BIEXCITON FLUORESCENCE LINE SHAPE IN CdS

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ABSTRACT

A careful experimental study of the M line in CdS is presented, with special attention to polarisation properties. The data can be fitted by a theoretical model of the line shape in both polarization ($E \perp C$ and $E // C$) taking into account the results of group theory, with the recombination of the molecule considered as giving two polaritons. A more precise value of the energy $E_B(o)$ of the ground state of the excitonic molecule is obtained $E_B(o)/2 = 2.5497$ eV ±0.2 meV.

I. INTRODUCTION

Much work has been already done on the biexciton luminescence in wurtzite type semiconductors.$^{1,2)}$ However, a complete agreement about the origin of the M line is far from being complete.$^{3,4)}$ We present here additional experimental results on the polarization properties of the M line in CdS, which are compared to a theoretical model more elaborate than the model proposed earlier by E. Hanamura.$^{2)}$ The good fit between the experiment and the theory provides a better proof of the existence of biexciton in CdS, and a more accurate value of its ground state energy $E_B(o)$.

II. EXPERIMENTAL SET UP

CdS platelets of good quality are immersed in pumped helium (T = 1.6 K). They are excited by the 4765 Å light of a cavity dumped A_r^+ laser, delivering 20 nsec pulses. At 15 W peak power focused in a spot of 60 µm in diameter, the excitation is about 0.5 MW/cm^2. The

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repetition rate was chosen in order to maintain the mean power below 10 mW. Emission spectra were taken in both polarization. A crucial point to select purely Γ_1 photon (E//C) is the use of a narrow vertical slit (the C axis of the crystal being horizontal) in order to select photons propagating in a narrow beam k⊥C. Another advantage of this geometry (k⊥C, E//C) is that one obtains a very good extinction of the I_2 line, which occurs in the same region as the M line. Since the M line is not so strongly forbidden in that geometry, one can observe it at a power density as low as 1 kW/cm^2 (see Fig. 3).

III. THEORETICAL MODEL[5)]

We take here the point of view that a biexciton decays into two polaritons, connected with the lowest A, n=1 exciton state. A given event:

$$\text{Biexciton}(\vec{K}_B, E_B) \rightarrow P(\vec{K}_1, E_1, \vec{\pi}_1) + P(\vec{K}_2, E_2, \vec{\pi}_2),$$

where $\vec{K}$, E and $\vec{\pi}$ refers respectively to wave vector, energy and polarization of the particle, has to be characterized by a matrix element; in addition the usual rules of conservation of energy and momentum are taken into account. Fig. 1 shows that this point of view gives significant changes with respect to the simple theory[2)] especially for biexciton of small momentum.

The matrix elements are determined in the approximation where one polariton is photon-like ($\vec{K}_1$ neglected) and the second is exciton-like ($\vec{K}_2 \sim \vec{K}_B$). We retain only the process allowed in the dipolar approximation.

Taking the z axis along C and the x axis along the momentum of the photon emitted we distinguish two cases:

1) E⊥C. The photon is of symmetry Γ_5. Since the biexciton is Γ_1, the emission of a Γ_5 exciton in the crystal is allowed (it can be purely transverse, or mixed). The emission of a Γ_6 exciton is forbidden. In

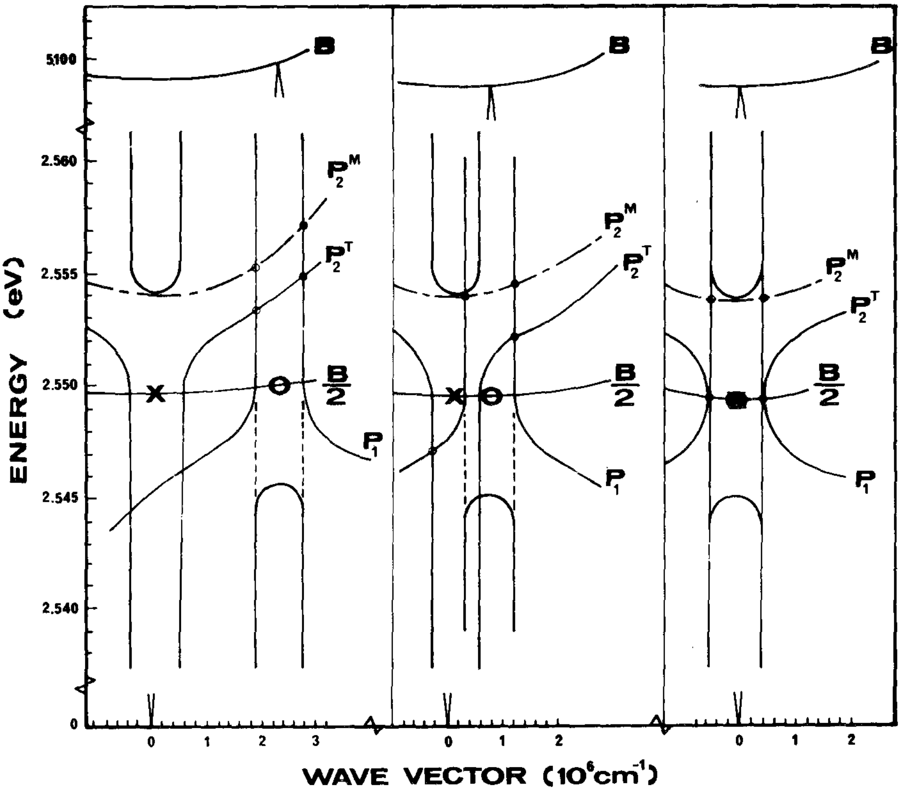

Fig.1. Schematic diagram showing the conservation of energy and momentum in the dissociation of a biexciton of momentum $\vec{K}_B$ into two polaritons. Here, the direction of momentum is restricted to a single direction perpendicular to the C axis.
In a) $\vec{K}_B$ is larger than the momentum of photons. One polariton is photon-like, the other exciton-like (longitudinal or transverse).
In b) K_B is of the order of the momentum of a photon.
In c) $K_B = 0$.

fact, the emission of two polaritons with polarizations perpendicular to each other is forbidden; this is why the matrix element in that case is taken as proportional to cos $\vec{\pi}_1 \cdot \vec{\pi}_2$.

2) E//C. The photon is of symmetry Γ_1. Then the process giving a Γ_5 (or a Γ_6) exciton is forbidden at the zone center. We have to take into account the results of group theory away from $\vec{K} = o$. It can be shown that the $\vec{K}\cdot\vec{P}$ theory can be applied to any eigenstate of a system with translational invariance; so we can use it for exciton or biexciton

states. The only mixing of interest occurring to first order in $\vec{K}$ is between Γ_1 and Γ_{5L} states and is proportional to $|\vec{K}_\perp|$ (Γ_{5L} is the state of polarization $\vec{\pi}$ parallel to $\vec{K}_\perp$). This means that for E//C, we can emit in the crystal only a mixed Γ_5 exciton (which becomes longitudinal if $\vec{K}_2 \perp C$), since in our approximation $\vec{K}_B = \vec{K}_2$. The matrix element is taken like $|\vec{K}_{B\perp}|$. The emission of Γ_5 transverse exciton is forbidden, as well as a Γ_6 exciton.

In addition, in the case E⊥C, there is a problem of probability p_e of escape of the polariton P_1 outside of the crystal. Since the total spectrum of the polariton created in the annihilation of a biexciton exhibits two peaks which are mirror like with respect to $E \sim E_B/2$, we assume a constant value of p_e for the lower energy peak and $p_e \sim 0$ for the upper peak.

Figure 2 gives the results of the line shape calculation, assuming Boltzmann distribution of the molecules with two different effective temperatures T_B. A few comments are of interest.

1) At low T_B, the line shape are much broader than expected when the simpler theory is used. This is due to the finite wave vector and the finite mass of both polaritons P_1 and P_2, and also the anisotropy of the exciton mass (related to the anisotropy of the valence band).

2) It is difficult to observe the longitudinal transverse splitting on the E⊥C spectrum, except at very low T_B. One reason is that in wurtzite crystal, the longitudinal mode is only a special case (k⊥C) of the mixed mode. The L. T. splitting is in fact more easily seen as a shift between the two curves for E⊥C and E//C.

3) Polaritons in the upper branch give negligible contribution to the spectrum.

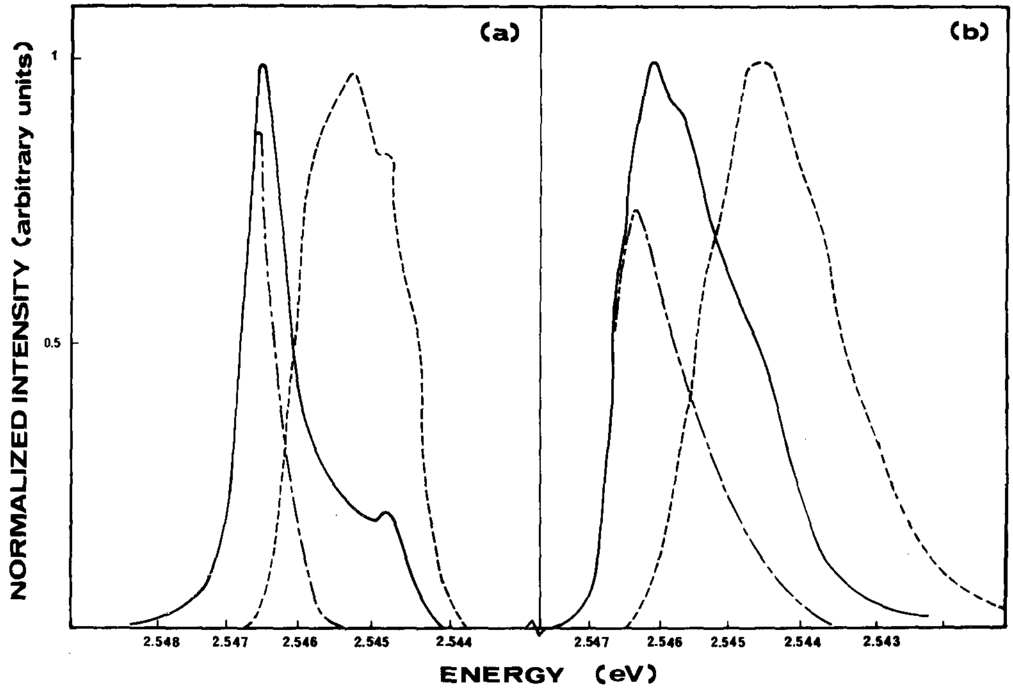

Fig.2. The theoretical M line shape for kT_b = 0.1 meV (a) and 0.5 meV (b) in Γ_5 (——) and Γ_1 (----) observation.
The numerical values used for calculation are summarized in note (6) of the text.
The two curves are arbitrarily normalized. In Γ_1 observation, only the emission of a "mixed" polariton p_2 is allowed. In Γ_5 observation, there are two contributions of equal integrated intensity. The transverse one is shown by (— — —).

IV. DISCUSSION OF THE RESULTS

Figure 3 shows the results obtained at a rather low excitation level for two different samples. A very good fit of the experimental line shape for E//C is obtained without any additional broadening and for T_B rather low. For E⊥C, it is just possible to verify that the theoretical line shape is compatible with the experimental one, which is still dominated by the I_2 line. A value of $E_B(o)/2$ = 2.5497 eV ± 0.2 meV gives the best fit to the data.6)

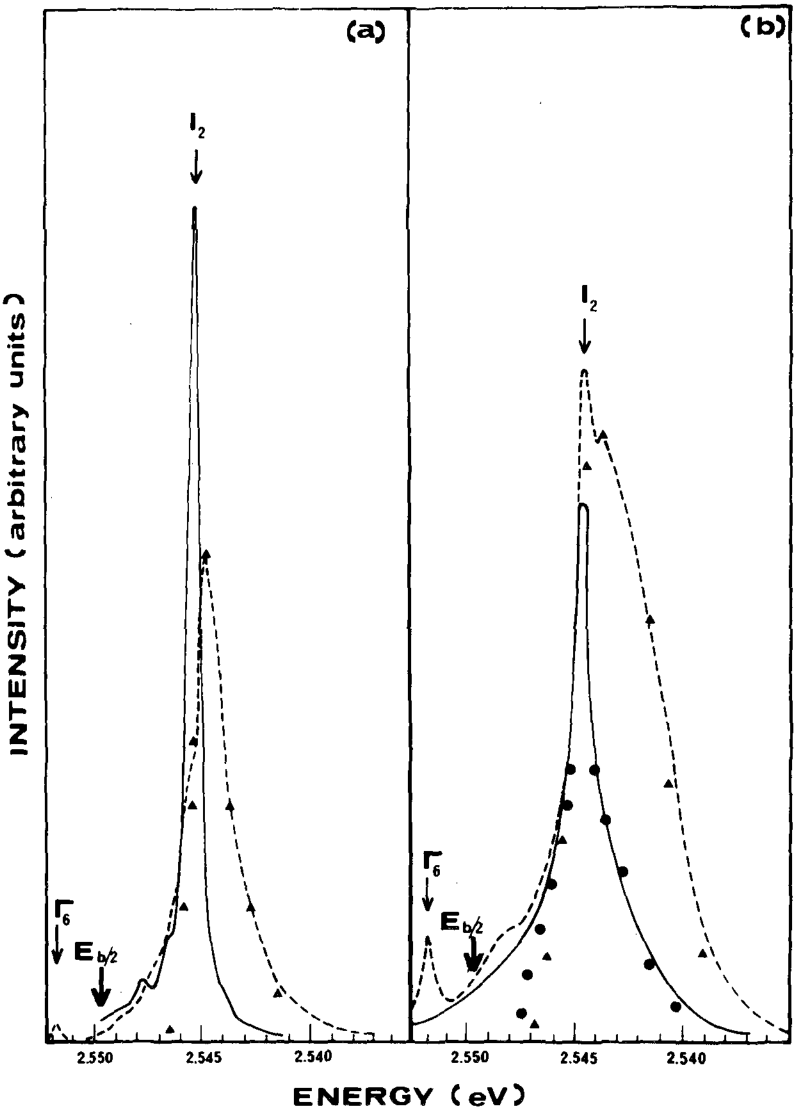

Fig.3. Experimental results in Γ_5 (——) and Γ_1 (----) observation of the M line at rather low ((a): 1 kW/cm^2) and intermediate ((b): 6 kW/cm^2) excitation level. The spectra in a) are taken from a purer sample than in b), so that the I_2 line is more extinguished by the Γ_1 observation.
When the M line is clearly distinguished, the fit gives satisfactory results (● in Γ_5 observation, ▲ in Γ_1 observation). The obtained values for kT_b are 0.4 meV (a), and 1.2 meV (b).

Figure 4 gives data at higher excitation (150 kW/cm^2). In that case, it is difficult to give a good fit for E//C, because in addition

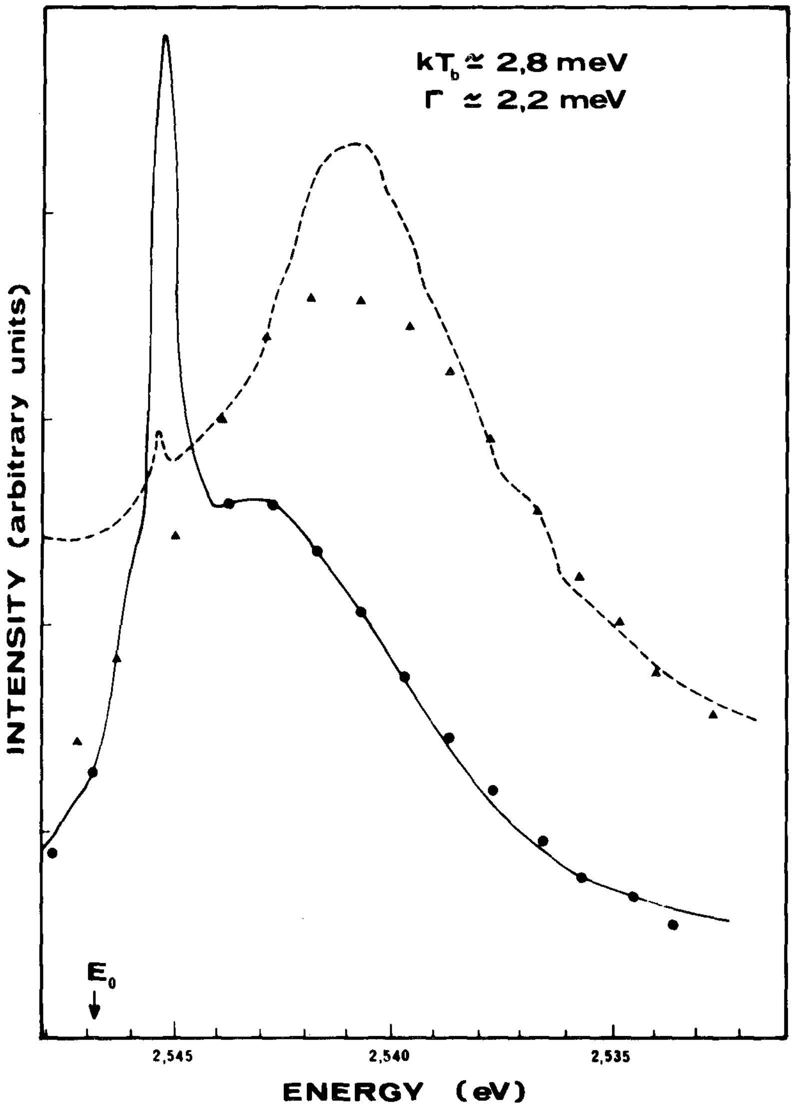

Fig.4. Experimental results in Γ_5 (———) and Γ_1 (- - - -) observation of the M line, at rather strong excitation level (150 kW/cm^2). Here the theoretical fitting is possible using the eqs.(1)(●) and (3)(▲) derived from the model of Hanamura. Although the energy dependence obviously differs in Γ_5 and Γ_1 observation, the fitting of the "forbidden" line is made difficult by the irregular background growing at these excitation levels, and in this configuration of observation. A possible theoretical curve, coherent with the results of Γ_5 observation is however shown.

to the M line, a rather large background appears between 2.556 and

2.540 eV, which could correspond to interaction between excitons, involving at least one exciton of band B. The E⊥C spectrum can be fitted by Hanamura's model, slighly modified to take into account the participation of both exciton modes (transverse and mixed) by an average exciton energy.

$$F(E) = (E_o-E)^{1/2}\exp\left[(E_o-E)/kT_B\right] \otimes \left[(E_o-E)^2 + \Gamma^2\right]^{-1} \qquad (1)$$

where $\otimes$ means convolution product with

$$E_o = E_B(o) - E^L_{ex}(o) + 5/8\,\Delta_{LT}\ . \qquad (2)$$

In that case, rather large biexcitonic temperature T_B and Lorentzian broadening parameter Γ are required, as in ref. (1). It should be noted that, by inspection of the 1 LO and 2 LO replica of the free exciton line, the temperature of excitons is close to T_B. The line E//C, after subtraction of the background emission is fitted by:

$$F(E) = (E^1_o-E)^{3/2}\exp\left[(E^1_o-E)/kT_B\right] \otimes \left[(E^1_o-E)^2 + \Gamma^2\right]^{-1} \qquad (3)$$

with

$$E^1_o = E_B(o) - E^L_{ex}(o)\ . \qquad (4)$$

The simultaneous fit of both line yields a value of $E_B(o)$ very close, to the one obtained at low excitation level, but with a poorer precision.

V. CONCLUSION

We think that these data give additional support to the existence of the biexciton in CdS, and the same experimental technique and theoretical analysis should be generalized to other wurtzite type material. We can predict the spectrum emitted by biexcitons at $k = 0$ (Bose condensation). In that case, P_1 and P_2 have opposite momentum and should have the same polarization, so they should have the same energy. A single sharp line at $E_B(o)/2$ should be emitted (and not at

E_o given by eq.(2)).

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6) We have used the following parameter for CdS: $\varepsilon_\infty = 7.3$, exciton masses $m_{/\!/} = 5.2\ m_o$, $m_\perp = 0.9\ m_o$; $E^L_{ex} = 2.5540$ and $\Delta_{LT} = 1.9$ meV. Our value of photon energies take into account the refractive index of air, a point which has been usually omitted, as in the well known paper of J. J. Hopfield and D. G. Thomas, Phys. Rev. 122 (1961) 35.