

## 1.8. Transport properties

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### 1.8.1. Introduction

The flow of either electricity or heat is regarded as ‘transport’. These flows are an extremely important characteristic of crystals. Some materials conduct heat or electricity well, while others conduct them poorly. Such properties are important for the use of materials in manufactured products, as some applications require good conductors, while others require poor conductors.

In this chapter, we review the transport properties of crystals. The primary concern is the flow of either electricity or of heat. The topic is restricted to steady-state flows and we do not treat a.c. currents. We also limit our discussion to *linear response*, which is defined precisely below. In general, it means that the flows of electricity and heat are small.

### 1.8.2. Macroscopic equations

The basic equations of transport are given below (Ziman, 1962; Goldsmid, 1986; Mahan, 1990). (The symbols used in this chapter are defined in Section 1.8.6.)

$$\mathbf{J} = \sigma(\mathbf{E} - \mathbf{S} \nabla T) \quad (1.8.2.1)$$

$$\mathbf{J}_Q = \mathbf{J}TS - \mathbf{K} \nabla T, \quad (1.8.2.2)$$

where  $\mathbf{J}$  and  $\mathbf{J}_Q$  are the current density and the heat current, respectively. The three main transport coefficients are the electrical conductivity  $\sigma$ , the thermal conductivity  $K$  and the Seebeck coefficient  $S$ . The electrical resistivity  $\rho$  is the inverse of the conductivity,  $\rho = 1/\sigma$ . In general, the currents, electric field and  $\nabla T$  are vectors while  $\sigma$ ,  $S$  and  $K$  are second-rank tensors. The number of independent tensor components is determined by the symmetry of the crystal (see Chapter 1.1). We assume cubic symmetry, so all of the quantities can be treated as scalars. Onsager relations require that the Seebeck coefficient  $S$  is the same in the two equations. A description of the transport properties of most crystals is simply given as a graph, or table, of how each of the three parameters ( $\sigma$ ,  $S$ ,  $K$ ) varies with temperature. The range of variation among crystals is enormous.

The above equations assume that there is no magnetic field and have to be changed if a magnetic field is present. This special case is discussed below.

### 1.8.3. Electrical resistivity

#### 1.8.3.1. Properties of the electrical resistivity

The electrical conductivity is usually written as (Ziman, 1962; Goldsmid, 1986; Mahan, 1990)

$$\sigma = \frac{n_0 e^2 \tau}{m^*}, \quad (1.8.3.1)$$

where  $n_0$  is the density of conduction electrons in units of  $m^{-3}$ ,  $e$  is the charge on the electron,  $\tau$  is the lifetime of the electron and  $m^*$  is the effective mass. Here we are assuming parabolic bands, so the energy of the electron is  $\varepsilon(k) = \hbar^2 k^2 / 2m^*$ .

If one measures  $\sigma$  as a function of temperature, then one has determined  $\tau(T)$ , assuming that one knows  $n_0$  and  $m^*$  from other measurements, e.g. Allen *et al.* (1986). The electron density  $n_0$  can sometimes be determined from the Hall effect, as discussed in Section 1.8.3.4. The effective mass  $m^*$  can be determined by a

cyclotron resonance experiment or a similar experiment that measures the properties of the Fermi surface. Also, the ratio  $n_0/m^*$  can be found by measuring the frequency dependence of the dielectric function in the infrared (Sievers, 1980):  $\varepsilon(\omega) = \varepsilon_\infty - 4\pi n_0 e^2 / (m^* \omega^2)$ . Here the factors  $n_0 e^2 / m^*$  occur in the same combination as found in the d.c. conductivity. The factors  $n_0$  and  $m^*$  can also be determined by numerical calculations of the band structure of the solid. In any case, we assume that these parameters are known. The only difficult parameter to find is the lifetime.

The lifetime of the electrons is usually determined by solving a Boltzmann equation for the distribution function of the electrons. The method of solution is described in many references (Ziman, 1962; Goldsmid, 1986; Mahan, 1990) and will not be repeated here. The Boltzmann equation is itself an approximate equation, since one must do some averaging over the particles in deriving it. This approximate equation can then be solved by a variety of methods: analytical with approximations, variationally or numerically with great accuracy. The latter is done quite easily with today’s computers. Here we shall summarize the main contributions to the lifetime.

The electrical resistivity is the inverse of the conductivity,

$$\rho = \frac{m^*}{n_0 e^2 \tau}. \quad (1.8.3.2)$$

The scattering rate of the electron can often be calculated using Fermi’s golden rule, which is an equation of the form

$$\frac{1}{\tau_i} = \frac{2\pi}{\hbar} \sum_f |M_{if}|^2 [1 - \cos \theta] \delta(E_i - E_f). \quad (1.8.3.3)$$

Here the lifetime of an initial state  $i$  is given by summing over all of the final states  $f$  that can be reached by a matrix element  $M_{if}$ . The factor of  $[1 - \cos \theta]$  is included to measure the amount of scattering, where  $\theta$  is the angle through which the electron scatters. Anything that scatters or interacts with an electron contributes to the lifetime. This includes the thermal vibrations of the ions, which is an intrinsic effect. There are also extrinsic effects such as scattering from impurities, grain boundaries, dislocations and the boundaries of the crystal. The latter is important in thin films or wires.

*Matthiessen’s rule* (Matthiessen & Vogt, 1864) states that the resistivities from each type of scattering process can simply be added. The total resistivity can be written as

$$\rho = \frac{m^*}{n_0 e^2} \sum_j \frac{1}{\tau_j}, \quad (1.8.3.4)$$

where  $\tau_j$  is the lifetime from one of the scattering mechanisms. There are several important disclaimers regarding this rule. It is far from rigorous. It is often untrue. Yet it works very well 95% of the time. We shall adopt the rule here for our discussion of the resistivity.

The major contributions to the resistivity of solids are:

(1) *Impurities*. Every crystal has impurities, as it is not possible to make a crystal without some defects. The reasons for this are well understood and here we just assume this fact. The formula for the lifetime contains two factors (Mahan, 1990): (a) the concentration of impurities  $n_i$  and (b) the phase shifts  $\delta_l(k)$  for scattering an electron of wavevector  $k$  and angular momentum  $l$ ,

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$$\frac{1}{\tau_i(k)} = \frac{4\pi n_i \hbar}{m^* k} \sum_l l \sin^2[\delta_l(k) - \delta_{l-1}(k)]. \quad (1.8.3.5)$$

Although this expression appears complicated, one can view it as consisting of three parts:

$$\frac{1}{\tau_i} = n_i v_k \sigma_c(k), \quad (1.8.3.6)$$

$$v_k = \frac{\hbar k}{m^*}, \quad (1.8.3.7)$$

$$\sigma_c = \frac{4\pi}{k^2} \sum_l l \sin^2[\delta_l(k) - \delta_{l-1}(k)]. \quad (1.8.3.8)$$

The three factors are the concentration  $n_i$  of impurities, the electron velocity  $v_k$  and the cross section  $\sigma_c$ . For each impurity, the cross section is a function of  $k$ . The lifetime is the density of impurities multiplied by a simple function of electron energy and is independent of temperature. A careful analysis shows that there is a temperature dependence to the scattering by impurities. However, this dependence is rather slight, and is dwarfed by the large temperature dependence of the electron scattering by phonons (Bass *et al.*, 1990). It is a common approximation to treat  $\tau_i$  as a constant independent of temperature. It is easy to determine this constant experimentally: the resistivity in the limit of zero temperature contains just the contribution from impurities and defects.

It is possible to add a known amount of impurities intentionally. Then a measurement of the impurity resistance provides a measurement of the cross section  $\sigma_c$ , since the Fermi velocity  $v_F$  is usually known.

(2) *Phonons in metals.* Crystals are composed of atoms, which vibrate. As the temperature increases, they vibrate with larger amplitude. These vibrations provide a noise spectrum for the electrons and cause the electrons to scatter. The scattering of electrons by phonons is an intrinsic process. For most solids, this process is the dominant contribution to the electrical resistivity at temperatures above 100 K.

Ziman (1962) first derived the following expression for the resistivity due to the scattering of electrons by phonons in a metal:

$$\rho(T) = C' \sum_{\lambda} \int q d^3 q |M_{\lambda}(\mathbf{q})|^2 (\hat{\xi}_{\lambda} \cdot \mathbf{q})^2 \left[ -\frac{\partial n_B(\omega)}{\partial \omega} \right]_{\omega=\omega_{\lambda}(\mathbf{q})} \quad (1.8.3.9)$$

$$C' = \frac{3\hbar v_0}{Me^2 16v_F^2 k_F^4}. \quad (1.8.3.10)$$

The constant  $C'$  collects numerous constants including the Fermi wavevector  $k_F$ , the Fermi velocity  $v_F$ , the ion mass  $M$  and the unit-cell volume  $v_0$ . The phonons have wavevector  $\mathbf{q}$  and different phonon bands (e.g. TA, LA, TO) are denoted by  $\lambda$ . The phonon frequencies are  $\omega_{\lambda}(\mathbf{q})$  and the matrix element for scattering the electron by wavevector  $\mathbf{q}$  is  $M_{\lambda}(\mathbf{q})$ .

Equation (1.8.3.9) is easy to evaluate using a computer code that generates all of the phonons at different points in the Brillouin zone. It is the formula used most often to calculate the temperature dependence of the resistivity of metals. However, the reader is warned that this formula is not exact, as it represents an approximate solution of the Boltzmann equation. In the only case in which the accuracy of equation (1.8.3.9) has been tested against numerically accurate solutions of the Boltzmann equation, Wu & Mahan (1984) found that (1.8.3.9) had an error of a few per cent. However, the formula is useful because it gives an answer that only errs by a few per cent and is relatively easy to calculate.

Equation (1.8.3.9) has one feature that is simple and important. At high temperature, the resistivity becomes proportional to

temperature. The Bose–Einstein occupation number  $n_B(\omega) \simeq k_B T / \hbar \omega$  and then the derivative with respect to  $\omega$  is simple. This gives the expression

$$\rho(T) = \frac{m^*}{n_0 e^2} \frac{1}{\tau(T)} \quad (1.8.3.11)$$

$$\frac{1}{\tau} = \frac{2\pi}{\hbar} \lambda_i k_B T \quad (1.8.3.12)$$

$$\lambda_i = \frac{m}{M} \frac{v_0}{16\pi^2 k_F^3} \int q d^3 q \frac{|M_{\lambda}(\mathbf{q})|^2 (\hat{\xi}_{\lambda} \cdot \mathbf{q})^2}{[\hbar \omega_{\lambda}(\mathbf{q})]^2}. \quad (1.8.3.13)$$

At high temperature, which in practice is above half of the Debye temperature, the inverse lifetime of the electron is proportional to the temperature. The coefficient is the dimensionless constant  $\lambda_i$ , which is called the ‘transport form of lambda’ (see Grimvall, 1981). This parameter gives the strength of the interaction between the electrons and the phonons. It ranges from very small values ( $\lambda_i \sim 0.1$ ) for the noble metals to values above 4 for heavy metals such as lead and mercury (see Grimvall, 1981).

Now we give some examples of the resistivity of common metals and show that the above formulas give a good account of the resistivity. Fig. 1.8.3.1 shows the intrinsic resistivity as a function of temperature for a simple metal (sodium). The data are taken from Bass *et al.* (1990). The impurity resistivity has been subtracted away. The resistivity is lowest at low temperature, increases at higher temperature and becomes linear at very high temperatures. In actual crystals, the low-temperature value is determined by scattering from impurities and is different for each piece of metal. If one subtracts the constant value and plots  $\rho(T) - \rho(0)$ , then the curve is the same for each crystal of sodium. This is just the phonon contribution to the resistivity.

At very high temperatures, the resistivity is found to deviate from being linear with temperature. This deviation is due to the thermal expansion of the crystal at high temperature. This can be suppressed by taking measurements at constant volume, as is the case for the results shown in Fig. 1.8.3.1. If the crystal is put under pressure to maintain constant volume, then the high-temperature resistivity is highly linear with temperature.

Also interesting is the behaviour of the resistivity at very low temperatures, say less than 1 K. For the alkali metals, the temperature dependence was found by Bass *et al.* (1990) to be

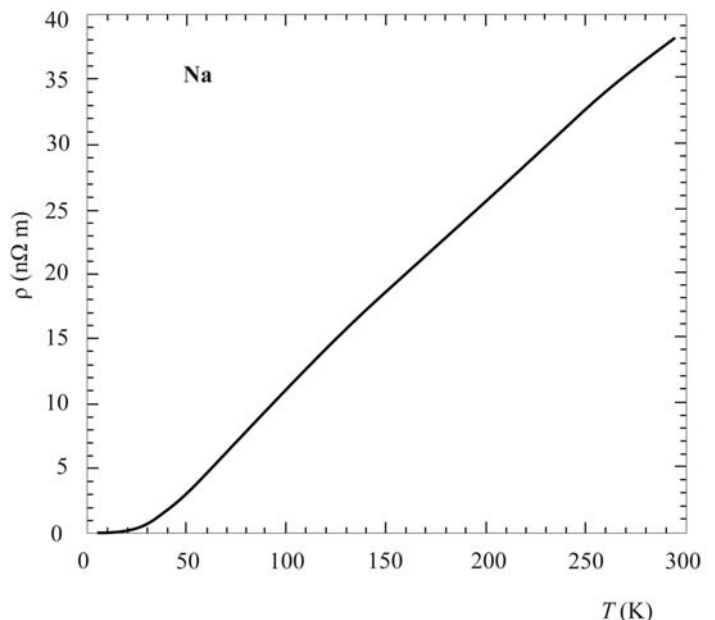


Fig. 1.8.3.1. The temperature dependence of the intrinsic electrical resistivity of sodium at constant density. The data are taken from Bass *et al.* (1990).

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$$\rho(T) = \rho_i(1 + BT^2) + AT^2. \quad (1.8.3.14)$$

The term  $\rho_i$  is the constant due to the impurity scattering. There is also a term proportional to  $BT^2$ , which is proportional to the impurity resistance. This factor is due to the Koshino–Taylor effect (Koshino, 1960; Taylor, 1964), which has been treated rigorously by Mahan & Wang (1989). It is the inelastic scattering of electrons by impurities. The impurity is part of the lattice and phonons can be excited when the impurity scatters the electrons. The term  $AT^2$  is due to electron–electron interactions. The Coulomb interaction between electrons is highly screened and makes only a small contribution to  $A$ . The largest contribution to  $A$  is caused by phonons. MacDonald *et al.* (1981) showed that electrons can interact by exchanging phonons. There are also terms due to boundary scattering, which is important in thin films: see Bruls *et al.* (1985).

Note that (1.8.3.14) has no term from phonons of  $O(T^5)$ . Such a term is lacking in simple metals, contrary to the assertion in most textbooks. Its absence is due to *phonon drag*. For a review and explanation of this behaviour, see Wiser (1984). The  $T^5$  term is found in the noble metals, where phonon drag is less important owing to the complexities of the Fermi surface.

### 1.8.3.2. Metal alloys

Alloys are solids composed of a mixture of two or more elements that do not form a stoichiometric compound. An example is  $\text{Cu}_x\text{Ni}_{1-x}$ , in which  $x$  can have any value. For small values of  $x$ , or of  $(1-x)$ , the atoms of one element just serve as impurities in the other element. This results in the type of behaviour described above. However, in the range  $0.2 < x < 0.8$ , a different type of resistivity is found. This was first summarized by Mooij (1973), who found a remarkable range of behaviours. He measured the resistivity of hundreds of alloys and also surveyed the published literature for additional results. He represented the resistivity at  $T = 300$  K by two values: the resistivity itself,  $\rho(T = 300)$ , and its logarithmic derivative,  $\alpha = d \ln(\rho)/dT$ . He produced the graph shown in Fig. 1.8.3.2, where these two values are plotted against each other. Each point is one sample as represented by these two numbers. He found that all of the results fit within a band of numbers, in which larger values of  $\rho(T = 300)$  are accompanied by negative values of  $\alpha$ . Alloys with very high values of resistivity generally have a resistivity  $\rho(T)$  that decreases with increasing temperature. The region where  $\alpha = 0$  corresponds to a resistivity of  $\rho^* = 150 \mu\Omega \text{ cm}$ , which appears to be a fixed point. As the temperature is increased, the resistivities of alloys with  $\rho > \rho^*$  decrease to this value, while the resistivities of alloys with  $\rho < \rho^*$  increase to this value.

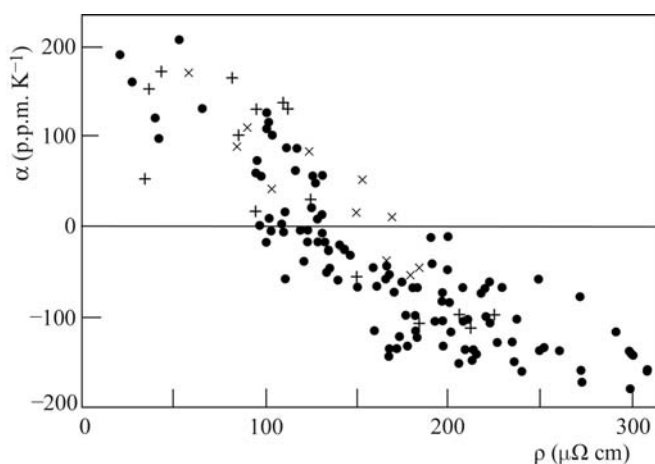


Fig. 1.8.3.2. The temperature coefficient of resistance *versus* resistivity for alloys according to Mooij (1973). Data are shown for bulk alloys (+), thin films (•) and amorphous alloys (x).

Mooij's observations are obviously important, but the reason for this behaviour is not certain. Several different explanations have been proposed and all are plausible: see Jonson & Girvin (1979), Allen & Chakraborty (1981) or Tsuei (1986).

Recently, another group of alloys have been found that are called *bad metals*. The ruthenates (see Allen *et al.*, 1996; Klein *et al.*, 1996) have a resistivity  $\rho > \rho^*$  that increases at high temperatures. Their values are outliers on Mooij's plot.

### 1.8.3.3. Semiconductors

The resistivity of semiconductors varies from sample to sample, even of the same material. The conductivity can be written as  $\sigma = n_0 e \mu$ , where  $e$  is the charge on the electron,  $\mu = e\tau/m^*$  is the mobility and  $n_0$  is the density of conducting particles (electrons or holes). It is the density of particles  $n_0$  that varies from sample to sample. It depends upon the impurity content of the semiconductor as well as upon temperature. Since no two samples have exactly the same number of impurities, they do not have the same values of  $n_0$ . In semiconductors and insulators, the conducting particles are extrinsic – they come from defects, impurities or thermal excitation – in contrast to metals, where the density of the conducting electrons is usually an intrinsic property.

In semiconductors, instead of talking about the conductivity, the more fundamental transport quantity (Rode, 1975) is the mobility  $\mu$ . It is the same for each sample at high temperature if the density of impurities and defects is low. There is an intrinsic mobility, which can be calculated assuming there are no impurities and can be measured in samples with a very low density of impurities. We shall discuss the intrinsic mobility first.

Fig. 1.8.3.3 shows the intrinsic mobility of electrons in silicon, from Rode (1972), as a function of temperature. The mobility generally decreases with increasing temperature. This behaviour is found in all common semiconductors. The mobility also decreases with an increasing concentration of impurities: see Jacoboni *et al.* (1977).

The intrinsic mobility of semiconductors is due to the scattering of electrons and holes by phonons. The phonons come in various branches called TA, LA, TO and LO, where T is transverse, L is longitudinal, A is acoustic and O is optical. At long wavelengths, the acoustic modes are just the sound waves, which

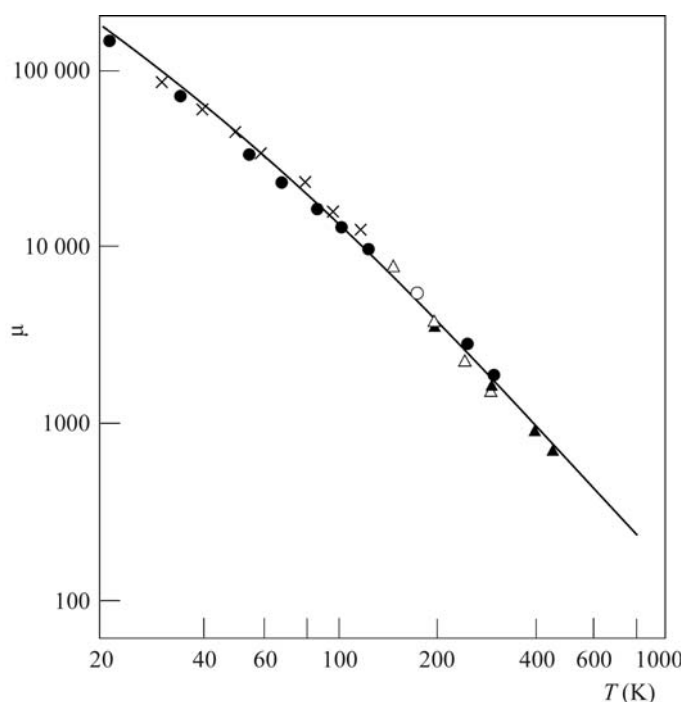


Fig. 1.8.3.3. The intrinsic mobility of electrons in silicon. Solid line: theory; points: experimental. After Rode (1972).

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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  $\mu_c$  and  $\mu_v$  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  $\sigma$  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  $\Lambda$  is the mean free path. To apply this to the present problem, take  $\Lambda$  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  $\Lambda$  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  $\Theta$ , 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,  $R_i \sim \text{constant}$ .

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### 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

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

The kinetic energy term of the ions is then

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

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

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

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

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

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  $R_I \sim \text{constant}$  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%  $^{12}\text{C}$  and 1%  $^{13}\text{C}$ . Anthony *et al.* (1990) showed that eliminating the  $^{13}\text{C}$  increases the thermal conductivity by a factor of nearly two (1.8 to  $3.2 \text{ kW m}^{-1} \text{ K}^{-1}$ ) 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  $\text{Ga}_x\text{Al}_{1-x}\text{As}$ . 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)

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

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

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

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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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  $\sigma$ . This relationship is called the *Wiedemann–Franz law* (Wiedemann & Franz, 1853).

$$K_e = \mathcal{L}_0 \sigma T \quad (1.8.4.11)$$

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

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):

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

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

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

where  $\mu$  is the chemical potential,  $e$  is the electron charge,

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

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

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

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:

$$\Sigma(\varepsilon) = N(\varepsilon) v_x(\varepsilon)^2 \tau(\varepsilon), \quad (1.8.5.6)$$

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  $\sigma TS$ ,  $S$  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  $\varepsilon$ . The function  $\partial n_F / \partial \varepsilon$  is a symmetric function of  $\varepsilon$ . Furthermore, it becomes very small when  $\varepsilon$  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  $\varepsilon$  that can be expanded in a Taylor series:

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

$$\sigma = e^2 \Sigma(\mu) \quad (1.8.5.8)$$

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

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:

$$\Sigma = 1 + C \frac{\gamma^2}{(\varepsilon - \mu - \varepsilon_0)^2 + \gamma^2}. \quad (1.8.5.10)$$

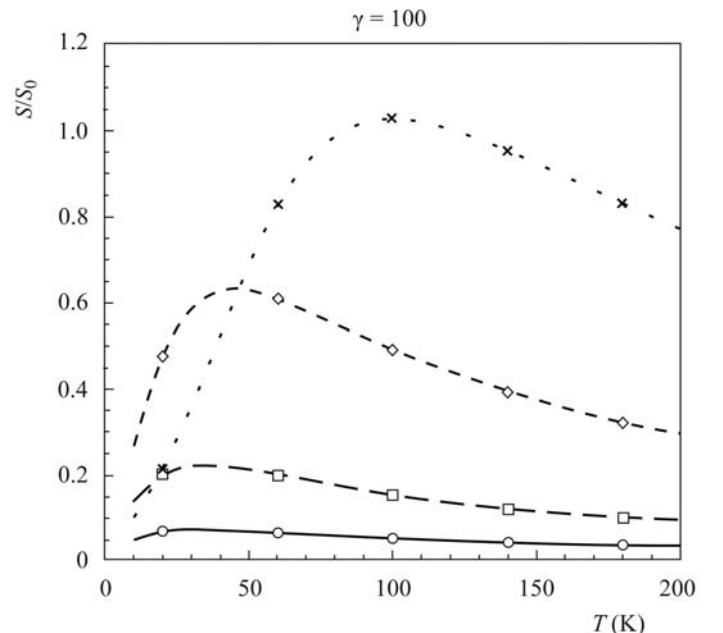


Fig. 1.8.5.1. The Seebeck coefficient  $S$  in units of  $S_0 = k_B/e$  for  $\Sigma(\varepsilon)$  containing a Lorentzian peak. The values of  $S$  increase as the resonance energy  $E_0$  increases away from the chemical potential.

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The peak of the Lorentzian is at  $\varepsilon_0$  and the width is  $\gamma$ . Fig. 1.8.5.1 shows the Seebeck coefficient calculated with this functional form. We arbitrarily took  $\gamma = k_B T_\gamma$  and  $T_\gamma = 100$  K. The four curves are for  $\varepsilon_0/k_B = 10, 30, 100$  and  $300$  K, and the larger  $\varepsilon_0$  has the larger Seebeck coefficient. All of the curves have a broad peak as a function of temperature. If  $\varepsilon_0 = 0$ , then  $S = 0$ , since the integrand is an odd function of  $(\varepsilon - \mu)$ . The vertical scale is  $S/S_0$  where  $S_0 = k_B/e = 86.17 \mu\text{V K}^{-1}$ . We see from Fig. 1.8.5.1 that it is difficult to get values of  $S/S_0$  very much larger than unity.

Another example is that of mixed-valence materials with  $f$  electrons. The  $f$  shells make electron states of narrow energy, which are approximated as Lorentzians. In this case,  $\Sigma(\varepsilon)$  equals the inverse of the right-hand side of (1.8.5.10). The argument for this is that  $1/\tau(\varepsilon)$  is proportional to the right-hand side of (1.8.5.10). Since  $\Sigma \propto \tau$ , it contains the inverse of (1.8.5.10). Interestingly enough, plots of the Seebeck coefficient by Jaccard & Sierro (1982) for this case also contain broad peaks in energy, where  $S/S_0$  has a maximum of about unity. In this case, a proper calculation includes the fact that both  $C$  and  $\gamma$  are functions of temperature. For a review, see Mahan (1997).

We give these examples of the Seebeck coefficient because they are the cases that occur most often. In many metals, the Seebeck coefficient is either linear with temperature or has broad peaks. The broad peaks are due to structure in  $\Sigma$  near the chemical potential. This structure is usually due either to variations in the density of states or in the electron lifetime.

In insulators, the Seebeck coefficient can become relatively large. The exact value depends upon the energy gap, the temperature and the density of impurities. This example is treated in many references, e.g. Goldsmid (1986) and Rowe (1995).

### 1.8.6. Glossary

$T$	temperature (K)
$\mathbf{J}$	current density ( $\text{A m}^{-2}$ )
$\mathbf{J}_Q$	heat current ( $\text{W m}^{-2}$ )
$\sigma$	electrical conductivity ( $\text{S m}^{-1}$ )
$\rho$	electrical resistivity
$K$	thermal conductivity ( $\text{W m}^{-1} \text{K}^{-1}$ )
$\mathbf{E}$	electric field ( $\text{V m}^{-1}$ )
$S$	Seebeck coefficient ( $\text{V K}^{-1}$ )
$k_B$	Boltzmann constant
$R_H$	Hall constant
$m^*$	effective mass of the electron
$\tau$	lifetime of the electron

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