Spin freezing below the nearest-neighbor percolation concentration in $Cd_{1-x}Mn_xTe$ and $Cd_{1-x}Mn_xSe$

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The very-low-temperature magnetization of $Cd_{1-x}Mn_xTe$ and $Cd_{1-x}Mn_xSe$ alloys shows spin-glass behavior for concentrations below the nearest-neighbor percolation limit. This is attributed to short-range exchange and dipolar interactions. New magnetic phase diagrams for both systems are presented.

I. INTRODUCTION

The generally accepted magnetic phase diagrams[1,2] of $Cd_{1-x}Mn_xTe$ and $Cd_{1-x}Mn_xSe$ show that there is spin-glass behavior below a spin-freezing temperature T_g for a wide range of Mn concentration. The phase diagrams also show that at high concentrations both systems show antiferromagnetic and mixed-crystal phases behavior while at low concentrations, below the nearest-neighbor percolation concentration $x \approx 0.20$, the two systems are believed to remain paramagnetic; the spin-glass behavior is generally accepted to be between these two concentrations ranges. However, preliminary measurements[3] below 1 K on $Cd_{1-x}Mn_xTe$ have shown that even at concentrations below $x \approx 0.20$ there is spin-glass behavior, presumably due to more distant neighbors. We report here an extensive investigation of this problem by studying the magnetization of $Cd_{1-x}Mn_xTe$ and $Cd_{1-x}Mn_xSe$ at very low temperatures for Mn concentrations in the range from $x = 0.15$ to 0.01. Contrary to general belief, spin-glass behavior is indeed observed for those samples, the spin-freezing temperatures extending down to the limit of our measurements, 0.01 K. From our results we present a new magnetic phase diagram for each system, extending it to concentrations well below the nearest-neighbor percolation limit.

$Cd_{1-x}Mn_xTe$ and $Cd_{1-x}Mn_xSe$ belong to a class of materials known as dilute magnetic semiconductors. They have been studied because of the wide range of fundamental magnetic phenomena achieved when x is varied and also because they are potentially important for devices[4] which can be controlled magnetically. Here we address a fundamental question, that of spin-glass behavior. This question has been extensively studied down to approximately 1 K using a variety of techniques such as susceptibility, EPR,[5,6] neutron scattering,[7] and specific heat[1,2,8] taken down to 0.5 K. These experiments have shown that the exchange interactions are antiferromagnetic and spin-glass effects occur in such insulating systems by a frustration mechanism.[9] The exchange interaction is a short-range one and hence it was reasonable in the above experiments to assume only nearest-neighbor interactions and use the percolation limits[10] of $x = 0.195$ for the fcc lattice (CdMnTe) and $x = 0.204$ for the hcp lattice (CdMnSe). On this model, many results were explained for both systems, and in particular, the then established, magnetic phase diagram. However, for low concentrations, problems arose in interpreting specific-heat[1] and magnetization data.[5] We show here, by going to low concentrations and low temperatures, that this model has to be modified as these systems cannot remain purely paramagnetic down to absolute zero.

II. EXPERIMENTS

Single-crystal samples[11] were prepared using a modified Bridgman technique. Their composition and homogeneity were analyzed by atomic-absorption and density measurements. The concentrations x are determined by atomic-absorption and high-temperature susceptibility measurements (assuming the spin $S = \frac{5}{2}$) and they agree to within 0.5% with the nominal concentrations. The homogeneity was also checked by EPR linewidth measurements on various parts of a large sample, and it was better than 0.1%. The samples actually originated from the same source as in Ref. 11, and were also used in the measurements of Ref. 5. In order to have a well-defined sample geometry, the crystals were ground with a mortar and pestle down to an approximate size of 50–100 μm and then packed into an epoxy holder. The sample was 2.5 mm in diameter and 6.2 mm long. Cooling was produced with a ^{3}He-^{4}He dilution refrigerator, the sample being inside the mixing chamber in the dilute phase. The magnetic flux from the sample in a magnetic field was coupled by means of a flux transformer (a static configuration) to a superconducting quantum-interference device, thus allowing the magnetization of the sample to be monitored[12] as a function of temperature, determined from the magnetization of a cerium magnesium nitrate (CMN) thermometer also located in the mixing chamber. The CMN thermometer was calibrated against a commercially calibrated germanium-resistance thermometer (Cryocal) and it had an accuracy of 2%. For the sample studied here the mag-

netization signal was large and the accuracy was better than 0.001% for magnetization changes between 4 and 0.01 K for a 5 at. % sample. The samples were cooled in a magnetic field of 1 Oe trapped in a niobium cylinder and measurements were taken on warming up, from the lowest temperature of 0.01 K, each point taking about 2–3 h at the lowest temperatures for equilibrium to be established between the sample and thermometer, and 1–2 h above the 250-mK range. Data were also taken on cooling down, but only above the spin-glass temperature. The warming data agreed very well with the cooling data, showing no thermal hysteresis above T_g.

III. RESULTS

The magnetization normalized to the field H and the concentration x is shown as a function of temperature in Fig. 1 for both systems. All the arrows indicate the spin-freezing temperatures T_g. There are no cusps here because the samples were field-cooled; the magnetometer measures dc magnetization. The "kinks" in the magnetization characterize the spin freezing, in agreement with higher concentration measurements of other groups.[5] The increase in magnetization below T_g at low magnetic fields is an interesting phenomenon attributed to "free" spins or groups of spins. All samples studied down to $x=0.01$ show spin freezing and presumably lower-concentration samples will also do the same at lower temperatures. However, analysis of magnetization data of a 0.05 at. % Mn sample in $Cd_{1-x}Mn_xTe$ of Ref. 3 shows single-impurity behavior, giving a hyperfine interaction ($A\mathbf{I}\cdot\mathbf{S}$) parameter A/k of 8.23 mK and a fine-structure parameter a/k of 4.04 mK in the fourth-order cubic term. A plot of the T_g for each concentration as determined in Fig. 1 against x gives the magnetic phase diagram for concentrations below the percolation limit. For completeness our results are joined to the $x \geq 0.20$ data from Refs. 1, 2, 5, and 13. This is shown in Fig. 2(a) for $Cd_{1-x}Mn_xTe$ and in Fig. 2(b) for $Cd_{1-x}Mn_xSe$, the telluride systems having the stronger interactions.

IV. ANALYSIS

The magnetic phase diagrams in Fig. 2 show two regimes. At concentrations above the percolation limits $x \approx 0.20$, the spin freezing is attributed to short-range antiferromagnetic exchange. It depends on the distance R between spins with a damping term β and is usually written in the form

$$J(R)=J_0(R)e^{-\beta R}. \tag{1}$$

It was first proposed by Bloembergen and Rowland[14] for insulators; the interaction between local moments is mediated by the polarization of valence-band electrons through virtual transitions. In their analysis $J(R)$ depends on $1/R^3$, while in the derivation of Abrikosov[15] the dependence is $1/R^{5/2}$. Equation (1) has also been derived by Sokel and Harrison.[16] The damping term β is equal to $[2E_g(m_e+m_h)]^{1/2}/h$ for semiconductors with a band gap E_g and electron and hole effective masses m_e and m_h respectively. Because of the strong dependence on R, $J(R)$ depends on the concentration x; it is strongly damped at distances greater than $1/\beta$.

Our observation that below the percolation limit of $x \approx 0.2$ spin freezing occurs is due to the fact the neighbors more distant than nearest neighbors start becoming important. Since the exchange interaction is strongly damped for large distances, we attribute the observed spin freezing at low concentrations to dipolar interactions between Mn spins or groups of Mn spins. Since this type of interaction is a long-range one, varying as $1/R^3$, it will be effective in coupling spins mainly at low concentrations, thus forming a dipolar spin glass. The dipole interaction is similar to a Ruderman-Kittel-Kasuya-Yosida interac-

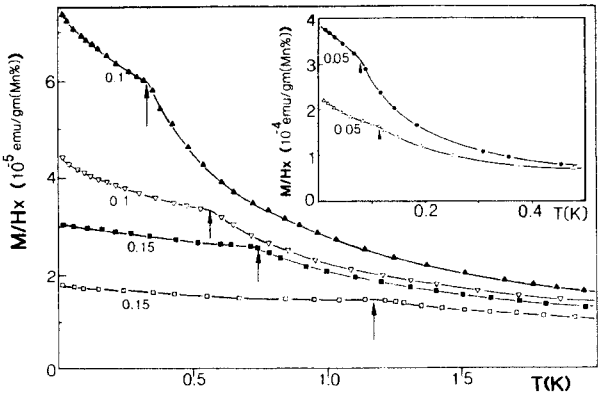

FIG. 1. Magnetization normalized to concentration x and magnetic field H of $Cd_{1-x}Mn_xTe$ (open symbols) and $Cd_{1-x}Mn_xSe$ (solid symbols) as a function of temperature. Arrows indicate spin-freezing temperatures T_g.

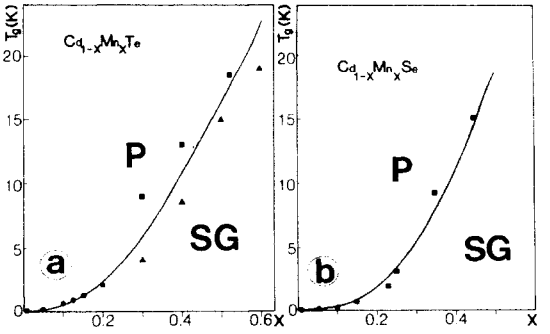

FIG. 2. Magnetic phase diagram for (a) $Cd_{1-x}Mn_xTe$ and (b) $Cd_{1-x}Mn_xSe$. The squares are data from Ref. 5 and the triangles are data from Ref. 13; the circles are our data. The solid line is a fit to all data using Eq. (2).

tion with competition between ferromagnetic and antiferromagnetic interactions and it has a $1/R^3$ dependence, thus leading to spin-glass behavior. To verify our hypothesis that we have an exchange and dipolar spin glass, we fit the complete magnetic phase diagram for both systems to

$$T_g = Ax + Bx \exp[-\alpha(x)x^{-1/3}] . \quad (2)$$

Here the first term is due to dipolar interactions and since it has a $1/R^3$ dependence it will vary as x, while the second term is due to the short-range exchange as presented in Eq. (1). The damping term α (proportional to β) varies with x because the energy gap E_g depends[17,18] on x. The parameters A and B are related to the dipole interaction and the exchange interaction, respectively. The best fit over the concentration ranges presented in Fig. 2 is achieved with $A=1.6$ K and $B=2.9\times10^4$ K for $Cd_{1-x}Mn_xSe$, and $A=2.4$ K and $B=7.2\times10^3$ K for $Cd_{1-x}Mn_xTe$. We have used, for the Se compound,[17]

$$\alpha(x)=3.3[E_g(x)]^{1/2} = 3.3(1.82+1.57x)^{1/2} , \quad (3)$$

and for the Te compound,[18]

$$\alpha(x)=2.8[E_g(x)]^{1/2} = 2.8(1.6+1.59x)^{1/2} , \quad (4)$$

neglecting the concentration dependence of the effective masses as it is small. The solid lines in Figs. 2(a) and 2(b) show the fit to Eq. (2) with the above parameters. The agreement is excellent and it does support the model that we proposed for the two types of spin-glass behavior, dipolar and exchange, the importance of each depending on the concentration range.

The values obtained in fitting the data are reasonable. For $Cd_{1-x}Mn_xTe$, Escorne *et al.*[13] obtain $\alpha=5.63$, which is higher than our value of 3.9 for $x=0.2$, as they did not consider the dipolar contribution. Magnetization measurements[19] on $Cd_{1-x}Zn_yMn_xTe$ at $y=0$ lead to a value of $\alpha\approx4.2$. A theoretical evaluation of $\alpha(x)$ using the expression for β presented earlier here (and with $m_e=m_0$ and the lattice constant $a=6.46$ Å) gives $0.43(1.6+1.59x)^{1/2}$, while we obtain experimentally $2.8(1.6+1.59x)^{1/2}$, implying that stronger exchange contributions may exist. The dipolar part also gives reasonable values, of the right order of magnitude, since a dipolar energy $3\mu^2/R_0^3$ corresponding to an average distance R_0, between two Mn magnetic dipoles μ, usually given by $\frac{4}{3}\pi(R_0/2)^3=a^3/4x$ for a fcc lattice of lattice constant a, is approximately $0.5Kx$; we measure $2.4Kx$ for the $Cd_{1-x}Mn_xTe$ system. A more precise value for the dipolar calculation would require the sum over all dipoles in a random distribution for the cubic structure of CdMnTe and for the hexagonal structure of CdMnSe. The nearest-neighbor separation[6] is 4.57 Å in $Cd_{1-x}Mn_xTe$ at $x=0.10$, while it is 4.28 Å in $Cd_{1-x}Mn_xSe$, at $x=0.08$. Hence, the dipolar interaction is comparable in both systems. It is difficult to be more precise at this point since our calculations at T_g are based on our low-x results and on the high-x values obtained from other groups, and those values have a large scatter. Within the experimental values of the magnetic phase diagram presented in Fig. 2, the dipolar interaction is equal to the exchange interaction at a concentration $x=0.10$ for $Cd_{1-x}Mn_xTe$.

V. CONCLUSIONS

We have presented data which have produced a new magnetic phase diagram for CdMnTe and CdMnSe, extending it to concentrations far below the nearest-neighbor percolation value. A model is presented to explain the new phase diagrams and it is based on Eq. (2). It is a phenomenological model and more work should be done to relate the parameters in Eq. (2) to the microscopic and structural characteristics of the system.

The temperature dependence of EPR linewidth data down to 1.4 K led to the suggestion[5] of spin-freezing temperatures T_g below 1 K for concentrations x ranging from 0.05 to 0.15, in agreement with the results presented here and the early preliminary results.[3] It is important that a wide range of concentrations be covered to get a clear manifestation of the model presented here. Over a small range of concentrations the data show a x^2 dependence[20] for T_g (with no physical justification), or they can be fitted,[19] at high concentrations, to only exchange interactions.

Our model can be used to explain the results of other groups in this field; the specific-heat data of Galazka *et al.*[1] for $Cd_{1-x}Mn_xTe$ at $x=0.10$ have an unexpected behavior and a nonrandom distribution of spins had to be assumed. Based on our model, their sample is a spin glass with a T_g of 0.5 K for $x=0.10$. The spins are randomly distributed, as evidenced by our data; this fact is supported by the high-magnetic-field measurements of Shapira *et al.*[21] for $x<0.1$ and hence there is probably no need to use clusters larger than statistically predicted.

The model presented here can be used for other insulating spin-glass systems. In $Eu_xSr_{1-x}S$ dipolar spin-glass behavior has been observed below the next-nearest percolation concentration of $x=0.13$ using ac-susceptibility measurements.[22] The authors claim that in their phase-diagram T_g is proportional to x for $0\le x\le0.5$. A much better fit to their data can be achieved by using an expression similar to Eq. (2). The concept of a dipolar spin glass was introduced by Holtzberg *et al.*[23] in studies of dilute $Eu_xSr_{1-x}S$. Although there has been a discussion of cluster models for dipolar spin glasses, our results do not deal with this aspect of the problem and we have no evidence from our data for clusters. Our model could possibly be extended to other spin-glass systems;[24,25] however, considering these would take us into areas of zero-gap semiconductors and damping due to mean-free-path effects,[26] which is beyond the scope of this paper. Finally, it is interesting to note that EPR linewidth studies[27] show that the distribution of internal fields as a function of Mn concentration in $Cd_{1-x}Mn_xTe$ has a shape similar to our Fig. 2. The spin freezing due to dipolar and exchange interactions proposed here has some similarity with nuclear magnetic ordering discussed in Ref. 28.

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