Theory of Electron-Phonon Enhancement of Thermoelectric Power in Metals

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The enhancement of the electron diffusion thermopower due to the electron-phonon interaction is studied microscopically. I find that the thermopower is enhanced not only by the mass enhancement but also significantly by a new mechanism independent of scattering. The result is justified in terms of the Landau-Boltzmann equation.

It is well known that the effect of electron-phonon mass renormalization does not appear in dc electrical conductivity.[1,2] Also, since the work of Prange and Kadanoff,[2] it has been believed that the above effect appears neither in thermal conductivity nor 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. They could explain their data[3] in aluminum with dilute gallium impurities only by including the effect of mass enhancement of 45%. However, it is not clear to what extent their semiclassical approach treats the effect of electron-phonon interaction and mass renormalization. In view of these developments, it seems necessary to resolve the situation by making a rigorous microscopic analysis. The present theory is based on Holstein's treatment[1] of electron-phonon system. I find that the thermopower is enhanced not only by the mass enhancement but also significantly by a new mechanism independent of scattering. The result is justified in terms of the Landau-Boltzmann equation.

I study a system of Bloch electrons interacting with the lattice and a low concentration of impurities at low temperature ($T \ll \Theta_D$, Debye temperature). One can easily generalize the result to other temperature regimes. The thermopower is given by[5]

$$\mathcal{S} = \langle\langle JK \rangle\rangle / eT \langle\langle JJ \rangle\rangle. \tag{1}$$

Here e is the electronic charge (negative) and

$$\langle\langle JK \rangle\rangle = \frac{1}{i} \frac{\partial}{\partial \omega} \mathcal{F}_{JK}(\hbar\omega + i0)\Big|_{\omega=0}. \tag{2}$$

The correlation function is given by

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

where the angular brackets denote the grand-canonical thermodynamic average, $\hbar\omega_r = k_B T 2\pi r i$, and $\beta^{-1} = k_B T$. Here r is an integer and k_B is Boltzmann's constant. $J(u)$ is in the imaginary-time Heisenberg representation. Finally, using the Frölich Hamiltonian,[1] K is given in terms of the charge-current operator J and the electronic energy current operator Q by

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

$$K_{\vec{k}',\vec{k}} \equiv (eQ - \mu J)_{\vec{k}',\vec{k}} = ev_{\vec{k}x}(\epsilon_{\vec{k}} - \mu)\delta_{\vec{k}',\vec{k}} + e\tfrac{1}{2}(v_{\vec{k}'x} + v_{\vec{k}x}) V_{\vec{q}}^{(0)} (b_{\vec{q}} + b_{-\vec{q}}^{\dagger}) \delta_{\vec{k}',\vec{k}+\vec{q}}, \tag{3}$$

where $\epsilon_{\vec{k}}$ and $v_{\vec{k}}$ are the Bloch energy and Bloch velocity of an electron of wave vector $\vec{k}$, and $V_{\vec{q}}^{(0)}$ is the bare electron-phonon interaction strength, assumed to be a function of the momentum transfer only. μ, $\delta_{\vec{k}',\vec{k}}$, and $b_{\vec{q}}$ ($b_{-\vec{q}}^{\dagger}$) are, respectively, the chemical potential, the Kronecker delta, and a Boson destruction (creation) operator. The temperature gradient is assumed to be in the x direction.

The correlation function in (2) is found in terms of the upper charge-current vertex correction (defined as EF-vertex part following Holstein's work[1]), which consists of ladders of single impurity lines and phonon lines. The lower vertex contains not only the first term of (3) but also terms arising from the second member of (3) and illustrated in Fig. 1. Here the curvy, solid, and incoming wiggly lines represent, respectively, phonon propagators, full electron propagators [to be denoted as $S_{\vec{k}}(z)$], and the external line. The electron-phonon vertices ($V_{\vec{q}}$) and the phonon frequency ($\omega_{\vec{q}}$) are dressed.[1]

One then finds

$$\langle\langle JK\rangle\rangle = \frac{e^2}{2\pi}\sum_{\vec{k}} v_{\vec{k}x}\int_{-\infty}^{\infty} dz\{[\epsilon_{\vec{k}}+M_{\vec{k}}(z)+m_{\vec{k}}(z)-\mu][-f^{(-)\prime}(z)]\varphi_{\vec{k}}(z)2\pi\delta[z-\epsilon_{\vec{k}}-M_{\vec{k}}(z)]$$

$$+\sum_{\pm}\pm(\epsilon_{\vec{k}}-\mu)f^{(-)}(z)\frac{S_{\vec{k}}'(z\pm i0)}{1-G_{\vec{k}}'(z\pm i0)}\frac{\partial}{\partial\omega}\Lambda_{\vec{k}}(z\pm i0, z+\hbar\omega\pm i0)\Big|_{\omega=0}\}, \quad (4)$$

where $f^{(-)}(z)$ and ω are the Fermi function and the external frequency, respectively. The prime means a derivative with respect to the argument. The electronic self-energy part is given in terms of its real and imaginary parts by $G_{\vec{k}}(z\pm i0)=M_{\vec{k}}(z)\mp i\Gamma_{\vec{k}}(z)$. The self-energy–like quantity $m_{\vec{k}}(z)$ is defined by

$$m_{\vec{k}}(z)=v_{\vec{k}x}^{-1}\sum_{\vec{k}'}\sum_{\pm}v_{\vec{k}'x}|V_{\vec{q}}|^2 f^{(\mp)}(\epsilon_{\vec{k}'})\delta_{\vec{k}',\vec{k}+\vec{q}}\mathcal{P}(z-\epsilon_{\vec{k}'}\pm\hbar\omega_{\vec{q}})^{-1}, \quad (5)$$

where $f^{(+)}\equiv 1-f^{(-)}$ and $\mathcal{P}$ indicates the principal part. The real part of the self-energy $M_{\vec{k}}(z)$ is obtained by replacing $v_{\vec{k}'x}$ in (5) by $v_{\vec{k}x}$. The distribution function $\varphi_{\vec{k}}(z)$ in (4) is related to the EF-vertex part $\Lambda_{\vec{k}}$ by[1] $\varphi_{\vec{k}}(z)=\hbar\Lambda_{\vec{k}}(z-i0, z+i0)/2\Gamma_{\vec{k}}(z)$ and to the (bare) transport relaxation time by $\varphi_{\vec{k}}(z)=v_{\vec{k}x}\tau_{\vec{k}}(z)$, where

$$\tau_{\vec{k}}(z)^{-1}=(2\pi N/\hbar)\sum_{\vec{k}'}|U_{\vec{k}',\vec{k}}|^2(1-\cos\theta_{\vec{k}',\vec{k}})\delta[z-\epsilon_{\vec{k}'}-M_{\vec{k}'}(z)]. \quad (6)$$

Here $U_{\vec{k}',\vec{k}}$ is the Fourier transform of the impurity potential, assumed to depend only on the scattering angle $\theta_{\vec{k}',\vec{k}}$, and N is the number of impurities. The quantity $\partial\Lambda_{\vec{k}}/\partial\omega$ in (4) is given by[6]

$$(\partial/\partial\omega)\Lambda_{\vec{k}}(z+i\eta 0, z+\hbar\omega+i\eta 0)|_{\omega=0}=(i\hbar)^{-1}\int_{-\infty}^{\infty}dx\sum_{\vec{k}}\sum_{\pm}\mp f^{(-)\prime}(x)|V_{\vec{q}}|^2\varphi_{\vec{k}'}(x)\delta[x-\epsilon_{\vec{k}'}-M_{\vec{k}'}(x)]$$

$$\times[\mathcal{P}(z-x\pm\hbar\omega_{\vec{q}})^{-1}-\pi i\eta\delta(z-x\pm\hbar\omega_{\vec{q}})], \quad \eta=\pm 1. \quad (7)$$

Although the phonon ladders do not contribute significantly to the scattering at low temperature, they are directly responsible for (7). Noting that $\varphi_{\vec{k}}(z)$ is inversely proportional to the concentration, (4) and (7) are given to the lowest-order in the latter quantity. Another smallness parameter in the present theory is the ratio of the sound velocity (c_s) to the Fermi velocity (v_F), or equivalently that of the Debye energy to the Fermi energy. The two terms $M_{\vec{k}}(z)+m_{\vec{k}}(z)$ in the parentheses of (4) arise from the processes shown in Fig. 1, and account for additional electronic energy current arising from the electron-phonon interaction. Although these quantities are small (i.e., of order of Debye energy), they vary rapidly over the range of the Debye energy [e.g., $\partial M_{\vec{k}}(z)/\partial z\sim 1$] and lead to an important contribution. The term proportional to $\partial\Lambda_{\vec{k}}/\partial\omega$ in (4) is apparently of higher order in electron-phonon interaction in view of (7). It is known[1] that the contribution from terms of this type of EF part is negligible for the charge conduction. However, in the present problem, the quantity $\partial\Lambda_{\vec{k}}/\partial\omega$ leads to a significant contribution. It turns out that the term proportional to $m_{\vec{k}}(z)$ in (4) cancels part of the above-mentioned contribution arising from $\partial\Lambda_{\vec{k}}/\partial\omega$. One then finds to the lowest order in the smallness parameters

$$\langle\langle JK\rangle\rangle=\tfrac{1}{3}(\pi e k_B T)^2\sum_{\vec{k}}v_{\vec{k}x}^2\{[1-M_{\vec{k}}'(\mu)](\partial/\partial\mu)[\tau_{\vec{k}}^{(0)}(\mu)\delta(\mu-\epsilon_{\vec{k}})]-m_{\vec{k}}''(\mu)\tau_{\vec{k}}^{(0)}(\mu)\delta(\mu-\epsilon_{\vec{k}})\}. \quad (8)$$

In (8), the "bare" relaxation time $\tau_{\vec{k}}^{(0)}(z)$ is defined via (6) by dropping $M_{\vec{k}'}(z)$ in the δ function, and use has been made of the relations

$$\tau_{\vec{k}}(\mu)\simeq\tau_{\vec{k}}^{(0)}(\mu), \quad \tau_{\vec{k}}'(\mu)=[1-M_{\vec{k}}'(\mu)]\tau_{\vec{k}}^{(0)\prime}(\mu),$$

and

$$(\partial/\partial\mu)[\tau_{\vec{k}}(\mu)\delta(\mu-\epsilon_{\vec{k}}-M_{\vec{k}}(\mu)]\simeq[1-M_{\vec{k}}'(\mu)](\partial/\partial\mu)[\tau_{\vec{k}}^{(0)}(\mu)\delta(\mu-\epsilon_{\vec{k}})].$$

Assuming $-M_{\vec{k}}'(\mu)$ ($\equiv\lambda$) to be isotropic at the Fermi surface, and using

$$\langle\langle JJ\rangle\rangle=e^2\sum_{\vec{k}}v_{\vec{k}x}^2\tau_{\vec{k}}^{(0)}(\mu)\delta(\mu-\epsilon_{\vec{k}})\equiv e^2\sigma^{(0)}(\mu), \quad (9)$$

one finds finally from (1) and (8)

$$\mathcal{S}=(1+\lambda)\mathcal{S}^{(0)}+(\pi^2 k_B^2 T/3e)[-m_{k_F}''(\mu)], \quad (10)$$

where the "bare" thermoelectric power $\mathcal{S}^{(0)}$ is given by

$$\mathcal{S}^{(0)} = (\pi^2 k_B{}^2 T/3e)(\partial/\partial\mu) \ln\sigma^{(0)}(\mu). \tag{11}$$

Note that only unrenormalized quantities enter (9) and (11). The first term of (10) corresponds to the enhancement through mass renormalization and arises from the first term of the curly brackets of (4) apart from the $m_{\vec{k}}(z)$ term. This term was obtained by Opsal and co-workers[3] semiclassically. The second term of (10) represents a new effect, whose noble physical origin will be discussed shortly. To make an order-of-magnitude estimate, one finds, using effective-mass and Debye approximations

$$-m_{\vec{k}_F}''(\mu) = \lambda/2\mu. \tag{12}$$

Comparing (12) with (10) and (11), it is seen that the second term of (10) constitutes a significant fraction of the thermopower. Although the bare relaxation time $\tau^{(0)}$ has been defined earlier by (6) for simplicity, $\tau^{(0)}$ in (9) and (11) should be understood as a generalized relaxation time; for example, it contains the effects of virtual recoil by impurities discussed by Nielsen and Taylor,[7] and the electron-phonon vertex correction to the impurity scattering discussed by Hasegawa.[8] This is achieved by modifying the irreducible scattering part accordingly.

Now, I justify (10), using the Landau-Boltzmann equation.[2] The latter leads to,[4] assuming cubic symmetry for simplicity,

$$\mathcal{S} = \frac{\pi^2}{3}\frac{k_B{}^2 T}{e}\frac{\partial}{\partial\mu}\ln\Big[\iint_{E_{\vec{k}}=\mu} dS\, v_{\vec{k}}^{(r)} \tau_{\vec{k}}^{(r)}(E_{\vec{k}})\Big]. \tag{13}$$

The integral in (13) is over the Fermi surface, and the renormalized relaxation time is given by[9] $\tau_{\vec{k}}^{(r)}(\mu) = (1+\lambda)\tau_{\vec{k}}^{(0)}(\mu)$. The quasiparticle energy and velocity are defined, respectively, by $E_{\vec{k}} = \epsilon_{\vec{k}} + M_{\vec{k}}(E_{\vec{k}})$ and

$$\vec{v}_{\vec{k}}^{(r)} = \frac{1}{\hbar}\nabla_{\vec{k}} E_{\vec{k}} = \frac{\vec{v}_{\vec{k}}}{1+\lambda} + \frac{1}{1+\lambda}\frac{1}{\hbar}\nabla_{\vec{k}} M_{\vec{k}}(z)\big|_{z=E_{\vec{k}}}. \tag{14}$$

The second term of (14) is of order c_s/v_F smaller than the first term and is insignificant for the electric conductivity. However, it varies very rapidly in energy and gives a significant contribution to (13). Using (14) in (13), one finds[3]

$$\mathcal{S} = (1+\lambda)\mathcal{S}^{(0)} + \frac{\pi^2}{3}\frac{k_B{}^2 T}{e}\left(\frac{1}{\hbar v_{k_{xF}}}\frac{\partial}{\partial k_{xF}} M_{\vec{k}_F}'(z)\right)_{z=\mu}, \tag{15}$$

the second term arising from that of (14). In (15) I have used $M_{\vec{k}_F}''(\mu) \sim c_s/v_F\mu \simeq 0$. When the electron-phonon matrix element is assumed to depend only on the momentum transfer, (15) reduces to (10). The former should be regarded as a more general result. Finally, the second term of (15) affects neither[10] the difference of the high-field and zero-field adiabatic magneto-thermopower,[3] $\mathcal{S}(\vec{H}) - \mathcal{S}(0)$, nor the high-field adiabatic Nernst-Ettingshausen effect.[11] This means that this term would not be observed in recent experimental investigations of mass enhancement in thermoelectricity.[3,11] A more detailed account of this work will be published elsewhere.

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[5]This formula is equivalent to that given by R. Kubo, M. Yokota, and S. Nakajima, J. Phys. Soc. Jpn. 12, 1203 (1957).
[6]This corresponds to the linear (in ω) term in (3.18) of Ref. 1.
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[9]This is seen from the fact that the dc conductivity ($\propto v_F(r)\tau(r)$) is unaffected by the mass enhancement (Refs. 1 and 2).
[10]This is strictly valid in a spherical model. See S. K. Lyo, to be published.
[11]R. Fletcher, Phys. Rev. B 14, 4329 (1976); B. J. Thaler, R. Fletcher, and J. Bass, to be published.

ERRATA

HEAVY-ION–INDUCED DEFECT PRODUCTION AT LOW TEMPERATURE IN SUPERCONDUCTING Nb_3Sn AND EFFECTS OF SATURATION. G. Ischenko, H. Adrian, S. Klaumünzer, M. Lehmann, P. Müller, H. Neumüller, and W. Szymczak [Phys. Rev. Lett. 39, 43 (1977)].

Part of a very important sentence has been omitted in the printed text. On page 44, second column, the sixth line should read as follows: "...the decrease of T_c due to the reduction of atomic long-range order and an increase of T_c due to a growing number of vacancies and interstitials."

POSITION AND DYNAMICS OF Ag IONS IN SUPERIONIC AgI USING EXTENDED X-RAY ABSORPTION FINE STRUCTURE. J. B. Boyce, T. M. Hayes, W. Stutius, and J. C. Mikkelsen, Jr. [Phys. Rev. Lett. 38, 1362 (1977)].

On page 1363, in the second paragraph, the fifth sentence should read "They give rise to the extensive structure between 1.6 and 3.8 Å which peaks at 2.56 Å, ..."

On page 1365 the fourth sentence should read: "..., in good agreement with the observed value of 3.0 ± 0.6."