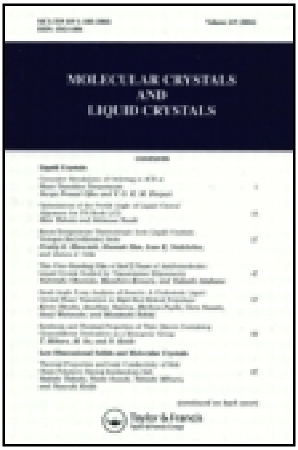

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Itsuko S. Suzuki, Masatsugu Suzuki, Hirohiko Sato & Toshiaki Enoki (2000): Successive Magnetic Phase Transitions of $Cu_cCo_{1-c}Cl_2$-$FeCl_3$ Graphite bi-intercalation Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 107-112

To link to this article: http://dx.doi.org/10.1080/10587250008025451

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 107-112
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Successive Magnetic Phase Transitions of $Cu_cCo_{1-c}Cl_2$-$FeCl_3$ Graphite bi-intercalation Compounds

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$Cu_cCo_{1-c}Cl_2$-$FeCl_3$ graphite bi-intercalation compounds (GBIC's) have a c-axis stacking sequence of -G-I_1-G-I_2-G-I_1-G-I_2-G- (G = graphite layer, $I_1 = Cu_cCo_{1-c}Cl_2$ layer, and $I_2 = FeCl_3$ layer). These compounds undergo magnetic phase transitions at T_h, T_{cu}, T_{cl}, T_{SG}, and T_{RSG} ($T_h > T_{cl} > T_{RSG} \approx T_{SG}$), depending on the Cu concentration. The phase transition at T_h is related to a helical spin order. The phase transitions at T_{cu} and T_{cl} are associated with a spin order of $Cu_cCo_{1-c}Cl_2$ layers. The re-entrant spin glass phase below T_{RSG} for $c \leq 0.4$ and the spin glass phase below T_{SG} for $c \geq 0.5$ are due to the spin frustration effect occurring in $FeCl_3$ layers. The nature of these phases has been studied using SQUID DC magnetization and SQUID AC magnetic susceptibility.

Keywords: helical spin order; spin glass; reentrant spin glass; random field effect; magnetic phase transition; SQUID AC susceptibility

INTRODUCTION

Magnetic graphite bi-intercalation compounds (GBIC's) offer possibilities for the formation of superlattices where two different intercalate layers alternate with a single graphite layer. The magnetic phase transitions of magnetic GBIC's have received attention, partly because of a helical spin order along the c axis [1, 2]. In this paper we study the magnetic phase transition of $Cu_cCo_{1-c}Cl_2$-$FeCl_3$ GBIC's ($0 \leq c \leq 1$) (hereafter referred as GBIC's) by SQUID DC magnetization and SQUID AC magnetic susceptibility. In these compounds, the $Cu_cCo_{1-c}Cl_2$

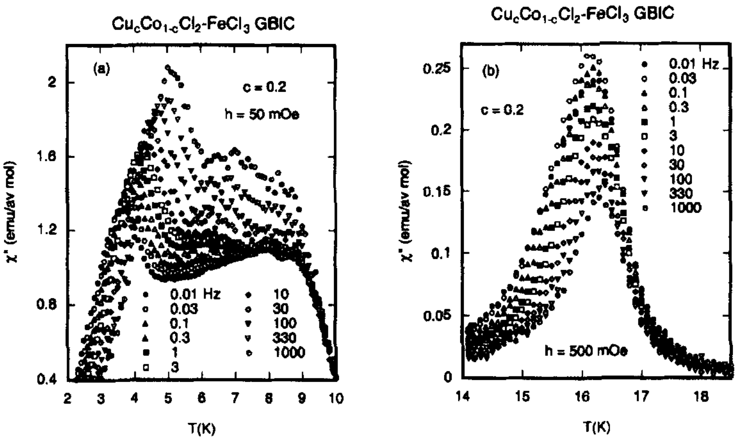
layer is formed with two different magnetic ions which are randomly distributed on the triangular lattice. The character of the average intraplanar exchange interaction in $Cu_cCo_{1-c}Cl_2$ layers changes from ferromagnetic to antiferromagnetic with increasing the Cu concentration c, while the intraplanar exchange interaction in $FeCl_3$ layers remains antiferromagnetic. The long-range spin order in the $Cu_cCo_{1-c}Cl_2$ layers is coupled with that in the $FeCl_3$ layers through an interplanar exchange interaction, leading to the helical spin order in GBIC's. The magnetic phase transitions of GBIC's are compared with those of stage-2 $Cu_cCo_{1-c}Cl_2$ GIC's [3, 4] and stage-2 $FeCl_3$ GIC [5].

EXPERIMENTAL PROCEDURE

The DC magnetization and AC susceptibility of GBIC's with c = 0, 0.1, 0.2, 0.4, 0.5, 0.7, 0.93, and 1 were measured using a SQUID magnetometer (Quantum Design, MPMS XL-5) with an ultra low field capability option. First, a remanent magnetic field was reduced to zero field (exactly less than 3 mOe) at 298 K for both DC magnetization and AC susceptibility measurements. Samples were then cooled from 298 K to 1.9 K in a zero field. (i) The measurements of the zero field cooled magnetization (M_{ZFC}) and the field cooled magnetization (M_{FC}). After an external magnetic field H (= 1 Oe) was applied perpendicular to the c axis at 1.9 K, M_{ZFC} was measured with increasing temperature (T) from 1.9 to 25 K, and subsequently M_{FC} was measured with decreasing T from 25 to 1.9 K. (ii) The measurement of M_{FC} in the presence of H perpendicular to the c axis. After annealing the sample for 10 minutes at 30 K in the presence of H, M_{FC} for each H was measured with decreasing T from 20 K to 1.9 K. (iii) The AC susceptibility measurement. The frequency (f) dependence of the dispersion (χ') and absorption (χ'') was measured at fixed T between 1.9 K to 18 K. After the measurement of frequency scan was completed for each T, the temperature was increased by 0.1 K. The amplitude of the ac magnetic field (h) is 50 mOe or 500 mOe and the frequency (f) range is between 0.01 Hz and 1 kHz.

RESULT

Figures 1(a) and (b) show the T dependence of χ'' for GBIC with c = 0.2. The absorption χ'' shows a small peak at T_h (=16.2 K), a very broad peak at T_{cu} (≈



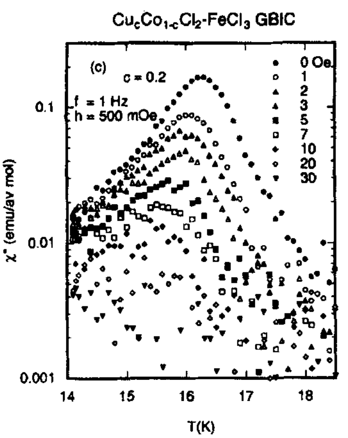


FIGURE 1 (a) and (b) χ" vs T for GBIC with c = 0.2 at various f. H = 0. h⊥c. (c) χ" vs T for c = 0.2 at various H (⊥c). h⊥c. f = 1 Hz.

7.9 K), a small peak at T_{cl} (≈ 6.2 - 6.4 K), and a sharp peak at T_{RSG}. The peak at T_{RSG} shifts to the high temperature side with increasing f. Figure 1(c) shows the T dependence of χ" for c = 0.2 in the presence of H perpendicular to the c axis. The peak temperature T_h shifts to the low temperature side with increasing H, while the peak height drastically decreases and disappears above 7 Oe. This result suggests that the resultant interplanar exchange interaction is antiferromagnetic and weak.

Figure 2 shows the T dependence of M_{FC} for c = 0.2 in the presence of H (≥3 Oe) perpendicular to the c axis. The increase of M_{FC} with decreasing T is made in two steps: it starts to increase at T_h and drastically increases below 10 K, and

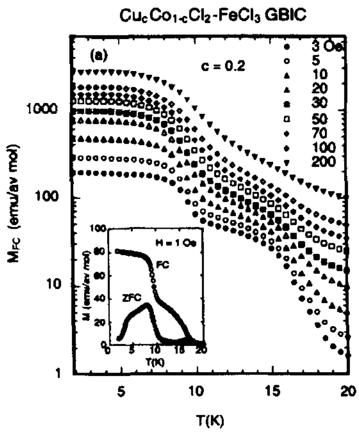


FIGURE 2 (a) H dependence of M_{FC} for c = 0.2 at various T. H⊥c. The T dependence of M_{FC} and M_{ZFC} for c = 0.2 is shown in the inset. H = 1 Oe.

reaches a saturated value below T_{cl}. The inset of Fig.2 shows the T dependence of M_{ZFC} and M_{FC} for c = 0.2, where H (= 1 Oe) is applied along the c plane. M_{ZFC} has a small peak at T_h = 16.0 K, a large peak at T_{cu} = 8.1 K, and a shoulder around T_{RSG} = 3.7 - 4.5 K. The deviation of M_{ZFC} from M_{FC} occurs below 21.3 K, indicating a irreversible effect of magnetization.

Figures 3(a) and (b) show the T dependence of χ" for GBIC's with c = 0.4 and c = 0.5, respectively. For c = 0.4 χ" has a very broad peak at T_{cu} (= 6.9 K) and a sharp peak at T_{RSG}. The peak at T_{RSG} shifts to the high temperature side with increasing f. No anomaly in χ" is observed around 16 K. For c = 0.5, χ" has a single peak at a temperature defined as T_{SG}, shifting to the high temperature side with increasing f.

DISCUSSION

Figure 4 shows the magnetic phase diagram for GBIC's. The critical temperatures T_h, T_{cu}, T_{cl}, and T_{RSG}, and T_{SG} are defined as temperatures at which χ" at f = 0.1 Hz has peaks. Our result is summarized as follows: (i) T_h ($\approx$ 16 K) and T_{cl} are observed only for $0 \leq c \leq 0.2$, (ii) T_{cu} and T_{cl} decrease with increasing Cu concentration and tend to reduce to zero around c = 0.5, (iii) T_{RSG} for $c \leq 0.4$ and T_{SG} for $c \geq 0.5$ are almost independent of Cu concentration. A helical spin order occurs below T_h. Below T_{cu} a two-dimensional (2D) ferromagnetic long range order appears in each $Cu_cCo_{1-c}Cl_2$ layer. Below T_{cl} these 2D ferromagnetic $Cu_cCo_{1-c}Cl_2$ layers are antiferromagnetically stacked along the c axis, forming a 3D antiferromagnetic phase. The spin glass phase occurs below T_{RSG} or T_{SG} in each $FeCl_3$ layer.

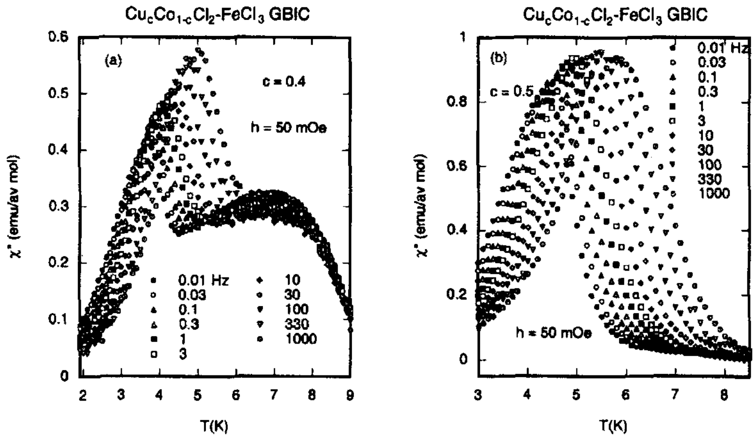


FIGURE 3 χ" vs T for (a) c = 0.4 and (b) c = 0.5 at various f. H = 0. h⊥c.

In the inset of Fig.4 we show the f dependence of T_{RSG} for GBIC's with c = 0.2 and 0.4, T_{SG} for GBIC's with c = 0.5 and 1, T_{RSG} for stage-2 $Cu_cCo_{1-c}Cl_2$ GIC with c = 0.8 [4], and T_{SG} for stage-2 $FeCl_3$ GIC [5]. The f dependence of T_{SG} for GBIC's with c = 0.5 and 1 is almost the same as that of T_{SG} for stage-2 $FeCl_3$ GIC. This result suggests that the SG behavior occurs in the $FeCl_3$ layer for GBIC's with $0.5 \leq c \leq 1$. Note that the value of T_{RSG} for GBIC's with c = 0.2 and 0.4 is lower than that of stage-2 $FeCl_3$ GIC at the same frequency, but is rather close to that of T_{RSG} for stage-2 $Cu_cCo_{1-c}Cl_2$ GIC with c = 0.8. In GBIC's

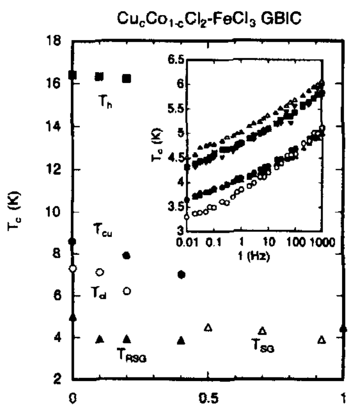


FIGURE 4 Magnetic phase diagram of GBIC's. T_h, T_{cu}, T_{cl}, T_{RSG}, and T_{SG} correspond to the peak temperatures in χ" vs T at f = 0.1 Hz. The inset shows the f dependence of T_{SG} and T_{RSG} for GBIC's with c = 0.2 (●), 0.4 (▲), 0.5 (■), and 1 (▼), stage-2 $Cu_cCo_{1-c}Cl_2$ GIC with c = 0.8 (○), and stage-2 $FeCl_3$ GIC (Δ).

with c = 0.2 and 0.4, the RSG behavior occurring inside the $FeCl_3$ layers may be modified by the random field effect arising from adjacent $Cu_cCo_{1-c}Cl_2$ layers. Because of the ferromagnetic spin order in $Cu_cCo_{1-c}Cl_2$ layers, the uniform interplanar exchange field may generate a random staggered magnetic field in each Fe^{3+} (Fe^{2+}) spin of the $FeCl_3$ layers. As shown in Figs.1(a) and 2(a), χ'' for GBIC's with c = 0.2 and 0.4 shows a plateau-like form between T_{cu} and T_{cl}, indicating that the phase transitions at T_{cu} and T_{cl} are partially destroyed by random field effects arising from the adjacent $FeCl_3$ layers through competing interplanar exchange interactions.

The phase transition at T_h is observed only in the system ($0 \leq c \leq 0.2$) where T_{cu} or T_{cl} are also observed. This result indicates that the helical spin order at T_h arises from competing interplanar exchange interactions. Because of weak interactions the phase transition at T_h is destroyed by a very weak magnetic field H_t (< 7 Oe for c = 0.2) along the c plane. For simplicity we consider the model of $CoCl_2$-$FeCl_3$ GBIC which is regarded as a 1D spin system: Co^{2+} and Fe^{3+} spins are alternatively arranged at equal distances along the c axis. A helical spin configuration with $\cos\theta = -J_1'/2J_2'$ is realized under the condition of $J_2'<0$ and $2|J_2'|>|J_1'|$, where θ is the rotation angle between spins in the adjacent layers, J_1' and J_2' are effective interplanar exchange interactions defined as $J_1' = J'_{Co-Fe}$ and $J_2' = J'_{Co-Co} + J'_{Fe-Fe}$. In the previous paper [2] we have estimated $J_1' = 7.0 \times 10^{-4}$ K and $J_2' = -1.66 \times 10^{-3}$ K for $CoCl_2$-$FeCl_3$ GBIC, which satisfy the above condition for the helical spin structure. Using these values of J_1' and J_2', θ is calculated as 78°, which is close to an angle (72°) of helical spin structure with periodicity of 10 magnetic layers.

Acknowledgment

We thank A.W. Moore for providing HOPG and H. Suematsu for providing single crystal of kish graphite. This work was partly supported by NSF DMR 9201656 and 9625829.

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