

## Effect of Phonon- and Electron-Electron-Induced $s$ - $d$ Transitions on the Thermopower of the Transition Metals\*

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Using a two-band model for the conduction electrons of the transition metals and assuming that only the lighter carriers contribute to charge transport, the effects of phonon-induced and electron-electron interband  $s$ - $d$  transitions are investigated. Provided that the total thermopower, not including the phonon-drag contribution, is given by  $S_T = (1/W_T) \sum_i W_i S_i$ , we find that interband electron-electron scattering may manifest itself in the total thermopower at low as well as at high temperatures. At lowest temperatures (near  $T/\Theta_D = 0.03$ ), depending upon the magnitudes and temperature dependences of electron-electron- and electron-phonon-scattering contributions, a well-defined extremum of the order of  $1\mu\text{V}/^\circ\text{K}$  may appear. At high temperatures the total thermopower, weighted as indicated above, may be dominated by electron-electron-scattering effects, and in that event, will exhibit a  $T^2$  temperature dependence. The effect of the variation of some of the parameters and the influence of the addition of impurities are discussed and the theoretical total thermopower is compared with available experimental data.

### I. INTRODUCTION

Recently there has been a resurgence of interest in the low-temperature resistivities of transition metals.<sup>1-4</sup> Although it has been known for some time<sup>5</sup> that the electrical resistivity  $\rho$  of some of the transition metals varies as  $T^2$  at the lowest temperatures, concomitant linear variations in the thermal resistivities  $W$  have only recently been observed. The origin of the  $T^2$  dependence of  $\rho$  is a problem of long standing. Although Baber<sup>6</sup> had proposed that electron-electron scattering was the cause for this variation, evidence to establish this proposal as valid has been slow in coming. Two of the major criticisms of Baber's proposal are the following:

(a)  $\rho$  is observed to vary as  $T^2$  in only a few of the transition metals rather than all of them as might be expected.

(b) Experimentally it is found that electron-electron scattering contributes a  $T^2$  term to  $\rho$  and consequently dominates the total resistivity at lowest temperatures where the contribution from phonon scattering eventually varies as  $T^5$ . Similarly at the highest temperatures where the lattice resistivity varies linearly with temperature, the electron-electron-scattering contribution should again be dominant. This latter behavior, however, has not been observed.

In an earlier paper,<sup>7</sup> one of us (L. C.) attempted to answer the first objection by a careful analysis of available experimental data. He was able to show that one could give a consistent theoretical interpretation of the ideal resistivities of the transition metals in terms of a two-band model and assuming (in all of the metals) the existence of a  $T^2$  term which may, however, be masked to a greater or lesser

degree by phonon scattering in different metals of the series.

Appel<sup>8</sup> attempted to answer the second objection to electron-electron scattering by appealing to numerical estimates of the two resistivity contributions. He argues that in some metals the  $T^2$  contribution will only "peak through" the phonon contribution at extremely high temperatures—near or above the melting point.

With increasing evidence for and interest in electron-electron scattering in transition metals, it seemed appropriate to consider the effect of these scattering processes on another electron transport phenomenon, the thermoelectric power. The calculation has been carried forward within the framework of the two-band model introduced by Mott<sup>9</sup> many years ago. Although the work assumes the "standard band structure" for the two bands, we have extended Mott's model somewhat by placing no *a priori* restriction on the curvatures of the bands; i. e., either the " $s$  band" or the " $d$  band" may be electron- or holelike. We also allow  $k_s > k_d$  as well as  $k_s < k_d$ , where  $\vec{k}_s$ ,  $\vec{k}_d$  are the Fermi wave vectors. Hence we consider four different situations, corresponding to two bands of identical or opposite curvature, with  $k_s > k_d$  and  $k_s < k_d$ . The subscripts  $s$  and  $d$  in this paper are used simply to denote a light-mass conduction band and a high-mass narrow band, respectively.

As we shall see, it is not possible to classify the results uniquely in terms of the above-mentioned four possibilities since two other parameters, the effective-mass ratio  $m_d/m_s$  and the "momentum gap"  $\eta$  defined by Eq. (6) which was introduced by Colquitt,<sup>7</sup> have a profound effect on the results.

In most situations electron-phonon scattering

dominates over electron-electron interband scattering in its effect on the thermopower at all temperatures and the temperature dependence of the thermopower is linear at elevated temperatures ( $T/\Theta_D > 1$ ). However, when the momentum gap is not too small, say 0.3 or more, we do find instances where the electron-electron contribution to the thermopower exhibits a well-defined extremum at very low temperatures. We also find conditions under which electron-electron interband scattering may dominate the effect of phonon-induced scattering at high temperatures and manifest itself in a more rapid temperature dependence (roughly  $T^2$ ) of the total thermopower.

In this investigation phonon drag was completely neglected. A more severe limitation, however, is the neglect of umklapp processes which in electron-electron scattering, at any rate, do not occur frequently enough to modify the transport coefficients significantly.<sup>10</sup> The reason appears to be that energy conservation severely restricts the possibility of electron-electron umklapp processes, in contrast to phonon-phonon or phonon-electron umklapp pro-

cesses. However, since umklapp processes depend sensitively on the details of the Fermi surface, it seemed to us that to include these processes in the parabolic band approximation would still not answer the difficult question of their importance in a more realistic situation. The calculation is, thus, in the spirit of a model calculation and we concern ourselves only with general qualitative conclusions.

In Secs. II and III, the effects of electron-phonon and electron-electron scattering on the different intrinsic transport properties are studied. In Sec. IV, the temperature dependence and sign of the total thermopower are discussed and figures for some typical cases are shown. In Sec. V, the effect of electron-electron scattering on the total thermopower at low and at elevated temperature is discussed and the results are compared with available experimental data.

## II. PHONON SCATTERING

The effects of electron-phonon scattering on the electrical and thermal resistivities of the transition metals in terms of a two-band model are given by<sup>7,11</sup>

$$\rho_{\text{pho}}(T) = \frac{3m_s P_{ss} h^3}{8\pi(2m_s)^{1/2} e^2 E_F^2} \left(\frac{T}{\Theta_D}\right)^3 \left\{ 2^{-1/3} n^{-2/3} \left(\frac{T}{\Theta_D}\right)^2 J_5\left(\frac{\Theta_D}{T}\right) + \omega_d \frac{m_d}{m_s} \frac{P_{sd}}{P_{ss}} \left[ J_3\left(\frac{\Theta_D}{T}\right) - J_3\left(\frac{\Theta_E}{T}\right) \right] \right\} \quad (1)$$

and

$$W_{\text{pho}}(T) = \frac{27m_s P_{ss} h^3 T}{16\pi^5 (2m_s)^{1/2} E_F^4} \left(\frac{T}{\Theta_D}\right)^3 \left(\frac{E_F}{k_B T}\right)^2 \left( J_5\left(\frac{\Theta_D}{T}\right) + 2^{-1/3} n^{-2/3} \left(\frac{T}{\Theta_D}\right)^2 \left[ \frac{2}{3} \pi^2 J_5\left(\frac{\Theta_D}{T}\right) - \frac{1}{3} J_7\left(\frac{\Theta_D}{T}\right) \right] + \omega_d \frac{m_d}{m_s} \frac{P_{sd}}{P_{ss}} \left\{ \frac{2}{3} \left[ J_5\left(\frac{\Theta_D}{T}\right) - J_5\left(\frac{\Theta_E}{T}\right) \right] + \frac{2}{3} \pi^2 \left[ J_3\left(\frac{\Theta_D}{T}\right) - J_3\left(\frac{\Theta_E}{T}\right) \right] \right\} \right). \quad (2)$$

Here  $n$  is the effective number of the lighter carriers per atom,  $\omega_d$  is the statistical weight (degeneracy) of the  $d$  states,  $P_{ss}$  and  $P_{sd}$  are proportional to the square of the matrix elements for phonon-induced  $s$ - $s$  and  $s$ - $d$  transitions, respectively,  $E_F$  is the Fermi energy,  $\Theta_D$  the Debye temperature, and  $k_B \Theta_E$  is the minimum energy of phonons that can induce  $s$ - $d$  transitions. The transport integrals  $J_n(x)$  are defined in Eq. (7).

In an early work, Mott<sup>9</sup> argues that the resistivities (electrical and thermal) due to phonon-induced  $s$ - $d$  transitions would contain a factor  $N_d(E_F)$ , the density of states in the  $d$  band. Wilson,<sup>11</sup> on the other hand, showed that if not all states on the  $d$  Fermi sphere could be reached from a given  $s$  state by phonon-induced transitions, the proportionality factor should be  $\omega_d m_d$ . In Mott's case, one assumes that the upper limit of the phonon wave vector  $|\vec{q}|$  inducing  $s$ - $d$  transitions is equal to  $k_s + k_d$ ,  $k_s$ , and  $k_d$  being the Fermi momenta of  $s$ - and  $d$ -type carriers, respectively. In the other case, the upper limit is

the Debye wave vector  $|\vec{q}_D|$ .

There is little distinction between these two cases when one is computing the magnitudes of the resistivities. However, as pointed out by Wilson, the thermopowers in the two cases are very different. In the first case in which one assumes that the largest momentum transferred is  $q_{\text{max}}^I = k_s + k_d < q_D$ , a situation which seems hardly realized in nature, the thermopower would be augmented by a factor proportional to  $\partial N_d(\epsilon)/\partial \epsilon$  which always has the same sign. In the second case where the largest momentum transferred is  $q_{\text{max}}^{II} = q_D < k_s + k_d$ , the thermopower will contain a contribution from  $\partial \Theta_E/\partial \epsilon$  which may be positive or negative depending on the relative magnitudes of the Fermi momenta and the relative curvatures of the two bands [see Eq. (5)].

We shall restrict ourselves to the latter case so that Wilson's model is the appropriate one. This is the reason that in Eqs. (1) and (2),  $\Theta_D$  appears in the transport integrals instead of  $\hbar u(k_s + k_d)/k_B$ , where  $u$  is the velocity of sound.

We now assume that the following expression, derived by Ziman<sup>12</sup> for low temperatures, is valid also when we allow interband as well as intraband transitions:

$$S_{\text{pho}} = \frac{\pi^2 k_B^2 T}{3e} \left[ -\frac{L_T}{L_0} \frac{\partial \ln \rho}{\partial \epsilon} + \left(1 - \frac{L_T}{L_0}\right) \frac{\partial \ln \sigma k_F}{\partial \epsilon} + \frac{3}{2\pi^2 E_F} \left(\frac{\Theta_D}{T}\right)^2 \left(\frac{k_F}{q_D}\right)^2 \frac{L_s}{L_0} \right]_{\epsilon=E_F}. \quad (3)$$

We note that in the high-temperature limit, Eq. (3)

$$S_{\text{pho}} = \frac{\pi^2 k_B^2 T}{3e} \left( \frac{3}{2E_F} + \frac{L_T}{L_0} \left[ \frac{1}{2E_F} \left\{ A \frac{(T/\Theta_D)^2}{m_s E_F^2} J_5 \left(\frac{\Theta_D}{T}\right) \pm \frac{m_d}{q_D \hbar^2} \left(\frac{\Theta_D}{T}\right) \left[ (-1)^j \frac{m_d}{m_s} k_d^{-1} + k_s^{-1} \right] G \left(\frac{\Theta_E}{T}\right) \right\} \right] \right. \\ \left. \left\{ A \frac{(T/\Theta_D)^2}{m_s E_F} J_5 \left(\frac{\Theta_D}{T}\right) + \frac{m_d}{m_s} \left[ J_3 \left(\frac{\Theta_D}{T}\right) - J_3 \left(\frac{\Theta_E}{T}\right) \right] \right\} - \frac{L_s}{L_0} \frac{3}{2\pi^2 E_F} \left(\frac{\Theta_D}{T}\right)^2 \left(\frac{k_s}{q_D}\right)^2 \right) \quad (5)$$

using the relation

$$\eta = \Theta_E / \Theta_D = |k_s - k_d| / q_D \quad (6)$$

to calculate the derivative  $\partial \Theta_E / \partial \epsilon$ . The following quantities and abbreviations have been introduced:

$$J_n(x) = \int_0^x \frac{z^n}{(e^z - 1)(1 - e^{-z})} dz, \\ A = \frac{(6\pi^2)^{2/3} \hbar^2 P_{ss}}{4a^2 \omega_d P_{sd}}, \quad (7)$$

$$G\left(\frac{\Theta_E}{T}\right) = \frac{(\Theta_E/T)^3}{(e^{\Theta_E/T} - 1)(1 - e^{-(\Theta_E/T)})},$$

where  $a$  is the lattice parameter and  $L_0$ ,  $L_T$ , and  $L_s$  are the Lorentz numbers defined by

$$L_0 = \frac{1}{3} \pi^2 (k_B/e)^2, \\ L_T = (\rho_{ss} + \rho_{sd}) / T(W_{ss} + W_{sd}), \quad (8)$$

$$L_s = \rho_{ss} / T W_{ss}.$$

The upper sign in the numerator in Eq. (5) corresponds to the case  $k_d < k_s$ , the lower one to  $k_d > k_s$ , and  $j$  is equal to 2 in the case of an inverted  $d$  band, and equal to 1 otherwise.

The sign of  $e$  is that of the lighter carriers. In our model we assume only that the carriers described by one band are substantially heavier than those of the other and that the former do not contribute to the charge transport. The dominant

reduces to the well-known formula

$$S_{\text{pho}} = -\frac{\pi^2 k_B^2 T}{3e E_F} \left[ E_F \frac{\partial \ln \rho}{\partial \epsilon} \right]_{\epsilon=E_F}. \quad (4)$$

We now substitute the electrical resistivity as given by Eq. (1) into Eq. (3). We assume, of course, that the two scattering processes, intraband and interband, are independent and contribute additively to the total resistivity. For the Fermi surface  $\sigma$  and the Fermi momentum  $k_F$ , we put in the corresponding values of the lighter carriers and obtain

charge carriers may be either electrons or holes.

The discussion of the effect on the total thermopower of phonon-induced scattering is complicated by the fact that the intrinsic thermopower must be weighted by the corresponding thermal resistivity. What we expect is that for  $T/\Theta_D > 1$  the quantity in the largest parentheses in Eq. (5) will be constant and  $S_{\text{pho}}$  therefore proportional to  $T$ . Below this temperature the contribution decreases mainly because the ratio of the Lorentz number diminishes. Below  $\Theta_E$  the exponential decay of  $s$ - $d$  transitions further reduces the contribution and  $S_{\text{pho}}$  may even reverse sign.

### III. ELECTRON-ELECTRON SCATTERING

If we assume that one can define a relaxation time for these processes, then the change with time of the distribution of the carriers due to collisions is given by<sup>13</sup>

$$\frac{\partial f(\vec{v}, \vec{r})}{\partial t} \Big|_{\infty 11} = -\frac{f(\vec{v}, \vec{r}) - f^0(\vec{v}, \vec{r})}{\tau(\vec{v}, \vec{r})}. \quad (9)$$

If we denote by<sup>14</sup>

$$\mathcal{Q}_{\vec{k}_1 \vec{k}_2}^{\vec{k}'_1 \vec{k}'_2} d\vec{k}_2 d\vec{k}'_1 d\vec{k}'_2 \quad (10)$$

the *a priori* transition probability that an electron in state  $\vec{k}_1$  collides with an electron in state  $(\vec{k}_2, \vec{k}_2 + d\vec{k}_2)$  and that the two particles are scattered into the states  $(\vec{k}'_1, \vec{k}'_1 + d\vec{k}'_1)$ ,  $(\vec{k}'_2, \vec{k}'_2 + d\vec{k}'_2)$ , respectively, and furthermore assume the electrons to be free and describe the interaction by a screened Coulomb potential, then we obtain<sup>15</sup>

$$\dot{f}_{\vec{k}_1} \Big|_{\text{coll}} = - \frac{32\pi^3 e^4}{\hbar k_B T V^2 v_2 v_3 v_4} \phi_{\vec{k}} \iiint \frac{\delta(\vec{k}_1 + \vec{k}_2 - (\vec{k}_3 + \vec{k}_4))}{(|\vec{k}_3 - \vec{k}_1|^2 + g^2)^2} dA_2 dA_3 dA_4$$

$$\times \iiint \Theta(\epsilon_1 + \epsilon_2 - \epsilon_3 - \epsilon_4) f_1^0 f_2^0 (1 - f_3^0) (1 - f_4^0) d\epsilon_2 d\epsilon_3 d\epsilon_4. \quad (11)$$

Here the subscripts 1, 2, 3, and 4 stand for  $\vec{k}_1$ ,  $\vec{k}_2$ ,  $\vec{k}'_1$ , and  $\vec{k}'_2$ , respectively. The  $v_i$ 's are the corresponding Fermi velocities,  $V$  is the volume of the Brillouin zone,  $\phi_{\vec{k}}$  stands for  $(\phi_1 + \phi_2 - \phi_3 - \phi_4)$ , where the  $\phi_i$ 's are defined by

$$f_i = f_i^0 - \phi_i \frac{\partial f_i^0}{\partial \epsilon_i}, \quad (12)$$

$g$  is the reciprocal of the screening radius,  $\delta(\vec{k})$  is the Dirac  $\delta$ , and the surface elements  $dA_i$  are defined in the Appendix. For a discussion of the properties of the energy conservation function  $\Theta(\epsilon)$  we refer to Ziman.<sup>16</sup>

We should like to mention that implicit in Eq. (11) is the fact that as a result of momentum conservation, normal intraband transitions provide no relaxation.

For the calculational details, we refer the reader to the Appendix and quote here merely the result

$$\dot{f}_{\vec{k}_1} \Big|_{\text{coll}} = - \frac{128\pi^5 e^4}{\hbar^4 k_B T V^2 v_2 v_3 v_4}$$

$$\times [(\pi k_B T)^2 + (\epsilon_1 - E_F)^2] f^0(\epsilon_1) [1 - f^0(\epsilon_1)]$$

$$\times \phi_{\vec{k}} (K_2 K_3 K_4 / |\vec{k}_1|) I(\Delta_{\text{min}}, \Delta_{\text{max}}), \quad (13)$$

where the integral  $I(\Delta_{\text{min}}, \Delta_{\text{max}})$  is given by Eqs. (A14) and (A15).

We now use Eqs. (9), (12), (13), and the property

$$\frac{\partial f_i^0}{\partial \epsilon_i} = - \frac{f_i^0 (1 - f_i^0)}{k_B T} \quad (14)$$

to obtain

$$\tau(\vec{k}_1) = \frac{\hbar^7 V^2}{128\pi^5 e^4} \frac{1}{m_2 m_3 m_4} \frac{|\vec{k}_1|}{I(\Delta_{\text{min}}, \Delta_{\text{max}})}$$

$$\times \frac{1}{(\pi k_B T)^2 + (\epsilon_1 - E_F)^2}. \quad (15)$$

In the usual framework of the theory of macroscopic transport coefficients, the electrical conductivity is given to first order by

$$\sigma(\epsilon) = \frac{e^2}{12\pi^3 \hbar} \int v_1 \tau(\vec{k}_1) dA_1. \quad (16)$$

Inserting Eq. (15) into Eq. (16), we obtain

$$\sigma(E_F) = \frac{\hbar^8 V^2}{384\pi^9 e^2} \frac{1}{m_1 m_2 m_3 m_4}$$

$$\times \frac{1}{(k_B T)^2} \frac{K_1^4}{I(\Delta_{\text{min}}, \Delta_{\text{max}})}. \quad (17)$$

From this expression we see that the most effective scattering processes are those in which  $(s, d) = (d', d')$ . The contribution of this type of process is larger than those of any other electron-electron-scattering processes by a factor greater than  $N_d(E_F)/N_s(E_F)$ . Hereafter we restrict our attention to these processes only and obtain for the electrical resistivity

$$\rho_{e-e} = \frac{384\pi^9 e^2}{\hbar^8 V^2} m_s m_d^3 \frac{I(\Delta_{\text{min}}, \Delta_{\text{max}})}{k_s^4} (k_B T)^2. \quad (18)$$

The lower and upper limits of  $I(\Delta_{\text{min}}, \Delta_{\text{max}})$  depend on the relative magnitudes of  $k_s$  and  $k_d$  as follows:

$$k_s < k_d: \Delta_{\text{min}} = k_d - k_s, \quad \Delta_{\text{max}} = k_d + k_s, \quad (19a)$$

$$k_s > k_d: \Delta_{\text{min}} = k_s - k_d, \quad \Delta_{\text{max}} = 2k_d. \quad (19b)$$

We require, of course, that  $\Delta_{\text{min}} < \Delta_{\text{max}}$  and hence in case of  $k_s > k_d$  we get the condition

$$k_s < 3k_d.$$

If this condition is violated, then there is no way for a scattering process to occur conserving linear momentum. Substituting the appropriate values for  $I(\Delta_{\text{min}}, \Delta_{\text{max}})$  according to Eq. (A15), we finally obtain

$$\rho_{e-e} = A_{e-e} \frac{m_s m_d^3}{k_s^5 k_d} \left( \frac{(\chi+1)}{(\chi+1)^2 + \chi^2} - \frac{1-\chi}{(1-\chi)^2 + \chi^2} + \frac{1}{\chi} \tanh^{-1} 2\chi^2 \right) T^2 \quad \text{for } \underline{k}_s < \underline{k}_d \quad (20a)$$

and

$$\rho_{e-e} = A_{e-e} \frac{m_s m_d^3}{k_s^5} \left( \frac{2\lambda}{4\lambda^2 + 1} - \frac{1-\lambda}{(1-\lambda)^2 + 1} + \tan^{-1} \frac{3\lambda - 1}{1 + 2\lambda(1-\lambda)} \right) T^2 \quad \text{for } \underline{k}_s > \underline{k}_d, \quad (20b)$$

where  $\chi = 1/\lambda = k_s/k_d$  and we have set  $g = k_s$ . The constant factor is

$$A_{e-e} = 192\pi^3 e^2 k_B^2 / \hbar^3 v^2. \quad (21)$$

From Eq. (4) we now find the intrinsic thermopower due to electron-electron scattering:

$$S_{e-e} = -\frac{\pi^2 k_B^2 T}{3e} \frac{m_d}{\hbar^2 k_d^2} \left[ \frac{[\chi^2 - (\chi+1)^2][(m_s/m_d)\chi^{-1} \mp 1]}{[\chi^2 + (\chi+1)^2]^2} + \frac{[\chi^2 - (1-\chi)^2][(m_s/m_d)\chi^{-1} \pm 1]}{[\chi^2 + (1-\chi)^2]^2} + \frac{2(m_s/m_d)\chi^{-1}(2\chi^2+1) \pm 4\chi}{1+4\chi^4} \right] /$$

$$\left( \frac{\chi+1}{(\chi+1)^2 + \chi^2} - \frac{1-\chi}{(1-\chi)^2 + \chi^2} + \chi^{-1} \tan^{-1} 2\chi^2 \right) - 4m_s/m_d \chi^{-2} \quad \text{for } k_s < k_d, \quad (22a)$$

$$S_{e-e} = -\frac{\pi^2 k_B^2 T}{3e} \frac{m_d}{\hbar^2 k_d^2} \left[ \frac{(\pm 2\lambda^{-1}(4\lambda^2-1))}{(4\lambda^2+1)^2} - \frac{[1-(1-\lambda)^2][(m_s/m_d) \pm \lambda^{-1}]}{[1+(1-\lambda)^2]^2} \frac{(m_s/m_d)(1+4\lambda^2) + 6\lambda \pm 5\lambda^{-1} - 4}{[1+2\lambda(1-\lambda)]^2 + (3\lambda-1)^2} \right] /$$

$$\left( \frac{2\lambda}{4\lambda^2+1} - \frac{1-\lambda}{(1-\lambda)^2+1} + \tan^{-1} \frac{(3\lambda-1)}{1+2\lambda(1-\lambda)} \right) - \frac{4m_s}{m_d} \quad \text{for } k_s > k_d. \quad (22b)$$

In Eqs. (22a) and (22b), the upper sign corresponds to the case of an inverted  $d$  band.

The total measured thermopower (discounting phonon drag) is the sum of the intrinsic thermopowers each weighted by the corresponding thermal resistivity. For electron-electron scattering we have<sup>17</sup>

$$W_{e-e} = [\rho_{e-e}/T(12-\pi^2)(k_B/e)^2]. \quad (23)$$

Since the expressions for  $S_{e-e}$  and  $W_{e-e}$  are rather complicated, it is difficult to predict the magnitude and sign of this contribution to the total thermopower in the general case. We do expect that if this contribution dominates that associated with electron-phonon scattering at high temperatures, the total thermopower will vary as  $\alpha T + \beta T^2$ , where the second term arises from electron-electron scattering. This follows from the expression for the total thermopower<sup>18</sup>

$$S_T = \frac{W_{pho} S_{pho} + W_{e-e} S_{e-e}}{W_{pho} + W_{e-e}} \quad (24)$$

and the fact that  $W_{pho}(\Theta_D) \gg W_{e-e}(\Theta_D)$ .  $W_{pho}$  at high temperatures is independent of  $T$ , whereas  $W_{e-e}$  and  $S_{e-e}$  are both linear in  $T$ . At still higher temperatures,  $W_{e-e}$  may become comparable to, or greater than,  $W_{pho}$  and where this happens the quadratic contribution in the total thermopower will diminish. In that event, the total thermopower will exhibit a linear temperature dependence even though electron-electron-scattering effects dominate over those of electron-phonon scattering. In some cases, this behavior is apparent from the calculated results and also in the data in some of the transition metals (see Secs. IV and V).

#### IV. TOTAL THERMOPOWER

The total thermopower for multiple-scattering mechanisms is given by<sup>18</sup>

$$S_T = \frac{1}{W_T} \sum_i W_i S_i \quad (25)$$

with

$$W_T = \sum_i W_i,$$

where  $S_i$  and  $W_i$  are the contributions to the thermopower and thermal resistivities of each mechanism independently. Thus, before we can construct the total thermopower, it is necessary to know the relative magnitudes of  $W_{e-e}$  and  $W_{pho}$ . As it is difficult to estimate these from first principles, we have resorted to an empirical estimate of the ratio  $\rho_{pho}(T)/\rho_{e-e}(T)$  by defining a parameter  $T_E$  by

$$\rho_{pho}(T_E) = \rho_{e-e}(T_E). \quad (26)$$

Estimates from experimental data<sup>5</sup> put  $T_E$  in the range 5–20 °K consistent with the evidence that  $W_{e-e}(\Theta_D) \ll W_{pho}(\Theta_D)$ . The theoretical total thermopower is plotted in Figs. 1–4, representing typical cases for different values of the gap parameter  $\eta$ , different effective-mass ratios  $m_d/m_s$ , and possible arrangements of the  $s$  and  $d$  bands.

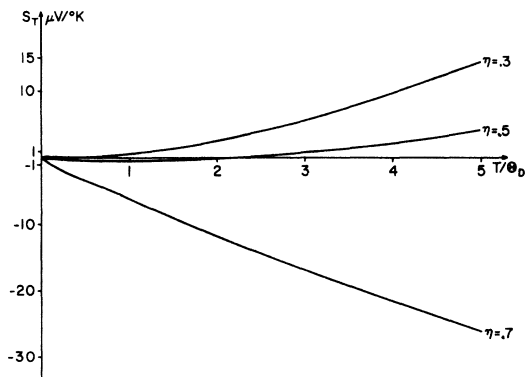


FIG. 1. Theoretical total thermopower in the case of an inverted  $d$  band;  $k_s < k_d$ ,  $m_d/m_s = 10$  for different gap parameters  $\eta$ .

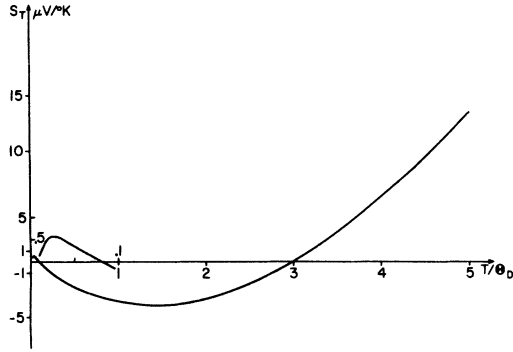


FIG. 2. Theoretical total thermopower in the case of an inverted  $d$  band;  $k_s < k_d$ ,  $m_d/m_s = 10$ ,  $\eta = 0.1$ . In the inset the details of a local maximum—not to be confused with a phonon-drag peak—are shown. This extremum is associated with the exponential decay of phonon-induced  $s$ - $d$  transitions at very low temperatures.

To aid our discussion we introduce  $S_{\text{pho}}^T$  and  $S_{\text{e-e}}^T$ , the weighted contributions of the two scattering processes to the total thermopower. These are defined by

$$S_{\text{pho}}^T = W_{\text{pho}} S_{\text{pho}} / W_T, \quad S_{\text{e-e}}^T = W_{\text{e-e}} S_{\text{e-e}} / W_T. \quad (27)$$

We now consider four distinct situations.

*Case I.* One band inverted relative to the other band.

(a)  $k_s < k_d$ :  $S_{\text{pho}}^T$  is negative at all temperatures<sup>19</sup> and dominant at low temperatures. For small and intermediate values of  $\eta$  ( $\leq 0.5$ ),  $S_{\text{e-e}}^T$  is positive. When  $m_d/m_s$  is large (10) it dominates  $S_{\text{pho}}^T$  at higher temperatures. In the case of large  $\eta$  (0.7),  $S_{\text{e-e}}^T$  is positive for  $m_d/m_s = 10$  only, and it is always smaller than  $S_{\text{pho}}^T$  throughout the temperature range. These results are shown in Fig. 1. If  $\eta = 0.1$  and  $m_d/m_s = 10$  we find a local extremum of the total

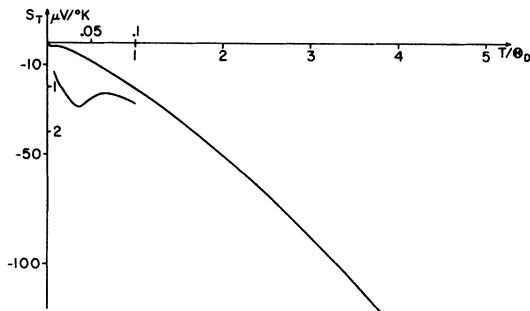


FIG. 3. Theoretical total thermopower in the case of an inverted  $d$  band;  $k_s > k_d$ ,  $m_d/m_s = 10$ ,  $\eta = 0.5$ . In the inset the details of a local minimum due to electron-electron-scattering effects are shown.

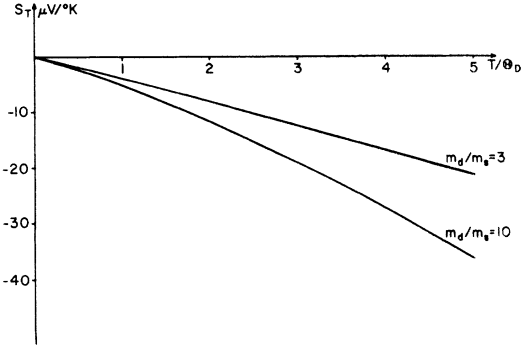


FIG. 4. Theoretical total thermopower in the case where the two bands have the same curvature,  $k_s < k_d$ ,  $\eta = 0.1$  for  $m_d/m_s = 3, 10$ .

thermopower at very low temperatures associated with the freezing out of phonon-induced  $s$ - $d$  transitions. A typical curve is shown in Fig. 2. On the other hand, in the case of  $\eta = 0.3$  and the same large ratio  $m_d/m_s$ , we find (depending upon the magnitude of  $k_s$ ) a local extremum due to electron-electron-scattering processes. Both these peculiarities will be discussed more in detail below (see Sec. V).

(b)  $k_s > k_d$ :  $S_{\text{pho}}^T$  is always negative and it is dominant at low temperatures.  $S_{\text{e-e}}^T$  is always negative and dominates  $S_{\text{pho}}^T$  at higher temperatures. Independent of the ratio  $m_d/m_s$ , we find for  $\eta = 0.5$  a strong local extremum associated with electron-electron-scattering effects. A representative curve for this behavior is shown in Fig. 3.

*Case II.* Both bands have curvatures of equal sign.

(a)  $k_s < k_d$ :  $S_{\text{pho}}^T$  as well as  $S_{\text{e-e}}^T$  are negative throughout the temperature range. For small and intermediate values of  $\eta$  and for large  $m_d/m_s$ ,  $S_{\text{e-e}}^T$  dominates at higher temperatures, but this is not the case if  $m_d/m_s$  is small (3). This change of the temperature dependence of the total thermopower with the effective-mass ratio is shown in Fig. 4.

(b)  $k_s > k_d$ :  $S_{\text{pho}}^T$  is dominant at low temperatures. The sign is negative<sup>20</sup> if  $m_d/m_s$  is small and  $\eta$  is small or intermediate ( $\leq 0.3$ ), or if  $m_d/m_s$  is large and  $\eta$  is small (0.1). The sign is positive if  $m_d/m_s$  is small and  $\eta$  is large ( $\geq 0.5$ ), or if  $m_d/m_s$  is large and  $\eta$  is intermediate or large ( $\geq 0.3$ ). Independent of the effective-mass ratio,  $S_{\text{e-e}}^T$  is positive for small and intermediate  $\eta$  ( $\leq 0.5$ ) and dominates  $S_{\text{pho}}^T$  at high temperatures. Under the same conditions as in case I (a) we obtain a local extremum characteristic for the exponential decay of the phonon-induced  $s$ - $d$  transitions at very low temperatures. We also find local extrema due to electron-electron-scattering effects which become more pronounced as the gap size increases ( $\eta \geq 0.3$ ) and the ratio  $m_d/m_s$  becomes larger.

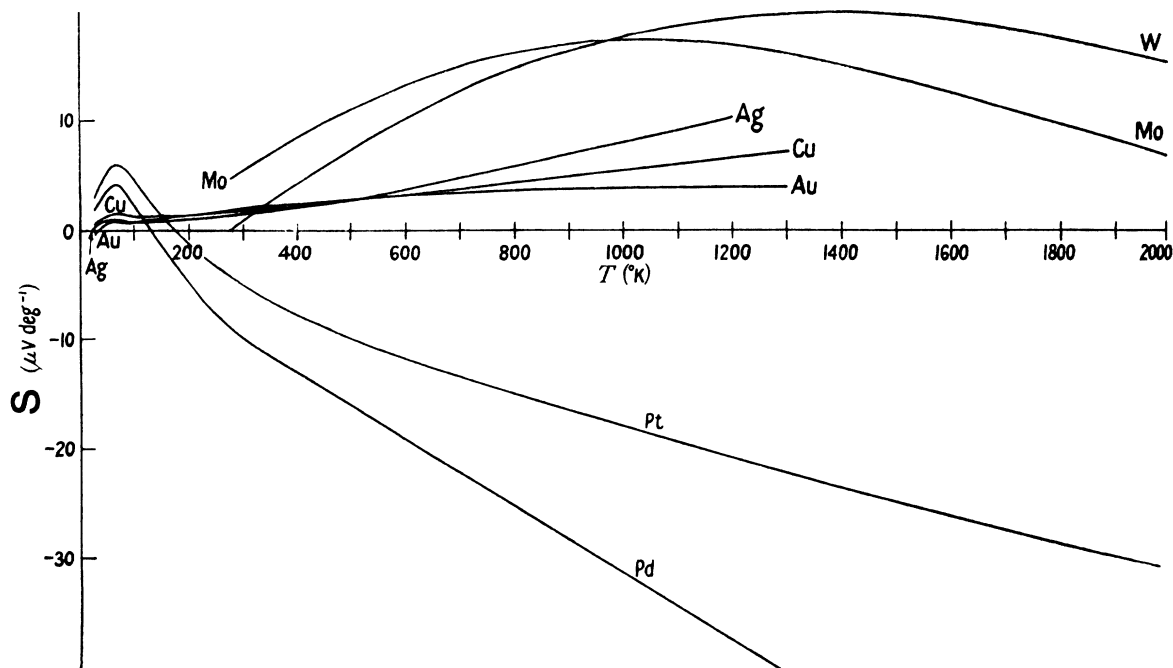


FIG. 5. Experimental thermopower of some of the transition metals taken from Cusack and Kendall (Ref. 22).

## V. DISCUSSION

There are several important limitations to our calculations which preclude a detailed comparison with the experimental data for each of the transition metals. First, we have used a spherical model for the Fermi surfaces of the conduction electrons in order to simplify the calculations. Although this is an obvious oversimplification of the actual Fermi surfaces in the transition metals, it perhaps suffices to represent the general features of these metals. The magnitudes of the quantities  $m_d/m_s$ ,  $a$ ,  $q_D$ ,  $k_s$ ,  $k_d$ ,  $\eta$ , and related derivatives with respect to the energy which enter the theory must then, however, be considered as empirical parameters. Second, we have omitted considerations of phonon-drag processes. Consequently, a comparison with the experimental data must be restricted to regions where  $T/\Theta_D$  is greater or much less than unity and phonon-drag effects have essentially disappeared. Finally, we neglected umklapp processes throughout this investigation.

Nonetheless, there are certain general features of the experimental data in these two limiting regions which seem to bear out our model calculation. For comparison we include the figure given by Cusack and Kendall<sup>22</sup> (Fig. 5) and refer also to more recent results.<sup>21</sup> In the high-temperature limit the thermopower for the transition metals is observed<sup>22,23</sup> to vary from large negative values (e.g., for Pd and Pt) to large positive values (e.g., for

W and Mo) at a given temperature as we pass from one metal to another. Although the argument that this variation is due to differences in the slope of the density of states of the  $d$  band is essentially correct (i.e., making no distinction between the Mott and Wilson models), it may be crucial in some cases to include the effects of electron-electron scattering. For example, the thermopower of W and Mo above the Debye temperature is given quite closely by

$$S_T = \alpha T - \beta T^2, \quad (28)$$

where the constants are  $\alpha \approx 4.5 \times 10^{-2} \mu\text{V}/^\circ\text{K}$ ,  $\beta \approx 2 \times 10^{-5} \mu\text{V}/(^\circ\text{K})^2$ , respectively. The second term may reflect the importance of electron-electron scattering on the thermopower at elevated temperatures. Moreover, in the low-temperature region (near  $10^\circ\text{K}$ ), the experimental data<sup>22</sup> for W display a peak of the order of  $0.2 \mu\text{V}/^\circ\text{K}$  which may be due to effects of electron-electron interband scattering. To understand this, we must look at the weighted contribution to the total thermopower, since from the linear temperature dependence of the corresponding intrinsic thermopower one would not expect such a behavior. From Eq. (27) we get the following temperature dependence:

$$S_{e-e}^T = AT^2/(BT^n + CT) \quad (29)$$

since we know that  $S_{e-e}$ , as well as  $W_{e-e}$ , are proportional to the temperature. In the case where we have intraband scattering induced by phonons

only (e.g., noble metals),  $n$  would be equal to 2. In our case, where in the temperature region of interest the probability of phonon-induced interband transitions drops exponentially,  $n$  will be larger than 2 but to a first approximation (up to the second term in the expansion of the exponential factor) still smaller than 3. We now differentiate with respect to temperature and obtain the following relation for the temperature at which the weighted contribution of electron-electron effects reaches a local extremum:

$$T_{\text{extr}} = \left( \frac{C}{(n-2)B} \right)^{1/(n-1)}. \quad (30)$$

The calculated thermopower exhibits such a local extremum only if  $T_{\text{extr}}$  lies below the characteristic temperature where effects due to phonon-induced interband scattering are diminished exponentially. Otherwise  $S_{\text{e-e}}^T$  not only diminishes with increasing temperature but the extremum will further be masked by  $S_{\text{pho}}^T$  which increases rapidly with increasing temperature. In the case of  $k_s > k_d$ , the local extremum becomes more pronounced as the ratio  $\lambda = k_d/k_s$  approaches  $\frac{1}{3}$ , for then only large-angle scattering events provide relaxation.

If the "momentum gap" is small ( $\eta = 0.1$ ), the phonon-induced  $s$ - $d$  transitions decay exponentially only at very low temperatures after essentially all contributions from electron-electron-scattering effects have diminished considerably. It is not surprising then, considering the complex temperature dependence of  $S_{\text{pho}}^T$  in this region, that we may find under these circumstances, and especially for a large ratio  $m_d/m_s$ , a local extremum quite similar to the one ascribed to electron-electron-scattering effects above.

Thus a local extremum in the case of small  $\eta$  is more likely to be associated with phonon-induced-scattering effects, whereas in case of intermediate or large  $\eta$  it might be due to the influence of electron-electron scattering.

We also might point out that in view of the rather complicated temperature dependence of  $S_{\text{pho}}^T$ , especially at low temperatures, and the interplay with  $S_{\text{e-e}}^T$  we must not be surprised if the general behavior of the total thermopower in this region is such that the thermopower, though it must surely vanish at absolute zero, does not appear to extrapolate to this value even if measurements are carried out to quite low temperatures, e.g.,  $1^\circ\text{K}$ .<sup>24</sup>

We also should like to mention briefly the influence of effects due to impurities. Since the corresponding thermal resistivity is proportional to  $T^{-1}$  and the intrinsic thermopower varies linearly with the temperature, we expect no qualitative change at higher temperature, but only a parallel shift in very impure materials. On the other hand,

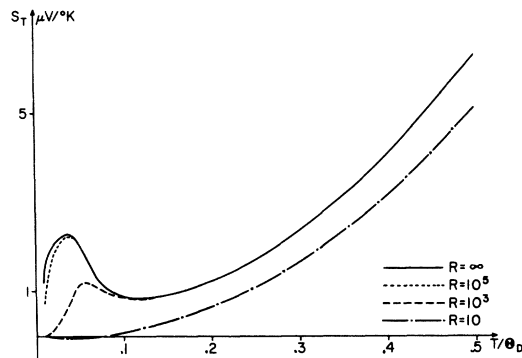


FIG. 6. Theoretical total thermopower in the case where the two bands have the same curvature,  $k_s > k_d$ ,  $m_d/m_s = 3$ ,  $\eta = 0.5$  for different values of the ratio  $R$ .

at low temperature there may arise a substantial change especially in the case where we have a local extremum in the ideal case. This situation is indicated in Fig. 6, where we show  $S$  vs  $T$  for various values of  $\rho(293^\circ\text{K})/\rho_{\text{res}} = R$ .

We should like to point out that Figs. 1-4 and 6 were obtained with an almost random choice (within our assumptions) of the parameters involved. In various portions of the temperature scale they qualitatively reflect some of the features of the experimental data shown in Fig. 5. A better fit to the experimental results could be obtained by adjusting the lattice constant  $a$  ( $3 \times 10^{-10}$  m), the statistical weight of  $s$ - $d$  transitions in the case of phononinduced scattering  $\omega_d P_{sd}/P_{ss}$  (2), the magnitude of the Fermi vector  $k_s$  ( $0.47$  to  $1.88 \times 10^{10}$   $\text{m}^{-1}$ ), and the Debye wave vector  $q_D$  ( $1.6 \times 10^{10}$   $\text{m}^{-1}$ ). The values in parentheses indicate our choice and were not changed with temperature.

In view of the various simplifying assumptions of the model calculations, such adjustment of parameters is of questionable value and we shall give one example, palladium. The difficulty is that we have too many parameters to vary and not much guidance to limit this freedom. There are a fair number of experimental results but one still has to estimate the values for  $m_d$ ,  $m_s$ ,  $k_s$ ,  $\eta$ , and  $T_E$  on which all of our theoretical results depend quite sensitively. The problem with  $k_s$  is not only that the real Fermi surface is not spherical, but that the complicated structure implies also that the electron surface centered at  $\Gamma$  consists of  $s$ - as well as  $d$ -like parts. Therefore, we have to find an effective value for the corresponding Fermi wave vector. The only experimental results which help us to choose the parameters reasonably are data for  $\rho$  or  $W$ .<sup>5</sup>

The calculated results for the theoretical total diffusion thermopower for Pd shown in Fig. 7 were obtained with the following choice of parameters:



$a = 3.8824 \times 10^{-10}$  m,<sup>25</sup>  $\Theta_D = 295$  °K,<sup>5</sup>  $m_s = 2.2m_e$ ,<sup>26</sup>  $m_d/m_s = 3.5$ ,<sup>26</sup>  $q_D = 1.57 \times 10^{10}$  m<sup>-1</sup>,<sup>25</sup>  $k_s = 1.03 \times 10^{10}$  m<sup>-1</sup>,<sup>26</sup>  $\eta = 0.1$ ,<sup>7</sup> and  $T_E = 5.0$  °K.<sup>5</sup> The difference between the theoretical curve and the experimental data could be due to the presence of impurities in the sample, the neglect of umklapp processes in our model, or could be minimized by lowering the value of  $k_s$  and readjusting  $m_d/m_s$  and  $T_E$ .

In the case of palladium, the large-hole effective mass suggests that these carriers do not contribute substantially to charge transport, so that our model, in which contributions to transport by the heavier carriers are neglected, may be a reasonable approximation. In tungsten and molybdenum, however, we encounter a rather more complex situation. To begin with, a four- rather than two-band model is undoubtedly more appropriate, and such a model was in fact employed by Aisaka and Shimizu.<sup>27</sup> If, however, we try to simplify to a two-band model, it is then not at all clear which group of carriers should properly be designated as the "lighter carriers," since effective masses are all of equal magnitude. If the dominant carriers were, indeed,  $d$ -band holes, the qualitative summaries following Eq. (27) would be modified in that all statements relating to the sign of the thermopower would have to be reversed. If this were a reasonable approximation to the true situation, the large positive thermopowers of the two metals and the nonlinear behavior at high temperature might be plausible in terms of case II (b) (with signs for  $S_{pho}^T$  and  $S_{\sigma}^T$  reversed).

It seems to us that such speculations must be viewed with enormous skepticism. The model we have employed is already a gross oversimplification for "two-band" metals such as palladium, and

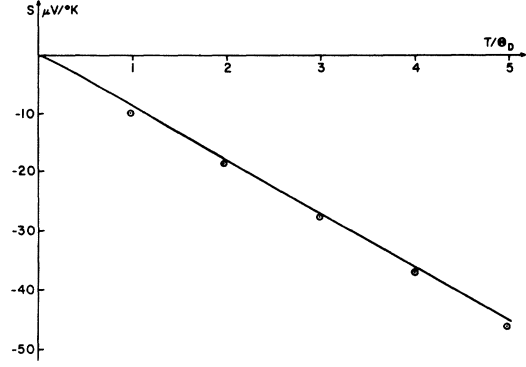


FIG. 7. Model calculation for Pd: theoretical thermopower, solid line; experimental data taken from Ref. 22, circles. Calculated result are based on the following parameters:  $a = 3.8824 \text{ \AA}$ ,  $\Theta_D = 295$  °K,  $m_s = 2.2m_e$ ,  $m_d/m_s = 3.5$ ,  $q_D = 1.57 \text{ \AA}^{-1}$ ,  $k_s = 1.03 \text{ \AA}^{-1}$ ,  $\eta = 0.1$ ,  $T_E = 5$  °K.

extension of arguments to include tungsten and molybdenum is of doubtful value. What we have tried to demonstrate and wherein we have, perhaps, succeeded, is that if electron-electron scattering is an important relaxation process in a transition metal it can have a substantial influence on the thermoelectric power as well as the resistivity. Moreover, in that case the simple model we have put forward is capable of reproducing the general features of available experimental data.<sup>28</sup>

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#### APPENDIX

We start with Eq. (11)

$$\begin{aligned} \hat{f}_{\vec{k}_1} \Big|_{\text{coll}} = & - \frac{32\pi^3 e^4}{\hbar^4 k_B T V^2 v_2 v_3 v_4} \phi_{\vec{k}} \iiint \frac{\delta(\vec{k}_1 + \vec{k}_2 - (\vec{k}_3 + \vec{k}_4))}{(|\vec{k}_3 - \vec{k}_1| + g)^2} dA_2 dA_3 dA_4 \\ & \times \iiint \Theta(\epsilon_1 + \epsilon_2 - \epsilon_3 - \epsilon_4) f_1^0 f_2^0 (1 - f_3^0) (1 - f_4^0) d\epsilon_2 d\epsilon_3 d\epsilon_4 \end{aligned} \quad (\text{A1})$$

and perform first the integration over energy. We made use of the relation

$$1 - f_i^0 = f_i^0 e^{(\epsilon_i - E_F)\beta}, \quad \beta = 1/k_B T \quad (\text{A2})$$

and of the property of  $\Theta(\epsilon)$  for large times to reduce the energy-dependent part to the form

$$\frac{1}{1 + e^{-(\epsilon_1 - E_F)\beta}} \int \frac{d\epsilon_3}{e^{(\epsilon_3 - E_F)\beta} + 1}$$

$$\times \int \frac{e^{(\epsilon_2 - E_F)\beta} d\epsilon_2}{(e^{(\epsilon_2 - E_F)\beta} + 1)(e^{(\epsilon_1 + \epsilon_2 - \epsilon_3 - E_F)\beta} + 1)}. \quad (\text{A3})$$

To evaluate the integral over  $\epsilon_2$ , we make the substitutions

$$e^{(\epsilon_1 - \epsilon_3)\beta} = a, \quad e^{(\epsilon_2 - E_F)\beta} = u. \quad (\text{A4})$$

Separation into the partial fraction

$$\frac{1}{(u+1)(au+1)} = \frac{1}{1-a} \left( \frac{1}{u+1} - \frac{1}{u+1/a} \right) \quad (\text{A5})$$

gives

$$\frac{1}{(1-a)\beta} \ln \frac{u+1}{u+1/a} \Big|_0^\infty = \frac{\epsilon_1 - \epsilon_3}{e^{(\epsilon_1 - \epsilon_3)\beta} - 1}. \quad (\text{A6})$$

With the further substitutions

$$e^{(\epsilon_1 - E_F)\beta} = b, \quad (\epsilon_1 - \epsilon_3)\beta = x, \quad (\text{A7})$$

we find for the whole energy-dependent part of Eq. (A1)<sup>29</sup>

$$\begin{aligned} & \frac{b}{2(b+1)^2\beta} [\pi^2 + (\ln b)^2] \\ &= \frac{(\pi k_B T)^2 + (\epsilon_1 - E_F)^2}{2(e^{(\epsilon_1 - E_F)\beta} + 1)(e^{-x} + 1)} \\ &= \frac{1}{2} [(\pi k_B T)^2 + (\epsilon_1 - E_F)^2] f^0(\epsilon_1) [1 - f^0(\epsilon_1)]. \quad (\text{A8}) \end{aligned}$$

This leaves us with the momentum-dependent part of Eq. (A1). We now define

$$2\pi \int \frac{dA_3}{(\Delta_1^2 + g^2)^2} \iint \frac{\Delta_{II} K_4^2}{k_2 k_4} \frac{K_2^2}{\Delta_{II}^2} \delta_{\Delta_I, \Delta_{II}} d\Delta_{II} dA(\vec{k}_2 - \vec{k}_4) = 2\pi K_2 K_4 \int \frac{dA_3}{\Delta_1(\Delta_1^2 + g^2)^2}. \quad (\text{A12})$$

In an analogous manner, we write

$$dA_3 = 2\pi K_3^2 \sin\varphi_I d\varphi_I = 2\pi(\Delta_I/k_1 k_3) K_3^2 d\Delta_I \quad (\text{A13})$$

and find that Eq. (A12) becomes

$$\begin{aligned} & 2\pi K_2 K_4 \int \frac{dA_3}{\Delta_1(\Delta_1^2 + g^2)^2} \\ &= 4\pi^2 \frac{K_2 K_3 K_4}{k_1} \int_{\Delta_{\min}}^{\Delta_{\max}} \frac{d\Delta_I}{(\Delta_1^2 + g^2)^2} \\ &= 4\pi^2 \frac{K_2 K_3 K_4}{k_1} I(\Delta_{\min}, \Delta_{\max}). \quad (\text{A14}) \end{aligned}$$

The integral  $I(\Delta_{\min}, \Delta_{\max})$  so defined is given by<sup>30</sup>

$$I(\Delta_{\min}, \Delta_{\max}) = \frac{1}{2g^2} \left( \frac{\Delta}{\Delta^2 + g^2} + \frac{1}{g} \tan^{-1} \frac{\Delta}{g} \right) \Big|_{\Delta_{\min}}^{\Delta_{\max}}. \quad (\text{A15})$$

$$\Delta_I^2 = |\vec{k}_3 - \vec{k}_1|^2 = k_1^2 + k_3^2 - 2k_1 k_3 \cos\varphi_I, \quad (\text{A9})$$

$$\Delta_{II}^2 = |\vec{k}_2 - \vec{k}_4|^2 = k_2^2 + k_4^2 - 2k_2 k_4 \cos\varphi_{II},$$

where the  $\varphi$ 's are the angles between the corresponding  $k$  vectors. First, we keep  $k_1$  and  $k_3$  fixed and vary  $k_4$  only; then

$$dA_4 = 2\pi K_4^2 \sin\varphi_{II} d\varphi_{II} = 2\pi(\Delta_{II}/k_2 k_4) K_4^2 d\Delta_{II}, \quad (\text{A10})$$

where  $K_i$  is the radius of the Fermi sphere of carriers of type (a). Similarly,

$$dA_2 = K_2^2 d\Omega_2 = (K_2^2/\Delta_{II}^2) dA(\vec{k}_2 - \vec{k}_4), \quad (\text{A11})$$

where  $\Omega_2$  is the space angle generated by  $\vec{k}_2$  (while  $\vec{k}_4$  varies) and  $A(\vec{k}_2 - \vec{k}_4)$  is the surface area swept out by the rotation of  $\vec{k}_2 - \vec{k}_4$ . Thus, the integrations  $dA_2$ ,  $dA_4$  can be evaluated as shown below:

Combining the above results, we obtain finally

$$\begin{aligned} \dot{f}_{\vec{k}_1}^* \Big|_{\text{c.o.l.l}} &= - \frac{128\pi^5 e^4}{\hbar^4 k_B T V^2 v_2 v_3 v_4} \\ &\times [(\pi k_B T)^2 + (\epsilon_1 - E_F)^2] f^0(\epsilon_1) [1 - f^0(\epsilon_1)] \\ &\times \phi_{\vec{k}} \frac{K_2 K_3 K_4}{|\vec{k}_1|} I(\Delta_{\min}, \Delta_{\max}). \quad (\text{A16}) \end{aligned}$$

We may point out here if we had not excluded intraband scattering already, their contribution to  $\dot{f}_{\vec{k}_1}^* \Big|_{\text{c.o.l.l}}$  would now be seen to vanish since in that case, particles 1, 2 and 3, 4 are indistinguishable and consequently  $\Delta_{I,II}$  and  $d\Delta_{I,II}$  must vanish [ $\varphi_I = \varphi_{II} = \pi$  in Eqs. (A9) or (A10) and (A13)].

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PHYSICAL REVIEW B

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## Effect of Fermi Surface Geometry on Electron-Electron Scattering\*

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In order to investigate the influence of Fermi-surface geometry on the lifetime of an electron due to interactions with other electrons, we have performed a calculation (using Fermi's "Golden Rule") of the energy- and temperature-dependent lifetime of an electron on a cylindrical Fermi surface. At zero temperature, the dominant energy dependence of the inverse lifetime or the decay rate is  $\epsilon^2 |\ln \epsilon|$  for small values of the parameter  $\epsilon$  which is the electron energy relative to the Fermi energy  $\mu$  measured in units of  $\mu$ . At finite temperatures the decay rate leads to an electrical resistivity proportional to  $T^2 |\ln kT/\mu|$  instead of the  $T^2$  dependence characteristic of a spherical Fermi surface. In addition, the similar calculation (using Fermi's "Golden Rule") for a spherical Fermi surface has been done exactly at zero temperature. The magnitude of the correction to the well-known  $\epsilon^2$  term has been obtained. Furthermore, in an appendix, written with N. D. Mermin, the dominating influence of the density of states on the wave-vector dependence of the susceptibility is demonstrated.

### I. INTRODUCTION

The possibility of observing the contribution of electron-electron scattering to the resistivity of metals is a subject of much current experimental and theoretical interest.<sup>1</sup> In the analysis of experimental data such scattering processes have usually been assumed to contribute a term proportional to  $T^2$  in the resistivity. The rationale for this is the well-known result<sup>2</sup> that the rate of decay due to electron-electron interactions of an electron in state  $\vec{p}_1$  with energy  $\epsilon_1$  (measured from the Fermi energy  $\mu$ ) is proportional to  $[(\pi kT)^2 + \epsilon_1^2]$ , when the Fermi surface is *spherical*. Such a rate of decay causes

a resistivity proportional to  $T^2$  provided a mechanism for degradation of the total momentum exists. This energy and temperature dependence of the decay rate is derived on the assumption that  $kT \ll \mu$  and  $\epsilon_1 \ll \mu$ , which is also the region of interest in the present investigation.

In this paper we report a calculation of the energy and temperature dependence of the decay rate of an electron on a *cylindrical* Fermi surface in order to illustrate the effect of geometry on the availability of phase space for the scattering. The cylindrical geometry is supposed to arise from a band-structure calculation that gives one-electron energies  $\epsilon_p = p^2/2m$ , where  $p$  is the magnitude of the compo-