

Transport in Metals. II. Effect of the Phonon Spectrum and Umklapp Processes at High and Low Temperatures*

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A calculation of the nonmagnetic transport coefficients of the alkali metals is made, with improvements designed to take into account the effect of the phonon spectrum on both the normal and umklapp regions of scattering. The phonon equations of motion are solved numerically to obtain a spectrum sample, and spectrum averages are then computed in a manner similar to specific heat calculations, although we do not need or compute the density of states directly. No average Debye temperatures are used, but rather the sums are obtained in terms of certain combinations of the elastic constants, which in principle are measurable. Also, improvements on the shielding part and on the ion part of the electronic matrix element are calculated and discussed. The results show that umklapp processes are important down to the lowest measurable temperatures in the ideal component of the electrical

and thermal resistivities, being completely dominant in the former. The low-temperature temperature dependence is therefore determined mainly from the umklapp term, which can show a faster variation than T^5 in the electrical resistivity, as is actually observed in sodium. The transverse phonon vibrations dominate the contributions at all temperatures and even the non-umklapp term at low temperatures. The computations give absolute magnitudes for the resistivities which are much too large at low temperatures. This is tentatively attributed in part at least to a spectrum which perhaps exaggerates the anisotropy of the transverse phonons. General expressions for the transport coefficients are calculated via the Kohler variational principle which are not restricted to the model of spherical energy surfaces. A general expression for the phonon-drag term in the thermo-electric power is given.

I

THE purpose of this paper is to present some improvements in the calculation of the electrical and thermal resistivities and thermoelectric power of the alkali metals. In Part I, we discuss the nature of the improvements and the results of numerical calculations. In Part II, we place a list of Appendices in which the details of the derivations and the methods of computation are explained.

1. Umklapp Processes and the Phonon Spectrum

One of the standard expressions for the thermal part of the electrical resistivity ρ_i is the Gruneisen interpolation formula^{1,2}

$$\rho_i = (\text{const}/\Theta) C^2 (T/\Theta)^5 J_5(\Theta/T), \quad (1)$$

where

$$J_5(x) = \int_0^x \frac{z^5 dz}{(e^z - 1)(1 - e^{-z})}, \quad (2)$$

and where the C in (1) is the interaction integral of Wilson [Eq. (9.3.8) of reference 2], and is related to the $I_{kk'}$ [Eq. (17b) below] of a previous article³ by the author (which we shall refer to as I) by

$$iCq = \mathbf{I}_{kk'} \cdot \boldsymbol{\xi}(j\boldsymbol{\sigma}). \quad (3)$$

On the left-hand side, we used q to denote the phonon wave vector, as does Wilson; whereas on the right-hand

side we use $\boldsymbol{\sigma}$ to denote the same thing, as in I and in the rest of this paper. $\boldsymbol{\xi}(j\boldsymbol{\sigma})$ is a unit vector in the direction of polarization of the phonon of wave vector $\boldsymbol{\sigma}$ and spectrum branch j . \mathbf{k} is the electron wave vector before, and \mathbf{k}' after the interaction with the phonon.

The first improvement relative to this expression is the inclusion of umklapp processes. An umklapp process is one where the electron wave vector satisfies the selection rule

$$\mathbf{s} \equiv \mathbf{k}' - \mathbf{k} = \boldsymbol{\sigma} + \mathbf{K}, \quad (4)$$

where \mathbf{K} is a vector of the reciprocal lattice. Since \mathbf{k} , \mathbf{k}' , and $\boldsymbol{\sigma}$ are reduced wave vectors, there is one and only one pair $\boldsymbol{\sigma}$, \mathbf{K} which will satisfy (4) for a given \mathbf{k} , \mathbf{k}' pair. Umklapp processes were first pointed out by Peierls.⁴ Bardeen⁵ later made a calculation which took them into account, assuming however that the wave vector for the phonons could be approximated by the maximum value σ_{max} for such processes. Ziman⁶ improved this by averaging the σ 's over the values consistent with keeping the electron wave vector difference $\mathbf{k} - \mathbf{k}'$ constant in magnitude. The geometry of such processes then allows for quite small σ 's to appear in this average. Bardeen and people previous to him concluded that umklapp processes would be negligible at low temperatures, because there is a lower limit on the energy of the phonons that can enter into such processes (which is what suggested the Bardeen approximation $\sigma = \sigma_{\text{max}}$ in the umklapp region). Ziman however showed that this energy can be quite small because of the range of σ 's in the average, and he concluded that the influence of umklapp processes would go down quite far in temperature, but at sufficiently low temperatures, the neglect of umklapp processes would become valid.

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¹ See, for example, N. F. Mott and H. Jones, *Theory of Metals and Alloys* (Dover Publications, Inc., New York, 1958), p. 274.

² A. H. Wilson, *Theory of Metals* (Cambridge University Press, New York, 1953), pp. 278 and 307.

³ M. Bailyn, *Phys. Rev.* **112**, 1587 (1958), Eq. (5).

⁴ R. Peierls, *Ann Physik* **5**, 121 (1932).

⁵ J. Bardeen, *Phys. Rev.* **52**, 668 (1937).

⁶ J. Ziman, *Proc. Roy. Soc. (London)* **A226**, 436 (1954).

Our work on this aspect of the calculation cannot be isolated from the second improvement, which is to take the phonon spectrum into account. In I, we investigated the effect of the nonequilibrium part of the phonon distribution, but our remarks in this paper refer only to the equilibrium part, and its spectrum. In 1956,⁷ Brooks and the author showed that in the alkali metals averaging over the phonon spectrum under the integral in (2), not outside it, increased the significance of the umklapp processes at all temperatures, but especially at low temperatures, where there seems to be no temperature low enough for the umklapp processes to become ineffective, at least until one is so deep in the impurity region that the thermal scattering can be neglected altogether. In fact our results were that if anything, *the non-umklapp part* could be neglected in the very low temperature region, at least as far as about 5°K, and that the umklapp contributions would be appreciable down to 2°K or lower.

Pfennig⁸ recently has come to the same conclusion, for more or less the same reasons.

We shall here indicate how the form of (1) changes when we make these improvements. The integral in (2) is changed from an integral over $z = \hbar\omega/kT$ where $\hbar\omega$ is the phonon energy, to an integral over scattering angle⁵ $\theta = \angle \mathbf{k}, \mathbf{k}'$. We shall have in mind a spherical Fermi surface, and scattering can take place from the vicinity of any point \mathbf{k} on the surface to any other point \mathbf{k}' . If we were limited to non-umklapp processes, we would have for body-centered cubic lattices $|\mathbf{k} - \mathbf{k}'|_{\max} = \sigma_{\max} = 2\frac{1}{2}k_0$ where k_0 is the radius of the Fermi sphere. This upper limit corresponds to a maximum phonon energy $\hbar\omega_{\max} = \kappa\Theta$ [see (1)]. With the inclusion of umklapp processes, $|\mathbf{k} - \mathbf{k}'|$ has an upper limit $2k_0$. The variable of integration is $u = \sin(\theta/2)$, and u goes from 0 to 1. For each value of u , there is a value of the electron wave vector difference $s = |\mathbf{k} - \mathbf{k}'|$, and for each such value there is a variety of possible σ 's. (For non-umklapp processes, all these σ 's have the same σ . For umklapp processes, even the σ magnitudes vary. There is also an "intermediate region" for which both umklapp and non-umklapp processes can occur with the same u —the latter is an extremely small region and is neglected, the cutoff between umklapp and non-umklapp taken at $u = 2^{-3} = 0.63$.) The Ziman average in the umklapp region concerned only the variation in σ magnitudes, whereas we attempt to take into account the spectrum of the phonons, and hence we must be concerned with the directions of σ also. The average we take then is in some sense analogous to the type of spectrum calculation made in specific heat theory, where the frequencies $\omega(\sigma)$'s are solved for particular σ values, and the density of states calculated. Here we do not calculate the density

of states directly, but we calculate the value of the resistivity "average-and" [see (B39), for example] at several σ 's, add the results, and then divide by the number of σ 's chosen.

We can see from (1) and (2) that the phonon phase velocity w , defined as ω/σ will cancel out when the Θ^{-6} factor in (1) multiplies the $z^5 dz$ factor in J_5 . Hence in the electrical resistivity the average over the spectrum will concern only the exponentials in (2). If we convert from Wilson's C to our $I_{kk'}$ as in (3), our $I_{kk'}$ incorporates an extra factor u , and (1) turns out to be of the form

$$\rho_i = \text{const } T^5 \int_0^1 du u^3 \left\langle \left\langle \frac{[I_{kk'} \cdot \xi(j\sigma)]^2}{(e^z - 1)(1 - e^{-z})} \right\rangle \right\rangle, \quad (5)$$

where we have not assumed that $I_{kk'}$ (or $I_{kk'}/u$) is constant, but rather have incorporated it as a function of u in the integral.⁵ The angle brackets imply an average over all σ consistent with a given u . This then is how we anticipate the transport coefficients will look under these improvements.

2. The Kohler Variational Principle and Distorted Fermi Surfaces

In Appendices A, B, and C we make the detailed calculation which leads to expressions like (5) for the electrical and thermal resistivities and the thermoelectric power. We use the variational principle of Kohler,⁹ adapted to take umklapp processes into account (see I). The variational principle provides the transport coefficients in the form of ratios of determinants of an arbitrary number of rows and columns. The accuracy increases with the number of rows and columns used. If we keep the usual number (1 for the electrical resistivity ρ , 2 for the thermal resistivity W , and 3 for the thermoelectric power S), and retain only terms in the lowest power of the smallness parameter $\Gamma = kT/\xi$, we get the expressions in (A1)–(A3) in Appendix A, where they are then adapted to take into account possible distortion of the Fermi surface. The effect of this distortion on the transport properties takes perhaps its simplest form in the integrals that appear in the variational principle. (Tsuji¹⁰ has already exploited this.) In particular, for the thermoelectric power, we have a high-temperature expression in (C5) which shows explicitly the effect of the Fermi surface shape independent of the details of the scattering mechanism, in the approximation of 3 rows and columns. (Keep in mind however footnote 9.)

⁹ M. Kohler, Ann. Physik **124**, 772 (1948); **125**, 679 (1949). See also reference 2. In everything that follows, it must be kept in mind that the variational principle, as we (and others) use it, starts from a distribution function of the form (A4) in Appendix A in which the "time of relaxation" represented by the curly brackets is assumed to depend only on the energy of the electron, but not on where on the energy surface the electron is. All our conclusions and discussions are subject to this limitation, which in fact may be severe.

¹⁰ M. Tsuji, J. Phys. Soc. (Japan) **13**, 818, 979 (1958).

⁷ M. Bailyn and H. Brooks, Bull. Am. Phys. Soc. **1**, 300 (1956); M. Bailyn, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry* (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 373; M. Bailyn thesis, Harvard University, 1956 (unpublished).

⁸ H. Pfennig, Z. Physik **155**, 332 (1959).

It is shown in Appendix B that a rigorous evaluation of the integrals yields averages exactly as in (5) so that the patch-work procedure used above has in fact a justification. Making no assumptions about the shape of the Fermi surface, we arrive at the general expressions (B28), (B29), and (C22), for ρ , W , and S , respectively. These expressions might be used to gain some idea of what happens under unusual circumstances, such as high pressure, for example. It is well known that the eventual effect of increasing pressure in the alkali metals is to increase the resistivity.¹¹ Ham¹² has indicated that the increase in pressure will make the distortion of the Fermi surface larger, and that the latter will probably make greater and greater contact as the pressure increases. Dugdale and Cohen have attributed the ultimate rise in ρ to this increasing contact. From our expression (B28) we may anticipate that the averages (i.e., what follows the integral sign) will change slightly, but also there may be a tendency for the electron velocities to become smaller on the Fermi surface since the distortion must have the effect of making narrower shapes out of the occupied region: because at the same time (1) the fraction of the zone filled must remain the same, and (2) the effect of pressure according to Ham is to have some of the filled region touch more and more the zone boundary. These narrower shapes will have smaller cross sections (than the undistorted sphere) and this implies smaller velocities on the surface.^{12a} Since in (B38) $\rho_i \sim [v(\zeta)]^{-2}$, where $v(\zeta)$ is the average velocity on the Fermi surface, we may expect that the effect of pressure is ultimately to raise the resistivity, through the decrease in $v(\zeta)$. Perhaps we have here the mechanism for the ultimate rise in ρ under pressure.¹³ (There are other effects of course, such as the change in the type of connections on the Fermi surface, changes in $I_{kk'}$, etc.)

If we use spherical energy surfaces, not necessarily in the effective mass approximation however, we get the results in (B39), (B40), and (C25), of which we cite the first two:

$$\rho_i = T^{-1} A_0 y_1^2 \int_0^1 \alpha(u) F_0(u) du, \quad (6)$$

$$W_i = T^{-2} L_0^{-1} A_0 y_1^2 \int_0^1 \alpha(u) \left(F_0 + \frac{3u^{-2}-2}{4\pi^2} F_2 \right) du, \quad (7)$$

¹¹ P. Bridgman, *Physics of High Pressures* (G. Bell and Sons, Ltd, London, 1949).

¹² F. Ham, *Bull. Am. Phys. Soc.* **5**, 161 (1960).

^{12a} Note added in proof.—As pointed out by Dugdale (private communication), one could have distortions that would not produce decreases in $v(\zeta)$. Hence, the statement in the text above must be regarded as a guess in which, however, we can now begin to have some faith as a result of Ham's calculations.¹³

¹³ The author is indebted to a talk given by M. Cohen, *Bull. Am. Phys. Soc.* **5**, 183 (1960), and to many conversations with and communications from J. S. Dugdale on this subject and from A. Gold on related subjects. F. Ham (private communication) has found substantial negative k^4 terms in the expansion of the energy function for K, Rb, and Cs which increase with decreasing lattice constant. This result tends to support the suggestion that $v(\zeta)$ decreases with increasing pressure.

where A_0 and L_0 are constants, y_1 is discussed below [see (11)], $\alpha(u)$ involves the matrix element $I_{kk'}$ [see (B43)], and the F_n are averages:

$$F_n = \left\langle \left\langle \frac{z^n}{(e^z - 1)(1 - e^{-z})} (\xi(j\sigma) \cdot s)^2 \right\rangle \right\rangle; \quad s \equiv \mathbf{s}/s, \quad (8)$$

which replace the J_n 's of references 1 and 2. (Note that F_0 corresponds to J_5 , F_2 to J_7 , etc.) The average in (8) is over all directions of \mathbf{s} (\mathbf{s} determines σ) for a given s magnitude, which then amounts to the exact same average as in (5).

Our results for the effect of including exchange and correlation corrections to the one electron energies can be seen from (B39), (B40), and (C25) to differ from Barrie's.¹⁴ What is sought is the ratio of the transport coefficient calculated with exchange effects to the result calculated on the effective mass approximation (EMA). Our expressions yield directly the ratio with respect to the *free* electron approximation. We can obtain the former ratio from the latter by defining three η_i 's as follows:

$$\eta_i = (m_0/m^*) y_i, \quad (9)$$

where from (B42), (C23), and (C6)

$$y_0 = 2\zeta_0 \left[\frac{d^2 E/dk^2}{(dE/dk)^2} \right]_{E=\zeta} = \frac{m^*}{m_0} \Big|_{\text{EMA}}, \quad (10)$$

$$y_1 = \frac{\hbar k_0/m_0}{v(\zeta)} = \frac{m^*}{m_0} \Big|_{\text{EMA}}, \quad (11)$$

$$y_2 = \frac{2\zeta_0}{3} \left[\frac{d}{dE} \ln v(E) A(E) \right]_{E=\zeta} = \frac{m^*}{m_0} \Big|_{\text{EMA}}. \quad (12)$$

Here $A(E)$ is the area of the surface of energy E , and $v(E)$ is the average velocity on that surface [see (A12)], and ζ_0 and k_0 [defined in (A10) and (A11)] are the Fermi energy (approximately) and the radius of the Fermi sphere, respectively. Translating Barrie's notation into ours, we get

$$\rho/\rho_{\text{EMA}} = W/W_{\text{EMA}} = \eta_1^3 \quad \left. \vphantom{\rho/\rho_{\text{EMA}}} \right\} \text{Barrie.} \quad (13a)$$

$$S/S_{\text{EMA}} = \frac{1}{2}(\eta_0 + \eta_1) \quad (13b)$$

We find from (B39), (B40), and (C25), however

$$\rho/\rho_{\text{EMA}} = W/W_{\text{EMA}} = \eta_1^2 \quad \left. \vphantom{\rho/\rho_{\text{EMA}}} \right\} \text{Here,} \quad (14a)$$

$$S/S_{\text{EMA}} = \frac{1}{3}(\eta_0 + 2\eta_1) \quad (14b)$$

where the exchange and correlation effect on the matrix element is ignored (for this, see Sec. 5 below), and where the change in the y_0 term in (C25) is not considered in (14).

¹⁴ R. Barrie, *Phys. Rev.* **103**, 1581 (1956).

3. The Phonon Spectrum

The method for computing the averages in (8) is explained in Appendix F. The solutions of the phonon equations of motion must be obtained, and up to next nearest interactions for bcc lattices they are of the form in (F1):

$$Dw^2/c_{44} = 8(a\sigma)^{-2} \left[1 - g_4 + \frac{c_{12} + c_{44}}{2c_{44}} \epsilon(\sigma) \right] \quad (15)$$

for the velocity w , where the c_{ij} 's are elastic constants, a the lattice parameter, D the density, g_4 given in (F4), and $\epsilon(\sigma)$ an eigenvalue that requires numerical computation. We solved on computers the equation (F2) for $\epsilon(\sigma)$ [and consequently for the eigenvectors $\xi(j\sigma)$] at several points, and with this information computed the averages in (8). More details are in Appendix F.

From a small sample of points in the elastic limit (long waves), we found⁷ the following characteristics of the spectrum. Let the three polarizations j be denoted by L (longitudinal), T_I , and T_{II} (transverse I and II), T_{II} being the one with the smallest velocity for a given σ . We find that the T vibrations have velocities which are considerably smaller than those of the L vibrations, and are highly anisotropic. In T_{II} , some velocities (in the 110 direction for example) become as low as $\frac{1}{8}$ the T velocities in the 100 direction. Also the cosines $(\xi(j\sigma) \cdot \sigma/\sigma)^2$ for T_I and T_{II} are very small but not zero. The early work on conductivity problems in metals approximated the transverse $\xi(T\sigma) \cdot \sigma/\sigma$ as zero, which would be valid for an isotropic substance (phonon velocities constant). Despite the smallness of these cosines, the exponential factors in (6) will favor the T modes (actually T_{II} mainly) at low temperatures sufficiently to make them dominate even the non-umklapp processes!⁷ (Pfennig⁸ has recently reached the same conclusion.) At high temperatures, however, the $(\xi \cdot \sigma/\sigma)^2$ factor cuts out the T modes in the non-umklapp term sufficiently so that that term is dominated by the L modes. The umklapp contributions are dominated by the T modes at high temperatures.

It should be emphasized that it would be very difficult to get the correlation between the disposition of σ magnitudes in the umklapp region and the tremendous anisotropy of the w 's if we did not make a "point calculation" as described above. This correlation turns out to be very important, since the small σ magnitudes frequently occur with small w 's, and this makes for a very large weighting in the F_n averages. Our early work on low temperatures in reference 7 was an estimate on very rough spectrum calculations neglecting the correlation, (of the same sort of accuracy as Pfennig's⁸) and our present more accurate calculations indicate that the preliminary results are qualitatively correct but quantitatively very bad. We discuss this below. We feel that more accurate computations and a more accurate spectrum are still very much needed.

TABLE I. The first row contains the temperature at which the resistivities of the following two rows were computed. The units of ρ are 10^{-5} ohm-cm. $A_0' = (m^*/m_0)^2 A_0$, where A_0 is given in (B41). It's units are 10^{-5} deg-ohm-cm. s_0 is defined in (F5) and s_1 in (F12). The units of the elastic constants are 10^{10} dynes/cm².

	Li	Na	K	Rb	Cs
T	297	125	70	211	158
ρ (th)	0.20	0.14	0.14	0.56	0.50
ρ (exp)	0.94	0.17	0.13	1.15	1.48
c_1	0.1	0.25	0.32	0.42	0.43
c_1/c_0	0.005	0.011	0.014	0.019	0.019 _s
A_0'	15.75	1.77	0.81	0.303	0.181
$s_0(4^\circ\text{K})$	0.044	0.148	0.196	0.232	0.273
$s_1(4^\circ\text{K})$	0.937	1.067	1.122	1.173	1.235
$c_{44}(4^\circ\text{K})$	13.58	6.02	2.65	2.03	1.68
$\theta(4^\circ\text{K})$	426	172	96.7	59.5	44.4
$c_{11} - c_{12}(4^\circ\text{K})$	2.83	1.089	0.516	0.400	0.344

4. On the Previous Neglect of Umklapp Processes at Low Temperatures

It should also be emphasized that the main reason the importance of umklapp processes at low temperatures was previously underestimated was that the spectrum averages were performed in effect outside the u integral. When an average Debye temperature is used, it corresponds to taking the bracket average in (5) outside the u integral, and this procedure underestimates the importance of the very small σ 's and the very small w 's which conspire together to provide tremendous umklapp contributions at the very low temperatures. It is nevertheless useful to have a parameter with a significance similar to a Debye temperature, but not involving misleading averages. We define therefore [see (F14)]

$$\theta = (\hbar k_0/\kappa)(c_{44}/\rho)^{1/2}, \quad (16)$$

which depends only on the lattice constant (through k_0) and on c_{44} . Values are given in Table I. We shall refer to this substance-characterizing quantity frequently in what follows.

5. The Matrix Element

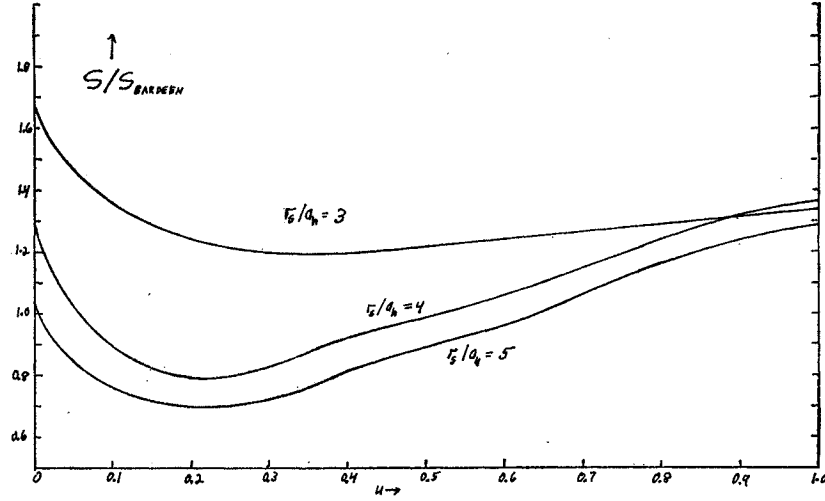
Our results (B39), (B40), and (C25) are in terms of a dimensionless quantity $\alpha(u)$:

$$\alpha(u) = (r_s/a_h)^2 (r_s/e)^4 u^3 I_{kk'}, \quad (17a)$$

$$I_{kk'} = N \int \psi(\mathbf{k}', \mathbf{r})^* \psi(\mathbf{k}, \mathbf{r}) \nabla v(\mathbf{r}) d^3r, \quad (17b)$$

where r_s is the radius of the Wigner-Seitz sphere, a_h the Bohr radius, and where $v(\mathbf{r})$ is the potential associated with the ion of the cell at $\mathbf{r}=0$ plus the electron cloud around it which shields the ion plus the electron hole around the electron which "antishields" the electron. Bardeen⁹ in 1937 calculated this quantity using the Hartree equations for the electrons. This takes into account shielding of the ion, but neglects the exchange and correlation hole effects. His result was that $I_{kk'}$

FIG. 1. The ratio of the shielding factor as calculated in this paper to the Bardeen result (reference 5).



could be written in the form,

$$I_{kk'} = S(s) I_{\text{ion}}(s) = \frac{1}{1 + S_{\text{Bardeen}}} I_{\text{ion}}(s), \quad (18)$$

$$I_{\text{ion}}(s) = N \int \psi(\mathbf{k}', \mathbf{r})^* \psi(\mathbf{k}, \mathbf{r}) \nabla v_{\text{ion}}(\mathbf{r}) d^3r, \quad (19)$$

where v_{ion} is the potential from the ion alone. In 1955, Bardeen and Pines¹⁵ treated the problem by means of the collective model for the N -particle electron system to take exchange and correlation effects into account. These authors concluded that for small wave-vectors $\mathbf{s} \equiv \mathbf{k}' - \mathbf{k}$, the 1937 Bardeen result still obtained, but that for large s there would be a correction that they did not attempt to work out. We have approached¹⁶ the exchange and correlation problem for the matrix element by employing the Hartree-Fock equation for the electrons and introducing the correlation correction simply by cutting off the long wave Fourier components of the Coulomb potential $1/r$ that appears in the exchange term. Our results can be written analogously to (18) as follows:

$$I_{kk'} = S(\mathbf{k}) I_{\text{ion}}(s) = \frac{1 - S_{\text{num}}'(k)}{1 - S_{\text{den}}'(s)} I_{\text{ion}}(s), \quad (20)$$

where S_{den} contains two terms, one arising from the Coulomb term in the Hartree-Fock equation and which reduces to the Bardeen term in (18) when the one-electron energy is treated in the effective mass approximation, the other arising from the exchange term in the Hartree-Fock equation, and which in the limit $s \rightarrow 0$ becomes negligible in comparison with the other terms, but otherwise is not negligible. The S_{num} depends on \mathbf{k} as well as $\mathbf{k} - \mathbf{k}'$, and hence wants to be averaged somehow. First one squares $I_{kk'}$, and then one averages over the circle of length talked about between (B24) and (B25). Unfortunately, reference 16 was written before

we had seen how the matrix element fits into the scheme of averages in (B25), and we averaged in reference 16 over the entire Fermi sphere. We repeated the calculation correctly for this paper however, the details being given in Appendix G, and the results in Fig. 1. It should be noted that if we pick any one of the points on the circle of length $l(s)$ we get the same value for S as for any other point on the circle. Therefore we do not in fact need to do anything extra to average, nor do we have to worry about averaging S^2 instead of S .

Our results indicate (except for a small wiggling) that for extremely small $|\mathbf{k} - \mathbf{k}'|$, the (1937) Bardeen result was too small and as $|\mathbf{k} - \mathbf{k}'|$ increases, S/S_{Bardeen} goes through a minimum and increases steadily up to the end of the umklapp region. The effect of the exchange and correlation hole is to increase the scattering over the Bardeen value, S^2 becoming as much as 1.6 times the Bardeen value in the umklapp region. Other consequences of our results are discussed in Appendix G. In particular, we note that our results do not reduce to the 1937 Bardeen result even right at $\mathbf{k} - \mathbf{k}' = 0$.

The disparity between our results and Bardeen and Pines' result has been reconciled by Pines¹⁷ (see also note added in proof to reference 16) who has been able to show that if one makes a canonical transformation which will remove the short-range electron-electron interaction (a term which in the Bardeen-Pines paper was neglected when they concluded that their results reduced to the 1937 Bardeen result for small s), and makes the adiabatic approximation, then their new results are identical with ours. Hence our one-electron model approach and the subsequent computations have been justified by a more rigorous argument.

An approximation that went into this computation was the use of plane waves for the electron wave functions. Brooks¹⁸ has shown how an improvement can

¹⁵ J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).

¹⁶ M. Baily, Phys. Rev. **117**, 974 (1960).

¹⁷ D. Pines (private communication).

¹⁸ H. Brooks (private communication). See also reference 16.

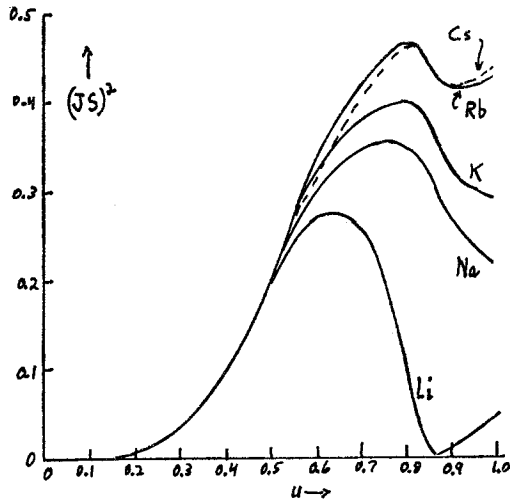


FIG. 2. The matrix element squared, using the Bardeen shielding factor. An error has crept into this figure. What is plotted is $\alpha(u)u^3(JS)^2$, not $(JS)^2$.

be made and suggests that the error in neglecting it may be large.

Also, we have used the first order exchange and correlation correction to the one-electron energies. The second order correction¹⁹ is certainly not negligible, and may play also a significant role numerically.¹⁸

The remainder of the computation of the matrix element concerns the ionic factor which we consider in the dimensionless form

$$J_{\text{ion}}(s) = N \frac{r_s}{a_h} \left(\frac{r_s}{c} \right)^2 \int \psi(\mathbf{k}', \mathbf{r})^* \psi(\mathbf{k}, \mathbf{r}) \nabla v_{\text{ion}}(\mathbf{r}) d^3r. \quad (21)$$

The approach we use to calculating (21) was introduced by Bardeen.⁵ The modifications that we make were suggested by Brooks. The first improvement is to use wave functions of the form

$$\psi(\mathbf{k}, \mathbf{r}) = N^{-1/2} a_0 e^{i\mathbf{k} \cdot \mathbf{r}} [u_0(r) + i f_{11}(\mathbf{r}) \mathbf{k} \cdot \mathbf{r} / r + \dots] \quad (22)$$

for which the necessary parameters to use in the Bardeen-type approach were obtained by Brooks by the quantum defect method²⁰ (see Appendix E). A second correction was the use of the Ewald sum technique²¹ to calculate the part of the integral in (21) that lies outside the cell in which the v_{ion} is situated.

We can sum up our results qualitatively as follows. (A) The quantity J becomes rather small in the umklapp region (for lithium it goes through a zero) and hence becomes sensitive to small corrections. Because of the factor F_n in the transport integrals [see (6), (7), etc.], the umklapp region is extremely important, and these small corrections have actually rather large effects.

¹⁹ J. G. Fletcher and D. Larson, *Phys. Rev.* **111**, 455 (1958).

²⁰ F. Ham, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1955), Vol. 1.

²¹ See texts such as M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).

(B) The improvement of the wave function, and the use of the Ewald technique in performing the lattice sum increases J in the umklapp region considerably, but not much in the non-umklapp region. We estimate the error in this part of our calculations to be of the order of 10%.

Despite the improvements on the matrix element, we feel that we are still far from having truly reliable values for $\alpha(u)$ ^{21a}. Consequently, we did not think that it was worth while making calculations that took more than a crude average effect of the improvements. In the umklapp region, we approximated α as a constant c_1 to be adjusted to fit the average theoretical calculation for each element. And in the non-umklapp region, we used a single curve for all the alkali's (see Fig. 2) with an adjustable multiplying constant c_0 :

$$\alpha(u) = c_0 u^5 h(u) \dots \quad 0 < u < 0.63 \text{ (non-umklapp)}, \quad (23)$$

$$= c_1 \dots \quad 0.63 < u < 1.0 \text{ (umklapp)},$$

$$c_0 = [JS/u]_{u=0^2}, \quad (24)$$

$$h(u) = 1 - 4.25u^2 + 6.25u^4 - 4.70u^8.$$

The form in (23), non-umklapp part, uses the 1937 Bardeen shielding factor. The adjusted c_0 and c_1 are given in Table I. We note from there that the umklapp region gets relatively more important as we go from Na to Cs. In Table I, c_0 and c_1 correspond to Fig. 2. These values were used in computing the results given in Fig. 3. We now give correction factors for certain approximations as follows: first the average of $(S/S_{\text{Bardeen}})^2$ in the umklapp region (i.e., the exchange adjustment of c_1); second this factor times the velocity correction of Eq. (14) adapted from Barrie's numbers; and third, $(S/S_{\text{Bardeen}})^2$ times the second order velocity correction adapted from Fletcher and Larson.¹⁹ We find: Na (1.92; 1.56; 4.66); K (1.56; 1.36; 4.53); Rb (1.43; 1.27; 4.22); Cs (1.34; 1.17; 3.90). Each of these numbers times the resistivity in Table I gives a new resistivity in the corresponding approximation. The third number in each case gives evidence that the second order effects are terribly large and provide very poor agreement with experiment. (It should be noted that the shielding factor used for the third number is the same as for the second, and does not include the second order correction to the one-electron energies in its calculation. Thus the third numbers are to this extent inconsistent. Nevertheless, the results are of interest.) We anticipate also a non-negligible effect of the second order exchange correction on the matrix element. This further cautions us that we cannot be confident in calculations of the matrix element. In the following section, the discussion

^{21a} Note added in proof.—In addition to the above-mentioned use of free-electron wave functions in computing the shielding factor, we mention the fact that the "vacuum fluctuations" of the phonons give rise to a temperature-dependent Debye-Waller factor in the matrix element J_{ion} . This factor depends exponentially on u^2 and may be very important when Bloch waves are used. A paper will appear shortly in *The Physical Review* on this point.

applies to the simplest case, the Bardeen shielding factor and no correction on the velocity. The same discussion would apply with the consistent first-order exchange correction made in the velocity and in the matrix element. However, the discussion below concerning magnitudes would not be applicable if the second-order exchange correction were contemplated.

At low temperatures, the extreme region, $u=1.0$ becomes relatively more important than at high temperatures. Therefore the same c_1 cannot be a correct average at all temperatures for a given substance. However in the temperature range, c_1 would vary by at most about 50%, whereas the transport coefficients for other reasons change by a factor of 10^3 or more. Hence we do not need to worry about this obscuring any temperature effects.

6. The Results of the Calculations

We here repeat the conclusions of a general nature that were first announced several years ago by Brooks and the author⁷ on the basis of preliminary calculations.

1. To the extent that the Born von Karman spectrum is valid, and the anisotropy of the relaxation time neglected (see footnote 9) the electrical resistivity is dominated by umklapp processes at all temperatures down to which we have calculated (8°K for sodium, 2°K for Cs, 20° for lithium). The thermal resistivity, subject to details of the matrix element, has about equal contributions from umklapp processes and non-umklapp processes, the latter beginning to become relatively less important at the lowest temperatures.

2. The transverse phonon modes dominate the electrical resistivity at all temperatures, and are of equal importance with the longitudinal in the thermal resistivity.

In our preliminary calculations, which employed an average Debye temperature in the umklapp region (for the low temperatures) we found quite good agreement with experiment in going from high to low temperatures.⁷ We were suspicious of this approximation, however, since there is a significant correlation between the anisotropy of the transverse phonons and the disposition of σ magnitudes in the umklapp region. Unfortunately, our worst fears were confirmed.²² In Fig. 3, (see also Table I), we indicate the experimental and theoretical curves that were obtained. (These were equated arbitrarily at some high temperature.) We notice that the resistivities (electrical and thermal) are in all cases too high as we go lower in temperature, the disagreement getting worse as the temperature gets lower, but setting in already at temperatures about $\frac{1}{2}$ the Debye-type temperature θ [see (16)]. The best

metal is cesium, the worst is sodium, while lithium (which is a metal which seems well to contemplate in a special category) is quite good. In the electrical resistivity, the disagreement in sodium at $\theta/T=20$ is such that the theoretical number is 10 times too large, for cesium about 2 times too large, the other metals ranging between these, potassium about 3 times, (and lithium, best of all, about 1.25). The magnitudes at some high temperature are listed in Table I, and we get good results for Na and K, rather poor results for the other metals, as is usually the case. It is interesting to note that if we multiply the factor that our high-temperature calculation is too low, by the factor that our low-temperature calculation is too high, we always get between about 5 and 10. For example, in sodium we get $(1)(10)=10$, for potassium, $(1)(5)=5$, for rubidium, $(2)(3)=6$, and for cesium, $(3)(2)=6$. In the case of lithium, the high-temperature value is too small by 4.0, but that is giving the matrix element a value which is probably too large. The total factor for lithium would be then larger than $(4)(1)=4$. We notice in addition that the sodium value is conspicuously larger than that of the other metals. We regard this as another aspect of the strange situation found in the specific heat²³ that all theoretical calculations for sodium based on an analysis of the spectrum yield Debye temperatures that go through a minimum as T gets down to about 10°K , where experimentally this is not observed; whereas a minimum *is* observed in potassium.²⁴

In a qualitative way, we have interpreted our results as implying that the spectrum we have used (that actually resembles the spectra that went into the specific heat calculations) has a shape that is worst suited for sodium from among all the alkali metals, and perhaps best suited for cesium. The characteristic of this theoretical spectrum is the high anisotropy in the transverse modes. We therefore draw the conclusion that this high anisotropy is actually fairly appropriate for cesium, but not for sodium, and the difference far more spectacular than merely some large change in the elastic constant parameters s_0 and s_1 . (See Fig. 4 and (F5) and (F12) for s_0 and s_1 .) This proposed systematic change from relatively small anisotropy to relatively large anisotropy as we go down the alkali metals would have significant consequences in the phonon drag effects

²³ See the review article by D. H. Parkinson, *Reports on Progress in Physics* (The Physical Society, London, 1958), Vol. 21, p. 226.

²⁴ Dr. D. L. Martin has pointed out to the author that the lack of a minimum in the Debye temperature of sodium at low temperatures probably has to do with the martensitic transformation in that metal at low temperatures. (See J. S. Dugdale and D. Guban, *Proc. Roy. Soc. (London)* A254, 184 (1960) for a recent analysis of the transformation in lithium and sodium. The other alkali metals have not revealed any such transformation despite great efforts to detect it.) About 50% of the specimen may be expected to convert to a faulted hcp lattice, and there has been some work which indicates that an hcp structure does not provide a pronounced minimum in the Debye temperature (see C. W. Garland and L. J. Slutsky, *J. Chem. Phys.* 28, 331, 1958). This would further our contention that sodium is somewhat of a special case. (We have come to a similar conclusion apropos of the phonon drag component of the thermo-electric power.²⁵)

²² The recent results of Pfennig⁶ are essentially equivalent to our preliminary calculations, the Blackman spectrum that he uses to get an average Debye temperature being of the same sort as ours. Our comments refer therefore equally well to his results as to our previous computations.

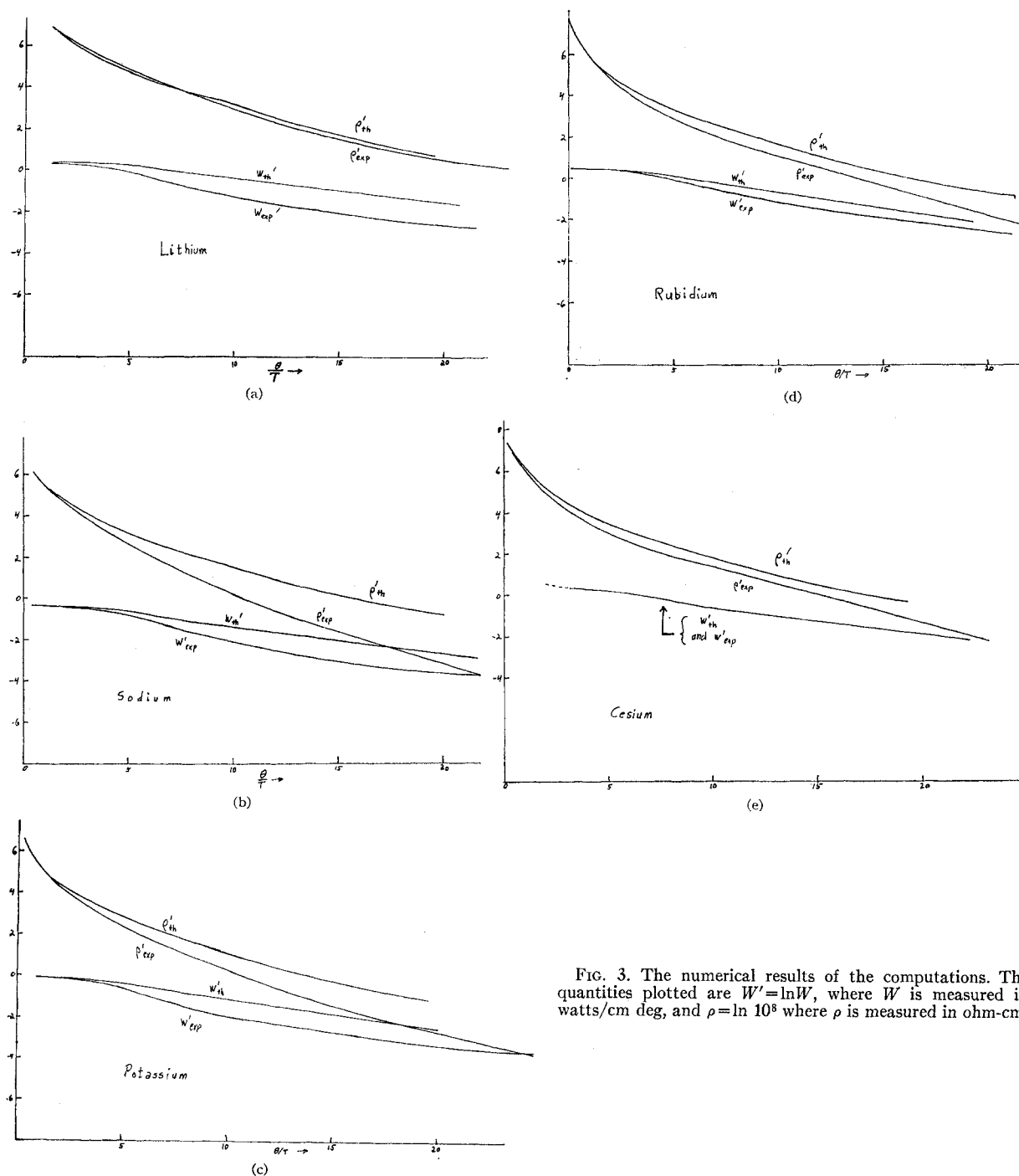


FIG. 3. The numerical results of the computations. The quantities plotted are $W' = \ln W$, where W is measured in watts/cm deg, and $\rho = \ln 10^8$ where ρ is measured in ohm-cm.

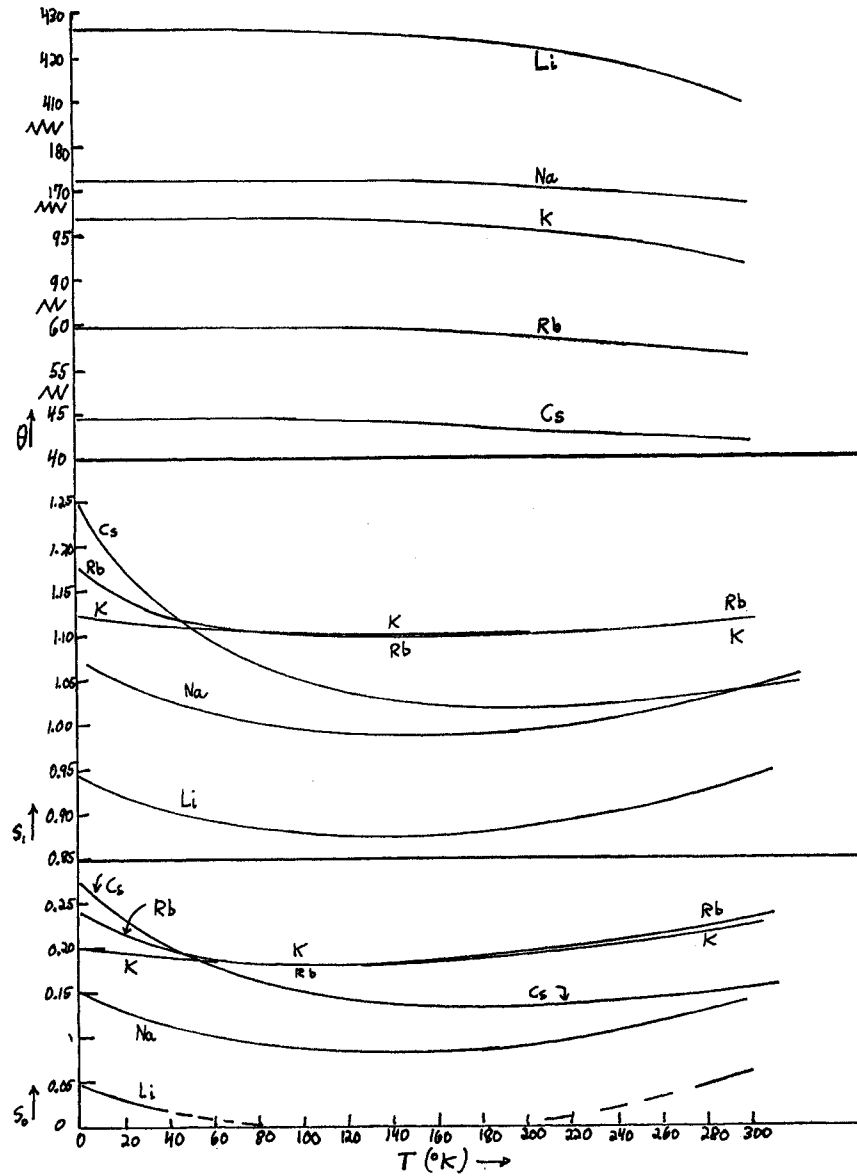
in the thermoelectric power,²⁵ and very likely in other contexts.

²⁵ M. Bailyn, Phil. Mag. (to be published). We have attributed the progressive increase in the positive character of the low-temperature thermoelectric power as we go from Na to Cs to many sources, the most significant to our minds heretofore being the progressive change in the matrix element. However, the progressive increase in anisotropy that we hypothesize from the results of this paper would be of equal significance. J. Ziman

There are other possible sources of our disagreement as we go from high to low temperatures. For example,

[Phil. Mag. 39, 371 (1959)] prefers to attribute the increase in positive character entirely to the progressive distortion of the Fermi surface as we go from Na to Cs. The problem of disentangling these effects is exceedingly complex, and it appears to the author unlikely that the relative importance will be determined in the near future, if only for the fact that one would need a much better spectrum than ours, and a much better description of the

FIG. 4. Elastic constant parameters as functions of temperature.



as we go down in temperature, the importance of the matrix element at $u=1.0$ becomes more and more important since F_0 becomes more and more greatly peaked at that point. Therefore, glancing at Fig. 2, we would expect for sodium and potassium that the effective c_1 should get smaller and smaller as we go down in temperature. (If we had relied on the 1937 Bardeen calculation, this effect would be increased.) It is however hard to see that this effect would be able to provide more than an increase of at most a factor of 2 for these metals (as mentioned above), even if we relied on the Bardeen matrix element. Thus we do not feel that this

distortion than is available, in order for the calculations to become significantly more accurate. However, our view is that the importance of the spectrum should not in any case be underestimated and surely not neglected.

can be the major origin of the discrepancy. Another possibility is the possibly poor extrapolation of the elastic constant parameters s_1 and s_0 . This however is totally inadequate to get alterations of the size needed. Distortion of the Fermi surface would also be inadequate, especially as that gets worse as we go from Na to Cs, whereas our discrepancies get worse in the other direction. One can however combine this effect with others to get changes in the right direction. *Note added in proof.* Dr. J. S. Dugdale has suggested that the correct spectrum might yield a general resistivity reduction that is similar for *all* the metals, but which would be compensated more and more as we go from Na to Cs by the increased distortion of the Fermi surface. This is an attractive alternative to attributing (as

we tentatively do) the discrepancy mainly to the spectrum. It should be noted that a distorted Fermi surface gives rise to smaller possible wave vectors in the umklapp region, and hence smaller possible phonon energies. This will have an effect therefore similar to some extent to an increase in anisotropy of the phonons, in the present problem. We are not convinced by these combinations, however, at this stage. Phonon drag effects are in the right direction, but they can be eliminated simply from the fact that there are no appreciable drag effects theoretically in the thermal resistivity (see I), whereas we get great discrepancies in the thermal resistivity calculations of this paper. There is a possibility that the spectrum points chosen in (F10) were not representative, but we avoided unrepresentative highly symmetric directions such as 110, and we had 25 points in $1/48$ of the sphere, so that this way out, although possible, seems to us unlikely. We therefore tentatively suggest that the origin of the discrepancy is a poor spectrum: the Born von Karman model including next-nearest neighbors may not be adequate for good quantitative comparison with experiment. In all this, we must not forget that the curly bracket in (A4) was assumed not to depend on the direction of \mathbf{k} . This may in fact hide serious errors.¹⁸

It should be noted that since the umklapp processes dominate the electrical resistivity, the T^5 law previously accepted as the limiting low-temperature T dependence does not set in until such extremely low temperatures, that the thermal component of the resistivity would not be large enough to distinguish from the impurity component. On the other hand, the umklapp term itself varies exponentially at low enough temperatures, and we may expect this to be measurable in some of the metals. Experimentally,²⁶ a T^6 law is found in sodium below 9°K, and this is quite consistent with our results, and could never be arrived at with just non-umklapp processes. However one would also expect something like this for lithium, and that is not observed. Possibly this has to do with the martensitic transformation which is more extensive in lithium than in sodium. Ultimately it must reflect something about the spectrum or the matrix element. In lithium, the possibility that the umklapp contribution is greatly weakened by a small matrix element in the umklapp region is not unlikely, especially if the zero in the matrix element occurs at $u=1.0$. Under such a situation, we would not expect the umklapp processes to dominate at the lowest temperatures (they usually do so through a great peak at $u=1.0$), and hence would not expect a T dependence more swift than the non-umklapp limit T^5 .

In the thermal resistivity, we find discrepancies of the same type as in the electrical resistivity as a function of temperature. They seem however to be generally

smaller, except for lithium. The reason for this is undoubtedly the fact that in the thermal resistivity, the non-umklapp contribution is significant and this is less sensitive than the umklapp part to the spectrum details. One important result of our calculation is that *there is no minimum in the ideal thermal conductivity* (or maximum in the thermal resistivity) as the temperature descends below $\theta/4$, except very slightly for rubidium, which more than likely arises from poor extrapolation of s_0 and s_1 or some other accidental error. Previous theories²⁷ have predicted such a minimum, which was never observed. It therefore seems certain that the spurious minimum in the thermal conductivity arose from an underestimate of umklapp processes, and of the effect of the spectrum on the umklapp processes. *Note added in proof.* A lessening of the anisotropy which we proposed three paragraphs above would not tend to produce again a maximum in the thermal resistivity provided the umklapp term remained important. Instead, it would make even more pronounced the steady decrease in the thermal resistivity as θ/T increases.

In the thermoelectric power, we do not have a quantity that is linear in the scattering mechanism (except in the phonon drag part which we neglect here). One can however rearrange terms as in Appendix D²⁸ to provide an expression

$$S = (eL_0T/\xi_0)S', \quad (25)$$

$$S' = W_0/W + 3(1 - W_0/W)S'', \quad (26)$$

where S'' can be estimated theoretically [see (D7)], and W_0/W , the ratio of the impurity component W_0 of the thermal resistivity to the total W , can be obtained from experiment. The resultant S' can then be calculated. We compare in Fig. 5 this calculation of S' at low temperatures with the straight lines assumed by MacDonald, Pearson, and Templeton.²⁹

Of far greater importance at low temperatures is the phonon drag effect. We have performed a numerical calculation of this effect based on an expression first derived in I. This has been written up in a separate paper referred to in footnotes 24 and 25. A derivation and discussion of the basic expression generalized to the case of distorted Fermi surfaces and more than one band is however included in Appendix H of the present paper.

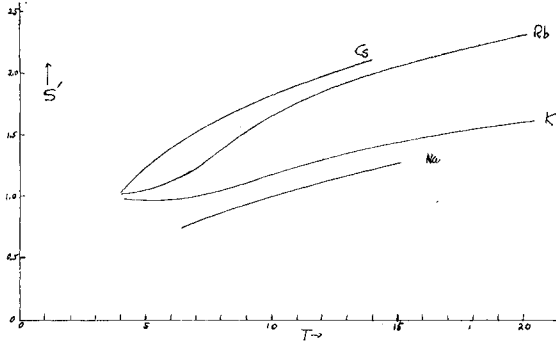
Finally, we take the opportunity to speculate on what might tend to smooth out the anisotropy of our spectrum as we go from Cs to Na. First of all, there is the possibility that the interactions of atoms more distant than next-nearest neighbors may not be negligible in the Born von Karman formulation of the problem. This is something that gets swiftly very complex, especially

²⁷ See reference 2, p. 309. See also Ziman, reference 6. Ziman went a good way toward getting rid of the minimum by means of his umklapp corrections.

²⁸ This type of manipulation has been made by M. Kohler, Z. Physik **126**, 481 (1949).

²⁹ D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, Proc. Roy. Soc. (London) **A248**, 107 (1958).

²⁶ For experiments see: D. K. C. MacDonald, G. K. White, and S. B. Woods, Proc. Roy. Soc. (London) **A235**, 358 (1956); and D. K. C. MacDonald and K. Mendelssohn, Proc. Roy. Soc. (London) **A202**, 103 (1950).

FIG. 5. The quantity S' of Eq. (D5).

since we then have to deal with more than 3 force constants, which cannot therefore all be reduced to the three elastic constants. One would have to appeal to x-ray data. Secondly, there is the possibility that the electron-electron interaction as treated by Bardeen and Pines¹⁵ would yield an increase of the "dressed" frequencies as opposed to the "bare" frequencies. [See Eqs. (3.12) and (4.8a) of reference 15.] Their results provided a *decrease* in the frequencies, but there may still be some loopholes by which alterations of the required sign could occur.

7. Conclusions

In the three basic nonmagnetic transport properties, we find that the umklapp processes are not only not negligible even at very low temperatures, but actually provide the distinguishing temperature dependence. In the electrical resistivity, the higher than T^5 law in sodium could only come from umklapp processes; in the thermal resistivity, the spurious minimum disappears when umklapp processes are taken into account; and in the thermoelectric power, it is the umklapp contribution to the phonon drag term that provides the anomalous positive sign. The first two of these results are discussed in the present paper; the latter was suggested by the author in I, and has since been computed numerically by Ziman³⁰ and the author.²⁵ The general expression is discussed below in Appendix H.

We find also that as a first approximation, it is far better to neglect the longitudinal phonons than the transverse phonons at any temperature, but especially at low temperatures.

Finally, the numerical results according to Fig. 3 are so far off that one begins to wonder what reliance can be put in the standard semiclassical transport theory. We feel, however, that the conclusion is not that the transport theory itself is inadequate for the phenomena discussed in this paper, but that the temperature dependence and numerical results in general in the alkali metals are unexpectedly sensitive to the details of a very anisotropic phonon spectrum which becomes more

and more important as the temperature decreases, because of the strange geometry (in wave-vector space) of the umklapp interactions. The success hitherto obtained with simple spectrum models in matching theory and experiment in sodium was not, in our view, a result of an ideal, but rather of a very unusual situation.²⁴ We suggest in fact that the ordinary transport properties are so sensitive to the lattice spectrum at low temperatures that these may in fact be as good a test of some aspects of the spectrum as is the specific heat.

ACKNOWLEDGMENTS

It is a pleasure to thank Professor Harvey Brooks for his direction during the original stages of this work and his continued advice during the completion of it. The author is also indebted to Dr. D. K. C. MacDonald, Mr. J. S. Dugdale, and Mr. A. Gold of the Low-Temperature Group at the National Research Council of Canada for their interest and encouragement.

II. APPENDICES

A. The Form for the Transport Coefficients

From Eqs. (84), (85), and (86) of I, neglecting phonon drag effects, we get

$$\rho = d_{00}/\alpha_0^2, \quad (\text{A1})$$

$$W = T d_{11}/\gamma_1^2, \quad (\text{A2})$$

$$(WS) = \frac{-\alpha_0\gamma_1 d_{10} + \alpha_1\gamma_1 d_{00} + \alpha_0\gamma_0 d_{11}}{\alpha_0^2\gamma_1^2}. \quad (\text{A3})$$

We change the expressions for the α_v 's, γ_v 's, and $d_{\mu\nu}$'s of reference 9 slightly in order to take into account distortions of the Fermi surface. The electron distribution function $f(k)$ is taken to be

$$f(k) = f_0 - \frac{m_0}{\hbar^2} (\nabla E)_x \frac{\partial f_0}{\partial E} \times \left\{ \mathcal{E}_x^* \sum_{\nu} a_{\nu} (E - \zeta)^{\nu} - \frac{1}{T} \frac{dT}{dx} \sum_{\nu} b_{\nu} (E - \zeta)^{\nu} \right\}, \quad (\text{A4})$$

where f_0 is the Fermi function, ζ the Fermi energy, and \mathcal{E}_x^* is defined in I (equals $\mathcal{E}_x + e^{-1} d\zeta/dx$, where \mathcal{E} is the electric field), and m_0 is the free electron mass. We would get the f used in reference 9 or in I by replacing $m_0\hbar^{-2}(\nabla E)_x$ by k_x . When (A4) is used in the Boltzmann equation, and in the variational principle, we have

$$\alpha_{\nu} = -e\gamma_{\nu-1} = \frac{m_0 e}{\hbar^3} \int (\nabla E)_x (\nabla E)_x \times \frac{\partial f_0}{\partial E} (E - \zeta)^{\nu} d^3k / 4\pi^3, \quad (\text{A5})$$

$$d_{\mu\nu} = -\left(\frac{m_0}{\hbar^2}\right)^2 \int (E - \zeta)^{\mu} (\nabla E)_x L \{ (E - \zeta)^{\nu} (\nabla E)_x \} \times d^3k / 4\pi^3, \quad (\text{A6})$$

³⁰ J. Ziman, Phil. Mag. **39**, 371 (1959). See also reference 23.

where for thermal scattering

$$L\{p\} = \sum_i \frac{\Delta}{8\pi^3} \int d^3k' (D_{kk'j}/N) \times [\Omega(-)\delta(-) + \Omega(+)\delta(+)] [-p(\mathbf{k}) + p(\mathbf{k}')]. \quad (\text{A7})$$

The L operator is obtained from Eq. (15) of I and is the collision operator in the Boltzmann equation. The α_v 's are obtained rather directly, and are

$$\alpha_0 = -\frac{3}{\pi^2} \frac{e}{(\kappa T)^2} \gamma_1 = -\frac{1}{12\pi^3} \frac{m_0 e}{\hbar^2} A(\zeta) v(\zeta) = -\frac{m_0}{m^*} \frac{e}{\hbar \Delta_0} \Big|_{\text{EMA}}, \quad (\text{A8})$$

$$\alpha_1 = -e\gamma_0 = -\frac{1}{36\pi} \frac{m_0 e}{\hbar^2} (\kappa T)^2 \left[\frac{d}{dE} v(E) A(E) \right]_{E=\zeta} = -\frac{\pi^2}{2} \frac{e}{\hbar \Delta_0} \zeta_0 \left(\frac{\kappa T}{\zeta_0} \right)^2 \Big|_{\text{EMA}}. \quad (\text{A9})$$

The last expressions in (A8) and (A9) are what one gets in the effective mass approximation (EMA). Here Δ_0 is the volume per atom, and

$$\zeta_0 = \frac{\hbar^2}{2m_0} \left(\frac{3\pi^2}{\Delta_0} \right)^{\frac{1}{3}} = \frac{\hbar^2 k_0^2}{2m_0} = \frac{m^*}{m_0} \zeta \Big|_{\text{EMA}}, \quad (\text{A10})$$

$$k_0^3 \Delta_0 = 3\pi^2. \quad (\text{A11})$$

The quantities ζ_0 and k_0 are defined (for any Fermi surface shape) by (A10) and (A11). $A(E)$ is the area of the surface of constant energy E , and $v(E)$ is the average velocity on that surface:

$$v(E) A(E) = \int_E dS v(E) = \frac{1}{\hbar} \int_E dS |\nabla E|. \quad (\text{A12})$$

In deriving (A8) and (A9) we have assumed cubic symmetry.

B. Reduction of the d_{mn} 's, and Calculation of the Resistivities

To calculate the d_{mn} 's we start from the formulas (16) and (44) of I neglecting phonon drag effects,

$$d_{\mu\nu} = B_1 \int \int d^3k d^3k' (D_{kk'j}/N) \times [\Omega(+)\delta(+) + \Omega(-)\delta(-)] \phi_{\mu\nu}. \quad (\text{B1})$$

$D_{kk'}$ is given by (9b) of I;

$$\Omega(\pm)\delta(\pm) = \Omega(E' - E \pm \hbar\omega) \delta(k' - k \pm \sigma \pm K);$$

and

$$\phi_{\mu\nu} = [-(E-\zeta)^\mu \nabla E + (E'-\zeta)^\mu \nabla E'] \cdot [-(E-\zeta)^\nu \nabla E + (E'-\zeta)^\nu \nabla E'], \quad (\text{B2})$$

$$B_1 = \left(\frac{m_0}{\hbar^2} \right)^2 \frac{\Delta}{8\pi^3} \frac{1}{4\pi^3} \frac{1}{3} \frac{1}{2}. \quad (\text{B3})$$

In B_1 the factor $1/(8\pi^3)$ comes from converting the k' sum to an integral (we do not count 2 for spin since interactions with phonons are assumed not to change the spin), the factor $1/(4\pi^3)$ comes from the definition [(32) of I] of d_{mn} , and the factor $\frac{1}{2}$ compensates adding the second term to the second bracket of (B2). We have made the velocity correction [replaced k_x by $(\nabla E)_x m_0 \hbar^{-2}$], and simplified for cubic symmetry [replaced $(\nabla E)_x (\nabla E)_x$ by $\frac{1}{3} \nabla E \cdot \nabla E'$].

We introduce a quantity dk_1' which denotes the differential segment perpendicular to the surfaces of constant energy at the point k' . The volume element $d^3k d^3k'$ is then

$$d^3k d^3k' = dS dk_1 dS' dk_1', \quad (\text{B4})$$

where dS' is the element of surface on the energy surface E' at k' . Now let us choose a k lying on an energy surface E , and integrate k_1' through some other point k' on the energy surface E . This integral will exercise the delta function nature of Ω and gives

$$\int dk_1' \Omega(\pm) F(k') = 2\pi \hbar F(k'(\mp)) [dE/dk_1']^{-1}, \quad (\text{B5})$$

where $k'(\pm)$ is obtained from k' (on E) by going along a line perpendicular to the energy surfaces from E an energy distance $\hbar\omega$ up $k'(+)$ or down $k'(-)$. We assume that there will always be a solution to the selection rule $k'(\pm) - k \pm \sigma \pm K = 0$ along this line that satisfies the energy condition $E' - E \pm \hbar\omega = 0$. dS' may now be taken as element on the energy surface E , and we must sum over the $+$ and $-$ cases.

Next the E (i.e., k_1) integral is performed. We regard the factors ∇E , $\nabla E'$ and $C_{kk'}$ [see Eqs. (9b) and (7) of I] as slowly varying with respect to the exponentials, in the vicinity of the Fermi surface. Outside the vicinity of the Fermi surface, the contributions are very small. Hence we take the above-mentioned quantities out at average values near the Fermi surface. Consider then two points k and k' (centered in dS and dS' , respectively) on the Fermi surface, and consider taking the two integrals dk_1 and dk_1' through k and k' . For every energy surface E that $dk_1(E)$ hits in the tail of the distribution, there will be contributions from two points $k'(E \pm \hbar\omega)$ hit by dk_1' , where $k'(E^+)$ is on the energy surfaces $E + \hbar\omega$, etc. Thus when we take out factors like $|\nabla E|/|\nabla E'|$ at average values in the tail, they should be averaged with this correlation in mind. (See Appendix C.)

Also, as we integrate through the tail of the distribution, the small changes of the phonon parameters σ , ω

are neglected. The σ used is the one appropriate to the dS, dS' pair on the Fermi surface.

The $\int dk_1$ is converted to an energy integral ($dk_1 = dE |\nabla E|^{-1}$) to regain the usual form for the integrals, and we find

$$d_{\mu\nu} = 2\pi\hbar B_1 \int \int dS dS' \frac{C_{kk'}}{\kappa T N} \times \left\{ \left| \frac{\nabla E}{\nabla E(-)'} \right| T_{\mu\nu}(-)^{(1)} + \left| \frac{\nabla E}{\nabla E(+)' } \right| T_{\mu\nu}(+)^{(1)} + \left| \frac{\nabla E(-)'}{\nabla E} \right| T_{\mu\nu}(-)^{(2)} + \left| \frac{\nabla E(+)' }{\nabla E} \right| T_{\mu\nu}(+)^{(2)} - \frac{\nabla E \cdot \nabla E(-)'}{|\nabla E| |\nabla E(-)'|} T_{\mu\nu}(-)^{(3)} - \frac{\nabla E \cdot \nabla E(+)' }{|\nabla E| |\nabla E(+)'|} T_{\mu\nu}(+)^{(3)} \right\}, \quad (\text{B6})$$

where

$$T_{\mu\nu}(-)^{(i)} = (\kappa T)^{\mu+\nu+1} [e^z - 1]^{-1}$$

$$\times \int_{-\infty}^{\infty} d\epsilon e^{\epsilon} f_0(E) f_0(E - \hbar\omega) X_{\mu\nu}(-)^{(i)}, \quad (\text{B7})$$

$$T_{\mu\nu}(+)^{(i)} = (\kappa T)^{\mu+\nu+1} (1 - e^{-z})^{-1}$$

$$\times \int_{-\infty}^{\infty} d\epsilon e^{\epsilon} f_0(E) f_0(E + \hbar\omega) X_{\mu\nu}(+)^{(i)}, \quad (\text{B8})$$

$$X_{\mu\nu}(\pm)^{(1)} = \epsilon^{\mu+\nu}$$

$$X_{\mu\nu}(\pm)^{(2)} = (\epsilon \pm z)^{\mu+\nu}, \quad (\text{B9})$$

$$X_{\mu\nu}(\pm)^{(3)} = \epsilon^{\mu} (\epsilon \pm z)^{\nu} + (\epsilon \pm z)^{\mu} \epsilon^{\nu},$$

and

$$\epsilon = (E - \zeta)/kT \quad z = \hbar\omega/kT. \quad (\text{B10})$$

The factors containing ∇E in (B6) [and the factors ∇_{mn} in (B15)–(B18) below] must be understood as averages over the tail of the Fermi distribution along lines perpendicular to the constant energy surface at \mathbf{k} and \mathbf{k}' , as discussed above. The energy integrals can be evaluated using Eq. (A.5.11) of Wilson.² We find for the relevant quantities [the curly brackets on the left referring to the corresponding brackets in (B6)]:

$$\{ \}_{00} = \nabla_{00} \kappa T z [(1 - e^{-z})(e^z - 1)]^{-1}, \quad (\text{B11})$$

$$\{ \}_{01} = \nabla_{01} \frac{1}{2} (\kappa T z)^2 [(1 - e^{-z})(e^z - 1)]^{-1}, \quad (\text{B12})$$

$$\{ \}_{11} = [\nabla_{11}^{(3)} (\kappa T z)^3 + \nabla_{11}^{(1)} L_1 \kappa T z] \times [(1 - e^{-z})(e^z - 1)]^{-1}, \quad (\text{B13})$$

where

$$L_1 = \pi^2 \kappa^2 T^2 / 3, \quad (\text{B14})$$

$$\nabla_{00} = \sum_{+-} \nabla_{00}(\pm) = \sum_{+-} \frac{|\nabla E - \nabla E(\pm)|^2}{|\nabla E| |\nabla E(\pm)'|} \cong 2 \frac{|\nabla E - \nabla E'|^2}{|\nabla E| |\nabla E'|}, \quad (\text{B15})$$

$$\nabla_{01} = \sum_{+-} \nabla_{01}(\pm) = \frac{|\nabla E|^2 - |\nabla E(-)'|^2}{|\nabla E| |\nabla E(-)'|} - \frac{|\nabla E|^2 - |\nabla E(+)'|^2}{|\nabla E| |\nabla E(+)'|}, \quad (\text{B16a})$$

$$= \left\{ |\nabla E| \left(\frac{1}{|\nabla E(-)'|} - \frac{1}{|\nabla E(+)'|} \right) \right\} + \left\{ \frac{|\nabla E(+)'| - |\nabla E(-)'|}{|\nabla E|} \right\}, \quad (\text{B16b})$$

$$\nabla_{11}^{(3)} = \sum_{+-} \nabla_{11}(\pm)^{(3)} = \frac{2}{3} \frac{|\nabla E - \nabla E'|^2}{|\nabla E| |\nabla E'|} + 2 \frac{\nabla E \cdot \nabla E'}{|\nabla E| |\nabla E'|}, \quad (\text{B17})$$

$$\nabla_{11}^{(1)} = \sum_{+-} \nabla_{11}(\pm)^{(1)} = \sum_{+-} \nabla_{00}(\pm). \quad (\text{B18})$$

The sum over $+$ and $-$ in d_{00} and d_{11} amounts to multiplying by 2, since accounting for the difference between $\nabla E(-)'$ and $\nabla E(+)'$ would give a very small correction. In d_{01} however, (B16) would give zero if we made the same approximation. When we expand as shown below it turns out that the first nonzero terms of d_{01} are of the same order as the terms in d_{11} that are calculated. We therefore must be rather careful in evaluating (B16).

Our results for the d_{mn} 's are given below in double angle brackets. These are defined to mean an average over all two-point connections on the Fermi surface:

$$\int \int dS dS' = A \langle \rangle_{\text{F.S.}} \quad (\text{B19})$$

Thus using (7) of I, we get

$$d_{00} = (B_2/\kappa T) A \langle \rangle^2 \langle \langle U_{00}(\mathbf{k}, \mathbf{k}') [(1 - e^{-z})(e^z - 1)]^{-1} \rangle \rangle_{\text{F.S.}}, \quad (\text{B20})$$

$$d_{01} = (B_2/\kappa T) A \langle \rangle^2 \langle \langle U_{01}(\mathbf{k}, \mathbf{k}') \frac{1}{2} \hbar\omega [(1 - e^{-z})(e^z - 1)]^{-1} \rangle \rangle_{\text{F.S.}}, \quad (\text{B21})$$

$$d_{11} = (B_2/\kappa T) A \langle \rangle^2 \langle \langle [L_1 U_{00}(\mathbf{k}, \mathbf{k}') + (\hbar\omega)^2 U_{11}(\mathbf{k}, \mathbf{k}')^{(3)}] [(1 - e^{-z})(e^z - 1)]^{-1} \rangle \rangle_{\text{F.S.}} = L_1 d_{00} + (B_2/\kappa T) A \langle \rangle^2 \langle \langle (\hbar\omega)^2 U_{11}(\mathbf{k}, \mathbf{k}')^{(3)} [(1 - e^{-z})(e^z - 1)]^{-1} \rangle \rangle_{\text{F.S.}}, \quad (\text{B22})$$

where

$$B_2 = 2\pi\hbar B_1 / 2NM, \quad (\text{B23})$$

M being the ionic mass, and

$$U_{00}(\mathbf{k}, \mathbf{k}') = \sum_j [\mathbf{I}_{kk'} \cdot \boldsymbol{\xi}(j\boldsymbol{\sigma})]^2 \nabla_{00}, \quad (\text{B24a})$$

$$U_{01}(\mathbf{k}, \mathbf{k}') = \sum_j [\mathbf{I}_{kk'} \cdot \boldsymbol{\xi}(j\boldsymbol{\sigma})]^2 \nabla_{01}, \quad (\text{B24b})$$

$$U_{11}(\mathbf{k}, \mathbf{k}')^{(3)} = \sum_j [\mathbf{I}_{kk'} \cdot \boldsymbol{\xi}(j\boldsymbol{\sigma})]^2 \nabla_{11}^{(3)}. \quad (\text{B24c})$$

The next step in reducing the d_{mn} 's in a general way is to isolate all the connections that have the same difference vector $\mathbf{s} = \mathbf{k}' - \mathbf{k}$, and to average over all such connections. If the Fermi surface is a sphere all these connections can be imagined to be enumerated by allowing a rigid rod of length s oriented in the direction of s to roll on the inside spherical shell. The tips of the rigid rod will each describe a circle of circumference $l(\mathbf{s}) = \pi s$. In general, for say ellipsoidal or other shapes, we will still have a length $l(\mathbf{s})$ covered by the tip of such a rigid rod rolling without change of orientation, but the length will not be precisely πs . The advantage of performing a preliminary average over all connections with a given s is that the phonon parameters do not change during it. We shall use $U_{mn}\{\mathbf{s}\}$ and $\{\{\}\}$ brackets to indicate averages over all \mathbf{k}, \mathbf{k}' with the same \mathbf{s} . Then

$$\langle\langle\{\{\}\}\rangle\rangle_{\text{F.S.}} = \langle\langle\{\{\}\}\rangle\rangle. \quad (\text{B25})$$

The double angle brackets on the right indicate an average over all $\mathbf{s}(s)$ for a given s . This is equal to the integral over all directions of $\mathbf{s}(s)$ with weighting factor equal to the ratio of the length $l(\mathbf{s})$ to the integral over all lengths for the given s magnitude:

$$\langle\langle\{\{\}\}\rangle\rangle = \int_{(s)} d\Omega\{\{\}\} \frac{l(\mathbf{s})}{\int_{(s)} d\Omega l(\mathbf{s})}. \quad (\text{B26})$$

(Here $\int d\Omega$ is the integral over solid angle of \mathbf{s} on a constant s -magnitude surface.) The single angle brackets in (B25) mean an average over all s magnitudes. This is equal to the integral over all s with weighting factor $\int d\Omega l(\mathbf{s}) / \int ds \int d\Omega l(\mathbf{s})$, the (normalized) composite lengths $l(\mathbf{s})$ associated with a magnitude s . Thus

$$\langle\langle\{\{\}\}\rangle\rangle_{\text{F.S.}} = \frac{\int ds \int_{(s)} d\Omega l(\mathbf{s}) \{\{\}\}}{\int ds \int_{(s)} d\Omega l(\mathbf{s})}. \quad (\text{B27})$$

The electrical and thermal resistivities due to thermal scattering (denoted by subscript i) are then

$$\rho_i = B_3 [\kappa T v(\dot{\tau})^2]^{-1} \int ds \int_{(s)} d\Omega l(\mathbf{s}) U_{00}\{\mathbf{s}\} [(1 - e^{-z})(e^z - 1)]^{-1} / \int ds \int_{(s)} d\Omega l(\mathbf{s}), \quad (\text{B28})$$

$$W_i = B_3 [L_0 \kappa T^2 v(\dot{\tau})^2]^{-1} \int ds \int_{(s)} d\Omega l(\mathbf{s}) [U_{00}\{\mathbf{s}\} + 3\pi^{-2} z^2 U_{11}\{\mathbf{s}\}^{(3)}] [(1 - e^{-z})(e^z - 1)]^{-1} / \int ds \int_{(s)} d\Omega l(\mathbf{s}), \quad (\text{B29})$$

where

$$B_3 = B_2 [12\pi^3 \hbar^2 m_0^{-1} e^{-1}]^2 = (\Delta_0 / M) (3\pi/4) (\hbar/e^2), \quad (\text{B30})$$

$$L_0 = \pi^2 k^2 / 3e^2. \quad (\text{B31})$$

The expressions in (B28) and (B29) apply to any shaped Fermi surface. If we wish to go any further, we must make some model of the shape. The advantage of (B28) and (B29) is that it is possible to extend calculations to shapes more complicated than the spherical. But in this paper we shall content ourselves with the usual spherical Fermi surface. If we call the radius k_0 , then from (B15) and (B17), we get $l(\mathbf{s}) = \pi s$, and:

$$\nabla_{00} = 2(\mathbf{k} - \mathbf{k}')^2 / (kk') \cong 4(1 - \cos\theta) = 8u^2, \quad (\text{B32})$$

$$\nabla_{11}^{(3)} = -\frac{4}{3}u^2 + 2, \quad (\text{B33})$$

$$u = \sin(\theta/2) \cdots 0 \leq u \leq 1, \quad (\text{B34})$$

$$U_{00} = \sum_j [\mathbf{I}_{kk'} \cdot \boldsymbol{\xi}(j\boldsymbol{\sigma})]^2 8u^2, \quad (\text{B35})$$

$$U_{11}^{(3)} = \sum_j [\mathbf{I}_{kk'} \cdot \boldsymbol{\xi}(j\boldsymbol{\sigma})]^2 (2 - 4u^2/3), \quad (\text{B36})$$

$$s = 2k_0 u, \quad (\text{B37})$$

and

$$\int ds \int_{(s)} d\Omega l(\mathbf{s}) = 8\pi^2 k_0^2. \quad (\text{B38})$$

Thus the resistivities due to thermal scattering are

$$\rho_i = A_0 T^{-1} y_1^2 \int_0^1 \alpha(u) F_0(u) du, \quad (\text{B39})$$

$$W_i = A_0 T^{-2} L_0^{-1} y_1^2$$

$$\times \int_0^1 \alpha(u) \left[F_0(u) + \frac{3u^2 - 2}{4\pi^2} F_2(u) \right] du, \quad (\text{B40})$$

where

$$A_0 = 16\pi^2 (4/9\pi)^{3/2} (m_0/M) (\hbar/\kappa), \quad (\text{B41})$$

$$y_1 = \frac{\hbar k_0 / m_0}{v(\dot{\tau})} = \frac{m^*}{m_0} \bigg|_{\text{EMA}}, \quad (\text{B42})$$

$$\alpha(u) = (I\{s\})^2 u^3 (r_s/a_n)^2 (r_s/e)^4, \quad (\text{B43})$$

and

$$F_n(u) = \left\langle \left\langle \frac{z^n}{(e^z - 1)(1 - e^{-z})} \left(\frac{\mathbf{s}}{s} \cdot \boldsymbol{\xi}(j\boldsymbol{\sigma}) \right)^2 \right\rangle \right\rangle. \quad (\text{B44})$$

The $F_n(u)$ are averages over all directions of \mathbf{s} for a given s magnitude. The average is indicated by the angle brackets. The factor $\alpha(u)$ is introduced for convenience in computations: it is dimensionless and of order of magnitude 1. It should be noted that what enters as a coefficient is γ_1 (squared) which is inversely proportional to the velocity; the effective mass, i.e., the second derivative of the energy does not enter directly into ρ_i and W_i .¹⁴

C. The Thermoelectric Power

The variational principle in the approximation of three rows and columns gives the expression (A2) and (A3) which can be reduced to

$$TS = \frac{\gamma_0}{\alpha_0} + \frac{\alpha_1 \rho T}{\gamma_1 W} - \frac{\gamma_1 d_{10}}{\alpha_0 d_{11}}, \quad (C1)$$

(where ρ and W are the total resistivities in this approximation), or using the values of α_v and γ_v in (A8) and (A9)

$$S = -\frac{\pi^2 k^2 T}{3 |e|} \left[\frac{d}{dE} \ln v(E) A(E) \right]_{E=\xi} \times \left(1 + \frac{\rho}{L_0 T W} - 2\delta \right), \quad (C2)$$

$$2\delta = \frac{d_{10}}{d_{11}} \left/ \left[\frac{d}{dE} \ln v(E) A(E) \right] \right|_{E=\xi}. \quad (C3)$$

At high temperatures and very low, where the Wiedemann Franz law holds, we have the general result that the first two terms in the circular bracket yield an expression S_0 independent of the details of scattering mechanism:

$$S = S_0(1 - \delta), \quad (C4)$$

$$S_0 = -\frac{\pi^2 k^2 T}{|e|} \frac{\gamma_2}{\xi_0}, \quad (C5)$$

$$\gamma_2 = \frac{2\xi_0}{3} \left[\frac{d}{dE} \ln v(E) A(E) \right]_{E=\xi} = \frac{m^*}{m_0} \bigg|_{\text{EMA}}, \quad (C6)$$

which displays in a simple way how the shape of the Fermi surface enters. At high temperatures an argument can be made that δ is often negligible. The neglect of δ cannot be made generally valid even at high temperatures, but we shall indicate how the argument, when valid, goes. If we substitute (B21) and (B22) into (C3), then with (B27)

$$\delta = \frac{2\xi_0}{3\gamma_2 L_1} \frac{\int ds \int d\Omega l(s) U_{01} \{ \mathbf{s} \}^{\frac{1}{2}} \hbar \omega [(1 - e^{-z})(e^z - 1)]^{-1}}{\int ds \int d\Omega l(s) [U_{00} \{ \mathbf{s} \} + (\hbar \omega / \kappa T)^2 (3/\pi^2) U_{11} \{ \mathbf{s} \}^{(3)}] [(1 - e^{-z})(e^z - 1)]^{-1}}. \quad (C7)$$

The second term in the curly brackets in the denominator is negligible at high temperatures; in any case it is positive and would help make δ small. The major problem is to estimate U_{01} , that is, to average ∇_{01} through the tail of the distribution. We shall refer to this as the "tail-average" or " T -average" in what follows. In (B16b), we notice that the numerator of the second curly bracket can be expanded

$$\frac{|\nabla E(+)'| - |\nabla E(-)'|}{|\nabla E|} = \frac{d|\nabla E'|}{dk_1'} \frac{dk_1'}{dE'} \frac{2\hbar\omega}{|\nabla E|} = \frac{2\hbar\omega}{|\nabla E|} \frac{d^2 E' / d(k_1')^2}{|\nabla E'|}, \quad (C8)$$

the T -average now being replaceable by the value (at the two points k and k') on the Fermi surface. We make no special notation for this average.

To get an analogous result for the first curly bracket of (B16b), we assume that ∇E is sufficiently smoothly varying so that the T -average of the ratio $|\nabla E|/|\nabla E(-)'|$ does not change significantly if we

step up the energy E by $2\hbar\omega$:

$$\left| \frac{\nabla E(E)}{\nabla E(E - \hbar\omega)'} \right| = \left| \frac{\nabla E(E + 2\hbar\omega)}{\nabla E(E + \hbar\omega)'} \right| \quad (C9)$$

both sides averaged through the E values in the tail of the distribution. [If ∇E is not sufficiently smooth, (C9) will still be valid at high temperatures, when the energy span of the tail is much larger than $\hbar\omega$.] Defining

$$b = d^2 E / dk_1^2, \quad (C10)$$

we get

$$\left| \frac{\nabla E}{\nabla E(-)'} \right| - \left| \frac{\nabla E}{\nabla E(+)' } \right| = \frac{|\nabla E(E + 2\hbar\omega)| - |\nabla E|}{|\nabla E(+)'|} = \frac{2\hbar\omega b}{|\nabla E| |\nabla E'|}, \quad (C11)$$

and from (B16b), (C8), and (C11),

$$\nabla_{01} = \frac{2\hbar\omega(b + b')}{|\nabla E| |\nabla E'|}. \quad (C12)$$

Defining

$$V_n = \{ \{ \sum_i (\mathbf{I}_{kk'} \cdot \xi(j\sigma))^2 \} \} z^n [(e^z - 1)(1 - e^{-z})]^{-1}, \quad (C13)$$

(see the discussion apropos of (B25) for the double curly brackets), we get

$$\delta = \frac{\xi_0}{\pi^2 y_2} \frac{\int ds \int d\Omega l(\mathbf{s}) V_2 \frac{b+b'}{|\nabla E| |\nabla E'|}}{\int ds \int d\Omega l(\mathbf{s}) \left[V_0 \frac{|\nabla E - \nabla E'|^2}{|\nabla E| |\nabla E'|} + \frac{3}{\pi^2} V_2 \nabla_{11}^{(3)} \right]}. \quad (\text{C14})$$

Now for the effective mass approximation (EMA)

$$\frac{|\nabla E - \nabla E'|^2}{|\nabla E| |\nabla E'|} \cong 4u^2 = \text{order } (2), \quad (\text{C15})$$

$$\frac{b+b'}{|\nabla E| |\nabla E'|} \cong \xi^{-1}. \quad (\text{C16})$$

Hence in this case the order of magnitude of δ is

$$\delta = \text{order} \left[\frac{1}{4\pi^2} \left(\frac{\hbar\omega}{\kappa T} \right)^2 \right], \quad (\text{C17})$$

since $y_2 = m^*/m_0 \cong 1$ in this case. If we take the effect of $(\kappa T/\hbar\omega)^2$ in V_0 to be of the order of a factor of 5 at high

temperatures, then δ is of the order $1/200$, a sufficiently small number. If we now distort the Fermi surface so as to cause the velocities $\hbar^{-1}\nabla E$ to average out to half their former selves, this would still not upset the smallness of δ . Thus we suggest that at high temperatures for situations that are not widely different from an isotropic Fermi surface, (and perhaps even then), we may neglect the δ . Thus (C5) should probably apply to the noble metals for example and to the alkali metals under pressure. (See however, footnote 9.)

If we are determined to get in general some more concrete estimate of δ , we may return to (B21) and (B22), writing these in terms of a double integral via (B19), and using (C12) and the high-temperature approximation for the exponentials. Then

$$\frac{d_{01}}{d_{11}} = B_2 \kappa T \frac{1}{\rho L_1 \alpha_0} \int \int dS dS' \sum_j (\mathbf{I}_{kk'} \cdot \xi(j\sigma))^2 \frac{b+b'}{|\nabla E| |\nabla E'|}, \quad (\text{C18})$$

where we have let $d_{11} = \rho L_1 \alpha_0^2$ at high temperatures. If we do the following drastic things, we can get a measure of this result in terms of the result for some standard substance like sodium: let us neglect the influence of $(\mathbf{I} \cdot \xi)^2$ in (C18), and let $b+b'$ be represented by the inverse of some effective mass m^* . Then the integral in (C18) is proportional to the square of the density of states at the Fermi surface, and we get

$$\frac{\delta}{\delta_{\text{Na}}} = \frac{[Dm^* y_2 \rho / \xi]_{\text{Na}}}{[Dm^* y_2 \rho / \xi]} \frac{\int dS |\nabla E|^{-1} \left(\int dS |\nabla E| \right)_{\text{Na}}}{\left(\int dS |\nabla E|^{-1} \right)_{\text{Na}} \int dS |\nabla E|}, \quad (\text{C19})$$

where D is the density M/Δ_0 which enters through the constant B_2 .

The final thing in this appendix will be to obtain from (C1) an expression for the thermoelectric power not restricted to high temperatures. From (C1), (A8), and (A9), we get

$$(WS)_i = -\frac{e}{\kappa T} \frac{B_3}{v(\xi)^2} \frac{3y_2}{2\xi_0} \int ds \int_{(\mathbf{s})} d\Omega l(\mathbf{s}) \left[2U_{00}\{\mathbf{s}\} + \frac{3z^2}{\pi^2} U_{11}\{\mathbf{s}\}^{(3)} - \frac{\hbar\omega\xi_0}{\pi^2 \kappa^2 T^2 y_2} U_{01}\{\mathbf{s}\} \right] \times [(e^z - 1)(1 - e^{-z})]^{-1} / \int ds \int_{(\mathbf{s})} d\Omega l(\mathbf{s}). \quad (\text{C20})$$

If we now divide by (B31) we get

$$S_i = (SW)_i / W_i = \frac{e L_0 T 3 y_2}{2 \xi_0} \frac{\int ds \int d\Omega l(\mathbf{s}) \left[2U_{00} + \frac{3z^2}{\pi^2} U_{11}^{(3)} - \frac{\hbar\omega\xi_0}{\pi^2 \kappa^2 T^2 y_2} U_{01} \right] [(e^z - 1)(1 - e^{-z})]^{-1}}{\int ds \int d\Omega l(\mathbf{s}) \left[U_{00} + \frac{3z^2}{\pi^2} U_{11}^{(3)} \right] [(e^z - 1)(1 - e^{-z})]^{-1}}. \quad (\text{C21})$$

This is the S analogous to (B30) and (B31); it makes no assumption about the Fermi surface shape. To go further,

we shall use spherical energy surfaces as in Appendix B. If we define

$$y_0 = 2\zeta_0 \left[\frac{(d^2E/dk^2)}{(dE/dk)^2} \right]_{E=\zeta} = \frac{m^*}{m_0} \bigg|_{\text{EMA}}, \quad (\text{C22})$$

then from (B24) and (C12) we get

$$U_{01}\{\mathbf{s}\} = \sum_i (\mathbf{l}_{kk'} \cdot \xi(j\sigma))^2 2\hbar\omega y_0 / \zeta_0.$$

We get finally by reducing (C20)

$$(SW)_i = -\frac{3|e|}{\zeta_0} \frac{A_0}{T} y_2 y_1^2 \int_0^1 \alpha(u) \left[F_0 + F_2 \frac{(3 - y_0/y_2)u^{-2} - 2}{8\pi^2} \right] du \quad (\text{C23})$$

$$S_i = \frac{(SW)_i}{W_i} = -\frac{\pi^2 k^2 T}{|e|\zeta_0} y_2 \frac{\int_0^1 \alpha(u) \left[F_0 + F_2 \frac{(3 - y_0/y_2)u^{-2} - 2}{8\pi^2} \right] du}{\int_0^1 \alpha(u) \left[F_0 + F_2 \frac{3u^{-2} - 2}{4\pi^2} \right] du}. \quad (\text{C24})$$

This reduces to S_0 [see (C5)] at high temperatures. Note that the S term in (C4) corresponds to the term in y_0 in (C24).

The expression S'' can be computed theoretically, W_0/W can be attempted theoretically or experimentally, and hence S' finally estimated.

D. The Ideal and Impurity Components of the Thermoelectric Power

The total thermoelectric power S is not the sum of the residual and thermal parts since S is not linear in the scattering cross section. However SW is. Let the residual and thermal parts of SW be denoted by the subscripts (0) and (i) , respectively. Similarly with W . Then we have

$$S = (SW)_0/W + (SW)_i/W. \quad (\text{D1})$$

For the residual part we shall assume the usual expression (see Mott and Jones¹, pp. 306 and 311)

$$\frac{(SW)_0}{W} = \frac{eL_0 T}{\zeta_0} \frac{W_0}{W}, \quad (\text{D2})$$

where $L_0 = \pi^2 k^2 / (3e^2)$. We can also write

$$1/W = (1 - W_0/W)/W_i$$

and then

$$\frac{(SW)_i}{W} = \left(1 - \frac{W_0}{W}\right) \frac{(SW)_i}{W_i}, \quad (\text{D3})$$

and using (B25) for $(SW)_i/W_i$

$$S = \frac{eL_0 T}{\zeta_0} S', \quad (\text{D4})$$

$$S' = \frac{W_0}{W} + 3 \left(1 - \frac{W_0}{W}\right) S'', \quad (\text{D5})$$

$$S'' = \frac{\zeta_0}{eL_0 T} \frac{(SW)_i}{W_i}$$

$$= y_2 \frac{\int du \alpha [F_0 + F_2 ((3 - y_0/y_2)u^{-2} - 2)/8\pi^2]}{\int du \alpha [F_0 + F_2 (3u^{-2} - 2)/4\pi^2]}. \quad (\text{D6})$$

E. Calculation of the Ionic Part of the Matrix Element

The quantity α that enters into our expressions for the transport coefficients is conveniently expressed as

$$\alpha(u) = (|JS|)^2 u^5, \quad (\text{E1})$$

where we hope there will be no confusion between the shielding factor S here (discussed in the text) and the thermoelectric power S of Appendix C. J is

$$J = i \frac{r_s}{a_h} \left(\frac{r_s}{e} \right)^2 N \int_{\text{crystal}} \psi(\mathbf{k}', \mathbf{r})^* \psi(\mathbf{k}, \mathbf{r}) \nabla v(\mathbf{r}) d^3 r. \quad (\text{E2})$$

One improvement discussed in this appendix arises from use of the wave function

$$\begin{aligned} \psi(\mathbf{k}, \mathbf{r}) &= N^{-1/2} a_\infty e^{i\mathbf{k} \cdot \mathbf{r}} u_k(r) \\ &= N^{-1/2} a_\infty e^{i\mathbf{k} \cdot \mathbf{r}} [u_0(r) + i f_{11}(r) \mathbf{k} \cdot \mathbf{r} / r + \dots], \end{aligned} \quad (\text{E3})$$

which is an extension from the plane wave approximation. The functions u_0 (the "s" function) and f_{11} (the "p" function) satisfy certain radial wave equations which we do not discuss here.³¹ The only numbers we actually need are the values on the surface of the Wigner-Seitz cell, and those can be obtained from the quantum defect method (reference 20, p. 185).

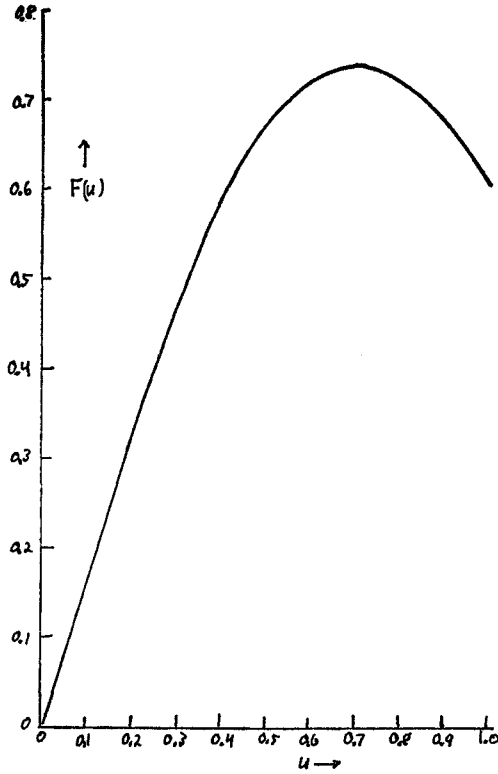
The normalization parameter a_∞ is obtained in terms of an auxiliary parameter γ

$$a_\infty = \gamma [\Delta_0 u_0^2(r_s)]^{-1/2}, \quad (\text{E4})$$

$$\gamma \equiv \Delta_0 u_0^2(r_s) / \int_{\text{cell}} u_0^2(r) d^3 r. \quad (\text{E5})$$

The general lines of computation follow Bardeen.⁶

³¹ J. Bardeen, J. Chem. Phys. **6**, 367, 372 (1938).

FIG. 6. The function $F(u)$ of Eq. (E13).

We make a separation of the integral into two parts, a part in the cell centered at $r=0$

$$J_{\text{in}} = N \frac{r_s}{a_h} \left(\frac{r_s}{e} \right)^2 \int_0^{r_s} [\psi(\mathbf{k}', \mathbf{r}) \psi^*(\mathbf{k}, \mathbf{r})] \nabla v_{\text{ion}} d^3r, \quad (\text{E6})$$

plus the part in the rest of the crystal

$$J_{\text{out}} = N \frac{r_s}{a_h} \left(\frac{r_s}{e} \right)^2 \times \sum_{\mathbf{R}_i \neq 0} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_i} \int_{\text{cell}} \psi(\mathbf{k}, \mathbf{r}) \psi^*(\mathbf{k}', \mathbf{r}) \nabla \frac{e^2}{|\mathbf{r}-\mathbf{R}_i|}, \quad (\text{E7})$$

where \mathbf{R}_i means the equilibrium position of the i th ion.

$$J_{\text{out}} = \frac{r_s}{a_h} \left(\frac{r_s}{e} \right)^2 \left\{ \frac{4\pi i e^2}{\Delta_0} \sum_{\mathbf{K}_i} \frac{\mathbf{k}-\mathbf{k}'+\mathbf{K}_i}{|\mathbf{k}-\mathbf{k}'+\mathbf{K}_i|^2} \exp \left[-\frac{|\mathbf{k}-\mathbf{k}'+\mathbf{K}_i|^2}{4Y^2} \right] \right. \\ \times \int_{\text{cell}} d^3r \psi(\mathbf{k}, \mathbf{r}) \psi^*(\mathbf{k}', \mathbf{r}) e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} + e^2 \sum'_{\mathbf{R}_i} \int_{\text{cell}} d^3r \frac{\mathbf{r}-\mathbf{R}_i}{|\mathbf{r}-\mathbf{R}_i|^3} \\ \left. \times \left[1 - 4\pi^{-\frac{1}{2}} \int_0^{(\mathbf{r}-\mathbf{R}_i)Y} t^2 \exp(-t^2) dt \right] \psi(\mathbf{k}, \mathbf{r}) \psi^*(\mathbf{k}', \mathbf{r}) e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_i} \right\}, \quad (\text{E11})$$

where Y is chosen to make the series converge rapidly. (We used $Y=1.20k_0$.) The primed R sum means that the term $\mathbf{R}=0$ contains only the second term in the square bracket. Although this looks formidable, the

J_1 is itself reduced by the method shown in reference 5 to a surface integral involving the total potential minus the integral of the gradient of the screening charge arising from the electrons which screen the ion. The exchange hole gives a constant potential (since the electron is always at its center) and does not enter in this part of the calculation, since it is the gradient of the potential that is required. In the surface integral, we used the recent values of the appropriate quantities on the surface of the Wigner-Seitz cell as computed by Brooks.²⁰ In the subtracted off potential, we made a detailed calculation using the u_0 value for lithium computed by Silverman²² and found that there was no significant difference from the free electron result. Since we expect the greatest deviation from free electron results for lithium, we assumed that this subtracted off term will be close to the free electron value for all the alkali metals. The result can then be written

$$J_{\text{in}} = \left\{ \gamma_2^2 \left(\frac{r_s}{a_h} \right)^2 [v(r_s) - E_0] j_1(x_s) + 3 \frac{r_s}{a_h} \frac{j_2(x_s)}{x_s} \right. \\ \left. + \frac{3}{2} \left(\frac{9\pi}{4} \right)^{\frac{1}{2}} g(3u - u^{-1}) j_2(x_s) \right\}, \quad (\text{E8})$$

$$x_s = |\mathbf{k}-\mathbf{k}'| r_s = 2(9\pi/4)^{\frac{1}{2}} u, \quad (\text{E9})$$

$$g = (df_{11}/dr)_{r=r_s/u_0(r_s)}, \quad (\text{E10})$$

where $v(r_s) - E_0$ refers to the total (including the electron-electron term) potential and energy, where the $j_n(x)$ are the spherical Bessel functions of order n , and where $v(r_s)$ and E_0 are in atomic units. $E_0 = E(\mathbf{k}=0)$. The last term in (E8) results from the cross terms in the square brackets in (E6) when $\psi\psi^*$ is written out.

The evaluation of J_2 was obtained by the Ewald sum technique²¹ first applied to this problem by Brooks. This has the consequence that the r integrals need extend only over a cell. The sum over \mathbf{R}_i is replaced by two sums, one over \mathbf{R}_i and one over \mathbf{K}_i , where the \mathbf{K}_i 's are the vectors of the reciprocal lattice. These sums have the advantage of being much more rapidly converging than the original sum as it appears in (E7). The result is

convergence is so rapid that the only significant terms were the $\mathbf{R}_i=0$, and $\mathbf{K}_i=0$ ones. The resulting expres-

²² R. Silverman, Phys. Rev. **85**, 227 (1952); also thesis, Harvard University (unpublished).

sion may be written

$$J_{\text{out}} = \frac{3}{2} \left(\frac{4}{9\pi} \right)^{\frac{1}{2}} \frac{r_s}{a_h} [u^{-1} \exp(-u^2/1.44) - P(u)], \quad (\text{E12})$$

where the P function is

$$P(u) = 2 \left(\frac{9\pi}{4} \right)^{\frac{1}{2}} \int_0^1 d \left(\frac{r}{r_s} \right) \gamma \left(\frac{u_0(r)}{u_0(r_s)} \right)^2 \times \left\{ j_1(|\mathbf{k} - \mathbf{k}'| r) \frac{4}{\pi^{\frac{1}{2}}} \int_0^{r^Y} x^2 \exp(-x^2) dx \right\}. \quad (\text{E13})$$

This has been estimated and the result is shown in Fig. 6. The factor γ in (E13) makes $P(u)$ roughly independent of the metal.

This in brief outline was how the ion part of the matrix element was calculated. An investigation of the error involved in neglecting the interference term in J_{out} , and in other neglects, was made and it was estimated that the error should not be more than about 10%, except for lithium. We have occasionally stated "except for lithium" in this discussion, and the reason is that in the surface integral in J_1 , the corrections arising from the extra term in (E3) were about 100%, and there seemed to be no sign of any convergence in sight, when we added a third "d" term in (E3). This lack of any semblance of convergence forces us to the conclusion that the free-electron approximation is a poor place to start a calculation for this substance, and that the methods used here simply are not good enough, even roughly. The lithium case is further complicated by the fact that the total J goes through a zero in the middle of the umklapp region, and the resulting contribution to the resistivity is very sensitive to where the zero occurs, since the umklapp contributions get more and more important as u approaches 1. We have used our results up to "d" terms in lithium just to get some numbers.

F. The Spectrum Calculation, the Method of Averaging in the Non-Umklapp and Umklapp Regions, and The Computation of Elastic Constants

The secular equation for the phonons on the Born von Karman model is obtained from de Launay³³ equation (11.7). The solutions are taken to be of the form

$$\frac{1}{4}(a\sigma)^2 D w^2 / c_{44} = 2(1 - \mathcal{G}_4) + [(c_{12} + c_{44}) / c_{44}] \lambda(\sigma), \quad (\text{F1})$$

where w is the velocity of the phonon, σ the wave vector, a the lattice constant, and D the density of the material. The elastic constants c_{ij} replace the force constants the relationship obtained by going to the limit $\sigma \rightarrow 0$. The force constant Δ is neglected, as was originally suggested by Born and von Karman. The function λ satisfies the

equation

$$\lambda^3 - t_1 \lambda^2 - t_2 \lambda - t_3 = 0, \quad (\text{F2})$$

which is what de Launay's (11.7) reduces to when our hypothesis (F1) is made. The rest of the symbols mean the following:

$$\begin{aligned} t_1 &= s_0 \mathcal{G}_1, \\ t_2 &= (1 - s_0^2) \mathcal{G}_2 - 3 \mathcal{G}_3, \\ t_3 &= \mathcal{G}_3 [s_0^3 + s_0 (\mathcal{G}_1 - 3) + 2 \mathcal{G}_4], \end{aligned} \quad (\text{F3})$$

$$\begin{aligned} \mathcal{G}_1 &= T_x + T_y + T_z, \\ \mathcal{G}_2 &= T_x T_y + T_y T_z + T_z T_x, \\ \mathcal{G}_3 &= T_x T_y T_z, \\ \mathcal{G}_4 &= [1 - \mathcal{G}_1 + \mathcal{G}_2 - \mathcal{G}_3]^{\frac{1}{2}}, \end{aligned} \quad (\text{F4})$$

where

$$\begin{aligned} T_i &= [\sin(\sigma_i a / 2)]^2, \\ s_0 &= (c_{11} - c_{44}) / (c_{12} + c_{44}). \end{aligned} \quad (\text{F5})$$

When the eigenvalues $w(j)$ ($j=1,2,3$) are obtained, the eigenvectors $\xi(j\sigma)$ which appear in (B44) can also be obtained by going back to the secular equation. In this way, if we are given σ , we can calculate the "average-and" in (B44).

The remaining task is to find what σ 's to average over in (B44): Here we must distinguish umklapp from non-umklapp processes. The separation comes at $u=0.63$ for a body-centered cubic material. For the two types of processes we have

$$\begin{aligned} \mathbf{s} &= \sigma \cdots & u < 0.63, \\ \mathbf{s} &= \sigma + \mathbf{K} \cdots & u > 0.63. \end{aligned} \quad (\text{F6})$$

Thus in the non-umklapp region, if we are given an s magnitude, the average in (B44) is over all σ 's of this same magnitude, but with differing directions:

$$\langle \langle \rangle \rangle = \langle \langle \rangle \rangle_{\sigma(\sigma)}, \quad \cdots \text{non-umklapp}, \quad (\text{F7})$$

which we have indicated by the symbol $\sigma(\sigma)$.

Although we could have performed the rest of the non-umklapp calculation in a way identical to the umklapp calculation as explained below, we found it more convenient to do it a different way, mainly because once the calculations issue from the machine, there is still a tedious amount of work to be done that can be simplified for the non-umklapp case. The simplification is to suppose that the variation of the eigenvectors and eigenvalues do not change much as σ magnitude increases for small σ (this is in fact just the elastic limit solution). Hence in (B40) and (B41) we shall be able to write

$$\begin{aligned} \int_0^{0.63} du I(s)^2 u^p F_n &= \left\langle \left\langle \langle \xi(j\sigma) \cdot \sigma / \sigma \rangle^2 \right. \right. \\ &\times \left. \int_0^{0.63} du \frac{I(s)^2 u^p}{(e^u - 1)(1 - e^{-u})} \right\rangle \rangle_{\sigma(\sigma)}, \end{aligned} \quad (\text{F8})$$

³³ J. de Launay, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2.

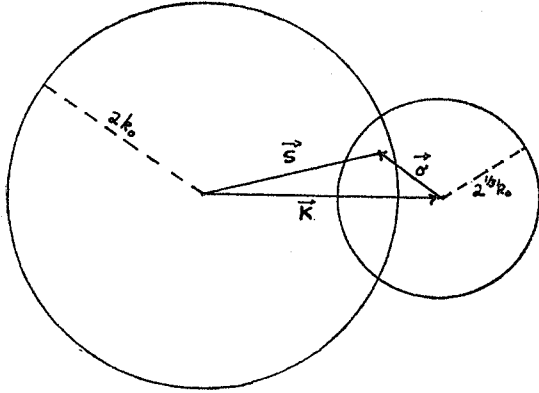


FIG. 7. The geometry of umklapp processes. The vector \mathbf{K} is a vector of the reciprocal lattice. The s sphere of radius $2k_0$ is the locus of scattered wave vectors $\mathbf{s} = \mathbf{k} - \mathbf{k}'$ in an interaction.

where the velocity appearing in z is the same for each σ for a given σ/σ . In other words, we have taken the average in front of the integral, and we use the elastic limit solutions. However, when eventually converting to an integral over z , it is essential to make the upper limit a function of the velocity even at extremely low temperatures. This general procedure is quite unjustified in the umklapp region.

In the umklapp region, we consider the s -sphere of radius $2k_0$. The geometry is as in Fig. 7. There will be associated with each of the 12 nearest neighbor K 's a region in the s -sphere (which will be a surface segment for a given s magnitude of course), and we need average over only one of these segments, in fact, because of the symmetry, over only $\frac{1}{4}$ of one. From (F6) we have for the choice of the reciprocal lattice vector $\mathbf{K} = (K/2^{\frac{1}{2}})(1,0,1)$:

$$\begin{aligned}\sigma_x &= s \sin\theta \cos\phi - 2^{-\frac{1}{2}}K, \\ \sigma_y &= s \sin\theta \sin\phi, \\ \sigma_z &= s \cos\theta - 2^{-\frac{1}{2}}K,\end{aligned}\quad (\text{F9})$$

where the polar angle θ is measured from the z direction. In this way if we are given an s magnitude in the umklapp region, we compute the σ 's from (F8) over the appropriate range of θ and ϕ , calculate the corresponding eigenvectors and eigenvalues from (F1) and (F2), and compute the corresponding "average-and" from (B44). The only remaining problem is to choose the various θ , ϕ 's to compute the σ 's for. The appropriate region to average over can be obtained by an examination of the geometry of the face-centered cubic reciprocal lattice. It is actually $1/48$ of the unit sphere, and the region is given by:

$$\begin{aligned}\text{I: } & 0 \leq \theta, \quad \phi \leq 45^\circ, \\ \text{II: } & 45^\circ \leq \theta \leq 54^\circ 44', \\ & 2^{-\frac{1}{2}} \leq \cos\phi \leq \cot\theta.\end{aligned}\quad (\text{F10})$$

We have taken the following points (where n and

TABLE II. The numbers from Eq. (F11).

n	4	8	10	14	16	20	22	26	28
m'/m	1/3	2/4	1/5	2/7	1/8	2/10	1/11	2/13	1/14
			4/5	5/7	4/8	5/10	4/11	5/13	4/14
					7/8	8/10	7/11	8/13	7/14
							10/11	11/13	10/14
									13/14

m'/m are given in Table II)

$$\begin{aligned}\theta &= (n/30)(\pi/4), \\ \phi &= (m'/m)(\pi/4),\end{aligned}\quad (\text{F11})$$

which neglect region II in (F10) but should give a good average, provided the Born-von Karman theory is sufficiently accurate in the nearest neighbor approximation.

In order to get numerical results, we have to know the elastic constants c_{ij} . These are obtained by the method of Fuchs (see reference 32, footnote 47), using for the room temperature compressibility values which we interpreted from the measurements of Bridgeman¹¹ and for low-temperatures values obtained in experiments by Swenson.³⁴ The compressibility seems to be a hard quantity to estimate from compressions, and we are not too sure what sort of accuracy is reflected by the results cited in Table I. We notice that at 4°K, the s_0 parameter rises as we go from lighter to heavier elements, but this trend starts to reverse itself at rubidium when we get to 77°K. At room temperature the same situation as at 77°K holds, except that cesium is now relatively quite low compared to rubidium. s_0 is very sensitive to the value of the compressibility, and we must regard these numbers with caution. It is interesting to note that at 77°K, we get a negative s_0 for lithium, which means that the longitudinal phonon in the 100 direction is slower than the transverse phonon, which implies instability. It is known that lithium undergoes a martensitic transition at about that temperature. Curiously however, at 4°K, we regain a positive s_0 for lithium. However, at 4°K, we have in units of 10^{10} erg/cm³, for lithium,

$$\begin{aligned}c_{11} - c_{44} &= 1/\chi + \frac{2}{3}(c_{11} - c_{12}) - c_{44} \\ &= 12.82 + 1.89 - 13.59 = 1.13.\end{aligned}$$

Hence a 5% error in the compressibility χ provides about a 50% error in $c_{11} - c_{44}$! (Lithium is more sensitive than the other metals, however.)

In Table I we give the values for s_0 and s_1 which are required in (F1), where

$$s_1 = (c_{12} + c_{44}) / (2c_{44}). \quad (\text{F12})$$

The values we chose to make our calculations for were 0.05, 0.15, and 0.30 for s_0 , and 0.9, 1.0, and 1.1 for s_1 . These were selected before we were aware of the work of Swenson, and were based on a range of values implied by some rather poor theoretical extrapolations for the

³⁴ C. A. Swenson, Phys. Rev. **99**, 423 (1955).

compressibility. Luckily our new s_0 values still lie in the above-mentioned range, but the s_1 values lie beyond 1.1 for the heavier elements. We therefore had to extrapolate s_1 for these elements.

Finally there is the elastic constant c_{44} that appears in the z of (B44). We introduce a temperature θ by

$$z = \hbar\omega/\kappa T = (\theta/T)(Dw^2/c_{44})^{1/2}(\sigma/k_0), \quad (\text{F13})$$

where the Dw^2/c_{44} is what we calculate in (F1), and where

$$\theta = (\hbar k_0/\kappa)(c_{44}/D)^{1/2} \quad (\text{F14})$$

depends on c_{44} . Numbers for θ are given in Table I, and we see that they are close to the ordinary Debye temperatures obtained from specific heat data. However, our θ 's are not averages over a spectrum: They are precisely defined by (F14). θ may be used in the specific heat or resistivity without any error arising from there being different averages involved. It is the rest of (F13) that gets averaged.

Since s_0 and s_1 are functions of temperature, we must use the appropriate values at the appropriate temperatures. The same is true for c_{44} and hence θ . However, in the range from 0°K to 77°K the density remains approximately the same (see reference 34) so that quantities which are functions of the density only do not change in this region. This includes c_{11} , c_{12} , c_{44} , and hence θ .

G. Evaluation of the Shielding Factor

In this appendix we shall have occasion to use the symbols p , x , z , θ , φ , L_0 , L , a , D , λ , and β with meanings

$$\langle a_s(\mathbf{k}) \rangle_{\text{ex}} = \frac{3}{4\pi k_0^3} \frac{\hbar^2 s^4}{2m_0} \int_{l < k_0} d^3l [E(\mathbf{l}) - E(\mathbf{l} + \mathbf{s})]^{-1} [|\mathbf{k}' + \mathbf{l}|^{-2} + |\mathbf{k} - \mathbf{l}|^{-2}] \cdots [|\mathbf{k}' + \mathbf{l}| > k_c; |\mathbf{k} - \mathbf{l}| > k_c], \quad (\text{G9})$$

where \mathbf{k}' satisfies (G2) and is on the Fermi surface and where k_c is the Bohn-Pines cutoff wave vector. In reference 16, (A9) was evaluated by first averaging \mathbf{k} over the Fermi surface. However, if \mathbf{s} is given, we should actually average only over the \mathbf{k} 's that lie on the circle of length $l(\mathbf{s})$ in (B26). The difference is that instead of averaging over the \mathbf{k} 's for a given s magnitude, we must average only over the k 's for a given \mathbf{s} vector, and in fact, we should average S^2 not S . What we shall do is evaluate (G9) directly as it stands without averaging over \mathbf{k} (or \mathbf{k}') at all, so long as it satisfies (G2). We shall then find that for all the proper \mathbf{k} 's, the result is the same and we need not average at all. This does not mean

different from what was used previously. The definitions are given below. S of course here means the shielding factor, not the thermoelectric power.

From reference 16 we get the shielding factor in the form [Eq. (32)]

$$S = \frac{1 + \lambda_0 [\langle a_s \rangle - \langle a_s(\mathbf{k}) \rangle]}{1 + \lambda_0 \langle a_s \rangle}, \quad (\text{G1})$$

where the denominator and $\langle a_s \rangle$ are evaluated in that reference. The electron wave vectors \mathbf{k} and \mathbf{k}' are on the Fermi surface and satisfy

$$\mathbf{k}' = \mathbf{k} + \mathbf{s}. \quad (\text{G2})$$

The energy function is

$$E(\mathbf{k}) = E_0 + (\hbar^2 k_0^2 / 2m_0)(px^2 - pqx^4), \quad (\text{G3})$$

$$x = k/k_0. \quad (\text{G4})$$

The parameters p and q appropriate to a given r_s/a_h are cited in reference 16. Finally from Eqs. (28), (A8), (A9) of that reference:

$$\lambda_0 = [12\pi(9\pi/4)^{1/2}]^{-1}(r_s/a_h)u^{-4}, \quad (\text{G5})$$

$$\langle a_s \rangle = \langle a_s \rangle_{\text{Coul}} + \langle a_s \rangle_{\text{ex}}, \quad (\text{G6})$$

$$\langle a_s \rangle_{\text{Coul}} = \langle a_s(\mathbf{k}) \rangle_{\text{Coul}} = 12u^2 F(u), \quad (\text{G7})$$

$$\langle a_s \rangle_{\text{ex}} = -12u^2 G(u; h). \quad (\text{G8})$$

In (G7), $\langle a_s(\mathbf{k}) \rangle_{\text{Coul}}$ does not depend on \mathbf{k} , hence it equals $\langle a_s \rangle_{\text{Coul}}$ and drops out of the numerator. The functions F and G in (G7) and (G8) are given in reference 16. The problem here is to evaluate

that the matrix element does not depend on \mathbf{k} ; it means that the dependence does not change so long as \mathbf{k} is on the circle of length $l(\mathbf{s})$.

To start, we shall change the variable of integration from \mathbf{l} to \mathbf{l}_1 in the term in \mathbf{k} in the square brackets where

$$\mathbf{l}_1 \equiv \mathbf{l} - \mathbf{k}, \quad (\text{G10})$$

the polar axis being now $-\mathbf{k}$. It can be shown that the two terms in the square bracket each contribute the same. We therefore consider only

$$\langle a_s(\mathbf{k}) \rangle = L_0 L, \quad (\text{G11})$$

$$L = k_0^{-1} \int_{k_c}^{2k_0} l_1^2 dl_1 \int_{\frac{1}{2}l_1/k_0}^1 \sin\theta d\theta \int_0^{2\pi} d\varphi l_1^{-2} k_0^2 [|\mathbf{l}_1 + \mathbf{k}|^2 - |\mathbf{l}_1 + \mathbf{k} + \mathbf{s}|^2 - (q/k_0^2)(|\mathbf{l}_1 + \mathbf{k}|^4 - |\mathbf{l}_1 + \mathbf{k} + \mathbf{s}|^4)]^{-1}, \quad (\text{G12})$$

$$L_0 = \frac{3k_0}{4\pi k_0^3} \frac{\hbar^2 s^4}{2m_0} \frac{2}{\hbar^2 k_0^2} \frac{2}{p} \frac{24}{\pi} \frac{u^4}{p}. \quad (\text{G13})$$

L_0 contains a factor 2 from the sum of the two terms in the square bracket of (G9). The limit we placed on the

θ integration can be obtained from a glance at the geometry of the l_1 -sphere. With a certain amount of algebra, and with $s^2 + 2\mathbf{k} \cdot \mathbf{s} = 0$, we can reduce (G11) to

$$\langle a_s(\mathbf{k}) \rangle = -\frac{6u^2}{\pi p} \int_{\beta}^2 dx \int_{x/2}^1 dz \int_0^{2\pi} [xb'D]^{-1} \left[\frac{1}{\cos t} + \frac{1}{D - \cos t} \right] dt, \quad (\text{G14})$$

where we have made the notational changes

$$\begin{aligned} x &= l_1/k_0, \\ z &= \cos \theta = -\hat{\mathbf{k}} \cdot \mathbf{l}_1/l_1, \\ \hat{\mathbf{z}} &= -\mathbf{k}/k_0, \end{aligned} \quad (\text{G15})$$

and where

$$\begin{aligned} D &= (a' + b'z)/b'u > 0, \\ a' &= 1 - 2q - 2qx^2, \\ b' &= 4qx, \\ \beta &= k_c/k_0, \end{aligned} \quad (\text{G16})$$

with

$$\cos t = \hat{\mathbf{s}} \cdot \mathbf{l}_1/l_1 = uz + [(1-u^2)(1-z^2)]^{1/2} \cos \varphi. \quad (\text{G17})$$

Here φ is the azimuthal angle of \mathbf{l}_1 around $\hat{\mathbf{z}}$ and we choose $\varphi=0$ at the azimuthal of \mathbf{s} around $\hat{\mathbf{z}}$. From standard integral tables³⁵ we find

$$\int_0^{2\pi} d\varphi [\cos t]^{-1} = 2\pi [z^2 + u^2 - 1]^{-1/2}, \quad (\text{G18})$$

$$\int_0^{2\pi} d\varphi [D - \cos t]^{-1} = 2\pi [a_2 + b_2 z + c_2 z^2]^{-1/2}, \quad (\text{G19})$$

provided the quantity contained in the square brackets is positive, the integrals are zero if the quantity in square brackets is negative. Here

$$\begin{aligned} a_2 &= (a'/b'u)^2 - 1 + u^2, \\ b_2 &= \frac{1-u^2}{u^2} \frac{2a'}{b'}, \\ c_2 &= (1-u^2)/u^2. \end{aligned} \quad (\text{G20})$$

The restriction requires that z^2 be greater than $1-u^2$ in (G18), but is automatically satisfied for all z in (G19). We indicate the remaining integrals:

$$\begin{aligned} \langle a_s(\mathbf{k}) \rangle &= -\frac{12u^3}{p} \left[\int_{\beta}^{2(1-u^2)^{1/2}} dx \int_{(1-u^2)^{1/2}}^1 dz + \int_{a(1-u^2)^{1/2}}^2 dx \int_{x/2}^1 dz \right] \frac{x^{-1}}{a' + b'z} \frac{1}{(z^2 - 1 + u^2)^{1/2}} \\ &\quad - \frac{12u^3}{p} \int_{\beta}^2 dx \int_{x/2}^1 dz \frac{x^{-1}}{a' + b'z} \frac{1}{(a_2 + b_2 z + c_2 z^2)^{1/2}} \cdots (1-u^2)^{1/2} > \beta/2 \\ &= -\frac{12u^3}{p} \int_{\beta}^2 dx \int_{x/2}^1 dz \frac{x^{-1}}{a' + b'z} \left[\frac{1}{(z^2 - 1 + u^2)^{1/2}} + \frac{1}{(a_2 + b_2 z + c_2 z^2)^{1/2}} \right] \cdots (1-u^2)^{1/2} < \beta/2. \end{aligned} \quad (\text{G21})$$

The z integrals can be obtained from standard tables.³⁶ We shall not indicate the quite complicated results of that integration. The final integral over x was carried out on the IBM-650 computer at Northwestern University.

The limiting case $u=0$, is of interest. We find

$$\lim_{u \rightarrow 0} \langle a_s(\mathbf{k}) \rangle_{\text{ex}} = -\frac{12u^4}{p} \frac{1}{1-2q} \frac{2}{\beta} \ln \frac{2}{\beta}, \quad (\text{G22})$$

$$\lim_{u \rightarrow 0} S = \frac{1 - [\pi(9\pi/4)^{1/2}]^{-1} (r_s/a_h) [p(1-2q)]^{-1} [6(\frac{1}{2} - \beta/2 + \beta^2/8) - \ln(2/\beta)]}{[\pi(9\pi/4)^{1/2}]^{-1} (r_s/a_h) u^{-2}}, \quad (\text{G23})$$

$$\lim_{u \rightarrow 0} \frac{S}{S_{\text{Bardeen}}} \cong \frac{p}{1+2q} - \left[\pi \left(\frac{9\pi}{4} \right)^{1/2} \right]^{-1} \frac{r_s}{a_h} \left[6 \left(\frac{1}{2} - \frac{\beta}{2} + \frac{\beta^2}{8} \right) - \ln \frac{2}{\beta} \right]. \quad (\text{G24})$$

The quantity in (G24) has the values 1.67, 1.30, and 1.04 for $r_s/a_h = 3, 4$, and 5, respectively.

³⁵ W. Grobner and N. Hofreiter, *Integraltafel* (Springer-Verlag, Wien, 1958), Vol. 2, formula 331 (41e, f).

³⁶ B. O. Pierce, *A Short Table of Integrals* (Ginn and Company, Boston, Massachusetts, 1929), 3rd. ed., formula 195.

In the theory of the phonon drag component of the thermoelectric power at low temperatures, the quantity

$$\left| \frac{(I(s)/u)_{u=0}}{I(s)_{u=1}} \right|^2 = \left| \frac{(S/u)_{u=0}}{S_{u=1}} \right|^2 \left| \frac{I_{\text{ion}}(0)}{I_{\text{ion}}(1)} \right|^2 \quad (\text{G25})$$

is important.²³ Our calculations give

$$\frac{(S_0/S_1)^2}{(S_0/S_1)_{\text{Bardeen}}^2}$$

equal to 1.54, 0.91, and 0.65 for r_s/a_h equal to 3, 4, and 5, respectively. Thus the Bardeen shielding factor considerably underestimates the growing importance of umklapp processes at $u=1$ to non-umklapp processes at $u=0$ as we go from lithium down the alkali's to cesium. (We are assuming that the tendency set up in going from $r_s/a_h=3$ to 5 will continue to 5.5, which is the appropriate value for cesium. We did not make this additional calculation as it would involve a considerable extra amount of numerical work.)

H. General Expression for the Phonon Drag Term of the Thermoelectric Power in Metals (Including Distortion and More Than One Band)

If the Fermi surface cuts more than one band, we describe the situation by the reduced wave vector \mathbf{k} and the band index l . A higher band is to be conceived as having been reduced into the first band by translations of the various portions by reciprocal lattice vectors. In terms of the reduced wave vector, we still get for any phonon transition the selection rule

$$\mathbf{k}' - \mathbf{k} = \boldsymbol{\sigma} + \mathbf{K} \quad (\text{or } -\boldsymbol{\sigma} - \mathbf{K}). \quad (\text{H1})$$

[See Eq. (4) of I.]

$$\alpha(j\boldsymbol{\sigma}; \mathbf{k}l, \mathbf{k}'l') = \frac{N^{-1}D_{\mathbf{k}\mathbf{k}'l'l'}\Omega(-)\delta(-)}{-\frac{dN_{0j}}{dz} \frac{1}{\kappa T \tau_j(\boldsymbol{\sigma})} + \sum_{\mathbf{k}\mathbf{k}'l'l'}^{[j\boldsymbol{\sigma}]} N^{-1}D_{\mathbf{k}\mathbf{k}'l'l'}\Omega(-)\delta(-)}. \quad (\text{H7})$$

The sums in (H6) and in the denominator of (H7) are over all interactions $\mathbf{k}l \leftrightarrow \mathbf{k}'l'$ in which the particular phonons $j\boldsymbol{\sigma}$ are permitted by the selection rules to enter. This includes interband umklapp processes as an example. $1/\tau_j(\boldsymbol{\sigma})$ is the sum of the reciprocals of the phonon-phonon collision time, the phonon-impurity and phonon-boundary collision times and any other phonon relaxation processes not involving electrons.

Considering a one-band metal, if we sum (H7) over all processes that involve one particular $j\boldsymbol{\sigma}$ and one particular umklapp type of process, we get back the relative probabilities $\alpha(j\boldsymbol{\sigma}; \boldsymbol{\sigma} + \mathbf{K})$ previously introduced in a paper on the phonon drag effect in the alkali metals.²⁵

From (H2) and (H5)–(H7), we get

$$S_g = \frac{1}{3|e|} \left(\frac{m}{N} \right)_{\text{eff}} \sum_{\sigma j} \frac{dN_{0j}}{dT} \nabla \omega \cdot \sum_{\mathbf{k}\mathbf{k}'l'l'}^{[j\boldsymbol{\sigma}]} \alpha(j\boldsymbol{\sigma}; \mathbf{k}l, \mathbf{k}'l') [\mathbf{v}(l\mathbf{k}) - \mathbf{v}(l'\mathbf{k}')], \quad (\text{H8})$$

From Eq. (86) of I, the phonon drag term is

$$S_g = T^{-1} \gamma_0' / \alpha_0. \quad (\text{H2})$$

For α_0 we may use from (A8)

$$\alpha_0 = -\frac{1}{12\pi^3} \frac{m_0 e}{\hbar^2} \sum_l A(l\zeta) v(l\zeta), \quad (\text{H3})$$

where $A(l\zeta)$ is the area of that part of the Fermi surface in the l th band, and where $v(l\zeta)$ is the average velocity on $A(l\zeta)$:

$$v(l\zeta) = \hbar^{-1} \int_{A(l\zeta)} dS |\nabla E| / A(l\zeta). \quad (\text{H4})$$

We may use (79) of I for γ_0' :

$$\gamma_0' = -\frac{1}{3N\Delta_0} \sum_{\sigma j} (dN_{0j}/dz) \nabla \omega \cdot \mathbf{Q}_0, \quad (\text{H5})$$

provided that in \mathbf{Q}_0 [see (76) of I] we replace \mathbf{k} by $m_0 \mathbf{v}(l\mathbf{k})/\hbar$

$$\mathbf{Q}_0(j\boldsymbol{\sigma}) = -m_0 \hbar^{-1} \sum_{\mathbf{k}\mathbf{k}'l'l'}^{[j\boldsymbol{\sigma}]} [\mathbf{v}(l\mathbf{k}) - \mathbf{v}(l'\mathbf{k}')] \times \alpha(j\boldsymbol{\sigma}; \mathbf{k}l, \mathbf{k}'l'). \quad (\text{H6})$$

Here $\alpha(j\boldsymbol{\sigma}; \mathbf{k}l, \mathbf{k}'l')$ is the relative probability that the phonon $j\boldsymbol{\sigma}$ will interact with electrons in a $\mathbf{k}l \leftrightarrow \mathbf{k}'l'$ transition:

where

$$\left(\frac{m}{N} \right)_{\text{eff}} = \frac{1}{N \Delta_0} \sum_l A(l\zeta) v(l\zeta) \rightarrow \left. \frac{m^*}{N} \right|_{\text{EMA}}, \quad (\text{H9})$$

where EMA means the effective mass approximation. N here refers to the number of atoms involved ($\Delta = N\Delta_0$).

The “normal” sign for S_g (for electrons) is negative. Since $dN_{0j}/dT > 0$, this means that normal contributions to S_g occur when

$$\nabla \omega \cdot [\mathbf{v}(l\mathbf{k}) - \mathbf{v}(l'\mathbf{k}')] < 0. \quad (\text{H10})$$

For the case of one band, and free electrons, we have $\mathbf{v} \sim \mathbf{k}$, and with $\nabla \omega \sim \boldsymbol{\sigma}$, we get from (H10)

$$\nabla \omega \cdot [\mathbf{v}(l\mathbf{k}) - \mathbf{v}(l'\mathbf{k}')] \sim \boldsymbol{\sigma} \cdot (\mathbf{k} - \mathbf{k}') = -\boldsymbol{\sigma} \cdot (\boldsymbol{\sigma} + \mathbf{K}). \quad (\text{H11})$$

Thus for non-umklapp processes ($\mathbf{K}=0$), (H11) is negative, and we get a normal contribution. For $\mathbf{K}=0$, (H11) yields a positive sign in general.

To analyze the effect of a higher band, we reduce it into the first Brillouin zone [in which now the \mathbf{k} and \mathbf{k}' of (H1) roam]. Consider the extreme case of a reduced zone whose *unoccupied* part is a sphere.

The velocities on the (Fermi) sphere are then directed *toward* the center rather than away from the center (as would occur if the sphere were occupied rather than unoccupied). Thus the velocity factor is (H10) changes sign from what it was when we considered (H11) in the previous paragraph, whereas $\nabla\omega$ does not, since that is still determined by the $\mathbf{k}-\mathbf{k}'$ in (H1). Hence for a sphere of holes, the non-umklapp interactions give an *anomalous* (positive) contribution to S_0 , whereas the umklapp processes would tend to give a normal contribution! If we have other shapes than a sphere, the situation becomes more complicated of course, but the general tendency seems to be that if the reduced zone is characterized by a large central hole, then we will get the results just described. One can contemplate inter-band transitions in a similar way, by reducing both bands into the first zone, and considering the directions of the velocities at \mathbf{k} on the l th band's surface to \mathbf{k}' on the l' th band's surface.

An important point is that once a band is reduced, and all \mathbf{k} space propagated periodically with this reduced zone, it cannot then make any difference where we choose the origin. As an example, let us take the two dimensional square lattice in which the Fermi surface does not quite reach to the corners in the first zone, yet bulges slightly through the face centers into the second zone. [See Mott and Jones,¹ Figure 39(b).] The first zone, when propagated throughout \mathbf{k} space consists of a lattice of small hole spheroids centered at the corners. Let us for this discussion treat these as spheres. If we take a new origin at the center of one of these spheres, it is evident that all processes are non-umklapp, and they will contribute anomalously to S_0

[i.e. (H10) will be positive]. If, however, we keep the origin at the center of the square as in the figure in Mott and Jones, then there is the possibility of corner to corner umklapp processes as well as non-umklapp processes from one point to another of the same corner. Nevertheless, when one examines (H10), one finds that each transition yields the same result in both descriptions, although sometimes it is regarded as an umklapp process in one and a non-umklapp process in the other.

So much for the first zone. If we propagate the reduced second zone to form a "second zone space," we get a lattice of small electron spheroids (henceforth regarded as spheres). If we place the origin of a new unit cell in this space at the center of one of them, keeping the zone edges parallel to the original propagating zone, then it is evident that the new unit cell contains in addition to the central sphere also bits at the corners. It can be seen from the geometry and from (H10) that all corner to corner transitions will give negative contributions to S_0 . [This must also follow from the fact that the corner bits combine to form a small electron spheroid. All transitions from one point to another on this spheroid must be capable of being treated as non-umklapp processes giving a normal (negative) S_0 .] In addition there are transitions from the central sphere to the corner bits. Some of these will be umklapp processes, some non-umklapp. We will have the usual result that the umklapp processes will generally give positive contributions; the non-umklapp, negative contributions. These results for the two bands will hold even if the spheroids are flat ellipsoids.

Finally there are the band to band transitions. We take as origin the center of an electron spheroid. There are then two halves of hole-spheres that fit in the first zone. The signs of the contributions will depend critically on the magnitude of the velocities, and we find nothing of a systematic nature to predict.