

Handout 10

Transport of heat and electricity in metals and semiconductors

10.1 Thermal and electrical conductivity of metals

10.1.1 The “Kinetic theory” of electron transport

We now apply our knowledge of bandstructure, Fermi surfaces and electron statistics to the problem of transport of heat and electricity by electrons. We are going to look initially at a metal with isotropic bands characterised by an effective mass m^* . This is in effect the Sommerfeld model with the additional refinement of an adjustable m^* which characterises the effect of the periodic lattice potential on the electrons; the Fermi surface will be spherical. (More complex Fermi surfaces will be mentioned later.) In Lecture 1 we used the Relaxation Time Approximation to derive the expression

$$\sigma = \frac{ne^2\tau}{m^*} \quad (10.1)$$

for the electrical conductivity σ of such a metal. Here n is the number density of electrons and τ^{-1} is the scattering rate. In addition, we used Kinetic Theory and the Sommerfeld model to obtain the expression

$$\kappa = \frac{1}{6}n\pi^2k_B^2\frac{T}{E_F}v_F^2\tau \quad (10.2)$$

for the electronic thermal conductivity κ . Here v_F is the Fermi velocity and E_F is the Fermi energy. Equations 10.1 and 10.2 were combined to give the Wiedemann–Franz Ratio or Lorenz number

$$L \equiv \frac{\kappa}{\sigma T} = \frac{\pi^2}{3}\frac{k_B^2}{e^2} \equiv L_0 \quad (10.3)$$

and it was found that this constant was in good agreement with many experimental data at room temperature. However, in many cases, experimental values of L differed markedly (by orders of magnitude!) from L_0 at lower temperatures.

The problem has arisen because two scattering times τ (which are not necessarily the same) have been cancelled in Equation 10.3. Acknowledging this fact we rewrite Equations 10.1 and 10.2 in the following form:

$$\sigma = \frac{ne^2\tau_\sigma}{m^*} \quad (10.4)$$

and

$$\kappa = \frac{1}{6}n\pi^2k_B^2\frac{T}{E_F}v_F^2\tau_\kappa, \quad (10.5)$$

i.e. we have distinguished the two scattering times.

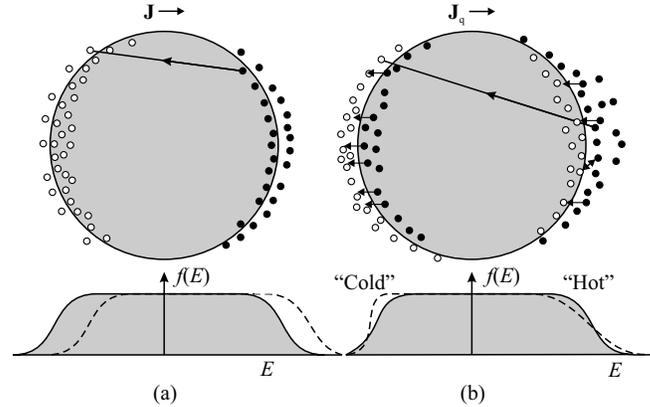


Figure 10.1: Top: representation of the alteration of the Fermi surface caused by electrical conduction (a) (current density \mathbf{J}) and thermal conduction (b) (heat flux \mathbf{J}_q); black circles represent filled states and white circles empty states. In electrical conduction, the Fermi surface is displaced by a tiny amount corresponding to the drift velocity caused by the electric field; thus, an excess of electrons travel towards the right. In thermal conduction, “hotter” electrons head right and “cooler” electrons head left. The effects of these changes are represented in the lower half of the Figures by plotting the Fermi-Dirac distribution functions for left-heading and right-heading electrons (dotted lines) compared to the equilibrium situation (grey shading). The long arrows indicate phonon scattering events of the kind encountered at room temperature, which lead to degradation of both the electrical and thermal currents. The short arrows are the phonon scattering processes encountered at low temperatures; note that these can degrade the thermal current both by “warming up” “cold” electrons and “cooling” “hot” electrons.

10.1.2 What do τ_σ and τ_κ represent?

In all of the following, we are going to be talking about the electron velocity \mathbf{v} . Previously, we have seen that $\mathbf{v} = (1/\hbar)\nabla_{\mathbf{k}}E(\mathbf{k})$; this means that electron velocities are always perpendicular to surfaces of constant energy. As always, the electrons at the Fermi surface are going to see most of the action; their velocities may be imagined as vectors normal to the Fermi surface, as the Fermi surface is *the* constant energy surface *par excellence*.¹

Consider first electrical conduction. In the absence of an electric field, there are as many electrons travelling in any one direction as in the opposite direction, so that no net current flows. When an electric field is applied, electrons at the Fermi surface acquire a small amount of extra velocity (the drift velocity derived in the Relaxation-Time Approximation). The effect is shown in Figure 10.1a; electrons on the right-hand side of the Fermi surface (with initial velocities parallel to the direction of the drift velocity) move up into slightly higher energy (velocity) states. Other electrons can then fill the states vacated. The net effect is to displace the Fermi surface by a very small amount $\sim m^*v_d/\hbar$, where v_d is the drift velocity (typically $v_d \sim 10^{-3}\text{ms}^{-1}$, whereas $v_F \sim 0.01c$).

In order to visualise the equivalent modification of the Fermi surface in the case of thermal conductivity, it is useful to recall the Kinetic Theory derivation of κ . Thermal conductivity occurs in gases because the gas molecules travelling in one direction have a higher characteristic thermal energy (or effective temperature) than those travelling in the opposite direction. The equivalent situation for electrons is represented in Figure 10.1b; the electrons travelling leftwards are “cooler” and therefore have a less smeared out Fermi-Dirac distribution function, whereas those going rightwards (in the direction of heat flow) are “hotter”, possessing a more broadened Fermi-Dirac distribution function characteristic of a higher temperature.

We can now identify what τ_κ and τ_σ represent.

- τ_σ represents the characteristic time to randomise/get rid of an electron’s excess of forward velocity (or deficiency of backward velocity). A single scattering event of the type shown by an arrow in

¹In the case of the simple bandstructure defined at the beginning of this discussion, \mathbf{v} and \mathbf{k} will be parallel; however, it is worth remembering that this will not usually be the case for bands in general.

Figure 10.1a would be sufficient for this purpose; an electron heading rightwards (in the direction of the current flow) has been scattered into an empty state on the opposite side of the Fermi surface with almost opposite momentum and velocity.

- τ_κ represents the characteristic time to randomise/get rid of an electron's excess/deficiency of thermal energy. This can be achieved in a variety of ways shown in Figure 10.1b; *e.g.* an electron can lose $\sim k_B T$ of energy, and drop into an empty state close by in k -space (vertical process) or it can be shot from the “hot” side of the Fermi surface to the “cold” side by a scattering event involving large momentum change (horizontal process).

10.1.3 Matthiessen's rule

In the following discussion, we are going to assume that the electronic scattering rates are additive, *i.e.*

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \frac{1}{\tau_3} + \dots, \quad (10.6)$$

where the τ_j^{-1} are scattering rates due to different processes (*e.g.* collisions with or emission/absorption of phonons, scattering from impurities *etc.*). Equation 10.6 implies that the scattering process with the shortest τ_j will dominate, allowing us to predict regions of temperature in which we can ignore all forms of scattering but one; *e.g.* it is reasonable to assume that scattering of electrons at high temperatures will be almost entirely due to phonons, because there are a lot of phonons around.

Equation 10.6 is known as *Matthiessen's rule*; it must be admitted that it is only a crude guide as to what to expect in the presence of more than one scattering mechanism. It fails most spectacularly when

- the outcome of one scattering process influences the outcome of another;
- one or more τ_j is a function of \mathbf{k} .

In the latter case, the conductivities κ and σ will involve total τ s due to all processes averaged over all \mathbf{k} , whereas Equation 10.6 implies the summation of reciprocals of each τ_j individually averaged over all \mathbf{k} ; these two operations are very unlikely to lead to the same result.

Having stated this *caveat*, we shall first think about highish temperatures, where electron–phonon scattering events predominantly determine τ_κ and τ_σ .

10.1.4 Emission and absorption of phonons

When discussing the idea of bands, we have seen that electrons are only scattered when something disturbs the periodicity of the crystal. We are first going to consider the role of phonons, which may be pictured as propagating local distortions of the crystal. Such distortions may scatter an electron; two processes must be considered.

1. **Elastic processes** Both the phonon and electron change wavevector and energy, constrained by conservation of energy and momentum.
2. **Inelastic processes** The phonon may be emitted or absorbed by an electron, causing the electron's wavevector and energy to change.

Our derivations of bandstructure also made a hidden assumption, that the positions of the ions were not affected by the presence of mobile electrons. This is of course somewhat unrealistic; electrons and ions are highly charged, and the passage of an electron will result in the distortion of the lattice around it. The electron can be scattered by this; in wave-mechanical terms it has emitted a phonon, causing its energy and momentum to change. This is another inelastic process.

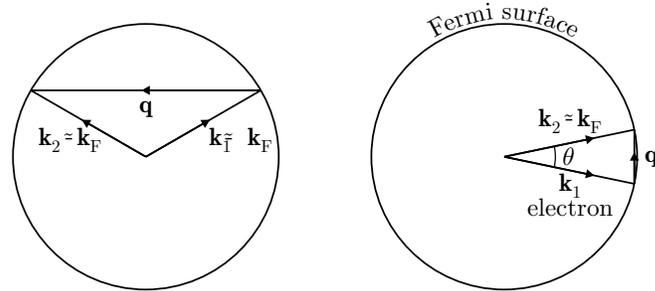


Figure 10.2: Geometry of electron-phonon scattering events at $T \sim \theta_D$ (left) and $T \ll \theta_D$ (right). In each case \mathbf{k}_1 and \mathbf{k}_2 are the initial and final electron wavevectors (both of magnitude $\approx k_F$) and \mathbf{q} is the phonon wavevector.

10.1.5 What is the characteristic energy of the phonons involved?

Phonons behave as massless bosons, that is to say they can be created and destroyed in a similar way to photons.² Phonons therefore have a “black-body” type of energy distribution, with a peak at an energy $\sim k_B T$, *i.e.* the characteristic phonon energy at a temperature T is $\hbar\omega \sim k_B T$. We therefore expect that when an electron scatters from or absorbs a phonon, that phonon will typically have an energy $\sim k_B T$.

But what about the emission of phonons? The form of the Fermi–Dirac distribution function for the electrons means that the only empty states below the Fermi energy have energies $E_F - (\sim k_B T)$. Similarly, the energy of the most energetic electrons will be roughly $E_F + (\sim k_B T)$. Therefore, an electron can only emit a phonon with energy $\sim k_B T$, *i.e.* even though the electron distorts the lattice at low temperatures, it cannot emit energetic phonons because there are no accessible final states for such a process!

The probability of emitting a phonon of energy $\sim k_B T$ will have a very similar temperature dependence to the probability of absorbing such a phonon. This is easy to see when one considers that the latter depends on the number of phonons around with such an energy (*i.e.* on the phonon density of states at an energy $\hbar\omega \sim k_B T$) whereas the former depends on the density of available final phonon states (*i.e.* the phonon density of states at an energy $\hbar\omega \sim k_B T$).

Therefore, in all that follows, I am just going to talk about elastic phonon scattering processes and inelastic phonon scattering processes where the latter means *either* emission *or* absorption of phonons; *i.e.* I shall assume that the probability of all processes involving phonons will follow a similar temperature dependence.

10.1.6 Electron–phonon scattering at room temperature

The Debye temperatures θ_D of most metals are less than or of the order of room temperature. Now θ_D is roughly the energy of the most energetic phonons in the metal, so that phonons with energy $\hbar\omega \sim k_B T$ will have wavevectors $q \approx$ (half the width of the Brillouin zone) $\sim k_F$, where k_F is the Fermi wavevector. Thus one phonon scattering event (inelastic or elastic) will scatter the electron to the opposite side of the Fermi surface (see Figure 10.2). Thus $\tau_\sigma^{-1} \approx \tau_\kappa^{-1} \propto$ (number of phonons with $\hbar\omega \sim k_B T$) $\propto T$.

10.1.7 Electron-phonon scattering at $T \ll \theta_D$

In this case, phonons with energy $\hbar\omega \sim k_B T$ will have energies $\ll k_B \theta_D$ and therefore $q \ll$ (Brillouin zone size), *i.e.* $q \ll k_F$. Thus, one *inelastic* phonon scattering event will be able to change the electron’s energy by $\sim k_B T$; hence $\tau_\kappa^{-1} \propto$ (number of phonons with $\hbar\omega \sim k_B T$) $\propto T^3$.³ However, one phonon scattering event (elastic or inelastic) will be unable to knock the electron to the other side of the Fermi

²See Statistical Mechanics books such as *e.g.* *Statistical Physics*, by Tony Guenault (Routledge, London 1988) page 124 .

³The T^3 power is well known from the Debye heat capacity derivation.

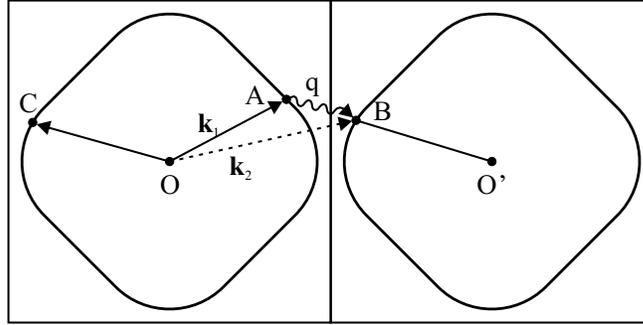


Figure 10.3: Geometry of electron-phonon umklapp scattering. A phonon with $|\mathbf{q}| < k_F$ is able to scatter an electron of wavevector \mathbf{k} with a positive velocity from the first Brillouin zone (A) to a state with a negative velocity (B) in the second Brillouin zone. The state at B is equivalent to that at C in the first Brillouin zone.

surface (see Figure 10.2) and so $\tau_\sigma \gg \tau_\kappa$. This is the reason for the failure of the Wiedemann–Franz ratio at low temperatures.

In order to take account of the fact that many, many scattering events are required before the excess forward velocity of the electron is thoroughly randomised, the scattering rate contains a weighting factor $(1 - \cos \theta)$, where θ is the scattering angle (see Figure 10.2). Now as θ is small,

$$1 - \cos \theta \approx 1 - \left(1 - \frac{\theta^2}{2}\right) = \frac{\theta^2}{2} \approx \frac{q^2}{2k_F^2} \approx \frac{\omega^2}{2k_F^2 v_\phi^2} \propto T^2, \quad (10.7)$$

where we have used the fact that the dispersion relationship for low energy phonons is close to $\omega = v_\phi q$, with v_ϕ the speed of sound. Therefore we have $\tau_\sigma \propto T^{-5}$ and $\tau_\kappa \propto T^{-3}$.

10.1.8 Departures from the low temperature $\sigma \propto T^{-5}$ dependence.

The $\sigma \propto T^{-5}$ temperature dependence is rarely if ever obeyed exactly. There are two main causes involving electron-phonon processes which contribute to this.

- **The periodicity of k -space** often allows phonons with small q to scatter electrons at the Fermi surface into empty states with energy $\sim E_F$ in an adjacent Brillouin zone; these states may have a velocity which is almost opposite to that of the initial state. This is shown schematically in Figure 10.3; the process is known as *electron umklapp scattering*.
- **Complicated Fermi surfaces** may have lobes, lozenges, ellipsoids *etc.* (plus their replicas, due to k -space periodicity, from other zones) all over the Brillouin zone. This means that phonons with short q can cause scattering of electrons between Fermi surface sections with very different characteristic velocities.

Both of these effects give a scattering rate which is roughly exponential, $\tau^{-1} \propto e^{-\theta_F/T}$, where θ_F is a characteristic temperature depending on the Fermi-surface geometry.

10.1.9 Very low temperatures and/or very dirty metals

In the case of very low temperatures, the phonon scattering becomes negligible and scattering of electrons by impurities and defects becomes dominant. Impurities have a different ionic core from the host metal, and therefore will often appear to be charged with respect to the background. The scattering of electrons by impurities is therefore like Rutherford scattering, with electrons being deflected through large angles. One “event” therefore degrades the transport of heat and electricity equivalently, so that $\tau_\kappa = \tau_\sigma = \text{constant}$ and the Wiedemann–Franz ratio again holds.

Temperature (scatterer)	Scattering times	κ σ	W-F ratio
Very low (impurities)	$\tau_\kappa \approx \tau_\sigma$ $\sim \text{const}$	$\kappa \propto T$, $\sigma \sim \text{const}$	L_0
$T \sim \theta_D/10$ (phonons)	$\tau_\kappa \propto T^{-3}$, $\tau_\sigma \propto T^{-5} \rightarrow e^{-\theta_F/T}$	$\kappa \propto T^{-2}$, $\sigma \propto T^{-5} \rightarrow e^{-\theta_F/T}$	$< L_0$
$T > \sim \theta_D$ (phonons)	$\tau_\kappa \approx \tau_\sigma$ $\propto T^{-1}$	$\kappa = \text{const}$, $\sigma \propto T^{-1}$	L_0

Table 10.1: Summary of the temperature dependences of scattering times and electrical and thermal conductivities.

10.1.10 Summary

A summary of the temperature dependences of scattering times and electrical and thermal conductivities is given in Table 1. Typical electrical resistivity and thermal conductivity data are shown in Figures 10.4 and 10.5. Note that for reasonably pure metals with reasonably simple bandstructures (*e.g.* alkali and noble metals), electrical resistivity data are all of a similar form, and when normalised to the value at $T = \theta_R$ lie roughly on the same curve when plotted against T/θ_R (see Figure 10.4); here θ_R is a characteristic temperature similar (but not identical) to θ_D .

10.1.11 Electron–electron scattering

In metals with simple Fermi surfaces, electron–electron scattering is relatively unimportant. Initial and final states for both electrons must have energies close to E_F and wavevectors close in magnitude to k_F ; in addition, energy and momentum must be conserved. The combination of these two requirements makes electron–electron scattering quite unlikely (and actually completely forbidden at $T = 0$).

However, electron–electron scattering becomes more important when

- the Fermi surface is complicated, so that there the conservation of energy and momentum becomes easy for a wider variety of possible scattering processes and/or
- the density of states at the Fermi energy is very large (because the effective mass is large), bumping up the number of initial and final states (*e.g.* transition metals, heavy fermion compounds).

Reasonably simple arguments⁴ show that electron–electron scattering leads to $\tau^{-1} \propto T^2$.

Some typical data for transition metals are shown in Figure 10.6. At low temperatures, the resistivities tend towards the T^2 dependence expected for electron–electron scattering.

10.2 Electrical conductivity of semiconductors

10.2.1 Temperature dependence of the carrier densities

Over wide ranges of temperature, the dominant contribution to the temperature dependence of the electrical conductivity is the rapidly varying number of free carriers. Recalling the results of Section 6.3.4, in order to find n and p when impurities are present we use the law of Mass Action (Equation 6.12)

$$np = T^3 W e^{-\frac{E_g}{k_B T}}$$

combined with the conservation law (Equation 6.17)

$$n - p = N_D - N_A,$$

where N_D is the density of donors and N_A is the density of acceptors (both are assumed to only provide one carrier each).

⁴See *e.g.* *Solid State Physics*, by N.W. Ashcroft and N.D. Mermin (Holt, Rinehart and Winston, New York 1976) page 347.

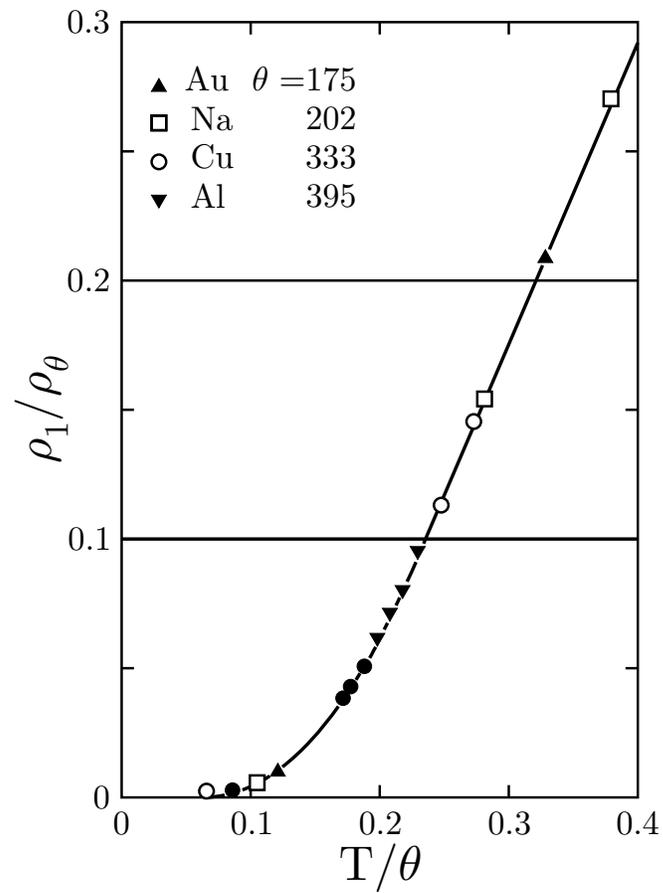


Figure 10.4: Normalised electrical resistivity data for several metals with reasonably simple Fermi surfaces plotted as a function of the normalised temperature T/θ_R . θ_R is shown in Kelvin for each metal at the top of the Figure.

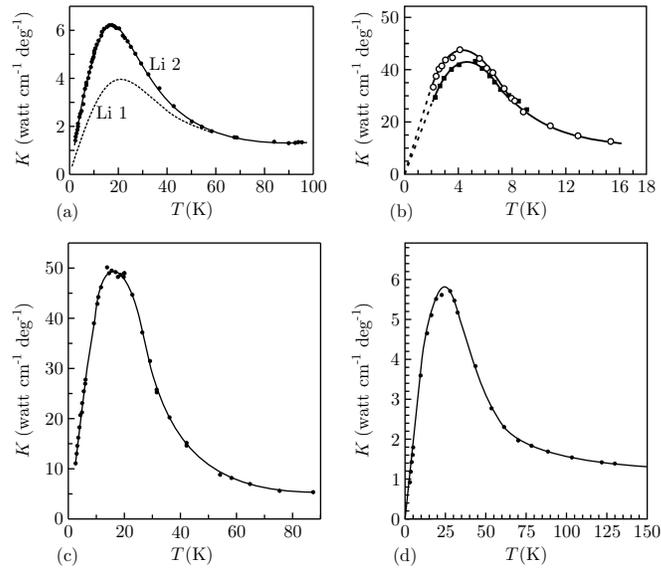


Figure 10.5: Thermal conductivity data for (a) Li (sample Li 1 is of lower purity than sample Li 2); (b) Na (again showing the effects of dirtier (lower curve) and cleaner (upper curve) samples); (C) Cu; (d) Cr.

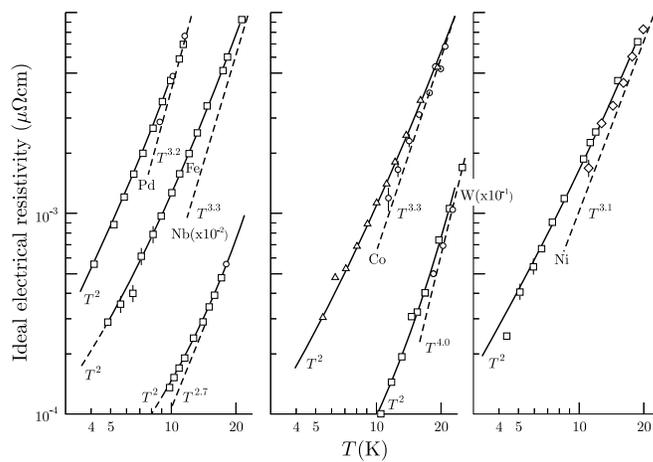


Figure 10.6: Resistivities of transition metals, showing the approach to T^2 at low temperatures.

The electrical conductivity of a semiconductor consists of a sum of contributions from all carrier types. The simple model of Section 6.3.4, which is a reasonable approximation for many semiconductors, has just two types, electrons and heavy holes. Therefore, the conductivity will contain just two contributions, *i.e.*

$$\sigma = ne\mu_c + pe\mu_{hh}, \quad (10.8)$$

where μ_c and μ_{hh} are the electron and hole mobilities respectively. The mobilities are defined as the drift velocity of the carrier per unit electric field; the Relaxation-Time Approximation (see the derivation of Equation 1.6) can be used to give

$$\mu_c = \frac{e\tau_c}{m_c^*} \quad (10.9)$$

and

$$\mu_{hh} = \frac{e\tau_{hh}}{m_{hh}^*}, \quad (10.10)$$

where τ_c^{-1} and τ_{hh}^{-1} are the scattering rates for the electrons in the conduction band and the heavy holes in the valence band respectively.

The temperature dependence of the electrical conductivity is therefore determined by convolutions of the temperature dependences of n and τ_c and p and τ_{hh} .

When $n \geq p$ (n-type or intrinsic semiconductors) the holes can be completely ignored in most cases; this is because in the majority of semiconductors, the electrons have a much smaller effective mass than the holes, resulting in a smaller density of states and hence a longer τ . Therefore the electron mobility is often much, much greater than that of the holes.

10.2.2 The temperature dependence of the mobility

There are two important sources of scattering.

1. **Impurities** ($T \ll \theta_D$). Charged impurity scattering is rather like Rutherford scattering; hence the scattering cross-section varies as E^{-2} . In the nondegenerate case, $E \sim k_B T$, so that the cross-section is proportional to T^{-2} ; hence the mean-free path is proportional to T^2 . The carrier speed is proportional to $E^{\frac{1}{2}}$, *i.e.* $T^{\frac{1}{2}}$. Therefore

$$\tau \propto \frac{T^{-\frac{1}{2}}}{T^{-2}} = T^{\frac{3}{2}}. \quad (10.11)$$

Note that this contrasts greatly with the situation in metals ($\tau \sim \text{constant}$ for impurity scattering), where all of the action goes on at or close to the Fermi surface; the carriers which scatter from the impurities in metals (see Section 10.1.9) have virtually constant (*i.e.* temperature-independent) energies. In non-degenerate semiconductors, the free carriers have a quasi-Boltzmann-like energy distribution, so that the average energy of the carriers varies with temperature.

2. **Phonons** ($T \sim \theta_D$). The number of phonons at such temperatures will be proportional to T (see Section 10.1.6), leading to a mean-free-path proportional to T^{-1} . As before, the speed is proportional to $T^{\frac{1}{2}}$. Therefore

$$\tau \propto \frac{T^{-1}}{T^{\frac{1}{2}}} = T^{-\frac{3}{2}}. \quad (10.12)$$

10.3 Reading

There are a large number of similar treatments of this topic *e.g.* (in increasing order of complexity) *Electricity and Magnetism*, by B.I. Bleaney and B. Bleaney, revised third/fourth editions (Oxford University Press, Oxford) Chapters 11, 17; *Solid State Physics*, by G. Burns (Academic Press, Boston, 1995) Sections 9.1-9.14; *Introduction to Solid State Physics*, by Charles Kittel, seventh edition (Wiley, New York 1996) Chapters 6 and 7; *Solid State Physics*, by N.W Ashcroft and N.D. Mermin (Holt, Rinehart and Winston, New York 1976) Chapters 1-3, 29. See also sections 4.23-4.27 of *Low temperature solid state physics*, by H.M. Rosenberg (OUP 1963).

