Magnetic susceptibility of $Zn_{1-x}Co_xS$ and $Zn_{1-x}Co_xSe$ alloys

A. Lewicki* and A. I. Schindler†

Department of Physics, Purdue University, West Lafayette, Indiana 47907

J. K. Furdyna and W. Giriat‡

Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

(Received 16 March 1989)

Static magnetic susceptibility has been investigated in two cobalt-based diluted magnetic semiconductors, $Zn_{1-x}Co_xS$ and $Zn_{1-x}Co_xSe$. The measurements were performed in the temperature range 4.2 K $\leq T \leq$ 300 K, using a vibrating-sample magnetometer. The Co concentration (determined by x-ray fluorescence) was $x \leq 0.145$ for the sulfide samples, and $x \leq 0.048$ for the selenides. The susceptibility in both systems displays a high-temperature Curie-Weiss behavior, which is qualitatively similar to that observed in Mn-based diluted magnetic semiconductors. From quantitative analysis of the high-temperature behavior within the framework of the mean-field approximation, we obtain the value of the Co^{2+} spin as 1.43 ± 0.10 for the sulfides, and 1.47 ± 0.10 for the selenides, i.e., in good agreement with the value of $\frac{3}{2}$ expected for the isolated Co^{2+} ion. The nearest-neighbor Co^{2+}-Co^{2+} exchange integral J/k_B for the sulfides and the selenides is found to be -47 ± 6 K and -54 ± 8 K, respectively. This value is at least three times as large as that for the Mn^{2+}-Mn^{2+} exchange integrals in $Zn_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xSe$ alloys. The origin of such strong antiferromagnetic coupling in Co alloys is not presently understood.

I. INTRODUCTION

Diluted magnetic semiconductors (DMS)'s—also referred to as semimagnetic semiconductors—are alloys based on II-VI semiconductor compounds in which a fraction of the nonmagnetic cations (Zn^{2+}, Cd^{2+}, or Hg^{2+}) has been randomly replaced by transition-metal ions (e.g., Mn^{2+}, Fe^{2+}, or Co^{2+}). The wide range of compositions (up to $x=0.85$ in $Zn_{1-x}Mn_xTe$) which is possible in these systems makes them unique in that one can then study the systematic evolution of magnetic properties from the very dilute to the highly concentrated limits. The results of experimental and theoretical investigations on these materials have been compiled in many reviews, for example, Refs. 1–3. Earlier studies dealt with the DMS compounds containing Mn^{2+} ions. Recently, DMS systems containing transition-metal ions such as Fe^{2+} and Co^{2+} have also been successfully synthesized. In particular, results on magnetic, electrical, and optical properties of $Cd_{1-x}Fe_xSe$ (Refs. 4–6), $Hg_{1-x}Fe_xSe$ (Refs. 4–6), $Zn_{1-x}Fe_xSe$ (Ref. 7), and $Cd_{1-x}Co_xSe$ (Ref. 8) have been published in the last three years.

In this paper we report on the magnetic properties of two Co^{2+}-based systems, $Zn_{1-x}Co_xS$ and $Zn_{1-x}Co_xSe$ systems. Single-crystal samples were prepared by chemical vapor transport. All materials studied here crystallize in the zinc-blende structure. The maximum concentrations of Co^{2+} ions are $x=0.145$ for $Zn_{1-x}Co_xS$, and $x=0.048$ for $Zn_{1-x}Co_xSe$. The precise values of x were obtained by x-ray fluorescence analysis, carried out at Goshen College. This analysis was necessary, because the real compositions differ significantly from the nominal values of x.

The x-ray powder diffraction analysis indicates no change (within the accuracy of the method) of the lattice parameter a as a function of the concentration of Co^{2+} ions. This observation is in contrast with the results for $Zn_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xSe$, where the lattice parameters obey Vegard's law, increasing linearly with x. Such difference between alloys containing cobalt and manganese can be related to the difference in the covalent (tetrahedral) radii of Zn, Co, and Mn. Namely, the increase of the lattice constant of $Zn_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xSe$ with increasing x results from the fact that the covalent radius of Mn ($r_{Mn}=1.326$ Å) is larger than that of Zn ($r_{Zn}=1.225$ Å) (Ref. 9). From the powder diffraction results on the Co-based alloys we therefore infer that the covalent radius of Co is significantly smaller than that of Mn and rather close to that of Zn.

II. Co^{2+} IONS IN THE TETRAHEDRAL CRYSTAL FIELD

In this section we provide a brief discussion of the properties of Co^{2+} ions under the action of the crystal field of a cubic tetrahedrally coordinated lattice. In both $Zn_{1-x}Co_xS$ and $Zn_{1-x}Co_xSe$ alloys the Co^{2+} ions randomly substitute for the Zn^{2+} cations. Each Co^{2+} ion is surrounded by four anions (S^{2-} or Se^{2-}), the axions forming a regular tetrahedron. The point charge model of the crystal-field theory expresses the energy-level structure of the Co^{2+} ion in a tetrahedral crystal field in terms of two parameters: the crystal-field amplitude Dq, and the spin-orbit coupling λ. Formally, the problem consists of finding the eigenvalues of a Hamiltonian operator, which is a sum of several terms. This can be performed analytically using the perturbation expansion.

The resulting energy-level diagram for a Co^{2+} ion[10,11]

is shown in Fig. 1. Using spectroscopic notation, the ground state of the Co^{2+} ion is the $^4A_2$ orbital singlet. The first $^4T_2$ excited state is separated from the ground state by an amount[10] $\Delta = 10Dq \sim 3750$ cm^{-1}. The next term—an orbital triplet $^4T_1$—is about $18Dq$ above the $^4A_2$ state. In the presence of the spin-orbit interaction, both orbital triplets split into four energy levels each, whereas the ground orbital singlet is shifted in energy, but remains unsplit (cf. Fig. 1). Only the application of a magnetic field removes the degeneracy of the ground state and splits $^4A_2$ into four levels ($S^z = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$). The value of Δ is much larger than the thermal energy at room temperature, and thus the occupations of all excited states are much smaller than that of the ground-state level. The magnetic susceptibility is therefore determined almost entirely by the properties of the singlet ground state $^4A_2$, with only a small admixture from the higher excited states. This mixing results in an increase of the g factor from the spin-only value.

The susceptibility in this system is given by a Curie law with an adjusted g factor. The values of the g factors for $Zn_{1-x}Co_xS$ and $Zn_{1-x}Co_xSe$ were determined by electron spin resonance in earlier investigations[12,13] and are $g = 2.248$ and $g = 2.274$, respectively. Except for the values of the spin S and the g factor, the behavior of the susceptibility of the Co^{2+} subsystem is of the same type as that for $3d^5$ ions (e.g., Mn^{2+}, Fe^{3+}), which have a half-filled $3d$ shell, with a singlet orbital $^6A_1$ ground state.

For completeness, we should comment at this point that some authors[11,14] point out the importance of the dy-

namic Jahn-Teller effect in explaining the optical absorption spectra of Co^{2+} ions in ZnS. This effect indeed leads to some additional splittings of the $^4T_2$ and $^4T_1$ levels, but leaves the $^4A_2$ state unchanged. Therefore, it does not influence the magnetic susceptibility of interest in this paper.

In order to analyze our experimental results, we must taken into account exchange interactions between the Co^{2+} ions. For the high-temperature regime, i.e., $k_BT \gg J$ (where J is the exchange integral between nearest Co^{2+} neighbors), the exchange interactions can be readily incorporated into the susceptibility by using the mean-field approximation. Assuming a random distribution of Co^{2+} ions over the cation sublattice, one can express the susceptibility in the form of the Curie-Weiss law[15]

$$\chi(T) = C(x)/[T - \Theta(x)] , \tag{1}$$

with the Curie constant per mole given by

$$C(x) = xN_A(g\mu_B)^2S(S+1)/3k_B , \tag{2}$$

and the Curie-Weiss temperature

$$\Theta(x) = 2xS(S+1)zJ/3k_B , \tag{3}$$

where x is the concentration of Co^{2+} ions, z is the number of cations in the first coordination sphere (12 for the zinc-blende structure), N_A is the Avogadro number, k_B is the Boltzmann constant, μ_B is the Bohr magneton, and S is the value of the spin ($S = \frac{3}{2}$ for the Co^{2+} ion). Alternatively, exactly the same expressions (1)–(3) would be obtained using the high-temperature expansion for a randomly dilute Heisenberg antiferromagnet.[16]

It should be remarked that the value of J obtained from the Curie-Weiss law is not *exactly* equal to the exchange integral between nearest neighbors, but is rather its upper estimate, since it also contains contributions from interactions between second-, third-, and higher-nearest neighbors. These contributions are usually (i.e., for other DMS materials) small, but not negligible,[17] and may amount to perhaps 10% of the total value of J.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The static susceptibility measurements in $Zn_{1-x}Co_xSe$ and $Zn_{1-x}Co_xS$ were carried out in the temperature range from 4.2 to 300 K using a vibrating-sample magnetometer, E.G.&G. model 155. The system was calibrated against a standard Ni sample with a known value of magnetic moment. We found that the susceptibility of the samples investigated is independent of the magnetic field, i.e., no saturation effects were observed up to the highest field used in the measurements (15 kOe) over the entire temperature range studied. The diamagnetic contributions for ZnS and ZnSe ($\chi_d = -0.405 \times 10^{-6}$ cm^3/g and -0.322×10^{-6} cm^3/g, respectively[18]), were subtracted from the χ data. The experimental error depended on the size of the detected signal, and varied from $\Delta\chi/\chi \approx 0.02$ to $\Delta\chi/\chi \approx 0.05$ for samples with the lowest concentration of Co^{2+} ions. In this work cgs Gaussian units are used.

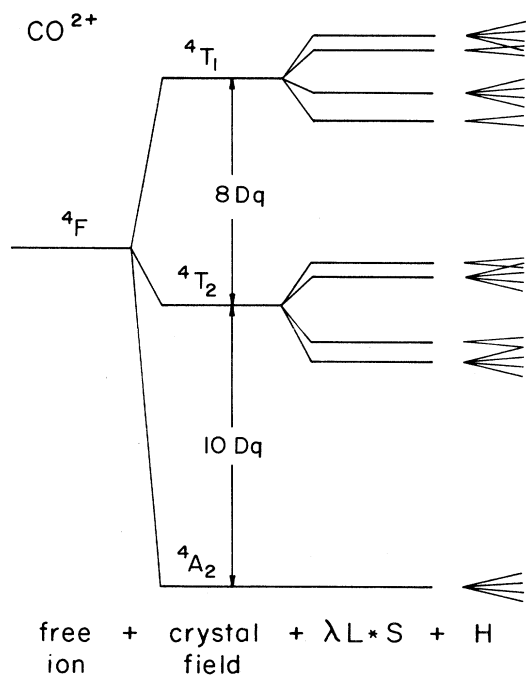The inverse molar susceptibility obtained for

FIG. 1. Energy-level diagram for states of the Co^{2+} ion in a tetrahedral crystal field (after Ref. 11). For the sake of clarity, distances between the levels are not in scale.

$Zn_{1-x}Co_xS$ is shown in Fig. 2. The straight lines represent the least-squares fits of the Curie-Weiss law to the experimental data in the high-temperature range. Below approximately 130 K, magnetic susceptibility does not follow the Curie-Weiss law. The occurrence of the deviation from the straight-line behavior at much higher temperatures than is observed for the manganese-based DMS alloys suggests a larger value of the exchange integral for $Zn_{1-x}Co_xS$ than for $Zn_{1-x}Mn_xS$ (Ref. 19).

The temperature dependence of the inverse molar susceptibility for $Zn_{1-x}Co_xSe$ is shown in Fig. 3. Here, too, χ^{-1} deviates from the Curie-Weiss behavior at a much higher temperature than in $Zn_{1-x}Mn_xSe$, indicating a higher value of J than in $Zn_{1-x}Mn_xSe$.

The least-squares fit to the Curie-Weiss law makes it possible to analyze the data quantitatively. Starting from Eqs. (2) and (3), we have determined microscopic parameters of the systems studied: the spin of the Co^{2+} ion, and the exchange integral between nearest-neighbor Co^{2+} ions. In Table I we present the results for both $Zn_{1-x}Co_xS$ and $Zn_{1-x}Co_xSe$. For comparison, we have also included parameters for $Zn_{1-x}Mn_xS$ (Ref. 19) and $Zn_{1-x}Mn_xSe$ (Ref. 20) in the same table. It is interesting to note that, whereas in the Mn-based alloys the value of J decreases with increasing anion size, this does not appear to be the case for the Co-based systems. We have observed that the value of the effective spin S, obtained from the susceptibility measurements for Co-based DMS alloys, is close to $\frac{3}{2}$. This indicates that the crystal-field model correctly predicts the total magnetic moment of the Co^{2+} ion in $Zn_{1-x}Co_xS$ and $Zn_{1-x}Co_xSe$. One notes from the table that the scatter of the J values is larger for

FIG. 3. Inverse molar magnetic susceptibility of $Zn_{1-x}Co_xSe$ as a function of temperature, for $x=0.045$ (two samples) and $x=0.048$.

the selenides than that for the sulfides. This is due to the fact that in the selenide samples available the concentration of magnetic ions was smaller ($x<0.05$), which led to a smaller signal amplitude, and consequently an increase of the experimental error in determining χ.

At low temperatures, the magnetic susceptibility continues to increase monotonically with decreasing T for all investigated samples, i.e., we do not observe the transition to the spin-glass state down to 4.2 K. It would be interesting to observe the influence of the exceptionally large exchange integral characterizing the Co-based DMS alloys on the transition temperature by extending these measurements to lower temperatures. This problem
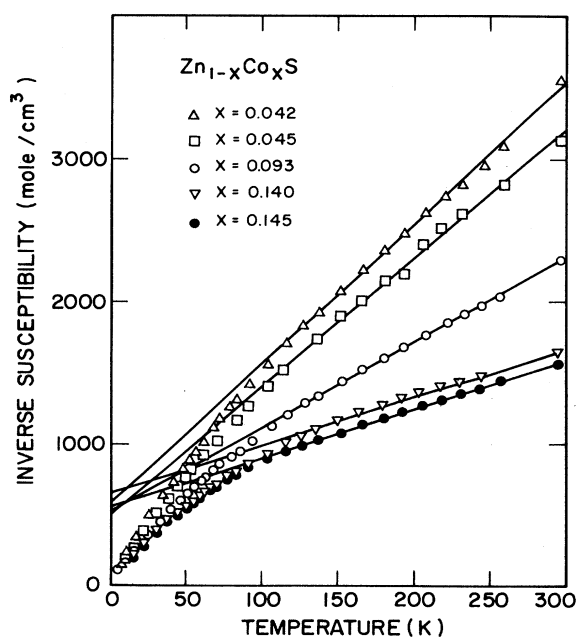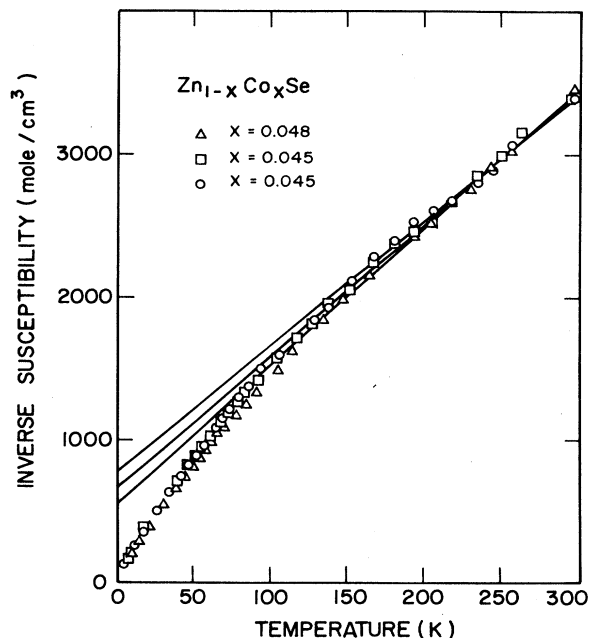

FIG. 2. Inverse molar magnetic susceptibility of $Zn_{1-x}Co_xS$ alloys as a function of temperature for various concentrations of Co^{2+} ions x.

TABLE I. Microscopic parameters of the systems studied.

Alloy	x	S	J/k_B (K)
$Zn_{1-x}Co_xS$	0.042	1.50±0.15	−46±8
	0.045	1.56±0.15	−45±10
	0.093	1.30±0.15	−44±8
	0.140	1.42±0.15	−55±10
	0.145	1.36±0.15	−45±6
(average)		(1.43±0.10)	(−47±6)
$Zn_{1-x}Mn_xS$ (Ref. 19)	≤0.025	2.5	−16.3±0.2
$Zn_{1-x}Co_xSe$	0.045	1.54±0.15	−63±11
	0.045	1.48±0.15	−53±10
	0.048	1.39±0.15	−45±10
(average)		(1.47±0.10)	(−54±8)
$Zn_{1-x}Mn_xSe$ (Ref. 20)	≤0.45	2.59±0.15	−13.5±0.95

is going to be investigated in the near future.

In summary, we have demonstrated and quantitatively investigated the antiferromagnetic interaction between Co^{2+} ions in $Zn_{1-x}Co_xS$ and $Zn_{1-x}Co_xSe$. The results reported are consistent with the general trends predicted by the theory of superexchange.[16] The values of the exchange integrals for the Co-based DMS alloys are about three times larger than those for their manganese-based counterparts. It is important to understand this striking and unambiguous behavior of the Co^{2+} systems. Theoretical work on quantitative formulation of J within the theory of superexchange would be particularly desirable at this time.

*Permanent address: Department of Solid State Physics, Akademia Górniczo-Hutnicza (AGH), PL-30-059 Kraków, Poland.

†Present address: Division of Materials Research, National Science Foundation, 1800 G Street, N.W. Washington, D.C. 20550.

‡Permanent address: Centro de Física, Instituto Venezolano de Investigaciones Científicas, Apartado 21827, Caracas 1020A, Venezuela.

[1]J. K. Furdyna and J. Kossut, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, Boston, 1988), Vol. 25.

[2]J. K. Furdyna, J. Appl. Phys. **64**, R29 (1988).

[3]R. R. Galazka and J. Kossut, in *Physics of II-VI and I-VII Compounds, Semimagnetic Semiconductors*, Vol. 17b of *Landbolt-Börnstein New Series, Group III*, edited by O. Madelung, M. Schulz, and H. Weiss (Springer,Berlin, 1982), p. 302.

[4]A. Mycielski, P. Dzwonkowska, B. Kowalski, B. A. Orlowski, M. Dobrowolska, M. Arciszewska, W. Dobrowolski, and J. M. Baranowski, J. Phys. C **19**, 3605 (1986).

[5]A. Lewicki, J. Spalek, and A. Mycielski, J. Phys. C **20**, 2005 (1987).

[6]A. Mycielski, J. Appl. Phys. **63**, 3279 (1988).

[7]A. Twardowski, M. von Ortenberg, and M. Demianiuk, J.

Cryst. Growth. **72**, 401 (1985).

[8]D. U. Bartholomew, E. K. Suh, A. K. Ramdas, S. Rodriguez, U. Debska, and J. K. Furdyna, Phys. Rev. B **39**, 5865 (1989).

[9]D. R. Yoder-Short, U. Debska, and J. K. Furdyna, J. Appl. Phys. **58**, 4056 (1985).

[10]H. A. Weakliem, J. Chem. Phys. **30**, 2117 (1962).

[11]A. J. Ryskin, A. L. Natadze, and S. A. Kazanskii, Zh. Eksp. Teor. Fiz. **64**, 910 (1973) [Sov. Phys.—JETP **37**, 462 (1973)].

[12]F. S. Ham, G. W. Ludwig, G. D. Watkins, and H. H. Woodbury, Phys. Rev. Lett. **5**, 468 (1960).

[13]J. C. M. Henning, H. van den Boom, and J. Dieleman, Philips Res. Rep. **21**, 16 (1966).

[14]P. Koidl, O. F. Schirmer, and U. Kaufmann, Phys. Rev. B **8**, 4926 (1973).

[15]J. Spalek (private communication).

[16]J. Spalek, A. Lewicki, Z. Tarnawski, J. K. Furdyna, R. R. Galazka, and Z. Obuszko, Phys. Rev. B **33**, 3407 (1986).

[17]A. Lewicki, J. Spalek, J. K. Furdyna, and R. R. Galazka, Phys. Rev. B **37**, 1860 (1988).

[18]D. J. Chadi, R. M. White, and W. A. Harrison, Phys. Rev. Lett. **35**, 1372 (1975).

[19]T. M. Giebultowicz, J. J. Rhyne, and J. K. Furdyna, J. Appl. Phys. **61**, 3537 (1987).

[20]J. K. Furdyna, N. Samarth, R. B. Frankel, and J. Spalek, Phys. Rev. B **37**, 3707 (1988).