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Variational Treatment of High-Frequency Transport Problems in Solids*

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A variational method of solving the Boltzmann transport equation in a magnetic field is extended to high-frequency problems. The variational functional does not have an extremum at the solution, but a saddle point. It is shown that the approximations to the conductivity satisfy a sum rule which is also satisfied by the exact result, provided reasonable trial functions are used. Alternative variational principles have been formulated by several authors and some of these are discussed. The variational equations used in this paper can also be derived by Blount's method, and this casts more light on their nature. It is shown that when the current carriers are not degenerate and the band is parabolic, the use of Sonine polynomials in the carrier energy as trial functions has certain formal advantages, but that in actual calculations simple powers of the energy give the same results. The method is applied to a calculation of the frequency-dependent magnetoconductivity for mixed ionized-impurity and polar optical-phonon scattering, using parameters appropriate to n-InSb at 77°K. The results are used to calculate the Faraday rotation and ellipticity as a function of magnetic field at a frequency of 35 Gc/sec. It is suggested that measurements of the Faraday ellipticity can give useful information about the scattering mechanisms in a material.

1. INTRODUCTION

It is well known that in treatments of transport problems starting from the Boltzmann equation, a magnetic field plays much the same role as a high-frequency electric field; the circular frequency ω of the electric field is simply replaced by the cyclotron frequency ω_c. This parallel is also apparent in the variational description of transport phenomena, and the magnetic operator M and the frequency operator Ω have the same formal properties. (The exact definition of these operators is given in Sec. 2.) The scattering operator L is Hermitian and positive definite, but M and Ω are anti-Hermitian. As a consequence, it is possible to set up a simple variational principle[1] which maximizes the conductivity when $\omega=\omega_c=0$, but the properties of M and Ω make this difficult when they are present.

In this paper variational principles in the presence of M and Ω are first considered, and the simple but nonextremal principle formulated some time ago[2] for problems in a magnetic field is extended to the frequency-dependent case. This form of the variational principle has been used in actual computations of solid-state properties.[3,4] It is shown that approximate solutions obtained by this method satisfy certain sum rules which also hold for the exact solutions. Other variational principles which have been formulated[5–7] are discussed, and their respective advantages for practical computations are compared.

The variational equations are then set up and formally solved, and it is shown that the use of Sonine polynomials as trial functions simplifies the formal treatment somewhat, but that it does not improve the convergence. The formalism is applied to a case of mixed polar-optical and ionized-impurity scattering, and the results of a calculation of the frequency-dependent magnetoconductivity and of the Faraday rotation and ellipticity are presented.

2. VARIATIONAL PRINCIPLES FOR THE BOLTZMANN EQUATION

If $\mathbf{k}$ is the wave vector of charge carriers in a solid, $E_\mathbf{k}$ the corresponding energy eigenvalue, and $f_\mathbf{k}^0$ the equilibrium distribution function, the presence of an external electric field sets up a nonequilibrium distribution $f_\mathbf{k}$ which, in the linear approximation, is customarily[1] written as

$$f_\mathbf{k}=f_\mathbf{k}^0-\Phi_\mathbf{k}(\partial f_\mathbf{k}^0/\partial E_\mathbf{k}). \tag{2.1}$$

This defines $\Phi_\mathbf{k}$ which is to be found by solving an equation of the form

$$R\Phi_\mathbf{k}=X_\mathbf{k}\equiv -e\mathbf{v}_\mathbf{k}\cdot\boldsymbol{\mathcal{E}}(\partial f_\mathbf{k}^0/\partial E_\mathbf{k}). \tag{2.2}$$

Here e is the charge of the carrier and $\mathbf{v}_\mathbf{k}$ the velocity of the state $\mathbf{k}$. Henceforth the label $\mathbf{k}$ will be omitted unless it is needed for clarity.

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[1] J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960).

[2] F. Garcia-Moliner and S. Simons, Proc. Cambridge Phil. Soc. **53**, 848 (1957).

[3] F. Garcia-Moliner, Phys. Rev. **130**, 2290 (1963), hereafter referred to as I.

[4] F. Garcia-Moliner, Proc. Roy. Soc. (London) **A249**, 73 (1958).

[5] B. B. Robinson and I. B. Bernstein, Ann. Phys. (N. Y.) **18**, 110 (1962).

[6] E. I. Blount, Phys. Rev. **131**, 2354 (1963).

[7] M. Bailyn, Phys. Rev. **126**, 2040 (1962).

In the presence of a magnetic field $\mathbf{H}$ and an electric field varying as $e^{i\omega t}$, the operator R is the following:

$$R=L+M+\Omega\,, \tag{2.3}$$

where L is the linear integral collision operator, extensively discussed by Ziman,[1] M is the magnetic operator

$$M\Phi=-(e/hc)(\partial f^0/\partial E)(\mathbf{v}\times)\mathbf{H}\cdot\nabla_{\mathbf{k}}\Phi\,, \tag{2.4}$$

and Ω is the frequency operator

$$\Omega\Phi=-i\omega(\partial f^0/\partial E)\Phi\,. \tag{2.5}$$

Thus Φ is in general a function of $\mathbf{k}$, $\mathbf{H}$, ω, and $\boldsymbol{\mathcal{E}}$, and it is a complex function if $\omega\neq 0$. For any two functions Φ and Ψ of the same space (assuming all appropriate boundary conditions) the scalar product will be defined as

$$\langle\Phi,\Psi\rangle\equiv\int\Phi^*\Psi d\mathbf{k}\,;\quad d\mathbf{k}\equiv(4\pi^3)^{-1}dk_1dk_2dk_3\,. \tag{2.6}$$

It can be shown that the following equalities hold:

$$\begin{aligned}\langle\Phi,L\Psi\rangle&=\langle\Psi,L\Phi\rangle^*\,;\\ \langle\Phi,M\Psi\rangle&=-\langle\Psi,M\Phi\rangle^*\,;\\ \langle\Phi,\Omega\Psi\rangle&=-\langle\Psi,\Omega\Phi\rangle^*\,,\end{aligned} \tag{2.7}$$

thus L is Hermitian, while M and Ω are anti-Hermitian. These properties of L and M are discussed by Ziman[1] for real functions Φ and Ψ.

One possible form of writing a variational principle is the following: Let $\Phi_\pm$ be the function Φ in a magnetic field $\pm\mathbf{H}$, and remember that * indicates complex conjugation, that is $i\to -i$ or $\Omega\to-\Omega$. A suitable variational functional is then

$$E(\Phi)=\langle\Phi_-{}^*,R\Phi_+\rangle-\langle\Phi_-{}^*,X\rangle-\langle X,\Phi_+\rangle\,. \tag{2.8}$$

By an extension of a formalism used elsewhere,[2] it is seen that independent variations of Φ_+ and $\Phi_-{}^*$ yield, respectively, the two conjugate forms of the Boltzmann equation

$$(L-M-\Omega)\Phi_-{}^*=X\,;\quad(L+M+\Omega)\Phi_+=X\,. \tag{2.9}$$

If Φ is expanded in some set of functions φ_r,

$$\Phi_+{}^{(N)}=\sum_{r=0}^{N}c_r\varphi_r\,,\quad\Phi_-{}^{*(N)}=\sum_{r=0}^{N}d_r\varphi_r\,, \tag{2.10}$$

then the variational equations, obtained by varying $E(\Phi)$ with respect to the coefficients d_r, are

$$\sum_{s=0}^{N}R_{rs}c_s=X_r\,, \tag{2.11}$$

where $R_{rs}=\langle\varphi_r,R\varphi_s\rangle$, $X_r=\langle\varphi_r,X\rangle$. When $M=\Omega=0$, one has a definite minimum principle for $E(\Phi)$. In the steady state $-E(\Phi)$ is precisely the current, so that the variational calculation maximizes the conductivity. Therefore, successive approximations approach monotonically the exact conductivity from below.

There is no difficulty in formally establishing variational principles in alternative forms, and many have been published in numerous references (usually for $\Omega=0$). The real questions concern, on the one hand, the physical meaning of the principle, and, on the other hand, its practical use as a method of calculation for solving transport problems. Ziman's book[1] reviews the relevant developments (for $\Omega=0$) up to 1960 and demonstrates the intimate relationship with irreversible thermodynamics. The meaning of the variational principle has also been discussed, for $\Omega\neq0$, by Robinson and Bernstein[5] for transport phenomena in a plasma, and by Blount.[6] The latter has shown that the functional $E(\Phi)$ of Eq. (2.8) has in the steady state a minimum with respect to variations of $(\Phi_++\Phi_-{}^*)$, which is the part of Φ even in both frequency and magnetic field, and a maximum with respect to variations of $(\Phi_+-\Phi_-{}^*)$, the part of Φ odd in both. Thus $E(\Phi)$ has a saddle point rather than an extremum.

Therefore for M or $\Omega\neq0$ the variational equations (2.11) do not set a limit to the conductivity. However, the variational approximation to the conductivity does share an interesting property with the exact result. Consider the case $M=0$, $\Omega\neq0$. Then the real part of the exact conductivity $\mathrm{Re}\sigma(\omega)$ satisfies the sum rule[8,9]

$$\int_0^\infty\mathrm{Re}\sigma(\omega)d\omega=\frac{\pi ne^2}{2m^*}\,, \tag{2.12}$$

where m^* is the conductivity effective mass of the carriers and n is their concentration. This equation follows from the solution of the problem of the initial acceleration of the carriers when an electric field is applied suddenly. The scattering mechanisms do not enter this problem, so it would be expected that the Nth-order variational approximation $\sigma^{(N)}$ would also satisfy (2.10) provided reasonable trial functions are chosen. This expectation is confirmed by an argument given in the Appendix. Hence

$$\int_0^\infty\mathrm{Re}\sigma^{(N)}(\omega)d\omega=\int_0^\infty\mathrm{Re}\sigma(\omega)d\omega=\frac{\pi ne^2}{2m^*}\,. \tag{2.13}$$

It should be noted that this relation is incompatible with monotonic convergence of $\mathrm{Re}\sigma^{(N)}(\omega)$ to the exact result from below.

This sum rule is easily generalized to the case where a magnetic field is also present, if the system is isotropic, or if it is a crystal and $\mathbf{H}$ is parallel to a threefold, fourfold, or sixfold symmetry axis. It is then convenient[9] to consider a circularly polarized electric field $\boldsymbol{\mathcal{E}}_\pm$ rotating in the (x,y) plane normal to $\mathbf{H}$:

$$\boldsymbol{\mathcal{E}}_\pm=|\mathcal{E}|e^{i\omega t}(1/\sqrt{2})(1,\mp i,0)\,. \tag{2.14}$$

The corresponding components of the conductivity

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[8] D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963), p. 136.

[9] N. K. Hindley, Phys. Status Solidi 7, 67 (1964).

tensor are written $\sigma_{\pm}$. The problem is now symmetric in ω and the cyclotron frequency ω_c, and $\sigma_{\pm}$ depends only on $(\omega\pm\omega_c)$. This implies sum rules like (2.12) in ω_c.

Bailyn[7] has remarked that (when $\Omega=0$) the even part of Φ is the solution of the equation

$$\mathcal{L}\Phi^{(e)}\equiv(L-ML^{-1}M)\Phi^{(e)}=X\,, \qquad (2.15)$$

for which there is an extremal principle, as $\mathcal{L}$ is positive definite and Hermitian. Using this principle, one arrives at Bailyn's formula (3.4a), which yields approximations which tend monotonically (from below) to the true value of the even part of the conductivity. Specifically, with $\mathbf{H}=(0,0,H)$, one has a calculation which maximizes σ_{xx}. However, the definition of $\mathcal{L}$ involves L^{-1}, which may be evaluated by using the ordinary variational principle. If these "internal" variational calculations are carried out to the same order of approximation as the "external" calculation, the same results are obtained as with the variational principle (2.8), if the same expansion functions are used throughout. To make this point more explicitly, consider an earlier publication,[3] (hereafter referred to as I) in which Eq. (2.8) was used to perform a calculation of galvanomagnetic effects for a semiconductor with polar-optical-mode scattering. Equations (36) and (37) of I are exactly equivalent to Bailyn's formulas (3.4a) and (3.4b), the matrices A and B of I being the representation of Bailyn's operators $\mathcal{L}$ and $-\mathcal{L}ML^{-1}$ in terms of the chosen expansion functions.

More complicated extremal principles have been given by Robinson and Bernstein,[5] and by Blount.[6] Blount's method consists in premultiplying the Boltzmann equation (2.2) by $R^{\dagger}T$, where $R^{\dagger}$ is the Hermitian adjugate of R, and T is any positive-definite Hermitian operator. The operator $R^{\dagger}TR$ is then Hermitian and positive definite, and an extremal principle applies. If T is chosen equal to L^{-1} the method is equivalent to Bailyn's. Blount[10] has pointed out that the Eqs. (2.11) can also be obtained from his variational principle, and this sheds more light on the nature of the earlier principle, Eq. (2.8). The appropriate variational functional for the Blount principle is

$$V(\Phi)=\langle\Phi,R^{\dagger}TR\Phi\rangle-\langle\Phi,R^{\dagger}TX\rangle-\langle X,TR\Phi\rangle. \qquad (2.16)$$

Expanding Φ in terms of the φ_r, as in Eq. (2.10), the Nth-order functional is

$$\begin{aligned}V_N=&\sum_{ijkl}^{N} c_i^*R_{ji}^*T_{jk}R_{kl}c_l-\sum_{ijk}^{N} c_i^*R_{ji}^*T_{jk}X_k\\ &\qquad\qquad-\sum_{ijk}^{N} X_i^*T_{ij}R_{jk}c_k\\ =&-\sum_{ij}^{N} X_i^*T_{ij}X_j+\sum_{jk}^{N} A_j^*T_{jk}A_k\,,\end{aligned}$$

where

$$A_i=\textstyle\sum_j R_{ij}c_j-X_i. \qquad (2.17)$$

Thus since T is positive definite V_N has a minimum value of $-\sum_{ij}{}^{N}X_i^*T_{ij}X_j$ when all the A_i are zero. But the equations $A_i=0$ are precisely the variational equations (2.11).

In the above argument the matrix T is arbitrary, but if $T=\frac{1}{2}(R^{-1}+R^{\dagger\,-1})$, then $\langle X,TX\rangle$ is the part of the conductivity even in both ω and H. The equations (2.11) minimize V_N, and therefore maximize the conductivity, for a given value of N. However, since it is not necessarily true that

$$\textstyle\sum_{ij}{}^{N+1}\,X_i^*T_{ij}X_j>\sum_{ij}{}^{N}\,X_i^*T_{ij}X_j\,,$$

monotonic convergence to the exact result does not follow. All we can conclude is that for a given set of N trial functions, equations (2.11) maximize the expression for the conductivity. In view of Eq. (2.13), perhaps this is the most that can be expected. Equations (2.11) will form the basis for the rest of this paper.

As has been mentioned, there is a symmetry between the frequency dependence of the conductivity and the magnetic-field dependence, with real and imaginary parts corresponding to parts even and odd in $\mathbf{H}$. Thus the same set of numerical results obtained in a given calculation can be interpreted to yield, for a suitably arranged geometry, either galvanomagnetic coefficients as a function of $\mathbf{H}$ or optical coefficients as a function of ω, or indeed magneto-optical coefficients as a function of $(\omega\pm\omega_c)$. This is obvious from the standard formulas when a relaxation time exists. Consider, however, the problem of polar-optical-mode scattering at arbitrary temperatures. The variational calculation reported in I, which ignored the field-theoretic complications of the polaron problem, yielded two functions of temperature and magnetic field F_c and F_H which are related to the conductivity mobility μ_c and the Hall mobility μ_H:

$$\mu_c=\bar{\mu}(z)F_c(z,Y)\,;\quad \mu_H=\bar{\mu}(z)F_H(z,Y)\,. \qquad (2.18)$$

Here $z=\hbar\omega_{\text{op}}/kT$, and ω_{op} is the frequency of the optical phonons; $Y=\bar{\mu}H/c$, and $\bar{\mu}$ is a known function of z of dimensions of mobility.

The real and imaginary parts of $\sigma_{\pm}(\omega,\omega_c)$ may be expressed in terms of the same functions if Y is reinterpreted as $Y_{\pm}$:

$$Y_{\pm}=m\bar{\mu}(\omega\pm\omega_c)/|e|\,, \qquad (2.19)$$

then

$$\begin{aligned}\sigma_{\pm}(\omega,\omega_c)=n|e|\bar{\mu}\{&F_c(z,Y_{\pm})\\ &-iY_{\pm}F_c(z,Y_{\pm})F_H(z,Y_{\pm})\}\,. \qquad (2.20)\end{aligned}$$

The derivation of this equation is considered in Sec. 4. The frequency- and magnetic-field-dependent dielectric function $\epsilon_{ij}(\omega,\omega_c)$ is related to the conductivity tensor $\sigma_{ij}(\omega,\omega_c)$ by

$$\epsilon_{ij}(\omega,\omega_c)=\epsilon_0\delta_{ij}-(4\pi i/\omega)\sigma_{ij}(\omega,\omega_c)\,, \qquad (2.21)$$

where δ_{ij} is the unit tensor and ϵ_0 the dielectric constant of the lattice. The free-carrier magneto-optical properties of a polar semiconductor can therefore be cal-

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[10] We wish to thank Dr. E. I. Blount for this suggestion and for several other very helpful comments.

culated from the data given in the tables of I. Unfortunately, for most values of z, the range of $Y_\pm$ covered by these tables is inadequate for practical ranges of variables in magneto-optical calculations.

3. THE VARIATIONAL EQUATIONS

After the above considerations the routine is straightforward. The variational equations (2.11) may be written

$$\sum_{s=0}^{N} (L_{rs}+M_{rs}+\Omega_{rs})c_s = X_r. \tag{3.1}$$

From now on it will be assumed that the solid is isotropic, or has cubic symmetry with the magnetic field $\mathbf{H}$ along a threefold or fourfold axis. The direction of $\mathbf{H}$ will be taken as the z axis of a right-handed Cartesian coordinate system with the x axis in the direction of $\mathcal{E}(\mathcal{E}\perp\mathbf{H})$. Unit vectors along the coordinate axes (x,y,z) will be denoted by $(\mathbf{u},\mathbf{u}',\mathbf{h})$, as in I. Let $\{\psi_r(E)\}$ be a set of functions of the carrier energy, which may be, for example, simple powers of E or polynomials in E. Expanding to Nth order,

$$\Phi^{(N)} = \sum_{r=0}^{N} c_r\psi_r\mathbf{k}\cdot\mathbf{u} + \sum_{r'=0}^{N} c'_{r'}\psi_{r'}\mathbf{k}\cdot\mathbf{u}', \tag{3.2}$$

the operator R has the following matrix representation:

$$R = \begin{bmatrix} L+\Omega & M \\ -M & L+\Omega \end{bmatrix}. \tag{3.3}$$

As in I, here L, M, and Ω are submatrices of the matrix R, and they have $(N+1)$ rows and columns each. Hence one easily obtains

$$\begin{aligned} \sigma_{xx}^{(N)} &= \mathcal{E}^{-2} \sum_{r,s=0}^{N} X_r[(L+\Omega)+M(L+\Omega)^{-1}M]_{rs}^{-1}X_s, \\ \sigma_{xy}^{(N)} &= -\mathcal{E}^{-2} \sum_{r,s=0}^{N} X_r[M+(L+\Omega)M^{-1}(L+\Omega)]_{rs}^{-1}X_s. \end{aligned} \tag{3.4}$$

It is convenient to express the results in terms of the conductivity components $\sigma_\pm$ corresponding to the circularly polarized electric fields of Eq. (2.14); these are given by

$$\sigma_\pm = \sigma_{xx} \mp i\sigma_{xy}. \tag{3.5}$$

Using the identity

$$(A+iB)^{-1} = (A+BA^{-1}B)^{-1} - i(B+AB^{-1}A)^{-1}, \tag{3.6}$$

one obtains

$$\sigma_\pm^{(N)} = \mathcal{E}^{-2} \sum_{r,s=0}^{N} X_r(L+\Omega\mp iM)_{rs}^{-1}X_s. \tag{3.7}$$

Also, for σ_{zz} one obtains

$$\sigma_{zz}^{(N)} = \mathcal{E}^{-2} \sum_{r,s=0}^{N} X_r(L+\Omega)_{rs}^{-1}X_s. \tag{3.8}$$

These then are the explicit formulas to calculate magnetic-field and frequency-dependent free-carrier properties, as the experimental coefficients can all be expressed in terms of the σ_{ij}. To evaluate the formulas explicitly one has to specify the model under study (scattering and band structure) and the functions $\psi_r(E)$. For example, for nondegenerate statistics and a standard parabolic band structure, the matrices M_{rs} and Ω_{rs}, and the vector X_r, take a particularly simple form if the $\psi_r(E)$ are taken to be Sonine polynomials.[11] The polynomials $S_m{}^r(y)$ are defined by

$$(1-t)^{-m-1}e^{-yt/(1-t)} = \textstyle\sum_r S_m{}^r(y)t^r, \tag{3.9}$$

and satisfy the orthogonality condition

$$\int_0^\infty e^{-x}S_m{}^p(x)S_m{}^q(x)x^m dx = \frac{\Gamma(m+p+1)}{\Gamma(p+1)}\delta_{pq}, \tag{3.10}$$

where δ_{pq} is the Kronecker delta symbol.

The trial functions $\psi_r(E)$ will be taken to be

$$\psi_r(E) = S_{3/2}{}^r(y), \quad y = E/kT. \tag{3.11}$$

The matrix element Ω_{rs} then becomes, using Eqs. (2.5), (2.6), and (3.10),

$$\begin{aligned} \Omega_{rs} &= -(i\omega/4\pi^3)\int (\mathbf{k}\cdot\mathbf{u})^2 S_{3/2}{}^r(y)S_{3/2}{}^s(y) \\ &\qquad\qquad \times(\partial f^0/\partial E)dk_1dk_2dk_3, \\ &= \frac{i\omega m^*n}{\hbar^2}\,\frac{\Gamma(r+\frac{5}{2})}{\Gamma(r+1)\Gamma(\frac{5}{2})}\delta_{rs}. \end{aligned} \tag{3.12}$$

Defining

$$\gamma_r = \frac{\Gamma(r+\frac{5}{2})}{\Gamma(r+1)\Gamma(\frac{5}{2})}, \tag{3.13}$$

one has

$$\Omega_{rs} = i\omega(m^*n/\hbar^2)\gamma_r\delta_{rs},$$

and similarly

$$\begin{aligned} M_{rs} &= -\omega_c(m^*n/\hbar^2)\gamma_r\delta_{rs}, \\ X_r &= (en/\hbar)\mathcal{E}\delta_{r0}. \end{aligned} \tag{3.14}$$

Thus M and Ω become diagonal matrices and all the X_r are zero except X_0. In general, however, L is not simplified, so the numerical work involved, principally the inversion of the matrix $(L+\Omega\mp iM)$, is not much reduced. However, there is one case in which L is diagonal too. This is the case in which scattering can be represented by a constant relaxation time τ. Then

$$L = -\frac{1}{\tau}\frac{\partial f^0}{\partial E}, \tag{3.15}$$

and

$$L_{rs} = (m^*n/\hbar^2\tau)\gamma_r\delta_{rs}. \tag{3.16}$$

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[11] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, London, England, 1939). Sonine polynomials have been used in a study of solid-state transport properties in a magnetic field by S. Devlin, thesis, Case Institute of Technology, Cleveland, Ohio, 1964 (unpublished).

Equation (3.7) now becomes

$$\sigma_{\pm}=(ne^2/m^*)\sum_{r,s=0}^{N}\delta_{r0}[(1/\tau)+i\omega\pm i\omega_c]^{-1}(1/\gamma_r)\delta_{rs}\delta_{s0},$$

$$=\frac{ne^2}{m^*}\frac{\tau}{1+i(\omega\pm\omega_c)\tau}. \tag{3.17}$$

This is of course the result obtained by solving the Boltzmann equation by elementary methods, and it is valid for all orders N of the variational calculation.

For energy-dependent relaxation times, the lowest variational approximation may be inaccurate. Then

$$L_{00}=\frac{m^*n}{\hbar^2}\langle 1/\tau\rangle\equiv\frac{m^*n}{\hbar^2}\frac{1}{\Gamma(\frac{5}{2})}\int_0^\infty\frac{1}{\tau}y^{3/2}e^{-y}dy, \tag{3.18}$$

and the dc conductivity in the absence of a magnetic field σ_0 is given to zero order by

$$\sigma_0^{(0)}=(ne^2/m^*)\langle 1/\tau\rangle^{-1}, \tag{3.19}$$

whereas the correct result has $\langle\tau\rangle$ for $\langle 1/\tau\rangle^{-1}$. For example, if $\tau=\tau_0 y^{3/2}$, which is approximately the case for ionized impurity scattering, the ratio of the exact result to the zero-order result is

$$\sigma_0/\sigma_0^{(0)}=\langle\tau\rangle\langle 1/\tau\rangle=32/3\pi=3.40. \tag{3.20}$$

However, a first-order calculation already gives a much better result:

$$\frac{\sigma_0}{\sigma_0^{(1)}}=\langle\tau\rangle\frac{\langle y^2/\tau\rangle\langle 1/\tau\rangle-\langle y/\tau\rangle^2}{(25/4)\langle 1/\tau\rangle-5\langle y/\tau\rangle+\langle y^2/\tau\rangle}$$

$$=\frac{128}{39\pi}=1.045. \tag{3.21}$$

It is interesting to note that when $\tau\propto y^{3/2}$, the exact solution for the distribution function is

$$\Phi=(e\hbar\mathcal{E}/m^*)\mathbf{k}\cdot\mathbf{u}\tau\propto y^{3/2}(\mathbf{k}\cdot\mathbf{u}), \tag{3.22}$$

which cannot be expanded in the form (3.2) if the ψ_r are taken to be polynomials in y. Yet the variational expression for the conductivity σ_0 still converges very quickly.

Since the Sonine polynomial $S_{3/2}{}^r(y)$ is of degree r, an Nth-order calculation using these polynomials as trial functions, up to $S_{3/2}{}^N(y)$, must give the same results as a calculation using powers of y up to y^N. This may also be checked directly. Therefore, Sonine polynomials do not improve the convergence of the method and give little or no advantage in numerical calculations.

4. SCOPE OF THE PRESENT CALCULATION: MIXED IMPURITY AND POLAR-OPTICAL-MODE SCATTERING

As a practical application of the variational method, a calculation has been made of the free-carrier magneto-optical properties of a semiconductor in which scattering by polar optical phonons is important. Since a relaxation time cannot be defined for this scattering mechanism except at very high and very low temperatures, a variational method is needed. The calculation was programmed in FORTRAN II for a digital computer, and the program was based on that used in I in a calculation of the magnetoresistance of a polar semiconductor: Practical use was thus made of the formal relation between the operators M and Ω. The trial functions $\psi_r(E)$ of (3.2) were taken to be

$$\psi_r(E)=y^r,\quad y=E/kT, \tag{4.1}$$

because these were the functions used in I, and because a power-series expansion yields the same results as an expansion in Sonine polynomials if carried to the same order.

As far as possible, results will be presented in a general dimensionless form to make them more convenient to use in the analysis of particular situations. However, the ranges of variables and parameters chosen are those appropriate to n-InSb under typical experimental conditions. Nonparabolicity of the conduction band, partial degeneracy, and other complications encountered in this semiconductor are outside the scope of the present calculation, which assumes a band of standard form and classical statistics. However, in order to be fairly realistic, ionized impurity scattering has been included as well as polar optical scattering. Many of the calculations have been made for a value of $z=\hbar\omega_{\mathrm{op}}/kT$ corresponding to a temperature of 77°K, which is a convenient temperature experimentally, and at which impurity scattering is important but the other complications mentioned above are not. The calculations have also been pushed to higher temperatures for pure polar scattering to study the dispersive properties of this scattering mechanism at different temperatures.

The matrix elements of the polar scattering operator with the basic functions (4.1) are[3,12]

$$L_{rs}{}^{(p)}=(n|e|/\hbar^2\bar{\mu})d_{rs}(z), \tag{4.2}$$

where the $d_{rs}(z)$ are dimensionless integrals identical with the $\delta_{rs}(z)$ of Howarth and Sondheimer,[12] and $\bar{\mu}$ is a quantity of dimensions of mobility

$$\bar{\mu}=\frac{3\gamma(kT)^{3/2}}{2^{7/2}\pi^{1/2}|e|m^{*3/2}}\frac{e^z-1}{e^{z/2}}. \tag{4.3}$$

Here γ^{-1}, which is proportional to the dimensionless coupling constant for the electron–polar-phonon interaction, is defined so that it is independent of the effective mass:

$$1/\gamma=(\omega_{\mathrm{op}}{}^2/4\pi)(1/\epsilon_\infty-1/\epsilon_s),$$

where ϵ_∞, ϵ_s are the dielectric constants of the lattice at frequencies $\omega\gg\omega_{\mathrm{op}}$ and $\ll\omega_{\mathrm{op}}$, respectively.

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

The Brooks-Herring formula[13] for the relaxation time for ionized-impurity scattering can be written

$$\tau^{-1}=\tau_0^{-1}g(ay)y^{-3/2}, \tag{4.4}$$

where

$$g(\xi)=\ln(1+\xi)-\xi/(1+\xi), \tag{4.5}$$

and where τ_0 and the screening constant a are independent of y. Using Eq. (3.15) the matrix elements of the impurity-scattering operator are found to be

$$L_{rs}^{(i)}=(m^*n/\hbar^2\tau_0)\lambda_{r+s}, \tag{4.6}$$

where

$$\lambda_n=\frac{1}{\Gamma(\frac{5}{2})}\int_0^\infty y^n g(ay)e^{-y}dy. \tag{4.7}$$

The integral λ_n can be evaluated in terms of tabulated functions by integrating the term involving $\ln(1+ay)$ by parts. The following recurrence relation is obtained:

$$\lambda_n/n!=\lambda_{n-1}/(n-1)!+[(n+1)/\Gamma(\tfrac{5}{2})]\times[A_n(1/a)-A_{n+1}(1/a)], \tag{4.8}$$

where

$$A_n(x)=\frac{1}{n!}\int_0^\infty\frac{y^n e^{-y}dy}{x+y}. \tag{4.9}$$

The integral λ_0 can be evaluated in the same way:

$$\lambda_0=(1+1/a)A_0(1/a)-1. \tag{4.10}$$

The integrals $A_n(x)$ have been studied and tabulated by Dingle *et al.*[14] The screening constant a is usually large, and in the present application an expansion of the $A_n(1/a)$ to order a^{-2} was used. The expansions are collected here for reference:

$$\begin{aligned}
\Gamma(\tfrac{5}{2})\lambda_0&=(1+2/a+3/2a^2)(\ln a-C)-1+1/a+3/4a^2,\\
\Gamma(\tfrac{5}{2})\lambda_1&=(1-3/2a^2)(\ln a-C)+2/a-5/4a^2,\\
(1/2!)\Gamma(\tfrac{5}{2})\lambda_2&=(\ln a-C)+\tfrac{1}{2}+1/a-7/4a^2,\\
\frac{\lambda_n}{n!}&=\frac{\lambda_{n-1}}{(n-1)!}+\frac{1}{\Gamma(\frac{5}{2})}\left[\frac{1}{n}-\frac{2}{a(n-1)n}+\frac{3}{a^2n(n-1)(n-2)}\right],\quad(n>2).
\end{aligned}\tag{4.11}$$

In the above, C is Euler's constant, 0.577216.

The total scattering matrix element L_{rs} is given by adding Eqs. (4.2) and (4.6):

$$L_{rs}=L_{rs}^{(i)}+L_{rs}^{(p)}=(ne/\hbar^2\bar{\mu})D_{rs}, \tag{4.12}$$

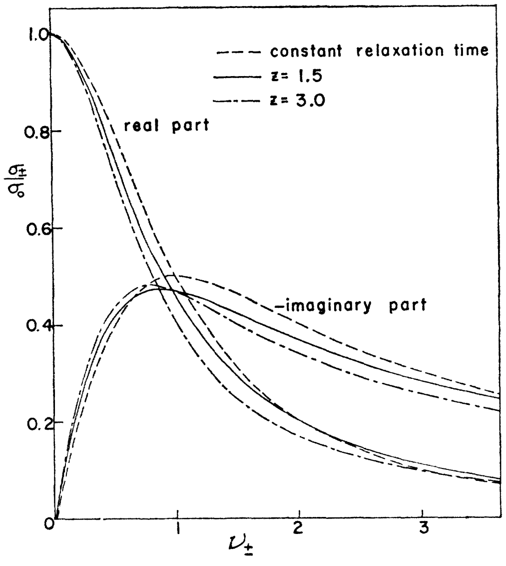

FIG. 1. The conductivity $\sigma_\pm/\sigma_0$ in the 3rd-order variational approximation as a function of $\nu_\pm=(\omega\pm\omega_c)\tau_{\mathrm{eff}}$ for pure polar scattering and two values of $z=\hbar\omega_{\mathrm{op}}/kT$. The curve for a constant relaxation time is also shown.

where

$$D_{rs}=d_{rs}+R\lambda_{r+s}, \tag{4.13}$$

and

$$R=\bar{\mu}m^*/|e|\tau_0. \tag{4.14}$$

The parameter R is a measure of the ratio of polar to impurity mobility. The matrix elements of M, Ω, and X are given by

$$\begin{aligned}
M_{rs}&=-\omega_c(m^*n/\hbar^2)\Gamma_{rs},\\
\Omega_{rs}&=i\omega(m^*n/\hbar^2)\Gamma_{rs},\\
X_r&=(en/\hbar)\mathcal{E}\Gamma_{r0},
\end{aligned}\tag{4.15}$$

where

$$\Gamma_{rs}=\Gamma(r+s+\tfrac{5}{2})/\Gamma(\tfrac{5}{2}). \tag{4.16}$$

The formulas (4.12) and (4.15) for the matrix elements are to be substituted in the general expression (3.7). The result may be expressed in the form

$$\sigma_\pm^{(N)}=n|e|\bar{\mu}F^{(N)}(z,Y_\pm), \tag{4.17}$$

where

$$F^{(N)}(z,Y_\pm)=\sum_{rs}\Gamma_{0r}(D+iY_\pm\Gamma)_{rs}^{-1}\Gamma_{s0}, \tag{4.18}$$

and

$$Y_\pm=m^*\bar{\mu}(\omega\pm\omega_c)/|e|. \tag{4.19}$$

The result may be written in a neater form if the matrix ν is introduced:

$$\nu=\Gamma^{-1}D+Y_\pm^2D^{-1}\Gamma. \tag{4.20}$$

Then by splitting Eq. (4.18) into real and imaginary parts, using Eq. (3.6), one finds

$$F^{(N)}(z,Y_\pm)=[\Gamma\nu^{-1}]_{00}+iY_\pm[\Gamma\nu^{-1}D^{-1}\Gamma]_{00}. \tag{4.21}$$

If this result is compared with the formulas for $F_c(z,Y)$

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[13] H. Brooks, Advan. Electron. Electron Phys. **7**, 156 (1955).

[14] R. B. Dingle, D. Arndt, and S. K. Roy, Appl. Sci. Res. **B6**, 144 (1957).

and $F_H(z,Y)$ given in Eq. (41) of I, Eq. (2.20) follows immediately.

The frequency- and magnetic-field-dependent dielectric function is defined by Eq. (2.21), which for circularly polarized radiation may be written

$$\epsilon_\pm = \epsilon_0 - (4\pi i/\omega)\sigma_\pm .$$

Hence

$$\epsilon_\pm^{(N)} = \epsilon_0[1 - i\eta F^{(N)}(z,Y_\pm)], \tag{4.22}$$

where

$$\eta = 4\pi n|e|\bar{\mu}/\epsilon_0\omega . \tag{4.23}$$

The refractive and absorption indices $N_\pm$ and $K_\pm$ are then defined by

$$(N_\pm - iK_\pm)^2 = \epsilon_\pm . \tag{4.24}$$

Thus knowledge of the function $F^{(N)}$ is all that is needed to evaluate the free-carrier magneto-optical properties of a polar semiconductor.

5. RESULTS

The function $F^{(N)}(z,Y)$, and the optical constants $N_\pm$ and $K_\pm$, were calculated for $z=3.77$ (77°K assuming an Einstein temperature for the optical phonons of 290°K, which is appropriate for InSb), and for a few typical values of R and η. In addition, $F^{(N)}(z,Y)$ was computed for pure polar scattering ($R=0$) for various temperatures. The calculations were carried to 3rd order (using 4×4 matrices).

Figures 1 and 2 show the real and imaginary parts of $\sigma_\pm^{(3)}/\sigma_0^{(3)} = F^{(3)}(z,Y)/F^{(3)}(z,0)$ as functions of $\nu_\pm$, where

$$\nu_\pm = Y_\pm F^{(3)}(z,0) = (\omega \pm \omega_c)\tau_{\text{eff}}^{(3)} . \tag{5.1}$$

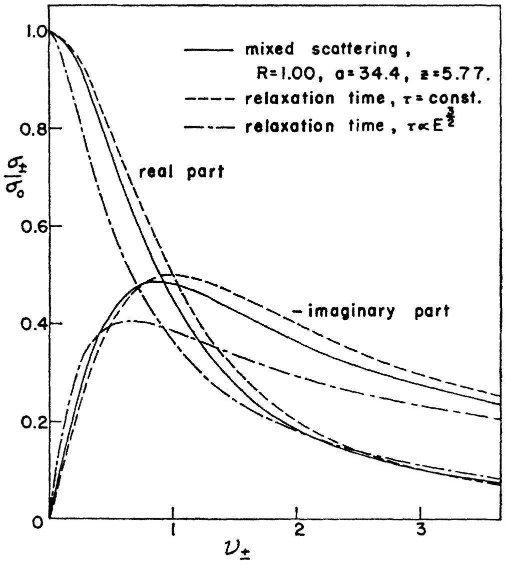

FIG. 2. The conductivity $\sigma_\pm/\sigma_0$ in the 3rd-order variational approximation as a function of $\nu_\pm = (\omega \pm \omega_c)\tau_{\text{eff}}$ for mixed polar-phonon and ionized-impurity scattering with parameters (corresponding to n-InSb at 77°K) as shown. Curves for constant relaxation time and for impurity scattering alone ($\tau \propto E^{3/2}$) are also shown.

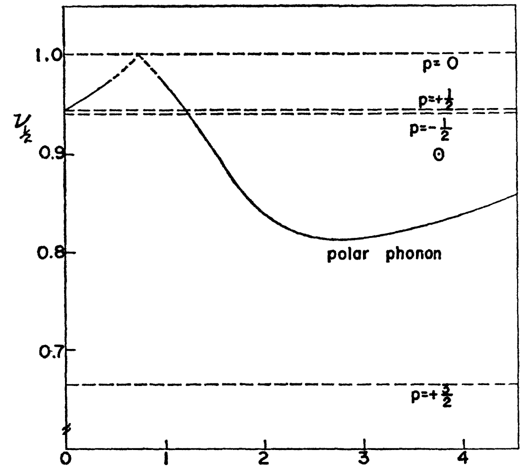

FIG. 3. The half-width $\nu_{1/2}$, the value of $\nu_\pm$ at which $\text{Re}\sigma_\pm = \frac{1}{2}\sigma_0$, as a function of z for pure polar scattering. Values for various energy-dependent relaxation times are also shown (broken lines), and the single point at $z=3.77$ is the value for mixed polar optical and impurity scattering for $R=1.00$, $a=34.4$.

Here $\tau_{\text{eff}}^{(N)}$ is an effective relaxation time chosen to give the Nth-order dc conductivity $\sigma_0^{(N)}$:

$$\sigma_0^{(N)} = (ne^2/m^*)\tau_{\text{eff}}^{(N)} . \tag{5.2}$$

Figure 1 shows the results for pure polar scattering, together with the standard Lorentzian curve obtained for a constant relaxation time. The curves show the kind of deviation from the Lorentzian shape which occurs, but for clarity results are plotted for only two values of z.

The departures from the Lorentzian curve are due to the dispersive nature of the scattering mechanism. A measure of this effect is given by $\nu_{1/2}$, the value of $\nu_\pm$ at which $\sigma_\pm = \frac{1}{2}\sigma_0$; for a constant relaxation time $\nu_{1/2}$ is 1, but for any other scattering mechanism it is less than 1. It is clear from Fig. 1 that for polar scattering $\nu_{1/2}$ is a function of temperature, and it is plotted on Fig. 3 as a function of z. The form of this curve between $z=\frac{1}{2}$ and $z=1$ is suggested by the fact that, at small values of z, polar scattering behaves like a positive dispersive mechanism (in the limit $z \to 0$ it can be represented by a relaxation time $\tau \propto E^{1/2}$), while for $z>1$ it behaves like a negative dispersive mechanism. This change of behavior is most clearly revealed by warm-carrier effects.[15] There should therefore be an intermediate temperature at which the mechanism shows no dispersion, though since a relaxation time does not exist, the precise temperature at which this happens may depend on the phenomenon considered. The form of the curve on Fig. 3 is very similar to the variation of the ratio μ_H/μ_c with z, studied in I, where μ_H, μ_c are the Hall and conductivity mobilities, respectively. This ratio is another measure of dispersive effects. Figure 3 also

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[15] D. Matz and F. Garcia-Moliner, Phys. Status Solidi 7, 205 (1964).

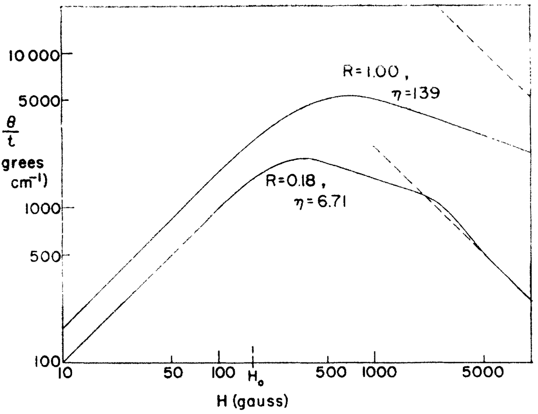

FIG. 4. Faraday rotation as a function of magnetic field H for mixed polar and impurity scattering (3rd-order variational approximation) at $z=3.77$ with parameters as shown. The broken lines are high-field asymptotes, H_0 is the cyclotron resonance field $mc\omega/|e|$.

shows the values of $\nu_{1/2}$ for various relaxation times $\tau \propto E^p$; in these cases $\nu_{1/2}$ is independent of temperature.

Figure 2 shows the variations of $\sigma_\pm/\sigma_0$ with $\nu_\pm$ for mixed polar optical and impurity scattering at $z=3.77$. The value of R is 1.00 and the screening constant $a=34.4$. A calculation with $R=0.18$, $a=600$ gave an almost identical curve. The value of $\nu_{1/2}$ for this curve is also shown on Fig. 3. The curves for a constant relaxation time and for $\tau \propto E^{3/2}$, which represents impurity scattering alone, are also plotted on Fig. 2. The mixed scattering curve shows less dispersion than either pure polar scattering or impurity scattering; this is clearly the result of combining a positive and a negative dispersive mechanism.

Note that the real part of $\sigma_\pm/\sigma_0$, plotted on Figs. 1 and 2, gives the absorption in a cyclotron resonance experiment with a circularly polarized electric field; in this case $\nu_{1/2}/\tau_{\text{eff}}$ is the half-width of the resonance line. The very small values of τ_{eff} encountered at the temperatures considered here would, of course, make this very difficult to observe. Note also that the sum rule (2.13) leads to an interesting relation, if Eqs. (5.1) and (5.2) are used:

$$\int_0^\infty \operatorname{Re}(\sigma_\pm^{(N)}/\sigma_0^{(N)})d\nu_\pm = \frac{\pi}{2}. \tag{5.3}$$

Thus the area under all the curves of $\operatorname{Re}(\sigma_\pm/\sigma_0)$ shown on Figs. 1 and 2 is the same.

Figures 4 and 5 show the Faraday rotation θ and the ellipticity δ as a function of magnetic field, calculated from the formulas

$$\begin{aligned} \theta &= (N_- - N_+)\omega t/2c, \\ \delta &= \tanh[(K_+ - K_-)\omega t/2c], \end{aligned} \tag{5.4}$$

where t is the thickness of the sample. The values of the parameters are $R=1.00$, $a=34.4$, $\eta=139$; and $R=0.18$, $a=600$, $\eta=6.71$. These values correspond to n-InSb with $n=1.23\times 10^{15}$ and 6×10^{13} carriers cm^{-3}, respectively, at a frequency of 35 Gc/sec. The corresponding values of $\omega\tau_{\text{eff}}$ are 0.306 and 0.690, respectively.

At high fields such that $\omega_c\tau_{\text{eff}}$ is very much greater than either $\omega\tau_{\text{eff}}$, 1, or the loss parameter $l=4\pi\sigma_0/\omega\epsilon_0$, the Faraday rotation approaches the limiting value

$$\lim_{H\to\infty}(\theta/t) = 2\pi ne/H\sqrt{\epsilon_0}. \tag{5.5}$$

This limit, which is independent of scattering mechanisms, is also shown on Fig. 4. The values of $l=\eta F^{(3)}(z,0)$ are 110 and 11.9 for the two samples, so both are very lossy and the high-field limit is not reached until the field is much greater than that at which the rotation is a maximum. The ellipticity also shows the typical behavior of lossy samples with small $\omega\tau_{\text{eff}}$. Figure 5 may be compared with curves given by Furdyna and Brodwin[16] for various scattering mechanisms represented by a relaxation time $\tau \propto E^p$. Their curves are for $\omega\langle\tau\rangle = 0.55$ and $l=3.9$, and have the qualitative features of the purer sample of Fig. 5.

Since the Faraday ellipticity is particularly sensitive to the nature of the scattering mechanism,[16] experimental measurement of this quantity as a function of magnetic field in the microwave region can, in principle, give useful information. Unfortunately, the theoretical expressions are quite complicated, and the only way information can be obtained from the results is to make a detailed comparison between theory and experiment. The three theoretical parameters R, η, and a

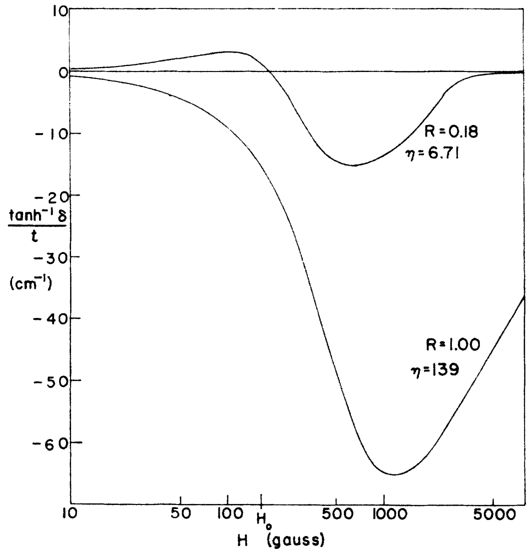

FIG. 5. Faraday ellipticity as a function of magnetic field H for mixed polar and impurity scattering (3rd-order variational approximation) at $z=3.77$ with parameters as shown. H_0 is the cyclotron resonance field $mc\omega/|e|$.

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[16] J. K. Furdyna and M. E. Brodwin, Phys. Rev. 124, 740 (1961).

are functions of carrier or impurity concentration, as well as the effective mass of the carriers and the dielectric constants ϵ_s and ϵ_∞. Thus it seems little information can be obtained by this method unless quite a lot is already known about the material.

The calculations presented here were made for values of the parameters corresponding to two particular samples of *n*-InSb. However, if computing facilities are available, it is not difficult to repeat them for other values of R, η, and a. The experiment can provide a valuable check on hypotheses as to the nature of the scattering mechanisms in a material, especially if the relevant parameters are known or can be estimated, for then detailed calculations can be made and compared with the experimental results. Good agreement would be a positive confirmation of the hypothesis. It would also be possible to determine the values of the parameters by calculating a family of curves, and choosing the one which gives the best agreement. If the hypothetical scattering mechanisms are polar optical and impurity scattering, the theory presented in Sec. 4 is directly applicable. The most suitable materials at the present time seem to be the III-V compounds, such as *n*-InSb or *n*-GaAs, for in many of these materials these two scattering mechanisms are thought to dominate between 77°K and room temperature.

6. CONCLUSIONS

It is well known that the variational principle has an appealing physical meaning for $M=\Omega=0$, in that it maximizes the entropy production, and also that it has the practical advantage of maximizing the conductivity. Variational principles for the cases when M or Ω are present have been devised by several authors, and some of these methods are, in principle, extremal. However, Bailyn's method[7] in the end gives the same results as the simpler principle, Eq. (2.8), unless care is taken that the various stages of the calculation converge independently. This requirement of independent convergence of the "internal" calculations may amount to a considerable complication in practice. Blount's method[6] includes Bailyn's as a special case, and it is also possible to derive the equations (2.11), used in this paper, from Blount's variational principle. This argument shows that for a given set of N trial functions, Eqs. (2.11) maximize the expression for the conductivity, but it does not guarantee monotonic convergence to the exact value as N is increased. Since a principle which maximizes the conductivity at all frequencies and magnetic fields is inconsistent with the sum rule Eq. (2.13) this is probably the best one can do.

More difficult and important in practice is the choice of suitable trial functions. In the present calculation, a power-series expansion in the carrier energy gives good convergence at low and high temperatures, but the convergence is slower at intermediate temperatures,[3] say $1<z<5$. The use of Sonine polynomials makes the matrices M and Ω diagonal, but it gives the same results as simple powers. In the theory of metals an expansion in powers of $(E-\zeta)$, where ζ is the Fermi energy, seems to give good convergence, and in anisotropic materials expansions in spherical harmonics suggest themselves. But the general problem of choosing the "best" trial functions would be well worth further study.

Measurements of the microwave Faraday ellipticity as a function of magnetic field can give useful information on the scattering mechanisms in the material, if supported by theoretical calculations. The theory presented in this paper is directly applicable to materials in which the dominant mechanisms are polar optical and impurity scattering, and it is suggested that measurements on the III-V compounds would be interesting.

ACKNOWLEDGMENTS

The numerical calculations were performed using the IBM 7094-1401 data processing system of the University of Illinois (partially supported by Grant No. NSFGP700 from the National Science Foundation). We wish to acknowledge the help of the staff of the Digital Computer Laboratory. We are grateful to Dr. R. F. Tucker and Dr. H. K. Rockstad for their helpful criticism of the manuscript.

APPENDIX

It was asserted in Sec. 2 that the sum rule Eq. (2.13) satisfied by the exact conductivity components is also satisfied by the Nth-order variational approximation. This will now be proved starting from the expression (3.8) for $\sigma^{(N)}(\omega)$:

$$\sigma^{(N)}=\mathcal{E}^{-2}\sum_{rs=0}^{N} X_r(L+\Omega)_{rs}^{-1}X_s. \tag{A1}$$

This expression was obtained using the trial functions (3.2) and assuming either isotropy or cubic symmetry with H along a threefold or fourfold axis. In Eq. (3.2) it is convenient here to replace $(\mathbf{k}\cdot\mathbf{u})$ by $(\mathbf{v}\cdot\mathbf{u})$, but the $\psi_r(E)$ will be left unspecified. We then find

$$(1/i\omega)\Omega_{rs}=K_{rs}, \tag{A2}$$

where

$$K_{rs}=-\int(\mathbf{v}\cdot\mathbf{u})^2\psi_r(E)\psi_s(E)(\partial f_0/\partial E)d\mathbf{k}. \tag{A3}$$

If the trial functions are chosen so that $\psi_0(E)=1$, then

$$X_r=e\mathcal{E}K_{r0}. \tag{A4}$$

Substituting in (A1), one finds

$$\sigma^{(N)}=e^2[K\{L+i\omega K\}^{-1}K]_{00}. \tag{A5}$$

Both L and K are Hermitian and positive definite. This property of K follows because we know that its eigenvalues are all real and positive; for an isotropic parabolic band the eigenfunctions of K are Sonine polynomials and the eigenvalues are $n\gamma_r/m^*$, with γ_r given by Eq. (3.13).

In the limit $\omega\rightarrow\infty$,

$$\sigma^{(N)}\rightarrow -i(e^2/\omega)K_{00}. \qquad \text{(A6)}$$

The meaning of K_{00} can be found by considering the dc conductivity under a scattering mechanism represented by a constant relaxation time. Under these conditions, from Eq. (3.22),

$$\sigma_0=e^2\tau K_{00}. \qquad \text{(A7)}$$

Hence

$$K_{00}=n/m^*, \qquad \text{(A8)}$$

where m^* is the effective mass determining the conductivity. A general expression for m^* is obtained by comparing Eqs. (A8) and (A3).

The poles of $\sigma^{(N)}$, regarded as a function of the complex variable ω, are the zeros of the determinant $|L+i\omega K|$, as all the matrix elements of L and K are finite. Consider the equation

$$|L-\lambda K|=0. \qquad \text{(A9)}$$

Because L and K are Hermitian and positive definite it follows that all the roots λ are real and positive. The poles of Eq. (A5) are then given by Eq. (A9) with $\lambda=-i\omega$. Hence $\sigma^{(N)}$ is analytic in the lower half of the ω plane, like the exact solution σ. By integration round an infinite semicircular contour closed round the lower half plane, using Eqs. (A6) and (A8), the sum rule (2.13) is obtained.

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Intrinsic and Extrinsic Recombination Radiation from Natural and Synthetic Aluminum-Doped Diamond

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The edge-recombination-radiation spectrum from natural semiconducting diamond has been re-examined and compared with spectra obtained for the first time from aluminum and nominally boron-doped General Electric synthetic diamond. The intrinsic components are due to the phonon-assisted decay of free indirect excitons of internal binding energy $\sim$0.08 eV. Comparison of the phonon energies with recently obtained dispersion curves for the fundamental lattice vibrations shows that the conduction-band minima are located at points $\frac{3}{4}$ of the way from the center to the $\langle 100\rangle$ boundaries of the reduced zone. Substructure has been observed in the intrinsic components due to the $\sim$7-meV spin-orbit splitting in the valence-band energy states at the zone center. The major extrinsic components are due to the zero-phonon and phonon-assisted decay of excitons bound to a characteristic acceptor center of semiconducting diamond ($E_A=0.36$ eV). The bound excitons have a thermal and optical ionization energy of $\sim$50 meV. These extrinsic components exhibit enhanced spin-orbit splitting ($\sim$12 meV). Radiation due to the zero-phonon and phonon-assisted recombination of free electrons at the neutral acceptor center has been detected. Infrared absorption measurements, neutron-activation analysis, and electrical-transport (Hall-effect) measurements have also been made. Intercomparison of these results and the edge-emission data shows that the acceptor center is due to isolated substitutional aluminum impurities. These acceptor centers are considerably more abundant in the synthetic diamonds, but the degree of compensation is generally much higher than in the available natural semiconducting specimens. Nitrogen donors with very deep energy levels apparently play a major role in the compensation.

I. INTRODUCTION

RECOMBINATION radiation of quantum energy close to the indirect energy gap, $E_g=5.5$ eV, of natural semiconducting diamond (type IIb)[1] has already been discussed.[2] Comparisons of results obtained from the latest edge-emission spectra with the lattice-vibrational dispersion curves recently measured by the inelastic scattering of slow neutrons[3] shows that the previous interpretation must be revised. The present paper shows that a very satisfactory description of the indirect gap transitions is obtained using the new lattice-dispersion data. The diamond spectra prove to be remarkably similar to the well-known recombination-radiation spectra of silicon,[4] the main differences arising from the very small spin-orbit valence-band splitting and the more compact wave functions for the electronic complexes in diamond.

In the previous work, edge emission from insulating General Electric synthetic diamonds was looked for

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