Phenomenological model for the remanent magnetization of dilute quasi-one-dimensional antiferromagnets

A. P. Vieira* and S. R. Salinas†
Instituto de Física, Universidade de São Paulo, Caixa Postal 66318, 05315-970 São Paulo, SP, Brazil
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We present a phenomenological model for the remanent magnetization at low temperatures in the quasi-one-dimensional dilute antiferromagnets $(CH_3NH_3)Mn_{1-x}Cd_xCl_3\cdot 2H_2O$ and $(CH_3)_2NH_2Mn_{1-x}Cd_xCl_3\cdot 2H_2O$. The model assumes the existence of uncompensated magnetic moments induced in the odd-sized segments generated along the Mn^{2+} chains upon dilution. These moments are further assumed to correlate ferromagnetically after removal of a cooling field. Using a (mean-field) linear-chain approximation and a reasonable set of model parameters, we are able to reproduce the approximate linear temperature dependence observed for the remanent magnetization in the real compounds.

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I. INTRODUCTION

At low temperatures, quasi-one-dimensional magnetic systems exhibit a wealth of interesting behavior, such as dimensional crossover,[1–3] random quantum paramagnetism,[4] order-by-disorder phenomena,[5,6] and Griffiths phases,[7,8] which have motivated many experimental and theoretical investigations. In most of these systems, three-dimensional (3D) order is eventually induced by interchain interactions. Taking advantage of the many analytical results available for one-dimensional model systems, this situation has been modeled in a variety of ways. Most of the existent approaches are based on linear-chain approximations,[9–11] which treat correlations along the chains in an exact way, while introducing interchain couplings via effective fields. These approximations have been quite successfully applied to pure systems and have given rise to generalized Ginzburg-Landau theories,[9,12] which account for fluctuations. Also, they have been widely used to explain disorder effects,[13–17] which are among the main topics of research on quasi-one-dimensional systems.

In the present work we consider a class of quasi-one-dimensional compounds,[18,19] represented by $(CH_3NH_3)MnCl_3\cdot 2H_2O$ (abbreviated MMC) and $(CH_3)_2NH_2MnCl_3\cdot 2H_2O$ (abbreviated DMMC), consisting of localized spin systems in which the Mn^{2+} ions (spin $S=\frac{5}{2}$) lie along the crystalline b axis, forming chains, and are antiferromagnetically coupled to each other by an intrachain interaction J/k_B around 3 K. Magnetic susceptibility and specific heat measurements[20] indicate the onset of 3D long-range order at Néel temperatures $T_N=4.12$ K for MMC and $T_N=6.36$ K for DMMC, with the magnetic moments aligning along the a axis. These temperatures are compatible with an interchain interaction $|J_\perp|\sim|J|\times 10^{-2}$. The character of this interaction is not reported in the literature. However, owing to the behavior of the materials upon dilution with nonmagnetic Cd^{2+} ions, it has been suggested (see below) that ferromagnetic interchain couplings are present. At temperatures above $T\sim 10$ K, susceptibility results are well described by a one-dimensional Heisenberg $S=\frac{5}{2}$ model, but at lower temperatures anisotropy effects (probably of dipolar origin) become relevant.[20] Calculations based on a classical anisotropic Heisenberg model, with parameters derived from experiments on DMMC, reinforce the importance of anisotropy.[15] In particular, the behavior of the correlation length along the chains is predicted to cross over from Heisenberg like to Ising like as the temperature is lowered.

Substitution of small amounts of nonmagnetic Cd^{2+} for Mn^{2+} ions induces the appearance of a remanent magnetization[18,19] below T_N, when samples are cooled in the presence of fields of a few Oe directed along the easy axis. This remanent magnetization is observed to vary linearly with temperature, except immediately below T_N, where demagnetization effects seem to be relevant.[18] Moreover, there is an excess parallel susceptibility, which is in general associated with the existence of uncompensated magnetic moments in odd-sized segments formed along the chains upon dilution.[21] Apparently, the linear temperature dependence of the remanent magnetization is of universal character, as inferred from measurements[19] performed on DMMC doped with Cd^{2+} (nonmagnetic) and Cu^{2+} $(S=\frac{1}{2})$. Experiments[22] performed on similar compounds $CsMnCl_3\cdot 2H_2O$ (CMC) and $CsMnBr_3\cdot 2H_2O$ (CMB) doped with Cu^{2+} (for which the signs of the interchain interactions are well known) revealed that a remanent magnetization appears in CMB, in which interchain couplings are ferromagnetic along one of the transversal directions and antiferromagnetic along the other; in contrast, no net magnetization is observable in CMC, where all interactions are antiferromagnetic. These experimental results, combined with the observation that some effective ferromagnetic coupling is expected in order to sustain a net remanent magnetization, have led to the idea that ferromagnetic interchain interactions should also be present in DMMC and MMC.[19] However, because of the lack of experimental data, up to now no conclusive evidence on this point seems to be available.

In this paper we introduce and discuss a phenomenological model for the low-temperature magnetic behavior of those compounds. By virtue of the previously discussed anisotropy effects, we believe the qualitative aspects to be captured by a $S=\frac{5}{2}$ Ising model, which in the pure limit (and in the simplest case) is described by the Hamiltonian

$$\mathcal{H}=J\sum_{\mathbf{r}} S_{\mathbf{r}}S_{\mathbf{r}+\mathbf{b}}+\sum_{\mathbf{r}}\sum_{\boldsymbol{\delta}} J^{\perp}_{\boldsymbol{\delta}}S_{\mathbf{r}}S_{\mathbf{r}+\boldsymbol{\delta}}, \tag{1}$$

where $J>0$, $\mathbf{r}$ is a lattice vector, $\mathbf{b}$ is the primitive vector along the crystalline b direction, $\boldsymbol{\delta}$ is a vector connecting a site to its nearest neighbors in the ac plane, $J^{\perp}_{\boldsymbol{\delta}}=J_{\perp}>0$ if $\boldsymbol{\delta}$ is parallel to the a axis, and $J^{\perp}_{\boldsymbol{\delta}}=-J_{\perp}$ if $\boldsymbol{\delta}$ is parallel to the c axis. Our approach is based on a linear-chain approximation, which treats the intrachain couplings (J) exactly, while introducing the weak interchain interactions ($J_{\perp}\ll J$) via Curie-Weiss terms connecting all spins (in such a way that a staggered effective field results, combining both ferro- and antiferromagnetic interchain interactions in a cooperative manner). At very low temperatures the chains are antiferromagnetically ordered, with a characteristic two-sublattice structure. Upon dilution, a very long chain breaks into finite segments, and uncompensated magnetic moments appear at the ends of odd-sized segments. On phenomenological grounds, we assume these moments to correlate ferromagnetically, with their direction determined in the experiments by the cooling field. For each segment of spins, the partition function can be exactly calculated; the total free energy of the chain is obtained by summing the free energies of segments of all sizes, with proper weighting factors. This procedure is detailed in Sec. II A. Then, in Sec. II B, we include the Curie-Weiss terms and discuss the results of the approximation. We show that this approach reproduces the linear temperature dependence of the remanent magnetization and the existence of an excess susceptibility. The final section is devoted to a discussion and conclusions.

II. PHENOMENOLOGICAL MODEL

A. Nearest-neighbor interactions

We initially consider an open segment of n Ising spins with antiferromagnetic couplings and alternating fields, described by the Hamiltonian

$$\mathcal{H}_n=J\sum_{j=1}^{n-1} S_jS_{j+1}-\sum_{j=1}^{n} h_jS_j-D\sum_{j=1}^{n} S_j^2, \tag{2}$$

where $J>0$ and $h_j=h_1$ (h_2) for odd (even) j; a crystal field D is also introduced. The spin variables S_j take the values $\pm\frac{1}{2}$, $\pm\frac{3}{2}$, and $\pm\frac{5}{2}$. The alternating fields are introduced to give room to a staggered effective field needed to describe long-range antiferromagnetic order in the presence of interchain interactions. According to the phenomenological hypothesis that there are uncompensated magnetic moments pointing in a preferred direction, determined by the cooling field, we assume that the spins at the ends of odd-sized segments are always under the action of a field h_1. When the field is removed, the moments would remain uncompensated due to pinning by the nonmagnetic impurities. For even-sized segments, the particular choice of a field h_1 at $j=1$ is of no consequence, since in this case the partition functions are symmetric under inversion.

As we are considering finite values of n, we must treat separately the cases of odd- and even-sized segments. Using the transfer-matrix technique, we can write the partition functions as

$$\mathcal{Z}^{\mathrm{odd}}_{n-1}=\langle \mathbf{v}_1|\mathbf{T}^{(n-2)/2}|\mathbf{v}_1\rangle \tag{3}$$

and

$$\mathcal{Z}^{\mathrm{even}}_{n}=\langle \mathbf{v}_1|\mathbf{T}^{(n-2)/2}\mathbf{T}_1|\mathbf{v}_2\rangle=\langle \mathbf{v}_2|\mathbf{T}_2\mathbf{T}^{(n-2)/2}|\mathbf{v}_1\rangle, \tag{4}$$

where n is an even number, $\mathbf{T}=\mathbf{T}_1\mathbf{T}_2$, the elements of the 6×6 matrices $\mathbf{T}_1$ and $\mathbf{T}_2$ are given by

$$T_1(S_i,S_j)=e^{-\beta JS_iS_j+\beta(h_1S_i+h_2S_j)/2+\beta D(S_i^2+S_j^2)/2}, \tag{5}$$

$$T_2(S_i,S_j)=T_1(S_j,S_i), \tag{6}$$

and the components of the vectors $\mathbf{v}_1$ and $\mathbf{v}_2$ are

$$v_1(S_j)=e^{\beta(h_1S_j+DS_j^2)/2}, \tag{7}$$

$$v_2(S_j)=e^{\beta(h_2S_j+DS_j^2)/2}. \tag{8}$$

The free energies associated with odd- and even-sized segments are

$$F^{\mathrm{odd}}_{n-1}=-k_BT\ln\mathcal{Z}^{\mathrm{odd}}_{n-1} \tag{9}$$

and

$$F^{\mathrm{even}}_{n}=-k_BT\ln\mathcal{Z}^{\mathrm{even}}_{n}. \tag{10}$$

We now consider a very long chain and assume that each of the N sites is occupied by a spin with probability p. For $0<p<1$, the chain is composed of finite segments of spins separated by empty sites. In the $N\to\infty$ limit, the number of segments of size n is $NP(n)=N(1-p)^2p^n$. Assuming that each segment is described by the Hamiltonian in Eq. (2), the total free energy per spin is given by the infinite series

$$f_{\mathrm{nn}}(h_1,h_2,T)=\frac{1}{p}\sum_{n\ \mathrm{even}}[P(n-1)F^{\mathrm{odd}}_{n-1}+P(n)F^{\mathrm{even}}_{n}]. \tag{11}$$

For $p<1$, as $nP(n)$ becomes negligible for sufficiently large n, this infinite series can be truncated and readily evaluated numerically.

Let us denote by type 1 (type 2) those spins under the action of a field h_1 (h_2). The numbers N_1 and N_2 of spins of either type in a chain can be determined by noting that in a segment of size n there are $n/2$ type-1 spins if n is even and $(n+1)/2$ type-1 spins if n is odd. Thus, the fractions of type-1 and type-2 spins are

$$\frac{N_1}{N}=\sum_{n\ \mathrm{odd}}P(n)\frac{n+1}{2}+\sum_{n\ \mathrm{even}}P(n)\frac{n}{2}=\frac{p}{1+p} \tag{12}$$

and

$$\frac{N_2}{N}=\sum_{n\ \mathrm{odd}}P(n)\frac{n-1}{2}+\sum_{n\ \mathrm{even}}P(n)\frac{n}{2}=\frac{p^2}{1+p}, \tag{13}$$

respectively. For $p<1$, the difference between the two fractions will obviously generate a nonzero magnetization at zero temperature.

B. Linear-chain approximation

In order to mimic the weak interchain coupling in the real compounds, we now assume that, in addition to the nearest-neighbor couplings inside each segment, there are also ferromagnetic Curie-Weiss (CW) interactions connecting all spins in the chain. We further assume that the CW interactions between two type-1 or two type-2 spins have strength J_{cw}/N, but that the CW interactions between a type-1 and a type-2 spin are weaker by a factor γ. This γ factor is introduced to allow for off-plane interchain couplings; in the pure limit ($p=1$) the chains are expected to exhibit antiferromagnetic order, so that γ must be smaller than unity. Upon dilution, we expect the antiferromagnetic arrangement to survive inside each segment, and in principle this could lead to a variation of γ with the concentration p, since the magnetic arrangement in the planes perpendicular to the chains could be disturbed. In any case, our results suggest that γ is very small, if not zero, in the compounds under consideration.

The contribution of the CW interactions to the total energy per spin is

$$\varepsilon_{cw}=-pJ_{cw}(m_1^2+2\gamma m_1 m_2+m_2^2), \tag{14}$$

where m_1 (m_2) is the magnetization per magnetic ion due to spins of type 1 (type 2). Since ε_{cw} depends only on the averages m_1 and m_2, and not on the detailed configuration of the spins, it is convenient to perform a change of variables. So we now introduce the Helmholtz potential per spin $a_{nn}(m_1,m_2,T)$, related to the nearest-neighbor interactions and defined by the Legendre transform

$$a_{nn}(m_1,m_2,T)=f_{nn}(\tilde{h}_1,\tilde{h}_2,T)+m_1\tilde{h}_1+m_2\tilde{h}_2, \tag{15}$$

where $\tilde{h}_1$ and $\tilde{h}_2$ are effective fields and

$$m_1=-\left(\frac{\partial f_{nn}}{\partial\tilde{h}_1}\right)_{\tilde{h}_2,T} \quad \text{and} \quad m_2=-\left(\frac{\partial f_{nn}}{\partial\tilde{h}_2}\right)_{\tilde{h}_1,T}. \tag{16}$$

For given values of m_1 and m_2 we can write the total Helmholtz potential

$$a(m_1,m_2,T)=a_{nn}(m_1,m_2,T)+\varepsilon_{cw}, \tag{17}$$

from which we obtain the relation between the external magnetic fields h_1, h_2 and the effective fields,

$$h_1=\left(\frac{\partial a}{\partial m_1}\right)_{m_2,T}=\tilde{h}_1-2pJ_{cw}(m_1+\gamma m_2) \tag{18}$$

and, similarly,

$$h_2=\left(\frac{\partial a}{\partial m_2}\right)_{m_1,T}=\tilde{h}_2-2pJ_{cw}(\gamma m_1+m_2). \tag{19}$$

Comparing these last results (for $\gamma=0$) with the local field at a site $\mathbf{r}$ due to its $q_\perp$ nearest neighbors in adjacent chains, as given by the Hamiltonian in Eq. (1), we conclude that J_{cw} can be estimated as

$$J_{cw}\simeq\frac{1}{2}pq_\perp J_\perp. \tag{20}$$

The thermodynamically stable magnetizations are those which minimize the free-energy functional

$$\Phi(h_1,h_2,T;m_1,m_2)=a(m_1,m_2,T)-m_1h_1-m_2h_2$$
$$=f_{nn}(\tilde{h}_1,\tilde{h}_2,T)-\varepsilon_{cw}. \tag{21}$$

For low temperatures and small ratios J_{cw}/J, setting $h_1=h_2=0$, the stable values of m_1 and m_2 have opposite signs. In the presence of dilution ($p<1$), since we have $|m_1|\neq|m_2|$, the model predicts a remanent magnetization per lattice site, m_r, given by

$$m_r=p(m_1+m_2). \tag{22}$$

In the $T\to0$ limit, m_r reaches a saturation value,

$$\lim_{T\to0}m_r=\frac{N_1-N_2}{N}S=\frac{p(1-p)}{(1+p)}S, \tag{23}$$

where $S=\frac{5}{2}$. The zero-field differential susceptibility χ_0 can be calculated by setting $h_1=h_2=h$ and taking the $h\to0$ limit,

$$\chi_0=\lim_{h\to0}\frac{\partial m_r}{\partial h}. \tag{24}$$

The Néel temperature is obtained from the solution of the equation

$$\left\{\frac{\partial^2\Phi}{\partial m_1^2}\frac{\partial^2\Phi}{\partial m_2^2}-\left(\frac{\partial^2\Phi}{\partial m_1\partial m_2}\right)^2\right\}_{m_1=m_2=0}=0, \tag{25}$$

in the absence of an external field.

In Fig. 1 we show the experimental data[19] for the temperature dependence of the remanent magnetization in DMMC doped with 4.5% Cd (this concentration was estimated from high-temperature fits to a Curie-Weiss law). We also show results of our calculations for the remanent magnetization with 4.5% dilution, $J_{cw}/J=1.5\times10^{-2}$, $\gamma=0$, and $D=0$. We obtained the best fit for the linear portion of the curve by setting the theoretical Néel temperature to 1.14 times the experimental value (which amounts to fitting J). This is a reasonable procedure, since our calculations are of a mean-field nature, and thus we do not expect to obtain

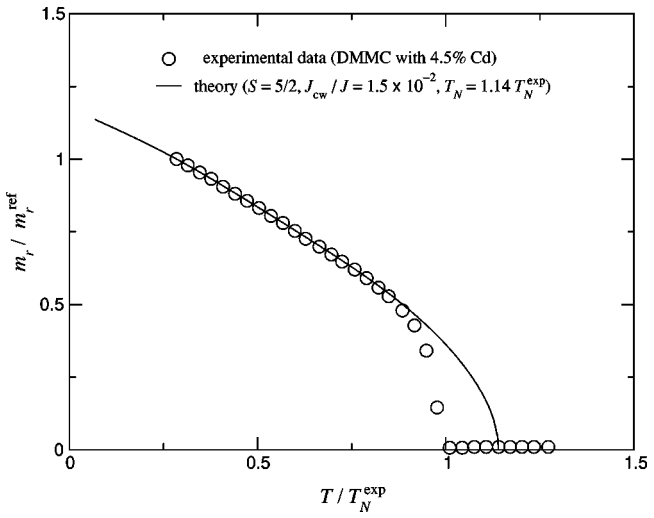

FIG. 1. Experimental data (circles) and theoretical calculation (solid curve) for the temperature dependence of the remanent magnetization in DMMC with 4.5% Cd. The magnetization is normalized to its value at the lowest temperature for which experimental data are available.

good quantitative results for the Néel temperature. Of course, the qualitative features of the calculations are not sensitive to small variations in the parameters; however, no strictly universal behavior (in the sense of data collapse) could be identified. We point out that setting the value of the crystal field to high positive values turns the system into a $S=\frac{1}{2}$ Ising model, and in this case the linear temperature dependence of m_r could not be so well reproduced. Note that, in view of Eq. (20), the value of J_{cw}/J used in the fit is fully compatible with the estimated experimental value of $J_\perp/J$ mentioned in the Introduction. The calculated ratio of the Néel temperatures of the diluted and pure systems is 0.86, compared to the

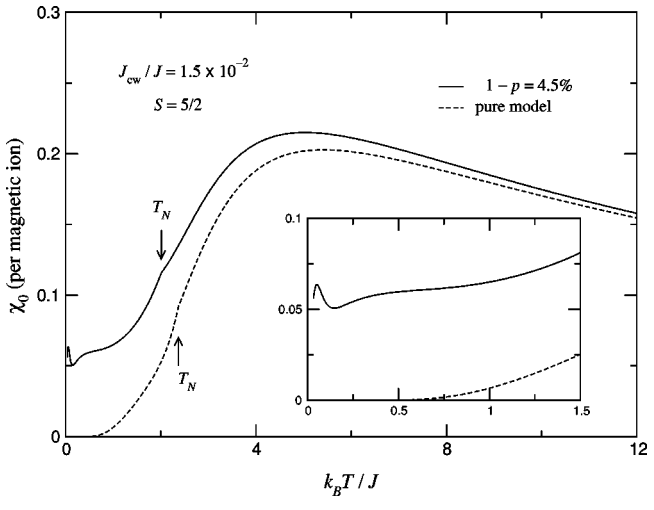

FIG. 2. Calculated zero-field susceptibility per magnetic ion in the pure limit (dashed curve) and for 4.5% dilution (solid curve), using the same parameters as in Fig. 1. The arrows indicate the corresponding Néel temperature, which is lower in the dilute case. The inset shows low-temperature behavior.

experimental estimate[19] of 0.99 for the real material. From Eq. (23), the saturation value of m_r for 1% dilution is 0.497% of the sublattice magnetization in the pure system, in excellent agreement with the experimental estimate[18] of 0.5% for MMC with 1% Cd.

In Fig. 2 we use the previous set of parameters to plot the calculated zero-field susceptibility χ_0 both in the pure limit and for 4.5% dilution. The broad maxima in the curves reflect short-range intrachain antiferromagnetic correlations, while the cusps (indicated in the figure by the arrows) correspond to the Néel temperatures (T_N). As is clear in the inset, for the dilute case we observe other features at lower temperatures. The small maximum close to $T=0$ is due to isolated spins, whose sole energy scale is given by the very weak interchain couplings, while the neighboring shoulder is due to small odd-sized segments, whose end spins are uncompensated (even-sized segments give negligible contributions to χ_0 at such low temperatures). This is in sharp contrast to the pure limit, in which the susceptibility vanishes exponentially for $T<T_N$.

It should be mentioned that the present approach is a generalization of that used by Slotte[23] to investigate the dilute $S=\frac{1}{2}$ Ising chain with competing short- and long-range interactions. However, owing to the presence of competition, his approach does not contemplate the possibility of long-range antiferromagnetic order at finite temperatures, even in the pure limit.

III. CONCLUSIONS

We introduced a phenomenological model for the remanent magnetization (m_r) in a class of dilute quasi-one-dimensional antiferromagnets, composed of weakly interacting spin chains. The model assumes the existence of uncompensated spins at the ends of odd-sized segments formed along the chains upon dilution. These spins are supposed to remain ferromagnetically correlated after a cooling field is removed. By using a linear-chain approximation, in which interchain interactions are treated at a mean-field level, we were able to reproduce the linear temperature dependence of m_r for a set of parameters compatible with experimental estimates.

Our linear-chain approximation is based on the assumption that, even upon dilution, each segment feels an staggered effective field. Of course, this assumption is subject to some restrictions. Depending on the impurity concentration $1-p$, the existence of uncompensated moments pointing in a preferred direction could lead to a complete destabilization of the magnetic ordering perpendicular to the chains (this can be seen by considering the effect, in a particular chain, of two neighboring nonmagnetic ions, which may invert the roles of the alternating sublattices). In this case, spins along the chains would feel the same interchain effective field, irrespective of their position. Actually, this would lead to a ferromagnetic transition (with a diverging susceptibility), and the long-range antiferromagnetic ordering would not be recovered even as $p\to 1$. We have performed calculations near this limit and have checked that the critical temperature depends linearly on $1-p$, being thus too small compared

with experimental findings. Moreover, it is not possible to reproduce the linear temperature dependence of the remanent magnetization. We conclude that, at least in the low impurity concentrations used here, for which the occurrence of two neighboring nonmagnetic atoms in the same chain is a rare event, our approximation is reasonable.

There remains the topic of identifying the precise mechanism responsible for the persistence of ferromagnetic correlations between the uncompensated spins. Monte Carlo simulations based on the Hamiltonian in Eq. (2) could be used to verify whether it is sufficient or necessary to have both ferro- and antiferromagnetic interchain interactions present in order to give rise to a remanent magnetization in quasi-one-dimensional systems.

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*Electronic address: apvieira@if.usp.br
†Electronic address: ssalinas@if.usp.br

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