

COLE-COLE ANALYSIS OF THE AC MAGNETIC SUSCEPTIBILITY OF SOME LAYERED HYBRID ORGANIC-INORGANIC MAGNETS

M. A. Girtu*

Department of Physics, Ovidius University, Constanta, RO-8700, Romania

This paper reports the magnetic studies on a family of triangular quantum Heisenberg antiferromagnets with weak additional Dzyaloshinskii-Moriya interaction, $\text{Cu}_2(\text{OH})_3(\text{C}_m\text{H}_{2m+1}\text{COO})$, $m = 7, 9$ and 11 . Below 20 K a complex phase with both canted-antiferromagnetism and spin glass-like characteristics is found. We present the results of a Cole-Cole analysis of the ac linear magnetic susceptibility, followed by a power-law fit of the relaxation times, which provide critical exponents characteristic for spin glass-like materials.

(Received July 21, 2003; accepted August 21, 2003)

Keywords: ac magnetic susceptibility, Canted antiferromagnet, Spin glass, Triangular antiferromagnet

1. Introduction

Hybrid organic-inorganic magnets are molecule-based magnets (systems in which electrons in molecular orbitals, consisting of superpositions of p and even s atomic orbitals, play a crucial role in the magnetic ordering) obtained by means of organic, organometallic or coordination chemistry methods [1]. Due to recent advancements in magneto-chemistry the concepts of “magnetic lattice engineering” or “magnets by design” are now much closer to reality, in many cases small changes in the chemical synthesis allowing the control and modulation of the overall magnetic properties [2].

The interest in molecular magnets is twofold, from both the basic and applied research perspectives. While room-temperature hybrid organic-inorganic magnets are of importance for applications as they might be able to replace in some applications typical magnetic materials such as ferrites [2], other new molecule-based materials are relevant because they represent unique experimental realizations for “exotic” theoretical models [1]. We discuss in this paper a family of materials that are significant for the latter reason, as they illustrate the role of small additional interactions in the magnetic ordering of triangular quantum Heisenberg antiferromagnets (TQHAF).

From a theoretical point of view classical triangular Heisenberg antiferromagnets reveal low-temperature noncollinear Neél long range order because the frustration, which occurs on a triangular lattice of antiferromagnetic bonds, can be released by spin configurations that are not antiparallel, as in the traditional Neél state [3]. In such case, the 120° planar spin configuration minimizes the total energy. The spin-1/2 system may have a disordered ground state, because of the quantum fluctuations present since the three component of the spin cannot be all well defined at the same time [4] (Fig. 1a). Other theoretical results proposed that the ground state of the TQHAF preserves at least a portion of the noncollinear Neél state obtained in the classical limit [5]. Although the latter possibility seems to prevail, a true consensus is yet to be reached. Research on TQHAF systems is, therefore, of current interest, especially as most of the experimental realizations have been systems with stacked lattices and three-dimensional ordering [6].

* Corresponding author: girtu@univ-ovidius.ro

In the paper [7] the magnetic behaviour of a 3-dimensional Fe-based hybrid organic-inorganic was reported. In other paper [8] we have shown that the unusual magnetic properties of hybrid organic-inorganic porphyrin-based magnets are due to one-dimensional ferromagnetic clusters that interact to form three-dimensional domains.

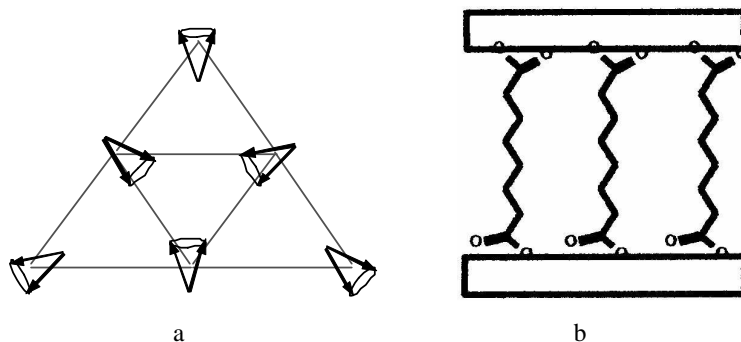


Fig. 1. a) Triangular quantum Heisenberg antiferromagnet. The quantum fluctuations take the spins away from the noncollinear 120° configuration; b) Layered structure of the family of magnets $\text{Cu}_2(\text{OH})_3(\text{C}_m\text{H}_{2m+1}\text{COO})$ $m = 7, 9$ and 11 . The interlayer distances are $24.1, 29.4,$ and 34.4 \AA , respectively.

Here we present magnetic studies of the recently reported hybrid organic/inorganic triangular quantum Heisenberg antiferromagnets with weak additional Dzyaloshinskii-Moriya (DM) interaction, $\text{Cu}_2(\text{OH})_3(\text{C}_m\text{H}_{2m+1}\text{COO})$, with $m = 7, 9$ and 11 [9]. These compounds are obtained by intercalation of saturated organic chains between inorganic layers of copper hydroxides [10]. The copper hydroxide salts $\text{Cu}_2(\text{OH})_3(\text{C}_m\text{H}_{2m+1}\text{COO})$, have a botallackite-type structure, in which two-crystallographically distinct Cu^{2+} ions lie in slightly different octahedral environments. The X-ray powder diffraction studies revealed the layered structure (Fig. 1b) with interlayer distances of $24.1, 29.4,$ and 34.4 \AA for $m = 7, 9,$ and $11,$ respectively.

The spin carrying units are $S = 1/2 \text{ Cu}^{2+}$ ions with no single-ion anisotropy, located on a planar lattice. The most important interaction consistent with the structure is the isotropic Heisenberg exchange [9], mediated by the bridging oxygen atoms. The magnetic lattice consists of non-equilateral triangles (different strengths of the exchange interaction, the average value of which is $\sim 60 \text{ K}$) due to the various Cu-O-Cu angles between adjacent pairs of Cu ions. The octahedral symmetry around the copper ions is slightly altered by the fact that the six oxygen ligands are not equivalent, some being part of an OH group others of an COO group. Given that the environment is different from site to site, the DM exchange [11] (estimated to $\sim 5 \text{ K}$ [9]), adds to the usual Heisenberg exchange.

Fits of the dc susceptibility data to high temperature series expansions were consistent with high temperature ($100 < T < 350 \text{ K}$) TQHAF behavior [9]. At low temperatures the deviations from the TQHAF predictions suggested a canted antiferromagnetic type of ordering, in accord with the strong peak in the second harmonic of the nonlinear ac susceptibility (at $\sim 20 \text{ K}$), which indicates the development of a spontaneous moment. The values of the saturation magnetization at 5 K , in fields of up to 5.5 T were about 4.5 times smaller than the ones expected for the $S = 1/2$ ferromagnet, consistent with canting and noncollinear spin configurations. Kouvel-Fisher scaling analyses indicated the divergence of the linear susceptibility with critical exponents $\gamma \sim 1.75$, characteristic for 2D Ising systems. The frequency dependence of the linear ac susceptibility and its harmonics, and the irreversibility in the field-cooled/zero-field-cooled magnetization reveal spin glass-like behavior near 20 K . We, therefore, proposed that instead of choosing between the resonant valence bond noncollinear Neél ground states, these three systems evolve due to the additional DM interaction toward a 2D Ising-like canted antiferromagnetic state with spin glass-like characteristics [9].

In this paper we present the results of a Cole-Cole analysis and show that the critical exponents obtained by power-law fitting of the temperature dependence of the mean relaxation time are consistent with our earlier report [9] that the low-temperature state is unusual, exhibiting a coexistence of magnetic order and disorder.

2. Experimental

The powder samples of $\text{Cu}_2(\text{OH})_3(\text{C}_m\text{H}_{2m+1}\text{COO})$, $m = 7, 9$ and 11 were sealed at room temperature in quartz tubes with known magnetic background signal. The measurements of the linear ac magnetic susceptibility were made with a Lake Shore 7225 ac Susceptometer/dc Magnetometer in various dc applied fields $0 \leq H_{\text{dc}} \leq 50$ kOe and in the temperature range $4 < T < 40$ K, either at constant field on warming, or at constant temperature, sweeping the field. Both the in-phase χ' and out-of-phase χ'' linear susceptibilities, $\chi = \chi' + i\chi''$, were measured under an ac field of amplitude 1 Oe and a wide range of frequencies ($5 \leq f \leq 10000$ Hz).

3. Results and discussion

The frequency dependence of the imaginary part of the linear magnetic susceptibility of $\text{Cu}_2(\text{OH})_3(\text{C}_9\text{H}_{19}\text{COO})$ is shown in Fig. 2. The peak temperature of χ'' varies with frequency, indicative of slow relaxation processes that characterize the glassy behavior [12].

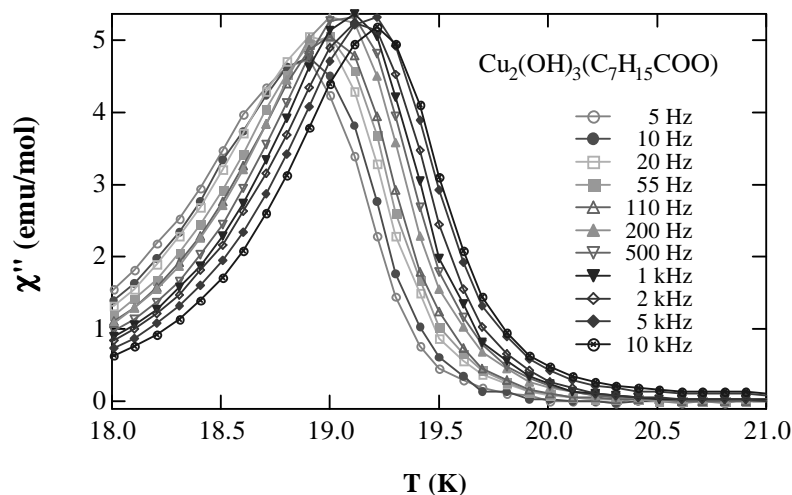


Fig. 2. Out-of-phase linear ac susceptibility versus temperature for $\text{Cu}_2(\text{OH})_3(\text{C}_7\text{H}_{15}\text{COO})$ at an ac field amplitude 1 Oe, no applied dc field, and frequencies of $5 \leq f \leq 10000$ Hz.

A detailed analysis of the relaxation times and their dependence on temperature can be made using the phenomenological description of Cole and Cole [13], which involves a modeling of the dynamics at a given temperature onto a distribution of relaxation times that is symmetric on the logarithmic time scale. The Cole-Cole formalism introduces a parameter α (where $0 < \alpha < 1$), which determines the width of the distribution of relaxation times $g(\ln \tau)$ around the median relaxation time, τ_c . The parameters α and τ_c determined from the Cole-Cole analysis at each T allow the construction of the distribution of relaxation times (Fig. 3). As the temperature is decreased through the transition τ_c increases, indicating the growth of the correlation length of the system of spins, while α also increases, reflecting the fact that the distribution of cluster sizes broadens. This behavior was seen in all three compounds, though only the analysis for the $m = 7$ sample is shown here.

The temperature dependence of the median relaxation time determined by Cole-Cole analysis for all three compounds, was found to vary almost six decades over less than three degrees. The divergence of the relaxation time was studied using power law scaling analysis, $\tau_c \propto (T - T_c)^{-z\nu}$ (Fig. 4), which gave for the dynamical critical exponents of the $m = 7, 9$, and 11 values of 5.5 to 6.1 , 7.7 , and 5.6 , respectively, characteristic for spin glasses ($5 \leq z\nu \leq 11$) [12] far from those characteristic for regular ferromagnets ($1.2 \leq z\nu \leq 2$) [14].

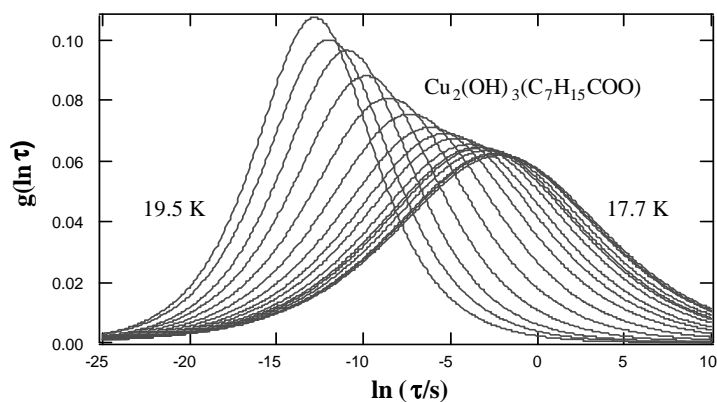


Fig. 3. Distribution of relaxation times obtained based on Cole-Cole analysis of the ac susceptibility, for $\text{Cu}_2(\text{OH})_3(\text{C}_7\text{H}_{15}\text{COO})$, at temperatures $17.7 = T = 19.5$ K (steps of 0.1 K).

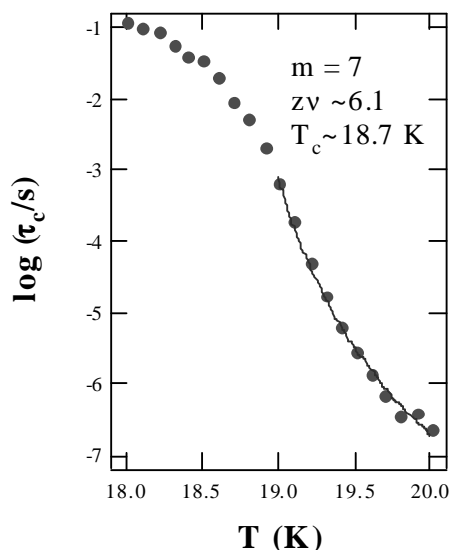


Fig. 4. Temperature dependence of the mean relaxation time τ_c obtained by Cole-Cole analysis for $\text{Cu}_2(\text{OH})_3(\text{C}_7\text{H}_{15}\text{COO})$. The line represents a the power law fit of the data.

While the Cole-Cole analysis was successful, providing critical exponents, the attempt to reach a data collapse by dynamic scaling analysis (following the standard linear scaling procedure [15]) failed for both power-law and activated types of dynamic behavior, for all three compounds, indicating that these systems are not typical spin glasses.

4. Conclusions

We showed that the frequency dependence of the linear ac susceptibility studied through Cole-Cole analysis indicates slow relaxation times characteristic of glassy behavior, while the failure of the dynamic scaling analysis suggests that the $\text{Cu}_2(\text{OH})_3(\text{C}_m\text{H}_{2m+1}\text{COO})$, ($m = 7, 9$ and 11) are not typical spin-glasses. We conclude that the results reported here are consistent with our previous claim that the low-temperature state is unusual, with a coexistence of spin glass-like and 2D Ising-like canted antiferromagnetic characteristics.

Acknowledgement

The author thanks C. M. Wynn, W. Fujita, K. Awaga and A. J. Epstein for the fruitful collaboration that made this work possible and the Romanian Ministry of Education and Research for financial support (CNCSIS A_T grant).

References

- [1] J. S. Miller, A. J. Epstein, *Angew. Chem. Int. Ed. Engl.* **33**, 385 (1994).
- [2] J. S. Miller, A. J. Epstein, *Chem. & Eng. News.* **73**, 30 91995).
- [3] G. Aeppli, P. Chandra, *Science* **275**, 177 (1997).
- [4] P. W. Anderson, *Mater. Res. Bull.* **8**, 153 (1973)
- [5] N. Elstner, R. R. P. Singh, A. P. Young, *Phys. Rev. Lett.* **71**, 1629 (1993).
- [6] M. F. Collins, O. A. Petrenko, *Can. J. Phys.* **75**, 605 (1997).
- [7] M. A. Gărtu, *J. Optoelectron. Adv. Mater.* **3**(1), 113 (2001).
- [8] M. A. Gărtu, *J. Optoelectron. Adv. Mater.* **4**(1), 85 (2002).
- [9] M. A. Gărtu, C. M. Wynn, W. Fujita, K. Awaga, A. J. Epstein, *Phys. Rev. B* **57**, 11058 (1998).
M. A. Gărtu, C. M. Wynn, W. Fujita, K. Awaga, A. J. Epstein, *Phys. Rev. B* **61**, 4117 (2000).
- [10] W. Fujita, K. Awaga, *Inorg. Chem.* **35**, 1915 (1996); W. Fujita, K. Awaga, T. Yokoyama, *Inorg. Chem.* **36**, 196 (1997).
- [11] T. Moriya, in *Magnetism*, G. T. Rado, H Suhl, eds., vol. I, Academic Press, New York, 1963.
- [12] J. A. Mydosh, *Spin Glasses: An Experimental Introduction*, Taylor and Francis, London, 1993.
- [13] K. S. Cole, R. H. Cole, *J. Chem. Phys.* **9**, 341 (1941).
- [14] P. M. Chaikin, T. C. Lubensky, *Principles of Condensed Matter Physics*, Cambridge University Press, New York, 1995.
- [15] S. Geschwind, D. A. Huse, G. E. Devlin, *Phys. Rev. B.* **41**, 4854 (1990).