

1.8. TRANSPORT PROPERTIES

can be modelled by a Debye model, $\omega_j(\mathbf{q}) = c_j q$, where c_j is the speed of sound for the mode j . At long wavelengths, the optical modes have a constant frequency which is represented by an Einstein model, $\omega_j(\mathbf{q}) = \omega_0$.

The intrinsic mobility is that for a low density of electrons or holes. The existing conducting particles are then confined to the lowest wavevector states near the minimum of the conduction band (electrons) or near the maximum of the valence band (holes). The phonons scatter the particles locally, so that the wavevector changes by small amounts, which can only be done by phonons of long wavelength. The above approximations, of using a Debye model for A modes and an Einstein model for O modes, is accurate. This is because one only needs to consider phonons of long wavelength: the approximations are inaccurate for phonons of short wavelength, but they are irrelevant.

The exception to this general behaviour is where the conduction band has several equivalent minima and the phonons scatter an electron from one minimum to another. This is called intervalley scattering. If the minima of the two electron pockets are separated by a wavevector \mathbf{q}_m , then one needs phonons of energy $\omega_j(\mathbf{q}_m)$. Again, these are a fixed set of constants, so one can assume an Einstein model with these phonons as the frequency. For the calculation of the intrinsic mobility of a semiconductor, one does not need to know all of the phonon modes in the solid, as one does for a metal. Instead, one needs to know only the phonons at selected points in the Brillouin zone.

The inverse lifetimes for each scattering process are simply added:

$$\frac{1}{\tau(k)} = \frac{1}{\tau_A(k)} + \frac{1}{\tau_O(k)} + \frac{1}{\tau_I(k)}. \quad (1.8.3.15)$$

The three terms are acoustic, optical and intervalley. First, we discuss the scattering by optical phonons. The inverse lifetime is proportional to the density of optical phonons N_0 :

$$\frac{1}{\tau_0} = \frac{N_0}{\tau}, \quad (1.8.3.16)$$

$$N_0 = \frac{1}{\exp(\hbar\omega_0/k_B T) - 1}. \quad (1.8.3.17)$$

The lifetime $\tau_0 \propto N_0^{-1} = \exp(\hbar\omega_0/k_B T) - 1$. This shows that the mobility increases exponentially at lower temperatures according to the factor $\exp(\hbar\omega_0/k_B T) - 1$. This feature is common to nearly all semiconductors.

The factor N_0 occurs because the electrons must absorb an optical phonon in order to scatter. The density of optical phonons in the crystal is proportional to the factor N_0 . Since usually $k_B T < \hbar\omega_0$ at room temperature, the thermally excited electrons have less energy than an optical phonon. In this case, the electrons cannot emit a phonon, since they are unable to lose that much energy: the process has no final state.

Notice that we have not yet discussed the mechanism by which the electron couples to the optical phonons. In general, there are two: the polar interaction and the deformation potential interaction. Polar interactions are found in crystals with different atoms and where there is some ionic bonding. When the charged ions vibrate, it results in oscillating dipoles that create long-range electric fields. Polar interactions are important in III–V and II–VI semiconductors such as GaAs or CdS. Polar interactions are not present in elemental semiconductors such as silicon and germanium, since each ion is neutral. However, the deformation potential interaction is present in these and could scatter strongly.

Next we discuss the intervalley scattering, where an electron moves between equivalent conduction-band minima. Here the phonons have a discrete energy $\hbar\omega_j(\mathbf{q}_m)$. At low temperatures, the electron can only absorb this phonon and the process is proportional to $N(\omega_j(\mathbf{q}_m))$. This behaves, in many ways, like the scattering by optical phonons. However, since $\omega_j(\mathbf{q}_m) < \omega_0$, the

temperature at which phonon emission can occur is lower. At low temperatures, the intervalley scattering also contributes exponential factors to the inverse lifetime. These contributions are usually lower than the optical phonon scattering. However, in silicon, Rode (1972) showed that the intervalley scattering dominates over the optical phonon scattering.

The scattering by acoustic phonons only is important at low temperature. For most semiconductors, the interaction between electrons and acoustic phonons is due to the deformation potential interaction. The standard calculation gives the inverse lifetime as proportional to $T^{3/2}$, which becomes smaller at low temperature. However, since the other phonon contributions become smaller with an exponential dependence upon temperature, at small enough temperatures the acoustic phonon term makes the largest contribution to the inverse lifetime. Therefore, at low temperatures, the scattering by acoustic phonons limits the mobility of the electron. Of course, this presumes that there is no contribution from the scattering by impurities. Since this contribution is a constant at low temperature, it is always the dominant contribution at low temperatures. Only in samples with a small concentration of impurities can one actually observe the limitation by acoustic phonons. For most samples, with a moderate density of impurities, the optical-phonon part forms the limit at intermediate temperatures, the impurity scattering forms the limit at low temperatures and one never observes the limit from acoustic phonons.

The discussion above covers the behaviour in the majority of cases. There are special types of crystal that show special behaviour. One of these is crystals that are strongly piezoelectric. The size of the electron–phonon interaction due to piezoelectricity is governed by the electromechanical coupling constant. In crystals where this number is relatively large, the scattering of electrons by acoustic phonons gives $\tau \propto T^{1/2}$ at low temperature, as shown by Mahan (1990). So far, the only class of crystals where this is found is the II–VI semiconductors with the wurtzite structure: ZnO and CdS. These are the most piezoelectric crystals found so far. They both show a dependence of the mobility upon $T^{1/2}$ at low temperature.

Finally, we should mention that semiconductors have an intrinsic conductivity that provides an absolute minimum to the conductivity of any sample. The value of this conductivity depends upon temperature. An electron is thermally excited above the energy gap, creating an electron and a hole. The density of electrons or holes is usually determined by the density of the various impurities or native defects, such as vacancies or interstitials. However, in a perfect crystal without defects, there will still be electrons and holes. The density of electrons (n) and holes (p) obeys the relationship

$$np = 4N_c N_v \left(\frac{2\pi\hbar^2}{m_c k_B T} \right)^{3/2} \left(\frac{2\pi\hbar^2}{m_v k_B T} \right)^{3/2} \exp(-E_G/k_B T), \quad (1.8.3.18)$$

where E_G is the energy gap between the electron and hole bands, and N_j and m_j are the number of equivalent bands and their effective masses. This formula comes from chemical equilibrium: the recombination of electrons and holes is controlled by phase space and the energy gap. The absolute minimum number of electrons and holes is where $n = p$, so that each is equal to the square root of the right-hand side of (1.8.3.18). If this minimum value is called $n_m = p_m$, then the minimum conductivity is $\sigma_m = n_m(\mu_c + \mu_v)$, where μ_c and μ_v are the mobilities of the electrons and the holes, respectively. The conductivity is never lower than this value.

1.8.3.4. The Hall effect

Measurement of the Hall effect is simple and often useful. One takes a crystal and applies a magnetic field B_z along the z axis.

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Then one imposes a current density j_x along the x axis. One finds that the Lorentz force induces a voltage, or the equivalent electric field E_y , in the y direction. The electric field is proportional to both the current and magnetic field. The ratio $E_y/(j_x B_z)$ is the *Hall constant* R_H . The inverse of R_H is just the charge e and the speed of light c multiplied by the density of electrons n_0 :

$$\frac{E_y}{j_x B_z} = R_H = \frac{1}{n_0 e c}. \quad (1.8.3.19)$$

This provides a simple and accurate method of measuring the density of electrons. It works well when there is only one kind of current carrier and works well in semiconductors with a low density of carriers. A typical experiment for a semiconductor is to measure the conductivity σ and the Hall constant R_H ; the mobility is then $\mu = c R_H \sigma$. If the conducting particles are holes in a semiconductor, the Hall constant has the opposite sign, which indicates positive charge carriers.

Measurement of the Hall effect does not work well if the semiconductor contains a mixture of different carriers, such as electrons and holes, or even electrons from different kinds of conduction bands. In these cases, the constant R_H is not easily interpreted. Similarly, measuring the Hall effect is rarely useful in metals. It only works well in the alkali metals, which have all of the electrons in the first Brillouin zone on a spherical Fermi surface. In most metals, the Fermi surface extends over several Brillouin zones and has numerous pockets or regions of different curvatures. Regions of positive curvature act as electrons and give a negative Hall constant; regions of negative curvature act as holes and give a positive contribution to the Hall constant. Again, it is difficult to interpret the Hall constant when both contributions are present. In general, the Hall effect is most useful in semiconductors.

1.8.3.5. Insulators

Insulators are crystals that do not conduct electricity by the flow of electrons or holes. We shall not mention this case. The band gaps E_G are sufficiently large that the intrinsic mobility is very small.

1.8.3.6. Ionic conductors

There are many ionic solids that have an appreciable electrical conductivity from the diffusive motion of ions. Any material in which the conductivity from the motion of ions is very much larger than that from the motion of electrons is useful as a battery material. For this reason, such materials have been investigated extensively, see *e.g.* Mahan & Roth (1976) or Salamon (1979).

1.8.4. Thermal conductivity

1.8.4.1. Introduction

The thermal conductivity determines the ability of the crystal to conduct heat. Device applications of crystals usually need an extreme value of the thermal conductivity: some applications need a low thermal conductivity, while others need a high thermal conductivity. At room temperature, the largest value of thermal conductivity is for diamond, which has $K = 1.8 \text{ kW m}^{-1} \text{ K}^{-1}$; see *e.g.* Spitzer (1970), Slack (1979) or Berman (1976). The lowest values are for amorphous materials, which have $K = 0.1 \text{ W m}^{-1} \text{ K}^{-1}$.

Heat flow can be carried by two kinds of excitations: phonons and electrons. The phonons carry most of the heat in insulators and semiconductors. Electrons carry appreciable amounts of heat only if there is a high density of conduction electrons, as in a metal. In metals, the electrons usually carry most of the heat. Of course, the heat conduction by phonons and electrons depends upon temperature. At high temperatures, the standard assumption is that the heat flows from phonons and electrons are inde-

pendent and can be calculated separately. However, there is an electron-phonon interaction, which causes a correlation between the two kinds of heat flow. This is called *phonon drag* and is an important phenomenon at low temperatures – typically less than 50 K. We are concerned mostly with higher temperatures, so will not discuss phonon drag here.

First consider the heat flow carried by phonons. As a rule of thumb, crystals with high values of thermal conductivity are those that are: (1) tetrahedrally bonded, (2) contain elements of low atomic number, and (3) lack impurities and defects (Spitzer, 1970; Berman, 1976; Slack, 1979).

The inverse of the thermal conductivity is called the thermal resistivity. There is an equivalent of Matthiessen's rule for thermal conductivity: it is a reasonable approximation to take the various contributions to the thermal resistivity and simply to add them. This is not a rigorous theorem; it is just a process that gives a reasonable answer most of the time. Here we shall discuss four contributions to the thermal resistivity: boundary scattering, impurity scattering, isotope scattering and anharmonic interactions:

$$R_K = R_B + R_i + R_l + R_A. \quad (1.8.4.1)$$

These various terms are discussed in order.

1.8.4.2. Boundary scattering

At low temperatures, the phonons that are thermally excited are those which have an energy near to or less than the thermal energy $\hbar\Omega(q) \leq k_B T$. This usually means acoustic modes of long wavelength. They tend to have a long mean free path, which can extend to the size of the crystal. In this case, the limiting process on the phonon scattering is simply bouncing off the walls of the crystal. The formula for this process is best derived from the classical formula for the thermal conductivity (see Ziman, 1962),

$$K = (1/3)C\bar{v}\Lambda, \quad (1.8.4.2)$$

where C is the heat capacity, \bar{v} is the average velocity and Λ is the mean free path. To apply this to the present problem, take Λ to be equal to the average dimension of the crystal and \bar{v} to be the speed of sound averaged over the various directions. At low temperatures, the heat capacity $C \propto T^3$, as given by the Debye theory. Since Λ and \bar{v} are constants, then $K \propto T^3$, which agrees well with the dependence found experimentally. Of course, the thermal resistance R_B is just the inverse of $R_B \propto T^{-3}$.

1.8.4.3. Impurity scattering

Impurities can be either point defects or extended defects such as dislocations. Here we confine our remarks to point defects. When acoustic phonons of long wavelength scatter from point defects, the process is very much like the Rayleigh scattering of light. The basic cross section varies as the fourth power of the frequency. Equivalently, at long wavelength, it varies as the fourth power of the wave number q of the phonons (see Ziman, 1962):

$$\frac{1}{\tau_i(q)} = n_i q^4 C_i, \quad (1.8.4.3)$$

where n_i is the concentration of impurities and C_i is a constant characteristic of the impurity. Of course, this lifetime for the phonon of wave number q must be averaged over all of the wavevectors in the crystal as a function of temperature. This averaging is actually mathematically delicate. At temperatures T less than the Debye temperature Θ , the average value of q is $q \sim k_B T / (\hbar v)$ and $R_i \sim T^4$. At high temperatures ($T > \Theta$), the average of $1/\tau(q)$ is a constant, since all values of q in the Brillouin zone are equally accessible. In this limit, $R_i \sim \text{constant}$.