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Electron-Electron Scattering and Transport Phenomena in Nonpolar Semiconductors

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The effect of electron-electron scattering processes due to Coulomb forces on the transport phenomena in nonpolar isotropic solids is treated in the framework of Kohler's variation principle. By considering the conduction electrons as a Fermi-Dirac gas of noninteracting free quasi-particles, each with charge $-e$ and mass m^*, electron-electron scattering is taken into account as a small perturbation, as is electron-phonon scattering in nonpolar solids. A shielded Coulomb potential which depends on two parameters—the effective dielectric constant and the shielding constant—is used as the interaction potential. These two parameters, for small concentrations of electrons, may be assumed to be independent of the distance between two electrons during a scattering process.

A general qualitative result is that electron-electron scattering causes the electrical conductivity to be reduced *less* than the electronic heat conductivity. The conductivities and the Wiedemann-Franz ratio will be reduced by an amount determined by the energy dependence of that perturbation of the electron distribution which is induced by primary scattering sources such as electron-phonon scattering or electron-impurity scattering. Quantitative results for nondegenerate semiconductors are obtained in terms of the variational method. With electron-phonon and electron-ion scattering assumed in turn as the primary scattering mechanism, the influence of electron-electron scattering on the electrical conductivity, the heat conductivity, and the Seebeck coefficient is calculated as function of temperature. The results are discussed with respect to the experimental situation.

The effect of electron-electron scattering on transport phenomena in metals is briefly considered. The applicability of the results obtained for isotropic semiconductors to an important class of anisotropic semiconductors is shown.

1. INTRODUCTION

IN the modern theory of electrons in nonpolar solids, the Coulomb interaction between conduction electrons is, for the most part, neglected. By a conduction electron we have in mind a free quasi-particle, of charge $-e$ and mass m^*, according to the free electron approximation. In this approximation, the periodic potential field of the fixed lattice particles and of all the other electrons is replaced by an almost constant potential field in order to describe the independent motion of a conduction electron (Hartree approximation). The ordinary theory of the electric transport phenomena is based upon the free-electron approximation. However, if the Coulomb interactions between conduction electrons are taken into account, some consequences of significance are obtained.

A first consequence is a change of the one-electron energy eigenvalues for a given momentum: When the Coulomb interaction between conduction electrons is taken into account, the one-electron excitation energy spectrum is somewhat altered.[1,2] The modification of the single-electron energy levels, via a corresponding change of the density of states, has some influence on the values of the transport coefficients but, even in the case of the monovalent metals, the corrections are temperature-independent and the Wiedemann-Franz ratio is not changed at all.[3] Thus, in calculating the transport coefficients we may neglect the influence of Coulomb interactions on the one-electron eigenstates. Furthermore, we assume that the influence of Coulomb interactions on the momentum distribution under thermal equilibrium conditions may be neglected. The momentum distribution of an interacting electron gas has been studied by several authors in recent years.[4]

A second consequence of Coulomb interaction between conduction electrons is the scattering of electrons by each other. The effect of this interaction on the transport phenomena in isotropic nonpolar semiconductors is the subject of this paper. The usual argument, that the total electric current is not changed because of the momentum conservation in an electron-electron scattering process, is correct only if the distribution of the electrons is the unperturbed distribution f_0 due to thermal equilibrium. However, when an external electrical field is applied, the electron-lattice interaction causes a perturbation of f_0 such that the steady-state distribution is $f=f_0+f_1$ ($f_1 \ll f_0$ for all electron energies E). Furthermore, when one takes electron-electron scattering into account it is exactly the perturbation f_1 which itself induces a further perturbation f_2. The perturbation f_1+f_2 determines the electrical conductivity. In the case of heat conduction, however, the pertinent quantity $E_1\mathbf{v}_1+E_2\mathbf{v}_2$ is not conserved in a single scattering process and, therefore, even if electron-phonon scattering is neglected, the electron-electron interaction itself will result in a nonzero heat resistivity.

In Appendix A it is shown that there exists an im-

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[1] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953); D. Pines, Phys. Rev. **92**, 626 (1953).

[2] P. Nozières and D. Pines, Phys. Rev. **109**, 741 (1960); **109**, 762 (1960).

[3] F. J. Blatt, Phys. Rev. **99**, 1735 (1955); R. Barrie, Phys. Rev. **103**, 1581 (1956).

[4] J. M. Luttinger, Phys. Rev. **119**, 1153 (1960); W. Kohn, Proc. Midwest Conf. Theoret. Phys.; Purdue University, Lafayette, April, 1960 (unpublished).

portant class of *anisotropic* semiconductors for which the above considerations also apply in principle.[5]

In restricting ourselves in this paper to isotropic conductors, we assume the free-electron approximation. The influence of all the interactions on the single-electron excitation spectrum is taken into account only to the extent that it is contained in the effective mass. The distribution of electrons on the one-electron states is given by the Fermi-Dirac statistics of noninteracting particles. The individual electron-electron scattering processes induce transitions between one-electron states. For the interaction potential we assume a screened Coulomb potential, first proposed empirically for a metal by Landsberg[6] and later determined systematically by Bohm and Pines.[1] The interaction potential and the ground state together determine another important physical quantity, the differential cross section.[7] In some cases the differential cross section can be expressed in terms of a transition probability calculated by first-order perturbation theory, which corresponds to the first Born approximation.[8] Even though this approximation may not be applicable, the change of the electron energy levels can still be neglected in nonpolar solids. Such a situation occurs in monovalent metals, where the cross section must be calculated by an exact method (see Appendix B). Some numerical values, applying to the conduction electrons in sodium, were calculated by Abrahams[9]; from these he estimates a mean free path of 2.5 cm at 4°K for electron-electron scattering.

In this investigation we avoid the concept of a free path or a relaxation time. This avoidance, according to our final results, turns out to be necessary, since it is impossible to define a uniform relaxation time for both charge and heat transport.[10] Thus, if both transport phenomena are superimposed (Peltier-effect), it is senseless to speak of a relaxation time for electron-electron scattering processes. Therefore, the theory of electrical transport phenomena is formulated by the variational method, first introduced by Kohler.[11] An important advantage of the variational method lies in its physical significance: The transport coefficients in the absence of a magnetic field are obtained by requiring that the steady-state distribution makes the rate of entropy production caused by all the scattering processes a maximum. A second advantage, connected with the mathematical procedure of the variational method, is the fact that different scattering mechanisms, represented formally by scattering operators, are additive. This means it is unnecessary to restrict the relative strengths of different scattering mechanisms.

The variation principle is discussed in the next section and its solutions are given in a general form. In Sec. 3, special questions connected with the electron-electron interaction—such as the interaction potential and the differential cross section—are discussed. In Sec. 4 the quantities determining the solution of the variation principle are given for Fermi-Dirac statistics, and in Sec. 5, by restricting the statistics to the nondegenerate case, explicit results are given for semiconductors with small electron concentrations. These results are applied to cases of practical interest in the last section and the numerical results are briefly discussed.

2. VARIATION PRINCIPLE

Formal Theory

For a gas of noninteracting free particles each with mass m^* and charge $-|e|$, the mean occupation numbers of the eigenstates are governed by the Fermi-Dirac statistics,

$$f_0=\left[\exp\left(\frac{E-\zeta}{k_BT}\right)+1\right]^{-1},\quad E=\frac{\hbar^2}{2m^*}|\mathbf{K}|^2. \tag{1}$$

The reduced wave vector $\mathbf{K}$ of a plane electron wave can be written in terms of the particle velocity vector $\mathbf{v}=(\hbar/m^*)\mathbf{K}$. From the mathematical point of view it is convenient to consider $\mathbf{K}$ and $\mathbf{v}$ interchangeably as quantum numbers of the one-electron states. Thus, the number of states per unit volume of the coordinate space is $2dK_xdK_ydK_z/(2\pi)^3$ or $2(m^*/h)^3dv_xdv_ydv_z$. The fundamental equation determining the steady-state distribution function f is the Boltzmann equation $(df/dt)=0$. For convenience we write

$$f=f_0-\frac{\Phi(\mathbf{v})}{k_BT}\frac{\partial f_0}{\partial\epsilon},\quad\text{where}\quad \epsilon=\frac{E}{k_BT}. \tag{2}$$

With an electric field F and a temperature gradient

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[5] The vector $e(\mathbf{v}_1+\mathbf{v}_2)$ is conserved in an individual electron-electron scattering process, provided one is concerned with nondegenerate energy surfaces in the wave vector space which are representable by a diagonalized quadratic form with energy-independent effective mass components. An example is n-germanium, where electron-electron scattering between energy surfaces belonging to the same energy minimum cannot change the electric current. Furthermore, if two electrons belonging to energy surfaces of two different equivalent energy minima (n-germanium) are scattered by each other, the vector $e(\mathbf{v}_1+\mathbf{v}_2)$ is conserved in normal (non-Umklapp) scattering processes.

[6] P. T. Landsberg, Proc. Phys. Soc. (London) **A162**, 49 (1949).

[7] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), p. 96.

[8] M. Born, Z. Physik **38**, 803 (1926).

[9] E. Abrahams, Phys. Rev. **95**, 839 (1954).

[10] This can easily be shown. An electric field may be applied to an isotropic conductor. If this field is switched off at $t=t_0$, the distribution for $t>t_0$ is given by

$$f(t)=f_0+[f(t_0)-f_0]\exp[(t-t_0)/\tau],$$

provided electron scattering can be described by a relaxation time τ. Now, assuming electron-electron scattering only, one finds $f(t)\approx f(t_0)$ because of the momentum conservation in each scattering process, and, thus, a relaxation time τ_{e-e} cannot be defined i.e., its value is infinite; however, if no electric field but a temperature gradient is applied, one finds $f(t\gg t_0)=f_0$, since in this case τ_{e-e} has a finite value.

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

$\partial T/\partial x$ in the x direction, we find the following integral equation for Φ when electron-electron scattering is included:

$$\frac{v_x}{k_BT}\frac{\partial f_0}{\partial \epsilon}\left[eF+T\frac{\partial}{\partial x}\left(\frac{\zeta}{T}\right)+k_B\epsilon\frac{\partial T}{\partial x}\right]=L_e(\Phi)+L_{e-e}(\Phi). \quad (3)$$

The operators L_e and L_{e-e} are given below; they are defined as linear integral operators because terms higher than first order in Φ are neglected.

The operator L_e includes those interactions of the electrons with the real crystal lattice which may be taken into account by time-dependent first-order perturbation theory. We may write

$$L_e(\Phi)=\frac{1}{8\pi^3k_BT}\int W_e(\mathbf{K},\mathbf{K}')f_0(1-f_0')(\Phi-\Phi')d\mathbf{K}', \quad (4)$$

where $f'_0=f_0(\mathbf{K}')$, etc.; W_e is a sum of transition probabilities, each normalized with respect to time and volume. For two important cases, considered below, the transition probabilities are noted explicitly. According to Bloch's theory[12] and its simple assumptions, the probability for the transition of an electron from an eigenstate defined by a wave vector $\mathbf{K}$ to a state $\mathbf{K}'$ induced by the collision with a longitudinal acoustical phonon of energy $\hbar\omega(\mathbf{q})=\hbar c_sq$, where $\mathbf{q}$ is a wave vector and c_s is the ($\mathbf{q}$-independent) phase velocity, can be written in terms of the Bloch constant C as

$$W_{e-\mathrm{ph}}(\mathbf{K},\mathbf{K}')=\frac{\pi}{\rho c_s}\left(\frac{2C}{3}\right)^2q[N\delta(E'-E-\hbar\omega)+(N+1)\delta(E'-E+\hbar\omega)]. \quad (5)$$

Here $\delta(x)$ denotes Dirac's delta function and ρ the density of the solid. Assuming that the deviation of the mean phonon occupation number $N(\mathbf{q})$ from thermal equilibrium may be neglected, we have $N=N_0$ where N_0 is the equilibrium phonon distribution.

The second type of scattering mechanism considered is the scattering of electrons by impurity atoms or by other atom-sized lattice imperfections. The general formula for the transition probability in such cases is

$$W_{e-i}(\mathbf{K},\mathbf{K}')=\frac{2\pi}{\hbar}\sum_i|\langle\mathbf{K}|\Delta V|\mathbf{K}'\rangle|^2\delta(E-E'), \quad (6)$$

where $\Delta V(\mathbf{r}-\mathbf{R}_j)$ is the perturbation potential associated with the lattice site $\mathbf{R}_j$.

Of primary interest in this investigation is the operator L_{e-e}, which, operating on Φ, gives the rate of change of the steady-state distribution f due to electron-electron scattering. From the mathematical theory of Fermi-Dirac gases[13] we know that this rate of change of f is given by

$$\left(\frac{\partial f}{\partial t}\right)_{e-e}=2\left(\frac{m^*}{h}\right)^3\int\int\int[f'f'_1(1-f)(1-f_1)-ff_1(1-f')(1-f'_1)]\alpha(\chi,g)\sin\chi d\chi d\gamma d\mathbf{v}_1. \quad (7)$$

The quantity $\alpha(\chi,g)$ is defined explicitly below[14]; $\mathbf{g}=\mathbf{v}-\mathbf{v}_1$ is the relative velocity of two electrons which undergo an electron-electron scattering process; χ is the deflection angle for $\mathbf{g}$ and γ is a second angle to fix $\mathbf{g}'=\mathbf{v}'-\mathbf{v}'_1$ with respect to $\mathbf{g}$. The occurrence of only five variable integrations in Eq. (7) instead of nine results from the two conservation laws

$$\epsilon+\epsilon_1=\epsilon'+\epsilon'_1, \quad (8a)$$

and

$$\mathbf{v}+\mathbf{v}_1=\mathbf{v}'+\mathbf{v}'_1, \quad (8b)$$

by which four variables are eliminated. If we neglect higher than first-order terms in Φ under the integral in Eq. (7), this equation can be rewritten in the simpler form

$$L_{e-e}(\Phi)=\frac{2}{k_BT}\left(\frac{m^*}{h}\right)^3\int\int\int\exp(\epsilon+\epsilon_1-2\zeta/k_BT)\times f_0f'_0f_{01}f'_{01}(\Phi+\Phi_1-\Phi'-\Phi'_1)\times\alpha(\chi,g)\sin\chi d\chi d\gamma d\mathbf{v}_1. \quad (9)$$

It can be seen that the factor

$$\exp(\epsilon+\epsilon_1-2\zeta/k_BT)f_0f'_0f_{01}f'_{01}$$

is invariant against interchange of $\mathbf{v}$, $\mathbf{v}_1$ with $\mathbf{v}'$, $\mathbf{v}'_1$ when Eq. (8a) is applied. Therefore, an important integral theorem, which for classical statistics is proved in detail by Chapman and Cowling,[15] is also true for Fermi-Dirac statistics. For integrable functions Φ_i we have

$$(\Phi_i,\Phi_j)_{e-e}=2\left(\frac{m^*}{h}\right)^3\int\Phi_iL_{e-e}(\Phi_j)d\mathbf{v}=(\Phi_j,\Phi_i)_{e-e}, \quad (10)$$

and

$$(\Phi_i,\Phi_i)_{e-e}\geq 0. \quad (11)$$

Now, including electron-electron scattering, the following formulation of the variation principle is convenient: Of all trial functions Φ_i, the solution Φ of Eq. (3) has the characteristic property of making the

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[12] H. Jones, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XIX, Part 1, p. 288.

[13] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, New York, 1958), p. 295; E. A. Uehling, and G. E. Uhlenbeck, Phys. Rev. 43, 552 (1933).

[14] The function $(2/g)\alpha(\chi,g)d\Omega$, where $d\Omega$ is the solid angle element $\sin\chi d\chi d\gamma$, represents the effective scattering cross section for electrons. The number of collision processes per time and volume unit between electrons in $d\mathbf{v}$ and $d\mathbf{v}_1$ such that the direction of the relative velocity $\mathbf{g}'$ lies in $d\Omega$ is given by

$$fd\mathbf{v}f_1d\mathbf{v}_12\alpha(\chi,g)d\Omega.$$

[15] See reference 13, p. 85.

integral $(\Phi_i,\Phi_i)=(\Phi_i,\Phi_i)_e+(\Phi_i,\Phi_i)_{e-e}$ a maximum subject to the subsidiary condition

$$(\Phi_i,\Phi_i)=2(m^*/h)^3\int\Phi_iF(\mathbf{v})d\mathbf{v},$$

where $F(\mathbf{v})$ is an abbreviation for the left-hand side of the integral equation (3).[16] The proof of the variation principle depends on the relations (10) and (11) and on similar relations for the scattering operator L_e.[11]

Transport Coefficients

The general formulation of the transport coefficients is straightforward as in the case for electron-lattice scattering only. The difference consists of formally replacing the operator L_e by L_e+L_{e-e}. To facilitate the calculation of the transport coefficients in our generalized case, we review briefly the mathematical procedure.[11] If we write

$$\Phi(\mathbf{v})=v_x\frac{m^*}{\hbar}c(\epsilon)$$

$$=v_x\left\{\left[eF+T\frac{\partial}{\partial x}\left(\frac{\zeta}{T}\right)\right]c^{(\frac{3}{2})}+\frac{1}{T}\frac{\partial T}{\partial x}c^{(\frac{5}{2})}\right\},\qquad(12)$$

and

$$L(\Phi)=v_x\frac{m^*}{\hbar}\mathfrak{L}(c)\quad\text{with}\quad\mathfrak{L}=\mathfrak{L}_e+\mathfrak{L}_{e-e},\qquad(13)$$

the integral equation (3) breaks into two equations,

$$\mathfrak{L}(c^{(n)})=\frac{(\epsilon k_BT)^{n-\frac{3}{2}}}{k_BT}\frac{\partial f_0}{\partial\epsilon},\quad n=\tfrac{3}{2},\tfrac{5}{2}.\qquad(14)$$

To find the solutions of Eq. (14), the trial functions $c^{(n)}$ are conveniently written in terms of the variables η, where $\eta=\epsilon-\zeta/k_BT$ (or $\eta=\epsilon$) for a degenerate (nondegenerate) electron gas. By expanding the trial functions as power series in η,

$$c^{(n)}=\sum_{r=0}^{\infty}c_r^{(n)}\eta^r,\qquad(15)$$

the coefficients $c_r^{(n)}$ may be determined through the Ritz procedure via the solution of a usual extremal problem of differential calculus. The perturbation functions $c^{(n)}$ determine the electric density J_x and the electronic heat current density W_x. To determine the transport coefficients we define

$$\beta_r^{(m)}=\frac{2}{k_BT}\left(\frac{m^*}{h}\right)^3\int v_x^2(k_BT\epsilon)^{m-\frac{3}{2}}\frac{\partial f_0}{\partial\epsilon}\eta^r d\mathbf{v}.\qquad(16)$$

If we also define in the usual form the symmetrical elements,

$$d_{rs}=d_{rs}^{(e)}+d_{rs}^{(e-e)}$$

$$=2\left(\frac{m^*}{h}\right)^3\int v_x^2\eta^r[\mathfrak{L}_e(\eta^s)+\mathfrak{L}_{e-e}(\eta^s)]d\mathbf{v},\qquad(17)$$

of the determinants

$$A=\det(d_{rs})\quad\text{and}\quad A_{m,n}=\begin{vmatrix}0&\beta_0^{(m)}&\beta_1^{(m)}&\cdots\\\beta_0^{(n)}&d_{00}&d_{01}&\cdots\\\beta_1^{(n)}&d_{10}&d_{11}&\cdots\\\cdot&\cdot&\cdot&\\\cdot&\cdot&\cdot&\\\cdot&\cdot&\cdot&\end{vmatrix},\qquad(18)$$

then the transport coefficients are given by the following formulas:

electrical conductivity

$$\sigma=(J_x/F)_{\partial T/\partial x=0}=-e^2(A_{\frac{3}{2},\frac{3}{2}}/A),\qquad(19)$$

heat conductivity

$$\kappa=\left(\frac{W_x}{\partial T/\partial x}\right)_{J_x=0}=-\frac{1}{T}\frac{A_{\frac{3}{2},\frac{3}{2}}A_{\frac{5}{2},\frac{5}{2}}-A_{\frac{3}{2},\frac{5}{2}}^2}{AA_{\frac{3}{2},\frac{3}{2}}},\qquad(20)$$

Seebeck coefficient

$$\alpha=\left(F+\frac{1}{e}\frac{\partial\zeta}{\partial x}\right)_{J_x=0}=-\frac{1}{eT}\frac{A_{\frac{3}{2},\frac{5}{2}}-\zeta A_{\frac{3}{2},\frac{3}{2}}}{A_{\frac{3}{2},\frac{3}{2}}}.\qquad(21)$$

To apply these formulas to concrete cases we will approximate the determinants A and $A_{m,n}$ by determinants with a finite number of rows. Sondheimer[11] has given explicit formulas for successive approximations of the electrical conductivity $\sigma^{(0)}$, $\sigma^{(1)}$, $\cdots$, the heat conductivity $\kappa^{(0)}$, $\kappa^{(1)}$, $\cdots$, and the Seebeck coefficient $\alpha^{(0)}$, $\alpha^{(1)}$, $\cdots$ (see also Wilson[17]). No general statements can be made on the convergence of successive approximations.

3. INTERACTION POTENTIAL, SCATTERING FORMULA, AND ELECTRON-ELECTRON SCATTERING OPERATOR

The electron-electron scattering operator L_{e-e} (Eq. 9) must be put into a form such that the quantities $d_{rs}^{(e-e)}$ and thereby the transport coefficients may be calculated quantitatively in a fairly simple manner. To this end, one must know the effective cross section $\alpha(\chi,g)$, which depends on the interaction potential $V(r)$.

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[16] The physical meaning of $(\Phi,\Phi)_{e-e}$ is easily understood if we write the entropy as

$$S=-2k_B(m^*/h)^3\int[f\ln f+(1-f)\ln(1-f)]d\mathbf{v},$$

and the entropy flow as

$$\mathbf{s}=-2k_B(m^*/h)^3\int[f\ln f+(1-f)\ln(1-f)]\mathbf{v}d\mathbf{v}.$$

Then we get [Dorn, Z. Naturforsch. **12A**, 739 (1957)].

$$\frac{\partial S}{\partial t}+\operatorname{div}\mathbf{s}=\frac{1}{T}(\Phi,\Phi)_e+\frac{1}{T}(\Phi,\Phi)_{e-e},$$

so that $(1/T)(\Phi,\Phi)_{e-e}$ represents the rate of entropy production per unit volume due to electron-electron scattering processes.

[17] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953), p. 310.

Interaction Potential

For the interaction potential $V(r=|\mathbf{r}_1-\mathbf{r}_2|)$ between two electrons with space vectors $\mathbf{r}_1$ and $\mathbf{r}_2$, we take the shielded Coulomb potential

$$V(r)=(e^2/\kappa r)\exp(-r/\lambda). \tag{22}$$

In a crystal which includes one of the cubic point groups in its symmetry operations, the interaction potential depends on two parameters: The effective dielectric constant κ and the shielding constant λ. Both these parameters take into account polarization effects. The dielectric constant κ describes what may be called the lattice polarization. This polarization is composed of two parts, namely, the polarization of the ion cores when the lattice particles are fixed, and of the displacement polarization which is associated with the readjusting of the positions of the lattice particles when an electron moves through the crystal. The shielding constant λ, as first pointed out by Macke,[18] describes the polarization of an electron cloud surrounding a given electron. For a nondegenerate electron gas the above formula for $V(r)$ results from the classical paper of Debye and Hückel.[19]

For semiconductors, there is no clear-cut theory of the dielectric constant for arbitrary electron concentration and arbitrary degree of polar bonding. Restricting ourselves to nonpolar semiconductors with small electron concentrations, we make the fairly reasonable assumption $\kappa=\kappa_0$, where κ_0 is the static dielectric constant. The dependence of κ on the velocities of two interacting electrons plays an essential role only if one is concerned with semiconductors characterized by polar bonding.[20] In nonpolar semiconductors, because of the small effective charge of the lattice particles, the lattice displacement polarization may be neglected. Thus, one assumes $\kappa_0 \simeq \kappa_\infty$ (κ_∞ = optical dielectric constant). We are left with the question of the r dependence of κ. According to Kohn,[21] for distances r large compared to the lattice constant d, one has $\kappa=\kappa_0$. Now, indeed, the minimum distance $r_{\min}$ of two electrons which undergo a scattering process is in general much greater than d. Assuming the extreme case of large angle scattering, namely, $g=v_1-v_2$, we may estimate the value of $r_{\min}$ from

$$(e^2/\kappa_0 r_{\min})\exp(-r_{\min}/\lambda)=\tfrac{1}{2}m_{\mathrm{red}}{}^*g^2, \quad m_{\mathrm{red}}{}^*=\tfrac{1}{2}m^*. \tag{23}$$

Substituting on the right for g its thermal average $\bar{g}$ and assuming reasonable data ($n=10^{15}$ cm^{-3}, $\kappa_0=16$, and $T=300$°K), we find $r_{\min}\simeq\frac{1}{10}\lambda$. The shielding constant λ is approximately 10^{-5} cm. At lower temperature, too, we have $r_{\min}(\bar{g})\gg d$. Hence, for the bulk of the electron pairs which undergo a scattering process in a nondegenerate semiconductor, it is reasonable to assume κ independent of r and equal to κ_0.[22] Furthermore, we may expect, as for electron-ion scattering,[23] that small-angle scattering is the dominant effect of electron-electron scattering on the transport phenomena.

The second parameter entering $V(r)$ is the shielding constant λ. For a nondegenerate electron gas, λ is given by the Debye length,

$$\lambda_D=(\kappa_0 k_B T/4\pi n e^2)^{\frac{1}{2}}. \tag{24}$$

Scattering Formula

The quantity $(2/g)\alpha(\chi,g)\sin\chi d\chi d\gamma$ is the effective scattering cross section in the center-of-mass coordinate system. It is calculated by solving the Schrödinger equation for the two-particle scattering problem in relative coordinates. As usual the equation

$$\tau(\chi,g)=\frac{\hbar}{2im_{\mathrm{red}}g^*}\sum_{l=0}^{\infty}(2l+1)[\exp(2i\delta_l)-1]P_l(\cos\chi) \tag{25}$$

defines the scattering amplitude in terms of partial waves. Here P_l denotes the Legendre polynomial of order l; the δ_l are phase constants which depend on g and $V(r)$. The scattering amplitude determines the function α, given by[24]

$$\alpha(\chi,g)=\tfrac{1}{2}g[\tfrac{1}{4}|\tau(\chi,g)+\tau(\pi-\chi,g)|^2 + \tfrac{3}{4}|\tau(\chi,g)-\tau(\pi-\chi,g)|^2], \tag{26}$$

when indistinguishability and spin of the particles are taken into account.

The calculation of the δ_l constitutes the mathematical problem. When $\delta_l \ll 1$ the Born approximation applies, i.e., $E\gg V(r)$ for $r\geq r_{\min}$. Obviously, then, the amplitude of the scattered wave is small compared to the amplitude of the plane wave. The criterion of the validity of the Born approximation is

$$(\lambda m_{\mathrm{red}}{}^* g/\hbar)\gg 1. \tag{27}$$

Assuming nondegenerate semiconductors, putting $\lambda=\lambda_D$ in Eq (27) and replacing g by its thermal overage $\bar{g}=0.73\bar{v}$, where $\bar{v}=(8k_BT/\pi m_{\mathrm{red}}{}^*)^{\frac{1}{2}}$, we see that the Born approximation holds for almost all electron pairs in the distribution $f_0(g)$. The Born approximation

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[18] W. Macke, Z. Naturforsch. **5a**, 192 (1952).

[19] P. Debye and E. Hückel, Z. Physik **24**, 185 (1923).

[20] H. Fröhlich, H. Pelzer, and S. Zienau, Phil. Mag. **XLI**, 221 (1950).

[21] W. Kohn, Phys. Rev. **105**, 509 (1957).

[22] In nearly degenerate semiconductors the above arguments do not hold. Since in such a case $r_{\min}$ may be of the order of the lattice constant, the dependence of κ and λ on r has to be taken into account. The theory must be revised by investigating electron-electron scattering in coordinate and momentum space together. In principle, the same is true for strong impurity scattering, a problem which is by no means settled [C. Herring, J. Phys. Chem. Solids **8**, 543 (1958)].

[23] L. Spitzer, Jr., and W. Härm, Phys. Rev. **89**, 977 (1953); C. Herring, Bell System Tech. J. **XXXIV**, 237 (1955).

[24] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1952); N. F. Mott, Proc. Roy. Soc. (London) **A126**, 259 (1930).

scattering amplitude is, with Eq. (22), given by

$$\tau(\chi,g)=-(2m_{\text{red}}^*e^2/\hbar^2\kappa_0)\times[\lambda_D^{-2}+(2^{\frac{1}{2}}m_{\text{red}}^*g/\hbar)^2(1-\cos\chi)]^{-1}. \quad (28)$$

Thus, the scattering formula reads

$$\alpha(\chi,g)=[e^4/2\kappa_0^2(m_{\text{red}}^*)^2g^3]\times[(\beta^2+1-\cos\chi)^{-2}+(\beta^2+1+\cos\chi)^{-2}-(\beta^2+1-\cos\chi)^{-1}(\beta^2+1+\cos\chi)^{-1}], \quad (29)$$

where

$$\beta=\hbar/2^{\frac{1}{2}}\lambda_D m_{\text{red}}^*g. \quad (30)$$

Electron-Electron Scattering Operator

When $\alpha(\chi,g)$ is given, it is possible in principle to calculate the scattering operator which describes electron-electron scattering in the framework of the variational method. Using a transformation, first introduced by Landshoff,[25] by which the x components of the velocity vectors under the integral in Eq. (9) are eliminated, the final form of the electron-electron scattering operator is given by

$$\mathfrak{L}_{e-e}(c)=\frac{2}{k_BT}\left(\frac{m^*}{h}\right)^3\frac{1}{v^2}\times\int\int\int\exp(\epsilon+\epsilon_1-2\zeta/k_BT)f_0f'_0f_{01}f'_{01}\times[\mathbf{v}\cdot\mathbf{v}c(\eta)+\mathbf{v}\cdot\mathbf{v}_1c(\eta_1)-\mathbf{v}\cdot\mathbf{v}'c(\eta')-\mathbf{v}\cdot\mathbf{v}'_1c(\eta'_1)]\times\alpha(\chi,g)\sin\chi d\chi d\gamma d\mathbf{v}_1. \quad (31)$$

This form of $\mathfrak{L}_{e-e}(c)$ has some advantage for introducing relative velocity coordinates, as shown below.

4. ON THE SOLUTION OF THE VARIATION PRINCIPLE

In this section a formal calculation of the $\beta_r^{(n)}$ and $d_{r-s}^{(e-e)}$ is carried out. For a degenerate electron gas, we use $\eta=\epsilon-\zeta/k_BT$, and the $\beta_r^{(n)}$ can easily be written in a form such that well-known results apply:

$$\beta_r^{(n)}=\frac{32\pi}{3\times2^{\frac{1}{2}}}\frac{(m^*)^{\frac{1}{2}}}{h^3}\int_{-\infty}^{+\infty}E^n\frac{\partial f_0}{\partial\eta}\eta^rd\eta, \quad n=\tfrac{3}{2},\tfrac{5}{2}. \quad (32)$$

The integral alone is denoted by $\alpha_r^{(n)}$ by Wilson,[17] who has given numerical values for it. Our value [Eq. (32)] is different by a constant factor, just the same as in the case of the $d_{rs}^{(e)}$, because of the formulation of the variation principle in **v** space instead **K** space (Wilson). Both descriptions are correct and equivalent when considering free quasi-particles. Here the **v** space is more convenient. Then, relative velocity coordinates can be introduced which describe conveniently the dynamics of binary scattering processes. From Eqs. (17) and (31), we have

$$d_{rs}^{(e-e)}=\frac{4}{k_BT}\left(\frac{m^*}{h}\right)^6\times\int_{\mathbf{v}}\int_{\mathbf{v}_1}\int_{\chi}\int_{\gamma}\exp(\epsilon+\epsilon_1-2\zeta/k_BT)f_0f_{01}f'_0f'_{01}\times\left(\frac{v_x}{v}\right)^2\eta^r[\mathbf{v}\cdot\mathbf{v}\eta^s+\mathbf{v}\cdot\mathbf{v}_1\eta_1^s-\mathbf{v}\cdot\mathbf{v}'(\eta')^s-\mathbf{v}\cdot\mathbf{v}'_1(\eta'_1)^s]\times\alpha(\chi,g)\sin\chi d\chi d\gamma d\mathbf{v}_1d\mathbf{v}. \quad (33)$$

This is an eightfold integral because the twelve velocity coordinates are reduced by four because of energy and momentum conservation. The introduction of relative velocity coordinates consists of relating the velocity vectors **v**, **v**₁; **v**′, **v**′₁ to the center-of-mass velocity **G** as shown in Appendix *C*. After the transformation, the $d_{rs}^{(e-e)}$ can be written in terms of the center-of-mass velocity and the relative velocity as integration variables:

$$d_{rs}^{(e-e)}=\frac{2^5}{k_BT}\left(\frac{m^*}{h}\right)^6\left(\frac{2k_BT}{m^*}\right)^4\int_{\mathfrak{G}=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\int_{\mathfrak{g}=0}^{\infty}\int_{\vartheta=0}^{\pi}\int_{\varphi=0}^{2\pi}\int_{\chi=0}^{\pi}\int_{\gamma=0}^{2\pi}\exp[2(\mathfrak{G}^2+\mathfrak{g}^2-\zeta/k_BT)]f_0f'_0f_{01}f'_{01}\times[\mathfrak{G}\cos\theta-\mathfrak{g}(\cos\vartheta\cos\theta+\sin\vartheta\sin\theta\cos\phi)]^2\frac{\eta^r}{\epsilon}\{\epsilon\eta^s+(\mathfrak{G}^2-g^2)\eta_1^s-[\mathfrak{G}^2+\mathfrak{g}^2\cos\chi-\mathfrak{g}\mathfrak{G}(\cos\vartheta+\cos\vartheta')](\eta')^s-[\mathfrak{G}^2-\mathfrak{g}^2\cos\chi-\mathfrak{g}\mathfrak{G}(\cos\vartheta-\cos\vartheta')](\eta'_1)^s\}\alpha'(\chi,\mathfrak{g})\sin\chi d\chi d\gamma\mathfrak{G}^2d\mathfrak{G}\sin\theta d\theta d\phi\mathfrak{g}^2d\mathfrak{g}\sin\vartheta d\vartheta d\varphi, \quad (34)$$

where $\alpha'(\chi,\mathfrak{g})=\alpha(\chi,g)$, $\cos\vartheta'=\cos\vartheta\cos\chi+\sin\vartheta\sin\chi\cos\gamma$.

As a consequence of momentum conservation [Eq. (11)] we have

$$d_{rs}^{(e-e)}=0, \quad \text{if } r \text{ or } s \text{ is zero.} \quad (35)$$

Now, the corresponding quantities for the interaction of electrons with phonons or with point imperfections do not vanish. Therefore, electron-electron scattering in isotropic conductors is to be considered a higher-order effect in the following sense:

The electron-electron scattering processes will affect only the energy-dependent terms in the series for the perturbations $c^{(n)}$; thus the zero-order term $c_0^{(n)}\eta^0$ is not influenced at all. However, this term to a great extent determines the electrical conductivity. There-

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[25] R. Landshoff, Phys. Rev. **76**, 904 (1949) and **82**, 442 (1951); an explicit deviation of this transformation is given by H. Schirmer and J. Friederich, Z. Physik **151**, 174 (1958).

fore, with respect to the variational method, the electrical charge transport is denoted as a zero-order transport phenomenon. The electrical resistivity would be zero if there were no other scattering mechanism besides electron-electron scattering. The thermal heat conduction, in the same sense, is a first-order transport phenomenon; it is primarily determined by the second term of the power series in η, $c_1^{(n)}\eta^1$. However, this term is affected by electron-electron scattering processes, because $(\mathbf{v}\eta+\mathbf{v}_1\eta_1)$ is not conserved in an electron-electron scattering process, so that $d_{11}^{(e-e)}\neq 0$. Thus, the electronic heat resistance is different from zero even if only electron-electron scattering is taken into account. The heat conduction is influenced in zero order because it itself is a first-order transport phenomenon.

We have emphasized the difference between charge and heat transport, which has also been pointed out by Keyes.[26] In our investigation the differing physical aspects of both transport phenomena come out quite naturally by applying an exact and straightforward mathematical method.[27] From this consideration we may conclude generally that, because of electron-electron scattering processes, the heat conductivity of isotropic conductors and of a certain important class of anistropic conductors (Appendix A) is reduced more than the electrical conductivity, and that the Wiedemann-Franz ratio is affected.

A quantitative calculation of the $d_{rs}^{(e-e)}$ for the general case of Fermi-Dirac statistics is difficult, since after integrating in Eq. (34) over θ, ϕ, and φ, which results in a factor $(8\pi^2/3)\epsilon$, we are left with five further integration variables and ζ as a parameter.

5. NONDEGENERATE SEMICONDUCTORS

For small electron concentrations, our calculations have a solid foundation with respect to the interaction potential [Eq. (22)] and the effective scattering cross section [Eq. (26)]. Furthermore, the calculations can be carried out avoiding numerical methods, since the Maxwell-Boltzmann function describes the unperturbed distribution, given by

$$f_0=\exp(-\epsilon+\zeta/k_BT), \tag{36}$$

$$\zeta=k_BT\ln[n/2(2\pi m^*k_BT/h^2)^{\frac{3}{2}}]. \tag{37}$$

The perturbations $c^{(n)}$ here are conveniently written in terms of $\eta=\epsilon$, and it follows from Eq. (16) that

$$\beta_r^{(n)}=-\frac{(r+n)!}{(\frac{3}{2})!}\frac{n(k_BT)^{n-\frac{3}{2}}}{m^*},\quad n=\tfrac{3}{2},\tfrac{5}{2};\quad r=0,1,2\cdots. \tag{38}$$

Electron-Electron Scattering

The important quantities $d_{rs}^{(e-e)}$ can be calculated analytically, since we have the identity

$$\exp[2(\mathfrak{G}^2+\mathfrak{g}^2-\zeta/k_BT)]f_0f'_0f_{01}f'_{01}\equiv\exp[-2(\mathfrak{G}^2+\mathfrak{g}^2-\zeta/k_BT)]. \tag{39}$$

Using this identity, we finally get, after considerable algebra, as the first few terms

$$\begin{aligned} &d_{r0}^{(e-e)}=0,\quad r=0,1,2\cdots,\\ &d_{11}^{(e-e)}=C(T)L_1(\delta^2),\\ &d_{21}^{(e-e)}=C(T)[\tfrac{7}{2}L_1(\delta^2)+7L_2(\delta^2)],\\ &d_{22}^{(e-e)}=C(T)[(77/4)L_1(\delta^2)+7L_2(\delta^2)+L_3(\delta^2)], \end{aligned} \tag{40}$$

where the factor $C(T)$ and the parameter δ^2 are given by

$$C(T)=\frac{2\pi^{\frac{1}{2}}}{3}\frac{n^2e^4}{(m^*k_BT)^{\frac{3}{2}}\kappa_0^2},\quad \delta^2=\frac{\hbar^2}{2\lambda_D^2m^*k_BT}. \tag{41}$$

The parameter integrals are defined by the formula

$$L_n(\delta^2)=\int_0^\infty \exp(-x^2)x^{2n+1} \times\{[5(1+\delta^2/x^2)-(1+\delta^2/x^2)^{-1}] \times\ln(1+2x^2/\delta^2)-10\}dx. \tag{42}$$

In general $\delta^2\ll 1$, so that the L_n can be fairly well approximated by simple formulas given in Appendix D.

Electron-Ion Scattering

The shielded Coulomb interaction potential for an electron and an ion is conveniently written in terms of a three-dimensional Fourier series:

$$V(\mathbf{r}-\mathbf{R}_j)=\frac{4\pi e^2}{\kappa_0}\sum_{\mathbf{q}}\frac{\exp[i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_j)]}{q^2+\lambda_D^2}. \tag{43}$$

Introducing Eq. (43) into Eq. (6), we find the corresponding transition probability, and after some calculations the scattering operator is given by[28]

$$\mathfrak{L}_{e-i}(c)=[2\pi e^4N_im^*f_0c(\epsilon)/\kappa_0^2\hbar^3k_BTK^3] \times\{\ln[1+(2\lambda_DK)^2]-[1+(2\lambda_DK)^2]^{-1}\}, \tag{44}$$

where N_i is the concentration of ionized impurity atoms. Transcribing this equation from the $\mathbf{K}$ to the $\mathbf{v}$ space,

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[26] R. W. Keyes, Bull. Am. Phys. Soc. 5, 150 (1960).

[27] There exists an interesting analogy to electron-electron scattering processes and their influence on the *electronic* heat conductivity. The *lattice* heat conductivity of an isotropic dielectric solid has a finite value if four-phonon normal scattering processes are taken into account. These four-phonon processes correspond directly to electron-electron scattering processes, if we think of phonons as of quasi-particles of the lattice. Not much is known about the lattice heat conduction, especially at higher temperatures ($T\gtrsim\theta_D$), and therefore the variational method seems to be a reasonable one to use to treat the insulator heat conductivity problem. I am indebted to Professor M. Kohler, Braunschweig, for a stimulating discussion concerning this point.

[28] If one writes $\mathfrak{L}_{e-i}(c)$ in terms of a relaxation time τ—$\mathfrak{L}_{e-i}(c)\propto c$—one has $\tau^{-1}=K_x\mathfrak{L}_{e-i}(c)/(f_0-f)$. The so-defined relaxation time is identical with the Brooks-Herring formula for $\tau(\epsilon)$.

TABLE I. Values of $\delta^2 = (\hbar^2/2\lambda^2{}_D m^* k_B T)$.

T (°K)	n (cm^{-3})	m^*/m	κ_0	λ_D (cm)	δ^2
300	10^{15}	1	16	1.5×10^{-5}	5.6×10^{-5}
10	10^{10}	1	16	8.8×10^{-4}	5.6×10^{-7}

we get the desired quantities:

$$d_{rs}{}^{(e-i)} = \frac{4(2\pi)^{\frac{1}{2}} e^4 N_i n}{3\kappa_0{}^2 (m^* k_B T)^{\frac{3}{2}}} M_{r+s}(\delta^2), \tag{45}$$

where the parameter integrals are defined by

$$M_{r+s}(\delta^2) = \int_0^\infty \exp(-y^2) y^{2(r+s+\frac{1}{2})} [\ln(1+4y^2/\delta^2) - (1+\delta^2/4y^2)] dy. \tag{46}$$

The interaction potential for electron-ion scattering [Eq. (43)] is assumed to be characterized by the same parameters (shielding constant λ and dielectric constant κ) as is the interaction potential for electron-electron scattering. Thus, δ^2 is the parameter given by Eq. (41); with $\delta^2 \ll 1$, approximation formulas given in Appendix D apply to the M_{r+s}.

Electron-Phonon Scattering

By specializing the formula (5) for the transition probability $W_{e-\mathrm{ph}}$ to nondegenerate semiconductors, neglecting the deviation of the phonon distribution from thermal equilibrium, and assuming elastic electron-phonon scattering processes, we find the corresponding scattering operator[29]

$$\mathfrak{L}_{e-\mathrm{ph}}(c) = \hbar K f_0 c(\epsilon)/m^* k_B T l_e, \tag{47}$$

where l_e is given in terms of Bloch's constant C by

$$l_e = 9\pi\rho\hbar^4 c_s{}^2/4C^2(m^*)^2 k_B T. \tag{48}$$

Transcribing Eq. (68) from the $\mathbf{K}$ to the $\mathbf{v}$ space, we obtain the $d_{rs}{}^{(e-\mathrm{ph})}$ in terms of l_e. However, with $\mathfrak{L} = \mathfrak{L}_{e-\mathrm{ph}}$ the perturbation $c(\epsilon)$ can, of course, be calculated directly from Eqs. (3) and (47). Then, the electrical conductivity can be calculated at once; the mobility $\mu_e = \sigma/ne$ is thereby defined and we can write l_e in terms of μ_e. Finally we get

$$d_{rs}{}^{(e-\mathrm{ph})} = [16ne/9\pi(m^*)^2\mu_e](r+s+2)!. \tag{49}$$

6. QUANTITATIVE RESULTS FOR SEMICONDUCTORS

Electron-Ion and Electron-Electron Scattering

In this section the case in which electron-ion scattering predominates over electron-phonon scattering is considered. Let us assume an isotropic one-band semiconductor with only one kind of impurity atoms with a single energy level in the forbidden zone. The concentration of ionized impurity atoms is then equal to the concentration of conduction electrons. If we assume that κ_0 and λ have the same values for electron-electron scattering and for electron-ion scattering, the quantities $d_{rs}{}^{(e-e)}$ and $d_{rs}{}^{(e-i)}$ have almost the same temperature dependence. Therefore, the temperature dependence of the transport coefficient for electron-ion scattering remain almost unaffected when electron-electron scattering is taken into account, but the numerical values of the coefficients are more or less changed. We define the quantities

$$e_{rs} = d_{rs}/d_{00}{}^{(e-i)}, \tag{50}$$

where $d_{rs} = d_{rs}{}^{(e-i)}$ when electron-electron scattering is neglected, and where $d_{rs} = d_{rs}{}^{(e-i)} + d_{rs}{}^{(e-e)}$ when electron-electron scattering is taken into account. In both cases the temperature dependences of the e_{rs} are exactly the same in the limit $\delta^2 = 0$. In practical cases δ^2 is usually small (Table I). We calculate the transport coefficients in the limit $\delta^2 = 0$, i.e., the Debye length is much larger than the electron wavelength. To this end, we need the values of e_{rs} listed in Table II, the $\beta_r{}^{(n)}$ for $r = 0$, 1, 2 [Eq. (38)], and $d_{00}{}^{(e-i)}$ [Eq. (45)]. For the electrical conductivity, ignoring and including electron-electron scattering (denoted by no subscript and the subscript e, respectively), we find

$$\begin{aligned} \sigma^{(0)} &= e^2(\beta_0{}^{(\frac{3}{2})})^2/d_{00}{}^{(e-i)}, & \sigma_e{}^{(0)} &= \sigma^{(0)}, \\ \sigma^{(1)} &= 3.25\sigma^{(0)}, & \sigma_e{}^{(1)} &= 1.93\sigma^{(0)}, \\ \sigma^{(2)} &= 3.39\sigma^{(0)}, & \sigma_e{}^{(2)} &= 1.94\sigma^{(0)}. \end{aligned} \tag{51}$$

Successive approximations for the electrical conductivity show rapid convergence after the first-order correction.[30] This convergence behavior of the $\sigma^{(n)}$ reflects the energy-dependence of the perturbation $c(\epsilon)$. For electron-ion scattering only, we have roughly $c_{e-i}(\epsilon) \propto \epsilon^{\frac{3}{2}}$. Therefore, more than one term in the series expansion for $c(\epsilon)$ must be taken into account. Similar considerations apply to the lowest-order approximations of the electronic heat conductivity. For the

TABLE II. Values of e_{rs}.

e_{rs}	Without $e-e$ scattering	Including $e-e$ scattering
e_{00}	1	1
e_{10}	1	1
e_{11}	2	$2+2^{\frac{1}{2}}$
e_{20}	2	2
e_{21}	6	$6+11/2^{\frac{1}{2}}$
e_{22}	24	$24+157/2^{\frac{3}{2}}$

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[29] J. Appel, Z. Naturforschg. **13a**, 386 (1958), Eq. (5a).

[30] In first-order approximation the electrical conductivity is given by

$$\sigma_e{}^{(1)} = \sigma^{(0)} \left[1 + \frac{(\frac{5}{2} - M_1/M_0)^2}{M_2/M_0 - (M_1/M_0)^2 + 2^{-\frac{3}{2}} n L_1/N_i M_0} \right], \quad \delta^2 \leqslant 1.$$

Assuming $n \gg N_i$, we have $\sigma_e{}^{(1)} = (1/3.25)\sigma^{(1)}$.

zero and first-order approximation we have

$$\kappa^{(0)}=\frac{4}{13}\frac{1}{T}\frac{(\beta_0{}^{(\frac{5}{2})})^2}{d_{00}{}^{(e-i)}},\quad \kappa_e{}^{(0)}=0.695\kappa^{(0)},$$
$$\kappa^{(1)}=6.50\kappa^{(0)}\qquad \kappa_e{}^{(1)}=1.64\kappa^{(0)}. \tag{52}$$

Here too, rapid convergence is to be expected after the first approximation. This statement may be shown to be correct by considering the Wiedemann-Franz ratios of successive approximations $L^{(n)}=\kappa^{(n)}/T\sigma^{(n)}$, for which we find

$$L^{(0)}=1.92(k_B/e)^2,\quad L_e{}^{(0)}=1.33(k_B/e)^2,$$
$$L^{(1)}=3.84(k_B/e)^2,\quad L_e{}^{(1)}=1.64(k_B/e)^2. \tag{53}$$

Already $L^{(1)}$ is very nearly $4(\kappa_B/e)^2$, which is the value to be expected for $L^{(\infty)}$ in the limit $\delta^2=0$. Also $L_e{}^{(1)}$ is probably close to $L_e{}^{(\infty)}$, as may be inferred from the work of Spitzer and Härm on the transport phenomena in a plasma.[23] The absolute thermoelectric power of a nondegenerate semiconductor depends primarily on the Fermi energy of the conduction electrons. Indeed, in zero-order approximation there is no influence of any scattering mechanism. Let us define successive approximations of the thermoelectric power by

$$\alpha^{(n)}=-(k_B/e)(\gamma^{(n)}-\zeta/k_BT). \tag{54}$$

Then we find

$$\gamma^{(0)}=\tfrac{5}{2},\qquad \gamma_e{}^{(0)}=\gamma^{(0)},$$
$$\gamma^{(1)}=3.65,\quad \gamma_e{}^{(1)}=3.31, \tag{55}$$
$$\gamma^{(2)}=4.02,\quad \gamma_e{}^{(2)}=3.22.$$

We see that electron-electron scattering has some influence on $\gamma^{(2)}$. This is to be expected physically since electron-electron scattering tends to bring the distribution of the current over the different energy shells ($\gamma^{(\infty)}=4$) toward the uniform distribution ($\gamma^{(0)}=\frac{5}{2}$).[31] In case of electron-phonon scattering as primary scattering source ($\gamma^{(\infty)}=2$) the effect of electron-electron scattering is in general negligible.

Electron-Phonon and Electron-Electron Scattering

Let us now assume that electron-phonon scattering predominates over electron-ion scattering. Here, it is convenient to define the quantities

$$g_{rs}=d_{rs}/d_{00}{}^{(e-\mathrm{ph})}, \tag{56}$$

where $d_{rs}=d_{rs}{}^{(e-\mathrm{ph})}$ or $d_{rs}=d_{rs}{}^{(e-\mathrm{ph})}+d_{rs}{}^{(e-e)}$ for electron-electron scattering omitted or included, respectively. We find $d_{00}{}^{(e-\mathrm{ph})}$ from Eq. (49). The values of g_{rs} are given in Table III, where

$$B=\tfrac{3}{16}\pi^{\frac{3}{2}}[e^3(m^*)^{\frac{1}{2}}n\mu_e/(k_BT)^{\frac{3}{2}}\kappa_0{}^2], \tag{57}$$

and the L_n are given by Eq. (40) in Sec. 5. With these values of g_{rs}, it is possible to obtain the electrical and the heat conductivities up to the second- and first-order approximations, respectively. However, we restrict ourselves to the calculation of $\sigma^{(0)}$, $\sigma^{(1)}$, and $\kappa^{(0)}$. The reason is that due to the energy-dependence of $c_{e-\mathrm{ph}}\propto\epsilon^{-\frac{1}{2}}$ there is already rapid convergence after the zero-order approximations. The electrical conductivity, ignoring and including electron-electron scattering (denoted by no subscript and subscript e, respectively), is given by[32]

TABLE III. Values of g_{rs}.

g_{rs}	Without $e-e$ scattering	Including $e-e$ scattering
g_{00}	1	1
g_{10}	3	3
g_{11}	12	$12+BL_1$
g_{20}	12	12
g_{21}	60	$60+B(L_2+7L_1/2)$
g_{22}	360	$360+B(77L_1/4+7L_2+L_3)$

$$\sigma^{(0)}=e^2(\beta_0{}^{(\frac{3}{2})})^2/d_{00}{}^{(e-\mathrm{ph})},\quad \sigma_e{}^{(0)}=\sigma^{(0)},$$
$$\sigma^{(1)}=\frac{13}{12}\sigma^{(0)},\qquad \sigma_e{}^{(1)}=\sigma^{(0)}\left(1+\frac{1}{12+4BL_1}\right). \tag{58}$$

The heat conductivity in the zero-order approximation is given by

$$\kappa^{(0)}=\frac{4}{13}\frac{1}{T}\frac{(\beta_0{}^{(\frac{5}{2})})^2}{d_{00}{}^{(e-\mathrm{ph})}},\quad \kappa_e{}^{(0)}=\frac{\kappa^{(0)}}{1+(4/13)(BL_1)}. \tag{59}$$

With the following data,

$$T=50^\circ\mathrm{K},\qquad \mu_e=10^4\ \mathrm{cm^2\ v^{-1}\ sec^{-1}},$$
$$n=10^{15}\ \mathrm{cm^{-3}},\quad \lambda_D=6\times10^{-6}\ \mathrm{cm},$$
$$m^*/m=1,\qquad \delta^2=2.4\times10^{-2},$$
$$\kappa_0=16,$$

we find $\sigma_e{}^{(1)}=0.991\sigma^{(1)}$ and $\kappa_e{}^{(0)}=0.89\kappa^{(0)}$. Here too, the heat conductivity is reduced more than the electrical conductivity and the Wiedemann-Franz ratio decreases. For the thermoelectric power the influence of electron-electron scattering processes may be neglected (see Sec. 6). We see that electron-electron scattering affects the transport coefficients less when electron-phonon scattering, and not electron-ion scattering, is the pertinent scattering mechanism. This difference is caused by the fact that the energy dependences of the perturbation $c_{e-\mathrm{ph}}(\epsilon)$ and $c_{e-i}(\epsilon)$ are different.

At higher temperatures, in the intrinsic range, all kinds of intercarrier scattering processes must be taken into account. Here we shall get some insight into the

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[31] C. Herring (private communication, in which $\gamma_e{}^{(\infty)}=0.8\gamma^{(\infty)}$ is suggested).

[32] If one assumes electron-electron scattering to be much stronger than electron-phonon scattering, i.e., $BL_1\gg1$, one has $\sigma_e{}^{(1)}=(12/13)\sigma^{(1)}$. From successive approximations for the electrical conductivity one may extrapolate that $\sigma_e{}^{(\infty)}=(9\pi/32)\sigma^{(\infty)}$.

roles of eletron-electron and hole-hole scattering. To this end we assume that in either case (electron-electron scattering and hole-hole scattering) the presence of an equal number of charge carriers with opposite sign can be taken into account via the shielding constant. Then, the screening of the potential field of an electron is enhanced by the holes. The shielding constant for electrons is given by Eq. (24) with n replaced by $2n$. Therefore, in the intrinsic range the presence of holes reduces electron-electron scattering and vice versa. Supposing as electron parameters

$$\begin{array}{ll} T=500^{\circ}\mathrm{K}, & \mu_e=2\times10^3\ \mathrm{cm}^2\ \mathrm{v}^{-1}\ \mathrm{sec}^{-1}, \\ n=5.5\times10^{17}\ \mathrm{cm}^{-3}, & \lambda_D=9.3\times10^{-7}\ \mathrm{cm}, \\ m^*/m=1, & \delta^2=2.7\times10^{-2}, \\ \kappa_0=16, & \end{array}$$

we find as the electrical and heat conductivities, due to electrons, $\sigma_e^{(1)}=0.977\sigma^{(1)}$ and $\kappa_e^{(0)}=0.73\kappa^{(0)}$, respectively.

In the intrinsic range the third kind of intercarrier scattering mechanism, namely electron-hole scattering, is probably more important than electron-electron scattering and hole-hole scattering.[33]

Discussion of Results

As an important consequence of electron-electron scattering processes, the electronic heat conductivity of isotropic conductors is reduced much more than is the electric conductivity. This difference arises because it is *impossible* to describe the influence of electron-electron scattering on the steady-state distribution of electrons in terms of a *true relaxation time*, i.e., a relaxation time which is independent of external force fields and which, up to a factor of the order of unity, is equal to the time between two electron-electron scattering processes of a given electron. The breakdown of the relaxation time concept is to be expected from physical reasons. Howarth and Sondheimer[34] have pointed out that, as a necessary condition for the existence of a relaxation time, the energy change of an electron in a scattering process must be small compared to the initial energy of the electron. In general, this condition does not apply to electron-electron scattering processes. When scattering processes cannot be described by a relaxation time, the Wiedemann-Franz law is no longer valid; because of intercarrier scattering, the Wiedemann-Franz ratio is reduced.

The reduction of the Wiedemann-Franz ratio, as a consequence of electron-electron scattering, can be easily understood by comparing the steady-state distribution functions f_σ and f_κ for the charge and the heat transport, respectively. The distribution f_σ arises from the unperturbed distribution f_0, in the first-order approximation, by shifting the midpoints of all the constant energy spheres away from $\mathbf{K}=0$ by the *same* amount. Thus, in the approximation $\sigma^{(0)}$, the differences in the shifts of different energy surfaces are entirely neglected. Therefore, electron-electron scattering, which is effective in randomizing electron energies, has no influence on $\sigma^{(0)}$. However, the electronic heat conduction is governed by f_κ, which is quite different from f_σ.[35] Here, the differences in the shifts of different energy surfaces (the energy dependence of Φ_κ) determines even the zero-order approximation $\kappa^{(0)}$. This energy dependence is directly influenced by electron-electron scattering via the scattering operator L_{e-e} [Eq. (9)].

There remains the important question of how much the electrical conductivity, the heat conductivity, and the Wiedemann-Franz ratio are reduced by electron-electron scattering. For isotropic conductors this depends first of all on the pertinent primary scattering source. The more strongly the corresponding perturbation of the electron distribution depends on energy, the more effective are electron-electron scattering processes. Therefore, in accordance with our results for semiconductors, electron-electron scattering has more influence on the transport coefficients when ionized impurity scattering is the pertinent scattering mechanism than it has when electron-phonon scattering predominates. This difference, as the above-stated difference in charge and heat transport, arises from the fact that electron-electron scattering processes have the tendency to randomize electron energies, but not electron momenta. Quantitative results were obtained for nondegenerate semiconductors with small electron concentrations, such that the Debye length is much larger than the electron wavelength. Assuming electron-ion scattering as the dominant scattering mechanism, we find that the electrical conductivity and the heat conductivity are smaller by factors 0.58 [Eq. (51)] and 0.25 [Eq. (52)], respectively, approximately independently of temperature. These results are in agreement with those calculated by Spitzer and Härm[23] and by Landshoff[25] using mathematical approaches

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[33] To include electron-hole scattering, we have to set up two Boltzmann equations, one for electrons and one for holes. Denoting the perturbations of the distribution functions of electrons and holes by Φ_e and Φ_h, respectively, we have as scattering operator which describes the scattering of electrons by holes

$$L_{e-h}(\Phi_e)=\frac{2}{k_BT}\left(\frac{m_h}{h}\right)^3\int\int\int \exp(\epsilon_e-\zeta_e/k\ \ T)$$
$$\times\exp(\epsilon_h-\zeta_h/k_BT)f_{0e}f_{0h}f'_{0e}f'_{0h}$$
$$\times(\Phi_e+\Phi_h-\Phi'_e-\Phi'_h)\alpha(\chi,g)\sin\chi d\chi d\gamma d\mathbf{v}_h.$$

Equation (4) must be extended by this expression; a corresponding equation holds for holes. Thus, we are left with two simultaneous integral equations for Φ_e and Φ_h. A generalized variational principle can be constructed in order to solve the two coupled Boltzmann equation for electrons and holes. Here, we will not further consider this interesting problem of electron-hole scattering except to state one important difference between electron-electron and electron-hole scattering processes. The latter, according to the above equation, influences the electrical conductivity σ already in its zero-order approximation $\sigma^{(0)}$.

[34] E. H. Sondheimer and D. J. Howarth, Proc. Roy. Soc. (London) **A219**, 53 (1953).

[35] See reference 29, Fig. 1.

different from each other and from ours.[36] The reduction of the Wiedemann-Franz ratio, $L_e^{(1)}=1.64(k_B/e)^2$ [Eq. (54)], could easily be verified if the phonon contribution to the heat transport were comparable to the electron contribution. Unfortunately, at low temperature the latter is several orders of magnitude smaller than the former. For higher electron concentrations our considerations are not appropriate—even if the ansatz 22 for the interaction potential is assumed to be valid—since the steady-state distributions of electrons and phonons are not independent of each other. Therefore, superposition effects occur which make it difficult to separate the heat conductivity into a phonon and an electron contribution.[37] That part of the thermoelectric power which corresponds to an average value of the electron energies—averaged with respect to the currents in different energy shells—is reduced by a factor 0.80 when electron-electron scattering is taken into account [Eq. (55)]. With increasing δ^2 the effect of electron-electron scattering on the transport coefficients decreases.

Assuming again small electron concentrations, but electron-phonon scattering as the pertinent scattering mechanism, electron-electron scattering is less effective, due to the slight energy dependence of $c_{\epsilon-\mathrm{ph}}(\epsilon)$. Thus, applying our results [Eqs. (58) and (59)] to a typical case, we see that at low temperature ($T=50$°K) the influence of electron-electron scattering on the electrical conductivity is of the order of 1%. In the intrinsic region ($T=500$°K) electron-electron and hole-hole scattering have a small influence on the electrical conductivity; the heat conductivity is reduced by about 27%. Here electron-hole scattering probably has much more influence on the electrical conductivity; $\sigma^{(0)}$ would already be affected.

Finally, we want to make a brief remark on the magnetoresistance. In zero magnetic field, electron-electron scattering affects the perturbation Φ more for higher electron energies than it does for lower ones. Now, with electron-phonon scattering only, in a magnetic field electrons with higher energies contribute relatively more to the electric current than they do in the absence of a field. Therefore, considering both these facts, electron-electron scattering will be more effective in randomizing electron energies when a magnetic field is applied. As a consequence, the magneto-resistance should be somewhat lower when electron-electron scattering is taken into account. However, the discrepancy that already exists between theory (saturation in strong fields) and experiment (linear increase in strong fields) for pure germanium at low temperatures is in the contrary direction.[38]

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APPENDIX A. ANISOTROPIC SEMICONDUCTORS

With respect to the electrical conductivity in isotropic solids, where $E(\mathbf{K})=(\hbar^2/2m^*)K^2$, it is shown in Sec. 4 that the influence of electron-electron scattering has to be considered as a higher-order effect. Namely, with electron-electron scattering as the only scattering mechanism, the electrical resistivity is zero.

Now, in anisotropic semiconductors the electrons have to be considered under the **K** aspect, appropriate to Bloch electrons. Thus, the conservation laws for a single electron-electron scattering process are

$$\mathbf{K}_1+\mathbf{K}_2=\mathbf{K'}_1+\mathbf{K'}_2, \tag{A.1}$$

$$E(\mathbf{K}_1)+E(\mathbf{K}_2)=E(\mathbf{K'}_1)+E(\mathbf{K'}_2). \tag{A.2}$$

According to whether the conservation law (A.1) is or is not equivalent to

$$\mathbf{v}_1+\mathbf{v}_2=\mathbf{v'}_1+\mathbf{v'}_2, \quad \text{where} \quad \mathbf{v}=\frac{1}{\hbar}\,\mathrm{grad}_{\mathbf{K}}E(\mathbf{K}), \tag{A.3}$$

electron scattering will or will not affect the electrical conductivity.

The conservation laws (A.1) and (A.3) are consistent with each other only if the effective mass tensor can be diagonalized simultaneously for all different wave vectors terminating on one energy surface and if the corresponding diagonal elements of different energy surfaces are the same. For electrons in a conduction band with the energy minimum located at $\mathbf{K}=0$, the energy E can be written in terms of those harmonic functions[39] which are associated with the identical representation of the corresponding crystal point group. In cubic crystals we have

$$E(\mathbf{K})=\sum_{m=1,2\cdots} a_{2m}K^{2m} +\sum_l b_l K^l\cdot H_l\left(\frac{K_x}{K},\frac{K_y}{K},\frac{K_z}{K}\right), \tag{A.4}$$

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[36] Spitzer and Härm describe the rate of change of f due to electron-electron scattering in terms of the Fokker-Planck equation [see also M. N. Rosenbluth, W. M. MacDonald, and D. L. Judd, Phys. Rev. **107**, 1 (1957)]. Landshoff applies the Chapman-Cowling method (reference 11, p. 107).

[37] J. Appel, *Progress in Semiconductor Physics*, edited by A. F. Gibson, [John Wiley & Sons, Inc., New York, (to be published)], Vol. V.

[38] G. Lautz and W. Ruppel, Z. Naturforsch. **10a**, 521 (1955), Fig. 5; J. Appel, H. Bruns and H. Schultz, *Meeting of the German Physical Society*, Heidelberg, October, 1957 (unpublished); H. Bruns, Dissertation, Braunschweig, 1961; C. Herring, *International Congress on Semiconductors*, Prague, August, 1960 (unpublished).

[39] D. G. Bell, Revs. Modern Phys. **26**, 11 (1954).

where a_{2m} and b_l are constants, H_l is the cubic harmonic of α type with order $l(\geq 4)$. Now, the most simple case for which obviously Eqs. (A.1) and (A.3) are not consistent with each other is given by such isotropic energy surfaces[40] that

$$E(\mathbf{K})=a_2K^2+a_4K^4. \tag{A.5}$$

On the other hand, there are anisotropic semiconductors with respect to the energy-band structures for which Eqs. (A.1) and (A.3) are consistent with each other. Such a case is given if the energy surfaces are nondegenerate for all different **K** vectors of a single band and if the energy can be represented by a diagonalized quadratic form with energy-independent effective mass components,

$$E(\mathbf{K})=\frac{\hbar^2}{2}\left[\frac{(K_x-K_x^{(0)})^2}{m_{xx}^*}+\frac{(K_y-K_y^{(0)})^2}{m_{yy}^*}+\frac{(K_z-K_z^{(0)})^2}{m_{zz}^*}\right], \tag{A.6}$$

where $\mathbf{K}^{(0)}$ is a wave vector corresponding to an energy extremum. Thus, it is evident that in n-germanium, electron-electron scattering between energy surfaces belonging to the same energy minimum (intravalley scattering) will not affect the electrical conductivity in zero order, although electrons of *different* effective mass are involved in scattering processes. If two electrons from different valleys are involved in an electron-electron scattering process, such that the electrons exchange their valleys by the scattering process (normal intervalley scattering), the current vector $e(\mathbf{v}_1+\mathbf{v}_2)$ is not changed. Only for a certain kind of scattering process, mentioned in Appendix B as Umklapp processes (Umklapp intervalley scattering), may the current vector be changed in a single scattering process. However, such Umklapp processes are expected to occur very seldom in n-germanium. The possibility of such scattering processes is small because the **K** star representing the energy minima contains only a few pairs of equivalent **K** vectors (equivalent **K** vectors are two vectors which differ by 2π times a vector of the reciprocal lattice).

APPENDIX B. METALS

To calculate the influence of electron-electron scattering on the transport phenomena in metals, the variation principle is an appropriate mathematical method for solving the Boltzmann equation and for determining the transport coefficients. Therefore, the variation principle has been formulated in Sec. 4 for the general case of Fermi-Dirac statistics. However, there exist some difficulties of more fundamental nature.

(1) It is difficult to define a two-electron interaction potential in terms of an appropriate dielectric constant. The usual assumption, that $\kappa=1$ in Eq. (33), is based on the work of Bohm and Pines,[1] where the problem of a dense electron gas interacting via Coulomb forces is treated assuming that the lattice is to be replaced by a positive, continuous charge background. From more recent work of Nozières and Pines[2] it does not seem possible to define an appropriate dielectric constant for the Coulomb interaction between two electrons in a metal. The concept of a dielectric constant dependent on frequency and wave vector does not apply to a pair of electrons, but to properly defined Fourier components of the density fluctuations of all the electrons.

(2) Assuming that the interaction potential is nevertheless given by Eq. (22) with $\kappa=1$, one finds that the Born approximation does not apply.[8] Exact calculations may be necessary to determine at least the lowest-order phases defined by Eq. (25).

(3) The possibility of Umklapp processes,

$$\mathbf{K}_1+\mathbf{K}_2=\mathbf{K}'_1+\mathbf{K}'_2+2\pi\mathbf{h}, \tag{B.1}$$

where **h** is a vector in the reciprocal lattice, occurs in first-order perturbation theory for electron-electron scattering. However, electron-electron Umklapp processes probably do not occur so often that the transport coefficients are changed to a measurable extent. The reason is that the energy conservation law will essentially restrict the possibility of Umklapp processes, in contrast to phonon-phonon and electron-phonon Umklapp processes. It can be seen that, in monovalent metals where the Fermi surface does not touch the Brillouin zone boundaries, electron-electron Umklapp processes can occur only for certain singular cases[41]. If the Fermi surface touches the Brillouin zone boundaries, of course, electron-electron Umklapp processes can occur more often.

It has been suggested that experimental evidence for electron-electron scattering is given by the temperature-dependence of the electrical resistivity of some transition metals at low temperatures. Baber[42] has made some calculations of the electrical resistivity due to electron-hole scattering on the basis of the Born approximation and assuming an isotropic two-band structure. He finds a T^2 proportionality for the electrical resistance. Approximately a T^2 dependence of the electrical resistance has been measured below 10°K by de Haas and de Boer[43] on platinum, by Justi[44] on indium and molybdenum, and by White and Woods[45] in a systematic investigation on several transition metals, particularly those with a relatively large electronic heat capacity. The measured coefficients of the T^2 proportionalities have the correct order of magnitude with respect to Baber's results after cor-

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[40] R. A. Silvermann and W. Kohn, Phys. Rev. **80**, 912 (1950).

[41] R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, 1956).

[42] W. G. Baber, Proc. Roy. Soc. (London) **A158**, 383 (1937).

[43] W. J. de Haas and J. H. de Boer, Physica **1**, 609 (1933).

[44] E. Justi, Z. Metallk. **51**, 1 (1960).

[45] G. K. White and S. B. Woods, Phil. Trans. **A251** (1959).

recting for the Born approximation. However, the measured heat resistivity of these transition metals also follows a T^2 law approximately.[45] Unfortunately, a T^2 dependence of the electronic heat resistivity may result from phonon-scattering of electrons into hole-eigenstates. Although we do not expect the Wiedemann-Franz law to apply for electron-hole scattering, i.e., we do not expect a linear dependence of the heat conductivity on temperature when electron-hole scattering is the pertinent scattering mechanism, at this time it is not clear whether or not electron-hole scattering affects the transport coefficients of some transition metals.[46] Generally speaking, up to now there is no conclusive evidence for an experimental manifestation of an influence of intercarrier scattering processes on transport phenomena in nonpolar solids.

APPENDIX C. RELATIVE VELOCITY COORDINATES

The following transformations are used to derive Eq. (34):

$$\mathbf{v}=\mathbf{G}-\tfrac{1}{2}\mathbf{g},\quad \mathbf{v}'=\mathbf{G}-\tfrac{1}{2}\mathbf{g}',$$
$$\mathbf{v}_1=\mathbf{G}+\tfrac{1}{2}\mathbf{g},\quad \mathbf{v}'_1=\mathbf{G}+\tfrac{1}{2}\mathbf{g}'. \qquad \text{(C.1)}$$

It is convenient to transform the velocities into dimensionless quantities with the help of

$$\boldsymbol{\mathfrak{G}}=(m^*/2k_BT)^{\frac{1}{2}}\mathbf{G} \quad \text{and} \quad \boldsymbol{\mathfrak{g}}=\tfrac{1}{2}(m^*/2k_BT)^{\frac{1}{2}}\mathbf{g}. \qquad \text{(C.2)}$$

The vectors $\boldsymbol{\mathfrak{G}}$ and $\boldsymbol{\mathfrak{g}}$ are related to the following polar coordinate systems: $\boldsymbol{\mathfrak{G}}(\mathfrak{G},\theta,\phi)$, with θ as polar angle between $\boldsymbol{\mathfrak{G}}$ and a fixed coordinate system; and $\boldsymbol{\mathfrak{g}}(\mathfrak{g},\vartheta,\varphi)$, with ϑ as polar angle between $\boldsymbol{\mathfrak{g}}$ and $\boldsymbol{\mathfrak{G}}$. Under the integral of Eq. (48) we have

$$mv_x{}^2/2k_BT=(\mathfrak{G}_x-\mathfrak{g}_x)^2=[\mathfrak{G}\cos\theta-\mathfrak{g}(\cos\vartheta\cos\theta$$
$$+\sin\vartheta\sin\theta\cos\phi)]^2, \qquad \text{(C.3)}$$

and, further,

$$\epsilon=|\boldsymbol{\mathfrak{G}}-\boldsymbol{\mathfrak{g}}|^2,\quad \epsilon'=|\boldsymbol{\mathfrak{G}}-\boldsymbol{\mathfrak{g}}'|^2,$$
$$\epsilon_1=|\boldsymbol{\mathfrak{G}}+\boldsymbol{\mathfrak{g}}|^2\quad \epsilon'_1=|\boldsymbol{\mathfrak{G}}+\boldsymbol{\mathfrak{g}}'|^2. \qquad \text{(C.4)}$$

The angles which occur in the scalar products are defined by

$$\chi=\sphericalangle(\boldsymbol{\mathfrak{g}},\boldsymbol{\mathfrak{g}}'),\qquad \vartheta=\sphericalangle(\boldsymbol{\mathfrak{g}},\boldsymbol{\mathfrak{G}}),$$
$$\vartheta'=\sphericalangle(\boldsymbol{\mathfrak{g}}',\boldsymbol{\mathfrak{G}}),\quad \cos\vartheta'=\cos\vartheta\cos\chi+\sin\vartheta\sin\chi\cos\gamma. \qquad \text{(C.5)}$$

APPENDIX D. THE INTEGRALS L_n AND M_n

Approximation formulas of the parameter integrals for small δ^2 are given by

$$\begin{aligned}
L_1&=2h(\delta^2)-3+2\delta^2h(\delta^2),\\
L_2&=4h(\delta^2)-4+\delta^2h(\delta^2),\\
L_3&=12h(\delta^2)-8,\\
M_0&=\tfrac{1}{2}h(\delta^2/2)-\tfrac{1}{2}+\tfrac{1}{8}\delta^2h(\delta^2/2),\\
M_1&=\tfrac{1}{2}h(\delta^2/2)-\tfrac{1}{8}\delta^3h(\delta^2/2),\\
M_2&=h(\delta^2/2)+\tfrac{1}{2}-\tfrac{1}{4}\delta^2h(\delta^2/2),\\
M_3&=3h(\delta^2/2)+\tfrac{5}{2}-\tfrac{3}{4}\delta^2h(\delta^2/2),\\
M_4&=12h(\delta^2/2)+13-3\delta^2h(\delta^2/2).
\end{aligned} \qquad \text{(D.1)}$$

In this approximation we have assumed $\delta^2\ll 1$ and, therefore, included terms of order $h(\delta^2)$ and $\delta^2h(\delta^2)$ only. The function $h(\delta^2)$ is defined by

$$h(\delta^2)\equiv\exp(\delta^2/2)[-\mathrm{Ei}(-\delta^2/2)], \qquad \text{(D.2)}$$

where

$$-\mathrm{Ei}(-x)\equiv\int_x^\infty\frac{\exp(-y)}{y}dy,$$

and for small δ^2 we may use the approximation

$$-\mathrm{Ei}(-x)=\ln(1/\gamma x)+x, \qquad \text{(D.3)}$$

where γ is Euler's constant ($\gamma=0.5772157\cdots$).

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[46] A. H. Wilson, Proc. Roy. Soc. (London) **167**, 580 (1938).