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Dilution of a layered antiferromagnet: Magnetism in $Mn_xZn_{1-x}PS_3$

Nirmala Chandrasekharan and Sukumaran Vasudevan
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

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The magnetic properties of the layered antiferromagnet $MnPS_3$ have been studied as a function of dilution with zinc. The magnetic susceptibility of $Mn_xZn_{1-x}PS_3$ can be accounted for reasonably well by a randomly diluted antiferromagnetic honeycomb lattice. For compositions above the percolation threshold the suceptibility was calculated using the high-temperature series expansion (HTSE) for a dilute magnetic lattice. For compositions below the percolation threshold uncompensated spins of the finite Mn clusters give rise to an additional Curie correction to the HTSE which is maximum near the p_c [S0163-1829(96)04445-1]

I. INTRODUCTION

This paper reports dilution studies on a layered Heisenberg antiferromagnet, manganese thiophosphate.[1] This study was initiated as part of an effort to understand the changes in magnetic properties, on intercalation, in this compound. The structure of the host compound is similar to that of transition-metal-diluted semiconductors and may be derived from the $CdCl_2$ type. The structure consists of $MnPS_3$ layers separated by a van der Waals gap.[2] The presence of the gap makes it possible to intercalate a wide variety of cationic species.[3] The mechanism of intercalation, however, is quite different from that in the structurally similar transition metal chalcogenides. Intercalation proceeds by an unusual ion exchange mechanism in which the electrical charge of the cationic guest species entering the van der Waals gap is counterbalanced by the loss of a Mn^{2+} ion from the layer. The loss of Mn^{2+} creates vacancies which are supposed to be randomly distributed within the layer.[4,5] The major change and in some cases the only change on intercalation is in the magnetic properties. Whereas the host structure is a Heisenberg antiferromagnet with $T_N = 78$ K,[1] the intercalated compounds show field-dependent susceptibility[6,7] and are weakly ferromagnetic. Intercalation in these compounds has generated considerable interest. It has been considered as an alternate approach to designing ferromagnets.[8] Moreover, since the cationic guest species retains much of its original properties on intercalation, it is possible to obtain a material that expresses the magnetic properties of the host as well as the properties of the guest species; e.g., the intercalation of a nonlinear optical (NLO) chromophore dimethyl stilbazonium cation in $MnPS_3$ has been reported.[9] The intercalated material exhibits both NLO properties as well as spontaneous magnetization at low temperatures due to the host lattice.

Two mechanisms have been suggested to explain the change in magnetic properties on intercalation: (i) a dilution effect, due to random vacancies in the layer (it has been suggested that this could lead to ferrimagnetism arising from uncompensated spins[8]) and (ii) a change in the local symmetry of Mn^{2+} around a vacancy leading to a canting of spins arising from a Dzyaloshinsky-Moriya type of interaction and/or zero-field splitting.[10] In order to understand the role of dilution we have examined the susceptibilities of a series of $Mn_xZn_{1-x}PS_3$ crystals both above and below the percolation threshold (p_c). Within a layer of $MnPS_3$, the Mn^{2+} ions have a honeycomb structure; the p_c is 0.7. The purpose of the present study was to investigate whether the effective spins of the Mn^{2+} and the nature of exchange change on dilution. In the literature, there are very few reports on magnetic susceptibilities below the percolation threshold in insulating two-dimensional (2D) Heisenberg systems. For example, in K_2MnF_4, a 2D Heisenberg antiferromagnet, with many similarities to $MnPS_3$, there are no reports of magnetic susceptibility studies for Mg dilution[11] for a range of concentrations below p_c.

We have measured the susceptibilities of the $Mn_xZn_{1-x}PS_3$ for $0 < x \leqslant 1$ over a wide temperature range and find that the high-temperature susceptibilities can be modeled reasonably well as a randomly diluted antiferromagnetic honeycomb lattice. The susceptibilities for $x > p_c$ were calculated using a high-temperature series expansion (HTSE) for a diluted honeycomb lattice. For compositions where $x < p_c$ an additional paramagnetic correction term was required to account for the contributions arising from uncompensated spins in the finite cluster. The Curie correction was found to scale with x. Our results imply that changes in magnetism on intercalation in $MnPS_3$ cannot be explained by a simple dilution model; some other mechanism would have to to be evoked to explain the spontaneous magnetization.

II. EXPERIMENT

Single crystals of $0 < x \leqslant 1$ were grown from the respective polycrystalline samples by chemical vapor transport using excess sulfur as the transporting agent.[3] The powders were synthesized using high-purity manganese, phosphorus, and sulfur, with phosphorus and sulfur being in slight excess, in evacuated sealed quartz ampoules and heated to 620 °C for 2 weeks. Subsequently, excess phosphorus and sulfur were distilled out at 300 °C. The $Mn_xZn_{1-x}PS_3$ powders were characterized by x-ray diffraction (XRD) and the stoichiometry by atomic absorption spectroscopy (AAS). Crystals were grown in a gradient furnace with the charge end being at 700 °C and the cooler end at 630 °C. Single crystals of typical size 5 mm $\times 5$ mm were obtained. The stoichiometry of the crystals was determined by AAS. The solid solutions are homogenous over the entire composition range. The

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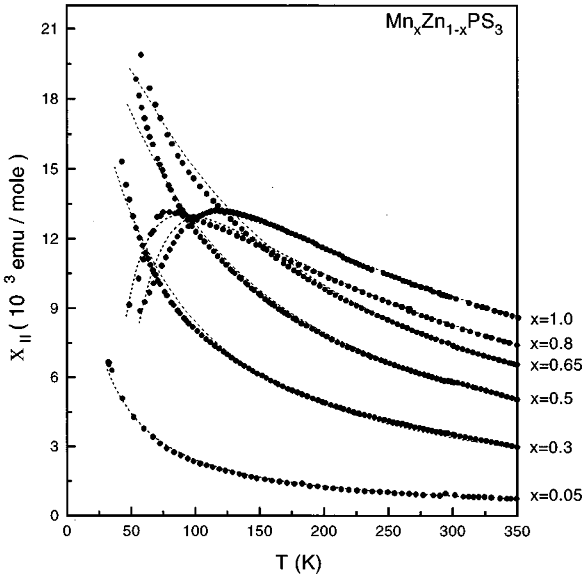

FIG. 1. The magnetic susceptibilities of $Mn_xZn_{1-x}PS_3$ single crystals parallel to the trigonal axis as a function of temperature. The dashed lines are the least squares fits of the susceptibility expressions of Eqs. (5) and (6) to the experimental susceptibilities. The values of the microscopic parameters are $J=-8.1$ K and $g=2.01$ while x was determined by atomic absorption spectroscopy.

lattice parameters obtained from XRD were found to obey Vegard's law, implying that the Zn^{2+} ions are randomly distributed in the lattice.

Static magnetic susceptibilities were measured in the temperature range 30–350 K, using a Faraday balance. The magnetic balance was calibrated using $HgCo(NCS)_4$. Crystals of $Mn_xZn_{1-x}PS_3$ were mounted on a quartz plate which was suspended from the balance by an arrangement similar to that described in Ref. 12. Susceptibilities both parallel and perpendicular to the ab basal plane were measured. (The magnetization axis of the pure $MnPS_3$ is perpendicular to the layer, i.e., the ab plane.) The diamagnetic susceptibilities of $Mn_xZn_{1-x}PS_3$ were calculated using Pascal constants and subtracted from the data. The diamagnetic contribution of the quartz plate and vacuum grease have also been subtracted. None of the samples showed any field dependence of the magnetization even at the lowest temperature studied, nor was any difference observed for field-cooled and zero-field-cooled samples.

III. RESULTS

The susceptibilities of $Mn_xZn_{1-x}PS_3$ are shown in Fig. 1. For values up to $x=0.7$, which is the percolation threshold for a honeycomb lattice, an antiferromagnetic transition is obtained. The percolation threshold being fairly high, we were unable to grow a sufficient range of compositions above the percolation threshold to make a quantitative correlation between T_N and $(p-p_c)$. Nevertheless, the effect of dilution on T_N can be clearly observed. The magnetization axis does not change on dilution. In pure $MnPS_3$, the Néel temperature is 78 K whereas for $x=0.8$ the T_N shifts to 54 K.

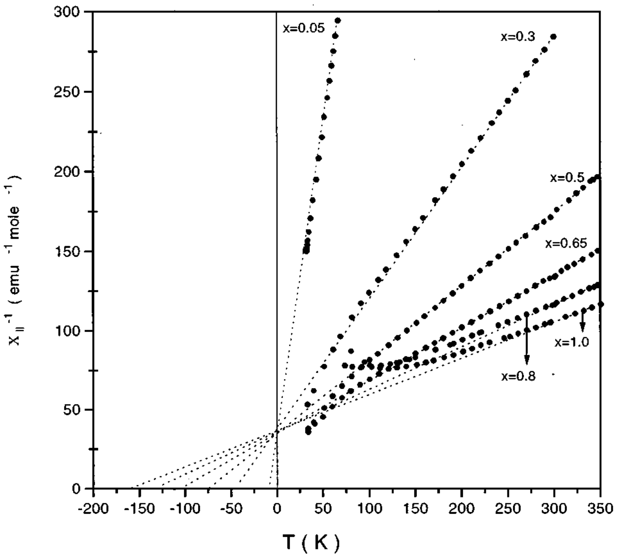

FIG. 2. The inverse magnetic susceptibilities of the $Mn_xZn_{1-x}PS_3$ single crystals parallel to the trigonal axis as a function of temperature for various concentrations of $0<x\leqslant 1$. The extrapolation of the high-temperature susceptibility curves to the negative temperature axis gives the Curie-Weiss temperature Θ_x.

The inverse susceptibilities are shown in Fig. 2. They fit reasonably well to a Curie-Weiss law for temperatures above 200 K. The Θ values obtained from an extrapolation of the Curie-Weiss law vary linearly with x, and are shown in Fig. 3. The Curie constants were also found to have a linear variation with concentration. It may be seen in Fig. 2 that at low temperatures the inverse susceptibilities for composition $x=0.65$, 0.5, and 0.3 show a downward deviation from the Curie-Weiss behavior. This is most evident for compositions close to p_c.

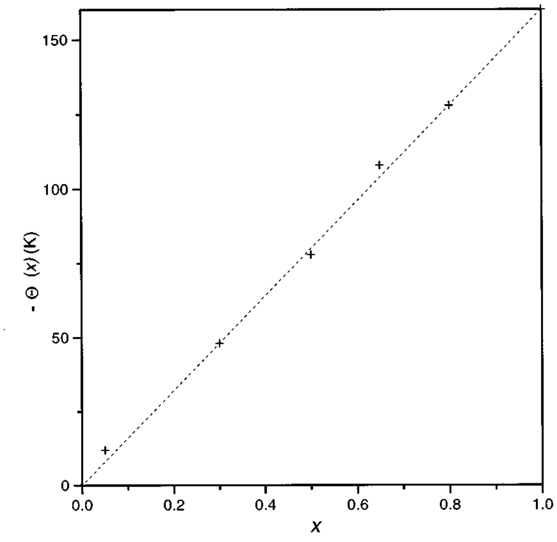

FIG. 3. The experimentally determined values (+) of the Curie-Weiss temperature $\Theta(x)$ as a function of temperature for single crystals of $Mn_xZn_{1-x}PS_3$. The dashed line denotes the $\Theta(x)$ calculated from that obtained for the parent $MnPS_3$.

The results can be understood if we represent the interactions between Mn^{2+} ions by the Heisenberg Hamiltonian for a randomly diluted antiferromagnet (it is assumed that the Mn^{2+} ions are orbitally nondegenerate, i.e., $L=0$):

$$\mathcal{H}=\sum_{ij} J_{ij}S_iS_j\xi_i\xi_j-g\mu_BH_{\mathrm{ext}}\sum_i \delta_i\xi_i, \qquad (1)$$

where sums i and j run over all the lattice sites ($i\neq j$) and $\xi=0$ or 1, depending on whether the cation site is occupied by a diamagnetic Zn^{2+} or the magnetic Mn^{2+} ion. J_{ij} is the exchange integral and S_i is the atomic spin of the magnetic ion located on the ith site. The second term is the Zeeman term with H_{ext} denoting the applied field. Since the distribution of the diamagnetic Zn^{2+} ions is random (quenched disorder), we have to average over all possible sequences of $\{\xi\}$. Such an averaging procedure yields $\xi_i=\xi^2=x$. In the mean-field approximation, the susceptibilities can be derived from the above Hamiltonian in the high-temperature limit and recast in the form of the Curie-Weiss law[13,14]

$$\chi=\frac{C(x)}{T-\Theta(x)}, \qquad (2)$$

with the Curie constant per unit volume,

$$C(x)=\frac{x(g\mu_B)^2S(S+1)N}{3k_B}, \qquad (3)$$

and the Curie-Weiss temperature

$$\Theta(x)=-\tfrac{2}{3}xS(s+1)\sum J_iz_i/k_B=\Theta_0x. \qquad (4)$$

Thus, if the distribution of diamagnetic ions is truly random, then the variation of the Curie-Weiss temperature should be linear with x. This is exactly what is observed for $\mathrm{Mn}_x\mathrm{Zn}_{1-x}\mathrm{PS}_3$ (Fig. 3). Θ_0 is the value for pure MnPS_3. It is also observed (Fig. 2) that the extrapolated high-temperature values of χ^{-1} at $T=0$ are independent of x, confirming the prediction of Eq. (2) and also confirming a random distribution of Mn^{2+} in the lattice. The above result along with results of Figs. 1 and 3 implies that the downward deviation from Curie-Weiss behavior in χ^{-1} plots at low temperature (Fig. 2) is not an impurity contribution. This downward deviation has been observed previously in many dilute semimagnetic semiconductors.[15] The origin of this downward deviation is probably a Curie contribution arising from uncompensated Mn^{2+} spins at the boundaries of the finite cluster which arises for $p<p_c$. These moments are not accounted for in the mean-field approximation; Eq. (2) is strictly valid only for the dilute infinite cluster.

The high-temperature susceptibility of MnPS_3 was modeled using the high-temperature series expansion (HTSE) for a two-dimensional honeycomb Heisenberg lattice and that of $\mathrm{Mn}_{0.8}\mathrm{Zn}_{0.2}\mathrm{PS}_3$ by the HTSE for a randomly dilute honeycomb lattice. The susceptibilities are expressed as a series expansion in J/kT:

$$\chi_{\mathrm{AFM}}=\frac{Ng^2\beta^2xS(S+1)}{3kT}\,\frac{1}{1+\sum_{i=1}^{6}(-1)^ib_i(x)(|J|/kT)^i}. \qquad (5)$$

The $(-1)^i$ accounts for the antiferromagnetic nature of exchange in this system. The coefficients $b_i(x)$'s were evaluated following the procedure of Morgan and Rushbrook.[16] It was verified that when $x=1$, the expression was similar to the HTSE expression of Rushbrook and Wood.[17] The exchange constant J was evaluated for MnPS_3 by fitting the above expression for $x=1$ to the experimental data. The best fit was obtained for $J/k=-8.1$ K and $g=2.01$. Using the value of J, the susceptibilities for $\mathrm{Mn}_{0.8}\mathrm{Zn}_{0.2}\mathrm{PS}_3$ were calculated after evaluation of the appropriate $b_i(x)$'s.[18] The calculated susceptibilities are shown as dashed lines in Fig. 1. It may be seen that the agreement is reasonably good over a wide temperature range.

For $\mathrm{Mn}_x\mathrm{Zn}_{1-x}\mathrm{PS}_3$ compositions where x is less than the percolation threshold (0.7) no long-range antiferromagnetic transition is observed. The Mn^{2+} ions are now part of finite clusters. For very small values of x (extreme dilution) it is possible to model the susceptibilities by the cluster model.[19] In this model the susceptibility is the sum of the magnetic susceptibilities of the various type of clusters of size $n=1,2,3,\ldots$, where n is the number of magnetic ions in the cluster. $\chi_{\mathrm{total}}=\Sigma N_i\chi_i$, where χ_i is the susceptibility of the ith cluster and N_i is the number of such clusters. N_i's depend on x and the type of lattice. However, for $x=p\sim p_c$ the evaluation of the various types of clusters and the calculation of their susceptibilities are computationally formidable. Consequently we have modeled the susceptibilities of $\mathrm{Mn}_x\mathrm{Zn}_{1-x}\mathrm{PS}_3$ ($x<0.7$) by considering the configurational average rather than the individual cluster configurations as in the cluster model. The susceptibility of the configurationally averaged clusters was treated as a sum of two terms: (i) a randomly diluted antiferromagnet susceptibility [Eq. (5)] with $J_{ij}=-8.1$ K, as in pure MnPS_3, and (ii) a Curie correction arising from local fluctuations of the uncompensated spins due to the finite size of the cluster not accounted for by the HTSE susceptibility:

$$\chi_{\mathrm{Total}}=\frac{x^{\gamma}C'}{T}+\chi_{\mathrm{AFM}}(x), \qquad (6)$$

where χ_{AFM} is as given by Eq. (5). The experimental susceptibility could be fitted reasonably well with $J/k=-8.1$ K and $\gamma=1$ for all compositions.

In systems like $\mathrm{Mn}_x\mathrm{Zn}_{1-x}\mathrm{PS}_3$, any formalism to explain the magnetic behavior would have to account for both the spin correlations which tend to suppress the total moment as well as local fluctuations arising from uncompensated spins which give rise to a paramagnetic contribution. In the dilute limit ($x=0.05$), spin correlations are relatively unimportant. It may be seen from Eq. (5) that when x is small, the fit of the HTSE is essentially Curie like and the formalism gives a good description to the magnetic data. At the other extreme ($x=1$) where spin correlations dominate, the HTSE is able to account reasonably well for the experimental susceptibilities. In the intermediate-concentration regime, for which both contributions are significant, while the HTSE can account reasonably well for the spin correlation, a Curie correction is required to fit the experimental data for x close to p_c.

The results of the present studies on the dilute two-dimensional antiferromagnet (AFM) $MnPS_3$ have an important consequence on the models used to describe the magnetic properties of intercalated $MnPS_3$. The present studies show that the uncompensated moments in the diluted 2D AFM can give rise to a Curie contribution but the lack of any field dependence of the magnetization suggests that they do not interact ferromagnetically to give a spontaneous magnetization down to the lowest temperature studied.

IV. CONCLUSIONS

The magnetic properties of $MnPS_3$ and that of $Mn_{0.8}Zn_{0.2}PS_3$ which occur above the percolation threshold ($x=0.7$) for a nearest-neighbor honeycomb lattice are adequately explained within the high-temperature series expansion (HTSE). The magnetic susceptibilities of the diluted zinc analogs below the percolation threshold were fitted by incorporating an additional Curie correction which was found to scale with x. Good agreement was observed between the fitted and experimental susceptibilities. Since no field dependence is observed for the diluted $Mn_xZn_{1-x}PS_3$, it may be concluded that dilution of the lattice cannot account for the spontaneous magnetization at the low temperatures observed in the intercalates of $MnPS_3$.

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