(as charge certainly is), then thermal currents will be degraded in precisely the same manner and to the same extent as electric currents. If, however, collisions do not conserve the energy ε of each electron, then a second mechanism becomes available for the degradation of a thermal current that has no electrical analogue: Collisions can alter the electron's energy ε as well as its velocity. Since such inelastic collisions will have a substantially different effect on thermal and electric currents, there is no longer any reason to expect a simple relation to hold between electrical and thermal conductivities.[14]

Evidently the Wiedemann-Franz law will hold to a good approximation, if energy is conserved to a good approximation. The crucial requirement is that the change in energy of each electron in a collision should be small compared with $k_B T$. It turns out that the scattering by thermal vibrations of the ions can satisfy this condition at high temperatures. Since such scattering is the dominant high-temperature source of collisions, the Wiedemann-Franz law is generally well obeyed at both high and low[15] temperatures. However, in the intermediate temperature range (roughly ten to a few hundred degrees K), where inelastic collisions are both prevalent and capable of producing electronic energy losses of order $k_B T$, one expects and observes failures of the Wiedemann-Franz law.

MATTHIESSEN'S RULE

Suppose there are two physically distinguishable sources of scattering (for example, scattering by impurities and scattering by other electrons). If the presence of one mechanism does not alter the way in which the other mechanism functions, then the total collision rate W will be given by the sums of the collision rates due to the separate mechanisms:

$$W = W^{(1)} + W^{(2)}. \tag{16.20}$$

In the relaxation-time approximation this immediately implies that

$$\frac{1}{\tau} = \frac{1}{\tau^{(1)}} + \frac{1}{\tau^{(2)}}. \tag{16.21}$$

If, in addition, we assume a k-independent relaxation time for each mechanism, then, since the resistivity is proportional to $1/\tau$, we will have

$$\rho = \frac{m}{ne^2\tau} = \frac{m}{ne^2} \frac{1}{\tau^{(1)}} + \frac{m}{ne^2} \frac{1}{\tau^{(2)}} = \rho^{(1)} + \rho^{(2)}. \tag{16.22}$$

This asserts that the resistivity in the presence of several distinct scattering mechanisms is simply the sum of the resistivities one would have if each alone were present.

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[14]   One sometimes encounters the assertion that the Wiedemann-Franz law fails because the relaxation time for thermal currents is different from the relaxation time for electric currents. This is, at best, a misleading oversimplification. The Wiedemann-Franz law fails, if inelastic scattering is present, because there are scattering processes that can degrade a thermal current without degrading an electric current. The failure is due not to the comparative *rates* at which electrons experience collisions, but to the comparative *effectiveness* of each single collision in degrading the two kinds of currents.

[15]   At low temperatures, as we have pointed out, the dominant source of collisions is elastic impurity scattering.

This proposition is known as Matthiessen's rule. At first glance its utility might seem questionable, since it is difficult to imagine how one might remove a source of scattering, keeping all other things constant. However, it does make certain general assertions of principle that are easily tested. For example, elastic impurity scattering should proceed at a temperature-independent rate (since neither the number of impurities nor their interaction with electrons is appreciably affected by the temperature), but the electron-electron scattering rate should go as T^2 (in the simplest theories: see Chapter 17). Thus Matthiessen's rule predicts a resistivity of the form $\rho = A + BT^2$ with temperature-independent coefficients A and B, if impurity and electron-electron scattering are the dominant mechanisms.

It is not hard to verify that Matthiessen's rule breaks down even in the relaxation-time approximation, if τ depends on k. For the conductivity σ is then proportional to some average, $\bar{\tau}$, of the relaxation time (see, for example, Eq. (13.25)). Thus the resistivity, ρ, is proportional to $1/\bar{\tau}$, and Matthiessen's rule requires that

$$1/\bar{\tau} = 1/\overline{\tau^{(1)}} + 1/\overline{\tau^{(2)}}. \tag{16.23}$$

However, Eq. (16.21) gives only relations such as

$$\overline{(1/\tau)} = \overline{(1/\tau^{(1)})} + \overline{(1/\tau^{(2)})}, \tag{16.24}$$

which are not equivalent to (16.23) unless $\tau^{(1)}$ and $\tau^{(2)}$ are independent of k.

A more realistic picture of collisions casts even graver doubts on the general validity of Matthiessen's rule, for the assumption that the scattering rate due to one mechanism is independent of the presence of the second becomes much less plausible as soon as the assumptions of the relaxation-time approximation are dropped. The actual rate at which an electron experiences collisions depends on the configuration of the other electrons, and this can be strongly affected by the presence of two competing scattering mechanisms unless, by some good fortune, it happens that the distribution function in the presence of each separate scattering mechanism is the same.

It can, however, be shown without making the relaxation-time approximation, that Matthiessen's rule holds as an inequality:[16]

$$\rho \geqslant \rho^{(1)} + \rho^{(2)}. \tag{16.25}$$

Quantitative analytic studies of the extent to which Matthiessen's rule fails are quite complex. The rule is certainly valuable as a crude guide to what to expect, but one must always bear in mind the possibility of gross failures—a possibility that is obscured by the naive relaxation-time approximation.

SCATTERING IN ISOTROPIC MATERIALS

It is sometimes asserted that the relaxation-time approximation can be justified in isotropic systems. This is an interesting and useful observation, but one must be aware

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[16]   See, for example, J. M. Ziman, *Electrons and Phonons*, Oxford, 1960, p. 286, and also Problem 4 below.