Fig. 20.50 The variation of the electrical conductivity of a substance with temperature is the basis of its classification as a metallic conductor, a semiconductor, or a superconductor. We shall see in Chapter 21 that conductivity is expressed in siemens per metre ($S\ m^{-1}$ or, as here, $S\ cm^{-1}$), where $1\ S = 1\ \Omega^{-1}$ (the resistance is expressed in ohms, Ω).
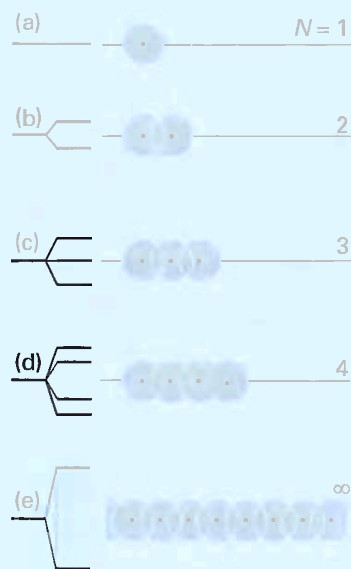

Fig. 20.51 The formation of a band of N molecular orbitals by successive addition of N atoms to a line. Note that the band remains of finite width as N becomes infinite and, although it looks continuous, it consists of N different orbitals.

free-electron approximation, the valence electrons are assumed to be trapped in a box with a periodic potential, with low energy corresponding to the locations of cations. In the **tight-binding approximation**, the valence electrons are assumed to occupy molecular orbitals delocalized throughout the solid. The latter model is more in accord with the discussion in the foregoing chapters, and we confine our attention to it.

We shall consider a one-dimensional solid, which consists of a single, infinitely long line of atoms. At first sight, this model may seem too restrictive and unrealistic. However, not only does it give us the concepts we need to understand conductivity in three-dimensional, macroscopic samples of metals and semiconductors, it is also the starting point for the description of long and thin structures, such as the carbon nanotubes discussed earlier in the chapter.

Suppose that each atom has one s orbital available for forming molecular orbitals. We can construct the LCAO-MOs of the solid by adding N atoms in succession to a line, and then infer the electronic structure using the building-up principle. One atom contributes one s orbital at a certain energy (Fig. 20.51). When a second atom is brought up it overlaps the first and forms bonding and antibonding orbitals. The third atom overlaps its nearest neighbour (and only slightly the next-nearest), and from these three atomic orbitals, three molecular orbitals are formed: one is fully bonding, one fully antibonding, and the intermediate orbital is nonbonding between neighbours. The fourth atom leads to the formation of a fourth molecular orbital. At this stage, we can begin to see that the general effect of bringing up successive atoms is to spread the range of energies covered by the molecular orbitals, and also to fill in the range of energies with more and more orbitals (one more for each atom). When N atoms have been added to the line, there are N molecular orbitals covering a band of energies of finite width, and the Hückel secular determinant (Section 11.6) is

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

where β is now the (s,s) resonance integral. The theory of determinants applied to such a symmetrical example as this (technically a 'tridiagonal determinant') leads to the following expression for the roots:

$$E_R = \alpha + 2\beta\cos\frac{k\pi}{N+1} \qquad k = 1, 2, \ldots, N \tag{20.21}$$

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

$$E_N - E_1 \rightarrow 4\beta \qquad \text{as} \quad N \rightarrow \infty \tag{20.22}$$

We can think of this band as consisting of N different molecular orbitals, the lowest-energy orbital ($k = 1$) being fully bonding, and the highest-energy orbital ($k = N$) being fully antibonding between adjacent atoms (Fig. 20.52). Similar bands form in three-dimensional solids.
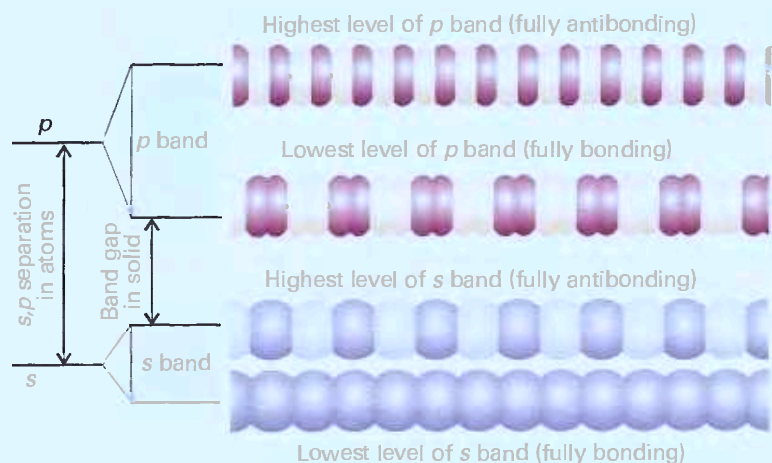
Highest level of p band (fully antibonding)

Lowest level of p band (fully bonding)

Highest level of s band (fully antibonding)

Lowest level of s band (fully bonding)

Fig. 20.52 The overlap of s orbitals gives rise to an s band and the overlap of p orbitals gives rise to a p band. In this case, the s and p orbitals of the atoms are so widely spaced that there is a band gap. In many cases the separation is less and the bands overlap.

Justification 20.5 *The width of a band*

The energy of the level with $k = 1$ is

$$E_1 = \alpha + 2\beta \cos\frac{\pi}{N+1}$$

As N becomes infinite, the cosine term becomes $\cos 0 = 1$. Therefore, in this limit

$$E_1 = \alpha + 2\beta$$

When k has its maximum value of N,

$$E_N = \alpha + 2\beta \cos\frac{N\pi}{N+1}$$

As N approaches infinity, we can ignore the 1 in the denominator, and the cosine term becomes $\cos \pi = -1$. Therefore, in this limit

$$E_N = \alpha - 2\beta$$

The difference between the upper and lower energies of the band is therefore 4β.

The band formed from overlap of s orbitals is called the **s band**. If the atoms have p orbitals available, the same procedure leads to a **p band** (as shown in the upper half of Fig. 20.52). If the atomic p orbitals lie higher in energy than the s orbitals, then the p band lies higher than the s band, and there may be a **band gap**, a range of energies to which no orbital corresponds. However, the s and p bands may also be contiguous or even overlap (as is the case for the $3s$ and $3p$ bands in magnesium).

(b) The occupation of orbitals

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

At $T = 0$, only the lowest $\frac{1}{2}N$ molecular orbitals are occupied (Fig. 20.53), and the HOMO is called the **Fermi level**. However, unlike in molecules, there are empty orbitals very close in energy to the Fermi level, so it requires hardly any energy to excite the uppermost electrons. Some of the electrons are therefore very mobile and give rise to electrical conductivity.
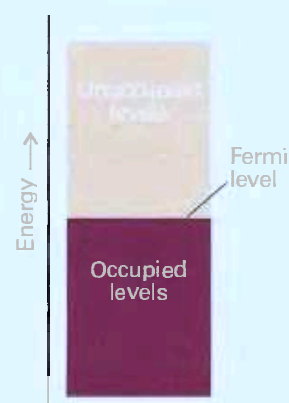

Fig. 20.53 When N electrons occupy a band of N orbitals, it is only half full and the electrons near the Fermi level (the top of the filled levels) are mobile.