

Anisotropy of two-photon absorption in GaAs and CdTe †

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The anisotropy in the two-photon absorption coefficient for GaAs and CdTe is reported for the first time. Variations of the order of 15% are observed at room temperature in the magnitude of the nonlinear absorption, and are seen to increase at 85°K, as the angle of the polarization vector of the incident 1.06-μm light is changed with respect to the crystal axes. The variation agrees with the predictions of nonlinear optics and a simple three-band model (neglecting excitons), but is too large at 85°K to be accounted for by the band model.

When an intense light beam traverses a material, nonlinear absorption often becomes of comparable magnitude with linear-absorption processes. In certain materials such as semiconductors, second-order nonlinear absorption can become the dominant loss mechanism if the light is sufficiently intense and $\hbar\omega < E_g < 2\hbar\omega$, where E_g is the energy gap and $\hbar\omega$ is the incident photon energy. Since some residual linear absorption is almost always present in this region, experimentalists usually describe the process by

$$\frac{dI}{dx} = -\alpha I - \beta I^2, \quad (1)$$

where β is the nonlinear absorption coefficient and the other quantities have their usual meaning. Theoretically, β is generally evaluated by the relationship

$$\beta = 2\hbar\omega W^{(2)} / I^2(\omega), \quad (2)$$

where $W^{(2)}$ is the second-order transition rate found from standard perturbation theory. Depending on the approximations used in determining the energy states in the crystal, the number arrived at using (2) may or may not be in good agreement with the experimental result. A fact that is usually hidden in these various approximations, is that the two-photon absorption coefficient is, in general, dependent on the orientation of the crystal axes of the material with respect to the \vec{k} vector of the incident light and its polarization. These dependences, however, are obvious when one considers the formulation of two-photon absorption (2PA) in the context of nonlinear optics.

For a single monochromatic beam of angular frequency ω_0 , the wave equation including the lowest order nonlinearity at ω_0 is

$$\frac{1}{\omega_0^2} \vec{\nabla} \times \vec{\nabla} \times \vec{E}(\vec{r}, t) + \frac{\epsilon(\omega_0)}{c^2} \vec{E}(\vec{r}, t) = -\frac{4\pi}{c^2} \vec{P}^{(3)}(\vec{r}, t), \quad (3)$$

where $\epsilon(\omega_0)$ is the complex linear dielectric con-

stant and we assume the following conventions for the field amplitudes:

$$\vec{E}(\vec{r}, t) = \int \vec{E}(\vec{r}, \omega) e^{i(\vec{k} \cdot \vec{r} - \omega t)} d\omega, \quad (4a)$$

$$\vec{E}(\vec{r}, \omega) = \frac{1}{2} [\vec{E}(\vec{r}) \delta(\omega - \omega_0) + \vec{E}^*(\vec{r}) \delta(\omega + \omega_0)], \quad (4b)$$

$$\begin{aligned} \vec{P}^{(3)}(\vec{r}, \omega) = & \int d\omega' d\omega'' \chi^{(3)}(-\omega, \omega', \omega'', \omega - \omega' - \omega'') \\ & \times \vec{E}(\vec{r}, \omega') \vec{E}(\vec{r}, \omega'') \vec{E}(\vec{r}, \omega - \omega' - \omega''). \end{aligned} \quad (4c)$$

We can solve Eq. (3) by separating $\vec{E}(\vec{r}, t)$ into transverse and longitudinal components. For the longitudinal component $E_{\text{long}}(\vec{r}, t)$, we find

$$E_{\text{long}} = -[4\pi/\epsilon(\omega_0)] P_{\text{long}}^{(3)}.$$

This component, which is also obtainable directly from the boundary conditions, will be negligible compared to the transverse component since we assume the nonlinear interaction is small. For the transverse component, we follow the standard approximation¹ that second derivatives of the slowly varying field $\vec{E}(\vec{r}, t)$ can be neglected; letting $\epsilon(\omega_0) = (\eta + ik)^2$, $k = (\omega_0/c)\eta$, and explicitly writing the tensor nature of $\chi^{(3)}(\omega_0)$, we find for the i th component of $\vec{E}(r)$,

$$\begin{aligned} -i \left(\frac{2\omega_0}{c} \eta \right) \frac{d}{dr} E_i(r) + \frac{\omega_0^2}{c^2} \kappa^2 E_i(r) - 2i\eta\kappa \frac{\omega_0^2}{c^2} E_i(r) \\ = \frac{4\pi\omega_0^2}{c^2} \chi_{ijkl}^{(3)} E_j(r) E_k(r) E_l^*(r). \end{aligned} \quad (5)$$

Substituting $E_i(r) = |E(r)|_i e^{i\phi(r)}$, Eq. (5) separates into real and imaginary parts

$$\begin{aligned} \frac{d}{dr} |E(r)|_i = -\frac{1}{2}\alpha |E(r)|_i - \frac{2\pi\omega_0}{\eta c} \\ \times [\text{Im}\chi^{(3)}(\omega_0)]_{ijkl} |E(r)|_i |E(r)|_j |E(r)|_l, \end{aligned} \quad (6a)$$

$$|E(r)|_i \frac{d\phi(r)}{dr} = -\frac{\omega_0}{2c\eta} \kappa^2 |E(r)|_i + \frac{2\pi\omega_0}{\eta c} \times [\text{Re}\chi^{(3)}(\omega_0)]_{ijkl} |E(r)|_j |E(r)|_k |E(r)|_l, \quad (6b)$$

where $\alpha = (2\omega_0/c)\kappa$. Multiplying both sides of (6) by $|E(r)|_i$ and summing over repeated subscripts, we find

$$\frac{dI(\omega_0, r)}{dr} = -\alpha I(\omega_0, r) - \frac{32\pi^2\omega_0}{\eta^2 c^2} F(\theta, \text{Im}\chi^{(3)}(\omega_0)) I^2(\omega_0, r), \quad (7a)$$

$$\frac{d\phi(r)}{dr} = -\frac{\omega_0 \kappa^2}{2\eta c} + \frac{16\pi^2\omega_0}{\eta^2 c^2} F(\theta, \text{Re}\chi^{(3)}(\omega_0)) I(\omega_0, r), \quad (7b)$$

where we have substituted $I(\omega_0, r) = (c\eta/8\pi)|E(r)|^2$ and the function F is determined by the crystal symmetry. Comparison of (1) with (7a) gives the experimental nonlinear absorption coefficient β in terms of the third-order susceptibility. Equation (7b) can be used to compute the intensity-dependent refractive index.

For zinc-blende semiconductors, $\chi_{ijkl}^{(3)}$, in general, will have four independent components (such as when one considers three-frequency mixing). For the special case of two-photon absorption from the same beam (or third-harmonic generation), there are only two independent components. They are

$$\begin{aligned} \chi_{ijkl}^{(3)} &= \chi_{1111}, & i=j=k=l=1, 2, 3 \\ &= \chi_{1122}, & i=j, \quad k=l \neq i=1, 2, 3 \\ & & i=k, \quad j=l \neq i=1, 2, 3 \\ & & i=l, \quad j=k \neq i=1, 2, 3. \end{aligned}$$

For the simple case of linearly polarized light, $F(\theta, \text{Im}\chi^{(3)}(\omega_0))$ becomes

$$F(\theta, \text{Im}\chi^{(3)}(\omega_0)) = \text{Im}\chi_{1111}(\epsilon_x^4 + \epsilon_y^4 + \epsilon_z^4) + 6 \text{Im}\chi_{1122}(\epsilon_x^2\epsilon_y^2 + \epsilon_x^2\epsilon_z^2 + \epsilon_y^2\epsilon_z^2), \quad (8)$$

where ϵ_x , ϵ_y , ϵ_z are the direction cosines of the polarization vector measured along the crystal-line cubic axes. In general, then, the nonlinear absorption coefficient will be anisotropic. Even if the incident light is unpolarized, F will depend on the direction of incidence, as indicated in Table I. For the special case of $\chi_{1111}(\omega) = 3\chi_{1122}(\omega)$, however, F (and hence β) will be isotropic for polarized or unpolarized light.

TABLE I. Values of F for different directions of normal incidence.

Direction of normal incidence	$F(\theta, \chi^{(3)}(\omega))$
[001] [*]	0.75($\chi_{1111} + \chi_{1122}$)
[110], [112]	0.5625 $\chi_{1111} + 1.3125\chi_{1122}$
[111]	0.5($\chi_{1111} + 3\chi_{1122}$)
[210]	0.63 $\chi_{1111} + 1.11\chi_{1122}$

The nonlinear optics formulation of 2PA has the advantage of showing immediately the form of the anisotropy present; however, in order to obtain specific information about χ_{1111} and χ_{1122} , one must use band-structure approximations for $\chi_{ijkl}^{(3)}$ which is equivalent to the more commonly used transition rate expressions,^{2,3} i.e.,

$$\text{Im}\chi_{1111}^{(3)}(\omega) = \frac{1}{16\hbar^3\pi^2\omega^4} \times \int d^3k \frac{\text{Re}p_{rstu}^{1111}}{(\omega_{sr}-\omega)(\omega_{ur}-\omega)} \delta(\omega_{tr}-2\omega), \quad (9)$$

$$\begin{aligned} \text{Im}\chi_{1122}^{(3)}(\omega) &= \frac{1}{96\hbar^3\pi^2\omega^4} \int d^3k \frac{\delta(\omega_{tr}-2\omega)}{(\omega_{sr}-\omega)(\omega_{ur}-\omega)} \\ &\times (p_{rstu}^{1122} + p_{rstu}^{1212} + p_{rstu}^{1221} \\ &\quad + p_{rstu}^{2211} + p_{rstu}^{2121} + p_{rstu}^{2112}). \end{aligned} \quad (10)$$

In this notation, r , s , t , and u represent energy bands (r is the initial state, t is the final state, u and s are intermediate states), 1 and 2 are crystalline axes, a summation over all possible energy bands is implied, and

$$p_{rstu}^{1122} = \left(\frac{e}{m}\right)^4 \langle r|p_1|s\rangle \langle s|p_1|t\rangle \langle t|p_2|u\rangle \langle u|p_2|r\rangle, \quad (11)$$

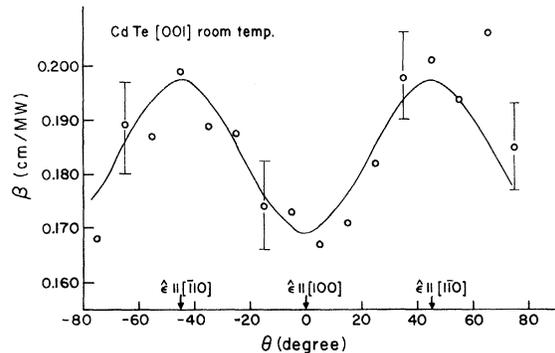


FIG. 1. Nonlinear absorption coefficient as a function of polarization angle for [001]-normal CdTe at 300°K.

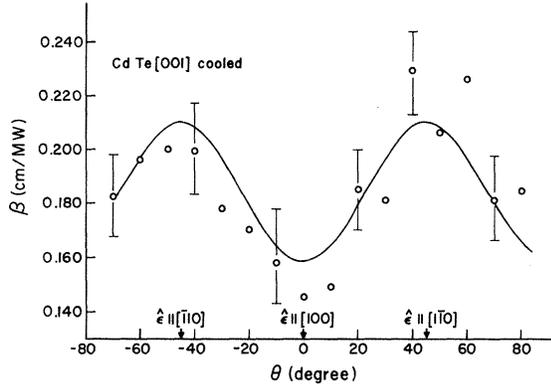


FIG. 2. Nonlinear absorption coefficient as a function of polarization angle for [001]-normal CdTe at 85°K.

etc.

Lee and Fan⁴ have proposed a model band structure for two-photon absorption including excitons. We have evaluated (9) and (10) using a similar model except that (i) excitons are not explicitly included, and (ii) the numerical values for the band parameters are derived from a full-zone $k \cdot p$ perturbation analysis.⁵ This model has been used successfully for the prediction of both first- and second-order optical effects by previous workers.^{5,6}

Samples of strain-free single-crystal CdTe and GaAs were investigated with a 1.06 μ -m Nd laser at both room temperature and 85°K. For the case of CdTe, the crystal was polished and oriented for [001] normal incidence. From (1), (7a), and (8), we find

$$\beta = \frac{32\pi^2\omega_0}{\eta^2 c^2} [\text{Im}\chi_{1111}^{(3)}(\omega)(\epsilon_x^4 + \epsilon_y^4 + \epsilon_z^4) + 6\text{Im}\chi_{1122}^{(3)}(\omega)(\epsilon_x^2\epsilon_y^2 + \epsilon_y^2\epsilon_z^2 + \epsilon_z^2\epsilon_x^2)] = B(\epsilon_x^2 + \epsilon_y^2 + \epsilon_z^2) + A(\epsilon_x^2\epsilon_y^2 + \epsilon_y^2\epsilon_z^2 + \epsilon_z^2\epsilon_x^2), \quad (12)$$

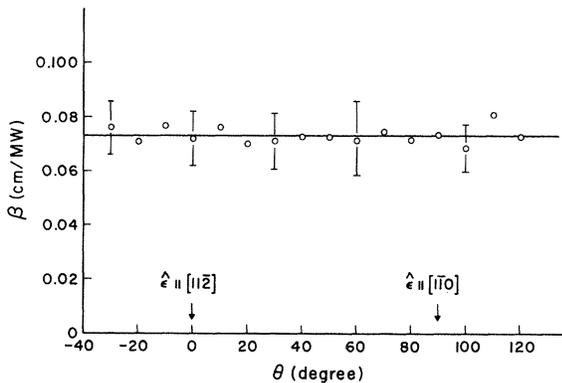


FIG. 3. Nonlinear absorption coefficient as a function of polarization angle for [111] GaAs.

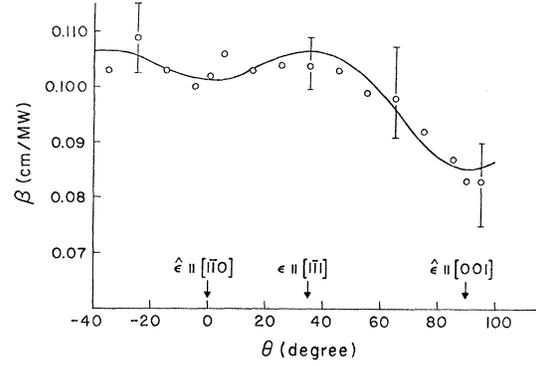


FIG. 4. Nonlinear absorption coefficient as a function of polarization angle for [110] GaAs at 300°K.

which for [001] normal incidence becomes

$$\beta = B(\sin^4\theta + \cos^4\theta) + A\sin^2\theta\cos^2\theta \quad (13)$$

[\$\theta\$ is measured from the [100] axis]. Figure 1 shows the results of the measurement at room temperature; the solid line is a least-squares fit of (13) and gives values of $A = 0.45$ cm/MW, $B = 0.17$ cm/MW, and $A/B = 2.63 \pm 0.50$ (since in general $\epsilon_x^4 + \epsilon_y^4 + \epsilon_z^4 = 1 - 2(\epsilon_x^2\epsilon_y^2 + \epsilon_y^2\epsilon_z^2 + \epsilon_z^2\epsilon_x^2)$, we see that at any frequency ω_0 , where $A/B = 2$, the nonlinear absorption coefficient β is isotropic). Figure 2 gives the results of the measurement at 85°K; the least-squares fit of (13) gives $A = 0.54$ cm/MW, $B = 0.16$ cm/MW, and $A/B = 3.34 \pm 0.54$.

A boule of GaAs was cut, oriented, and polished for both [111] and [110] normal incidence experiments. For the [111] orientation, no anisotropy was found in the nonlinear absorption coefficient β , as shown in Fig. 3. In addition, the magnitude of β did not change from the room temperature value at 85°K. For [110] normal incidence, however, an anisotropy was noted at room temperature, which, as in the case of CdTe, increased at 85°K. These results are shown in Figs. 4 and 5.

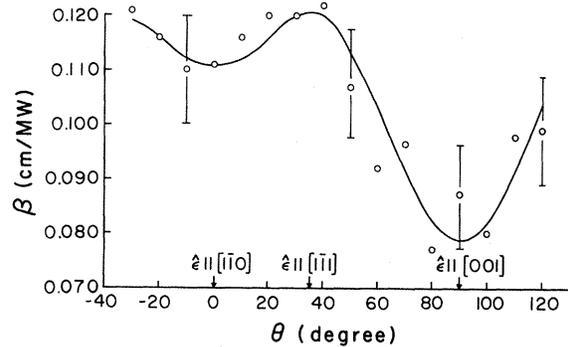


FIG. 5. Nonlinear absorption coefficient as a function of polarization angle for [110] GaAs at 85°K.

TABLE II. Summary of experimental results and predictions of the theory.

	A	B	A/B	β (cm/MW)	
[001] CdTe 300 °K	0.448	0.170	2.63 ± 0.50	...	(expt)
	0.160	0.65	2.46	...	[Eq. (12)]
[001] CdTe 85 °K	0.535	0.160	3.34 ± 0.54	...	(expt)
	0.128	0.052	2.46	...	[Eq. (12)]
[111] GaAs 300 °K	0.072	(expt)
	0.214	0.096	2.23	0.102	[Eq. (12)]
[111] GaAs 85 °K	0.080	(expt)
	0.172	0.074	2.32	0.080	[Eq. (12)]
[110] GaAs 300 °K	0.235	0.086	2.73 ± 0.6	...	(expt)
	0.214	0.096	2.23	...	[Eq. (12)]
[110] GaAs 85 °K	0.283	0.078	3.61 ± 0.9	...	(expt)
	0.172	0.074	2.32	...	[Eq. (12)]

The solid line in Figs. 3–5 is a least-squares fit of Eq. (12), which becomes for these orientations

$$[111]: \beta = \frac{1}{2}A + \frac{1}{4}B \text{ (isotropic)}, \quad (14)$$

$$[110]: \beta = \frac{1}{4}A \cos^2\theta(1 + 3 \sin^2\theta) + B(\frac{1}{2} \cos^2\theta + \sin^2\theta). \quad (15)$$

Since there is no anisotropy for the [111] direction, we cannot find independent values of A and B . However, for [110] incidence, we find for the room-temperature case $A = 0.235$ cm/MW, $B = 0.086$ cm/MW, and $A/B = 2.73 \pm 0.6$. Similarly, the values of A and B at 85 °K are $A = 0.283$ cm/MW, $B = 0.078$ cm/MW, and $A/B = 3.61 \pm 0.9$.

In order to predict the nonlinear absorption from theory, one needs to truncate the sum over energy bands in (9) and (10). As in the model previously described,⁴ if one considers only transitions involving the valence bands and the lowest conduction band [labeled by r and t , respectively, in Eqs. (9) and following], there is no predicted anisotropy in β . When one includes the next-higher conduction band, an anisotropy begins to appear but it is small due to the relatively large energy

denominators involved for these terms in Eq. (9) and following. At low temperatures, we assumed that the only parameters that changed in the calculation were the energy gaps; for our sample of CdTe, we measured on a Cary 14 a widening of the $k=0$ gap by 5%, and for GaAs a 6% widening was noted. These percentage widenings were also applied to the E'_0 gap (labeled E'_g in Ref. 4).

A summary of the experimental results is given in Table II. The predictions for A/B are in agreement within the experimental error at room temperature but deviate from the prediction at 85 °K. However, considering the lack of knowledge about the band parameters at this temperature (for example, the knowledge of the behavior of the band effective masses is not well resolved^{7,8}) this is not surprising. In addition exciton effects, which may become important at low temperatures, are not included.

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