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Magnetic Susceptibility and the Spin-Glass Transition of $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ at Low Temperatures

Y. Q. YANG,* P. H. KEESOM, AND J. K. FURDYNA

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

AND W. GIRIAT

Centro de Fisica, Instituto Venezolano de Investigaciones Cientificas,
Apartado 1827, Caracas 1010A, Venezuela

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Low-field magnetic susceptibility of the diluted magnetic semiconductors $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ was measured between 4.2 and 30 K for the Mn concentration range $0.25 < x < 0.40$. When $x > 0.25$, both of these ternary systems show a spin-glass transition in the above temperature range, as evidenced by a somewhat rounded cusp in the susceptibility and by the presence of irreversible effects. Because these materials are insulators at low temperatures, and the interactions between the Mn ions are only antiferromagnetic, the observed spin-glass behavior is attributed to frustration inherent in the *hcp* lattices of these compounds. The phase diagrams for the boundary of the paramagnetic and the spin-glass phases are presented for the two alloy systems, and the difference between the two phase diagrams is discussed.

I. Introduction

Ternary semiconductor alloys with controlled quantities of magnetic ions, referred to as diluted magnetic (or "semimagnetic") semiconductors, have recently been extensively investigated (*1*, *2*). These investigations included the studies of magnetic and/or thermal properties of $Cd_{1-x}Mn_xTe$ (*3*, *4*), $Hg_{1-x}Mn_xTe$ (*5*), $Hg_{1-x}Mn_xSe$ (*6*), and $Cd_{1-x}Mn_xSe$ (*4*, *7*).

In this paper we report low dc-field magnetic susceptibility measurements for $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$. These compounds are new members of the diluted magnetic semiconductor (DMS) family, forming single crystallographic phases with the wurtzite structure for the composition range $0 \leq x \leq 0.45$ in the case of $Cd_{1-x}Mn_xS$, and for $0.10 \leq x \leq 0.45$ in the case of $Zn_{1-x}Mn_xS$ (*8*). For $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$, the Cd and Mn or the Zn and Mn ions are distributed randomly over their respective *hcp* sublattices. In this the present compounds resemble $Cd_{1-x}Mn_xSe$, but they differ from the remaining DMS compounds studied so far, where the distribution of Mn ions is over an *fcc* sublattice.

Magnetic susceptibilities of $Zn_{1-x}Mn_xS$ and $Cd_{1-x}Mn_xS$ were studied earlier by others (*9*, *10*) in the dilute Mn limit ($x <$

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* Permanent address: Dept. of Physics, University of Science and Technology of China, Hefei, Anhui, China.

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0.075), i.e., where the materials are paramagnetic. Our susceptibility measurements were carried out for x from 0.25 to 0.40 at temperatures between 4.2 and 30 K. The samples with $x = 0.25$ remained paramagnetic down to 4.2 K. The higher concentration samples ($x \geq 0.30$) show a spin-glass transition in the temperature range covered. This is similar to the behavior of the other members of the DMS family (*3–7*).

II. Experimental Procedure

The samples of $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ were prepared by sintering. The constituent binary alloys (prereacted CdS and MnS or ZnS and MnS) were ground into a fine powder, thoroughly mixed, and pressed into a pellet, which was placed in a quartz ampule. The ampule was heated to 1200°C and kept at this temperature for 10 days. The sample so sintered was again finely ground and mixed thoroughly, and the heating process was repeated for another 10 days. This procedure ensures that the atomic fraction of Mn in the final product is the same as that of starting materials, and that the composition is homogeneous throughout the sample.

A superconducting magnet in the persistent mode provided a constant field of 15 G. A superconducting quantum interference device (rf-SQUID) measured the change in magnetization when the temperature was varied between 4.2 and 30 K. The value of the magnetization at a given temperature was measured by pulling the sample through a pair of oppositely wound coils spaced 4 cm apart. The superconducting transition of a small piece of lead (about $\frac{1}{2}$ mg) was used to calibrate the sensitivity of the system (*11*).

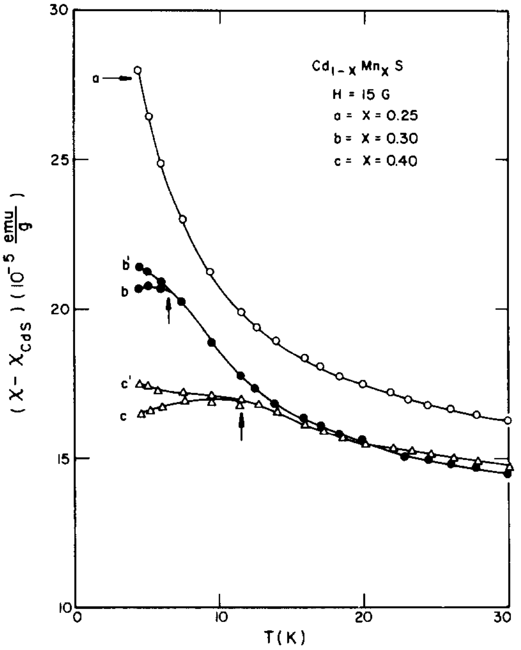

FIG. 1. Magnetic susceptibilities of $Cd_{1-x}Mn_xS$ as a function of temperature for various Mn concentrations x. Curves marked by unprimed letters correspond to zero-field-cooled (ZFC) susceptibility, and primed letters indicate the field-cooled (FC) susceptibility. No difference between FC and ZFC data is observed for curve a, indicating the absence of irreversible effects above 4.2 K for $x = 0.25$. Vertical arrows mark the point where the FC and ZFC curves converge for the remaining compositions, indicating T_g.

III. Results and Discussion

Both systems $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ show remarkable similarity in their magnetic behavior. For samples with $x \geq 0.30$ the value of the dc susceptibility $\chi = M/H$ was dependent on their past magnetic history, i.e., whether the specimen had been cooled in the presence or in the absence of the applied magnetic field. For the latter (zero-field-cooled) case, the samples were first cooled in a magnetic field of less than 0.03 G and then a field of 15 G was applied. The susceptibility for both sets of samples is shown as a function of temperature in Figs. 1 and 2. The diamagnetic contribution $\chi_d = -1.04 \times 1\text{-}^{-5}$ emu/g for CdS (*12*), and $\chi_d = -0.63 \times 10^{-5}$ emu/g for ZnS (*13*), were subtracted from the measured value. A rounded but unmistakable break in

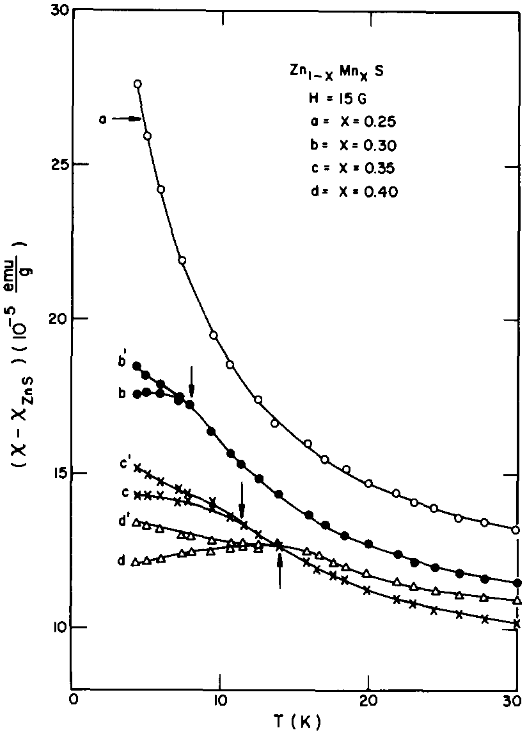

FIG. 2. Magnetic susceptibilities of $Zn_{1-x}Mn_xS$ as a function of temperature for various Mn concentrations x. Curves marked by unprimed letters correspond to zero-field-cooled (ZFC) susceptibility, and primed letters indicate the field-cooled (FC) susceptibility. No difference between FC and ZFC data is observed for curve a, indicating the absence of irreversible effects above 4.2 K for $x = 0.25$. Vertical arrows indicate T_g for the remaining compositions.

the zero-field-cooled susceptibility is observed for every sample with $x \geq 0.30$ at some temperature T_g, and is identified as the spin-glass transition. The smoothness of the χ vs T curve at the transition (a rounded "knee" rather than a sharp cusp) probably arises from small local fluctuations of the composition around the nominal value of x in the sintered samples (on the scale of ±2%). The field-cooled susceptibility is identical to the zero-field-cooled χ above T_g, but differs from the latter below T_g, indicating the presence of irreversible effects, as expected for the spin-glass phase. For samples with $x = 0.25$ we observed no knee in the susceptibility, and no difference in field-cooled and zero-field-cooled susceptibilities in our temperature range, indicating that probably the spin-glass transition takes place below 4 K. This general behavior is then very close to that of the other diluted magnetic semiconductor spin-glasses $Cd_{1-x}Mn_xTe$ (*3, 4*), $Hg_{1-x}Mn_xTe$ (*5*), $Hg_{1-x}Mn_xSe$ (*6*), $Cd_{1-x}Mn_xSe$ (*4, 7*), and $Zn_{1-x}Mn_xTe$ (*14*).

In Fig. 3 we present a plot of T_g vs x, constituting magnetic phase diagrams for $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ for $T > 4$ K. The existence of two magnetic phases is qualitatively in agreement with the theoretical analysis of De Seze (*15*), who predicted the presence of a spin-glass phase as a consequence of frustration in an *fcc* lattice when the magnetic ions interact antiferromagnetically. Although his arguments refer explicitly to an *fcc* lattice, they can be equally applied to the wurtzite crystal structure of $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$, where up to next nearest neighbors the crystal structure is essentially identical to *fcc*. The phase diagram cannot be extended above $x = 0.45$, since no single crystallographic phase of $Cd_{1-x}Mn_xS$ and

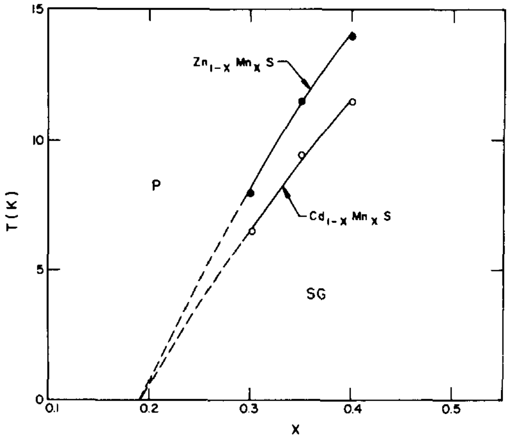

FIG. 3. Magnetic phase diagram for the system $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$. The curves separate the paramagnetic region (P) from the spin-glass region (SG). Dashed lines are extrapolated.

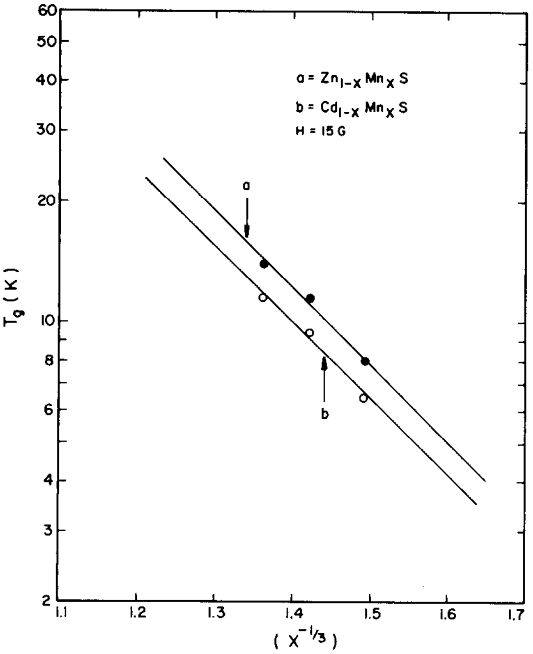

FIG. 4. Logarithm of the spin-glass transition temperature T_g vs $x^{-1/3}$ for the systems $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$.

$Zn_{1-x}Mn_xS$ exists above that concentration (*8*).

In Fig. 3 we show that for any given Mn concentration x the spin-glass transition temperature T_g for the $Zn_{1-x}Mn_xS$ is higher than for $Cd_{1-x}Mn_xS$. Now, the ionic radius of Zn^{2+} ion is 0.74 Å and is smaller than the ionic radius of 0.97 Å for Cd^{2+}. Furthermore, the size of the unit cell for ZnS (a = 3.820 Å, c = 6.260 Å) is considerably smaller than that for the CdS (a = 4.1368 Å, c = 6.7163 Å) and this difference will also hold for ternary Mn alloys based on these compounds (*8*). Since the Cd and Mn ions or the Zn and Mn ions are distributed randomly over an *hcp* sublattice, it is clear that the interacting Mn ions in $Zn_{1-x}Mn_xS$ are separated by a smaller distance, with smaller intervening group II ions, than in the case of $Cd_{1-x}Mn_xS$.

We recall from the Heisenberg model that the energy of interaction of spins $\mathbf{S}_i$ and $\mathbf{S}_j$ is represented by a term

$$U = -2J\mathbf{S}_i \cdot \mathbf{S}_j, \qquad (1)$$

where J is the exchange integral, which is related to the overlap of the charge distributions of the Mn ions i and j. Since the Mn–Mn distance in $Zn_{1-x}Mn_xS$ is smaller than in $Cd_{1-x}Mn_xS$, the exchange integral for the former compound must be greater, i.e., the energy of interaction between Mn ions in $Zn_{1-x}Mn_xS$ is stronger than in $Cd_{1-x}Mn_xS$. Thus, for the same Mn concentration, spin-glass freezing is expected to take place at a higher temperature in zinc compounds than in cadmium compounds. This interpretation is consistent with the observed difference of the spin-glass transition temperatures between $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ for the same value of x for $x \geq 0.3$. On the other hand, the *onset* of *hcp* lattice frustration responsible for the spin-glass behavior occurs at a percolation concentration which depends on the topology of the lattice, but not on specific ions involved. The fact that both the $Cd_{1-x}Mn_xS$ and the $Zn_{1-x}Mn_xS$ curves tend to extrapolate to the same $x \approx$ 0.18–0.19 at T = 0 K (dashed curves in Fig. 3) is consistent with this picture.

Recently, Escorne *et al.* (*16*) have proposed a phenomenological relation between T_g and x

$$\log T_g = Ax^{-1/3} + B, \qquad (2)$$

where A and B are positive constants. In Fig. 4 we plot log T_g vs $x^{-1/3}$ for samples $Zn_{1-x}Mn_xS$ and $Cd_{1-x}Mn_xS$. The linear relation between log T_g and $x^{-1/3}$ is fairly well satisfied in the whole range $0.30 \leq x \leq 0.40$, in agreement with the phenomenological law (2).

For completeness, we have also shown in Fig. 5 the inverse susceptibility vs T of the x = 0.25 samples of $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$, which remain paramagnetic down to 4.2 K. At higher temperatures, the χ^{-1} curves tend to a linear Curie–Weiss behavior which corresponds to antiferromag-

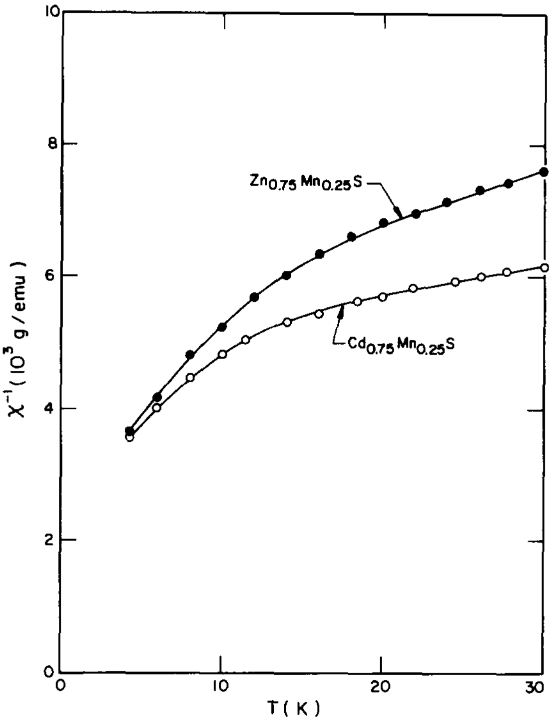

FIG. 5. Inverse susceptibility vs temperature for the $x = 0.25$ samples, which remain paramagnetic above 4.2 K. Note the characteristic downturn of χ^{-1}, common to all DMS at low temperatures.

netic Mn–Mn interaction. As the temperature decreases, χ^{-1} shows a characteristic downturn from the Curie–Weiss behavior, which has been ascribed to cluster formation (*3*). The behavior shown in Fig. 5 is typical of the paramagnetic range of all DMS compounds studied so far (*1*).

In conclusion, we have shown that the magnetic susceptibilities of $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ are quite similar to those of other members of this family of diluted magnetic semiconductors. For low values of x the system is paramagnetic. For $x > 0.30$, a spin-glass phase due to the frustration of the lattice is observed in both ternary systems above 4 K. An extrapolation of the observed T_g vs x behavior indicates that the spin-glass behavior can be expected to occur down to about $x \approx 0.2$ at progressively lower temperatures. When the Mn ions substitute for either Cd or Zn, the exchange interactions between Mn ions is different due to the difference in the ionic radii of the group II constituents. This is apparently responsible for the difference of the spin-glass transition temperatures observed for $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ at any given value of x.

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