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Spontaneous and Stimulated Luminescence in CdS and ZnS Excited by Multiphoton Optical Pumping

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Spontaneous and stimulated emission at 85 °K in CdS and ZnS single crystals is reported. The exciting source was a ruby laser and its second harmonic. The two-photon spectrum of CdS shows stimulation effects in the phonon-assisted excitonic lines at a pumping level of about 10^{26} (photons/cm²)/sec. The same effect is observed in cubic ZnS with the second-harmonic light. A three-photon excited spontaneous luminescence is also obtained in this last sample. The results are in good agreement with the theoretical predictions of multiphoton-absorption theory.

I. INTRODUCTION

Several authors have reported spontaneous and stimulated emission in II-VI compounds.[1-3] The mechanism responsible for most of the lasing transitions is reported[4] to involve bound excitons and acoustical-phonon-assisted transitions, particularly at very low temperatures (4.2 °K) and in the presence of impurity centers. At liquid-nitrogen temperature, line-shape measurements[1] in the spontaneous-emission spectrum have shown that in pure CdS, CdSe, and ZnO, the laser transitions involve the E_{exc}-LO line, i.e., the longitudinal optical-phonon-assisted emission of free excitons.

Other recombination mechanisms which can give laser action in II-VI compounds are the exciton-exciton[2] interaction and the excitonic-molecule recombination.[5] This last effect is difficult to observe experimentally owing to the small binding energy of the excitonic molecule, while the first

one may become prominent at very low temperatures. Generally, the laser emission has been obtained by electron-beam pumping,[1,2] by linear optical pumping with ultraviolet laser light,[6] and by two-photon excitation with a ruby laser.[7]

In the present work we report stimulated emission in pure CdS and ZnS samples at a temperature of 85 °K under two-photon optical pumping, and three-photon excited spontaneous luminescence in ZnS at the same temperature.

II. BASIC THEORY

The fundamental energy gap E_g of CdS and ZnS (cubic) are, at 77 °K, 2.5 and 3.8 eV; the photon energy of the ruby laser is $\hbar\omega_1 = 1.78$ eV and that of its second harmonic is $\hbar\omega_2 = 3.56$ eV.

The nonlinear cross section γ_n for an n-photon process is defined by

$$W^{(n)} = N\gamma_n I^n , \qquad (1)$$

where $W^{(n)}$ is the transition rate for unit volume, N is the density of active atoms, and I is the exciting photon flux (photons/cm²)/sec; γ_n is then measured in $cm^{2n} sec^{n-1}$. For small absorption it may be assumed that I is constant along the thickness of the sample.

The two-photon absorption coefficient has been firstly calculated by means of perturbation theory by Braunstein and Ockman.[8] More recently, the nonlinear cross sections γ_2 and γ_3 have been calculated by Bassani and Hassan[9] for band-band transitions in semiconductors.

Using a parabolic band model with direct gap, γ_2 is

$$\gamma_2 = \frac{8\pi\hbar^3 e^4}{n^2 m^4 c^2} \frac{|P_{cm}|^2 |P_{nv}|^2}{N(\hbar\omega)^2} \frac{1}{(\alpha_c + \alpha_v)(\beta_c + \beta_v)^{1/2}} \times \frac{(2\hbar\omega - E_g)^{1/2}}{\{\Delta_n - \hbar\omega + [(\alpha_n + \alpha_v)/(\alpha_c + \alpha_v)](2\hbar\omega - E_g)\}^2}$$

$$\times \left[1 - \frac{2}{3} \frac{B}{\beta_e + \beta_v} \frac{2\hbar\omega - E_g}{\Delta n - \hbar\omega + [(\alpha_n + \alpha_v)/(\alpha_c + \alpha_v)](2\hbar\omega - E_g)} \right], \quad (2)$$

where $i = \hbar^2/2m_{i\perp}$, $i = \hbar^2/2m_{i\parallel}$ ($i = v, c, n$, where v is the valence band, c the conduction band, and n the intermediate band), P_{ij} is the momentum matrix element between bands i and j, Δn is the energy difference between the minima of the intermediate band and the maximum of the valence band, and B is an anisotropy factor which for CdS equals 0.35 in units of $\hbar^2/2m$. The other symbols have their usual meaning.

With a similar derivation, γ_3 is

$$\gamma_3 = \frac{4\pi^2 \hbar^5 e^6}{n^6 m^6 c^3 N} \frac{1}{(\hbar\omega)^3 \alpha_c^{3/2}}$$

$$\times \frac{36|(1 + \mathscr{P}_{nm}) P_{cm} P_{mn} P_{nv}|^2}{[\Delta_n - \hbar\omega + (\alpha_n/\alpha_c)(3\hbar\omega - E_g)]^2}$$

$$\times \frac{(3\hbar\omega - E_g)^{1/2}}{[\Delta m - \hbar\omega + (\alpha m/\alpha c)(3\hbar\omega - E_g)]^2}, \quad (2')$$

where now two intermediate bands n and m are taken into account and $\mathscr{P}_{nm}$ indicates a permutation over n and m.

For CdS and ZnS, respectively, one gets, from Eqs. (2) and (2'),

CdS: $\gamma_2 \simeq 10^{-48} cm^4 sec$ ($\hbar\omega = 1.78$ eV);

$\gamma_2 \simeq 210^{-49} cm^4 sec$ ($\hbar\omega = 3.56$ eV),

ZnS:

$\gamma_3 \simeq 10^{-80} cm^6 sec^2$ ($\hbar\omega = 1.78$ eV).

The theoretical values of γ_2 and γ_3 have been found in good agreement with the experimental determination by nonlinear photoconductivity measurements.[10,11]

We can now consider the conditions for a negative absorption coefficient in phonon-assisted transitions.

The absorption coefficient for indirect transition may be written[1]

$$\alpha(\nu) = (n/c)A(\nu)[N_p(N_k + 1) - (N_p + 1)N_k], \quad (3)$$

where n is the refractive index at frequency ν and c is the velocity of light. $A(\nu)$ is a proportionality constant which depends on ν. N_k and N_p are the numbers of the excitons and phonons per state. At low temperature, a negative absorption coefficient is possible because the number of LO phonons present is very small.

Particularly, by Eq. (3), in very good agreement with experiments on II-VI compounds, one finds that the required exciton density δ_{exc} at 77 °K for stimulated emission is $10^{16}-10^{17} cm^{-3}$, values that should be achieved using two-photon optical pumping.[12,13] In fact, the threshold condition to achieve this population inversion is that the rate of upward transitions must exceed that of downward transitions, i.e., $W = N\gamma_2 I^2 > \delta_{exc}/\tau$, where τ is the spontaneous lifetime.

Assuming $\tau \simeq 10^{-8}$ sec, $N \simeq 10^{22} cm^{-3}$, and $\gamma_2 \simeq 10^{-48} cm^4 sec$, the previous condition is verified for laser beam intensity $I \simeq 10^{26}$ (photons/cm²)/sec.

III. EXPERIMENTAL PROCEDURE

We used monocrystals of CdS and cubic ZnS obtained from Semielements Inc. They were cut in the form of a rectangular prism with a pair of carefully treated plane parallel faces, forming a planar resonator. The cavity length is about 5 mm. The dimensions of the other edge were also of the order of several millimeters. The samples were fixed to the copper cold finger of a vacuum cryostat operating at 85 °K.

For CdS, we have recorded the luminescence spectrum under one-photon excitation using the blue Ar^+ line ($\lambda = 4880$ Å) or alternatively with the 3650-Å Hg line. The two-photon luminescence was excited by a Q-switched ruby laser, with a pulse duration of 20 nsec and 200-MW peak power.

The energy of every pulse was monitored with a photodiode intercepting a small fraction of the beam. The emission light, collected in a direction perpendicular to that of the exciting beam, was analyzed by a 0.6-m grating monochromator with a 1P28 photomultiplier whose output was fed to a

storage oscilloscope.

Alternatively, the luminescence was recorded photographically, using a spectrograph; in fact for CdS, one laser shot gives an observable spectrum.

The ZnS emission spectra induced by three- and two-photon excitation were obtained using, respectively, the beam of the ruby laser and its second harmonic. The maximum power of second-harmonic light was about 10 MW.

IV. RESULTS AND DISCUSSION

The one-photon CdS emission spectrum, excited by the Ar^+ laser is shown in Fig. 1 (dashed line). The strong green emission which is typical of CdS is due to bound-to-bound transitions and their LO-phonon replicas ($\hbar\omega_{LO} = 38$ meV).

The blue excitonic luminescence is not observed in the one-photon spectrum and this fact is probably due to the small penetration depth of the exciting light. The two-photon excited spectrum, which is due to bulk excitation (Fig. 1, solid line) shows this last region which includes two peaks at λ = 4946 Å (2.507 eV) and λ = 5022 Å (2.469 eV) corresponding to free-exciton recombinations assisted by one and two LO phonons, respectively.

The spectra of Fig. 1 were recorded in the absence of a resonator, i.e., on a sample with natural surfaces.

The peak intensity of the blue and green luminescence is plotted versus excitation intensity in
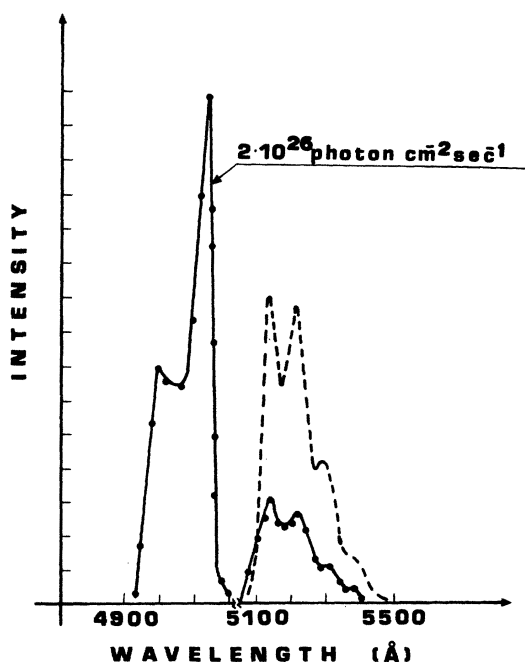
FIG. 1. CdS photoluminescence spectrum one-photon excitation (dashed line) and two-photon excitation (solid line).
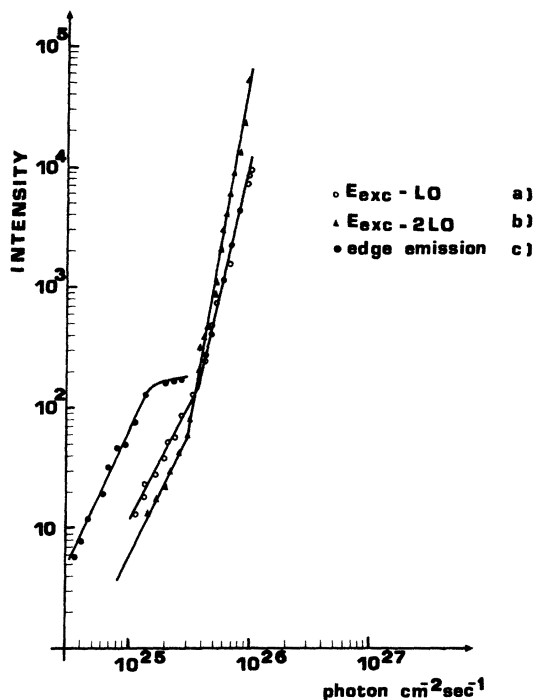
FIG. 2. Peak luminescence intensity vs incident flux for CdS.

Fig. 2 for three energies, corresponding to the E_{exc}-LO, E_{exc}-2LO and the largest edge emission peak λ = 5140 Å (2.412 eV). It is evident from this figure that the peak intensity of the edge emission has a quadratic dependence on the laser intensity that is typical of a two-photon absorption process. At a pump level I of 10^{25} (photons/cm^2)/sec the green luminescence begins to saturate, in agreement with the fact that such emission is due to transitions involving impurity states.

The peak intensity of E_{exc}-LO and E_{exc}-2LO lines, on the other hand, has first a quadratic dependence, then shows a faster rise ($\sim I^6$). For $I > 2 \times 10^{26}$ (photons/cm^2)/sec the superquadratic rise is quite generally followed by saturation effects. The threshold I_s for the superquadratic rise is 5×10^{25} and 3×10^{25} (photons/cm^2)/sec for the E_{exc}-LO and E_{exc}-2LO lines, respectively.

This superquadratic dependence may be attributed essentially to the onset of stimulated emission, which produces a sharpening of the peaks. The experimentally observed thresholds give a critical exciton density: $\delta_{exc} = N\gamma_2 I_s^2\tau \sim 10^{16}-10^{17}$ excitons/cm^3 which is in agreement with the theoretical estimates.

Figure 3 shows the excitonic region spectrum of the same sample with two surfaces lapped to form a plane parallel resonator. In this figure one may see that at an excitation level of 2×10^{26} (photons/cm^2)/sec (the same level used in Fig. 1) the half-
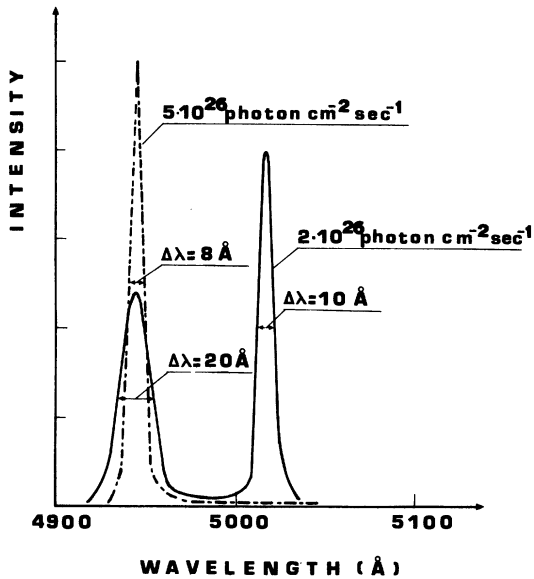
FIG. 3. Stimulated emission of CdS in the phonon-assisted excitonic lines.

width of the E_{exc}-LO is 4.9 meV, which is smaller than KT (about 7.1 meV). At higher excitation levels the E_{exc}-2LO line disappears while the E_{exc}-LO sharpens up to an half-width of 4 meV at 5×10^{26} (photons/cm^2)/sec. This two-photon induced laser effect is in good agreement with the observations of Basov et al.[7]

In Fig. 4 the spontaneous emission spectrum of a cubic ZnS sample excited by the ruby light is reported. The two bands at $\lambda = 3315$ Å (3.740 eV). and $\lambda = 3355$ Å (3.696 eV) are also due (as for CdS) to phonon-assisted excitonic recombinations ($\hbar\omega_{LO}$ = 43 meV). These peaks in fact correspond to that observed in one-photon luminescence at 4.2 °K,[14] allowing for the thermal shift of 15 meV between 4.2 and 85 °K. At this last temperature the energy
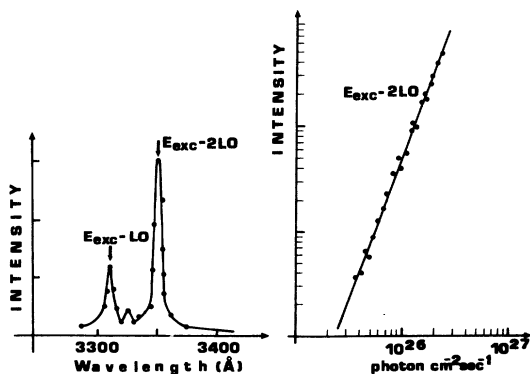

FIG. 4. Emission spectrum of ZnS under three-photon excitation and dependence of the luminescence on the photon flux (E_{exc} – 2LO line).
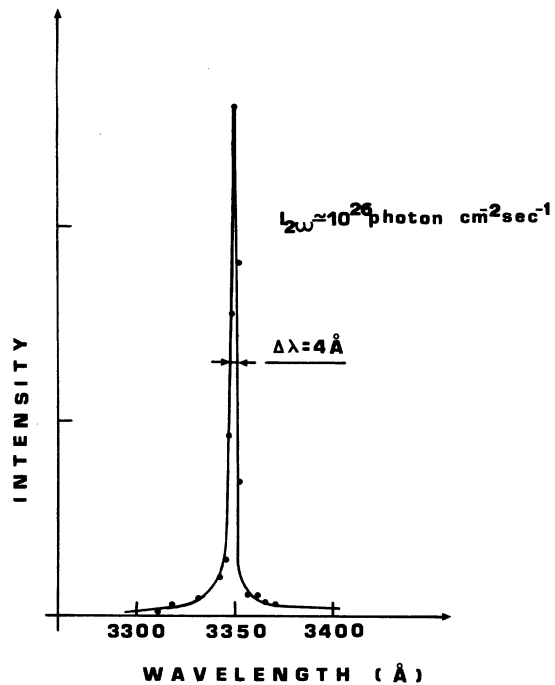

FIG. 5. Stimulated emission of ZnS induced by two-photon excitation.

gap[15] of cubic ZnS is about 3.8 eV, and then an interband excitation is only possible by a three-photon process. This is confirmed by the excitation intensity dependence of luminescence, which shows (Fig. 4) a cubic rise typical of a three-quantum excitation. To our knowledge, this is the first time that a three-photon excited intrinsic luminescence is observed in ZnS. It is worth noting, however, that this effect is quite reasonable, because from Eq. (2') and the previous measurements[10,11] the nonlinear cross section is $\gamma_3 \simeq 10^{-80}$ cm^6 sec^2. This gives, at a pumping level of 10^{26} (photons/cm^2)/sec, a transition rate of $\simeq 10^{20}$ sec^{-1} cm^{-3} of the same order of magnitude of that used in the one-photon luminescence. In a manner similar to CdS, zinc sulphide also shows stimulated emission under two-photon excitation (Fig. 5). This is obtained using the second harmonic of the ruby light focused on a sample treated to obtain an optical cavity. At a pump level of 10^{26} (photons/cm^2)/sec the E_{exc}-2LO peak has an half-width of 4 meV. The peak luminescence dependence vs I is at first quadratic and then superquadratic as for CdS.

V. CONCLUSIONS

The stimulation threshold of phonon-assisted excitonic lines in CdS and ZnS has been investigated under multiphoton excitation. The results show a good agreement with the threshold excitonic densities determined by electron-beam-pumped experi-

ments, and are consistent with calculated and
measured values of the nonlinear cross sections
γ_2 and γ_3.

The stimulation effect is first observed on the
E_{exc}-2LO line, and at increasing excitation levels
shifts towards higher energies (E_{exc}-LO line). This
effect may be due to the relatively high temperature,
which favors the two-phonon line.[4] A similar shift
of the gain towards high energies is also observed
in electron-beam-pumped CdS at lower tempera-

tures.

Finally, a three-photon excitonic luminescence
in ZnS is observed for the first time.

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Exchange-Induced Hyperfine Fields in the Samarium Monochalcogenides*

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We have observed large negative shifts of the Se^{77} nuclear magnetic resonance in SmSe and
SmS$_c$Se$_{1-c}$ solid solutions. These shifts, which depend markedly on temperature and vary linearly with
the sulfur concentration, are found to be correlated with the expectation value of the rare-earth spin.
Simple models for the temperature and concentration dependence are used to obtain the hyperfine field
at the selenium site and the approximate dependence of this quantity on the lattice spacing. For SmSe
the hyperfine field per unit $4f$ spin is -29 ± 4 kOe, where the error includes all probable temperature
dependences of the relevant exchange integrals. In the pseudobinary compounds the dominant
contribution to the concentration dependence of the shift is due to the dependence of the hyperfine
field on the lattice spacing. The data suggest an inverse-seventh power relationship for this dependence.

I. INTRODUCTION

The usual mechanism for ferromagnetic exchange
in rare-earth compounds is indirect exchange via
conduction electrons,[1] and in rare-earth insulators
the dominant interaction between the paramagnetic
ions is expected to be antiferromagnetic.[2] Thus,
the discovery[3] of ferromagnetism in the ionic semi-
conductor EuO was a great surprise. This pro-
vided the stimulus for extensive experimental in-
vestigations of the europium monochalcogenides,
and it is now well documented[4] that all of these com-
pounds exhibit unusually large Eu^{2+}-Eu^{2+} exchange.

Recently much effort has been devoted[5,6] to a the-
oretical explanation of the microscopic origins of
this anomalously large exchange, but as yet the de-
tailed mechanisms are not well understood. In
particular, there is considerable controversy about
the dominant mechanism in the ferromagnetic in-
teraction J_1 between nearest-neighbor Eu^{2+} ions.
This controversy is centered on the question of the
relative importance of indirect exchange resulting
from virtual transitions of localized $4f$ states to ex-
tended $5d$ states[5] and indirect valence-shell ex-
change due to the polarized (by the $4f$ spins) $5p$ and
$6s$ closed shells of the rare-earth ions.[6] It is gen-