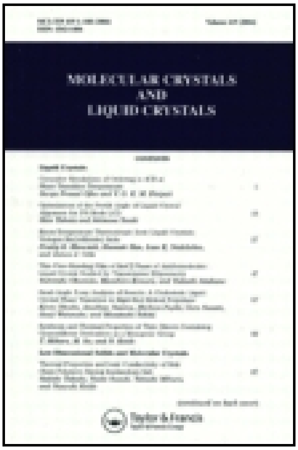

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Magnetic Order and Disorder in a Family of Layered Organic/Inorganic Nanocomposites

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We report magnetic studies of a family of triangular quantum Heisenberg antiferromagnets (TQHAFs) with weak additional Dzyaloshinskii-Moriya interaction, $Cu_2(OH)_3(C_mH_{2m+1}COO)$, m = 7, 9 and 11. The three compounds have nearly identical magnetic properties, despite the large differences in the interlayer separation, indicative of 2D behavior. While the high temperature dc susceptibility data suggest TQHAF behavior, at low temperatures the deviations from the TQHAF predictions imply a canted antiferromagnetic type of ordering, consistent with both the strong peak in the second harmonic of the nonlinear ac susceptibility (at ≈ 20 K) and the low saturation magnetization observed in the low temperature hysteresis curves. We propose that the interplay of Heisenberg and Dzyaloshinskii-Moriya exchanges leads to an unusual state with both 2D Ising-like canted antiferromagnetic and spin glass-like characteristics, a state in which order and disorder appear to coexist.

Keywords: triangular quantum Heisenberg antiferromagnets; TQHAF; spin glass; two-dimensional magnets

INTRODUCTION

The recent interest in geometrically frustrated systems has been spurred by the new phenomena predicted or already observed at low temperatures: noncollinear Neèl long range order (LRO), order by disorder, partial order, quantum disorder, etc.[1,2,3,4,5,6]

Triangular Heisenberg AFs recently have been intensely studied both theoretically and experimentally but most of the experimental realizations have been systems with stacked lattices and three-dimensional ordering.[7] Regarding the triangular spin-1/2 (quantum) Heisenberg antiferromagnet (TQHAF), the suggestion that this is the simplest system to have a resonating valence bond ground state,[5] as opposed to the noncollinear semiclassical Neèl state,[7] has resulted in much debate and controversy and, although the later possibility seems to prevail, a true consensus is yet to be reached. Research on TQHAF systems is, therefore, of current interest.

We review and extend here magnetic studies of the recently reported[8,9,10] hybrid organic/inorganic triangular quantum Heisenberg antiferromagnets with weak additional Dzyaloshinskii-Moriya (DM) interaction, $Cu_2(OH)_3(C_mH_{2m+1}COO)$, with m = 7, 9 and 11. These compounds are obtained by intercalation of saturated organic chains between inorganic layers of copper hydroxides.[11,12] The copper hydroxy salts $Cu_2(OH)_3(C_mH_{2m+1}COO)$, m = 0, exhibit a botallackite-type structure, in which two-crystallographically distinct copper atoms lie in slightly different octahedral environments.[13] X-ray powder diffraction[13] and EXAFS[14] studies revealed the layered structure with interlayer distances of 24.1, 29.4, and 34.4 Å for m = 7, 9, and 11, respectively. Based on the width of the diffraction peaks we estimate the size of the crystallites to ~300 Å consistent with values obtained from TEM studies.[15] The TEM photographs revealed interference patterns usually observed only in structurally ordered materials.[15]

The spin carrying units are $S = 1/2$ 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, $H_H = -\sum 2J_{ij}\vec{S}_i \cdot \vec{S}_j$, mediated by the bridging oxygen atoms. As there are four distinguishable Cu-O-Cu angles between adjacent pairs of Cu ions,[14] the varying strength of the exchange interaction (the average value of which is[10] $2J \sim 60$ K) may also vary causing the magnetic lattice to consist of nonequilateral triangles. The octahedral symmetry around the copper ions is slightly altered by the fact that of the six oxygen ligands not all are equivalent. Given the varying small anisotropy the DM exchange[16] $H_{DM} = \sum \vec{D}_{ij} \cdot (\vec{S}_i \times \vec{S}_j)$, with various DM vectors $\vec{D}_{ij}$ (estimated[10] to $D \sim 5$ K), adds to the usual Heisenberg exchange.

The interlayer interactions are expected to be very small, likely negligible.

Also, dipole-dipole interactions[17] are likely negligible (~10^{-4} K) due to the large interlayer distances. It is, therefore, very likely that these compounds are good realizations of 2D systems.

Fits of the dc susceptibility data to high temperature series expansions[18] were consistent with high temperature ($100 \leq T \leq 350$ K) TQHAF behavior.[8] 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 ≈ 20 K), which indicates the development of a spontaneous moment.[8,9,10] 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.[10] Kouvel-Fisher scaling analyses indicated the divergence of the linear susceptibility with critical exponents $\gamma \approx 1.75$, characteristic for 2D Ising systems.[10] 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.[8,9,10] Instead of choosing between the resonant valence bond[5] noncollinear Neel ground states,[1] we proposed that these three systems evolve due to the additional DM interaction toward a 2D Ising-like canted antiferromagnetic state with spin glass-like characteristics.

In this paper we extend our previous studies, reporting new results of ac susceptibility measurements in the presence of an applied dc field. We show that these results are consistent with our previous suggestion that the interplay between Heisenberg and DM exchanges leads to an unusual state in which order and disorder appear to coexist.

EXPERIMENTAL

The powder samples of $Cu_2(OH)_3(C_mH_{2m+1}COO)$, 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 H_{dc} to 50 kOe and $5 \leq T \leq 40$ K, either at constant field on warming, or at constant temperature, sweeping the field. Both the in-phase (χ_l') and out-of-phase (χ_l'') linear susceptibilities, $\chi_l = \chi_l' + i\chi_l''$, were measured under an ac field $H_{ac} = h_O \sin(2\pi f t)$ of amplitude h_O = 1 Oe and a wide range of frequencies ($5 \leq f \leq 10000$ Hz).

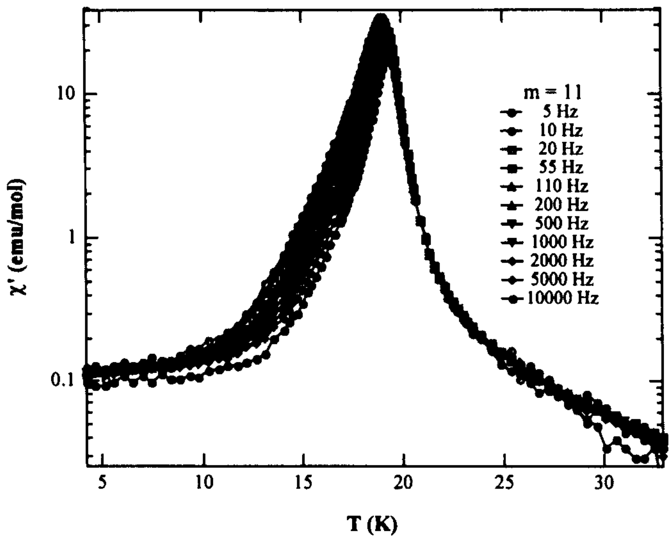

FIGURE 1: ac susceptibility versus temperature for $Cu_2(OH)_3(C_9H_{19}COO)$ at an ac field amplitude $h_0 = 1$ Oe, no applied dc field, and various frequencies $5 \leq f \leq 10000$ Hz.

RESULTS AND DISCUSSION

The frequency dependence of the real part of the linear magnetic susceptibility of $Cu_2(OH)_3(C_9H_{19}COO)$ is shown in Fig. 1. The peak temperature of χ_1' increases while the peak height decreases with increasing frequency indicative of slow relaxation processes that characterize the glassy behavior.[19] The values of the relative variation of the peak temperature per decade of frequency, $(\Delta T_P/T_P)/\Delta(\log_{10} f) = 0.003$, 0.008, and 0.008, for m = 7, 9, and 11, respectively,[8,9,10] are in the range of canonical spin glasses.[20]

The Cole-Cole formalism[20] 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.[21] Based on the Cole-Cole equation for the ac susceptibility one can determine an expression for $\chi_1''(\chi_1')$ which allows the fit of the experimental data.[21] Such fits (with α and τ_c as parameters) are presented for $Cu_2(OH)_3(C_9H_{19}COO)$ in the Argand plot of Fig. 2, where the phenomenological Cole-Cole model is described by circular arcs with a maximum at $2\pi\tau_c f = 1$. Noteworthy is the shift of the data points from a

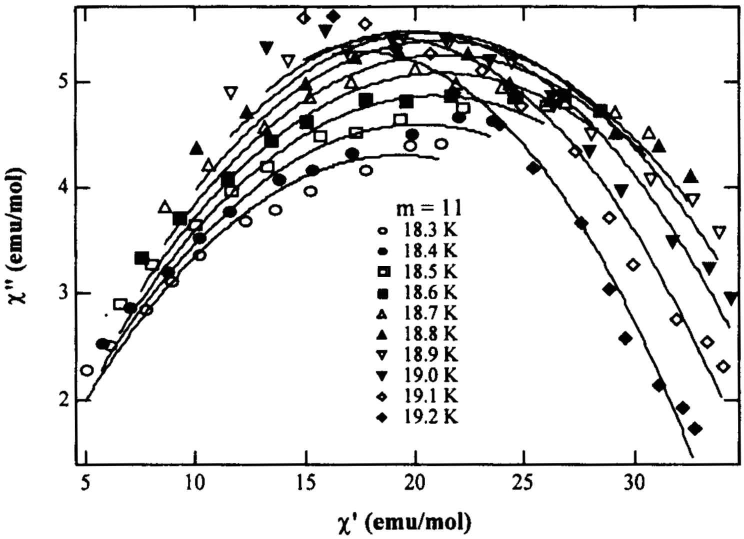

FIGURE 2: Argond plots and Cole-Cole analysis of the ac susceptibility data of Fig. 1, for $Cu_2(OH)_3(C_9H_{19}COO)$, at various temperatures $18.3 \leq T \leq 19.2$ K.

nearly isothermal susceptibility above 19.2 K to a nearly adiabatic susceptibility below 18.3 K. As it will be seen below, this behavior corresponds to a large increase of the median relaxation time when decreasing the temperature by a few degrees through the transition.

The parameters α and τ_c determined from the Cole-Cole analysis at each T allow the construction of the distribution of relaxation times. 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. Similar behavior was seen in all three compounds.[8,9,10]

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 which gave[10] for the dynamical critical exponents values characteristic for spin glasses.[19]

Results of dynamic susceptibility measurements in the presence of a constant dc magnetic field are shown in Fig. 3. The overall shape of the temperature dependence of χ_l' remains qualitatively the same in all dc fields: χ_l' increases with decreasing T, has a peak, decreases and then levels off at low temperatures. The magnitude of χ_l' (which describes the fluctuations in magnetization) decreases monotonically with increasing H_{dc}, as expected, indicating that as the applied field is raised more and more spins are "locked," oriented by the dc field and do not participate in fluctuations. Also, the peak in the in-phase susceptibility shifts toward higher temperatures as H_{dc} is increased (see the inset of Fig. 3). The presence of the field compensates for the disordering effect of thermal fluctuations, allowing the "ordering" to occur at higher T. Such behavior has been seen in Monte Carlo simulations of 2D Ising magnets.[22] The broadening of the peak in the presence of the dc field may be caused by the distribution of crystallites in the powder sample. While in the absence of the field all crystallites are equivalent, given the anisotropy of each crystallite, as the H_{dc} is increased the various crystallites may reach some kind of ordering at different temperatures.

While the usual 2D Ising magnet has vanishing susceptibility as T decreases to zero,[22] the constant low T χ_l' seen in Fig. 3 indicates that fluctuations do not disappear for these samples, consistent with the zero field dc data. Therefore, some spin degrees of freedom are preserved at low T, which is in accord with frustration playing a crucial role in these systems. It is likely that, as it was argued previously,[10] the periodic magnetic lattice (with nonuniform but periodic Heisenberg and DM exchange coupling strengths) may lead to the coexistence of magnetic order and disorder, as it is possible that one or more sublattices order below the critical temperature T_C while at least one sublattice stays disordered at all T.

The out-of phase linear susceptibility χ_l'' has a sharp peak, suggesting a divergence, only at the limit of zero applied field. At higher H_{dc} the peak is broader, extending toward lower temperatures.

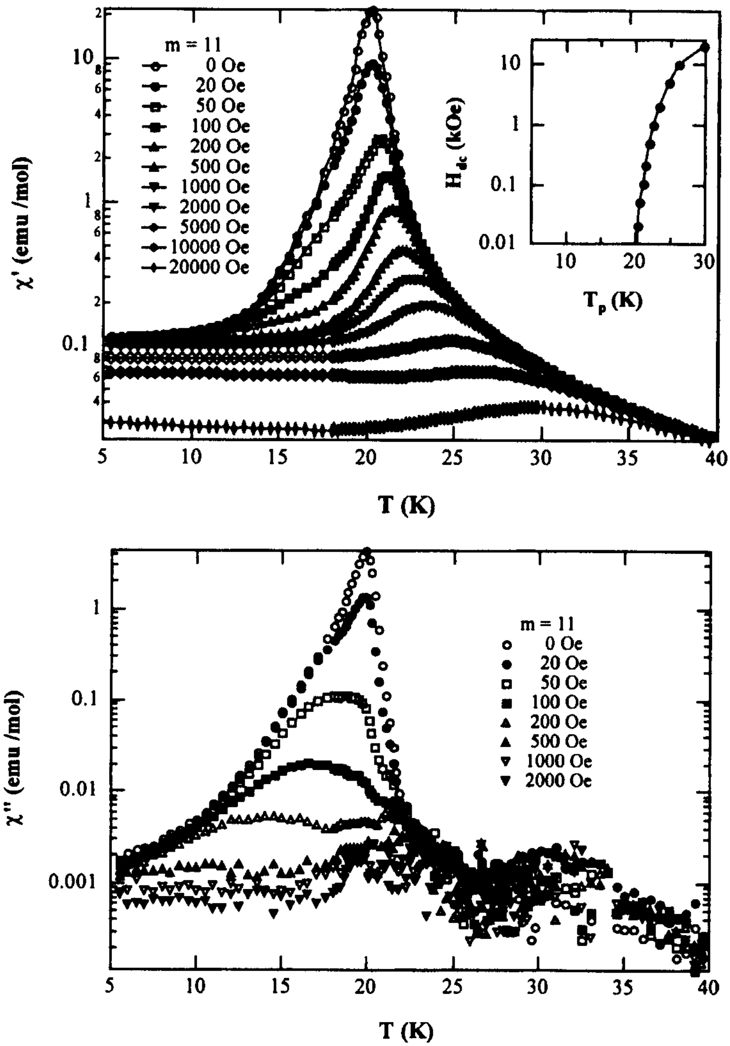

FIGURE 3: Real (top) and imaginary (bottom) parts of χ_1 versus T for $Cu_2(OH)_3(C_9H_{19}COO)$ in an ac field of f = 1000 Hz and h_o = 1 Oe, and various dc applied fields $0 \leq H_{dc} \leq 20000$ Oe. Inset: H_{dc} versus peak temperature in χ_1'.

The linear in-phase and out-of-phase ac susceptibility data at various temperatures are plotted versus H_{dc} in Fig. 4. The overall shape of the field dependence of χ_l' changes with *T*. At 5 K χ_l' varies weakly with H_{dc} at fields below 10 kOe, decreasing more rapidly at higher fields. As the temperature is increased, χ_l' has a more abrupt variation at small fields (H_{dc} = 1 kOe), the magnitude increasing monotonically for all $T \leq 20$ K (filled symbols in Fig. 5). As *T* is increased further (empty symbols in Fig. 5), the magnitude of χ_l' decreases monotonically while the field dependence gradually becomes weaker, especially at $H_{dc} > 1$ kOe, the $\chi_l'(H_{dc})$ curves changing shape. A qualitative similar behavior is observed for χ_l''.

This behavior is generally expected, as at low temperatures, even small fields are strong enough to reduce fluctuations. As *T* is increased stronger and stronger fields are needed to diminish the fluctuations, which grow towards the $T_c \approx 20$ K. Above the transition, as *T* is increased further, the magnetization fluctuations decrease again, such that smaller and smaller dc fields are able to lower χ_l'. The fast decrease of χ_l' in the higher field regime (H_{dc} = 10 kOe), similar for all temperatures, suggests that such fields are strong enough to "lock" the spins and suppress fluctuations.

CONCLUSIONS

We conclude that the results reported here are consistent with and strengthen our previous suggestion that the interplay between Heisenberg and DM exchanges leads to an unusual state in which order and disorder appear to coexist.

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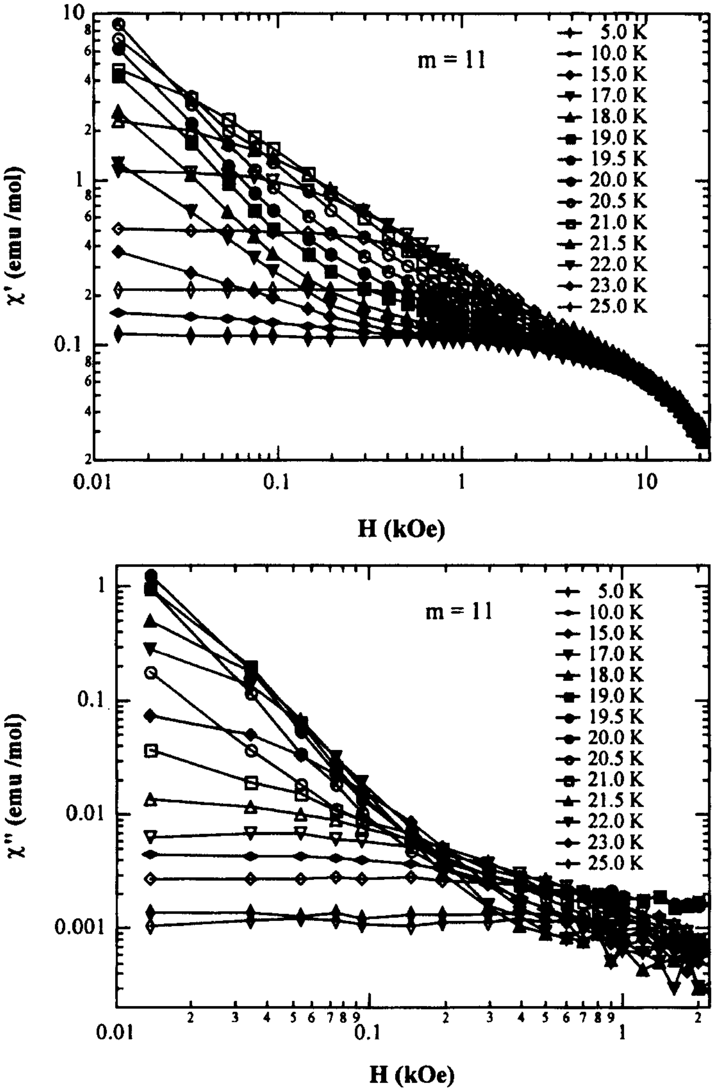

FIGURE 4: Real (top) and imaginary (bottom) parts of the ac susceptibility versus applied dc field for $Cu_2(OH)_3(C_9H_{19}COO)$ in an ac field of f = 1000 Hz and h_o = 1 Oe, at various temperatures $5 \leq T \leq 25$ K.

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