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Theory of Thermoelectric Power
In Metals and Alloys^{*}

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ABSTRACT

The electron-diffusion thermoelectric power (thermopower) of metals and dilute alloys is investigated over a wide range of temperatures in a simple model of free electrons with scattering characterized by a relaxation time τ . It is found that second-order corrections to the T-matrix for electron scattering involving intermediate virtual phonon states result in strongly energy-dependent corrections to τ , and thus greatly influence the thermopower. The primary results are first, that there exists a contribution to the electron-diffusion thermopower of a metal which has the same magnitude and general temperature-dependence as that due to phonon-drag, and second, that there is a term in the thermopower of an alloy which is strongly dependent upon the type of impurity present, and is important at low temperatures. The significance of these results in interpreting experimental data is discussed.

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I. INTRODUCTION

It is observed experimentally that when a metal, alloy, or semiconductor is subjected to a temperature gradient, there arises within the material an electric field. This field is proportional to the magnitude of the temperature gradient, and the constant of proportionality, which itself may be a function of the mean temperature about which the temperature gradient is established, is known as the absolute thermoelectric power, or thermopower, of the material. Mathematically, one finds a relationship of the form

$$\underline{E} = \underline{\vec{S}}(T) \cdot \nabla T \quad (1-1)$$

In an anisotropic material, the thermopower $\underline{\vec{S}}$ is a tensor quantity, though in most cases we deal with materials of sufficient symmetry that $\underline{\vec{S}}$ can be taken to be of the form $S_{ij} = S\delta_{ij}$. Throughout the remainder of this work, we will make this simplifying assumption.

Theoretically, a few simple arguments suffice to show why a relationship of the form (1-1) ought to exist. When a temperature gradient is established across a material, the electrons on one end are on the average "hotter", or more energetic, than those on the other end. Should the scattering of electrons be energy-dependent then (for example) the "hot" electrons from the hot end, may on the average travel further down the length of the material than the "cold" electrons from the other end, and electrons will diffuse from the hot to the cold end until an excess charge has been built

up which causes an electric field, re-establishing equilibrium and preventing further diffusion. Thermopower which arises in this fashion is known as electron-diffusion thermopower, and depends essentially on the energy derivative of the scattering cross section for electrons at the Fermi level. The scatterers which enter into a calculation of electron-diffusion thermopower are primarily impurities at low temperatures and phonons at high temperatures.

In addition to electron-diffusion thermopower, there is also a contribution due to phonon-drag, and which arises from the net phonon flux which is directed from the hot end of the sample to the cold end. These phonons, crudely speaking, exert a pressure on the electrons and sweep them along from the hot to the cold end.

While it has long been known that electron-diffusion and phonon-drag effects ought to account for the observed thermopowers in various systems, theoretical work has been unable to account unambiguously for experimental results, particularly at low temperatures. This state of affairs arises from the fact that theoretical expressions for S are invariably in the form of a sum of various terms of the same magnitude and differing signs. Thus, the final result is strongly dependent on the model and method of calculation employed. In such a situation, theoretical work has the most hope of being successful when it can point out general trends which ought to occur independent of the exact details of the way in which they are calculated. Accordingly, in the present work we demonstrate

on the basis of simple models certain new effects in electron-diffusion thermopower, and show how the interpretation of experimental data is thereby simplified.

A general expression for the electron-diffusion thermopower of a metal or alloy is¹

$$S = \frac{1}{eT} \frac{\int (\epsilon - \zeta) \sigma(\epsilon) \frac{\partial f}{\partial \epsilon} d\epsilon}{\int \sigma(\epsilon) \frac{\partial f}{\partial \epsilon} d\epsilon} \quad (1-2)$$

where e is the electronic charge (a negative quantity), ζ the Fermi level, $f(\epsilon)$ the Fermi function, and $\sigma(\epsilon)$ the conductivity which the metal would have (at $T=0$) if the Fermi level were at ϵ . Equation (1-2) can be written in the form

$$S = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \left[\frac{\partial \ln \sigma(\epsilon)}{\partial \epsilon} \right]_{\epsilon=\zeta} \quad (1-2a)$$

if corrections of order $(k_B T/\zeta)^2$ are neglected. It is Eq. (1-2a) that is the most common expression for the electron-diffusion thermopower, and the one that we use in the present work. It is often convenient to express Eq. (1-2a) in terms of a dimensionless thermopower parameter ξ , given by

$$\xi = \left[\frac{\partial \ln \sigma(\epsilon)}{\partial \ln \epsilon} \right]_{\epsilon=\zeta} \quad (1-3)$$

and in terms of which (1-2a) is written as

$$S = S_0 \xi, \quad S_0 \equiv \frac{\pi^2 k^2 T}{3 e \zeta}.$$

If we assume that the electron scattering can be characterized in terms of a relaxation time $\tau(\epsilon)$, a general expression for $\sigma(\epsilon)$ is²

$$\sigma(\epsilon) = \frac{2e^2}{3\Omega} v^2(\epsilon) \tau(\epsilon) D(\epsilon),$$

where Ω is the volume of the sample and $D(\epsilon)$ the energy density of states for electrons of one spin orientation. In a system of "free" electrons, for which $\epsilon = k^2$, it follows that ξ can be written as

$$\xi = \frac{3}{2} - \left[\frac{\partial \ln(1/\tau)}{\partial \ln \epsilon} \right]_{\zeta}. \quad (1-4)$$

We have written Eq. (1-4) in terms of the inverse relaxation time $1/\tau$, because it is this quantity that is proportional to the total electron scattering cross section, and is most naturally computed theoretically. In our subsequent work, we generally treat the electrons as free and study the energy-dependence of $1/\tau(\epsilon)$, using Eq. (1-4) to obtain our final answer for ξ .

The effects that we consider here arise in second-order corrections to the T-matrix for electron scattering. We find a class of second-order terms that add coherently to the first order terms, and are proportional to a Fermi function, thus being strongly energy-dependent near $\epsilon = \zeta$, and providing an important contribution

to Eq. (1-4). The motivation for this investigation can be found in the Kondo effect,³ in which internal degrees of freedom in the electron scatterers destroy the cancellation which normally occurs between the occupancy factors f and $(1-f)$ for second-order scattering processes in which an intermediate electron and hole respectively participate. In a similar way, we find electron scattering processes involving virtual intermediate phonons to result in a strongly energy-dependent contribution.

In preliminary work⁴ we applied this concept of virtual recoil to the low-temperature thermopower of dilute alloys. In the present work we apply these ideas to both pure metals (Chapter II) and dilute alloys (Chapter III), treating finite as well as vanishingly small temperatures. Two significant results emerge from this study. First, we find a contribution to the electron-diffusion thermopower which has the same magnitude and temperature dependence as that due to phonon drag. Second, we find a contribution to the thermopower of a dilute alloy which is proportional to the difference in the potentials of the solute and solvent ions, and which can dominate observed thermopowers at low temperatures. The significance of these results in explaining various experimental data is discussed in Chapter IV, and a discussion and summary are given in Chapter V.

II. Thermopower in Pure Metals

To illustrate the way in which virtual phonon and multi-phonon processes can influence the thermopower of a metal, we begin by studying these effects in a "pure metal", which we take to be a Bravais lattice of identical ions, each of which presents a potential $V(\underline{r})$ to a conduction electron. Of course, in any real metal one has also effects due to various impurities, but we defer a consideration of these to a later chapter. If we assume a rigid-ion model, the potential seen by a conduction electron is given by

$$V(\underline{r}) = \sum_{\underline{l}} V(\underline{r} - \underline{l} - \underline{\gamma}_{\underline{l}}) \quad (2-1)$$

where $\{\underline{l}\}$ are the vectors to the lattice sites, and $\underline{\gamma}_{\underline{l}}$ is the displacement of the ion at $\underline{l}$ from its equilibrium position due to thermal vibrations. To second order in $\underline{\gamma}_{\underline{l}}$, Eq. (2-1) may be expressed in the notation of second quantization as²

$$\begin{aligned} V(\underline{r}) = & \sum_{\underline{R}, \underline{R}'} c_{\underline{R}'}^{\dagger} c_{\underline{R}} V_{\underline{R}'\underline{R}} N \left[\Delta(\underline{R} - \underline{R}') + i \sum_{\underline{q}, \underline{s}} (\underline{R} - \underline{R}') \cdot \hat{\underline{s}} g(\underline{q}, \underline{s}) \right. \\ & \times B_{\underline{q}, \underline{s}} \Delta(\underline{R} - \underline{R}' + \underline{q}) - \frac{1}{2} \sum_{\substack{\underline{q}, \underline{s} \\ \underline{q}', \underline{s}'}} (\underline{R} - \underline{R}') \cdot \hat{\underline{s}} (\underline{R} - \underline{R}') \cdot \underline{s}' g(\underline{q}, \underline{s}) g(\underline{q}', \underline{s}') B_{\underline{q}, \underline{s}} B_{\underline{q}', \underline{s}'} \\ & \left. \times \Delta(\underline{R} - \underline{R}' + \underline{q} + \underline{q}') \right] \quad (2-2) \end{aligned}$$

where $V_{\underline{k}', \underline{k}} = \frac{1}{\Omega} \int e^{i(\underline{k} - \underline{k}') \cdot \underline{r}} V(\underline{r}) d\underline{r}$, Ω being the volume of the sample,

$c_{\underline{k}}^{\dagger}, c_{\underline{k}}$ are creation and annihilation operators for free-electron states of wave vector $\underline{k}$,

$$B_{qs} = a_{-qs}^{\dagger} + a_{qs}; \quad a_{qs}^{\dagger}, a_{qs} \text{ being creation and annihilation operators for phonon modes of wave vector } q \text{ and polarization } \hat{s},$$

$$g(q,s) = (Q/2MN\omega_{q,s})^{1/2}.$$

N = Number of ions in the sample, and

$$\Delta(k) = \sum_g \delta(k-g), \quad g \text{ a vector of the reciprocal lattice.}$$

As we have seen in Chapter I, it is the energy derivative of the probability for an electron in a state k at the Fermi level to be scattered that is influential in determining the thermopower of a metal, and thus we are interested in computing the T-matrix for scattering due to the potential (2-2) to second order:

$$T = V + V(\epsilon - H_0)^{-1} V \quad (2-3)$$

The various terms which appear in square brackets in Eq. (2-2) correspond to the scattering of an electron with emission or absorption of zero, one, or two phonons. Because of the wavevector conservation which arises from the invariance of the potential under translations $\underline{L}$, the case of no-phonon scattering need not be considered. Thus, we see that diagrammatically Eq. (2-3) may be represented as illustrated in Fig. 1. (see page 8).

The first-order term denoted (1a) is the one usually considered in the theory of electron-phonon scattering² and is clearly larger than any of the other terms, since by Migdal's Theorem⁵ higher order terms in the electron-phonon interaction must be smaller than the first order term by powers of (m/M) , the ratio of electronic to ionic masses. However, it must be recalled that

Fig. 1 - Diagrammatic Representation of T-matrix

it is not the relative magnitude of these terms that is important in determining the thermopower, but rather the relative magnitude of their energy derivatives at the Fermi level. Thus, while terms of type (1a) may in themselves be sufficient to account for observed conductivities, higher order terms may well be necessary to account adequately for the thermopower.

The problem that arises, then, is to determine which second order terms will have a strong energy dependence, and it is natural to seek these among those terms that add coherently with the first-order term, in that they connect the same initial and final states. Such terms can be constructed from the totality of terms represented by the diagrams labeled (2b) and (2c) in Fig. 1, provided that we have a virtual intermediate phonon state - that is, one of the phonons absorbed or emitted must be subsequently emitted or absorbed. In Fig. 2, then, we show diagrammatically those terms which on physical grounds may be expected to provide important thermopower contributions.

Fig. 2 - First and Second-Order Terms Contributing Coherently to Electron-Phonon Scattering

The second-order terms which appear in Fig. 2 are somewhat symbolic in nature, in that both the intermediate electron and phonon states may be either "particles" or "holes". That is, the sequence of electron operators for scattering from $\underline{k}$ to $\underline{k}'$ may be either $c_{\underline{k}'}^\dagger c_{\underline{k}''}^\dagger c_{\underline{k}''} c_{\underline{k}}$ or $c_{\underline{k}''}^\dagger c_{\underline{k}'}^\dagger c_{\underline{k}''} c_{\underline{k}}$, where $\underline{k}''$ is some intermediate state while the sequence of phonon operators may be $B_{\underline{q}s} a_{\underline{q}'s'}^\dagger a_{\underline{q}'s'}$, $B_{\underline{q}s} a_{\underline{q}'s'} a_{\underline{q}'s'}^\dagger$, $a_{\underline{q}'s'}^\dagger a_{\underline{q}'s'} B_{\underline{q}s}$, or $a_{\underline{q}'s'} a_{\underline{q}'s'}^\dagger B_{\underline{q}s}$, ($\underline{q}'s'$) being an intermediate phonon state. In each of these cases, the "energy denominator", $(\epsilon - H_0)^{-1}$, appearing in Eq. (2-3) will be different. Furthermore, the various possibilities will depend in different ways on the occupancies $f_{\underline{k}''}$ and $n_{\underline{q}s}$ of the intermediate states. This raises the possibility that certain terms in the T-matrix represented by Fig. 2 may be proportional to the Fermi function, and thus strongly energy-dependent at the Fermi level. While it is well known³ that in the case of purely elastic electron scattering the "hole" and "particle" processes contribute equally and effects due to the occupancy of the intermediate state cancel, we shall see that the extra degree of freedom introduced by the intermediate phonon states results in this no longer being the case, and that strongly energy-dependent second-order terms do,

in fact, occur. It is these terms that provide the new and important thermopower contributions discussed in this work.

In an Appendix, we show that the contributions to T illustrated in Fig. 2 can be written in the form

$$T = T_1^{(\pm)} + T_2^{(\pm)}, \text{ where} \quad (2-4)$$

$$T_{1k\bar{k}}^{(\pm)} = -iNV_q \sum_s g(q,s) \underline{q} \cdot \hat{s} \left(\frac{1}{2} \text{ctnh}(\hbar\omega_{qs}/2k_B T) \mp \frac{1}{2} \right)^{\frac{1}{2}} \quad (2-4a)$$

and

$$T_{2k\bar{k}}^{(\pm)} = -2iN^2 \sum_{q's's'} g^2(q's') g(q,s) V_{q'} V_{\underline{q}-\underline{q}'} \underline{q}' \cdot \hat{s}' (\underline{q}-\underline{q}') \cdot \hat{s} \\ \times (\underline{q}-\underline{q}') \cdot \hat{s} \frac{2\hbar\omega_{q's'} f_{Bq'}}{(E_k - E_{k-q'})^2 - (\hbar\omega_{q's'})^2} \left(\frac{1}{2} \text{ctnh}(\hbar\omega_{qs}/2k_B T) \mp \frac{1}{2} \right)^{\frac{1}{2}} \quad (2-4b)$$

In deriving Eqs. (2-4), we have retained only those second-order terms that are proportional to a Fermi function, and have taken $\underline{k}' = (\underline{k} + \underline{q})$ (via an intermediate state $\underline{k}'' = \underline{k} + \underline{q}'$ in the second-order case). We have also assumed that the Fourier transform of the potential, $V_{\underline{k}',\underline{k}}$, is a function only of the momentum transfer $|\underline{k}' - \underline{k}|$, and that the occupancy factor for phonons is given by the Bose function, or that

$$n_{qs} = \frac{1}{2} \left\{ \text{ctnh}(\hbar\omega_{qs}/2k_B T) - 1 \right\}$$

We thus take the phonon system to be in equilibrium, and are there-

fore dealing only with the electron-diffusion contribution to the thermopower. The (upper/lower) signs in Eqs. (2-4) refer to processes in which a phonon of wave vector $\pm \underline{q}$ is (absorbed/emitted).

From Eqs. (2-4), we find that to third order in V the intrinsic probability for electrons to be scattered from $\underline{k}$ to $\underline{k}'$ is given by

$$\begin{aligned} Q^{(\pm)}(\underline{k}, \underline{k}') &= \frac{2\pi}{\hbar} |T_{\underline{k}'\underline{k}}^{(\pm)}|^2 \delta(\epsilon_{\underline{k}} - \epsilon_{\underline{k}'} \pm \hbar\omega_{\underline{q}}) \\ &= \frac{2\pi}{\hbar} \left[|T_{1\underline{k}'\underline{k}}^{(\pm)}|^2 + 2 \operatorname{Re} T_{1\underline{k}'\underline{k}}^{(\pm)*} T_{2\underline{k}'\underline{k}}^{(\pm)} \right] \delta(\epsilon_{\underline{k}} - \epsilon_{\underline{k}'} \pm \hbar\omega_{\underline{q}}). \end{aligned}$$

It is convenient to write this transition probability in the form

$$Q^{(\pm)}(\underline{k}, \underline{k}') = Q^0(\underline{k}, \underline{k}') \frac{1}{2} (\coth(\hbar\omega_{\underline{q}}/2k_B T) \mp 1) \delta(\epsilon_{\underline{k}} - \epsilon_{\underline{k}'} \pm \hbar\omega_{\underline{q}}) \quad (2-5)$$

where

$$Q^0(\underline{k}, \underline{k}') = Q_1(\underline{k}, \underline{k}') + Q_2(\underline{k}, \underline{k}') ; \quad (2-6)$$

$$Q_1(\underline{k}, \underline{k}') = \frac{2\pi}{\hbar} N^2 V_{\underline{q}}^2 g^2(\underline{q}) q^2, \text{ and} \quad (2-6a)$$

$$\begin{aligned} Q_2(\underline{k}, \underline{k}') &= \frac{2\pi}{\hbar} 4N^3 g^2(\underline{q}) V_{\underline{q}} \sum_{\underline{q}'} g^2(\underline{q}') V_{\underline{q}'} V_{\underline{q}-\underline{q}'} \\ &\quad \times \frac{q' \cdot (\underline{q} - \underline{q}') q \cdot (\underline{q} - \underline{q}')}{(\epsilon_{\underline{k}} - \epsilon_{\underline{k}+\underline{q}})^2 - (\hbar\omega_{\underline{q}})^2} \quad (2-6b) \end{aligned}$$

In deriving Eqs. (2-6), we have assumed the phonon frequencies to

be independent of polarization, and have summed over the three polarization vectors $\hat{s}$. This simplifying assumption, while not directly applicable to any real metal, is justified within the framework of a calculation such as this which seeks only to show that certain effects exist and to estimate the order of magnitude of these effects.

We are now in a position to use Eq. (2-5) to compute the relaxation time for electrons of wave vector $\underline{k}$, and to determine the energy dependence of the additional term represented by Eq. (2-6b). We do this by finding an approximate solution to the linearized Boltzmann equation, which can be written as⁶

$$\underline{v}_k f_k (1 - f_k) = \sum_{k'} Q(\underline{k}, \underline{k}') f_{k'} (1 - f_{k'}) (\underline{\Lambda}_k - \underline{\Lambda}_{k'}) \quad (2-7)$$

where $\underline{\Lambda}_k$ is the vector mean free path for electrons of wave vector $\underline{k}$. The important point to be considered in determining the relaxation time from Eq. (2-7) is that because of the inelastic nature of the scattering $f_{k'} \neq f_k$, and the difference between the two, at the Fermi level, can be significant. If we assume that the electron group velocity $\underline{v}_k$ and $\underline{\Lambda}_k$ are in the direction $\hat{k}$ of the electron wave vector, and are functions only of the electron energy ϵ_k , then (7) may be transformed into a scalar equation for the inverse relaxation time $1/\tau_k \equiv v_k/\Lambda_k$:

$$\frac{1}{\tau_k} = \sum_{k'} Q(\underline{k}, \underline{k}') \left(\frac{1 - f_{k'}}{1 - f_k} \right) \left(1 - \frac{\Lambda_{k'}}{\Lambda_k} \cos \theta_{kk'} \right) \quad (2-8)$$

By making use of the fact that the Fermi function $f(\epsilon)$ can be written as

$$f(\epsilon) = \frac{1}{2} \left[1 - \tanh \left(\frac{\epsilon - \epsilon_F}{2k_B T} \right) \right],$$

and that $\epsilon_{k'} = \epsilon_k \pm \hbar\omega_q$, we can write

$$f(\epsilon_{k'}) = f(\epsilon_k) + \mathcal{Z}(\epsilon_k, q), \quad \text{where} \quad (2-9)$$

$$\begin{aligned} \mathcal{Z}(\epsilon, q) = & \mp \frac{1}{2} \tanh \left(\frac{\hbar\omega_q}{2k_B T} \right) \pm \frac{\tanh^2 \left(\frac{\epsilon - \epsilon_F}{2k_B T} \right) \tanh \left(\frac{\hbar\omega_q}{2k_B T} \right)}{1 \pm \tanh \left(\frac{\epsilon - \epsilon_F}{2k_B T} \right) \tanh \left(\frac{\hbar\omega_q}{2k_B T} \right)} \\ & + \frac{1}{2} \frac{\tanh \left(\frac{\epsilon - \epsilon_F}{2k_B T} \right) \tanh^2 \left(\frac{\hbar\omega_q}{2k_B T} \right)}{1 \pm \tanh \left(\frac{\epsilon - \epsilon_F}{2k_B T} \right) \tanh \left(\frac{\hbar\omega_q}{2k_B T} \right)} \end{aligned} \quad (2-9a)$$

Thus, if we assume Λ_k to be a slowly varying function of energy, Eq. (2-8) can be written as

$$\frac{1}{\tau_k} = \sum_{k'} Q(k, k') \left(1 - \frac{\mathcal{Z}(\epsilon_k, q)}{1 - f_k} \right) (1 - \cos \theta_{kk'}) \quad (2-10)$$

We use Eqs. (2-5, 6, 10) to compute the inverse relaxation time and its energy derivative at the Fermi level. First, we consider the inverse relaxation time at the Fermi level τ . From Eq. (2-9a), we see that $\mathcal{Z}(\tau) = \mp \frac{1}{2} \tanh(\hbar\omega_q/2k_B T)$, and since $f(\tau) = \frac{1}{2}$, it follows from Eqs. (2-10) and (2-5) that

$$\begin{aligned}
 \frac{1}{\tau(\xi)} &= \sum_{\underline{k}'} Q^0(\underline{k}, \underline{k}') \frac{1}{2} (\coth(\hbar\omega_q/2k_B T) \mp 1) (1 \pm \tanh(\hbar\omega_q/2k_B T)) \\
 &\quad \times (1 - \cos \theta_{\underline{k}\underline{k}'}) \delta(\epsilon_{\underline{k}} - \epsilon_{\underline{k}'} \pm \hbar\omega_q) \\
 &= \sum_{\underline{k}'} Q^0(\underline{k}, \underline{k}') \operatorname{csch}(\hbar\omega_q/k_B T) (1 - \cos \theta_{\underline{k}\underline{k}'}) \\
 &\quad \times \delta(\epsilon_{\underline{k}} - \epsilon_{\underline{k}'} \pm \hbar\omega_q) \quad (2-11)
 \end{aligned}$$

In evaluating Eq. (2-11), we recognize that $Q_1(\underline{k}, \underline{k}')$ will be an adequate approximation to $Q^0(\underline{k}, \underline{k}')$, while when at a later stage we desire to evaluate $\partial(1/\tau)/\partial\epsilon$ both $Q_1(\underline{k}, \underline{k}')$ and $Q_2(\underline{k}, \underline{k}')$ must be considered. Thus, from Eqs. (2-6a) and (2-11) we have

$$\begin{aligned}
 \frac{1}{\tau(\xi)} &= \frac{2\pi}{\hbar} N^2 \sum_{\underline{q}} V_{\underline{q}}^2 \frac{\hbar}{2MN\omega_{\underline{q}}} q^2 \left(1 - \frac{\underline{k}}{|\underline{k}+\underline{q}|} - \frac{\underline{k}-\underline{q}}{k|\underline{k}+\underline{q}|} \right) \\
 &\quad \times \operatorname{csch}(\hbar\omega_q/k_B T) \delta(\epsilon_{\underline{k}} - \epsilon_{\underline{k}'} \pm \hbar\omega_q) \quad (2-12)
 \end{aligned}$$

where it is now understood that $|\underline{k}| = k_F$, the Fermi radius. An exact solution of Eq. (2-12) would require a knowledge of the way in which $V_{\underline{q}}$ behaves as a function of q , and is complicated somewhat by the $\hbar\omega_{\underline{q}}$ which appears in the delta function. However, we note that corrections to $|\underline{k}+\underline{q}|/k = 1$ are of order $\hbar\omega_q/k$, and are thus 10^{-2} or less. Consequently, all of the important effects due to the inelastic nature of the scattering are contained in the $\operatorname{csch}(\hbar\omega_q/k_B T)$ term, so that to a good approxima-

tion we have

$$\frac{1}{\tau(\xi)} = \frac{4\pi}{\hbar} N^2 \sum_q V_q^2 \frac{\hbar}{2MN\omega_q} q^2 \left(-\frac{\mathbf{k} \cdot \mathbf{q}}{k^2} \right) \times \text{csch}(\hbar\omega_q/k_B T) \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}}) \quad (2-13)$$

where a factor of 2 has come in from the summation of those processes in which phonons are absorbed and emitted, and which contribute equally in this approximation. Equation (2-13) is easily evaluated if we adopt a simple model in which V_q is some constant value V , and the phonon spectrum is a simple Debye spectrum with a cut-off wave vector $q_d = k_B \theta / \hbar s$, s being the speed of sound. Performing the summation on q by an integral over q -space, we find directly:

$$\frac{1}{\tau(\xi)} = \frac{3}{2} \frac{2\pi}{\hbar} \frac{(NV)^2}{k_B \theta} \left(\frac{m}{M} \right) \frac{N}{N'} \left(\frac{T}{\theta} \right)^5 G_4(\theta/T) \quad (2-14)$$

where N is the number of ions, N' the number of electrons, and

$$G_n(x) \equiv \int_0^x \xi^n \text{csch} \xi \, d\xi.$$

We note that as $T \rightarrow \infty$, $G_4(\theta/T) \rightarrow \frac{1}{4}(\theta/T)^4$, while as $T \rightarrow 0$, $G_4(\theta/T)$ approaches a constant value. Thus, in Eq. (2-14) we recognize the usual result¹ for the electron-phonon resistivity of a T and T^5 behavior in the high- and low-temperature limits respectively. At

this point, it should be mentioned that by cutting the summation over q off at q_d , we are neglecting electron-phonon Umklapp processes. To include these in any reasonable way would require taking into account the specific crystal structure of the metal under consideration and the Bloch nature of the electron wave functions, and would increase considerably the complexity of the calculation without producing qualitative changes in our final results. Thus, in the spirit of the approximations already made, we defer a consideration of Umklapp processes to a more detailed investigation to be undertaken in the future.

Next, we consider the somewhat more difficult question of the energy-derivative of $1/\tau$ at the Fermi level. From Eq. (2-10), we have

$$\begin{aligned} \frac{\partial}{\partial \epsilon_k} \frac{1}{\tau_k} = & \sum_{k'} \left(\frac{\partial}{\partial \epsilon_k} Q(k, k') \right) \left(1 - \frac{Z(\epsilon_k, q)}{1 - f_k} \right) (1 - \cos \theta_{kk'}) \\ & - \sum_{k'} Q(k, k') \frac{\partial}{\partial \epsilon_k} \left(\frac{Z(\epsilon_k, q)}{1 - f_k} \right) (1 - \cos \theta_{kk'}) \end{aligned} \quad (2-15)$$

From Eq. (2-9a), it follows that

$$\frac{\partial}{\partial \epsilon_k} \left(\frac{Z(\epsilon_k, q)}{1 - f_k} \right) = \frac{1}{2k_B T} \tanh \left(\frac{\hbar \omega_q}{2k_B T} \right) \left[\tanh \left(\frac{\hbar \omega_q}{2k_B T} \right) \pm 1 \right],$$

so that at $\epsilon_k = \epsilon_F$, Eq. (2-15) becomes

$$\begin{aligned}
\frac{\partial}{\partial \epsilon_{\mathbf{k}}} \left(\frac{1}{\tau_{\mathbf{k}}} \right) &= \sum_{\mathbf{k}'} \frac{\partial}{\partial \epsilon_{\mathbf{k}}} \left[Q^0(\mathbf{k}, \mathbf{k}') \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'} \pm \hbar \omega_q) \right] (1 - \cos \theta_{\mathbf{k}\mathbf{k}'}) \\
&\quad \times \frac{1}{2} \left(\coth(\hbar \omega_q / 2k_B T) \mp 1 \right) \left(1 \pm \tanh(\hbar \omega_q / 2k_B T) \right) \\
&\quad - \frac{1}{2k_B T} \sum_{\mathbf{k}'} Q^0(\mathbf{k}, \mathbf{k}') \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'} \pm \hbar \omega_q) (1 - \cos \theta_{\mathbf{k}\mathbf{k}'}) \tanh\left(\frac{\hbar \omega_q}{2k_B T}\right) \\
&\quad \times \frac{1}{2} \left(\coth\left(\frac{\hbar \omega_q}{2k_B T}\right) \mp 1 \right) \left(\tanh\left(\frac{\hbar \omega_q}{2k_B T}\right) \pm 1 \right) \\
&= \sum_{\mathbf{k}'} \frac{\partial}{\partial \epsilon_{\mathbf{k}}} \left[Q^0(\mathbf{k}, \mathbf{k}') \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'} \pm \hbar \omega_q) \right] (1 - \cos \theta_{\mathbf{k}\mathbf{k}'}) \operatorname{csch}\left(\frac{\hbar \omega_q}{k_B T}\right) \\
&\quad \mp \frac{1}{2k_B T} \sum_{\mathbf{k}'} Q^0(\mathbf{k}, \mathbf{k}') \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'} \pm \hbar \omega_q) \\
&\quad \times (1 - \cos \theta_{\mathbf{k}\mathbf{k}'}) \operatorname{sech}^2\left(\frac{\hbar \omega_q}{2k_B T}\right) \quad (2-16)
\end{aligned}$$

We see from Eq. (2-16) that the term due to the variation of $\frac{1}{\tau_{\mathbf{k}}}$ with energy is of opposite sign for processes in which phonons are absorbed or emitted and will tend to cancel out. The cancellation is, in fact, easily seen to be exact to order $\hbar \omega_q / \epsilon$, and accordingly we neglect this term and evaluate

$$\begin{aligned}
\frac{\partial}{\partial \epsilon_{\mathbf{k}}} \left(\frac{1}{\tau_{\mathbf{k}}} \right) &= \sum_{\mathbf{k}'} \frac{\partial}{\partial \epsilon_{\mathbf{k}}} \left[Q^0(\mathbf{k}, \mathbf{k}') \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'} \pm \hbar \omega_q) \right] \\
&\quad \times (1 - \cos \theta_{\mathbf{k}\mathbf{k}'}) \operatorname{csch}(\hbar \omega_q / k_B T) \quad (2-16a)
\end{aligned}$$

Recalling that $Q^0(\mathbf{k}, \mathbf{k}') = Q_1(\mathbf{k}, \mathbf{k}') + Q_2(\mathbf{k}, \mathbf{k}')$, we see that

Eq. (2-16a) contains two terms. The first is easily evaluated in the same way as Eq. (2-13), and we obtain the result

$$\sum_{\mathbf{k}'} \frac{\partial}{\partial \epsilon_{\mathbf{k}}} \left[Q_1(\mathbf{k}, \mathbf{k}') \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'} \pm \hbar \omega_{\mathbf{q}}) \right]_S (1 - \cos \theta_{\mathbf{k}\mathbf{k}'}) \operatorname{csch}(\hbar \omega_{\mathbf{q}} / k_B T)$$

$$= \frac{3}{2} \frac{2\pi}{k} \frac{(NV)^2}{k_B \Theta} \left(\frac{m}{M} \right) \frac{N}{N'} \left(\frac{T}{\Theta} \right)^5 G_4 \left(\frac{\Theta}{T} \right) \frac{1}{3} \left[2 \frac{\partial \ln V}{\partial \ln \epsilon} - \frac{3}{2} \right] \quad (2-17)$$

We must consider the second term in greater detail however. It is this term that has not previously been considered in theories of thermopower, and which leads to new and interesting results. From Eq. (2-6b), we recognize immediately that the only factor in $Q_2(\mathbf{k}, \mathbf{k}')$ which is sufficiently energy-dependent to make a contribution to Eq. (2-16a) is the factor $f_{\mathbf{k}+\mathbf{q}'} \left[(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}'})^2 - (\hbar \omega_{\mathbf{q}'})^2 \right]^{-1}$. Accordingly, we must evaluate

$$\left. \frac{\partial}{\partial \epsilon_{\mathbf{k}}} \frac{1}{\tau_{\mathbf{k}}^{(2)}} \right]_S = \frac{2\pi}{k} (NV)^3 \frac{4k^2}{MN} \frac{\partial}{\partial \epsilon_{\mathbf{k}}} \sum_{\mathbf{q}'} \frac{f_{\mathbf{k}+\mathbf{q}'}}{(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}'})^2 - (\hbar \omega_{\mathbf{q}'})^2}$$

$$\times \sum_{\mathbf{q}'} \frac{k}{2MN\omega_{\mathbf{q}'}} \operatorname{csch} \left(\frac{\hbar \omega_{\mathbf{q}'}}{k_B T} \right) \mathbf{q}' \cdot (\mathbf{q} - \mathbf{q}') \mathbf{q} \cdot (\mathbf{q} - \mathbf{q}')$$

$$\times \left(-\frac{\mathbf{k} \cdot \mathbf{q}'}{k^2} \right) \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}) \quad (2-18)$$

The same assumptions have been made in writing down Eq. (2-18) as were made in evaluating Eq. (2-13). Now if we take $\mathbf{k}$ as the direction of the polar axis, and (θ, ϕ) and (θ', ϕ') are the angles

of q and q' respectively towards this axis, the summation on q is easily performed as an integral over q -space, and we are left with:

$$\begin{aligned} & \sum_q \frac{\hbar}{2mN\omega_q} \operatorname{csch}\left(\frac{\hbar\omega_q}{k_B T}\right) q'_x(q-q'_x) q_y(q-q'_y) \left(-\frac{\hbar \cdot q}{R^2}\right) \delta(\epsilon_R - \epsilon_{|R+q|}) \\ &= -\frac{3}{8} \frac{m}{\hbar} \frac{1}{k_B T} \frac{q_d^3}{R^3} \left(\frac{T}{\Theta}\right)^7 \left\{ \eta^2 \left[\frac{3}{8} \frac{q^2}{R^2} G_6\left(\frac{\Theta}{T}\right) - \frac{1}{2} \frac{q^2}{q_d^2} \left(\frac{\Theta}{T}\right)^2 G_4\left(\frac{\Theta}{T}\right) \right] \right. \\ & \quad + \eta \left[\frac{1}{2} \frac{q'}{R} G_6\left(\frac{\Theta}{T}\right) + \frac{1}{2} \frac{q'^3}{R q_d^2} \left(\frac{\Theta}{T}\right)^2 G_4\left(\frac{\Theta}{T}\right) \right] \\ & \quad \left. + \left[-\frac{1}{8} \frac{q'^2}{R^2} G_6\left(\frac{\Theta}{T}\right) + \frac{3}{2} \frac{q'^2}{q_d^2} \left(\frac{\Theta}{T}\right)^2 G_4\left(\frac{\Theta}{T}\right) \right] \right\} \end{aligned} \quad (2-19)$$

where $n = \cos\theta'$, and the $G_n(\Theta/T)$ are as previously defined. Equation (2-19) must now be substituted into Eq. (2-18), and the summation over q' performed. We note that all of the summations to be performed are of the form

$$\begin{aligned} S_{nm} &= \frac{\partial}{\partial \epsilon_R} \sum_{q'} \frac{q'^n \eta^m f_{\underline{k}+\underline{q}'}}{(\epsilon_R - \epsilon_{\underline{k}+\underline{q}'})^2 - (\hbar\omega_{q'})^2} \\ &= \frac{\Omega}{8\pi^3} \int_0^{q_d} q'^{n+2} dq' \\ & \quad \times \frac{\partial}{\partial \epsilon_R} \int_{-1}^1 d\eta \frac{\eta^m f\left(\epsilon_R + \frac{\hbar^2}{2m} (q'^2 + 2kq'\eta)\right)}{\left[\frac{\hbar^2}{2m} (q'^2 + 2kq'\eta)\right]^2 - (\hbar\omega_{q'})^2} \end{aligned} \quad (2-20)$$

In performing integrals of type (2-20), it is convenient to make a change of variables in the integration over η , and define $\Delta = \hbar^2(q'^2 + 2kq'\eta)/2m$. Then Eq. (2-20) reduces to the form

$$S_{nm} = \frac{\Omega}{8\pi^3} \frac{2\pi m}{k^2 k} \int_0^{q_d} q'^{n+1} dq' \times \frac{\partial}{\partial \epsilon_k} \int_{\Delta_-}^{\Delta_+} d\Delta \frac{\left(\frac{m}{k^2 k q'} \Delta - \frac{q'}{2k} \right) f(\epsilon_k + \Delta)}{\Delta^2 - (k\omega_{q'})^2} \quad (2-20a)$$

where $\Delta_{\pm} = \pi^2(q'^2 \pm 2kq')/2m$. Next, we take the energy derivative inside the integral over Δ . Three terms arise, one due to the energy dependence of the integrand, and two due to the energy dependence of $\Delta_{\pm}$. These latter terms are easily shown to be smaller than the former by a factor of order $(k_B\theta/\zeta)^2$, and may thus be ignored. Consequently, ignoring the weak energy dependence of the factor $(m\Delta/k^2 k q' - q'/2k)^m$, we have

$$S_{nm} = \frac{\Omega}{4\pi^2} \frac{m}{k^2 k} \int_0^{q_d} q'^{n+1} dq' \int_{\Delta_-}^{\Delta_+} d\Delta \left(\frac{m}{k^2 k q'} \Delta - \frac{q'}{2k} \right)^m \times \frac{\partial f(\epsilon_k + \Delta)/\partial \epsilon_k}{\Delta^2 - (k\omega_{q'})^2} \quad (2-20b)$$

Now

$$\left. \frac{\partial f(\epsilon_k + \Delta)}{\partial \epsilon_k} \right|_{\zeta} = - \frac{1}{4k_B T} \operatorname{sech}^2(\Delta/2k_B T),$$

and is sufficiently great as to cause Eq. (2-18) to be of the same order of magnitude as Eq. (2-17), and to provide a new and important thermopower contribution. However, the factor $\operatorname{sech}^2(\Delta/2k_B T)$ poses certain computational difficulties in Eq. (2-20b) which, in the light of approximations already made, do not warrant the effort necessary to overcome them. Accordingly, in evaluating Eq. (2-20b) we approximate $\partial f(\epsilon_k + \Delta)/\partial \epsilon_k|_{\zeta}$ by a "square pulse" of height $-\frac{1}{4} k_B T$ and width $4k_B T$, centered about $\Delta=0$. From Fig. 3, it is evident that the error thereby incurred is negligible, as both functions

have the same height and area, and both tend to a delta function as $T \rightarrow 0$.

Fig. 3 - Exact and Approximate Fermi Function Derivatives

Thus, we assume

$$\left[\frac{\partial f(\epsilon + \Delta)}{\partial \epsilon} \right]_{\epsilon} = \begin{cases} 0 & \Delta < -2k_B T \\ -\frac{1}{4} k_B T & -2k_B T < \Delta < 2k_B T \\ 0 & \Delta > 2k_B T \end{cases}$$

With this approximation, Eq. (2-20b) becomes

$$S_{nm} = -\frac{\Omega}{4\pi^2} \frac{m}{\kappa^2 \kappa} \frac{1}{4k_B T} \int_0^{q_d} q'^{n+1} dq' \times \int_{\Delta_-}^{\Delta_+} d\Delta \frac{\left(\frac{m}{\kappa^2 \kappa q'} \Delta - \frac{q'}{2\kappa} \right)^m}{\Delta^2 - (\frac{1}{\kappa} \omega_{q'})^2} \quad (2-20c)$$

where now $\Delta_{\pm} = \pm 2k_B T$, unless $\left| \frac{\kappa^2}{2m} (q'^2 \pm 2\kappa q') \right| < 2k_B T$. In practice, $\Delta_{\pm}$ may be taken as $\pm 2k_B T$ over the whole range of integration of

q' , as corrections for extremely small q' are negligible. Using the fact that

$$\int_{\Delta_-}^{\Delta_+} \frac{\Delta^l d\Delta}{\Delta^2 - (k\omega)^2} = \frac{\Delta^{l-1}}{l-1} \Big|_{\Delta_-}^{\Delta_+} + (k\omega)^2 \int_{\Delta_-}^{\Delta_+} \frac{\Delta^{l-2} d\Delta}{\Delta^2 - (k\omega)^2},$$

we can express all the integrals over Δ in terms of

$$\int_{\Delta_-}^{\Delta_+} \frac{d\Delta}{\Delta^2 - (k\omega)^2} = \frac{1}{k\omega} \log \left| \frac{\Delta_+ - k\omega}{\Delta_+ + k\omega} \right|,$$

due to the fact that for l odd, $\int_{\Delta_-}^{\Delta_+} \frac{\Delta^l d\Delta}{\Delta^2 - (k\omega)^2}$ must vanish.

The subsequent integrals over q' are all of the form⁷

$$\begin{aligned} \int x^n \log(a+bx) dx &= \frac{1}{n+1} \left[x^{n+1} - \frac{(-a)^{n+1}}{b^{n+1}} \right] \log(a+bx) \\ &+ \frac{1}{n+1} \sum_{k=1}^{n+1} \frac{(-1)^k x^{n-k+2} a^{k-1}}{(n-k+2) b^{k-1}}, \end{aligned}$$

so that all integrals of the form (2-20c) can be performed, and

Eq. (2-18) can be evaluated. The final result obtained is

$$\frac{\partial}{\partial \epsilon_R} \left(\frac{1}{T_h^{(2)}} \right)_j = \frac{2\pi}{\kappa} \frac{g}{16} \frac{(NV)^3}{(R_0\theta)^3} \left(\frac{m}{M} \right)^2 \left(\frac{I}{\theta} \right)^6 \left(\frac{2N}{N'} \right)^2 H(\tau/\theta) \quad (2-21)$$

where

$$H\left(\frac{T}{\theta}\right) = \frac{1}{20} \left(\frac{2N}{N'}\right)^{2/3} \left[\frac{3}{8} G_6\left(\frac{\theta}{T}\right) - \frac{3}{2} \left(\frac{N'}{2N}\right)^{2/3} \left(\frac{\theta}{T}\right)^2 G_4\left(\frac{\theta}{T}\right) \right] L_4\left(\frac{2T}{\theta}\right) \\ - \frac{1}{3} \left[\frac{3}{8} G_6\left(\frac{\theta}{T}\right) - \frac{3}{2} \left(\frac{N'}{2N}\right)^{2/3} \left(\frac{\theta}{T}\right)^2 G_4\left(\frac{\theta}{T}\right) \right] L_2\left(\frac{2T}{\theta}\right)$$

(2-22)

and

$$L_n(2T/\theta) = \int_0^1 \xi^n \log \left| \frac{\xi - 2T/\theta}{\xi + 2T/\theta} \right| (n+1) d\xi$$

(2-22a)

and we have neglected terms of order $(k_B \theta / \zeta)^2$ and less. Thus, using Eqs. (2-14, 17, 21) we obtain

$$\left. \frac{\partial \ln(1/\tau)}{\partial \ln \xi} \right|_s = -\frac{3}{2} + 2 \left. \frac{\partial \ln V}{\partial \ln \xi} \right|_s \\ + \frac{3}{2} \frac{(NV)\zeta}{(k_B \theta)^2} \left(\frac{m}{N}\right) \frac{N}{N'} \Phi\left(\frac{T}{\theta}\right)$$

(2-23)

where

$$\Phi(T/\theta) = \frac{(T/\theta) H(T/\theta)}{G_4(\theta/T)}$$

(2-24)

So that for a "pure metal", we see that the thermopower parameter ξ must be of the form

$$\xi = 3 - 2 \left. \frac{\partial \ln V}{\partial \ln \epsilon} \right|_{\xi} - \frac{3}{2} \frac{(NV)}{(k_B \theta)^2} \left(\frac{m}{M} \right) \frac{N}{N'} \phi(T/\theta) . \quad (2-25)$$

Thus we see that ξ should be the constant term predicted by earlier theories⁸ plus a complicated function of temperature, $\phi(T/\theta)$, multiplied by a constant of order unity. We now show the way in which this function varies with temperature. We write out $\phi(T/\theta)$ explicitly as

$$\begin{aligned} \Phi\left(\frac{T}{\theta}\right) = \left(\frac{T}{\theta}\right) & \left\{ \frac{1}{20} \left(\frac{2N}{N'}\right)^{2/3} \left[\frac{3}{8} \frac{G_6(\theta/T)}{G_4(\theta/T)} - \frac{3}{2} \left(\frac{N'}{2N}\right)^{2/3} \left(\frac{\theta}{T}\right)^2 \right] L_4\left(\frac{2T}{\theta}\right) \right. \\ & \left. - \frac{1}{3} \left[\frac{3}{8} \frac{G_6(\theta/T)}{G_4(\theta/T)} - \frac{3}{2} \left(\frac{N'}{2N}\right)^{2/3} \left(\frac{\theta}{T}\right)^2 \right] L_2\left(\frac{2T}{\theta}\right) \right\} \quad (2-26) \end{aligned}$$

$$L_4\left(\frac{2T}{\theta}\right) = \log \left| \frac{2T/\theta - 1}{2T/\theta + 1} \right| - \left(\frac{2T}{\theta}\right)^5 \log \left| 1 - \left(\frac{\theta}{2T}\right)^2 \right| - \frac{1}{2} \left(\frac{2T}{\theta}\right) - \left(\frac{2T}{\theta}\right)^3 \quad (2-26a)$$

$$L_2\left(\frac{2T}{\theta}\right) = \log \left| \frac{2T/\theta - 1}{2T/\theta + 1} \right| - \left(\frac{2T}{\theta}\right)^3 \log \left| 1 - \left(\frac{\theta}{2T}\right)^2 \right| - \left(\frac{2T}{\theta}\right) \quad (2-26b)$$

We consider the limiting behavior of $\phi(T/\theta)$ as $T \rightarrow 0$ and as $T \rightarrow \infty$.

First, we consider the low-temperature limit. As $T \rightarrow 0$, it is easy to show that

$$G_n(\theta/T) \rightarrow \int_0^\infty x^n \operatorname{csch} x \, dx = \frac{2^{n+1} - 1}{2^n} \Gamma(n+1) \zeta(n+1) , \text{ where}$$

$\Gamma(n+1) = n!$, and $\zeta(x)$ is Riemann's zeta function. Furthermore, we have

$$\lim_{T \rightarrow 0} L_4(2T/\theta) = -\frac{5}{2} \left(\frac{2T}{\theta} \right)$$

$$\lim_{T \rightarrow 0} L_2(2T/\theta) = -3 \left(\frac{2T}{\theta} \right)$$

Thus, we obtain the result

$$\begin{aligned} \lim_{T \rightarrow 0} \Phi\left(\frac{T}{\theta}\right) &= \left(\frac{T}{\theta}\right)^2 \left\{ -\frac{1}{4} \left(\frac{2N}{N'}\right)^{2/3} \left[\frac{3}{8} \frac{G_6(\infty)}{G_4(\infty)} - \frac{3}{2} \left(\frac{N'}{2N}\right)^{2/3} \left(\frac{\theta}{T}\right)^2 \right] \right. \\ &\quad \left. + 2 \left[+\frac{3}{8} \frac{G_6(\infty)}{G_4(\infty)} - \frac{3}{2} \left(\frac{N'}{2N}\right)^{2/3} \left(\frac{\theta}{T}\right)^2 \right] \right\} \\ &= \left(\frac{T}{\theta}\right)^2 \Phi_1 + \Phi_2 \end{aligned} \quad (2-27)$$

where

$$\Phi_1 = \left[\frac{3}{4} - \frac{3}{32} \left(\frac{2N}{N'}\right)^{2/3} \right] \frac{(2^7-1)6! \zeta(7)/2^6}{(2^5-1)4! \zeta(5)/2^4} \quad (2-27a)$$

and

$$\phi_2 = \left[-3 \left(\frac{N'}{2N} \right)^{2/3} + \frac{3}{8} \right] \quad (2-27b)$$

We see, then, that at low temperatures the correction factor to ϵ due to virtual multi-phonon processes approaches a constant negative value, and increases from it as T^2 .

In the high-temperature limit on the other hand, we have

$$\lim_{T \rightarrow \infty} G_n(\theta/T) = \frac{1}{n} \left(\frac{\theta}{T} \right)^n$$

$$\lim_{T \rightarrow \infty} L_4(2T/\theta) = -\frac{5}{6} \frac{\theta}{T}$$

$$\lim_{T \rightarrow \infty} L_2(2T/\theta) = -\frac{3}{4} \frac{\theta}{T}$$

so that

$$\begin{aligned} \lim_{T \rightarrow \infty} \Phi\left(\frac{T}{\theta}\right) &= -\frac{1}{16} \left(\frac{2N}{N'} \right)^{2/3} \left[\frac{3}{8} \cdot \frac{4}{6} - \frac{3}{2} \left(\frac{N'}{2N} \right)^{2/3} \right] \left(\frac{\theta}{T} \right)^2 \\ &\quad + \frac{1}{2} \left[\frac{3}{8} \cdot \frac{4}{6} - \frac{3}{2} \left(\frac{N'}{2N} \right)^{2/3} \right] \left(\frac{\theta}{T} \right)^2 \\ &= \left(\frac{\theta}{T} \right)^2 \Phi_3 \end{aligned} \quad (2-28)$$

where

$$\phi_3 = \left[-\frac{1}{4} \left(\frac{N'}{2N} \right)^{2/3} - \frac{1}{64} \left(\frac{2N}{N'} \right)^{2/3} + \frac{7}{32} \right] \quad (2-28a)$$

so we see that as $T \rightarrow \infty$, $\phi(T/\theta)$ falls to zero as T^{-2} . In Fig. 4, we sketch the way in which we expect ξ to behave for a pure metal in the light of this theory. It will be noted that the temperature dependence of the "hump" due to the virtual multi-phonon processes has the same temperature dependence as that normally attributed to phonon drag.⁸ Due to the fact that V , representing an attractive potential, is of necessity negative, we see that the virtual recoil contribution to ξ will be negative, or of opposite sign from the phonon-drag contributions normally attributed to "normal" processes.

Fig. 4. - Thermopower parameter ξ for Pure Metal, with Corrections due to Virtual Multi-Phonon Processes.

These corrections are of sufficient magnitude to be observable experimentally, and in Chapter IV we discuss in detail the interpretation of various data in the light of these new corrections. However, for a complete theory, it is first necessary to consider

the effect of impurity scattering, as these effects are also significant in the low-temperature region where the multi-phonon corrections are greatest. Accordingly, we turn our attention to the thermopower of an alloy, discussed in the next chapter.

III. Thermopower in Alloys

No real metal approaches the ideal described in Chapter II. There are invariably various impurities which contribute to the scattering of electrons, and thus ought to influence the observed thermopower. In fact, it is easy to show in a simple way that at a given temperature, the scattering mechanism that dominates the scattering of electrons provides the greatest contribution to the observed thermopower. If we suppose that there are n independent scattering mechanisms, and that the i th mechanism acting alone would produce an inverse relaxation time $1/\tau_i$, then the total effect is given by

$$1/\tau = \sum_{i=1}^n 1/\tau_i \quad (3-1)$$

The logarithmic derivative of this inverse relaxation time is in consequence given by

$$\begin{aligned} \frac{\partial \ln(1/\tau)}{\partial \ln \xi} &= \frac{\xi}{(1/\tau)} \sum_{i=1}^n \frac{\partial(1/\tau_i)}{\partial \xi} \\ &= \sum_{i=1}^n \frac{(1/\tau_i)}{(1/\tau)} \frac{\partial \ln(1/\tau_i)}{\partial \ln \xi} \end{aligned} \quad (3-2)$$

From Eq. (3-2), we see that in a system where various scattering mechanisms are at work, the thermopower parameter ξ will contain a term due to each mechanism acting separately, weighted by the

fraction of the total inverse relaxation time contributed by that particular mechanism. Thus, at any given temperature, the dominant scattering mechanism provides the major contribution to the observed thermopower. This gives a clear indication of why the observed low-temperature thermopowers of "pure" metals often exhibit strange behavior, with different samples often giving widely different results.^{9,10} Every metal contains some impurities, responsible for the so-called residual resistance. In the low-temperature residual resistance region, it is these impurities that determine the thermopower, and not the metal itself. Thus, the observed experimental results are clearly understandable if there is a means by which $\frac{\partial}{\partial \epsilon} (1/\tau)$ may be a strong function of the type of impurity present. In earlier work,⁴ we have shown how virtual recoil processes can account for such behavior in the extreme low-temperature limit; and we now extend this work to finite temperatures, taking into account both impurity scattering and the phonon scattering discussed in Chapter II.

The simplest system to consider is that of a dilute alloy. In such a system, we know clearly the nature of the impurities present, and can readily compare theory with experiment. Let us suppose, then, that we have a metal like that of Chapter II, except that now a fraction c of the N sites are occupied by impurity ions, and $(1-c)N$ sites by host ions, with $c \ll 1$. Then if $V(\underline{r})$ is the potential due to a host ion, and $V'(\underline{r})$ that due to an impurity ion, the total potential in which a conduction electron moves is given by

$$\begin{aligned}
 W(\underline{r}) &= \sum_{\underline{l}_1} V(\underline{r}-\underline{l}_1-\underline{y}_{\underline{l}_1}) + \sum_{\underline{l}_2} V'(\underline{r}-\underline{l}_2-\underline{y}_{\underline{l}_2}) \\
 &= \sum_{\underline{l}} V(\underline{r}-\underline{l}-\underline{y}_{\underline{l}}) + \sum_{\underline{l}} U_{\underline{l}}(\underline{r}-\underline{l}-\underline{y}_{\underline{l}}) \quad (3-3)
 \end{aligned}$$

where $\{\underline{l}_1\}$ are the vectors to host sites, $\{\underline{l}_2\}$ the vectors to impurity sites, and $\{\underline{l}\} = \{\underline{l}_1\} + \{\underline{l}_2\}$. We have further defined

$$U_{\underline{l}}(\underline{r}-\underline{l}) = \begin{cases} V'(\underline{r}-\underline{l}) - V(\underline{r}-\underline{l}) & \underline{l} \in \{\underline{l}_2\} \\ 0 & \text{otherwise} \end{cases}$$

As in Chapter II, we express $W(\underline{r})$ in second-quantized form.

Symbolically, we write

$$W = V + U \quad (3-4)$$

where V is given by Eq. (2-2) and

$$\begin{aligned}
 U &= \sum_{\underline{k}\underline{k}'} e^{i(\underline{k}-\underline{k}')\cdot\underline{l}} U_{\underline{k}\underline{k}'}(\underline{l}) c_{\underline{k}'}^\dagger c_{\underline{k}} \left[1 + i \sum_{\underline{q}\underline{s}} e^{i\underline{q}\cdot\underline{l}} (\underline{k}-\underline{k}')\cdot\hat{\underline{s}} g(\underline{q},\underline{s}) B_{\underline{q}\underline{s}} \right. \\
 &\quad \left. - \frac{1}{2} \sum_{\substack{\underline{q}\underline{s} \\ \underline{q}'\underline{s}'}} e^{i(\underline{q}+\underline{q}')\cdot\underline{l}} (\underline{k}-\underline{k}')\cdot\hat{\underline{s}} (\underline{k}-\underline{k}')\cdot\hat{\underline{s}}' g(\underline{q},\underline{s}) g(\underline{q}',\underline{s}') B_{\underline{q}\underline{s}} B_{\underline{q}'\underline{s}'} \right] \quad (3-5)
 \end{aligned}$$

We see that the form of U is much the same as the form of V , except that since $U_{k,k'}(\underline{l})$ is not independent of $\underline{l}$, we can no longer immediately perform the summation over $\underline{l}$, and thus do not obtain the momentum-conserving Δ -functions. Scattering by impurities, therefore, may be either elastic or inelastic with emission and absorption of phonons. We again compute the T-matrix for electron scattering to second order:

$$\begin{aligned} T &= W + W(\epsilon - H_0)^{-1}W \\ &= V + V(\epsilon - H_0)^{-1}V + U + U(\epsilon - H_0)^{-1}U \\ &\quad + U(\epsilon - H_0)^{-1}V + V(\epsilon - H_0)^{-1}U \end{aligned} \quad (3-6)$$

The first two terms in Eq. (3-6) represent scattering processes already considered in Chapter II. The other four terms are new, and represent additional ways in which scattering can occur due to the presence of impurities. Some of the processes represented by these new terms are illustrated in Fig. 5, where we denote by $\otimes$ an interaction via U as opposed to V .

In Fig. 5 (see page 33), we note that there are two types of impurity scattering possible: elastic and inelastic. There will thus be three inverse relaxation times in a dilute alloy, those due to inelastic phonon scattering, elastic impurity scattering, and inelastic impurity scattering. We denote these $1/\tau_1$, $1/\tau_2$, and $1/\tau_3$ respectively. The first of these, as well as its

Fig. 5. - Scattering Processes Involving Impurities

logarithmic derivative, have been calculated in Chapter II, so we now turn our attention to $1/\tau_2$ and $1/\tau_3$. As we shall see, the most important of these is $1/\tau_2$, which remains finite as $T \rightarrow 0$ and gives rise to the residual resistance. Terms contributing to $1/\tau_2$ are illustrated in Fig. 5(A) and (C). Those of Fig. 5(A), in which all interactions are via a U , have been considered in our earlier work⁴ in the limit $T \rightarrow 0$. There are in addition terms such as those illustrated in Fig. 5(C), in which both a U and a V participate. Such terms can also add coherently to the first order term of Fig. 5(A).

By a method analogous to that of the Appendix, one can show that the T -matrix for elastic impurity scattering is given by

$$T_2 = T_{2a} + T_{2b} + T_{2c}, \text{ where} \quad (3-7)$$

$$T_{2a}^{k'k} = \sum_{\underline{l}} e^{i(\underline{k}-\underline{k}') \cdot \underline{l}} U_{k'k}(\underline{l}) \quad (3-7a)$$

$$T_{2b}^{k'k} = \sum_{\substack{\underline{l}, \underline{l}', q, s \\ k''}} e^{i(\underline{k}''-\underline{k}'+q) \cdot \underline{l}} e^{i(\underline{k}-\underline{k}''-\underline{l}') \cdot \underline{l}'} \frac{2k\omega_{qs} f_{k''}}{(\epsilon_k - \epsilon_{k''})^2 - (k\omega_{qs})^2} \times g^2(q, s) U_{k'k''}(\underline{l}) U_{k''k}(\underline{l}') \quad (3-7b)$$

$$T_{2c}^{k'k} = 2N \sum_{q, s} e^{i(\underline{k}-\underline{k}') \cdot \underline{l}} U_{k', k-\underline{l}}(\underline{l}) V_{k, k-\underline{l}} q \cdot \hat{s} (\underline{k}-\underline{k}-\underline{l}) \cdot \hat{s} \times g^2(q, s) \frac{2k\omega_{qs} f_{k-\underline{l}}}{(\epsilon_k - \epsilon_{k-\underline{l}})^2 - (k\omega_{qs})^2} \quad (3-7c)$$

Equation (3-7a) represents direct scattering by an impurity, while Eqs. (3-7b) and (3-7c) are second-order terms in which scattering is twice by an impurity, and once by an impurity and once by a phonon, respectively. All of these processes can connect the same initial and final states, and thus add coherently.

Using Eqs. (3-7), we find the probability of transition to be proportional to

$$|T_2^{k'k}|^2 = |T_{2a}^{k'k}|^2 + 2\text{Re } T_{2a}^{*k'k} \left[T_{2b}^{k'k} + T_{2c}^{k'k} \right],$$

which is given by

$$\begin{aligned}
 |T_2^{k'k}|^2 &= \sum_{\underline{l}, \underline{l}'} e^{i(\underline{k}-\underline{k}') \cdot (\underline{l}'-\underline{l})} U_{\underline{k}'\underline{k}}(\underline{l}) U_{\underline{k}\underline{k}'}(\underline{l}') \\
 &- 2 \operatorname{Re} \sum_{\substack{\underline{l}, \underline{l}', \underline{l}'' \\ \neq \underline{k}''}} e^{i(\underline{k}-\underline{k}') \cdot \underline{l}} e^{i(\underline{k}''-\underline{k}'+\underline{q}) \cdot \underline{l}'} e^{i(\underline{k}-\underline{k}''-\underline{q}) \cdot \underline{l}''} \\
 &\times U_{\underline{k}'\underline{k}}(\underline{l}) U_{\underline{k}'\underline{k}''}(\underline{l}') U_{\underline{k}''\underline{k}}(\underline{l}'') g^2(\underline{q}) \\
 &\times (\underline{l}'-\underline{l}'') \cdot (\underline{l}-\underline{l}'') \frac{2\hbar\omega_{\underline{q}} f_{\underline{k}''}}{(\epsilon_{\underline{k}} - \epsilon_{\underline{k}''})^2 - (\hbar\omega_{\underline{q}})^2} \\
 &+ 4N \operatorname{Re} \sum_{\underline{l}, \underline{l}', \underline{q}} e^{i(\underline{k}-\underline{k}') \cdot (\underline{l}'-\underline{l})} U_{\underline{k}'\underline{k}}(\underline{l}) U_{\underline{k}', \underline{k}-\underline{q}}(\underline{l}') \\
 &\times V_{\underline{k}, \underline{k}-\underline{q}} \underline{q} \cdot (\underline{k}-\underline{k}'-\underline{q}) g^2(\underline{q}) \\
 &\times \frac{2\hbar\omega_{\underline{q}} f_{\underline{k}-\underline{q}}}{(\epsilon_{\underline{k}} - \epsilon_{\underline{k}-\underline{q}})^2 - (\hbar\omega_{\underline{q}})^2}
 \end{aligned}$$

(3-8)

Equation (3-8) was derived under the same assumptions used in deriving Eqs. (2-6) for the pure-metal case. Since the sums over lattice sites are independent of one another and extend over the

whole crystal, we can rearrange these sums such that $\underline{r}$ is the origin for subsequent summations, thus making use of the translational symmetry of the crystal. If in the first and third term of Eq. (3-8) we define $\underline{L} = \underline{r}_1' - \underline{r}_1$, and in the second we define $\underline{L} = \underline{r}_1' - \underline{r}_2$, and $\underline{L}' = \underline{r}_2' - \underline{r}_1$, and then sum over these new variables, we can write Eq. (3-8) in the form

$$\begin{aligned}
 |T_2^{kk}|^2 = & \sum_{\underline{L}} e^{i(\underline{k}-\underline{k}') \cdot \underline{L}} U_{\underline{k}, \underline{k}'}(\underline{L}) U_{\underline{k}, \underline{k}'}(\underline{L}+\underline{L}) \\
 & - 2 \operatorname{Re} \sum_{\substack{\underline{L}, \underline{L}' \\ \underline{q}, \underline{q}''}} e^{i(\underline{k}-\underline{k}') \cdot \underline{L}} e^{i(\underline{k}-\underline{k}''-\underline{q}) \cdot \underline{L}'} U_{\underline{k}, \underline{k}'}(\underline{L}) U_{\underline{k}, \underline{k}''}(\underline{L}+\underline{L}') \\
 & \times U_{\underline{k}, \underline{k}''}(\underline{L}+\underline{L}+\underline{L}') (\underline{k}'-\underline{k}'') \cdot (\underline{k}-\underline{k}'') g^2(\underline{q}) \frac{2\hbar\omega_{\underline{q}} f_{\underline{k}''}}{(\epsilon_{\underline{k}}-\epsilon_{\underline{k}''})^2 - (\hbar\omega_{\underline{q}})^2} \\
 & + 4N \operatorname{Re} \sum_{\underline{L}, \underline{q}} e^{i(\underline{k}-\underline{k}') \cdot \underline{L}} U_{\underline{k}, \underline{k}'}(\underline{L}) U_{\underline{k}, \underline{k}'}(\underline{L}+\underline{L}) V_{\underline{k}, \underline{k}-\underline{q}} \\
 & \times \underline{q} \cdot (\underline{k}-\underline{k}-\underline{q}) g^2(\underline{q}) \frac{2\hbar\omega_{\underline{q}} f_{\underline{k}-\underline{q}}}{(\epsilon_{\underline{k}}-\epsilon_{\underline{k}-\underline{q}})^2 - (\hbar\omega_{\underline{q}})^2} .
 \end{aligned}
 \tag{3-8a}$$

In this form, it is clear that at low concentrations c of impurity the most important contribution to Eq. (3-8a) comes from the terms in which $\underline{L} = \underline{L}' = 0$, for then all the terms in the summation over $\underline{r}$ add in phase. In this sense, $\underline{L}$ and $\underline{L}'$ play the role of correlation lengths, and as c is increased, terms involving non-vanishing $\underline{L}, \underline{L}'$ will become increasingly important. In the case

of a dilute alloy, however, such terms may safely be neglected, so that we have for the transition probability that enters into $1/\tau_2$:

$$Q_2(\underline{k}, \underline{k}') = Q_{2a}(\underline{k}, \underline{k}') + Q_{2b}(\underline{k}, \underline{k}') + Q_{2c}(\underline{k}, \underline{k}') \quad , \quad (3-9)$$

where

$$Q_{2a}(\underline{k}, \underline{k}') = \frac{2\pi}{\hbar} cN |U_{\underline{k}', \underline{k}}|^2 \delta(\epsilon_{\underline{k}} - \epsilon_{\underline{k}'}), \quad (3-9a)$$

$$\begin{aligned} Q_{2b}(\underline{k}, \underline{k}') &= -\frac{2\pi}{\hbar} 2cN \sum_{\underline{q}, \underline{R}''} U_{\underline{k}', \underline{R}} U_{\underline{k}, \underline{R}''} U_{\underline{R}, \underline{R}''} g^2(\underline{q}) \\ &\times (\underline{k}' - \underline{R}'') \cdot (\underline{k} - \underline{R}'') \frac{2\hbar\omega_{\underline{q}} f_{\underline{R}''}}{(\epsilon_{\underline{R}} - \epsilon_{\underline{R}''})^2 - (\hbar\omega_{\underline{q}})^2} \\ &\times \delta(\epsilon_{\underline{R}} - \epsilon_{\underline{R}'}), \end{aligned} \quad (3-9b)$$

$$\begin{aligned} Q_{2c}(\underline{k}, \underline{k}') &= \frac{2\pi}{\hbar} 4cN^2 \sum_{\underline{q}} U_{\underline{k}', \underline{R}} U_{\underline{R}, \underline{R}-\underline{q}} V_{\underline{k}, \underline{R}-\underline{q}} g^2(\underline{q}) \\ &\times \underline{q} \cdot (\underline{k} - \underline{R}' - \underline{q}) \frac{2\hbar\omega_{\underline{q}} f_{\underline{R}-\underline{q}}}{(\epsilon_{\underline{R}} - \epsilon_{\underline{R}-\underline{q}})^2 - (\hbar\omega_{\underline{q}})^2} \\ &\times \delta(\epsilon_{\underline{R}} - \epsilon_{\underline{R}'}), \end{aligned} \quad (3-9c)$$

and we have used the fact that in summing over $\underline{R}$ there are cN terms which are non-vanishing, and have defined $U_{\underline{k}', \underline{k}}$ as $U_{\underline{k}', \underline{k}}(\underline{R})$ for a site $\underline{R}$ known to be occupied by an impurity ion. In Eqs. (3-9) we recognize the standard result² that for dilute alloys

the impurity scattering, and thus the residual resistance, are proportional to the concentration c of impurity.

We must now use Eqs. (3-9) in solving the linearized Boltzmann equation for $(1/\tau_2)$ and $\partial(1/\tau_2)/\partial\epsilon$. For elastic scattering, Eq. (2-8) takes the particularly simple form

$$\frac{1}{\tau_k} = \sum_{k'} Q(k, k') (1 - \cos\theta_{kk'}) \quad (3-10)$$

As in Chapter II, we find the first order term (3-9a) to be sufficient for calculating $1/\tau_2$ at the Fermi level. Using Eqs. (3-10) and (3-9a), we find

$$\begin{aligned} \frac{1}{\tau_2} &= \frac{2\pi}{k} cN \sum_{k'} |U_{kk'}|^2 (1 - \cos\theta_{kk'}) \delta(\epsilon_k - \epsilon_{k'}) \\ &= \frac{2\pi}{k} \frac{c}{4} \frac{c}{5} (N U)^2 \frac{N}{N} \end{aligned} \quad (3-11)$$

where the same assumptions have been made as were made in evaluating Eq. (2-13).

Next, we consider the energy derivative of $1/\tau_2$ at the Fermi level, and must include effects due to the "virtual recoil" terms represented by Eqs. (3-9b,c). From Eqs. (3-9,10), we have

$$\begin{aligned} \frac{\partial}{\partial\epsilon} \frac{1}{\tau_2} &= \sum_{k'} \frac{\partial}{\partial\epsilon_k} \left[Q_{2a}(k, k') + Q_{2b}(k, k') + Q_{2c}(k, k') \right] \\ &\quad \times (1 - \cos\theta_{kk'}) \end{aligned} \quad (3-12)$$

We consider in turn each of the three terms which occur in Eq. (3-12). In a manner analogous to that used in calculating Eq. (3-11), it follows immediately that

$$\begin{aligned} \sum_{k'} \frac{\partial}{\partial \epsilon_k} Q_{2a}(k, k') (1 - \cos \Theta_{kk'}) \\ = \frac{2\pi}{k} \frac{3}{4} \frac{C}{g^2} (Nu)^2 \frac{N'}{N} \left[\frac{1}{2} + 2 \frac{\partial \ln u}{\partial \ln \epsilon} \right] , \end{aligned} \quad (3-13)$$

so that we are left with the problem of calculating the contributions to Eq. (3-12) from the second-order terms $Q_{2b}(k, k')$ and $Q_{2c}(k, k')$.

Thus, we consider next the contribution to Eq. (2-13) from $Q_{2b}(k, k')$, which is given by

$$\begin{aligned} \sum_{k'} \frac{\partial}{\partial \epsilon_k} Q_{2b}(k, k') (1 - \cos \Theta_{kk'}) = -\frac{2\pi}{k} \frac{ac k^2}{m} \sum_{k'} \frac{\partial}{\partial \epsilon_k} \sum_{k''} u_{k'k} u_{kk''} \\ \times u_{k''k} (\underline{k} - \underline{k}'') \cdot (\underline{k} - \underline{k}') \frac{f_{k''}}{(\epsilon_k - \epsilon_{k''})^2 - (\hbar \omega_p)^2} \delta(\epsilon_k - \epsilon_{k'}) \end{aligned} \quad (3-14)$$

In evaluating Eq. (3-14), as in evaluating Eq. (2-17), we recognize

that only the "energy denominator" $[(\epsilon_k - \epsilon_{k'})^2 - (\hbar\omega_q)^2]^{-1}$ is sufficiently strongly energy-dependent to provide a significant contribution. Consequently, making the usual assumptions, we find that Eq. (3-14) can be written in the form

$$\sum_{k'} \frac{\partial}{\partial \epsilon_k} Q_{2b}(\underline{k}, \underline{k}') (1 - \cos \theta_{kk'}) = -\frac{2\pi}{K} \frac{2ek^2}{M} U^3 \times \sum_{k'} Y(\underline{q}, \underline{k}, \underline{k}') \delta(\epsilon_k - \epsilon_{k'}) \quad (3-15)$$

where

$$Y(\underline{q}, \underline{k}, \underline{k}') = \frac{\partial}{\partial \epsilon_k} \sum_{k''} (\underline{k}' - \underline{k}'') \cdot (\underline{k} - \underline{k}'') \frac{f_{k''}}{(\epsilon_k - \epsilon_{k''})^2 - (\hbar\omega_q)^2} \\ = \frac{\partial}{\partial \epsilon} \int_0^\infty D(\epsilon'') \frac{f(\epsilon'')}{(\epsilon - \epsilon'')^2 - (\hbar\omega_q)^2} d\epsilon'' \frac{1}{4\pi} \int_\Omega d\Omega'' (\underline{k}' - \underline{k}'') \cdot (\underline{k} - \underline{k}'') \quad (3-15a)$$

We evaluate $Y(\underline{q}, \underline{k}, \underline{k}')$ by performing first the integral over angles, and then over energy. Taking $\underline{k}$ as the polar axis, and assuming $\underline{k}'$ to lie in the x - z plane making an angle α with $\underline{k}$, we have for the angular integration in Eq. (3-15a),

$$\frac{1}{4\pi} \int_\Omega d\Omega'' (\underline{k}' - \underline{k}'') \cdot (\underline{k} - \underline{k}'') = k''^2 + k^2 \cos \alpha = \frac{2m}{K^2} (\epsilon'' + \epsilon \cos \alpha),$$

so that

$$Y(\underline{q}, \underline{k}, \underline{k}') = \frac{\partial}{\partial \tilde{\epsilon}} \int_{-\epsilon}^{\infty} D(\tilde{\epsilon} + \epsilon) \frac{f(\tilde{\epsilon} + \epsilon)}{\tilde{\epsilon}^2 - (\hbar\omega_q)^2} \frac{2m}{\hbar^2} [\tilde{\epsilon} + \epsilon (1 + \cos\alpha)] d\tilde{\epsilon} ,$$

where we have made the change of variables $\tilde{\epsilon} = \epsilon'' - \epsilon$. We now take the derivative inside the integral and evaluate it at the Fermi level. A term due to the variation of the lower limit with energy vanishes, and we are left with

$$Y(\underline{q}, \underline{k}, \underline{k}') = \int_{-\epsilon}^{\infty} \frac{2m}{\hbar^2} [\tilde{\epsilon} + \epsilon (1 + \cos\alpha)] D(\tilde{\epsilon} + \epsilon) \frac{\partial f(\tilde{\epsilon} + \epsilon) / \partial \epsilon}{\tilde{\epsilon}^2 - (\hbar\omega_q)^2} d\tilde{\epsilon} .$$

We evaluate this last integral making the same approximation to $\partial f / \partial \epsilon$ as was made in evaluating Eq. (2-20), and find

$$Y(\underline{q}, \underline{k}, \underline{k}') = - \frac{2m}{\hbar^2} \frac{D(\epsilon)}{4k_B T} \left[\frac{\epsilon(1 + \cos\alpha)}{\hbar\omega_q} \log \left| \frac{\hbar\omega_q - 2k_B T}{\hbar\omega_q + 2k_B T} \right| \right. \\ \left. + \frac{\hbar\omega_q}{2\epsilon} \log \left| \frac{\hbar\omega_q - 2k_B T}{\hbar\omega_q + 2k_B T} \right| + \frac{2k_B T}{\epsilon} \right] .$$

(3-16)

We now substitute Eq. (3-16) into Eq. (3-15) and perform the summation over q to find

$$Y(\underline{k}, \underline{k}') \equiv \sum_{\underline{q}} Y(\underline{q}, \underline{k}, \underline{k}')$$

$$= -\frac{2m}{\hbar^2} \frac{D(\underline{q})}{4k_B T} 3N \left[\frac{S(1+\cos\alpha)}{2k_B \theta} L_1(2T/\theta) \right.$$

$$\left. + \frac{k_B \theta}{8S} L_3(2T/\theta) + \frac{2}{3} \frac{k_B T}{S} \right]$$

(3-17)

where the functions $L_n(x)$ are as defined in Eq. (2-22a). Finally, substituting Eq. (3-17) into Eq. (3-15) and performing the summation over $\underline{k}'$, we have

$$\sum_{\underline{k}} \frac{\partial}{\partial \epsilon_R} Q_{2b}(\underline{k}, \underline{k}') (1-\cos\alpha) = \frac{2\pi}{\hbar} \frac{27C}{4} \frac{(N\hbar)^3}{4k_B T S^2} \frac{m}{M} \left(\frac{N'}{N}\right)^2 \Psi_I\left(\frac{T}{\theta}\right) \quad (3-18)$$

where

$$\Psi_I\left(\frac{T}{\theta}\right) = \frac{S}{3k_B \theta} L_1\left(\frac{2T}{\theta}\right) + \frac{k_B \theta}{8S} L_3\left(\frac{2T}{\theta}\right) + \frac{2}{3} \frac{k_B T}{S}$$

(3-18a)

The final contribution to $\partial(1/\tau_2)/\partial\epsilon$ that we must consider is that due to $Q_{2c}(\underline{k}, \underline{k}')$:

$$\sum_{\mathbf{R}} \frac{\partial}{\partial \epsilon_{\mathbf{R}}} Q_{2c}(\mathbf{R}, \mathbf{R}') (1 - \cos \theta_{\mathbf{R}\mathbf{R}'}) = \frac{2\pi}{\hbar} \frac{4C\hbar^2}{m} N \frac{\partial}{\partial \epsilon_{\mathbf{R}}} \sum_{\mathbf{R}'\mathbf{q}} U_{\mathbf{R}'\mathbf{R}} U_{\mathbf{R}'\mathbf{R}-\mathbf{q}} \\ \times V_{\mathbf{R}, \mathbf{R}-\mathbf{q}} \frac{\mathbf{q} \cdot (\mathbf{R} - \mathbf{R}' - \mathbf{q})}{(\epsilon_{\mathbf{R}} - \epsilon_{\mathbf{R}-\mathbf{q}})^2 - (\hbar\omega_{\mathbf{q}})^2} \frac{f_{\mathbf{R}-\mathbf{q}} (1 - \cos \theta_{\mathbf{R}\mathbf{R}'}) \delta(\epsilon_{\mathbf{R}} - \epsilon_{\mathbf{R}'})}{(3-19)}$$

Equation (3-19) bears a strong resemblance to Eq. (2-18) in the way in which the wave vectors of the intermediate electron and phonon states are connected. The mathematics involved in evaluating Eq. (3-19) is thus entirely analogous to that of Chapter II. The result we finally obtain is

$$\sum_{\mathbf{R}} \frac{\partial}{\partial \epsilon_{\mathbf{R}}} Q_{2c}(\mathbf{R}, \mathbf{R}') (1 - \cos \theta_{\mathbf{R}\mathbf{R}'}) = \frac{2\pi}{\hbar} c \frac{m}{m} \frac{(N\mathcal{U})^2 NV}{k_B \theta (4k_B T) S} \left(\frac{N'}{2N} \right)^{\frac{2}{3}} L_2 \left(\frac{2T}{\theta} \right) \quad (3-20)$$

Equations (3-11, 13, 18, 20) enable us to determine the logarithmic derivative of $(1/\tau_2)$ at the Fermi level as

$$\left. \frac{\partial \ln(1/\tau_2)}{\partial \ln \epsilon} \right|_F = \frac{1}{2} + 2 \left. \frac{\partial \ln \mathcal{U}}{\partial \ln \epsilon} \right|_F + 9 \frac{N\mathcal{U}}{4k_B T} \left(\frac{m}{m} \right) \frac{N'}{N} \Psi \left(\frac{T}{\theta} \right) \\ + \frac{2}{3} \frac{(NV) S}{4k_B T (k_B \theta)} \left(\frac{m}{m} \right) \left(\frac{2N}{N'} \right)^{\frac{1}{3}} L_2 \left(\frac{2T}{\theta} \right) \quad (3-21)$$

From Eqs. (1-4) and (3-2), we see that Eq. (3-21) will determine the thermopower of an alloy when $1/\tau_2$ is the greatest contribution to $1/\tau$. This will clearly be in the low-temperature region, since $1/\tau_2$ remains finite as $T \rightarrow 0$, while $1/\tau_1$ vanishes as T^5 . It is thus of interest to consider the low-temperature limit of (3-21). Now it is easy to show that

$$\lim_{T \rightarrow 0} L_1(2T/\theta) = -8T/\theta$$

$$\lim_{T \rightarrow 0} L_2(2T/\theta) = -6T/\theta$$

$$\lim_{T \rightarrow 0} L_3(2T/\theta) = -16T/3\theta$$

So that

$$\lim_{T \rightarrow 0} \bar{\Psi}\left(\frac{T}{\theta}\right) = \frac{\xi}{3k_B\theta} \left(-\frac{8T}{\theta}\right) + \frac{k_B\theta}{8\xi} \left(-\frac{16T}{3\theta}\right) + \frac{2}{3} \frac{k_B T}{\xi} = -\frac{8}{3} \frac{\xi}{k_B\theta} \frac{T}{\theta}$$

and we are left with

$$\begin{aligned} \lim_{T \rightarrow 0} \left. \frac{\partial \ln(1/\tau_2)}{\partial \ln \varepsilon} \right|_S &= \frac{1}{2} + 2 \left. \frac{\partial \ln \mathcal{U}}{\partial \ln \varepsilon} \right|_S - 6 \frac{(N\mathcal{U})^2}{(k_B\theta)^2} \left(\frac{m}{M}\right) \left(\frac{N'}{N}\right) \\ &\quad - \frac{(N\mathcal{U})^2}{(k_B\theta)^2} \left(\frac{m}{M}\right) \left(\frac{2N}{N'}\right)^{1/3} \end{aligned} \quad (3-22)$$

Eq. (3-22) leads to the low-temperature thermopower derived in our

earlier work,⁴ except for the fourth term, which results from scattering processes not previously considered. We note that the third term is proportional to U , and may thus be either positive or negative, depending on whether the impurity may be considered attractive or repulsive. The fourth term, on the other hand, is invariably positive, since we know that V will be attractive. Thus, the relative magnitudes of the third and fourth terms with respect to each other and to the first two terms are very important in determining the sign of the observed low-temperature thermopower. It is clear, then, why such a wide variety of behavior has been observed in low-temperature thermopower measurements on various alloys.

In the high-temperature limit, it is straightforward to show that

$$\lim_{T \rightarrow \infty} L_1(2T/\theta) = -2\theta/3T$$

$$\lim_{T \rightarrow \infty} L_2(2T/\theta) = -3\theta/2T$$

$$\lim_{T \rightarrow \infty} L_3(2T/\theta) = -4\theta/5T$$

and thus we see that the "virtual recoil" corrections to $\partial \ln(1/\tau_2)/\partial \ln \epsilon$ decay as T^{-2} in the high-temperature limit. However, the high-temperature behavior of Eq. (3-21) is not of such importance as the low-temperature behavior, since at high temperatures $1/\tau_2$ has ceased to be the dominant contribution

to $1/\tau$, and in consequence Eq. (3-21) contributes little to the thermopower in this temperature region.

There is one other relaxation time to be considered if we are to complete our theory of thermopower in dilute alloys, and that is $1/\tau_3$, which is due to inelastic scattering from impurity sites. Scattering processes of this type have been illustrated in Fig. 5(b). However, on simple physical grounds, it is easy to argue that these processes are of minimal importance in determining the thermopower. In the low temperature limit, $1/\tau_3$ must surely go to zero, since it is dependent upon the emission and absorption of phonons. Consequently, $1/\tau_2$ must be greater than $1/\tau_3$ in this limit, and must by Eq. (3-2) be the dominant factor in determining the thermopower. In the high-temperature limit, on the other hand, while $1/\tau_3$ must become greater than $1/\tau_2$, it will inevitably be much less than $1/\tau_1$, since the transition probabilities for impurity scattering are all reduced by a factor of c from those for pure metal scattering. In figurative terms, as there are only a fraction c of impurities, it is much more likely that an electron will "collide" with a pure metal phonon than an impurity phonon. Thus, $1/\tau_1$ determines the thermopower at high temperatures, just as $1/\tau_2$ is the dominant term at low temperatures. We therefore recognize that $1/\tau_3$ will not be important unless there is some intermediate temperature region in which it manages to be greater than both $1/\tau_1$ and $1/\tau_2$ simultaneously. Thus, we compute $1/\tau_3$ and compare with the relaxation times we have already computed.

As before, we find first order theory to be sufficient in calculating $1/\tau_3$. Eq. (3-5) tells us that the first-order term in the T-matrix T_3 for inelastic impurity scattering is given by

$$T_{3a}^{kk'} = \sum_{qs} e^{i(\underline{k}-\underline{k}'+\underline{q}) \cdot \underline{R}} U_{k'R}(\underline{R}) \tilde{c}(\underline{k}-\underline{k}') \cdot \hat{s} g(q, s) \\ \times \frac{1}{\sqrt{2}} \left[\coth(\hbar\omega_q/2k_B T) \mp 1 \right]^{1/2},$$

so that the transition probability is given to first order by

$$Q_{3a}^{(\pm)}(\underline{k}, \underline{k}') = \frac{2\pi}{\hbar} |U_{k'R}|^2 |\underline{k}-\underline{k}'|^2 CN \delta(\epsilon_k - \epsilon_{k'} \pm \hbar\omega_q) \\ \times \sum_q g^2(q) \frac{1}{2} \left[\coth(\hbar\omega_q/2k_B T) \mp 1 \right] \quad (3-23)$$

Thus, using the linearized Boltzmann equation (2-10) which is appropriate for inelastic scattering, we have

$$\frac{1}{\tau_3} = \frac{2\pi}{\hbar} U^2 CN \sum_{k'} |\underline{k}-\underline{k}'|^2 (1 - \cos \theta_{kk'}) \delta(\epsilon_k - \epsilon_{k'} \pm \hbar\omega_q) \\ \times \sum_q \frac{\hbar}{2mN\omega_q} \operatorname{csch}(\hbar\omega_q/k_B T) \quad (3-24)$$

Equation (3-24) is easily evaluated in the same manner as Eq. (2-12). We find

$$\frac{1}{\tau_3} = \frac{2\pi}{k} 8c \frac{(N\mathcal{U})^2}{k_B\theta} \left(\frac{N'}{N}\right) \left(\frac{m}{M}\right) \left(\frac{T}{\theta}\right)^2 G_1(\theta/T) \quad (3-25)$$

At low temperatures, $G_1(\theta/T)$ approaches a constant value, and we see that $1/\tau_3$ goes to zero as T^2 . At high temperatures, on the other hand, $G_1(\theta/T)$ approaches the limiting value (θ/T) , so that $1/\tau_3$ increases linearly in this limit. Such a term due to inelastic impurity scattering has been investigated previously,^{11,12} and found in general to be negligible compared to the terms contributed by other scattering processes. To show why this is the case, we compare the magnitudes of $1/\tau_1$, $1/\tau_2$, and $1/\tau_3$. These are given by Eqs. (2-14), (3-11), and (3-25) respectively. First, we consider the ratio

$$\frac{(1/\tau_3)}{(1/\tau_1)} = 8c \left(\frac{N'}{N}\right)^2 \left(\frac{\mathcal{U}}{V}\right)^2 \left(\frac{\theta}{T}\right)^3 \frac{G_1(\theta/T)}{G_4(\theta/T)} \quad (3-26)$$

At high temperatures, we see that this ratio approaches a constant value of order c , in accord with the physical reasoning previously presented. Thus, for dilute alloys such as we are considering here, $1/\tau_3$ cannot be an important factor in the thermopower, and will affect the observed value by at most a few percent. However, at low temperatures, $1/\tau_3$ must eventually become greater than $1/\tau_1$, as it falls off as T^2 , instead of T^5 . In the limit of low tem-

peratures, G_1 and G_4 approach constant values of order unity, so that the ratio (3-26) will be significant for $(\theta/T)^3 c > 1$, or $T < c^{1/3} \theta$. For dilute alloys, this means something like $T < \theta/10$. The ratio of $1/\tau_3$ to $1/\tau_2$, on the other hand, is given by

$$\frac{(1/\tau_3)}{(1/\tau_2)} = 8 \frac{\epsilon}{k_B \theta} \frac{m}{M} \left(\frac{T}{\theta}\right)^2 G_1(\theta/T) \quad (3-27)$$

We see immediately from Eq. (3-27) that when T is sufficiently small so that $1/\tau_3 > 1/\tau_1$, $1/\tau_2$ is already many times greater than $1/\tau_3$. For example, for $T = \theta/10$, (3-27) is of order 10^{-4} . Clearly, then, by Eq. (3-2), we need not consider $1/\tau_3$ in our simple theory for the thermopower of a dilute alloy.

A complete model for the thermopower of a dilute alloy may thus be constructed around Eqs. (1-4), (2-14), (2-23), (3-2), (3-11), and (3-21). Detailed comparison with various experimental data is given in Chapter IV; for the moment we content ourselves with a qualitative discussion of what types of behavior can be expected from this theory.

At very low temperatures, Eq. (3-22) tells us that the thermopower parameter ξ may be either positive or negative, while at high temperatures, Eq. (2-25) tells us that ξ should approach a constant positive value. In the region in between, $1/\tau_2$ falls off as $1/\tau_1$ increases and the contributions to ξ due to each are an important part of the total value. In Fig. 6 we show qualitative sketches of how $(1/\tau_1)/(1/\tau)$, $(1/\tau_2)/(1/\tau)$,

$\partial \ln(1/\tau_1)/\partial \ln \epsilon$ and $\partial \ln(1/\tau_2)/\partial \ln \epsilon$ vary with temperature. In Fig. 7 we show the thermopower parameter ξ and thermopower S that result from this behavior.

Fig. 6 - Temperature Behavior of Factors Contributing to the Thermopower of a Dilute Alloy

A brief comparison of Fig. 7 with some of the experimental curves shown, for example, in MacDonald's book⁸ reveals that such behavior is, in fact, observed. An interesting point to note is that what we have calculated here is only the "electron diffusion" contribution to the thermopower, as opposed to the "phonon drag" component. Such "humps" as appear in Fig. 7 are invariably attributed to phonon drag effects in previous theories.¹³ This raises the interesting possibility that such effects have been misinterpreted

Fig. 7 - Thermopower of a Dilute Alloy

in the past, and that the standard technique¹⁴⁻¹⁶ of expanding the low temperature thermopower in the form $S = AT + BT^3$ and attributing the T^3 component solely to phonon drag may be in error. These and other interesting questions raised by this work are discussed in the next chapter, where we discuss our theories in the light of experimental data.

IV Applications

We now proceed to show more quantitatively the way in which the results of Chapters II and III serve to shed light upon experimental thermopower data. There are two predictions of the present theory which do not appear in earlier work. These are a low-temperature limit dependent upon the sign of the impurity potential, and a "phony phonon drag" contribution due solely to electron diffusion via virtual multiphonon processes. The former is far easier to verify in an unambiguous manner than the latter, which presumably exists at the same time as true phonon drag, and is thus difficult to distinguish. Thus, we consider first examples taken from low-temperature thermopower data on dilute alloys, and then discuss the higher temperature "phony phonon drag" effect.

Equation (3-22) tells us that for a dilute alloy, in the limit of low temperature, the thermopower parameter ξ is given by

$$\xi = 1 - 2 \left[\frac{\partial \ln \eta}{\partial \ln \epsilon} \right]_T + \frac{\sum}{(k_B \theta)^2} \frac{m}{M} \left[6(NU) \left(\frac{N'}{N} \right) + (NV) \left(\frac{2N}{N'} \right)^{\frac{1}{2}} \right] \quad (4-1)$$

As we have mentioned, Eq. (4-1) differs from the results of our previous work on low-temperature alloys⁴ in that there is a term proportional to V in addition to the term proportional to U . This second term will invariably be negative, as it represents the attractive ionic potential, while the first term may be either positive or negative, representing the difference between impurity

and host potentials. We see that for U attractive, the correction term in (4-1) must be greater than for U repulsive, as in the former case the two terms in brackets add, and in the latter case they subtract. Indeed, for a monovalent impurity in a monovalent host lattice, for example, we expect V to be greater in magnitude than U , and thus we expect the correction term to reduce ξ from its "free electron" value.

As an example, we consider again the data of Guénault and MacDonald¹⁷ for dilute alloys of Na, Rb, and Cs in K. If we use the same potentials U and V as were used in our earlier work on this system,⁴ we obtain from Eq. (4-1) the results shown in Table I.

Solute	ξ (Expt)	ξ_1	ξ_2	ξ_3
Na	0.86	3.50	1.46	1.38
Rb	-0.19	-0.19	-0.40	-0.19
Cs	-0.43	-1.42	-1.03	-0.72

TABLE I - The Thermopower Parameter ξ for Dilute Alloys of Potassium. ξ_1 is the theoretical value from Reference (4), ξ_2 and ξ_3 have been computed from Eq. (4-1) as explained in the text.

In the column of Table I labeled ξ_2 , we show the results obtained directly from Eq. (4-1) with $\theta = 100^\circ\text{K}$, $\zeta = 2.1 \text{ eV}$, and $m/M = 1.39 \times 10^{-5}$. In the column labeled ξ_3 , we show the results if we assume the quantity in brackets in Eq. (4-1) to be multiplied by some constant of order unity, and adjust that constant such that the result for KRb agrees with experiment. The reasoning behind

this last adjustment is that while we have assumed V_q to be a constant, it does, in fact, vary with momentum transfer q and in general decreases as q increases. Thus, we expect that the U 's and V 's appropriate to Eq. (4-1) should be something less than the $q=0$ pseudopotentials used.

For comparison, we have included in Table I the experimental results of Guénault and MacDonald¹⁷ for 0.2 at.% solute at $T = 3^\circ K$, and the theoretical results of our previous work, labeled $\xi(\text{expt})$ and ξ_1 , respectively. We see immediately that ξ_2 and ξ_3 are in far better agreement with the experimental values than is ξ_1 . In particular, the partial cancellation of the terms proportional to U and V has served to bring the results for Na down considerably, and has brought the value of ξ for KNa much more into line with the observed value. Our belief in virtual recoil as the dominant contribution to the low-temperature thermopower of dilute alloys is much strengthened by these results, as it is clear that this mechanism accounts semiquantitatively for the behavior of the system considered. Indeed, it must be said that the agreement is remarkable, considering the crudity of the model used.

Another striking example of the influence of virtual recoil on low-temperature thermopower can be found in the hydrogen-palladium system. In Figure 8, we sketch the low-temperature thermopower of pure Pd and of some Pd-H alloys as recently determined by Fletcher, et al.¹⁸ We note that the addition of hydrogen to palladium, even in as small an amount as 3%, is sufficient to change the thermopower of the system from negative to positive. We

Fig. 8 - Low-Temperature Thermopower of Pd-H Alloys

note further that the initial slopes of S for the various alloys, which are proportional to ξ , are more or less independent of the concentration of impurity, in accord with the prediction of Eq. (4-1), for example. Finally, as Fletcher et al.¹⁸ point out, these results do not find their explanation in existing theories of Pd and its alloys, which generally invoke impurity-induced s - d scattering and predict a negative thermopower upon the addition of impurities such as silver and hydrogen which add electrons to the metal.¹⁹ It thus seems likely that the behavior of this system can be attributed to the influence of virtual recoil, and it is therefore of interest to make a theoretical calculation for comparison with these experimental results.

A difficulty immediately arises, however, in that the theory of Chapter III assumed a substitutional alloy, while it is well-known²⁰ that in PdH , the hydrogen impurities are located in

interstitial positions in the f.c.c. host lattice. Fortunately, it is easy to make a simple model for describing the scattering due to these impurities. The inelastic-neutron-scattering data of Bergsma and Goedkoop²¹ show clearly that one can associate with the hydrogen impurities in PdH a vibrational mode of frequency $\hbar\omega = 0.056$ eV. Such behavior can be accounted for by considering the protons as being trapped in an interstitial cage of palladium ions, and vibrating inside like 3-dimensional harmonic oscillators of characteristic frequency ω . At low temperatures, we expect scattering from these oscillators to provide the dominant contribution to $1/\tau$, just as in the previous chapter, and thus to determine the thermopower.

A further difficulty is of course due to the fact that Pd is a transition metal, and thus has a complex band structure. The validity of a "free electron" calculation of the sort performed in Chapter III is consequently not immediately obvious. However, the Fermi surface of Pd is known²² to consist of an electron surface of primarily s-p character located at the center of the Brillouin zone, and two hole surfaces of primarily d character. If we make the reasonable assumption that the s electrons contribute the greatest amount to the conductivity, then these ought to be of primary importance in determining the thermopower.⁸ A reasonable calculation can thus be made by treating only the electron surface, which is approximately spherical with a radius of about 0.5 atomic units.²² Important parameters relating to this surface are available through de Haas-van Alphen data²² on Pd, and can be used as

input into a theoretical calculation.

Expressing these ideas more mathematically, we take the potential seen by an electron in the s-band of $\underline{\text{PdH}}$ to be of the form

$$W(\underline{r}) = \sum_{\underline{l}} V(\underline{r}-\underline{l}-\underline{\gamma}_{\underline{l}}) + \sum_{\underline{l}'} U(\underline{r}-\underline{l}'-\underline{\gamma}_{\underline{l}'}) , \quad (4-2)$$

where $\{\underline{l}\}$ are the sites of the Pd host lattice, and $\{\underline{l}'\}$ are the interstitial sites occupied by hydrogen impurities. This potential can be expressed in the notation of second-quantization as

$$W = V + U , \quad \text{where} \quad (4-3)$$

$$V = \sum_{\underline{R}\underline{R}'} C_{\underline{R}'}^{\dagger} C_{\underline{R}} V_{\underline{R}\underline{R}'} N \left[\Delta(\underline{R}-\underline{R}') + i \sum_{\underline{q}\underline{s}} (\underline{R}-\underline{R}') \cdot \hat{\underline{s}} \right. \\ \left. \times g(\underline{q},\underline{s}) (a_{\underline{q},\underline{s}}^{\dagger} + a_{\underline{q},\underline{s}}) \Delta(\underline{R}-\underline{R}'+\underline{q}) + \dots \right] , \quad (4-3a)$$

and

$$U = \sum_{\underline{R}\underline{R}'\underline{\alpha}} C_{\underline{R}'}^{\dagger} C_{\underline{R}} U_{\underline{R}\underline{R}'} e^{i(\underline{R}-\underline{R}') \cdot \underline{\alpha}'} \left[1 + i \sum_{\underline{\alpha}} (\underline{R}-\underline{R}') \cdot \hat{\underline{\alpha}} \right. \\ \left. \times \left(\frac{\hbar}{2m'\omega} \right)^{1/2} (d_{\underline{\alpha}}^{\dagger} + d_{\underline{\alpha}}) + \dots \right] . \quad (4-3b)$$

In Eq. (4-3b), we have taken the motion of the hydrogen ions about their equilibrium sites ($\underline{1}'$) to be that of a 3-dimensional harmonic oscillator of frequency ω , and have assumed no correlation in the motion of the impurities at each site. The operators $d_{\alpha}^{\dagger}, d_{\alpha}$ are creation and annihilation operators for motion along the coordinate direction α , and M' is the mass of the hydrogen ion (proton). Equation (4-3a), of course, represents nothing more than the pure metal electron-phonon interaction discussed in Chapter II.

We note that this model for the PdH system with interstitial impurities differs from the model of Chapter III in two respects. First, the potential U that appears is the full potential of the impurity, and not the difference between impurity and host potentials. Thus, it is clear that in this system U must be a negative quantity. Second, the motions of the impurities and host ions are independent of one another and are treated as separate excitations of the system. In all other respects, this system is the same as that of Chapter III, and the analysis can proceed in an analogous manner. Again we find that there are three types of scattering present and contributing to the relaxation time: phonon scattering, elastic impurity scattering, and inelastic impurity scattering. Using first order theory, we easily find that the inverse relaxation times $1/\tau_1$, $1/\tau_2$, and $1/\tau_3$ due to each of these in the order mentioned are given by

$$\frac{1}{\tau_1} = \frac{3}{4} \frac{2\pi}{\kappa} \left(\frac{NV}{k_B\theta} \right)^2 \left(\frac{m}{M} \right) \frac{N}{N'} \left(\frac{T}{\theta} \right)^5 G_4(\theta/T) \quad , \quad (4-4a)$$

$$\frac{1}{\tau_2} = \frac{8}{4} \frac{2\pi}{h} \frac{C}{S} (N'U)^2 \frac{N'}{N} \quad , \quad (4-4b)$$

$$\frac{1}{\tau_3} = 4 \frac{2\pi}{h} \frac{C}{h\omega} (N'U)^2 \left(\frac{m}{M'}\right) \frac{N'}{N} \operatorname{csch}(\hbar\omega/k_B T) \quad . \quad (4-4c)$$

Equations (4-4a) and (4-4b) are, of course, identical with the relaxation times similarly labeled in Chapter III. The relaxation time τ_3 , however, is seen to be somewhat different from that of Chapter III, as a result of the different vibrational motion assumed for the impurities here. We note, however, that at low temperatures Eq. (4-4c) becomes exponentially small, while at high temperatures it becomes proportional to $k_B T/\hbar\omega$. Thus, it is easy to show that at all temperatures $1/\tau_3$ is much smaller than $1/\tau_1$ or $1/\tau_2$, and is not an important factor to consider in determining the thermopower. As in Chapter III, then, a determination of $\partial(1/\tau_2)/\partial\varepsilon$ at the Fermi level of Pd will enable us to predict the thermopower of this system.

To second order in U , the T-matrix for elastic scattering is found to be given by

$$\begin{aligned} T_{k'k} = & \sum_{k''} U_{k'k''} e^{i(\underline{k}-\underline{k}') \cdot \underline{R}'} - \frac{\hbar^2}{M'} \sum_{k''k'''} (\underline{k}'-\underline{k}'') \cdot (\underline{k}-\underline{k}'') \\ & \times U_{k''k'''} U_{k''k} \frac{f_{k''}}{[\varepsilon_k - \varepsilon_{k''}]^2 - (\hbar\omega)^2} e^{i(\underline{k}-\underline{k}') \cdot (\underline{R}' - \underline{R}'')} \quad , \quad (4-5) \end{aligned}$$

where again we have kept only strongly energy-dependent second-order terms. We note that there are two differences between Eq. (4-5) and the analogous Eqs. (3-7) for the substitutional alloy. First, of course, there is no summation over frequencies ω , as all impurities are treated here as Einstein oscillators. Second, and more important, there is no "mixed term" involving both a U and a V . This, of course, is a result of the fact that in the present case the displacements of the hydrogen and palladium ions are governed by different excitations. There is thus no "mixed term" that can add coherently with the first order term in (4-5).

The calculation of $\partial \ln(1/r_2)/\partial \ln \epsilon$ from Eq. (4-5) is easily done in a manner analogous to that used in calculating Eq. (3-18). In the limit of low temperatures, we find the result

$$\lim_{T \rightarrow 0} \xi = 1 - 2 \left. \frac{\partial \ln U}{\partial \ln \epsilon} \right|_s + \frac{8}{3} \cdot U D(\xi) \frac{m^*}{M'} \left(\frac{q}{k\omega} \right)^2 \quad (4-6)$$

In Eq. (4-6), we have taken $\xi = \hbar^2 k^2 / 2m^*$, where m^* is the cyclotron mass and k the mean radius of the s -band electron surface. The factor $UD(\xi) = -\frac{1}{2}$, if we take the $q=0$ limit of a screened potential. Similarly, assuming a screened potential, one can estimate $\partial \ln U / \partial \ln \epsilon = -0.15$. We write Eq. (4-6) in the form $\xi = \xi_0 + \Delta\xi$, where ξ_0 is the prediction of simple first-order

theory, and $\Delta\xi$ is a correction due to virtual recoil. We note that ξ_0 is positive, while $\Delta\xi$ is negative, as it must be if the thermopower is to be positive, as observed experimentally.¹⁸

Using $m^* = 2.2 m$ and $k = 0.52$ a.u. as determined by Vuillemin,²² we find from (4-6) the result $\Delta\xi = -1.4$, while experimentally^{18,23} the results shown in Table II are found.

H/Pd	S(3°K) ($\mu V/\text{deg}$)	$\Delta\xi$
0	-0.18	-
0.03	+0.13	-4.25
0.11	+0.18	-5.38
0.42	+0.185	-5.50

TABLE II - Observed Low-temperature Thermopowers of Dilute PdH Alloys

We note that while our theoretical value of $\Delta\xi = -1.4$ is somewhat lower than the observed experimental results, it is of the same order of magnitude and predicts the same qualitative behavior - a change of S from negative to positive upon the addition of hydrogen, the low temperature behavior being approximately independent of the concentration of impurity. When we consider the crudity of our model for the PdH system, these results appear as convincing proof of the operation of virtual recoil in this system. This is especially true in light of the fact that no other theoretical explanation has been advanced which can account for this behavior.

Finally, we turn our attention from alloys to "pure" metals;

that is, metals where the concentration of impurities is sufficiently low that the electron-phonon contribution to the inverse relaxation time remains the dominant contribution down to fairly low temperatures, say 8/10 or less. In such a system, we should expect to observe a thermopower parameter ξ given by Eq. (2-25), which we repeat here for convenience:

$$\xi = 3 - 2 \left. \frac{\partial \ln V}{\partial \ln \epsilon} \right|_F - \frac{3}{2} \frac{(NV)}{(k_B \theta)^2} \left(\frac{m}{M} \right) \frac{N}{N'} \Phi(\chi) \quad (4-7)$$

where $\chi = T/\theta$, and

$$\begin{aligned} \Phi(\chi) = \chi \left\{ \frac{1}{20} \left(\frac{2N'}{N} \right)^{\frac{2}{3}} \left[\frac{3}{8} \frac{G_6(1/\chi)}{G_4(1/\chi)} - \frac{3}{2} \left(\frac{N'}{2N} \right)^{\frac{2}{3}} \left(\frac{1}{\chi} \right)^2 \right] L_4(2\chi) \right. \\ \left. - \frac{1}{3} \left[\frac{3}{8} \frac{G_6(1/\chi)}{G_4(1/\chi)} - \frac{3}{2} \left(\frac{N'}{2N} \right)^{\frac{2}{3}} \left(\frac{1}{\chi} \right)^2 \right] L_2(2\chi) \right\} . \end{aligned} \quad (4-7a)$$

It is the term proportional to $\Phi(\chi)$ that is new in this work, and which is due to virtual multiphonon processes. We have shown in Chapter II that as $\chi \rightarrow \infty$, $\Phi(\chi) \propto 1/\chi^2$, while as $\chi \rightarrow 0$, $\Phi(\chi) \propto A+B\chi^2$. We thus have from this term a contribution to S which varies as T^3 and as $1/T$ in the low and high temperature limits respectively, and behaves in this respect exactly as the "phonon drag" contribution to S is predicted to behave.⁸ It

must be emphasized at this point that throughout the present calculation we have assumed the phonon system to be in equilibrium. Thus, the term proportional to $\phi(\chi)$ presumably exists independent of and in conjunction with the term due to phonon drag. Therefore, it is clearly of interest to study the magnitude of this term to see how it behaves and how large it is relative to the observed "phonon drag" humps which appear in the thermopowers of various metals.

Using the fact that $S = S_0 \xi$, where $S_0 \propto T$, we can write the thermopower due to Eq. (4-7) in the form

$$S = S_1 \chi - S_2 \chi \phi(\chi) \quad (4-8)$$

where

$$S_1 = \left[3 - 2 \frac{\partial \ln V}{\partial \ln \xi} \right] S_0(\theta) \quad (4-8a)$$

and

$$S_2 = \frac{3}{2} \frac{(NV)^2}{(k_B \theta)^2} \left(\frac{m}{M} \right) \frac{N}{N'} S_0(\theta) \quad (4-8b)$$

The first term in (4-8) is the usual electron-diffusion thermopower term which varies linearly with temperature. The second is the correction due to virtual multiphonon processes, which we now wish to investigate in greater detail. The quantity $\chi \phi(\chi)$ is a function which is the same for all metals of the same valency, while the coefficient S_2 is an amplitude factor which will vary

from one metal to another. In Fig. 9 we show the behavior of $\chi^*(\chi)$, as determined by a numerical calculation for a monovalent metal.

Fig. 9 - The Function $\chi^*(\chi)$ Related to Virtual Multiphonon Thermopower

We note that $-\chi^*(\chi)$ rises rapidly to a maximum of about 0.48 at $T \approx 0.4\theta$, and then dies off fairly rapidly, being less than 0.1 for $T > \theta$. Such behavior ought certainly to be observable, should the amplitude S_2 be sufficiently great. In Table III, we present data relating to this amplitude for the monovalent metals. We note immediately from Table III and Fig. 9 that the magnitude of Eq. (4-8b) is such that it should indeed provide a significant contribution to the total electron-diffusion thermopower as given by Eq. (4-8). The question that arises, then, is to what extent has this effect been misinterpreted as, or masked by, phonon drag?

	$\theta(^{\circ}\text{K})^a$	$\epsilon(\text{eV})^a$	M/m	$S_2(\mu\text{V/deg})$
Li	335	4.7	1.28×10^4	3.64
Na	156	3.1	4.24	1.55
K	91.1	2.1	7.20	1.06
Rb	55.5	1.8	15.7	0.682
Cs	39.5	1.5	24.4	0.515
Cu	343	7.0	11.7	0.574
Ag	226.2	5.5	19.9	0.399
Au	102.4	5.5	36.2	0.481

TABLE III Thermopower Correction Amplitudes for Monovalent Metals. (a) Representative values from Kittel.²⁴

Is there any way in which virtual multiphonon-mediated electron diffusion can be separated from true phonon drag? In an attempt to answer these questions we turn to a survey of the present status of phonon drag thermopower.

It would appear that phonon-drag thermopower is one of those areas of physics where a lot can be done in a formal sense, but very little can be done in the practical sense of comparing theory with experiment, simply because the theory involves too many quantities about which little is known. For example, one of the more recent expressions for the thermopower contribution S_g due to phonon drag is that derived by Bailyn:²⁵

$$S_g = \frac{k_B}{ie} \sum_{j,q} \left[\frac{\partial n(j,q)}{\partial E_g} \right] \sum^{(19)} \alpha(j,q; k, k')$$

$$\times \left[v(k) \tau(k) - v(k') \tau(k') \right] - v(j,q)$$

$$\times \left\{ \sum v^2(k) \tau(k) \left[-\partial f^0 / \partial E \right] \right\}^{-1} \quad (4-9)$$

In this awesome expression, $\alpha(j,q; k, k')$ is the probability relative to all other things that might happen to it that a phonon of polarization j and wave vector q will scatter an electron from state k in band ℓ to state k' in band ℓ' . The v 's and τ 's are group velocities and (anisotropic) relaxation times for electrons in the states by which they are labeled. The exact details of Eq. (4-9) are, however, unimportant. What is important is that it depends strongly upon inputs, especially the α 's, about which very little can be said. Thus, it is virtually impossible to produce from equations like (4-9) an unambiguous theoretical prediction for S_g which can be compared with experiment. In the past, for example,¹³ it has been assumed that the α 's are constants which can be removed from the summation in which they occur, and their values then adjusted such that S_g gives the best agreement with observed deviations in S from linearity in T . One can proceed, of course, to more esoteric formulations²⁵ for the quantities appearing in Eq. (4-9), but in the end not much more can

be concluded then that within a range of reasonable parameters for a given model, phonon drag can be made to account for observed experimental behavior.

Such an approach to phonon drag is acceptable, provided one assumes that this mechanism is the only major cause for S not to vary linearly with T . We now propose that virtual multiphonon processes also provide a contribution to S which is non-linear in T and which is significant in precisely the same temperature region where phonon drag effects are expected to occur. A question therefore arises as to whether or not existing interpretations of the low-temperature thermopowers of metals are accurate.

In order to gain a feeling for the types of effects we are discussing here, we present in Figures 10-12 the thermopowers of the monovalent metals.

Fig. 10 - Thermopower of Noble Metals²⁶

Fig. 11 - Thermopower of Alkali Metals²⁷

Fig. 12 - Thermopower of Li²⁶

The deviations from linear behavior are quite marked, and are of order $1 \mu\text{V}/\text{deg}$ in most cases. This is the same order of magnitude as would be predicted from Eq. (4-8) (cf. Table III). The location of the maximum deviation, however, is typically around $T/\theta = 0.2$, while Eq. (4-8) peaks at a somewhat higher temperature, $T = 0.4\theta$. This may be the result of the approximations made in our calculation. On the other hand, should it indeed turn out that the contribution to S due to virtual multiphonon processes does peak at a temperature higher than that due to phonon drag, there is some hope that observed curves might be resolved into two superimposed curves, thus demonstrating unambiguously the operation of this mechanism. In this regard, the oscillatory behavior in the thermopower of Na is somewhat interesting, though such behavior can also be produced with appropriate assumptions from phonon-drag con-

siderations alone.¹³

It has recently been suggested to us²⁸ that while in a given metal the separation of phonon-drag and "phony phonon-drag" effects may not be possible, an unambiguous demonstration of the presence of our mechanism may be possible through an investigation of the thermopowers of a series of alloys of the same host metal. This is so because it is to be expected that the presence of impurities will affect the two contributions in different ways. The magnitude of the phonon-drag contribution to the thermopower is dependent upon the relative probability that a phonon will scatter with an electron as opposed to all other scattering mechanisms.⁸ Adding impurities gives rise to the possibility of phonon-impurity scattering, and thus reduces the phonon-drag thermopower. If we assume the force constants to be unaffected by the presence of impurities, then the mass difference, ΔM , between host and impurity ions will be the primary factor in determining the amount of phonon-impurity scattering, and simple theories^{1,29} predict that the inverse relaxation time $1/\tau_{\text{imp}}$ for scattering of phonons by impurities should go as $(\Delta M/M)^2$.

Our mechanism, on the other hand, is affected by the presence of impurities in a different way. First and most important, the presence of impurities will give rise to the "virtual recoil" effects predicted by Eq. (3-21), and these will contribute to the thermopower in the amount by which the residual resistance contributes to the total resistivity. This contribution will, in a

first approximation, depend upon the valence difference, Δz , between host and impurity ions, and not upon the mass difference. A second and somewhat less important contribution arises from the perturbation of the phonon spectrum due to the presence of impurities. It is well-known³⁰ that heavy and light impurities give rise to resonance and localized modes of low and high frequency, respectively. Summations of the type (3-14), which go as ω^{-2} , ought thus to be somewhat enhanced by heavy impurities and reduced by light impurities. It thus seems likely that starting with a given metal, and then comparing its thermopower with those of alloys chosen specifically to modify phonon-drag or "phony phonon-drag" in a given way, the two effects may indeed be separable.

If for the moment we suppose that the peaks of the two contributions to S do occur at the same temperature, we can subtract the maximum deviation $S_2\chi^\Phi(\chi)_{\max}$ due to virtual multiphonon processes from the observed maximum deviation, $\Delta S_{\max}$, and thus estimate the deviation due to phonon drag, ΔS_g . These estimates are presented in Table IV and were obtained by extrapolating the linear portion of the S - T curve to $T=0$ and subtracting the extrapolated value from the observed value at the local maximum in S . Table IV is of interest for the fact that it points out that "true" phonon drag in some of the alkali metals may well be negative. Such a negative phonon drag hump is the prediction of the simplest theories of phonon drag, in which electron-phonon unklapp processes are neglected, and would be expected in the

	$S_2 \chi^{\phi}(\chi)_{\max}$	$\Delta S_{\max}$	$\Delta S_g = \Delta S_{\max} - S_2 \chi^{\phi}(\chi)_{\max}$
Li	1.74	1.00	-0.74
Na	0.74	-0.00	-0.74
K	0.51	0.26	-0.25
Rb	0.33	1.56	1.23
Cs	0.25	3.03	2.78
Cu	0.28	1.10	0.82
Ag	0.19	1.06	0.87
Au	0.23	1.06	0.83

TABLE IV - Estimate of Thermopower Deviation ΔS_g due to True Phonon Drag. All values are in $\mu V/\text{deg}$.

limit of very low temperatures for a material with a spherical Fermi surface.⁸ Table IV suggests that such simple considerations may be closer to the truth than has been realized. It may well be that important trends in the true phonon drag have been masked by a virtual multiphonon contribution of the same order of magnitude, thus confusing the theoretical interpretation of experimental results. Thus, when proper account is taken of the contribution we have derived here, phonon drag theory may advance in consequence, and perhaps more definitive results can be obtained.

The examples presented in this Chapter clearly show that energy-dependent second-order terms of the type we have considered lend new insight into the problem of thermoelectricity. A reinter-

pretation of past results in the light of this theory may well advance our knowledge of transport phenomena in metals and alloys. Our results are summarized and discussed in the next Chapter.

V - Discussion and Conclusions

In the preceding chapters, we have shown how second-order corrections to the electron scattering probability in a metal, while not themselves large in magnitude, can be important in phenomena such as the thermoelectric power in which it is the energy derivative of this scattering probability that comes into play. This importance arises because of the strong energy dependence of second-order terms involving a virtual phonon in the intermediate state. Such terms are proportional to the Fermi function, and thus have large derivatives in the region of the Fermi level.

As a consequence of the energy-dependence thus introduced into the scattering cross sections for electrons by both impurities and phonons, two significant effects arise. First, as discussed in Chapter II, there exists a term in the electron-diffusion thermopower of a pure metal which is of the same order of magnitude, and has the same temperature dependence, as the term caused by phonon drag. The existence of this term casts new light upon experimental results for the thermopowers of metals at lower temperatures, and suggests that previous theoretical work on phonon drag has been hampered by the assumption that this mechanism was alone responsible for deviations in S from linear behavior. Important trends in the phonon-drag component of S may well have been obscured by the virtual multiphonon term, thus preventing insights that might have aided theoretical work in this area.

In this respect, it is felt that the term due to virtual multiphonon processes should be much less sensitive to the details of the model used in calculating it than the phonon-drag term, which (cf. Eq. 4-9) depends strongly on the assumptions and model used in calculating it. This holds out the hope that it may not be too difficult to subtract the effect of multiphonon processes from the observed experimental curves, and thus make possible the study of "true" phonon drag. An experimental study formulated along the lines suggested in Chapter IV would be very useful in demonstrating unambiguously the presence of the "phony phonon drag" mechanism, and might also reveal how closely the magnitude corresponds to our rough estimates.

The second important effect arising from the processes considered in this work is a term in the impurity dominated thermopower which is of the same order of magnitude as terms previously considered in theories of impurity thermopower, and which is proportional to the sign of the difference between the potentials of the solute and solvent. This effect is much easier to demonstrate than the pure-metal "phony phonon drag" effect, simply because it can be shown on quite general grounds (cf. Eq. 3-2) that at sufficiently low temperatures impurity scattering must dominate the thermopower. We feel that the examples presented in Chapter IV offer convincing evidence that the mechanism of virtual recoil is present in the low-temperature thermopowers of the systems considered.

In light of the present work, then, it is clear that any attempt to deal quantitatively with thermoelectric effects in metals and alloys requires a consideration of virtual multiphonon and virtual recoil effects. A more detailed theory than the present one must inevitably fall back upon numerical computation, so as to include the effects of, for example, the Bloch nature of the electron wave functions, the energy dependence of the scattering pseudopotential, and (in the case of alloys) the increasing perturbation of the phonon spectrum with concentration of impurities. This last effect, it should be noted, is believed by us to account for the concentration dependence found in the low-temperature thermopowers of alkalis in alkalis¹⁷ but not predicted by Eq. (4-1), which was derived assuming the phonon spectrum to be unperturbed by the presence of impurities. In this respect, it is of interest to note that in the PdH system, where we treat virtual recoil independent of the phonon spectrum of the host lattice, the experimental thermopowers are approximately independent of concentration,¹⁸ as predicted by Eq. (4-6). Some work on corrections to the theory of Chapter III, based on corrections to the phonon spectrum using the recently developed lattice dynamics of Taylor and Wu³¹ is currently in progress.

While there are thus many areas in which the quantitative aspects of this theory can be improved, there is no reason to believe that the qualitative results ought not to be accurate. We thus conclude that virtual recoil and "phony phonon drag" are concepts which must enter into any real understanding of thermoelectric

effects .

Appendix

Energy-Dependent Second-Order Contributions to the T-Matrix

In this Appendix, we derive in detail Eqs. (2-4), thus showing how these strongly energy-dependent corrections arise. From Eqs. (2-2) and (2-3), we have

$$T = T^{(1)} + T^{(2)} \quad , \quad (A-1)$$

$$T^{(1)} = \sum_{\underline{k}, \underline{k}', s} V_{\underline{k}', \underline{k}} C_{\underline{k}'}^{\dagger} C_{\underline{k}} i(\underline{k} - \underline{k}') \cdot \hat{s} g(q, s) B_{qs} N \Delta(\underline{k} - \underline{k}' + \underline{q}) \quad (A-1a)$$

$$\begin{aligned} T^{(2)} = \sum_{\substack{\underline{k}_1, \underline{k}_2, \underline{k}_3, \underline{k}_4 \\ q, s, q', s', q'', s''}} & \left\{ -\frac{i}{2} V_{\underline{k}_1, \underline{k}_2} C_{\underline{k}_1}^{\dagger} C_{\underline{k}_2} (\underline{k}_2 - \underline{k}_1) \cdot \hat{s} (\underline{k}_2 - \underline{k}_1) \cdot \hat{s}' g(q, s) \right. \\ & \times g(q', s') B_{qs} B_{q's'} N \Delta(\underline{k}_2 - \underline{k}_1 + \underline{q} + \underline{q}') (E - H_0)^{-1} \\ & \times V_{\underline{k}_3, \underline{k}_4} C_{\underline{k}_3}^{\dagger} C_{\underline{k}_4} (\underline{k}_4 - \underline{k}_3) \cdot \hat{s}'' g(q'', s'') B_{q''s''} N \Delta(\underline{k}_4 - \underline{k}_3 + \underline{q}'') \\ & - \frac{i}{2} V_{\underline{k}_1, \underline{k}_2} C_{\underline{k}_1}^{\dagger} C_{\underline{k}_2} (\underline{k}_2 - \underline{k}_1) \cdot \hat{s}'' g(q'', s'') B_{q''s''} N \Delta(\underline{k}_2 - \underline{k}_1 + \underline{q}'') \\ & \times (E - H_0)^{-1} V_{\underline{k}_3, \underline{k}_4} C_{\underline{k}_3}^{\dagger} C_{\underline{k}_4} (\underline{k}_4 - \underline{k}_3) \cdot \hat{s} (\underline{k}_4 - \underline{k}_3) \cdot \hat{s}' g(q, s) \\ & \left. \times g(q', s') B_{qs} B_{q's'} N \Delta(\underline{k}_4 - \underline{k}_3 + \underline{q} + \underline{q}') \right\} \end{aligned}$$

(A-1b)

We see from Eq. (A-1b) that we have terms to consider which are of the form

$$a) \quad C_{k_1}^\dagger C_{k_2} B_{q_3} B_{q'_4} (\epsilon - H_0)^{-1} C_{k_3}^\dagger C_{k_4} B_{q''_5}$$

and

$$b) \quad C_{k_1}^\dagger C_{k_2} B_{q''_3} (\epsilon - H_0)^{-1} C_{k_3}^\dagger C_{k_4} B_{q_5} B_{q'_6}$$

We wish to choose the indices on terms (a) and (b) in such a way that Eq. (A-1b) adds coherently with Eq. (A-1a), in which electrons are scattered from $\underline{k}$ to $\underline{k}'$ with the absorption/emission of a phonon of wave vector $\underline{q}$. There are several ways in which this can be done, and each gives rise to a different "energy denominator" $(\epsilon - H_0)^{-1}$. For the electron operators, the two possibilities are

$\underline{1}$	$\underline{2}$
$k_1 = k'$	$k_1 = k''$
$k_2 = k''$	$k_2 = k$
$k_3 = k''$	$k_3 = k'$
$k_4 = k$	$k_4 = k''$

while for the phonon operators the four possibilities are

$$\text{A} \quad a_{q's'} \frac{1}{E-H_0} a_{q's'}^\dagger B_{qs}$$

$$\text{B} \quad B_{qs} a_{q's'} \frac{1}{E-H_0} a_{q's'}^\dagger$$

$$\text{C} \quad a_{q's'}^\dagger \frac{1}{E-H_0} a_{q's'} B_{qs}$$

$$\text{D} \quad B_{qs} a_{q's'}^\dagger \frac{1}{E-H_0} a_{q's'}$$

The energy denominators that arise in each of these cases are, in an obvious notation,

<u>CASE</u>	<u>$(E-H_0)$</u>
1A	$E_k - E_{k''} - \hbar\omega_{q's'} \pm \hbar\omega_{qs} = E_{k'} - E_{k''} - \hbar\omega_{q's'}$
1B	$E_k - E_{k''} - \hbar\omega_{q's'}$
1C	$E_k - E_{k''} + \hbar\omega_{q's'} \pm \hbar\omega_{qs} = E_{k'} - E_{k''} + \hbar\omega_{q's'}$
1D	$E_k - E_{k''} + \hbar\omega_{q's'}$
2A	$E_{k''} - E_{k'} - \hbar\omega_{q's'} \pm \hbar\omega_{qs} = - (E_k - E_{k''} + \hbar\omega_{q's'})$
2B	$E_{k''} - E_{k'} - \hbar\omega_{q's'} = - (E_{k'} - E_{k''} + \hbar\omega_{q's'})$
2C	$E_{k''} - E_{k'} + \hbar\omega_{q's'} \pm \hbar\omega_{qs} = - (E_k - E_{k''} - \hbar\omega_{q's'})$
2D	$E_{k''} - E_{k'} + \hbar\omega_{q's'} = - (E_{k'} - E_{k''} - \hbar\omega_{q's'})$

Similarly, the numerators in each of these cases are

CASE	NUMERATOR
1A	$C_k^+ C_k C_k^+ C_k a_{q's}^+ a_{q's}^+ B_{qs} =$
1B	$C_k^+ C_k C_k^+ C_k B_{qs} a_{q's}^+ a_{q's}^+ =$
1C	$C_k^+ C_k C_k^+ C_k a_{q's}^+ a_{q's}^+ B_{qs} =$
1D	$C_k^+ C_k C_k^+ C_k B_{qs} a_{q's}^+ a_{q's}^+ =$
	$\left. \begin{array}{l} \\ \\ \\ \end{array} \right\} (1-f_k'')(1+n_{q's}) C_k^+ C_k B_{qs}$
2A	$C_k^+ C_k C_k^+ C_k a_{q's}^+ a_{q's}^+ B_{qs} =$
2B	$C_k^+ C_k C_k^+ C_k B_{qs} a_{q's}^+ a_{q's}^+ =$
2C	$C_k^+ C_k C_k^+ C_k a_{q's}^+ a_{q's}^+ B_{qs} =$
2D	$C_k^+ C_k C_k^+ C_k B_{qs} a_{q's}^+ a_{q's}^+ =$
	$\left. \begin{array}{l} \\ \\ \\ \end{array} \right\} -f_k''(1+n_{q's}) C_k^+ C_k B_{qs}$

Taking appropriate matrix elements $T_{k'k}^{(\pm q)}$, we can combine the terms as indicated, including all the relevant factors from Eq. (A-1b).

A factor of 2 is introduced due to the fact that as one sums over q , q' and q'' , there will be a coherent term when any of the two wave-vectors on the one side equal the one on the other.

1A + 2D

$$-N^2 V_{k'k''} V_{k''k} i(\underline{k}''-\underline{k}') \cdot \underline{\hat{s}}' (\underline{k}-\underline{k}'') \cdot \underline{\hat{s}}' (\underline{k}-\underline{k}'') \cdot \underline{\hat{s}} g^2(q',s') g(q,s) \left[\frac{n_{qs}}{n_{qs}+1} \right]^{1/2} \\ \times \frac{1+n_{q's'}-f_{k''}}{\epsilon_{k'}-\epsilon_{k''}-\hbar\omega_{q's'}} \Delta(\underline{k}-\underline{k}''+\underline{q}-\underline{q}') \Delta(\underline{k}''-\underline{k}'+\underline{q}') .$$

1B + 2C

$$-N^2 V_{k'k''} V_{k''k} i(\underline{k}''-\underline{k}') \cdot \underline{\hat{s}}' (\underline{k}-\underline{k}'') \cdot \underline{\hat{s}}' (\underline{k}-\underline{k}'') \cdot \underline{\hat{s}} g^2(q',s') g(q,s) \left[\frac{n_{qs}}{n_{qs}+1} \right]^{1/2} \\ \times \frac{1+n_{q's'}-f_{k''}}{\epsilon_{k'}-\epsilon_{k''}-\hbar\omega_{q's'}} \Delta(\underline{k}-\underline{k}''+\underline{q}-\underline{q}') \Delta(\underline{k}-\underline{k}''+\underline{q}') .$$

1C + 2B

$$-N^2 V_{k'k''} V_{k''k} i(\underline{k}''-\underline{k}') \cdot \underline{\hat{s}}' (\underline{k}-\underline{k}'') \cdot \underline{\hat{s}}' (\underline{k}-\underline{k}'') \cdot \underline{\hat{s}} g^2(q',s') g(q,s) \left[\frac{n_{qs}}{n_{qs}+1} \right]^{1/2} \\ \times \frac{n_{q's'}+f_{k''}}{\epsilon_{k'}-\epsilon_{k''}+\hbar\omega_{q's'}} \Delta(\underline{k}-\underline{k}''+\underline{q}-\underline{q}') \Delta(\underline{k}''-\underline{k}'+\underline{q}') .$$

1D + 2A

$$-N^2 V_{k'k''} V_{k''k} i(\underline{k}''-\underline{k}') \cdot \underline{\hat{s}}' (\underline{k}-\underline{k}'') \cdot \underline{\hat{s}}' (\underline{k}-\underline{k}'') \cdot \underline{\hat{s}} g^2(q',s') g(q,s) \left[\frac{n_{qs}}{n_{qs}+1} \right]^{1/2} \\ \times \frac{n_{q's'}+f_{k''}}{\epsilon_{k'}-\epsilon_{k''}+\hbar\omega_{q's'}} \Delta(\underline{k}''-\underline{k}'+\underline{q}-\underline{q}') \Delta(\underline{k}-\underline{k}''+\underline{q}') .$$

These may be further combined, and if we keep only those parts of the resulting sum proportional to a Fermi function, we obtain

$$(1A + 2D) + (1C + 2B)$$

$$N^2 V_{k'k''} V_{k''k} i(\underline{k}'' - \underline{k}') \cdot \hat{S}'(\underline{k} - \underline{k}'') \cdot \hat{S}'(\underline{k} - \underline{k}') \cdot \hat{S} g^2(q', s') g(q, s) \left[\frac{n_{qs}}{n_{qs+1}} \right]^{1/2} \\ \times \frac{2\hbar\omega_{q's'} f_{k''}}{(\epsilon_{k'} - \epsilon_{k''})^2 - (\hbar\omega_{q's'})^2} \Delta(\underline{k}'' - \underline{k}' + \underline{q} - \underline{q}') \Delta(\underline{k}'' - \underline{k}' + \underline{q}') \quad (A-2)$$

$$(1B + 2C) + (1D + 2A)$$

$$N^2 V_{k'k''} V_{k''k} i(\underline{k}'' - \underline{k}') \cdot \hat{S}'(\underline{k} - \underline{k}'') \cdot \hat{S}'(\underline{k}' - \underline{k}') \cdot \hat{S} g^2(q', s') g(q, s) \left[\frac{n_{qs}}{n_{qs+1}} \right]^{1/2} \\ \times \frac{2\hbar\omega_{q's'} f_{k''}}{(\epsilon_{k'} - \epsilon_{k''})^2 - (\hbar\omega_{q's'})^2} \Delta(\underline{k}'' - \underline{k}' + \underline{q} - \underline{q}') \Delta(\underline{k}'' - \underline{k}' + \underline{q}') \quad (A-2a)$$

We note that if we interchange k and k' in Eq. (A-2), it becomes

$$N^2 V_{kk''} V_{k''k'} i(\underline{k}'' - \underline{k}) \cdot \hat{S}'(\underline{k}' - \underline{k}'') \cdot \hat{S}'(\underline{k}' - \underline{k}') \cdot \hat{S} g^2(q', s') g(q, s) \left[\frac{n_{qs}}{n_{qs+1}} \right]^{1/2} \\ \times \frac{2\hbar\omega_{q's'} f_{k''}}{(\epsilon_k - \epsilon_{k''})^2 - (\hbar\omega_{q's'})^2} \Delta(\underline{k}' - \underline{k}'' + \underline{q} - \underline{q}') \Delta(\underline{k}'' - \underline{k} + \underline{q}') \quad (A-2b)$$

which is the same as Eq. (A-2a), but opposite in sign. Likewise, Eq. (A-1a) changes sign if k and k' are interchanged. Thus, for purposes of computing $|T|^2$ one need only take Eq. (A-2a) as the 2nd order term in T , multiplying it by a factor of two. One thus

obtains directly Eq. (2-4b), upon making use of the Δ -function relations.

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