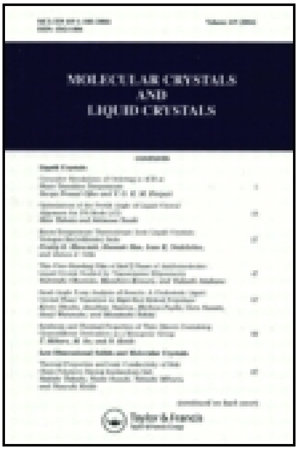

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

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Version of record first published: 23 Oct 2006.

To cite this article: S. Flandrois, P. Biensan, J. M. Louis, G. Chouteau, T. Roisnel, G. Andre & F. Bouree (1994): Magnetic Order in A Bi-Intercalation Compound, Graphite - $CrCl_3$ - $CoCl_2$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 245:1, 105-110

To link to this article: http://dx.doi.org/10.1080/10587259408051673

Mol. Cryst. Liq. Cryst. 1994, Vol. 245, pp. 105–110
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Printed in the United States of America

MAGNETIC ORDER IN A BI-INTERCALATION COMPOUND, GRAPHITE - $CrCl_3$ - $CoCl_2$

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Abstract $CoCl_2$ has been intercalated in a stage-3 $CrCl_3$-GIC to give a pseudo stage-1 GBIC with intercalate stacking sequence -A-B-B-A-, where A = $CrCl_3$ and B = $CoCl_2$. The magnetic properties have been studied by SQUID magnetometry and a.c. susceptibility experiments, and the magnetic structure investigated by neutron diffraction. The data provide evidence for an antiferromagnetic order along the C-axis below 11 K and a helical magnetic phase between 11 and 15 K.

INTRODUCTION

Graphite intercalation compounds offer an opportunity to synthesize novel magnetic compounds with various intraplanar or interplanar arrangements. Systems of special interest are those known as graphite bi-intercalation compounds (GBIC) containing a regular sequence of two kinds of intercalated layers[1] which can be both magnetic or one magnetic and the other non-magnetic. While the latter case allows greater separation between the magnetic planes relative to that in the associated binary GIC's, the former offers the possibility of studying the interaction between the two types of magnetic guests.

$CrCl_3$ is particularly convenient for this purpose. It undergoes a magnetic phase transition below T = 16.8 K to an antiferromagnetic state, with the spins lying in the basal planes and forming ferromagnetic layers which alternate in direction along the C-axis[2]. It can be intercalated into graphite to give well-defined stage-3 compounds and the intercalation temperature (800°C) is such that the compounds are stable up to 650°C at least. Thus, it can be sequentially intercalated with another metal chloride to give a GBIC. In this paper, we investigate the magnetic properties and especially the magnetic ordering at low temperature for a pseudo stage-1 $CrCl_3$-$CoCl_2$-GBIC.

EXPERIMENTAL

The stage-3 $CrCl_3$-GIC samples were prepared from single crystals of Madagascar natural graphite by vapor reaction of $CrCl_3$ in a chlorine atmosphere ($T = 800°C$, $P_{Cl} = 4$ atm). Then, the stage-3 $CrCl_3$-GIC was heated in the presence of $CoCl_2$ under the same reaction conditions that are required for the preparation of stage-1 $CoCl_2$-GIC ($T = 600°C$, $P_{Cl} = 3$ atm). The so produced materials are pseudo-stage-1 GBIC with intercalate stacking sequence A/B/B/A where A = $CrCl_3$, B = $CoCl_2$ and / = graphite layer. The synthesized samples were structurally characterized by (00 l) and precession X-ray diffraction techniques, revealing that, after intercalation, both the chloride layers and the graphite layers have kept the same crystallographic aspects as those found in the corresponding pristine materials. The composition deduced from analyses is $C_{21}CrCl_3(CoCl_2)_2$.

The magnetic properties were studied by SQUID magnetometry and a.c. susceptibility experiments (f = 127 Hz, a.c. field ~ 1 Oe).

Neutron diffraction data (λ = 2.426 Å) were recorded at eleven different temperatures from 1.5 to 20.6 K on the G4-1 two-axis spectrometer of the Laboratoire Léon Brillouin.

RESULTS AND DISCUSSION

Figure 1 shows the results of low-field (2.1 Oe) SQUID magnetometry measurements performed with the field applied perpendicular and parallel to the layers. Below 15 K a large hysteresis behavior is exhibited between the zero-field-cooled (ZFC) and field-cooled (FC) magnetizations, as in the case of the binary GIC's. The FC curve with H//c exhibits two peaks at 15 K and 10.5 K, with a shoulder at about 9 K. When H//a, the peak at T = 15 K has disappeared. These results are corroborated by a.c. susceptibility measurements (Figure 2).

Figure 3 shows the neutron diffraction patterns obtained at 20.6 K and 1.5 K on a powder sample. The 20.6 K pattern is nuclear only and characteristic of a pseudo stage-1 GIC : all the Bragg peaks can be indexed either as (00 l) reflections of the GBIC (with l = 3n) or as (hk0) reflections of the intercalated chlorides. The selection rule for the (00l) peaks (l = 3n) can be accounted for by a nuclear structure factor F_N calculation. Taking a $CrCl_3$ plane, as the origin of the C-axis, F_N can be written as :

$$F_N = b_{CrCl_3} + 2\, b_{CoCl_2} \cos(2\pi l/3) + 7\, b_C \left[(-1)^l + 2\cos(2\pi l/6)\right]$$

where b_i is the coherent scattering length. The third term is the most important contribution and is maximum for l = 3 n

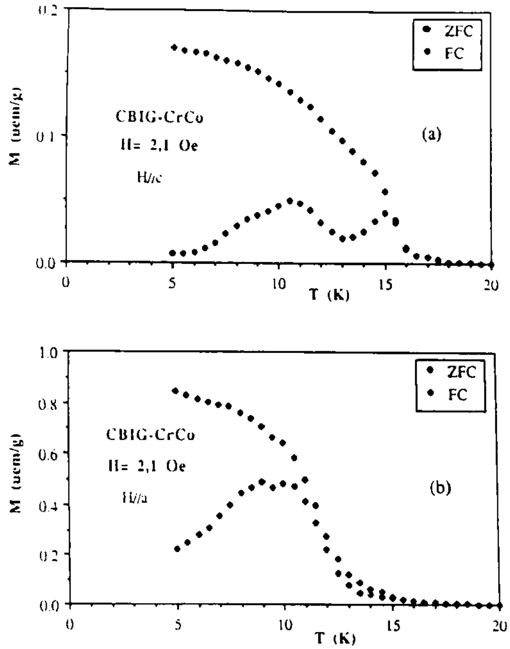

Figure 1 : The Z.F.C. and F.C. magnetization measured with the field applied (a) perpendicular and (b) parallel to the layers.

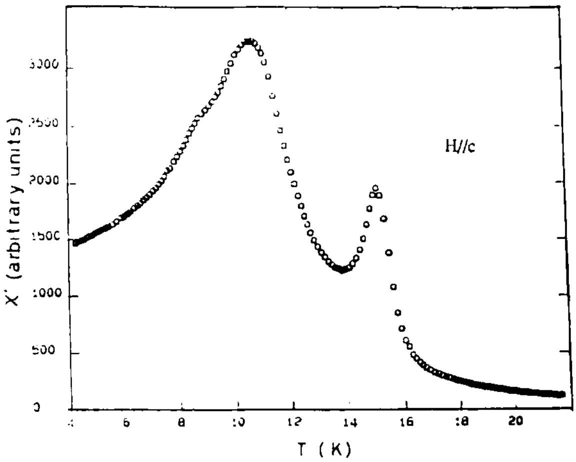

Figure 2 : The temperature dependence of the a.c. susceptibility parallel to the C-axis

($F_N = b_{CrCl_3} + 2\ b_{CoCl_2} + 2\ l\ b_C\ (-1)^{l/3}$ for $l = 3n$ and $F_N = b_{CrCl_3} - b_{CoCl_2}$ for $l \neq 3n$). As the coherent scattering lengths of $CrCl_3$ and $CoCl_2$ are almost equal, this GBIC with a period I_C presents the same neutron diffraction pattern as a stage-1 compound of period $I_C/3$.

At 1.5 K, some superstructure peaks appear which can be attributed to magnetic signals. Due to their weak intensity, the analysis was realized after substracting the nuclear contribution (20.6 K pattern). The peaks appearing at $2\ \theta = 7.5°$, $22.5°$ and $38°$ can be indexed, in a magnetic unit cell of period $I_{CM} = 2I_C$, as (003), (009) and (0015) reflections, respectively. The intensities of these reflexions decrease with increasing temperature and become zero between 10 and 11 K (Figure 4).

The determination of the magnetic order along the c-axis results from a magnetic structure factor calculation, assuming (i) colinear magnetic structure, with the magnetic moments perpendicular to the c-axis (ferromagnetic planes), (ii) identical magnetic moments on Cr^{3+} ($S = 3/2$) and Co^{2+} ($S = 3/2$) ions, (iii) identical in-plane concentrations in the Cr and Co layers.

The magnetic structure factor for (00l) reflections can be written as : $F_M(00l) = M \sum_i \varepsilon_i \exp\left(2i\pi \vec{k}.\vec{r}_i\right)$ with $\varepsilon_i = \pm 1$ (Figure 5). The $F_M.F_M^*$ quantity, directly proportional to the observed magnetic intensities, then becomes :

$F_M.F_M^* = 2M^2\ [3 + C_1 \cos(\pi l/3) + C_2 \cos(2\pi l/3) + C_3 \cos(\pi l)]$ with

$$C_1 = \varepsilon_0 + \varepsilon_4 + \varepsilon_0\varepsilon_1 + \varepsilon_1\varepsilon_2 + \varepsilon_2\varepsilon_3 + \varepsilon_3\varepsilon_4$$

$$C_2 = \varepsilon_1 + \varepsilon_3 + \varepsilon_0\varepsilon_4 + \varepsilon_1\varepsilon_3 + \varepsilon_2\varepsilon_4 + \varepsilon_0\varepsilon_2$$

$$C_3 = \varepsilon_2 + \varepsilon_0\varepsilon_3 + \varepsilon_1\varepsilon_4$$

The observed selection rule $l = 6n \pm 3$ leads to the unique solution : $\varepsilon_0 = \varepsilon_2 = \varepsilon_4 = -1$ and $\varepsilon_1 = \varepsilon_3 = +1$, which means an antiferromagnetic order along the C-axis.

Magnetic contributions are also observed on the (100) and (110) reflections of chromium chloride and (100) of cobalt chloride. These peaks present a Warren-type profile characteristic of a 2-D order, and this magnetic contribution is the signature of long-range ferromagnetic order inside Cr^{3+} and Co^{2+} planes. The temperature where this magnetic contribution disappears can also be estimated to be around 11 K.

It can also be noted that the FWHM of the (00l) magnetic peaks is larger than the instrumental resolution, which indicates an imperfect magnetic long range order. From the Scherrer formula, the magnetic coherence length along the c-axis can be estimated to be roughly 110 Å, i.e. about 12 magnetic layers, in agreement with values previously determined for stage-1 $CoCl_2$-GICs[3,4].

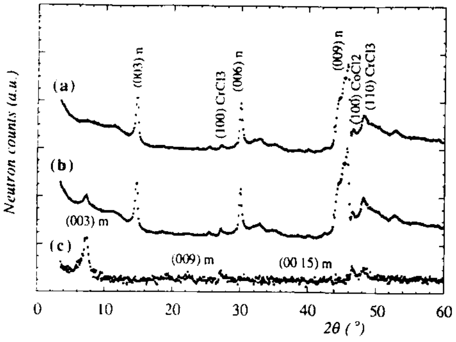

Figure 3 : Neutron diffraction patterns (a) at T = 20.6 K, (b) at T = 1.5 K, (c) difference (x4)

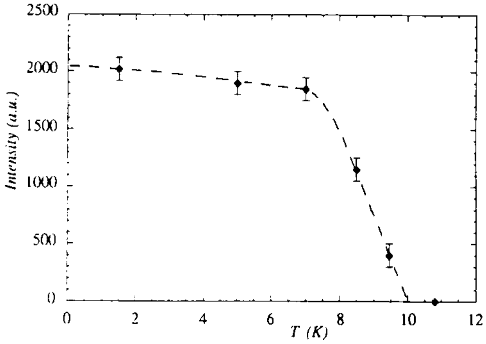

Figure 4 : The temperature dependence of the intensity of the magnetic peak at 2θ = 7.5°

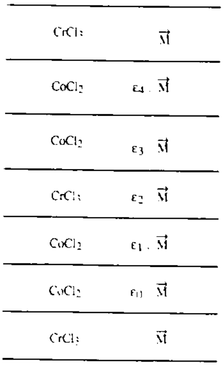

Figure 5 : The magnetic unit cell : magnetic moment configuration (lines represent graphene)

Between 10.8 K and 15.6 K only one weak magnetic peak can be observed at $2\theta = 6°$, which could be indexed as a magnetic satellite of the (001) nuclear Bragg peak with a modulation propagation vector $\vec{k} = (0,0,1/5)$. In such a commensurate magnetic unit cell ($I_{CM} = 5I_C$), this peak is indexed as $(006)_M$. With the assumption of an helimagnetic structure (rotation angle = $2\pi/5$), a magnetic structure factor calculation shows that the only existing $(00l)_M$ peaks correspond to $l_M = 5n \pm 1$ and have the following positions and intensities :

l_M	(h k l) nuclear cell	2 θ (°)	I_M (a.u.)
1	$(000)^{\pm}$	0.99	1000
4	$(001)^{-}$	3.97	62
6	$(001)^{+}$	5.96	27
9	$(002)^{-}$	8.94	12
11	$(002)^{+}$	10.94	8

In such a situation, the (001) peak cannot be experimentally observed, due to its low 2θ angular position and the (004) peak can blend into the small angle magnetic diffuse scattering.

Thus, the susceptibility peak at 15 K could be the signature of the appearance of an helical magnetic order, which in turn is transformed at 11 K into an antiferromagnetic ordering. It is worth noticing that the helical magnetic structure is in agreement with the magnetic susceptibility anisotropy. The ratio of the susceptibilities parallel and perpendicular to the helical axis is known[5] to be related with the rotation angle of the magnetic moments. We found $\chi_c/\chi_a = 3.6$ at 15 K, after correction for demagnetizing effects, which gives an angle of 69°, in good agreement with the value of 72° deduced from neutron diffraction.

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