P. J. Price

The Linear Hall Effect

Abstract: A new method for handling the Boltzmann equation is used to obtain, without approximation, a general formula for the linear Hall effect in a solid electronic conductor. Expressions for the conductivity in no magnetic field and for the quadratic magnetoconductivity are also obtained. These formulas introduce a vector mean free path, not in general parallel to the electron velocity, which is related to the velocity by an integral equation. Some possible cases of the formula for the Hall effect are analyzed. The solution of the integral equation for the vector mean free path is discussed, and methods of approximation are proposed.

Contents

Introduction

The mathematical problem of the solution of the Boltzmann equation for the free electrons arose at the founding, by Drude and Lorentz, of the theory of electronic transport processes in solids; and it has remained a prominent aspect of solid state physics. While knowledge of the free states of the electrons, and of the scattering transitions between the states, was still very limited, crude methods of approximating the solution of the Boltzmann equation were appropriate. At the present time, however, detailed knowledge of the ingredients of the equation, for many metals and semiconductors, is growing up rapidly, and increasingly refined and extensive experimental data on the transport processes are being obtained. Accordingly there is an interest in more precise and more general mathematical methods.

The present paper describes an application to the galvanomagnetic effects of a method which was found useful originally in the theory of non-linear conduction (conduction in strong electric fields), but which evidently has a number of potential applications. The method is explained in a paper where it is used in the theory of thermal conduction by electrons.[1] (This paper will be referred to here as "LN.") The idea is to introduce a suitable integrating factor so that the Boltzmann equation integrates to give directly a formula for the flux (e. g. electric current) characterizing the transport effect. The intermediate step of solving for the electron distribution function, for the "force" (e. g., electric field) in question, is bypassed. The resulting formula gives the flux in terms of an average, over the *thermal* distribution f_0, of an expression containing a new unknown, the "conjugate" of the magnitude (e. g., electron velocity) measured by the flux. This conjugate is in turn given by an integral equation related to the Boltzmann equation. Something is gained in this exchange of mathematical problems, however:

a) The same conjugate is shared by more than one transport effect (for example, by zero-field conductivity and linear Hall effect: see Section 3).

b) A general expression, not subject to any approximations beyond those implicit in the Boltzmann equation itself, is obtained for the transport coefficient. From the form of this expression, physical insights and definite conclusions can be derived (see, for example, the discussion of the linear Hall effect for general crystal symmetry in Section 3).

c) The problem of solution of the equation for the conjugate is amenable to physical intuition in ways that the analysis of the original Boltzmann equation is not. In Section 5, a number of approaches to the problem of the calculation of the conjugate to the velocity are proposed: In particular, a minimum principle is used to obtain a generalization of a well-known formula for the effect of anisotropy in quasi-elastic scattering.

It is proposed to call this technique "the integral method."

In the present paper, formulas are obtained for the first three terms of the power series for the conductivity as a function of magnetic field: i. e. the terms proportional to the zero'th, first and second powers of the field. The formulas are completely general except that they assume that the diagonal elements of the reduced electron density matrix are given by the Boltzmann equation, and hence they depend for example on the applicability of the one-electron model. Therefore the present results might be modified by correlation phenomena and by the unknown influence of the effect which appears as a dependence of the electron levels on temperature. The formula for the third term of the expansion (magnetoconductivity), which is derived in Section 4, introduces a further "conjugate" which *in general* does not, apparently, reduce to an explicit function of the conjugate of the velocity. Thus it appears that the method does not lead, as the conventional relaxation-time approximation does,[2] to a formula for the conductivity in a magnetic field of arbitrary strength: This question has not, however, been studied further.

1. The phenomenological theory

The purpose of this section is to review the general phenomenological theory of conduction in the presence of a magnetic field, **H**, and to introduce the terminology and notation to be used. The phenomenological theory has been discussed by Juretschke,[3] by Okada,[4] and by Keyes,[5] who discuss in detail the situation for some specific crystal symmetries. The system of vector notation used here (which is similar to that of Keyes) is explained in the Appendix, where also some required formulas of vector algebra are stated.

The theory presented in this paper, like kinetic theories of transport effects generally, naturally yields formulas for the electric current **J** caused by a given electric field **E** (rather than **E** for a given **J**), and hence for the conductivity $\boldsymbol{\sigma}(\mathbf{H})$. The Onsager relation[6] for electrical conduction states that[7]

$$\boldsymbol{\sigma}(\mathbf{H})^{\sim}=\boldsymbol{\sigma}(-\mathbf{H}). \tag{1.1}$$

Therefore the symmetric part of $\boldsymbol{\sigma}$ is an even function, and the antisymmetric part an odd function, of **H**. It follows that we may write the antisymmetric part in the form

$$\hat{\boldsymbol{\sigma}}=\mathbf{H}\cdot\boldsymbol{\Phi}, \tag{1.2}$$

where the triadic $\boldsymbol{\Phi}$ is an even function of **H** and

$$\boldsymbol{\Phi}^{(2\sim 3)}=-\boldsymbol{\Phi}. \tag{1.3}$$

Then by Eq. (A2) of the Appendix we may express the conductivity in the form (A3):

$$\boldsymbol{\sigma}=\tilde{\boldsymbol{\sigma}}-\mathbf{H}\cdot\boldsymbol{\beta}\times\boldsymbol{\varepsilon}, \tag{1.4}$$

where

$$\boldsymbol{\beta}\equiv\tfrac{1}{2}\boldsymbol{\Phi}^{(2\times 3)}. \tag{1.5}$$

Since $\tilde{\boldsymbol{\sigma}}$ and $\boldsymbol{\beta}$ are even functions of **H**, the power series for them are of the form

$$\tilde{\boldsymbol{\sigma}}(\mathbf{H})=\boldsymbol{\sigma}(0)+\mathbf{HH}:\boldsymbol{\Psi}+\ldots\ldots, \tag{1.6}$$

$$\boldsymbol{\beta}(\mathbf{H})=\boldsymbol{\beta}(0)+\mathbf{HH}:\boldsymbol{\Omega}+\ldots\ldots. \tag{1.7}$$

In the following sections formulas for the first two terms of (1.6), and for the first term of (1.7), are derived from the first three terms of the expansion

$$\mathbf{J}=(\boldsymbol{\sigma}(0)+\mathbf{H}\cdot\boldsymbol{\Phi}(0)+\mathbf{HH}:\boldsymbol{\Psi}+\ldots..)\cdot\mathbf{E}. \tag{1.8}$$

According to (1.4), the relation between **J** and **E** is of form

$$\mathbf{J}=\tilde{\boldsymbol{\sigma}}\cdot\mathbf{E}-\mathbf{H}\cdot\boldsymbol{\beta}\times\mathbf{E}, \tag{1.9}$$

where the second term on the right expresses the Hall effect. The more conventional expression of the Hall effect is, however, by the second term of the inverse relation

$$\mathbf{E}=\tilde{\boldsymbol{\rho}}\cdot\mathbf{J}+\mathbf{H}\cdot\boldsymbol{\alpha}\times\mathbf{J}, \tag{1.10}$$

$\boldsymbol{\alpha}$ being the Hall constant. (Again, the appropriate Onsager relation requires that $\tilde{\boldsymbol{\rho}}$ and $\boldsymbol{\alpha}$ be even functions of **H**.) In practice it is the coefficients of (1.10), rather than those of (1.9), which are determined directly by measurements. Therefore it is important to have available the formulas which relate $\tilde{\boldsymbol{\rho}}$ and $\boldsymbol{\alpha}$ to $\tilde{\boldsymbol{\sigma}}$ and $\boldsymbol{\beta}$. These are given at once by (A5) and (A6), and are

$$\tilde{\boldsymbol{\rho}}=\frac{\tilde{\boldsymbol{\sigma}}^{-1}+\boldsymbol{\rho}^{H}}{1+\tilde{\boldsymbol{\sigma}}:\boldsymbol{\rho}^{H}}, \tag{1.11}$$

$$\boldsymbol{\alpha}=\frac{\boldsymbol{\beta}\cdot\tilde{\boldsymbol{\sigma}}}{D(1+\tilde{\boldsymbol{\sigma}}:\boldsymbol{\rho}^{H})}, \tag{1.12}$$

where

$$\boldsymbol{\rho}^{H}\equiv\mathbf{H}\cdot\boldsymbol{\beta}\;\mathbf{H}\cdot\boldsymbol{\beta}/D,$$

$$D\equiv\det.\ \tilde{\boldsymbol{\sigma}}\quad.$$

In zero magnetic field the Hall constant is

$$\boldsymbol{\alpha}(0)=\boldsymbol{\beta}(0)\cdot\boldsymbol{\sigma}(0)/D(0). \tag{1.13}$$

When $\boldsymbol{\alpha}=\alpha\boldsymbol{\varepsilon}$, and similarly for $\boldsymbol{\beta}$, $\tilde{\boldsymbol{\sigma}}$ and $\tilde{\boldsymbol{\rho}}$ (these are mutually consistent only for $\mathbf{H}=0$), then there is a unique scalar Hall mobility

$$\mu^H \equiv c\beta/\sigma. \tag{1.14}$$

In general, however, there is no unique way of defining a *dyadic* Hall mobility. It might be defined as $c\tilde{\boldsymbol{\sigma}}\cdot\boldsymbol{\alpha}$, or as $c\tilde{\boldsymbol{\rho}}\cdot\boldsymbol{\beta}$.

The Onsager relations do not require $\boldsymbol{\beta}$ (or $\boldsymbol{\alpha}$) to be symmetric. If, however, $\boldsymbol{\beta}$ is not symmetric then a vector

$$2\mathbf{s} \equiv \boldsymbol{\beta}^{(\times)} \tag{1.15}$$

may be formed from its elements; and $\mathbf{s}$ must be an even function of $\mathbf{H}$, since $\boldsymbol{\beta}$ is. Consequently $\mathbf{s}$ must correspond to an inherent polarity of the substance. If an antisymmetric component of $\boldsymbol{\beta}$ should exist in some conditions, then (1.9) could be written in the form

$$\mathbf{J} = \tilde{\boldsymbol{\sigma}}\cdot\mathbf{E} - \mathbf{H}\cdot\tilde{\boldsymbol{\beta}}\times\mathbf{E} + (\mathbf{H}\times\mathbf{s})\times\mathbf{E}. \tag{1.16}$$

The contribution from the third term of (1.16) might be referred to as a "polar Hall effect."

2. General results for galvanomagnetic effects

In this section some general results, to be applied in the following sections, for galvanomagnetic transport phenomena will be derived. The notation and method are as explained in Section 3 of LN. The distribution function for the electrons is supposed to be expanded in a series

$$f = f_0 + f_1 + f_2 + \ldots\ldots \tag{2.1}$$

such that f_n is proportional to the n'th power of the driving force, which in the present case is the electric field $\mathbf{E}$. Then from the fundamental Boltzmann equation we obtain a linear inhomogeneous equation for f_1 in terms of f_0, the Fermi distribution function:

$$\mathfrak{D}_0 f_1 + \frac{e}{c}(\mathbf{v}\times\mathbf{H})\cdot\frac{\partial f_1}{\partial \mathbf{p}} = \left(\frac{e}{kT}\right)\mathbf{E}\cdot\mathbf{v}f_0(1-f_0), \tag{2.2}$$

where the linearized relaxation operator $\mathfrak{D}_0$ is given by

$$\mathfrak{D}_0 g(\Gamma) \equiv I(\Gamma')\left\{g(\Gamma')T(\Gamma';\Gamma) - g(\Gamma)T(\Gamma;\Gamma')\right\}. \tag{2.3}$$

Here Γ stands for all the variables specifying the electron state and $I(\Gamma)$ for integration, $\int d^3\mathbf{p}\ldots\ldots$, over pseudo-momentum together with summation over the other variables, band index q and an electron spin component ϑ.[8] The charge of the electron is $-e$, ϵ is its (Hartree-Fock) energy, and $\mathbf{v}$ is its group velocity $\partial\epsilon/\partial\mathbf{p}$. The collision function $T(\Gamma;\Gamma')$ is the usual one, $S(\Gamma;\Gamma')$ (see eq. (24) of LN), with a "correction" for Fermi statistics (for when f_0 is not $\ll 1$), and is defined by eq. (30) of LN. In the conditions for which (2.18) and (5.4) hold, T is given by eq. (31) of LN:

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

As in LN we define the relaxation time, τ, by the equation

$$\frac{1}{\tau} \equiv I(\Gamma')T(\Gamma;\Gamma'), \tag{2.4}$$

and we define for any function $\psi(\Gamma)$ a conjugate function, $\psi^\dagger(\Gamma)$, by the equation[9]

$$\psi^\dagger(\Gamma) - I(\Gamma')T(\Gamma;\Gamma')\tau(\Gamma')\psi^\dagger(\Gamma') = \psi(\Gamma). \tag{2.5}$$

The following consequence of (2.4) and (2.5) is the fundamental theorem of the integral method: if $\psi(\Gamma)$ and $g(\Gamma)$ are any functions such that the double sum-integrals involved are uniformly convergent, then

$$I\,\psi g = -I\,\psi^\dagger\tau\mathfrak{D}_0 g. \tag{2.6}$$

The use of the theorem is illustrated by the applications in the following sections and in LN.

To obtain the required results we further expand f_1 in a series

$$f_1 = f_{1,0} + f_{1,1} + f_{1,2} + \ldots\ldots \tag{2.7}$$

such that $f_{1,m}$ is proportional to the m'th power of $\mathbf{H}$, and set up corresponding series for the electric current density $\mathbf{J} = -eh^{-3}I\,\mathbf{v}f$, so that

$$\mathbf{J}^{(n,m)} = -eh^{-3}I\,\mathbf{v}f_{n,m}. \tag{2.8}$$

We seek to calculate $\mathbf{J}^{(1,0)}$, $\mathbf{J}^{(1,1)}$ (Section 3) and $\mathbf{J}^{(1,2)}$ (Section 4), and hence are concerned with $f_{1,0}$, $f_{1,1}$ and $f_{1,2}$. From (2.2) we find

$$\mathfrak{D}_0 f_{1,0} = (e/kT)\mathbf{E}\cdot\mathbf{v}f_0(1-f_0); \tag{2.9}$$

$$\mathfrak{D}_0 f_{1,m} = (e/c)\mathbf{H}\cdot\mathbf{g}f_{1,m-1}, \qquad m \geqslant 1. \tag{2.10}$$

Here the differential operator $\mathbf{g}$ is the same as[10] Herring's $\boldsymbol{\gamma}$ and Wilson's $\boldsymbol{\Omega}/\hbar^2$:

$$\mathbf{g} \equiv \mathbf{v}\times\partial/\partial\mathbf{p}, \tag{2.11}$$

and hence

$$(\mathbf{v}\times\mathbf{H})\cdot\partial/\partial\mathbf{p} = -\mathbf{H}\cdot\mathbf{g}.$$

The result of operating with $\mathbf{g}$ on a magnitude which depends on $\mathbf{p}$ only through being a function of ϵ is zero. For example, $\mathbf{g}f_0 = 0$. Also, as may be shown by "integration by parts",[11]

$$I\,\phi(\mathbf{g}\psi) = -I\,\psi(\mathbf{g}\phi). \tag{2.12}$$

From these two rules follows the further result

$$[\phi\,\mathbf{g}\,\psi] = -[\psi\,\mathbf{g}\,\phi], \tag{2.13}$$

where, as in LN, we introduce the convenient "square bracket" notation

$$h^{-3}If_0(1-f_0)\psi \equiv [\psi]. \tag{2.14}$$

A "flux" for the electron distribution disturbed by the driving force $\mathbf{E}$ has the form of the density, $h^{-3}I\psi f$, of a one-electron magnitude $\psi(\Gamma)$. To calculate the term $h^{-3}I\psi f_{1,m}$, we make use of the foregoing results to transform it to an expression of form $h^{-3}I\psi' f_{1,m-1}$, hence in turn to one of form $h^{-3}I\psi'' f_{1,m-2}$, and so on down a ladder ending with an expression of the form (2.14). For the final stage, we apply the general result obtained by substituting (2.6) in (2.9) with $g = f_{1,0}$:

$$I\psi f_{1,0} = -(e/kT)\mathbf{E}\cdot If_0(1-f_0)\mathbf{v}\tau\psi^\dagger. \tag{2.15}$$

From (2.8) with $m=0$ and (2.15) we have, for the conductivity in zero magnetic field,

$$\boldsymbol{\sigma}(0)=\tilde{\boldsymbol{\sigma}}(0)=(e^2/kT)[\,\mathbf{l}\ \mathbf{v}\,], \tag{2.16}$$

where

$$\mathbf{l}\equiv\mathbf{v}^\dagger\tau. \tag{2.17}$$

The vector $\mathbf{l}$ may be called the mean free path for electric currents. It was shown in LN that if the crystal substrate which scatters the electrons is in thermal equilibrium, so that the detailed balance theorem applies to the electron state without reference to any other variables, then

$$[\psi\tau\phi^\dagger]=[\phi\tau\psi^\dagger]. \tag{2.18}$$

It follows from (2.17) and (2.18) that $[\mathbf{lv}]=[\mathbf{vl}]$: that the dyadic (2.16) actually is symmetric, and hence that the result obtained here for $\boldsymbol{\sigma}$ in zero magnetic field satisfies the Onsager relation (1.1). The other Onsager relations for electric current and heat current in zero magnetic field were also found in LN to be consequences of (2.18).

By applying (2.18) to (2.15) we obtain the formula

$$h^{-3}I\psi f_{1,0}=-(e/kT)[\,\psi\ \mathbf{l}\,]\cdot\mathbf{E}. \tag{2.19}$$

On the other hand, for $m\geqslant 1$ we have, by (2.6) and (2.10),

$$I\psi f_{1,m}=-(e/c)\mathbf{H}\cdot I\tau\psi^\dagger\mathbf{g}f_{1,m-1}$$

and hence, by (2.12),

$$I\psi f_{1,m}=(e/c)\mathbf{H}\cdot If_{1,m-1}\mathbf{g}(\tau\psi^\dagger). \tag{2.20}$$

From (2.19) and (2.20) we obtain the second of a sequence of relations of which (2.19) is the first:

$$\begin{aligned}h^{-3}I\psi f_{1,1}&=-(e/kT)(e/c)\mathbf{H}\cdot[(\mathbf{g}(\tau\psi^\dagger))\,\mathbf{l}\,]\cdot\mathbf{E}\\&=+(e/kT)(e/c)\mathbf{H}\cdot[\tau\psi^\dagger\mathbf{g}\,\mathbf{l}\,]\cdot\mathbf{E}.\end{aligned} \tag{2.21}$$

This result is applied in Section 3 to the calculation of the Hall effect. To obtain the third relation of the sequence we apply (2.20) twice. Then, for $m\geqslant 2$,

$$I\,\psi f_{1,m}=(e/c)^2\,\mathbf{H}\cdot If_{1,m-2}\,\mathbf{g}(\tau\lambda^\dagger),$$

where

$$\lambda\equiv\mathbf{H}\cdot\mathbf{g}\,(\tau\psi^\dagger).$$

Therefore, by (2.19),

$$h^{-3}I\psi f_{1,2}=-(e/kT)(e/c)^2\,\mathbf{H}\cdot[(\mathbf{g}(\tau\lambda^\dagger))\,\mathbf{l}\,]\cdot\mathbf{E}.$$

By (2.13) and (2.18),

$$[(\mathbf{g}(\tau\lambda^\dagger))\,\mathbf{l}\,]=-[\tau\lambda^\dagger\mathbf{g}\,\mathbf{l}\,]=-[\tau\lambda(\mathbf{g}\ \mathbf{l})^\dagger]$$

and hence, finally,

$$h^{-3}I\psi f_{1,2}=\frac{e}{kT}\left(\frac{e}{c}\right)^2\mathbf{HH}:[\tau(\mathbf{g}(\tau\psi^\dagger))(\mathbf{g}\ \mathbf{l})^\dagger]\cdot\mathbf{E}. \tag{2.22}$$

This last result is used in Section 4 to calculate the magnetoconductivity.

When $\psi=-e\mathbf{v}$, (2.19), (2.21) and (2.22) become the first three terms on the right of (1.8). If, on the other hand, we substitute $\psi=\epsilon\mathbf{v}$ they become the first three terms in the expansion of the energy flux density, and so represent the Peltier and Ettingshausen effects in a weak magnetic field.

3. The linear Hall effect

The linear Hall effect is given by $\mathbf{J}^{(1,1)}$. By (2.8) we have, on substituting $\psi=\mathbf{v}$ in (2.21) and making use of (2.17),

$$\mathbf{J}^{(1,1)}=(e^2/kT)(e/c)\mathbf{H}\cdot[(\mathbf{g}\ \mathbf{l})\,\mathbf{l}\,]\cdot\mathbf{E}$$

and hence, by (1.8),

$$\boldsymbol{\Phi}(0)=(e^2/kT)(e/c)[(\mathbf{g}\ \mathbf{l})\,\mathbf{l}\,]. \tag{3.1}$$

We may verify from (3.1) that $\mathbf{H}\cdot\boldsymbol{\Phi}(0)$ is antisymmetric, as it should be, since by (2.13)

$$[(\mathbf{g}\ \mathbf{l})\,\mathbf{l}\,]=-[(\mathbf{g}\ \mathbf{l})\,\mathbf{l}\,]^{(2-3)}.$$

By (3.1) and (1.5), the linear Hall effect is given by the dyadic

$$\boldsymbol{\beta}(0)=\tfrac{1}{2}(e^2/kT)(e/c)[(\mathbf{g}\ \mathbf{l})\times\mathbf{l}\,]. \tag{3.2}$$

Eq. (3.2), together with the definitions of its terms, is the central result of this paper.

We now consider the consequences of some special cases of the functions $\epsilon(\Gamma)$ and $\mathbf{l}(\Gamma)$. If $\mathbf{v}$ and $\mathbf{v}^\dagger$ are parallel, and hence $\mathbf{v}$ and $\mathbf{l}$ are parallel, for all of the range of Γ contributing to the sum-integral, then (3.2) reduces to

$$\boldsymbol{\beta}(0)=\tfrac{1}{2}(e^2/kT)(e/c)[\,\mathbf{l}\times\boldsymbol{\gamma}\times\mathbf{l}\,] \tag{3.3}$$

where $\boldsymbol{\gamma}$ (Keyes' $\boldsymbol{\alpha}/m$) is the inverse mass dyadic:

$$\boldsymbol{\gamma}\equiv\frac{\partial^2\epsilon}{\partial\mathbf{p}\partial\mathbf{p}}. \tag{3.4}$$

Since $\boldsymbol{\gamma}$ is symmetric, the dyadic (3.3) is symmetric. If $\boldsymbol{\gamma}$ is a constant (for example, in the range of Γ giving the contribution to $\boldsymbol{\beta}$ from the neighborhood of a simple band-edge point in a semiconductor or semimetal) then (3.3) reduces to

$$\boldsymbol{\beta}(0)=\frac{1}{2}\,\frac{e^2}{kT}\left(\frac{e}{c}\right)(\boldsymbol{\Xi}\cdot\boldsymbol{\gamma}\cdot\boldsymbol{\Xi})^{(1-3)}:[\,\mathbf{l}\,\mathbf{l}\,] \tag{3.5}$$

(where the left-hand side is the contribution from, and the sum-integral on the right-hand side is taken over, the range of Γ for which $\boldsymbol{\gamma}$ has the given constant value). The components of the tetradic are readily calculated for rectangular cartesian axes parallel to the principal axes of $\boldsymbol{\gamma}$. For example, the (i,i,k,k) component is $-\gamma_{jj}$ and the (i,k,i,k) component is $+\gamma_{jj}$. If the principal axes of $[\,\mathbf{l}\,\mathbf{l}\,]$ are in the same directions as those of $\boldsymbol{\gamma}$, we then have

$$[\,\mathbf{l}\times\boldsymbol{\gamma}\times\mathbf{l}\,]_{ii}=-\gamma_{jj}[\,l_k^2]-\gamma_{kk}[\,l_j^2],\ \text{etc.}$$

With $\mathbf{l}$ parallel to $\mathbf{v}$, we might have written

$$\mathbf{l}\equiv\tau_d\mathbf{v},$$

or

$$\mathbf{v}^\dagger\equiv(\tau_d/\tau)\mathbf{v} \tag{3.6}$$

(the subscript stands for "diffusion"). In the theory of Jones and Zener,[12] (2.2) is solved by assuming that $\mathfrak{D}_0 f_1$ may be replaced by $-f_1/\tau$; and if the diffusion time τ_d be substituted for τ in this assumption then the result (3.3) is obtained. The foregoing analysis (a) discloses the actual condition for a result of the form (3.3) to hold; (b) provides a general expression for the diffusion time, for this case; and (c) shows that the same diffusion time, and the same condition for its application, apply for $\mathfrak{Z}(0)$ as for $\boldsymbol{\sigma}(0)$.

When $\mathbf{v}$ and $\mathbf{v}^\dagger$ are not parallel it would be natural to generalize (3.6) by making τ_d a dyadic:

$$\mathbf{l}=\boldsymbol{\tau}_d\cdot\mathbf{v}. \tag{3.7}$$

Dumke[13] and Herring and Vogt[14] both introduce a tensor relaxation time. Dumke treats only conduction without a magnetic field (i. e. he calculates $\boldsymbol{\sigma}(0)$). He writes

$$f_1\equiv-(e/kT)f_0(1-f_0)\mathbf{E}\cdot\boldsymbol{\tau}\cdot\mathbf{v},$$

which is permissible and correct in general, and gets an equation for the components of $\boldsymbol{\tau}$ which appears to be equivalent to (2.5) with $\psi=\mathbf{E}\cdot\mathbf{v}$. Herring and Vogt include the effect of a magnetic field but introduce a tensor relaxation time by an assumption. They expand f_1, in the neighborhood of a simple band-edge point, in spherical harmonics of $\mathbf{v}^*\equiv\boldsymbol{\gamma}^{-\frac{1}{2}}\cdot\mathbf{v}$ and then assume that the term transforming like $\mathbf{v}^*$ ($\mathbf{v}^*\phi^{(1)}(\epsilon)$, say) satisfies

$$\mathfrak{D}_0\phi^{(1)}\mathbf{v}^*=-\phi^{(1)}\boldsymbol{\tau}_{HV}{}^{-1}\cdot\mathbf{v}^*.$$

Since $\mathbf{J}$ depends only on this term, they obtain expressions for the terms of (1.8) as functions of $\boldsymbol{\gamma}$ and $\boldsymbol{\tau}_{HV}$. They also give an expression (their eq. (11)) for the components of $\boldsymbol{\tau}_{HV}$ in certain conditions. From the point of view of the present paper, it would not be appropriate *in the most general case* to introduce a dyadic relaxation time by the relation (3.7), since the relation does not uniquely define $\boldsymbol{\tau}_d$ but merely imposes three conditions on its components. However, where the relation of the functions $\mathbf{l}(\Gamma)$, $\mathbf{v}(\Gamma)$ allows it we could partially predetermine our $\boldsymbol{\tau}_d$ by assuming fixed directions for the three principal axes, the same over the whole region of the variables Γ involved in a particular calculation;[15] and then the three magnitudes specifying $\boldsymbol{\tau}_d$ in these conditions are uniquely given by (3.7), and conversely they uniquely determine $\mathbf{l}$. Both Dumke and Herring and Vogt make this assumption of fixed principal axes, which is appropriate to their calculations. The transformation of our results—for example (3.2)—to the form obtained by substituting (3.7) with fixed principal axes for $\boldsymbol{\tau}_d$ is laborious but straightforward. Here we just examine the special case where $\boldsymbol{\gamma}$ is constant and $\mathbf{l}(\Gamma)$ is of the form

$$\mathbf{l}=\tau'(\Gamma)\boldsymbol{\nu}\cdot\mathbf{v} \tag{3.8}$$

with $\boldsymbol{\nu}$ a fixed constant tensor (or, in other words, all the components of $\boldsymbol{\tau}_d$, (3.7), maintain fixed ratios to each other as they vary with Γ). Then

$$(\mathbf{gl})\times\mathbf{l}=\tau'\mathbf{v}\times(\boldsymbol{\gamma}\cdot\boldsymbol{\nu}^\sim\times\boldsymbol{\nu})\cdot(\tau'\mathbf{v}).$$

On substituting this result in (3.2), and taking the dyadic function of $\boldsymbol{\nu}$ and $\boldsymbol{\gamma}$ outside the sum-integral, we find

$$\left.\begin{aligned}&\mathfrak{Z}(0)=\tfrac{1}{2}(e^2/kT)(e/c)\boldsymbol{\Theta}:[\,\mathbf{l}'\mathbf{l}'\,],\\&\text{where } \mathbf{l}'\equiv\tau'\mathbf{v}\text{ and}\\&\boldsymbol{\Theta}\equiv-((\boldsymbol{\nu}^\sim\times\boldsymbol{\nu})\cdot\boldsymbol{\gamma}\cdot\boldsymbol{\Xi})^{(1\sim3)}.\end{aligned}\right\} \tag{3.9}$$

This result generalizes (3.5) by substituting $\boldsymbol{\Theta}$ for the corresponding tetradic there. If $\boldsymbol{\nu}$ is symmetric with principal axes parallel to those of $\boldsymbol{\gamma}$, then $(\boldsymbol{\nu}^\sim\times\boldsymbol{\nu})_{ijk}=-\Xi_{ijk}\nu_{ii}\nu_{kk}$. We then have, for the non-zero components of $\boldsymbol{\Theta}$, $\Theta_{iijj}=-\gamma_{kk}\nu_{jj}\nu_{kk}$ etc., and $\Theta_{ijij}=+\gamma_{kk}\nu_{ii}\nu_{kk}$, etc. These results are simple generalizations of those for (3.5).

The other special case of (3.7) which we consider is where $\boldsymbol{\tau}_d$ is a function of ϵ only, in its dependence on $\mathbf{p}$, and is symmetric. Then the derivative of $\boldsymbol{\tau}_d$ with respect to $\mathbf{p}$ makes no contribution to $\mathbf{gl}$. Consequently

$$\mathfrak{Z}(0)=\tfrac{1}{2}(e^2/kT)(e/c)[\mathbf{v}\times\boldsymbol{\gamma}\cdot\boldsymbol{\tau}_d\times\boldsymbol{\tau}_d\cdot\mathbf{v}]. \tag{3.10}$$

This is the formula appropriate to the approximation (5.16).

The general result (3.2), expressed in terms of rectangular cartesian components, reads:

$$\beta(0)_{ij}=\tfrac{1}{2}\left(\frac{e^2}{kT}\right)\left(\frac{e}{c}\right)\Sigma_r\Sigma_s\Sigma_t\Sigma_u\,\Xi_{irs}\,\Xi_{jtu}\left[v_r\left(\frac{\partial}{\partial p_s}l_t\right)l_u\right].$$

On specializing to cubic symmetry we obtain, for the Hall mobility,

$$\mu^H=e[v_j(l_k\partial l_j/\partial p_k-l_j\partial l_k/\partial p_k)]/[l_iv_i], \tag{3.11}$$

where $i\neq k$. (Here μ^H is defined as in (1.14) so that it may have either sign, the negative sign being usually associated with "electrons" rather than "holes.") When, as for (3.3), $\mathbf{l}$ and $\mathbf{v}$ are parallel, (3.11) reduces to

$$\mu^H=e[l_jl_k\gamma_{jk}-l_j^2\,\gamma_{kk}]/[l_iv_i]. \tag{3.12}$$

4. Quadratic magnetoconductivity

Before calculating $\boldsymbol{\Psi}$ (see eq. (1.8)) explicitly, we note a general formula for the effect of a magnetic field on conductivity which may be obtained from (2.2) and (2.6). On multiplying (2.2) by $h^{-3}\tau\psi^\dagger$ and operating with I we obtain

$$h^{-3}I\,\psi f_1+(e/kT)[\tau\psi^\dagger\mathbf{v}]\cdot\mathbf{E}=h^{-3}(e/c)\mathbf{H}\cdot I(\mathbf{g}\tau\psi^\dagger)f_1. \tag{4.1}$$

When $\psi=-e\mathbf{v}$, (4.1) becomes

$$(\boldsymbol{\sigma}-\boldsymbol{\sigma}(0))\cdot\mathbf{E}=-(e^2/c)\mathbf{H}\cdot h^{-3}I(\mathbf{gl})f_1. \tag{4.2}$$

The right-hand side of (4.2) is proportional to $\mathbf{E}$, and represents both the Hall effect and the magnetoconductivity.

From (2.22) with $\psi=-e\mathbf{v}$ we have

$$\boldsymbol{\Psi}=-(e^2/kT)(e/c)^2\,[\tau(\mathbf{g}\,\mathbf{l})(\mathbf{g}\,\mathbf{l})^\dagger]^{(2\sim3)}. \tag{4.3}$$

By making use of the Onsager relation (2.18) together with (2.22), we would have obtained, instead of (4.3),

$$\boldsymbol{\Psi}=-(e^2/kT)(e/c)^2\,[\tau(\mathbf{g}\,\mathbf{l})^\dagger\mathbf{g}\,\mathbf{l}]^{(2\sim3)}. \tag{4.4}$$

Actually (4.4), rather than (4.3), is the result that would have been obtained if no use at all of (2.18) had been made;[16] and we adopt it here as our standard formula in preference to (4.3). The result for $\boldsymbol{\gamma}$ constant [as in (3.5)], and $\mathbf{l}=\tau_d(\epsilon)\,\mathbf{v}$, is

$$\boldsymbol{\Psi}=-\frac{e^2}{kT}\left(\frac{e}{c}\right)^2[\tau\mathbf{l}\,\mathbf{l}^\dagger]:\left\{(\boldsymbol{\Xi}\cdot\boldsymbol{\gamma}\,\boldsymbol{\Xi}\cdot\boldsymbol{\gamma})^{(135246)}\right\}. \tag{4.5}$$

When the result (5.22) of the following section applies, we have

$$[\tau(\mathbf{g}\ \mathbf{l})^\dagger \mathbf{g}\ \mathbf{l}\ ] = [\mathbf{v}\cdot\boldsymbol{\tau}_d \times \boldsymbol{\gamma}\cdot\boldsymbol{\tau}_d\ \ \mathbf{v}\times\boldsymbol{\gamma}\cdot\boldsymbol{\tau}_d]. \tag{4.6}$$

The contribution to $\boldsymbol{\Psi}$ from a region of the zone in which $\boldsymbol{\gamma}$ is constant (i. e. from one valley) is then given by the contribution to $[\boldsymbol{\epsilon}\ \boldsymbol{\tau}_d\ \boldsymbol{\tau}_d\ \boldsymbol{\tau}_d]$. When, as is to be expected, the principal axes of $\boldsymbol{\tau}_d$ and $\boldsymbol{\gamma}$ are parallel in the same valley, the contribution from that valley to Ψ_{ijkl} (where the coordinate axes are chosen parallel to the principal axes) is

$$-\frac{2}{3}\frac{e^2}{kT}\left(\frac{e}{c}\right)^2 \Sigma_n \Xi_{ikn} \Xi_{jln} \gamma_{kk}\gamma_{ll}\gamma_{nn}[\epsilon\tau_k\tau_l\tau_n]. \tag{4.7}$$

For Boltzmann statistics ($f_0 \ll 1$) this is evidently the same result as Herring and Vogt's (reference 14, eq. (20)) with $\boldsymbol{\tau}_{HV}$ replaced by $\boldsymbol{\tau}_d(\epsilon)$.

The form of $\boldsymbol{\Psi}$ for a cubic crystal is determined by the result given by Seitz (reference 2, eq. (1)) as

$$\mathbf{HH}: \boldsymbol{\Psi} = \beta H^2 \boldsymbol{\varepsilon} + \gamma \mathbf{HH} + \delta(H_i^2 \mathbf{ii} + H_j^2 \mathbf{jj} + H_k^2 \mathbf{kk}), \tag{4.8}$$

where $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ are unit vectors parallel to the three crystal axes and β, γ, δ are scalar parameters specifying $\boldsymbol{\Psi}$ in this case. By comparison of (4.8) with (4.4) we find

$$\left.\begin{aligned} \beta &= A_{ijij}\ , \\ \gamma &= A_{iijj} + A_{ijji}\ , \\ \beta+\gamma+\delta &= A_{iiii}\ , \end{aligned}\right\} \tag{4.9}$$

where

$$A_{mnrs} \equiv -(e^2/kT)(e/c)^2[\tau(g_m l_n)^\dagger g_r l_s].$$

For an *isotropic* region of a band, with $\boldsymbol{\gamma} = \boldsymbol{\varepsilon}/m^*(\epsilon)$ and $\mathbf{l} = \tau_d(\epsilon)\mathbf{v}$,

$$\mathbf{g}\ \mathbf{l} = (\tau_d/m^*)\mathbf{v}\times\boldsymbol{\varepsilon}.$$

Therefore, for the contribution to $\boldsymbol{\Psi}$ from such a region, with m^* a constant, we have from (4.9)

$$\left.\begin{aligned} \delta &= 0, \\ \beta &= -\gamma = -\tfrac{1}{3}(e^2/kT)(e/m^*c)^2[\tau(\tau_d\mathbf{v})^\dagger\cdot\tau_d\mathbf{v}]. \end{aligned}\right\} \tag{4.10}$$

If in addition the scattering is *elastic*, the expression in the square bracket of (4.10) is equal to $v^2\tau_d^3$. Then (4.10) becomes a special case of the result given by (4.7).

5. Calculation of the vector mean free path

The foregoing prescription for the calculation of the transport coefficients $\boldsymbol{\sigma}(0)$, $\boldsymbol{\beta}(0)$ would not be complete without some indication of how the "vector mean free path" $\mathbf{l}(\Gamma)$ may be obtained in practice. The evaluation of the magnetoconductivity constant $\boldsymbol{\Psi}$, eq. (4.4), requires the calculation of $(\mathbf{g}\,\mathbf{l})^\dagger$ also. Therefore we have to consider the solution of (2.5) for $\psi^\dagger$. The solution is not unique, but any two solutions can differ only by a/τ, where a is constant (or piece-wise constant, as described below). To prove this statement, we let two solutions of (2.5) be $\psi^\dagger$ and $\psi^\dagger + \chi(\Gamma)/\tau$.

Then

$$I(\Gamma')(\chi(\Gamma)-\chi(\Gamma'))T(\Gamma;\Gamma') = 0. \tag{5.1}$$

On multiplication by $2\chi(\Gamma) f_0(\Gamma)(1-f_0(\Gamma))$, and summation-integration over Γ, (5.1) becomes

$$I(\Gamma)I(\Gamma')(\chi(\Gamma)-\chi(\Gamma'))^2 R(\Gamma;\Gamma') = 0. \tag{5.2}$$

Here R is the function defined in LN,

$$R(\Gamma;\Gamma') \equiv f_0(\Gamma)(1-f_0(\Gamma))T(\Gamma;\Gamma'), \tag{5.3}$$

and we have made use of the symmetry property

$$R(\Gamma;\Gamma') = R(\Gamma';\Gamma), \tag{5.4}$$

which follows from the detailed balance principle. Since $R \geqslant 0$, (5.2) cannot be satisfied unless $\chi(\Gamma') = \chi(\Gamma)$ for any two points Γ, Γ', connected by scattering processes. Such pairs of points must form chains which either link together the whole domain of Γ or else divide it into a set of sub-domains which are not connected with each other by any scattering processes but in each of which all points are linked together. Therefore χ must be constant in each domain, but may have different values in different domains (be piece-wise constant). The replacement of $\psi^\dagger\tau$ by $\psi^\dagger\tau + \chi$ then has no effect on the value of the right-hand side of (2.6); and therefore the results of Sections 3 and 4, deduced from (2.6), are unique.[17] One may verify this in each specific case, for example on adding a constant vector to $\mathbf{l}\ (\Gamma)$ in (3.2) and (4.4). Obviously, this conclusion is related to the uniqueness of the solution of (2.2) for f_1.

Eq. (2.5) may be written as

$$(1-\mathcal{O})\psi^\dagger = \psi, \tag{5.5}$$

in terms of the operator $\mathcal{O}$ introduced in LN and defined by

$$\mathcal{O}\phi \equiv I(\Gamma')T(\Gamma;\Gamma')\tau(\Gamma')\phi(\Gamma'),$$

or alternatively as

$$(1-\mathcal{L})\tau\psi^\dagger = \tau\psi, \tag{5.6}$$

in terms of the operator $\mathcal{L}$ defined by

$$\mathcal{L}\phi \equiv \tau(\Gamma)I(\Gamma')T(\Gamma;\Gamma')\phi(\Gamma').$$

A solution of (5.5) is

$$\psi^\dagger = (1+\mathcal{O}+\mathcal{O}^2+\ldots\ldots.)\psi, \tag{5.7}$$

provided the series converges; and similarly (5.6) is inverted by the operator $1+\mathcal{L}+\mathcal{L}^2+\ldots\ldots.$ For $f_0 \ll 1$ and with scattering by acoustic phonons alone, in the neighborhood of a simple band-edge point,[18] one may expect to find, in some cases, that

$$\mathcal{O}\mathbf{v} \ll \mathbf{v}. \tag{5.8}$$

When (5.8) is satisfied, the series solution

$$\mathbf{v}^\dagger - \mathbf{v} = \mathcal{O}\mathbf{v} + \mathcal{O}^2\mathbf{v} + \ldots\ldots. \tag{5.9}$$

should converge rapidly, since one would expect to find $\mathcal{O}^2\mathbf{v} \ll \mathcal{O}\mathbf{v}$, etc., at the same time. On the other hand, for scattering predominantly by impurity ions (5.8) may be far from the truth, according to present ideas,[18] since small angles of scattering may be very probable. There is in fact no obvious reason to expect the series (5.7) to converge in all possible cases. The natural physical interpretation of the successive terms of the series (5.9), where it converges, is as giving the effect, on the transport constants, of persistance of velocity after one, two, ... etc. collisions following an initial free path.[19]

There is an especially simple solution of (5.5) if $(\mathcal{O}\psi)/\psi$ is unchanged when operated on by $\mathcal{O}$. In this case

$$\psi^\dagger = \psi/(1-(\mathcal{O}\psi)/\psi). \tag{5.10}$$

One would not expect (5.10) to be valid unless the change in energy on scattering is negligible, since otherwise there are in general two distinct sets of final states connected to a given initial state by scattering. If the scattering is virtually elastic, and if the Brillouin zone has spherical symmetry (ϵ,τ, etc. are functions of p only, in their dependence on $\mathbf{p}$), then we have, as a special case of (5.10), the standard result[19, 20]

$$\left.\begin{aligned}&\tau_d = \tau/(1-\kappa),\\ \text{where}\quad &\mathcal{L}\mathbf{v} \equiv \kappa(\Gamma)\mathbf{v}\end{aligned}\right\} \tag{5.11}$$

and τ_d is given by (3.6). (The two possible definitions of κ, in terms of $\mathcal{L}$ and of $\mathcal{O}$, are equivalent here; but we shall find below that when there *is* a distinction it is the above definition, in terms of $\mathcal{L}$, that we want.)

For the problems in the theory of the transport effects posed by actual solids, the scattering probability function $S(\Gamma;\Gamma')$ is frequently very complicated. Since there is the prospect of the scattering function becoming known reliably in detail, for some of these cases, it is important to have methods of getting good approximate solutions of (5.5), or (5.6), systematically and without losing touch with intuitive ideas about the result. One such method may be provided by the following minimum principle:[21] Let

$$W(\phi) \equiv$$
$$I(\Gamma)I(\Gamma')(\phi(\Gamma)-\phi(\Gamma'))^2R(\Gamma;\Gamma') - 4I\phi\psi f_0(1-f_0), \tag{5.12}$$

where R is given by (5.3). Then if

$$\phi = \tau\psi^\dagger, \tag{5.13}$$

where $\psi^\dagger$ satisfies (2.5),

$$W(\phi+\chi) - W(\phi) = I(\Gamma)I(\Gamma')(\chi(\Gamma)-\chi(\Gamma'))^2R(\Gamma;\Gamma')$$

for any arbitrary function χ. Therefore W is a minimum when ϕ satisfies (5.13) (and is the same for any two solutions, ϕ_1/τ, ϕ_2/τ, of (2.5)). The minimum value of W is

$$-2I\tau\psi^\dagger\psi f_0(1-f_0).$$

It follows that the functional

$$W(\mathbf{h}) \equiv I(\Gamma)I(\Gamma')|\mathbf{h}(\Gamma)-\mathbf{h}(\Gamma')|^2R(\Gamma;\Gamma')$$
$$-4I\mathbf{h}\cdot\mathbf{v}f_0(1-f_0) \tag{5.14}$$

is a minimum when $\mathbf{h}(\Gamma)=\mathbf{l}$. Alternatively, for an arbitrary direction in space the functional

$$U_i \equiv (e^2/kT)[2h_iv_i - (h_i/\tau)(1-\mathcal{L})h_i] \tag{5.15}$$

has a *maximum* of $\sigma_{ii}(0)$ when $h_i = l_i$. It therefore gives a *lower bound* to the (i, i) component of $\boldsymbol{\sigma}(0)$, for an arbitrary function $h_i(\Gamma)$. It should be noted that this property of the maximum of (5.15) guarantees that successive improvements in the solution for $\mathbf{l}$, indicated by reductions of (5.14) or increases of (5.15), correspond to successively more accurate values of $\boldsymbol{\sigma}(0)$, but that we have not proved that the same guarantee applies for $\boldsymbol{\beta}(0)$. It seems reasonable to expect, however, that variational solutions for $\mathbf{l}$ may be obtained which give good values for $\boldsymbol{\beta}(0)$ along with good values of $\boldsymbol{\sigma}(0)$.

The minimum principle leads to a generalization of the solution (5.11) for the more realistic conditions where the Brillouin zone does not have spherical symmetry but where the change in electron energy on scattering still is negligible. We set

$$l_i = \tau_i(\epsilon)v_i \tag{5.16}$$

and seek the "best" solution for τ_i. The result is

$$\left.\begin{aligned}&\tau_i = \overline{v_i^2}/\overline{(v_i^2(1-\kappa_i)/\tau)},\\ \text{where}\quad &\mathcal{L}v_i \equiv \kappa_i(\Gamma)v_i.\end{aligned}\right\} \tag{5.17}$$

The bar in (5.17), as in LN, signifies averaging over a constant-energy "surface":

$$\overline{\psi}(\epsilon') \equiv I(\Gamma)\psi\delta(\epsilon'-\epsilon(\Gamma)), \tag{5.18}$$

where δ is Dirac's function. For a simple band-edge neighborhood with $\boldsymbol{\gamma}$ constant, (5.17) reduces to the result given by Herring and Vogt (reference 14, eq. (11)). It should be noted that it is *not* assumed in the derivation of (5.17) that τ is a function of ϵ only. Solutions (5.16), (5.17) of (2.5) may be obtained, with consistency, for three directions but not more than three. The three solutions may then be incorporated into a dyadic $\boldsymbol{\tau}_d(\epsilon)$ which gives $\mathbf{l}$ in terms of $\mathbf{v}$ by a relation of the form (3.7). Different dyadics $\boldsymbol{\tau}_d(\epsilon)$ will be obtained for different choices of the three directions, and obviously the "best" choice could be found by minimizing (5.14); but one would expect the correct choice to be usually clear from the symmetry of the energy "surface."

The solution of (2.5) for $\mathbf{l}$ obtained in the preceding paragraph may be generalized to take into account changes in ϵ on scattering. The best solution, according to the minimum principle, of (5.16) for $\tau_i(\epsilon)$ is that given by the integral equation

$$\overline{(v_i^2/\tau)}\tau_i - \int Z_i(\epsilon;\epsilon')\tau_i(\epsilon')d\epsilon' = \overline{v_i^2}, \tag{5.19}$$

where

$$Z_i(\epsilon_1;\epsilon_2) \equiv$$
$$I(\Gamma)I(\Gamma')\delta(\epsilon_1-\epsilon(\Gamma))\delta(\epsilon_2-\epsilon(\Gamma'))v_i(\Gamma)T(\Gamma;\Gamma')v_i(\Gamma'). \tag{5.20}$$

Thus, at the expense of the approximation (5.16), eq. (2.5) is reduced to a *one-dimensional* integral equation. (To generalize (5.19) for τ_i a function of ϵ, ϑ and q, one just replaces $I(\Gamma)$, $I(\Gamma')$, in (5.18) and (5.20) by $\int d^3\mathbf{p}$ . . . . and $\int d^3\mathbf{p}'$ . . . .) If the change of energy on scattering, and hence the "width" of the kernel $Z_i(\epsilon;\epsilon')$, is small enough, we may replace $\tau_i(\epsilon')$ by $\tau_i(\epsilon)$ in the second term on the left of (5.19). The ordinary algebraic equation for τ_i then obtained is identical with (5.17). For n-germanium and n-silicon, at ordinary temperatures, intra-valley scattering by acoustic lattice vibrations may be taken as elastic in calculating $\mathbf{J}^{(1)}$, but for intra-valley scattering by optical modes and inter-valley scattering the energy change may not be neglected. Herring and Vogt[14] point out, however, that, whereas intra-valley scattering by acoustic modes is virtually "conserving", the rest of the scattering by lattice vibrations is virtually "randomizing": it has small persistence of velocity. Thus, according to this view, we may split the scattering function into two terms,

$$T = T_c + T_r,$$

such that $T_c(\Gamma;\Gamma')$ connects states for which, as in deriving (5.17), we may take $\epsilon(\Gamma) = \epsilon(\Gamma')$, while T_r has the property

$$I(\Gamma')T_r(\Gamma;\Gamma')\mathbf{v}(\Gamma') \ll \mathbf{v}(\Gamma)/\tau_r(\Gamma),$$

where τ_r is defined analogously to (2.4). Since ϵ is virtually constant (though differing from its initial value) among the states in a given valley to which an electron is scattered, by any one lattice mode, from a given state, we may to the same approximation drop the "randomizing" contribution to Z_i. We then obtain from (5.19) the solution (5.17) with $v_i^2(1-\kappa_i)/\tau$ replaced by

$$(v_i^2/\tau) - v_i I(\Gamma')T_c(\Gamma;\Gamma')v_i(\Gamma').$$

Therefore

$$\frac{1}{\tau_i(\epsilon)} = \frac{1}{\tau_i^c} + \frac{\overline{(v_i^2/\tau_r)}}{\overline{v_i^2}},$$

where τ_i^c is the value of τ_i according to (5.17) if the "randomizing" collisions are neglected altogether. But, for the same conditions, τ_r is virtually a function of ϵ only.[18] Hence, finally,

$$\frac{1}{\tau_i} = \frac{1}{\tau_i^c} + \frac{1}{\tau_r}. \tag{5.21}$$

The result on which (4.6) is based may be derived from the foregoing considerations. If $\mathbf{I} = \mathbf{v}\cdot\boldsymbol{\tau}_d(\epsilon)$, then

$$\mathbf{g}\,\mathbf{I} = \mathbf{v}\times\boldsymbol{\gamma}\cdot\boldsymbol{\tau}_d(\epsilon).$$

Now, $\boldsymbol{\gamma}$ is a constant of intra-valley scattering, but of course changes in the scattering from one valley to another. If inter-valley scattering is randomizing, however, these processes in which $\boldsymbol{\gamma}$ changes make no contribution to the difference between $(\mathbf{gI})$ and $(\mathbf{gI})^\dagger$. Similarly, since intra-valley processes are either randomizing or conserving, $\boldsymbol{\tau}_d(\epsilon)$ may be taken as constant. Consequently $(\mathbf{gI})^\dagger$ is obtained on replacing $\mathbf{v}$ by $\mathbf{v}^\dagger$ in $\mathbf{gI}$:

$$(\mathbf{g}\,\mathbf{I})^\dagger = \mathbf{v}\cdot\boldsymbol{\tau}_d\times\boldsymbol{\gamma}\cdot\boldsymbol{\tau}_d/\tau. \tag{5.22}$$

In metals at low temperatures the change of ϵ in scattering is $\sim kT$. Then the width of the kernel Z_i in (5.19) may not be neglected. For intermediate temperatures it might be approximated by taking the first two or three terms of the Taylor series for $\tau_i(\epsilon') - \tau_i(\epsilon)$. A linear differential equation of first or second order for $\tau_i(\epsilon)$ would result.

It is obvious that perturbation methods may be developed to approximate solutions of the linear inhomogeneous equation (2.5). Suppose, for example, that $\psi^\dagger{}_0$ is believed to be a good approximation to $\psi^\dagger$. If

$$\psi^\dagger \equiv \psi^\dagger{}_0 + \psi^\dagger{}_1,$$

then we have

$$(1-\mathcal{O})\psi^\dagger{}_1 = \psi - (1-\mathcal{O})\psi^\dagger{}_0. \tag{5.23}$$

If $\psi^\dagger{}_0$ is in fact a good approximation to $\psi^\dagger$, the right-hand side of (5.23) will be small and hence the solution, $\psi^\dagger{}_1$, may be expected to be small compared to $\psi^\dagger{}_0$. Then an approximate solution of (5.23) may be good enough. There is no reason, however, to expect a series solution of form (5.7) for (5.23) to converge rapidly although the corresponding solution of (2.5) did not. If the series solution of (2.5) does not converge satisfactorily (for example, if the scattering is predominantly through small angles and we are seeking a solution for $\mathbf{I}$) it is natural to try as a first approximation the function

$$\left.\begin{aligned} &\psi^\dagger{}_0 = b\psi, \\ &\text{where} \\ &b(1-\mathcal{O})\psi \equiv \psi. \end{aligned}\right\} \tag{5.24}$$

(This "brute force solution" is just the result (5.10) proposed irrespective of whether the necessary condition, that $(\mathcal{O}\psi)/\psi$ is unchanged when operated on by $\mathcal{O}$, is satisfied.) Substitution of (5.24) into (5.23) results in the equation

$$(1-\mathcal{O})\psi^\dagger{}_1 = \mathcal{O}(b\psi) - b\mathcal{O}\psi. \tag{5.25}$$

Thus $\psi^\dagger{}_1$ is proportional to a measure of the violation of the condition for (5.10) to be an exact solution. If the condition is fairly well satisfied, so that the right-hand side of (5.25) (ψ_1, say) is small compared to ψ, and if application of the procedure a second time to solve (5.25) leads to an equation of which the right-hand side is in turn small compared with ψ_1, a rapidly converging sequence might be obtainable. It could be useful in practice, if a sufficient knowledge of T and τ were available in suitable form, even though the general term could not be reduced to a simple algebraic expression, like the general term of (5.7). Of course one could start instead from the approximation, $\psi^\dagger{}_0$, given by (5.16) and (5.17) or (5.19).

A different kind of situation for which perturbation methods are appropriate is where a good solution of (2.5) is known for a scattering function, T_0, which is an approximation to the actual function T. Thus we would know the solution, $\psi^\dagger{}_0$, of the equation

$$\psi^\dagger{}_0 - \mathcal{O}_0\psi^\dagger{}_0 = \psi, \tag{5.26}$$

and require the solution of

$$\psi^\dagger - \mathcal{O}\psi^\dagger = \psi \tag{5.27}$$

where $\mathcal{O} \simeq \mathcal{O}_0$. The difference between $\mathcal{O}$ and $\mathcal{O}_0$ might be due to scattering processes not included in T_0 (for example to inter-valley scattering or to a *small* amount of scattering by optical lattice quanta or by impurities); or the difference might be due to the effect of a shear strain on inter-valley scattering.[22] Let

$$\psi^\dagger \equiv \psi^\dagger{}_0 + \phi,$$

$$\mathcal{O} \equiv \mathcal{O}_0 + \mathcal{P}.$$

Then, by (5.26) and (5.27), ϕ is given exactly by

$$\phi - \mathcal{O}\phi = \mathcal{P}\psi^\dagger{}_0. \tag{5.28}$$

If $\mathcal{O} \simeq \mathcal{O}_0$ then ϕ is approximately equal to ϕ_1 where

$$\phi_1 - \mathcal{O}_0\phi_1 = \mathcal{P}\psi^\dagger{}_0. \tag{5.29}$$

Eq. (5.29) gives the first term of a series solution of (5.28), $\phi_1 + \phi_2 + \ldots\ldots$, of which the general term satisfies

$$\phi_{n+1} - \mathcal{O}_0\phi_{n+1} = \mathcal{P}\phi_n \tag{5.30}$$

for $n \geqslant 1$.

Acknowledgments

I am indebted to Mr. G. D. Whitfield for pointing out some erroneous arguments and statements in the manuscript version of this paper; to Mr. P. B. Linhart, who was associated with some of the work from which the theory presented here originated; and to Dr. H. Frisch for an informative conversation on the literature of the kinetic theory of gases.

Appendix: vector notation and formulas

The notation and terminology used here for vector calculus are those of Gibbs,[23] with the following modifications and extensions: Vectors are denoted by boldface latin letters, dyadics by boldface lower-case greek letters, and triadics, tetradics, etc. by boldface capital greek letters. The unit dyadic is $\boldsymbol{\varepsilon}$:

$$\mathbf{a}\cdot\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}\cdot\mathbf{a} = \mathbf{a},\ \boldsymbol{\alpha}\cdot\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}\cdot\boldsymbol{\alpha} = \boldsymbol{\alpha}, \text{ etc.}$$

The unit skew triadic is $\boldsymbol{\Xi} \equiv -\boldsymbol{\varepsilon}\times\boldsymbol{\varepsilon}$. It has the property

$$(\mathbf{ab}):\boldsymbol{\Xi} = \mathbf{a}\cdot\boldsymbol{\Xi}\cdot\mathbf{b} = \boldsymbol{\Xi}:(\mathbf{ab}) = \mathbf{b}\times\mathbf{a},$$

and its rectangular cartesian components Ξ_{ijk} are usually denoted by e_{ijk}. The transpose of a dyadic $\boldsymbol{\alpha}$ is $\boldsymbol{\alpha}^{\sim}$:

$$(\mathbf{ab})^{\sim} \equiv \mathbf{ba}.$$

The vector of a dyadic $\boldsymbol{\alpha}$ is

$$\boldsymbol{\alpha}^{(\times)} \equiv -\boldsymbol{\alpha}:\boldsymbol{\Xi}.$$

The symmetric and antisymmetric ("selfconjugate" and "anti-selfconjugate") parts of a dyadic $\boldsymbol{\alpha}$ are

$$\tilde{\boldsymbol{\alpha}} \equiv \tfrac{1}{2}(\boldsymbol{\alpha} + \boldsymbol{\alpha}^{\sim}), \quad \hat{\boldsymbol{\alpha}} \equiv \tfrac{1}{2}(\boldsymbol{\alpha} - \boldsymbol{\alpha}^{\sim}).$$

The extension to polyadics of the notation for transpose and vector of a dyadic is indicated by the examples following:

$$(\mathbf{abc})^{(2\sim3)} = \mathbf{acb},$$

$$(\mathbf{abcd})^{(1\sim3)} = \mathbf{cbad},$$

$$(\mathbf{abcd})^{(2\times3)} = \mathbf{ab}\times\mathbf{cd},$$

$$\boldsymbol{\Xi}^{(1\times2)} = 2\boldsymbol{\varepsilon}.$$

A complicated succession of transposes is also indicated (see eq. (4.5)) by specifying the final order of the factors of the component polyads. E. g.

$$(\mathbf{abcde})^{(35241)} = \mathbf{cebda}.$$

If a dyadic $\boldsymbol{\alpha}$ is antisymmetric then[24] it is equal to $-\frac{1}{2}\boldsymbol{\alpha}^{(\times)}\times\boldsymbol{\varepsilon}$. Therefore, for a general dyadic $\boldsymbol{\alpha}$,

$$\hat{\boldsymbol{\alpha}} = \boldsymbol{\alpha}:(\tfrac{1}{2}\boldsymbol{\Xi}\times\boldsymbol{\varepsilon}). \tag{A1}$$

Similarly for a triadic if $\boldsymbol{\Phi}^{(2\sim3)} = -\boldsymbol{\Phi}$ then

$$\boldsymbol{\Phi} = -\tfrac{1}{2}\boldsymbol{\Phi}^{(2\times3)}\times\boldsymbol{\varepsilon}, \tag{A2}$$

and so on. According to (A1), a general dyadic may be expressed in the form

$$\boldsymbol{\alpha} = \boldsymbol{\omega} + \mathbf{t}\times\boldsymbol{\varepsilon}, \tag{A3}$$

where $\boldsymbol{\omega}$ is symmetric. Let its inverse, if it exists, be

$$\boldsymbol{\alpha}^{-1} \equiv \boldsymbol{\omega}' - \mathbf{t}'\times\boldsymbol{\varepsilon}. \tag{A4}$$

Then it can be shown that

$$\boldsymbol{\omega}' = \frac{\boldsymbol{\omega}^{-1}D + \mathbf{tt}}{D + \mathbf{t}\cdot\boldsymbol{\omega}\cdot\mathbf{t}}, \tag{A5}$$

$$\mathbf{t}' = \frac{\mathbf{t}\cdot\boldsymbol{\omega}}{D + \mathbf{t}\cdot\boldsymbol{\omega}\cdot\mathbf{t}}, \tag{A6}$$

where $D \equiv \det.\boldsymbol{\omega}$. These last results are used in Section 1 to convert the general expression for conductivity into one for resistivity.

The Einstein summation convention is not used in this paper. Repeated indices are summed only where it is explicitly indicated.

References and footnotes

1. P. J. Price, "The Lorenz Number," *IBM Journal* **1,** 147 (1957).
2. F. Seitz, *Phys. Rev.* **79,** 372 (1950).; B. Abeles and S. Meiboom, *Phys. Rev.* **95,** 31 (1954).; M. Shibuya, *Phys. Rev.* **95,** 1385 (1954).
3. H. Juretschke, *Acta Cryst.* **8,** 716 (1955).
4. T. Okada, *Memoirs of the Faculty of Science of Kyusyu University*, Series B, **1,** 157 (September, 1955).
5. R. W. Keyes, *J. Electronics* **2,** 279 (1956).
6. S. R. de Groot, *Thermodynamics of Irreversible Processes*, North-Holland Publishing Company, Amsterdam 1951, § 21.
7. It is convenient to express the relation in terms of **H** rather than the magnetic induction: There is no ambiguity so long as there is no magnetic hysteresis in the substance. In the following sections it will be assumed that the susceptibility is negligible, so as to avoid ambiguities over the Lorentz force acting on an individual electron; and then there is naturally no hysteresis.
8. Where the spin degeneracy is lifted by spin-orbit coupling, so that the two independent spin states are mixed together in the single-electron states, the significance of ϑ is different. None of the work in this paper is affected by the change.
9. The uniqueness of $\psi^\dagger$ according to this definition is discussed at the beginning of Section 5.
10. C. Herring, *Bell System Tech. J.* **34,** 234 (1955); A. H. Wilson, reference 12.
11. The derivation of this result makes the assumption that a double partial derivative of ϵ with respect to two components of **p** is unchanged by reversing the order of the differentia-

tions (i. e. that Υ, eq. (3.4), is symmetric). This is not true at branch points of the energy function, such as occur at the degenerate points where two bands "stick together"; but it seems obvious that the proof can be re-established in such cases by some formulation which excludes from the integrals the neighborhood of a branch point. I have not, however, investigated this question.

12. See A. H. Wilson, *The Theory of Metals*, Second Edition, Cambridge 1953, Section 8.551.
13. W. P. Dumke, *Phys. Rev.* **101**, 531 (1956).
14. C. Herring and E. Vogt, *Phys. Rev.* **101**, 944 (1956).
15. This is possible when nowhere in this region are $\mathbf{l}$ and $\mathbf{v}$ parallel to two different principal axes.
16. The *general* result was given in the form (2.22) because this is simpler than the form obtained if the "Onsager relation" (2.18) is not assumed. For $\mathbf{\Psi}^{\bullet}$—the effect of a magnetic field, in the order $\mathbf{H}^2$, on *electric current*—it makes no difference to the simplicity of the result.
17. The argument immediately following eq. (61) of LN is not accurate, though the conclusion is still correct. If the scattering is elastic, then $\tau((\mathbf{v}\epsilon)^{\dagger}-\mathbf{v}^{\dagger}\epsilon)$ must equal an arbitrary (vector) function of ϵ. It is easily verified that the numerator of the right-hand side of eq. (60) of LN then still vanishes.
18. C. Herring, reference 10, Appendix A.
19. J. H. Jeans, *The Dynamical Theory of Gases*, Fourth Edition, Dover, New York 1954, Section 371.
20. N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys*, Clarendon Press, Oxford 1936, Chapter 7, eq. (47); F. Seitz, *The Modern Theory of Solids*, McGraw-Hill, New York 1940, Section 127, eq. (29); A. H. Wilson, reference 12, Section 9.4; W. Shockley, *Electrons and Holes in Semiconductors*, D. Van Nostrand, New York 1950, Section 11.2.
21. For a discussion of an equivalent variation principle for a formally similar equation, see A. H. Wilson, reference 12, Chapter 10.
22. R. W. Keyes, *Phys. Rev.* **103**, 1240 (1956).
23. J. W. Gibbs (E. B. Wilson, ed.), *Vector Analysis*, Yale University Press, New Haven 1925. See also P. M. Morse and H. Feshbach, *Methods of Theoretical Physics*, McGraw-Hill, New York 1953, Chapter 1.
24. J. W. Gibbs, reference 23, Section 112.

Received April 22, 1957