13

Electronic conductivity in solids

- How are donor atoms and acceptor atoms in semiconductors differentiated?
- What is a quantum well?
- What are Cooper pairs?

The electronic conductivity of solids varies widely (Figure 13.1). Solids that allow an electric current to flow when a small voltage is applied are called conductors. Solids that do not allow a current to flow are called insulators. Semiconductors fall between these two classes. As gauged from Figure 13.1, it is a matter of degree whether a solid is a conductor, semiconductor or an insulator but, irrespective of the magnitude of the effect, conductivity requires the presence of mobile charge carriers. In this chapter, solids that have reasonable numbers of mobile charge carriers present, either because of their native electronic properties or because they have been deliberately introduced by doping, are considered. In addition, superconductors, a group of materials that appear not to use 'normal' conductivity mechanisms, are described.

13.1 Metals

13.1.1 Metals, semiconductors and insulators

One of the defining physical properties of a metal is its electrical conductivity. (Section S4.6 gives definitions of this and related terms.) Electrical conductivity in a solid is attributable to electrons that are free to move (i.e. that gain energy) under the influence of an applied electric field. The metallic bonding model, described in Sections 2.3.2 and 2.3.3, allows conductivity to be understood most easily. In this model, the electrons on the atoms making up the solid are allocated to energy bands that run throughout the whole of the solid. A simple one-dimensional band-structure diagram, called a flat-band diagram (Figure 13.2), allows the broad distinction between conductors, semiconductors and insulators to be understood.

If the number of electrons available fills the energy band completely, and the energy gap between the top of the filled band and the bottom of the next higher (empty) energy band is large, the material is an insulator (Figure 13.2a). This is because the electrons have no means of taking up the additional energy needed to allow them to move under a low voltage, because all of the energy levels are filled or inaccessible. Only a considerable voltage will cause electrons to jump from the

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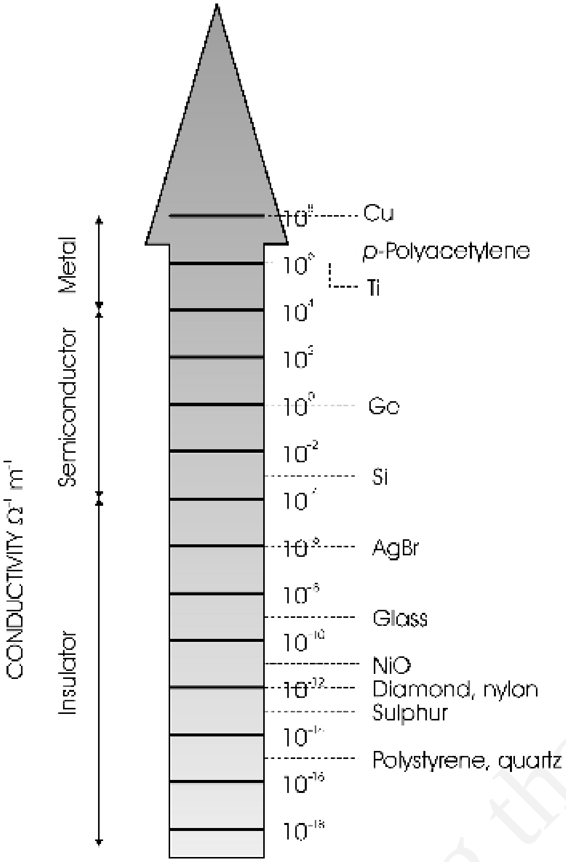


Figure 13.1 The range of electronic conductivity in solids

completely filled band to the next-highest empty band, and when such a transfer does occur the insulator has broken down.

If the energy gap between the filled and empty band is small enough that thermal energy is sufficient to cause some electrons to jump from the lower filled band to the upper empty band, the electronic properties change. Such materials are called intrinsic semiconductors (Figure 13.2b). Once electrons arrive in the empty band, they can contribute to electrical conductivity, as there are empty energy levels around them and the solid is transformed from an insulator into a poor electronic conductor. The now almost filled band is called the valence band, and the almost empty band is called the conduction band. The energy gap is the band gap, E_g.

Although this picture is simple, it reveals an important feature. It is found that the 'vacancies' left in the valence band when electrons are promoted to the conduction band also contribute to the conduction process. To a good approximation, these vacancies can be equated to positive electrons, and move in the opposite direction to the electrons in an applied field. They are called positive holes, or just holes. Semiconductors are characterised by an increase in conductivity with temperature because the number of mobile charge carriers, electrons and holes, will increase as the temperature increases.

If the band gap is so small that thermal energy at normal temperatures is sufficient to generate a very high number of charge carriers in each band the material is classed as a degenerate semiconductor. At 0 K intrinsic semiconductors become insulators.

Semiconductivity can arise in an insulator if the material contains an appreciable number of impurities (added intentionally or not). Similarly, the conductivity of an intrinsic semiconductor can be manipulated by adding suitable impurities. The impurities can act as donors, donating electrons to the conduction band to form n-type semiconductors (Figure 13.2c), or as acceptors, accepting electrons from the valence band, and thus donating holes to the valence band, to form p-type semiconductors (Figure 13.2d). When all of the impurities are fully ionised (i.e. when all the donor levels have lost an electron or all the acceptor levels have gained an electron) the exhaustion range has been reached. If the donors and acceptors are present in equal numbers the material is said to be a compensated semiconductor. At 0 K these materials are also insulators. It is difficult in practice to distinguish between compensated extrinsic semiconductors and intrinsic semiconductors.

When there are insufficient electrons to fill the highest band (the valence band becomes indistinguishable from the conduction band in this case) even small amounts of energy will be able to move the topmost electrons into higher energy levels, and small voltages will produce significant conductivity and the solid is a metal (Figure 13.2e). The

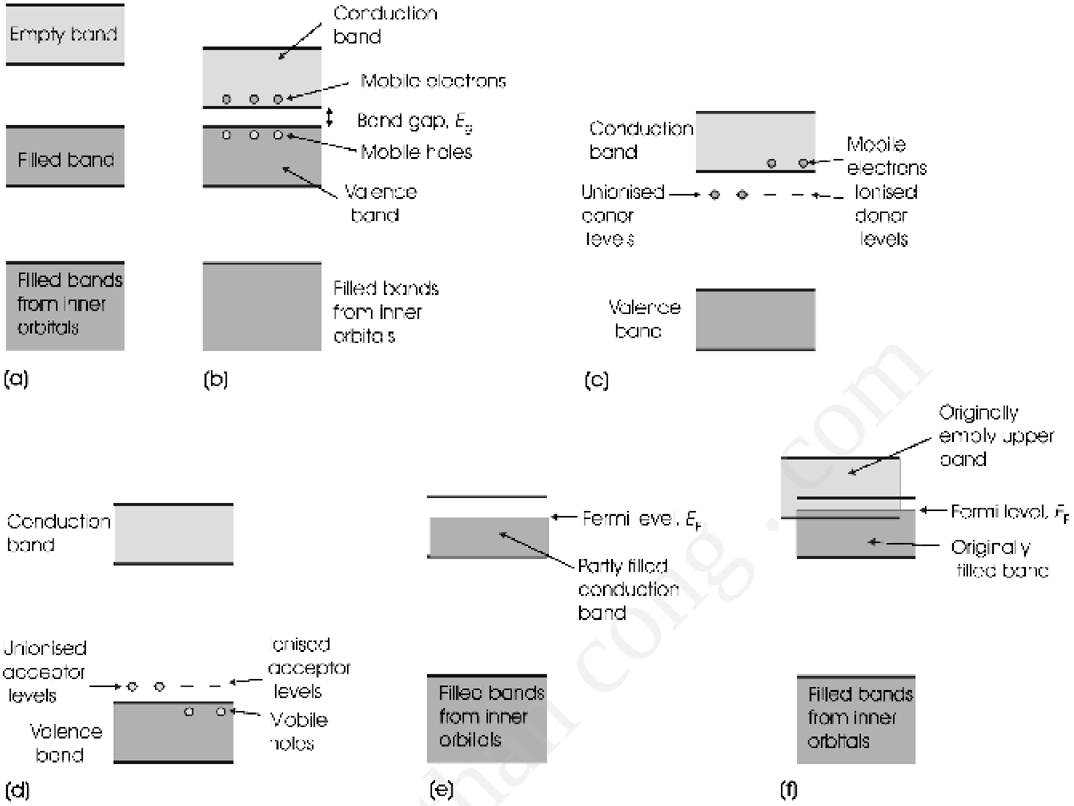


Figure 13.2 Energy-band representations of materials: (a) insulators, (b) intrinsic semiconductors, (c) n-type extrinsic semiconductors, (d) p-type extrinsic semiconductors, (e) metals and (f) semimetals. The innermost filled energy bands are omitted in parts (c) and (d)

uppermost filled energy levels form the Fermi surface. Should the bottom of the $(n+1)$th band lie energetically lower than the top of a full nth band, electrons will spill over into the bottom of the empty band until the Fermi level intersects both sets of bands. Holes and electrons now exist, and coexist at 0 K. This type of material is called a semimetal (Figure 13.2f).

From the point of view of metallic conductivity, the nature of the atoms composing the structure is not important. The primary point is that there should be an upper band, a conduction band, which is party filled with electrons. This depends on crystal structure and the extent to which the outer electron orbitals overlap. A large number of compounds have sufficient overlap of the outer orbitals to generate bands of reasonable width, and can loosely be classed as metals. Many oxides, including ReO_3 and TiO, as well as nitrides, phosphides and silicides have high conductivities and can often be considered as metals or semimetals. Large numbers of sulphides and selenides are considered to be best classified as high-conductivity semiconductors, whereas tellurides tend to be regarded as metallic.

13.1.2 Conductivity of metals and alloys

Although the conductivity of a metal is dependent on the shape of the Fermi surface, a good idea of the conduction properties of metals can be gained by considering the properties of a metal with a half-filled conduction band and a spherical Fermi

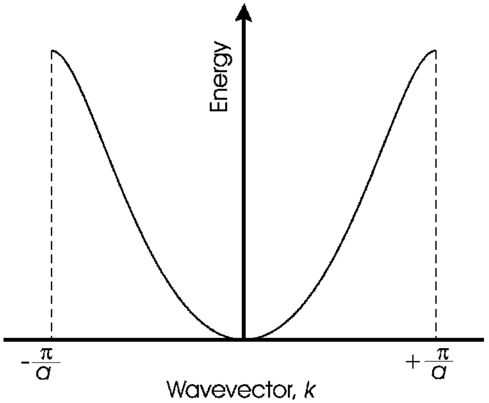


Figure 13.3 The energy versus wave vector curve for a free electron in a metal

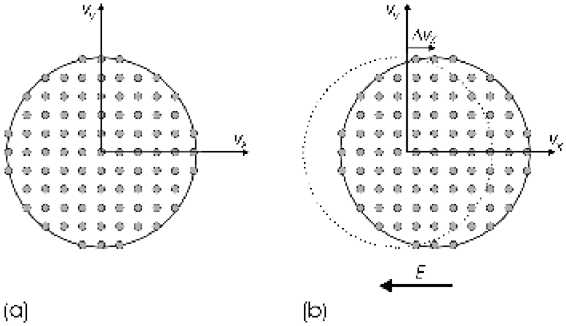


Figure 13.4 The Fermi surface (circled) marks the boundary up to which velocity states (shaded circles) of free electrons in a 'two-dimensional' metal are occupied. (a) In the absence of an electric field, equal numbers of electrons are moving in all directions, and the sum of the velocities is zero. (b) In an electric field, $\boldsymbol{E}$, the distribution of velocities changes (solid outer boundary compared with the dotted boundary), causing more to move against the direction of the electric field. This overfall drift velocity is observed as electronic conductivity

surface. The ideas already described with respect to the metallic bond (Section 2.3) are able to account for this.

Return to the simple energy versus wave-vector diagram of a 'one-dimensional' metal (Figure 13.3). The wave vector, $\boldsymbol{k}$, can be expressed in terms of the velocity or the momentum of the electrons:

$$\boldsymbol{k} = \frac{2\pi}{\lambda} = \left(\frac{2\pi}{h}\right)\boldsymbol{p} = \left(\frac{2\pi m}{h}\right)\mathbf{v} \qquad (13.1)$$

where λ is the wavelength of the electron wave, $\boldsymbol{p}$ is the momentum of the electron, m is the mass of the electron, $\mathbf{v}$ is the velocity of the electron, and h is Planck's constant. Thus $\boldsymbol{k}$ is proportional to both momentum and velocity. Each energy level is then associated with an electron velocity, which increases as the Fermi surface is approached. The Fermi surface therefore divides the occupied velocity states from the unoccupied states.

In the case of a 'two-dimensional' metal, the Fermi surface can be represented as a circle, with velocity components along the x and y axes (Figure 13.4a). Because velocity states are filled up to the Fermi surface, when the metal is at normal equilibrium the velocities sum to zero. Thus, although the electrons are in motion, no current flows.

When an electric field, $\boldsymbol{E}$, is applied to the metal, each electron experiences a force $-e\boldsymbol{E}$ and a change in momentum, $\Delta\boldsymbol{p}$, which is equivalent to a change in the value of the wave vector, $\Delta\boldsymbol{k}$, and velocity, $\Delta\mathbf{v}$, of the electrons. An electric field applied along the x axis will translate the velocity distribution parallel to the x axis by a small amount opposite to the direction of the applied field, shown as the solid-line outer circle as compared with the dotted circle in Figure 13.4b. The velocities no longer sum to zero along x, and electrons drift in a direction opposite to that of the applied field. A current then flows. The effect is limited by collisions with atoms, impurities and defects and a steady current is reached.

The electronic conductivity of a metal can be estimated from this model. It is found (see Section S4.7) that the conductivity, σ, and its reciprocal, the resistivity, ρ, are given by:

$$\sigma = \frac{e^2 n\tau}{m_e^*}$$

$$\rho = \frac{m_e^*}{e^2 n\tau}$$

where e is the electron charge, n is the number of mobile electrons in the metal, τ is the average time an electron spends between two successive scattering events, and m_e^* is the effective mass of the electrons. This latter term is used to account for the fact that the dynamics of electrons in solids is quite different from that in a vacuum, and measurements show that the mass that applies to electrons in a vacuum (the rest mass) needs to be replaced by an effective mass. The effective mass is not a constant but depends on temperature and the direction in the crystal that the electron is travelling.

If it is assumed that the velocity of an electron is reduced to zero each time it is scattered, then it is seen that the current will decay to zero in a time τ after the voltage is turned off. The term τ, the time between successive scattering processes, is also called the relaxation time. The mean free path of the electron, which is the length of the path between successive scattering events, is given by:

$$\Lambda = \tau \mathrm{v}_\mathrm{F}$$

where v_F is the electron velocity at the Fermi surface.

The conductivity is often written in terms of another variable, the mobility of the electrons, μ_e:

$$\sigma = ne\mu_\mathrm{e}$$

where the mobility is given by:

$$\mu_\mathrm{e} = \frac{e\tau}{m_\mathrm{e}^*}$$

Scattering is the main cause of resistivity. The electron wave can be scattered in a variety of ways, of which three are of most importance. The first is the interaction of the electron wave with lattice vibrations, called phonons. This is called thermal scattering. As the temperature increases so do the lattice vibrations, and the resistivity rises. At low temperatures the resistivity drops gradually to a finite value, maintained at absolute zero (Figure 13.5), except for the superconductors, described later in this chapter. This is an intrinsic property of a metal and cannot be altered. Structural imperfections present in the solid also contribute to resistivity. These are mainly defects such as dislocations and grain boundaries, or else impurities. As with lattice vibrations, they scatter the electron waves and so increase resistivity. Defects and impurities are extrinsic features that can be removed by careful processing.

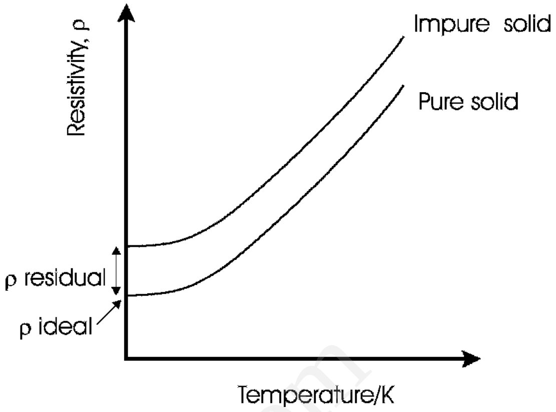


Figure 13.5 The variation of the resistivity of a metal with temperature; impure solids and alloys have a higher resistivity than pure metals, at all temperatures

The different scattering processes can be allocated relaxation times as follows. Suppose that the distance between thermal scattering events is Λ_th. The number of scattering events per second, n_thermal, will be given by:

$$\begin{aligned} n_\mathrm{thermal} &= \frac{\mathrm{v}_\mathrm{F}}{\Lambda_\mathrm{th}} \\ &= 1/\tau_\mathrm{th} \end{aligned}$$

where v_F is the electron velocity at the Fermi surface, and τ_th is the thermal relaxation time. Analogous equations can be written in respect of the distance between defect scattering, Λ_def, and between impurity scattering, Λ_imp. Thus the resistivity can be written:

$$\rho = \frac{m_\mathrm{e}^*}{e^2 n_\mathrm{F} \tau_\mathrm{th}} + \frac{m_\mathrm{e}^*}{e^2 n_\mathrm{F} \tau_\mathrm{def}} + \frac{m_\mathrm{e}^*}{e^2 n_\mathrm{F} \tau_\mathrm{imp}}$$

Taking into account these features, the total resistivity can be written as:

$$\rho = \rho_\mathrm{phonons} + \rho_\mathrm{defects} + \rho_\mathrm{impurities}$$

This is known as Mattiesen's rule, sometimes written as:

$$\rho = \rho_\mathrm{ideal} + \rho_\mathrm{residual}$$

where ρ_ideal is the intrinsic component due to phonon interactions and ρ_residual is the extrinsic contribution.

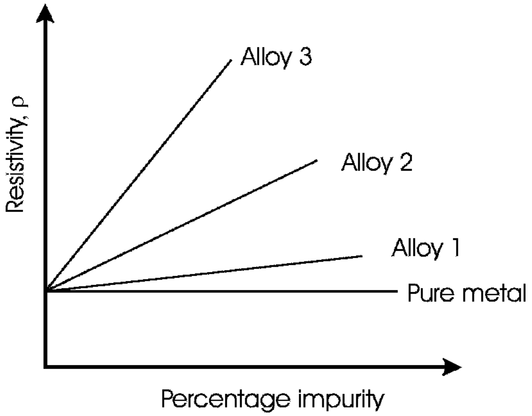


Figure 13.6 The variation of the resistivity of alloys with concentration of the alloying elements

The resistivity of a substitutional solid solution alloy will generally be greater than that of a pure metal because the elements added to form the alloy have the same effect as impurities (Figure 13.6). If the alloying atoms order to form a new crystal structure, the disruptive scattering of the electron wave is suppressed and the resistivity will drop.

A consequence of the electron collisions is a transfer of energy from the mobile electrons to the structure. This is revealed as heat energy and accounts for the fact that an electric current generates heat. This effect, which takes place uniformly along the length of the conductor, is called Joule heating. The amount of heat generated is:

$$P = I^2R$$

where P is the power output (W), I is the current (A), and R is the resistance (Ω). This heating poses problems for closely packed electronic circuits, which have to be cooled to function correctly.

13.2 Semiconductors

13.2.1 Intrinsic semiconductors

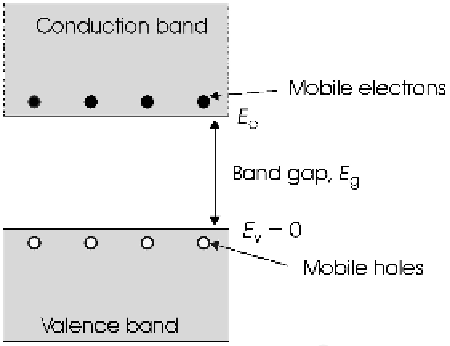


Figure 13.7 The simplest 'flat-band' energy-band description of an intrinsic semiconductor

The simplest band picture of a semiconductor is drawn in Figure 13.7. The energy gap between the top of the valence band, E_v, and the bottom of the conduction band, E_c, is called the band gap, E_g. Electron energy increases (and is defined to be positive) when measured *upwards* from the top of the valence band, which is usually taken as the energy zero. Hole energy increases (and is defined to be positive) when measured *downwards* from the top of the valence band. At absolute zero, the valance band will be full and the conduction band empty. As the temperature increases, some electrons will be promoted across the narrow band gap, and the material will show a small degree of conductivity. Because the number of electrons promoted will increase with temperature, the conductivity will rise with temperature. This increase is characteristic of a semiconductor and is of greater importance than the magnitude of the conductivity. Remember that for metals conductivity falls with increasing temperature.

The conductivity, σ, of a semiconductor is made up of two components, one due to electrons,

$$\sigma_e = ne\mu_e$$

and one due to holes,

$$\sigma_h = pe\mu_h$$

so that the overall conductivity will be given by:

$$\sigma(\text{total}) = ne\mu_e + pe\mu_h$$

where the subscripts e and h refer to electrons and holes, respectively; the number of electrons is given by n; the number of holes is given by p; and the mobility is given by μ.

It is possible to determine the number of electrons excited into the conduction band by thermal energy in an intrinsic semiconductor using Fermi–Dirac statistics (see Section 2.3.7 and Section S4.12). It is found that:

$$n \propto \exp\left(-\frac{E_g}{2kT}\right)$$

where n is the number of electrons in the conduction band, E_g is the band gap between the top of the valence band and the bottom of the conduction band, k is the Boltzmann constant, and T is the absolute temperature. As the number of holes is equal to the number of electrons in an intrinsic semiconductor,

$$p \propto \exp\left(-\frac{E_g}{2kT}\right)$$

The total conductivity, σ, which is proportional to the number of electrons and holes, can be expressed in the form:

$$\sigma = \sigma_0 \exp\left(-\frac{E_g}{2kT}\right)$$

where σ_0 is a constant, E_g is the band gap between the top of the valence band and the bottom of the conduction band, k is the Boltzmann constant, and T is the absolute temperature. Taking logarithms of each side of this equation, we obtain

$$\ln \sigma = \ln \sigma_0 - \frac{E_g}{2kT}$$

The gradient of a plot of conductivity versus $1/T$ will therefore yield a value for the (thermal) band gap (Figure 13.8).

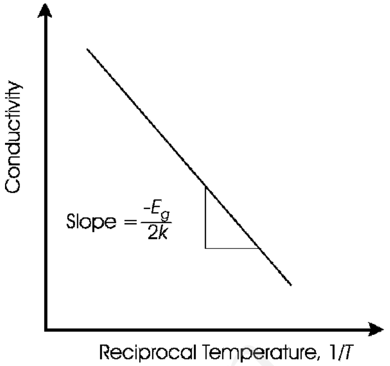


Figure 13.8 The variation of resistivity versus reciprocal temperature for an intrinsic semiconductor

An alternative method of obtaining the magnitude of the band gap is via the absorption of radiation. In a semiconductor, almost all of the energy levels below the conduction band are occupied. This means that low-energy radiation directed at a crystal will not interact with the electrons, and the crystal will be transparent. As the energy gradually increases, eventually the energy will just be sufficient to promote an electron from the top of the valence band to the bottom of the conduction band. The radiation will now be absorbed and the crystal will become opaque. The (optical) band gap can be equated to the energy at which this change occurs. Thus,

$$E_g = h\nu_g$$

where $h\nu_g$ is the energy of the photon required to promote an electron from the valence band and create a hole in its place.

Note that the absorption of radiation is more complex than this simple model suggests, and a more complete description will be given in Section 14.1.3. Moreover, the measured value of the optical band gap is usually slightly different from the thermal band gap. This is simply a reflection of the fact that the bands in a semiconductor are not flat as drawn in Figure 13.7 but have a more complex curved shape.

Approximate values for the band gap in some semiconductors is given in Table 13.1. The band gap decreases as the atom size increases (i.e. as one moves down the relevant group in the periodic table). Thus, within the group of elements listed, diamond is best regarded as an insulator, whereas grey tin is regarded as a metal. The second group

Table 13.1 Approximate values for the band gap of some semiconductors

Compound	Symbol or formula	Band gap/eV
Elements:		
Diamond	C	5.47
Silicon	Si	1.12
Germanium	Ge	0.66
Grey tin	Sn	0.08
III–V semiconductors:		
Gallium nitride	GaN	3.36
Gallium phosphide	GaP	2.26
Gallium arsenide	GaAs	1.42
II–VI semiconductors:		
Cadmium sulphide	CdS	2.42
Cadmium selenide	CdSe	1.70
Cadmium telluride	CdTe	1.56

Note: the band gap is normally given in electron volts in most compilations; 1 eV is equal to 1.60219×10^{-19} J.

are called III–V semiconductors because they are compounds of elements in groups III and V (now groups 13 and 15) of the periodic table. The last compounds listed are called II–VI semiconductors because they are compounds of elements in groups II and VI (now groups 12 and 16) of the periodic table.

The decrease in band gap with size of atom is simply a consequence of the fact that the outer orbitals of larger atoms overlap more and give rise to wider bands. As a consequence, the gaps are narrower.

13.2.2 Carrier concentrations in intrinsic semiconductors

To determine more accurate values for the number of holes and electrons present in an intrinsic semiconductor it is appropriate to use Fermi–Dirac statistics and the density of states at the bottom of the conduction band (see Section S4.8). To a good approximation, it is found that the number of electrons in the conduction band per unit volume, n_i, which is equal to the number of intrinsic holes in the valence band, p_i, at an absolute temperature, T, is:

$$n_i = p_i = 4.826 \times 10^{21} \left(\frac{m_e^* m_h^*}{m_e^2} \right)^{3/4} T^{3/2} \exp\left(-\frac{E_g}{2kT} \right) \tag{13.2}$$

where m_e^* is the effective mass of the electron, m_h^* is the effective mass of a hole, and E_g is the band gap. In an intrinsic semiconductor

$$n = p = n_i = p_i$$

Equation (13.2) shows that, at a given temperature

$$np = \text{constant}$$

The temperature dependence of the equilibrium constant is given by:

$$np = 2.33 \times 10^{43} \left(\frac{m_e^* m_h^*}{m_e^2} \right)^{3/2} T^3 \exp\left(-\frac{E_g}{kT} \right)$$

Assuming that the effective mass of electrons and holes is independent of temperature, we obtain

$$np \propto T^3 \exp\left(-\frac{E_g}{kT} \right)$$

This equation applies to doped semiconductors as well as to intrinsic semiconductors, a finding of considerable practical importance. To a good approximation, the Fermi energy lies at the centre of the band gap (Section S4.8):

$$E_F = \frac{1}{2} E_g + \frac{3}{4} kT \ln\left(\frac{m_h^*}{m_e^*} \right) \approx \frac{1}{2} E_g$$

Writing the total conductivity, $\sigma(\text{total})$, as

$$\sigma(\text{total}) = ne\mu_e + pe\mu_h$$

we obtain

$$\sigma(\text{total}) = 773.1 \left(\frac{m_e^* m_h^*}{m_e^2} \right)^{3/4} T^{3/2} (\mu_e + \mu_h) \times \exp\left(-\frac{E_g}{2kT} \right) \tag{13.3}$$

Although the mobility of electrons and holes decreases with temperature, exactly as in a metal, it is found that the conductivity of an intrinsic semiconductor increases with temperature, as the exponential term in Equations (13.2) and (13.3) dominates the other terms.

13.2.3 Extrinsic semiconductors

The deliberate addition of carefully chosen impurities to silicon, germanium and other semiconductors is called doping. It is carried out so as to modify the electronic conductivity, and the dopants are chosen so as to add either electrons or holes to the material. It is possible to gain a good idea of how this is achieved very simply. Suppose that an atom such as phosphorus, P, ends up in a silicon crystal. This can occur, for example, if a small amount of phosphorus impurity is added to molten silicon before the solid is crystallised. Experimentally the impurity atom is found to occupy a position in the crystal that would normally be occupied by a silicon atom, and so forms a substitutional defect.

Silicon adopts the diamond structure, in which each atom is linked to four tetrahedrally disposed neighbours by four sp^3 hybrid bonds (Section 5.3.6). These use all of the four ($3s^2$, $3p^2$) valence electrons available. Phosphorus is found one place to the right of silicon in the periodic table, which indicates that the atom has one more electron in its complement. The outer electron structure of phosphorus is $3s^2$, $3p^3$, and, after forming four sp^3 hybrid bonds, one electron is spare and still associated with the phosphorus atom (Figure 13.9a.i). This electron is available to enhance the electrical conductivity if it can enter the conduction band. Atoms such as phosphorus are called donors when they are added to silicon as they can donate the unused valence electron to the conduction band.

The simplest model to employ for the estimation of the energy needed to free the electron uses the Bohr theory of the hydrogen atom. To recall this model, a single electron is attracted to a positive nucleus consisting of a single proton. The energy needed to free this electron is given by:

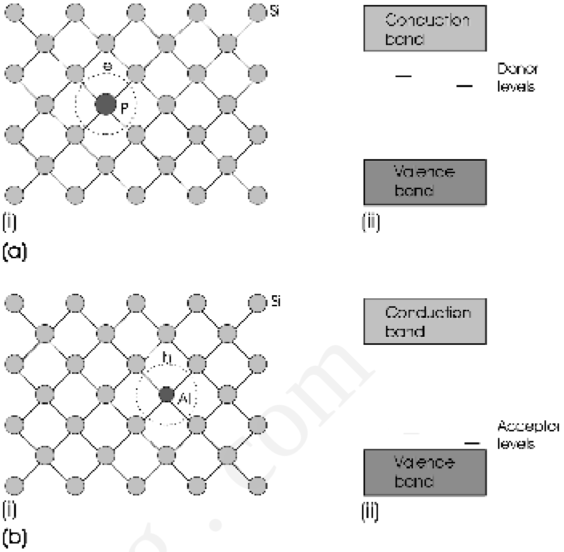


Figure 13.9 (a) (i) Donor impurity in a crystal of an extrinsic semiconductor and (ii) the associated energy-band diagram; donor impurities add donor energy levels below the conduction band. (b) (i) Acceptor impurity in a crystal of an extrinsic semiconductor and (ii) the associated energy-band diagram; acceptor impurities add acceptor energy levels above the valence band

$$E = -\frac{m_e e^4}{8\varepsilon_0^2 h^2}$$

where m_e is the mass of the electron, e is the electron charge, ϵ_0 is the permittivity of free space, and h is the Planck constant. The value of E is -2.18×10^{-18} J (-13.6 eV). The negative value reflects the fact that zero is taken as the energy of a completely free electron. To apply this to an electron located at a phosphorus atom, suppose that the attraction of the phosphorus nucleus is 'diluted' by the relative permittivity of silicon, ϵ_r, and the mass of the electron is replaced by the effective mass m_e^*. The energy to free the electron is now:

$$E(\mathrm{P}) = -\frac{m_e^* e^4}{8\varepsilon_0^2 \varepsilon_r^2 h^2}$$

$$= \frac{E m_e^*}{m_e \varepsilon_r^2}$$

As the effective mass of an electron in silicon is approximately one tenth of the electron rest mass, and as the relative permittivity of silicon is about 10, the energy needed to free the electron is about one hundredth of the band gap, which suggests that the electron should be very easily liberated. Donor energies are often represented by an energy level, the donor level, drawn under the conduction band (Figure 13.9a.ii).

An analogous situation arises if silicon is doped with an element such as aluminium. Aluminium is also found to form a substitutional defect. However, aluminium is found one place to the left of silicon in the periodic table, with a valence electron configuration $3s^2$, $3p^1$, and has one valence electron less than silicon. One of the four resulting sp^3 hybrid bonds will be an electron short. This is equivalent to the introduction of a positive hole, which is localised on the aluminium impurity (Figure 13.9b.i). Providing that the energy needed is not too great, an electron from the full valance band can be promoted to fill the bond, leaving a hole in the valence band. The energy needed to free the hole, calculated using the Bohr model, is similar to that of an electron. Once in the valance band, the hole is free to move and to contribute to the conductivity. Dopant atoms from the left of silicon in the periodic table, such as aluminium, are called acceptors, because they can be imagined to accept an electron from the filled valence band and so create a hole that takes part in conductivity. These impurities can also be represented by energy levels, drawn just above the top of the valence band (Figure 13.9b.ii).

The energy to liberate donor electrons and acceptor holes is about 8×10^{-21} J (0.05 eV). These values are comparable to room temperature thermal energy, and most extrinsic electrons and holes should be free at room temperature. In this state, the donors and acceptors are said to be ionised, and the semiconductor crystal will be a reasonable conductor. If donor atoms are present in great numbers, they will govern the conductivity, which will be by electrons. The material is said to be n-type. If acceptors are present in greatest quantities, then holes will control the conduction, and the material is said to be p-type. When both electrons and holes are present and both contribute to the conductivity we talk of majority and minority carriers.

The number of holes and electrons present is not solely dependent on the number of donors and acceptors present. The equilibrium equation,

$$np = \text{constant} = n_i^2 \qquad (13.4)$$

governs populations. If large numbers of donors are added, so that n increases, the number of holes decreases accordingly. Similarly, if large numbers of acceptors are added, the population of holes increases and the number of electrons decreases. This vital fact makes it possible to fabricate silicon-chip electronic circuits, founded on the ability to transform n-type to p-type silicon, and vice versa, at will. If the relationship given in Equation (13.4) did not hold, successive doping cycles would simply increase overall conductivity.

13.2.4 Carrier concentrations in extrinsic semiconductors

The electronic properties of an extrinsic semiconductor are determined by the number of mobile charge carriers, electrons and holes, both intrinsic and extrinsic, and by the position of the Fermi energy (Figure 13.10). The total numbers of mobile electrons and holes is related to n_i and p_i, the numbers of intrinsic electrons, and holes by:

$$np = \text{constant} = n_i^2 = p_i^2$$

The number of holes created by the addition of the acceptors is equal to N_a^-, where the number of acceptor atoms per unit volume is N_a, and the number of acceptors that have gained an electron,

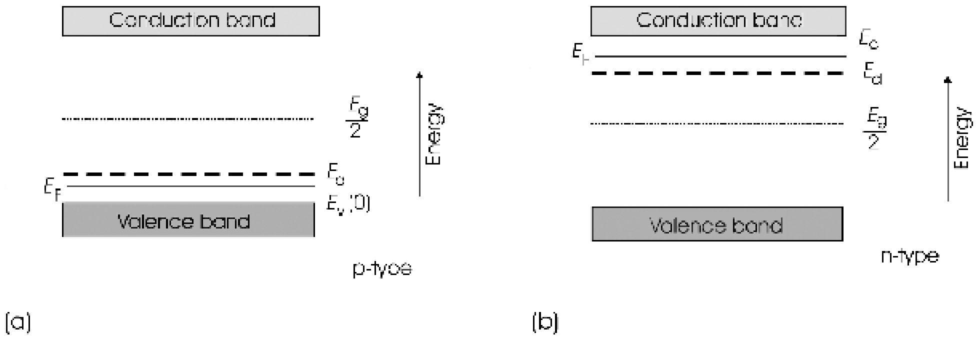


Figure 13.10 The position of the Fermi energy in (a) a p-type semiconductor and (b) an n-type semiconductor at low temperatures

ionised acceptors, is N_a^-. Similarly, the number of electrons created by the addition of the donors is equal to N_d^+, where the number of donor atoms per unit volume is N_d, and the number of donors that have lost an electron, ionised donors, is N_d^+. As a doped crystal must remain electrically neutral,

$$n + N_a^- = p + N_d^+ \qquad (13.5)$$

Equations (13.4) and (13.5) allow the numbers of mobile charge carriers and the position of the Fermi level to be found as a function of dopant concentration, using a similar approach to that outlined in Section S4.8 for intrinsic semiconductors. Unfortunately, the results are not easily expressed analytically or displayed graphically.

At elevated temperatures, most of the donors and acceptors will be ionised, and the electroneutrality condition, Equation (13.5), can be written as:

$$n + N_a = p + N_d \qquad (13.6)$$

In cases where an n-type semiconductor contains only donors, and at high temperatures, so that the donors are completely ionised, Equations (13.4) and (13.6) give the number of electrons and holes as

$$n(\text{n-type}) \approx N_d$$

$$p(\text{n-type}) \approx \frac{n_i^2}{N_d}$$

Similarly, for a p-type semiconductor crystal that contains only acceptors at high temperatures, the number of electrons and holes is:

$$n(p\text{-}type) \approx \frac{n_i^2}{N_a}$$

$$p(p\text{-}type) \approx N_a$$

The position of the Fermi level is a function of the temperature and the concentration of the electrons and holes (Figure 13.11). At low temperatures, the position of the Fermi level approaches the conduction band in n-type materials and the valence band in p-type materials. In effect, the Fermi level changes in order to maintain a balance between the charges (Figure 13.12). As the temperature increases, the contribution from the intrinsic electrons and holes increases. In essence, the semiconductor gradually changes from an extrinsic towards an intrinsic material. Because of this, the Fermi level approaches the position found in intrinsic semiconductors, near to the middle of the band gap. The rapidity of this change will depend on the concentrations of donors and acceptors in the semiconductor. A semiconductor will maintain its extrinsic character to higher temperatures when doped with higher concentrations of impurities.

13.2.5 Characterisation

Although the resistance of a metal can be measured easily by attaching two contacts, this gives

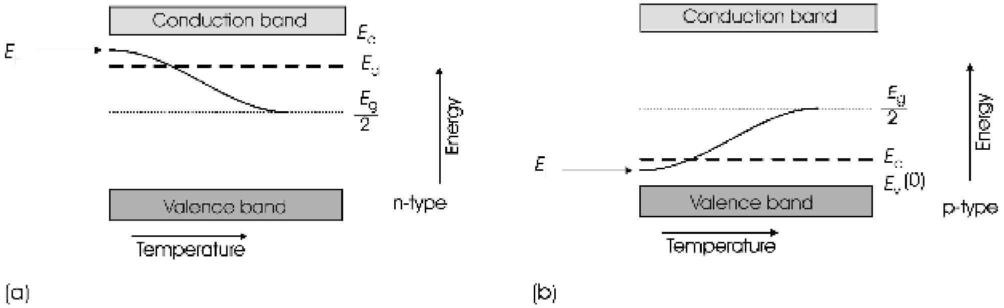


Figure 13.11 The variation of the position of the Fermi energy of (a) an n-type and (b) a p-type semiconductor with temperature

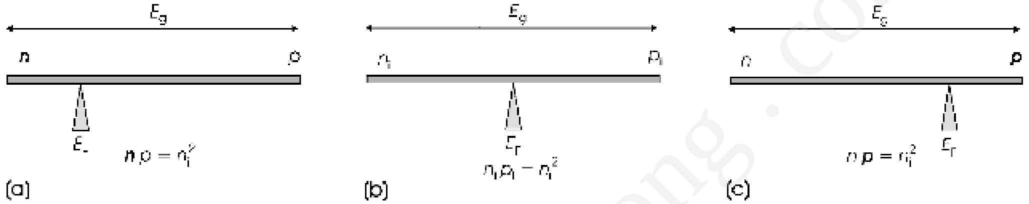


Figure 13.12 The position of the Fermi energy in semiconductors varies with temperature and dopant concentration so as always to maintain the relationship np = constant: (a) in an n-type semiconductor the concentration of electrons is much higher than the concentration of holes, and the Fermi energy is to the left-hand side of the ‘balance’; (b) in an intrinsic semiconductor the concentration of holes and electrons is equal and the Fermi energy is central; (c) in an n-type semiconductor the concentration of holes is much higher than the concentration of electrons, and the Fermi energy is to the right-hand side of the ‘balance’. As the temperature increases the intrinsic contribution to the hole and electron concentrations becomes more important, and the Fermi energy tends towards the centre

unreliable results for semiconductors. For these materials, the resistivity is most often determined by using a four-point probe on rectangular (Figure 13.13a) or disc-shaped (Figure 13.13b) samples. The probes are sharply pointed, equally spaced, needles and press down with a known force on the surface of the sample. The current passes between two outer probes, and the voltage drop is measured between the two inner probes. The relationship between the measured

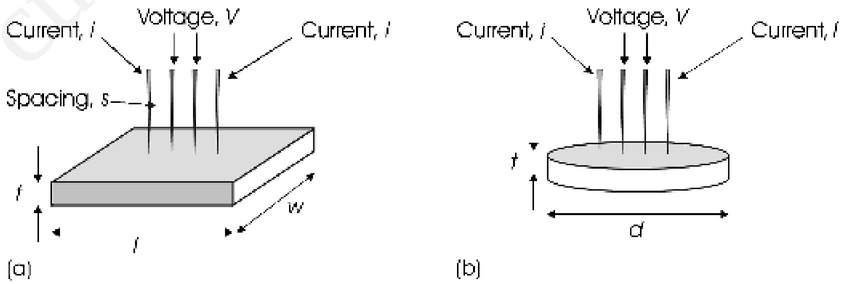


Figure 13.13 Arrangement in the four-point probe method of measurement of resistance of semiconductors for (a) rectangular specimen and (b) a disc. The spacing, s, of the probes is much smaller than the dimensions of the specimen. The current is measured between the outer probes, and the voltage drop is measured between the inner two probes

voltage and current and the resistivity depends on the geometry of the experimental setup. For a bulk specimen, in which the thickness of the sample is much greater than the spacing between the probes,

$$\rho = 2\pi s\left(\frac{V}{I}\right)$$

where ρ is the resistivity of the material, s is the distance between the probe needles, V is the voltage drop between the middle two needles, and I is the current between the outer two needles. In the case of a thin film, in which the probe spacing, s, is much greater than the film thickness, t, and much smaller than the distance to the edge of the film, that is $l, w \gg s \gg t$ (Figure 13.13a), or $d \gg s \gg t$ (Figure 13.13b), the expression for the resistivity is:

$$\rho = \frac{\pi t}{\ln 2}\frac{V}{I}$$

$$\approx 4.54t\frac{V}{I}$$

This formula is independent of the probe spacing, s.

The resistance of thin films is sometimes reported as the sheet resistance, R_s. This is defined in terms of the bulk resistance of a material, R, of resistivity ρ, and the dimensions of the sample. For a rectangular specimen (Figure 13.13a):

$$R_s = \frac{\rho}{t}$$

$$\rho = \frac{Rwt}{l}$$

hence

$$R_s = \frac{Rw}{l}$$

The sheet resistance is quoted in unit of ohms per square (Ω/□). Thus

$$\rho = R_s t\,(\Omega\, m)$$

The carrier type can be found in two ways, via the Hall effect or the Seebeck effect. The second technique is described in Section 15.2.2. The Hall effect, discovered in 1879, relies on the displacement of moving charges in a magnetic field to determine the nature of the mobile carriers. A slab of material is arranged so that the current flow is normal to a fairly strong (0.2 T), magnetic induction (Figure 13.14a). The moving charges will experience a force due to the magnetic induction in the solid that is normal both to current direction and to magnetic field. That is, if the current I is along the x axis and the magnetic induction is along the z axis the charge carriers will be deflected in the y-axis direction. This deflection will build up until the electric field density is just strong enough to oppose further charge displacement. The result is a voltage, the Hall voltage, along the y-axis. Perhaps counterintuitively the charge carriers will be deflected in the same direction, irrespective of the charge that they carry, and the sign of the voltage will give the sign of the charge carriers. The value of the Hall voltage, V, can be appreciable.

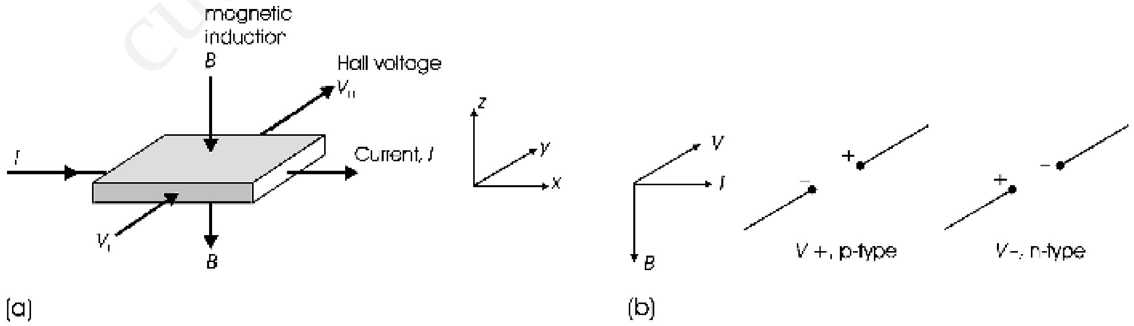


Figure 13.14 (a) Arrangement of the measurement of the Hall effect, showing the axes used; (b) the sign of the Hall voltage with respect to the direction of the current and magnetic induction

The relationship between the current, magnetic induction and electric field is:

$$\boldsymbol{E}_y = \pm R_{\mathrm{H}} \boldsymbol{J}_x \boldsymbol{B}_z \tag{13.7}$$

where $\boldsymbol{E}_{\mathrm{y}}$ is the electric field along the y axis, measured in $\mathrm{V\,m^{-1}}$, $\boldsymbol{J}_x$ is the current density along the x axis, measured in $\mathrm{A\,m^{-2}}$, and $\boldsymbol{B}_z$ is the magnetic induction along the z axis, measured in T. The constant of proportionality, the Hall coefficient, R_{H}, has units $\mathrm{m^3\,C^{-1} = V\,m\,A^{-1}\;T^{-1}}$. The sign of the Hall coefficient differentiates n-type and p-type semiconductors. For example, if the magnetic induction is aligned along $-z$ (Figure 13.14a), a positive Hall voltage compared with the orthogonal *V, B* and *I* axes, yields a positive value for R_{H} and the material is p-type, whereas a negative voltage and negative R_{H} indicates that the material is n-type (Figure 13.14b).

The Hall coefficient is related in a simple way to the number of mobile charge carriers. Suppose that the current is made up of electrons flowing parallel to x with a drift velocity v_x. The magnetic field present will exert a force, $\boldsymbol{F}$, on an electron:

$$\boldsymbol{F} = e\mathbf{v}_x\boldsymbol{B}_z$$

The force exerted by an electric field, $\boldsymbol{E}_{\mathrm{y}}$, on an electron is given by

$$\boldsymbol{F} = \boldsymbol{E}_{\mathrm{y}}\, e$$

When the two forces are equal and equilibrium is achieved,

$$\boldsymbol{E}_{\mathrm{y}} = \mathbf{v}_x\boldsymbol{B}_z$$

The current density is given by:

$$\boldsymbol{J} = -ne\mathbf{v}_x$$

where n is the number of mobile electrons per unit volume. Substituting the expressions for $\boldsymbol{E}_y$ and $\boldsymbol{J}$ into Equation (13.7), and rearranging, we obtain:

$$R_{\mathrm{H}} = \frac{-1}{ne}$$

where n is the number of electrons per unit volume, each with a charge of $-e$. For a flow of positive holes:

$$R_{\mathrm{H}} = \frac{1}{pe}$$

where p is the number of mobile holes per unit volume, each with a charge of $+e$.

In general, only one mobile charge carrier, either electrons or holes, is present. In this case, by measuring both the conductivity, σ, and the Hall coefficient, R_{H}, it is possible to determine the number of charge carriers and their mobility as:

$$\sigma_{\mathrm{e}} = ne\mu_{\mathrm{e}}$$
$$-R_{\mathrm{H}}\sigma_{\mathrm{e}} = \mu_{\mathrm{e}}$$

or

$$\sigma_{\mathrm{h}} = pe\mu_{\mathrm{h}}$$
$$+R_{\mathrm{H}}\sigma_{\mathrm{h}} = \mu_{\mathrm{h}}$$

If both electrons and holes are present:

$$\begin{aligned}\sigma(\text{total}) &= ne\mu_{\mathrm{e}} + pe\mu_{\mathrm{h}}\\ &= |e|(n\mu_{\mathrm{e}} + p\mu_{\mathrm{h}})\end{aligned}$$

and

$$R_{\mathrm{H}} = \frac{n\mu_{\mathrm{e}}^2 + p\mu_{\mathrm{h}}^2}{(n\mu_{\mathrm{e}} + p\mu_{\mathrm{h}})^2}\,\frac{1}{|e|}$$

The mobility derived from a Hall measurement is often called the Hall mobility to distinguish it from the drift mobility (see Section S4.7).

For noncubic single crystals the Hall coefficient varies with direction, although the effect is averaged when measurements are made on polycrystalline samples. A number of ordinary metals have positive Hall coefficients, including Be, Al, Cd, In, As and W. These results could not be explained in terms of the classical 'electron gas' model. In some metals, such as Er and Ho, the Hall coefficient varies from negative to positive as a function of crystallographic direction. The explanation of these findings requires a detailed knowledge of the three-dimensional shape of the Fermi surface in these metals.

13.2.6 The p–n junction diode

The electrical behaviour that emerges when a region of p-type semiconductor is adjacent to a region of n-type semiconductor, a p–n junction diode, often just called a diode, is different from the behaviour of the separate components. (Note that p–n junction diodes are fabricated by selective doping of different regions of a semiconductor crystal and not by joining separate crystals together.)

The simplest band picture of a p–n junction is shown in Figure 13.15. In separated materials, the Fermi energies are unequal (Figures 13.15a and 13.15b). When a p-type region abuts an n-type

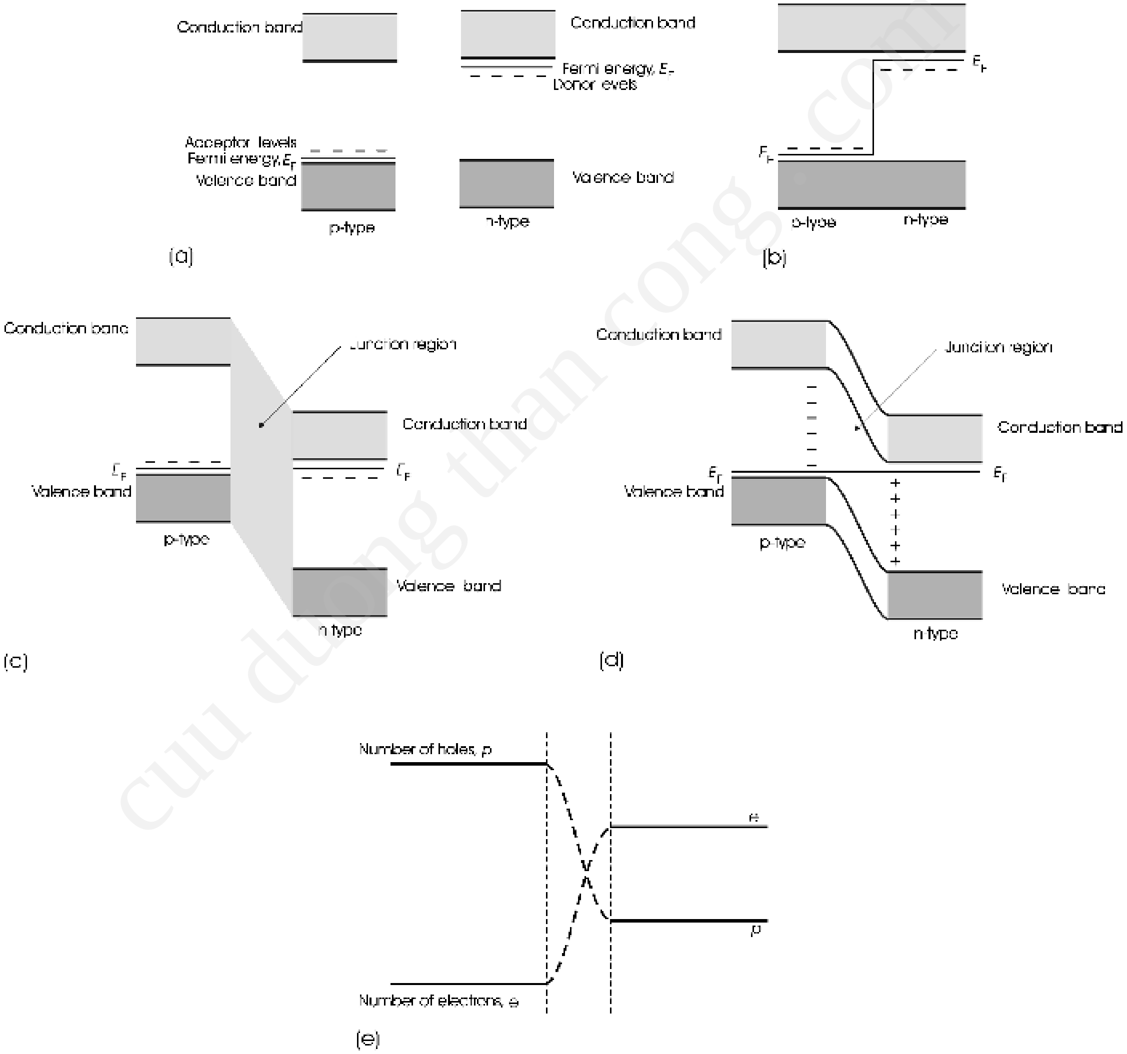


Figure 13.15 The p–n junction. (a) energy bands of separated p-type and n-type materials; (b) schematic energy bands for juxtaposed p-type and n-type materials. (c) energy bands on joining; (d) distorted energy bands in the junction region at equilibrium; and (e) the numbers of electrons and holes across the junction region at equilibrium

region, electrons move into the p-type region from the n-type side, and holes move into the n-type region from the p-type region, by diffusion. This can be thought of as electrons spilling *down* the Fermi surface, E_F, from p to n, and holes spilling *up* the Fermi surface, E_F, from p to n. Most of these moving displaced charge carriers will recombine, holes with electrons in the n region, and electrons with holes in the p region. As electrons leave the n-type material, positively charged donor atoms are left behind, and negatively charged acceptor atoms are left in the p-type material as holes leave. These charges will create an electric potential, the contact potential, of about 0.3 V. At equilibrium, the Fermi level must be the same on each side of the junction (Figure 13.15c). The energy levels have been shifted vertically with respect to each other, by the difference in E_F values, to give a distorted band structure in the junction region (Figure 13.15d), and the electron and hole populations change dramatically as the junction is traversed (Figure 13.15e).

The transition region has a width of about 1 μm. The density of mobile charge carriers in the transition region is low, and for this reason the transition region is also called the depletion region. At equilibrium (thermal and electrical) there will still be an exchange of carriers at the junction, but the current in each direction will be the same. Dynamic equilibrium holds.

The conductivity of the p–n junction in one direction is totally different from that in the other. An applied voltage, which will drop across the transition region, because of the absence of mobile charge carriers, can be applied with the positive side connected either to the p-type region or to the n-type region. The arrangement in which the positive voltage is connected to the p-type region is called forward bias. This causes the potential barrier to be reduced. The Fermi level changes to allow electrons to 'roll down' the Fermi level and the holes 'roll up' the Fermi level, causing a current to flow (Figure 13.16a). Under a forward bias there is a rapid increase in the current flowing across the junction. The situation when the negative voltage is applied to the p-type region is called reverse bias (Figure 13.16b). The effect of the reverse bias is to raise the potential barrier, so that electrons cannot pass up it or holes down it. Current flow now virtually ceases.

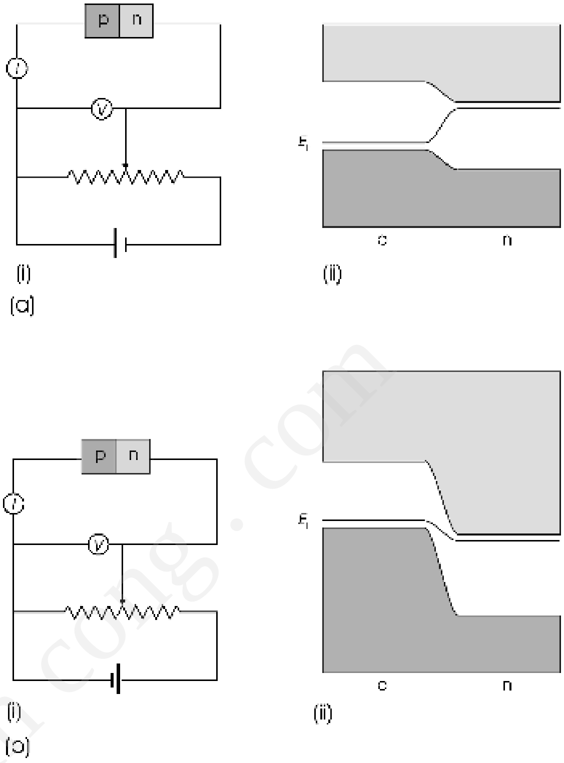


Figure 13.16 (a) (i) A p–n junction under forward bias and (ii) band structure of the junction; (b) (i) a p–n junction under reverse bias and (ii) band structure of the junction

The change of current with applied voltage is given by the Shockley equation. In a simplified form this is:

$$I = I_0 \left[\exp\left(\frac{eV}{kT}\right) - 1 \right]$$

where I_0 is a constant term, the saturation current, determined by the junction geometry and the doping levels; e is the charge on the electrons and holes; V is the applied voltage; k is the Boltzmann constant; and T is the temperature (Figure 13.17).

The total current across the device, which is constant for any applied voltage, is made up of

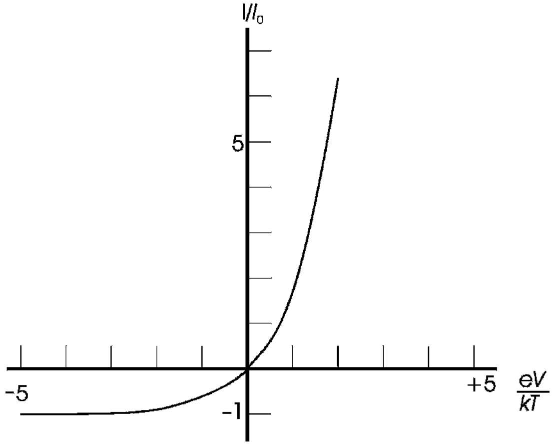


Figure 13.17 The ideal current–voltage characteristics for a p–n junction. Note: I and I_0, the current and the saturation current, respectively; e, charge on the electrons and holes; V, applied voltage; k, the Boltzmann constant; T, temperature

hole and electron flows in opposite directions. Consider the situation when a forward bias is applied (Figure 13.18). The number of electrons moving to the left will increase rapidly, by a factor of $\exp(V/kT)$. If V is 0.1 V, this is a factor of about ×55 at room temperature. Thus the number of electrons appearing at the p-type boundary is about 55 times higher than the equilibrium concentration there. A similar situation describes the holes appearing at the n-type boundary. In general, the hole current will be greater than the electron current under forward bias, but the actual currents on each side will depend on the doping levels.

When the electrons reach the p-type region they are annihilated by combination with holes. The penetration depth depends on a number of factors, but can be taken to be about 1 mm. In order to maintain charge neutrality, the hole population must be replenished and holes must be move into the p-type region from the left to balance the electron density. Similarly, the holes that arrive in the n-type region are gradually annihilated by recombination with electrons. In order to maintain charge balance, an extra electron current must flow into the n-type region from the right.

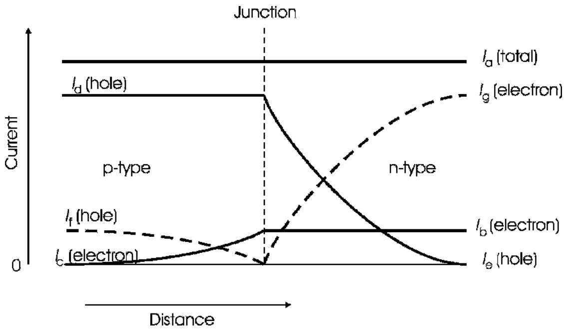


Figure 13.18 The currents I_a–I_g flowing across a p–n junction under forward bias

The total current flowing will be made up of six components (Figure 13.18):

- I_a, total current (constant) $= I_b + I_e + I_g = I_c + I_d + I_f$;
- I_b, electron current flowing in the n-type region (constant);
- I_c, injected electron current in p-type region (decaying);
- I_d, hole current in p-type region (constant);
- I_e, injected hole current in n-type region (decaying);
- I_f, declining hole current in p-type region to balance and annihilate I_c;
- I_g, declining electron current in n-type region to balance and annihilate I_e.

This is quite different than in a metal, in which an applied voltage allows the mobile electrons to acquire a drift voltage. In a p–n junction, minority carriers are injected into both regions. They were not there originally and arise as a consequence of the applied voltage.

From what has been said, it can be seen that a p–n junction diode acts as a rectifier. That is, the device exhibits a very low resistance to current flow in one direction and a very high resistance in the other.

13.2.7 Modification of insulators

The properties of insulators can be modified in the same way as the properties of semiconductors, and an insulator can be transformed into a semiconductor by suitable doping. The impurities can act as donors, donating electrons to the conduction band, or as acceptors, accepting electrons from the valence band, and thus donating holes to the valence band. Nickel oxide, NiO, has the *halite* (B1) structure and can be considered to be an ionic oxide, containing equal numbers of Ni^{2+} and O^{-} ions. Green nickel oxide can be reacted with colourless lithium oxide, Li_2O, to give a black solid solution $Li_xNi_{1-x}O$. The Li^+ ions occupy Ni^{2+} sites in the structure to form substitutional defects. In order to maintain charge neutrality, every Li^+ ion in the crystal must be balanced by a Ni^{3+} ion. This can be regarded as a Ni^{2+} ion together with a trapped hole. The situation is thus analogous to that of Al^{3+} doped into silicon, and the defect can be regarded as an acceptor (Figure 13.19a). The process of creating electronic defects in a crystal in this way is called valence induction. Black $Li_xNi_{1-x}O$ is a p-type semiconductor, and as the holes are only weakly bound to the cations the material posses a high conductivity.

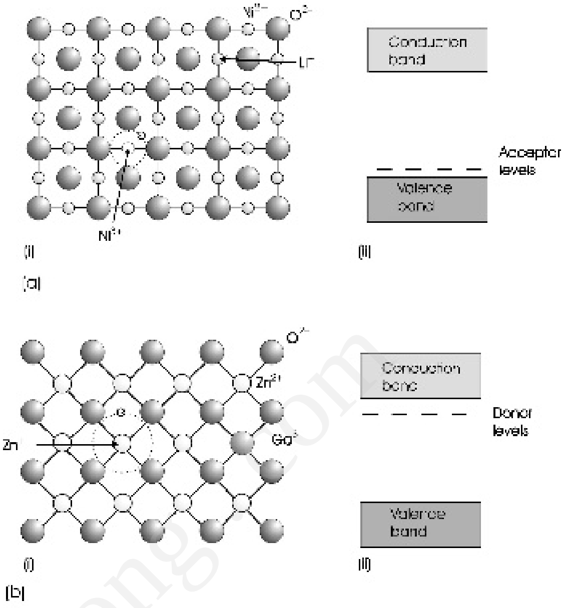


Figure 13.19 The conversion of insulating oxides into semiconductors. (a) (i) Nickel oxide (NiO) doped with lithium oxide (Li_2O), making it a p-type semiconductor, and (ii) the energy-band structure of Li^+-doped NiO. (b) (i) Zinc oxide (ZnO) doped with gallium oxide (Ga_2O_3), making it an n-type semiconductor, and (ii) the energy-band structure of Ga^{3+}-doped ZnO

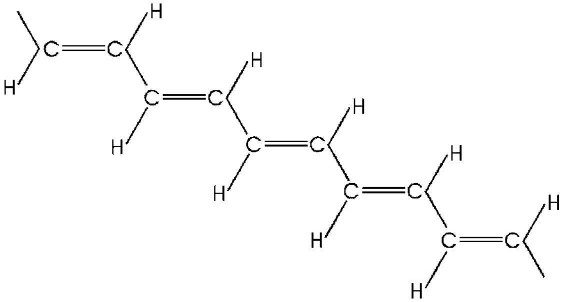
It is equally possible to impart n-type conductivity to an insulator by suitable doping. An example is provided by the reaction of small amounts of gallium oxide, Ga_2O_3, with zinc oxide, ZnO. In this case, Ga^{3+} ions substitute for Zn^{2+} ions in the zinc oxide structure to form $Ga_xZn_{1-x}O$. To maintain charge neutrality, one electron must be added to balance each Ga^{3+} ion in the structure. It is generally believed that these rest on Zn^{2+} ions to generate Zn^+ ions in the crystal. The electrons are not strongly attached to the Zn^{2+} ions, and each Zn^+ ion can be regarded as a donor (Figure 13.19b).

The key to valence induction is that the cation of the host structure can take two valence states, one of which is regarded as the host cation plus a weakly bound hole or electron.

The electronic properties of complex oxides can be changed in the same way, provided that one of the cations present can take part in the valence change. $SrVO_3$ provides an example. The structure of this phase is of the cubic *perovskite* type. This material, which is an insulator, contains Sr^{2+} ions in the large sites between the metal–oxygen octahedra and V^{4+} ions in the octahedra. If some of the Sr^{2+} ions are replaced by La^{3+} ions, charge neutrality is maintained by transforming some V^{4+} ions into V^{3+} ions. The V^{3+} ions can be regarded as V^{4+} ions plus a trapped electron, and are donors. Thus although $SrVO_3$ is a poor electronic conductor, $La_xSr_{1-x}VO_3$ is quite a good one.

13.2.8 Conducting polymers

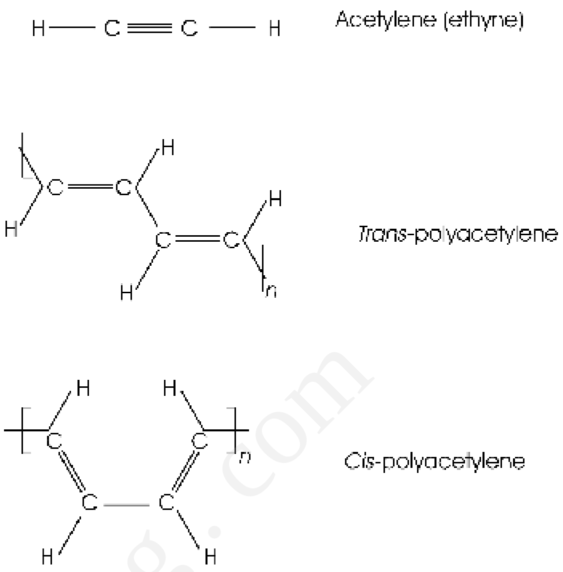
Ordinary polymers are good insulators, and they are widely used in this capacity, as insulating covering



Scheme 13.1 Part of a conjugated hydrocarbon molecule, in which carbon atoms are linked alternately by single and double bonds. Note: C, carbon; H, hydrogen; bonds connecting the atoms are shown as lines

on cables and other electrical conductors. The molecular feature that allows polymers to become electronically conducting is the presence of conjugated double and single bonds (Scheme 13.1). The framework of the molecule is composed of sp^2 hybrid σ bonds, at 120 ° to each other (see Section 2.2.6). The double bonds are formed by overlap of π orbitals above and below the plane of the carbon chains. These are not located between specific pairs of carbon atoms, as drawn, but are spread over all of the molecule as delocalised π orbitals, similar to those above and below the planes of the sheets of carbon atoms in graphite. A long molecule will have extensive delocalised π orbitals, and it could be anticipated that these would lead to high electronic conductivity along the backbone of the molecule, to give a 'one-dimensional' metal.

The first conducting polymer to be synthesised was polyacetylene. When polymerised, acetylene (ethyne) forms a silvery flexible film of polyacetylene. Acetylene (ethyne) has a formula C_2H_2. The carbon atoms are linked by a triple bond, consisting of 1 sp-hybrid σ bond and two π bonds (Scheme 13.2). Generally, polymerisation leads to the all-*cis* polymer. At room temperature this changes to the thermodynamically stable all-*trans* form. These two forms are geometrical isomers (see Section S2.1). Both are poor insulators, with the *trans* form having a conductivity similar to that of silicon (approximately 10^{-3} S m^{-1}), and the *cis* form with a conductivity similar to that of water (approximately 0.1 S cm^{-1}).



Scheme 13.2 Schematic structures of polyacetylenes: (a) acetylene (ethyne), (b) repeating unit of the *trans* polymer and (c) repeating unit of the *cis* polymer

This is rather surprising if the band structure of these materials is considered. The sp^2 hybrid orbitals are filled and would give lower-energy filled bands that do not contribute to the conductivity. The remaining p_z orbitals on each carbon contain one electron. A chain of CH units, each with one unpaired outer electron, is analogous to a chain of alkali metal atoms such as lithium. On the one hand, if the separation of the carbon atoms is rather large, each electron would be completely localised on each carbon and the polymer would be a magnetic insulator, possibly ferromagnetic or antiferromagnetic (Figure 13.20a; see Section 12.3). On the other hand, if the intercarbon distance is small, each electron is able to delocalise over all of the carbon atoms in a π band. Each atom would contribute just one electron, which would produce a half-full band and the material should show metallic conductivity (Figure 13.20b).

The discrepancy is resolved in the following way. A linear chain of equispaced atoms in a metal, such as a chain of sodium atoms, is found to be energetically unstable. Instead, the spacing between the atoms will adjust itself so that an energy gap opens

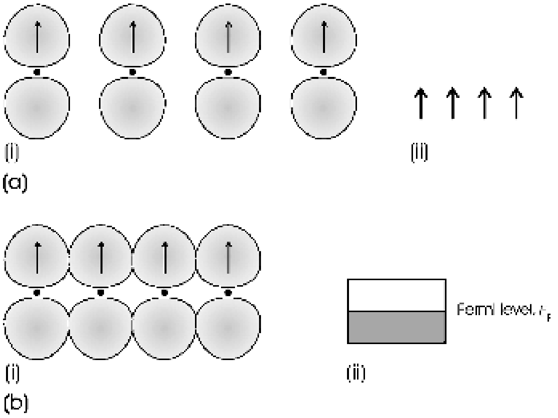


Figure 13.20 (a) (i) A chain of isolated half-occupied p orbitals, which will lead to a magnetic insulator and (ii) the magnetic dipoles in one possible orientation. (b) (i) A chain of overlapping p orbitals, which will lead to (ii) a half-filled conduction band and metallic conductivity

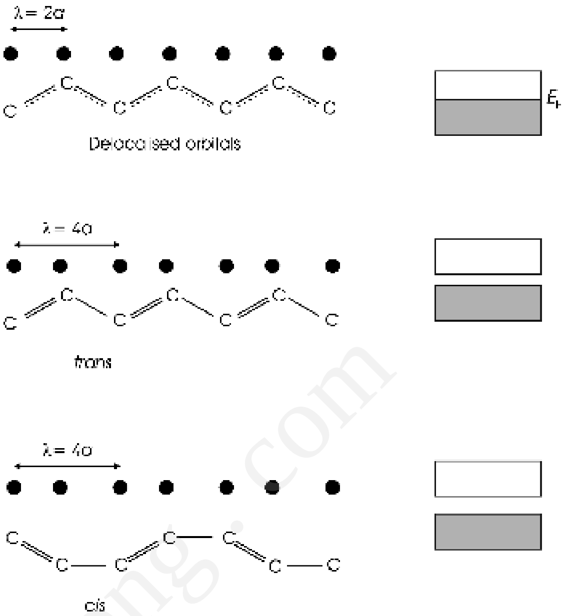


Figure 13.21 (a) Delocalised orbitals along a polymer chain leads to equally spaced atoms and a half-filled energy band. Peierls distortion in (b) *trans*-polyacetylene and (c) *cis*-polyacetylene, leads to alternating short and long bonds and a band structure similar to that of an intrinsic semiconductor

at the Fermi level. The variation in spacing is called a Peierls distortion. As a consequence, the half-filled band is transformed into two – a filled band and an empty band – and, as a result the solid becomes a semiconductor (Figure 13.21). In agreement with this, C–C bonds along the chain in *trans* and *cis* polyacetylene alternate between two lengths. The band gap is approximately 1.8 eV (2.88×10^{-19} J) in the *trans* form and about 2 eV (3.20×10^{-19} J) in the *cis* form of the polymer.

Polyacetylene is transformed into a metallic conductor by doping. This involves oxidation or reduction of the polymer. Electron acceptors such as halogens (chlorine, iodine, etc.) oxidise the polymer. In this process, electrons are taken from the filled lower band and used to form halide ions, leaving holes, which result in a 'p-type' material. A typical reaction is:

$$[\mathrm{CH}]_n + \frac{3x}{2}\mathrm{I}_2 \rightarrow [(\mathrm{CH})_n^{x+}x(\mathrm{I}_3^-)]$$

The iodine enters the polymer between the molecular chains.

Doping with alkali metals (lithium, sodium, etc.) reduces the polymer. In this process, the alkali metal donates electrons to the empty band, forming an alkali metal ion and transforming the polymer into an 'n-type' material. A typical reaction can be written as:

$$[\mathrm{CH}]_n + x\mathrm{Li} \rightarrow [(\mathrm{CH})^{x-}x\mathrm{Li}^+]$$

Conductivity of these doped materials is of the order of 10^8 S m^{-1}, similar to that of copper or silver. The variation of the conductivity with dopant concentration is illustrated in Figure 13.22. Notice that much greater concentrations of dopant are needed (at %) than those used in the traditional semiconductors such as silicon (parts per million). Heavy doping has transformed the insulating polymer into a material that seems to be metallic. This is an example of an insulator-to-metal transition.

However, the conductivity and other electrical properties of both the semiconducting and the

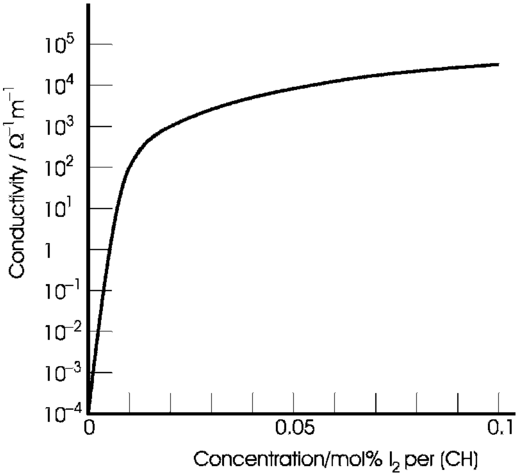


Figure 13.22 Schematic variation of the conductivity of polyacetylene doped with iodine. The concentration is in moles of I_2 per CH unit. The conductivity changes from that typical of an insulator to that associated with a metal

metallic region are not identical to those of the semiconductors and metals already discussed. For example, the conductivity in the metallic region of iodine-doped polyacetylene decreases as the temperature decreases (Figure 13.23) whereas in an ordinary metal the reverse is true. Moreover, the resistivity seems to have an Arrhenius-like temperature dependence:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$

where E_a is the activation energy, k is Boltzmann's constant, T is the temperature, and σ_0 is a constant (Figure 13.23). This suggests that the dopant does not simply add mobile carriers to a conduction or valence band, as with silicon.

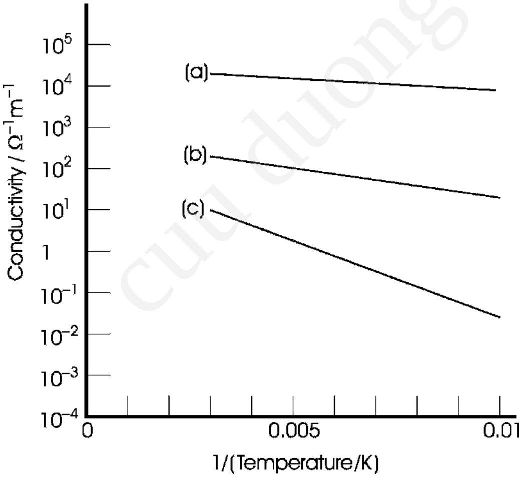


Figure 13.23 Schematic variation of the conductivity of polyacetylene doped with iodine versus reciprocal temperature. Dopant concentration is approximately (a) 0.15 mol%, (b) 0.01 mol% and (c) 0.005 mol% of I_2 per CH unit

The explanation of this feature is bound up with both the microstructure and the nanostructure of the polymer. Polyacetylene is composed of ordered, fairly crystalline, regions linked by disordered regions in which the polymer chains are twisted and coiled, which indicates that the band picture is a severe approximation. This is why dopants do not simply add mobile charge carriers to bands. The dopants, in fact, modify the nanostructure of the polymer chains. Acetylene polymerises preferentially to form the *cis* isomer, and this transforms into the stable *trans* form. The transformation process is initiated at random, rather like the nucleation of a crystal in a liquid. In the same way that crystallites grow together to form a polycrystalline mass, when two regions of polymer chain that have transformed from *cis* to *trans* meet there is frequently a mismatch (Figure 13.24). This mismatch is called a soliton, which can be thought of as an interruption in the orderly pattern of conjugated double bonds, extending over several adjacent carbon atoms. In some cases there will be a π electron missing, which will give the soliton a positive charge. In other cases, the soliton can attract an unbound π electron to give a neutral soliton, or two

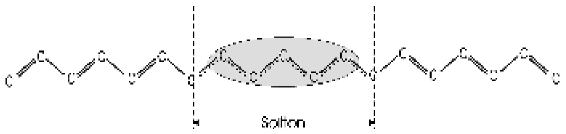


Figure 13.24 A soliton in *trans*-polyacetylene. The shaded ellipse in the centre of the soliton may represent either an electron hole (creating a positively charged soliton), a single electron (creating a neutral soliton) or two electrons (creating a negative soliton)

π electrons to give a negative soliton. Doping adds to the soliton density along the polymer chains by extracting or adding electrons.

Solitons give rise to two effects. First, at the soliton, the alternating bond lengths required for the Peierls transition are suppressed. Ultimately, when enough solitons are present, the Peierls transition fails and a half-filled band is reinstated, recreating the metallic state. Second, the solitons give rise to impurity energy levels in the band gap. When enough of these are present, they merge and bridge the band gap, again making high conductivity possible.

The conduction process is not simply the spread of electron waves throughout the solid, as in a crystalline metal. Instead, the charge on the soliton jumps from one location to a neighbouring one under the influence of an electric field. This is similar to ionic conductivity, and this produces the Arrhenius-like behaviour.

The conductivity of the polymer depends on the microstructure of the solid. Stretching the polymer sheet at moderate temperatures increases the alignment of the chains and leads to significant improvement in properties along the chain direction. In this form, polyactylene is widely used as an electrode material in lightweight batteries.

13.3 Nanostructures and quantum confinement of electrons

Section 3.2.5 introduced the ideas of quantum wells, quantum wires and quantum dots. These structures have unique electronic and optical properties because of the way in which electrons are localised, or confined. In bulk solids, electrons are located on atom cores in ionic solids, in localised bonds in normal covalent solids, delocalised over molecular orbitals, as in graphite, or completely delocalised, as in metals. Quantum nanostructures confine the electrons (and holes in semiconductors) at a scale different from any of these, and this gives rise to the novel properties that such structures possess. An electron or hole bonding energy much greater than thermal energy characterises strongly confined charge carriers.

13.3.1 Quantum wells

A quantum well is constructed by laying down a thin layer of a semiconductor with a smaller band gap within a semiconductor with a larger band gap. The most studied quantum well structures are those formed from a layer of gallium arsenide, GaAs, sandwiched in gallium aluminium arsenide, GaAlAs (Figure 13.25a). Gallium arsenide has a band gap of about 1.42 eV, whereas aluminium arsenide has a band gap of about 2.16 eV. Gallium

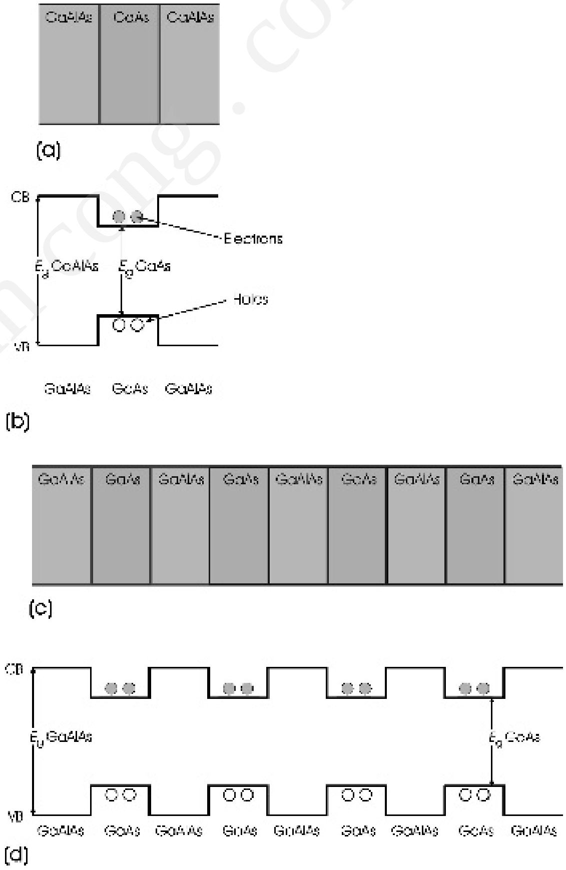


Figure 13.25 (a) A single quantum well of gallium arsenide, GaAs, formed from a thin layer in gallium aluminium arsenide, GaAlAs; (b) the energy band structure of the quantum well; (c) a multiple quantum well superlattice in gallium arsenide; and (d) the schematic energy band structure of the superlattice. Note: CB, conduction band; VB; valence band; E_g, band gap

aluminium arsenide alloys have band gaps between these values. The electrons in the thin GaAs layer are effectively trapped in the 'well' formed in the conduction band of the composite material (Figure 13.25b). Similarly, the holes in the thin layer of semiconductor are trapped at the 'hill' in the valence band of the composite material.

The properties of single quantum wells are enhanced when a number of these features are combined to form a multiple quantum well or superlattice (Figures 13.25c and 13.25d).

The dimension at which quantum confinement becomes important, Δx, is derived from the Heisenberg uncertainty principle (see Section 1.2.1). It is found that

$$\Delta x \approx \left(\frac{h^2}{m_e^* kT}\right)^{1/2}$$

for electrons, and

$$\Delta x \approx \left(\frac{h^2}{m_h^* kT}\right)^{1/2}$$

for holes, where h is the Planck constant, m_e^* is the effective mass of the electron in the semiconductor, m_h^* is the effective mass of the hole in the semiconductor, k is the Boltzmann constant, and T is the temperature (in kelvin). For quantum confinement to be important, quantum wells must be about 10 atom layers or less in thickness.

The energy of an electron in a quantum well can be calculated using the approach outlined in Section 2.3.6. If it is assumed that the electron is free, and trapped by an infinite boundary potential, the same equations for a free electron in a metal apply. Thus, the energy, E, of a free electron in a rectangular parallelepiped with edges a, b and c is given by Equation (2.15):

$$E(n_x, n_y, n_z) = \frac{h^2}{8m_e}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

where h is the Planck constant, m_e is the mass of the electron, and n_x, n_y and n_z are the quantum numbers along the three axes. Exactly the same equation will apply to a free electron confined to a slab of material, although it is better to replace the electron mass with the effective mass, m_e^*. In the case of a quantum well, the electron is confined in one dimension, say x, and unconfined in two directions, which can be taken as y and z, so it is convenient to rewrite Equation (2.15) as:

$$E(n_x, n_y, n_z) = \left(\frac{h^2}{8m_e^*}\right)\left(\frac{\mathrm{n_x}^2}{\mathrm{a}^2}\right) + \left(\frac{\mathrm{h}^2}{8m_e^*}\right)\left(\frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \tag{13.7}$$

The values of b and c can be taken as about 1 cm, and the value of a is about 10^{-8} m. The energy is therefore dominated by the first term in Equation (13.7). This introduces a new set of energy levels, associated with electron waves trapped in the well (Figure 13.26). The electron energy level in the lowest, $n = 1$, state is raised by $h^2/8m_e^* a^2$ compared with the base of the well. These energy levels are called electron subbands, and when the energy levels trap the electron strongly the electrons are strongly confined.

Exactly the same equations apply to holes, where the effective mass m_h^* replaces m_e^*. The energy levels that arise from trapped holes are called hole subbands.

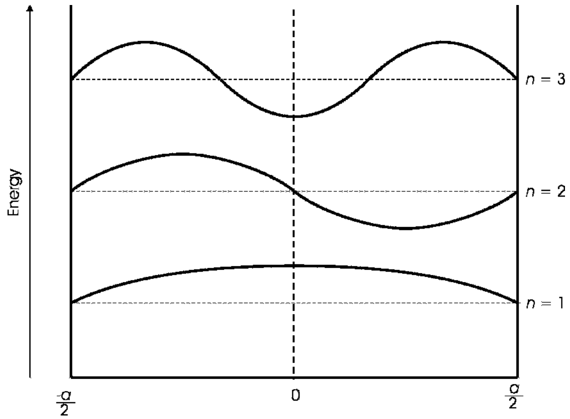


Figure 13.26 The first three energy levels for an electron trapped in a one-dimensional quantum well are the same as an electron trapped on a line (Section 2.3.6, Figure 2.27, page 48)

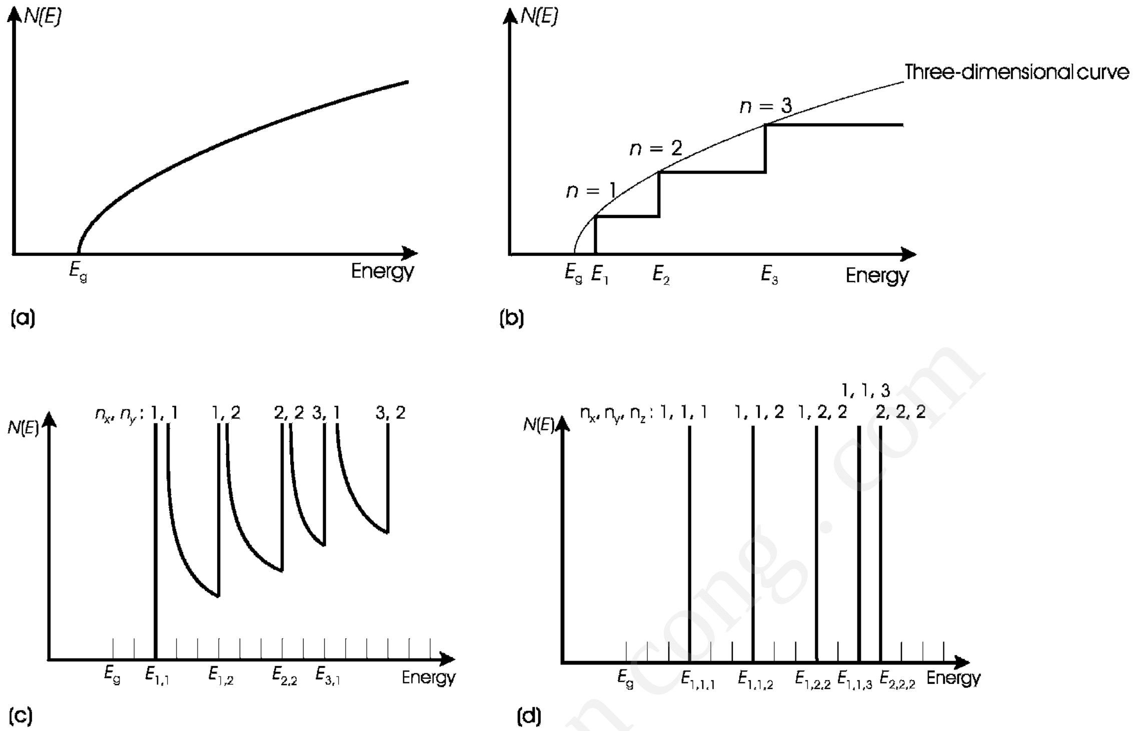


Figure 13.27 (a) The density-of-states function, $N(E)$, for a free electron in a metal; (b) the step-like density-of-states function for an electron trapped in a quantum well; (c) the density-of-states function of an electron trapped on a quantum wire; and (d) the density-of-states function of an electron trapped in a quantum dot

The density of states for a free electron is parabolic in shape (Figures 2.29, page 49, and 13.27a). The imposition of the quantum well changes the curve, and the smooth continuum is now broken into steps (Figure 13.27b). The height of the steps depends on the dimensions of the quantum well material.

The optical properties of quantum wells are described in Section 14.11.1.

13.3.2 Quantum wires and quantum dots

The above considerations can be applied equally well to confinement in two or three dimensions – so-called quantum wires and quantum dots (see Section 3.2.5). For a quantum wire with restricted dimensions along a and b, the free electron confined in an infinite potential well will have energy levels given by:

$$E(n_x, n_y, n_z) = \left(\frac{h^2}{8m_e^*}\right)\left(\frac{n_x^2}{a^2}\right) + \left(\frac{h^2}{8m_e^*}\right)\left(\frac{n_y^2}{b^2}\right) + \left(\frac{h^2}{8m_e^*}\right)\left(\frac{n_z^2}{c^2}\right) \tag{13.8}$$

where a and b are small, and c is large. The density-of-states curve for this situation is drawn in Figure 13.27(c). In the case of the quantum dot, Equation (13.8) is retained, but the third dimension, c, is also small. The density-of-states curve for a quantum dot is shown in Figure 13.27(d).

The interesting optical properties of these structures are described in Section 14.11.2.

13.4 Superconductivity

13.4.1 Superconductors

In 1911 H. Kamerlingh Ohnes found that mercury lost all electrical resistance when cooled to the temperature of liquid helium (4.2 K) and reached the superconducting state. Subsequently, a large number of materials, including metallic elements, alloys, organic compounds, sulphides, oxides and nitrides have been found to exhibit superconductivity. In the superconducting state all electrical resistance is lost and electrical current, once started, will flow forever without diminishing (Figure 13.28). Superconductivity is a quantum mechanical feature, one of the few that are apparent in the 'macroscopic' world, and some of its features are puzzling when viewed from the standpoint of classical physics.

The temperature at which most materials become superconducting is called the superconducting transition temperature, T_c, (Figure 13.28). Most metallic elements have a T_c that is below 10 K. For many years the highest value of T_c recorded was close to 18 K, and this seemed to be a genuine limit, but new techniques of preparation pushed this up to 23.2 K, in the alloy Nb_3Ge, by 1970. This temperature stood as the record until the ceramic superconductors were discovered, in 1986. Although the T_c of the first ceramic compound recognised as a superconductor, $La_{1.85}Ba_{0.15}CuO_4$, was only about 30 K, the very existence of superconductivity in a ceramic led to an explosion of research that produced large numbers of new ceramic superconductors. The current record for T_c, 138 K, is held by the oxide $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8.33}$.

13.4.2 The effect of magnetic fields

The defining characteristic of superconductors is the loss of all electrical resistivity. However, other features are important. When a superconductor is cooled in a magnetic field it expels the magnetic induction, $\boldsymbol{B}$, in its interior. This is called the Meissner effect. Ideally, this expulsion is complete so that a superconductor behaves as perfectly diamagnetic (see Figures 13.29a and 13.29b). In effect, in the superconducting state a surface current is produced that is sufficient to generate an internal magnetic field that exactly cancels the magnetic induction. This current also distorts the external magnetic field so that it does not penetrate the superconductor, which is thus screened (Figure

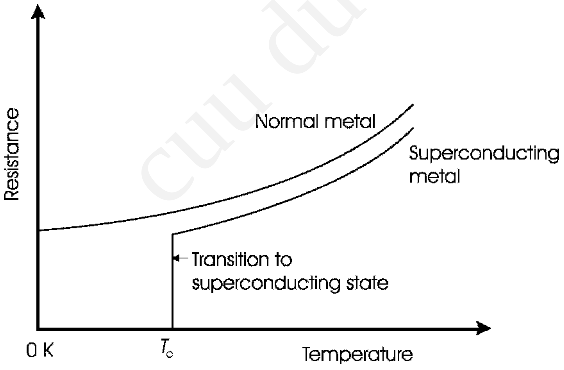


Figure 13.28 The variation of the resistance of a normal metal compared with that of a superconducting metal as the temperature approaches 0 K. In a superconducting metal all resistance is lost at the transition temperature, T_c, which is close to 0 K

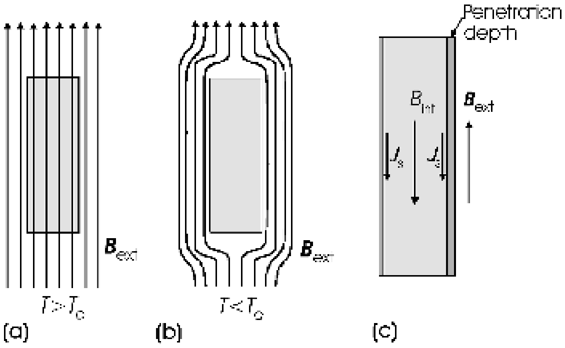


Figure 13.29 The Meissner effect; (a) a normal metal or a superconducting metal above the transition temperature, T_c, allows the penetration of magnetic flux into the bulk; (b) in a superconducting metal below the transition temperature, the magnetic flux is 'expelled'; (c) a surface current, $\boldsymbol{J}_s$, is induced in the superconductor below the transition temperature which creates an internal magnetic flux, $\boldsymbol{B}_{int}$, that cancels the external flux, $\boldsymbol{B}_{ext}$

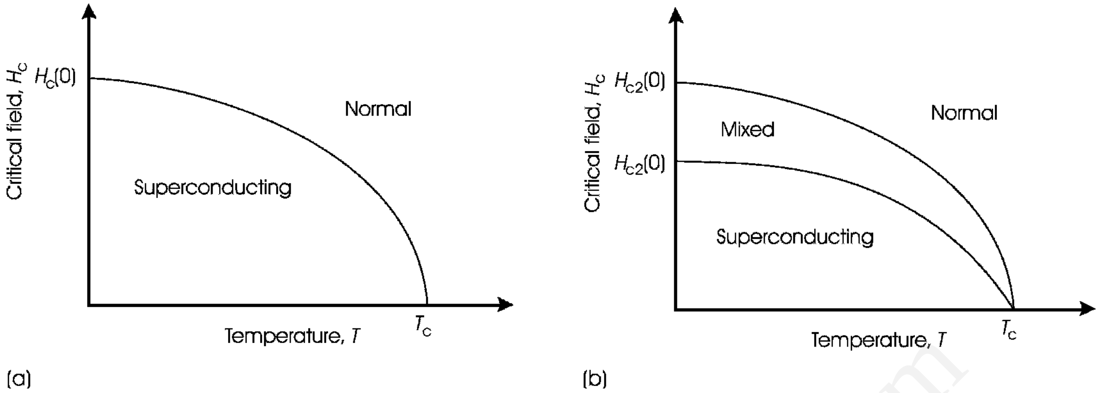


Figure 13.30 The variation of the superconducting properties with the external magnetic field: (a) a type-I superconductor $H_c(0)$ is the critical field at 0 K; (b) a type-II superconductor; $H_{c2}(0)$ and $H_{c1}(0)$ are, respectively, the upper and lower critical fields at 0 K

13.29c). The surface current is confined to a thin layer, called the penetration depth, which has a value of between 10 nm and 100 nm. The exclusion of the magnetic induction costs energy, and when that cost outweighs the energy gained by the formation of the superconducting state the material reverts to normal behaviour. This occurs at a critical field, H_c, in Type-I superconductors. The value of the critical field, H_c, is temperature-dependent so that a phase boundary can be mapped out in H–T phase space (Figure 13.30a). The relationship between H_c and the critical temperature, T_c, is given by the approximation:

$$H_c \approx H_c(0)\left[1-\left(\frac{T}{T_c}\right)^2\right] \qquad (13.9)$$

where $H_c(0)$ is the critical magnetic field at 0 K, and T is the absolute temperature. [Note that values of the critical field are often quoted in tesla, the unit of magnetic induction, not the unit of magnetic field, A m^{-1}. In these cases, equate the ‘field’ in tesla to $\mu_0 H$, where $\boldsymbol{H}$ is the true field, measured in A m^{-1}.]

In many superconductors the transition between the superconducting and normal state is not sharp. When the external magnetic field reaches some lower critical magnetic field value, H_{c1}, magnetic flux starts to penetrate the material. The material becomes normal when the magnetic field reaches a higher value, the upper critical field, H_{c2}. This behaviour characterises type-II superconductors (Figure 13.30b). The temperature dependence given in Equation (13.9) holds if H_c is relaced by $H_{c2}(0)$.

When the field reaches H_{c1}, filaments of magnetic flux cross the superconductor. These regions are no longer superconducting, so that some of the sample is in the superconducting state and some is normal (Figure 13.31). These small cylindrical regions of normal material are isolated from the superconducting matrix by surface currents forming a vortex.

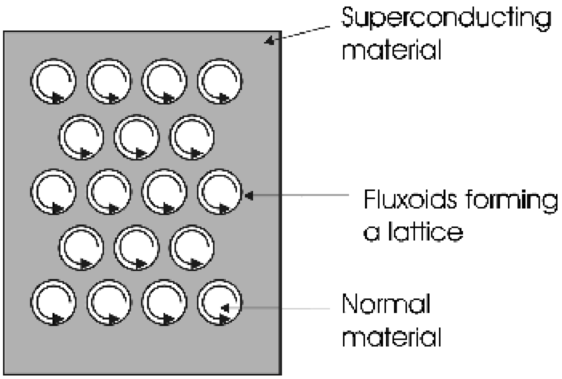


Figure 13.31 A type-II superconductor in the mixed state. The solid contains small threads of normal material, fluxoids, which penetrate the superconducting bulk. These repel each other by virtue of the surface currents, and so form a regular array, a fluxoid lattice

The normal threads are called vortices or fluxoids. The currents act so as to repel each other, so that the flux lines form an ordered structure called a fluxon lattice, flux lattice or vortex lattice. At the core of each flux vortex the material is effectively normal, but is surrounded by a region of superconductor.

The magnetic flux enclosed by a loop of superconductor must be quantised in multiples of $h/2e$, where h is the Planck constant, and e is the electronic charge. The unit of flux is called the flux quantum, or fluxon, Φ_o, with a value of 2.07×10^{-15} Wb (T m^2). The flux enclosed in any circuit must then be $nh/2e$, with n taking integral values.

As the magnetic field increases, the amount of normal phase also increases relative to the superconducting part. Ultimately, the flux lines are so close together that no superconducting material exists between them, and the solid becomes normal. The field that finally destroys the superconductivity is the upper critical field, H_{c2}.

13.4.3 The effect of current

Although a superconducting solid exhibits no resistivity, at a certain current, the critical current, J_c, a superconductor reverts to a normal resistive state. The critical current is a function of the temperature and the external magnetic field, and hence the superconducting state of a solid can be mapped out as a volume with respect to current, field and temperature axes (Figure 13.32). As either temperature or magnetic field increase, the critical current decreases. The critical current is also greatly influenced by the microstructure of the solid, and careful processing is needed to obtain superconducting samples with high values of the critical current. For working devices a value of J_c of about 10^6 A cm^{-2} or greater needs to be achieved.

13.4.4 The nature of superconductivity

In a normal metal, resistivity is the result of interactions of the current-carrying electrons with the crystal structure. This clearly does not happen in the superconducting state and a completely different theory of electrical conduction is needed to account for the properties that superconductors possess.

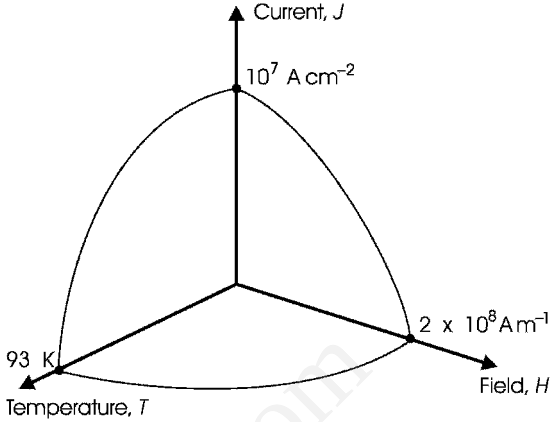


Figure 13.32 The region supporting superconductivity depends on the field, the temperature and the current in the solid. The values shown here for the critical field, temperature and current are typical of the high-temperature ceramic superconductor $YBa_2Cu_3O_{7-x}$

Type-I superconductors are well explained by the Bardeen–Cooper–Schrieffer (BCS) theory. In this, the superconducting state is characterised by having the mobile electrons coupled in pairs. Each pair consists of two electrons with opposite spins, called Cooper pairs. At normal temperatures, electrons strongly repel one another. As the temperature falls and the lattice vibrations diminish, a weak attractive force between pairs of electrons becomes significant. In Type-I superconductors the 'glue' between the Cooper pairs are phonons (lattice vibrations).

The coupling can be envisaged in the following way. As an electron passes through a crystal, it interacts with the surrounding positively charged atomic cores, weakly attracting them (Figure 13.33). This leads to a slightly enhanced region of positive charge in the neighbourhood of the passing electron. Naturally, this weak attraction is swamped at high temperatures by thermal vibrations. At low temperatures another electron is able to feel the influence of the distortion. This second electron is weakly attracted to the slightly positive region

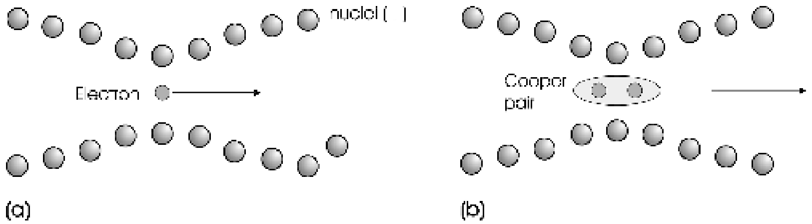


Figure 13.33 (a) An electron passing through a solid attracts the positively charged atomic nuclei slightly, creating a slightly enhanced region of positive charge; (b) at low temperatures, another electron can be attracted into this positive region to form a Cooper pair, which behaves as a single particle

generated by the first electron, and is carried along with it. The two electrons are thus linked.

Formally, this is described as linkage by the quanta of lattice vibration called phonons. When an electron in a Cooper pair passes through the crystal, the atom cores are attracted and then spring back as the electron passes. This causes a phonon to be emitted that is picked up by the other electron in the Cooper pair. At the same time, this electron is also causing phonons to be emitted, which are picked up by the first electron. This phonon exchange acts as the weak glue between the electron pairs. This coupling is easily destroyed even at low temperatures, and Cooper pairs are constantly forming and breaking apart. The pairs of electrons behave quite differently from single electrons. For example, they share the same wavefunction and are able to pass through the crystal unimpeded.

In the newly discovered high-temperature superconductors (described in Section 13.4.5) it has been shown that the electrons are also paired. Unfortunately, the BCS theory is not able to account for the much stronger coupling that must occur in these solids, and no satisfactory theory has yet been suggested.

13.4.5 Ceramic 'high-temperature' superconductors

High-temperature superconductors are copper oxides that maintain the superconducting state to temperatures above that of liquid nitrogen. One of the most interesting features of these new oxide superconductors is that they are all nonstoichiometric oxides and the superconductivity is closely correlated to this feature. The stoichiometric variation of greatest significance with respect to superconductivity is the oxygen content. Some representative materials are listed in Table 13.2.

Crystallographically, the phases are all related to the *perovskite* structure type, ABO_3, where A is a

Table 13.2 Some high-temperature superconducting oxides

Compound[a]	T_c/K
$La_{1.85}Sr_{0.15}CuO_4$	34
$Nd_{2-x}Ce_xCuO_4$	20
$YBa_2Cu_3O_{6.95}$	93
Double Bi-O or Tl–O layers:	
$Bi_2Sr_2CuO_6$	10
$Bi_2CaSr_2Cu_2O_8$	92
$Bi_2Ca_2Sr_2Cu_3O_{10}$	110
$Tl_2Ba_2CuO_6$	92
$Tl_2CaBa_2Cu_2O_8$	119
$Tl_2Ca_2Ba_2Cu_3O_{10}$	128
$Tl_2Ca_3Ba_2Cu_4O_{12}$	119
Single Tl–O or Hg–O layers:	
$TlCaBa_2Cu_2O_7$	103
$TlCa_2Ba_2Cu_3O_9$	110
$HgBa_2CuO_4$	94
$HgCaBa_2Cu_2O_6$	127
$HgCa_2Ba_2Cu_3O_8$	133
$Hg_{0.8}Tl_{0.2}Ca_2Ba_2Cu_3O_{8.33}$	138
$HgCa_3Ba_2Cu_4O_{10}$	126

[a] The formulae are representative and do not always show the exact oxygen stoichiometry for the optimum T_c values given.

Note: T_c, superconducting transition temperature.

large cation and *B* is copper (see Section 5.4.3). The structures of the superconductors can be built up of slices of *perovskite* structure linked by slabs with structures mainly equivalent to slices of the *halite* and *fluorite* structures. The copper valence in most compounds lies between the formal values of Cu^{2+} and Cu^{3+}. Moreover, the appearance of superconductivity and the transition temperature are closely connected to the composition of these nonstoichiometric solids, which all exhibit considerable degrees of oxygen composition variation.

13.4.5.1 Lanthanum cuprate, La_2CuO_4

The phase La_2CuO_4 contains trivalent La and divalent Cu and adopts a slightly distorted version of the K_2NiF_4 structure in which the CuO_6 octahedra are lengthened along the *c* axis compared with the regular octahedra in the parent phase (Figure 13.34). The structure can be thought of as sheets of the *perovskite*-type one CuO_6 octahedron in thickness, and can also be described as built from CuO_2 and LaO layers, stacked in the sequence . . . CuO_2, LaO, LaO, CuO_2 . . . .

When prepared in air by heating the oxides CuO and La_2O_3, the compound is usually stoichiometric, with oxygen content close to 4.00. Electronically, the material is an insulator. The substance can be transformed into a superconductor via valence induction to generate Cu^{3+} ions. Replacing some of the La^{3+} cations with the alkaline earth cations Ba^{2+}, Sr^{2+} or Ca^{2+} achieves this. In the resulting compounds the dopant A^{2+} cations substitute for La^{3+}. Because these ions have a lower charge than the La^{3+}, charge neutrality can be maintained by creating one Cu^{3+} ion for each A^{2+}, to give a formula $La_{2-x}A_xCu^{2+}_{1-x}Cu^{3+}_xO_4$.

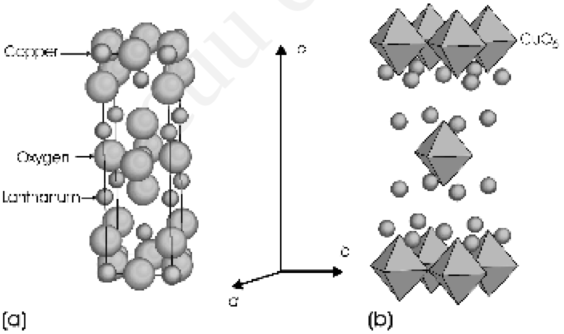


Figure 13.34 The crystal structure of La_2CuO_4, shown as (a) atom packing and (b) CuO_6 octahedra. The dimensions of the room-temperature orthorhombic unit cell are $a_0 = 0.535$ nm, $b_0 = 0.540$ nm, and $c_0 = 1.314$ nm

The first copper oxide superconductor, $La_{2-x}Ba_xCuO_4$, was produced in this way, although the isostructural material $La_{2-x}Sr_xCuO_4$ has been investigated in most detail. This latter compound shows a maximum T_c of 37 K at a composition near to $La_{1.85}Sr_{0.15}CuO_4$. Charge neutrality can be maintained in one of two ways in this compound. If valence induction occurs, one Cu^{3+} forms for each Sr^{2+} substituent, to give a formula $La_{2-x}Sr_xCu^{2+}_{1-x}Cu^{3+}_xO_4$. It is also possible to generate one oxygen vacancy for every two Sr^{2+} added, to give a charge-neutral formula $La_{2-x}Sr_xCu^{2+}O_{4-(x/2)}$.

The balance between these two alternatives is very delicately poised, and leads to a surprising situation. Initially, the Cu^{3+} option is preferred. Because Cu^{3+} can be looked on as Cu^{2+} together with a trapped hole, valence induction generates a hole population which leads to a superconducting state. As the Sr^{2+} concentration rises the Cu^{3+} population rises, peaking when *x* is approximately 0.2. As more Sr^{2+} is added, the preferred defect now becomes the oxygen vacancy and the oxygen content of the parent phase falls below 4.0. The number of Cu^{3+} ions decreases as oxygen vacancies form, and when the concentration of Sr^{2+} reaches approximately 0.32 all of the compensation is via vacancies and the material is no longer a superconductor (Figure 13.35). The nature of the defects in the phase is, therefore, directly related to the appearance of superconductivity.

13.4.5.2 Yttrium barium copper oxide (123), $YBa_2Cu_3O_7$

The compound $YBa_2Cu_3O_7$ has been widely studied because it is relatively easy to prepare and it was the first superconductor discovered with a T_c above the boiling point of liquid nitrogen. The crystal

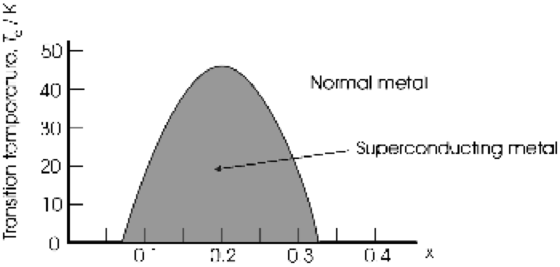


Figure 13.35 The variation of the superconducting transition temperature, T_c, with composition parameter x, for $La_{2-x}Sr_xCuO_4$. The superconducting state exists over only a small region of composition. Outside of this, the solid does not show superconducting behaviour

structure of $YBa_2Cu_3O_7$ consists of three perovskite-like unit cells stacked one on top of the other (Figure 13.36). The middle perovskite unit contains Y as the large *A* atom and Cu as the smaller *B* atom. The cells above and below this contain Ba as the *A* atom and Cu as the *B* atom, to give a metal formula of YBa_2Cu_3 as one would expect for a tripled perovskite cell, $A_3B_3O_9$. The unit cell of the superconductor should contain nine oxygen atoms. Instead the seven oxygen atoms present are arranged in such a way as to give the copper atoms square pyramidal and square planar coordination, rather than octahedral coordination as in the normal perovskites. If the ions are allocated the normal formal charges of Y^{3+}, Ba^{2+} and O^{2-}, the Cu must take an average charge of 2.33, which can be considered to arise from the presence of two Cu^{2+} ions and one Cu^{3+} ion per unit cell.

The appearance of superconductivity in this material is closely related to the oxygen content, and, like La_2CuO_4, it is a hole superconductor. At the exact composition $YBa_2Cu_3O_{7.0}$ the material is an insulator. Superconductivity appears when a small amount of oxygen is lost. The compound can readily lose oxygen down to a composition of $YBa_2Cu_3O_{6.0}$, and the superconducting transition temperature changes continuously over this composition range (Figure 13.37). The maximum value of T_c, close to 93 K, is found near to the composition $YBa_2Cu_3O_{6.95}$. As more oxygen is removed the value of T_c falls to a plateau of approximately 60 K, when the composition lies between the approximate limits of $YBa_2Cu_3O_{6.7}$ to $YBa_2Cu_3O_{6.5}$. Continued oxygen removal down to the phase limit of $YBa_2Cu_3O_{6.0}$ rapidly leads to a loss of superconductivity. The exact behaviour of any

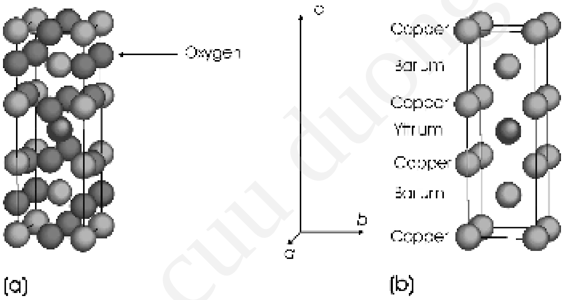


Figure 13.36 (a) The crystal structure of the high-temperature ceramic superconductor $YBa_2Cu_3O_7$; (b) the crystal structure showing cations only, revealing that the metal skeleton of the material is identical to a stack of three *perovskite*-like unit cells. The oxygen atoms are distributed so that no copper ions have six oxygen neighbours, as they would in a *perovskite*. Some copper ions have only four oxygen neighbours, thus changing the composition from $YBa_2Cu_3O_9$ to $YBa_2Cu_3O_7$. The dimensions of the orthorhombic unit cell are $a_0 = 0.381$ nm, $b_0 = 0.388$ nm, and $c_0 = 1.165$ nm

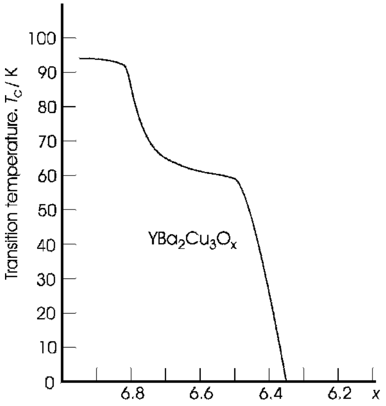


Figure 13.37 The variation of the superconducting transition temperature, T_c, with oxygen content, x, for $YBa_2Cu_3O_x$. Outside of the approximate range of x of 6.95–6.35 the material behaves as a typical insulating ceramic

sample depends on the defects present and this in turn depends on whether the samples are cooled quickly or slowly.

The oxygen atoms are not lost at random during reduction but come solely from the CuO_4 square planar units. This has the effect of converting the copper coordination from square planar to linear, resulting in CuO_2 chains running through the structure. This structural feature is of vital importance in allowing the superconducting transition to take place.

13.4.6 Josephson junctions

Cooper pairs can tunnel through a thin layer of insulator, called a weak link, separating two superconducting regions, without destroying the coupling between them or the superconductivity of the adjoining phases. In such cases a direct current (dc) flows across the insulating layer without the application of an accompanying voltage. This is called the dc Josephson effect. In essence, the insulator behaves as if it were a superconductor. The Josephson effect persists only for a certain range of currents and, eventually, above a critical current, i_c, a voltage develops across the junction.

When two Josephson junctions are connected in parallel (Figure 13.38a), the maximum current, i_c, that can flow across the device is function of the magnetic flux enclosed in the loop. As the magnetic flux penetrating the loop varies, the value of i_{cmax} varies from a maximum at zero flux or an integral number of flux quanta to a minimum for a half-integer number of flux quanta. The relationship is given by:

$$i_{cmax} = 2I_J \cos\left(\frac{\pi\Phi}{\Phi_0}\right)$$

where I_J is a constant depending on the junction geometry, Φ is the enclosed magnetic flux, and Φ_0 is the flux quantum.

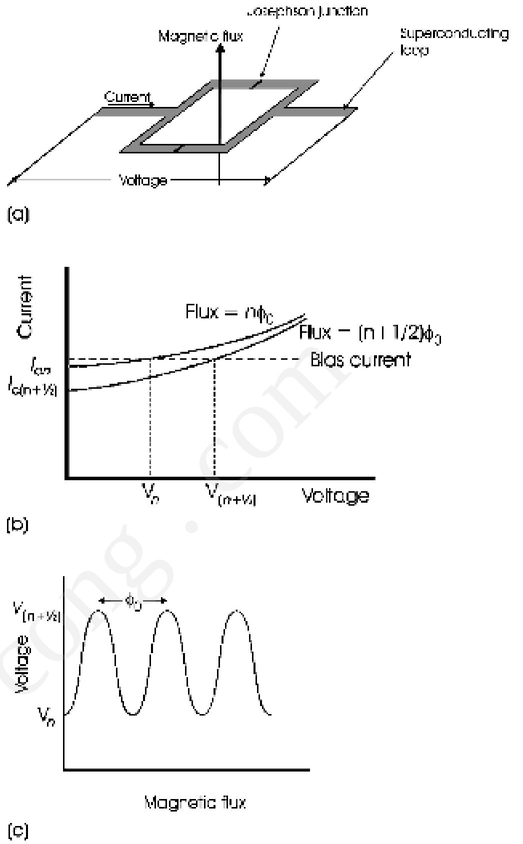


Figure 13.38 (a) A dc (direct-current) SQUID (superconducting quantum interference device) circuit, consisting of a loop of superconducting material containing two Josephson junctions, one in each arm. (b) With a bias current above the critical current, i_c, the voltage depends on the number of flux quanta that penetrate the loop. (c) In a varying magnetic field, the voltage cycles sinusoidally, with a period equal to the flux quantum

A dc SQUID is a device based on this effect, used for the measurement of microscopic magnetic fields. The acronym SQUID stands for superconducting quantum interference device. In operation, a bias current is used which is just above that needed to produce a voltage across the circuit. The critical current i_{cn} when a whole number of flux quanta penetrate the loop is higher than when an odd half number of flux quanta penetrate the loop, $i_{c[n+(1/2)]}$. Because of this, the voltage recorded, V_n, $V_{n+(1/2)}$, or an intermediate value, depends on the magnetic flux penetrating the loop (Figure 13.38b), and as the magnetic flux changes the voltage varies in a sinusoidal fashion (Figure 13.38c). A SQUID is a magnetic flux to voltage converter. Typically, the gain is about 1 volt per flux quantum. As fractions of a volt are easily measured, a SQUID has a sensitivity of approximately 10^{-4} to 10^{-6} of a flux quantum. This is sensitive enough to measure the magnetic fields produced by changes in the electrical activity of the brain.

Answers to introductory questions

How are donor atoms and acceptor atoms in semiconductors differentiated?

Donor atoms donate electrons to the conduction band in a semiconductor. This means that they have at least one extra valence electron over that required to fulfil the local bonding requirements of the structure. This electron can be promoted to the conduction band and enhance the number of mobile electrons present. For the elemental semiconductors silicon and germanium, this indicates atoms to the right of group 14 in the periodic table. The converse is true for acceptors. These have one less valence electron than required to fulfil the local bonding requirements in the structure. This shortfall is made up by appropriating an electron from the valence band, leaving behind a hole that adds to the existing hole population. For the elemental semiconductors silicon and germanium, this indicates atoms to the left of group 14 in the periodic table.

What is a quantum well?

A quantum well consists of a thin layer of a semiconductor with a smaller band gap within a semiconductor with a larger band gap. The most studied quantum well structures are those formed from a layer of gallium arsenide, GaAs, sandwiched in gallium aluminium arsenide, GaAlAs. The electrons in the thin GaAs layer are effectively trapped in the 'well' formed in the conduction band of the composite material. Similarly, the holes in the thin layer of semiconductor are trapped at the 'hill' in the valence band of the composite material.

What are Cooper pairs?

Cooper pairs are pairs of mobile electrons that form at very low temperatures. Each pair consists of two electrons with opposite spin. The electrons share the same wavefunction and are able to pass through the crystal unimpeded.

At normal temperatures, electrons strongly repel one another. As the temperature falls and the lattice vibrations diminish, a weak attractive force between pairs of electrons becomes significant. In Type-I superconductors the 'glue' between the Cooper pairs are phonons (lattice vibrations). When an electron in a Cooper pair passes through the crystal, the atom cores are attracted and then spring back as the electron passes. This causes a phonon to be emitted that is picked up by the other electron in the Cooper pair. At the same time, this electron is also causing phonons to be emitted, which are picked up by the first electron. This coupling is easily destroyed even at low temperatures, and Cooper pairs are constantly forming and breaking apart.

Further reading

A. Cottrell, 1988, *Introduction to the Modern Theory of Metals*, Institute of Metals, London.

P.A. Cox, 1987, *The Electronic Structure and Chemistry of Solids*, Oxford University Press, Oxford.

W.B. Pearson, 1972, *The Crystal Chemistry and Physics of Metals and Alloys*, Wiley-Interscience, New York, especially Ch. 5.

M. Aldissi, 1987, 'Recent Advances in Inherently Conducting Polymers and Multicomponent Systems', *Journal of Materials Education* **9** 333.

A.P. Epstein, 1997, 'Eletrically Conducting Polymers: Science and Technology', *Materials Research Society Bulletin* **22** (June) 6.

A.J. Heeger, 2001, 'Semiconducting and Metallic Polymers: The Fourth Generation of Polymeric Materials', *Materials Research Society Bulletin* **22** (November) 900.

J.R. Waldron, 1996, *Superconductivity of Metals and Cuprates*, Institute of Physics, Bristol.

The following articles in *Scientific American* (in order of publication) give a good overview of superconductivity

R.M. Hazen, 1988, 'Perovskites', *Scientific American* **258**, (June) 52.
A.M. Wolsky, R.F. Giese, E.J. Daniels, 1989, 'The New Superconductors: Prospects for Applications', *Scientific American* **260** (February) 44.
R.J. Cava, 1990, 'Superconductors Beyond 1–2–3', *Scientific American* **263** (August) 24.
J. Clarke, 1994, 'SQUIDs', *Scientific American* **271** (August) 36.
R. de B. Ouboter, 1997, 'H.K. Oness's Discovery of Superconducivity', *Scientific American* **276** (March) 84.

A number of review articles, which give an indication of the rapid progress made in the science and engineering of high-temperature superconductor compounds, are to be found in

Materials Research Society Bulletin **XIV** (January 1989).
Materials Research Society Bulletin **XV** (June 1990).
Materials Research Society Bulletin **XVII** (August 1992).
Materials Research Society Bulletin **XIX** (September 1994).

Problems and exercises

Quick quiz

1 An insulator is a material with a full valence band, an empty conduction band and:
- (a) No band gap
- (b) A small band gap
- (c) A large band gap

2 An intrinsic semiconductor is a material with a full valence band, an empty conduction band and:
- (a) No band gap
- (b) A small band gap
- (c) A large band gap

3 In an intrinsic semiconductor, the current is carried by:
- (a) Electrons
- (b) Holes
- (c) Electrons and holes

4 A degenerate semiconductor has:
- (a) Few electrons and holes present
- (b) Only electrons or else holes present
- (c) Large numbers of electrons and holes present

5 Donors make a semiconductor:
- (a) p-type
- (b) n-type
- (c) Degenerate

6 Acceptors make a semiconductor:
- (a) p-type
- (b) n-type
- (c) Degenerate

7 A compensated semiconductor has:
- (a) Equal numbers of donors and acceptors present
- (b) Equal numbers of electrons and holes present
- (c) No intrinsic electrons and holes present

8 A metal has:
- (a) A partly filled uppermost band
- (b) Overlapping uppermost bands
- (c) Zero band gap between the two uppermost bands

9 A semimetal has:
- (a) A partly filled uppermost band
- (b) Overlapping uppermost bands
- (c) Zero band gap between the two uppermost bands

10 In a metal *not* carrying a current:
- (a) The electrons are stationary
- (b) The electrons at the Fermi surface are moving with random velocities
- (c) The average velocity of all electrons sums to zero

11 The conductivity of a metal:
  (a) Increases as the temperature increases
  (b) Falls as the temperature increases
  (c) Is insensitive to temperature

12 The conductivity of a semiconductor:
  (a) Increases as the temperature increases
  (b) Falls as the temperature increases
  (c) Is insensitive to temperature

13 The resistivity of a metal arises from:
  (a) Electron scattering from vibrations of the atoms in the material
  (b) Electron scattering from defects
  (c) Electron scattering both from defects and from atomic vibrations

14 The conductivity of a semiconductor increases as the energy band gap:
  (a) Decreases
  (b) Increases
  (c) Varies

15 A semiconductor crystal is transparent to radiation with energy:
  (a) Greater than the band gap
  (b) Less than the band gap
  (c) Exactly equal to the band gap

16 The band gap of a semiconductor:
  (a) Does not depend on atom size
  (b) Increases with increasing atom size
  (c) Decreases with increasing atom size

17 Atoms to the right of silicon and germanium in the periodic table act as:
  (a) Donors
  (b) Acceptors
  (c) Neither

18 Atoms to the left of silicon and germanium in the periodic table make the material:
  (a) n-type
  (b) p-type
  (c) Neither

19 Electrons give rise to:
  (a) A positive Hall coefficient
  (b) A negative Hall coefficient
  (c) A neutral Hall coefficient

20 When a current flows across a p–n junction under forward bias it is made up of:
  (a) Six components
  (b) Four components
  (c) Two components

21 Doping a transition metal oxide with a cation of lower valence will make it:
  (a) p-type
  (b) n-type
  (c) Cause no change

22 Conducting polymers contain:
  (a) Metal atoms in the structure
  (b) Conjugated double bonds
  (c) Conjugated triple bonds

23 Doping polyacetylene with sodium makes it:
  (a) A metallic conductor.
  (b) A p-type semiconductor
  (c) An n-type semiconductor

24 A semiconductor quantum well is:
  (a) A thin layer of a semiconductor on an insulator
  (b) Alternating layers of two semiconductors on an insulator
  (c) A thin layer of a semiconductor within a different semiconductor

25 Electrons in a quantum wire are strongly confined:
  (a) In one-dimension
  (b) In two dimensions
  (c) In three dimensions

26 A type-I superconductor:
  (a) Does not interact with magnetic fields
  (a) Draws an external magnetic field into itself
  (c) Expels internal magnetic fields

27 A material in the superconducting state can be thought of as:
  - (a) A perfect diamagnetic solid
  - (b) A perfect paramagnetic solid
  - (c) A perfect ferromagnetic solid

28 A superconductor carrying a current becomes a normal conductor:
  - (a) Below the critical current
  - (b) At the critical current
  - (c) Above the critical current

29 Superconductivity in conventional (low-temperature) superconductors is due to:
  - (a) Pairs of electrons
  - (b) Pairs of holes
  - (c) Electron–hole pairs

30 Ceramic superconductors mostly have structures closely related to:
  - (a) Spinel
  - (b) Perovskite
  - (c) Halite

31 A Josephson junction consists of:
  - (a) A very thin layer of insulator separating two superconducting regions
  - (b) A very thin layer of superconductor separating two insulating regions
  - (c) A thin layer of superconducting material separating two metallic regions

32 A SQUID measures:
  - (a) Resistivity
  - (b) Superconductivity
  - (c) Magnetic fields

Calculations and questions

13.1 The electrical resistivity of gold, at 273 K, is $2.05 \times 10^{-8}\,\Omega$ m. Gold adopts the A1 structure with a cubic lattice parameter, a_0, of 0.4078 nm. The velocity of electrons at the Fermi surface is 1.40×10^{6} m s^{-1}. Each gold atom contributes one electron to the structure. Calculate the relaxation time, τ, and the mean free path, Λ, of the electrons. Compare Λ with the interatomic spacing of gold atoms in the crystal.

13.2 The electrical resistivity of silver, at 273 K, is $1.47 \times 10^{-8}\,\Omega$ m. Silver adopts the A1 structure with a cubic lattice parameter, a_0, of 0.4086 nm. The velocity of electrons at the Fermi surface is 1.39×10^{6} m s^{-1}. Each silver atom contributes one electron to the structure. Calculate the relaxation time, τ, and the mean free path, Λ, of the electrons. Compare Λ with the interatomic spacing of silver atoms in the crystal.

13.3 The electrical resistivity of rubidium, at 273 K, is $11.5 \times 10^{-8}\,\Omega$ m. Rubidium adopts the A2 structure with a cubic lattice parameter, a_0, of 0.5705 nm. The velocity of electrons at the Fermi surface is 8.1×10^{7} m s^{-1}. Each rubidium atom contributes one electron to the structure. Calculate the relaxation time, τ, and the mean free path, Λ, of the electrons. Compare Λ with the interatomic spacing of rubidium atoms in the crystal.

13.4 The electrical resistivity of magnesium, at 273 K, is $4.05 \times 10^{-8}\,\Omega$ m. Magnesium adopts the A3 structure with hexagonal lattice parameters of $a_0 = 0.3209$ nm, and $c_0 = 0.5211$ nm. The velocity of electrons at the Fermi surface is 1.58×10^{6} m s^{-1}. Each magnesium atom contributes two electrons to the structure. Calculate the relaxation time, τ, and the mean free path, Λ, of the electrons. Compare Λ with the interatomic spacing of magnesium atoms in the crystal.

13.5 The electrical resistivity of liquid mercury as a function of temperature is given in Table 13.3. The velocity of electrons at the Fermi

Table 13.3 Data for Question 13.5

$\rho/(10^{-8}\,\Omega\,\text{m})$	94.1	103.5	128.0	214.0	630.0
T/°C	0	100	300	700	1200

surface is $1.52 \times 10^6\,\mathrm{m\,s^{-1}}$. Determine how the mean free path, Λ, varies with temperature. The density of liquid mercury is $13456\,\mathrm{kg\,m^{-3}}$. Assume that this does not vary with temperature and that each mercury atom contributes two mobile electrons to the liquid.

13.6 The resistivity of cadmium metal crystals at room temperature is $7.79 \times 10^{-8}\,\Omega\,\mathrm{m}$ parallel to the c axis, and $6.54 \times 10^{-8}\,\Omega\,\mathrm{m}$ parallel to the a axis. Cadmium adopts the A3 structure with hexagonal unit cell parameters of $a_0 = 0.2979\,\mathrm{nm}$, $c_0 = 0.5620\,\mathrm{nm}$ and each Cd atom contributes two mobile electrons to the crystal. Calculate the mobility of the electrons along the unit cell axes.

13.7 The resistivity of zinc metal crystals at room temperature is $6.05 \times 10^{-8}\,\Omega\,\mathrm{m}$ parallel to the c axis, and $5.83 \times 10^{-8}\,\Omega\,\mathrm{m}$ parallel to the a axis. Zinc adopts the A3 structure with hexagonal unit cell parameters of $a_0 = 0.2665\,\mathrm{nm}$, $c_0 = 0.4947\,\mathrm{nm}$ and each Zn atom contributes two mobile electrons to the crystal. Calculate the mobility of the electrons along the unit cell axes.

13.8 The resistivity of a sample of brass containing 70 wt% Cu and 30 wt% zinc is $6.3\times 10^{-8}\,\Omega\,\mathrm{m}$ at 0 °C, compared with that of pure copper, which is $1.54 \times 10^{-8}\,\Omega\,\mathrm{m}$ at the same temperature. Determine the residual resistivity at this temperature.

13.9 The resistivity of a sample of bronze containing 90 wt% Cu and 10 wt% tin is $1.36\times 10^{-7}\,\Omega\,\mathrm{m}$ at 0 °C, compared with that of pure copper, which is $1.54 \times 10^{-8}\,\Omega\,\mathrm{m}$ at the same temperature. Determine the residual resistivity at this temperature.

13.10 The resistivity at 0 °C for nickel and for a number of nickel alloys is given in Table 13.4. Plot the resistivity against the amount of nickel in the alloy. Comment on the shape of the plot in terms of the possible structures of the alloys. [Note: graph is not shown in the answers at the end of this book.]

13.11 The resistivity at 0 °C aluminium and for a number of aluminium alloys is given in Table 13.5. Plot the resistivity against the amount of aluminium in the alloy. Comment on the shape of the plot in terms of the possible structures of the alloys. [Note: graph is not shown in the answers at the end of this book.]

13.12 The resistivity at 0 °C for copper and for a number of copper alloys is given in Table 13.6. Plot the resistivity against the amount of copper in the alloy. Comment on the shape of the plot in terms of the possible structures of the alloys. [Note: graph is not shown in the answers at the end of this book.]

Table 13.4 Data for Question 13.10

	Nickel	Alumel	Chromel P	Nichrome	Monel
Resistivity/$10^{-8}\,\Omega\,\mathrm{m}$	6.16	28.1	70	107.3	42.9
Wt% Ni	100	95	90	77.3	67.1

Table 13.5 Data for Question 13.11

	Aluminium	RR59	RR57	Alpax gamma	Lo-Ex
Resistivity/$10^{-8}\,\Omega\,\mathrm{m}$	2.42	3.5	3.95	3.5	3.95
Wt% Al	100	93	89	87	85

Table 13.6 Data for Question 13.12

	Copper	Bronze	Manganin	Brass	German silver	Constanin
Resistivity/$10^{-8}\,\Omega$ m	1.54	19.8	41.5	6.3	40	49
Wt% Cu	100	90	84	70	62	60

13.13 Estimate the number of intrinsic electrons, n, and holes, p, and the product np, for a crystal of silicon at 300 K taking the effective mass of electrons and holes as equal to the electron rest mass, m_e. The band gap, E_g, is 1.12 eV.

13.14 Estimate the number of intrinsic electrons, n, and holes, p, and the product np, for a crystal of gallium arsenide, GaAs, at 300 K, taking the effective mass of electrons and holes as equal to the electron rest mass, m_e. The band gap, E_g, is 1.42 eV.

13.15 Estimate the number of intrinsic electrons, n, and holes, p, and the product np, for a crystal of gallium arsenide, GaAs, at 300 K, taking the effective mass of electrons to be $0.067m_e$ and holes as $0.082m_e$. The band gap, E_g, is 1.42 eV.

13.16 Estimate the number of intrinsic electrons, n, and holes, p, and the product np, for a crystal of cadmium selenide, CdSe, at 300 K, taking the effective mass of electrons to be $0.13m_e$ and holes as $0.45m_e$. The band gap, E_g, is 1.70 eV.

13.17 Determine the band gap, E_g, of silicon from the conductivity data given in Table 13.7. What is the minimum frequency, ν, of light that will excite an electron across the band gap?

13.18 Determine the band gap, E_g, of germanium from the conductivity data given in Table 13.8. What is the minimum frequency, ν, of light that will excite an electron across the band gap?

13.19 Calculate the donor energy-level position in silicon doped with phosphorus using the ‘Bohr model’. The effective mass of an electron is $0.33m_e$ and the relative permittivity of silicon is 11.7.

13.20 Calculate the acceptor energy-level position in germanium doped with aluminium using the ‘Bohr model’. The effective mass of a hole is $0.16m_e$ and the relative permittivity of germanium is 16.0.

13.21 Calculate the donor energy-level position in indium phosphide, InP, doped with tin, using the ‘Bohr model’. The effective mass of an electron is $0.067m_e$ and the relative permittivity of indium phosphide is 12.4.

13.22 Calculate the acceptor energy level position in gallium arsenide, GaAs, doped with zinc, using the ‘Bohr model’. The effective mass

Table 13.7 Data for Question 13.17

Temperature /°C	227	277	327	377	427	477	527
Conductivity/Ω^{-1} m^{-1}	3×10^{-4}	9×10^{-4}	3×10^{-3}	8×10^{-3}	2.5×10^{-2}	6×10^{-2}	8×10^{-2}

Table 13.8 Data for Question 13.18

Temperature /°C	5	47	82	122	162	240	344	441
Conductivity/Ω^{-1} m^{-1}	0.0001	0.0008	0.004	0.009	0.05	0.1	0.6	1.0

Table 13.9 Data for Question 13.29

Current (along x)/mA	8	16	24	32	40
Voltage (along y)/V	0.081	0.159	0.233	0.318	0.401

of a hole is $0.082m_e$ and the relative permittivity of gallium arsenide is 13.2.

13.23 The energy gap for gallium arsenide, GaAs, is 1.4 eV at 300 K. The effective mass of electrons is $0.067m_e$ and of holes is $0.082m_e$. How near to the band gap centre is the Fermi level?

13.24 The energy gap for gallium phosphide, GaP, is 2.26 eV at 300 K. The effective mass of electrons is $0.82m_e$ and of holes is $0.60m_e$. How near to the band gap centre is the Fermi level?

13.25 A semiconductor containing 10^{20} holes m^{-3} and 10^{18} electrons m^{-3} has a conductivity of $0.455\ \Omega^{-1}\ m^{-1}$. The ratio of the mobilities of electrons and holes, μ_e/μ_h, is 10. What are the hole and electron mobilities?

13.26 Gallium arsenide, GaAs, is doped with 10^{18} donor atoms. The hole mobility is $0.04\ m^2\ V^{-1}\ s^{-1}$, and the electron mobility is $0.85\ m^2\ V^{-1}\ s^{-1}$. Using the results of Question 13.15, determine the conductivity of the sample.

13.27 A 1-cm cube of n-type germanium supports a current of 6.4 mA when a voltage is applied across two parallel faces. The charge carriers have a mobility of $0.39\ m^2\ V^{-1}\ s^{-1}$. Determine the Hall coefficient of the crystal assuming that only the majority charge carriers need be considered.

13.28 (a) Estimate the Hall coefficient, R_H, for intrinsic silicon, using the following values: $n_i = 1 \times 10^{16}\ m^{-3}$; mobility of electrons $= 0.15\ m^2\ V^{-1}\ s^{-1}$; and mobility of holes $= 0.045\ m^2\ V^{-1}\ s^{-1}$. (b) Calculate the Hall voltage, V, for a 1-cm cube of pure silicon at 20 °C, in a magnetic induction of 0.2 T, when a current of 10^{-3} A is applied to a cube face.

13.29 A single crystal of germanium doped with antimony to make it p-type is used in a Hall experiment. The crystal dimensions are 20 mm × 10 mm × 1 mm in the x, y, and z directions, respectively. In a constant induction of 0.9 T along the z direction, the current (along x) and voltage (along y) readings were obtained, as given in Table 13.9. Calculate the Hall coefficient, R_H, and the carrier density, ρ.

13.30 Using Figure 13.23, estimate the activation energy for the conductivity of polyacetylene doped with iodine for the three concentrations shown; that is, for (a) 0.15 mol%, (b) 0.01 mol% and (c) 0.005 mol% of I_2 per CH unit.

13.31 The transition metal titanium forms two slightly nonstoichiometric oxides, TiO_2 and Ti_2O_3. The oxide TiO_2 loses a small amount of oxygen to form TiO_{2-x}. Is it likely to show p-type or n-type semiconductivity? The oxide Ti_2O_3 gains a slight amount of oxygen to form Ti_2O_{3+x}. Is it likely to show n-type or p-type semiconductivity?

13.32 The oxide $LaCoO_3$ is an insulator. What are the charges on the cations present? The compound is doped with Sr^{2+} to form $La_{1-x}Sr_xCoO_3$, in which the Sr^{2+} substitutes for the La. What are the valences of the ions in this material? Is the doped material a p-type or an n-type semiconductor?

13.33 The compound Mg_2TiO_4 is an inverse *spinel*, which can be written as (Mg)[Mg Ti]O_4, where the round brackets indicate cations in tetrahedral sites and the square brackets indicate cations in octahedral sites. The compound $MgTi_2O_4$ is a normal *spinel*, (Mg)[Ti_2]O_4. (see Section 5.3.10). Both compounds are insulators. What are the charges on the ions? A small amount of $MgTi_2O_4$ is doped into Mg_2TiO_4 to form $Mg_{2-x}Ti_{1+x}O_4$. What are the charges on the ions and how are they distributed in the spinel structure? Will the material be a p-type or an n-type conductor?

13.34 Gallium arsenide has an electron effective mass of $0.067m_e$ and a hole effective mass of $0.082m_e$. Calculate the dimension at which quantum confinement becomes significant for (a) n-type and (b) p-type gallium arsenide at 300 K. Check the units of the calculation. (c) The crystal structure of gallium arsenide consists of layers of GaAs each 0.327 nm in thickness; how many layers are needed for quantum confinement of electrons or holes?

13.35 Gallium phosphide, GaP, has an electron effective mass of $0.82m_e$ and a hole effective mass of $0.60\,m_e$. Calculate the dimension at which quantum confinement becomes significant for (a) n-type and (b) p-type gallium phosphide. (c) The crystal structure of gallium phosphide consists of layers of GaP each 0.315 nm in thickness; how many layers are needed for quantum confinement of electrons or holes?

13.36 Compare the energy of the $n = 1$ energy level in the three directions for a quantum well of dimensions 1 cm × 1 cm × 10 nm, in a material in which the effective mass of the electron is $0.1m_e$.

13.37 Determine the energies of the lowest three states in a gallium arsenide–aluminium arsenide quantum well structure in which the potential well has a width of 9.8 nm, corresponding to 30 GaAs layers. The electron effective mass is $0.067m_e$.

13.38 Determine the energy of the $n = 1$ energy level in a fragment of n-type gallium nitride 20 nm × 393 nm × 1700 nm. The effective mass of electrons in this material is $0.19m_e$.

13.39 The critical field of the superconductor $PbMo_5S_6$ is given as 60 T. What is the critical field in A m^{-1}?

13.40 The critical field, H_{c2}, for the type-II superconductor Nb_3Sn at 15 K is given as 7 T. Estimate the value of the critical field at 0 K. The superconducting transition temperature, T_c, is 25 K.

13.41 What value of the critical field, B_{c2}, will cause the superconductivity of the type-II superconductor Nb_3Ge to be lost at 20 K. The value of the critical field at 0 K is given as 37 T, and the superconducting transition temperature is 23.6 K.

13.42 The superconductor $Nd_{1-x}Ce_xCuO_4$ is derived from the insulator Nd_2CuO_4 by substitution of some Nd^{3+} by Ce^{4+}. What are the charges on the Cu ions present? Will the superconductivity be via holes or electrons?

13.43 The compound $La_2SrCu_2O_6$ can take up oxygen to a composition $La_2SrCu_2O_{6.2}$. What are the charges on the Cu ions present in each of these phases? Are either potential high-temperature superconductors and, if so, would the superconductivity be via holes or electrons?