Contribution to the theory of the thermal conductivity of metals at low temperatures

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An exact expression is obtained for the electronic thermal conductivity of an anisotropic metal under conditions when scattering of electrons by phonons predominates in the low-temperature limit (when the thermal momentum of the phonons is smaller than all the characteristic dimensions of the Fermi surface).

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The electronic thermal conductivity of metals at low temperatures, under conditions when scattering of electrons by phonons predominates, was considered long ago by Peierls[1] and is constantly a center of attention. The usual method of calculating the thermal conductivity consists of determining from the kinetic equation the nonequilibrium electron distribution function

$$f_{\mathbf{k}}=f_{\mathbf{k}}^{0}-\frac{\partial f_{\mathbf{k}}^{0}}{\partial \varepsilon_{\mathbf{k}}}\Phi_{\mathbf{k}}$$

and of a determination of the heat flux associated with this function. In the calculation of $\Phi_{\mathbf{k}}$ there arise in natural fashion two problems, that of the dependence of $\Phi_{\mathbf{k}}$ on the energy $\varepsilon_{\mathbf{k}}$ and that of the dependence of $\Phi_{\mathbf{k}}$ on the direction of the wave vector $\mathbf{k}$. For an isotropic metal, only the first of these problems exists, since the angular dependence of $\Phi_{\mathbf{k}}$ is trivial, viz., $\Phi_{\mathbf{k}} \propto \hat{\mathbf{k}}\nabla T$ $(\hat{\mathbf{k}}=\mathbf{k}/k)$.[2]

If we substitute in the kinetic equation

$$\Phi_{\mathbf{k}}=c(\varepsilon_{\mathbf{k}})\hat{\mathbf{k}}\nabla T, \tag{1}$$

we obtain for $c(\varepsilon_{\mathbf{k}})$ an integral equation similar to Bloch's equation in the electric conductivity problem[1,3]:

$$\eta=\int_0^\infty dx\,\frac{x^2}{e^x-1}\left\{\frac{e^\eta+1}{e^\eta+e^{-x}}[c(\eta+x)-c(\eta)]+\frac{e^{-\eta}+1}{e^{-\eta}+e^{-x}}[c(\eta-x)-c(\eta)]\right\}, \tag{2}$$

where $\eta=(\varepsilon_{\mathbf{k}}-\mu)/T$ and μ is the chemical potential. This equation cannot be solved analytically; only the temperature dependence of the thermal conductivity, $\varkappa \propto T^{-2}$, can be established.[1] Equation (2) is usually solved by a variational method, but the convergence of the result is slow and a rather large number of trial functions must be used. An exact solution of (1) was obtained by Klemens[3] by numerical integration.

The energy dependence of $\Phi_{\mathbf{k}}$ in the isotropic case has thus been sufficiently well investigated. In the case of an anisotropic metal, the angular dependence of $\Phi_{\mathbf{k}}$ is also important. Apart from several variational calculations (e.g., Ref. 4), however, there are no reported studies of this question.

It will be shown in this paper that in the general anisotropic case, in the low-temperature limit (when the wave vector of the thermal phonon q_T is less than the smallest of the characteristic dimensions of the Fermi surface $k_{\min}$) the energy and angle variables can be separated in the kinetic equation. Therefore $\Phi_{\mathbf{k}}$ is represented as the product

$$\Phi_{\mathbf{k}}=c(\varepsilon_{\mathbf{k}})G(\hat{\mathbf{k}}), \tag{3}$$

with the function $c(\varepsilon\mathbf{k})$ the same as in (1), but $G(\hat{\mathbf{k}})$ can be found in explicit form. This yields a closed equation for the thermal conductivity of a metal with an arbitrary Fermi surface and with an arbitrary phonon spectrum.

The kinetic equation for the electrons under conditions of perdominant electron-phonon scattering is of the form[2]

$$-\frac{\varepsilon_{\mathbf{k}}-\mu}{T}\frac{\partial f_{\mathbf{k}}^{0}}{\partial \varepsilon_{\mathbf{k}}}\mathbf{v}_{\mathbf{k}}\nabla T=-\frac{1}{T}\sum_{\mathbf{k}'q\lambda}(\Phi_{\mathbf{k}}-\Phi_{\mathbf{k}'})\sum_{G}\frac{2\pi}{\hbar}|g_{\mathbf{k}\mathbf{k}'}^{\lambda}|^2 f_{\mathbf{k}}^{0}(1-f_{\mathbf{k}'}^{0})[n_{q\lambda}^{0}\delta(\varepsilon_{\mathbf{k}'}-\varepsilon_{\mathbf{k}}-\hbar\omega_{q\lambda})\delta_{\mathbf{k}'-\mathbf{k}-\mathbf{q},G}+(1+n_{q\lambda}^{0})\delta(\varepsilon_{\mathbf{k}'}-\varepsilon_{\mathbf{k}}+\hbar\omega_{q\lambda})\delta_{\mathbf{k}'-\mathbf{k}+\mathbf{q},G}], \tag{4}$$

where $g_{\mathbf{k}\mathbf{k}'}^{\lambda}$ is the matrix element of the electron-phonon interaction, $\mathbf{q}$ and λ are the wave vector and the polarization of the phonon, and G is the reciprocal-lattice vector.

We introduce in place of $\mathbf{k}$ the variables $\varepsilon_{\mathbf{k}}$ and $\mathbf{f}$, where $\mathbf{f}$ is a vector having the same direction as $\mathbf{k}$, but terminating on the Fermi surface. As a function of $\mathbf{f}$, $\Phi_{\mathbf{k}}$ changes significantly over intervals $\gtrsim k_{\min}$, and varies substantially as a function of $\varepsilon_{\mathbf{k}}$ over the width of the thermal smearing of the Fermi distribution. Inasmuch as in the low-temperature limit $|\mathbf{k}'-\mathbf{k}| \sim q \ll k_{\min}$ and $\varepsilon_{\mathbf{k}'}-\varepsilon_{\mathbf{k}} \sim \hbar\omega_{\mathbf{q}} \sim T$, the angular dependence of $\Phi_{\mathbf{k}}$ is weak compared with the energy dependence[5]; we can therefore put in (4)

$$\Phi_{\mathbf{k}}-\Phi_{\mathbf{k}'} \approx \Phi(\varepsilon_{\mathbf{k}}, \mathbf{f})-\Phi(\varepsilon_{\mathbf{k}'}, \mathbf{f}).$$

In addition, we can put $\varepsilon_{\mathbf{k}} \approx \varepsilon_{\mathbf{k}'} \approx \varepsilon_F$ in the slowly varying energy functions (such as $\mathbf{v}_{\mathbf{k}}$). These assumptions are equivalent to neglecting the terms $\sim(Tq_D/\Theta k_{\min})^2$ and $\sim T/\varepsilon_F$ (q_D is the Debye wave vector of the phonon) and are fully justified for the calculation of the thermal conductivity; we note that in the case of electric conductivity these terms play a principal role and cannot be neglected.[1,5]

As a result of the approximations made, the kinetic equation acquires the following structure:

$$-(\varepsilon-\mu)\frac{\partial f^{0}(\varepsilon)}{\partial \varepsilon}\mathbf{v}_{\mathbf{f}}\nabla T=-\int d\varepsilon'[\Phi(\varepsilon, \mathbf{f})-\Phi(\varepsilon', \mathbf{f})]Q_{\mathbf{f}}(\varepsilon, \varepsilon') \tag{5}$$

and is not an integral equation in the angle variable $\mathbf{f}$. The expression for the kernel $Q_{\mathbf{f}}(\varepsilon, \varepsilon')$ is obtained from (4):

$$Q_{\mathbf{f}}(\varepsilon, \varepsilon')=\int\frac{dS_{\mathbf{f}'}}{(2\pi)^3\hbar v_{\mathbf{f}'}}\sum_{\lambda}\frac{2\pi}{\hbar}|g_{\mathbf{f}\mathbf{f}'}^{\lambda}|^2 f^{0}(\varepsilon)[1-f^{0}(\varepsilon')]$$
$$\times n^{0}(\varepsilon-\varepsilon')\{\delta(\varepsilon'-\varepsilon-\hbar\omega_{\mathbf{f}'-\mathbf{f},\lambda})-\delta(\varepsilon'-\varepsilon+\hbar\omega_{\mathbf{f}'-\mathbf{f},\lambda})\}. \tag{6}$$

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We note that under the assumptions made we need not worry specially about the umklapp processes: for open Fermi surfaces the choice of G in (4) is uniquely determined by the requirement that k and k′ be close, and transitions through a finite gap in the case of closed surfaces are frozen-out.

Since f and f′ are close, all the functions f′ in (6) can be expanded in terms of $\mathbf{q}=\mathbf{f}'-\mathbf{f}$, with only the principal term retained. The section of the Fermi surface near f can be regarded as planar and we can go from integration with respect to f′ to integration with respect to q:

$$\int dS_{\mathbf{f}'} \to \int_0^\infty q\,dq \int_0^{2\pi} d\varphi_{\hat{\mathbf{q}}}.$$

Here $\varphi_{\hat{\mathbf{q}}}$ is an angle in the plane tangent to the surface at the point f; the upper limit in the first integral was set equal to infinity in view of the rapid convergence. We use also the fact that at small q the phonon frequency $\omega_{\mathbf{q}\lambda}=s_{\hat{\mathbf{q}}\lambda}q$, while the matrix element is

$$|g^{\lambda}_{\mathbf{f}'\mathbf{f}}|^2=q\hbar\,|\hat{q}_i e_j^{\lambda}(\hat{\mathbf{q}})\,\Lambda_{ij}(\mathbf{f})\,|^2/2\rho s_{\hat{\mathbf{q}}\lambda}\equiv qM^{\lambda}_{\mathbf{f}\hat{\mathbf{q}}}, \tag{7}$$

where $s_{\hat{\mathbf{q}}\lambda}$ and $e^{\lambda}(\hat{\mathbf{q}})$ are the phase velocity and polarization vector of the phonon, Λ_{ij} is the deformation potential, and ρ is the density of the metal; summation over repeated indices is implied. As a result, the expression for $Q_{\mathbf{f}}(\varepsilon,\varepsilon')$ reduces to

$$Q_{\mathbf{f}}(\varepsilon,\varepsilon')=D(\varepsilon,\varepsilon')\Gamma_{\mathbf{f}}; \tag{8}$$

$$D(\varepsilon,\varepsilon')=f^0(\varepsilon)[1-f^0(\varepsilon')]n^0(\varepsilon-\varepsilon')(\varepsilon'-\varepsilon)^2\operatorname{sgn}(\varepsilon'-\varepsilon),$$

$$\Gamma_{\mathbf{f}}=\frac{2\pi}{\hbar}\frac{1}{(2\pi)^3\hbar v_{\mathbf{f}}}\sum_{\lambda}\int_0^{2\pi}d\varphi_{\hat{\mathbf{q}}}\frac{M^{\lambda}_{\mathbf{f}\hat{\mathbf{q}}}}{(\hbar s_{\hat{\mathbf{q}}\lambda})^3}. \tag{9}$$

The kernel of the integral equation is thus degenerate, so that we can find in explicit form the angular dependence of $\Phi_{\mathbf{k}}$:

$$\Phi(\varepsilon,\mathbf{f})=\frac{\mathbf{v}_{\mathbf{f}}\nabla T}{\Gamma_{\mathbf{f}}}\frac{1}{T^3}c\left(\frac{\varepsilon-\mu}{T}\right). \tag{10}$$

For the function $c(\eta)$ we obtain the universal equation

$$\eta\frac{\partial f^0(\eta)}{\partial\eta}=\int_{-\infty}^{\infty}d\eta'\{c(\eta)-c(\eta')\}f^0(\eta)[1-f^0(\eta')]$$
$$\times n^0(\eta-\eta')(\eta'-\eta)^2\operatorname{sgn}(\eta'-\eta),$$

which reduces after simple transformations to the form (2). Since the solution of (2) was obtained by Klemens[3] (Fig. 1), it follows that (10) yields the complete solution of the kinetic equation (4).

Calculating with the aid of (10) the heat flux

$$\mathbf{U}=-2\sum_{\mathbf{k}}(\varepsilon_{\mathbf{k}}-\mu)\mathbf{v}_{\mathbf{k}}\frac{\partial f_{\mathbf{k}}^0}{\partial\varepsilon_{\mathbf{k}}}\Phi_{\mathbf{k}},$$

we obtain the thermal conductivity tensor in the form

$$\varkappa_{nn'}=\frac{1}{T^2}\int_{-\infty}^{\infty}d\eta\,\eta\frac{\partial f^0(\eta)}{\partial\eta}c(\eta)\int\frac{2dS_{\mathbf{f}}}{(2\pi)^3\hbar v_{\mathbf{f}}}\frac{v_{\mathbf{f}}^n v_{\mathbf{f}}^{n'}}{\Gamma_{\mathbf{f}}}.$$

The first integral yields a universal constant whose numerical value can be obtained with the aid of the Klemens solution:

$$\int_{-\infty}^{\infty}d\eta\,\eta\frac{\partial f^0(\eta)}{\partial\eta}c(\eta)=-\int_{-\infty}^{\infty}\frac{\eta}{(e^{\eta}+1)(e^{-\eta}+1)}c(\eta)\,d\eta\approx 0.130.$$

We obtain thus for the thermal conductivity of the metal the closed expression

$$\varkappa_{nn'}=\frac{0.130}{T^2}2\int dS_{\mathbf{f}}v_{\mathbf{f}}^n v_{\mathbf{f}}^{n'}\left(\frac{2\pi}{\hbar}\sum_{\lambda}\int_0^{2\pi}d\varphi_{\hat{\mathbf{q}}}\frac{M^{\lambda}_{\mathbf{f}\hat{\mathbf{q}}}}{(\hbar s_{\hat{\mathbf{q}}\lambda})^3}\right)^{-1}. \tag{11}$$

Expressing $M^{\lambda}_{\mathbf{f}\hat{\mathbf{q}}}$ in terms of the deformation potential, we obtain finally

$$\varkappa_{nn'}=\frac{0{,}0827}{T^2}\frac{\rho}{\hbar}\int dS_{\mathbf{f}}v_{\mathbf{f}}^n v_{\mathbf{f}}^{n'}\left(\sum_{\lambda}\int_0^{2\pi}d\varphi_{\hat{\mathbf{q}}}\frac{|\hat{q}_i e_j^{\lambda}(\hat{\mathbf{q}})\Lambda_{ij}(\mathbf{f})|^2}{(\hbar s_{\hat{\mathbf{q}}\lambda})^4}\right)^{-1}. \tag{12}$$

We recall that the integration with respect to f is over the Fermi surface, and the integration with respect to $\varphi_{\hat{\mathbf{q}}}$ is in a plane tangent to the surface at the point f.

In the foregoing calculations we disregarded the disequilibrium of the phonons, i.e., we used Bloch's hypothesis. It is known, however, that in the case of the thermal conductivity the dragging of the phonons is of little importance.[1] In fact, eliminating the phonon distribution function from the kinetic equation for the electrons (with the aid of the kinetic equation for the phonons) and substituting $\Phi_{\mathbf{k}}$ in the form (3) with odd $c((\varepsilon-\mu)/T)$ and $G(\hat{\mathbf{k}})$, we easily verify that the terms connected with dragging have an additional smallness $\sim(T/\Theta)^2$ or T/ε_F compared with the principal term, i.e., of the same order as the terms discarded in the calculation. Compensated metals constitute a special case,[6] in which a divergence appears in the terms of higher order in T/ε_F (which are neglected in the present paper) if no account is taken of the umklapp processes. When umklapp is allowed for, these terms turn out to increase exponentially as $T\to 0$, and at extremely low temperatures they become the principal terms and lead to an exponential temperature dependence of the thermal conductivity: $\varkappa\sim\exp(T/T^*)$ (T^* is the temperature at which the umklapp process freeze out). This, however, occurs only at temperatures low enough to allow the large value of the Peierls exponential to compensate for the initial smallness of these terms, i.e.,

$$T<T^*/\ln(\varepsilon_F/T)\sim 1\ \text{K}$$

(see Ref. 6). Except for this temperature region, formula (12) is valid also for compensated metals.

It is easy to obtain a preliminary estimate for the thermal conductivity of noble metals. Inasmuch as the deformation potential is large on the necks,[7] while the Fermi velocity is small, we can neglect in (12) the integrals over the necks. Using the cubic symmetry of the metals, assuming for simplicity the phonon spectrum to be isotropic, and assuming that the deformation potential $|\Lambda_{ij}|=(2/3)\varepsilon_F\delta_{ij}$ on the spherical part of

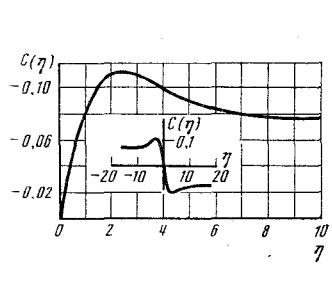

FIG. 1. Solution of the integral equation (2), obtained by Klemens[3] by numerical integration.

the Fermi surface, i.e, equal to the value for the free electrons, we obtain

$$\varkappa \approx \frac{0{,}497\hbar}{kT^2}\rho s_t^4 \frac{S_1}{S_0} \qquad (13)$$

(restoring the dimensionality of the Boltzmann constant k), where s_t is the speed of sound for the longitudinal mode, S_1 is the area of the essentially spherical part of the Fermi surface (without the necks), and S_0 is the area of the free-electron sphere. Putting $S_1 \approx 0.6 S_0$ and taking s_t to be the speed of sound for the most symmetrical direction [100], we obtain for W/T^2 (W is the thermal resistance) the values 1.3, 2.7, and 2.1 (in units of 10^{-5} cm/W·K) for Cu, Ag, and Au, respectively.

To compare these values with experiment it is necessary first to separate the temperature interval for which such a comparison is correct. The upper bound of the temperature is determined by the principal assumption $q_T \ll k_{\min}$. In noble metals, $k_{\min}$ corresponds to the dimension of the neck and amounts to $\approx q_D/5$, so that expression (12) is valid at $T \ll \Theta/5 \approx 40$–$60$ K. On the other hand, at the very lowest temperatures scattering by impurities always predominates and distorts the temperature dependence of the thermal conductivity (owing to the deviations from the Matthiessen rule). The lower bound of the temperature is therefore determined by the requirement that the thermal conductivity due to scattering by phonons be substantially larger than that connected with the impurities and with the lattice defects. For the purest samples of Cu and Ag this is satisfied at $T > 7$–10 K.

For extremely pure Ag samples, the relation $W \propto T^2$ is observed in the interval 5–16 K (Ref. 8); the value $W/T^2 = 3.0 \times 10^{-5}$ cm/W·K obtained in this case (see also Ref. 9) agrees with the estimate above. The available experimental data for copper are insufficient for a reliable determination of the temperature dependence of W in the pure metal. The thermal resistance, however, obtained by an estimate at $T \sim 10$ K, is close to the experimental values for the purest samples (Fig. 2).

An estimating formula of the type (13) can be obtained also for metals described by the pseudopotential theory. In the general case it cannot be stated that the deformation potential Λ_{ij} is large near a Bragg plane. However, even from the fact that its off-diagonal components differ from zero and have the usual value $\sim \varepsilon_F$ (as well as because of a certain decrease of the Fermi velocity), the contribution made to the integral (12) from the vicinities of the Bragg planes turns out to be several times weaker. Inasmuch as in many metals the free-electron sphere is strongly cut up by the Bragg planes, $\varkappa$ can be considerably smaller than for a spherical Fermi surface. These simple considerations explain

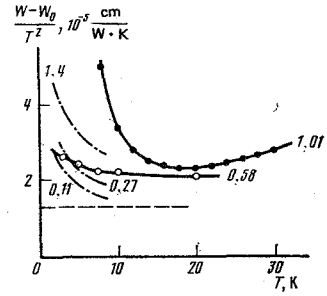

FIG. 2. Experimental data on the thermal conductivity of CU: •) Powell *et al.*[10]; ○) Schriempf (see the table in Ref. 11); dash-dot) Rumbo.[12] W is the measured thermal resistance, $W_0 = \rho_0/LT$ (L is the Lorentz number); the numbers indicate the residual resistivity ρ_0 of the sample in units of 10^{-9} Ω-cm. Dashed line—temperature dependence of W for a pure metal as estimated from formula (13).

why the experimental values of W/T^2 for noble metals turn out to be among the lowest ones[3] (in accordance with the fact that these are the best conductors at room temperature). Indeed, for these metals, that part of the Fermi surface which is far from the Bragg planes has a relatively large area; at the same time they are characterized by a high density and speed of sound. For example, the value of ρs^4 for copper (according to the data for the polycrystal) are larger than for all the nontransition metals except Be (Al has practically the same value of s_t^4 as Cu).

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[1]R. Peierls, Ann. Phys. (Leipzig) **4**, 121 (1930). H. Bethe and A. Sommerfeld, Elektronentheorie der Metalle, inL Handbuch der Physik, Vol. 24, Part 2, Springer, 1933. §§39, 42.
[2]J. M. Ziman, Electrons and Phonons, Oxford, 1960, Chap. VII, §4, Chap. IX, §§5, 6.
[3]P. G. Klemens, Austr. J. Phys. 7, 64 (1954). P. G. Klemens, transl. in: Fizika nizkikh temperature (Low Temperature Physics), A. I. Shal'nikov, ed., IIL, 1959, p. 224.
[4]A. P. Zhernov and Yu. M. Kagan, Fiz. Tverd. Tela (Leningrad) **20**, 3306 (1978) [Sov. Phys. Solid State **20**, 1906 (1978)].
[5]E. M. Lifshitz and L. P. Pitaevskiĭ, Fizicheskaya kinetika (Physical Kinetics), Nauka, 1979, §82.
[6]V. N. Flerov, Fiz. Tverd. Tela (Leningrad) **16**, 55 (1974) [Sov. Phys. Solid State **16**, 33 (1974)].
[7]R. E. McFarlane and J. A. Rayne, Phys. Rev. **162**, 532 (1967).
[8]A. C. Erlich and J. T. Schriempf, Sol. St. Commun. **14**, 469 (1974).
[9]J. F. Kos, Phys. Rev. Lett. **31**, 1314 (1973).
[10]R. L. Powell, H. M. Roder, and W. J. Hall, Phys. Rev. **115**, 314 (1959).
[11]M. E. Breit and J. E. Black, Can. J. Phys. **55**, 521 (1977).
[12]E. R. Rumbo, J. Phys: F **6**, 85 (1976).

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