

Magnetic susceptibility of stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ graphite intercalation compounds

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dc magnetic susceptibility measurements were carried out on stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ graphite intercalation compounds which approximate two-dimensional randomly mixed ferromagnets with XY spin symmetry. The average effective magnetic moment and the Curie-Weiss temperature are determined as a function of cobalt concentration and discussed in terms of the molecular-field approximation. The results indicate that (i) the Co^{2+} and Ni^{2+} spins are randomly distributed on the triangular lattice sites inside the intercalate layer and (ii) the intraplanar interaction between Co^{2+} and Ni^{2+} is enhanced and larger than that between Co^{2+} and Co^{2+} and that between Ni^{2+} and Ni^{2+} : $J(\text{Co-Ni}) = 1.28[J(\text{Co-Co})J(\text{Ni-Ni})]^{1/2}$.

In recent years, ternary graphite intercalation compounds (TGIC's) have received considerable attention from both chemists and physicists.¹ These compounds provide an opportunity to synthesize exotic compounds and to explore their novel physical properties. Of particular interest among these compounds are the magnetic ternary GIC's such as graphite bi-intercalation compounds (GBIC's) and random-mixture GIC's (RMGIC's). The magnetic GBIC is quite an exotic type of GIC with a stacking sequence along the c axis, $\cdots GI_1GI_2GI_1GI_2G \cdots$, where the two different intercalate layers (I_1 and I_2) alternate with a single graphite layer (G), both intercalants being of the acceptor type ($I_1, I_2 = \text{NiCl}_2, \text{CoCl}_2, \text{FeCl}_3$).² The magnetic RMGIC is also a new type of GIC. The random mixture $A_cB_{1-c}\text{Cl}_2$ ($A, B = \text{Ni, Co, Mn, Fe}$) is directly intercalated into the graphite substrate and forms a stage- N ($N = 1, 2, \dots$) RMGIC, where c is a concentration ($0 \leq c \leq 1$). The dimensionality of this random magnetic system changes from three dimensional (3D) to two dimensional (2D) with increasing stage number.

In this paper, we report the results of dc magnetic-susceptibility measurements on stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ -GIC. The adjacent $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ intercalate layers are separated by two graphite layers. The Co^{2+} and Ni^{2+} ions are randomly distributed on the triangular lattice sites in the intercalate $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ layer. The Curie-Weiss temperature θ , the average effective magnetic moment P_{eff} , and the critical temperature T_c are determined as functions of Co concentration. The deviation of θ from linearity will be discussed in terms of the molecular-field theory as first proposed by Hashimoto.³

The stage-2 CoCl_2 - and NiCl_2 -GIC's have attracted considerable attention because they approximate 2D XY -like ferromagnets. The spin Hamiltonian for Co^{2+} ions in the stage-2 CoCl_2 -GIC can be written in terms of the fictitious spin $S = \frac{1}{2}$ as

$$H = -2J(\text{Co-Co}) \sum_{(i,j)} \mathbf{S}_i \cdot \mathbf{S}_j + 2J_A(\text{Co-Co}) \sum_{(i,j)} S_i^z S_j^z + 2J'(\text{Co-Co}) \sum_{(i,m)} \mathbf{S}_i \cdot \mathbf{S}_m, \quad (1)$$

where the first two sums extend over nearest neighbors within the intercalate layer, and the last sum is over the nearest neighbors in adjoining layers. The z axis coincides with the c axis. The constants $J(\text{Co-Co})$, $J'(\text{Co-Co})$, and $J_A(\text{Co-Co})$ are the ferromagnetic intraplanar, antiferromagnetic interplanar, and anisotropic exchange interactions: $J(\text{Co-Co}) = 7.75$ K, $J'(\text{Co-Co})/J(\text{Co-Co}) \approx 8 \times 10^{-4}$, and $J_A(\text{Co-Co})/J(\text{Co-Co}) = 0.48$.⁴⁻⁶ The spin Hamiltonian for Ni^{2+} ions in the stage-2 NiCl_2 -GIC can be described with $S = 1$ as

$$H = -2J(\text{Ni-Ni}) \sum_{(i,j)} \mathbf{S}_i \cdot \mathbf{S}_j + D(\text{Ni}) \sum_i (S_i^z)^2 + 2J'(\text{Ni-Ni}) \sum_{(i,m)} \mathbf{S}_i \cdot \mathbf{S}_m, \quad (2)$$

where $D(\text{Ni})$ is the single-ion anisotropy: $D(\text{Ni}) = 0.80$ K, $J(\text{Ni-Ni}) = 8.75$ K, and $J'(\text{Ni-Ni})/J(\text{Ni-Ni}) \approx 10^{-3}$.^{4,7} The XY anisotropy is much smaller than in stage-2 CoCl_2 -GIC.

To prepare crystals of stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ -GIC, first, single crystals of $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ were grown from the anhydrous CoCl_2 and NiCl_2 powders of that nominal weight composition in a Bridgeman furnace at temperatures around 900°C . Since CoCl_2 and NiCl_2 are very similar chemically, the composite crystal is one where the two magnetic ions are distributed randomly throughout the samples. Then the stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ -GIC was prepared by intercalation of $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ single crystal into single crystals of Kish graphite in a Cl_2 gas atmosphere at 740 Torr for 20 days at 540°C . The Co concentration in the GIC thus obtained is assumed to coincide with that in the bulk cobalt-nickel chloride single crystal.

The stoichiometry of the GIC's was determined by the weight uptake measurement. The c -axis stacking sequence was confirmed by (00L) x-ray diffraction to be well-defined stage 2.

The dc magnetic susceptibility measurements of these compounds were made with a Cahn Electrobalance with an applied magnetic field H oriented perpendicular to the c axis of the crystal. dc susceptibility was measured from 4.2 to 300 K.

We have measured the dc magnetic susceptibility of stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ -GIC's with Co concentration $c=0.10, 0.19, 0.40, 0.52, 0.63,$ and $0.80,$ with the external magnetic field $H=4.0$ kOe. The susceptibility obeys the Curie-Weiss law

$$\chi_M = \chi_{M^0} + \frac{C_M}{T - \theta} \quad (\text{emu/ave mol}) \quad (3)$$

in the paramagnetic phase, where χ_{M^0} is the temperature-independent molar susceptibility, C_M the Curie-Weiss constant, and θ the Curie-Weiss temperature. The least-squares fit of the data to Eq. (3) yields $C_M, \theta,$ and χ_{M^0} in the temperature range $150 \leq T \leq 300$ K. The susceptibility data of C_M and θ for the stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ -GIC are listed in Table I. The average effective magnetic moment P_{eff} is related to the Curie-Weiss constant by

$$C_M = \frac{N_A \mu_B^2 P_{\text{eff}}^2(\text{ave})}{3k_B} \cong \frac{1}{8} P_{\text{eff}}^2(\text{ave}). \quad (4)$$

The average effective magnetic moment $P_{\text{eff}}(\text{ave})$ is also listed in Table I. Figure 1 shows $P_{\text{eff}}(\text{ave})$ as a function of Co concentration $c,$ where $P_{\text{eff}}(\text{Ni})=3.29\mu_B$ for the stage-2 NiCl_2 -GIC (Ref. 7) and $P_{\text{eff}}(\text{Co})=5.54\mu_B$ for the stage-2 CoCl_2 -GIC.⁵ The average effective magnetic moment $P_{\text{eff}}(\text{ave})$ increases monotonically with increasing Co concentration $c.$ This monotonic change of $P_{\text{eff}}(\text{ave})$ suggests that Ni and Co ions exist in the divalent state inside the intercalate layer.

Figure 2 shows the Curie-Weiss temperature θ as a function of Co concentration $c.$ The data for $c=0, \theta=70$ K, is from Suematsu *et al.*⁷ The data for $c=1, \theta=23.2$ K, is from Wiesler *et al.*⁵ A monotonic increase in $\theta,$ as a function of Co concentration $c,$ is observed.

It is well known that stage-2 CoCl_2 - and NiCl_2 -GIC's undergo two magnetic phase transitions at T_{cl} and $T_{cu}:$ ⁴⁻⁷ $T_{cl}=8.0$ K and $T_{cu}=9.1$ K for the stage-2 CoCl_2 -GIC, and $T_{cl}=17.5$ K and $T_{cu}=22.0$ K for stage-2 NiCl_2 -GIC. Above $T_{cu},$ the system is in the paramagnetic phase. Between T_{cl} and $T_{cu},$ 2D ferromagnetic ordering occurs inside the intercalate layers. Below $T_{cl},$ 3D antiferromagnetic ordering occurs with the 2D ferromagnetic sheets aligned antiferromagnetically along the c axis.

TABLE I. Magnetic susceptibility data of stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ -GIC with the stoichiometry $C_n\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2.$

c	n	$P_{\text{eff}} (\mu_B/\text{ave mol})$	θ (K)	T_c (K)	$\gamma = \theta/T_c$
0.00 ^a	12.71	3.29	70.0	22.0	3.18
0.10	10.97	3.80	60.8	20.3	3.00
0.19	13.24	3.79	55.5	16.2	3.43
0.40	10.95	4.47	42.9	14.4	2.98
0.52	11.33	4.71	38.0	12.5	3.04
0.63	10.76	5.15	31.3	11.8	2.65
0.80	12.33	5.05	28.5	10.7	2.66
1.00 ^b	10.60	5.54	23.2	9.1	2.55

^aReference 7.

^bReference 5.

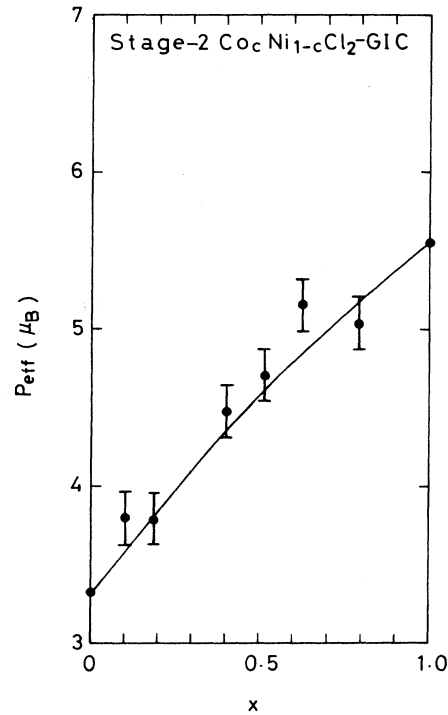


FIG. 1. Average effective magnetic moment P_{eff} of stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ -GIC as a function of Co concentration $c.$ The solid line is a plot of Eq. (9).

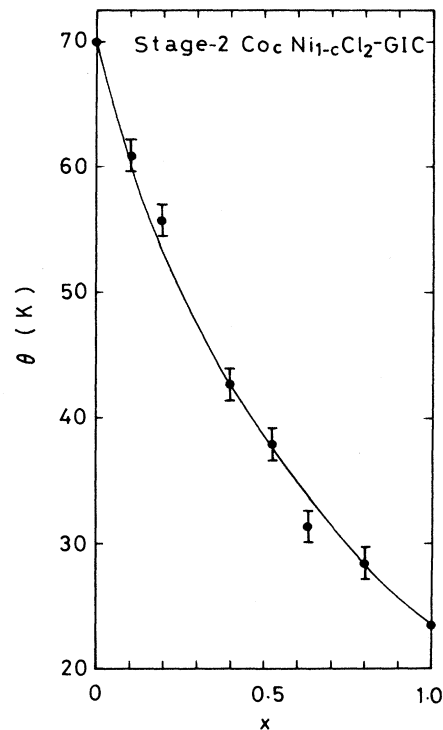


FIG. 2. Curie-Weiss temperature θ of stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ -GIC as a function of Co concentration $c.$ The solid line is a plot of Eq. (10) with $\alpha=1.28.$

We have also measured the dc magnetic susceptibility of stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2\text{-GIC}$ below 30 K at a low field H ($=100$ Oe) to determine the critical temperature T_c as a function of Co concentration.

The magnetic susceptibility measured by the Faraday balance method is the sum of the susceptibility χ and M_0/H , where M_0 is a magnetization proportional to the saturation magnetization. The data of susceptibility versus temperature undergoes a second-order turning point: the curve concavity changes. The M_0/H portion is concave down and is extrapolated to the temperature axis to determine the critical temperature T_c , which may correspond to T_{cu} .⁷ Figure 3 shows the critical temperature T_c versus Co concentration c for the stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2\text{-GIC}$. The data of T_c are listed in Table I. The critical temperature T_c decreases monotonically from $T_c=22.0$ K for $c=0$ to $T_c=9.1$ K for $c=1$. The ratio of θ to T_c , γ , for each Co concentration is listed in Table I. The ratio monotonically decreases with Co concentration: $\gamma=3.18$ at $c=0$ and $\gamma=2.55$ at $c=1.0$.

We note that the intercalate layer in the stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2\text{-GIC}$ may be formed of small islands which are on the order of 100–400 Å. The existence of small islands is a common feature of the acceptor-type GIC's, where the boundary regions of the islands provide acceptor sites for electrons transferred from the host graphite layers.^{4,8} In this discussion, we do not take the finite-size effect into account. For simplicity, we suppose that Co^{2+} and Ni^{2+} spins are randomly distributed on the triangular lattice sites in the intercalate layers. The intraplanar exchange interactions between adjacent magnetic ions Co-Co, Co-Ni, and Ni-Ni are denoted by $J_{11}=J(\text{Co-Co})$,

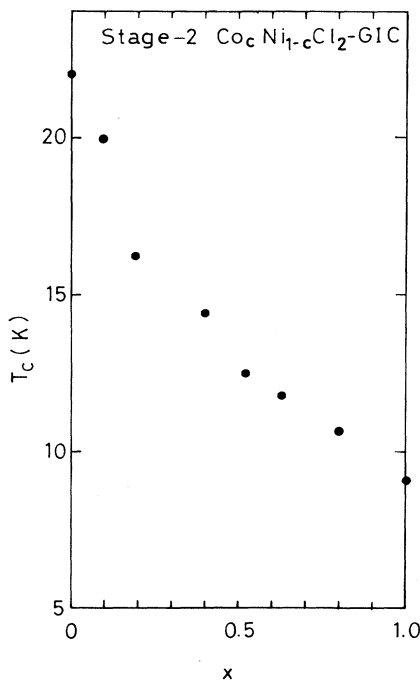


FIG. 3. Critical temperature T_c of stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2\text{-GIC}$ as a function of Co concentration.

$J_{12}=J(\text{Co-Ni})$, and $J_{22}=J(\text{Ni-Ni})$. The ranges of the exchange interactions are limited to the nearest neighbors. By using the molecular-field approximation as first applied by Hashimoto,³ the total magnetization M can be calculated as

$$M = cM_1 + (1-c)M_2, \quad (5)$$

where M_1 and M_2 are the magnetizations of the induced Co^{2+} and Ni^{2+} spins. The M_i ($i=1,2$) are given by

$$M_i = N_A g_i \mu_B \langle S_i \rangle = \frac{C_{ii}}{T} H(i), \quad (6)$$

where $g_1=6.40$, $g_2=2.33$, and C_{ii} ($i=1,2$) are defined by

$$C_{ii} = \frac{N_A \mu_B^2 P_{\text{eff}}^2(i)}{3k_B}. \quad (7)$$

Here, N_A is the Avogadro number, k_B the Boltzmann constant, μ_B the Bohr magneton, $P_{\text{eff}}(1)$ and $P_{\text{eff}}(2)$ the effective magnetic moments of the Co^{2+} and Ni^{2+} ions of the stage-2 $\text{CoCl}_2\text{-}$ and $\text{NiCl}_2\text{-GIC}$'s, respectively, and $\langle S_1 \rangle$ and $\langle S_2 \rangle$ the average spins of the Co^{2+} and Ni^{2+} ions, respectively. When the first term of the spin Hamiltonians [Eqs. (1) and (2)] is assumed to dominate the second and third terms, i.e., the system behaves like a 2D Heisenberg-type ferromagnet, the molecular fields at the Co and Ni sites, $H(1)$ and $H(2)$, can be described by

$$H(1) = H + \frac{2z}{g_1 \mu_B} [cJ_{11} \langle S_1 \rangle + (1-c)J_{12} \langle S_2 \rangle] \quad (8a)$$

and

$$H(2) = H + \frac{2z}{g_2 \mu_B} [cJ_{12} \langle S_1 \rangle + (1-c)J_{22} \langle S_2 \rangle], \quad (8b)$$

respectively, where z is the coordination number ($z=6$) and H is the applied magnetic field. The exchange interaction between Co^{2+} and Ni^{2+} spins, J_{12} , is taken as a trial function of the geometric mean of the two interactions with a multiplicative parameter α , $J_{12} = \alpha(J_{11}J_{22})^{1/2}$. Then the average effective magnetic moment and the Curie-Weiss temperature can be derived as

$$P_{\text{eff}}(\text{ave}) = [cP_{\text{eff}}^2(1) + (1-c)P_{\text{eff}}^2(2)]^{1/2}, \quad (9)$$

and

$$\theta = \frac{c^2 C_{11}^2 q_{11} + (1-c)^2 C_{22}^2 q_{22} + 2c(1-c)C_{11}C_{22}q_{12}}{cC_{11} + (1-c)C_{22}} \quad (10)$$

with

$$q_{ij} = \frac{2zJ_{ij}}{N_A g_i g_j \mu_B^2}. \quad (11)$$

We now discuss the data of Figs. 1 and 2 in terms of Eqs. (9) and (10). The data on $P_{\text{eff}}(\text{ave})$ vs Co concentration c in Fig. 1 agree well with the solid line corresponding to Eq. (9) with $P_{\text{eff}}(1)=5.54\mu_B$ and $P_{\text{eff}}(2)=3.29\mu_B$. This result indicates that the actual Co concentration inside the intercalate layer may be close to the nominal Co concentration. By using Eq. (10), the concentration dependence of θ can be calculated with α as a parameter:

$J_{12} = \alpha(J_{11}J_{22})^{1/2}$. The data on θ vs Co concentration in Fig. 2 agree very well with the solid line corresponding to Eq. (10) with $\alpha = 1.28$. This result indicates that the intraplanar exchange interaction between the Co^{2+} and Ni^{2+} spins is ferromagnetic and larger than $J_{11} = J(\text{Co-Co})$ and $J_{22} = J(\text{Ni-Ni})$: $J_{12} = J(\text{Co-Ni}) = 10.54$ K. The straight line connecting the two end points ($\theta = 70$ K at $c = 0$ and $\theta = 22.0$ K at $c = 1$) is given by Eq. (10) with

$$J_{12} = \frac{1}{2} \left[\frac{g_2}{g_1} J_{11} + \frac{g_1}{g_2} J_{22} \right]. \quad (12)$$

Since $g_1 = 6.40$ and $g_2 = 2.33$, α , corresponding to the straight line, can be estimated as $\alpha = 1.63$. For $\alpha < 1.63$, the θ vs c curve is concave.

We note that the value of α ($= 1.28$) thus obtained for the stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ -GIC is very close to the factor α ($= 1.29$) which has been reported by Ikeda, Abe, and Hatta⁹ for the 2D random antiferromagnet $\text{Rb}_2\text{Co}_c\text{Ni}_{1-c}\text{F}_4$. They used this α to explain the dependence of the Néel temperature T_N on the Co concentration. A similar result is also observed for the 2D random antiferromagnet $\text{K}_2\text{Co}_c\text{Ni}_{1-c}\text{F}_4$.¹⁰ However, the dependence of the critical temperature T_c on Co concentration in the stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ -GIC may not be discussed in terms of the molecular-field approximation where (i) the short-range spin fluctuation and (ii) XY spin symmetry are not taken into account. In fact, the data of T_c vs c in Fig. 3 for the stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ -GIC is not exactly proportional to the data of θ vs c in Fig. 2. As mentioned above, the ratio of θ to T_c changes slightly from $\gamma = 3.18$ at $c = 0$ to $\gamma = 2.55$ at $c = 1$, indicating that the shift of T_c is weaker than that of θ in the concentration range $0.7 < c < 1.0$. A similar result has been obtained for the specific-heat measurement of the bulk $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$, by Kostryukova,¹¹ who concluded that the weak shift of the Néel temperature T_N for $0.7 < c < 1.0$ indicates that the exchange interaction $J(\text{Co-Ni})$ is the same order as $J(\text{Co-Co})$. How-

ever, this conclusion is not the case for the stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ -GIC because $J(\text{Co-Ni})$ is larger than both $J(\text{Co-Co})$ and $J(\text{Ni-Ni})$.

The Co^{2+} spins in the stage-2 CoCl_2 -GIC are oriented in the c plane with large XY anisotropy. The Ni^{2+} spins in the stage-2 NiCl_2 -GIC are also aligned in the c plane, but the XY anisotropy is much smaller than in the stage-2 CoCl_2 -GIC. The critical temperature of the stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ -GIC may be determined by (i) the intraplanar exchange interactions $J(\text{Co-Co})$, $J(\text{Ni-Ni})$, and $J(\text{Co,Ni})$ and (ii) the XY anisotropy. The XY anisotropy may gradually increase with increasing Co concentration. To explain the concentration dependence of T_c , we need a sophisticated theory where the XY anisotropy of Co^{2+} and Ni^{2+} is taken into account.

In conclusion, the stage-2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ -GIC is the first case where a random magnetic mixture has been intercalated into the graphite host. The following results can be derived from the dc magnetic susceptibility of these compounds. (i) The Co^{2+} and Ni^{2+} spins are randomly distributed throughout the intercalate islands. (ii) The intraplanar exchange interaction between Co^{2+} and Ni^{2+} is enhanced and larger than those between Co^{2+} and Co^{2+} and those between Ni^{2+} and Ni^{2+} . (iii) The critical temperature T_c , which may correspond to T_{cu} , decreases with increasing Co concentration.

Further details of the magnetic phase transitions at T_{cl} and T_{cu} for each Co concentration will be investigated by using ac susceptibility and neutron scattering. We will conduct x-ray-scattering experiments to determine d spacing for each Co concentration.

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