Electron-phonon enhancement of thermoelectricity in metals

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The many-body effect of the electron-phonon interaction on the electron-diffusion thermopower is calculated microscopically. It is found that the thermopower is enhanced not only by the mass enhancement but also significantly by a new mechanism, arising from the electron-phonon modification of the quasiparticle velocity. The result is justified, using a simple phenomenological treatment based on the Landau-Boltzmann theory. The effect of the above result on some of the magnetic-thermoelectric phenomena is discussed semiclassically.

I. INTRODUCTION

The interaction of electrons with the lattice vibration is responsible for many interesting phenomena in solids. For example, it enhances the mass of the electron and, therefore, the electronic-specific-heat capacity. The effect of the electron-phonon mass renormalization is known to be absent from many of the dc transport coefficients such as the dc electric conductivity[1,2] and the thermal conductivity.[2] Also, after the work of Prange and Kadanoff,[2] it has been believed that the above effect does not appear in the thermoelectric effect.

Recently, Opsal, Thaler, and Bass[3] argued, using Mott's formula,[4] that the impurity-dominated electron-diffusion thermopower is enhanced by the electron-phonon mass renormalization.[5] They could explain their data[3] on aluminum with dilute gallium impurities only by assuming the effect of mass enhancement of 45%. However, it is not clear to what extent their semiclassical approach treats the effect of the electron-phonon interaction. It is felt that a definitive conclusion can be drawn only from a first-principles calculation. In view of these developments, it seems necessary to resolve the situation by making a rigorous microscopic analysis. A brief summary of a part of this work has been published earlier.[6]

Thermoelectric power is the heat transported per carrier per unit temperature. The contribution to the heat current from electrons just below and above the Fermi level tends to cancel out. As a result, the thermopower depends sensitively on the energy derivative of various quantities contributing to the conductivity at the Fermi level. For this reason, one has to consider all the higher-order terms with sensitive dependence on energy in calculating the thermoelectric power, unlike in calculating the dc conductivity. As will become clear later, this seems to have been the basic source of difficulty and confusion in the previous theories. We find that the thermopower is enhanced not only by the mass enhancement[3] but also significantly by a new mechanism, arising from the electron-phonon modification of the quasiparticle velocity.

In Sec. II we present a simple phenomenological treatment of the thermoelectric power based on the Landau-Boltzmann theory. In Sec. III, a microscopic justification for the result obtained in Sec. II is given. We discuss the effect of the electron-phonon interaction on magneto-thermoelectricity semiclassically in Sec. IV. Concluding remarks are given in Sec. V.

II. PHENOMENOLOGICAL THEORY

In this section we give a semiclassical analysis of the thermopower. In the presence of an applied electric field $\vec{\mathcal{E}}$ and a uniform temperature gradient ∇T, the electric and thermal currents $\vec{J}$ and $\vec{U}$ are given by[7]

$$\vec{J}=L_{EE}\vec{\mathcal{E}}+L_{ET}\nabla T\ ,\quad \vec{U}=L_{TE}\vec{\mathcal{E}}+L_{TT}\nabla T\ . \tag{2.1}$$

The various tensor transport coefficients in (2.1) can be expressed in terms of the perturbed electron distribution function[8]

$$f_{\vec{k}}=f_{0\vec{k}}+(-f'_{0\vec{k}})[e\vec{\mathcal{E}}\cdot\vec{\phi}_{\vec{k}}-k_B\nabla T\cdot\vec{\psi}_{\vec{k}}]\ , \tag{2.2}$$

where $f_{0\vec{k}}$ is the equilibrium distribution function (i.e., Fermi function) for a quasiparticle of momentum $\vec{k}$ and energy $E_{\vec{k}}$ and e (negative) is the electronic charge. The prime denotes a derivative with respect to the argument, and k_B is Boltzmann's constant. The quasiparticle energy $E_{\vec{k}}$ is given by the Brillouin-Wigner perturbation equation

$$E_{\vec{k}}=\epsilon_{\vec{k}}+M_{\vec{k}}(E_{\vec{k}})\ , \tag{2.3}$$

where $\epsilon_{\vec{k}}$ is the bare electronic energy and $M_{\vec{k}}(z)$ is the real part of the electronic self-energy, arising mainly from a virtual one-phonon process, in which a phonon is emitted and then absorbed.

One then obtains,[8,9] using (2.2),

$$L_{EE}=\sigma(\mu)\,, \tag{2.4}$$

$$L_{TE}=\frac{1}{e}\int_0^{\infty} dz\left(-\frac{\partial f_0(z)}{\partial z}\right)(z-\mu)\sigma(z)$$
$$=\frac{\pi^2}{3e}(k_BT)^2\left.\frac{d\sigma(z)}{dz}\right|_{z=\mu}, \tag{2.5}$$

with the conductivity tensor given by

$$\sigma(z)=\frac{e^2}{4\pi^3\hbar}\int_{z=E_{\vec{k}}}\frac{dS}{v^*_{\vec{k}}}\,\vec{v}^*_{\vec{k}}\,\vec{\psi}_{\vec{k}}\,. \tag{2.6}$$

In (2.6) the integration is over the quasiparticle energy surface $z=E_{\vec{k}}$ and over the bands. The quasiparticle velocity $\vec{v}^*_{\vec{k}}$ is given by

$$\vec{v}^*_{\vec{k}}=(1/\hbar)\nabla_{\vec{k}}E_{\vec{k}}\,. \tag{2.7}$$

Hereafter, we assume a cubic symmetry for convenience. Using, then, the Onsager relation (dagger means the transpose)

$$L_{ET}(\vec{H})=-L^{\dagger}_{TE}(-\vec{H})/T\,, \tag{2.8}$$

the thermoelectric power is given by

$$S=-(L_{ET}/L_{EE})_{xx}=\frac{\pi^2}{3e}k_B^2T\left(\frac{\partial\ln\sigma_{xx}(z)}{\partial z}\right)_{z=\mu}. \tag{2.9}$$

In (2.8) $\vec{H}$ is a static magnetic field, which is zero in this section. The temperature gradient is assumed to be in the x direction. Making a relaxation time approximation, one sets $\vec{\psi}_{\vec{k}}=\vec{v}^*_{\vec{k}}\tau^*_{\vec{k}}$, obtaining

$$\sigma_{xx}(z)=\frac{e^2}{12\pi^3\hbar}\int_{z=E_{\vec{k}}} dS\,v^*_{\vec{k}}\,\tau^*_{\vec{k}}\,. \tag{2.10}$$

The quasiparticle velocity is obtained from (2.3) and (2.7),

$$\vec{v}^*_{\vec{k}}=\frac{\vec{v}_{\vec{k}}}{1-M'_{\vec{k}}(E_{\vec{k}})}+\frac{1}{1-M'_{\vec{k}}(E_{\vec{k}})}\left.\frac{1}{\hbar}\nabla_{\vec{k}}M_{\vec{k}}(z)\right|_{z=E_{\vec{k}}}, \tag{2.11}$$

where $\vec{v}_{\vec{k}}\equiv(1/\hbar)\nabla_{\vec{k}}\epsilon_{\vec{k}}$. The quantity $M_{\vec{k}}(z)$ varies extremely slowly with respect to $\vec{k}$, and the second term is negligibly small. Namely, noting that $(1/\hbar)\nabla_{\vec{k}}M_{\vec{k}}(z)\sim(M_{\vec{k}}/E_{\vec{k}})\vec{v}_{\vec{k}}$, the second term of (2.11) is of order $|M_{\vec{k}}/E_{\vec{k}}|\sim k_B\Theta_D/\mu\sim c_s/v_F$ smaller than the first term near the Fermi level. Here Θ_D, c_s, and v_F are the Debye temperature, sound, and Fermi velocities, respectively. However, the second term of (2.11) varies much more rapidly [i.e., $-M'_{\vec{k}}(z)\sim 1$] with energy than the first term. Namely, the former varies significantly over the phonon energy scale, whereas the latter only over the electronic energy ($E_{\vec{k}}$) scale. For this reason, both terms in (2.11) give important contributions to $(\partial/\partial E_{\vec{k}})\vec{v}^*_{\vec{k}}$ and, therefore, to the thermoelectric power.

As shown by Opsal *et al.*,[3] the first term of (2.11), inserted in (2.10) and (2.9), leads to[10]

$$S_1\equiv(1+\lambda)\frac{\pi^2}{3e}k_B^2T\left(\frac{\partial\ln\sigma^{(0)}_{xx}(z)}{\partial z}\right)_{z=\mu}, \tag{2.12}$$

where the bare conductivity is given by

$$\sigma^{(0)}_{xx}=\frac{e^2}{12\pi^3\hbar}\int_{z=\epsilon_{\vec{k}}} dS\,v_{\vec{k}}\tau^{(0)}_{\vec{k}}\,. \tag{2.13}$$

Here $\lambda\,[\equiv -M'_{\vec{k}}(\mu)]$ is assumed to be isotropic, and use is made of the relationship $v^*_{\vec{k}}\tau^*_{\vec{k}}=v_{\vec{k}}\tau^{(0)}_{\vec{k}}$ ($\tau^{(0)}_{\vec{k}}$ is the bare relaxation time). The latter relationship follows from the fact that the dc conductivity given in (2.1) is unaffected [i.e., $\sigma_{xx}(\mu)=\sigma^{(0)}_{xx}(\mu)$] by the renormalization.[1,2] Note that only unrenormalized quantities enter (2.13). The nutshell of the argument[3] leading to (2.12) is that (a) the energy derivative in (2.9) with respect to the quasiparticle energy can be replaced by $\partial/\partial z=\partial/\partial E_{\vec{k}}=(1+\lambda)(\partial/\partial\epsilon_{\vec{k}})$ and (b) the renormalized conductivity σ_{xx} in (2.9) equals the bare conductivity $\sigma^{(0)}_{xx}$ given in (2.13).

To obtain the remaining contribution to the thermopower, we insert the second term of (2.11) in (2.10) and (2.9). Using[11] $M''_{\vec{k}_F}(\mu)\sim c_s/v_F\mu\simeq 0$, one finds

$$S_2\equiv\frac{\pi^2}{3e}k_B^2T[\sigma^{(0)}_{xx}(\mu)]^{-1}\left(\frac{e^2}{12\pi^3\hbar}\right)\times\int_{\mu=\epsilon_{\vec{k}}} dS\,\frac{[\vec{v}_{\vec{k}}\cdot(1/\hbar)\nabla_{\vec{k}}M'_{\vec{k}}(\mu)]\tau^{(0)}_{\vec{k}}(\mu)}{v_{\vec{k}}}\,. \tag{2.14}$$

Defining

$$\xi=\left(\frac{1}{\hbar v_{kx}}\frac{\partial}{\partial k_x}M'_{\vec{k}_F}(z)\right)_{z=\mu=\epsilon_{\vec{k}}}$$

and assuming ξ to be isotropic, one obtains from (2.14)

$$S_2=(\pi^2\xi/3e)k_B^2T\,. \tag{2.15}$$

To make an order of magnitude estimate, one finds, using effective mass and Debye approximations,[11]

$$\xi=\lambda/2\mu\,. \tag{2.16}$$

Comparing (2.15), (2.16) with (2.12) and using

$$\left(\frac{\partial}{\partial z}\ln\sigma^{(0)}_{xx}(z)\right)_{z=\mu}\sim\frac{1}{\mu}\,,$$

it is seen that S_2 constitutes a significant fraction of the thermoelectric power ($S=S_1+S_2$).

III. MICROSCOPIC THEORY

In this section we give a microscopic justification for the result obtained in Sec. II. The analysis in the previous section has been quite general except for the relaxation time approximation introduced for simplicity. In this section, however, we will specifically study, for simplicity, a system of Bloch electrons interacting with the lattice and a low concentration of static impurity centers at low temperatures ($T \ll \Theta_D$). One can easily generalize the result to other regimes of temperature. For the electron-phonon system we use the Frölich Hamiltonian. The transport properties of this system have been studied extensively by Holstein,[1] and the present treatment is based on his formalism. We carry out the analysis to higher order than that found in the latter work for the reason discussed in Sec. I. In this theory, the smallness parameter of the perturbation expansion is the ratio of the phonon energy to the Fermi energy, or equivalently that of the sound velocity c_s to the Fermi velocity v_F. An additional smallness parameter in the present theory is the concentration of the impurities.

The Hamiltonian is then given by

$$H = \sum_{\vec{k}} \epsilon_{\vec{k}} a^\dagger_{\vec{k}} a_{\vec{k}} + \sum_{\vec{q}} \hbar\omega^{(0)}_{\vec{q}} \left(b^\dagger_{\vec{q}} b_{\vec{q}} + \frac{1}{2}\right)$$

$$+ \sum_{\vec{k}\vec{q}} V^{(0)}_{\vec{q}} a^\dagger_{\vec{k}+\vec{q}} a_{\vec{k}} (b_{\vec{q}} + b^\dagger_{-\vec{q}})$$

$$+ \sum_{\vec{k}'\vec{k}} \sum_{j=1}^{N} \exp[i(\vec{k}-\vec{k}')\cdot\vec{R}_j]\, U_{\vec{k}'\vec{k}}\, a^\dagger_{\vec{k}'} a_{\vec{k}} \,, \quad (3.1)$$

where $a^\dagger_{\vec{k}}$, $a_{\vec{k}}$ are Fermion creation and destruction operators, and $b^\dagger_{\vec{q}}$ ($b_{\vec{q}}$) creates (destroys) a phonon of "momentum" q and bare frequency $\omega^{(0)}_{\vec{q}}$. The first two terms in (3.1) describe independent Bloch electron motion and harmonic lattice vibration. The third term describes the bare electron-phonon interaction, assumed to depend only on the momentum transfer[12]

$$V^{(0)}_{\vec{q}} = C|\vec{q}|\,[\hbar/2\mathfrak{N}M\omega^{(0)}_{\vec{q}}]^{1/2} \,, \quad (3.2)$$

where C is the phenomenological Sommerfeld-Wilson interaction constant, $\mathfrak{N}$ the number of atoms in the sample, and M the atomic mass. The last term of (3.1) represents elastic scattering by impurity centers (assumed to be substitutional) at $\vec{R}_j$. The quantities N and $U_{\vec{k}'\vec{k}}$ are the number of impurities and the Fourier transform of the impurity potential, respectively. Other notations are defined in Sec. II.

According to the linear-response theory, the thermopower is given by[13]

$$\mathcal{S} = \langle\langle \hat{J}\hat{K} \rangle\rangle / eT \langle\langle \hat{J}\hat{J} \rangle\rangle \,, \quad (3.3)$$

where

$$\langle\langle \hat{J}\hat{K} \rangle\rangle = \frac{1}{i}\frac{\partial}{\partial\omega}\, \mathfrak{F}_{JK}(\hbar\omega + i0)\Big|_{\omega=0} \,. \quad (3.4)$$

The correlation function is given by

$$\mathfrak{F}_{JK}(\hbar\omega_r) = \int_0^\beta \langle \hat{J}(u)\hat{K} \rangle \exp(\hbar\omega_r u)\, du \,, \quad (3.5)$$

where the angular brackets denote the grand canonical thermodynamic average, $\hbar\omega_r = 2\pi r i k_B T$ (r is an integer), and $\beta^{-1} = k_B T$. The operator $\hat{J}(u)$ is in the imaginary time Heisenberg representation. In (3.3), $\hat{J}$ is the charge current operator

$$\hat{J} = e\sum_{\vec{k}} v_{\vec{k}x} a^\dagger_{\vec{k}} a_{\vec{k}} \quad (3.6)$$

and $\hat{K}/e$ is the heat current operator defined in terms of the energy current operator $\hat{Q}$ by

$$K \equiv eQ - \mu J$$

$$= e\sum_{\vec{k}\vec{k}'} a^\dagger_{\vec{k}'} a_{\vec{k}} \Big(v_{\vec{k}x}(\epsilon_{\vec{k}} - \mu)\delta_{\vec{k}',\vec{k}} + \frac{1}{2}(v_{\vec{k}'x} + v_{\vec{k}x})$$

$$\times \sum_{\vec{q}} V^{(0)}_{\vec{q}} (b_{\vec{q}} + b^\dagger_{-\vec{q}})\delta_{\vec{k}',\vec{k}+\vec{q}} \Big) \,, \quad (3.7)$$

where $\delta_{\vec{k}',\vec{k}}$ is the Kronecker delta. The second term in (3.7) represents an additional heat current due to the electron-phonon interaction. The energy current operator $\hat{Q}$ is derived in the Appendix.

The correlation function in (3.4) is conveniently evaluated in terms of the upper charge-current vertex correction (to be defined as EF-vertex part following Holstein's work[1]), which consists of ladders of the irreducible scattering part. The latter contains a single impurity line, a phonon line, and their higher-order corrections such as virtual recoil by impurities discussed by Nielsen and Taylor[15] and the electron-phonon vertex correction to the impurity scattering discussed by Hasegawa.[16] Although the phonon ladders do not contribute to the scattering at low temperatures, they give a significant contribution to the thermopower through higher-order corrections of the EF-vertex part [cf. (3.13)]. The lower heat current vertex contains not only the first term of (3.7) but also terms arising from the electron-phonon interaction, namely, the second member of (3.7). The latter is illustrated in Fig. 1. Here the curvy, solid, and incoming wiggly lines represent, respectively, phonon propagators, full electron propagators, and the external line.

The full electron propagator is given, in the complex z plane, by[1,17]

$$S_{\vec{k}}(z) = 1/[z - \epsilon_{\vec{k}} - G_{\vec{k}}(z)] \,, \quad (3.8)$$

where $G_{\vec{k}}(z)$ is the electronic self-energy part.

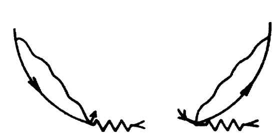

FIG. 1. Effective electronic heat current vertex arising from the electron-phonon interaction.

The phonon contribution to $G_{\vec{k}}(z)$ is given, to the lowest order, by

$$G^{ph}_{\vec{k}}(z)=\sum_{\vec{k}'\vec{q}}\sum_{\pm}\frac{|V_{\vec{q}}|^2 f^{(\mp)}(\epsilon_{\vec{k}'})\delta_{\vec{k}',\vec{k}+\vec{q}}}{z-\epsilon_{\vec{k}'}\pm\hbar\omega_{\vec{q}}}\ . \qquad (3.9)$$

Here $V_{\vec{q}}$, $\omega_{\vec{q}}$, $f^{(-)}(x)$ are renormalized electron-phonon interaction, renormalized phonon frequency,[1] Fermi function, and $f^{(+)}(x)=1-f^{(-)}(x)$. One defines, slightly below the real axis,

$$G_{\vec{k}}(z-i0)=M_{\vec{k}}(z)+i\Gamma_{\vec{k}}(z)\ . \qquad (3.10)$$

For the real part $M_{\vec{k}}(z)$, only the phonon contribution [i.e., the real part of $G^{ph}_{\vec{k}}(z-i0)$] is important because of its rapid variation in energy at the Fermi level. Namely, the quantity $M'_{\vec{k}}(\mu)$ is of order unity. At the Fermi level, the phonon contribution to the imaginary part $\Gamma_{\vec{k}}(z)$ is negligibly small at low temperature, and $\Gamma_{\vec{k}}(z)$ becomes linear in impurity concentration. With an increasing value of $|z-\mu|$, $\Gamma_{\vec{k}}(z)$ increases rapidly and saturates near $|z-\mu|\sim\hbar\omega_D$, leading to the rapid variation of $M_{\vec{k}}(z)$ in z. As is well known, the above properties are due to the fact that a particle (hole) with a large excitation energy decays rapidly to the Fermi level by emitting phonons of large energy, because the phonon density of states is large. However, a particle with a smaller excitation energy decays slowly, because it can emit only small energy phonons which are scarce.

The correlation function is then given by[18]

$$\begin{aligned}\mathfrak{F}_{JK}(\hbar\omega+i0)=-\frac{e^2}{2\pi i}\sum_{\vec{k}}v_{\vec{k}x}\int_{-\infty}^{\infty}dz\,[\epsilon_{\vec{k}}+M_{\vec{k}}(z)+m_{\vec{k}}(z)-\mu]\\ \times\{2\Gamma_{\vec{k}}(z)\omega(-f^{(-)\prime}(z))\phi_{\vec{k}}(z)S_{\vec{k}}(z-i0)S_{\vec{k}}(z+i0)\\ +\Lambda_{\vec{k}}(z-i0,z+\hbar\omega-i0)f^{(-)}(z+\hbar\omega)S_{\vec{k}}(z-i0)S_{\vec{k}}(z+\hbar\omega-i0)\\ -\Lambda_{\vec{k}}(z+i0,z+\hbar\omega+i0)f^{(-)}(z)S_{\vec{k}}(z+i0)S_{\vec{k}}(z+\hbar\omega+i0)\}\ .\end{aligned} \qquad (3.11)$$

The quantity $\phi_{\vec{k}}(z)$ is the distribution function [cf. (2.3)] and is related to the EF-vertex part $\Lambda_{\vec{k}}$ by[1] $\phi_{\vec{k}}(z)=\hbar\Lambda_{\vec{k}}(z-i0,z+i0)/2\Gamma_{\vec{k}}(z)$. According to Holstein,[1] the latter satisfies the Boltzmann equation. One then finds

$$\phi_{\vec{k}}(z)=v_{\vec{k}x}\tau_{\vec{k}}(z)\ , \qquad (3.12a)$$

where the transport relaxation time is given by

$$\tau_{\vec{k}}(z)^{-1}=\frac{2\pi N}{\hbar}\sum_{\vec{k}'}|T_{\vec{k}'\vec{k}}|^2(1-\cos\Theta_{\vec{k}'\vec{k}})\delta(z-\epsilon_{\vec{k}'}-M_{\vec{k}'}(z))\ , \qquad (3.12b)$$

$T_{\vec{k}'\vec{k}}$ being the transition amplitude for scattering from $\vec{k}$ to $\vec{k}'$. The approximations leading to (3.12b) will be given shortly [cf. (3.16)]. Also, one finds $(\eta=\pm 1)$[19]

$$\Lambda_{\vec{k}}(z+i\eta 0,z+\hbar\omega+i\eta 0)=v_{\vec{k}x}-i\omega\sum_{\vec{k}'\vec{q}}\sum_{\pm}\int_{-\infty}^{\infty}dx\ \frac{[-f^{(\mp)\prime}(x)]|V_{\vec{q}}|^2\phi_{\vec{k}'}(x)\delta_{\vec{k}',\vec{k}+\vec{q}}\delta(x-\epsilon_{\vec{k}'}-M_{\vec{k}'}(x))}{z-x\pm\hbar\omega_{\vec{q}}+i\eta 0}\ . \qquad (3.13)$$

Finally, the quantity $m_{\vec{k}}(z)$ in (3.11) is given by

$$m_{\vec{k}}(z)=v_{\vec{k}x}^{-1}\sum_{\vec{k}'\vec{q}}\sum_{\pm}v_{\vec{k}'x}|V_{\vec{q}}|^2 f^{(\mp)}(\epsilon_{\vec{k}'})\delta_{\vec{k}',\vec{k}+\vec{q}}\,P\,\frac{1}{z-\epsilon_{\vec{k}'}\pm\hbar\omega_{\vec{q}}}\ , \qquad (3.14)$$

P indicating the principal part. The quantity $m_{\vec{k}}(z)$ also varies rapidly in energy [i.e., $m_{\vec{k}}(\mu)'\sim 1$] at the Fermi level. Both $m_{\vec{k}}(z)$ and $M_{\vec{k}}(z)$ are of order of the phonon energy. The quantity $M_{\vec{k}}(z)+m_{\vec{k}}(z)$ in (3.11) arises from the processes illustrated in Fig. 1, and accounts for additional electronic energy current due to the electron-phonon interaction. As is discussed in Sec. I, it leads to an important contribution because of its sensitive dependence on energy. Also, the last two terms in the curly brackets of (3.11) give an important contribution, unlike in charge conduction problem where terms of this type are insignificant.[1]

The distribution function $\phi_{\vec{k}}$ is inversely proportional to the concentration (c). Therefore, the first term in the curly brackets of (3.11) is linear in ω and c^{-1}. For other terms we retain contributions linear in ω and c^{-1} in view of (3.4). We set $\omega=0$ for the last two terms in the curly brackets of (3.11) except for the EF-vertex parts $\Lambda_{\vec{k}}$, because the second term of (3.13) is already linear in these quantities. The first term of (3.13) leads to a higher-order (in c) contribution and will be dropped hereafter. In evaluating (3.11), it is convenient to introduce an identity

$$S_{\vec{k}}(z+i\eta_1 0)S_{\vec{k}}(z+\hbar\omega+i\eta_2 0) = \frac{S_{\vec{k}}(z+i\eta_1 0)-S_{\vec{k}}(z+\hbar\omega+i\eta_2 0)}{\hbar\omega - G_{\vec{k}}(z+\hbar\omega+i\eta_2 0)+G_{\vec{k}}(z+i\eta_1 0)}\ . \quad (3.15)$$

Using this expression in (3.11), it is clear that one has to perform a summation of the type $\sum_{\vec{k}} Q_{\vec{k}} S_{\vec{k}}$. When $Q_{\vec{k}}$ is a slowly varying function of $\vec{k}$ (i.e., $\partial Q_{\vec{k}}/\partial\epsilon_{\vec{k}} \sim Q_{\vec{k}}/\epsilon_{\vec{k}}$), one can expand[1,20]

$$S_{\vec{k}}(z+\hbar\omega+i\eta 0) = \frac{1}{z-\epsilon_{\vec{k}}+i\eta 0} - [\hbar\omega - G_{\vec{k}}(z+\hbar\omega+i\eta 0)] \times \frac{\partial}{\partial\epsilon_{\vec{k}}}\ \frac{1}{z-\epsilon_{\vec{k}}+i\eta 0} + \cdots \quad (3.16)$$

which, combined with (3.15), yields

$$S_{\vec{k}}(z-i0)S_{\vec{k}}(z+i0) \simeq \pi\delta(z-\epsilon_{\vec{k}}-M_{\vec{k}}(z))/\Gamma_{\vec{k}}(z)\ , \quad (3.17a)$$

$$\lim_{\omega\to 0} S_{\vec{k}}(z+i\eta 0)S_{\vec{k}}(z+\hbar\omega+i\eta 0) = -\frac{S'_{\vec{k}}(z+i\eta 0)}{1-G'_{\vec{k}}(z+i\eta 0)} \simeq \frac{\partial}{\partial\epsilon_{\vec{k}}}\ \frac{1}{z-\epsilon_{\vec{k}}+i\eta 0}\ . \quad (3.17b)$$

Using (3.4), (3.11), (3.13), and (3.17), one finds

$$\langle\!\langle \hat{J}\hat{K}\rangle\!\rangle = \mathrm{I}+\mathrm{II}\ , \quad (3.18a)$$

where

$$\mathrm{I} = e^2\sum_{\vec{k}} v_{\vec{k}x}\int_{-\infty}^{\infty} dz[z-\mu+m_{\vec{k}}(z)][-f^{(-)\prime}(z)]\phi_{\vec{k}}(z)\delta(z-\epsilon_{\vec{k}}-M_{\vec{k}}(z)) \quad (3.18b)$$

and

$$\mathrm{II} = e^2\sum_{\vec{k}\vec{k}'\vec{q}}\sum_{\pm}\pm\int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dx\,[-f^{(-)\prime}(z)]\phi_{\vec{k}}(z)\delta(z-\epsilon_{\vec{k}}-M_{\vec{k}}(z))f^{(-)}(x)(\epsilon_{\vec{k}'}-\mu)\delta_{\vec{k}',\vec{k}+\vec{q}}$$
$$\times|V_{\vec{q}}|^2\left(P\frac{1}{z-x\pm\hbar\omega_{\vec{q}}}\ \frac{1}{\hbar}\ \frac{\partial}{\partial k'_x}\delta(x-\epsilon_{\vec{k}'})-\delta(z-x\pm\hbar\omega_{\vec{q}})\frac{1}{\hbar}\ \frac{\partial}{\partial k'_x}P\frac{1}{x-\epsilon_{\vec{k}'}}\right). \quad (3.18c)$$

After a lengthy algebra, which involves integrations by parts in k'_x, one reduces (3.18c) to

$$\mathrm{II} = e^2\sum_{\vec{k}}\int_{-\infty}^{\infty}dz[-f^{(-)\prime}(z)]\phi_{\vec{k}}(z)\delta(z-\epsilon_{\vec{k}}-M_{\vec{k}}(z))$$
$$\times\left[-v_{\vec{k}x}m_{\vec{k}}(z)+(z-\mu)\sum_{\vec{k}'\vec{q}}\sum_{\pm}\pm v_{\vec{k}'x}|V_{\vec{q}}|^2\delta_{\vec{k}',\vec{k}+\vec{q}}\left(f^{(-)\prime}(\epsilon_{\vec{k}'})P\frac{1}{z-\epsilon_{\vec{k}'}\pm\hbar\omega_{\vec{q}}}\right.\right.$$
$$\left.\left.-[f^{(-)}(\epsilon_{\vec{k}'})-f^{(-)}(z\pm\hbar\omega_{\vec{q}})]P'\frac{1}{z-\epsilon_{\vec{k}'}\pm\hbar\omega_{\vec{q}}}\right)\right]. \quad (3.19)$$

It is seen that terms proportional to $m_{\vec{k}}(z)$ in (3.18b) and (3.19) cancel each other. Defining the rest of the terms as I′ and II′, respectively,

$$\mathrm{I}' = \tfrac{1}{3}(\pi e k_B T)^2\frac{\partial}{\partial z}\left(\sum_{\vec{k}} v_{\vec{k}x}\phi_{\vec{k}}(z)\delta(z-\epsilon_{\vec{k}}-M_{\vec{k}}(z))\right)_{z=\mu} \quad (3.20a)$$

and

$$\mathrm{II}' = -\tfrac{1}{3}(\pi e k_B T)^2\sum_{\vec{k}} v_{\vec{k}x}m''_{\vec{k}}(\mu)\phi_{\vec{k}}(\mu)\delta(\mu-\epsilon_{\vec{k}})\ . \quad (3.20b)$$

Inserting (3.12) in (3.20), and using (3.3), the thermopower is given by

$$\mathcal{S} = \mathcal{S}_1+\mathcal{S}_2\ , \quad (3.21a)$$

where

$$\mathcal{S}_1 = \frac{e\pi^2k_B^2T}{3\sigma_{xx}^{(0)}}\sum_{\vec{k}} v_{\vec{k}x}^2[1-M'_{\vec{k}}(\mu)] \times\frac{\partial}{\partial z}[\tau_{\vec{k}}^{(0)}(z)\delta(z-\epsilon_{\vec{k}})]_{z=\mu} \quad (3.21b)$$

and

$$\mathcal{S}_2 = -\frac{e\pi^2k_B^2T}{3\sigma_{xx}^{(0)}}\sum_{\vec{k}} v_{\vec{k}x}^2 m''_{\vec{k}}(\mu)\tau_{\vec{k}}^{(0)}(\mu)\delta(\mu-\epsilon_{\vec{k}})\ . \quad (3.21c)$$

The "bare" relaxation time $\tau_{\vec{k}}^{(0)}(z)$ is obtained from (3.12b) by dropping the self-energy correction [e.g., $M_{\vec{k}}(z)$]. Note that $\tau_{\vec{k}}^{(0)}(\mu)=\tau_{\vec{k}}(\mu)$ and $\tau'_{\vec{k}}(\mu) = [1-M'_{\vec{k}}(\mu)]\tau_{\vec{k}}^{(0)\prime}(\mu)$. The bare conductivity is given by a well known expression[21]

$$\sigma_{xx}^{(0)} = e^2\sum_{\vec{k}} v_{\vec{k}x}^2\tau_{\vec{k}}^{(0)}(\mu)\delta(\mu-\epsilon_{\vec{k}})\ .$$

It is seen that (3.21b) constitutes the enhancement of the thermoelectric power through the mass enhancement factor $1-M'_{\vec{k}}(\mu)$ discussed in Sec. I. The quantity in (3.21c) represents new effects discussed earlier in Sec. II.

The expression in (3.21c) can be identified with that given in (2.14) in the following way. Starting from an expression [cf. (3.9)]

$$M_{\vec{k}}(z)=\sum_{\vec{k}'}\sum_{\pm} f^{(\mp)}(\epsilon_{\vec{k}'})|V_{\vec{k}-\vec{k}'}|^2 \times P\,\frac{1}{z-\epsilon_{\vec{k}'}\pm\hbar\omega_{\vec{k}-\vec{k}'}}, \qquad (3.22)$$

we find

$$\frac{1}{\hbar}\nabla_{\vec{k}}M'_{\vec{k}}(z)=-\sum_{\vec{k}'} f^{(\mp)}(\epsilon_{\vec{k}'})\frac{1}{\hbar}\nabla_{\vec{k}}\times\left(|V_{\vec{k}-\vec{k}'}|^2 P'\,\frac{1}{z-\epsilon_{\vec{k}'}\pm\hbar\omega_{\vec{k}-\vec{k}'}}\right) -\vec{v}_{\vec{k}}m''_{\vec{k}}(z). \qquad (3.23)$$

For $z=\mu$, the first term of the above expression vanishes on integrating by parts, yielding

$$(1/\hbar)\nabla_{\vec{k}}M'_{\vec{k}}(\mu)=-\vec{v}_{\vec{k}}m''_{\vec{k}}(\mu), \qquad (3.24)$$

and, therefore,

$$\mathcal{S}_2=\frac{\pi^2k_B^2T}{3e\sigma_{xx}^{(0)}}\left(\frac{e^2}{12\pi^3\hbar}\right)\times\int_{\mu=\epsilon_{\vec{k}}} dS\,\frac{[\vec{v}_{\vec{k}}\cdot(1/\hbar)\nabla_{\vec{k}}M'_{\vec{k}}(\mu)]\tau_{\vec{k}}^{(0)}(\mu)}{v_{\vec{k}}}. \qquad (3.25)$$

This expression is identical to that of (2.14). Note that in the above calculation [namely, in deriving (3.23) from (3.22)], we have assumed that the electron-phonon coupling strength depends only on the momentum transfer in according with the approximation of the present section. However, the expression given in (2.14) is general and free of this assumption. This means that the latter will follow from a general expression of the energy current operator given in the Appendix [i.e., (A5)]. This point is under investigation.

IV. MAGNETO-THERMOELECTRIC POWER

In this section we examine the effect of the electron-phonon interaction on magneto-thermoelectric power semiclassically. For this purpose we introduce a static external magnetic field $\vec{H}$ along the x direction to the problem studied in Sec. II. Using Onsager's relation (2.8) and assuming a cubic symmetry (with $\vec{H}$ along a symmetry axis), one finds from (2.1), (2.4), and (2.5),

$$J_x=\sigma_{xx}\mathcal{E}_x+\sigma_{xy}\mathcal{E}_y-eL_0T\left(\sigma'_{xx}\frac{\partial T}{\partial x}+\sigma'_{xy}\frac{\partial T}{\partial y}\right)\equiv 0, \qquad (4.1a)$$

$$J_y=\sigma_{yx}\mathcal{E}_x+\sigma_{yy}\mathcal{E}_y-eL_0T\left(\sigma'_{yx}\frac{\partial T}{\partial x}+\sigma'_{yy}\frac{\partial T}{\partial y}\right)\equiv 0, \qquad (4.1b)$$

$$U_y=eL_0T^2(\sigma'_{yx}\mathcal{E}_x+\sigma'_{yy}\mathcal{E}_y)+L_{TT}^{yx}\frac{\partial T}{\partial x}+L_{TT}^{yy}\frac{\partial T}{\partial y}. \qquad (4.2)$$

Here $L_0=\frac{1}{3}(\pi k_B/e)^2$ is the Lorentz number and the prime on the conductivity tensors means the derivative with respect to the Fermi energy. In (4.1) we have set $\vec{J}=0$, because the electric current does not flow in the thermoelectric power measurement.

For simplicity we assume a single relaxation time $\tau_{\vec{k}}^*$ for distribution functions $\vec{\phi}_{\vec{k}}$ and $\vec{\psi}_{\vec{k}}$ in (2.2). This assumption is valid, for example, for elastic scattering. Using the Landau-Boltzmann equation,[2] one then finds $\vec{\psi}_{\vec{k}}=-(E_{\vec{k}}-\mu)\vec{\phi}_{\vec{k}}/k_BT$ and $\vec{\phi}_{\vec{k}}=\tau_{\vec{k}}^*\vec{v}_{\vec{k}}^*$, obtaining

$$L_{TT}=L_0T\sigma(\mu). \qquad (4.3)$$

A. Adiabatic effect

If the sample surfaces are in contact with the vacuum in the y direction, the heat current U_y vanishes in (4.2). Defining $\mathcal{S}(\vec{H})\equiv\mathcal{E}_x/(\partial T/\partial x)$ and the Nernst-Ettingshausen coefficient $\mathcal{S}_{NE}\equiv\mathcal{E}_y/(\partial T/\partial x)$, one obtains from (4.1) to (4.3), for a large magnetic field (i.e., $\omega_c\tau^*\gg 1$, ω_c is the cyclotron resonance),

$$\mathcal{S}_{NE}(\vec{H})=eL_0T\left(\frac{\sigma_{xy}^{(0)}(\vec{H})}{\sigma_{yy}^{(0)}(\vec{H})}\right)\frac{d}{dz}\ln\sigma_{xy}(\vec{H})\Big|_{z=\mu} \qquad (4.4a)$$

and

$$\Delta\mathcal{S}\equiv\mathcal{S}(\vec{H})-\mathcal{S}(\vec{H}\equiv 0) =eL_0T\left(2\frac{d}{dz}\ln\sigma_{xy}(\vec{H}) -\frac{d}{dz}\ln[\sigma_{yy}(\vec{H})\sigma_{xx}(\vec{H}=0)]\right)_{z=\mu}. \qquad (4.4b)$$

In (4.4a) the conductivity tensors in the parentheses have been replaced by their bare values. The result in (4.4b) has been derived by Averback and Wagner[9] in a slightly different form. The major difficulty in calculating the thermoelectric coefficients is that they usually contain contributions arising from the energy derivative of the relaxation time. It will become clear shortly that the latter contribution is absent in (4.4a), because $\sigma_{xy}(\vec{H})$ is independent of the relaxation time. Also, it is only weakly present in (4.4b), because the relaxation times in the second term of (4.4b) tend to cancel out.[9]

For uncompensated metals without open orbits perpendicular to the magnetic field, one has[22] $\sigma_{xy}(z)=ec[n_e(z)-n_h(z)]/H$ where c, $n_e(z)$, and $n_h(z)$ are the speed of light, the number of electrons, and holes contained within the energy surface $E_k=z$, respectively. It is interesting to note that the quasiparticle velocity given in (2.11) does not appear in the off-diagonal tensor σ_{xy}. Therefore, there is no contribution of the type of (2.14) arising from the electron-phonon modification of the quasiparticle velocity. Using the argument presented in the paragraph following (2.11), the high-field Nernst-Ettingshausen coefficient given in (4.4a) is simply enhanced by the mass renormalization factor $1+\lambda$ [cf. (2.12)] alone. This enhancement has apparently been seen in recent experiments by Fletcher[23] and by Thaler, Fletcher, and Bass[23] in molybdenum and aluminum, respectively.

Also, it follows that the first term on the right hand side of (4.4b) is enhanced by a factor $1+\lambda$. For the second term, one writes[24]

$$\sigma_{yy}(\vec{H}) = \frac{1}{4\pi^3\hbar}\left(\frac{c\hbar}{H}\right)^2 \int_{E_{\vec{k}}=\mu} \frac{dS\tilde{K}_x^2}{v_{\vec{k}}^* \tau_H^*}, \quad (4.5)$$

where $\tilde{K}_x$ is the x component of the wave vector measured from the centroid of the electron's orbit and τ_H^* is a field dependent relaxation time.[24] The only dependence on the quasiparticle velocity is explicitly contained in the denominator in (4.5). In a spherical model, the quasiparticle velocities in (2.10) and (4.5) are factored out of the integral, and contributions to $\Delta\mathcal{S}$ arising from the energy dependence of the quasiparticle velocity are cancelled out in the second term of (4.4b). Again, this means that there is no contribution arising from the electron-phonon correction of the quasiparticle velocity. One then concludes in a similar way as before that $\Delta\mathcal{S}$ is simply enhanced by a factor $1+\lambda$. However, for a general band structure, there is some contribution from the electron-phonon modification of the quasiparticle velocity. The observation of the enhancement of $\Delta\mathcal{S}$ in aluminum has been reported by Opsal *et al.*[3]

B. Isothermal effect

If the temperature gradient in the y direction is zero (i.e., $\partial T/\partial y = 0$), then one obtains from (4.1)

$$\mathcal{S}(\vec{H}) = \frac{1}{2} eL_0 T \frac{d}{dz} \ln[\sigma_{yy}(\vec{H})^2 + \sigma_{xy}(\vec{H})^2]. \quad (4.6)$$

In the absence of the magnetic field, the above result reduces to the adiabatic result (2.9). For a strong magnetic field (i.e., $\omega_c\tau^* \gg 1$), one has $\sigma_{yy}/\sigma_{xy} \sim 1/H \ll 1$ for uncompensated metals without open orbits.[21] In this limit, (4.6) becomes

$$\mathcal{S}(\vec{H}) = eL_0 T \frac{d}{dz} \ln\sigma_{xy}(\vec{H}). \quad (4.7)$$

Using the previous argument, $\mathcal{S}(\vec{H})$ is then simply enhanced by a factor $1+\lambda$. The contributions from the derivative of the relaxation time and from electron-phonon modification of the quasiparticle velocity are absent. It is interesting to note that these two contributions always accompany each other, as is clearly seen from the fact they appear in (2.10) and (4.5) as a product. Other thermoelectric coefficients contain these contributions and will not be presented here.

V. CONCLUSION

The effect of the electron-phonon interaction on the electron diffusion thermoelectric power in metals has been studied microscopically. It is demonstrated that the semiclassical Mott's rule based on Landau-Boltzmann theory leads to a correct (microscopic) result. It is found that the thermoelectric power is enhanced not only by the mass enhancement factor $1+\lambda$ but also by a new effect, arising from the electron-phonon modification of the quasiparticle velocity. Higher-order processes are shown to be important for the thermoelectric phenomena unlike in dc conductivity, because the thermoelectric power depends delicately on energy at the Fermi level. The effect of the electron-phonon interaction on some magneto-thermoelectric coefficients has also been studied.

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APPENDIX

In this appendix we derive the electronic part of the energy current operator $\hat{Q}$. The energy current $\vec{Q}$ is related to the energy density ρ, by the continuity equation

$$\partial\rho/\partial t = -\nabla\cdot\vec{Q}, \quad (A1)$$

where

$$\rho = \tfrac{1}{2}(\psi^* H\psi + \text{c.c.}),$$

the second term meaning complex conjugate. The total wave function satisfies the Schrödinger equation $i\hbar\partial\psi/\partial t = H\psi$. One then finds

$$\frac{\partial\rho}{\partial t} = -\frac{\hbar}{4im}\nabla\cdot[\psi^*\nabla(H\psi) - (\nabla\psi^*)H\psi] + \text{c.c.}, \quad (A2)$$

m being the electronic mass. Comparing (A2) with (A1) and introducing a field operator Ψ and its Hermitian conjugate $\Psi^\dagger$, the energy current operator is given by

$$\hat{Q} = \frac{1}{2m}\int \Psi^\dagger \hat{p} H\Psi d^3r + \text{H.c.}. \quad (A3)$$

Here $\hat{p}$ and H.c. mean momentum operator and Hermitian conjugate, respectively. Separating H

$= H_0 + H'$, where H_0 is the Bloch Hamiltonian: $H_0|\vec{k}\rangle = \epsilon_{\vec{k}}|\vec{k}\rangle$, one has,[14] for $\vec{q} = \vec{k}' - \vec{k}$,

$$\langle \vec{k}'|1/m\hat{p}|\vec{k}\rangle = \vec{v}_{\vec{k}}\delta_{\vec{k}',\vec{k}} + 1/\hbar(\nabla_{\vec{k}'} + \nabla_{\vec{k}})V^{(0)}_{\vec{k}',\vec{k}}(b_{\vec{q}} + b^{\dagger}_{-\vec{q}}) . \tag{A4}$$

Inserting (A4) in (A3) and using second quantized operators, we obtain to the first order in electron-phonon interaction

$$\hat{Q} = \sum_{\vec{k}} \vec{v}_{\vec{k}}\epsilon_{\vec{k}}a^{\dagger}_{\vec{k}}a_{\vec{k}} + \sum_{\vec{k}'\vec{k}\vec{q}} \frac{\vec{v}_{\vec{k}'} + \vec{v}_{\vec{k}}}{2} V^{(0)}_{\vec{k}',\vec{k}}a^{\dagger}_{\vec{k}'}a_{\vec{k}}(b_{\vec{q}} + b^{\dagger}_{-\vec{q}})\delta_{\vec{k}',\vec{k}+\vec{q}}$$
$$+ \sum_{\vec{k}'\vec{k}\vec{q}} \frac{\epsilon_{\vec{k}'} + \epsilon_{\vec{k}}}{2} [1/\hbar(\nabla_{\vec{k}'} + \nabla_{\vec{k}})V^{(0)}_{\vec{k}',\vec{k}}] a^{\dagger}_{\vec{k}'}a_{\vec{k}}(b_{\vec{q}} + b^{\dagger}_{-\vec{q}})\delta_{\vec{k}',\vec{k}+\vec{q}} . \tag{A5}$$

When the electron-phonon interaction depends only on the momentum transfer (i.e., $V^{(0)}_{\vec{k}',\vec{k}} = V^{(0)}_{\vec{k}'-\vec{k}}$), the last term vanishes and (A5) reduces to $\hat{Q}$ defined in (3.7).

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[1]T. Holstein, Ann. Phys. (N.Y.) 29, 410 (1964).

[2]R. E. Prange and L. P. Kadanoff, Phys. Rev. A 134, 566 (1964).

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

[4]N. F. Mott and H. Jones, *Theory of Metals and Alloys* (Clarendon, Oxford, 1936).

[5]See also B. J. Thaler and J. Bass, J. Phys. F 6, 2315 (1976); J. L. Opsal and D. K. Wagner, *ibid.* 6, 2323.

[6]S. K. Lyo, Phys. Rev. Lett. 39, 363 (1977).

[7]J. M. Ziman, *Electrons and Phonons* (Oxford U.P., Oxford, 1960).

[8]M. Ia. Azbel, M. I. Kaganov, and I. M. Lifschitz, Zh. Eksp. Teor. Fiz. 32, 1188 (1957) [Sov. Phys.-JETP 5, 967 (1957)].

[9]R. S. Averback and D. K. Wagner, Solid State Commun. 11, 1109 (1972).

[10]A general expression for S_1 is given in (3.21b).

[11]This is obtained readily from (2.40) of Ref. 1.

[12]The effect of this approximation is discussed in the Appendix and later in the text.

[13]By evaluating (3.3)–(3.5) in terms of exact eigenstates, one can readily show that this formula is equivalent to that given by R. Kubo, M. Yokota, and S. Nakajima, J. Phys. Soc. Jpn. 12, 1203 (1957).

[14]W. Kohn and J. M. Luttinger, Phys. Rev. B 108, 590 (1957).

[15]P. E. Nielsen and P. L. Taylor, Phys. Rev. Lett. 21, 893 (1968).

[16]A. Hasegawa, Solid State Commun. 15, 1361 (1974).

[17]A. A. Abrikosov, L. P. Gor'kov, and I. Ye Dzyaloslinskii, *Quantum Field Theoretical Methods in Statistical Physics* (Pergamon, New York, 1965); A. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).

[18]The derivation is similar to that of (3.19) of Ref. 1.

[19]This corresponds to (3.18) of Ref. 1.

[20]Note that $G_{\vec{k}}(z)$ and $m_{\vec{k}}(z)$ are slowly varying functions of $\vec{k}$. See, for example, Ref. 1.

[21]This expression is equivalent to that of (2.13).

[22]I. M. Lifshitz, M. Ia. Azbel, and M. I. Kaganov, Zh. Eksp. Teor. Fiz. 30, 220 (1955) [Sov. Phys.-JETP 3, 143 (1956)].

[23]R. Fletcher, Phys. Rev. B 14, 4329 (1976); B. J. Thaler, R. Fletcher, and J. Bass, J. Phys. F (accepted for publication).

[24]D. K. Wagner, Phys. Rev. B 5, 336 (1972).