PHYSICAL REVIEW B VOLUME 50, NUMBER 22 1 DECEMBER 1994-II

Axial anisotropy of Co^{2+} in CdS from magnetization-step and high-frequency EPR

V. Bindilatti, A. N. Anisimov, and N. F. Oliveira, Jr.
Instituto de Física, Universidade de São Paulo, CP 20516, 01498-970 São Paulo, São Paulo, Brazil

Y. Shapira
Department of Physics, Tufts University, Medford, Massachusetts 02155
and Groupe d'Études des Semiconducteurs, Université Montpellier II, Place E. Bataillon, 34095 Montpellier Cedex 5, France

M. Goiran and F. Yang
Laboratoire de Physique des Solides, Service des Champs Magnétiques Intenses, Institut National des Sciences Appliquées,
Complexe Scientifique de Rangueil, 31077 Toulouse-Cedex, France

S. Isber and M. Averous
Groupe d'Études des Semiconducteurs, Université Montpellier II, Place E. Bataillon, 34095 Montpellier Cedex 5, France

M. Demianiuk
Institute of Technical Physics, Wojskowa Akademia Techniczna, 00908 Warsaw, Poland

(Received 22 July 1994)

A magnetization step due to isolated Co^{2+} spins in $Cd_{1-x}Co_xS$ was observed at 30 mK. The magnetic field at this step gave $2D=1.32\pm0.04$ cm^{-1} for the single-ion axial anisotropy constant of Co^{2+}. This value is close to those obtained by other methods. EPR experiments at 96 GHz gave $2D=1.28\pm0.04$ cm^{-1}. The EPR data suggest the existence of a Koster-Statz term in the spin Hamiltonian.

I. INTRODUCTION

Several types of magnetization steps (MST's) have been observed in dilute magnetic semiconductors (DMS). The most frequently studied type involves MST's arising from pairs (dimers) of spins. Such MST's are used to determine the antiferromagnetic exchange constant J for the two spins in the pair.[1,2] A completely different type of MST arises from isolated spins (singles) when the spin Hamiltonian (SH) contains an axial anisotropy term. The MST arising from isolated spins has been recently observed by our group in $Cd_{1-x}Co_xS$ and $Cd_{1-x}Co_xSe$, which have the wurtzite structure.[3] A similar effect has been observed previously in several concentrated magnetic materials with weak interactions between the magnetic ions.[4,5]

In principle, the MST due to isolated ions can be used to determine the single-ion axial anisotropy constant D. To achieve a reasonable accuracy, however, the MST must be relatively sharp. This means that the concentration x of magnetic ions must be quite low, because the MST is broadened by interactions between the magnetic ions. In the previous work[3] the cobalt concentration was not sufficiently low for this purpose. (Later measurements of x, including atomic absorption, showed that the value $x=1.3\%$ quoted in Ref. 3 should be changed to 1.6%.) The present experiments were carried out on a $Cd_{1-x}Co_xS$ sample with $x=0.5\%$. The MST (due to singles) in this sample was sufficiently sharp to determine D with an accuracy of 3%. New electron paramagnetic resonance (EPR) data at 96 GHz, which give D more directly, are also presented. Both of our values for D are close to previous results, from EPR at lower frequencies[6] and from specific heat,[7] and they also agree with recent Raman data.[8]

II. THEORETICAL BACKGROUND

When a Co^{2+} ion is placed in a II-VI DMS, the ^4F ground level of the free ion is split by the tetrahedral crystal field into three levels. The lowest of these is the $^4A_2$ level.[9,10] This lowest level controls the magnetic behavior at room temperature and below. It is therefore customary to represent the Co^{2+} ion as an effective spin $S=\frac{3}{2}$. If the DMS is cubic then all four states ($S_z=\pm\frac{1}{2}$ and $\pm\frac{3}{2}$) are degenerate at zero magnetic field. This degeneracy is partially lifted in the wurtzite structure of $Cd_{1-x}Co_xS$, because of the axial term in the crystal field. Among the resulting two Kramers doublets, one corresponds to $S_z=\pm\frac{1}{2}$, and the other to $S_z=\pm\frac{3}{2}$.

Choosing the z axis to be parallel to the hexagonal axis (c axis) of the crystal, the conventional SH for an isolated Co^{2+} ion is

$$\mathcal{H}=g_{\parallel}\mu_B B_z S_z+g_{\perp}\mu_B(B_x S_x+B_y S_y)+D[S_z^2-(1/3)S(S+1)]\ , \qquad (1)$$

where $\mathbf{B}$ is the magnetic field, $g_{\parallel}$ and $g_{\perp}$ are the g factors parallel and perpendicular to the c axis, respectively, μ_B is the Bohr magneton, and D is the single-ion axial anisotropy constant. For $Cd_{1-x}Co_xS$ the constant D is positive, so that the energy of the $S_z=\pm\frac{3}{2}$ Kramers doublet is $2D$ higher than that of the $S_z=\pm\frac{1}{2}$ doublet. Early

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EPR data gave $g_{\parallel}=2.269$, $g_{\perp}=2.286$, and $2D=1.34$ cm^{-1} (corresponding to 1.93 K).

Figure 1 shows the energy levels obtained from Eq. (1) when **B** is parallel to the c axis. One important feature is the level crossing at B_{cr}, at which the ground state changes. This change increases the magnitude of S_z for the ground state from $-\frac{1}{2}$ to $-\frac{3}{2}$, which gives rise to a MST if the temperature T is sufficiently low ($k_B T \ll D$). Below B_{cr} the magnetization M at such low temperatures follows the Brillouin function for spin-$\frac{1}{2}$, with a saturation value corresponding to $S_z=-\frac{1}{2}$. The MST then increases M by a factor of 3. The width δB of the MST is controlled by several factors: (1) the temperature T (thermal broadening), (2) interactions between the Co^{2+} ions (which increase with increasing x), and (3) any spread in the values of D arising from local strains. The field B_{cr} at the center of the MST is related to D as

$$g_{\parallel}\mu_B B_{\mathrm{cr}}=2D \ , \tag{2}$$

which allows D to be determined from the position of the MST.

Figure 1 also shows some possible EPR transitions when $\mathbf{B}\parallel c$ and when the photon energy $h\nu$ is larger than $2D$. The allowed transitions (i.e., transitions with $\Delta S_z=1$) are labeled as K, L, and M. Transition N is one of the "forbidden" transitions ($\Delta S_z=2$). It is easy to show that the resonance fields B_i for a fixed frequency ν satisfy the following relations:

$$B_N=(1/2)B_L \ , \tag{3}$$

$$\Delta B_{LK}\equiv B_L-B_K=B_{\mathrm{cr}} \ , \tag{4}$$

and

$$\Delta B_{KM}\equiv B_K-B_M=B_{\mathrm{cr}} \ . \tag{5}$$

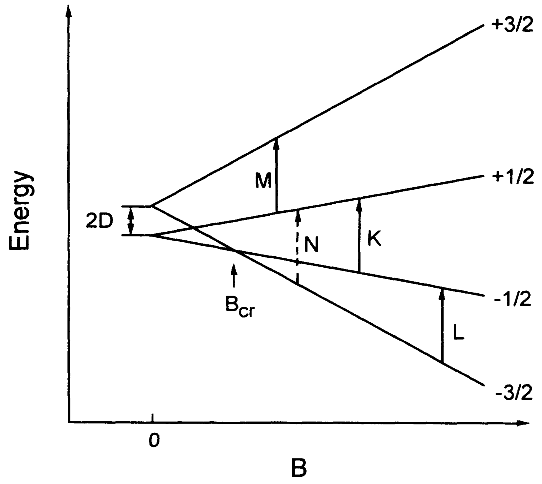

FIG. 1. Schematic of the lowest-energy levels of an isolated Co^{2+} ion in CdS. The magnetic field **B** is along the c axis. Note the change of the ground state at B_{cr}. The allowed EPR transitions ($\Delta S_z=1$) for $h\nu>2D$ are K, L, and M. One of the "forbidden" transitions is N.

It should be emphasized that these equations are exact only within the framework of the conventional SH, given by Eq. (1). The measured differences ΔB_{LK} or ΔB_{KM} can be used to determine D [via Eqs. (4), (5), and (2)] provided that $g_{\parallel}$ is known. This determination does not depend on knowing the frequency ν exactly.

III. MAGNETIZATION STEP

Magnetization data were taken on a $\mathrm{Cd}_{1-x}\mathrm{Co}_x\mathrm{S}$ sample with $x=0.5\%$. The measurements were made in a plastic dilution refrigerator[11] operated at 30 mK. The choice of the refrigerator was motivated by the requirement $k_B T \ll D \cong 1$ K, and the need to minimize eddy-current heating due to time-varying magnetic fields. The magnetization was measured with a capacitance force magnetometer, using an alternating magnetic-field gradient to produce an ac force proportional to the magnetization.[3,12] The main magnetic field, on which the ac field gradient was superimposed, was produced by a superconducting coil, and was parallel to the c axis.

Figure 2(a) shows the magnetization data. A reasonably sharp MST is clearly visible. Its position was determined from the peak in the derivative dM/dB, shown in

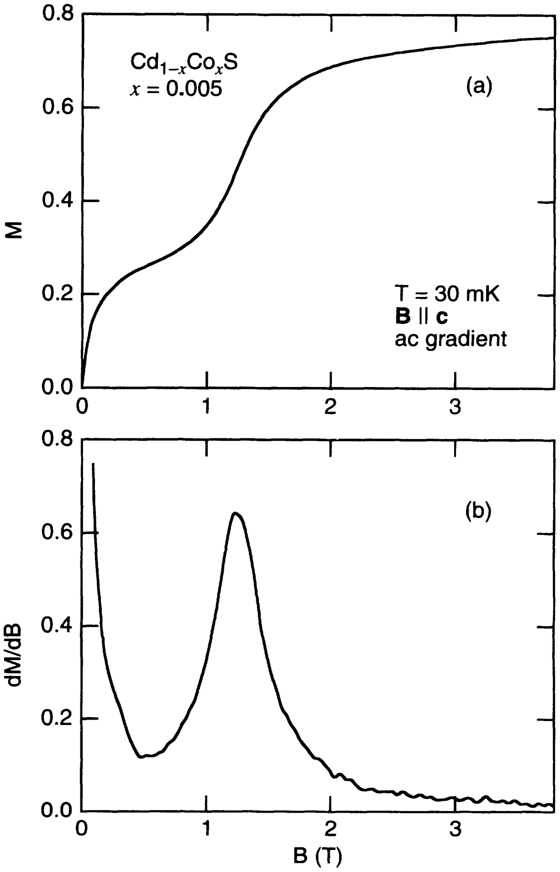

FIG. 2. (a) Magnetization curve of $\mathrm{Cd}_{1-x}\mathrm{Co}_x\mathrm{S}$, with $x=0.005$, at $T=30$ mK. The magnetic field **B** is along the c axis. The ordinate axis is in arbitrary units. (b) The derivative dM/dB obtained by a numerical differentiation of the curve in part (a).

Fig. 2(b). This derivative was obtained by a numerical differentiation of the data in Fig. 2(a). To obtain B_{cr}, the small monotonic background on which the peak was superimposed was subtracted. The field at the maximum (after background subtraction) then gave $B_{cr}=1.25\pm0.04$ T. Using $g_{\parallel}=2.269$ (from Ref. 6, and confirmed by the data below) this result for B_{cr} gives $2D=1.32\ \pm0.04$ cm^{-1}.

IV. EPR RESULTS

EPR measurements at 96 GHz were performed on a $Cd_{1-x}Co_xS$ sample with $x=1.6\%$. The radiation was produced by a GaAs Gunn oscillator. The sample, 0.7 mm thick, was placed at the end of a waveguide. The transmission through the sample was measured in the Faraday geometry by recording the photocurrent in an InSb detector cooled to 4.2 K. A pulsed field magnet was used, although the fields required at 96 GHz were rather modest. The data analysis concentrated mainly on the down portion of the pulse, which lasted much longer, about 1 s. The field **B** was parallel to the *c* axis, to within 3°. The magnetic field calibration was checked by EPR measurements on diphenylpicrylhydrazyl. Most data were taken at 4.2 K, but some data were taken in temperatures up to 35 K. At higher temperatures the absorption in the sample was too high, presumably due to the presence of charge carriers which froze out only at the lower temperatures.

Figure 3 shows some typical data. Four resonances are observed, superimposed on a background of monotonically increased transmission. The two resonances at the higher fields are much more prominent. The other two resonances can be seen more clearly by subtracting the background and expanding the vertical scale, as shown in the inset. All four resonances (including that with the weakest intensity) were reproducible. No other resonances were observed in fields up to 33 T. The monotonic background in Fig. 3 may be due to a magnetic freeze-out of the remaining conduction carriers.

The four resonances are easily identified as the *K*, *L*, *M*, *N* resonances in Fig. 1. Values for the resonance fields were obtained by averaging over all experimental traces. The resonance field $B_k=3.04$ T confirms the known value of $g_{\parallel}$ (Ref. 6) to within 1%. The measured ratio $B_N/B_L=0.502$ is very close to the value 0.500 expected from the conventional SH, Eq. (3). On the other hand, the difference $\Delta B_{LK}=B_L-B_K$ is 6% smaller than the difference $\Delta B_{KM}=B_K-B_M$, contrary to the equality expected from the conventional SH [Eqs. (4) and (5)]. Ignoring the difference between ΔB_{LK} and ΔB_{KM} for the moment, and taking the average, we obtain $B_{cr}=1.211\pm0.04$ T. Here, use was made of Eqs. (4) and (5), and the uncertainty was chosen to cover the two slightly different values obtained from these equations. Using Eq. (2) and the known value of $g_{\parallel}$, we then obtained $2D=1.28\pm0.04$ cm^{-1}. This result is close to 1.32 ± 0.04 cm^{-1} from the MST, and is also in reasonable agreement with 1.34 ± 0.02 cm^{-1} from the early EPR work[6] and 1.35 ± 0.04 cm^{-1} from specific-heat data.[7]

Various possible causes for the difference between ΔB_{LK} and ΔB_{KM} were considered, beginning with possible systematic experimental errors. Uncertainties arising from the finite linewidths of the resonances were judged to be too small. An error in the field calibration (over the field range between resonances *M* and *L*) is very unlikely, particularly when the measured ratio B_N/B_L is so close to the predicted ratio. A misalignment of **B** relative to the *c* axis can lead to the observed results. However, the required misalignment angle is 8°, which is far too large.

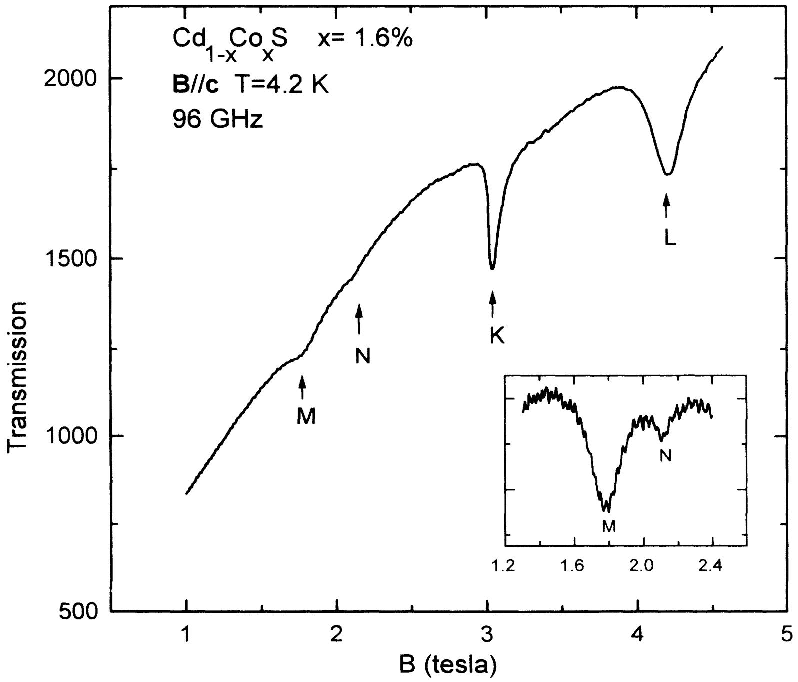

FIG. 3. Transmission (in arbitrary units) of 96-GHz waves through a $Cd_{1-x}Co_xS$ sample, with $x=0.016$. The magnetic field **B** is along the *c* axis. The inset shows an expanded view of the transmission near resonances *M* and *N*, with the monotonic background subtracted.

(The orientation of the flat face of the sample which was used for mounting it at the end of the waveguide was reconfirmed later by x-ray measurements.)

The other possibility is that a small correction term should be added to the conventional SH, Eq. (1). For cubic materials, Koster and Statz (KS),[13] and Bleaney,[14] suggested that terms proportional to $B_i S_i^3 (i = x,y,z)$ should be added to the conventional SH. The existence of such terms was verified experimentally by Ham *et al.*[15] To explain our results in $Cd_{1-x}Co_xS$, with $\mathbf{B} \| c$, we add to the conventional SH a KS term $u_{\|}\mu_B B_z S_z^3$, where $u_{\|}$ is a dimensionless parameter. When this term is added to Eq. (1), the zero-field splitting between the two Kramers doublets is still equal to $2D$, but the slopes of the straight lines in Fig. 1 are changed. The changes in the slopes lead to a difference between ΔB_{LK} and ΔB_{KM}. Good agreement with the observed difference between ΔB_{LK} and ΔB_{KM}, and also with the observed ratio B_N / B_L, is obtained with $u_{\|} = 0.009$. This value for $u_{\|}$ is comparable to typical values found in cubic materials.[15] The sign of $u_{\|}$ is the same as that of the corresponding term along the [111] direction in cubic ZnSe and ZnS, but opposite to that in ZnTe.

Although the data at 96 GHz suggest the existence of a KS term, a definitive proof is lacking. If the KS term exists then the difference between ΔB_{LK} and ΔB_{KM} should increase as the frequency ν is increased. Thus, resonance experiments in the far infrared should be helpful in resolving this issue. A resonance experiment at a wavelength of 890 μm (336.8 GHz) was actually carried out by us at 4.2 K, using a molecular gas laser pumped by a CO_2 laser. Unfortunately, at this higher frequency only the L line was observed, presumably because the initial states for the K and M transitions were practically unoccupied at 4.2 K. On the basis of resonance L alone, no firm conclusion concerning the existence of the KS term could be reached. (The field $B_L = 11.75$ T was halfway between the values calculated with and without the KS term, but the uncertainty was large enough to bring it into agreement with either possibility.) Measurements of the *differences* ΔB_{LK} and ΔB_{KM} would have provided a more definitive test of the existence of the KS term. Unfortunately, attempts to observe the other resonances by increasing the temperature failed because the strong increase in the absorption led to an undetectable transmission.

The values of D deduced from the MST and from our EPR data will be affected if the KS term is included in the data analysis. In both cases, D will increase by 1% relative to the values quoted above, which were based on the conventional SH. This small change is well within the quoted uncertainties.

ACKNOWLEDGMENTS

We are grateful to A. Twardowski, Z. Wilamowski, and V. Orera for useful discussions. This work was supported by CNPq Grant Nos. 300.477/92-9, 910.071/92-6, and 460.675/92-1, by CNRS, and by NSF Grant Nos. DMR-9219727 and INT-9216424.

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