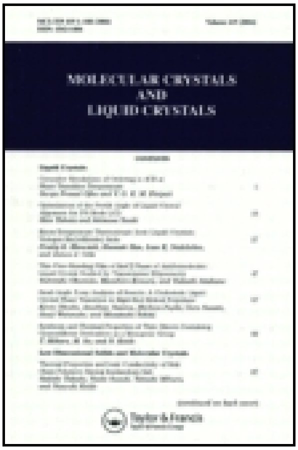

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# Percolation Behavior in $Co_cMg_{1-c}Cl_2$ and Stage-2 $Co_cMg_{1-c}Cl_2$ Graphite Intercalation Compounds

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# PERCOLATION BEHAVIOR IN $Co_cMg_{1-c}Cl_2$ AND STAGE-2 $Co_cMg_{1-c}Cl_2$ GRAPHITE INTERCALATION COMPOUNDS

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Abstract The magnetic phase transition of bulk $Co_cMg_{1-c}Cl_2$ and stage-2 $Co_cMg_{1-c}Cl_2$ GIC has been studied by dc and ac magnetic susceptibility, and low field SQUID magnetization measurements. The critical temperature decreases with the dilution of nonmagnetic $Mg^{2+}$ ions and reduces to zero at the percolation threshold $c_p$: $c_p \approx 0.5$ for stage-2 $Co_cMg_{1-c}Cl_2$ GIC and $c_p \approx 0.36$ for $Co_cMg_{1-c}Cl_2$. A possible one-dimensional character of stage-2 $Co_cMg_{1-c}Cl_2$ GIC near $c = c_p$ and the irreversible effect of magnetization below the critical temperature for stage-2 $Co_cMg_{1-c}Cl_2$ GIC ($0.74 \leq c \leq 1$) are discussed.

## INTRODUCTION

Pristine $Co_cMg_{1-c}Cl_2$ and stage-2 $Co_cMg_{1-c}Cl_2$ graphite intercalation compounds (GIC's) ($0 \leq c \leq 1$) approximate site-diluted three-dimensional (3D) and two-dimensional (2D) XY spin systems, respectively.[1-3] The $Co_cMg_{1-c}Cl_2$ and stage-2 $Co_cMg_{1-c}Cl_2$ GIC are layered compounds in which the $Co_cMg_{1-c}Cl_2$ layers are stacked along the c-axis. The $Co^{2+}$ and $Mg^{2+}$ ions are randomly distributed on the triangular lattice sites within each $Co_cMg_{1-c}Cl_2$ layer. Since the adjacent $Co_cMg_{1-c}Cl_2$ layers are separated by two graphite layers in the stage-2 $Co_cMg_{1-c}Cl_2$ GIC, the interplanar exchange interaction of stage-2 $Co_cMg_{1-c}Cl_2$ GIC is much weaker than that of $Co_cMg_{1-c}Cl_2$. Thus the $Co_cMg_{1-c}Cl_2$ and stage-2 $Co_cMg_{1-c}Cl_2$ GIC are expected to provide model systems of 3D and 2D site-random spin systems on the triangular lattice, respectively. The stage-2 $Co_cMg_{1-c}Cl_2$ GIC undergoes a phase transition between the paramagnetic phase and the 2D ferromagnetic phase at a critical temperature $T_c$, while $Co_cMg_{1-c}Cl_2$ undergoes a phase transition between the paramagnetic phase and the 3D antiferromagnetic phase at a Néel temperature $T_N$. The critical temperatures $T_c$ and $T_N$ defined in Ref. 3 decrease with decreasing Co concentration and reduce to zero at the percolation threshold $c_p$: $c_p \approx 0.36$ for $Co_cMg_{1-c}Cl_2$ and $c_p \approx 0.5$ for stage-2 $Co_cMg_{1-c}Cl_2$ GIC.[3]

The magnetic phase transitions of these two systems have been studied by using dc and ac magnetic susceptibility, and low field SQUID magnetization measurements. The effect of dilution with Mg ions on the magnetic phase transition is discussed in association with the dimension of systems. A possible 1D behavior for stage-2 $Co_cMg_{1-c}Cl_2$ GIC near $c = c_p$ and the irreversible effect of magnetization for stage-2 $Co_cMg_{1-c}Cl_2$ GIC ($0.74 \leq c \leq 1$) are also examined by SQUID magnetization measurements.



## EXPERIMENT

Single crystals of $Co_cMg_{1-c}Cl_2$ ($0.35 \leq c \leq 1$) were grown by heating a mixture of dehydrated $CoCl_2$ and $MgCl_2$ with nominal weight composition in quartz sealed in vacuum at 900 °C. Stage-2 $Co_cMg_{1-c}Cl_2$ GIC's ($0.46 \leq c \leq 1$) were synthesized by intercalation of single-crystal $Co_cMg_{1-c}Cl_2$ into single-crystal kish graphite in a chlorine gas atmosphere at 740 Torr for 20 days at 540 °C. The Co concentration of stage-2 $Co_cMg_{1-c}Cl_2$ GIC was determined from the fact that the Curie-Weiss temperature is proportional to an actual Co concentration.[3] We find that the Co concentration of GIC's is a little larger than that of intercalants. The c-axis stacking sequence was confirmed by (00L) x-ray diffraction to be well-defined stage-2. The magnetic properties of these compounds were studied by dc and ac magnetic susceptibility, and SQUID magnetization. The low field SQUID magnetization measurements ($H = 1$ Oe) were performed as follows: (i) First the sample was cooled from 300 to 2 K in the absence of magnetic field. A magnetic field of 1 Oe was then applied along the direction perpendicular to the c-axis. (ii) The temperature dependence of ZFC magnetization ($M_{ZFC}$) was measured with increasing temperature from 2 to 10 K. (iii) The sample was again cooled at the field of 1 Oe and the temperature dependence of FC magnetization ($M_{FC}$) was measured with decreasing temperature from 10 to 2 K.

## RESULTS AND DISCUSSION

Figure 1(a) shows the ratio R of the critical temperature to the Curie-Weiss temperature $\Theta$ of $Co_cMg_{1-c}Cl_2$ and stage-2 $Co_cMg_{1-c}Cl_2$ GIC as a function of Co concentration.[3] The ratio $T_N/\Theta$ of $Co_cMg_{1-c}Cl_2$ decreases from 0.60 to 0.31 as the concentration c decreases from $c = 1$ to $c = 0.5$. The ratio $T_c/\Theta$ of stage-2 $Co_cMg_{1-c}Cl_2$ GIC decreases from 0.30 to 0.17 as the concentration c decreases from $c = 1$ to $c = 0.61$. It is experimentally known that the value of R decreases as the dimension of the system decreases.[3] The value of R for $Co_cMg_{1-c}Cl_2$ is much larger than that for stage-2 $Co_cMg_{1-c}Cl_2$ GIC for $c \geq 0.7$, indicating that $Co_cMg_{1-c}Cl_2$ and stage-2 $Co_cMg_{1-c}Cl_2$ GIC approximate 3D and 2D spin systems, respectively. In the stage-2 $Co_cMg_{1-c}Cl_2$ GIC, the value of R is assumed to be lower than 0.1 for $0.5 \leq c \leq 0.55$, suggesting a possible 1D character of the system near the percolation threshold. Figure 1(b) shows the phase diagram of these compounds. The reduced critical temperature $T_c(c)/T_c(c = 1)$ of stage-2 $Co_cMg_{1-c}Cl_2$

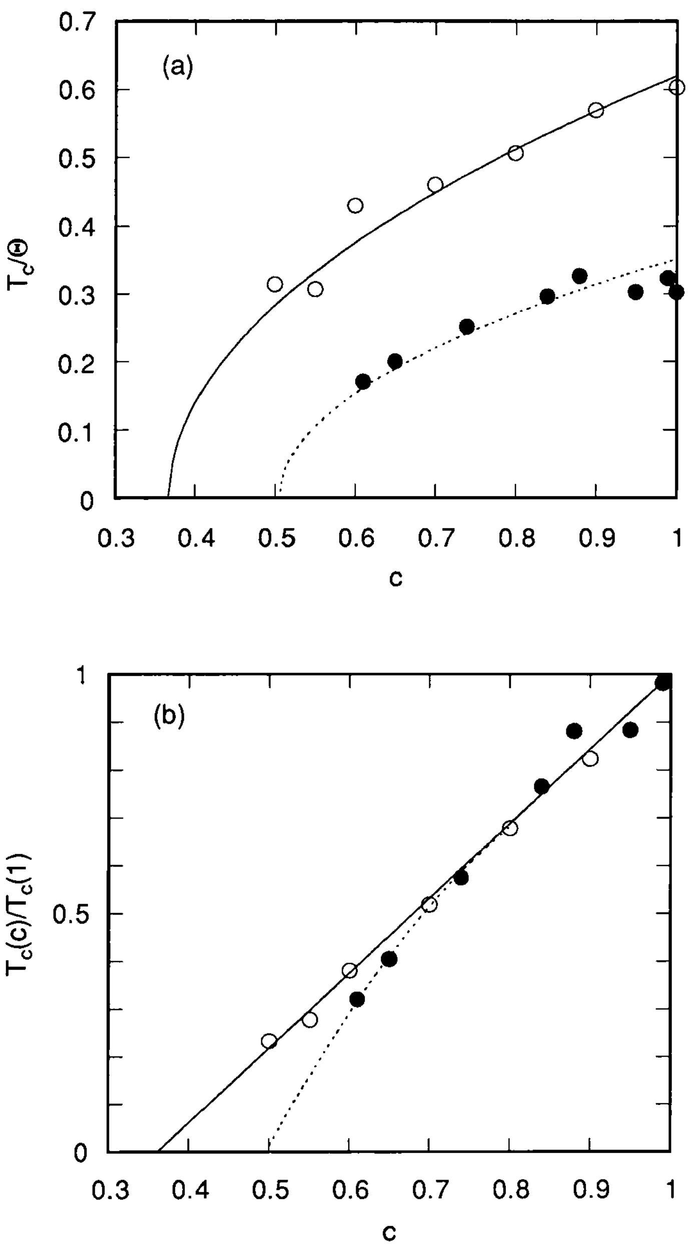


FIGURE 1 (a) $T_c(c)/\Theta(c)$ vs c, and (b) reduced critical temperature $T_c(c)/T_c(1)$ vs c for stage-2 $Co_cMg_{1-c}Cl_2$ GIC (closed circles) and $Co_cMg_{1-c}Cl_2$ (open circles). The solid and dotted lines are guides to the eyes (Ref. 4).

GIC is almost the same as $T_N(c)/T_N(c = 1)$ of $Co_cMg_{1-c}Cl_2$ for $c > 0.7$. The effect of the dimension on the dilution with Mg ions becomes significant below $c \approx 0.7$. The percolation threshold for $Co_cMg_{1-c}Cl_2$ is $c_p \approx 0.36$, close to the theoretical value (0.295) for the 2D triangular lattice with nearest neighbor (n.n.) and next nearest neighbor (n.n.n.) exchange interactions, and the percolation threshold for stage-2 $Co_cMg_{1-c}Cl_2$ GIC is $c_p \approx 0.5$, close to the theoretical value (0.5) for the 2D triangular lattice with n.n. exchange interaction. From these results the stage-2 $Co_cMg_{1-c}Cl_2$ GIC is expected to behave like one-dimensional ferromagnet in the concentration just above $c_p$.

Figure 2 shows the magnetic susceptibility for c = 0.61 and 0.46 at the magnetic field of 50 Oe. The solid line corresponds to the exact solution of the 1D Heisenberg ferromagnet with S = 1/2 theoretically derived by Bonner and Fisher.[5] The measured susceptibilities for c = 0.61 and 0.46 deviate from the theoretical line denoted by the solid line. In these compounds the intercalate layers are formed of small islands, whose diameter is typically on the order of 500 Å. The deviation from the theoretical estimate may be due to the finite-size effect of these small islands and the possible Co concentration gradient within samples. We have not succeeded in synthesizing a stage-2 $Co_cMg_{1-c}Cl_2$ GIC sample with the Co concentration just above the percolation threshold

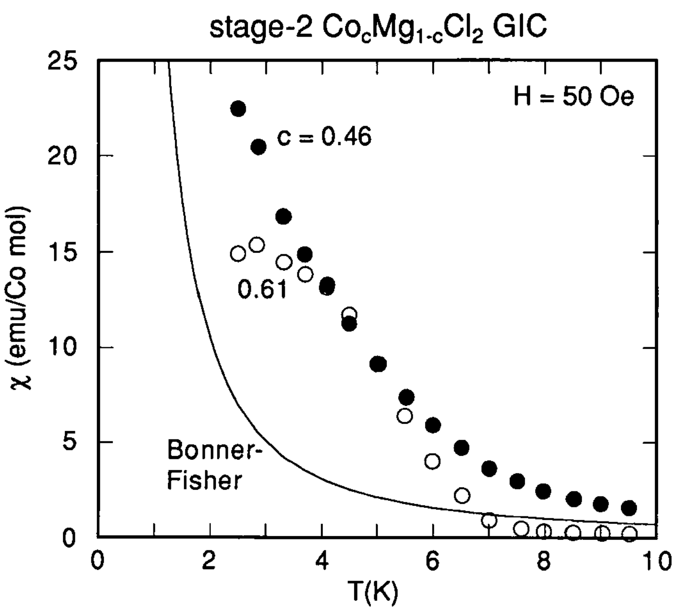


FIGURE 2 Susceptibility at low temperature for stage-2 $Co_cMg_{1-c}Cl_2$ GIC's with c = 0.46 (closed circles), and c = 0.61 (open circles). The solid line is the exact solution of the 1D Heisenberg ferromagnet with S = 1/2.[5]

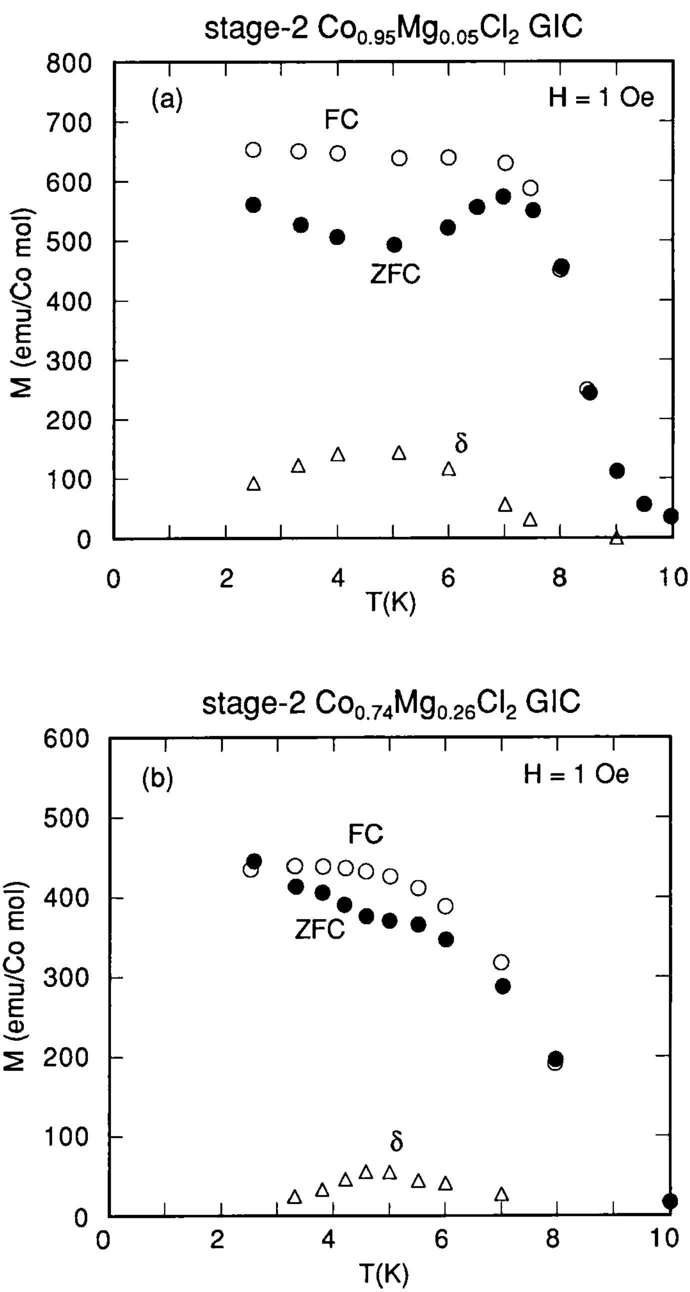


FIGURE 3 Low field magnetization for stage-2 $Co_cMg_{1-c}Cl_2$ GIC's with (a) c = 0.95, and (b) c = 0.74.

partly because the Co concentration of GIC's is usually larger than that of the intercalant. Here we also note that the susceptibility of site-diluted quasi-2D XY ferromagnet $K_2Cu_cZn_{1-c}F_4$ with c = 0.6 ($c_p$ = 0.59) is well described by the exact solution of the 1D Heisenberg ferromagnet with S = 1/2.[6]

The low field SQUID magnetization was measured for stage-2 $Co_cMg_{1-c}Cl_2$ GIC's with c = 1, 0.95, 0.88, and 0.74 at 1 Oe in the temperature range between 2 and 10 K. The temperature dependence of $M_{ZFC}$ and $M_{FC}$ is shown in Fig. 3 for (a) c = 0.95 and (b) c = 0.74. The difference between $M_{ZFC}$ and $M_{FC}$ denoted by $\delta$ is also shown in Fig. 3. For c = 0.95 $M_{ZFC}$ has a broad peak at $T_{max}$ (= 7 K). The magnetization $M_{FC}$ begins to deviate upward from $M_{ZFC}$ below $T_c$ (= 8.5 K), indicating the appearance of an irreversible effect below $T_c$. Note that there is no anomaly in $\delta$ around $T_{max}$. The temperature dependence of $M_{ZFC}$ and $M_{FC}$ for c = 0.88 is similar to that for c = 0.95. For c = 0.74, an irreversible effect still appears below 7.8 K but no broad peak of $M_{ZFC}$ is observed.

The irreversible effect may be explained by a cluster glass model:[4] The intercalate layers are formed of islands. Below $T_c$ the spins within each island are ferromagnetically aligned, forming a ferromagnetic cluster. The spin direction of these ferromagnetic clusters is frozen at low temperature because of frustrated inter-island interactions such as dipole-dipole interactions between islands in the same intercalate layer, and antiferromagnetic interplanar exchange interactions between islands in the different layers. When a part of $Co^{2+}$ ions is replaced by non-magnetic $Mg^{2+}$ ions, the ferromagnetically connected bonds between $Co^{2+}$ ions are disconnected. The destruction of 2D ferromagnetic spin order within each island for c < 0.74 leads to the disappearance of the irreversible effect.

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