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THE CONDUCTION OF ELECTRICITY IN SOLIDS

The conduction of electricity in solids is principally concerned with the motion of electrons within a solid due to electric and magnetic fields. A solution or gas containing ions conducts but an ionic solid doesn't because the bonding is too strong. Table 1 lists the resistivities of a few solids at room temperature.

TABLE 1

CONDUCTORS	RESISTIVITY / Ωm
SILVER	161×10^{-8}
COPPER	169×10^{-8}
ALUMINIUM	262×10^{-8}
SODIUM	459×10^{-8}
IRON	10^{-7}
SEMICONDUCTORS	
GERMANIUM	0.6
SILICON	2300
INSULATORS	
GLASS	$10^{10} - 10^{14}$
SULPHUR	10^{15}
FUSED QUARTZ	7.5×10^{16}

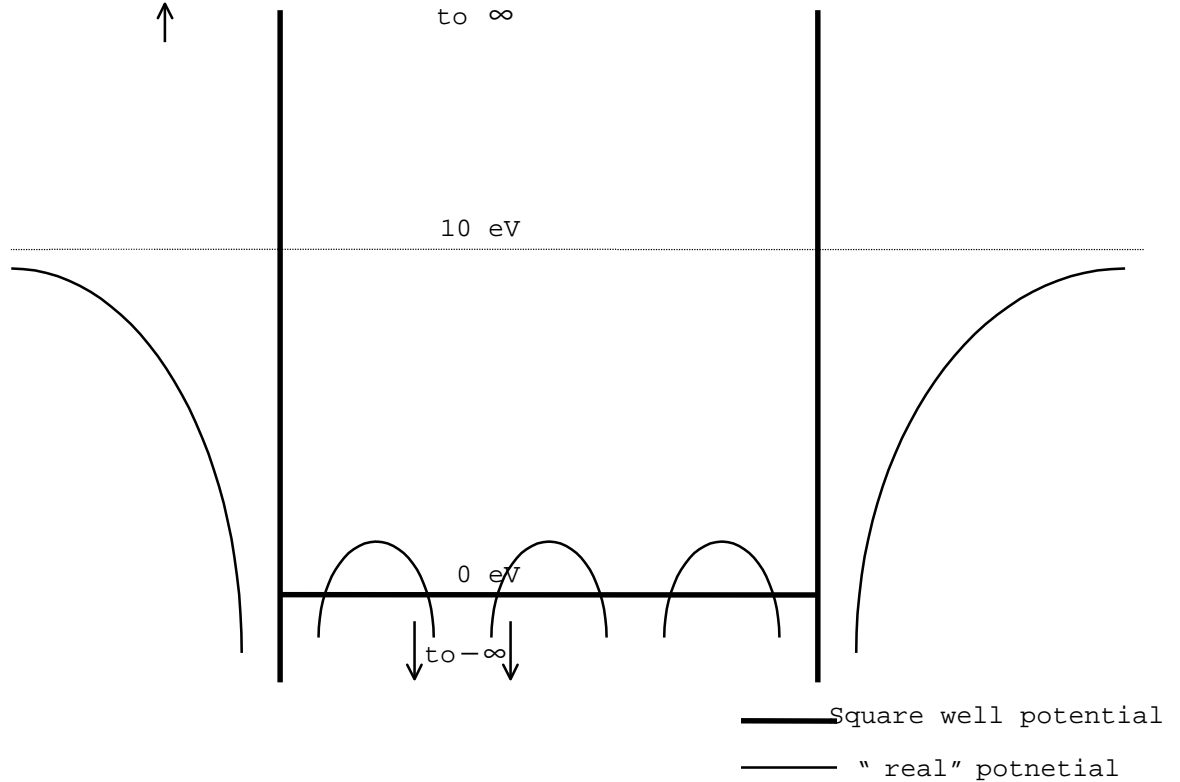
In this essay I will discuss the basic concepts of conduction in metals and in semiconductors.

THE FREE ELECTRON MODEL

In a metal the atoms' valence electrons are delocalised and their wavefunctions extend throughout the crystal. If we consider a line of 5

ions in a metal. The potential, as an electrons sees it, is shown approximately by figure 1. The free electron model however ignores all interactions between electrons and ions and takes the potential outside the metal to be infinite.

FIGURE 1



potential.

If we consider a cube of side L whose potential is 0 inside and infinite outside and has one corner at the origin the solution of the Time Independent Schrodinger Equation is

$$\Psi = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{2a\pi x}{L}\right) \sin\left(\frac{2b\pi y}{L}\right) \sin\left(\frac{2c\pi z}{L}\right).$$

a , b and c are integers. The permitted energy values of a particle in a box are:

$$E = \frac{h^2 k^2}{8\pi^2 m} = \frac{h^2}{8m L^2} (a^2 + b^2 + c^2),$$

h , k and m have their usual meanings. Of course not all pieces of metal are cubic; but that's not important. By turning L^3 into V the density of states equation can be derived; $g(k) = \frac{V k^2}{2\pi^2}$.

Electrons are fermions which means that no two electrons of the same spin can occupy the same quantum-mechanical state. The degree of occupation of the states is given by the Fermi-Dirac equation

$$f(E) = \frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right) + 1}$$

where μ is the chemical potential, k_B is Boltzmann's constant and T is the temperature. The Fermi temperature of a typical metal is of the order of 10000K. At room temperature the distribution is approximately a "step" function. Each electron can be thought of as occupying part of a sphere in "k-space". The radius of this sphere is the Fermi wavenumber, k_F .

THE EFFECTS OF A UNIFORM ELECTRIC FIELD

Electrons are accelerated by d.c. electric fields.

$$\underline{a} = -\frac{e}{m_e} \underline{E}$$

where $-e$ is the electronic charge and m_e isn't the electron's mass but its effective mass;

$$m_e = \frac{\hbar^2}{4\pi^2} \left(\frac{d^2E}{dk^2} \right)^{-1}$$

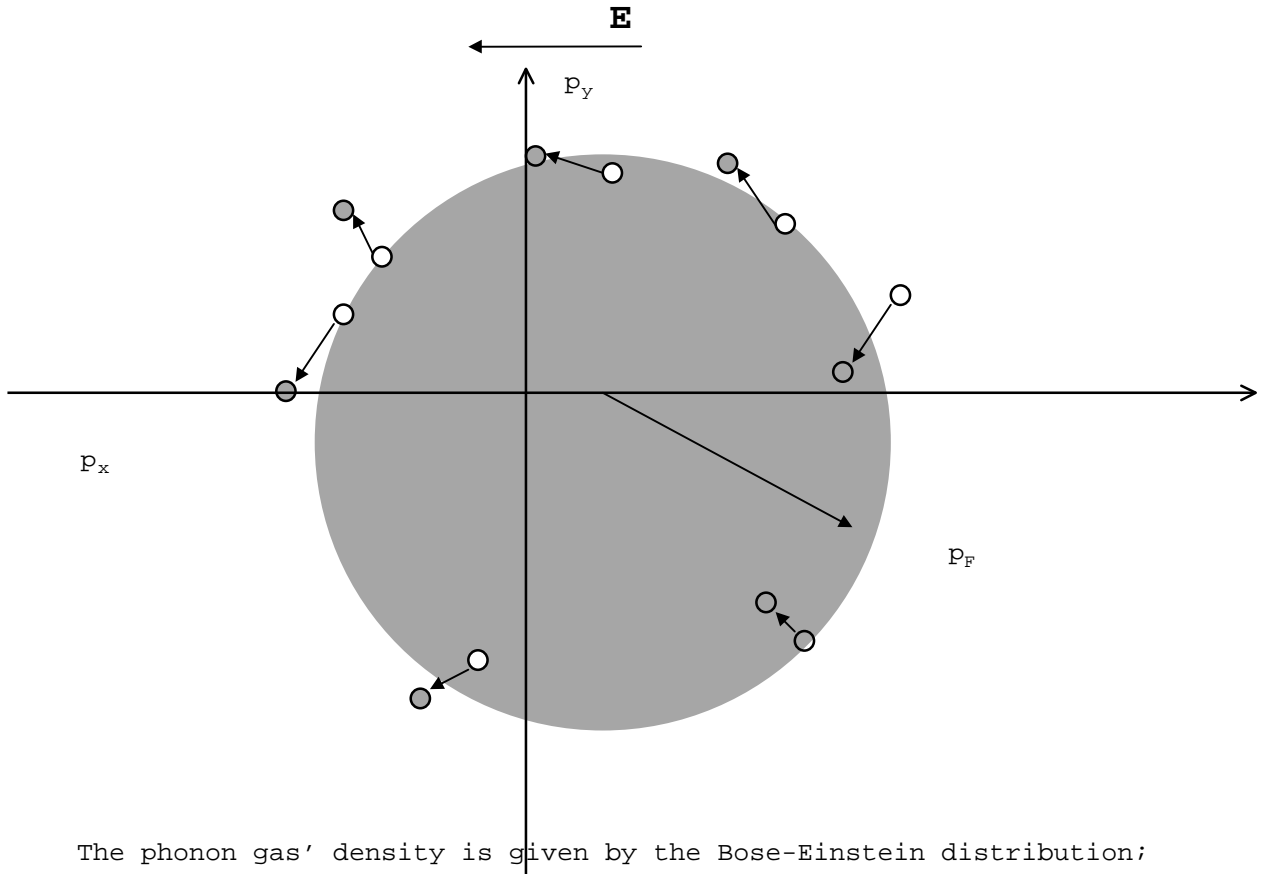
In the case of free electron model, $m = m_e$. When the lattice potential is taken into account this is not the case. The resistivity of a conductor is given by Ohm's law;

$$\rho = \frac{m_e}{ne^2\tau}$$

where n is the electron density and τ is mean time between collisions, if it were the case that an electron loses all of the drift velocity that it has accumulated in a collision. Sodium is a metal that obeys the free electron model very well. At room temperature $\tau = 26 \times 10^{-14}$ s. the Fermi velocity of the electrons is $\approx 11 \times 10^6 \text{ms}^{-1}$ and so the mean free path is $\approx 29 \text{nm}$. As this is very much larger than the atomic separation in sodium this implies that the electrons are not scattered by the ions. Electron-electron scattering does take place but the most important type of scattering is electron-phonon scattering. A phonon is a quantum of vibrational energy. The energy of a phonon is $\frac{\hbar\omega}{2\pi}$ or $k_B\Theta_D$ where ω is

the natural frequency of oscillation of the lattice and Θ_D is the Debye temperature, which for most metals is between 100K and 500K. Phonons have no mass and are bosons. A metal can be thought of as containing a gas of electrons and a gas of phonons. Figure 3 displays the kinds of momentum transfer that can take place when an electron is scattered by a phonon. The Fermi sphere is slightly off-centre, due to the field. The Debye temperature of any metal is much lower than its Fermi temperature. This, together with the Pauli Exclusion principle, means that only electrons close to the Fermi surface can be scattered by phonons.

FIGURE 2



$$n = \frac{1}{\exp\left(\frac{\hbar\omega}{2\pi k_B T}\right) - 1} = \frac{1}{\exp\left(\frac{\Theta}{T}\right) - 1}$$

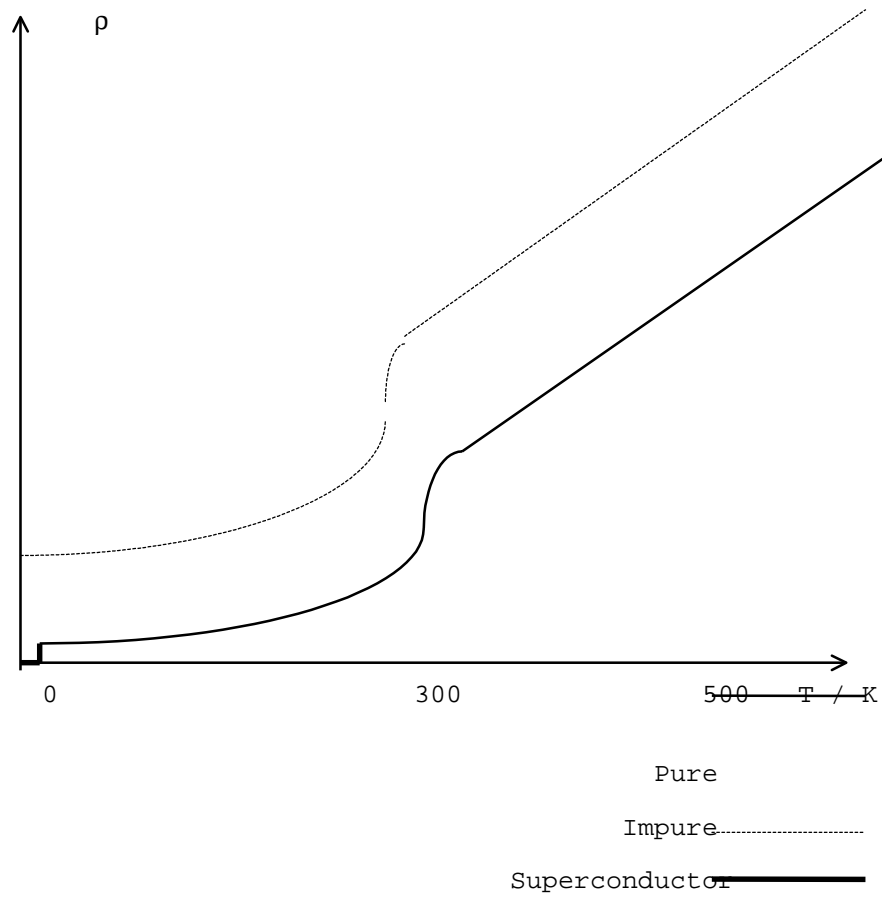
If $T \gg \Theta$, $n \approx \frac{T}{\Theta}$.

At high temperatures the phonon density is proportional to the temperature. So too is the resistivity.

If $T \ll \Theta$ it turns out that the resistivity is approximately proportional to T^5 .

At $T=0$ the resistivity ought to be 0. However all crystalline materials have dislocations and electrons can be scattered by these. Electrons can also be scattered by any impurity atoms in the metal. Figure 3 outlines how the resistivity changes with temperature for two samples of metal, one of them is pure but the other is impure. The impurities increase the resistivity by roughly the same amount at all temperatures.

FIGURE 3

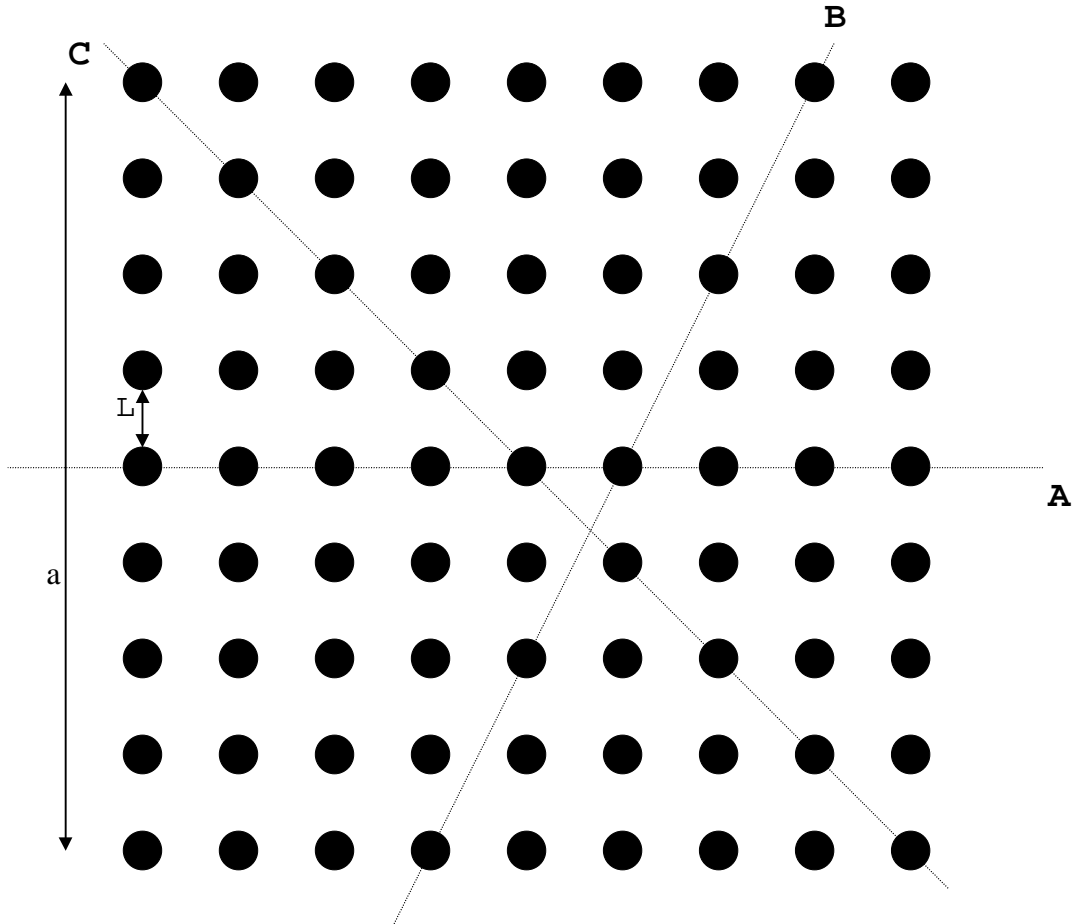


The resistivity of any sample of metal at absolute 0 is called its residual resistivity. This is assuming that the metal doesn't become a superconductor. Many metals, at temperatures below a certain critical temperature (between 0K and 10K) do become superconductors. Many metal oxides also become superconductors but these do so at higher temperatures (10 - 100K). As far as anyone can tell the resistivity of a superconductor is 0; or if it is not then it is below $10^{26} \Omega m$.

BAND GAPS

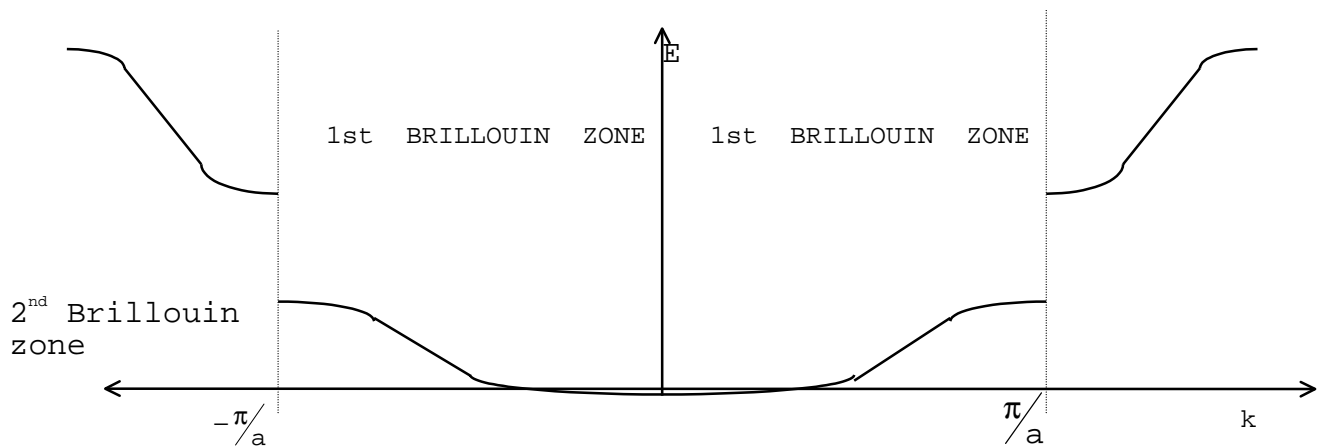
Figure 4 shows a square lattice of ions.

FIGURE 4



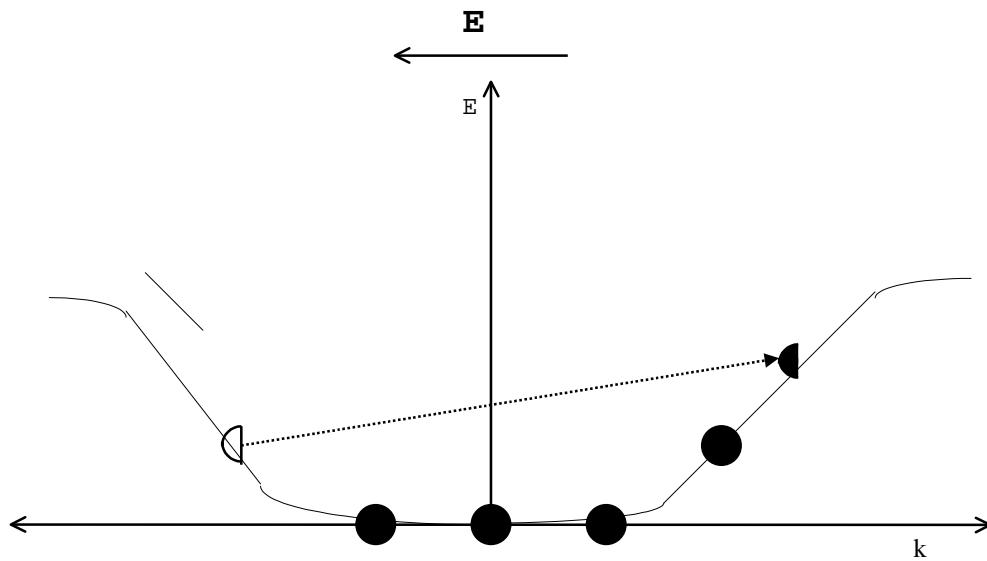
If we have an electron moving along path A, the way in which the electron's energy depends on its wavenumber is shown approximately in figure 5.

FIGURE 5



This dispersion relationship is a deformed parabola. The wavenumber axis is divided up into Brillouin zones. At each zone boundaries there is an energy band gap. The permitted wavenumber states are $\frac{2n\pi}{L}$ where n is an integer. There are nine permitted states in the first zone: $k = -\frac{8\pi}{L}, -\frac{6\pi}{L}, -\frac{4\pi}{L}, \dots, \frac{8\pi}{L}$. There are nine more states in the second zone and another nine in the third. Each zone can therefore accommodate 18 electrons. If there is one valence electron per atom present half of the first zone is full. Each half-circle in figure 6 represents an electron. One has been shifted from the left-hand side to the right by an electric field. This transfer requires very little energy.

FIGURE 6

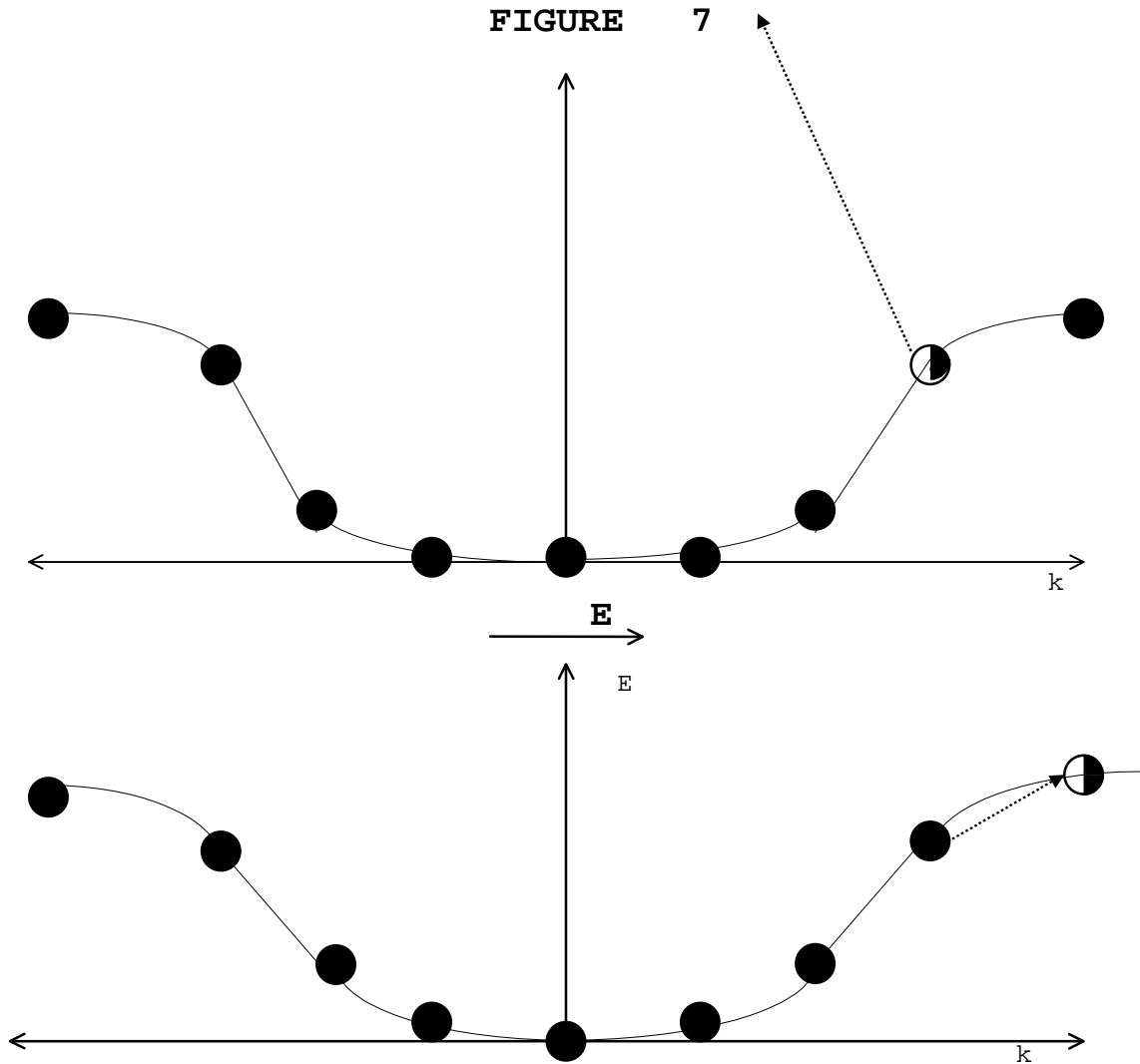


If the atoms are divalent the whole of the first zone is filled. For conduction to take place additional energy must be given to the electrons for them to jump the gap. If the atoms are trivalent the first zone is filled and second zone is half filled. Conduction is possible in this case. One might think that no element with an even number of valence electrons per atom can be a conductor. The alkaline earth metals are divalent however and so are most metals in the transitional series. The reason becomes apparent when the situation is considered in two dimensions. The separation of atoms along line B on figure 4 is larger than the separation along line A. Along line C it is larger again. The energy of a valence electron therefore depends not only on the direction of its wavevector as well as its magnitude. In the free electron case it depended only on its magnitude. It is possible, if the band gaps are quite small, that the highest energy in the first zone, looking along one direction, is higher than the lowest energy in the second zone, looking along another. If such an overlap exists the element can conduct. If not; it is a semiconductor or an insulator.

HOLES

In the case of a divalent element the energy band above the band gap is called the conduction band because only electrons in this band can conduct. The energy band below the band gap is called the valence band. In figure 7 an electron has been taken from the valence band and added to the conduction band. There is now a "hole" in the valence. A hole

will shift in the presence of an electric field and act like a positive charge carrier.



If the only charge carrier in a metal were electrons then all metals would have negative Hall coefficients. Some metals though, such as cadmium, have positive Hall coefficients and this is due to holes.

SEMICONDUCTORS

The resistivities given for Silicon and Germanium in Table 1 are for the pure semiconductor at 298K. A semiconductor's resistivity though is highly dependent on temperature and can be affected by "donor" and "acceptor" impurity atoms. Both types of charge carrier are present in a semiconductor. An alternative method of displaying the dispersion relationship is shown in figure 9. The effective masses, m_e and m_h , are considered as constants, since the effective masses at band gaps come to a stationary point as figure 8 shows. Only electrons near a band gap are liable to cross the gap.

FIGURE 8

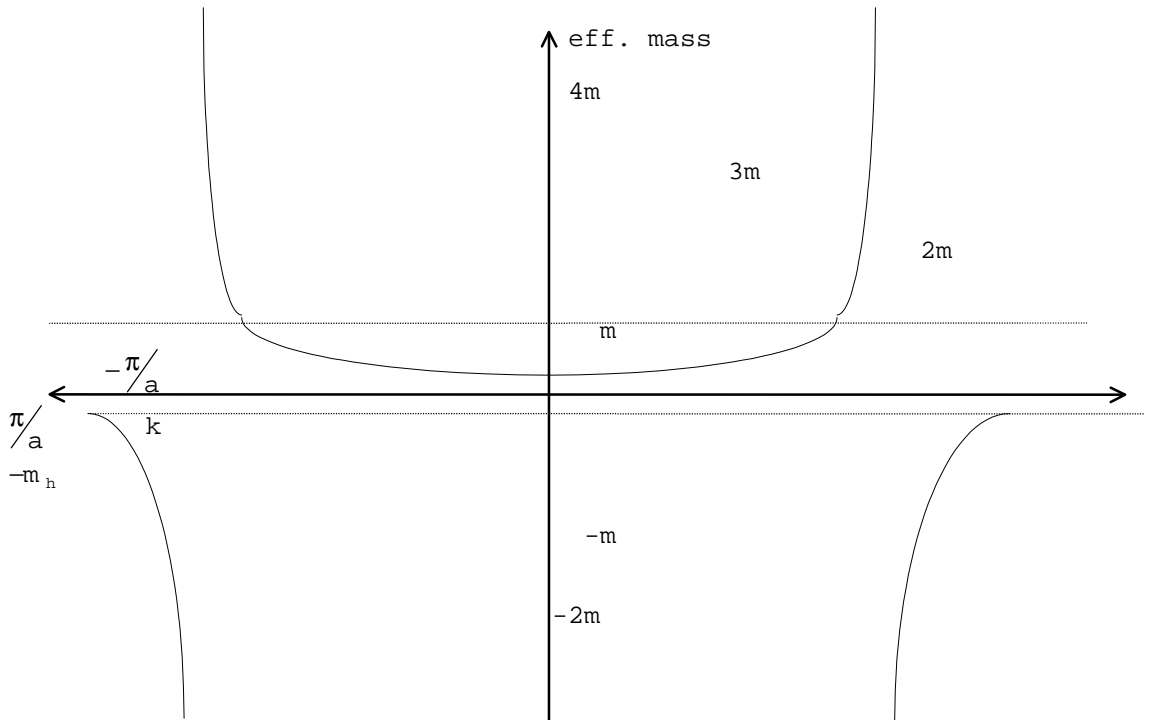
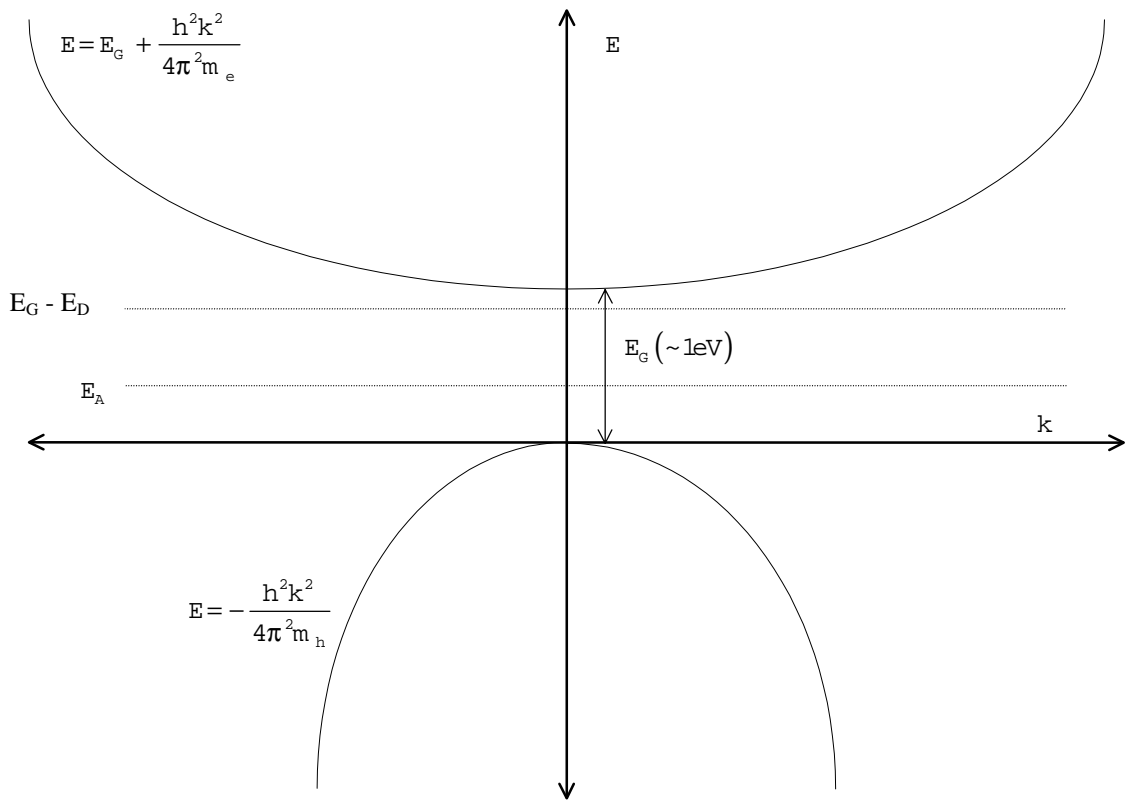


FIGURE 9



The density of states in the conduction band is

$$g(E) = \frac{V\pi}{h^3} (2m_e)^{3/2} (E - E_G)^{1/2}.$$

In the valence band

$$g(E) = \frac{V\pi}{h^3} (2m_h)^{3/2} (-E)^{1/2}.$$

The conduction electron density is

$$\frac{2}{V} \int_{E_G}^{\infty} f(E) g(E) dE.$$

The hole density is

$$\frac{2}{V} \int_{-\infty}^0 [1 - f(E)] g(E) dE.$$

If one assumes that the chemical potential at room temperature is near the centre of the band gap and that $f(E)$ is a step function the integrals can be evaluated.

$$n = N_c \exp\left(\frac{\mu - E_G}{k_B T}\right) \quad \text{where} \quad N_c = 2 \left(\frac{2\pi m_e k_B T}{h^2}\right)^{3/2},$$

$$p = N_v \exp\left(-\frac{\mu}{k_B T}\right) \quad \text{where} \quad N_v = 2 \left(\frac{2\pi m_h k_B T}{h^2}\right)^{3/2}.$$

The two concentrations must equal each other in a pure semiconductor:

$$n = p = N_c N_v^{1/2} \exp\left(-\frac{E_G}{k_B T}\right).$$

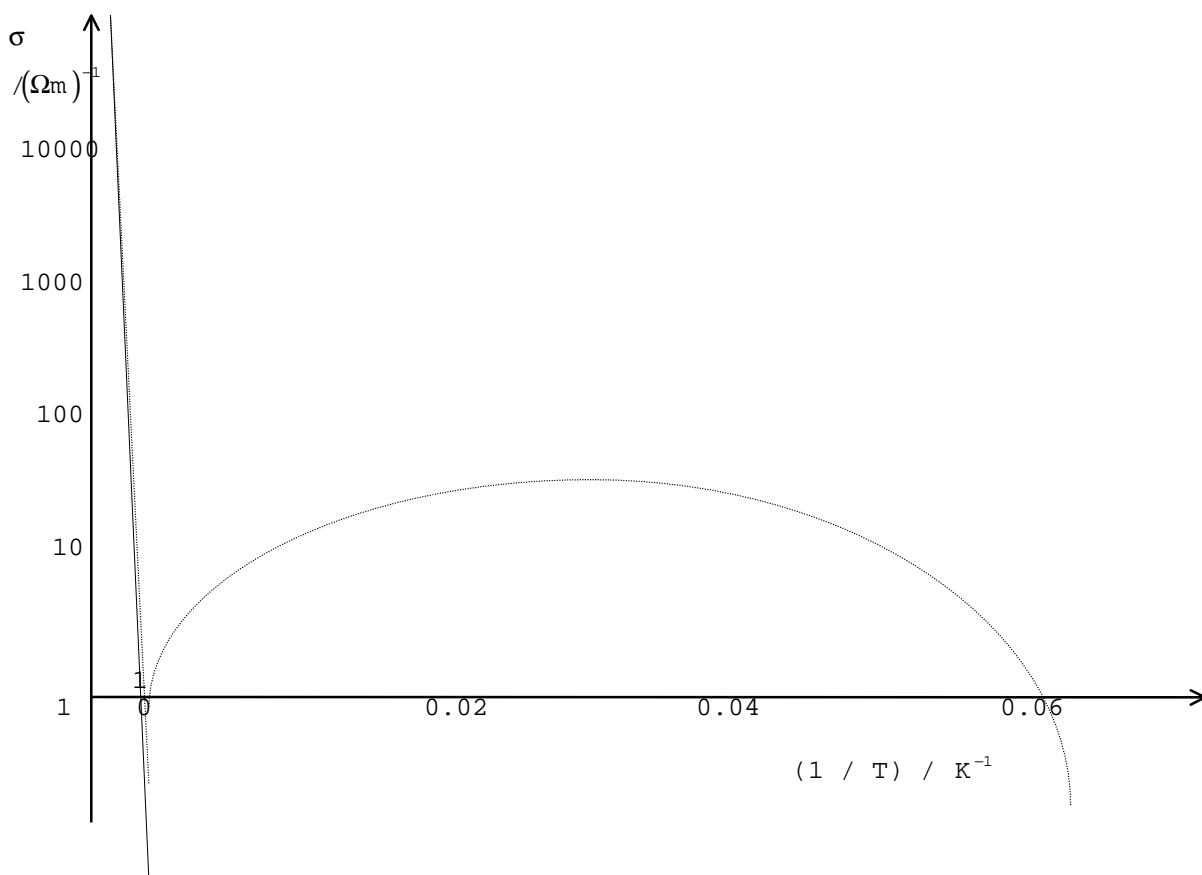
The chemical potential of a pure semiconductor is

$$\mu \approx \frac{1}{2} E_G + \frac{3}{4} k_B T \ln\left(\frac{m_h}{m_e}\right).$$

Since $1 \text{ eV} \gg k_B T$ at room temperature the assumptions made earlier are acceptable.

The solid line on figure 10 shows how the conductivity of a pure semiconductor changes with temperature. Below 50K a semiconductor is practically an insulator.

FIGURE 10



DONOR AND ACCEPTOR IMPURITIES

Silicon and germanium are members of group IV in the periodic table. Each atom forms four covalent bonds with neighbouring atoms. A group IV atom can be replaced by a group V atom like arsenic. That atom, having formed four bonds, has one spare valence electron that can join the conduction band. Alternatively a group IV atom can be replaced by a group III atom like aluminium. This atom needs an extra electron to form the four bonds. It takes one from the valence band, thus creating a hole.

Donor and acceptor atoms introduce new energy bands, as shown on figure 9. If a semiconductor contains N_D donors and N_A acceptors the number of ionised donors is

$$N_D^+ = N_D [1 - f(E_G - E_D)]$$

and the number of acceptors is

$$N_A^- = N_A f(E_A).$$

The dotted line on figure 10 shows how the conductivity semiconductor doped with donors (~ 1 atom in 10^9) changes with temperature. The chemical potential of this semiconductor is

$$\mu \approx E_G - k_B T \ln \left(\frac{N_c}{N_D} \right).$$

At very low temperatures, $\mu > E_D$ and so very few donors are ionised. As the temperature increases μ drops below E_D and more donors become

ionised. The conductivity increases up to a point when all the donors have become ionised. It then starts to fall again due to phonon scattering. At about 500K it starts to rise sharply, following the path that a pure semiconductor takes.

REFERENCES

Most of the material has been taken from "Solid State Physics" by J.R. Hook and H.E. Hall, second edition.

Table 1 data taken from "Book of Chemistry Data" by J.G. Stark and H.G. Wallace, Second Edition.