PHYSICAL REVIEW B VOLUME 31, NUMBER 6 15 MARCH 1985

Temperature dependence of the diffusion thermopower in metals

W. Hänsch*

I. Institut für Theoretische Physik, Universität Hamburg, 2000 Hamburg 36, Jungiusstrasse 9, Federal Republic of Germany

(Received 23 March 1984)

We calculate the diffusion thermopower for a system of electrons interacting with static impurities and longitudinal-acoustical phonons. Our calculation is based on a many-body transport equation developed earlier. We compare our results with conjectures from Kubo's formula and find agreement. For a simple model, we present the temperature variation of the corresponding vertex functions over a wide temperature range. We find a pronounced temperature dependence between $0.2\Theta_D$ and $1.0\Theta_D$; here Θ_D is the Debye temperature. We discuss the implications on the use of Mott's relationship.

I. INTRODUCTION

Thermoelectrical phenomena were discovered in the first half of the last century. Since then, a vast amount of experimental material has been accumulated to challenge the theorists.[1,2] Among the large variety, the thermopower and the Wiedemann-Franz law deserve special attention. Both provide an excellent tool to test the underlying models of transport against the experimental results.[3] The early theory of transport in solids predicts, at least at high temperature, the right order of magnitude of the thermopower and gives reasonable agreement for the Wiedemann-Franz law. In the low-temperature region, agreement is usually poor within the framework of that simple theory. Here different scattering mechanisms compete and phonon drag effects become important. The aim of this paper is to add a contribution to the discussion of the diffusion thermopower in an electron system interacting with phonons and static impurities. In particular, we question whether Mott's relationship is sufficient to describe the diffusion thermopower in such systems.

Diffusion thermopower is a result of a very sensitive balance of energy current by electrons in a small shell right above and below the Fermi energy. This makes it a second-order process compared with the conductivity. Many effects contribute, such as electron-phonon renormalization, multiple phonon scattering, and many-body corrections of various kinds. A calculation usually considers one effect alone in absence of all others, and even this is a formidable task. Approximations are usually made in order to understand at least a particular aspect. In this sense, our work is to be understood as an attempt to study the diffusion thermopower in a system where both elastic (electron-impurity) and inelastic (electron-phonon) scattering of the electrons are present.

There has been recent work on the diffusion thermopower in the systems under consideration. Lyo,[4] and Vilenkin and Taylor,[5] studied many-body corrections to the thermopower. In particular, they investigated the problem of electron-phonon mass enhancement. While the appearance of electron-phonon mass enhancement is experimentally[6] and theoretically[7] verified for the low-temperature diffusion thermopower in high magnetic fields, experiments in zero magnetic field usually do not show this factor directly. An exception seems to be some amorphous metals where the temperature dependence of the thermopower follows that of the electron-phonon mass enhancement.[8,9] In contrast, the simple metals (pure and dilute alloys) usually show a ratio of the low-temperature slope of the diffusion thermopower S_d versus T and its high-temperature equivalent, which is 1 order of magnitude larger than that expected from simple arguments.[10–12] Krempasky and Schmid[13] presented a calculation of the diffusion thermopower, following the ideas of Nielsen and Taylor,[14] taking interference effects of phonon and impurity scattering in the electron self-energy into account. They predicted a modification of the low-temperature thermopower.

It was shown[15] that Mott's relationship for the diffusion thermopower S_d is true for a system of independent electrons interacting with static impurities:

$$S_d=\frac{\pi^2}{3}\frac{k_B^2T}{e\epsilon_F}\frac{\partial\ln\sigma(\epsilon)}{\partial\ln\epsilon}\bigg|_{\epsilon=\epsilon_F}. \tag{1.1}$$

The energy-dependent part of the conductivity is given by

$$\sigma=\int d\epsilon\left[-\frac{\partial n_F(\epsilon)}{\partial\epsilon}\right]\sigma(\epsilon)\,. \tag{1.2}$$

Here $n_F(\epsilon)$ is the Fermi-Dirac distribution function for the electrons. General arguments show that Eq. (1.1) is true whenever the many-body Hamiltonian can be decomposed into a sum of single-particle Hamiltonians.[16] Jonson and Mahan[17] showed that Mott's relationship and the Wiedemann-Franz law are valid for an electron-phonon impurity system in the static phonon approximation. Within classical transport theory one can derive that Eq. (1.1) holds if the scattering of the electrons is elastic.[18] Electron-phonon scattering is not elastic at low and intermediate temperatures. It is therefore interesting to study the diffusion thermopower in a wider temperature range.

Unfortunately, S_d is not directly accessible by experiment because the experimental results always contain both phonon drag and diffusion thermopower. The extraction of S_d is believed to be possible in the extreme regions of low and high temperature.[19] In the intermediate region S_d remains essentially hidden. For a smooth variation of the density of states near the Fermi energy and the absence of resonant bound states near ϵ_F, one expects a smooth variation of the energy-dependent conductivity $\sigma(\epsilon)$. This gives a weak temperature dependence of its energy derivative. Therefore, we infer from Mott's relationship a linear temperature dependence of the diffusion thermopower, especially in the low-temperature region. Here a plot of S/T versus T^2 shall give a straight line. Its intersection with the S/T axis gives S_d/T and its slope is proportional to the phonon drag contribution.[19] Systematic deviations from the straight line are reported by De Vroomen *et al.*[10] However, the experimental points usually follow a straight line.[20]

The calculation of the thermopower is a transport problem and therefore can be solved either with Kubo's formulation of linear response or a Boltzmann-type transport equation. In a recent series of papers, Mahan and Hänsch[7,21,22] derived and applied a modified transport equation for a many-body system. In Ref. 22 we have shown for several examples that this new transport equation gives results which are equivalent to that derived from Kubo's formula. In Ref. 7 we included a magnetic field and could confirm the suggestion of Opsal *et al.*[6] concerning the electron-phonon mass enhancement of the low-temperature diffusion power in high magnetic fields. This work was based on the validity of Mott's relationship. More recently, Mahan[23] used that formulation to explain the linear magnetic field dependence of the longitudinal magnetoresistivity. All of these examples show that the new transport equation provides a good tool to calculate transport properties in many-body systems.

So far we have not included a temperature gradient and therefore were unable to calculate the thermopower directly. We will do this here.

The organization of this paper is as follows. In Sec. II we will reformulate the theory extensively described in Ref. 22 when a temperature gradient is present. In Sec. III we will discuss some limiting cases of the resulting equations and their consequences on the diffusion thermopower. For the simple model of a free-electron gas interacting with static impurities and longitudinal Debye phonons, we calculate the temperature dependence of the diffusion thermopower over a wide range of temperature in Sec. IV. This work closes in Sec. V with a summary and a discussion of our findings.

II. TRANSPORT EQUATION WITH $\Delta T \neq 0$

To derive a transport equation for the many-body distribution function $n(\vec{R},\tau,\vec{k},\omega)$, we have used a nonequilibrium formulation of statistical mechanics as given, for instance, by Kadanoff and Baym[24] and Keldysh.[25] In Refs. 7 and 22 a detailed account of the calculations is given. We briefly summarize these here. Because energy and momentum are independent variables in a many-body system, we have to retain this independence in the distribution function too. In contrast to the classical distribution function, its many-body counterpart depends now on four variables: space $(\vec{R})$, time (τ), momentum $(\vec{k})$, and energy (ω). Once $n(\vec{R},\tau,\vec{k},\omega)$ is known, we can calculate the generated currents. For the charge current we have, for instance,

$$\vec{j}(\vec{R},\tau) = e\sum_{\vec{k}} \int \frac{d\omega}{2\pi} \vec{v}_k n(\vec{R},\tau,\vec{k},\omega) \ . \tag{2.1}$$

Both the Kadanoff and Baym[24] and the Keldysh[25] formulation are equivalent.[26] The latter resembles the ordinary equilibrium statistical mechanics. That means diagrammatic representation of perturbation theory is possible and Dyson's equation holds. We only have to replace all quantities like Green's functions and self-energies with 2×2 matrices. For the Green's function, for example, the diagonal elements are the causal and anticausal Green's functions G and $\overline{G}$, respectively, and the nondiagonal parts $G^<$ and $G^>$ are related to the many-body distribution function. In particular we have

$$n(\vec{R},\tau,\vec{k},\omega) = -iG^<(\vec{R},\tau,\vec{k},\omega) \ , \tag{2.2}$$

It is convenient to work in Wigner coordinates, which are center-of-mass $(\vec{R},\tau)$ and relative $(\vec{r},t)$ coordinates. The transport equation is then derived by using a gradient-expansion technique for the center-of-mass coordinates and Fourier transform $(\vec{r},t)$. So far we have only calculated $G^<$ self-consistently for a homogeneous and static electromagnetic field[27] as generated by a vector potential $\vec{A}(\vec{R},\tau)$.[28] Because the fields always appear in connection with the generalized velocity, we employ the transformation $\vec{k}-(e/c)\vec{A}(\vec{R},\tau)\rightarrow\vec{k}$, and therefore shift the field dependence to the space and time derivatives. Finally, we linearize in the fields and diffusion terms [compare Eq. (2.27) in Ref. 7]. For a metal, where we neglect the momentum dependence of the self-energies, we obtain in the steady state $(\tau\rightarrow\infty)$ and zero magnetic field

$$e\vec{E}\cdot\vec{v}\,\mathrm{Im}\Sigma^r \frac{\partial n_F(\omega)}{\partial\omega} A^2 = G^>\Sigma^< - \Sigma^> G^< \ . \tag{2.3}$$

On the left-hand side, Eq. (2.3) shows the drift of the electrons in an electric field. Here A is the exact spectral function of the electrons, $\mathrm{Im}\Sigma^r$ the imaginary part of their retarded self-energy, and $\vec{v}$ their velocity $\vec{v}=\vec{\nabla}_{\vec{k}}\epsilon(k)$. The right-hand side exhibits the force counterbalancing the drift of the electrons. It is attributed to the interaction of the electrons with, for example, phonons and/or impurities and corresponds to the transport relaxation time τ_{tr}^{-1}. The generalization to include a temperature gradient is straightforward as well. The nonequilibrium propagator is a time-ordered product of an electron creation and destruction operator $\psi^\dagger$ and ψ, respectively,

$$G(x_1,x_2) = -i\langle T[\Psi(x_1)\Psi^\dagger(x_2)]\rangle, \quad x=(\vec{r},t) \tag{2.4}$$

where the time-ordering operator acts on a different contour than the equilibrium one and therefore produces the matrix structure.[25] This is not important for the following. The expectation value is different from zero only in the region $|\vec{r}_1-\vec{r}_2|<l$, where l is the mean free path of the electrons. Even if this is large on a microscopic scale, as a few thousand or ten thousand angstroms, it is still small on a macroscopic one. If there is no appreciable

change in the temperature over that distance, it is legitimate to introduce a local temperature field $T(\vec{R})$, $\vec{R}=\frac{1}{2}(\vec{r}_1+\vec{r}_2)$. If this is not possible, the evaluation of the expectation value might not be defined. The introduction of a temperature field in that way gives another dependence of the Green's function in the center-of-mass set of the Wigner variables; we have to replace $\vec{\nabla}_{\vec{R}}\rightarrow\vec{\nabla}_{\vec{R}}+(\vec{\nabla}_{\vec{R}}T)\partial/\partial T$, wherever it appears during the calculation. Therefore, we produce an additional term on the left-hand side of Eq. (2.3):

$$e\vec{E}\cdot\vec{v}\,\mathrm{Im}\Sigma^{r}\frac{\partial n_F(\omega)}{\partial\omega}A^2+\frac{\vec{\nabla}T}{T}\cdot\vec{v}\omega\,\mathrm{Im}\Sigma^{r}\frac{\partial n_F(\omega)}{\partial\omega}A^2 =G^{>}\Sigma^{<}-\Sigma^{>}G^{<}\ . \quad (2.5)$$

The new term describes the effect of a temperature gradient on the electrons. In the quasiparticle approximation, the left-hand side duplicates the driving term in the Boltzmann equation.[29] In a many-body system, however, we have to keep the independence of energy and momentum. We will solve Eq. (2.5) self-consistently with the ansatz

$$\begin{aligned}G^{<}(\vec{k},\omega)=iA(\vec{k},\omega)n_F(\omega)-ie\vec{E}\cdot\vec{v}_{\vec{k}}&\\ \times\frac{\partial n_F(\omega)}{\partial\omega}A(\vec{k},\omega)\Lambda(\vec{k},\omega)&\\ +i\frac{\vec{\nabla}T}{T}\cdot\vec{v}_{\vec{k}}\omega\frac{\partial n_F(\omega)}{\partial\omega}A(\vec{k},\omega)\Phi(\vec{k},\omega)\ .&\quad (2.6)\end{aligned}$$

We dropped the dependence on $\vec{R}$ and τ because we consider now only the steady-state and homogeneous driving fields. From our previous work on the dc conductivity in metals[21] we know that Λ has the meaning of a vertex function for charge transport. We can interpret Φ in a quite similar way as the vertex function for energy transport.[30] In the quasiparticle approximation both are the same.[21] In many-body systems, however, one has to distinguish them. As shown by Jonson and Mahan,[17] it is just their difference that gives the correct results in the well-understood special cases of elastic scattering. In the next section we will reveal the results presented by Jonson and Mahan.[17]

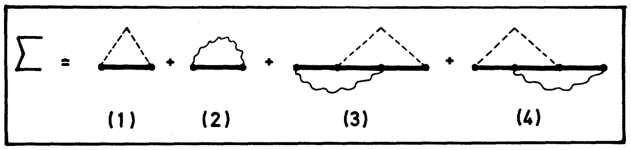

FIG. 1. Self-energy diagrams up to first order; average over randomly distributed impurities (dashed lines); phonon propagator (wavy lines); electron propagator (double lines).

We now specify the self-energy for the electrons interacting with static impurities and longitudinal phonons. One is tempted to follow the usual argument, keeping the lowest-order terms only. These are the first two diagrams shown in Fig. 1. This cannot be done without a word of caution. Due to the nature of the thermopower, it is determined by energy derivatives of certain quantities and not their magnitude. This makes a rigorous use of Midgal's theorem difficult because it states the relative magnitudes of higher-order phonon contributions and says nothing about their energy dependence. However, we follow the argument by Vilenkin and Taylor[5] and neglect higher-order phonon contributions. This is more a compromise between correctness and tractability than a justified approximation. A more serious matter is the interference diagrams shown as third and fourth contribution in Fig. 1. Even if we stay in lowest order they are present. Although they do not contribute to the conductivity, they do have, at least at zero temperature, a nonnegligible energy derivation at $\omega=0$. In fact, they enter, as shown by Krempasky and Schmid,[13] as vertex corrections to the impurity scattering. We show in Appendix A that this correction is less important for finite frequencies. To be consistent we also have to consider these contributions in the nonequilibrium self-energies $\Sigma^{>,<}$. As we show in Appendix B, their contribution is less important and can be neglected. Neglecting the interference diagrams, therefore, causes uncertainties whenever we have to take the static limit of an energy derivative of the imaginary part of the electron's self-energy. We will see that this does not influence the problem we are facing. With all of this in mind we can follow the calculations of Ref. 22 and derive equations for Λ and Φ:

$$\begin{aligned}X^{n}(\vec{k},\omega)=\tfrac{1}{2}\omega^{n}A(\vec{k},\omega)+\frac{1}{2\Gamma(\omega)}\sum_{\vec{q}}|V(\vec{q})|^{2}\frac{\vec{v}_{\vec{k}}\cdot\vec{v}_{\vec{k}+\vec{q}}}{\vec{v}_{\vec{k}}^{\,2}}A(\vec{k}+\vec{q},\omega)X^{n}(\vec{k}+\vec{q},\omega)&\\ +\frac{1}{2\Gamma(\omega)}\sum_{\vec{q}}|M_{\vec{q}}|^{2}\frac{\vec{v}_{\vec{k}}\cdot\vec{v}_{\vec{k}+\vec{q}}}{\vec{v}_{\vec{k}}^{\,2}}\Big\{A(\vec{k}+\vec{q},\omega+\omega_{\vec{q}})X^{n}(\vec{k}+\vec{q},\omega+\omega_{\vec{q}})[n_B(\omega_{\vec{q}})+n_F(\omega+\omega_{\vec{q}})]&\\ +A(\vec{k}+\vec{q},\omega-\omega_{\vec{q}})X^{n}(\vec{k}+\vec{q},\omega-\omega_{\vec{q}})\{n_B(\omega_{\vec{q}})+[1-n_F(\omega-\omega_{\vec{q}})]\}\Big\}\ ,&\end{aligned} \quad (2.7)$$

where we have used

$$X^{n=0}(\vec{k},\omega)=\Lambda(\vec{k},\omega)\ , \quad (2.8a)$$

$$X^{n=1}(\vec{k},\omega)=\Phi(\vec{k},\omega)\ . \quad (2.8b)$$

The second term in Eq. (2.7) is attributed to electron-impurity scattering with its matrix element $V(\vec{q})$ and the impurity concentration n_i. The third term describes electron-phonon scattering. $M_{\vec{q}}$ is the corresponding interaction matrix element, $n_B(\omega)$ is the Bose-Einstein distribution function for the phonons, and $\Gamma = -\mathrm{Im}\Sigma^r$.

The vertex functions Λ and Φ are related to the diffusion power S_d by virtue of Eqs. (2.1), (2.2), and (2.6):

$$S_d = \frac{\pi^2}{3}\frac{k_B^2 T}{e}\left.\frac{\dfrac{\partial}{\partial\omega}\sum_{\vec{k}}\vec{v}_{\vec{k}}^{\,2}A(\vec{k},\omega)\Phi(\vec{k},\omega)}{\sum_{\vec{k}}\vec{v}_{\vec{k}}^{\,2}A(\vec{k},\omega)\Lambda(\vec{k},\omega)}\right|_{\omega=0} . \tag{2.9}$$

To derive Eq. (2.9) we further assumed that both the electrical field and the temperature gradient are parallel. Equation (2.9) turns into Mott's relationship whenever $\Phi = \Lambda$. We separate the major part of the momentum dependence in Φ and Λ coming from the spectral function $A(\vec{k},\omega)$. With the new, only weakly-momentum-dependent functions $\overline{\Phi}$ and $\overline{\Lambda}$,[32]

$$\Lambda(\vec{k},\omega) = \tfrac{1}{2}A(\vec{k},\omega) + \frac{1}{2\Gamma(\omega)}[\overline{\Lambda}(\vec{k},\omega) - 1] , \tag{2.10a}$$

$$\Phi(\vec{k},\omega) = \tfrac{1}{2}A(\vec{k},\omega) + \frac{1}{2\Gamma(\omega)}[\overline{\Phi}(\vec{k},\omega) - 1] , \tag{2.10b}$$

we obtain from Eq. (2.8) in the limit $\Gamma \ll \epsilon_F$,

$$\begin{aligned}\overline{X}^n(\vec{k},\omega) = \omega^n &+ \tfrac{1}{2}n_i\sum_{\vec{q}} |V(\vec{q})|^2 \frac{\vec{v}_{\vec{k}}\cdot\vec{v}_{\vec{k}+\vec{q}}}{\vec{v}_{\vec{k}}^{\,2}} A(\vec{k}+\vec{q},\omega)\frac{\overline{X}^n(\vec{k}+\vec{q},\omega)}{\Gamma(\omega)} \\ &+ \tfrac{1}{2}\sum_{\vec{q}} |M_{\vec{q}}|^2 \frac{\vec{v}_{\vec{k}}\cdot\vec{v}_{\vec{k}+\vec{q}}}{\vec{v}_{\vec{k}}^{\,2}} \left[A(\vec{k}+\vec{q},\omega+\omega_{\vec{q}})\frac{\overline{X}^n(\vec{k}+\vec{q},\omega+\omega_{\vec{q}})}{\Gamma(\omega+\omega_{\vec{q}})}[n_B(\omega_{\vec{q}}) + n_F(\omega+\omega_{\vec{q}})] \right. \\ &\qquad\qquad \left. + A(\vec{k}+\vec{q},\omega-\omega_{\vec{q}})\frac{\overline{X}^n(\vec{k}+\vec{q},\omega-\omega_{\vec{q}})}{\Gamma(\omega-\omega_{\vec{q}})}[n_B(\omega_{\vec{q}}) + 1 - n_F(\omega-\omega_{\vec{q}})] \right] . \end{aligned} \tag{2.11}$$

Although Eq. (2.11) still contains the full momentum dependence of the problem it is usually weak. Therefore, proceeding with Eq. (2.9), we replace $\overline{\Lambda}(\vec{k},\omega)$ and $\overline{\Phi}(\vec{k},\omega)$ by their momentum averages over the Fermi surface. Inserting now Eqs. (2.10a) and (2.10b) we derive for the diffusion thermopower

$$S_d = \frac{\pi^2}{3}\frac{k_B^2 T}{e\epsilon_F}\left.\left[\left\{[1+\lambda]\eta - \epsilon_F\frac{\Gamma(\omega)'}{\Gamma(\omega)}\right\}\frac{\overline{\Phi}(\omega)}{\overline{\Lambda}(\omega)} + \epsilon_F\frac{\overline{\Phi}(\omega)'}{\overline{\Lambda}(\omega)}\right]\right|_{\omega=0} , \tag{2.12}$$

$$\eta = \left.\frac{\partial \ln v(\epsilon)}{\partial \ln\epsilon}\right|_{\epsilon=\epsilon_F} . \tag{2.13}$$

Here the prime means the derivative with respect to ω, $v(\epsilon)$ is the average of $v_k = |\vec{\nabla}_k\epsilon(\vec{k})|$ over a surface of constant energy, and λ is the energy derivative of the real part of the electron's retarded self-energy. That is, $1+\lambda$ is essentially the electron-phonon mass enhancement factor. To derive Eq. (2.12), we assumed momentum-independent self-energies and again $\Gamma \ll \epsilon_F$. Both are usually fulfilled to a high degree in metals. Therefore we believe that Eq. (2.12) shall give a good starting point to discuss the diffusion thermopower in metals. A closer inspection of Eq. (2.12) is worthwhile. In the first place it is interesting to study its deviations from Mott's relationship as given by Eq. (1.1). The energy-dependent part of the conductivity is easily inferred from Eqs. (2.5) and (2.6) with $\vec{\nabla}T = 0$. As a result, we obtain

$$\sigma(\omega) \sim \sum_{\vec{k}} \vec{v}_{\vec{k}}^{\,2} A(\vec{k},\omega)\frac{\overline{\Lambda}(\vec{k},\omega)}{\Gamma(\omega)} , \tag{2.14}$$

where $\overline{\Lambda}(\vec{k},\omega)$ is again the solution of Eq. (2.11) with $n = 0$. This gives, by virtue of Eq. (1.1),

$$S_d = \frac{\pi^2}{3}\frac{k_B^2 T}{e\epsilon_F}\left.\left[\left\{(1+\lambda)\eta - \epsilon_F\frac{\Gamma(\omega)'}{\Gamma(\omega)}\right\} + \epsilon_F\frac{\overline{\Lambda}(\omega)'}{\overline{\Lambda}(\omega)}\right]\right|_{\omega=0} . \tag{2.15}$$

Comparison of Eqs. (2.12) and (2.15) shows clearly where we can expect deviations: The static limit of the ratios $\overline{\Phi}/\overline{\Lambda}$ and $\overline{\Phi}'/\overline{\Lambda}'$. The physical reason for this comes from the differences of the charge and energy transport vertex functions as discussed earlier. We notice that the quantity in parentheses is the same for Eqs. (2.12) and (2.15). The electron-phonon mass enhancement appears also in Mott's relationship, evaluated in a proper way. Unfortunately, the mass enhancement is not the only contribution. As we see, the other term comes from the energy derivative of the imaginary part of the electron's self-energy. Within our model this contribution is negligible because the impurity part is only very weakly energy dependent and its derivative therefore vanishes. The phonon part is an even function of energy and therefore its derivative vanishes at $\omega=0$ exactly. This situation is quite different, at least at low temperatures, when we include the interference diagrams. In the static limit, $\omega\to 0$, the expression $\epsilon_F\Gamma'/\Gamma$ does not vanish. It is proportional to the electron-phonon coupling strength λ [see Eq. (A11)]. This compensates, in part, the mass enhancement factor, which is multiplied by the structure-dependent quantity η. We have to leave the discussion here because, as it turns out, an important contribution is still missing. At this point, we would like to emphasize that we do not want to give a quantitative calculation of the diffusion thermopower, rather, we concentrate our effort on investigating the deviations from Mott's relationship which are exhibited in the ratios $\overline{\Phi}(0)/\overline{\Lambda}(0)$ and $\overline{\Phi}(0)'/\overline{\Lambda}(0)'$.

III. SPECIAL CASES

In this section we discuss some special solutions of Eq. (2.4) presented in Sec. II. We derive nothing new here, but only reproduce already well-known results in a somewhat different way. The rationale is to show that our more unfamiliar many-body approach gives results which are comparable to or equal to the sophisticated methods used in evaluating Kubo's formula. Particularly interesting cases are impurity scattering, the static phonon approximation, and the high-temperature phonon scattering limit. In all these cases scattering of the electrons is elastic and therefore Mott's relationship is assumed to be true. In the language of the usual linear-response theory the diffusion thermopower is expressed through the ratio of the charge-current—charge-current and charge-current—heat-current correlation functions L_{QQ} and L_{QE}, respectively,[32,33]

$$S_d=L_{QE}/L_{QQ}\ . \tag{3.1}$$

The interesting point in evaluating these correlation functions is that the heat-current operator is not given by its classical equivalent:

$$\vec{j}_E=\sum_{\vec{k}}\vec{v}_{\vec{k}}(\epsilon(\vec{k})-\epsilon_F)c^{\dagger}_{\vec{k}}c_{\vec{k}}\ . \tag{3.2}$$

Here $c^{\dagger}_{\vec{k}}$ ($c_{\vec{k}}$) is a creation (destruction) operator of an electron in state k. There are additional terms caused by the interaction of the electrons with phonons and/or impurities.[32] Only if these new terms are included one can derive the correct result.[17] The reproduction of Jonson and Mahan's[17] result is quite simple in our formulation. The limit of static phonon means to neglect the phonon frequency $\omega_{\vec{q}}$ whenever it appears in connection with other energies. We do not want to discuss the validity of this approximation here, but refer it to Ref. 17. As a result we obtain from Eq. (2.11),

$$\overline{X}^{n=0}(\vec{k},\omega)=\frac{\overline{X}^{n=1}(\vec{k},\omega)}{\omega}\ , \tag{3.3}$$

or in the notation introduced in Eq. (2.8),

$$\overline{\Lambda}(\vec{k},\omega)=\overline{\Phi}(\vec{k},\omega)\ . \tag{3.4}$$

Mott's relationship holds true.

Another interesting example is the high-temperature limit. Here electron-phonon scattering dominates and we can neglect the impurity part. For high temperatures we have for the statistical factors

$$\begin{aligned}&n_B(\omega_{\vec{q}})+n_F(\omega+\omega_{\vec{q}})\to\frac{k_BT}{\omega_{\vec{q}}}\ ,\\ &n_B(\omega_{\vec{q}})+[1-n_F(\omega-\omega_{\vec{q}})]\to\frac{k_BT}{\omega_{\vec{q}}}\ ,\end{aligned} \tag{3.5}$$

and for the imaginary part of the electron's self-energy

$$\Gamma(\omega)\to\tfrac{1}{2}\Gamma_0k_BT\ . \tag{3.6a}$$

Γ_0 is a frequency-independent constant. Inserting Eqs. (3.5) and (3.6a) in Eq. (2.11) and neglecting the impurity term, we obtain

$$\overline{\Lambda}(\vec{k},\omega)=1+\frac{1}{\Gamma_0}\sum_{\vec{q}}\left|\frac{M_{\vec{q}}}{\omega_{\vec{q}}}\right|^2\frac{\vec{v}_{\vec{k}}\cdot\vec{v}_{\vec{k}+\vec{q}}}{\vec{v}_k^{\,2}}[A(\vec{k}+\vec{q},\omega+\omega_{\vec{q}})\overline{\Lambda}(\vec{k}+\vec{q},\omega+\omega_{\vec{q}})+A(\vec{k}+\vec{q},\omega-\omega_{\vec{q}})\overline{\Lambda}(\vec{k}+\vec{q},\omega-\omega_{\vec{q}})]\ , \tag{3.6b}$$

$$\begin{aligned}\omega\overline{\Phi}(\vec{k},\omega)=\omega+\frac{1}{\Gamma_0}\sum_{\vec{q}}\left|\frac{M_{\vec{q}}}{\omega_{\vec{q}}}\right|^2\frac{\vec{v}_{\vec{k}}\cdot\vec{v}_{\vec{k}+\vec{q}}}{\vec{v}_{\vec{k}}^{\,2}}&[A(\vec{k}+\vec{q},\omega+\omega_{\vec{q}})(\omega+\omega_{\vec{q}})\overline{\Phi}(\vec{k}+\vec{q},\omega+\omega_{\vec{q}})\\ &+A(\vec{k}+\vec{q},\omega-\omega_{\vec{q}})(\omega-\omega_{\vec{q}})\overline{\Phi}(\vec{k}+\vec{q},\omega-\omega_{\vec{q}})]\ .\end{aligned} \tag{3.6c}$$

Differentiating Eq. (3.6c) with respect to ω we derive an equation which is already close to Eq. (3.6b):

$$\begin{aligned}[\omega\overline{\Phi}(\vec{k},\omega)]'=1+\frac{1}{\Gamma_0}\sum_{\vec{q}}\left|\frac{M_{\vec{q}}}{\omega_{\vec{q}}}\right|^2\frac{\vec{v}_{\vec{k}}\cdot\vec{v}_{\vec{k}+\vec{q}}}{\vec{v}_k^{\,2}}&\{A(\vec{k}+\vec{q},\omega+\omega_{\vec{q}})[(\omega+\omega_{\vec{q}})\overline{\Phi}(\vec{k}+\vec{q},\omega+\omega_{\vec{q}})]'\\ &+A(\vec{k}+\vec{q},\omega-\omega_{\vec{q}})[(\omega-\omega_{\vec{q}})\overline{\Phi}(\vec{k}+\vec{q},\omega-\omega_{\vec{q}})]'\}\end{aligned}$$

$$+\frac{1}{\Gamma_0}\sum_{\vec{q}}\left|\frac{M_{\vec{q}}}{\omega_{\vec{q}}}\right|^2\frac{\vec{v}_{\vec{k}}\cdot\vec{v}_{\vec{k}+\vec{q}}}{\vec{v}_k^{\,2}}\{A(k+\vec{q},\omega+\omega_{\vec{q}})'[(\omega+\omega_{\vec{q}})\Phi(\vec{k}+\vec{q},\omega+\omega_{\vec{q}})]$$

$$+A(\vec{k}+\vec{q},\omega-\omega_{\vec{q}})'[(\omega-\omega_{\vec{q}})\overline{\Phi}(\vec{k}+\vec{q},\omega-\omega_{\vec{q}})]\}\ . \tag{3.7}$$

In Eq. (3.7) the last term is of order ω_D/ϵ_F smaller than the second. We neglect this term and find by inspection

$$\overline{\Lambda}(\vec{k},\omega)=[\omega\overline{\Phi}(\vec{k},\omega)]'\ , \tag{3.8}$$

which gives in the static limit $\overline{\Lambda}(\vec{k},0)=\overline{\Phi}(\vec{k},0)$. A similar discussion of the first energy derivative of Eq. (3.6b) and the second energy derivative of Eq. (3.6c) gives

$$\overline{\Lambda}(\vec{k},\omega)'=\tfrac{1}{2}[\omega\overline{\Phi}(\vec{k},\omega)]''\ , \tag{3.9}$$

which is in the static limit $\overline{\Lambda}(\vec{k},0)'=\overline{\Phi}(\vec{k},0)'$. As we expected, Mott's relationship is valid in the high-temperature limit. An interesting observation, however, is that in contrast to the impurity limit, charge and energy vertex functions are in general not the same. They have the same value only in the static limit.

Another interesting feature we can study in the high-temperature limit are the magnitudes of $\overline{\Lambda}(0)$ and $\overline{\Lambda}(0)'$. To this end we write the vertex function $\overline{\Lambda}$ in the following form:

$$\overline{\Lambda}(\vec{k},\omega)=\overline{\Lambda}_0(\vec{k},\omega)+\frac{\omega}{\epsilon_F}\overline{\Lambda}_1(\vec{k},\omega) \tag{3.10}$$

and consider $\overline{\Lambda}_0$ and $\overline{\Lambda}$ as constants. This is a plausible approximation considering the weak frequency dependence of the self-energy at high temperatures. Inserting Eq. (3.10) into Eq. (3.5) and differentiating once with respect to ω we obtain

$$\overline{\Lambda}_1=\overline{\Lambda}_0^2\frac{\epsilon_F}{\Gamma}\frac{\partial}{\partial\epsilon_{\vec{k}}}\left[-\frac{\mathrm{Im}\Sigma^r(\vec{k},\omega)}{T}\right]. \tag{3.11}$$

In Eq. (3.11) we cannot neglect the momentum dependence of the self-energy because its derivative with respect to k is multiplied by the large number ϵ_F/Γ, and therefore the product can give a finite non-negligible number. To estimate an order of magnitude we replace the momentum derivative $\partial/\partial\epsilon_k\rightarrow 1/2\epsilon_F$.[34] Large and small numbers cancel, and the result is

$$\overline{\Lambda}_1\simeq\tfrac{1}{2}\overline{\Lambda}_0^2 \tag{3.12}$$

and

$$S_d^{T\rightarrow\infty}=\frac{\pi}{3}\frac{k_B^2T}{e\epsilon_F}\eta(1+\overline{\Lambda}_0^{T\rightarrow\infty}/2\eta) \tag{3.13}$$

for the diffusion power, using Eq. (2.15). In a very similar way, we can derive the low-temperature limit of S_d. To do this we neglect the phonon scattering term in Eq. (2.11), which means a restriction to the residual resistivity region, where impurity scattering dominates the transport relaxation:

$$S_d^{T=0}=\frac{\pi}{3}\frac{k_B^2T}{\epsilon_F}\eta(1+\lambda)(1+\overline{\Lambda}^{T=0}/2\eta)\ . \tag{3.14}$$

Equation (3.14) has been derived within our approximation of neglecting the interference diagrams. Although they do not contribute significantly to the scattering term, their influence on the imaginary part of the electron's self-energy is important whenever we have to calculate its energy derivative in the static limit. If we include them initially, the ratio Γ'/Γ in Eq. (2.15) does not disappear. According to Eq. (A11) it gives a finite correction term. However, we produce the very same term in calculating $\overline{\Lambda}'/\overline{\Lambda}$; therefore it does not contribute [compare Eq. (4.9)], and Eq. (3.14) holds true again.

In both limits, very high and very low temperatures, the vertex function $\overline{\Lambda}$ has a simple meaning: It is the ratio of the transport relaxations time τ_{tr} and the quasiparticle lifetime τ. They are in general different because in τ_{tr} large-angle scattering is favored over small-angle scattering.

Although we disregarded the phonon scattering term in Eq. (2.9) to derive Eq. (3.14), phonon effects remain present in the low-temperature or impurity-dominated region. The mass enhancement factor is usually not directly apparent in experiments with zero magnetic fields in simple metals. However, there is evidence that the temperature dependence of the thermopower of amorphous metals follows that of the electron-phonon mass enhancement factor closely.[8,9] Here the transport is controlled by impurity scattering over a wide temperature range and phonon scattering is of minor importance, so that Eq. (3.14) might be valid over a considerable temperature range.

IV. A SIMPLE MODEL

We now turn to the solution of Eq. (2.11). This gives both the vertex functions $\overline{\Lambda}(n=0)$ and $\overline{\phi}(n=1)$. In general such a task is a very complicated problem. Solutions of similar equations can be found in the literature on transport phenomena in electron-phonon systems.[35] Usually only the vertex functions are needed and not their energy derivatives. This is not the case in the problem under investigation, although we have shown in the preceding section that the energy derivative of the vertex function is of order ω_D/ϵ_F. This smallness is compensated by the multiplication with ϵ_F [compare Eqs. (2.12) and (2.15)] and, as it turns out, gives the dominant contribution at high temperatures. Therefore, we have to repeat all steps leading to the standard form of a Fredholm integral equation for the vertex functions $\overline{\Lambda}$ and $\overline{\Phi}$ and collect contributions of order ω_D/ϵ_F which are usually neglected.[32] We will not do this in the most general form possible but for a special model of free electrons interacting with static impurities and Debye phonons. For convenience, we also consider a constant electron-phonon matrix element. Although this last approximation is certainly poor for a quantitative analysis, it should reflect the qualitative behavior well enough.[36] Of course this model oversimplifies reality, but might have some merit in the low-temperature limit in simple metals. However, at the end of this section we will give some arguments of how an extension to a more realistic situation can be accomplished.

To solve Eq. (2.11) we use a product ansatz of the form (for the moment we will consider $n=0$ only)

$$\overline{\Lambda}(\vec{k},\omega)=\chi(\vec{k},\omega)R(\vec{k},\omega)\ . \tag{4.1}$$

The function χ is supposed to solve the impurity part in the absence of phonon scattering:

$$\chi(\vec{k},\omega)=1+\tfrac{1}{2}n_i\sum_{\vec{q}}|V(\vec{q})|^2\frac{\vec{v}_{\vec{k}}\cdot\vec{v}_{\vec{k}+\vec{q}}}{\vec{v}_{\vec{k}}^{\,2}}\times A(\vec{k}+\vec{q},\omega)\frac{\chi(\vec{k}+\vec{q},\omega)}{\Gamma(\omega)}\ . \tag{4.2}$$

For free electrons Eq. (4.2), evaluated at $k=k_F$, turns into

$$\chi(k_F,\omega)=1+\frac{n_i}{8\pi^2}\int_0^\infty\frac{dq\,q}{v_F}|V(q)|^2\int_{\epsilon_q-v_Fq}^{\epsilon_q+v_Fq}d\xi\left[1-\frac{1}{2}\left[\frac{q}{k_F}\right]^2+\frac{\xi}{2\epsilon_F}\right]A(\xi,\omega)\frac{\chi(\xi=0,\omega)}{\Gamma(\omega)}\ . \tag{4.3}$$

In the limit of weak momentum dependence of χ, this can be expressed after a rearrangement by

$$\chi(\omega)=\frac{\Gamma(\omega)}{\Gamma^{\mathrm{ph}}(\omega)+\Gamma_{\mathrm{tr}}^{\mathrm{im}}(\omega)},\quad\Gamma(\omega)=\Gamma^{\mathrm{ph}}(\omega)+\Gamma^{\mathrm{im}}(\omega)\ . \tag{4.4}$$

Here Γ is the total level broadening by the interactions. The superscripts ph and im refer to the phonon and impurity part, respectively. The subscript tr means the corresponding transport broadening. For the impurity part we obtain

$$\begin{aligned}\Gamma^{\mathrm{im}}(\omega)&=\frac{n_i}{8\pi^2}\int_0^\infty\frac{dq\,q}{v_F}|V(q)|^2\int_{\epsilon_q-v_Fq}^{\epsilon_q+v_Fq}d\xi\,A(\xi,\omega)\ ,\\ \Gamma_{\mathrm{tr}}^{\mathrm{im}}(\omega)&=\frac{n_i}{16\pi^2}\int_0^\infty\frac{dq\,q}{v_F}|V(q)|^2\int_{\epsilon_q-v_Fq}^{\epsilon_q+v_Fq}d\xi\left[\left[\frac{q}{k_F}\right]^2-\frac{\xi}{\epsilon_F}\right]A(\xi,\omega)\ ,\end{aligned} \tag{4.5}$$

and for its energy derivatives

$$\begin{aligned}&\Gamma^{\mathrm{im}}(\omega)'=0\ ,\\ &\Gamma_{\mathrm{tr}}^{\mathrm{im}}(\omega)'=-\frac{1+\lambda}{2\epsilon_F}\Gamma^{\mathrm{im}}(\omega)\ .\end{aligned} \tag{4.6}$$

For the energy derivative of $\chi(\omega)|_{\omega=0}$ we get by virtue of Eqs. (4.4) and (4.6)

$$\chi(\omega)'|_{\omega=0}=\frac{1+\lambda}{2\epsilon_F}\frac{\Gamma^{\mathrm{im}}(\omega)}{\Gamma^{\mathrm{ph}}(\omega)+\Gamma_{\mathrm{tr}}^{\mathrm{im}}(\omega)}\chi(\omega)\bigg|_{\omega=0}\ . \tag{4.7}$$

In the limit of very low temperature the (transport) mean free path l (l_{tr}) is completely determined by impurity scattering, therefore the Eqs. (4.4) and (4.7) read

$$\chi(\omega)=\frac{\Gamma(\omega)}{\Gamma^{\mathrm{ph}}(\omega)+\epsilon_F/k_Fl_{\mathrm{tr}}}\ , \tag{4.8a}$$

$$\frac{\chi(\omega)'}{\chi(\omega)}=\frac{1+\lambda}{2\epsilon_F}\frac{\epsilon_F/k_Fl}{\Gamma^{\mathrm{ph}}(\omega)+\epsilon_F/k_Fl_{\mathrm{tr}}}\bigg|_{\omega=0}\ . \tag{4.8b}$$

In the limit where phonon scattering is absent, Eq. (4.8a) turns into the earlier mentioned result $\chi=\tau_{\mathrm{tr}}/\tau$. Equations (4.7) and (4.8b) are exact when we neglect contributions from the interference diagrams. As discussed in Sec. II, this approximation is usually a good one for nonzero frequency; however, Eqs. (4.7) and (4.8b) are evaluated in the limit $\omega=0$. To complete the analysis of the impurity part, we quote the result if the interference diagrams are included in the quasiparticle level broadening:

$$\frac{\chi(\omega)'}{\chi(\omega)}\bigg|_{\omega=0}=\frac{1+\lambda}{2\epsilon_F}\frac{\epsilon_F/k_Fl}{\Gamma^{\mathrm{ph}}(\omega)+\epsilon_F/k_Fl_{\mathrm{tr}}}+\frac{\Gamma(\omega)'}{\Gamma(\omega)}\bigg|_{\omega=0}\ . \tag{4.9}$$

The function R is essentially determined by the electron-phonon scattering. Inserting Eq. (4.1) together with Eq. (4.8a) into Eq. (2.11), we obtain an equation for R:

$$\begin{aligned}R(\vec{k},\omega)=1+\tfrac{1}{2}\sum_{\vec{q}}|M_{\vec{q}}|^2\frac{\vec{k}\cdot(\vec{k}+\vec{q})}{k^2}\bigg[&A(\vec{k}+\vec{q},\omega+\omega_{\vec{q}})\frac{R(\vec{k}+\vec{q},\omega+\omega_{\vec{q}})}{\Gamma^{\mathrm{ph}}(\omega+\omega_{\vec{q}})+\epsilon_F/k_Fl_{\mathrm{tr}}}(\cdots)\\ &+A(\vec{k}+\vec{q},\omega-\omega_{\vec{q}})\frac{R(\vec{k}+\vec{q},\omega-\omega_{\vec{q}})}{\Gamma^{\mathrm{ph}}(\omega-\omega_{\vec{q}})+\epsilon_F/k_Fl_{\mathrm{tr}}}(\cdots)\bigg]\ .\end{aligned} \tag{4.10}$$

To derive Eq. (4.10) we have assumed that $R(\vec{k},\omega)$ depends only weakly on momentum. The ellipses represent the statistic factors as given in Eq. (2.11).

A very similar equation can be derived from the $n=1$ component of Eq. (2.11). Corresponding to Eq. (4.1), we call the phonon part $Q(\vec{k},\omega)$. In the new notation the thermopower reads

$$S_d=\frac{\pi^2}{3}\frac{k_B^2T}{e\epsilon_F}\eta\left[\left[(1+\lambda)+\frac{\epsilon_F X(\omega)'}{\eta X(\omega)}-\frac{\epsilon_F\Gamma(\omega)'}{\eta\Gamma(\omega)}\right]\frac{Q(\omega)}{R(\omega)}+\frac{\epsilon_F Q(\omega)'}{\eta R(\omega)}\right]\Bigg|_{\omega=0} . \tag{4.11}$$

The term in brackets is attributed to impurity scattering alone and contains only information about the elastic scattering channel. The inelastic and more interesting contributions in our context are represented by the ratios Q/R and Q'/R. If we exclude systems with magnetic impurities, causing Kondo anomalies, it is not completely farfetched to assume that the impurity part, or the elastic channel, will determine the low-temperature magnitudes of S_d. In the high-temperature limit this quantity is decreasing with temperature and eventually gives one. By virtue of Eqs. (4.9) and (4.11) we finally derive for the diffusion thermopower

$$S_d=\frac{\pi^2}{3}\frac{k_BT}{e\epsilon_F}\eta\left[(1+\lambda)\left[1+\frac{1}{2\eta}\frac{\epsilon_F/k_Fl}{\Gamma^{\mathrm{ph}}(\omega)+\epsilon_F/k_Fl_{\mathrm{tr}}}\right]\frac{Q(\omega)}{R(\omega)}+\frac{\epsilon_F Q(\omega)'}{\eta R(\omega)}\right]\Bigg|_{\omega=0} . \tag{4.12}$$

Our discussion of the diffusion thermopower is based on this equation. We now have to calculate R, Q, and their derivatives at $\omega=0$. Assuming, as is usually true in simple metals, only a weak $\vec{k}$ dependence of $R(\vec{k},\omega)$ we can disregard it completely[21,22] and set $k=k_F$. In the now standard procedure we derive, for $R(\omega)=R(k_F,\omega)$ keeping terms of order ω_D/ϵ_F,

$$\begin{aligned}R(\omega)=1&+\frac{1}{4\pi}\int_{\omega/v_F}^{2k_F(1+c/v_F)+\omega/v_F}\frac{dq\,q}{v_F}|M_q|^2\left[1-\frac{1}{2}\left[\frac{q}{k_F}\right]^2+\frac{1}{2}\frac{\omega+\omega_q}{\epsilon_F}\right]\frac{R(\omega+\omega_q)}{\Gamma^{\mathrm{ph}}(\omega+\omega_q)+\epsilon_F/k_Fl_{\mathrm{tr}}}(\cdots)\\&+\frac{1}{4\pi}\int_{\omega/v_F}^{2k_F(1-c/v_F)+\omega/v_F}\frac{dq\,q}{v_F}|M_q|^2\left[1-\frac{1}{2}\left[\frac{q}{k_F}\right]^2+\frac{1}{2}\frac{\omega-\omega_q}{\epsilon_F}\right]\frac{R(\omega-\omega_q)}{\Gamma^{\mathrm{ph}}(\omega-\omega_q)+\epsilon_F/k_Fl_{\mathrm{tr}}}(\cdots) .\end{aligned} \tag{4.13}$$

Here v_F is the Fermi velocity and c the velocity of sound.

For the q integration the Debye vector q_D is a natural upper bound. In our model it is consistent to use the relation $q_D=(2/Z)^{1/3}k_F$.[36] Here Z is the valence of the atoms constituting the metal. q_D is less than the actual upper limit for $|\omega|\lesssim\epsilon_F$ and therefore we can replace it by q_D:

$$\begin{aligned}R(\omega)=1+\frac{1}{4\pi}\int_{-q_D}^{q_D}\frac{dq\,d}{v_F}|M_q|^2\left[1-\frac{1}{2}\left[\frac{q}{k_F}\right]^2+\frac{1}{2}\frac{\omega+\omega_q}{\epsilon_F}\right]\frac{R(\omega+\omega_q)}{\Gamma^{\mathrm{ph}}(\omega+\omega_q)+\epsilon_F/k_Fl_{\mathrm{tr}}}\\ \times[n_B(\omega_q)+n_F(\omega+\omega_q)][1-\Theta(\omega-v_Fq)\Theta(\omega+v_Fq)] .\end{aligned} \tag{4.14}$$

Equation (4.14) is further simplified by using a constant matrix element $|M_q|^2=(\lambda/\omega_D)N(0)$ and proper normalized energies (units of $2\epsilon_F$), and momentum vectors (units of k_F)

$$R(\omega)=1+\frac{1}{4\pi}\int_{-1}^{1}d\Omega\,\Omega[1-\tfrac{1}{2}q_D^2\Omega^2+\omega_D(\omega+\Omega)]\frac{R(\omega+\Omega)}{\Gamma^{\mathrm{ph}}(\omega+\Omega)+\gamma}[n_B(\Omega)+n_F(\omega+\Omega)][1-\Theta(c\omega-\Omega)\Theta(c\omega+\Omega)] . \tag{4.15}$$

In an analogous way we derive an equation for $Q(\omega)$,

$$Q(\omega)=1+\frac{1}{\omega 4\pi}\int_{-1}^{1}d\Omega\,\Omega[1-\tfrac{1}{2}q_D^2\Omega^2+\omega_D(\omega+\Omega)]\frac{(\omega+\Omega)Q(\omega+\Omega)}{\Gamma^{\mathrm{ph}}(\omega+\Omega)+\gamma}[n_B(\Omega)+n_F(\omega+\Omega)][1-\Theta(c\omega-\Omega)\Theta(c\omega+\Omega)] . \tag{4.16}$$

In this notation the phonon broadening Γ^{ph} and γ read

$$\Gamma^{\mathrm{ph}}(\omega)=\int_{-1}^{1}d\Omega\,\Omega[n_B(\Omega)+n_F(\omega+\Omega)] , \tag{4.17}$$

$$\gamma=\Gamma_{\mathrm{tr}}^{\mathrm{im}}=\frac{2}{\pi}\frac{1}{\lambda\omega_Dq_D^2}\frac{1}{k_Fl_{\mathrm{tr}}}\simeq\frac{10^3}{k_Fl_{\mathrm{tr}}} . \tag{4.18}$$

The numerical value of γ is chosen to represent a typical metal. With Eqs. (4.15)—(4.18) the problem is well defined and can, in principle, be solved on a computer. Because ω_D is a very small number compared to 1, for numerical convenience it is appropriate to look for a solution of the form

$$R(\omega)=R_0(\omega)+\omega_D R_1(\omega)\ , \tag{4.19}$$

With Eq. (4.19) we derive a coupled system of integral equations for R_0 and R_1. If we disregard contributions of order ω_D^2, these systems decouple and we have two simple Fredholm equations to solve,

$$R_0(\omega)=1+\int_{-1}^{1} d\Omega\,\Omega(1-\tfrac{1}{2}q_D^2\Omega^2)\frac{R_0(\omega+\Omega)}{\Gamma^{\rm ph}(\omega+\Omega)+\gamma}[n_B(\Omega)+n_F(\omega+\Omega)][1-\Theta(c\omega-\Omega)\Theta(c\omega+\Omega)]\ , \tag{4.20}$$

$$\begin{aligned}R_1(\omega)=&\int_{-1}^{1} d\Omega\,\Omega\frac{(\omega+\Omega)R_0(\omega+\Omega)}{\Gamma^{\rm ph}(\omega+\Omega)+\gamma}[n_B(\Omega)+n_F(\omega+\Omega)][1-\Theta(c\omega-\Omega)\Theta(c\omega+\Omega)]\\&+\int_{-1}^{1} d\Omega\,\Omega(1-\tfrac{1}{2}q_D^2\Omega^2)\frac{R_1(\omega+\Omega)}{\Gamma^{\rm ph}(\omega+\Omega)+\gamma}[n_B(\omega)+n_F(\omega+\Omega)][1-\Theta(c\omega-\Omega)\Theta(c\omega+\Omega)]\ ,\end{aligned} \tag{4.21}$$

$$Q_0(\omega)=1+\frac{1}{\omega}\int_{-1}^{1} d\Omega\,\Omega(1-\tfrac{1}{2}q_D^2\Omega^2)\frac{(\omega+\Omega)Q_0(\omega+\Omega)}{\Gamma^{\rm ph}(\omega+\Omega)+\gamma}[n_B(\Omega)+n_F(\omega+\Omega)][1-\Theta(c\omega-\Omega)\Theta(c\omega+\Omega)]\ , \tag{4.22}$$

$$\begin{aligned}Q_1(\omega)=&\frac{1}{\omega}\int_{-1}^{1} d\Omega\,\Omega\frac{(\omega+\Omega)^2Q_0(\omega+\Omega)}{\Gamma^{\rm ph}(\omega+\Omega)+\gamma}[n_B(\Omega)+n_F(\omega+\Omega)][1-\Theta(c\omega-\Omega)\Theta(c\omega+\Omega)]\\&+\frac{1}{\omega}\int_{-1}^{1} d\Omega\,\Omega(1-\tfrac{1}{2}q_D^2\Omega^2)\frac{(\omega+\Omega)Q_1(\omega+\Omega)}{\Gamma^{\rm ph}(\omega+\Omega)+\gamma}[n_B(\Omega)+n_F(\omega+\Omega)][1-\Theta(c\omega-\Omega)\Theta(c\omega+\Omega)]\ .\end{aligned} \tag{4.23}$$

Equations (4.20)–(4.23) are now solved on a computer by iteration. It is easy to verify that the following relation holds for Q and R:

$$f_n(\omega)=(-1)^n f_n(-\omega),\quad n=0,1\ . \tag{4.24}$$

From this we can infer that the zero components do not contribute to the derivative in the static limit and that the 1 components vanish at $\omega=0$. We calculate the derivative by the limit $f_1'(\omega)=\lim_{\omega\to 0}f_1(\omega)/\omega$. For the numerical evaluation we set $q_D=1$ which corresponds to a bivalent metal. For γ we choose the values $\gamma=0$, 10^{-1}, and 10^{-2} to study the sensitivity on the impurity concentration. In Fig. 2 we show the ratio $Q(0)/R(0)$. According to Mott's relationship [compare Eq. (2.15)] it should be 1. This value is approached for finite impurity scattering at very low and high temperatures. At high temperatures the electron-phonon scattering is quasielastic and therefore one expects a behavior independent of the impurity concentration because electron-phonon scattering is dominant. This is clearly seen in Fig. 2. Although at very low temperatures impurity scattering dominates and therefore $Q(0)/R(0)$ approaches 1, its behavior is very sensitive on the impurity concentration. The deviation from the ideal value $Q(0)/R(0)=1$ is largest in the intermediate temperature range at approximately $T\simeq 0.2\Theta_D$. It is in this region that the inelastic phonon scattering is most efficient. In the very same temperature range, also the phonon drag contribution shows a pronounced temperature dependence.[1,2] A remark on the pure metal ($\gamma=0$) is in order. $Q(0)/R(0)$ does not approach 1 in the low-temperature region. In fact, in the limit $T=0$, the ratio $Q(0)/R(0)$ will vanish because here $R(0)$ will increase rapidly with decreasing temperature and eventually will become infinite. In fact, it can be shown that the zero-temperature limit of Eq. (4.20) produces a misbehaved solution. The reason for this is that a pure metal turns into an ideal conductor at $T=0$. However, this is a somewhat academic problem because even the purest samples contain a residual of impurities and thermopower experiments require a finite-temperature gradient and therefore $T\neq 0$. In Figs. 3 and 4 we show, for comparison, the ratios $Q(0)'/R(0)$ and $R(0)'/R(0)$. Our analysis in Sec. III is now confirmed that this ratio plays the dominant part in the high-temperature region. In general, they are not so sensitive on the impurity concentration as $Q(0)/R(0)$ was, especially in the low-temperature region. They too show a very pronounced temperature dependence in the vicinity of the Debye temperature Θ_D. The resulting temperature dependence of S_d is given by the combination of $Q(0)/R(0)$ and $Q(0)'/R(0)$. The former contribution is still to be weighted by the impurity part and the electron-phonon mass enhancement factor, both also having a temperature dependence. The situation is simplified in the low-temperature range, e.g., $T\leq 0.1\Theta_D$. Here the temperature dependence of the impurity part and the electron-phonon mass enhancement is weak and we

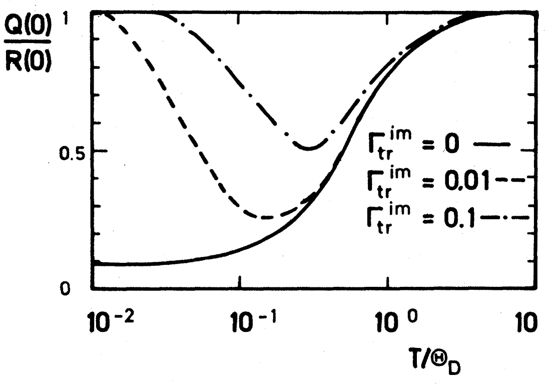

FIG. 2. Ratio of the derivative $R'(\omega)$ and $R(\omega)$ in the static limit; Γ_{tr}^{im} is defined by Eq. (4.18).

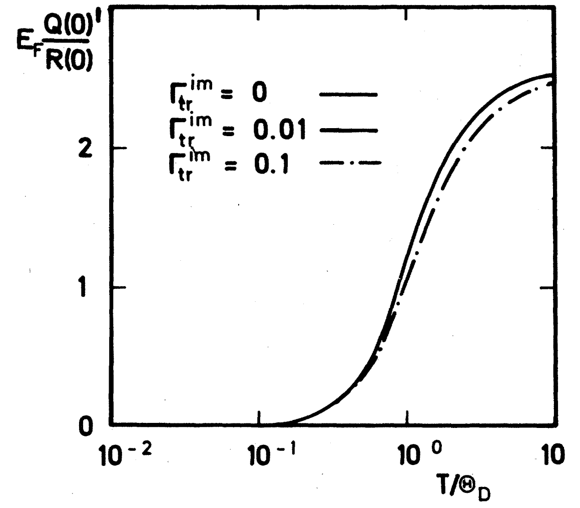

FIG. 3. Ratio of the vertex functions $Q(\omega)$ and $R(\omega)$ in the static limit; Γ_{tr}^{im} is defined by Eq. (4.18).

can use their zero-temperature limits. Furthermore, $\epsilon_F Q(0)'/R(0)$ is negligibly small and can be disregarded. We then obtain for the diffusion thermopower S_d,

$$S_d \simeq (1+\lambda) S_d^{im} \frac{Q(0)}{R(0)} . \tag{4.25}$$

Here S_d^{im} is the diffusion thermopower determined by impurity scattering alone in absence of electron-phonon interaction [compare Eq. (3.14)]. It is now convenient to normalize S/T to its zero-temperature value $S/T\,|_{T=0}$ because this directly gives the ratio $Q(0)/R(0)$,

$$\frac{S_d/T}{S_d/T\,|_{T=0}} = 1-\Delta . \tag{4.26}$$

Δ accounts for deviations from Mott's relationship after which Eq. (4.26) should be 1,

$$\Delta = 1 - Q(0)/R(0) . \tag{4.27}$$

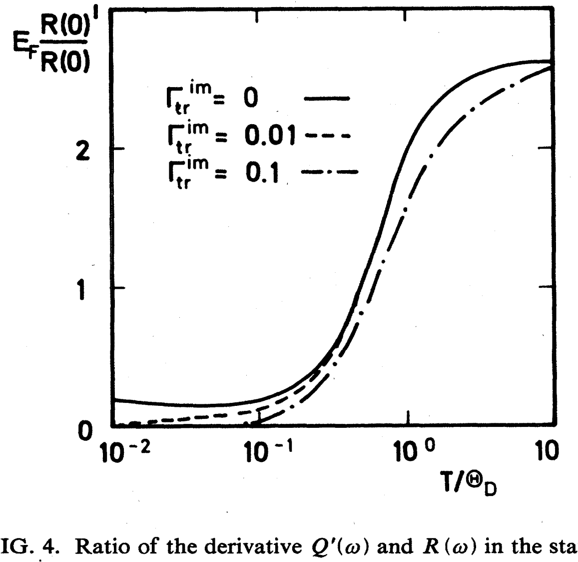

FIG. 4. Ratio of the derivative $Q'(\omega)$ and $R(\omega)$ in the static limit; Γ_{tr}^{im} is defined by Eq. (4.18).

Δ can be obtained from experiment in the low-temperature region where phonon-drag contributions vary as T^3 and can be separated. This is usually accomplished by plotting S^{exp}/T versus T^2. A tangent placed at $T=0$ then represents the phonon-drag part. In the absence of Kondo anomalies caused by magnetic impurities such a procedure should be working in principle. However, there is an ambiguity caused by the position of the tangent in respect to the experimental data points because the point $T=0$ is only approximately reached. Appropriate for comparison, at least qualitatively, of our calculation with experiment, are thermopower measurements at low temperature on the simple metals and their dilute alloys. Although much material can be found in the literature,[37] only a little is available with a complete analysis of the phonon-drag term.[10,11,12,37] The measurements of De Vroomen *et al.* on a variety of Al samples seem to be the most suited because they measured the thermopower down to 2 K and show a general structure which is absent in measurements of other groups which did not proceed to such low temperatures. In Fig. 5 we show the comparison of the experimental data, now normalized according to Eq. (4.26), and our calculation. We picked a dirty sample (A13) and a pure one (A12a). From their residual resistivity we can estimate the transport mean free path's $l_{tr} \simeq 10^{+3}$ (A13) and $l_{tr} \simeq 10^{+5}$ (A12a) measured in units of the Fermi vector. For the temperature range of interest the calculated deviation Δ for the dirty sample is negligibly small and therefore the data points shall follow a straight line, as they in fact do. The situation is different for the pure sample. Although we cannot produce a quantitative agreement our simple theory clearly shows the right tendencies.

Before we conclude this section we have to comment on a possible extension to a more realistic situation. We have assumed free electrons, Debye phonons, and a constant electron-phonon matrix element. The first approximation is generally accepted for simple metals, the latter two are not. In the low-temperature region which is of particular interest because we can separate phonon drag, only the magnitudes of the vertex functions $R(\omega)$ and $Q(\omega)$ are important and not their derivatives. Following the usual arguments[32] we can neglect in Eq. (4.13) all contributions of order ω_D/ϵ_F. As a result we obtain the standard form of vertex equations for an electron-phonon system,

$$R_0(\omega) = 1 + \int_{-1}^{1} d\Omega [\alpha^2 F(\Omega) - \alpha^2 F(\Omega)_{tr}] \times \frac{R_0(\omega+\Omega)}{\Gamma^{ph}(\omega+\Omega)+\gamma} \times [n_B(\Omega) + n_F(\omega+\Omega)] , \tag{4.28}$$

$$Q_0(\omega) = 1 + \frac{1}{\omega} \int_{-1}^{1} d\Omega [\alpha^2 F(\Omega) - \alpha^2 F(\Omega)_{tr}] \times \frac{(\omega+\Omega) Q_0(\omega+\Omega)}{\Gamma^{ph}(\omega+\Omega)+\gamma} \times [n_B(\Omega) + n_F(\omega+\Omega)] . \tag{4.29}$$

Here $\alpha^2 F(\Omega)$ is the McMillan function and $\alpha^2 F_{tr}(\Omega)$ its

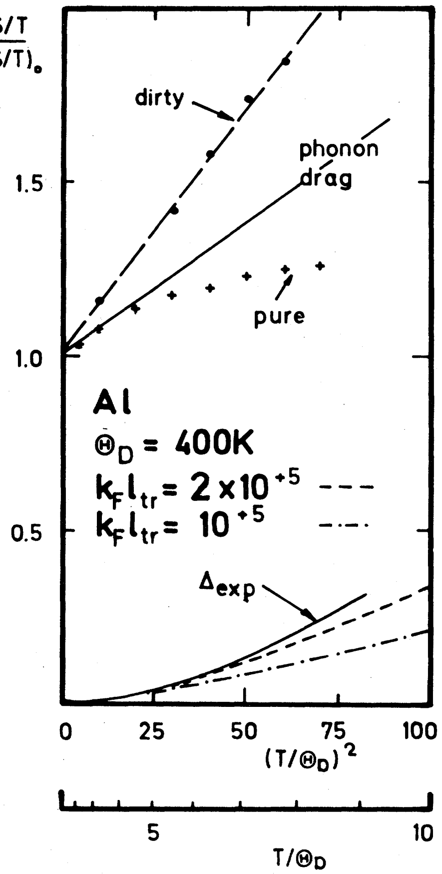

FIG. 5. Comparison of the presented calculation with experiment. Upper half is experimental data from Ref. 10: dirty samples (open circles), and pure sample (crosses). The straight line is the phonon drag contribution as extracted from experiment. Lower half is experimentally determined deviations from the linear temperature dependence in the diffusion thermopower S_d (solid line): calculated deviations based on Eq. (4.27) for different mean free path.

transport equivalent.[32] Both are averages of electron-phonon scattering as restricted on the Fermi surface using realistic phonon dispersion relations and electron-phonon matrix elements. Solutions of both equations can be found in the literature,[38,39] although in a different context than studied here.

V. CONCLUSION

It is Mott's relationship that plays a central role in the diffusion thermopower of metals. There has been quite a lot of work done concerning the sign and magnitude of the diffusion thermopower based on this formula,[1] but already less is concerned with the question of the validity range of that relation in real metals.[16-18] Here the electrons are scattered by impurities and phonons. Mott's relationship has been shown to hold true for elastical scattering only. However, electron-phonon scattering is inelastic. Therefore, it is worthwhile to study the diffusion thermopower and its relation to Mott's formula when electron-phonon scattering is present. The usual way to do this is to calculate the corresponding correlation functions in linear-response theory which has been done by various authors.[4,5,17] Unfortunately, most recently they were more or less concerned with many-body corrections to Mott's relationship in form of the electron-phonon mass enhancement factor. We presented in the previous sections a calculation under a different aspect. We focused our attention on deviations from Mott's relationship in the presence of electron-phonon scattering. To this end we employed the many-particle transport equation derived earlier.[21] The equivalence to Kubo's formulation has been shown already for several examples. We derived a result in Sec. III which was a conjecture from Kubo's formula reported by Jonson and Mahan.[17]

The more interesting results, however, were presented in Sec. IV where, for a simple model, we calculated the vertex functions Λ and Φ and their derivatives over a wide temperature range. Although the model oversimplifies reality and will therefore not give quantitative results, we believe that the qualitative features presented will hold in a more realistic calculation. As a basic result we find a strong temperature dependence in the intermediate-temperature range between $0.2\Theta_D$ and $1.0\Theta_D$. Such a pronounced temperature dependence is usually attributed to phonon drag alone. This makes the situation in that temperature range even more complicated. A separation of diffusion and phonon drag, necessary to compare existing theories of both with experiments, is most likely impossible in the simple way proposed by Hübner.[2] However, the situation becomes clear in the low- and high-temperature limit where the qualitative behavior of phonon drag is known. In the latter, Mott's relationship holds because electron-phonon scattering can be considered as quasielastic. It is noteworthy that this region is approached in such a way that it is independent of the impurity concentration. This is nothing else than the fact that electron-phonon scattering is dominant. Another interesting observation is that the energy derivation of the vertex function seems to be more important here than its magnitude. This part is usually not considered because it is of order ω_D/ϵ_F in the magnitude and therefore neglected. In the low-temperature limit contributions from the derivatives of the vertex functions are negligibly small and the diffusion thermopower can be expressed as a product of the pure impurity part and a correction term given by the ratio of the two vertex functions $Q(0)$ and $R(0)$. As a by-product we retain that the diffusion thermopower is indeed enhanced by $1+\lambda$, the electron-phonon mass enhancement factor. Mott's relationship is true when Q/R is 1. This value is approached in the limit $T \rightarrow 0$ for a finite impurity scattering rate. However, it depends in a very sensitive way on the impurity concentration. We can say in a simple and intuitive way that Mott's relationship holds true in larger temperature ranges when the impurity scattering rate increases. There is some evidence for this result if we compare our calculation with experiment. However, this is not free from ambiguity because the data contain both diffusion thermopower and phonon drag. To separate S_d the phonon drag has to be removed. This depends in a very sensitive way on the resolution of experimentally determined data points in the vicinity of $T=0$.

To support the presented idea requires measurements of the thermopower of simple metals with a good resolution for very low temperatures. An understanding of the low-temperature dependence of the diffusion thermopower is not only interesting in itself (with regard to Mott's relationship), but can also be an important prerequisite to understanding its global temperature behavior. This is necessary, on the other hand, to separate the phonon drag. When this work was prepared for publication, the work of Goedsche *et al.*[40] came to our attention. Based on Zubarev's correlation-function approach, they studied the thermopower of metals and came up, in principle, with similar results as presented here. Unfortunately, a detailed analysis on the temperature dependence is missing in that work.

We will close with a comment on the impurity term as it appears in the low-temperature limit. From Eq. (3.14) we can learn that its magnitude is determined in an essential way by the ratio l_{tr}/l where l_{tr} and l are the impurity transport and quasiparticle mean free path. For impurity scattering alone, a typical value of this ratio is of the order of 2—3. However, if we speculate for a moment that this ratio represents the total elastic scattering, this ratio can vary over a considerable range and would be very sensitive to the sample preparation. This, in fact, is observed in experiments. A simple argument shows that the ratio l_{tr}/l tends to have large values if the scattering centers are large. Then low momentum transfers dominate and we will have $\Gamma^{\mathrm{im}} \gg \Gamma_{\mathrm{tr}}^{\mathrm{im}}$ [compare Eq. (4.5)]. This can account for the large values of the low-temperature values observed in simple metals.[10–12] Of course this speculation assumes that there are no magnetic impurities which can cause Kondo anomalies and lead therefore to an enhanced magnitude. We also cannot explain the change of sign observed.

APPENDIX A: INTERFERENCE DIAGRAMS-EQUILIBRIUM CASE

In this appendix we calculate the contribution from the interference diagrams to the equilibrium retarded self-energy of the electron. This has been done already by Krempasky and Schmid.[13] However, their calculation contains a mistake and therefore it is worthwhile to repeat it here. In the finite-temperature Matsubara formalism[32] we have for the diagram no. 3 of Fig. 1,

$$\Sigma(\vec{k},\omega)=-T\sum_{\vec{q}}\sum_{\Omega}|M_{\vec{q}}|^2 D(\vec{q},\Omega)G(\vec{k}-\vec{q},\omega-\Omega)\sum_{\vec{q}\,'}|V(\vec{k}-\vec{q}\,')|^2 G(\vec{q}\,',\omega)G(\vec{q}\,'-\vec{q},\omega-\Omega)\ . \tag{A1}$$

Here T is the temperature, D and G are the equilibrium phonon and electron Green's function, and M and V are the interaction matrix elements of the electrons with phonons and impurities. If we consider for the time being a constant matrix element V, the $\vec{q}\,'$ summation can be done in the free-electron case,

$$\sum_{\vec{q}\,'}|V(\vec{k}-\vec{q})|^2 G(\vec{q}\,',\omega)G(\vec{q}\,'-\vec{q},\omega-\Omega)=V^2\left[\frac{m^2}{4\pi}\right]^2\frac{1}{q}\int_{-\epsilon_F}^{\infty}d\xi_{q'}\int_{(q'-q)/2m-\epsilon_F}^{(q'+q)/2m-\epsilon_F}d\xi_p\,G(\xi_{q'},\omega)G(\xi_p,\omega-\Omega)\ . \tag{A2}$$

Because only an energy region close to the Fermi energy is important, we can extend the limits of both the integrals to infinity and obtain[13]

$$\sum_{\vec{q}\,'}|V(\vec{k}-\vec{q}\,')|^2 G(\vec{q}\,',\omega)G(\vec{q}\,'-\vec{q},\omega-\Omega)=-\tfrac{1}{4}V^2m^2\mathrm{sgn}(\omega)\mathrm{sgn}(\omega-\Omega)\ . \tag{A3}$$

Inserting this into Eq. (A1) we have

$$\Sigma(\vec{k},\omega)=\tfrac{1}{4}V^2m^2\mathrm{sgn}(\omega)T\sum_{\Omega}\sum_{\vec{q}}\left|\frac{M_{\vec{q}}}{q}\right|^2 D(\vec{q},\omega-\Omega)G(\vec{k}-\vec{q},\Omega)\mathrm{sgn}(\Omega)\ . \tag{A4}$$

Equation (A4) corresponds to Eq. (A8) in Ref. 13. The difference is that there is an additional factor of sgn(Ω) and therefore it can no longer be expressed by the electron-phonon self-energy as it was in Ref. 13. However, the Ω summation can still be done exactly. After analytic continuation to the real axis we obtain

$$\Sigma^r(\vec{k},\omega)=-i\frac{V^2m^2}{4\pi^2}\sum_{\vec{q}}\left|\frac{M_{\vec{q}}}{q}\right|^2\int\frac{d\Omega}{2\pi}\int\frac{d\Omega'}{2\pi}\frac{B(\vec{q},\Omega)A(\vec{k}-\vec{q},\Omega')}{\omega-\Omega-\Omega'+T\delta}$$
$$\times\{\mathrm{Re}\Psi(\tfrac{1}{2}[1+i(\omega-\Omega/\pi T)])-\mathrm{Re}\Psi(\tfrac{1}{2}(1+i\Omega'/\pi T))\}\ . \tag{A5}$$

Here $B(\vec{q},\omega)$ and $A(\vec{q},\omega)$ are the phonon and electron spectral functions, ψ is the Euler Ψ function,[41] and Re means the real part. In the limit $T\rightarrow\infty$ the right-hand side of Eq. (A5) vanishes and for $T\rightarrow 0$ we derive

$$\Sigma^r(\vec{k},\omega)=-i\frac{V^2m^2}{4\pi}\sum_{\vec{q}}\left|\frac{M_{\vec{q}}}{q}\right|^2\int\frac{d\Omega}{2\pi}\int\frac{d\Omega'}{2\pi}B(\vec{q},\Omega)A(\vec{k}-\vec{q},\Omega')\frac{P}{\omega-\Omega-\Omega'}\ln\left|\frac{\omega-\Omega}{\Omega'}\right|\ . \tag{A6}$$

In the limit $\omega \to 0$ we obtain, using the spectral functions for the noninteracting system,

$$\Sigma^r(\vec{k},\omega) = -i\frac{1}{8\tau_{\rm im}}\lambda\frac{\omega_D}{\epsilon_F}(q_D/k_F)^2\omega \ . \tag{A7}$$

Here we have used $\tau_{\rm im}^{-1} = 2\pi V^2 N(0)$. Both diagrams have the very same contribution. If we finally collect all impurity parts shown in Fig. 1 we have for the negative imaginary part of the electron's self-energy, as attributed to impurity scattering,

$$\Gamma^{\rm im}(\omega) = \frac{\epsilon_F}{k_F l}[1 + \tfrac{1}{2}\lambda(q_D/k_F)^2(\omega/\epsilon_F)] \ . \tag{A8}$$

For the phonon part alone we have

$$\Gamma^{\rm ph}(\omega) = \frac{\pi}{2}\lambda\omega_D(q_D/k_F)^2(\omega/\omega_D)^2 \ . \tag{A9}$$

Equations (A8) and (A9) give for the total level broadening $\Gamma(\omega)$,

$$\Gamma(\omega) = \frac{\epsilon_F}{k_F l} + \frac{\pi}{2}\lambda\omega_D(q_D/k_F)^2(\omega/\omega_D)^2 \times [1 + (\omega_D/\pi\omega)(1/k_F l)] \ . \tag{A10}$$

From Equation (A10) we can deduce that for finite frequencies $\omega \neq 0$ the interference term is only a minor correction for pure and moderately dirty samples. This, however, changes, if we consider the static limit of the ratio $\epsilon_F\Gamma'/\Gamma$ [compare Eqs. (2.12) and (2.15)],

$$\epsilon\frac{\Gamma(0)'}{F\Gamma(0)} = \tfrac{1}{2}\lambda(q_D/k_F)^2 \ , \tag{A11}$$

which is no longer small.

APPENDIX B: INTERFERENCE DIAGRAMS—NONEQUILIBRIUM CASE

The nonequilibrium self-energies $\Sigma^<$ and $\Sigma^>$ are calculated in the Keldysh formalism.[25] Applying the rules given in Ref. 25, we obtain for the interference diagrams the contributions

$$\Sigma^<(\vec{k},\omega) = -2i\int\frac{d\Omega}{2\pi}\sum_{\vec{q}}|M_{\vec{q}}|^2 D^<(\vec{q},\Omega)G^<(\vec{k}-\vec{q},\omega-\Omega)\sum_{\vec{q}\,'}|V(\vec{k}-\vec{q}\,')|^2 {\rm Im}[G(\vec{q}\,'-\vec{q},\omega-\Omega)G(\vec{q}\,',\omega)] \ , \tag{B1}$$

$$\Sigma^>(\vec{k},\omega) = 2i\int\frac{d\Omega}{2\pi}\sum_{\vec{q}}|M_{\vec{q}}|^2 D^>(\vec{q},\Omega)G^>(\vec{k}-\vec{q},\omega-\Omega)\sum_{\vec{q}\,'}|V(\vec{k}-\vec{q}\,')|^2 {\rm Im}[\bar{G}(\vec{q}\,'-\vec{q},\omega-\Omega)\bar{G}(\vec{q}\,',\omega)] \ . \tag{B2}$$

Here $G^{>,<}$ and $D^{>,<}$ are the corresponding nonequilibrium propagators. The bar means the anti-time-ordered quantity. To derive Eqs. (B1) and (B2) we have to assume that the phonons remain in equilibrium. This is of course not true in the present situation. However, diffusion thermopower has to be considered as attributed to nonequilibrium electrons alone, disregarding a possible phonon drag effect. Therefore Eqs. (B1) and (B2) are exact for our purpose. Together with the other two contributions Eqs. (B1) and (B2) have to be inserted in the right-hand side of Eq. (2.5):

$$G^>\Sigma^< - G^<\Sigma^> = G^>\Sigma^< - G^<\Sigma^>|_{1,2} + G^>\Sigma^< - G^<\Sigma^>|_{3,4} \ . \tag{B3}$$

Here the numbers refer to the corresponding parts of the self-energy as shown in Fig. 1. We pay special attention on the second term in Eq. (B3) labeled 3,4. Its equilibrium contribution vanishes by virtue of the statistic factors contained in $G^>$, $G^<$, $D^>$, and $D^<$. The term linear in the driving fields is

$$\begin{aligned} G^>\Sigma^< - G^<\Sigma^>|_{3,4}^{(1)} = i\Bigg[& G^>(\vec{k},\omega)\int\frac{d\Omega}{2\pi}\sum_{\vec{q}}|M_{\vec{q}}|^2 D^<(\vec{q},\Omega)G^<(\vec{k}-\vec{q},\omega-\Omega) \\ & - G^<(\vec{k},\omega)\int\frac{d\Omega}{2\pi}\sum_{\vec{q}}|M_{\vec{q}}|^2 D^>(\vec{q},\Omega)G^>(\vec{k}-\vec{q},\omega-\Omega)\Bigg]^{(0)} U^{(1)}(\vec{k},\vec{q},\omega,\Omega) \\ + i\Bigg[& G^>(\vec{k},\omega)\int\frac{d\Omega}{2\pi}\sum_{\vec{q}}|M_{\vec{q}}|^2 D^<(\vec{q},\Omega)G^<(\vec{k}-\vec{q},\omega-\Omega) \\ & - G^<(\vec{k},\omega)\int\frac{d\Omega}{2\pi}\sum_{\vec{q}}|M_{\vec{q}}|^2 D^>(\vec{q},\Omega)G^>(\vec{k}-\vec{q},\omega-\Omega)\Bigg]^{(1)} U^{(0)}(\vec{k},\vec{q},\omega,\Omega) \ . \end{aligned} \tag{B4}$$

The superscript refers to the order of the driving fields. The first term vanishes because it is essentially the equilibrium expression and the statistic factors cancel. In the second term the zero-order contribution of the vertex function U is

$$\begin{aligned} U^{(0)}(\vec{k},\vec{q},\omega,\Omega) = {} & [1-2n_F(\omega)]\sum_{\vec{q}\,'}|V(\vec{k}-\vec{q}\,')|^2 A(\vec{q}\,',\omega){\rm Re}G(\vec{q}\,'-\vec{q},\omega-\Omega) \\ & + [1-2n_F(\omega-\Omega)]\sum_{\vec{q}\,'}|V(\vec{k}-\vec{q}\,')|^2 A(\vec{q}\,'-\vec{q},\omega-\Omega){\rm Re}G(\vec{q}\,',\omega) \ , \end{aligned} \tag{B5}$$

and the term in large parrentheses is very similar to the first term in Eq. (B3) labeled 1,2. It is straightforward to show

$$U^{(0)} \sim \frac{1}{k_F l}\frac{\omega_D}{\epsilon_F}\,, \tag{B6}$$

$$[U^{(0)'}] \sim \frac{1}{k_F l}\frac{1}{\epsilon_F}\,. \tag{B7}$$

For an order-of-magnitude argument we can now write Eq. (B3) as

$$G^{>}\Sigma^{<} - G^{<}\Sigma^{>} \sim (G^{>}\Sigma^{<} - G^{<}\Sigma^{>})\,|_{1,2}\left[1+\frac{1}{k_F l}\frac{\omega_D}{\epsilon_F}\right]. \tag{B8}$$

The influence of the interference diagrams is, even for moderately dirty samples, still several magnitudes smaller than ω_D/ϵ_F. Therefore we can neglect this contribution, even if we collect terms which are of order ω_D/ϵ_F.

---

[*] Present address: Robert Koch Strasse 22, 8012 Ottobrunn, Federal Republic of Germany.

[1] F. J. Blatt, P. A. Schroeder, C. L. Foiles, and D. Grieg, *Thermoelectric-Power of Metals* (Plenum, New York, 1976).

[2] R. P. Huebner, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1972), Vol. 27, p. 64.

[3] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976).

[4] S. K. Lyo, Phys. Rev. B **17**, 2545 (1978).

[5] A. Vilenkin and P. L. Taylor, Phys. Rev. B **18**, 5280 (1978).

[6] J. L. Opsal, B. J. Thaler, and J. Bass, Phys. Rev. Lett. **36**, 1211 (1976).

[7] W. Hänsch and G. D. Mahan, Phys. Rev. B **28**, 1886 (1983).

[8] B. L. Gallagher, J. Phys. F **11**, L207 (1981).

[9] A. B. Kaiser, J. Phys. F **12**, L223 (1982).

[10] A. R. De Vroomen, C. Van Baarle, and A. J. Cuelenaere, Physica (Utrecht) **26**, 19 (1960).

[11] F. J. Blatt, Helv. Phys. Acta **41**, 693 (1968).

[12] R. J. Gripshover, J. B. Van Zytveld, and J. Bass, Phys. Rev. **163**, 163 (1967); R. S. Averbeck, C. H. Stephan, and J. Bass, J. Low Temp. Phys. **12**, 319 (1973).

[13] J. J. Krempasky and A. Schmid, J. Low Temp. Phys. **34**, 197, (1979).

[14] P. E. Nielsen and P. L. Taylor, Phys. Rev. B **10**, 4061 (1974).

[15] N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1971).

[16] V. Chester and A. Thellung, Proc. Phys. Soc. London **77**, 1005 (1961).

[17] M. Jonson and G. D. Mahan, Phys. Rev. B **21**, 4223 (1980).

[18] I. M. Lifschitz, M. Ja. Asbel, and M. I. Kaganov, *Elektronentheorie der Metalle* (Akademie, Berlin, 1975).

[19] See, for instance, F. J. Blatt, P. A. Schroeder, C. L. Foiles, and D. Grieg, in *Thermoelectric Power of Metals*, Ref. 1.

[20] It is amazing to observe that the experimental data can follow a straight line independent of the way it is plotted, e.g., S/T vs T, T^2, and T^3; compare Ref. 12.

[21] G. D. Mahan and W. Hänsch, J. Phys. F **13**, L47 (1983).

[22] W. Hänsch and G. D. Mahan, Phys. Rev. B **28**, 1902 (1983).

[23] G. D. Mahan, J. Phys. F **13**, L257 (1983).

[24] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (Benjamin, New York, 1962).

[25] L. V. Keldysh, Zh. Eksp. Teor. Fiz. **47**, 1515 (1964) [Sov. Phys.—JETP **20**, 1018 (1965)].

[26] We used the Kadanoff and Baym method in Refs. 21 and 22 and the Keldysh approach in Ref. 7. Both give the very same result.

[27] A generalization to the ac case has been done by T. Wu and G. D. Mahan (unpublished).

[28] Gauge invariance is shown in Ref. 22.

[29] J. Callaway, *Quantum Theory of the Solid State (Student Edition)* (Academic, New York, 1976).

[30] The vertex functions Λ and Φ correspond to the correlation functions usually calculated in Kubo's linear-response theory. Λ corresponds to the charge-current—charge-current and Φ to the charge-current—heat-current correlation function.

[31] Because of a technical error in their calculation we repeat it in Appendix A.

[32] G. D. Mahan, *Many Particle Physics* (Plenum, New York, 1981).

[33] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1964).

[34] This choice is justified by the calculation presented in Sec. IV.

[35] G. Grimvall, *The Electron Phonon Interaction in Metals*, Vol. 16 of *Selected Topics in Solid State Physics*, edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1981), p. 207.

[36] For a discussion of the electron-phonon matrix element, see Ref. 35 or the very detailed discussion by D. J. Scalapino, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), Vol. 1, p. 449.

[37] For a complete list of experiments up to 1972, see R. P. Huebner, in *Solid State Physics*, Ref. 2.

[38] K. Takegahara and S. Wang, J. Phys. F **7**, L293 (1977).

[39] C. R. Leavens, J. Phys. F **7**, 163 (1977).

[40] F. Goedsche, R. Richter, H. Wegener, and G. Röpke, Phys. Status Solidi **120**, 631 (1983).

[41] I. S. Gradshteyn and I. M. Ryshik, *Table of Integrals, Series and Products* (Academic, New York, 1965), Sec. 8.36.