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A NEW CONTRIBUTION TO THE NONLINEAR OPTICAL SUSCEPTIBILITY ARISING FROM UNEQUAL ATOMIC RADII

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Compounds containing a first-row atom are shown to have an important additional contribution to the nonlinear optical susceptibility d_{ijk}. Inclusion of this effect explains the anomalous sign of d_{33} for ZnO and leads to excellent agreement with experiment.

Recently Miller and Nordland[1] have measured the absolute signs in a variety of nonlinear materials. They observed a remarkable change of sign in d_{ijk} between ZnO (d_{33}) which is negative and the other measured semiconductors which are all positive [e.g., ZnTe (d_{14}), CdS (d_{33}) GaAs (d_{14}), etc.]. There are at least two reasons why this result is surprising. First, the ionicity f_i of ZnO is very similar to all the other II-VI's. Secondly, the bond-charge calculation[2] of nonlinear optical susceptibilities which has been highly successful in accounting for the magnitude and signs of the normal III-V and II-VI semiconductors (i.e., GaAs, CdS, etc.) predicts the wrong sign for ZnO.

Nevertheless, ZnO is unusual since there is a large difference in size between the Zn and O atoms, (the Zn covalent volume[3] is about 6 times larger than that of O). In fact most compounds containing a first-row element will be anomalous because the covalent radii[3] r_α of first-row elements are much smaller than those of any other row.

The bond charge q will be situated very close to the intersection of r_α and r_β since this is where the atomic overlap that produces q is a maximum. When the bond charge is acentrically located (i.e., $r_\alpha \neq r_\beta$) we will demonstrate that in addition to the usual antisymmetric potential (C) contribution to d_{ijk}, there is a further contribution arising from the homopolar energy gap E_h. In fact the electric field dependence of E_h is also necessary in order to explain the sign of the third-order nonlinear susceptibility[4] C_{ijkl}.

The average homopolar gap that the bond charge experiences is experimentally[5] given by

$$E_h^2 = a/r_0^{2s}, \tag{1a}$$

$$(\chi_h)_{\text{av}} = (4\pi)^{-1}\Omega_p^2/E_h^2, \tag{1b}$$

where r_0 is the average radius $= \frac{1}{2}(r_\alpha + r_\beta) = \frac{1}{2}d$, $s = 2.48$, a is a known constant, and χ_h is the average homopolar susceptibility of the bond charge. Although Eq. (1) is completely adequate for describing the linear susceptibility, the nonlinear susceptibility is more sensitive to the crystal potentials and hence a more accurate microscopic description of E_h is necessary. Both atoms α and β contribute to the average susceptibility:

$$(\chi_h)_{\text{av}} = \tfrac{1}{2}[(\chi_h)_\alpha + (\chi_h)_\beta], \tag{2a}$$

$$(\chi_h)_\alpha = (4\pi)^{-1}\Omega_p^2/(E_h^2)_\alpha, \tag{2b}$$

where Eq. (2b) is a generalization of Eq. (1b). In order to generalize Eq. (1a) we replace the average radius r_0 by the actual radius r_α at which the bond charge is located. Thus,

$$(E_h^2)_\alpha = a'(r_\alpha - r_{c\alpha})^{-2s}, \tag{2c}$$

where a' is another constant and $r_{c\alpha}$ is the core radius of atom α. This $r_{c\alpha}$ must be included since the valence-electron wave functions are orthogonal to those of the core. Hence, the probability of finding a valence electron in the core region is very small, and the contribution to the susceptibility from these states must also be small. In order to simplify the calculation we will replace $r_{c\alpha}$ and $r_{c\beta}$ by a typical average core radius $r_c = 0.3r_0$ which is its value[3] in ZnO.

Combining Eqs. (2) yields

$$(E_h)_\alpha^{-2} = \frac{1}{2}\left[\frac{(r_\alpha - r_c)^{2s}}{a'} + \frac{(r_\beta - r_c)^{2s}}{a'}\right]. \qquad (3)$$

It should be remarked that the results of calculating the linear susceptibility $\chi = (4\pi)^{-1}\Omega_p^{\,2}/E_g^{\,2}$ ($E_g^{\,2} = E_h^{\,2} + C^2$) using Eq. (3) agree just as well with experiment as using Eq. (1a). In particular using the same individual gaps $(E_h^{\,2})_\alpha$ for an interrelated set of crystals (e.g., InAs, InSb, GaAs, GaSb) gives good agreement with the total experimental gaps $E_h^{\,2}$.

An electric field $\mathcal{E}$ will displace the bond charge[6] q by an amount Δr_α given by

$$P = \chi\mathcal{E} = Nq\Delta r_\alpha \equiv (\nu/d^3)q\Delta r_\alpha, \qquad (4)$$

where N is the number of bonds/cm^3 ($\nu = 3\sqrt{3}/4$ for zinc blende and wurtzite structures). This displacement will change both the ionic and covalent energy gaps[2,5] ΔC and ΔE_h, and hence the linear susceptibility becomes electric field dependent. Thus, identifying[2] the coefficient of the linear $\mathcal{E}$ term with the nonlinear susceptibility, we arrive at the total nonlinearity d_{ijk}. Physically Miller's $\Delta_{ijk} = d_{ijk}/\chi^3$ is more fundamental than d_{ijk} since Δ should be proportional to the total acentricity of the bond. The results of this calculation are

$$\begin{aligned} \Delta_{ijk} &= \Delta_{ijk}(C) + \Delta_{ijk}(E_h), \\ \Delta_{ijk}(C) &= [4\pi(300)\gamma]\frac{G_{ijk}d}{(\Omega_p)^2}C, \\ \Delta_{ijk}(E_h) &= \left[\frac{4\pi(40)}{\nu}\frac{G_{ijk}d^2E_h^{\,2}}{(\Omega_p)^2 q}\right]\rho, \end{aligned} \qquad (5)$$

where $\Delta(C)$ (derived in Ref. 2) and $\Delta(E_h)$ refer to the contribution arising from the electric field dependence of C and E_h, respectively. The $\Delta(E_h)$ term is completely new; its crucial importance has not been realized previously. G_{ijk} is the geometrical factor,[2] and $\rho = (r_\alpha - r_\beta)/(r_\alpha + r_\beta)$ is the normalized measure of the displacement of q from the exact center of the bond.

Equation (5) shows that Δ_{ijk} depends on the total acentricity of the bond, which can be thought of as arising from two distinct sources. One type of acentricity $[\Delta(C)]$ is the electronegativity difference between the bonding atoms as measured by the ionic energy gap C. The second acentricity $[\Delta(E_h)]$ is the displacement ρ or q off center.

Because $\Delta(E_h)$ vanishes when $\rho = 0$ (e.g., GaAs) this term is only important for crystals like ZnO which contain a first-row element, and hence have widely different sized atoms. In crystals laking a first-row element, ρ is so small (e.g., $\rho = 0.04$, ZnS; $\rho = 0.068$, InAs) that ρ is not significantly different from zero within the uncertainty for the determination of r_α (at least 5%) and thus for simplicity we take $\rho = 0$ for this case.

The sign of Δ is vitally important since a theory which gives the wrong sign (even if it coincidentally gives the correct magnitude) may be missing some important physics. Fundamentally the signs of $\Delta(C)$ and $\Delta(E_h)$ reflect whether the potentials increase or decrease upon the application of a positive field $\mathcal{E}$. The sign of ρ is positive if the metal atom is larger (e.g., $\rho > 0$, ZnO) and negative otherwise ($\rho < 0$, BAs); while the sign of $\Delta(E_h)$ is opposite to that of ρ (remenber $q < 0$).

Table I lists all the AB semiconductors for which ρ is large,[3] and for comparison, ZnTe. The agreement with experiment is excellent both in magnitude and sign and is obtained without adjustable parameters. The relative importance of the two effects (electronegativity C, displacement ρ) can vary widely. For example in ZnTe $\rho \simeq 0$, and C is large, while in BAs $C \simeq 0$, and ρ is large. For the interesting intermediate case of BeO both acentricities oppose one another so that the bond appears to have no net asymmetry and Δ is an order of magnitude smaller[7] than the

Table I. Comparison of theory and experiment for the nonlinear optical coefficient d_{ijk}. For wurtzite (w) d_{33} is given, for zinc blende (z) d_{14} is given, while for left quartz (l) d_{11} is given. The asterisk means that good index of refraction data are unavailable (we used that of Ref. 6); hence the calculation is less accurate for these materials.

Crystal	ρ	$d_{ijk}(C)$	$d_{ijk}(E_h)$	d_{ijk} calc	d_{ijk} expt
		(10^{-9} esu)		(10^{-9} esu)	
InN(w)*	+0.323	+94	−212	−118	
ZnO(w)	+0.288	+25	−53	−28	−22[a]
GaN(w)*	+0.260	+52	−115	−63	
AlN(w)	+0.211	+43	−84	−41	
SiC(w)	+0.205	+70	−268	−198	
SiC(z)	+0.205	+61	−232	−171	
BeO(w)	+0.180	+7.1	−8.4	−1.3	−0.75[b,c]
BAs(z)*	−0.179	+28	+846	+874	
SiO_2(l)	+0.268	−0.96	+2.18	+1.22	+1.2[c]
ZnTe(z)	$\simeq 0$	+300	$\simeq 0$	+300	+310[c]

[a] Ref. 1.

[b] Ref. 8.

[c] R. C. Miller, private communication. The sign of Δ for BeO is based on etch patterns.

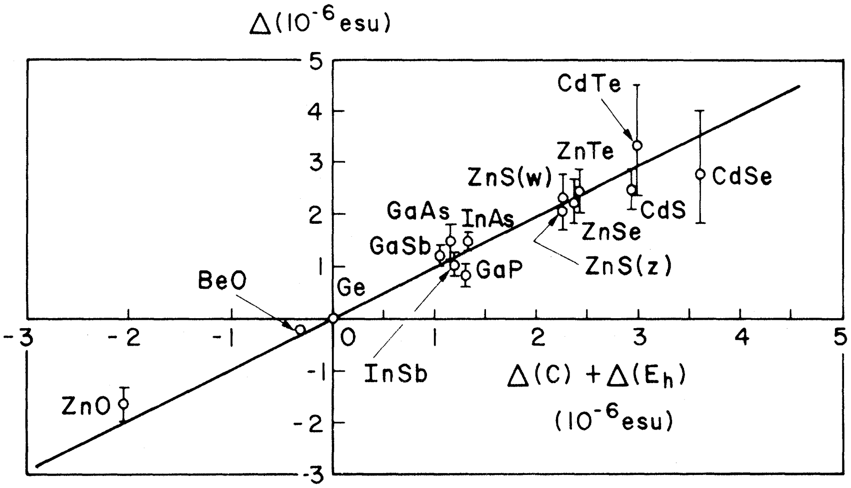

FIG. 1. Plot of theory (the straight line uses no adjustable parameters) versus experiment for Miller's Δ.

average value. The small value of Δ in $LiGaO_2$[8] is probably also due to such a near cancellation. Note especially that the anomalous negative sign of Δ_{33} in ZnO is completely explained, as is the anomalous sign of the more complicated crystal SiO_2.

Figure 1 exhibits more clearly the excellent agreement in magnitude and sign between theory, given by the straight line [Eq. (5)], and experiment. The experimental signs for most (see Ref. 1 and Table I, Ref. c) of the materials shown are known. Note again how the anomalous negative sign of Δ_{33} in ZnO is clearly explained.

It is very useful to obtain a simple physical measure of the total bond acentricity, which we will denote by δ. Using several reasonable approximations, Eq. (5) can be simplified to

$$\Delta \simeq 3.7\times 10^{-6}\delta \text{ esu};\quad \delta = f_i - 4\rho. \tag{6}$$

Figure 2 dramatically demonstrates the good fit of Eq. (6) for both positive and negative δ (i.e., both first-row and nonfirst-row crystals). It is satisfying that there is complete symmetry between positive and negative δ. In particular, for these crystals δ has the corresponding maximum and minimum values of about ±0.75, with Δ having the extreme values of about $\pm 3\times 10^{-6}$ esu.

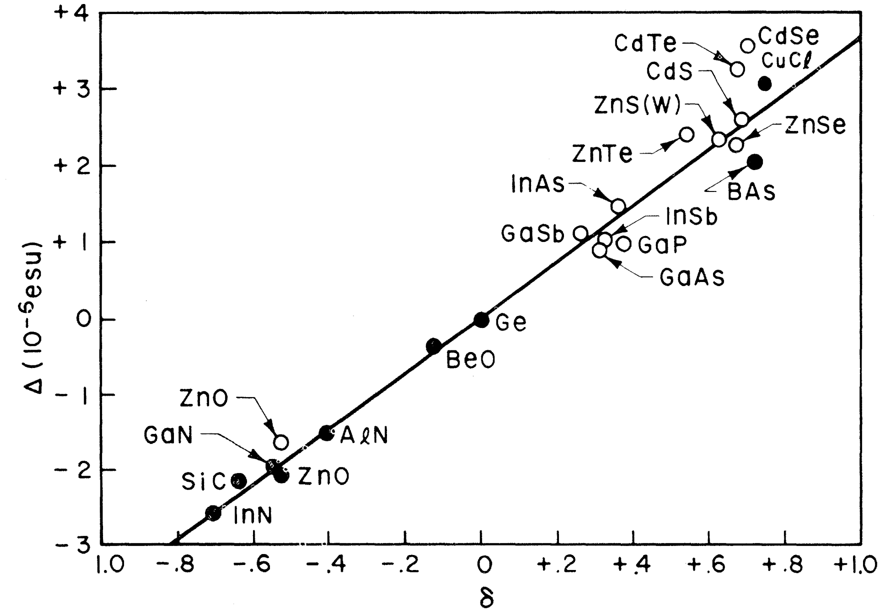

FIG. 2. Plot of Miller's $\Delta = 3.7\times 10^{-6}\delta$ esu against the total bond acentricity $\delta = f_i - 4\rho$. Open circles are experimental points (see Ref. 2 for references); closed circles are calculated from Eq. (5).

Another satisfying feature of δ is that the peculiar BAs which has $f_i \simeq 0$ and a large negative value for ρ (making δ positive) is right on the curve of Fig. 2 along with say ZnSe which has about the same positive δ (but which arises from the opposite situation $\rho = 0$ and large f_i). This is powerful evidence that δ is truly a fundamental measure of the total fractional acentricity. In this light we can say that CuCl and InN which have δ's of $\simeq \pm 75\,\%$, respectively, are about as close to the maximum possible distortion ($\delta = \pm 100\,\%$) and consequently the largest Δ (4×10^{-6} esu) one can get in these crystals before there is a phase change[5] to a six-fold-coordinated structure.

In conclusion, we have shown the importance of the acentricity produced by the displacement of the bond charge off center. Without adjustable parameters, this effect completely explains the "anomalous" sign of ZnO and SiO_2 as well as the very small value for Δ in BeO. It is very important to be aware of such possible cancellations (i.e., $\delta \simeq 0$) if one wants to find materials with large nonlinear coefficients.

We are grateful to Robert C. Miller, W. A. Nordland, and J. Jerphagnon for making their results available prior to publication.

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[2] B. F. Levine, Phys. Rev. Lett. 22, 787 (1969).

[3] J. A. Van Vechten and J. C. Phillips, to be published.

[4] This additional term was not included in Ref. 2 but is discussed in B. F. Levine, to be published.

[5] J. A. Van Vechten, Phys. Rev. 182, 891 (1969), and 187, 1007 (1969).

[6] A complete discussion of the determination of q is given in Ref. 5. The result $\gamma = 6$ for these crystals, which was used in Ref. 2, arises from a direct calculation using the correct value of q for each material. The order of magnitude of q for these semiconductors is $\simeq \frac{1}{2}e$, although it varies somewhat.

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ISING MODEL WITH A TRANSVERSE FIELD

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The phase transition in the Ising model has been studied as a function of an applied transverse field, by Green's function and series-expansion methods. The critical indices are probably independent of the applied field except at $T = 0$ where they appear to be related to those of the Ising model in one higher dimension.

The Ising model in a transverse field can be represented by the Hamiltonian

$$\mathcal{H} = -\Gamma \sum_i S_{ix} - \tfrac{1}{2} \sum_{ij} J_{ij} S_{iz} S_{jz}, \qquad (1)$$

where S_{ix}, S_{iz} are spin-$\frac{1}{2}$ operators and where the sums extend over the points of a lattice. This model corresponds to the pseudospin formulation of phase-transition problems and may be used to study order-disorder ferroelectrics with a tunneling effect[1] or the magnetic ordering in materials with singlet crystal-field ground states.[2] It is one of the simplest models where a phase transition takes place at a finite external field.[3] There exists a phase boundary in the Γ-T plane as shown in Fig. 1, where results calculated by various methods for a simple cubic lattice with nearest-neighbor interactions are plotted. The curve is limited by the points $\Gamma = 0$, $T = T_c$ (Ising model) and $T = 0$, and $\Gamma = \Gamma_c$, where Γ_c is the critical transverse field. In the region above the curve the S_z components are disordered although $\langle S_{ix} \rangle \neq 0$. The transverse field plays a role which is in many ways similar to the temperature and the critical temperature decreases as the field increases.

The system has first been studied using a Green's function method,[4] where the equations of motion for the Green's functions were decoupled by a scheme introduced by Callen[5] for the Heisenberg model. The high-temperature susceptibility is calculated in a self-consistent way and diverges at the critical temperature. The phase boundary curve thus obtained is plotted in Fig. 1 (curve 3). In the limit $\Gamma \to 0$ this approximation corresponds to the spherical model of the Ising case.

A better result is obtained from a series expansion of the susceptibility[6] in $(\beta J)^n$, where $\beta = 1/kT$:

$$\chi = \sum_{n=0}^{\infty} \alpha_n (\beta\Gamma)(J\beta)^n. \qquad (2)$$

This series has been calculated up to $n = 5$ from