

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 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 ∇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)

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

where n_0 is the density of conduction electrons in units of m^{-3} , e is the charge on the electron, 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,

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

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 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

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

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 ,