Transmittance, luminescence, and photocurrent in CdS under two-photon excitation

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Two-photon transitions in CdS have been investigated at a single wavelength by measuring the nonlinear transmittance, photocurrent, and luminescence. The exciting source was the beam of a Q-switched ruby laser ($\hbar\omega = 1.78$ eV). The nonlinear cross section γ_2 for two-photon transitions has been measured and compared with the predictions of existing theories. The luminescence shows, at room temperature, stimulation effects at a pumping level $I_s \geq 4 \times 10^{25}$ photons/cm^2 sec. On the other hand, the photocurrent increases quadratically at low excitation levels and shows saturation effects near the threshold of stimulated emission. This saturation can be correlated to the light-emission stimulation.

INTRODUCTION

In this work we report the results of a study of two-photon optical transitions in cadmium sulphide. The two-photon process has been detected using three different techniques: nonlinear transmittance (NLT), nonlinear photoconductivity (NLP), and nonlinear luminescence (NLL). By combining these techniques, the following results have been achieved: (a) direct determination of the nonlinear cross section γ_2 for a two photon process; (b) measurement of $\mu\tau$ product of majority carriers in the bulk of the semiconductor; (c) spontaneous and stimulated excitonic emission at room temperature (RT). A photocurrent-saturation effect which may be correlated to the onset of stimulated emission has been also observed. It is worth noting that the whole results of this study show that two-photon experiments may be very useful to give the values of optoelectronic parameters in the bulk of the sample, thus avoiding the influence of the surfaces on accuracy of the measurement.

EXPERIMENTAL PROCEDURE

Figure 1 shows the experimental set-up used for the simultaneous measurement of transmittance, photocurrent, and luminescence under two-photon excitation. The incident beam of intensity I_0(photons/cm^2 sec) was obtained from a Q-switched ruby laser ($\hbar\omega = 1.78$ eV) with 200-MW peak power and 20-nsec pulse duration. The beam cross section was about 1.5 cm^2. The energy of every pulse was monitored with a beam-splitter and an SGD 100A photodiode. Measurements were carried out on a highly photosensitive monocrystal of CdS ($E_g = 2.4$ eV), cut in the shape of a rectangular prism with a pair of carefully treated parallel faces which formed a plane-parallel resonator. The cavity length was about 5 mm. Indium contacts vacuum deposited on two opposite faces were used for photocurrent measurements. The experimental details of these last measurements have been previously described.[1] The total charge Q induced by two-photon transitions can be written[2]

$$Q = e V_0 NL \mu\tau^2 (1 - e^{-\tau_L/\tau}) \frac{\gamma_2 I_0^2}{1 + 2LN\gamma_2 I_0} , \qquad (1)$$

where V_0 is the collecting voltage, L is the thickness of the sample along the laser beam, μ is the mobility of free carriers, τ is their free lifetime, N is the concentration of active atoms, γ_2 is the two-photon nonlinear cross section, and τ_L is the laser-pulse duration.

The luminescence, collected in a direction perpendicular to the exciting beam, was analyzed using a grating monochromator with a photomultiplier followed by a storage oscilloscope. Alternatively, the light emission was recorded photographically with a spectrograph and a 3000 ASA Polaroid film. Two laser shots gave an observable spectrum with a slit width of 20 μm.

The transmittance measurements were performed as it is shown in Fig. 1. The measuring set-up

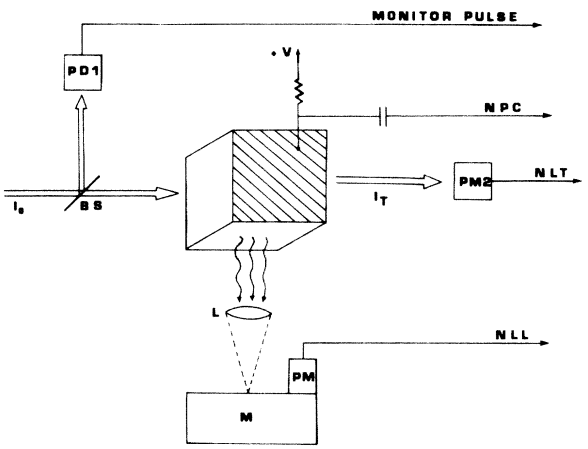

FIG. 1. Experimental set-up for simultaneous measurement of NLT, NLL, and NLP.

was tested for linearity and calibrated with a thermocouple calorimeter. When there is an one-photon contribution to absorption, the two-photon transmittance formula becomes[3]

$$I_T = \frac{I_0 e^{-\alpha L}}{1 + 2N\gamma_2 I_0 L\,[(1 - e^{-\alpha L})/\alpha L]} \quad , \tag{2}$$

where I_T is the transmitted intensity and α is the one-photon absorption coefficient. A plot of I_0/I_T vs I_0 gives a straight line whose intercept on the ordinate axis is $e^{\alpha L}$. For $\alpha L \ll 1$ assuming $\gamma_2 \approx 10^{-49}$ cm^4 sec, $L \approx 1$ cm, and $N \simeq 10^{22}$ cm^{-3} I_T/I_0 becomes about 0.5 for $I_0 \sim 5\times10^{25}$ photons/cm^2 sec, which corresponds to about 15 MW/cm^2 of ruby-laser light, i.e., to an optical pumping well below the damage threshold of CdS ($\simeq$100 MW/cm^2).

RESULTS AND DISCUSSION

The plot of I_0/I_T vs I_0 is shown in Fig. 2 for a nominally undoped CdS sample. The linear dependence is in good agreement with Eq. (2). The straight line has an ordinate-axis intercept which differs from unity and this is an evidence of the contribution of the one-photon process. The following values are obtained for α and γ_2 using $L = 0.5$ cm and $N = 2\times10^{22}$ atoms/cm^3:

$$\alpha = 0.33 \text{ cm}^{-1} ,$$

$$\gamma_2 = 2.5\times10^{-49} \text{ cm}^4 \text{ sec} \quad .$$

The low value of α may be due to an impurity absorption, and the order of magnitude of γ_2 is consistent with previous indirect experimental determinations.[2,4] On the other hand, two-photon spectroscopy measurements,[5] made by using the two-beam technique, give, for $\hbar\omega + \hbar\omega_L = 3.56$ eV and $I_{\omega_L} = 10^{26}$ photons/cm^2 sec, $\alpha \simeq 1$ cm^{-1}, corresponding to $\gamma_2 = 5\times10^{-49}$ cm^4 sec.

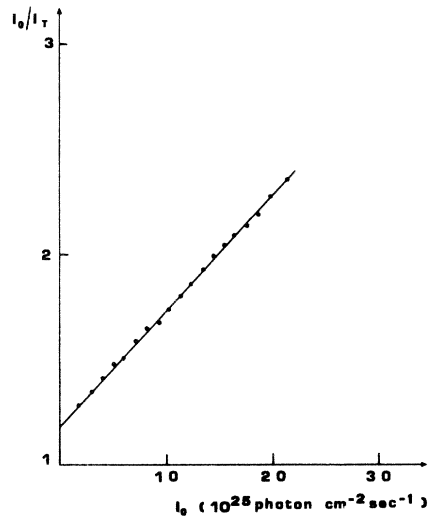

FIG. 2. Attenuation ratio I_0/I_T vs I_0 for two-photon processes in CdS.

The comparison of the γ_2 experimental value may be done using the calculations reported in the Appendix. From the formula for allowed-allowed (a-a) transitions [Eq. (A1)] and our experimental result, it is possible to evaluate the product of the square of the momentum matrix elements $|P_{cn}|^2|P_{nv}|^2$:

$$|P_{cn}|^2|P_{nv}|^2 = 39\times10^{-76} \text{ erg}^2\text{g}^2 \quad .$$

Assuming $P_{cn} \approx P_{nv}$ this result is consistent with the usual order of magnitude of matrix element for allowed transitions.[6] On the other hand, Eqs. (A2) and (A3), which are valid for allowed-forbidden (a-f) transitions give the following values for the momentum matrix element of the allowed transition $|P|^2$:

$$|P|^2 = \begin{cases} 6\times10^{-40} \text{ erg g} & \text{from Eq. (A2),} \\ 1.7\times10^{-35} \text{ erg g} & \text{from Eq. (A3).} \end{cases}$$

It is clear then that our experimental value is not consistent with (a-f) transitions.

It is worth noting that the two models give results very different from another. Particularly, the Basov equation gives too high a transition rate for the two-photon process using a matrix element with the correct order of magnitude. We wish also to note that a more conclusive answer may be only obtained from the frequency dependence of γ_2 [$\frac{1}{2}$ for (a-a) and $\frac{3}{2}$ for (a-f) transitions]. Such result may be achieved using the NLT technique with a tunable dye laser as exciting source.

The results of the two other measurements (NLL and NLP) are strongly interdependent. In Fig. 3 it is shown the emission spectrum at room temperature of CdS at a pumping intensity of 8.8×10^{25} photons/cm^2 sec. The emission peak is centered at 5290 Å and shows a long-wavelength tail; its half-width is $\simeq$20 meV. This luminescent emission has been observed in cathodoluminescence experiments by various authors,[7,8] who also report stimulation at this wavelength at room temperature. The nature of such transition has been ascribed to an exciton-exciton collision process.[8] The peak luminescence intensity and the photo-induced charge Q are plotted versus I_0 in Fig. 4. At relatively low intensities both dependences are quadratic and this demonstrates that the two effects are due to a two photon excitation. By increasing I_0, for $I_0 \geq I_S = 4\times10^{25}$ photon/cm^2 sec the two dependences change dramatically. In fact, while the luminescence grows superquadratically ($\sim I^{5.4}$), the photocurrent saturates.

This behavior may be understood assuming that there is competition between charge collection to electrodes and radiative recombination via exci-

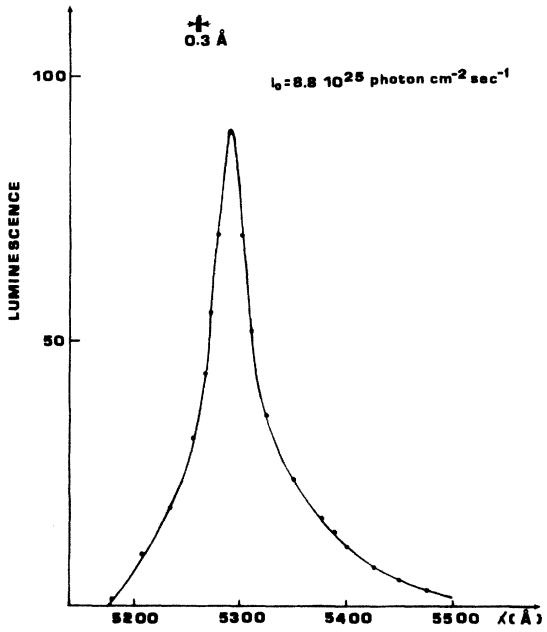

FIG. 3. Luminescence spectrum of CdS at room temperature with two-photon excitation.

tonic states. Below I_s the luminescence is essentially spontaneous and both processes follow the excitation rate. Above I_s, the luminescence emission begins to be stimulated; this shortens the free lifetime of carriers and gives the photocurrent saturation. A similar effect has been observed by electron-beam pumping in CdSe.[9]

By combining the results of NLT and NLP and using Eq. (1) it is possible to get a value of $\mu\tau$ for CdS, which in our case is 6.2×10^{-5} cm^2/V. This technique is particular interesting because gives a $\mu\tau$ value which essentially reflects the bulk properties of the medium, owing to the uniform excitation. We wish to note that by measuring the photocurrent decay time, one gets an independent value of τ and then it is possible to measure the bulk mobility. In our measurements the photocurrent decay shows two components, one fast, about 0.2 μsec and the other slower, i.e., 5 μsec. This last component may be due to trapping effects. At this stage of investigation it is not possible to give a satisfying explanation of this behavior. A detailed analysis of the decay mechanism will be the subject of a next experiment with three-photon excitation using a Nd laser.

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APPENDIX

The nonlinear cross section γ_2 for a two-photon process is defined by

$$w^{(2)} = N\gamma_2 \mathcal{I}^2 \ ,$$

where $w^{(2)}$ is the unit volume transition rate, N the density of active atoms, and $\mathcal{I}$ the photon flux at the considered point. γ_2 is measured consequently in cm^4 sec. γ_2 has been calculated for band-band transitions and using a parabolic-band model by various authors.[3,10,11]

The calculation of Ref. 10 has been extended by Hassan[11] for allowed-allowed (a-a) transitions, to take into account crystal anisotropy.

The resulting equation, when the approximation $x \ll 1$ is dropped, becomes

$$\gamma_2 = \frac{4\pi\sqrt{2}e^4}{c^2 m^{5/2} n^2} \frac{|P_{cn}|^2 |P_{nv}|^2}{N(\hbar\omega)^2} \frac{1}{M(BM)^{1/2}} \frac{1}{\alpha_c + \alpha_v} \times \left(\frac{x}{1+x^2} + \arctan x\right) \ ,$$

with

$$B = (\beta_v + \beta_n) - \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v}(\beta_c + \beta_v) \ ,$$

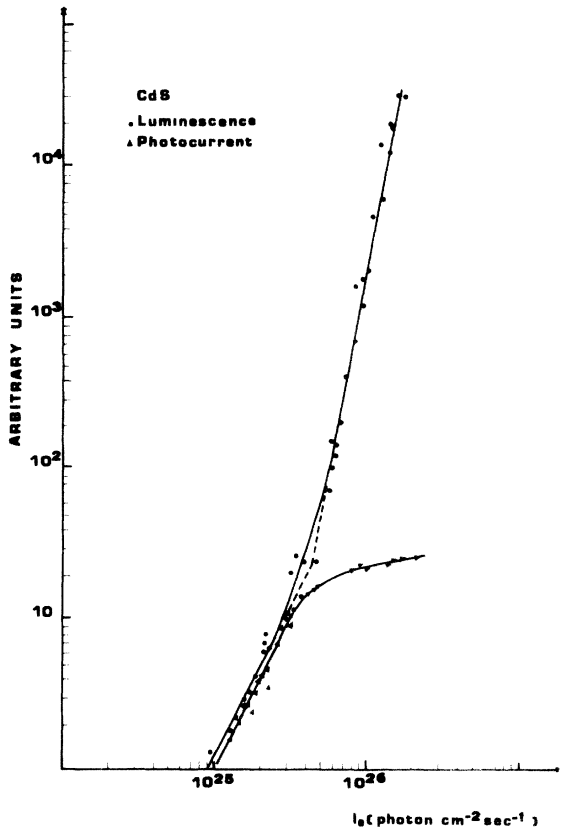

FIG. 4. NLL and NLP dependence on excitation intensity I_0.

$$M = \Delta E - \hbar\omega + \frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v}(2\hbar\omega - E_g) \quad , \tag{A1}$$

$$x = \left(\frac{B}{M}\,\frac{2\hbar\omega - E_g}{\beta_c + \beta_v}\right)^{1/2} \quad .$$

α_i and β_i are the inverse effective masses perpendicular and parallel to the c axis, respectively, and P_{ij} are the momentum matrix elements between states i and j, v is the valence band, c is the conduction band, and n is intermediate band. ΔE is the energy difference between the top of valence band and the bottom of intermediate band. The other symbols have the usual meaning. Assuming the effective-mass values of Ref. 12 and $\Delta E = 9.4$ eV, Eq. (A1) gives for CdS

$$\gamma_2 = (6.42\times10^{25})\,|P_{cn}|^2\,|P_{nv}|^2 \ \text{cm}^4\,\text{sec} \quad .$$

The anisotropy effect ($B \neq 0$) is not very important in this case and the results obtained with $B = 0$ differ by less than a few percent. In addition to (a-a) transitions, two other types of transitions are to be considered: allowed-forbidden (a-f) and forbidden-forbidden (f-f). These last ones gives a very small transition rate and may be discarded. The (a-f) transitions have been calculated with different assumptions by Basov and by Braunstein. The results are,[3,10] respectively,

$$\gamma_2' = \frac{2^{17/2}\pi e^4 |P_{cv}|^2 (2\hbar\omega - E_g)^{3/2}}{n^2 c^2 m^{3/2} N(\hbar\omega)^4 (\alpha_c + \alpha_v)^{1/2}} \tag{A2}$$

and

$$\gamma_2'' = \frac{16\sqrt{2}\,\pi e^4 m^{1/2}}{3c^2 n^2 (m_T)^2}\,\frac{|P_{vn}|^2}{N(\hbar\omega)^2}\,\frac{1}{(\alpha_v + \alpha_c)^{5/2}} \times \frac{(2\hbar\omega - E_g)^{3/2}}{\{\Delta E - \hbar\omega + [(\alpha_n + \alpha_v)/(\alpha_c + \alpha_v)](2\hbar\omega - E_g)\}^2}, \tag{A3}$$

where m_T is an effective mass for the forbidden transition. The main difference between (A2) and (A3) is that in Eq. (A2) the intermediate states are valence and conduction states, while in (A3) a third band n is used as intermediate state. For CdS we obtain

$$\gamma_2' = 3.78\times10^{-10}\,|P_{cv}|^2 \quad ,$$

$$\gamma_2'' = 1.59\times10^{-14}\,|P_{vn}|^2 \quad .$$

[1] I. M. Catalano, A. Cingolani, and A. Minafra, Phys. Rev. B 5, 1629 (1972).

[2] A. Cingolani, F. Ferrero, A. Minafra, and D. Trigiante, Nuovo Cimento 4B, 217 (1971).

[3] N. G. Basov, A. Z. Grasyuk, I. G. Zubarev, V. A. Katulin, and O. N. Krokhin, Zh. Eksp. Teor. Fiz. 50, 551 (1966) [Sov. Phys.-JETP 23, 366 (1966)].

[4] I. M. Catalano, A. Cingolani, and A. Minafra, Phys. Rev. B 4, 1488 (1973).

[5] F. Pradere and A. Mysyrowicz, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors*, edited by S. P. Keller, J. C. Hensel, and F. Stern (U. S. AEC, Division of Technical Information, Washington, D. C., 1970), p. 101.

[6] F. Bassani and A. R. Hassan, Nuovo Cimento B 7, 313 (1972).

[7] F. H. Nicoll, Appl. Phys. Lett. 10, 69 (1967).

[8] J. M. Hvam, Phys. Rev. B 4, 4459 (1971).

[9] J. M. Hvam, in *Proceedings of the International Conference on the Physics of Semiconductors, Prague*, 1972 (PWN-Polish Scientific Publishers, Warsaw, 1972), p. 697.

[10] R. Braunstein and N. Ockman, Phys. Rev. 134, A499 (1964).

[11] A. R. Hassan, Nuovo Cimento B 70, 21 (1970).

[12] J. J. Hopfield and D. G. Thomas, Phys. Rev. 122, 35 (1961).