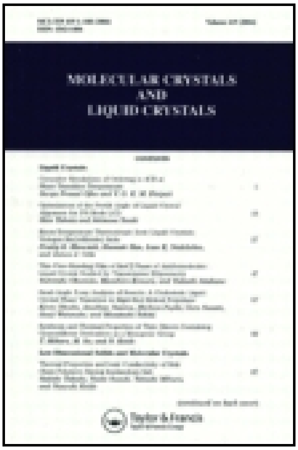

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Magnetic Properties of Random-Mixture Graphite Intercalation Compounds

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MAGNETIC PROPERTIES OF RANDOM-MIXTURE GRAPHITE INTERCALATION COMPOUNDS

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Abstract Random-mixture GICs such as stage-2 $Ni_cMn_{1-c}Cl_2$ GICs and stage-2 $Co_cMn_{1-c}Cl_2$ GICs provide model systems for studying 2D random spin systems with spin frustration effects. The magnetic properties of these compounds have been studied by dc and ac magnetic susceptibility, and low field SQUID magnetization measurements. An irreversible effect of magnetization for stage-2 $Ni_cMn_{1-c}Cl_2$ GICs ($0.8 \leq c \leq 1$) and stage-2 $Co_cNi_{1-c}Cl_2$ GICs ($0 \leq c \leq 1$) indicates an occurrence of cluster glass phase below a critical temperature where the spin directions of ferromagnetic clusters are frozen because of frustrated inter-island interactions.

INTRODUCTION

Magnetic binary graphite intercalation compounds (GICs) such as stage-2 $CoCl_2$ GIC and stage-2 $NiCl_2$ GIC have proven to be extremely fruitful for fundamental studies in the physics of two-dimensional (2D) magnetism.[1,2] Magnetic ternary GICs promise to continue this trend and even enhance the versatility of binaries by adding another degree of freedom to the design of these synthetic compounds. The magnetic random-mixture graphite intercalation compounds (RMGICs) such as $Co_cNi_{1-c}Cl_2$ GICs,[3-5] $Ni_cMn_{1-c}Cl_2$ GICs,[6] and $Co_cMn_{1-c}Cl_2$ GICs[7] are novel types of GIC where the intercalate layer is formed of a random mixture of two kinds of intercalants such as $CoCl_2$, $NiCl_2$, and $MnCl_2$. These magnetic RMGICs form a class of materials whose dimension can be systematically controlled by the number of graphite layers between adjacent intercalate layers, i.e., the stage number. Because of recent progress in sample preparation these magnetic RMGICs provide model systems for studying the magnetic phase transitions of two-dimensional (2D) random spin systems where various kinds of spin frustration effect occur as a result of the competing intraplanar ferromagnetic and antiferromagnetic interactions and the competing spin anisotropies between Ising, XY and Heisenberg symmetry. The intercalate layers of these magnetic RMGICs have a unique 2D complex lattice formed of small islands. The peripheral chlorine ions at the island boundary provide acceptor sites for charges transferred from the graphite layer to the intercalate layer. The island diameter of intercalate layers is on the order of 500 Å. The growth of spin correlation length within intercalate layers may be limited by the existence of small islands.

We have undertaken extensive studies on magnetic properties and magnetic phase transitions of stage-2 $Ni_cMn_{1-c}Cl_2$ GICs and stage-2 $Co_cNi_{1-c}Cl_2$ GICs by dc and ac magnetic susceptibility, and SQUID magnetization measurements. The Curie-Weiss temperature Θ and the critical temperature T_c are determined as a function of concentration and discussed in terms of the molecular field theory. The low field magnetization shows an irreversible effect below T_c for stage-2 $Ni_cMn_{1-c}Cl_2$ GICs with $0.7 \le c \le 1$ and stage-2 $Co_cNi_{1-c}Cl_2$ GICs with $0 \le c \le 1$. Possible phases such as cluster glass phase and spin glass phase are discussed.

EXPERIMENT

The dehydration of ACl_2 and BCl_2 (A, B = Co, Ni, Mn) was done at 400 °C in the presence of HCl gas at a pressure of one atmosphere. Single crystals of $A_cB_{1-c}Cl_2$ over the entire range of A-concentrations are grown by using the Bridgeman method: a mixture of dehydrated ACl_2 and BCl_2 with the nominal weight composition was heated in quartz sealed in vacuum at 990 °C. The stage-2 $A_cB_{1-c}Cl_2$ GICs were synthesized by intercalating single crystal $A_cB_{1-c}Cl_2$ into single-crystal kish graphite in a chlorine gas atmosphere at a pressure of 740 Torr. The reaction was continued at 540 °C for 20 days. The stage of these RMGIC samples was confirmed to be well-defined stage-2 by (00L) x-ray scattering experiments using a Huber double-circle diffractometer with a Siemens 2.0 kW x-ray generator.

The dc magnetic susceptibility was measured by the Faraday balance method in the temperature range between 1.5 K and 300 K. A magnetic field of 100 Oe $\le H \le$ 2 kOe was applied in an arbitrary direction in the c-plane of the samples. The ac magnetic susceptibility was measured by a conventional ac Hartshorn bridge method in the temperature range between 2.6 K and 30 K. An ac magnetic field of 330 Hz was applied in an arbitrary direction in the c-plane of the samples. The highly sensitive measurements of magnetization were carried out with a SQUID magnetometer (Model VTS-905 SQUID system, manufactured by S.H.E. Corporation). The measurements were performed in three steps. (i) A sample having a weight of 4 - 7 mg was first cooled to a temperature 4.2 K from 300 K in five minutes in the absence of magnetic field. A field of 1 Oe was then applied in an arbitrary direction in the c-plane of the sample, and held constant while the measurements were made from 4.2 K to 30 K. (ii) The temperature dependence of zero-field cooled (ZFC) magnetization, M_{ZFC}, was measured at increasing temperature from 4.2 K to 30 K. (iii) The sample was again cooled while the field of 1 Oe and the temperature dependence of field-cooled (FC) magnetization, M_{FC}, was measured at decreasing temperature from 30 K to 4.2 K.

The actual concentration of stage-2 $A_cB_{1-c}Cl_2$ GIC samples may be different from the concentration of pristine compound $A_cB_{1-c}Cl_2$ used as intercalants. We determined the concentration of RMGIC samples by electron microprobe measurement. The measurement was carried out by using a scanning electron microscope (Model Hitachi S-450). Figure 1 shows the relationship between the concentration (c_b) of the pristine compounds and the concentration (c_e) determined from the electron microprobe for stage-2 $Ni_cMn_{1-c}Cl_2$ GICs. The data of c_e vs c_b in stage-2 $Ni_cMn_{1-c}Cl_2$ GICs agree well with a straight line with $c_e = c_b$ in the entire concentration of c_b, suggesting that the actual concentration c is the same as the concentration of the pristine compounds used as intercalant.

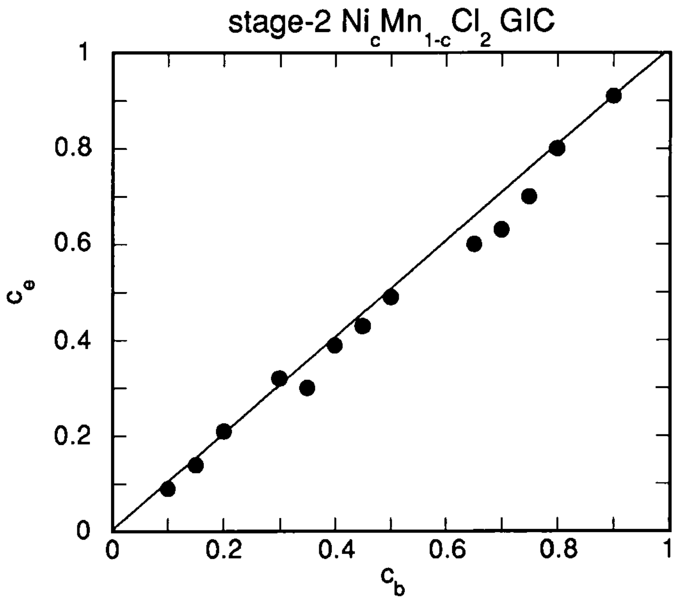


FIGURE 1 Relationship between bulk concentration (c_b) of intercalants and concentration (c_e) determined from the electron microprobe measurement for stage-2 $Ni_cMn_{1-c}Cl_2$ GICs.

RESULTS AND DISCUSSION

Stage-2 $Ni_cMn_{1-c}Cl_2$ GICs are 2D random-spin systems with competing ferromagnetic J(Ni-Ni) and antiferromagnetic J(Mn-Mn) exchange interactions.^{6} Figures 2(a) shows

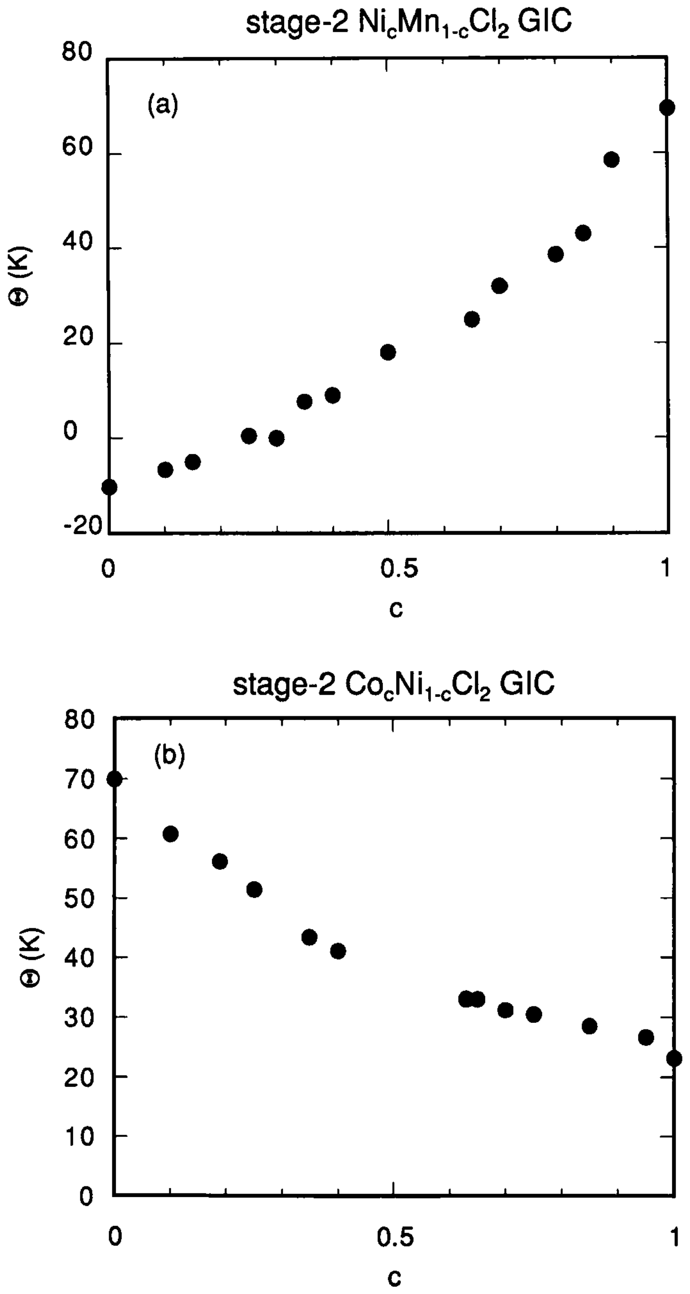


FIGURE 2 Θ vs c in (a) stage-2 $Ni_cMn_{1-c}Cl_2$ GICs (Ref. 6) and (b) stage-2 $Co_cNi_{1-c}Cl_2$-GICs (Ref. 4).

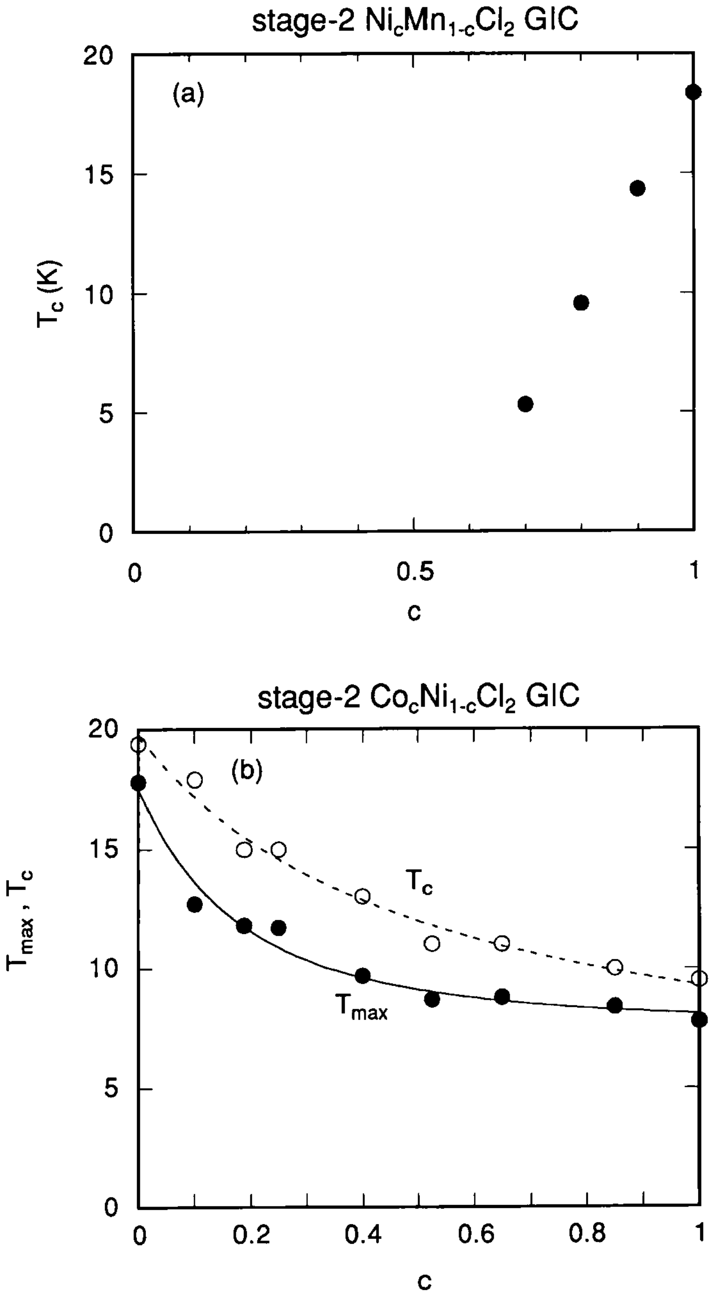
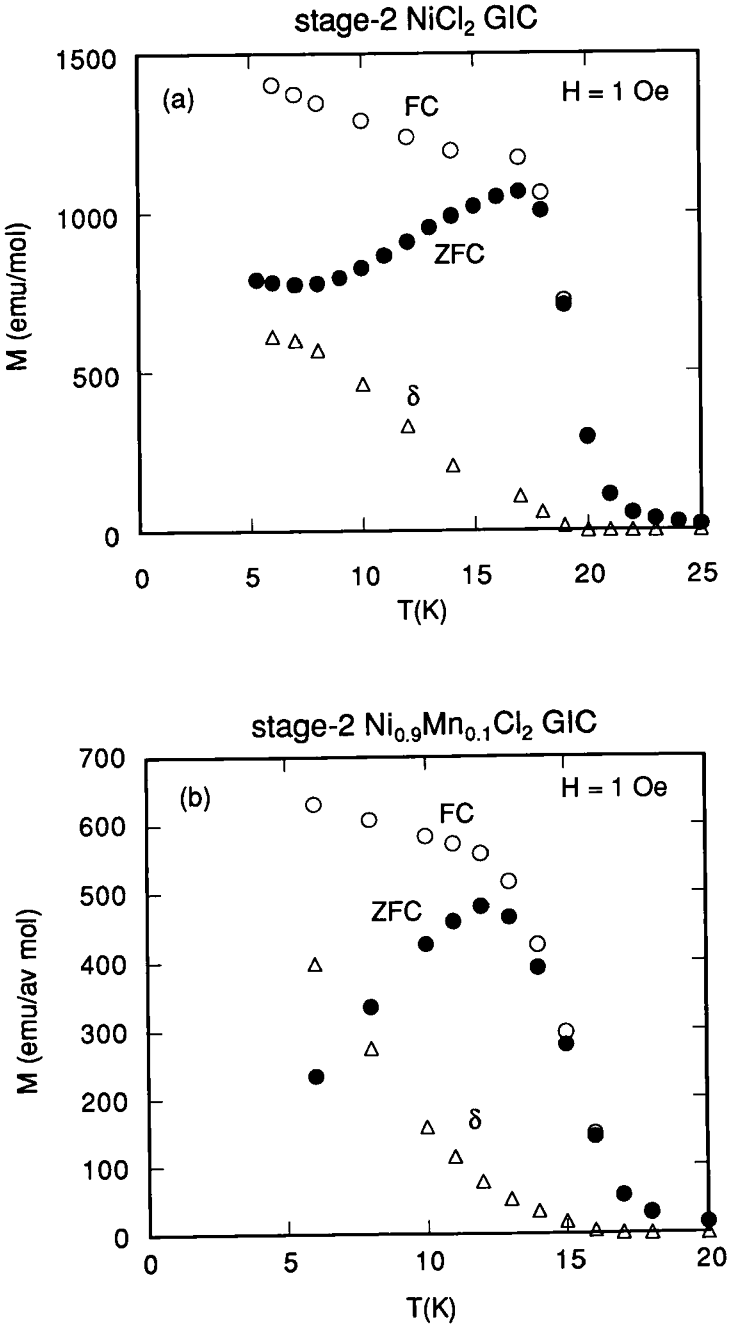


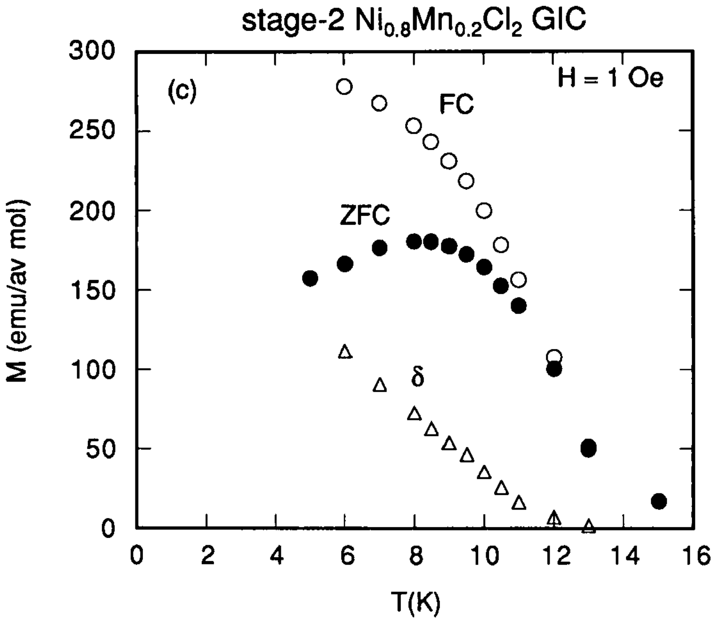
FIGURE 3 (a) T_c vs c in stage-2 $Ni_cMn_{1-c}Cl_2$ GICs (Ref. 7). (b) T_c vs c and T_{max} vs c in stage-2 $Co_cNi_{1-c}Cl_2$-GICs (Ref. 8). The solid and dotted lines are guides to the eyes.

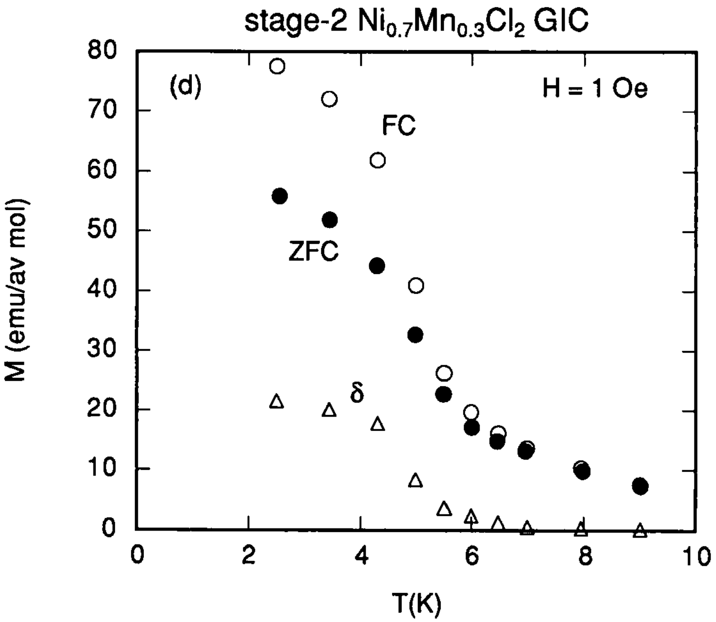
the Ni concentration dependence of Curie-Weiss temperature Θ. The monotonic increase of Θ with Ni concentration suggests that both Ni and Mn ions are randomly distributed on the triangular lattice sites of the $Ni_cMn_{1-c}Cl_2$ intercalate layers. The sign of Θ changes from negative to positive around $c \approx 0.22$. The comparison of Θ vs c with the prediction from molecular field theory indicates that the exchange interaction between Ni and Mn spins is ferromagnetic and is described by $J(Ni\text{-}Mn) = 1.09\,[J(Ni\text{-}Ni)\,|J(Mn\text{-}Mn)|]^{1/2} = 1.44$ K. Figure 3(a) shows the Ni concentration dependence of critical temperature T_c. The critical temperature T_c rapidly decreases with a dilution of Mn and tends to reduce to zero below $c \approx 0.6$, suggesting that Mn^{2+} ions behave like nonmagnetic ions. The large initial slope of $[d\ \ln T_c/dc]_{c=1} = 2.38$ is ascribed to the two-dimensional Heisenberg-like character of stage 2 $NiCl_2$-GIC. The magnetic properties of stage-2 $Co_cMn_{1-c}Cl_2$ GICs are similar to those of stage-2 $Ni_cMn_{1-c}Cl_2$ GICs.[7] The Curie-Weiss temperature monotonically increases with increasing Co concentration. Its sign changes from negative to positive around $c \approx 0.2$. The exchange interaction between Co and Mn spins is ferromagnetic and described by $J(Co\text{-}Mn) = 1.2\,[J(Co\text{-}Co)\,|J(Mn\text{-}Mn)|]^{1/2} = 1.49$ K.

Stage-2 $Co_cNi_{1-c}Cl_2$ GICs magnetically behave like a quasi 2D Heisenberg ferromagnet with XY spin anisotropy,[3-5] where the intraplanar exchange interaction such as J(Co-Co) and J(Ni-Ni) are ferromagnetic. The spin symmetry continuously changes from Heisenberg-like at $c = 0$ to XY-like at $c = 1$. The effective XY spin anisotropy parameter g_{eff} almost linearly changes from 7.62×10^{-3} at $c = 0$ to 0.48 at $c = 1$: $g_{eff} = 1$ for the ideal XY symmetry. Figures 2(b) shows the Co concentration dependence of Θ. The comparison of Θ vs c with the prediction from molecular field theory indicates that the intraplanar exchange interaction J(Co-Ni) between the different spins is larger than that between like spins, J(Co-Co) or J(Ni-Ni): $J(Co\text{-}Ni) = 1.2\,[J(Co\text{-}Co)\,J(Ni\text{-}Ni)]^{1/2}$. Figure 3(b) shows the Co concentration dependence of T_c. We have shown in Ref. 5 that the ratio of T_c to Θ is well described by $T_c/\Theta = Ag_{eff}^{1/\phi} + B$ with $\phi = 1.34$, $A = 0.229$ and $B = 0.224$. The first term and second term of T_c/Θ are due to the XY spin anisotropy effect in the 2D system and the 3D effect through interplanar exchange interaction, respectively.

Figure 4 shows the temperature dependence of M_{ZFC}, M_{FC} and the difference δ (= $M_{FC} - M_{ZFC}$) of stage-2 $Ni_cMn_{1-c}Cl_2$ GICs with c = 1, 0.9, 0.8, 0.7, 0.65, and c = 0.6. For c = 1, 0.9, and 0.8, M_{FC} coincides with M_{ZFC} at sufficiently high temperatures and begins to deviate upward from M_{ZFC} at T_c. This irreversible effect below T_c is considered to arise from spin frustration effects occurring in the $Ni_cMn_{1-c}Cl_2$ intercalate layers. The magnetization M_{ZFC} exhibits a broad peak at T_{max} ($<T_c$), while δ does not show any anomaly at T_{max}. This result indicates that T_{max} is not a critical temperature.


stage-2 NiCl$_2$ GIC
(a)
H = 1 Oe
FC
ZFC
δ
M (emu/mol)
1500
1000
500
0
0
5
10
15
20
25
T(K)
stage-2 Ni$_{0.9}$Mn$_{0.1}$Cl$_2$ GIC
(b)
H = 1 Oe
FC
ZFC
δ
M (emu/av mol)
700
600
500
400
300
200
100
0
0
5
10
15
20
T(K)


stage-2 Ni0.8Mn0.2Cl2 GIC
(c)
H = 1 Oe
FC
ZFC
δ
M (emu/av mol)
T(K)
0
50
100
150
200
250
300
0
2
4
6
8
10
12
14
16


stage-2 Ni0.7Mn0.3Cl2 GIC
(d)
H = 1 Oe
FC
ZFC
δ
M (emu/av mol)
T(K)
0
10
20
30
40
50
60
70
80
0
2
4
6
8
10

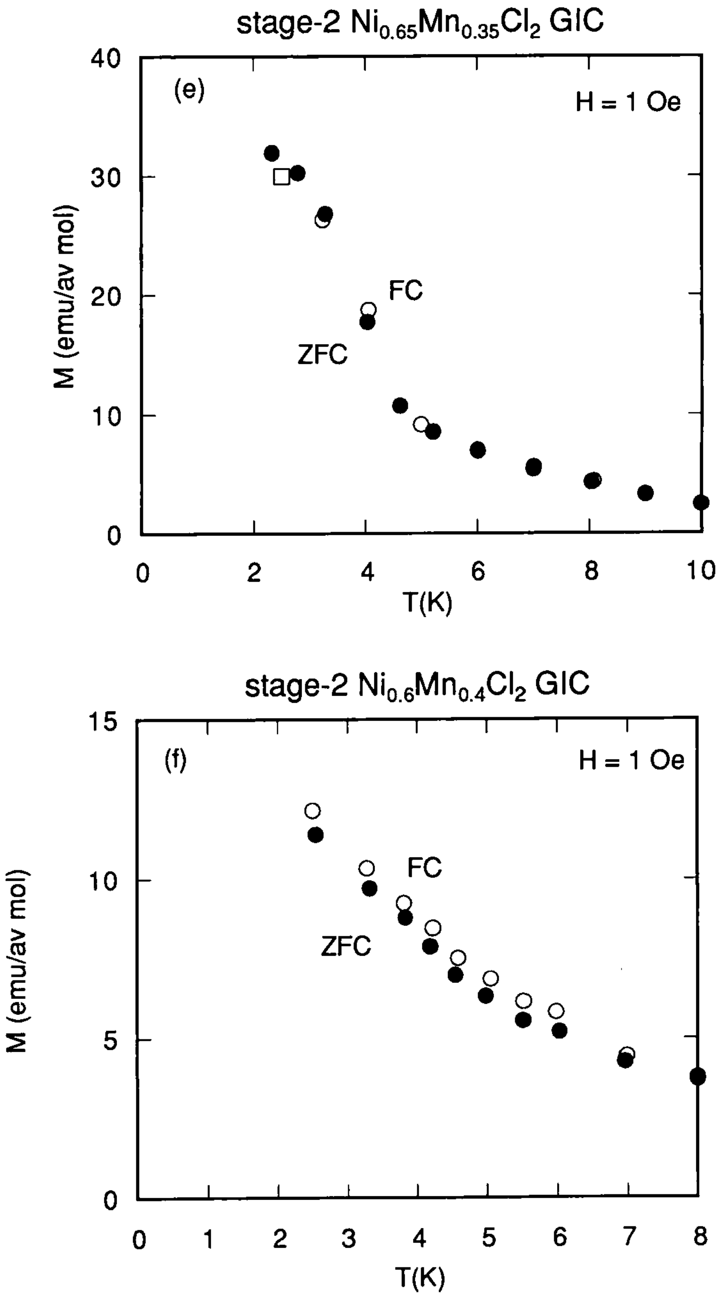


FIGURE 4 Temperature variation of M_{FC} (o), M_{ZFC} (•) and δ (= M_{FC} - M_{ZFC}) (Δ) for stage-2 $Ni_cMn_{1-c}Cl_2$ GICs. H = 1 Oe. H ⊥ c. (a) c = 1, (b) c = 0.9, (c) c = 0.8, (d) c = 0.7, (e) c = 0.65, and (f) c = 0.6.

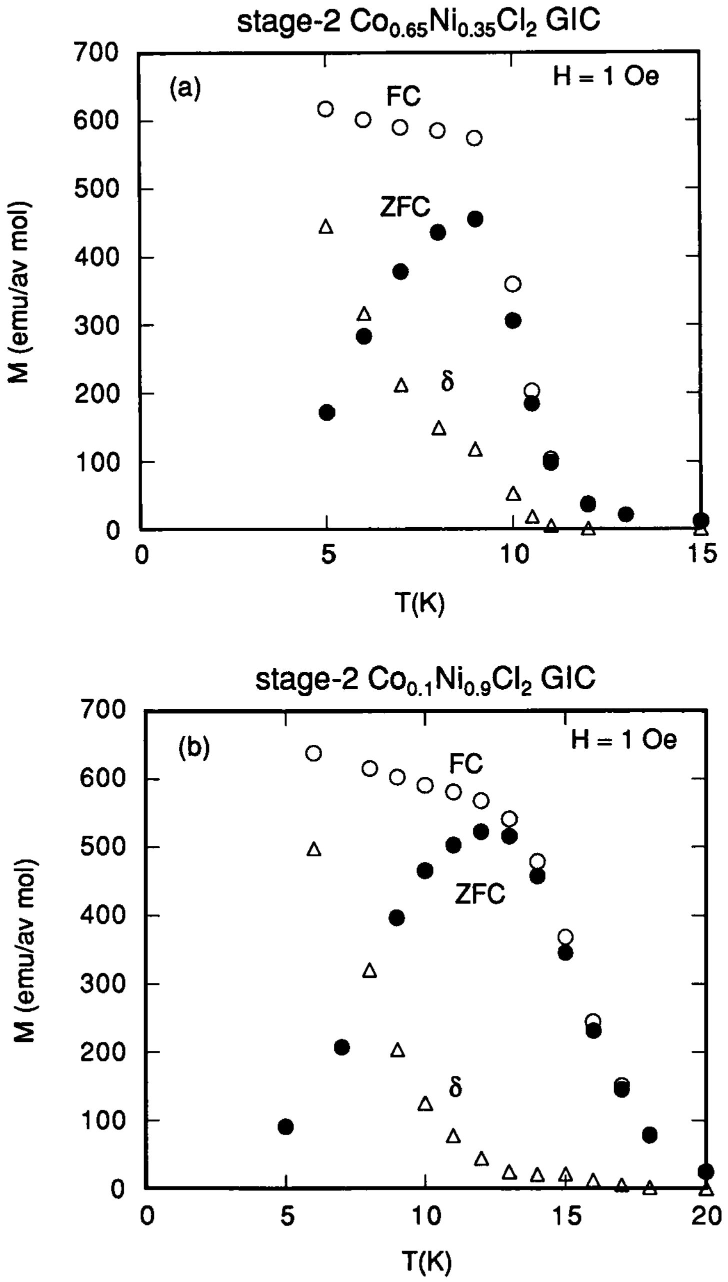


FIGURE 5 Temperature variation of M_{FC} (o), M_{ZFC} (•) and δ (= M_{FC} - M_{ZFC}) (Δ) for stage-2 $Co_cNi_{1-c}Cl_2$ GICs. H = 1 Oe. H ⊥ c. (a) c = 0.65 and (b) c = 0.1.

For $c = 0.7$ the irreversible effect still appears below T_c, but M_{ZFC} does not show any peak below T_c. For $c = 0.65$ and 0.60 M_{FC} coincides with M_{ZFC}, implying no irreversible effect at any temperature. Figure 5 shows the temperature dependence of M_{ZFC} and M_{FC} for stage-2 $Co_cNi_{1-c}Cl_2$ GICs with $c = 0.65$ and 0.1. We find that for $0 \le c \le 1$ M_{ZFC} shows a broad maximum at T_{max} and that the irreversible effect appears below T_c.[8] The difference δ monotonically increases with decreasing temperature and does not show any anomaly around T_{max} for any Co concentration. The Co concentration dependence of T_{max} and T_c is shown in Fig. 3(b).

For the type I compounds (stage-2 $Ni_cMn_{1-c}Cl_2$ GICs with $c = 1$, 0.9, and 0.8, and stage-2 $Co_cNi_{1-c}Cl_2$ GICs with $0 \le c \le 1$), the intraplanar ferromagnetic interactions are dominant compared to the intraplanar antiferromagnetic interactions. The magnetic phase transition of the type I compounds is understood as follows. Below T_c, spins within each island are ferromagnetically aligned, forming ferromagnetic clusters. There appears a cluster glass phase below T_c where the spin directions of ferromagnetic clusters are frozen because of frustrated inter-island interaction consisting of the combination of dipole-dipole interaction and interplanar antiferromagnetic interaction.[8] When the temperature is close to T_{max}, the thermal energy becomes comparable to the magnitude of the frustrated inter-island interaction. Above T_{max} the spin direction of ferromagnetic clusters becomes random. The spins in the ferromagnetic clusters are still coupled through the ferromagnetic intraplanar exchange interaction. Above T_c the spins in islands become disordered. For the type II compounds (stage-2 $Ni_cMn_{1-c}Cl_2$ GICs with $c = 0.7$) where the intraplanar antiferromagnetic interactions are comparable to the intraplanar ferromagnetic interactions, a spin glass-like phase is considered to occur within each island below T_c. The directions of spins within each island are frozen because of the spin frustrated effect arising from the competition between ferromagnetic J(Ni-Ni) and antiferromagnetic J(Mn-Mn) interactions. For the type III compounds (stage-2 $Ni_cMn_{1-c}Cl_2$ GICs with $c = 0.65$ and 0.6) each island is in the paramagnetic phase.

It may be concluded from these results that the ferromagnetic phase, spin-glass phase and paramagnetic phase corresponding to the concentration may be realized within each island. Ozeki and Nishimori[9] have studied the phase diagram of the 2D asymmetric $\pm J$ Ising model on the square lattice by the numerical transfer matrix method. In this model the exchange interaction J_{ij} is only in the nearest neighbor bonds and is randomly distributed at each bond with the probability weight c of ferromagnetic bonds ($J_{ij} = J$) and the probability weight $(1 - c)$ of antiferromagnetic bonds ($J_{ij} = -J$). The c-T phase diagram consists of a ferromagnetic phase for $c > c_u$ (≈ 0.89) and a possible random antiphase state (RAS) for $c_l < c < c_u$ ($c_l \approx 0.8$). This RAS characterized by the existence of long-range order and zero magnetization may correspond to a spin glass-like phase. Our experimental results are qualitatively explained by this model.

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