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## **Nonlinear Luminescence in CdI<sub>2</sub> under Pulsed Laser Excitation**

Cadmium iodide has been studied from the point of view of nonlinear processes by experiments of optical amplification under two photon excitation. The two photon absorption (2PA) coefficient is determined by nonlinear transmittance technique. By means of two and three photon comparative luminescence measurements carried out using a ruby and neodymium laser, the three photon absorption (3PA) coefficient is determined. The experimental values of the absorption coefficients are compared with the predictions of the existing theories.

Keywords: cadmium iodide, optical amplification, absorption coefficients

### **1. Introduction**

The existence of high intensity lasers has made multiphoton spectroscopy an important tool in the study of the electronic structure of solids. In quantitative studies of multiphoton absorption processes in solids, photoluminescence technique has been widely used. In recent years, three photon spectroscopy has become a powerful tool to investigate electronic and excitonic properties in insulators and semiconductors. Some workers (SINGH et al.) have studied quantitatively the nonlinear photoconductivity properties of CdI<sub>2</sub> using the fundamental and frequency doubled Nd:YAG laser. The transition mechanism related to MPA processes depends on frequency and material parameters. Since CdI<sub>2</sub> is known to have crystal structure with 4H polytypism, it is a better system for ascertaining the predictions of multiphoton processes made by earlier workers (WALTER et al.). Also the energy gap of CdI<sub>2</sub> (3.5 eV at 80 K) is approximately in resonance with the two photon of ruby ( $2 h\nu = 3.56$  eV) and three photon of neodymium ( $3 h\nu = 3.51$  eV) laser. Recently, the emission characteristics of CdI<sub>2</sub> have been investigated using N<sub>2</sub> laser under one photon absorption and the optical amplification in the crystal has been confirmed at LNT for various emission components (AJITH KUMAR et al.). In view of the aforesaid facts, it is found desirable to study the optical amplification under two photon absorption and to determine the 2PA coefficient by nonlinear transmittance (NLT) method. Moreover, the 3PA coefficient of the crystal has been determined by the comparative nonlinear luminescence (NLL) measurements for the first time. The experimental values are then compared with the predictions of the existing theories.

### **2. Experimental**

Highly pure good quality single crystals of CdI<sub>2</sub> were grown from melt by using the horizontal zone melting and refining technique (AJITH KUMAR et al.). The crystals grown from the melt are found to be predominantly of the 4H type. High quality samples (8 x 6 x

3 mm<sup>3</sup>) were selected to use the maximum possible available power density for the excitation. The maximum value which was allowed without crystal damage was about 90 MW/cm<sup>2</sup> with 7 ns pulse duration for both lasers. The nonlinear transmittance and luminescence measurements were carried out at the liquid nitrogen temperature (80 K). For the stimulated luminescence measurements an orthogonal excitation collection geometry was adopted (CATALANO et al.). For the measurement of 3PA coefficient the experimental arrangement reported elsewhere (CINGOLANI et al.) was employed. The broad emission from self-trapped excitons (STE) of CdI<sub>2</sub> has been recorded and the optical amplification under two photon excitation has been studied.

### 3. Results and discussion

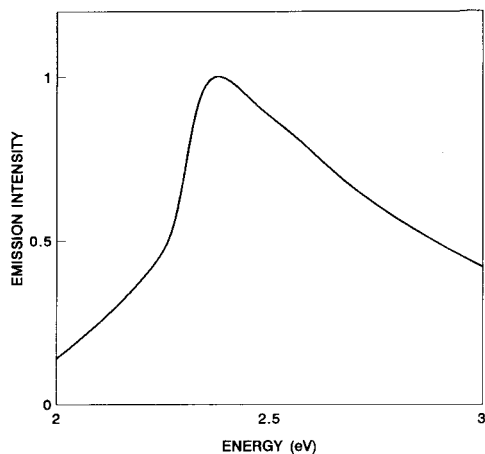


Fig. 1: Stimulated emission spectrum of CdI<sub>2</sub> at LNT.

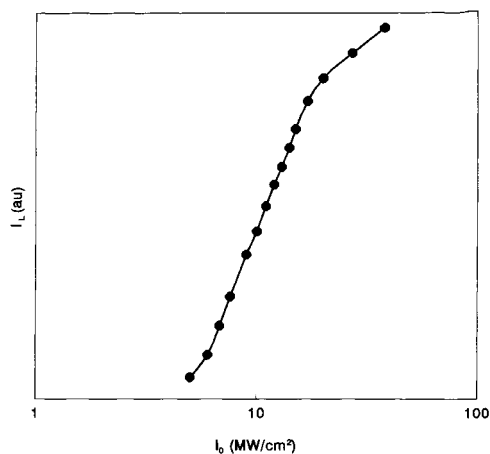


Fig. 2: Stimulated emission intensity vs. two photon pumping power.

Under two photon pumping by means of ruby laser the stimulated emission spectrum of CdI<sub>2</sub> at 80 K (Figure 1) shows a broad band with its maximum at about 523 nm (2.37 eV). The dependence of the emission intensity at the maximum wavelength  $\lambda_{\max} = 523$  nm on the excitation intensity of ruby laser is reported in Figure 2. Above the threshold of about 7 MW/cm<sup>2</sup> the slope becomes super quadratic and the emission shows lasing features, up to the saturation threshold of about 25 MW/cm<sup>2</sup>. This means that also under two photon pumping, the optical amplification processes due to self trapped excitons works properly. This result is quite analogous to the optical amplification process under one photon pumping using a nitrogen laser (AJITH KUMAR et al.).

The nonlinear transmittance technique gives directly the two photon absorption coefficient  $\beta$  by measuring the attenuation ratio  $I_T/I_0$ . Actually, where there is also a one photon contribution to the absorption characterised by an absorption coefficient  $\alpha$ , the two photon reciprocal transmittance formula becomes (ADDUCCI et al.)

$$\frac{I_0}{I_T} = e^{\alpha l} + \frac{2\beta I_0}{\alpha} (e^{\alpha l} - 1) \quad (1)$$

Plotting  $I_0/I_T$  vs.  $I_0$  gives a straight line which intercepts the ordinate axis at  $e^{\alpha l}$  (Figure 3). The one photon absorption coefficient obtained is 5.5 cm<sup>-1</sup>. From the slope  $\beta$  can be determined to be  $3.8 \times 10^{-2}$  cm/MW.

A combination of nonlinear transmittance and nonlinear luminescence method allows the quantitative determination of the 3PA coefficient. When the photon energies of the two photon excitation flux  $I_{Rb}$  and three photon excitation flux  $I_{Nd}$  are such that  $2 \hbar\omega_{Rb} \approx 3 \hbar\omega_{Nd}$ , the same quantum efficiency can be assumed in both absorption processes. Then by arranging an appropriate experimental configuration one can have (CATALANO et al.).

$$\gamma = \frac{I_3}{I_2} \frac{I_{Rb}^2}{I_{Nd}^3} \beta(1-\alpha L) \tag{2}$$

where  $I_3$  and  $I_2$  are the luminescence intensities at the neodymium and ruby frequencies respectively. At  $\lambda = 523$  nm, the  $CdI_2$  luminescence emission is found to have the maximum optical gain (AJITH KUMAR et al.). The dependence of the emission intensity on the exciting intensities  $I_{Rb}$  and  $I_{Nd}$  corresponding to the ruby and neodymium laser beam respectively is shown in Figure 4. Each experimental point is obtained by averaging over several measurements. In the neodymium excitation case, the straight line causing the experimental points has a slope around 3, which is consistent with the three photon absorption process. On the other hand, the slope of 2 obtained for ruby excitation shows a two photon process. Assuming the same luminescence intensity ( $I_3 = I_2$ ) for both the processes, in Figure 4 and from equation (2) and by knowing the two photon absorption coefficient at the ruby frequency, the 3PA coefficient at neodymium frequency can be deduced. One gets, then

$$\gamma = 4.6 \times 10^{-2} \text{ cm}^3/\text{GW}^2 \tag{3}$$

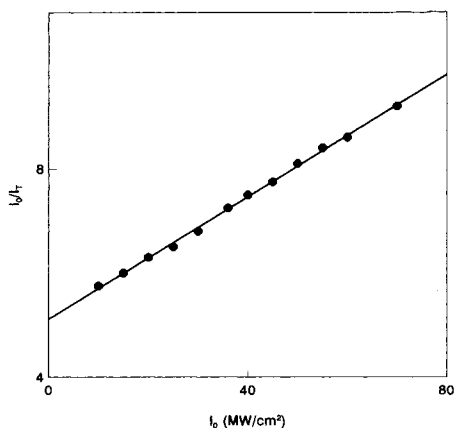


Fig. 3: Reciprocal transmittance vs. incident power.

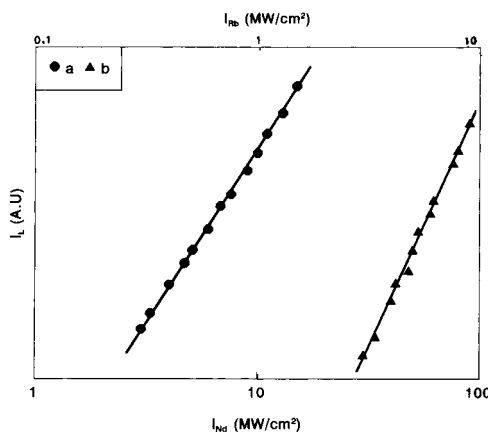


Fig. 4: Luminescence intensity vs. laser input power: (a) Ruby laser and (b) Neodymium laser.

We have compared the experimental values with the predictions of the existing theories (BASSANI et al., JONES et al.) and the earlier reported values (Table 1). In the case of perturbative method the theoretical 2PA value is more in line with the experimental one, while the 3PA value underestimates the experimental one by only an order of magnitude. This consistency arises from the four band model, anisotropy and nonparabolicity adopted for the perturbative method. On the other hand the nonperturbative method greatly underestimates the TPA coefficients. This is due to the simple two band model adopted in spite of the nonparabolicity and anisotropy introduced in this method. Thus it can be said that multiphoton processes will become more competitive at high photon densities and that it is

possible by means of two and three photon comparative photoluminescence measurements to determine quantitatively the 3PA coefficient. It should also be noted that an appropriate choice of the laser intensities is crucial in the experimental evaluation of the absorption coefficients. Moreover, the result of the stimulated emission of CdI<sub>2</sub> in particular has a relevant practical interest as a tunable laser material at least in the low temperature region.

Absorption coefficient	Perturbative method	Nonperturbative method	Experimental results
$\beta$	$3.5 \times 10^{-2}$ cm/MW	$6 \times 10^{-5}$ cm/MW	$3.8 \times 10^{-2}$ cm/MW (present work) $4.0 \times 10^{-2}$ cm/MW (CATALANO et al.)
$\gamma$	$3.4 \times 10^{-3}$ cm <sup>3</sup> /GW <sup>2</sup>	$1.3 \times 10^{-10}$ cm <sup>3</sup> /GW <sup>2</sup>	$4.6 \times 10^{-2}$ cm <sup>3</sup> /GW <sup>2</sup> (present work)

Table 1: Theoretical and experimental values of 2PA ( $\beta$ ), 3PA ( $\gamma$ ) coefficients of CdI<sub>2</sub>.

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