1.8. TRANSPORT PROPERTIES

1.8.4.4. *Isotope scattering*

The perfect crystal is defined as having each atom in its expected position, with no vacancies, interstitials or other defects. Such a crystal would still have a type of disorder that scatters phonons. Most elements have several natural isotopes for their nuclei. Natural crystals usually reflect this mixture of isotopes. Special crystals can be made that are composed of a single isotope, and these lack the resistive term from isotope scattering. However, most crystals have isotope scattering. The scattering is from the mass difference of the nuclei. The interaction term comes from the kinetic energy of the ion vibrational motion. If there are two isotopes with masses M_1 and M_2, with concentrations c and $(1-c)$, respectively, then the average of the mass in the kinetic energy term as discussed by Klemens (1955) is

$$\left\langle \frac{1}{M} \right\rangle = \frac{c}{M_1} + \frac{1-c}{M_2}. \tag{1.8.4.4}$$

The kinetic energy term of the ions is then

$$\sum_i \frac{P_j^2}{2M_j} = \sum_i \frac{1}{2}P_i^2 \left[\left\langle \frac{1}{M} \right\rangle + \left(\frac{1}{M_j} - \left\langle \frac{1}{M} \right\rangle \right) \right]. \tag{1.8.4.5}$$

The second term is the perturbation. When we evaluate the golden rule for scattering, we square the matrix element and then average the square:

$$\left\langle \left(\frac{1}{M_j} - \left\langle \frac{1}{M} \right\rangle \right)^2 \right\rangle = c\left(\frac{1}{M_1} - \left\langle \frac{1}{M} \right\rangle \right)^2 + (1-c)\left(\frac{1}{M_2} - \left\langle \frac{1}{M} \right\rangle \right)^2 \tag{1.8.4.6}$$

$$= c(1-c)\left(\frac{1}{M_1} - \frac{1}{M_2} \right)^2 \tag{1.8.4.7}$$

$$= c(1-c)\left(\frac{\Delta M}{M_1 M_2} \right)^2. \tag{1.8.4.8}$$

The isotope scattering depends upon the concentration in the form $c(1-c)$ and upon the square of the mass difference $\Delta M = M_2 - M_1$. The isotope fluctuations act as point defects. The total expression for the scattering cross section also includes a factor of q^4 in addition to the factors given above. Thus their temperature dependence is identical to that of the point defects: $R_I \sim T^4$ at low temperature and $R_I \sim$ constant at high temperature.

This behaviour is found experimentally. The isotope scattering is usually a small contribution to the thermal resistivity. It is only important in temperature regions where the other resistivities are small. This occurs, of course, at the maximum value of the thermal conductivity, since that is where all of the resistivities are small. Changing the isotopic mix of a crystal changes the thermal conductivity in the temperature regions where it is large. One example is diamond, which is usually 99% ^{12}C and 1% ^{13}C. Anthony *et al.* (1990) showed that eliminating the ^{13}C increases the thermal conductivity by a factor of nearly two (1.8 to 3.2 kW m^{-1} K^{-1}) at room temperature. Another example is germanium, where isotope scattering makes a sizeable contribution to the thermal resistance (see Berman, 1976).

1.8.4.5. *Alloy scattering*

Alloys are mixtures of two or more different crystal 'ingredients'. We assume that the atoms are randomly located on the different atom sites. Some alloys are ordered, but that makes them crystals. An example of a disordered alloy is $Ga_xAl_{1-x}As$. Since GaAs and AlAs have the same crystal structure and nearly the same lattice constant, the mixed crystal permits any value of x. The Ga and Al atoms randomly occupy the cation site in the zinc blende lattice. Experimentally, it is found that the thermal resistance as a function of x is (see Ziman, 1962; Berman, 1976)

$$R(x) = xR_{\text{GaAs}} + (1-x)R_{\text{AlAs}} + x(1-x)R_A. \tag{1.8.4.9}$$

The first two terms just average the thermal resistance of the two lattices. The third term is the scattering of the phonons from the alloy fluctuations. It is derived in the same way as the equivalent factor of $c(1-c)$ in the discussion of isotope scattering in Section 1.8.4.4. In alloys, the fluctuations are due to two factors: the mass difference at the atoms sites (as in isotope scattering) and the difference in the bonding between Ga and Al. The constant R_A depends on these factors. It is not small: Yao (1987) showed that the term $x(1-x)R_A$ is four or five times larger than the others at $x = 1/2$. Although we have cited a particular example of alloy scattering, this dependence is quite universal. Alloy fluctuations typically dominate the thermal resistivity of alloys.

1.8.4.6. *Anharmonic interactions*

In crystals that are relatively pure, *i.e.* those that lack large numbers of impurities, the important limitation on thermal conductivity at high temperature is from anharmonic interactions (Ziman, 1962). The vibrational potential between neighbouring atoms is not perfectly harmonic. Besides the quadratic dependence on vibrational distance, there is usually a term that depends upon the third and perhaps fourth powers of the relative displacements of the ions. These latter terms are the anharmonic part of the vibrational potential energy. They cause the crystal to expand with temperature and also contribute to the thermal resistance.

For most crystals, the cubic term is important. Its contribution is best explained using the language of phonons. The cubic term means that three phonons are involved. This usually means that one phonon decays into two others, or two phonons combine into one. Both processes contribute to the lifetime of the phonons. On rare occasions, the phase space of the phonons does not permit these events. For example, silicon has a very high frequency optical phonon branch (62 meV at the zone centre) while the acoustic phonons have rather low frequencies. The optical phonons are unable to decay into two of lower frequency, since the two do not have enough energy. This explains, in part, why silicon has a high thermal conductivity. However, this case is unusual. In most crystals, the phonons have similar energy and one can decay into two of lower energy.

The three-phonon events have a simple dependence upon temperature. When one phonon goes to two, or *vice versa*, the rate depends upon the density of phonons $n_B(\omega_q)$ as given by the Bose–Einstein occupation number. At high temperature, *i.e.* about half of the Debye temperature, this function can be expanded to

$$n_B(\omega_q) = \frac{1}{\exp(\hbar\omega_q/k_BT) - 1} \simeq \frac{k_BT}{\hbar\omega_q} \tag{1.8.4.10}$$

and the thermal resistance is proportional to temperature. Thus a plot of the inverse thermal conductivity *versus* temperature usually shows a linear behaviour at high temperature. This linear term is from the anharmonic interactions. There are two main reasons for deviations from linear behaviour: the thermal expansion of the crystal and the contribution of the anharmonic quartic terms, which tend to go as $O(T^2)$.

1.8.4.7. *Thermal conductivity of metals*

Heat conduction in metals can occur by either phonons or electrons. The conduction by phonons has been discussed above. In metals, there is another contribution to the thermal resistance: the absorption of the phonons by the electrons. Metals have low-energy excitations, which consist of exciting an electron just below the chemical potential to an occupied state just above the

chemical potential. The separation in energy between these two electron states can be arbitrarily small and can be small enough to be equal to the energy of a phonon. By this process, the energy of the phonon can be absorbed by the electron gas, which contributes to the thermal resistance of the phonons.

However, in metals, the electrons tend to carry more heat than the phonons. The latter play a secondary role. Thus, we divide the thermal conductivity into electronic and phonon parts, $K = K_e + K_p$. This choice of separation is rather interesting. Note that we do not combine their inverses, as we do for the components of each separate contribution.

The thermal resistance due to the electrons is related to the electrical resistance. Both depend upon the lifetime of the electrons. Because of this, there is a simple relationship between the electronic part of the thermal conductivity and the electrical conductivity σ. This relationship is called the *Wiedemann–Franz law* (Wiedemann & Franz, 1853).

$$K_e = \mathcal{L}_0 \sigma T \tag{1.8.4.11}$$

$$\mathcal{L}_0 = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2. \tag{1.8.4.12}$$

The parameter $\mathcal{L}_0$ is called the *Lorenz number*. The value given above is for a metal with a well defined Fermi surface, so the electrons obey Fermi–Dirac statistics. In the other limit of classical statistics, its value is $2(k_B/e)^2$. We caution that this simple relation between the electrical and thermal conductivities is not exact. The reason for this is that the two lifetimes are not identical: the electrical conductivity uses the lifetime for changing the momentum of the electron, while the thermal conductivity uses the lifetime for changing the energy current. However, the two lifetimes are similar. In practice, the Wiedemann–Franz law is found to work quite well. It seems to be valid regardless of the mechanisms that scatter the electrons: whether the scattering is by phonons, impurities or spin excitations. It can be used to estimate the thermal conductivity from electrons in metals, or in semiconductors with large densities of conduction electrons or holes.

1.8.5. Seebeck coefficient

The Seebeck coefficient S is the third transport coefficient that enters into the fundamental equations (1.8.2.1) and (1.8.2.2). Here we discuss some of its basic properties. First, we write down three integrals for the transport coefficients according to Goldsmid (1986):

$$\sigma = e^2 \int_{-\infty}^{+\infty} d\varepsilon \left(-\frac{\partial n_F}{\partial \varepsilon}\right) \Sigma(\varepsilon) \tag{1.8.5.1}$$

$$T\sigma S = e \int_{-\infty}^{+\infty} d\varepsilon \left(-\frac{\partial n_F}{\partial \varepsilon}\right) \Sigma(\varepsilon)(\varepsilon - \mu) \tag{1.8.5.2}$$

$$TK_e = \int_{-\infty}^{+\infty} d\varepsilon \left(-\frac{\partial n_F}{\partial \varepsilon}\right) \Sigma(\varepsilon)(\varepsilon - \mu)^2, \tag{1.8.5.3}$$

where μ is the chemical potential, e is the electron charge,

$$\left(-\frac{\partial n_F}{\partial \varepsilon}\right) = \frac{1}{k_B T} \frac{\exp\left[(\varepsilon - \mu)/k_B T\right]}{\{\exp\left[(\varepsilon - \mu)/k_B T\right] + 1\}^2}, \tag{1.8.5.4}$$

$\Sigma(\varepsilon)$, which we will call the transport distribution function, is given by

$$\Sigma(\varepsilon) = \sum_{\mathbf{k}} v_x(\mathbf{k})^2 \tau(\mathbf{k}) \delta(\varepsilon - \varepsilon(\mathbf{k})), \tag{1.8.5.5}$$

where the summation is over the first Brillouin zone, $v_x(\mathbf{k})$ is the group velocity of the carriers with wavevector $\mathbf{k}$ in the direction of the applied field, $\tau(\mathbf{k})$ is the lifetime of the carriers and $\varepsilon(\mathbf{k})$ is

the dispersion relation for the carriers. In cases in which many bands contribute to the transport process, the summation has to be extended to all the bands. In some particular cases, such as for parabolic bands, the transport distribution defined in (1.8.5.5) takes a much simpler form:

$$\Sigma(\varepsilon) = N(\varepsilon) v_x(\varepsilon)^2 \tau(\varepsilon), \tag{1.8.5.6}$$

where $N(\varepsilon)$ is the density of states.

The Seebeck coefficient is defined in (1.8.5.2). Since the left-hand side of this equation contains σTS, S is defined as the ratio of the two integrals in (1.8.5.1) and (1.8.5.2). The magnitude of the function $\Sigma(\varepsilon)$ is immaterial for S, since the magnitude cancels in the ratio. All that matters is the dependence of $\Sigma(\varepsilon)$ upon the energy ε. The function $\partial n_F/\partial \varepsilon$ is a symmetric function of ε. Furthermore, it becomes very small when ε is more than a few thermal energies $(k_B T)$ away from the chemical potential. The Seebeck coefficient depends upon how $\Sigma(\varepsilon)$ varies within this small energy range. The usual case is that it is a smooth function of ε that can be expanded in a Taylor series:

$$\Sigma(\varepsilon) \simeq \Sigma(\mu) + (\varepsilon - \mu)\frac{\partial \Sigma(\mu)}{\partial \mu} + O((\varepsilon - \mu)^2) \tag{1.8.5.7}$$

$$\sigma = e^2 \Sigma(\mu) \tag{1.8.5.8}$$

$$S = \frac{\pi^3 k_B^2 T}{3e} \frac{\partial}{\partial \mu} \ln[\Sigma(\mu)]. \tag{1.8.5.9}$$

The Seebeck coefficient has a linear dependence upon temperature. The coefficient of this term depends upon the energy variations in $\Sigma(\varepsilon)$ at the chemical potential. In most metals, a linear dependence upon temperature is observed (*e.g.* Rowe, 1995), particularly at high temperature. This linearity is found when one simple criterion is satisfied: that the function $\Sigma(\varepsilon)$ has a smooth dependence upon energy near the chemical potential.

Any deviation from linear behaviour in the Seebeck coefficient implies that the function $\Sigma(\varepsilon)$ has a more complicated behaviour near the chemical potential. Here we review several possible shapes. One is a simple Lorentzian peak:

$$\Sigma = 1 + C \frac{\gamma^2}{(\varepsilon - \mu - \varepsilon_0)^2 + \gamma^2}. \tag{1.8.5.10}$$
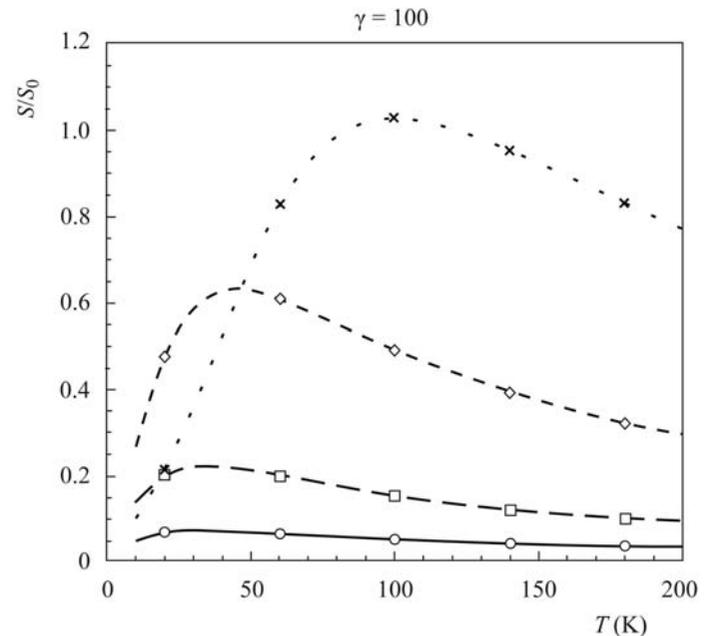
Fig. 1.8.5.1. The Seebeck coefficient S in units of $S_0 = k_B/e$ for $\Sigma(\varepsilon)$ containing a Lorentzian peak. The values of S increase as the resonance energy E_0 increases away from the chemical potential.