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Magneto-optical studies of excitons bound to Ag and Cu acceptors in *p*-type CdTe

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The linear and quadratic Zeeman effects have been studied for two different neutral-acceptor—bound-exciton complexes, (Ag,X) and (Cu,X), in high-purity p-type CdTe. For both complexes, the results are consistent with a bound-exciton ground state $J=\frac{1}{2}$ in T_d symmetry. The relevant electron g value is $g_e=-1.77\pm0.02$ for the electron, and $K=+0.61\pm0.04$ and $L=-0.04\pm0.02$ for the hole parameters describing the isotropic and anisotropic Zeeman effects, respectively. The diamagnetic shift observed for the neutral-acceptor—bound-exciton complex is well explained in terms of the pseudodonor model.

I. INTRODUCTION

Recently, a systematic study of acceptor impurities has been carried out in CdTe by photoluminescence experiments on various high purity p-type materials and impurity doped materials.[1-3] In p-type materials, the residual impurities are found to be Ag and Cu, which introduce acceptor levels at 108 and 146 meV above the valence band, respectively. The associated principal bound-exciton (PBE) lines have also been identified at 1.5885 eV (Ag) and 1.5896 eV (Cu).[2,3]

In this paper, we report on a Zeeman study of these PBE lines. The linear Zeeman effects are consistent with the model of exciton recombination at neutral acceptors in T_d symmetry, indicating that Ag and Cu acceptors are indeed on Cd sites.[2] The bound-exciton ground state is a $J=\frac{1}{2}$ state for both Ag and Cu. The diamagnetic shift of the bound-exciton ground state has also been analyzed. The results show that the complex of exciton bound to neutral acceptor (A^0,X) is well described by the pseudodonor model discussed by Rühle and Bimberg.[4]

II. EXPERIMENTAL RESULTS

The high-purity p-type CdTe crystals were grown by B. Schaub [Laboratoire d'Electronique et de Technologie d'Informatique (LETI) Grenoble], using a modified Bridgman method. The uncompensated total acceptor concentrations were about 5×10^{14} cm^{-3}. The photoluminescence (PL) was excited with the 4880-Å line of the Ar$^+$ laser, and analyzed through a high-resolution monochromator [trés haute resolution (THR) Jobin-Yvon]. All measurements were made with the sample immersed in liquid helium pumped below the λ point ($T\sim1.8$ K). Magnetic fields up to 45 kG were produced by a superconducting split coil magnet. Zeeman spectra were recorded in both Voigt and Faraday configurations, and the samples could be rotated with the

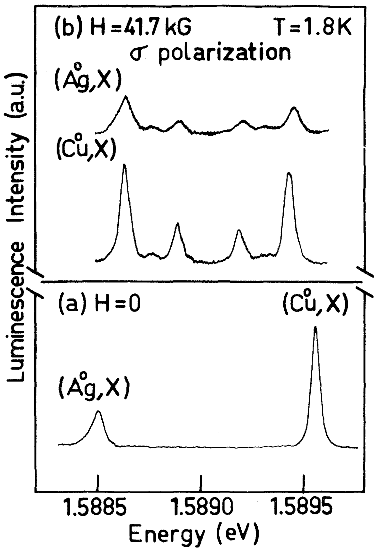

FIG. 1. (a) Neutral-acceptor—bound exciton lines (A^0,X) for Ag and Cu acceptors in high-purity p-type CdTe. (b) Comparison of Zeeman effects on the (Ag^0,X) and (Cu^0,X) lines for $H\,||\,\langle 110\rangle$ and σ polarization in the Voigt configuration.

magnetic field in a (110) plane.

Figure 1(a) shows the PL spectrum at zero magnetic field. The two sharp lines at 1.5896 and 1.5885 eV have been identified by Chamonal *et al.*[2] as due to the recombination of excitons bound to neutral Cu and Ag acceptors, respectively. These PBE lines are very similar to the strong A_x^0 line at 1.590 eV and the weaker A_{2x}^0 line at 1.589 eV observed by Malyavkin[5] in vapor-phase grown *p*-type crystals. Since recent back doping experiments[2] showed that Cu and Ag are the residual impurities in high-purity *p*-type CdTe it is tempting to associate A_x^0 to (Cu,*X*) and A_{2x}^0 to (Ag,*X*). In fact, A_x^0 and A_{2x}^0 lines have the same relative energy position and relative intensity as (Cu,*X*) and (Ag,*X*) lines, the only difference being a small systematic shift to higher energies of about 0.5 meV for the A_x^0 and A_{2x}^0 lines [compare Fig. 1(a) with Fig. 1 of Ref. 5]. In Ref. 5 however, the strong A_x^0 line was attributed to exciton recombination at a neutral (unidentified) acceptor, and the weaker A_{2x}^0 line to the recombination of a bound multiple exciton complex[6] (BMEC) consisting of two excitons bound to a neutral acceptor. The main argument was based on the observation of a superlinear dependence of the PL intensity I on the pumping power P for the A_{2x}^0 line: $I(A_{2x}^0) \sim P^{1.4}$ and $I(A_x^0) \sim P$. As shown in Fig. 2, only a linear dependence was observed for both (Ag,*X*) and (Cu,*X*) lines, even at the pumping power ~30 W cm^{-2} used in Ref. 5. This is consistent with the assignment of these lines as PBE lines.[1-3] Whether A_x^0 and A_{2x}^0 lines are (Cu,*X*) and (Ag,*X*) lines or not, the answer needs further investigations.

In magnetic fields, the Cu and Ag PBE lines linearly split into six well-resolved components. Their Zeeman spectra are the same within our experimental errors [see Fig. 1(b)], so, in the following, we will only present the data of the strong Cu PBE line, and it is understood that those of the weaker Ag PBE line are identical.

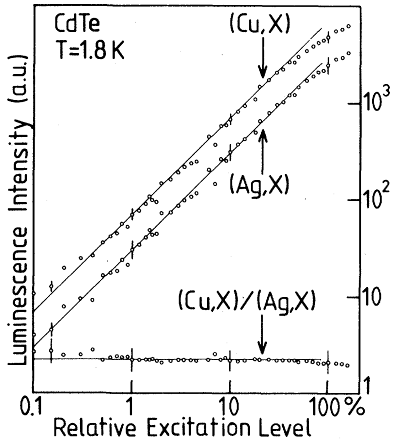

FIG. 2. Photoluminescence intensity of the (Ag^0,*X*) and (Cu^0,*X*) lines vs excitation power. The 100% excitation corresponds to ~300 W cm^{-2} (the maximum power used is ~200 mW, the laser beam being focused on a spot diameter of ~0.2–0.3 mm).

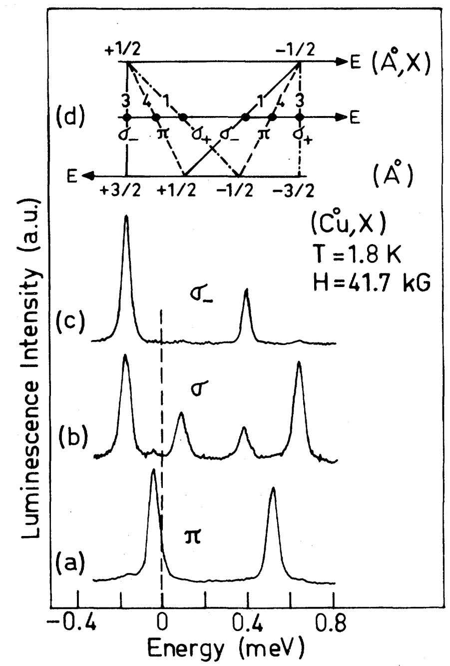

FIG. 3. (a) and (b) Zeeman effects on the (Cu^0,*X*) line for σ and π polarizations in the Voigt configuration, and for H in a (110) plane at about 24° from a ⟨001⟩ direction. (c) σ_- polarization in the Faraday configuration, for $H \| \langle 111 \rangle$. The vertical dotted line indicates the position of the (Cu^0,*X*) line at zero magnetic field. Optical selection rules for the polarizations and the relative oscillator strengths (in the Voigt configuration), of the transitions resulting from a $J=\frac{1}{2}$ (neutral acceptor bound exciton) $\rightarrow J=\frac{3}{2}$ (neutral acceptor) transition in magnetic field, and for $g_e<0, K>0, L\sim 0$ are shown in (*d*).

The Zeeman spectra are strongly polarized. In the Voigt configuration there are four magnetic subcomponents with the σ polarization and two magnetic subcomponents with the π polarization [Figs. 3(a) and 3(b)]. In the Faraday configuration, there are two pairs of magnetic subcomponents with the σ_- polarization [Fig. 3(c)] and σ_+ polarization. This polarization study will be particularly useful for the analysis of the linear Zeeman effect in Sec. III.

An overall shift of the spectrum toward higher energies is observed with increasing magnetic fields. It is due to diamagnetic effects as clearly shown in Fig. 4. In the figure, the shift of the gravity center of the spectrum has been plotted versus H^2 (H is the

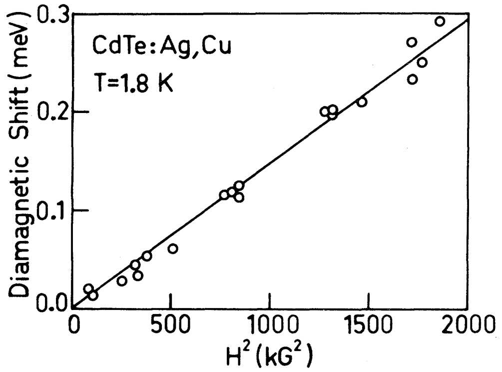

FIG. 4. Diamagnetic shift of the (Cu^0,X) line. The straight line is a fit to Larsen's theory (Ref. 15), assuming $\epsilon=9.8$ and an effective mass $m^*=0.093m_e$.

magnetic field) for various orientations of the magnetic field. The shift rate is isotropic and is about 1.47×10^{-4} meV kG^{-2}.

III. DISCUSSION

The linear Zeeman effects are well accounted for by a model of exciton recombination at neutral acceptor in T_d symmetry. The bound exciton complex is made up with two holes with $j=\frac{3}{2}$ and one electron with $j=\frac{1}{2}$.[6] In the j-j coupling scheme, this will result in bound exciton states described by a total angular momentum $J=\frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$. The state of lowest energy which is the initial state of the transition cannot be predicted. However, it can be unambiguously determined from polarization studies. The final state of the transition is the neutral acceptor state $J=\frac{3}{2}$. Therefore, one would expect two π magnetic subcomponents for an initial $J=\frac{1}{2}$ state, and four π subcomponents for an initial $J=\frac{3}{2}$ or $\frac{5}{2}$ state. The fact that only two π subcomponents are observed in the Zeeman spectrum [see Fig. 3(a)] indicates that the bound exciton ground state is the $J=\frac{1}{2}$ state.

The optical selection rules used in this work are shown in Fig. 3(d). They are in good agreement with our observations. It should be noted that the signs of the electron and hole g factors have been obtained also from polarization studies. The Zeeman effect was nearly isotropic, so, the isotropic hole g factor K of the hole is much greater than the anisotropic g factor L. In this case, it can be easily shown that the signs of the circular polarizations of the outer Zeeman components depend only on the sign of K. In the present case, the lowest energy Zeeman component is σ_- polarized [see Fig. 3(c)], which is only possible with $K>0$. Then the analysis of the relative intensities of the magnetic subcomponents shows that the electron g factor g_e is negative. This feature (i.e., $K>0$, $g_e<0$) is in good agreement with the signs of g factors in CdTe reported recently by Simmonds *et al.*[7]

A quantitative analysis of the linear Zeeman effects has been made by using the effective spin Hamiltonian

$$\mathcal{H}_{1/2}=g_e\mu_B\vec{J}\cdot\vec{H}\ , \tag{1}$$

for the initial bound-exciton state $J=\frac{1}{2}$ and

$$\mathcal{H}_{3/2}=\mu_B[K\vec{J}\cdot\vec{H}+L(J_x^3H_x+J_y^3H_y+J_z^3H_z)]\ , \tag{2}$$

for the final acceptor state $J=\frac{3}{2}$ in cubic symmetry.[8,9] μ_B is the Bohr magneton, g_e is the electron g factor, K and L are the hole parameters describing the isotropic and anisotropic Zeeman effects, respectively. The solutions of Eqs. (1) and (2) are well known.[8,9] Best fit to the data for various orientations of the magnetic field has been obtained with the following set of parameter values:

$$\begin{aligned} g_e &= -1.77\pm0.02\ ,\\ K &= +0.61\pm0.04\ ,\\ L &= -0.04\pm0.02\ . \end{aligned} \tag{3}$$

The electron g factor has the same (negative) sign than for the conduction electron, $g_e=-1.59\pm0.02$.[10] However, the absolute value is somewhat different. It is interesting to note that EPR experiments[11] also yield a different value, $|g_e|=1.6803\pm0.0005$, for the shallow (unidentified) donors in undoped and n-type CdTe. This seems to indicate that the actual g value depends on the nature of the electron state: free electron state for the conduction electron or bound electron state for the donor and the (A^0,X) complex. Such effect has been observed by Weber *et al.*[12] for exciton bound to neutral donor and isoelectronic trap in Si.

To our knowledge, there is no previous report on the values of the hole parameters K and L, although Zeeman effects have been studied for some (A^0,X) lines at ~1.59 eV.[5,13] Only recently, Simmonds *et al.*[7] have reported the value $K=0.5$ for a doublet at 1.589 eV related to an (unidentified) acceptor level at 69 meV above the valence band, in n-type CdTe. The hole effective g factor has been measured by Malyavkin[5] for the A_x^0 line at 1.590 eV. For the magnetic field approximately directed along $\langle 221\rangle$, he obtained $g_{1/2}=0.52\pm0.05$ and $g_{3/2}=0.45\pm0.05$, by assuming that $g_e=-1.6$. This would give $K=0.32$ and $L=0.07$. With our K and L values (3), we obtain $g_{1/2}=0.49$ and $g_{3/2}=0.53$ for the magnetic field directed along $\langle 221\rangle$ axis. This is in reasonable agreement with the result of Malyavkin, considering that the actual electron g value is -1.77.

In addition to the linear Zeeman effect, we have observed diamagnetic effects.[4,14–17] For the (A^0,X) complex, one would expect two types of diamagnetic effects[4,16]: (i) a "diamagnetic splitting" effect in the acceptor ground state $J=\frac{3}{2}$ which splits apart the gravity center of the $m_J=\pm\frac{1}{2}$ Zeeman components from the $m_J=\pm\frac{3}{2}$ components; (ii) a "diamagnetic shift" effect in the initial bound exciton state and in the final acceptor state. Both effects are proportional to $(a_0H)^2$, where a_0 is the radius of the wave function of the state of interest (i.e., acceptor state or bound exciton state), and H is the magnitude of the applied magnetic field. The first effect (i.e., diamagnetic splitting) is negligibly small for the (Cu,X) and (Ag,X) complexes in CdTe since the Zeeman spectra are symmetrical within our experimental errors (see Fig. 3). This indicates that the bound hole is fairly localized, and therefore, it is reasonable to assume that the diamagnetic shift effect, shown in Fig. 4, mainly comes from the more extended bound exciton state.

The observed diamagnetic shift has been fitted by using a simple hydrogenic model. From first-order perturbation calculations, the diamagnetic shift of the 1s ground state is given by

$$\Delta E=\tfrac{1}{2}R^*\gamma^2 \tag{4}$$

with $\gamma=\hbar\omega_c/2R^*$ where $\hbar\omega_c$ is the cyclotron resonance energy, and $R^*=m^*e^4/2\hbar^2\epsilon^2$ is the effective rydberg, m^* is the effective mass, and ϵ is the static dielectric constant. Note that Eq. (4) is only valid in the low-field regime.

In fact, deviations from more accurate calculations[15,18,19] are found to be less than 5% for $\gamma \leq 0.2$. This limiting value of γ would correspond to $H \lesssim 45$ kG for the effective mass donor in CdTe. We have used Eq. (4) to fit the data in Fig. 4, with the effective mass m^* as an adjustable parameter. Due to the uncertainty in the published values of the static dielectric constant ϵ (Refs. 1 and 20–22) we have taken $\epsilon=9.8\pm0.2$. The best result has been obtained for $m^*=(0.093\pm0.005)m_e$, and the values of γ vary from 0 to 0.2 in Fig. 4, so the error due to the use of the first-order perturbation theory [Eq. (4)] is less than 5%. The fitted effective mass value m^* is very close to the electron effective mass value $m_e^*=(0.0963\pm0.0008)m_e$.[23,24]

This strongly supports the pseudodonor model for the (A^0,X) complex suggested by Rühle and Bimberg.[4] In the model, the two holes of the complex are strongly bound by the short-range potential of the acceptor, thus producing a long-range Coulomb potential which binds the electron in donorlike states. Similar experimental evidence of this model has been reported for deep acceptor bound exciton complexes in GaAs (Refs. 14, 16, and 25) and GaSb.[4]

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