Series II

The experimentally observed states and their energies are

State	Energy
$1S$	$14\,931\pm3$ cm^{-1}
$2S-2P_{\pm1}$	$15\,032\pm2$ cm^{-1}
$2\,P_0$	$15\,022\pm3$ cm^{-1}

The series limit may be estimated to be $15\,050\pm15$ cm^{-1} with an effective rydberg of $Ry=120\pm10$ cm^{-1}.

Series III

The $1S$ state was observed at $18\,218\pm10$ cm^{-1}, with an estimated series limit at $18\,340\pm20$ cm^{-1}.

The difference in the series limits between the first and second series corresponds to a crystal field splitting of the valence band of 200 ± 15 cm^{-1}. The difference between the limits for the first and third series corresponds to a spin-orbit splitting of the valence band of 3490 ± 20 cm^{-1}.

Interband Electron-Electron Scattering and Transport Phenomena in Semiconductors

JOACHIM APPEL

John Jay Hopkins Laboratory for Pure and Applied Science, General Atomic Division of General Dynamics Corporation, San Diego, California

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The effect of interband electron-electron scattering (electron-hole scattering, light hole–heavy hole scattering, etc.) on the electrical transport phenomena is studied with a variational method obtained by a generalization of Kohler's variation principle to a multiband conductor. To this end we make the following assumptions: (1) The electronic structure is given by parabolic conduction and valence bands, separated from each other by $\Delta E\gg k_BT$; the valence band may be twofold degenerate; (2) The average occupation numbers of electronic eigenstates are given by Fermi-Dirac statistics; (3) The dynamical interaction between charge carriers is described by a shielded Coulomb potential.

Assuming nondegenerate semiconductors, we consider acoustical and optical phonon scattering and ion scattering, besides electron-electron scattering. Quantitative results are obtained for the electrical conductivity, the heat conductivity, and the Seebeck coefficient, including the ambipolar effect. The results can easily be applied to cases of physical interest; we discuss here hole-hole scattering and mobility of p germanium, intercarrier scattering and mobility of intrinsic germanium, transient conductivity of charge carriers in germanium produced by short pulses of high-energy electrons, intercarrier scattering and its influence on the heat conductivity, and the Wiedemann-Franz ratio of intrinsic semiconductors.

I. INTRODUCTION

IN a previous paper[1] the effect of electron-electron scattering on the electrical transport phenomena was studied on the basis of the free-electron approximation and under the assumption of a shielded Coulomb potential describing the pair interaction between conduction electrons. The allowed electron eigenstates were restricted to one band only. For such a simple model, because of momentum conservation in a single (non-umklapp) scattering process, the electrical conductivity is not affected in its zero-order approximation. However, in first and higher order, the electrical conductivity changes. The reason for this change lies in the energy dependence of the perturbation f_1, which, as a consequence of the electron-lattice interaction, adds to the unperturbed Fermi-Dirac distribution f_0. The perturbation f_1 is modified because electron-electron scattering randomizes energies. The effect on the electrical conductivity of semiconductors is shown in Fig. 1, assuming electron-ion scattering as the primary scattering source.

The effect of electron-electron scattering becomes more important for the electrical conductivity when the electrons are distributed over two or more partly filled energy bands. Transition metals and intrinsic semiconductors are examples of a multiband structure. In considering the electrical conduction of such substances, it is convenient to distinguish between intraband and interband electron-electron scattering processes. The former have been discussed in A, while the latter may be understood as scattering processes in which each of the two participants belongs to a *different* band (the first to a conduction band, the other to a valence band, etc.). The transition probabilities are the same whether each of the two electrons stays in its original band or whether the two electrons exchange bands. Both direct and exchange transitions will be called interband scattering processes. Physically, the difference between intraband and interband scattering is trivial: In the first case the momentum conservation in a single scattering event implies the velocity conservation $v_1+v_2=v_1'+v_2'$, whereas in the second case usually $v_1+v_2\neq v_1'+v_2'$. In other words, interband scattering processes affect the electrical conductivity primarily because of a current

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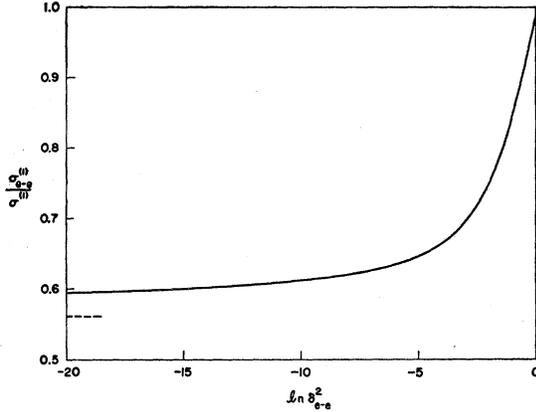[1] J. Appel, Phys. Rev. **122**, 1760 (1961), hereafter referred to as A.

FIG. 1. Effect of electron-electron scattering on the Brooks-Herring formula; $\sigma_{e\text{-}e}{}^{(1)}$ is the first-order approximation of the electrical conductivity for electron-ion and electron-electron scattering, $\sigma^{(1)}$ is the first-order approximation of the Brooks-Herring conductivity formula; the parameter $\delta_{e\text{-}e}$ (Eq. 40 of A) is proportional to electron wavelength over Debye length.

change in most scattering events and secondarily because energies are randomized. Special cases of physical interest are electron-hole scattering and light hole—heavy hole scattering in semiconductors.

The purpose of the present paper is to discuss the combined influence on the electrical transport coefficients due to intraband and interband electron-electron scattering which results from the dynamical interaction of charge carriers via a shielded Coulomb potential. As a basis for this discussion we consider a three-band model with one-electron eigenstates given by the free-electron approximation. As is usual, electrons in inverted bands (valence bands) are replaced by positive holes. Thus, we assume one conduction band and two valence bands as shown in Fig. 2; m_e, m_h, and m_l are the effective masses of the electrons and of the heavy and light holes, respectively. The energy gap ΔE is assumed to be large compared to $k_B T$, so that transitions of electrons from the conduction band to the valence band and vice versa, do not occur as a consequence of single-phonon scattering processes.[2] However, interband transitions of holes between the light hole band and the heavy hole band, induced by phonons, may be important.[3] These transitions can be incorporated in our calculations provided one knows the corresponding transition probabilities. Here, for the sake of simplicity, the formal theory will be restricted to intraband phonon scattering. However, in applying the final results to a concrete case, such as germanium, interband phonon scattering is taken into

[2] However, if $k_B\theta_D \ll \Delta E$ (θ_D=Debye temperature), or if one considers two overlapping bands, the upper band being a conduction band and the lower band being a valence band (transition metals), interband scattering of electrons induced by thermal phonons has to be taken into account. Then it is convenient to relate the energies of the electrons in the conduction band (s electrons) and the valence band (d electrons) to the same zero energy; see A. H. Wilson, Proc. Roy. Soc. (London) **A167**, 580 (1938).

[3] H. Ehrenreich and A. W. Overhauser, Phys. Rev. **104**, 331 and 649 (1956).

account by retaining an appropriate mobility ratio for the phonon-scattering of light and heavy holes.

The main mathematical problem consists in solving simultaneously three coupled Boltzmann equations. To this end, we shall apply a mathematical procedure which is a generalization of Kohler's variation principle to a multiband conductor. Besides intraband and interband electron-electron scattering, we shall consider intraband scattering due to longitudinal acoustical phonons, longitudinal optical phonons, and ionized impurities.

II. VARIATION PRINCIPLE FOR A MULTIBAND CONDUCTOR

Let us consider the following system of three linear integral equations for the perturbations Φ_e, Φ_h, Φ_l of the distribution functions of electrons, heavy holes, and light holes, respectively,

$$\frac{v_{e,x}}{k_B T}\frac{\partial f_{0e}}{\partial \epsilon_e}\left[eF+T\frac{\partial}{\partial x}\left(\frac{\zeta_-}{T}\right)+k_B\epsilon_e\frac{\partial T}{\partial x}\right]$$

$$=L_e(\Phi_e)+L_{e\text{-}e}(\Phi_e)+L_{e\text{-}h}(\Phi_e+\Phi_h)$$

$$+L_{e\text{-}l}(\Phi_e+\Phi_l), \quad (1a)$$

$$\frac{v_{h,x}}{k_B T}\frac{\partial f_{0h}}{\partial \epsilon_h}\left[eF+T\frac{\partial}{\partial x}\left(\frac{\zeta_+}{T}\right)+k_B\epsilon_h\frac{\partial T}{\partial x}\right]$$

$$=L_h(\Phi_h)+L_{h\text{-}h}(\Phi_h)+L_{h\text{-}e}(\Phi_h+\Phi_e)$$

$$+L_{h\text{-}l}(\Phi_h+\Phi_l), \quad (1b)$$

$$\frac{v_{l,x}}{k_B T}\frac{\partial f_{0e}}{\partial \epsilon_l}\left[eF+T\frac{\partial}{\partial x}\left(\frac{\zeta_+}{T}\right)+k_B\epsilon_l\frac{\partial T}{\partial x}\right]$$

$$=L_l(\Phi_l)+L_{l\text{-}l}(\Phi_l)+L_{l\text{-}e}(\Phi_l+\Phi_e)+L_{l\text{-}h}(\Phi_l+\Phi_h). \quad (1c)$$

The same notation is used as in A; however, the suffixes e, h, and l refer to different species of charge carriers. For electrons we write

$$\Phi_e=k_B T(f_e-f_{0e})/(\partial f_{0e}/\partial \epsilon_e), \quad (2)$$

where $\epsilon_e=E_e/k_B T$ and f_{0e} is the Fermi-Dirac distribution for electrons (Fermi energy ζ_-). Although the original Boltzmann equations are nonlinear in the f's, Eqs. (1a) through (1c) have been linearized in the Φ's. The linear integral operators L describe the interactions of the charge carriers with the real crystal lattice and with each other. Thus, L_e, L_h, and L_l include the scattering of electrons and of light and heavy holes by acoustical and optical phonons and by point imperfections, respectively; L_e is given by Eq. (4) of A, and L_h, and L_l are defined correspondingly. The nine operators characterized by a pair of subindices, $L_{e\text{-}e}$, etc., describe Coulomb scattering of charge carriers by each other. In the case of electrons, the three electron-carrier scattering operators which determine the rate of change of the steady-state distribution f_e due to electron–heavy hole scattering, electron–light hole scattering and electron–

electron scattering are given, respectively, by

$$L_{e-h}(\Phi_e+\Phi_h)=\frac{2}{k_BT}\left(\frac{m_h}{h}\right)^3$$

$$\times\int\int\int \exp(\epsilon_e+\epsilon_h-\zeta_-/k_BT-\zeta_+/k_BT)$$

$$\times f_{0e}f_{0h}f_{0e}'f_{0h}'(\Phi_e+\Phi_h-\Phi_e'-\Phi_h')$$

$$\times\alpha_{e-h}\sin\chi\,d\chi\,d\gamma\,dv_h, \qquad (3)$$

$L_{e-l}(\Phi_e+\Phi_l)$ is obtained from Eq. (3) by replacing index h by l; $L_{e-e}(\Phi_e)$ is given by Eq. (9) of A observing the appropriate notation $(\alpha=\alpha_{e-e}, \zeta=\zeta_-)$. The functions $\alpha_{e-h}, \alpha_{e-l}$, and α_{e-e} are related to the effective scattering cross sections for electrons. Explicit formulas for all α's will be given below. The variables χ and γ denote the polar and the azimuthal deflection angles, respectively, for the relative velocity $\mathfrak{g}$ due to a single scattering event.

The main mathematical problem consists in finding the solutions of the three simultaneous integral equations (1a) through (1c). These solutions will be obtained by means of a generalized variation principle which applies to a multiband conductor. The following formulation of the variation principle is convenient:

Let us consider the following integral which is a quadratic functional of allowed trial functions Ψ_e, Ψ_h, and Ψ_l:

$$\{\Psi_e,\Psi_h,\Psi_l\}=2\left(\frac{m_e}{h}\right)^3\int\Psi_e L_e(\Psi_e,\Psi_h,\Psi_l)dv_e$$

$$+2\left(\frac{m_h}{h}\right)^3\int\Psi_h L_h(\Psi_h,\Psi_e,\Psi_l)dv_h$$

$$+2\left(\frac{m_l}{h}\right)^3\int\Psi_l L_l(\Psi_l,\Psi_e,\Psi_h)dv_l, \qquad (4)$$

where, for example,

$$L_e(\Psi_e,\Psi_h,\Psi_l)=L_e(\Psi_e)+L_{e-e}(\Psi_e)$$
$$+L_{e-h}(\Psi_e+\Psi_h)+L_{e-l}(\Psi_e+\Psi_l).$$

Then, the variation principle implies that of all trial functions the solutions Φ_e, Φ_h, and Φ_l of Eqs. (1a) through (1c) have the characteristic property of making the integral $\{\Psi_e,\Psi_h,\Psi_l\}$ a maximum subject to the subsidiary conditions

$$\int\Psi_e L_e(\Psi_e,\Psi_h,\Psi_l)dv_e=\int\Psi_e F(v_e)dv_e, \qquad (5a)$$

$$\int\Psi_h L_h(\Psi_h,\Psi_e,\Psi_l)dv_h=\int\Psi_h G(v_h)dv_h, \qquad (5b)$$

$$\int\Psi_l L_l(\Psi_l,\Psi_h,\Psi_e)dv_l=\int\Psi_l G(v_l)dv_l, \qquad (5c)$$

where $F(v_e)$, $G(v_h)$, and $G(v_l)$ are abbreviations for the left-hand sides of Eqs. (1a), (1b), and (1c), respectively.

The proof of the generalized variation principle as a maximum principle consists in a systematic generalization of Kohler's original mathematical procedure.[4] It relies on two integral theorems which correspond to the relations (10) and (11) of A and which are obtained by considering all kinds of intercarrier scattering processes. We mention that $(1/T)\{\Phi_e,\Phi_h,\Phi_l\}$ represents the rate of entropy production per unit volume due to the scattering processes of all charge carriers.

III. TRANSPORT COEFFICIENTS

In order to calculate the electrical conductivity σ, the heat conductivity κ, and the Seebeck coefficient α, it is convenient—in view of the linearity of the operators L—to rewrite the variation principle for the Φ's in a slightly different form. To this end we make the usual ansatz:

$$\Phi_e=v_{e,x}\left(eF_-c^{(\frac{3}{2})}+\frac{1}{T}\frac{\partial T}{\partial x}c^{(\frac{5}{2})}\right), \qquad (6a)$$

$$\Phi_h=v_{h,x}\left(eF_+b^{(\frac{3}{2})}+\frac{1}{T}\frac{\partial T}{\partial x}b^{(\frac{5}{2})}\right), \qquad (6b)$$

$$\Phi_l=v_{l,x}\left(eF_+\bar{b}^{(\frac{3}{2})}+\frac{1}{T}\frac{\partial T}{\partial x}\bar{b}^{(\frac{5}{2})}\right), \qquad (6c)$$
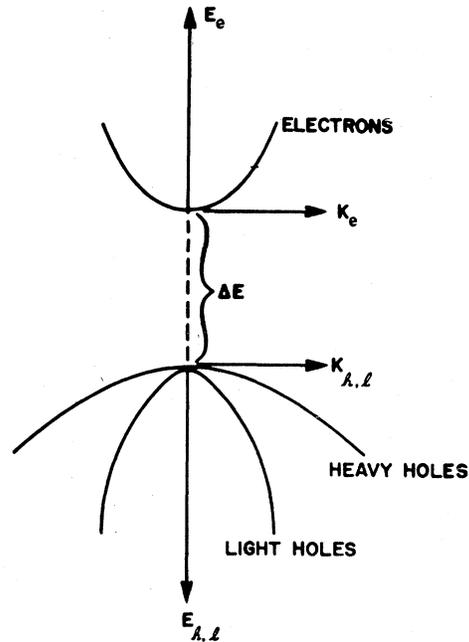

FIG. 2. Schematic sketch of the electronic structure consisting of a conduction band and a twofold degenerate valence band; the energy extrema occur at the center of the Brillouin zone.

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where

$$F_{\mp} = eF \pm T \frac{\partial}{\partial x}\left(\frac{\zeta_{\mp}}{T}\right). \qquad (7)$$

Assuming thermal equilibrium we have

$$\frac{\partial}{\partial x}\left(\frac{\zeta_+}{T}\right) = -\frac{\partial}{\partial x}\left(\frac{\zeta_-}{T}\right). \qquad (8)$$

Assuming nonequilibrium we consider the quasi-Fermi level for electrons ζ_- and the one for holes ζ_+ to be independent of x.[5] With the help of Eqs. (6a) through (6c) new scattering operators $\mathfrak{L}$ are defined and the three integral equations (1a) through (1c) break into three pairs of equations for the $c^{(n)}$, $b^{(n)}$, and $\bar{b}^{(n)}$. Of all the scattering operators $\mathfrak{L}$ occurring in these six integral equations we shall discuss the ones for electrons only; those for holes have the same analytical form. The integral operator $\mathfrak{L}_e$ is given in Wilson's textbook on metals.[6] Of primary interest here are the three operators $\mathfrak{L}_{e-e}$, $\mathfrak{L}_{e-h}$, and $\mathfrak{L}_{e-l}$. Using Landshoff's transformation by which the x components of the velocity vectors under the integral of Eq. (3) are eliminated, the final form of the three scattering operators, assuming Fermi-Dirac statistics, is given by

$$\mathfrak{L}_{e-h}(c^{(n)}, b^{(n)}) = \frac{2}{k_B T}\left(\frac{m_h}{h}\right)^3 \frac{1}{v_e^2}$$

$$\times \int\int\int \exp[\epsilon_e + \epsilon_h - (\zeta_- + \zeta_+)/k_B T] f_{0e} f_{0h} f_{0e}' f_{0h}'$$

$$\times [\mathbf{v}_e \cdot \mathbf{v}_e c^{(n)}(\epsilon_e) - \mathbf{v}_e \cdot \mathbf{v}_e' c^{(n)}(\epsilon_e')$$

$$+ \mathbf{v}_e \cdot \mathbf{v}_h b^{(n)}(\epsilon_h) - \mathbf{v}_e \cdot \mathbf{v}_h' b^{(n)}(\epsilon_h')] \alpha_{e-h} \sin\chi \, d\chi \, d\gamma \, d\mathbf{v}_h; \quad (9)$$

$\mathfrak{L}_{e-l}(c^{(n)}, \bar{b}^{(n)})$ is obtained from Eq. (9) by replacing b by $\bar{b}$ and index h by l; $\mathfrak{L}_{e-e}(c^{(n)})$ is given by Eq. (31) of A observing the notation rules. The problem of solving the three pairs of integral equations for the $c^{(n)}$, $b^{(n)}$, and $\bar{b}^{(n)}$ is reformulated as variation principle, in complete analogy to the consideration given in Sec. I, which, however, applies to the Eqs. (1a) through (1c). The appropriate variational function and the associated subsidiary conditions can easily be derived from Eqs. (4) through (6c).

The variational problem is solved by a direct method (Ritz procedure). Thus, the trial functions are expanded in power series

$$c^{(n)} = \sum_{r=0}^{\infty} c_r^{(n)} \eta_e^r, \qquad (10a)$$

$$b^{(n)} = \sum_{r=0}^{\infty} b_r^{(n)} \eta_h^r, \qquad (10b)$$

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[5] Then Eq. (8) is an identity if $T = $const.
[6] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953), 2nd ed., p. 302.

$$\bar{b}^{(n)} = \sum_{r=0}^{\infty} \bar{b}_r^{(n)} \eta_l^r, \qquad (10c)$$

where $\eta_e = \epsilon_e - \zeta_-/k_B T$ (or $\eta_e = \epsilon_e$) for metals (semiconductors). The expansion coefficients satisfy the following simultaneous systems of linear equations ($s = 0$ to ∞, $n = \frac{3}{2}, \frac{5}{2}$)

$$\sum_s (D_{rs}^{(e)} c_s^{(n)} + h_{rs}^{(e-h)} b_s^{(n)}$$
$$+ h_{rs}^{(e-l)} \bar{b}_s^{(n)}) - \alpha_r^{(n)} = 0, \quad (11a)$$

$$\sum_s (D_{rs}^{(h)} b_s^{(n)} + h_{rs}^{(h-e)} c_s^{(n)}$$
$$+ h_{rs}^{(h-l)} \bar{b}^{(n)}) - \delta\beta_r^{(n)} = 0, \quad (11b)$$

$$\sum_s (D_{rs}^{(l)} \bar{b}_s^{(n)} + h_{rs}^{(l-e)} c_s^{(n)}$$
$$+ h_{rs}^{(l-h)} b_s^{(n)}) - \delta\gamma_r^{(n)} = 0, \quad (11c)$$

where

$$D_{rs}^{(e)} = d_{rs}^{(e)} + d_{rs}^{(e-e)} + g_{rs}^{(e-h)} + g_{rs}^{(e-l)},$$
$$D_{rs}^{(h)} = d_{rs}^{(h)} + d_{rs}^{(h-h)} + g_{rs}^{(h-e)} + g_{rs}^{(h-l)}.$$

The coefficients of Eq. (11a) are defined as follows:

$$d_{rs}^{(e)} = \int \eta_e^r \mathfrak{L}_e(\eta_e^s) \omega d\mathbf{v}_e, \qquad (12a)$$

$$d_{rs}^{(e-e)} = \int \eta_e^r \mathfrak{L}_{e-e}(\eta_e^s) \omega d\mathbf{v}_e, \qquad (12b)$$

$$g_{rs}^{(e-h)} = \int \eta_e^r \mathfrak{L}_{e-h}(\eta_e^s, 0) \omega d\mathbf{v}_e, \qquad (12c)$$

$$g_{rs}^{(e-l)} = \int \eta_e^r \mathfrak{L}_{e-l}(\eta_e^s, 0) \omega d\mathbf{v}_e, \qquad (12d)$$

$$h_{rs}^{(e-h)} = \int \eta_e^r \mathfrak{L}_{e-h}(0, \eta_h^s) \omega d\mathbf{v}_e, \qquad (12e)$$

$$h_{rs}^{(e-l)} = \int \eta_e^r \mathfrak{L}_{e-l}(0, \eta_l^s) \omega d\mathbf{v}_e, \qquad (12f)$$

$$\alpha_r^{(n)} = \int (k_B T \epsilon_e)^{n-\frac{3}{2}} \frac{\partial f_{0e}}{\partial \epsilon_e} \eta_e^r \omega d\mathbf{v}_e, \qquad (12g)$$

where $\omega = 2(m_e/h)^3 v_{e,x}^2$. The coefficients of Eqs. (11b) and (11c) are defined correspondingly. We observe the following type of symmetry relations:

$$d_{rs}^{(e)} = d_{sr}^{(e)}, \quad g_{rs}^{(e-h)} = g_{sr}^{(e-h)}, \quad h_{rs}^{(e-h)} = h_{sr}^{(h-e)}. \quad (13)$$

The solutions of the infinite set of Eqs. (11a) through (11c) are obtained as quotients of infinite determinants. Correspondingly the three transport coefficients can be obtained in terms of the determinants

$$A_{m,n} = \begin{vmatrix} 0 & \alpha_0^{(m)} & \delta\beta_0^{(m)} & \delta\gamma_0^{(m)} & \cdots \\ \alpha_0^{(n)} & D_{00}^{(e)} & h_{00}^{(e-h)} & h_{00}^{(e-l)} & \cdots \\ \delta\beta_0^{(n)} & h_{00}^{(h-e)} & D_{00}^{(h)} & h_{00}^{(h-l)} & \cdots \\ \delta\gamma_0^{(n)} & h_{00}^{(l-e)} & h_{00}^{(l-h)} & D_{00}^{(l)} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \end{vmatrix}, \quad (14)$$

and A. The determinant A is derived from $A_{m,n}$ by omitting its first row and column. With these definitions for $A_{m,n}$ and A the general expressions of the transport coefficients are given elsewhere.[1] However, for practical purposes the infinite determinants are to be replaced by determinants with a finite number of rows. Thus, successive approximations of the electrical conductivity $\sigma^{(0)}$, $\sigma^{(1)}$, $\cdots$, the heat conductivity $\kappa^{(0)}$, $\kappa^{(1)}$, $\cdots$, and the Seebeck coefficient $\alpha^{(0)}$, $\alpha^{(1)}$, $\cdots$, are given by determinants $A_{m,n}^{(j)}$ and $A^{(j)}$ with $3j+1$ and $3j$ rows ($j=1, 2, \cdots$), respectively. We observe rapid convergence of successive approximations of σ, κ, and α in the case of semiconductors.

IV. NONDEGENERATE SEMICONDUCTORS

Assuming small carrier concentrations some simplifications occur since (1) the effective cross sections for intercarrier scattering are given by the Born approximation and (2) the Fermi-Dirac distribution can be approximated by the Maxwell-Boltzmann function.

Scattering Operators

The rate of change of the electron distribution due to scattering by longitudinal acoustical and optical phonons and ionized impurities is proportional to

$$\mathfrak{L}_e(c) = \mathfrak{L}_{e\text{-ac}}(c) + \mathfrak{L}_{e\text{-op}}(c) + \mathfrak{L}_{e\text{-}i}(c), \tag{15}$$

where

$$\mathfrak{L}_{e\text{-ac}}(c) = \hbar K_e f_{0e} c / m_e k_B T \lambda_{e\text{-ac}}(C_e^2), \tag{16}$$

$$\mathfrak{L}_{e\text{-op}}(c) = (D_e^2 K^2 f_{0e} c / 2^{\frac{1}{2}} \pi \hbar^2 k_B^{\frac{3}{2}} T^{\frac{1}{2}} \theta)$$
$$\times [N(\epsilon_e + \theta/T)^{\frac{1}{2}} + (N+1)(\epsilon_e - \theta/T)^{\frac{1}{2}} h(\epsilon_e - \theta/T)], \tag{17}$$

$\mathfrak{L}_{e\text{-}i}(c)$ is given by Eq. (44) of A. The operator $\mathfrak{L}_{e\text{-ac}}$ is derived elsewhere,[7] and the free path $\lambda_{e\text{-ac}}$ for elastic scattering of electrons by acoustical phonons is given in terms of Bloch's constant C_e by Eq. (48) of A. The operator $\mathfrak{L}_{e\text{-op}}$ which describes inelastic scattering of electrons by optical phonons with energy $k_B \theta$ is obtained with Seitz's expression for the transition probability[8]; D_e is the Seitz constant and $\mathbf{K}$ is a wave vector terminating on the surface of the first Brillouin zone. Heaviside's unit step function $h(x)$ is defined as follows: $h(x) = 0$ if $x < 0$, $h(x) = 1$ if $x > 0$. The operator $\mathfrak{L}_{e\text{-}i}$ is derived in A; however, the shielding parameter λ_D is the one given below.

The operators $\mathfrak{L}$ describing electron-carrier scattering are given by Eq. (9) and two similar equations. The scattering formulas are

$$\alpha_{e\text{-}h} = (e^4/\kappa_0^2 m_{\text{red}}^2 g^3)(\beta^2 + 1 - \cos\chi)^{-2}, \tag{18}$$

where $\beta = \hbar/2^{\frac{1}{2}}\lambda_D m_{\text{red}} g$; m_{red} is the reduced effective mass, and κ_0 is the static dielectric constant; $\alpha_{e\text{-}l}$ has the same analytical form as $\alpha_{e\text{-}h}$; $\alpha_{e\text{-}e}$ is given by Eq. (29).

of A with $m_{\text{red}} = m_e/2$ and λ_D as given below. The α's which determine the effective scattering cross sections are obtained with the Born approximation assuming a shielded Coulomb potential to describe the dynamical interaction between charge carriers. The shielding parameter is the Debye length λ_D given by

$$\frac{1}{\lambda_D^2} = \frac{1}{\lambda_{De}^2} + \frac{1}{\lambda_{Dh}^2} + \frac{1}{\lambda_{Dl}^2} = \frac{\kappa_0 k_B T}{4\pi e^2 (n + p + \bar{p})}, \tag{19}$$

where n, p, and $\bar{p}$ are the concentrations of electrons, heavy holes, and light holes, respectively. The use of the scattering formulas given above puts two (independent) upper limits on the carrier concentration for a particular temperature. The first restriction is imposed by the Born approximation: Electron wavelength is to be smaller than λ_D. The second, more serious restriction occurs because the pair interaction potential with λ_D as screening length is derived in the Debye-Hückel limit[9]: many charge carriers in a Debye sphere. This latter condition is not satisfied in several cases of physical interest. However, it has been pointed out by Herring[10] that results obtained in the Debye-Hückel limit seem to be valid beyond the range where its derivation is clearly justified.

General Results

Successive approximations of σ, κ, and α are determined by the elements of the determinants $A_{m,n}^{(i)}$ and $A^{(i)}$. We have calculated those elements necessary to find the first and the second approximation of the transport coefficients. For electrons we obtain with the scattering operators given above the following results:

Acoustical phonon scattering.

$$d_{rs}^{(e\text{-ac})} = \frac{16ne}{9\pi m_e^2 \mu_{e\text{-ac}}}(r + s + 2)!, \tag{20}$$

where $\mu_{e\text{-ac}}$ is the electron mobility.

Optical phonon scattering.

$$d_{00}^{(e\text{-op})} = A(2K_1 + zK_0/2), \tag{21a}$$

$$d_{10}^{(e\text{-op})} = A[(6 + z^2/2)K_1 + 3zK_0/2], \tag{21b}$$

$$d_{11}^{(e\text{-op})} = A[(24 + 11z^2/4)K_1 + (6z + z^3/2)K_0], \tag{21c}$$

where

$$A = \frac{2^{\frac{1}{2}} n D_e^2 K^2 m_e^{\frac{1}{2}} \exp(\frac{1}{2}z)}{3\pi^{\frac{1}{2}} \rho \hbar^2 (k_B T)^{\frac{1}{2}} \exp z - 1}, \tag{22}$$

[7] J. Appel, Z. Naturforsch. 13a, 386 (1958), Eq. (5a).

[8] F. Seitz, Phys. Rev. 73, 549 (1948), Eqs. (27) and (45a); see also D. T. Howarth and E. H. Sondheimer, Proc. Roy. Soc. (London) 219, 53 (1953).

[9] In the framework of a continuum approach the derivation of λ_D for a completely ionized plasma is given by N. Rostoker and M. N. Rosenbluth, Phys. Fluids 3, 1 (1960).

[10] C. Herring, Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovakian Academy of Sciences, Prague, 1961), p. 82; see also H. Brooks, Advances in Electronics and Electron Physics, edited by L. Marton (Academic Press Inc., New York, 1955), Vol. 7, p. 85.

$K_m = K_m(z/2)$ is the Bessel function defined elsewhere [11] and $z = \theta/T$.

Ionized impurity scattering. $d_{rs}^{(e-i)}$ is given by Eq. (45) of A with δ^2 replaced by $2\delta_{e-i}^2$, where

$$\delta_{e-i}^2 = \hbar^2/4\lambda_D^2 m_e k_B T.$$

Electron–heavy hole scattering.

$$g_{00}^{(e-h)} = B(m_h/m_e)J_0, \tag{23a}$$

$$g_{10}^{(e-h)} = B(m_h/m_e + m_h)[5J_0/2 + (m_h/m_e)J_1], \tag{23b}$$

$$g_{11}^{(e-h)} = B[m_e m_h/(m_e+m_h)^2][55J_0/4 + 5(m_h/m_e)J_1 + (m_h/m_e)^2 J_2 + 2(m_h/m_e)I_1]; \tag{23c}$$

$g_{rs}^{(h-e)}$ is obtained from $g_{rs}^{(e-h)}$ by interchanging indices e and h;

$$h_{00}^{(e-h)} = -(m_e/m_h)g_{00}^{(e-h)}, \tag{23d}$$

$$h_{10}^{(e-h)} = -(m_e/m_h)g_{10}^{(e-h)}, \tag{23e}$$

$$h_{01}^{(e-h)} = -(m_h/m_e)g_{10}^{(h-e)}, \tag{23f}$$

$$h_{11}^{(e-h)} = -B[m_e m_h/(m_e+m_h)^2]\{55J_0/4 + (5/2) \times [(m_e/m_h)+(m_h/m_e)]J_1 + J_2 - 2I_1\}; \tag{23g}$$

where

$$B = \frac{2^{\frac{5}{2}}\pi^{\frac{1}{2}}e^4 n_p}{3[(m_e+m_h)m_e m_h]^{\frac{1}{2}}\kappa_0^2(k_B T)^{\frac{3}{2}}}, \tag{24}$$

$J_n = J_n(\delta_{e-h}^2)$ and $I_n = I_n(\delta_{e-h}^2)$ are parameter integrals given in Appendix A; and

$$\delta_{e-h}^2 = \hbar^2/4\lambda_D^2(m_e m_h/m_e + m_h)k_B T.$$

Electron–light hole scattering. $g_{rs}^{(e-l)}$, $g_{rs}^{(l-e)}$, and $h_{rs}^{(e-l)}$ are obtained from Eqs. (23a)–(23g) by replacing index h by l.

Electron–electron scattering. $d_{rs}^{(e-e)}$ is given by Eqs.
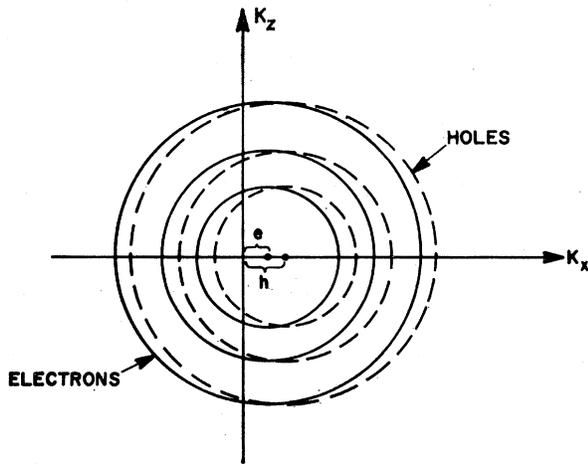

FIG. 3. Schematic diagram to illustrate the displacement of the electron and hole distributions associated with the zero-order approximation of the electronic heat conductivity. Assuming acoustical phonon scattering we have e: $h = (\lambda_{e-ac}/\lambda_{h-ac})(m_h/m_e)^{\frac{5}{2}}$.

[11] A. H. Watson, *Theory of Bessel Functions* (Cambridge University Press, Cambridge, 1958), p. 77.

(40) of A with $\delta^2 = \delta_{e-e}^2 = \hbar^2/2\lambda_D^2 m_e k_B T$. The determinantal elements for heavy and light holes are obtained by appropriate interchange of indices e, h, l, and of n, p, $\bar{p}$.

Ambipolar effects can be taken into account correctly to all orders for both the heat conductivity and the Seebeck effect by adding a potential energy $\Delta E(T)/2k_B T$ to the kinetic energy of the charge carriers in the brackets of Eqs. (1a) through (1c). Then $\alpha_r^{(\frac{3}{2})}$ remains unchanged [Eq. (12g)]; however, for $r = \frac{5}{2}$ we have

$$\alpha_r^{(\frac{5}{2})} = -\frac{n_e k_B T}{m_e}\frac{1}{(\frac{3}{2})!}\left[(\tfrac{5}{2}+r)! + (\tfrac{3}{2}+r)!\frac{\Delta E}{2k_B T}\right]. \tag{25}$$

V. QUANTITATIVE RESULTS AND DISCUSSION

Two-Band Semiconductor

Assuming two parabolic bands, a conduction band and an inverted or valence band separated from each other by an energy gap $\Delta E \gg k_B T$, we can easily obtain the zero-order approximation for the three transport coefficients. The results are:

Electrical Conductivity

$$\sigma^{(0)} = \frac{\sigma_e^{(0)} + \sigma_h^{(0)} - \sigma_e^{(0)}\sigma_h^{(0)}[(1-n/p)+(1-p/n)]CJ_0}{1+[(n/p)\sigma_h^{(0)}+(p/n)\sigma_e^{(0)}]CJ_0}, \tag{26}$$

where

$$C = \frac{2^{\frac{5}{2}}\pi^{\frac{1}{2}}e^2(m_e m_h)^{\frac{1}{2}}}{3\kappa_0^2(k_B T)^{\frac{3}{2}}(m_e+m_h)^{\frac{1}{2}}}, \tag{27}$$

and $J_0 = J_0(\delta_{e-h}^2)$; the electrical conductivity of electrons and holes obtained in zero-order approximation is denoted as $\sigma_e^{(0)}$ and $\sigma_h^{(0)}$, respectively.[12]

Heat Conductivity

$$\kappa^{(0)} = \left(\frac{k_B}{e}\right)^2 T \frac{(5+\Delta E/k_B T)^2}{(1/\sigma_e^{(0)})+(1/\sigma_h^{(0)})}. \tag{28}$$

Seebeck Coefficient

$$\alpha^{(0)} = -\frac{5k_B}{2e}\frac{\sigma_e^{(0)}-\sigma_h^{(0)}}{\sigma_e^{(0)}+\sigma_h^{(0)}}. \tag{29}$$

The simple formula [Eq. (26)] for the electrical conductivity is understood easily. We consider two cases:

(1) For $n = p$ the additional term in the denominator represents the effect of electron-hole scattering on the conductivity in complete analogy to the effect of electron-ion scattering on $\sigma_{e-ac}^{(0)}$. Indeed, assuming

$$m_h/m_e \rightarrow \infty,$$

we find

$$1/\sigma^{(0)} = 1/\sigma_{e-ac}^{(0)} + 1/\sigma_{e-i}^{(0)},$$

[12] Assuming electron-hole scattering to be weak compared to electron-lattice scattering, $\sigma^{(0)}$ has been calculated by D. Dorn [Z. Naturforsch. **383**, 11a (1961)] for an intrinsic semiconductor. His result is in agreement with the one obtained from Eq. (26) if the correct value for the screening length is introduced.

where $\sigma_{e-i}{}^{(0)}$ is the correct zero-order approximation of the Brooks-Herring formula [see Eq. (51) of A].

(2) For $n \neq p$, the bracket term in the numerator of Eq. (26) is different from zero. The first and second terms in the bracket are proportional to the drag which electrons impose on holes and vice versa, respectively. A drag effect on the mobility of minority carriers was first observed and discussed in detail by Paige[13] and McLean.[14]

The formulas (28) and (29) for the thermoelectric effects apply if $\zeta_{+} = \zeta_{-}$. The heat conductivity $\kappa^{(0)}$ is the exact zero-order approximation including the conductivity due to the transfer of pair excitation energies as electron-hole pairs flow from the hot to the cold region of a crystal. Thereby the total electric current is zero. Thus, the finite heat conductivity $\kappa^{(0)}$ is implied by steady-state distributions of electrons and holes as shown in Fig. 3. It is in the approximation $\kappa^{(1)}$ that those terms occur which correspond to the usual electronic heat conductivity of a single band. Therefore, $\kappa^{(1)}$ is affected also by electron-electron scattering. However, in intrinsic semiconductors the ambipolar diffusion term given by Eq. (28) is predominant.[15] Assuming $\sigma_{e,h}{}^{(0)}$ to be due to phonon scattering, we find that $\kappa^{(0)}$ is a good approximation (correct to $\sim 10\%$) for the exact ambipolar diffusion term of a two-band semiconductor. Thus, electron-hole scattering reduces the ambipolar heat conduction by approximately a factor

$$F(\delta_{e-h}{}^2) = \frac{1}{1 + (\sigma_e{}^{(0)}\sigma_h{}^{(0)}/\sigma_e{}^{(0)} + \sigma_h{}^{(0)})(n/p + p/n - 2)2CJ_0},$$

$$\delta_{e-h}{}^2 < 1. \quad (30)$$

The Wiedemann-Franz ratio $L^{(0)}$ given by Eqs. (26) and (28) is larger than the corresponding ratio obtained by ignoring electron-hole scattering. The thermoelectric power $\alpha^{(0)}$ is not changed [Eq. (29)] and in higher order the effect of intercarrier scattering is usually small in intrinsic semiconductors.

p-Germanium

An interesting application is provided by p-germanium and, of course, other semiconductors of the zincblende type which have a similar valence band structure. The electrical conductivity which we shall consider here is in its zero-order approximation given by Eq. (26) with the minus signs in the numerator replaced by plus signs. We have calculated the first-order approximation $\sigma^{(1)}$ of p-germanium at 77°K as a function of the concentration of ionized impurity centers assuming this concentration to be equal to the concentration of light

[13] E. G. S. Paige, J. Phys. Chem. Solids 16, 207 (1960).
[14] T. P. McLean and E. G. S. Paige, J. Phys. Chem. Solids 16, 220 (1960).
[15] P. J. Price, Proc. Phys. Soc. (London) B69, 851 (1956); O. Madelung, Encyclopedia of Physics, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20.
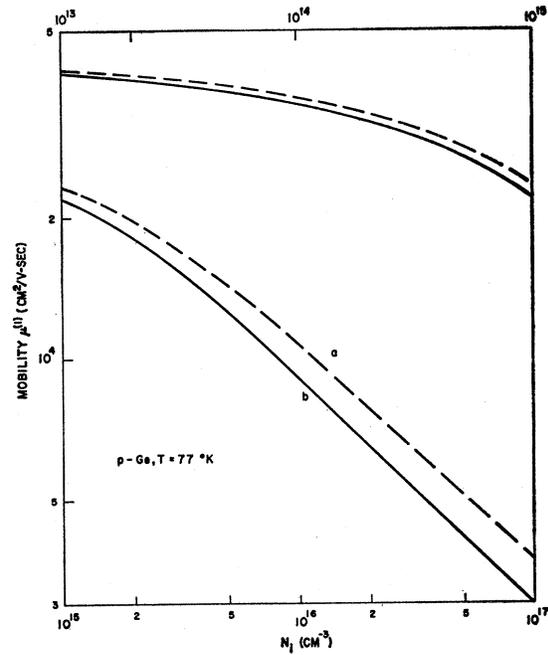
FIG. 4. The mobility of p-germanium (a) ignoring and (b) including hole-hole scattering.

and heavy holes. The following parameter values are appropriate[16]:

$$\kappa_0 = 16, \quad m_l = 0.043m, \quad m_h = 0.35m,$$

$$\mu_{ac} = \frac{\mu_{e-ac} + (m_h/m_l)^{\frac{3}{2}}\mu_{h-ac}}{1 + (m_h/m_l)^{\frac{3}{2}}} = 580\ 000\left(\frac{15°K}{T}\right)^{\frac{3}{2}} \text{cm}^2/\text{v-sec.}$$

Optical phonon scattering is correctly taken into account by determining the Seitz constant $D_h = D_l$ from the measured mobility at room temperature. We find

$$D_h = 8.1 \text{ ev}$$

with $\theta = 436°K$ and with

$$K = \pi/a \quad (a = 2.81 \times 10^{-8} \text{ cm}).$$

The results are shown in Fig. 4 for $\mu^{(1)} = \sigma^{(1)}/(p+\bar{p})e$ ignoring and including hole-hole scattering, respectively. A discussion of these results and their comparison with experiments will be given elsewhere.[17] We mention that two parameters determine the relative influence of hole-hole scattering on μ: the hole concentration and the screening length (see also Fig. 1).

Intrinsic Germanium

The characteristic feature of an intrinsic semiconductor is the well-known exponential temperature

[16] R. Bray and D. M. Brown, Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovakian Academy of Sciences, Prague, 1961), p. 60.
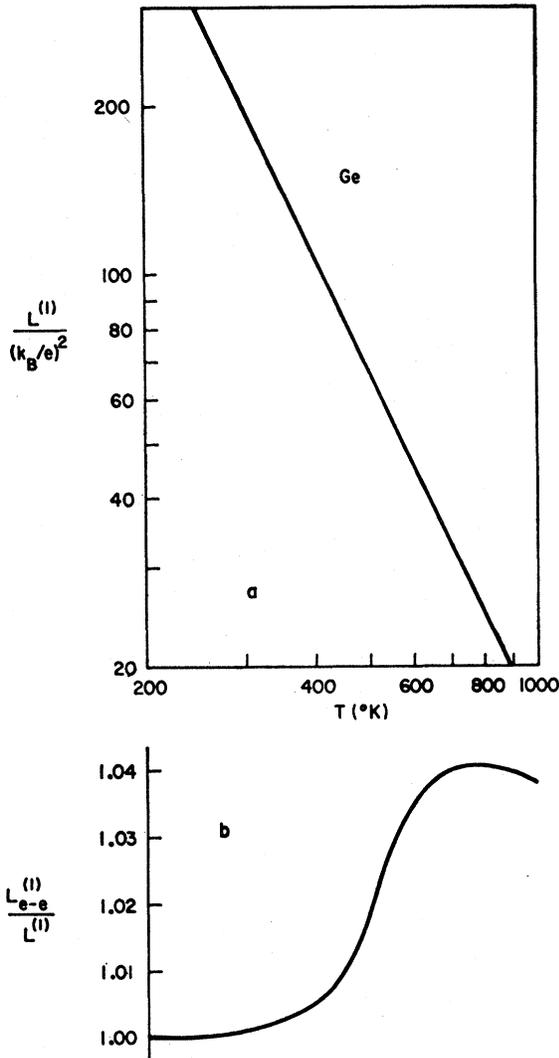[17] J. Appel and R. Bray (to be published).

Fig. 5. (a) The first-order approximation for the mobility of intrinsic germanium $\mu^{(1)}=\sigma^{(1)}/e(n+p+\bar{p})$, ignoring intercarrier scattering. (b) Ratio of the mobility $\mu_{e\text{-}e}^{(1)}$ (lattice and intercarrier scattering) and $\mu^{(1)}$.

dependence of the charge carrier concentration. With increasing electron-hole concentration, Coulomb scattering processes will occur more often. However, since the interaction potential becomes weaker with increasing number of carriers, the effective scattering cross sections decrease. In the limit of a degenerate electron gas (metals), the screening becomes so strong that electron-electron scattering is unimportant for the electrical resistivity, except at very low temperatures. Therefore, we may expect that in an intrinsic semiconductor the relative influence of intercarrier scattering on the mobility does not monotonically increase as the temperature rises. This is verified by Fig. 5 for the case of germanium. The electronic mobilities $\mu^{(1)}$ and $\mu_{e\text{-}e}^{(1)}$ have been calculated as a function of temperature assuming for holes the parameters given above and for

electrons the following:

$$m_e = 0.22m,$$

$$\mu_{e\text{-ac}} = 34\,000(80°K/T)^{\frac{3}{2}}\ cm^2/\text{v-sec},$$

$$D_e = 4.1\ ev.$$

The Wiedemann-Franz ratio for intrinsic germanium is shown in Fig. 6. It is true in general that the quotient $L_{e\text{-}e}/L>1$, provided that the ambipolar term is the predominant one in the electronic heat conductivity. Then, $L_{e\text{-}e}/L$ is determined primarily by electron-hole scattering processes. The latter, however, affect the momentum distributions of electrons and holes more strongly by shifting both momentum distributions in K space, than by randomizing the energies of electrons and holes. We mention the fact that in the case of a one-band conductor the Wiedmann-Franz ratio is always reduced by electron-electron scattering.

Transient Mobility of Ge

In an intrinsic semiconductor the carrier concentration increases with temperature. As the temperature rises the scattering of electrons and holes by the thermal lattice vibrations becomes more important, and, therefore, the relative influence of intercarrier scattering on the mobility is only a few percent. However, it is possible to increase the carrier concentration by several orders of magnitude without changing the temperature by exposing the crystal to high-energy primary electrons for short time intervals (1–5 μsec). These primary electrons are supplied by an electron linear accelerator, and the dynamical interaction between primary electrons and crystal valence electrons results in the latter being excited to the conduction band. The resultant free-electron-hole pairs give rise to an increased conductivity. Since the lifetime of the excess carriers is usually quite short—approximately 20 μsec for an initial electron concentration of 10^{14} in n-Ge—the transient conductivity is to be measured by special experimental methods.[18] The result to be expected for the transient mobility of germanium at 77°K is shown in Fig. 7.

ACKNOWLEDGMENTS

APPENDIX A. PARAMETER INTEGRALS

The integrals occurring in Eqs. (23a) through (23g) are defined as follows:

$$J_n(y) = \int_0^\infty \exp(-x^2)x^{2n+1}$$
$$\times [\ln(1+2x^2/y)-(1+y/2x^2)^{-1}]dx, \quad (A1)$$

[18] E. G. Wikner (private communication); V. A. J. van Lint, General Atomic Report GA-1827, 1960 (unpublished).

$$I_n(y) = \int_0^\infty \exp(-x^2)x^{2n+1}$$

$$\times [2(1+y/x^2)\ln(1+2x^2/y)-4]dx. \quad (A2)$$

Both integrals can be expressed in a closed form for $n>0$.

APPENDIX B. TRANSITION METALS

In order to investigate in the framework of the Boltzmann equation the influence of interband electron-electron scattering on the electrical and heat conductivities of transition metals, some difficulties must be
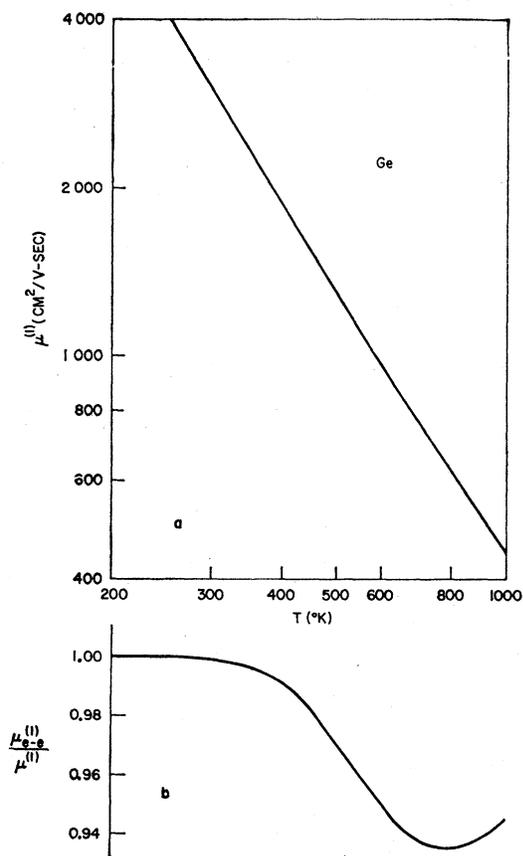

FIG. 6. (a) The Wiedemann-Franz ratio $L^{(1)}=\kappa^{(1)}/\sigma^{(1)}T$ for intrinsic germanium. (b) Ratio of $L_{e-e}^{(1)}$ (lattice and intercarrier scattering) and $L^{(1)}$.
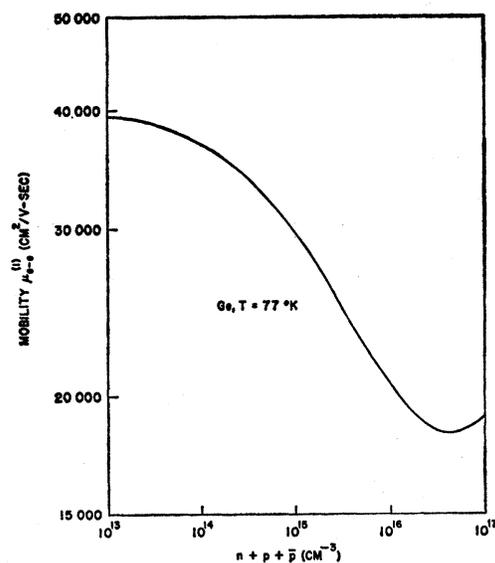

FIG. 7. The mobility $\mu_{e-e}^{(1)}$ (lattice and intercarrier scattering) of germanium as a function of the electron-hole concentration.

overcome which have been outlined before.[1] One may expect, however, that a theoretical consideration based on the Boltzmann equation gives the correct temperature dependences of the transport coefficients because the low-frequency phenomena in metals can be described *completely* in terms of *appropriately* defined quasi-particles,[19] the interaction of these quasi-particles with impurities, and their interaction with each other via a screened Coulomb potential. Therefore, also in the case of metals, the electrical conductivity and the heat conductivity in zero-order approximation are given by formulas of the type presented by Eqs. (26) and (27), respectively, with $CJ_0 \propto (k_B T/\zeta)^2$. Thus, a contribution to the low-temperature resistivity which is proportional to T^2, caused by interband electron-electron scattering, should be accompanied by a heat resistivity contribution which is proportional to T^1. Experimentally, a T^2 contribution to the electrical resistivity has been confirmed by White and Woods;[20] however, a T^1 contribution to the heat resistivity has not been observed yet.

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[19] J. S. Langer, Phys. Rev. 124, 1003 (1961).
[20] G. K. White and S. B. Woods, Phil. Trans. Roy. Soc. (London) A251, 273 (1959).