Pair spectra in copper-doped zinc telluride

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The first observation of discrete donor-acceptor pair lines in copper-doped ZnTe is reported. The spectral analysis shows that the two impurities are located on the same sublattice (type-I spectrum) and gives $E_A^{Cu}+E_D=168\pm1$ meV and $\epsilon\simeq9.15$. The binding energy of the acceptor is obtained from the $n=2$ orbital states with even and odd parity evidenced from photoexcitation spectra and resonant luminescence of distant pairs. It is deduced that $E_A^{Cu}\simeq149$ meV, $E_D\simeq19$ meV, confirming that the dominant acceptors in ZnTe are Cu atoms on Zn sites and giving direct information on the site occupied by the unidentified shallow donor (s) in this material.

The near-gap low-temperature photoluminescence spectra (PL) of refined p-type ZnTe ($N_A-N_D\leq5\times10^{15}$ cm^{-3}) are dominated by a series of sharp bound exciton lines involving neutral acceptors and photoneutralized donors.[1] These lines are accompanied by two-hole (two-electron) transitions which are crucial for the analysis of impurities present in the samples.[1,2] A few tens of meV below, particularly on doped samples ($N_A-N_D\geq10^{16}$ cm^{-3}), donor-acceptor pair (DAP) transitions involving principally hydrogenlike acceptors (Li, P) have been observed and recently studied by photoexcitation spectroscopy.[3,4] In this paper we are concerned with the DAP band involving the deeper acceptor a at E_V+149 meV observed on ZnTe crystals doped by diffusion with copper.

The acceptor a has been related in the past to the second level of the zinc vacancy, but it has been established since the work of Dean *et al.*[1] that it is related to an impurity which has been identified recently from optical and electrical measurements as copper probably on a zinc site with a tetrahedral symmetry.[5] We confirm here this assignment and give some information on the shallow donor(s) in ZnTe.

Since copper has a very high diffusion coefficient, it is necessary to use a double-diffusion technique to introduce a high concentration of copper on zinc sites and to avoid the formation of complex centers.[5] On the other hand, by varying the first-diffusion temperature, the uncompensated s_{Cu} concentration (where $[s_{Cu}]$ represents the substitution of copper on a zinc site) can be controlled between 5×10^{16} and 5×10^{17} cm^{-3}. In Fig. 1 we show the PL spectra excited with the 4880-Å line of an Ar^+ laser on several ZnTe samples: as grown [Fig. 1 (a)] and doped 5×10^{16} [Fig. 1 (b)] and 3×10^{17} cm^{-3} [Fig. 1 (c)]. On the as-grown sample we observe the principal bound-exciton (PBE) line A_1^q at 2.374(6) eV (5219.8 Å) with its associated two-hole transition series near 2.25 eV (5500 Å) corresponding to parity allowed transitions between the ground state and the $nS_{3/2}$ states of the acceptor a. As copper is introduced we observe a rapid increase of the band (D^0, A^0_{Cu}) due to distant DAP recombination with a progressive decrease of two-hole transitions. When $N_A-N_D\simeq3\times10^{17}$ cm^{-3} the

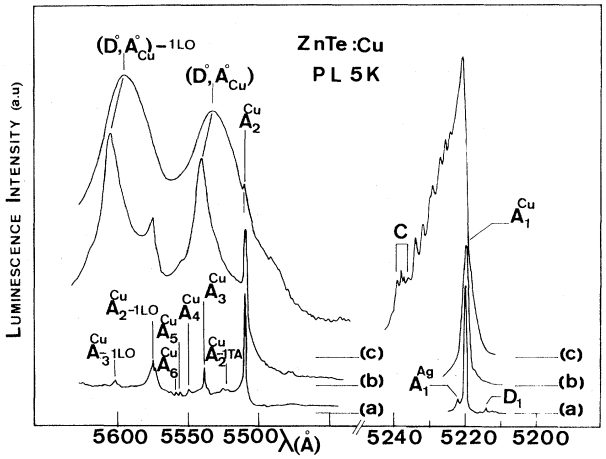

FIG. 1. Photoluminescence spectra of ZnTe recorded at 5 K with low excitation intensity: (a) ZnTe as grown 8×10^{14} cm^{-3}; (b) ZnTe:Cu 5×10^{16} cm^{-3}; (c) ZnTe:Cu 3×10^{17}cm^{-3}. The bound-exciton lines with their two-hole transitions are indexed as in Ref. 1 (a: copper, g: silver). The donor-acceptor pair (D^0, A^0_{Cu}) is strongly enhanced by copper diffusion. The bound-exciton line is broadened due to exciton transfer between acceptors pairs. The undulations result from statistical variation of acceptor pair distribution with distance.

PBE line is strongly broadened with undulations appearing on the low-energy tail. This process results at high doping from the recombination of excitons bound on interacting acceptor pairs[6] similar to the undulation spectra reported in GaP:N:Zn.[7] The (D^0,A^0_{Cu}) band corresponds to the "yellow" transition presently observed by other authors in poorly refined ZnTe (Ref. 8) with its characteristic phonon coupling well described in Hopfield's theory ($\bar{N} \simeq 1,5$).[9] The broadening and the displacement of the maximum to higher energy with increasing doping are due, respectively, to the relative increase of close-pair contributions and to the decrease of the mean distance ($R_{max} \propto N_A^{-1/3}$) between donors and acceptors.

Figure 2 shows the high-energy side of (D^0,A^0_{Cu}) at high excitation levels revealing numerous sharp lines. This spectrum, comparable to those obtained for ZnSe,[10] corresponds to the recombination of electrons and holes trapped on close pairs with the discrete internuclear distances determined by the zinc-blende–lattice structure while the (D^0,A^0_{Cu}) band corresponds to recombination at unresolved widely separated pairs. The assignment of each line is made using the intensity pattern[10] of a type-I configuration for which both the donor and the acceptor are on the same sublattice. An impurity system of type II (the two impurities on different sublattices) cannot fit the results since the gaps observed for $m = 14, 30, 46, \ldots$ should not occur in this case.[11] Satisfactory agreement between the calculated intensity distribution and experiment is obtained, except

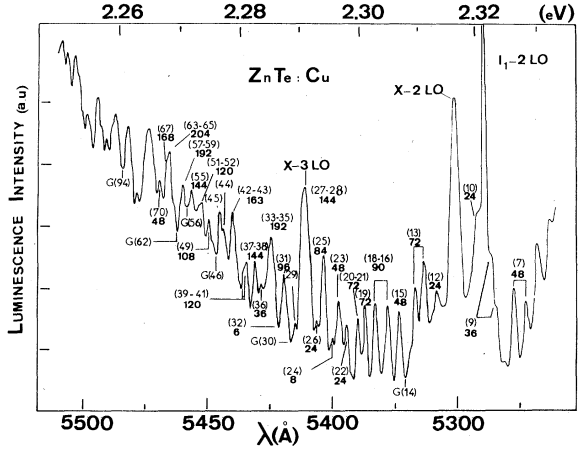

FIG. 2. Discrete donor-acceptor pairs observed on the high-energy tail of (D^0,A^0_{Cu}) band and identified according to a type-I spectrum. The shell number m is given in parentheses, the other number indicates the site degeneracy. Empty shells for which gaps are anticipated are denoted by $G(m)$.

for shells 16 to 18 where splittings arising from nonequivalent sites within a given shell probably mix the different lines. In Fig. 3 we have plotted the energy of pair lines as a function of r. For $r \geq 30$ Å the energy radiated by pair recombination is well-described by the Coulomb model (curve C). The best fit is obtained with a dielectric constant $\epsilon \simeq 9.15$ in good agreement with the value deduced from donor states[3] and gives $E_A + E_D \simeq 168 \pm 1$ meV by extrapolating to $r \to \infty$.

For $r \leq 30$ Å we have the typical deviation from Coulombic law which is clearly not adequately represented on a large scale by the van der Waals term (curve C + vdW). Indeed as the bound-electron wave function has a large extension in real space ($a_D \simeq 40$ Å) (Ref. 12) we have already a large overlap for close pairs, and in this case the electron-hole correlations are poorly described by a dipole-dipole interaction.

The binding energies of the two impurities are not directly obtained from DAP analysis. The acceptor depth can be estimated at 148 ± 2 meV from free-to-bound transitions observed at 20 K.[5] In order to get more precise values for the ionization energies we have performed excitation spectroscopy experiments on the (D^0,A^0_{Cu}) band to observe the excited states of the acceptor.[3,13] The excitation source is a coumarin-6 dye pumped with a 4-W Ar^+ laser. The sample is immersed in liquid helium ($T \simeq 1.8$ K).

Figure 4 (a) shows the photoexcitation spectra of distant pairs for several detection energies, i.e., for different pair distances. Three peaks are observed which shift with a constant rate with excitation energy. They correspond to the enhancement of the luminescence intensity radiated by the selected pair when the laser excitation is resonant with the transition between the acceptor excited state and the donor ground state[14] (see the insert of Fig. 4). Thus a given peak appears when the relation

$$h\nu_{ex} = E_g - (E_A^* + E_D) + e^2/\epsilon r \qquad (1)$$

is satisfied. (E_A^* refers to the acceptor excited states.)

From comparison with the theoretical calculations of acceptor states in ZnTe,[15] infrared absorption,[5] and PL spectra,[1] the peaks K, L, M are related, respectively, to the $2P_{3/2}, 2S_{3/2}, 2P_{5/2}(\Gamma_8)$ states (see Table I for excitation and binding energies of these levels). As the transitions are produced between two different sites in space the transition probability is only determined by the electron-hole wave-function overlap, whatever their parity. Thus the P states can be observed but the intensity of the excitation peak is proportional to the overlap term which explains that, as

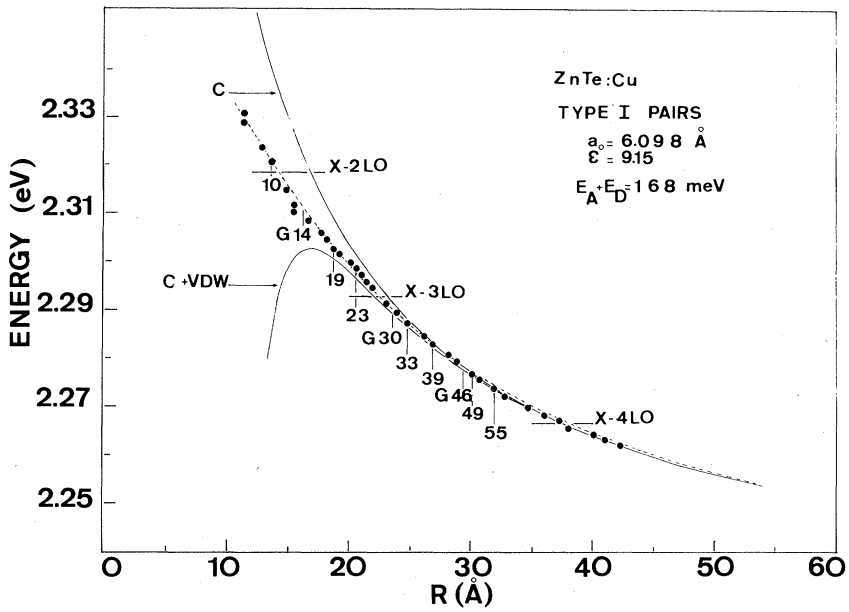

FIG. 3. Photon energy of the discrete pair lines versus lattice separation. The position of the bound exciton which masks pair lines are indicated. The solid curves are the plots of the Coulomb term without (C) and with (C+vdW) the van der Waals interaction. Because of polarization interaction, systematic deviations occur for $r \leq 20$ Å.

shown in Fig. 4 (a), transitions between even states $2S(A) \rightarrow 1S(D)$ are more efficient than $2P(A) \rightarrow 1S(D)$ transitions.

The complementary experiment which consists of exciting selectively DAP luminescence with below-band-gap photons in the region corresponding to excitation energy of pairs is shown in Fig. 4 (b).[16] Superimposed on the broad band, lumines-

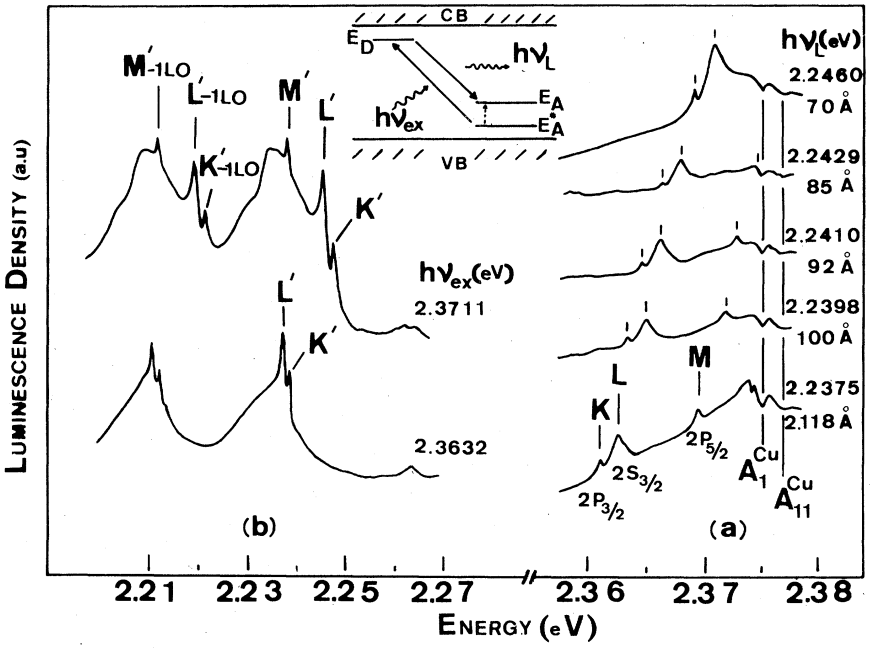

FIG. 4. (a) Photoexcitation spectra of the donor-acceptor pair (D^0,A^0_{Cu}) recombination for different pairs separation. The lines appearing in absorption are related to impurity bound-exciton states. (b) Resonant luminescence of donor-acceptor pairs for two excitation energies. These two experiments reveal the odd and even acceptor states (see Table I) which give accurate binding energy. The inset describes the excitation process (PE) of DAP recombination (PL) through the acceptor excited state.

TABLE I. Excitation energy ($E_{1S}-E_{nS,nP}$) of excited states of s_{Cu} acceptor in ZnTe obtained from two-hole transitions (THT), free-to-bound ($F \rightarrow B$) recombination, infrared absorption (ir), photoexcitation (PE) and resonant luminescence (RL) of DAP. The last line indicates the theoretical binding energies ($E_V - E_{nS,nP}$) of the hydrogenlike acceptor in ZnTe.

Experiment \ E (meV)	$2S_{3/2}$	$2P_{3/2}$	$2P_{5/2}(\Gamma_8)$	$2P_{5/2}(\Gamma_7)$	E_A^{Cu}	E_D
THT (Ref. 1)	125.1				149	
$F \rightarrow B$ DAP					149	19
ir (Ref. 5)			133	137	149.5	
PE	125.3	124.0	132.8		148.5	
RL	125.4	123.8	132.5		148.5	
Effective mass theory (Ref. 15)	17.5	23.7	16.2	13.2	62	18.5

cence lines (K', L', M') appear. They shift to lower energies when the excitation energy is decreased and K' disappears for $h\nu_{ex} < 2.365$ eV. The spectral shift between $h\nu_{ex}$ and lines K', L', M' is the same as for excitation peaks K, L, M (Table I). The possibility of electronic Raman scattering on holes bound on s_{Cu} acceptors has been excluded because the transitions $S \rightarrow P$ are forbidden and because the number of Raman lines should be independent of excitation energy. These lines correspond to DAP with different separations excited resonantly through the acceptor excited state and decaying radiatively after the rapid deexcitation of the hole to the acceptor ground state (Fig. 4). The relation (1) is also valid in this case, but for each acceptor excited state, r is the variable on the opposite side of photoexcitation spectroscopy where the variable was $h\nu_{ex}$. Thus, the spectral shift between $h\nu_{ex}$ and lines K', L', M' is the same as for K, L, M excitation lines and verifies the equation

$$h\nu_{ex} - h\nu_{lum} = E_A - E_A^*. \quad (2)$$

From relation (1) we see that when $h\nu_{ex}$ decreases r must be increased to conserve the equality. In particular for $h\nu_{ex} < 2.365$ eV the pairs excited through the $2P_{5/2}(\Gamma_8)$ level (line M') have a separation greater than 220 Å. Thus the radiative recombination probability $W(r)$ which is a function of overlap [$W(r) \propto e^{-\alpha r}$] is very low and this line cannot be observed, probably due to energy transfer towards closer pairs or other decay channels. This can explain why higher excited states with $n > 3$ are not observed in our experiments.

The results of the two techniques are compared in Table I. It appears that the excitation energy deduced from lines L and L' which involves the $2S_{3/2}$ level coincides exactly with the value obtained from two-hole transitions for the acceptor a on the as-grown crystal. This is a clear confirmation that the acceptor introduced by copper diffusion is the acceptor a. By adding the theoretical binding energy of P states[15] to the excitation energy of lines K (K') and L (L') we obtain $E_A^{Cu} \simeq 148.5$ meV. Then from the value of $E_A + E_D$ deduced from discrete DAP we have $E_D \simeq 19$ meV.

In conclusion, this paper describes the first observation of discrete donor-acceptor pairs in copper-doped ZnTe. The analysis of the spectrum is considerably extended by photoexcitation and resonant-luminescence experiments which allow the accurate determination of acceptor ground state as well as excited state. This is particularly useful for high doping when bound-exciton spectroscopy becomes less efficient. We have thus shown that copper on a zinc site is the persistent acceptor a at $E_V + 149$ meV confirming other optical and electrical measurements. On the other hand, shallow donor(s) yet unidentified at $E_C - 19$ meV have been shown to be also on the zinc site. These donors are unidentified until now, but the preceding remark restricts the field of investigation to elements of column III (Al, Ga, In).

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