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

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Abstract. Magnetic properties of stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ graphite intercalation compounds (GICs) for $0 \leq c \leq 1$ have been studied by DC magnetic susceptibility. These compounds can be considered to approximate two-dimensional randomly mixed ferromagnets with XY spin symmetry. As a function of Co concentration c the average effective magnetic moment P_{eff} , and the Curie–Weiss temperature Θ have been determined. The measurements indicate that Co^{2+} and Ni^{2+} spins are distributed randomly on triangular lattice sites of each intercalate layer. It is found that the intraplanar exchange interaction $J(\text{Co–Ni})$ between the different spins is larger than that between like spins, $J(\text{Co–Co})$ or $J(\text{Ni–Ni})$: $J(\text{Co–Ni}) = 1.2 [J(\text{Co–Co})J(\text{Ni–Ni})]^{1/2}$. As a function of concentration, the susceptibility shows a rounding effect at the magnetic phase transition for a series of compounds with $c = 0.1, 0.19, 0.35, 0.40, 0.52, 0.63, 0.80$ and 1.0 . We have assumed a Gaussian distribution of transition temperatures to determine the average value of transition temperature $\langle T_c \rangle$, the distribution of transition temperature σ and the critical exponent β . It appears that the critical exponent β is unchanged for $0.35 \leq c \leq 1.0$: $\beta = 0.09 \pm 0.01$. We obtain for the initial slope of $\langle T_c \rangle$ versus c at $c = 0$ the value -1.21 ± 0.02 . The ratio $\sigma/\langle T_c \rangle$ shows a broad peak centred at $c = 0.5$ which is explained here qualitatively by both finite size effect and macroscopic Co concentration gradient within the intercalate layer.

1. Introduction

Considerable effort has been reported recently on magnetic ternary graphite intercalation compounds (TGICs) in which two different magnetic species are intercalated into the galleries between graphite layers (Solin and Zabel 1988). Included in the magnetic TGICs are graphite bi-intercalation compounds (GBICs) and random mixture graphite intercalation compounds (RMGICs). In the case of the magnetic GBIC, two different magnetic intercalate layers (I_1 and I_2) alternate with graphite layers (G), forming a stacking sequence $\dots \text{GI}_1\text{GI}_2\text{GI}_1\text{GI}_2 \dots$ along the c axis (Suzuki *et al* 1984b, Herold *et al* 1985, Rancourt *et al* 1988). In the case of the magnetic RMGIC, the random mixture $\text{A}_c\text{B}_{1-c}\text{Cl}_2$ (A, B = Ni, Co and Mn) is intercalated into the graphite host, where c is the concentration of A ($0 \leq c \leq 1$). Stage N magnetic RMGICs are formed with $N = 1, 2, \dots$, and the dimensionality of the system changes from three-dimensional (3D) to two-dimensional (2D) as N increases. Different kinds of frustration effects can be studied in these systems: competition between ferromagnetic and antiferromagnetic interactions

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leading to spin glass behaviour, competing spin anisotropies between XY and Ising models, and the formation of a 2D antiferromagnet on the triangular lattice sites.

We believe that the measurements reported here on stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs describe the first randomly mixed magnetic system which has been studied in magnetic RMGIC research. We analyse the structural properties of these compounds by x-ray scattering, and the magnetic properties using DC magnetic susceptibility. Stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs approximate 2D randomly mixed ferromagnets with XY spin symmetry (Yeh *et al* 1989), stage 2 meaning that adjacent $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ intercalate layers are separated by two graphite layers. There are triangular lattice sites in the intercalate layer on which it is expected that the Co^{2+} and Ni^{2+} ions are randomly distributed. It is along the c plane of the single crystals that the spins of both Co^{2+} and Ni^{2+} are oriented.

Stage 2 CoCl_2 GICs have been studied intensively and much is known about it (Murakami *et al* 1983, Suzuki *et al* 1983, Hun and Flandrois 1984, Wiesler *et al* 1986, 1987). There is a three-layer sandwich of Cl–Co–Cl layers which comprises the CoCl_2 intercalate layer. In nearly the same configuration as in the pristine compound, each layer forms a triangular lattice. The intercalate layer is translationally incommensurate with the graphite host, but rotated 30° with respect to it. The in-plane lattice constant a is 3.55 Å, while the c -axis repeat distance is 12.70 Å. In terms of a fictitious spin $S = \frac{1}{2}$, the spin Hamiltonian for the Co^{2+} ions in stage 2 CoCl_2 GIC can be given as

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

where $J(\text{Co-Co})$ is the ferromagnetic intraplanar exchange interaction, $J'(\text{Co-Co})$ is the antiferromagnetic interplanar exchange interaction, and $J_A(\text{Co-Co})$ is the anisotropic exchange interaction: $J(\text{Co-Co}) = 7.75$ K, $J'(\text{Co-Co})/J(\text{Co-Co}) \approx 8 \times 10^{-4}$, and $J_A(\text{Co-Co})/J(\text{Co-Co}) = 0.48$. In equation (1) we take the z axis to coincide with the c axis. The first two sums in the spin Hamiltonian are taken over nearest neighbours within the intercalate layer. The last sum extends over nearest neighbours in adjoining layers. $P_{\text{eff}}(\text{Co})$, the effective magnetic moment of the Co^{2+} ions is given by $P_{\text{eff}}(\text{Co}) = g(\text{Co})[S(S+1)]^{1/2}$. With $S = \frac{1}{2}$ and $g(\text{Co}) = 6.40$ we obtain $P_{\text{eff}}(\text{Co}) = 5.54 \mu_B$ (Wiesler *et al* 1986). There are two magnetic phase transitions in stage 2 CoCl_2 GIC. The paramagnetic phase with 2D spin fluctuations, but no spin ordering, exists above T_{cu} ($=9.1$ K). The onset of 2D ferromagnetic ordering in the intercalate layer occurs at T_{cu} . When the temperature is lowered to T_{cl} ($=8.0$ K), 3D spin correlations arise. Short-range antiferromagnetic correlations between the spins in neighbouring layers develop below T_{cl} (Murakami *et al* 1983). In table 1 we have displayed magnetic and structural data for this compound.

In stage 2 NiCl_2 GIC, the graphite galleries in the host are occupied by the intercalant in the same arrangement described above. In this case the intercalate layer is translationally incommensurate with the host graphite with a rotation angle of 0° . Here the in-plane lattice constant is $a = 3.46$ Å, while the c -axis repeat distance is 12.70 Å. In this case also, the magnetic properties are similar to those described above (Suematsu *et al* 1983, Suzuki *et al* 1983, 1984a). Here the magnetic phase transition temperatures are T_{cu} ($=22.0$ K) and T_{cl} ($=17.5$ K) (Suzuki *et al* 1983). In terms of $S = 1$ the spin Hamiltonian for the Ni^{2+} ions in stage 2 NiCl_2 GIC can be given as

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

where $D(\text{Ni})$ is the single-ion anisotropy; $D(\text{Ni}) = 0.80$ K, $J(\text{Ni-Ni}) = 8.75$ K, and

Table 1. Structural and magnetic properties of stage 2 CoCl₂ GIC and stage 2 NiCl₂ GIC, where a is the in-plane lattice constant and d is the c -axis repeat distance (Suematsu *et al* 1983, Wiesler *et al* 1986).

	Stage 2 CoCl ₂ GIC	Stage 2 NiCl ₂ GIC
Spin S	$\frac{1}{2}$	1
J (K)	7.75	8.75
D (K)	—	0.80
J_A (K)	3.72	—
T_{c1} (K)	8.0	17.5
T_{c2} (K)	9.1	22.0
Θ (K)	23.2	70.0
C_M (emu K/mol)	3.84	1.35
P_{eff} (μ_B)	5.54	3.29
g	6.40	2.33
d (Å)	12.70	12.70
a (Å)	3.55	3.46

$J'(\text{Ni-Ni})/J(\text{Ni-Ni}) \approx 10^{-3}$. The XY anisotropy here is much smaller than above. $P_{\text{eff}}(\text{Ni})$, the effective magnetic moment of Ni²⁺ ions is given by $P_{\text{eff}}(\text{Ni}) = g(\text{Ni})[S(S+1)]^{1/2}$. With $S = 1$ and $g(\text{Ni}) = 2.33$ we obtain $P_{\text{eff}}(\text{Ni}) = 3.29 \mu_B$ (Suematsu *et al* 1983). In table 1 we have also displayed the magnetic and structural data for this compound.

From the DC magnetic susceptibility above 150 K at 4.0 kOe, we have determined the effective magnetic moment and the Curie–Weiss temperature as a function of Co concentration. From the measurement below 30 K at 100 Oe, we have also studied the magnetic phase transition. The measured DC susceptibility exhibits a rounding effect at the magnetic phase transition, making it difficult to determine the transition temperature. We have assumed a Gaussian distribution of transition temperatures to determine the critical exponent β , the average transition temperature $\langle T_c \rangle$ and the degree of distribution of transition temperature σ . We exhibit the results as a function of Co concentration and discuss the concentration dependence of $\langle T_c \rangle$, β , and the ratio $\sigma/\langle T_c \rangle$.

2. Molecular field approximation

To understand how the Co²⁺ and Ni²⁺ ions interact when they randomly occupy lattice sites, we make a molecular field approximation as first applied by Hashimoto (1963) and developed by Yeh *et al* (1989). Here the first term of the spin Hamiltonians in equations (1) and (2) is assumed to dominate the second and third terms. The stage 2 CoCl₂ and NiCl₂ GICs can be approximated as 2D Heisenberg ferromagnetic systems. The magnetic ions form a regular triangular lattice with z nearest neighbours (z is referred to as the coordination number, $z = 6$ in this case). The interactions of i -spin ($i = 1$ for Co²⁺ and $i = 2$ for Ni²⁺) can be described by the Hamiltonian

$$\mathcal{H}(i) = -2 \sum_{j=1}^z J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - g_i \mu_B \mathbf{H} \cdot \mathbf{S}_i \quad (3)$$

where the summation runs over the nearest neighbours of i -spin. The intraplanar

exchange interactions between adjacent magnetic ions Co–Co, Co–Ni, and Ni–Ni are denoted by $J_{11} = J(\text{Co–Co})$, $J_{12} = J(\text{Co–Ni})$, and $J_{22} = J(\text{Ni–Ni})$. The ranges of the exchange interactions are limited to the nearest neighbours. Expanding the summation and treating the spins of 1- and 2-ions as their respective mean values, $\langle S_1 \rangle$ and $\langle S_2 \rangle$, the spin Hamiltonians become

$$\mathcal{H}(i) = -g_i \mu_B [\mathbf{H} + (2z/g_i \mu_B)(J_{i1} \langle S_1 \rangle P_{i1} + J_{i2} \langle S_2 \rangle P_{i2})] \cdot \mathbf{S}_i \quad (4)$$

where $P_{11} (=c)$ is the probability for a Co^{2+} ion to have another Co^{2+} ion as its nearest neighbour, $P_{12} (=1-c)$ the probability for a Co^{2+} ion to have a Ni^{2+} ion as its nearest neighbour. Similarly, we have $P_{22} = 1-c$, and $P_{21} = c$. Notice also that $J_{12} = J_{21}$. The magnetization M_i for ion i can be approximated by the Curie law,

$$M_i = C_{ii} H_i / T \quad (5)$$

with the Curie–Weiss constant

$$C_{ii} = N_A (g_i \mu_B)^2 S_i (S_i + 1) / 3k_B. \quad (6)$$

Using the molecular field H_i of equation (4), the magnetization M_i can be described by

$$M_1 = (C_{11}/T)[H + cq_{11}M_1 + (1-c)q_{12}M_2] \quad (7)$$

and

$$M_2 = (C_{22}/T)[H + cq_{12}M_1 + (1-c)q_{22}M_2] \quad (8)$$

with

$$q_{ij} = 2zJ_{ij}/(N_A g_i g_j \mu_B^2). \quad (9)$$

Thus the total magnetization, M , is given by

$$M = cM_1 + (1-c)M_2. \quad (10)$$

Then the DC magnetic susceptibility defined by M/H can be derived as

$$\chi = \frac{T[cC_{11} + (1-c)C_{22}] + [c(1-c)C_{11}C_{22}(2q_{12} - q_{22} - q_{11})]}{T^2 - [C_{11}q_{11}c + C_{22}q_{22}(1-c)]T + [c(1-c)C_{11}C_{22}(q_{11}q_{22} - q_{12}^2)]}. \quad (11)$$

By expanding equation (11) by $1/T$ and comparing it with the Curie–Weiss law

$$\chi = C/(T - \Theta) \quad (12)$$

the Curie–Weiss constant C and the Curie–Weiss temperature Θ can be obtained as

$$C = cC_{11} + (1-c)C_{22} \quad (13)$$

and

$$\Theta = \frac{c^2 C_{11}^2 q_{11} + (1-c)^2 C_{22}^2 q_{22} + 2c(1-c)C_{11}C_{22}q_{12}}{cC_{11} + (1-c)C_{22}}. \quad (14)$$

The average effective magnetic moment P_{eff} can be expressed by

$$P_{\text{eff}} = [cg_1^2 S_1(S_1 + 1) + (1-c)g_2^2 S_2(S_2 + 1)]^{1/2} = [cP_{\text{eff}}^2(\text{Co}) + (1-c)P_{\text{eff}}^2(\text{Ni})]^{1/2} \quad (15)$$

where $P_{\text{eff}}(\text{Co})$ and $P_{\text{eff}}(\text{Ni})$ are the effective magnetic moments of the stage 2 CoCl_2 and NiCl_2 GICs. These results of the molecular field approximation will be used to explain

Table 2. *c*-axis repeat distance of stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs with the stoichiometry of $\text{C}_n\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$.

<i>c</i>	<i>n</i>	<i>d</i> (Å)
0.00	12.71	12.70
0.10	10.97	12.67
0.19	13.24	12.69
0.40	10.95	12.72
0.52	11.33	12.68
0.63	10.76	12.74
0.80	12.33	12.71
1.00	10.60	12.70

the experimental results of the DC magnetic susceptibility for the stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs.

3. Experimental procedure

The 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 the nominal weight composition in a Bridgeman furnace at temperatures around 900 °C. 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 obtained coincides with that in the bulk cobalt–nickel chloride single crystal. The stoichiometry of each sample ($\text{C}_n\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$) was determined from its weight uptake measurement before and after intercalation (table 2).

In order to accurately determine the *c*-axis repeat distance, $(00\bar{L})$ x-ray scattering of these GIC samples was performed by using a Huber double-circle diffractometer with a Siemens 2.0 kW x-ray generator equipped with a sealed Mo tube and a flat graphite monochromator.

The DC magnetic susceptibility measurements of these GIC samples were performed with a Cahn electrobalance with an applied magnetic field *H* oriented perpendicular to the *c* axis of the crystal. The GIC sample of ~5 mg was placed in a fused quartz sample holder of known susceptibility. The DC magnetic susceptibility was measured from 30 K to 300 K at *H* = 4.0 kOe, and from 4.2 K to 30 K at 100 Oe.

4. Result and discussion

We have performed x-ray scattering experiments on the stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GIC samples with various Co concentrations at 300 K. The *c*-axis repeat distance (*d*-spacing) of these compounds is determined from the $(00\bar{L})$ x-ray diffraction patterns. A typical $(00\bar{L})$ x-ray diffraction pattern for *c* = 0.52 is shown in figure 1 as a function of wave number Q_c with Mo $K\alpha$ x-ray radiation. The Bragg reflections appear at $Q_c = (2\pi/d)\bar{L}$ ($\bar{L} = 1, 2, \dots$) with *d* = 12.68 Å. The (002) peak is much broader than (003) and (004) peaks. Such a differential peak broadening, which is common among acceptor-type GICs, indicates that this sample is mainly stage 2 but with small fraction of other stage numbers. The

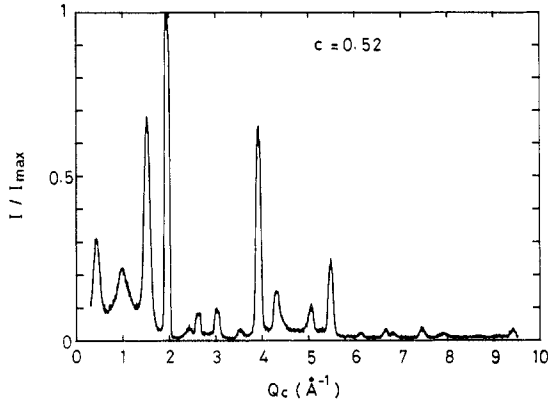


Figure 1. $(00\bar{L})$ x-ray diffraction pattern of stage 2 $\text{Co}_{0.52}\text{Ni}_{0.48}\text{Cl}_2$ GIC with Mo $K\alpha$ radiation source at 300 K. $Q_c = (2\pi/d)\bar{L}$ with $d = 12.68 \text{ \AA}$.

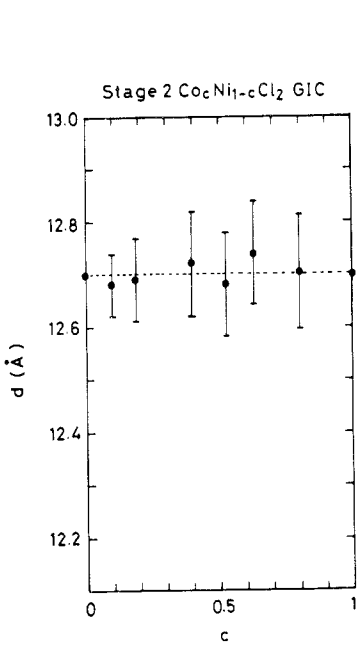


Figure 2. c -axis repeat distance versus Co concentration c of stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs.

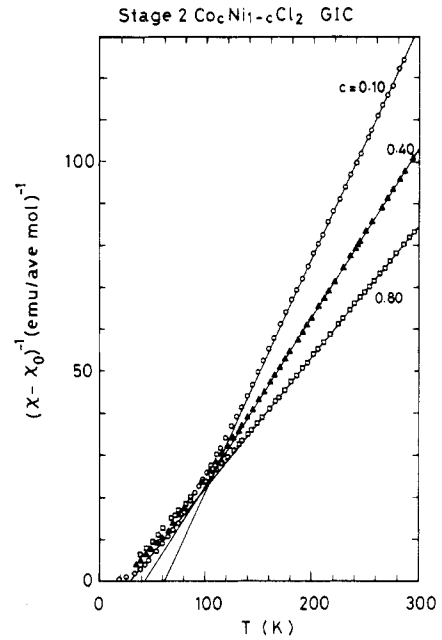


Figure 3. Reciprocal DC magnetic susceptibility $(\chi - \chi_0)^{-1}$ versus temperature for stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs with $c = 0.10$ (\circ), 0.40 (\triangle) and $c = 0.80$ (\square). $H = 4.0 \text{ kOe}$. $H \parallel c$ plane. The solid line is the least squares fit to the Curie-Weiss law for $150 \leq T \leq 300 \text{ K}$.

values of the d -spacing of our samples with stoichiometry $\text{C}_n\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ are listed in table 2. Figure 2 shows the plot of the d -spacing as a function of Co concentration for our samples. The d -spacing seems to be independent of Co concentration ($d = 12.70 \text{ \AA}$)

Table 3. Curie–Weiss constant C (emu K/ave mol), temperature-independent susceptibility χ_0 (emu/ave mol), Curie–Weiss temperature Θ (K) and effective magnetic moment P_{eff} (μ_B /ave mol) of stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs.

c	C (emu K/ave mol)	χ_0 (emu/ave mol)	Θ (K)	P_{eff} (μ_B /ave mol)
0.00	1.354	—	70.0	3.29
0.10	1.803	-5.41×10^{-5}	60.78	3.80
0.19	1.775	-5.16×10^{-4}	56.13	3.77
0.35	—	—	43.39	—
0.40	2.484	-5.20×10^{-4}	43.39	4.46
0.52	2.749	-1.08×10^{-3}	38.92	4.69
0.63	3.255	-9.68×10^{-4}	33.07	5.10
0.80	3.225	-5.14×10^{-4}	27.51	5.08
1.00	3.840	-8.50×10^{-5}	23.2	5.54

within experimental error. Since the d -spacing of stage 2 CoCl_2 GIC is equal to that of stage 2 NiCl_2 GIC ($d = 12.70 \text{ \AA}$), our result is consistent with the prediction from Vegard's law (d -spacing is proportional to c).

We have measured the DC magnetic susceptibility of stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs with Co concentration $c = 0.10, 0.19, 0.40, 0.52, 0.63$ and 0.80 in the temperature range $30 \text{ K} \leq T \leq 300 \text{ K}$, where an external magnetic field is applied along the direction perpendicular to the c axis ($H = 4.0 \text{ kOe}$). It is found that the DC magnetic susceptibility data obey the Curie–Weiss law

$$\chi = \chi_0 + C/(T - \Theta) \quad (\text{emu/ave mol}) \quad (16)$$

in the temperature range $150 \text{ K} \leq T \leq 300 \text{ K}$, where χ_0 is the temperature-independent molar susceptibility, C the Curie–Weiss constant, and Θ the Curie–Weiss temperature. The least squares fit of the DC susceptibility data to equation (16) yield the values of C , Θ and χ_0 for each Co concentration, which are listed in table 3. Figure 3 shows the reciprocal susceptibility data of these compounds, denoted by $(\chi - \chi_0)^{-1}$, as a function of temperature for the Co concentration $c = 0.10, 0.40$ and $c = 0.80$ (figure 3), where the solid lines are described by $(\chi - \chi_0)^{-1} = (T - \Theta)/C$ with C and Θ listed in table 3. It is found from figure 3 that the slope corresponding to $1/C$ and the T -axis intercept corresponding to Θ monotonically decrease with increasing Co concentration. The average effective magnetic moment P_{eff} is related to the Curie–Weiss constant C by

$$C = N_A \mu_B^2 P_{\text{eff}}^2(\text{ave})/3k_B \approx \frac{1}{3} P_{\text{eff}}^2(\text{ave}) \quad (17)$$

where N_A is the Avogadro's number, k_B the Boltzmann constant, and μ_B the Bohr magneton. The average effective magnetic moment $P_{\text{eff}}(\text{ave})$ is also listed in table 3 for each Co concentration. Figure 4(a) shows the plot of $P_{\text{eff}}(\text{ave})$ as a function of Co concentration, where the data for $c = 0$ are from Suematsu *et al* (1983) ($P_{\text{eff}}(\text{Ni}) = 3.29 \mu_B$), and the data for $c = 1$ are from Wiesler *et al* (1986) ($P_{\text{eff}}(\text{Co}) = 5.54 \mu_B$). The average effective magnetic moment $P_{\text{eff}}(\text{ave})$ increases with increasing Co concentration. This monotonic change of $P_{\text{eff}}(\text{ave})$ suggests that Ni and Co exist as divalent ions inside the intercalate layer. Figure 4(b) shows the Curie–Weiss temperature, Θ , as a function of Co concentration. The data for $c = 0$ are from Suematsu *et al* (1983)

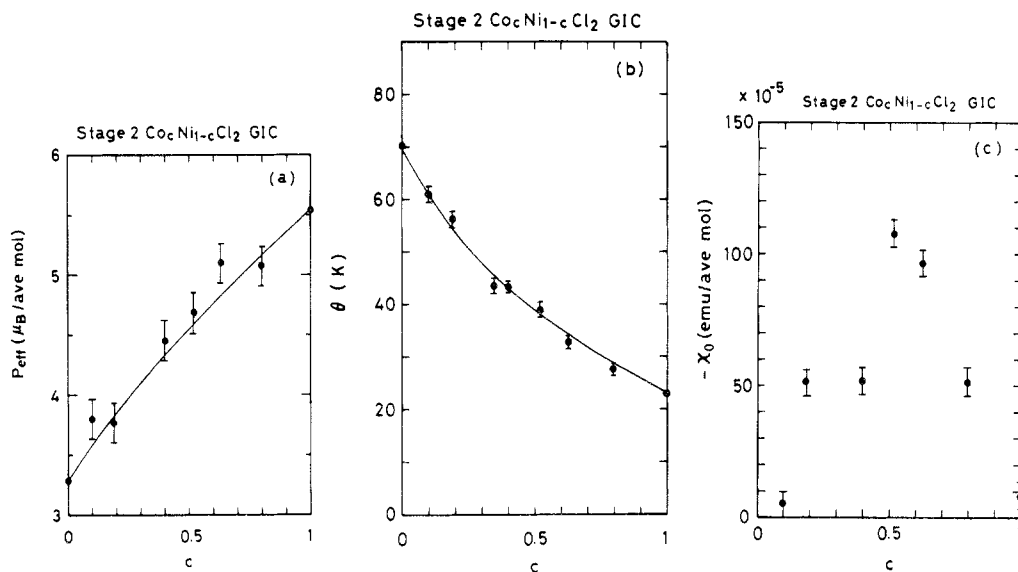


Figure 4. (a) Average effective magnetic moment, P_{eff} , versus Co concentration c of stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs (Yeh *et al* 1989). The solid line is a plot of equation (15). (b) Curie-Weiss temperature, Θ (K), versus Co concentration c (Yeh *et al* 1989). The solid line is a plot of equation (14) with $k = q_{12}(q_{11}q_{22})^{-1/2} = 1.2$. (c) Absolute value of temperature-independent susceptibility ($-\chi_0$) versus Co concentration, where χ_0 is negative for $0 \leq c \leq 1$.

($\Theta = 70$ K). The data for $c = 1$ are from Wiesler *et al* (1986) ($\Theta = 23.2$ K). From figure 4(b), the initial slope of Θ versus c is obtained as

$$(1/\Theta) \partial\Theta/\partial c = -1.13 \pm 0.02 \quad (18)$$

at $c = 0$. We now discuss the data of figures 4(a) and (b) in terms of equations (15) and (14). The data on $P_{\text{eff}}(\text{ave})$ versus Co concentration c in figure 4(a) agree well with the solid line corresponding to equation (15) with $P_{\text{eff}}(\text{Co}) = 5.54 \mu_B$ and $P_{\text{eff}}(\text{Ni}) = 3.29 \mu_B$. This result indicates that the actual Co concentration inside the intercalate layer may be close to the nominal Co concentration. By using equation (14), the concentration dependence of Θ can be calculated, where J_{12} is taken as a trial function of the geometric mean of the two interactions with a multiplicative parameter, k , $J_{12} = k(J_{11}J_{22})^{1/2}$. The data on Θ versus Co concentration in figure 4(b) agree very well with the solid line corresponding to equation (14) with $k = 1.2$. 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 $J_{22} = J(\text{Ni-Ni})$: $J_{12} = J(\text{Co-Ni}) = 9.88$ K. We note that the value of k ($=1.2$) thus obtained for stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs is very close to the factor k ($=1.29$) which has been reported by Ikeda *et al* (1981) for the 2D random antiferromagnet $\text{Rb}_2\text{Co}_c\text{Ni}_{1-c}\text{F}_4$, although they use this value of k to explain the dependence of the transition temperature, T_N , on the Co concentration.

As is shown in table 3, the temperature-independent susceptibility χ_0 is diamagnetic (negative) for any Co concentration. Figure 4(c) shows the value of $-\chi_0$ as a function of Co concentration, where the data at $c = 1$ is from Wiesler *et al* (1986). A noticeable feature of figure 4(c) is that the value of $-\chi_0$ has a maximum around $c = 0.5$. The diamagnetic contribution to the susceptibility from cores, $\chi(\text{core})$, can be calculated as

$\chi(\text{core}) = -12.8 \times 10^{-5}$ emu/ave mol for the stage 2 CoCl_2 GIC with stoichiometry of $\text{C}_{10.60}\text{CoCl}_2$, and as $\chi(\text{core}) = -14.0 \times 10^{-5}$ emu/ave mol for the stage 2 NiCl_2 GIC with stoichiometry of $\text{C}_{12.71}\text{NiCl}_2$. Here we use the core diamagnetic susceptibility of $\chi_{\text{C}} = -6 \times 10^{-6}$, $\chi_{\text{Cl}} = -26 \times 10^{-6}$, $\chi_{\text{Co}} = -12 \times 10^{-6}$ and $\chi_{\text{Ni}} = -12 \times 10^{-6}$ (all units of emu/gram-ion) (Mulay 1966). The value of χ_0 at $c = 1$ ($\chi_0 = -8.50 \times 10^{-5}$ emu/ave mol) is close to the diamagnetic susceptibility from cores. We do not have the data of χ_0 at $c = 0$ available. However, it is found that the value of χ_0 at $c = 0.1$ ($\chi_0 = -5.41 \times 10^{-5}$ emu/ave mol) is also close to the diamagnetic susceptibility from cores. The strong enhancement of diamagnetic contribution in χ_0 around $c = 0.5$ may come from the orbital contribution from conduction electrons, which is expected to be paramagnetic for the donor-type GICs and diamagnetic for the acceptor-type GICs. Note that the room temperature powder susceptibility of stage 1 $\text{K}_c\text{Cs}_{1-c}$ GICs (Furdin *et al* 1975), which are donor-type, is paramagnetic and shows a sharp peak around $c = 0.5$. Both stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs and stage 1 $\text{K}_c\text{Cs}_{1-c}$ GICs form a 2D triangular lattice in the intercalate layer.

Now we assume that our sample with stoichiometry $\text{C}_{11.33}\text{Co}_{0.52}\text{Ni}_{0.48}\text{Cl}_2$ ($c = 0.52$) is composed of two parts $\text{C}_{11.33}$ and $\text{Co}_{0.52}\text{Ni}_{0.48}\text{Cl}_2$ which are completely isolated. Then the diamagnetic susceptibility from the graphite part of $\text{C}_{11.33}$ can be estimated as $\chi_1 = -99.6 \times 10^{-5}$ emu/ave mol by using the value of -7.32×10^{-6} emu g^{-1} at room temperature for pristine graphite (DiSalvo *et al* 1979). The core diamagnetic susceptibility of graphite part $\text{C}_{11.33}$ is given by $\chi_2 = -6.78 \times 10^{-5}$ emu/ave mol. The core diamagnetic susceptibility of the $\text{Co}_{0.52}\text{Ni}_{0.48}\text{Cl}_2$ part is given by $\chi_3 = -6.4 \times 10^{-5}$ emu/ave mol. Thus the total susceptibility is calculated as $\chi_1 + \chi_2 + \chi_3 = -112.8 \times 10^{-5}$ emu/ave mol, which is in good agreement with the experimental result of χ_0 for $c = 0.52$ ($\chi_0 = -108 \times 10^{-5}$ emu/ave mol). This result may suggest that there is no structural correlation between the graphite layer and the intercalate layer around $c = 0.5$.

In order to study the magnetic phase transition of these compounds, we have measured the DC magnetic susceptibility of these compounds with $c = 0.10, 0.19, 0.35, 0.40, 0.52, 0.63$ and 0.80 below 30 K, where a low field H ($= 100$ Oe) is applied along the direction perpendicular to the c axis. Figure 5 shows the DC magnetic susceptibility of our samples with $c = 0.10, 0.19, 0.40, 0.52, 0.80$ and 1.0 as a function of temperature. The data for $c = 1.0$, which is observed by Wiesler *et al* (1986), is shown in figure 5 for comparison. It is evident from figure 5 that there is a rounding of the transition temperature which seems to increase as the Co concentration decreases.

The DC magnetic susceptibility measured by the Faraday balance is the sum of the susceptibility arising from short range spin fluctuation and M_0/H , where M_0 is a magnetization proportional to the saturation magnetization M_s . The temperature variation of the measured DC susceptibility below the transition temperature is assumed to be determined mainly by that of the saturation magnetization. In fact, the DC susceptibility of stage 2 CoCl_2 GIC at 4.2 K already reaches about $\frac{1}{2}$ of M_s/H even for $H = 100$ Oe, where $M_s(\text{Co}) = N_{\text{Ag}}(\text{Co}) \mu_{\text{B}} S(\text{Co}) = 1.787 \times 10^4$ emu/mol. Figure 6 shows the plot of the maximum value of DC magnetic susceptibility, χ_{max} , as a function of the Co concentration. The monotonic increase of χ_{max} with increasing Co concentration indicates that (i) $M_s(\text{Co})$ is larger than $M_s(\text{Ni})$, and that (ii) the actual Co concentration after intercalation is almost the same as the nominal Co concentration of intercalant before intercalation. The solid line is the result of a least-squares fit of the data to a straight line in figure 6: $\chi_{\text{max}} = 31.8c + 58.9$ emu/ave mol. Although the magnetization

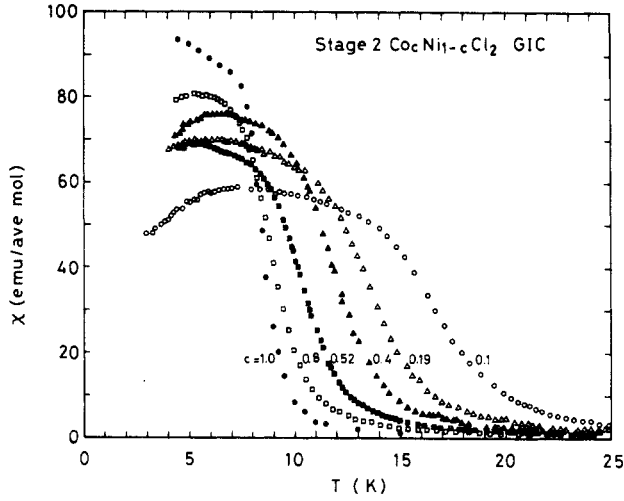


Figure 5. DC magnetic susceptibility versus temperature for stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs with Co concentration $c = 0.10$ (\circ), 0.19 (\triangle), 0.40 (\blacktriangle), 0.52 (\blacksquare), 0.80 (\square) and $c = 1.0$ (\bullet). $H = 100$ Oe. $H \parallel c$ plane.

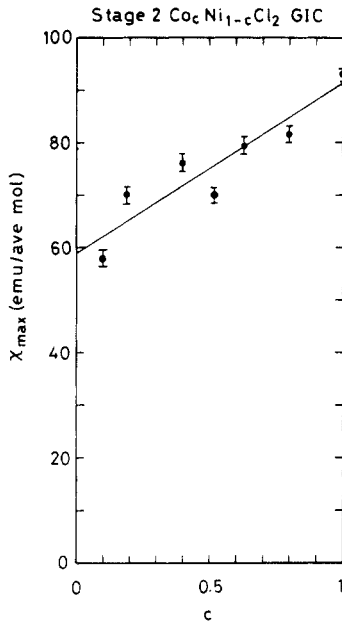


Figure 6. Maximum value of the DC magnetic susceptibility in figure 5, χ_{max} , as a function of Co concentration c .

of stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs is not saturated at $H = 100$ Oe, the dependence of χ_{max} on the Co concentration is similar to that of the theoretical value of

$$M_s/H = 5585 [3.20 c + 2.33 (1 - c)]/H = 48.6 c + 130.1$$

at $H = 100$ Oe. This result indicates that the measured DC susceptibility coincides with the magnetization below the transition temperature.

It is difficult to determine a transition temperature for each curve from figure 5. The measured DC susceptibility shows a tail around the transition temperature, which may arise from (i) short range spin fluctuations, and (ii) the finite size effect of islands within intercalate layers. In order to determine the average transition temperature $\langle T_c \rangle$ quantitatively, we assume a Gaussian distribution of the transition temperature with mean value $\langle T_c \rangle$ and width σ , which is described by

$$f(T_c) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[-\frac{1}{2} \left(\frac{T_c - \langle T_c \rangle}{\sigma} \right)^2 \right]. \quad (19)$$

Then the magnetization can be expressed by a power law with a critical exponent β ,

$$M(T) = M(0) \int_T^\infty D \left(1 - \frac{T}{T_c} \right)^\beta f(T_c) dT_c \quad (20)$$

where D is defined by

$$D^{-1} = \operatorname{erfc}(x = -\langle T_c \rangle / \sqrt{2}\sigma) \quad (21)$$

with the error function

$$\operatorname{erfc}(x) = \frac{1}{\sqrt{\pi}} \int_x^\infty \exp(-y^2) dy. \quad (22)$$

We do not use the data well above $\langle T_c \rangle$ for the least-squares fitting calculation because the contribution from short range spin fluctuation is not negligible even well above $\langle T_c \rangle$. When the data used are found to be well above $\langle T_c \rangle$ after the calculation, the data are removed from the calculation and the calculation is repeated until consistent results are obtained. In figures 7(a)–(c), we again show the plot of DC susceptibility as a function of temperature for $c = 0.19, 0.40$ and 0.80 to make it easy to compare between experimental data and calculations. We also have a least-squares fit of the data at $c = 0$ obtained by Suematsu *et al* (1983) ($H = 87.7$ Oe) to equation (20). The solid lines in figure 7 are the results of the least-squares fits to a power law with Gaussian distribution of the transition temperature. We have an excellent agreement between data and calculation. The values of $\langle T_c \rangle$, β and σ for each Co concentration are listed in table 4. Figure 8(a) shows the $\langle T_c \rangle$ versus Co concentration for stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs. The average transition temperature, $\langle T_c \rangle$, decreases monotonically from $\langle T_c \rangle = 20.06$ K for $c = 0$ to $\langle T_c \rangle = 8.78$ K for $c = 1$. Here it should be noted that $\langle T_c \rangle$ is between T_{c1} and T_{c0} for the case of $c = 0$ and 1. The average transition temperature $\langle T_c \rangle$ falls below a straight line connecting between $\langle T_c \rangle$ at $c = 0$ and 1. From figure 8(a), the initial slope of $\langle T_c \rangle$ versus c is obtained as

$$(1/\langle T_c \rangle) \partial \langle T_c \rangle / \partial c = -1.21 \pm 0.02, \quad (23)$$

at $c = 0$. The data on $\langle T_c \rangle$ versus c in figure 8(a) are not exactly proportional to the data on Θ versus c in figure 4(b). The ratio of Θ to T_c , $\gamma (= \Theta/T_c)$, monotonically decreases with Co concentration: $\gamma = 3.49$ at $c = 0$ and $\gamma = 2.64$ at $c = 1.0$. The dependence of $\langle T_c \rangle$ on Co concentration can not be explained in terms of the molecular field approximation. The effects of spin fluctuation and spin symmetry such as Ising, XY and Heisenberg are dominant factors in determining the transition temperature. In the molecular field approximation, of course, these effects are not taken into account at all. 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

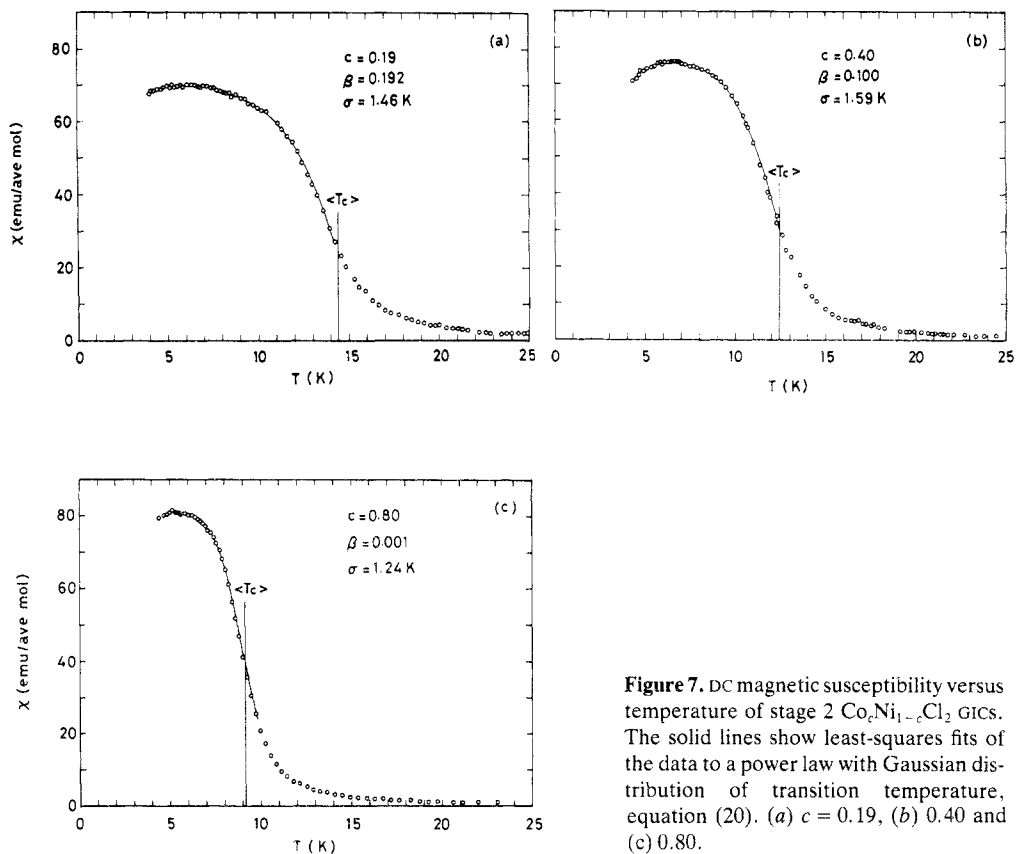


Figure 7. DC magnetic susceptibility versus temperature of stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs. The solid lines show least-squares fits of the data to a power law with Gaussian distribution of transition temperature, equation (20). (a) $c = 0.19$, (b) 0.40 and (c) 0.80.

Table 4. Critical exponent β , average critical temperature $\langle T_c \rangle$ and distribution of the transition temperature σ , of stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs.

c	$\langle T_c \rangle$ (K)	β	σ (K)
0.00	20.06	0.122	1.90
0.10	17.68	0.152	2.24
0.19	14.40	0.192	1.46
0.35	13.14	0.090	1.68
0.40	12.39	0.100	1.59
0.52	10.8	0.090	1.39
0.63	10.22	0.098	1.32
0.80	9.15	—	1.22
1.00	8.78	0.082	0.62

is much smaller than in the stage 2 CoCl_2 GIC. It is found from figure 8(a) that the slope defined by $-\partial\langle T_c \rangle/\partial c$ decreases with Co concentration and is nearly equal to zero for $0.8 \leq c \leq 1.0$. This small slope for $0.8 \leq c \leq 1.0$ indicates that (i) the exchange interaction $J(\text{Co-Ni})$ is of the same order as $J(\text{Co-Co})$, and that (ii) the XY anisotropy gradually changes over this region of Co concentration.

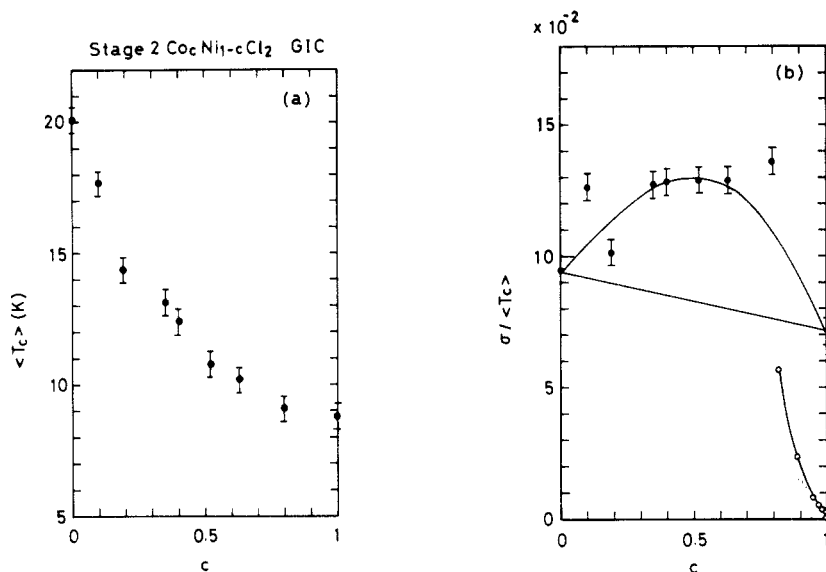


Figure 8. (a) Average transition temperature $\langle T_c \rangle$ versus Co concentration c (Yeh *et al* 1989). (b) $\sigma / \langle T_c \rangle$ versus Co concentration c for the stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs (●). For comparison, the results of $\sigma / \langle T_c \rangle$ versus c for $\text{Rb}_2\text{Co}_c\text{Mg}_{1-c}\text{F}_4$ (○) are shown (Ikeda *et al* 1979). The solid lines are guides to the eyes.

The value of β for $0.35 \leq c \leq 1.0$ is smaller than that for $0 \leq c \leq 0.19$, and is almost independent of the Co concentration: $\beta = 0.09 \pm 0.01$ for $0.35 \leq c \leq 1.0$. This value of β is smaller than that for the 2D Ising system ($\beta = 0.125$) and may be attributed to the 2D XY-character of these systems. The scaling relation $\alpha + 2\beta + \gamma = 2$ is valid, where α and γ are the critical exponents of specific heat and susceptibility. If $\alpha = 0$ is assumed, then the value of γ is estimated as $\gamma = 1.82 \pm 0.02$. This value of γ is smaller than that obtained from the AC susceptibility versus temperature for the stage 2 NiCl_2 GIC: $\gamma = 2.02 \pm 0.05$ for $t > 1.3 \times 10^{-1}$ where $t = (T - T_{\text{cu}}) / T_{\text{cu}}$ (Suzuki and Ikeda 1981). The distribution of transition temperature, σ , tends to become broader from $\sigma = 0.62$ K at $c = 1$ to $\sigma = 1.90$ K at $c = 0$ as the Co concentration decreases. Note that the values of σ are much larger than the temperature fluctuations within the samples, typically ± 0.1 K. The fact that σ is the largest for the stage 2 NiCl_2 GIC ($\sigma = 1.90$ K at $c = 0$) indicates that the rounding of the transition temperature observed for samples with any Co concentration may arise not only from the gradient of the Co concentration within the intercalate layer, because there is, of course, no gradient of Co concentration in the stage 2 NiCl_2 GIC.

Here we note that the stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs belong to acceptor-type GICs. The intercalate layers of these compounds are formed of small islands, whose size is on the order of 400–500 Å. On the boundary of these small islands, there exist dangling bonds of chlorine atoms, which provide acceptor sites for electrons transferred from the host graphite layers to the intercalate layers (Flandrois *et al* 1981, Wertheim 1981, Baron *et al* 1982, Flandrois *et al* 1983). For the stage 2 CoCl_2 GIC based on single crystals of Kish graphite, the diameter of islands is reported to be $L = 450$ Å from the high resolution x-ray measurement (Wiesler *et al* 1987). The size of islands inside the $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ intercalate layer is assumed to be given by $L \sim a/\rho$. Here ρ is the charge transfer from one C atom in the graphite layer to the intercalate layer, and a is the in-plane lattice

constant: $\rho = 0.012$ (Flandrois *et al* 1981) for $c = 0$ and $\rho = 0.0093$ for $c = 1$ (Hun and Flandrois 1984). The in-plane lattice constant is almost independent of Co concentration: $a = 3.46 \text{ \AA}$ for $c = 0$, and $a = 3.55 \text{ \AA}$ for $c = 1$. Thus the size of islands L depends only on the charge transfer ρ : $L \sim 1/\rho$. We assume that the rounding of the transition temperature could be due to the finite size of islands. According to finite size scaling (Fisher and Ferdinand 1967), the ratio $\sigma/\langle T_c \rangle$ may be described by

$$\sigma/\langle T_c \rangle \sim L^{-\lambda} \sim \rho^\lambda \quad (24)$$

where $\lambda = 1/\nu$ and ν is the critical exponent of the spin correlation length. Since λ is positive, the ratio $\sigma/\langle T_c \rangle$ increases as the charge transfer ρ decreases. Figure 8(b) shows the ratio of $\sigma/\langle T_c \rangle$ as a function of Co concentration for the stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs. The value of $\sigma/\langle T_c \rangle$ at $c = 1$ is smaller than that at $c = 0$, suggesting that the size of islands in the stage 2 CoCl_2 GIC is larger than that in the stage 2 NiCl_2 GIC. In fact, the diameter of islands for the stage 2 NiCl_2 GIC base on Madagascar natural graphite has been reported as $L = 170 \text{ \AA}$ from small angle neutron scattering experiments (Flandrois *et al* 1983), and is smaller than the diameter of islands for the stage 2 CoCl_2 GIC. The exponent λ is estimated as $\lambda = 0.3$ using the values of $\sigma/\langle T_c \rangle$ and L at $c = 0$ and 1. However, this value gives us only rough estimate of λ because the size of islands depends on the quality of the graphite host in GIC samples.

It is found from figure 8(b) that the ratio $\sigma/\langle T_c \rangle$ seems to have a broad peak around $c = 0.5$. There is no reason why the charge transfer ρ has a peak at $c = 0.5$. We assume that the charge transfer ρ changes monotonically with Co concentration. According to equation (24), then, the ratio $\sigma/\langle T_c \rangle$ is predicted to change monotonically with Co concentration. Thus the broad peak of $\sigma/\langle T_c \rangle$ around $c = 0.5$ is not explained only from the finite size scaling. The large value of $\sigma/\langle T_c \rangle$ around $c = 0.5$ may be attributed to a macroscopic concentration gradient over the intercalate layers, which may be the largest at $c = 0.5$ when two pure systems CoCl_2 and NiCl_2 are mixed randomly within the intercalate layer. In figure 8(b), we also show the data of $\sigma/\langle T_c \rangle$ versus c for the 2D Ising-like antiferromagnets $\text{Rb}_2\text{Co}_c\text{Mg}_{1-c}\text{F}_4$ (Ikeda *et al* 1979). The distribution of transition temperature σ is assumed to arise from a macroscopic gradient of Co concentration across the sample. In these systems, the ratio $\sigma/\langle T_c \rangle$ is almost zero at $c = 1$, and rapidly increases with decreasing Co concentration. Such a rapid increase of $\sigma/\langle T_c \rangle$ around $c = 1$ is also observed in the stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs. Note that the change of $\sigma/\langle T_c \rangle$ from $c = 1$ to 0.8 in $\text{Rb}_2\text{Co}_c\text{Mg}_{1-c}\text{F}_4$ is on the same order as that in the stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs. Therefore, it may be concluded that both the finite size of islands and the macroscopic concentration give rise to a smearing of the transition temperature for any c except $c = 0$ and 1. The value of σ can be described by

$$\sigma = (\sigma_s^2 + \sigma_c^2)^{1/2} \quad (25)$$

where σ_s is the smearing of T_c due to finite size effect and given by equation (24), and σ_c is the smearing of T_c due to the concentration gradient. In figure 8(b), the ratio $\sigma_s/\langle T_c \rangle$ may correspond to the straight line which connects between values of $\sigma/\langle T_c \rangle$ at $c = 0$ and 1. The ratio $\sigma_c/\langle T_c \rangle$ may show a broad peak at $c = 0.5$.

5. Conclusion

For the first time, random magnetic mixtures have been intercalated into a graphite host, and these compounds, stage 2 $\text{Co}_c\text{Ni}_{1-c}\text{Cl}_2$ GICs, approximate two-dimensional

site-random XY ferromagnets. Our DC magnetic susceptibility measurements indicate that the Co^{2+} and Ni^{2+} spins are randomly distributed in the intercalate layers in agreement with average effective magnetic moment calculations using the molecular field approximation. We have determined that the intraplanar exchange interaction between Co^{2+} and Ni^{2+} is $J(\text{Co-Ni}) = 9.88$ K. This is larger than the exchange interactions between like ions, which were $J(\text{Ni-Ni}) = 8.75$ K and $J(\text{Co-Co}) = 7.75$ K. We have determined that the temperature independent contribution to the magnetic susceptibility is diamagnetic, and the absolute value of this contribution has a peak around $c = 0.5$.

The average transition temperature $\langle T_c \rangle$, distribution of transition temperature σ , and the critical exponent β were determined by assuming a Gaussian distribution of transition temperatures. $\langle T_c \rangle$, the average transition temperature, decreases with increasing Co concentration, the initial slope $\partial(\ln\langle T_c \rangle)/\partial c$ at $c = 0$ being -1.21 ± 0.02 . $\langle T_c \rangle$ may be between T_{cu} and T_{cl} . The small value of the slope $-\partial\langle T_c \rangle/\partial c$ for $0.8 \leq c \leq 1$ is consistent with our result that $J(\text{Co-Ni})$ and $J(\text{Co-Co})$ have nearly the same magnitude. We found that the critical exponent β is almost independent of Co concentration for $0.35 \leq c \leq 1.0$: $\beta = 0.09 \pm 0.01$. The finite size effect and the macroscopic gradient of Co concentration may cause smearing of the transition temperature. We found that the ratio $\sigma/\langle T_c \rangle$ arising from the finite size effect is almost independent of Co concentration. However $\sigma/\langle T_c \rangle$ coming from the concentration gradient depends strongly on Co concentration.

The understanding of the magnetic phase transitions of random magnetic mixtures intercalated into graphite hosts would be improved by specific heat, AC magnetic susceptibility and neutron scattering measurements. It would be particularly interesting to examine how the magnetic phase transition temperatures T_{cu} and T_{cl} observed for $c = 0$ and 1 change as Co concentration is altered.

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References

- Baron F, Flandrois S, Hauw C and Gaultier J 1982 *Solid State Commun.* **42** 759–62
- DiSalvo F J, Safran S A, Waszczak J V and Fischer J E 1979 *Phys. Rev. B* **20** 4883–8
- Fisher M E and Ferdinand A E 1967 *Phys. Rev. Lett.* **19** 169–72
- Flandrois S, Hewat A H, Hauw C and Bragg R H 1983 *Synth. Met.* **7** 305–12
- Flandrois S, Masson J-M, Rouillon J-C, Gaultier J and Hauw C 1981 *Synth. Met.* **3** 1–13
- Furdin G, Carton B, Herold A and Zeller C 1975 *CR Acad. Sci. Paris B* **280** 653–6
- Hashimoto T 1963 *J. Phys. Soc. Japan* **18** 1140–7
- Hérolid A, Furdin G, Guerard D, Hachim L, Lelaurain M, Nadi N E and Vangelisti R 1985 *Synth. Met.* **12** 11–17
- Hun B and Flandrois S 1984 *J. Chim. Phys.* **81** 869–74
- Ikeda H, Abe T and Hatta I 1981 *J. Phys. Soc. Japan* **50** 1488–94
- Ikeda H, Suzuki M and Hutchings M T 1979 *J. Phys. Soc. Japan* **46** 1153–60

- Mulay L N 1966 *Magnetic Susceptibility* (New York: Interscience)
- Murakami Y, Matsuura M, Suzuki M and Ikeda H 1983 *J. Magn. Magn. Mater.* **31-34** 1171-2
- Rancourt D G, Hun B and Flandrois S 1988 *Can. J. Phys.* **66** 776-90
- Solin S A and Zabel H 1988 *Adv. Phys.* **37** 87-254
- Suematsu H, Nishitani R, Yoshizaki R, Suzuki M and Ikeda H 1983 *J. Phys. Soc. Japan* **52** 3874-85
- Suzuki M and Ikeda H 1981 *J. Phys. C: Solid State Phys.* **14** L923-8
- Suzuki M, Ikeda H and Endoh Y 1983 *Synth. Met.* **8** 43-51
- Suzuki M, Ikeda H, Murakami Y, Matsuura M, Suematsu H, Nishitani R and Yoshizaki R 1983 *J. Magn. Magn. Mater.* **31-34** 1173-4
- Suzuki M, Koga K and Jinzaki Y 1984a *J. Phys. Soc. Japan* **53** 2745-51
- Suzuki M, Oguro I and Jinzaki Y 1984b *J. Phys. C: Solid State Phys.* **17** L575-80
- Wertheim G K 1981 *Solid State Commun.* **38** 633-5
- Wiesler D G, Suzuki M, Chow P C and Zabel H 1986 *Phys. Rev. B* **34** 7951-7
- Wiesler D G, Suzuki M and Zabel H 1987 *Phys. Rev. B* **36** 7051-62
- Yeh M, Suzuki M and Burr C R 1989 *Phys. Rev. B* **40** 1422-5