Dispersion of Nonlinear Optical Susceptibilities in Hexagonal II-VI Semiconductors*

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We have determined the dispersion of three independent nonlinear optical susceptibilities, $|d_{15}|$, $|d_{31}|$, and $|d_{33}|$, for CdS and CdSe. Tunable dye lasers (0.73 to 1.0 μm) were used. In spite of the large absorption at the second harmonic and/or fundamental wavelengths, Kleinman's relation ($d_{15}=d_{31}$) holds. The ratio $|d_{33}/d_{31}|$ exhibits dispersion and deviates from Robinson's relation (ratio of 2). The relative phase angles between d_{15} and d_{31} and between d_{31} and d_{33} were measured at two wavelengths by a new reflection interference technique.

A II-VI semiconductor with $6mm$ point group has three independent nonlinear optical coefficients, d_{15}, d_{31}, and d_{33}.[1] Several calculations[2,3] have suggested that additional symmetries exist among the components of the d tensor. For a lossless and dispersionless crystal, Kleinman[2] predicted $d_{15}=d_{31}$. Robinson,[3] using symmetry properties of isolated AB_4 tetrahedra, further predicted $d_{33}=-2d_{31}$. More recent calculations,[4,5] based on Phillips's dielectric theory of electronegativity,[6,7] have yielded similar relations among the components of the d tensor. Levine[5,8] has calculated both the absolute magnitudes and signs of the nonlinear optical coefficients. These are in excellent agreement with experiment.[9] Recently, numerous experiments[10-12] and theory[13,14] have considered the dispersion of the nonlinear optical coefficients of $\bar{4}3m$ crystals in the region where $2\hbar\omega$ is strongly absorbed. However, none of the theoretical and experimental results have dealt with crystals of $6mm$ symmetry in the absorption region. This paper will present the dispersion measurements of $|d_{33}|$, $|d_{15}/d_{31}|$, and $|d_{33}/d_{31}|$ in the range where the second-harmonic photon energy $2\hbar\omega$ is near and much larger than the exciton energy gaps of CdS and CdSe. The relative phases among d_{15}, d_{31}, and d_{33} will also be presented at several wavelengths. Dispersion measurements of d coefficients in $6mm$ crystals will enable one to test the generality of the additional symmetry relations in the d tensor.

The experimental arrangement and apparatus used in this investigation have been reported previously.[12] The tunable dye lasers[15] (0.7 to 1.0 μm) were pumped by a Q-switched ruby laser. The second-harmonic photons generated by transmission from the quartz monitor[16] and generated by reflection from the sample under study were detected by two photomultipliers (EMI 9635QD). The two photocurrent outputs were digitized by a gated electronic pulse integrator which had the capability of accumulating data from successive laser pulses. The CdS and CdSe single crystals were oriented with their a axes as the face normal and their c axes in the crystal face. Since the generation of reflected second harmonic requires careful crystal preparation, the crystal surfaces were polished with Linde C, A, and B abrasives in succession and were then mildly etched.[17] The quality of the crystal surface was judged in two ways. First, the crystal surface had to have good mirrorlike reflection. This prevented large beam divergence and poor definition of the face normal. Second, the reflected harmonic intensity had to adhere to polarization selection rules. The "forbidden" intensity was at most $\frac{1}{20}$ of the "allowed" intensity for all the wavelengths we investigated.

For optically isotropic crystals, such as $\bar{4}3m$ semiconductors, the formula relating the reflected harmonic intensity $I_R(2\omega)$ to the nonlinear optical coefficient has been presented by Bloembergen and Pershan.[18] For uniaxial crystals, such as $6mm$ semiconductors, the formulas relating $I_R(2\omega)$ to the three independent d coefficients are somewhat more involved. The fundamental and harmonic polarizations must be decomposed into ordinary and extraordinary rays or a mixture of the two. Several calculations[19-21] have dealt with the reflected harmonic radiation from uniaxial crystals. The most thorough treatment was that by Fischer.[21] Because of an unfortunate choice of axes to represent the reflected electric field at $2\hbar\omega$, Fischer's results were only correct for a few special crystal orientations and polarizations of the fundamental and harmonic radiations. We have corrected Fischer's results. The details will be reported elsewhere.

To measure the dispersion of the modulus of the nonlinear coefficients, the crystal and the polarizations of the fundamental and harmonic field must be so oriented that $I_R(2\omega)$ arises only from one element of the d tensor. To specify these orientations we shall define the following angles: (i) α, the angle between the vertical and the c axis; (ii) β, the angle between the vertical and the polarization axis of the analyzer; (iii) θ, the angle of incidence and thus, the angle of reflection. The polarization of the incident electric field was always vertical.

To measure the dispersion of $|d_{33}|$, $\alpha = 0$, $\beta = 0$, and $\theta = 45°$. In this case, the formula connecting $I_R(2\omega)$ to $|d_{33}|$ reduces to that derived by Bloembergen and Pershan. The linear extraordinary dielectric constants should be used. The $I_R(2\omega)$ from the II-VI semiconductors were compared to the transmitted second harmonic intensity from an ammonium dihydrogen phosphate (ADP) crystal.[22] Figure 1(a) shows the dispersion of $|d_{33}|$ in CdS and CdSe normalized to that of $|d_{36}|$ in ADP. We chose ADP because the dispersion of $|d_{36}|$ is small in this wavelength range and because its absolute value has been well determined.[23] For CdS, one observes a peak in $|d_{33}|$ at the exciton energy gap[24] ($E_{\mathrm{ex}} \approx 2.5$ eV). This peak at $2\hbar\omega = E_{\mathrm{ex}}$ is much less pronounced than that observed from the low-temperature experiments with CuCl.[10] For CdSe, the enhancement of $|d_{33}|$ when $2\hbar\omega$ is larger than 3.0 eV can be associated with the E_1 peaks in its joint density of states[25] ($E_1 = 4.98$ eV).

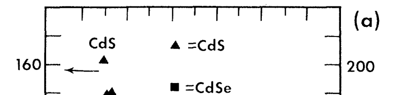

FIG. 1. (a) The dispersion of $|d_{33}|$ in CdS and CdSe normalized to that of $|d_{36}|$ in ADP. The error bar results from a 10% uncertainty of the linear extraordinary dielectric constant. (b) The dispersion of $|d_{33}/d_{31}|$ and $|d_{15}/d_{31}|$ in CdS. The error bars in these ratios result from a 10% uncertainty in the linear extraordinary index of refraction relative to the ordinary index of refraction. (c) Same as (b) except that the crystal is CdSe.

To measure the dispersion of $|d_{31}|$, $\alpha = 90°$, $\beta = 90°$, and $\theta = 45°$. The reflected harmonic polarization is a mixture of ordinary and extraordinary rays. The more generalized nonlinear reflection formula must be used in relating $I_R(2\omega)$ to $|d_{31}|$. The ratio $|d_{33}/d_{31}|$ in CdS and CdSe is shown in Figs. 1(b) and 1(c), respectively. The $|d_{33}/d_{31}|$ measurements were repeated at $\theta = 14°$ [see Figs. 1(b) and 1(c)] in order to make two checks: (i) the repeatability of our measurements and (ii) the correctness of our nonlinear optics reflection formula which is a function of θ. The data with $\theta = 45°$ and 14° agreed well. When CdS is transparent to both $2\hbar\omega$ and $\hbar\omega$, $|d_{33}/d_{31}|$ obeys the theoretical prediction[3-5] of 2. As $2\hbar\omega$ approaches E_{ex}, a peak in the ratio was observed. For $2\hbar\omega > E_{\mathrm{ex}}$, $|d_{33}/d_{31}|$ approaches 1.5. In CdSe for $2\hbar\omega > E_{\mathrm{ex}}$ ($E_{\mathrm{ex}} = 1.8$ eV for CdSe)[26] the ratio $|d_{33}/d_{31}|$ was also less than 2.

To measure the dispersion of $|d_{15}|$ we chose $\theta = 14°$. The other angles were set with $\beta = 45°$, which in turn was orthogonal to the c axis ($\alpha = 45°$). For this orientation, the $I_R(2\omega)$ contributions from $|d_{33}|$ and $|d_{31}|$ were less than 5%. The dispersion of $|d_{15}/d_{31}|$ is also shown in Figs. 1(b) and 1(c) for CdS and CdSe, respectively. Much to our surprise, $|d_{15}/d_{31}| = 1$ for both crystals throughout the photon energy range. One would expect the Kleinman symmetry condition to be invalid when $2\hbar\omega$ and $\hbar\omega$ are strongly absorbed by the nonlinear medium. At present, we can give no explanation for the experimental result $|d_{15}/d_{31}| = 1$.

Absorption at $2\hbar\omega$ or at $\hbar\omega$ makes an absolute sign determination by Maker fringe[27,28] techniques difficult.[9] The additional symmetry relations for $6mm$ crystals not only predict the magnitude of the ratios, but also predict the relative phase angles between d_{15} and d_{31} ($\Delta\Phi_A = 0$) and between d_{33} and d_{31} ($\Delta\Phi_B = \pi$). We decided to measure these two relative phase angles $\Delta\Phi_A$ and $\Delta\Phi_B$. That is, we wished to test the generality of the relative phase-angle predictions in the absorbing region, even though the absolute phase angles of the d coefficients are known to be complex.[9,11,29]

Relative phase information can be deduced by observing $I_R(2\omega)$ as the crystal is rotated about its face normal. Specifically, one varies the angle α, while keeping β at either 0° or 90°, $\theta = 45°$, and the incident polarization vertical. At arbitrary angle α, the contribution to $I_R(2\omega)$ from each of the three nonlinear coefficients depends on their relative phase angles. The determination of the relative phase angle by using the interference among the independent d coefficients has been reported previously for transmission-type harmonic generation experiments.[30-32]

Figure 2(a) shows, for four combinations of $\Delta\Phi_A$ and $\Delta\Phi_B$, theoretical plots of $I_R(2\omega)$ as a function of α with $\beta = 0$. Figure 2(b) shows the case for $\beta = 90°$. In both cases the experimental measured $|d_{15}/d_{31}|$ and $|d_{33}/d_{31}|$ values at 1.7 eV were used. Our experimental data for CdS at $\hbar\omega = 1.7$ eV are shown in Figs. 2(a) and 2(b). The good fit between the calculated and experimental data implies that $\Delta\Phi_A = 0$ and $\Delta\Phi_B = \pi$, as the additional symmetry relations had predicted. We repeated our measurements for CdS at $\hbar\omega = 1.25$ eV, in order to make $2\hbar\omega = E_{\mathrm{ex}}$. The experimental data were compared with the theoretical plot with $\Delta\Phi_A = 0$ and $\Delta\Phi_B = \pi$ [see Fig. 2(c)].

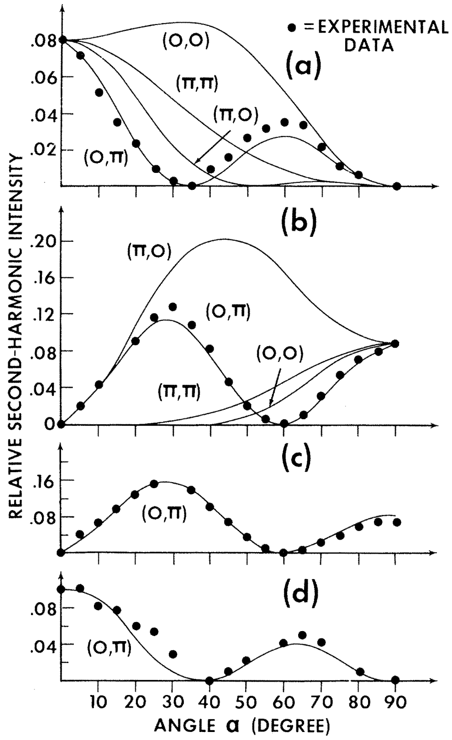

FIG. 2. (a) The relative second harmonic intensity as a function of angle α for different combinations of the relative phase angles between d_{15} and d_{31} ($\Delta\Phi_A$) and between d_{33} and d_{31} ($\Delta\Phi_B$). Four combinations are shown ($\Delta\Phi_A, \Delta\Phi_B$). The experimental data measured in CdS at $\hbar\omega = 1.7$ eV are shown as solid circles. The harmonic polarization is vertical, $\beta = 0°$. (b) Same as (a) except that the harmonic polarization is horizontal, $\beta = 90°$. (c) Only $\Delta\Phi_A = 0$ and $\Delta\Phi_B = \pi$ are shown along with the experimental data measured in CdS at $\hbar\omega = 1.25$ eV and with $\beta = 90°$. (d) Only $\Delta\Phi_A = 0$ and $\Delta\Phi_B = \pi$ are shown along with the experimental data measured in CdSe at $\hbar\omega = 1.7$ eV and with $\beta = 0°$. Theories that are applicable for the transparency region of the crystal predict $\Delta\Phi_A = 0$ and $\Delta\Phi_B = \pi$.

For CdSe at $\hbar\omega = 1.7$ eV, similar results for $\Delta\Phi_A$ and $\Delta\Phi_B$ were also obtained [see Fig. 2(d)]. At $\hbar\omega = 1.17$ eV, Miller and Nordland[9] also found $\Delta\Phi_B \approx \pi$ for CdSe. In fact, they measured the absolute phase angle and found for d_{33} an angle of $180° - 44° \pm 180°$ and for d_{31} an angle of $-49° \pm 180°$ In the absorbing region, it is indeed surprising that even though the absolute phase angles are no longer 0 or π, the relative phase angle of d_{15} to d_{31} is still 0, and that of d_{33} to d_{31} is still π.

In summary, we have measured, for CdS and CdSe, the dispersions of $|d_{33}|$, $|d_{15}/d_{31}|$, and $|d_{33}/d_{31}|$ in the region where $2\hbar\omega$ and/or $\hbar\omega$ are absorbed. Throughout the wavelength range (0.7 to 1.0 μm), $|d_{15}/d_{31}| = 1$ while $|d_{33}/d_{31}|$ exhibited dispersion and deviated from the ratio 2. We have also measured relative phase angles among the d coefficients at two different wavelengths corresponding to $\hbar\omega = 1.25$ and 1.7 eV. Within our experimental error, the relative phase of d_{15} to d_{31} was found to be 0 and that for d_{33} to d_{31} was found to be π for both CdS and CdSe. It is remarkable how well the additional symmetry predictions, predicted for the transparency region, were found to be valid in the region where both $2\hbar\omega$ and $\hbar\omega$ were strongly absorbed. We hope that our experimental results may further stimulate theorists to extend their calculations to regions of absorption and dispersion, where the electronic energy bands must be accounted for.

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Density of Zeros on the Lee-Yang Circle for Two Ising Ferromagnets*

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Extrapolations of high-field and high-temperature series expansions have been used to construct numerical approximations to the density of zeros $g(\theta)$ on the Lee-Yang circle for the Ising ferromagnets on a two-dimensional square and a three-dimensional diamond lattice. For temperatures above the critical temperature the density is zero for $|\theta| < \theta_G$ and then varies as $(\theta - \theta_G)^\mu$, with $\mu \simeq -0.1$ and $+0.1$ for the square and diamond lattices, respectively.

Lee and Yang[1] in 1952 pointed out that the thermodynamic properties of an Ising ferromagnet in the thermodynamic limit, in the presence (or absence) of a magnetic field H, are determined by the limiting density of zeros of the partition function, $g(\theta)$, on the unit circle $z = e^{i\theta}$ in the complex $z = \exp(-2H/T)$ plane (with H and T in suitable dimensionless units). There have been many studies of the thermodynamic properties of Ising ferromagnets, especially near the critical point,[2] but despite the fact that $g(\theta)$ (as a function of T) contains all this information, and is of fundamental significance for the theory of phase transitions,[3] very little is known about its actual form. We present below results of what we believe to be the first systematic investigation of $g(\theta)$, based on extrapolations of high-temperature and high-field series, for two Ising ferromagnets which exhibit a phase transition and a critical point: the square lattice and the diamond lattice, with nearest-neighbor interactions.

We have obtained quantitative information about some features of g previously anticipated such as the existence of a gap $|\theta| < \theta_G(T)$, centered at $\theta = 0$, in which g is zero if the temperature exceeds the critical temperature T_c. (Such a gap implies that the free energy is an analytic function of H for all real values of H including $H = 0$, and thus there is no phase transition as a function of H.[3] Such analyticity, and thereby the existence of a