

# Chapter 2

## Structure and Bonding

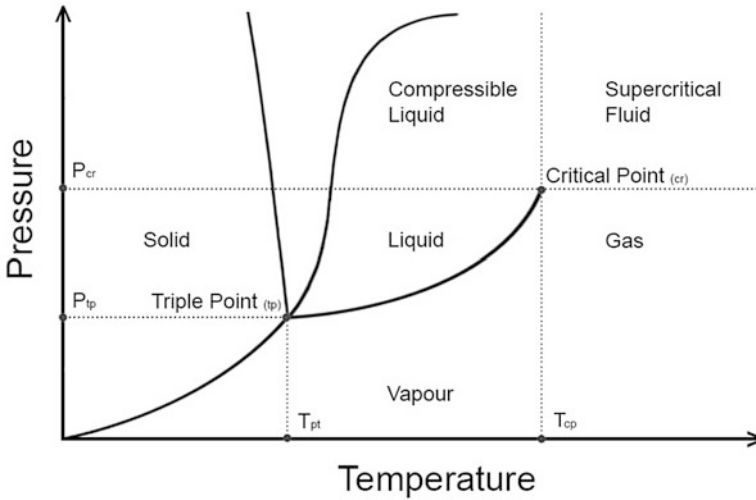
### 2.1 Introduction

Matter is composed of atoms and molecules. Gases, liquids and solids are different states of matter (there can be some other states also under some extreme conditions of matter). However they can get converted into one another depending upon their stability at different pressure, temperature or variation of both. For example, as illustrated in Fig. 2.1, water molecule ( $\text{H}_2\text{O}$ ) can be in gaseous state (vapour), liquid state (water) or solid state (ice) depending on the temperature and pressure. Water vapour can be converted into liquid water or ice by cooling. Similarly ice can be turned into water and then vapour by heating. At the triple point, solid, liquid and gas co-exist. Critical point as shown in Fig. 2.1 is a point at which some critical values of temperature and pressure are reached. Beyond this point there is no distinction between gas and liquid phase.

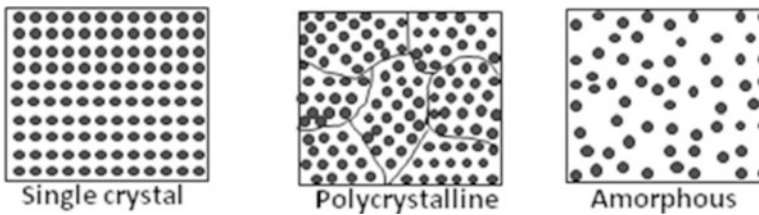
Density of gas is usually very low  $\sim 10^{19}$  atoms/cc, whereas that of solids and liquids is high viz  $\sim 10^{23}$  atoms/cc (we are not considering here porous forms of solids). Correspondingly the distances between atoms (or molecules) in gases are 3 to 4 nm. In solids and liquids the distances between the atoms or molecules are typically 0.2–0.4 nm, an order of magnitude smaller than in gases.

One can see that the density and distances between the atoms or molecules for both liquids and solids are comparable. However a liquid does not have a particular shape and takes the shape of its container. Atoms or molecules in a liquid, as in a gas, are under a state of continuous, random motion known as Brownian motion. In solids the situation is different. There the atoms and molecules also are in a state of motion, but the motion is about their fixed positions. Atoms and molecules vibrate about their fixed positions with some characteristic frequencies.

Let us now consider a solid like  $\text{Al}_2\text{O}_3$ . It can appear as a transparent, opaque or translucent even without change of its chemical formula or presence of impurities. Why is it so? What is the origin of such a change one may wonder!



**Fig. 2.1** Phase diagram showing different states of matters, which depend upon pressure and temperature



**Fig. 2.2** Different types of solids

Figure 2.2 illustrates schematically three different forms of solids known as single crystal, polycrystalline and amorphous. In what is known as a ‘single crystal’ there is almost infinitely long arrangement of atoms or molecules with certain symmetry characteristics of the material. When we say infinite distance, it means a length many a times larger than the distance between two atoms.

In a polycrystalline solid, there are some ‘grain boundaries’. Size of the grain can depend upon the processing and typically can be few  $\mu\text{m}^3$ . Each grain itself is a ‘single crystal’ but the orientations of these different crystals are different or random. Each grain also has a kind of ‘grain wall’ in which atoms may be more or less randomly distributed. The thickness of such walls is often very crucial in determining the various properties of materials such as mechanical, optical or electrical. At the grain boundary the long range periodicity of the solid is broken.

If each grain in the material becomes too small, comparable to the distance between the atoms or molecules, we get what is known as ‘amorphous’ solid. In amorphous solids, the grain boundaries disappear. Although the distances and even

the arrangement between nearest or even next nearest atoms may look similar for most of the atoms, they lack long-range order as in a poly or single crystal. The situation is similar to a liquid where a snapshot of atoms if taken would be similar to what we get in amorphous solid.

Thus transparent, precious form of  $\text{Al}_2\text{O}_3$  known as ‘sapphire’, a gemstone, is a single crystal; its translucent form is a polycrystalline and the opaque form is an amorphous solid. Further, with same type of atoms or molecules even different single crystals can be formed with altogether different properties. Consider for example diamond and graphite, two well known crystalline forms of carbon. Diamond is transparent, colourless and very hard. Graphite with the same chemical constituent viz. carbon is soft, black and opaque. Diamond is electrically insulating but graphite is conducting. Why two materials made of the same constituents should differ so much? For this, one should try to understand how the atoms in two materials are arranged, how the arrangement of atoms affects the bonding of atoms and ultimately the properties. In fact differences in the properties are usually correlated to the arrangement of atoms or structure and bonding. By studying a large number of solids, scientists have been able to understand how atoms are arranged in different crystal structures. This has led them to make a classification and develop some useful techniques by which one can identify atomic arrangements in some unknown sample. We shall start with some definitions in order to understand all this.

## 2.2 Arrangement of Atoms

**Lattice:** It is an arrangement of points repeated in one, two or three directions making it a one dimensional, two dimensional or three dimensional lattice.

However, for the sake of simplicity we may often take examples of two-dimensional lattices (Fig. 2.3).

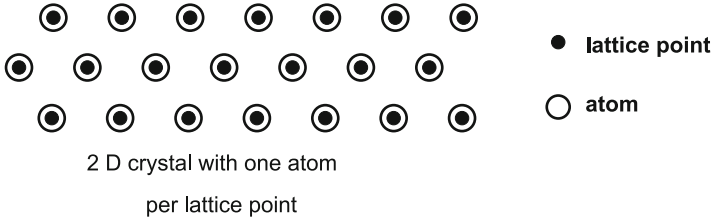
**Crystal:** When an atom or a group of atoms are attached to each lattice point, it forms a crystal (Fig. 2.4).

**Unit Cell:** Crystal structures can be understood in terms of unit cell, which when translated in any direction can fill the complete space without leaving any space in between or without overlapping. *Unit cell is a conventional cell* and can be of any volume, size, orientation or shape (see Fig. 2.5). However it is often taken in such a way that it has atoms at some corners or centre.

**Primitive Cell:** Unit cell with smallest volume is known as ‘*primitive cell*’ (see Fig. 2.6). It is also necessary to consider the *unit cell vectors* which define the

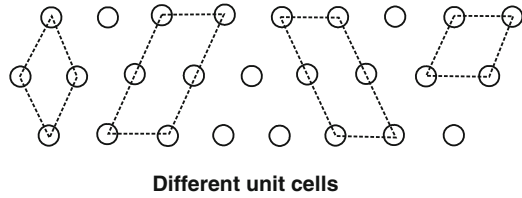


Fig. 2.3 A periodic arrangement of points in two dimensions makes a lattice

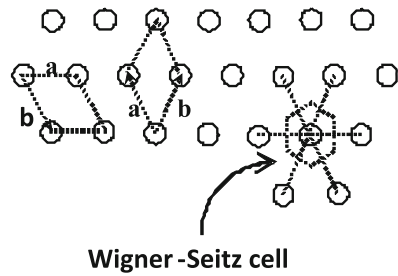


**Fig. 2.4** A lattice + atom makes a solid or crystal

**Fig. 2.5** Different unit cells in the same arrangement of atoms



**Fig. 2.6** Some primitive cells



boundaries or edges of unit cell. It can be seen that in direction of **a**, if we translate the cell by ‘a’ unit, the cell is repeated. Same is true for **b**. Thus **a** and **b** are translation vectors.

*Translation vectors of primitive or smallest unit cell are known as ‘primitive vectors’.* It is not always necessary to consider primitive vectors but one can have ‘unit vectors’ of any convenient length.

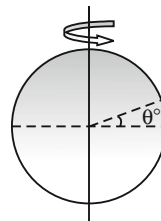
$$\text{Volume of the cell } V = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c} \tag{2.1}$$

As is clear from above figure, the choice of unit cell, unit vector, primitive cell or primitive vector is not unique.

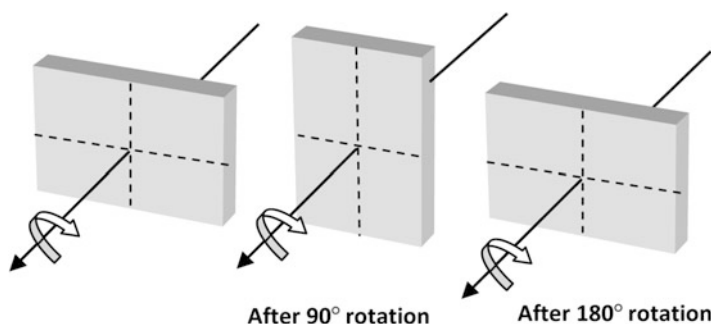
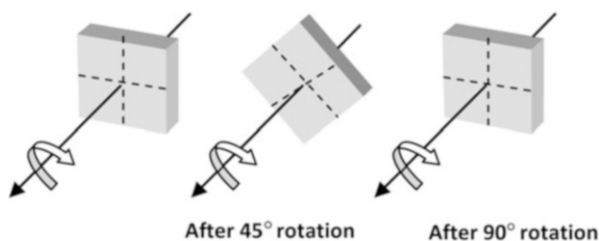
In order to classify the crystals further, it is necessary to understand certain symmetry operations around a point (also known as point operation, which helps to classify the crystals).

**Symmetry:** Symmetry transformation about a point is the one which leaves the system invariant or without any change even after some operation.

**Fig. 2.7** A circle can be rotated around an axis passing through its centre through any angle and would appear as if unmoved



**Fig. 2.8** Point symmetry of a square



**Fig. 2.9** Point symmetry of a rectangle

**Rotational Symmetry:** Consider for example a circle (Fig. 2.7). Circle is a perfectly symmetric object which can be rotated about an axis through its centre by any angle  $\theta$  without it appearing as if it was rotated. Thus by rotating through any angle we make an invariant transformation for a circle or a sphere.

But this is not true for any lower symmetry object. Consider now a square (Fig. 2.8). You can rotate it by  $90^\circ$  about an axis passing through its midpoint which appears as if it has not been rotated. This can be done only four times successively in any direction (clockwise or anticlockwise). The square is said to have a fourfold symmetry. The square would also have a twofold symmetry.

Consider now a rectangle. If you rotate it through  $90^\circ$ , you see the difference as shown in Fig. 2.9, but if you rotate it through  $180^\circ$  it looks similar to the original state. This you can do twice. Therefore, rectangle is an object with twofold symmetry.

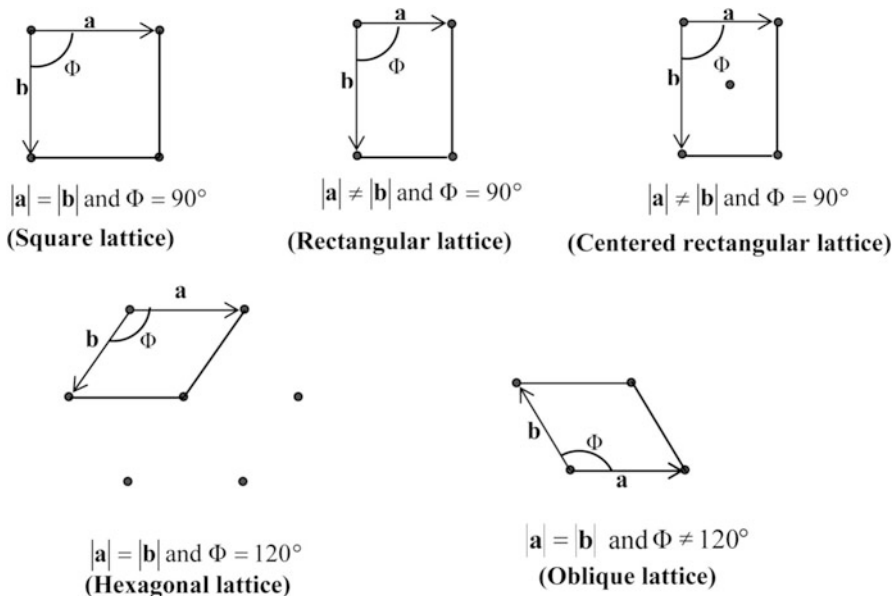


Fig. 2.10 Five two-dimensional Bravais lattices

There are various angles through which one can rotate an object. But it has to be consistent with translational symmetry to make it a crystal. In other words just rotational symmetry is not sufficient to describe a real crystal. It has to be consistent with translational symmetry too. It can be shown that there are only  $2\pi/1$ ,  $2\pi/2$ ,  $2\pi/3$ ,  $2\pi/4$  and  $2\pi/6$  possible rotations consistent with translation symmetry which can leave the crystal structure invariant.

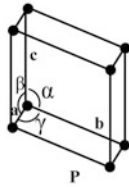
### 2.3 Two Dimensional Crystal Structures

Although by choosing different vectors, it is possible to construct variety of unit cells, it turns out that there are only *five types* of units or *Bravais lattices* as shown in Fig. 2.10 required to describe all observed two dimensional crystal structures.

### 2.4 Three Dimensional Crystal Structures

Three dimensional solids are divided into *seven crystal systems* and fourteen Bravais lattices as illustrated in Fig. 2.11. Any three dimensional crystalline solid (except quasicrystals to be discussed later in this chapter) would be one or the other type of the fourteen Bravais lattices.

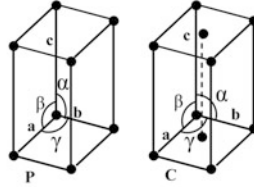
1. Triclinic



$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma$$

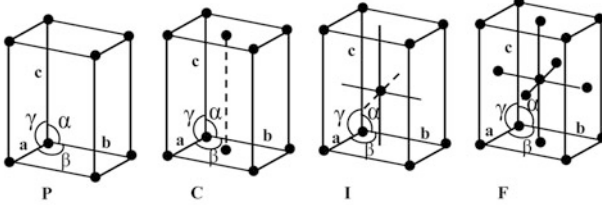
2. Monoclinic



$$a \neq b \neq c$$

$$\alpha = \beta = 90^\circ \neq \gamma$$

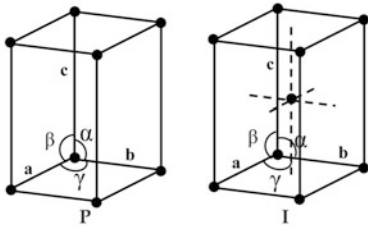
3. Orthorhombic



$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

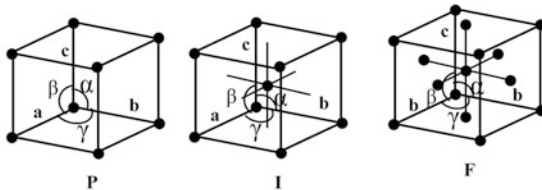
4. Tetragonal



$$a = b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

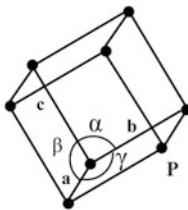
5. Cubic



$$a = b = c$$

$$\alpha = \beta = \gamma = 90^\circ$$

6. Triagonal



$$a = b = c$$

$$\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$$

Fig. 2.11 Fourteen Bravais lattices in three dimensions (*P* Primitive cell, *I* Body centred cell, *F* Face centred cell, *C* Base centred cell)

## 7. Hexagonal

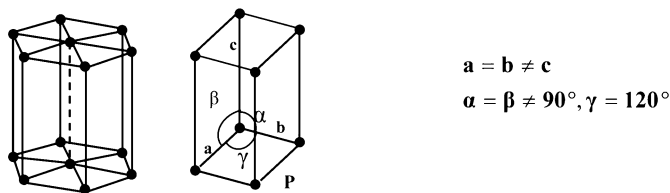


Fig. 2.11 (continued)

## 2.5 Some Examples of Three Dimensional Crystals

### 2.5.1 Body Centred Cube (bcc) (Fig. 2.12)

## 2.6 Planes in the Crystals

Planes in the crystals are denoted by what is known as ‘*Miller indices*’ and are determined as follows.

Consider the intercepts on **a**, **b**, **c** (the primitive axes or non-primitive axes of unit cell). For example as in Fig. 2.13, let the axial lengths be 0.8, 0.4 and 0.4 nm along **a**, **b** and **c** respectively. Let the intercepts be 0.2, 0.4 and 0.4 nm respectively. Fractional intercepts would be  $\frac{1}{4}$ , 1 and 1. Miller indices of the plane would be 4, 1 and 1 or conventionally written as (411). Miller indices are written in the round brackets.

Few examples are illustrated in Fig. 2.14.

## 2.7 Crystallographic Directions

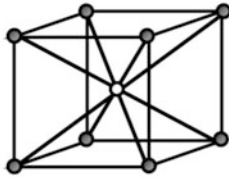
Directions are denoted by smallest length of unit vectors i.e. **a** as [100], **b** as [010] and **c** as [001]. Direction numbers are always placed in the square brackets. See Fig. 2.15.

## 2.8 Reciprocal Lattice

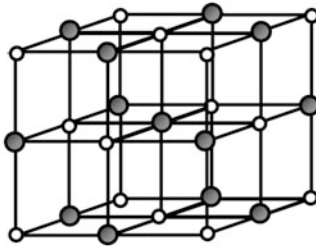
Using X-rays, electrons or neutrons having wavelength  $\sim 0.1$  to 0.2 nm, length comparable to distance between atoms or planes in a solid, it is possible to obtain a diffraction pattern (more details about diffraction pattern will be given in Chap. 7 on Analysis Techniques). Analysis of diffraction patterns leads to the determination



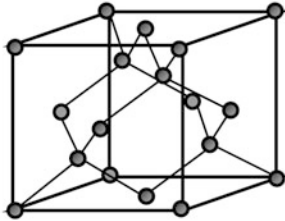
**CsCl** : Body Centred Cubic (bcc),  $\text{Cs}^+$  ion at (000), two atoms/cell,  $\text{Cl}^-$  ion at  $(1/2, 1/2, 1/2)$  co-ordinates. It is a conventional unit cell.



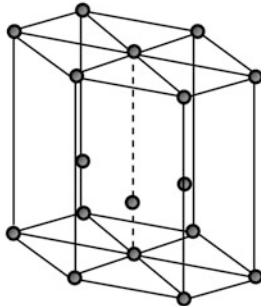
**NaCl**: Face Centred Cubic (fcc), alternate arrangement of  $\text{Na}^+$  and  $\text{Cl}^-$  ions in  $x, y$  and  $z$  directions. It is a conventional unit cell.



**Diamond**: Cubic, interpenetrating cubes, eight atoms/cell

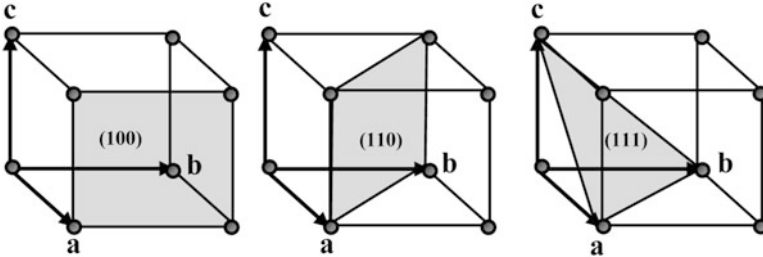
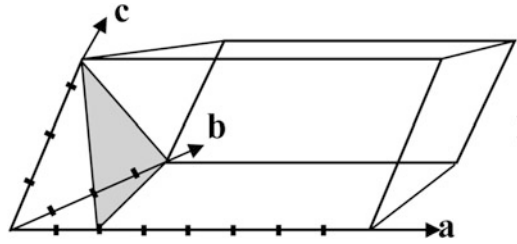


**Graphite**: Hexagonal hcp ABAB...  $c/a = 1.633$



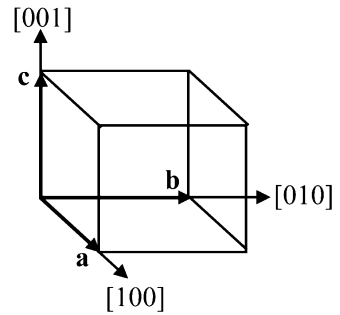
**Fig. 2.12** Schematic diagram illustrating CsCl, NaCl, diamond and graphite crystal structures

**Fig. 2.13** Plane having Miller indices (411)



**Fig. 2.14** Examples of (100), (110), (111) planes in a cubic crystal

**Fig. 2.15** Crystallographic directions



of crystal structure (Bravais lattice). However diffraction pattern is obtained in the *reciprocal space*. Points in the reciprocal space are related to real space. Each point in the reciprocal space represents a set of planes in real lattice.

It is therefore often convenient to use the concept of reciprocal lattice to deal with the crystals. Reciprocal Lattice Vectors **A**, **B** and **C** are defined in terms of the vectors **a**, **b** and **c** in real lattice as

$$\begin{aligned}
 \mathbf{A} &= \frac{2\pi (\mathbf{b} \times \mathbf{c})}{(\mathbf{a} \cdot \mathbf{b} \times \mathbf{c})} \\
 \mathbf{B} &= \frac{2\pi (\mathbf{c} \times \mathbf{a})}{(\mathbf{a} \cdot \mathbf{b} \times \mathbf{c})} \\
 \mathbf{C} &= \frac{2\pi (\mathbf{a} \times \mathbf{b})}{(\mathbf{a} \cdot \mathbf{b} \times \mathbf{c})}
 \end{aligned}
 \tag{2.2}$$

In the resulting network of reciprocal points, position vector  $\mathbf{G}$  can be written as

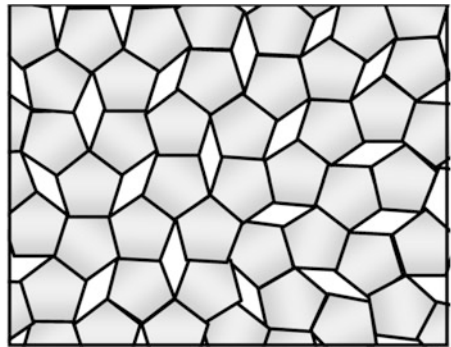
$$\mathbf{G} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C} \quad (2.3)$$

where  $h, k, l$  are Miller indices of the planes as discussed in Sect. 2.6.

## 2.9 Quasi Crystals

As far as point symmetry is concerned,  $360/5 = 72^\circ$  is a possible rotation. However if one tries to translate a pentagon in two dimensional space, it cannot fill the space completely as can be seen from the Fig. 2.16. Therefore fivefold rotation does not satisfy the criterion viz. rotation plus translation symmetry to make a crystal. Therefore for quite long time it was thought that crystals having fivefold symmetry cannot exist. Same is the situation with sevenfold symmetry (there are overlapping regions) and you will find that for solids, in the old text books it is considered to be a forbidden geometry for atomic arrangement in crystals. In fact as discussed earlier, only 1, 2, 3, 4 and 6 fold axes of rotation are crystallographically allowed.

However there are now evidences after the experimental work by Dan Shechtman in 1982 that in some crystalline matter fivefold symmetry does exist. Indeed in some alloys like Al-Mn, Al-Pd-Mn and Al-Cu-Co, fivefold, eightfold or tenfold symmetries have been observed. Dan Shechtman got the Nobel Prize for this discovery in 2011. This kind of aperiodic symmetry can be explained by a different kind of space filling method than using simple geometries like rectangles or squares. The credit for it goes to astrophysicist Penrose and is known as '*penrose tiling*' (Interestingly penrose tiling was made by Roger Penrose way back in 1970s just to show an aperiodic tiling. Before Penrose's suggestions such tiling could be seen in Islamic culture). What Penrose suggested is that instead of using a single unit cell for the translation, use two-unit cells like a thin and a fat rhombus or a kite and a dart as shown in Fig. 2.17.



**Fig. 2.16** Five-fold pattern

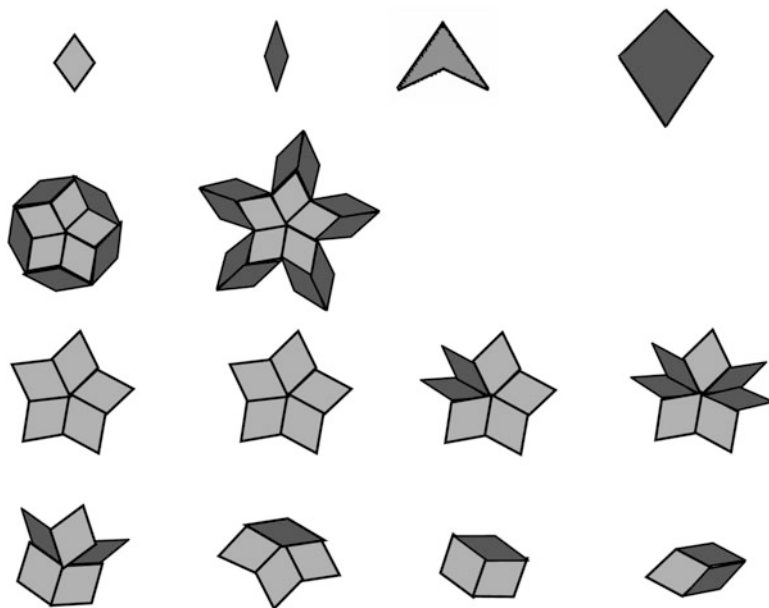


Fig. 2.17 Penrose tiles (*first line*) and various motifs generated using them

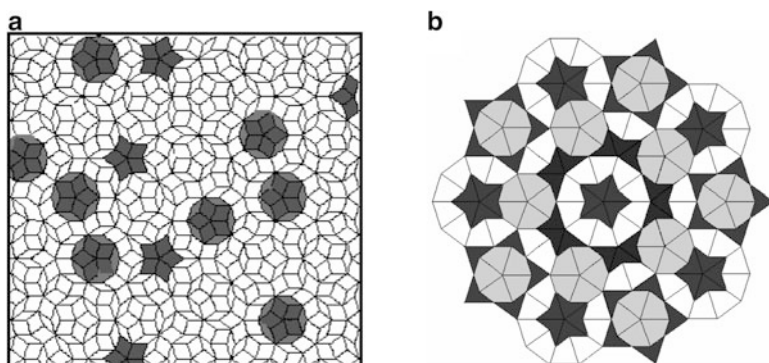


Fig. 2.18 Penrose tiling: (a) using fat and thin rhombus and (b) using kite and dart

Now we can see (Fig. 2.18) how they fit into each other filling a large region without leaving spaces in between or overlapping with each other. Such aperiodic materials which exhibit X-ray diffraction patterns are known as *quasi crystals*. Properties of such alloys are quite interesting. For example they are poor heat and electricity conductors. They also do not get rusted easily. Interestingly Shechtman was not aware of Penrose tiling for a long time.

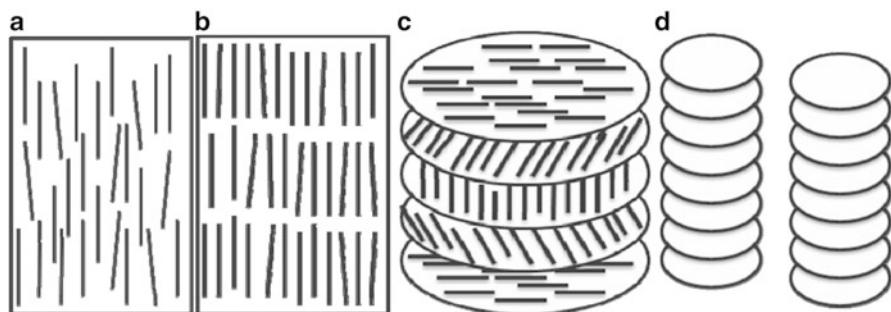
**Box 2.1: Revised Definition of a Crystal**

Crystals are defined as solids with periodic arrangement of atoms or molecules. Until 1982 all the known crystals were found to follow the translational and rotational symmetry operations in which only 1, 2, 3, 4 and 6 fold rotations are allowed. However after the observation of quasi crystals by Shechtman it was apparent that even 5, 7 and 10 fold rotations are also possible in solids. Therefore, International Organisation of Crystallographers revised the definition of crystals in 1991. A crystal can be defined now as any solid having a distinct diffraction pattern. We shall learn about the diffraction from crystals in a later chapter.

## 2.10 Liquid Crystals

Similar to quasicrystals, liquid crystal is another class of unconventional crystals. Unlike quasicrystals the work on liquid crystals began as early as 1888 when Friedrich Reinitzer noticed that the cholesteryl benzoate, when heated, became a cloudy liquid at 145 °C and clear liquid at 179 °C. After hearing about this curious behaviour of cholesteryl benzoate molecules, Otto Lehman looked into more details and not only confirmed Reinitzer's results but also gave the name *liquid crystals* in 1889 to it and similarly behaving materials. He found that some molecules before melting pass through a (liquid) phase in which they flow like liquids. However they have interesting optical properties and have some attributes of crystals. As the name suggests it has liquid-like as well as crystal-like properties. Although credit on the discovery of liquid crystals is given to Reinitzer, he himself has quoted similar observations by Julius Planer from 1861.

Many molecules have rod-like shapes and are the candidates of different types of liquid crystals like nematic, cholesteric, smectic and discotic (see Fig. 2.19). In



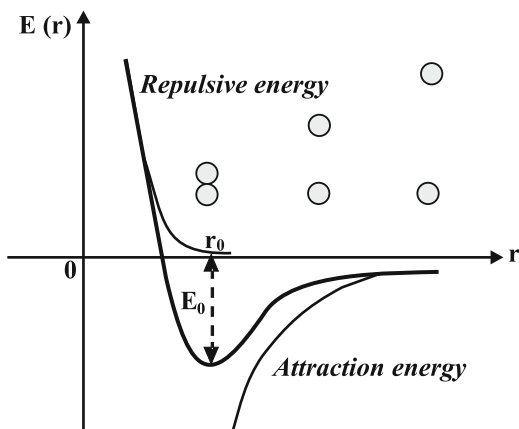
**Fig. 2.19** (a) Nematic (b) Smectic (c) Cholesteric (d) Discotic liquid crystals

nematic crystals the molecules are almost parallel to each other in the vertical direction but their positions are random. Thus there is orientation order like in a crystal but positional disorder like in a liquid. The smectic crystals are characterized by slabs of oriented molecules which are disordered with respect to each other. In the cholesteric (also called chiral nematic) the molecules are oriented in the same direction as in a nematic crystal in a single plane but there is rotation of molecules from plane to plane like twisting. There are some disc-like molecules which arrange themselves randomly in a plane but form vertical stacks to form what is known as discotic liquid crystals.

Although for decades the liquid crystal research was driven only by scientific curiosity, their optical properties showed that they have a huge potential in display panels. They are widely used in the display screens of televisions, computers, watches and many other applications.

## 2.11 Bonding in Solids

When two atoms approach each other, they start interacting. The type and the amount of interaction depend upon the distance between the two atoms and the type (element or electronic configuration) of the atom. However, in general, one can understand this interaction as follows with the help of Fig. 2.20. Consider two atoms. At infinity or a very large distance compared to their sizes, the electrons have no interatomic interaction of any type and both the atoms have all the properties independent of each other. However, as soon as they start coming closer, their electron clouds start interacting with each other. This results into an attractive force and a repulsive force between the two atoms due to mutual electrostatic interaction. The electrostatic interaction between the atoms arises due to the positive charges of nuclei and negative charges of electron clouds. All other forces like gravitation have negligible effect compared to electrostatic interaction and can be neglected.



**Fig. 2.20** Interatomic potential vs. interatomic distance. Here  $E_0$  is the bond energy and  $r_0$  is the bond length

A distance dependent energy curve has two parts viz. an attractive (negative energy) part and the repulsive (positive energy) part. At certain distance between the two atoms, the attractive interaction dominates as compared to the repulsive interaction. At this distance, say  $r_0$ , the two atoms can form what is known as 'bond' with 'bond energy'  $E_0$ . The two atoms enjoy the state of lower energy by being together than remaining as separate ones. This can give rise to the formation of a molecule. As we shall see below, there can be different types of bonds with different bonding strengths or value of  $E_0$ . The equilibrium distance at which the energy is  $E_0$  is the 'bond length' of the molecule. As the atoms come closer or have a distance smaller than  $r_0$  between them, their electron charge clouds start overlapping. Due to similar charges they start repelling each other. This can be understood in terms of Pauli exclusion principle, which states that no two electrons can have same quantum numbers. Even in solids the atoms are held together due to mutual interaction between the atoms and we have bond energy and bond length as in a molecule. However in a solid there are not just two atoms as we discussed above but a very large number of atoms (even many molecules have more than two atoms and different bonds within a single molecule). It is still possible to consider the interaction between the atoms using a simple diagram as discussed above. The energy difference between energy of free atoms and that of crystal is known as *cohesive energy*.

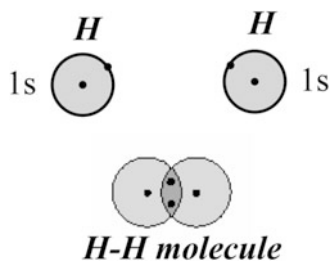
Let us now discuss various types of bonds that occur in some molecules and solids. They are classified into different types of bonds as: (1) Covalent bond, (2) Ionic bond, (3) Metallic bond, (4) Mixed bond and (5) Secondary bond.

Covalent, ionic and metallic bonds are known as primary bonds and others are known as secondary bonds. There are also bonds which are not pure ionic, covalent or metallic but have some partial character of different bonds and are known as mixed bonds. We shall briefly discuss each type of bond with some examples.

### 2.11.1 Covalent Bond

When two atoms form a molecule by sharing some of their valence electrons, a covalent bond is established. Sometimes atoms may use even all the valence electrons for sharing. Consider a simple example of  $H_2$  molecule. Hydrogen atomic number is 1 and it has its one electron in 1s shell. We know that in atoms stable orbits can be formed with certain electronic configurations, like two electrons in 1s shell. Thus hydrogen atom is more stable if there are two electrons in 1s shell. When two hydrogen atoms come very close to each other so that their 1s shells overlap (See Fig. 2.21), then both have as if two electrons. Therefore they form a molecule attaining a state of lower energy together than both were independent. There are many other molecules like  $CH_4$ ,  $O_2$  or  $N_2$  which are covalent in nature.

In solids we have covalent bonds in many crystals like diamond, silicon, germanium etc. We shall discuss the covalent bond in solids with the example of diamond crystal. Diamond is made up of carbon atoms. Carbon has atomic number

**Fig. 2.21** Hydrogen molecule**Table 2.1** Examples of some covalent bonds, their equilibrium bond lengths and energies

Bond	Bond length (nm)	Bond energy (eV)
H–H	0.07414	4.5
O–O	0.12074	1.4
P–P	0.18931	2.2
Cl–Cl	0.19879	2.5
C–C	0.12425	3.6
Si–Si	0.2246	1.8
Ge–Ge	0.2403	1.6

6 and its electron configuration is  $1s^2 2s^2 2p^2$ . Thus, it lacks four atoms in p shell to attain the stable or lowest possible energy configuration. In crystal each carbon atom is coordinated (or surrounded by nearest neighbours as shown in Fig. 2.12) by four carbon atoms. Instead of just using two valence electrons from 2p shell, all four electrons from principal quantum number 2 or L shell are used by each carbon atom. This enables each carbon atom to have four bonds (known as  $sp^3$  bonds) which are then shared with four neighbouring carbon atoms. In this way each carbon atom shares one electron with every other neighbouring carbon atom forming covalent bonds. This also gives rise to a tetrahedral arrangement of carbon atoms so that angle between C–C–C atoms is equal.

In Table 2.1 we give some more examples of covalent bonds and their bond energies along with bond lengths.

### 2.11.2 Ionic Bond

This type of chemical bond is formed when atoms are in the vicinity and electron(s) from one atom is transferred to another. The one able to transfer the electron or electrons is termed as electropositive and the one which has a tendency to accept electron or electrons is known as electronegative. The ions thus formed are called cations and anions respectively. NaCl, KCl and  $\text{CaCl}_2$  are good and simple examples of ionic bond formation. Let us consider the example of NaCl. Sodium (Na) has atomic number 11 and electronic configuration  $1s^2 2s^2 2p^6 3s^1$ . We can easily see that if there was not an electron in 3s orbit of sodium, it would have been stable like



inert gas element neon. On the other hand chlorine with atomic number 17 (electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^5$ ) lacks one electron to attain a stable configuration like that in argon (Ar) with 18 electrons. Thus we have a situation here that one atom has extra electron and another is short of an electron to attain the stable configuration. When two such atoms are at a sufficiently short distance the electron from Na gets transferred to Cl forming an ionic bond and both gaining a state of lower energy. The bond thus formed is known as *ionic bond*. However there is energy required to remove an electron from metal atom like sodium atom in this example. This energy is known as *energy of ionization*.

In solid of NaCl, as illustrated in Fig. 2.12, the crystal structure is face centre cubic (FCC) with each ion of one type surrounded by six ions of opposite charge. Also each ion has oppositely charged neighbours. Note that there is a difference in the sizes of Na and Cl ions.

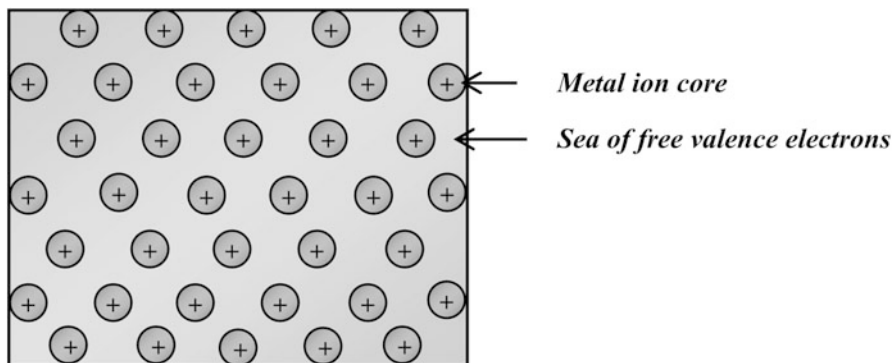
However there is ionization energy required to remove an electron from sodium atom. Ionic crystals are easily soluble in polar liquids like water. The ionic crystals have high melting point. In general they are electrically and thermally non-conducting.

### 2.11.3 Metallic Bond

Atoms like Na, K, Cu, Au, Ag, Fe, Co and Ca in which there are one or more electrons which can be easily removed (valence electrons) from them form metals and the bond that holds the crystal together is known as *metallic bond*. The loose electrons are able to move quite easily from one atom to another and cannot be localized to a particular atom or the other. Such electrons form what is known as an *electron gas* (of free electrons) and are responsible for the *metallic bond* which is an electrostatic interaction between the positive ions of atoms that have lost the electrons and are unable to move themselves (however, ions vibrate about their mean positions) in the crystal. This is schematically shown in Fig. 2.22. In metals the bond is not directional and usually the metal ions try to come as close as possible forming a compact structure with high coordination number of ions. It is therefore possible to move ions in any direction quite easily by applying a force. The metals are thus ductile. The free electrons in metals respond to electric or magnetic field quite easily making them electrically or thermally good conducting materials.

### 2.11.4 Mixed Bonds

It is often found that bonds have a mixed character. We saw in case of diamond or silicon crystals, we have pure covalent bonds. However if we consider a crystal like that of NaCl, KCl, GaAs, InP or ZnS we find that there is no pure covalent or pure ionic bond amongst the atoms. A class of materials ( $Al_2O_3$ , MgO etc.)



**Fig. 2.22** A metal considered as a periodic arrangement of positive ions (*circles*) embedded in an electron gas (*grey background*) of negatively charged electrons contributed by each atom

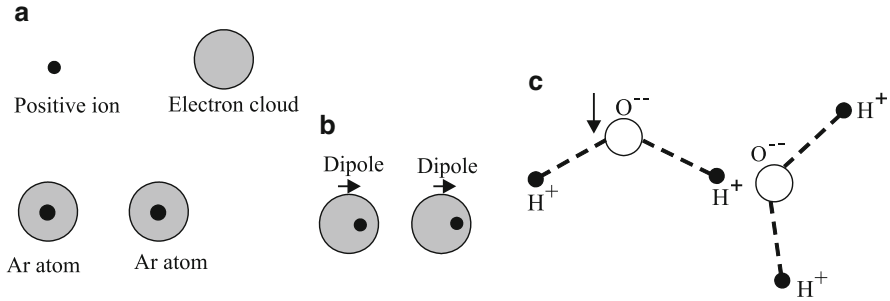
**Table 2.2** Examples of covalent and mixed bonds

Materials	Ionic %	Covalent %
Si	0	100
Ge	0	100
ZnO	62	38
CdS	69	31
GaAs	31	69

known as ‘ceramics’ also have partial metallic and non-metallic characters (ionic and covalent mix bonding). Their properties also change correspondingly. They may not be completely insulators nor conductors of heat and electricity. Such crystals are known to have mixed type of bonding. Often it is useful to find out the percentage of each type (See Table 2.2).

### 2.11.5 Secondary Bonds

These are very weak bonds compared to ionic, covalent and metallic bonds. Typical examples are found in rare gas atom solids (obtained at low temperatures), solidified  $\text{CO}_2$ , solidified  $\text{C}_2\text{H}_4$ , water and some molecular crystals. These weak bonds are due to formation of instantaneous dipoles in rare gas atoms and molecules which leads to what is known as *Van der Waals bond*. As illustrated in Fig. 2.23, although rare gas atoms have stable electronic configurations and cannot interact with other atoms when they are very close to each other, at any instance they have small dipoles with positive and negative ends due to movement of charges inside. At high temperature the kinetic energy of atoms is very large and atoms move with high velocities without any interactions between the dipoles. However at low temperatures and small distances the dipoles can interact. The interaction between the dipoles can



**Fig. 2.23** Centre of positive charge and negative charges, over a long period (average), coincides as in (a) but at any instance a dipole can exist due to displacement of electric charge cloud as in (b). Dipole-dipole interaction (c)

be attractive as well as repulsive. But there can be a weak net attractive interaction. This gives a small value of  $E_0$  or bond energy.

It is also likely that some molecules (see Fig. 2.23c) have already some permanent dipoles on them which can then interact with each other. Molecules with permanent dipoles on them are known as *polar molecules*. Consider for example a water molecule  $\text{H}_2\text{O}$ . In water molecule, oxygen attracts two electrons from two hydrogen atoms. Therefore within the molecule we have ionic bonds. Oxygen is negatively charged and two hydrogen atoms are positively charged. This gives rise to a permanent dipole on water molecule (Each oxygen ion can attract positively charged hydrogen atom and each hydrogen atom can in principle get attracted to other  $\text{H}_2\text{O}$  molecule). Such dipoles then can interact with each other forming weak van der Waals bonds but are referred to as *hydrogen bonds*. These are slightly stronger than the fluctuating dipoles discussed earlier but still lie in the category of secondary bonds. In some cases an atom of hydrogen is responsible to bond two electronegative atoms simultaneously. For example two fluorine (chlorine etc.) atoms are simultaneously bonded with single hydrogen atom. Hydrogen atom loses its electron to one of the fluorine atom (ionic bond) and the proton is attracted and is positively charged which bond with the second fluorine atom. Thus a difluoride  $\text{HF}_2^-$  is formed by *hydrogen bond*.

Van der Waals bonding is also observed in long chains of carbon or C–H. The chains themselves may have various atoms bonded by covalent and ionic bonds but the inter chain reactions may be weak due to Van der Waals interaction, as in polymers.

## 2.12 Electronic Structure of Solids

We discussed in the previous sections about geometrical structures and bonding in solids. Materials can be identified with appropriate structure and bonding. However to further understand different mechanical, thermal, electrical, magnetic

and optical properties it is necessary to further know the *electronic structure* of solids. The electronic structure of nanomaterials would certainly be different from atoms, molecules or solids. Nanomaterials in fact are intermediate form of solids. They are too small to be considered as bulk, three dimensional solids and too big to be considered as molecules. If we start with an atom, we know that bringing two atoms together to form a molecule changes the electronic structure. If three atoms come together there is further change. In fact addition of each atom would change the electronic structure till the number of atoms becomes too large. Depending upon the type of atoms, at large number the clusters of such atoms would reach bulk electronic structure. Bulk electronic structures or those of atoms and molecules can be learnt in standard text books on these topics. Here we shall briefly discuss how such electronic structures are useful to classify the materials as metals, semiconductors and insulators.

As a simple picture one can consider a one dimensional solid in which atoms are periodically arranged on a line (one dimensional case which can be readily extrapolated to take into account a three dimensional solid). Each atom can then be considered to contribute one electron (becoming a positive ion) which is free to move in the solid.

We can consider first free electron motion and see how such concept leads to band structure of solids.

### 2.12.1 Free Electron Motion

We saw in Chap. 1 that Schrödinger equation for an electron in one dimension is given as

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} \right) \psi(x) + V(x)\psi(x) = E\psi(x) \quad (2.4)$$

and the wave function  $\psi(x)$  for a free particle is

$$\psi(x) = A \sin \left( \frac{n_x \pi x}{a} \right) \quad (2.5)$$

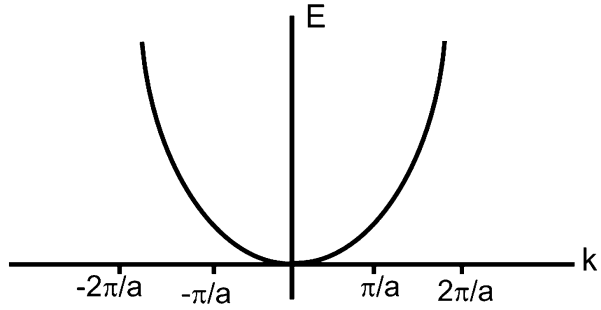
with  $n_x = 0, 1, 2 \dots$

### 2.12.2 Bloch's Theorem

From the free electron motion we go to the electron states in a one dimensional periodic potential, which can be written as

$$V(x) = V(x + a) \quad (2.6)$$

**Fig. 2.24** Electron energy levels at different wave vector  $k$



It was realized by Bloch that the wave function satisfies the relation

$$\psi(x + a) = \psi(x)e^{ika} \quad (2.7)$$

### 2.12.3 Origin of Band Structure

We now give an intuitive argument for the presence of bands. We know that

$$E_k = \frac{\hbar^2 k^2}{2m} \quad (2.8)$$

for travelling wave in one direction.

The electron spectrum is as shown in Fig. 2.24.

$\psi(+)$  =  $e^{\frac{i\pi x}{a}}$  and  $\psi(-)$  =  $e^{-\frac{i\pi x}{a}}$  are oppositely moving waves.

For a pure travelling wave

$$|\psi| = e^{ikx} e^{-ikx} = 1 \quad (2.9)$$

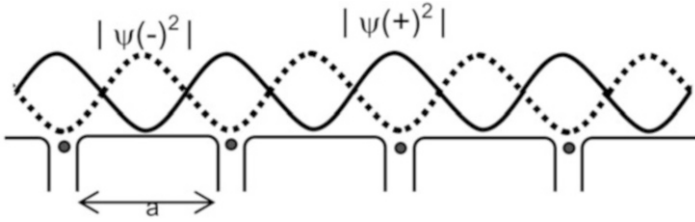
But if electron waves are reflected at  $k = \pm\pi n/a$ , the standing waves are generated as

$$\psi(+)= e^{\frac{i\pi x}{a}} + e^{-\frac{i\pi x}{a}} = 2 \cos\left(\frac{\pi x}{a}\right) \quad (2.10)$$

$$\text{and } \psi(-) = e^{\frac{i\pi x}{a}} - e^{-\frac{i\pi x}{a}} = 2 \sin\left(\frac{\pi x}{a}\right) \quad (2.11)$$

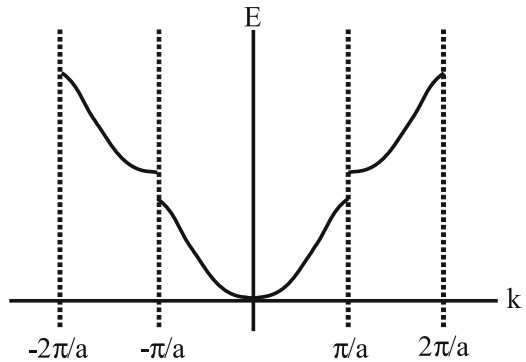
$\psi(+)$  and  $\psi(-)$  pile up electrons in different regions as shown in Fig. 2.25.

$$\text{Probability density } \rho(+)= |\psi(+)|^2 = 4\cos^2 \frac{\pi x}{a} \quad (2.12)$$



**Fig. 2.25** Electron probability distribution in periodic potential

**Fig. 2.26** Energy levels separated by band gap at zone boundary

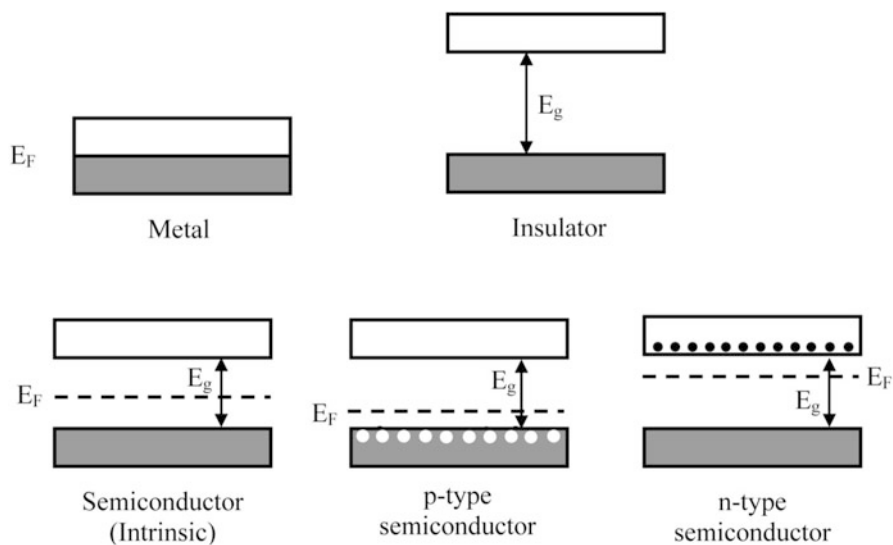


$$\text{and } \rho(-) = |\psi(-)|^2 = 4\sin^2 \frac{\pi x}{a} \quad (2.13)$$

This gives rise to energy gaps in the free electron curve of Fig. 2.24 as illustrated in Fig. 2.26.

This is a very important result as details about amount of energy gap, overlap of energy bands, curvature of bands determine the properties of solids. The bands in solids have closely spaced energy levels. They are filled upto Fermi level according to Pauli exclusion principle viz. no two electrons can exist in an energy state with all the quantum numbers same. The Fermi level is the highest occupied level at absolute zero temperature.

A qualitative picture representing metal, insulator and semiconductors is given in Fig. 2.27. A metal would have its outermost electron filled band (valence band) overlapping with empty band (conduction band). If there is a small gap between valence and conduction band (upto  $\sim 2-3$  eV) then it is a semiconductor. If the gap is larger, the material is an insulator. Interestingly, by introducing small amount of dopant (atoms different compared to those in the host material), some localized energy states can be introduced in the energy gap. Depending upon whether such levels are close to valence band or close to conduction band, semiconductor becomes *p* or *n* type semiconductor. The electrical conductivity in many semiconductor devices is controlled by such dopants.



**Fig. 2.27** Different types of materials viz. metals, semiconductors and insulators can be understood on the basis of the overlap or separation between outer filled valence and empty conduction bands

A band picture of solids thus enables one to understand differences between metals, semiconductors and insulators. Moreover detailed analysis also helps to understand other physico-chemical properties of solids.

## Further Reading

- M. Chandra, *Atomic Structure and Chemical Bond*, 3rd edn. (Tata McGraw Hill Publishing Co Ltd, New Delhi, 1991)  
 C. Kittel, *Introduction to Solid State Physics*, 5th edn. (Wiley, New Delhi, 1995)



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