THREE-PHOTON ABSORPTION AND SUBSEQUENT EXCITED-STATE ABSORPTION IN CdS

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The nonlinear absorption of single picosecond light pulses (λ = 1.06 μm) in CdS is investigated at very high light intensities. Three-photon absorption and subsequent excited-state absorption of the generated electrons and holes explain the rapid decrease of transmission with increasing intensity. A three-photon absorption cross-section of $\sigma^{(3)} = (2 \pm 0.5) \times 10^{-80}$ cm^6 s^2 and an average excited state absorption cross-section of $\sigma_{ex} = (7 \pm 3) \times 10^{-18}$ cm^2 was determined.

Three-photon absorption in CdS crystals has been reported by several authors [1–4]. In previous experiments Q-switched Nd–glass lasers and pulse trains from mode-locked Nd–glass lasers were used. Two-photon absorption of laser light (λ = 1.06 μm, $h\nu_L$ = 1.17 eV) is not possible, since CdS has an energy gap of $E_g \simeq$ 2.42 eV at room temperature. The three-photon absorption of laser light in CdS was detected indirectly by measuring the luminescence or the photoconductivity. The reported three-photon absorption cross-sections differ by one order of magnitude.

In this paper we study the nonlinear absorption of single picosecond light pulses (λ = 1.06 μm) in a CdS crystal at room temperature. The absorption is directly determined by transmission measurements. Three-photon absorption alone cannot explain our experimental data. Light absorption by electrons and holes generated by three-photon absorption has to be taken into account. The three-photon absorption cross-section and the average excited state absorption cross-section for electrons and holes are determined.

In our experiments, we used a mode-locked Nd–glass laser [5]. A single picosecond light pulse was selected from the early part of the pulse train by an electro-optical shutter. The single pulse was amplified to an energy of approximately 3 mJ. The laser pulses had a pulse duration of $\Delta t_L \simeq 6$ ps (fwhm) and a spectral width of $\Delta\tilde{\nu}_L \simeq 3$ cm^{-1} (fwhm). The pulses were nearly bandwidth limited. The single light pulses passed through single CdS crystals of 0.1 cm and 0.31 cm thickness. The c-axis of the crystal was oriented perpendicular to the propagation axis and to the polarization direction of the laser beam. The intensity of the picosecond light pulse at the sample was varied with filters and lenses and it was measured with the method of a saturable absorber [6]. The light transmission through the crystal was measured with two photocells. A schematic drawing of our experimental setup is shown in fig. 1.

Before discussing the results of three-photon absorp-

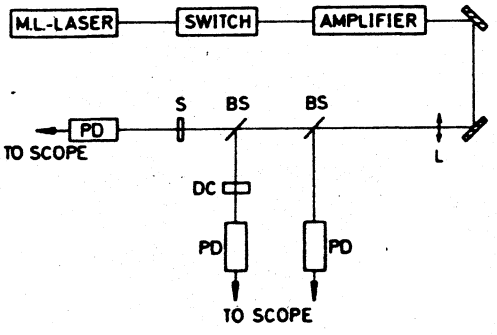

Fig. 1. Experimental setup for nonlinear absorption measurements. L = lens, BS = beam splitter, S = CdS sample, PD = photodetector, DC = saturable absorber for intensity detection.

tion and subsequent excited-state absorption the following remarks should be made:

i) In our experiments we avoided self-focusing in CdS by using short sample lengths (0.1 cm and 0.31 cm), large beam diameters (> 1 mm) and divergent beams ($2\theta > 10^{-3}$ rad).

ii) We made sure that no appreciable loss of laser light occurred by stimulated Raman scattering [7] or stimulated parametric three- [8] or four-photon interactions [9]. In the parametric three-photon interaction $\omega_L \rightarrow \omega_S + \omega_i$ phase matching is possible at $\lambda \simeq 1.12$ μm (laser light perpendicular to optical axis). In the case of parametric four-photon interaction $\omega_L + \omega_L \rightarrow \omega_S + \omega_i$ phase matching is obtained at $\lambda \simeq 9100$ Å and $\lambda \simeq 9550$ Å (laser light parallel to optical axis). The transmitted light was spectrally investigated in the range between 6000 Å and 12000 Å with a 0.3 m Ebert polychromator and an optical multi-channel analyser consisting of a silicon vidicon and a data processing system. No new frequency components could be detected.

iii) To ascertain that three-photon transitions between the valence band and the conduction band occur, we observed the fluorescence following the laser excitation. The emitted light was measured in nearly forward direction within the spectral range from 5000 to 6000 Å with a 0.25 m double monochromator and a photomultiplier. The fluorescence maximum occurred at $\lambda \simeq 5300$ Å. Our fluorescence spectra are similar to that of ref. [10] which were obtained by two-photon absorption of light from a Q-switched ruby laser.

The differential equation for three-photon absorption accompanied by excited-state absorption of the generated electrons and holes is given by

$$\frac{\partial I_L(r, t', z)}{\partial z} = -\alpha^{(3)} I_L(r, t', z)^3 - 2\sigma_{ex} N_{ex}(r, t', z, I_L) I_L(r, t', z), \tag{1}$$

$\alpha^{(3)} = \sigma^{(3)} N/(h\nu_L)^2$ is the three-photon absorption coefficient in cm^3/W^2. $\sigma^{(3)}$ is the three-photon absorption cross-section measured in $cm^6\ s^2$. σ_{ex} is the mean linear absorption cross-section for excited electrons and holes. N_{ex} denotes the number density of excited electrons or holes. It is defined by the following equation.

$$N_{ex}(r, t', z, I_L) = -\frac{1}{3h\nu_L} \frac{\partial}{\partial z} \int_{-\infty}^{t'} I_L(r, t, z)\, dt. \tag{2}$$

The recombination of electrons and holes within the pulse duration ($\Delta t_L \simeq 6$ ps) is neglected.

If the excited state absorption is negligible ($\sigma_{ex} \rightarrow 0$) eq. (1) can be solved easily. We find

$$I_L(r, t', z) = I_L(r, t', 0)[1 + 2\alpha^{(3)} z I_L^2(r, t', 0)]^{-1/2}. \tag{3}$$

The energy transmission for gaussian light pulses is obtained by integration over space and time

$$T_E(I) = \frac{4}{\sqrt{\pi}} \int_0^{\infty} dr\, r \exp(-r^2) \int_0^{\infty} dt\, \{\exp(-t^2)[1 + 2\alpha^{(3)} I_{0L}^2 \exp\{-2(r^2 + t^2)\}]^{-1/2}\}. \tag{4}$$

If the excited-state absorption cannot be neglected ($\sigma_{ex} > 0$), eqs. (1) and (2) represent a complicated system of coupled nonlinear differential equations. We solved the system approximately by setting the result of eq. (3) into eq. (2). This procedure leads to

$$N_{ex}(r, t', z) = \frac{\alpha^{(3)}}{3h\nu_L} \int_{-\infty}^{t'} I_L^3(r, t, 0)[1 + 2\alpha^{(3)} I_L^2(r, t, 0) z]^{-3/2} dt. \tag{5}$$

We obtain an approximate solution of eq. (1) by adding a loss factor to eq. (3).

$$I_{L,ex}(r, t', z) = I_L(r, t', z) \exp\left(-2\sigma_{ex} \int_0^z N_{ex}(r, t', x) dx\right). \tag{6}$$

Integration over space and time leads to the energy transmission

$$T_{E,ex}(I) = \int_0^{\infty} 2\pi r\, dr \int_{-\infty}^{\infty} dt\, I_{L,ex}(r, t', z) \Big/ \int_0^{\infty} 2\pi r\, dr \int_{-\infty}^{\infty} dt\, I_L(r, t', 0).$$

For gaussian input pulses $I_L(r, t, 0) = I_{0L} \exp[-(r/r_L)^2 - (t/t_L)^2]$ we find

$$T_{E,ex}(I) = \frac{2}{\sqrt{\pi}} \int_0^\infty dr\, r \exp(-r^2) \int_{-\infty}^{\infty} dt \exp(-t^2)[1 + 2I\alpha^{(3)} I_{0L}^2 \exp(-2r^2 - 2t^2)]^{-1/2}$$

$$\times \exp\left[-\frac{2\sigma_{ex} I_{0L}^2 t_L \exp(-r^2)}{3h\nu} \left(\int_{-\infty}^{t} \exp(-t'^2)\, dt' \right.\right.$$

$$\left.\left. - \int_{-\infty}^{t} dt' \exp(-t'^2)[1 + 2I\alpha^{(3)} I_{0L}^2 \exp(-2r^2 - 2t'^2)]^{-1/2} \right) \right] . \quad (7)$$

This equation was solved numerically after averaging the integral over t'.

In fig. 2 the experimental points show the nonlinear transmission of laser light in dependence of the input peak intensity for a crystal of 0.1 cm length. The strong decrease of energy transmission at increasing laser intensity cannot be accounted for by three-photon absorption of laser light alone (dashed curves). The excited-state absorption of the generated electrons and holes by three-photon absorption of laser light is responsible for the rapid decrease in transmission. The experimental points can be fitted best with a three-photon absorption cross-section of

$$\sigma^{(3)} = (2.0 \pm 0.5) \times 10^{-80} \text{ cm}^6 \text{ s}^2$$

$$(\alpha^{(3)} \simeq (1.1 \pm 0.3) \times 10^{-2} \text{ cm}^3/\text{GW}^2)$$

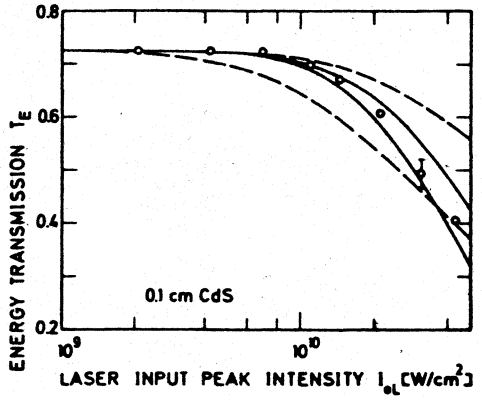

Fig. 2. Energy transmission of picosecond light pulses (λ = 1.06 μm, Δt_L = 6 ps) through 0.1 cm CdS. The experimental points are compared to theoretical curves. The dashed curves describe three-photon absorption. Upper curve, $\sigma^{(2)} = 2 \times 10^{-80}$ cm^6 s^2; lower curve, $\sigma^{(2)} = 1.5 \times 10^{-79}$ cm^6 s^2. The curves do not fit the data. The solid curves are calculated for three-photon absorption and subsequent excited-state absorption of generated electrons and holes. The parameters are $\sigma^{(3)} = 2 \times 10^{-80}$ cm^6 s^2 together with $\sigma_{ex} = 4 \times 10^{-18}$ cm^2 (upper curve) and $\sigma_{ex} = 1 \times 10^{-17}$ cm^2 (lower curve).

and a mean excited-state absorption cross-section for electrons and holes of $\sigma_{ex} \simeq (7 \pm 3) \times 10^{-18}$ cm^2.

In fig. 3 the nonlinear light transmission is shown for a CdS crystal of 0.31 cm length. The same nonlinear cross-sections $\sigma^{(3)}$ and σ_{ex} as in fig. 2 give excellent agreement with the experimental data.

In ref. [11] the free electron absorption cross-section was measured to be $\sigma_{el} \simeq 5 \times 10^{-19}$ cm^2 for λ = 1.06 μm. Our average value of σ_{ex} indicates that hole absorption and possibly hot carrier absorption is larger than σ_{el} of ref. [11].

In table 1 the experimental results on three-photon absorption in CdS are presented. With nanosecond light pulses from Q-switched Nd-glass lasers considerably larger three-photon absorption cross-sections have been reported. Carrier absorption was not taken into consideration, but may be responsible for the large values of $\sigma^{(3)}$. The absorption coefficients obtained with mode-locked pulse trains are in good agreements with our observed value. In these measurements photo-con-

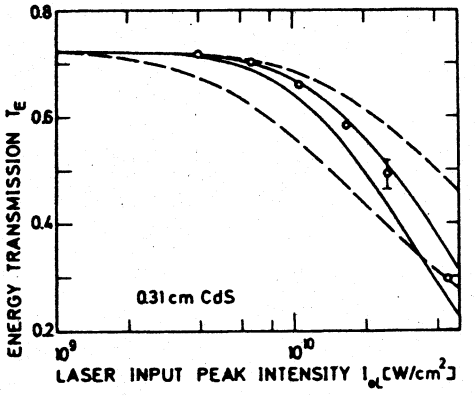

Fig. 3. Nonlinear transmission of picosecond light pulses through 0.31 cm CdS. The curves belong to the same parameters as in fig. 2. The experimental points are best fitted by the values $\sigma^{(3)} = (2 \pm 0.5) \times 10^{-80}$ cm^6 s^2 and $\sigma_{ex} = (7 \pm 3) \times 10^{-18}$ cm^2.

Table 1
Three-photon absorption in CdS.

Sample	Temp. [K]	Excitation	Method	Information	Ref.
Unspecified	77	Q-switched Nd–glass laser	Luminescence	$I_S \propto I_L^{3.4}$; $\sigma^{(3)} \simeq 2 \times 10^{-79}$ cm^6 s^2	[1]
Unspecified		Mode-locked Nd–glass laser	Luminescence	$\sigma^{(3)} \simeq 3.5\ 10^{-80}$ cm^6 s^2	[2]
Single crystal	300	Mode-locked Nd–glass laser	Conductivity	$I_S \propto I_L^{2.86}$; $\sigma^{(3)} \simeq 2.3 \times 10^{-80}$ cm^6 s^2	[3]
Polycrystal	300	Mode-locked Nd–glass laser	Conductivity	$I_S \propto I_L^{2.8}$ $\sigma^{(3)} \simeq 7 \times 10^{-80}$ cm^6 s^2	[3]
Single crystal	80	Q-switched Nd–glass laser	Luminescence	$\sigma^{(3)} \simeq 10^{-79}$ cm^6 s^2	[4]
Single crystal with $E_L \perp c$	300	Mode-locked Nd–glass laser; single pulse	Transmission	$\sigma^{(3)} \simeq (2 \pm 0.5) \times 10^{-80}$ cm^6 s^2 $\sigma_{ex} \simeq (7 \pm 3) \times 10^{-18}$ cm^2	This work

ductivity and luminescence were measured, so that only a very small part of the laser pulse had to be absorbed in the sample. The generated concentration of electrons and holes was kept small and excited-state absorption could be neglected. In our direct study of three-photon absorption by transmission measurements considerable amount of laser light is absorbed and excited-state absorption plays an important role.

In conclusion we wish to point out that direct three-photon absorption measurements were carried out with picosecond light pulses. The application of intense picosecond light pulses together with picosecond light continua make two- [12] and three-photon spectroscopy possible. The different selection rules for single-photon, two-photon, and three-photon transitions make picosecond multi-photon spectroscopy a fruitful spectroscopic tool.

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