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Enhanced Two-Photon Absorption in "Pure" CdS

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Abstract We report the observation of anti-Stokes luminescence from the bulk of "pure" CdS. This phenomenon is explained by a cooperative absorption mechanism of two photons enhanced by excitons in the crystal.

The so-called anti-Stokes luminescence has been observed before in doped-materials[1,2,3], but to our knowledge nobody has reported a similar effect in pure materials. Since both sequencial and cooperative mechanismshave been proposed as explanation of that phenomenom[4] it is interesting to look for systems where the intermediate states are short-lived, since in this case for a low laser excitation the contribution of a sequencial mechanism will be negligible.

In this paper we report for the first time the observations of exciton enhanced luminescence in the bulk of "pure" CdS, excited by two photons in a cooperative mechanism. We have used a conventional light scattering set up with an argon ion laser for the excitation lines. The experiment was performed at 10 K in a non intentionaly doped platelets of CdS. The phenomenom was observed already with a few milliwatts of laser power.

A pure CdS would show in the band gap region only exciton lines, these states have normally very short life times, and at 10 K these lines are near the Ar^+ laser energies. In figure 1 we show the anti-Stokes spectra for "pure" CdS at 10 K obtained with 4880 Å, 4965 Å and 5145 Å excitations lines. Prominent Stokes luminescence can be seen in the spectrum excited by 4880 Å line, Since the exciton lines at 10 K start at energies near 19,436 cm^{-1} (5145 Å) our results indicate a two-photon absorption process enhanced by the intermediateexcitonlevels w_i.

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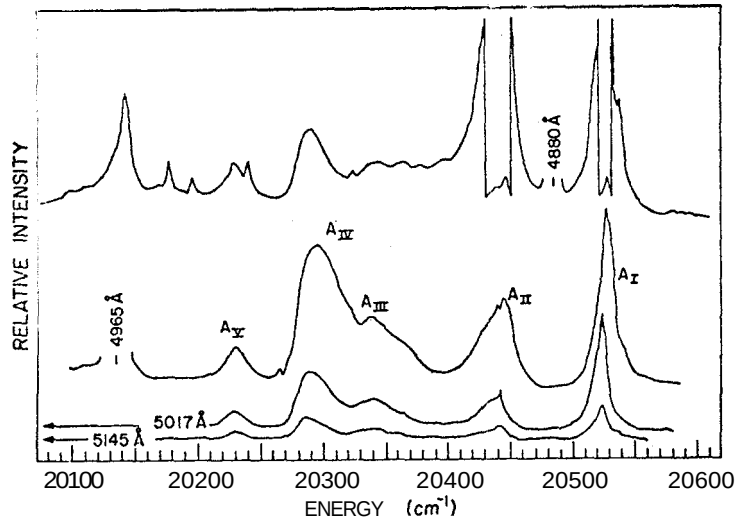

Fig.1 - Luminescence spectra of "pure" CdS excited by two photons in a cooperative mechanism, the laser intensities corresponding to less than 10^{24} photons/(s.m^2).

It is well known[6] that the transition matrix element for two-photon absorption process is proportional to

$$\left| \sum_i \frac{\vec{\varepsilon}_L \cdot \vec{D}_{fi} \; \vec{\varepsilon}_s \cdot \vec{D}_{io}}{\omega_L - \omega_i} \right|^2$$

where $\vec{D}_{ij}$ is the matrix element of the electric-dipole moment between states $|i\rangle$ and $|j\rangle$, $\vec{E}_{L,s}$ are the light polarization vectors, ω_L is the laser frequency and ω_i is the frequency obtained from the energy difference between any excited states $|i\rangle$ and the ground states of the electronic Hamiltonian of the crystal. The symbols o and f stand for the ground and the final states respectively. In general, ω_i is greater than ω_f, which makes $(\omega_L - \omega_i)^{-1}$ smaller than $(\omega_L - \omega_f)^{-1}$. But if it happens that the intermediate state is between the initial and final states ($\omega_o < \omega_i < \omega_f$) and has non-zero electric dipole matrix elements, the-

re would be an enhancement of the transitions matrix element. In the present case these conditions can be fulfilled by excitonic levels present in the band gap near the conduction band[5]. Supposing that there is only one intermediate exciton level coritributing to the process, the luminescence intensity must be proportional to $(\omega_L-\omega_i)^{-2}$. This is shown in figure 2, where we have plotted the reciprocal square root of obser-

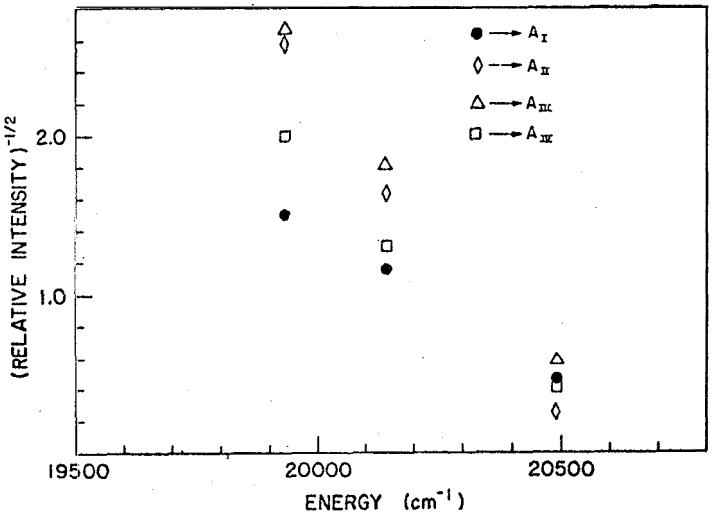

Fig.2 - Reciprocal square root of the observed intensities vs laser energies.

ved intensities vs laser frequencies (the intensities with 5145 Å laser line are very weak, so we did not use them in the figure 2). From figure 2 we obtein the intermediate exciton frequency ω_i equal to 20,780±250 cm^{-1}, which is close to the exciton frequencies in CdS.

In conclusion we claim that the so called anti-Stokes luminescence we observed in "pure" CdS is nothing more than the luminescence resulting from absorption of two photon (cooperative mechanism), enhanced by the sxistence of the intermediate exciton state between the ground and final state.

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RESUMO

O presente trabalho apresenta resultados da observação de luminescência anti-Stokes do interior de um cristal de CdS "puro". Este fenômeno é explicado por mecanismo de absorção cooperativa de dois fótons enaltecido por níveis de excitons no cristal.