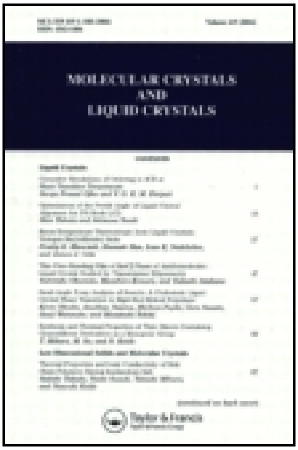

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# Magnetic Properties of Metal Halides-Graphite Intercalation Compounds Under Pressure

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# MAGNETIC PROPERTIES OF METAL HALIDES-GRAPHITE INTERCALATION COMPOUNDS UNDER PRESSURE

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Abstract Magnetization measurements under pressure of 0-10 kbar have been carried out on GIC's with $CoCl_2$ (stage 1), $NiCl_2$ (stage 2), $MnBr_2$ (stage 3), $CrCl_3$ (stage 3) and biintercalated $CrCl_3$-$CoCl_2$ (pseudo stage 1). For the three former ones, the ordering temperature $T_c$ increases with increasing pressure in agreement with the smaller interlayer distance and the corresponding J' increase. However, for GIC's containing $CrCl_3$, an unexpected decrease of $T_c$ is observed.

## INTRODUCTION

Intercalation of magnetic species into graphite gives interesting systems to study the relationship between dimensionality, magnetism and related phase-transition behavior[1,2]. With this class of materials, it is possible to vary the lattice dimensionality by changing the number of carbon layers which separate two successive magnetic layers (the stage of the compound). A great number of magnetic halides (mainly chlorides) have been intercalated into graphite for this purpose. The studies of magnetic properties by ESR or static magnetism show the increase in 2-D character by intercalation. Generally, a 3-D magnetic order appears at low temperature, at a value $T_c$ much smaller than the ordering temperature of the pristine halide, but which is almost stage-independent.

Another way of changing the interlayer magnetic interaction is applying pressure. Studies of GIC's under pressure have been mainly devoted to transport properties and structural modifications[3]. Only one recent paper[4] is dealing with the effect of pressure on the magnetic properties of graphite-$CoCl_2$ compounds, measured in a.c. field. The results show a shift of the 3-D antiferromagnetic ordering temperature to a higher temperature with increasing pressure, in agreement with the increase of the antiferromagnetic interlayer coupling J'. We have performed similar measurements in static field and have extended them to other intercalation compounds of graphite with antiferromagnetic halides.

## EXPERIMENTAL

Intercalation compounds of graphite with $CoCl_2$ (stage 1), $NiCl_2$ (stage 2) and $CrCl_3$ (stage 3) have been synthesized in the usual way by heating a mixture of powdered graphite and anhydrous chloride in chlorine atmosphere. For the preparation of the bi-intercalation compound[5] graphite-$CrCl_3$-$CoCl_2$ (pseudo stage 1), the synthesized stage 3 $CrCl_3$ GIC (in which two graphite interlayer galleries out of three remain unoccupied) was used as a precursor and, hence, was subsequently fully intercalated with $CoCl_2$. The compound graphite-$MnBr_2$ (stage 3) has been prepared[6] from stage 3 graphite-$CdBr_2$ by a displacement reaction $MnBr_2 \rightarrow CdBr_2$. All the synthesized samples were structurally characterized by (00 l) and precession X-ray diffraction techniques.

The magnetization measurements were carried out using a SQUID magnetometer (SHE Corp.) and a Be-Cu clamp type pressure cell allowing measurements to be performed up to 10 kbar. Pressure is applied at room temperature. The pressure loss between 300 K and 4 K is about 30 % and the pressure inhormogeneity is of the order of 0.5 kbar.

## RESULTS AND DISCUSSION

Figure 1 gives the in-field-cooled magnetization for a sample of stage 1 graphite-$CoCl_2$, measured in an applied magnetic field of 5.9 Oe at ambient pressure, 4.7 kbar and 9.3 kbar. Under pressure the curves are shifted to higher temperature. Taking the inflexion point of the curves as the transition temperature $T_c$ from the paramagnetic phase at high temperature to the antiferromagnetic phase at low temperature, $T_c$ changes from 9.7 K at ambient pressure to about 10.3 K at 9.3 kbar. At first glance, the pressure dependence of $T_c$ appears linear : $T_c(P) = T_c(0)\ (1 + \alpha P)$. The value of $\alpha = 6.6 \times 10^{-3}$ $kbar^{-1}$ is in good agreement with the results of Nicholls et al[4].

In the same way, stage 2 $NiCl_2$-graphite compounds (figure 2) and stage 3 $MnBr_2$-graphite compounds (figure 3) exhibit $T_c$ shifts to higher temperature with increasing pressure, with $\alpha$ values of about $2.6 \times 10^{-3}$ $kbar^{-1}$ and $6.1 \times 10^{-3}$ $kbar^{-1}$, respectively. If the compressibility of these compounds is assumed to be due mainly to the compressibility along the c-axis, the $T_c$ increase must result from the decrease with pressure of the interlayer distance and the correlative increase of the magnetic interlayer coupling J'.

On the other hand, in the case of the stage 3 $CrCl_3$-graphite compound (figure 4) and $CrCl_3$-$CoCl_2$-graphite biintercalation compound (figure 5), an unexpected decrease

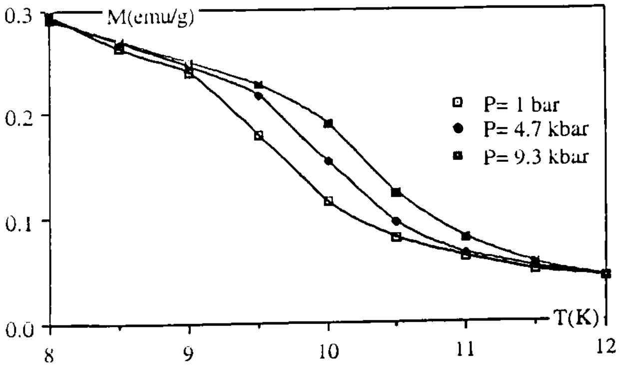

Figure 1 Magnetization of stage 1 $CoCl_2$ GIC under pressure (H=5.9 Oe)

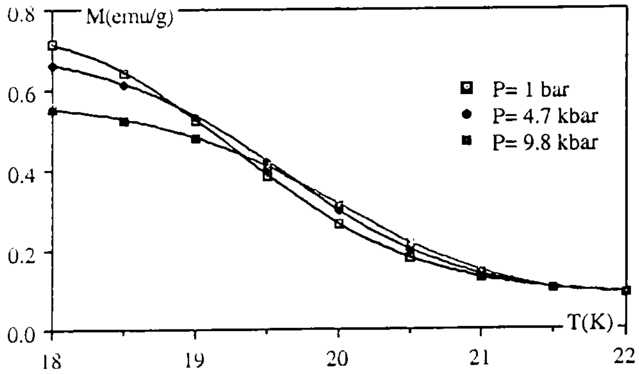

Figure 2 Magnetization of stage 2 $NiCl_2$ GIC under pressure (H=4.7 Oe)

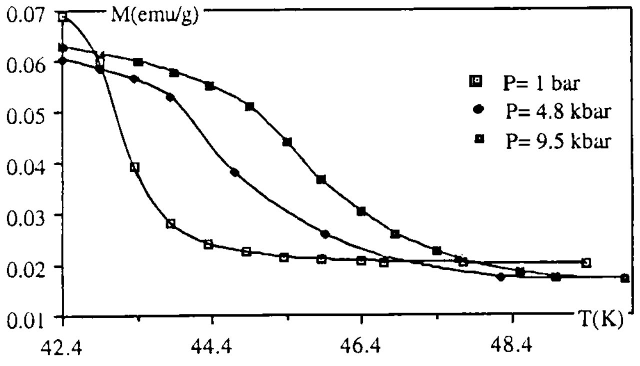

Figure 3 Magnetization of stage 3 $MnBr_2$ GIC under pressure (H=73.5 Oe)

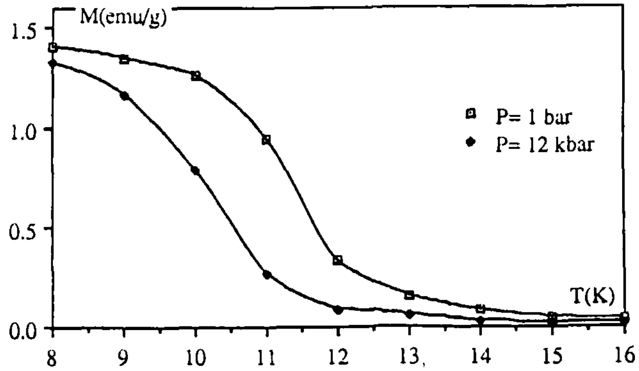

Figure 4 Magnetization of stage 3 $CrCl_3$ GIC under pressure (H=25 Oe)

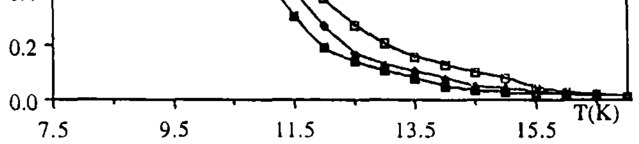

Figure 5 Magnetization of pseudo stage 1 $CrCl_3$-$CoCl_2$ GBIC under pressure (H=3.8 Oe)

of $T_c$ is observed, with $\alpha$ values of $-8 \times 10^{-3}$ kbar$^{-1}$ and $-7 \times 10^{-3}$ kbar$^{-1}$, respectively. It can also be observed that for the biintercalation compound, the shoulder appearing at T = 15 K on the curve at 1.5 kbar, characteristic of the transition to a helical magnetic phase[5,7], disappears at higher pressure.

Several interpretations of the decrease in $T_c$ with increasing pressure are possible, based on pressure-induced structure changes. If one assumes that the transition temperature in these systems is given by $kT_c \sim J'S^2 (\xi_a/a)^2$, where $\xi_a$ is the value of the in-plane spin correlation length and is the intercalate lattice constant, the increase in J' resulting from applying pressure must be more than compensated by a decrease of $\xi_a$ or/and an increase of a. This could result from a distortion of the chlorine octahedra, more likely for a trichloride like $CrCl_3$ than for dichlorides such as $CoCl_2$ or $NiCl_2$. This effect could be enhanced by the slight non-hydrostaticity, since an helical magnetic structure could be more sensitive to uniaxial stress than a simple antiferromagnetic one. On the other hand, the filling factors of the intercalated layers is rather low[5] for $CrCl_3$ layers as well as for $CoCl_2$ layers in the biintercalation compound. As a result, displacements of the intercalated islands are possible under pressure, leading eventually to higher stages. X-ray diffraction experiments performed after coming back to ambient pressure did not show any change, but the phenomenon could be reversible. Diffraction experiments under pressure are needed to clear up the matter.

## REFERENCES

1. G. Dresselhaus and M.S. Dresselhaus, in Intercalation in Layered Materials, vol. 148 of NATO-ASI Series B : Physics, edited by M.S. Dresselhaus (Plenum, New York, 1986), p.
2. D.G. Rancourt, in Chemical Physics of Intercalation, vol. 172 of NATO-ASI Series B ; Physics, edited by A.P. Legrand and S. Flandrois (Plenum, New York, 1987), P. 79
3. R. Clarke and C. Uher, Adv. Phys., 33, 469 (1984)
4. J.T. Nicholls, C. Murayama, H. Takahashi, N. Mori, T. Tamegai, Y. Iye and G. Dresselhaus, Phys. Rev. B, 41, 4953 (1990)
5. P. Biensan, Thesis, University of Bordeaux I (1991)
6. O. Gonzalez, S. Chehab, J. Amiell, B. Agricole, S. Flandrois and E. Stumpp, Mat. Sci. Forum, 91-93, 619 (1992).
7. S. Flandrois, P. Biensan, J.M. Louis, G. Chouteau, T. Roisnel, G. André and F. Bourée, These proceedings.