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Coexistence of glassiness and canted antiferromagnetism in triangular quantum Heisenberg antiferromagnets with weak Dzyaloshinskii-Moriya interaction

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We present magnetic studies of three triangular quantum Heisenberg antiferromagnets (TQHAF's) with weak additional Dzyaloshinskii-Moriya interaction, $Cu_2(OH)_3(C_mH_{2m+1}COO)$, $m=7$, 9, and 11. Fits of the dc susceptibility data to high-temperature series expansions agree with high-temperature TQHAF behavior. At low temperatures the deviations from the TQHAF predictions suggest a canted antiferromagnetic type of ordering, while the strong peak in the second harmonic of the nonlinear ac susceptibility indicates the development of a spontaneous moment. The frequency dependence of the linear ac susceptibility and the irreversibility in the field-cooled/zero-field-cooled magnetization show that frustration is strong enough to cause glassiness. We propose that the interplay of Heisenberg and Dzyaloshinskii-Moriya exchanges leads to the unusual coexistence of glassiness and canted antiferromagnetism in these geometrically frustrated systems. [S0163-1829(98)51710-9]

The debate whether frustration alone is strong enough to destroy magnetic order has preoccupied both the experimental and theoretical communities. Traditionally, spin glass behavior required both disorder and frustration.[1,2] It has been argued that frustration alone can lead to large ground-state degeneracies, accompanied by extensive ground-state entropies, but cannot produce a sufficiently ''rough'' free energy landscape necessary for the development of glassiness.[3] Since the effects of frustration are more pronounced in lower dimensions, the best candidates for disorder-free glassiness are two-dimensional (2D) antiferromagnets on triangular or *kagomé* lattices.[3,4] Such systems have been intensely studied in recent years, glassiness being found in *kagomé* systems[5] as well as in other materials,[6,7] all having continuous symmetry spins and sharing the same basic building block—the triangular plaquette—for their lattices. Each of these materials has its strengths and weaknesses as examples of spin glasses.[4]

Theoretically, the suggestion that the triangular spin-1/2 (quantum) Heisenberg antiferromagnet (TQHAF) is the simplest system to have a resonating valence bond (RVB) ground state (GS),[8] as opposed to the noncollinear semiclassical Néel state, has resulted in much debate and controversy. Other RVB-type variational wave functions have been proposed,[9] supporting the disordered spin liquid GS, but lower energy variational states preserving some of the long-range 120° noncollinear Néel-type order have been found.[10] Exact diagonalization of small clusters[11] suggested no magnetic long-range order (MLRO), while two more recent calculations reached opposite conclusions regarding the existence of MLRO.[12,13] Spin-wave theory,[14] high-temperature series expansions,[15] and renormalization group effective field theories[16] support various degrees of long-range noncollinear Néel ordering, however a consensus is yet to be reached.

The previously studied magnetic realization of TQHAF's has provided interesting results regarding the nature of the GS. While difficulties in the preparation of $NaTiO_2$ have so far impeded extensive studies, preliminary results are consistent with a disordered low-temperature phase.[17] Recent reports on thin films of K/Si (Ref. 18) and ^{3}He/graphite[19] presented various realizations of TQHAF's but did not show whether frustration is strong enough to lead to glassiness. Therefore, other systems are needed for addressing the controversy concerning the GS of TQHAF's.

In this paper we report, to our knowledge, the first evidence for hybrid organic/inorganic TQHAF's, $Cu_2(OH)_3(C_mH_{2m+1}COO)$, $m=7$, 9, and 11. Based on dc magnetization and magnetic irreversibility studies, and on linear and nonlinear ac susceptibility data we show that these compounds have an unusual magnetic behavior, presenting, due to the additional Dzyaloshinskii-Moriya (DM) interaction, neither the RVB nor the noncollinear Néel GS. Instead, we propose that the interplay between the Heisenberg antiferromagnetic exchange, causing frustration, and the DM interaction, leading to spin canting, allow these systems to evolve into an unusual state with both canted antiferromagnetic and spin glasslike characteristics.

The samples we have studied are compounds obtained by intercalation of saturated organic chains between inorganic layers of copper hydroxides.[20] The copper hydroxy salts $Cu_2(OH)_3X$ ($X=NO_3$, $C_mH_{2m+1}COO$, $m\geq 0$, etc.) exhibit a botallackite-type structure,[21] in which two crystallographically distinct copper atoms lie in different octahedral environments.[20] X-ray powder diffraction studies revealed

the layered structure with interlayer distances of 24.1, 29.4, and 34.4 Å for $m=7$, 9, and 11, respectively.[20] 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. The TEM photographs revealed interference patterns usually observed in structurally ordered materials.[22] Extended x-ray absorption fine structure (EXAFS) measurements showed[23] that the powder samples of the intercalation compounds maintain the basic framework of the crystalline inorganic layer $Cu_2(OH)_3NO_3$, with slight distortions of the local octahedral symmetry.

The Cu^{2+} ions with no single ion anisotropy are associated with $S=1/2$ isotropic Heisenberg spins located on nonequilateral planar triangular magnetic lattices.[20,21] The most important interactions consistent with this structure are the Heisenberg (symmetric) superexchange ($\mathcal{H}_H = -\Sigma 2J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$) through oxygen atoms[24] and the weaker DM (antisymmetric) exchange ($\mathcal{H}_{\rm DM}=\Sigma\mathbf{D}_{ij}\cdot\mathbf{S}_i\times\mathbf{S}_j$) (Ref. 25) caused by the spin-orbit interactions and the different local environments of adjacent copper sites.[23] DM interaction recently was shown to be responsible for canted antiferromagnetic behavior in another 2D oxygen bridged copper system, the parent compounds for high-temperature superconductors.[26]

The ac magnetic susceptibility was measured with a Lake Shore 7225 ac susceptometer/dc magnetometer in zero dc applied field and in the temperature range $5\leqslant T\leqslant 30$ K, on warming. Both the in-phase (χ_1') and out-of-phase (χ_1'') linear susceptibilities, $\chi_1=\chi_1'+i\chi_1''$, were measured under an ac field $H_{\rm ac}=1$ Oe and a wide range of frequencies ($5\leqslant f\leqslant 10000$ Hz). The second and third harmonics of the magnetic susceptibility χ_2 and χ_3 were obtained by reading the $2f$ and $3f$ lock-in responses, respectively, to an ac field with frequency f. The harmonics were measured on warming, in zero applied magnetic field, at fixed ac field amplitude (1.3 Oe) and frequencies between 10 and 3330 Hz. The magnetization was measured with a Quantum Design MPMS 5 SQUID magnetometer for $5\leqslant T\leqslant 350$ K and $0\leqslant H_{\rm dc}\leqslant 55000$ Oe.

The temperature dependence of the static susceptibility $\chi_{\rm dc}$ is shown as the $\chi_{\rm dc}T$ product in Fig. 1. Upon decreasing T from room temperature $\chi_{\rm dc}T$ first decreases, indicating antiferromagnetic correlations and then, below 50 K, increases, with a peak around 20 K. In the inset the curves (normalized by their Curie constants) overlay each other. The independence on interlayer distances suggests true 2D behavior. The fit to the high T series expansions for TQHAF (Ref. 15) confirms this behavior for $120\leqslant T\leqslant 350$ K. The values of the two free parameters, the average exchange coupling constant[24] and the Curie constant (or, equivalently, the Landé g factor), are similar for the three compounds: $-2J=62$, 56, 54 K and $C=0.53$, 0.54, 0.58 emu K/mol ($g=2.37$, 2.40, 2.48), for $m=7$, 9, and 11, respectively. The substantial increase in interlayer separation correlates with a small decrease in the exchange and a small increase in the g factor of the copper spins.

The upward trend of the $\chi_{\rm dc}T$ product below 50 K indicates ferromagnetic correlations between the spins, the sharp peak suggesting a transition with a critical temperature $T_c \approx 20$ K for all three compounds. This behavior is likely due

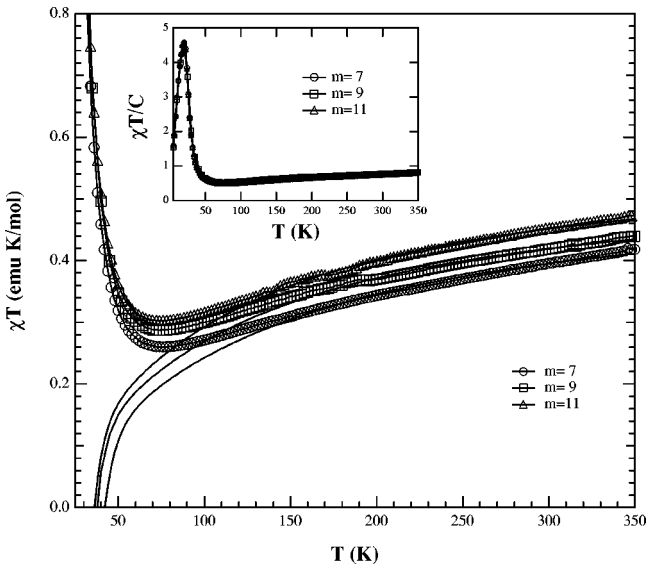

FIG. 1. $\chi_{\rm dc}T$ product for $Cu_2(OH)_3(C_mH_{2m+1}COO)$, $m=7$, 9, and 11 at $H_{\rm dc}=5000$ Oe, and fit to high-temperature series expansions predictions. Inset: the $\chi_{\rm dc}T$ product is normalized to the Curie constant.

to the spin canting caused by the additional DM exchange, whose strength[25] is $D_{ij}\sim[(g-2)/g]2J_{ij}\sim 2J_{ij}/5$.

The fit to the Curie-Weiss law $\chi_{\rm dc}^{-1}=(T+\Theta_{\rm CW})/C$ for $T\geqslant 200$ K gave mean field ordering temperatures $\Theta_{\rm CW}$ of 140, 130, and 120 K, for $m=7$, 9, and 11, respectively. This quantity allows the calculation of a parameter $\Theta_{\rm CW}/T_c = f_R$, which describes the degree of frustration of geometrically frustrated systems.[7] We obtained for our compounds values of 7, 6.5, and 6, respectively, suggesting moderate strength frustration.

The lowest frequency (5 Hz) χ_1' data for the three compounds is displayed in the inset of Fig. 2. The independence of the peak temperatures ($T_p=19.1$, 19.3, and 19.0 K, for $m=7$, 9, and 11, respectively) on the interlayer distances indicates that the magnetic behavior is governed by the intralayer interactions and, therefore, that these compounds are true 2D systems. The sharp peaks suggest divergencies of the susceptibility and, therefore, true phase transitions. Kouvel-Fisher scaling analyses[27] give similar critical exponents γ, with values close to that of a 2D Ising system, $\gamma=1.75$.[28]

The peak temperature of χ_1' increases and the peak height decreases with increasing frequency, Fig. 2, indicative of slow relaxation processes that characterize the glassy behavior.[2,29] 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, place these compounds in the range of canonical spin glasses.[2]

The field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves for the $m=7$ compound ($m=9$ and 11 compounds have almost identical behavior[28]), Fig. 3, show, with decreasing T, a rapid rise just above 20 K. At lower T the ZFC magnetization deviates below the FC magnetization indicating history dependence of the magnetization processes in the T range where χ_1' shows frequency dependence. The field dependence of the bifurcation point T_b between the FC and ZFC curves (T_b decreases with increasing the applied dc

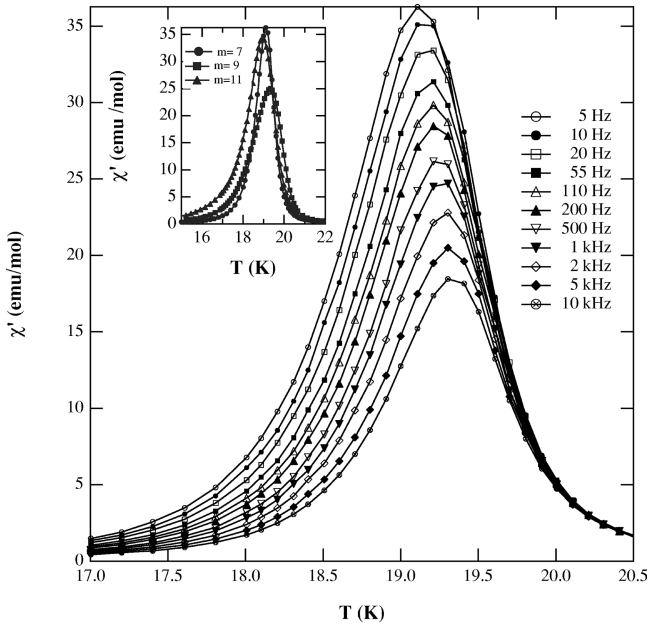

FIG. 2. χ_1' of $Cu_2(OH)_3(C_7H_{15}COO)$, in $H_{dc}=1$ Oe (zero applied dc field) at frequencies $5 \leqslant f \leqslant 10000$ Hz. Inset: χ_1' of $Cu_2(OH)_3(C_mH_{2m+1}COO)$, $m=7$, 9, and 11, in $H_{ac}=1$ Oe (zero applied dc field) at $f=5$ Hz.

field) reinforces the glassy behavior description.[30,31]

Even harmonics can be observed only if a system exhibits a spontaneous magnetization, due to the lack of inversion symmetry with respect to the applied field.[32] Therefore, for a spin glass only odd harmonics are expected while for ferromagnets both even and odd harmonics should be present.[33] Both second and third harmonics ($2f$ and $3f$ responses, respectively), for the $m=7$ compound, Fig. 4 (again the $m=9$ and 11 compounds have almost identical behavior[28]), have sharp peaks suggesting divergencies of both these quantities and, therefore, true magnetic transitions. The peak in the second harmonic indicates that a spontaneous moment is

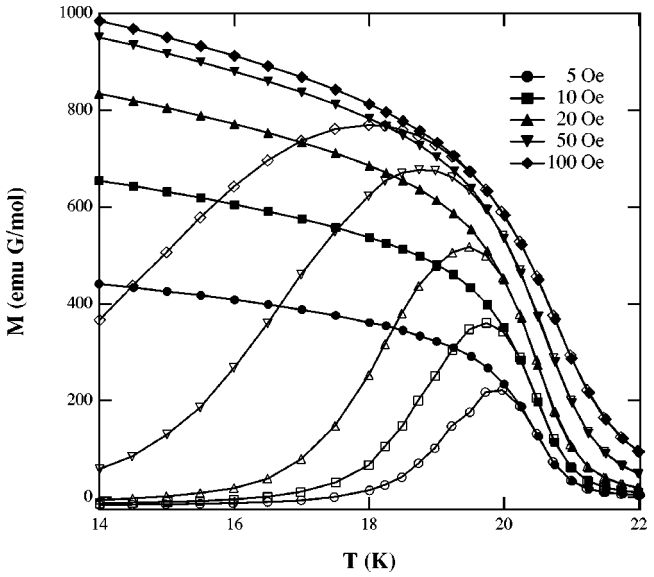

FIG. 3. FC (filled symbols) and ZFC (empty symbols) magnetization of $Cu_2(OH)_3(C_7H_{15}COO)$ in dc applied fields of $5 \leqslant H_{dc} \leqslant 200$ Oe.

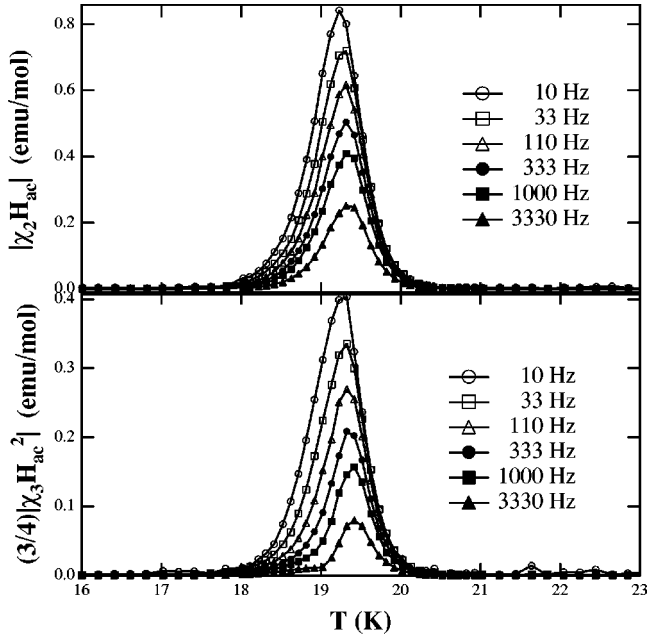

FIG. 4. Nonlinear susceptibilities $|\chi_{2,\mathrm{exp}}H_{ac}|$ and $|\frac{3}{4}\chi_{3,\mathrm{exp}}H_{ac}^2|$ of $Cu_2(OH)_3(C_7H_{15}COO)$ measured at $2f$ and $3f$, respectively, in $H_{ac}=1.3$ Oe (zero dc field) at frequencies $10 \leqslant f \leqslant 3330$ Hz.

formed at that transition while the frequency dependence of both components of the nonlinear susceptibility suggests slow relaxation processes and glassiness.

Hysteresis curves give[28] saturation magnetization values of ~1440, 1480, and 1550 emu Oe/mol-Cu, for $m=7$, 9, and 11, respectively, well below the value of 5585 emu Oe/mol expected for a spin-1/2 $g=2$ ferromagnet. That these values are smaller than the ferromagnetic limit is consistent with both the spin canting and/or spin freezing pictures. The small increase of the saturation magnetization with the interlayer distance is in agreement with the slight increase in the g factor of the copper spins.

Thus, all three systems show very similar magnetic properties. High-temperature TQHAF behavior is in accord with the fit to high-temperature series expansions. The frequency dependence of the linear ac susceptibility and the field dependence of the bifurcation point of the field-cooled/zero-field-cooled magnetization data suggest that geometrical frustration is strong enough to cause slow relaxation and glassiness. The low-temperature dc susceptibility and the second harmonic of the nonlinear ac susceptibility indicate that frustration cannot prevent the additional DM interaction from leading to a canted antiferromagnetic type of ordering.

In real compounds, there usually exist either symmetry-reducing lattice distortions[4] or additional interactions[7] which relieve frustration and allow the system to order at a temperature determined by the dominant interaction strength. The existence of a phase transition at finite temperatures for geometrically frustrated Ising and Heisenberg systems depends on the connectedness of the different GS's.[34] The process by which the system can eventually select the GS for which the density of low-lying excited states is a maximum was called ''order by disorder.''[35] If, on the other hand, zero-temperature disorder contaminates the whole system at finite temperatures no phase transition occurs at any T.[36] A third possibility, of coexistence below a finite T of partial order

and partial disorder, was called ''order with disorder.''[34]

We, therefore, propose that the unusual behavior of these three TQHAF systems is determined by the interplay between the Heisenberg exchange, causing geometrical frustration and glassiness, and the DM exchange, causing spin canting and 2D Ising-like behavior. Instead of choosing between the RVB (spin liquid) or noncollinear Néel GS's, these systems evolve towards a phase in which order and disorder appear to coexist.

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