<div align="center">1.8. TRANSPORT PROPERTIES</div>

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

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

The kinetic energy term of the ions is then

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

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

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

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

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

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$_x$Al$_{1-x}$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)

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

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

$$n_B(\omega_q) = \frac{1}{\exp(\hbar\omega_q/k_B T) - 1} \simeq \frac{k_B T}{\hbar\omega_q} \qquad (1.8.4.10)$$

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

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