Effect of Correlation on the High-Frequency Conductivity of an Electron Gas

P. A. WOLFF

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 12 July 1963)

The equation of motion method is used to study the high-frequency conductivity of a single-component plasma in which carriers have a nonquadratic energy-momentum relation. In such a medium current is not conserved in electron-electron collisions, and there are important correlation corrections to the conductivity. The expression for the correction involves the perturbed correlation function in the plasma, and explicitly shows that the correction vanishes in the case of a quadratic energy-momentum relation. Evaluation of the correlation function is only possible if the electron-electron interaction is weak. An approximate calculation is made in this limit, which yields a formula for the conductivity that is correct to second order in the electron-electron interaction.

INTRODUCTION

RECENTLY, a number of theoretical papers[1] have dealt with the question of correlation corrections to the high-frequency conductivity of a plasma. This work has concerned itself with multicomponent plasmas in which the constituent particles satisfy an energy-momentum relation of the form $E(\mathbf{k})=k^2/2m$.[2] It is well known, of course, that in a *single*-component plasma with such an energy-momentum relation, the conductivity is unaffected by correlation. This result follows from the fact that, in such a medium, the particle current is proportional to the momentum, and therefore is conserved in particle-particle collisions. In most metallic and semiconducting plasmas, however, the energy-momentum relationship is not of the free particle form, and this argument is inapplicable. Hence, it is of considerable interest to study correlation corrections in a single-component plasma whose constituents do not obey a quadratic dispersion relation. Such an investigation is the aim of this paper.

In previous treatments[1] of the conductivity of quantum-mechanical plasmas, calculations have been carried out with many-body perturbation theory using diagrammatic techniques. We wish to attack the problem somewhat differently, using the equation of motion method[3] which is a simplified version of the Martin-Schwinger[4] Green's function formalism. This method, though not a completely general one, is entirely adequate for the present purpose, and has the advantage of closely paralleling the technique that is used in classical plasma problems. As in the classical case, the basic approximation is the factorization of higher order correlation functions into products of lower order ones. Such a procedure is valid when the average interaction energy

of particles in the plasma is small compared to their kinetic energy.

Though the basic ideas of the equation of motion method are quite simple, its application involves a good deal of algebra. The equations are lengthy, and the final formula for the conductivity is very complicated. To date, no attempt has been made to apply it to a physically interesting situation, but it is hoped that it will ultimately prove useful in studying the properties of real metals.

THE TOTAL CURRENT

In the following we are concerned with a many-body system described by the Hamiltonian

$$H_0=\sum_{\mathbf{k}} \left[E(\mathbf{k})a_{\mathbf{k}}^*a_{\mathbf{k}}\right]$$
$$+\tfrac{1}{2}\sum_{\mathbf{k}\mathbf{k}';\,\mathbf{q}}{}' \left[a_{\mathbf{k}+\mathbf{q}}{}^* a_{\mathbf{k}'-\mathbf{q}}{}^* \left(\frac{4\pi e^2}{q^2}\right)a_{\mathbf{k}'}a_{\mathbf{k}} \right], \quad (1)$$

in which $a_{\mathbf{k}}^*$ and $a_{\mathbf{k}}$ are the usual creation and annihilation operators, for states of wave vector $\mathbf{k}$, that satisfy the anticommutation relation

$$[a_{\mathbf{k}}^*,a_{\mathbf{k}'}]_+=\delta(\mathbf{k}-\mathbf{k}'). \quad (2)$$

The prime on the summation in Eq. (1) indicates that terms with $\mathbf{q}=0$ are to be omitted, since we presume the plasma neutralized by a uniform fixed background of positive charge. $E(\mathbf{k})$, the single-particle energy function, is left arbitrary, though we are particularly interested in the case in which it is not of the free particle form. Equation (1) is a single-band version of the sort of Hamiltonian that is commonly used to describe Bloch electrons. Actually, in many cases, the interband matrix elements that are omitted from it may be absorbed into a background dielectric constant, or the definition of the energy function. This will often be true for semiconductors or semimetals, and for them this Hamiltonian is fairly accurate. In good metals it is less correct, but does contain the essential features that we wish to investigate.

Let us now imagine that the system described by Eq. (1) is perturbed by the application of a weak,

---

[1] J. Dawson and C. Oberman, Phys. Fluids **5**, 517 (1962); C. Oberman, A. Ron, and J. Dawson, Phys. Fluids **5**, 1514 (1962); V. I. Perel and G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. **41**, 886 (1961) [translation: Soviet Phys.—JETP **14**, 633 (1962)]; D. F. DuBois, V. Gilinsky, and M. G. Kivelson, Phys. Rev. **129**, 2376 (1963); A. Ron and N. Tzoar, Phys. Rev. (to be published).

[2] We set $\hbar=1$ throughout this paper.

[3] David Pines, *The Many-Body Problem* (W. A. Benjamin Company, New York, 1961).

[4] P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).

uniform, time-varying field whose coupling to it is described by the interaction

$$H_1 = -\left(\frac{1}{c}\right)\int \mathbf{J}(\mathbf{r})\cdot\mathbf{A}(\mathbf{r},t)d^3r$$

$$\simeq -\frac{e}{c}\sum_{\mathbf{k}}\left[a_{\mathbf{k}}^*a_{\mathbf{k}}\mathbf{v}(\mathbf{k})\cdot\mathbf{A}e^{-i(\omega+i\epsilon)t}\right]. \qquad (3)$$

In this expression $\mathbf{A}$ is the vector potential of the external field, and $\mathbf{v}(\mathbf{k})=\nabla_{\mathbf{k}}E(\mathbf{k})$ the velocity of an electron in state $\mathbf{k}$. Quadratic terms in $\mathbf{A}$ are omitted from Eq. (3) since, to obtain the conductivity, we need only compute the induced current to first order in the field. For the system we are considering, the ith component of the current operator is

$$J_i = e\sum_{\mathbf{k}}\left[v_i\left(\mathbf{k}-\frac{e}{c}\mathbf{A}\right)a_{\mathbf{k}}^*a_{\mathbf{k}}\right], \qquad (4)$$

where

$$v_i(\mathbf{k}) = \frac{\partial E(\mathbf{k})}{\partial k_i}. \qquad (5)$$

Since $\mathbf{A}$ is assumed small this expression may be approximated as follows:

$$J_i \simeq e\sum_{\mathbf{k}}\left\{\left[v_i(\mathbf{k})-\frac{e}{c}\sum_{j}\left(\frac{\partial^2E}{\partial k_i\partial k_j}A_j\right)\right]a_{\mathbf{k}}^*a_{\mathbf{k}}\right\}$$

$$\equiv J_i^{(1)}+J_i^{(2)}. \qquad (6)$$

If the energy-momentum relation were quadratic $(E=k^2/2m)$ the second term in this formula would take the form

$$-\frac{e}{mc}A_i\sum_{\mathbf{k}}\left[n(\mathbf{k})\right] = -\frac{eNA_i}{mc}, \qquad (7)$$

where $n(\mathbf{k})=a_{\mathbf{k}}^*a_{\mathbf{k}}$ is the number operator and N the total number of particles in the system. We see presently [Eq. (19)] that, in the case of a quadratic energy-momentum relation, $\mathbf{J}^{(1)}$ vanishes. Thus, we may immediately calculate the conductivity of such a system from Eq. (7). The result is the familar expression (in which n is the particle density) for the high-frequency conductivity of an electron gas;

$$\sigma = ne^2/im\omega. \qquad (8)$$

In the more general case of a nonquadratic energy function the corresponding contribution to σ arising from the $\mathbf{J}^{(2)}$ term in Eq. (6) (which may now be a tensor) is

$$\sigma_{ij}^{(2)} = \frac{e^2}{i\omega}\sum_{\mathbf{k}}\left[\frac{\langle n(\mathbf{k})\rangle}{\Omega}\frac{\partial^2E(k)}{\partial k_i\partial k_j}\right]. \qquad (9)$$

In this relation Ω is the volume of the system and $\langle n(\mathbf{k})\rangle = \mathrm{tr}[\rho n(\mathbf{k})]$, where ρ is the density matrix for the interacting, but unperturbed, plasma. For our purposes,

the crucial feature of this formula is the fact that it has exactly the same frequency dependence as the conductivity [Eq. (8)] of a gas of particles with a quadratic energy-momentum relation. Thus, though some correlation effects are contained in Eq. (9), they are not of great interest and we make no attempt to further evaluate this formula.

The important correlation corrections to σ arise from the expectation value, with respect to the perturbed density matrix, of the first term, $\mathbf{J}^{(1)}$, in the current operator. These have a different frequency dependence from that of Eqs. (8) and (9) and are complex, rather than purely imaginary, indicating that here correlation introduces dissipative processes into the conductivity. We now turn to this aspect of the calculation, which is the principal problem of the paper.

FORMULA FOR $\langle\mathbf{J}^{(1)}\rangle$

In this section the quantity we wish to evaluate is

$$\langle\mathbf{J}^{(1)}\rangle = e\sum_{\mathbf{k}}\left[\mathbf{v}(\mathbf{k})\langle a_{\mathbf{k}}^*a_{\mathbf{k}}\rangle\right], \qquad (10)$$

which contains the expectation value of the operator $a_{\mathbf{k}}^*a_{\mathbf{k}}$ calculated with respect to the *perturbed* density matrix of the many-body system. If one assumes the density matrix expanded in powers of $\mathbf{A}$ one may write

$$\rho \simeq \rho_0+\rho_1+\cdots \qquad (11)$$

and

$$\langle a_{\mathbf{k}}^*a_{\mathbf{k}}\rangle \simeq \mathrm{tr}(\rho_0 a_{\mathbf{k}}^*a_{\mathbf{k}})+\mathrm{tr}(\rho_1 a_{\mathbf{k}}^*a_{\mathbf{k}})$$

$$\equiv \langle a_{\mathbf{k}}^*a_{\mathbf{k}}\rangle_0+\langle a_{\mathbf{k}}^*a_{\mathbf{k}}\rangle_1. \qquad (12)$$

Only the second term of Eq. (12) contributes to the current, so one obtains the following expression for $\langle\mathbf{J}^{(1)}\rangle$:

$$\langle\mathbf{J}^{(1)}\rangle = e\sum_{\mathbf{k}}\left[\mathbf{v}(\mathbf{k})\langle a_{\mathbf{k}}^*a_{\mathbf{k}}\rangle_1\right]. \qquad (13)$$

We use the equation of motion method—which here must be extended to second order in the electron-electron interaction—to evaluate $\langle a_{\mathbf{k}}^*a_{\mathbf{k}}\rangle_1$. The resulting formalism is somewhat similar to that discussed by Suhl and Werthamer[5] in connection with the second-order random-phase approximation. To begin, we consider the equation of motion—in the Heisenberg representation—of the number operator $a_{\mathbf{k}}^*a_{\mathbf{k}}$. Its time derivative is determined, in the usual way, by the commutator with the Hamiltonian:

$$i\frac{\partial}{\partial t}(a_{\mathbf{k}}^*a_{\mathbf{k}}) = [a_{\mathbf{k}}^*a_{\mathbf{k}}, H_0+H_1]$$

$$= \sum_{\mathbf{k}';\mathbf{q}}'\left\{a_{\mathbf{k}}^*a_{\mathbf{k}'-\mathbf{q}}^*\left(\frac{4\pi e^2}{q^2}\right)a_{\mathbf{k}'}a_{\mathbf{k}-\mathbf{q}}\right\}$$

$$-\sum_{\mathbf{k}';\mathbf{q}}'\left\{a_{\mathbf{k}+\mathbf{q}}^*a_{\mathbf{k}'-\mathbf{q}}^*\left(\frac{4\pi e^2}{q^2}\right)a_{\mathbf{k}'}a_{\mathbf{k}}\right\}. \qquad (14)$$

[5] H. Suhl and N. R. Werthamer, Phys. Rev. **122**, 359 (1961).

Here it is important to notice that the equation does *not* explicitly contain the perturbation $\mathbf{A}$. Thus, the occupation numbers $a_\mathbf{k}^*a_\mathbf{k}$ are not directly altered by the field, but only in an indirect way through its effect on the operators $a_\mathbf{k}^*a_{\mathbf{k}'-\mathbf{q}}^*a_{\mathbf{k}'}a_{\mathbf{k}-\mathbf{q}}$ and $a_{\mathbf{k}+\mathbf{q}}^*a_{\mathbf{k}'-\mathbf{q}}^*a_{\mathbf{k}'}a_\mathbf{k}$, which describe pair correlation in the plasma. By taking the trace of Eq. (14) with the first-order correction ρ_1 to the density matrix, we may now obtain an expression for the average that appears in Eq. (13). Since the perturbation is harmonic in time, all first-order expectation values vary as $e^{-i(\omega+i\epsilon)t}$. Thus, one finds

$$i\frac{\partial}{\partial t}\langle a_\mathbf{k}^*a_\mathbf{k}\rangle_1 = (\omega+i\epsilon)\langle a_\mathbf{k}^*a_\mathbf{k}\rangle_1$$

$$= \sum_{\mathbf{k}';\mathbf{q}}' \left\{\left(\frac{4\pi e^2}{q^2}\right)[\langle a_\mathbf{k}^*a_{\mathbf{k}'-\mathbf{q}}^*a_{\mathbf{k}'}a_{\mathbf{k}-\mathbf{q}}\rangle_1 \right.$$
$$\left. - \langle a_{\mathbf{k}+\mathbf{q}}^*a_{\mathbf{k}'-\mathbf{q}}^*a_{\mathbf{k}'}a_\mathbf{k}\rangle_1]\right\} . \quad (15)$$

When substituted into Eq. (13), this expression yields the result

$$\langle \mathbf{J}^{(1)}\rangle = \left(-\frac{e}{\omega}\right)\sum_{\mathbf{k},\mathbf{k}';\mathbf{q}}' \left\{\left(\frac{4\pi e^2}{q^2}\right)[\mathbf{v}(\mathbf{k})-\mathbf{v}(\mathbf{k}+\mathbf{q})]\right.$$
$$\left. \times\langle a_{\mathbf{k}+\mathbf{q}}^*a_{\mathbf{k}'-\mathbf{q}}^*a_{\mathbf{k}'}a_\mathbf{k}\rangle_1\right\} , \quad (16)$$

which may be summetrized in $\mathbf{k}$ and $\mathbf{k}'$ with the aid of the commutation relation, which implies that

$$a_{\mathbf{k}+\mathbf{q}}^*a_{\mathbf{k}'-\mathbf{q}}^*a_{\mathbf{k}'}a_\mathbf{k} = a_{\mathbf{k}'-\mathbf{q}}^*a_{\mathbf{k}+\mathbf{q}}^*a_\mathbf{k}a_{\mathbf{k}'} , \quad (17)$$

and

$$\langle a_{\mathbf{k}+\mathbf{q}}^*a_{\mathbf{k}'-\mathbf{q}}^*a_{\mathbf{k}'}a_\mathbf{k}\rangle_1 = \langle a_{\mathbf{k}+\mathbf{q}}^*a_\mathbf{k}a_{\mathbf{k}'-\mathbf{q}}^*a_{\mathbf{k}'}\rangle_1$$
$$+ \langle n(\mathbf{k}+\mathbf{q})\rangle_1\delta(\mathbf{k}+\mathbf{q}-\mathbf{k}') . \quad (18)$$

The final form is

$$\langle \mathbf{J}^{(1)}\rangle = \left(-\frac{e}{2\omega}\right)\sum_{\mathbf{k},\mathbf{k}';\mathbf{q}}' \left\{\left(\frac{4\pi e^2}{q^2}\right)\langle a_{\mathbf{k}+\mathbf{q}}^*a_\mathbf{k}a_{\mathbf{k}'-\mathbf{q}}^*a_{\mathbf{k}'}\rangle_1 \right.$$
$$\left. \times[\mathbf{v}(\mathbf{k})+\mathbf{v}(\mathbf{k}')-\mathbf{v}(\mathbf{k}+\mathbf{q})-\mathbf{v}(\mathbf{k}'-\mathbf{q})]\right\} . \quad (19)$$

The second term of Eq. (18) does not contribute to this formula since the velocity term vanishes when $\mathbf{k}'=\mathbf{k}+\mathbf{q}$.

Equation (19) is an exact expression for $\langle\mathbf{J}^{(1)}\rangle$. Its form shows immediately that there is no correlation correction if $E(k)=k^2/2m$ for, under these circumstances, the factor $[\mathbf{v}(\mathbf{k})+\mathbf{v}(\mathbf{k}')-\mathbf{v}(\mathbf{k}+\mathbf{q})-\mathbf{v}(\mathbf{k}'-\mathbf{q})]$ is zero. To use it to determine the conductivity, one must approximately evaluate the perturbed correlation function $\langle a_{\mathbf{k}+\mathbf{q}}^*a_{\mathbf{k}'-\mathbf{q}}^*a_{\mathbf{k}'}a_\mathbf{k}\rangle_1$. We consider this question in the next section.

CALCULATION OF THE PERTURBED CORRELATION FUNCTION

To evaluate the function $\langle a_{\mathbf{k}+\mathbf{q}}^*a_\mathbf{k}a_{\mathbf{k}'-\mathbf{q}}^*a_{\mathbf{k}'}\rangle_1$, it is convenient to consider the equation of motion of the operator $a_{\mathbf{k}+\mathbf{q}}^*(0)a_\mathbf{k}(0)a_{\mathbf{k}'-\mathbf{q}}^*(t)a_{\mathbf{k}'}(t)$ whose average value is the two-particle *autocorrelation* function. The advantage of this procedure is that the perturbed autocorrelation function obeys, at least in the random-phase approximation, a quite simple integral equation, whereas that which determines $\langle a_{\mathbf{k}+\mathbf{q}}^*a_\mathbf{k}a_{\mathbf{k}'-\mathbf{q}}^*a_{\mathbf{k}'}\rangle_1$ is very involved. Of course, one must always pay a price for such a simplification. In this case, it is that the perturbed autocorrelation function is given in terms of the corresponding unperturbed function which must then, itself, be calculated. Thus, there are a number of steps in the analysis, but no one of them is particularly difficult.

A straightforward computation shows that the equation of motion of the operator $a_{\mathbf{k}+\mathbf{q}}^*(0)a_\mathbf{k}(0)a_{\mathbf{k}'-\mathbf{q}}^*(t)a_{\mathbf{k}'}(t)$ is

$$i\frac{\partial}{\partial t}[a_{\mathbf{k}+\mathbf{q}}^*(0)a_\mathbf{k}(0)a_{\mathbf{k}'-\mathbf{q}}^*(t)a_{\mathbf{k}'}(t)] = a_{\mathbf{k}+\mathbf{q}}^*(0)a_\mathbf{k}(0)[a_{\mathbf{k}'-\mathbf{q}}^*(t)a_{\mathbf{k}'}(t),H]$$

$$= [E(\mathbf{k}')-E(\mathbf{k}'-\mathbf{q})][a_{\mathbf{k}+\mathbf{q}}^*(0)a_\mathbf{k}(0)a_{\mathbf{k}'-\mathbf{q}}^*(t)a_{\mathbf{k}'}(t)]$$

$$+ \sum_{\mathbf{l}';\mathbf{q}'}' \left\{a_{\mathbf{k}+\mathbf{q}}^*(0)a_\mathbf{k}(0)a_{\mathbf{k}'-\mathbf{q}}^*(t)a_{\mathbf{l}'-\mathbf{q}'}^*(t)\left(\frac{4\pi e^2}{q'^2}\right)a_{\mathbf{l}'}(t)a_{\mathbf{k}'-\mathbf{q}'}(t)\right\}$$

$$- \sum_{\mathbf{l}';\mathbf{q}'}' \left\{a_{\mathbf{k}+\mathbf{q}}^*(0)a_\mathbf{k}(0)a_{\mathbf{k}'-\mathbf{q}+\mathbf{q}'}^*(t)a_{\mathbf{l}'-\mathbf{q}'}^*(t)\left(\frac{4\pi e^2}{q'^2}\right)a_{\mathbf{l}'}(t)a_{\mathbf{k}'}(t)\right\}$$

$$- \frac{e}{c}[\mathbf{v}(\mathbf{k}')-\mathbf{v}(\mathbf{k}'-\mathbf{q})]\cdot\mathbf{A}e^{-i(\omega+i\epsilon)t}[a_{\mathbf{k}+\mathbf{q}}^*(0)a_\mathbf{k}(0)a_{\mathbf{k}'-\mathbf{q}}^*(t)a_{\mathbf{k}'}(t)] . \quad (20)$$

This is a very complicated equation which, through the Coulomb interaction, couples two- and three-particle operators. To make any progress in solving it one must somehow approximate the latter by simpler functions.

The usual procedure is to replace three-particle correlations by suitable products of one- and two-particle correlation functions. Such an approximation is valid when the plasma is weakly coupled, in the sense that

the average potential energy of a pair of electrons in it is small compared to their kinetic energy. Henceforth we assume that this is the case. We also retain only those terms in the linearization which arise from *direct* Coulomb interactions—that is, terms from the summations in Eq. (20) that contain a factor $\delta(\mathbf{q}-\mathbf{q}')$. These introduce a factor $(4\pi e^2/q^2)^2$ into Eq. (16) that is highly divergent in the limit $q \rightarrow 0$. Thus, such terms can be large even if the electron-electron interaction is very weak, and they must be retained if one is to obtain sensible results from a plasma calculation. Keeping them is equivalent to summing, in the sense discussed by Gell-Mann and Brueckner,[6] the most divergent terms in perturbation theory. Other terms (representing exchange effects) which result from the linearization of Eq. (20), do *not* lead to this difficulty in lowest order and can be omitted. Thus, our basic approximation is to replace the average of the three-particle operator by the following expression:

$$\langle a_{\mathbf{k}+\mathbf{q}}{}^*(0)a_{\mathbf{k}}(0)a_{\mathbf{k}'-\mathbf{q}}{}^*(t)a_{\mathbf{l}'-\mathbf{q}'}{}^*(t)a_{\mathbf{l}'}(t)a_{\mathbf{k}'-\mathbf{q}'}(t)\rangle$$
$$\simeq \langle a_{\mathbf{k}+\mathbf{q}}{}^*(0)a_{\mathbf{k}}(0)a_{\mathbf{l}'-\mathbf{q}}{}^*(t)a_{\mathbf{l}'}(t)\rangle$$
$$\times \langle a_{\mathbf{k}'-\mathbf{q}}{}^*a_{\mathbf{k}'-\mathbf{q}}\rangle\delta(\mathbf{q}-\mathbf{q}'). \quad (21)$$

It should be realized that this factorization represents a very drastic simplification of Eq. (20) which, however, is equivalent to that made in the well-known random phase approximation.[3] The terms of first order in $\mathbf{A}$ that appear in Eq. (21) are then

$$\langle a_{\mathbf{k}+\mathbf{q}}{}^*(0)a_{\mathbf{k}}(0)a_{\mathbf{l}'-\mathbf{q}}{}^*(t)a_{\mathbf{l}'}(t)\rangle_1\langle a_{\mathbf{k}'-\mathbf{q}}{}^*a_{\mathbf{k}'-\mathbf{q}}\rangle_0\delta(\mathbf{q}-\mathbf{q}')$$
$$+\langle a_{\mathbf{k}+\mathbf{q}}{}^*(0)a_{\mathbf{k}}(0)a_{\mathbf{l}'-\mathbf{q}}{}^*(t)a_{\mathbf{l}'}(t)\rangle_0$$
$$\times \langle a_{\mathbf{k}'-\mathbf{q}}{}^*a_{\mathbf{k}'-\mathbf{q}}\rangle_1\delta(\mathbf{q}-\mathbf{q}'). \quad (22)$$

We have seen earlier, however, that the operator $a_{\mathbf{k}'-\mathbf{q}}{}^*a_{\mathbf{k}'-\mathbf{q}}$ is only indirectly affected by the perturbation. As a consequence, the second term of Eq. (22) is of higher order in the electron-electron interaction than the first, and may be omitted.

We now multiply Eq. (20) by the density matrix, take its trace, and collect terms of first order in $\mathbf{A}$. After making the approximations outlined above we obtain a relatively tractable equation for the perturbation of the two-particle autocorrelation function. It is

$$\left[i\frac{\partial}{\partial t}+E(\mathbf{k}'-\mathbf{q})-E(\mathbf{k}')\right]F_1(\mathbf{k},\mathbf{k}';t)$$

$$=[n(\mathbf{k}'-\mathbf{q})-n(\mathbf{k}')]\left(\frac{4\pi e^2}{q^2}\right)\sum_{\mathbf{l}'}[F_1(\mathbf{k},\mathbf{l}';t)]$$

$$-\frac{e}{c}[\mathbf{v}(\mathbf{k}')-\mathbf{v}(\mathbf{k}'-\mathbf{q})]\cdot\mathbf{A}e^{-i(\omega+i\epsilon)t}F_0(\mathbf{k},\mathbf{k}';t), \quad (23)$$

───────────
[6] M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).

where

$$F_0(\mathbf{k},\mathbf{k}';t)=\langle a_{\mathbf{k}+\mathbf{q}}{}^*(0)a_{\mathbf{k}}(0)a_{\mathbf{k}'-\mathbf{q}}{}^*(t)a_{\mathbf{k}'}(t)\rangle_0, \quad (24)$$

$$F_1(\mathbf{k},\mathbf{k}';t)=\langle a_{\mathbf{k}+\mathbf{q}}{}^*(0)a_{\mathbf{k}}(0)a_{\mathbf{k}'-\mathbf{q}}{}^*(t)a_{\mathbf{k}'}(t)\rangle_1, \quad (25)$$

and

$$n(\mathbf{k})=\langle a_{\mathbf{k}}{}^*a_{\mathbf{k}}\rangle_0. \quad (26)$$

Here F_0 is the unperturbed autocorrelation function, and F_1 its change due to the field. Equation (23) is simplified by removing the $e^{-i(\omega+i\epsilon)t}$ time dependence through the substitution

$$F_1(\mathbf{k},\mathbf{k}';t)=e^{-i(\omega+i\epsilon)t}T(\mathbf{k},\mathbf{k}';t), \quad (27)$$

and by Fourier transformation. The transforms,

$$T(\mathbf{k},\mathbf{k}';x)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{ixt}T(\mathbf{k},\mathbf{k}';t)dt,$$
$$\quad (28)$$
$$F_0(\mathbf{k},\mathbf{k}';x)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{ixt}F_0(\mathbf{k},\mathbf{k}';t)dt,$$

obey a simple integral equation

$$[x+\omega+i\epsilon+E(\mathbf{k}'-\mathbf{q})-E(\mathbf{k}')]T(\mathbf{k},\mathbf{k}';x)$$

$$-\left(\frac{4\pi e^2}{q^2}\right)[n(\mathbf{k}'-\mathbf{q})-n(\mathbf{k}')]\sum_{\mathbf{l}'}[T(\mathbf{k},\mathbf{l}';x)]$$

$$=-\frac{e}{c}[\mathbf{v}(\mathbf{k}')-\mathbf{v}(\mathbf{k}'-\mathbf{q})]$$
$$\cdot\mathbf{A}F_0(\mathbf{k},\mathbf{k}';x)\equiv S(\mathbf{k},\mathbf{k}';x), \quad (29)$$

which has the solution

$$T(\mathbf{k},\mathbf{k}';x)=\left\{\frac{1}{x+\omega+i\epsilon+E(\mathbf{k}'-\mathbf{q})-E(\mathbf{k}')}\right\}$$

$$\times\left\{S(\mathbf{k},\mathbf{k}';x)+\left(\frac{4\pi e^2}{q^2}\right)\left[\frac{n(\mathbf{k}'-\mathbf{q})-n(\mathbf{k}')}{\mathfrak{D}(x+\omega+i\epsilon)}\right]\right.$$

$$\left.\times\sum_{\mathbf{l}'}\left[\frac{S(\mathbf{k},\mathbf{l}';x)}{x+\omega+i\epsilon+E(\mathbf{l}'-\mathbf{q})-E(\mathbf{l}')}\right]\right\}, \quad (30)$$

where

$$\mathfrak{D}(z)=1+\left(\frac{4\pi e^2}{q^2}\right)\mathcal{L}_0(z), \quad (31)$$

and

$$\mathcal{L}_0(z)=\sum_{\mathbf{l}'}\left[\frac{n(\mathbf{l}')-n(\mathbf{l}'-\mathbf{q})}{z+E(\mathbf{l}'-\mathbf{q})-E(\mathbf{l}')}\right]. \quad (32)$$

$\mathfrak{D}(z)$ is the usual random-phase approximation[3] expression for the wave vector and frequency dependent dielectric constant of a plasma. Equation (30) relates the change in the pair distribution function to the corresponding unperturbed function. Thus, as the final step in the calculation, we must evaluate $F_0(\mathbf{k},\mathbf{k}';x)$. This part of the problem is discussed in the next section.

CALCULATION OF THE UNPERTURBED CORRELATION FUNCTION

In this section we discuss the calculation of the function $F_0(\mathbf{k},\mathbf{k}';x)$, which determines the pair correlation in the unperturbed plasma. For this purpose it is most convenient to consider, not the correlation function itself, but the closely related Green's function defined by the equation

$$G_r(t) = -i\theta(t)\langle[a_{\mathbf{k}'-\mathbf{q}}{}^*(t)a_{\mathbf{k}'}(t),a_{\mathbf{k}+\mathbf{q}}{}^*(0)a_{\mathbf{k}}(0)]\rangle, \quad (33)$$

where

$$\begin{aligned}\theta(t) &= 1 \quad t \geq 0\\ &= 0 \quad t < 0.\end{aligned} \quad (34)$$

Equation (33) defines the retarded Green's function; there is also a corresponding expression for the advanced Green's function, $G_a(t)$, obtained by replacing $-i\theta(t)$ by $i\theta(-t)$ in Eq. (33). The advantage of working with Green's functions, rather than the correlation function, is that their value at $t=0$ is determined by the com-

mutation relations and the single-particle occupation probabilities, whereas the value of $F_0(\mathbf{k},\mathbf{k}';t)$ at $t=0$ must, itself, be calculated. Fortunately, in thermal equilibrium, there is a direct relation between the Green's functions and the corresponding correlation function. Such relations have been discussed at length by Zubarev,[7] and we may use his analysis to show that (see Appendix)

$$F_0(\mathbf{k},\mathbf{k}';x) = i\left[\frac{G_r(\mathbf{k},\mathbf{k}';x) - G_a(\mathbf{k},\mathbf{k}';x)}{(e^{\beta x}-1)}\right], \quad (35)$$

where $\beta = (\kappa T)^{-1}$, κ is Boltzmann's constant, and T the absolute temperature. The derivation of this result specifically assumes that the system in question is in thermal equilibrium. We assume that this is the case (before the perturbation $\mathbf{A}$ is applied) of the plasmas we consider.

To calculate G_r and G_a we again use the equation of motion method. One may easily show that G_r is determined by the equation

$$i\frac{\partial G_r}{\partial t} + [E(\mathbf{k}'-\mathbf{q}) - E(\mathbf{k}')]G_r = [n(\mathbf{k}) - n(\mathbf{k}-\mathbf{q})]\delta(\mathbf{k}+\mathbf{q}-\mathbf{k}')\delta(t)$$

$$- i\theta(t)\sum_{\mathbf{l}';\mathbf{q}'}{}'\left\{\left(\frac{4\pi e^2}{q'^2}\right)\langle[a_{\mathbf{k}'-\mathbf{q}}{}^*(t)a_{\mathbf{l}'-\mathbf{q}'}{}^*(t)a_{\mathbf{l}'}(t)a_{\mathbf{k}'-\mathbf{q}'}(t),a_{\mathbf{k}+\mathbf{q}}{}^*(0)a_{\mathbf{k}}(0)]\rangle\right\}$$

$$+ i\theta(t)\sum_{\mathbf{l}';\mathbf{q}'}{}'\left\{\left(\frac{4\pi e^2}{q'^2}\right)\langle[a_{\mathbf{k}'-\mathbf{q}+\mathbf{q}'}{}^*(t)a_{\mathbf{l}'-\mathbf{q}'}{}^*(t)a_{\mathbf{l}'}(t)a_{\mathbf{k}'}(t),a_{\mathbf{k}+\mathbf{q}}{}^*(0)a_{\mathbf{k}}(0)]\rangle\right\}. \quad (36)$$

This equation is exact, and correspondingly complicated. To solve it we make the same approximations as were used in deriving Eq. (23) from Eq. (20). The result is a simple integral equation for $G_r(\mathbf{k},\mathbf{k}';x)$;

$$[x+i\delta+E(\mathbf{k}'-\mathbf{q}) - E(\mathbf{k}')]G_r(\mathbf{k},\mathbf{k}';x)$$

$$-\left(\frac{4\pi e^2}{q^2}\right)[n(\mathbf{k}'-\mathbf{q}) - n(\mathbf{k}')]\sum_{\mathbf{l}}[G_r(\mathbf{k},\mathbf{l};x)] = \left[\frac{n(\mathbf{k}+\mathbf{q}) - n(\mathbf{k})}{2\pi}\right]\delta(\mathbf{k}+\mathbf{q}-\mathbf{k}'), \quad (37)$$

whose solutions is

$$G_r(\mathbf{k},\mathbf{k}';x) = \left\{\frac{1}{x+i\delta+E(\mathbf{k}'-\mathbf{q}) - E(\mathbf{k}')}\right\}$$

$$\times\left\{\frac{[n(\mathbf{k}+\mathbf{q}) - n(\mathbf{k})]\delta(\mathbf{k}+\mathbf{q}-\mathbf{k}')}{2\pi} + \left(\frac{4\pi e^2}{q^2}\right)\frac{[n(\mathbf{k}+\mathbf{q}) - n(\mathbf{k})][n(\mathbf{k}'-\mathbf{q}) - n(\mathbf{k}')]}{2\pi\mathfrak{D}(x+i\delta)[x+i\delta+E(\mathbf{k}) - E(\mathbf{k}+\mathbf{q})]}\right\}. \quad (38)$$

The advanced Green's function G_a is obtained from this equation by replacing δ by $-\delta$.

We have now calculated the two correlation functions (perturbed and unperturbed) that are needed to determine $\langle\mathbf{J}^{(1)}\rangle$. The final result is obtained by combining Eqs. (19), (29), (30), (31), and (38). After a good deal of algebra one obtains the following formula for $\langle\mathbf{J}^{(1)}\rangle$:

$$\langle\mathbf{J}^{(1)}\rangle = \left(+\frac{ie^2}{2\omega^2 c}\right)\sum_q\int_{-\infty}^{\infty}\left(\frac{4\pi e^2}{q^2}\right)^2\frac{dx}{2\pi(e^{\beta x}-1)}\left\{\frac{[\mathfrak{L}_0(x+\omega+i\epsilon) - \mathfrak{L}_0(x+i\delta)][\mathfrak{L}_2(x+\omega+i\epsilon) - \mathfrak{L}_2(x+i\delta)]\cdot\mathbf{A}}{\mathfrak{D}(x+i\delta)\mathfrak{D}(x+\omega+i\epsilon)}\right.$$

$$\left. - \frac{[\mathfrak{L}_1(x+\omega+i\epsilon) - \mathfrak{L}_1(x+i\delta)][\mathfrak{L}_1(x+\omega+i\epsilon) - \mathfrak{L}_1(x+i\delta)]\cdot\mathbf{A}}{\mathfrak{D}(x+i\delta)\mathfrak{D}(x+\omega+i\epsilon)} - \text{same terms with } \delta \leftrightarrow -\delta\right\}, \quad (39)$$

[7] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [translation: Soviet Phys.—Uspekhi **3**, 320 (1960)].

where

$$\mathfrak{L}_1 = \sum_{l'} \left\{ \frac{[\mathbf{v}(l'-\mathbf{q}) - \mathbf{v}(l')][n(l') - n(l'-\mathbf{q})]}{z + E(l'-\mathbf{q}) - E(l')} \right\}, \tag{40}$$

and $\mathfrak{L}_2$ is the tensor

$$\mathfrak{L}_2 = \sum_{l'} \left\{ \frac{[\mathbf{v}(l'-\mathbf{q}) - \mathbf{v}(l')][\mathbf{v}(l'-\mathbf{q}) - \mathbf{v}(l')][n(l') - n(l'-\mathbf{q})]}{z + E(l'-\mathbf{q}) - E(l')} \right\}. \tag{41}$$

Equation (39) is a general expression for the second-order correlation correction to the conductivity of a plasma with an arbitrary energy versus momentum relation. It may easily be shown to reduce to the result of Ron and Tzoar[1] in the case in which the function $E(k)$ consists of several pockets below the Fermi surface, in each of which the carriers satisfy an energy-momentum relation of the form $E_s(\mathbf{k}) = (\mathbf{k} - \mathbf{k}_s)^2/2m_s$. The formula also reduces to a result previously derived by the author[8] when the frequency dependence of the screening functions, $\mathfrak{D}(x+i\delta)$ and $\mathfrak{D}(x+\omega+i\epsilon)$, is ignored.

Equation (39), in general, yields a complex value for $\langle \mathbf{J}^{(1)} \rangle$, indicating that correlation produces a dissipative term in the conductivity. This dissipation arises from processes in which a pair of electrons, that are interacting with each other, absorb a photon and share its energy. Such a process is not possible, of course, for a *single* free electron, since it always violates the energy-momentum conservation laws. However, when correlation is appreciable, an electron that interacts with the field may transfer momentum to other electrons in the medium. As a consequence, the restrictions imposed by the conservation laws are greatly relaxed and it becomes possible for the plasma to absorb high-frequency radiation. The totality of such processes—which at high frequencies may also result in plasmon emission—are responsible for the dissipative part of $\mathbf{J}^{(1)}$. The Kramers-Kronig relations then require that there be a corresponding reactive correction to the current, which is contained in $\mathbf{J}^{(2)}$ and the real part of $\mathbf{J}^{(1)}$.

ACKNOWLEDGMENTS

APPENDIX

To prove Eq. (35) of the text we consider two different correlation functions;

$$F_0(\mathbf{k}, \mathbf{k}'; t) = \langle a_{\mathbf{k}+\mathbf{q}}^*(0) a_{\mathbf{k}}(0) a_{\mathbf{k}'-\mathbf{q}}^*(t) a_{\mathbf{k}'}(t) \rangle \tag{A1}$$

and

$$E_0(\mathbf{k}, \mathbf{k}'; t) = \langle a_{\mathbf{k}'-\mathbf{q}}^*(t) a_{\mathbf{k}'}(t) a_{\mathbf{k}+\mathbf{q}}^*(0) a_{\mathbf{k}}(0) \rangle. \tag{A2}$$

In an equilibrium ensemble these formulas may be

[8] P. A. Wolff, Phys. Rev. **116**, 544 (1960).

rewritten in the form

$$F_0(\mathbf{k}, \mathbf{k}'; t) = Z^{-1} \operatorname{tr}[e^{-\beta H_0} a_{\mathbf{k}+\mathbf{q}}^*(0) a_{\mathbf{k}}(0) a_{\mathbf{k}'-\mathbf{q}}^*(t) a_{\mathbf{k}'}(t)] \tag{A3}$$

and

$$E_0(\mathbf{k}, \mathbf{k}'; t) = Z^{-1} \operatorname{tr}[e^{-\beta H_0} a_{\mathbf{k}'-\mathbf{q}}^*(t) a_{\mathbf{k}'}(t) a_{\mathbf{k}+\mathbf{q}}^*(0) a_{\mathbf{k}}(0)], \tag{A4}$$

where H_0 is the Hamiltonian defined in Eq. (1) and $Z = \operatorname{tr}(e^{-\beta H_0})$. Next, we introduce a complete set of eigenfunctions of H_0 to evaluate the matrix elements that appear here. The expression for $F_0(\mathbf{k}, \mathbf{k}'; t)$ that results is

$$F_0(\mathbf{k}, \mathbf{k}'; t) = Z^{-1} \sum_{n,n'} \{ e^{-\beta E_n} \langle n | a_{\mathbf{k}+\mathbf{q}}^* a_{\mathbf{k}} | n' \rangle$$
$$\times e^{iE_{n'}t} \langle n' | a_{\mathbf{k}'-\mathbf{q}}^* a_{\mathbf{k}'} | n \rangle e^{-iE_n t} \}, \tag{A5}$$

with the Fourier transform

$$F_0(\mathbf{k}, \mathbf{k}'; x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ixt} F_0(\mathbf{k}, \mathbf{k}'; t) dt$$
$$= Z^{-1} \sum_{n,n'} \{ e^{-\beta E_n} \langle n | a_{\mathbf{k}+\mathbf{q}}^* a_{\mathbf{k}} | n' \rangle$$
$$\times \langle n' | a_{\mathbf{k}'-\mathbf{q}}^* a_{\mathbf{k}'} | n \rangle \delta(x + E_{n'} - E_n) \}. \tag{A6}$$

In a similar way one may show that

$$E_0(\mathbf{k}, \mathbf{k}'; x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ixt} E_0(\mathbf{k}, \mathbf{k}'; t) dt$$
$$= Z^{-1} \sum_{n,n'} \{ e^{-\beta E_n} \langle n | a_{\mathbf{k}'-\mathbf{q}}^* a_{\mathbf{k}'} | n' \rangle$$
$$\times \langle n' | a_{\mathbf{k}+\mathbf{q}}^* a_{\mathbf{k}} | n \rangle \delta(x + E_n - E_{n'}) \}. \tag{A7}$$

After interchanging the indices n and n', and making use of the relation between E_n and $E_{n'}$ is that required by the delta function, one finds

$$E_0(\mathbf{k}, \mathbf{k}'; x) = Z^{-1} \sum_{n,n'} \{ e^{-\beta(E_n - x)} \langle n | a_{\mathbf{k}+\mathbf{q}}^* a_{\mathbf{k}} | n' \rangle$$
$$\times \langle n' | a_{\mathbf{k}'-\mathbf{q}}^* a_{\mathbf{k}'} | n \rangle \delta(x + E_{n'} - E_n) \}. \tag{A8}$$

Comparison of Eqs. (A6) and (A8) then shows that

$$F_0(\mathbf{k}, \mathbf{k}'; x) = e^{-\beta x} E_0(\mathbf{k}, \mathbf{k}'; x). \tag{A9}$$

This is a key relation from which we may now derive Eq. (35) relatively easily. The retarded Green's function [see Eq. (33)] may be written as follows in terms of

E_0 and F_0:

$$G_r(t) = -i\theta(t)[E_0(\mathbf{k},\mathbf{k'}; t) - F_0(\mathbf{k},\mathbf{k'}; t)]$$

$$= -i\theta(t)\int_{-\infty}^{\infty} e^{-ix't}[E_0(\mathbf{k},\mathbf{k'}; x') - F_0(\mathbf{k},\mathbf{k'}; x')]dx'$$

$$= -i\theta(t)\int_{-\infty}^{\infty} e^{-ix't}(e^{\beta x'}-1)F_0(\mathbf{k},\mathbf{k'}; x')dx'. \quad (A10)$$

The Fourier transform of G_r is

$$G_r(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \frac{(e^{\beta x'}-1)F_0(\mathbf{k},\mathbf{k'}; x')dx'}{(x-x'+i\delta)}. \quad (A11)$$

An expression for the Fourier transform of the advanced Green's function is obtained by changing the sign of δ in this equation. Thus

$$(G_r - G_a) = \frac{1}{2\pi}\int_{-\infty}^{\infty} (e^{\beta x'}-1)F_0(\mathbf{k},\mathbf{k'}; x')$$

$$\times\left[\frac{1}{x-x'+i\delta} - \frac{1}{x-x'-i\delta}\right]dx'$$

$$= -i(e^{\beta x}-1)F_0(\mathbf{k},\mathbf{k'}; x), \quad (A12)$$

which is exactly Eq. (35) of the text.

Optical Properties of 15R SiC: Luminescence of Nitrogen-Exciton Complexes, and Interband Absorption

Lyle Patrick, D. R. Hamilton, and W. J. Choyke

Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

(Received 30 July 1963)

Optical experiments on 15R SiC are reported, and the results are compared with those given earlier for 6H SiC. The absorption edge is due to indirect, exciton-producing transitions, across an exciton energy gap of 2.986 eV at 6°K. Two distinct photoluminescence spectra are found, due to two kinds of nitrogen-exciton complexes. These spectra consist of series of lines, from which 18 phonon energies are obtained. Only four series of lines are observed in each spectrum, although there are five inequivalent nitrogen sites in 15R SiC. The four nitrogen donor ionization energies are found to be approximately 0.14, 0.16, 0.16, and 0.20 eV. These, and other binding energies, are somewhat smaller than in 6H SiC. As in the 6H SiC data, we find evidence of exciton hopping, of localized vibrations, of the presence of six conduction band minima, and of a second valence band, split off 4.8 meV by spin-orbit interaction.

I. INTRODUCTION

UNTIL recently, the study of SiC polytype differences has been largely limited to x-ray investigations of the numerous stacking orders found in this material.[1-3] We are now reporting results of optical experiments on polytype 15R SiC, and we make many comparisons with results of similar experiments[4,5] on the most common SiC polytype, 6H. Since many SiC properties are nearly the same for all polytypes, it is interesting to speculate on the reasons for any marked differences.

Crystallographically, the SiC polytypes differ only in the stacking order (along the c axis) of close-packed atomic planes. The various polytypes can be represented by ordered sequences of the three letters, ABC, each

letter representing a plane of Si atoms, and another plane of C atoms. In this notation, rhombohedral 15R SiC (space group R3m) is ABCACBCABACABCB; hexagonal 6H SiC (space group P6₃mc) is ABCACB. A short description of polytype structural differences is given in Sec. III.

The energy gaps of 6H and 15R SiC differ by only about 1%. That the difference is so little is probably accidental, for the energy gap of cubic SiC is considerably smaller,[6] and the energy gap of the 4H polytype is about 10% larger (see Fig. 1). All three polytypes shown in Fig. 1 have structure in their absorption edges which is characteristic of indirect optical transitions with the creation of excitons. In this respect they resemble Ge and Si.[7] The absorption edge of 15R SiC is shown in more detail in Sec. IX.

Considerable information on donors, phonons, and carriers in 6H SiC has been derived from recent studies

[1] A. R. Verma, *Crystal Growth and Dislocations* (Butterworths Scientific Publications Ltd., London, 1953), Chap. 7.

[2] R. S. Mitchell, Z. Krist. **109**, 1 (1957). This paper contains many references to x-ray results.

[3] P. Krishna and A. R. Verma, Proc. Roy. Soc. (London) **A272**, 490 (1963).

[4] W. J. Choyke and Lyle Patrick, Phys. Rev. **127**, 1868 (1962).

[5] D. R. Hamilton, W. J. Choyke, and Lyle Patrick, Phys. Rev. **131**, 127 (1963).

[6] Lyle Patrick, W. J. Choyke, and D. R. Hamilton, Bull. Am. Phys. Soc. **8**, 484 (1963). For cubic SiC, $E_{Gx}=2.39$ eV.

[7] G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. **108**, 1377 (1957); **111**, 1245 (1958); R. J. Elliott, *ibid.* **108**, 1384 (1957).