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The Lorenz Number

Abstract: The theory of the Lorenz number of a conducting crystal is developed for the common models of the electron assembly. For the one-electron model it is shown that, provided scattering is elastic to an approximation which is examined, the Lorenz number is equal to the square fluctuation of the thermoelectric power. For the phenomenological band model an equivalent result is obtained. It is hypothesized that these results are special cases of a more general one. Some applications, including the theory of the bipolar anomaly for semiconductors, are discussed.

Contents

1. Introduction

The law of Wiedemann and Franz (1853) states that all metals have the same ratio of thermal conductivity to electrical conductivity, at any given temperature. At ordinary temperatures it holds quite well, except for a few metals, over a range of about two decades in the values of K and σ. The law was refined by the conclusion of Lorenz (1872) that the ratio is proportional to the absolute temperature. Thus, if we write

$$K=\Lambda\sigma T, \tag{1}$$

where K and σ are the thermal and electrical conductivities respectively, then the Wiedemann-Franz-Lorenz law states that the "Lorenz Number" Λ is the same for all metals at all temperatures.

There is at present a growing interest in the application of the law to *semiconductors*,[1] partly as a natural consequence of the revelation of failures of the law by recent measurements, partly of technological origin and because the efficiency of conversion of thermal to electrical energy by a thermocouple is proportional to σ/K. For these substances, which are poor electrical conductors, an appreciable part (K_0, say) of the thermal conductivity originates in transfer of energy in ways other than by motion of the conducting electrons. The proper form of the Wiedemann-Franz-Lorenz law is then[2]

$$K=K_0+\Lambda\sigma T. \tag{2}$$

The non-electronic part, K_0, of K normally arises from transfer of energy by moving lattice vibration quanta.

It will be convenient in this paper to discuss the value of the dimensionless magnitude χ defined by

$$\Lambda\equiv\chi(k/e)^2, \tag{3}$$

where k is Boltzmann's constant and e the charge of the electron, rather than that of Λ itself. The theoretical value of χ for metals, in conditions where the Weidemann-Franz-

Lorenz law holds, is $\pi^2/3$: this fact was first established by Sommerfeld For metals even where the value of χ deviates distinctly from the Sommerfeld value it remains of this order of magnitude. For semiconductors on the other hand it may be shown,[3] on the basis of the band model, that values of χ large compared to one should occur; and at least one of the cases[4] of anomalous dependence of K on T which have been found may evidently be accounted for by the predicted anomalous values of χ: this is the so-called "bipolar" effect.

The main part (Sections 3 to 5) of the present paper deals with the theory of the Lorenz number, and the possible anomalous values of χ, according to the single-electron (self-consistent field) model. It is shown that normally $(kT)^2\chi$ is equal to the mean square fluctuation, over all possible energies, of the electron energy, with the contribution, at each energy, to the electric current due to an electric field as weighting factor. That is to say, $(kT)^2\chi$ is the mean square fluctuation of the Peltier heat. (The exception to this result occurs where the changes in electron energy on scattering are not small compared with thermal energy kT.) Essentially the same result is obtained for the phenomenological theory presented in Section 2; and it is suggested in Section 6 that the result may be quite general, rather than depending on certain approximations for the collective states of the electrons of the substance, and may even have an extension to the totality of thermal excitations of the substance

2. Phenomenological theory for several conducting bands

Before examining the theory of electronic thermal conductivity on the basis of the one-electron model, it is worthwhile to discuss the theory in terms of the phenomenological model in which conduction is supposed to be the sum of contributions from a number of distinct conducting "bands," for each of which there is a distinct range of energy for the current carriers. This model originated from the results of the one-electron model for crystals but it is possible, and expedient here, to introduce the "band" model in phenomenological terms not depending on the concepts from which it originated. Actually the phenomenological band model is, for semiconductors at least, probably of more general validity. The analysis of the electronic thermal conductivity of semiconductors in terms of a single effective conduction (electron) band and a single effective valence (hole) band originally led to the prediction, by Davydov and Shmushkevich,[3] of anomalously large values of χ for a semiconductor in which both valence and conduction bands contribute appreciably to σ. In this section the phenomenological theory of this phenomenon is generalized to apply to a homogeneous conductor with any number of conducting bands.[5]

For convenience, we assume isotropic or cubic symmetry: then the linear phenomenological equations for simultaneous electrical and thermal conduction may be written in the form

$$\mathbf{J}=\sigma(\mathbf{E}+\Omega\mathrm{grad}T), \tag{4}$$

$$\mathbf{W}=(L+\phi)\mathbf{J}-K\mathrm{grad}T. \tag{5}$$

Here $\mathbf{J}$ and $\mathbf{W}$ are the electric current density and energy current density respectively, $\mathbf{E}$ is the electric field and ϕ the potential. We generalize these equations by expressing $\mathbf{J}$ and $\mathbf{W}$ in terms of the individual contributions from the bands:

$$\mathbf{J}=\Sigma_s\mathbf{J}_s,\quad \mathbf{W}+K_0\mathrm{grad}T=\Sigma_s\mathbf{W}_s, \tag{6}$$

where

$$\mathbf{J}_s=\sigma_s(\mathbf{E}+\Omega_s\mathrm{grad}T), \tag{7}$$

$$\mathbf{W}_s=(L_s+\phi)\mathbf{J}_s-K_s\mathrm{grad}T. \tag{8}$$

The subscript $s=1, 2, \ldots$ labels the band. By making use of the first of (6), (7) may be written in the form

$$\mathbf{J}_s=(\sigma_s/\sigma)\{\mathbf{J}+\Sigma_t\sigma_t(\Omega_s-\Omega_t)\mathrm{grad}T\}. \tag{9}$$

On substituting (9) into (8), and the result in turn into the second of (6), we obtain an equation of the form of (5) with

$$L=\Sigma_sL_s\sigma_s/\sigma \tag{10}$$

and

$$K=K_0+\Sigma_s\{K_s-(\sigma_s/\sigma)L_s\Sigma_t\sigma_t(\Omega_s-\Omega_t)\}. \tag{11}$$

If we write

$$K_s\equiv\chi_s\sigma_sT(k/e)^2 \tag{12}$$

for the individual contributions of the bands to the electronic thermal conductivity, then comparison of (11) with (2) and (3) yields the formula

$$\chi=\Sigma_s\frac{\sigma_s}{\sigma}\chi_s+\sum\sum_{s<t}\frac{\sigma_s\sigma_t}{\sigma^2}\,\frac{(L_s-L_t)(\Omega_t-\Omega_s)}{T(k/e)^2}. \tag{13}$$

The phenomenological coefficients L and Ω are related to the Peltier heat Π and the thermoelectric power Q by the formulas[6]

$$e\Pi=\zeta+eL,\quad eQ=d\zeta/dT-e\Omega, \tag{14}$$

where ζ is the chemical potential of the electrons (the Fermi energy in the one-electron model). In virtue of (10) and the corresponding relation for Ω in terms of the Ω_s we may therefore write

$$\Pi=\Sigma_s\Pi_s\sigma_s/\sigma,\quad Q=\Sigma_sQ_s\sigma_s/\sigma, \tag{15}$$

defining

$$e\Pi_s\equiv\zeta+eL_s,\quad eQ_s\equiv d\zeta/dT-e\Omega_s. \tag{16}$$

Then (13) becomes

$$\chi-\Sigma_s\frac{\sigma_s}{\sigma}\chi_s=\left(\frac{e}{kT}\right)^2\sum\sum_{s<t}\frac{\sigma_s\sigma_t}{\sigma^2}T(Q_s-Q_t)(\Pi_s-\Pi_t)$$

$$=\left(\frac{e}{kT}\right)^2\Sigma_s\frac{\sigma_s}{\sigma}T(Q_s-Q)(\Pi_s-\Pi). \tag{17}$$

Thus the anomaly in χ is proportional to the correlation between the band contributions to Π and to TQ. If the Kelvin relation

$$TQ=\Pi \tag{18}$$

is satisfied for each band separately,

$$T Q_s = \Pi_s \tag{19}$$

then this correlation is at its greatest, and we have

$$\chi - \Sigma_s \frac{\sigma_s}{\sigma}\chi_s = \sum\sum_{s<t} \frac{\sigma_s \sigma_t}{\sigma^2}\left(\frac{e(\Pi_s - \Pi_t)}{kT}\right)^2$$

$$= \Sigma_s \frac{\sigma_s}{\sigma}\left(\frac{e(\Pi_s - \Pi)}{kT}\right)^2 . \tag{20}$$

Since the right-hand side of (17) may be written, taking (18) into account, as

$$\left(\frac{e}{kT}\right)^2 \Sigma_s \frac{\sigma_s}{\sigma}\left\{\left(\frac{\Pi_s + TQ_s}{2} - \Pi\right)^2 - \left(\frac{\Pi_s - TQ_s}{2}\right)^2\right\},$$

the correction to (20) is proportional to the *squares* of deviations from (19). (See Section 4.)

In terms of (20), the origin of the bipolar anomaly in χ for semiconductors[3] is a large contribution to the right-hand side from the conduction ($s=1$) and valence ($s=2$) bands. Then

$$\chi - \frac{\sigma_1}{\sigma}\chi_1 - \frac{\sigma_2}{\sigma}\chi_2 = \frac{\sigma_1 \sigma_2}{\sigma^2}\left(\frac{e(\Pi_1 - \Pi_2)}{kT}\right)^2 .$$

Since $\zeta - e\Pi_s$ is the average, weighted by the electron velocities in the presence of an electric field, of the electron energies in the band, the factor $e(\Pi_2 - \Pi_1)$ must be not less than the forbidden energy gap Δ. Since normally $\Delta \gg kT$, there will hence be a large anomaly when σ_1 and σ_2 are comparable. Actually $e(\Pi_2 - \Pi_1) - \Delta \sim kT$,[7] and so the anomaly in χ cannot be very much greater than $(e\Delta/2kT)^2$ in practice (but see footnote 7). Normally χ_1 and χ_2 will not be anomalously large.

The question naturally arises whether other combinations of bands may give rise to such an effect. Another kind of combination does actually exist, and may in principle be realised in *p*-silicon: as in germanium the valence band is split by spin-orbit coupling so that the band-edge is double, but in silicon the separation of the two valence band edges (i.e. at the zone center) is thought to be only 0.035 ev [8]. Thus this separation (Δ_{s0}, say) is of order kT at around 400° K. In this case the contributions from thermal excitation of holes to Π_a and to Π_b (where "a" refers to the degenerate upper valence band and "b" to the split off lower valence band) are both positive, and tend to cancel in $\Pi_b - \Pi_a$. Then for *p*-silicon

$$\chi - \frac{\sigma_a}{\sigma}\chi_a - \frac{\sigma_b}{\sigma}\chi_b \simeq \frac{\sigma_a \sigma_b}{\sigma^2}\left(\frac{\Delta_{s0}}{kT}\right)^2 . \tag{21}$$

In practice we will also have

$$\sigma_b/\sigma_a = (m_b/m_a)^{3/2}(\mu_b/\mu_a)\exp(-\Delta_{s0}/kT), \tag{22}$$

where m_a, m_b are the density-of-states masses and μ_a, μ_b the mobilities of the bands (in case "a", for the degenerate sub-bands in combination). From present knowledge[8] it appears that $m_b \simeq 0.3 m_a$. Then the condition for the value of (21) at the temperature of its maximum to be large is that $\mu_b \gg \mu_a$. In contrast to the situation for the bipolar effect, for the effect being discussed the contribution to K may be monotonically increased by doping and is proportional to σ. However, for the contribution to K to be comparable to K_0, in silicon at the temperature of the maximum, σ would need to be some thousands of inverse ohm-cm; and this leaves the possibility of observing any anomaly in this case somewhat in question.[9] The situation should be improved by alloying the silicon with germanium, which would presumably increase Δ_{s0}, and hence increase the temperature for the maximum of χ, and hence both increase Λ and decrease K_0 at the maximum, and at the same time further decrease the competing lattice conductivity K_0 on account of the decrease with alloying at fixed temperature;[1] but all this can be expected to result in only a modest reduction in the values of σ needed. More favorable cases, among other semiconductors, may possibly exist.[10]

By the first of (16), the right-hand side of (20) is proportional to the square fluctuation of L_s, and hence essentially of the band energies, over the phenomenological bands, with σ_s/σ as weighting factor. The question naturally arises: can this result be generalized (to represent χ rather than just the anomalous part) by including the fluctuation of carrier energy *within* each band? We shall see in the following two sections that if conduction is treated in terms of the one-electron model then, subject to a certain restriction, this idea is right. The generalization is expressed by eq. (43).

3. Theory for the one-electron model

According to the one-electron (self-consistent field) model, the possible wave functions for all the electrons participating in transport phenomena in a conducting crystal are Slater determinants specified by occupation numbers, $\nu(\mathbf{p},\vartheta,q) = 0$ or 1, of single-electron states, which in turn are specified by the pseudomomentum $\mathbf{p}$ ($\mathbf{p}/\hbar$ is the wave vector of a Bloch function), a spin component $\vartheta = \pm\frac{1}{2}$, and the band index q. The word "band" is here used in the strict sense which it has in the Bloch-Brillouin theory. For each band there is an energy function which in the absence of a net magnetization may be taken to depend only on $\mathbf{p}$. Then $\epsilon = \epsilon(\mathbf{p},q)$. Corresponding to each single-electron state there is also a particle velocity $\mathbf{v} = \partial\epsilon/\partial\mathbf{p} = \mathbf{v}(\mathbf{p},q)$. A homogeneous stationary condition of the crystal may be represented by an ensemble of quantum states for all the electrons, each characterized by one such wave function and hence by a set of occupation numbers $\nu(\mathbf{p},\vartheta,q)$. For the present purpose this ensemble is sufficiently characterized by the mean values, $f(\mathbf{p},\vartheta,q)$, of the ν. In the case of thermal equilibrium at absolute temperature T, f is a function of ϵ only:

$$f(\mathbf{p},\vartheta,q) = f_0(\epsilon) \equiv \left\{1 + \exp\left(\frac{\epsilon - \zeta}{kT}\right)\right\}^{-1} . \tag{23}$$

In a non-equilibrium steady state, f is caused to differ from f_0 by disturbances due to the external "driving forces." The transport phenomena arise when the disturbance originates in a space gradient: for example a gradient of temperature, grad T, or of electric potential, grad $\phi = -\mathbf{E}$. These are treated by supposing the distribution function to depend also on position in the crystal: $f = f(\mathbf{p},\vartheta,q;\mathbf{r})$.

Then the fundamental equation describing the steady-state distribution function for the system is the Boltzmann equation[12]

$$\Sigma_{q'}\Sigma_{\vartheta'}\int d^3\mathbf{p}'\{f(\mathbf{p}',\vartheta',q')S(\mathbf{p}',\vartheta',q';\mathbf{p},\vartheta,q)(1-f(\mathbf{p},\vartheta,q)) - f(\mathbf{p},\vartheta,q)S(\mathbf{p},\vartheta,q;\mathbf{p}',\vartheta',q')(1-f(\mathbf{p}',\vartheta',q'))\} = \mathbf{F}\cdot\frac{\partial f(\mathbf{p},\vartheta,q)}{\partial \mathbf{p}}+\mathbf{v}\cdot\frac{\partial f(\mathbf{p},\vartheta,q)}{\partial \mathbf{r}}, \tag{24}$$

where $\mathbf{F}$ is the Lorentz force acting on each electron and $S(\mathbf{p}',\vartheta',q';\mathbf{p},\vartheta,q)(1-f(\mathbf{p},\vartheta,q))d^3\mathbf{p}$ is the probability per unit time for an electron to be scattered from the state characterized by $(\mathbf{p}',\vartheta',q')$ to any of those belonging to the volume element $d^3\mathbf{p}$ of $\mathbf{p}$-space about the state characterized by $(\mathbf{p},\vartheta,q)$.

The present section is concerned with the solution of (24), to first order in the deviation of f from f_0, when the driving forces are an electric field and a temperature gradient and when it may be assumed that the scattering function S of (24) represents scattering by a crystal "substrate" *which does not deviate appreciably from its thermal equilibrium state*. In virtue of this last assumption, it follows at once from the principle of detailed balancing[13] that the function

$$f_0(\epsilon(\mathbf{p},q))S(\mathbf{p},\vartheta,q;\mathbf{p}',\vartheta',q')(1-f_0(\epsilon(\mathbf{p}',q'))) \equiv R(\mathbf{p},\vartheta,q;\mathbf{p}',\vartheta',q') \tag{25}$$

is symmetric with respect to the primed and unprimed variables:

$$R(\mathbf{p}',\vartheta',q';\mathbf{p},\vartheta,q)=R(\mathbf{p},\vartheta,q;\mathbf{p}',\vartheta',q'). \tag{26}$$

The left-hand side of (24) then vanishes when (23) is satisfied. To obtain the equation for the deviation of f from f_0 to first order in the driving forces (i.e. the Boltzmann equation for the *linear* transport effects), (24) is linearized by substituting $f=f_0+f_1$ into it and equating the terms on the *left* which are of first degree in f_1 to the terms on the *right* which are linear in the "driving forces."[14] In the present case the driving forces are the space gradients of ζ and T, introduced by the term in $\partial f_0/\partial \mathbf{r}$ on the right of (24), and the electric field $\mathbf{E}$ in the Lorentz force $\mathbf{F}=-e\mathbf{E}$. Then the contribution of the right-hand side of (24) to the linearized Boltzmann equation is

$$g(\mathbf{p},q)=-\mathbf{v}\cdot(\mathbf{A}+\epsilon\,\mathbf{B})f_0(1-f_0), \tag{27}$$

where

$$\mathbf{A}\equiv\frac{-e\mathbf{E}+(\zeta/T-d\zeta/dT)\mathrm{grad}T}{kT},\quad \mathbf{B}\equiv-\frac{\mathrm{grad}T}{kT^2}. \tag{28}$$

Before writing down the complete linearized Boltzmann equation for f_1, and proceeding, it is convenient to simplify the notation by letting a single symbol, Γ, stand for the set of variables $\mathbf{p},\vartheta,q$ specifying an electron state, and to let $I(\Gamma)$ stand for the sum-integral operator $\Sigma_q\Sigma_\vartheta\int d^3\mathbf{p}\ \ldots$. Then the linearized Boltzmann equation for f_1 is

$$I(\Gamma')\{f_1(\Gamma')T(\Gamma';\Gamma)-f_1(\Gamma)T(\Gamma;\Gamma')\}=g(\Gamma), \tag{29}$$

where g is defined by (27) and

$$T(\Gamma;\Gamma')\equiv S(\Gamma;\Gamma')(1-f_0(\Gamma'))+f_0(\Gamma')S(\Gamma';\Gamma). \tag{30}$$

In virtue of the relation (25), (26), an alternative form of (30) is

$$T(\Gamma;\Gamma')=S(\Gamma;\Gamma')\left\{\frac{1-f_0(\Gamma')}{1-f_0(\Gamma)}\right\}. \tag{31}$$

The form of (29) suggests the definition of a collision relaxation time τ by:

$$\frac{1}{\tau(\Gamma)}\equiv I(\Gamma')T(\Gamma;\Gamma'). \tag{32}$$

We wish to find expressions, in terms of the driving forces, for the flux of electrons and flux of electron energy, which are given respectively by

$$\mathbf{N}=h^{-3}I\,\mathbf{v}f, \tag{33}$$

$$\mathbf{W}_{\mathrm{elec.}}=h^{-3}I\,\mathbf{v}\epsilon f \tag{34}$$

(where I is the sum-integral operator defined above and here operating on the electron state variables for the magnitudes $\mathbf{v}$, ϵ, f on the right). To obtain a formal solution for $\mathbf{N}$ and $\mathbf{W}_{\mathrm{elec.}}$, with f on the right of (33) and (34) replaced by f_1, we make use of the following theorem: Let $\psi(\Gamma)$ be any one-electron function and let a "conjugate" function $\psi^\dagger$ be defined by the relation

$$\psi^\dagger(\Gamma)-I(\Gamma')T(\Gamma;\Gamma')\tau(\Gamma')\psi^\dagger(\Gamma')=\psi(\Gamma). \tag{35}$$

Then, by (29) and (32),

$$If_1\psi=-Ig\tau\,\psi^\dagger. \tag{36}$$

Eqns. (27), (28) and (36) at once yield the formal linear macroscopic transport equations, with $\mathbf{v}$, $\mathbf{v}\epsilon$, etc. for ψ. It is convenient to make the further abbreviation

$$h^{-3}I\,\psi f_0(1-f_0)\equiv[\psi]. \tag{37}$$

Then the linear transport equations are[15]

$$\mathbf{N}=\mathbf{A}\cdot[\tau\mathbf{v}\,\mathbf{v}^\dagger]+\mathbf{B}\cdot[\tau\epsilon\mathbf{v}\,\mathbf{v}^\dagger], \tag{38}$$

$$\mathbf{W}_{\mathrm{elec.}}=\mathbf{A}\cdot[\tau\mathbf{v}(\mathbf{v}\epsilon)^\dagger]+\mathbf{B}\cdot[\tau\epsilon\mathbf{v}(\mathbf{v}\epsilon)^\dagger]. \tag{39}$$

From (38), the electrical conductivity tensor has components

$$\sigma_{ij}=(e^2/kT)[\tau v_j v_i^\dagger]. \tag{40}$$

The electronic thermal conductivity is given by the value of $\mathbf{W}_{\mathrm{elec.}}$ in the presence of a temperature gradient when the electric field is such that the current density $\mathbf{J}=-e\mathbf{N}$ is zero. Thus we have to solve for $\mathbf{A}$ in (38), for $\mathbf{N}=0$, and substitute the result in (39). It is expedient at this point to specialize to the case of cubic crystal symmetry. Then, for $\mathbf{J}=0$,

$$3kT^2[\tau\mathbf{v}\cdot\mathbf{v}^\dagger]\mathbf{W}_{\mathrm{elec.}} = \{[\tau\mathbf{v}\cdot(\mathbf{v}\epsilon)^\dagger][\tau\epsilon\mathbf{v}\cdot\mathbf{v}^\dagger]-[\tau\mathbf{v}\cdot\mathbf{v}^\dagger][\tau\epsilon\mathbf{v}\cdot(\mathbf{v}\epsilon)^\dagger]\}\mathrm{grad}\,T$$

and hence, if we identify $-\mathbf{W}_{\mathrm{elec.}}$ with $(K-K_0)\mathrm{grad}\,T$, by (2) and (3)

$$\chi=\left(\frac{1}{kT}\right)^2\left\{\frac{[\tau\epsilon\mathbf{v}\cdot(\mathbf{v}\epsilon)^\dagger]}{[\tau\mathbf{v}\cdot\mathbf{v}^\dagger]}-\frac{[\tau\epsilon\mathbf{v}\cdot\mathbf{v}^\dagger]}{[\tau\mathbf{v}\cdot\mathbf{v}^\dagger]}\frac{[\tau\mathbf{v}\cdot(\mathbf{v}\epsilon)^\dagger]}{[\tau\mathbf{v}\cdot\mathbf{v}^\dagger]}\right\}. \tag{41}$$

If the scattering were perfectly elastic (i.e. connected initial and final states only with the same value of ϵ) then

we would have

$$(\mathbf{v}\epsilon)^\dagger = \mathbf{v}^\dagger\epsilon. \tag{42}$$

(For the proof of this statement, see the beginning of Section 5.) On substituting (42) into (41) the latter reduces to

$$\chi = \left[\tau \quad \mathbf{v}^\dagger\left(\epsilon - \frac{[\tau\mathbf{v}\cdot\mathbf{v}^\dagger\epsilon]}{[\tau\mathbf{v}\cdot\mathbf{v}^\dagger]}\right)^2\right] / (kT)^2[\tau\mathbf{v}\cdot\mathbf{v}^\dagger]. \tag{43}$$

Thus $\chi(kT)^2$ becomes simply the square fluctuation of ϵ over the levels, with $\tau\mathbf{v}\cdot\mathbf{v}^\dagger f_0(1-f_0)$ (proportional to the contribution per one-electron state to the conductivity) as weighting factor. The Sommerfeld value, $\chi = \pi^2/3$, for metals results from (43) in special conditions which are discussed below (Section 5) together with the conditions for (43) to be a good approximation to (41). The result (43) itself is the generalization of (20) which was proposed in the last paragraph of Section 2.

4. Comparison of the two models; the reciprocal relations

In this section we examine the correspondence of the results for the one-electron model to those for the phenomenological band model. Eq. (41) may be rewritten as

$$\chi = \frac{[\tau(\mathbf{v}\epsilon - \mathbf{v}w)\cdot((\mathbf{v}\epsilon)^\dagger - \mathbf{v}^\dagger w^\dagger)]}{(kT)^2[\tau\mathbf{v}\cdot\mathbf{v}^\dagger]}, \tag{44}$$

where w and $w^\dagger$ are defined by the relations

$$\left.\begin{aligned}[\tau\epsilon\mathbf{v}\cdot\mathbf{v}^\dagger] &\equiv w[\tau\mathbf{v}\cdot\mathbf{v}^\dagger],\\ [\tau\mathbf{v}\cdot(\mathbf{v}\epsilon)^\dagger] &\equiv w^\dagger[\tau\mathbf{v}\cdot\mathbf{v}^\dagger].\end{aligned}\right\} \tag{45}$$

On comparing (45) with (4), (5), (14), (38), and (39) it is found that

$$w = \zeta - eTQ, \quad w^\dagger = \zeta - e\Pi. \tag{46}$$

An analogy between (44) and (17), with $\Sigma_s(\sigma_s/\sigma)$ . . . corresponding to $h^{-3}I\, f_0(1-f_0)(\tau\mathbf{v}\cdot\mathbf{v}^\dagger/[\tau\mathbf{v}\cdot\mathbf{v}^\dagger])$ . . . , is then evident. [It makes no difference to the result (44) if ϵ is replaced by $\epsilon - \zeta$ in both (44) and (45).]

We have to assure ourselves that the Kelvin relation (18) holds for the model of a conductor studied in Section 3. Eq. (46) shows that what is required is to verify that

$$w = w^\dagger. \tag{47}$$

It is expedient to deal with this question at the present point in the discussion, and to do so by proving the following theorem: If ϕ and ψ are any two functions of Γ (of course, such that the double sum-integral in (49) is uniformly convergent), then

$$[\tau\phi^\dagger\psi] = [\tau\psi^\dagger\phi]. \tag{48}$$

The proof entails writing out the left-hand side according to the definition (37) and then substituting for ψ in terms of $\psi^\dagger$ by (35):

$$h^3[\tau\phi^\dagger\psi] = I\tau\phi^\dagger\psi^\dagger f_0(1-f_0)$$
$$-I(\Gamma)I(\Gamma')\tau(\Gamma)\phi^\dagger(\Gamma)\, f_0(\Gamma)(1-f_0(\Gamma))T(\Gamma;\,\Gamma')\tau(\Gamma')\psi^\dagger(\Gamma').$$

Now, by (25) and (31),

$$f_0(\Gamma)(1-f_0(\Gamma))T(\Gamma;\,\Gamma') = R(\Gamma;\,\Gamma').$$

Hence

$$h^3[\tau\phi^\dagger\psi] = I\tau\phi^\dagger\psi^\dagger f_0(1-f_0)$$
$$-I(\Gamma)I(\Gamma')\phi^\dagger(\Gamma)\tau(\Gamma)R(\Gamma;\,\Gamma')\tau(\Gamma')\psi^\dagger(\Gamma'). \tag{49}$$

The first term on the right of (49) is symmetrical in $\phi^\dagger$ and $\psi^\dagger$. By (26), the second term on the right is also symmetrical. Hence we arrive at (48). It is a significant property of the theorem that it is true in virtue of the principle of detailed balancing as expressed by (26), and hence depends on the assumption that the crystal substrate—the agent of the scattering—is in thermal equilibrium. It is not true when there is an appreciable phonon drag effect.[16] Eq. (48), applied in conjunction with (36), embodies the Onsager reciprocal relations[17] for the transport effects of the system of electrons considered here. With ϕ and ψ set equal to two components, v_i and v_j, of $\mathbf{v}$, it follows at once from (40) that $\sigma_{ij} = \sigma_{ji}$. This result is, of course, one of the Onsager relations for a crystal in zero magnetic field. Similarly the coefficient of $\mathbf{B}$ in (39) is a symmetric tensor. Finally, the (i,j) component of the coefficient of $\mathbf{B}$ in (38) is equal to the (j,i) component of the coefficient of $\mathbf{A}$ in (39). This last result is just the Onsager relation for the thermoelectric coefficients in zero magnetic field.[18] For a cubic crystal it reduces to (47), which we set out to prove. The Kelvin relation (18) is thus verified.[19]

We may now examine how the results of the one-electron model, (41), (43), and (44), may be explicitly reduced to (13), (17) and (20) of the phenomenological model. The natural expectation is that a one-one correspondence between sets of one-electron states in "Γ-space" and the "bands" of the phenomenological band model should be found. An implicit idea of the latter was that the correspondence would be between the *phenomenological* "bands" labeled by the index s of Section 2 and the *Bloch* bands, of one-electron states, labeled by the index q of Section 3. It is more enlightening, however, to proceed by arbitrarily dividing up the entirety of states over which Γ ranges in the formulas of the preceding section into sets "1," "2," . . . "α," . . . which cover the whole range without overlapping, and which are otherwise quite general except that for convenience we require that each set still constitute a system with cubic symmetry, and simply rewriting (41) in terms of magnitudes for each set analogous to χ, w and $w^\dagger$. We write

$$h^{-3}I_\alpha\psi f_0(1-f_0) \equiv [\psi]_\alpha, \tag{50}$$

where $I_\alpha(\Gamma)$ stands for summation and integration over the set "α," and define

$$\sigma_\alpha \equiv (e^2/3kT)[\tau\mathbf{v}\cdot\mathbf{v}^\dagger]_\alpha, \tag{51}$$

$$\left.\begin{aligned}[\tau\epsilon\mathbf{v}\cdot\mathbf{v}^\dagger]_\alpha &\equiv w_\alpha[\tau\mathbf{v}\cdot\mathbf{v}^\dagger]_\alpha,\\ [\tau\mathbf{v}\cdot(\mathbf{v}\epsilon)^\dagger]_\alpha &\equiv w^\dagger{}_\alpha[\tau\mathbf{v}\cdot\mathbf{v}^\dagger]_\alpha,\end{aligned}\right\} \tag{52}$$

$$\chi_\alpha \equiv \frac{[\tau(\mathbf{v}\epsilon - \mathbf{v}w_\alpha)\cdot((\mathbf{v}\epsilon)^\dagger - \mathbf{v}^\dagger w^\dagger{}_\alpha)]_\alpha}{(kT)^2[\tau\mathbf{v}\cdot\mathbf{v}^\dagger]_\alpha}. \tag{53}$$

By the above definitions,

$$\sigma=\Sigma_\alpha\sigma_\alpha,\ w=\Sigma_\alpha\frac{\sigma_\alpha}{\sigma}w_\alpha,\ w^\dagger=\Sigma_\alpha\frac{\sigma_\alpha}{\sigma}w^\dagger{}_\alpha. \tag{54}$$

Then (41) transforms to

$$\chi-\Sigma_\alpha\frac{\sigma_\alpha}{\sigma}\chi_\alpha=\sum_{\alpha<\beta}\sum\frac{\sigma_\alpha\sigma_\beta}{\sigma^2}\frac{(w_\alpha-w_\beta)(w_\alpha{}^\dagger-w^\dagger{}_\beta)}{(kT)^2}$$

$$=\Sigma_\alpha\frac{\sigma_\alpha}{\sigma}\frac{(w_\alpha w^\dagger{}_\alpha-ww^\dagger)}{(kT)^2}$$

$$=\Sigma_\alpha\frac{\sigma_\alpha}{\sigma}\frac{(w_\alpha-w)(w^\dagger{}_\alpha-w^\dagger)}{(kT)^2}\ . \tag{55}$$

The substitutions

$$w_\alpha\equiv\zeta-eTQ_\alpha,\ \ w^\dagger{}_\alpha\equiv\zeta-e\Pi_\alpha, \tag{56}$$

which are consistent with (15), (46) and (54), and whose relation to (46) is analogous to the relation of (19) to (18), complete the formal analogy between (55) and (17).

So far, however, the partitioning of the one-electron states into sets, each to be identified with one of the phenomenological bands of Section 2, has been arbitrary, and so the correspondence between (55) and the results of the theory developed in Section 2 may be expected to be in general formal rather than physical. For example, one can imagine the states to make up each set chosen from all over the whole range of values of ϵ, so that all the w_α (or alternatively all the $w^\dagger{}_\alpha$) are equal. In this case (55) vanishes. The value of χ has of course not been changed by this procedure. Rather this choice of the sets makes the χ_α larger, since by (53) they essentially measure the dispersion of energies ϵ in each set. We expect the sets to be chosen rather so as to partition the scale of electron energy into ranges in a physically natural way. A further reasonable criterion of the suitability of the sets to correspond to what is usually had in mind by the phenomenological band model is that the relations (19) should hold, to a good approximation, for them. We are therefore interested in the condition for the relations

$$w_\alpha=w^\dagger{}_\alpha \tag{57}$$

to hold to a good approximation. These latter relations are, as is evident from the definitions (52), satisfied for any choice of the sets if (42) is satisfied; but in that case (41) reduces to (43), and then the partitioning of χ into the contributions from the χ_α and the "inter-set" contributions on the right of (55) is indeed arbitrary. (What is of concern in this case is just the distribution, over the range of electron energy ϵ, of contributions to σ, without regard to the classification of the contributing electron states: see Section 5.) Here we are concerned with the conditions for (57) to hold when (42) is not in general satisfied.

The conditions for (57) to hold may be studied by adapting the proof of (48), and hence of (47), given above. By the same process as yields (49), one finds

$$[\tau\phi^\dagger\psi]_\alpha-[\tau\psi^\dagger\phi]_\alpha=h^{-3}\{I_\alpha(\Gamma)I^\alpha(\Gamma')$$
$$-I^\alpha(\Gamma)I_\alpha(\Gamma')\}\tau(\Gamma)R(\Gamma;\,\Gamma')\tau(\Gamma')\phi^\dagger(\Gamma')\psi^\dagger(\Gamma), \tag{58}$$

where the operator I^α stands for summation and integration over all states *except* those belonging to the set α:

$$I^\alpha\equiv I-I_\alpha.$$

The right-hand side of (58) vanishes if there are no transitions between the set α and other sets (so that R vanishes when Γ belongs to α while Γ' does not), and is otherwise proportional to the probability of inter-set transitions. In fact the fractional difference between $[\tau\phi^\dagger\psi]_\alpha$ and $[\tau\psi^\dagger\phi]_\alpha$ is of the order of magnitude of the fraction of the transitions given by R which are inter-set transitions.

On the other hand, if an appreciable fraction of the transitions for the set α are to or from the other sets then w_α and $w^\dagger{}_\alpha$, defined by (57), no longer respectively give precisely the current contributed by the set α in the presence of a temperature gradient and the energy flux contributed by the set α in the presence of an electric field. The identification (56) has still a formal validity in that (17) is satisfied, but it is inappropriate physically in that (16) is then not consistent with (7) and (8). To see that the values of w_α and $w^\dagger{}_\alpha$ deviate, in proportion to the probability of inter-set transitions, from those corresponding to the physical meaning (56) which we would like to attribute to w_α and $w^\dagger{}_\alpha$, we observe that the generalization of (36) for an arbitrary set α of states is

$$I_\alpha f_1\psi+I_\alpha g\tau\psi^\dagger=\{I^\alpha(\Gamma)I_\alpha(\Gamma')$$
$$-I_\alpha(\Gamma)I^\alpha(\Gamma')\}f_1(\Gamma)T(\Gamma;\,\Gamma')\tau(\Gamma')\psi^\dagger(\Gamma'). \tag{59}$$

The right-hand side of (59) vanishes for the same condition as for the vanishing of the right-hand side of (58). Thus if we carry through the argument leading to the equations, corresponding to (38) and (39), for the contributions from the set α to $\mathbf{N}$ and $\mathbf{W}_{\text{elec.}}$ we will find additional terms on the right originating from the right-hand side of (59) and proportional to the probability of transitions into and out of the set. Consideration of the forms of the right-hand sides of (58) and (59) indicates that there is not a general condition for them to cancel each other out so that (19) is satisfied. If inter-set transitions occur then in general (19) is not satisfied. The situation disclosed is similar to that concerning the calculation of the thermoelectric coefficients, and the formulation of the Kelvin relations, when the phonon drag effect is appreciable.[20] The further analysis of this situation is beyond the scope of the present paper. The conclusion we note for the purposes of the present paper is that the convenient relations (19) for the phenomenological theory are approached closest *when the sets into which the one-electron states are divided are such that transitions between them have the least probability.*

The criterion which we have arrived at, for choosing the sets of electron states to be treated phenomenologically as acting together in "bands," is the one which would be suggested by intuition. It is, also, likely to be satisfied when the sets chosen coincide with the *Bloch* bands of the one-electron theory, since transitions within these bands are normally more probable than transitions between them. The selection rules and matrix elements for transitions are governed by the symmetry of the wavefunctions of the initial state and the final state, and the classification of the one-electron wave functions into Bloch bands is actually a classification by symmetry. Generally the intra-band tran-

sitions entail emission or absorption of a phonon. On the other hand, transitions *between* bands separated by a forbidden gap of more than the maximum lattice-mode quantum energy will entail emission or absorption of a photon, and be much less frequent. Inter-band transitions by phonon absorption or emission are thought to occur between the degenerate pair of valence bands in germanium, and to amount to an appreciable fraction of the relaxation processes for either band.[21] However, since they have a common band-edge point it should anyhow be more reasonable and convenient to combine these bands for the present purpose, treating the states belonging to them as a single set which is to be identified with one of the phenomenological bands of Section 2. On the other hand, it would be natural to divide up the states of the conduction band of germanium into sets each belonging to one of the "valleys" of the energy function[22] and to treat each set as a phenomenological band. Each such band taken separately does not have cubic symmetry and hence their contributions to the thermoelectric crossterms of the fluxes (38) and (39) *in the direction of the electric field and temperature gradient* would not be all equal, and hence there should be a contribution to the right-hand side of (17) in spite of the equivalence of the valleys. It is believed that inter-valley transitions are an appreciable fraction—though not the majority—of all relaxation processes for any one of the valleys,[23] so that (20) would not be valid and allowance should be made for the departure from (19).

5. Further discussion and applications

We consider first the condition for validity, and the consequences, of (43). Eq. (41) may be rewritten, making use of (47), as

$$\chi-\frac{[\tau\mathbf{v}\cdot\mathbf{v}^\dagger(\epsilon-w)^2]}{(kT)^2[\tau\mathbf{v}\cdot\mathbf{v}^\dagger]}=\frac{[\tau(\epsilon-w)\mathbf{v}\cdot((\mathbf{v}\epsilon)^\dagger-\mathbf{v}^\dagger\epsilon)]}{(kT)^2[\tau\mathbf{v}\cdot\mathbf{v}^\dagger]}, \tag{60}$$

where the second term on the left is the expression (43) and the right-hand side is the possible correction in which we are now interested. (The second term of the factor $\epsilon-w$ on the right is arbitrary, in the sense that, by (45) and (47), adding any constant to this factor would not change the value of the numerator. The motive for the choice of the form $\epsilon-w$ is to facilitate the reasoning leading to (63).) In discussing this correction it is convenient to adopt an abbreviated notation for the operator acting on $\psi^\dagger$ in the second term on the left of (35), such that (35) reads

$$(1-\mathcal{O})\psi^\dagger=\psi.$$

Then, for arbitrary functions $\phi(\Gamma)$, $\psi(\Gamma)$,

$$(1-\mathcal{O})((\phi\psi)^\dagger-\psi^\dagger\phi)=\mathcal{O}\psi^\dagger\phi-\phi\mathcal{O}\psi^\dagger.$$

In particular,

$$(1-\mathcal{O})((\mathbf{v}\epsilon)^\dagger-\mathbf{v}^\dagger\epsilon)$$
$$=I(\Gamma')T(\Gamma;\Gamma')\tau(\Gamma')(\epsilon(\Gamma')-\epsilon(\Gamma))\mathbf{v}^\dagger(\Gamma'). \tag{61}$$

If the scattering is elastic, the right-hand side of (61) vanishes. Then $(\mathbf{v}\epsilon)^\dagger$ and $\mathbf{v}^\dagger\epsilon$ can differ only by a *vector* function of Γ which is nullified by the operator $1-\mathcal{O}$. In general such does not exist, and so we arrive at (42). If the scattering is not quite elastic, the order of magnitude of (61) is $\mathbf{v}^\dagger$ times that of the average change in energy on scattering from the state Γ. This should then also be the order of magnitude of $(\mathbf{v}\epsilon)^\dagger-\mathbf{v}^\dagger\epsilon$. Consequently, if we define $\epsilon^*(\Gamma)$ by

$$\mathbf{v}\cdot((\mathbf{v}\epsilon)^\dagger-\mathbf{v}^\dagger\epsilon)\equiv\epsilon^*\mathbf{v}\cdot\mathbf{v}^\dagger, \tag{62}$$

then ϵ^* should be of the order of magnitude of the changes in energy on scattering. Let us consider now the situation where (as normally in a metal or extrinsic semiconductor) substantially all the contributions to the sum-integrals of (60) come from a single range of allowed values of ϵ, and hence from a range $\sim kT$ in extent. The numerator on the right of (60) vanishes if ϵ^* is constant, and otherwise will be of order of magnitude $(kT)^2[\tau\mathbf{v}\cdot\mathbf{v}^\dagger]$ times the order of magnitude of $d\epsilon^*/d\epsilon$ in this range, where the bar over ϵ^* signifies averaging in the usual way over all values of Γ for a given electron energy ϵ. Hence

$$\chi-\frac{[\tau\mathbf{v}\cdot\mathbf{v}^\dagger(\epsilon-w)^2]}{(kT)^2[\tau\mathbf{v}\cdot\mathbf{v}^\dagger]}\sim\frac{d\overline{\epsilon^*}}{d\epsilon}\sim\frac{\overline{\epsilon^*}}{kT}\quad, \tag{63}$$

the right-hand side being understood to be evaluated in the range of ϵ contributing substantially all the conduction. The condition for the correction to (43) to be small is evidently that $\epsilon^*\ll kT$.

The single type of scattering process whose consequences it is the most important to understand in the present connection is absorption or emission of a Debye phonon. If the velocity of these is s, the change of electron energy is $\pm s|\mathbf{p}'-\mathbf{p}|$. For a metal normally the lengths of the wavevectors, $\mathbf{p}/\hbar$, of the electron states contributing to conduction are of the order of magnitude of the inverse of a lattice constant. The change in electron energy on scattering is hence $\sim k\theta$, where θ is the Debye temperature, unless $T\ll\theta$. Since scattering with a change in energy large compared with kT is in general improbable, if $T\ll\theta$ the change in energy is $\sim kT$. (What then happens is that for nearly all the scattering the angle between $\mathbf{p}'$ and $\mathbf{p}$ is small.) Hence if $T\ll\theta$ the right-hand side of (63) is of order unity and cannot be neglected (except compared to an anomalous large contribution, which is not in question here), but if $T\gg\theta$ it is $\sim\theta/T$ and may be neglected. Similar considerations for an extrinsic semiconductor with a non-degenerate band ($f_0\ll 1$ or $1-f_0\ll 1$) lead to the conclusion that in this case (63) is small except at the very low temperatures of order ms^2/k or less (where anyhow other types of scattering process will be dominant). Evidently anomalously *large* values of χ are likely to arise as a consequence of (43), and hence are to be explained in terms of it rather than by deviations from it.

We now consider the possible values of χ predicted by (43) for various cases. It is useful to write the sum-integrals as simple integrals with ϵ as the variable, by introducing a factor $G(\epsilon)$ such that $G\delta\epsilon$ is the number of electron states, per unit volume of the crystal, in the infinitesimal range $\delta\epsilon$, and defining

$$\eta(\epsilon) \equiv \overline{\tau \mathbf{v} \cdot \mathbf{v}^{\dagger}}. \tag{64}$$

Then

$$-\frac{eQ}{k} = \frac{w-\zeta}{kT} = \frac{\int(\epsilon-\zeta)\eta G f_0(1-f_0)d\epsilon}{kT\int \eta G f_0(1-f_0)d\epsilon}, \tag{65}$$

$$\chi + \left(\frac{eQ}{k}\right)^2 = \frac{\int(\epsilon-\zeta)^2\eta G f_0(1-f_0)d\epsilon}{(kT)^2\int \eta G f_0(1-f_0)d\epsilon}, \tag{66}$$

where the integrals extend over all accessible levels for the electrons included in the system of one-electron states. If, as in metals, the range of energy ϵ contributing appreciably to the integrals of (65) and (66) is from many times kT less than ζ to many times kT greater than ζ, and if ηG does not vary appreciably over this range, then we may cancel out ηG from the integrals and take them from $-\infty$ to $+\infty$. To this approximation

$$\left.\begin{aligned} &(e/k)\,Q = 0; \\ &\chi = \int_{-\infty}^{\infty}(\epsilon-\zeta)^2 f_0(1-f_0)d\epsilon \Big/ (kT)^2 \int_{-\infty}^{\infty} f_0(1-f_0)d\epsilon \\ &= \pi^2/3 = 3.29. \end{aligned}\right\} \tag{67}$$

Thus we obtain the Sommerfeld value for χ. If the above conditions are relaxed to the extent that small but finite derivatives $(d^n\eta G/d\epsilon^n)_{\epsilon=\zeta}$ are admitted, then the right-hand side of (65) becomes a power series in the odd derivatives times $(kT)^n$, the right-hand side of (66) in the even derivatives times $(kT)^n$. With a few exceptions (such as bismuth and some metal alloys) even the leading terms of these series (of course excluding the term of (66) with $n=0$) are small at ordinary temperatures. Normally (but see the next paragraph) the term of degree n is of order $(kT/|\zeta-\epsilon_0|)^n$, where ϵ_0 is a band-edge energy and $|\zeta-\epsilon_0| \sim$ an ev, but exceptions can occur where the Fermi energy ζ is very near the sharp minimum in G which occurs when the allowed energy ranges of two bands just slightly overlap.

Appreciable values for the right-hand side of (66) can be foreseen to occur for metals when $T \ll \theta$, though of course in this case (66) is not accurately true. As explained above, in this case the change in energy for phonon scattering is $\sim kT$. Consequently the second factor on the right of (31) will in general differ appreciably from unity when the first factor is nonzero. It is possible to infer qualitative features of the function $\lambda(\Gamma)$, defined to be such that the value of (32) is $1/\lambda$ times what it would have been if this second factor on the right of (31) had not been present, from the order of magnitude of the changes of electron energy on scattering. As $\epsilon-\zeta$ increases from minus a few times kT to plus a few times kT, λ increases from a value less than one to a maximum greater than one (for $\epsilon-\zeta \sim +kT$) and finally tends to one for $\epsilon-\zeta$ several times kT. Thus the effect on the integrals of (65) and (66) is to tend to cut off the half of the range of integration for which $\epsilon < \zeta$, and to make ηG a maximum, with $d^2(\eta G)/d\epsilon^2 \sim -(kT)^{-2}$, at $\epsilon-\zeta \simeq kT$. Consequently the contribution to χ on the left of (60) is reduced below the Sommerfeld value. The right-hand side of (60) is negative, according to the discussion of it above, and hence acts in the same direction to decrease χ below the Sommerfeld value.

From the foregoing discussion it may be concluded that in metals for $T \ll \theta$, if the scattering is by emission and absorption of phonons, χ should in general be substantially less than $\pi^2/3$. This result is a long-standing one of the theory of metals, and is confirmed by experiment.[24] The purpose of the discussion here was to give an insight, from the point of view of the present paper, into the origin of the result, and to suggest—though of course on a far from rigorous basis—that it is generic to inelastic scattering rather than an "accidental" outcome of the mathematically elaborate theories for specific actual metals. At still lower temperatures the dominant relaxation process in practice is scattering by impurities. It is customary to assume that this scattering is *elastic*. Then (a), Eq. (66) is rigorously correct (provided the phonon drag effect is negligible); and (b), the second factor on the right of (31) is rigorously equal to unity, and we may hence again expect ηG to vary very little over a range $\sim kT$ about $\epsilon = \zeta$ and in any case, so far as the one-electron model itself is a good approximation, to vary at a rate independent of T. Hence

$$\chi - \pi^2/3 \simeq (kT/\Delta_1)^2, \tag{68}$$

where normally, as for $T \gg \theta$, $\Delta_1 \sim |\zeta-\epsilon_0|$. This prediction (68) of the standard theory is also confirmed by experiment.[24] It is found that as T decreases from values $\sim\theta$ the value of χ decreases to a minimum and increases again towards $\pi^2/3$.

For semiconductors, so far as the phonon drag effect may be neglected, (43) or (66) is the general result of the one-electron model except at the very lowest temperatures.[25] However, the results (67) are *not* valid, even for an extrinsic semiconductor, because G and η vary strongly over the states contributing to conduction. For an extrinsic semiconductor it is convenient to write (43) in the form

$$\chi = \frac{\int(\epsilon-\epsilon_0)^2\eta G f_0(1-f_0)d\epsilon}{(kT)^2\int \eta G f_0(1-f_0)d\epsilon} - \left\{\frac{\int(\epsilon-\epsilon_0)\eta G f_0(1-f_0)d\epsilon}{kT\int \eta G f_0(1-f_0)d\epsilon}\right\}^2, \tag{69}$$

where ϵ_0 is the band-edge energy, rather than in the form (66). The value of χ depends altogether on the particular dependence of η and G on $\epsilon-\epsilon_0$. It is normally—not always—correct to take G to be proportional to $(\pm(\epsilon-\epsilon_0))^{1/2}$. The standard theory of the scattering leads to the result[26] that η is also proportional to $(\pm(\epsilon-\epsilon_0))^{1/2}$. Then ηG is proportional to $\pm(\epsilon-\epsilon_0)$: this dependence is assumed in deriving (70) and (71). If the Fermi level is many times kT beyond the band-edge on the "forbidden" side, the distribution is non-degenerate,

$$f_0(1-f_0) \simeq \exp\{\pm(\zeta-\epsilon_0)/kT\},$$

and (69) gives the standard result

$$\chi = 3! - (2!)^2 = 2. \tag{70}$$

As the Fermi level moves into the band, the value of χ changes from that given by (70) to that given by (67). At the intermediate point where $\zeta = \epsilon_0$, we have from (69)

$$\left.\begin{aligned} \frac{e}{k}Q &= \frac{\zeta(2)}{\ln 2} = 2.36; \\ \chi &= \frac{9\zeta(3)/2}{\ln 2} - \left(\frac{\zeta(2)}{\ln 2}\right)^2 = 2.23. \end{aligned}\right\} \tag{71}$$

(Here $\zeta(n)$ is the Riemann function.)

From the account given by Ioffé[1] of the results of Devyatkova[2] on n-PbTe, χ was 1.9 in the non-degenerate state and increased to a limit of 2.7 on doping to the degenerate state.[27] These results, when compared with (67), (70) and (71), indicate that in the "degenerate" state $\zeta-\epsilon_0$ was of order kT (perhaps several times kT) rather than $\gg kT$. This conclusion is consistent with the figure quoted by Ioffé for the electron density and the assumption that G was roughly equal to $2\pi(2m/h^2)^{3/2}(\epsilon-\epsilon_0)^{1/2}$. It is necessary, however, to account for the evident tendency (see Fig. 8 of Ioffé, reference 1) for χ to approach a limiting value, for high doping, substantially less than the Sommerfeld value. Now, provided the donor states, because of the strength of the mutual interaction of donor electron orbitals, form part of the system of one-electron states, so that (even if there is no compensation) they can by themselves accomodate twice as many electrons as the donors introduce, the Fermi level cannot rise above the uppermost of these donor-derived levels. It is a plausible assumption, in these conditions, that the resulting contribution ($G_d(\epsilon)$, say) to the density-of-states function should overlap the contribution ($G-G_d\equiv G_0(\epsilon)$, say) of the undoped substance, so as to form a single continuous spectrum. If the energy range of G_d were of order kT, the condition $\zeta-\epsilon_0\sim kT$ would then be realized. It might not be reasonable, however, to assume that the curve of G would be thus "fattened up" without being distorted. It may be, on the other hand, that there was only a small overlap of the G_d and G_0 spectra, so that the donor-derived levels formed a tail to the main distribution, with $d(\eta G_d)/d\varepsilon<1$. It would be interesting to know whether the thermoelectric power did or did not become small compared to k/e in the high-conductivity limit.

In terms of (65), (66), the conditions for the bipolar anomaly are that there be a "forbidden" energy range in which ηG is zero or very small, separating two ranges of finite ηG by an energy large compared to kT, and that the Fermi level lie in the middle of the forbidden range so that the contributions to the conductivity come not from energies $\epsilon\simeq\zeta$ but from the "wings" of the curve of $f_0(1-f_0)$ where $|\epsilon-\zeta|\gg kT$. The second moment of the function $\eta G f_0(1-f_0)$ of ϵ is then large compared to $(kT)^2$ if the actual position of the Fermi level is such that the two contributions to the conductivity σ are comparable. It is possible, at least in principle, for this situation to be inverted so that χ according to (66) is *small* compared to one. The requirement is for the conduction to arise from a single range—of width Δ, say—of finite ηG, with forbidden gaps of width $\gg kT$ above and below it. Then χ must be less than$(\Delta/kT)^2$, and hence if these conditions can be maintained when $T\gg\Delta/k$ then χ must become $\ll 1$. The point which the foregoing discussion is intended to bring out is that determination of Q and Λ may serve as a crude "spectrometer" in giving information about the distribution of electron levels with η, the measure of their contributions to σ, as weighting factor.

6. Possible generalizations

In the one-electron theory of Sections 3 and 4, the Lorenz number was related to the mean square fluctuation of ϵ over the levels, with the mobility factor η giving their relative weight. This result failed to hold just in the conditions which might have been expected—when the magnitude of the energy change on scattering was great enough for the resulting loss of definition of the energy of the electrons taking part in conduction to be appreciable relative to the root mean square fluctuation of the energy. The form of the result suggests that it is not just a special one for the one-electron model but has a "thermodynamic" generality; and this suspicion is somewhat born out by the fact that the result of the same form arrived at in Section 2 does not depend on the one-electron model for validity, but only on the Kelvin relations (19) for the phenomenological "bands" of the model. Many-electron correlations within these would not in themselves make (20) fail. If, however, the result (43) derives from one of such a generality then at least it ought to refer, in terms of the one-electron model, to averages over γ-space rather than over μ-space.[28] That this is a reasonable interpretation of the actual result is shown by the following consideration: Let us label the levels in μ-space by subscripts i, j, etc. and set $z_i\equiv\exp\{(\zeta-\epsilon_i)/kT\}$. If $\nu_i=0$ or 1 is the occupation of the i'th level, then

$$((\nu_i))=z_i/(1+z_i)\equiv f_0, \tag{72}$$

where the double bracket (( )) denotes an average over the grand canonical ensemble. Let A and B be two magnitudes of form

$$A\equiv\Sigma_i a_i\nu_i,\ B\equiv\Sigma_i b_i\nu_i. \tag{73}$$

Then it is easily shown that

$$\begin{aligned}((AB))-((A))((B)) \\ =\Sigma_i a_i b_i\{((\nu_i))-((\nu_i))^2\}=Iabf_0(1-f_0).\end{aligned} \tag{74}$$

Thus the substitution of the factor $f_0(1-f_0)$ for the factor f_0, in the averages $If_0(1-f_0)\ldots$ which give the relation of fluxes to forces in the linear transport theory, is just the change which appears, for Fermi statistics, in going from a correlation in μ-space to one in γ-space. We cannot apply this result literally to (43), to justify the proposed interpretation, because the factor $\tau^*\equiv\tau\mathbf{v}\cdot\mathbf{v}^\dagger/v^2$ is by its nature defined for μ-space, not for γ-space.

The same considerations apply to the remaining part of the thermal conductivity, K_0, where this comes from phonons, excitons, and plasmons which do not interact appreciably. These are localizable "particles" (with crystal momentum $\mathbf{p}$, energy ϵ and velocity $\mathbf{v}=\partial\epsilon/\partial\mathbf{p}$) which are bosons whose number is not conserved in certain allowed transitions which occur among the relaxation processes. The equilibrium distribution function $N_0(\epsilon)$ is therefore the Planck function; and there will be a Boltzmann equa-

tion, for the effect of a temperature gradient, which can be linearized to an equation corresponding to eq. (24) but for $N_1 \equiv N - N_0$ rather than for f_1. If, to save trouble consistently with the present purpose, we write the rate of relaxation of N_1, corresponding to the left-hand side of (24), as $-N_1/\tau$, then we find

$$K_0 = (1/3kT^2)h^{-3} I\, \tau |\mathbf{v}\epsilon|^2 N_0(1+N_0). \tag{75}$$

Here the operator I stands for integration over **p**-space and summation over indices specifying the nature of the excitation (phonon, etc.), and direction of polarization, mode of vibration, spin state, etc. The result (75) differs from the corresponding one for electrons in that the factor $N_0(1+N_0)$ replaces $f_0(1-f_0)$. The fluctuation formula corresponding to (74), on the other hand, differs from (74) in just the same way: $N_0(1+N_0)$ replaces $f_0(1-f_0)$ on the right-hand side. Thus the right-hand side of (75) also may be interpreted as expressing a contribution to the thermal conductivity in terms of the square fluctuation of the energy flux for the "γ-space" ensemble, except that there is the same difficulty over the factor τ.

Presumably this difficulty could be resolved by formulating a Boltzmann equation for the localized many-particle distribution function, instead of for the localized reduced one-particle function, and solving it for thermal conduction. If interactions between the particles need not be excluded,[29] it might be possible to establish in its general form the conclusion suggested here: that the thermal conductivity can be expressed—by a formula corresponding to those arrived at here but involving the complete set of microscopic variables of the whole system—in terms of the square fluctuation, weighted by the relaxation time for the energy flux as a function of the microscopic variables, of the energy flux.[30] Kubo[31] has given a formula for the *electrical* conductivity which seems to satisfy just this prescription, and he remarks[32] that a formula similar to his exists for thermal conductivity. Kubo's formula involves a time correlation rather than a relaxation time, and hence, as he points out, recalls the general theories of noise and Brownian motion.

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References and footnotes

1. For a recent review of this question (including an account of the work of the Leningrad school, which only recently became generally accessible in the non-Soviet world) see A. F. Ioffé, Proceedings of the Ottawa Conference, Canadian Journal of Physics **34**, no. 12A, 1342 (December 1956). See also reference 4 here, and the papers by Busch and Schneider and by Fröhlich and Kittel in the Proceedings of the Amsterdam Conference, Physica **20**, 1084 (1954).
2. The dependence of K on σ, corresponding to eq. (2), for a semiconductor has been demonstrated by Devyatkova by measurements of K over a range of impurity concentrations, and hence over a range of values of σ, at a fixed temperature, for PbTe. See Fig. 8 (page 1348) of the article by Ioffé, reference 1, for the resulting curve of K *versus* σ.
3. Davydov and Shmushkevich, Uspekhi Fiz. Nauk **24**, 21 (1940). [This reference is taken from Ioffé, reference 1. For a more accessible account of the theory see P. J. Price, Phil Mag. **46**, 1252 (1955).]
4. The case of Bi_2Te_3. See H. J. Goldsmid, Proc. Phys. Soc. **B69**, 203 (1956); P. J. Price, Proc. Phys. Soc. **B69**, 851 (1956).
5. The treatment here is comparable to that given, in a somewhat different formulation, for two bands by J. Tauc, Czech. J. Phys. **6**, 108 (1956), Section 6, except that he assumes the relations (19) from the beginning. See also reference 13, chapter 8.
6. P. J. Price, Phys. Rev. **104**, 1223 (1956), Section 1.
7. This value may be considerably enhanced by the phonon drag effect.
8. See, for example, E. O. Kane, J. Phys. Chem. Solids **1**, 82 (1956).
9. If the doping went so far that band (a) became degenerate, the effective value of Δ_{s0} in (21) would be reduced, but also the value of σ_b/σ_a would be less than that given by (22) with the new effective value of Δ_{s0}.
10. It has been found possible, for example, to grow lead telluride with high enough electrical conductivity for $\Lambda\ T\sigma$ to exceed K_0 even though the value of χ was not anomalous. (See footnote 2.)
11. See, for example, R. E. Peierls, *Quantum Theory of Solids*, Clarendon Press, Oxford 1955, Chapters IV and VI.
12. This equation (24) presupposes that the electron energy function $\epsilon(\mathbf{p}, q)$ does not depend on temperature, and this restriction may impose a serious limitation on the applicability of the theory given here. For a partial and rather arbitrary discussion of the question of the influence of variation of ϵ with temperature on the transport effects, see reference 6, Section 2c.
13. See, for example, S. R. de Groot, *Thermodynamics of Irreversible Processes*, North-Holland Publishing Co., Amsterdam 1951, § 64.
14. In the present case the latter are all terms in f_0, but in the presence of a magnetic field **H** there would also be a term proportional to **H** and to f_1.
15. These results are the natural generalizations of the primitive theory in which the left-hand side of (29) is replaced by $-f_1/\tau$. The factor $\mathbf{v}\cdot\mathbf{v}\dagger/v^2$ in (38) for cubic symmetry, for example, is the general correction in this case for "persistence of velocities": for elastic scattering, if τ is a function of ϵ only in its dependence on **p**, it reduces to an expression which is essentially the well known Lorentz correction. The effects of a magnetic field (Hall, Nernst, Righi-Leduc) may be included by a somewhat more elaborate application of the same methods. For Boltzmann statistics (f_0 or $1-f_0$ very small) the same approach, making use of (35), may be used to generalize the results for the linear case to the case of an indefinitely large electric field. The reformulation of the Bloch equations for conduction in metals which was suggested by Dingle, Physica **22**, 698 (1956), somewhat resembles the method described here. However, Dingle defines relaxation times differing according to the nature of the *force*, whereas if the results of my method are put in terms of equivalent relaxation times the latter differ according to the nature of the *flux*. The relaxation time defined by eq. (32) here always

"exists," but the relations between it and the coefficients of the transport effects according to the primitive theory are not correct in general.
16. C. Herring, Phys. Rev. **96,** 1163 (1954).
17. Reference 13, chapters 1, 4, and 8.
18. For a discussion of the thermodynamics of thermoelectricity in anisotropic substances see C. A. Domenicali, Rev. Mod. Phys. **26,** 237 (1954).
19. As has been emphasized, the proof here depends on the assumption that there is no appreciable phonon drag effect. Sondheimer[20] has given a proof which allows for the influence on f_1 of the disturbance of the phonon distribution, and includes the contribution to Π from the flux of phonon energy. However, his proof is for a model in which the only relaxation processes for phonons are those, due to coupling of electron and lattice states, in which an electron is deflected (scattered) in course of the emission or absorption of a phonon. This model, from which other phonon relaxation processes are excluded, represents a system which *would never reach a steady state* in the presence of transport "driving forces" (such as an electric field), though it may be imagined to apply to an ideal system in which the other relaxation processes were too weak to affect the values of the thermoelectric coefficients appreciably but still present and serving to ensure a steady state. Sondheimer's criticism of some published theories of the phonon drag effect—that they give results, for the thermoelectric coefficients, which do not satisfy the Kelvin relation—retains its cogency although these theories do attempt to take into account other phonon relaxation processes and hence are based on more realistic models to which his proof of the Kelvin relation does not apply.
20. E. H. Sondheimer, Proc. Roy. Soc. **A234,** 391 (1956).
21. H. Ehrenreich and A. W. Overhauser, Phys. Rev. **104,** 331 (1956).
22. C. Herring, Bell System Tech. J. **34,** 237 (1955).
23. W. P. Dumke, Phys. Rev. **101,** 531 (1956).
24. A. H. Wilson, *The Theory of Metals*, Cambridge University Press, Second Ed., 1953, Section 9.7.
25. Scattering by phonons can, however, become sufficiently inelastic to cause appreciable deviations from (66) at temperatures much greater than ms^2/k if the electron distribution becomes degenerate (as it always does in practice for *n*-InSb, for example).
26. This relationship occurs much more frequently in the literature of the transport effects of semiconductors than in nature.
27. Ioffé quotes 1.92 and 3 respectively, but from the data he gives in his Fig. 8 it is evident that the ratio of the values of χ in the high-conductivity and low-conductivity limits is 2.7/1.9. Absolute values of χ for each limit cannot be deduced directly from the data because the temperature is not given.
28. Here "μ-space" and "γ-space" are used with the conventional meanings, and so it is the *former* which is "Γ-space" in the notation of this paper.
29. See for example H. S. Green, *The Molecular Theory of Fluids*, Interscience Publishers, New York 1952.
30. The following, admittedly vague, conclusion seems worth pointing out as an immediate application of this hypothesis: the phonon drag effect should increase the thermal conductivity, since it will cause a positive correlation between the lattice and electron contributions to the energy flux. (The increase presumably is relative to the value K would have if (a) f_1 were the solution of the Boltzmann equation when the scattering function S is as it would be if N_1 were zero, while (b) conversely N_1 had the values it would have if f_1 were zero.) Just the same conclusion was arrived at in Section 2, in terms of the phenomenological theory, for the bipolar effect (see footnote 7).
31. R. Kubo, Proceedings of the Ottawa Conference, Canadian Journal of Physics **34,** no. 12A, 1274 (December 1956).
32. Reference 31, note (8).

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