

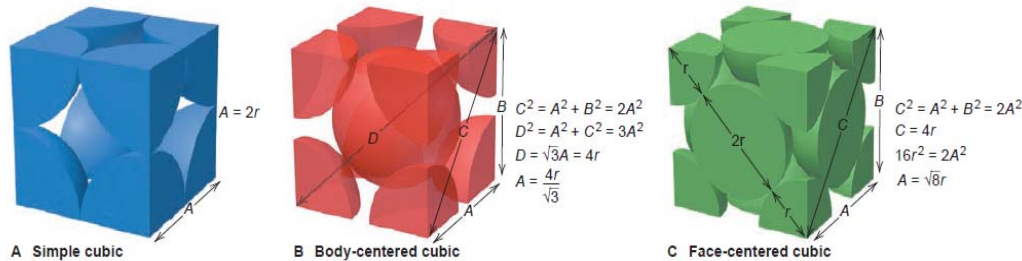
Packing Efficiency and the Creation of Unit Cells

Suppose we arrange the first layer of spheres. Then

$$pf = \frac{\text{volume of atoms in unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{(4/3)\pi r^3 \cdot \text{No of atoms / unit cell}}{a^3}$$

The relationship between lattice parameter and atomic radius



Material solids can be classified according to Bonds as following

1-Metallic Solids

The simplest model that accounts for the properties of metals is the electron-sea model. It proposes that all the metal atoms in a sample pool their valence electrons to form an electron “sea” that is delocalized throughout the piece. The metal ions are submerged within this electron sea in an orderly array. Rather, *the valence electrons are shared among all the atoms in the sample*, and the piece of metal is held together by the mutual attraction of the metal cations for the mobile, highly delocalized valence electrons.

The *regularity*, but not rigidity, of the metal-ion array and the *mobility* of the valence electrons account for the physical properties of metals. Metals have moderate to high melting points because the attractions between the cations and the delocalized electrons are not broken during melting, but boiling points are very high because each cation and its electron(s) must break away from the others. Gallium provides a striking example: it melts in your hand (mp 29.8°C) but doesn't boil until 2403°C. The alkaline earth metals have higher melting points than the alkali metals because of greater attraction between their 2 cations and twice the number of valence electrons

When struck by a hammer, metals usually bend or dent rather than crack or shatter. Instead of repelling each other, the metal cations slide past each other through the Electron Sea and end up in new positions. Compare this behavior with that of an ionic solid. As a result, many metals can be flattened into sheets (malleable) and pulled into wires (ductile). Gold is in a class by itself: 1 g of gold (a cube 0.37 cm on a side) can be hammered into a 1.0-m² sheet that is only 230 atoms (50 nm) thick or drawn into a wire 165 m long and 20 μm thick!

Metals are good electrical conductors because the mobile electrons carry the current, and they conduct heat well because the mobile electrons disperse heat more quickly than do the localized electron pairs or fixed ions in other materials

Molecular Solids

The lattice positions that describe unit cells of molecular solids represent molecules or monatomic elements. Although the bonds

within molecules are covalent and strong, the forces of attraction *between* molecules are much weaker. They range from hydrogen bonds and weaker dipole–dipole interactions in polar molecules such as H₂O and SO₂ to very weak dispersion forces in symmetrical, nonpolar molecules such as CH₄, CO₂, and O₂ and monatomic elements, such as the noble gases. Because of the relatively weak intermolecular forces of attraction, molecules can be easily displaced. Thus, molecular solids are usually soft substances with low melting points. Because electrons do not move from one molecule to another under ordinary conditions, molecular solids are poor electrical conductors and good insulators.

Covalent Solids

Covalent solids (network solids) can be considered giant molecules that consist of covalently bonded atoms in an extended, rigid crystalline network. Diamond and quartz are examples of covalent solids. Because of their rigid, strongly bonded structures, *most* covalent solids are very hard and melt at high temperatures. Because electrons are localized in covalent bonds, they are not freely mobile. As a result, covalent solids are *usually* poor thermal and electrical conductors at ordinary temperatures. (Diamond, however, is a good conductor of heat; jewelers use this property to distinguish diamonds from imitations.)

An important exception to these generalizations about properties is *graphite*, an allotropic form of carbon. The overlap of an extended electron network in each plane makes graphite an excellent

conductor. The very weak attraction between layers allows these layers to slide over one another easily. Graphite is used as a lubricant, as an additive for motor oil, and in pencil “lead” (combined with clay and other fillers to control hardness).

Ionic Solids

Most salts crystallize as ionic solids with ions occupying the unit cell, such as NaCl. Many other salts crystallize in the sodium chloride (face-centered cubic) arrangement. Examples are the halides of Li^+ , K^+ , and Rb^+ , and $\text{M}^{2+} \text{X}^{2-}$ oxides and sulfides such as MgO, CaO, and MnO. Two other common ionic structures are those of cesium chloride, CsCl (simple cubic lattice), and zinc blende, ZnS (face-centered cubic lattice). Salts that are isomorphous with the CsCl structure include CsBr, CsI, NH_4Cl , TlCl , TlBr , and TlI . The sulfides of Be, Cd, and Hg, together with CuBr, CuI, AgI, and ZnO, are isomorphous with the zinc blende structure.

The ions in an ionic solid can vibrate only about their fixed positions, so ionic solids are poor electrical and thermal conductors. Liquid (molten) ionic compounds are excellent conductors, however, because their ions are freely mobile

Some properties of solids :

1- Mechanical properties

The fundamental concepts for the discussion of the mechanical properties of solids are stress and strain. The **stress** on an object

is the applied force divided by the area to which it is applied. The **strain** is the resulting distortion of the sample. The general field of the relations between stress and strain is called **rheology**.

Stress may be applied in a number of different ways. Thus, **uniaxial stress** is a simple compression or extension in one direction (Fig. 47); **hydrostatic stress** is a stress applied simultaneously in all directions, as in a body immersed in a fluid. A **pure shear** is a stress that tends to push opposite faces of the sample in opposite directions.

A sample subjected to a small stress typically undergoes **elastic deformation** in the sense that it recovers its original shape when the stress is removed. For low stresses, the strain is linearly proportional to the stress. The response becomes nonlinear at high stresses but may remain elastic. Above a certain threshold, the strain becomes **plastic** in the sense that recovery does not occur when the stress is removed. Plastic deformation occurs when bond breaking takes place and, in pure metals, typically takes place through the agency of dislocations. Brittle solids, such as ionic solids, exhibit sudden fracture as the stress focused by cracks causes them to spread catastrophically.

The response of a solid to an applied stress is commonly summarized by a number of coefficients of proportionality known as ‘module’:

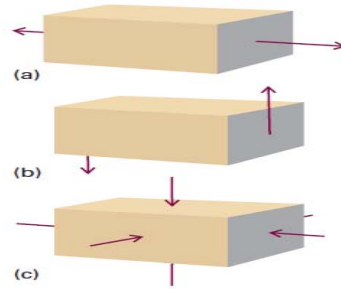


Fig. 47 Types of stress applied to a body. a) Uniaxial stress b) shear stress c) hydrostatic pressure

$$\text{Young's modulus : } E = \frac{\text{normal stress}}{\text{normal strain}} \quad (16a)$$

$$\text{Bulk modulus : } K = \frac{\text{pressure}}{\text{fractional change in volume}} \quad (16b)$$

$$\text{Shear modulus : } G = \frac{\text{shear stress}}{\text{shear strain}} \quad (16c)$$

Where ‘normal stress’ refers to stretching and compression of the material, as shown in Fig. 48a and ‘shear stress’ refers to the stress depicted in Fig. 20.48b. The bulk modulus is the inverse of the isothermal compressibility, κ , ($\kappa = -(\partial V/\partial p)T/V$). A third ratio indicates how the sample changes its shape:

$$\text{Poisson's ratio : } \nu_p = \frac{\text{transverse strain}}{\text{normal strain}} \quad (17)$$

The modules are interrelated:

$$G = \frac{E}{2(1 + \nu_p)}, \quad K = \frac{E}{3(1 - 2\nu_p)} \quad (18)$$

We can use thermodynamic arguments to discover the relation of the module to the molecular properties of the solid. Thus, in the *Justification* below, we show that, if neighboring molecules interact by a Lennard-Jones potential, then the bulk modulus and

the compressibility of the solid are related to the Lennard-Jones parameter ε (the depth of the potential well) by

$$K = \frac{8N_A\varepsilon}{V_m} \quad \text{and} \quad k = \frac{1}{K} = \frac{V_m}{mN_A\varepsilon} \quad (19)$$

We see that the bulk modulus is large (the solid stiff) if the potential well represented by the Lennard-Jones potential is deep and the solid is dense (its molar volume small).

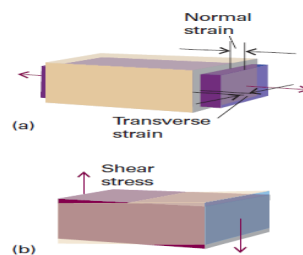


Fig.48 (a) Normal stress and the resulting strain. (b) Shear stress. Poisson's ratio indicates the extent to which a body changes shape when subjected to a uniaxial stress.

The typical behavior of a solid under stress is illustrated in Fig. 49. For small strains, the stress–strain relation is a Hooke's law of force, with the strain directly proportional to the stress. For larger strains, though, dislocations begin to play a major role and the strain becomes plastic in the sense that the sample does not recover its original shape when the stress is removed.

The differing rheological characteristics of metals can be traced to the presence of **slip planes**, which are planes of atoms that under stress may slip or slide relative to one another. The slip planes of a ccp structure are the close-packed planes, and careful inspection of a unit cell shows that there are eight sets of slip planes in different directions. As a result, metals with cubic

close-packed structures, like copper, are malleable: they can easily be bent, flattened, or pounded into shape. In contrast, a hexagonal close-packed structure has only one set of slip planes; and metals with hexagonal close packing, like zinc or cadmium, tend to be brittle.

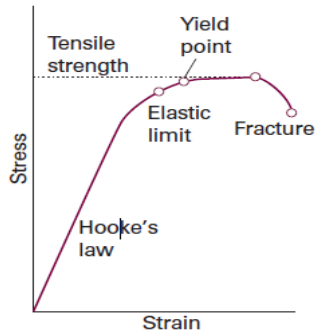


Fig. 20.49 At small strains, a body obeys Hooke's law

2- Electrical properties

We shall confine attention to electronic conductivity, but note that some ionic solids display ionic conductivity. Two types of solid are distinguished by the temperature dependence of their electrical conductivity (Fig. 50): A **metallic conductor** is a substance with a conductivity that decreases as the temperature is raised.

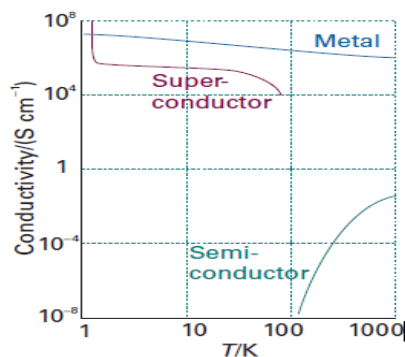


Fig. 50 The variation of the electrical conductivity of a substance with temperature

A **semiconductor** is a substance with a conductivity that increases as the temperature is raised.

A semiconductor generally has a lower conductivity than that typical of metals, but the magnitude of the conductivity is not the criterion of the distinction. It is conventional to classify semiconductors with very low electrical conductivities, such as most synthetic polymers, as insulators. We shall use this term, but it should be appreciated that it is one of convenience rather than one of fundamental significance. A superconductor is a solid that conducts electricity without resistance.

(a) The formation of bands

The central aspect of solids that determines their electrical properties is the distribution of their electrons. There are two models of this distribution. In one, the nearly free-electron approximation, the valence electrons are assumed to be trapped in a box with a periodic potential, with low energy corresponding to the locations of cations. In the tight-binding approximation, the valence electrons are assumed to occupy molecular orbitals delocalized throughout the solid. The latter model is more in accord with the discussion in the foregoing chapters, and we confine our attention to it.

We shall consider a one-dimensional solid, which consists of a single, infinitely long line of atoms. At first sight, this model may seem too restrictive and unrealistic. However, not only does it give us the concepts we need to understand conductivity

in three-dimensional, macroscopic samples of metals and semiconductors, it is also the starting point for the description of long and thin structures, such as the carbon nanotubes discussed earlier in the chapter.

Suppose that each atom has one s orbital available for forming molecular orbitals. We can construct the LCAO-MOs of the solid by adding N atoms in succession to a line, and then infer the electronic structure using the building-up principle.

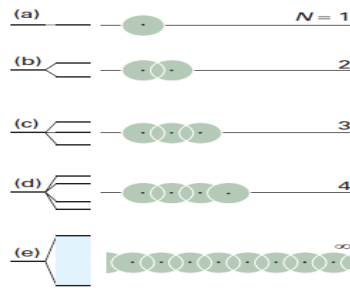


Fig. 51 The formation of a band of N molecular orbitals by successive addition of N atoms to a line. Note that the band remains of finite width as N becomes infinite and, although it looks continuous, it consists of N different orbitals.

One atom contributes one s orbital at certain energy (Fig. 51). When a second atom is brought up it overlaps the first and forms bonding and antibonding orbitals. The third atom overlaps its nearest neighbor (and only slightly the next-nearest), and from these three atomic orbitals, three molecular orbitals are formed: one is fully bonding, one fully antibonding, and the intermediate orbital is nonbonding between neighbors. The fourth atom leads to the formation of a fourth molecular orbital. At this stage, we can begin to see that the general effect of bringing up successive atoms is to spread the range of energies covered by the

molecular orbitals, and also to fill in the range of energies with more and more orbitals (one more for each atom). When N atoms have been added to the line, there are N molecular orbitals covering a band of energies of finite width, and the Hückel secular determinant is

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \dots & 0 \\ \beta & \alpha - E & \beta & 0 & 0 & \dots & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & \dots & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & \dots & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \dots & \vdots \\ 0 & 0 & 0 & 0 & 0 & \dots & \alpha - E \end{vmatrix} = 0$$

Where β is now the (s, s) resonance integral,

The theory of determinants applied to such a symmetrical example as this (technically a ‘tridiagonal determinant’) leads to the following expression for the roots:

$$E_R = \alpha + 2\beta \cos \frac{k\pi}{N-1} \quad \text{where } k = 1, 2, \dots, N \quad (21)$$

When N is infinitely large, the difference between neighboring energy levels (the energies corresponding to k and $k + 1$) is infinitely small, but, as we show in the following *Justification*, the band still has finite width overall:

$$E_N - E \rightarrow 4\beta \quad \text{when } N \rightarrow \infty \quad (22)$$

We can think of this band as consisting of N different molecular orbitals, the lowest energy orbital ($k = 1$) being fully bonding, and the highest-energy orbital ($k = N$) being fully antibonding between adjacent atoms (Fig. 52). Similar bands form in three-dimensional solid

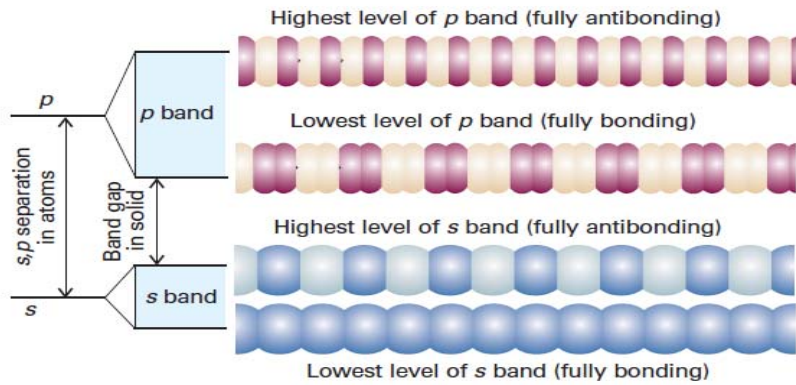


Fig. 52 The overlap of *s* orbitals gives rise to an *s* band and the overlap of *p* orbitals gives rise to a *p* band. In this case, the *s* and *p* orbitals of the atoms are so widely spaced that there is a band gap. In many cases the separation is less and the bands overlap.

The band formed from overlap of *s* orbitals is called the *s* band. If the atoms have *p* orbitals available, the same procedure leads to a *p* band (as shown in the upper half of Fig 52). If the atomic *p* orbitals lie higher in energy than the *s* orbitals, then the *p* band lies higher than the *s* band, and there may be a band gap, a range of energies to which no orbital corresponds. However, the *s* and *p* bands may also be contiguous or even overlap (as is the case for the 3*s* and 3*p* bands in magnesium).

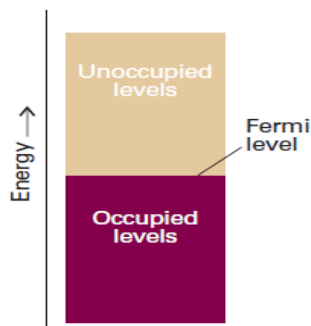


Fig. 53 When *N* electrons occupy a band of *N* orbitals, it is only half full and the electrons near the Fermi level (the top of the filled levels) are mobile.

(b) The occupation of orbitals

Now consider the electronic structure of a solid formed from atoms each able to contribute one electron (for example, the alkali metals). There are N atomic orbitals and therefore N molecular orbitals packed into an apparently continuous band. There are N electrons to accommodate.

At $T = 0$, only the lowest $1/2 N$ molecular orbitals are occupied (Fig. 53), and the HOMO is called the Fermi level. However, unlike in molecules, there are empty orbitals very close in energy to the Fermi level, so it requires hardly any energy to excite the uppermost electrons. Some of the electrons are therefore very mobile and give rise to electrical conductivity.

At temperatures above absolute zero, electrons can be excited by the thermal motion of the atoms. The population, P , of the orbitals is given by the Fermi–Dirac distribution, a version of the Boltzmann distribution that takes into account the effect of the Pauli principle:

$$p = \frac{1}{e^{(E-\mu)/kT} + 1} \quad (23)$$

The quantity μ is the chemical potential, which in this context is the energy of the level for which $P = 1/2$ (note that the chemical potential decreases as the temperature increases). The chemical potential in eqn 23 has the dimensions of energy, not energy per mole.

The shape of the Fermi–Dirac distribution is shown in Fig. 54. For energies well above μ , the 1 in the denominator can be neglected, and then

$$p = e^{-(E-\mu)/kT} \quad (24)$$

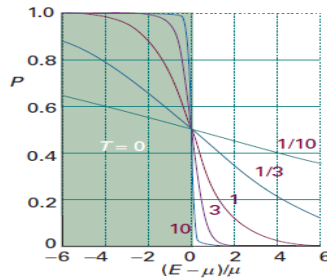


Fig. 54 The Fermi–Dirac distribution, which gives the population of the levels at a temperature T . The high-energy tail decays exponentially towards zero. The curves are labeled with the value of μ/kT . The pale green region shows the occupation of levels at $T = 0$.

The population now resembles a Boltzmann distribution, decaying exponentially with increasing energy. (The higher the temperature, the longer the exponential tail), The electrical conductivity of metallic solid decreases with increasing temperature even though more electrons are excited into empty orbitals. This apparent paradox is resolved by noting that the increase in temperature causes more vigorous thermal motion of the atoms, so collisions between the moving electrons and an atom are more likely. That is, the electrons are scattered out of their paths through the solid, and are less efficient at transporting charge.

(c) Insulators and semiconductors

When each atom provides two electrons, the $2N$ electrons fill the N orbitals of the s band. The Fermi level now lies at the top of the band (at $T = 0$), and there is a gap before the next band begins (Fig.55). As the temperature is increased, the tail of the

Fermi–Dirac distribution extends across the gap, and electrons leave the lower band, which is called the valence band, and populate the empty orbitals of the upper band, which is called the conduction band. As a consequence of electron promotion, positively charged ‘holes’ are left in the valence band. The holes and promoted electrons are now mobile, and the solid is an electrical conductor. In fact, it is a semiconductor, because the electrical conductivity depends on the number of electrons that are promoted across the gap, and that number increases as the temperature is raised. If the gap is large, though, very few electrons will be promoted at ordinary temperatures and the conductivity will remain close to zero, resulting in an insulator. Thus, the conventional distinction between an insulator and a semiconductor is related to the size of the band gap and is not an absolute distinction like that between a metal (incomplete bands at $T = 0$) and a semiconductor (full bands at $T = 0$).

Fig. 55 depicts conduction in an intrinsic semiconductor, in which semiconduction is a property of the band structure of the pure material. Examples of intrinsic semiconductors include silicon and germanium. A compound semiconductor is an intrinsic semiconductor that is a combination of different elements, such as GaN, CdS, and many *d*-metal oxides. An extrinsic semiconductor is one in which charge carriers are present as a result of the replacement of some atoms (to the extent of about 1 in 10^9) by dopant atoms, the atoms of another

element. If the dopants can trap electrons, they withdraw electrons from the filled band, leaving holes which allow the remaining electrons to move (Fig. 56a). This procedure gives rise to

p- type semiconductivity, the p indicating that the holes are positive relative to the electrons in the band. An example is silicon doped with indium. We can picture the semiconduction as arising from the transfer of an electron from a Si atom to a neighboring in atom. The electrons at the top of the silicon valence band are now mobile, and carry current through the solid. Alternatively, a dopant might carry excess electrons (for example, phosphorus atoms introduced into germanium), and these additional electrons occupy otherwise empty bands, giving n-type semiconductivity, where n denotes the negative charge of the carriers (Fig. 56b). The preparation of doped but otherwise ultrapure materials was described in *Impact I6.2*.

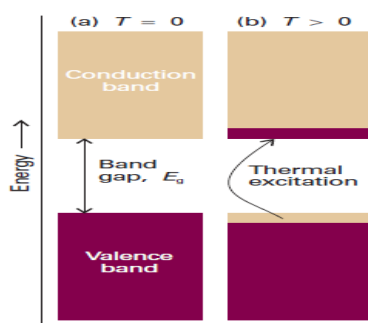


Fig. 20.55 (a) When $2N$ electrons are present, the band is full and the material is an insulator at $T = 0$. (b) At temperatures above $T = 0$, electrons populate the levels of the upper *conduction band* and the solid is a semiconductor.

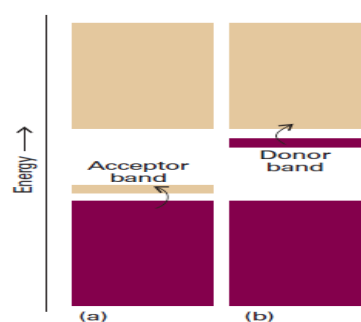


Fig. 20.56 (a) A dopant with fewer electrons than its host can form a narrow band that accepts electrons from the valence band. The holes in the band are mobile and the substance is a p-type semiconductor. (b) A dopant with more electrons than its host forms a narrow band that can supply electrons to the conduction band. The electrons it supplies are mobile and the substance is an n-type semiconductor.

Now we consider the properties of a **p–n junction**, the interface of a p-type and n type semiconductor. Consider the application of a ‘reverse bias’ to the junction, in the sense that a negative electrode is attached to the p-type semiconductor and a positive electrode is attached to the n-type semiconductor (Fig. 57a). Under these conditions, the positively charged holes in p-type semiconductor are attracted to the negative electrode and the negatively charged electrons in the n-type semiconductor are attracted to the positive electrode. As a consequence, charge does not flow across the junction. Now consider the application of a ‘forward bias’ to the junction, in the sense that the positive electrode is attached to the p-type semiconductor and the negative electrode is attached to the n-type semiconductor (Fig. 57b). Now charge flows across the junction, with electrons in the n-type semiconductor moving toward the positive electrode and holes moving in the opposite direction. It follows that a p–n junction affords a great deal of control over the magnitude and direction of current through a material. This control is essential for the operation of transistors and diodes, which are key components of modern electronic devices.

As electrons and holes move across a p–n junction under forward bias, they recombine and release energy. However, as long as the forward bias continues to be applied, the flow of charge from the electrodes to the semiconductors will replenish them with electrons and holes, so the junction will sustain a

current. In some solids, the energy of electron–hole recombination is released as heat and the device becomes warm. This is the case for silicon semiconductors, and is one reason why computers need efficient cooling systems.

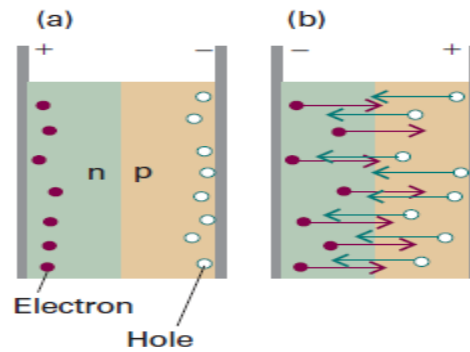


Fig. 57 A p–n junction under (a) reverse bias, (b) forward bias.