Induced net spontaneous magnetization by nonmagnetic impurities in the quasi-one-dimensional antiferromagnet $(CH_3NH_3)Mn_{1-x}Cd_xCl_3\cdot 2H_2O$

A. Paduan-Filho and C. C. Becerra
Instituto de Física da Universidade de São Paulo, Caixa Postal 66318, CEP 05315-970 São Paulo, Brazil

F. Palacio
Instituto de Ciencia de Materiales de Aragon, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain
(Received 16 March 1998)

We report effects induced by the partial substitution of the Mn^{++} ions by Cd^{++} ones in the magnetic properties of the quasi-one-dimensional Heisenberg-like antiferromagnet compound $(CH_3NH_3)Mn_{1-x}Cd_xCl_3\cdot 2H_2O$ at very low fields. A three-dimensional (3D) ordering of the linear chains occurs at $T_N=4.12$ K ($x=0$). Samples with $x\sim 0.01$ were investigated. We observe the appearance of a remanent magnetization (M_r) below T_N when the sample is cooled through T_N, in a small axial magnetic field (as low as few mOe) applied along the axis of antiferromagnetic alignment. The magnitude of M_r is of the order of 1% of the sublattice magnetization of the antiferromagnet. Samples cooled in axial fields below 0.02 Oe may exhibit an inversion of the sign of M_r at a temperature below T_N. In this case the susceptibility measurements show two strong singularities: one at T_N and the second at the temperature where the inversion point occurs. It was found that this inversion is due to a polarization of the bulk of the sample by its surface that orders at $T_N=3.95$ K and causes a demagnetization field in which the bulk polarizes at a lower temperature ($T_p=3.55$ K). These results are compared with those previously observed in some diluted three-dimensional antiferromagnets and it is shown that for applied fields above 0.1 Oe, M_r obeys at temperatures below T_p the same universal behavior previously found for M_r in other low anisotropy 3D systems.
[S0163-1829(98)09229-7]

I. INTRODUCTION

The introduction of disorder in a three-dimensional antiferromagnetic system by means of the substitution of magnetic ions by nonmagnetic ones can change substantially its magnetic properties. When an antiferromagnet is cooled in a low magnetic field to a temperature below the Néel temperature T_N, no net magnetization is expected to be observed in the system. However, the substitution of magnetic ions in the lattice by nonmagnetic ones (dilution) can in principle introduce mechanisms that may favor the appearance of a net magnetization. This occurs, for example, when some diluted three-dimensional (3D) antiferromagnets are cooled below T_N in an applied magnetic field (FC). In this case the presence of random fields is at the origin of an excess magnetization (ΔM) that should be absent when the same sample is cooled in zero applied field (ZFC).[1] The magnitude of ΔM increases with a power of the applied field H and is relevant only at fields above some few kOe. Recently, the observation of phenomena, consisting in the appearance below T_N of a remanent magnetization M_r, has renewed interest on diluted antiferromagnets.[2,3] Such anomalous M_r is observed to appear when the crystal is oriented parallel to the easy axis of antiferromagnetic alignment in fields as low as few mOe. This M_r has been observed in compounds of the series $A_2Fe_{1-x}In_xCl_5\cdot H_2O$ where $A=$K or Rb (we abbreviate these systems in this paper as K-Fe/In and Rb-Fe/In, respectively) and $Mn_{1-x}Zn_xF_2$ (abbreviated as Mn/Zn). All of them are 3D systems with low magnetic anisotropy. The magnetic ion is in an S state with spin $\frac{5}{2}$. One remarkable characteristic of these compounds is that the temperature dependence of M_r below T_N seems to be x and compound independent. This universal-like behavior of M_r has been discussed previously.[4–6] The aim of this paper is to explore the extent of the referred magnetic behavior, to the case of a system with marked one-dimensional character.

Magnetic susceptibility and magnetic phase diagram studies in chainlike quasi-1D systems, with small interactions between the chains, show that the inclusion of impurities in low concentrations, of about 1%, can affect whole magnetic properties.[7,8] This occurs because the introduction of impurities limits the growth of the correlation length along the chain, thus leading to drastic effects on the long-range magnetic ordering.[8]

The 1D compound $(CH_3NH_3)MnCl_3\cdot 2H_2O$, (MMC), is a system that in principle can be adequate for the comparative purpose of the work since the magnetic ion has the same electronic structure of the 3D systems previously studied but in a lower dimensionality structure. From the behavior of the susceptibility[9,10] and from the x-ray structure,[11] it is known that the Mn ions are arranged in chains along the b direction of the crystal, coupled with an intrachain antiferromagnetic interaction of $J_{\text{intra}}/k=-3.01$ K. The susceptibility and specific-heat data at temperatures down to 1 K indicate that a 3D long-range antiferromagnetic order occurs below $T_N=4.12$ K, the magnetic moments being aligned along the a axis. This 3D order can be accounted for by an interchain interaction J' that is of the order of 10^{-2} of J_{intra}.[10] From the magnetic phase diagram[12] an estimate of the ratio of the anisotropy to the exchange field $\alpha=H_A/H_E=4\times 10^{-3}$ was

found. Thus, this compound can be described as a low anisotropy 1D system.

Small amounts of Cd, in substitution of Mn, can be introduced in the lattice. In this paper, the effect of such a dilution in the magnetic properties is investigated particularly when a very small magnetic field is applied. It is shown that a remanent magnetization develops in samples of $(CH_3NH_3)Mn_{1-x}Cd_xCl_3 \cdot 2H_2O$, (MMC/Cd), with small concentrations of Cd. This is observed below the Néel temperature when samples are cooled in fields of few Oe. Preliminary data of magnetization in the low field of MMC diluted with Cd and Cu has been published recently.[13] Special attention is given here to magnetization experiments performed at fields of a few mOe, where a phenomenon related to an inversion of the remanent magnetization was found.

II. EXPERIMENTAL METHODS

The diluted compounds $(CH_3NH_3)Mn_{1-x}Cd_xCl_3 \cdot 2H_2O$ crystallize in the monoclinic $P2_1/c$ structure.[11] The crystals are prismatic in shape, elongated along the *b* axis. The easy axis of the antiferromagnetic phase is parallel to the *a* axis. Single crystals of MMC-Cd with a concentration around $x = 0.01$ were used in the measurements. They were grown from solutions containing $(CH_3NH_3)Cl_3$ and $MnCl_2 \cdot 4H_2O$ in the molar ratio of 2:3. Small amounts of $CdCl_2 \cdot 2H_2O$ were added to the solutions. The concentration *x* was determined from the ordering temperature $T_N(x)$ of each sample following a procedure previously established for this series compound.[9] In order to identify the existence of concentration gradients, measurements were made in several samples cut from a unique crystal.

Magnetization measurements were made using a VSM (vibrating sample magnetometer) and a SQUID (superconducting quantum interference device). The ac susceptibility was measured in the SQUID magnetometer with excitation fields of 0.1 to 10 Oe at frequencies ranging from 0.1 to 1000 Hz.

Fields above 80 Oe in the VSM and 10 Oe in the SQUID were produced by means of a superconducting magnet. Lower fields were obtained by means of a small copper coil mounted with its axis coaxial with the measuring pickup coils. The local axial field at the site of the sample, due basically to the axial component of the Earth's magnetic field and to local environmental sources, was carefully compensated for by setting a very small current through the copper coil. Typically, this axial field is of the order of 0.1 Oe and can even change its sign depending on the position of nearby equipment and dewars. The value of this residual field was repeatedly checked and compensated for during the runs in order to ensure the best possible reproducibility of the results between different runs. The procedure used to set the field is described in Ref. 3. With this procedure the applied field can be set with a resolution of the order of 0.001 Oe in the sample region when using the VSM setup. Here the amplitude of the vibrating movement is of the order of 1 mm. Although with the SQUID the sensitivity is ~ 100 times higher than that of the VSM at such low fields, in the process of the measurements the sample is subjected to a movement that can be of several centimeters. The homogeneity of the field in such a length may change by several mOe and can result in differences between the two methods. As we will see, some of the effects reported in this paper occur for fields below 0.02 Oe, thus this is an important issue that cannot be ignored.

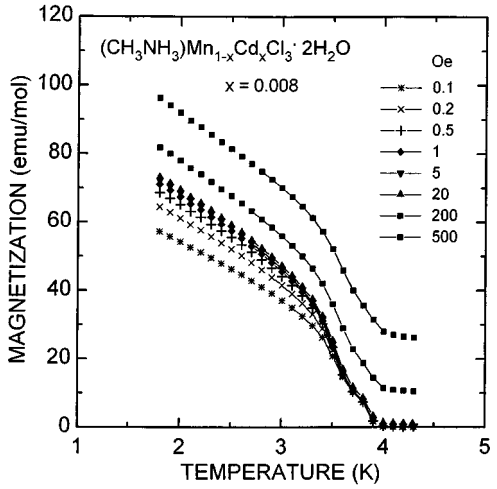


FIG. 1. Magnetization as a function of temperature for a sample of MMC/Cd with $x = 0.008$ and for different cooling axial fields applied along the axis of antiferromagnetic alignment. These measurements were made in a SQUID magnetometer.

Unless otherwise noted, the typical dimension of the crystals used were $2 \times 2 \times 3$ mm. Since very small fields of the order of a few mOe can be of importance, it is possible that the demagnetization factor play an important role in the observed effects. In some measurements, samples with different demagnetization factors, cut from the same single crystal, were also used in the experiments.

III. EXPERIMENTAL RESULTS

Figure 1 shows the measured magnetization as a function of temperature for a sample of MMC/Cd with $x = 0.008$. In these data the sample was field cooled from the paramagnetic phase at fields ranging from 0.1 to 500 Oe. The field was applied along the axis of antiferromagnetic alignment, and magnetization was measured along this same direction. The measured magnetization is $M(T) = M_r(T) + \chi_{\|}(T)H$, where $M_r(T)$ is the magnetization measured after the field *H* is set to zero (remanent magnetization) and $\chi_{\|}(T)$ is the parallel susceptibility. This last term, $(\chi_{\|}H)$, is almost negligible when compared to $M_r(T)$ for fields below 1 Oe. Even at the highest fields used (500 Oe), the $M_r(T)$ term is still larger than $\chi_{\|}H$. In Fig. 2 the temperature dependence of $M_r(T)$ for another sample of the same batch at fields between 0.08 and 8 Oe is shown. The principal features of these data can be summarized as follows: (1) a remanent magnetization M_r along the axis of easy magnetization is observed in diluted samples for temperatures below T_N. Independent checks made in undiluted samples $(x = 0)$ with the VSM magnetometer revealed that, if a remanent magnetization exists in this case, it is below the sensitivity of the instrument. No net magnetization was found in directions perpendicular to the easy axis of the sample in the diluted systems; (2) a kink in the $M_r(T)$ curve is always present at a temperature T_p slightly below T_N. For the samples shown in Figs. 1 and

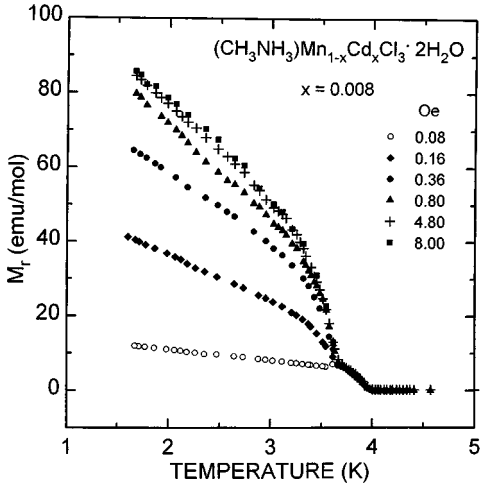


FIG. 2. Remanent magnetization M_r for an MMC/Cd sample with $x=0.008$ measured with the VSM magnetometer. These data are for fields below 8 Oe. The measurements were made after removing the applied field below the transition temperature T_N. Note the change of M_r behavior with two different regimes of saturation. Above 3.55 K, saturation occurs for cooling fields as low as 0.08 Oe.

2, T_N and T_p are, respectively, 3.9 K and 3.55 K. For the undiluted system ($x=0$), T_N is 4.12 K; (3) this kink divides the saturation behavior of $M_{r,s}$ in two regimes: for $T<T_p$, M_r has tendency to saturation for fields of the order of few Oe. This is clear in Fig. 1. For $T_p<T<T_N$, M_r saturates at fields two orders of magnitude smaller (below 0.050 Oe). This last feature is particularly evident in Fig. 2.

The in-phase χ' and out-of-phase χ'' components of the ac susceptibility χ were taken for several frequencies and applied fields. Data measured at a frequency of 1 Hz with a modulation field of 0.2 Oe at the local axial field of the laboratory are shown in Fig. 3. Two peaks are observed in χ', at 3.9 and 3.55 K. These peaks correspond to the onset of the remanent magnetization and to the kink observed in the

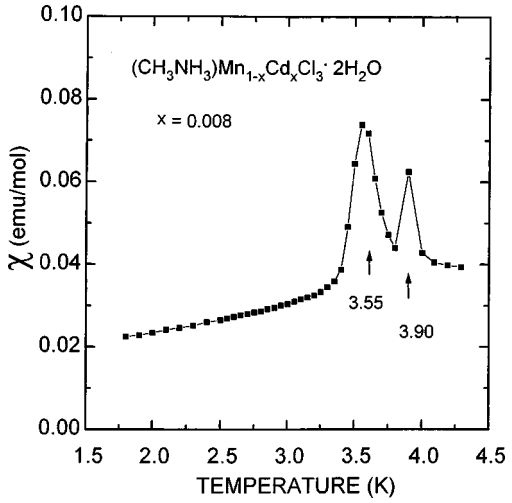


FIG. 3. ac magnetic susceptibility as a function of temperature showing the two peaks at $T_p=3.55$ K and $T_N=3.9$ K that correspond to the singularities in the M_r vs T curves.

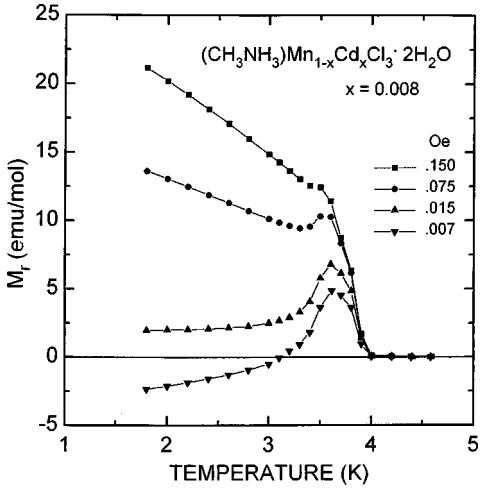


FIG. 4. M_r vs T curves for very low applied cooling fields (below 0.15 Oe). Note the inversion of M_r for the lowest field (0.007 Oe).

magnetization curves. The two peaks are observed in all the investigated diluted samples, indicating their intrinsic character. Variation of the Cd concentration only changes slightly the value of T_N and T_p.

The data shown in Figs. 1 and 2 are for cooling fields above a tenth of 1 Oe. A closer look at the behavior of M when the sample is cooled at lower fields revealed a striking behavior. The kink observed at T_p becomes more pronounced and changes into a peak as it is shown in Fig. 4 for fields between 0.007 and 0.15 Oe. At even smaller fields (less than 0.015 Oe), an inversion of the magnetization occurs where M_r changes sign at a temperature slightly below T_p. Figure 5 shows a set of data obtained for magnetic fields in the interval between $+0.007$ and -0.007 Oe. The temperature at which the magnetization reverses its sign depends on the applied field; the smaller the field, the higher the temperature. Extrapolation of curves like those in Fig. 5 indicate that, in the limit of zero field, M_r reverses at $T=3.55$ K, the same value of T_p. The appearance of a magnetization antiparallel to the applied field below the charac-

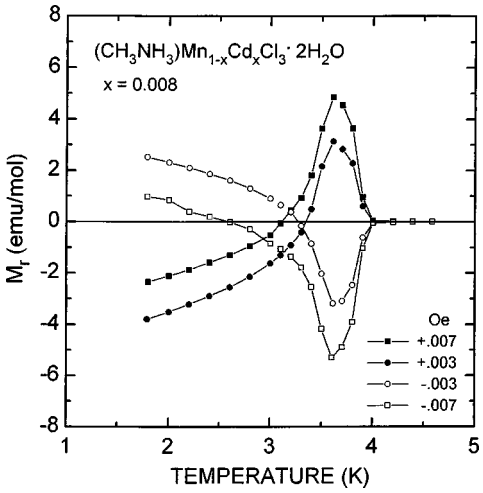


FIG. 5. M_r vs T for two values of the cooling field where inversion in M_r is observed. Note the symmetry of M_r upon inversion of the sign of the cooling field.

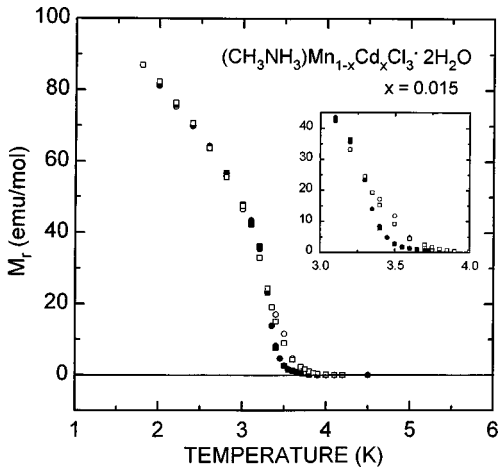


FIG. 6. Remanent magnetization for two samples cut from the same crystal but with a demagnetization factor that varies by a factor of 2.5. Open symbols refer to samples with higher demagnetization factor. The samples were cooled in a field of 0.41 Oe. Note that at low temperatures the remanent magnetization of both samples agree but that a substantial difference occurs just below T_N.

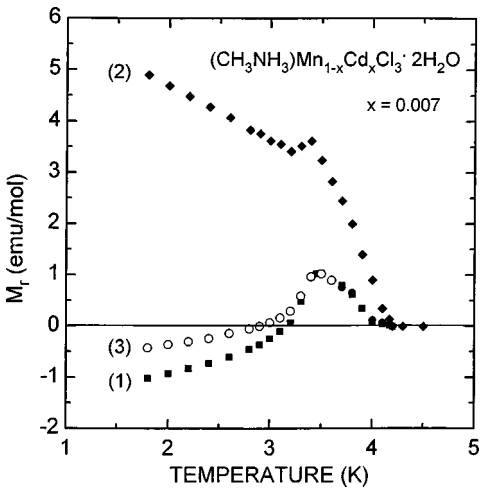


FIG. 7. In curve 1 (■) the sample was cooled in a field of 0.005 Oe. Curve 2 (♦) is for a cooling field of 0.025 Oe. In curve 3 the sample was initially cooled through T_N in the field of 0.005 Oe (●) and at $T=3.6$ K the applied field was switched to 0.025 Oe (○).

teristic temperature T_p found in MMC/Cd was carefully checked in several samples grown with different Cd concentrations ($x=0.005$ to 0.015). The typical dimensions of those samples were $2\times2\times3$ mm. It is important to emphasize that this behavior was observed in the measurements made with either the VSM or the SQUID magnetometers. In particular, the data shown in Fig. 2 were taken in the VSM. Data in Figs. 1, 4, and 5 were obtained with the SQUID magnetometer. Since the outcome of the measurements seems to be very sensitive to a very small local axial field at the sample site, the demagnetization field of the sample should be of importance. To verify this assumption, we have performed measurements in two samples with $x=0.015$ cut from the same crystal. The samples were cylindrical with a diameter of 2.5 mm, and with different lengths: one was 9 mm long while the other was 2.5 mm. Their demagnetization factor (DM) are in the ratio of 1/(2.5). Figure 6 shows the results obtained for these two samples. The magnetization for both samples is compared for the same cooling field of 0.41 Oe. The sample with higher DM develops a remanent magnetization at a slightly higher temperature than the sample with the smaller DM (see the inset in Fig. 6). As the temperature decreases, the magnetization of both samples converge towards the same values.

In order to further explore the behavior of the remanent magnetization at such very low fields, some experiments were conducted in which a sample that shows the inversion of M_r was initially cooled, starting from the paramagnetic phase, in a field below the threshold field in which M_r reversal occurs. Then, at a temperature below the onset of the remanent magnetization, the field is switched to a higher value above this threshold. Figure 7 illustrates this kind of experiment. The data are for a sample with $x=0.007$ and were taken in the VSM setup where the position of the sample oscillates within 1 mm in the measurement. Data were first taken by the process of FC at a field $H_1=0.005$ Oe (■). In this field the inversion in M occurs around $T=3.2$ K for this sample. In a second run (♦), the cooling field was set at $H_2=0.025$ Oe, a field in which no inversion is observed but where the distinctive peak at T_p is present. Finally, in a third run the sample was FC in the field $H_1=+0.005$ Oe down to $T=3.5$ K (●). Below this temperature the field was switched to $H_2=+0.025$ Oe, a field at which no inversion is observed in a FC run, and the sample was further cooled down to $T=1.75$ K (○). This third run shows that a switching field of 0.025 Oe is unable to suppress the inversion of M. The outcome of this experiment is that, once a value of the remanent magnetization is established for the axial cooling field $H_1=+0.005$ Oe, the switching of this field to $H_2=+0.025$ Oe does not lead to a change in the general behavior of the magnetization at lower temperatures but only to a slight modification of $M(T)$. However, we verified that switching to fields above 0.1 Oe does produce a change in the trend of the $M(T)$ curve and the inversion is suppressed. These results are important since they help us to understand why, in spite of the very low field in which these effects are observed, the VSM and SQUID results are consistent with each other. As already pointed out, in the measuring process at the SQUID system, the sample is subject to a movement that extends over several centimeters. Certainly the field homogeneity, although high, cannot be guaranteed within some few mOe. However, once the sample is cooled below T_N in a very low field (below 0.015 Oe for the sample whose data are in Figs. 4 and 5), only switching fields above 0.1 Oe can change the sign of the remanent moment.

Some considerations about the degree of orientation needed to observe the mentioned inversion can be formulated. The local transversal Earth's magnetic field is of the order of 0.5 Oe. Considering that an axial field of roughly ±0.025 Oe is necessary to obtain a magnetization that is always positive (or negative), and since in our setup only the axial field can be compensated, a small misalignment of the easy axis of the sample with respect to the axial field can produce a low field along the easy axis of the sample. Then, a small misalignment of the crystal of the order of $\theta\cong25/500$ rad (3°) can prevent the inversion of M. We have checked this point by slightly tilting the crystal and also by

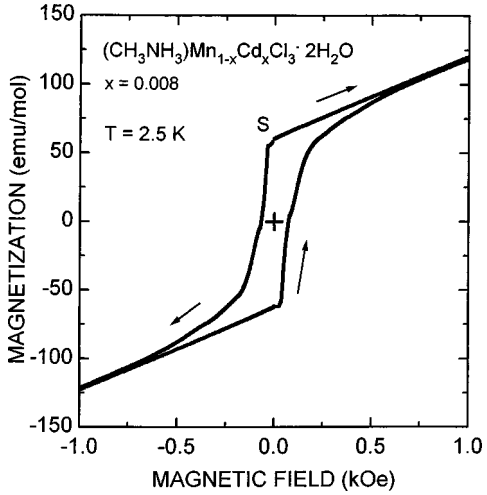


FIG. 8. Hysteresis cycle obtained for a sample with $x=0.008$ at $T=2.5$ K. The sample was cooled at a field of $H=4$ Oe. The cycle starts at S. Arrows indicate the cycling direction of the applied field H. A full saturation of M after inversion of H is achieved only at fields $H\sim\pm 700$ Oe.

introducing a transverse field provided by a set of Helmholtz coils mounted externally to the experimental setup. In this case we observed that samples carefully oriented, which do show inversion in fields below 0.025 Oe, had their inversion suppressed by transverse fields above 2 Oe provided by the Helmholtz coils. This indicates that our alignment is of the order of one to two degrees.

The behavior exhibited by the diluted samples below T_N upon field cycling is shown in the hysteresis curves of Figs. 8 and 9. Figure 8 shows the hysteresis curve obtained at $T=2.5$ K for a sample with $x=0.008$. The sample was FC in the remanent field of the superconducting coil. This field is of the order of few Oe and is sufficient to saturate M_r. The field was cycled in the interval ± 2000 Oe but only the central part of the cycle is shown in the figure. At this temperature the coercive field for this sample is roughly 70 Oe. A hysteresis curve obtained at $T=3.6$ K is shown in Fig. 9. In

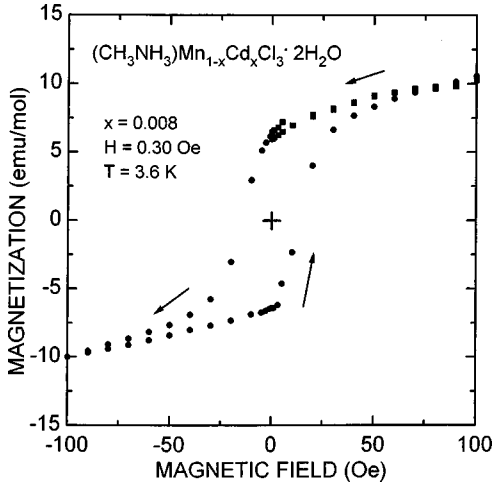
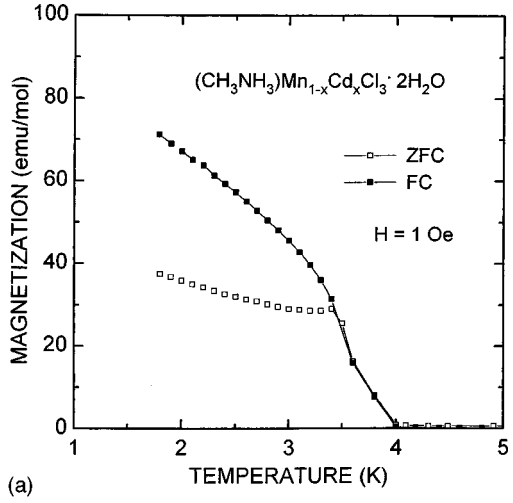


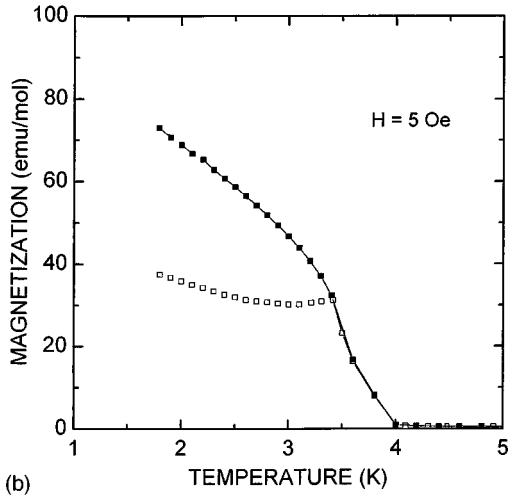
FIG. 9. Hysteresis cycle obtained at $T=3.6$ K. Starting point of the cycle and direction of cycling are indicated. The sample was cooled to 3.6 K in a field of 0.30 Oe. At this temperature saturation of M_r is already obtained for this cooling field.

this temperature region ($T_p<T<T_N$), the saturation is achieved at very low field. For this experiment the sample was cooled in a field of 0.30 Oe. This field is already sufficient to saturate the remanent magnetization at this temperature. However, the same field in the region below T_p does not saturate M_r and leads to open loops in the hysteresis cycle. The coercive field increases with decreasing the temperature, for this sample being of the order of 200 Oe at $T=1.5$ K and of about 15 Oe at $T=3.6$ K. Saturation of M_r after being reversed occurs for fields of the order of 1 kOe at $T=2.5$ K and 75 Oe at $T=3.6$ K. It should be emphasized that, in the closed loops that are always obtained when the field is high enough to saturate M_r, the magnetization is reversible in the linear regions of $M(H)$.

In another set of experiments the magnetization of the diluted samples was measured following ZFC (field heating after zero-field cooling) and FC (field heating after field cooling) procedures. The measurements were made in a diluted crystal with $x=0.008$ at applied fields in the range between 1–1000 Oe. Figures 10(a)–10(c) show representative curves corresponding to fields of 1, 5, and 100 Oe. The same experimental condition was applied for each measurement. The sample was first cooled from $T=15$ K down to 1.8 K at the local magnetic field of the laboratory once the remanence of the superconducting coil had been suppressed. In these measurements no effort was made to compensate the local axial field at the sample site, which is estimated to be of about 0.1 Oe. Once the temperature of the sample was stabilized at $T=1.8$ K, the magnetic field was set to the experimental value (1, 5, or 100 Oe for the curves in Figs. 10) and measurements were then run up to $T=7$ K (ZFC procedure). From this temperature the sample was cooled down to $T=1.8$ K with the applied field maintained at the experimental value and measurements were then run up to $T=7$ K (FC procedure). As the experimental data represented in Figs. 10 show, below a given temperature T_S, the magnetic fields in the ZFC process cannot carry the remanent magnetization up to the value attained in the FC process. Above T_S no difference is observed between the magnetization data taken with the ZFC and FC processes.

The dc magnetic susceptibility for MMC and MMC/Cd were measured using the SQUID with a field of 1000 Oe applied along the easy axis of antiferromagnetic alignment. Results for the undiluted and for the diluted ($x=0.008$) are shown in Fig. 11. The susceptibility has a broad maximum around $T=30$ K, due to the development of the antiferromagnetic correlations within the linear chains. At a lower temperature ($T_N=4.12$ K) three-dimensional long-range ordering occurs between the antiferromagnetic linear chains. In the diluted MMC/Cd sample the susceptibility showed similar temperature dependence as MMC down to the maximum of the susceptibility. Below $T=30$ K, the susceptibility starts to increase as a consequence of magnetic moments that appear due to the breaking of the chains by the impurities. The application of a magnetic field polarizes the magnetic moments coming from unpaired spins at the end of the chains. This is a well-established behavior that has been experimentally observed in other linear chain systems.[7,8,14–16] The difference between the dc susceptibility of the pure and the diluted samples $[\Delta\chi=\chi(x)-\chi(0)]$ is also represented in the figure.





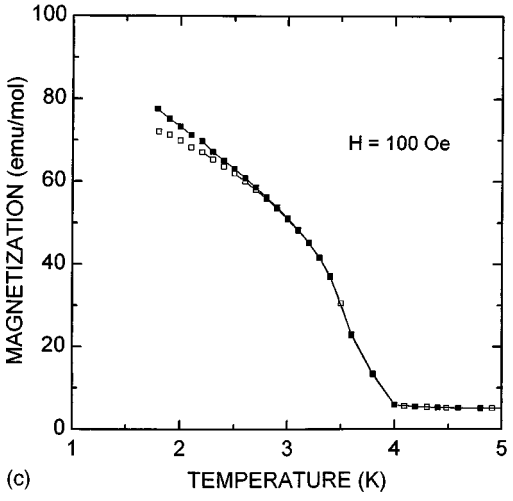


FIG. 10. FC-ZFC cycles for a MMC/Cd sample with $x = 0.008$. (a) 1 Oe; (b) 5 Oe, and (c) 100 Oe. In the ZFC process the sample was initially cooled in zero applied field to the lowest temperature and measurements were made upon heating after the field was applied at the lowest T. The temperature where the irreversibility occurs decreases with increasing field.

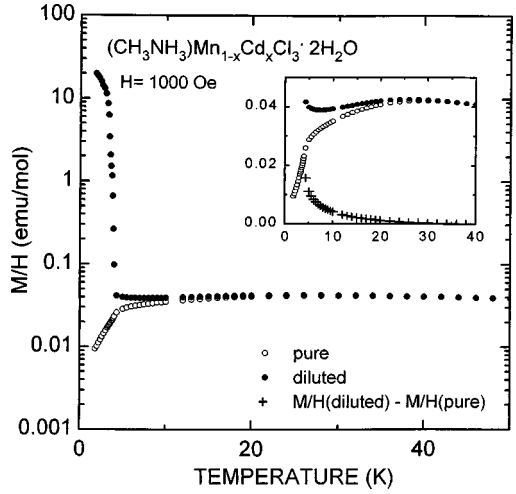


FIG. 11. dc susceptibility up to 50 K for a sample of MMC/Cd with $x = 0.008$ (full circles) and for a sample of pure MMC (open circles). The applied field was of 1000 Oe. Note that χ_{dc} for the pure sample tends to zero below T_N, while for the diluted sample tends to diverge. The difference between the dc susceptibility of the two samples $\Delta\chi$ is shown in the insert (+). Note that $\Delta\chi$ increases below 30 K as the temperature decreases.

IV. DISCUSSION

Let us summarize the principal features observed in these diluted samples: (a) below 30 K down to the ordering temperature (~ 4 K) the difference between the dc susceptibilities of the diluted and the undiluted compound increases with decreasing T. At the ordering temperature this susceptibility difference tends to diverge. (b) At the ordering temperature T_N a net magnetization starts to develop and it increases as T decreases. (c) In general, M vs T shows a characteristic kink in the curve at a temperature T_p below T_N. In the region $T_p < T < T_N$, the saturation occurs at fields of the order of 50 mOe; at lower temperatures the saturation of this magnetization occurs at higher fields, of the order of 1 Oe. (d) This characteristic kink in the M vs T curve is associated with the inversion of M at very low fields (below 0.025 Oe). These two characteristic temperatures T_N and T_p are accompanied by marked sharp singularities in the ac susceptibility. (e) If samples cut from the same crystal but with very different demagnetization factors are compared, it is observed that in the sample with higher DM an enhancement of the magnetization just below the ordering temperature occurs. (f) The field cycling experiments (hysteresis cycles) made at fixed temperatures below T_N, the field switching at very low fields and the FC-ZFC temperature cycles indicate that the observed remanent magnetization is accompanied by irreversibilities.

The observed remanent magnetization is a characteristic feature of the MMC samples in which the manganese ion is substituted by a different one. This magnetization appears only along the direction parallel to the axis of antiferromagnetic alignment. The effect does not occur only when the ion is substituted by a nonmagnetic one, but as already pointed out, substitution by Cu also originates a net magnetization in the samples.[13] In the case of Cd substituted samples discussed in this paper, the inclusion of only 1% of Cd generates a net magnetization that when saturated at the lowest

temperatures, is of the order of 0.5% of M_{sub}. The sublattice magnetization (M_{sub}) of the undiluted system is 13 900 emu/mol. This indicates that an uncompensated magnetic moment is generated by almost half of the nonmagnetic impurities. If we assume that each diamagnetic ion causes a break in the magnetic chain, the remanent magnetization could be attributed to the contribution of the uncompensated moments at the ends of the chains. Statistically, only half of the broken chains will have an uncompensated moment.

The analysis of the susceptibility difference $\Delta\chi$ between the dc susceptibilities of the diluted and undiluted compounds indicates that it follows a Curie-Weiss behavior above 5 K and diverges at the ordering temperature. The differences in the susceptibilities start to appear around 30 K; this is a temperature where the antiferromagnetic correlations in the chain start to be dominant. It seems clear that the uncompensated moments in the magnetic chain segments are responsible for the difference in the dc susceptibilities and for the remanent magnetization. An attempt to fit $\Delta\chi$ to a Curie-Weiss law was made in the region above 5 K; the obtained Curie constant is consistent with a content of 1% of Cd. Since this region is dominated by antiferromagnetic correlations within the chains, and since the interchain interactions also start to play a relevant role that will lead ultimately to the three-dimensional ordering of these chains, deviations of this behavior are expected, and the value of the fitted parameter should be viewed with caution.

The remanent magnetization observed in this linear diluted compound resembles the general shape found in other 3D diluted systems structure when a process of field cooling in low applied magnetic fields is undertaken. It was found that the resulting M_r vs T curve for the K-Fe/In,[3] Rb-Fe/In,[6] and for Mn/Zn (Ref. 2) diluted systems, follow a universal behavior. In the present case, however, some differences are observed. In the MMC/Cd a remanent magnetization appears first at $T_N = 3.9$ K, then a kink is found at $T_p = 3.55$ K, while for the 3D compounds the curve is smooth in the entire range of temperature. At very low applied fields, usually below 0.025 Oe, an inversion of M_r is observed in MMC/Cd that is not observed in the 3D samples with comparable DM factors. In addition, MMC/Cd shows two regimes of saturation. Between T_p and $T_{N,}$, M_r saturates at fields of $H \sim 0.08$ Oe while saturation below T_p arises at a field ten times larger (when completely saturated, the remanent magnetization is represented by $M_{r,s}$). In the previously mentioned 3D system the saturation occurs at fields ranging from 1 to 5 Oe.

The remanent magnetization upon field and temperature cycling, illustrated in Figs. 8 to 10, suggest that its behavior is affected by a domain structure formed in the crystal. The smooth process of the reversal of the magnetization in the hysteresis loops indicates a smooth rotation in the moments via wall movement. However, this is not always the case since the hysteresis cycle followed by crystals of K-Fe/In present strong avalanchelike effects.[17]

The magnetization curves in Fig. 10 show, for each applied field, a temperature T_s below which the magnetization measured with ZFC is lower than that measured with FC. At temperatures below T_s, the applied field cannot polarize the moments frozen through the ZFC process up to the extent reached in the presence of the field (FC). It is interesting to represent the value of T_s obtained for different applied fields.

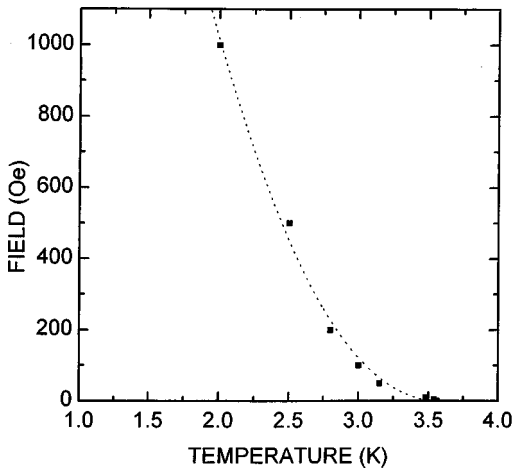


FIG. 12. Dependence of the ''irreversibility point'' T_S as a function of the applied field. The broken line is a fit to a power law $T_0 - T = H^{2/\varphi}$, with $T_0 = 3.6$ K and $\varphi \sim 4.1$.

This is illustrated in Fig. 12. The increase in the slope of the curve as the applied field increases illustrates how stiff the domain walls become as the temperature decreases. The data points can be fitted to a power law $T_0 - T = H^{2/\varphi}$, with $T_0 = 3.6$ K and $\varphi \sim 4.1$. This value for the exponent indicates that the stiffness of the domain walls in this compound increases very rapidly as the temperature decreases. The field switching experiments shown in Fig. 7 and already described also support the stiffness of the domain walls.

The 3D ordering temperature is related to the interchain exchange that in this case is of the order $10^{-2}\ J_{\text{intra}}$. Two facts should be explained by any model attempting to explain the appearance of the remanent magnetization in this system. First, the two distinctive peaks shown in the ac susceptibility and the two different saturation regimes observed in the remanent magnetization curves. The two peaks shown in the ac susceptibility corresponding to T_N and to T_p could be indicative of a transition occurring in two steps. We do not know what is the origin of this two-step process, but a simple picture to explain it can be provided as follows: in a first step, the onset of the magnetization starts to develop from the surface of the crystal; this would generate an internal local field that opposes the direction of the magnetization. Then, in a second step, the rest of the moments will align in this local field, generating an opposite magnetization. If the external applied field is higher than the local field generated by the magnetization in the first step, then it will dominate and all the moments will orient in the external axial field (H_{axial}). This simple argument can in principle explain the magnetization inversion, provided that the external field in which the initial ordering occurs is kept below 0.050 Oe. Otherwise, the uncompensated moments will align in H_{axial} at T_N and T_p. The two regimes of saturation of the magnetization can in this context be understood if we consider that the moments at the surface of the crystal should be more easily saturated than those in the bulk. If this is so, the shape of the crystal should affect the outcome of the measurements in the region near T_N.[18]

The experiments performed on samples cut from the same single crystal but with a different DM factor (see Fig. 6)

seem to support the above model. The sample with a smaller DM factor has a smaller contribution to M_r in the region ''above'' T_p. It is noted in the insert of Fig. 6 that in this particular crystal the magnetization at 3.6 K is three times larger than in the higher DM sample. This suggests that the magnetization is strongly dependent on the number of magnetic moments at the crystal surface. At low temperatures, when all the uncompensated moments in the crystal are oriented by the cooling field of 0.41 Oe, the magnetization of both samples are equal. An estimate of the demagnetization factor for the sample with the largest DM (length=2.5 mm) gives $N/(4\pi)\approx 0.3$. The corresponding demagnetization field $H_d=NM=N\rho M$, where M is the magnetization in emu/cm^3 and ρ is the density, at 3.6 K is $H_d=0.3\times 4\pi \times 1.83\times 0.02=0.134$ Oe and $H_d=0.05$ Oe at 3.8 K. The direction of this field opposes the direction of the magnetization. Thus, for applied fields below 0.025 Oe, the field where suppression of the inversion is observed, the negative demagnetization field will tend to set the overall magnetization of the sample in the region below T_p, while for applied fields higher than 0.025 Oe, it is the applied external field that will set the orientation of M.

The behavior of the saturated remanent magnetization $M_{r,s}$ below T_p seems to follow the same universal behavior previously found for other 3D systems. In Fig. 13 the data of MMC/Cd at 0.041 Oe, where M_r is already saturated, are compared with the data obtained for the 3D diluted compound $Mn_{1-x}Zn_xF_2$, $(x=0.25)$. The data is plotted in a reduced temperature scale $t=T/T_N$ and the magnetization of all the systems was normalized at $t=0.5$. The absolute remanent magnetization of the Mn/Zn sample is two orders of magnitude smaller than the MMC/Cd sample. The similarity is striking and indicates that the temperature dependence of $M_{r,s}$ has the same physical origin for all these systems whose undiluted compounds have different crystals structures and very different magnetic ordering properties.

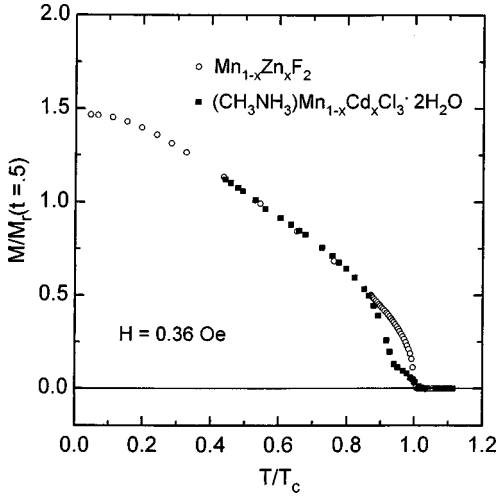


FIG. 13. Reduced magnetization for MMC/Cd with $x=0.008$ compared with the corresponding magnetization observed in Mn/Zn $(x=0.25)$. The reduced temperature $t=T/T_c$ was used to scale both curves in temperature. Apart from the region close to T_N, where presumably the surface polarizing effects are dominant, the overall agreement between the two sets of data is very good. The absolute remanent magnetization of the Mn/Zn sample is two orders of magnitude smaller than the MMC/Cd sample. The magnetization of both samples were normalized at the reduced temperature $t=0.5$.

V. CONCLUSIONS

In this work we show that a remanent magnetization appears in diluted samples of the linear chain antiferromagnet $(CN_3NH_3)Mn_{1-x}Cd_xCl_3\cdot 2H_2O$. We also show that a magnetization inversion occurs for very low fields in the mOe range. The cause of this inversion is unknown, but we advanced a simple model based on the polarization of the bulk of the sample by its surface that can in principle explain the experimental features encountered. The hysteresis cycles and the FC-ZFC behavior indicate that a structure of domains is formed in the sample at the ordering temperature. The behavior of the remanent magnetization at low temperatures is analogous to that found in other low anisotropy 3D antiferromagnets, and this may be an indication of a universal-like behavior as the origin of this magnetization. If this is the case, it is possible that the remanent magnetization could be linked to an excess of magnetization in the walls of antiferromagnetic domains. Until now, no theoretical treatments have tried to explain the excess of magnetization found in all these diluted low anisotropy antiferromagnets.

ACKNOWLEDGMENTS

This research was supported by Brazilian agencies FAPESP (Grant Nos. 96/12051-1 and 96/06208-5), CNPq, FINEP, by research Grant No. MAT97-0951 from the Comisión Interministerial de Ciencia y Tecnología (CICYT), and by cooperative grants from CCInt-USP and CNPq-CSIC (Brazil-Spain).

[1] P. Pollak, W. Kleemann, and D. P. Belanger, Phys. Rev. B **38**, 4773 (1988).
[2] T. Fries, Y. Shapira, A. Paduan-Filho, C. C. Becerra, and F. Palacio, J. Phys.: Condens. Matter **5**, 8083 (1993).
[3] C. C. Becerra, A. Paduan-Filho, T. Fries, Y. Shapira, and F. Palacio, J. Phys.: Condens. Matter **6**, 5725 (1994).
[4] F. Palacio, M. Gabas, J. Campo, C. C. Becerra, and A. Paduan-Filho, Phys. Scr. **I55**, 163 (1994).
[5] C. C. Becerra, A. Paduan-Filho, T. Fries, Y. Shapira, and F. Palacio, J. Magn. Magn. Mater. **140**, 1475 (1995).
[6] F. Palacio, M. Gabás, J. Campo, C. C. Becerra, A. Paduan-Filho, and V. B. Barbeta, Phys. Rev. B **56**, 3196 (1997).
[7] C. Dupas and J. P. Renard, Phys. Rev. B **18**, 401 (1978).
[8] N. Fujiwara, J. R. Jeitler, C. Navas, M. M. Turnbull, T. Goto, and N. Hosoito, J. Magn. Magn. Mater. **140-144**, 1663 (1995).
[9] R. Mégy, Ph.D. thesis, Universite Paris Sud-Orsay, France, 1987.
[10] S. Simizu, J. Chen, and S. A. Friedberg, J. Appl. Phys. **55**, 2398 (1984).
[11] W. Depmeier and K. Klaska, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **36**, 1065 (1980).
[12] A. Paduan-Filho and N. F. Oliveira Jr., J. Phys. C **17**, L857 (1984).

[13] A. Paduan-Filho, C. C. Becerra, and F. Palacio, J. Appl. Phys. **79**, 5236 (1996).
[14] J. C. Schouten, K. Kopinga, and W. J. M. de Jonge, J. Phys. C **15**, 783 (1982).
[15] C. Dupas, J. P. Renard, J. Seiden, and A. Cheikh-Rouhou, Physica B & C **108B**, 1319 (1981).
[16] P. M. Richards, Phys. Rev. B **14**, 1239 (1976).
[17] C. C. Becerra, V. B. Barbeta, A. Paduan-Filho, F. Palacio, J. Campo, and M. Gabás, Phys. Rev. B **56**, 3204 (1997).
[18] D. L. Mills, Phys. Rev. B **3**, 3887 (1971).