

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

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 σ . 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 μ 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 σTS , 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 ε . The function $\partial n_F / \partial \varepsilon$ is a symmetric function of ε . Furthermore, it becomes very small when ε 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 ε 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:

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

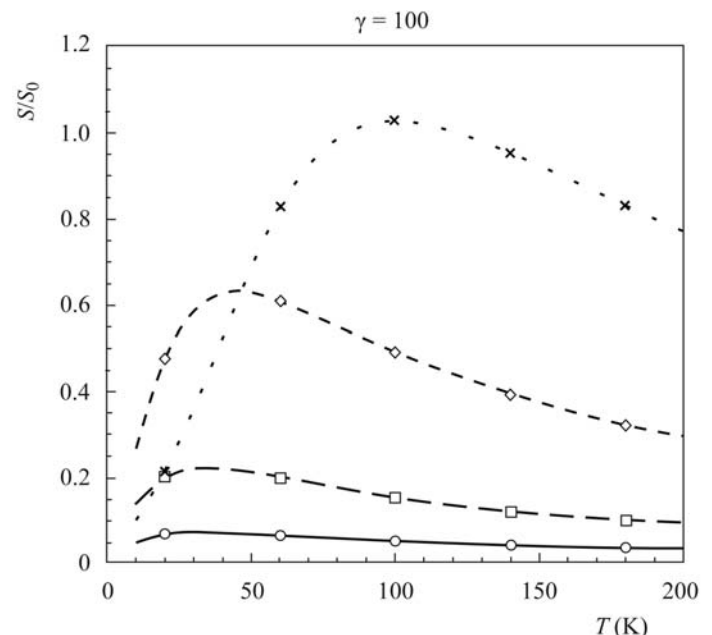


Fig. 1.8.5.1. The Seebeck coefficient S in units of $S_0 = k_B/e$ for $\Sigma(\varepsilon)$ containing a Lorentzian peak. The values of S increase as the resonance energy E_0 increases away from the chemical potential.

1.8. TRANSPORT PROPERTIES

The peak of the Lorentzian is at ε_0 and the width is γ . 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 ε_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 γ 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 Σ 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 (A m^{-2})
\mathbf{J}_Q	heat current (W m^{-2})
σ	electrical conductivity (S m^{-1})
ρ	electrical resistivity
K	thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
\mathbf{E}	electric field (V m^{-1})
S	Seebeck coefficient (V K^{-1})
k_B	Boltzmann constant
R_H	Hall constant
m^*	effective mass of the electron
τ	lifetime of the electron

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