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Magnetic susceptibility of diluted magnetic semiconductor alloys $Cd_{1-x}Co_xS$ in the temperature range 40 mK $\leq T \leq$ 400 K

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The magnetic susceptibility of $Cd_{1-x}Co_xS$ has been measured over the temperature range 40 mK $\leq T \leq 400$ K for alloy compositions $0.0016 \leq x \leq 0.082$. The value of the effective exchange integral was obtained from the susceptibility data using the pair-correlation approximation and the mean-field approach, yielding $J_{\text{eff}}/k_B = -22 \pm 4$ K and -20 ± 4 K, respectively. The dependence of χ on T indicates the presence of a small temperature-independent contribution, which has been found to be consistent with the prediction of the crystal-field model for a Co^{2+} ion in a wurtzite-structure lattice. Results of the crystal-field model, together with the pair-correlation approximation, were also successfully applied to describe the susceptibility anisotropy observed at very low temperatures.

I. INTRODUCTION

The $Cd_{1-x}Co_xS$ alloys are diluted magnetic semiconductors (DMS's) in which a fraction x of nonmagnetic cations is randomly replaced by substitutional magnetic Co^{2+} ions. The DMS material has the same crystallographic structure as the host nonmagnetic compound. The concentration of Co^{2+} ions may vary from zero to some maximum value, the maximum concentration depending on the host compound.

The main purpose of this paper is to determine the value of the exchange integral between Co^{2+} ions for $Cd_{1-x}Co_xS$, using either the pair-correlation approximation PA (also called the nearest-magnetic-neighbor pair-correlation approximation[1,2]) or the mean-field approximation. Differences between these two approaches will be discussed in Sec. II. Furthermore, we wish to verify the presence of a temperature-independent contribution to the magnetic susceptibility that has been predicted by the crystal-field theory[3,4] for a single Co^{2+} ion in a wurtzite-structure lattice.

The $Cd_{1-x}Co_xS$ wurtzite lattice structure is slightly distorted along the $\hat{c}$ axis. The c/a ratio for CdS is equal[5] to 1.623, i.e., it is smaller than that for the ideal hcp structure ($c/a = \sqrt{8/3} \cong 1.633$). This small distortion, however, combined with a uniaxial symmetry contribution to the crystal field originating from more distant ions, leads to an important change of magnetic properties, namely, to a magnetic anisotropy at low temperatures. In earlier magnetic studies of $Cd_{1-x}Co_xS$ alloys, the angular dependence of the magnetic susceptibility was measured at a fixed temperature ($T = 4.2$ K) and was found to agree with a uniaxial anisotropy model.[6] For $x \geq 0.03$, a magnetic-susceptibility maximum was observed at low temperatures and was ascribed to a transition from the paramagnetic to the spin-glass state.[7] Specific heat data for $Cd_{1-x}Co_xS$ were also reported,[8] giving a precise value of the zero-field splitting parameter D (see discussion in Sec. II).

In this paper we report systematic magnetic-susceptibility measurements on $Cd_{1-x}Co_xS$, for concentrations $x \leq 0.082$ in the temperature range from 40 mK to 400 K. Three types of experimental apparatus were necessary to cover such a wide temperature range. To cover the higher temperature range we used a vibrating-sample magnetometer (2–300 K) and a high-field superconducting quantum interference device (SQUID) magnetometer (100–400 K). At very low temperatures ($T \leq 4.2$ K), samples were attached to a cold finger of a dilution refrigerator and a standard ac mutual-inductance bridge operating at 26 Hz was used.[7] These ac susceptibility results were calibrated by comparing them with the data from the vibrating-sample magnetometer (VSM) in the overlapping temperature range from 2 to 4 K. The experimental error varied from $\Delta\chi/\chi \simeq 0.03$ (for the VSM and SQUID) ac method.

The concentration of Co^{2+} ions (except for the sample with $x \cong 0.0016$) was determined by electron microprobe analysis and by atomic absorption spectroscopy. We have observed some nonsystematic discrepancies (up to $\Delta x/x = 0.1$) between the results from the two techniques. The discrepancies are probably too large to be attributed to measuring error alone. The value of Δx was included in the uncertainties of the experimental results given in Sec. II.

II. RESULTS AND ANALYSIS

The magnetic susceptibility of the $Cd_{1-x}Co_xS$ samples cannot be interpreted without considering the effect of the crystal field on Co^{2+} ions. The calculation of energy levels of Co^{2+} in a tetrahedral-symmetry crystal field with a small admixture of the trigonal-symmetry potential has been thoroughly discussed by several authors.[3,4,9] We will therefore present only the most important results, essential for the analysis of our data.

A. Theoretical details

The ground orbital state ${}^4A_2$ is separated from the excited states by the energy[9] of $\Delta/k_B \cong 4750$ K. In the presence of the trigonal-symmetry potential, the ${}^4A_2$ state divides into two Kramers doublets. The difference in energy of these doublets is usually defined (at $H=0$) as $2D$. The energy levels can then be described by the following spin Hamiltonian[3] for a single Co^{2+} ion:

$$\mathcal{H}_S = D(S_z^2-\tfrac{5}{4})+g_\perp \mu_B S_x H_x + g_\parallel \mu_B S_z H_z + G_\perp H_x^2 + G_\parallel H_z^2 , \tag{1}$$

where

$$G_\perp = \frac{\mu_B^2}{\lambda}(0.5g_\perp - 1) = \frac{\mu_B^2}{4D}(g_\parallel - g_\perp)(g_\perp - 2) , \tag{2}$$

$$G_\parallel = \frac{\mu_B^2}{\lambda}(0.5g_\parallel - 1) = \frac{\mu_B^2}{4D}(g_\parallel - g_\perp)(g_\parallel - 2) , \tag{3}$$

μ_B is the Bohr magneton, λ is the spin-orbit coupling constant, S_x, S_z, H_x, and H_z are the components of spin and of magnetic field, and $g_\perp$ and $g_\parallel$ are g factors for $\mathbf{H}\perp\hat{c}$ and $\mathbf{H}\parallel\hat{c}$, respectively. Using the Hamiltonian given by Eq. (1), one can calculate the magnetic susceptibility, which is found to be anisotropic at low temperatures, and which at high temperatures follows a Curie law with an additional temperature-independent term[6] $G_\perp$ or $G_\parallel$:

$$\chi_{S\perp} = \frac{5g_\perp^2\mu_B^2}{4k_BT} - 2G_\perp = \frac{C_\perp}{T} + \chi_{0\perp} , \tag{4}$$

$$\chi_{S\parallel} = \frac{5g_\parallel^2\mu_B^2}{4k_BT} - 2G_\parallel = \frac{C_\parallel}{T} + \chi_{0\parallel} . \tag{5}$$

$G_\perp$ and $G_\parallel$ are both negative. These temperature-independent terms can be estimated from Eqs. (2) and (3), using the published value of the zero-field splitting parameter[8] $D/k_B = 0.97$ K, and the g factors ($g_\perp = 2.286 \pm 0.008$ and $g_\parallel = 2.269 \pm 0.005$) from electron paramagnetic resonance measurements.[10] This estimate yields $N_A G_\perp \simeq -4.7 \times 10^{-4}$ cm³/mol and $N_A G_\parallel \simeq -4.4 \times 10^{-4}$ cm³/mol, where N_A is Avogadro's number.

B. Magnetic susceptibility at high temperatures

Figure 1 shows the temperature dependence of the inverse susceptibility for a $\mathrm{Cd}_{1-x}\mathrm{Co}_x\mathrm{S}$ sample with $x=0.0075$, where the diamagnetic contribution of the Cd^{2+} and S^{2-} ions[11] ($\chi_{\mathrm{CdS}} = -0.369 \times 10^{-6}$ cm³/g) has already been subtracted. The data points do not follow a straight-line dependence predicted by a Curie-Weiss law alone. They can, however, be fit quite well to a theoretical curve when the temperature-independent term $G_\parallel$ is included (solid line in Fig. 1). A discussion of this theoretical calculation will be given below.

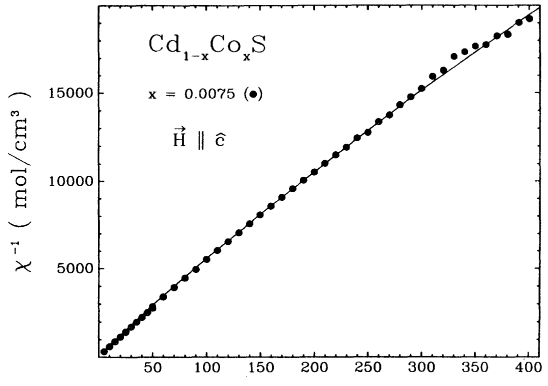

FIG. 1. Inverse molar susceptibility of $\mathrm{Cd}_{1-x}\mathrm{Co}_x\mathrm{S}$ as a function of temperature for $x=0.0075$.

Single-crystal samples of $\mathrm{Cd}_{1-x}\mathrm{Co}_x\mathrm{S}$ with a larger concentration of Co^{2+} ions have also been measured and used for determining the exchange integral. Experimental results are shown in Fig. 2 for $x=0.044$ and 0.082. The solid lines in Fig. 2 represent the best fit of the pair-correlation approximation[2] to the data. This approximation is based on the assumption that, instead of taking into account interactions between all magnetic ions, one calculates only pairwise contributions, neglecting larger clusters of magnetic ions and interactions between pairs. The total magnetic susceptibility has been calculated as a sum of contributions from pairs containing nearest neighbors (NN), next-nearest neighbors (NNN), and so on, each contribution multiplied by a probability P_i of finding a specific pair,

$$P_i(x) = (1-x)^{n_i - 1} - (1-x)^{n_i} , \tag{6}$$

$$n_i = \sum_{\nu=1}^{i} z_\nu, \quad n_0 = 0 , \tag{7}$$

where z_ν is the number of cation sites in the νth coordination sphere. The value of exchange integrals has been

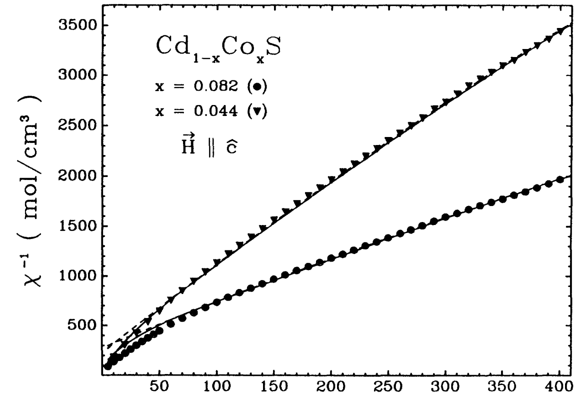

FIG. 2. Temperature dependence of the inverse susceptibility of $\mathrm{Cd}_{1-x}\mathrm{Co}_x\mathrm{S}$, $x=0.044$ and 0.082. Solid lines represent the pair-correlation approximation, whereas dashed lines are obtained from the mean-field approach.

obtained from the expression

$$J_i(R_i)=J_1\left[\frac{R_i}{R_1}\right]^{-n}, \quad i=1,2,\ldots, \tag{8}$$

where J_i is the exchange integral, R_i is the distance between NN, NNN, etc., and n is a parameter which determines how rapidly J_i decreases as a function of R_i. For the wurtzite-structure lattice, ratios R_i/R_1 are known and therefore all values of $J_i(R_i), i=1,2,\ldots$, can be calculated as a function of only two parameters: J_1 and n.

The Co^{2+}-Co^{2+} pair Hamiltonian for the wurtzite-structure symmetry of the crystal field may be written as a sum of two Hamiltonians for noninteracting ions [$\mathcal{H}_{S1}$ and $\mathcal{H}_{S2}$ given by Eq. (1)] and Heisenberg exchange term,

$$\mathcal{H}_P=\mathcal{H}_{S1}+\mathcal{H}_{S2}-2J_i\mathbf{S}_1\cdot\mathbf{S}_2 \tag{9}$$

$$\begin{aligned}&=D(S_{z1}^2+S_{z2}^2)-J_i(2S_{z1}S_{z2}+S_{+1}S_{-2}+S_{-1}S_{+2})\\&\quad+0.5g_\perp\mu_BH_x(S_{+1}+S_{+2}+S_{-1}+S_{-2})\\&\quad+g_\parallel\mu_BH_z(S_{z1}+S_{z2})+2G_\perp H_x^2+2G_\parallel H_z^2 ,\end{aligned} \tag{10}$$

where S_{+1}, S_{-1}, S_{+2}, S_{-2} are spin-shift operators for the first and second ion, respectively. Eigenvalues of the above pair Hamiltonian have been found using a numerical diagonalization of the $\mathcal{H}_P$ matrix. These eigenvalues depend on the following parameters: D, J_1, n, and on the magnetic field $\mathbf{H}$ (both its value and its direction). Two of these were taken from specific-heat results[8] ($D/k_B=0.97$ K, $n=6$) and fixed. To obtain a theoretical expression for the magnetic susceptibility, the free energy $F_i=F_i(J_i,H)$ for a pair of ith neighbors has been numerically calculated as a function of H (up to the second-order term). The pair contribution to the susceptibility may then be obtained from the well-known equation

$$\chi_i=-\left[\frac{\partial^2F_i}{\partial H^2}\right]_T \tag{11}$$

and the total susceptibility

$$\chi=\chi(T,J_1,x)=\sum_{i=1}^{N}\tfrac{1}{2}\chi_i(T,J_1)P_i(x)+\left[1-\sum_{i=1}^{N}P_i(x)\right]\chi_S , \tag{12}$$

where x is the concentration of Co^{2+} ions. The summation in Eq. (12) runs up to $N=25$. Since $J_{26},J_{27},\ldots,J_\infty \ll J_1$, we have assumed that all remaining ions contribute to the total susceptibility in the same way[6] as noninteracting ions, designating such contribution by χ_S. The only two adjustable parameters in Eq. (12) are J_1 and x. The latter was allowed to vary only within the range determined by the accuracy of the composition analysis, e.g., $x=0.083\pm0.003$. Since we intend to compare the results of the pair-correlation approximation with the mean-field approach, which includes only one effective exchange integral J_{eff}, this quantity was also calculated from[12]

$$J_{\text{eff}}z_1=\sum_{i=1}^{N}J_iz_i=J_1\sum_{i=1}^{N}z_i\left[\frac{R_i}{R_1}\right]^{-n} . \tag{13}$$

For the two concentrated samples, the best fit of Eq. (12) to the experimental data has been obtained with the following parameters: $x=0.044$, $J_{\text{eff}}/k_B=-20$ K and $x=0.082$, $J_{\text{eff}}/k_B=-26$ K. For the previously discussed dilute sample ($x=0.0075$), $J_{\text{eff}}/k_B=-20$ K has also been used. For $x=0.0075$ and 0.044 the theoretical curves obtained from the PA model agree well with the experimental data over the whole temperature range. However, for the most concentrated sample ($x=0.082$) a discrepancy has been observed for temperatures below 100 K which cannot be accounted for by an adjustment of parameters. We ascribe this discrepancy to the presence of larger clusters of Co^{2+} ions, the occurrence of which becomes more probable as x increases.

An alternative theoretical approach to the description of the magnetic interactions is the mean-field approximation.[13] This model is correct only in the high-temperature regime, i.e., when $k_BT \gg J_1$. If the mean field is applied to Eqs. (4) or (5), then one can get the following expression for the inverse susceptibility[14] of an interacting system of Co^{2+} ions:

$$\chi_\alpha^{-1}=\frac{T}{C_\alpha+\chi_{0\alpha}T}-\frac{\Theta}{C_\alpha} , \tag{14}$$

where

$$\Theta=8xS(S+1)J_{\text{eff}}/k_B=30xJ_{\text{eff}}/k_B ,$$

$$C_\alpha=(g_\alpha\mu_B)^2xS(S+1)N_A/(3k_B)\cong0.470xg_\alpha^2 ,$$

x is the concentration of Co ions, and the subscript α denotes $\perp$ or $\parallel$. If the temperature-independent term $\chi_{0\alpha}$ is equal to zero, then Eq. (14) reduces to a Curie-Weiss law. In our analysis we assume the same value of $\chi_{0\alpha}$ as for the PA, and then we fit Eq. (14) to the experimental data for $T>100$ K (dashed line in Fig. 2). In this case, the best fit has been obtained with $J_{\text{eff}}/k_B=-18$ K, $x=0.0445$ and $J_{\text{eff}}/k_B=-22$ K, $x=0.085$. The above values of J_{eff} and x are quite close to those calculated from the PA model.

The comparison of the mean-field results with the PA approach shows that the value of J_{eff} obtained from PA is systematically larger by 10–15% than that obtained from Eq. (14). The PA method has a decided advantage over the mean-field approximation at low temperatures, but is limited to low concentrations of magnetic ions ($x\leq0.1$).

C. Magnetic anisotropy in a very dilute limit

We have also measured the magnetic susceptibility of a very dilute $\mathrm{Cd}_{1-x}\mathrm{Co}_x\mathrm{S}$, $x=0.0016$, at very low temperatures, starting from $\simeq 40$ mK (Fig. 3). In this temperature range the susceptibility is strongly anisotropic and the *temperature dependence* $\chi(T)$ for $\mathbf{H}\parallel\hat{\mathbf{c}}$ is also different from that for $\mathbf{H}\perp\hat{\mathbf{c}}$. The calculation based on the PA method (depicted by the two solid lines in Fig. 3) agrees well with the experimental data. Obviously, for such a small concentration of magnetic ions, exchange interactions produce only a minor correction to the crystal-field

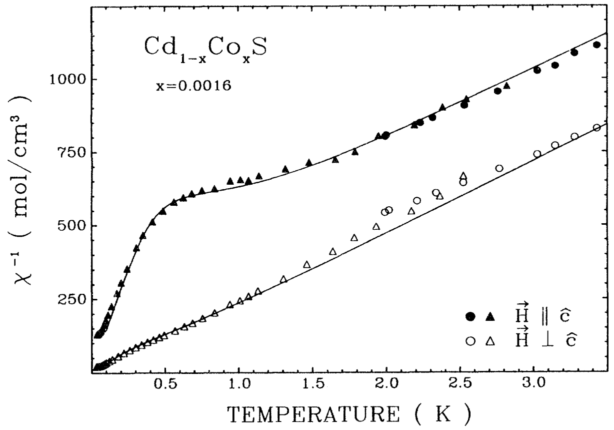

FIG. 3. Low-temperature anisotropic susceptibility of $Cd_{1-x}Co_xS$, $x=0.0016$, for $\mathbf{H}\parallel\hat{c}$ and $\mathbf{H}\perp\hat{c}$. Circles and triangles denote data obtained from VSM and ac mutual inductance magnetometers, respectively.

Hamiltonian [Eq. (1)]. Below approximately 100 mK the experimental data deviate from the theoretical curve. This effect, however, is likely to have an instrumental rather than a physical origin: the weak thermal contact between the cold finger of the dilution refrigerator and the sample (which is itself a poor thermal conductor at low temperatures) can result in the inability to achieve good thermal equilibrium. We will therefore not discuss the magnetic susceptibility for $T<100$ mK.

In addition to the rigorous numerical calculation, an intuitive explanation of the observed behavior may be provided. When the magnetic field H is parallel to the c axis and small (i.e., $g_{\parallel}\mu_B H \ll 2D$), the lower pair of energy levels corresponds to states with $S_z=\pm\frac{1}{2}$, whereas the higher pair corresponds to states with $S_z=\pm\frac{3}{2}$ [Fig. 4(a)]. At $T \ll 2D/k_B$ only the lower doublet is occupied and hence Co^{2+} ions behave like $S=\frac{1}{2}$ ions instead of $S=\frac{3}{2}$ ions. This leads to an effective reduction of the atomic magnetic moment, and therefore to a smaller susceptibility. For $\mathbf{H}\perp\hat{c}$, on the other hand, *both* doublets are represented by linear combinations of $S_z=\pm\frac{1}{2}$ and $\pm\frac{3}{2}$ states [Fig. 4(b)]. The magnetic moment is not reduced even at very low temperatures and the total susceptibility is larger than that for $\mathbf{H}\parallel\hat{c}$.

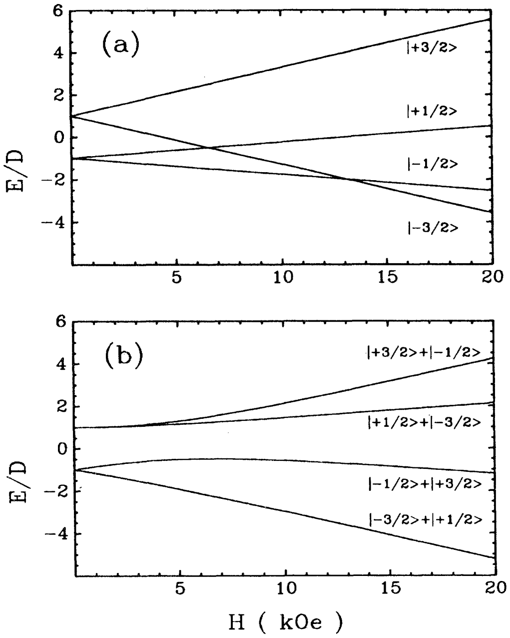

FIG. 4. Diagrams of the energy levels of a Co^{2+} ion in a wurtzite crystal structure (a) for $\mathbf{H}\parallel\hat{c}$, and (b) for $\mathbf{H}\perp\hat{c}$.

III. SUMMARY

Summarizing, we have obtained the value of the effective exchange integral $J_{\text{eff}}/k_B=-22\pm4$ K (an average of the various compositions examined). The pair-correlation approximation and the mean-field approach were found to give comparable J_{eff} for $x\leq0.1$. The temperature-independent term of the magnetic susceptibility was observed, in agreement with the crystal-field theory. And, finally, the susceptibility at very low temperatures was found to be anisotropic. The observed anisotropy can be readily interpreted using the energy-level diagram obtained from the spin Hamiltonian.

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