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The magnetic susceptibility of graphite biintercalated with CoCl₂ and GaCl₃

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Résumé. — Nous présentons les premiers résultats obtenus par susceptibilité magnétique sur le composé de bi-insertion du graphite avec CoCl₂-GaCl₃ et nous les comparons à ceux du composé d'insertion graphite-CoCl₂ de deuxième stade. L'ajustement de la partie haute température du pic de susceptibilité présente deux régimes. Dans le régime haute température, les valeurs de γ obtenues sont élevées, et plus élevées encore dans le biinséré. Ceci indique que le couplage tridimensionnel est encore plus faible dans ce dernier. Dans le régime basse température, près de la transition, la susceptibilité est gouvernée par la nature insulaire des couches insérées.

Abstract. — We present the first results of magnetic susceptibility on CoCl₂-GaCl₃ biintercalated in graphite, and compare them with those obtained in second stage CoCl₂-graphite. A fit by a power law above the maximum of the susceptibility present two regimes: in the high temperature one, the γ values are high and even higher in the CoCl₂-GaCl₃ compound. This indicates that the three-dimensional coupling is lower in the biintercalation compound. In the low temperature regime, near the transition, the susceptibility is driven by the islandic nature of the intercalate layer.

1. Introduction.

The phase transitions in two dimensional (2D) systems present different situations depending on the dimension of the order parameter. Onsager has given the exact solution for the Ising model [1]. For the 2D ferromagnetic plane rotator, Kosterlitz and Thouless [2] have developed a theory in which the low temperature phase presents an algebraic quasi-long range order induced by magnetic vortex interaction. The 2D Heisenberg model does not present phase transition [3]. However, experimental magnetic systems are not as ideal as described by models: the spin dimensionality is an adjustable parameter, the size of the samples is always finite and no true 2D magnetic systems can exist because of the absence of screening of the dipole-dipole interaction.

CoCl₂ is a layered material where the cobalt atoms form a triangular lattice in the octahedral sites defined by two triangular chlorine lattices. At low temperature the cobalt layers are ferromagnetic and they are stacked antiferromagnetically. The critical temperature is \( T_0 = 24.9 \) K. The magnetism of pristine CoCl₂ can be analyzed with the following Hamiltonian:

\[
H = - J \sum_{ij} (S^i_x S^j_x + S^i_y S^j_y + \lambda' S^i_z S^j_z) + J' \sum_{ij} (S^i_x S^j_x + S^i_y S^j_y + \lambda' S^i_z S^j_z) \tag{1}
\]

where \( J \) is the in-plane ferromagnetic exchange between nearest neighbours and \( J' \) the antiferromagnetic exchange between nearest neighbours in adjacent layers. From the neutron scattering investigation of the magnetic excitations in pristine CoCl₂, Hutchings [4] has found the following values:

\( J = 28.5 \) K, \( J'/J = -0.0756 \), \( \lambda = 0.44 \) and \( \lambda' = 0.56 \).
An old idea [5] to reduce the dimensionality was to take advantage of the interaction of the CoCl\textsubscript{2} in graphite. As the crystallographic structure of the CoCl\textsubscript{2} layer intercalated in graphite is almost the same as in pristine CoCl\textsubscript{2}, it was supposed that the nature of the magnetism of the layers would not be modified by the intercalation process. Its only effect would then be to modify the interaction between the magnetic layers and hence to reduce the dimensionality of the space.

The graphite biintercalation compounds are a new family of synthetic materials formed by a sequence of layers with an identity period which corresponds to four ordered layers \(G-I_1-G-I_2\) where \(I_1\) and \(I_2\) are two different species [6] and \(G\) is a graphène (carbon) layer.

We present here the first results on the magnetic susceptibility of a graphite biintercalation compound made of magnetic (CoCl\textsubscript{2}) and non magnetic (GaCl\textsubscript{3}) layers. We also present a similar study on second stage CoCl\textsubscript{2} intercalated in graphite (the stage is the number of graphite layers which separate two intercalated layers). The comparison between the magnetic susceptibility of the intercalated and biintercalated compounds can be very useful to understand their magnetism. Some preliminary results of this work have been published elsewhere [7].

Several magnetic susceptibility experiments have been published on CoCl\textsubscript{2} intercalated in graphite. Karimov [5] first pointed out a phase transition near 8.1 K by a magnetic susceptibility maximum. On the basis of a careful study of the magnetic field dependence, he claimed a double transition at 9.05 K and 8.1 K. The upper transition was identified with a paramagnetic to 2D state and the lower one with a 2D to 3D transition. He also pointed out the role of the finite in-plane crystalline correlation length on the appearance of the 2D magnetic phase and on the 3D coupling. More recently Elahy et al. [8] have repeated the measurements in stage 2, 4 and 5 compounds and interpreted their results with the Kosterlitz-Thouless model [2]. Though their analysis is not very convincing, due to additional \textit{ad hoc} parameters, the strong effect of the applied magnetic field is consistent with a Kosterlitz-Thouless phase. Indeed the analysis of Jose et al. [9] predicts that the intermediate phase is unstable against an uniaxially applied field and the two temperatures move towards each other [8]. Suzuki et al. [10] have also performed experiments on second stage samples. They have obtained very similar results.

Even that the crystallographic structure of the CoCl\textsubscript{2} layer intercalated in graphite is the same as in the pristine material, it is now well established that the layer is not continuous. It is made of islands [11] of variable size. The size of these islands affects drastically the magnetism. Very recently Rancourt [12] has developed an approach adapted to the islandic nature of the sample by considering the superparamagnetic interaction between islands.

2. Samples and experimental set-up.

We shall give now some details on sample preparation because we think that the difference in published results arises mainly from the difference in preparation and hence the nature of the samples.

We have used for both samples the same type of pristine graphite i.e. HOPG (Highly Oriented Pyrolytic Graphite). The intercalation of CoCl\textsubscript{2} is made by direct action of CoCl\textsubscript{2} vapour in the presence of excess chlorine gas. After introduction of the graphite in the reaction tube the cobalt chloride is purified by double distillation: the first one under vacuum and the second one under atmosphere of dry chlorine. The reactor tube is finally sealed under a controlled pressure of chlorine gas (740 mm Hg), and placed in a two zone furnace whose temperatures determine the stage of the final compound, in our case stage 2 [13]. The compound is further analysed by (00 \(l\)) X-ray reflections which show a pure stage 2 compound.

The biintercalated compound is obtained by intercalation of GaCl\textsubscript{3} in the stage 2 CoCl\textsubscript{2} compound, at a much lower temperature. The biintercalation process is also monitored by observation of the (00 \(l\)) X-ray lines. This second intercalation was made under the appropriate thermodynamic conditions for obtaining a saturated compound. X-ray diagrams show that in the biintercalation compound the identity period is equal to the addition of the identity periods of the first stage intercalation compounds of the two chlorides. This new method produces compounds in which the intercalated species are completely separated and ordered in the sequency \(G-I_1-G-I_2\). Previously another method has been used [14, 8] to intercalate CoCl\textsubscript{2} in graphite. In this method the action of a volatile CoAlCl\textsubscript{4} complex gives a mixed graphite intercalation compound of sequency \(G-\text{(CoCl}_2\text{)}_1-G(\text{AlCl}_3)_y\) in the second stage. In this case the AlCl\textsubscript{3} is introduced in the intercalate layer between the CoCl\textsubscript{2} islands.

In the CoCl\textsubscript{2} compounds an excess of chlorine compensates the charge transfer which occurs between carbon and intercalate layers in the intercalation process. We have then only Co\textsuperscript{2+} ions in the compound and then the Hamiltonian is not modified. From the chemical analysis of second stage CoCl\textsubscript{2} control samples prepared under the same conditions as our samples we obtain the formula \(\text{C}_{10.3}\text{CoCl}_{12.12}\) instead of the stoichiometric formula \(\text{C}_{8.3}\text{CoCl}_{12}\) based on crystallographic studies. The comparison of both formulae shows that the CoCl\textsubscript{2} covers 81 % of the graphite surface. Furthermore if we suppose that the excess chlorine defines the border of the island we obtain islands of 200 Å of diameter. This corresponds to about 5 500 spins/island.

We have used long parallelepiped samples (0.5 \(\times\) 3 \(\times\) 6 mm\(^3\)) with the long side perpendicular to the c-axis. In order to measure the AC susceptibility we have used a classical modulation technique at 111 Hz, and a modulation field of 0.1 Oe parallel to the layers.
plane. We measure the AC signal produced in two concentric coils of a few thousands turns connected in series-opposition and compensated to 0.2% in the absence of the sample. The AC signal is detected by a low noise amplifier and fed into a phase sensitive detector. Particular care was taken to the phase of the detected signal, in quadrature with the modulation AC current, in order to be sure to measure only the real part of the magnetic susceptibility, because an admixture of some imaginary susceptibility signal can modify strongly the shape of the curves versus the temperature. The data acquisition and temperature programming and stability is made by a DEC MINC 11/23 micro computer. We have used signal averaging, to minimize the noise, so that each point corresponds to averaging 100 data points.

3. Results.

In figure 1 we present the magnetic susceptibility \( \chi \) as a function of the temperature for both samples without applied magnetic field. We observe in both cases a single peak, at 6.8 K for the second stage CoCl\(_2\) graphite intercalation compound and at 6.1 K for the CoCl\(_2\) and GaCl\(_3\) graphite biintercalation compound. However the maxima are relatively flat. Figure 2 shows the effect of an applied magnetic field \( H \), parallel to the layers plane, on the magnetic susceptibility \( \chi \) of the biintercalated compound : G-CoCl\(_2\)-G-GaCl\(_3\). One observes that \( \chi \) is very sensitive to an applied field : its amplitude decreases very strongly, and the position of the maximum shifts to higher temperatures. These results are similar to those obtained in the intercalated CoCl\(_2\) [5]. Due to the strong variation of \( \chi \) with an applied magnetic field, we were obliged to use very small modulation fields. This is what we have done by using 0.1 Oe, a value below what we did not observe any variation in the susceptibility. But we did not try to shield the earth magnetic field. In stage 2 CoCl\(_2\), the temperature which corresponds to the maximum of the susceptibility is lower than that found by other authors [8,10], and this is due to two larger island dimensions in our case.

The scaling law for the susceptibility as a function of the temperature at zero applied magnetic field is

\[
\chi \approx (T - T_c)/T_c^{\gamma}
\]

for \( T > T_c \) where \( T_c \) is the transition temperature. In figure 3 we have plotted \( 1/\chi \) as a function of \( T - T_c \) taking for \( T_c \) in each case the temperature of the maximum. This figure shows clearly two regimes for \( \gamma \) as a function of the temperature with a narrow intermediate region.

As we have mentioned each intercalated layer is made of islands of about 200 Å in diameter. As the temperature decreases below the magnetic ordering temperature of an infinite layer (\( T_c \approx JS^2 \approx 7 \text{ K} \)) according to the value of \( J \) in the pristine material a strong intra-island spin-spin correlation appears in the sample. Then a relatively strong inter-island intra-plane ferromagnetic coupling and an inter-plane inter-island antiferromagnetic coupling develop. The origin of these interactions is the dipole-dipole coupling. As it was first mentioned by Rancourt [12] this kind of model explains the shape and the very high
Fig. 3. — The inverse of the magnetic susceptibility of intercalated and biintercalated graphite as a function of reduced temperature, on a double logarithmic scale.

magnitude of the maximum of the magnetic susceptibility in graphite-NiCl₂.

In the high temperature regime of figure 3 the in-plane correlation length increases until it reaches at a temperature $T_i$ the size of the island. The numerical value of $\gamma$ obtained for this region is summarized for each sample in table I. The temperature $T_i$ can be estimated for the CoCl₂ graphite intercalation compound at $7.5 \pm 0.2$ K and for the CoCl₂-GaCl₃ graphite biintercalation compound at $7.2 \pm 0.2$ K. For both GICs we have found two characteristic temperatures $T_e$ and $T_{et}$, which can be used to reinter- prete the experimental data of other workers which were interpreted as a Kosterlitz-Thouless phase transition with two other temperatures $T_{cl}$ and $T_{eu}$. As the biintercalation process is performed at lower temperature than the intercalation of CoCl₂ the size of the CoCl₂ islands should be the same in both compounds. This explains the quasi-equality of the $T_e$ values, but the difference between the $\gamma$ values shows that the three-dimensional coupling plays also an important role. In both intercalated and biintercalated samples the c-axis crystalline correlations are very weak because of stacking faults and finite size of the islands as it was measured in FeCl₃ intercalated 

Table I. — Parameters for the fit of $\chi \sim ((T - T_e)/T_e)^{-\gamma}$ for both compounds. $\gamma_1$ is obtained by a fit above $T_i$ and $\gamma_2$ on the all range above $T_e$ after the correction by formula (3).

<table>
<thead>
<tr>
<th></th>
<th>$T_i$ (K)</th>
<th>$T_e$ (K)</th>
<th>$\gamma_1$</th>
<th>$\gamma_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-CoCl₂</td>
<td>7.5 ± 0.2</td>
<td>6.8</td>
<td>2.10</td>
<td>2.42</td>
</tr>
<tr>
<td>G-GaCl₃</td>
<td>7.2 ± 0.2</td>
<td>6.1</td>
<td>2.56</td>
<td>3.07</td>
</tr>
</tbody>
</table>

[15]. It is hence impossible that the magnetic correlation length can be smaller than the crystalline one in any range. Because of the nature of the dipole-dipole interaction, the only way to decrease it is to increase the distance between the layers (which is realized here) or the size of the islands, which appears to be difficult experimentally.

An alternative treatment is to extrapolate the experimental results to those of an infinite size sample and then to analyse the results with the scaling law. One simple way to extrapolate is to impose that the observed maximum correspond to a divergence if the sample would have an infinite size. We have then

$$\chi_{\text{th}} = \chi(1 - \chi/\chi_{\text{max}}). \tag{3}$$

$\chi_{\text{th}}$ is the magnetic susceptibility for an infinite system, $\chi$ is the measured one and $\chi_{\text{max}}$ the maximum of the measured value. This formula introduces important corrections for values between $T_i$ and $T_e$.

The determination of $\gamma$ in this case is given in figure 4. The numerical values of $\gamma$ obtained for both samples are also summarized in table I. The Kosterlitz-Thouless theory predicts

$$\ln \chi = b \exp(- \ln ((T - T_e)/T_e)/2)$$

the agreement of the experimental results with the Kosterlitz-Thouless theory [2] is not good in any range for any value of the parameter $T_e$.

Table I shows clearly two features: the increase of the $\gamma$ value and the reduction of the temperature of the maximum susceptibility when going from the intercalation compound to the biintercalation one. Furthermore the high numerical $\gamma$ values indicate strong fluctuations.

Fig. 4. — The inverse of the magnetic susceptibility of the intercalated and biintercalated graphite, corrected for finite size effects, as a function of reduced temperature on a double logarithmic scale.
For the 2D \(-XY\) model \((J' = \lambda = \lambda' = 0)\) the critical temperature for the ferromagnetic plane rotator is given by [2]

\[
T_{KT} = \pi JS^2/2
\]  
(4)

with \(S = 1/2\) here. If we add to the \(XY\) system \((\lambda = \lambda' = 0)\) a small 3D coupling \((J'/J \ll 1)\) the variation of the critical temperature is given by (2)

\[
T_s(J')/T_{KT} = 1 + 9/\ln^2 (J'/J)
\]  
(5)

however for a 2D system \((J' = 0)\) with \(\lambda \neq 0\) we have for the variation of the critical temperature the following expression [16] :

\[
\lim_{\lambda \to 1} T_s(\lambda) = -2/\ln(1 - \lambda).
\]  
(6)

The latter two examples which refer to two limiting cases show that the critical temperature is reduced by either the 3D coupling \(J'\) or by increasing the third component of the spin \(\lambda\). So the reduction of the critical temperature can be due to one effect, to the other or to a combination of both effects, when one goes from CoCl\(_2\)-GIC to the biintercalation product.

To choose between both effects is not easy and we need other assumptions. As we suppose that only Co\(^{2+}\) ions are present in the intercalation compound we take for \(\lambda\) the same value as in pristine CoCl\(_2\). Then the reduction of the critical temperature between the pristine material and the intercalation compound is caused by the reduction of \(J'\). If we also suppose, as we have previously explained, that the biintercalation does not affect the structure of the CoCl\(_2\) layer, though the charge transfer of the CoCl\(_2\) layer can be modified, then the reduction of the temperature is also caused by the reduction of \(J'\).

If we assume in addition that the biintercalation compound is the real 2D compound according to formula [5] we estimate for the CoCl\(_2\) GIC \(J'/J \approx 2.5 \times 10^{-4}\) then \(J' \approx 7 \times 10^{-3}\) K. The actual value of \(J'\) if the biintercalation compound is not pure 2D is hence larger than \(7 \times 10^{-3}\) K.

4. Conclusion.

The biintercalation of magnetic species in graphite allows us to obtain relatively good two-dimensional compounds. Indeed the biintercalation of CoCl\(_2\) and GaCl\(_3\) in graphite increases the two dimensional character of the CoCl\(_2\) intercalated in graphite. Moreover it seems that the CoCl\(_2\) compounds have the same spin dimensionality as in the pristine material \((\lambda = 0.44)\) : they are not very good \(XY\) systems. However, the in-plane anisotropy is very small [4], and the in-plane invariance by rotation is quite good. As it was just mentioned above, it is possible to extend the Kosterlitz-Thouless theory in this case (formula (6)).

In the high temperature region, \(T > T_i\), the magnetic susceptibility shows the strong fluctuations of low-dimensional systems, but the difference of the \(\gamma\) values shows that the \(c\)-axis coupling is not negligible. In the intermediate range, between \(T_c\) and \(T_i\), the magnetic susceptibility seems to be driven by the islandic nature of the compounds which modifies the in-plane coupling, but also induces a \(c\)-axis dipole-dipole coupling among islands. It should be also noted that, even in the high temperature range (above \(T_i\)), the Kosterlitz-Thouless theory does not explain the magnetic susceptibility, but we are very far away from \(T_c\) in this range, and the theory is not valid any more. The small size of the islands does not allow the development of vortices and hence their dissociation which explains this kind of transitions, which should be affected by the edge effects. A competition between the development of in-plane vortices and the \(c\)-axis antiferromagnetism which both minimize the dipole-dipole interaction in the same range of energy should explain the observed maximum of the magnetic susceptibility.

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