k-linear-term and polariton effects on the $Z_{1,2}$ excitons in CuBr

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The $Z_{1,2}$ excitons in CuBr are investigated by magnetoreflectance and magnetoluminescence. The reflectance anomaly at the energy of the degenerate (Γ_4,Γ_3) states is explained as owing to the k-linear term of the Γ_8 valence band coupled with the finite exciton wave vector $\vec{K}$. Based on this coupling scheme, the polariton effect on the exciton states is elucidated. The "bottleneck" for the polariton relaxation is found to be on the spin-triplet exciton state.

Recently, intense efforts have been made to investigate the internal structure and electron-hole exchange interactions (including L-T splitting) of highly degenerate exciton states in semiconductors by the use of external perturbations.[1-4] In zinc-blende crystals, the excitons associated with the Γ_8 hole and Γ_6 electron states are represented by $\Gamma_5+\Gamma_4+\Gamma_3$. Here Γ_5 represents the dipole allowed state and Γ_4, Γ_3 represent the dipole inactive spin-triplet states. The Hamiltonian of the exchange interaction is represented by

$$H_{\text{exch}}=\tilde{\Delta}_1(\vec{J}\cdot\vec{\sigma}-\tfrac{3}{4})+\tilde{\Delta}_2(\sigma_x J_x^3+\sigma_y J_y^3+\sigma_z J_z^3)+E_{L\text{-}T}\tfrac{1}{3}(3\cos^2\theta-1). \quad (1)$$

Here $\vec{J}$ and $\vec{\sigma}$ are the hole and electron angular momentum operators. $\tilde{\Delta}_1$ and $\tilde{\Delta}_2$ represent the isotropic and anisotropic spin-exchange splittings. The last term corresponds to the L-T splitting of the exciton due to the dipole $(\vec{\mu})$–dipole interaction with $\theta^2=(\vec{K}\cdot\vec{\mu})^2/K^2\mu^2$. Though the exchange splitting between the Γ_5 and Γ_4, Γ_3 states and $E_{L\text{-}T}$ of the Γ_5 state[5] have become generally recognized, almost no information is available on the anisotropic spin-exchange splitting $(-\tfrac{3}{2}\tilde{\Delta}_2)$ between the Γ_4 and Γ_3 states.[4] The effect due to coupling of the k-linear term inherent in the Γ_8 band and the exciton translational momentum $\vec{K}$ suggests a relaxation of the selection rules.[6]

We have measured normal incidence reflectance and luminescence spectra of the $Z_{1,2}$ excitons in CuBr on a {110} cleaved surface by using a Xe discharge lamp and the 3250-Å line of a He-Cd laser, respectively. As shown in Fig. 1, the reflectance spectrum is composed of two structures: a main broad-reflectance peak (Γ_5) and an anomalous sharp spike due to the spin-triplet states.[7] The luminescence spectrum at low temperatures is, however, composed mainly of a sharp structure just around the reflectance spike. A weak broad-luminescence hump at around the high-energy edge of the main reflectance peak becomes distinct at 77 K. From a line-shape analysis of the reflectance spectrum, we evaluate the resonance energies of the longitudinal (L), transverse (T), and spin-triplet (t) states. We obtain $E_{L\text{-}t}=13.5$–14.0 meV and $E_{T\text{-}t}=1.5$ meV. Thus $E_{L\text{-}T}$ is evaluated as 12.0–12.5 meV. In the Faraday configuration under magnetic fields, we have measured the difference between the σ_{+1} and σ_{-1} spectra [referred to as MCR for magnetic circular reflectance and MCP for magnetic circular polarization of luminescence] by the circular polarization modulation technique. Here σ_{+1} corresponds to the $M_J=+1$ exciton state. The effective g value is defined by $[E(\sigma_{+1})-E(\sigma_{-1})]/\mu_B H$.

Figure 2(a) shows the reflectance and MCR spectra of the $Z_{1,2}$ excitons in CuBr for $\vec{H}\parallel\vec{K}\parallel[110]$. The two MCR structures yield g values of -2.2 ± 0.1 and $+0.22\pm0.05$ (by line-shape analysis) for the reflectance spike and the main peak, respectively. We assign the second MCR structure $(g=+0.22)$ to the Γ_{5T} exciton state. The finite oscillator strength of the reflectance spike, being almost independent of samples, cannot be explained without considering an intrinsic mechanism which mixes the Γ_4, Γ_3, and Γ_5 states. The possibility

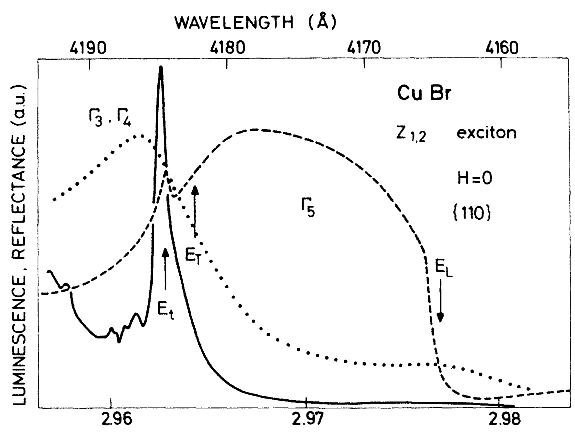

FIG. 1. Reflectance (dashed line) and luminescence (solid) spectra of the $Z_{1,2}$ excitons in CuBr at 4.5 K. The luminescence spectrum at 77 K (dotted) is included by subtracting the energy shift due to the temperature change.

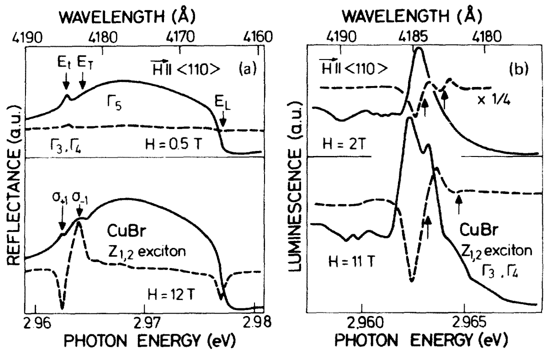

FIG. 2. Magneto-optical spectra of the $Z_{1,2}$ excitons in CuBr at 4.5 K. (a) Reflectance (solid) and MCR (dashed) spectra; (b) luminescence (solid) and MCP (dashed) spectra.

of an internal stress effect is unambiguously excluded by the clear selection rules observed under magnetic fields.

Now we consider the Hamiltonian due to the k-linear term effect represented by

$$H_K=\hbar K_t[K_x\{(J_y^2-J_z^2)J_x\}+\text{c.p.}]\,[m_0/(\gamma_1 m_e^*+m_0)], \tag{2}$$

where $\{AB\}=\frac{1}{2}(AB+BA)$, c.p. means cyclic permutation, and K_t, γ_1, and m_e^* are the coefficients of the k-linear term of the Γ_8 band, the Luttinger parameter, and the electron mass, respectively. If $\hbar K_t \neq 0$, the finite oscillator strength of the Γ_4, Γ_3 states is explicable even at zero field. In the Faraday configuration with $\vec{H} \parallel \vec{K} \parallel [110]$, the $|J^{(t)}=2, M_J=\mp 2\rangle$ states (abbreviated as $|2,\mp 2\rangle$) of the Γ_4, Γ_3 excitons become optically allowed in the $\sigma_{\mp 1}$ polarizations, respectively.[6]

We will further examine the following two possibilities: (a) $-\frac{3}{2}\tilde{\Delta}_2>0$ or (b) $-\frac{3}{2}\tilde{\Delta}_2=0$. In case of (a), the threefold degenerate Γ_4 states are expected to be responsible for the first MCR structure ($g=-2.2$). Owing to the k-linear term effect, two states of the Γ_4 excitons can be partially polarized for σ_{-1} and σ_{+1} ($\vec{H} \parallel \vec{K} \parallel [110]$), since they include the $|2,+2\rangle$ and $|2,-2\rangle$ states in unequal amounts (9 to 1 with respect to the oscillator strength). One of the twofold degenerate Γ_3 states also becomes dipole allowed due to the k-linear term effect. In the Voigt configuration with $\vec{H} \parallel [110]$ and $\vec{K} \parallel [1\bar{1}0]$, a single σ structure is expected from Γ_4. The splitting between the Γ_4 and Γ_3 states is predicted as at most 2.5 meV (corresponding to the limiting case of $-\frac{3}{2}\tilde{\Delta}_2 \gg -2\tilde{\Delta}_1$) using the experimental values of $E_{L\text{-}T}$ and $E_{T\text{-}t}$. The oscillator strength of the Γ_3 state is calculated to be more than 8% of the oscillator strength of the Γ_4 states. On the contrary, we have never observed (even at 12 T) any additional reflectance structure or a sharp luminescence peak in the above-mentioned energy region. The Zeeman component of the reflectance spike observed in the σ_{+1} (σ_{-1}) spectrum did not show a structure in the σ_{-1} (σ_{+1}) spectrum by use of a steady circular polarizer in $\vec{H} \parallel \vec{K} \parallel [110]$. A clear doublet splitting of the reflectance spike in the σ spectrum with $\vec{H} \parallel [110]$ and $\vec{K} \parallel [1\bar{1}0]$ disproves the possibility of (a). We conclude that the anisotropic spin-exchange splitting $-\frac{3}{2}\tilde{\Delta}_2$ is less than the half-width of the reflectance spike. The smallness of $\tilde{\Delta}_2$ is also suggested from a theoretical point of view. Considering that the second exchange term in Eq. (1) has a nonvanishing matrix element between $|2,\mp 2\rangle$ states,[4] $|\frac{3}{2},\mp\frac{3}{2}\rangle$ states of the Γ_8 valence band should not be pure down- or up-spin states in order to yield a finite $\tilde{\Delta}_2$. The mixture of β spin state into $(x+iy)\alpha$, for example, is possible, through the $d\gamma$ (x^2-y^2 and $3z^2-r^2$) orbitals of d-like functions or higher-order angular momentum states. From the known band scheme of CuBr,[8] however, this mixing is expected to be very small.

Thus we discuss the experimental results by the model (b). Here the five components of the Γ_4, Γ_3 states are degenerate at zero field but for the k-linear term effect. Then, the energy splitting between the T and t states is represented by

$$E_{T\text{-}t}=-2\tilde{\Delta}_1-\tfrac{1}{3}E_{L\text{-}T}\ . \tag{3}$$

Using $E_{T\text{-}t}=1.5$ meV, and $E_{L\text{-}T}=12.0$–12.5 meV, we obtain $-2\tilde{\Delta}_1=5.5$–5.7 meV. The leading off-diagonal matrix elements due to the k-linear term are represented below for $|2,\mp 2\rangle$, $|2,\pm 1\rangle$, and $|1,\pm 1\rangle$ states in the case of $\vec{H} \parallel \vec{K} \parallel [110]$:

$$\begin{pmatrix} 0 & \mp iT & \mp i\sqrt{3}T \\ \pm iT & 0 & 0 \\ \pm i\sqrt{3}T & 0 & E_{T\text{-}t} \end{pmatrix}, \tag{4}$$

where $T=9\hbar K_t K m_0/16(\gamma_1 m_e^*+m_0)$. The relative oscillator strength of the degenerate Γ_4, Γ_3 states compared with that of the Γ_5 state (experimentally evaluated to be 0.02) is represented by

$$4\pi\beta(\Gamma_4,\ \Gamma_3)/4\pi\beta(\Gamma_5)=(\sqrt{3}\ T/E_{T\text{-}t})^2. \tag{5}$$

Taking $K=3.5\times 10^5$ cm^{-1}, $m_e^*=0.3m_0$, $\gamma_1=0.71$,[9] and $E_{T\text{-}t}=1.5$ meV, we obtain $\hbar K_t=0.7\times 10^{-9}$ eV cm, which will yield a splitting of about 0.2 meV at the above-mentioned K value. This splitting is, however, not observed due to the half-width of the reflectance spike.

Diagonalizing the exciton matrix, Eq. (4), we obtain three eigenenergies $E_{Ti}(K)$; $i=1, 2, 3$ and the corresponding oscillator strengths $4\pi\beta_i(K)$. The polariton dispersion curves are described by

$$\frac{(\hbar cK)^2}{E^2}=\epsilon_\infty+\sum_{i=1,2,3}\frac{4\pi\beta_i(K)}{1-[E/E_i(K)]^2}\ , \tag{6}$$

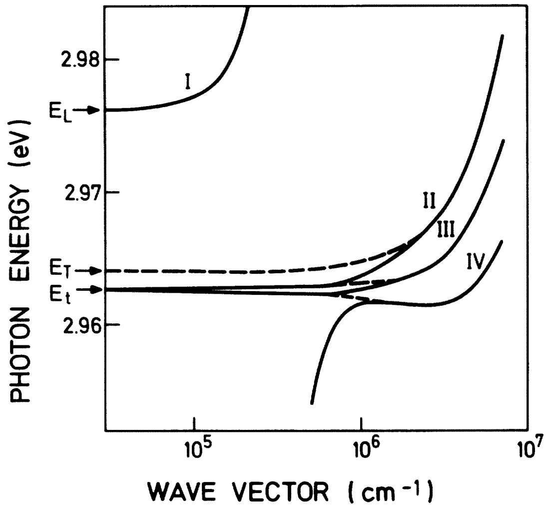

FIG. 3. Polariton dispersion curves (solid) calculated for the $Z_{1,2}$ excitons in CuBr at zero field, together with the uncoupled mechanical exciton states (dashed). The parameters are $\epsilon_\infty = 5.4$, $m_{ex} = 1.7m_0$, $\sum_i 4\pi\beta_i = 4.4\times 10^{-2}$, $E_{T\text{-}t} = 1.5$ meV, $\tilde{\Delta}_2 = 0$, and $\hbar K_t = 0.7\times 10^{-9}$ eV cm.

where $E_i(K) = E_{Ti}(K) + \hbar^2K^2/2m_{ex}$. Figure 3 shows the calculated result at zero field. The branch I is the upper polariton (UP) of the Γ_5 state. The branch IV is the lower polariton (LP) of the Γ_4, Γ_3 states. The branch III has UP (Γ_4, Γ_3) character at small K and LP (Γ_4, Γ_3) character at large K. On the other hand, the dispersion II is assigned to UP (Γ_4, Γ_3) at small K but continues to LP (Γ_5) in the region with large K.

Figure 2(b) shows the luminescence and MCP spectra of the main peak. At $H = 0$, no MCP signal is observed. At low magnetic fields, we observed the two MCP structures indicated by the arrows. The first MCP structure at lower energies results from the main luminescence peak, the doublet splitting of which is directly observable at 11 T. The second structure results from the high-energy tail of the main peak. With increasing magnetic field, the first MCP structure relatively increases, due to the enlarged Zeeman splittings and the preferential population into the low-energy state. The g value of the main luminescence peak is $g = -1.9 \pm 0.2$ at 11 T, in close agreement with that of the reflectance spike. Thus the main luminescence peak is assigned to the Γ_4, Γ_3 states. We notice that the second MCP structure has also a negative g value. It is also assigned to the Γ_4, Γ_3 states.

Finally, we discuss the luminescence associated with the Γ_5 state (I and II). No MCP signal is observed from the broad luminescence hump placed at the high-energy edge of the reflectance peak (77 K), which indicates a small g value of this structure. Since the peak energy of this luminescence hump coincides with E_L, we assign this structure to the UP (Γ_5).[10] Since the dispersion curve II is a very smooth function of K, there is no anomaly (so-called bottleneck) on this curve where the radiative lifetime becomes much smaller than that due to the intrabranch phonon scattering. Accordingly, the LP (Γ_5) luminescence is so inconspicuous in CuBr.[10] Owing to the k-linear term effect, the exciton oscillator strengths responsible for III and IV states monotonically increase as functions of K^2. Therefore, the probability of the interbranch polariton scattering by acoustic phonons increases as the energy increases from E_t. The polaritons on the branch II thus easily relax to III and IV states. Consequently, the bottleneck lies on the branch IV. The main luminescence peak is reasonably assigned to this state. Then the second MCP structure which appears just on the high-energy tail of the main MCP structure is identified as originating from the bottom part of the polariton states II and III. Though III is more populated at low temperatures, we cannot discriminate the contributions from the II and III states because of the small energy difference and the similar g values of them at small K.

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