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# THE THEORY OF THE TRANSPORT PHENOMENA IN METALS

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## Abstract

Exact expressions, valid for all temperatures, are obtained in the form of infinite determinants for the electrical conductivity, the thermal conductivity and the thermo-electric power of a degenerate gas of quasi-free electrons interacting with the ionic lattice of a metal. It is shown that the values of the electrical and thermal conductivities, in general, exceed the values given by the approximate interpolation formulae due to Bloch, Wilson and others, and, in particular, that the Grüneisen-Bloch formula for the ideal electrical resistance is appreciably in error in the region close to the Debye temperature. It is further shown that the residual and ideal resistances of an impure metal are not strictly additive in the region where the two are of the same order of magnitude. The behavior of the thermal conductivity is shown to agree qualitatively with the discussion based on Wilson's formula given by Makinson; the numerical values of the thermal conductivity, however, are increased appreciably, particularly for an ideal metal at low temperatures. The thermoelectric power is also discussed, but no simple results can be given for the intermediate temperature range.
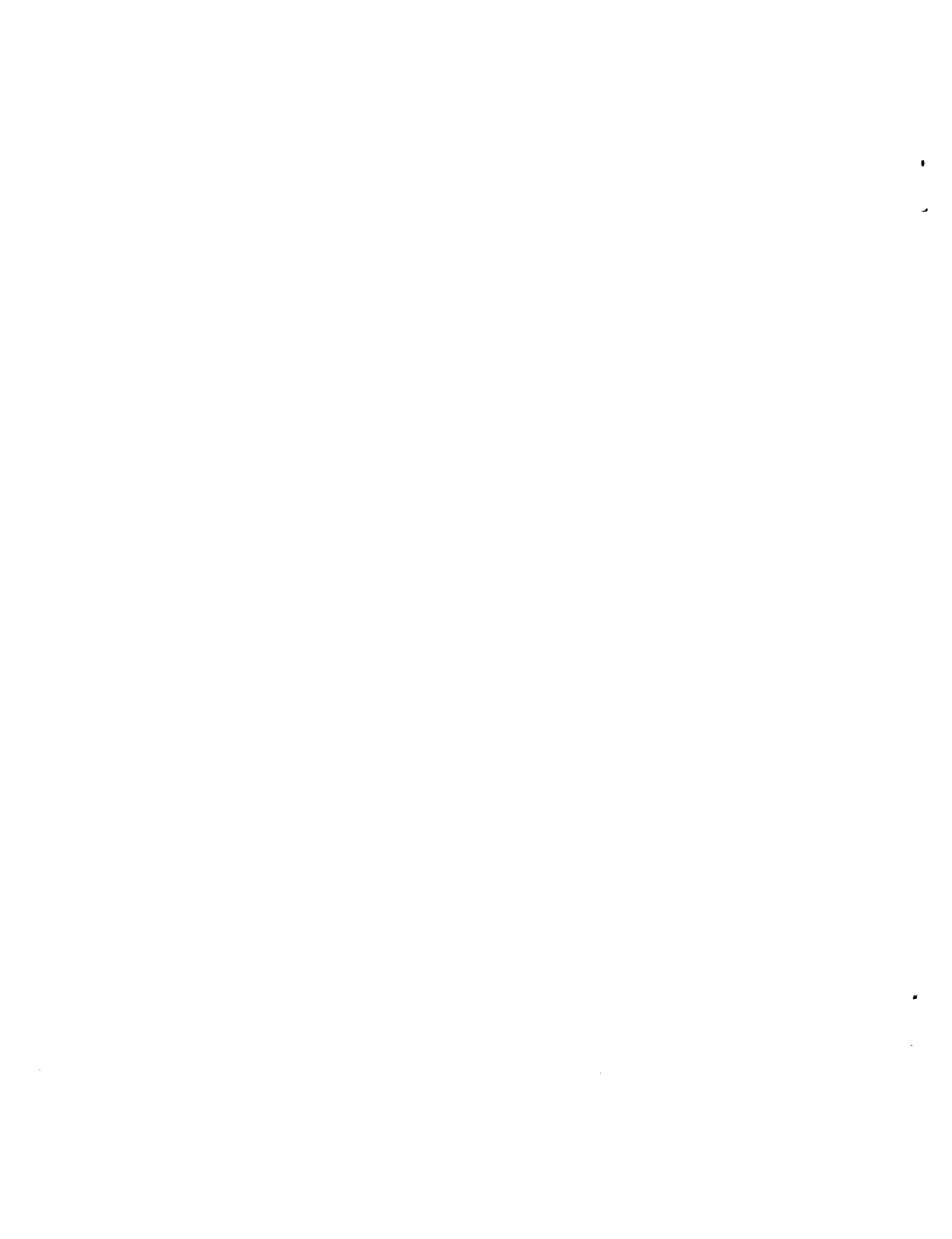
# THE THEORY OF THE TRANSPORT PHENOMENA IN METALS

## 1. Introduction

The theoretical study of the transport phenomena in metals requires the solution of a complicated integral equation for the velocity distribution function of the conduction electrons. This equation has so far been solved only for the simplest model in which the electrons are assumed to be quasi-free; even for this case, no satisfactory and generally valid solution has yet been given, although much effort has been devoted towards obtaining solutions in a variety of special cases. At high temperatures, such that $(\Theta/T)^2$ can be neglected, where $\Theta$ is the Debye temperature, the integral equation reduces to an ordinary equation, and a solution is easily obtained (see, for example, p. 208, (1); and the terms of higher order in $(\Theta/T)^2$ may be obtained by a method of successive approximations, Section 2, (2). The case of an impure metal at very low temperatures can also be treated by a method of successive approximations, which amounts to an expansion in descending powers of the residual resistance, Section 3, (2) and (3); but the higher order terms become very complicated, and the method cannot be applied to the case of an ideally pure metal. The electrical conductivity of a pure metal can be obtained by a special method of Bloch (4); but this gives only the leading term at low temperatures, and it cannot be used at all to deal with the second order effects such as the thermal conductivity and the thermoelectric power.

More general methods, applicable in principle to the whole temperature range, have been given by Kroll (5,6) and more recently by Kohler (7,8). Kroll transformed the integral equation into an infinite set of linear equations and obtained a solution by the use of infinite determinants; he confined himself to an evaluation of the leading terms in the thermal conductivity and the thermoelectric power of an ideal metal at low temperatures. It is shown in Section 5 of the present paper that Kroll's original result for the thermal conductivity is, in fact, incorrect; see also Kroll (9) and Umeda and Yamamoto (10). Kohler transformed the integral equation into a variational problem, and attempted to obtain a solution by expanding the distribution function as a power series and by using the variation principle to determine the coefficients. He evaluated explicitly the approximations of lowest order only, and found that they lead to expressions for the electrical and thermal conductivities which are identical with the interpolation formulae previously obtained by Wilson (2) for an impure metal, assuming the general validity of Matthiessen's rule concerning the additivity of the residual and ideal resistances. (The expression for the ideal electrical resistance obtained by these methods is identical with the well known Grüneisen-Bloch interpolation formula.) These formulae are, however, known to lead to incorrect results at intermediate temperatures (3), and no explicit expressions for the transport magnitudes which are exact for all temperatures have so far been given.

Such expressions are provided in the present paper, which represents a synthesis and further development of Kroll's and Kohler's methods of solution. In Section 2 the

variational method as developed by Kohler (8) is recapitulated, and it is shown that it leads to equations which are identical with those obtained earlier by Kroll (5) by means of an arbitrary procedure.* In Section 3 the calculations are completed without approximation; the transport magnitudes for a degenerate electron gas are finally obtained as the ratio of two infinite determinants (Eqs. 38, 39 and 40). The results may be evaluated numerically to any desired degree of accuracy by breaking off the determinants at a finite number of rows and columns, but no attempt is made to give a general discussion of the convergence of the method. Wilson's interpolation formulae are obtained on retaining only the lowest terms in the determinants which give a non-zero result, and it is shown in Section 3.31 that the effect of the higher approximations is to increase the electrical and thermal conductivities above the values given by Wilson.

The electrical conductivity is discussed in detail in Section 4, and numerical values are given. It is shown that the Grüneisen-Bloch formula leads to values of the ideal electrical conductivity which are appreciably too low at temperatures close to the Debye temperature, in agreement with the experimental facts. For an impure metal it is found that Matthiessen's rule breaks down in the important temperature region where the residual and ideal resistances are of the same order of magnitude. The deviations from the rule are small and positive, in qualitative agreement with experiment. A result obtained by Dube (3), which seems to indicate that the deviations from Matthiessen's rule are negative, is discussed in Section 4.22 and is shown to admit of no such interpretation.

The second order phenomena are considered in Section 5. It is shown that Wilson's formula for the thermal conductivity, discussed in detail by Makinson (13), is qualitatively correct; and the existence of a minimum at intermediate temperatures is confirmed. The numerical values of the thermal conductivity are increased appreciably at intermediate and (for an ideal metal) at low temperatures. The paper concludes with a brief discussion of the thermoelectric power in Section 5.2.

## 2. General Theory

2.1. The integral equation. We restrict the discussion to monovalent metals and assume that the electrons are quasi-free, so that the energy E is related to the wavevector $\underset{\sim}{k}$ by $E = h^2|\underset{\sim}{k}|^2/(8\pi^2 m)$, where m is the effective mass of an electron. In the presence of an electric field $\mathcal{E}$ and a temperature gradient $\partial T/\partial x$ parallel to the x axis, the distribution function f of the conduction electrons is most conveniently written in the form

$$f = f_o - k_1 \, c(\eta) \, \frac{\partial f_o}{\partial E} \tag{1}$$

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*After completion of the present work, there came to the author's notice a paper by Umeda (11) in which the variational derivation of Kroll's equations is given independently of Kohler's work. Some particular results of the present paper have been anticipated by later Japanese work on Kroll's method (10, 12).

where $\eta = (E - \zeta)/kT$ ($\zeta$ is the Fermi energy level and k is Boltzmann's constant*), $f_o$ is the Fermi function $1/(e^\eta + 1)$, and $c(\eta)$ is a function of $\eta$ which has to be determined.

When scattering by both impurities and the lattice vibrations is taken into account, the integral equation for $c(\eta)$ is (reference (2), Eqs. 3 and 19)

$$4\Lambda\left(\frac{h^2}{8\pi^2 m}\right)^{3/2} \left(\frac{\Theta}{T}\right)^3 E^{3/2} \left(\epsilon\,\mathcal{E} + T\,\frac{\partial}{\partial x}\left(\frac{\zeta}{T}\right) + \frac{E}{T}\,\frac{\partial T}{\partial x}\right) = L(c) \tag{2}$$

where

$$L(c) = -\Lambda M\left(\frac{\Theta}{T}\right)^3 E^2\, c(\eta) - \int_{-\Theta/T}^{\Theta/T} \left[E\,c(\eta) - c(\eta + z)\left(E + \frac{1}{2}kTz - D\left(\frac{T}{\Theta}\right)^2 z^2\right)\right]$$

$$\times \frac{e^\eta + 1}{e^{\eta+z} + 1}\,\frac{z^2\,dz}{|1 - e^{-z}|} \tag{3}$$

and $-\epsilon$ is the electronic charge, M is a constant depending on the number and scattering power of the impurities, and $\Lambda$ and D are constants characteristic of the pure metal. The explicit form of $L(c)$ will not be needed for the general results to be proved in the present section.

2.2 The variation principle. Since the integral equation is linear, it is sufficient to solve it when the left-hand side is replaced by $E^n$; the corresponding solution is denoted by $c^{(n)}$. To obtain a solution we make use of a variational formulation of Kohler (7,8). Kohler has shown that the correct solution $c^{(n)}$ is such as to make the integral**

$$\left(c^{(n)},\ c^{(n)}\right) = \int_{-\infty}^{\infty} c^{(n)}\,L\left(c^{(n)}\right)\frac{\partial f_o}{\partial \eta}\,d\eta \tag{4}$$

a maximum, subject to the subsidiary (normalizing) condition

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* The use of k in two different senses, to denote the wave-vector $\underset{\sim}{k}$ with components $k_1$, $k_2$, $k_3$, and to denote Boltzmann's constant k, should not cause any confusion.

** The relation between the present notation and that of Kohler (8) is most easily found by comparing Eqs. 2 and 3 of the present paper with Eqs. 1a, 1b and 1c of Kohler's paper. Kohler writes the curly bracket on the left-hand side of Eq. 2 in the form

$$\left(\epsilon\,\mathcal{E} + \frac{\partial \zeta}{\partial x}\right) + k\eta\frac{\partial T}{\partial x}$$

and separates the integral equation accordingly; this procedure is in some respects more convenient than ours, which is that used by Wilson (2), but the final results are the same. Equations 4 and 5 of the present paper are essentially equivalent to Eqs. 5a, 5b, 6a and 6b of Kohler's paper.

$$\int_{-\infty}^{\infty} c^{(n)} \, L\left(c^{(n)}\right) \frac{\partial f_o}{\partial \eta} \, d\eta = \int_{-\infty}^{\infty} E^n \, c^{(n)} \, \frac{\partial f_o}{\partial \eta} \, d\eta \quad . \tag{5}$$

Kohler has also proved generally that, if $\phi_1$ and $\phi_2$ are any functions of $\eta$,

$$(\phi_1, \, \phi_2) = (\phi_2, \, \phi_1) \quad , \tag{6}$$

and

$$(\phi_1, \, \phi_1) \geqslant 0 \quad . \tag{7}$$

2.21.  We now expand $c^{(n)}$ as a power series in $\eta$,

$$c^{(n)}(\eta) = \sum_{\mu=0}^{\infty} c_{\mu}^{(n)} \eta^{\mu} \quad , \tag{8}$$

and use the variation principle to determine the coefficients. Equations 4 and 5 become

$$\left(c^{(n)}, \, c^{(n)}\right) = \sum_{\mu=0}^{\infty} \sum_{\nu=0}^{\infty} d_{\mu\nu} \, c_{\mu}^{(n)} \, c_{\nu}^{(n)} \quad , \tag{9}$$

and

$$\sum_{\mu=0}^{\infty} \sum_{\nu=0}^{\infty} d_{\mu\nu} \, c_{\mu}^{(n)} \, c_{\nu}^{(n)} = \sum_{\mu=0}^{\infty} a_{\mu}^{(n)} \, c_{\mu}^{(n)} \quad , \tag{10}$$

where*

$$d_{\mu\nu} = (\eta^{\mu}, \, \eta^{\nu}) = \int_{-\infty}^{\infty} \eta^{\mu} \, L(\eta^{\nu}) \frac{\partial f_o}{\partial \eta} \, d\eta = d_{\nu\mu} \tag{11}$$

and

$$a_{\mu}^{(n)} = \int_{-\infty}^{\infty} E^n \eta^{\mu} \frac{\partial f_o}{\partial \eta} \, d\eta \quad . \tag{12}$$

By differentiating with respect to $c_{\mu}^{(n)}$ for example, it is found that the maximum value of expression 9, subject to the condition of Eq. 10, is obtained if the coefficients $c_{\mu}^{(n)}$ satisfy the infinite set of equations

$$\sum_{\nu=0}^{\infty} d_{\mu\nu} \, c_{\nu}^{(n)} = a_{\mu}^{(n)}, \quad \mu = 0, 1, 2, \ldots \tag{13}$$

Equation 13 could have been obtained formally from Eq. 2 by multiplying by

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* Apart from a multiplicative constant, the quantity $d_{\mu\nu}$ defined here is the same as that used by Kohler (8), Eq. 8c. Also $a_{\mu}^{(3/2)}$ and $a_{\mu}^{(5/2)}$ correspond to Kohler's $a_{\mu}$ and $\beta_{\mu}$, but are not identical with them for the reasons given in the second footnote on page 3.

$\eta^{\mu}(\partial f_{o}/\partial \eta)$, where $\mu = 0,1,2,\ldots$, and integrating with respect to $\eta$. This is, in fact, the procedure adopted (without special justification) by Kroll (5); see also Section 6.5, (1).

2.3. The current densities. If $\underset{\sim}{v}$ is the velocity of an electron ($h\underset{\sim}{v} = 2\pi \, grad_{k} \, E$), the electric current is given by

$$J = -\frac{\epsilon}{4\pi^{3}} \iiint v_{x} \, f \, dk_{1} \, dk_{2} \, dk_{3} = \frac{16\pi^{2}}{3h^{4}} (2m)^{3/2} \, \epsilon \int_{-\infty}^{\infty} E^{3/2} \, c(\eta) \frac{\partial f_{o}}{\partial \eta} \, d\eta$$

$$= \mathcal{K}_{\frac{3}{2}, \frac{3}{2}} \left( \epsilon^{2} \, \mathcal{E} + \epsilon T \frac{\partial}{\partial x} \left( \frac{\zeta}{T} \right) \right) + \mathcal{K}_{\frac{3}{2}, \frac{5}{2}} \frac{\epsilon}{T} \frac{\partial T}{\partial x} \quad , \tag{14}$$

and the heat current is given by

$$\omega = \frac{1}{4\pi^{3}} \iiint v_{x} \, E \, f \, dk_{1} \, dk_{2} \, dk_{3}$$

$$= \mathcal{K}_{\frac{5}{2}, \frac{3}{2}} \left( -\epsilon \, \mathcal{E} - T \frac{\partial}{\partial x} \left( \frac{\zeta}{T} \right) \right) - \mathcal{K}_{\frac{5}{2}, \frac{5}{2}} \frac{1}{T} \frac{\partial T}{\partial x} \quad , \tag{15}$$

where, using Eqs. 8 and 12,

$$\mathcal{K}_{m,n} = \frac{8\Lambda}{3\pi h} \left( \frac{\Theta}{T} \right)^{3} \int_{-\infty}^{\infty} E^{m} \, c^{(n)}(\eta) \frac{\partial f_{o}}{\partial \eta} \, d\eta = \frac{8\Lambda}{3\pi h} \left( \frac{\Theta}{T} \right)^{3} \sum_{\mu=0}^{\infty} a_{\mu}^{(m)} \, c_{\mu}^{(n)} = \mathcal{K}_{n,m} . \tag{16}$$

(Note that our notation for the $\mathcal{K}$'s differs slightly from that used by Wilson (2)).

2.31. Solving the infinite set of Eqs. 13 for the $c_{\mu}^{(n)}$ and substituting the result in Eq. 16, it is easily shown that

$$\mathcal{K}_{m,n} = -\frac{8\Lambda}{3\pi h} \left( \frac{\Theta}{T} \right)^{3} \frac{\mathcal{D}_{m,n}}{\mathcal{D}} \quad , \tag{17}$$

where $\mathcal{D}$ is the determinants of the $d_{\mu\nu}$'s,

$$\mathcal{D} = |d_{\mu\nu}| \quad , \tag{18}$$

and where

$$\mathcal{D}_{m,n} = \begin{vmatrix} 0 & a_{0}^{(m)} & a_{1}^{(m)} & a_{2}^{(m)} & \cdots \\ a_{0}^{(n)} & d_{00} & d_{01} & d_{02} & \cdots \\ a_{1}^{(n)} & d_{10} & d_{11} & d_{12} & \cdots \\ a_{2}^{(n)} & d_{20} & d_{21} & d_{22} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \end{vmatrix} \tag{19}$$

All the transport effects of interest are readily expressed in terms of the $\mathcal{K}_{m,n}$, and hence in terms of the quantities $d_{\mu\nu}$ and $a_\mu^{(n)}$.

The electrical conductivity is given by

$$\sigma = \epsilon^2 \mathcal{K}_{\frac{3}{2},\frac{3}{2}} = -\frac{8\epsilon^2\Lambda}{3\pi h}\left(\frac{\Theta}{T}\right)^3 \frac{\mathcal{D}_{\frac{3}{2},\frac{3}{2}}}{\mathcal{D}} \quad . \tag{20}$$

The thermal conductivity is

$$K = \frac{\mathcal{K}_{\frac{3}{2},\frac{3}{2}}\mathcal{K}_{\frac{5}{2},\frac{5}{2}} - \mathcal{K}_{\frac{3}{2},\frac{5}{2}}^2}{\mathcal{K}_{\frac{3}{2},\frac{3}{2}}\,T} = \frac{8\Lambda}{3\pi h\Theta}\left(\frac{\Theta}{T}\right)^4\left(-\frac{\mathcal{D}_{\frac{5}{2},\frac{5}{2}}}{\mathcal{D}} + \frac{\mathcal{D}_{\frac{3}{2},\frac{5}{2}}^2}{\mathcal{D}_{\frac{3}{2},\frac{3}{2}}\mathcal{D}}\right) \quad . \tag{21a}$$

As shown by Kohler, Sylvester's theorem (see, for example, (14)) may be used to write this in the simpler form

$$K = -\frac{8\Lambda}{3\pi h\Theta}\left(\frac{\Theta}{T}\right)^4 \frac{\mathcal{D}_{\frac{3}{2},\frac{3}{2},\frac{5}{2},\frac{5}{2}}}{\mathcal{D}_{\frac{3}{2},\frac{3}{2}}} \quad , \tag{21b}$$

where

$$\mathcal{D}_{\frac{3}{2},\frac{3}{2},\frac{5}{2},\frac{5}{2}} = \begin{vmatrix} 0 & 0 & a_0^{(3/2)} & a_1^{(3/2)} & a_2^{(3/2)} & \cdots \\ 0 & 0 & a_0^{(5/2)} & a_1^{(5/2)} & a_2^{(5/2)} & \cdots \\ a_0^{(3/2)} & a_0^{(5/2)} & d_{00} & d_{01} & d_{02} & \cdots \\ a_1^{(3/2)} & a_1^{(5/2)} & d_{10} & d_{11} & d_{12} & \cdots \\ a_2^{(3/2)} & a_2^{(5/2)} & d_{20} & d_{21} & d_{22} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \end{vmatrix} \quad . \tag{22}$$

Finally, the absolute thermoelectric power per degree is $-\mathcal{G}/\epsilon$, where

$$\mathcal{G} = \frac{\mathcal{K}_{\frac{3}{2},\frac{5}{2}} - \zeta\mathcal{K}_{\frac{3}{2},\frac{3}{2}}}{\mathcal{K}_{\frac{3}{2},\frac{3}{2}}\,T} = \frac{\mathcal{D}_{\frac{3}{2},\frac{5}{2}} - \zeta\mathcal{D}_{\frac{3}{2},\frac{3}{2}}}{\mathcal{D}_{\frac{3}{2},\frac{3}{2}}\,T} \quad . \tag{23}$$

## 3. Explicit Evaluation of the Transport Magnitudes
## for a Degenerate Electron Gas

3.1. The quantities $a_\mu^{(n)}$ and $d_{\mu\nu}$ defined by Eqs. 12 and 11, (L being the integral operator (3)), may be evaluated by expanding in powers of $\eta$ and using the usual methods for integrals involving the Fermi distribution function. The calculations are straightforward but (in the case of the $d_{\mu\nu}$) somewhat lengthy; details are given in Appendix 1, and only the final results will be quoted here.

It is found that

$$a_\mu^{(n)} = -\zeta^n a_\mu - \zeta^n \sum_{r=2,4,6\ldots}^{\infty} \frac{n(n-1)(n-2)\ldots(n-r+1)}{r!} a_{\mu+r} \gamma^r \qquad (24a)$$

if $\mu$ is even (including $\mu = 0$), and that

$$a_\mu^{(n)} = -\zeta^n \sum_{r=1,3,5\ldots}^{\infty} \frac{n(n-1)(n-2)\ldots(n-r+1)}{r!} a_{\mu+r} \gamma^r \qquad (24b)$$

if $\mu$ is odd, where $\gamma = kT/\zeta$ is the degeneracy parameter, and where

$$a_0 = 1 \quad,$$

$$a_{2s} = 2\,(2s)! \sum_{\ell=1}^{\infty} \frac{(-1)^{\ell+1}}{\ell^{2s}} = (2^{2s} - 2)\, B_s\, \pi^{2s} \qquad (s \geqslant 1) \quad, \qquad (25)$$

and $B_s$ is the sth Bernoulli number.

Further,

$$d_{\mu\nu} = \Lambda\, M\left(\frac{\Theta}{T}\right)^3 \zeta^2 \left(a_{\mu+\nu} + \gamma^2 a_{\mu+\nu+2}\right) + 2D\left(\frac{T}{\Theta}\right)^2 F_{\mu\nu} \qquad (26a)$$

if $\mu+\nu$ is even, and

$$d_{\mu\nu} = 2\gamma\, \Lambda\, M\left(\frac{\Theta}{T}\right)^3 \zeta^2 a_{\mu+\nu+1} + 2\gamma\, D\left(\frac{T}{\Theta}\right)^2 F_{\mu\nu} \qquad (26b)$$

if $\mu+\nu$ is odd, where

$$F_{\mu\nu} = a_{\mu+\nu} \mathcal{J}_5 + \sum_{k=3,5,7\ldots}^{\mu-1,\mu} \binom{\mu}{k} \frac{a_{\mu+\nu-k+1}}{\mu+\nu-k+1} \left(\mathcal{J}_{k+4} - \frac{\zeta}{D}\left(\frac{\Theta}{T}\right)^2 \mathcal{J}_{k+2}\right)$$

$$+ \sum_{k=3,5,7\ldots}^{\nu-1,\nu} \binom{\nu}{k} \frac{a_{\mu+\nu-k+1}}{\mu+\nu-k+1} \left(\mathcal{J}_{k+4} - \frac{\zeta}{D}\left(\frac{\Theta}{T}\right)^2 \mathcal{J}_{k+2}\right)$$

$$+ \frac{\zeta}{D} \left(\frac{\Theta}{T}\right)^2 \sum_{k=3,5,7\ldots}^{\mu+\nu+1} \binom{\mu+\nu+1}{k} \frac{a_{\mu+\nu-k+1}}{\mu+\nu+1} \mathcal{J}_{k+2}$$

$$+ (-1)^\mu \frac{\mu! \, \nu!}{(\mu+\nu+1)!} \left( \mathcal{J}_{\mu+\nu+5} - \frac{\zeta}{D} \left(\frac{\Theta}{T}\right)^2 \mathcal{J}_{\mu+\nu+3} \right) \tag{27a}$$

if $\mu+\nu$ is even, and where

$$F_{\mu\nu} = \frac{\zeta}{D} \left(\frac{\Theta}{T}\right)^2 \left[ \left( \frac{1}{4}(\mu+\nu) + \frac{1}{2} \mu\nu \right) a_{\mu+\nu-1} \mathcal{J}_5 \right.$$

$$- \sum_{k=4,6,8\ldots}^{\mu-1,\mu} \left\{ \binom{\mu+1}{k+1} - \frac{1}{2} \binom{\mu}{k} \right\} \frac{a_{\mu+\nu-k+1}}{\mu+\nu-k+1} \mathcal{J}_{k+3}$$

$$- \sum_{k=4,6,8\ldots}^{\nu-1,\nu} \left\{ \binom{\nu+1}{k+1} - \frac{1}{2} \binom{\nu}{k} \right\} \frac{a_{\mu+\nu-k+1}}{\mu+\nu-k+1} \mathcal{J}_{k+3}$$

$$\left. + \sum_{k=4,6,8\ldots}^{\mu+\nu+1} \binom{\mu+\nu+2}{k+1} \frac{a_{\mu+\nu-k+1}}{\mu+\nu+2} \mathcal{J}_{k+3} + \frac{1}{2} (-1)^\mu (\mu-\nu) \frac{\mu! \, \nu!}{(\mu+\nu+2)!} \mathcal{J}_{\mu+\nu+4} \right] \tag{27b}$$

if $\mu+\nu$ is odd. In these expressions the symbol

$$\sum_{k=3,5,7\ldots}^{\mu-1,\mu} \quad ,$$

for example, means that the upper limit of the summation is to be taken as $\mu-1$ or $\mu$ according as $\mu$ is even or odd, and moreover that the summation is to be omitted entirely if $\mu < 3$. It is evident by inspection that $F_{\mu\nu} = F_{\nu\mu}$; as particular cases, we have

$$F_{o\nu} = F_{\nu o} = \sum_{k=1,3,5\ldots}^{\nu+1} \binom{\nu+1}{k} \frac{a_{\nu-k+1}}{\nu+1} \mathcal{J}_{k+4} \tag{28a}$$

if $\nu$ is even, and

$$F_{o\nu} = F_{\nu o} = \frac{1}{2} \frac{\zeta}{D} \left(\frac{\Theta}{T}\right)^2 \sum_{k=2,4,6\ldots}^{\nu+1} \binom{\nu+1}{k} \frac{a_{\nu-k+1}}{\nu+1} \mathcal{J}_{k+3} \tag{28b}$$

if $\nu$ is odd. Finally, in the above expressions

$$\mathcal{J}_n = \int_o^{\Theta/T} \frac{z^n \, dz}{(e^z - 1)(1 - e^{-z})} \quad . \tag{29}$$

It should be particularly noted that the calculations have been carried out retaining all powers of $\gamma$. The expressions for $a_\mu^{(n)}$ are infinite series in ascending powers of $\gamma^2$, while the $d_{\mu\nu}$ involve powers of $\gamma$ up to and including the second only.

3.2 The transport magnitudes can now be evaluated explicitly by substituting the expressions 24 and 26 in Eqs. 20, 21 and 23. For a degenerate electron gas it is sufficient to retain only the lowest terms in an expansion in ascending powers of $\gamma^2$. This enables us to simplify the resulting expressions considerably; it should be noted, however, that this approximation does not, in general, allow us to break off the infinite determinants at a finite number of rows and columns.

It follows from Eqs. 18 and 26, for example, that the leading term in the determinant $\mathcal{D}$ is independent of $\gamma$, and is

$$
\mathcal{D} = \begin{vmatrix}
d'_{00} & 0 & d'_{02} & 0 & d'_{04} & \cdots \\
0 & d'_{11} & 0 & d'_{13} & 0 & \cdots \\
d'_{20} & 0 & d'_{22} & 0 & d'_{24} & \cdots \\
0 & d'_{31} & 0 & d'_{33} & 0 & \cdots \\
d'_{40} & 0 & d'_{42} & 0 & d'_{44} & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots &
\end{vmatrix} ,
$$

where $d'_{\mu\nu}$ is the coefficient of the lowest power of $\gamma$ in $d_{\mu\nu}$. Rearranging rows and columns, we obtain

$$
\mathcal{D} =
\begin{vmatrix}
d'_{11} & d'_{13} & d'_{15} & \cdots & 0 & 0 & 0 & \cdots \\
d'_{31} & d'_{33} & d'_{35} & \cdots & 0 & 0 & 0 & \cdots \\
d'_{51} & d'_{53} & d'_{55} & \cdots & 0 & 0 & 0 & \cdots \\
\vdots & \vdots & \vdots & & \vdots & \vdots & \vdots & \\
0 & 0 & 0 & \cdots & d'_{00} & d'_{02} & d'_{04} & \cdots \\
0 & 0 & 0 & \cdots & d'_{20} & d'_{22} & d'_{24} & \cdots \\
0 & 0 & 0 & \cdots & d'_{40} & d'_{42} & d'_{44} & \cdots \\
\vdots & \vdots & \vdots & & \vdots & \vdots & \vdots &
\end{vmatrix}
=
\begin{vmatrix}
d'_{11} & d'_{13} & d'_{15} & \cdots \\
d'_{31} & d'_{33} & d'_{35} & \cdots \\
d'_{51} & d'_{53} & d'_{55} & \cdots \\
\vdots & \vdots & \vdots &
\end{vmatrix}
\times
\begin{vmatrix}
d'_{00} & d'_{02} & d'_{04} & \cdots \\
d'_{20} & d'_{22} & d'_{24} & \cdots \\
d'_{40} & d'_{42} & d'_{44} & \cdots \\
\vdots & \vdots & \vdots &
\end{vmatrix}
$$

(30)

Similarly, we find

$$\mathscr{D}_{\frac{3}{2},\frac{3}{2}} =$$

$$\zeta^3 \begin{vmatrix} 0 & a_0 & 0 & a_2 & 0 & \cdots \\ a_0 & d'_{00} & 0 & d'_{02} & 0 & \cdots \\ 0 & 0 & d'_{11} & 0 & d'_{13} & \cdots \\ a_2 & d'_{20} & 0 & d'_{22} & 0 & \cdots \\ 0 & 0 & d'_{31} & 0 & d'_{33} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{vmatrix} = \zeta^3 \begin{vmatrix} d'_{11} & d'_{13} & d'_{15} & \cdots \\ d'_{31} & d'_{33} & d'_{35} & \cdots \\ d'_{51} & d'_{53} & d'_{55} & \cdots \\ \vdots & \vdots & \vdots \end{vmatrix} \times \begin{vmatrix} 0 & a_0 & a_2 & a_4 & \cdots \\ a_0 & d'_{00} & d'_{02} & d'_{04} & \cdots \\ a_2 & d'_{20} & d'_{22} & d'_{24} & \cdots \\ a_4 & d'_{40} & d'_{42} & d'_{44} & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix},$$

$$(31)$$

and, after somewhat more complicated manipulations,

$$\mathscr{D}_{\frac{3}{2},\frac{3}{2},\frac{5}{2},\frac{5}{2}} = \gamma^2 \zeta^8 \begin{vmatrix} 0 & a_2 & a_4 & a_6 & \cdots \\ a_2 & d'_{11} & d'_{13} & d'_{15} & \cdots \\ a_4 & d'_{31} & d'_{33} & d'_{35} & \cdots \\ a_6 & d'_{51} & d'_{53} & d'_{55} & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix} \times \begin{vmatrix} 0 & a_0 & a_2 & a_4 & \cdots \\ a_0 & d'_{00} & d'_{02} & d'_{04} & \cdots \\ a_2 & d'_{20} & d'_{22} & d'_{24} & \cdots \\ a_4 & d'_{40} & d'_{42} & d'_{44} & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix},$$

$$(32)$$

and

$$\mathscr{D}_{\frac{3}{2},\frac{5}{2}} - \zeta \mathscr{D}_{\frac{3}{2},\frac{3}{2}} = \gamma^2 \zeta^4 \begin{vmatrix} 0 & a_0 & \frac{3}{2}a_2 & a_2 & \frac{3}{2}a_4 & a_4 & \cdots \\ \frac{3}{2}a_2 & d'_{00} & d'_{01} & d'_{02} & d'_{03} & d'_{04} & \cdots \\ a_2 & 0 & d'_{11} & 0 & d'_{13} & 0 & \cdots \\ \frac{3}{2}a_4 & d'_{20} & d'_{21} & d'_{22} & d'_{23} & d'_{24} & \cdots \\ a_4 & 0 & d'_{31} & 0 & d'_{33} & 0 & \cdots \\ \frac{3}{2}a_6 & d'_{40} & d'_{41} & d'_{42} & d'_{43} & d'_{44} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{vmatrix},$$

$$(33)$$

only the lowest power of $\gamma^2$ being retained in each case.

3.3 The final results are most conveniently expressed in terms of the approximate interpolation formulae for the electrical and thermal conductivities of an impure metal given by Wilson (2), p. 378. From Eq. 26 we readily obtain

$$d'_{\mu\nu} = \frac{8\,\epsilon^2\zeta^3\Lambda}{3\pi h}\,(\frac{\Theta}{T})^3\left(\frac{a_{\mu+\nu}}{\sigma_r} + \frac{F_{\mu\nu}}{\mathcal{J}_5\sigma_i}\right) \tag{34a}$$

if $\mu+\nu$ is even, and

$$d'_{\mu\nu} = \frac{8\,\epsilon^2\zeta^3\Lambda}{3\pi h}\,(\frac{\Theta}{T})^3\left(\frac{2a_{\mu+\nu+1}}{\sigma_r} + \frac{F_{\mu\nu}}{\mathcal{J}_5\sigma_i}\right) \tag{34b}$$

if $\mu+\nu$ is odd, where $1/\sigma_r = \rho_r = 3\pi h M/(8\epsilon^2\zeta)$ is the residual electrical resistance, and where

$$\frac{1}{\sigma_i} = \rho_i = \frac{3\pi h D}{4\epsilon^2\zeta^3\Lambda}\,(\frac{T}{\Theta})^5\,\mathcal{J}_5 \tag{35}$$

is the Grüneisen-Bloch interpolation formula for the ideal electrical resistance. Alternatively we may write, for $\mu+\nu$ even,

$$d'_{\mu\nu} = \frac{8\pi k^2\zeta^3\Lambda\,\Theta}{9h}\,(\frac{\Theta}{T})^2\left(\frac{a_{\mu+\nu}}{K_r} + \frac{1}{3}\,\pi^2\,\frac{F_{\mu\nu}}{F_{11}\,K_i}\right) \tag{36}$$

($F_{11}$ is obtained from Eq. 27a, and $K_r = \frac{1}{3}\,(\pi k/\epsilon)^2\,\sigma_r T$ is the residual thermal conductivity; note that the present notation differs slightly from Wilson's), and where

$$\frac{1}{K_i} = \frac{27h}{8\pi^3 k^2\zeta^2\Lambda\,\Theta}\,(\frac{T}{\Theta})^2\left(\mathcal{J}_5 + \frac{D}{\zeta}(\frac{T}{\Theta})^2\,(\frac{2\pi^2}{3}\,\mathcal{J}_5 - \frac{1}{3}\,\mathcal{J}_7)\right) \tag{37}$$

is Wilson's interpolation formula for the ideal part of the thermal resistance.*

Combining Eqs. 20, 30, 31 and 34a and removing a common factor from numerator and denominator, we obtain the final expression for the electrical conductivity

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* This formula is introduced here for mathematical convenience; we may note (see Section 5) that, unlike Eq. 35, it cannot be used as an interpolation formula for the ideal resistance in the absence of impurities.

$$\sigma = -\frac{\begin{array}{c|cccc} & 0 & a_0 & a_2 & a_4 \\ \hline a_0 & \left(\dfrac{1}{\sigma_r}+\dfrac{1}{\sigma_i}\right) & \left(\dfrac{a_2}{\sigma_r}+\dfrac{F_{02}}{\}5\sigma_i}\right) & \left(\dfrac{a_4}{\sigma_r}+\dfrac{F_{04}}{\}5\sigma_i}\right)\cdots \\ a_2 & \left(\dfrac{a_2}{\sigma_r}+\dfrac{F_{20}}{\}5\sigma_i}\right) & \left(\dfrac{a_4}{\sigma_r}+\dfrac{F_{22}}{\}5\sigma_i}\right) & \left(\dfrac{a_6}{\sigma_r}+\dfrac{F_{24}}{\}5\sigma_i}\right)\cdots \\ a_4 & \left(\dfrac{a_4}{\sigma_r}+\dfrac{F_{40}}{\}5\sigma_i}\right) & \left(\dfrac{a_6}{\sigma_r}+\dfrac{F_{42}}{\}5\sigma_i}\right) & \left(\dfrac{a_8}{\sigma_r}+\dfrac{F_{44}}{\}5\sigma_i}\right)\cdots \\ \vdots & \vdots & \vdots & \vdots \end{array}}{\begin{array}{cccc} \left(\dfrac{1}{\sigma_r}+\dfrac{1}{\sigma_i}\right) & \left(\dfrac{a_2}{\sigma_r}+\dfrac{F_{02}}{\}5\sigma_i}\right) & \left(\dfrac{a_4}{\sigma_r}+\dfrac{F_{04}}{\}5\sigma_i}\right)\cdots \\ \left(\dfrac{a_2}{\sigma_r}+\dfrac{F_{20}}{\}5\sigma_i}\right) & \left(\dfrac{a_4}{\sigma_r}+\dfrac{F_{22}}{\}5\sigma_i}\right) & \left(\dfrac{a_6}{\sigma_r}+\dfrac{F_{24}}{\}5\sigma_i}\right)\cdots \\ \left(\dfrac{a_4}{\sigma_r}+\dfrac{F_{40}}{\}5\sigma_i}\right) & \left(\dfrac{a_6}{\sigma_r}+\dfrac{F_{42}}{\}5\sigma_i}\right) & \left(\dfrac{a_8}{\sigma_r}+\dfrac{F_{44}}{\}5\sigma_i}\right)\cdots \\ \vdots & \vdots & \vdots \end{array}} \tag{38}$$

(the $a_\mu$'s are given by Eq. 25 and the $F_{\mu\nu}$'s by Eq. 27a).

Similarly, combining Eqs. 21b, 31, 32 and 36, we obtain the thermal conductivity

$$K = -\frac{3}{\pi^2}\frac{\begin{array}{c|cccc} & 0 & a_2 & a_4 & a_6 \\ \hline a_2 & \dfrac{1}{3}\pi^2\left(\dfrac{1}{K_r}+\dfrac{1}{K_i}\right) & \left(\dfrac{a_4}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{13}}{F_{11}K_i}\right) & \left(\dfrac{a_6}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{15}}{F_{11}K_i}\right)\cdots \\ a_4 & \left(\dfrac{a_4}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{31}}{F_{11}K_i}\right) & \left(\dfrac{a_6}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{33}}{F_{11}K_i}\right) & \left(\dfrac{a_8}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{35}}{F_{11}K_i}\right)\cdots \\ a_6 & \left(\dfrac{a_6}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{51}}{F_{11}K_i}\right) & \left(\dfrac{a_8}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{53}}{F_{11}K_i}\right) & \left(\dfrac{a_{10}}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{55}}{F_{11}K_i}\right)\cdots \\ \vdots & \vdots & \vdots & \vdots \end{array}}{\begin{array}{cccc} \dfrac{1}{3}\pi^2\left(\dfrac{1}{K_r}+\dfrac{1}{K_i}\right) & \left(\dfrac{a_4}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{13}}{F_{11}K_i}\right) & \left(\dfrac{a_6}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{15}}{F_{11}K_i}\right)\cdots \\ \left(\dfrac{a_4}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{31}}{F_{11}K_i}\right) & \left(\dfrac{a_6}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{33}}{F_{11}K_i}\right) & \left(\dfrac{a_8}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{35}}{F_{11}K_i}\right)\cdots \\ \left(\dfrac{a_6}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{51}}{F_{11}K_i}\right) & \left(\dfrac{a_8}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{53}}{F_{11}K_i}\right) & \left(\dfrac{a_{10}}{K_r}+\dfrac{1}{3}\pi^2\dfrac{F_{55}}{F_{11}K_i}\right)\cdots \\ \vdots & \vdots & \vdots \end{array}}, \tag{39}$$

and, combining Eqs. 23, 31, 33 and 34, we obtain the thermoelectric power

$$
\mathfrak{S} = \frac{k^2 T}{\zeta}\;
\frac{
\begin{vmatrix}
0 & a_0 & \frac{3}{2}a_2 & a_2 & \frac{3}{2}a_4 & \cdots \\[2ex]
\frac{3}{2}a_2 & \left(\frac{1}{\sigma_r}+\frac{1}{\sigma_i}\right) & \left(\frac{2a_2}{\sigma_r}+\frac{F_{01}}{\sqrt{5}\,\sigma_i}\right) & \left(\frac{a_2}{\sigma_r}+\frac{F_{02}}{\sqrt{5}\,\sigma_i}\right) & \left(\frac{2a_4}{\sigma_r}+\frac{F_{03}}{\sqrt{5}\,\sigma_i}\right) & \cdots \\[2ex]
a_2 & 0 & \left(\frac{a_2}{\sigma_r}+\frac{F_{11}}{\sqrt{5}\,\sigma_i}\right) & 0 & \left(\frac{a_4}{\sigma_r}+\frac{F_{13}}{\sqrt{5}\,\sigma_i}\right) & \cdots \\[2ex]
\frac{3}{2}a_4 & \left(\frac{a_2}{\sigma_r}+\frac{F_{20}}{\sqrt{5}\,\sigma_i}\right) & \left(\frac{2a_4}{\sigma_r}+\frac{F_{21}}{\sqrt{5}\,\sigma_i}\right) & \left(\frac{a_4}{\sigma_r}+\frac{F_{22}}{\sqrt{5}\,\sigma_i}\right) & \left(\frac{2a_6}{\sigma_r}+\frac{F_{23}}{\sqrt{5}\,\sigma_i}\right) & \cdots \\[2ex]
a_4 & 0 & \left(\frac{a_4}{\sigma_r}+\frac{F_{31}}{\sqrt{5}\,\sigma_i}\right) & 0 & \left(\frac{a_6}{\sigma_r}+\frac{F_{33}}{\sqrt{5}\,\sigma_i}\right) & \cdots \\[1ex]
\vdots & \vdots & \vdots & \vdots & \vdots &
\end{vmatrix}
}{
\begin{vmatrix}
0 & a_0 & 0 & a_2 & 0 & \cdots \\[2ex]
a_0 & \left(\frac{1}{\sigma_r}+\frac{1}{\sigma_i}\right) & 0 & \left(\frac{a_2}{\sigma_r}+\frac{F_{02}}{\sqrt{5}\,\sigma_i}\right) & 0 & \cdots \\[2ex]
0 & 0 & \left(\frac{a_2}{\sigma_r}+\frac{F_{11}}{\sqrt{5}\,\sigma_i}\right) & 0 & \left(\frac{a_4}{\sigma_r}+\frac{F_{13}}{\sqrt{5}\,\sigma_i}\right) & \cdots \\[2ex]
a_2 & \left(\frac{a_2}{\sigma_r}+\frac{F_{20}}{\sqrt{5}\,\sigma_i}\right) & 0 & \left(\frac{a_4}{\sigma_r}+\frac{F_{22}}{\sqrt{5}\,\sigma_i}\right) & 0 & \cdots \\[2ex]
0 & 0 & \left(\frac{a_4}{\sigma_r}+\frac{F_{31}}{\sqrt{5}\,\sigma_i}\right) & 0 & \left(\frac{a_6}{\sigma_r}+\frac{F_{33}}{\sqrt{5}\,\sigma_i}\right) & \cdots \\[1ex]
\vdots & \vdots & \vdots & \vdots & \vdots &
\end{vmatrix}
}
\tag{40}
$$

3.31. An alternative form for $\sigma$ and $K$, which is particularly convenient for numerical evaluation, may be obtained as follows. Let $S^{(2n)}$ be the determinant obtained by breaking off the denominator of Eq. 38 at the $(n+1)$th row and column (the element in the bottom right-hand corner being $a_{4n}/\sigma_r + F_{2n,\,2n}/\sqrt{5}\,\sigma_i$). Also let $S^{(2n)}_{a,a}$ be the determinant of $n+2$ rows and columns obtained by bordering $S^{(2n)}$ with $0$, $a_0$, $a_2$, $\ldots$, $a_{2n}$, and let $S^{(2n)}_a$ be the determinant obtained from $S^{(2n)}$ on replacing the last column by $a_0$, $a_2$, $\ldots$, $a_{2n}$. Then Sylvester's theorem gives

$$\begin{vmatrix} S^{(2n)} & S_a^{(2n)} \\ S_a^{(2n)} & S_{a,a}^{(2n-2)} \end{vmatrix} = S^{(2n-2)} \; S_{a,a}^{(2n)} \qquad ,$$

or, rearranging,

$$-\frac{S_{a,a}^{(2n)}}{S^{(2n)}} + \frac{S_{a,a}^{(2n-2)}}{S^{(2n-2)}} = \frac{\left(S_a^{(2n)}\right)^2}{S^{(2n-2)} \; S^{(2n)}} \tag{41}$$

Also

$$-\frac{S_{a,a}^{(0)}}{S^{(0)}} = \sigma^{(0)} \tag{42}$$

where

$$\frac{1}{\sigma^{(0)}} = \frac{1}{\sigma_r} + \frac{1}{\sigma_i} \tag{43}$$

is the expression for the electrical resistance obtained by assuming the general validity of Matthiessen's rule; $\sigma_i$ is given by Eq. 35.

In Eq. 41 put $n = 1, 2, 3, \ldots$, and add each of the resulting expressions to Eq. 42. This gives

$$\sigma = \sigma^{(0)} + \sum_{n=1}^{\infty} \frac{\left(S_a^{(2n)}\right)^2}{S^{(2n-2)} \; S^{(2n)}} \qquad . \tag{44}$$

Similarly, for the thermal conductivity,

$$K = K^{(0)} + \frac{3}{\pi^2} \sum_{n=1}^{\infty} \frac{\left(K_a^{(2n)}\right)^2}{K^{(2n-2)} \; K^{(2n)}} \tag{45}$$

where

$$\frac{1}{K^{(0)}} = \frac{1}{K_r} + \frac{1}{K_i} \qquad . \tag{46}$$

Here $K_i$ is given by Eq. 37, and $K^{(2n)}$ is the determinant obtained by breaking off the denominator of Eq. 39 at the $(n + 1)$th row and column, while $K_a^{(2n)}$ is obtained from $K^{(2n)}$ on replacing the last column by $a_2, a_4, \ldots, a_{2n+2}$.

In Eqs. 44 and 45 the correction terms to Wilson's interpolation formulae are exhibited explicitly. It may be shown that the determinants $S^{(2n)}$ and $K^{(2n)}$ are positive (this is essentially due to the fact that the $d_{\mu\nu}$ defined by Eq. 11 are the coefficients of a positive definite quadratic form), and the series of Eqs. 44 and 45 are therefore monotonically increasing sequences.

# 4.  The Electrical Conductivity

4.1  Equations 38 and 44 for the electrical conductivity are valid for all temperatures (provided that it is permissible to treat the electron gas as completely degenerate), and for ideally pure as well as for impure metals.  Previous solutions have all been confined to the regions of temperatures high and low compared with the Debye temperature, for which the complicated general expressions reduce to comparatively simple ones.  At high temperatures, Wilson, Section 2, (2) has shown that the conductivity is given by Eq. 43, correct to terms of order $(\Theta/T)^2$ and $M\Theta/T$.*  Further, Bloch (4) has shown that the ideal part (Eq. 35) of Eq. 43 represents the leading term in the expression for the conductivity of an ideal metal at very low temperatures, and Wilson, Section 3, (2) has shown that Eq. 43 also gives the conductivity of an impure metal at low temperatures, correct to terms of order $\sigma_r/\sigma_i$.  (These special results can, of course, be shown to follow directly from Eqs. 38 and 44; the proofs will not be given here.)  At sufficiently high and low temperatures, therefore, $\sigma = \sigma^{(0)}$, Matthiessen's rule is valid, and the correction terms represented by the infinite sum in Eq. 44 are negligible.  At intermediate temperatures (such that T is comparable with $\Theta$, or $\sigma_r$ with $\sigma_i$) the correction terms become appreciable and increase the electrical conductivity above the value given by Eq. 43.  For an ideal metal, each correction term is proportional to $(\Theta/T)^5$ at high temperatures and to $(\Theta/T)^3$ at low temperatures ($\sigma^{(0)}$ is proportional to $\Theta/T$ and $(\Theta/T)^5$ respectively); while, for an impure metal, each correction term is proportional to $(T/\Theta)^{10}/M^3$ at low temperatures, where $\sigma^{(0)}$ is proportional to $1/M$.  It is, in general, no longer possible to separate the resistivity into a part depending upon $\rho_r$ only and a part depending upon $\rho_i$ only; no simple formula can be given for the deviations from Matthiessen's rule, but they are evaluated numerically below for some typical cases.

4.2  The magnitude of the correction terms has to be estimated by numerical methods.  For this purpose it is convenient to rewrite Eq. 44 in terms of the notation introduced by Makinson (13).  The ideal electrical resistance at high temperatures, such that $(\Theta/T)^2$ can be neglected compared with unity, is (1), p. 208,

$$\frac{1}{\sigma_i} = \frac{AT}{\Theta} \quad , \tag{47}$$

where

$$A = \frac{3\pi h\, D}{(16\, \epsilon^2\, \zeta^3\, \Lambda\,)} \quad . \tag{48}$$

With this notation, we easily obtain from Eq. 44

---

* In discussing the high temperature limit Wilson actually confined himself to the case of an ideally pure metal (M = 0), but his method is easily extended to include the impurity term.

$$4A\sigma = \frac{4A}{\rho} = \frac{1}{\left(\frac{T}{\Theta}\right)^5 \mathcal{J}_5 + \frac{\rho_r}{4A}} + \sum_{n=1}^{\infty} \frac{\left(\xi_a^{(2n)}\right)^2}{\xi^{(2n-2)}\,\xi^{(2n)}} \tag{49}$$

where

$$\xi^{(2n)} = \begin{vmatrix} \left(\left(\frac{T}{\Theta}\right)^5 F_{00} + \frac{\rho_r}{4A}\right) & \left(\left(\frac{T}{\Theta}\right)^5 F_{02} + a_2\frac{\rho_r}{4A}\right) & \cdots & \left(\left(\frac{T}{\Theta}\right)^5 F_{0,2n} + a_{2n}\frac{\rho_r}{4A}\right) \\[2mm] \left(\left(\frac{T}{\Theta}\right)^5 F_{20} + a_2\frac{\rho_r}{4A}\right) & \left(\left(\frac{T}{\Theta}\right)^5 F_{22} + a_4\frac{\rho_r}{4A}\right) & \cdots & \left(\left(\frac{T}{\Theta}\right)^5 F_{2,2n} + a_{2n+2}\frac{\rho_r}{4A}\right) \\[2mm] \cdots & \cdots & \cdots & \cdots \\[2mm] \left(\left(\frac{T}{\Theta}\right)^5 F_{2n,0} + a_{2n}\frac{\rho_r}{4A}\right) & \left(\left(\frac{T}{\Theta}\right)^5 F_{2n,2} + a_{2n+2}\frac{\rho_r}{4A}\right) & \cdots & \left(\left(\frac{T}{\Theta}\right)^5 F_{2n,2n} + a_{4n}\frac{\rho_r}{4A}\right) \end{vmatrix} \tag{50}$$

and where $\xi_a^{(2n)}$ is obtained from $\xi^{(2n)}$ on replacing the last column by $a_0, a_2, \ldots, a_{2n}$. The $a_\mu$'s are given by Eq. 25 and the $F_{\mu\nu}$'s by Eqs. 27a and 28a. The parameter $\rho_r/4A$ is a measure of the amount of impurity present, and it is seen that the quantity $4A\sigma$ depends upon $T/\Theta$, $D/\zeta$ and $\rho_r/4A$ only. For monovalent metals, which alone are considered in the present paper, we have $D/\zeta = 2^{-1/3}$ (reference 13).

4.21.   Equation 49 may be used to compute successive approximations to $\sigma$ by retaining successive terms of the infinite series; the value obtained by retaining N terms of the series will be denoted by $\sigma^{(2N)} = 1/\rho^{(2N)}$. In the approximation of zero order, Matthiessen's rule is valid and the resistance is given by Eq. 43.* If $\rho_i^{(2N)}$ denotes the resistance of the ideal metal in the Nth approximation, the deviation $\Delta^{(2N)}$ from Matthiessen's rule is

$$\Delta^{(2N)} = \rho^{(2N)} - \left(\rho_i^{(2N)} + \rho_r\right) ; \tag{51}$$

in general it will depend both upon the temperature and upon the amount of impurity present.

The first three approximations have been evaluated numerically. Table 1 gives values of $\rho_i^{(2N)}/4A$ for the pure metal, and of $\rho^{(2N)}/4A$ and $\Delta^{(2N)}/4A$ for two values of the impurity parameter $\rho_r/4A$. Explicit expressions for the $a_\mu$'s and the $F_{\mu\nu}$'s required in these calculations, and a table of values of the integrals $\mathcal{J}_n$ defined by Eq. 29, are given in Appendix 2.

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* Kohler (8) attempted to evaluate the first correction term, and claimed to show that it is zero for a completely degenerate electron gas. This (incorrect) result is due to an error in Kohler's evaluation of the quantity $d_{22}$ (Eq. 18 of Kohler's paper).

Table 2.   The Thermal Conductivity of Monovalent Metals

| $\frac{T}{\Theta}$ | $\rho_r/4A = 0$ | | | $\rho_r/4A = 0.01$ | | | $\rho_r/4A = 0.03$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\frac{12A}{\pi^2 L_0 \Theta} K_i^{(0)}$ | $\frac{12A}{\pi^2 L_0 \Theta} K_i^{(2)}$ | $\frac{12A}{\pi^2 L_0 \Theta} K_i^{(4)}$ | $\frac{12A}{\pi^2 L_0 \Theta} K^{(0)}$ | $\frac{12A}{\pi^2 L_0 \Theta} K^{(2)}$ | $\frac{12A}{\pi^2 L_0 \Theta} K^{(4)}$ | $\frac{12A}{\pi^2 L_0 \Theta} K^{(0)}$ | $\frac{12A}{\pi^2 L_0 \Theta} K^{(2)}$ | $\frac{12A}{\pi^2 L_0 \Theta} K^{(4)}$ |
| $\ll 1.0$ | $0.012757 \left(\frac{\Theta}{T}\right)^2$ | $0.015705 \left(\frac{\Theta}{T}\right)^2$ | $0.016957 \left(\frac{\Theta}{T}\right)^2$ | $30.396 \frac{T}{\Theta}$ | $30.396 \frac{T}{\Theta}$ | $30.396 \frac{T}{\Theta}$ | $10.132 \frac{T}{\Theta}$ | $10.132 \frac{T}{\Theta}$ | $10.132 \frac{T}{\Theta}$ |
| 0.05 | 5.175 | 6.404 | 6.835 | 1.1748 | 1.2086 | 1.2117 | 0.4614 | 0.4644 | 0.4644 |
| 0.0769 | 2.246 | 2.807 | 3.036 | 1.1457 | 1.2548 | 1.2799 | 0.5786 | 0.5990 | 0.6013 |
| 0.1 | 1.4180 | 1.7552 | 1.8872 | 0.9669 | 1.0972 | 1.1348 | 0.5909 | 0.6294 | 0.6370 |
| 0.125 | 1.0347 | 1.2362 | 1.3132 | 0.8132 | 0.9229 | 0.9585 | 0.5695 | 0.6140 | 0.6257 |
| 0.167 | 0.8005 | 0.8912 | 0.9265 | 0.6913 | 0.7534 | 0.7762 | 0.5431 | 0.5763 | 0.5874 |
| 0.2 | 0.7446 | 0.7955 | 0.8162 | 0.6634 | 0.7009 | 0.7158 | 0.5445 | 0.5669 | 0.5753 |
| 0.25 | 0.7372 | 0.7604 | 0.7708 | 0.6720 | 0.6901 | 0.6982 | 0.5710 | 0.5827 | 0.5878 |
| 0.333 | 0.7909 | 0.7983 | 0.8023 | 0.7336 | 0.7397 | 0.7429 | 0.6408 | 0.6450 | 0.6472 |
| 0.5 | 0.9214 | 0.9225 | | 0.8687 | 0.8697 | | 0.7796 | 0.7803 | |
| 0.667 | 1.0133 | 1.0136 | | 0.9651 | | | 0.8811 | | |
| 0.833 | 1.0718 | 1.0718 | | 1.0282 | | | 0.9510 | | |
| 1.0 | 1.1094 | | | 1.0703 | | | 0.9999 | | |
| 1.25 | 1.1440 | | | 1.1106 | | | 1.0492 | | |
| $\gg 1.0$ | 1.2158 | | | 1.2158 | | | 1.2158 | | |

An idea of the magnitude of the correction terms, and of the rapidity with which the series (Eq. 49) converges, can be obtained by an inspection of Table 1. It is seen that the deviations from the zero order values of the resistance are negative (as noted in Section 3.31) are largest in relative value when $T/\Theta$ is of the order of 0.2 but decrease rapidly for higher and lower temperatures, and are most important for very pure specimens; the maximum value of the correction to the ideal resistance amounts to about 10 percent. The deviations $\Delta$ from Matthiessen's rule are positive, increase with the amount of impurity present and are largest in the region where the residual and ideal resistances are of the same order of magnitude. They are very small in relative magnitude, and for the range of values shown in Table 1, $\Delta$ is always less than one percent of the total resistance.

The measured resistance values are usually separated into an ideal and a residual part by assuming the validity of Matthiessen's rule, and the temperature variation of the ideal resistance is assumed to be given by the Grüneisen-Bloch formula, Eq. 35 (15). It is now seen that both these assumptions are incorrect, and in particular that Eq. 35 leads to values of the ideal resistance which are considerably too high at intermediate temperatures. Also Matthiessen's rule is strictly valid at high temperatures only, and at very low temperatures such that the residual resistance is large compared with the ideal resistance; but the rule always represents a good approximation, and the deviations from it need only be taken into account if high accuracy is required. The experimental data (compare the tables given by Grüneisen (15)) are not sufficiently accurate to be compared in detail with the theoretical results, but they are in general agreement with the predictions outlined above. The observed values of the ideal resistance at intermediate temperatures are in most cases smaller than the values calculated from Eq. 35, and the magnitude of the deviations is of the order predicted by the present theory. The observed deviations from Matthiessen's rule are in many cases too large to be explained by the present theory, although they agree qualitatively with its predictions. To account for their order of magnitude it is, in general, necessary to employ models more complicated than the one-band, free-electron model discussed here ((16), p. 450; (17)).

4.22. Kohler (17) has proved generally that the deviations $\Delta$ from Matthiessen's rule are always positive (or zero), and we have seen above that the behavior of the free-electron model is in agreement with this result. A calculation of Dube (3) is in apparent contradiction with Kohler's theorem. Dube attempted to obtain an estimate of $\Delta$ for the free-electron model by using Wilson's method of successive approximations (2) to calculate the resistance of an impure metal at low temperatures, correct to terms of order $(\rho_i/\rho_r)^2$. Dube's result is (using his notation)

$$\rho = \rho_r + \rho_i - \left(g(T) - 1\right) \rho_i^2/\rho_r \quad , \tag{52}$$

where $\rho_i$ is given by Eq. 35, and where $g(T) - 1$ is a complicated function of T which

tends to a constant positive value at very low temperatures. (An expression corresponding to Eq. 52 may easily be obtained from Eq. 44 by expanding in powers of $\sigma_r/\sigma_i$, but owing to the restricted validity of such an expansion this question will not be considered further here.)

Dube used his result to conclude that the deviation from Matthiessen's rule is

$$\Delta = \rho - (\rho_r + \rho_i) = -\left(g(T) - 1\right) \rho_i^2/\rho_r \quad , \tag{53}$$

which is negative. This argument is fallacious. The reason is that, in the approximation considered by Dube, it is not correct to identify Eq. 35 with the ideal resistance. In fact, Eq. 35 represents merely the leading term in an expansion for the true ideal resistance $\rho_i'$ at low temperatures, of the form

$$\rho_i' = \rho_i \left[1 - C(\frac{T}{\Theta})^2 + O\left((\frac{T}{\Theta})^4\right)\right] \quad , \tag{54}$$

where C is a positive constant. The leading term in the expression for $\Delta$ at low temperatures is therefore given by

$$\Delta = \rho - (\rho_r + \rho_i') = C\rho_i \, (\frac{T}{\Theta})^2 \quad , \tag{55}$$

and not by Dube's expression, Eq. 53; the latter is of higher order in $T/\Theta$. $\Delta$ is therefore positive, in agreement with the general result, and it is clear that Dube's calculation by itself cannot be used to draw any conclusions whatsoever concerning the nature of the deviations from Matthiessen's rule.

## 5. Second Order Phenomena

5.1. The thermal conductivity. The general expressions of Eqs. 39 and 45 for the thermal conductivity are analogous to those for the electrical conductivity, and may be discussed in similar fashion. The zero order approximation $K^{(0)}$ given by Eqs. 37 and 46 was first obtained by Wilson (2) and has been discussed in detail by Makinson (13). We must now consider how this expression has to be modified to take into account the effect of the higher order correction terms. Wilson has shown that $K^{(0)}$ is the correct expression for the thermal conductivity at high temperatures, including terms of order $(\Theta/T)^2$ and $M\Theta/T$, and that it holds also for an impure metal at low temperatures, correct to terms of order $K_r/K_i$. There is one important difference compared with the case of the electrical conductivity. Bloch's method (4), which is used to show that the ideal electrical resistance at low temperatures is given correctly by Eq. 35, cannot be applied to the second order effects such as the thermal conductivity, and in fact the ideal thermal conductivity at low temperatures is not given by Eq. 37, contrary to statements made by Kroll (6) and Wilson (1), p. 219. This matter is discussed further below, but the difference in status between Eqs. 35 and 37 should be carefully noted.

5.11. To evaluate the thermal conductivity numerically, we use the notation of Section 4.2 to write Eq. 45 in a form which corresponds to Eq. 49. This is

$$\frac{12A}{\pi^2 L_0 \Theta} K = \frac{\frac{T}{\Theta}}{(\frac{T}{\Theta})^5 F_{11} + a_2 \frac{\rho_r}{4A}} + \frac{9}{\pi^4} \frac{T}{\Theta} \sum_{n=1}^{\infty} \frac{\left(\chi_a^{(2n)}\right)^2}{\chi^{(2n-2)} \chi^{(2n)}} , \qquad (56)$$

where A is given by Eq. 48, $L_0 = \frac{1}{3}(\pi k/\epsilon)^2$ is the 'normal' (high temperature) value of the Wiedemann-Franz ratio, and where

$$\chi^{(2n)} =$$

$$\begin{vmatrix} \left((\frac{T}{\Theta})^5 F_{11} + a_2 \frac{\rho_r}{4A}\right) & \left((\frac{T}{\Theta})^5 F_{13} + a_4 \frac{\rho_r}{4A}\right) & \cdots & \left((\frac{T}{\Theta})^5 F_{1,2n+1} + a_{2n+2} \frac{\rho_r}{4A}\right) \\ \left((\frac{T}{\Theta})^5 F_{31} + a_4 \frac{\rho_r}{4A}\right) & \left((\frac{T}{\Theta})^5 F_{33} + a_6 \frac{\rho_r}{4A}\right) & \cdots & \left((\frac{T}{\Theta})^5 F_{3,2n+1} + a_{2n+4} \frac{\rho_r}{4A}\right) \\ \cdots & \cdots & \cdots & \cdots \\ \left((\frac{T}{\Theta})^5 F_{2n+1,1} + a_{2n+2} \frac{\rho_r}{4A}\right) & \left((\frac{T}{\Theta})^5 F_{2n+1,3} + a_{2n+4} \frac{\rho_r}{4A}\right) & \cdots & \left((\frac{T}{\Theta})^5 F_{2n+1,2n+1} + a_{4n+2} \frac{\rho_r}{4A}\right) \end{vmatrix} ,$$

$$(57)$$

while $\chi_a^{(2n)}$ is obtained from $\chi^{(2n)}$ on replacing the last column by $a_2, a_4, \ldots, a_{2n+2}$. The value of the thermal conductivity obtained by retaining N terms of the infinite series in Eq. 56 will be denoted by $K^{(2n)}$. (The first two terms of the series for the case of an ideally pure metal have been obtained and discussed by Kroll (9) and by Umeda and Yamamoto (10).) The $F_{\mu\nu}$'s required for evaluating the first three approximations are given explicitly in Appendix 2; the results of the calculations for a monovalent metal, both in the absence of impurities and for two values of the impurity parameter $\rho_r/4A$, are shown in Table 2 and are displayed graphically in Figs. 1, 2 and 3.

As a particular result it should be noted that, for an ideal metal at low temperatures, each term of the series of Eq. 56 is proportional to $(\Theta/T)^2$; the ideal thermal conductivity is therefore proportional to $T^{-2}$, as stated by Makinson, but the proportionality constant cannot be given in closed form. (It may be obtained from Eq. 39 as the ratio of two infinite determinants.) In the presence of impurities, however, the zero order approximation is exact at sufficiently low temperatures (as stated above), being proportional to $(T/\Theta)/(\rho_r/4A)$, whereas each correction term is proportional to $(T/\Theta)^7/(\rho_r/4A)^3$. At high temperatures $K^{(0)}$ is independent of T, and each correction term (for a pure metal) is proportional to $(\Theta/T)^4$.

The zero order curves in Figs. 1 to 3 correspond to Makinson's approximation (cf. Fig. 1 of Makinson's paper). The present theory shows that Makinson's formula

Table 1. The Electrical Resistance of Monovalent Metals

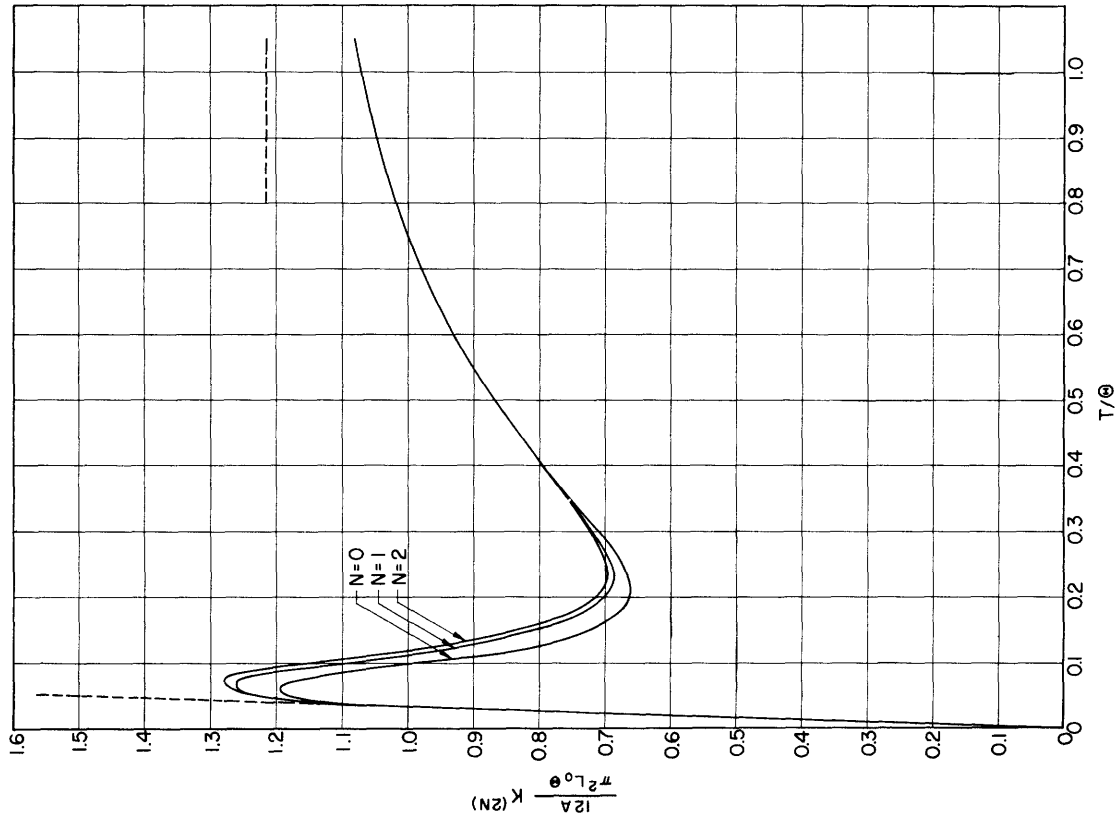| $\dfrac{T}{\Theta}$ | $100\,\dfrac{\rho_i^{(0)}}{4A}$ | $100\,\dfrac{\rho_i^{(2)}}{4A}$ | $100\,\dfrac{\rho_i^{(4)}}{4A}$ | $100\,\dfrac{\rho^{(0)}}{4A}$ | $100\,\dfrac{\rho^{(2)}}{4A}$ | $100\,\dfrac{\rho^{(4)}}{4A}$ | $100\,\dfrac{\Delta^{(2)}}{4A}$ | $100\,\dfrac{\Delta^{(4)}}{4A}$ | $100\,\dfrac{\rho^{(0)}}{4A}$ | $100\,\dfrac{\rho^{(2)}}{4A}$ | $100\,\dfrac{\rho^{(4)}}{4A}$ | $100\,\dfrac{\Delta^{(2)}}{4A}$ | $100\,\dfrac{\Delta^{(4)}}{4A}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $100\,\rho_r/4A = 0$ | | | $100\,\rho_r/4A = 1$ | | | | | $100\,\rho_r/4A = 3$ | | | | |
| 0.01 | $1.2443 \times 10^{-6}$ | $1.2429 \times 10^{-6}$ | $1.2429 \times 10^{-6}$ | | | | | | | | | | |
| 0.025 | $1.2152 \times 10^{-4}$ | $1.2068 \times 10^{-4}$ | $1.2065 \times 10^{-4}$ | | | | | | | | | | |
| 0.05 | $3.8882 \times 10^{-3}$ | $3.7821 \times 10^{-3}$ | $3.7786 \times 10^{-3}$ | 1.00390 | 1.00384 | 1.00384 | 0.00006 | 0.00006 | 3.0039 | 3.0039 | — | 0.0001 | — |
| 0.0769 | 0.033166 | 0.031171 | 0.031069 | 1.03316 | 1.03167 | 1.03167 | 0.0005 | 0.0006 | 3.0332 | 3.0322 | 3.0322 | 0.0010 | 0.0011 |
| 0.1 | 0.11638 | 0.10674 | 0.10601 | 1.1164 | 1.1083 | 1.1080 | 0.0016 | 0.0020 | 3.1164 | 3.1102 | 3.1102 | 0.0035 | 0.0042 |
| 0.125 | 0.30968 | 0.28090 | 0.27807 | 1.3097 | 1.2841 | 1.2822 | 0.0032 | 0.0041 | 3.3097 | 3.2886 | 3.2879 | 0.0077 | 0.0098 |
| 0.167 | 0.91141 | 0.83202 | 0.82217 | 1.9114 | 1.8382 | 1.8301 | 0.0062 | 0.0079 | 3.9114 | 3.8481 | 3.8423 | 0.0161 | 0.0201 |
| 0.2 | 1.6084 | 1.4881 | 1.4721 | 2.6084 | 2.4964 | 2.4821 | 0.0083 | 0.0100 | 4.6085 | 4.5098 | 4.4984 | 0.0217 | 0.0263 |
| 0.25 | 2.8797 | 2.7192 | 2.6941 | 3.8797 | 3.7292 | 3.7060 | 0.0100 | 0.0119 | 5.8796 | 5.7458 | 5.7258 | 0.0266 | 0.0317 |
| 0.333 | 5.2554 | 5.0847 | 5.0536 | 6.2555 | 6.0944 | 6.0651 | 0.0097 | 0.0115 | 8.2556 | 8.1110 | 8.0846 | 0.0263 | 0.0310 |
| 0.5 | 10.0915 | 9.9746 | 9.9487 | 11.0915 | 10.9805 | 10.9557 | 0.0059 | 0.0070 | 13.0916 | 12.9907 | 12.9679 | 0.0161 | 0.0192 |
| 0.667 | 14.747 | 14.677 | 14.660 | 15.748 | 15.680 | 15.663 | 0.003 | 0.003 | 17.747 | 17.686 | 17.670 | 0.0091 | 0.010 |
| 0.833 | 19.253 | 19.210 | 19.198 | 20.253 | 20.211 | — | 0.001 | — | 22.253 | 22.214 | — | 0.004 | — |
| 1.0 | 23.662 | 23.634 | 23.626 | 24.662 | 24.635 | — | 0.001 | — | 26.662 | 26.637 | — | 0.003 | — |
| 1.25 | 30.165 | 30.150 | 30.145 | 31.165 | 31.150 | — | 0.000 | — | 33.165 | 33.151 | — | 0.001 | — |

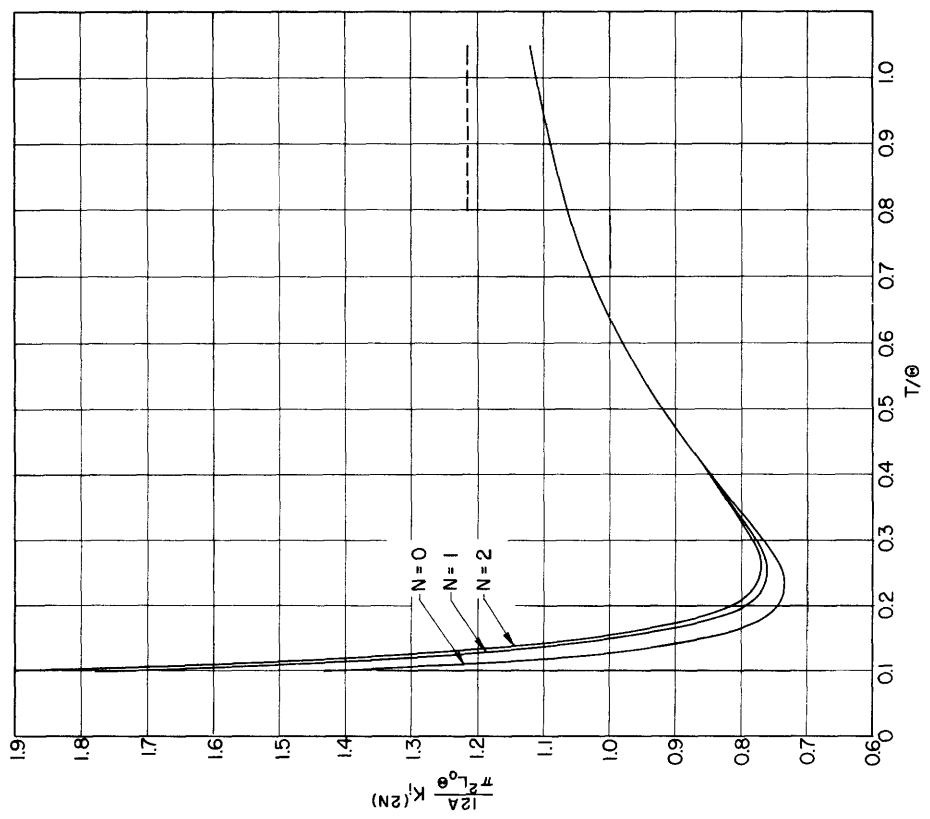Fig. 2 The thermal conductivity of monovalent metals. $\rho_r/4A = 0.01$.



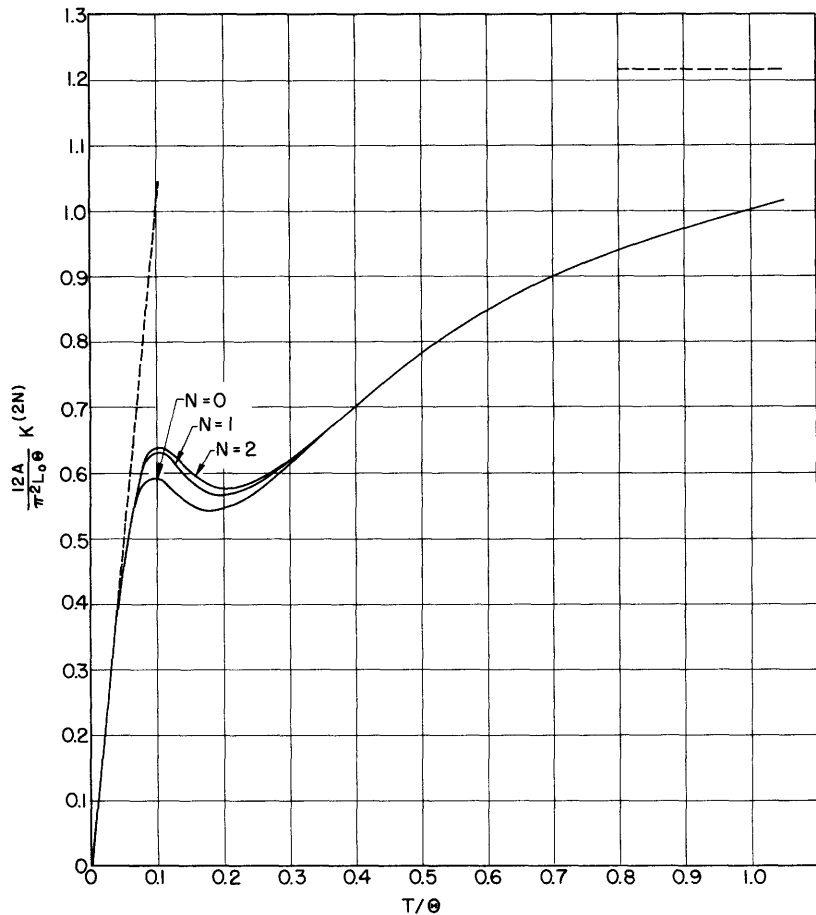Fig. 1. The thermal conductivity of monovalent metals. $\rho_r/4A = 0$.

Fig. 3

The thermal conductivity of monovalent metals. $\rho_r/4A = 0.03$.

for the thermal conductivity is qualitatively correct, and in particular it confirms the existence of a minimum in $K$ at intermediate temperatures, provided that the amount of impurity is not too high.* The numerical values of the thermal conductivity are increased at intermediate temperatures in all cases, and are increased particularly at low temperatures in the case of an ideally pure metal. The position of the minimum in $K$ is shifted towards slightly higher temperatures, and the same is true for the low temperature maximum in $K$ which occurs for impure metals. The correction terms are, in general, larger than in the case of the electrical conductivity; the first correction to the ideal thermal conductivity alone amounts to about 25 percent at low temperatures. This means that the Lorenz number $L = K/\sigma T$ is increased above Makinson's values; numerical estimates of $L$ may be obtained by combining corresponding values of $\sigma$ and $K$ given

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* It may be objected that inclusion of the higher approximations might invalidate this result. This is not so, since the thermal conductivity at high temperatures must decrease at first as the temperature is lowered (2), p. 376.

in Tables 1 and 2.

The experimental results on the thermal conductivity have been discussed by Makinson; they are not sufficiently accurate to justify renewed discussion in the light of the present theory. There is fair agreement between theory and experiment, both qualitatively and in orders of magnitude, but the minimum in $K$ predicted by the theory does not seem to have been observed.

5.2. The thermoelectric power. The general expression, Eq. 40, for the thermoelectric power is more complicated in character than the corresponding expressions for the electrical and thermal conductivities, and will not be discussed in the same detail. It is known that, at high temperatures,

$$S = \pi^2 k^2 T / \zeta \tag{58}$$

and that, at very low temperatures,

$$S = \pi^2 k^2 T / 3\zeta \quad . \tag{59}$$

This latter result, in particular, is valid both for an ideal metal and in the presence of impurities (5); pp. 177, 220, (1). The correction terms of order $(\Theta/T)^2$ at high temperatures, and of order $\sigma_r/\sigma_i$ for an impure metal at low temperatures, have been obtained by Wilson (2). These results may be shown to follow as special cases from Eq. 40, which provides the connection formula for the transition from Eq. 59 at low temperatures to Eq. 58 at high temperatures, and which replaces the simple approximate interpolation formulae given by Kohler (8) and Sondheimer (18). Kohler's formula, in particular, is obtained if the infinite determinants in Eq. 40 are broken off at the third row and column, and higher approximations to $S$ may be obtained by retaining additional rows and columns. It does not seem possible to make any general statements regarding the effect on $S$ of retaining the higher terms. There is therefore no point in discussing them in detail, particularly in view of the well known inadequacy of the free-electron model to serve as a basis for discussing the observed thermoelectric effects in real metals.

Appendix 1.  Evaluation of $a_\mu^{(n)}$ and $d_{\mu\nu}$

1.1.  Consider first

$$a_\mu^{(n)} = \int_{-\infty}^{\infty} E^n \eta^\mu \frac{\partial f_o}{\partial \eta} \, d\eta \tag{A-1}$$

where $\eta = (E - \zeta)/kT$.  Put $\gamma = kT/\zeta$, and suppose that $E^n$ can be expanded in the series

$$E^n = \zeta^n (1 + \gamma\eta)^n = \zeta^n + \zeta^n \sum_{r=1}^{\infty} \frac{n(n-1)(n-2)\ldots(n-r+1)}{r!} (\gamma\eta)^r \tag{A-2}$$

so that (assuming that the series can be integrated term by term)

$$a_\mu^{(n)} = \zeta^n \int_{-\infty}^{\infty} \eta^\mu \frac{\partial f_o}{\partial \eta} \, d\eta + \zeta^n \sum_{r=1}^{\infty} \frac{n(n-1)(n-2)\ldots(n-r+1)}{r!} \gamma^r \int_{-\infty}^{\infty} \eta^{r+\mu} \frac{\partial f_o}{\partial \eta} \, d\eta \ . \tag{A-3}$$

Now according to Wilson (1), Appendix 1.3,

$$\int_{-\infty}^{\infty} \eta^r \frac{\partial f_o}{\partial \eta} \, d\eta = - \int_{-\infty}^{\infty} \frac{\eta^r e^{-\eta}}{(1 + e^{-\eta})^2} \, d\eta = - a_r \quad (r \text{ even}),$$
$$= 0 \quad (r \text{ odd}) \ , \tag{A-4}$$

where

$$a_o = 1 \ ,$$

$$a_{2s} = 2(2s)! \sum_{\ell=1}^{\infty} \frac{(-1)^{\ell+1}}{\ell^{2s}} \quad (s \geqslant 1) \ . \tag{A-5}$$

Combining Eqs. A-3 and A-4, we obtain Eqs. 24a and 24b of the main text.

1.2.  We have, next, combining Eqs. 3 and 11 of the main text and putting $E = \zeta(1 + \gamma\eta)$,

$$d_{\mu\nu} = - \zeta \int_0^{\Theta/T} \frac{z^2 dz}{e^z - 1} I_{\mu\nu}(z) \ , \tag{A-6}$$

where

$$I_{\mu\nu}(z) = \int_{-\infty}^{\infty} \eta^\mu \left[ \left( (1 + \gamma\eta)\eta^\nu - (\eta + z)^\nu \left(1 + \gamma\eta + \frac{1}{2}\gamma z - \frac{D}{\zeta} \left(\frac{T}{\Theta}\right)^2 z^2\right) \right) \frac{e^\eta + 1}{e^\eta + e^{-z}} \right.$$

$$\left. + \left( (1 + \gamma\eta)\eta^\nu - (\eta - z)^\nu \left(1 + \gamma\eta - \frac{1}{2}\gamma z - \frac{D}{\zeta} \left(\frac{T}{\Theta}\right)^2 z^2\right) \right) \frac{e^\eta + 1}{e^{\eta-z} + 1} \right] \frac{\partial f_o}{\partial \eta} \, d\eta \ . \tag{A-7}$$

(The term corresponding to the presence of impurities has been omitted.)

We shall consider in detail only the case where $\mu$ and $\nu$ are both odd.  The other cases are dealt with similarly.  In Eq. A-7, expand $(\eta \pm z)^\nu$ in powers of $\eta$, and put

$$J_s^{\pm}(z) = \int_{-\infty}^{\infty} \eta^s \left( \frac{e^{\eta} + 1}{e^{\eta} + e^{-z}} \pm \frac{e^{\eta} + 1}{e^{\eta - z} + 1} \right) \frac{\partial f_o}{\partial \eta} \, d\eta \quad . \tag{A-8}$$

This gives, after some rearrangement,

$$I_{\mu\nu} = z^{\nu} \left( \frac{D}{\zeta} \left( \frac{T}{\Theta} \right)^2 z^2 - 1 \right) J_{\mu}^{-} - \frac{1}{2} \gamma z^{\nu+1} J_{\mu}^{+} + \frac{D}{\zeta} \left( \frac{T}{\Theta} \right)^2 z^2 J_{\mu+\nu}^{+} - \left( \nu + \frac{1}{2} \right) \gamma z \, J_{\mu+\nu}^{-}$$

$$+ \sum_{r=2,4,6\ldots}^{\nu-1} \left[ \binom{\nu}{r} \left\{ \frac{D}{\zeta} \left( \frac{T}{\Theta} \right)^2 z^2 - 1 \right\} J_{\mu+\nu-r}^{+} - \gamma z \left\{ \frac{1}{2} \binom{\nu}{r} + \binom{\nu}{r+1} \right\} J_{\mu+\nu-r}^{-} \right] z^r$$

$$+ \sum_{r=1,3,5\ldots}^{\nu-2} \left[ \binom{\nu}{r} \left\{ \frac{D}{\zeta} \left( \frac{T}{\Theta} \right)^2 z^2 - 1 \right\} J_{\mu+\nu-r}^{-} - \gamma z \left\{ \frac{1}{2} \binom{\nu}{r} + \binom{\nu}{r+1} \right\} J_{\mu+\nu-r}^{+} \right] z^r \quad . \tag{A-9}$$

1.21 To evaluate the integrals $J_s^{\pm}(z)$ we use the following result, which is a slight generalization of a formula given by Wilson (2) Eq. 11:

$$\int_{-\infty}^{\infty} \frac{\eta^s}{(e^{-\eta} + 1)(e^{\eta+z} + 1)} \, d\eta = \frac{1}{(s+1)(e^z - 1)} \int_{-\infty}^{\infty} \frac{\eta^{s+1} - (\eta - z)^{s+1}}{(e^{\eta} + 1)(e^{-\eta} + 1)} \, d\eta \quad . \tag{A-10}$$

This gives

$$J_s^{+}(z) = \frac{1}{(s+1)(1 - e^{-z})} \int_{-\infty}^{\infty} \left( (\eta + z)^{s+1} - (\eta - z)^{s+1} \right) \frac{\partial f_o}{\partial \eta} \, d\eta \quad , \tag{A-11a}$$

and

$$J_s^{-}(z) = \frac{1}{(s+1)(1 - e^{-z})} \int_{-\infty}^{\infty} \left( 2\eta^{s+1} - (\eta + z)^{s+1} - (\eta - z)^{s+1} \right) \frac{\partial f_o}{\partial \eta} \, d\eta \quad . \tag{A-11b}$$

Expanding $(\eta \pm z)^{s+1}$ in powers of $\eta$ and using Eq. A-4, we obtain

$$J_s^{+}(z) = -\frac{2}{(s+1)(1 - e^{-z})} \sum_{t=1,3,5\ldots}^{s+1} \binom{s+1}{t} a_{s-t+1} z^t \quad , \qquad J_s^{-}(z) = 0 \tag{A-12a}$$

if s is even, and

$$J_s^{+}(z) = 0, \qquad J_s^{-}(z) = \frac{2}{(s+1)(1 - e^{-z})} \sum_{t=2,4,6\ldots}^{s+1} \binom{s+1}{t} a_{s-t+1} z^t \tag{A-12b}$$

if s is odd.

1.22. From Eq. A-9 and Eq. A-12, we now obtain

$$I_{\mu\nu} = \frac{2z^{\nu}}{(\mu + 1)(1 - e^{-z})} \left( \frac{D}{\zeta} \left(\frac{T}{\Theta}\right)^2 z^2 - 1 \right) \sum_{t=2,4,6\ldots}^{\mu+1} \binom{\mu+1}{t} a_{\mu-t+1} z^t$$

$$- \frac{2}{(\mu + \nu + 1)(1 - e^{-z})} \frac{D}{\zeta} \left(\frac{T}{\Theta}\right)^2 z^2 \sum_{t=1,3,5\ldots}^{\mu+\nu+1} \binom{\mu+\nu+1}{t} a_{\mu+\nu-t+1} z^t$$

$$- \frac{2}{1 - e^{-z}} \left( \frac{D}{\zeta} \left(\frac{T}{\Theta}\right)^2 z^2 - 1 \right) \left[ \sum_{r=2,4,6\ldots}^{\nu-1} \frac{1}{\mu+\nu-r+1} \binom{\nu}{r} z^r \sum_{t=1,3,5\ldots}^{\mu+\nu-r+1} \binom{\mu+\nu-r+1}{t} a_{\mu+\nu-r-t+1} z^t \right.$$

$$\left. - \sum_{r=1,3,5\ldots}^{\nu-2} \frac{1}{\mu+\nu-r+1} \binom{\nu}{r} z^r \sum_{t=2,4,6\ldots}^{\mu+\nu-r+1} \binom{\mu+\nu-r+1}{t} a_{\mu+\nu-r-t+1} z^t \right] . \qquad \text{(A-13)}$$

The double sum in Eq. A-13 may be simplified by collecting together all the terms involving a fixed power of z, say $z^k$. The square bracket in Eq. A-13 then becomes

$$\sum_{k=3,5,7\ldots}^{\nu} A_{\mu\nu,k} \frac{a_{\mu+\nu-k+1}}{(\mu+\nu-k+1)!} z^k + \sum_{k=\nu+2,\nu+4\ldots}^{\mu+\nu+1} B_{\mu\nu,k} \frac{a_{\mu+\nu-k+1}}{(\mu+\nu-k+1)!} z^k ,$$

$$\text{(A-14)}$$

where

$$A_{\mu\nu,k} = \sum_{r=1}^{k-1} (-1)^r \binom{\nu}{r} \frac{(\mu+\nu-r)!}{(k-r)!} , \qquad \text{(A-15a)}$$

and

$$B_{\mu\nu,k} = \sum_{r=1}^{\nu-1} (-1)^r \binom{\nu}{r} \frac{(\mu+\nu-r)!}{(k-r)!} . \qquad \text{(A-15b)}$$

The summations in Eq. A-15 may be evaluated to give (supposing that $\mu \leqslant \nu$)

$$A_{\mu\nu,k} = (\mu+\nu-k)! \left\{ \binom{\mu}{k} + \binom{\nu}{k} \right\} - \frac{(\mu+\nu)!}{k!} \qquad \text{(A-16a)}$$

if $k \leqslant \mu$,

$$A_{\mu\nu,k} = (\mu+\nu-k)! \binom{\nu}{k} - \frac{(\mu+\nu)!}{k!} \qquad \text{(A-16b)}$$

if $\mu + 2 \leqslant k \leqslant \nu$,

$$B_{\mu\nu,k} = \frac{\mu!}{(k-\nu)!} - \frac{(\mu+\nu)!}{k!} \qquad \text{(A-16c)}$$

if $\nu + 2 \leqslant k \leqslant \mu + \nu - 1$, and

$$B_{\mu\nu,\,\mu+\nu+1} = \frac{1}{\mu+1} - \frac{1}{\mu+\nu+1} - \frac{\mu!\,\nu!}{(\mu+\nu+1)!} \qquad \text{(A-16d)}$$

Combining Eqs. A-13, A-14 and A-16 and simplifying, we obtain

$$I_{\mu\nu} = -\frac{2}{1-e^{-z}}\left[\frac{D}{\zeta}\left(\frac{T}{\Theta}\right)^2 z^3\, a_{\mu+\nu} + \sum_{k=3,5,7\ldots}^{\mu+\nu+1} \binom{\mu+\nu+1}{k}\frac{a_{\mu+\nu-k+1}}{\mu+\nu+1}\, z^k\right.$$

$$+ \left(\frac{D}{\zeta}\left(\frac{T}{\Theta}\right)^2 z^2 - 1\right)\left\{\sum_{k=3,5,7\ldots}^{\mu}\binom{\mu}{k}\frac{a_{\mu+\nu-k+1}}{\mu+\nu-k+1}\,z^k + \sum_{k=3,5,7\ldots}^{\nu}\binom{\nu}{k}\frac{a_{\mu+\nu-k+1}}{\mu+\nu-k+1}\,z^k\right.$$

$$\left.\left. - \frac{\mu!\,\nu!}{(\mu+\nu+1)!}\,z^{\mu+\nu+1}\right\}\right]. \qquad \text{(A-17)}$$

The same result is obtained if $\mu > \nu$, and combination of Eqs. A-6 and A-17 now leads to Eqs. 26a and 27a of the main text. The impurity term has here been omitted; it is easily evaluated by the method used in Appendix 1.1 above, and the details will not be given.

### Appendix 2. Numerical Evaluation of the Transport Magnitudes

2.1. We collect below explicit expressions for the $a_\mu$'s and $F_{\mu\nu}$'s required for evaluating the first three approximations to the electrical and thermal conductivities according to Eqs. 49 and 56. Equation 25 gives

$$a_0 = 1, \quad a_2 = \frac{1}{3}\pi^2, \quad a_4 = \frac{7}{15}\pi^4, \quad a_6 = \frac{31}{21}\pi^6, \quad a_8 = \frac{127}{15}\pi^8, \quad a_{10} = \frac{2555}{33}\pi^{10}$$
$$\text{(A-18)}$$

Further, Eqs. 27a and 28a give, for $\mu$ and $\nu$ even,

$$F_{00} = \oint_5 \qquad \text{(A-19)}$$

$$F_{02} = \frac{1}{3}\pi^2\,\oint_5 + \frac{1}{3}\,\oint_7 \qquad \text{(A-20)}$$

$$F_{22} = \frac{7}{15}\pi^4\,\oint_5 + \frac{1}{30}\,\oint_9 + \frac{\zeta}{D}\left(\frac{\Theta}{T}\right)^2\left(\frac{2}{3}\pi^2\,\oint_5 + \frac{1}{6}\,\oint_7\right) \qquad \text{(A-21)}$$

$$F_{04} = \frac{7}{15}\pi^4\,\oint_5 + \frac{2}{3}\pi^2\,\oint_7 + \frac{1}{5}\,\oint_9 \qquad \text{(A-22)}$$

$$F_{24} = \frac{31}{21}\pi^6\,\oint_5 + \frac{7}{15}\pi^4\,\oint_7 + \frac{1}{105}\,\oint_{11} + \frac{\zeta}{D}\left(\frac{\Theta}{T}\right)^2\left(\frac{28}{15}\pi^4\,\oint_5 + \pi^2\,\oint_7 + \frac{2}{15}\,\oint_9\right) \qquad \text{(A-23)}$$

$$F_{44} = \frac{127}{15}\pi^8\,\oint_5 + \frac{124}{63}\pi^6\,\oint_7 + \frac{1}{630}\,\oint_{13} + \frac{\zeta}{D}\left(\frac{\Theta}{T}\right)^2\left(\frac{248}{21}\pi^6\,\oint_5 + \frac{98}{15}\pi^4\,\oint_7 + \frac{4}{3}\pi^2\,\oint_9 + \frac{23}{210}\,\oint_{11}\right) \qquad \text{(A-24)}$$

and, for $\mu$ and $\nu$ odd,

$$F_{11} = \frac{1}{3}\pi^2 \mathcal{J}_5 - \frac{1}{6}\mathcal{J}_7 + \frac{1}{2}\frac{\zeta}{D}\left(\frac{\Theta}{T}\right)^2 \mathcal{J}_5 \tag{A-25}$$

$$F_{13} = \frac{7}{15}\pi^4 \mathcal{J}_5 + \frac{1}{6}\pi^2 \mathcal{J}_7 - \frac{1}{20}\mathcal{J}_9 + \frac{\zeta}{D}\left(\frac{\Theta}{T}\right)^2\left(\frac{1}{2}\pi^2 \mathcal{J}_5 + \frac{1}{4}\mathcal{J}_7\right) \tag{A-26}$$

$$F_{33} = \frac{31}{21}\pi^6 \mathcal{J}_5 + \frac{7}{30}\pi^4 \mathcal{J}_7 - \frac{1}{140}\mathcal{J}_{11} + \frac{\zeta}{D}\left(\frac{\Theta}{T}\right)^2\left(\frac{21}{10}\pi^4 \mathcal{J}_5 + \pi^2 \mathcal{J}_7 + \frac{3}{20}\mathcal{J}_9\right) \tag{A-27}$$

$$F_{15} = \frac{31}{21}\pi^6 \mathcal{J}_5 + \frac{7}{6}\pi^4 \mathcal{J}_7 + \frac{1}{6}\pi^2 \mathcal{J}_9 - \frac{1}{42}\mathcal{J}_{11}$$
$$+ \frac{\zeta}{D}\left(\frac{\Theta}{T}\right)^2\left(\frac{7}{6}\pi^4 \mathcal{J}_5 + \frac{5}{6}\pi^2 \mathcal{J}_7 + \frac{1}{6}\mathcal{J}_9\right) \tag{A-28}$$

$$F_{35} = \frac{127}{15}\pi^8 \mathcal{J}_5 + \frac{341}{126}\pi^6 \mathcal{J}_7 + \frac{7}{60}\pi^4 \mathcal{J}_9 - \frac{1}{504}\mathcal{J}_{13}$$
$$+ \frac{\zeta}{D}\left(\frac{\Theta}{T}\right)^2\left(\frac{155}{14}\pi^6 \mathcal{J}_5 + \frac{77}{12}\pi^4 \mathcal{J}_7 + \frac{4}{3}\pi^2 \mathcal{J}_9 + \frac{19}{168}\mathcal{J}_{11}\right) \tag{A-29}$$

$$F_{55} = \frac{2555}{33}\pi^{10}\mathcal{J}_5 + \frac{127}{6}\pi^8 \mathcal{J}_7 + \frac{31}{63}\pi^6 \mathcal{J}_9 - \frac{1}{2772}\mathcal{J}_{15}$$
$$+ \frac{\zeta}{D}\left(\frac{\Theta}{T}\right)^2\left(\frac{635}{6}\pi^8 \mathcal{J}_5 + \frac{3875}{63}\pi^6 \mathcal{J}_7 + 14\pi^4 \mathcal{J}_9 + \frac{5}{3}\pi^2 \mathcal{J}_{11} + \frac{23}{252}\mathcal{J}_{13}\right). \tag{A-30}$$

2.2.  The integrals

$$\mathcal{J}_n(x) = \int_0^x \frac{z^n dz}{(e^z - 1)(1 - e^{-z})} \tag{A-31}$$

(with $x = \Theta/T$) are most conveniently evaluated by means of the series

$$\mathcal{J}_n(x) = n!\sum_{s=1}^\infty \frac{1}{s^n} - \frac{x^n}{e^x - 1} - n!\sum_{s=1}^\infty \frac{e^{-sx}}{s^n}\left(1 + sx + \frac{(sx)^2}{2!} + \ldots + \frac{(sx)^{n-1}}{(n-1)!}\right),$$
$$\tag{A-32}$$

valid for large x, and

$$\mathcal{J}_n(x) = x^{n-1}\left(\frac{1}{n-1} - \sum_{s=1}^\infty (-1)^{s-1}\frac{B_s}{(2s)!}\frac{2s-1}{2s+n-1}x^{2s}\right), \tag{A-33}$$

valid for small x, where the $B_s$ are the Bernoulli numbers. Numerical values are given in Table 3, correct to five significant figures (a table of values of $\mathcal{J}_5$ only has previously been given by Grüneisen (15)).

Table 3.  Values of $\oint_n(\Theta/T)$

| T/Θ \ n | 5 | 7 | 9 | 11 | 13 | 15 | 17 |
|---|---|---|---|---|---|---|---|
| 0 | 124.43 | 5082.1 | $3.6361 \times 10^5$ | $3.9937 \times 10^7$ | $6.2278 \times 10^9$ | $1.3077 \times 10^{12}$ | $3.5569 \times 10^{14}$ |
| 0.05 | 124.42 | 5078.2 | $3.6180 \times 10^5$ | $3.9083 \times 10^7$ | $5.8160 \times 10^9$ | $1.1030 \times 10^{12}$ | $2.5004 \times 10^{14}$ |
| 0.076923 | 123.14 | 4809.8 | $3.0344 \times 10^5$ | $2.5647 \times 10^7$ | $2.6594 \times 10^9$ | $3.0916 \times 10^{11}$ | $3.8962 \times 10^{13}$ |
| 0.1 | 116.38 | 3972.1 | $1.9743 \times 10^5$ | $1.2123 \times 10^7$ | $8.4470 \times 10^8$ | $6.3770 \times 10^{10}$ | $5.0803 \times 10^{12}$ |
| 0.125 | 101.48 | 2798.8 | $1.0353 \times 10^5$ | $4.4849 \times 10^6$ | $2.1340 \times 10^8$ | $1.0785 \times 10^{10}$ | $5.6799 \times 10^{11}$ |
| 0.16667 | 70.873 | 1328.9 | 31011 | $8.1272 \times 10^5$ | $2.2840 \times 10^7$ | $6.7201 \times 10^8$ | $2.0417 \times 10^{10}$ |
| 0.2 | 50.263 | 705.56 | 11953 | $2.2377 \times 10^5$ | $4.4520 \times 10^6$ | $9.2226 \times 10^7$ | $1.9661 \times 10^9$ |
| 0.25 | 29.488 | 281.75 | 3167.4 | 38845 | $5.0260 \times 10^5$ | $6.7413 \times 10^6$ | $9.2781 \times 10^7$ |
| 0.33333 | 12.771 | 72.010 | 468.43 | 3291.4 | 24264 | $1.8479 \times 10^5$ | $1.4409 \times 10^6$ |
| 0.5 | 3.2293 | 8.3763 | 24.717 | 78.230 | 258.74 | 881.95 | 3072.9 |
| 0.66667 | 1.1199 | 1.6538 | 2.7649 | 4.9460 | 9.2329 | 17.748 | 34.851 |
| 0.83333 | 0.47907 | 0.45534 | 0.48883 | 0.56090 | 0.67116 | 0.82665 | 1.0399 |
| 1.0 | 0.23662 | 0.15665 | 0.11700 | 0.093343 | 0.077632 | 0.066444 | 0.058071 |
| 1.25 | 0.098845 | 0.041987 | 0.020100 | 0.010273 | 0.0054720 | 0.0029989 | 0.0016782 |

# References

(1) A. H. Wilson: The Theory of Metals (Cambridge University Press, 1936).

(2) A. H. Wilson: Proc. Camb. Phil. Soc. 33, 371 (1937).

(3) G. P. Dube: Proc. Camb. Phil. Soc. 34, 559 (1938).

(4) F. Bloch: Z. Phys. 59, 208 (1930).

(5) W. Kroll: Z. Phys. 80, 50 (1933).

(6) W. Kroll: Z. Phys. 81, 425 (1933).

(7) M. Kohler: Z. Phys. 124, 772 (1948).

(8) M. Kohler: Z. Phys. 125, 679 (1949).

(9) W. Kroll: Sci. Pap. Inst. Phys. Chem. Res., Tokyo, 34, 194 (1938).

(10) K. Umeda and T. Yamamoto: J. Fac. Sci. Hokkaidô Univ. (Ser. 2) 3, 249 (1949).

(11) K. Umeda: Sci. Pap. Inst. Phys. Chem. Res., Tokyo, 39, 342 (1942).

(12) K. Umeda and T. Toya: J. Fac. Sci. Hokkaidô Univ. (Ser. 2) 3, 257 (1949).

(13) R. E. B. Makinson: Proc. Camb. Phil. Soc. 34, 474 (1938).

(14) G. Kowalewski: Einführung in die Determinantentheorie, Section 41; (Verlag von Veit and Co., Leipzig, 1909).

(15) E. Grüneisen: Ann. Phys., Leipzig, (5), 16, 530 (1933).

(16) E. H. Sondheimer and A. H. Wilson: Proc. Roy. Soc. A190, 435 (1947).

(17) M. Kohler: Z. Phys. 126, 495 (1949).

(18) E. H. Sondheimer: Proc. Camb. Phil. Soc. 43, 571 (1947).