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HAL Id: jpa-00246730
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Submitted on 1 Jan 1993

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Magnetic behaviour of spin 1/2 finite chains intercalated into graphite. Example of the copper chloroaluminate complex

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(Received 11 June 1992, accepted in final form 9 July 1992)

Résumé. — Des nouveaux composés chloroaluminates de cuivre et de cobalt ont été préparés puis insérés dans le graphite. Dans le cas du composé au cuivre l'analyse aux rayons X montre une structure en chaînes. Les propriétés magnétiques s'interprètent bien dans un modèle de chaînes finies de spins 1/2 portés par les ions Cu^{2+}. A basse température la contribution des chaînes impaires est dominante et du type loi de Curie.

Abstract. — New chloroaluminate compounds with copper and cobalt have been prepared and intercalated into graphite. For the copper intercalated compound X ray analysis shows a chain structure. The magnetic properties are consistent with a model of finite chain distribution of spin 1/2 Cu^{2+} ions. The contribution to the susceptibility of the short chains containing an odd number of spins is a paramagnetic-like tail which is dominant at low temperatures.

1. Introduction.

The weak Van der Waals coupling between the graphene layers in graphite allows intercalation of a wide variety of chemical species. The distance between two planes is changed in proportionality with the guest size. The intercalation process is also driven by the amount of charge which can be exchanged between the intercalated specie and the graphite. The resulting compounds have a layered structure and are good model systems for the study of many physical

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properties, like transport properties and magnetism as a function of the effective dimensionality. The magnetic properties of many transition metal chlorides have been studied in the pristine compounds and more intensively in the graphite intercalation compounds (GIC’s). In most cases they can be interpreted within the framework of 2D models. A way for reducing the magnetic dimensionality parameter $|J'/J|$ (inter- to intraplane interaction ratio) consists in increasing the layer spacing while keeping a large intraplane $J$ value. This is realized in GICs in which the exchange interaction is much greater in one direction than in the others. The intrinsic magnetism of such low-dimensional lattices continues to request a fundamental interest. Copper (II) compounds usually provide a large variety of structures which have led to many interesting and significant spin-1/2 Heisenberg magnetic systems, including 1D and 2D ferromagnets $[1, 2]$, 1D antiferromagnets $[3, 4]$, as well as more complicated polymeric systems $[5]$. Jahn-Teller distortion effects play probably an important role in the wide variety of magnetic properties of these compounds. In the present work, the structure and magnetic properties of new GIC with the complex molecule CuAl$_2$Cl$_8$ are studied and interpreted in the framework of a spin-1/2 finite chains description.

2. Structural aspect and synthesis.

The CuAl$_2$Cl$_8$ complex seems to exist in two different crystal structures, monoclinic $[6]$ and triclinic $[7]$. In both forms, the coordinates of Cu$^{2+}$ and Al$^{3+}$ are the same; nearly square plane for copper ions and tetrahedral for Al ions. The networks composed of AlCl$_4^-$ and CuCl$_6^-$ distorted octahedra lie parallel to the $bc$-plane of the unit cell, forming a layered structure of chains.

The molecule is intercalated into highly oriented pyrolytic graphite (HOPG) at 300 °C. Synthesis and structural characterization will be given in more details elsewhere $[8]$. The final compound of first stage$^{(1)}$ has an average formula C$_{22}$CuAl$_2$Cl$_8$ which shows that the filling factor is of about 85 % when compared to the theoretical composition $[9]$. This filling factor is very good and comparable to the one usually obtained in the majority of GIC’s. It is now well established that the structure of the intercalated molecule layers is far from being ideal and exhibits many defects like voids and islands $[10]$. The identity period along the graphite $c$-axis is $I_c = 9.47$ Å, comparable to that of G-CuCl$_2$ ($9.37$ Å). The three-dimensional stacking consists in the three-layer sequence Cl-M-Cl ; (M = Cu, Al with the ratio 1 : 2) as proved by the measured electronic density profile $\rho(z)$. The in-plane structure of the intercalants is a hexagonal array with the parameter $a = 13.8$ Å. The in-plane coherence length for this structure is of the order of 300 Å.


The measured in-plane static susceptibility $\chi = M/H$ as reported in figure 1 does not show any characteristic feature of a magnetic ordering : neither discontinuity nor peak. It is almost independent of the temperature below $T_M \approx 31$ K except for a drastic increase at very low temperature far below $T_M$. In the region $4 < T < 25$ K, $\chi$ is satisfactorily described by the law : $\chi = \chi_0 + C/T$ where the second term is dominant. We evaluated $C = 0.100$ K.emu/mol. yielding an effective moment $\mu_{\text{eff}} = 0.89 \mu_B$ per copper (II) ion. This moment is smaller than the free ion Cu$^{2+}$ moment value (1.9$\mu_B$). The additional term is small : $\chi_0 \approx 0.008$ emu/mol.

$^{(1)}$ The stage is defined as the number of adjacent graphene layers separating two successive planes of the intercalated specie.
After substraction of the paramagnetic term, $C/T$, the remaining susceptibility also represented in figure 1 displays a very broad maximum around $T_M$. Such a maximum is expected for an antiferromagnetic linear chain system [11]. Broad susceptibility maxima could also occur in systems of isolated clusters or two-dimensional sheets of exchange coupled spins [12].

The anomalous paramagnetic behavior observed at low temperature, may originate in: i) the existence of diluted or isolated spins (or clusters of spins) which behave as a localized paramagnetic moments [13], ii) the presence of loose spins which arises in frustrated systems [14, 15] or iii) unpaired spins at the free ends of independent chains containing an odd finite number of spins [11, 16]. This latter possibility is more consistent with the structure of the present compound. Within this interpretation the "substracted susceptibility" $\chi(T) - C/T$ would be essentially due at low temperature, to even spin chains and/or to long chains. The temperature at which the maximum of $\chi(T) - C/T$ occurs gives an evaluation of the intra-chain interaction $J$ which is responsible for the short-range correlation between the spins. A semi-quantitative analysis within the one dimensional magnetic models is possible if the system is considered, in a crude approximation, as made of independent identical antiferromagnetic chains. Following this assumption, we have found that the Fisher model [17] adapted for finite antiferromagnetic Heisenberg chains by Smith and Friedberg [18] provides a good representation of our results with an antiferromagnetic exchange integral $J/k_B \approx -40$ K. At high temperatures far above $T_M$, the measured susceptibility follows a Curie-Weiss law: $\chi = C/(T - \theta)$. The asymptotic Curie-Weiss temperature $\theta$ is negative ($\theta \approx -44$ K) and in good agreement with the quantity $\frac{2}{3}zS(S+1)\frac{J}{k_B}$, ($S = 1/2, z = 2, J = -40$ K), which is predicted for Heisenberg linear finite-chains in the high temperature limit [16]. The effective moment ($\mu_{eff} \approx 1.64\mu_B$) calculated from $C'$ ($C' \approx 0.334$ K.emu/mol) is consistent with a free paramagnetic Cu$^{2+}$ distribution at
high temperature. The interchain coupling becomes significant only at very low temperature ($T < 4$ K) where it induces a three-dimensional ordering. In this range the approximation of independent chains is no more valid.

The presence of uncompensated spins within the odd chains has been confirmed by the measurements of the magnetization versus field. Representative isotherms are reported in figure 2. The magnetization $M(H)$ contains two types of contributions: i) a low field part which exhibits below 4 K a positive curvature characteristic of an antiferromagnetic contribution, ii) a high field part corresponding to the orientation process of individual spins in the magnetic field direction.

![Magnetization curves](image)

Fig. 2. — Magnetization curves at various temperatures as function of the applied magnetic field. The insert shows the low field shape of $M(H)$ at 1.85 K. Note that the average magnetic moment measured in 12 T is $0.33 \mu_B$/Cu$^{2+}$.

The average saturation moment obtained by zero field extrapolation of the high field part of $M(H)$ curves is $\mu_S = 0.30 \mu_B$/Cu$^{2+}$ (at 1.85 K). If all the moments were aligned in the magnetic field one should find the free ion theoretical value $\mu_S = 1\mu_B$. (for Cu$^{2+}$). We can thus conclude that about 30% of copper ion spins are unpaired and that a field of 12 T is not strong enough to break the antiferromagnetic interaction $J$.

The small positive curvature of $M(H)$ observed in the low field region may be related to the “thermal spin flopping” which arises usually in long even antiferromagnetic chains. It corresponds to a change in the susceptibility regime due to the lowering of the energy states by the magnetic field [16]. In the pure CuCl$_2$ crystal, a spin-flop transition has been observed at a field $H_{sf} = 4.1$ T (at 4.2 K) along the antiferromagnetic $b$-axis. The jump of the magnetization at this field is very small $(0.012\mu_B$/Cu$^{2+}$) [19]. In the case of the present compound, such a transition could be masked by the dominant paramagnetic contribution at low temperatures of the odd chains. For the same reason an accurate determination of the eventual spin-flop transition from magnetization measurements has not been possible for the CuCl$_2$GIC [20].

We have reported experimental evidence of antiferromagnetic spin 1/2 finite chain behaviour in the new CuCl$_2$.2AlCl$_3$ graphite intercalated complex, using susceptibility and high field magnetization measurements. Our results are consistent with the extension of the Fisher model developed by Smith and Friedberg for finite antiferromagnetic Heisenberg chains. Full quantitative analysis is made difficult because calculations are performed in zero field and our results show that the susceptibility is very field sensitive at least at low temperatures. In addition, the structure is disordered and the compound must be described as an assembly of chains of various sizes. The susceptibility must be averaged, for a given field, over the sizes distribution: \( \chi(T, J, J') = \Sigma_n f_n(T, J, J') \cdot \chi_n(T, J, J') \) where \( f_n \) is the fraction of chains containing \( n \) spins (odd or even), \( \chi_n \) is the susceptibility of the chain with \( n \) spins and \( J(J') \) is the intra- (inter-) chain exchange coupling. Although the contribution of odd chains is dominant, an accurate calculation must include the statistical distribution of chains due to finite size effects. Parallel to this study, cobalt chloraluminate CoCl$_2$.2AlCl$_3$ has also been intercalated into graphite. This compound is very attractive because its structure is formed of very well decoupled linear Co$^{2+}$ chains in the c-direction (of the monoclinir unit cell) [21, 22]. This GIC offers the possibility of obtaining a canted spin magnetic structure which arises more commonly with linear chain systems and originates from antisymmetric spin coupling [23, 24]. Weak ferromagnetism may occur due to an incomplete antiferromagnetic alignment of the spins as observed in CsCoCl$_3$.2H$_2$O and CoCl$_2$.2D$_2$O [25-27]. The canting becomes important when strong anisotropy exists as for the Co$^{2+}$ ion. Another very interesting chloraluminate could be the Ni-complex. This compound is structurally isomorphous to the Co-chloroaluminate and is formed by Ni$^{2+}$ chains with an integer spin value (\( S = 1 \)). Graphite intercalation of this molecule is of particular interest to check the special Haldane conjecture [28] which is predicted for \( S = 1 \) Heisenberg antiferromagnets. Experimentally such a conjecture was observed in a few systems as NENP [29]. It is characterized by an energy gap between the singlet ground state and the first excited states.

In conclusion, the advantage of graphite intercalation, is the possibility of reducing the effective magnetic dimensionality and to explore 1D, 2D and 3D magnetic systems.

Acknowledgements.

We wish to thank Pr. A.A. Stepanov for many discussions and Dr. J.P. Boucher for a number of useful suggestions.

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