Effect of XY spin anisotropy on the critical temperature in stage-2 $Co_cNi_{1-c}Cl_2$-graphite intercalation compounds

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Stage-2 $Co_cNi_{1-c}Cl_2$ graphite intercalation compounds behave magnetically like a quasi-two-dimensional Heisenberg ferromagnet with XY spin anisotropy. The spin symmetry continuously changes from Heisenberg-like at $c=0$ to XY-like at $c=1$. The effect of spin anisotropy on the critical behavior of these compounds has been studied by using ac and dc magnetic susceptibility. The ratio of critical temperature T_c to Curie-Weiss temperature Θ as a function of effective XY spin anisotropy parameter $g_{\rm eff}$ is well described by $T_c/\Theta = Ag_{\rm eff}^{1/\phi} + B$ with $A=0.229$, $B=0.224$, and the crossover exponent $\phi(=1.34)$. The first and second terms of T_c/Θ are due to the spin anisotropy effect in the two-dimensional system and the three-dimensional effect, respectively. The extrapolated value of $Ag_{\rm eff}^{1/\phi}$ at $g_{\rm eff}=1$ may give an estimate for the ratio of the Kosterlitz-Thouless temperature to the intraplanar exchange interaction.

I. INTRODUCTION

Magnetic binary graphite intercalation compounds (GIC's), 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 GIC's 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.[3] The magnetic random mixture GIC's are typical examples of magnetic ternary GIC's. Two kinds of magnetic intercalant species are intercalated into the same gallery of the host graphite. Recent progress in preparation of magnetic random mixture GIC's, such as stage-2 $Co_cMn_{1-c}Cl_2$ GIC's and stage-2 $Co_cNi_{1-c}Cl_2$ GIC's, makes it possible for one to study various kinds of spin frustration effect such as competing ferromagnetic and antiferromagnetic interactions and competing spin anisotropies between Ising, XY, and Heisenberg.[4-7]

The stage-2 $Co_cNi_{1-c}Cl_2$ GIC's provide a model system for studying the magnetic phase transition of 2D Heisenberg-like ferromagnets with XY spin anisotropy. In these compounds the XY-like Co^{2+} spins with spin $S=\frac{1}{2}$ and the Heisenberg-like Ni^{2+} ions with spin $S=1$ are randomly distributed within the same intercalate layers. In a previous paper[4] we have studied the magnetic properties of these compounds by dc magnetic susceptibility. We found that the Co concentration dependence of Curie-Weiss temperature and effective magnetic moment is explained well in terms of the molecular field theory, indicating that Co^{2+} and Ni^{2+} are randomly distributed in the $Co_cNi_{1-c}Cl_2$ intercalate layer. The nearest-neighbor intraplanar exchange interaction between Co^{2+} and Ni^{2+} is ferromagnetic and is larger than ferromagnetic intraplanar interactions between like ions. We also found that the magnetization below 30 K at 100 Oe shows a rounding effect at the phase transition, making it difficult to determine the critical temperature T_c.[4] A Gaussian distribution function of critical temperature was assumed to analyze the data of magnetization versus temperature. In these compounds the intercalate layers are formed of small islands, which is a feature common to acceptor type GIC's.[1,2] The island size is typically on the order of 500 Å. The boundary of these islands provides acceptor sites for electrons which are transferred from the graphite π band. Both the finite-size effect of these small islands and the possible Co concentration gradient within samples may cause a smearing of critical temperature.[4]

In this paper we study the magnetic phase transition of stage-2 $Co_cNi_{1-c}Cl_2$ GIC's. We measure the dc and ac magnetic susceptibility of samples newly synthesized and samples used in the previous paper.[4] The dc magnetic susceptibility above 150 K at 4.0 kOe obeys the Curie-Weiss law. The Curie-Weiss temperature Θ is determined as a function of Co concentration. The ac magnetic susceptibility shows a broad peak around a critical temperature T_c. When the critical temperature is defined as a temperature at which the ac magnetic susceptibility has a maximum, the ratio T_c/Θ can be obtained as a function of Co concentration. The spin symmetry of these compounds is predicted to change from Heisenberg-like to XY-like with increasing Co concentration (Sec. V). The effect of XY spin anisotropy on the ratio T_c/Θ is discussed in the light of theoretical predictions of critical temperature for the 2D Heisenberg system with XY spin anisotropy.

II. BACKGROUND

A. Phase transition and spin Hamiltonian

The stage-2 $CoCl_2$ GIC and stage-2 $NiCl_2$ GIC undergo two magnetic phase transitions at T_{cl} and T_{cu}: $T_{cl}=8.0$ K and $T_{cu}=9.1$ K for stage-2 $CoCl_2$ GIC,[8,9]

and $T_{cl}=17.5$ K and $T_{cu}=22.0$ K for stage-2 $NiCl_2$ GIC.[10,11] The finite size of small islands is a crucial element in the magnetic phase transition of these compounds. The effective interplanar exchange interaction $J'_{\rm eff}$ between spins over the in-plane spin correlation length ξ in adjacent magnetic intercalate layers is described by $J'_{\rm eff}=J'(\xi/a)^2$, where a is the in-plane lattice constant. The growth of ξ is limited by the island size as the temperature is decreased. Suppression of the increase in $J'_{\rm eff}$ leads to the realization of 2D spin ordering between T_{cl} and T_{cu}. Below T_{cl} there occurs 3D spin ordering where the 2D ferromagnetic layers are antiferromagnetically stacked along the c axis. The stage-2 $CoCl_2$ GIC and stage-2 $NiCl_2$ GIC magnetically behave like a 2D Heisenberg-like ferromagnet with XY spin anisotropy. The spin Hamiltonian of Co^{2+} in the stage-2 $CoCl_2$ GIC is described as[4]

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

in terms of a fictitious spin $S(\text{Co})=\frac{1}{2}$, where the z axis coincides with the c axis, J(Co-Co) is the ferromagnetic intraplanar exchange interaction, J'(Co-Co) is the antiferromagnetic interplanar exchange interaction, and J_A(Co-Co) is the anisotropic exchange interaction: J(Co-Co)$=7.75$ K, $\Delta(\text{Co})=J'(\text{Co-Co})/J(\text{Co-Co})\approx 8\times10^{-4}$, and J_A(Co-Co)$=3.72$ K. The first two sums are taken over all nearest-neighbor pairs of spins within the intercalate layer. The last sum extends over nearest-neighbor pairs of spins in adjoining intercalate layers. The spin Hamiltonian of Ni^{2+} in the stage-2 $NiCl_2$ GIC is described as[4]

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

in terms of spin $S(\text{Ni})=1$, where D(Ni) is the single-ion anisotropy [$D(\text{Ni})=0.80$ K], $J(\text{Ni-Ni})=8.75$ K, and $\Delta(\text{Ni})=J'(\text{Ni-Ni})/J(\text{Ni-Ni})\approx10^{-3}$.

B. Theory for critical temperature of quasi-2D XY spin system

Hikami and Tsuneto[12] have predicted the critical temperature of a quasi-2D Heisenberg ferromagnet with XY anisotropy in terms of a scaling argument for the crossover effect. The expression for the critical temperature of the system with $g\approx0$ and $\Delta=0$ can be derived from a scaling argument for the crossover from 2D Heisenberg behavior to 2D XY behavior,[13] where g is the XY spin anisotropy parameter and Δ is the ratio of interplanar to intraplanar exchange interaction. The in-plane spin correlation length ξ becomes large as the temperature is decreased to the critical temperature. The true phase transition may appear under the condition

$$g\xi^2\approx x_1\ , \tag{3}$$

where x_1 is a finite value. The in-plane spin correlation length ξ is assumed to coincide with the spin correlation length of the 2D Heisenberg model ξ_H

$$\xi_H\approx\exp\left[\frac{2\pi J}{T}\right]\ , \tag{4}$$

in the limit of $g\approx0$. Then the critical temperature is estimated from Eqs. (3) and (4) as

$$\frac{T_c(g,\Delta=0)}{J}=\frac{4\pi}{\ln\left[\frac{x_1}{g}\right]}\quad(g\to0)\ . \tag{5}$$

Similarly, the expression for the critical temperature of the system with $g=1$ and $\Delta\neq0$ can be derived from a scaling argument for the crossover from 2D XY behavior to 3D XY behavior.[12,13] As the temperature is decreased to the critical temperature, the in-plane correlation length of the 2D XY model, ξ_{XY}, becomes large as

$$\xi_{XY}\approx\exp\left\{b\left[\frac{T-T_K}{T_K}\right]^{-1/2}\right\}\ , \tag{6}$$

where b is a constant ($b\approx1.5$). The phase transition may occur under the condition

$$\Delta(\xi_{XY})^2=x_2\ , \tag{7}$$

where x_2 is a finite value. Then the critical temperature is estimated from Eqs. (6) and (7) as

$$\frac{T_c(g=1,\Delta)}{J}=\frac{T_K}{J}\left[1+\frac{4b^2}{\left\{\ln\left[\frac{x_2}{\Delta}\right]\right\}^2}\right]\ . \tag{8}$$

Note that this critical temperature is a monotonically increasing function of Δ.

In the general case $0<\Delta<g<1$, according to Hikami and Tsuneto,[12] the crossover from 2D Heisenberg with XY anisotropy to 3D XY occurs, and the critical temperature is given by

$$\frac{T_c(g,\Delta)}{J}=A_2g^{1/\phi}+\frac{B_2}{\left[\ln\frac{x_2}{\Delta}\right]^2}\ , \tag{9}$$

where A_2, B_2, and x_2 are constants. The first term is a conventional form of the shift in the critical temperature due to spin anisotropy and is derived from a standard treatment of the crossover scaling for spin anisotropy,[14–16] where ϕ is a crossover exponent. The second term is due to the crossover of the dimensionality.

III. EXPERIMENTAL PROCEDURE

The single crystals of $Co_cNi_{1-c}Cl_2$ ($0\le c\le1$) were grown from anhydrous $CoCl_2$ and $NiCl_2$ powders of the nominal weight composition in a Bridgeman furnace at temperatures around 980 °C. The stage-2 $Co_cNi_{1-c}Cl_2$ GIC was prepared by intercalation of $Co_cNi_{1-c}Cl_2$ single crystal into single crystals of graphite in a Cl_2 gas atmo-

sphere at 740 Torr. The reaction was continued at 540 °C for 20 days. The Co concentration in the GIC obtained was confirmed to coincide with that in the bulk cobalt-nickel chloride single crystal from the dc magnetic susceptibility. The stoichiometry of each sample ($C_nCo_cNi_{1-c}Cl_2$) was determined from its weight uptake measurement before and after intercalation. The stage of these GIC samples was confirmed to be stage-2 from the (00L) x-ray scattering experiment by using a Huber double-circle diffractometer with a Siemens 2.0-kW x-ray generator.

The ac magnetic susceptibility of stage-2 $Co_cNi_{1-c}Cl_2$ GIC's was measured by using an ac Hartshorn bridge method. An ac magnetic field with frequency $\nu=330$ Hz and amplitude $h=300$ mOe was applied along the c plane of the samples. The dc magnetic susceptibility of stage-2 $Co_cNi_{1-c}Cl_2$ GIC's was measured by using the Faraday balance method. The GIC sample of 10 mg was placed in a fused quartz sample holder of known susceptibility.

IV. RESULT

The dc magnetic susceptibility of stage-2 $Co_cNi_{1-c}Cl_2$ GIC's was measured in the temperature range $30 \le T \le 300$ K in the presence of an external magnetic field ($H=4.0$ kOe) along the direction perpendicular to the c axis. The dc magnetic susceptibility data obey the Curie-Weiss law in the temperature range $150 \le T \le 300$ K. Figure 1 shows the Curie-Weiss temperature Θ of stage-2 $Co_cNi_{1-c}Cl_2$ GIC's as a function of Co concentration, where Θ is determined from the least-squares fit of the susceptibility data to the Curie-Weiss law. We find a monotonic decrease of Θ from $\Theta(\text{Ni})=70.0$ K at $c=0$ to $\Theta(\text{Co})=23.2$ K at $c=1.0$.

The real part of the ac magnetic susceptibility of stage-2 $Co_cNi_{1-c}Cl_2$ GIC's was measured in the temperature range $2.6 \le T \le 25$ K. The samples used in this measurement were the same ones used in the dc magnetic susceptibility measurement. Figure 2 shows the real part of ac magnetic susceptibility, χ', in stage-2 $Co_cNi_{1-c}Cl_2$ GIC's with various Co concentrations, as a function of temperature. The real part χ' shows a broad peak for each Co concentration because of a smearing of critical temperature arising from the finite-size effect of small islands and the possible Co concentration gradient within intercalate layers. The peak height of χ' tends to decrease with increasing Co concentration. The critical temperature T_c, defined as a temperature at which the real part χ' has a maximum, shifts to the high-temperature side with decreasing Co concentration. The full width at half maximum of the peak in χ' around the critical temperature ΔT increases from 2.2 to 6 K as the Co concentration decreases. The Co concentration dependence of T_c is shown in Fig. 3, indicating a large decrease of T_c from $c=0$ to 0.5 and a slight decrease of T_c from $c=0.5$ to 1. Note that the critical temperatures T_c at $c=0$ and 1 coincide with the lower critical temperatures T_{cl} of stage-2 $NiCl_2$ GIC and $CoCl_2$ GIC, respectively, where the real part χ' has a peak. The real part χ' of stage-2 $NiCl_2$ GIC and $CoCl_2$ GIC is known to show a shoulder at T_{cu} in the limit of $h \approx 0$.[2] Such a shoulder is not seen in χ' of Fig. 3, which was measured at $h=300$ mOe. The upper critical temperature T_{cu} is considered to be a temperature at which the in-plane spin correlation length becomes the same size as islands inside intercalate layers.

Figure 4 shows a log-log plot of χ' versus reduced temperature t ($=T/T_c-1$) for $c=0.85$. The real part χ'

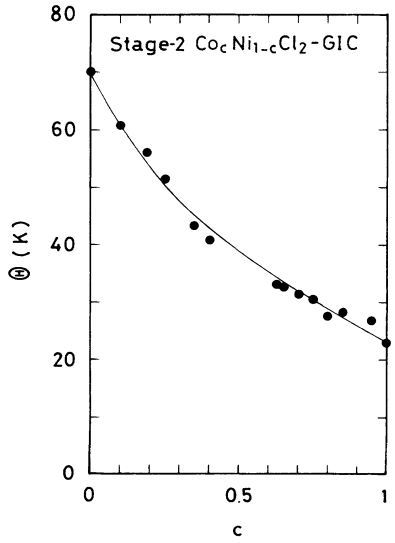

FIG. 1. Curie-Weiss temperature Θ vs Co concentration of stage-2 $Co_cNi_{1-c}Cl_2$ GIC's. The solid line is described by Eq. (14) with $\Theta(\text{Co-Ni})=p[\Theta(\text{Co})\Theta(\text{Ni})]^{1/2}$ and $p=1.2$.

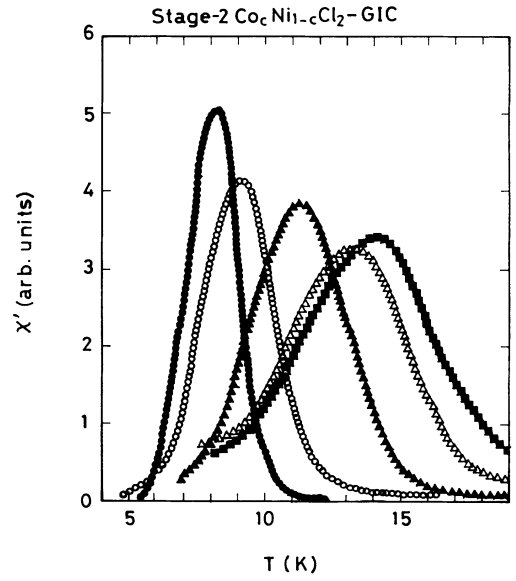

FIG. 2. Real part of ac magnetic susceptibility (χ') of stage-2 $Co_cNi_{1-c}Cl_2$ GIC's vs temperature. $c=0.1$ (■), 0.19 (Δ), 0.40 (▲), 0.63 (○), and 1.0 (●). The ac magnetic field of $\nu=330$ Hz and $h=300$ mOe is applied along the c plane.

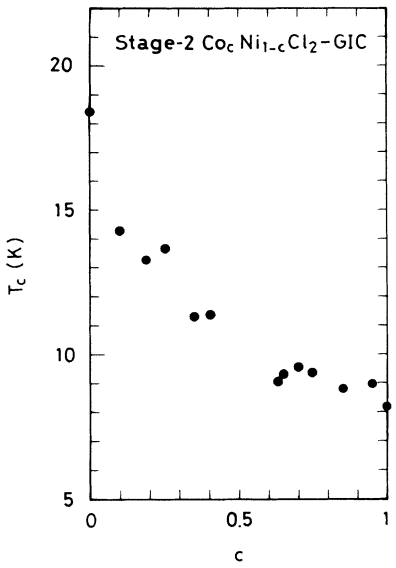

FIG. 3. Co concentration dependence of critical temperature T_c of stage-2 $Co_cNi_{1-c}Cl_2$ GIC's.

above T_c may be described by a power law $\chi' \sim t^{-\gamma}$. In the temperature range of $0.21 \leq t \leq 0.58$, the least-squares fit of the data to the power law yields the critical exponent $\gamma = 2.02 \pm 0.02$. For $t < 0.21$, the slope of the curve $\log_{10}\chi'$ vs $\log_{10} t$ decreases with the decrease of t probably because of intrinsic behavior such as crossover effect or smearing of critical temperature. Similar behavior of χ' versus temperature has been reported by Dupas

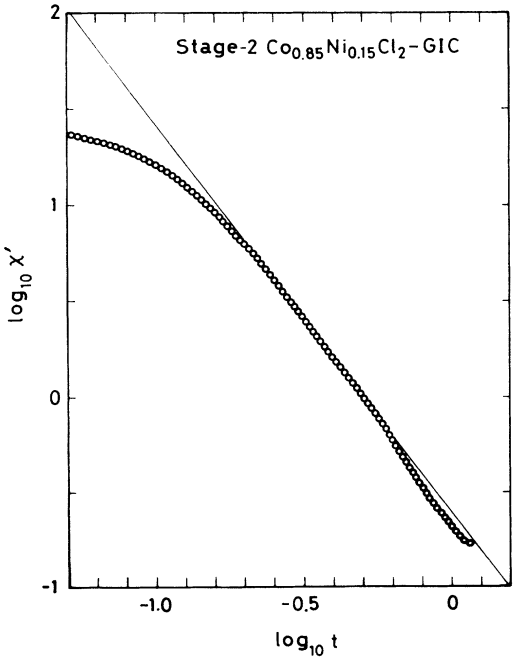

FIG. 4. Log-log plot of χ' vs t $(t = T/T_c - 1)$ for stage-2 $Co_cNi_{1-c}Cl_2$ GIC's with $c = 0.85$. The solid line denotes a least-squares fit to the power law with $\gamma = 2.02$.

TABLE I. Critical temperature T_c, Curie-Weiss temperature Θ, critical exponent γ, the fitting temperature range t for γ, and critical exponent β of stage-2 $Co_cNi_{1-c}Cl_2$ GIC's.

c	T_c (K)	Θ (K)	γ	t	β
0	18.38	70.00	1.99	0.15–0.18	0.122
0.10	14.23	60.78			0.152
0.19	13.24	56.13	2.09	0.19–0.28	0.192
0.25	13.66	51.44			
0.35	11.28	43.39	2.48	0.19–0.23	0.090
0.40	11.36	41.11	2.18	0.14–0.27	0.100
0.63	9.09	33.07	2.12	0.20–0.26	0.098
0.65	9.29	32.99	2.02	0.25–0.35	
0.70	9.62	31.23	1.94	0.14–0.33	
0.75	9.38	30.54	2.10	0.19–0.29	
0.85	8.81	28.59	2.02	0.21–0.58	
0.95	9.00	26.75	1.85	0.16–0.36	
1	8.20	23.20	2.07	0.10–0.18	0.082

and Renard[17] for a quasi-2D XY-like ferromagnet K_2CuF_4: $\gamma = 1.00 \pm 0.05$ for $10^{-4} < t < 2 \times 10^{-3}$ and γ increases to a maximum value of $\gamma = 1.9$ at $t = 0.5$. The values of γ and the fitting temperature range for each Co concentration are listed in Table I. The values of γ for mixed systems are likely to be close to those of pure systems except for $c = 0.35$: $\gamma = 2.07 \pm 0.02$ for stage-2 $CoCl_2$ GIC and $\gamma = 1.99 \pm 0.02$ for stage-2 $NiCl_2$ GIC. Rogiers, Grundke, and Betts[18] have shown from a high-temperature series expansion for the 2D XY model that the susceptibility has a conventional power-law divergence with $\gamma = 2.51 \pm 0.25$ rather than an exponential singularity. This theoretical value of γ, which is a little larger than the values of γ in the stage-2 $Co_cNi_{1-c}Cl_2$ GIC's, indicates the 2D XY character of the critical behavior in these compounds. In a previous paper[4] we have

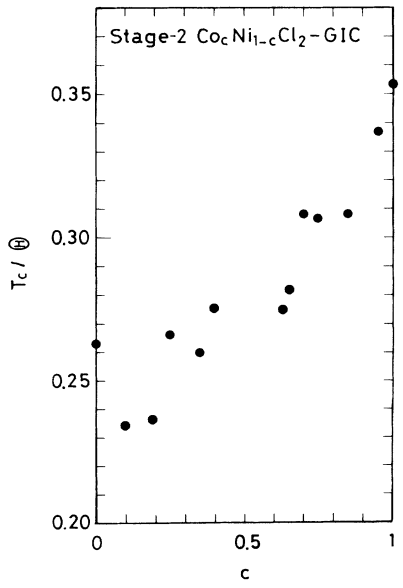

FIG. 5. Ratio of T_c/Θ vs Co concentration of stage-2 $Co_cNi_{1-c}Cl_2$ GIC's.

determined the values of critical exponent β of magnetization for several samples by assuming a Gaussian distribution function of critical temperature with average critical temperature and width. The values of β thus obtained are also listed in Table I. We find from Table I that the critical exponent β seems to be independent of the Co concentration: $\beta \approx 0.1$ except for $c=0.10$ and 0.19.

In Fig. 5 we show the Co concentration dependence of the ratio of T_c/Θ, which is calculated from the values of T_c and Θ for each Co concentration in Table I. The ratio T_c/Θ is 0.263 at $c=0$, and has a minimum value of 0.234 around $c=0.1$. With further increase of the Co concentration from $c=0.1$, the ratio T_c/Θ monotonically increases and reaches 0.353 at $c=1$. This behavior of T_c/Θ is explained below in terms of the effect of XY spin anisotropy on the phase transition of these compounds.

V. DISCUSSION

The stage-2 $Co_cNi_{1-c}Cl_2$ GIC's magnetically behave like a 2D Heisenberg-like ferromagnet with XY spin anisotropy. The spin Hamiltonian of these compounds may be described as[4]

$$H=-\sum_{\langle i,j\rangle} 2J_{ij}(\mathbf{S}_i\cdot\mathbf{S}_j-g_{ij}S_i^zS_j^z)+\sum_{\langle i,m\rangle} 2J'_{im}\mathbf{S}_i\cdot\mathbf{S}_m \ , \quad (10)$$

where J_{ij} (>0) is a ferromagnetic intraplanar exchange interaction between ions on i and j sites of the same intercalate layer, J'_{im} (>0) is an antiferromagnetic interplanar exchange interaction between i and m ions of adjacent intercalate layers, and g_{ij} (>0) is an XY spin anisotropy parameter between ions on i and j sites. The value of g_{ij} in stage-2 $NiCl_2$ GIC is much smaller than that in stage-2 $CoCl_2$ GIC; $g(\text{Co-Co})=J_A(\text{Co-Co})/J(\text{Co-Co})=0.48$ and $g(\text{Ni-Ni})=D(\text{Ni})/[2zJ(\text{Ni-Ni})]=7.62\times10^{-3}$. For $J'_{im}=0$ in Eq. (10), the spin Hamiltonian can be rewritten as

$$H=-\sum_{\langle i,j\rangle} 2J_{\text{eff}}(c)\{\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_j-g_{\text{eff}}(c)\sigma_i^z\sigma_j^z\} \ , \quad (11)$$

by using spin operators σ_i normalized by the spin values of i ions. Within the framework of a molecular field approximation, the effective XY spin anisotropy parameter $g_{\text{eff}}(c)$ of stage-2 $Co_cNi_{1-c}Cl_2$ GIC's is given by

$$\begin{aligned} g_{\text{eff}}(c)=&\{c^2[P(\text{Co})]^2\Theta(\text{Co})g(\text{Co-Co})+(1-c)^2[P(\text{Ni})]^2\Theta(\text{Ni})g(\text{Ni-Ni}) \\ &+2c(1-c)\Theta(\text{Co-Ni})P(\text{Co})P(\text{Ni})g(\text{Co-Ni})\}/\{c^2[P(\text{Co})]^2\Theta(\text{Co}) \\ &+(1-c)^2[P(\text{Ni})]^2\Theta(\text{Ni})+2c(1-c)\Theta(\text{Co-Ni})P(\text{Co})P(\text{Ni})\} \ , \end{aligned} \quad (12)$$

where $P(\text{Co})$ ($=5.54\mu_B$) and $P(\text{Ni})$ ($=3.29\mu_B$) are the effective magnetic moments, and $\Theta(\text{Co})$ ($=23.2$ K) and $\Theta(\text{Ni})$ ($=70.0$ K) the Curie-Weiss temperatures of the stage-2 $CoCl_2$ GIC and stage-2 $NiCl_2$ GIC, respectively. In a previous paper[4] we assumed that the intraplanar exchange interaction between Co^{2+} and Ni^{2+} spins is given by $J(\text{Co-Ni})=p[J(\text{Co-Co})J(\text{Ni-Ni})]^{1/2}$ with constant p, leading to the definition $\Theta(\text{Co-Ni})=p[\Theta(\text{Co})\Theta(\text{Ni})]^{1/2}$. Further, we assume here that the XY spin anisotropy parameter between Co^{2+} and Ni^{2+} spins is described by $g(\text{Co-Ni})=q[g(\text{Co-Co})g(\text{Ni-Ni})]^{1/2}$ with constant q. The effective intraplanar exchange interaction $J_{\text{eff}}(c)$ is related to the Curie-Weiss temperature $\Theta(c)$ of stage-2 $Co_cNi_{1-c}Cl_2$ GIC's by

$$J_{\text{eff}}(c)=\frac{3\Theta(c)}{2z}=\frac{\Theta(c)}{4} \ , \quad (13)$$

where $\Theta(c)$ is given by[4]

$$\Theta(c)=\frac{c^2[P(\text{Co})]^2\Theta(\text{Co})+(1-c)^2[P(\text{Ni})]^2\Theta(\text{Ni})+2c(1-c)\Theta(\text{Co-Ni})P(\text{Co})P(\text{Ni})}{c[P(\text{Co})]^2+(1-c)[P(\text{Ni})]^2} \ . \quad (14)$$

In Fig. 1 the solid line is a theoretical curve of $\Theta(c)$ given by Eq. (14) where $\Theta(\text{Co-Ni})=p[\Theta(\text{Co})\Theta(\text{Ni})]^{1/2}$ with $p=1.2$. The data of Θ agree well with the solid line, indicating that $J(\text{Co-Ni})$ is ferromagnetic and is given by 9.88 K. The effective interaction J_{eff} monotonically decreases from $\Theta(\text{Ni})/4=17.5$ K at $c=0$ to $\Theta(\text{Co})/4=5.8$ K at $c=1$ with increasing Co concentration. When q is assumed to be equal to $p=1.2$, the value of $g(\text{Co-Ni})$ is estimated as $g(\text{Co-Ni})=0.0726$, which is close to the value observed for $K_2Co_cNi_{1-c}F_4$: $g(\text{Co-Ni})=0.05\pm0.02$.[19] Figure 6 shows the effective XY spin anisotropy parameter $g_{\text{eff}}(c)$ as a function of Co concentration where three values of $g(\text{Co-Ni})$ are chosen: $g(\text{Co-Ni})=0$, 0.0726, and 0.1. As the Co concentration increases from $c=0$ to 1, the parameter g_{eff} monotonically increases from 7.62×10^{-3} to 0.48, indicating a continuous change of the spin symmetry from Heisenberg-like to XY-like.

Now we discuss the effect of XY spin anisotropy and the interplanar exchange interaction on the ratio T_c/Θ in the stage-2 $Co_cNi_{1-c}Cl_2$ GIC's. We find in Fig. 5 that as the Co concentration changes from $c=0$ to 0.1 the ratio T_c/Θ begins to decrease and shows a minimum around $c=0.1$. This minimum of T_c/Θ around $c=0.1$ is qualitatively explained as follows. The effective XY spin anisotropy g_{eff} is a monotonically increasing function of Co concentration (Fig. 6). On the other hand, the ratio Δ may change slightly from $\Delta(\text{Ni})=10\times10^{-4}$ at $c=0$ to $\Delta(\text{Co})=8\times10^{-4}$ at $c=1$. The first term of Eq. (9) due to the XY spin anisotropy may remain unchanged for $0\le c\le0.1$ because of very small change in g_{eff} (Fig. 6),

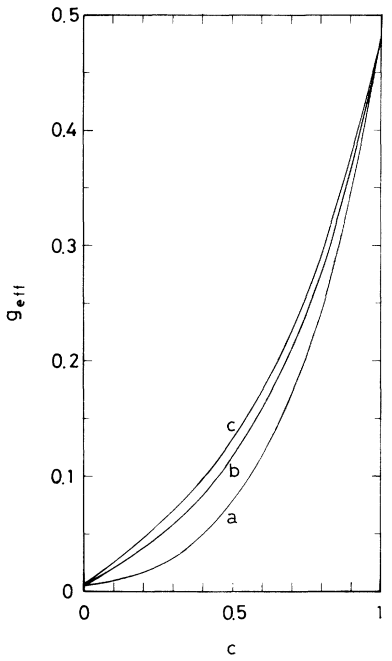

FIG. 6. XY spin anisotropy parameter g_{eff} vs Co concentration described by Eq. (12), where g(Co-Ni) is changed as a parameter: (a) g(Co-Ni)=0, (b) 0.0726, and (c) 0.1.

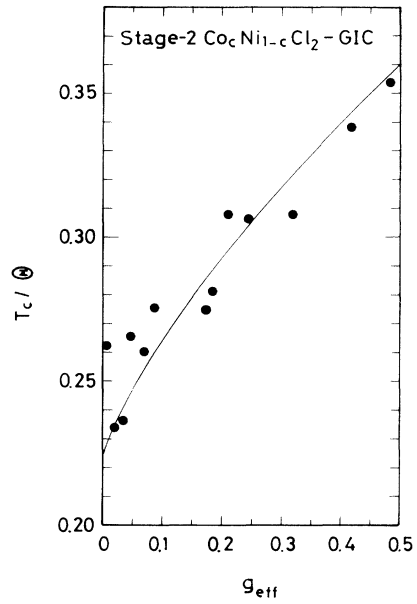

FIG. 7. Plot of T_c/Θ as a function of XY spin anisotropy parameter g_{eff} with g(Co-Ni)=0.0726. The solid line is a result of least-squares fit of the data to Eq. (15) with $A=0.229$, $B=0.224$, and $\phi=1.34$.

while the second term of Eq. (9) due to the effect of interplanar exchange interaction decreases slightly because of the possible decrease of Δ from $\Delta(\text{Ni})=10\times10^{-4}$ to $\Delta(\text{Co})=8\times10^{-4}$ for $0\le c\le0.1$. For $c\ge0.1$ the ratio Δ is assumed to be equal to $\Delta(\text{Co})=8\times10^{-4}$ and the effective XY spin anisotropy g_{eff} is assumed to change drastically. Then Eq. (9) may be rewritten as

$$\frac{T_c(c)}{\Theta(c)}=A\{g_{\text{eff}}(c)\}^{1/\phi}+B\ , \tag{15}$$

where A and B are constants. Figure 7 shows the plot of the ratio T_c/Θ as a function of g_{eff} for the case of g(Co-Ni)$=1.2[g(\text{Co-Co})g(\text{Ni-Ni})]^{1/2}=0.0726$. The least-squares fit of the data of T_c/Θ vs g_{eff} to Eq. (15) yields the values of $A=0.229$, $B=0.224$, and $\phi=1.34$. We also obtain the values of $A=0.196$, $B=0.224$, and $\phi=1.78$ for the case of g(Co-Ni)=0, and $A=0.238$, $B=0.224$, and $\phi=1.25$ for the case of g(Co-Ni)=0.1. The crossover exponent ϕ is found to increase with decreasing g(Co-Ni). Here we adopt the value of g(Co-Ni)=0.0726 for the stage-2 $Co_cNi_{1-c}Cl_2$ GIC's. Our result of $\phi=1.34$ is found to be close to the theoretical value of crossover exponent for the crossover from 3D Heisenberg-like to 3D XY-like behavior, $\phi=1.25$[20] suggesting a 3D antiferromagnetic ordered phase with XY-character below T_c. The extrapolated value of T_c/Θ at $g_{\text{eff}}=0$ is equal to the value of B (=0.224). However, we note that the value of B obtained from the relation of T_c/Θ vs g_{eff} for a series of compounds $(C_nH_{2n+1}NH_3)_2CuCl_4$ ($n=1-10$) (Ref. 21) is $B=0.22$. These also magnetically behave like a quasi-2D Heisenberg-like ferromagnet with XY spin anisotropy: $S=\frac{1}{2}$ and $\Delta=2.5\times10^{-4}-5.5\times10^{-4}$. This close agreement of B between stage-2 $Co_cNi_{1-c}Cl_2$ GIC's and $(C_nH_{2n+1}NH_3)_2CuCl_4$ may indicate that the ratio T_c/Θ in the limit of $g_{\text{eff}}=0$ takes a universal value (=0.22–0.224) for quasi-2D Heisenberg-like ferromagnets with XY spin anisotropy ($\Delta\neq0$). Here it should be noted that for $\Delta=0$ the value of T_c/Θ at $g_{\text{eff}}=0$ is equal to 0 because the 2D Heisenberg system has no phase transition above 0 K.

Here we discuss a possibility for determining an expression of the Kosterlitz-Thouless (KT) temperature T_K in an ideal 2D XY spin system, based on the assumption that Eq. (15) is still valid at $g_{\text{eff}}=1$. In Eq. (15) the extrapolated value of T_c/Θ at $g_{\text{eff}}=1$ is estimated as $A+B=0.453$ with $A=0.229$ and $B=0.224$. The term A arising from the XY spin anisotropy effect may correspond to the ratio T_K/Θ: $T_K/\Theta=A=0.229$. The Curie-Weiss temperature Θ is described by $\Theta=2zJS(S+1)/3$, where S is the spin, J the intraplanar exchange interaction, and z the number of nearest-neighbor spins. For the stage-2 $CoCl_2$GIC with $S=\frac{1}{2}$ and $z=6$, the ratio T_K/J is estimated as

$$\frac{T_K}{zJ}=\frac{2}{3}AS(S+1)=0.115\ . \tag{16}$$

This ratio may be compared with the result of Monte Carlo simulations.[22,23] For an ideal 2D XY spin system on a square lattice ($z=4$), the ratio T_K/J is predicted to be described as $T_K/2J=0.887S^2(z/4)$, leading to the ratio $T_K/zJ=0.11$ for $S=\frac{1}{2}$. This value of T_K/zJ is in excellent agreement with our result ($T_K/zJ=0.115$). Thus it may be concluded that the ratio T_K/zJ takes a universal value (=0.11–0.115) for ideal 2D XY spin systems.

Finally we consider the magnetic phase transition of stage-2 $CoCl_2$ GIC. We define the 3D and 2D spin ordering temperatures as T_{3D} and T_{2D}, respectively. By using T_{3D} and T_{2D}, Eq. (15) may be rewritten as

$$\frac{T_{3D}}{\Theta}=\frac{T_{2D}}{\Theta}+B\ , \tag{17}$$

where $T_{3D}>T_{2D}$ because of $B>0$. For the stage-2 $CoCl_2$ GIC T_{3D} is considered to coincide with the lower critical temperature T_{cl}: $T_{cu}>T_{cl}=T_{3D}>T_{2D}$. Here T_{2D} is an ideal temperature at which the in-plane spin correlation length ξ is assumed to diverge when the intercalate layer forms a perfect triangular lattice, and T_{cu} is a temperature at which ξ is comparable to the size of islands in the intercalate layer. From Eq. (17) with $B=0.224$, $\Theta=23.2$ K, and $T_{3D}=T_{cl}=8.2$ K, the value of T_{2D} is estimated as $T_{2D}=3.0$ K, which is much lower than T_{cl}. Such a behavior has been reported in the 2D planar ferromagnet K_2CuF_4.[24,25] The actual critical temperature (=6.25 K) is higher than the estimated KT transition temperature (=5.5 K). It may be understood that the phase transition of K_2CuF_4 is basically the KT-type transition but modified by the weak interplanar interaction. The phase transition of stage-2 $CoCl_2$ GIC may be dominantly caused by the Kosterlitz-Thouless transition, but is modified by the finite-size effect of small islands and the antiferromagnetic interplanar exchange interaction. The intermediate phase between T_{cl} and T_{cu} is a purely 2D ordered phase. The growth of the in-plane spin correlation length ξ is limited by the size of small islands.

VI. CONCLUSION

We have investigated the magnetic phase transition of stage-2 $Co_cNi_{1-c}Cl_2$ GIC's which approximate quasi-two-dimensional Heisenberg ferromagnets with XY spin anisotropy. The phase transition at the critical temperature T_c is caused by both the XY spin anisotropy effect and the 3D effect through interplanar exchange interaction. While the interplanar exchange interaction is almost independent of Co concentration, the spin symmetry drastically changes from Heisenberg-like to XY-like with increasing Co concentration. We have shown that the ratio of T_c to the Curie-Weiss temperature Θ is well described by $T_c/\Theta=Ag_{\rm eff}^{1/\phi}+B$ 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, respectively. The extrapolated value of $Ag_{\rm eff}^{1/\phi}=A$ at $g_{\rm eff}=1$ may suggest that the Kosterlitz-Thouless temperature T_K of an ideal 2D XY system is described by $T_K/zJ=0.115$, where J is the intraplanar exchange interaction and z is the number of nearest-neighbor spins.

For further discussion we need ac magnetic susceptibility measurements in the presence of an external magnetic field. The value of $g_{\rm eff}$ for each Co concentration can then be estimated from the value of spin-flop field. We also need a theory of the critical temperature for the 2D Heisenberg-like ferromagnet with XY anisotropy where magnetic ions with $S=\frac{1}{2}$ and 1 are randomly distributed on the triangular lattice. The exchange interaction between magnetic ions with different spins is considered to have a significant effect on the critical temperature.

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