PHYSICAL REVIEW B VOLUME 25, NUMBER 7 1 APRIL 1982

Spin-glass versus antiferromagnetic clustering in $Cd_{1-x}Mn_xTe$

M. Escorne
Laboratoire de Physique des Solides, Centre National de la Recherche Scientifique
1 Place A. Briand, 92190 Meudon, France

A. Mauger*
Department of Physics, University of California, Irvine, California 92717
(Received 9 November 1981)

Magnetic properties of single crystals $Cd_{1-x}Mn_xTe$ $(0.05 \leq x \leq 0.5)$ have been studied. The low-field susceptibility has been measured for temperatures ranging from 0.07 to 30 K, and is compared with high-field magnetization data. It is shown that these semimagnetic semiconductors do not behave like canonical spin-glasses. A detailed analysis of the data based on a magnetic-cluster description of mictomagnetic alloys is presented. Some features, such as the particular x dependence of the freezing temperature and the coexistence of infinite and finite spin clusters in a definite range of concentrations x above the percolation threshold, are correlated to the short-range nature of the exchange interaction between Mn ions.

I. INTRODUCTION

Spin-glasses are dilute solid solutions of magnetic ions in a nonmagnetic matrix. In the past, attention has been focused on metallic spin-glasses, the matrix being, for example, a noble metal. In such a case, however, it is not always easy to separate the part of the conduction electrons from that of the localized moments, for instance in the specific heat.[1,2] Then, recently, Villain pointed out the interest to have more experimental data in insulating spin-glasses.[3] The best way to obtain them is to use frustrated sytems with only antiferromagnetic interactions, as suggested by De Sèze[4] and Aharony.[5] $Cd_{1-x}Mn_xTe$ has been considered as an insulating spin-glass of this kind, which motivated previous studies of the magnetic properties[6–9] and of the specific heat[9] on this material. Recently, we have shown that, in the range $0.2 < x < 0.6$, a cusp in the susceptibility curve occurs at a temperature T_g, depending on x according to the law[10]

$$\ln T_g = -\gamma x^{-1/3} + \beta \ , \tag{1}$$

where γ and β are positive constants, displaying a short-range magnetic interaction between the localized Mn^{2+} ions:

$$J(r) = J_0 e^{-\alpha r} \ , \qquad \alpha = \frac{\gamma}{a}\left(\frac{2\pi}{3}\right)^{1/3} \ , \tag{2}$$

where a is the lattice constant.

Our purpose is to present an investigation of the low-field magnetic susceptibility up to 30 K, which not only completes the previous studies, but also sheds some light on the freezing process in this material. The experimental results are reported in Sec. II. In particular, superparamagnetism is evidenced at $T > T_g$ for $x > 0.25$, and in the whole range of temperatures investigated $0.07 < T < 30$ K for smaller Mn concentrations. The results are analyzed in Sec. III and discussed in Sec. IV.

II. EXPERIMENTS

Single crystals $Cd_{1-x}Mn_xTe$ were grown in the zinc-blende phase by a modified Bridgman technique at the Institute of Polish Academy of Sciences (Warsaw), and at the Laboratoire de Physique des Solides at Bellevue. The compositions were determined by chemical analysis, electron microprobe analysis, and confirmed by means of the linear dependence of the free exciton energy versus the concentration x.[11] It was checked that the low-field susceptibility hereunder reported is just the same within experimental uncertainty for all samples, whatever their origin, in the whole range of Mn concentrations investigated.

Magnetic measurements were performed on a vibrating sample magnetometer at Bellevue at $T > 1.5$ K and by an extraction method at Grenoble below 1.5 K. Due to the presence of irreversible effects, the magnetization was composed of both reversible and irreversible contributions at the low magnetic fields investigated $(15 < H < 80$ G) for $x \geq 0.2$. The reversible magnetic susceptibility χ is deduced from the slope of the magnetization at low fields. The curves $\chi^{-1}(T)$ are reported in Fig. 1. For $x \geq 0.25$, susceptibility cusps are observed at temperatures

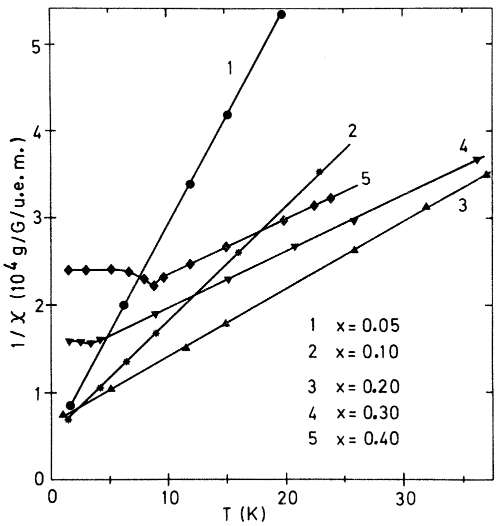

FIG. 1. Inverse of the magnetic susceptibility in $Cd_{1-x}Mn_xTe$, as a function of temperature.

which satisfy Eq. (1) with

$$\beta = 9.74, \quad \gamma = 5.63 \ , \tag{3}$$

in agreement with previous results.[10] At $x \leqslant 0.20$ no cusp was observed above 1 K. At the boundary between these two ranges of Mn concentrations, the $x = 0.25$ case is of a particular interest. First it should be noticed that the susceptibility cusp is well pronounced at 2.15 K in the $x = 0.25$ sample, as it can be seen in Fig. 2. This is the usual behavior met in systems where the dilute magnetic ions are coupled by a weak and short-range magnetic interaction. In particular, χ strongly decreases upon cooling at $T \lesssim T_g$. In contrast to the curves for the lower concentrations, $\chi(T)$ for $x \geqslant 0.30$ is much more characteristic of large-scale freezing. The curves show a rapid drop just above T_g, while below T_g, $\chi(T)$ varies much more slowly with temperature and is practically flat in the range $1\ K < T < T_g$. This feature is illustrated in Fig. 2 for $x = 0.3$ where $T_g = 4.0$ K. These results show that below T_g, the whole assembly of manganese ions is frozen at $x \geqslant 0.30$. However, the spin system is not frozen in an ordered state at such concentrations since neutron experiments and specific-heat measurements reveal that long-range antiferromagnetic ordering takes place only at $x \sim 0.6$.[9]

From our magnetic measurements, it is then possible to define a critical concentration x_c, with $0.25 < x_c < 0.30$, which makes a separation between two different magnetic behaviors at low temperatures. The variations of the remanent magnetization (RM) as a function of temperature are also quite different on both sides of $x = x_c$ as illustrated in Fig. 3, and reflect the behavior of $\chi(T)$: RM is almost temperature independent below T_g in $x = 0.30$ sample and increases upon cooling in the $x = 0.25$ sample. This parameter did not depend on time at the scale of one-half hour.

At $T > T_g$, χ^{-1} varies linearly with temperature up to about 30 K for all Mn concentrations investigated,

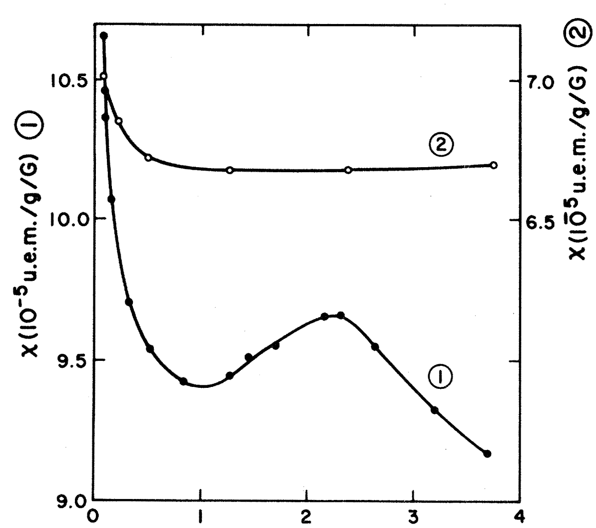

FIG. 2. Magnetic susceptibility as a function of temperature for $Cd_{1-x}Mn_xTe$ with $x = 0.25$ (curve 1) and $x = 0.30$ (curve 2).

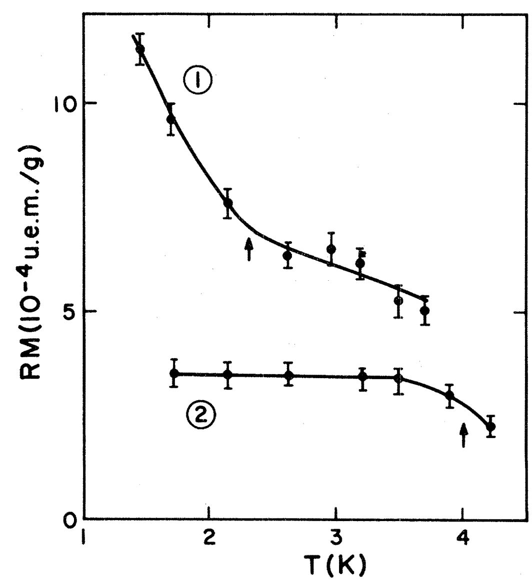

FIG. 3. Remanent magnetization RM as a function of temperature in $Cd_{1-x}Mn_xTe$ with $x = 0.25$ (curve 1) and $x = 0.30$ (curve 2). The freezing temperatures defined by the susceptibility cusps are marked by arrows.

as can be seen in Fig. 1. A Curie-Weiss law is then satisfied, which will be analyzed in Sec. III.

III. ANALYSIS

We have already emphasized the difference of the magnetic behavior on both sides of x_c at $T \lesssim T_g$. This difference still persists at very low temperature below 1 K.

A. Low-temperature regime ($T < 1$ K)

In the case $x > x_c$, a small increase of $\chi(T)$ is observed when the temperature is decreased to 0.07 K, which can be imputed to the contribution from residual paramagnetic impurities to the magnetic susceptibility. This contribution satisfies the Curie law and provides the order of magnitude for the concentration of such impurities: $N_i \sim 10^{18}$ cm^{-3}.

In the case $x < x_c$, a strong increase of χ is observed in the range $0.07 < T < 1$ K, the variations being systematically at least four times larger than for $x > x_c$. This feature is illustrated in Fig. 2. We then infer that such variations, too large to be imputed to impurities, are an intrinsic property of the material. In fact, such an increase of χ upon cooling is expected in incommensurate spin-glasses, i.e., spin-glasses where the conduction band has minima at vectors incommensurate with the lattice parameter.[12] However, our samples are crystallized in the zinc-blende structure which implies that the only maximum of interest for the conduction band is at the Γ point. Furthermore, in incommensurate spin-glasses, χ increase like $|\log T|$ or $|\log T|^3$ upon cooling. This law is not satisfied in our samples. Thus, it is clear that the behavior of $\chi(T)$ in our samples is not a spin-glass effect. In fact, the magnetic susceptibility below 1 K is the superposition of two different contributions, when impurity effects are neglected for such low concentrations $x < x_c$: (i) The contribution χ_1 arises from those of Mn spins which are frozen in an infinite antiferromagnetic cluster. As it can be seen from the data at $x > x_c$, this contribution is almost temperature independent. (ii) The contribution χ_2 comes from the fraction of the Mn spins which can be considered as loose, either because they do not belong to any cluster (single spins) or because they are located at a place where the internal fields coming from different neighbors cancel or at least do not give a resultant larger than the thermal energy $k_B T$. This situation is likely to occur at the boundary of finite spin clusters. For such spins, the Curie law is satisfied:

$$\chi_2 = \frac{C'}{T}, \quad C' = \frac{N' S(S+1) g^2 \mu_B^2}{3 k_B} \quad , \tag{4}$$

where g is the Lande factor μ_B the Bohr magneton,

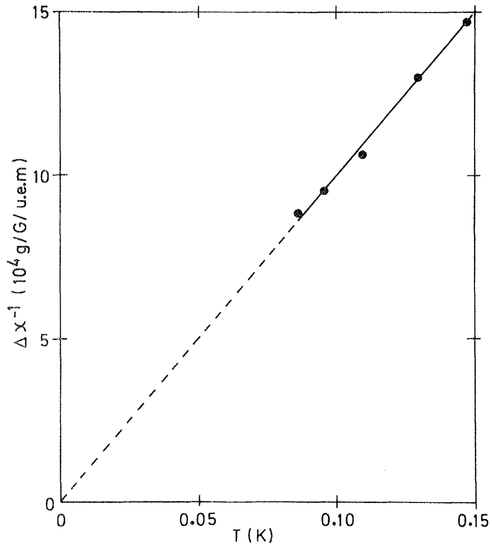

FIG. 4. Plot of $[\chi(T) - \chi(T_0)]^{-1}$ vs temperature in $Cd_{0.75}Mn_{0.25}Te$, where $T_0 = 1$ K is defined by the minimum of the susceptibility curve $\chi(T)$.

k_B the Boltzmann constant, and N' is the concentration of loose spins. Since χ_2 takes significant values only at temperatures low enough so that χ increases upon cooling, we can write $\chi_2(T_0) \simeq 0$, where T_0 is the temperature at which $\chi(T)$ goes through a minimum ($T_0 = 1$ K for $x = 0.25$). We can then express the magnetic susceptibility under the form:

$$\chi(T) - \chi(T_0) = \frac{C'}{T} \quad . \tag{5}$$

The plot of $[\chi(T) - \chi(T_0)]^{-1} = \Delta\chi^{-1}$ as a function of T is reported in Fig. 4, and shows that Eq. (5) is fairly well satisfied. From the slope of this curve, we can deduce the fraction N'/N_0 of Mn spins which are loose: for $x = 0.25$, $N'/N_0 \sim 2 \times 10^{-4}$.

B. High-temperature regime

We have shown that loose spins exist even far below T_g in the case $x < x_c$. In the same way, we can wonder whether all spins are free above T_g. The answer is most easily given by the analysis of the remanent magnetization. We can see in Fig. 3 that RM does not vanish at T_g, and irreversible processes persist up to 30 K. This illustrates that, on both sides of x_c, frozen antiferromagnetic clusters still exist in a superparamagnetic state at $T_g < T < 30$ K. In this range of temperatures the N unfrozen spins give a contribution to the magnetic susceptibility which satisfies the Curie-Weiss law as can be seen in Fig. 1:

$$\chi = \frac{N/N_0}{T + \Theta} \frac{N_0 S(S+1) g^2 \mu_B^2}{3 k_B} \quad . \tag{6}$$

TABLE I. Numerical results of magnetization and susceptibility measurements in $Cd_{1-x}Mn_xTe$. The sets $(\Theta, N/N_0)$ deduced from the Brillouin law for the high-field magnetization in columns 2 and 3 are from Ref. 14. The sets $(\Theta, N/N_0)$ deduced from the Curie law for $\chi(T)$ at low field are reported in the two last columns.

Composition x (at.%)	Magnetization Θ (K)	Parameters N/N_0	Susceptibility Θ (K)	Parameter N/N_0
5	2.29	0.62	1.8	0.59
10	3.84	0.43	4	0.41
20	7.3	0.28	8.3	0.35
30	14.9	0.21	19	0.26
40			27.8	0.21

The temperature Θ is proportional to the mean strength of the internal field to which such spins are submitted, and should not be confused with the paramagnetic Curie temperature deduced from the high-temperature susceptibility data at $T >> 30$ K, where all spins are in a paramagnetic configuration.[6] This difference is evidenced by the fact that at $T > 30$ K, a curvature of $\chi^{-1}(T)$ is observed, the situation being similar to that observed in $Hg_{1-x}Mn_xTe$.[13] The values of N/N_0 and Θ fitting the experimental cruves $\chi(T)$ are reported in Table I. Magnetization measurements on such samples at 1.5 K, made at Service National des Champs Intenses (SNCI) (Grenoble) in the range $0.2 < H < 15.5$ T have been reported elsewhere by Gaj *et al.*[14] who have shown that the magnetization curves fit the Brillouin law

$$(S_z) = \frac{N}{N_0} S B_{5/2}\left[\frac{g\mu_B S H}{k_B(T+\Theta)}\right] , \qquad (7)$$

where $B_{5/2}$ is the Brillouin function for spins $S = 5/2$. The sets $(N/N_0, \Theta)$ fitting Eq. (7) are also reported in Table I for comparison. In the special case $x = 0.3$, the magnetization curve was measured at a temperature lower than T_g so that the results cannot be directly compared with those deduced from the low-field magnetic susceptibility. For the others concentrations a very good agreeement between the two sets of parameters $(N/N_0, \Theta)$ is found. This emphasizes that the molecular-field approximation describes fairly well the magnetic properties of $Cd_{1-x}Mn_xTe$ and that Θ does not depend significantly on temperature, in the definite temperature range $T_g < T < 30$ K.

IV. DISCUSSION

To complete the above description of the magnetic properties on mictomagnetic $Cd_{1-x}Mn_xTe$ in terms of clustering in the vicinity of the temperature T_g defined by the susceptibility cusp, it is necessary to discuss the freezing processes at T_g itself in the framework of the percolation model. In the site problem, the percolation transition with the formation of an infinite spin cluster occurs at $x_p^1 \simeq 0.20$ in the fcc lattice when only first nearest neighbors are considered,[15,16] and at $x_p^2 = 0.136$ when next-nearest neighbors are also considered.[17] Oseroff *et al.*[8] have reported experimental evidence that the infinite spin cluster is observed at $x_p \sim 0.15$ in $Cd_{1-x}Mn_xTe$, so that $x_p \sim x_p^2$. This shows that the percolation theory does apply to this material, which implies that the range of the magnetic interactions is smaller than the mean distance between the Mn ions at such concentrations. This is in agreement with the model of a magnetic interaction decreasing exponentially with the distance in Eq. (2). The ratio of the exchange integrals between nearest and next-nearest neighbors, deduced from Eqs. (1)–(3) is $J_1/J_2 \simeq 8$. This shows that J_2, even small, is not negligible compared with J_1, which explains why $x_p \sim x_p^2$. However, a complex magnetic behavior is expected for manganese concentrations $x_p^2 < x < x_p^1$, because the smallness of J_2 favors the coexistence of finite spin clusters with the infinite clusters in this range of concentrations. Our results show that this coexistence is indeed observed up to x_c which compares well with x_p^2. Moreover, the difference between x_p^2 and x_c may be correlated to an anisotropic distribution of Mn ions which has been evidenced by specific-heat measurements.[9]

We have shown that a lot of order exists above T_g and a lot disorder below T_g in $Cd_{1-x}Mn_xTe$. This is well understood in the percolation model for spin-glasses and mictomagnets developed by Smith.[18] In this model, an infinite cluster occurs at T_g, but order is present inside a finite cluster above T_g and disorder is associated with the existence of finite clusters disconnected from the infinite one below T_g. Our analysis allowed us to give an estimation of the extent of the persisting disorder below T_g in terms of the ratio $N'/N_0 \lesssim 2\times10^{-4}$ of Mn which remain loose. This ratio is then very small, so that the freezing of $Cd_{1-x}Mn_xTe$ looks much like a phase transition. However, we must keep in mind that the specific-heat data show no critical behavior for the range of concentrations x which we investigated,[9] and that neutron measurements show that there is no long-range magnetic order in the low-temperature phase, in contradiction with the assertion of Oseroff *et al.,* deduced from magnetic susceptibility and electron paramagnetic resonance measurements.[8] Our own magnetic susceptibility data could be analyzed in terms of mictomagnetic compounds, without making the hypothesis of any long-range ordering whatsoever.

The magnetic properties above T_g could be understood in the framework of the molecular-field approximation. Such is not the case in metallic spin-glasses, since the oscillation of the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction at long distance lead to striking derivations of the magnetization curve from the Brillouin law, for example.[19,20]

V. CONCLUSION

The magnetic properties of $Cd_{1-x}Mn_xTe$ have been analyzed in detail in the vicinity of susceptibility cusp at the temperature T_g. The whole freezing process of Mn spins could be analyzed in terms of clustering and supports the percolation description of mictomagnets by Smith. Some specific properties such as the law $T_g(x)$, the occurrence of an infinite cluster at the percolation threshold, and the validity of a molecular-field approximation above T_g were shown to be specific features of short-range magnetic interactions decreasing exponentially upon the distance. Their generality should then overcome the particular case of $Cd_{1-x}Mn_xTe$.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Dr. R. Galazka, R. Triboulet, and G. Didier for supplying the samples. Helpful discussions of one author (A.M.) with Dr. J. L. Tholence, J. A. Gaj, and J. Souletie are also gratefully acknowledged.

---

*Permanent adress: Laboratoire de Physique des Solides, CNRS, 1 Place A. Briand, 92190 Meudon, France.

[1]W. Marshall, Phys. Rev. 118, 1519 (1960).
[2]J. Kondo, Prog. Theor. Phys. 33, 575 (1965).
[3]J. Villain, Z. Phys. B 33, 31 (1979).
[4]L. DeSeze, J. Phys. 10, L353 (1977).
[5]A. Aharony, J. Phys. C 11, L457 (1978).
[6]V. Sondermann, J. Magn. Magn. Mater. 2, 216 (1976).
[7]M. F. Deigen, V. Ya. Zevin, V. M. Maevskii, I. V. Potikevich, and B. D. Smanina, Fiz. Tverd. Tela. 9, 983 (1967) [Sov. Phys. Solid State 9, 773 (1967)].
[8]S. B. Oseroff, R. Calvo, and W. Giriat, Solid State Commun. 35, 539 (1980).
[9]R. R. Galazka, S. Nagata, and P. H. Keesom, Phys. Rev. B 22, 3344 (1980).
[10]M. Escorne, A. Mauger, R. Triboulet, and J. L. Tholence, Physica (Utrecht) 108B+C, 309 (1981).
[11]J. A. Gaj, R. R. Galazka, and M. Naurocki, Solid State Commun. 25, 193 (1978).
[12]A. A. Abrikhosov, Adv. Phys. 29, 869 (1980).
[13]U. Sondermann and E. Vogt, Physica (Utrecht) 86–88B, 419 (1977).
[14]J. A. Gaj, R. Planel, and G. Fishman, Solid State Commun. 29, 435 (1979).
[15]H. L. Frisch, J. M. Hammersley, and D. J. A. Welsch, Phys. Rev. 126, 949 (1962).
[16]M. F. Sykes and J. W. Essam, Phys. Rev. 133A, 310 (1964).
[17]C. Domb and N. W. Dalton, Proc. Phys. Soc. London 89, 859 (1966).
[18]D. A. Smith, J. Phys. 5, 2148 (1975).
[19]A. J. Larkin and D. E. Khmelnitski, Zh. Eksp. Teor. Fiz. 58, 1789 (1970) [Sov. Phys. JETP 31, 958 (1970)].
[20]K. Matho, Physica (Utrecht) 86B, 854 (1977).