Electron paramagnetic resonance of Mn-doped Cd$_{1-x}$Hg$_x$Te

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The crystal-field splittings of the ground state of Mn in Cd$_{1-x}$Hg$_x$Te have been measured using electron paramagnetic resonance. The values are similar to those of Mn in II-VI compound semiconductors and are much smaller than the values assumed recently for Mn in semimagnetic semiconductor alloys.

I. INTRODUCTION

Considerable interest has been shown in the "semimagnetic semiconductors" (SMSC's) which have unusual properties because of the presence of a magnetic transition element in a semiconducting environment.[1] Evidence for a spin-glass phase in these materials has come from specific-heat measurements of Hg$_{1-x}$Mn$_x$Te,[2] Hg$_{1-x}$Mn$_x$Se,[3] Cd$_{1-x}$Mn$_x$Te,[4] and Cd$_{1-x}$Mn$_x$Se.[5] In each case, the specific heat shows a magnetic-field-dependent component in addition to the lattice contribution. The excess component was explained previously in terms of a contribution from pairs of Mn ions.[4] Recently it has been suggested that the excess component is due in part to a large crystal-field splitting of single Mn ions.[5] In one case, the data was fitted by a cubic splitting into a doublet and a quartet separated by 0.8 K, and in another case by a splitting into three doublets separated by 0.4 and 0.7 K, which is the result one expects from an axial field.

It is suggested that the splitting is caused by distortions of the crystal lattice which result from the replacement of the group-II ions Cd (ionic radius of 0.097 nm) or Hg (ionic radius of 0.110 nm) by the smaller Mn ion (ionic radius of 0.08 nm). The possibility that single Mn ions are the explanation has not been suggested previously because EPR measurements of Mn in low concentrations in II-VI semiconductors such as CdTe and ZnSe show that the crystal-field splitting of the Mn levels is much smaller (0.004 K) than that assumed above.[6] It is suggested in the new model that when the concentration of Mn exceeds about 5 at. %, some of the Mn ions are affected by a proposed distortion of the lattice which is peculiar to the alloy environment.

Unfortunately, it is not possible to check this hypothesis directly by EPR because, for concentrations above 0.01 at. %, the Mn EPR spectrum is broadened into a single line[7] which yields no information of use in the present context. We have attempted to test the hypothesis by forming the alloy out of two II-VI compound semiconductors instead of making Mn one of the components of the alloy, which would disguise its EPR spectrum. In particular, we have studied the Mn-doped alloy, Cd$_{1-x}$Hg$_x$Te:Mn. The ionic radii of Cd and Hg differ almost as much as that of Cd and Mn, so that if the alloy environment produces a lattice distortion sufficient to cause a large crystal-field splitting in the case of

Cd$_{1-x}$Mn$_x$Te and other semimagnetic semiconductors, it should do so also in the case of Cd$_{1-x}$Hg$_x$Te:Mn. However, in the latter alloy, one can expect to see evidence of the distortion in the Mn EPR spectrum, which should be well resolved because of the low Mn concentration.

II. EXPERIMENTAL PROCEDURE

The polycrystalline samples of Cd$_{1-x}$Hg$_x$Te:Mn ($0.35 \leq x \leq 0.92$) were prepared from finely ground mixtures of II-VI compound semiconductors and a trace of Mn. The mixtures were placed in quartz tubes, sealed off under vacuum, and annealed at about 850 °C for several days. EPR measurements were performed in conventional X-band and Q-band spectrometers at room temperature and 77 K. Since the exact composition of the alloys is not important in the present context, the atomic values quoted are calculated from the weights of the constituents used in forming the alloy.

III. THEORY

The EPR spectrum described below is due to Mn^{2+} ions in a $^6S_{5/2}$ state with electron spin $S = \frac{5}{2}$ and nuclear spin $I = \frac{5}{2}$. Since the Mn^{2+} is in alloys formed from semiconductors with cubic symmetry, one might expect the local symmetry of the substitutional Mn^{2+} site to be cubic also. Indeed x-ray-diffraction results from our samples show that the alloys retain the overall cubic symmetry of the constituent CdTe and HgTe. However, we show below that the results can only be explained by local axial symmetry. The appropriate spin Hamiltonian has the form

$$\mathscr{H} = g\beta\vec{H}\cdot\vec{S} + D[S_z^2 - \tfrac{1}{3}S(S+1)] + A\vec{S}\cdot\vec{I} - g_N\beta_N\vec{H}\cdot\vec{I} \ ,$$

(1)

where all the symbols have their usual meaning and the z axis is the direction of the axial-symmetry axis. For the purpose of EPR, the electron states can be labeled by the magnetic quantum numbers M and m corresponding to the electron and nuclear spins, respectively. The axial term in Eq. (1) splits the Mn ground state into three levels with $M = \pm\frac{1}{2}$, $\pm\frac{3}{2}$, and $\pm\frac{5}{2}$ separated by $2D$ and $4D$, respectively, where D is the crystal-field parameter in Eq. (1). The EPR spectrum consists of six strong lines corresponding to transitions of the form $|M, m\rangle$

$\rightarrow |M-1,m\rangle$ with $M=\frac{1}{2}$ and $m=-\frac{5}{2}$, $-\frac{3}{2}$, $-\frac{1}{2}$, $\frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$. The strong angular dependence of the other fine-structure lines $(M\neq\frac{1}{2})$ means that they are too broad to be observed from a powder sample. In addition, a total of ten much weaker transitions of the type $|\frac{1}{2}, m\rangle\rightarrow|-\frac{1}{2}, m\pm1\rangle$ are visible between the main lines.

Expressions for the positions and relative intensities of the 16 transitions referred to above have been obtained using perturbation theory up to third order.[8] The third-order corrections are much less than the linewidth in our case and therefore the following second-order expressions are adequate for explaining the data below. First, the separations δH_m^S of successive strong $|\frac{1}{2}, m\rangle\rightarrow|-\frac{1}{2}, m\rangle$ and $|\frac{1}{2}, m-1\rangle\rightarrow|-\frac{1}{2}, m-1\rangle$ transitions are given by[9]

$$\delta H_m^S = -A'[1-(A'/2H_0)(2m-1)], \qquad (2)$$

where H_0 is the resonant magnetic field for $A=D=0$ and $A'=A/g\beta$. Second, the separations δH_m^W of the weak transitions $|\frac{1}{2}, m\rangle\rightarrow|-\frac{1}{2}, m-1\rangle$ and $|\frac{1}{2}, m-1\rangle\rightarrow|-\frac{1}{2}, m\rangle$ are given by[9]

$$\delta H_m^W = -17(A')^2/2H_0+2g_N\beta_N H/g\beta. \qquad (3)$$

Unfortunately, neither of the last two expressions involves the crystal-field parameter D which determines the crystal-field splitting which we seek. However, the parameter D can be estimated from the spectrum in several ways. The first and most reliable method is to plot the ratio of the intensity of each of the main lines to the intensity of the high-field line $(m=\frac{5}{2})$ and compare with the theoretical ratios which have been calculated for various values of D.[10] Second, the ratio R_I of the weak- $(|\frac{1}{2}, m\rangle\rightarrow|-\frac{1}{2}, m-1\rangle)$ to strong- $(|\frac{1}{2}, m\rangle\rightarrow|-\frac{1}{2}, m\rangle)$ line transition involves the crystal-field parameter D and is given by[9]

$$R_I = \frac{512}{15}(\frac{35}{4}-m^2+m)\frac{D^2}{g^2\beta^2H_0^2}. \qquad (4)$$

Other consequences of the axial field are that, with increasing m, the weak lines broaden and shift to higher fields and the strong lines appear to split into doublets because of the powder line shape. In the present case, the relatively large linewidth prevents the observation of the latter two effects.
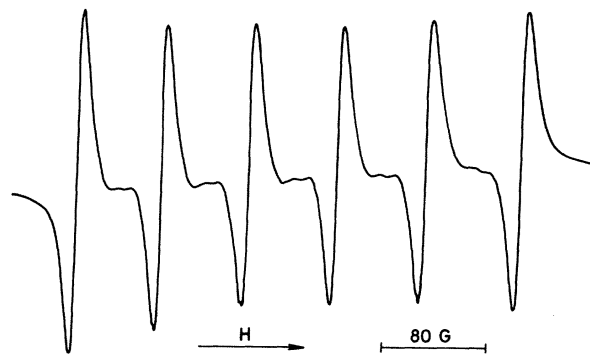

FIG. 1. EPR spectrum from Mn in $Cd_{0.92}Hg_{0.08}Te$.

IV. RESULTS AND DISCUSSION

The EPR spectrum of $Cd_{0.92}Hg_{0.08}Te$:Mn is shown in Fig. 1. The six prominent lines are the main transitions. The ten weak lines between them can be seen much more clearly with higher gain. The magnitude of D can be determined from the EPR spectrum in the ways described above and the required measurements are summarized in Table I. The second column gives the integrated intensity of the lines which were obtained by digitizing individual spectra at about 500 points and numerically integrating the result using a microcomputer. By measuring different series of spectra we found that the errors in these measurements are 10%. The next two columns give the separations δH_m^S of successive strong-line transitions and the separations δH_m^W of the successive pairs of weak-line transitions, respectively, for the m values given in the table. The last column gives the separation ΔH of the $|\frac{1}{2}, m\rangle$ strong-line transition and the average of the positions of the two weak-line transitions $|\frac{1}{2}, m\rangle\rightarrow|-\frac{1}{2}, m+1\rangle$ and $|\frac{1}{2}, m+1\rangle\rightarrow|-\frac{1}{2}, m\rangle$. The separations of the strong and weak lines can be fitted by Eqs. (2) and (3) using $A=-62.4$ G as shown in Table I. This value of A is similar to the value of -61.6 G found for Mn^{2+} in $CdTe$.[6]

The magnitude of D can be estimated from the relative intensities of the six main lines. Figure 2 shows a plot of the ratio of the intensity of each of the main lines to the high-field line $(m=\frac{5}{2})$. The relative intensities show a minimum for the $m=\pm\frac{1}{2}$ lines which is characteristic of

TABLE I. Properties of the EPR signal from $Cd_{0.92}Hg_{0.08}Te$:Mn. The separations δH_m^S and δH_m^W of the strong and weak lines and the separation ΔH are explained in the text. Theoretical values are from Eqs. (2) and (3).

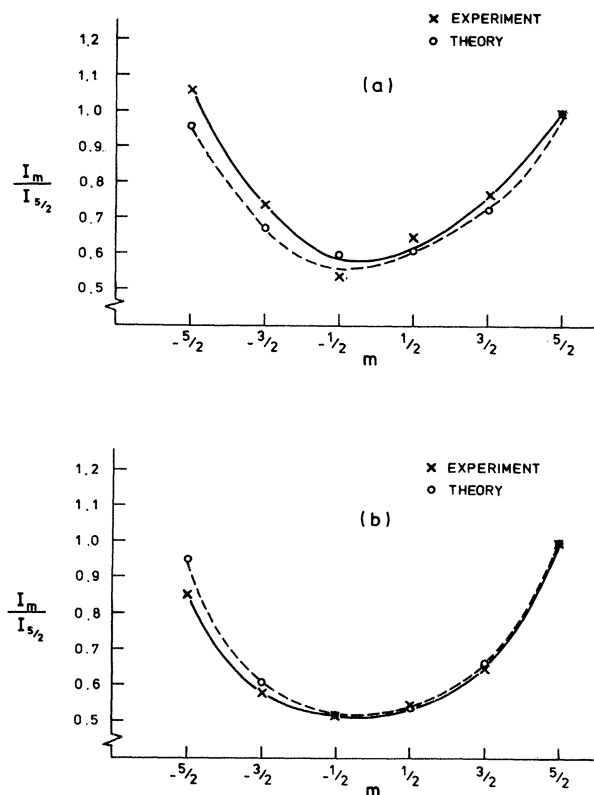| Nuclear magnetic quantum number	Intensity of strong line (arb. units)	δH_m^S (G)		δH_m^W (G)		ΔH (G)
		Expt.	Theory	Expt.	Theory	
$-\frac{5}{2}$	2.74					31.5
$-\frac{3}{2}$	1.93	60.4	60.0	11	13	32.6
$-\frac{1}{2}$	1.37	61.5	61.2	11	13	32.8
$\frac{1}{2}$	1.70	61.8	62.4	12	13	33.2
$\frac{3}{2}$	2.02	63.5	63.6	12	13	34.5
$\frac{5}{2}$	2.66	64.8	64.8	12	13	

FIG. 2. Ratio of the intensity of each of the strong lines to that of the high-field line ($m = \frac{5}{2}$) as a function of magnetic quantum number m for (a) $Cd_{0.92}Hg_{0.08}Te$, and (b) $Cd_{0.65}Hg_{0.35}Te$.

an axial field.[10] For the cubic symmetry, on the other hand, the relative intensities show a monotonic decrease with increasing m value as in the case of MgO:Mn.[10] Therefore we conclude that the predominant crystal-field component is due to an axial field. The magnitude of the axial parameter D can be obtained by fitting the data in Fig. 2 from the numerical results given in Ref. 10. The theoretical fit shown is obtained with $D=0.016$ K for $Cd_{0.92}Hg_{0.08}Te$:Mn. The value of D does not vary greatly with composition; for example, $D=0.018$ K for $Cd_{0.65}Hg_{0.35}Te$:Mn as shown in Fig. 2(b).

A second way of determining D is from the ratio R_I of the weak-line transitions to the strong-line transitions which is given by Eq. (4). For $D=0.016$ K, one expects $R_I \sim 0.3$, which is larger than the value which we estimate from the height multiplied by the width squared (width^2) of the lines. However, our estimate of R_I is very approximate because the weak lines are overlapping, and are spread out over a wider field range because they have a greater angular dependence than the strong lines. Finally, as a consequence of the crystal-field term, the weak lines

should broaden and shift to higher fields for increasing m. That trend is indicated in our results by the values of ΔH in Table I. The shift cannot be fitted accurately to a value of D without computer simulation of the powder spectrum, but it is of the correct order of magnitude.

Therefore all the aspects of the spectrum are compatible with an axial-field environment resulting in a crystal-field parameter of $D=0.016$ K. This value of D is of the same order of magnitude as for Mn^{2+} in the axial-field environment of hexagonal II-VI compound semiconductors[6] for which $D=0.01$ K. However, the axial-field component demonstrated by the EPR results for the alloys has a different origin. The alloys are formed from semiconductors which have cubic structure, and the x-ray results confirm that the atoms occupy sites on a cubic lattice. However, the occupancy of those sites by the group-II elements is random, and thus the local symmetry about each site is lower than cubic. It has been found that D values of the order of 2 K result from the random occupancy by two different atoms of nearest-neighbor sites in cubic crystals.[11] Therefore it is not surprising that an axial-field component is found in the present case where the second-nearest-neighbor sites are randomly occupied. The many different arrangements of the occupancies of the second-nearest-neighbor sites will give rise to a distribution in the magnitude and direction of the axial field similar to the distribution found in glasses.[12] Since the field is a result of an average, it should not depend greatly on composition, in agreement with our preliminary results on other alloy compositions. The axial field identified in this work must also occur in the SMSC's and may have an effect on the magnetic properties of those materials, as it does, for example, in amorphous metallic alloys.[13]

V. CONCLUSION

The EPR results show that the Mn ion occupies a site with axial symmetry in the $Cd_{1-x}Hg_xTe$:Mn alloys studied. The variation of the intensity of the strong EPR lines is very well fitted by a crystal-field parameter $D \sim 0.018$ K. This means that in zero field, the Mn ground state consists of three doublets, separated by 0.036 and 0.072 K, respectively. The energy-level scheme would result in a peak in the specific heat due to the Mn at an extremely low temperature (about 0.04 K). There does not seem to be any reason why the crystal-field splitting should be an order of magnitude larger in the alloy environment of the SMSC's than in the Hg-Cd-Te alloy. Therefore it does not seem that isolated Mn ions can be the explanation of the peak in the excess specific heat in the SMSC's.

ACKNOWLEDGMENTS

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