Phonon-Drag Part of the Thermoelectric Power in Metals

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A formula for the phonon-drag part S_g of the thermoelectric power in metals is obtained by assuming that the electron scattering processes can be described by a relaxation time $\tau(\mathbf{k})$. The formula differs from the simplest variational expression only by having extra factors of τ in numerator and denominator. The signs of the contributions of S_g and the low-temperture limit are discussed.

1. INTRODUCTION AND DERIVATION

RECENTLY, Van Baarle[1] and Fletcher and Dugdale[2] have suggested that the impurity scattering of *electrons* may play an important role in the phonon-drag part S_g of the thermoelectric power in metals. This at first sight would seem to be unlikely. Consider the simplest approximation to S_g given by[3]

$$S_g=\frac{\kappa}{|e|}\frac{\frac{2}{3}e^2\sum_{\mathbf{q}j}(\partial N_0(j\mathbf{q})/\partial\kappa T)\sum^{(\mathbf{q}j)}\alpha(j\mathbf{q};\mathbf{k}l,\mathbf{k}'l')[\mathbf{v}(\mathbf{k}l)-\mathbf{v}(\mathbf{k}'l')]\cdot\mathbf{v}(j\mathbf{q})}{\frac{2}{3}e^2\sum v(\mathbf{k}l)^2[-\partial f_0/\partial E]} \tag{1}$$

in which $\alpha(j\mathbf{q};\mathbf{k}l,\mathbf{k}'l')$ is the relative probability that the $j\mathbf{q}$ phonon will engage in the interaction that sends the electron state from $\mathbf{k}l$ to $\mathbf{k}'l'$ (relative to all other interactions that the phonon $j\mathbf{q}$ may enter); $\mathbf{v}(\mathbf{k}l)$ is the velocity of the electron in reduced wave-vector state $\mathbf{k}$ and band l; and $N_0(j\mathbf{q})$ is the equilibrium distribution of phonons in state $j\mathbf{q}$, frequency $\omega(j\mathbf{q})$, and velocity $\mathbf{v}(j\mathbf{q})$. The second sum $\sum^{(j\mathbf{q})}$ is over all states and transitions that need the $\mathbf{q}j$ phonon. The factors 2 in the numerator and denominator come from a sum over spin, and the factors $\frac{1}{3}$ come from converting $v_x(\mathbf{k}l)v_x(j\mathbf{q})$ to $3^{-1}\mathbf{v}(\mathbf{k}l)\cdot\mathbf{v}(j\mathbf{q})$ valid for cubic materials.

The quantity α does not depend on the scattering of the *electron* by impurities, but only on the scattering of the *phonon* by impurities (it enters as just another of the processes that the phonon can enter into when the relative probability is calculated). How then can the impurity scattering of the electrons affect the S_g term?

There is, in fact, an impurity effect on the electrons that may matter here, but it is lost in the very simple approximations used in manipulating the variational principle.

An expression for S_g which is almost as simple as Eq. (1) but which shows the effect of electron scattering by impurities can be obtained by assuming a relaxation time $\tau(\mathbf{k},l)$, in the collision terms of the generalized Boltzmann equation.[4,5] Such a procedure allows the equation to be solved without any trouble, and without recourse to the variational principle. Furthermore, the solution for S_g reduces to Eq. (1) when the assumed relaxation time is approximated by a constant. We feel, therefore, that the approximation of a relaxation time is in all respects better than the first variational approximation, especially when the impurity scattering of electrons is larger than the phonon scattering, in which situation the use of a relaxation time is probably quite good altogether. τ is not, however, treated as a constant over the Fermi surface, the anisotropy assumed being crucial to the subsequent discussion.

The derivation of the new result will only be sketched briefly. A knowledge of some of the equations in Ref. 4 will be necessary, and is assumed without discussion. The electron distribution function $f(\mathbf{k}l)$ is expanded in the usual way:

$$f(\mathbf{k}l)=f_0(E(\mathbf{k}l))-(\partial f_0/\partial E)g(\mathbf{k}l), \tag{2}$$

where f_0 is the Fermi function, and $g(\mathbf{k}l)$ the new unknown. The generalized Boltzmann equation is obtained by solving the phonon Boltzmann equation in terms of g and then substituting into the electron Boltzmann equation, the result being Eq. (14) of Ref. 4,

$$-(\partial f/\partial t)_{\text{drift}}-U=L(g). \tag{3}$$

Here U is the "drag" correction to the drift term, and $L(g)$ is a generalized scattering term containing not only the ordinary electron-phonon scattering L_{ph} and the impurity scattering of electrons L_{imp}, but also a "drag" correction L_{ph}'. The effects from L_{ph}' were called "phonon relaxation" effects in Ref. 4 and "reaction" effects in Ref. 5, to distinguish them from the effects from U. Thus

$$L(g)=L_{\text{ph}}(g)+L_{\text{ph}}'(g)+L_{\text{imp}}(g). \tag{4}$$

We shall assume that at low enough temperatures the dominant scattering term is L_{imp}, for which the relaxa-

[1] C. Van Baarle, Physica **33**, 424 (1967).
[2] R. Fletcher and J. S. Dugdale, Proceedings of the International Low-Temperature Conference, Moscow, 1966 (unpublished).
[3] M. Bailyn, Phys. Rev. **120**, 381 (1960). See Appendix H, in particular Eq. (H8).
[4] M. Bailyn, Phys. Rev. **112**, 1587 (1958). See Eq. (14). The first to set up an equation of this type was L. Gurevich, J. Phys. (U.S.S.R.) **10**, 67 (1946).
[5] See also M. Tsuji, J. Phys. Soc. Japan **14**, 618 (1959).

tion-time approximation is probably quite good. For $L_{\rm ph}$ and $L_{\rm ph}'$ the reader is referred to Refs. 4 and 5. Whether $L_{\rm ph}$ and $L_{\rm ph}'$ are neglected altogether or simply approximated, we make the hypothesis that the total $L(g)$ can be written in terms of a single $\mathbf{k}l$-dependent relaxation time $\tau(\mathbf{k}l)$:

$$L(g)\cong\tau(\mathbf{k}l)^{-1}(\partial f_0/\partial E)g(\mathbf{k}l). \tag{5}$$

It should be noted that this is the second relaxation-time approximation made in solving the coupled Boltzman equation: the first (see Ref. 4) was in assuming that all phonon-phonon collision terms could be treated in terms of a phonon relaxation time. Further, these are the only two approximations made in the whole argument leading to Eq. (6) below, aside, of course, from allowing the Boltzmann equation itself to be linearized.

Equation (3) can be solved without further ado, and the result can be inserted in the expression for the thermoelectric power obtained by computing J_x and setting it equal to zero. The answer for the drag part is

$$S_g=\frac{\kappa}{|e|}\frac{\frac{2}{3}e^2\sum[\partial N_0(\mathbf{q}j)/\partial\kappa T]\sum^{(jq)}\alpha(j\mathbf{q};\mathbf{k}l,\mathbf{k}'l')[\mathbf{v}(\mathbf{k}l)\tau(\mathbf{k}l)-\mathbf{v}(\mathbf{k}'l')\tau(\mathbf{k}'l')]\cdot\mathbf{v}(j\mathbf{q})}{\frac{2}{3}e^2\sum v(\mathbf{k}l)^2\tau(\mathbf{k}l)[-\partial f_0/\partial E]}. \tag{6}$$

Equation (6) is the new approximate formula containing the influence of the impurities as well as of the phonons.[6,7] It reduces to Eq. (1) whenever τ is a function of energy[6] only.

It is convenient at this point to rewrite the result in terms of an internal sum

$$\mathbf{w}(\mathbf{k}l)=(\partial f_0/\partial E)^{-1}\sum_{\mathbf{k}'l'}[-\alpha(j\mathbf{q};\mathbf{k}l,\mathbf{k}'l')+\alpha(j\mathbf{q};\mathbf{k}'l',\mathbf{k}l)]\times[\partial N_0(j\mathbf{q})/\partial\kappa T]\mathbf{v}(j\mathbf{q}) \tag{7}$$

having the units of velocity. Then Eq. (6) becomes

$$S_g=-\frac{\kappa}{e}\frac{\frac{2}{3}e^2\sum\tau\mathbf{v}\cdot\mathbf{w}[-\partial f_0/\partial E]}{\frac{2}{3}e^2\sum\tau v^2[-\partial f_0/\partial E]}, \tag{8}$$

where all quantities depend on $\mathbf{k}l$.

2. DISCUSSION

Apropos of Eq. (6), we have three comments. First, and most important perhaps, we conclude that at low temperatures S_g may be quite sensitive to the impurity content through the $\tau(\mathbf{k}l)$ factors in Eq. (6). Such a sensitivity, if present, would emerge by a given impurity affecting the positive parts of the contributions to S_g differently from the negative parts, or by the relative $+-$ influences of one impurity being different from those of another. (The signs of contributions are discussed more fully below).

Second, pursuing the idea that different regions of the Fermi surface act differently, it is possible to divide the Fermi surface into different sections labelled i, the division being arbitrary, and to separate S_g into a sum of terms corresponding to each i with a weighting factor σ_i/σ:

$$S_g=\sum_i(\sigma_i/\sigma)S_{gi}, \tag{9}$$

where σ_i has the significance of the conductivity of region i and S_{gi} that of the phonon-drag thermopower of region i.

Equation (9) can be arrived at in various ways. At low enough temperatures, the important $\mathbf{q}$'s are very small. Thus the phonon transitions between the regions i form a small part of the total number of transitions and can be neglected. Thus the numerator of Eq. (6) turns into a sum over regions i, and the quantities in Eq. (9) are

$$\sigma_i=\tfrac{2}{3}e^2\sum_{\mathbf{k}l}^{(i)}\tau(\mathbf{k}l)v(kl)^2[-\partial f_0/\partial E], \tag{10}$$

$$S_{gi}=-\frac{\kappa}{e}\frac{\frac{2}{3}e^2\sum_{jq}[\partial N_0(j\mathbf{q})/\partial\kappa T]\sum^{(jq,i)}\alpha(j\mathbf{q};\mathbf{k}l,\mathbf{k}'l')[\mathbf{v}(\mathbf{k}l)\tau(\mathbf{k}l)-\mathbf{v}(\mathbf{k}'l')\tau(\mathbf{k}'l')]\cdot\mathbf{v}(j\mathbf{q})}{\frac{2}{3}e^2\sum^{(i)}v(\mathbf{k}l)^2\tau(\mathbf{k}l)[-\partial f_0/\partial E]}. \tag{11a}$$

The electron sums are all restricted to the $\mathbf{k}l$'s in region i. Here σ_i and S_{gi} have the significance of the conductivity and thermopower from regions i, although of course τ, depending as it does on the impurity scattering, involves in its evaluation a large number of transitions *between* regions, no matter what the temperature.

Use of Eq. (11a) implies that Eq. (9) is a low-temperature approximation. If, however, we start from Eq. (8), we can obtain Eq. (9) without approximation

[6] Tsuji (Ref. 5) must have had this formula, or its equivalent, written down in his notes. But since he assumed that $\tau(\mathbf{k})$ was a function of E, his formulas allowed the τ factor to cancel out, thus proving long ago that the simplest variational expression emerged from an isotropic τ approximation, rather than pointing out the possible anisotropic effects. At the time of Tsuji's article, there was of course no experimental indication that such effects might be significant.

[7] J. M. Ziman, Advan. Phys. **10**, 1 (1961), in using his version of the variational principle, was the first to encorporate $\tau(k)$'s in the phonon-drag expressions. They entered through a variational trial function suggested by the Boltzmann equation. His results do not reduce to ours.

by defining

$$S_{gi}=-\frac{\kappa\,\frac{2}{3}e^2\sum^{(i)}\tau\mathbf{v}\cdot\mathbf{w}[-\partial f_0/\partial E]}{e\;\frac{2}{3}e^2\sum^{(i)}\tau v^2[-\partial f_0/\partial E]}. \tag{11b}$$

Since this resembles Eq. (8), we are led to describe it as the phonon-drag part of region i, much in the same way that Eq. (10) is the conductivity of region i, noting, however, that $\mathbf{w}$ now involves in its evaluation transitions to other regions, just as τ does.

An expansion as in Eq. (9) has a great convenience if the regions i are so chosen that within each one, τ is fairly constant. Then the τ's cancel out in Eqs. (11). The separation would be even more useful if the regions i were not only of constant τ but of a single sign.

The conclusions obtained concerning the sensitivity of S_g to impurity scattering of electrons, and to the separation as in Eq. (9), are in agreement with the suggestions of Fletcher and Dugdale[2,8] and Van Baarle[1] mentioned at the outset.

The third comment concerns the sign of S_g. Using Eq. (6) for the basic expression, we note that the sign depends on the sum of contributions from all transitions $\mathbf{k}l\rightarrow\mathbf{k}'l'$ and that each of these provides a + or − contribution depending on whether

$$Z\equiv[\mathbf{v}(\mathbf{k}l)\tau(\mathbf{k}l)-\mathbf{v}(\mathbf{k}'l')\tau(\mathbf{k}'l')]\cdot\mathbf{v}(j\mathbf{q}) \tag{12}$$

is + or −. Of course the selection rule, explicit[3] in the α's,

$$\mathbf{k}'-\mathbf{k}=\mathbf{q}+\mathbf{K}, \tag{13}$$

must also be satisfied, where $\mathbf{K}$ is a reciprocal-lattice vector. Notice that it is $\mathbf{v}$ that appears in Eq. (12) not $\mathbf{k}$ or $\mathbf{q}$. This $\mathbf{v}$ can easily be traced back to the *field* terms of the Boltzmann equations, and does not stem from an assumption as to the form of g in Eq. (2).

The standard sign for S_g is negative, and this comes about from Eq. (12) in the simple situation characterized by (1) τ constant, (2) nonumklapp processes, and (3) free-electron spherical energy surfaces. For then $\mathbf{v}-\mathbf{v}'$ is proportional to $-\mathbf{q}$, whence Z is negative. It was pointed out in Ref. 4 that an umklapp process, all other conditions remaining the same, tends to give an anomalous sign, since $\mathbf{v}-\mathbf{v}'\sim-(\mathbf{q}+\mathbf{K})$ is generally in a direction opposite to $\mathbf{q}$. And in Ref. 3, Appendix H, it was shown that a hole surface provides the opposite behavior (negative contribution for umklapps and positive for nonumklapps).

When approaching rather bizarre surfaces, it would be encouraging if some sort of general rule existed for when + and − contributions occur. Unfortunately, about the only valid statement is a generalization[7] of the filled-sphere–empty-sphere cases cited above, namely, that when the shortest surface connection between $\mathbf{k}$ and $\mathbf{k}_0'$ (in the extended zone scheme, where $\mathbf{k}_0'$ is the equivalent state to $\mathbf{k}'$ that is closest to $\mathbf{k}$) lies on a convex strip of surface (relative to the filled part), the contribution tends to be normal (negative), but if the strip lies on a concave part, the contribution tends to be anomalous (positive).

At low enough temperatures, where only the small q's are excited, this tendency becomes stronger and stronger,[9] since if $\mathbf{q}$ is small enough the region on the Fermi surface containing $\mathbf{k}$ and $\mathbf{k}'$ can be approximated by a shape with a constant curvature.

An expansion[10] of Z in powers of q demonstrates this clearly. Using d/dk_q to mean a directional derivative toward $\mathbf{q}$, and $\rho_\mathrm{q}(\mathbf{k}l)$ to mean the algebraic radius of curvature of the "normal" section on the Fermi surface containing $\mathbf{v}(\mathbf{k}l)$, the normal, and $\mathbf{q}$, we get

$$\begin{aligned}\lim_{q\rightarrow0}Z&=-q\frac{\partial}{\partial k_\mathrm{q}}[\mathbf{v}(\mathbf{k}l)\tau(\mathbf{k}l)]\cdot\mathbf{v}(j\mathbf{q})\\&=-q\left\{\frac{\partial}{\partial k_\mathrm{q}}|v(\mathbf{k}l)\tau(\mathbf{k}l)|\,\hat{v}(\mathbf{k}l)\cdot\mathbf{v}(j\mathbf{q})\right.\\&\qquad\left.+v(\mathbf{k}l)\tau(\mathbf{k}l)[t\hat{b}+\rho_\mathrm{q}^{-1}\hat{q}]\cdot\mathbf{v}(j\mathbf{q})\right\},\end{aligned} \tag{12a}$$

where t is the "torsion" and $\hat{b}=\hat{v}(\mathbf{k}l)\times\hat{q}$. Note that $\hat{v}(\mathbf{k}l)\cdot\hat{q}\rightarrow0$ as $q\rightarrow0$. Now *if* we suppose that $\mathbf{v}(j\mathbf{q})$ is in the direction of $\mathbf{q}$, then

$$\lim_{q\rightarrow0}Z=-v(\mathbf{k}l)\tau(\mathbf{k}l)\omega(j\mathbf{q})\rho_\mathrm{q}(\mathbf{k}l)^{-1}. \tag{12b}$$

In this case, the sign of Z depends only on the sign of the radius of curvature ρ_q and not, for example, directly on τ or $\mathbf{v}(kl)$ or their derivatives.

In considering a point $\mathbf{k}$ on the Fermi surface, notice that the sign of Z may change from $\mathbf{q}$ direction to $\mathbf{q}$ direction even for very small $\mathbf{q}$ (as on a "neck" surface, where transitions along the neck have concave connections, those around convex), and that an average over

[8] R. Fletcher and J. S. Dugdale (Ref. 2) actually used $S_g=\sum_i\alpha_i\times(\sigma_i/\sigma)S_{gi}$. Where α_i was estimated to be W_i/W, where W_i is the lattice thermal resistance associated with region i. (They noted however, that the α_i's could be included in S_{gi}'s themselves). Their separating off of this factor α_j gives us some insight into our own α's. The only real difference between the two is that their α refers to a whole region whereas ours refers to an individual transition. Our α is the relative probability of a transition involving a particular phonon. Such a probability may be described as an inverse relaxation time for the phonons, so that symbolically

$$\alpha(j\mathbf{q};\mathbf{k}\mathbf{k}')=\frac{\tau^{-1}(j\mathbf{q};\mathbf{k}\mathbf{k}')}{\sum\tau^{-1}(j\mathbf{q};\mathbf{k}_1\mathbf{k}_2)+\tau_\mathrm{other}^{-1}}.$$

If now we suppose that it is legitimate to average this over a region i, and further to average numerator and denominator separately, and finally if we note that the denominator will refer to all regions i in general, so that its average spans the whole Fermi surface, we get Fletcher and Dugdale's formula, provided we define W_i to be proportional to $\langle\tau^{-1}\rangle_i$. The appearance of a thermal resistance in the denominator of the phonon-drag term is not unrelated to Ziman's (Ref. 7) variational version of the expression.

[9] This was pointed out to me by Dr. Dugdale and Dr. Guénault.

[10] An expansion of this type was first done by Ziman in Ref. 7 in terms of effective mass.

directions is not particularly easy, since the phonon velocities, which enter as $v(j\mathbf{q})^{-3}$, ultimately (see below) may cause a considerable weighting.

This concludes the discussion of Eq. (6). In the Appendix, the entire expression for S_{gi} is integrated out for small q (low temperatures) a good deal of the way. And in the following paper, the results are applied to the noble metals.

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APPENDIX. THE LOW-TEMPERATURE LIMIT

The results obtained in the text simplify considerably if one allows T to get very small, a situation corresponding to many of the experiments. The simplification arises because the factor $\partial N_0/\partial T$ insures that only the very small q's will matter if T is small enough. Thus the low-T limit leads to a small-q approximation, which simplifies the mathematics.

We have already seen at the end of Sec. 2 how Z reduces for small q. Referring to Eq. (11a) we see that there remains α to evaluate. From Eq. (H7) of Ref. 3. and Eqs. (9b) and (7) of Ref. 4, we find, neglecting phonon-impurity and phonon-phonon interactions,

$$\alpha(j\mathbf{q};\mathbf{k},\mathbf{k}+\mathbf{q})=\frac{|\mathbf{I}_{\mathbf{k},\mathbf{k}+\mathbf{q}}\cdot\xi(j\mathbf{q})|^2 f_0(E(\mathbf{k}))[1-f_0(E(\mathbf{k}+\mathbf{q}))]\delta(E(\mathbf{k}+\mathbf{q})-E(\mathbf{k})-\hbar\omega)}{\sum_{\mathbf{k}'}|\mathbf{I}_{\mathbf{k}',\mathbf{k}'+\mathbf{q}}\cdot\xi(j\mathbf{q})|^2 f_0(E(\mathbf{k}'))[1-f_0(E(\mathbf{k}'+\mathbf{q}))]\delta(E(\mathbf{k}'+\mathbf{q})-E(\mathbf{k}')-\hbar\omega)}, \tag{A1}$$

where $\hat{\xi}$ is the direction of polarization of the $j\mathbf{q}$ phonon, and where

$$\mathbf{I}_{\mathbf{k},\mathbf{k}+\mathbf{q}}=\int\psi_{+\mathbf{q}}^*\psi_{\mathbf{k}}\nabla V_0\xrightarrow[(\mathbf{q}\to 0)]{}\mathbf{q}\cdot\int(\nabla_{\mathbf{k}}\psi_{\mathbf{k}}^*)\psi_{\mathbf{k}}\nabla V_0, \tag{A2}$$

V_0 being the potential from one cell on the rigid ion expansion of the crystal potential, and $\psi_{\mathbf{k}}$ the electron wave function.

We wish now to integrate the denominator of Eq. (A1) for an arbitrary Fermi surface. The crux of the matter lies in the fact that the energy delta function together with the factor $f_0(E(\mathbf{k}))[1-f_0(E(\mathbf{k}+\mathbf{q}))]$ will restrict the $\mathbf{k}$'s to lie on certain lines on the Fermi surface, these lines well defined once the shape of the Fermi surface and the vector $\mathbf{q}$ are specified. For a spherical surface, the lines are circles lying in a plane perpendicular to the vector $\mathbf{q}$, with radius $(k_F^2-q^2/4)^{1/2}$. For vanishingly small $\mathbf{q}$ on an arbitrary surface, the lines are those on which $\mathbf{q}$ is tangent to the Fermi surface. We shall denote these by the symbol $\mathrm{LT}(\mathbf{q})$, meaning "lines of tangency of $\mathbf{q}$." For arbitrary $\mathbf{q}$ and an arbitrary surface, nothing general can be said except that such lines exist; for simplicity we will call them "lines of intersection of $\mathbf{q}$." It would only be for surfaces exactly cylindrical in some region that a line could develop into an *area*, and we shall omit this exceptional circumstance from the argument.

Thus the way to integrate over $\mathbf{k}'$ in the denominator is to separate as follows:

$$\sum_{\mathbf{k}'}=\frac{V}{8\pi^3}\int dE'\int dk_1 dk_2 J\frac{1}{\hbar v(\mathbf{k}')}, \tag{A3}$$

where k_1 is to mean a direction along the appropriate "line of intersection of $\mathbf{q}$", and k_2 is to mean a direction chosen for convenience, such that the integral will eliminate the delta function. J is the appropriate Jacobian.

Consider now the integral over k_2. Let the intersection of the k_2 axis with the line of intersection of $\mathbf{q}$ be called $\mathbf{k}_0$. Then $E(\mathbf{k}_0+\mathbf{q})-E(\mathbf{k}_0)-\hbar\omega=0$. Expanding from $\mathbf{k}_0$ in the direction of k_2 we have

$$\begin{aligned}\int dk_2\delta[E(\mathbf{k}'+\mathbf{q})-E(\mathbf{k}')-\hbar\omega]&=\int dk_2\delta\left[k_2\frac{\partial}{\partial k_2}(E(\mathbf{k}'+\mathbf{q})-E(\mathbf{k}'))\right]\\&=\left|\frac{\partial}{\partial k_2}[E(\mathbf{k}'+\mathbf{q})-E(\mathbf{k}')]\right|^{-1},\end{aligned} \tag{A4}$$

which is evaluated at $\mathbf{k}_0$. For small q

$$\begin{aligned}\frac{\partial}{\partial k_2}[E(\mathbf{k}'+\mathbf{q})-E(\mathbf{k}')]|_{\mathbf{k}_0}&\to\frac{\partial}{\partial k_2}(\hbar\mathbf{v}(\mathbf{k}')\cdot\mathbf{q})|_{\mathbf{k}_0}\\&=\hbar v(\mathbf{k}_0)[-t\hat{b}+\rho^{-1}\hat{k}_2]\cdot\mathbf{q},\end{aligned} \tag{A5}$$

where t is the torsion and ρ the radius of curvature of a normal section through $v(\mathbf{k}_0)$ in the direction k_2, $\hat{k}_2$ is a unit vector in the k_2 direction at k_0, and $\hat{b}=\hat{k}_2\times\hat{v}(\mathbf{k}_0)$ [In writing Eq. (A5), we used the fact that $\mathbf{v}(\mathbf{k}_0)\cdot\mathbf{q}=0$.]

It is now clear how best to choose the direction k_2. If we choose it in the direction of $\mathbf{q}$, then $\hat{b}\cdot\mathbf{q}=0$. Let us call the corresponding radius of curvature $\rho_{\hat{q}}(\mathbf{k}_0)$. Then finally

$$\lim_{q\to 0}\int dk_2\delta[E(k'+q)-E(k')-\hbar\omega]=\frac{\rho_{\hat{q}}(\mathbf{k}_0)}{\hbar v(\mathbf{k}_0)q}, \tag{A6}$$

and the Jacobian J is $\sin\gamma$ where γ is the angle between $\mathbf{q}$ and dk_1.

For convenience let us now call k_1 by k_q. Then α becomes

$$\alpha(j\mathbf{q};\mathbf{k},\mathbf{k}+\mathbf{q})=\frac{f_0(E(\mathbf{k}))[1-f_0(E(\mathbf{k}+\mathbf{q}))]\delta(E(\mathbf{k}+\mathbf{q})-E(\mathbf{k})-\hbar\omega)\,|\,\mathbf{I}_{\mathbf{k},\mathbf{k}+\mathbf{q}}\cdot\hat{\xi}(j\mathbf{q})\,|^2}{\int dE' f_0(E')[1-f_0(E'+\hbar\omega(j\mathbf{q}))]V(8\pi^3\hbar^2 q)^{-1}\int_{\mathrm{LT}(\mathbf{q})} dk_q\,|\,\mathbf{I}_{\mathbf{k}',\mathbf{k}'+\mathbf{q}}\cdot\hat{\xi}\,|^2 w(\mathbf{k}'\hat{q})}, \tag{A7}$$

where a weight factor w has been introduced:

$$w(\mathbf{k}'\hat{q})=\frac{\sin\gamma\,|\rho_{\hat{\mathbf{q}}}(\mathbf{k}')|}{|v(\mathbf{k}')|^2}. \tag{A8}$$

When α in the form of Eq. (A7) is placed into Eq. (11a), there arise two routes by which the remaining expression can be reduced. On the one hand the $\mathbf{k}$ integral can be performed first; on the other hand, the $\mathbf{q}$ integral can be performed first. We shall do it both ways for the reason that the former conforms to what we believe is the essential quality of phonon drag (namely the effect on the electron system, phonon by phonon), while the latter allows us to see directly how the various parts of the Fermi surface enter in, and makes a numerical calculation perhaps more accessible.

If $\mathbf{k}$ is integrated first, there is no real change at all from what took place in the denominator. The only ultimate difference comes in the weighting of the final integral over "lines of tangency of $\mathbf{q}$," for there is the extra factor Z to include. The sum over $\mathbf{q}$ can be changed to an integral over $z=\hbar\omega/\kappa T$, which can be evaluated for small enough T, and an integral over angles $d\Omega_q$. When all that is done, the remainder is

$$S_{gi}=\frac{\kappa}{|e|}\sum_j\int d\Omega_q\left(\frac{T}{\vartheta(\hat{q}_j)}\right)^3\beta_i(\hat{q}_j), \tag{A9}$$

where

$$\beta_i(\hat{q}j)=\frac{4\pi^4}{15}\frac{k_F^2}{A_i}\frac{\int_{\mathrm{LT}(\mathbf{q})}^{(i)} dk_q w'(\mathbf{k}\hat{q})\,|\,\mathbf{I}\cdot\xi\,|^2}{\int_{\mathrm{LT}(\mathbf{q})} dk_q w(\mathbf{k}\hat{q})\,|\,\mathbf{I}\cdot\xi\,|^2}, \tag{A10}$$

A_i being the area of the ith part of the Fermi surface,

$$\int_{\mathrm{LT}(\mathbf{q})}^{(i)} dk_q$$

signifying integration along the parts of the LT(q) lying in the ith region, and

$$\vartheta(\mathbf{q}j)=\hbar v(j\mathbf{q})k_F/\kappa, \tag{A11}$$

where k_F is the radius of a sphere in k space having the same volume as that actually occupied, i.e.,

$$2\frac{4\pi}{3}k_F^2\frac{V}{8\pi^3}=N, \tag{A12}$$

where N is the number of electrons. The new weighting factor in the numerator of Eq. (A10) is

$$w'(\mathbf{k}\hat{q})=-\mathrm{sgn}\rho_{\hat{\mathbf{q}}}\sin\gamma\frac{k_F}{v(\mathbf{k})}\frac{\tau(\mathbf{k})}{\langle v\tau\rangle_i}, \tag{A13}$$

the angle brackets indicating an average over the entire ith region of the Fermi surface.

Equation (A9) shows how each phonon (direction) contributes to the thermoelectric power. The weighting goes as $v(j\mathbf{q})^{-3}$ and as β. We note that β is obviously a rather complicated quantity making reference to all the points on the Fermi surface at which $\mathbf{q}$ is tangent. The weighting in the numerator, w', is quite different from that in the denominator, w, and it is hard to make any statements about β without first obtaining some idea of the lines of tangency for $\mathbf{q}$.

Next we go back to Eq. (11a) and integrate over $\mathbf{q}$ first, ending up with an integral over the Fermi surface:

$$S_{gi}=\frac{\kappa}{|e|}\frac{1}{A_i}\int_i dS_k\sum_j\int d\varphi_q\left(\frac{T}{\vartheta(\hat{q}j)}\right)^3\beta_i'(\hat{q}j\,|\,\mathbf{k}), \tag{A14}$$

where the dimensionless β' is

$$\beta_i'(\hat{q}j\,|\,\mathbf{k})=\frac{k_F w''(fj\,|\,\mathbf{k})\,|\,\mathbf{I}_{\mathbf{k},\mathbf{k}+\mathbf{q}}\cdot\hat{\xi}(j\mathbf{q})\,|^2}{\int_{\mathrm{LT}(\mathbf{q})} dk_q w(\mathbf{k}'\hat{q})\,|I_{\mathbf{k}',\mathbf{k}'+\mathbf{q}}\cdot\hat{\xi}(j\mathbf{q})\,|^2} \tag{A15}$$

in terms of a new weighting

$$w''(\hat{q}j\,|\,\mathbf{k})=-\frac{k_F^2}{v(\mathbf{k})}\frac{\tau(\mathbf{k})}{\langle v\tau\rangle_i}\frac{1}{\rho_q}. \tag{A16}$$

The integral over φ_q in Eq. (A14) is over all phonon directions tangent to the Fermi surface at $\mathbf{k}$.

We notice that a full integration over $\mathbf{q}$ is impossible

without first having a good deal of information about the Fermi surface, and would be even if the phonons were isotropic. (See, for example, the denominator of β'.) Thus a neat separation of phonon from Fermi-surface effects is not in general possible.

Notice that the weighting w'' in Eq. (A15) is different from the w' in Eq. (A10). The difference consists mainly in an extra factor $|\rho_q|^{-1}$ in the former. This may at first glance seem surprising, but if it is noted that Eq. (A14) contains an integral over the Fermi *surface* whereas Eq. (A9) has one only over a *line* of tangency, we can see the connection. If, in fact, we performed part of the surface integral in Eq. (A14) we would get another factor $|\rho_q|$ which would cancel the $|\rho_q|^{-1}$ already present. Thus if we seek the contribution to S_{gi} from some particular phonon (direction), then the weighting along a line of tangency should not include the magnitude $|\rho_q|^{-1}$ but only the sign, $\mathrm{sgn}\rho_q$.

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Anisotropy of Relaxation Times and Phonon Drag in the Noble Metals

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The effect of impurities on the phonon-drag part S_g of the thermoelectric power at very low temperatures is examined for alloys of copper, silver, and gold. S_g is separated into three terms corresponding to: (1) the neck regions in the ⟨111⟩ directions, (2) the convex belly regions around the ⟨100⟩ directions, and (3) the concave belly regions around the ⟨110⟩ directions. We find that in gold the concave belly region is most important and in silver the necks are most important. The sign of the neck contribution is examined through the behavior of the ⟨110⟩ phonons at the zone boundary, and it is found that the positive contributions dominate there. The experimental results for three types of impurities, (A) uncharged, (B) charged, and (C) transition-metal, are discussed, and qualitative agreement with the theory is found.

1. INTRODUCTION

IN what follows we wish to apply the results obtained in the previous paper[1] (henceforth referred to as I) to a particular example, that of phonon-drag S_g in the noble metals at very low temperatures.

Recent experiments[2–4] have shown very strikingly that the magnitude and even, in some cases, the sign of S_g in the noble metals varies with the kind of impurity which dominates the electron scattering. For example, in silver S_g is positive down to the lowest temperatures in all the samples so far studied.[2] Where, however, the scattering is by 'uncharged' impurities (Au or Cu in Ag), S_g is much larger than when the scattering is by 'charged' impurities (e.g., Ge, In). In gold, it has recently been found that although S_g is normally positive it becomes negative at low temperatures when the scattering is by Pt impurity.

Explanations of this dependence of S_g on the type of impurity scattering have already been put forward.[3,5] Here we extend and to some extent modify these ideas inthe light of I.

We saw, in I, that the sign of the contribution to S_g from a transition along a particular strip of the Fermi surface depended at very low temperatures on its concavity or convexity with respect to the occupied states. In the noble metals we can distinguish three regions which differ in this respect: (1) the convex belly regions associated roughly with ⟨100⟩ directions (2) the *concave* belly regions centered mainly around the ⟨100⟩ directions, and (3) the neck regions, (in the ⟨111⟩ directions) where the principal radii of curvature have opposite signs.

For simplicity it is often assumed that apart from the necks, the Fermi surfaces of the noble metals are nearly spherical. There are, however, substantial concave regions which are particularly conspicuous in Cu and Au. These can be seen clearly in the diagrams given by Segall[6] and by Roaf[7] and even more strikingly

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