PHYSICAL REVIEW VOLUME 112, NUMBER 5 DECEMBER 1, 1958

Transport in Metals: Effect of the Nonequilibrium Phonons

M. BAILYN
Department of Physics, Northwestern University, Evanston, Illinois

(Received March 10, 1958)

The coupled Boltzmann equations for phonons and electrons in a metal are solved simultaneously using first-order perturbation theory. Use is made of the Kohler variational principle to put the transport coefficients in terms of determinants. The final results are in the form of integrals involving the phonon-phonon relaxation time $\tau(\boldsymbol{\sigma})$ and the electron-electron relaxation time. The details of how a finite electrical conductivity exists by means of umklapp processes even when $\tau(\boldsymbol{\sigma})\rightarrow\infty$ (the Peierls equilibrium problem) is revealed in the electrical conductivity expression. In general, the effects may be described as "phonon relaxation" effects, altering all the transport coefficients somewhat when $\tau(\boldsymbol{\sigma})$ gets large, and "phonon-drag" or drift effects, altering appreciably only the thermoelectric power.

I. INTRODUCTION

THE problem of transport in metals is to a large extent the history of how electrons and phonons interact. We shall neglect impurity and boundary scattering in this paper. There are three types of such interactions involved: (1) electron-electron, (2) electron-phonon, and (3) phonon-phonon. In addition there are external parameters which cause a change in the distributions, namely the electric field and a temperature gradient. We shall not consider magnetic fields. The first work on electron transport problems[1] ignored (1) and (3), and regarded each collision of type (2) to commence with the phonons in equilibrium distributions, which implied that collisions of type (3) are frequent enough to maintain phonon equilibrium. The possibility of the phonons not having an equilibrium distribution was well understood, and equations were written down showing where the nonequilibrium component appeared. Peierls[2] in particular pointed out the rather grave problem of equilibrium at low temperatures, when the ignored collisions of type (3) were shown not to be sufficient to provide equilibrium; and other mechanisms had to be invoked, namely umklapp (UK) processes to maintain a steady state. However electron-phonon UK processes were thought to diminish too fast at low temperatures to provide what was necessary. Recent work[3] has shown that the contribution of UK processes had been greatly underestimated, and unless very low temperatures indeed were contemplated (say 2 or 3 degrees K), there were enough UK processes to satisfy the most skeptical.

In 1945, Gurevich[4] proposed that the nonequilibrium component of the phonon distribution could not reasonably be neglected in the thermoelectric power of metals. He set up the coupled Boltzmann equations for the phonons and for the electrons, representing collisions of type (3) by a relaxation time. He calculated out some results, but did not attempt to solve the Boltzmann equations simultaneously. Since then, much work[5] has been done on this phonon-drag effect in semiconductors.

In 1949, Kohler[6] showed how a variational method could be applied to transport properties of metals, and how by this means a more general electron distribution function could be employed. The electrical conductivity so calculated could be formulated in a monotonically increasing series.

The burden of this paper is to solve the coupled Boltzmann equations of the phonons and electrons, and to obtain expressions for the transport coefficients by a method identical to Kohler's, but applied to the more general problem. A variety of assumptions has been employed, chief among which are these six:

(1) The phonon-phonon collisions may be represented by a relaxation time $\tau_j(\boldsymbol{\sigma})$, a function of the phonon wave vector $\boldsymbol{\sigma}$ and polarization index j:

$$[\partial N_j(\boldsymbol{\sigma})/\partial t]_{\text{ph-ph coll.}}=-(N_j-N_{0j})/\tau_j(\boldsymbol{\sigma}).$$

(2) The perturbation potential in collisions of electrons with vibrating ions may be written in the form

$$\Delta V=\sum_l \nabla v(\mathbf{r}-\mathbf{r}(l))\cdot\mathbf{u}(l),$$

where the ∇v may be a factor times the gradient of the ion potential, or may be more complex. The index l represents the cell number. $\mathbf{u}(l)$ is the displacement of the lth ion.

(3) Electron-electron interactions may be represented by a relaxation time $\tau(\mathbf{k})$, a function of the wave vector $\mathbf{k}$:

$$(\partial f/\partial t)_{\text{elec-elec coll.}}=-(f-f_0)/\tau(\mathbf{k}).$$

(4) First-order perturbation theory is applicable.

---

[1] For example, A. Sommerfeld and H. Bethe, in *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. XXIV, Part 2. Our displacement function Eq. (3) is identical to Bethe's, except for where the mass factor appears.

[2] R. E. Peierls, Ann. Physik 4, 121 (1930).

[3] M. Bailyn, thesis, Harvard University, 1956 (unpublished); M. Bailyn and H. Brooks, Bull. Am. Phys. Soc. Ser. II, **1**, 300 (1956). See also note by M. Bailyn in *Low Temperature Physics and Chemistry* [Proceedings of the Fifth International Conference, University of Wisconsin Press, 1958], p. 373.

[4] L. Gurevich, J. Phys. (U.S.S.R.) **9**, 477 (1945); **10**, 67 (1946).

[5] See references in J. M. Blatt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4, p. 359.

[6] M. Kohler, Z. Physik **124**, 772 (1948); **125**, 679 (1949); **126**, 495 (1949). E. H. Sondheimer, Proc. Roy. Soc. (London) **A203**, 75 (1950).

(5) The steady-state statistical average[7] electron distribution function f may be written

$$f_n(\mathbf{k})=f_0(E_n(\mathbf{k}))-(\partial f_0/\partial E)g(\mathbf{k}),$$
$$g(\mathbf{k})=\mathcal{E}_x{}^*\varphi_1(\mathbf{k})-(dT/dx)\varphi_2(\mathbf{k})/T,$$
$$\mathcal{E}_x{}^*=\mathcal{E}_x+e^{-1}d\zeta/dx,$$
$$f_0=(e^\epsilon+1)^{-1},$$
$$\epsilon=[E_n(\mathbf{k})-\zeta]/\kappa T,$$

where $\mathbf{k}$ is the reduced electron wave vector, and $E_n(\mathbf{k})$ is the energy in the nth band. $\mathcal{E}$ is the electric field, and ζ is the Fermi energy.

(6) The steady-state statistical-average[7] phonon distribution function may be represented by an occupation number $N_j(\boldsymbol{\sigma})$:

$$N_j(\boldsymbol{\sigma})=N_{0j}(\omega_j(\boldsymbol{\sigma}))-(\partial N_{0j}/\partial\hbar\omega)G_j(\boldsymbol{\sigma}),$$
$$N_{0j}=(e^\gamma-1)^{-1},$$
$$\gamma=\hbar\omega_j(\boldsymbol{\sigma})/\kappa T,$$

where $\omega_j(\boldsymbol{\sigma})$ is the frequency of the jth vibration branch. The final expressions obtained in this paper are integrals involving $\tau_j(\boldsymbol{\sigma})$ and $\tau(\mathbf{k})$. Umklapp processes are taken into account exactly, for if they were neglected, our expression for the electrical conductivity would go to infinity in the limit of large $\tau_j(\boldsymbol{\sigma})$.

II. DERIVATION OF THE BOLTZMANN EQUATIONS

The Boltzmann equation for the electron distribution function is

$$-\left(\frac{\partial f}{\partial t}\right)_{\text{drift}}=\left(\frac{\partial f}{\partial t}\right)_{\text{coll.}}$$
$$=\sum_{\mathbf{k}'n'}\{-P(n\mathbf{k}\to n'\mathbf{k}')f_n(\mathbf{k})[1-f_{n'}(\mathbf{k}')]$$
$$+P(n'\mathbf{k}'\to n\mathbf{k})f_{n'}(\mathbf{k}')[1-f_n(\mathbf{k})]\}-\frac{f-f_0}{\tau(\mathbf{k})},\quad(1)$$

where $P(n\mathbf{k}\to n\mathbf{k}')$ is the probability per unit time of a transition from state $n\mathbf{k}$ to $n'\mathbf{k}'$. By first-order perturbation theory, it is

$$P(n\mathbf{k}\to n'\mathbf{k}')=\sum_{\mathfrak{N}}\hbar^{-2}|(n'\mathbf{k}'\mathfrak{N}'|\Delta V|n\mathbf{k}\mathfrak{N})|^2$$
$$\times\Omega(E(\mathfrak{N}')+E_{n'}(\mathbf{k}')-E(\mathfrak{N})-E_n(\mathbf{k})),\quad(2)$$
$$\Omega(x)=\left[\frac{\sin(xt/2\hbar)}{xt/2\hbar}\right]^2 t,$$

where $\mathfrak{N}$ indicates the phonon configuration. Only one initial state $\mathfrak{N}$ is considered. A statistical average is later taken. The quantity $\Omega(x)$ acts as a delta function.

We use for the displacement function

$$\mathbf{u}(l)=[NM]^{-\frac{1}{2}}\sum_{\sigma j}\boldsymbol{\xi}_j(\boldsymbol{\sigma})$$
$$\times\{a_j(\boldsymbol{\sigma})\exp[i\boldsymbol{\sigma}\cdot\mathbf{r}(l)]+a_j{}^*(\boldsymbol{\sigma})\exp[-i\boldsymbol{\sigma}\cdot\mathbf{r}(l)]\},\quad(3)$$

where N is the number of cells in the periodic block, M is the ion mass, where the sum contains only one of the two $(\boldsymbol{\sigma},-\boldsymbol{\sigma})$, where a_j is a destruction operator and $a_j{}^*$ a creation operator, and where $\boldsymbol{\xi}_j(\boldsymbol{\sigma})$ is the unit displacement vector for waves of wave vector $\boldsymbol{\sigma}$ and polarization j $(j=1,2,3)$. The matrix element in (2) is then

$$(n'\mathbf{k}'\mathfrak{N}'|\Delta V|n\mathbf{k}\mathfrak{N})$$
$$=\mathbf{I}_{\mathbf{k}\mathbf{k}'}\sum_{\sigma\mathbf{K}j}\{\hbar/[2NM\omega_j(\boldsymbol{\sigma})]\}^{\frac{1}{2}}\boldsymbol{\xi}_j(\boldsymbol{\sigma})$$
$$\times\{[N_j(\boldsymbol{\sigma})]^{\frac{1}{2}}\Omega(E_{n'}(\mathbf{k}')-E_n(\mathbf{k})-\hbar\omega)\delta(\mathbf{k}'-\mathbf{k}-\boldsymbol{\sigma}-\mathbf{K})$$
$$+[N_j(\boldsymbol{\sigma})+1]^{\frac{1}{2}}\Omega(E_{n'}(\mathbf{k}')-E_n(\mathbf{k})+\hbar\omega)$$
$$\times\delta(\mathbf{k}'-\mathbf{k}+\boldsymbol{\sigma}+\mathbf{K})\},\quad(4)$$
$$\mathbf{I}_{\mathbf{k}\mathbf{k}'}=N(\mathbf{k}'n'|\nabla v|\mathbf{k}n)=\mathbf{I}_{\mathbf{k}'\mathbf{k}}.\quad(5)$$

$\mathbf{K}$ represents some reciprocal lattice vector. The electron wave functions are normalized over the whole crystal. The $\mathbf{k}$ delta functions select out $\boldsymbol{\sigma}$ and $\mathbf{K}$ for a given $\mathbf{kk}'$ pair, since $\mathbf{kk}'$ and $\boldsymbol{\sigma}$ are reduced wave vectors. Thus

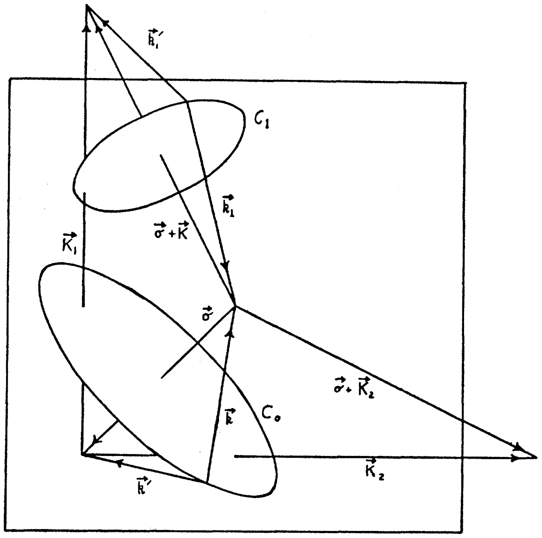

FIG. 1. Two umklapp types of scattering, $\mathbf{K}=0$, and $\mathbf{K}=\mathbf{K}_1$, are shown schematically for the phonon wave vector $\boldsymbol{\sigma}$, and a third type is indicated. C_0 is a curve denoting the locus of origins of $\mathbf{kk}'$ pairs satisfying the delta-function condition for type $\mathbf{K}=0$, C_1 for type $\mathbf{K}=\mathbf{K}_1$. The angle between $\mathbf{k}$ and $\boldsymbol{\sigma}+\mathbf{K}$ is fixed by the energy delta function. The sums in the text over all possible $\mathbf{kk}'$ pairs (for a given $\boldsymbol{\sigma}j$) satisfying the delta-function conditions [Eq. (8) for example] would reduce in this case to all $\mathbf{kk}'$ pairs with origin on C_0, C_1, C_2 (not shown), and any other possible C_i's.

---

[7] By "statistical average" is meant an average over the grand canonical ensemble as, for example, are meant the n's in (7.606) and (7.705) of D. Ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, Inc., New York, 1954). See also (6.110).

$$
\begin{aligned}
(\partial f/\partial t)_{\text{coll.}}= &\sum_{\mathbf{k}'n'j} (1/N)C_{\mathbf{kk}'j} \\
&\times\{\Omega(E'-E-\hbar\omega_j)\delta(\mathbf{k}'-\mathbf{k}-\boldsymbol{\sigma}-\mathbf{K}) \\
&\times[-N_j(\boldsymbol{\sigma})f(1-f')+(N_j(\boldsymbol{\sigma})+1)f'(1-f)] \\
&+\Omega(E'-E+\hbar\omega_j)\delta(\mathbf{k}'-\mathbf{k}+\boldsymbol{\sigma}+\mathbf{K}) \\
&\times[-(N_j(\boldsymbol{\sigma})+1)f(1-f')+N_j(\boldsymbol{\sigma})f'(1-f)]\} \\
&-(f-f_0)/\tau(\mathbf{k}), \qquad (6)
\end{aligned}
$$

$$
C_{\mathbf{kk}'j}=[2\hbar\omega_j(\boldsymbol{\sigma})M]^{-1}|\mathbf{I}_{\mathbf{kk}'}\cdot\xi_j(\boldsymbol{\sigma})|^2=C_{\mathbf{k}'\mathbf{k}j}>0. \qquad (7)
$$

If $\mathbf{k}$ is fixed, and $\mathbf{k}'$ roams over reduced space, the first two terms [each square bracket in (6) contains two "terms"] will be nonzero for $\mathbf{k}'$'s different in general from those corresponding to the last two. The reciprocal lattice vector $\mathbf{K}$ is appropriately chosen so as to allow the delta function to be nonzero, if possible.

The phonon Boltzmann equation may be written directly from (6), for whereas the second and fourth terms of (6) provide gains to the electron distribution, it is the second and third which provide gains to the phonon distribution. Similarly the first and fourth provide losses to the phonon distribution. Hence

$$
\begin{aligned}
-[\partial N_j(\boldsymbol{\sigma})/\partial t]_{\text{drift}} \\
=[\partial N_j(\boldsymbol{\sigma})/\partial t]_{\text{coll.}}=\tfrac{1}{2}&\sum_{\mathbf{k}_1\mathbf{k}_1'}^{[\sigma j]} (C_{\mathbf{k}_1\mathbf{k}_1'j}/N) \\
&\times\{\Omega(E_1'-E_1-\hbar\omega_j)\delta(\mathbf{k}_1'-\mathbf{k}_1-\boldsymbol{\sigma}-\mathbf{K}) \\
&\times[-N_j(\boldsymbol{\sigma})f(1-f')+(N_j(\boldsymbol{\sigma})+1)f'(1-f)] \\
&-\Omega(E_1'-E_1+\hbar\omega)\delta(\mathbf{k}_1'-\mathbf{k}_1+\boldsymbol{\sigma}+\mathbf{K}) \\
&\times[-(N_j(\boldsymbol{\sigma})+1)f(1-f')+N_j(\boldsymbol{\sigma})f'(1-f)]\} \\
&-[N_j(\boldsymbol{\sigma})-N_{0j}]/\tau_j(\boldsymbol{\sigma}), \qquad (8)
\end{aligned}
$$

where we have introduced the relaxation by phonon-phonon collisions in terms of a relaxation time. The sum means for a given $\boldsymbol{\sigma}j$ over all possible $\mathbf{kk}'$ pairs satisfying the delta-function conditions. *This means also over all possible* UK *processes for each* $\boldsymbol{\sigma}$. (See Fig. 1.) The factor $\frac{1}{2}$ before the $\mathbf{k}_1\mathbf{k}_1'$ sum insures that each interaction is counted only once.

We shall introduce abbreviations here to shorten the expressions. Let

$$
\begin{aligned}
&\Omega(\pm)=\Omega(E'-E\pm\hbar\omega_j), \\
&\Omega_1(\pm)=\Omega(E(\mathbf{k}_1')-E(\mathbf{k}_1)\pm\hbar\omega_j), \\
&\delta(\pm)=\delta(\mathbf{k}'-\mathbf{k}\pm\boldsymbol{\sigma}\pm\mathbf{K}), \\
&\delta_1(\pm)=\delta(\mathbf{k}_1'-\mathbf{k}_1\pm\boldsymbol{\sigma}\pm\mathbf{K}_1), \qquad (9a) \\
&g(\mathbf{k}')=g', \\
&g(\mathbf{k}_1')=g_1', \\
&G_j(\boldsymbol{\sigma})=G_j, \\
&D_{\mathbf{kk}'j}=\frac{C_{\mathbf{kk}'j}}{\kappa T}\frac{f_0(E)f_0(E')}{|e^{-\epsilon}-e^{-\epsilon'}|}=D_{\mathbf{k}'\mathbf{k}j}>0. \qquad (9b)
\end{aligned}
$$

Further, we drop reference to bands. The δ-function conditions arose from use of Bloch wave functions of the form $u_{n\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r})$ where the exponential factor gives rise to the δ function no matter what n is involved.

Using assumption (5), anticipating the delta-function nature of the Ω, and neglecting products of small quantities, we get

$$
\begin{aligned}
\left(\frac{\partial f}{\partial t}\right)_{\text{coll.}}=&\sum_{\mathbf{k}'j}\frac{1}{N}D_{\mathbf{kk}'j}[\Omega(-)\delta(-)(-G_j-g+g') \\
&+\Omega(+)\delta(+)(G_j-g+g')]+\frac{g}{\kappa T}\frac{\partial f_0}{\partial\epsilon}\frac{1}{\tau(\mathbf{k})}, \qquad (10)
\end{aligned}
$$

$$
\begin{aligned}
\left[\frac{\partial N_j(\boldsymbol{\sigma})}{\partial t}\right]_{\text{coll.}}=&\tfrac{1}{2}\sum_{\mathbf{kk}'}^{[\sigma j]}\frac{1}{N}D_{\mathbf{kk}'j}[\Omega(-)\delta(-)(-G_j-g+g') \\
&-\Omega(+)\delta(+)(G_j-g+g')]+\frac{G_j}{\kappa T}\frac{\partial N_{0j}}{\partial\gamma}\frac{1}{\tau_j(\boldsymbol{\sigma})}. \qquad (11)
\end{aligned}
$$

Before having gone from (6) and (8) to (10) and (11), we may regard a statistical average[7] as having been taken. If the phonon-electron interaction and fields are turned off, then the average of a typical term, say $Nf(1-f')$ is the product of the average of N and of $f(1-f')$. Knowing the averages of N and of f to be N_0 and f_0, respectively, one can use the equilibrium condition to solve for the average of ff' and show that it too is the product of the individual averages. Then when the electron-phonon interaction and fields are turned on, we assume that the new average is a perturbation of $N_0f_0(1-f_0')$, and of the form $(N_0+N_1)(f_0+f_1)\times(1-f_0'-f_1')$, where now N_1, f_1, and f_1' are perturbations of the statistical averages. This is what is implied in assumptions 5 and 6.

III. PROOF OF THE APPLICABILITY OF THE VARIATIONAL METHOD

First we shall combine (10) and (11). Equation (11) solved for $G_j(\boldsymbol{\sigma})$ yields

$$
\begin{aligned}
G_j(\boldsymbol{\sigma})=&\left[\frac{\partial N_j(\boldsymbol{\sigma})}{\partial t}\right]_{\text{drift}}\frac{1}{F_j(\boldsymbol{\sigma})}-\frac{1}{F_j(\boldsymbol{\sigma})}\tfrac{1}{2}\sum_{\mathbf{k}_1\mathbf{k}_1'}^{[\sigma j]}\frac{1}{N}D_{\mathbf{k}_1\mathbf{k}_1'j} \\
&\times[\Omega_1(-)\delta_1(-)-\Omega_1(+)\delta_1(+)](g_1-g_1') \\
=&\left[\frac{\partial N_j(\boldsymbol{\sigma})}{\partial t}\right]_{\text{drift}}\frac{1}{F_j(\boldsymbol{\sigma})}-\frac{2}{F_j(\boldsymbol{\sigma})}\tfrac{1}{2}\sum_{\mathbf{k}_1\mathbf{k}_1'}^{[\sigma j]}\frac{1}{N}D_{\mathbf{k}_1\mathbf{k}_1'j} \\
&\times\Omega_1(-)\delta_1(-)(g_1-g_1'), \qquad (12)
\end{aligned}
$$

where

$$
\begin{aligned}
F_j(\boldsymbol{\sigma})=&-\frac{dN_{0j}}{d\gamma}\frac{1}{\kappa T}\frac{1}{\tau_j(\boldsymbol{\sigma})}+\sum_{\mathbf{k}_1\mathbf{k}_1'}^{[\sigma j]}\frac{1}{N}D_{\mathbf{k}_1\mathbf{k}_1'} \\
&\times[\Omega_1(-)\delta_1(-)+\Omega_1(+)\delta_1(+)] \\
=&-\frac{dN_{0j}}{d\gamma}\frac{1}{\kappa T}\frac{1}{\tau_j(\boldsymbol{\sigma})}+2\sum_{\mathbf{k}_1\mathbf{k}_1'}^{[\sigma j]}\frac{1}{N}D_{\mathbf{k}_1\mathbf{k}_1'j} \\
&\times\Omega_1(-)\delta_1(-)>0. \qquad (13)
\end{aligned}
$$

The second forms for (12) and (13) arise from exchanging the dummy indices $\mathbf{k}_1$ and $\mathbf{k}_1'$, and using (9b). It is here that we must keep in mind that the $\boldsymbol{\sigma}$ and $\mathbf{K}$ which find themselves in the delta function are the ones which will make a nonzero value. For when we switch **k** and **k′**, the second term in (12) resembles the first, except for the particular **K** vector. It must be understood, however, that the delta function arose when **k** and **k′** were given, and was taken to represent a selection from all $\boldsymbol{\sigma}$ [in the $\boldsymbol{\sigma}$ sum of (3)] of the one $\boldsymbol{\sigma}$ combined with the one **K** which would give a nonzero value. When we switch **k** and **k′** in (12) in the second term, the sum over $\boldsymbol{\sigma}$ and **K** will select out the ones to satisfy the delta function, and hence the **K** will be the same that gives a nonzero value in the first term. $F_j(\boldsymbol{\sigma})$ is always positive since $dN_{0j}/d\gamma$ is negative.

Substitution of (12) into (10) gives

$$-(\partial f/\partial t)_{\text{drift}}-U(\mathbf{k})=L(g), \tag{14}$$

which is a generalized Boltzmann equation. Here

$$L(g)=L_1(g)+L_2(g)+L_3(g), \tag{15}$$

$$L_1(g)=\sum_{\mathbf{k}'j}(1/N)D_{\mathbf{k}\mathbf{k}'j}\times[\Omega(-)\delta(-)+\Omega(+)\delta(+)](-g+g'),$$

$$L_2(g)=\sum_{\mathbf{k}'j}(1/N)D_{\mathbf{k}\mathbf{k}'j}[\Omega(-)\delta(-)-\Omega(+)\delta(+)]\times[1/F_j(\boldsymbol{\sigma})]\sum_{\mathbf{k}_1\mathbf{k}_1'}^{[\sigma j]}(1/N)D_{\mathbf{k}_1\mathbf{k}_1'j}\times\Omega_1(-)\delta_1(-)(g_1-g_1'), \tag{16}$$

$$L_3(g)=\frac{g}{\kappa T}\frac{df_0}{d\epsilon}\frac{1}{\tau(\mathbf{k})},$$

$$U(\mathbf{k})=\sum_{\mathbf{k}_1'j}(1/N)D_{\mathbf{k}_1\mathbf{k}_1'j}\times[-\Omega_1(-)\delta_1(-)+\Omega_1(+)\delta_1(+)]\times\left[\frac{\partial N_j(\boldsymbol{\sigma})}{\partial t}\right]_{\text{drift}}\frac{1}{F_j(\boldsymbol{\sigma})}. \tag{17}$$

In making use of the variational principle, we treat U as a drift term, and propose to show that if $h(\mathbf{k})$ is any function, then

$$\sum_{\mathbf{k}}h(\mathbf{k})L(g)=\sum_{\mathbf{k}}g(\mathbf{k})L(h),\quad \sum_{\mathbf{k}}g(\mathbf{k})L(g)<0. \tag{18}$$

These two conditions are the prerequisites for use of the variation principle.

It is immediately obvious that L_3 satisfies (18) since $df_0/d\epsilon$ is negative, and $\tau(\mathbf{k})$ is positive.

The coefficient of $-g(\mathbf{k})+g(\mathbf{k}')$ in L_1 is symmetrical in **k** and **k′**. Hence, if we multiply by $h(\mathbf{k})$ and sum, and then exchange dummy indices **k** and **k′**, the result will be identical to the unexchanged form except that $h(\mathbf{k})$ has become $-h(\mathbf{k}')$:

$$\begin{aligned}2\sum_{\mathbf{k}}hL_1(g)&=\sum_{\mathbf{k}\mathbf{k}'j}(1/N)D_{\mathbf{k}\mathbf{k}'j}[\Omega(-)\delta(-)+\Omega(+)\delta(+)]\times(-g+g')(h-h')\\&=\sum_{\mathbf{k}\mathbf{k}'j}(2/N)D_{\mathbf{k}\mathbf{k}'j}\Omega(-)\delta(-)(-g+g')(h-h').\end{aligned} \tag{19}$$

The second form is obtained by exchanging **k** and **k′**. We now form

$$\sum hL_2(g)=\sum_{\mathbf{k}\mathbf{k}'j}(1/N)D_{\mathbf{k}\mathbf{k}'j}\times[\Omega(-)\delta(-)-\Omega(+)\delta(+)]h(\mathbf{k})\times[1/F_j(\boldsymbol{\sigma})]\sum_{\mathbf{k}_1\mathbf{k}_1'}^{[\sigma j]}(1/N)D_{\mathbf{k}_1'\mathbf{k}_1j}\Omega_1(-)\delta_1(-)(g_1-g_1').$$

Interchange **k** and **k′**. When this is done the square bracket becomes the negative of itself, with the same $\boldsymbol{\sigma}$. When the reversed member **k′k** is calculated, it will select out the same $\boldsymbol{\sigma}$, the only differences being that it comes from the second term in the square bracket instead of the first, and that there is a change in sign. Thus when the original is added to the interchanged expression, we get a factor $h(\mathbf{k})-h(\mathbf{k}')$. Also, the second term in the square bracket will add up to the same quantity as the first term. (Interchange **k** and **k′** in the second term.) Thus

$$2\sum_{\mathbf{k}}hL_2(g)=\sum_{\mathbf{k}\mathbf{k}'j}(2/N)D_{\mathbf{k}\mathbf{k}'j}\Omega(-)\delta(-)(h-h')\times[1/F_j(\boldsymbol{\sigma})]\sum_{\mathbf{k}_1\mathbf{k}_1'}^{[\sigma j]}(1/N)D_{\mathbf{k}_1\mathbf{k}_1'j}\times\Omega_1(-)\delta_1(-)(g_1-g_1'). \tag{20}$$

From here, the simplest procedure is to add the L_1 and L_2 terms, and multiply L_1 above and below by $F_j(\boldsymbol{\sigma})$. Then we rewrite the $\mathbf{k}\mathbf{k}'j$ sum as

$$\sum_{\mathbf{k}\mathbf{k}'j}=\sum_{\sigma j}\sum_{\mathbf{k}\mathbf{k}'}^{[\sigma j]}, \tag{21}$$

which means that for each $\boldsymbol{\sigma}j$ all possible $\mathbf{k}\mathbf{k}'$ combinations are first summed. (See Fig. 1.) The $\boldsymbol{\sigma}$'s are summed over the reduced zone, and the $\mathbf{k}\mathbf{k}'$ sum for each $\boldsymbol{\sigma}$ will involve all possible UK processes associated with that $\boldsymbol{\sigma}$. (21) is permissible because of the presence of the **k** delta function, which in any case will allow only one $\boldsymbol{\sigma}$ for a given $\mathbf{k}\mathbf{k}'$. Thus

$$\begin{aligned}2\sum_{\mathbf{k}}h[L_1(g)+L_2(g)]=\sum_{\sigma j}\frac{1}{F_j(\boldsymbol{\sigma})}\sum_{\mathbf{k}\mathbf{k}'}^{[\sigma j]}\sum_{\mathbf{k}_1\mathbf{k}_1'}^{[\sigma j]}&\times\left\{-\frac{dN_{0j}}{d\gamma}\frac{1}{\kappa T}\frac{1}{\tau_j(\boldsymbol{\sigma})}\frac{1}{N}D_{\mathbf{k}\mathbf{k}'j}\Omega(-)\delta(-)\right.\\&\times(-g+g')(h-h')+\frac{1}{N}D_{\mathbf{k}_1\mathbf{k}_1'j}\Omega_1(-)\delta_1(-)\\&+\frac{2}{N}D_{\mathbf{k}\mathbf{k}'j}\Omega(-)\delta(-)(-g+g')(h-h')\\&+\frac{1}{N}D_{\mathbf{k}_1\mathbf{k}_1'j}\Omega_1(-)\delta_1(-)\frac{2}{N}D_{\mathbf{k}\mathbf{k}'j}\Omega(-)\delta(-)\\&\left.\times(g_1-g_1')(h-h')\right\}.\end{aligned} \tag{22}$$

It is evident from this that the first of Eqs. (18) is satisfied. To get the second, let us define

$$A_{\mathbf{kk}'j}(\boldsymbol{\sigma}) \equiv (2/N) D_{\mathbf{kk}'j}\Omega(-)\delta(-) \geq 0, \qquad b_{\mathbf{kk}'} \equiv g - g'. \tag{23}$$

The term in $\tau_j(\boldsymbol{\sigma})$ in (22) will always be ≤ 0 when $h=g$. We need concern ourselves only with the others. If we call the just-mentioned term $-B$, then

$$2\sum_{\mathbf{k}} g[L_1(g)+L_2(g)] = -B - \sum_{\sigma j}[1/2F_j(\boldsymbol{\sigma})] \sum_{\mathbf{kk}'}^{[\sigma j]} \sum_{\mathbf{k}_1\mathbf{k}_1'}^{[\sigma j]} \times A_{\mathbf{k}_1\mathbf{k}_1'j} A_{\mathbf{kk}'j}(b_{\mathbf{kk}'}^2 - b_{\mathbf{kk}'}b_{\mathbf{k}_1\mathbf{k}_1'}). \tag{24}$$

But it will always be true that

$$\sum_{\mathbf{kk}'}^{[\sigma j]} \sum_{\mathbf{k}_1\mathbf{k}_1'}^{[\sigma j]} A_{\mathbf{kk}'j}A_{\mathbf{k}_1\mathbf{k}_1'j}(b_{\mathbf{kk}'} - b_{\mathbf{k}_1\mathbf{k}_1'})^2 \geq 0, \tag{25}$$

and

$$\sum_{\mathbf{kk}'}^{[\sigma j]} \sum_{\mathbf{k}_1\mathbf{k}_1'}^{[\sigma j]} A_{\mathbf{kk}'j}A_{\mathbf{k}_1\mathbf{k}_1'j}(b_{\mathbf{kk}'}^2 - b^2_{\mathbf{k}_1\mathbf{k}_1'}) = 0, \tag{26}$$

since the ranges of $\mathbf{kk}'$ and $\mathbf{k}_1\mathbf{k}_1'$ are the same. Thus the $\mathbf{kk}'$ and $\mathbf{k}_1\mathbf{k}_1'$ sum in (24) is positive, and the whole expression is negative. This proves the second of equations (18), and we may now employ the variational principle.

The physical significance of the various terms are as follows. $L_1(g)$ represents the relaxation of nonequilibrium electrons by equilibrium phonons. $L_2(g)$ would represent the excitation of electrons by those nonequilibrium phonons which themselves were excited out of equilibrium by the nonequilibrium electrons, provided the first term in F is neglected. The fact that (24) is negative states that the excitation by the above-mentioned phonons is always slower than the relaxation by the rest of the phonons. This must be the case, of course, since otherwise the situation would not remain a first-order perturbation. The first term in F shows the effect of the phonons in interacting among each other in relaxing back to equilibrium. Its effect on the electrons is to make the excitation by nonequilibrium phonons less pronounced. The second term in F represents the effect of the electron-phonon collisions in relaxing the phonons. The quantity U [Eq. (17)] describes the exciting effect on the electrons, arising from those nonequilibrium phonons which were themselves excited out of equilibrium by the temperature gradient.

IV. THE VARIATIONAL PROCEDURE

Although there are several treatments of the variational principle in the literature, it was thought worth while to present here the important steps in the derivation, since the final determinants are different in structure from the ordinary ones.

First, the customary drift terms are

$$\left(\frac{\partial f_0}{\partial t}\right)_{\text{drift}} = \left(\frac{e\hbar}{m}\mathcal{E}_x^* + \frac{\hbar}{m}\frac{E-\zeta}{T}\frac{dT}{dx}\right)k_x\frac{\partial f_0}{\partial E}, \tag{27}$$

$$\left(\frac{\partial N_0}{\partial t}\right)_{\text{drift}} = \frac{dN_0}{d\gamma}\gamma\frac{d\omega}{d\sigma_x}\frac{1}{T}\frac{dT}{dx}. \tag{28}$$

Then we define $H_x(\mathbf{k})$ by

$$U(\mathbf{k}) = H_x(\mathbf{k})(dT/dx)/T. \tag{29}$$

Using assumption (5) and the above, we get the separated equations

$$\frac{e\hbar}{m}k_x\frac{\partial f_0}{\partial E} = -L(\varphi_1), \tag{30}$$

$$\frac{\hbar}{m}(E-\zeta)k_x\frac{\partial f_0}{\partial E} - H_x = -L(\varphi_2). \tag{31}$$

Finally we define the per-unit-volume integrals (from here on the sums are converted to integrals):

$$(\varphi,\psi) = -\int \varphi(\mathbf{k})L(\psi)d\mathbf{k}/4\pi^3 = (\psi,\varphi). \tag{32}$$

The variational principle then says that if trial functions φ_1 and φ_2 are chosen with adjustable parameters, then the requirement

$$\delta(\varphi_1,\varphi_1) = 0, \tag{33}$$

with side condition

$$(\varphi_1,\varphi_1) = \frac{e\hbar}{m}\int k_x\frac{\partial f_0}{\partial E}\varphi_1\frac{1}{4\pi^3}d\mathbf{k}, \tag{34}$$

leads to Eq. (30); and the requirement

$$\delta(\varphi_2,\varphi_2) = 0, \tag{35}$$

with side condition

$$(\varphi_2,\varphi_2) = -\int\left[\frac{\hbar}{m}\frac{\partial f_0}{\partial E}(E-\zeta)k_x + H_x\right]\varphi_2\frac{1}{4\pi^3}d\mathbf{k}, \tag{36}$$

leads to (31). The proof of these statements depends on the validity of (18), and we shall be content with having proved (18). (For more details see reference 6.)

We employ now functions of the form*

$$\varphi_1 = \sum_{\nu=0}^{n} a_\nu(E-\zeta)^\nu k_x; \quad \varphi_2 = \sum_{\nu=0}^{n} b_\nu(E-\zeta)^\nu k_x. \tag{37}$$

With this, we get

$$(\varphi_1,\varphi_1) = \sum_{\mu\nu=0}^{n} d_{\mu\nu}a_\mu a_\nu, \tag{38}$$

$$(\varphi_2,\varphi_2) = \sum_{\mu\nu=0}^{n} d_{\mu\nu}b_\mu b_\nu; \tag{39}$$

---

* The a_ν's and b_ν's are constants to be determined.

and the side conditions become

$$\sum_{\mu\nu=0}^{n} d_{\mu\nu}a_\mu a_\nu=\sum_{\nu=0}^{n}\alpha_\nu a_\nu, \tag{40}$$

$$\sum_{\mu\nu=0}^{n} d_{\mu\nu}b_\mu b_\nu=\sum_{\nu=0}^{n}\beta_\nu b_\nu, \tag{41}$$

where

$$\alpha_\nu=\frac{e\hbar}{m}\int k_x^2\frac{\partial f_0}{\partial E}(E-\zeta)^\nu\frac{1}{4\pi^3}d\mathbf{k}, \tag{42}$$

$$\beta_\nu=-\int\left[\frac{\hbar}{m}\frac{\partial f_0}{\partial E}(E-\zeta)^{\nu+1}k_x^2+H_x(E-\zeta)^\nu k_x\right]\frac{1}{4\pi^3}d\mathbf{k}, \tag{43}$$

$$d_{\mu\nu}=((E-\zeta)^\mu k_x,\ (E-\zeta)^\nu k_x). \tag{44}$$

It will be convenient in the future to use

$$\gamma_\nu=-(\hbar/m)\int(\partial f_0/\partial E)(E-\zeta)^{\nu+1}k_x^2d\mathbf{k}/4\pi^3. \tag{45}$$

In the ordinary theory $\gamma=\beta$. The electric current J_x and the energy current w_x are given by

$$\begin{aligned}J_x&=(e\hbar/m)\int k_xg(\mathbf{k})(\partial f_0/\partial E)d\mathbf{k}/4\pi^3\\&=\textstyle\sum_\nu a_\nu\alpha_\nu\mathcal{E}_x^*-\sum_\nu b_\nu\alpha_\nu(dT/dx)/T,\end{aligned} \tag{46}$$

$$\begin{aligned}w_x&=-(\hbar/m)\int k_xg(\mathbf{k})[E-\zeta+\zeta](\partial f_0/\partial E)d\mathbf{k}/4\pi^3\\&=-J_x\zeta/e+\textstyle\sum_\nu a_\nu\gamma_\nu\mathcal{E}_x^*-\sum_\nu b_\nu\gamma_\nu(dT/dx)/T.\end{aligned} \tag{47}$$

Thus the electrical conductivity with no temperature gradient is σ_0:

$$\sigma_0=\textstyle\sum_\nu a_\nu\alpha_\nu; \tag{48}$$

the thermal conductivity of the electrons, with no current, is κ, where

$$T\kappa=-[(\textstyle\sum_\nu a_\nu\gamma_\nu\sum_\mu b_\mu\alpha_\mu)/\sum_\nu a_\nu\alpha_\nu]+\sum_\nu b_\nu\gamma_\nu; \tag{49}$$

and the thermoelectric power with no current is S, where

$$TS=(\textstyle\sum_\nu b_\nu\alpha_\nu)/\sum_\nu a_\nu\alpha_\nu. \tag{50}$$

The equations of the variational problem are

$$\sum_{\nu=0}^{n}d_{\mu\nu}a_\nu=\alpha_\mu,\qquad \sum_{\nu=0}^{n}d_{\mu\nu}b_\nu=\beta_\mu; \tag{51}$$

and the solutions are

$$a_\nu=(\textstyle\sum_\mu\alpha_\mu d^{\mu\nu})/D, \tag{52}$$

$$b_\nu=(\textstyle\sum_\mu\beta_\mu d^{\mu\nu})/D, \tag{53}$$

where $d^{\mu\nu}$ is the cofactor of $d_{\mu\nu}$ in the d matrix (whose determinant is D). From Eqs. (51) we can form $\sum_{\mu\nu}d_{\mu\nu}a_\nu b_\mu$ in two ways, and find the relation

$$\textstyle\sum_\mu a_\mu b_\mu=\sum_\mu\beta_\mu a_\mu. \tag{54}$$

Now, in general, for a symmetric matrix $d_{\mu\nu}$, we will have

$$D_{pq}\equiv\sum_{\mu\nu=0}^{n}p_\mu q_\nu d^{\mu\nu}=-\left\|\begin{matrix}d_{00}&d_{01}&\cdots&d_{0n}&p_0\\d_{10}&d_{11}&\cdots&d_{1n}&p_1\\\vdots&\vdots&&\vdots&\vdots\\d_{n0}&d_{n1}&\cdots&d_{nn}&p_n\\q_0&q_1&\cdots&q_n&0\end{matrix}\right\|. \tag{55}$$

Hence

$$\textstyle\sum a_\nu\alpha_\nu=-D_{\alpha\alpha}/D, \tag{56a}$$

$$\textstyle\sum a_\nu\gamma_\nu=-D_{\alpha\gamma}/D, \tag{56b}$$

$$\textstyle\sum b_\nu\alpha_\nu=\sum\beta_\mu a_\mu=-D_{\beta\alpha}/D, \tag{56c}$$

$$\textstyle\sum b_\nu\gamma_\nu=-D_{\beta\gamma}/D. \tag{56d}$$

Whence Eqs. (48) to (50) become

$$\sigma_0=-D_{\alpha\alpha}/D, \tag{57}$$

$$T\kappa=+[D_{\alpha\gamma}\textstyle\sum_{\alpha\beta}-D_{\beta\gamma}D_{\alpha\alpha}]/[DD_{\alpha\alpha}]=-\dfrac{D_{\alpha\beta;\,\alpha\gamma}}{D_{\alpha\alpha}}, \tag{58}$$

$$ST=D_{\beta\alpha}/D_{\alpha\alpha}. \tag{59}$$

The second form in (58) arises from use of "Sylvester's theorem." Even though our determinants are different from Kohler's, the theorem still applies. We have

$$D_{\alpha\beta;\,\alpha\gamma}\equiv\left\|\begin{matrix}d_{00}&d_{01}&\cdots&d_{0n}&\alpha_0&\beta_0\\d_{10}&d_{11}&\cdots&d_{1n}&\alpha_1&\beta_1\\\vdots&\vdots&&\vdots&\vdots&\vdots\\d_{n0}&d_{n1}&\cdots&d_{nn}&\alpha_n&\beta_n\\\alpha_0&\alpha_1&\cdots&\alpha_n&A_1&A_2\\\gamma_0&\gamma_1&\cdots&\gamma_n&A_3&A_4\end{matrix}\right\| \tag{60}$$

where A_1, A_2, A_3, and A_4 all have the value zero. If A^1, etc., are the minors of these elements, then the theorem states that

$$A^1A^4-A^2A^3=DD_{\alpha\beta;\,\alpha\gamma}. \tag{61}$$

But in our previous terminology, $A^1=D_{\beta\gamma}$, $A^2=D_{\alpha\gamma}$, $A^3=D_{\alpha\beta}$, $A^4=D_{\alpha\alpha}$. The second form for (58) then follows.

Finally we write down the first terms of (57) through (59).

$$\sigma_0=\alpha_0^2/d_{00}, \tag{62}$$

$$\begin{aligned}T\kappa=(\alpha_0\gamma_1-\gamma_0\alpha_1)(\beta_1\alpha_0-\beta_0\alpha_1)/&\\ [d_{00}\alpha_1^2-2d_{10}\alpha_0\alpha_1+\alpha_0^2d_{11}],&\end{aligned} \tag{63}$$

$$TS=\frac{[-\alpha_1\beta_1d_{00}+d_{10}(\alpha_0\beta_1+\alpha_1\beta_0)-d_{11}\alpha_0\beta_0]}{-\alpha_1^2d_{00}+2\alpha_0\alpha_1d_{10}-\alpha_0^2d_{11}}. \tag{64}$$

Many ot the terms will be very small, owing to the presence of powers of $\kappa T/\zeta$.

V. CALCULATION OF $F_j(\boldsymbol{\sigma})$ [EQ. (13)]

The problem of integrating over $\mathbf{k}_1\mathbf{k}_1'$ pairs for a given $\boldsymbol{\sigma}$ can be carried out almost completely. We assume that $\mathbf{I}_{\mathbf{kk}'}$ depends only on $\boldsymbol{\sigma}+\mathbf{K}$. It will thus change when we go from one type of UK to another, but it will remain the same for all $\mathbf{kk}'$ combinations for a particular UK type. So will $\xi_j(\boldsymbol{\sigma})$, which does not even differ from one UK type to another. Thus we introduce a dimensionless parameter of order of magnitude 10^{-3}:

$$B_{j\sigma;\,\sigma+\mathbf{K}}=(2a_h^3/e^4)\,|\,\xi_j(\boldsymbol{\sigma})\cdot\mathbf{I}_{\mathbf{kk}'}|^2/|\boldsymbol{\sigma}+\mathbf{K}|, \qquad (65)$$

where a_h is the Bohr radius.

The $\mathbf{k}$ sum is transformed:

$$\sum_{\mathbf{k}}\rightarrow\frac{N\Delta_0}{4\pi^3}\frac{dE}{|\nabla_{\mathbf{k}}E|}k^2d(\cos\theta)d\varphi, \qquad (66)$$

where Δ_0 is the atomic volume, and θ is the polar angle, which will be the angle between $\mathbf{k}$ and $\boldsymbol{\sigma}+\mathbf{K}$ for each $\mathbf{K}$. Also

$$\int\Omega(-)\delta(-)d(\cos\theta)=[2m\pi/(\hbar k|\boldsymbol{\sigma}+\mathbf{K}|)]$$
$$\times\delta(E'-E-\hbar\omega)\delta(\mathbf{k}'-\mathbf{k}-\boldsymbol{\sigma}-\mathbf{K}). \qquad (67)$$

The φ integral is 2π for each $\mathbf{K}$. There remains only the E integral:

$$\int_0^\infty dE\,f_0(E)f_0(E+\hbar\omega)e^{\epsilon}=\hbar\omega_j/(e^{\gamma}-1). \qquad (68)$$

Thus

$$F_j(\boldsymbol{\sigma})=\frac{dN_{0j}}{d\gamma}\frac{1}{\kappa T\tau_c}\left[\frac{\tau_c}{\tau_j(\boldsymbol{\sigma})}+\sum_{\mathbf{K}}^{[\sigma j]}B_{j\sigma;\,\sigma+\mathbf{K}}\right], \qquad (69)$$

where

$$\tau_c=(M/m)(a_h^3/\Delta_0)(4\pi a_h/\alpha_{00}c), \qquad (70)$$

where α_{00} is the fine structure constant, c the velocity of light, and a_h the Bohr radius. Thus the whole integral has reduced to a sum over reciprocal lattice vectors associated with a given $\boldsymbol{\sigma}$.

To give some idea of the numbers involved, Table I is provided, giving values of τ_c for the alkali metals, and representative values for B taken from reference 3. The third row τ' are values of $\tau_j(\boldsymbol{\sigma})$ which will make the first term in the square bracket of (69)† equal the second. From Kittel's book,[8] we expect $\tau_j(\boldsymbol{\sigma})$ to be of the order 10^{-12} or 10^{-13} sec at 90°K or so.

VI. DISCUSSION OF THE PARAMETERS

In this section we shall estimate the α's, β's, γ's, and $d_{\mu\nu}$'s to the extent of eliminating the small terms in Eqs. (62) to (64) and of giving some qualitative picture of the type and significance of any new effects on the transport coefficients.

TABLE I. Numerical values for the parameters in Eq. (69). The numbers are designed to reveal only the order of magnitude. τ' is defined in the text after Eq. (70).

	Li	Na	K	Rb	Cs
τ_c[a]	0.27	0.53	0.47	0.82	1.10
$B_{j\sigma;\,\sigma+\mathbf{K}}$	0.003	0.002	0.001	0.0005	0.0004
τ'[a]	45.	130.	250.	820.	1400.

[a] The units of τ_c and τ' are 10^{-13} sec.

The α's are the same as Kohler's α's, and the γ's are the same as Kohler's β's:

$$\alpha_0=-\frac{e}{\hbar\Delta_0}, \qquad \alpha_1=-\frac{\pi^2}{2}\frac{e\zeta}{\hbar\Delta_0}\left(\frac{\kappa T}{\zeta}\right)^2, \qquad (71)$$

$$\gamma_0=\frac{\pi^2}{2}\frac{\zeta}{\hbar\Delta_0}\left(\frac{\kappa T}{\zeta}\right)^2, \quad \gamma_1=\frac{\pi^2}{3}\frac{\zeta^2}{\Delta_0\hbar}\left(\frac{\kappa T}{\zeta}\right)^2. \qquad (72)$$

Our β's may be written in the form

$$\beta_\nu=\gamma_\nu+\gamma_\nu', \qquad (73)$$

where

$$\gamma_\nu'=-\frac{1}{\Delta}\sum_{\mathbf{kk}'j}(E-\zeta)^\nu k_x\frac{1}{N}D_{\mathbf{kk}'j}$$
$$\times[-\Omega(-)\delta(-)+\Omega(+)\delta(+)]\frac{dN_{0j}}{d\gamma}\gamma\frac{d\omega_j}{d\sigma_x}\frac{1}{F_j(\sigma)}. \qquad (74)$$

The γ_ν''s are actually collision integrals similar to the $d_{\mu\nu}$'s but they appear in the present formalism in the guise of drift integrals. One way of treating them is to transform by the usual method to

$$\gamma_\nu'=(1/3\Delta)\sum_{\sigma j}(dN_{0j}/d\gamma)[\gamma/F_j(\boldsymbol{\sigma})]\nabla_\sigma\omega_j\cdot\sum_{\mathbf{kk}'}(\boldsymbol{\sigma}j)$$
$$\times[(E-\zeta)^\nu\mathbf{k}-(E'-\zeta)^\nu\mathbf{k}'](1/N)$$
$$\times D_{\mathbf{kk}'j}\Omega(-)\delta(-), \qquad (75)$$

where it is recognized that in a cubic crystal the calculation along an x, y, or z axis must yield the same value, so that we could sum over x, y, and z and divide by three. The reduction (21) was also used. We make use of the sums

$$\mathbf{Q}_\nu(j\boldsymbol{\sigma})=-[2/F_j(\boldsymbol{\sigma})]\sum_{\mathbf{kk}'}^{[\sigma j]}[(E-\zeta)^\nu\mathbf{k}-(E'-\zeta)^\nu\mathbf{k}']$$
$$\times(1/N)D_{\mathbf{kk}'j}\Omega(-)\delta(-), \qquad (76)$$

$$\mathbf{Q}_0(j\boldsymbol{\sigma})=\{\sum_{\mathbf{K}_1}^{[\sigma j]}(\boldsymbol{\sigma}+\mathbf{K}_1)B_{j\sigma;\,\sigma+\mathbf{K}_1}\}/$$
$$\{[\tau_c/\tau_j(\boldsymbol{\sigma})]+\sum_{\mathbf{K}_1}^{[\sigma j]}B_{j\sigma;\,\sigma+\mathbf{K}_1}\}, \qquad (77)$$

---

† The various terms in the square bracket of (69) indicate the relative importance of relaxing by phonon-phonon interactions and by the various UK interactions, for a given $\boldsymbol{\sigma}$.

[8] C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1956), second edition, p. 139.

$$\mathbf{Q}_1(j\boldsymbol{\sigma})=\{\sum_{\mathbf{K}_1}^{[\sigma j]}(\boldsymbol{\sigma}+\mathbf{K}_1)\hbar\omega_j(\boldsymbol{\sigma})$$
$$\times[\hbar\omega_j(\boldsymbol{\sigma})/(\hbar^2|\boldsymbol{\sigma}+\mathbf{K}_1|^2/4m)]B_{j\sigma;\sigma+\mathbf{K}_1}\}$$
$$\times\{[\tau_c/\tau_j(\boldsymbol{\sigma})]+\sum_{\mathbf{K}_1}^{[\sigma j]}B_{j\sigma;\sigma+\mathbf{K}_1}\}^{-1}. \quad (78)$$

These were evaluated by using the delta function to sum over $\mathbf{k}'$, and by converting to an integral over $\mathbf{k}$. The polar axis is chosen along $\boldsymbol{\sigma}+\mathbf{K}_1$, and the Ω becomes a delta function for the angle between $\mathbf{k}$ and $\boldsymbol{\sigma}+\mathbf{K}_1$. The K_1's represent possible umklapp processes for the given $\boldsymbol{\sigma}$. These can be obtained by adding $\mathbf{K}_1$ to $\boldsymbol{\sigma}$ and seeing whether or not the result is a vector smaller in magnitude than $2k_0$, where k_0 is the electron wave vector at the Fermi level. The sum over $\mathbf{K}_1$ is then a sum over all such possible $\mathbf{K}_1$'s.

We find

$$\gamma_0'=-(1/3\Delta)\sum_{\sigma j}(dN_{0j}/d\gamma)\gamma\nabla_\sigma\omega_j\cdot\mathbf{Q}_0, \quad (79)$$

$$\gamma_1'=-(1/3\Delta)\sum_{\sigma j}(dN_{0j}/d\gamma)\gamma\nabla_\sigma\omega_j\cdot\mathbf{Q}_1. \quad (80)$$

In the same manner, neglecting terms in $\tau(\mathbf{k})$, we find

$$d_{00}=\sum_{\mathbf{kk}'}(1/N)D_{\mathbf{kk}'j}\Omega(-)\delta(-)\tfrac{1}{3}(\boldsymbol{\sigma}+\mathbf{K})$$
$$\cdot(\boldsymbol{\sigma}+\mathbf{K}-\mathbf{Q}_0), \quad (81)$$

$$d_{10}=\sum_{\mathbf{kk}'}(1/N)D_{\mathbf{kk}'j}\Omega(-)\delta(-)$$
$$\times\tfrac{1}{3}[-\mathbf{k}(E-\zeta)+\mathbf{k}'(E'-\zeta)][\boldsymbol{\sigma}+\mathbf{K}-\mathbf{Q}_0], \quad (82)$$

$$d_{11}=\sum_{\mathbf{kk}'}(1/N)D_{\mathbf{kk}'j}\Omega(-)\delta(-)$$
$$\times\tfrac{1}{3}[-\mathbf{k}(E-\zeta)+\mathbf{k}'(E'-\zeta)]$$
$$\times[\mathbf{k}'(E'-\zeta)-\mathbf{k}(E-\zeta)-\mathbf{Q}_1]. \quad (83)$$

VII. THE TRANSPORT COEFFICIENTS

In Eqs. (62) to (64) we shall include in the usual fashion terms only of lowest order in $(\kappa T/\zeta)^2$, a very small quantity for metals at ordinary temperatures. The results above show that the corrections to d_{00}, d_{01}, and d_{11} will not alter their orders of magnitude in this sense. Thus we take the usual theory's results: d_{00} of zero order, d_{01} and d_{11} of first order. [Kohler's expressions and our "usual theory's" differ only in the contemplated method of calculation (see reference 3) and in the inclusion of UK processes.] We find

$$\sigma_0=\alpha_0^2/d_{00}, \quad (84)$$

$$T\kappa=\frac{\gamma_1^2}{d_{11}}\left[1+\frac{\gamma_1'}{\gamma_1}-\frac{\alpha_1}{\alpha_0}\frac{\gamma_0'}{\gamma_1}\right]\approx\frac{\gamma_1^2}{d_{11}}\left(1+\frac{\gamma_1'}{\gamma_1}\right), \quad (85)$$

$$TS=\left(1+\frac{\gamma_1'}{\gamma_1}\right)\frac{-\alpha_0\gamma_1d_{10}+\alpha_1\gamma_1d_{00}}{\alpha_0^2d_{11}}+\frac{\gamma_0}{\alpha_0}\left(1+\frac{\gamma_0'}{\gamma_0}\right). \quad (86)$$

The effects can be classified into two groups: (1) relaxation effects in the $d_{\mu\nu}$'s, and (2) drift effects in the γ_ν''s.

In the electrical conductivity, if $\tau_j\rightarrow\infty$ and UK processes are neglected, then $\sigma_0\rightarrow\infty$ as is well known on general grounds[2] but had not previously been shown to result from a statistical calculation. Thus when $\tau\rightarrow\infty$, the phonons which cannot participate in UK processes cannot contribute any resistance to the charge flow, but those that can participate in UK processes can contribute both through UK and non UK processes. With this cutoff of long-wave phonons, the resistivity varies ultimately not as T^5 but exponentially.

The details of how, in the limit $\tau\rightarrow\infty$, the UK processes can produce a nonzero scattering can now be seen. The limit $\tau\rightarrow\infty$ means that the phonons cannot dissipate energy or momentum fast enough to the surface and outside the crystal and thus interact principally only with the electrons. This implies a closed electron-phonon system. If momentum were conserved, the initial electron unbalance caused by the electric field would remain shared between the electrons and phonons even if the field is subsequently turned off. This ability to maintain the unbalance in the absence of the field is described as an infinite conductivity. Equation (81) shows that this will occur not merely when UK processes are neglected, but also whenever there is only one UK type of process possible for a phonon, whether that type has $\mathbf{K}=0$ or not. (However, the only cases where only one UK type is possible are the long-wave phonons, and the type is $\mathbf{K}=0$.)

To begin the description of how the infinite conductivity is prevented, we find it convenient to restate the facts upon which the phenomenon rests: (1) there are processes which do not conserve momentum, and (2) certain phonons may engage in more than one UK type of collision. Peierls' original discussion of a general nature centered on Fact 1. We find it convenient to emphasize both these aspects. (Fact 1 is necessary for the validity of Fact 2, but not sufficient.) Let us return to Eqs. (19) and (20), the latter referring to the momentum change caused by the nonequilibrium component of the phonon distribution tossing back some of the momentum that the electrons tried to get rid of. In the following discussion we regard the $g(\mathbf{k})$ in $L(g)$ as referring to the electron distribution, with g proportional to k_x and $h(\mathbf{k})$ as the quantity being scattered, in this case momentum, also proportional to k_x. (19) and (20) then correspond to d_{00}. x denotes the direction of the electric field.

The right-hand side of (19) is of the form

$$\sum(k_x-k_x')P_{\mathbf{kk}'}[k_x-k_x']. \quad (87a)$$

The first k_x-k_x' is the momentum loss associated with the collision. $P_{\mathbf{kk}'}$ is an intrinsic probability of collision. The second k_x-k_x' arises from the difference in the nonequilibrium components of the statistical average of the distributions of $\mathbf{k}$ and $\mathbf{k}'$. The main points of the argument to follow are not dependent on the assumption $g(\mathbf{k})\sim\mathbf{k}$, however. We shall use the word "net-probability" to exclude that part of the transition probability which corresponds to equilibrium behavior, and which, when summed, cancels to zero. Specifically we denote $P_{\mathbf{kk}'}[k_x-k_x']$ as the "net-probability" that the processes $\mathbf{k}\leftrightarrow\mathbf{k}'$ will produce excess phonons. We continue to refer to it as a probability even though it is unnormalized, i.e., even though it really represents the total *number* of excess phonons produced. To convince oneself that this indeed is what is represented, one may compare (11) with (19), it being clear in (11) that the expressions denote changes in $N_j(\boldsymbol{\sigma})$.

We pause here to make some remarks on the net-probability concept. If one traces the terms in (10) back to the terms in (6), one can show that the g and g' in the first square bracket of (10) arise from the destruction and creation terms, respectively, of the first square bracket in (6). This means that if, say, $g'>g$, there is a net-probability for a gain in the statistically averaged number of phonons above the equilibrium, which in fact is reflected in the $g-g'$ factor of the first bracket in (11). If this were all that was involved, the average number of $\boldsymbol{\sigma}$ phonons would increase without limit. To achieve a steady state (neglecting phonon-phonon interactions), we say that this average excess number is also the average excess number destroyed per unit time. But where can we find the interactions by which to destroy the excess? The answer is: in interactions involving the excess itself, once it is produced. We thus envisage a cycle: by an ordinary interaction, an excess phonon is produced; then by an extraordinary interaction it is destroyed. The number created must equal the number destroyed to maintain a steady state. On this picture, then, once an excess phonon is produced, its total probability of being destroyed is 1. The fact that without a temperature gradient and allowing $\tau_j(\boldsymbol{\sigma})\rightarrow\infty$, the average net rate of phonon production through collisions is zero does not mean that the net rate of electron momentum change through collisions is zero. This in fact is just the Peierls' paradox.

The right-hand side of (20) is of the form

$$\sum\{-(k_x-k_x')P_{\mathbf{kk}'}\langle k_x-k_x'\rangle_{\mathrm{UK\ Av}}\}. \tag{87b}$$

The first k_x-k_x' has the same significance as before. So does $P_{\mathbf{kk}'}$. However, the nonzero net-probability of the transition here is not the direct result of the difference between the nonequilibrium components of $\mathbf{k}$ and $\mathbf{k}'$, but an indirect result in the form of interactions with the nonequilibrium component of the $\boldsymbol{\sigma}$ phonons. We shall refer to this component as if it corresponded to an increase in the number, although it could, of course, equally well correspond to a decrease. The existence of such a nonequilibrium component for the phonons reflects the fact stated above that there is a greater probability for the phonon creation-destruction cycle to proceed by first a creation and then a destruction than the other way around. Now this component arises through, and its magnitude depends on, *all* the UK types of interaction which can produce the given $\boldsymbol{\sigma}$, not just on the type corresponding to the destruction collision at hand in (87b). When referred to the electron distribution unbalances, this component will reflect an average over all these types. If there is only one type possible, then this average has no significance, with the result that (87b) would cancel (87a). That is, even though there is a net probability for being first created and then destroyed, there is nevertheless a certainty that if it is created it will be destroyed, and if it gets created and destroyed in the same type of process, it will give back what it took in the way of electron momentum, and we indeed get no net change in the electron momentum. When there is more than one type of UK process available, the average becomes important, and keeps (87b) from canceling (87a). In the limit $\tau\rightarrow\infty$, the sum of (87a) and (87b) is then

$$\sum P_{\mathbf{kk}'}(k_x-k_x')-\sum P_{\mathbf{kk}'}(k_x-k_x')\times\left\{\frac{\sum(k_{1x}-k_{1x}')P_{\mathbf{k}_1\mathbf{k}_1'}}{\sum P_{\mathbf{k}_1\mathbf{k}_1'}}\right\}=\{\sum\sum P_{\mathbf{kk}'}P_{\mathbf{k}_1\mathbf{k}_1'}\times[(k_x-k_x')^2-(k_x-k_x')(k_{1x}-k_{1x}')]\}/\sum P_{\mathbf{kk}'}. \tag{87c}$$

To make clear what is involved in there being a nonequilibrium component to the phonon distribution and what the significance of Facts 1 and 2 is, let us follow the career of phonons $\boldsymbol{\sigma}j$ which may engage in two UK types of interaction, which we label 1 and 2. The relative net-probability of being created in a type-1 process is $P_1[\sigma_x+K_{1x}]$, and in a type-2 process is $P_2[\sigma_x+K_{2x}]$. The polarization index j, strictly speaking, should appear on all the P's, but for convenience we shall avoid this encumbrance. The total net probable change in electron momentum in creating these phonons is

$$(\sigma_x+K_{1x})P_1[\sigma_x+K_{1x}]+(\sigma_x+K_{2x})P_2[\sigma_x+K_{2x}], \tag{88a}$$

where the first σ_x+K_x represents the actual momentum change per collision. Each term is nonzero because of the deviation from equilibrium of the electron distribution function, reflected in the second factor σ_x+K_x. The expression shows the net tendency for the electron nonequilibrium component to produce a nonequilibrium component to the phonon distribution. In the absence of phonon-phonon interactions, our new phonons may be considered the deviation from equilibrium of the phonon distribution.

The total probability for an excess phonon to be destroyed is 1, as emphasized above. But the destruction may take place by means of a process of UK type 1 or 2 irrespective of how the excess phonon was produced. This is the crux of the matter. The relative probability that it will be destroyed in a collision of type 1 is $P_1/(P_1+P_2)$ and of type 2 is $P_2/(P_1+P_2)$. The "relative net-probability" of phonons being created in a type-1 process and destroyed in a type-1 process is $P_1[\sigma_x+K_{1x}]P_1/(P_1+P_2)$, and the corresponding net-probable electron momentum change *in the destruction collision of type 1* is

$$-(\sigma_x+K_{1x})\frac{P_1P_1}{P_1+P_2}[\sigma_x+K_{1x}].$$

The relative net-probable electron momentum change *in the destruction collisions of type 2*, corresponding to the death of excess phonons which were created in a type 1 process, is

$$-(\sigma_x+K_{2x})\frac{P_1P_2}{P_1+P_2}[\sigma_x+K_{1x}].$$

The sum of these last two expressions is to be added to the change given by the first term of Eq. (88a), (which we multiply above and below by P_1+P_2), in order to obtain the net-probable electron momentum change associated with both the life and the death of phonons σ if they were created in a type-1 process:

$$\langle\Delta k_{1x}\rangle=\frac{P_1P_2}{P_1+P_2}[(\sigma_x+K_{1x})^2-(\sigma_x+K_{1x})(\sigma_x+K_{2x})].$$

As it stands, this could be either positive or negative. If the phonons were created in a type-2 process, the net-probable electron momentum change is

$$\langle\Delta k_{2x}\rangle=\frac{P_1P_2}{P_1+P_2}[(\sigma_x+K_{2x})^2-(\sigma_x+K_{1x})(\sigma_x+K_{2x})].$$

This could also be positive or negative. The sum of these two expressions gives the total net-probable electron momentum change associated with the life history of σ phonons:

$$\langle\Delta k_{1x}\rangle+\langle\Delta k_{2x}\rangle=\frac{P_1P_2}{P_1+P_2}(K_{1x}-K_{2x})^2>0. \qquad (88b)$$

Thus the electron system will always lose momentum. (88b) corresponds to (87c). This discussion in fact paraphrases the argument which leads to Eqs. (22) to (26).

The above expression (88b) may be derived more directly still, and in a manner to emphasize the significance of the momentum nonconservation. $P_1P_2/(P_1+P_2)$ is the relative intrinsic probability of a collision of type 1 being followed by one of type 2 (or vice versa). $P_1P_2[\sigma_x+K_{1x}]/(P_1+P_2)$ is the relative net-probability that a process of type 1 because of the electron unbalance will not average to zero and will be followed by a process of type 2. $K_{1x}-K_{2x}$ is the momentum loss from the whole system in such a sequence of interactions. Thus

$$(K_{1x}-K_{2x})\frac{P_1P_2}{P_1+P_2}[\sigma_x+K_{1x}]$$

is the net-probable momentum loss from the system, i.e., the momentum nonconserved. Further

$$(K_{2x}-K_{1x})\frac{P_1P_2}{P_1+P_2}[\sigma_x+K_{2x}]$$

is the corresponding loss associated with the sequence 2 followed by 1. The sum is the total net-probable loss from the system associated with the creation and destruction of a phonon when the electron distribution has a nonequilibrium component, since sequences 1 followed by 1, and 2 followed by 2 give a zero loss each. The sum referred to gives just the expression in Eq. (88b).

The situation may be described in words as follows: there is a stronger correlation between momentum change and net probability of occurrence for processes which tend to produce than for processes which tend to reduce the phonon unbalance, and this for the reason that once the nonequilibrium phonon is created, it forgets how it was created, and thus loses a measure of correlation. The relation between momentum change and net probability is such as always to reduce the momentum unbalance of the electron-phonon system.

If one makes a list of the possible momentum losses $K_{ix}-K_{jx}=\Delta K_{mx}$ which can occur for any phonon (there are only a very few), and defines an effective matrix element in the limit $\tau\rightarrow\infty$:

$$R_{j\sigma}{}^{(m)}=\tfrac{1}{2}\Big[\sum_{\substack{i\neq l\\ \mathbf{K}_i-\mathbf{K}_l=\Delta\mathbf{K}_m}}^{[\sigma j]} B_{j\sigma;\,\sigma+\mathbf{K}_m}B_{j\sigma;\,\sigma+\mathbf{K}_l}\Big]\Big/\sum_{\mathbf{k}}^{[\sigma j]} B_{j\sigma;\,\sigma+\mathbf{K}}$$

for each of these, then one can write d_{00} in a form which parades the importance of these momentum nonconservation processes:

$$d_{00}=\frac{1}{\kappa T\tau_c}\sum_m(\Delta K_{mx})^2\sum_\sigma(-)\frac{1}{6}\frac{dN_{0j}}{d\gamma}R_{j\sigma}{}^{(m)}. \qquad (89)$$

If the phonons interact among themselves, then the phonon unbalance will be partly relaxed by transitions which have nothing to do with the electron momentum. In this case, $\tau_c/\tau_j(\boldsymbol{\sigma})$ is to be interpreted as the probability of such interactions, relative to $B_{j\sigma;\sigma+\mathbf{K}}$, the relative probability of UK type $\mathbf{K}$. When impurity scattering of the phonons is considered, it is to be expected that another term will be added to the denominator of the **Q**'s.

An estimate of the importance of this correction can be obtained from Table I. $\mathbf{Q}_0$ is of order of magnitude

$$k_0B/\{[\tau_c/\tau_j(\boldsymbol{\sigma})]+B\}.$$

This will have the value $0.1k_0$ when $\tau_j(\boldsymbol{\sigma})$ is of the order $10^2\tau_c$, i.e., 10^{-11} sec, which is the order of magnitude to be expected at low temperatures. Thus a low-temperature correction may be anticipated.

The significance of the correction to d_{10} is similar. But the correction to d_{11} entails the removal of energy from the electrons during the phonon relaxation. It is apparent that $\mathbf{Q}_1$ corrects for this, but with the peculiar and very small weighting factor

$$\tfrac{1}{2}\hbar\omega \bigg/ \left[\frac{\hbar^2|\boldsymbol{\sigma}+\mathbf{K}_1|^2}{2m}\right].$$

The correction to d_{11} is small because of the energy origin chosen in the expansions (37). The cancellation of plus and minus contributions is very large. (If one chose zero energy as origin, one can see that $\mathbf{Q}_1$ would reveal a character analogous to $\mathbf{Q}_0$.) The choice of energy origin favors a swift convergence of the series into which the transport coefficients may be put.

Orders of magnitude of γ_0' and γ_1' may be obtained by neglecting UK processes. The results will be too large, and probably of the wrong sign. But they are useful in eliminating small quantities in the transport coefficients, and can be calculated easily. We take the limit of large $\tau_j(\boldsymbol{\sigma})$ and low temperatures:

$$\lim_{\tau\to\infty}\gamma_0' = \sum_j \frac{\kappa T}{\hbar\Delta_0}\left(\frac{T}{\Theta_j}\right)^3 3\sum_{s=1}^{\infty}\frac{1}{s^3}, \tag{90}$$

$$\lim_{\tau\to\infty}\gamma_1' = \sum_j \frac{(\kappa T)^2}{\hbar\Delta_0}\left(\frac{T}{\Theta_j}\right)^3 \frac{\kappa\Theta_j}{\hbar^2\sigma_{\max}{}^2/2m}\frac{3}{2}\sum_{s=1}^{\infty}\frac{1}{s^3}, \tag{91}$$

where

$$\kappa\Theta_j = \hbar(\omega_j)_{\max} = \hbar\sigma_{\max} w_j.$$

The phonon velocity $\mathbf{w}_j = \nabla_\sigma \omega_j(\boldsymbol{\sigma})$ is treated as isotropic, dispersionless, and in the direction $\boldsymbol{\sigma}$ for the present purpose. Thus

$$\frac{\gamma_0'}{\gamma_0} = \sum_j \frac{\zeta}{\kappa T}\left(\frac{T}{\Theta_j}\right)^3 \frac{6}{\pi^2}\sum_{s=1}^{\infty}\frac{1}{s^3}, \tag{92}$$

$$\frac{\gamma_1'}{\gamma_1} = \sum_j \frac{\kappa\Theta_j}{\hbar^2\sigma_{\max}{}^2/2m}\left(\frac{T}{\Theta_j}\right)^2 \frac{9}{2\pi^2}\sum_{s=1}^{\infty}\frac{1}{s^3}. \tag{93}$$

It is at once evident that γ_1'/γ_1 will be small compared to 1, whereas γ_0'/γ_0 will not. If τ_j gets small, these ratios get smaller still, since both terms in the denominator of γ_0' and γ_1' are of the same sign. For convenience, we rewrite the transport coefficients taking advantage of the negligibility of the small terms:

$$T\kappa = \gamma_1{}^2/d_{11}, \tag{94}$$

$$TS = [-\alpha_0\gamma_1 d_{10} + \alpha_1\gamma_1 d_{00} + \alpha_0\gamma_0 d_{11}]/\alpha_0{}^2 d_{11} + \gamma_0'/\alpha_0. \tag{95}$$

It was originally to understand the thermoelectric power that Gurevich and others began to study the "phonon-drag" effects. Unfortunately, it is just for the thermoelectric power that even a qualitative appraisal of the new effects is hard to obtain without extensive calculations. Certain things of very general nature may be said, however. First, there are two effects, one the relaxation effect in d_{00} and d_{10}, (which makes d_{00} always smaller, but not necessarily d_{10}), the other the effect of a new drift term. Second, a significant effect in S need not be reflected in the conductivities.

What one would like to know most of all is the *sign* of the new term. The new term has an interesting characteristic in this regard. All $\mathbf{K}=0$ interactions give a negative value (i.e., providing a term of same sign as the usual term), whereas all UK interactions provide a positive value. This results from the fact that

$$\nabla_\sigma\omega_j\cdot(\boldsymbol{\sigma}+\mathbf{K}) \approx w_j(\boldsymbol{\sigma}/\sigma)\cdot(\boldsymbol{\sigma}+\mathbf{K})$$

will be positive when $\mathbf{K}=0$, and from the nature of umklapps, it will be negative when a Bragg reflection bounces the electron back. Our experience in transport calculations has been that UK processes dominate the scattering.[3] If this is still the case for γ_0', then an explanation for the low-temperature anomalies in Rb and Cs may be at hand.[9] Numerical calculations are planned by the author to answer this question.

To get some sort of order of magnitude estimate of the additional term in the thermoelectric power, we use 10^{-13} sec, as an order of magnitude underestimate for $\tau_j(\boldsymbol{\sigma})$ at 30°K. The contribution is then of the order of magnitude of the measured thermoelectric power. Thus the τ can at the same time be small enough not to alter the conductivities by much, and large enough to cause an appreciable effect in the thermoelectric power. However the fact that UK and non-UK processes tend to cancel each other out will greatly diminish the effect. A low-temperature T^3 dependence (first found by Gurevich) seems to be predicted by the present derivation, although the temperature dependence of τ may alter this, as will also the influence of T on the balance between UK and non-UK processes.

We also note that the $1/\Theta_j{}^3$ factor in the new term more than compensates the effect of τ_c from (70) when we go from Na to Cs, so that we expect the effect on Rb and Cs to be larger than on Na and K, which seems to be what the experiments indicate. The positive thermoelectric power of Li seems to escape the theory. It could possibly enter through an unexpectedly large UK weighting in $B_{j\sigma;\sigma+\mathbf{K}}$.

A high-temperature correction is not to be ruled out. A rough order-of-magnitude estimate indicated an effect one order of magnitude smaller than the observed values. Considering the roughness of these estimates, we cannot eliminate such a possibility.

VIII. OTHER EFFECTS

The scattering of electrons by impurities may be taken into account by adding a term $L_4(g)$ to $L(g)$ in (15) in the usual manner. It will affect the $d_{\mu\nu}$'s only.

Additional scattering mechanisms for the phonons would affect the $F_j(\boldsymbol{\sigma})$'s and hence would affect the

---

[9] For the experimental work, see MacDonald, White, and Woods, Proc. Roy. Soc. (London) **A235**, 358 (1956), and D. K. C. MacDonald and W. B. Pearson, Proc. Roy. Soc. (London) **A219**, 373 (1953).

relaxation corrections in the $d_{\mu\nu}$'s and the γ_ν''s. They would also affect Eq. (14) by adding another drift term similar to $U(\mathbf{k})$, and hence would affect the β integrals.

The transport of energy by phonons would affect the thermal conductivity. It can be written down and developed using (12), assumption 5, (37), and (46), whence

$$\begin{aligned} w_{\text{phonons}} &= (1/8\pi^3)\sum_j \int d\boldsymbol{\sigma}\, \hbar\omega_j(\boldsymbol{\sigma}) \nabla_\sigma \omega_j \\ &\qquad \times[-(dN_{0j}/d\gamma)G_j(\boldsymbol{\sigma})/\kappa T] \\ &= -[\kappa_0 + (1/T)(\textstyle\sum_\nu a_\nu\lambda_\nu)(\sum_\nu b_\nu\alpha_\nu)/ \\ &\qquad (\textstyle\sum_\nu a_\nu\alpha_\nu) - (1/T)\sum_\nu b_\nu\lambda_\nu](dT/dx) \\ &= -[\kappa_0 + D_{\alpha\beta;\alpha\lambda}/(D_{\alpha\alpha}T)], \end{aligned} \tag{96}$$

where

$$\kappa_0 = [24\pi^3 T\kappa T]^{-1} \sum_j \int d\boldsymbol{\sigma}\, \hbar\omega_j (\nabla_\sigma\omega_j)^2 \times (dN_0/d\gamma)[\gamma/F_j(\boldsymbol{\sigma})](dN_0/d\gamma),$$

$$\lambda_\nu = [24\pi^3\kappa T]^{-1} \sum_j \int d\boldsymbol{\sigma}\, \hbar\omega_j(\nabla_\sigma\omega_j\cdot \mathbf{Q}_\nu) dN_0/d\gamma = -\gamma_\nu'.$$

κ_0 is quite negligible. The other term to a first approximation will alter (63) to the extent of replacing γ_0 and γ_1 by $\gamma_0+\lambda_0$ and $\gamma_0+\lambda_1$, respectively. λ_1 is small compared to γ_1, but λ_0 is not small compared to γ_0. But every term in which γ_0 appears is so small because of other factors that λ_0 will have no sizable effect in metals. The effect of "electron drag" is negligible.‡

IX. THE ONSAGER RELATIONS

Our results must satisfy the Onsager relations, since we have employed detailed balancing, and have treated the electron-phonon interaction symmetrically. To show the verification, we rewrite the currents as

$$\begin{aligned} J_x &= L_{11}\mathcal{E}_x^{**} + L_{12}\left(-\frac{1}{T}\frac{dT}{dx}\right), \\ w_x &= w_{\text{electron}} + w_{\text{phonon}} = L_{21}\mathcal{E}_x^{**} + L_{22}\left(-\frac{1}{T}\frac{dT}{dx}\right), \end{aligned} \tag{97}$$

where

$$\mathcal{E}_x^{**} = \mathcal{E}_x - \frac{T}{e}\frac{d}{dx}\frac{\zeta}{T} = \mathcal{E}_x^{*} + \frac{\zeta}{e}\left(-\frac{1}{T}\frac{dT}{dx}\right). \tag{98}$$

The "proper forces" $\mathcal{E}^{**}$ and $-(dT/dx)/T$ are the ones appropriate to the streams J_x and w_x.[10] Our Eqs. (46), (47), and (96) become

$$\begin{aligned} J_x &= L_{11}'\mathcal{E}_x^{*} + L_{12}'\left(-\frac{1}{T}\frac{dT}{dx}\right) \\ &= L_{11}'\mathcal{E}_x^{**} + \left(L_{12}' - \frac{\zeta}{e}L_{11}'\right)\left(-\frac{1}{T}\frac{dT}{dx}\right), \\ w_x &= L_{21}'\mathcal{E}_x^{*} + L_{22}'\left(-\frac{1}{T}\frac{dT}{dx}\right) \\ &= L_{21}'\mathcal{E}_x^{**} + \left(L_{22}' - \frac{\zeta}{e}L_{21}'\right)\left(-\frac{1}{T}\frac{dT}{dx}\right), \end{aligned} \tag{99}$$

where

$$\begin{aligned} L_{11}' &= \textstyle\sum a_\nu\alpha_\nu, \\ L_{12}' &= \textstyle\sum b_\nu\alpha_\nu = \sum a_\nu\beta_\nu, \\ L_{21}' &= \textstyle\sum a_\nu[\gamma_\nu - (\zeta/e)\alpha_\nu - \lambda_\nu] = \sum a_\nu\beta_\nu - (\zeta/e)\alpha_\nu, \\ L_{22}' &= \textstyle\sum b_\nu(\gamma_\nu - \lambda_\nu) + T\kappa_0 = \sum b_\nu\beta_\nu + T\kappa_0. \end{aligned} \tag{100}$$

The Onsager relation which we verify is that $L_{12}-L_{21}=0$. By Eqs. (99) and (100) this is

$$\begin{aligned} L_{12}' - (\zeta/e)L_{11}' - L_{21}' \\ = \textstyle\sum\{a_\nu\beta_\nu - (\zeta/e)a_\nu\alpha_\nu - a_\nu[\beta_\nu - (\zeta/e)\alpha_\nu]\} = 0, \end{aligned}$$

which proves the relation.

Added note.—Since writing this paper, the author has become aware of recent work[11] on the variational principle. None of those papers takes the same approach as ours, however. A note by Tsuji,[12] on the other hand, indicates a procedure similar to ours.

---

‡ The last relation in (96) shows that the electron drag on phonon heat conduction will cancel, to first order in drag quantities, the phonon drag on electron heat conduction. The present theory provides the correction second order in drag quantities, although we have not written it down.

[10] H. B. Callen, Phys. Rev. **73**, 1349 (1948).

[11] J. Ziman, Can. J. Phys. **34**, 1256 (1956); D. Dorn, Z. Naturforsch. **12a**, 739 (1957); G. E. Tauber, Bull. Am. Phys. Soc. Ser. II, **3**, 104 (1958); I. I. Hanna and E. H. Sondheimer, Proc. Roy. Soc. (London) **A239**, 247 (1957).

[12] M. Tsuji, J. Phys. Soc. Japan **13**, 426 (1958). His article has appeared in Mem. Fac. Sci., Kyushu Univ., Ser. B, **2**, No. 4. Tsuji has not taken account of umklapp processes, however.