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Composition-induced metamagnetism and static magnetic properties of $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$

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Mixed magnetic $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$ has been studied by dc magnetization and susceptibility measurements over the complete composition range. The two components are three-dimensional Ising (Fe) and Heisenberg (Ni) antiferromagnets, ordering at 21.9 K and at 7.25 K (with a 6.31 K spin reorientation transition), respectively. Each contains $MCl_2MCl_2M\ldots$ chemical (and structural) chains, with ferromagnetic intrachain exchange and weaker but significant antiferromagnetic interchain exchange. Curie-Weiss fits, $\chi_M = C/(T-\theta)$, to high temperature powder susceptibilities of mixtures yield Curie and Weiss constants. Though imperfectly regular, $\theta(x)$ exhibits an overall composition dependence which implies that unlike-ion exchange is ferromagnetic and slightly stronger than like-ion interactions. In all but the end mixtures ($x=0.10$ and 0.90), two susceptibility maxima are observed, usually with one predominant. The form of $\chi(T)$ evolves with composition, and implies homogeneous mixing rather than crude admixture of components. Transition temperatures can often be estimated; these display a weak but regular composition dependence. Even in end mixtures there are subtle differences from pure component behavior for magnetization versus field isotherms. Dramatically different properties are observed for intermediate compositions, from $x=0.30-0.80$, where field-induced transitions in the 6–10 kG range occur for temperatures below 8 K. Significant hysteretic effects also appear. This corresponds to composition-induced metamagnetism. Mean-field analysis of the hysteresis suggests that the ratio of interchain to intrachain exchange is somewhat larger than in the pure components. The temperature dependence of the hysteresis loop area does not support the notion of an activation process for domain wall motion or growth. Comparison can be made with previously studied $Co_{1-x}Ni_xCl_2 \cdot 2H_2O$, with respect to which there are some similarities but also major differences in behavior.

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I. INTRODUCTION

Of fundamental interest in condensed matter physics are phase transitions occurring under the influence of random disorder. Especially important in this regard are mixed magnetic systems based on insulating materials, where the dominant exchange interactions are short range in nature. Two categories of binary mixed magnets (each component having a spin) have been of the greatest interest. One group is those systems with competing orthogonal spin anisotropies, a major consequence of which is the existence of a "tetracritical" point in the $T-x$ magnetic phase diagram. Important theoretical attention[1,2] and experimental effort[3–7] have been devoted to such materials. The other major group is systems in which strongly competing ferromagnetic and antiferromagnetic interactions occur, which often gives rise to frustration and can lead to spin glass phases.[8,9] A vast theoretical and experimental literature exists on spin glasses. Significant experimental examples among insulating materials include $Fe_{1-x}Mn_xTiO_3$,[10] $Rb_2Mn_xCr_{1-x}Cl_4$,[11,12] $Co_{1-x}Mn_xCl_2 \cdot 2H_2O$,[13,14] and $Co_{1-x}Mn_xCl_2 \cdot H_2O$.[15,16]

Most mixed magnetic materials, while exhibiting randomness, contain neither of the special competitions described above. Nevertheless, interesting effects peculiar to the mixture but not the pure components can still arise. Thus, many different theoretical forms for the ordering temperature versus composition have been obtained.[17–19] $T_c(x)$ may exhibit more or less curvature of either sign, different curvatures in different composition ranges, as well as maxima or minima or even both a maximum and a minimum in the same $T-x$ phase diagram. Far from all possible forms for $T_c(x)$ obtained theoretically have been observed. Also interesting is the occurrence of other than simple antiferromagnetic behavior in a mixture of conventional antiferromagnets. Such can arise from different, though not orthogonal, anisotropy axes of the pure components. Another complicating factor is the appearance of new exchange interactions in the mixture that significantly alter the balance among all relevant interactions, which in general will include those characteristic of the pure components as well as any new ones.

In this paper we examine the static magnetic properties of mixed magnetic $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$ over the entire composition range. The structures of the two components, although not identical, have many similarities. In each of $FeCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 2H_2O$ occur linear chains of chloride bibridged metal ions, with the Cl-M-Cl bridging angles slightly less than 90°. In the nickel system, a slight relative tilting of adjacent $NiCl_4$ planar coordination moieties along the chain yields a repeat unit of two nickel centers.[20] In the iron system there is no tilting and so one $FeCl_4$ moiety is the repeat unit.[21] Each substance crystallizes in a monoclinic $C2/m$ structure, with $MCl_2MCl_2M\ldots$ chains along the b axis in $NiCl_2 \cdot 2H_2O$ and along the c axis in $FeCl_2 \cdot 2H_2O$. The upper sections of Fig. 1 illustrate some of these relations. The ratio of the lengths of these two axes in the two materials is 1.893, similar to the 2:1 periodicity ratio just noted. It is reasonable then to expect substitutional replacement of either metal ion along the chain to occur. Hydrogen bonding serves to couple the chains together structurally in either substance, the specifics differing somewhat because of the different tilt characteristics. Unit cell volumes per formula unit are 113.2 and 105.0 Å^3 for $FeCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 2H_2O$, respectively, for a difference of 7.2%. This is somewhat larger than the 4.2%

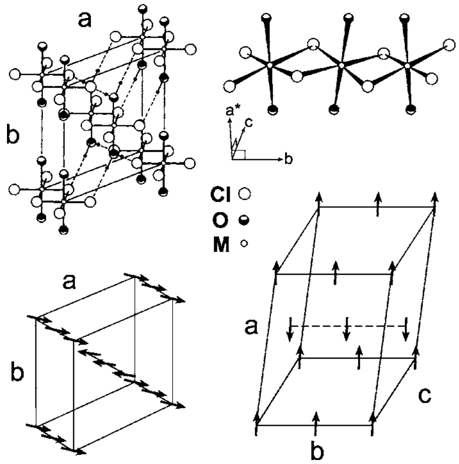

FIG. 1. Upper left: crystal structure of $FeCl_2 \cdot 2H_2O$; upper right: tilt variation in structural chain of $NiCl_2 \cdot 2H_2O$ and relation to crystal axes of this system; lower left and right, respectively: ordered spin arrangements in $FeCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 2H_2O$.

for $Co_{1-x}Ni_xCl_2 \cdot 2H_2O$ studied previously,[22] but comparable to the 7.8% difference of $Co_{1-x}Mn_xCl_2 \cdot 2H_2O$,[13,14] and smaller than the 11.7% difference of $Mn_{1-x}Ni_xCl_2 \cdot 2H_2O$,[23] in all of which homogeneous mixing occurred. In the following all indications are that homogeneous mixing in the present case has occurred.

$FeCl_2 \cdot 2H_2O$ is a well studied three-dimensional (3D) Ising antiferromagnet ordering at 22.3 K.[24–28] Spins in the $FeCl_2FeCl_2Fe\ldots$ chemical chains are in the ac plane perpendicular to b, with the spins in a given chemical chain running along c ferromagnetically aligned. The spin direction is 32° from the c axis, with the alignment antiparallel for neighboring chains separated by $\pm(a \pm b)/2$, yielding overall antiferromagnetic ordering. This is illustrated in the lower left section of Fig. 1. Successive metamagnetic transitions occur at 39.2 and 45.6 kG, for $T \ll 22$ K, to states of increasing ferromagnetic alignment. $NiCl_2 \cdot 2H_2O$ is a much more isotropic 3D Heisenberg antiferromagnetic ordering at 7.25 K, with a spin reorientation transition occurring at 6.31 K.[29–31] The spins in each $NiCl_2NiCl_2Ni\ldots$ chemical chain are ferromagnetically aligned along a^*, which is normal to both b and c. The spins of chains separated by $\pm(a \pm c)/2$ are oppositely directed to give overall antiferromagnetism. This is illustrated in the lower right section of Fig. 1. In $NiCl_2 \cdot 2H_2O$ also, successive metamagnetic transitions occur, at 19, 56, and 82 kG near 0 K, to states of increasing ferromagnetic alignment.[30]

In $NiCl_2 \cdot 2H_2O$, spins align along or very nearly along metal-oxygen bonds, which are nearly normal to the $MCl_2MCl_2M\ldots$ chains. In $FeCl_2 \cdot 2H_2O$ spins align perpendicular to the metal-oxygen bonds. There is the potential then for achieving competing orthogonal spin anisotropies, unless even small departure from strictly 90° angles between the ordered nickel and iron spins is critical and prohibitive. Each pure system is characterized by strong ferromagnetic intrachain and somewhat weaker but still quite significant antiferromagnetic interchain exchange. Although interactions of both signs exist, the distribution is unlikely to be such that marked competition, leading to spin frustration, develops in mixtures.

The results reported here are largely consistent with the foregoing expectations. Neither multicritical behavior nor spin glass properties are observed. But the antiferromagnetic susceptibility maxima and nearby transition temperatures show a quite unusual composition dependence, of a form hardly seen before. Two successive transitions appear except for compositions very near the extremes. The Weiss constant, from fits to high temperature susceptibility data, also shows an interesting composition dependence. Most notable, perhaps, is the field dependence of the magnetization as a function of composition. Nonlinearities in M versus H are strong for a broad range of compositions, and pronounced hysteretic behavior is also evident. Metamagnetic transitions occur at fields much smaller than those characterizing the pure components.

II. EXPERIMENTAL

An aqueous solution of $FeCl_2$ was prepared, and any Fe^{3+} present was reduced by heating in the presence of iron filings and a small excess of HCl, followed by purging of dissolved oxygen with Ar(g). The Fe^{2+} concentration was determined by standard methods. Appropriate stoichiometric amounts of $NiCl_2 \cdot 6H_2O$ were dissolved in portions of the parent Fe^{2+} solution, in order to yield a series of solutions ranging from 0.10 to 0.90 mole fraction Fe^{2+}. The resulting solutions were purged again, then placed in a vacuum oven which was flushed with Ar(g), and held at 80 °C for several days until reaching dryness. The polycrystalline solid materials obtained were confirmed to be dihydrate by thermogravimetric analysis. Elemental analysis for iron and nickel by atomic absorption spectrophotometry gave values agreeing with nominal compositions to within 0.018 mole fraction unit rms, comparable with experimental uncertainty. In the following nominal compositions are used.

X-ray powder diffraction patterns were obtained for various mixture compositions and for the pure components. Similarities exist between the patterns for the two pure components, though differences in peak positions and intensity distributions also occur because of the nonidentical crystal structures. In each case, agreement with known patterns for $NiCl_2 \cdot 2H_2O$ or $FeCl_2 \cdot 2H_2O$ was satisfactory, with no indications of the presence of higher hydrates. As x varies from either composition extreme, peak positions shift modestly but systematically from pure component locations, typically to intermediate values. There is no indication that either component is present separately in the mixtures, neither with respect to individual peak locations nor with respect to the total number of peaks. The x-ray data suggest that at the level probed by x-rays microscopically homogeneous mixtures were obtained. The magnetic data to be presented are also consistent with this inference.

A variable-temperature vibrating sample magnetometer system was used to make magnetization and susceptibility measurements. Susceptibility data are field-cooled measurements and are corrected for demagnetization and diamagnetism. Polycrystalline samples of approximately 100–150 mg size were packed into nonmagnetic sample holders under dry conditions, accurately weighed, and then screwed onto a

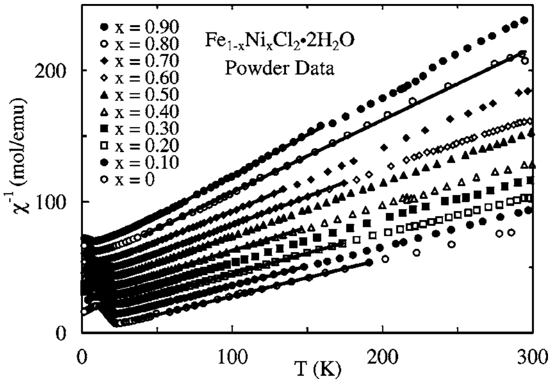

FIG. 2. Inverse molar magnetic susceptibility vs temperature for various compositions of $Fe_{1-x}Ni_xCl_2\cdot 2H_2O$. Lines correspond to Curie-Weiss fits described in text. For clarity, data sets for $x=0.10, 0.20, \ldots, 0.90$ are shifted up $7, 14, \ldots, 63$ mol/emu.

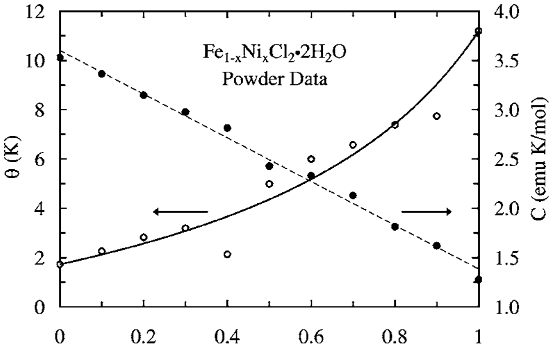

FIG. 3. Curie constant (closed circle) and Weiss theta (open circle) vs composition for $Fe_{1-x}Ni_xCl_2\cdot 2H_2O$. The dashed line through $C(x)$ is a linear fit. The curve connecting $\theta(1)$ and $\theta(2)$ is according to Eq. (3) with $p=1.15_5$.

nonmagnetic sample rod in immediate proximity to a calibrated resistance thermometer. Temperatures are believed to be accurate to within ±0.005 to 0.5 K, depending on the range. Magnetic field values are accurate to ±max (2 G, 0.1%), while magnetization and susceptibility values are accurate to 1.5%, though with substantially better precision.

III. RESULTS OF MEASUREMENTS

A. Magnetic susceptibility

The reciprocal molar magnetic susceptibilities of the various compositions of $Fe_{1-x}Ni_xCl_2\cdot 2H_2O$ studied here appear in Fig. 2, with corrections applied. Fits to the data based on the Curie-Weiss form $\chi_M = C/(T-\theta)$ appear as lines in the figure. For most compositions, data at higher temperature display either above-average noise or signs of inadequate thermal equilibrium. Hence, a maximum fitting temperature significantly lower than 300 K was adopted, but one still high enough that the fitting range is adequately broad and linear. The typical minimum fitting temperature was 40 K, chosen in order to avoid the denser data at lower temperatures and the common deviations from linearity which tend to appear there. Modest variations of 5 to 10 K in the limiting fit temperatures led to only quite small variations in the resulting best fit parameters C and θ.

The Curie and Weiss constant fit parameters appear in Fig. 3. Statistical uncertainties in C and θ are about 0.008 emu K/mol and 0.3 K, respectively; these are, in the same order, about equal to and somewhat larger than symbol size. The variation of C with composition is not quite linear, with $C(x)$ values showing a tendency to bow above a line connecting $C(0)$ and $C(1)$. The latter were determined by us for the pure components using the same apparatus. A linear $C(x)$ dependence emerges from the application of mean-field theory to a two-component homogeneous magnetic mixture.[32,33] A Curie constant can be expressed in general as

$$C = N_o \mu_B^2 P^2 / 3k, \tag{1}$$

where P, dimensionless, is the average effective moment for the mixed system and is related to the individual moments of components 1 (of mole fraction x) and 2, $P(1)$, and $P(2)$, by

$$P(x) = [xP(1)^2 + (1-x)P(2)^2]^{1/2}. \tag{2}$$

The linear behavior of $C(x)$ referred to above follows immediately. This may be seen as a consequence of the single-ion character of the Curie constant, i.e., not affected by exchange interactions even when $|\theta|$ in the Curie-Weiss form is substantial. If one allows for the possibility that the pure component Curie constants are in significant error, a fairly acceptable line (shown dashed in the figure) can be put through the collection of C values with mostly modest deviations apparent (though often larger than the statistical uncertainties).

The same mean-field treatment gives for the Weiss θ composition dependence

$$\theta(x) = \{x^2 P(1)^2 \theta(1) + (1-x)^2 P(2)^2 \theta(2) + 2px(1-x)P(1)P(2)[\theta(1)\theta(2)]^{1/2}\}/P(x)^2, \tag{3}$$

where p is an exchange ratio parameter defined as $J(1,2)/[J(1,1)J(2,2)]^{1/2}$, i.e., the ratio of the unlike-ion exchange to the geometric mean of the like-ion exchange interactions in the mixture (the latter assumed the same as in the pure systems). One employs the observed $\theta(x)$ values, along with those determined for the pure systems, $\theta(1) = \theta(NiCl_2\cdot 2H_2O) = 11.2$ K and $\theta(2) = \theta(FeCl_2\cdot 2H_2O) = 1.73$ K, in Eq. (3) in order to find an optimal value for the one free parameter p. For this purpose $P(x)$ is also needed, and is obtained from Eq. (2) employing $P(i)$ values for the pure components deduced from their C values; these are $P(1)=3.19$ and $P(2)=5.31$, for the nickel and iron systems respectively. The optimal value found for p is $1.15_5 \pm 0.04$; the solid curve in Fig. 2 is that calculated according to Eq. (3) with this p. The positive value indicates that exchange interactions between Ni and Mn ions are ferromagnetic. That $|p|$ is greater than unity implies that the unlike-ion exchange is stronger than the like-ion exchange interactions. It is evident that the fitted curve leaves several data points exhibiting substantial deviations from it. The reason for the high degree of scatter in the observed $\theta(x)$, definitely larger than in the

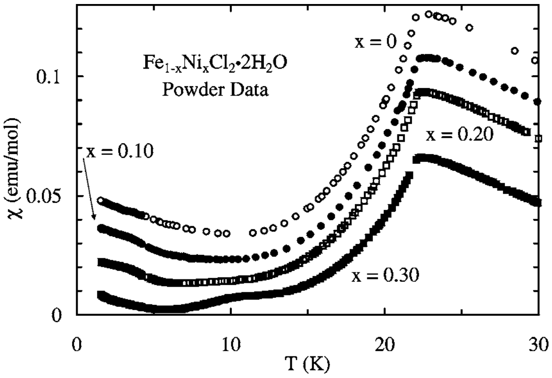

FIG. 4. Molar magnetic susceptibility vs temperature for low x compositions of $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$. For clarity, data sets have been shifted down; thus, $x=0$, 0.10, 0.20, and 0.30 by 0.015, 0.025, 0.035, and 0.055 emu/mol, respectively.

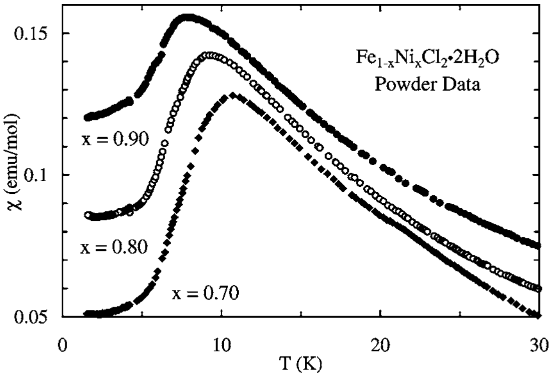

FIG. 6. Molar magnetic susceptibility vs temperature for high x compositions of $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$. For clarity, data sets are shifted; thus $x=0.70$ and 0.80 down by 0.035 and 0.020 emu/mol, respectively, and $x=0.90$ up by 0.010 emu/mol.

majority of mixed magnets examined by us, is not understood.

The molar magnetic susceptibility at low temperatures is shown for the various compositions in Figs. 4–6. Antiferromagnetic maxima are evident in all data sets and occur at the expected locations for $FeCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 2H_2O$ (not shown but appearing in Ref. 22). For most mixtures two maxima (or, often, a major maximum and an incipient maximum or shoulder) appear. Only for the pure components and for the least admixed $x=0.10$ and 0.90 compositions is there but a single maximum. Although the features are quite weak there are discernible (more clearly on specially scaled plots) shoulders at approximately 10.8 K in $x=0.20$ and at 21.2 K in $x=0.80$, in addition to the prominent maxima at 22.6 K and 9.2 K, respectively, in these compositions. In $x=0.30$ the roughly similarly located shoulder is clearly more prominent than in $x=0.20$, while the same can be said for the high temperature shoulder in $x=0.70$ relative to that in $x=0.80$. For the three interior compositions of $x=0.40$, 0.50, and 0.60, the two maxima are decidedly more similar (if not quite equal) in prominence. It must be emphasized, however, that with respect to neither the precise locations of the maxima or shoulders, and even less so with respect to their relative sizes, can the observed susceptibilities be accounted for as mole-fraction weighted crude mixtures of $FeCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 2H_2O$. In general, for such crude mixtures the weaker maxima (or shoulders) would be much more pronounced than they are observed to be. Thus, in addition to the x-ray implications, there is intrinsic evidence in the susceptibilities for homogeneous mixing.

In Fig. 7 appear the $T_{\max}$ locations for the various compositions, and where possible also an estimated T_c taken as the position of a maximum in $d\chi/dT$ when this can be plausibly identified. The latter provides the best available estimate for the antiferromagnetic ordering temperature.[34] When the maximum derivative location is ambiguous, there is sometimes evident an anomaly in $\chi(T)$; in such cases, e.g., the higher temperature transition in $x=0.60$, this is used for the T_c estimate.

Uncertainties in $T_{\max}$ and T_c are estimated to be 0.2 to 0.3 K, comparable with symbol size. An imperfect but fairly evident tendency for the upper $T_{\max}$ and T_c values to decrease weakly with increasing x appears. Also evident is a tendency, again imperfect, for the lower temperature $T_{\max}$ and T_c to increase with decreasing x; the variation is somewhat stronger here than for the upper temperature features. There is some indication for a maximum in the lower tem-

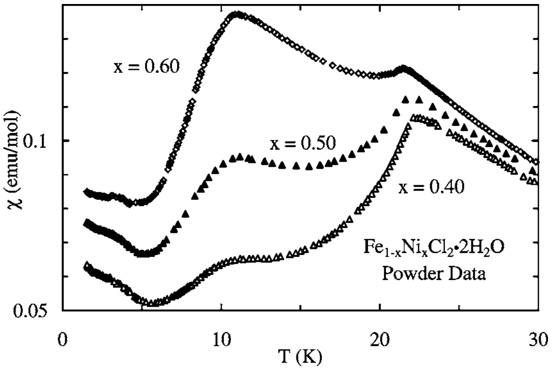

FIG. 5. Molar magnetic susceptibility vs temperature for intermediate x compositions of $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$. For clarity, data for $x=0.40$ and $x=0.60$ have been shifted down 0.010 and up 0.0025 emu/mol, respectively, with $x=0.50$ unshifted.

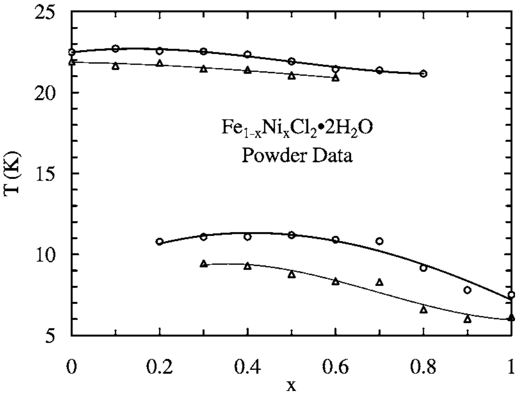

FIG. 7. Temperatures of susceptibility maxima (circles) and estimated antiferromagnetic transitions (triangles) vs composition for $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$. Curves through results are guides to the eye only.

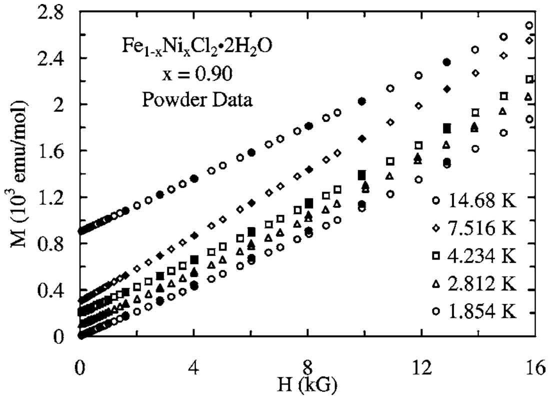

FIG. 8. Molar magnetization vs field (increasing, open symbols; decreasing, closed symbols) at various temperatures for an $x=0.90$ composition of $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$. For clarity successively higher temperature isotherms are shifted up 100, 200, 300, and 900 emu/mol.

perature T_{max} near $x=0.5$. The form of the T versus x diagram is highly unusual, and we will return to this in Sec. IV.

B. Magnetization

Magnetization isotherms at 4.2 K for each of the pure components were consistent with literature results. Essentially linear M versus H was seen for $FeCl_2 \cdot 2H_2O$ up to the maximum 15.9 kG field of our magnet, which is well below the 39 kG metamagnetic transition. Linearity up to about 9 kG, with moderate upward curvature between 9 and 16 kG (probably anticipatory of the 19 kG metamagnetic transition) was present for $NiCl_2 \cdot 2H_2O$. The hysteresis, on decreasing the field from 15.9 kG back down to zero, was negligible in both materials.

In mixtures, more interesting behavior appears even for very weak admixture. Thus for $x=0.10$ (not displayed) while hysteresis remains negligible (as for the pure iron material) in all isotherms up to 15.9 kG and back down, there were evident at 1.85 K, 4.23 K, 7.93 K, and even 14.77 K small degrees of curvature in M versus H, and even subtle curvature changes, not present in $FeCl_2 \cdot 2H_2O$. In $x=0.90$, Fig. 8, while 7.52 K and higher temperature isotherms are very close to linear, for each of 4.23 K, 2.81 K, and 1.85 K there is more general upward curvature throughout the field range than for $NiCl_2 \cdot 2H_2O$ as well as some hysteresis, growing with decreasing temperature, not present in the pure nickel material. In neither of these end compositions, however, did any reliable indications of field-induced transitions appear. Another example of a composition displaying subtle features implying not quite conventional M versus H behavior, but without clear signs of field-induced transitions, is $x=0.20$ in Fig. 9. Hysteresis is always negligible, and so only the field-increasing data are shown, for selected temperatures. At 11.83 K (as also at 25.99 K, not shown) the dependence is very close to linear. At 4.230 K, however, there is evident (more visible on optimally scaled plots) a subtle curvature change appearing near 10 kG; i.e., the overall shape has slight S character. This is also so for 2.81 K (not shown), but for 1.856 K the shape of M versus H is of a modest general downward curvature.

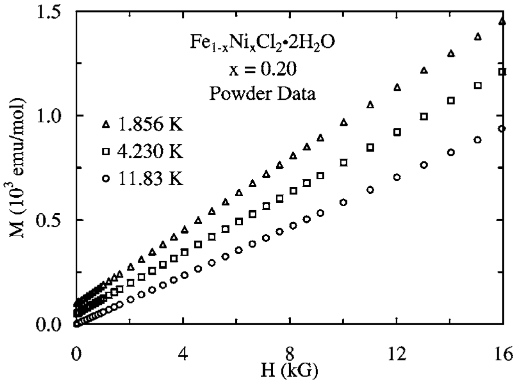

FIG. 9. Molar magnetization vs field (increasing) at various temperatures for an $x=0.20$ composition of $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$. For clarity, the 4.230 K and 1.856 K isotherms are shifted up 50 and 100 emu/mol, respectively.

The most striking behavior occurs for compositions from $x=0.30$ through 0.80. In each case, though more weakly for $x=0.30$, there is evidence of field-induced transitions with characteristic fields varying with temperature, and of significant temperature-dependent hysteresis as well. The field-increasing data are shown for $x=0.60$ in Fig. 10. The 11.78 K isotherm is essentially linear. Definite curvature appears already at 9.564 K. But for lower temperatures than this, one can discern two regimes in each isotherm, a low field and a high field region, which are either fairly linear or at least approximately linear. (There is actually some concave downward curvature in the high field regions where sufficient data are available; for the two lowest temperatures this is not evident.) Lines were drawn through the regions described. The resulting intersections are taken as upper critical fields $H_c(+)$. A similar procedure was applied to each $M(H)$ isotherm on decreasing the applied field from the 15.9 kG maximum to near zero (see next paragraph); this yields lower critical fields $H_c(-)$.

A few examples of the hysteresis in $x=0.60$ appear in Fig. 11. One somewhat surprising point (also evident in data for

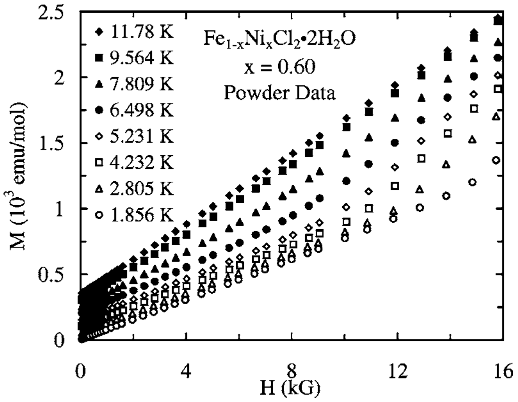

FIG. 10. Molar magnetization vs field (increasing) at various temperatures for an $x=0.60$ composition of $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$. For clarity, successively higher temperature isotherms are shifted up 50, 100, 150, 200, 250, 300, and 350 emu/mol.

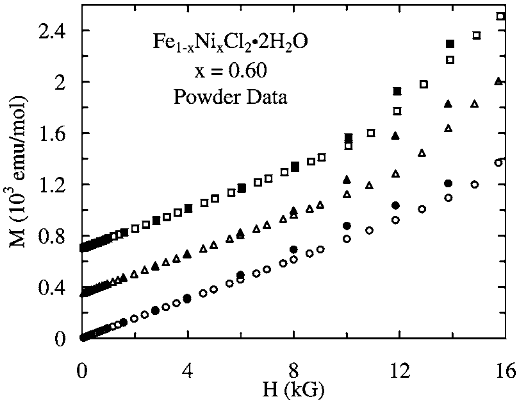

FIG. 11. Hysteresis in molar magnetization vs field for an $x=0.60$ composition of $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$ at the lowest temperatures of 1.856 K (circles), 2.805 K (triangles), and 4.232 K (squares). Open symbols are increasing field, and closed symbols decreasing field, data. For clarity, the 2.805 K and 4.232 K data are shifted up 350 and 700 emu/mol, respectively.

$x=0.40$, 0.50, and 0.70 and to a lesser degree for $x=0.30$ and 0.80) is that the extent of the hysteretic field range is somewhat greater for the lowest 1.8 K temperature while the magnitude of the hysteresis [difference between M(down) and M(up) at given field] appears less than at the higher 2.8 K temperature. Presumably this is related to the fact that the upturn in the increasing field data is just coming in above 14 kG and near the field limit of the measurements for the 1.8 K isotherm.

The average of $H_c(+)$ and $H_c(-)$ is the best measure of the correct equilibrium transition field at a given temperature. This, called simply H_c, appears in Fig. 12 for $x=0.60$. Because the dependence on temperature is somewhat unexpected, also shown is the directly determined $H_c(+)$, to which the unusual hysteretic behavior at the very lowest temperatures just mentioned does not contribute. The very modest downturn in H_c below 2.8 K appears to result from the surprisingly low $H_c(-)$ at the lowest temperature. The very weak decline in H_c with increasing temperature above 4.2 K, and extending so to at least 9 K, is unexpected. For the other mixtures in which unmistakable hysteretic effects were seen, $x=0.30$, 0.40, 0.50, 0.70, and 0.80, the behavior of H_c and $H_c(+)$ was similar, though more erratic for $x=0.80$. The magnitudes of the critical fields were also rather similar, though with a modest tendency toward smaller values for larger x, most markedly so for $x=0.80$. The dependence of $H_c(+)$ on composition in Fig. 12 is mostly similar to that seen previously in those compositions of $Co_{1-x}Ni_xCl_2 \cdot 2H_2O$ showing field-induced transitions.[22] But at the higher temperatures here, in both $H_c(+)$ and (consequently) in H_c, the decrease in critical field is much softer than appeared in the Co/Ni mixture.

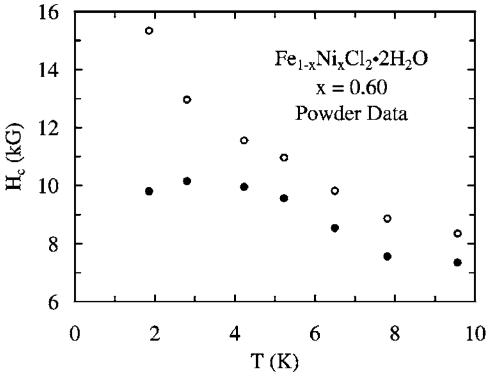

FIG. 12. Transition fields vs temperature for $x=0.60$ $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$. Open circles are $H_c(+)$ and closed are the equilibrium value, the average of $H_c(+)$ and $H_c(-)$.

Regarding compositions not shown, in $x=0.80$ the upturns in M versus H are somewhat softer than in the $x=0.60$ data displayed. The degree of hysteresis is only moderately smaller than in $x=0.60$, but does not extend as high in temperature—being just discernible at 5.24 K and negligible at 6.53 K, though there are still indications in M versus H of a field-induced transition as high as 7.90 K. In $x=0.30$ the transitions are not significantly less clear than in $x=0.60$, but the hysteresis is much smaller. It is just discernible at 5.17 K and hardly apparent at 6.51 K; the existence of a field-induced transition persists through 7.93 K, however. In $x=0.40$ the hysteresis is approximately intermediate in magnitude between that of $x=0.30$ and of $x=0.60$, and remains just discernible at 6.46 K; the existence of a field-induced transition persists through 7.80 K. The behavior in $x=0.50$ is fairly similar to that in $x=0.40$, while that for $x=0.70$ is somewhat intermediate between the behaviors in $x=0.60$ and 0.80.

IV. ANALYSIS AND DISCUSSION

Major characteristics of the magnetic data show that the mixtures examined are microscopically homogeneous rather than crude mixtures of the separate constituents. The observed $\chi(T)$ are quite inconsistent with a weighted average of pure component susceptibilities. Although the composition dependences of the locations of the two susceptibility maxima (one near 22 K and prominent for low x, the other near 9 K and prominent for high x) are weak or moderate, there is some systematic variation. That for the latter feature is especially evident. Most striking, the magnetization behavior in mixtures is qualitatively different from that of either pure component. In the high field, high hysteresis regions of $x=0.60$ for example, it is clear that a different kind of magnetically ordered state exists. This is also so for all compositions from $x=0.30$ through $x=0.80$.

Significant frustration effects were not expected in the present mixed system, and is supported by comparison of the Weiss θ parameters obtained from the susceptibility analysis with the observed ordering temperatures. The ratio $|\theta|/T_c$ has been proposed[35] as a measure of frustration in systems with mainly antiferromagnetic interactions. Values substantially greater than unity are found for magnets with high frustration. For each of the mixture compositions examined here, as well as for the pure constituents $FeCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 2H_2O$, the ratio is not large. However, the existence of major ferromagnetic interactions in the present materials makes $|\theta|/T_c$ a less conclusive indicator of frustration in any case.

The magnetization isotherms for $x=0.60$ (as well as 0.30, 0.40, 0.50, 0.70, and 0.80, not shown) suggest metamagnetic behavior. The pure components undergo metamagnetic transitions only at much larger fields, 19 and 39 kG for the nickel and iron materials respectively (with additional transitions at yet higher fields). The substantial hysteresis observed is also suggestive of first-order transitions. Such are the rule in metamagnets for temperatures well below that of antiferromagnetic ordering.

A mean-field theory of metamagnetic transitions was applied to $FeCl_2$ in a classic paper of Jacobs and Lawrence.[36] Previous results were extended to calculate the maximum hysteresis of the first-order metamagnetic transition as a function of temperature. The predictions depend parametrically on the ratio of intra- to intersublattice exchange field coefficients, Γ and A. These occur in the effective field (at a sublattice site) expression

$$\underline{H}_{\rm eff}^{\pm} = H - AM^{\mp} + \Gamma M^{\pm}, \tag{4}$$

where $M^{\pm}$ is the magnetization for either the up (+) or down (−) sublattices of the low field antiferromagnetically ordered state. A ferromagnetic intrasublattice interaction ($\Gamma > 0$) is found to be necessary for a first-order transition to occur. For a metamagnetic transition to develop, the anisotropy strength has to exceed that of the antiferromagnetic exchange between sublattices.

In each pure component of the present mixture the intrasublattice exchange (along $MCl_2MCl_2M\ldots$ chains) is ferromagnetic (positive Γ) and the intersublattice exchange (between the chains) is antiferromagnetic (positive A); hence, the situation is suitable for applying the foregoing model. Before considering the temperature dependence of the hysteresis, we first apply a relation emerging from the mean-field treatment[36]

$$\Gamma/A = (kT_{\rm N}/\mu H_{\rm c})[3S/(S+1)] - 1, \tag{5}$$

where μ is the magnetic moment per magnetic ion, $T_{\rm N}$ is the Néel temperature, and $H_{\rm c}$ is the transition field at 0 K. The magnetic moment can be calculated from the Curie constant via $C=N_{\rm o}\mu^2/3k$; for a mixed system the average effective moment of a particular composition must be calculated this way, from the empirical C value.

If one uses the previously noted values of $T_{\rm N}$ and $H_{\rm c}$ (near 0 K) for $FeCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 2H_2O$, along with μ values derived from the Curie constants determined here, together with $S_{\rm Fe}=2$ and $S_{\rm Ni}=1$, the values of Γ/A which emerge are 2.1_3 and 1.2_6, respectively. Expressions for the mean-field coefficients in terms of the primary exchange interactions are $A=2z_{\rm AF}J_{\rm AF}/N$ and $\Gamma=2z_{\rm F}J_{\rm F}/N$, where each z is the number of neighbors interacting with a given ion via the corresponding J and where N is the number of ions in the sample.[36] There are $z_{\rm F}=2$ neighbors along a chain. A given ion on a chain interacts with $z_{\rm AF}=4$ ions on neighboring chains of the opposite sublattice. Thus the ratios Γ/A indicate that the intrachain ferromagnetic interactions are somewhat stronger than the interchain antiferromagnetic, by from 2.5 (Ni) to 4 (Fe) times. This is qualitatively consistent with conclusions arrived at previously by other means.[24,28,30]

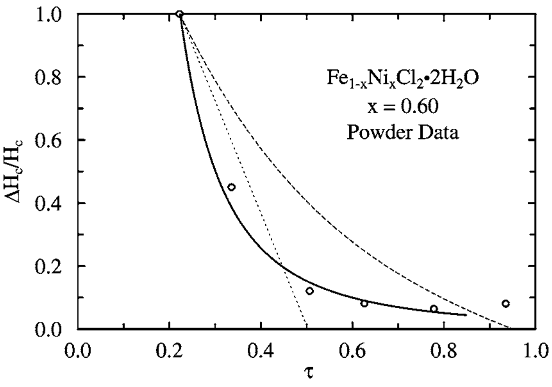

FIG. 13. Fractional hysteresis at equilibrium critical field vs reduced temperature for $x=0.60$ $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$. Curve through results is a guide to the eye only. Also shown are mean-field predictions (from Ref. 36) for $\Gamma/A=9$ (longer dash curve) and $\Gamma/A=0.6$ (shorter dash curve), scaled as described in text.

Apply now the same method to the $x=0.60$ composition using a $T_{\rm N}$ value of 8.35 K and estimated 0 K transition field of 10.0 kG. The measured Curie constant yields the effective moment 4.31_7. The average mixture spin is taken as $[(1-x)S_{\rm Fe}^2+xS_{\rm Ni}^2]^{1/2}$, with $S_{\rm Fe}=2$ and $S_{\rm Ni}=1$ as above. The resulting Γ/A is 4.16, significantly larger than the ratios for the pure components primarily because of the substantially smaller critical field of the mixture.

Also emerging from mean-field theory, in the limit of Ising type anisotropy,[36] is the prediction that the first-order metamagnetic transition becomes continuous at a sufficiently high temperature T^*, the so-called tricritical temperature. In terms of a reduced temperature $\tau=T/T_{\rm N}$ needed later,

$$\tau^* = 1 - A/3\Gamma, \tag{6}$$

with $\Gamma/A=4.16$ the result is $\tau^*=0.92$. Hence, for $x=0.60$ the prediction is that $T^*=7.68$ K. The hysteresis decreases markedly with increasing temperature and is barely discernible at 7.809 K in this mixture. The similarity between the temperature of this isotherm and T^* seems satisfactory.

The hysteresis as a function of temperature can also be analyzed based on a mean-field model.[36] Define $\Delta H_{\rm c}$ as the difference between apparent transition fields for increasing and decreasing field. Then $\Delta H_{\rm c}/H_{\rm c}$, where $H_{\rm c}$ is the estimated equilibrium transition field, is a field-normalized measure of hysteresis, and is predicted to depend on Γ/A. The hysteresis disappears at τ^* and decreases markedly with increasing temperature, more rapidly the smaller is Γ/A.

In Fig. 13 are plotted $\Delta H_{\rm c}/H_{\rm c}$ versus τ for the $x=0.60$ composition. The behavior is more erratic for higher temperatures, but the overall dependence is fairly regular. Shown as well are the mean-field predictions obtained in Ref. 36 for two values of Γ/A, 9 and 0.6. These have been scaled so that the calculated $\Delta H_{\rm c}/H_{\rm c}$ is 1.00 at the lowest temperature measured, $\tau=0.22_2$. (Theory generally predicts substantially larger hysteresis than observed, because certain mechanisms in real crystalline materials, e.g., demagnetization effects and structural imperfections, tend to reduce the hysteresis.[36]) While the observed temperature dependence differs from ei-

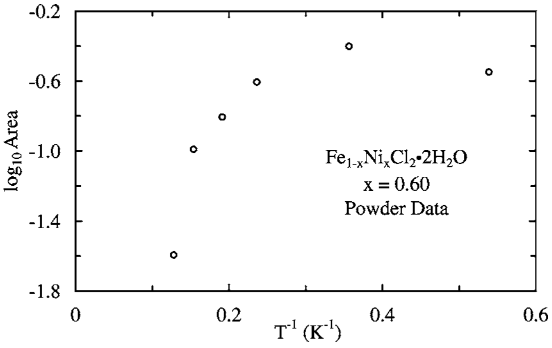

FIG. 14. Logarithm of hysteresis loop area (arbitrary units) vs reciprocal temperature for $x=0.60$ $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$.

ther calculated curve, it is quite plausible that what is seen corresponds to a Γ/A value intermediate between 9 and 0.6, consistent with the earlier estimate. It is also very likely that the difference in shape between observed and calculated dependences is due to the polycrystalline nature of the sample studied here.

The areas enclosed by the hysteresis loops for $x=0.60$, from 1.856 K through 7.809 K, were determined, and the logarithm of the area versus reciprocal temperature appears in Fig. 14. The motivation is to check a relation previously reported for $FeCl_2$,[37] and subsequently observed by us for $Co_{1-x}Ni_xCl_2 \cdot 2H_2O$,[22] that the loop area was proportional to $\exp(\delta/T)$, with δ a characteristic activation energy presumably associated with domain growth or domain wall motion. It is evident that such a relation fails in the present case, with no really plausible linear behavior evident anywhere in Fig. 14. Nor can this be ascribed simply to apparent abnormalities (referred to earlier) associated with the lowest temperature isotherms, as the curvature evident in the figure seems general. In $Co_{1-x}Ni_xCl_2 \cdot 2H_2O$ the hysteresis loops appeared to be better formed, possibly because the transitions fields were somewhat lower so that more of the desirable field range above the transition was within reach. In the present Fe/Ni mixture more uncertainty is encountered for the lowest 1.8 K temperature in particular. Still, it is not obvious that for higher temperatures than this any ambiguities are so severe as to create serious problems.

It is important to consider also other differences between the behavior in $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$ and in previously studied $Co_{1-x}Ni_xCl_2 \cdot 2H_2O$. The $T(x)$ diagrams of the two mixed systems have somewhat similar structures. There is a set of higher temperature susceptibility maxima and associated transitions and an analogous set at lower temperature. While the locations of these features in mixtures are in the vicinity of corresponding pure component features, there are also systematic differences including at least modest composition dependence. Particularly noteworthy is that the range of compositions in which both the higher and lower temperature features appear is much broader in the present Fe/Ni mixed system than in Co/Ni. In the latter mixture it was only in a relatively narrow range from about $x=0.20$ to slightly above $x=0.40$ that this occurred, whereas in the present case the phenomenon is seen from $x=0.20$ through $x=0.80$.

The existence of two maxima in $\chi(T)$ and associated transitions might suggest tetracritical behavior. But that explanation is almost certainly not applicable here. Based on experience with a number of candidate systems for such behavior, it seems likely that essentially perfect orthogonality of the ordered spin directions of the two components is needed. The tilt characteristics of the nickel coordination moieties very likely spoils this condition. And, indeed, the temperatures of the maxima and associated transitions in Fig. 7 are quite inconsistent with any plausible set of ordering lines meeting at a tetracritical point.

We would offer an explanation for the observed $T(x)$ in $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$ similar to that previously proposed for the Co/Ni mixture.[22] The spin alignment tendencies of the iron and nickel centers almost certainly differ, being nearly if not quite orthogonal; the difference is in fact much larger than for the Co/Ni mixture, where the spin alignment directions should be close to the same. It is possible then that over substantial composition ranges neither the iron nor the nickel spin anisotropy sufficiently dominates as to favor a single ordering direction. First one alignment tendency, and then the other, appears as the temperature is varied. Only at quite low and quite high x does the majority spin character so dominate that but a single alignment tendency appears. The broader x range, compared to the Co/Ni mixed system, over which both alignment tendencies appear in the $\chi(T)$ data is due to the strongly differing tendencies of the two spin types.

Very interestingly, it was approximately in the same narrow composition range ($x=0.25$ to 0.41) of the Co/Ni mixture that the most marked hysteretic effects in M versus H and the most well-defined first-order field-induced transitions occurred.[22] Near 0 K the estimated equilibrium transition fields in $x=0.27_2$ and 0.40_9 compositions of $Co_{1-x}Ni_xCl_2 \cdot 2H_2O$ were 9.1 and 9.4×10^3 kG, respectively. It is undecided whether transitions even near such field values occur for x smaller than the above; the available data suggest at least somewhat lower H_c values. It is quite clear, however, that for higher x values in the Co/Ni mixed system any transition fields are significantly larger than 9–10 kG.

In contrast, in $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$ there is evidence of field-induced transitions occurring in the vicinity of 10 kG near 0 K for compositions extending from x=0.30 through 0.80. There is no sign, as in the Co/Ni mixture, that with increasingly high nickel content the transition field value approaches that in the pure nickel material (19 kG), though it is natural to assume this must occur in the $x \rightarrow 1$ limit. The detailed hysteretic behavior definitely differs from that in $Co_{1-x}Ni_xCl_2 \cdot 2H_2O$. This is most pronounced at the lowest 1.8 K temperature examined, where data suggest that the $H_c(+)$ value is as high as 14.3 kG while the $H_c(-)$ is a much lower 4.8 kG. Such difference did not appear in the Co/Ni mixture data. Moreover, there is a major qualitative difference between the appearance of these 1.8 K data and those at an only moderately higher temperature of 2.8 K, where the difference between $H_c(+)$ and $H_c(-)$ becomes much smaller. In general, however, the hysteresis loops in the Fe/Ni mixture are of similar size to those seen in the Co/Ni mixture. As already noted, the temperature dependence of the loop area in the Fe/Ni mixture is not of the simple form seen in the Co/Ni system; nor do we believe that this can be a mere consequence of uncertainties in evaluating these areas.

In seeking a rationale for the rather different $T(x)$ and detailed $M(H)$ behaviors in $Co_{1-x}Ni_xCl_2 \cdot 2H_2O$ and $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$, one might consider other differences between the properties of the cobalt and iron components of these mixed systems. The most obvious differences are T_c (Néel) values and the metamagnetic critical fields. The ordering temperature is 27% higher for $FeCl_2 \cdot 2H_2O$ than for $CoCl_2 \cdot 2H_2O$. Probably the only direct consequence of this is that the upper temperature maxima and associated transitions are correspondingly higher in $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$ than in $Co_{1-x}Ni_xCl_2 \cdot 2H_2O$. Of more significance is likely to be that H_c in the pure iron compound is 25% higher than in the pure cobalt. Yet the H_c value in $x=0.60$ $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$ is only 5–10% larger than in those compositions of $Co_{1-x}Ni_xCl_2 \cdot 2H_2O$ ($x=0.27_2$ and 0.40_9) where the clearest metamagnetic behavior occurred. If, however, one focuses on $H_c(+)$ values, there is more marked difference between the two mixed systems. In each of the above cited compositions of the Co/Ni mixture, $H_c(+)$ exceeded 10 kG only at the lowest 1.8–1.9 K temperature, and was still clearly less than 11 kG. In the Fe/Ni system, on the other hand, $H_c(+)$ exceeds 14 kG at a similar temperature for each of the compositions $x=0.30$ through $x=0.70$ (it is just less than 12 kG for $x=0.80$). If one consults instead the 2.8 K isotherms, which are such as to allow more precise determinations of $H_c(+)$, this quantity still exceeds 12 kG (except for $x=0.80$ where it is 11.6 kG). In the Co/Ni system at a similar temperature $H_c(+)$ was near 9.5 kG for each of the above cited compositions.

It seems likely that the differences in behavior between the Co/Ni and Fe/Ni mixtures result from either or both of differences in the character of the dominant anisotropies in $CoCl_2 \cdot 2H_2O$ and $FeCl_2 \cdot 2H_2O$ and differences in ordered spin orientations. The nature of the magnetic states on either side of the two field-induced transitions in each material is the same. At the lower transition (31.3 kG in the cobalt and 39.2 kG in the iron system), one-third of the saturation magnetization achieved at the higher transition (44.9 kG in the cobalt and 45.6 kG in the iron material) is attained. A six-sublattice structure has been proposed for the intermediate state, and its existence is believed to be due to a secondary antiferromagnetic intrasublattice interaction (the dominant one is ferromagnetic). As to the character of the anisotropy, it is considered strictly of single-ion type in $FeCl_2 \cdot 2H_2O$, i.e., a term DS_z^2 with respect to the $S=2$ spin and with D/k variously estimated as 8.3 or 13.7 K.[28] In $CoCl_2 \cdot 2H_2O$, on the other hand, at low temperatures the effective spin becomes $S'=1/2$ with associated anisotropic effective exchange interaction.[38] It is established that this difference leads to the existence of multimagnon bound states in the cobalt compound, which can be observed,[38] while any such which might exist in the iron compound are not.[25] We cannot judge whether these anisotropy differences account for the distinctions in $T(x)$ and $M(H)$ properties in the Co/Ni and Fe/Ni mixed materials; a difficult theoretical treatment would doubtless be needed.

It is far from evident how the nearly orthogonal ordering tendencies of the cobalt and iron spins in $Co_{1-x}Ni_xCl_2 \cdot 2H_2O$ and $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$ can explain the very different composition dependence in the metamagnetism exhibited. But the earlier proposed explanation for the different $T(x)$ appearance in the two mixed systems may provide a phenomenological rationale. The narrow composition range in $Co_{1-x}Ni_xCl_2 \cdot 2H_2O$ in which two susceptibility maxima were observed also corresponds fairly well with that including compositions showing very clear metamagnetic transitions with rather similar H_c. In $Fe_{1-x}Ni_xCl_2 \cdot 2H_2O$ the composition range exhibiting two susceptibility maxima is much broader, and it is just over this range that metamagnetic transitions are seen with only small variation in the value of H_c. It appears doubtful that these correlations can be mere coincidence, though of course no deeper explanation is thereby provided. Unanswered as well, and surely worth theoretical attention, is why the metamagnetic critical field is reduced, in each of the Co/Ni and the Fe/Ni mixed systems, relative to values in the pure components.

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