Optical gain by self-trapped excitons in CdI_2

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The stimulated emission in CdI_2 at temperatures between 10 K and room temperature has been studied under N_2-laser and dye-laser optical pumping. The observed spectra consist of only one broad band due to a strong saturation effect, but the unsaturated optical gain spectrum shows that the stimulated emission is due to the overlapping of four main amplified transitions. These transitions are highly consistent with the model of self-trapped excitons in ionic crystals.

The luminescence of self-trapped excitons (STE) in ionic crystals consists of broad bands in the near ultraviolet and visible spectral region. The calculated threshold for laser action from STE requires a population inversion $\Delta N \cong 10^{16}$ cm^{-3} in order to obtain an optical gain of 1 cm^{-1}. At present such a population threshold can be achieved under high excitation density (HED) optical pumping by means of pulsed laser sources, resonant in energy with the excitonic absorption. The configuration coordinate diagram of a self-trapped exciton in ionic crystals is highly consistent with a four-levels laser pumping scheme.[1] Then the laser action involving STE transitions is a prime candidate for new tunable laser sources; the tunability results from the homogeneously broadened emission linewidth.

In order to study laser action from ionic crystals a good candidate is CdI_2, a layered compound that shows a broad spontaneous emission from STE;[2] its direct energy gap ($E_g = 3.5$ eV at 4.2 K) is approximately in resonance with the nitrogen laser ($h\nu = 3.68$ eV).

Matsumoto and co-workers[3,4] observed stimulated emission from CdI_2 at 80 K under HED, but they suggested that the optical amplification was due to the formation of self-trapped biexcitons, since the stimulated emission was localized at lower energies than the spontaneous one.

In this paper we report the results of a systematic study of unsaturated optical gain spectra and of stimulated emission of CdI_2, containing Pb impurities; the HED was achieved by means of a nitrogen laser or a dye laser. The experimental results are consistent with the optical amplification model proposed for the self-trapped excitons in Ref. 1, but they do not agree with the hypothesis of self-trapped biexcitons.

Single crystals of CdI_2 were grown from the melt by using the Bridgmann technique.[5] The CdI_2 crystals grown from the melt have been reported to be predominantly of the 4*H*-type polytype. This is confirmed by the Raman spectrum of our samples, reported in Fig. 1: in this spectrum the very narrow line detected at 15.8 cm^{-1} corresponds to the E_2^2 mode of the polytype 4*H* [space group C_{6v}^4 ($P6_3mc$)], while the two further lines at 45 and 111.5 cm^{-1} are assigned to E_1^1 and A_1^1 modes, respectively, originating from the various polytypes of the point-group symmetry C_{6v}, C_{3v}, and D_{3d}.[6] Optical absorption measurements performed by means of photoacoustic spectroscopy show an absorption band below the indirect energy gap. This band (centered at 3.1 eV at RT) is due to the presence of Pb^{++} impurities in our samples;[7] this presence is also confirmed by the spontaneous luminescence spectrum of CdI_2 at 10 K under PPO dye laser optical pumping in resonance with the impurity band. In such a condition the spectrum shows the three typical emission bands of Pb^{++} in CdI_2,[8] i.e., two narrow bands at 388 and 397 nm, respectively, and another broad band centered at 518 nm.

To achieve the HED in CdI_2 we used three different laser sources: (1) a nitrogen laser ($I_{max} = 10$ MW/cm^2), whose 337.1-nm light lies in the direct excitonic absorption region of CdI_2; (2) a flow-type nitrogen pumped dye laser ($I_0 = 1$ MW/cm^2) tuned at 367 nm, i.e., in the indirect energy gap absorption region;[9] (3) the same dye laser tuned at 387 nm, i.e., in resonance with the absorption band of Pb^{++} impurities at 10 K.

The HED experiments were carried out at temperatures between 10 and 300 K and an orthogonal excitation-collection geometry was adopted. The photoelectric detection apparatus was described elsewhere.[10] The experimental technique to measure the unsaturated optical gain was similar to that developed by Shaklee, Nahory, and Leheny:[11] the sample excited length was controlled down to 0.1 μm.

In Fig. 2 we report the unsaturated optical gain spectrum

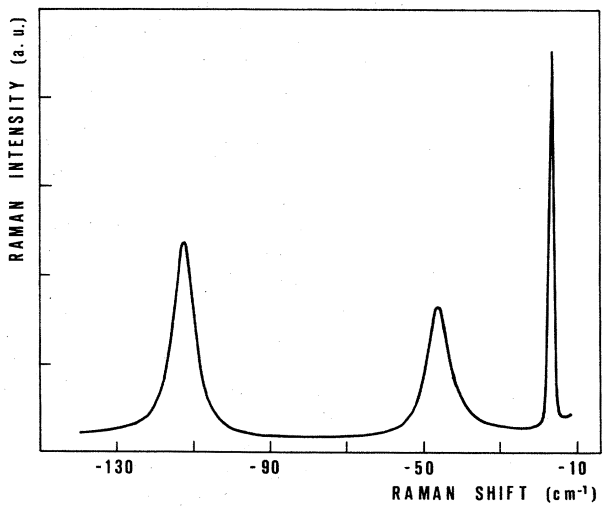

FIG. 1. Raman spectrum of CdI_2 single crystal at RT: $x(xy)z$ orientation; 300-mW excitation at 488 nm by an unfocused argon laser beam.

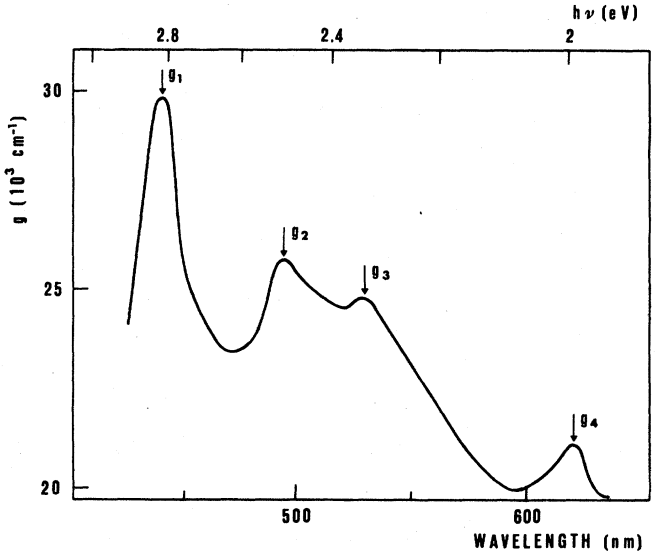

FIG. 2. Unsaturated optical gain spectrum of CdI_2 at LNT under nitrogen laser excitation.

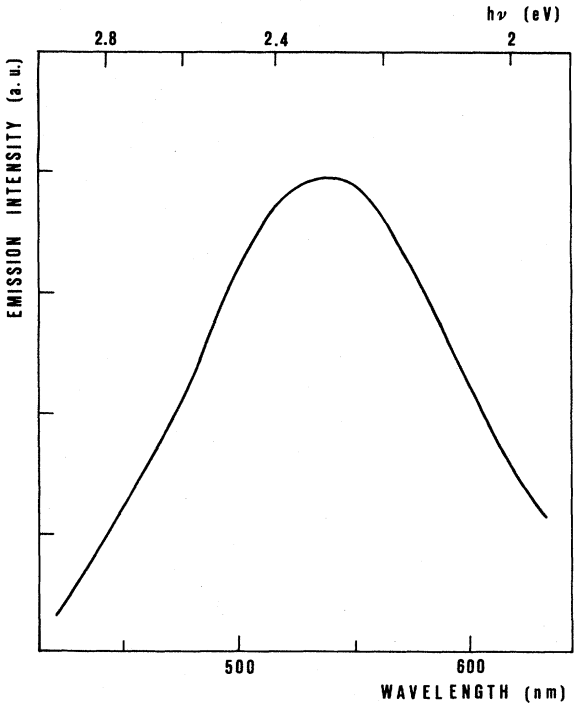

FIG. 3. Stimulated emission spectrum of CdI_2 at 80 K under 1-MW/cm^2 nitrogen laser pumping: excited length $l = 3$ mm.

of CdI_2 at 80 K under N_2 laser pumping at $I_0 = 1$ MW/cm^2. It is worth noting that the gain coefficient $g(\lambda)$ holds values above 10^3 cm^{-1} in a broad range between 420 and 630 nm. Moreover, $g(\lambda)$ depends linearly on the excitation intensity up to the maximum delivered by the nitrogen laser. On the contrary, no evidence of optical gain was achieved by means of optical pumping resonant either with the indirect gap or with the Pb^{++} impurity band. This proves that the optical amplification effect is related to the generation of a high excitonic density. The highest value of g is achieved at liquid-nitrogen temperature (LNT), whereas at 10 K also the maximum value is below 600 cm^{-1}; on the other hand, at $T > 80$ K, at fixed I_0, the optical gain decreases quickly. In Fig. 2 four main peaks can be recognized: g_1 at 2.81 eV, g_2 at 2.53 eV, g_3 at 2.37 eV, and g_4 at 2 eV. Experimental evidence of g_1 and g_3 was reported in Ref. 3, though the value of g_1 resulted to be one-half of g_3.

In common opinion the self-trapped excitons in CdI_2 are well approximated by the excited states of the $(Cd^{2+}X^{-}_6)^{-4}$ complex molecular ions, where X^- is a halogen ion.[12] The energy diagram of this complex ion in D_{3d} symmetry field could allow us to associate g_1, g_3, and g_4 to the transition called V, G, and Y,[12] experimentally observed at low excitation intensity. In our spontaneous emission spectra of CdI_2, at suitable excitation intensity and temperature, we also observe V, G, and Y bands and, moreover, the band associated to g_2. Nevertheless, we cannot assign the peaks of our optical gain spectrum on the basis of the energy diagram of $(Cd^{2+}I^{-}_6)^{4-}$ complex molecular ions in D_{3d} symmetry field as in Ref. 13, since we have shown that our CdI_2 samples have a C_{6v} symmetry field and the Pb^{++} impurities can give place to a different configuration coordinates diagram of STE in CdI_2 with respect to undoped samples.

In Fig. 3 we show the broad stimulated emission spectrum of CdI_2 obtained in the same experimental conditions of Fig. 2, with an excited length $l = 3$ mm. This spectrum shows only a broad Gaussian band with its maximum at about 2.3 eV. In Fig. 4 we report the dependences of the stimulated emission intensity at the wavelengths of the gain peaks g_1, g_2, g_3, and g_4 on the excited length l of the sample from 10 to 70 μm. The values of g obtained at $I_0 = 1$ MW/cm^2 and $T = 80$ K from the slope of the unsaturated region for $l < 10$ μm are indicated in Fig. 2. These values of g increase linearly with the pumping intensity.

It is evident from Fig. 4 that the stimulated emission saturation depends strongly on the wavelength. Particularly, it must be noted that at $\lambda_1 = 440.5$ nm the stimulated emis-

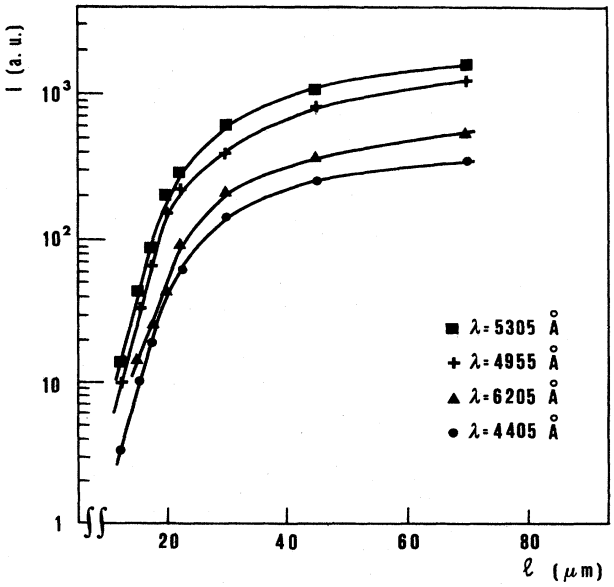

FIG. 4. Stimulated emission intensity vs the sample excited length l ($l > 10$ μm) at the wavelengths of the gain peaks on Fig. 2.

sion intensity quickly grows with l and shows a large gain (g_1), though it saturates at relatively small levels of emitted intensity or of excited length. On the contrary, at larger wavelengths (i.e., $\lambda_2 = 495.5$ nm) the optical gain $g_2 < g_1$, but the saturation effect is observed at an emission intensity which is almost an order of magnitude larger than at λ_1. Moreover, for $\lambda = 530.5$ nm and $\lambda = 620.5$ nm we obtain $g_4 < g_3 < g_2$, but the saturation for $\lambda = 530.5$ nm is achieved at higher values of l. Such a spectral behavior of the optical gain explains why the unsaturated optical gain spectrum shows four well-distinguishable peaks, whereas the stimulated emission spectrum obtained at $l > 100$ μm always results in only one broadband centered on the wavelength with the highest saturation threshold.

In conclusion, our experimental results show that four different optical transitions with a high optical gain contribute to the optical amplification process in $4H$-type CdI_2 under HED. The dependence of g on the pumping photon energy confirms that the nature of the stimulated emission is related to STE. Moreover, since the optical gain strongly decreases below LNT, it can be excluded, according to previous observations in semiconductors, that the population inversion mechanism is due to self-trapped biexcitons. On the other hand it seems, more reasonably, that the mechanisms observed for CdI_2 are consistent with the general scheme of four-levels laser proposed in Ref. 1 for self-trapped excitons in ionic crystals.

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