

TRANSPORT PROPERTIES OF METALS AND ALLOYS

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Three aspects on electronic conduction in solids are briefly reviewed. (1) Accurate resistance measurements on Pb by Pokorný show the existence of a thermally induced liquid-like lattice defect which might be envisaged as atomic disorder next to a vacancy. (2) 'Saturation' effects in the electronic part of the thermal conductivity of pure transition metals are discussed and compared with the well-known saturation in the electrical conductivity. (3) In macroscopically inhomogeneous materials (composite materials), the spatial fluctuation in the electric field may be very large, also within the individual phases of the composite.

1. Introduction

This paper reviews some aspects of electron transport properties of metals and alloys by three examples of current interest. We first consider the electrical resistivity of a simple metal (Pb) at intermediate and high temperatures. A theoretical analysis of accurate measurements reveals the existence of a new kind of thermally induced lattice defect. We next turn to transport properties at high temperatures and in highly resistive metals and alloys. It is experimentally well known that the resistivity shows a saturation effect, but it still lacks a generally accepted explanation. A similar saturation is also known to occur in the phonon mediated thermal conductivity of insulators. Here we shall discuss saturation in the electronic part of the thermal conductivity of pure metals. In the last section we consider transport in macroscopically inhomogeneous materials. This is a field which has connections both with practical aspects on engineering materials and with fundamental theories on percolation.

2. A liquid-like thermal defect

The electrical resistivity is often used to study defects in a lattice, for instance the recovery of an irradiated sample [1] or the vacancy concentration in quenched specimens [2]. Then the resistivity in the defect-free crystal has to be sub-

tracted from the total measured value. This is not very difficult in the cases just mentioned, because the defect concentration during the measurement is much higher than what corresponds to thermodynamic equilibrium. A study of defects in equilibrium, on the other hand, requires that the phonon limited resistivity ρ_{ep} is accurately separated out. At least in simple metals, ρ_{ep}/T varies slowly enough with T to allow a study of the vacancy contribution [2, 3]. As one approaches the melting temperature T_m , one might expect to see scattering by, e.g., divacancies or interstitials. Since the free energies of the solid and the liquid phases are equal at T_m , one may also see precursors of the liquid state. For instance, we can imagine that the atoms surrounding a vacancy in the solid lattice leave their equilibrium positions and form what might be envisaged as a microscopic liquid drop.

Pokorný [4] measured the resistance of lead from 300 K to its melting temperature $T_m = 601$ K with a hitherto unmatched precision (0.001%). In addition to the contribution which could be represented by a polynomial in T (i.e. ρ_{ep}) the fit to the data gave two terms of the form $b_i \exp(-Q_i/k_B T)$. The larger of them ($i = 1$) corresponds to vacancy scattering. It is detectable at all temperatures in the measured range. Starting at about 540 K there is also a term with $Q_2 \approx 3.70Q_1$ and $b_2/b_1 \approx 10^7$. The value for b_2 is not consistent with a static defect (such as an interstitial) since we then expect that $b_2 \approx b_1$. However, a liquid-like defect structure would enhance b_2

by a factor $\exp(S_2/k_B)$, where the entropy S_2 is due to the disorder that arises when the atoms take no definite lattice positions. A simple estimate [4], based on the known entropy difference per atom between the liquid and the solid states, shows that $b_2/b_1 \approx 10^7$ can be explained by a microscopic liquid-like defect comprising about 17 atoms. In view of the uncertainty of this estimate, it is in satisfactory agreement with the idea of a disordered structure surrounding a vacant site. A preliminary analysis shows the same effect in Al [5]. It is worth stressing that the numerical analysis of the experimental data requires a detailed consideration as regards numerical stability etc. [4, 5].

A defect structure closely related to the one discussed above has been independently suggested by other authors, and for different systems. Seeger and Chik [6] argued that 'extended' vacancies, with nearest neighbours around a vacancy forming a liquid-like structure, could explain the self-diffusion in Ge. Gösele, Frank and Seeger [7] used the same idea to account for the slow rate of vacancy-interstitial recombination in Si, and introduced the concept of an 'entropy barrier' associated with the disordered structure. Sherby et al. [8] associated the self diffusion in ϵ -Pu with an activated liquid-like structure. Fluss et al. [9] noted the similarity between positron annihilation data in Ni at vacancies and in the liquid phase. Nachtrieb and Handler [10] discussed diffusion mediated by a liquid-drop defect similar to the one mentioned here, but without reference to the importance of the entropy.

3. Saturation effects in the thermal conductivity of metals

Moof [11] drew attention to the empirical fact that the electrical resistivity of highly resistive systems does not obey Matthiessen's rule or increase with the temperature, but shows what is usually referred to as resistivity saturation. A similar saturation occurs for the thermal conductivity of non-metallic solids [12-13]. In spite of many attempts, the phenomenon has got no gen-

erally accepted explanation [14-16]. In this paper we shall briefly discuss the thermal conductivity κ in metals. In order to elucidate some trends, our approach is first within the Boltzmann theory, and Matthiessen's rule etc are assumed to be valid. In a pure metal we take $\kappa_{\text{tot}} = \kappa_{\text{ep}} + \kappa_{\text{ph}}$. The terms refer to the total conductivity, the phonon limited electronic part and the heat carried by phonons, respectively. For the latter term, we take $1/\kappa_{\text{ph}} = 1/\kappa_{\text{ph,e-p}} + 1/\kappa_{\text{ph,an}}$, where the two parts give the phonon scattering due to electron-phonon and anharmonic interactions, respectively. We now seek an estimation for the ratio $\kappa_{\text{ph,e-p}}/\kappa_{\text{ep}}$. From expressions given in the appendix, one finds

$$\kappa_{\text{ph,e-p}}/\kappa_{\text{ep}} = [81/(2\pi^2)] [(\hbar q_D)^2 (N_v(E_F)) \langle v_k^2 \rangle]^{-1}. \quad (1)$$

In the free-electron case, with a valency Z ,

$$\kappa_{\text{ph,e-p}}/\kappa_{\text{ep}} = kZ^{4/3}, \quad (2)$$

where $k \approx 1$ (in our model, $k = (9/\pi^2)(2)^{1/3}$). A similar result has been derived by Klemens [17] for low temperatures.

When the electron band structure is far from free-electron-like we must resort to (1). Note that $(N_v(E_F))^{-2} \langle v_k^2 \rangle$ is essentially $(\int v^{-1} dS) \times (\int v dS) \approx (\int dS)^2 = S^2$, where the integration is over the Fermi surface S_F . Therefore we expect that band-structure effects in transition metals (which can lead to a high ρ_{ep} ; see the appendix) do not significantly increase the ratio $\kappa_{\text{ph,e-p}}/\kappa_{\text{ep}}$ above its value for simple metals. Since κ_{tot} is in addition limited by anharmonicity, the thermal conductivity of transition metals should be well approximated by κ_{e} at high temperatures, provided that the Boltzmann equation etc is adequate.

Guided by the Wiedemann-Franz law, we plot in fig. 1 ρ_{ep} and $L_0 T / \kappa_{\text{tot}}$ versus T for pure W, V and U. There is a conspicuous similarity between the two sets of curves. The thermal conductivity shows a saturation effect in V and U and the Wiedemann-Franz law is well obeyed in spite of the supposed [14-16] breakdown of the Boltzmann equation when saturation occurs. Tungsten shows no saturation but the

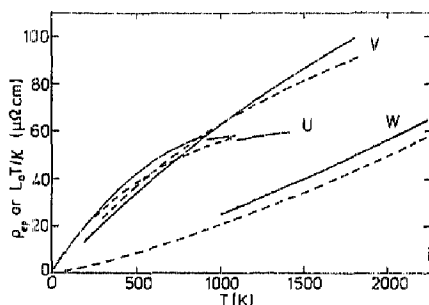


Fig. 1. Experimental data for ρ_{cp} (solid lines) and $L_0 T / \kappa_{cp}$ (dashed lines) for V [20, 22], U [21, 22] and W [19, 22].

Wiedemann–Franz law is equally well obeyed. We also calculate an apparent Lorenz number $L^* = \kappa_{tot} / (\rho_{cp} T)$ at 1500 K from experimental data on ρ_{cp} for Ti, Zr, Hf, Nb [19], V [20] and U [21] (at 1200 K for U) and with recommended values [22] for κ_{tot} . The result is $L^* = (2.5 \pm 0.2) \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$, to be compared with the ‘ideal’ value $2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$. A similar analysis has been done by Khoder et al. [18] for V_3Si and V_3Si_3 .

4. Conduction in macroscopically inhomogeneous materials

Many materials of practical importance are macroscopically inhomogeneous. We shall consider cases where the size of a single grain is much larger than the electron mean free path. The conductance properties of such systems are described by classical physics and thus rest on theories developed more than a century ago. In spite of that, the field has recently received much attention. One reason is the increased use of composite materials, e.g. for selective solar absorption, and another reason is the connection with percolation problems.

To be specific, we consider two-phase materials in which the phases 1 and 2 have conductivities σ_1 and σ_2 and concentrations (volume fractions) f_1 and $f_2 (= 1 - f_1)$. The two phases are assumed to be so distributed that the system is

(on a large scale) isotropic and homogeneous, with an effective conductivity σ_e . Pioneering work by Hashin and Shtrikman [23] and others established bounds on σ_e : $\sigma_e < \sigma_c < \sigma_u$, with

$$\sigma_e = \sigma_1 + \frac{f_2}{[1/(\sigma_2 - \sigma_1)] + [f_1/(d\sigma_1)]}. \quad (3)$$

Here d is the dimensionality of the system and $\sigma_1 < \sigma_2$. (In one dimension, $d = 1$, we simply get the series coupling of resistors.) The upper bound, σ_u , is obtained if indices 1 and 2 are interchanged in (3). One can show that (3) is the best possible bound, because there are geometries (‘coated sphere’ systems [23, 24]) for which it is attained. More narrow bounds require additional knowledge about the geometrical distribution of the two phases. Much work has recently been done in this field, e.g. by Milton [25–27] and Bergman [28]. They show how (3) is one step in a hierarchy of bounds and also how (3) is generalised to include materials with complex dielectric constants. Fig. 2 exemplifies how σ_e varies with f_2 in two dimensions ($d = 2$).

The local field $E_1(r)$ (r is in phase 1) varies with the position r . The spatial fluctuations in $E_1(r)$ can be very large when $f_1 \approx f_2$ and $\sigma_2/\sigma_1 \gg 1$ (or $\ll 1$). As an example, consider a two-dimensional system, e.g. an inhomogeneous film on a substrate or conduction perpendicular to the fibers in a fiber bundle (cf. fig. 3). Suppose

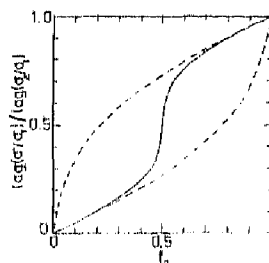


Fig. 2. The solid line is [30] $\sigma_e(f_2)$ for a generalised checkerboard geometry where ‘white’ ($\sigma_1 = 1$) areas continuously expand to cover the board ($f_2 = 0$) or shrink until the board is ‘black’ ($\sigma_1 = \infty$). The dashed lines are the Hashin–Shtrikman bounds σ_c and σ_u .

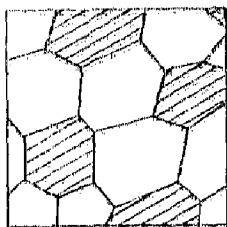


Fig. 3. A schematic structure of a two-phase composite material which is, on a large scale, isotropic and homogeneous.

that the structure is symmetric in the sense that if the phases 1 and 2 are interchanged when $f_1 = f_2$ ($\approx 1/2$), one gets back the same kind of material. Then, for $f_1 = f_2$ [29, 30], $\alpha_3 = (\alpha_1\alpha_2)^{1/2}$. Further,

$$\frac{\langle E^2 \rangle_i}{\langle E \rangle_i^2} = \frac{1}{4} \left(\sqrt{\frac{\alpha_1}{\alpha_2}} + \sqrt{\frac{\alpha_2}{\alpha_1}} + 2 \right), \quad (4)$$

where $\langle \rangle_i$ denotes a spatial average over the phase 1. If E_a is the applied field over the entire specimen $\langle E \rangle_1/E_a = (c_1\sqrt{\alpha_2} + c_2\sqrt{\alpha_1})/\sqrt{\alpha_2}$ [29, 30]. Relations for phase 2 are obtained if indices 1 and 2 are interchanged in the expressions given here. Fig. 4 exemplifies how $\langle E \rangle_i$ and $\langle E^2 \rangle_i$ ($i = 1, 2$) vary with f_i . The large, and un-

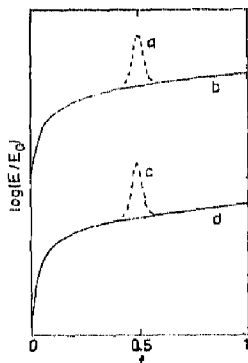


Fig. 4. Characteristic behaviour of $\log(E/E_a)$ where E is $\sqrt{\langle E^2 \rangle}_1$ (a), $\langle E \rangle_1$ (b), $\sqrt{\langle E^2 \rangle}_2$ (c) and $\langle E \rangle_2$ (d). The peak heights in (a) and (c) are half the distance between (b) and (d).

avoidable, high local fields near $f_i \approx 1/2$ have been seen as a non-ohmic behaviour in Au films on glass [31].

Appendix A

The phonon-limited electrical resistivity can be written [32, 33]

$$\rho_{\text{ep}} = \frac{8\pi^2 k_B \lambda_U T}{\hbar \omega_p^2} = \frac{3\pi \Omega_a k_B \lambda_U T}{\hbar \omega^2 N_a(E_F) \langle v_F^2 \rangle}, \quad (\text{A.1})$$

where ω_p is the plasma frequency, Ω_a the atomic volume, $\langle v_F^2 \rangle$ a Fermi level average of the electron velocity v_a , λ_U a 'transport' electron-phonon interaction parameter and $N_a(E_F)$ the electron density of states at the Fermi level (per atom and spin). In free-electron-like metals, $\omega_p^2 = 4\pi n e^2/m$, which gives

$$\rho_{\text{ep}} = (2\pi k_B m)/(3\hbar n e^2) \lambda_U T. \quad (\text{A.2})$$

Saturation occurs when ρ_{ep} is high. However, this is not related to a large electron-phonon coupling parameter λ_U ($\lambda_U = \lambda$ with $\lambda = 0.4$ – 1.0 for many transition metals but $\lambda = 1.5$ for Pb). Instead, the high ρ_{ep} of transition metals arises from band structure effects, i.e. a small $N_a(E_F) \times \langle v_F^2 \rangle$.

The Wiedemann-Franz law gives κ_{ep} as

$$\kappa_{\text{ep}} = (\pi^2/3)(k_B/e)^2 T \rho_{\text{ep}} = L_0 T / \rho_{\text{ep}}, \quad (\text{A.3})$$

where L_0 is the Lorenz number.

From the usual expression for the thermal conductivity of a gas, $\kappa = (1/3) c v^2 \tau$, with the phonon life-time $\tau_{\text{ph,e-p}}$ expressed in λ [33, 34] and a Debye model for phonons ($\hbar \omega_D = c_{\text{ph}} q_D$) one finds

$$\kappa_{\text{ph,e-p}} = 9 k_B [2\pi \hbar q_D^2 N_a(E_F) \Omega_a \lambda]^{-1}. \quad (\text{A.4})$$

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