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LETTER TO THE EDITOR

An A centre in CdTe

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Abstract. Application of electron paramagnetic resonance to neutron-irradiated CdTe shows the presence of a new centre, labelled XA, having mirror symmetry C_s. In terms of a spin Hamiltonian for an effective spin $S = \frac{1}{2}$, its g-values are $g_1 = 2.0034$, $g_2 = 2.0840$ and $g_3 = 2.2020$, where axis 1 corresponds to a [110] direction. We show that an A centre consisting of a Cd vacancy and either a group VII donor on a neighbouring Te site or an impurity isoelectronic to Te can account for the observed EPR. In this model, it is assumed that the bound hole of the A centre is distributed among two neighbouring Te ions.

Isolated intrinsic defects and their combinations with doping elements are frequently discussed in the context of the unipolar conduction type of most II–VI compounds [1]. Among these defects, the so-called A centres, which each consist of a cation vacancy and a neighbouring donor on an anion or cation site, have been identified by electron paramagnetic resonance (EPR) in ZnS [2], ZnSe [3], $ZnS_{1-x}Se_x$ [4] and ZnTe [5]. To our knowledge, however, an A centre has not been reported for CdTe. In this Letter we present EPR spectra obtained for neutron-irradiated CdTe, which are consistent with the model of an A centre in CdTe.

The CdTe single crystal investigated was grown by the Bridgman method without any intentional doping. EPR investigations performed at 20 K in the X band (9.7 GHz) and Q band (35 GHz) showed the Fe^{3+} spectrum of isolated iron on a Cd site [6]. This sample was then irradiated inside a nuclear reactor by neutrons at a temperature of approximately 45 °C. During irradiation, the sample was shielded by a Cd container which absorbed most of the thermal neutrons but only a small fraction of the fast ones. The dose measured inside the container was 1.1×10^{17} cm^{-2}, consisting mainly of neutrons with energies higher than 0.1 MeV.

After neutron irradiation, the EPR spectrum of Fe^{3+} was unchanged, but a new, additional spectrum appeared, which we call the XA spectrum. As shown in figure 1, it consists of two lines for the magnetic field $\boldsymbol{B}$ parallel to ⟨100⟩ (for the convention specifying the directions, see [7]), which split into up to seven lines as the magnetic field is turned within a {110} plane. Because of the rather small signal-to-noise ratio, neither hyperfine structure (HFS) nor ligand hyperfine structure (LHFS) could be observed. It is reasonable to attribute the spectrum to intrinsic defects formed by the neutron bombardment.

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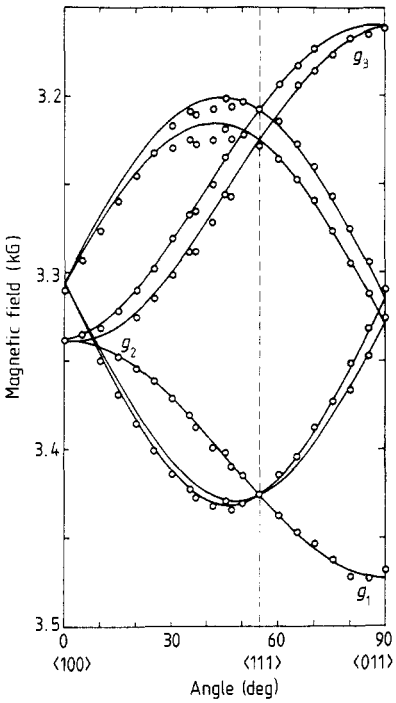

Figure 1. The angular dependence of EPR lines in the neutron-irradiated sample of CdTe. The circles represent measurements in the X band (9.7 GHz) at 20 K; the full curves show the fit with the g-values $g_1 = 2.0034$, $g_2 = 2.0840$ and $g_3 = 2.2020$, and a tilting angle $\tau = 3°$.

The angular dependence of the spectrum in figure 1 shows that the minimum and maximum magnetic resonance fields occur for $\boldsymbol{B}$ approximately parallel to ⟨011⟩ directions. If the axes of the diagonalised **g** tensor lie in {011} planes, two of the three components of **g** have to correspond to these extrema.

Fitting the angular dependence with a Hamiltonian of spin $S = \frac{1}{2}$, the best result is obtained with an orthorhombic **g** tensor, describing C_s symmetry, with

$$g_1 = 2.0034 \qquad g_2 = 2.0840 \qquad G_3 = 2.2020$$

where axis 1 is exactly parallel to ⟨110⟩. There are two possibilities for defining the orientation of the two other axes. The tetrahedral point group (T_d) of the CdTe lattice contains two subgroups which have two axes perpendicular to the [110] direction of axis 1. The first one is that of the C_{2v} symmetry. In this case, axis 2 and axis 3 are first chosen parallel to the [001] and [1$\bar{1}$0] directions, respectively. Then they are rotated about axis 1 through an angle $\tau = \pm 3°$ to give the observed C_s symmetry. The second possibility is a distorted C_{3v} symmetry. Here the axes 2 and 3 are parallel to [$\bar{1}$12] and [1$\bar{1}$1] respectively, with subsequent rotation around axis 1 through $-32.3°$ or $-38.3°$ (i.e. $\alpha \pm \tau$, where α is 35.3°, the angle between [011] and [111]).

Most of the known A centres in II–VI compounds are described by C_{3v} symmetry, with a small distortion ($\tau < 7°$) produced by the nearby donor, which lowers the symmetry to C_s. This symmetry is appropriate for a hole that is bound either to one or to three anion neighbours. In the case of the A centres in ZnS : Cl and ZnS : Br even a thermal activation for the hopping of the bound hole between the three anion neighbours is observed [8]. In the case of our XA centre, the description by a distorted C_{3v} symmetry appears rather unlikely, because of the large rotation angle necessary to fit the observed data.

The other possibility, the description of the XA spectrum in terms of a distorted C_{2v} symmetry, is consistent with an A centre in which the bound hole is distributed over two

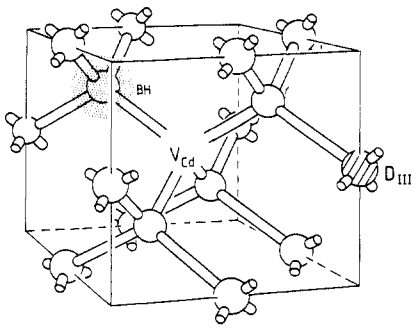

Figure 2. A model of an A centre in CdTe formed by a Cd vacancy (V_{Cd}) and a group III donor (D_{III}) on a nearest Cd site. Most probably the bound hole (BH) will go to the Te site which is most distant from the positively charged donor. Thus the symmetry is nearly C_{3v}.

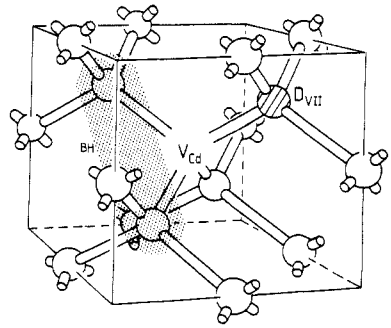

Figure 3. A model of an A centre in CdTe formed by a Cd vacancy (V_{Cd}) and a group VII donor (D_{VII}) on a neighbouring Te site. The C_{2v} symmetry can be explained as corresponding to a spontaneous Jahn–Teller-like distortion causing the bound hole (BH) to be located on two Te neighbours.

neighbouring anion atoms. Such an interpretation was given for the A centres $V_{Zn}SSe_2Cl$ and $V_{Zn}SSe_2Br$ ion $ZnS_{1-x}Se_x$ [4] (the notation for these centres nominates first the cation vacancy and then the four neighbouring atoms on the surrounding anion places). For these two centres, the C_{2v} symmetry is inherent, because of the two different species of anion neighbours. In CdTe, the reduction from T_d to C_{2v} symmetry can be explained by a spontaneous Jahn–Teller-like distortion. Then the hole wavefunction is located on two Te neighbours. The additional lowering of symmetry to C_s in the model of the A centre can be explained by assuming the presence of either a nearby donor on a cation or anion site, or an isoelectronic, group VI impurity on an anion site with higher electronegativity than that of Te, like Se or S.

Because of the lack of HFS and LHFS, the microscopic nature of the centre responsible for the XA spectrum cannot be deduced. If the model of an A centre is correct, there are in principle two possibilities for the associated shallow donor. It can be either a group III donor (D_{III}) on a nearest cation site or a group VII donor (D_{VII}) on a neighbouring anion site.

The D_{III} could form $V_{Cd}Te_4Cd_{11}D_{III}$, using a notation that lists all atoms, up to the second-nearest-neighbour shell. In this defect, one of the four Te atoms is more distant from the D_{III} atom than the other three (see figure 2). In the model of the A centre, the associated donor is positively charged. Hence, it is reasonable to locate the bound-hole wavefunction, which also represents a positive charge, at the Te neighbour that is most distant from the Cd vacancy. In this situation, however, the symmetry would be a C_{3v} one, which is not the one observed for the XA centre.

A shallow donor, D_{VII}, on a Te site, in contrast, could form $V_{Cd}Te_3D_{VII}$. For this defect, the three Te neighbours are at the same distance from the shallow donor, as shown in figure 3. A spontaneous Jahn–Teller-like distortion of the defect causes bonding of the hole to two of the three Te neighbours. This gives the symmetry needed to explain the XA centre. In addition, the *g*-shifts of the XA centre have the same sign and order as those of the A centres observed in $ZnS_{1-x}Se_x$ [4].

When the observed XA centre consists of a Cd vacancy and an isoelectronic impurity on a Te site with a higher electronegativity than Te, the same arguments as for a group VII donor hold. So this is another possible explanation of the observed EPR spectrum.

In table 1, the *g*-shifts are compiled for the XA centre ($V_{Cd}Te_3X$) and for the two A

Table 1. A summary of the g-shifts observed for A centres in cubic $ZnS_{1-x}Se_x$ [4] and for the XA centre described in this Letter.

Centre	Δg_1	Δg_2	Δg_3	Angle (deg)
$V_{Zn}SSe_2Cl$	0.0102	0.0953	0.1763	16 ± 2
$V_{Zn}SSe_2Br$	0.0037	0.1016	0.1817	13 ± 2
$V_{Cd}Te_3X$	0.0011	0.0817	0.1997	3 ± 1

centres with the same symmetry, mentioned above. All three g-values of the XA centre and of the two other centres exhibit a positive g-shift, i.e. the g-values are larger than $g_0 = 2.0023$, the value for the free electron. This might seem to be in contradiction to the understanding of the A centres, as mentioned by Bittebierre and Cox [5] in their reference 35 for ZnTe : Al. In the present case of the XA centre, however, we assume that the bound hole is shared by two Te neighbours. The usual estimate for the g-shift from the spin–orbit coupling should thus not hold, because the centre is not centrosymmetric and the wavefunction, described in a molecular orbital picture, is made of two dangling, non-collinear atomic orbitals [4].

Instead, in order to estimate the g-shift for the XA centre, we consider the following simple reasoning. Watkins [3] reported on the defect $V_{Zn}Se_3Te$ in Te-doped ZnSe, in which the spin is located at the Te ligand in a $\langle 111 \rangle$ dangling bond, with $g_\parallel = 1.873$ and $g_\perp = 2.258$. Assuming that a hole bound to a single Te ligand in CdTe has the same g-values, we can estimate the components of the **g** tensor for our $V_{Cd}Te_2TeX$ complex, where the bound hole is shared by the two Te ligands. Taking a linear combination of atomic orbitals of the two dangling bonds directed to $\langle 111 \rangle$ and $\langle 1\bar{1}\bar{1} \rangle$ for our case, we get $g_1 = 2.0095$, $g_2 = 2.1374$ and $g_3 = 2.258$. These values are too large, but they have the same ordering as the observed ones and all of them are larger than the value of the free electron. This argument shows that our model is consistent with earlier observations of A centres.

Because of the above properties of the XA centre, we propose a model of an A centre in CdTe formed by a Cd vacancy and either a group VII donor or an isoelectronic impurity, like Se or S on a neighbouring Te site.

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