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Electron-paramagnetic-resonance study of a deep Cl-associated center in ZnTe:Cl

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We describe EPR studies of ZnTe doped with chlorine. The characteristic EPR spectrum is observed under optical illumination at low temperature. A defect, which has a trigonal symmetry, is identified as Cl^- occupying a tellurium site associated with a positively charged ion which is tentatively assumed to be a Sn^{2+} or a Pb^{2+} ion. Under illumination, the associated defect should become paramagnetic by trapping an electron. Super-hyperfine-splitting lines are also observed and account for the Te nuclei. The Hamiltonian parameters of the center have been obtained. Luminescence, thermoluminescence, and optically detected magnetic-resonance experiments on the same crystals lead to the conclusion that part of the chlorine impurity behaves as a hydrogenic shallow donor but some of the chlorine atoms also form the Cl^{2-} associate center which is a deep center.

I. INTRODUCTION

ZnTe is a II-VI compound semiconductor with zinc-blende structure and a direct energy gap close to 2.39 eV at low temperature. Unlike all other widegap II-VI semiconductors, ZnTe is *p* type, whether or not it is deliberately doped with potential donors or acceptors. Properties of the most important acceptors in ZnTe are well known,[1] so ZnTe doped with impurities expected to introduce donors should now be investigated.

It is known that chlorine, substituting for the chalcogen, introduces shallow donor in CdS and ZnSe.[2] While associated with a Zn vacancy it gives the well-known *A* center.[3] Moreover, it has been reported that in CdTe chlorine does not act as a hydrogenic impurity, but forms a deep center.[4]

We report here on EPR studies of ZnTe doped with chlorine. Under optical illumination at low temperature, a characteristic EPR spectrum is observed. Section II gives the experimental procedure, while experimental results and a qualitative discussion are reported in Sec. III. In Sec. IV, the Hamiltonian parameters of the defect are discussed, and spectra calculated using these parameters are compared to the experimental ones. In Sec. V, the nature of the center is discussed using the chemical analysis of the crystals. Finally, in Sec. VI, the dual behavior of chlorine in ZnTe is discussed. Photo- and thermal excitation or quenching of the center will be described in a forthcoming paper.[5]

II. EXPERIMENTAL PROCEDURE

Two types of crystals have been studied. The first was grown by a Bridgman method (B. Schaub, Laboratoire d'Electronique et de Technologie de l'Informatique, Grenoble) with chlorine added as $CdCl_2$. The others were grown by the traveling heater method (THM) with $ZnCl_2$ added in the first pass of molten Te. For these samples, several passes of pure Te have provided subsequent impurity purification, but in these cases the EPR signal disappears (Table I).

From capacitance versus reverse-voltage measurements made on Schottky diodes (In-ZnTe) and from admittance-spectroscopy measurements,[6] the concentration of acceptors N_A and donors N_D are deduced, and N_A is essentially the well-known Cu

TABLE I. N_A and N_D are the acceptor (essentially Cu) and donor impurity concentration as deduced using Schottky-diode and admittance spectroscopy technique. Concentrations (a) and (b) are deduced from luminescence and EPR experiments, respectively. Related spectra are strong (+ +), weak (+), or absent (0).

	Electrical measurement ($\times 10^{15}$ cm^{-3})		Concentrations (a)		Concentrations (b)
Crystal	N_A	N_D	Deep level	Shallow level	Cl-related center
THM 1	13.4	11	+ +	+ +	+ +
THM 2	13	0.8	+0	+ +	0
THM 3	11	0.03	0	+	0
Bridgman	10	0.8	+ +	+ +	+ +

acceptor.[7] These results are listed in Table I. The relative intensity of the observed spectra is indicated qualitatively (+ + strong, + weak, 0 absent) as deduced from luminescence and EPR experiments.

The EPR measurements were performed on an X-band spectrometer with a variable temperature cryostat adapted to the microwave cavity. This cavity has a window to allow illumination of the sample. A filtered 250-W xenon lamp is used for optical excitation or quenching of the EPR signal. The crystals used were in the form of parallelepiped with the $\langle 110 \rangle$ axis lying along the main axis. The magnetic field was rotated in a plane perpendicular to this axis.

III. RESULTS AND QUALITATIVE DISCUSSION

At room temperature, no resonance signal is observed with or without optical illumination. At low temperature ($T < 50$K), the sample shows a paramagnetic absorption signal when filters passing $\lambda \leq 556$ nm (2.23 eV) are used while no signal appears with filters passing $\lambda \geq 590$ nm (2.10 eV).

When the temperature decreases from 50 K, there is an enhancement of the EPR signal. The signal is maximum for $T = 32$ K and a decrease of the signal amplitude is observed for $T < 32$ K. At 12 K, the absorption signal has disappeared, even if the microwave power is reduced.

Typical EPR spectra of ZnTe:Cl at 32 K with the magnetic field parallel to the $\langle 100 \rangle$ or $\langle 110 \rangle$ axis and excitation wavelength of 556 nm are shown in Fig. 1. A set of four strong well-resolved main lines (a,b,c,d) of comparable intensities is seen. On each side of the main lines, a group of weak lines ($d_1, d_2, c_1, \ldots$) can be seen which are related to the same center.

A dual sample cavity is used to determine the concentration of the observed centers by comparison with a calibrated standard. The measurement on the crystals THM 1 and Bridgman leads to an estimated concentration of $\simeq 10^{15}$ cm^{-3}.

The pattern of four lines (with comparable intensities) suggests an interaction with a nucleus of spin-$\frac{3}{2}$. This isotope must be nearly 100% abundant. Of the several ways of achieving this, only interaction with Cl or Cu nuclei is reasonable. However, a close examination of the resolved lines d and d' on Fig. 1, clearly favors chlorine. Indeed, lines d and d' account for the difference in the nuclear moments of ^{35}Cl and ^{37}Cl ($I = \frac{3}{2}$, relative abundances 0.754 and 0.246, nuclear moments $0.82091\mu_I$ and $0.6833\mu_I$, μ_I is the nuclear magneton), while the difference in the nuclear moments of ^{63}Cu and ^{65}Cu would induce a weak line on the outer side of line d (as reported, for instance, in ZnO:Cu).[8] Typical values of the parameters which describe the observed center are given in Table II.

Two situations are likely for a chlorine ion in the cubic ZnTe structure: One is substitutional at a Te site, and the other interstitial. The former

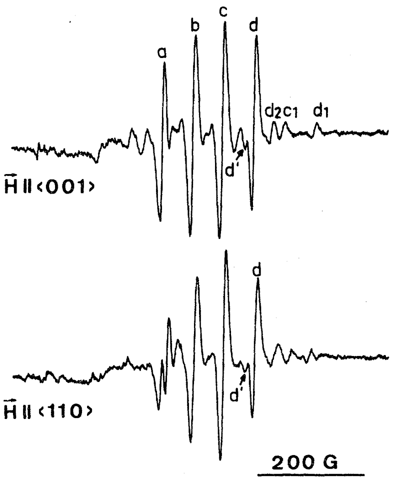

FIG. 1. Typical EPR spectra. $T = 32$ K. The sample is irradiated with light of wavelength 556 μm.

TABLE II. Typical values of the parameters which describe the observed center associated with ZnTe doped with chlorine.

Cl^- associated defect in ZnTe:Cl	
$g_{\parallel}$	1.965
$g_{\perp}$	1.963
$A_{\parallel}(Cl^{35})$	51.7×10^{-4} cm^{-1}
$A_{\perp}(Cl^{35})$	44.7×10^{-4} cm^{-1}
$A_{\parallel}(Sn^{115})$	226.8×10^{-4} cm^{-1}
$A_{\perp}(Sn^{115})$	171.6×10^{-4} cm^{-1}
A(Te)	55.9×10^{-4} cm^{-1}

should behave as an electron trap while the latter should trap a hole. The deviation Δg of the value of g from that of a free electron is definitely negative. This is a characteristic of an electron and could favor the substitutional or quasisubstitutional model.

The relatively small value of Δg indicates that the observed center is a deep center so hyperfine splitting (HFS) can be observed: For shallow donors in ZnTe, $|g|\simeq 0.4$.[9] The HFS associated with Cl nuclei is nearly isotropic and relatively large, implying that the wave functions of the unpaired electrons have rather strong overlap with chlorine s-type orbitals.

The delocalization of the electron orbitals and interaction with nearby nuclei can account for the less intense lines which are observed on each side of the four-line pattern (Fig. 1) as the following discussions shows. If a trigonal symmetry defect is assumed, the center will consist of a substitutional or quasisubstitutional Cl^- on a Te site associated with an impurity on the first-neighbor Zn site (or at least in the $\langle 111 \rangle$ direction). Moreover, for this defect, the super-hyperfine-splitting (SHFS) of only three (of the twelve) Te nuclei which are on the second shell around the Cl^- ion must be taken into account, as well as the SHFS of the three Zn nuclei which are the first neighbors of the Cl nucleus.

For such a defect, the simplest spectrum occurs when the magnetic field is parallel to the $\langle 001 \rangle$ axis. The spectrum in Fig. 1 shows that the line labeled d_1 can be the HFS line of the impurity on a Zn site while d_2 is the SHFS line related to the three Te nuclei. These two lines are associated with the main line d, and the line c_1 will be the equivalent of the d_1 line for the main line c.

So an $I=\frac{1}{2}$ spin is assumed for the impurity on the Zn site. The natural abundance of this nucleus can be estimated using the experimental value of the relative intensity of the HFS line d_1 (compared to that of the d line). The observed value 0.09 implies a natural abundance of about 16%. These two results rule out ^{67}Zn, ^{29}Si, or ^{39}K as possible candidates for the HFS lines. The remaining reasonable possibilities are HFS with Sn, Pb, or Cd nuclei ($I=\frac{1}{2}$, total natural abundances 16.70, 21.1, and 25%, respectively).

IV. THE SPIN HAMILTONIAN OF THE DEFECT

We use as the spin Hamiltonian

$$H=\mu_\beta SgH+I\,(\mathrm{Cl})A\,(\mathrm{Cl})S+I(X)A(X)S+\sum_{i=1}^{3} I\,(\mathrm{Te})A\,(\mathrm{Te})S\ .$$

The first term describes the Zeeman interaction of the paramagnetic electron with the external field. The other terms are related to the HFS interaction with the ^{35}Cl and ^{37}Cl nuclei, the HFS interaction with an X nucleus on Zn site, and the SHFS interaction with three Te nuclei (^{123}Te and ^{125}Te), as reported above. In this expression, several terms have been left out for simplicity (nuclear Zeeman or quadrupolar interaction), although their effects are not completely negligible.

The proposed model for the defect has trigonal symmetry, so three sets of two parameters are required to specify g, A(Cl), and $A(X)$. It will be shown that A(Te) can be reasonably assumed to be isotropic. These parameters are deduced from the EPR spectra taken at various orientations; see, for example, Fig. 1.

Satisfactory results are obtained with the parameters given in Table I. These values are used to calculate the expected derivative EPR signal. The results of this calculation are shown in Fig. 2 for a Cl_{Te}-Sn_{Zn} defect (^{35}Cl, ^{37}Cl, ^{115}Sn, ^{117}Sn, ^{119}Sn, ^{123}Te, and ^{125}Te are taken into account): Gaussian-shaped lines of 9-G width peak-to-peak are assumed.

The relative intensities of the calculated line d_1 (related to Sn nucleus) and d_2 (related to Te nuclei) for H parallel to the $\langle 001 \rangle$ axis are given in Table III. In the same table, we give experimental values of the intensities as well as those calculated for Pb or Cd nuclei instead of Sn. It can be seen that the best fit occurs for Sn or Pb. This result is somewhat surprising since the two members of the associated Cl_{Te} and Sn_{Zn} (or Pb_{Zn}) are donorlike species, while it is easier to imagine such an association with Cd_{Zn}. Moreover, chemical analysis of the crystal (Sec. V) reveals a high concentration of cadmium (2000 or 3000 ppm).

In the calculated curves of Fig. 2, the SHFS due to Zn nuclei has not been taken into account (there are three Zn nuclei as first neighbors of the Cl^- ion). For H parallel to the $\langle 001 \rangle$ axis, the maximum expected relative intensity of these SHFS lines is only 0.02 (natural abundance of ^{67}Zn is 4.11% and $I=\frac{5}{2}$). So we think that either the related SHFS lines are too weak to be observed or the SHF interaction is too small to be resolved.

By comparing spectra in Figs. 1 and 2, it can be seen that when the magnetic field is parallel to the $\langle 001 \rangle$ axis, the experimental spectrum is asymmetric while the calculated one is not (see line d' for instance). Preliminary optically detected magnetic resonance (ODMR) experiments have shown that forbidden $\Delta m = 1$ transitions can be observed if the microwave power is increased.[10] This result can explain the slight asymmetry observed on the experimental curve.

A rough approximation of the HFS parameter A is given by Blumenfeld *et al.*[11] for a pure S electron:

$$A=\frac{8}{3}\frac{R\alpha^2 g(I) Z^3}{n_0^3} .$$

R is the Rydberg constant, α the fine-structure constant, $g(I)=\mu_I/I$ the nuclear g factor, n_0 the effective quantum number, and Z the effective nuclear charge.

Chlorine Cl^{2-} has the same electronic structure as potassium K^0 ($4s^1$). Using the above equation with the parameter of the K atom gives 116×10^{-4} cm^{-1} as an estimated value for $A(Cl^{2-})$. Thus the value reported in Table I (50×10^{-4} cm^{-1}) is comparable to the free-ion value. This is a clear indication that the center is a deep center (for example, for the shallow gallium and indium donors in ZnO, the HFS is only $0.1-1$ % of the free Ga^{2+}, In^{2+} ion value.[12,13]

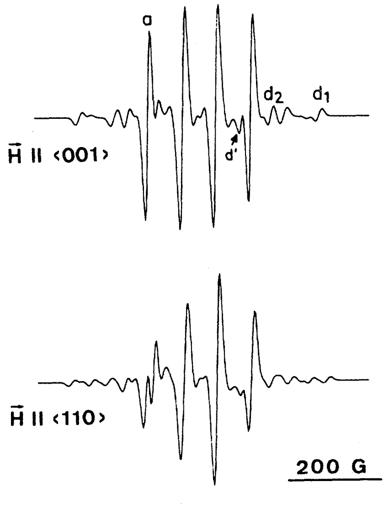

FIG. 2. Calculated EPR spectra for a Cl_{Te}-Sn_{Zn} defect, using parameters of Table II and Gaussian-shaped lines of 9-G width peak-to-peak.

TABLE III. Relative values of experimental and calculated intensities of the EPR spectrum for H parallel to the $\langle 001 \rangle$ axis. d_1 and d_2 are HSF and SHFS lines related to X and Te nucleus, respectively.

	$\frac{d_1}{d}$	$\frac{d_2}{d}$
Experimental	0.09 ± 0.01	0.10 ± 0.01
X=Sn	0.07	0.1
X=Pb	0.10	0.115
X=Cd	0.12	0.143

The experimental value of the HFS parameter A(Cl) as well as its nearly isotropic nature imply a strong contribution of chlorine s-type orbital. However, as g differs markedly from the free-electron value (2.0023), a contribution of p orbitals of the neighboring ions must be invoked. For the calculated spectrum, it has been shown that the electron interacts with only three of the twelve Te which are the nearest neighbors of the chlorine. We presume that these three Te are the nearest neighbors of the cationic impurity, that is, the delocalization of the paramagnetic electron occurs preferentially towards the cationic impurity.

It was reported that in ZnS or ZnSe crystals, a pure s electron of Sn^{3+} ion has a HFS parameter $A \simeq 5000\times10^{-4}$ cm^{-1}.[14,15] The experimental A(Sn) value (200×10^{-4} cm^{-1}) means that the contribution of the 5s orbital of Sn is weak ($\sim$5%). Finally, the charge state of the paramagnetic defect will be essentially $(Cl^{2-}_{Te}\text{-}Sn^{2+})^0$. This remark is also applicable if the nucleus is Pb.

V. CHEMICAL ANALYSIS OF THE CRYSTALS

Mass-spectroscopy analysis of the crystals reveals that the main residual impurities are silicon and potassium (4 and 10 ppm, respectively). The major difference between the two types of crystal is the higher concentrations of chlorine and cadmium (30 and 3000 ppm) for the Bridgman crystal relative to the THM crystals (6 and 2 ppm). Moreover, for these latter crystals, the analyzed Cl content remains unchanged although passes of tellurium induce an apparent purification since the donor content decreases markedly (see Table I).

These results show that there is no simple correlation between the concentration of the main impurities and that of the observed center. However, it is to be noted that in any case, the concentration of the center as deduced from EPR experiments (10^{15} cm^{-3}) is much lower than that of the chlorine impurity ($\sim 10^{18}$ cm^{-3}) so a Cl related center can be involved. In addition, the high concentration of cadmium, especially in the Bridgman crystals, favors this impurity as the X ion of the observed center. However, this impurity has a natural abundance somewhat too large so a large discrepancy occurs between the calculated and the experimental curves (see Table III). Sn or Pb nucleus remains a better candidate as X ion.

VI. CONCLUSION

Chlorine is normally thought to act as a shallow donor as observed in CdS or ZnSe.[2] Indeed, a shallow center associated with chlorine doping is observed in our crystals using luminescence experiments.[16,17] An isotropic donor center is identified with an ionization energy $E_D^{\mathrm{Cl}} = 20.1$ meV (compared to the persistent donor observed in as-grown ZnTe which has $E_D = 18.3$ meV) and a typical D-A luminescence band corresponding to a Cl-donor—Cu-acceptor pair centered at 5500 Å, is observed.

The existence of a distinct deep chlorine-associated defect is confirmed by the fact that a broad thermoluminescence band in the red (7500 Å), with a peak near 25 K, is observed simultaneously with the EPR signal. Moreover, this thermoluminescence broad band disappears, as well as the EPR signal for a "purified" crystal (THM 2, THM 3 in Table I). ODMR experiments have revealed also that the EPR signal is associated with the near-infrared luminescence band.[10]

So EPR and luminescence experiments indicate that one part of the chlorine in ZnTe behaves as a substitutional hydrogenic donor and another part forms an associated defect which is a deep center (as reported above, only a very small fraction of the chlorine content is involved in deep centers). This defect, which has a trigonal symmetry, is identified as a Cl^- ion occupying a tellurium site associated with a positively charged ion on one of the four Zn sites nearest to the Cl^-. This positively charged ion has been tentatively assumed to be a Sn ion but a Pb ion could also be involved. SHFS lines are also observed and account for three of the twelve Te nuclei which are on the second shell around the Cl site. The parameters of the spin Hamiltonian are reported.

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