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Biexcitonic luminescence for "allowed" and "forbidden" polarization

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We present theoretical and experimental results on biexcitons in CdS. On the basis of an accurate selection of the polarization of luminescence light from the M line, we obtain a good agreement with the hypothesis of the biexciton and a precise value for its ground-state half-energy (2.5497 eV ± 0.1 meV). We also discuss previous results obtained by other authors.

I. INTRODUCTION

Much work has been done recently to obtain more precise knowledge of the excitonic molecule (biexciton) in CdS and CdSe. Shionoya *et al.*[1] observed a new line M in the luminescence spectra of these compounds under strong excitation, and assigned it to the radiative recombination of biexcitons. Subsequently, Hanamura[2] performed a line-shape analysis of their data. This analysis appears to be inadequate to explain the results we present at lower excitation levels. Moreover, it overestimates the biexcitonic temperature and the collision broadening, even at strong excitation levels. This will be shown in Sec. II, where we put forward a more accurate analysis, which takes into account the longitudinal-transverse splitting, the mass anisotropy of excitons, and the polariton effects. Although some approximations are still made, it leads to a better fit of the experimental results which we present in Sec. III. The experiment is performed with a careful selection of emergence and polarization angles of the observed photons. This observation technique is more suitable than previously published ones, as it permits the observation of the M line at lower excitation levels. It provides a more precise value of the biexciton ground energy.

II. THEORETICAL

For our purpose, we confine hereafter to the biexciton ground state of Γ_1 symmetry,[3] which has a momentum $\hbar K_b$.

The radiative recombination of such a biexciton is interpreted as the dissociation into two polaritons: (i) one of them, labeled P_1, travels in the direction of observation $\vec{k}$, and is detected if it can be transmitted at the surface of the crystal; (ii) the second polariton, labeled P_2, ensures the energy and momentum global conservation and is generally not detected: the possibility that the polariton P_2 travels also in the $\vec{k}$ direction and is observed (if transmitted) in the M line has not been considered. The reason is that, taking into account the refractive index n of the material and the aperture f of optics, the probability for any emitted polariton to be detected is of the order of $(1/4\pi)(f/n)^2 \sim 0.2\%$, much less if a slit is interposed (see Sec. III). Thus, the conditional probability that, P_1 traveling along $\vec{k}$, P_2 may be also detected is of the same order of magnitude and cannot affect our results.

As shown in Sec. III, we select the emitted photons propagating perpendicularly to the c axis of the crystal (we assume $\vec{c} \parallel \vec{z}$ and $\vec{k} \parallel \vec{x}$ and define, for any vector $\vec{V}$, the parallel and perpendicular components with respect to c: $V_\parallel$ and $V_\perp$).

The selection of the luminescence polarization parallel or perpendicular to the c axis distinguishes the photons of either Γ_1 or Γ_5^y symmetry. It follows that P_1 lies on the dispersion curve of either Γ_1 photons (uncoupled with A excitons) or transverse Γ_5^y polaritons (see Fig. 1).

Hereafter we only consider P_1 and P_2 to belong to the $A_{n=1}$ band, which is a consequence of the energy position of the M line.

In this framework, P_2 may belong to the Γ_5 or Γ_6 representations of the crystal point group, which stem from the exchange interaction; the Γ_5 polaritons (Γ_5 excitons are optically active) may correspond to a purely transverse mode (Γ_5^T) or to a "mixed"[4] mode (Γ_5^M) depending on the relative orientation of their electric dipoles and wave vectors. The "mixed"-mode polariton is purely longitudinal (respectively transverse) when the wave vector lies in the xy plane: $K_{2\parallel}=0$ (respectively in the z direction: $K_{2\perp}=0$). A general case is illustrated in Fig. 1.

A. Evaluation of the transition strengths

Our purpose here is not an exhaustive computation of the transition strengths implied in the problem; we just want to point out the essential results needed to interpret our experiments, in the framework of the dipolar approximation. This approximation seems sufficient considering that,

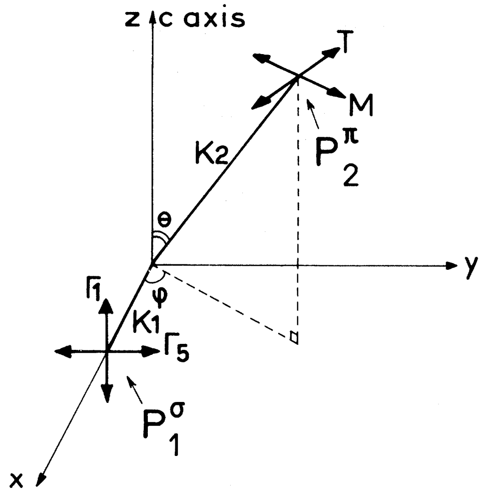

FIG. 1. Wave vectors $\vec{K}_1$ and $\vec{K}_2$ of the P_1 and P_2 polaritons in $\vec{K}$ space: P_1 propagating along the x direction, its (transverse) polarization is either perpendicular to c (Γ_5^y symmetry) or parallel to c (Γ_1 symmetry). A polariton P_2 of Γ_5^x symmetry would be purely longitudinal and not transmitted at the surface of the crystal. If P_2 gets a dipole (Γ_5 symmetry), it lies in the xy plane. So, $\vec{K}_2$ lying in any direction, P_2 may be either purely transverse, or "mixed," depending on the relative orientation of its dipole with $\vec{K}_2$.

for biexcitonic temperatures T_b over 1 °K, most polaritons P_2 are excitonlike with wave vectors $\vec{K}_2$ much larger than those of P_1 (photonlike). It will be justified *a posteriori* by the results of computation, as shown below.

If one uses the N-particle wave functions for the elementary excitations involved, the matrix element α for optical transition will be

$$\langle \phi_b^{\vec{K}_b}(\vec{r}_1, \ldots, \vec{r}_i, \ldots, \vec{r}_N)| \times \sum_{i=1}^{N} \vec{A}_\sigma(\vec{r}_i)\cdot\vec{p}_i |\phi_{\mathrm{ex},\pi}^{\vec{K}_2}(\vec{r}_1, \ldots, \vec{r}_i, \ldots, \vec{r}_N)\rangle , \quad (1)$$

where $\phi_b^{\vec{K}_b}$ (respectively $\phi_{\mathrm{ex},\pi}^{\vec{K}_2}$) is a biexciton (respectively exciton) wave function, with wave vector $\vec{K}_b$ (respectively $\vec{K}_2$). π labels the remaining polariton P_2 ($\pi = \Gamma_5 T$, $\Gamma_5 M$, or Γ_6) and σ the photon selected polarization ($\sigma = \Gamma_5$ or Γ_1).

It reduces, in the dipolar approximation, to

$$\alpha(\vec{K}_b, \sigma, \pi) = \vec{A}_\sigma \cdot \langle \phi_b^{\vec{K}_b}(r_1, \ldots, r_i, \ldots, r_N)| \times \vec{P} |\phi_{\mathrm{ex},\pi}^{\vec{K}_2}(r_1, \ldots, r_i, \ldots, r_N)\rangle = \vec{A}_\sigma \cdot \langle \vec{P}_\pi^{\vec{K}_b}\rangle , \quad (2)$$

where $\langle \vec{P}_\pi^{\vec{K}_b}\rangle$ is the total momentum matrix element between the considered states.

At this stage, the zero-order approximation in $\vec{K}_b$, used until now in this problem[2] states that $\langle \vec{P}_\pi^{\vec{K}_b}\rangle \sim \langle \vec{P}_\pi^0\rangle$, and elementary-group-theory considerations show that only the two components $\langle P_{\Gamma_5}^0\rangle_{x \text{ or } y}$ differ from zero so that the emitted light is totally polarized perpendicularly to the c axis of the crystal.

To go to first order in $\vec{K}_b$, we must consider that the well-known $\vec{K}\cdot\vec{P}$ perturbation theory can be applied to any system of N particles, with translational invariance. This is demonstrated in the Appendix. The formal application of $\vec{K}\cdot\vec{P}$ perturbation theory, where $\vec{K}$ and $\vec{P}$ are, respectively, the total wave vector and momentum operator of the N-particle system, is then possible: from Eq. (2), when Γ_1 (respectively Γ_5) photons are observed, the relevant matrix elements of $\vec{P}$ are $\langle P_\pi^{\vec{K}_b}\rangle_z$ (respectively $\langle P_\pi^{\vec{K}_b}\rangle_y$). In Table I are listed the symmetries of $\vec{K}=0$ states and of their first-order term in $\vec{K}$ for different directions of $\vec{K}$. One deduces easily the dependence of the squared matrix element on the wave vector of the biexciton, $\vec{K}_b$, and on the nature π of P_2 (in the dipolar approximation $\vec{K}_b = \vec{K}_2$). The results are summarized in Table II.

If one does not neglect the wave vector of photonlike polaritons ($\vec{K}_2 \neq \vec{K}_b$), the situation is more complicated. One sees from Table I that several terms in $K_{2\perp}$ and $K_{b\perp}$ appear in the matrix element for Γ_1 polarization, due to the rectangular products of the biexciton and Γ_5^M exciton wave functions. Let us remark that it would be contradictory to assert $\vec{K}_2 \neq \vec{K}_b$ in the framework of the dipolar approximation, which assumes $\vec{K}_1 = 0$. One could deduce for example that $\alpha(\vec{0}, \Gamma_1, M) \neq 0$. This is probably erroneous because in this case (where the wave vector of photons is not neglected), we should use a more accurate analysis.[5] Actually, the choice we have made,

$$|\alpha(\vec{K}_b, \Gamma_1, M)|^2 = d|K_{b\perp}|^2, \quad \text{instead of } d|K_{2\perp}|^2 ,$$

is more satisfactory from the point of view of symmetry. Moreover, we have checked this choice to be of negligible influence on the computed line shapes for $T_b > 1$ °K (see Sec. II C). This seems a good justification of the dipolar approximation in such conditions.

B. Computation of the emerging polariton energy

The computation of the energy of P_1, associated to the dissociation of a biexciton with wave vector $\vec{K}_b$, *and* traveling along the $\vec{k}$ direction, can be performed from the principles of wave vector and energy conservation. This is shown in Fig. 2, for both Γ_5 and Γ_1 observations. We first want to emphasize that, $\vec{K}_b$ and $\vec{k}$ being given, the dissociation into P_1 and P_2 is always possible, with either transverse of "mixed" P_2-Γ_5 polariton. The effects which are neglected in the simple theory used by Hanamura[2] are listed as follows:

TABLE I. Representations (and partner of bidimensional representations) of the wave functions involved in the problem: Biexciton (Φ_b), "mixed" and transverse mode Γ_5 excitons (Φ_{ex}^M and Φ_{ex}^T), Γ_6 excitons ($\Phi_{ex}^{\Gamma_6}$). The notation is that used for the group C_{6V} in G. F. Koster, J. O. Dimmock, R. S. Wheeler, and H. Statz, *Properties of the 32-Point Groups* (MIT, Cambridge, Mass., 1963). The wave functions are considered for $\vec{K}=0$ and for $\vec{K}\neq 0$ lying in the three main directions (see Fig. 1). The representations are given for the zero- and first-order term in $\vec{K}$ of the wave functions.

Wave vector	Polar angles	Order	Φ_b	Φ_{ex}^M	Φ_{ex}^T	$\Phi_{ex}^{\Gamma_6}(\times 2)$
$\vec{K}=0$		0, 1	Γ_1	$\Gamma_5(\times 2)$		$\Gamma_6(\times 2)$
$\vec{K}\parallel\vec{c}$	$\theta=0$	0, 1	Γ_1	$\Gamma_5(\times 2)$		$\Gamma_6(\times 2)$
$\vec{K}\perp\vec{c}$	$\theta=\frac{1}{2}\pi$	0	Γ_1	Γ_5^x	Γ_5^y	$\Gamma_6(\times 2)$
and $\vec{K}\parallel\vec{x}$	and $\varphi=0$	1	Γ_5^x	Γ_1, Γ_6^y	Γ_2, Γ_6^x	Γ_3, Γ_4, $\Gamma_5(\times 2)$
$\vec{K}\perp\vec{c}$	$\theta=\frac{1}{2}\pi$	0	Γ_1	Γ_5^y	Γ_5^x	$\Gamma_6(\times 2)$
and $\vec{K}\parallel\vec{y}$	and $\varphi=\frac{1}{2}\pi$	1	Γ_5^y	Γ_1	Γ_2	$\Gamma_5(\times 2)$

(i) The remaining polariton P_2 may be, for both polarizations of P_1, emitted in a pure transverse or "mixed" mode. It does not mean that the M line should be duplicated with an energy shift Δ^{LT} (the longitudinal-transverse splitting) because, in the "mixed" mode, only the Γ_5 excitons with momentum perpendicular to the c axis are purely longitudinal.

Depending on the zenital angle θ between $\vec{K}_2$ and the c axis, the energy of the "mixed" mode, for $\Delta^{LT}\ll E^T$, is given by

$$E^M(\theta,\vec{K}_2)=E^T(\vec{K}_2)+\Delta^{LT}(\vec{K}_2)\sin^2\theta$$
$$=E^L(\vec{K}_2)-\Delta^{LT}(\vec{K}_2)\cos^2\theta; \quad (3)$$
$$E^L(\vec{K}_2)=E^L(\vec{0})+\hbar^2K^2/2M$$

is the energy of purely longitudinal uncoupled excitons with mass M; $E^T(\vec{K}_2)$ is the energy of purely transverse polaritons; $\Delta^{LT}(\vec{K}_2)$ is constant out of the bottleneck region.

From Eq. (3), and a constant density of states in $\vec{K}$ space, one computes easily the distribution of energies $n(\epsilon)$ of excitonic polaritons for a fixed $\vec{K}_2$. In an isotropic model

$$n(\epsilon)\propto\delta(\epsilon-E^T(\vec{K}_2))$$
$$+\{4\Delta^{LT}(\vec{K}_2)[E^L(\vec{K}_2)-\epsilon]\}^{-1/2}, \quad (4)$$

with

$$E^T(\vec{K}_2)\leq\epsilon\leq E^L(\vec{K}_2).$$

The effect of the longitudinal-transverse splitting is non-negligible for all values of $\vec{K}_b$, that is, for all biexcitonic temperatures T_b. It should lead to the appearance of two peaks (for $T_b<10$ °K), provided that one can neglect the other broadening factors considered below, and especially the mass anisotropy. In fact, such an approximation is not valid.

(ii) For small $\vec{K}_b$, the longitudinal-transverse splitting is increased because of the coupling of transverse excitons with photons, and the energy E_2 of P_2 is lowered. As a consequence the energy E_1 of the associated P_1 is increased. The importance of this effect depends on the proportion of biexcitons emitting bottleneck polaritons. Thus, it has an influence only at low temperature ($T_b<10$ °K), but being associated with small $\vec{K}_b$, it appears to be negligible for the emission of Γ_1 photons as soon as $T_b>1$ °K (see Sec. II A).

(iii) In a given experiment $\vec{k}$ is fixed parallel to x, but the direction of $\vec{K}_b$ (and, consequently, of $\vec{K}_2$) is not. For example, the typical values $\pm 2\times 10^6$ cm^{-1} in the x direction are equally probable, but the associated energies of P_2 differ by more than 1 meV, because of the band curvature and the nonzero photon wave vector.

This broadening effect is even greater for larger $\vec{K}_b$ (and high temperatures T_b) as well as for small

TABLE II. Strength of transition $S_\sigma(\vec{K}_b,\pi)$. It only depends, in the dipolar approximation, on $\vec{K}_b$ and on the nature of P_1 and P_2. It may be calculated from Table I, with constant coefficient D and d, the ratio of which depends on the mixing of the A valence band with the others. The angles θ and φ are the polar angles of $\vec{K}_b$, as defined in Fig. 1 ($\vec{K}_2=\vec{K}_b$ in the dipolar approximation). We have neglected second-order terms in $\vec{K}_b$ for S_{Γ_5}, and fourth-order terms for S_{Γ_1}.

$\pi \backslash \sigma$	$\Gamma_5(\perp c)$	$\Gamma_1(\parallel c)$
Γ_5, T	$D\cos^2\varphi$	0
Γ_5, M	$D\sin^2\varphi$	$d\lvert\vec{K}_b\rvert^2\sin^2\theta$
$\Gamma_6(\times 2)$	0	0

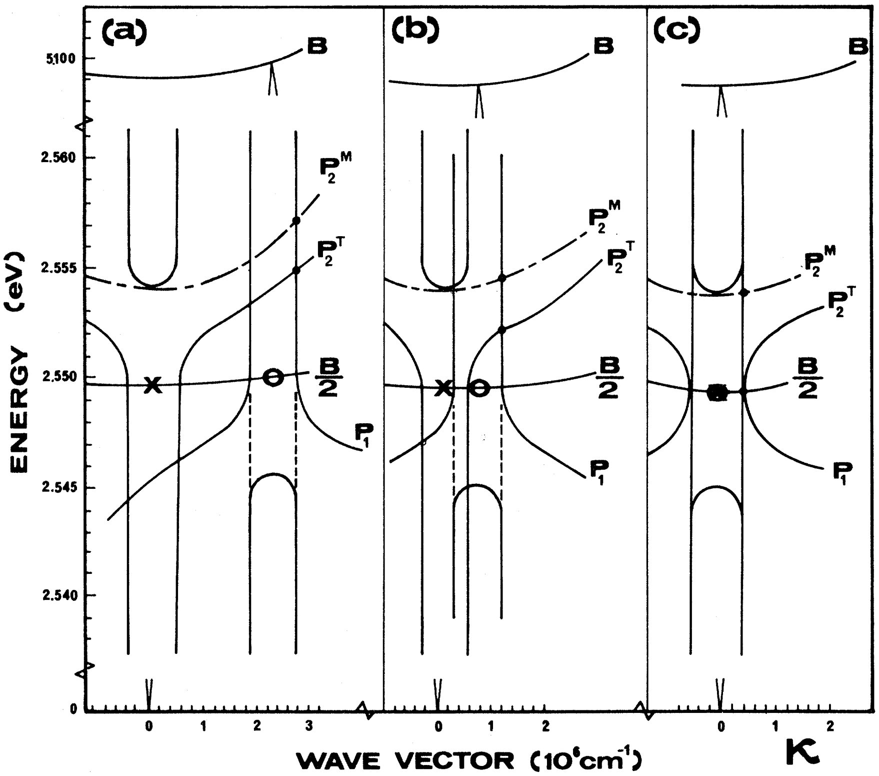

FIG. 2. Possible dissociations of a biexciton $B(E_b, \vec{K}_b)$ into two polaritons P_1 and P_2. In a four-dimensional space, the five relevant dispersion laws can be noted $B(E_b, \vec{K}_b) = 0$, $P_1^\sigma(E_1, \vec{K}_1) = 0$ and $P_2^\pi(E_2, \vec{K}_2) = 0$, with $\sigma = \Gamma_1$ or Γ_5, and $\pi = T$ or M. They are represented by five hypersurfaces and, as we restrict P_1 polaritons to travel parallel to x, $P_1(E_1, \vec{K}_1)$ reduces to a one-dimensional curve. The principle is to represent $P_1(E_b - E_1, \vec{K}_b - \vec{K}_1) = 0$, so that the intersection points of these curves with $P_2(E_2, \vec{K}_2)$ satisfy $E_1 + E_2 = E_b$ and $\vec{K}_1 + \vec{K}_2 = \vec{K}_b$. Here, we have represented the case of $\vec{K}_b \| \vec{\kappa}$ so that (i) only the intersection points (•) travel along $\vec{\kappa}$; (ii) the "mixed" mode (dashed-solid line) is purely longitudinal; (iii) the apparent effective masses of biexcitons and excitons are their transverse masses. P_2^T and $P_1^{\Gamma_5}$, strongly coupled with excitons, are represented by a solid line and $P_1^{\Gamma_1}$, uncoupled, by a dashed line. The point $(E_b(0)/2, 0)$ (X) refers to the biexciton half energy and by the transformation we make, it corresponds to the point $(E_b/2, K_b)$ (O), which lies on the "half energy" biexciton dispersion hypersurface: $B(2E, K) = 0$ (noted $\frac{1}{2}B$).

$\vec{K}_b$, when the polariton effect complicates the shape of the intersection surfaces in momentum space.

(iv) A fourth important broadening effect is not seen in Fig. 1: it is due to the strong anisotropy of excitonic and biexcitonic masses in CdS, related to the A-valence-band anisotropy. For a given biexciton energy, E_1 depends on the orientation of K_2. This effect appears to be important for $T_b \lesssim 20\,°K$. It does not appear in the simple model of Hanamura where $\vec{K}_1 = \vec{0}$. Moreover, if a thermal distribution is assumed, most of the biexcitons have their momentum along the c axis of the crystal, with a heavier mass; the "mixed" mode P_2 they emit will be more transverse than expected from a simple generalization of Eq. (4). This will broaden and flatten the "mixed" mode contribution to the M line.

C. Computation of the M line shape

The M line shape is given by

$$W(E_1^\sigma) = \mathcal{T}(E_1^\sigma) \sum_\pi \int n(\vec{K}_b) P(\vec{K}_b) S_\sigma(\vec{K}_b, \pi) \times \delta(E_b(\vec{K}_b) - E_1^\sigma - E_2^\pi(\vec{K}_b, \vec{\kappa}))\, d\vec{K}_b\,, \tag{5}$$

where the indexes σ and π are defined as in Eq. (1); $n(\vec{K}_b)$ is the (constant) density of states of biexcitons in momentum space; $P(\vec{K}_b)$ is the population factor of biexcitons in this space, which has been assumed to be a Boltzmann factor with an effective temperature T_b; the mass anisotropy is taken into account; $S(\vec{K}_b, \pi)$, the strength of transition, is taken in accordance with the results in Table II. Let us just recall that they imply that $\vec{\kappa}$, the direction of observation, is taken strictly perpendicular to the c axis of the crystal.

All the remarks made in Sec. II B are included in the complexity of the δ functions: from $\vec{K}_b$, $\vec{\kappa}$, and σ, one can compute, as illustrated in Fig. 2, the energy and momentum of two couples of polaritons

$$\{P_1^\sigma, P_2^T\} \text{ and } \{P_1^\sigma, P_2^M\},$$

which satisfy the energy and momentum conservation, P_1 being traveling in the $\vec{\kappa}$ direction and situated on the pure (Γ_5 or Γ_1) dispersion curve.

The coefficient characteristic of the "transfer" out of the crystal, $\mathcal{T}(E_1)$ applies only for P_1 because, as shown above, the probability that P_2 may *also* be detected is very weak.

We have evaluated numerically[6] the integral in Eq. (5) for different values of E_1, using a rectangular function of 0.1-meV width as a substitute for the δ functions. Having to tabulate the polariton dispersion curve, we should limit our computations to $T_b \geq 1$ °K. (A typical result is shown in Fig. 3 for the Γ_5 observation and $kT_b = 0.2$ meV.) In these conditions, the P_1 polaritons yield into two symmetric lines M and M'. The M line appears to be formed with (Γ_5 or Γ_1) P_1 situated below 2.547 eV, and the M' line with P_1 above 2.553 eV, and situated on the lower branch of the dispersion curve. In such conditions, the calculation of $\mathcal{T}(E_1)$ is trivial[7] and has been assumed to be constant for the whole M line, and zero for its symmetric M'.

The theoretical M line shapes are presented in Fig. 4 for two typical biexciton temperatures T_b, and for the two configurations of observations. In our theory, the biexciton ground-state energy may influence the line shape and has been chosen in accordance with the experimental data. The numerous effects that we have considered in Sec. II B lead to an apparent width of the M line larger than kT_b, even at biexcitonic temperatures as low as 10 °K.

In Γ_5 configuration of observation, these effects make it difficult to observe separately the transverse and "mixed" mode contributions. The integrated intensity of the latest should decrease at very low temperatures because, when $\vec{\kappa}$ is parallel to the x direction, a small $\vec{K}_b$ makes $\vec{K}_2$ lie predominantly in the $-x$ direction. This effect does not play any significative role as long as $T_b \gtrsim 1$ °K; both contributions are then equal.

In Γ_1 configuration, and at rather low T_b, the effect of longitudinal-transverse splitting of P_2 polaritons is clearly seen, because of the zero contribution of P_2^T; this leads to a shift of the line towards the low energies (with respect to the Γ_5 line), by a quantity of the order of Δ^{LT}. At higher T_b, the effect of the K_b-dependent matrix element dominates; it shifts also the line towards the low energies, of a quantity of the order of kT_b.

III. EXPERIMENTAL

A. Setup

The CdS platelet is immersed in pumped liquid helium ($T \sim 1.6$ °K) and excited by the 4765-Å light of a cavity-damped Ar^+ laser. With 20-nsec pulses

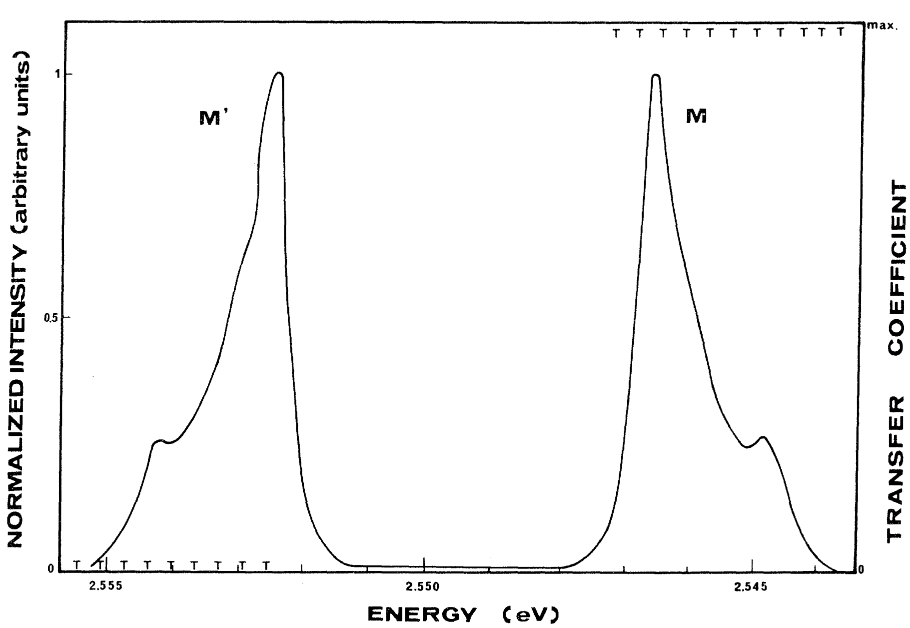

FIG. 3. Result of the calculation of the integral in Eq. (5) for $kT_b = 0.2$ meV ($T_b \sim 2$ °K) and Γ_5 observation. If one neglects the temperature broadening of the biexcitonic distribution, the two lines M and M' are symmetric with respect to the biexciton ground-state half energy. The transfer coefficient $\mathcal{T}$ is just represented (T) for energies where it is obviously constant or slowly varying (see Ref. 7).

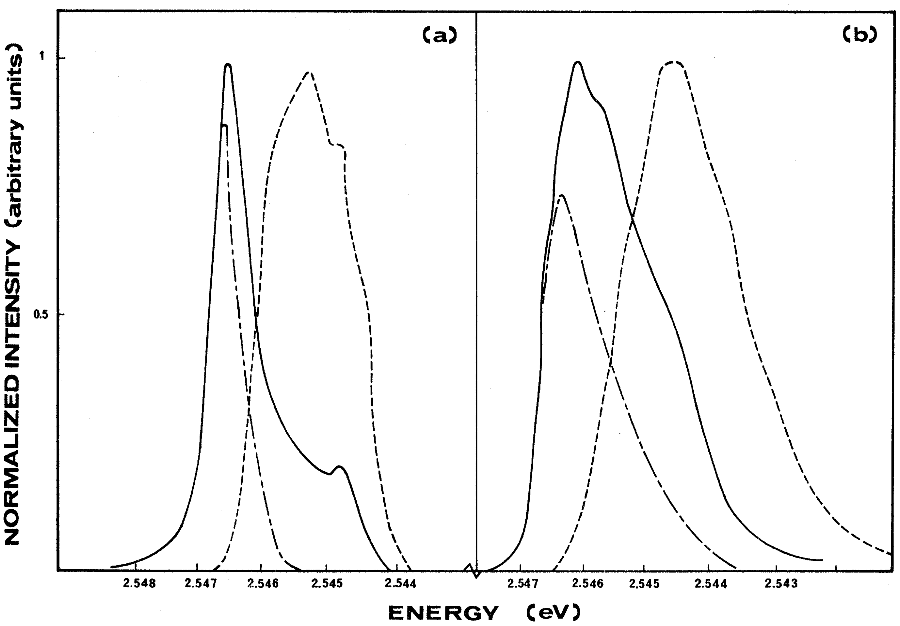

FIG. 4. Theoretical M lineshape for (a) $kT_b = 0.1$ meV and (b) 0.5 meV in Γ_5 (solid) and Γ_1 (dashed) observation. The two curves are normalized. In Γ_1 observation, only the emission of a "mixed" polariton P_2 is allowed. In Γ_5 observation, there are two contributions; the transverse one is shown by a dashed-solid line.

of peak power 15 W, focused in a spot of diameter ~60 μm, we get an exciting power up to 0.5 MW/cm^2.

The crucial point of the experiment is to select pure Γ_1 photons, using a narrow vertical slit perpendicular to the c axis of the crystal. The emergence and polarization angle of luminescence can be adjusted to be, respectively, 90° and 0° with respect to the c axis, by the extinction of the excitonic "mixed" mode luminescence Γ_{5L}.[4] An angular aperture of 2° is enough to eliminate most mixed photons. In those conditions, the mere rotation of the polarizer selects equally pure Γ_5 and Γ_1 photons.

Selecting pure Γ_1 photons is essential: first to make visible the M line shape associated to "forbidden" transitions, second to decrease at most the I_2 line which is more strongly Γ_5 polarized than the M line. When no special precaution is taken, one essentially observes the Γ_5 luminescence, because the associated matrix elements are much stronger (see Sec. II A).

More than ten samples have been investigated, giving concordant results.

B. Experimental results

Typical spectra are shown in Figs. 5 and 6. The main features resulting from the study of Γ_1 luminescence are the following: (i) The permanence of the two narrow excitonic lines Γ_6 and Γ_{5L} (the latest being only seen for emergence angles slightly differing from 90°), even at the strongest excitations obtained. No broadening has been observed on these lines. (ii) The growth of a rather flat continuum between 2.556 and 2.540 eV. It may be related to transitions involving B levels, which are allowed in this configuration. (iii) The rate of polarization of the M line, considered as the ratio of intensities at maximum in Γ_5 and Γ_1 configuration; it decreases with exciting power and may be less than 25. This is to be compared with the rate of polarization of the I_2 line, in the same conditions of observation, which may be greater than 500. (iv) The observation of the M line at rather low exciting power, due to a good extinction of the I_2 line in Γ_1 configuration: even if not clearly resolved from the latest, it may be observed at excitation density such as 150 W/cm^2.

Let us now examine in detail the results at different excitation levels.

1. Strong excitation levels

At strong excitation levels (approximately over 10 kW/cm^2), the fit of the M line shape can be done using the theory of Hanamura[2] because the broadening he attributes to the elastic collision of biexcitons is clearly observed (see Fig. 5). Thus, it is vain to attempt to distinguish between this broadening and those due to the effects pointed out in Sec. II B. In view of the theoretical results we have obtained, and of the poor accuracy of the fitting procedure (see below), it is sufficient to include all of them into a global broadening β.

In Hanamura's theory, the matrix element is constant and the dispersion curves of biexcitons and excitons are assumed to be parabolic:

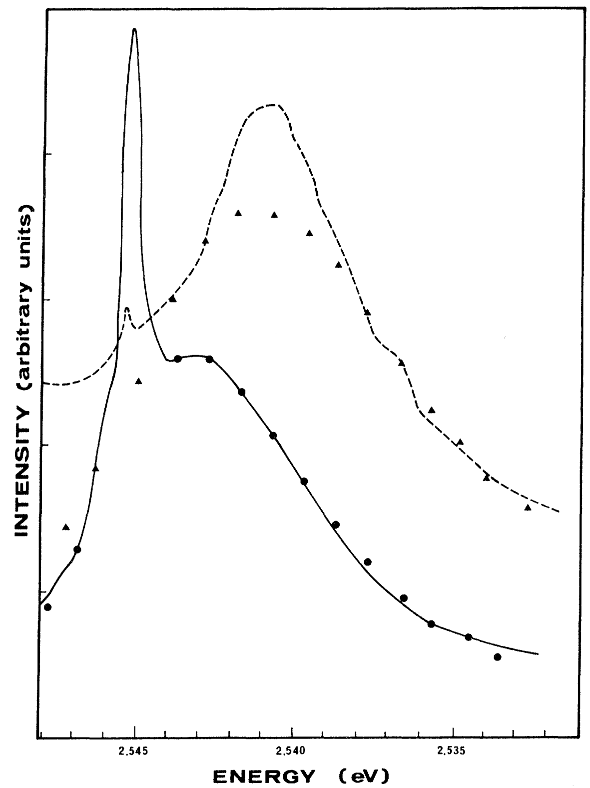

FIG. 5. Experimental results in Γ_5 (solid) and Γ_1 (dashed) observation of the M line, at rather strong excitation level (150 kW/cm²). The fit in Γ_1 observation is rendered difficult by the irregular background growing at these excitation levels. However, a possible theoretical curve derived from Eq. (6b) (▲) is shown; it is coherent with the fit in Γ_5 observation using Eq. (6a) (●). The obtained values are $kT_b = 2.8$ meV and $\beta = 2.2$ meV.

$$E_b(\vec{K}) = E_b(\vec{0}) + \hbar^2 K^2/4M ,$$

$$E_{ex}(\vec{K}) = E_{ex}(\vec{0}) + \hbar^2 K^2/2M .$$

No longitudinal-transverse splitting is taken into account and one obtains a Boltzmann line shape:

$$(E_0 - E)^{1/2} \exp[-(E_0 - E)/kT_b] ,$$

where $E_0 = E_b(0) - E_{ex}(0)$, convoluted by a Lorentzian $[(E_0 - E)^2 + \beta^2]^{-1}$ to account for a broadening β.

We just improve it in two ways: (i) by introducing a matrix element proportional to $\vec{K}_b$ in Γ_1 configuration of observation; (ii) by considering that the ground state $E_{ex}(\vec{0})$ of the parabolic excitons must be an average over the possible remaining excitons; that is the M excitons for Γ_1 observation, the T and M excitons for Γ_5 observation.

The method for computing the pseudo ground state of the corresponding parabolic dispersion curves and the density of states is shown in effect (i) of Sec. II B. We use it with a constant Δ^{LT}, because the quasitotality of remaining excitons are now out of the bottleneck region (high T_b leads to great $\vec{K}_2$). From Eq. (4) we get two averaged value for the exciton ground-state energy to be used in this problem:

$$\langle E_{ex}(\vec{0})\rangle^5 = \tfrac{1}{2}[\langle E^M_{ex}(\vec{0})\rangle + E^T_{ex}(\vec{0})] = E^L(\vec{0}) - \tfrac{5}{8}\Delta^{LT}$$

and

$$\langle E_{ex}(\vec{0})\rangle^1 = \langle E^M_{ex}(\vec{0})\rangle = E^L(\vec{0}) - \tfrac{1}{4}\Delta^{LT} .$$

Thence, it is possible to fit the experimental data with

$$\{(E^5_0 - E)^{1/2} \exp[-(E^5_0 - E)/kT_b]\} * [(E^5_0 - E)^2 + \beta^2]^{-1} \quad (6a)$$

for the Γ_5 observation, and

$$\{(E^1_0 - E)^{3/2} \exp[-(E^1_0 - E)/kT_b]\} * [(E^1_0 - E)^2 + \beta^2]^{-1} \quad (6b)$$

for the Γ_1 observation; where

$$E^i_0 = E_b(\vec{0}) - \langle E_{ex}(\vec{0})\rangle^i .$$

We obtain good results for the minimization of the mean quadratic deviation. There is no doubt that a matrix element $\alpha(\Gamma_1, \vec{K}_b)$ linear in $\vec{K}_b$ provides a good interpretation of the compared shapes of the M line in Γ_1 and Γ_5 configurations.

The accurate determination of the three physical parameters kT_b, β and, mainly, $E_b(\vec{0})$ which should be independent of the conditions of excitation, is more delicate: including the scaling factor and an adjustable ground level (especially for the Γ_1 configuration), we had to adjust five parameters. At excitation levels situated in the range 10–100 kW/cm², the fits of the Γ_1 spectra are more accurate, because of the good extinction of I_2 line. At stronger excitation, the background becomes important and the Γ_5 spectra are more suitable.

At these excitation levels, the effective kT_b varies from 1 to 3 meV and the apparent broadening β from $0.5kT_b$ to kT_b with increasing excitation. The excitonic temperatures, which can be measured by analysis of the LO-phonon-assisted exciton lines in the same conditions of excitation, are of the same order of magnitude than T_b, that is much higher that the lattice temperature. Great care has been taken to avoid the local heating of the lattice by an average excitation power smaller than 10 mW. Using the numerical values listed in Ref. 6, the most probable value for $E_b(\vec{0})$ that we have found in all analyzed spectra of this type is 5.0998 eV ±0.4 meV $[\tfrac{1}{2}E_b(0) = 2.5499$ eV ±0.2 meV$]$. This precision is doubtless greater than provided by the mere Γ_5 observation.

Our experimental results are in good agreement with those of Shionoya *et al.*[1] However, we do not obtain the same value for $E_b(\vec{0})$ because we take into account the averaged effect of the longitudinal-transverse splitting of the remaining excitons. We also think that a ratio β/kT_b always greater than 0.5 is inconsistent with attributing β only to the elastic collision between biexcitons. It seems necessary to subtract a constant broadening of, typically, 0.7 meV, to obtain a good connection with the fits at lower excitations, where no collision broadening has to be introduced.

2. *Intermediate and low excitation levels*

For excitation levels smaller than 10 kW/cm^2, the fit of the M line shape with the slightly modified theory of Hanamura [Eqs. (6)] becomes impossible. On the other hand, the theoretical shapes presented in Sec. II agree fairly well with the experimental shapes at intermediate excitation levels [Fig. 6(b)] and are not in contradiction with the few data obtained at rather low excitation levels [Fig. 6(a)]. The determination of kT_b can be done easily by superposition of the theoretical and experimental curves, with a precision better than 0.05 meV. No additional broadening has to be assumed. The Γ_1 observation being much more significative in these cases, the extinction of the I_2 line becomes crucial.

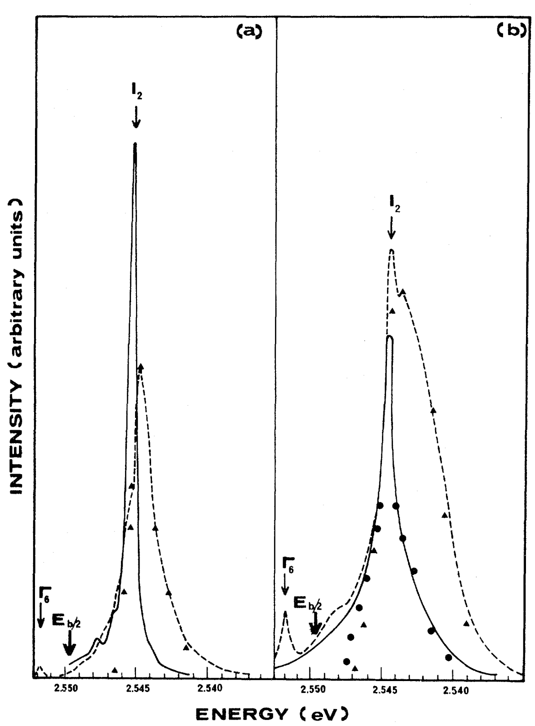

FIG. 6. Experimental results in Γ_5 (solid) and Γ_1 (dashed) observation of the M line at rather low [(a): 1 kW/cm^2] and intermediate [(b) 6 kW/cm^2] excitation levels. The spectra in (a) are taken from a purer sample, so that the extinction of the I_2 line is better in Γ_1 observation. When the M line is clearly distinguished, the fit with Eq. (5) gives satisfactory results (● in Γ_5, ▲ in Γ_1 observation). The obtained values for kT_b are (a) 0.4 meV and (b) 1.2 meV.

The biexciton temperature we find in the spectra of this type varies from 0.2 to 1.5 meV. It appears to be possible to observe the M line with a characteristic T_b near the lattice temperature, even with nonresonant exciting light.

The biexciton ground energy is found to be

$$E_b(0) = 5.0994 \pm 0.2 \text{ meV},$$

$$\tfrac{1}{2}E_b(0) = 2.5497 \pm 0.1 \text{ meV}.$$

3. *Relative intensity of "forbidden" transitions*

The product of the rate of polarization τ of the M line, with the biexcitonic temperature deduced from the fits remains roughly constant. This is consistent with our theoretical analysis and provides information on the relative intensity of the strength of transition S_{Γ_1}.

From $\tau kT_b \sim 100$ meV, we deduce that the ratio d/D (as defined in Fig. 1) is of the order of 2×10^{-15} cm^2. It means that for a Γ_1 biexciton (or a Γ_5 exciton) with a typical wave vector $K = 10^6$ cm^{-1}, the greater of both mixing coefficients with Γ_5 (or Γ_1) states is of the order of $(2\times10^{-3})^{1/2} \sim 0.05$ (in an isotropic model).

IV. DISCUSSION

Although the theoretical and experimental considerations we have presented in this paper are not decisive to answer the question: "Excitonic molecule or not?," we think they add some credibility to this hypothesis for the case of CdS; first, we have shown why the M line seems much broader then a realistic kT_b, even at intermediate excitation levels. Second, we have shown by the polarization study of the M line that it is most probably related to a traveling excitation, with some associated momentum.

The observation, in "forbidden" polarization, of the M line at rather low excitation level, and with high focusing of the laser beam, may exclude the hypothesis of stimulated emission, as well as the very good reproductibility of those experiments from one sample to another. We think that the M line being observed at lower level in better quality samples (that is, purer samples) may not be related to impurity centers, as proposed by Dite *et al.*[8]

On the other hand, we can question the interpretation of some experimental results more recently published:

(i) Voigt and Mauersberger[9] have attributed a luminescent line M_v situated at[6] 2.5486 eV and appearing in high-purity CdS samples, to the radiative recombination of "cold," of $\vec{K}_b \sim \vec{0}$ biexcitons. Contrarily to their opinion, we have shown in Sec. II that the emission of two transverse Γ_5 polaritons is possible for $\vec{K}_b = 0$ biexcitons: they have the same energy $[E^T = \frac{1}{2}E_b(\vec{0})]$, opposite wave vectors and parallel dipoles. These polaritons should be observed, because, around the biexciton half-energy, the "transfer" coefficient $\mathcal{T}(E^T)$ is nonzero. The emission, from $\vec{K}_b = \vec{0}$ biexcitons, of two polaritons with different energies, such as the process invoked by Voigt, Mir, and Kehrberg,[10] is forbidden because these two polaritons would lie on two different dispersion curves (T and M) and so have orthogonal dipoles. The dissociation into Γ_5 polaritons being always possible, it results that the dissociation of a biexciton emitting a Γ_6 exciton, forbidden in the dipolar approximation, remains negligible for all values of $\vec{K}_b$. Thus, it may not influence the total lifetime of biexcitons.

(ii) We have shown in Sec. II that there is no drastic modification of the M line shape and position for temperature over 1 °K. We deduce that, in all experiments performed in pumped liquid helium ($T \sim 2$ °K), if sharp lines (typically narrower than 1 meV) are attributed to the recombination of biexcitons, this prescribes the Bose condensation of the biexcitons.[11] As predicted by Hanamura,[12] this should lead to numerous striking effects which have not yet been observed in CdS.

(iii) What should be the emission spectrum of $\vec{K}_b = \vec{0}$ biexcitons? As shown in (i), it should be a sharp peak at energy $\frac{1}{2}E_b(\vec{0})$ in Γ_5 polarization and the transition is forbidden in pure Γ_1 configuration of observation. If the emergence angle θ of the observed polariton wave vectors with the c axis differs from 90°, the sharp peak remains in Γ_5 polarization (still perpendicular to c); in the orthogonal polarization (which is generally neither parallel nor perpendicular to the c axis) there should appear one peak at the same energy, associated to the emission of two mixed polaritons, with opposite wave vector, parallel dipoles and the same energy: $E^M = \frac{1}{2}E_b(\vec{0})$. The intensity of this peak would be proportional to the transverse part of the mixed polariton in the considered direction of propagation, that is to $\cos^2\theta$ (θ referred to the inside of the crystal).

(iv) We deduce from (iii) that, if Bose condensation occurs, no line should be observed at energy $E_0 = E_b(\vec{0}) - E_{ex}(\vec{0})$. This seems contradictory with the observation of Kuroda *et al.*[13] in CdSe under picosecond-pulse excitation.

Concerning the M_v line observed by Voigt *et al.*,[9] the biexciton energy which they deduce from their interpretation[6] (5.1007 eV) is not in agreement with ours, no more than the result obtained if we state that the M_v line lies at $\frac{1}{2}E_b(\vec{0})$ (5.0974 eV). This disagreement, in addition to the remarks made in (iii) and to other experimental results,[14] lead us to think that the M_v line is not due to the recombination of biexcitons.

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APPENDIX

Let us consider a N-particle system, represented by a wave function $\Phi_S(\vec{r}_1, \ldots, \vec{r}_i, \ldots, \vec{r}_N)$, solution of a Hamiltonian of the form

$$H = \left(\sum_i \frac{-\hbar^2}{2m_i} \nabla^2_{\vec{r}_i}\right) + V(\vec{r}_1, \ldots, \vec{r}_i, \ldots, \vec{r}_N).$$

Here, S refers to all suitable characteristic quantum numbers of the system and V is a potential term, periodic, which may include interaction between particles, but using only multiplicative terms.

One easily shows that a new set of coordinates $\{\vec{\rho}_i\}$ can be chosen so that: (i) the $\{\vec{\rho}_i\}$ are linear combinations of the $\{\vec{r}_i\}$; (ii) $\vec{\rho}_1$ is the coordinate of the center of mass of the system:

$$\vec{\rho}_1 = \left(\sum_i m_i \vec{r}_i\right) \Big/ \left(\sum_i m_i\right);$$

(iii) all the lines of the transformation matrix $\{T_{ij}\}$ are mutually orthogonal.

Then, one can put $\Phi_S(\vec{r}_1, \ldots, \vec{r}_i, \ldots, \vec{r}_N) = \exp(i\vec{K}\cdot\vec{\rho}_1)U_{\vec{K},\sigma}(\vec{\rho}_1, \ldots, \vec{\rho}_i, \ldots, \vec{\rho}_N)$ so that $\vec{K}$ and σ form a new set of quantum numbers, $U_{\vec{K},\sigma}$ is periodic in ρ_1 and is solution of a "pseudo-Schrödinger" equation:

$$\begin{aligned} H_{\vec{K}} U_{\vec{K},\sigma} &= \left[\sum_{j=1}^{N}\left(-\frac{\hbar^2}{2M_j}\nabla_{\vec{\rho}_j} - i\frac{\hbar^2}{M'}\vec{K}\cdot\nabla_{\vec{\rho}_j}\right) + V(\vec{\rho}_1, \ldots, \vec{\rho}_j, \ldots, \vec{\rho}_N)\right] U_{\vec{K},\sigma} \\ &= [E_\sigma - (\hbar^2/2M)K^2]\, U_{\vec{K},\sigma}, \end{aligned}$$

where

$$\frac{1}{M_j} = \frac{1}{m_j}\sum_i T^2_{ij}$$

and

$$1/M' = N/M_1.$$

The last term is the analog of the $\vec{K}\cdot\vec{P}$ perturbation term in one-electron-band theory. $\vec{K}$ is the conjugate variable of the coordinate of the center of mass of the system: $\vec{\rho}_1$, $-i\hbar\nabla_{\vec{\rho}_1}$ is the total momentum operator $\vec{P}$, associated to $\vec{\rho}_1$.

[1]S. Shionoya, H. Saito, E. Hanamura, and O. Akimoto, Solid State Commun. 12, 223 (1973).

[2]The main consequences of Hanamura's theory are summarized in III B1. See also E. Hanamura, in *Luminescence of Crystals, Molecules and Solutions*, edited by F. Williams (Plenum, New York, 1973), p. 121.

[3]F. Bassani, J. J. Forney, and A. Quattropani, Phys. Status Solidi B 65, 2, 591 (1974).

[4]C. Benoit à la Guillaume, A Bonnot, and J. M. Debever, Phys. Rev. Lett. 24, 22, 1235 (1970).

[5]Taking into account the momentum of photons in the frame of the dipolar approximation is generally incorrect. This is shown, for the example of excitons in V. S. Cherepanov and V. S. Galishev, Fiz. Tverd Tela 3, 1085 (1960) [Sov. Phys.-Solid State 3, 790 (1960)].

[6]In computing the photon energies, we included the refractive index of air: E(eV), λ(Å) = 12 394.5. This was not done by J. J. Hopfield and D. G. Thomas [Phys. Rev. 122, 1 (1961)] whose numerical values we used for CdS. In Sec. IV, we have also "corrected" the values given in Ref. 9 for comparison with ours. Thus, the numerical values used in the calculation of Eq. (5) are $E_{ex}^{L}(0) = 2.5540$ eV, $\Delta^{LT} = 1.9$ meV, $\epsilon_{\infty} = 7.3$ and excitonic masses $m_{\parallel} = 5.2 m_0$, $m_{\perp} = 0.9 m_0$.

[7]In the "transfer coefficient," we must include the possibility of phonon scattering before reaching the surface, as well as the transmission coefficients of polaritons through the surface. This problem is analogous to the one of polariton fluorescence line shape where it appears rather clear that, for lower-branch polaritons, $\mathcal{T} = 0$ above 2.553 eV and reduces to light transmission under 2.547 eV. See A. Bonnot and C. Benoit à la Guillaume, Proceedings of Taormina Research Conference, edited by Burstein and de Martini, p. 197, 1972 (unpublished).

[8]A. F. Dite, V. L. Revenko, V. R. Timofeev, and P. D. Altukhov, Zh. Eksp. Teor. Phys. Pis'ma Red. 18, 579 (1973) [Sov. Phys.-JETP Lett. 18, 341 (1973).]

[9]J. Voigt and G. Mauersberger, Phys. Status Solidi B 60, 679 (1973).

[10]J. Voigt, F. Mir, and G. Kehrberg, Phys. Status Solidi B 70, 625 (1975).

[11]We cannot discuss here in details the results that Voigt and Rückmann have obtained in absorption experiments [Phys. Status Solidi B 61, K85 (1974)]. But the problem is quite similar and: either the peak they associate to the longitudinal exciton is not wide enough to be related to the fusion of "mixed" polaritons and photons; or such as sharp peak prescribes the Bose condensation of longitudinal excitons!

[12]E. Hanamura, J. Phys. Soc. Jpn. 37, 6, 1545 (1974).

[13]H. Kuroda, S. Shionoya, H. Saito, and E. Hanamura, Solid State Commun. 12, 533 (1973).

[14]A line situated at the same position, about 1 meV wide, has often been observed by ourselves in ordinary CdS platelets at very low excitation level. Its kinetic is similar to the one of the I_2 and free exciton lines.