Electron-phonon contribution to the thermopower of metals

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A theorem is proved for the thermopower when limited by the electron-phonon interaction. It is shown for simple metals that the thermopower is given by the Mott formula plus a correction term. The correction term is evaluated and shown to be small for simple metals. Thus we are able to show that Mott's formula is valid for phonon scattering by electrons, even when the energy dependence of the phonons is taken into account. This proof extends our earlier result, which only applied to static impurities, and to phonons in the adiabatic approximation.

I. INTRODUCTION

The thermoelectric power of metals continues to be a phenomenon that intrigues both theorists and experimentalists.[1-26] One issue, which has dominated the theoretical effort, is the role of electron-phonon interactions in limiting the thermopower. The situation is understood at high temperatures, and also at high magnetic fields. The situation is controversial at low temperatures, in the absence of a magnetic field. The experiments show a complicated dependence which is not understood. The theorists argue about whether the low-temperature results are affected by the electron-phonon mass enhancement. Much theoretical work has been brought to bear on this point.[7,12-23]

The purpose of the present paper is to prove a theorem regarding the electron-phonon contribution to the electronic part of the thermopower. Our theorem is that even for a fully interacting electron-phonon system, and including the inelastic nature of the electron scattering by the phonons, the thermopower is still given by the Mott formula plus a small correction term

$$S = S_M + \delta S \; , \tag{1}$$

$$S_M = \frac{\pi^2}{3}\left[\frac{k_B}{e}\right] k_B T \left[\frac{d\ln[\sigma(\varepsilon)]}{d\varepsilon}\right]_{\varepsilon=0} , \tag{2}$$

where S_M is the Mott formula, while δS is a correction term. The energy point $\varepsilon = 0$ is at the chemical potential. We provide an explicit evaluation for the correction term, and show that its leading term is of the fourth power in the electron-phonon matrix element. Although such high-order terms can often be neglected in transport calculations, this need not be so for the thermopower, which depends on how various quantities *change* at the Fermi level. However, we show explicitly that δS is negligible at both high and low temperatures, so that the Mott formula can be utilized in the evaluation of the thermopower. This theorem should save much work, since $\sigma(\varepsilon)$ is just the energy-dependent scattering function needed for the electrical conductivity.

The first exact theorem on the thermopower was by Chester and Thellung,[2] who showed the Mott formula is valid for electron scattering by static impurities. The present theorem is a continuation of our earlier work[18] on the Mott formula. Our earlier proof also considered phonons, but treated them in the adiabatic approximation which neglects the energy of the phonon. The present generalization to phonons of nonzero frequency greatly increases the power and usefulness of the Mott formula.

There are three separate regimes in simple metals.

(1) At large magnetic fields, experiments[8-11] showed that there is mass enhancement to the thermopower. Hänsch and Mahan[19] showed that theory predicted this result at high fields. This region seems understood.

(2) At high temperatures, in the absence of a field, the Mott formula is quite accurate. Here the theory also agrees with experiment.[24,25] Electron-phonon effects are important at high temperatures.

(3) At low temperatures, in the absence of a field, the situation is largely not understood.

The present discussion will mainly treat case (3), although we will also discuss case (2) briefly.

There has been much previous work on electron-phonon contributions to the thermopower in metals. Much of it has centered around the issue of whether the electron-phonon mass enhancement affects the results. The first discussion by Prange and Kadanoff[4] concluded that it did not. Later experimental work discovered mass enhancement in the thermopower,[8-11] which showed electron-phonon effects to be important. However, these experiments were at high magnetic field, and the measurements were for off-diagonal components of the thermopower tensor. Later theory[19,26] showed that the mass-enhancement factor λ did enter the thermopower for this experiment, in agreement with experiments.

However, the issue which has been discussed most often is whether electron-phonon interaction affects the longitudinal thermopower in zero magnetic field. This issue has been treated by Lyo,[12] Vilenkin,[13,14] Taylor,[13,15] Ono,[15,16] and a long sequence of other theorists.[17-23] Generally speaking, each successive calculation considered more terms in the diagrammatic expansion, and found these terms are important. Thus the result is getting longer with each published paper. There are two important interactions that scatter electrons at low temperatures—impurities and phonons. Their contributions interfere, and the mass-enhancement factors depend on the strength of the impurity scattering.

Our theorem has little to say regarding this topic. We prove that all of the complicated contributions are in the Mott term in the thermopower. However, that does not make them easier to calculate.

The early theories in this historical sequence were trying to just calculate the Mott contribution. Hänsch[21] was the first to realize the Mott term had corrections, and tried to calculate them. Using his formulas, we have been able to show the correction terms are small.

Recent calculations[24,25] showed that the Mott expression gave good values for the thermopower of alkali metals at high temperature. These results provide confirmation of our suggestion that the correction term δS to the thermopower, which results from the phonon energy, is small and can be neglected. We find that the correction term δS becomes increasingly small at high temperatures, while S_M is becoming larger, so that the Mott formula is increasingly accurate at high temperatures.

Many of our derivatives use techniques analogous to the method of "force-force" correlation functions. It is well known that this technique is not exact, and gives only approximate expressions for correlation functions.[27] However, here we use the method only to show whether contributions are large or small. In particular, we use it to estimate corrections to the Mott expressions. Since our results are qualitative, the use of force-force correlation functions is justified. That is, we use it to show the terms are negligibly small.

II. FORMALISM

In the previous paper[18] (hereafter called I) we studied the thermoelectric power S of a system of independent electrons interacting with static impurities, and adiabatic phonons, as described by the Hamiltonian

$$H=\sum_k \varepsilon_k c_k^\dagger c_k+\sum_q U(q)\rho(q)+\sum_{q\lambda}\hbar\omega_{q\lambda}a_{q\lambda}^\dagger a_{q\lambda} , \tag{3}$$

where ρ is the electron density operator, and for future reference we have introduced the notation

$$U(q)\equiv\frac{1}{\Omega}V^{\mathrm{imp}}(q)\rho^{\mathrm{imp}}(q)+\sum_\lambda W_\lambda(q)Q_\lambda(q) . \tag{4}$$

In I the heat current corresponding to Eq. (1) was found to be

$$\mathbf{j}_Q=\sum_k \xi_k\mathbf{v}_k c_k^\dagger c_k+\sum_q U(q)\mathbf{j}(q)+\sum_q \mathbf{B}(q)\rho(q) , \tag{5}$$

$$\xi_k=\varepsilon_k-\mu , \tag{6}$$

$$\mathbf{j}(q)=\tfrac{1}{2}\sum_k(\mathbf{v}_k+\mathbf{v}_{k+q})c_k^\dagger c_k , \tag{7}$$

$$\mathbf{B}(q)=\frac{-i}{M}\sum_\lambda[\nabla_q W_\lambda(q)]P_\lambda(q) , \tag{8}$$

$$P_\lambda(q)=M\dot{Q}_\lambda(q) . \tag{9}$$

There is also a term[13] from inelastic impurity scattering, which we neglect. In I it was shown that the Mott formula (2) for the thermopower is exact in the approximation where the energy of the phonons is neglected. In this approximation, the phonon displacement $Q_\lambda(q)$ is treated as a c number, while the phonon momentum $P_\lambda(q)$ is neglected.

Now we evaluate the electron-phonon contribution to the thermopower while including the energy of the phonons. A small correction term is derived to the Mott formula. To this end, we need to evaluate the transport coefficients $L^{ij}\equiv\lim_{\omega\to 0}[\mathrm{Re}\mathbb{L}^{ij}(\omega+i\delta)]$, where in dimension d

$$\mathbb{L}^{11}(i\omega)=-\frac{iT}{(i\omega)\hbar d\Omega}\int_0^{\hbar\beta}d\tau\, e^{i\omega\tau}\langle T_\tau\mathbf{j}(\tau)\cdot\mathbf{j}(0)\rangle , \tag{10}$$

$$\mathbb{L}^{12}(i\omega)=-\frac{iT}{(i\omega)\hbar d\Omega}\int_0^{\hbar\beta}d\tau\, e^{i\omega\tau}\langle T_\tau\mathbf{j}_Q(\tau)\cdot\mathbf{j}(0)\rangle . \tag{11}$$

The symbols $\mathbf{j}(0)$ and $\mathbf{j}(\tau)$ denote (7) evaluated at $\mathbf{q}=0$, but with τ either zero or nonzero. The thermopower is related to these transport coefficients

$$S=\frac{1}{eT}\frac{L^{12}}{L^{11}} . \tag{12}$$

These formulas are all needed for the derivation of the thermopower.

III. PROOF OF THEOREM

To prove the validity of the Mott formula, we will show that if $\sigma(\epsilon)$ is implicitly defined from its relation to L^{11} as given below, then L^{12} also has the following form:

$$L^{11}=\frac{T}{e^2}\int_{-\infty}^{\infty}d\epsilon\left[\frac{-dn_F(\epsilon)}{d\epsilon}\right]\sigma(\epsilon) , \tag{13}$$

$$L^{12}=\frac{T}{e^2}\int_{-\infty}^{\infty}\epsilon\, d\epsilon\left[\frac{-dn_F(\epsilon)}{d\epsilon}\right]\sigma(\epsilon)+\delta L^{12} . \tag{14}$$

In the energy integrals the factor of $dn_F/d\epsilon$ is symmetric in ϵ. If $\sigma(\epsilon)$ and $\epsilon\sigma(\epsilon)$ are expanded in powers of ϵ, the integrals therefore get nonzero contributions from even terms. The first term in (14) is the Mott contribution L_M^{12}. The two energy integrals can to lowest order in k_BT/E_F be approximated as

$$L^{11}\approx\frac{T}{e^2}\sigma(0) , \tag{15}$$

$$L_M^{12}\approx\frac{\pi^2k_B^2T^3}{3e^2}\left[\frac{d\sigma(\epsilon)}{d\epsilon}\right]_{\epsilon=0} . \tag{16}$$

The units are such that $\sigma(0)$ is the conductivity. The ratio of these two quantities, as in (12), produces the Mott expression (2) for the thermopower. The correction term δS in (1) comes from δL^{12}.

In order to show the relationship between L^{11} and L^{12} implied above, we take a slightly different route than in I. Define a function $F(\tau,\tau')$ which is the current-current correlation function when $\tau=\tau'$:

$$F(\tau,\tau')\equiv\sum_k \mathbf{v}_k\cdot\langle c_k^\dagger(\tau)c_k(\tau')\mathbf{j}(0)\rangle\ , \tag{17}$$

$$F(\tau,\tau^-)=\langle T_\tau \mathbf{j}(\tau)\cdot\mathbf{j}(0)\rangle\ . \tag{18}$$

Define its Fourier transform in the Matsubara formalism as

$$F(\tau,\tau')=\frac{1}{(\hbar\beta)^2}\sum_{ip,ip'}F(ip,-ip')e^{ip\tau}e^{ip'\tau'}\ . \tag{19}$$

It follows from Eq. (23) of I that

$$\mathbb{L}^{11}=-\frac{iT}{(i\omega)\hbar d\Omega}\frac{1}{\hbar\beta}\sum_{ip}F(ip,ip+i\omega)\ . \tag{20}$$

One can perform the summation over the complex frequency ip and cast the right-hand side in the form of (13) which derives an expression for

$$\sigma(\varepsilon)=\frac{e^2}{\hbar d\Omega}[F(\epsilon-i\delta,\epsilon+i\delta)-\mathrm{Re}F(\epsilon+i\delta,\epsilon+i\delta)]\ . \tag{21}$$

Now consider another function $S(\tau,\tau')$ related to F by

$$S(\tau,\tau')\equiv\frac{\hbar}{2}\left(\frac{\partial}{\partial\tau}-\frac{\partial}{\partial\tau'}\right)F(\tau,\tau')\ . \tag{22}$$

The "time" derivatives implied by (22) are evaluated using the equations of motion

$$\hbar\frac{\partial}{\partial\tau}c_k^\dagger(\tau)=[H,c_k^\dagger]=\xi_k c_k^\dagger+\sum_q U(q)c_{k+q}^\dagger\ , \tag{23}$$

$$\hbar\frac{\partial}{\partial\tau}c_k(\tau)=[H,c_k(\tau)]=-\xi_k c_k-\sum_q U(q)c_{k-q}\ . \tag{24}$$

It then follows from (17) and (22) that

$$S(\tau,\tau^-)=\sum_k \xi_k\mathbf{v}_k\cdot\langle T_\tau c_k^\dagger(\tau)c_k(\tau)\mathbf{j}(0)\rangle+\tfrac{1}{2}\sum_{qk}(\mathbf{v}_k+\mathbf{v}_{k+q})\cdot\langle T_\tau U(q,\tau)c_{k+q}^\dagger(\tau)c_k(\tau)\mathbf{j}(0)\rangle\ . \tag{25}$$

Compare this expression to (5). The right-hand side of the above equation has the form $\langle T_\tau \mathbf{j}_Q(\tau)\cdot\mathbf{j}(0)\rangle$ except the last term in $\mathbf{j}_Q$ is missing. Thus we can write

$$\langle T_\tau \mathbf{j}_Q(\tau)\cdot\mathbf{j}(0)\rangle=S(\tau,\tau^-)\ +\sum_q\langle T_\tau\rho(q,\tau)\mathbf{B}(q,\tau)\cdot\mathbf{j}(0)\rangle\ , \tag{26}$$

which relates $S(\tau,\tau')$ to $\mathbb{L}^{12}$ in (11). The last term in the above equation causes δL^{12}, which becomes from the third term in the expression (5) for the heat current. The first term on the right gives the Mott contribution. It is interesting that early theories[12] of the thermopower neglected the last term in the heat current. Vilenkin and Taylor[13] were the first to derive this term in the heat current, but neglected it as small. They were right.

We show that the first term in (26) gives the Mott expression by taking the Fourier transform

$$\int_0^{\hbar\beta}d\tau\, e^{i\omega\tau}S(\tau,\tau^-)=\frac{1}{2\beta}\sum_{ip}[(ip)+(ip+i\omega)]F(ip,ip+i\omega)\ . \tag{27}$$

The summation over frequency can be evaluated. Equation (5) is similar to Eq. (20) for $\mathbb{L}^{11}(i\omega)$ except for the energy factor of $\frac{1}{2}[(ip)+(ip+i\omega)]$. This factor gives the extra factor of ϵ in the integrand of (14). The result is the first term on the right-hand side of (14), which gives the Mott expression for the thermopower.

The small term δL^{12} stems from the third term in Eq. (5) for the heat current. An explicit evaluation of δL^{12} is provided in the Appendix, where we derive

$$\delta L^{12}=\frac{2\hbar k_F}{3\pi k_B}\int_0^{\omega_D}u\,du\,\alpha_{(2)}^2(u)F(u)n_B(u)[1+n_B(u)]\times\left[1-\left(\frac{\hbar\beta u}{2}\right)\coth\left(\frac{\hbar\beta u}{2}\right)\right]\ . \tag{28}$$

Here $\alpha_{(2)}^2(u)F(u)$ is related to the McMillan function α^2F.

We observe that while the leading contribution to L^{12} is inversely proportional to the square of the electron-phonon interaction ($L^{12}\sim W^{-2}$), δL^{12} is proportional to the square of the electron-phonon interaction ($\delta L^{12}\sim W^2$). It is smaller than L^{12} by four powers of the interaction. Usually such terms can be neglected in transport calculations. This is also true for δL^{12} in this case. An estimate of this term can be obtained at low temperatures. In the Appendix we show that at small u one can approximate $\alpha_{(2)}^2F\sim-\lambda_{(2)}u^2/\omega_D^2$, where ω_D is the Debye frequency and $\lambda_{(2)}$ is dimensionless and of order unity. Then at low temperature we get

$$\delta S\sim 8\lambda_{(2)}\zeta(3)\left(\frac{k_B}{e}\right)\left(\frac{k_BT}{\hbar\omega_D}\right)^2\left(\frac{k_F\rho}{R_H}\right)\ . \tag{29}$$

Here the value of the Riemann ζ function is $\zeta(3)\approx 1.2$, and $R_H=h/e^2\approx 25.8$ kΩ is the quantum resistance. This can be compared with the free-electron Mott expression,

$$S_0=\frac{\pi^2}{2}\left(\frac{k_B}{e}\right)\left(\frac{k_BT}{E_F}\right)\ . \tag{30}$$

Hence the relative importance of the correction term is given by

$$\frac{\delta S}{S_0}=\frac{16\lambda_{(2)}\zeta(3)}{\pi^2}\frac{E_Fk_BT}{(\hbar\omega_D)^2}\left(\frac{k_F\rho}{R_H}\right)\equiv b\rho T\ . \tag{31}$$

We estimate that for simple metals with $\lambda_{(2)}\sim 1$ then $b\sim 10^4/(\Omega\,\mathrm{cm\,K})$. This value is very small. Typically at low temperature, $T\sim 1$ K, the resistivity is $\rho\sim 10^{-8}\ \Omega\,\mathrm{cm}$, so that $\delta S/S_0\sim 10^{-4}$. Thus the correction term seems entirely negligible at low temperatures.

Since δS increases its value with $O(T^2)$ as T increases, the correction term appears to be more important at higher temperature. However, this is not the case. It is also shown in the Appendix that at high temperature then δL^{12} tends to a constant, which is quite negligible compared to the first term in (14) which is $O(T^3)$. The first term in (14) gives the Mott term S_M in (2), while $\delta S \sim \delta L^{12}/TL^{11}$. The correction term becomes increasingly negligible at high temperature, $k_B T \gg \hbar\omega_D$. Its relative importance is given by

$$\frac{\delta S}{S_0} \sim \frac{\lambda_{(2)}\lambda_t}{12}\left[\frac{\hbar\omega_D}{k_B T}\right]^2 , \tag{32}$$

where λ_t, the transport version of the electron-phonon coupling constant, can be of order unity for simple metals. Hence, it is indeed small also at high temperature. Since it is negligible at both high and low temperatures, we conclude that it is negligible at all temperatures.

Finally, we would like to make a comment regarding the contribution to L^{12} from the two terms in the heat current which arise from the electron-phonon interaction:

$$\mathbf{j}_Q^{(3)} = \sum_{q\lambda} W_\lambda(q) Q_\lambda(q) \mathbf{j}(q) , \tag{33}$$

$$\mathbf{j}_Q^{(4)} = -\frac{i}{M}\sum_{\lambda}[\nabla_q W_\lambda(q)] P_\lambda(q)\rho(q) . \tag{34}$$

From the relation $(\partial/\partial\tau)Q_\lambda(q) = -iP_\lambda(q)/M$, where the time derivative gives rise to a factor of the phonon frequency $\omega_{q\lambda}$, it has been argued[13] that the contribution to L^{12} from $\mathbf{j}^{(4)}$ should be smaller than that from $\mathbf{j}^{(3)}$ by a factor of c_s/v_F, where c_s is the sound velocity and v_F is the Fermi velocity. However, this conjecture is not borne out by an explicit calculation (see the Appendix). There we show that treating $\mathbf{j}^{(3)}$ in the same way as $\mathbf{j}^{(4)}$ gives an exponentially small contribution at low temperatures. This term, which in contrast to $\mathbf{j}^{(4)}$ is contained in the Mott formula, does, however, make an important contribution at high temperatures, where it can be of the same order of magnitude as the free-electron Mott term (30) (see the Appendix). This is interesting because this contribution to the thermopower is of the fourth order in the electron-phonon matrix element. Such terms are often neglected in transport calculations. However, in this case it is not small.

Of course, these are not the only two terms in the energy current which contain the electron-phonon interaction. Since the Hamiltonian (3) contains the electron-phonon interaction, the first two terms in the energy current (5) also contribute electron-phonon terms to the energy current. They are the ones which are important at both high and low temperatures.

IV. DISCUSSION

In conclusion, we have shown that the Mott formula for the thermoelectric power is approximately valid for a system of independent electrons interacting with static impurities and with harmonic phonons. The inelastic nature of the scattering of electrons by phonons makes a small correction to the Mott formula. We have derived this correction, and have explicitly shown that it is small at both low and high temperatures.

Thus the Mott formula can be used as a starting formula for discussing the thermopower, even for the system of electrons and phonons. This should make easier any future work on this topic.

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APPENDIX

Here we calculate explicitly the contributions to L^{12} from the two terms in the heat current which arise from the energy currents $\mathbf{j}_Q^{(3)}$ and $\mathbf{j}_Q^{(4)}$ given in (33) and (34). The contribution from $\mathbf{j}_Q^{(4)}$, which gives rise to the correction δL^{12} in (28), and which is the largest one at low temperatures, will be evaluated first. It can be expressed as

$$\delta L^{12} = \frac{T}{d\Omega\hbar}\lim_{\omega\to 0}\mathrm{Im}\left[\frac{R^{(4)}(\omega+i\delta)}{\omega}\right] ,$$

$$R^{(4)}(i\omega) = \sum_{q\lambda}\int_0^{\hbar\beta} d\tau\, e^{i\omega\tau}[\nabla_q W_\lambda(q)] \times\langle T_\tau \dot{Q}_\lambda(q,\tau)\rho(q,\tau)\mathbf{j}(0)\rangle .$$

After integrating by parts and using the cyclic properties of the trace we get

$$R^{(4)}(i\omega) = \sum_{q\lambda}[\nabla_q W_\lambda(q)]\cdot\frac{1}{i\omega}\left[\langle \dot{Q}_\lambda[\mathbf{j}(0),\rho(q)]\rangle + \int_0^{\hbar\beta} d\tau\, e^{i\omega\tau}\left\langle T_\tau \dot{Q}_\lambda(q,\tau)\rho(q,\tau)\left[\frac{\partial}{\partial\tau'}\mathbf{j}(\tau')\right]_{\tau'=0}\right\rangle\right] . \tag{A1}$$

The first term on the right contributes a real term to $R^{(4)}$ which can be neglected since we want its imaginary part. In the second term on the right, we have

$$\frac{\partial}{\partial\tau}\mathbf{j}(\tau) = \frac{1}{\hbar}[H,\mathbf{j}] = -\frac{1}{m}\sum_{q'}\mathbf{q}' U(q')\rho(q') . \tag{A2}$$

The interaction $U(q)$ is given in (4). To lowest order in the electron-phonon interaction, the only nonzero terms in (A1) have $\mathbf{q}' = -\mathbf{q}$. The second term above gives

$$R^{(4)}(i\omega)=\frac{\hbar}{2m}\sum_{q\lambda}\frac{\mathbf{q}\cdot\nabla_q W_\lambda^2(q)}{2M\omega_{q\lambda}}\frac{1}{i\omega}\int_0^{\hbar\beta}d\tau\, e^{i\omega\tau}\chi(q,\tau)\frac{\partial}{\partial\tau}D_\lambda(q,\tau)\ , \tag{A3}$$

$$D(q,\tau)\equiv-\langle T_\tau[a_{q\lambda}(\tau)+a^\dagger_{-q\lambda}(\tau)][a_{-q\lambda}(0)+a^\dagger_{a\lambda}(0)]\rangle\ , \tag{A4}$$

$$\chi(q,\tau)\equiv-\langle T_\tau\rho(q,\tau)\rho(-q,0)\rangle\ . \tag{A5}$$

The quantity $D(q,\tau)$ is the phonon Green's function, while $\chi(q,\tau)$ is the density-density correlation function, which is related to the inverse of the longitudinal dielectric function.

The conventional symbol for the electron-phonon matrix element is $M_\lambda(q)=W_\lambda(q)(\hbar/2M\omega_{q\lambda})^{1/2}$. In Fourier space the above expression becomes

$$R^{(4)}(i\omega)=\frac{1}{2m}\sum_{q\lambda}\frac{\mathbf{q}\cdot\nabla_q[\omega_{q\lambda}|M_\lambda(q)|^2]}{\omega_{q\lambda}}\frac{1}{i\omega}\frac{1}{\hbar\beta}\sum_{iq}(iq)D_\lambda(q,iq)\chi(q,iq+i\omega)\ , \tag{A6}$$

$$D_\lambda(q,iq)=\frac{2\omega_{q\lambda}}{(iq)^2-\omega_{q\lambda}^2}\ . \tag{A7}$$

On performing the Matsubara sum one finds that

$$\delta L^{12}=\frac{T}{md\hbar\Omega}\sum_{q\lambda}\{\mathbf{q}\cdot\nabla_q[\omega_{q\lambda}|M_\lambda(q)|^2]\}\frac{d\,\mathrm{Im}\chi(q,\omega_{q\lambda}+i\delta)}{d\omega_{q\lambda}}\left[\frac{dn_B}{d\omega_{q\lambda}}+\frac{\omega_{q\lambda}}{2}\frac{d^2n_B}{d\omega_{q\lambda}^2}\right]\ ,$$

where $n_B(\omega_{q\lambda})$ is the Bose-Einstein factor. In the limit of small frequency the density-density response function becomes in $d=3$ dimensions

$$\mathrm{Im}\chi(q,\omega_{q\lambda})=-\frac{\omega_{q\lambda}m^2v\Theta(2k_{F-q})}{2\pi\hbar^2q\epsilon(q)^2}\ , \tag{A8}$$

where $\epsilon(q)$ is the static dielectric function of the electron gas, and v is the volume of a primitive unit cell. It is useful to express the integrals over phonon frequency with the help of the McMillan function α^2F,

$$\alpha^2(u)F(u)=\frac{v}{(2\pi\hbar)^2v_F}\times\int_0^{2k_F}q\,dq\left|\frac{M_\lambda(q)}{\epsilon(q)}\right|^2\delta(u-\omega_{q\lambda})\ . \tag{A9}$$

Here we need a slightly different version, which we call $\alpha^2_{(2)}F$,

$$\alpha^2_{(2)}(u)F(u)=\frac{v}{8\pi^2\hbar^2v_F}\times\sum_\lambda\int_0^{2k_F}\frac{q^2dq}{\omega_{q\lambda}\epsilon(q)^2}\frac{d}{dq}[\omega_{q\lambda}|M_\lambda(q)|^2]\times\delta(u-\omega_{q\lambda})\ . \tag{A10}$$

Using this dimensionless function enables us to express δL^{12} as

$$\delta L^{12}=\frac{2\hbar k_F}{3\pi k_B}\times\int_0^{\omega_D}u\,du\,\alpha^2_{(2)}(u)F(u)n_B(u)[1+n_B(u)]\times\left[1-\left[\frac{\hbar\beta u}{2}\right]\coth\left[\frac{\hbar\beta u}{2}\right]\right]\ . \tag{A11}$$

This result shows that δL^{12} is of the order of the square of the electron-phonon matrix element. Since L^{11} is proportional to the electric conductivity, which is proportional to $L^{11}\sim|M|^{-2}$, then the ratio $\delta S=\delta L^{12}/L^{11}\sim O(M^4)$. It is not surprising therefore that δS is rather small and can be neglected.

It is interesting to examine δS in the limit of low temperature. Here all phonons but the acoustic modes of long wavelength are frozen out. In this regime of small q, we can accurately approximate $\omega_{q\lambda}=c_\lambda q$, $|M_\lambda(q)|^2\sim q^{-3}$, and $\epsilon(q)=1+k_{TF}^2/q^2$. Note that in the present notation $M_\lambda(q)$ is the *unscreened* electron-phonon matrix element. By changing to the dimensionless variable $x\equiv u/k_BT$ in Eqs. (A9) and (A10), it is straightforward to show that $\delta L^{12}\sim T^4$. If the conductivity is taken to be a constant, from impurity scattering, then $\delta S\sim T^2$ at low temperature. A simple estimate of the coefficient is obtained at low temperatures by writing

$$\alpha^2_{(2)}F\sim-\lambda_{(2)}\frac{u^2}{\omega_D^2},\ \lambda_{(2)}\sim\frac{0.3}{Z}\frac{M}{m}\left[\frac{\hbar\omega_D}{E_F}\right]^2\ , \tag{A12}$$

$$\delta L^{12}\sim-\frac{\lambda_{(2)}2k_F(k_BT)^4l}{3\pi k_B\hbar^3\omega_D^2}\ , \tag{A13}$$

$$l\equiv\int_0^\infty x^3dx\frac{1}{2(\cosh x-1)}\left[1-\frac{x}{2}\coth\left[\frac{x}{2}\right]\right]\ , \tag{A14}$$

$$l=-6\zeta(3)\ . \tag{A15}$$

Here the dimensionless constant $\lambda_{(2)}$ is of order unity, and $\zeta(3)\sim1.2$ is a value of Riemann ζ function. From the above estimate of δL^{12} it follows that δS is given by (29) and is negligible at low temperature as discussed in the main text.

Another interesting limit is a high temperature. Here we can show that δL^{12} goes to a constant, since all of the thermal factors cancel:

$$\lim_{k_B T \gg \hbar\omega_D} \delta L^{12} = -\frac{\hbar k_F}{18\pi k_B}\int_0^{\omega_D} u\, du\, \alpha_{(2)}^2(u)F(u) \ . \quad \text{(A16)}$$

At high temperature, the electrical conductivity is dominated by electron-phonon scattering. It is then given in terms of the transport-version λ_t of the electron-phonon coupling constant,

$$\lim_{k_B T \gg \hbar\omega_D} \sigma = e^2\hbar n_0/(2\pi m \lambda_t k_B T) \ . \quad \text{(A17)}$$

This coupling constant is similar to (A9), but has an additional factor of $q^2/(2k_F^2)$ in the integrand. From (12) and (15) we see that $\delta S \sim O(T^{-1})$. The correction term becomes smaller at large temperature. Since the Mott term in (2) is proportional to T, it becomes larger while δS is becoming smaller. Thus the Mott expression becomes increasingly accurate at high temperature. A crude estimate is obtained by using the *small*-frequency limit $\alpha_{(2)}^2 F \sim -\lambda_{(2)} u^2/\omega_D^2$ for *all* frequencies. One finds that at high temperatures

$$\delta S \sim \lambda_{(2)}\lambda_t \frac{\pi^2}{24}\frac{(\hbar\omega_D)^2}{E_F k_B T} \ , \quad \text{(A18)}$$

and the relative importance $\delta S/S_0$ is given by (32).

The contribution of $\mathbf{j}_Q^{(3)}$ to L^{12}, which we shall call $L_{(3)}^{12}$ is *included* in the Mott formula (2). Nevertheless, it is interesting to examine its magnitude at low and high temperatures and compare it to the other contribution from the electron-phonon interaction to the heat current $\mathbf{j}_Q^{(4)}$. We have

$$L_{(3)}^{12} = \frac{T}{d\Omega\hbar}\lim_{\omega\to 0} \mathrm{Im}\left[\frac{R^{(3)}(\omega+i\delta)}{\omega}\right] \ ,$$

$$R^{(3)}(i\omega) = \sum_{q\lambda} W_\lambda(q)\int_0^{\hbar\beta} d\tau\, e^{i\omega\tau}\langle T_\tau Q_\lambda(q,\tau)\mathbf{j}(q,\tau)\cdot\mathbf{j}(0)\rangle \ .$$

Integrating by parts, and using the cyclic properties of the trace, we find

$$R^{(3)}(i\omega) = \sum_{q\lambda} W_\lambda(q)\frac{1}{i\omega}\left[\Big\langle Q_\lambda(q)[\mathbf{j}(0)\cdot\mathbf{j}(q)]\Big\rangle + \int_0^{\hbar\beta} d\tau\, e^{i\omega\tau}\Big\langle T_\tau Q_\lambda(q,\tau)\mathbf{j}(q,\tau)\cdot\left[\frac{\partial}{\partial\tau'}\mathbf{j}(\tau')\right]_{\tau'=0}\Big\rangle\right] \ .$$

The first term of this expression is real and does not contribute to the answer. The second term is evaluated to lowest order in the electron-phonon matrix element by taking terms with $\mathbf{q}'=-\mathbf{q}$. Using (A14), and the equation of continuity $\partial\rho(q)/\partial\tau = \mathbf{q}\cdot\mathbf{j}(q)$, we find

$$R^{(3)}(i\omega) \approx \frac{1}{i\omega m}\sum_{q\lambda}|M_\lambda(q)|^2\int_0^\beta d\tau\, e^{i\omega\tau}D_\lambda(q,\tau)\frac{\partial}{\partial\tau}\chi(q,\tau)$$

$$= -\frac{1}{i\omega}\frac{1}{m}\sum_{q\lambda}|M_\lambda(q)|^2\frac{1}{\hbar\beta}\sum_{iq}(iq+i\omega)D_\lambda(q,iq)\chi(q,iq,+i\omega) \ .$$

Compare this expression with (A6) for $R^{(4)}(i\omega)$. They differ in their matrix elements. They also differ in that one has a factor of (iq) while the other has a factor of $(iq+i\omega)$. This difference changes the thermal occupation factors. The result can be expressed as

$$L_{(3)}^{12} = -\frac{4\hbar k_F}{3\pi k_B}\int_0^{\omega_D} u\, du\, \alpha^2 F(u) n_B(u)[1+n_B(u)]\left[1-\left[\frac{\hbar\beta u}{4}\right]\coth\left[\frac{\hbar\beta u}{2}\right]\right] \ . \quad \text{(A19)}$$

At low temperature this expression vanishes, since the integral equivalent to (A14) is zero. Thus it does not contribute anything at low temperature [more precisely, there is an exponentially small contribution, as in (A14), the upper integration limit $\hbar\omega_D/k_B T$ has been approximated by infinity].

At high temperatures ($k_B T \gg \hbar\omega_D$) expression (A19) becomes

$$\lim_{k_B T \gg \hbar\omega_D} L_{(3)}^{12} = -\frac{\lambda k_F k_B T^2}{3\pi\hbar} \ , \quad \text{(A20)}$$

$$\lambda \equiv 2\int_0^{\omega_D}\frac{du}{u}\alpha^2(u)F(u) \ . \quad \text{(A21)}$$

This term increases according to $O(T^2)$, in contrast to (A16), which goes to a constant at high temperature. These two terms are similar at low temperature, but not at high temperature, where using (A17) the contribution to the thermopower corresponding to (A20) is (A9), but has an additional factor of

$$\lim_{k_B T \gg \hbar\omega_D} S_{(3)} = -\pi^2\lambda\lambda_t\left[\frac{k_B}{e}\right]\left[\frac{k_B T}{E_F}\right] \ . \quad \text{(A22)}$$

This expression is interesting because it is of the order of the fourth power of the electron-phonon matrix element. Thus it is neglected by the usual treatments. However, this expression is not small, since both λ and λ_t can be of order one for simple metals. Hence it is of the same order of magnitude as the free-electron contribution (30), which is of zeroth order in the electron-phonon interaction. There are other terms in the Mott expression which depend upon the electron-phonon coupling constant besides this one. They give the standard expression of Ziman.[3]

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