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Theory of thermoelectric effects in metals and alloys*

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The electron-diffusion Seebeck coefficient of metals and dilute alloys is investigated in a simple model in which free electrons are scattered by phonons or by substitutional impurities bound in the lattice. Second-order corrections to the T matrix for electron scattering involving intermediate virtual phonon states are found to be of small magnitude but to have a very strong energy dependence. They thus make a large contribution to the thermoelectric coefficients while leaving the conductivities essentially unaltered. The pronounced temperature dependence of these second-order contributions allows an interpretation of experimental results that relies less on the phonomenon of phonon drag then has previously been the case.

I. INTRODUCTION

The thermoelectric effects in metals depend on the electronic structure of the materials involved in a manner sufficiently subtle to render their interpretation difficult. In a Peltier experiment, for example, an electric current flows through the sample in the absence of a temperature gradient, and the resulting heat current is measured. This flow of thermal energy, however, is found[1] to be limited to the small imbalance between the opposing heat currents carried by electrons with energies respectively greater than or less than the chemical potential ζ. A further complication may be added in the form of the heat current carried by the phonons which have been scattered by the conduction electrons in the phenomenon known as phonon drag.[2] Consequently, theoretical predictions of thermoelectric coefficients depend on such delicate quantities as the energy derivative of the scattering of the electrons; they are frequently highly dependent on the model chosen, since there are few other experiments that can be called on to justify any given value for the energy dependence of electron scattering cross sections. In fact, it is not merely the details of the scattering that differ in the various published calculations; the fundamental mechanisms giving rise to the energy dependence of the scattering may be totally different. One school of thought,[3] for example, treats the scattering as a single-particle problem and produces an energy-dependent scattering as a consequence of the energy dependence of the pseudopotentials of the scattering ions. The present authors, on the other hand, have investigated[4–6] the scattering as a many-particle problem, and have found the effects of the electron-phonon interaction to dominate the sign as well as the magnitude of the thermoelectric effects.

In the present paper, a detailed discussion is given of the effects reported briefly in Refs. 4–6. In Sec. II the Boltzmann equation and vector mean free path are briefly discussed, and then in Sec. III the calculation of the scattering amplitude is described. The effects of the second-order terms in the scattering amplitude on the thermoelectric effects in pure metals are evaluated in Sec. IV, while Sec. V consists of the calculation of the additional contributions to be expected in a dilute alloy, where virtual recoil of the solute atoms is possible. The summary of these results, included in the discussion in Sec. VI, is intended to be comprehensible without reference to the details of the derivation.

II. THE BOLTZMANN EQUATION

Of the available formalisms for calculating transport coefficients, we choose the simplest, and consider the predictions of a solution for the Boltzmann equation. The reasons for this choice are twofold. Firstly, we shall be working in second-order perturbation theory, the range of validity of which is, in some cases, related to that of the Boltzmann equation itself. For example, the reduction of the Kubo formula to produce the Boltzmann equation breaks down when the ladder sum contains crossed phonon lines; such terms are of the fourth order in the electron-phonon interaction, and it is thus consistent to ignore their effect in the present calculation. Secondly, we wish to allow the possibility of extending the calculation to anisotropic materials, for which the Boltzmann equation alone presents a major computational obstacle.[7] In the present paper, however, we confine our attention to a free-electron model having a spherical Fermi surface.

The results of this approach are that the Seebeck coefficient, or thermopower, S, is given[1] by the expression

$$S=(L_0 eT/\zeta)\xi \; . \tag{1}$$

Here L_0 is $\pi^2 k_B^2/3e^2$, the free-electron Lorenz number, k_B is Boltzmann's constant, T the absolute temperature, e the electronic charge, and ζ the chemical potential, equal to the Fermi energy in this instance. The dimensionless parameter ξ is customarily taken to be equal to the fractional change in the quantity

$$\sum_k \vec{v}_k \cdot \vec{\Lambda}\delta(\mathcal{E}-\mathcal{E}_k) \; , \tag{2}$$

per fractional change in energy $\mathcal{E}$, evaluated at $\mathcal{E}=\zeta$ and with $\vec{v}_k$ the electron velocity for wave number $\vec{k}$, and with $\vec{\Lambda}_k$ the vector mean free path[8,9]; in the present paper a more delicate expression for this quantity will be required in some instances. It is common to write ξ in the form

$$\xi=\frac{\partial \ln\sigma(\zeta)}{\partial \ln\zeta} \; , \tag{3}$$

with σ the conductivity for a metal with Fermi energy ζ. This would be inappropriate in the present case, in which many-body effects are to be taken into account. We shall see that there are important contributions to the scattering that are functions of $\mathcal{E}_k-\zeta$; the changes in expression (2) that lead to corresponding contributions to S are then found by studying the variation of Λ_k with $\mathcal{E}$ *while* ζ *is kept fixed.* Allowing ζ to vary with $\mathcal{E}$ would lead to a spurious disappearance of these terms from the final expression for S.

In the present calculation it will be possible for the most part to write

$$\xi=\frac{3}{2}-\left(\frac{\partial \ln(\tau^{-1})}{\partial \ln\mathcal{E}}\right)_{\mathcal{E}=\zeta} \; , \tag{4}$$

with τ^{-1} the inverse relaxation time found from the linearized Boltzmann equation,[7]

$$\tau_k^{-1}=\sum_{k'} Q(\vec{k},\vec{k}')\left(\frac{1-f_{k'}}{1-f_k}\right)\left(1-\frac{\Lambda_{k'}}{\Lambda_k}\cos\theta_{kk'}\right) \; .$$

The term equal to $\frac{3}{2}$ in Eq. (4) is characteristic of the density of states of the free-electron system, while in Eq. (5) the quantity $Q(\vec{k},\vec{k}')$ is the intrinsic probability for an electron to be scattered from an occupied state $\vec{k}$ to an empty one $\vec{k}'$, the probability of occupation of a state $\vec{k}$ is f_k, and $\theta_{kk'}$ is the angle between $\vec{k}$ and $\vec{k}'$. The fact that Λ is treated as a scalar indicates that the assumption has been made that the scattering is isotropic, so that $Q(\vec{k},\vec{k}')$ is invariant under rotation of the crystal axes. Having thus simplified the model to the greatest extent that is profitable, we now turn to the core of the problem and study the energy dependence of the scattering.

III. THE SCATTERING PROBABILITY

Until a few years ago it was commonly assumed that the exclusion principle could be ignored for the intermediate state in second-order perturbation calculations of the scattering of conduction electrons. It was argued that any contribution from scattering through occupied intermediate states need not be included because another set of scattering processes existed which exactly cancelled these particular terms in the scattering amplitude. In 1964 Kondo[10] pointed out that such a procedure is invalid if the scatterer may exchange spin with the scattered electron, as then the two terms in second order that had been expected to cancel differ in that one term contains a product of spin raising and lowering operators of the form S^+S^- while the other contains S^-S^+. As these operators do not commute, a term containing $f_{k''}$, the occupancy of the intermediate state of the electron, exists in the scattering probability, and the well known resistance minimum results.[11] In general terms, one may say that the Kondo effect occurs because the scatterer possesses an internal degree of freedom. It thus is reasonable to ask whether the degrees of freedom of an ion that allow it to participate in lattice vibrations might also have measurable consequences in second-order scattering processes.

Another common practice has been the neglect of the effects of the renormalization of vertices in electron scattering processes that occurs when additional electron-phonon interactions are included. While the importance of such effects on the forward-scattering amplitude (and hence on the electronic specific heat) have long been recognized,[12] little note appears to have been taken of the corrections caused to the general electron-scattering probabilities. This is probably a consequence of the smallness of the parameter m/M, the ratio of the electron mass to the ion mass. However, while it is perfectly true that the magnitude of the scattering cross section may only be changed by a very small amount, the energy derivative of the cross section may be radically altered. As we shall in fact see, the fractional change in the energy derivative of the cross section is typically of the order of $(m/M)(V\zeta/k_B^2\Theta^2)$, with V a parameter related to the ionic potential and $k_B\Theta$ the Debye energy. Such corrections are at least significant, and in many cases dominant.

For simplicity we consider a rigid-ion model of a random substitutional alloy. The potential $W(\vec{r})$ acting on an electron is then

$$W(\vec{r})=\sum_l V(\vec{r}-\vec{l}-\vec{y}_l)+\sum_l U_l(\vec{r}-\vec{l}-\vec{y}_l) \; , \tag{6}$$

where $V(\vec{r})$ is the potential due to a single screened solvent ion and U_l vanishes at solvent-ion sites and is equal to the difference between solute and solvent potentials at the solute-ion sites, which are a small fraction c of the total number of sites. The displacements $\vec{y}_l$ of the ions from their equilibrium positions may be expressed in terms of the normal modes of vibration of the lattice, which is assumed to be of Bravais form. Equation (6) may then be written in second-quantized form as

$$W = V + U$$

with

$$V=\sum_{k,k'} c^\dagger_{k'} c_k V_{k'k}\Big(N\Delta(\vec{K}) + iN^{1/2}\sum_{q,s}\Delta(\vec{K}+\vec{q})(\hbar/2M\omega_{qs})^{1/2}(\vec{K}\cdot\vec{S})(a_{qs}+a^\dagger_{-qs}) - \frac{1}{2}\sum_{q,s,q',s'}\Delta(\vec{K}+\vec{q}+\vec{q}\,')(\vec{K}\cdot\vec{S})(\vec{K}\cdot\vec{S}\,')(\hbar/2M\omega_{qs})^{1/2}(\hbar/2M\omega_{q's'})^{1/2}(a_{qs}+a^\dagger_{-qs})(a_{q's'}+a^\dagger_{-q's'})+\cdots\Big)\ , \tag{7}$$

and

$$U=\sum_{k,k'} c^\dagger_{k'} c_k U_{k'k}\Big(NR(\vec{K}) + iN^{1/2}\sum_{q,s} R(\vec{K}+\vec{q})(\hbar/2M\omega_{qs})^{1/2}(\vec{K}\cdot\vec{S})(a_{qs}+a^\dagger_{-qs})+\cdots\Big)\ . \tag{8}$$

The notation here is that of Ref. 1, Chap. 5, in which c_k annihilates an electron of wave number $\vec{k}$ and a_{qs} annihilates a phonon of wave number $\vec{q}$, polarization $\vec{s}$, and frequency ω_{qs}. The ionic mass, assumed equal for solvent and solute, is M; and $V_{k'k}$ and $U_{k'k}$ are, respectively, the Fourier transform of the potential due to a single ion, and Fourier transform of the difference between the potentials due to solute and solvent ions; and $\vec{K}=\vec{k}-\vec{k}'$. The function R is defined as

$$R(\vec{K}) = N^{-1}\sum e^{i\vec{K}\cdot\vec{l}}\ , \tag{9}$$

with the sum proceeding only over solute sites, while

$$\Delta(\vec{K}) = \sum_g \delta_{K,g}\ ,$$

with $\vec{g}$ the vectors of the reciprocal lattice.

When the scattering amplitude $T_{\vec{k}\vec{k}'}$ between electron states is calculated to second order, a large number of terms are obtained. Of these, we ignore contributions from the terms in V that are of zeroth order in the phonon coordinates, as these will merely change the electron wave functions from plane waves to Bloch waves. A selection of the remaining terms of lowest order is illustrated in Fig. 1, in which electrons are represented by smooth lines, phonons by wavy lines, and scattering by the impurity potential by a vertex marked with a cross. For brevity, no distinction is made between phonon absorption or emission in this illustration. We shall assume the resistivity to be calculable from the diagrams shown in Figs. 1(a) and 1(b) alone; this point has already been the subject of some discussion in the literature.[13] The thermoelectric effects, on the other hand, require the examination of terms of higher order, and in particular of those terms of second order that add coherently to terms of first order. As an example we note diagrams like Figs. 1(c)–1(f), which may represent the same net process as Fig. 1(a), and Figs. 1(g)–1(l) which may be coherent with Fig. 1(b). It is permissible to neglect these terms in calculating the resistivity because of an almost complete cancellation that occurs between, for example, the diagrams of Figs. 1(c) and 1(e). The fact that the cancellation is not complete is due to the energy of the phonon present in the intermediate state of the system; the small contribution that does not cancel is found to be highly energy dependent, and thus crucial in calculating the Seebeck coefficient.

IV. EFFECTS IN PURE MATERIALS

We consider first inelastic scattering from the pure-metal potential V, and confine our attention to those processes of which the net result is the

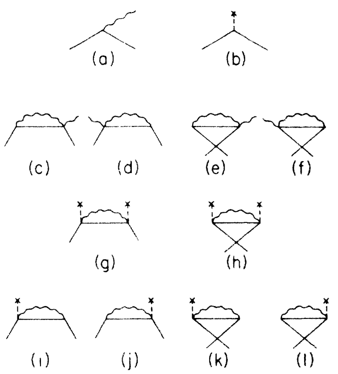

FIG. 1. Possible low-order scattering processes. An electron (straight line) may be scattered by absorption or emission of a phonon (wavy line), by an impurity (vertical dashed line), or by both simultaneously.

scattering of an electron from $\vec{k}$ to $\vec{k}'$, and the creation or destruction of a single phonon of wave number $\vec{q}$ and polarization $\vec{s}$. In the second-order terms we retain only those containing the Fermi occupation function $f_{k''}$ of the intermediate electron state $\vec{k}''$, and find

$$T = T_1^{(\pm)} + T_2^{(\pm)}$$

where

$$\langle \vec{k}', n_q \pm 1 \,|\, T_1^{(\pm)} \,|\, \vec{k}, n_q \rangle = -iV_q \sum_s \vec{q} \cdot \vec{s} \left(\frac{N\hbar}{4M\omega_{qs}} \right)^{1/2} \left[\coth\left(\frac{\hbar\omega_{qs}}{2k_B T} \right) \pm 1 \right]^{1/2} , \tag{10}$$

and

$$\langle \vec{k}', n_q \pm 1 \,|\, T_2^{(\pm)} \,|\, \vec{k}, n_q \rangle = -4iN^{1/2} \sum_{s, q', s'} \left(\frac{\hbar}{4M\omega_{qs}} \right)^{1/2} \left(\frac{\hbar}{2M\omega_{q's'}} \right) V_{q'} V_{q-q'} \vec{q}' \cdot \vec{s}' (\vec{q} - \vec{q}') \cdot \vec{s}' (\vec{q} - \vec{q}') \cdot \vec{s}$$

$$\times \frac{\hbar\omega_{q's'}}{(\mathcal{E}_k - \mathcal{E}_{k+q'})^2 - (\hbar\omega_{q's'})^2} f_{k+q'} \left[\coth\left(\frac{\hbar\omega_{qs}}{2k_B T} \right) \pm 1 \right]^{1/2} . \tag{11}$$

The upper (lower) signs are appropriate to those processes in which a phonon of wave vector $\vec{q}$ is emitted (absorbed). The phonon system has been assumed to be in equilibrium, and so the phenomenon of phonon drag[2] will be absent from our results. The approximation is made that the energy $\hbar\omega_{qs}$ of the real phonon that is absorbed or emitted is small compared with that of the virtual phonon $\vec{q}'$ that is present in the intermediate state in diagrams like Figs. 1(d), 1(e), etc. This will be a valid step at low temperatures, as $\hbar\omega_{qs} \sim k_B T$, while the principal contribution from virtual phonons comes from those for which $\hbar\omega_{q's'} \sim k_B \Theta$, the Debye energy; at high temperatures the invalidity of this particular approximation becomes irrelevant, as processes involving virtual phonons then make a negligible contribution.

To third order in V the probability $Q^{\pm}(\vec{k}, \vec{k}')$ for an electron in the occupied state $\vec{k}$ to be inelastically scattered to the empty state $\vec{k}'$ is

$$Q^{\pm}(\vec{k}, \vec{k}') = \frac{2\pi}{\hbar} \left(|T_1^{(\pm)}|^2 + 2\,\mathrm{Re}\, T_1^{(\pm)*} T_2^{(\pm)} \right) \delta(\mathcal{E}_k - \mathcal{E}_{k'} \mp \hbar\omega_q) . \tag{12}$$

Here the simplifying assumption has been made that ω_{qs} is independent of s. Substitution of Eqs. (10)–(12) in Eq. (5) gives the energy-dependent relaxation time τ_k. We assume the magnitude Λ_k of the vector mean free path to be a slowly varying function of energy, so that $\Lambda_{k'}/\Lambda_k = 1$ to order $\hbar\omega/\zeta$. Further, the energy-conserving delta function in Eq. (12) requires $\mathcal{E}_{k'} = \mathcal{E}_k \mp \hbar\omega$, so that if $\mathcal{E}_k = \zeta$ we find

$$(1 - f_{k'})/(1 - f_k) = 1 \mp \tanh(\hbar\omega_q / 2k_B T) .$$

Equation (5) thus becomes

$$\frac{1}{\tau_k} = \sum_{k', \pm} \left(\frac{2\pi}{\hbar} \right) \left(|T_1^{(\pm)}|^2 + 2\,\mathrm{Re}\, T_1^{(\pm)*} T_2^{(\pm)} \right)$$

$$\times [1 \mp \tanh(\hbar\Omega_q / 2k_B T)](1 - \cos\theta_{kk'})$$

$$\times \delta(\mathcal{E}_k - \mathcal{E}_{k'} \mp \hbar\omega_q) . \tag{13}$$

An average relaxation time of sufficient accuracy to provide a value for the conductivity is found from this expression in the usual way when terms in T_2 are neglected. We assume here a simple model in which V_q is equal to some constant V and the phonon spectrum is of isotropic Debye form with characteristic temperature Θ. With N the number of ions and N' the number of electrons, one finds[14]

$$\frac{1}{\tau(\zeta)} = \frac{3}{2} \frac{2\pi}{\hbar} \frac{(NV)^2}{k_B \Theta} \frac{m}{M} \frac{N}{N'} \left(\frac{T}{\Theta} \right)^5 G_4(\Theta/T) , \tag{14}$$

where

$$G_n(x) = \int_0^x \xi^n \operatorname{csch}\xi \, d\xi . \tag{15}$$

Electron-phonon umklapp processes have not been included in this expression, as they increase considerably the complexity of the calculation without qualitatively changing the final result.

The energy derivative of the inverse relaxation time is composed of the two parts that arise from the terms in $|T_1|^2$ and $\mathrm{Re}\, T_1^* T_2$ in Eq. (13). The first part is readily calculated with the aid of approximations similar to those used in deriving Eq. (14). One finds a contribution of

$$\frac{d}{d\mathcal{E}_k} \left(\frac{1}{\tau} \right)_1 = \frac{1}{\mathcal{E}_k \tau} \left(2 \frac{\partial \ln |V|}{\partial \ln \mathcal{E}} - \frac{3}{2} \right) , \tag{16}$$

which in the absence of other effects would, on substitution in Eq. (4), yield the result

$$\xi_1 = 3 - 2 \left(\frac{\partial \ln |V|}{\partial \ln \mathcal{E}} \right)_{\mathcal{E} = \zeta} . \tag{17}$$

The second part, to which attention was first drawn in Ref. 5, requires more careful consideration. Combination of Eqs. (10), (11), and (13) yields a contribution to the inverse relaxation time of

$$\left(\frac{1}{\tau}\right)_2 = \frac{2\pi}{\hbar}(NV)^3 \frac{4\hbar^2}{MN}\sum_{q,q'} \frac{\hbar}{2MN\omega_q}\vec{q}'\cdot(\vec{q}-\vec{q}')\vec{q}\cdot(\vec{q}-\vec{q}')$$
$$\times \operatorname{csch}\left(\frac{\hbar\omega_q}{k_B T}\right)(1-\cos\theta_{kk'})\frac{f_{k+q'}}{(\mathcal{E}_k-\mathcal{E}_{k+q'})^2-(\hbar\omega_{q'})^2}\,\delta(\mathcal{E}_k-\mathcal{E}_{k+q}\pm\hbar\omega_q)\,, \tag{18}$$

when the same approximation of an isotropic Debye model is made for the phonon system. The summation over $\vec{q}$ is easily performed; one finds

$$\sum_q \frac{\hbar}{2MN\omega_q}\operatorname{csch}\left(\frac{\hbar\omega_q}{k_B T}\right)\vec{q}'\cdot(\vec{q}-\vec{q}')\vec{q}\cdot(\vec{q}-\vec{q}')\left(-\frac{\vec{k}_F\cdot\vec{q}}{k_F^2}\right)\delta(\mathcal{E}_k-\mathcal{E}_{k+q})$$
$$= -\frac{3}{8}\frac{m}{M}\frac{1}{k_B\Theta}\frac{q_D^5}{k_F^3}\left(\frac{T}{\Theta}\right)^5\left[\left(\frac{(3\eta^2-1)q'^2}{8k_F^2}+\frac{\eta}{2}\frac{q'}{k_F}\right)\left(\frac{T}{\Theta}\right)^2 G_6(\Theta/T)+\left(\frac{(3-\eta^2)q'^2}{2q_D^2}+\frac{\eta q'^3}{2k_F q_D^2}\right)G_4(\Theta/T)\right], \tag{19}$$

where η is the cosine of the angle between $\vec{q}'$ and $\vec{k}$, and q_D is the Debye radius and k_F the Fermi radius.

The summation over $\vec{q}'$ is then seen to require evaluation of a set of terms of the form

$$A_{nl} = \sum_{\vec{q}'} \frac{q'^n \eta^l f(\mathcal{E}_{k+q'})}{(\mathcal{E}_k-\mathcal{E}_{k+q'})^2-(\hbar\omega_{q'})^2}\ .$$

These are most easily evaluated in the geometry shown in Fig. 2, in which one coordinate is measured normal to the surfaces of constant electron energy. To an adequate approximation we then find

$$A_{nl} = \frac{(-1)^l m\Omega}{2^{l+2}\pi^2\hbar^2 k_F^{l+1}}\int_0^{q_D}(q')^{l+n+1}\,dq'$$
$$\times\int_{-\mathcal{E}_k}^{\infty}\frac{f(\mathcal{E}_k+\hat{\mathcal{E}})}{\hat{\mathcal{E}}^2-(q'k_B\Theta/q_D)^2}\,d\hat{\mathcal{E}}\ .$$

At this point we note that the energy derivative $(\partial/\partial\mathcal{E}_k)(1/\tau)_2$ of the partial inverse relaxation time found in this way may itself vary appreciably within the thickness of the Fermi surface, and so Eq. (4) ceases to be strictly accurate. It is then advantageous to return to an earlier stage in the theory of the thermolectric coefficients[15] to find that these higher-order processes can be expected to contribute to the parameter ξ an amount

$$\Delta\xi = \frac{3\zeta}{\pi^2 k_B^2 T^2 (1/\tau)_1}\int\left(\frac{1}{\tau}\right)_2(\mathcal{E}_k-\zeta)\frac{\partial f_k^0}{\partial\mathcal{E}}\,d\mathcal{E}_k\ . \tag{20}$$

Substitution in Eq. (20) of Eqs. (14), (18) and (19) then yields

$$\Delta\xi_1 = -\left(\frac{9\zeta NV}{2\pi^2 k_B^2 T^2}\right)\left(\frac{m}{M}\right)\int_0^1\left\{\frac{3}{2}\left(\frac{2N}{N'}\right)^{1/3}\rho^3-\frac{3}{8}\left(\frac{2N}{N'}\right)\rho^5\right.$$
$$\left.-\left[\frac{3}{8}\left(\frac{2N}{N'}\right)\rho^3-\frac{3}{32}\left(\frac{2N}{N'}\right)^{5/3}\rho^5\right]\left(\frac{T}{\Theta}\right)^2\frac{G_6(\Theta/\tau)}{G_4(\Theta/\tau)}\right\}d\rho$$
$$\times\int_{-\infty}^{\infty} z\,\operatorname{sech}^2 z\,dz\int_{-\infty}^{\infty}\frac{\tanh u}{(u-z)^2-(\rho\Theta/2T)^2}\,du\ . \tag{21}$$

The integrals over z and u are evaluated in the Appendix, and yield a function that at low temperatures approaches $-4\pi^2T^2/3\Theta^2\rho^2$. In this limit, the integrations over ρ are trivial and yield a correction to ξ that is temperature independent and of a magnitude comparable to or greater than the previously accepted result given by Eq. (17).

At intermediate temperatures the results may be written as

$$\Delta\xi_1 = \frac{\zeta NV}{k_B^2\Theta^2}\frac{m}{M}\Psi_1(T/\Theta)\ , \tag{22}$$

where the dimensionless function $\Psi_1(T/\Theta)$ is shown in Fig. 3 for various valences. Because the product of constants multiplying Ψ_1 in Eq. (22) has a magnitude of approximately unity and an inherently negative sign (the potential due to an ion being attractive), we find ξ to contain a large negative contribution at low temperatures from virtual multiphonon processes. Because these effects are attenuated at higher temperatures, one find a positive hump to be added to the Seebeck coefficient S. An example of this for a monovalent metal is shown in Fig. 4, in which the plotted S is the sum of a contribution from multiphonon processes and a negative linear term from the familiar effects described by Eq. (17). It will not escape notice that just such a form for the temperature dependence of the Seebeck coefficient has frequently been observed experimentally, and has usually been attributed to the effects of phonon drag.[2] A current of phonons, however, would normally be expected to sweep a current of electrons down the crystal in its own direction, thus giving rise to a *negative* hump in S, and it has formerly been necessary to invoke some very particular types of umklapp scattering in order to explain humps that occur in a

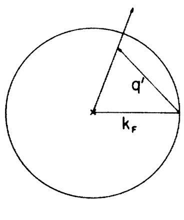

FIG. 2. Geometry used in reducing Eq. (19).

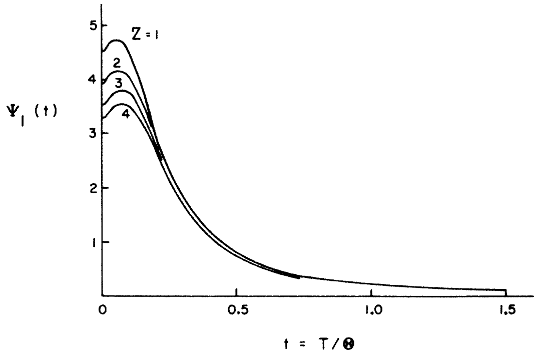

FIG. 3. Temperature dependence of the contribution to the thermoelectric parameter ξ of virtual phonons in a pure metal for various values of the valence Z. The temperature is measured in units of the Debye temperature Θ.

positive direction.[16] The recognized presence of virtual multiphonon processes thus considerably modifies the interpretation of experimental data.

V. EFFECTS IN ALLOYS

In a dilute substitutional alloy, the total thermopower will be the sum of contributions from a number of effects. In addition to the processes discussed in the previous section, there will also be scattering at the impurity sites, and some of these scattering events may be accompanied by the emission of a phonon as the impurity atom recoils. In second order, the possibility of processes involving virtual phonons arises; it was in studying this phenomenon of virtual recoil that the importance of second-order phonon interactions to the thermoelectric coefficients was first noticed.[4]

The scattering processes involving impurity ions may be either elastic or inelastic. The contribution of the inelastic scattering to the thermoelectric coefficients will be negligible as a consequence of the fact that the amplitudes for these processes will not be coherent with either of the lowest-order processes represented in Figs. 1(a) and 1(b). While the process of Fig. 1(a) conserves wave number and that of Fig. 1(b) conserves energy, inelastic scattering at impurities will in general conserve neither. Terms in the scattering probability involving virtual intermediate phonons can thus only occur in higher order, and may be safely neglected.

Second-order elastic scattering processes involving virtual phonons will be of two kinds—those involving repeated scattering at an impurity and those involving one scattering at an impurity and one by a wave-number-conserving phonon interaction. The former are depicted in Figs. 1(g) and 1(h), while the latter are shown in Figs. 1(i)–1(l). The total elastic scattering from all these processes is then calculated to be

$$Q(\vec{k},\vec{k}') = \frac{2\pi}{\hbar} cN\delta(\mathcal{E}_k - \mathcal{E}_{k'})(\mathfrak{Q}_A + \mathfrak{Q}_B + \mathfrak{Q}_C) , \tag{23}$$

where

$$\mathfrak{Q}_A = |U_{k'-k}|^2 ,$$

$$\mathfrak{Q}_B = -\frac{2\hbar^2}{MN} \sum_{q,k''} U_{k'k} U_{kk''} U_{k''k'} (\vec{k}' - \vec{k}'') \cdot (\vec{k} - \vec{k}'') \times \frac{f_{k''}}{(\mathcal{E}_k - \mathcal{E}_{k''})^2 - (\hbar\omega_q)^2} ,$$

$$\mathfrak{Q}_C = \frac{4\hbar^2}{M} \sum_q U_{k'k} V_{k,k+q} U_{k+q,k'} \vec{q} \cdot (\vec{k}' - \vec{k} - \vec{q}) \times \frac{f_{k+q}}{(\mathcal{E}_{k+q} - \mathcal{E}_k)^2 - (\hbar\omega_q)^2} .$$

The lowest-order term $\mathfrak{Q}_A$ is sufficient for a calculation of the partial inverse relaxation time due to impurities, and one finds

$$\left(\frac{1}{\tau}\right)_3 = \frac{3\pi}{2\hbar\zeta} \frac{N'}{N} c(NU)^2$$

when $U_{kk'}$ is taken as constant and the Born approximation assumed adequate. In the absence of inelastic scattering this would yield a thermopower parameter ξ_2 of magnitude

$$\xi_2 = \frac{5}{2} - 2\left(\frac{\partial \ln|U|}{\partial \ln \mathcal{E}}\right)_{\mathcal{E}=\zeta} . \tag{24}$$

The contribution from the term $\mathfrak{Q}_B$, representing double scattering at an impurity, may eventually be reduced to the form

$$\Delta\xi_B = 6 \frac{NU\zeta}{(k_B\Theta)^2} \frac{m}{M} \frac{N'}{N} \left[\frac{-6}{\pi^2} \frac{T}{\Theta} \int_0^{\Theta/2T} \gamma^2 \Phi(\gamma)\, d\gamma\right] \tag{25}$$

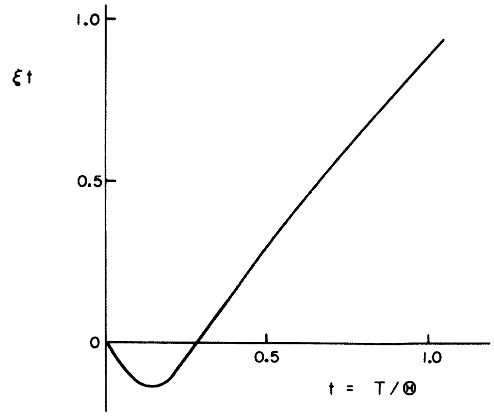

FIG. 4. Typical form of the negative of the Seebeck coefficient S to be expected in a pure meterial in the absence of phonon drag. Here $\xi T/\Theta$, which is proportional to $-S$, is plotted for the case where $\xi = 1 - \frac{1}{2}\Psi_1(T/\Theta)$ in a monovalent metal.

where $\Phi(\gamma)$ is the function discussed in the Appendix. The expression in square brackets reduces to unity in the limit of low temperatures. The contribution from the term $\mathfrak{Q}_C$, representing mixed scattering, is similarly found to be

$$\Delta\xi_C = \frac{NV\zeta}{(k_B\Theta)^2}\,\frac{m}{M}\left(\frac{2N}{N'}\right)^{1/3}\left[\frac{-24}{\pi^2}\left(\frac{T}{\Theta}\right)^2\int_0^{\Theta/2T}\gamma^3\Phi(\gamma)\,d\gamma\right], \tag{26}$$

where again the expression in square brackets has a low-temperature limit of unity.

At finite temperatures, the Seebeck coefficient of an alloy will exhibit these effects as well as the pure-material effects described in the previous section. It is easily shown that the contribution of each effect to the thermoelectric power is approximately proportional to its contribution to the resistance; so if the impurity and lattice contributions to the resistivity are ρ_R and ρ_T respectively, one finds a resultant Seebeck parameter ξ given by

$$\xi = \frac{\rho_R(\xi_2 + \Delta\xi_B + \Delta\xi_C) + \rho_T(\xi_1 + \Delta\xi_1)}{\rho_R + \rho_T}\,. \tag{27}$$

The various contributions here are those defined in Eqs. (17), (21), (24), (25), and (26).

VI. DISCUSSION

The most important feature of the correction terms that we have calculated is their magnitude. The ratio of the magnitudes of these correction terms to those of the lowest-order terms (which are the only ones considered in the standard works on thermoelectric effects) is of order $(m/M)(NV\zeta/k_B^2\Theta^2)$. The first factor is the ratio of the electron mass to the ionic mass, and is indeed small, being perhaps of order 10^{-5}, a fact which no doubt accounts for its previous neglect in the theory of thermoelectric effects. The second factor, however, is of the order of the square of the ratio of the Fermi energy to the Debye energy, and is sufficiently large to compensate for the smallness of the first factor, and yield a product of order unity. It will thus be necessary to consider all the effects that we have described in predicting the temperature dependence and size of the Seebeck coefficient of any given dilute alloy.

Let us now attempt to summarize our results graphically to give a prescription for calculating the theoretically predicted thermopower. The discussion proceeds most simply in terms of the parameter ξ, but is easily converted to a discussion of the Seebeck coefficient S through the relation

$$S = \pi^2 k_B^2 T\xi/3e\zeta$$

with ζ the Fermi energy, and e the (negative) electronic charge.

The contributions to ξ to be expected in a pure material are twofold: firstly there is the temperature-independent term

$$\xi_1 = 3 - 2\left(\frac{\partial \ln|V|}{\partial \ln\mathcal{E}}\right)_{\mathcal{E}=\zeta}$$

calculated from the energy dependence of the ionic pseudopotential. To this must be added the inherently negative temperature-dependent term

$$\Delta\xi_1 = \frac{\zeta NV}{(k_B\Theta)^2}\,\frac{m}{M}\,\Psi_1(T/\Theta)\,,$$

where the function Ψ_1 is shown in Fig. 3, and

$$NV = \Omega_1^{-1}\int V(\vec{r})\,d\vec{r}\,,$$

with Ω_1 the volume of a unit cell, and $V(\vec{r})$ the screened pseudopotential of a single ion.

Adding a small concentration of solute to this pure material involves three new terms in the Seebeck parameter. There is the familiar term

$$\xi_2 = \frac{5}{2} - 2\left(\frac{\partial \ln|U|}{\partial \ln\mathcal{E}}\right)_{\mathcal{E}=\zeta}\,,$$

due to the energy dependence of the density of states and of the impurity scattering potential, to which must be added the two terms

$$\Delta\xi_B = 6\,\frac{\zeta NU}{(k_B\Theta)^2}\,\frac{m}{M}\,\frac{N'}{N}\,\Psi_2(T/\Theta)\,,$$

$$\Delta\xi_C = \frac{\zeta NV}{(k_B\Theta)^2}\,\frac{m}{M}\left(\frac{2N}{N'}\right)^{1/3}\Psi_3(T/\Theta)\,.$$

The functions Ψ_2 and Ψ_3 are shown in Figs. 5 and 6, and the ratio N'/N is the valence. While $\Delta\xi_C$ is inherently negative, the sign of $\Delta\xi_B$ will be the same as the sign of the net scattering potential of the impurity, and may be positive or negative, depending on whether the solute presents a net repulsive or attractive potential in comparison with the solvent ion for which it has been substituted. These three impurity-generated terms must then be combined with the pure-solvent contributions as indicated in Eq. (27).

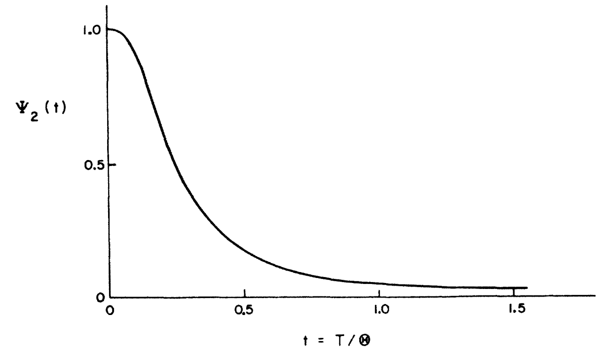

FIG. 5. Temperature dependence of the contribution to the thermoelectric parameter ξ of processes in which an electron is twice scattered by an impurity ion exhibiting virtual recoil.

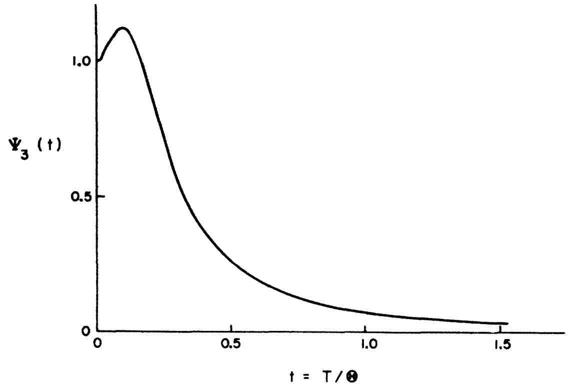

FIG. 6. Temperature dependence of the contribution to the thermoelectric parameter ξ of processes in which an electron is scattered both by an impurity exhibiting virtual recoil and in a wave-number-conserving phonon interaction.

Since attention was first drawn to the importance of multiphonon processes in the thermopowers of pure materials, the experimentalist observing a low-temperature hump in the Seebeck coefficient has faced a problem of interpretation in that these effects yield a temperature dependence of S that is similar to that caused by disequilibrium in the lattice-wave distribution function. Indeed, the present authors[5] were tempted in a euphonic moment to refer to the manifestation of second-order processes as "phony phonon drag." It is therefore important to ask in what respects these two effects differ sufficiently to be distinguishable.

Firstly, the presence of phony phonon drag (PPD) in pure materials will frequently be felt in the form of a *positive* hump in S, while true phonon drag (PD) in its most direct form yields a *negative* hump.[2] In anisotropic materials, however, umklapp processes may invert the sign of the PD component,[16] and so this test alone is insufficient. A feature of PD is that its low-temperature contribution varies as T^3, and yields a form of $S(T)$ that is initially convex, changing to concave as the maximum of the hump is approached, while PPD effects give rise to a form of $S(T)$ that, *in an ideally pure material*, varies from linearity as $T^3 \ln T$, but which is also initially convex. However, caution is required in interpreting experiments on "pure" metals, as the criterion $\rho_T \gg \rho_R$ must be obeyed if alloy effects are to be negligible.[17] This is seldom the case for helium temperatures, and the value of many measurements in allegedly pure materials is compromised by the fact that the Seebeck coefficient is then determined by scattering from unknown impurities at all temperatures below 10K.

Any decisive method of separating PD and PPD contributions in pure metals must rest on the different physical mechanisms involved, and would require measurements on several samples, or at least on more than one state of the same sample. For example, it might be possible to alter the PD contribution by further annealing of a sample while leaving the PPD contribution unaltered. In some materials it might be possible to see a shift in the position of the maximum in the PPD hump by working with a sample of a different isotope of a metal.[18]

In dilute alloys the presence of virtual-recoil terms is more readily confirmed, the recent discussion by Dudenhoeffer and Bourassa[19] of the thermopower of dilute aluminum alloys being particularly persuasive. The interpretation of the low-temperature thermopowers of dilute alloys of alkali metals in potassium is facilitated by the presence of the term $\Delta\xi_C$, which was absent in our preliminary publication[4] on this subject. While too many uncertainties remain for a precise comparison of theory with experiment to be meaningful, the general behavior of ξ in these alloys is readily interpreted in terms of the dominating effect of $\Delta\xi_B$. Our present results differ from those of Ref. 4 in a number of respects. At the time that the preliminary account of the importance of the term $\Delta\xi_B$ was published the effects of consecutive scattering by a phonon and by a recoiling impurity atom had not been considered, and so the term $\Delta\xi_C$ was missing. This omission has been corrected. as has a numerical error in the treatment of the scattering in Ref. 4. In addition, two suggestions made by Meyer and Young[3] in a comment on the preliminary calculation have been followed; the parameters U and V were taken to be the Animalu-Heine pseudopotentials[20,21] evaluated at $q = \frac{2}{3}k_F$ and suitably renormalized, and the energy dependence of the d-wave component of the scattering was allowed for by attributing a value of 0.9 to the term $\partial \ln |U| / \partial \ln \mathcal{E}$. The results are shown in Table I, in which the theoretical predictions are compared with the experimental results of Guénault and MacDonald.[22] It must be emphasized that the contribution of $\Delta\xi_B$ to the theoretical result is extremely sensitive to the choice of potential, and leads to an uncertainty of at least ± 0.5 in ξ.

The complete temperature variation of the See-

TABLE I. Comparison with experiment of the theoretical prediction of the thermopower parameter ξ at low temperatures for dilute alloys of alkali metals in potassium. Experimental results are from Ref. 22.

Solute	ξ (theory)	ξ (expt.)
Na	0.86	0.86
Rb	−0.27	−0.19
Cs	−0.46	−0.43

beck parameter ξ has been shown to be due to a number of effects. In addition to the effects of true phonon drag (which are undoubtedly a large contribution in many measurements, although perhaps not quite so many as has been hitherto believed) there are the contributions $\Delta\xi_B$ and $\Delta\xi_C$ which are important (and frequently dominant) at low temperatures, but which decrease in magnitude as the temperature is raised. At temperatures sufficiently high that the phonon resistivity ρ_T is comparable with the residual resistivity ρ_R the parameter ξ begins to change from its impurity-dominated form to the phonon-dominated form, which itself has the temperature variation of $\Delta\xi_1$. A large variety of behaviors of $S(T)$, even involving several changes in sign over the complete temperature range, is readily obtainable when the various constants take on appropriate values.

To complete this paper, we recall the approximations that have been made, and draw attention to improvements that are necessary if more detailed comparisons of theory and experiment are to be made. Firstly, we note that terms to second order in the perturbation expansion of the T matrix have been calculated and found to be important, but that higher-order terms have been ignored. This appears to be reasonable on the ground that advancing to higher order would introduce terms smaller by a further factor of m/M without increasing the energy dependence in any compensating way.

Of the second-order terms, no account has been taken of the effect of the coherent interference between the first-order effect of intrinsic two-phonon processes and the second-order effect of one-phonon processes. The justification for this is that, within the framework of the Boltzmann equation, both phonons are real rather than virtual, and thus too sparse to be important at low temperatures. On the other hand, more exact transport formalisms in which these scattering processes occur as part of a ladder sum, might well pick up an appreciable contribution from such scatterings.

A more serious shortcoming of the present analysis has been the assumption of a free-electron model and the neglect of umklapp processes; these must undoubtedly be important in polyvalent materials and could well introduce further factors of two or three into the final results. The assumed constancy of the Fourier transforms of the ionic potentials U and V of solute and solvent is not a serious defect of the theory, as the detailed form of these functions may readily be inserted in the formalism at the cost of some additional numerical integrations. The assumption that solute and solvent ions had equal mass was necessary to allow the motion of the solute atoms to be described simply in terms of the phonon coordinates of the pure solvent lattice. While this will be a reasonable approximation for many systems, it may introduce error when the masses of the two constituents are markedly different. The limiting cases of very light and very heavy solutes present few difficulties, and lead to results broadly similar to those presented here, an example being the *Pd*H system.[6] One thus might expect an alloy of which the components are only moderately different in mass to be reasonably well described in the present approximation; this must remain a conjecture for the time being, however, in view of the difficulties associated with describing the dynamics of disordered systems.

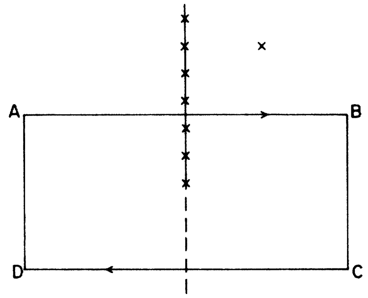

FIG. 7. Contour used in deriving expression for $\Phi(\gamma)$. The line *AB* lies along the real axis.

ACKNOWLEDGMENT

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APPENDIX

Reduction of Eq. (21) requires evaluation of the integral

$$\Phi(\gamma)=\frac{1}{2\gamma}\int_{-\infty}^{\infty} z\,\mathrm{sech}^2 z\int_{-\infty}^{\infty}\tanh u\times\left(\frac{1}{u-z-\gamma}-\frac{1}{u-z+\gamma}\right)dz\,du\ .$$

The poles of $\tanh u$ occur at $u=(n+\frac{1}{2})i\pi$ where n is any integer, and one accordingly performs the integral over u to find

$$\Phi(\gamma)=\frac{\pi i}{2\gamma}\sum_{n=0}^{N}\int_{-\infty}^{\infty} z\,\mathrm{sech}^2 z\left(\frac{1}{(n+\frac{1}{2})i\pi-z-\gamma}+\frac{1}{(n+\frac{1}{2})i\pi+z+\gamma}-\frac{1}{(n+\frac{1}{2})i\pi-z+\gamma}-\frac{1}{(n+\frac{1}{2})i\pi+z-\gamma}\right)dz\ .$$

The upper limit N of the summation is a large integer that will tend to infinity at a later stage of the calculation.

The poles of the integrand in the z plane are at $z=(m+\frac{1}{2})i\pi$, with m any integer, and at $z=\pm\gamma \pm(n+\frac{1}{2})i\pi$. For simplicity, the contour may be closed in the half plane that does not contain the isolated pole, as illustrated in Fig. 7 for the term

$$\int_{-\infty}^{\infty} \frac{z\,\mathrm{sech}^2 z}{(n+\frac{1}{2})i\pi - z - \gamma}\, dz\ ,$$

which is the integral along the line AB. Along the line DC the variable z has the value $x-Ni\pi$. Only the component odd in γ survives in the final expression for Φ, and so from the integral along DC we retain only the contribution

$$\frac{-2Ni\pi\gamma}{[(N+n+\frac{1}{2})i\pi]^2}\ .$$

When the residues at $(m+\frac{1}{2})i\pi$ are included, one finds

$$\Phi(\gamma)=\sum_{n=0}^{N}\left(-\frac{4N}{(N+n+\frac{1}{2})^2}+\sum_{m=0}^{N}\frac{4\pi^2}{(m+n+1)^2\pi^2+\gamma^2} - \sum_{m=0}^{N}\frac{8\pi^4(m+\frac{1}{2})(m+n+1)}{[(m+n+1)^2\pi^2+\gamma^2]^2}\right)\ .$$

In the limit $N\to\infty$ this reduces to

$$\Phi(\gamma)=-2+4\sum_{u=1}^{\infty}\left(\frac{(\gamma/\pi)^2 u}{[(\gamma/\pi)^2+u^2]^2}\right)\ ,$$

which at high temperatures may be replaced by the power series expansion for small γ

$$\Phi(\gamma)=-2+4(\gamma/\pi)^2\zeta(3)-8(\gamma/\pi)^4\zeta(5)+\cdots\ ,$$

where $\zeta(n)$ is the Riemann zeta function. At low temperatures one requires an approximation for $\Phi(\gamma)$ when γ is large, and this may be obtained by use of the Poisson summation formula. One finds

$$\Phi(\gamma)=8\sum_{p=1}^{\infty}\int_0^{\infty}\frac{(\gamma/\pi)^2 x\cos 2\pi p x}{[x^2+(\gamma/\pi)^2]^2}\,dx$$

$$=-\frac{\pi^2}{3\gamma^2}-\frac{\pi^4}{15\gamma^4}-\cdots+R_n(\gamma)\ .$$

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