Evidence of nonparabolic-band effect on two-photon spectrum of ZnSe

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The magnitude and frequency dependence of the two-photon-absorption (TPA) coefficient in ZnSe have been measured for photon energies significantly greater than the energy-band gap E_g. Valence-band degeneracy and nonparabolicity effects on the TPA mechanism for a typical zinc-blende semiconductor are proven.

Experiments on two-photon absorption (TPA) in zinc-blende structure semiconductors in a condition of excitation near resonance with fundamental optical gap $(h\nu_1 + h_{\nu_2}) \geq E_g$ have shown that the α_2 value depends greatly on both valence-band degeneracy and exciton state density.[1,2] This is in perfect agreement with theoretical hypotheses. On the other hand, TPA experiments on the same type of semiconductors, but for excitation energies greater than energy gap $(h\nu_1 + h\nu_2) >> E_g$, yield results which are in disagreement with theoretical hypotheses.[1,3,4] Recently, this discrepancy has been ascribed to the fact that the α_2 theoretical values do not consider the nonparabolic-band effect which becomes significant at high excitation energies. Moreover, TPA spectroscopy experiments carried out at fixed laser frequency utilizing different zinc-blende structure compounds with energy gaps varying from 0.18 eV (InSb) to 1.5 eV (CdTe) seem to confirm theoretical hypotheses.[5]

The purpose of this paper is to verify the degeneracy and nonparabolicity effects of the energy bands both on the magnitude and frequency dependence of the two-photon-absorption coefficient in a particular zinc-blende semiconductor ZnSe by means of tunable TPA spectroscopy in the $(h\nu_1 + h_{\nu_2}) >> E_g$ experimental conditions. Measurements were carried out on ZnSe single crystals (energy gap at 300 K: $E_g = 2.58$ eV) characterized by a triply degenerate valence-band maximum Γ_{15} and a direct energy gap more than twice the energy of the neodymium-ytrrium aluminum garnet (YAlG) laser ($2h\nu_1 = 2.34$ eV) at room temperature. High quality crystals were selected to prevent damage from high power density excitation and to avoid experimental value dependence on the sample purity degree.

TPA coefficient absolute value at $(h\nu_1 + h\nu_2) = 3.56$ eV was measured at room temperature by means of the "absolute two-channel normalization TPA method." This method uses a reference channel allowing elimination of relative absorption dependence on laser spatial and temporal fluctuations. This is achieved by placing a filter of a certain attenuation F value in front of the reference sample and comparing the laser beam attenuation in two different TPA absorbers.

The unknown nonlinear attenuation coefficient is thus given in terms of both the filter attenuation factor and the reference known TPA coefficient product. The details of this method are reported in Ref. 2.

A CdS single crystal was used as a reference sample. The absolute TPA coefficient value ($\alpha_2 = 0.056$ cm/MW) of this semiconductor has been previously measured by Lotem and co-workers at ruby frequency.[6] The experimental value of the ZnSe TPA coefficient obtained by means of the aforementioned technique has a 10% accuracy. The experimental setup used for measuring both the absolute TPA coefficient and its frequency dependence is similar to the one reported in Ref. 6. A neodymium-YAlG Q-switched laser (20-nsec pulse duration, 100-MW peak power) was used both as a source for the high intensity beam at ν_1 frequency and for pumping a visible dye laser ν_2 by means of its second- and third-harmonic generations. For the measurements of the TPA aboslute coefficient the Nd-YAlG and dye laser beams, combined through a dichroic mirror in two collinear beams, were split by a Glan prism into the CdS reference sample and the ZnSe examined sample. The tunable dye beam was used as a probe. The experimental apparatus used allowed measurements of two-photon spectroscopy in the energy range 3 eV $\leq (h\nu_1 + h\nu_2) \leq$ 4.5 eV.

The experimental values of the ratio ρ between the transmitted energies in the CdS reference crystal and in the ZnSe sample as a function of the laser intensity and of the filter transmission F at $(h\nu_1 + h\nu_2) = 3.56$ eV are reported in Fig. 1. From the data in this figure it is evident that the ratio ρ results are independent of I_0 for $1.33 < F < 1.53$. The ZnSe absolute TPA coefficient value at $(h\nu_1 + h\nu_2) = 3.56$ eV, obtained from the experimental data in Fig. 1 and from Eq. (5) of Ref. 6, is $\alpha^{(2)} = 0.08$ cm MW^{-1}. On the other hand, by utilizing the band effective masses for the intraband momentum matrix element

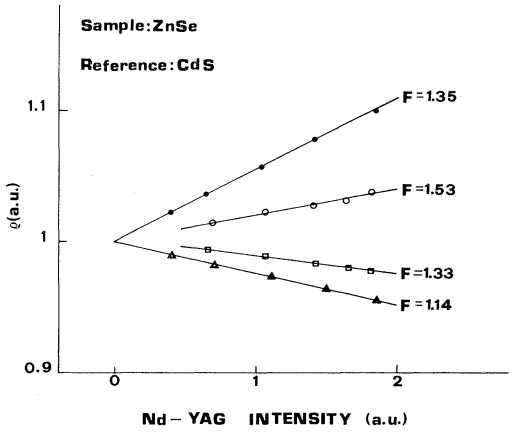

FIG. 1. Ratio ρ (between the transmitted energies in the sample and reference sample) as a function of the laser intensity and the filter transmission F at $(h\nu_1 + h\nu_2) = 3.56$ eV.

and the nonparabolic expression

$$E_{cv}=E_g\left(1+\frac{\hbar^2K^2}{m_{cv}^*E_g}\right)^{1/2}$$

for intraband energy difference E_{cv}, the following theoretical TPA coefficient expression in Basov's approximation,[7]

$$\alpha_2^{\text{nonparab}}=\frac{2^3\pi e^4E_g^{-3/2}}{3\epsilon_\infty c^2(m_{cv}^*)^{1/2}}\frac{[(h\nu_1+h\nu_2)^2-E_g^2]^{3/2}}{[(h\nu_1+h\nu_2)/2]^4}\quad,\qquad(1)$$

where m_{cv}^* is the reduced effective mass of the bands v and c and the other symbols have the usual meaning, was obtained. Equation (1) reduces to the equation

$$\alpha_2^{\text{parab}}=\frac{2^{7/2}\pi e^4E_g}{e\epsilon_\infty c^2(m_{cv}^*)^{1/2}}\frac{(h\nu_1+h\nu_2-E_g)^{3/2}}{[(h\nu_1+h\nu_2)/2]^5}\qquad(2)$$

related to parabolic approximation when $(h\nu_1+h\nu_2)\cong E_g$. It is worth noting that the two different above-mentioned approximation types cause differences both in the TPA coefficient line shape and in its absolute value. In fact, the ZnSe theoretical TPA coefficient values related to parabolic- and nonparabolic-band approximation obtained from the (1) and (2) formula, are $\alpha_2^{\text{nonparab}}=0.02$ cm MW^{-1} and $\alpha_2^{\text{parab}}=0.011$ cm MW^{-1}, respectively. The comparison between the ZnSe theoretical and experimental TPA coefficient values shows that the theoretical value obtained from the nonparabolic model, proposed for $(h\nu_1+h\nu_2)\gg E_g$ and for semiconductors with degenerate energy bands, gives a better approximation of the experimental data than the one given by classical parabolic approximation.

Figure 2 shows the ZnSe two-photon-absorption line shape obtained by using a neodymium-YAlG and dye laser and by supplying a two-photon pumping with $(h\nu_1+h\nu_2)\gg E_g$. The continuous curves a and b in Fig. 2, calculated theoretically by Eqs. (1) and (2), are related to nonparabolic and parabolic approximation, respectively. The good fit between the experimental points and the nonparabolic theoretical line shape yields definitive evidence of the nonparabolic-band effect importance in TPA processes for zinc-blende semiconductors in excitation conditions $(h\nu_1+h\nu_2)\gg E_g$.

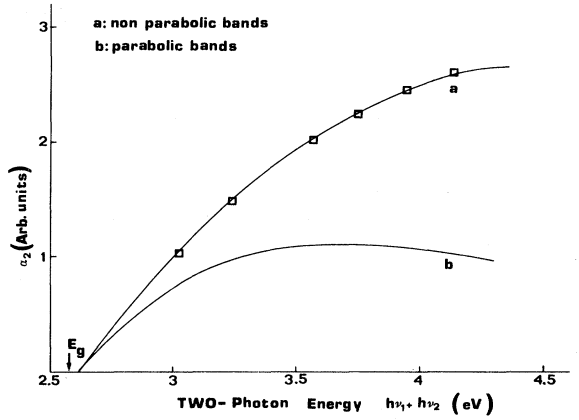

FIG. 2. Two-photon-absorption coefficients vs $(h\nu_1+h\nu_2)$ for a ZnSe single cyrstal. Full lines a and b are calculated for nonparabolic and parabolic bands, respectively. The symbols indicate experimental results.

In conclusion, we have demonstrated that in direct gap degenerated materials at excitation energies much greater than the fundamental optical gap the absolute TPA coefficient value and its energy dependence are in agreement only with the theoretical coefficients calculated including nonparabolicity and degeneracy of the energy bands.

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