PHYSICAL REVIEW B VOLUME 9, NUMBER 10 15 MAY 1974

Local field effects and the dielectric response matrix of insulators: A model

David Linton Johnson*
Michelson Laboratory, Naval Weapons Center, China Lake, California 93555

(Received 4 February 1974)

A simple model relating the low-optical-frequency dielectric response matrix of Adler and Wiser, $\epsilon_{\vec{K},\vec{G}}$, to the random-phase-approximation dielectric constant and to the Fourier coefficients of the valence-charge density, is presented. The model is derived by use of Kramers-Kronig relations and f sum rules. The results of a recent band-structure calculation and other model calculations are compared with this model.

I. INTRODUCTION

Recently, serious interest has emerged in the effects of the nondiagonal dielectric response matrix of crystals in an electric field.[1-7] When a real solid is polarized by an electric field, microscopic electric fields which vary on the scale of atoms are established. In crystals, a (macroscopic) electric field $E(\vec{q},\omega)$ will establish (microscopic) fields $E(\vec{q}+\vec{K},\omega)$ ($\vec{K}$ is a reciprocal lattice vector) whose time average is not zero; the local or effective field which polarizes the charge in the crystal is a properly weighted average of these fields. The microscopic fields $E(\vec{q}+\vec{K},\omega)$ are related to the macroscopic field $E(\vec{q},\omega)$ by means of the dielectric matrix $\epsilon_{\vec{K},\vec{G}}(\vec{q},\omega)^2$,

$$E(\vec{q}+\vec{K},\omega)=(\epsilon^{-1}_{\vec{0},\vec{K}}/\epsilon^{-1}_{\vec{0},\vec{0}})\,E(\vec{q},\omega)\;, \tag{1.1}$$

hence, the term "off-diagonal response." Effects of this nature are sometimes called "local field effects." In this paper we develop an approximate treatment of $\epsilon_{\vec{K},\vec{G}}$ in nonmetal crystals at zero temperature for frequencies small compared to electronic frequencies but large compared to lattice-vibration frequencies. Adler and Wiser (AW)[1] have derived, essentially by an extension of the random-phase approximation (RPA), an approximation to $\epsilon_{\vec{K},\vec{G}}$ for longitudinal fields,

$$\epsilon_{\vec{K},\vec{G}}(\vec{q},\omega)=\delta_{\vec{K},\vec{G}}-\frac{4\pi e^2}{\Omega|\vec{q}+\vec{K}|\,|\vec{q}+\vec{G}|}\sum_{\vec{k}ll'}\frac{f_0[\mathcal{E}_{l'}(\vec{k}+\vec{q})]-f_0[\mathcal{E}_l(\vec{k})]}{\mathcal{E}_{l'}(\vec{k}+\vec{q})-\mathcal{E}_l(\vec{k})-\hbar\omega+i\hbar\alpha}$$
$$\times\langle\vec{k}+\vec{q},l'|e^{i(\vec{q}+\vec{K})\cdot\vec{r}}|\vec{k},l\rangle\langle\vec{k},l|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}|\vec{k}+\vec{q},l'\rangle\;, \tag{1.2}$$

where $|\vec{k},l\rangle$ and $\mathcal{E}_l(\vec{k})$ are the eigenstates and eigenvalues of the unperturbed crystal Hamiltonian, f_0 is the temperature-dependent Fermi-Dirac distribution function and Ω is the crystal volume. $\epsilon_{\vec{0},\vec{0}}(\vec{q},\omega)$ is the usual RPA dielectric constant for crystals as given by Cohen and Ehrenreich[8] (CE). The macroscopic dielectric constant is derived from Eq. (1.2) according to[1]

$$\epsilon_{\mathrm{macro}}(\vec{q},\omega)=1/[\epsilon^{-1}(\vec{q},\omega)]_{\vec{0},\vec{0}}\;, \tag{1.3}$$

which can be rewritten[9]

$$\epsilon_{\mathrm{macro}}(\vec{q},\omega)=\epsilon_{\vec{0},\vec{0}}-\sum_{\vec{K},\vec{G}}{}'\,\epsilon_{\vec{0},\vec{K}}S^{-1}_{\vec{K},\vec{G}}\epsilon_{\vec{G},\vec{0}}\;, \tag{1.4}$$

where $S=\epsilon$ restricted to $\vec{K}\neq\vec{0}\neq\vec{G}$. Of course, for light at or below optical frequencies, $\vec{q}\approx\vec{0}$ and $\epsilon_{\mathrm{macro}}$ (longitudinal) $=\epsilon_{\mathrm{macro}}$ (transverse). We will consider Eqs. (1.2) and (1.3) to be the extended RPA (ERPA) result. According to Eq. (1.4),

$$\epsilon_{\mathrm{macro}}\approx\epsilon_{\vec{0},\vec{0}}\;, \tag{1.5}$$

only if $\epsilon_{\vec{0},\vec{K}}$ is negligible for $\vec{K}\neq\vec{0}$. The usual CE approximation [Eq. (1.5)] is valid only when microscopic field effects can be neglected; this is true for most metals and for most covalent solids as will be further discussed in Sec. III. The off-diagonal matrix elements are an important physical effect which can be determined indirectly [compare Eqs. (1.3) and (1.4)] and, in some cases, directly; the existence of electric fields $E(\vec{q}+\vec{K},\omega)$ due to the influence of light $E(\vec{q},\omega)$ [Eq. (1.1)] allows one, in prinicple, to Bragg scatter Doppler-shifted x rays[5] through a change in wave vector $\vec{q}+\vec{K}$ in addition to the static scattering $\Delta\vec{k}=\vec{K}$. The scattering efficiency for the former process is proportional[2,5] to a quantity $|\phi_{\vec{K}}|^2$, where

$$\phi_{\vec{K}}=(\epsilon_{\vec{0},\vec{0}}-1)\,\epsilon^{-1}_{\vec{0},\vec{K}}/\epsilon_{\vec{0},\vec{0}}\;. \tag{1.6}$$

To date efforts to observe such an effect have failed, presumably because the $\phi_{\vec{K}}$'s are too small.

Equation (1.3) is not, as claimed by AW,[1] equivalent to the classical Clausius-Mossotti (CM) relation[10] between the dielectric constant and the polarizability $[(\epsilon_{\vec{0},\vec{0}}-1)/4\pi N$ may be thought of as an atomic-like polarizability (see Wiser[1])], even in the tight-binding limit; this was shown by Sinha *et al.*,[6] who found it necessary to include exchange-correlation corrections to the electron-electron interaction in order to retrieve the CM equation. It is known, from pressure-dependent measurements, that the CM relation is obeyed in certain crystals.[3] Nonetheless, the difference between Eqs. (1.3) and(1.5) is correctly referred to as a "local field effect" because the microscopic polarizing electric field is different from the macroscopic electric field and the AW formalism (ERPA), modified for exchange correlation as suggested by Sinha *et al.*,[6] provides a viable band-theoretic starting point for analyzing such effects in crystals. (One need not necessarily do an additional electronic calculation, additional sums over the Brillouin zone, etc.)

Although many authors have, for a wide range of materials, calculated $\epsilon_{\vec{0},\vec{0}}$ band theoretically as an approximation to ϵ_{macro}, apparently the work of Van Vechten and Martin[2] (VVM), on diamond remains the only detailed calculation of the $\epsilon_{\vec{K},\vec{G}}$ matrix, via Eq. (1.2), in insulators. They found for $\vec{q}\approx\vec{0}$, ω arbitrary, that use of Eq. (1.3) generally increased the existing disparity between $\epsilon_{\vec{0},\vec{0}}$ and experiment; in particular, they found ($\vec{q}=\vec{0}$, $\omega <$ band gap) that $1/(\epsilon^{-1}_{\vec{0},\vec{0}}) < \epsilon_{\vec{0},\vec{0}} < \epsilon$ (experiment). ment). Use of the CM local field always increases the low-frequency dielectric constant over that obtained by its neglect, i.e., $\epsilon_{\vec{0},\vec{0}}$ in this case. In order to achieve better agreement with experiment, VVM invoked a particular *Ansatz* (quite different from Sinha's)of frequency-dependent correlation corrections that go beyond ERPA, namely,

$$\epsilon_{\text{cor}}(\omega)=\frac{1}{\epsilon^{-1}_{\vec{0},\vec{0}}(\omega)}+\beta\left(\frac{1}{\epsilon^{-1}_{\vec{0},\vec{0}}(\omega)}-\epsilon_{\vec{0},\vec{0}}(\omega)\right)\times\frac{[\epsilon_{\vec{0},\vec{0}}(\omega)-1]^2}{\epsilon_{\vec{0},\vec{0}}(\omega)}\quad. \tag{1.7}$$

This assumption of the first term in large parentheses to a large extent merely undoes the damage done by use of Eq. (1.3) instead of (1.5); if $\beta=-\epsilon_{\vec{0},\vec{0}}(0)/[\epsilon_{\vec{0},\vec{0}}(0)-1]^2$, then $\epsilon_{\text{cor}}(0)=\epsilon_{\vec{0},\vec{0}}(0)$. Nonetheless, use of Eq. (1.7) did generally improve agreement with the experimental $\epsilon_2(\omega)$ curve. VVM[2] also found the largest $\phi_{\vec{K}}$ [in ERPA, see Eq. (1.6)] to be $\phi_{111}\approx 0.03$ which goes a long way toward explaining why the Doppler-shifted Bragg-scattered x-ray effect has not been observed in diamond. However, in view of Eq. (1.7) it is not clear what will be the effect on $\epsilon_{\vec{K},\vec{G}}$ of correlations beyond ERPA, at least for diamond. The ERPA formulation is, nonetheless, a useful band-theoretic starting point for off-diagonal effects in solids and modification of the ERPA result, to include correlation and exchange, can, in some cases, be approximated by modification of the electron-electron interaction $v(\vec{Q})$ as suggested by Sinha *et al.*[6]

This paper is concerned with the dielectric response matrix $\epsilon_{\vec{K},\vec{G}}$ in ERPA only [Eq. (1.2)] as applied to nonmetals at zero temperature. Section II is devoted to Kramers-Kronig (KK) relations, asymptotic ($\omega\to\infty$) values, and f sum rules. In Sec. III these results are used to present a simple model which relates $\epsilon_{\vec{K},\vec{G}}(\omega\approx 0)$ to $\epsilon_{\vec{0},\vec{0}}$ and to the spatial distribution of valence-charge density; there are no adjustable parameters in the usual sense. The model is presented not as a calculational aid (the Sinha factorization scheme[6] is far superior, when applicable, as it can be inverted by hand), but merely to exhibit the close relationship between the off-diagonal response and the spatial distribution of valence-charge density. The results are compared with those of VVM.[2] This model, like the ERPA upon which it is based, is never equivalent to the CM equation. In Sec. IV other phenomenological models are compared. Section V is a summary.

II. KRAMERS-KRONIG RELATIONS, ASYMPTOTIC VALUES, AND f SUM RULES

Equation (1.2) can be rewritten

$$\epsilon_{\vec{K},\vec{G}}(\vec{q},\omega)=H_{\vec{K},\vec{G}}(\vec{q},\omega)+iA_{\vec{K},\vec{G}}(\vec{q},\omega)\ , \tag{2.1}$$

where

$$H_{\vec{K},\vec{G}}=\delta_{\vec{K},\vec{G}}-\frac{4\pi e^2}{|\vec{q}+\vec{K}|\;|\vec{q}+\vec{G}|\,\Omega}\sum_{\vec{k}ll'}\{f_0[\mathcal{E}_{l'}(\vec{k}+\vec{q})]-f_0[\mathcal{E}_l(\vec{k})]\}\langle\vec{k}+\vec{q},l'|e^{i(\vec{q}+\vec{K})\cdot\vec{r}}|\vec{k},l\rangle\langle\vec{k},l|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}|\vec{k}+\vec{q},l'\rangle\,\mathcal{P}(\omega)\ , \tag{2.2a}$$

$$\mathcal{P}(\omega)=\frac{\mathcal{E}_{l'}(\vec{k}+\vec{q})-\mathcal{E}_l(\vec{k})-\hbar\omega}{[\mathcal{E}_{l'}(\vec{k}+\vec{q})-\mathcal{E}_l(\vec{k})-\hbar\omega]^2+\alpha^2}\to P\left(\frac{1}{\mathcal{E}_{l'}(\vec{k}+\vec{q})-\mathcal{E}_l(\vec{k})-\hbar\omega}\right), \tag{2.2b}$$

$$A_{\vec{K},\vec{G}}=\frac{4\pi e^2}{|\vec{q}+\vec{K}|\,|\vec{q}+\vec{G}|\,\Omega}\sum_{\vec{k}ll'}\{f_0[\mathcal{E}_{l'}(\vec{k}+\vec{q})]-f_0[\mathcal{E}_l(\vec{k})]\}\langle\vec{k}+\vec{q},l'|e^{i(\vec{q}+\vec{K})\cdot\vec{r}}|\vec{k},l\rangle\langle\vec{k},l|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}|\vec{k}+\vec{q},l'\rangle\,\mathfrak{D}(\omega), \tag{2.2c}$$

$$\mathfrak{D}(\omega)=\frac{\alpha}{[\mathcal{E}_{l'}(\vec{k}+\vec{q})-\mathcal{E}_l(\vec{k})-\hbar\omega]^2+\alpha^2}\to\pi\delta[\mathcal{E}_{l'}(\vec{k}+\vec{q})-\mathcal{E}_l(\vec{k})-\hbar\omega]\ . \tag{2.2d}$$

(The arrows signify $\alpha \rightarrow 0^+$, P means principal part.) $H_{\vec{K},\vec{G}}$ ($A_{\vec{K},\vec{G}}$) is the dispersive (absorptive) part of $\epsilon_{\vec{K},\vec{G}}$. Both $H_{\vec{K},\vec{G}}$ and $A_{\vec{K},\vec{G}}$ are Hermitian; they are real and therefore symmetric if (and, it will be shown, only if) the crystal has an inversion center. Because the time dependence of the fields was assumed[1] to be $e^{i\omega t}$, $A_{\vec{K},\vec{K}} < 0$ if $\omega > 0$ and conversely. Let $\Delta\mathcal{E} = \mathcal{E}_{l'}(\vec{k}+\vec{q}) - \mathcal{E}_l(\vec{k})$, then

$$\frac{\mathfrak{D}(x)}{x-\omega} = \frac{A}{x-\omega} + \frac{B}{x-\Delta\mathcal{E}+i\alpha} + \frac{C}{x-\Delta\mathcal{E}-i\alpha}\ , \tag{2.3}$$

where

$$A = \alpha/[(\omega-\Delta\mathcal{E})^2+\alpha^2], \tag{2.4a}$$

$$B = -i/2(\omega-\Delta\mathcal{E}+i\alpha)\ , \tag{2.4b}$$

$$C = B^*\ . \tag{2.4c}$$

Integrating Eq. (2.3) over a standard double-semicircle contour in the complex x plane (Fig. 29 of Landau and Lifschitz[11]) one finds

$$\frac{P}{\pi}\int_{-\infty}^{\infty} \frac{\mathfrak{D}(x)}{x-\omega}\,dx = \mathcal{P}(\omega)\ , \tag{2.5}$$

which, together with Eqs. (2.2), implies

$$H_{\vec{K},\vec{G}}(\vec{q},\omega) = \delta_{\vec{K},\vec{G}} + \frac{P}{\pi}\int_{-\infty}^{\infty} \frac{A_{\vec{K},\vec{G}}(\vec{q},x)}{\omega-x}\,dx \tag{2.6a}$$

$$= \delta_{\vec{K},\vec{G}} + \frac{2}{\pi}P\int_0^{\infty} \frac{A_{\vec{K},\vec{G}}(\vec{q},x)}{\omega^2-x^2}\,x\,dx \tag{2.6b}$$

where $A_{\vec{K},\vec{G}}(\vec{q},-\omega) = -A_{\vec{K},\vec{G}}(\vec{q},\omega)$ will be proven. Similarly,

$$A_{\vec{K},\vec{G}}(\vec{q},\omega) = \frac{P}{\pi}\int_{-\infty}^{\infty} \frac{H_{\vec{K},\vec{G}}(\vec{q},x) - \delta_{\vec{K},\vec{G}}}{x-\omega}\,dx \tag{2.7}$$

and there is no difficulty associated with exchanging the limit $\alpha \rightarrow 0^+$ with the x integration.[12] Equations (2.6) and (2.7) are analogues of the ordinary KK relations[11] between ϵ_1 and ϵ_2 but contain more information because $A_{\vec{K},\vec{G}}$ and $H_{\vec{K},\vec{G}}$ are, in general, complex valued. We now derive asymptotic forms for $\epsilon_{\vec{K},\vec{G}}$ as $\omega \rightarrow \infty$. Let

$$F_{\vec{K},\vec{G}} = \sum_{\vec{k}ll'} \frac{f_0[\mathcal{E}_{l'}(\vec{k}+\vec{q})] - f_0[\mathcal{E}_l(\vec{k})]}{\mathcal{E}_{l'}(\vec{k}+\vec{q}) - \mathcal{E}_l(\vec{k}) - \hbar\omega + i\alpha}$$
$$\times\langle\vec{k}+\vec{q},l'|e^{i(\vec{q}+\vec{K})\cdot\vec{r}}|\vec{k},l\rangle\langle\vec{k},l|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}|\vec{k}+\vec{q},l'\rangle\ , \tag{2.8}$$

so that

$$\epsilon_{\vec{K},\vec{G}} = \delta_{\vec{K},\vec{G}} - \frac{4\pi e^2}{|\vec{q}+\vec{K}|\,|\vec{q}+\vec{G}|\,\Omega}\,F_{\vec{K},\vec{G}}\ . \tag{2.9}$$

Consider

$$T = \sum_{\vec{k}ll'} \frac{f_0[\mathcal{E}_{l'}(\vec{k}+\vec{q})]}{\mathcal{E}_{l'}(\vec{k}+\vec{q}) - \mathcal{E}_l(\vec{k}) - \hbar\omega + i\alpha}$$
$$\times\langle\vec{k}+\vec{q},l'|e^{i(\vec{q}+\vec{K})\cdot\vec{r}}|\vec{k},l\rangle\langle\vec{k},l|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}|\vec{k}+\vec{q},l'\rangle\ . \tag{2.10}$$

If one makes the substitution $\vec{k}' = -(\vec{k}+\vec{q})$ (drop the prime) and interchanges (l,l'), one finds

$$T = -\sum_{\vec{k}ll'} \frac{f_0[\mathcal{E}_l(\vec{k})]}{\mathcal{E}_{l'}(\vec{k}+\vec{q}) - \mathcal{E}_l(\vec{k}) + \hbar\omega - i\alpha}$$
$$\times\langle\vec{k}+\vec{q},l'|e^{i(\vec{q}+\vec{K})\cdot\vec{r}}|\vec{k},l\rangle\langle\vec{k},l|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}|\vec{k}+\vec{q},l'\rangle\ , \tag{2.11}$$

where we have assumed time-reversal symmetry in the absence of spin-orbit coupling,[13] but have not assumed inversion symmetry. (Note that $\vec{k}$ and $\vec{k}+\vec{q}$ can always simultaneously be taken within the first Brillouin zone.) Equation (2.8) becomes

$$F_{\vec{K},\vec{G}} = -2\sum_{\vec{k}ll'} f_0[\mathcal{E}_l(\vec{k})]\langle\vec{k}+\vec{q},l'|e^{i(\vec{q}+\vec{K})\cdot\vec{r}}|\vec{k},l\rangle\langle\vec{k},l|e^{i(\vec{q}+\vec{G})\cdot\vec{r}}|\vec{k}+\vec{q},l'\rangle \frac{\mathcal{E}_{l'}(\vec{k}+\vec{q}) - \mathcal{E}_l(\vec{k})}{[\mathcal{E}_{l'}(\vec{k}+\vec{q}) - \mathcal{E}_l(\vec{k})]^2 - (\hbar\omega - i\alpha)^2} \tag{2.12}$$

and one can immediately see that $H_{\vec{K},\vec{G}}(\vec{q},-\omega) = H_{\vec{K},\vec{G}}(\vec{q},\omega)$ and $A_{\vec{K},\vec{G}}(\vec{q},-\omega) = -A_{\vec{K},\vec{G}}(\vec{q},\omega)$. As $\omega \rightarrow \infty$ the leading term can be written in the form

$$\underset{\omega\rightarrow\infty}{L} F_{\vec{K},\vec{G}} = \frac{1}{(\hbar\omega)^2}\sum_{\vec{k},l} f_0[\mathcal{E}_l(\vec{k})]\sum_{l'}\{[\mathcal{E}_{l'}(\vec{k}+\vec{q}) - \mathcal{E}_l(\vec{k})]\langle\vec{k}+\vec{q},l'|e^{i(\vec{q}+\vec{K})\cdot\vec{r}}|\vec{k},l\rangle\langle\vec{k},l|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}|\vec{k}+\vec{q},l'\rangle$$
$$+ [\mathcal{E}_{l'}(\vec{k}-\vec{q}) - \mathcal{E}_l(\vec{k})]\langle\vec{k},l|e^{i(\vec{q}+\vec{K})\cdot\vec{r}}|\vec{k}-\vec{q},l'\rangle\langle\vec{k}-\vec{q},l'|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}|\vec{k},l\rangle\}\ . \tag{2.13}$$

Let $\mathcal{H}$ be the appropriate (unperturbed) one-electron crystal Hamiltonian, assumed by AW[1] to be a local operator,

$$\mathcal{H}|\vec{k},l\rangle = \mathcal{E}_l(\vec{k})|\vec{k},l\rangle\ , \tag{2.14}$$

then

$$[[\mathcal{H}, e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}],\ e^{i(\vec{q}+\vec{K})\cdot\vec{r}}] = (-\hbar^2/2m)\,e^{i(\vec{K}-\vec{G})\cdot\vec{r}}(\vec{q}+\vec{K})\cdot(\vec{q}+\vec{G})\ , \tag{2.15}$$

taking the matrix element of Eq. (2.15) on both sides with $|\vec{k},l\rangle$ and using the completion relation

$$\sum_{\vec{k},l} |\vec{k},l\rangle\langle\vec{k},l| = I \, ,$$

we find

$$\sum_{l'} \{ [\mathcal{E}_{l'}(\vec{k}+\vec{q}) - \mathcal{E}_l(\vec{k})] \langle\vec{k},l|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}|\vec{k}+\vec{q},l'\rangle\langle\vec{k}+\vec{q},l'|e^{i(\vec{q}+\vec{K})\cdot\vec{r}}|\vec{k},l\rangle + [\mathcal{E}_{l'}(\vec{k}-\vec{q}) - \mathcal{E}_l(\vec{k})]$$
$$\times\langle\vec{k},l|e^{i(\vec{q}+\vec{K})\cdot\vec{r}}|\vec{k}-\vec{q},l'\rangle\langle\vec{k}-\vec{q},l'|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}|\vec{k},l\rangle\}$$
$$= \frac{\hbar^2}{m}(\vec{q}+\vec{K})\cdot(\vec{q}+\vec{G})\langle\vec{k},l|e^{i(\vec{K}-\vec{G})\cdot\vec{r}}|\vec{k},l\rangle \; . \qquad (2.16)$$

Comparing Eq. (2.16) with Eqs. (2.9) and (2.13) gives

$$\underset{\omega\to\infty}{L} \epsilon_{\vec{K},\vec{G}}(\vec{q},\omega) = \underset{\omega\to\infty}{L} H_{\vec{K},\vec{G}}(\vec{q},\omega)$$
$$= \delta_{\vec{K},\vec{G}} - (4\pi e^2 n/m\omega^2)$$
$$\times f(\vec{K}-\vec{G})\,\hat{e}(\vec{q}+\vec{K})\cdot\hat{e}(\vec{q}+\vec{G}) \, , \qquad (2.17)$$

where $\hat{e}(\;)$ indicates unit vector in the direction of the argument, n is the average-number density of electrons in the crystal, and

$$f(\vec{G}) = \frac{1}{n}\sum_{\vec{k},l} f_0[\mathcal{E}_l(\vec{k})]\langle\vec{k},l|e^{i\vec{G}\cdot\vec{r}}|\vec{k},l\rangle \qquad (2.18)$$

is the Fourier transform of the total-number density of electrons normalized to $f(\vec{0})=1$. When $\vec{K}=\vec{G}=\vec{0}$ we get the ordinary RPA result

$$\underset{\omega\to\infty}{L} \epsilon_{\vec{0},\vec{0}}(\vec{q},\omega) = 1 - \omega_p^2/\omega^2 \, , \qquad (2.19a)$$

$$\omega_p^2 = 4\pi n e^2/m \, . \qquad (2.19b)$$

Comparing Eq. (2.17) with Eq. (2.6b) we find the new f sum rule

$$\int_0^\infty \omega A_{\vec{K},\vec{G}}(\vec{q},\omega)\,d\omega = -\tfrac{1}{2}\pi\omega_p^2 f(\vec{K}-\vec{G})$$
$$\times\hat{e}(\vec{q}+\vec{K})\cdot\hat{e}(\vec{q}+\vec{G}) \, . \qquad (2.20)$$

It is clear that A, and hence H, are, in general, real only if the crystal has an inversion center. When $\vec{K}=\vec{G}=\vec{0}$, Eq. (2.20) reduces to the usual f sum rule on the RPA dielectric function $\epsilon_{\vec{0},\vec{0}}$,

$$\int_0^\infty \omega\,\mathrm{Im}[\epsilon_{\mathrm{RPA}}(\vec{q},\omega)]d\omega = -\tfrac{1}{2}\pi\omega_p^2 \, . \qquad (2.21)$$

The equivalent relations on $\epsilon_{\mathrm{macro}}$ [Eq. (1.3)] are unaffected. Write Eq. (2.17) in the form

$$\underset{\omega\to\infty}{L} \epsilon_{\vec{K},\vec{G}}(\vec{q},\omega) = \left(1 - \frac{\omega_p^2}{\omega^2}\right)\delta_{\vec{K},\vec{G}} - \frac{\omega_p^2}{\omega^2} J_{\vec{K},\vec{G}} \, , \qquad (2.22)$$

where J has only off-diagonal elements independent of ω. Using

$$(I-B)^{-1} = I + B + B^2 + B^3 \cdots \, , \qquad (2.23)$$

it is easy to show that

$$\underset{\omega\to\infty}{L} \epsilon_{\mathrm{macro}}(\vec{q},\omega) = 1 - \omega_p^2/\omega^2 \qquad (2.24)$$

to lowest order, as it must since Eq. (2.24) is a model-independent result.[14] [Neither Eq. (2.24) nor (2.17) is necessarily a good approximation for $\omega\approx\omega_p$.] The KK relations on $\epsilon_{\mathrm{macro}}$ are also model independent, depending on causality arguments alone,[11] so the f sum rule

$$\int_0^\infty \omega\,\mathrm{Im}[\epsilon_{\mathrm{macro}}(\vec{q},\omega)]d\omega = -\tfrac{1}{2}\pi\omega_p^2 \qquad (2.25)$$

still holds.[14] Equation (2.20) shows that all solids except jellium have a nonzero dielectric response matrix $\epsilon_{\vec{K},\vec{G}}$ for all $(\vec{K},\vec{G})$; the f sum rule [Eq. (2.20)] is quite different from the acoustic sum rule of Pick, Cohen, and Martin[15] since it puts a condition on each element.

In the next section Eqs. (2.6b) and (2.20) will be used to develop a simple model for the dielectric response matrix of nonmetals at low frequency in ERPA.

III. MODEL FOR THE DIELECTRIC RESPONSE MATRIX IN INSULATORS AND SEMICONDUCTORS AT LOW OPTICAL FREQUENCIES

We wish to develop a simple model for the $\omega\approx 0$ elements of $\epsilon_{\vec{K},\vec{G}}$ in ERPA and apply the model to diamond. Specfically, we intend to relate $\epsilon_{\vec{K},\vec{G}}$ to ϵ_{RPA} and the spatial distribution of valence-charge density.

We observe that, for a fairly large class of semiconductors and insulators,[3] the absorption spectrum $\epsilon_2(\vec{q}=\vec{0},\omega)$ is a single sharply peaked function of ω, at least as far as its effect (through the KK relation) on $\epsilon_1(\omega=0)$ is concerned; the structure in ϵ_2 is more related to the structure of the bands $\mathcal{E}_l(\vec{k})$ than to the matrix elements, as long as the f sum rule is obeyed. We make the one-oscillator approximation[3]

$$A_{\vec{K},\vec{G}}(\vec{q},\omega) = C(\vec{q}+\vec{K},\vec{q}+\vec{G})\,\delta[\hbar\omega - E(\vec{q}+\vec{K},\vec{q}+\vec{G})] \, . \qquad (3.1)$$

This approximation is trivially satisfied by a solid whose valence band and conduction band are perfectly flat; for $\vec{q}=\vec{0}$, the bands need only be parallel. The (truncated) f sum rule [Eq. (2.20)] yields the value of $C(\vec{q}+\vec{K},\vec{q}+\vec{G})$ and Eq. (3.1) substituted into Eq. (2.6b) gives

$$\epsilon_{\vec{K},\vec{G}}(\vec{q},\omega) = \delta_{\vec{K},\vec{G}} + \left[\frac{\hbar\omega_p}{E(\vec{q}+\vec{K},\vec{q}+\vec{G})}\right]^2 f_v(\vec{K}-\vec{G})$$
$$\times\hat{e}(\vec{q}+\vec{K})\cdot\hat{e}(\vec{q}+\vec{G}) \, , \qquad (3.2)$$

where ω_p and $f_v(\vec{G})$ refer only to the valence bands.[16]

For $\vec{K}=\vec{G}=\vec{0}$ we have merely reproduced the result of Penn's model,[17] upon which Phillips has based a theory of bonding,[18]

$$\epsilon_{\vec{0},\vec{0}}(\vec{q},\omega=0)=1+[\hbar\omega_p/E(\vec{q},\vec{q})]^2\ . \tag{3.3}$$

[Our energy $E(\vec{q},\vec{q})$ differs slightly from Penn's.] That Eq. (3.3) applies for $\vec{q}\neq\vec{0}$ can be seen by referring to the calculation of Walter and Cohen[19] on Si. If $E(\vec{q},\vec{q})$, for a given $\vec{q}$, is determined by setting the right-hand side of Eq. (3.3) equal to the calculated value of $\epsilon_{\vec{0},\vec{0}}(\vec{q},0)$, one obtains energies that correlate well with peaks in the calculated absorption spectrum $\text{Im}\,\epsilon_{\vec{0},\vec{0}}(\vec{q},\omega)$ of Ref. 19, although for $\vec{q}\gtrsim(100)(\pi/a)$ (X in the Brillouin zone) the approximation of Eq. (3.1) is hardly valid. Walter and Cohen[19] calculated $\text{Re}\,\epsilon_{\vec{0},\vec{0}}$ directly and used KK analysis to determine $\text{Im}\,\epsilon_{\vec{0},\vec{0}}$; for this reason their calculation of $\text{Im}\,\epsilon_{\vec{0},\vec{0}}$ changes sign below the absorption edge.

We write Eq. (3.2) as follows:

$$\epsilon_{\vec{K},\vec{G}}(\vec{q},0)=\delta_{\vec{K},\vec{G}}+(\epsilon_{\text{RPA}}-1)g[\vec{q}+\tfrac{1}{2}(\vec{K}+\vec{G});\ \vec{K}-\vec{G}]\times f_v(\vec{K}-\vec{G})\,\hat{e}(\vec{q}+\vec{K})\cdot\hat{e}(\vec{q}+\vec{G})\ , \tag{3.4}$$

where

$$\epsilon_{\text{RPA}}=\epsilon_{\vec{0},\vec{0}}(\vec{q}=\vec{0},\omega=0)=1+[\hbar\omega_p/E(\vec{0},\vec{0})]^2, \tag{3.5a}$$

$$g[\vec{q}+\tfrac{1}{2}(\vec{K}+\vec{G})\ ;\ \vec{K}-\vec{G}]=[E(\vec{0},\vec{0})/E(\vec{q}+\vec{K},\vec{q}+\vec{G})]^2\ . \tag{3.5b}$$

$E(\vec{0},\vec{0})$ is chosen so that ϵ_{RPA} equals the calculated value $\epsilon_{\vec{0},\vec{0}}(\vec{q}=\vec{0},\omega=0)$ and *not*, for our purposes, the experimental value ϵ_{macro} as Penn and Srinivasan[17] have done. Equation (3.4) is not a tautology; since $g\geq 0$, Eq. (3.4) makes a definite prediction about the phase of $\epsilon_{\vec{K},\vec{G}}$. It may happen that $(\vec{q}+\vec{K})\cdot(\vec{q}+\vec{G})=0$ and/or $f_v(\vec{K}-\vec{G})\equiv 0$ either of which predicts $\epsilon_{\vec{K},\vec{G}}=0$. Since, for longitudinal fields

$$\vec{P}(\vec{q},\vec{K})=\hat{e}(\vec{q}+\vec{K})\,|\vec{P}|\ , \tag{3.6a}$$

$$\vec{E}(\vec{q},\vec{K})=\hat{e}(\vec{q}+\vec{K})\,|\vec{E}|\ . \tag{3.6b}$$

Equation (3.4) says that only components of $\vec{E}$ along $\vec{P}$ contribute to the polarization, which is certainly reasonable but not necessary. This point will be discussed in Sec. IV. We seek an approximate formula for $g[\vec{q}+\frac{1}{2}(\vec{K}+\vec{G})\ ;\ (\vec{K}-\vec{G})]$ and we anticipate that it will not depend on the details of the bands, such as matrix elements, the point being that with a reasonable choice of such a function, $\epsilon_{\vec{K},\vec{G}}$ can be related primarily to ϵ_{RPA} and $f_v(\vec{K}-\vec{G})$.

Actually, Penn[17] has already suggested such a formula in the case when $\vec{K}-\vec{G}=\vec{0}$, namely,

$$g[\vec{q}+\tfrac{1}{2}(\vec{K}+\vec{K})\ ;\ \vec{0}]=\left(1+\frac{\hbar^2}{2mE(\vec{0},\vec{0})}\ (\vec{q}+\vec{K})^2\right)^{-2} \tag{3.7a}$$

$$=\left(1+\frac{\hbar(\epsilon_{\text{RPA}}-1)^{1/2}}{2m\omega_p}\ (\vec{q}+\vec{K})^2\right)^{-2}. \tag{3.7b}$$

This gives

$$\epsilon_{\vec{K},\vec{K}}(\vec{q})=\epsilon_{\vec{0},\vec{0}}(\vec{q}+\vec{K})=1+(\epsilon_{\text{RPA}}-1)\Big/\left(1+\frac{\hbar(\epsilon_{\text{RPA}}-1)^{1/2}}{2m\omega_p}\ (\vec{q}+\vec{K})^2\right)^2, \tag{3.8}$$

where ϵ_{RPA} is taken (in the present work) to be the calculated $\epsilon_{\vec{0},\vec{0}}(\vec{q}=\vec{0},\omega=0)$. The origin of Eq. (3.8) is that when $\vec{q}+\vec{K}=\vec{0}$, $\epsilon_{\vec{0},\vec{0}}=\epsilon_{\text{RPA}}$ and when $|\vec{q}+\vec{K}|\to\infty$,

$$\epsilon_{\vec{K},\vec{K}}(\vec{q},\omega=0)\to 1+\{\hbar\omega_p/[(\hbar^2/2m)(\vec{q}+\vec{K})^2]\}^2\ , \tag{3.9}$$

i.e., for large $|\vec{q}+\vec{K}|$, band effects are negligible and one obtains the free electron (Lindhard) result[20] of which Eq. (3.9) represents the leading terms. That $\epsilon_{\vec{K},\vec{K}}(\vec{q})$ decreases to unity as $|\vec{q}|\to\infty$ is due to the nonlocal response (in real space) of the valence electrons. Walter and Cohen[21] found that $\epsilon_{\vec{0},\vec{0}}(\vec{q},\omega=0)$, calculated band theoretically, is an exceptionally isotropic function for Si, Ge, GaAs, and ZnSe, as is Eq. (3.8), although the latter has the inadequacy, first pointed out by Brust,[22] that it appreciably overestimates $\epsilon_{\vec{0},\vec{0}}(\vec{q})$ at intermediate values of $\vec{q}$. We are more interested in rough, yet reasonable, values of $\epsilon_{\vec{0},\vec{0}}(\vec{K})$, however, and Eq. (3.8) may not be such a bad approximation in those cases. In this spirit, it is interesting that Eq. (3.8), based on a model small-gap semiconductor, is very similar to $\epsilon_{\vec{0},\vec{0}}(\vec{q})$ based on models of large-gap insulators.[23]

We arbitrarily extend Penn's approximation [Eq. (3.7)] to include

$$g[\vec{q}+\tfrac{1}{2}(\vec{K}+\vec{G})\ ;\ \vec{K}-\vec{G}]=\{1+\kappa(\vec{K}-\vec{G})\,[\vec{q}+\tfrac{1}{2}(\vec{K}+\vec{G})]^2\}^{-2}\ , \tag{3.10}$$

κ is a measure of the extent of the nonlocal response (in real space) of the valence-electron gas to an electric field. For elements $\epsilon_{\vec{K},\vec{G}}$, where $|\vec{K}-\vec{G}|$ is "large" corresponding to well-localized components of the valence-charge density, one may reasonably expect that nonlocal effects are negligible, i.e., $\kappa\to 0$. We arbitrarily cut off κ when $|\vec{K}-\vec{G}|>2\vec{k}_F$ corresponding to the end of the predominance of first-order scattering between states on the surface of the unperturbed Fermi sphere and the onset of the predominance of higher-order scattering processes.[18] The model of this paper for the dielectric response matrix of insulators and semiconductors in ERPA at zero frequency is, therefore,

$$\epsilon_{\vec{K},\vec{G}}(\vec{q})=\delta_{\vec{K},\vec{G}}+\frac{(\epsilon_{\text{RPA}}-1)f_v(\vec{K}-\vec{G})\hat{e}(\vec{q}+\vec{K})\cdot\hat{e}(\vec{q}+\vec{G})}{\{1+\kappa[\vec{q}+\frac{1}{2}(\vec{K}+\vec{G})]^2\}^2}\ , \tag{3.11a}$$

where

$$\kappa = \hbar(\epsilon_{\mathrm{RPA}} - 1)^{1/2}/2m\omega_p \quad \text{if} \quad |\vec{K} - \vec{G}| < 2k_F$$
$$= 0 \quad \text{if} \quad |\vec{K} - \vec{G}| > 2k_F . \qquad (3.11\text{b})$$

The model has no adjustable parameters in the usual sense because ϵ_{RPA} is chosen equal to the calculated value $\epsilon_{\vec{0},\vec{0}}(\vec{q} = \vec{0}, \omega = 0)$; as mentioned previously, $\epsilon_{\mathrm{RPA}} - 1$ may be thought of as the polarizability. The model relates $\epsilon_{\vec{K},\vec{G}}$ to $f_v(\vec{K} - \vec{G})$ and band energies $E(\vec{q} + \vec{K}, \vec{q} + \vec{G})$; the latter have been eliminated in favor of ϵ_{RPA} alone by means of Eqs. (3.5) and (3.10). The particular choice [Eq. (3.10)] is arbitrary and is only meant to illustrate the close connection between $\epsilon_{\vec{K},\vec{G}}$ and ϵ_{RPA}, $f_v(\vec{K} - \vec{G})$ with use of some reasonable function, g, such as is given by Eq. (3.10). The spirit of this article is that the valence electrons reside in valence states, which have a certain similarity to each other; the success, in Ge, of the Baldereschi mean-value point[24] stems from this point of view. We do not choose, for example, to further simplify the diamond-valence states in terms of atomic charges and bond charges,[18] although the particular choice of Eq. (3.10) is reminiscent of Phillips's arguments. The appearance of $f_v(\vec{K} - \vec{G})$ is not at all surprising when one considers the effects of other short-wavelength electric fields, but for the geometrical factor which picks out the longitudinal-longitudinal component of each tensor $\overleftrightarrow{\epsilon}_{\vec{K},\vec{G}}$, Eq. (2.17) could be used to discuss ordinary Bragg scattering of x rays.[25]

The only existing band-theoretic calculation of $\epsilon_{\vec{K},\vec{G}}$ in ERPA [Eq. (1.2)] is that by VVM on diamond.[2] They found[26] $\epsilon_{\vec{0},\vec{0}}(\vec{q} = \vec{0}, \hbar\omega = 1.5\ \mathrm{eV}) = 5.4779$; we accordingly set $\epsilon_{\mathrm{RPA}} = 5.4779$. [The model of Eq. (3.11) has been derived for $\omega = 0$ but well below the band gap most of the weak dispersion can be absorbed in ϵ_{RPA}.] In order to obtain $f_v(\vec{G})$ we have taken the experimental data of Göttlicher and Wölfel[27] (and Renninger[28] for $F[222]$) as rescaled by Dawson,[29] divided out their assumed Debye-Waller factor, and then subtracted off the calculated core form factor of McWeeny[30] in order to get $f_v(\vec{G})$ for a frozen lattice at the room-temperature lattice constant used by VVM. The experimental $f_v(\vec{G})$'s are essentially the same as those tabulated by Kleinman and Phillips[31] except for $f_v[111]$ which is perhaps more accurately determined by Kleinman and Phillips[31] and so we have used their result for $f_v[111]$. VVM calculated $\epsilon_{\vec{K},\vec{G}}$ for reciprocal lattice vectors through the set [222]; the model of Eq. (3.11) requires $f_v(\vec{G})$ through the set [444] and all of these $f_v(\vec{G})$'s are listed in Table I. It would perhaps make more sense to use $f_v(\vec{G})$ as calculated by VVM but the experimental values of Table I are more readily determined. Since $|f_v(\vec{G})| \ll |f_{\mathrm{core}}(\vec{G})| \approx |f_{\mathrm{total}}(\vec{G})|$ when $|\vec{G}| > |220|$, our values of the corresponding $f_v(\vec{G})$'s are probably not very accurate, even as to sign, but we present them anyway. However, $f_v[222]$ is quite accurate because $f_{\mathrm{core}}[222] \equiv 0$ by virture of spherical symmetry, and its sign is determined by assuming it corresponds to a charge accumulation in the bond region. Table I could be determined very nearly by mere inspection of Fig. 1 of Ref. 27. The room-temperature lattice constant[27] determines k_F and ω_p.

Table II contains the values of the diagonal elements and largest off-diagonal elements $\epsilon_{\vec{K},\vec{G}}(\vec{q} = 0, \hbar\omega = 1.5\ \mathrm{eV})$ as calculated by VVM[2,26] in ERPA [Eq. (1.2)] compared with the corresponding elements calculated from the present model [Eq. (3.11)] using the input of Table I and $\epsilon_{\mathrm{RPA}} = 5.4779$. Table II also lists the respective values of $\epsilon_{\mathrm{macro}}$ [Eq. (1.3)] and the largest value of $\phi_{\vec{K}}$ [Eq. (1.6)]; the size of the dielectric matrix was 59×59 corresponding to $\vec{K}$ vectors through the set [222] and was inverted numerically in each case. For $|\vec{K} - \vec{G}| = 0$, $|111|$, $|311|$, and $|222|$ our calculation agrees fairly well with VVM, although the diagonal elements do exhibit the aforementioned overestimation discussed by Brust[22]; for $|\vec{K} - \vec{G}| \geq |400|$, our values of $f_v(\vec{K} - \vec{G})$ are not at all accurate but the pertinent $\{\epsilon_{\vec{K},\vec{G}}\}$ are generally small compared to the other off-diagonal elements, as expected. Our values of $\epsilon_{\vec{K},\vec{G}}$ when $|\vec{K} - \vec{G}| = |220|$ are of the opposite sign of VVM's;[2] evidently,[16] $\int_0^\infty \omega A_{\vec{K},\vec{G}}(\vec{q} = 0, \omega)\, d\omega$ and $\int_0^\infty [A_{\vec{K},\vec{G}}(\vec{q} = 0, \omega)/\omega]\, d\omega$ have opposite signs and there is no simple way Eq. (3.11) can be modified to accommodate this. The second law of thermodynamics[11] requires $\mathrm{Im}\, \epsilon \leq 0$; this is automatically satisfied by $A_{\vec{K},\vec{K}}$ in ERPA,

TABLE I. Fourier coefficients of the normalized valence charge density in diamond obtained according to the method described in Sec. III of the text. Error bars reflect experimental errors only and do not include calculational errors associated with the core states.

$\vec{G}$	$f_v(\vec{G})$
000	1.000
111	-0.245 ± 0.001
220	-0.046 ± 0.002
311	0.011 ± 0.001
222	0.038 ± 0.003
400	0.036 ± 0.002
331	0.003 ± 0.001
422	0.007 ± 0.001
511 333	-0.001 ± 0.001
440	-0.015 ± 0.003
531	0.006 ± 0.001
620	0.004 ± 0.001
533	0.001 ± 0.001
444	0.0

TABLE II. Comparison of the diagonal and largest off-diagonal elements of $\epsilon_{\vec{K},\vec{G}}$ [$\vec{q}=\delta\ (100)$; $\hbar\omega = 1.5$ eV] as calculated by Van Vechten and Martin[a] for diamond using the Adler-Wiser[b] formalism, with the same elements calculated from the model of Sec. III using the data of Table I. ϵ_{macro} and $\phi_{\vec{K}}$ are defined in the text.

$\lvert\vec{K}-\vec{G}\rvert$	$\vec{K}$	$\vec{G}$	$\epsilon_{\vec{K},\vec{G}}$ (VVM)	$\epsilon_{\vec{K},\vec{G}}$ (Present work)
000	000	000	5.4779	5.4779
	111	111	1.2621	1.3858
	200	200	1.1829	1.2527
	220	220	1.0572	1.0814
	311	311	1.0203	1.0464
	222	222	1.0170	1.0396
111	000	111	-0.2342	-0.2469
	111	200	0.0466	0.0616
	111	220	0.0308	0.0387
	111	222	-0.0254	-0.0267
	200	311	-0.0199	-0.0241
	220	311	0.0128	0.0145
	311	222	0.0085	0.0103
200	000	200	0.0000	0.0000
220	000	220	0.0230	-0.0215
	111	$\bar{1}\bar{1}1$	0.0171	0.0211
	111	$31\bar{1}$	-0.0112	0.0043
	200	020	-0.0132	0.0000
	200	222	0.0091	-0.0035
	220	022	-0.0091	0.0030
	000	022	0.0000	0.0000
311	000	311	0.0615	0.0446
	000	131	0.0494	0.0149
	111	$\bar{2}00$	-0.0093	-0.0284
	111	$22\bar{2}$	-0.0208	-0.0164
	200	131	0.0109	0.0149
	220	$3\bar{1}1$	-0.0075	-0.0210
	220	113	-0.0093	-0.0210
222	000	222	0.0967	0.0982
	111	$\bar{1}\bar{1}\bar{1}$	-0.1371	-0.1702
	200	022	-0.0094	0.0000
400	111	$\bar{3}11$	0.0091	-0.0281
	220	$2\bar{2}0$	0.0059	0.0000
331	111	$\bar{2}\bar{2}0$	-0.0214	-0.0110
	111	$\bar{2}\bar{2}2$	0.0116	0.0045
	200	$\bar{1}31$	-0.0100	-0.0041
420	111	$\bar{3}\bar{1}1$	0.0060	0.0000
333	111	$\bar{2}\bar{2}\bar{2}$	0.0134	0.0045
	220	$\bar{1}\bar{1}3$	0.0067	-0.0019
440	220	$\bar{2}\bar{2}0$	-0.0179	0.0672
444	222	$\bar{2}\bar{2}\bar{2}$	-0.0060	0.0000
ϵ_{macro}			5.0	5.089
ϕ_{111}			0.03	0.03744

[a] References 2 and 26.

[b] Reference 1.

but there is no corresponding requirement on the phase of the off-diagonal elements. If either $f_v(\vec{K}-\vec{G})=0$ or $(\vec{q}+\vec{K})\cdot(\vec{q}+\vec{G})=0$, Eq. (3.11) predicts $\epsilon_{\vec{K},\vec{G}}=0$ in cases where this need not be so, as can be seen in Table II. We observe that the physically observable quantities, ϵ_{macro} and $\phi_{\vec{K}}$, are in rather good agreement with those calculated by VVM, although, according to Eq. (1.4), $\epsilon_{0,0} - \epsilon_{\text{macro}}$ is the quantity that ought to be compared. Again, we emphasize that this model is not to be thought of as a calculational aid[32] but it merely exhibits the close connection between $\epsilon_{\vec{K},\vec{G}}$ and ϵ_{RPA}, $f_v(\vec{K}-\vec{G})$, for $\omega \approx 0$.

IV. DISCUSSION

In this section we discuss certain aspects of the model of Sec. III. In particular, this model, like the Sinha factorization scheme[6] based on ERPA, is never equivalent to the CM equation. We consider our model in the appropriate limit.

As discussed by Wiser,[1] the microscopic electric field

$$E(\vec{r}) = \sum_{\vec{K}} E(\vec{q},\vec{K})\, e^{-i(\vec{q}+\vec{K})\cdot\vec{r}} \tag{4.1}$$

is different from the macroscopic or average electric field

$$E_{\text{macro}}(\vec{r}) = E(\vec{q},\vec{0})\, e^{-\vec{q}\cdot\vec{r}}\ . \tag{4.2}$$

The various components of the polarizability are related to the components of the microscopic electric field by

$$P(\vec{q},\vec{K}) = N_0 \sum_{\vec{G}} \alpha(\vec{q},\vec{K},\vec{G})\, E(\vec{q},\vec{G}) \tag{4.3}$$

(N_0 is the density of unit cells), where it can be shown[1]

$$\alpha(\vec{q},\vec{K},\vec{G}) = (1/4\pi N_0)(\epsilon_{\vec{K},\vec{G}} - \delta_{\vec{K},\vec{G}})\ . \tag{4.4}$$

$\alpha(\vec{q},\vec{0},\vec{0})$ is the polarizability of a crystal, relating the macroscopic polarization to the macroscopic *local* electric field

$$P(\vec{q},\vec{0}) = N_0\, \alpha(\vec{q},\vec{0},\vec{0})\, E_{\text{loc}}(\vec{q})\ . \tag{4.5}$$

$E_{\text{loc}}(\vec{q})$ is, in general, different from the macroscopic average electric field, $E(\vec{q},\vec{0})$, giving rise to the difference between Eqs. (1.3) and (1.5). We will transform to real space but it must be remembered that each element $\alpha(\vec{q},\vec{K},\vec{G})$ is itself really a tensor operator and we have focused on the longitudinal-longitudinal component of $\overleftrightarrow{\alpha}$; Eq. (4.4) should be rewritten

$$\hat{e}(\vec{q}+\vec{K})\cdot\overleftrightarrow{\alpha}(\vec{q},\vec{K},\vec{G})\cdot\hat{e}(\vec{q}+\vec{G}) = (1/4\pi N_0)(\epsilon_{\vec{K},\vec{G}} - \delta_{\vec{K},\vec{G}})\ , \tag{4.6}$$

i.e., any polarizability tensor $\overleftrightarrow{\alpha}(\vec{q},\vec{K},\vec{G})$ satisfying Eq. (4.6) will guarantee

$$\vec{P}(\vec{q},\vec{K})\cdot\hat{e}(\vec{q}+\vec{K})=\frac{1}{4\pi}\sum_{\vec{G}}[(\epsilon_{\vec{K},\vec{G}}-\delta_{\vec{K},\vec{G}})\,\vec{E}(\vec{q},\vec{G})\cdot(\vec{q}+\vec{G}), \tag{4.7}$$

when substituted in the vector Eq. (4.3) (the direction of $\vec{E}$ changes with $\vec{r}$). Using the model of Sec. III, $\overleftrightarrow{\alpha}$ can be taken[33] as

$$\overleftrightarrow{\alpha}(\vec{q},\vec{K},\vec{G})=\frac{\alpha_0}{\{1+\kappa(\vec{K}-\vec{G})[q+\frac{1}{2}(\vec{K}+\vec{G})]^2\}^2}\times f_v(\vec{K}-\vec{G})\,\overleftrightarrow{I}\ , \tag{4.8}$$

where $\alpha_0=(\epsilon_{RPA}-1)/4\pi N_0$. The CM relation assumes a *local* polarizability,

$$\overleftrightarrow{\alpha}(\vec{r},\vec{r}\,')=\alpha_0\delta(\vec{r}-\vec{r}\,')\,\overleftrightarrow{I}\ , \tag{4.9}$$

relative to the local effective field

$$\vec{P}(\vec{r})=N_0\int d\vec{r}\,'\,\overleftrightarrow{\alpha}(\vec{r},\vec{r}\,')\,\vec{E}_{loc}(\vec{r}\,') \tag{4.10a}$$

$$=\alpha_0N_0\vec{E}_{loc}(\vec{r})\ . \tag{4.10b}$$

(It is then further argued for isotropic systems that $\vec{E}_{loc}=\vec{E}_{macro}+\frac{4}{3}\pi\vec{P}$; see, e.g., Fröhlich.[34]) Fourier transforming Eq. (4.9) gives

$$\alpha(\vec{q})=\alpha_0=\text{const}\ . \tag{4.11}$$

Accordingly, in order to test our model in the CM limit, we set $\kappa\equiv0$ in Eq. (4.8). When transformed back into real space, the present model predicts

$$\overleftrightarrow{\alpha}(\vec{r},\vec{r}\,')=\alpha_0\rho_v(\vec{r})\,\delta(\vec{r}-\vec{r}\,')\,\overleftrightarrow{I}\ , \tag{4.12}$$

so that the polarization at a point $\vec{r}$ due to the microscopic (not local-effective) field at $\vec{r}$ is proportional to the density of polarizable valence electrons $\rho_v(\vec{r})$. Utilizing Eqs. (4.12) and (4.10a),

$$\vec{P}(\vec{r})=\alpha_0N_0\rho_v(\vec{r})\,\vec{E}(\vec{r}) \tag{4.13a}$$

$$=\alpha_0N_0\vec{E}_{loc}(\vec{r})\ . \tag{4.13b}$$

One may further average Eq. (4.13b) over a unit cell in order to get the relationship between the (macroscopic) polarization and the macroscopic local-effective field in this model. From Eq. (4.10) it is apparent that if the valence electrons are uniformly spread out $\rho_v(\vec{r})\equiv1$, then $\vec{E}_{loc}=\vec{E}_{macro}=\vec{E}_{micro}$. The derivation of the classical CM equation assumes well localized atoms (in fact, point atoms) with no appreciable overlap of neighbors. Accordingly, we consider the extreme case when $\rho_v(\vec{r})$ is given by a summation of δ functions centered on atomic sites, i.e., $f_v(\vec{G})\equiv1$. (For simplicity we consider a monatomic unit cell fcc or bcc.) The dielectric matrix of Sec. III, taken in the limit of well separated atoms ($\kappa\equiv0, f_v\equiv1$) simplifies to

$$\epsilon_{\vec{K},\vec{G}}=\delta_{\vec{K},\vec{G}}+(\epsilon_{RPA}-1)\,\hat{e}(\vec{q}+\vec{K})\cdot\hat{e}(\vec{q}+\vec{G})\ . \tag{4.14}$$

This is of the same form as that considered by Sinha *et al.*[6] as the tight-binding limit and is now invertible by hand. The result is

$$\epsilon_{macro}=1+(\epsilon_{RPA}-1)/[1+\tfrac{1}{3}N(\epsilon_{RPA}-1)] \tag{4.15a}$$

$$=1+\ 4\pi N_0\alpha_0/[1+\tfrac{1}{3}N(4\pi N_0\alpha_0)] \tag{4.15b}$$

($N+1$ is the dimension of the ϵ matrix and should, strictly speaking, be taken as infinite), which contrasts sharply with the classical CM equation[10,34]

$$\epsilon_{CM}=1+\ 4\pi N_0\alpha_0/[1-\tfrac{1}{3}(4\pi N_0\alpha_0)]\ . \tag{4.16}$$

Equation (4.15) always lowers the dielectric constant relative to that obtained by neglect of local-field effects $\epsilon(\text{neglect})=1+4\pi N_0\alpha_0$ (in fact, if one really considers $f_v(\vec{G})\equiv1$ for all $\vec{G}$, $\epsilon_{macro}=1$), whereas the CM equation always increases the dielectric constant relative to $\epsilon(\text{neglect})$. The Sinha factorization scheme,[6] which is exact in the tight-binding two-band limit, reproduces Eq. (4.15) when the electron-electron interaction is taken as

$$v(\vec{Q})=4\pi e^2/\Omega\vec{Q}^2\ , \tag{4.17}$$

i.e., the ERPA of AW.[1] In order to retrieve the CM relation [Eq. (4.16)], Sinha had to remove a self-interacting term from $v(\vec{Q})$ to account for the exchange-correlation hole, as can be done by various methods,[35]

$$v(\vec{Q})=(4\pi e^2/\Omega\vec{Q}^2)\,[1-f_{ec}(\vec{Q})]\ . \tag{4.18}$$

In this sort of treatment the factor $1/[\,|\vec{q}+\vec{K}|\,|\vec{q}+\vec{G}|\,]$ in Eq. (1.2) is modified by multiplication with $[1-f_{ec}(\vec{q}+\vec{K})]$. This is an effect which goes beyond the correlations of the ERPA of AW[1] in which each electron responds to the average field of every electron including itself.

The main difference between the present model and Sinha *et al.*[6] [apart from the modification of $v(\vec{Q})$] is that $f_v(\vec{Q})$, used in this paper, refers directly to the normalized valence-charge density only and appears in the form $f_v(\vec{K}-\vec{Q})$ whereas the $\{f_s(\vec{Q})\}$ used by Sinha *et al.*[6] are merely conveniently chosen functions which, even in the tight-binding two-band limit where the scheme is exact, represent the Fourier transform of a weighted product of valence- and conduction-band states and appear in the form $f_s(\vec{q}+\vec{K})\,f^*_{s'}(\vec{q}+\vec{G})$.[32]

The bond charge model (BCM) of Freund and Levine[5] bears a similarity to the present model. They have proposed

$$\overleftrightarrow{\alpha}_{BCM}(\vec{r},\vec{r}\,')=\alpha_0\rho_B(\vec{r})\,\delta(\vec{r}-\vec{r}\,')\,\overleftrightarrow{I}\ , \tag{4.19}$$

which has a Fourier transform

$$\overleftrightarrow{\alpha}_{BCM}(\vec{q},\vec{K},\vec{G})=\alpha_0f_B(\vec{K}-\vec{G})\,\overleftrightarrow{I}\ , \tag{4.20}$$

to be compared with Eq. (4.8). The BCM has predicted a scattering factor ϕ_{111} an order of magnitude larger than that calculated by VVM.[2,26] It is easy to see why. First, since $\overleftrightarrow{\alpha}_{BCM}(\vec{r},\vec{r}\,')$ is a local response, $\alpha_{BCM}(\vec{q},\vec{K},\vec{G})$ does not decrease with $\vec{q}$ [or $\vec{q}+\frac{1}{2}(\vec{K}+\vec{G})$]. Secondly, $\rho_B(\vec{r})$ is the normalized bond-charge density only; it is more highly localized than the entire valence-charge density and so $f_B(\vec{G})$ is larger than $f_v(\vec{G})$. As a consequence, the dielectric matrix $\epsilon_{\vec{K},\vec{G}}$ based on Eq. (4.19) gives larger off-diagonal, and even diagonal, elements than does Eq. (4.8), which agrees reasonably well with VVM and consequently it predicts larger values of $\phi_{\vec{K}}$.

V. SUMMARY

We have derived a model for the dielectric response matrix, $\epsilon_{\vec{K},\vec{G}}$, of Adler and Wiser[1] (ERPA) for $\omega \rightarrow 0$. There are no adjustable parameters in this model which has as inputs the dielectric constant calculated in RPA (neglect of local-field effects) and the Fourier coefficients of the valence-charge density. The model is in fairly good agreement with the matrix calculated band theoretically for diamond by VVM.[2] The model, like the ERPA upon which it is based, is never equivalent to the classical CM relation between the dielectric constant and the polarizability, although the situation can be remedied by the introduction of a correlation-exchange factor[35] in the model.

ACKNOWLEDGMENTS

The author is grateful to the NRC and to the staff of the Michelson Laboratory for the excellent opportunities afforded him as a Postdoctoral Associate. The author acknowledges many useful comments and ideas from M. Kastner, who initiated interest in the problem; from J. A. Van Vechten and S. K. Sinha, who contributed unpublished work of their own; and from J. Hermanson and J. Scherfinski. The excellence of the staff and facilities of the Computer Sciences Branch and Mathematics Division of Michelson Laboratory are appreciated.

---

*National Research Council Postdoctoral Research Associate.

[1] S. L. Adler, Phys. Rev. 126, 413 (1962); N. Wiser, Phys. Rev. 129, 62 (1963). We have adopted the convention of Ref. 2 for $\epsilon_{\vec{K},\vec{G}}$.

[2] J. A. Van Vechten and R. M. Martin, Phys. Rev. Lett. 28, 446 (1972); 28, 646(E) (1972).

[3] M. Kastner, Phys. Rev. B 6, 2273 (1972); 7, 5237 (1973), and references therein.

[4] T. K. Bergstresser and G. W. Rubloff, Phys. Rev. Lett. 30, 794 (1973).

[5] I. Freund and B. F. Levine, Phys. Rev. Lett. 25, 1241 (1970); P. M. Eisenberger and S. L. McCall, Phys. Rev. A 3, 1145 (1971).

[6] S. K. Sinha, Phys. Rev. 177, 1256 (1969); R. P. Gupta and S. K. Sinha, J. Appl. Phys. 41, 915 (1970); S. K. Sinha, R. P. Gupta, and D. L. Price, Phys. Rev. Lett. 26, 1324 (1971); R. P. Gupta and S. K. Sinha, Phys. Rev. B 3, 2401 (1971); S. K. Sinha, R. P. Gupta, and D. L. Price (unpublished).

[7] R. M. Martin, J. A. Van Vechten, J. E. Rowe, and D. E. Aspnes, Phys. Rev. B 6, 2500 (1972).

[8] H. Ehrenreich and M. H. Cohen, Phys. Rev. B 115, 786 (1959).

[9] F. Ayres, Jr., *Theory and Problems of Matrices* (Schaum, New York, 1962), Chap. 7, p. 57.

[10] W. K. H. Panofsky and M. Phillips, *Classical Electricity and Magnetism* (Addison-Wesley, Reading, Mass., 1962); D. R. Corson and P. Lorrain, *Introduction to Electromagnetic Fields and Waves* (Freeman, San Francisco, 1962).

[11] L. D. Landau and E. M. Lifschitz, *Electrodynamics of Continuous Media* (Addison-Wesley, Reading, Mass., 1960).

[12] This is not true of metals because $\epsilon_{\vec{0},\vec{0}}(\vec{q}=0,\omega)$ has a a pole at $\omega=0$ (Wiser, Ref. 1). This can be taken into account (Ref. 11).

[13] C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963).

[14] D. Pines, *Elementary Excitations in Solids* (Benjamin, New York, 1964).

[15] R. M. Pick, M. H. Cohen, and R. M. Martin, Phys. Rev. B 1, 910 (1970).

[16] Truncation of the f sum rule may be dangerous because Eq. (2.16) includes transitions to the core. See Ref. 14. Such effects do not occur unless the "core" states are near the valence band in energy. J. A. Van Vechten, Phys. Rev. 182, 891 (1969). They are separated by some 250 eV in diamond. F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[17] D. R. Penn, Phys. Rev. 128, 2093 (1962); G. Srinivasan, *ibid* 178, 1244 (1969). See also V. Heine and R. O. Jones, J. Phys. C 2, 719 (1969).

[18] J. C. Phillips, *Covalent Bonding in Crystals, Molecules, and Polymers* (University of Chicago, Chicago, 1969).

[19] J. P. Walter and M. L. Cohen, Phys. Rev. B 5, 3101 (1972).

[20] F. Stern, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 15, p. 299.

[21] J. P. Walter and M. L. Cohen, Phys. Rev. B 2, 182 (1970).

[22] D. Brust, J. Phys. C 4, L278 (1971); Phys. Rev. B 5, 435 (1972).

[23] J. Hermanson, Phys. Rev. 150, 660 (1966); J. L. Fry, Phys. Rev. 179, 892 (1969).

[24] A. Baldereschi, Phys. Rev. B 7, 5212 (1973).

[25] R. W. James in Ref. 20, Vol. 15, p. 77.

[26] J. A. Van Vechten (private communication). Reference 2 incorrectly quoted the calculated values of $\epsilon_{\vec{0},\vec{0}}(\vec{q}=\vec{0}, \hbar\omega=1.5\text{ eV})$. 1.5 eV was chosen because it is a convenient optical frequency (e.g., Bragg scattering, Ref. 5). We are most grateful to Dr. Van Vechten for communicating his unpublished results.

[27] S. Göttlicher and W. Wölfel, Z. Elektrochem. 63, 891 (1959).

[28] M. Renninger, Acta Crystallogr. 8, 606 (1955).

[29] B. Dawson, Proc. R. Soc. A 298, 264 (1967).

[30] R. McWeeny, Acta Crystallogr. 7, 180 (1954).

[31] L. Kleinman and J. C. Phillips, Phys. Rev. 125, 819 (1962).

[32] The Sinha scheme (Ref. 6) has been able to fit the calculated values of Ref. 2 [J. A. Van Vechten (private

communication)].

[33] An arbitrary dyadic $\overleftrightarrow{C}$ such that $(\vec{q}+\vec{K})\cdot\overleftrightarrow{C}\cdot(\vec{q}+\vec{G})=0$ could be added to the right side of Eq. (4.8) but our choice is simplest.

[34] H. Fröhlich, *Theory of Dielectrics* (Oxford U. P., London, 1949).

[35] K. S. Singwi, A. Sjölander, M. P. Tosi, and R. H. Lond, Phys. Rev. B 1, 1044 (1970; D. J. W. Geldart and R. Taylor, Can. J. Phys. 48, 155 (1970); 48, 167 (1970); F. Toigo and T. O. Woodruff, Phys. Rev. B 2, 3959 (1970); V. S. Mashkevich and K. B. Tolpygo, Zh. Eksp. Teor. Fiz. 32, 520 (1957) [Sov. Phys.-JETP 5, 435 (1957)].