Absolute two-photon absorption line shape in ZnTe

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By measuring, as a function of temperature, the nonlinear light transmittance from neodymium and ruby lasers, the ZnTe two-photon absorption (TPA) has been studied both near the direct band gap and close to the critical point E_1. The TPA absolute coefficients have been determined by means of the two-channel normalization technique. It has been found that for $2\hbar\omega \geq E_g$, the TPA spectrum line shape has a dependence that is peculiar to absorption involving exciton levels, while for $2\hbar\omega$ close to E_1, the line shape has a $(2\hbar\omega\text{-}E_g)^{3/2}$ dependence, which is typical of the "allowed-forbidden" mechanisms corresponding to the two-band model. By comparing the TPA experimental and theoretical values, it has been found that the TPA is strongly influenced both by the exciton effect and by the valence-band degeneracy.

I. INTRODUCTION

Multiphoton processes are important in investigating many nonlinear optical phenomena in solids. In particular, as regards the two-photon-absorption processes (TPA), the selection rules are generally different from those of one-photon absorption; there follows that the measured TPA properties are complementary to the linear ones. Information about the magnitude of the transition-matrix element, the density of states, and the energy eigenvalues may be obtained from the TPA-coefficient absolute measurements and in particular from its frequency dependence.

To calculate the two-photon-absorption coefficient, several theories have been proposed. These theories make use of the time-dependent perturbation approach in the gauge $\vec{A}\cdot\vec{p}$. In employing this approach the virtual states have been considered as being associated either with the conduction and valence bands (two-band model)[1-3] or with a higher-lying band (three-band model).[4-7] The exciton effect has not been taken into consideration in these treatments. Only two models have taken into account the exciton effect. The first model[8,9] assumed simple conduction and valence bands. The second one[10] instead considered a simple conduction band and a degenerate valence band.

Both the intermediate states and the final ones in the last model have been associated with exciton levels (the final states being the exciton continuum). This theory shows that the valence-band degeneracy strongly increases the two-photon-absorption coefficient α_2/I (cm/MW) and that the exciton-effect contribution to α_2/I grows with the ratio between the exciton binding energy E_b and the difference $2\hbar\omega - E_g$, where $2\hbar\omega$ is the two-photon energy and E_g is the energy gap.

The purpose of this paper is to study the spectral dependence of the TPA coefficient in ZnTe and hence to elucidate the transition mechanisms involving exciton states and degenerate valence bands. Zinc telluride is a semiconductor with a zinc-blende structure having a triply degenerate maximum Γ_{15} of the valence band and a direct energy gap E_g at room temperature RT quasiresonant with twice the energy of the neodymium-laser photon ($2\hbar\omega = 2.34$ eV). On the other hand, the interband transition $\Lambda_3 - \Lambda_1$, corresponding to the critical point E_1, is quasiresonant with twice the frequency of the ruby laser ($2\hbar\omega = 3.56$ eV).[11]

By varying the sample temperature and therefore the energy gap E_g, by means of fixed-wavelength lasers as the ruby and the neodymium ones it is possible to study the dependence of α_2/I on $2\hbar\omega - E_g$.

The absolute values of the TPA coefficients have been measured at several temperatures, by means of the nonlinear transmittance technique, according to: (i) "the standard one-beam method" or (ii) "the two-channel-normalization TPA method."

Experimental results provide good evidence of the contributions of the valence-band degeneracy and of the exciton states to the TPA coefficient.

II. EXPERIMENTAL PROCEDURE

The measurements were carried out on crystals of ZnTe, grown from the vapor phase without intentionally added impurities and having the typical thickness $d = 0.15$ cm. The samples showed p-type conductivity with a hole mobility $\mu = 110$ cm^2/V sec and a carrier concentration $p > 10^{12}$ cm^{-3}. High-quality crystals were selected to prevent damage, due to high-power density excitation. The allowed maximum value without crystal damage was about 25 MW/cm^2.

The experimental setup used for measuring the nonlinear transmittance by the standard one-beam

TPA method has been previously reported.[12] In our case some modifications were introduced in order to allow measurements in the temperature range from 77 to 400 °K and to use either a ruby or a neodymium Q-switched laser as exciting sources. Both lasers used had 20-nsec pulse duration and 200-MW peak power, and the beam cross section of the lasers was 1.5 cm^2. Since the light of high-power laser beams is not uniformly distributed over their cross section, we took much care in reducing and testing, as in Ref. 13, the influence of beam nonuniformity on the TPA-coefficient value. A rather good performance was achieved by selecting particular zones of the beam by means of an aperture of 3-mm diam. placed in the laser cavity. By measuring the attenuation ratio $I(z=d)/I_0$ as a function of I_0, the standard method cited above gave directly the two-photon absorption coefficient α_2/I.

Actually, when there is a one-photon contribution, characterized by an absorption coefficient α, the two-photon reciprocal transmittance formula becomes

$$\frac{I_0}{I(z=d)} = \left(\frac{e^{\alpha d}}{(I-R)^2} + \frac{\beta(e^{\alpha d}-1)}{\alpha(1-R)} I_0\right) \times \left(\frac{1+e^{\alpha d}/R+(e^{\alpha d}/R)^2}{2+e^{\alpha d}/R+(e^{\alpha d}/R)^2}\right), \quad (1)$$

where $\beta = \alpha_2/I$, $I(z=d)$ is the intensity of the transmitted beam for a sample of thickness d, I_0 is the laser intensity function at $z=0$, and R is the reflection coefficient.

A 25% accuracy can be afforded by means of this technique because of the irreproducibility of the laser-pulse spatial and temporal profile. The dependence of the measurement on the laser parameters has been eliminated by using the two-channel normalization TPA method proposed by Lotem *et al.*[14] consisting of the comparison between the attenuations of the laser beam through two different samples. The ratio ρ between the energies transmitted by two different two-photon absorbers for identical laser pulses is given by

$$\rho = \frac{e^{-\alpha_r d_r}(1-R_r)^2 \int \frac{I_0(x,y,t)\,dx\,dy\,dt}{1+\beta_r/\alpha_r I_0(1-R_r)(1-e^{-\alpha_r d_r})}}{e^{-\alpha_s d_s}(1-R_s)^2 \int \frac{I_0(x,y,t)\,dx\,dy\,dt}{1+\beta_s/\alpha_s I_0(1-R_s)(1-e^{-\alpha_s d_s})}}, \quad (2)$$

where the indices r and s stand for the reference and the sample, respectively; and $I_0(x,y,t)$ is the laser-beam intensity $I(x,y,z,t)$ calculated for $z=0$. If the laser beam impinging on the reference sample is attenuated by an extra filter of transmission F, the term I_0 in the numerator of Eq. (2) should be replaced by FI_0.

By checking the intensity dependence of ρ it is possible to find, experimentally, the value of F which makes the ratio ρ between the signals from the samples independent of the laser intensity I_0. In this case the two denominators of the integrands in Eq. (2) become equal and the ratio β_s/β_r can be evaluated. Since the F value is independent of the laser-beam properties, the value of the measured nonlinear absorption coefficient is also independent of the coherence properties of the laser beam. In our case we used as reference samples GaAs and CdS crystals for the Nd and ruby laser, respectively.

The absolute TPA coefficients of these semiconductors where previously measured by Lotem *et al.*[14]

The experimental values of the TPA coefficient obtained by means of this technique for ZnTe at different temperatures and for both lasers have an accuracy of 10%.

III. RESULTS AND DISCUSSION

Figure 1 shows the two-photon-absorption line shape obtained by using a neodymium laser and by supplying a two-photon pumping with $2\hbar\omega$ near the direct band gap of ZnTe. The experimental points were determined by means of the two-channel-normalization TPA method. At different temperatures, the relative error on α_2/I was about 10%. The absolute values of α_2/I and the line shape of α_2/I vs $(2\hbar\omega - E_g)$ are in agreement with the previous experimental results reported in Ref. 10. In the latter reference the TPA measurements were performed by "the standard one-beam method," i.e., with a relative error of about 25%.

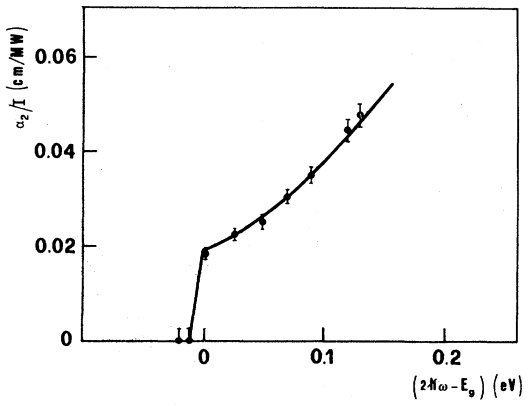

FIG. 1. Two-photon-absorption coefficients vs $2\hbar\omega - E_g$ for a ZnTe sample and neodymium-laser excitation.

The continuous curve of Fig. 1 was theoretically calculated by the equation

$$\alpha_2/I \propto e^{X\pi}/\sinh \pi X ,$$

where $X=[E_b/(2\hbar\omega - E_g)]^{1/2}$ and $E_b = 12$ meV is the binding energy of the free exciton. The preceding equation gives the characteristic dependence of the absorption coefficient on the density of exciton states. The good fit between the experimental points and the theoretical line shape yields evidence for the importance of the exciton effect in the TPA processes. Moreover, Fig. 1 shows that the TPA coefficient is not measurable below 130 °K since $2\hbar\omega - (E_g - E_b) < 0$ for $T \leq 130$ °K.

Figure 2 shows the results obtained by using a ruby laser, i.e., with $2\hbar\omega \gg E_g$ and close to the interband transition $\Lambda_3 - \Lambda_1$ corresponding to the critical point E_1 of ZnTe. In this case the measurements were also made by means of the experimental methods (i) and (ii). Within the different relative errors, we found that the corresponding values were consistent.

The experimental points of Fig. 2 fit well the equation

$$\alpha_2/I \propto (2\hbar\omega - E_g)^{3/2} .$$

This dependence excludes the exciton effect in TPA processes when $2\hbar\omega \gg E_g$. On the other hand, there is evidence that the interband transitions are of the type "allowed-forbidden."

The equations resulting from the various theoretical models proposed by different authors are summarized in Table I. The same table shows the α_2/I equations where both the valence-band-degeneracy and the exciton-level effects are taken into account either together or separately.

Table II is a summary of the absolute experimental and theoretical TPA coefficients obtained by means of the various models drawn in Table I, which allows a comparison among the models. This comparison was made at room temperature both for $2\hbar\omega$ near the energy gap E_g and far from it.

In order to make the calculations within all the theoretical models presented in Table I, we assumed, as momentum matrix element, Kane's approximated expression

$$|P_{ij}|^2 = \tfrac{3}{2} m(\alpha_c - 1)E_g(E_g + \Delta)/(3E_g + 2\Delta) ,$$

where Δ is the spin-orbit splitting of the valence band and α_c is the inverse conduction-band effective mass.

It is worth noting that the last assumption which is typical of the first-order absorption processes, gives good results particularly when the theoretical model assumes a Hamiltonian interaction in the gauge $\vec{A}\cdot\vec{p}$. The other parameters which are necessary for the calculations were taken from Refs. 11 and 15.

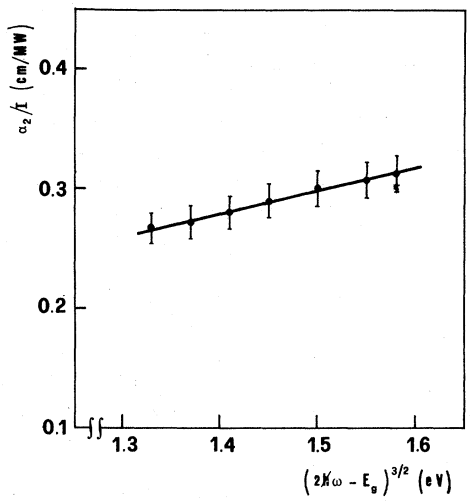

FIG. 2. Two-photon-absorption coefficient vs $2\hbar\omega - E_g$ for a ZnTe sample and ruby-laser excitation.

It is clear from Table II that when $2\hbar\omega$ is close to E_g a good agreement is found between experimental and theoretical values of α_2/I if we take into account the degenerate-valence-band and the exciton-level contributions as intermediate and final states.

In practice, the exciton effect increases the TPA coefficient by one order of magnitude. This contribution is quite important when the valence band is degenerate as in the ZnTe case. In fact, if we calculate the excitonic contribution for a simple valence band, we find that α_2/I increases only by a factor 3. Therefore both the line shape and the absolute value of α_2/I in the TPA spectrum of Fig. 1 can be correctly interpreted by taking into account the effect of the different branches of the degenerate valence band and that of the three excitonic series. In the case $2\hbar\omega \gg E_g$, one can see, as from Table II, that the experimental value of the TPA coefficient is in good agreement with the theoretical one obtained by Basov's theory. The same does not apply to other theoretical values that differ from the aforementioned one by about one order of magnitude. This discrepancy suggests that the other theoretical models cease to be a good approximation when energy states deep in the bands are involved. This result is in accordance with previous TPA experiments performed, for $2\hbar\omega \gg E_g$, in GaAs and InP compounds.[10] Actually the line shape in Fig. 2 relative to the critical point E_1 corresponds to al-

TABLE I. Calculation synopsis for two-photon transitions. The symbols $\mu_0, X_v, J_v, r_v, \rho_1, \rho_2$ have been defined by Lee and Fan in Eqs. (17), (26), (25), and (38) of Ref. 10; $a, \ldots, f$ are numerical coefficients; E_{bv} is the binding energy of an exciton involving valence band v; $\alpha_i = \hbar^2/2m_i$ are the relative inverse effective masses (v is the valence band, c the conduction band, n the intermediate band); ΔE is the separation between v and n band extrema; the c_i's are defined by Eqs. (17) and (18) of Ref. 16. The other symbols have the usual meaning.

Author	Model	Calculation scheme	Result of the calculation
Lee-Fan Ref. 10	Simple valence band	Exciton	$\frac{a_2}{I} = \frac{2^8\pi}{\sqrt{2}\times 15}\frac{e^4}{c^2m^4}\frac{\mu_0^{5/2}}{n}\frac{1}{(\hbar\omega)^3}\left[(1+X^2)\frac{\pi X e^{\pi X}}{\sinh\pi X}\frac{J^2 A}{X^3 E_b^{1/2}}\right]$ $A = P^2(ar^2 + b\rho_2^2 + c\rho_1^2\rho_2^2 + dr\rho_2 + er\rho_1\rho_2 + f\rho_1\rho_2^2)$
Braunstein-Ockman Ref. 4		No exciton	$\frac{a_2}{I} = \frac{2^{11/2}e^4\pi n}{3c^2m^{3/2}}\frac{\lvert P_{vn}\rvert^2}{(\hbar\omega)^3}(a_c+a_v)^{-1/2}\frac{(2\hbar\omega - E_g)^{3/2}}{M^2}$ $M = \left[\Delta E - \hbar\omega + \frac{a_n+a_v}{a_c+a_v}(2\hbar\omega - E_g)\right]$
Lee-Fan Ref. 10		Exciton	$\frac{a_2}{I} = \frac{2^8\pi}{\sqrt{2}\times 15}\frac{e^4}{c^2m^4}\frac{\mu_0^{5/2}}{n(\hbar\omega)^3}\sum_{v=1}^{3}\left[(1+X_v^2)\frac{\pi X_v e^{\pi X_v}}{\sinh\pi X_v}\frac{J_v^2 A_v}{X_v^3 E_{bv}^{1/2}}\right]$ $A_v = P^2(a_v r_v^2 + b_v\rho_2^2 + c_v\rho_1^2\rho_2^2 + d_v r_v\rho_2 + e_v r_v\rho_1\rho_2 + f_v\rho_1\rho_2^2)$
Lee-Fan Ref. 10	Degenerate valence band	No exciton	$\frac{a_2}{I} = \frac{2^8\pi}{\sqrt{2}\times 15}\frac{e^4}{c^2m^4}\frac{\mu_0^{5/2}}{n}\frac{1}{(\hbar\omega)^5}\sum_{v=1}^{3}\frac{E_{bv}^{3/2}A_v}{X_v^3}$
Basov *et al.* Ref. 1		No exciton	$\frac{a_2}{I} = \sum_{i=1}^{3}\frac{2^{17/2}e^4\pi}{n^2c^2m^{3/2}}\frac{\lvert P_{cvi}\rvert^2}{(\hbar\omega)^5}(a_c+a_{vi})^{-1/2}(2\hbar\omega - E_g)^{3/2}$
Fossum-Chang Ref. 16		No exciton	$\frac{a_2}{I} = \sum_{i=1}^{3}\frac{16\sqrt{2}}{15}\frac{\pi}{n^2}\frac{e^4}{c^2}\frac{C_i^2\lvert P\rvert^2}{(\hbar\omega)^5 m^{3/2}}(a_c+a_{vi})^{-1/2}(2\hbar\omega - E_g)^{3/2}$

TABLE II. Comparison of experimental data (present work) with numerical results of theoretical models.

		Model	Calculation scheme	a_2/I (cm/MW)
$2\hbar\omega \geq E_g$	Theoretical results	Simple valence band	Exciton Ref. 10	0.0017
		Degenerate valence band	Exciton Ref. 10	0.032
			No exciton Ref. 10	0.0025
	Experimental results			0.035
$2\hbar\omega \gg E_g$	Theoretical results	Simple valence band	No exciton Ref. 4	0.012
			No exciton Ref. 10	0.035
		Degenerate valence band	No exciton Ref. 1	0.26
			No exciton Ref. 16	0.087
	Experimental results			0.26

lowed-forbidden transitions, and the absolute values of α_2/I are in agreement with a two-band model which assumes a degenerate valence band.

Finally, from the results of this work and by taking into account the previous comparison[12,13,17] of the experimental and theoretical values of the TPA coefficient, it is possible to conclude that in degenerate semiconductors the Lee and Fan theory gives a satisfactory estimate of the TPA coefficients when $2\hbar\omega$ is close to E_g, while in the case $2\hbar\omega \gg E_g$ the two-band model gives good results for allowed-forbidden transitions. The three-band model is satisfactory for allowed-allowed transitions.

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