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Ternary Mixed Magnetic Co/Mn/Ni Dichloride Dihydrate

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Abstract

Ternary mixed magnetic $Co_{1-x}Mn_yNi_{x-y}Cl_2 \cdot 2H_2O$ has as its components three well studied antiferromagnets. Each is characterized by MCl_2MCl_2M…chemical and structural chains, with intrachain exchange interactions antiferromagnetic for the Mn component but ferromagnetic for the other two components. Competing ferromagnetic and antiferromagnetic intrachain exchange interactions occur in two different pairwise combinations. Reported here is the magnetic behavior of an equimolar mixture of the three components. One maximum appears in the magnetic susceptibility vs temperature, at 4.85 ± 0.05 K, a quite interesting result since decidedly lower than the locations of susceptibility maxima in the pure components. A pronounced upturn in the susceptibility below 2.3 K also appears. Magnetization vs field isotherms display increasingly strong convex upward curvature and associated hysteresis with decreasing temperature. All of these characteristics differ markedly from those of the pure components.

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I. Introduction

Most studies of randomly mixed magnetic materials have dealt with binary systems. While two components is the simplest situation, the more complicated case of a ternary mixed magnet is also worth attention. Suitable systems are decidedly less common, but an attractive one we developed is $Co_{1-x}Mn_yFe_{x-y}Cl_2\cdot 2H_2O$.[1-3] We initiate here the study of a new ternary insulating magnetic mixture, which we believe to be only the second (after the above) examined systematically from a phase diagram perspective, $Co_{1-x}Mn_yNi_{x-y}Cl_2\cdot 2H_2O$. The three $MC1_2\cdot 2H_2O$ components are characterized by chemical and structural MCl_2MCl_2M…chains, and known from past work on each of the three possible binary systems[4-6] to mix homogeneously. Each of the three mixtures $Co_{1-x}Mn_xCl_2\cdot 2H_2O$ [4], $Co_{1-x}Ni_xCl_2\cdot 2H_2O$ [5] and $Mn_{1-x}Ni_xCl_2\cdot 2H_2O$ [6] shows quite distinct magnetic behavior and a unique T vs x magnetic phase diagram. Because in each component spins in the antiferromagnetic ordered states are along or nearly along M-O coordination bonds, competing orthogonal spin anisotropies [7] should be absent. Observed differences in behavior among the three binary mixtures are due then to variations in the detailed intrachain interaction distribution consequent on mixing, supplemented by single ion anisotropy effects of the individual metal ions along with variations in the distribution of antiferromagnetic interchain interactions.

The quite contrasting magnetic properties of the above three binary mixtures makes the properties of the present ternary mixed system intriguing. Fruitful comparison may also emerge with results on the earlier ternary mixed magnet $Co_{1-x}Mn_yFe_{x-y}Cl_2\cdot 2H_2O$, where $FeCl_2\cdot 2H_2O$ rather than $NiCl_2\cdot 2H_2O$ was one of the components. Indeed, for the equimolar composition studied here a susceptibility maximum occurs at a substantially lower temperature than for any of the three components. This differs from the behavior in the Co/Mn/Fe ternary material.

2. Experimental

Ternary mixtures were prepared very much as were the binary mixtures of the same components earlier. Confirmation that dihydrate material was obtained was by thermogravimetric analysis. The composition reported here is nominal. Based on previous experience this is expected to hold up well when eventual atomic absorption analysis of all samples examined is performed. Samples were handled so as to minimize exposure to atmospheric water vapor. Magnetization measurements were made on ca. 100 mg samples using a PAR vibrating sample magnetometer mated with a Janis Supervaritemp cryostat. Temperatures were measured with a calibrated carbon glass resistance thermometer located very near the sample. Magnetic susceptibilities are corrected for diamagnetism and demagnetization, both rather small effects.

3. Measurements and Analysis

Displayed in Fig. 1 is the molar susceptibility of an equimolar composition of $Co_{1-x}Mn_y$ $Ni_{x-y}Cl_2 \cdot 2H_2O$, i.e., $x = 0.66_6$, $y = 0.33_3$. No features of interest appear at temperatures above those shown. The most notable aspect of the plot is the well formed maximum, at 4.85 ± 0.05 K. This is definitely (much) lower than the locations of antiferromagnetic maxima in the pure components: near 17.9 K, 7.0 K and 7.6 K for the Co, Mn and Ni materials, respectively. Nor are even minor anomalies at these pure component characteristic temperatures evident in the data for the present mixture. The $MCl_2 \cdot 2H_2O$ systems are three-dimensional magnetically, and ordering temperatures occur only a few percent below the corresponding T_{max}. It is somewhat difficult however to identify in the data of Fig. 1 a maximum in $d\chi/dT$, the usual signature, on the low temperature side of the maximum, to assign to an antiferromagnetic transition [8]. For the present, it will be assumed that such a transition occurs below but close to T_{max}.

Also very obvious in the plot is a pronounced upturn in the susceptibility below about 2.3-2.4 K. Such a feature, though usually less well-defined and prominent than that occurring here, has appeared in certain other mixed magnets examined by us in which a hydrate of $MnCl_2$ was a component. The tendency to turn over at temperatures below 1.7 K has also been seen in such cases. A possible explanation is a mixed magnetic hydration state impurity involving $MnCl_2$.

Worth noting is that a fit of much higher temperature data according to a Curie-Weiss form, $\chi_M = C/(T - \theta)$, yields a C of 2.70 emu-K/mol and a θ of -4.7_4 K. The former is 7.5% lower than calculated as a mole fraction weighted average of the known Curie constants for the pure components. This represents a similar level of modestly imperfect agreement as seen over a range of compositions of the Co/Mn/Fe ternary mixture previously studied. A similarly calculated theta value is -3.6_0 K. It is not necessarily expected that θ(obs) in particular should agree with such a calculated value, since theta is a multi-ion interaction parameter and new interactions arise in a mixture. But the level of similarity just noted is comparable, again, with that seen over many compositions of the Co/Mn/Fe ternary system.

In Fig 2 appears the molar magnetization vs field and temperature for the same equimolar composition sample. The isotherm at 6.06 K, well above T_{max} = 4.85 K of the magnetic susceptibility, is essentially linear and without hysteresis. But the isotherms at 4.23 K and below, all at lesser temperature than T_{max}, show a convex upward curvature which becomes stronger at temperature decreases. The degree of hysteresis also increases with decreasing temperature. An attempt was made to identify possible characteristic fields, perhaps associated with a field-induced transition, by locating the intersection points of linear approximations to the low-moderate and high field portions of each isotherm displaying curvature. While rather

satisfactory lines could be drawn through these regions for each isotherm at or below 4.23 K, all intersections occurred between 5.9 and 6.9 kG and failed to show a completely regular temperature dependence. Hence we tend to reject this interpretation.

4. Discussion

In the present equimolar mixture one antiferromagnetic maximum appears in the susceptibility and located well below temperatures where maxima occur for the individual components. In $Co_{1-x}Mn_xCl_2 \cdot 2H_2O$ the phase boundary T(x) descended from both composition extremes (x = 0, 1) [4]. It also did so in $Mn_{1-x}Ni_xCl_2 \cdot 2H_2O$ [6], though with quite a different general form. In $Co_{1-x}Ni_xCl_2 \cdot 2H_2O$ T(x) was extremely unusual, with substantial or even remarkably broad composition ranges extending from either extreme in which T(x) varied only very modestly [5]. It is certainly unclear then what sort of T(x) should be expected in the present mixed system, and many more compositions will need to be explored in order to determine it. But it is evident that T(x,y) for transitions in the present system will differ significantly from that determined for the Co/Mn/Fe ternary system [3]. In the earlier system a susceptibility maximum did not occur at an unexpectedly low temperature for an approximately equimolar composition.

The pattern of curvature in the magnetization isotherms, and associated hysteresis, as it evolves with temperature, is different from that of any of the pure components. It also differs markedly from that exhibited by the binary mixed system $Mn_{1-x}Ni_xCl_2 \cdot 2H_2O$, involving two of the three components here. Magnetization isotherms in $Co_{1-x}Mn_xCl_2 \cdot 2H_2O$ tended to be, when not simply linear, of opposite curvature (concave downward) to those in the present ternary mixture. In $Co_{1-x}Ni_xCl_2 \cdot 2H_2O$ curvature characteristics were qualitatively similar to those seen here, but much more pronounced, with substantially larger hysteresis. A metamagnetic transition was deduced. In contrast to the situation for the present isotherms, described in the last

paragraph of the previous section, it was possible to infer a reliable transition field which varied with temperature in a plausible way for such a phenomenon. Therefore, we conclude that the situation is quite different in the present ternary mixture, at any rate for the particular equimolar composition studied here.

In the space available we will note that an intriguing range of behavior has appeared in this new ternary material based on results for certain other compositions. Thus a 20% Co, 40% Mn, 40% Ni composition exhibits no susceptibility maximum nor other notable feature suggestive of a transition. Moreover, its magnetization isotherms display opposite curvature (concave downward) to those of the equimolar composition shown in the present paper. No less striking, a 60% Co, 20% Mn, 20% Ni composition exhibits two susceptibility maxima, one near 5.0 K and the other near 13.5 K. Its magnetization isotherm curvature characteristics are qualitatively similar to those of the present equimolar mixture, but quite different in detail.

It should be mentioned also that small time dependent effects were observed in the magnetization for the present equimolar composition at the lowest temperatures on decreasing the field back down below about 5 kG. This is possibly indication of a spin glass state [9, 10]. Similar effects were observed in $Co_{1-x}Mn_xCl_2 \cdot 2H_2O$, though interestingly not in the other two (Mn/Ni, Co/Ni) related binary systems. In order to sort out the details of behavior in this new ternary mixed magnet, additional experiments like time-dependent thermoremanent magnetization, etc. will be performed. Naturally, also, many additional compositions need to be prepared and examined.

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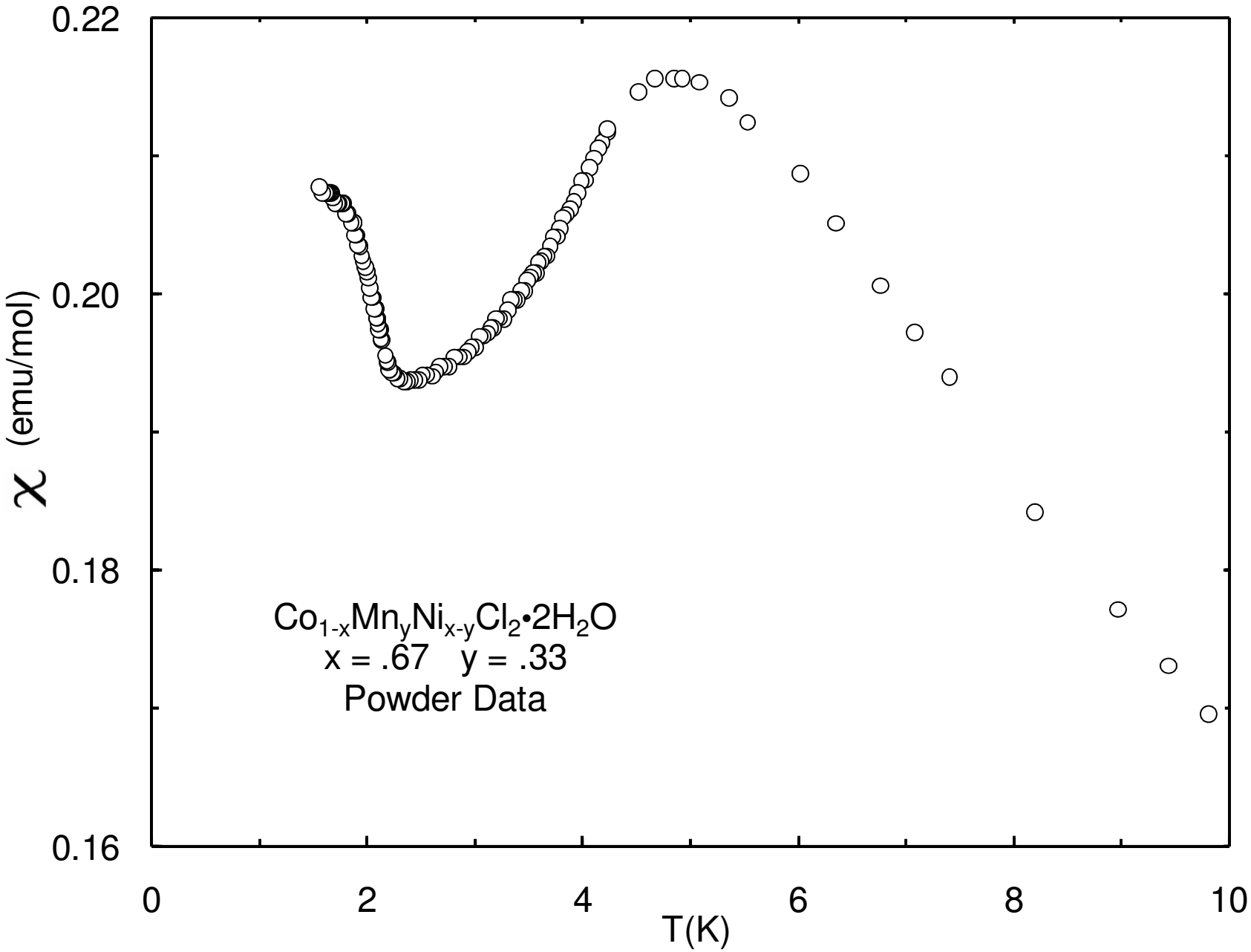
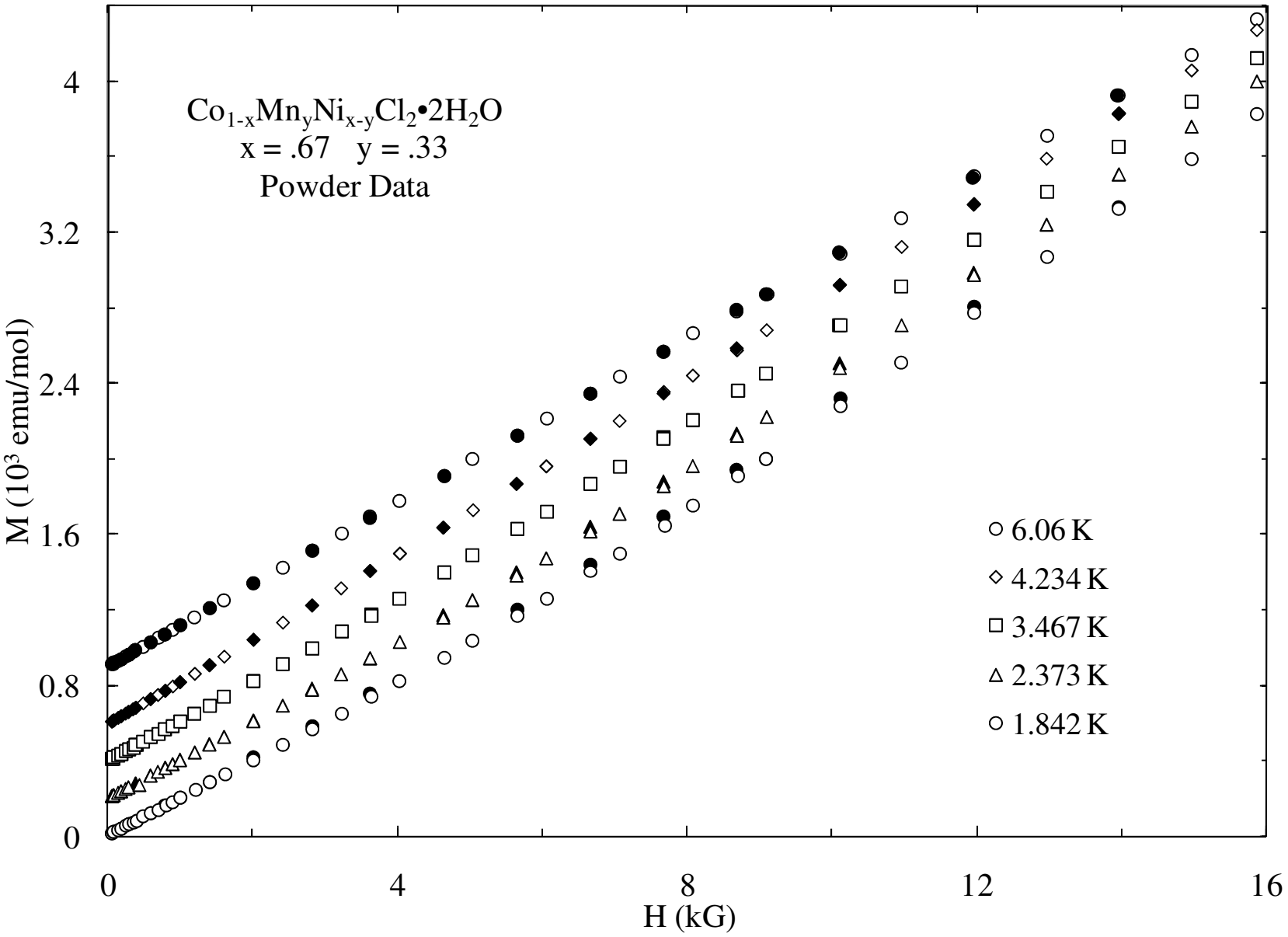
Figure Captions

Fig. 1. Molar magnetic susceptibility vs temperature for an equimolar composition of $Co_{1-x}Mn_yNi_{x-y}Cl_2 \cdot 2H_2O$.

Fig. 2. Molar magnetitization vs field for an equimolar composition of $Co_{1-x}Mn_yNi_{x-y}Cl_2 \cdot 2H_2O$. Open symbols are field-up data, closed symbols field-down. For clarity data for isotherms at higher temperatures are shifted up 200, 400, 600 and 900 emu/mole successively.


0.22
0.20
0.18
0.16
χ (emu/mol)
0
2
4
6
8
10
T(K)
Co1-xMnyNix-yCl2•2H2O
x = .67 y = .33
Powder Data


$Co_{1-x}Mn_yNi_{x-y}Cl_2•2H_2O$
x = .67 y = .33
Powder Data
6.06 K
4.234 K
3.467 K
2.373 K
1.842 K
M (10^3 emu/mol)
H (kG)
0
0.8
1.6
2.4
3.2
4
0
4
8
12
16