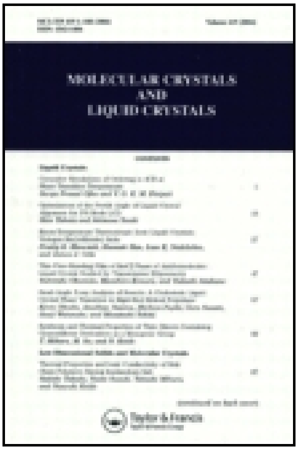

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MAGNETIC PROPERTIES OF GRAPHITE BIINTERCALATION COMPOUNDS

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Abstract The magnetic properties of $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBICs have been studied by using dc magnetic susceptibility and low and high field SQUID magnetization measurements. The effect of biintercalation on the magnetic properties is discussed in comparing the experimental results of $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBICs with those of stage-2 $Co_cMn_{1-c}Cl_2$ GICs.

INTRODUCTION

Magnetic graphite biintercalation compounds (GBICs) offer possibilities for the formation of superlattices with a stacking sequence of $GI_1GI_2GI_1GI_2$...along the c-axis, where two different intercalate layers (I_1 and I_2) alternate with a single graphite layer (G): I_1 = $Co_cNi_{1-c}Cl_2$ and $Co_cMn_{1-c}Cl_2$ ($0 \le c \le 1$) and I_2 = $FeCl_3$. These compounds provide not only challenges for exploring novel physical phenomena associated with the crossover from two-dimensional (2D) to three-dimensional (3D) behavior and associated with randomness in the 2D systems, but also opportunities for testing the existing fundamental theories of 2D physics. In the present study we have prepared $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBIC samples with well-defined c-axis stacking sequences. The magnetic properties of these compounds have been studied by dc magnetic susceptibility, and low and high field SQUID magnetization measurements. We report results on (i) the temperature dependence of dc magnetic susceptibility, (ii) the temperature dependence of zero-field cooled (ZFC) and field-cooled (FC) magnetization (H = 1 Oe), and (iii) the field dependence of magnetization ($0 \le H \le 1$ kOe). The magnetic properties of $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBICs are compared with those of stage-2 $Co_cMn_{1-c}Cl_2$ GIC.[1]

EXPERIMENT

Samples of $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBICs were prepared by a sequential intercalation method:[2] the intercalant $FeCl_3$ was intercalated into the empty graphite galleries of stage-2 $Co_cMn_{1-c}Cl_2$ GIC. A mixture of well-defined stage-2 $Co_cMn_{1-c}Cl_2$ GIC based on single-crystal kish graphite and single-crystal $FeCl_3$ inside pyrex glass tubing sealed in vacuum was kept at 330 °C for two weeks. The stacking sequence of these GBIC samples was checked by a (00L) x-ray scattering experiment. For example the c-axis repeat distance is d = 18.88 ± 0.02 Å for $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBIC with c = 0.6. The concentration of samples determined by electron microprobe measurements was consistent with that determined from weight uptake measurements. The experimental procedures of dc magnetic susceptibility and SQUID magnetization measurements are described in detail elsewhere.[3]

RESULT AND DISCUSSION

The temperature dependence of dc magnetic susceptibility for $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBICs with c = 1, 0.9, 0.8, 0.7, 0.6, and 0.25 was measured by the Faraday method (H = 2 kOe and H ⊥ c). The dc magnetic susceptibility of these compounds is found to obey the Curie-Weiss law above 130 K. Figure 1 shows the Co concentration dependence of the Curie-Weiss temperature Θ for stage-2 $Co_cMn_{1-c}Cl_2$ GICs and $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBICs. Here the prediction from the molecular field theory is denoted by a dotted line.[1] We find that the sign of Θ changes at c ≈ 0.2 for stage-2 $Co_cMn_{1-c}Cl_2$ GICs and c ≈ 0.7 for $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBICs. Ohhashi and Tsujikawa[4] have shown that Θ is negative for $FeCl_3$ GIC (Θ = - 8.2 ± 0.8 K for stage-1 and Θ = - 6.0 ± 1.0 K for stage-2), indicating an antiferromagnetic intraplanar interaction between Fe^{3+} ions in the $FeCl_3$

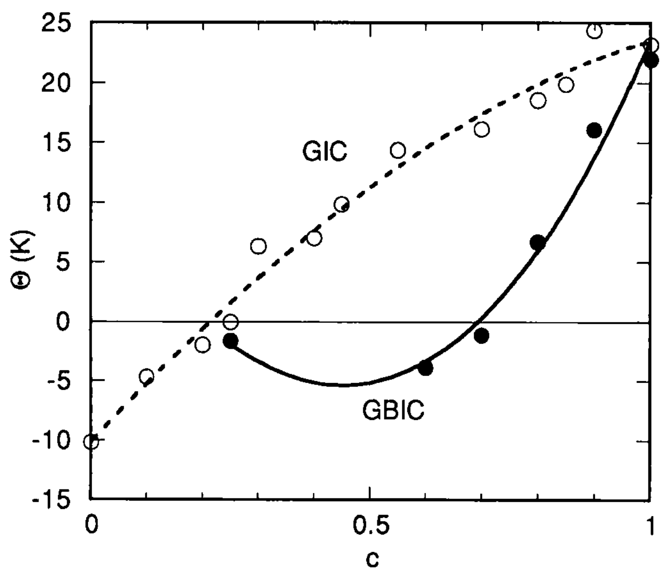

FIGURE 1 Concentration dependence of Θ for $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBICs (•) and stage-2 $Co_cMn_{1-c}Cl_2$ GICs (o). The solid line is a guide to the eye.

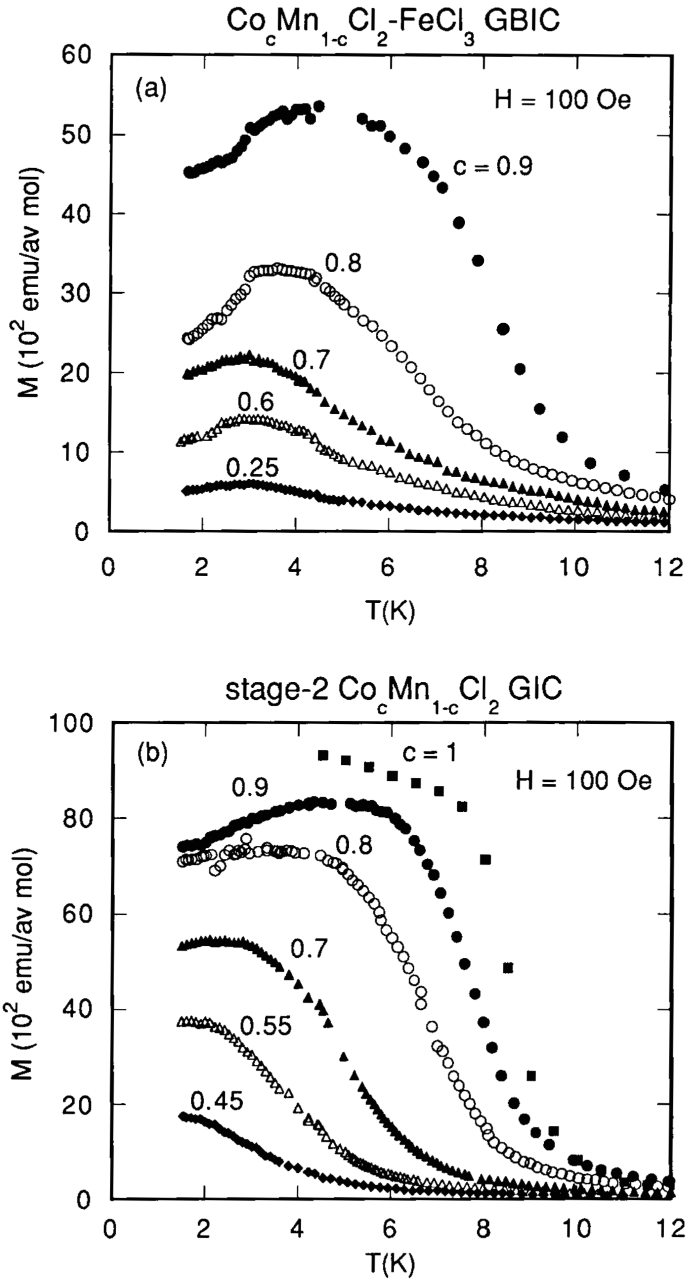

FIGURE 2 Temperature dependence of dc magnetic susceptibility for (a) $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBICs and (b) stage-2 $Co_cMn_{1-c}Cl_2$ GICs (Ref.1). H = 100 Oe. H $\perp$ c.

layer. The value of Θ for $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBICs ($0.6 \leq c \leq 0.8$) is much smaller that for stage-2 $Co_cMn_{1-c}Cl_2$ GICs with the same c because of $FeCl_3$ layers in GBICs. Figure 2 shows the temperature dependence of dc magnetization M for $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBICs and stage-2 $Co_cMn_{1-c}Cl_2$ GICs which was measured by the Faraday method (H = 100 Oe and $H \perp c$). We find that (i) a broad peak appears in the temperature range between 3 K and 4 K for $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBICs with c = 0.8, 0.7, 0.6 and 0.25, and that (ii) the magnetization of GBICs ($0.25 \leq c \leq 0.7$) is much smaller than that of GICs with the same c. Simon et al.[5] have shown from magnetic neutron scattering studies that the stage-1 $FeCl_3$ GIC undergoes an antiferromagnetic phase transition at T_N = 3.8 K but that the stage-2 $FeCl_3$ GIC does not show any phase transition down to 1.5 K. The 2D short range spin correlation develops below 20 K in both stage-1 and stage-2. The broad peak observed in GBICs may indicate an appearance of antiferromagnetic long range order in the $FeCl_3$ layer below 4 K.

Figure 3 shows the temperature dependence of zero-field cooled magnetization (M_{ZFC}), field cooled magnetization (M_{FC}), and the difference δ (= M_{FC} - M_{ZFC}) for $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBICs with c = 1 and 0.7. The magnetization M_{ZFC} for c = 1 has a broad peak, while M_{ZFC} for c = 0.7 reduces to zero in two steps as the temperature increases. We find that the irreversible effect of magnetization appears in GBICs for $0.45 \leq c \leq 1$ and in GICs for $0.8 \leq c \leq 1$ because of the spin frustration effect.[3] The spin frustration effect in GBICs may arise from both competing interplanar interactions between $Co_cMn_{1-c}Cl_2$ layer and $FeCl_3$ layer and competing intraplanar interactions within $Co_cMn_{1-c}Cl_2$ layer, and may be enhanced near $c \approx 0.5$ corresponding to a percolation threshold of the triangular lattice, where M_{FC} of GBICs is comparable to the magnetization of stage-2 $FeCl_3$ GIC.

Figure 4 shows the field dependence of SQUID magnetization M for $CoCl_2$-$FeCl_3$ GBIC at T = 2.5 K and 6 K when H was increased from 1 Oe to 1 kOe. The following procedure was followed before the measurement: (i) the sample was cooled from 300 K to 2.5 K at H = 0 in five minutes, (ii) H was increased from 0 to 50 kOe at 2.5 K (M = 1.54×10^4 emu/av mol at T = 2.5 K and H = 50 kOe), and (iii) H was decreased from 50 kOe to 1 Oe. We find that the value of M at 2.5 K is larger than that at 6 K for $H<H_c$ ($\approx$ 20 Oe) and is almost the same for $H>H_c$, where H_c corresponds to the spin flop field for the antiferromagnetic phase of stage-2 $CoCl_2$ GIC where the 2D ferromagnetic layers are antiferromagnetically stacked along the c-axis.[6] This result indicates that the antiferromagnetic interplanar interaction between adjacent $CoCl_2$ layers in GBIC is greatly reduced by the appearance of antiferromagnetic long range order of Fe^{3+} within the $FeCl_3$ layer below 4 K.

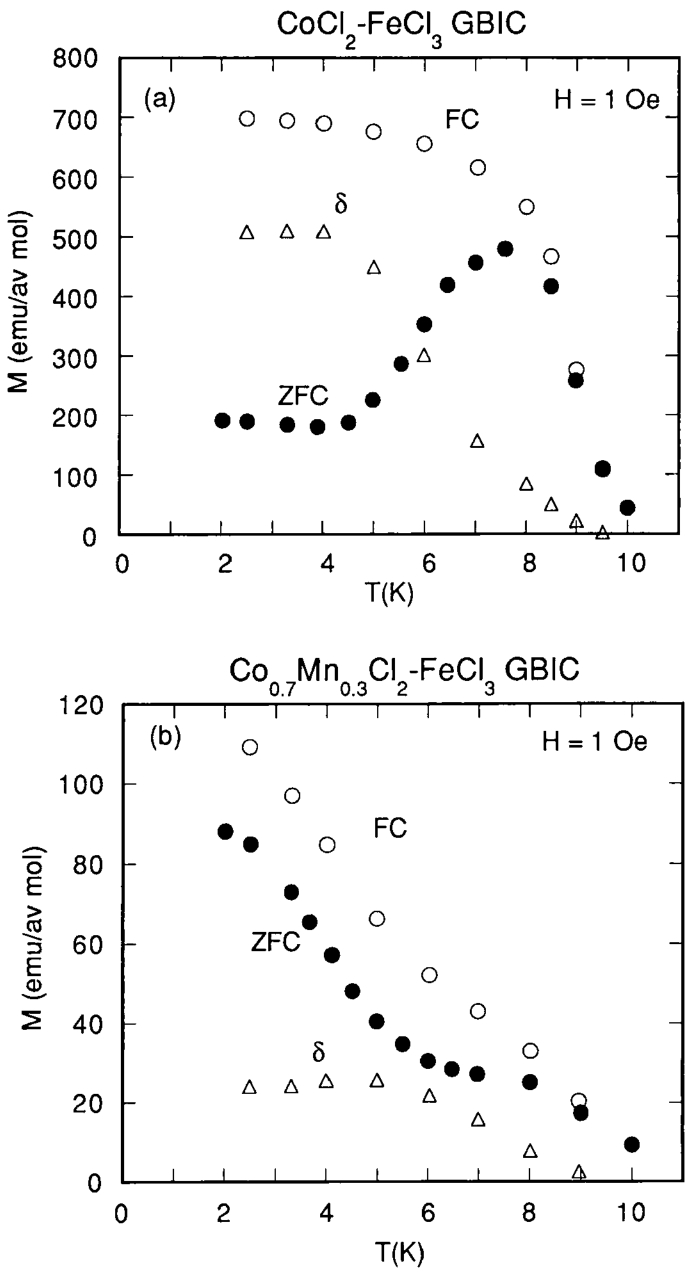

FIGURE 3 Temperature variation of M_{FC} (o), M_{ZFC} (•) and δ (= M_{FC} - M_{ZFC}) (Δ) for $Co_cMn_{1-c}Cl_2$-$FeCl_3$ GBIC. H = 1 Oe. H ⊥ c. (a) c = 1. (b) c = 0.7.

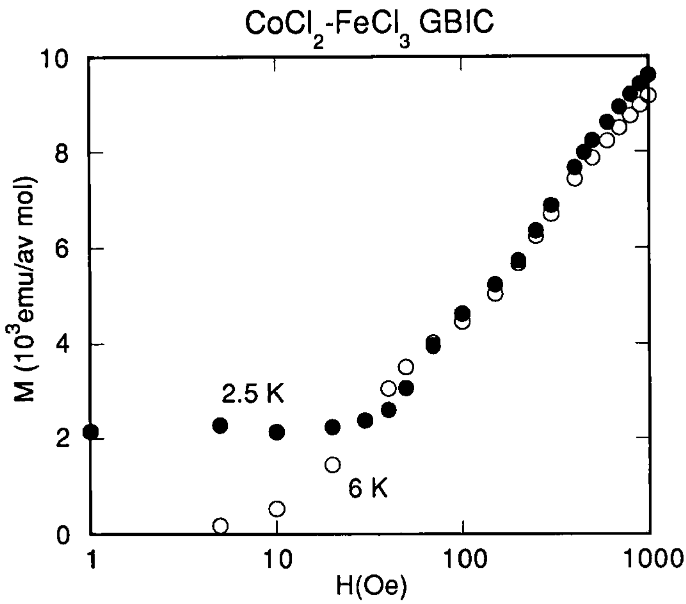

FIGURE 4 Field dependence of magnetization for $CoCl_2$-$FeCl_3$ GBIC. H ⊥ c. T = 2.5 K (•) and 6 K (o).

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