

Composition induced lowering of metamagnetic critical field and static magnetic properties of $\text{Co}_{1-x}\text{Ni}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

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The magnetic behavior of $\text{Co}_{1-x}\text{Ni}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ has been studied by dc magnetization and susceptibility measurements on mixtures spanning the entire composition range. The pure components are three-dimensional Ising (Co) and Heisenberg (Ni) antiferromagnets, ordering at 17.2 K and at 7.25 K (with a 6.31 K spin reorientation transition), respectively. Each contains $\text{MCl}_2\text{MCl}_2\text{M}\dots$ 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 that vary regularly with composition. C vs x is close to linear. The $\theta(x)$ dependence is less conventional, exhibiting only weak variation for small x , a marked increase between $x \geq 0.2$ and $x \leq 0.4$, and a steady increase from $x > 0.4$ to 1. In the susceptibilities of all mixtures below 20 K antiferromagnetic maxima appear. For Ni-rich mixtures only one maximum occurs, with T_{max} increasing weakly but uniformly from $x=1$ (7.47 K) to $x=0.56_4$ (8.8₃ K). A maximum in this region persists even down to $x=0.27_2$ (9.1₅ K); for $x=0.21_0$ only a shoulder in $\chi(T)$ near 9 K appears. For Co-rich mixtures a maximum near 18 K occurs, becoming merely incipient for $x \sim 0.4$; its location varies weakly between 17.9₅ and 18.2₅ K. Transition temperatures, slightly lower than the associated T_{max} , can often be estimated; these display a weak but regular composition dependence as well. Magnetization vs field isotherms evolve with composition. For high x the appearance of $M(H)$ is similar to that of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$. For low x somewhat more curvature in $M(H)$ occurs than for $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, and there is a suggestion of qualitatively different behavior, though hysteresis effects are very small. Dramatically different properties are observed for $x=0.27_2$ and 0.40₉, where field induced transitions in the 6 to 10 kG range occur for temperatures below 7 K. Major hysteretic effects, especially below 2 K, also appear. The overall behavior is reminiscent of metamagnets, and since the inferred transition fields are two or more times smaller than those previously determined for the pure components, this is a composition induced effect. A mean-field theory analysis of the temperature dependence of the hysteresis is made, suggesting that the ratio of interchain to intrachain exchange is somewhat larger in the $x=0.27_2$ and 0.40₉ mixtures than in the pure components. The temperature dependence of the hysteresis loop area suggests the presence of an activation process with a characteristic temperature of the order of 1 K.

I. INTRODUCTION

Mixed magnetic systems, especially those based on insulating materials in which any exchange interactions are short range, have long played an important role in the study of phase transitions influenced by the presence of random disorder. Mixed magnets in which competing orthogonal spin anisotropies occur constitute one major class of system which has received attention, both theoretical^{1,2} and experimental;³⁻⁷ tetracritical points in the phase diagrams of such systems have frequently been observed. Also of great importance are mixed magnets in which strongly competing ferromagnetic and antiferromagnetic interactions exist, leading to frustration and often to spin-glass behavior.^{8,9} A number of experimental systems have been examined,¹⁰⁻¹³ and the theoretical literature is extremely extensive.

It is still possible, however, to uncover and study effects in mixed magnetic systems in which neither competing orthogonal anisotropies nor frustrated exchange interactions occur. For example, a wide variety of possible forms for the dependence of ordering temperature on composition have been obtained theoretically.¹⁴⁻¹⁶ $T_c(x)$ may display lesser or greater curvature of either sign, different curvatures in dif-

ferent composition (x) ranges, maxima or minima, or even both a maximum and a minimum in the same T - x phase diagram. Few of these unusual shapes have actually been observed in real systems. Also interesting is the appearance of other than simple antiferromagnetic behavior in a mixture of otherwise normal antiferromagnets. This might occur because of different, though not orthogonal, anisotropy axes of the pure components, or because of the appearance of new exchange interactions in the mixture that markedly alter the balance among such interactions.

This paper examines the static magnetic properties of mixed magnetic $\text{Co}_{1-x}\text{Ni}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ over the complete composition range. The structures of the two components, while not identical, have many similarities. Each is characterized by linear chains of chloride bridged metal ions, with slightly less than 90° Cl-M-Cl bridging angles. In $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ slight relative tilting of adjacent NiCl_4 planar coordination units along the chain leads to a repeat unit of two nickel centers,¹⁷ vs only one cobalt center in $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ where no tilting occurs.¹⁸ Both substances crystallize in a monoclinic $C2/m$ structure, with $\text{MCl}_2\text{MCl}_2\text{M}\dots$ chains along the b axis in $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ and along the c axis in

$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$. The lengths of these axes in the two materials are in the ratio 1.937:1, quite close to 2:1 (i.e., the different periodicity along chains in $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$). Thus, substitutional replacement of either metal ion along the chain may be expected. In both substances the chains are coupled structurally by hydrogen bonding, though details differ due to the different tilting characteristics. The unit-cell volumes per formula unit are 109.6 and 105.0 Å³, for $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$, respectively. The 4.2% difference is sufficiently small that homogeneous mixing may be expected. In previously studied^{6,7,11} binary mixtures of the Mn, Co, and Fe systems, the differences in the unit cell volumes were typically this large or even larger. In $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ a subtle structural transition occurs at 230 K, leading to a doubling of the *c* axis and slight shifting of certain $\text{NiCl}_2\text{NiCl}_2\text{Ni} \dots$ chains relative to others.¹⁹ The effects of such a transition in the high-temperature susceptibilities of nickel rich compositions examined here appear to be evident.

$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ is a well-studied three-dimensional (3D) Ising antiferromagnet ordering at 17.2 K.^{20–23} Spins in the $\text{CoCl}_2\text{CoCl}_2\text{Co} \dots$ chemical chains are ferromagnetically aligned along *b*, with the spins of chains separated by $\pm(a \pm b)/2$ oppositely directed to give overall antiferromagnetism. For $T \ll 17.2$ K a metamagnetic transition occurs at 31.3 kG, and then a second transition at 44.9 kG, to a state of greater ferromagnetic alignment. $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ is a much more isotropic 3D Heisenberg antiferromagnet ordering at 7.25 K, with a spin reorientation transition occurring at 6.31 K.^{24,19} The spins in each $\text{NiCl}_2\text{NiCl}_2\text{Ni} \dots$ 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. In $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ also, a metamagnetic transition occurs at 19 kG near 0 K, this is followed by transitions at 56 and 82 kG, to states of increasing ferromagnetic alignment.¹⁹

In each of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ spins align along or very nearly along metal-oxygen bonds, which are essentially normal to the $\text{MCl}_2\text{MCl}_2\text{M} \dots$ chains. Therefore, in the mixed spin chains, competing orthogonal spin anisotropies should not occur. 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 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 not heretofore seen. The Weiss constant, from fits to high-temperature susceptibility data, also shows an interesting composition dependence. Most remarkable perhaps is the field dependence of the magnetization as a function of composition. Nonlinearities in *M* vs *H* are especially strong for certain compositions, and pronounced hysteretic behavior is also evident. Metamagnetic transitions occur at fields much smaller than those characterizing the pure components.

II. EXPERIMENT

Aqueous solutions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in various relative proportions were prepared and evaporated to

dryness at 80 °C over a period of a few days and with occasional grinding to prevent occlusion of water. That the dihydrate was obtained was confirmed by thermogravimetric analysis of the materials. These were fine grained and uniform in appearance. Colors ranged from dark red at the cobalt end of the composition series to yellow green at the nickel end. Care was taken to minimize exposure of samples to atmospheric water vapor.

X-ray powder diffraction patterns of mixtures and pure components were obtained. Significant variations in peak positions and distribution of peaks for the pure components occurs, because of the different relations between unit-cell axes and local coordination and linkage axes. As *x* decreases from 1 toward 0, mixture patterns evolve in form from that of the nickel to that of the cobalt material. For compositions nearest the *x*=0,1 extremes, mixture patterns are similar to those of the corresponding pure component, with modest shifts of 1–2° for most diffraction peaks. For more intermediate compositions, the patterns differed more markedly from those of either pure component. There was no indication that either component was present separately in the mixtures, neither with respect to individual peak positions nor with respect to the total number of peaks. Thus the x-ray data suggest that a gradual shift from one structure to the other occurs as admixture proceeds. The quality of the x-ray data are not such as to permit conclusions to be drawn concerning the precise nature of any intermediate composition structure. The implication that microscopically homogeneous mixtures were obtained, at the level probed by x rays, is also consistent with the observed magnetic behavior.²⁵ Cobalt and nickel concentrations were determined by atomic absorption spectrometry.

Magnetization and susceptibility measurements were performed with a variable-temperature vibrating sample magnetometer system. Susceptibility data are field cooled measurements and are corrected for demagnetization and diamagnetism. The latter is estimated as an essentially constant -9.0×10^{-5} emu/mol. A correction for temperature-independent paramagnetism was also made; this is estimated to vary between 2.4×10^{-4} and 4.3×10^{-4} emu/mol for the pure nickel and cobalt systems, respectively, with a mole fraction weighted average correction applied. Polycrystalline samples of from 100 to 150 mg were packed under dry conditions into nonmagnetic sample holders, accurately weighed, and then screwed onto a nonmagnetic sample rod in close proximity to a calibrated carbon-glass resistance thermometer. The accuracy of temperatures reported is from ± 0.005 to 0.5 K, depending on the range. Magnetic-field values are accurate to $\pm \max(2G, 0.1\%)$, and magnetization and susceptibility values to 1.5%, though the precision is substantially better than this.

III. RESULTS OF MEASUREMENTS

A. Magnetic susceptibility

The reciprocal molar susceptibilities of seven mixtures and the pure components examined in this paper are shown vs temperature in Fig. 1; corrections (relatively small) for demagnetization, diamagnetism, and temperature-independent paramagnetism are already applied. Fits to the

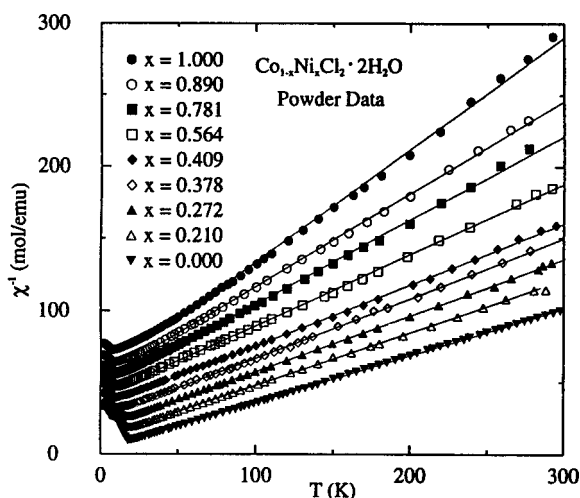


FIG. 1. Inverse molar magnetic susceptibility vs temperature for various compositions of $\text{Co}_{1-x}\text{Ni}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. The $x=0$ data are unshifted; for clarity data sets with successively larger x are shifted up 8, 16, . . . , 64 mol/emu. Lines are Curie-Weiss fits described in text.

data according to a Curie-Weiss form, $\chi_M = C/(T - \theta)$, also appear in Fig. 1, and were made for similar temperature ranges, ca. 30–300 K. At other temperatures deviations from linearity were evident. Modest variations of 5–10 K in the limiting fit temperatures led to only very minor variations in C and θ . The results for C and θ vs composition appear in Fig. 2. Statistical uncertainties in C and θ are about 0.2 emu K/mol and 1 K, respectively, comparable with or slightly larger than symbol sizes. Both C and θ vary with x in a smooth fashion. A straight line connecting $C(0)$ and $C(1)$ is the anticipated mean-field theory dependence on composition of $C(x)$ for a mixture; there appear some small systematic deviations of observed $C(x)$ above the line in Fig. 2. The $\theta(x)$ dependence is much more unusual, showing little variation for small x , a marked rise between $x=0.2$ and 0.4 , followed by an increasingly rapid increase as x approaches 1.

The molar susceptibility in the low-temperature region is shown in Figs. 3 and 4. Antiferromagnetic maxima are evident, and these occur at the expected locations for $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$

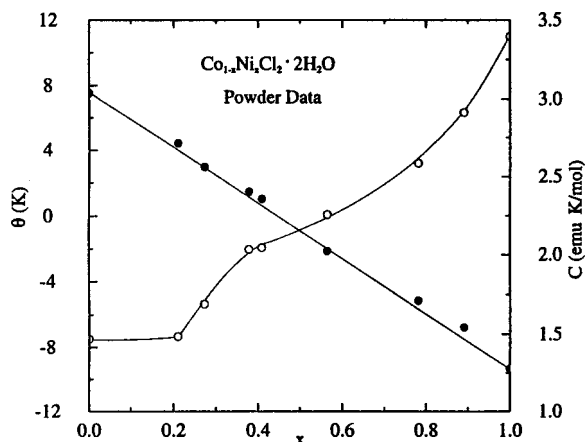


FIG. 2. Curie constant (\bullet) and Weiss θ (\circ) vs composition for $\text{Co}_{1-x}\text{Ni}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. A straight line connects C values for $x=0$ and 1. The curve associated with the θ values is a guide to the eye only.

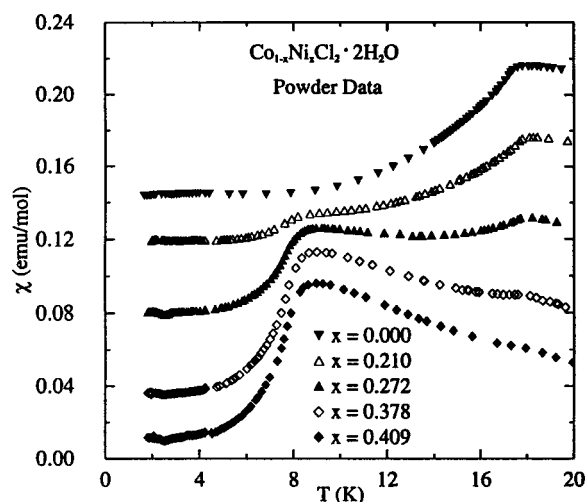


FIG. 3. Molar magnetic susceptibility vs temperature below 20 K for Co-rich compositions of $\text{Co}_{1-x}\text{Ni}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. For clarity the $x=0.0, 0.210, 0.272, 0.378,$ and 0.409 sets are shifted by $+0.11, +0.08, +0.03, -0.02,$ and -0.05 emu/mol, respectively.

and $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$. For the mixtures there appear one or two maxima in $\chi(T)$. Compositions $x=0.56_4$ through 0.89_0 show only one maximum, located in the 8–9 K range and displaying a modest but clear position dependence on concentration. Compositions $x=0.21_0$ through 0.40_9 show two maxima, one of them in some cases only incipient, occurring near 18 K and near 8 K. While the locations of these maxima, especially that near 18 K, show only weak composition dependence, the relative prominence of the two features varies strongly with concentration. The approximately 18 K maximum, reminiscent of the corresponding feature in $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, becomes dramatically weaker with increasing x . The approximately 8 K maximum, reminiscent of the corresponding feature in $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$, becomes dramatically stronger with increasing x . However, the relative prominence of the two features cannot be rationalized simply on the basis of the relative amounts of cobalt and nickel ion complex

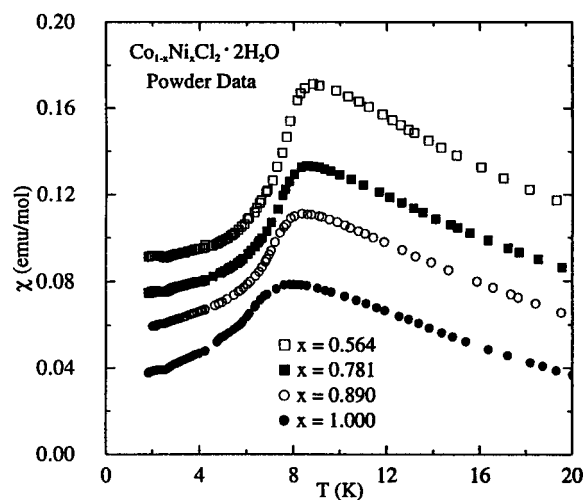


FIG. 4. Molar magnetic susceptibility vs temperature below 20 K for Ni-rich compositions of $\text{Co}_{1-x}\text{Ni}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. For clarity the $x=0.564, 0.781, 0.890,$ and 1.0 sets are shifted by $+0.02, 0, -0.02,$ and -0.04 emu/mol, respectively.

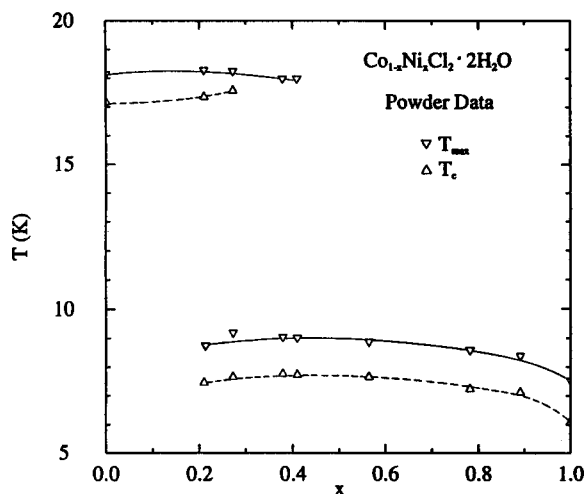


FIG. 5. Temperatures of susceptibility maximum (∇) and anti-ferromagnetic transitions (Δ) vs composition for $\text{Co}_{1-x}\text{Ni}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. Curves through results are guides to the eye only.

present. A mole-fraction weighted summation of the susceptibilities of the two pure components differs greatly from the observed $\chi(T)$ for each mixture.

Where possible the location of a maximum in $d\chi/dT$, on the low-temperature side of each susceptibility maximum, was estimated. This is assumed to correspond to the location T_c , of an antiferromagnetic transition.²⁶ Such an estimate can be made for the more prominent of the maxima in any given mixture, but frequently cannot be made for the weaker one. In Fig. 5 appear T_{max} and T_c vs composition. Uncertainties in these quantities are estimated to be approximately 0.1 K, comparable with symbol size. The T_c obtained here for $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ agree very well with literature values. The weak composition dependence of T_{max} and T_c is remarkable, while the form of the T - x diagram is unique as far as we know.

B. Magnetization

Magnetization isotherms measured for the pure components at 4.2 K were consistent with literature results. For $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ M vs H is essentially linear to our 15.9 kG maximum field, which is well below the 31.3 kG metamagnetic transition. For $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ the isotherm was linear to approximately 9 kG, with moderate upward curvature between 9 and 16 kG; the latter behavior is presumably anticipatory of the 19 kG metamagnetic transition in this substance. On decreasing the field from 15.9 kG to near zero the hysteresis in $M(H)$ was negligible in both materials.

The mixtures exhibit more interesting behavior. Isotherms for $x=0.21_0$ appear in Fig. 6. Even at 15 K some small curvature is present. For 4.232 K one can also discern two approximately linear regimes, one up to 8 kG and another from 10 to nearly 16 kG (there is slight concave downward curvature for the highest fields). Lines drawn through these regimes intersect at 8870 ± 50 G. Only very weak hysteresis was present for the 4.2 K isotherm, while the hysteresis was negligible at 15 K.

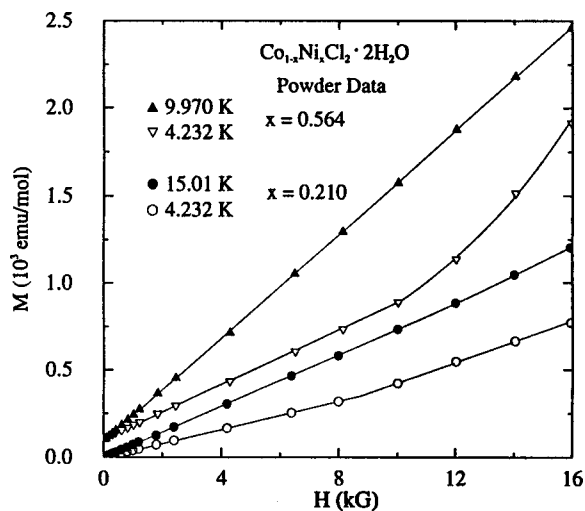


FIG. 6. Molar magnetization vs field (increasing) at various temperatures for $x=0.21_0$ and 0.56_4 compositions of $\text{Co}_{1-x}\text{Ni}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. For clarity the $x=0.56_4$ data are shifted up 100 emu/mol. Lines or curves through data are guides to the eye only.

The behavior for $x=0.27_2$ is more remarkable yet. A series of isotherms from 10.07 to 1.866 K appears in Fig. 7. That for 10.07 K is essentially linear, except for some weak upward curvature at the highest fields. The overall nonlinearity of M vs H becomes more pronounced with decreasing temperature. The low to moderate field sections of each isotherm are, however, fairly linear. The high-field sections show some concave downward curvature, but linear regimes exist in these over a few kG. Lines were drawn through the low-moderate field sections and through the near linear portion of the high-field sections. The resulting intersections are defined as the upper critical fields $H_c(+)$. A similar analysis performed for $M(H)$ taken on decreasing H back down (see next paragraph) yields lower critical fields $H_c(-)$. The $x=0.40_9$ mixture exhibited magnetization behavior qualitatively very similar to that of 0.27_2 .

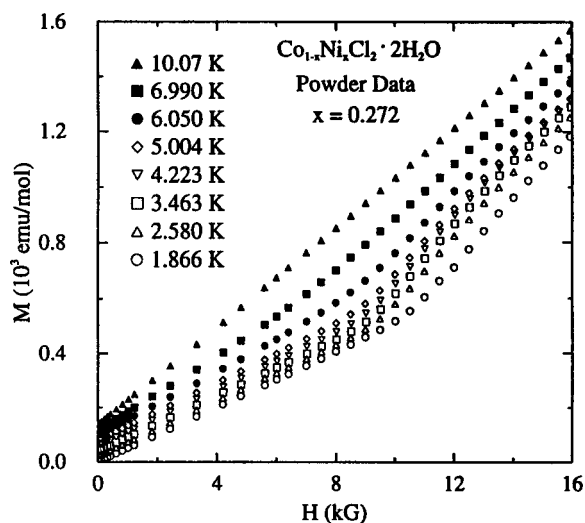


FIG. 7. Molar magnetization vs field (increasing) at various temperatures for an $x=0.27_2$ composition of $\text{Co}_{1-x}\text{Ni}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. For clarity the sets for successively higher temperatures than 1.866 K are shifted up by 20, 40, . . . , 140 emu/mol, respectively.

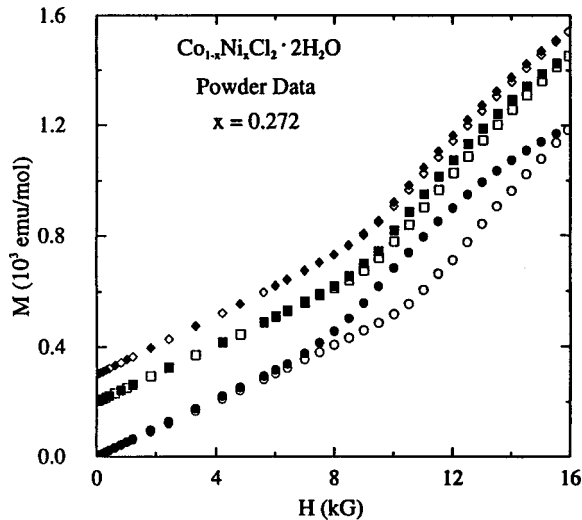


FIG. 8. Hysteresis in molar magnetization vs field for an $x=0.272$ composition of $\text{Co}_{1-x}\text{Ni}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ at 1.866 K (circles), 3.463 K (squares), and 5.004 K (diamonds); data for latter two temperatures are shifted up 200 and 300 emu/mol, respectively. Closed symbols are on decreasing the field.

Major hysteresis properties are also observed for the isotherms of $x=0.272$ and 0.409 . Examples appear in Fig. 8, for the former composition at three temperatures. The hysteresis for $x=0.409$ is very similar in magnitude and in general appearance. In Fig. 8, at 1.866 K, large hysteresis is evident from the highest field (15.9 kG) down to approximately 7 kG, below which the hysteresis is very small and qualitatively different. For each successively higher-temperature isotherm the hysteresis decreases substantially; it is, however, still much greater at 4.2 K for $x=0.272$ (and 0.409) than it is for $x=0.210$ or for mixtures with $x>0.5$.

The best available measure of the correct equilibrium transition field at a given temperature is the average of $H_c(+)$ and $H_c(-)$. This is displayed for the $x=0.272$ and 0.409 compositions in Fig. 9. The temperature dependencies are qualitatively very similar for the two mixtures, and apart

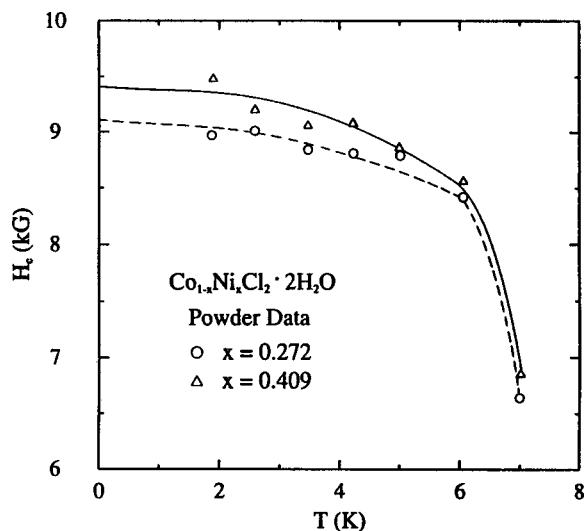


FIG. 9. Equilibrium transition field vs temperature for $x=0.272$ and 0.409 compositions of $\text{Co}_{1-x}\text{Ni}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. Curves through results are guides to the eye only.

from minor deviations are rather typical for such quantities in that substantial falloff in $H_c(T)$ occurs only fairly close to the Néel temperature. Critical fields for $x=0.409$ are slightly higher than for $x=0.272$.

A few isotherms were collected for $x=0.378$. Their appearance (not shown) was rather similar to those of $x=0.272$ and 0.409 at comparable temperatures. For $x=0.564$, however, a major qualitative difference is apparent; the two isotherms taken appear in Fig. 6. For 9.970 K the dependence is essentially linear, rather like the comparable temperature isotherms of $x=0.409$ and 0.272 . But the 4.232 K isotherm does not show the sharp upturn, with modest concave downward curvature at the highest fields, exhibited by the 4.2 K isotherms of $x=0.409$ and 0.272 . Instead the curvature is gradual and uniform. The hysteresis (not shown) was also much weaker than for the 4.2 K isotherms of $x=0.409$ and 0.272 .

Isotherms for $x=0.781$ (not shown) were qualitatively similar to those for $x=0.564$: linear near 10 K, with some curvature appearing for temperatures below 7 K, but without sharp upturns and with only very weak hysteresis at any temperature. For the 4.2 K isotherm of $x=0.781$, significant curvature appears only near and above 12 kG, a somewhat higher field than the corresponding 10 kG value characterizing the 4.2 K isotherm of $x=0.564$. Isotherms for $x=0.890$ (not shown) exhibited similar characteristics, with behavior rather similar to that observed for the pure nickel system.

IV. ANALYSIS AND DISCUSSION

Several 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 in strong disagreement with a weighted average of the pure component susceptibilities, as noted in Sec. III A. Also, although the composition dependencies of the locations of the two susceptibility maxima (one near 18 K for $x=0$ through $x=0.409$, the other near 8 K for $x=0.272$ through $x=1$) are weak, there is some systematic variation as close inspection of Fig. 5 reveals. Thus T_{max} varies monotonically from 9.15 K at $x=0.272$ to 7.47 K at $x=1$. Most striking perhaps, the magnetization behavior in mixtures, especially for $x=0.272$ and 0.409 , is qualitatively different from that of either pure component. In the high-field, high-hysteresis regions in particular, it is clear that a different kind of magnetically ordered state exists. In $x=0.272$ and 0.409 some weak time dependencies in the magnetization were observed for the lowest temperatures (1.866 K, 1.896 K) only, and in these cases only within the major hysteresis loops at higher fields. The size of these loops was much greater at 1.8–1.9 K than at higher temperatures. It is reasonable to conclude that the time dependencies are not related to any spin-glass characteristics but rather to domain-wall motion associated with the hysteresis loops. In lower and higher x mixtures the high-field hysteretic properties of the $x=0.272$ and 0.409 compositions did not develop.

That significant frustration effects would not occur in the present mixed system was anticipated, and is supported by comparison of the Weiss θ parameters obtained from the susceptibility analysis with the observed ordering tempera-

tures. The ratio $|\theta|/T_c$ has been proposed²⁷ 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 $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$, the ratio is less than one and often substantially less. However, the existence of major ferromagnetic interactions in the present materials makes $|\theta|/T_c$ a less conclusive indicator of frustration.

There are indications in the susceptibilities of very Ni-rich mixtures of the high-temperature structural phase transition characterizing $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$.¹⁹ Modest shifts in $\chi^{-1}(T)$ appear between 220 and 240 K for $x=1$, and between 200 and 225 K for $x=0.89_0$ and 0.78_1 , the shifts being smaller for the latter two compositions. If the Curie-Weiss fits are redone to exclude the four highest temperature data for each of these compositions, small increases in C (from 2.3 to 3.4%, approximately the symbol width in Fig. 2) and small decreases in θ (from 0.8 to 2.0 K, or two to four symbol widths) occur. These shifts do not alter the $C(x)$ and $\theta(x)$ dependencies in Fig. 2 in any essential way.

In Fig. 2 the $C(x)$ dependence is close to linear as expected from mean-field theory.²⁸ However, the $\theta(x)$ dependence clearly indicates the existence of at least two concentration regimes, one from $x=0$ to ≤ 0.4 and the other for $x \geq 0.4$. The composition dependencies of T_{\max} and T_c in Fig. 5 are quite different from that of $\theta(x)$. But the existence of two composition regimes on either side of $x \approx 0.4$ is evident.

The existence of two maxima in the susceptibilities of the compositions $x=0.21_0$ through 0.40_9 is remarkable. The arguments against an inhomogeneity-based explanation have been provided. While successive transitions for a given composition are typically observed in tetracritical systems, that explanation is not applicable here. Not only is tetracritical behavior not expected in the present mixture on magnetic/structural grounds, the temperatures at which the maxima occur for the above compositions are inconsistent with any plausible set of ordering lines meeting at a tetracritical point.

Certain mixed systems are known in which successive transitions occur^{29,30} but for which tetracritical behavior has not been claimed. The additional transitions are thought to be spin reorientation in character, arising from the tendencies of different species to order along different directions or in different patterns. As discussed in Sec. I, the spin alignment directions of the cobalt and nickel ions are anticipated to be close to the metal-oxygen bonds. These tendencies are determined by local anisotropy effects associated with metal ion coordination geometries. But based on the local geometries in the pure compounds, such M-O bond directions probably differ slightly depending on cobalt vs nickel site occupancy. It is possible that over some limited composition range neither the cobalt nor the nickel ion anisotropy sufficiently dominates so as to favor a single ordering direction in a cooperative transition. Rather, first one and then the other alignment tendency appears as the temperature is varied. At the present stage, and especially lacking single-crystal samples, this suggestion must of course be considered speculative.

The magnetization isotherms for $x=0.27_2$ in Figs. 7 and 8 suggest metamagnetic behavior. The pure components undergo metamagnetic transitions only at much larger fields,

approximately 19 and 31 kG for the nickel and cobalt materials, respectively (with additional transitions at yet higher fields). The substantial hysteresis observed for $x=0.27_2$ (and 0.40_9) is also suggestive of first-order transitions. Such are indeed the rule in metamagnets for temperatures well below that of antiferromagnetic ordering.

Mean-field and associated theories of metamagnetic transitions, with particular application to FeCl_2 , were employed in a classic paper of Jacobs and Lawrence.³¹ 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

$$H_{\text{eff}}^{\pm} = H - AM^{\mp} + \Gamma M^{\pm}, \quad (1)$$

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. Of course in order for a metamagnetic transition to develop the anisotropy strength has to be sufficiently strong, exceeding that of the antiferromagnetic exchange between the sublattices.

The present mixed system is suitable for applying the foregoing model, because in both components the intrasublattice exchange (along $\text{MCl}_2\text{MCl}_2\text{M}\dots$ chains) is ferromagnetic (positive Γ) and the intersublattice exchange (between the chains) is antiferromagnetic (positive A). Preliminary to consideration of the temperature dependence of the hysteresis, we first apply the following relation emerging from the mean-field treatment³¹

$$\Gamma/A = (kT_N/\mu H_c)[3S/(S+1)] - 1, \quad (2)$$

where μ is the magnetic moment per magnetic ion, T_N is the Néel temperature, and H_c is the transition field at 0 K. The magnetic moment can be calculated from the Curie constant via $C = N_0\mu^2/3k$; 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_N and H_c (near 0 K) for $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ along with μ values derived from the Curie constants determined here, together with $S_{\text{Co}} = 3/2$ and $S_{\text{Ni}} = 1$, the values of Γ/A that emerge are 1.9_9 and 1.2_6 , respectively. Expressions for the mean-field coefficients in terms of the primary exchange interactions are $A = 2z_{AF}J_{AF}/N$ and $\Gamma = 2z_F J_F/N$, 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.³¹ There are $z_F = 2$ neighbors along a chain. A given ion on a chain interacts with $z_{AF} = 4$ 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 (Co) times. This is qualitatively consistent with conclusions arrived at previously by other means.^{19,23}

We apply the same method to the $x=0.27_2$ and 0.40_9 compositions, using T_N values (Fig. 5) of 7.69 and 7.77 K and estimated for 0 K transition fields of 9.1 and 9.4

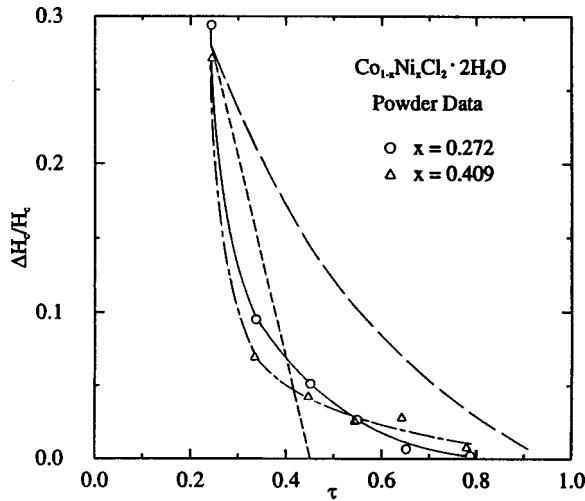


FIG. 10. Fractional hysteresis at equilibrium critical field vs reduced temperature for $x=0.272$ and 0.409 compositions of $\text{Co}_{1-x}\text{Ni}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. Curves through results (solid- and short-long dash, respectively) are guides to the eye only. Also shown are the mean-field predictions (from Ref. 31) for $\Gamma/A=9$ (long-dash curve) and $\Gamma/A=0.6$ (short-dash curve), scaled as described in text.

$\times 10^3$ G, respectively. The measured Curie constants yield the effective moments 4.19_6 and $4.02_7 \mu_B$ in the same order. The average mixture spin is taken as $[(1-x)S_{\text{Co}}^2 + xS_{\text{Ni}}^2]^{1/2}$, with $S_{\text{Co}}=3/2$ and $S_{\text{Ni}}=1$ as above. The resulting Γ/A are each 4.2_2 , significantly larger than the ratios for the pure components primarily because of the substantially smaller critical fields of the mixtures.

Another prediction which emerges from mean-field theory, in the limit of Ising type anisotropy,³² is 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 $\tau=T/T_N$, which will be needed later,

$$\tau^* = 1 - A/3\Gamma. \quad (3)$$

With $\Gamma/A=4.2_2$ the result is $\tau^*=0.92_1$. Hence, for $x=0.27_2$ and 0.40_9 , the prediction is that $T^*=7.08$ and 7.16 K, respectively. As noted previously, the hysteresis decreases markedly with increasing temperature. It is barely discernible at the highest temperatures measured at which a field-induced transition is still observed, 6.990 and 7.005 K for $x=0.27_2$ and 0.40_9 , respectively.

Analysis of the hysteresis as a function of temperature can also be made based on a mean-field model.³¹ Define ΔH_c as the difference between apparent transition fields for increasing and decreasing field. Then $\Delta H_c/H_c$, where H_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. 10 are plotted $\Delta H_c/H_c$ vs τ for the $x=0.27_2$ and 0.40_9 compositions. The behavior is more erratic for higher temperatures in the latter mixture, but the magnitude and temperature dependencies of $\Delta H_c/H_c$ are similar for the two mixtures. Also shown are the mean-field predictions obtained in Ref. 31 for two values of Γ/A , 9 and 0.6. These

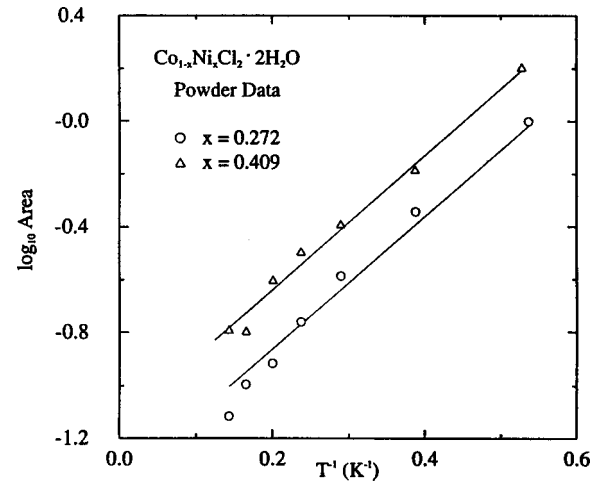


FIG. 11. Logarithm of hysteresis loop area (arbitrary units) vs reciprocal temperature for $x=0.272$ and 0.409 compositions of $\text{Co}_{1-x}\text{Ni}_x\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. Linear approximations to each set are shown.

have been scaled so that the calculated $\Delta H_c/H_c$ is 0.28 at the lowest temperature(s) measured ($\tau=0.243$ and 0.244 for $x=0.27_2$ and 0.40_9 , respectively). (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.³¹) While the observed temperature dependencies differ from either 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 estimates for the two compositions. It is also very likely that the difference in shape between observed and calculated dependencies is due to the polycrystalline nature of the samples studied here.

In a magneto-optical study of FeCl_2 an interesting relation was found for the temperature dependence of the hysteresis,³³ although the data were limited to the narrow, low-temperature range of 1.34 – 2.1 K [for FeCl_2 , $T_N=23.55$ K, with an empirical tricritical temperature of 21.15 K (Ref. 31)]. Specifically, the area enclosed by the H increasing and decreasing magnetization curves was found to be proportional to $\exp(\delta/T)$, with $\delta=14.2$ K. Possible inferences are that domain-wall motion associated with the progress of the metamagnetic transition is thermally activated, or alternatively that the nucleation of the domains is so activated.

We have calculated the areas enclosed by the moderate-high-field hysteresis loops of the $x=0.27_2$ and 0.40_9 compositions at various temperatures. The logarithm of the loop area (in arbitrary units) is plotted vs reciprocal temperature in Fig. 11. The $x=0.40_9$ results are more nearly linear, though with substantial scatter. The $x=0.27_2$ results exhibit systematic curvature. However, in either case a straight line can be drawn which is a plausible mean representation of the results. The slope of the line is about 1.2 K in either case. This is an order of magnitude smaller than the value found for FeCl_2 in Ref. 33.

From $\theta(x)$, $T_{\text{max}}(x)$, and $T_c(x)$, and the composition dependence of magnetization isotherms, it is apparent that the region from somewhat above $x=0.2$ to slightly above $x=0.4$ is special. Theta increases markedly here, two suscep-

tibility maxima occur, and metamagnetic behavior is accentuated, with a first-order transition at fields much less than for either pure component. We are unaware of any theory of composition dependent metamagnetism in a mixture of two magnetic components having different spin anisotropies. It is hoped that the present results may serve to stimulate such work.

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