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.)

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

$$\mathbf{J}_Q = \mathbf{J}T\mathbf{S} - \mathbf{K}\,\overrightarrow{\nabla T}, \qquad (1.8.2.2)$$

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 σ, the thermal conductivity K and the Seebeck coefficient S. The electrical resistivity ρ is the inverse of the conductivity, $\rho = 1/\sigma$. In general, the currents, electric field and $\overrightarrow{\nabla T}$ are vectors while σ, 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 (σ, 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)

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

where n_0 is the density of conduction electrons in units of m^{-3}, e is the charge on the electron, τ 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 σ 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): $\epsilon(\omega) = \epsilon_\infty - 4\pi n_0 e^2/(m^*\omega^2)$. 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,

$$\rho = \frac{m^*}{n_0 e^2} \frac{1}{\tau}. \qquad (1.8.3.2)$$

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

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

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 θ 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

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

where τ_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,

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

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

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

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

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

The three factors are the concentration n_i of impurities, the electron velocity v_k and the cross section σ_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 τ_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 σ_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:

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

(1.8.3.9)

$$C' = \frac{3\hbar v_0}{Me^2 16 v_F^2 k_F^4}.$$ (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 λ. 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 ω is simple. This gives the expression

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

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

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

(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 λ_t, 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 ($\lambda_t \sim 0.1$) 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 supressed 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
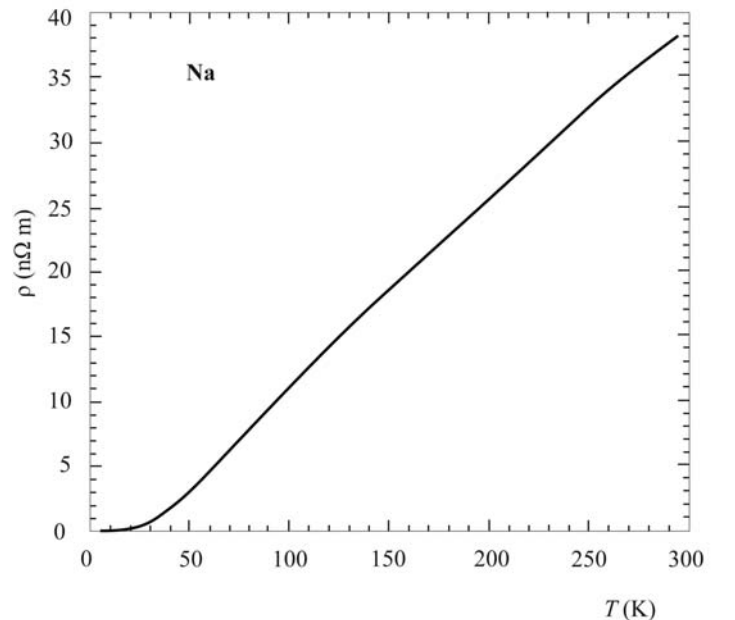

Fig. 1.8.3.1. The temperature dependence of the intrinsic electrical resistivity of sodium at constant density. The data are taken from Bass *et al.* (1990).

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

The term ρ_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 $Cu_x Ni_{1-x}$, 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 α. 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 $\rho^* = 150\,\mu\Omega\,cm$, which appears to be a fixed point. As the temperature is increased, the resisitivities of alloys with $\rho > \rho^*$ decrease to this value, while the resisitivities of alloys with $\rho < \rho^*$ increase to this value.

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 μ. 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
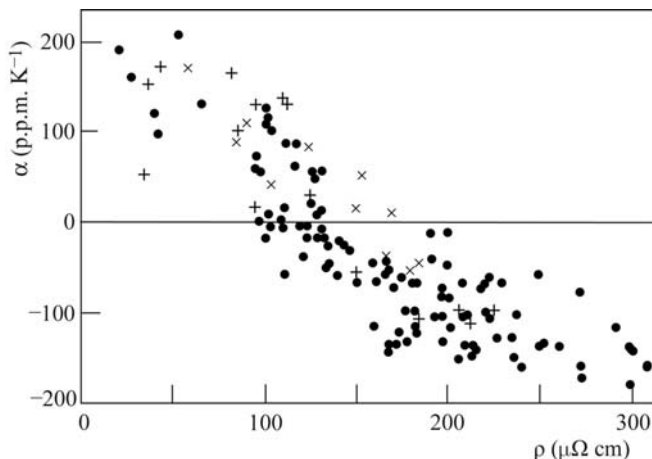

Fig. 1.8.3.2. The temperature coefficient of resistance *versus* resistivity for alloys according to Mooij (1973). Data are shown for bulk alloys ($+$), thin films ($\bullet$) and amorphous alloys ($\times$).
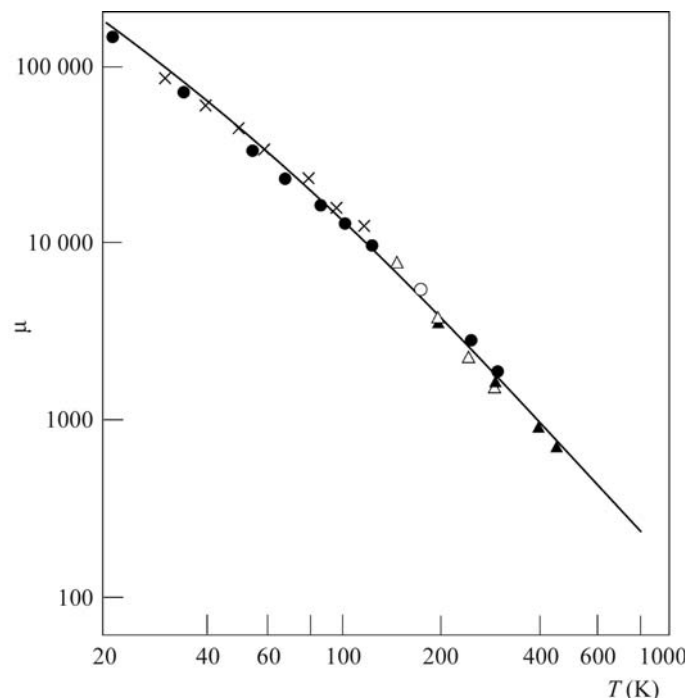

Fig. 1.8.3.3. The intrinsic mobility of electrons in silicon. Solid line: theory; points: experimental. After Rode (1972).