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Identification of the chlorine *A* center in CdTe

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The chlorine *A* center has been identified in CdTe using photoluminescence and optically detected magnetic-resonance techniques. The *A* center is found to be an acceptor with a binding energy $E_a = 120 \pm 3$ meV and consists of a Cd vacancy and a Cl donor on a nearest Te site. The defect has trigonal symmetry with $g_{\parallel} = 2.2$ and $g_{\perp} = 0.4$, assuming an effective spin $S = \frac{1}{2}$. The interactions with the three Te neighbors are also resolved and the measured isotropic ligand hyperfine interaction amounts to $(2.7 \pm 0.4) \times 10^{-2}$ cm^{-1}.

The use of wide-band-gap II-VI semiconductors in electronic and optoelectronic applications is often limited by self-compensation.[1,2] This renders the materials *n* type (ZnS,ZnSe) or *p* type (ZnTe) regardless of doping. That these materials can be doped *n* type and not *p* type, or vice versa, can be explained if the self-compensating defects are donors in some materials and acceptors in the others.[3-7] Despite intensive research, the reasons for this classical problem are still not settled.

In a study of the ternary system $Cd_{1-x}Zn_xTe$ it was shown that an abrupt change from *n*- to *p*-type conductivity occurs at $x \geq 0.7$, independent of doping.[3] This behavior can be explained by extrinsic impurities or intrinsic defects, as well as by intrinsic defects paired off with doping impurities (self-compensation). The *p*-type conductivity observed for $x \geq 0.7$ could, in principle, be the result of extrinsic acceptors such as Cu or Ag. Cu is an especially dominant contaminant, but since its solubility does not change dramatically from ZnTe to CdTe, it is unlikely that Cu accounts for the observed conductivity change.[8] Similar arguments hold for the other known impurities. Examples of intrinsic acceptor defects are metal vacancies (isolated or complexed) or, as recently discussed, cation antisite defects (Zn_{Te} and Cd_{Te}), which have also been suggested to be responsible for the *p*-type conductivity of these materials.[9]

The intrinsic defects, argued to be most important in the *p*-type self-compensation mechanism of II-VI compounds, are the cation vacancies and the cation-impurity pairs (*A* centers).[3] The atomic structure of the *A* centers has been extensively studied in ZnS, ZnSe, and ZnTe.[10,11] They consist of a metal vacancy paired off with a donor located either on the group-VI-element sublattice (e.g., Cl_{Te}) or on the group-II-element sublattice (e.g., Ga_{Zn}). The *A* centers behave as acceptors with energy levels 0.16 eV (ZnTe), 0.6 eV (ZnSe), and 1 eV (ZnS) above the valence band.

Compared with these II-VI compounds, the doping behavior of CdTe is different, considering that it can be made both *n* and *p* type. Since the *A* centers were never identified in CdTe despite extensive research efforts, and due to the possibility of *n*-doping CdTe, it can be argued that *A* centers are not formed in CdTe.[12] This view was supported by thermodynamic calculations that showed a smaller probability for the formation of vacancies in the narrow-band-gap material CdTe ($E_g = 1.6$ eV) than in other II-VI compounds.[13] The situation in CdTe can, in turn, be used as an argument that *A* centers, in fact, are responsible for the self-compensation in *p*-type ZnTe. In a recent theoretical work on intrinsic defects in ZnSe, the authors showed that centers including native defects (such as the *A* center) are not responsible for the self-compensation mechanism.[6]

The present identification of the *A* centers in CdTe, on which we report, therefore clarifies several aspects in the role of these defects in the self-compensation mechanism in CdTe, ZnTe, and $Cd_{1-x}Zn_xTe$. In particular, we will present evidence that the *A* centers represent only a minor fraction of the defects responsible for the compensation mechanism in ZnTe.

Most investigations of photoluminescence (PL) in CdTe report on the presence of a 1.4 eV PL band, which, including the more- or less-pronounced phonon replicas, ranges from 1.3 to 1.5 eV.[14] This band, which occurs independent of growth technique, has not been identified, and its origin is therefore widely discussed. Our investigations clearly show that the emission in this spectral range consists of (at least) three independent emission bands. The first band, located at 1.45 eV and exhibiting 21-meV LO-phonon replicas [Fig. 1(a)], originates in the donor-acceptor recombination between a shallow Cl donor (the dopant in our crystals, binding energy 14 meV) and, possibly, a Cu acceptor.[8] The second band, which is of unknown origin, has a strong line at 1.475 eV (Ref. 15) and an additional, weaker line at higher energy [Fig. 1(b)]. The third band has a zero-phonon line at

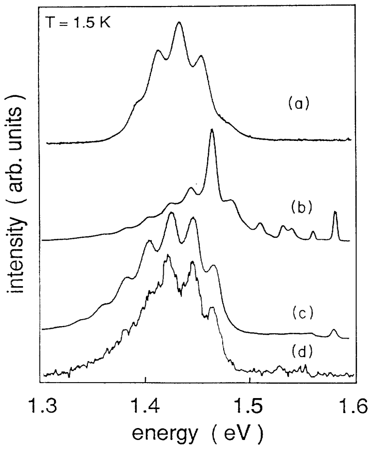

FIG. 1. Photoluminescence signals obtained in different CdTe:Cl samples. At least three different defects are observed: (a) donor-acceptor recombination between the (assumed) Cu acceptor and the shallow Cl donor; (b) unidentified spectrum; (c) the emission from the donor-acceptor recombination between the Cl donor and the A-center acceptor; (d) excitation spectrum of the A-center ODMR signal.

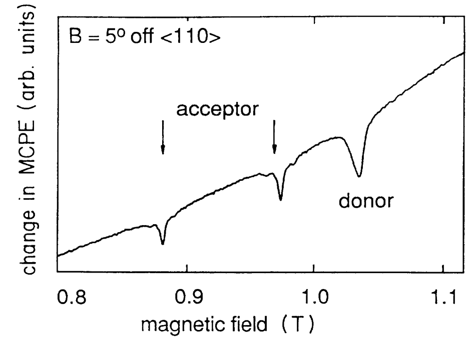

FIG. 2. The MCPE spectrum of CdTe:Cl showing the Cl donor resonance and the new resonances identified as originating in the A center. The signals appear as an $\approx 5\%$ decrease of the MCPE signal, $T = 1.5$ K and the microwave energy is 24 GHz.

1.478 eV followed by six LO-phonon replicas, which show an intensity distribution according to the Poisson distribution $I(n) = e^{-S}(S^n/n!)$ and a Huang-Rhy factor of $S = 2.2 \pm 0.1$ [see Fig. 1(c)]. This PL band arises from a D-A recombination involving the A centers, as will be shown below. It should be noted that these three bands, which have almost the same energies, are totaly mixed in many crystals, and have, therefore, caused considerable confusion.

For the structure identification, we combine PL and electron paramagnetic resonance by performing optically detected magnetic-resonance (ODMR) experiments.[16] Instead of detecting synchronous changes of the total PL intensity as a function of chopped microwaves, we use the fact that the emission is circularly polarized. By combining a stress modulator and a linear polarizer, differences between left and right circularly polarized emission light are monitored. The temperature and magnetic-field dependence of this signal [magnetic circularly polarized emission (MCPE)] proved that the population difference of the emitting states can be changed by resonant 24-GHz microwaves, allowing the detection of the ODMR signals of the recombination defects.[17] At resonance, the MCPE intensity decreases up to 5%, and both donor and acceptor resonances could be observed (Fig. 2). Figure 1(d) presents the excitation spectrum of the ODMR signal, showing that the resonances originate in the luminescence band shown in Fig. 1(c).

The shallow Cl donor resonance at 1.036 T is isotropic, and corresponds to $g = 1.69$ (spin $S = \frac{1}{2}$), in agreement with the g value obtained for donor centers in other experiments.[18] The acceptor resonances are anisotropic. Their field positions as a function of the sample orientation when the crystal is rotated in a $\{110\}$ plane are shown in Fig. 3. The rotation pattern is consistent with a trigonal defect, and the effective g value g_{eff} (i.e., assuming $S = \frac{1}{2}$) can be described by the spin Hamiltonian[19]

$$H = \mu_B \mathbf{B} \cdot \overleftrightarrow{g}_{\mathrm{eff}} \cdot \mathbf{S} \;, \tag{1}$$

$$g_{\mathrm{eff}} = (g_{\parallel,\mathrm{eff}}^2 \cos^2\theta + g_{\perp,\mathrm{eff}}^2 \sin^2\theta)^{1/2} \;. \tag{2}$$

Here θ denotes the angle between the magnetic field $\mathbf{B}$ and a trigonal $\langle 111 \rangle$ symmetry axis. A best fit to the measured data is obtained using $g_{\parallel,\mathrm{eff}} = 2.2$ and $g_{\perp,\mathrm{eff}} = 0.4$, as shown by the solid lines in Fig. 3.

Each of the acceptor lines in Fig. 2 is accompanied by four satellites of lower intensity (Fig. 4). The intensities of the two stronger and the two weaker satellites are about 12% and 1% of the central line, respectively. The splittings are, within the experimental accuracy, constant when the crystal is rotated in the magnetic field (a de-

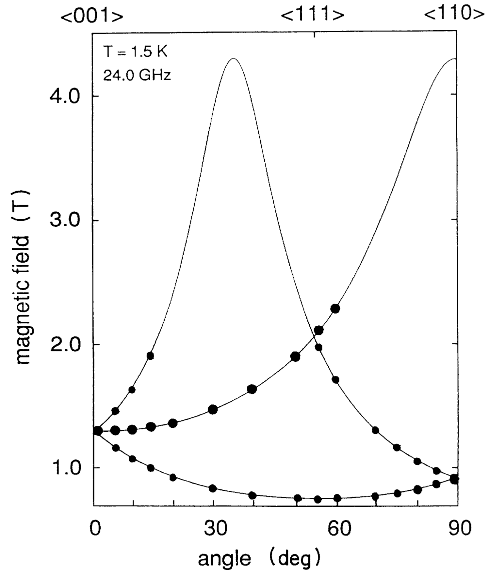

FIG. 3. Angular dependence of the positions of the fine structure lines of the A center in CdTe:Cl obtained at 24.0 GHz. The magnetic field is rotated in a $\{110\}$ plane. The experimental data are plotted as closed circles. The calculated angular dependence (trigonal symmetry) is plotted as solid lines.

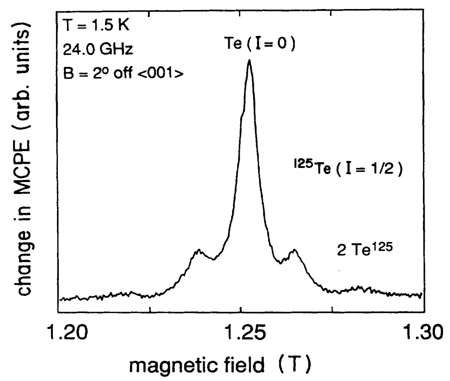

FIG. 4. The ligand interactions from the three Te nearest neighbors are clearly resolved. The different resonance peaks correspond to 0, 1, and 2 of the 3 Te neighbors having an isotope with nuclear spin $I=\frac{1}{2}$.

tailed discussion of this isotropic behavior of the ligand interaction can be found in Ref. 11). Considering the intensities and positions of the peaks observed, the spectrum cannot be explained in terms of hyperfine interactions with a central nucleus of the defect. However, the set of five lines can be explained well by the hyperfine interaction with three equivalent nearest-neighbor Te ligands. About 92% of the Te isotopes have nuclear spin $I=0$, and 8% have $I=\frac{1}{2}$. Among the isotopes with $I=\frac{1}{2}$, ^{125}Te (7%) has a nuclear moment $\mu=0.88\mu_N$ and ^{123}Te (0.9%) $\mu=0.73\mu_N$. The difference in their magnetic moments, however, is too small to be resolved in our measurements, and will therefore not be considered further. By definition, an A center has three nearest Te neighbors. The sites of these Te atoms can be occupied either by an isotope with $I=0$ or $\frac{1}{2}$. Taking into account the statistical weights, the defects surrounded by one Te atom with $I=\frac{1}{2}$ should account for 13%, the defects surrounded by two Te atoms with $I=\frac{1}{2}$ should account for 0.5%, and the defects surrounded by three Te atoms with $I=\frac{1}{2}$ should account for 0.001% of the intensity. The latter are difficult to observe, but the experimental data are otherwise in excellent agreement with such a model. The measured value of the ligand interaction is $a_{\mathrm{Te}}=2.7\pm0.4\times10^{-2}\ \mathrm{cm}^{-1}$.

Based on the observation of three (out of four) Te neighbors, the trigonal symmetry, and the acceptor character of the defect, we identify the defect as a Cd vacancy paired with a Cl donor, i.e., as an A center. This model is consistent with the single-acceptor picture of the A center $[(V_{\mathrm{Cd}}{}^{2-}\mathrm{Cl}_{\mathrm{Te}}{}^{+})^{-}$ and $(V_{\mathrm{Cd}}{}^{-}\mathrm{Cl}_{\mathrm{Te}}{}^{+})^{0}$, of which the neutral charge state is observed in our recombination experiment]. the lack of a hyperfine interaction with the Cl donor is consistent with results observed for A centers in other II-VI semiconductors.[20]

The PL energy is given by

$$h\nu=E_g-E_d-E_a+e^2/4\pi\epsilon\epsilon_0 R\ . \tag{3}$$

Since E_d, the electron binding energy of the shallow Cl donors in CdTe, is 14 meV, and the Coulomb term accounts for 5–7 meV (considering the doping concentrations used in our samples), a hole binding energy of $E_a=120\pm3$ meV is calculated for the A center acceptor. Comparing this value with the ones for the shallow effective-mass acceptors in CdTe,[21] e.g., Na with $E_a=54$ meV, we realize that the A center is not a true deep-level defect. This is supported by the PL line shape, which shows a weak coupling to the lattice (compare the deep A centers in ZnSe and ZnS, which exhibit strong phonon coupling as evidenced by the ≈0.3-eV broad Gaussian emission bands). A further argument for the shallow-level character of the A center stems from an analysis of the observed g values. A shallow acceptor can be described as being formed by a $J=\frac{3}{2}$ hole from the top of the valence band. According to the Hamilton operator

$$H=\mu_B\mathbf{B}\cdot\overleftrightarrow{g}\mathbf{J}+\mathbf{D}J_z^2\ , \tag{4}$$

a trigonal perturbation splits the $J=\frac{3}{2}$ state into $J=\pm\frac{1}{2}$ and $\pm\frac{3}{2}$. If the $J=\pm\frac{3}{2}$ states are lowest in energy, and the trigonal splitting is strong, the expected g values of the $S=\frac{1}{2}$ Hamiltonian of Eq. (1) are $g_{\perp,\mathrm{eff}}=0$ and $g_{\parallel,\mathrm{eff}}=3\cdot g_{\parallel}$. Using our measured value of $g_{\parallel,\mathrm{eff}}=2.2$, we can deduce $g_{\parallel}=0.73$. This is in the range of the g values for shallow effective-mass-like acceptors in CdTe.[22] Again there is a distinct difference to the A centers in ZnSe and ZnS, where the g values ($g_{\perp}$ and $g_{\parallel}$) are close to 2. However, the g values of the A center in CdTe are close to the g values of the A centers in ZnTe.[11]

Based on our identification of the A centers in CdTe, we address the question as to whether they are responsible for the p-type conductivity in ZnTe, and the crossover from n- to p-type conductivity in $\mathrm{Cd}_{1-x}\mathrm{Zn}_x\mathrm{Te}$ at $x\geq0.7$. We have studied the PL band of the Cl A center through the ternary system. The binding energy increases slightly from $E_a=120\pm3$ meV in CdTe to $E_a=160\pm10$ meV in ZnTe. The latter value is very close to that already reported for the Al A center in ZnTe.[11] We also note that the concentration of the A centers does not change considerably from CdTe to ZnTe, and therefore cannot account for the changes in resistivity from a few Ω cm n-type (CdTe) to a few Ω cm p-type (ZnTe). We thus conclude that the A centers are indeed present in CdTe, but can hardly account for the p-type conversion leading to p-type ZnTe.

These results are in line with the conclusions of Mandel[3,23] that the A centers represent only a small fraction of the defects responsible for the self-compensation. From his experiments, he requires doubly ionized defects, such as isolated cation vacancies or the cation antisite defects, to explain the self-compensation. However, any definite identification of the electronic and atomic structure of these defects has not yet been established.

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