Exciton Contributions to the Nonlinear Optical Susceptibility

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By using a simple hydrogenic model, we are able to account for the magnitude, sign, and tensor character of the exciton contribution to the nonlinear optical susceptibility in CuCl and ZnO.

Haueisen and Mahr,[1] and more recently Kramer, Parsons, and Bloembergen,[2] have done a beautiful series of experiments on the excitonic contribution to the nonlinear optical susceptibility. By tuning a dye laser (at frequency ω) so that the generated second harmonic frequency (2ω) swept through the exciton resonances, Haueisen and Mahr[1] were able to experimentally determine the magnitude, the sign, and the dispersion of the exciton contribution to the second-order nonlinear optical susceptibility d_{ijk}^{ex}, in CuCl and ZnO. Kramer, Parsons, and Bloembergen[2] also measured the dispersion of the exciton nonlinearity in CuCl using a different technique, namely resonant third-order mixing. We suggest below an extremely simple and physically transparent model which adequately accounts for the magnitude and sign of the exciton nonlinear polarizability and its close relationship to the exciton linear polarizability.

However, before describing this model it is instructive to examine first the equation of motion of the exciton and the total polarization P_i of the crystal. Following Yablonovitch, Flytzanis, and Bloembergen[3] and Kramer, Parsons, and Bloembergen[2] these are given by

$$M(\ddot{Q}_i+\Gamma\dot{Q}_i+\omega_T{}^2Q_i)=e_i{}^*E_i+\tfrac{1}{2}\,\alpha_{ijk}E_jE_k \tag{1}$$

and

$$P_i=Ne_i{}^*Q_i+\chi_{ii}E_i+N\alpha_{ijk}E_jQ_k+d_{ijk}E_jE_k\,, \tag{2}$$

where Q, Γ, ω_T, e^*, M, N, and α_{ijk} are the exciton internal coordinate, damping, transverse resonant frequency, effective charge, reduced mass, number density, and transverse "Raman" coefficient, respectively; χ_{ii} and d_{ijk} are the electronic linear and second-order susceptibilities, respectively. By combining Eqs. (1) and (2) to second order, the total linear $\chi_{ii}{}^{\mathrm{tot}}(\omega)$ and nonlinear susceptibility $d_{ijk}{}^{\mathrm{tot}}(\omega)$ can be obtained as[2,3]

$$\chi_{ii}{}^{\mathrm{tot}}(\omega)=\chi_{ii}+\frac{N(e_i{}^*)^2/M}{\omega_T{}^2-\omega^2+i\omega\Gamma}\,, \tag{3}$$

and

$$d_{ijk}{}^{\mathrm{tot}}(\omega)=d_{ijk}+\frac{\frac{3}{2}Ne_i{}^*\alpha_{ijk}/M}{\omega_T{}^2-\omega^2+i\omega\Gamma}\,, \tag{4}$$

where the second terms in Eqs. (3) and (4) are the resonant exciton contributions. At high frequencies ($\omega \gg \omega_T$) only the nonresonant electronic contribution remains whereas in the low-frequency limit ($\omega \ll \omega_T$) the exciton contributions to the linear $\chi_{ii}{}^{\mathrm{ex}}$ and nonlinear $d_{ijk}{}^{\mathrm{ex}}$ susceptibilities tend toward constant values,

$$\chi_{ii}{}^{\mathrm{tot}}(0)=\chi_{ii}+N(e_i{}^*)^2/M\omega_T{}^2\equiv\chi_{ii}+\chi_{ii}{}^{\mathrm{ex}}\,, \tag{5}$$

$$d_{ijk}{}^{\mathrm{tot}}(0)=d_{ijk}+\frac{3}{2}\;\frac{Ne_i{}^*\alpha_{ijk}}{M\omega_T{}^2}\equiv d_{ijk}+d_{ijk}{}^{\mathrm{ex}}\,. \tag{6}$$

In the notation of Haueisen and Mahr[1] these low-frequency excitonic contributions are denoted as A and B, i.e.,

$$B\equiv4\pi\chi_{ii}{}^{\mathrm{ex}}=4\pi N(e_i{}^*)^2/M\omega_T{}^2 \tag{7}$$

and

$$A\equiv d_{ijk}{}^{\mathrm{ex}}=\tfrac{3}{2}Ne_i{}^*\alpha_{ijk}/M\omega_T{}^2\,. \tag{8}$$

By fitting the expressions for the frequency-dependent susceptibilities $\chi_{ii}{}^{\mathrm{tot}}(\omega)$ and $d_{ijk}{}^{\mathrm{tot}}(\omega)$ [i.e., Eqs. (3)–(8)] to their resonant second-harmonic measurements, Haueisen and Mahr[1] determined the excitonic linear and nonlinear polarizabilities B and A.

Because of the complexity of CuCl and ZnO, wave functions of sufficient accuracy are not available (i.e., CuCl has important d-band contributions and the Zn and O atoms have much different covalent radii), and thus a fundamental microscopic quantum mechanical calculation of $d_{ijk}{}^{\mathrm{ex}}$ would be difficult. We are therefore led to attempt a much simpler macroscopic approach.

For the basis of our model we assume that the origin of the exciton nonlinearity, i.e., the origin of the electric field dependence of the exciton polarizability, is associated with the dependence of the core screening on the applied electric field. That is, an applied optical field changes the crystal dielectric constant ϵ (via the electronic nonlinearity d_{ijk}) and hence changes the effective core charge $Z_{\text{eff}} = Z/\epsilon$ of a hydrogenic-like exciton (where Z is the unscreened core charge). The hydrogenic problem can of course be solved exactly, and it is trivial to show that the linear polarizability of a hydrogenic system is proportional to $(Z_{\text{eff}})^{-4}$, and therefore

$$\chi^{\text{ex}} \propto \epsilon^4 . \tag{9}$$

Physically the reason that χ^{ex} increases as ϵ^4 is that the exciton binding energy E_{ex} decreases with ϵ $[E_{\text{ex}} \propto (Z_{\text{eff}})^2 \propto \epsilon^{-2}]$, while the exciton radius a_{ex} increases with ϵ $[a_{\text{ex}} \propto Z_{\text{eff}} \propto \epsilon]$, both of which increase the exciton polarizability $[\chi^{\text{ex}} \propto (a_{\text{ex}})^2/E_{\text{ex}} \propto \epsilon^4]$. Thus, since ϵ is a function of field (via d_{ijk}) the exciton screening and polarizability are nonlinear. More precisely, an examination of the $d_{ijk}E_jE_k$ term in Eq. (2) shows that the change in the electronic dielectric constant $\Delta\epsilon$ caused by an optical field E_k can be written as

$$\Delta\epsilon_{ij} = 8\pi d_{ijk} E_k . \tag{10}$$

As Eq. (9) shows, this change $\Delta\epsilon$ of the electronic polarizability will produce a corresponding change in the exciton polarizability $\Delta\chi^{\text{ex}}$ of an amount

$$\Delta\chi_{ij}^{\text{ex}} = (4\chi_{ii}^{\text{ex}}/\epsilon)(8\pi d_{ijk}E_k). \tag{11}$$

Using the definition of the exciton nonlinearity d_{ijk}^{ex} corresponding to that for the electronic nonlinearity of Eq. (10), namely

$$\Delta(4\pi\chi_{ij}^{\text{ex}}) = 8\pi d_{ijk}^{\text{ex}} E_k , \tag{12}$$

yields our final result, namely

$$d_{ijk}^{\text{ex}} = 4(4\pi\chi_{ii}^{\text{ex}}/\epsilon) d_{ijk} . \tag{13}$$

In the notation of Haueisen and Mahr,[1] i.e., Eqs. (7) and (8), and defining $d_{ijk} \equiv d^\infty$, Eq. (13) can be written as

$$(A/d^\infty) = 4(B/\epsilon). \tag{14}$$

Our expression for d_{ijk}^{ex} [Eqs. (13) and (14)] predicts a number of remarkably simple results.[4] First the exciton nonlinearity d_{ijk}^{ex} is proportional to both the electronic linear χ_{ii} and nonlinear d_{ijk} susceptibilities. Thus, the selection rules for the allowed d_{ijk}^{ex} coefficients are determined by the requirement that both d_{ijk} and χ_{ii} not vanish. For example, the A exciton in CdS is only strong for E perpendicular to the c axis (i.e., $\chi_{11}^{\text{ex}} \neq 0$, $\chi_{33}^{\text{ex}} \simeq 0$). Therefore, $d_{333}^{\text{ex}} \simeq 0$, $d_{311}^{\text{ex}} \simeq 0$, but $d_{113}^{\text{ex}} \neq 0$ which is, of course, a strong violation of the Kleinman symmetry relation $d_{ijk}^{\text{ex}} = d_{kji}^{\text{ex}}$. Further, for nonzero χ_{ii}^{ex}, Eq. (13) implies (a) that the absolute signs of the excitonic and electronic nonlinearities are the same, (b) that all the different tensor components of d_{ijk}^{ex} have nearly the same proportionality constant, i.e., the ratio $d_{ijk}^{\text{ex}}/d_{ijk}$ is almost independent of the tensor indices *ijk* (since χ_{ii}^{ex} is quite isotropic for zinc-blende and wurtzite crystals), and (c) that the ratio of the fractional contribution of the exciton nonlinear polarizability [i.e., $d_{ijk}^{\text{ex}}/d_{ijk} \equiv A/d^\infty$] to the fractional contribution of the exciton linear polarizability [i.e., $4\pi\chi_{ii}^{\text{ex}}/\epsilon \equiv B/\epsilon$] is independent of any crystal parameters and is, in fact, a *pure constant*, i.e., $(d_{ijk}^{\text{ex}}/d_{ijk})/(4\pi\chi_{ii}^{\text{ex}}/\epsilon) = +4$, as shown by Eqs. (13) and (14).

We can now compare the experimental values of Haueisen and Mahr[1] with our theoretical predictions based on Eqs. (13) and (14), for the various components d_{ijk}^{ex} for both CuCl and ZnO. In this connection it is important to note that the crystal dielectric constant ϵ appearing in Eqs. (13) and (14) (and elsewhere) is that appropriate to the particular exciton of interest for which the linear and nonlinear susceptibilities χ_{ii}^{ex} and d_{ijk}^{ex} have been determined. The reason for this is that it is well known that the appropriate effective dielectric screening is a function of the exciton radius,[5,6] i.e., $\epsilon = \epsilon(r)$. This is true since for large-orbit excitons the lattice motion can follow the slowly moving exciton and hence the relevant dielectric constant is the static one ϵ_0. However, for small-radius excitons the exciton motion is too rapid for lattice screening to be effective and hence the optical-frequency dielectric constant ϵ_∞ is appropriate. For excitons of intermediate radius, the effective dielectric screening constant varies smoothly between these limits.

Table I shows that the magnitude and sign of the experimental values of $d_{ijk}^{\text{ex}}/d_{ijk}$ are in good agreement with the predicted value of $16\pi\chi_{ii}^{\text{ex}}/\epsilon$.[11] It is especially noteworthy that the experimental values of $d_{ijk}^{\text{ex}}/d_{ijk}$ are the same for both the d_{333}^{ex} and d_{311}^{ex} exciton resonances as predicted by Eqs. (13) and (14), even though the nonlinear coefficients d_{333}^{ex} and d_{311}^{ex} differ not only in magnitude by a factor of 2, but also in sign (i.e., $d_{333}^{\text{ex}}/d_{311}^{\text{ex}} = -2$). Further, it is worth mentioning that this good agreement is obtained in spite of the complexity of the electronic nonlinearity in CuCl and ZnO. That is, CuCl and ZnO are among the few *negative* nonlinear susceptibilities [i.e., $d_{333}(\text{ZnO}) < 0$, $d_{123}(\text{CuCl}) < 0$] in

TABLE I. The experimental measurements of Haueisen and Mahr (Ref. 1) for the ratio of the excitonic to electronic second-order nonlinear susceptibilities ($d_{ijk}^{\text{ex}}/d_{ijk}$) are compared with our theory [Eqs. (13) and (14)], and are seen to be in good agreement. The experimental absolute signs of d_{ijk} are shown (note especially d_{333} and d_{311} of ZnO) to indicate that the ratio $d_{ijk}^{\text{ex}}/d_{ijk}$ is independent of these signs as predicted by Eq. (13).

Crystal	Coefficient (Sign)	Exciton Symmetry	ω_T (eV)	ϵ	$4\pi\chi^{\text{ex}}$ (10^{-3})	$d^{\text{ex}}_{ijk}/d_{ijk}$ (10^{-3}) Theory	$d^{\text{ex}}_{ijk}/d_{ijk}$ (10^{-3}) Experiment
CuCl[a,b]	$d_{123}(-)$	$1f(\Gamma_6\times\Gamma_7)$	3.204	5.4	20	+15	+17
CuCl[a,b]	$d_{123}(-)$	$1d(\Gamma_6\times\Gamma_8)$	3.268	6	50	+33	+24
ZnO[a,c]	$d_{333}(-)$	$C(\Gamma_7\times\Gamma_7)$	3.420	8.6	30	+14	+17
ZnO[a,c]	$d_{311}(+)$	$C(\Gamma_7\times\Gamma_7)$	3.420	8.6	30	+14	+17
GaAs[d]	$d_{123}(+)$	$(\Gamma_1\times\Gamma_5)$	1.515	12.6	1.6	+0.51	
InP[e]	$d_{123}(+)$		1.419	12.1	2.35	+0.78	
ZnS[f]	$d_{123}(+)$	A	3.799	8.1	10.4	+5.1	
ZnSe[f]	$d_{123}(+)$	A	2.799	8.7	5.4	+2.5	
ZnTe[f]	$d_{123}(+)$	A	2.381	9.7	4.4	+1.8	
CdTe[f]	$d_{123}(+)$	A	1.596	9.7	4.8	+2.0	
CdS[f]	$d_{113}(-)$	A	2.554	8.5	12.5	+5.9	
CdS[f]	$\begin{Bmatrix} d_{113}(-) \\ d_{333}(+) \\ d_{311}(-) \end{Bmatrix}$	B	2.569	8.5	8.2	+3.9	

[a] Ref. 1.
[b] Ref. 6.
[c] Ref. 7.
[d] Ref. 8.
[e] Ref. 9.
[f] Ref. 10.

the class of tetrahedral semiconductors; most of the other compounds such as GaAs are simpler and *positive.*[12] This unusual behavior for these two crystals arises from unrelated complications. In CuCl there is a significant *d*-band contribution from the noble-metal *d* electrons,[13] whereas in ZnO it is the unequal covalent radii of the Zn and O atoms which produce the negative nonlinearity.[13] Therefore, it would certainly be of great interest to do this type of exciton-resonance experiment on a simpler crystal such as GaAs which has an extremely well characterized[8] and closely hydrogenic exciton, and for which $d_{123} > 0$. To encourage such measurements we have listed our theoretical predictions for GaAs as well as for other common zinc-blende and wurtzite semiconductors in Table I. The predicted large differences between the III-V, II-VI, and I-VII semiconductors provide good opportunities to test this theory.

In conclusion, by the use of an extremely simple physically transparent model [i.e., Eq. (9)] we have been able to adequately account for the magnitude, sign, and tensor character of the exciton contribution d_{ijk}^{ex} to the second-order nonlinear optical susceptibility in CuCl and ZnO. We have also predicted d_{ijk}^{ex} for a variety of common III-V, II-VI, and I-VII zinc-blende and wurtzite semiconductors.

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[4] Of course these simple expressions can only be expected to hold for the ground state ($n = 1$ exciton). The excited states ($n = 2, 3,$ etc.) are obviously more complex and a quantum mechanical treatment would be required. For example, the $n \approx 2$ C exciton in ZnO ($\omega_T = 3.465$ eV) has a nonlinearity (from Ref. 1) of ($d_{ijk}^{\text{ex}}/d_{ijk}$) $\simeq -0.05$, whereas the value calculated from Eq. (13) is $+0.005$. This sign change and order of magni-

tude increase (for the $n = 2$ excited state) over the ground state ($n = 1$) calculation may be related to the nearly degenerate $2s$ and $2p$ exciton energy levels $E(2s)$ and $E(2p)$. In fact $[E(2p) - E(1s)]/[E(2p) - E(2s)] \simeq -17$ [R. Dinges, D. Fröhlich, B. Staginnus, and W. Staude, Phys. Rev. Lett. 25, 922 (1970).

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New Bond-Charge Model for the Lattice Dynamics of Diamond-Type Semiconductors

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A new bond-charge model for phonons in semiconductors of diamond structure is presented. I show that the flattening of the transverse acoustic phonon branches in these materials can be understood by interactions involving the bond charges, when these move adiabatically. The phonon spectrum of Ge is calculated using only four parameters, all of which are physically meaningful, and very good agreement with experimental values is obtained.

The phonon dispersion relations of all semiconductors with diamond or sphalerite structure[1] exhibit one characteristic feature, from which only diamond itself is excepted: The transverse acoustic (TA) phonon branches have very low frequencies and are very flat away from the zone center, although the corresponding shear moduli have rather high values. In the following, I show that this can be understood by interactions involving the bond charges (BC's), if these are allowed to move adiabatically. My model also enables us to elucidate the differences in the nature of the binding forces in the group IV materials.

Based on Phillips's bond-charge model[2] for covalent crystals, Martin[3] has used a dielectric screening model to calculate the phonon spectrum of Si. He assumed that the bare-ion-core potentials are screened in a nearly free-electron-like manner; i.e., by the diagonal elements of the inverse dielectric function $\epsilon^{-1}(\vec{q}+\vec{G}, \vec{q}+\vec{G}')$. This metallike binding gives rise to short-range central forces between the ions, which die out rapidly beyond nearest neighbors. The effect of the off-diagonal elements of ϵ^{-1} is described by Coulombic interactions involving the BC's. These forces represent the covalent character of the binding; they lead to effective noncentral forces between the ions, which produce the stability of the diamond structure against shear. The specific assumption was made that the BC's were fixed midway between the ions, even when the latter are displaced. Martin obtained fair agreement with experimental dispersion curves, except that the flattening of the TA phonons could not be reproduced.

In 1959, Cochran[4] pointed out that this flattening of TA branches, which in a Born and von Kármán model requires very long-range force constants,[5] is in fact due to mainly short-range ion-electron and electron-electron interactions. Cochran's shell model (SM), however, has many drawbacks. The noncentral two-body forces, which are crucial for the stability against shear, are not adequately understood.[6] Further, the electrons in a bond are shared by two atoms and it is unphysical to divide them between the two.[7] Finally, it turned out to be impossible to extend the SM to III-V compounds without introducing many new parameters, although the phonon spectra are very similar.[1]

The starting point of my work is the bond-charge model; i.e., I describe the effect of the