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ELECTRICAL AND THERMAL TRANSPORT IN MATERIALS

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CONTENTS

I. INTRODUCTION

1. Some simple formulae – are they useful?

Almost any textbook in solid state physics contains the formula

$$\sigma = ne^2\tau/m \tag{1.1}$$

which expresses the electrical conductivity σ in the number n of conduction electrons per volume, the electron charge e, the scattering time τ and the electron mass m. The electrical resistivity ρ is

$$\rho = 1/\sigma. \tag{1.2}$$

Matthiessen's rule is another formula encountered in most textbooks. It says that the total electrical resistivity ρ_{tot} of, e.g., a dilute alloy is the sum of two parts referring to the resistivity ρ_{ph} of the pure metal ("ep" stands for ρ limited by the electron–phonon interaction) and the resistivity ρ_{def} caused by the impurities ("defects");

$$\rho_{tot} = \rho_{ep} + \rho_{imp} \tag{1.3}$$

The Wiedemann–Franz law,

$$\kappa_e = \sigma L_o T \tag{1.4}$$

relatesthe thgermal conductivity κ_e due to the electrons and the corresponding electrical conductivity σ, through the Lorenz number L_o and the temperature T. In an ideal model,

$$L_o = (\pi^2/3)(k_B/e)^2 \tag{1.5}$$

where k_B is Boltzmann's constant and e is the electron charge.

The total thermal conductivity κ_{tot} of a metal has a contribution κ_{el} from the conduction electrons (cf. Eq. 1.4) and a contribution κ_{ph} from phonon transport. In an insulator, only κ_{ph} remains. A standard expression for that term is

$$\kappa_{ph} = (1/3)C_V C\ell \tag{1.6}$$

where C_V is the phonon heat capacity per volume, C is an average sound velocity and ℓ is an average phonon mean free path.

Much of this lecture series will be devoted to the validity of the relations (1.1) – (1.6). In particular, we shall see that often these expressions are too approximate in theoretical calculations for real materials (which are far from the idealised cases mentioned in textbooks) or – even worse – the relations are simply not valid because they do not rest on a physically acceptable model. For instance, the concept of a mean–free path ℓ can not be maintained if the scattering is so strong that ℓ of a certain phonon would be shorter than the wavelength associated with the phonon.

The material in these lecture notes is, to a large extent, covered in depth in a book by Grimvall (1986). That work and some other general and specialised references are listed at the end of these notes.

II. ELECTRICAL CONDUCTIVITY

1. The formula $\sigma = ne^2\tau/m$

The relaxation time τ in (1.1) is very difficult to calculate. We therefore first assume that somehow τ is known. It must vary with the electron state (here denoted by its wave vector $\mathbf{k}$) and as a first approximation we may think of τ in (1.1) as an average over the Fermi surface, i.e. $\tau = <\tau(\mathbf{k})>$. If we also know the energies $\epsilon(\mathbf{k})$ and the velocities $v_\mathbf{k}$ of the electron states, a linear–response solution of the Boltzmann transport equation leads to the following expression for the conductivity σ:

$$\sigma = -(2e^2/3V) \sum_\mathbf{k} v_\mathbf{k}^2\, \tau(\mathbf{k})\, (\partial f_\mathbf{k}^0/\partial \epsilon_\mathbf{k}) \qquad (2.1)$$

V is the total crystal volume and f^0 is the Fermi–Dirac statistical factor. The sum is over all conduction electron states $\mathbf{k}$ (the number of states is proportional to V so σ is independent of V), but the derivative $(\partial f_\mathbf{k}^0/\partial \epsilon_\mathbf{k})$ is strongly peaked at the Fermi level. As a check on (2.1), let us replace $-(\partial f_\mathbf{k}^0/\partial \epsilon_\mathbf{k})$ by a delta–function $\delta(\epsilon_\mathbf{k}-\epsilon_F)$ at the Fermi level ϵ_F, assume a free–electron model and take a constant τ. The sum over $\mathbf{k}$ is transformed into an integral by the usual prescription

$$\sum_\mathbf{k} \to V(2\pi)^{-3} \int d^3\mathbf{k} = V(2\pi)^{-3} \int 4\pi k^2\, (dk/d\epsilon)\, d\epsilon \qquad (2.2)$$

Then, after some algebra, we get Eq. (1.1). As a modification towards real systems, we use an effective–mass approximation for $\epsilon(\mathbf{k})$ at the Fermi level, i.e. $d\epsilon/dk = \hbar^2 k_F/m_b$, and explicitly allow $\tau(\mathbf{k})$ to be anisotropic but retain the assumption of the free–electron model result $k_F = (3\pi^2 n)^{1/3}$. Then

$$\sigma = ne^2 <\tau(\mathbf{k})>/m_b \qquad (2.3)$$

If we allow both $v(\mathbf{k})$ and $\tau(\mathbf{k})$ to be anisotropic but still assume that $-(\partial f_\mathbf{k}^0/\partial \epsilon_\mathbf{k})$ can be replaced by a delta–function $\delta(\epsilon_\mathbf{k}-\epsilon_F)$, we get

$$\sigma = (2e^2/3V) \sum_\mathbf{k} v_\mathbf{k}^2\, \tau(\mathbf{k})\, \delta(\epsilon_\mathbf{k}-\epsilon_F) \qquad (2.4)$$

Next, suppose that $\tau(\mathbf{k})$ in (2.4) can be separated out as multiplicative factor. The remaining part of σ contains

$$\omega_{pl}^2 \equiv (8\pi e^2/3V) \sum_\mathbf{k} v_\mathbf{k}^2\, \delta(\epsilon_\mathbf{k}-\epsilon_F) \qquad (2.5)$$

The plasma frequency ω_{pl} is a quantity which can be obtained from ordinary band structure calculations. Then we may write

$$\sigma = (\omega_{pl}^2/4\pi) <\tau> \qquad (2.6)$$

Note that with the familiar free–electron expression $\omega_{pl}^2 = 4\pi ne^2/m$, we recover Eq. (1.1) from (2.6).

2. A variational result for the resistivity

We shall not dwell on details but merely state that there is a variational formulation of the transport problem (Ziman, 1960) which allows us to write an expression for the electrical resistivity ρ which corresponds to Eq. (2.3) for σ,

$$\rho \le (m_b/ne^2) <1/\tau(\mathbf{k})> \qquad (2.7)$$

This should be compared with an "exact" solution $\rho = 1/\sigma = (m_b/ne^2)/<\tau(k)>$. Cf. Schwartz's inequality in mathematics which implies that $<1/\tau> \geq 1/<\tau>$. The reason for considering $<1/\tau>$ instead of $<\tau>$ is that the former quantity expresses a scattering rate which is directly obtainable from the "Golden Rule" of quantum mechanics. We now make the following assumptions. The inequality in (2.7) is replaced by an equality and m_b is generalised to the plasma frequency ω_{pl} as in (2.6). A calculation of $<1/\tau>$ contains matrix elements for the scattering of an electron from a state **k** to a state **k'**. If the scattering is due to phonons, its temperature dependence is governed by Bose–Einstein factors which are functions of phonon frequencies ω. Then it is convenient to replace scattering probabilities in **k**–space with a coupling function $\alpha^2_{tr}F(\omega)$ which is a function only of the phonon energy $h\omega$ which is absorbed or emitted, irrespective of the wave vectors **k** and **k'** involved in the scattering event. $\alpha^2_{tr}F(\omega)$ is called the Éliashberg transport coupling function. In a simple description it may be thought of as an electron–phonon coupling $\alpha^2_{tr}(\omega)$ (matrix element squared), multiplied by a phonon density of states $F(\omega)$ which measures the number of scattering modes involving the phonon frequency ω. If $<1/\tau>$ is calculated from $\alpha^2_{tr}F$, (2.7) yields

$$\rho = (4\pi/\omega_{pl})^2 \int_0^{\omega_{max}} \beta\omega\, \alpha^2_{tr}F(\omega)\,[e^{\beta\omega}-1]^{-1}\,[1-e^{-\beta\omega}]^{-1}\,d\omega \qquad (2.8)$$

where $\beta\omega = \hbar\omega/k_BT$. Although based on several approximations, this expression may be considered a natural starting point for numerical work or further approximations.

3. The Bloch–Grüneisen formula

We assume that the phonons are described by a Debye model, i.e. $\omega = Cq$ where C is the sound velocity. Then $\omega_{max} = Cq_D$ and $F(\omega) \sim \omega^2 \sim q^2$. We also take a model in which there is no coupling to Umklapp processes and let $\alpha^2 \sim q^2 \sim \omega^2$, so that the resulting

$\alpha^2F(\omega) \sim \omega^4 \sim q^4$. The expresssion (2.8) takes the form

$$\rho_{BG}(T) = (c_1/T)\int_0^{q_D} q^5\,[e^y-1]^{-1}\,[1-e^{-y}]^{-1}\,dq \qquad (2.9)$$

where $y = \hbar Cq/k_BT$ and c_1 is a constant. This is the well–known Bloch–Grüneisen resistivity formula. We note that it does not give the absolute magnitude of ρ since c_1 is not calculated, but it often gives a very good account of the temperature dependence of ρ from, say, $T = 0.2\theta_D$ to $1.5\theta_D$ (θ_D = Debye temperature $\approx \hbar Cq_D/k_B$).

4. The resistivity in an Einstein model

Let us assume an Einstein phonon model, i.e. $\alpha^2_{tr}F(\omega) = c_E\delta(\omega-\omega_E)$, where c_E is a constant (depends on the strength of the scattering matrix elements) and ω_E is the Einstein frequency. Then, from (2.8),

$$\rho_E(T)/T = c'_E\, C_E(h\omega/k_BT) \qquad (2.10)$$

C_E is the Einstein heat capacity of phonons and c'_E is closely related to c_E. Thus the temperature dependence of the phonon–limited $\rho(T)/T$ and of the heat capacity are identical in an Einstein phonon model. (This has no deep physical origin but is an accidental result of how Bose–Einstein and Fermi–Dirac factors enter (2.8)). It is well known that the temperature dependence of the lattice heat capacity is not very sensitive to details in the phonon spectrum $F(\omega)$. Then it is not surprising that also the temperature dependence of the electrical resistivity is insensitive to details in $\alpha^2_{tr}F(\omega)$. We may now understand the empirical correlation, Fig. 1, between the temperature dependence of the lattice heat capacity and the electrical resistivity that was noted by Grüneisen (Berichte Deutsche physikal. Ges. 15, 1913, p. 186), long before quantum mechanics would explain the behaviour of $\rho(T)$. We also understand why the Bloch–Grüneisen formula ρ_{BG} is so good. Its original derivation rests on a number of quite crude approximations, but only the shape of $\alpha_{tr}^2 F(\omega)$ matters, and that may be modelled by a Debye spectrum. In fact, there is in general no reason to prefer the Bloch–Grüneisen formula ρ_{BG} to, e.g., the Einstein model result ρ_E. In particular this is so because the T^5 behaviour at low T implied by ρ_{BG} is usually wrong, for various reasons.

5. The high–temperature limit

Consider the high–temperature limit of Eq. (2.8), i.e. $\beta\omega_{max} << 1$ (in practice $\beta\omega_{max} \lesssim 1$ will do). Then,

$$\rho = (8\pi^2 k_B T/\hbar\omega_{pl}^2)\ \lambda_{tr} \tag{2.11}$$

where λ_{tr} is a dimensionless parameter which measures the strength of the electron–phonon coupling,

$$\lambda_{tr} = 2\int_0^{\omega_{max}} \alpha_{tr}^2 F(\omega)\ (d\omega/\omega) \tag{2.12}$$

The parameter λ_{tr} is closely related to the electron–phonon coupling strength λ that appears, e.g., in the BCS theory of superconductivity and as an enhancement factor $1 + \lambda$ in the low–temperature electronic heat capacity. (The essential difference between λ_{tr} and λ is the average of a factor $1 - \cos\theta_{kk'}$ where $\theta_{kk'}$ is the scattering angle of the conduction electron.) For most metallic systems (simple metals and transition metals, as well as alloys and compounds) λ_{tr} and λ lie between 0.15 and 1.5, cf. Table I.

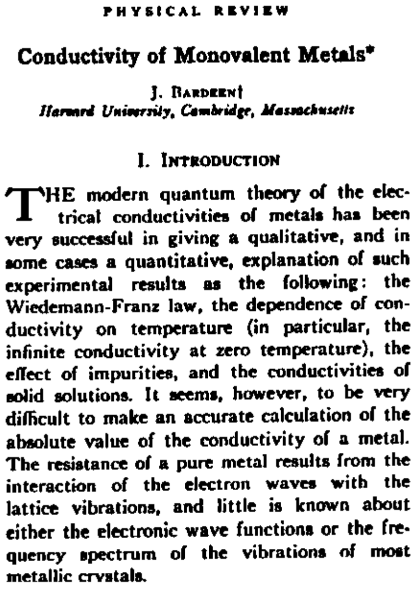
Table I: P.B. Allen (Phys. Rev. B36, 1987, p. 2920) used Eq. (2.11), ρ from experiments and ω_{pl} from electron band–structure calculations to get semiempirical values for λ_{tr}.

element	Li	Al	Pb	V	Nb	Mo	W	Ir	Pd
λ_{tr}	0.35	0.39	1.48	1.09	1.06	0.32	0.26	0.50	0.47

6. Calculations for real metals

The Bloch–Grüneisen formula or related expressions can give a good account of the temperature dependence of ρ, but it remains to find its absolute value. The first attempts at a calculation of ρ for real metals are those of Mott and Jones (1936) and Bardeen (1937). For sodium, they obtained at room temperature $\rho = 3.1\ \mu\Omega$cm (Mott and Jones) and 2.6 – 4.7 $\mu\Omega$cm (Bardeen), while the experimental value is $\rho_{exp} = 4.78\ \mu\Omega$cm. The most ambitious calculation for sodium to date is probably that of Shukla and Taylor (J. Phys. F 6, 1976, p. 531) who used a pseudopotential approach and obtained $\rho = 4.63\ \mu\Omega$cm. One of the very few realistic calculations for transition metals is that of Allen et al. (1986), Fig. 2

From J. Bardeen,
Phys. Rev. 52 (1937), 688.



PHYSICAL REVIEW

Conductivity of Monovalent Metals*

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I. Introduction

THE modern quantum theory of the electrical conductivities of metals has been very successful in giving a qualitative, and in some cases a quantitative, explanation of such experimental results as the following: the Wiedemann-Franz law, the dependence of conductivity on temperature (in particular, the infinite conductivity at zero temperature), the effect of impurities, and the conductivities of solid solutions. It seems, however, to be very difficult to make an accurate calculation of the absolute value of the conductivity of a metal. The resistance of a pure metal results from the interaction of the electron waves with the lattice vibrations, and little is known about either the electronic wave functions or the frequency spectrum of the vibrations of most metallic crystals.

Figure 1: In an Einstein phonon model, the quantity ρ/T has the same temperature dependence as the heat capacity C_p and the lattice part of the thermal expansion coefficient β. This behaviour is approximately obeyed also in many metallic elements. The figure shows data for aluminum. (From Grimvall, 1986).

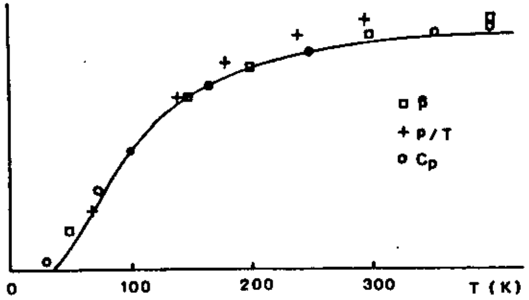
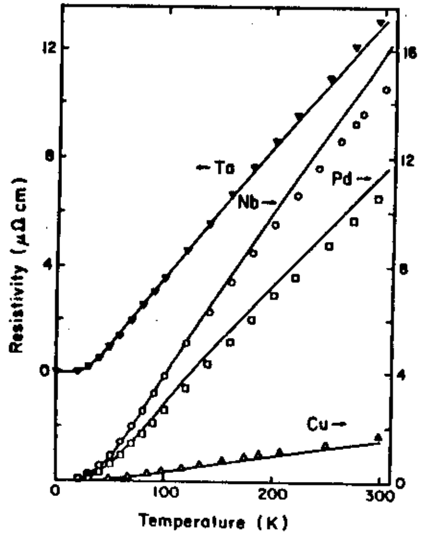


Figure 2: In non–transition metals (such as Na and Al) pseudopotential methods allow ρ to be calculated with an accuracy of 3 – 10 % at room temperature. A calculation of ρ in transition metals is difficult. The figure shows results from one of the very few realistic calculations which are available. (Allen et al., Phys. Rev. B 34, 1986, p. 4331).



III. THERMAL CONDUCTIVITY

1. Introduction

Metals are good thermal conductors because heat is carried by the conduction electrons. Yet the best thermal conductor of any solid at room temperature is not a metal but an insulator – diamond. In diamond, as in other insulators, the heat is carried by the phonons. However, diamond is a special case and usually the phonon part κ_{ph} in metals and alloys is negligible compared to the electronic contribution κ_{el}. Heat carried by photons (in semi–transparent solids) or by spin waves may be of importance in some cases, which are not considered here. Electrical superconductivity has no counterpart in thermal transport. In particular, the conventional superconductors conduct heat better in their normal states.

2. Thermal transport by conduction electrons

The thermal conductivity κ_{el} can be written in a form which is the counterpart of the electronic conductivity σ in Eq. (2.3). It reads

$$\kappa_{el} = (nk_B^2T/m_b) < [(\epsilon-\epsilon_F)/k_BT]^2\ \tau(k,\epsilon_k) > \qquad (3.1)$$

Since the Fermi surface average < ...> involves an energy–dependent function $(\epsilon-\epsilon_F)^2$ we have explicitly written out the dependence of τ on the electron energy ϵ_k. If there is no strong dependence of τ on ϵ_k, we can perform the energy integral as

$$<...>_\epsilon = \int_{-\infty}^{\infty} [(\epsilon-\epsilon_F)/k_BT]^2\ [-\partial f^0(\epsilon)/\partial\epsilon]\ d\epsilon \qquad (3.2)$$

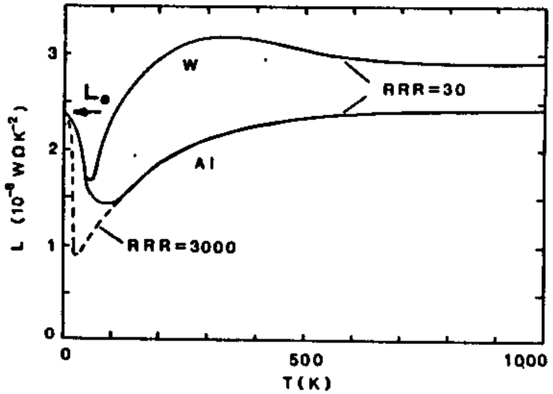
The integral is equal to $\pi^2/3$, and we recover κ_{el} as given by the Wiedemann–Franz law if we compare with Eqs. (3.1), (2.3) and (1.4). We can also consider the high–temperature limit and get

$$1/\kappa_{el} = (2\pi m_b k_B / L_0 n e^2 \hbar)\, \lambda_{tr} \tag{3.3}$$

3. Deviations from the Wiedemann–Franz law

In a real metal, $\tau(\mathbf{k},\epsilon)$ has a non–negligible energy dependence for $|\epsilon-\epsilon_F| < \hbar\omega_{max}$. Further, the electron density of states $N(\epsilon)$ may have a significant energy dependence near ϵ_F. Then <...> in (3.2) will vary with T and be different from $\pi^2/3$. As a consequence, the Wiedemann–Franz law is not fully obeyed. We can define an apparent Lorenz number $L \equiv (\kappa_{el}/\sigma T)$ where κ_{el} and σ are experimental values. Fig. 3 shows L as a function of T for Al, W and an Al alloy. When impurity scattering dominates, τ is independent of ϵ (cf. Sec. IV.1). This explains why the Wiedemann–Franz law is better obeyed for impure systems.

Figure 3.: The apparent Lorenz number $L \equiv (\kappa_{el}/\sigma T)$ from experimental values of κ_{el} and σ for almost pure Al and W and for an Al alloy. RRR is the residual resistance ratio. (From Grimvall, 1986).



4. Lattice thermal conductivity

The expression $\kappa_{ph} = (1/3)C_V C\ell$ given in Eq. (1.6) is the result for thermal conduction in a classical gas. It can be applied also to conduction in a solid since the lattice vibrations can be considered as a gas of phonons (massless bosons). Let (q,λ) denote the wave vector (in the first Brillouin zone) and the mode (longitudinal or transverse; acoustic or optical) of a phonon of frequency $\omega(q,\lambda)$. Its group velocity is $C_g(q,\lambda) = |\nabla_q \omega(q,\lambda)|$, the mean free path is $\ell(q,\lambda)$ and the heat capacity is $c(q,\lambda)$. Then the lattice thermal conductivity can be written, as a generalisation of the classical gas expression,

$$\kappa_{ph} = (1/3V) \sum_{q,\lambda} c(q,\lambda) C_g(q,\lambda) \ell(q,\lambda) \tag{3.4}$$

Under certain assumptions we may replace ℓ by $C_g \tau$ where τ is a relaxation time. In analogy to the case of the electrical conductivity, the theoretical difficulties lie in the scattering time τ or the mean free path ℓ of the phonons. But there is a major difference between the two cases. We noted that the temperature dependence of the electrical conductivity could be well accounted for by simple models such as a Debye or Einstein phonon spectrum, although the absolute magnitude of the conductivity was more difficult to calculate. In the case of the lattice conductivity, there is no such simplification. Both the temperature dependence and the absolute magnitude are quite uncertain (except at low temperatures – see below). An approximate description of κ_{ph} gives the following result.

High temperatures: Consider Eq. (3.4). The heat capacity per mode, $c(q,\lambda)$, has its classical value $k_B/2$. Neglect the temperature dependence of the group velocity C_g, i.e. anharmonic shifts in $\omega(q,\lambda)$. The phonon mean free path ℓ is limited by scattering against other phonons. The probability for three–phonon scattering (one phonon scatters into two phonons, or two phonons scatter into one phonon) depends on Bose–Einstein factors

$$n(q,\lambda) = [\exp(\beta\omega_{q\lambda}) - 1]^{-1}, \tag{3.5}$$

which govern the absorbtion and stimulated emission of bosons. The net result, at high temperatures, is that ℓ varies as $1/T$. (In a classical picture, ℓ would vary inversely with the number of other gas particles present, i.e. as $1/n \sim T$ in our case). The magnitude of ℓ depends on the phonon–phonon matrix element. That is an anharmonic effect, which is sometimes crudely modeled by the Grüneisen parameter γ_G which appears in the lattice thermal expansion. Under a number of other simplifying approximations, one may finally arrive at the Leibfried–Schlömann formula (cf. Klemens, in "Thermal conductivity", 1969) for the phonon–limited lattice conductivity,

$$\kappa_{ph-ph} = B(2\pi)^{-3}\,[Ma\omega_D^3 / \gamma_G^2 T] \tag{3.6}$$

Here B is a dimensionless constant of the order of 1 (Klemens suggests $B = 1.6$), M is the atomic mass, a is an interatomic distance given by $(4\pi/3)a^3 = \Omega_a$ where Ω_a is the atomic volume, and $\omega_D = k_B\theta_D/\hbar$ is the Debye frequency. It is obvious that this result can give little more than a rough estimate. Further, experiments usually show a more rapid decrease of κ_{ph-ph} than the $1/T$ dependence in (3.6). Am empirical relation of some value is

$$\kappa_{ph-ph} = \kappa^*(T_m/T)^{\eta} \tag{3.7}$$

where κ^* is a fitted constant, T_m is the melting temperature and η typically is 1.3. The main reason for $\eta \neq 1$ is that thermal expansion (i.e. an effect of anharmonicity) lowers ω_D.

Intermediate temperatures: As the temperature is lowered through the Debye temperature, certain scattering processes of fundamental importance for κ_{ph-ph} (Umklapp–processes) are "frozen out". Then ℓ increases roughly exponentially in θ_D/T and we may write

$$\kappa_{ph-ph} = \kappa_0 \exp(-\theta_D/T) \tag{3.8}$$

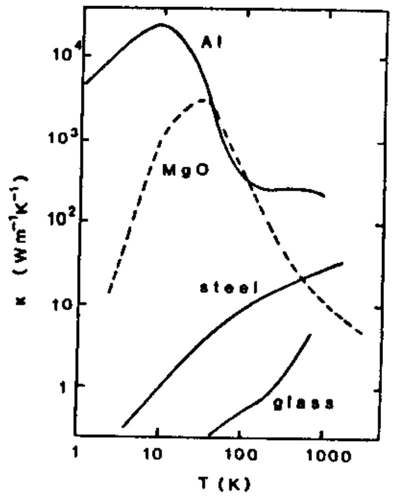
The prefactor κ_0 is difficult to calculate but can be fitted to experiments. The Debye temperature θ_D to be used in (3.8) may be quite different from the standard θ_D that is found from the low–T lattice heat capacity. Thus, Eq. (3.8) is only a crude description of the dominating temperature dependence in κ_{ph-ph}.

Low temperatures: As the temperature decreases further, phonon–phonon scattering becomes less important than the (unavoidable) defect scattering. The number of defects does not depend on the temperature. Therefore, at low enough T, $\ell(q,\lambda)$ is independent of T. The only temperature dependence of κ_{ph} comes from the heat capacities $c(q,\lambda)$, which vary as T^3 at low T. Hence,

$$\kappa_{ph} = AT^3 \tag{3.9}$$

where A is a constant which depends on the defects present.

Figure 4: The thermal conductivity κ for some metals and non–metals (from Grimvall, 1986).



5. Diamond and other materials with high thermal conductivity

It has already been said that diamond has the highest known thermal conductivity of any material, at room temperature. This can be qualitatively understood as follows. The frequency of an oscillator is $\omega = \sqrt{k/M}$, where k is a force constant and M is the vibrating mass. Now compare with diamond. Carbon has one of the smallest atomic masses and the interatomic forces in diamond are exceptionally large. Therefore a typical vibrational frequency, and hence θ_D, is very large. In fact, $\theta_D \approx 2000$ K for diamond, which is the highest Debye temperature known for any solid. At room temperature, Umklapp processes are almost completely frozen out. If the specimen is very pure, we are in the regime where $\kappa \sim \exp(-\theta_D/T)$ is very large, cf. Eq. (3.8).

In analogy to the case of diamond, we would expect elements or compounds with strong (i.e. covalent) interatomic forces and small atomic masses to have a high thermal conductivity at room temperarture, provided that they do not contain too many defects. This is indeed the case for, e.g., Si and several hard materials such as carbides and nitrides. This fact is of considerable practical importance. In semiconductors the generated heat is efficiently carried away, which prevents overheating and malfunction in devices. Edges in cutting tools are made of hard materials which should be good thermal conductorrs to avoid deterioration due to overheating.

6. Calculations of κ_{ph} in real materials

There are at least one hundred more or less accurate calculations of σ for real metals. Almost all of those refer to simple (i.e. non–transition) metals such as K and Al. Through the Wiedemann–Franz law, the results may apply also to the electronic thermal conductivity κ_{el}. More detailed work aiming at a direct calculation of κ_{el} (i.e. not assuming that $L = L_0$) has been published for, e.g., K (Leung et al., Phys. Rev. B 16, 1977, p. 4358) and Zn (Tomlinson, Phys. Rev. B 19, 1979, p. 1893). It may then be surprising to learn

that there are only a few calculations of the lattice thermal conductivity for real systems, which do not invoke a fitting of parameters such as B (Eq. 3.6), κ^* (Eq. 3.7) or κ_0 (Eq. 3.8). Not even for a solid like NaCl has much been done. The most ambitious calculation to date is that of Petterson (J. Phys. C 20, 1987, p. 1047) for the alkali halides. Typically, the uncertainty in calculations of κ_{ph-ph} is almost an order of magnitude larger than in the best calculations of σ for simple metals. A major reason is the difficuly to find accurately the matrix element for the anharmonic phonon–phonon interaction.

IV. SCATTERING BY DEFECTS

1. Electrical conductivity

We assume that the conduction electrons are scattered by defects as well as by phonons. A useful expression for the total scattering rate is the scattering time approximation

$$1/\tau_{tot}(\mathbf{k},\epsilon_{\mathbf{k}}) = 1/\tau_{ep}(\mathbf{k},\epsilon_{\mathbf{k}}) + 1/\tau_{def}(\mathbf{k}) \tag{4.1}$$

The defect scattering is elastic (i.e. the electron does not lose or gain energy) and hence $\tau_{def}(\mathbf{k})$ is independent of $\epsilon_{\mathbf{k}}$. The relation (4.1) used in $\rho = (m_b/ne^2)<1/\tau_{tot}>$, cf. Eq. (2.7), would immediately give Matthiessen's rule, Eq. (1.3). If we now still rely on (4.1) but use the more correct expression $1/\rho = \sigma = (ne^2/m_b)<\sigma>$ we get ρ $1/<\tau_{ep}\tau_{def}/(\tau_{ep} + \tau_{def})>$. Then there will be deviations from Matthiessen's rule (DMR) unless $\tau_{ep}(\mathbf{k},\epsilon_{\mathbf{k}})/\tau_{def}(\mathbf{k})$ is independent of k and $\epsilon_{\mathbf{k}}$. A significant DMR may occur well below room temperature (below θ_D). At high temperatures, we can neglect the $\epsilon_{\mathbf{k}}$ dependence of $\tau(\mathbf{k},\epsilon_{\mathbf{k}})$ and then the DMR is smaller although not always negligible.

For small defect concentrations c, ρ_{def} is proportional to c,

$$\rho = \pi(16\pi/3)^{1/3}\, r_s^2\, (a_0/\ell)\, (a_0\hbar/e^2) \qquad (5.1)$$

The prefactor $\pi(16\pi/3)^{1/3}\, r_s^2$ typically is 40. If ℓ is larger than the nearest neighbour distance, we have $\ell/a_0 \gtrsim 6$. This gives an upper limit $\rho \lesssim 150$ μΩcm from (5.1), in good qualitative agreement with Mooij's rule. [We may note that the fundamental unit of resistivity $a_0\hbar/e^2$ can also be written $\hbar^3/(me^4)$.]

Figure 5: The electrical resistivity of metals seems to "saturate" at about 100 – 150 μΩcm. (From Grimvall, 1986).

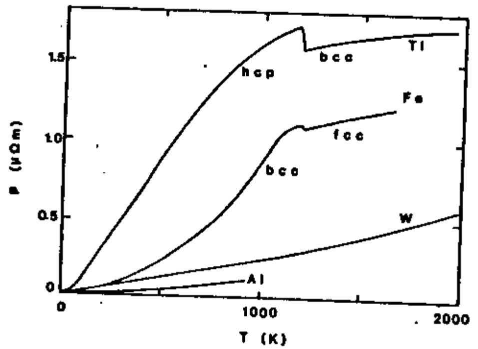
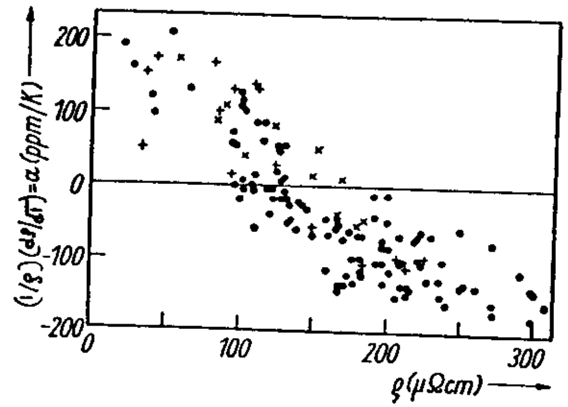


Figure 6: In highly resistive metals and alloys, $d\rho/dT$ may be small or negative. Data for bulk alloys (+), thin films (o) and amorphous alloys (×). (From Mooij, 1973).



There is no generally accepted theory for electron transport in the regime where Mooij's rule applies, although there have been many attempts (cf. Gantmakher et al., Pramana – J. Phys. 28, 1987, p. 509). The **"shunt resistor model"** of Wiesmann et al. (Phys. Rev. Lett. 38, 1977, p. 782) often gives a useful phenomenological description. Let $\rho_{ideal}(T)$ be the resistivity if no saturation would take place and ρ_{sat} be a parameter characteristic of the system and of the order of 150 μΩcm. The total measured resistivity is approximately given by

$$1/\rho_{tot}(T) = 1/\rho_{ideal}(T) + 1/\rho_{sat} \qquad (5.2)$$

2. Thermal conductivity

In analogy to the case of electrical conduction we expect a breakdown of the simple lattice thermal conductivity formula based on the Boltzmann equation when the phonon mean free path $\ell(q,\lambda)$ is a short as the corresponding phonon wavelength $2\pi/q$. Consider Eq. (3.4) and assume that the heat capcity has its clasical value, $k_B/2$ per phonon mode (q,λ). Replace $C_g(q,\lambda)$ by a Debye model sound velocity C_D and take a simple cubic lattice with lattice parameter a so that $(1/3V)\Sigma_{q,\lambda} = 1/a^3$. Let ℓ be at least equal to the nearest–neighbour distance a. Then κ_{ph} must be larger than $k_B C_D a/a^3 = k_B C_D/a^2$. We rewrite this as an expression for a saturation value $(\kappa_{ph})_{sat}$,

$$(\kappa_{ph})_{sat} \approx k_B(C_D q_D)/a^2 q_D \approx k_B\omega_D/4a = k_B^2\theta_D/4a\hbar \qquad (5.3)$$

where we have used that $q_D = (6\pi^2)^{1/3}/a$. Taking the typical values $\theta_D = 300$ K and $a = 3\times10^{-10}$ m we get $(\kappa_{ph})_{sat} \sim 0.5$ W/m·K. This is an underestimation of $(\kappa_{ph})_{sat}$ since we have gone to the extreme limit of $\ell = a$ for all phonon modes, but it suffices to explain why the thermal conductivity of many strongly disordered materials of quite different kinds

$$\rho_{def} = c\rho^*_{def} \tag{4.2}$$

where ρ^*_{def} is a resistivity characteristic of the defect and the host material. For high defect concentrations, such as in concentrated alloys, it is very difficult to account theoretically for the total defect resistivity. Sometimes, Nordheim's rule

$$\rho_{def} = c(1-c)\rho^*_{def} \tag{4.3}$$

gives an acceptable description. See, however, Section V on saturation phenomena.

2. Thermal conductivity

We assume, as in the case of the electrical conductivity, that the scattering time approximation with

$$1/\tau_{tot}(q,\lambda) = 1/\tau_{ph-ph}(q,\lambda) + 1/\tau_{ph-def}(q,\lambda) \tag{4.4}$$

is valid for the combined scattering of phonons (q,λ) by anharmonic phonon–phonon interactions and by phonon–defect interactions. We now write $\ell = C_g\tau_{tot}$ in Eq. (3.4). In analogy to the case of conduction electrons (cf. Section IV.1) there would be a "Matthiessen's rule" for the lattice thermal conductivity only if τ_{ph-ph} and τ_{def} have the same dependence on (q,λ). Only then could we use $\ell = C_g\tau_{tot}$ in Eq. (3.4) to get for the thermal resistivities $W \equiv 1/\kappa$

$$W_{tot} = 1/\kappa_{tot} = 1/\kappa_{ph-ph} + 1/\kappa_{ph-def} = W_{ph-ph} + W_{ph-def} \tag{4.5}$$

However, the necessary condition on $\tau_{ph-ph}(q,\lambda)/\tau_{ph-def}(q,\lambda)$ is usually not fulfilled. For the electronic part of thermal conductivity, on the other hand, Matthiessen's rule is often a

good approximation (at not too low T),

$$(W_{el})_{tot} = (W_{el})_{ep} + (W_{el})_{def} \tag{4.6}$$

V. SATURATION EFFECTS

1. Electrical conductivity

According to the simple theory, Eq. (2.11), ρ increases linearly with T. As a rule, one observes a more rapid increase for simple metals. The main reason is that the electron–phonon coupling contains $1/\omega^2(q,\lambda)$ where $\omega(q,\lambda)$ are phonon frequencies which decrease with increasing T, mainly as an indirect effect of thermal expansion. Contrary to this T–dependence, many transition metals show a $\rho(T)$ which increases less rapidly than linearly in T, and sometimes has a pronounced tendency for "saturation" as in Fig. 5. In many transition metal alloys with ρ larger than about 100 μΩcm, $d\rho/dT$ is experimentally found to be negative, cf. Fig. 6. This is known as Mooij's rule (Mooij, phys. stat. sol. (a) 17, 1973, p. 521) but like many other rules it is not without exceptions. The effect can be given a qualitative explanation. The key idea is that the usual formulae for the resistivity should break down when the electron scattering is so strong that the electron mean free path ℓ is of the order of the distance between neighbouring atoms. As an illustration, consider Eq. (2.6), let $\ell = v_F\tau$ and take the free–electron result for ω_{pl}. (Although the systems now of interest do not have the Fermi surface of a free electron gas.) We may express ρ in the dimensionless parameter r_s which measures the electron concentration $[(4\pi/3)r_s^3 = 1/n]$, the ratio ℓ/a_0 where a_0 is the Bohr radius (0.5 A) and $a_0\hbar/e^2 = 0.22$ μΩm which is a fundamental unit of resistivity. Then, (alloys, ceramics, ionic solids, polymers) seems to saturate at a rather universal value. Slack reviewed the field some time ago (Solid State Physics vol. 34, 1979, p. 1) and not much has been clarified since then.

Finally, we add that very little is known about the electronic contribution to the thermal conductivity when there is "saturation". However, it seems that the Wiedemann–Franz law is still valid (Grimvall, Physica 127 B, 1984, p. 165).

VI. ANISOTROPIC CONDUCTIVITY

1. Single–crystal anisotropy

The conductivities σ and κ are tensors of rank two. If such a tensor has cubic symmetry, it reduces to a diagonal form with all elements equal to σ or κ. This was assumed in the previous sections. We now consider the important case of hexagonal symmetry. (The same relations hold for trigonal and tetragonal symmetry.) Let θ be the angle between the current j and the crystallographic c–axis. The resistivity $\rho(\theta) \equiv E(\theta)/|j|$ can be written

$$\rho(\theta) = \rho_{\parallel} \cos^2\theta + \rho_{\perp} \sin^2\theta \qquad (6.1)$$

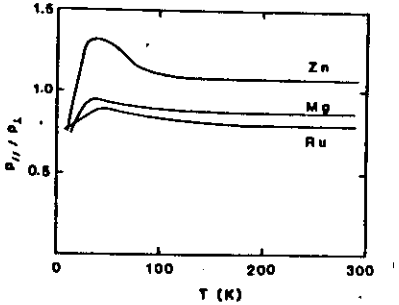
This describes the current flow in, e.g., a wire. Next we let the field E have a specified angle θ to the c–axis (e.g., E is applied across a slab). The conductivity $\sigma(\theta) \equiv j(\theta)/|E|$ is

$$\sigma(\theta) = \sigma_{\parallel} \cos^2\theta + \sigma_{\perp} \sin^2\theta \qquad (6.2)$$

Note that although $\sigma_{\perp} = 1/\rho_{\perp}$ and $\sigma_{\parallel} = 1/\rho_{\parallel}$, one has $\sigma(\theta) \neq \rho(\theta)$. Often, the anisotropy in

the conductivity of hexagonal metals is rather small, cf. Fig. 7. In hexagonal graphite, however, the anisotropy is large.

Figure 7: The anisotropy of the electrical resistivity in Zn, Mg and Ru. (From Grimvall, 1986).



2. Polycrystalline materials

Let the diagonal elements of the conductivity matrix of a single crystal be σ_a, σ_b and σ_c. A polycrystalline specimen of this material is quasi–isotropic and we may ask for its effective conductivity σ_e. One can show (Molyneux, J. Math. Phys. 11, 1970, p. 1172) that σ_e is bounded by

$$3[1/\sigma_a + 1/\sigma_b + 1/\sigma_c]^{-1} \le \sigma_e \le (1/3)[\sigma_a + \sigma_b + \sigma_c] \qquad (6.3)$$

One knows that a material can be constructed such that the upper bound is attained, so in this respect this is the best possible bound. Less is known about the lower bound.

In the case of hexagonal symmetry, $\sigma_a = \sigma_b = \sigma_{\perp}$ and $\sigma_c = \sigma_{\parallel}$. Then, one may use an effective–medium result (Bolotin and Moskalenko, J. Appl. Mech. Tech. Phys. 8, 1967, p. 3) which gives the effective conductivity σ_e as the solution of the equation

$$4y^3 - (y/5)\,[4x^2 + 12x - 1] - x^2 = 0 \qquad (6.4)$$

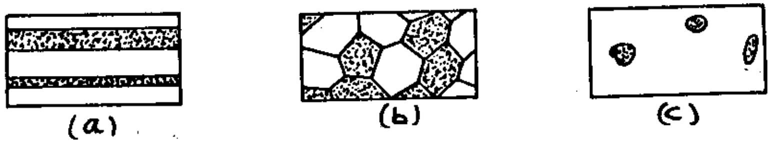
where $x = \sigma_a/\sigma_c$ and $y = \sigma_e/\sigma_c$. We also note that the bounds in Eq. (6.3) may be quite close. For instance, in a hexagonal symmetry with $\sigma_\perp/\sigma_\parallel = 1.2$, the upper and lower bounds in (6.3) differ by less than 1 %.

VII. MULTIPHASE MATERIALS

1. Introduction

Consider a material made up of a regular or a random arrangement of two phases of different conductivities σ_1 and σ_2 (or κ_1 and κ_2). In a geometry such as in Fig. 8a, it is trivial to calculate the resulting conductivity, just by a series or parallel coupling of the properties of the phases, with their volume fractions f_1 and f_2. The case of a random dilute suspension of one phase in the other, Fig. 8c, is also not to difficult to handle. But for a quasi–isotropic mixture such as that in Fig. 8b, there is no general expression for the overall effective (and isotropic) conductivity σ_e. However, one can find useful bounds to σ_e.

Figure 8: Some geometrical phase distributions in inhomogeneous materials.



The macroscopic transport of electric charge and heat is goverened by the equations $j = \sigma E$ and $q = \kappa(-\nabla T)$, respectively. Two other equations, of exactly the same mathematical structure, are $D = \epsilon E$ for dielectric and $B = \mu H$ for magnetic properties, respectively.

Much of the research on effective transport properties of inhomogeneous systems has been done with dielectric or magnetic applications in mind. Therefore, important results for σ_e or κ_e are often to be inferred from work in those two other fields of physics. We also note that the related question of effective properties for elastic parameters poses a different mathematical problem, because even for an isotropic material one needs two elastic parameters in a complete description (e.g., the bulk and the shear moduli, or the longitudinal and the transverse sound velocities).

2. Wiener and Hashin–Shtrikman bounds

One may show (Wiener, Abh. Math.–Physik. Kl. Königl. Sachs. Ges. Wiss. 32, 1912, p. 509) that whatever the geometrical arrangement of the two phases is, the overall conductivity σ_e is bounded by the series and parallel coupling results,

$$[f_1/\sigma_1 + f_2/\sigma_2]^{-1} \le \sigma_e \le f_1\sigma_1 + f_2\sigma_2 \qquad (7.1)$$

The bounds are attained for geometries such as in Fig. 8a, so there can be no better bounds if any geometrical distribution is to be allowed. But for a random (i.e. quasi–isotropic) mixture such as in Figs. 8b and 8c, there are more narrow bounds, due to Hashin and Shtrikman (J. Appl. Phys. 33, 1962, p. 3125). They give for σ_e

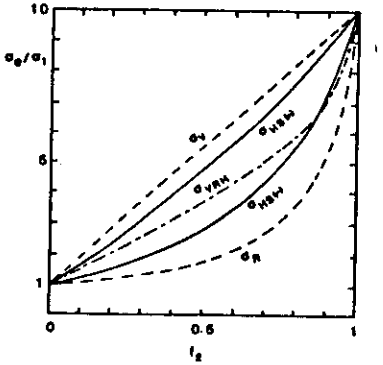
$$\sigma_\ell \le \sigma_e \le \sigma_u \qquad (7.2)$$

where the lower bound σ_ℓ is (labelling chosen such that $\sigma_2 > \sigma_1$)

$$\sigma_\ell = \sigma_1 + f_2\,[1/(\sigma_2 - \sigma_1) + f_1/(3\sigma_1)]^{-1} \qquad (7.3)$$

and the upper bound σ_u is obtained from (7.3) by interchanging all indices 1 and 2. Fig. 9 shows examples of the Wiener and the Hashin–Shtrikman bounds.

Figure 9: The upper and lower Wiener bounds (sometimes referred to as the Voigt and Reuss bounds, respectively), their average $\sigma_{VRH} = (\sigma_V + \sigma_R)/2$ (sometimes referred to as the Voigt–Reuss–Hill estimate) and the upper and lower Hashin–Shtrikman bounds σ_{HS}. The ratio σ_2/σ_1 for the conductivities of the pure components is 10. (From Grimvall, 1986.)



3. Dilute suspensions

Let phase 1 form a dilute suspension in a matrix of phase 2. When the shape of the inclusions is ellipsoidal, and in the dilute limit $f_1 \ll 1$, there is an exact expression for the effective conductivity σ_e (cf. Osborn, Phys. Rev. 67, 1945, p. 341 or Stoner, Phil. Mag. 36, 1945, p. 803). For spherical inclusions the solution was found already in 1892 by Rayleigh (Phil. Mag. 34, p. 481). One has, for any ratio σ_2/σ_1,

$$\sigma_e = \sigma_2 \left[1 - 3f_1(\sigma_2 - \sigma_1)/(2\sigma_2 + \sigma_1)\right] \tag{7.4}$$

4. Effective–medium theories

In the previous section we considered dilute spheres of phase 1 in a matrix 2. If the volume fraction f_1 is not small, we may still use a similar approach but let spheres of phase 1 be embedded in a medium of conductivity σ_e. Then

$$\sigma_e = \sigma_2 - 3f_1\sigma_e(\sigma_2 - \sigma_1)/(2\sigma_e + \sigma_1) \tag{7.5}$$

This formula can be derived in a stricter fashion (cf. Landauer, J. Appl. Phys. 23, 1952, p. 779) and also extended to a mixture of N phases i = 1, ..., N, with conductivities σ_i. In the effective–medium approach,

$$\sum_i f_i\,(\sigma_e - \sigma_i)/(\sigma_i + 2\sigma_e) = 0 \tag{7.6}$$

We finally remark that there are various similar results which are also referred to as effective–medium theories. We may also note that the effective–medium result in the dilute limit agrees not only with the result for spherical suspensions (Eq. 7.4) but also with the dilute–limit lower (or upper if 1 and 2 are interchanged) Hashin–Shtrikman bound.

LITERATURE

Much of the contents of these lecture notes is dealt with in detail in
G. Grimvall, "Thermophysical properties of materials". North–Holland, 1986.

A useful and detailed reference work to electron and phonon transport in solids, as the theory was developed until the end of the 1950's, is
J. Ziman, "Electrons and Phonons". Clarendon Press, 1960. [Reprinted later].

A recent book on the electrical conductivity is
P.L. Rossiter, "The electrical resistivity of metals and alloys". Cambridge University Press, 1987.

Two other useful books on the electrical and thermal conductivity are
J.S. Dugdale, "The electrical properties of metals and alloys". Arnold, 1977
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Thermal conduction is dealt with by
P.G. Klemens, in "Thermal conductivity", edited by R.P. Tye. Academic Press, 1969.
G.A. Slack, in "Solid State Physics" vol. 34, edited by H. Ehrenreich et al., Academic Press, 1979, p. 1.

For experimental data see, e.g., the recent Landolt–Börnstein tables and the CINDAS volumes "Thermophysical properties of matter", edited by Y.S. Touloukian et al.