Calculation of Local Effective Fields: Optical Spectrum of Diamond

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The random-phase-approximation formalism describing local fields developed by Adler and by Wiser is evaluated for an insulator for the first time. It is shown that umklapp effects decrease the low-frequency electronic dielectric constant, contrary to what is required to reconcile theory with experiment for most semiconductors. A simple prescription for effects of dynamical correlation is shown to improve agreement with experiment for diamond.

The concept of the local electric field dates back at least 100 years to the work of Mossotti. Although the concept has been widely applied, it is still rather poorly developed and understood. The fundamental point is that when any medium is polarized, the polarization density is nonuniform, and therefore, it induces electric fields which fluctuate on the scale of the atoms involved rather than with the wavelength of the applied field. The *macroscopic*[1] field $\overline{\vec{E}}$ is the Fourier component of the internal field which varies with frequency ω and wave vector $\vec{q}$ of a long-wavelength applied field. We term all components of the internal field with frequency ω but with different spatial variation as *microscopic* fields. These are the fundamental quantities in the "local field problem" because appropriate weighted averages of the microscopic fields define any of the various "local effective fields" which are useful in specific models. We are concerned with crystals, in which case microscopic fields have wave vectors $\vec{q}+\vec{K}$, where $\vec{K}$ is a reciprocal lattice vector, and are generated by the long-wavelength field through umklapp processes. The purpose of this paper is to present the results of a numerical calculation of the microscopic fields in an insulator and their effect upon the long-wavelength, frequency-dependent macroscopic dielectric function.

Of course, there are instantaneous field fluctuations with Fourier components other than $\vec{q}+\vec{K}, \omega$. These fluctuating fields do not appear explicitly in the linear dielectric theory because their expectation values vanish. Fluctuations nevertheless produce dynamical correlations among the electrons, such that expectation values of products of the fields do not vanish. In principle, their effect is included[2,3] in the magnitude of the components of the dielectric function. We shall demonstrate the necessity of incorporating correlation effects upon the dielectric function.

For simplicity we consider only cubic crystals in this paper so that the dielectric tensor is diagonal in Cartesian coordinates. We shall omit these Cartesian-coordinate indices from our expressions. The dielectric-function matrix[2-5] for longitudinal fields may be defined[6] as a matrix in reciprocal lattice vectors $\vec{K}$ and $\vec{K}'$ [note $\vec{E}(\vec{q}+\vec{K},\omega)=E(\vec{q}+\vec{K},\omega)(\vec{q}+\vec{K})/|\vec{q}+\vec{K}|$, etc.],

$$\epsilon_{\vec{K},\vec{K}'}(\vec{q},\omega)=\frac{\partial E_{\text{ext}}(\vec{q}+\vec{K},\omega)}{\partial E(\vec{q}+\vec{K}',\omega)}, \tag{1}$$

where $\vec{q}$ is in the first Brillouin zone, E_{ext} is a longitudinal component of an external applied field, and E is the ω component of the total field inside the crystal, i.e., $\overline{\vec{E}}(\vec{q},\omega)$ is the macroscopic field $\overline{\vec{E}}$ and $\vec{E}(\vec{q}+\vec{K},\omega)$, $\vec{K}\neq 0$, are the microscopic fields. Although the "proper" response function[7,8] $\epsilon_{\vec{K},\vec{K}'}$ is the quantity most readily calculated, it is its matrix inverse $\epsilon^{-1}{}_{\vec{K},\vec{K}'}$ that relates to measurable quantities. The macroscopic dielectric constant $\bar{\epsilon}(\omega)$ is[4,8]

$$\bar{\epsilon}(\omega)=\lim_{q\to 0}[1/\epsilon^{-1}{}_{0,0}(\vec{q},\omega)], \tag{2}$$

and the microscopic fields are given by

$$E(\vec{q}+\vec{K},\omega)=\frac{\epsilon^{-1}{}_{0,\vec{K}}(\vec{q},\omega)}{\epsilon^{-1}{}_{0,0}(\vec{q},\omega)}E(\vec{q},\omega). \tag{3}$$

The dielectric constant defined in (2) is also the square of the index of refraction (which may be viewed as a consequence of gauge invariance[3,7,8]). Thus, $\text{Re}\{\bar{\epsilon}(\omega)\}$ and $\text{Im}\{\bar{\epsilon}(\omega)\}$ are to be identified with $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$, the real and imaginary parts of the dielectric constant.

Adler[4] and Wiser[5] (A-W) have generalized the Cohen-Ehrenreich (C-E) dielectric function to incorporate umklapp effects. They worked within the Hartree or random-phase approximation (RPA) which completely ignored dynamical correlations. In terms of a sum over states in band n at wave vector $\vec{k}$ with wave function $\psi_{n,\vec{k}}$, energy $E_{n,\vec{k}}$, and occupation number $f_{n,\vec{k}}$, they find the RPA dielectric matrix $\tilde{\epsilon}_{\vec{K},\vec{K}'}(\vec{q},\omega)$ to be[4-6] (the tilde always denotes RPA)

$$\tilde{\epsilon}_{\vec{K},\vec{K}'}(\vec{q},\omega)=\delta_{\vec{K},\vec{K}'}-\frac{4\pi e^2}{V|\vec{q}+\vec{K}||\vec{q}+\vec{K}'|}\sum_{n,n',\vec{k}}\frac{\langle n,\vec{k}|e^{-i\vec{K}\cdot\vec{r}}|n',\vec{k}+\vec{q}\rangle\langle n',\vec{k}+\vec{q}|e^{i\vec{K}\cdot\vec{r}}|n,\vec{k}\rangle(f_{n,\vec{k}}-f_{n',\vec{k}+\vec{q}})}{\hbar\omega+E_{n,\vec{k}}-E_{n',\vec{k}+\vec{q}}}. \tag{4}$$

Here V is the crystal volume and $\langle | \rangle$ denotes integration over the primitive cell. The relation $X^{-1}=\mathrm{P}(X^{-1})+i\pi\delta(X)$ separates (4) into Hermitian (real) and anti-Hermitian (imaginary) parts. Equation (4) is the generalization of the commonly used C-E dielectric function to incorporate umklapp effects within the RPA approximation. To our knowledge, umklapp terms ($\vec{K}\neq\vec{K}'$) in Eq. (4) have never been calculated for an insulator.

We have calculated the RPA dielectric-function matrix including all reciprocal lattice vectors through the set (222) for diamond. Energy intervals of 1 eV up to 40.5 eV were used, and the resulting 59×59 matrix at each energy was inverted numerically. For the calculation we used a nontruncated pseudopotential derived from Animalu's[9] free-atom factors corrected for screening and the effect of bond charges according to the approach of Phillips.[10] The band structure resulting from this calculation, discussed by Van Vechten, Martin, and Henvis,[11] is very similar to those of Herman[12] and of Saslow, Bergstresser, and Cohen.[13] In Fig. 1 we see the experimental $\epsilon_2(\omega)$ spectrum obtained by Roberts and Walker[14] compared with two results of our calculation, $\mathrm{Im}\{\tilde{\epsilon}_{0,0}(\omega)\}$, i.e., ϵ_2(C-E), and $\mathrm{Im}\{1/\tilde{\epsilon}^{-1}{}_{0,0}(\omega)\}$, i.e., ϵ_2(A-W). The important result is that the strength in ϵ_2(A-W) is shifted to higher energies than in ϵ_2(C-E), which already had its strength significantly higher than the experimental ϵ_2. This also affects the low-frequency dielectric function. For example, the experimental value at $\omega=1.5$ eV is 5.7, the C-E value is 5.4, and the A-W value is 5.0.

The discrepancy between the A-W result and that required to bring the C-E dielectric function into agreement with experiment is not restricted to diamond. In general, the C-E analysis underestimates both real and imaginary parts of the dielectric function of covalent solids at frequencies below the main peak of the spectrum and overestimates them above this peak.[15] However, a matrix identity[2,3] requires

$$\bar{\epsilon}\equiv 1/\epsilon^{-1}{}_{0,0}=\epsilon_{0,0}-\sum_{\vec{K},\vec{K}'\neq 0}\epsilon_{0,\vec{K}}S^{-1}{}_{\vec{K},\vec{K}'}\epsilon_{0\vec{K}'}{}^{*}, \tag{5}$$

where $S_{\vec{K},\vec{K}'}$ is $\epsilon_{\vec{K},\vec{K}'}$ restricted to $\vec{K},\vec{K}'\neq 0$. Note that $S_{\vec{K},\vec{K}}>1.0$ below the band gap because of the $\delta_{\vec{K},\vec{K}'}$ in Eq. (4). In our calculation the off-diagonal components of $\tilde{\epsilon}_{\vec{K},\vec{K}'}$ are all smaller than 1.0. We believe this will always be the case for covalent solids (i.e., except in the tight-binding limit) so that all eigenvalues of $S_{\vec{K},\vec{K}'}$ are positive. Therefore, the final term in Eq. (5) is negative definite and $\bar{\epsilon}<\epsilon_{0,0}$. In the RPA this means ϵ(A-W) $<\epsilon$(C-E) $<\epsilon$(expt) below the band gap. This general result is somewhat surprising since the Mossotti-Lorentz local field always increases the dielectric constant below the band gap.

In order to reconcile these results with experiment, it is necessary to incorporate effects of dynamical correlations upon the dielectric function. Here we neglect bound excitons and concentrate upon effects above the band gap. Lacking a tractable rigorous procedure for treating correlations, we propose a form, discussed in Ref. 11, with one adjustable parameter. The corrections

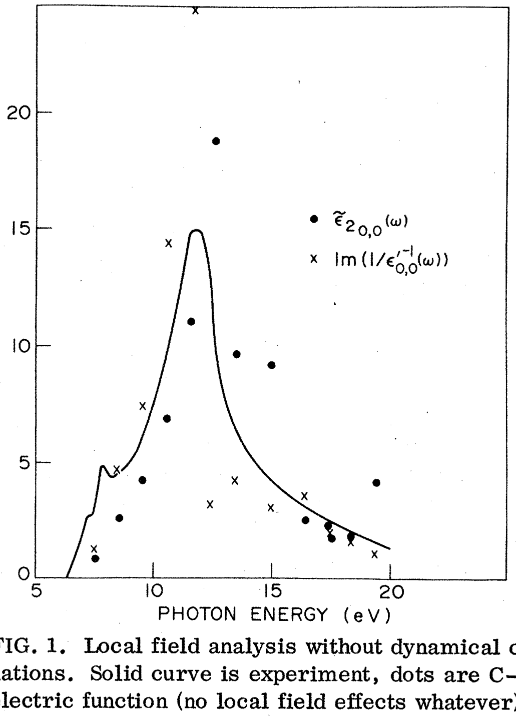

FIG. 1. Local field analysis without dynamical correlations. Solid curve is experiment, dots are C-E dielectric function (no local field effects whatever), crosses are A-W dielectric function (local fields treated in RPA).

to the dielectric function are proportional to the difference between the average of products of the instantaneous field operators and the product of the average of the fields. One such correction has already been calculated: The matrix inversion procedure for including umklapp corrections to the C-E dielectric function is equivalent to allowing products of microscopic fields in the expression for the macroscopic dielectric function. We make the *Anzatz* that the *frequency dependence* of the dynamical correlation correction is proportional to that of the umklapp correction already calculated in the RPA, i.e., the frequency dependence contains a factor $A(\omega)=1/\tilde{\epsilon}^{-1}{}_{0,0}(\omega)-\tilde{\epsilon}_{0,0}(\omega)$. In addition, physically, the corrections to Eq. (4) arise from the interaction of the fluctuating instantaneous polarization of the electrons induced at various points in the crystal. We feel that there is a close analogy to the Van der Waals interaction of the spontaneous polarization of atoms, which also has zero expectation value but nonzero effect because the interaction is proportional to the product of correlated fluctuations. To a first approximation this correction should be proportional to $B(\omega)=[\tilde{\epsilon}_{0,0}(\omega)-1]^2/\tilde{\epsilon}_{0,0}(\omega)$, which has the form of a screened Van der Waals interaction strength. We are led to a corrected complex dielectric function $\epsilon'(\omega)$ with the form

$$\epsilon'(\omega)=1/\tilde{\epsilon}^{-1}{}_{0,0}(\omega)+\alpha A(\omega)B(\omega), \tag{6}$$

where $A(\omega)$ and $B(\omega)$ are defined above and α is adjusted so that $\epsilon'(0)$ equals the experimental static dielectric constant.

The resulting $\epsilon_2'(\omega)=\mathrm{Im}\,\epsilon'(\omega)$ is shown in Fig. 2. We see that the imaginary part of the dielectric function incorporating the proposed correction for dynamical correlation effects gives reasonable agreement with experiment and resolves the previous discrepancy. In this calculation a mesh of only 31 points in the $\frac{1}{48}$ of the Brillouin zone was used; a finer mesh would produce a smoother curve in better agreement with experiment.

One motivation for the present work is the recent proposal[16,17] to measure by x-ray scattering the magnitude of charge-density waves accompanying a photon, i.e., for directly measuring the microscopic fields. The scattering efficiency[16] is proportional to a factor $|\Phi_{\vec{K}}|^2$ in the notation of Sinha, Gupta, and Price,[18] which from Eq. (3) may be shown to be

$$\Phi_{\vec{K}}=\epsilon^{-1}{}_{\vec{K},0}\epsilon_{0,0}/(\epsilon_{0,0}-1). \tag{7}$$

In the present RPA calculation we find the largest Φ to be $\Phi_{111}\approx 0.03$, which would yield a scattering efficiency about an order of magnitude lower than predicted for diamond in Ref. 16 on the basis of a rigid-bond charge model.

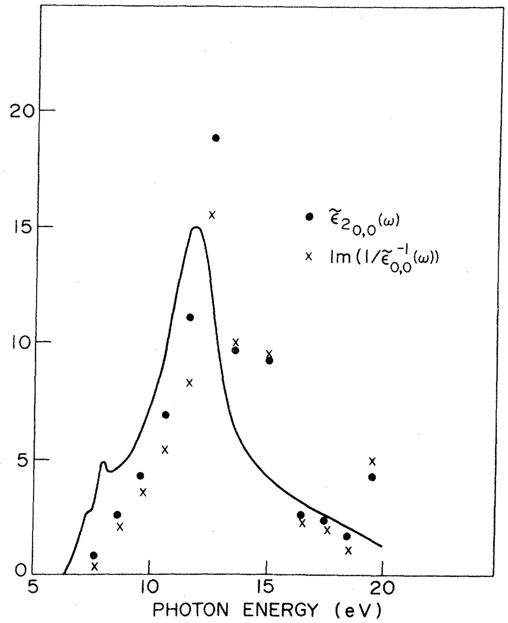

FIG. 2. Local field analysis with dynamical correlations. As in Fig. 1, solid curve is experiment and dots are C-E dielectric function; but crosses represent dielectric function $\epsilon'(\omega)$ including local fields with dynamical correlations given by Eq. (6).

One other result of the present calculation is that all elements $\tilde{\epsilon}_{\vec{K},\vec{K}+200}$, and elements related by symmetry to these, are small whereas, e.g., $\tilde{\epsilon}_{\vec{K},\vec{K}+111}$ is large. This is because there is no (200) Fourier component of the unperturbed crystal potential V whereas V_{111} is the largest component of V (after V_0). This is a band effect which is easily expressed in reciprocal space. In terms of approximations to ϵ pictured in real space, such as the factorization scheme of Sinha, Gupta, and Price[18] or a bond-charge mode,[19] such a result is more difficult to explain.

In summary, we have evaluated the RPA analysis of the local field effects for diamond. Results in that case, and for a wide variety of other covalent materials, deviate further from experiment than does the uncorrected analysis. A formula for incorporating effects of short-range dynamical correlations at frequencies above the band gap yielded good agreement with experiment over a wide frequency range. Finally, the Adler-Wiser RPA dielectric analysis has provided a "first-principles" estimate of the magnitude of the local fields, direct measurement of which appears feasible in proposed x-ray experiments.

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Magnetic Tricritical Points in Ising Antiferromagnets

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The thermodynamic properties of the antiferromagnetic Ising simple cubic and square lattices with nearest-neighbor and next-nearest-neighbor interactions have been studied using a Monte Carlo technique. Although both systems were found to possess magnetic tricritical points, their behavior in the "tricritical region" differed from that found in He^3-He^4 mixtures.

Over the past decade tremendous interest has been generated regarding the thermodynamic properties of both magnetic and gas-liquid systems near their critical points. New stimulus has been added recently by Griffiths[1] who examined the region of the two-fluid critical mixing point in He^3-He^4 mixtures and pointed out that the critical temperature corresponded to a thermodynamic "tricritical point," T_t. In addition, his examination of the experimental results showed that "classical theory"[2] clearly failed near T_t. Since there is no reason to expect any relation to the ordinary critical region, the "tricritical region" represents a totally new thermodynamic puzzle. Analogous tricritical behavior is also to be expected in magnetic systems (with suitable transformation of variables), and indeed magnetic tricritical points have been observed in $FeCl_2$,[3] $Ni(NO_3)\cdot 2H_2O$,[4] and dysprosium aluminum garnet (DyAlG).[5] Unfortunately, the experiments on these systems were not intended to probe the tricritical region and only in the case of DyAlG was the experimental resolution sufficient to map out the thermodynamic behavior near T_t. In DyAlG, however, the situation is complicated by the dominance of long-range dipolar interactions. Griffiths[1] used general arguments to propose a "scaling" form for the free energy. This expression appears quite successful for He^3-He^4, and an analogous form should apply to magnetic systems. Beyond this, theoretical support is very sparse.[6] Molecular field theory [7-9] does predict the existence of tricritical points in magnetic systems with competing interactions; however, this model fails completely in the ordinary critical region and should not be expected to be reliable near T_t. Because of the difficulty of including both competing interactions and a magnetic field in the Hamiltonian, series expansions have not been derived for any lattice. (The nearest neighbor only case has been considered.[10]) Thus, the only information available regarding magnetic systems comes from a small number of experimental reports of tricritical points in anisotropic systems.

It was our desire to investigate simple two- and three-dimensional magnetic systems in or-