

Local-Field Effects on Electroreflectance Line Shapes: the Contact Exciton

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Rowe and Aspnes have calculated the effect of a Slater-Koster interaction, or contact exciton, on the electroreflectance line shape of a semiconductor. We comment that their result is equivalent with the Lorentz-Lorenz result for the effect of a local electric field.

It has been noted¹⁻³ that one-electron-approximation calculations do not predict experimentally observed optical-modulation line shapes for any semiconductor modulation experiment. Rowe and Aspnes have investigated^{1,2} the effect of including a Slater-Koster interaction, or contact exciton, on the dielectric function at interband frequencies and, in particular, on the predicted electroreflectance line shape of Ge. If we denote⁴ by $\bar{\epsilon}(q, q', \omega)$ the one-electron dielectric function to which this contact-exciton correction is applied, i. e., the dielectric function defined by Ehrenreich and Cohen,⁵ then the result obtained by Rowe and Aspnes for the corrected dielectric function, $\epsilon(q, q', \omega)$, may be written as

$$\epsilon(q, q', \omega) - 1 = \frac{\bar{\epsilon}(q, q', \omega) - 1}{1 - g[\bar{\epsilon}(q, q', \omega) - 1]}. \quad (1)$$

In (1), q and q' denote the wave vectors of the macroscopic average electric field $E(q', \omega)$; ω is macroscopic average electric field $E(q', \omega)$; ω is their common frequency. The parameter g is proportional to the depth of the assumed square-well interaction between the electron and hole in the contact-exciton model. The parameter g is fitted to experiment for each critical point of the observed spectrum, but is assumed to be constant across the width of the electroreflectance signal associated with each critical point.

Rowe and Aspnes^{1,2} showed that this correction to the dielectric function greatly improved the calculated electroreflectance line shape. However, they did not realize that Eq. (1) is a widely used result of a simple Lorentz-Lorenz treatment of the local effective electric field⁶ in a solid with overlapping atoms. Such a correction must be made to $\bar{\epsilon}$ because Ehrenreich and Cohen neglected all polarization fields except that having the fre-

quency and wave vector of the applied field.^{5,7} Thus $\bar{\epsilon}$ is analogous to the "atomic polarizability" in the Clausius-Mossotti model in the sense that both are defined in terms of the polarization that would occur if the single-particle wave functions of the medium responded independently (i. e., with random phases) to the external applied field. In a Lorentz-Lorenz treatment one introduces an average field $E_e(q', \omega)$ effective in polarizing the medium. Except for the dependence on the small wave vector q' of the external field, $E_e(q', \omega)$ is defined to be constant throughout the unit cell. It is in fact the average of the full local field, which varies rapidly with position in the unit cell and fluctuates in time (at frequencies other than that of the driving field ω), weighted by the local polarizability of the medium.^{4,7,8} The Lorentz-Lorenz local effective field is often written as⁶

$$E_e(q', \omega) = E(q', \omega) + \frac{1}{3} \pi f P(q', \omega), \quad (2)$$

where $P(q', \omega)$ is the macroscopic average polarization. In Eq. (2) the parameter f is the ratio of the actual value of the Lorentz-Lorenz effective field to the value calculated for a Clausius-Mossotti model, $E = \frac{1}{3} \pi P$. (In a noncubic material, f is a tensor.) Equation (1), with $f = 3g$, may be derived from Eq. (2) by writing

$$P(q, \omega) = \chi(q, q', \omega) E(q', \omega) = \bar{\chi}(q, q', \omega) E_e(q', \omega) \quad (3)$$

and solving for χ in terms of $\bar{\chi}(q, q', \omega) = [\bar{\epsilon}(q, q', \omega) - 1]/4\pi$, i. e., the polarizability that would result in the absence of all local-field corrections.

The reason that the contact exciton and the Lorentz-Lorenz local-field treatments give the same correction to the Cohen-Ehrenreich dielectric function $\bar{\epsilon}(q, q', \omega)$ is that they represent the same approximation to the energy arising from the correlation of the induced polarization, or, equiva-

lently, the electron-hole pairs. As the spacial average of a dipole electric field is zero, the full local field would not affect the polarizability if it were not for the fact that the microscopic polarization induced at various points is correlated in time and in space.⁴ Both the Lorentz-Lorenz and the contact-exciton treatments replace the effect of these correlations (both umklapp and dynamical) with an interaction which is constant in the unit cell and independent of frequency. Then the value of either f or g is adjusted so that calculation and experiment agree for some limited optical feature or phenomenon. Different values of f and g would be required to fit different optical features or phenomena in the same material.^{1,2,6} It is very easy to evaluate the correlation energy $U(f)$ in the Lorentz-Lorenz picture:

$$U(f) = \int_0^f -\frac{1}{2} P(f) dE_e(f) = -\frac{1}{2} \int_0^f \frac{4}{3} \pi (\chi E)^2 df \\ = -\frac{f(\tilde{\chi} E)^2}{1 - \frac{4}{3} \pi f \tilde{\chi}} \quad (4)$$

The contact-exciton picture must give the same correlation energy $U(g) = U(f)$ for the same change in $\epsilon(q, q', \omega)$ in order that energy be conserved in that picture. This is difficult to show in general but for the limit $\hbar\omega \ll \mathcal{E}_k$, where \mathcal{E}_k is an excitation energy, the total energy of a solid in the presence of a field E can be written (see Appendix)

$$W(E) = W(0) = \frac{1}{2} \chi(q, q', \omega) E^2. \quad (5)$$

Thus the ground-state energy $W(0)$ is lowered by the induced polarization and for the same change in the polarizability $\tilde{\chi} - \chi$, both models result in the same change in total energy.

It seems that the question of whether or not the contact-exciton treatment of the electron-hole interaction is *identically* the same as the crude Lorentz-Lorenz treatment of the local fields resulting from the polarization of the medium is not well defined. If one restricts the consideration of each to the estimate of the energy resulting from the correlation of the induced polarization, then they are the same. If one considers the dynamics of the induced polarization, or the electron-hole pairs, then there is a question of how the models are to be adapted to the situation in a real material. It has been shown that the Clausius-Mossotti model can be adapted⁹ to give a good explanation of the pronounced anisotropy of the third-order electronic susceptibility¹⁰ in Si and Ge. This adaptation consisted of placing the dipoles at the bond site between the atoms rather than on the nuclei and computing the dependence of the field at the various bond sites on the direction of the applied field. These calculated local-field strengths were used to determine the proper value of the f parameter

in the Lorentz-Lorenz model in order to calculate the Franz-Keldysh-Aspnes effect at the E_0 critical point. From this, the third-order susceptibility⁹ for different field orientations was obtained. It seems likely that a similar adaptation of the contact-exciton model could be made, but we have not attempted this. Because of the simple form of the classical formalism, it appears that the local-field treatment can be applied to a wide range of problems in addition to the two examples discussed above.

As a final comment we will note that workers in the field of modulation spectroscopy generally neglect local-field effects, and occasionally assert that they are negligible in semiconductors.¹¹ Workers in the field of nonlinear optics observe the same physical effects, the electric field dependence of the optical index of refraction, as those which account for electroreflectance. These workers have long acknowledged the importance of local fields and invoked them to achieve agreement between theory and experiment.¹² A similar correlation exists between infrared absorption, where the full Lorentz-Lorenz correction is assumed, and stress-modulation experiments, where no correction is assumed. It would seem that it is time that the close connection between these experiments should be appreciated¹³; effects which are important in one must be present in the other.

APPENDIX

Equation (5) is usually derived by classical methods using a longitudinal geometry with associated boundary conditions. It is therefore of some interest to show that the energy lowering due to the electric field is independent of this geometry since the boundary condition which relates the field to the total energy can be replaced by the variational principle. Here we derive Eq. (5) by quantum methods suggested by Halperin.¹⁴

The Hamiltonian of a solid in an applied field E is

$$H = H_0 - \lambda E \sum_k (\alpha_k^\dagger \beta_{-k}^\dagger + \alpha_k \beta_{-k}), \quad (A1)$$

where H_0 is the unperturbed Hamiltonian and λ is a dipole matrix element assumed constant. The second term in Eq. (A1) is just the classical induced polarization interaction $\vec{P} \cdot \vec{E}$. The operator $\alpha_k^\dagger \beta_{-k}^\dagger$ creates an electron-hole pair with relative momentum k and no center-of-mass momentum (i. e., direct transitions). The wave function can be written

$$|\psi\rangle = (1 + E \sum_k f(k) \alpha_k^\dagger \beta_{-k}^\dagger) |0\rangle \quad (A2)$$

in terms of the unperturbed state $|0\rangle$. The mixing coefficients $f(k)$ can be determined from the variational principle which gives the result

$$f(k) = \lambda / \mathcal{E}_k, \quad (A3)$$

where \mathcal{E}_k is an optical transition energy. These excitation energies correspond to the direct inter-band gaps \mathcal{E}_k^0 in the one-electron approximation but are lowered by the electron-hole interaction which shifts oscillator strength to lower photon energies. By combining Eqs. (A1)–(A3) one obtains

$$\Delta W = \langle \psi | H | \psi \rangle - \langle 0 | H_0 | 0 \rangle = -\lambda^2 E^2 \sum_k \mathcal{E}_k^{-1}. \quad (\text{A4})$$

The susceptibility is defined as

$$\chi = \frac{\partial}{\partial E} \langle \psi | P | \psi \rangle = 2\lambda \sum_k f(k), \quad (\text{A5})$$

and using Eqs. (A3) and (A4)

$$\Delta W = -\lambda^2 E^2 \sum_k \mathcal{E}_k^{-1} = \frac{1}{2} \chi E^2, \quad (\text{A6})$$

which is the classical result obtained by using the variational principle instead of solving a boundary-value problem. The classical boundary-condition solution does not make clear the equivalence of transverse and longitudinal fields in the long-wavelength low-frequency limit with respect to the total energy of the solid.¹⁵

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Nuclear Quadrupole Resonance and Magnetic Relaxation in $(LaGd)Al_2$ [†]

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Nuclear-quadrupole-resonance and relaxation measurements have been made at low temperatures in the dilute $(LaGd)Al_2$ system at zero and low applied magnetic fields. The results complement those of McHenry, Silbernagel, and Wernick at high fields, and are consistent with the onset of magnetic order in the Gd random-spin system.

McHenry, Silbernagel, and Wernick¹⁻³ (hereafter referred to as MSW) have recently reported a series of nuclear-resonance and relaxation measurements in the pseudobinary alloy system $(LaGd)Al_2$. Their results were consistent with the absence of long-range magnetic order in this system, even in alloys with up to 10 at. % Gd and at temperatures below 4.2 K. Magnetization measurements in the same system⁴ indicated that, on the contrary, magnetic order is formed at or above 1.5 K for Gd concentrations above 2 at. %. Thus an apparent discrepancy exists between the nuclear-relaxation and magnetization results. MSW point out, however, that their relaxation measurements were carried out in applied magnetic fields

of greater than 2.5 kOe, whereas the magnetization measurements were made for the most part in low fields, of the order of 250–500 Oe. MSW speculated that the ordering process might affect magnetization and high-field nuclear-relaxation measurements quite differently, and also that the field might itself strongly influence the magnetic order.

We wish to report the results of Al^{27} nuclear-quadrupole-resonance (NQR) and relaxation measurements on the $(LaGd)Al_2$ system in zero and small applied fields which confirm qualitatively the first, and possibly the second, of the above speculations. The Al^{27} nuclei are situated in non-cubic sites in the cubic Laves-phase $LaAl_2$ lattice,^{5,6} and in zero static field exhibit the usual NQR spec-