Chapter **1**

The Science of Engineering Materials

1.1 Introduction

'Engineering Materials' is a term, which is used to include a wide variety of materials that are used for construction, in a general sense, and the materials used in the generation and transmission of energy. The engineer, whether he is dealing with an engine, a dam or a power plant, has to be concerned with the properties and the behaviour of the materials used in their construction. Consequently, his field of interest is very wide, from steel to rubber, from concrete to oil and so forth. In selecting the right type of material the engineer has to consider such properties as formability, machinability, mechanical and chemical stability, electrical behaviour, radiation changes and certainly the cost. Because of these responsibilities of the engineer, the scope of the Chemistry of Engineering Materials is widened to such an extent that it is very difficult to define its limits.

A gear, for instance, has to be made of a material which is, to begin with, soft, so that proper shape can be given to it. The material should be such that after giving the shape its properties can be so altered that it becomes tough and will retain the shape. It is a skill of this kind, for example, that is gained by a study of the Chemistry of Engineering Materials. It also enables one to anticipate the behaviour of a material in a new or different situation and also the direction in which to proceed in search of new types of materials. Engineering design has made vast progress in many directions. It is easy to design equipment for very high pressure or high temperature operations, but the design will remain on paper as long as material to withstand the pressure or temperature is not produced.

The materials being numerous, it is not possible for any one to have detailed knowledge of them. Therefore, we shall try to study the *principles* that govern the properties of all materials. This will lead us to the consideration of the structure of materials–gross structure, the grains and the crystals and the atomic structure; and the effect of the service conditions on the properties of the materials.

Such knowledge very often permits the prediction of properties in a material and trial-and-error becomes unnecessary. For example, knowledge of the behaviour of electrons in materials resulted in the development of semiconductors which are used in many equipments such as transistors and solar batteries.

This study is fascinating as it can lead to answers to simple yet baffling questions. Why are metals good conductors and not bad conductors ? Why is

a mixture (an alloy) of gold and silver, both of which individually are very good conductors, not so good a conductor ? At higher temperatures the chemical activity increases, but why does the electrical conductivity of a metal decrease whereas it increases in a non-metal ? What makes a certain material a lubricant and another material an abrasive ? Why are metals ductile ? One can go on posing many such questions.

The engineer is also concerned with the life of material used in the equipment made. This has wide connotations. He has to study the lubricants without which movement of solid surfaces with respect to each other become difficult if not impossible. There is also the problem of deterioration of the material in the environment, which leads to the study of corrosion.

Questions of this kind have led the scientist to investigate engineering materials along new lines. It has now become possible to relate qualitatively almost all the engineering properties of materials to the fundamentals. Quantitative derivations for most of the properties are still awaited. These studies have led to the origin of a new branch of study known as 'Materials Science'. This is beyond the scope of this book although hints will be given wherever possible.

Although "Chemistry of Engineering Materials" deals with all types of materials useful to the engineers, "Materials Science" deals with materials primarily in the solid state. It is a utility-oriented interdisciplinary study of solid materials. Solid state physics and solid state chemistry provide important tools for investigating the relationship between properties and structure of materials. Disciplines like metallurgy, ceramics and polymer science have greatly contributed to the development of materials science. The inter-disciplinary studies have also resulted in systematic study of composite materials, which are gaining in importance.

The new understanding of the materials has originated from recognition of the fact that properties of all the materials are due to their structure. The structure depends upon the manner in which the atoms of the material join to form molecules or crystals or amorphous structures. Most of the engineering properties of materials are the properties of aggregate, i.e., collections or groups of particles. Further, the materials have imperfections which greatly affect their properties.

Materials Science has developed rapidly because firstly, the users of the engineering materials are more concerned with the physical properties, and secondly, the rules which govern the joining of atoms and molecules in

groups and of these groups into large aggregates, are common for all materials. This being so an understanding of the rules and the structure of the materials will enable one to understand the behaviour and properties of all materials. Such an understanding has not only led to the development of new materials but also made the study of materials rational and satisfying to the intellect.

No material has all the properties that can be desired, and in addition, for any use several properties may be desired. Therefore, the engineer has to choose or develop a material so that there is the desired compromise of properties. Understanding of the principles enables the scientist to foretell the structure that will have the needed compromise of properties. He then proceeds to develop a material that will have the desired structure. Thus new materials are developed.

Often only one material does not serve the purpose and different parts of the equipment or machine are made of different materials. This idea is used even in making simple devices, for example an aluminum pan for boiling has a wooden handle. Fibre reinforced metals have been developed which have high strengths. High polymers are now fast replacing steel in some fields of construction and in automobile industries.

1.2 Effect of Structure

Atoms are the fundamental units that compose all materials. Therefore, physical, chemical and mechanical properties must depend upon the nature of the atoms. It is reasonable to think that knowing some characteristics of the atoms forming a material, it should be possible to calculate the values of these properties. From this point of view the properties can he considered to be either *structure-insensitive properties or structure-sensitive properties.* The properties which do not depend upon, or are insensitive to, small discontinuities in structure or small changes in composition are known as structure-insensitive properties. Elastic constants, intrinsic magnetisation, heat of sublimation, specific heat and thermal expansion are properties of this type. Many of the engineering and other properties such as fracture, conductivity, viscosity, diffusibility, elastic limit and strength are sensitive to small changes in structure or composition of the material. Such properties are called structure-sensitive properties. The present state of knowledge of these properties is only qualitative and cannot be used for engineering calculations. In spite of this fact, the atomistic theories help to correlate a large number of physical, chemical and mechanical properties.

The engineer very frequently uses the data given in the various handbooks. The data regarding the structure-sensitive properties should be used very carefully. It should be ascertained that the material being used has the same history as the material whose properties are taken from the handbooks. The danger of such mistakes in structure-insensitive properties is much less.

1.2.1 The Atom

Except for density and specific heat, the engineering properties of materials seem to be little influenced by the atomic weights. The engineering properties, just as the chemical properties, of the various elements can be explained to a considerable extent, by the behaviour of electrons in the outer shells. These electrons influence the mechanical and strength characteristics as these properties are dependent upon inter-atomic bondings which are decided by the outer electrons; they influence the optical properties, the size of the atom and the electrical conductivity. In order to understand these and similar properties, it is necessary to study the distribution and energy levels of the electron. The planetary theory of the structure of the atom, given by the eminent physicist Neils Bohr, has been very useful in many respects. It is, however, open to several objections and has been replaced by the wave theory of matter. A study of this kind is fascinating but is beyond the scope of this text.

The classical theory of mechanics failed to explain the stability of atoms. According to the old theory moving electrons should emit electromagnetic waves, lose energy, gradually slow down and ultimately collapse in the nucleus. This is against experimental observations. The second difficulty came because the atoms give sharp spectral lines. According to the classical theory there should be a continuous series of lines corresponding to continuous motion of the electrons. Some explanations were offered to meet these objections. In attempting to give more satisfactory explanations quantum mechanics was developed which has culminated in wave mechanics.

According to Heisenberg's indeterminacy principle, it is not possible to determine simultaneously both position and momentum of a moving body. This holds good for all moving bodies but its calculation for the small particles, like the electrons show very different results from those obtained by the simple mechanical calculations. This view leads to the conclusion that the exact position of an electron cannot be predicted but the location where there is the probability of finding it can be foretold.

The nucleus of an atom is about 10^{-12} cm in diameter and has nearly all the mass. Some properties of the nucleus have been considered in the chapter on Nuclear Fuels. The electrons are assumed to occupy certain orbitals or energy levels which are three dimensional and determine the probabilities of

the electrons being located in various regions of space around the nucleus. Each orbital is described by three quantum numbers, viz., the principal quantum number which tells about the size of the orbital (the distance from nucleus); the azimuthal quantum number gives the shape and the magnetic quantum number denotes the orientation of the orbitals in the space. The maximum number of electrons in each orbital is determined by the Pauli's Exclusion Principle.

Accordingly, each of these orbitals in an atom can have at most two electrons. The electrons belonging to the same orbitals are distinguished in terms of the spin quantum number which gives the direction of rotation of an electron about its axis. A pair of electrons at a particular energy level spin in opposite directions, thus balancing their magnetic moments. This spin is important in explaining the magnetic properties of materials.

Mass number (A) of an element is the number of protons plus the number of neutrons in the nucleus of the atom. Atomic number, which is represented by Z is the number of protons in the atom. Thus the value of A for isotopes of an element is different, but the value of Z is the same. Most of the physical and mechanical properties of materials do not depend on isotopes. Certain properties, like diffusion, which depend upon the atomic weight are affected by the isotope present. For example, the properties of steel have not been found to depend on the isotope of carbon present in it. But, palladium foil is more permeable to ordinary hydrogen than to an isotope of hydrogen like deuterium.

1.2.2 Forces of Attraction

Most of the engineering properties of materials are due to the forces that hold the particles and the atoms together. These forces, the inter-atomic forces, are due to the electronic structure of the atoms. They are of two types: 1. Strong or primary forces (or bonds) and 2. Weak or secondary forces (van der Waal's forces).

1.2.3 Primary Forces

The *ionic bond* is the simplest of primary forces of attraction. It is due to, transfer of valence electrons of the atoms of one element to those of the other. This results in the positively and negatively charged ions which attract each other, as in a NaCl molecule. It should be noted that a Na^+ is attracted not only by Cl^- of the same molecule but by all the Cl^- in the entire mass of sodium chloride, i.e., it is surrounded by a number of Cl^-. If it were not so, sodium chloride could not have the physical properties it has. Thus all the positively charged ions are attracted by all the negatively charged ions in the mass and all the negatively charged ions are attracted by all the positively charged ions. The ionic solids are better conductors than the covalent solids, but not as good conductors as the metals. The ionic solids fracture more easily than the covalent solids.

In many cases such a simple transfer of electrons is not feasible, and atoms share electrons giving rise to *covalent bond*. Two hydrogen atoms on coming close to one another share the electrons (provided the electrons spin in opposite directions, if the spins are the same, the two atoms are repelled). Thus they acquire a helium type shell. It is noteworthy that each electron belongs to the system as a whole, and therefore covers both the protons. Thus the electrons move in a molecular orbit instead of an atomic orbit. In a similar manner two atoms of chlorine share two electrons completing their shells. The hydrocarbons are examples of this type of bonding. Most of these substances have very strong forces of attraction within the molecule (i.e., intra-molecular attraction) but attraction between different molecules is weak (weak inter-molecular attraction). The result is that these substances have low melting and low boiling points. The covalent bond is strong and directional (see 'Hardness' in this Chapter), therefore it gives fairly hard solids which resist deformation. It has resulted in the hardest material, the diamond. The carbon atom has four electrons in the outer shell and needs four more electrons to have a stable shell. This is achieved by sharing four electrons of adjoining carbon atoms resulting in a three-dimensional lattice in space.

The third type of bond is *metallic bond*. Its exact nature is complicated, but in a greatly simplified form we may say that when an atom has fewer valence electrons, these are not held so strongly by the remaining 'core', hence are removed easily. With the removal of the valence electrons the 'core' becomes a positive ion with a complete-shell structure. These electrons may be considered to be 'free' electrons and constitute what is called the electron 'cloud' or 'gas' (see Fig. 1.1). The electron cloud is not attached firmly to a particular positively charged core but may be considered to be common to all. It is this attraction between the negatively charged electron cloud and positively charged core that brings the metal atoms together. This accounts for close packing of atoms, which gives high density, and absence of directional properties. This arrangement shows that there are no bonds in a metal between one atom and another. The nuclei (i.e., the positively charged spheres or ions) repel each other. Thus the atoms are relatively free to change their positions because it does not involve the breaking up of atomic bonds. This fact explains some of the important mechanical properties, e.g., plasticity of the metals, formation of alloys, etc. The electron cloud or gas, which is common to all the atoms of the metal permeates the whole mass and causes the positively charged particles to pack together closely and give coherence to the metal.
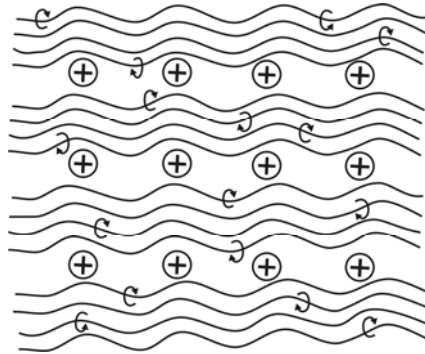
Fig. 1.1 Metallic bond.

In ionic bond, the valence electrons remain near a single ion; in covalent bonds, the valence electrons are shared by a few atoms. Thus in both these cases electrons are closely associated with corresponding ions or atoms. In metallic bond the valence electrons are not closely associated with ions but are free to move within the volume of the metal.

This picture can provide explanations for a number of properties of metals, the important ones being the following :

1. High electrical conductivity of metals is due to the fact that the electrons constituting the electron cloud are free to move in an electric field.
2. High thermal conductivity of metals largely arises because the electron cloud absorbs kinetic energy and being more free to move helps in the transfer of thermal energy from a high temperature level to a low temperature level.
3. The absence of atom to atom bond explains many mechanical properties (discussed later in this Chapter).
4. The free electrons absorb light energy and vibrate at frequency equal to that of the light striking them. These vibrating electrons emit light giving a metallic lustre.

It was stated earlier that the full explanation of metallic bonding is quite complex. The mechanism explained above suggests that it is due to electrostatic attraction between the electron cloud and the positive nuclei of the atoms. This would result in a relatively weak bond, as is the case with metals like sodium and potassium. This weak bonding explains why the alkali metals are soft and wax-like and have relatively low melting points and low specific gravities. Besides alkali metals, other metals of engineering importance that have this type of bonding dominant are magnesium, zinc, mercury, lead, tin and silver. The atomic structure of a number of metals is such that an inner orbital is not filled completely. This results in strong covalent bonding between the atoms which extends throughout the length

and breadth of the grain or the crystal. This provides an explanation for the hardness and high melting points of chromium, manganese, iron, nickel, tungsten, etc.

As there are no atom to atom bonds in metals the atoms have greater freedom. This enables a metal to mix with other metals easily and form alloys. This also explains why metals join or weld easily with each other.

The metallic bond is non-directional. Therefore there is a pull or attraction in all directions. This results in the atoms tightly fitting, one another and causing the metals to be heavy and dense.

Thus it can be said that the metallic bonding is a combination of electrostatic attraction between the electrons and the positive nuclei of the atoms and covalent bonding due to the presence of un-filled d-orbitals.

1.2.4 Secondary Forces of Attraction

There are several types of weaker forces that also cause inter-atomic attraction. In many cases their effect is insignificant but in some cases they are the only forces at work, hence they need to be considered briefly. Often these are called *van der Waals' forces*. For example, in the inert gases the outer shell is complete and none of the three types of bonding discussed so far is operative. Hence, these gases remain monatomic. At extremely low temperatures the thermal vibrations are greatly reduced and then the effect of these weak forces is seen and the gases condense.

The number of electrons and protons in each atom is the same and it shows no electric charge. In the presence of another atom of same kind the centers of negative and positive charges do not coincide giving rise to slight eccentricity. Thus weak van der Waals' forces originate.

The formation of *electrical dipoles* contributes greatly to the existence of van der Waals' forces. Hydrogen fluoride is a good example which has unusually high boiling point (19.4^{o}) for this type of molecule.
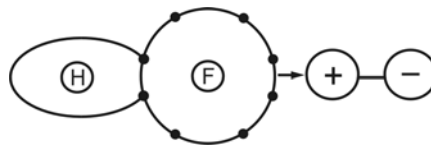
Fig. 1.2 Formation of an electrical dipole.

In this type of sharing, eight shared electrons surround the positive charge of the fluorine nucleus more completely than the two shared electrons surround the positive charge of the hydrogen nucleus. The result is that the centre of the positive charge of the whole molecule is different from the centre of the negative charge and an electrical dipole is created.

See Fig. 1.2. This happens in asymmetric (not having symmetry) molecules and attraction between the molecules results. See Fig. 1.3.
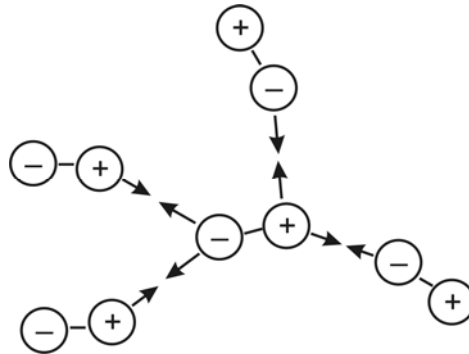
Fig. 1.3 Attraction between the asymmetric molecules.

In a similar manner water molecules are also dipolar and are much more strongly attracted not only to one another but also to other polar molecules. The non-polar molecules like benzene are attracted to one another much less strongly. This explains why benzene and water will not mix. If these two are shaken together, the water molecules strongly attract each other, squeeze out the benzene molecules, and come together to form a separate layer.

In symmetrical atoms, like noble gas atoms the electrons surround the nucleus uniformly with the result that the centre of positive charge and the centre of negative charge coincide. Due to the random movement or the electrons the centre of the negative charge is fluctuating. Therefore, even in symmetrical atoms momentarily the centre of the negative charge does not coincide with the centre of the positive charge. The result is that there is momentary polarization of the atoms of the molecules. In other words, the atoms are attracted to each other. According to quantum mechanics such shifting of the centres is likely to take place when there is another atom nearby. This weak and momentary attraction between the atoms causes the noble gases to condense though at very low temperatures.

1.2.5 Aggregates

The properties of engineering materials can be better understood by considering aggregates of atoms. All materials have kinetic and potential energies in the atoms and molecules that comprise them. There is the kinetic energy of motion and the potential energy of the forces that exist between the atoms and the molecules. The difference between the kinetic and potential energies decides the physical state–solid, liquid or gaseous–of the material. The kinetic energy mostly depends upon the temperature and the potential energy upon the distance between the molecules.

In a gas, the molecules are far apart and the forces of attraction between them are weaker. Hence, the molecules are free to move about, i.e., their kinetic energy is high. As the temperature is reduced (i.e., kinetic energy is reduced) or the pressure increased (i.e., the distance between the molecules is decreased) the attraction between the molecules increases and they become less free to move and the liquid state results. Thus the gases fill the volume of the container in which they are put but the liquids have their own definite volumes. In the liquids, the forces of attraction are not so high as to prevent them from seeking their own levels and from taking the shapes of the containers in which they are placed.

In the gases the space between the atoms or molecules is large. They may be several atomic diameters apart. In the liquids and solids the atoms and molecules are very close to each other. Application of pressure reduces the space between them and reduction in temperature reduces their vibration, therefore, the gases condense when the pressure is applied and temperature reduced. The solids and the liquids are incompressible because the space between the atoms and the molecules is small. The atoms can also be brought near to each other by chemical affinity. Thus hydrogen and oxygen, both difficult to condense by physical means, easily give a liquid, viz. water, by chemical means.

When the atoms are brought very close to each other, forces of repulsion become pronounced. These forces are weak at long distances, but at shorter range are stronger than the attractive forces. When two atoms are brought near each other, i.e., compressed, they meet increasing repulsive force.

Forces of attraction as well as forces of repulsion are at work on the particles. There is the attraction between the positively charged nucleus and the negatively charged electrons. The nuclei repel each other. When two atoms are brought nearer to each other the forces of attraction try to keep them together. As the distance decreases, the repulsive force of the positively charged nuclei is exerted, and at a certain distance the forces balance each other and energy has to be spent in increasing or decreasing the distance i.e., in compressing or expanding the material. Atoms occupy these equilibrium positions. The X-ray diffraction photograph shows these positions. As the temperature increases the atoms vibrate and the photograph becomes blurred.

Certain materials, like hydrogen, oxygen and nitrogen have stronger inter-atomic forces and when they form molecules, there is only a small residual affinity left. Therefore, the molecules do not come close to each other. This accounts for the difficulty in liquifying them. Many organic compounds have small residual affinity, therefore, on the application of a small amount of heat they volatalize or are disrupted. The liquids, and more especially the metal particles, have a large amount of residual energy which causes them to be held together firmly.

In the solids, the potential energy predominates and they maintain their shapes. Thus the solids have basically different engineering properties. Both

gases and liquids are mobile and are called fluids. Gases offer less resistance when their particles move past other particles of gas; liquids offer more resistance. This resistance is called *viscosity*. The consideration of viscosity is important in the science of lubrication.

1.3 The Solid State

The solid state differs from the liquid and gaseous states in not being fluidic. The solids are of two types, crystalline and amorphous.

In the crystalline solids the atoms are arranged in a regular way. Their positions in space with respect to other atoms are fixed and they take up definite geometrical arrangements. If space is divided in equal volumes by continuous intersecting planes, then seven shapes or patterns are obtained. These shapes constitute the seven *crystal* patterns. When an arrangement repeats in space, the *lattice* structure, which is characteristic of a crystalline material, is produced. The space lattice is represented by a three-dimensional network of straight lines. The intersections of the lines are called lattice points. The centres of the atoms are located at the lattice points. Thus, a space lattice describes the locations and arrangement of atoms in a given crystal. There are fourteen such arrangements or space lattices. (In certain crystal patterns there are more than one possible lattices and in others only one. For   example, there are two lattices for tetragonal and monoclinic, three for cubic, four for orthorhombic and only one for rhombohedral, triclinic and hexagonal crystals.) In each lattice there is a fundamental pattern or grouping of atoms which is repeated indefinitely in all the three dimensions. This grouping, which has the complete pattern of the crystal, is called a *unit cell*. Each unit cell is bounded by plane surfaces which meet at definite angles. See Fig. 1.4.

Unit Cells   Crystals
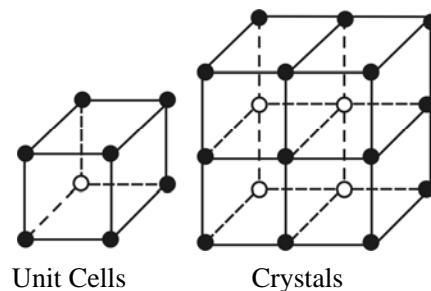
Fig. 1.4 Making crystals from unit cells.

In the amorphous solids the atoms are not arranged in a regular way. These solids are supposed to be super-cooled liquids. Glass is a common example of an amorphous solid. The structure of an amorphous solid is more complex than that of a crystalline solid. A metal wire bends easily but a glass rod breaks. The metal is said to be ductile whereas, glass is brittle. Metal is a

good conductor but glass is an insulator. Glass is transparent but a metal-sheet (unless extremetly thin) is opaque. Such differences in properties arise from the difference in the manner in which the atoms are arranged in the materials.

Arrangement of atoms in a regular manner helps in the conduction of electric current. Metals are crystalline solids and are conductors. When the arrangement is disturbed, the conductivity falls, as happens on heating a metal. In molten state the metal atoms are more free to move about and as the crystalline structure is destroyed, the electrical conductivity is lower than in the solid state. All these facts go to show the nature of the solid state. The dimensions of a unit cell depend on the dimensions of the atoms forming the cell and the arrangement in the unit cell. The atomic diameter is the distance between the centres of two adjoining atoms.

The four types of unit cells which are most common in engineering materials will be discussed only briefly.

1.   **Simple Cubic** lattice has the centres of the atoms located at the eight corners of a cube. The crystal is built up in a manner similar to the building up of a large cube from cubical bricks except that the corner atoms are shared by the adjoining cubes as shown in Fig. 1.4. Ionic crystals, such as NaCl and LiF have cubic lattice.

2.   **Body Centred Cubic** (B.C.C.) lattice is similar to the cubic except that an additional atom is situated at the centre of the cube (Fig. 1.5). α-iron, which is the stable form of iron at room temperature, has this type of arrangement. Sodium, potassium, chromium, tungsten, etc. also form B.C.C. crystals. The actual arrangement is more complicated than it looks from the simple Figure. All the atoms, whether at the centre or the corners of a cell, are surrounded by eight adjacent atoms, hence they have the same geometric environment. (Atoms at the centres of eight adjoining unit cells when joined form a cube and there is an atom at the centre.)

Face centred   Body centred   Hexagonal close
cubic   cubic   packed
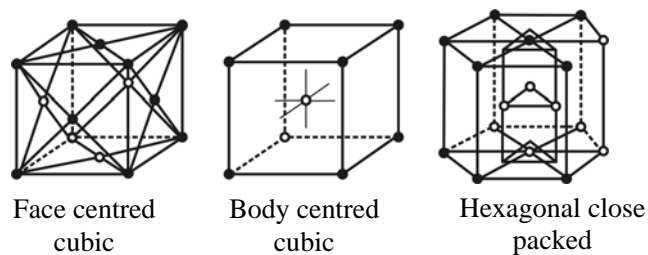
Fig. 1.5

3. **Face Centred Cubic** (F.C.C.) lattice is similar to the simple cubic but has additional atoms at the centres of the faces and none at the centre of the cube. This is a more common structure in metals than the body centred cubic lattice. γ-iron, which is the stable form of iron at higher temperature forms F.C.C. crystals. Other common metals like aluminium, copper, gold, nickel and silver have this type of lattice.

4. **Hexagonal Close Packed** (H.C.P.) latice is a hexagonal prism in shape, with twelve atoms at the twelve corners, and one each at the centre of the two hexagonal faces and three more at the centre of the prism. Magnesium, zinc, cobalt and titanium have this type of lattice (Fig. 1.6).
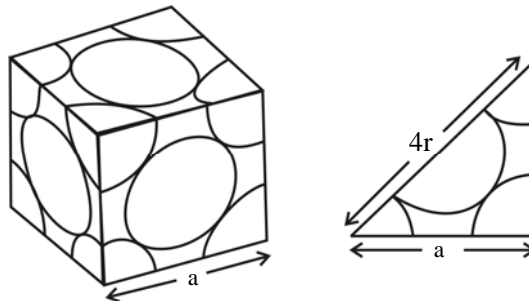
Fig. 1.6

Each of the eight corner atoms of the cubic unit cell is shared by eight unit cells. In other words, each atom is common to eight cells. Therefore only one-eighth of each atom belongs to a cell. Thus one eighth of eight atoms i.e., one atom, belongs to a unit cubic cell.

In the body centred cubic cell an atom is added in the centre, making two atoms per unit cell. The atom at the face of face centred cubic lattice is shared by two cells, so half of each such atom belongs to a cell. There are six atoms at the six faces contributing three atoms to the cell, and there is one atom due to the atoms at the corners of the cube. Therefore, four atoms belong to each face centred cubic unit cell.

In the F.C.C. and H.C.P. structures the atoms are packed more closely than in other structures. This fact can be best realised by taking balls and trying to make the structure. If crystal models are made, with wooden balls representing the atom, balls (or the atoms), in F.C.C. and H. C. P. structures, 74 percent of the volume of the unit cell is occupied by the atoms, 68% in B.C.C. unit cell and only 52% of the volume is occupied by the atoms in simple cubic unit cell. This fact is expressed by saying that the packing factors of the F.C.C. and H.C.P. structures are 0.74 and of B.C.C. is 0.68 and of simple cubic is 0.52.

Knowing the crystal structure, the atomic weight and the atomic radius of an element, it is possible to calculate its density. For example, aluminium forms F.C.C. crystals and has an atom radius of 1.431 $\overset{o}{A}$. (1 $\overset{o}{A}$ = 10^{-8} cm). Its density can be calculated as follows :

$$(4r)^2 \; = 2a^2 \; \text{or} \; a = 2\sqrt{2}r$$

$$= 2 \times 1.414 \times 1.431 \; \overset{o}{A} = 4.046 \; \overset{o}{A}$$

$$= 4.046 \times 10^{-8} \text{ cm} = \text{lattice constant.}$$

It has already been shown that each unit cell of F.C.C. crystal has 4 atoms.

$$\text{Density} = \frac{\text{weight per unit cell}}{\text{volume per unit cell}}$$

$$= \frac{(\text{atoms per cell}) \times (\text{wt. in g. per atom})}{(\text{lattice constant})^3}$$

$$= \frac{4 \times 27 / (6.02 \times 10^{23})}{(4.046 \times 10^{-8})^3} = 2.71 \text{ g/cm}^2$$

(Note – Atomic weight of aluminium is 27 and Avogadro's number is 6.02×10^{23})

It is noteworthy that the experimental value of the density of pure aluminium is 2.699. It has been found that the experimental values are always slightly lower than the calculated densities. It is, therefore, concluded that some atoms are missing from the lattice sites. This leads us to the consideration of crystal defects.

1.3.1 Crystallisation from the Liquid State

It may be noted that in the crystal lattice the adjacent cells share atoms which are located on the faces or at the corners of the cells. When a pure metal is cooled from the liquid state and the temperature approaches its melting point the atoms begin to join together to form unit cells and lattices which may subsequently again pass into the liquid state. If, however, the liquid is cooled to a temperature below the melting point the unit cells and the lattices formed are stable and act as solid nuclei around which other atoms, which have lost sufficient energy, join and thus the nuclei grow in size. The energy released during solidification raises the temperature to the true melting point.

Under-cooling needed for starting nucleation has been depicted in the cooling curve shown in Fig. 1.7(a). This type of nucleation is known as homogeneous nucleation.

(a) Homogeneous nucleation   (b) Heterogeneous nucleation
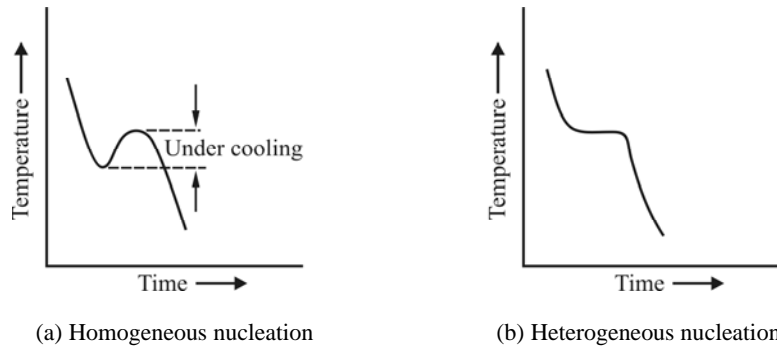
Fig. 1.7 Cooling curve.

Impurities of higher melting points present in the liquid metal at its melting point provide solid nuclei over which atoms arrange themselves and crystal growth or solidification starts at the melting point itself without any sign of under-cooling. This process, known as heterogeneous nucleation, has been shown in Fig. 1.7(b).

After the solid nuclei have been formed they begin to grow in all directions with the result that a number of crystals compete for the same space and perfect external shape is difficult to maintain. This results in the formation of crystals which do not have regular external shape. These are called *grains*. A grain is a crystal but it does not generally have the regular external shape of the crystal. See Fig. 1.8.

Nuclei   Grains   Grain boundaries
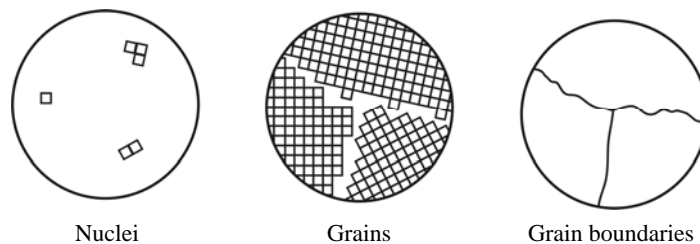
Fig. 1.8 Formation of grain boundaries.

Rapid cooling of a metal from the molten state provides a large under-cooling giving a higher rate of nucleation. Thus a large number of nuclei are formed with the result that a large number of grains are produced per unit volume. The structure so produced has fine (or small) grains which gives rise to superior mechanical strength (the explanation for this has been

given in this Chapter under "Deformation of Rigid Bodies"). As this is of considerable practical importance, it may be added that a small percentage of a high melting metal is added to a molten metal before it reaches its melting point so that a number of nuclei are provided and a fine grained structure, with higher mechanical strength, results. This is known as grain refining.

This type of formation affects the properties of the materials very greatly. In some respects, a single crystal has different properties along different directions due to the arrangement of the atoms. In non-cubic crystals, properties, such as electrical and thermal conductivities, coefficient of expansion, and rate of chemical attack, differ in different directions in the crystal. Graphite crystals have a 100 times greater electrical conductivity along one axis than on a perpendicular axis. Such directionality of properties in different directions, is called *anisotropy*. But the engineering materials consist of numerous grains developed at random with the result that the properties of a material are found to be the same along all directions of the material. Of course, there are a few exceptions to this generalization.

In the gaseous and liquid states the properties are the same in all directions and these states are called *isotropic*.

There are zones in which the adjacent crystals meet. These form the *grain boundaries*. The atoms lying in these zones are like the 'buffer land' between countries. They do not wholly belong to either of the grains, and therefore have different properties. The grains are comparatively small blocks lying at various angles to each other.

In 1863 Sorby developed a technique for observing the structure of metals. He polished the metal surface and treated it with a weak chemical which attacked different constituents at different rates. The chemical, usually acidic in nature, is called an etching agent. Metals cannot be observed as biological specimens are observed, because the metals are opaque. Sorby directed light rays on metal surface and the reflected light was viewed.

The etching agent attacks the gain boundaries more easily and grooves are formed. The grain lying at different angles are also attacked at different rates. Depending upon the structure of the metal the surface becomes uneven. On observing it by reflected light under a microscope some areas appear bright and others dark. This enables one to observe the size and shape of the grains, foreign inclusions, surface defects and the phases. All these help to understand the behaviour of the metal.

1.3.2 Crystal Imperfections

Study of unit cells and crystals shows the perfect order existing in them. In the actual crystalline materials that one handles there are always present *imperfections* or *defects*. The grain boundaries, described above, are such imperfections which alter the structure-sensitive properties. Another important type of defect, known as *line defect* or *dislocation* has been considered later in this Chapter along with deforrnation of rigid bodies, as the dislocations offer explanations of certain important mechanical properties. It is, therefore, proposed to consider here only the *impurity atoms* and *point defects*.

Impurity atoms : By the terrn "impurity atoms" is meant atoms entering the crystal structure and not the accidental or otherwise inclusions of foreign matter like the slags, oxides, etc. introduced during the preparation of the metals. The impurity atoms form what is known as a *solid solution*. A solid solution may be defined as a homogeneous mixture of two or more kinds of atoms in a solid state. The nature of bond in the metals is such that usually they act as solvents and can dissolve at least small amount of many other elements. The impurity atoms may (a) occupy small interstitial sites between the solvent atoms, forming *interstitial solid solution* or (b) replace or substitute the solvent atoms forming *substitutional solid solution*. See Fig. 1.9.
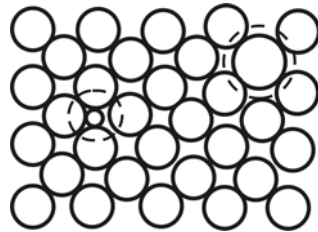
Fig. 1.9 Solid solution (left) interstitial, (right) substitutional.

Since atoms in metals are densely packed, the interstitial sites available for the impurity atoms are limited. Higher the packing factor less is the space available in between the atoms. Therefore, mostly small atoms such as hydrogen, boron, carbon, nitrogen, oxygen and lower atomic weight metals dissolve interstitially in metals. Besides the size of the atoms, chemical differences often restrict the interstitial solubilities. In spite of such solubility there is distortion of the crystal structure in the surrounding region. An important exception is titanium, in which upto 33 atomic percent oxygen dissolves.

The transition elelments, e.g., iron and nickel, have higher interstitial solubility. This is supposed to be due to their electronic structure i.e., incomplete shell inside the outer valence shell.

The interstitial solid solutions may have properties very different from the original metal e.g. pure iron has poor mechanical properties whereas steel, with less than 0.5% carbon, can be very hard and strong.

Substitutional solid solutions are formed when the solute atoms are similar in size and chemical nature of the solvent atoms. There is complete solid solubility when the radii of elements differ by not more than 8% and they have the same crystal structure. If the atomic radii differ by more than 15%, the range of solubility is limited. Common examples of complete solid solubilities are of copper-nickel, both having F.C.C. lattice and of niobium-tantalum, both having B.C.C. lattice, and having nearly identical atomic diameters.

The effect of dissolving aluminium or phosphorus in germanium or silicon, resulting in semi-conductivity will be discussed later in this chapter.

Substitution of foreign atoms in ionic crystals also takes place, provided electrical neutrality is maintained. Substitution of impurity cations is more common. When the charge of the impurity ion is different from that of the host ion another defect is created. For example, when Ca^{2+} is introduced in a sodium chloride crystal, it displaces two Na^+ so as to maintain electronic neutrality, but it can occupy only one site with the result that removal of another Na^+ creates a cation vacancy which affects the electrical properties of the ionic material. The cation vacancy can be repeated by exchanging positions with the neighbouring cations in an electric field. This causes electrical conductivity.

Point defects are local imperfections occurring at isolated lattice points. The defect being local its influence extends to only a few atom diameters beyond its location. These defects arise during crystallization of the metal but thermal vibrations at a later stage may also introduce the point defects.

A *vacancy* is created when an atom is missing from the lattice site. See Fig. 1.10. More than one vacancy may condense to form di or tri-vacancy. As the temperature increases the vacancies increase but even near the melting temperature the vacancy concentration reaches only a value of about 1 in 10^4. The vacancies can move about in the crystal by exchanging positions with neighbouring atoms. They play an important part in the solid state reactions.
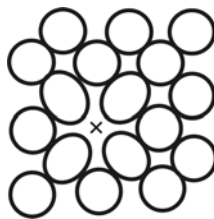
Fig. 1.10

Interstitialcies have already been discussed. Self-interstitialcies, i.e., atoms dislodged from the lattice site and occupying interstitial spaces in the same crystal are less common, because this causes a great deal of structural disorder.

In ionic solids a cation-anion pair may be missing so that electrical neutrality of the crystal as a whole is maintained. A cation-anion vacancy pair as illustrated in Fig. 1.11 is called *Schottky Defect*. The missing ions generally take up positions on the surface and do not require any interstitial.
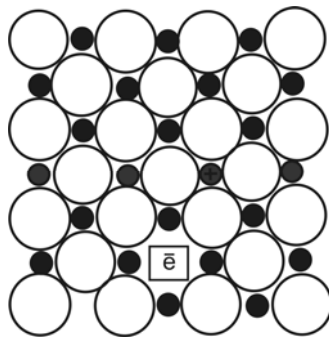
Fig. 1.11 Schottky defect.

Another point defect is known as *Frankel defect*. In this case there is an interstitial cation (or anion) very near another cation (or anion) vacacy. The displacement of a cation to an instital position is shown in Fig. 1.12 (a). This is quite a common defect. However, sometimes the dissolved cation may occupy a position at the surface, as shown in Fig. 1.12 (b). The movement of anions is less likely due to their bigger sizes.

(a)   (b)
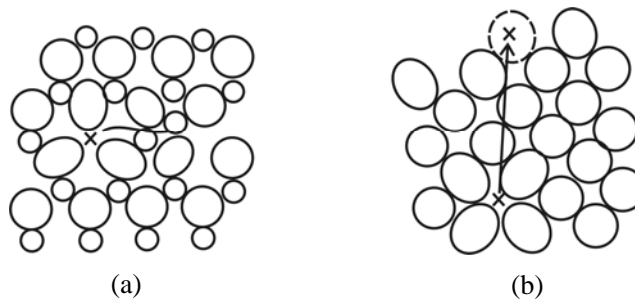
Fig. 1.12 Frankel defect.

Close packed structures have more of vacancies and Schottky defects than interstitialcies and Frenkel defects because to force atoms in between regular positions of atoms requires additional energy.

1.3.3 The Metallic State

Metals are substances which are characterized by high conductivitities, opacity, strength, ductility, lustre, etc. But such definition is unsatisfactory because there are some non-metallic elements which exhibit these properties under certain conditions, There are also conditions in which the metals do not exhibit these properties–at high temperatures the strength is lost and at low temperatures ductility is lost. One of the best ways to define a metallic state is in terms of electrical resistance. The electrical resistance of the metals increases with rise in temperature whereas it decreases in the case of non metals. This definition, however, does not give a satisfactory idea about what a metal is.

The term *metallic* has two distinct meanings. In the chemical sense, it refers to certain behaviour of the atomic particles, for example, the metals form basic oxides, evolve hydrogen from the acids and form salts. In the metallurgical sense, one is concerned with large aggregates of matter which give rise to certain physical and mechanical properties. These properties are not possessed by the atomic paticles and depend, to a large extent, on the manner in which aggregetes are formed. This term also refers to alloy systems which play a vary important role in the work of the engineers. An understanding of the metallic state can be gained by studying the structure of the atoms and the mechanisms of their joining together into larger aggregates of matter.

It is thus seen that the matallic state is a crystalline state which is characterized by an orderly internal arrangement of atoms. The regular arrangement of the atoms gives to the crystal its regular shape. The faces of the crystal and the planes within it have layers of atoms. There are rows of atoms on the edges of the crystals. The common physical properties, such as thermal and electrical conductivities, coefficient of expansion, strength and solubility, depend upon the nature of atoms and also on their arrangement in the space lattice.

1.4   Engineering Properties of Materials

1.4.1 Hardness

In general, the covalent bond produces harder solids than those produced by the ionic bond. The hardest materials are the diamond and corundum both of which have covalent bonds in their crystal structures. The role of covalent bonds can be understood by considering the carbon crystal. Each carbon atom has four electrons which it shares with its four nearest neighbours. The bonds are directed in four directions. Each of these four neighbours in itself sharing its electrons with four carbon atoms and so on and on. Thus a

perfectly symmetrical giant molecule interlocking the various atoms is formed, with the result that to disturb any of its atoms is to cause disturbance in a large number of atoms (Fig. 1.13).

Fig. 1.13 A diamond crystal.

Such a crystal has powerful cohesive forces and is extremely hard and has a very high melting point (3750°). Silicon and germanium have similar structures but their valence etectrons are much less tightly bound because of larger atomic diameters (i.e., the valence electrons are situated further away from the nucleus). Therefore, the cohesive forces are less strong and Si and Ge are neither so hard nor have so high melting points (1421° for silicon and 958° for germanium).

The diamond structure is similar to the structure of methane. In graphite carbon atoms join to form hexagonal sheet-like crystals as they do in benzene (Fig. 1.14). Each carbon atom forms a covalent bond with its 8 neighbouring atoms. Thus, each carbon atom contributes a spare electron which can move freely in sheet. The sheets are joined to one another by weak forces which permit the graphite crystals to slide over each other easily. Thus graphite is a good conductor of electricity, useful as a writing material and a lubricant.
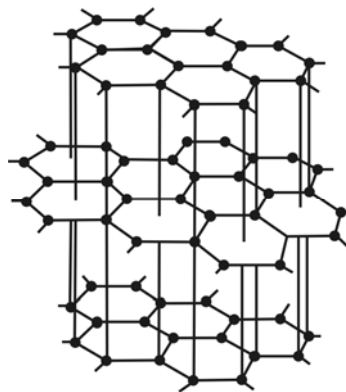
Fig. 1.14 A graphite crystal.

The electrons cannot move to the sheets in the perpendicular direction. Graphite, thus, conducts electricity parallel to the sheets, but is an insulator perpendicular to them.

Next to these in hardness are materials like quartz which have mixed ionic-covalent bonds. Minerals like fluorite and apatite which have ionic bonds are not as hard as quartz. With regards to such interpretations, however, one needs to be careful, because several factors often contribute to a property like hardness. Talc is a very soft material. Its molecules are formed by covalent bonds. It forms sheet-like crystals, which are held together by van der Waals' forces of attraction which are relatively weak forces. Therefore the sheets can easily be separated from one another making talc very soft. Most of the engineering metals and alloys in pure state have quite low hardness, but they can be hardened by heat treatment which produces hard structures. The principles and techniques of heat treatment are discussed in a later Chapter. The hardness of metals and alloys can also be increased by cold work.

1.4.2 Deformation of Rigid Bodies

Resistance to mechanical forces is one of the most useful properties of metallic materials. It is desired in some cases that the material may not be completely resistant to deformation. A good illustration is that of a spring. It is meant to deform under load and to regain its original shape when the load is removed.

For understanding the mechanical properties, it is helpful to briefly review what happens to the crystals under elastic and plastic deformations. When, on being subjected to a load, a solid changes its shape but regains its original shape once the load is removed, the phenomenon is known as *elastic deformation*. If the load produces a permanent change in shape it is known as *plastic deformation*. In both cases, a displacement of atoms takes place.

In elastic deformation the atoms come back to their original positions and in plastic deformation the displacement of atoms takes place to such an extent that new stable positions are acquired. In other words, in plastic deformation the atoms move away sufficiently from their original crystal lattices so as to acquire new lattices which have essentially the same pattern as the original lattices. See Fig. 1.15.
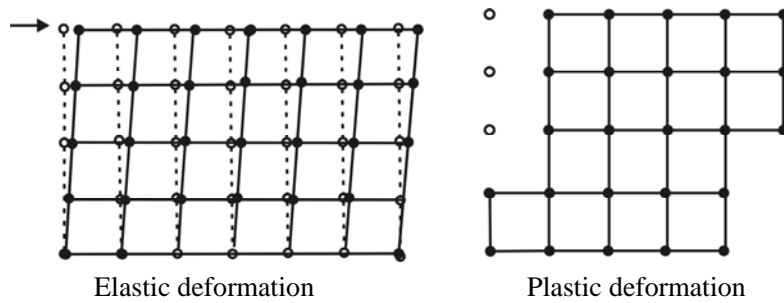
Elastic deformation   Plastic deformation

Fig. 1.15

In plastic deformation, *slip* takes place along those crystallographic planes which have the largest number of atoms, the reason being that in such cases the mean distance between the atoms is the smallest, and hence the movement of atoms from one stable position to another is easiest. Consequently slip takes place only in certain directions.

The presence of slip planes in the crystal of a metal has been verified by metallographic examination. When a metal specimen is squeezed in a vice it is found that its surface becomes crossed with fine lines. These lines are straight and parallel in each grain. In different grains they run in different directions indicating that different grains are oriented in different directions. Observation under a microscope shows the formation of steps at the surface. See Fig. 1.16. The movement has been compared to sliding as happens in a pack of playing cards. This view has been supported by deformation of large single crystals of metals. The *plastic flow* is different from the flow of gases and liquids. It takes place along certain crystal axes. It depends upon the regular arrangement of atoms within the crystal. As has already been explained, the arrangement repeats itself in a crystal. Therefore when a slip plane shears away from it neighbouring atoms and acquires a new position, it fits into the new surroundings as it did before. In a perfect crystal the original properties and the internal structure of the crystals are thus restored. In the bulk materials, as are handled by the engineers, there are defects which alter the properties.
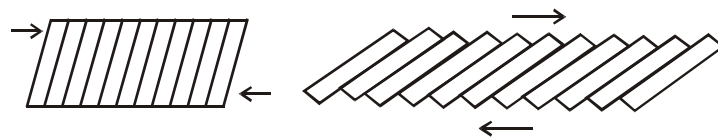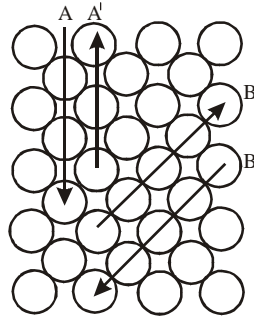

Fig. 1.16 Parallel lines formed on stressing a metal indicate that slip takes place in certain crystal planes in each grain.

This is easy to understand with the help of Fig. 1.17. The atoms are more closely packed on planes B and B' than on A and A'. It is also seen that


Fig. 1.17 Slip planes.

movement of plane A with respect to A' involves greater disturbance, i.e., more energy is required in the movement, than the movement of plane B against B', it is noteworthy that planes B and B' are further apart than planes A and A'. Slip takes place more easily along planes which are separated than along planes which are close to each other. Thus deformation takes place by shearing of planes of atoms. Tensile and compressive forces can also be resolved into shear forces and whether a metal is subjected to compression or tension, planes of atoms slip against other planes and deformation takes place.

The mechanism of deformation explains an important phenomenon. Suppose a piece of metal is passed between roll and the thickness is reduced. This would mean that there has been a movement of atoms along certain planes. These planes would be those along which the movement is easiest leaving behind planes along which further movement is more difficult. This means that the metal has become harder. It would now need more power to reduce the thickness than was necessary in the case of the original sample. This phenomenon is known as *work hardening* or *strain hardening* of metals. The operation is known as *cold working*. This explains why most metals after mechanical working (like rolling, forging, etc.) possess improved mechanical properties.

Work hardening, besides enabling the engineer to improve the properties of metals, has another very important practical use. Tar, pitch or a sheet of paper if pressed into a die becomes thin at a point and tears. If a sheet of metal is pressed into a die it also becomes thin at a point, but this point becomes hard by work hardening. Consequently the deformation shifts to the thicker parts which are weaker. Thus uniform deformation takes place. This phenomenon enables the metals to be deep drawn and made into useful shapes.

Above a certain temperature, known as critical temperature, which is fixed for each metal the atoms have sufficient energy to regain the strain free positions. Therefore, no strain hardening takes place. This is known as *hot working*.

Slip takes place along a particular crystallographic plane in a crystal, and it may not continue in the same direction in the adjacent crystal (or grain). The reason is that the plane of least resistance in the new crystal (or grain) may be oriented in a different direction. Therefore the direction of slip has to change whenever a new grain is met. It follows from this that the larger the number of times the direction of slip has to change, the greater is the resistance that the metal offers to slip (or deformation). In a metal of a given section if the grain (or crystals) are smaller, (thereby the number of grains per unit volume is larger), then the direction of slip changes more often, see Fig. 1.18. Therefore metals with smaller grains are stronger than those with coarser grains. These principles form the basis of the theory of *metal working*.
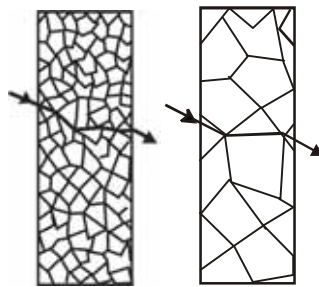
Fig. 1.18 Deformation of a plolycrystalline material.

This mechanism of slip qualitatively explains satisfactorily deformation of metals. When calculations of strength of materials are made on this basis, it is found that the calculated strength is 100 to 1000 times more than the actual strength. The first reaction to this discrepancy was that the theory is incorrect. Later, when very thin fibres or whiskers of metals were made, it was found that they approached the theoretical strength (see the chapter on Composite Materials). The discrepancy is now explained on the basis of the presence of imperfections or irregularities known an *dislocations* in the crystals.

1.4.3 Dislocation

Sir Nevil Mott, a leading solid state physicist, once brought out the difference between slip and dislocation by a simple example. If there is a heavy carpet spread on a floor and it has to be moved a little, there are two ways of moving it. If one tries to pull or slide the entire carpet as one piece, it

offers great resistance. The other way is to form a wrinkle and the wrinkle can be pushed forward easily and the carpet is pushed forward bit by bit. The former process corresponds to slip and the latter to dislocation. Deformation or plastic flow of a metal takes place by the movement of dislocations, like the movement of a wrinkle in the above example. It is due to this fact that the actual strength of metals in much smaller than the strength calculated on the basis of slip.

Dislocations are defects in crystals. The simplest of these is due to the presence of an extra half plane of atoms as shown in the Fig. 1.19. It is called a *line defect*. The presence of this plane of atoms displaces elastically the adjacent atoms, which exert elastic forces on both sides of the dislocation. These forces are balanced, therefore the dislocation, or the plane of atoms, can move easily on either side. When subjected to shear force only the dislocation moves in one direction and the metal undergoes deformation as shown in Fig. 1.19. It is noteworthy that in this case only a row of atoms has moved successively and not the entire half crystal as shown in the mechanism of slip in Fig. 1.15. This requires much less energy and explains why the metals have much lower strength than the calculated strength for perfect crystals.
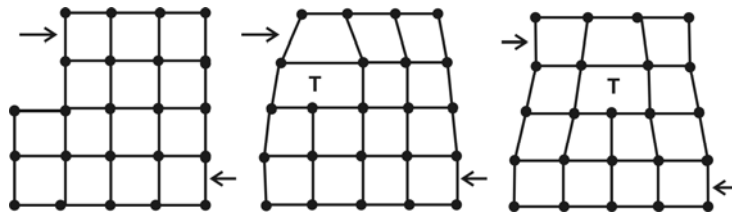
Fig. 1.19 The movement of a dislocation.

The dislocation described above is known as *edge dislocation* and the direction of slip lies at right angles to the dislocation line. When the direction of slip is parallel to the dislocation line or follows a helical or screw path, the dislocation is known as *screw dislocation*. Metals commonly have not only both the types of dislocations but also have a complex network of interconnected dislocations. Other defects, like the vacancies and impurity atoms, are also persent. The result is that while a dislocation moves, its ends remain tied or anchored to the network of dislocations or to other defects.

It has just been explained, and is clear from Fig. 1.19, that the addition of the plane of atoms pushes the adjacent atoms which exert elastic stress on both sides of the dislocation and the stress is balanced. This is true if the dislocation is wide and there are a large number of atoms on both the sides. In a narrow dislocation the forces will not be balanced and large shear force will be required to move the dislocation.

As the metals do not have atom to atom bonds, the dislocations in metals are wide. A material like diamond has carbon atoms bound on all sides by covalent bonds, therefore it cannot have wide dislocations. In a narrow dislocation the forces around it are not balanced so a large external stress is needed for moving the dislocation. Therefore, a material like diamond is hard in spite of the presence of dislocations.

The metal has defects like vacancies, impurity atoms and grain boundaries. A dislocation coming across any of these gets stuck up or its ends get tied. The dislocation is unable to move. Due to the applied stress the dislocation line bends and forms a curve, like a bow. On drawing an arrow on a bow it becomes harder to draw as the bow bends, so also the movement of the dislocation becomes more difficult as the bend increases. As the stress is further increased loops are formed which break away from the original and result in new dislocations. This is known as *Frank-Read source* and it becomes a dislocation multiplier and the number of dislocations increases.

When a number of dislocations are thus formed, only a few move opposite to each other and get neutralized. Most of the dislocations move at an angle to each other. Further, they are unable to cross the grain boundaries. The result can be better visualized by considering the example of a number of moving vehicles arriving at a crossing. This results in a traffic jam. In a similar manner, a large number of dislocations get stuck up and the movement stops. If further plastic deformation is to take place, higher stress has to be applied, i.e., the metal has become harder. This is known as *work hardening* or *strain hardening*.

Work hardening is an important tool in the hand of the engineer for increasing strength of metals. Thus any factor which obstructs the movement of dislocations causes hardening or strengthening of metals. This is the reason why metals having smaller grains are stronger than those with larger grains. The grain boundaries obstruct the movement of the dislocations. A similar thing happens when foreign atoms are added to a metal. They cause local distortion with the result that movemeut of dislocations is impeded. This explains why alloys are harder and stronger than the parent metals. On heating, the atoms get more energy, the grains grow, and the metal becomes softer and further plastic deformation becomes easier. In some alloys, like duralumin which is an alloy of aluminium with small amounts of alloying elements, on heating slightly or in course of time some intermetallic compounds are precipitated. These act as strong barriers to the movement of the dislocations. The result is that the alloy becomes hard. This is known as *age hardening*.

1.4.4 Strength and Ductility

Of all the mechanical properties strength is considered to be very important. It usually connotes resistance to deformation. Ductility is a characteristic property of metals and represents the capacity for plastic deformation at the breaking point of the metal. These two properties seem to be the opposite of each other, but non-ductile metals are not necessarily strong. They may be brittle and may break easily. However, the strength and ductility of most materials are usually inversely proportional. Of course, this generalization does not take into consideration lack of strength on account of inherent defects (like cracks) in the materials. For most satisfactory applications it is necessary to have a balance between strength and ductility.

Slip takes place along planes which have the maximum number of atoms because it involves movement of atoms through a minimum distance for acquiring new stable positions. Slip takes place more easily in metals which have the close-packed structures, namely face centred cubic and hexagonal close-packed structures. Therefore, these metals are more ductile and malleable than those having body centred cubic structure. In the close-packed structures, face centred cubic lattice is more symmetrical than the hexagonal. Face centred cubic structures therefore have close-packed rows of atoms running in several directions with the result that slip can take place in several directions. This means that when a metal having face centred cubic crystal lattice is deformed, slip takes place in several directions, and the crystal changes shape and adjusts so as to fit in neighbouring grains or crystals without leaving holes or causing crack. It is this property which is known as *ductility* and *malleability*. Therefore, the metals which have face centred cubic lattice are most ductile. The hexagonal close packed lattice does not permit freedom of slip to such a great extent, therfore such metals are more brittle than the former and are liable to develop cracks when mechanically worked. Body centred cubic metals are still more brittle and difficult to work mechanically.

With rise in temperature, the strength of a metal decreases and ductility increases. At higher temperatures the kinetic energy of the atoms increases thereby weakening the atomic bonds. Thus the metal loses strength, and ductility increases because the metal can deform more easily. *Failure or rupture* of most metals at room temperature takes place along intra-crystalline planes, i.e., through the crystals. This happens because less energy is required to shift the atoms along slip planes than by breaking many atomic bonds at grain boundaries. The atoms at the grain boundaries are not arranged in an orderly manner and therefore their shifting requires more energy. As the temperature is raised, the individual atoms lying at the grain boundaries oscillate more than the atoms in the grains. Therefore failure at higher temperatures is along the grain boundaries. This occurs quite suddenly

and without any appreciable deformation. Thus under a microscope the specimen looks like a brittle failure (this takes place suddenly and without deformation) in spite of the fact that the metal is more ductile at higher temperatures.

1.4.5 Toughness

Toughness is related to ductility as well as to strength, because it is a measure of energy required to break a material. Of two metals that have the same strength, the one which is more ductile is tougher, because in its case slip within the crystals can occur to a greater extent without rupture of the metal (Strength is a measure of the load that the material can take before breaking). If an element like phosphorus is present in steel it forms an eutectic. It does not fit into the crystal lattice, hence it concentrates at the grain boundaries. When such a sample of steel receives a shock, the slip takes place at the grain boundaries and the steel cracks; therefore phosphorus is an undesirable impurity in steel. Steel thus becomes *cold short*. If sulphur is present as FeS it forrns a network at the grain boundaries. It melts readily and makes steel brittle at red hot. This is known as *red shortness*. If sulphur is present as MnS the harmful effect of sulphur is minimized because MnS forms small globules which do not facilitate slip as FeS does.

1.4.6 Cohesion

It is a common experience that a particle cannot be easily torn off from a piece of metal. Different metals form alloys over a wide range of compositions. The metals can be joined easily. All this raises the question, what holds the metal particles together ? Such questions cannot be answered in a very satifactory manner in simple terms.

The metal atoms are not held in crystals by any chemical bond. Therefore their positions can be interchanged more easily with other atoms than the positions of the atoms of non-metal, which are bound by chemical bond. Consequently, when clean surfaces of a metal, or different metals, are brougbt in close contact as in welding or soldering, the atoms diffuse and change places readily. The free electrons move freely from one surface to the other and hold the particles together. It is this free electron cloud which acts as glue and holds the particles, which are positively charged, together. The free movement of electrons across the grain boundaries gives high cohesive strength to grain boundaries in metals. This view is supported by the fact that it is very difficult to break a cold metal along its grain boundaries. Fracture along the grain boundaries takes place either when impurities are present at the boundaries or at higher temperatures.

1.4.7 Electrical Conductivity

Many of the electrical and magnetic properties can be quantitatively explained. Such an understanding has resulted in the development of the fine particle permanent magnets, ferrites and the transistors which play an important role in the electronics industry, because both the size and the power requirement are greatly reduced.

Electrical conductivity is one of the most widely varying of all physical quantities. It is usually expressed as resistivity which is reciprocal of conductivity. The resistivities of good insulating materials like polystyrene and silica are about 10^{23} times that of good conductols like silver and copper. Between these two extremes lie the semi-codductors. For some applications high electrical resistance is needed, as in the coil of a heater. Low electrical resistance is necessary for such uses as long distance transmission lines.

Resistivity is highly sensitive to traces of impurities and to temperature, and in some cases to light. It is well-known that traces of impurities in conductors greatly increase the resistivity. It is only beginning to be recognised that traces of impurities can also considerably decrease the resistivity. This is what happens in semiconductors. One part of gallium or arsenic in 10^9 parts of germanium increases its conductivity 1000 times and makes it suitable for use as a semiconductor. A little further addition increases the conductivity of germanium 100,000 times. Pure nickel oxide is a very bad conductor but the addition of 1% lithium decreases its resistivity from 10^3 ohms per cm^3 to 1 ohm per cm^3.

In most cases change in resistivity with change in temperature is not sudden although in some cases it is sudden. Vanadium sesqui-oxide provides a good example. Its resistivity just below 150° Kelvin is about 10^6 ohms per cm^3, but just above this temperature it is about 10^{-1} ohm per cm^3.

Electrical conduction involves movement of electrical charge from one location to another. This takes place either by the movement of ions or the electrons. When the carriers of the charge are either negative or positive ions, the phenomenon is called ionic conductivity. In electronic conductivity the charge is carried by electrons.

1.4.8 Ionic Conductivity

In a material thermal agitation causes the movement of ions in various directions. This results in their collisions with other ions and atoms and the net result is that there is no conduction of electricity in any direction. When an external potential is applied the ions move to the opposite poles and electricity is conducted. If the temperature is raised the ionic mobility is increased and ionic conductivity also increases.

Ionic conduction in solids is low because energy sufficient for displacement of ions is not available. In liquids, the atoms are not as rigidly fixed as in solids with the result that movement of ions requires less energy. Therefore, ionic conductivity is more significant for the liquids.

1.4.9 Electronic Conductivity

The metallic bond theory postulates that a metal is made up of positively charged atoms (ions) and a cloud of free electrons which wander at random through the metal with no particular electron attached to individual atoms. The metal is coherent and compact because of the electrostatic attraction between the electron cloud and the positively charged atoms in the lattice. In the absence of external potential the free electrons move with equal ease in all directions in the metal (It has been shown that the average speed of a free electron in a metal is about 10^8 cm per second). This does not cause any net flow of current because there are as many electrons flowing in one direction as in the opposite direction. The result is that there is no flow of electric current through the metal and the metal is electrically neutral.

If a potential difference is imposed between the two ends of the metal the free electrons moving towards the positive pole are accelerated. Movement towards the negative electrode consumes energy and the velocity in that direction is decreased. Thus electricity flows through the metal, and electric current is proportional to the applied potential. Therefore, the metals obey *Ohm's law*, If the crystal lattice of the metal were perfect, then the only force to be overcome by the electrons would be the electrostatic attraction and the metal would have offered only a small resistance. But the lattices of all the metals have imperfections and electrons collide with the ions. If the crystal lattices are distorted, say by mechanical work, the frequency of these collisions is increased. The collisions cause the charged atoms (i.e., ions) of the metal to vibrate with increased amplitude. This is recorded as a rise in temperature and is expressed by **$H = RI^2t$**. This explains why metals offering resistance get heated when an electric current flows through them.

At higher temperatures there is greater oscillation of the metal ions, and also the spacing between the ions in the crystal lattice becomes less regular, therefore the mean free path for the flow of the electrons is reduced. This causes obstruction in the flow of electrons and electrical conductivity of metals decreases with rise in temperature. See Fig. 1.20.
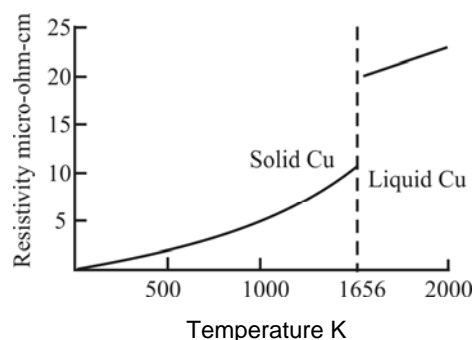
Fig. 1.20 Electrical resistivity of copper.

It is interesting to recall that at higher temperatures the mobility of atoms increases and molten metals loose their characteristic rigidity. The molten metals are mechanically weak but offer higher resistance to the flow of electrons. Fig. 1.20 shows change of resistance of copper with change in temperature. It is noteworthy that at the melting temperature, the resistance suddenly increases. This happens because although the free electrons have higher kinetic energy, the thermal oscillation of the ions also increases and becomes the dominant influence. The oscillating ions obstruct or resist the movement of electrons and electric resistance increases. As the temperature of a metal is lowered, resistance to the movement of electrons decreases with the result that electrical conductivity increases. Some metals exhibit abrupt and large increase in electrical conductivity as the temperature approaches absolute zero. This phenomenon is known as *super conductivity*. Super conductivity of metals has been demonstrated experimentally. A ring is made of a pure metal and a part of it is placed in a magnetic field when an electric current begins to flow. The temperature is reduced by the use of liquid gases. If the temperature is sufficiently low, the current will continue to flow indefinitely on the removal of the magnetic field. No satisfactory explanation for the phenomenon of super-conductivity has as yet been found. According to quantum mechanics, at absolute zero in a perfect crystal there could be no thermal oscillations and therefore there would be no obstruction to flow of electrons on this account. According to the principle of indeterminacy, given by Heisenderg there will be uncertainty in position of particles even at absolute zero. Accordingly, there would be slight ionic oscillation which would be negligible as compared to the resistance due to impurities and defects in the crystal lattice.

The case of non-metal is different. They do not have free electrons and are perfect insulators at absolute zero. With rise in temperature the thermal vibrations enable some electrons to over-come the atomic forces and they escape. These electrons are responsible for the slight electrical conductivity of non-metals at atmospheric temperature. As the temperature is increased, more electrons are made available and electrical conductivity of non-metal in-creases. See Fig. 1.21.
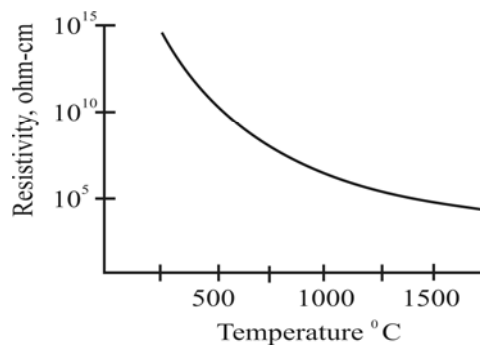

Fig. 1.21 Electrical resistivity of silica.

In a metal also with rise in temperature a few additional electrons become available for conduction of electricity, but as there are already present a very large number of conduction electrons, the effect of these additional electrons is insignificant. The disturbance or obstruction due to thermal agitation of the particles is the dominant factor. This explains why electrical conductivity of a non-metal increases with rise in temperature where as electrical conductivity of a metal decreases.

Presence of foreign elements also disturbs the regularity of the crystals, therefore impurities reduce the electrical conductivity. Both silver and gold are very good conductors of electricity. If some gold is mixed with silver, the electrical conductivity of the alloy falls greatly because the uniformity and geometry of the lattices of silver and of gold are disturbed and the electrons cannot flow easily. In the same way residual stresses and cold-work also adversely affect electrical conductivity by affecting the lattices.

This picture of electronic conductivity is based on the hypothesis proposed by Drude in 1900. His hypothesis explained successfully, and in a simple manner, several observations connected with electronic as well as thermal conductivities. He assumed that all the valence electrons take part in conduction. If this is the case, then quite a large amount of energy would be required to raise the temperature of a material. In other words, its specific heat would be high. Actually a much smaller amount of energy raises the temperature. Moreover, if a large fraction of the valenec electrons were available as conduction electrons, the conductivities of all pure metals would be almost the same. This is not the case. It is, therefore, concluded that only a very small fraction of the valence electrons take part in conduction.

Some of the questions which could not be answered by Drude's hypothesis have been answered by quantum mechanics. For such an understanding at least an elementary knowledge of energy levels is necessary. The concept of energy levels can be illustrated by taking the example of an isolated single atom of sodium. Fig. 1.22 (a) shows the commonly used simplified sketch of a sodium atom. Need for having subshells arises because of the fact that no orbital can have more than two electrons (Pauli's principle). This is depicted in Fig. 1.22 (b). The electrons in different subshells have different energy levels. These have been plotted in Fig. 1.22 (c). The energy levels are distinct and separate and electrons cannot occupy spaces between these energy levels. Electrons occupy the lowest available energy level. Therefore each successive sub shell is filled before higher energy level subshells are occupied. Analogy of water can help to explain this point. Suppose there are several inter-connected tanks placed at different levels. If water is allowed to flow in, the tank at the lowest level is first filled up. Then the tanks at higher levels are filled with water. Similar is the case with electron shells of different energy levels.

<div align="center">(a)   (b)   (c)   (d)</div>
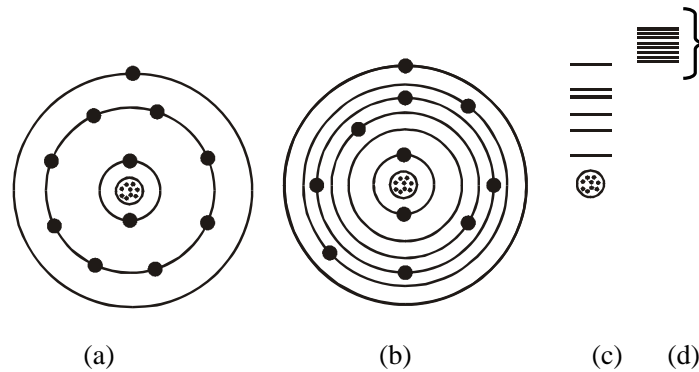
<div align="center">**Fig. 1.22** Energy levels of a sodium atom.</div>

An electron can be moved to the next higher energy level only if a definite quantity of energy, called a quantum of energy is supplied. As not more than two electrons can occupy a subshell there cannot be more than two electrons having the same energy level (The two electrons of a subshell or energy level are mirror images of each other and spin in opposite directions).

The principles stated above apply to individual, isolated atoms. When the atoms are brought together, as in a crystal which may have 10^{20} or more atoms, the situation changes. The atoms are no more isolated from each other. There is an interplay of forces of attraction and repulsion. As the nonvalence electrons are closely associated with their respective nuclei, they do not interact significantly. The valence electrons are relatively free and interact, and new energy levels are established. The defference between them is very small and they may be considered to form a group or an *energy band*, Fig. 1.22 (d). Therefore an electron may be considered to be able to occupy any level within the band because change from one level to another requires a very small amount of energy. Although the difference in the energy levels in a band is extremely small, there does exist a difference. The number of discrete levels in an energy band is the same as the number of atoms in the unit cell of a crystal.

Each energy level in a band can have two electrons. Each of the monovalent atoms contributes only one electron. Therefore the energy bands of monovalent atoms are only half filled. The net result is that the valence electrons are so arranged that they form a band, the energy levels of the lower half having the electrons and the upper half of the band remaining empty. Addition of negligible energy raises a valence electron to an empty state where it is free to move inside the crystal and to conduct electricity. This upper portion of the energy band is called the *conduction band*.

Let us now examine the case of a divalent element, like magnesium. As each atom contributes two electrons to the band, there are enough electrons to supply two electrons to each of the energy levels. It so happens

that the energy level of the first valence band overlaps the energy level of the second valence band. In other words, the energy required to occupy the lowest levels in the second band is less than the energy required in the highest levels in the first band. This results in the overflow of electrons into the second band as depicted in Fig. 1.23 (a). The electrons which now occupy the lower part of the second band can be raised by the addition of small amount of energy to an empty state, see Fig. 1.23 (b), called conduction band, just as is the case with monovalent elements, and can conduct electricity.
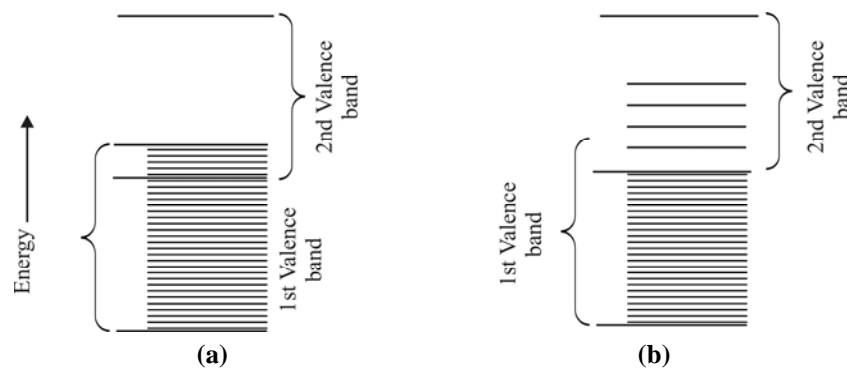

Fig. 1.23 Energy bands of magnesium.

(a) Magnesium is divalent and all of its valence electrons could fill the first valence band. As first and second valence band overlap, less energy is required to reach the lower levels in the second band than the top level in the first (b) In an external field the electrons of the second valence band are raised to the empty state and are free to move to the positive electrode.

On the application of an external electric field to an element of the type described above, the electrons get a small amount of additional energy. This raises some of the electrons to higher energy levels which were empty. The energised electrons are accelerated to the positive pole. The electrons moving in the opposite direction are decelerated. As the energising process removes electrons from some of the lower levels, vacancies are created in these levels and decelerated electrons fall into them. These two movements–acceleration of some electrons to the positive pole and reduction in the number of electrons moving in the opposite direction–cause the net flow of electricity in a direction. The materials that have such structures, as described above, are the conductors. Most metals have electronic structures of this type.

The energy bands of only a few materials, like the alkaline earths, overlap. In many cases they are separated and there is an energy gap between two adjacent bands. The size of the energy gap varies from material to material. For example, elements in the fourth group of the periodic table form covalent compounds and the crystals are cubic, like diamond crystals. Therefore, they all have high resistance. Their energy bands are full. The

energy gap between the filled band and the conduction band is different for these elements. Carbon has the biggest gap, silicon comes next, then comes germanium, and tin has the smallest gap. Therefore a small electric field raises electrons of tin to a conduction band. In germanium and silicon the gaps are not too difficult to bridge and they become semiconductors. Diamond is an insulator because the energy gap is too large. See Fig. 1.24.
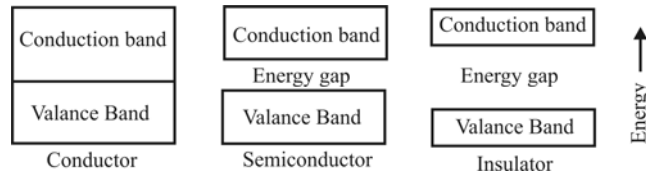
Fig. 1.24 Energy bands of conductor, semiz-conductor and insulator.

Quantum mechanics has shown that the earlier hypothesis, the Drude hypothesis, was incorrect in assuming that the mean free path of the electrons is the distance between the atoms. The movement of electrons in a crystal is like a wave. As they approach an ion, they get excited with the result that they spend comparatively little time near the ions. The result is that under ideal conditions, according to quantum mechanics, there is no collision between the traveling electrons and the ionic core of the crystal. This means that there is no resistance to an electron's travel and the conductivity is infinite. The thermal vibrations and defects in the real crystals cause collisions and scatter some of the electrons. The net result is that the mean free path of electrons is large and this explains the high electrical conductivity of the metals. The scattering of electrons further explains why only a fraction of electrons are travelling in the direction of applied voltage. The travel direction of some electrons is altered due to scattering. At higher temperatures the ionic oscillation is higher and consequently there is increased electron scattering, with the result that conductivity decreases.

1.4.10 Semiconductors

Semiconductors are, basically, classed as non-metals. In pure state and at low temperatures they do not conduct electricity. However, with increase in temperature some electrons in the valence band may be thermally excited and occupy the conduction band. The number of such electrons in the conduction band depends upon the width of the energy gap and the temperature. The promotion of electrons from valence band can take place even at the ambient temperature. The electrons promoted to the conduction band leave vacancies in the valence band which are known as holes and may be considered as positive current carriers. At any temperature, the product of the numbers of free electrons and holes is constant. Under the influence of an electrical field both move but in opposite directions and contribute to the net flow of electricity. Such a semiconductor is known as *Intrinsic*

Semiconductor and has equal numbers of free electrons and holes. The conductivity of an intrinsic semiconductor can be increased to many folds when traces of other materials are added.

Silicon and germanium are widely used as commercial semiconductors. A silicon atom, for instance, has four valence electrons which are shared by neighbouring atoms giving a structure similar to that of diamond. Thus the energy bands are filled up and pure silicon has negligible conductivity. When very small quantities (one part per million parts) of phosphorus or aluminium are added to it so as to form a solid solution with silicon, the electrical properties of silicon change greatly and it becomes an extrinsic semiconductor. Phosphorus has five valence electrons and is now in covalent structure of silicon which has four valence electrons.

Thus there is one *extra electron* which does the trick. It is not a member of the electron pair. It is a free electron and moves throughout the material. On the application of an external electrical field it is raised to higher energy level in its band and its motion is accelerated in one direction. Thus electric current is couducted. Silicon is thus "doped" with phosphorus and becomes a semicondctor of n-type. The letter 'n' stands for negative charge contributed by the additional electrons. The action of phosphorus on germanium is similar. See Fig. l.25 (a).

The solid solution of alluminium in silicon also improves the conductivity of the semi-conductor. Aluminium has three valence electrons. When an aluminium atom enters the covalent structure of silicon, see Fig. 1.25 (b), there is a shortage of one electron and a "hole" or gap is formed. This results in the valence energy band remaining unfilled. When this material is placed in an external field, an electron can move to fill the electron hole. This produces another hole which is filled by the electron of a neighbouring atom. Thus electron holes move in succession in a direction opposite to the electric field and electric current is conducted. A semiconductor of this type conducts electric current by the movement of positive holes and is called p-type semiconductor. The effect of aluminium on germanium is similar.

(a)   (b)
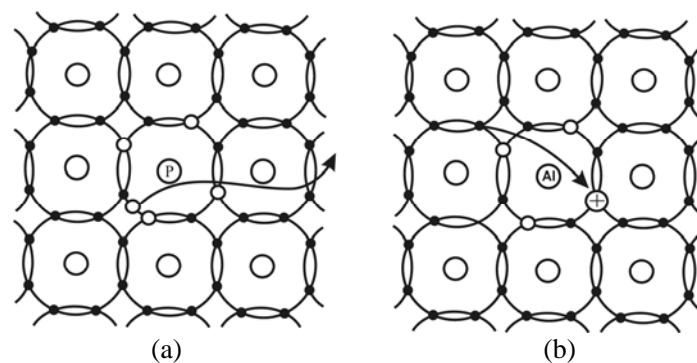
Fig. 1.25 Semiconductivity due to impurity atoms.

Thus a trace of V-group element present as solid solution in IV-group element produces n-type semiconductor and a III-group element in IV-group element gives rise to p-type semiconductor. Some other combinations also make semiconductors. There should be on an average four electrons per atom and the elements should form a covalent bond and not form ions. Although silicon and germanium are most commonly used at present, several other materials are also used as semiconductors. Some common compounds used as semiconductors are : barium oxide which is used in oxide coated cathodes, lead sulphide is useful due to its photoconductive property, and cesium antimonide finds application in photomultipliers.

The semiconductors find wide applications in making rectifiers. When a semiconductor and a metal are placed in contact, electric current flows more easily in one direction than in another. Such a device, called a *transistor*, is used in radio receivers in place of a vacuum tube. In the n-typ semiconductors the electron flows from the semiconductor to a metal but not in the opposite direction.

To summarise, the difference between conductors, semiconductors and insulators is in the energy required to cause a drift of electrons in one direction. A small electric field supplies sufficient energy to cause the drift of free electrons of a metal. In a semiconductor, free electrons are not present but on supplying a substantial amount of energy (which is often thermal or light energy) the chemical bonds are broken and conduction electrons are released. In insulators the chemical bonds are much stronger and a large amount of energy is required for releasing the electrons. Under such high voltage the insulators suffer a breakdown, like a building struck by lightning.

1.4.11   Electro-Mechanical Properties

Some crystalline materials do not have a centre of symmetry, i.e. do not have a point in the crystal about which the lattice sites and atoms are arranged symmetrically. The result is that the centres of positive and negative charges do not coincide. This gives rise to the formation of an electrical dipole. This property is generally exhibited by ionic crystals. Quartz, SiO_2, is a common example of such a material. Barium titanate, $BaTiO_3$, is still more interesting in the sense that above 120° it forms cubic crystals with the oxygen ions at the centre of each face and a titanium ion at the centre of the cube, barium ions occupying the corners. Below 120° its crystals are tetragonal with an oxygen ion near the centre (not at the centre) of each face and a titanium ion near the centre of the cell. Thus each cell has positive and negative sides and acts as small electric dipole. A number of such unit cells align in the same direction in a domain giving an enhanced dipole effect, i.e., there is a build up of negative charge on one end of the crystal and positive charge at the other end.
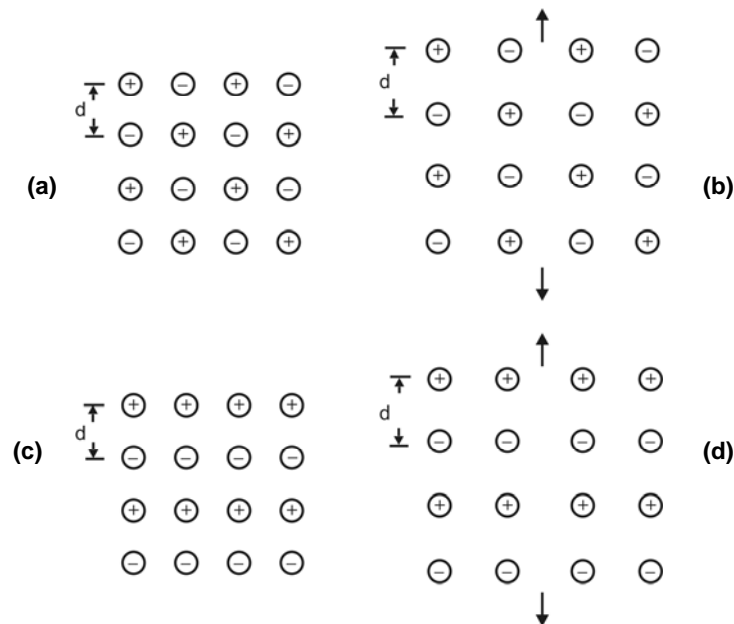
Fig. 1.26 (a) An ionic crystal with a center of symmetry (b), no induced dipole moment is formed under tensile strain (c), In an ionic crystal with no center of symmetry (d), a dipole moment is formed under tensile strain.

Fig. 1.26 (a) depicts an ionic crystal with a centre of symmetry and Fig. 1.26 (b) makes it clear how no dipole moment can be induced in such a crystal. Fig. 1.26 (c) is of an ionic crystal with no centre of symmetry and in Fig. 1.26 (d) it is clear why a dipole moment is induced on applying a stress.

Rochelle salt (potassium sodium tartrate) is more sensitive than barium titanate but is easily attacked by moisture and can be used in the temperature range 18° to $24\ ^oC$. Other salts commonly used are ammonium dihydrogen phosphate (ADP) and potassium dihydrogen phosphate (KDP). Lead titanate ceramics are used for higher temperature applications than barium titanate (whose crystal changes to the cubic form at 120°).

When such a crystal is compressed (or pulled) with a stress, the dipole length d is changed and if there is a conducting path the charge difference between the two ends is decreased, otherwise a voltage differential is obtained. On the application of an external voltage across the crystal the dipole length decreases (Fig. 1.27(a)) or the length increases (Fig. 1.27(b)) depending upon the electrode applied. Thus there is a change in the dimension on the application of an electric potential or a potential difference is produced on the applications of stress. Such a combination of mechano$\rightarrow$electrical and electro$\rightarrow$mechanical actions is called *piezo electric effect*. "Piezo" means "pressure".
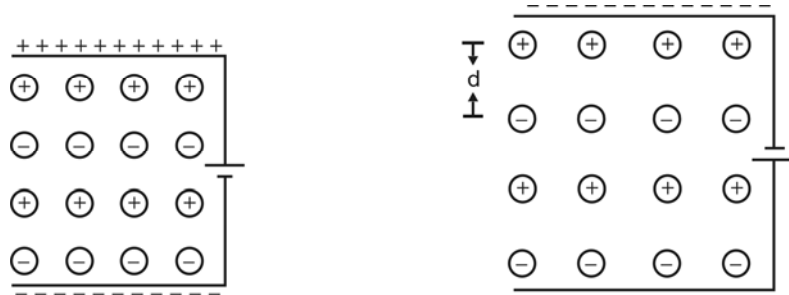
Fig. 1.27 Electric field induces dimensional changes in a piezo electric material.

In an alternating electric field the crystal vibrates with the frequency of the alternating field. This pheonomenon has enabled the production of devices called *transducers* which are used in micro-phones, phonograph pickups, pressure measuring devices for high pressures, strain gauges, under-water sound equipments for both picking up and sending sound waves, ultrasonic vibrators, etc.

1.4.12   Thermal Conductivity

Like electrical conductivity the thermal conductivity of metals is primarily due to free electrons. In the latter case, the driving energy is a difference in temperature between the two ends of a metallic bar. The electrons at the hotter end of the bar acquire more kinetic energy and move to the colder end, thus transferring the energy and heat to the colder end. The electrons from the colder end are pushed by the energised electrons to the hotter end where they also get energised. Thus metals are good conductors of electricity as well as of heat. At a particular temperature there is a direct relationship between the electrical and thermal conductivity of a metal. Impurities reduce both types of conductivity. Hence alloys are poorer conductors of heat than pure metals. Although the electrical conductivity of metals falls with a rise in temperature, the thermal conductivity does not fall at that rate because at a higher temperature each electron carries more energy (although it carries the same quantity of electricity) and so transfers more thermal energy to the colder end. This is offset to some extent by the increased resistance to electron flow because of an increased rate of oscillation of the ions at the higher temperature. The thermally excited lattice vibrations also make notable contibution to the thermal conductivity of the solids. In metals and semi-conductors both the electrnoic conduction and lattice conduction may occur. However, in metals electronic conduction due to free electrons dominates. The mechanism of thermal conductivity of non-metals is a little more complicated but can be explained in a similar manner.

1.4.13   Magnetism

The magnetic properties of materials were put to use long before the cause of magnetism came to be understood. For ages the needle of a compass has enabled the traveller to find the direction. Use of magnetism in the generation of electricity on a wide scale is well-known. Magnetic properties of materials help to reproduce sound and visual images. They help to energise electric motors and to turn speedometers. They enable a computer to store information. Even in small devices, say like the door latch of a refrigerator, the magnetic property of a material proves handy. But the cause of magnetism has only come to be understood during the last few decades. Even now a number of questions remain to be answered.

Magnetic properties of materials are usually grouped in three classes. Iron, cobalt and nickel and some specialized alloys are highly rnagnetic. They are strongly attracted to a magnetic field. They can be easily made into powerful magnets. This property is known as *ferromagnetism*. The ferromagnetic materials become more magnetic in a relatively weak magnetic field. The majority of metals like magnesium and tin and many other materials are very weakly attracted to a magnet. This property, known as *paramagnetism*, is also exhibited by the ferromagnetic materials above a specific temperature. The other metals, like antimony and bismuth and all non-metals show magnetic response in a direction opposite to the applied field, i.e., they are weakly repelled by magnetized objects. This very weak property, known as *diamagnetism*, has not yet proved to be of any practical significance.

In 1820, more than a century before the present theory of magnetism was propounded, H. C. Oersted made an important discovery which can be considered to be the forerunner of the modern theory of magnetism. He found that an electric current affects a magnetic needle. Later, both Ambere and Arago magnetized steel needles by placing them in a helix of wire carrying an electric current. This simple experiment that a moving electric charge creates a magnetic field, seems to have inspired the great exponents of quantum mechanics theory to explain the subtleties of magnetic behaviour. Briefly stated, the idea is that the moving electrons of the atoms are like an electric current flowing through a wire and give rise to a magnetic field. In 1926 Goudsmit and Uhlenbeck enlarged upon Pauli's idea and proposed the spinning electron as the fundamental magnetic particle. The quantum theory of magnetic behaviour was then rapidly developed by Heisenberg (1928) and others.

The atoms of a ferromagnetic material have permanent magnetic moments. There are three factors that can cause magnetic moment in an atom. Nuclei of some atoms also act as magnets. In most cases their effect is negligible because magnetic moment is inversely proportional to the mass. Therefore, magnetic moment due to the nuclei is about 2000th part of the magnetism due to the electrons and can be neglected.

Electrons contribute to magnetism in two ways. An electron moves round the nucleus in an orbit and also spins on its axis. Both these cause magnetism along the axis of rotation. Of these two factors, the spin of the electron makes a more important contribution to magnetism. S. J. Barnett and others have experimentally established that when magnetization of an iron group of elements is changed, the direction of spin of some of the electrons in the atoms also changes but their orbital motions remain practically unchanged. The orbital moments of electrons of rare-earth elements and in compounds contribute to magnetism substantially.

In most of the atoms, as they are arranged in molecules and solids, there exists a tendency in electrons to form antiparallel and self-neutralizing pairs with the adjacent electrons (An antiparallel pair means that if one of the electrons of the pair spins in clockwise direction, the other spins parallel to it but in anti-clockwise direction). Thus the spin and orbital angular moments of the pair get neuturalized and the total magnetism being zero, most of the materials are classed as 'non-magnetic'. They really have extremely weak magnetic properties. The application of an external magnetic field causes slight unbalance in the pairing. In the case of some metals, the unbalance is only in the spin pairing of electrons. This results in weak paramagnetism. In other cases the orbital pairing gets slightly unbalanced and diamagnetism results.

The tendency to form antiparallel pairs is in accord with the requirements of Pauli's exclusion principle and quantum mechanics which state that two electrons cannot occupy the same state i.e. there cannot be two electrons, having the same spin and angular movement, moving in a particular orbit. This objection is overcome by forming an antiparallel pair, thereby two electrons occupy the same orbit. It is believed that the two electrons completely interpenetrate each other and are in away, superimposed on each other. The positive charge of the nucleus attracts the electrons and prevents them from flying away. The antiparallel behaviour has been mathematically worked out by Heisenberg in terms of quantum mechanical forces of exchange which act between electrons in neighbouring atoms. The exchange forces are a function of the ratio of the atomic spacing in a metal crystal to the diameter of the 3d subshell. If this ratio is within a narrow limit the exchange forces are positive and ferromagnetism results. Only four elements (Fe, Ni, Co, and Gd) have positive values and are ferromagnetic. In other cases the exchange forces are not positive. For example, all the five electrons in the 3d subshell of a chromium spin in the same direction. Its exchange force being negative, the atoms do not so align as to have magnetic moment in the same direction with the result that chromium is not ferromagnetic in spite of the fact that a single atom of chromium has five electrons with spin in one direction and an iron atom has only four such electrons. Besides the exchange forces, there are electro-static and magnetic forces. A more detailed discussion of the subject is beyond the scope of this book.

From the foregoing discussion it can be generalized that all the elements that have an even number of electrons are non-magnetic, and those which have an odd number of electrons will have an unpaired electron per atom and such elements should exhibit feeble magnetic properties. Even in such a case the outer unpaired electron forms an antiparallel pair with an electron of another atom of its kind which comes near it in the solid state.

The transition metals and rare earths are characterized by unfilled electron shells i.e., some electrons occupy outer shells before inner shells have been completely filled. This introduces deviations from the generalization that we have just now made. The outer valence shell of these elements has a pair of anti-parallel electrons but some of the inner shells are unpaired. For example, in iron, cobalt and nickel the third shell is incomplete whereas the fourth shell has a pair of electrons. The outermost pair of electrons may be considered to form a protective layer and prevents the inner unpaired electrons from forming pairs with similar electrons of a neighbouring atom. This can be illustrated by taking the example of iron, which has been shown in Fig. 1.28.
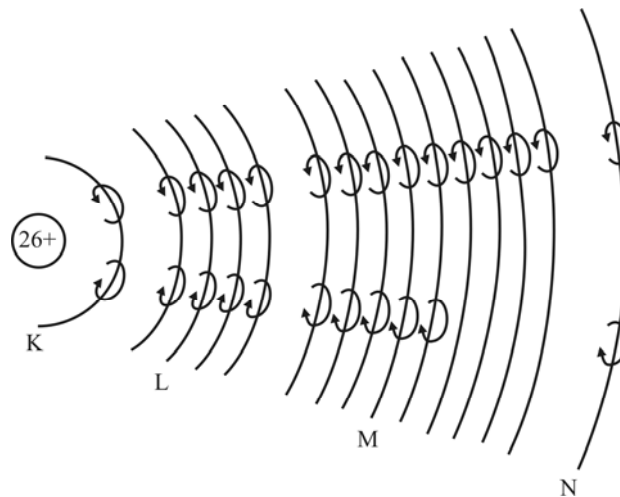
Fig. 1.28 Electron shells of iron. Four unpaired electrons of 3d subshell make iron ferromagnetic.

The 3d subshell can have 10 electrons moving in 5 pairs in 5 electron orbitals. In an iron atom it is unfilled and has a pair of anti parallel electrons and 4 unpaired electrons moving in 4 orbital. There is a pair of electrons in 4s subshell. The unpaired electrons with spin in the same direction make an iron atom a small permanent magnet. A cobalt atom has 3 unpaired electrons spinning in the same direction and similarly a nickel atom has 2 electrons. When the atoms of these elements come close together, as in the solid state, the pair of antiparallel electrons of the 4s subshell of an atom gets disrupted

and forms free electrons or the "electron cloud" and these electrons take part in electrical conduction. The spins of electrons of neighbouring atoms, in small volumes called *domains*, are held parallel by strong quantum mechanical forces which exercise a coupling effect. This effect is a short-range effect and electron screening limits its field with the result that the domain volumes are very small. When the temperature of a magnet is raised, the energy of thermal agitation tries to counter act the coupling effect and above a definite temperature the thermal energy overcomes the alignment and the material ceases to act as a magnet. This temperature is known as *Curie temperature*. It has been experimentally observed that the saturation magnetization of a ferromagnetic material decreases with increase in temperature, becoming zero at the Curie tempurature. On cooling to a temperature below the Curie temperature the quantum mechanical forces again become the stronger forces causing coupling of atoms with parallel electrons spins. Curie temperature of iron is 780°, cobalt is 1175°, nickel is 365° and of gadolium is 16°.

Another interesting behaviour of the coupling effect may be mentioned. Some materials like chromium, copper chloride, ferrous fluoride, manganese fluoride, manganese oxide and nickel oxide show feeble magnetic properties and are paramagnetic. The magnetic susceptibility of such a material increases as it is cooled to a temperature known as *Neel point*. Below this temperature atoms with opposite spins form antiparallel couples and no magnetism is observed. This property is known as *anti-ferromagnetism*. As the temperature is increased above the Neel point, the increased thermal agitation destroys, more and more, the regular alignment of atoms with spin in the same direction and magnetism decreases. The Neel point, for example, of manganese fluoride is minus 206°.

The structures of certain ceramic compounds, which contain iron, nickel, cobalt or manganese are such that they exhibit a property known as *ferrimagnetism* (not ferromagnetism). These have lower magnetic moments than the ferromagnetic materials. The important materials of this class are (magnetic) *ferrites* and *garnets*. These can be represented by the general formula AB_2O_4. The A cations are divalent (Ni^{2+}, Mn^{2+}, Fe^{2+}. etc.) and the B cations are covalent (Fe^{3+}). The crystals are cubic and the structure is decided by oxygen ions which are larger than the metal ions. There are two kinds of positions that are available to the metal ions to occupy. The metal ions occupying one kind of position have their magnetic moments pointing in one direction and those occupying the other kind of position have their magnetic moments in the opposite direction, i.e., the two sides are antiparallel. The two magnetic moments try to neutralize each other, but they are unequal with the result that the material shows a certain amount of net magnetic moment in one direction. For example, in magnetite the magnetic moment to two iron atoms point in one direction and one in the opposite direction. The net result is that in every three atoms the magnetic property is due to one atom.

Ferrimagnetic materials have certain advantages over ferromagnetic materials. When the latter are subjected to changing fields at high frequencies, as in communication engineering, eddy currents are formed causing energy losses. These losses are reduced by using a material that has high electrical resistance. Efforts to produce such materials led to the use of non-metallic refractory materials, called ferrites having resistance of the order of 10^6 ohm. Proper mixtures of the oxides in the powdered form are pressed into the required shape and heated to over 1000°. On cooling a hard, strong and brittle material is obtained. As these have very high electrical resistances the eddy current formation is eliminated. Their hysteresis loops are such that they are very useful for certain applications, as in high frequency appliances. In these materials only some of the atomic magnets point in the same direction therefore the maximum induction attainable is much lower than in ferromagnets. Moreover, these are brittle, hence are unsuitable for use in transformers, generators and motors.

We have so far considered the behaviour of magnetic materials on the atomic scale. The forces of exchange, whose existence has been established by quantum mechanics, cause the parallel alignment of the electron spins in a number of atoms. These atoms form small cubes (about 0.02 mm side) which are called *domains*. The domain theory was first proposed by Weiss in 1907 but his description, with slight modification, was accepted in the 1960s. According to him the magnetic strength of a material is the sum or the magnetic strength of the domains. The domains lying at different angles tend to cancel the strength of each other. In a magnetic field the domains align and point in a direction with the result that the magnetic field is greatly increased. The existence of the domains was first established by Barkhausen who connected amplifier and headphones to magnet. On changing the magnetic field clicks were heard indicating changes in the domain structure. The existence of domains has been confirmed by studying the distribution of magnetic powder on the surface of a magnet.

It is a well-known principle of physics that all systems tend to attain a state possessing minimum energy. Therefore, the stable configuration is that for which the total energy is the minimum. It is seen from Fig. 1.29 that as a magnet is subdivided, the external lines of force of a magnet are shrunk. In other words, when a magnet is sub-divided, or the number of domains is increased, the energy of the external field is reduced. At the same time, as the
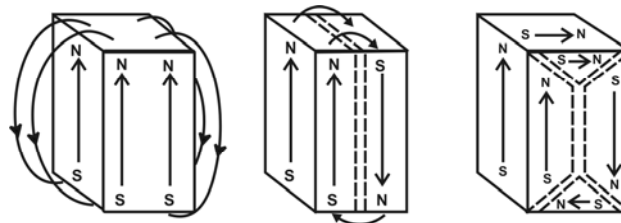
Fig. 1.29 Formation of domains.

number of domains increases the short range coupling energy increases because domain boundaries increase and a larger number of magnets have to be held in anti parallel alignment as can be seen from Fig. 1.29. At a certain subdivision an equilibrium is established between these two opposite effects and state of minimum energy is reached. If the domains are of larger size then the external field energy is higher and if the domains are smaller then the coupling energy is higher. It is the equilibrium state which determines the domain size.

The domains with antiparallel alignment are separated by a wall (called the Block wall, named after the discoverer) which is a few hundred atoms thick. In this wall the atoms gradually change direction from one side to the other side of the wall and point in the opposite direction.

Within a domain all of the atoms are aligned parallel and a domain acts like a tiny little magnet. In an 'unmagnetized' ferromagnetic material the domains lie at different angles cancelling the magnetism of each other. On applying a magnetic field the domains (with the atoms in each domain still remaining parallel to each other) turn so as to align more nearly with the applied magnetic field. In some materials this happens easily and in others with difficulty. In other words, some materials are easy to magnetize and also easy to demagnetize after the magnetizing field is removed. These are called magnetically *soft*. The materials that are difficult to magnetize and demagnetize are *hard*. Mechanically hard materials are magnetically hard also, and the same rule applies for soft materials.

In 1885 Ewing noticed that a ferromagnetic material continued to show magnetism even after the external field was reduced to zero. On reversing the field it got magnetized in the reverse direction and on removing the field some magnetism persisted in that direction. To reduce the magnetism to zero it was necessary to apply a certain field in the opposite direction. This happens because some of the domains do not return to their original positions after removing the field. This tendency to retain induced magnetization after the removal of magnetization is called *hysteresis*.

In hard materials more energy is required for turning the domains. Therefore, more of the induced magnetism remains in hard materials than in the soft materials. Hard materials are necessary whenever permanent magnets are requird, as in loudspeakers, telephone receivers, meters of various kinds, electric clocks and magnetos. Soft materials give higher efficiency whenever intensity of the field is to be changed, as in the case of a generator, motor or transformer.

As both hard and soft magnetic materials are important for various uses, the causes which contribute to one or the other kind of property have been studied and a number of new materials have been developed.

Hysteresis is best depicted by plotting the intensity of magnetization against the field strength. When the field is reversed, the demagnetization curve does not follow the magnetization curve and within the two curves is enclosed an area known as the hysteresis loop. This area is small for soft materials and large for hard materials. This gives an idea of the energy loss, which appears as heat energy in the process of the magnetization, demagnetization and remagnetization cycle.

The application of a magnetic field can affect the domains in two ways. If the field is of low, or of medium strength, the domain walls, move and the size of the domains whose magnetization is parallel to the applied field increases and the size of domains with antiparallel magnetization decreases. The movement of the domain walls is reversed when the field is reversed. The application of a strong field causes the movement to such an extent that the domain walls are pushed between the imperfections and impurities present in the material. The result is that when the field is brought to zero, the domains which pushed the imperfections cannot return to their original positions. This causes residual magnetism. The more the imperfections and obstacles, the greater will be the residual magnetism and the harder will be the material. The material for making soft magnets should therefore have a minimum of imperfections and the crystals should preferably be oriented in the same direction. Cold working and increasing the imperfections makes a ferromagnetic material suitable for making a permanent magnet. Heat treatment, like annealing reduces internal stresses and the material becomes more suitable for making a soft magnet.

The foregoing discussion also explains the cause of the observed phenomenon known as *magnetostriction*. The change in the degree of magnetization of a ferromagnetic material is accompanied by a small corresponding change in its length. In most cases the length increases in the direction of magnetization. This happens because magnetization is an anisotropic property i.e. it is different in different directions of the crystal. There are certain preferred directions in a crystal in which magnetization takes place easily. Magnetostriction is made use of in making oscillators giving high frequency and low amplitude vibrations, certain supersonic generators for testing metal and underwater radar. From this it can be expected that mechanical stress will affect magnetic properties. Large stresses which cause plastic deformation of the material decrease the permeability (i.e., the magnetization becomes more difficult). Stresses within the elastic limit may increase or decrease permeability depending on the nature of the material. It is believed that the humming sound made by the transformers is due to magnetostriction i.e., due to stretching of the crystals in the direction of magnetization. The direction being reversed so frequently in the ransformers, the domains change shape giving the humming sound. Magneto striction also causes more energy losses (hysteresis losses).

Another source of energy loss is from eddy currents induced by field changes. This increases with increase in the frequency of the changes. This source of loss can be lowered by increasing electrical resistance e.g., by introducing impurities. Another way to cut down eddy current is by making the magnet from sheets of the metal with alternate layers of an insulating meterial. This reduces the area of the conducting metal and eddy currents are reduced. Considerable attention is being paid to the development of magnetic materials particularly suitable for electrical industry. Several materials have been developed which have low hysteresis losses. One of the early materials developed was by N. P. Goss in 1934. He prepared steel with 3% silicon and subjected it to a series of mechanical working and heat treatment processes whereby most of the crystal grains were oriented in the same direction. Thus hysteresis lossess are reduced. Due to silicon it has higher electrical resistance. This decreases eddy current which is another source of energy loss. Other alloys using silicon in steel have also been developed, for example, 1 to 3% silicon is used for those magnets which need to have mechanical strength, as for the rotating parts of the motor and generator. Higher amounts of silicon help to reduce eddy currents but make steel too brittle. In transformers 4.5% of silicon has been used. 6.5% silicon makes steel too brittle with no magnetostriction.

For some applications it is more important to reduce hysteresis losses than to save on the cost of material. In such cases costlier alloys like *permalloy* (78.5% nickel and 21.5% iron) are used. In this alloy both magnetostriction and anisotropy are very low. Addition of molybdenum reduces both these disadvantages to zero. Permalloy is suitable for transformers that transmit weak signals communication apparatus. *Hipernik* (50% nickel and 50% iron) has low hysteresis losses and high permeabilities in the stronger magnetic fields as for transmission of power. The properties of these alloys are further improved by heat treatment. *Supermalloy* (79% nickel, 5% molybdenum and 16% iron) after heat treatment in pure hydrogen at 1200 $^{\circ}$C has very high permeability.

Some alloys of iron and cobalt (containing 35% to 40% cobalt) show higher intensities of magnetization than either iron or cobalt alone. Another important alloy is *perminvar* (25% cobalt, 30% iron and 45% nickel) whose permeability is independent of field strength over a relatively wide range. Heat treatment alters its magnetic properties and makes it more useful for certain applications. In most cases, cited above, no satisfactory explanation has as yet been found to explain the special magnetic properties of the alloys.

Mention may be made of the materials for permanent or hard magnets. *Alnico* (about 55% iron, 18% nickel, 12% cobalt, 10% aluminium and 5% copper) and *MK steel* (about 55% iron, 30% nickel and 15% aluminium) are some of the widely used alloys of this type. Fore making the magnets, alloys of this type are melted and poured into moulds having cold bottoms and hot sides. Freezing takes place from the bottom upwards producing elongated crystals. These alloys are of the precipitation hardened type. It is believed that the very small particles, having single domains are precipitated. These particles point in the same direction, and therefore give highly permanent magnets. "*Lodex*" is essentially an alloy of iron and cobalt embedded in lead. This also gives permanent magnets and has the advantage that due to the presence of lead, it can be easily made into the desired shapes.

Applications of magnetic materials seem to be unending. Requirements of the digital computer may be mentioned briefly. Its memory unit is of a magnetic material which should be hard enough to store information for a long time. If it is too hard then the information will not be neatly and rapidly read-in and read-out. Therefore, the material must have properties in between hard and soft magnets. To attain this, tapes coated with ferrites are being used.

1.4.14   Optical Properties

For obvious reasons the optical properties in the visible range are of special interest. Infra-red and ultra-violet radiations are also of interest as they cover some frequencies which bring about certain electronic transition in metals. On passing through the solid, depending on its nature, some or all of the intensity of light is absorbed through electronic interactions. Thus as light travel through the solid, its intensity decreases continuously. Some of the light reaching the back surface is internally reflected and the remainder passes out of the material.

The metals are opaque and have high reflectivity. In a metal, just above occupied level in the conduction band, there are many empty electronic states. Electrons excited to higher energies by incident radiations of wide range of frequencies are absorbed in them. This causes light to be absorbed within a metal surface on traversing a very short distance. Thus light is transmitted only through metal films of thickness of the order of 10^{-4} mm or even less. The excited state of electrons being unstable, they quickly fall back to the lower energy levels causing re-emission of light. This total

process, of absorption of incident radiation, electrons excitation to higher energy levels and their falling back to the lower energy levels emitting radiations, is the cause of reflectance of the metals. If certain frequencies of the incident white light are not remitted, the surface looks coloured. As the electronic structures of different metals (especially of the filled '*d*' band and the empty '*s*' band) differ from each other, different wave lengths in the visible region are preferentially absorbed. This gives different colours to different metals. Many metals have high density in the electronic slates in different part of the '*d*' band causing low reflectivity throughout the visible range. This gives them a grayish colour.

It is more difficult to make a simple generalization of the optical properties of *non-metals*. Depending on their band structure they may be opaque or transparent and may look coloured or clear. This is due to, as already explained, the selective nature of the absorption, reflection, scattering and transmission processes. The atomic vibration frequencies of most metals are comparable to the photon frequencies. Photon absorption also takes place because of the interaction with electric dipoles included by the atomic vibrations.

In many *semiconductors* the light frequencies are able to execite electrons from the valence band to the conduction band. Thus visible radiations get absorbed and the material is opaque and has dark gray colour and dull metallic lustre. When the energy gap corresponds to certain photon frequency in the visible range, distinctive colour is observed.

Materials like inorganic glass, polymethyl methacrylate, diamond, common salt and ice are *electrical insulators*. They have large energy gap and light cannot excite the electrons to the higher energy states with the result that they have very small reflection and are transparent.

The noncubic polycrystalline materials have different index of refraction in different directions and light is scattered or reflected in different directions at the grain boundaries. This makes them milky white in colour or translucent.

Materials which are normally transparent but have porosity appear opaque. This explains opaqueness of most *ceramic materials*. Thin sections of polycrystalline alumina is transparent but sintered alumina, which has pores, is opaque.

1.4.15 Solid State Chemistry

In this chapter the engineering properties of materials have, in general, been considered mainly from the physicist's point of view. In many cases it is neither possible nor proper to make a rigid distinction between physics and chemistry. In this Section an attempt will be made to point out how the so-called laws of chemistry, which the student is apt to apply only to reactions in which at least one reactant is a liquid or a gas, also apply to the solid state. The applications of these laws have not only thrown new light on the understanding of physical properties of materials, but have also contributed to the development of new and more useful materials.

The previous Section of this chapter have shown the importance of defects or imperfections in the crystals on the physical properties of the materials. One of the most important contributions of chemistry in the field of solid state is the study of these defects. The technique of the chemist can be explained by a simple example. In the simple experiments which every student performs in the chemistry laboratory, he focusses his attention on the minor components like the solute and ignores the major component like the solvent e.g., water. He mainly concerns himself with the reactants like the various acids, bases and indicators which are in small quantities as compared to the water in which they have been dissolved. In the same way the chemist pays special attention to the minor constituents i.e. the defects in the solids, which greatly affect their properties. This approach helps to produce defects in a controlled manner thereby introducing the desired properties in the materials.

In the solid state, several important chemical reactions take place due to lattice defects. One such defect, called a *vacancy*, is the absence of an atom from its site in the crystal lattice. At room temperatures about one vacancy per 1000 sites is present in the crystals. The vacancies can move throughout the crystal, the neighbouring atoms or ions taking their places, similar to the movement of the extra electron as explained in this Chapter in the Section on semiconductors. The importance of vacancy can be shown by considering the photographic process. The emulsion on the photographic plate has ionic crystals of silver bromide. An electron is released from one of the bromide ions when light strikes the crystals. This electron is trapped by an impurity atom in the crystal. As this atom has negative charge, it becomes a centre of attraction for positively charged silver ions. The movement of the silver ions in the solid state takes place by migrating through the vacancies. The cluster of silver ions thus formed produces the latent image which is subsequently made prominent by the developing process.

Phosphorescence is another solid state reaction. Phosphors are mainly based on zinc sulphide and are used as the coating on television screen. These get activated by an electron stream. In zinc sulphide crystals the electrons are released by ultra-violet rays or by the impact of a stream of electrons. The electrons so released are temporarily raised to higher energy level and may quickly fall back into their old positions. In the presence of an impurity atom they may be trapped at some higher energy level which is a matastable position. Tbe electron may later escape from the trap and fall back to its old energy level. In this process a quantum of light is released. Similar phenomenon takes place in the paints which shine in darkness. Along similar lines photo-conductivity, i.e. conduction of electricity by the action of light, can be explained.

Application of the law of mass action can be taken as another illustration. In the common salt analysis this law is applied for the precipitation or removal of a constituent as an insoluble solid by common ion effect. In the same way, in a crystal an ion or atom can be removed from its place. If an atom is displaced from its position in a crystal it has two effects. A vacancy is created in the place from which the atom has been displaced. The displaced atom then occupies a place where there was normally no atom, thus interstitial defect is created. If the temperature is high enough, a neighbouring atom can jump into the vacancy leaving its original place vacant. Thus the vacancy as well as the interstitial atom can move through the crystal lattice. The law of mass action governs the concentrations of these defects. If a divalent ion is introduced in a lattice, it displaces two monovalent ions. If calcium chloride is introduced in a crystal of sodium chloride each calcium ion occupies the position of a sodium ion and also displaces another sodium ion creating a vacancy. According to the law of mass action, the product of the concentrations of vacancy and interstitial ions is constant. Therefore, increase in the concentration of vacancy causes a decrease in the concentration of interstitial ions. The technique enables one to adjust the concentrations of vacancies and interstitial ions and thereby certain properties can be adjusted.

Suppose there is a saturated solution of oxalic acid. If some oxalic acid crystals are added to the solution, the crystals do not dissolve and settle below the solution. On adding an alkali solution to it, the undissolved oxalic acid crystals dissolve. This simple experiment shows that the presence of an alkali increases the solubility of an acid. This principle has been applied for developing a semiconductor crystal having a positive-negative junction. A portion of the crystal is 'doped' with a donor of electrons and the balance with an acceptor of electrons. Arsenic (which is pentavalent) atoms in silicon (which is tetravalent) crystal can donate electrons whereas aluminium (which is trivalent) atoms act as acceptors. Such a junction allows the electrons to flow in one direction only i.e., from the donor to acceptor (or from positive to negative junction). A system of this kind helps to build

transistors. On joining a positive-negative junction with a negative-positive junction, a current amplifier is built. The contribution of chemistry in such a field of study is clear from the example of the increase of the solubility of an acid by the presence of an alkali. The solubility of an acceptor (like aluminium in silicon) is increased by the presence of a donor (like arsenic or phosphorus) in silicon. In a similar way the mechanical properties can be adjusted by influencing the dislocations.

Precipitation experiments are familiar to all the students of chemistry. If hydrogen chloride is added to a saturated solution of sodium chloride pure sodium chloride precipitates because of the increase in the concentration of chloride ions. In a similar manner, aggregates of atoms can be pushed out of the solid solution and deposited at various places in the crystal (Solid solutions are homogeneous mixtures of two or more components in a solid state). As an illustration, a solid solution of lithium in silicon can be considered. Lithium donates electrons to the solid solution. If another electron donating substance is added to this solution, the solubility of lithium will be decreased and lithium atoms will precipitate out of the solid solution. By adjusting the concentrations of the constituents, it is possible to form small aggregates or particles of lithium. In the Section on semiconductors the influence of such defects on electrical conductivity has been shown. In a similar manner, precipitates can be formed which influence mechanical properties like brittleness, plasticity or strength of a crystalline material.

The chemical laws have been verified in the solid state more accurately than in the solutions. The combined efforts of the physicists and the chemists have resulted in a better understanding of the principles of the properties of materials. This has resulted not only in the more efficient use of the materials but also has helped to develop new materials.

These are only some of the illustrations which show how the reactions in the solid state influence the properties of the materials. As understanding of the subject develops, it is hoped that like other traditional branches, solid state chemistry will form a well-defined branch of study.

1.4.16   Factors Affecting Engineering Properties

The strength of a single perfect crystal of a metal is over a hundred times more than that of the same metal as generally used. The metal in its commercial form consists of a number of crystals or grains and, therefore, is polycrystalline. The lower strength of the metal is due to (i) defects or dislocations within the grains and the presence of the grain boundaries and (ii) presence of foreign matter or imperfections introduced during the manufacture of the metal. The foreign matter or imperfections, like non-metallic inclusions, alloying elements, dissolved gases, porosity, etc., tend to segregate or concentrate at certain points in the body of the metal.

Starting with a metal having the aforesaid limitations, its properties can be altered by the following factors or operations :

1. Control of grain size
2. Mechanical working.
3. Alloying other elements
4. Heat treatment.

The reasons for improvement in properties due to the control of grain size and mechanical working have already been outlined in this Chapter. Alloying and heat treatment will be dealt with in later Chapters. It may suffice here to say that heat treatment is a very important factor in controlling the properties, but it applies only to alloys. Pure metals have little response to heat treatment.