

## Optical orientation of excitons in CdS

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The optical orientation by circularly polarized light of free and bound excitons in CdS is reported and discussed. The observed degrees of polarization are generally large and vary significantly with the exciting energy (a "negative" polarization is sometimes obtained). These results, together with the effects of a magnetic field, provide a lot of information about the levels excited, the luminescent levels (lifetimes and disorientation times), and the transfer of polarization from the first to the second. The optical orientation by linearly polarized light is also observed for the first time in solids. It is shown why these unusual effects can be seen on free excitons and not on other levels. The additional information that they provide leads to a better comprehension of the mechanisms of thermalization of the excitons, and of the symmetry properties of  $K \neq 0$  exciton states.

### I. INTRODUCTION

It is well known, from Lampel's earlier works<sup>1,2</sup> that spin orientation by optical pumping can be achieved in semiconductors. This effect is quite analogous to the optical pumping between atomic levels in gases.<sup>3</sup> Spin orientation had first been performed on band-to-band or band-to-impurity transitions in cubic III-V compounds like GaSb, GaAs, and Ga<sub>1-x</sub>Al<sub>x</sub>As,<sup>4-6</sup> and it must be emphasized that the possible orientation results from the spin-orbit splitting of the valence bands.

In noncubic crystals like II-VI compounds (i. e., CdS, ZnO, CdSe, etc.), the degeneracy of the valence bands is totally lifted, due to both the crystal-line field and spin-orbit coupling. For these semiconductors, the situation seems more favorable, but this case is complicated by the anisotropy of the considered crystals. Moreover, it is well known that the strong interaction between electrons and holes leads to excitons, and one cannot treat separately the two created particles as has been done in the previous cubic compounds where the Rydberg unit of the excitons is very small. The first observation of optical orientation of excitons was achieved in CdSe by Gross, Ekimov, Razbirin, and Safarov,<sup>7</sup> then in InP by Weisbuch and Lampel and in CdS by ourselves.<sup>8</sup>

Dealing first with circularly polarized light, we show here that orientation of excitons can be achieved in CdS (Secs. II and III) and develop some theoretical considerations about the rate of conservation of the orientation through the transfer of excitations (Sec. IV) in the crystal. The exposition of our experimental conditions (Sec. V) includes an important presentation of the samples we used. Experimental results on orientation of free and bound excitons are presented and partially discussed in Sec. VI and VII. We deduce from these results,

and from the effects of a magnetic field (Sec. VIII) information about disorientation and lifetime of excitons. For the sake of simplicity, we have joined in Sec. IX the theoretical preliminaries and experimental results which concern optical orientation by linearly polarized light, and in Sec. X a more delicate analysis of the transfer of excitation through  $\vec{K} \neq 0$  exciton states is given, which yields a satisfactory explanation of experimental results in both circular and linear configurations.

### II. STRUCTURE OF EXCITONIC LEVELS IN CdS

The band structure of CdS has been well established by the studies of Thomas and Hopfield. They have given in great detail<sup>9-11</sup> the symmetry of the excitonic levels occurring from the different non-degenerate valence bands (i. e., *A*, *B*, *C* series). From these symmetries, they deduced selection rules for light absorption, which are summarized in Table I.

The optical transitions in perpendicular (parallel) polarization to the *c* axis of the crystal involve levels of twofold  $\Gamma_5$  (single fold  $\Gamma_1$ ) symmetry. Because of the longitudinal-transverse (LT) splitting of excitons, the  $\Gamma_5$  excitons remain doubly degenerate only when their wave vector is parallel to the

TABLE I. The selection rules for interaction of light with the  $n=1$  excitons of the *A*, *B*, and *C* series in a wurtzite-type crystal. The criterion is the direction of the associated electric field, perpendicular ( $\perp$ ) or parallel ( $\parallel$ ) to the *c* axis (see Ref. 9).

		<i>A</i>	<i>B</i>	<i>C</i>
$n=1$	<i>S</i>	$\perp$	$\perp, \parallel$	$\perp, \parallel$
	<i>S</i>	$\perp$	$\perp, \parallel$	$\perp, \parallel$
$n=2$	$P_0$	$\perp$	$\perp, \parallel$	$\perp, \parallel$
	$P_{\pm}$	$\perp, \parallel$	$\perp, \parallel$	$\perp, \parallel$

$c$  axis, while they split when propagating perpendicular to it. Therefore, in an optical-pumping experiment, one must choose a suitable direction of propagating for the absorbed and emitted photons. According to these considerations, we are now only concerned with the twofold degenerate  $\Gamma_5$  levels, propagating along the  $c$  axis.

It can easily be shown that each multifold excitonic hydrogenic state reduces in the crystal point group into several irreducible representations with at least one  $\Gamma_5$  level. Our purpose is to show that spin orientation of this level can be achieved by optical pumping in propagation parallel to the  $c$  axis. In addition, we will show that these general consideration can be also applied to excitons bound to impurities.

### III. CIRCULARLY POLARIZED LIGHT ABSORPTION DUE TO EXCITON LEVELS

The optical absorption due to an excitonic state  $\psi_{\lambda, \vec{k}}$  ( $\lambda$  is the exciton level index,  $\vec{k}$  is the exciton wave vector) is governed by a matrix element  $M$  which can be written in the form

$$M = M_+ + M_-, \quad (1)$$

$M_+$  and  $M_-$  being readily found to be

$$\begin{aligned} M_+ &\propto a_+ \langle \psi_{\lambda \vec{k}} | p_+ e^{-i(\omega t - \vec{k} \cdot \vec{z})} | \Phi \rangle, \\ M_- &\propto a_- \langle \psi_{\lambda \vec{k}} | p_- e^{-i(\omega t - \vec{k} \cdot \vec{z})} | \Phi \rangle, \end{aligned} \quad (2)$$

where  $\Phi$  is the ground state,  $a_+$  and  $a_-$  are the left ( $\sigma^+$ ) and right ( $\sigma^-$ ) circular component of the complex potential vector of the exciting light, and  $p_+$  and  $p_-$  are the circular components of the momentum operator.

In the zero-photon wave-vector approximation, and for an S-like exciton,  $M_+$  and  $M_-$  are<sup>12</sup>

$$\begin{aligned} M_+ &\propto a_+ U_{\lambda}(\vec{0}) \langle u_{c,i} | p_+ | u_{v,j} \rangle, \\ M_- &\propto a_- U_{\lambda}(\vec{0}) \langle u_{c,i} | p_- | u_{v,j} \rangle, \end{aligned} \quad (3)$$

where  $U_{\lambda}(\vec{1})$  is the envelope function of the exciton and where  $u_{c,i}$  ( $u_{v,j}$ ) is the wave function of  $\vec{k} \approx 0$

electron (hole) states involved in the formation of the exciton. The two indexes  $i$  and  $j$  can be interpreted as the total angular momentum of these states.

The relations (3) show that the selection rules in circularly polarized light only involve the symmetry of the bands through the one-particle matrix elements of  $p_{\pm}$  which correspond to band-to-band transitions. The wave function of valence and conduction band of CdS were calculated by Gutsche and Jahne<sup>13</sup> and their results are summarized in Table II.

Using Koster's *et al.* table,<sup>14</sup> the selection rules in circularly polarized light are then deduced:

$$\begin{aligned} \langle S | p_+ | X_- \rangle &= P, & \langle S | p_- | X_- \rangle &= 0, \\ \langle S | p_+ | X_+ \rangle &= 0, & \langle S | p_- | X_+ \rangle &= -P. \end{aligned} \quad (4)$$

From Table II and relations (4), it is easy to calculate the relative probability of optical transition in circularly polarized light between the ground level and the different  $\Gamma_5$  excitonic levels corresponding to S-like excitons. As shown in Fig. 1, a consequence of our index convention is that the absorption of resonant  $\sigma^+$  ( $\sigma^-$ ) light creates exciton states labeled with  $m = 1$  ( $m = -1$ ) which expresses the conservation of the total angular momentum component along the  $c$  axis.

Let us emphasize that a  $\sigma^+$  light resonant with the  $A_{n=1,S}$  excitonic level creates an exciton involving an electron spin  $|\uparrow\rangle$  and an hole spin  $|\uparrow\rangle$ . In the case of B and C excitons, we get the opposite result concerning only the electron spin (the B and C valence bands are not pure of spin: see Table II).

We conclude that it is theoretically possible, by circularly polarized light excitation, to obtain a 100% spin orientation of the two particles bound in a  $\Gamma_5$  free exciton. Assuming that such an orientation is achieved, a possible detection of the orientation is to analyze the polarization of the fluorescent light,<sup>15</sup> because absorption and recombination processes are ruled by complex-con-

TABLE II. The  $\vec{k}=0$  wave functions involved in the formation of  $\Gamma_5$  excitons in a wurtzite-type crystal. The values of  $\alpha$  and  $\beta$  can be found in Ref. 13.

		Electron taken from the valence band		Electron created in the conduction band	
$A_{\Gamma_5}$	$\psi_A^{-1}$	$u_{A,+3/2}$	$X_+  \uparrow\rangle$	$u_{c,+1/2}$	$S  \uparrow\rangle$
	$\psi_A^{+1}$	$u_{A,-3/2}$	$X_-  \uparrow\rangle$	$u_{c,-1/2}$	$S  \uparrow\rangle$
$B_{\Gamma_5}$	$\psi_B^{-1}$	$u_{B,+1/2}$	$\alpha X_+  \uparrow\rangle + \beta Z  \uparrow\rangle$	$u_{c,-1/2}$	$S  \uparrow\rangle$
	$\psi_B^{+1}$	$u_{B,-1/2}$	$\alpha X_-  \uparrow\rangle + \beta Z  \uparrow\rangle$	$u_{c,+1/2}$	$S  \uparrow\rangle$
$C_{\Gamma_5}$	$\psi_C^{-1}$	$u_{C,+1/2}$	$-\beta X_+  \uparrow\rangle + \alpha Z  \uparrow\rangle$	$u_{c,-1/2}$	$S  \uparrow\rangle$
	$\psi_C^{+1}$	$u_{C,-1/2}$	$-\beta X_-  \uparrow\rangle + \alpha Z  \uparrow\rangle$	$u_{c,+1/2}$	$S  \uparrow\rangle$

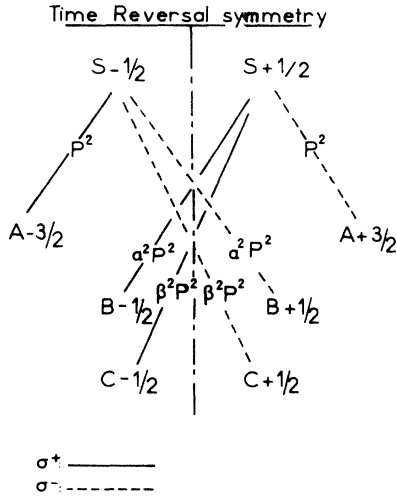


FIG. 1.  $\sigma^+$  and  $\sigma^-$  transitions between the A, B, and C valence band and the conduction (S) band for wurtzite-type crystal. The values of  $\alpha$  and  $\beta$  can be found in Ref. 13.

jugate matrix elements. This result is available for  $\Gamma_5$  excitons in any compound.

#### IV. DEGREE OF POLARIZATION OF A LUMINESCENT LEVEL INTERACTING WITH AN ORIENTED EXCITED LEVEL

Let us label  $\mu$  a primary excited level. The excitations can decay into the observed fluorescent states, labeled  $\nu$ .  $n^*(\mu)$  [ $n^-(\mu)$ ] being the population of the state  $\phi^*(\mu)$  [ $\phi^-(\mu)$ ] created by absorption of a  $\sigma^+$  [ $\sigma^-$ ] photon, let us define the orientation  $P(\mu)$  of the level  $\mu$

$$P(\mu) = \frac{n^*(\mu) - n^-(\mu)}{n^*(\mu) + n^-(\mu)}. \quad (5)$$

The degree of polarization (DOP) of the fluorescence due to the level  $\nu$ , in equilibrium with the level  $\mu$ , is given by

$$\rho(\mu, \nu) = P(\nu) = \frac{n^*(\nu) - n^-(\nu)}{n^*(\nu) + n^-(\nu)}. \quad (6)$$

The rate equations describing the equilibrium between the two levels are, for a  $\sigma^+$  excitation,

$$\begin{aligned} \frac{d}{dt} [n^*(\mu) + n^-(\mu)] &= J - [n^*(\mu) + n^-(\mu)] \tau^{-1}(\mu), \\ \frac{d}{dt} [n^*(\mu) - n^-(\mu)] &= p_f J - [n^*(\mu) - n^-(\mu)] \\ &\quad \times [\tau^{-1}(\mu) + T_1^{-1}(\mu)], \\ \frac{d}{dt} [n^*(\nu) + n^-(\nu)] &= \pi [n^*(\nu) + n^-(\nu)] \\ &\quad - [n^*(\nu) + n^-(\nu)] \tau^{-1}(\nu), \\ \frac{d}{dt} [n^*(\nu) - n^-(\nu)] &= \Theta(\mu - \nu) [n^*(\nu) - n^-(\nu)] \\ &\quad - [n^*(\nu) - n^-(\nu)] [\tau^{-1}(\nu) + T_1^{-1}(\nu)], \end{aligned} \quad (7)$$

with  $p_f = 1$  for a 100% pumping rate, where  $J$  is the rate of creation of the elementary excitations at level  $\mu$ ;  $\tau(\mu$  or  $\nu)$  and  $T_1(\mu$  or  $\nu)$  are, respectively, the lifetime and disorientation time for the level  $\mu$  or  $\nu$ . The annihilation of the  $\mu$  states through the channel  $\nu$  is described by the probability of conversion of the  $\mu$  into the  $\nu$  states,  $\pi$ , and by the phenomenological parameter  $\Theta(\mu - \nu)$  which characterizes the rate of transfer of the orientation.

Solving the rate equations (7), we obtain

$$P(\mu) = \frac{\epsilon p_f T_1(\mu)}{\tau(\mu) + T_1(\mu)}, \quad (8)$$

$$\rho(\mu, \nu) = P(\nu) = \frac{\Theta(\mu - \nu) P(\mu) T_1(\nu)}{\tau(\nu) + T_1(\nu)},$$

$\epsilon = +1$  ( $\epsilon = -1$ ) for a  $\sigma^+$  ( $\sigma^-$ ) exciting light. We will always assume  $\sigma^+$  exciting light in the following.

It must be pointed out that the sign of  $\Theta(\mu - \nu)$  is determined by the symmetries of the two levels  $\mu$  and  $\nu$ . For example, the transfer from the B exciton to the A exciton yields a negative value of  $\Theta$ , as is easily verified from Table II.

#### V. EXPERIMENTAL

Our experiment requires monochromatic exciting light obtained by a monochromator  $M_1$  (see Fig. 2). The fluorescence is analyzed by a second monochromator  $M_2$ . The sample is cooled by immersion in a pumped-liquid-helium vessel ( $T = 1.6^\circ \text{K}$ ). The exciting light is circularly polarized using a linear polarizer coupled with a quarter-wave plate. The fluorescent light is then analyzed using an identical circular analyzer which can be set in  $\sigma^+$  or  $\sigma^-$  configuration.

This experimental setup is suited to experiments of luminescence spectra with a monochromatic exciting light, as well as excitation spectra (ES) of selected luminescence lines. These two types of spectra illustrate a unique physical reality: the transfer of elementary excitations from an excited to an emitting level. This study is not our purpose in this paper and has been reported by several authors,<sup>16-18</sup> but we must emphasize here

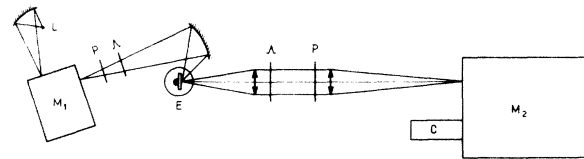


FIG. 2. Experimental setup.  $M_1$  and  $M_2$  are the two monochromators; L is a 100-W high-pressure mercury lamp, E the sample, C a photomultiplier, P a linear polarizer and A a quarter wave plate.

its importance for our subject, from both experimental and theoretical points of view.

The sample we used was obtained by growing an epitaxial layer of CdS on a massive single crystal of CdS cut perpendicularly to the  $c$  axis. It is a doped, or "bad", sample from the point of view of ES of excitonic luminescence; they are essentially characterized by sharp LO-phonon replicas with a negligible flat continuum. Therefore, on the basis of a previous study of several types of samples,<sup>18</sup> we can assert the following in this case.

(i) Most of excitonic luminescence is due to free excitons created by indirect absorption in their band, with emission of one LO phonon. The free electrons and holes directly created (when exciting energy  $h\nu_e$  is larger than the gap) are trapped on impurities and do not contribute to the formation of free and bound excitons.

(ii) Of all the free excitons created in their band with finite  $\vec{K}_c$ , only those with kinetic energy  $(N-1)\hbar\Omega$  [ $\hbar\Omega$  is the LO-phonon energy,  $N$  (integer)  $\geq 1$ ] will be able to reach, by successive emissions of LO phonons, the bottom of the band, of energy  $E(A_{n-1})$ , and will decay radiatively. If  $\tau_{LO}$  and  $\tau_{ac}$  are the mean interaction time with LO and acoustic phonons, and  $\tau$  is the total lifetime of free excitons, we characterize this situation by  $\tau_{LO} < \tau < \tau_{ac}$ . The lifetime involved is in fact rather difficult to define with much precision. As shown in Ref. 18, there is no thermalization of excitons in their band, and  $\tau$  characterizes the probability that an exciton can leave its band, by trapping at an impurity, indirect radiative decay, and, mainly, nonradiative decay. So, it may be dependent on the  $\vec{K}$  of excitons. At the  $\vec{K}=0$  point, the radiative probability shortens the total lifetime. But we implicitly consider in the following that the free-exciton luminescence comes, in fact, from the transmission of  $\vec{K}||c$  polaritons through the surface.

This explains the existence of sharp regular peaks in the ES of free-exciton luminescence. Because the implied indirect absorption coefficient is zero for  $\vec{K}=0$ ,<sup>18</sup> the larger peak corresponds to  $N=2$ , that is, to  $h\nu_e = E(A_{n-1}) + 2\hbar\Omega$  and a kinetic energy of the created excitons  $\hbar\Omega$ .

(iii) The same type of arguments explains the existence of one or two (or more) series of peaks appearing in the ES of other excitonic recombination lines.

Such a situation seems experimentally unfavorable, because of the poor radiative efficiency of the excitonic luminescence due to lack of the contribution of direct absorption. But it turns out to our advantage, because we can follow the elementary excitations through a small number of steps, from the absorption to the reemission of light. Moreover, as we will see in Sec. IX, the

loss of coherence between the electron and the hole, inherent in the free electron-hole pairs, would ruin our hope to observe some important degree of linear polarization on luminescent light.

Because of the poor radiative efficiency, which requires the use of wide slits, we detect after  $M_2$  a part of the exciting light, diffused by the surface of the sample. We must subtract this parasite light to measure the DOP of luminescence. This is, in fact, more easily achieved on the luminescence spectra than on the ES which we often present here for the sake of comprehension. However, this parasite light was sometimes an important limitation to the accuracy of our experiments.

## VI. ORIENTATION OF FREE EXCITON

### A. $A_T$ line

This line is due to the direct annihilation of a  $A_{n-1}$  free exciton of  $\Gamma_5$  symmetry. Its ES (see Fig. 3) shows that the radiative efficiency is non-negligible for exciting energies  $h\nu_e$  around

$$h\nu_e = E(A_{n-1}) + N\hbar\Omega \quad [N(\text{integer}) \geq 1]$$

(the LO-phonon replicas) and

$$h\nu_e = E(A_{n-2})$$

(a "transit" line), where  $E(A_{n-2})$  is the energy of the  $(A_{n-2}, \vec{K}=0)$  states of  $\Gamma_5$  symmetry. The DOP of the  $A_T$  line is given for various exciting energies in Table III.

For  $h\nu_e$  resonant with the  $A_{n-2}$  level, we get from (8):

$$P(A_{n-2}) = T_1(A_{n-2}) / [T_1(A_{n-2}) + \tau(A_{n-2})], \quad (9)$$

and the DOP of the  $A_T$  line is given by

$$\rho(A_{n-2}, A_{n-1}) = \frac{\Theta(A_{n-2} - A_{n-1}) P(A_{n-2}) T_1(A_{n-1})}{T_1(A_{n-1}) + \tau(A_{n-1})}. \quad (10)$$

As we shall see in Sec. VIB, we can determine directly  $P(A_{n-2})$ , which is found to be 0.78. We deduce from this and (10)

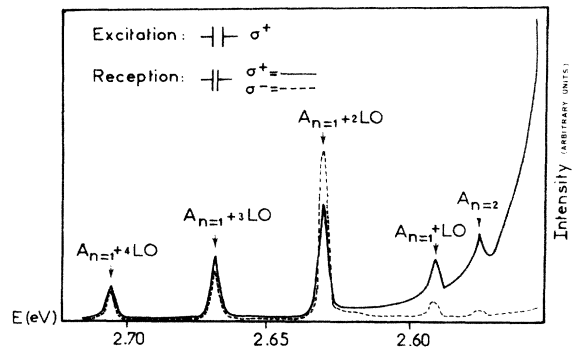


FIG. 3. ES of  $A_T$  line in circular configuration.

TABLE III. Degree of polarization of the  $A_T$  line for various exciting energies in both configurations.

Line in the ES	Exciting energy in eV	DOP in circular configuration (+, -)	DOP in linear configuration (X, Y)
$A_{n=2}$	2.576	+0.70	+0.80
$A_{n=1} + \text{LO}$	2.590	+0.28	+0.32
$A_{n=1} + 2\text{LO}$	2.629	-0.20	+0.36
$A_{n=1} + 3\text{LO}$	2.668	+0.05	+0.25

$$\frac{\Theta(A_{n=2} \rightarrow A_{n=1}) T_1(A_{n=1})}{T_1(A_{n=1}) + \tau(A_{n=1})} = 0.9.$$

This result implies that

$$T_1(A_{n=1}) \geq 10 \tau(A_{n=1}), \quad (11)$$

the equality standing if  $\Theta(A_{n=2} \rightarrow A_{n=1}) = 1$ , that is, if the transfer of excitation from an  $A_{n=2}$  to  $A_{n=1}$  exciton does not affect the orientation. We think it is the real situation, and this can be supported by the following considerations: the transfer from the  $(A_{n=2}, \vec{K}=0)$  states to the  $A_{n=1}$  band can only occur with emission of acoustic phonons. First-order processes, involving one phonon, lead to  $(A_{n=1}, \vec{K} \neq 0)$  excitons which must then lose their kinetic energy by emission of several acoustic phonons to reach the  $\Gamma$  point where they can radiate. Such processes are expected to be disorienting (see Sec. X). But we have shown in Ref. 18, and noted in Sec. V, that their contribution to luminescence is negligible. On the other hand, one second-order process can transfer directly  $(A_{n=2}, \vec{K}=0)$  to the  $(A_{n=1}, \vec{K}=0)$  level, involving a virtual intermediate state only. These processes may conserve the orientation (see Fig. 10).

Concerning the other lines of the ES presented in Table III, and which correspond to indirectly created excitons, a precise interpretation of the measured DOP is more difficult because of the several interactions occurring between excitons and phonons in the processes of creation and thermalization. This will be discussed in Sec. X.

#### B. $A_{n=2}$ - LO line

The  $A_{n=2}$ -LO line is due to the recombination of  $A_{n=2}$  excitons with one LO-phonon emission, and appears when  $h\nu_e$  is resonant with the  $A_{n=2}$  level, whereas, in the same experimental conditions, the  $A_{n=1}$ -LO line is not observable when  $h\nu_e = E(A_{n=1})$ . We have precisely described and interpreted this surprising effect in Ref. 19, and showed there that  $(A_{n=2}, \vec{K}=0)$  created excitons radiate with emission of one LO phonon without any transit through a real intermediate state. So it is possible to detect the orientation of  $(A_{n=2}, \vec{K}=0)$  excitons through the DOP of the  $A_{n=2}$ -LO line:  $\rho(A_{n=2}, A_{n=2}\text{-LO}) = P(A_{n=2})$ . It is found to be

0.78 in  $\sigma^+\sigma^-$  configuration [Fig. 4(a)] and this value implies

$$T_1(A_{n=2}) \approx 3.5 \tau(A_{n=2}). \quad (12)$$

### VII. ORIENTATION OF EXCITONS BOUND TO IMPURITIES

#### A. $A$ exciton bound to a neutral donor: $I_{2A}$ line

In the lowest energy level of this complex, the spatial symmetry of the wave function requires an antisymmetric-spin wave function for the two electrons.<sup>11</sup> Taking into account the spin of the hole, the level presents a twofold degeneracy. Each state can decay radiatively according to the scheme of Fig. 5(a).

The selection rules of Fig. 5(a) are deduced from the results summarized in Fig. 1. Let us remark that the DOP of the  $I_{2A}$  line (4869 Å at 1.6 °K) is determined by the orientation of the hole bound in the complex.

The ES of this line shows at least two series of LO-phonon replicas, and "transit" lines at energies  $E(A_{n=2})$  and  $E(A_{n=1})$ .<sup>17,18</sup> The experimental limitations evoked in Sec. V make difficult a measure of  $\rho(A_{n=1}, I_{2A})$ . However, we could orient the  $I_{2A}$  center by excitation on the  $A_{n=2}$  level. We found

$$\rho(A_{n=2}, I_{2A}) = 0.4.$$

We deduce from (8) and (12)

$$T_1(I_{2A})/[T_2(I_{2A}) + \tau(I_{2A})] \geq 0.5,$$

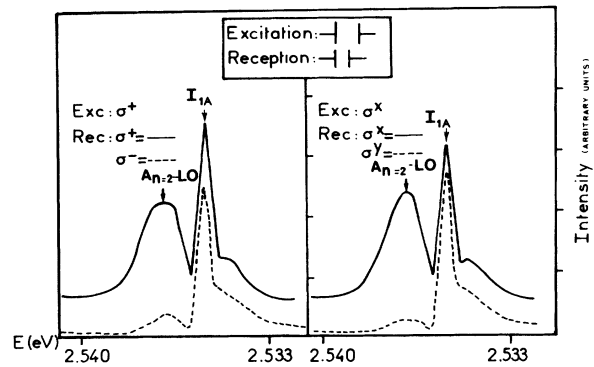


FIG. 4. Luminescence spectra of  $A_{n=2}$ -LO and  $I_1$  line in circular (a) and linear (b) configurations. The exciting energy is 2.576 eV ( $A_{n=2}$  level).

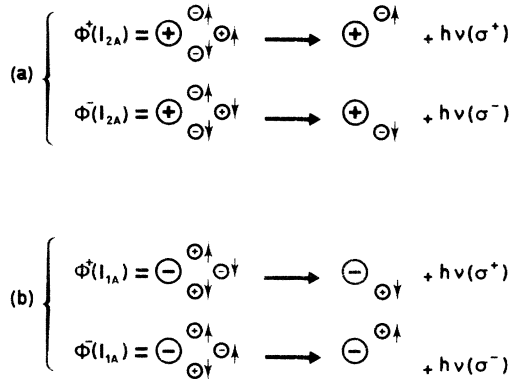


FIG. 5. Schemes which illustrate the radiative recombination of an exciton bound to a neutral donor (a) or acceptor (b), depending on the spin of the hole (a) or of the electron (b).

the equality standing if  $\Theta(A_{n=2} \rightarrow I_{2A}) = 1$ . This is problematic, because the excitations transfer through real intermediate states ( $A_{n-1}$ ,  $\vec{K} \neq 0$ ), as it will be shown on the example of  $I_{1A}$  center.<sup>20</sup> However, since the lifetime of  $I_{2A}$  center is 0.6 nsec,<sup>21</sup> the disorientation time for the hole bound in  $I_{2A}$  seems to be of the same order of magnitude as for the electron bound in  $I_{1A}$  (see Sec. VIII). This situation is very different in III-V compounds.<sup>22</sup>

#### B. A exciton bound to a neutral acceptor: $I_{1A}$ line

Following the same arguments given in VIIA, the radiative decay of this level is described by the scheme of Fig. 5(b). The DOP of  $I_{1A}$  luminescence (4888 Å at 1.6 °K) is determined by the orientation of the electron bound in the complex.

The great binding energy of the complex (18 meV) allows various accurate experiments. The ES of  $I_{1A}$  is shown on Fig. 6, and some DOPs are listed in Table IV. We shall now restrict ourselves to the analysis of the "transit" lines of this ES, which correspond to the direct creation of some oriented level with resonant exciting light.

(a) The cases of "transit" levels  $I_{1B}$ ,  $A_{n=1}$ ,  $B_{n=1}$  and  $A_{n=2}$  can be treated from the same point of view, because we have just to follow the orientation of the electron in the transfer to  $I_{1A}$ . Using (8), we deduce from the experimental DOP several equalities or inequalities between lifetimes and disorientation times of the transit levels, and information about the transfer factors  $\Theta$ . These results, listed in Table V, are obtained using the values  $\tau(I_{1A}) = 1$  nsec found by Henry and Nassau,<sup>21</sup> and  $T_1(I_{1A}) = 1$  nsec which we have obtained from the analysis of the Hanle effect on the  $I_{1A}$  level (Sec. VIII). The signs of the transfer factors  $\Theta(\mu \rightarrow I_{1A})$  are theoretically obtained from the com-

pared symmetries of the wave functions. Concerning the  $I_{1B}$  complex, which involves two holes of different valence bands, we just followed the electron spin orientation through the transfer. This qualitative analysis is only justified because of the limited resolution on the excitation, with respect to the splitting of the  $I_{1B}$  level.<sup>11</sup>

The transfer factor  $\Theta(A_{n=2} \rightarrow I_{1A})$ , which is found to be  $\approx 0.25$ ,<sup>20</sup> requires some explanation. One could expect that

$$\Theta(A_{n=2} \rightarrow I_{1A}) = \frac{\Theta(A_{n=2} - A_{n=1}) T_1(A_{n=1})}{[T(A_{n=1}) + \tau(A_{n=1})]} \Theta(A_{n=1} \rightarrow I_{1A})$$

which would lead to

$$\Theta(A_{n=2} \rightarrow I_{1A}) > 0.45.$$

In fact, the transfer factor which we have calculated previously dealt with  $\vec{K} = 0$  states. The binding of an exciton on an impurity is not as selective as the direct creation or recombination and ( $A_{n=1}$ ,  $\vec{K} \neq 0$ ) must be considered as probable real intermediate states. As we will see in Sec. X, this leads to the partial depolarization of the whole population.

(b) The "transit" level  $I_{2B}$  must be treated apart, because, corresponding to a  $B$  exciton bound to a neutral donor, it involves two electrons. The reason why its excitation may be transferred into an  $I_{1A}$  complex is that its energy is located in the  $A_{n=1}$  exciton band. So,  $I_{2B}$  may be autoionized in  $A_{n=1}$  excitons which then are bound to neutral acceptors. An  $I_{2B}$  oriented center contains two electrons with antisymmetrized-spin wave functions, and  $I_{1A}$  only one electron, uncoupled to the holes. So the two final states  $\phi^+(I_{1A})$  and  $\phi^-(I_{1A})$  are equally probable. The transfer can occur through  $\Gamma_6$  as well as  $\Gamma_5$  free  $A$  exciton. This is in good agreement with the experimental  $\rho(I_{2B} \rightarrow I_{1A})$ .

#### VIII. EFFECT OF A TRANSVERSE MAGNETIC FIELD

In a magnetic field, the well-known precession of spins around the direction of the field gives rise

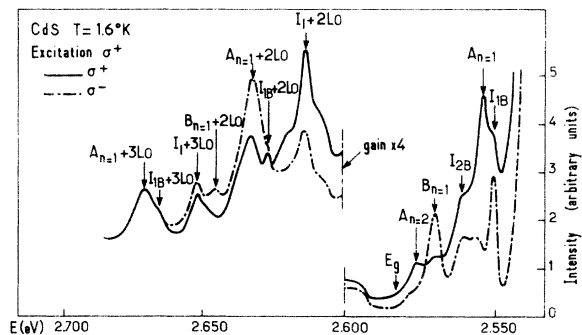


FIG. 6. ES of  $I_{1A}$  line in circular configuration.

TABLE IV. Degree of polarization of the  $I_{1A}$  line for various exciting energies in both configurations.

Line in the ES	Exciting energy in eV	DOP in circular conf. (+, -)
$I_{1B}$	2.549	-0.26
$A_{n=1}$	2.553	+0.50
$I_{2B}$	2.560	+0.04
$B_{n=1}$	2.569	-0.50
$A_{n=2}$	2.576	+0.10 <sup>a</sup>
$I_{1A} + 2LO$	2.611	+0.13
$A_{n=1} + 2LO$	2.629	-0.18

<sup>a</sup>See Ref. 20.

to a depolarizing effect, similar to the Hanle effect in gases. The mean value of the orientation along the  $c$  axis is given by

$$P(H_t) = \frac{P(0)}{1 + (g_t \mu_B H_t T'_1 / \hbar)^2}, \quad (13)$$

where  $g_t$  is the transverse component of the  $g$  factor,  $H_t$  the magnitude of the transverse magnetic field,  $\mu_B$  the Bohr magneton, and  $T'_1$  the total lifetime of the orientation:

$$T'^{-1}_1 = T^{-1}_1 + \tau^{-1}. \quad (14)$$

A.  $I_{1A}$  line

Hopfield has shown that the  $g$  factor of the  $I_{1A}$  complex is the same as that of the bound electron and is isotropic ( $g = 1.76$ ).<sup>11</sup> The DOP of the  $I_{1A}$  fluorescence, as a function of  $H_t$ , follows a classical Lorentzian, with a half-width  $H_0 = 125$  G (see Fig. 7). We deduce from (13)  $T'_1 = \hbar/g_t \mu_B H_0 = 0.52$  nsec, and using  $\tau(I_{1A}) = 1$  nsec found by Henry and Nassau<sup>21</sup>:  $\tau(I_{1A}) \approx T_1(I_{1A}) \approx 1$  nsec.

B.  $I_{2A}$  and  $A_{n=1}$  lines

In a magnetic field, the  $I_{2A}$  complex behaves as a hole in the  $A$  valence band, with  $g_t = 0$ .<sup>11</sup> So, no depolarizing effect is observed on this line. The same result occurs for the free exciton, in agree-

ment with previous observations by Gross *et al.* in CdSe.<sup>7</sup>

## IX. ORIENTATION OF EXCITONS BY LINEARLY POLARIZED LIGHT

## A. Linearly polarized light absorption

The formal identity between the two-dimensional space of  $\Gamma_5$  transverse excitons and the space of configuration of photons for  $\vec{k} \parallel c$ , appeared in the discussion of Sec. III. This analogy led us to choose as an orthonormal basis for this  $\Gamma_5$  space the two excitons related, as illustrated on Fig. 1, to circular  $\sigma^+$  and  $\sigma^-$  light by relations (4). These relations may be written using a two-particle (or excitonic) formalism:

$$\begin{aligned} \langle \Phi | p^+ | \Gamma_5^+ \rangle &= - \langle \Phi | p^- | \Gamma_5^- \rangle = P, \\ \langle \Phi | p^- | \Gamma_5^+ \rangle &= \langle \Phi | p^+ | \Gamma_5^- \rangle = 0, \end{aligned} \quad (15)$$

where  $\Phi$  is the crystal ground state,  $\Gamma_5^+$  and  $\Gamma_5^-$  are, for example, the two  $A$  excitons  $|S^+\rangle \otimes |X+\rangle$  and  $|S^+\rangle \otimes |X-\rangle$ .

Having chosen two arbitrary perpendicular transverse directions  $X$  and  $Y$ , and using the usual relations between Cartesian and circular components of the momentum operator, we find

$$\begin{aligned} \langle \Phi | p^X | (i/\sqrt{2})(\Gamma_5^+ + \Gamma_5^-) \rangle \\ &= \langle \Phi | p^Y | -(1/\sqrt{2})(\Gamma_5^+ - \Gamma_5^-) \rangle = -iP, \\ \langle \Phi | p^X | (-1/\sqrt{2})(\Gamma_5^+ - \Gamma_5^-) \rangle \\ &= \langle \Phi | p^Y | (i/\sqrt{2})(\Gamma_5^+ + \Gamma_5^-) \rangle = 0. \end{aligned} \quad (16)$$

These relations allow us to say that the exciton which we call

$$\Gamma_5^X = (i/\sqrt{2})(\Gamma_5^+ + \Gamma_5^-) \quad (17a)$$

is created by absorption of and will recombine with emission of a  $\sigma^X$  photon. Its orthogonal partner

$$\Gamma_5^Y = -(1/\sqrt{2})(\Gamma_5^+ - \Gamma_5^-) \quad (17b)$$

has the same properties with regard to  $\sigma^X$  photons.

TABLE V. The deductions made from the experimental DOP listed in Table IV which involve  $\vec{K} = 0$  primary excited levels. We have used the values  $T_1(I_{1A}) \approx \tau(I_{1A}) \approx 1$  nsec found in Sec. VII and Ref. 21.

Primary excited level: $\mu$	Spin of the electron in $\mu$	Measured $\rho(\mu, I_{1A})$	Theoretical sign of $\Theta(\mu \rightarrow I_{1A})$	Experimental $T_1(\mu), \tau(\mu), \Theta(\mu \rightarrow I_{1A})$
$I_{1B}$	$ \uparrow\rangle$	-0.26	-	$\Theta < 0$
$A_{n=1}$	$ \uparrow\rangle$	+0.50	+	$T_1 \gg \tau, \Theta = +1$
$I_{2B}$		+0.04	0	$\Theta \approx 0$
$B_{n=1}$	$ \uparrow\rangle$	-0.50	-	$T_1 \gg \tau, \Theta = -1$
$A_{n=2}$	$ \uparrow\rangle$	+0.10	+	$\Theta \approx 0.25^a$

<sup>a</sup>See Ref. 20.

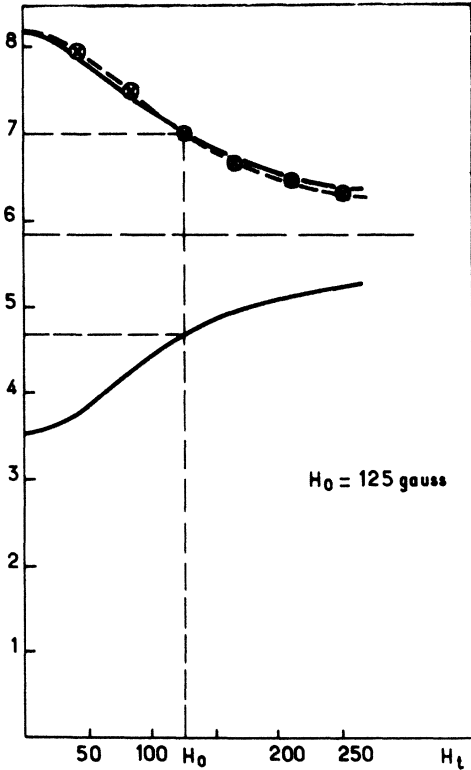


FIG. 7. Hanle effect on the  $I_{1A}$  fluorescence in circular configurations. The  $\odot$  shows the theoretical Lorentzian profile.

#### B. Nonequivalence of linear and circular orientations

However, optical orientation in  $(\sigma^x, \sigma^y)$  configuration is unusual in semiconductors, and has not yet been observed experimentally to our knowledge (excepting the case of localized impurities more relevant to atomic physics). Actually, our experimental results in these two configurations are quite different and we wish to emphasize, before presenting them, that the equivalence, for the description of polarization, of both circular and linear configurations (and of any other orthonormal set of two polarization states) may be broken when the light is interacting with matter. The space of eigenfunctions of the electronic system can be divided into two parts, related by time reversal symmetry. The  $\{\Gamma_5^+, \Gamma_5^-\}$  basis for orientation states of  $\Gamma_5$  excitons has the property that the two functions are mutually Kramers-conjugate. So the electron-hole and photon spaces are divided, in the  $(+, -)$  configuration, into two symmetric parts, having the same properties.

More precisely, and considering as an example the  $A$  excitons in CdS, let us choose two arbitrary bases for the  $\Gamma_5$  space of electrons  $\{\vec{e}_1, \vec{e}_2\}$  and the  $\Gamma_7$  space of holes  $\{\vec{h}_1, \vec{h}_2\}$ , respectively. The ten-

orial product  $\{\vec{e}_1, \vec{e}_2\} \otimes \{\vec{h}_1, \vec{h}_2\}$  will form a basis for the space of electron-hole pairs (or excitons), which may split into two two-dimensional spaces  $\Gamma_5$  and  $\Gamma_6$ . One can easily check, from the symmetry considerations pointed out above, that the only two bases satisfying

$$\begin{aligned} \{\vec{e}_1 \otimes \vec{h}_1, \vec{e}_2 \otimes \vec{h}_2\} &\in \Gamma_5, \\ \{\vec{e}_1 \otimes \vec{h}_2, \vec{e}_2 \otimes \vec{h}_1\} &\in \Gamma_6 \end{aligned} \quad (18)$$

are the ones we choose in relations (4). In other words,  $\Gamma_5^+$  and  $\Gamma_5^-$  form the only basis function of  $\Gamma_5$  space which can be expressed as a single tensorial product of electron and hole basis functions: the basis function  $\Gamma_5^+$  is only a product of an electron  $S\uparrow$  and a hole  $X\uparrow$  and both particles can be considered as completely oriented "by themselves" in this product. In the  $(+, -)$  configuration, a 100% orientation may be created among electrons and holes, as well as among excitons. This is not the case in any other basis, the  $(X, Y)$  configuration being the opposite, where no orientation can be assigned to the electron or the hole alone, although excitons may be 100% oriented.

This can be verified on the example of  $I_{1A}$  centers, where the electron contains all the information about orientation, because of the required antisymmetrization of the two holes: A straightforward calculation shows that such centers cannot decay in linearly polarized light, each linear polarization in this configuration being equiprobable for any orientation of the electron. The same type of calculation is obviously available for  $I_{2A}$  centers, and for any situation where the memory of polarization is lost for one of the two particles (i. e., band-to-band recombination in a  $n$ - or  $p$ -type crystal, etc.).

Moreover, one is easily convinced that the mere exchange of particles between free electron-hole pairs destroys the orientation of the whole population, as soon as this population is numerous enough to mix up the original pairings.

All these cases, where no optical pumping effect is expected *a priori* in  $(X, Y)$  configuration, could be described in more general terms of the "loss of coherence" between the electron and the hole. We wish to point out that these effects have nothing to do with ordinary relaxation of spin orientation. They are related to the fact that, strictly speaking, the photon coming out cannot in general be described by a pure quantum state, but by a mixed state.<sup>23</sup>

#### C. Degrees of polarization

It results from these limitations that in the  $(\sigma^x, \sigma^y)$  configuration a nonzero DOP will be generally observed on free-exciton luminescent lines ( $A_{n=1}, A_{n=2}$ -LO) and not on excitons bound to neutral



impurity lines ( $I_{1A}, I_{2A}$ ). [The case of exciton bound to a ionized donor, which gives rise to the  $I_3$  line, could not be properly studied in our sample. But optical pumping in  $(X, Y)$  may be expected on this line.]

This appears very clearly on the luminescence spectra, and no residual polarization has ever been observed on  $I_{1A}$  or  $I_{2A}$  lines [compare Fig. 4(a) and 4(b)].

The Fig. 8 shows the ES of  $A_T$  line in the  $(\sigma^X, \sigma^Y)$  configuration (the measured DOP are listed in Table III), and Fig. 4(b) the  $A_{n=2}$ -LO line in luminescence with excitation resonant with the  $A_{n=2}$  level. (The measured DOP is 0.80.)

When  $h\nu_e = E(A_{n=2})$ , the measured DOP in  $(\sigma^X, \sigma^Y)$  are about the same as in the  $(\sigma^+, \sigma^-)$  configuration, for both  $A_T$  and  $A_{n=2}$ -LO lines. It is quite satisfying and the calculated transfer factors and disorientation ratios seems roughly the same in both configurations.

One could easily show that, if longitudinal ( $T_1$ ) and transverse ( $T_2$ ) disorientation times are properly defined for excitons with respect to the  $c$  axis in the usual phenomenological way, the depolarization in circular configuration is actually relevant to  $T_1$ , and in linear configuration to  $T_2$ . However, when there is no perturbation applied (such as magnetic field parallel to  $c$  or uniaxial stress perpendicular to  $c$ ), there is no reason why they should be different. Our experimental results corroborate this point of view for  $A_{n=2}$  excitons: with the use of the analog of relation (8) in  $(X, Y)$  configuration, they provide [see relation (12)]

$$T_1(A_{n=2}) \simeq T_2(A_{n=2}) \simeq 3.5\tau(A_{n=2}). \quad (19)$$

For  $A_{n=1}$  excitons, we can only conclude that [see relation (11)]

$$T_1(A_{n=1}) \gtrsim 10\tau(A_{n=1}) \text{ and } T_2(A_{n=1}) \gtrsim 10\tau(A_{n=1}) \quad (20)$$

with good presumptions that the equality stands.

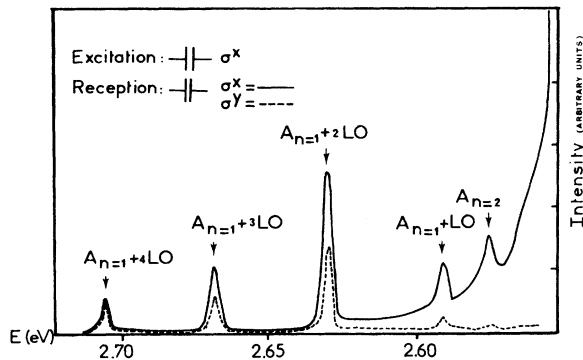


FIG. 8. ES of  $A_T$  in linear configuration.

The other exciting energies presented in Table III correspond to indirectly created excitons, and the corresponding DOP will be discussed in Sec. X.

#### D. Effect of a longitudinal magnetic field

We could hope to observe the Hanle effect on the free excitons  $A_{n=1}$  or  $A_{n=2}$ , due to a longitudinal (with respect to the  $c$  axis) magnetic field. The splitting of  $\Gamma_5^+$  and  $\Gamma_5^-$  induces, in this case, a rotation of the mean polarization plane of the fluorescent light. This rotation can be compared fruitfully to a "resonant Faraday effect."

Calculations have been made, using the well-known description of the population of  $\Gamma_5$  excitons in terms of density operators, and the rotation angle has been found to be

$$\alpha = \arctan(\frac{1}{2}\omega T_2'), \quad (21)$$

and the corresponding DOP

$$\Theta \frac{T_2}{T_2 + \tau} \frac{1}{(1 + \omega^2 T_2'^2)^{1/2}}, \quad (22)$$

where  $\Theta$  is the transfer factor from the exciton level,  $\hbar\omega$  the  $\Gamma_5^+$ ,  $\Gamma_5^-$  splitting, and

$$T_2'^{-1} = T_2^{-1} + \tau^{-1}.$$

Measurement of  $\alpha$  and knowledge of the longitudinal  $g$ -factor component of excitons serves to determine  $T_2'$  and check the sign of the  $g$  factor.

We have made this experiment in a ferromagnet providing 12 kG, and the rotation was measured by classical methods of Faraday-effect studies. Taking into account the several experimental restrictions mentioned in Sec. V, and enhanced by the necessity of propagating along the magnetic field, we were limited to measure a rotation greater than 0.05 rad. No rotation has been observed on  $A_{n=1}$  or  $A_{n=2}$ -LO luminescence.

Using the longitudinal component of  $g$  for the  $A_{n=1}$  exciton provided by Hopfield and Thomas,<sup>10</sup>  $g = 0.62$ , should mean that  $T_2' < 2 \cdot 10^{-12}$  sec, for both  $A_{n=1}$  and  $A_{n=2}$  excitons. Because of relations (19) and (20), this must be due to the very short lifetime of excitons in our sample. This is not surprising in view of the ES, as reminded in Sec. V.

#### X. EFFECTS OF THE INDIRECT CREATION OF EXCITONS

In the preceding sections, we have restricted ourselves to the discussion of the most intelligible cases for the transfer of excitations: after direct creation in a  $\vec{K} = 0$  or impurity level  $\mu$ , the orientation of excitons could be detected on a  $\vec{K} = 0$  or impurity level  $\nu$ . For example, the transfers

$$(A_{n=2}, \vec{K} = 0 \rightarrow A_{n=1}, \vec{K} = 0), \quad (A_{n=1}, \vec{K} = 0 \rightarrow I_{1A}), \\ (I_{1B} \rightarrow I_{1A})$$

illustrate three different cases we have met, which

are included in the analysis made in Sec. IV. The case of the  $A_{n=2}$ -LO line is particularly simple for  $\mu = \nu$ , and the orientation of the created level can be directly measured in this case.

Often, we have found simple arguments to show that  $\Theta(\mu \rightarrow \nu)$  should be very close of 1, 0 or -1, and this was checked experimentally. In fact, we generally could, out of all the possible "paths" of excitons on an  $(E, \vec{K})$  diagram, pick up one to be the most probable and containing  $\vec{K} = 0$  real intermediate states. So we did not have to deal with two complications arising from transit of excitons through  $\vec{K} \neq 0$  real intermediate states: (i) the effect of longitudinal-transverse (LT) splitting of excitons, and (ii) the effect of  $A, B$  and  $C$  exciton band mixing.

We will now take these effects into account to explain the observed DOP, in  $(+, -)$  and  $(X, Y)$  configurations, of the  $A_T$  line when exciting energy is situated on the LO-phonon replicas of its ES.<sup>18</sup> Although it could be done also for bound-exciton luminescence by an easy generalization, the corresponding experimental results are not accurate enough to improve the verification of our theories.

Generally speaking, from obvious symmetry considerations, many paths involving  $\vec{K} \neq 0$  intermediate states are possible. But they will not lead to the same final state at the  $\Gamma$  point, and we will have to sum over all these directions to obtain the interesting properties of the final mixed state.

#### A. LT splitting

Optically active excitons having nonzero kinetic energy remain doubly degenerate only if propagating along the  $c$  axis of the crystal. For, as pointed out in Sec. II, the LT splitting  $\delta_{LT}$  is constant for a given direction of  $\vec{K}$  (providing we remain beyond the region of strong coupling between excitons and photons), but depends on the azimuthal angle  $\theta$  of  $\vec{K}$  and the  $c$  axis:  $\delta_{LT} = \delta_0 \sin^2 \theta$ .

So, for example, created  $\Gamma_5^+$  excitons will evolve in different ways if they "stay" the same time  $\bar{\tau}_{ac}$  in different points of the  $K$  space before reaching the  $\vec{K} = 0$  level where they will be detected (see Fig. 9). If  $\bar{\tau}_{ac} > \hbar/\delta_{LT}$ , they are projected into the "good" states transverse and longitudinal with respect to  $\vec{K}$ , and the averaged polarization over the polar angle of  $\vec{K}$  will be zero. If  $\bar{\tau}_{ac} < \hbar/\delta_{LT}$ , they will not have time to be depolarized.

If the transition between the two situations were abrupt and the time  $\bar{\tau}_{ac}$  equal for all excitons, a transfer factor  $\Theta$  ranging between 0 and 1 is given by the mere computation of the DLT and NDLT areas:

$$\bar{\tau}_{ac} = \frac{\hbar}{\delta_0(2\Theta - \Theta^2)} \approx \frac{10^{-12}}{2\Theta - \Theta^2} \quad (23)$$

with  $\delta_0 = 0.6$  meV from earlier works.<sup>24</sup>

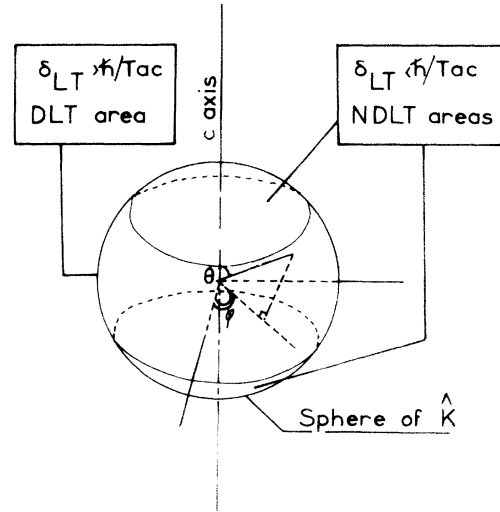


FIG. 9. On the sphere of the direction of  $\vec{K}$ , the excitons are not disoriented on the caps but may be disoriented on the equatorial zone if they "stay" a time longer than  $\hbar/\delta_{LT}$ .

A more precise analysis would be complicated because several phonons with various directions and different interaction times are implied in the scatterings of an exciton. The time  $\bar{\tau}_{ac}$  which is determined is nothing but an order of magnitude of the mean time that excitons spend out of  $\vec{K} = 0$  states.

Reviewing now the various possible transfers of excitation which we have to deal with in our sample (see Sec. V and Ref. 18), we find it suitable to divide them into two categories (see Fig. 10).

*a. Nondisorienting by LT splitting (NDLT).* The transfer channels involve only  $\vec{K} \approx 0$  states ( $A_{n=1}, \vec{K} = 0 - I_{1A}$ ), or virtual  $\vec{K} = 0$  intermediate states ( $A_{n=2}, \vec{K} = 0 - A_{n=1}, \vec{K} = 0$ ), or real  $\vec{K} \neq 0$  intermediate states, but are occupied during a time shorter than  $\hbar/\delta_0 \approx 10^{-12}$  sec. The last case corresponds to the indirect creation of excitons able to reach the bottom of the band by LO-phonon emissions only (the interaction time  $\tau_{LO}$  may be considered to be  $10^{-13}$  to  $10^{-14}$  sec<sup>25</sup>). It happens for exciting energies  $\hbar\nu_e = E(A_{n=1}, \vec{K} = 0) + N\hbar\Omega$  [ $N(\text{integer}) \geq 2$ ], and gives rise to the  $(A_{n=1} + 2, 3, \dots, \text{LO})$  replicas in the ES of the  $A_T$  line, because the indirect absorption is forbidden for  $\vec{K} = 0$  created excitons.<sup>18</sup>

*b. Disorienting by LT splitting (DLT).* The transfer channels involve  $\vec{K} \neq 0$  real intermediate states occupied during a time longer than  $\hbar/\delta_0$ . This is the case for the few excitons created at kinetic energies slightly higher than  $(N-1)\hbar\Omega$  ( $N \geq 1$ ), which reach the bottom of the band by several interaction with acoustic phonons. They provide a negligible contribution to the  $(A_{n=1} + 2, 3, \dots, \text{LO})$

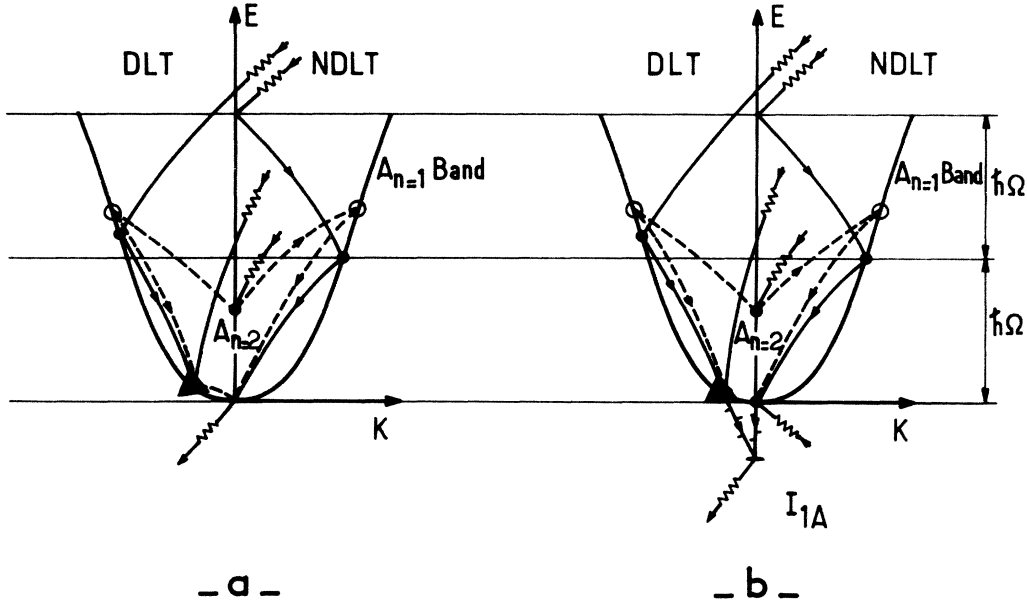


FIG. 10. Some possible channels for the transfer of excitation from indirectly ( $A_{n-1} + \text{NLO}$ ) or directly ( $A_{n-1}$ ,  $A_{n-2}$ ) created excitons, in the case of the direct annihilation (a) and of the trapping on  $I_1$  center (b) of  $A_{n-1}$  excitons. On the left part of each band are shown DLT channels; on the right, NDLT channels. Between the exciting and the emitted photons, the acoustical scatterings (dashed line) and the trappings (spiked line) are slow, while the LO scatterings (solid line) are rapid. So the  $\vec{K} \neq 0$  real intermediate states may be disoriented ( $\blacktriangle$ ) by LT splitting, or nondisoriented ( $\bullet$ ) as the  $\vec{K} = 0$  ones. The virtual intermediate states (O) are not disoriented.

replicas, but give rise to the  $A_{n-1} + \text{LO}$  replica at exciting energy  $h\nu_e = E(A_{n-1}) + \hbar\Omega$ , for which the NDLT channel is forbidden.

This explains qualitatively the experimental DOP on the  $A_{n-1} + \text{LO}$  replica, which are similar in both configuration and suggest that depolarization effects due to LT splitting are very important. They provide, from (23),  $\bar{\tau}_{ac} \approx 2 \times 10^{-12}$  sec. From the same point of view, the trapping of a free exciton on an impurity is not very selective. Although the ( $A_{n-1}$ ,  $\vec{K} = 0 \rightarrow I_{1A}$ ) transfer is NDLT, the ( $A_{n-2}$ ,  $\vec{K} = 0 \rightarrow I_{1A}$ ) is DLT because excitons transit through real states  $A_{n-1}$  with  $\vec{K} \neq 0$ . Actually, the corresponding transfer factor (see Table V) is 0.25. It seems to be larger than 0.4 (see Sec. VIIA) for  $I_{2A}$ , suggesting that the trapping on a neutral donor is more selective than on a neutral acceptor. This is in qualitative agreement with the compared width of the LO-phonon replicas in the ES of  $I_{1A}$  and  $I_{2A}$ .<sup>17, 18</sup>

#### B. Band mixing

In contrast to the single LO-phonon replicas, the 2nd, 3rd, ... LO-phonon replicas of the ES of the  $A_T$  line are mainly contribution of NDLT channels. But, as the kinetic energy of exciton increases, we must take into account the mixing of the  $A$ -valence band with  $B$ - and  $C$ -valence bands. This must be of primary importance for the ( $A_{n-1}$

+ 2LO) replica, because excitation is then quasi-resonant with the fundamental  $\Gamma_5 C$  exciton: it increases the contribution of this virtual intermediate state to the indirect absorption. As we have seen in Secs. VI and VII, such a contribution may lead to a negative value of the DOP, in the (+, -) configuration, which obviously could not be obtained by mere relaxation effects.

(a) Dealing now with the ( $A_{n-1} + 2\text{LO}$ ) replica, we consider, in view of symmetry considerations developed in Sec. II that the absorption of one  $\sigma^+$  photon (at the proper energy) leads, after emission of two LO phonons with opposite wave vector  $\vec{K}_c$  and  $-\vec{K}_c$ , to an  $A_{n-1}$  exciton in the bottom of its band in some pure state  $\alpha\Gamma_5^+ + \beta\Gamma_5^-$ . This general  $\Gamma_5$  exciton can be compared to, and actually radiate into an elliptically polarized light. This obviously breaks the symmetry of our situation, and this can only be due to the occurrence of the particular direction of  $\vec{K}_c$ . Let us define it by  $\theta$  and  $\phi$ , its azimuthal and polar angles with respect to the  $c$  axis, and make two reasonable hypotheses. (i) The ellipticity of the created  $\Gamma_5$  exciton is  $\phi$  independent. (ii) The polar angle of, for example, the great axis of the ellipse is, apart from an additive constant,  $\phi$ .

Without any more loss of generality, we can now write this  $\Gamma_5$  state

$$\Delta_5^*(\theta, \phi) = A(\theta)\Gamma_5^+ + B(\theta)e^{-2i\phi}\Gamma_5^- \quad (24a)$$

with  $A(\theta)$  real and  $A(\theta)^2 + |B(\theta)|^2 = 1$ .

We need not be precise about  $A(\theta)$  and  $B(\theta)$ , although we could assert that  $A(\theta) = 1$  for  $\theta = 0$  or  $\pi$  (the symmetry is then no more broken), and that  $B(\theta)$  is probably real so that the direction of the great axis is parallel to  $\vec{K}_c$ .

We need specify the  $\Gamma_5^-$  state resulting from the absorption of one  $\sigma^-$  photon with no more precision. Probably it is not the orthogonal partner of  $\Delta_5^+$ , because the great axis of the ellipse would be orthogonal too. It may be the same ellipse, described in the opposite way, or more probably its symmetric with respect to the  $(\vec{K}_c, c)$  plane. We will write this state:

$$\Delta_5^-(\theta, \psi) = A(\theta)\Gamma_5^- + B'(\theta)e^{+2i\phi}\Gamma_5^+ \quad (24b)$$

with  $B' = -B^*$ , or  $B^*$ , or  $B$  for the three different hypothesis.

The only important facts are in the modules of  $A(\theta)$  and  $B(\theta)$ , which assert that  $\Delta_5^-$  is "described" in the opposite way to  $\Delta_5^+$ , and in the sign of the exponential, which asserts that  $\Delta_5^-$  is rotated with  $\phi$  as  $\Delta_5^+$ .

(b) Assuming now a  $\sigma^+$  exciting light, and that the probability  $p$  of one particular LO-phonon emission is  $\phi$  independent, we can write from (24) the density operator of the excitons in the bottom of their band, on the  $\{\Gamma_5^+, \Gamma_5^-\}$  basis.

$$\begin{aligned} \rho_{+-} &= \frac{1}{4\pi} \sum_{\theta, \phi} [ |\Delta_5^+(\theta, \phi)\rangle \langle \Delta_5^+(\theta, \phi)| + |\Delta_5^-(\theta, \phi)\rangle \langle \Delta_5^-(\theta, \phi)| ] p(\theta) \\ &= \frac{1}{2} \sum_{\theta} [ A(\theta)^2 |\Gamma_5^+\rangle \langle \Gamma_5^+| + |B(\theta)|^2 |\Gamma_5^-\rangle \langle \Gamma_5^-| ] p(\theta) \\ &= A^2 |\Gamma_5^+\rangle \langle \Gamma_5^+| + B^2 |\Gamma_5^-\rangle \langle \Gamma_5^-| \end{aligned} \quad (25)$$

with  $A^2 = \frac{1}{2} \sum_{\theta} A(\theta)^2 p(\theta)$  and  $B^2 = \frac{1}{2} \sum_{\theta} |B(\theta)|^2 p(\theta)$ .

This density operator corresponds to a maximum DOP (without any spin-relaxation effects):

$$P_{\max}^{\sigma^+} = A^2 - B^2 = 2A^2 - 1.$$

On the other hand,  $\sigma^x$  and  $\sigma^y$  photons create, respectively,

$$\begin{aligned} \Delta_5^x(\theta, \phi) &= (i/\sqrt{2}) [ \Delta_5^+(\theta, \phi) + \Delta_5^-(\theta, \phi) ], \\ \Delta_5^y(\theta, \phi) &= - (1/\sqrt{2}) [ \Delta_5^+(\theta, \phi) - \Delta_5^-(\theta, \phi) ], \end{aligned} \quad (26)$$

The density operator of the population created by a  $\sigma^x$  excitation is

$$\begin{aligned} \rho_{XY} &= \frac{1}{4\pi} \sum_{\theta, \phi} | \Delta_5^x(\theta, \phi) \rangle \langle \Delta_5^x(\theta, \phi) | p(\theta) \\ &= \frac{1}{2} ( |\Gamma_5^+\rangle \langle \Gamma_5^+| + |\Gamma_5^-\rangle \langle \Gamma_5^-| ) \\ &\quad + A^2 |\Gamma_5^-\rangle \langle \Gamma_5^+| + A^2 |\Gamma_5^+\rangle \langle \Gamma_5^-| \end{aligned}$$

[remembering that  $|B'(\theta)|^2 = |B(\theta)|^2$  and  $A^2 + B^2 = 1$ ]. In the  $\{\Gamma_5^x, \Gamma_5^y\}$  basis, it becomes

$$\begin{aligned} \rho_{XY} &= \frac{1}{2} (1 + A^2) | \Gamma_5^x \rangle \langle \Gamma_5^x | \\ &\quad + \frac{1}{2} (1 - A^2) | \Gamma_5^y \rangle \langle \Gamma_5^y |, \end{aligned} \quad (27)$$

which corresponds to a maximum DOP in the  $(X, Y)$  configuration:

$$P_{\max}^{XY} = A^2.$$

(c) Including now relaxation effects, we get for the observed DOP

$$0 \leq P^{*-} \leq 2A^2 - 1, \quad \text{if } A^2 \geq \frac{1}{2}$$

or

$$0 \geq P^{*-} \geq 2A^2 - 1, \quad \text{if } A^2 < \frac{1}{2}$$

and

$$P^{XY} \leq A^2. \quad (28)$$

From Table III, we are in the case  $A^2 < \frac{1}{2}$ , and we may check that  $-0.20 = P^{*-} > 2P^{XY} - 1 = -0.28$ . If we describe the relaxation effects by two coefficients  $R_{+-}$  and  $R_{XY}$ , so that

$$P^{*-} = R_{+-} P_{\max}^{\sigma^+}$$

and

$$P^{XY} = R_{XY} P_{\max}^{XY},$$

we deduce that  $0.72/R_{XY} + 0.20/R_{+-} = 1$  so that  $1 > R_{XY} > 0.90$  and, correlatively,  $0.71 < R_{+-} < 1$ . If we suppose  $R_{XY} \approx R_{+-}$ , which seems reasonable on the view of results of Sec. IX, we get  $R_{XY} \approx R_{+-} \approx 0.90$ . In any case, these results show that, roughly speaking, the disorientation times (transverse and longitudinal) of excitons are longer than 10 times their lifetime at the bottom of the band.

The situation is more complicated for the third LO-phonon replica, ( $A_{n=1} + 3\text{LO}$  line in the ES of  $A_T$ ), because three LO phonons are implied in the processes with the condition  $\vec{K}_1 + \vec{K}_2 + \vec{K}_3 = 0$ . But we may assert that the nearly zero DOP in  $(+, -)$  configuration is partly due to a compensation effect of this type, because some polarization remains in  $(X, Y)$  configuration (0.25).

Let us remark that the experimental result  $|B| > A$  in our calculation implies a rather important mixing of the bands at kinetic energy  $\hbar\Omega$ . However, the contribution of  $C$  is increased by the quasiresonance of this level with the incoming photons, and one cannot deduce that there is more than 50% of  $C$  (and  $B$ ) in the  $A$ -exciton band at this energy.

## XI. CONCLUSION

We have shown in this paper that the optical orientation of free and bound excitons can be achieved in circular polarization in CdS. We often observed very important degrees of polarization of emitted light for two different reasons. (i) The theoretical possible orientation are 100%, because of the

nondegenerate valence bands. (ii) The lifetimes of excitons in our sample were rather short, decreasing correlatively the influence of depolarization times ( $\tau < T_1$ ).

The second point is difficult to separate from the fact that we had a lot of information about the transfer of the excitations in the crystal. In particular, we have pointed out the importance of the creation of excitons in their band with participation of LO phonons. Most probably, the transfer through electron-hole pairs would be more difficult to interpret.

These good conditions provided us with much information about the disorientation times and lifetimes of excitons. Much work should be done now to deduce the precise physical meaning of these parameters, which we have introduced in a rather phenomenological way, in the case of excitons.

The observation of optical pumping in linear configuration confirms the distinction between excitons, and free electron-hole pairs which more often lose any memory of their conditions of creation (the linear polarization as well as the energy of the exciting light).<sup>26</sup> A linearly polarized emission can only result from the proper orientation of two particles (in fact an exciton) and not from the orientation of individual electrons or holes. Optical-pumping experiments may help in understanding the kinetics of elementary excitations, as has been illustrated in Sec. X of this paper.

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<sup>1</sup>G. Lampel, Thèse d'Etat (Faculté des Sciences d'Orsay, 1968) (unpublished).

<sup>2</sup>G. Lampel, Phys. Rev. Lett. **20**, 491 (1968).

<sup>3</sup>C. Cohen-Tannoudji and A. Kastler, *Progress in Optics*, edited by B. Wolff (North-Holland, Amsterdam, 1966), Vol. 5.

<sup>4</sup>R. R. Parsons, Phys. Rev. Lett. **23**, 1152 (1969).

<sup>5</sup>B. P. Zakharchenya, V. G. Fleisher, R. I. Dzhidev, Yu. P. Veshchunov, and I. B. Rusanov, Zh. Eksp. Teor. Fiz. **13**, 195 (1971) [JETP Lett. **13**, 137 (1971)].

<sup>6</sup>A. I. Ekimov and V. I. Safarov, Zh. Eksp. Teor. Fiz. **12**, 293 (1970) [JETP Lett. **12**, 198 (1970)].

<sup>7</sup>E. F. Gross, A. I. Ekimov, B. S. Razbirin, and V. I. Safarov, Zh. Eksp. Teor. Fiz. **14**, 108 (1971) [JETP Lett. **14**, 70 (1971)].

<sup>8</sup>C. Weisbuch and G. Lampel, in *Proceedings of the International Conference on Semiconductor Physics, Warsaw* (Polish Scientific, Warsaw, 1972), p. 1327; A. Bonnot, R. Planel, C. Benoit a la Guillaume, and G. Lampel, *ibid.*, p. 1334.

<sup>9</sup>D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).

<sup>10</sup>J. J. Hopfield and D. G. Thomas, Phys. Rev. **122**, 35 (1961).

<sup>11</sup>D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962).

<sup>12</sup>R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

<sup>13</sup>E. Gutsche and E. Jahne, Phys. Stat. Sol. **21**, 57 (1967).

<sup>14</sup>G. F. Koster, J. O. Dimmock, R. S. Wheeler and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT Press, Cambridge, Mass. 1963),

<sup>15</sup>R. R. Parsons, Can. J. Phys. **49**, 1850 (1971).

<sup>16</sup>E. F. Gross, S. A. Ppermogorov, V. V. Travnikov, and A. V. Selkin, J. Phys. Chem. Solids **31**, 2595 (1970).

<sup>17</sup>H. Malm and R. R. Hearing, Can. J. Phys. **49**, 2970 (1971).

<sup>18</sup>R. Planel, A. Bonnot and C. Benoit a la Guillaume, Phys. Stat. Sol. B **58**, 251 (1973).

<sup>19</sup>A. Bonnot, R. Planel, and C. Benoit a la Guillaume, Solid State Commun. (to be published).

<sup>20</sup>New experiments with a better resolution lead us to rectify the value of  $\rho(A_{n=2} \rightarrow I_{1A})$  given in Ref. 8. Thence,  $\Theta(A_{n=2} \rightarrow I_{1A}) < 1$ , as may be  $\Theta(A_{n=2} \rightarrow I_{2A})$ . So we get less information about the  $I_{2A}$  center than previously hoped.

<sup>21</sup>C. H. Henry and K. Nassau, Phys. Rev. B **1**, 1628 (1970).

<sup>22</sup>B. P. Zakharchenya, in Ref. 8, p. 1315.

<sup>23</sup>G. Fishman, C. Hermann, and G. Lampel, Colloq. Montpellier (France) (to be published).

<sup>24</sup>E. Gutsche and J. Voigt, in *Proceedings of the International Conference on II-VI Semiconductors, Providence*, 1967, edited by D. G. Thomas (Benjamin, New York, 1967), p. 337.

<sup>25</sup>R. Stratton, Proc. Roy. Soc. Lond. **A246**, 406 (1958).

<sup>26</sup>The possibility of observing the optical orientation of free excitons in linear configuration has also been considered by G. L. Bir and G. E. Pikus, in Ref. 8, p. 1341.