Glassiness and canted antiferromagnetism in three geometrically frustrated triangular quantum Heisenberg antiferromagnets with additional Dzyaloshinskii-Moriya interaction

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We report results of extensive 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 are consistent with high-temperature TQHAF behavior. At low temperatures the deviations from the TQHAF predictions suggest a canted antiferromagnetic type of ordering, consistent with the strong peak in the second harmonic of the nonlinear ac susceptibility, which 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 reveal spin-glass-like behavior. Glassy behavior also is suggested by the specific heat data, which show only a weak broad feature at the transition. We propose that, instead of choosing between the resonant valence bond or noncollinear Néel ground states expected for the ideal TQHAF, these systems undergo, due to the additional Dzyaloshinskii-Moriya interaction, a finite temperature phase transition to a state with both Ising-like canted antiferromagnetic and glassy characteristics. The interplay of Heisenberg exchange, causing frustration, and Dzyaloshinskii-Moriya interaction, determining spin canting, leads to an unusual state in which order and disorder appear to coexist.

I. INTRODUCTION

In the past decade there has been increased interest in systems that exhibit new types of magnetic ordering as a consequence of competing interactions.[1] Frustration (occurring when no spin configuration can simultaneously minimize all the interactions) is generated by the competition between interactions of different kind (e.g., competing ferro- and antiferromagnetic interactions or competing nearest-neighbor and next-nearest-neighbor interactions) or by the topology of the lattice (e.g., triangular, kagomé, pyrochlore lattices with antiferromagnetic nearest-neighbor interactions, etc.).[2]

The recent interest in geometrically frustrated systems is 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] Noncollinear Neèl LRO occurs when frustration can be released by spin configurations that are not antiparallel, as in the traditional Neèl state. Simple examples are the triangular Heisenberg or XY antiferromagnets (AF) with classical spins, in which cases 120° configurations minimize the total energy. Order by disorder is a phenomenon that occurs in systems with high degeneracy of the classical ground state (GS), by which the system can select, by means of thermal, quantum, or quenched fluctuations, the most ''flexible'' subset of the GS manifold, the one for which density of low-lying excited states is a maximum.[3,4] The coexistence, below a finite T, of partial order and partial disor-

der was called ''order with disorder.''[5] Such coexistence in an equilibrium state of magnetic order and disorder occurs when one or more sublattices order below the critical temperature T_c, while at least one sublattice stays disordered at all temperatures.[5,6] Quantum disorder can be manifest in the quantum spin-liquid GS associated initially with triangular[7] and more recently with pyrochlore[8] AF's.

Recently, increased numbers of experimental realizations of such geometrically frustrated systems have been achieved.[1,9–11] Extensive experimental studies of such materials showed in some cases evidence of spin-glass-like behavior, which may not always be due to the presence of disorder, as in the case of spin glasses.[12–16] These results raise questions such as whether the glassy behavior is intrinsic to the pure frustrated system or even the smallest degree of disorder (very difficult to detect) is sufficient to be responsible for the spin-glass-like characteristics, whether the glassiness found in the pure frustrated systems is identical to the one observed in the random frustrated systems (spin glasses), and what is the universality class, if any.

Traditionally, spin-glass behavior required both randomness and frustration.[17,18] One of the main conclusions of the a review on spin glasses[17] was that although many of the pure frustrated models have nonperiodic GS's, the state at finite temperature is always a simple periodic magnetic structure, and no spin-glass phase could be found. However, there can be long-lived nonperiodic metastable states such that the dynamic properties of such systems are more spin-glass-like than the static properties. Moreover, if disorder is

added fully frustrated systems could be made into spin glasses.

The theoretical possibility for disorder-free glassiness in the case of frustrated Heisenberg systems remains controversial even for the most highly frustrated systems.[19] It was argued that structural disorder could have either an ordering or a disordering effect depending on the type (site or bond) and degree of disorder, the properties of the degeneracy manifold, and the space dimension.[4,19,20] For some nominally disorder-free geometrically frustrated compounds[12–16] additional interactions may be necessary to explain the spin freezing and glassiness observed.[9,19] Single-ion anisotropy (SIA) has been the most common additional interaction proposed to be responsible for the glassy behavior,[16,19] while the Dzyaloshinskii-Moriya (DM) interaction has not been extensively considered, though it can become crucial for $S = 1/2$ systems, for which there is no SIA.

Triangular Heisenberg AF's recently have been intensely studied both theoretically and experimentally.[11] Most of the experimental realizations have been systems with stacked lattices. Various noncollinear states (and in particular the 120° GS) predicted theoretically were actually observed, however the ordering in these systems is three-dimensional.[11] It was determined that interlayer interactions and SIA play an important role in the magnetic ordering, while site disorder did not affect significantly the ordered GS in such systems.[11]

Regarding the triangular spin-1/2 (quantum) Heisenberg antiferromagnet (TQHAF), the suggestion that this is the simplest system to have a resonating valence bond (RVB) ground state,[7] as opposed to the noncollinear semiclassical Néel state, has resulted in much debate and controversy. Other RVB-type variational wave functions have been proposed,[21] supporting the disordered spin liquid GS, but lower energy variational states preserving some of the long-range 120° noncollinear Néel-type order also have been found.[22] Exact diagonalization of small clusters[23] suggested no long range order, while two more recent calculations reached opposite conclusions regarding the existence of magnetic LRO.[24,25] Spin-wave theory,[26] high-temperature series expansions,[27] and renormalization group effective field theories[28] support various degrees of long-range noncollinear Néel ordering, however a true consensus is yet to be reached.

The previously studied magnetic realization of TQHAF's has not provided conclusive results regarding the nature of the GS. The difficulties in the preparation of NaTiO$_2$ have impeded extensive studies, though preliminary results are consistent with a disordered low-temperature phase.[29] The interest in TQHAF's has recently increased due to new theoretical and experimental studies on nonmagnetic analogues.[30–34] However, these reports did not settle the controversy concerning the GS of TQHAF's, and new systems are needed to address it.

In this paper we present extensive magnetic studies of the recently reported[35] hybrid organic/inorganic TQHAF's with weak additional Dzyaloshinskii-Moriya interaction, $Cu_2(OH)_3(C_mH_{2m+1}COO)$, $m = 7$, 9, and 11. These hybrid nanocomposites are examples of molecule-based magnets[36] with a two-dimensional (2D) magnetic lattice, the most important interactions being Heisenberg and DM exchanges.[35] Based on dc magnetization and magnetic irreversibility stud-

ies, and on linear and nonlinear ac susceptibility data we showed[35] 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 proposed[35] that the interplay between the Heisenberg antiferromagnetic exchange, causing frustration, and the DM interaction, leading to spin canting, allow these systems to evolve, into a new, unusual state with both 2D Ising-like canted antiferromagnetic and spin-glass-like characteristics. Here we expand those studies, presenting extensive data for all three compounds. Based on dc magnetization and magnetic irreversibility studies, linear and nonlinear ac susceptibility data, and specific heat data we show that these three compounds have a similar but unusual magnetic behavior. Moreover, static scaling analyses of the magnetization and of the susceptibility as well as dynamic scaling and Cole-Cole analyses strengthen our previous conclusions.

The paper is organized as follows: In Sec. II we introduce the materials, discussing their structure as well as the main interactions likely to be responsible for their magnetic behavior. We follow with a description of the experimental apparatus and the measurement techniques used. Section III presents the experimental data together with the results of static and dynamic scaling analyses. In Sec. IV we discuss the correlation between structure and magnetic behavior, the role of additional interactions, structural disorder, and quantum fluctuations. We speculate on the possibility of partial order in these compounds. Section V is devoted to conclusions.

II. EXPERIMENT

A. Materials

The samples studied are compounds obtained by intercalation of saturated organic chains between inorganic layers of copper hydroxides.[37,38] The copper hydroxy salts $Cu_2(OH)_3C_mH_{2m+1}COO$, $m \geqslant 0$, exhibit a botallackite-type structure,[39] Fig. 1(a), in which two-crystallographically distinct copper atoms lie in slightly different octahedral environments.[37] Extended x-ray absorption fine structure measurements showed[40] that the powder samples of the intercalation compounds maintain the basic framework of the crystalline inorganic layer of the parent compound $Cu_2(OH)_3NO_3$, with only minor distortions of the local environment. The 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.[37] 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 only in structurally ordered materials.[41]

The spin-carrying units are $S = 1/2$ Cu^{2+} ions with no single-ion anisotropy, located on a planar lattice.[37,40] The most important interaction consistent with the structure presented in Fig. 1(a) is the isotropic Heisenberg (symmetric) exchange: $\mathcal{H}_H = -\Sigma 2J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$. The (super-) exchange interaction[42] is mediated by two types of bridging oxygen atoms, one from the OH groups, the other from COO groups. As there are unique Cu-O-Cu angles between each pair of Cu
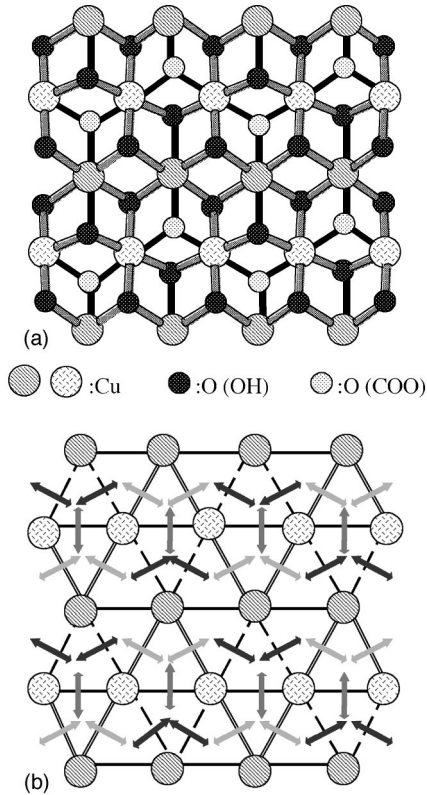
FIG. 1. (a) Proposed intralayer structure of $Cu_2(OH)_3(C_mH_{2m+1}COO)$, $m=7$, 9, and 11 based on the structure of the parent compound $Cu_2(OH)_3NO_3$ (Ref. 43). Arrows show the directions of slight anisotropy. (b) Suggested magnetic lattice of $Cu_2(OH)_3(C_mH_{2m+1}COO)$, $m=7$, 9, and 11. The different symbols for the lines connecting the spin sites suggest different strengths of the Heisenberg exchange coupling, while the arrows show probable orientations of the various DM vectors $\mathbf{D}_{ij}$. The interactions are distributed periodically throughout the lattice.

ions, the strength of the exchange interactions also vary[40] causing the magnetic lattice to consist of nonequilateral triangles.

According to the Goodenough-Kanamori[42] rules the exchange coupling constant depends on the angles between magnetic ion–ligand–magnetic ion, angles of 180° (strong orbital overlap) and 90° (orthogonal orbitals) leading to strong antiferromagnetic and ferromagnetic interactions, respectively. For intermediate angles, even small deviations from 90° and/or the presence of side groups coupled to the ligands may be sufficient for the interactions to become antiferromagnetic.[43] In the $Cu_2(OH)_3(C_mH_{2m+1}COO)$, $m=7$, 9, and 11 compounds, given the Cu-O-Cu angles and the presence of the side groups bound to the oxygen ligands,[43] the intralayer exchange interaction was found to be antiferromagnetic.[40,44]

When the local environments of adjacent spin sites are different the DM (antisymmetric) exchange,[45] $\mathcal{H}_{DM} = \Sigma \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j$, caused by the spin-orbit interaction, can add to the usual Heisenberg exchange. This additional interaction is always weaker than the Heisenberg exchange and favors perpendicular spin alignments. The direction of the DM axial vector $\mathbf{D}_{ij}$ could be determined based on the symmetries relating adjacent spin sites. In particular, if an inversion center is located half way between the two sites $\mathbf{D}_{ij}$ is zero, while if

there is a mirror plane including the two sites $\mathbf{D}_{ij}$ is perpendicular to that plane.[46] For the compounds reported here the octahedral symmetry around the Cu ions is slightly altered by the inequivalency of the six oxygen ligands, some being part of an OH group others of an COO group.[37] This small anisotropy varies from site to site leading to a variety of DM vectors.

Figure 1(b) shows the suggested simplified magnetic lattice of $Cu_2(OH)_3(C_mH_{2m+1}COO)$, $m=7$, 9, and 11. The different symbols for the lines connecting the spin sites suggest different strengths of the Heisenberg exchange coupling. The arrows show probable directions of the DM vectors $\mathbf{D}_{ij}$ (not necessarily in the plane of the lattice), the different symbols suggesting different interaction strengths. The interactions are distributed periodically but not uniformly throughout the lattice. Though this suggested magnetic lattice is clearly oversimplified (especially in predicting the directions of the DM vectors) it represents the principal magnetic interactions and could constitute a starting point for theoretical studies.

The interlayer interactions are expected to be very small, likely negligible. The direct exchange between unpaired electrons located in adjacent layers is very small because of the negligible overlap of the orbitals involved, due to the large interlayer separation. The exchange through spin polarization is also negligible as the organic chains have only saturated carbon atoms. Also, the interlayer dipole-dipole interactions are likely negligible ($\sim 10^{-4}$ K) due to the large interlayer distances, which are about tenfold larger than the intralayer spin-spin distances. The dipolar interactions[47] probably play an important role only at low temperatures. It is, therefore, very likely that these compounds are good realizations of 2D systems.

B. Measurement techniques

The powder samples, with masses of ~ 20 mg, were sealed at room temperature in quartz tubes with known magnetic background signal. The measurements of the linear ac magnetic susceptibility and its harmonics were made with a Lake Shore 7225 AC Susceptometer/DC Magnetometer in the temperature range $5 \leq T \leq 30$ 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 $H_{ac} = h_0 \sin(2\pi f t)$ with $h_0 = 1$ Oe (in zero dc applied field) and a wide range of frequencies ($5 \leq f \leq 10000$ 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 linear ac magnetic susceptibility was also measured in various dc applied fields $0 \leq H_{dc} \leq 50$ kOe and in the temperature range $5 \leq T \leq 40$ K, at constant field on warming.

The magnetization was measured with a Quantum Design MPMS 5 SQUID magnetometer. The temperature dependence of the static susceptibility was determined based on magnetization data collected on cooling between 350 K and 5 K in a dc applied field of 5000 Oe. Hysteresis curves were obtained at 5 K for applied fields of $-55000 \leq H_{dc}$

≤55000 Oe, after cooling with no applied field through the transition. The remanent magnetization was measured after taking precautions for properly zeroing the applied dc field, to within 0.05 Oe. The sequence for the measurements consisted of: cooling the system in a small dc field (5 Oe at first) from 50 K (a temperature at least twice the T_c) to 5 K, well below the transition; turning the applied field to zero at 5 K; taking data on warming in zero applied dc field at ~0.2 K/min; repeating the sequence for higher fields, up to 50 Oe. (Fields higher than 50 Oe were avoided because of the danger of trapping flux in the superconducting magnet, which would than compromise the zeroing of the dc field. Fields lower than 5 Oe lead to noisy data.) Field-cooled and zero-field-cooled magnetization data were collected on warming in the range $5 \leq T \leq 30$ K in various applied dc fields. The sequence for the measurements consisted of: cooling the system in zero applied dc field from 50 K to 5 K; turning the applied field on at 5 K; taking zero-field-cooled (ZFC) data on warming at ~0.5 K/min in the applied dc field; cooling the system in the same applied dc field from 50 K to 5 K; taking FC data on warming in the applied dc field; repeating the sequence for higher fields ($5 \leq H_{dc} \leq 200$ Oe).

The specific heat data were collected with a Quantum Design PPMS. The samples were cut from pressed pellets (masses between 7.5 and and 9.8 mg) and were mounted on the sample holder using a small amount of Apiezon N grease. To separate the contribution of the sample heat capacity from the addenda, the heat capacity of the sample holder with the grease was measured over the full temperature range ($1.9 \leq T \leq 300$ K) prior to mounting each sample. All measurements were done in the absence of an applied magnetic field. Each data point corresponds to a single relaxation measurement, where the sample holder is heated at constant power for half the characteristic time-constant of the calorimeter, followed by a cooling period. The heat-capacity values were extracted from the temperature response curves by fitting to the solution of a dual time-constant thermal model,[48] thus minimizing thermal contact artifacts.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. Canted antiferromagnetic behavior

The temperature dependence of the static susceptibility χ_{dc} for $Cu_2(OH)_3(C_mH_{2m+1}COO)$, $m=7, 9$, and 11, was presented elsewhere as $\chi_{dc}T$ vs T.[35] It was shown that upon decreasing T from room temperature the $\chi_{dc}T$ product first decreases, indicating antiferromagnetic correlations and then, below 50 K, increases, with a peak at ~20 K. The $\chi_{dc}T$ curves for $m=7, 9$, and 11 normalized by their Curie constants overlay each other, demonstrating independence on interlayer distances and suggesting true 2D behavior.

The fit to the high-T series expansions for TQHAF[27] is consistent with such behavior for $120 \leq T \leq 350$ K. The values of the two free parameters, the average exchange coupling constant, and the Curie constant (or, equivalently, the Landé g factor), were found[35] 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 large increase in interlayer separation correlates
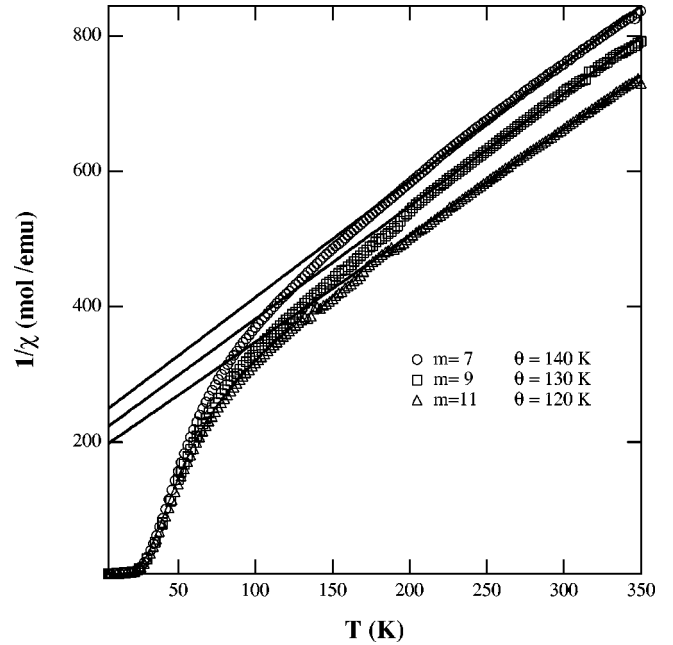

FIG. 2. χ_{dc}^{-1} vs T for $Cu_2(OH)_3(C_mH_{2m+1}COO)$, $m=7, 9$, and 11 at $H_{dc} = 5000$ Oe, and fits to Curie-Weiss mean field predictions.

with a small decrease in the exchange and a slight increase in the g factor of the copper spins.

The upward trend of the $\chi_{dc}T$ product below 50 K indicated[35] 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 to the spin canting caused by the additional DM exchange, whose strength is estimated[46] at $D_{ij} \sim [(g-2)/g]J_{ij} \approx 5$ K.

The fit to the Curie-Weiss law $\chi_{dc}^{-1} = (T + \Theta_{CW})/C$ for $T \geq 200$ K (Fig. 2) gives mean field Θ_{CW} of 140, 130, and 120 K, for $m=7, 9$, and 11, respectively. This quantity allows the calculation of the ratio Θ_{CW}/T_c, which may correlate with the degree of frustration.[9] We obtain values of 7, 6.5, and 6, respectively, suggesting moderate strength frustration.[9] A better estimate of the degree of frustration is $f_R = \Theta_{CW}/T_N$ which relies on the use of the Neèl temperature, corresponding to an antiferromagnetic transition (in this case in the absence of the DM interaction, perhaps due to 3D interactions, etc.). Thus, we estimate even stronger frustration, as T_N would very likely be much lower than 20 K.

Hysteresis curves at 5 K (Fig. 3) give saturation magnetization values of ~1440, 1480, and 1550 emu Oe/mol-Cu (below the value of 5585 emu Oe/mol expected for a spin-1/2 $g = 2$ ferromagnet), and coercive fields of 600, 900, and 1000 Oe for $m=7, 9$, and 11, respectively. The saturation magnetizations correlate with the g values determined from the high-temperature static susceptibility. It is noted that both g and the saturation magnetization increase monotonically with m. If instead of the spin-only value for the g factor $g=2$ we use the values obtained above from the fit to high-temperature series expansions ($g = 2.37, 2.40, 2.48$) we calculate expected ferromagnetic saturation magnetizations values of 6620, 6700, and 6925 emu Oe/mol. Therefore, the experimental saturation magnetizations are significantly smaller
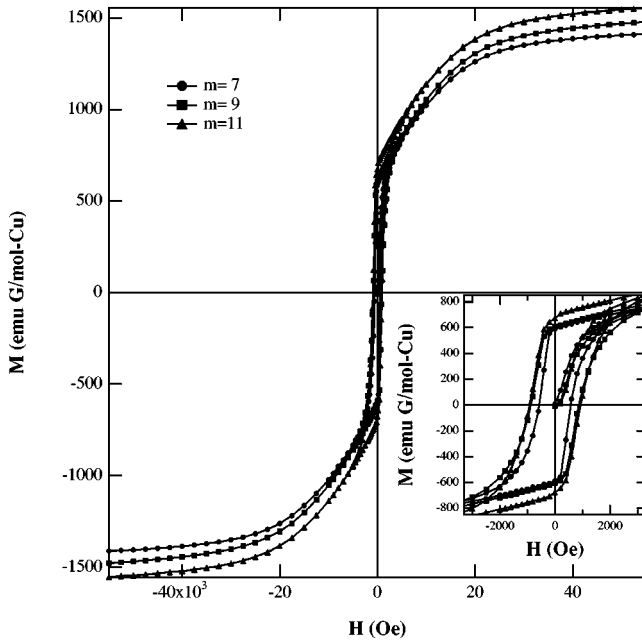
FIG. 3. Hysteresis curves for $Cu_2(OH)_3(C_mH_{2m+1}COO)$, $m = 7, 9,$ and 11 at $T = 5$ K. Inset: details of the low-field region showing the coercive fields.

(~ 4.5 fold) than the ones expected for a ferromagnetic material, consistent with spin canting and/or noncollinear spin configuration pictures.

The lowest frequency (5 Hz) χ_1', Fig. 4, data demonstrates 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. Thus the magnetic behavior is governed by the intralayer interactions and, therefore, these compounds are true 2D systems.

The sharp peaks (variations of almost three orders of magnitude over less than three degrees) suggest divergencies of the susceptibility and, therefore, true phase transitions.
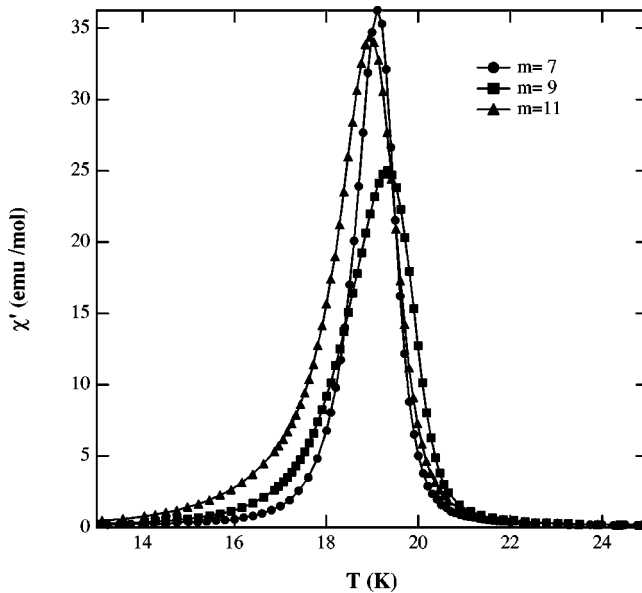

FIG. 4. χ_1' of $Cu_2(OH)_3(C_mH_{2m+1}COO)$, $m = 7, 9,$ and 11, in $h_0 = 1$ Oe (zero applied dc field) at $f = 5$ Hz.

The divergence of the magnetic susceptibility can be studied using Kouvel-Fisher scaling analysis,[49] which makes use of the scaling law:

$$\chi \propto (T - T_c)^{-\gamma} \qquad (1)$$

and defines a new function:

$$X_{KF} = \frac{1}{\chi(d\chi^{-1}/dT)} \qquad (2)$$

to determine T_c and γ:

$$X_{KF} = \frac{T - T_c}{\gamma}. \qquad (3)$$

Kouvel-Fisher scaling analyses of the linear susceptibility data (Fig. 4) are presented in Fig. 5 for all three compounds. The parameters obtained through such analyses are $T_c = 19.0, 19.7,$ and 19.5 K and $\gamma = 1.81, 1.75,$ and 1.78 for $m = 7, 9,$ and 11, respectively. The error in the determination of the γ values is estimated to about ± 10–15 %, mainly due to the various choices for the temperature ranges where data were fitted to a straight line. The final choices reflect the best fits in ranges of reduced temperature of about $0.01 \leqslant (T - T_c)/T_c \leqslant 0.15$.

All three compounds have similar critical exponents γ, with values close to that of a 2D-Ising system, $\gamma = 1.75$, significantly larger than 1.24 for 3D Ising or 1.39 for 3D-Heisenberg systems.[50] Although the error in these fits is relatively large, it is clear that the lower bound for the γ exponent would still be far above the 3D ones, suggesting that these systems have Ising-like behavior, despite the absence of single-ion anisotropy. Such a behavior is likely due to the anisotropy caused by the additional DM interaction.

The field dependence of the remanent magnetization and the normalized remanent magnetization—obtained dividing the actual value at each T by the value at the lowest temperature measured 5 K, $M(T)/M(5K)$—for all three compounds are shown in Fig. 6. The low-field normalized remanence data are consistently above the higher-field values and show sharper temperature variations, the transition being best probed at the lowest applied field of 5 Oe. These data were used for static scaling analyses, to find T_c and the critical exponent β:

$$M \propto (T_c - T)^{\beta}. \qquad (4)$$

The fits to the power law behavior below T_c, Fig. 6, give $T_c = 19.9, 19.8,$ and 19.5 K and unusually large values of $\beta = 0.81, 0.76,$ and 0.80 for $m = 7, 9,$ and 11, respectively. The errors in the determination of these values is estimated to about ± 10–15 %, mainly due to the various possible choices for the temperature ranges where data were fitted. The final choices were made such that the region fitted was beyond saturation and within the critical regime (ranges of reduced temperature of roughly $0.005 \leqslant (T - T_c)/T_c \leqslant 0.1$) and such that the best fit could be obtained.

All three compounds have similar critical exponents β, with values significantly larger than the 0.125 (0.3 experimentally) for 2D Ising, 0.32 for 3D Ising, or 0.36 for 3D-Heisenberg systems.[50] Even though the errors of these fits

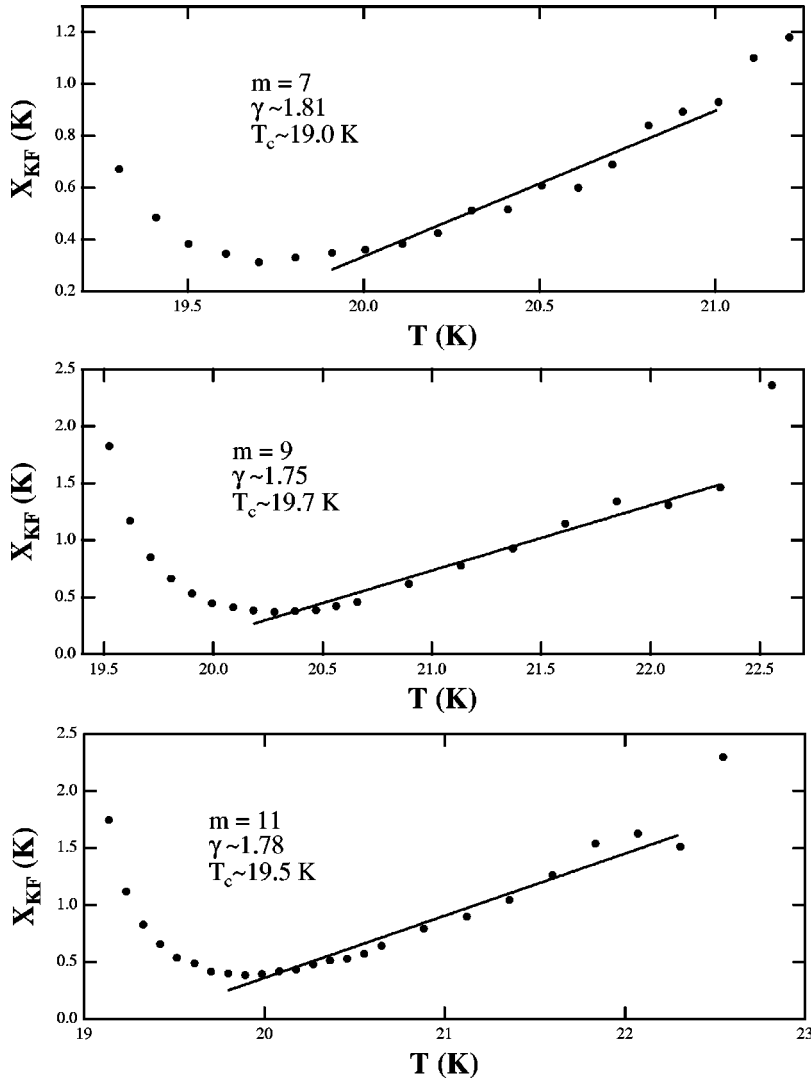FIG. 5. Kouvel-Fisher scaling analysis of χ_1' data of Fig. 6 for $Cu_2(OH)_3(C_mH_{2m+1}COO)$, (a) $m=7$, (b) $m=9$, and (c) $m=11$.

are relatively large, the lower limit of the values for the critical exponents are still much larger than any of the known β exponents. These large values deserve further study.

The nonlinear susceptibility can provide important information regarding the existence of a phase transition, the nature of the transition, and the dynamics near the transition. For a ferromagnet (FM) the magnetization M can be expanded in a power series with respect to the magnetic field, H, as:

$$M_{FM} = M_0 + \chi_1 H + \chi_2 H^2 + \chi_3 H^3 + \cdots, \quad (5)$$

where M_0 is the spontaneous magnetization, χ_1 the linear magnetic susceptibility, and χ_2, χ_3, etc. are the nonlinear components of the susceptibility. The even nonlinear components can be observed because of the lack of inversion symmetry with respect to the applied field.[51] For a SG there is no spontaneous magnetization and M can be expressed in terms of only the odd powers of H:[52]

$$M_{SG} = \chi_1 H + \chi_3 H^3 + \cdots. \quad (6)$$

In the case of a small amplitude ac field and no applied dc field the linear and nonlinear susceptibilities are related to the harmonics measured experimentally by:[53]

$$\chi_{1,exp} = \chi_1 + \frac{3}{4}\chi_3 h_o^2 + \cdots \approx \chi_1, \quad (7)$$

$$\chi_{2,exp} h_o = \chi_2 h_o + \chi_4 h_o^3 + \cdots \approx \chi_2 h_o, \quad (8)$$

$$\frac{3}{4}\chi_{3,exp} h_o^2 = \frac{3}{4}\chi_3 h_o^2 + \frac{15}{16}\chi_5 h_o^4 + \cdots \approx \frac{3}{4}\chi_3 h_o^2. \quad (9)$$

Both second and third harmonics ($2f$ and $3f$ responses, respectively), for the $m=9$ compound (again the $m=7$ and 11 compounds have almost identical behavior[35]), Fig. 7, have relatively sharp peaks (variations of almost three orders of magnitude over a temperature range less than one degree) suggesting divergencies of both these quantities and, therefore, true magnetic transitions. The peak in the second harmonic indicates that a spontaneous moment is formed at that transition, while the frequency dependence of both components of the nonlinear susceptibility suggests slow relaxation processes and glassiness.

We note that the fluctuations surveyed by both the linear and nonlinear ac susceptibilities start above the transition and peak (in the low-frequency limit) at the critical point. Similarly, the remanent magnetization measured in the dc experiment has nonzero values even above the transition.
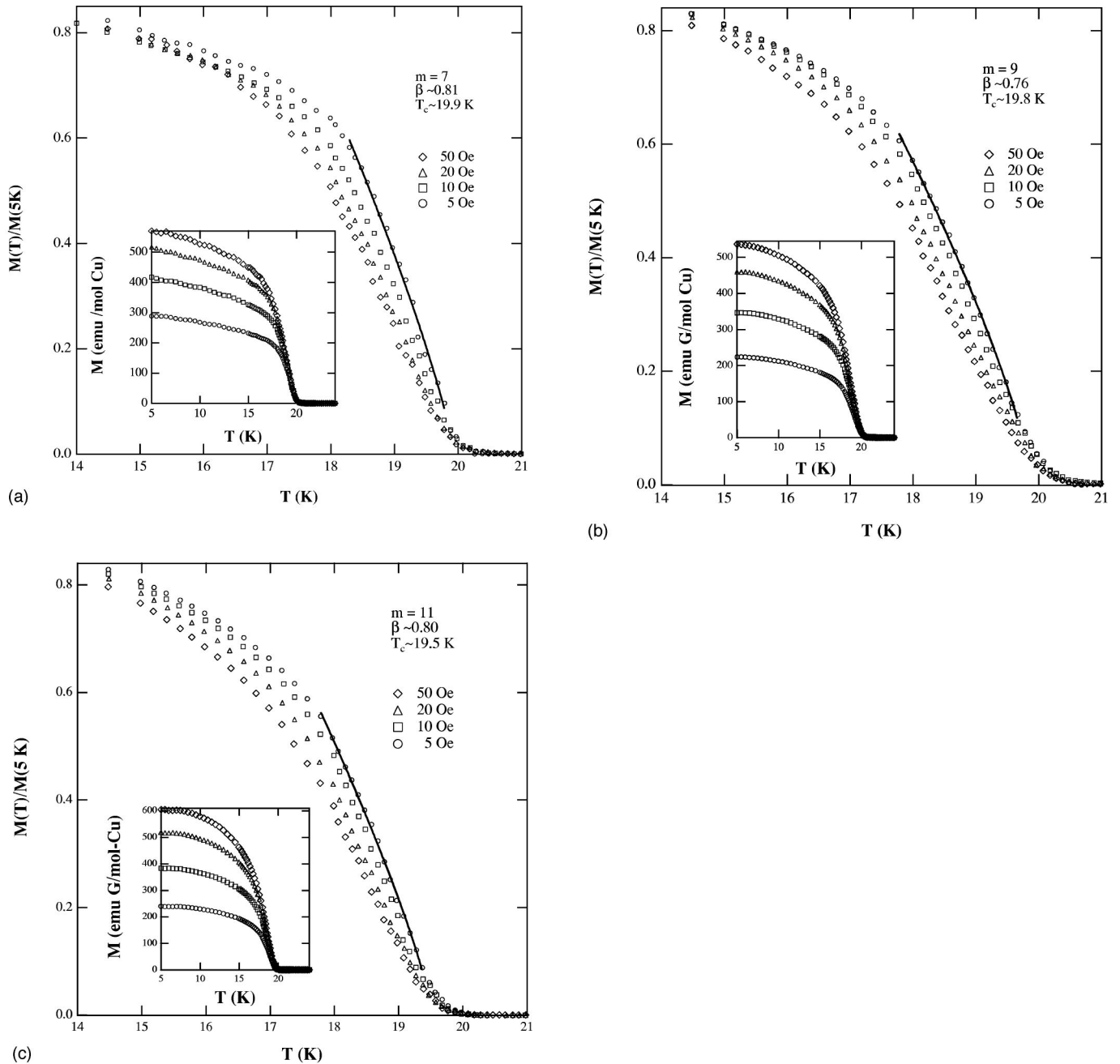
FIG. 6. Normalized remanent magnetization for $Cu_2(OH)_3(C_mH_{2m+1}COO)$, (a) $m=7$, (b) $m=9$, and (c) $m=11$ at $5 \leqslant H_{dc} \leqslant 50$ Oe with power law fits. Inset: the unnormalized data.

These effects may be caused by impurities, the finite size of the system, the time of measurement, etc., but mostly by the instrumental resolution for measuring the applied fields and the response of the system.[54,55]

B. Spin-glasslike behavior

The frequency dependence of the real and imaginary part of the linear susceptibility is shown in Fig. 8. The peak temperature of χ_1' increases while the peak height decreases strongly with increasing frequency indicative of slow relaxation processes that characterize glassy behavior.[18,56] 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,[35] place these compounds within the range of canonical spin glasses.[18]

Given the glassy behavior observed in the ac susceptibility data, we attempted to perform dynamic scaling analyses for all three compounds, using the linear scaling procedure.[57] This procedure allows the determination of T_c, and the spin-glass critical exponents separately and independently, avoiding the usual log-log plot that often conceals departures from scaling. Attempts to achieve data collapse using the spin-glass scaling expressions were not successful, likely due to the complex behavior of these systems (apparent divergence in the linear susceptibility and the presence of the second harmonic of the susceptibility to be discussed below). Thus these materials are not typical spin glasses.
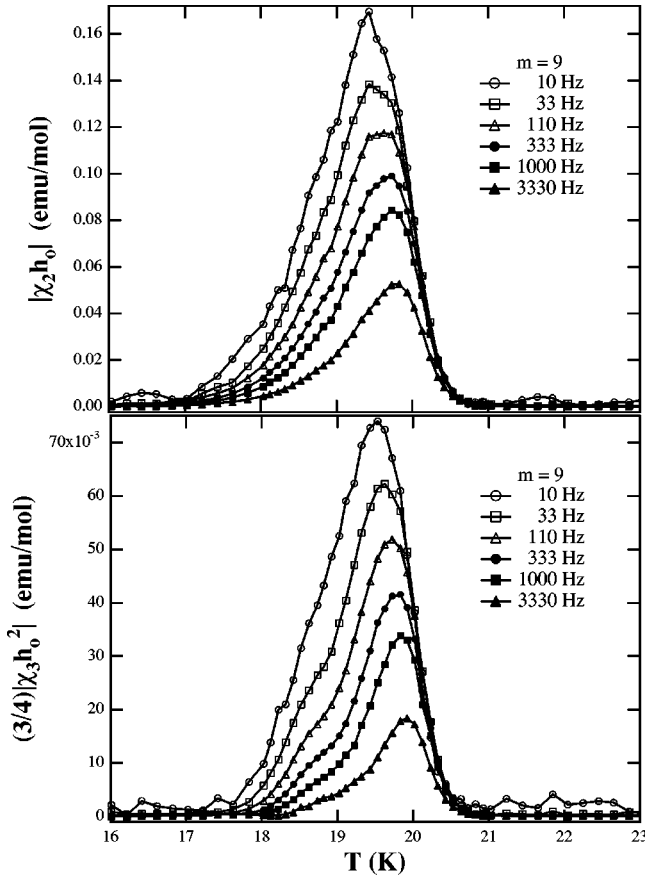
FIG. 7. Nonlinear susceptibilities $|\chi_{2,exp}h_0|$ and $|\frac{3}{4}\chi_{3,exp}h_0^2|$ of $Cu_2(OH)_3rm(C_9H_{19}COO)$ measured at $2f$ and $3f$, respectively, in $h_0=1.3$ Oe (zero dc field) at frequencies $10 \leqslant f \leqslant 3330$ Hz.

The frequency dependence of the ac susceptibility presented in Fig. 8 indicates long relaxation times. A detailed analysis of these relaxation times and their dependence on temperature can be made using the phenomenological description of Cole and Cole,[58] 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 ($0<\alpha<1$), which determines the width of the distribution of relaxation times, $g(\ln \tau)$, around the median relaxation time, τ_c:[59]

$$g(\ln \tau) = \frac{1}{2\pi} \frac{\sin(\alpha\pi)}{\cosh[(1-\alpha)\ln(\tau/\tau_c)] - \cos(\alpha\pi)}. \quad (10)$$

This distribution is determined based on the Cole-Cole equation for the complex linear susceptibility:

$$\chi_{1,CC} = \chi_S + \frac{\chi_0 - \chi_S}{1+(i\omega\tau_c)^{1-\alpha}}, \quad (11)$$

where χ_0 and χ_S are the isothermal ($\omega \to 0$) and adiabatic ($\omega \to \infty$) susceptibilities, respectively.

Based on the Cole-Cole equation one can determine an expression for $\chi_1''(\chi_1')$, which allows the fit of the experimental data.[59] Such fits (with α, τ_c, and the isothermal susceptibility as parameters) are presented in the Argand plot of Fig. 9, where the phenomenological Cole-Cole model is de-
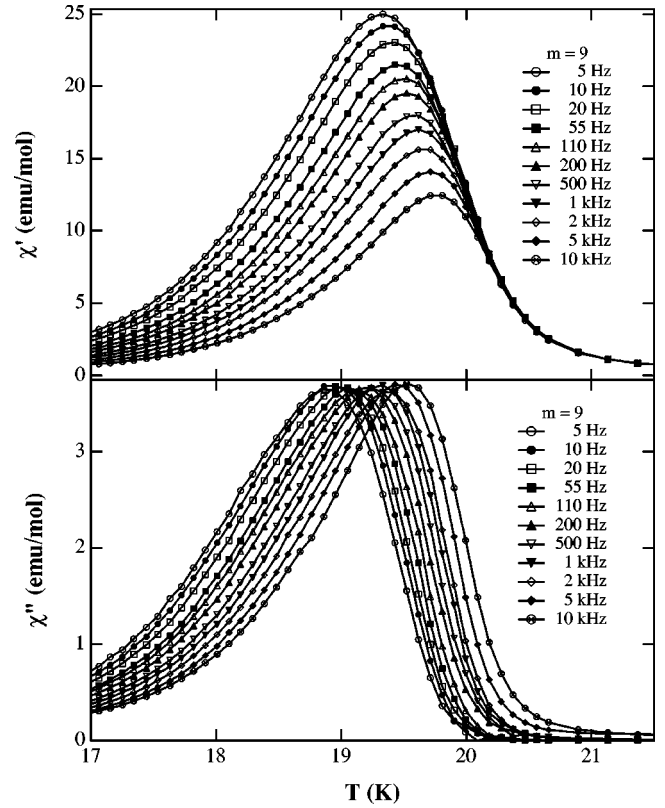

FIG. 8. χ_1' and χ_1'' of $Cu_2(OH)_3(C_9H_{19}COO)$, in $h_0=1$ Oe (zero applied dc field) at various frequencies $5 \leqslant f \leqslant 10000$ Hz.

scribed by circular arcs of size $(1-\alpha)\pi$ cutting the χ_1' axis at χ_0 and χ_S with a maximum at $\omega\tau_c=1$. Noteworthy is the shift of the data points from a nearly isothermal susceptibility above 19.5 K to a nearly adiabatic susceptibility below 18.7 K. As it will be seen below, this behavior corresponds to a large increase of the median relaxation time when decreasing the temperature 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
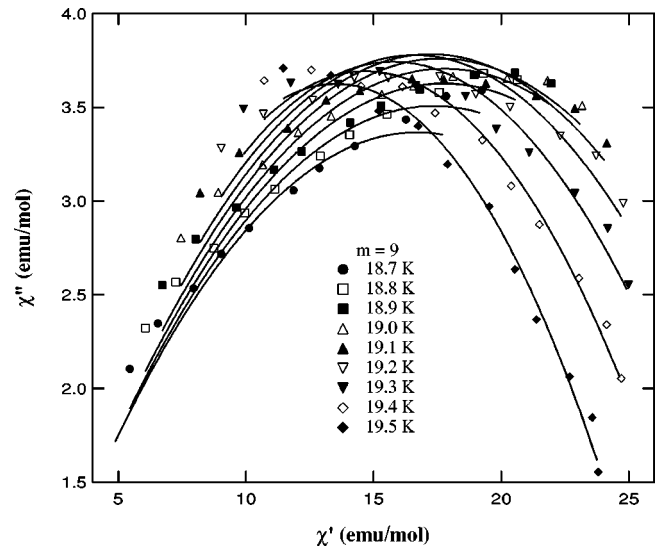

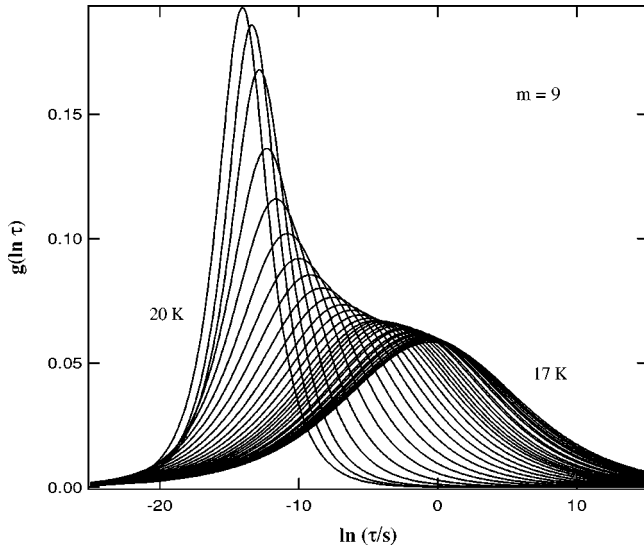FIG. 9. Argand plots, $\chi_1''(\chi_1')$, and Cole-Cole analysis of data shown in Fig. 9, for $Cu_2(OH)_3(C_9H_{19}COO)$ at $18.7 \leqslant T \leqslant 19.5$ K.

FIG. 10. Distribution of relaxation times $g(\tau)$ for $Cu_2(OH)_3(C_9H_{19}COO)$ obtained through Cole-Cole analysis of the data shown in Fig. 9, at $17 \leqslant T \leqslant 20$ K.

of relaxation times (Fig. 10). As the temperature is decreased through the transition the median relaxation time increases, indicating the growth of the correlation length of the system of spins, while the parameter α, describing the width of the distribution of relaxation times, increases, reflecting the fact that the distribution of cluster sizes broadens. Such a behavior was seen in all three compounds, though only the analysis for the $m=9$ sample (based on the data of Fig. 8) is shown here.

The temperature dependence of the median relaxation time determined by Cole-Cole analysis for all three compounds, presented in Fig. 11, shows that τ_c varies almost six decades over less than three degrees. The divergence of the relaxation time can be studied using scaling analysis based on the scaling law:

$$\tau_c \propto (T-T_c)^{-z\nu}. \tag{12}$$

The parameters obtained through such analyses are $T_c = 18.7, 18.6,$ and 18.3 K and $z\nu = 6.1, 7.7,$ and 5.6 for $m = 7, 9,$ and 11, respectively. The error in the determination of these values is estimated to about $15-20\%$, again mainly due to the various choices for the temperature ranges where data were fitted to a straight line. The final choices reflect the best fits in ranges of reduced temperature of about $0.02 \leqslant (T-T_c)/T_c \leqslant 0.25$. These values are much larger than those found in pure systems without frustration, where $z \sim 2$ and $\nu \sim 0.6$, but comparable to those found in spin glasses, where $z\nu$ is larger than 5, in some cases even larger than 10.[50,56]

The field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves for the $m=9$ compound ($m=7$ and 11 compounds have almost identical behavior[35]), Fig. 12, 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
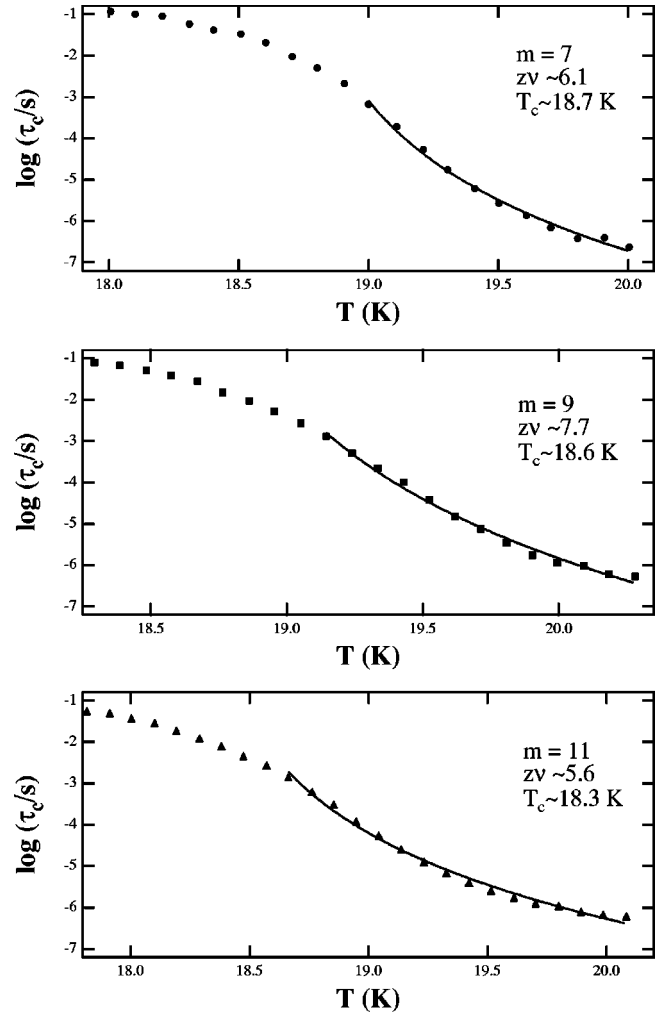

FIG. 11. Temperature dependence of the mean relaxation time obtained through Cole-Cole analysis of the χ_{ac} data for $Cu_2(OH)_3(C_mH_{2m+1}COO)$, (a) $m=7$, (b) $m=9$, and (c) $m=11$ with power-law fits.

and ZFC curves (T_b decreases with increasing the applied dc field) reinforces the glassy behavior description.[60,61]

Specific heat data is plotted as the ratio C/T vs T in Fig. 13(a). In the absence of a nonmagnetic sample with a similar structure isolation of the magnetic component of the specific heat is not obvious. However, a weak broad feature in the total specific heat is observed just above the temperature for the magnetic transition, at about 21 K, where there is a modest change in slope, which we attribute to the magnetic specific heat. Weak features in the magnetic specific heat are very common in spin glasses and spin-glass-like systems[17] because of the gradual freezing of the magnetic degrees of freedom starting well above the spin-glass transition.

The log-log plot of the specific heat shown in Fig. 13(b) reveals a roughly quadratic power law behavior. More precisely, the exponents are about $1.9 < n < 2.2$, depending on the region of the fit, being closer to $n \sim 2$ below the transition. This result is expected for both phonons and antiferromagnetic spin waves on a 2D lattice. It is, therefore, likely that the layered crystalline structure causes a T^2 behavior of the specific heat in the temperature range probed. The crossover to T^3, expected for any 3D solid, probably takes place at temperatures below 1 K.
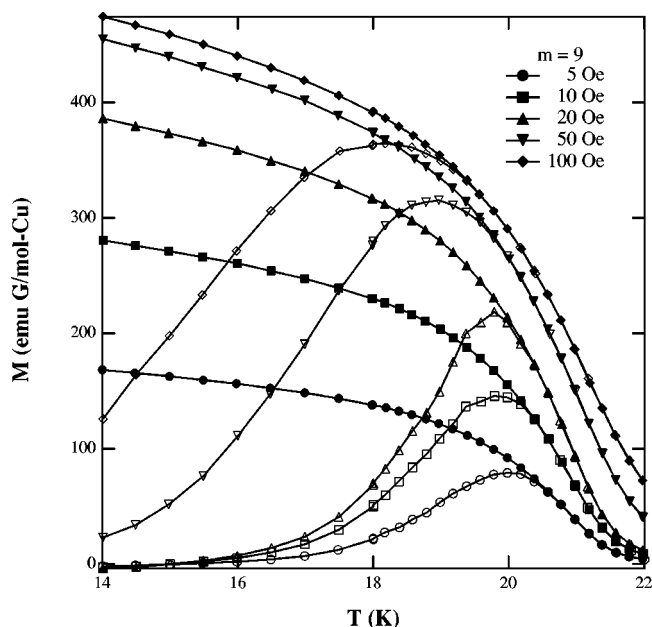
FIG. 12. FC (filled symbols) and ZFC (empty symbols) magnetization of $Cu_2(OH)_3(C_9H_{19}COO)$ in dc applied fields of $5 \leqslant H_{dc} \leqslant 200$ Oe.
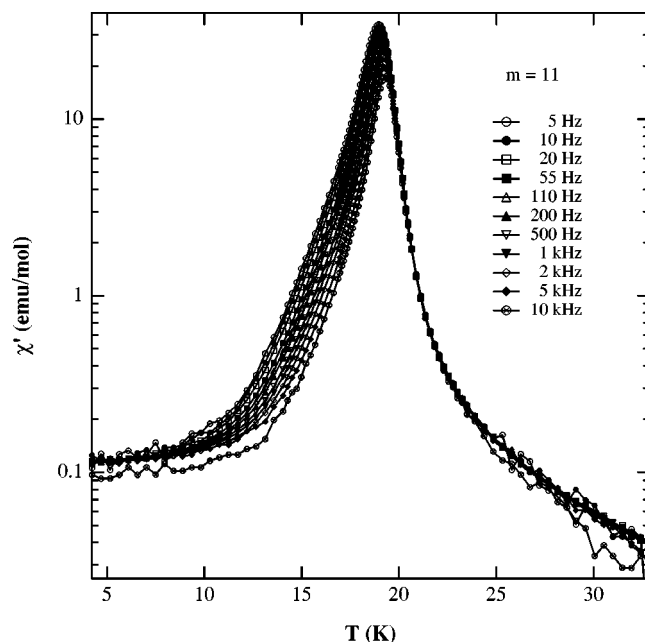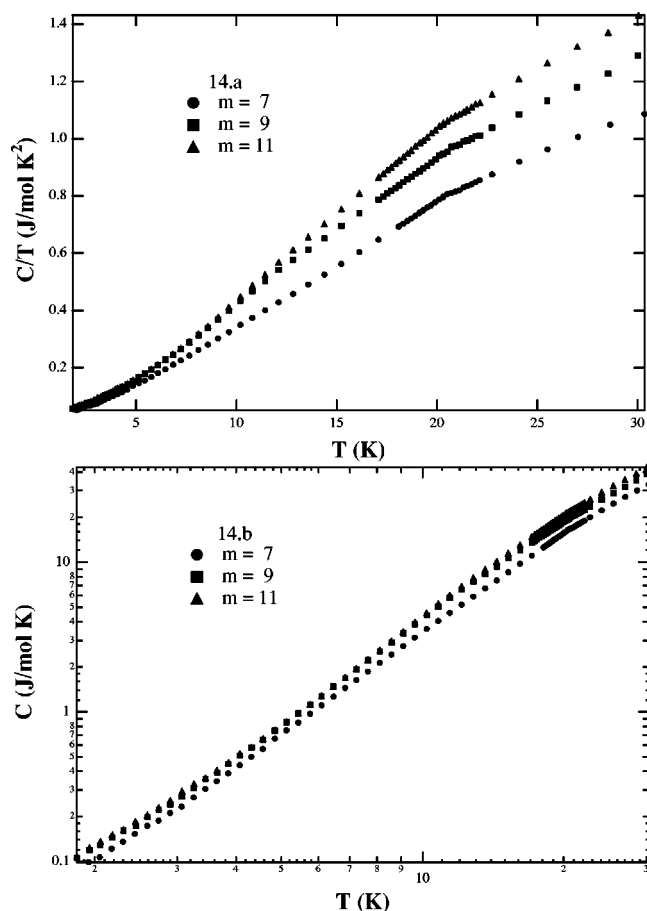
FIG. 13. Specific heat of $Cu_2(OH)_3(C_mH_{2m+1}COO)$, $m = 7, 9,$ and 11, plotted as the ratio C/T vs T, (a), and as a log-log plot of C vs T, (b).

FIG. 14. χ'_1 of $Cu_2(OH)_3(C_{11}H_{23}COO)$, in $h_0 = 1$ Oe (zero applied dc field) at various frequencies $5 \leqslant f \leqslant 10000$ Hz.

The low-temperature dynamic susceptibility in zero applied dc field and various frequencies and in the presence of various constant dc magnetic fields are shown in Fig. 14 and Fig. 15, respectively for the compound with $m = 11$. Figs. 14 and 15 display the data on logarithmic scales and in a wider range of temperatures, which allows the examination of the magnetic behavior especially below the ≈ 20 K transition.

The overall shape of the temperature dependence of χ'_1 remains qualitatively the same regardless of frequency (Fig. 14) or dc fields (Fig. 15). The in-phase susceptibility increases with decreasing T, has a peak and then levels off at low temperatures. The magnitude of χ'_1 (which describes the

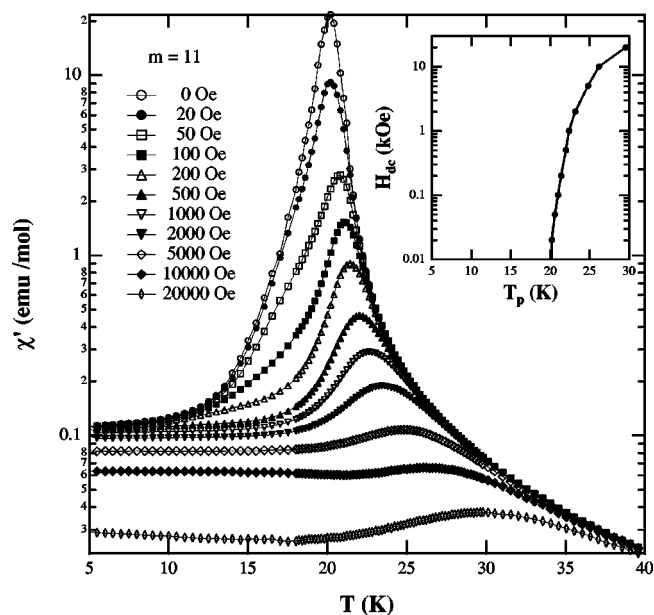

FIG. 15. χ'_1 of $Cu_2(OH)_3(C_{11}H_{23}COO)$, in $h_0 = 1$ Oe at $f = 1000$ Hz and various dc applied fields $0 \leqslant H_{dc} \leqslant 20000$ Oe. Inset: H_{dc} at the peak in χ'_1 vs peak temperature T_p.

fluctuations in magnetization) decreases monotonically with increasing H_{dc} (Fig. 15), 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 T as H_{dc} is increased (inset of Fig. 15). 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.[62]

It is important to note the leveling off of χ_1' at low temperatures. While the usual 2D-Ising magnet has vanishing susceptibility as T decreases to zero,[62] the constant low T χ_1' seen in Fig. 15 indicates that fluctuations do not disappear for these compounds, consistent with the zero field dc data of Fig. 12. Therefore, some spin degrees of freedom are preserved at low T, which is in accord with frustration playing a crucial role in these systems. Given the nonuniform but periodic magnetic lattice, it is possible that one or more sublattices order below the critical temperature of ≈ 20 K, while at least one sublattice remains disordered even below 5 K.[1]

IV. DISCUSSION

All three systems show very similar magnetic properties despite the large differences between the interlayer distances. The magnetic behavior must, therefore, be determined by the intralayer interactions, which are expected to be very similar, based on the intralayer structural similarities between the three compounds. The absence of single-ion anisotropy at the spin carrying sites and the presence of oxygen mediated superexchange pathways lead to strong isotropic Heisenberg antiferromagnetic exchange, which on a triangular lattice causes spin frustration. The slight differences in the environment of adjacent Cu sites causes a weak DM exchange, which favors spin canting leading to anisotropies.

The antiferromagnetic correlations revealed by the dc susceptibility data show that the Heisenberg antiferromagnetic exchange is indeed the dominant interaction. Moreover, the fits to high-temperature series expansions indicate that the high-temperature behavior of these compounds is consistent with that of a TQHAF. At low temperatures the deviations from the TQHAF predictions, together with the strong peaks in both the linear ac susceptibility and its harmonics (the second harmonic indicating the developing of a spontaneous moment) suggest a canted antiferromagnetic type of ordering, consistent with the presence of weak DM interaction.

The nature of the low-temperature phase is very unusual, however. The sharpness of the peaks in the linear and nonlinear susceptibilities (orders of magnitude variations over only a few degrees) suggests divergencies and, therefore, a true phase transition. The critical exponents obtained by Kouvel-Fisher scaling analysis of the linear susceptibility suggest a 2D Ising-like low-temperature phase. However, this simple picture is complicated by the strong frequency dependence of the linear ac susceptibility and the irreversibilities present in the FC/ZFC magnetization data (with field dependence of the bifurcation temperature) which indicate spin-glass-like behavior. Moreover, the dynamic critical exponents obtained through Cole-Cole analysis of the dynamic susceptibility, followed by fitting the temperature dependence of the median relaxation times to power laws, have large values, reminescent of glassy dynamics. The specific heat data has only a weak broad feature at the transition, consistent with the spin-glass-like behavior. The small value of the 5 K saturation magnetization, which is only a small fraction of the value expected for a spin-1/2 system, is consistent with spin canting and/or noncollinear spin configurations as well as with partial order. Furthermore, the leveling off below 10 K of the linear ac susceptibility with or without a superimposed dc magnetic field suggests that some spin degrees of freedom are preserved below the transition. It appears that the interplay of Heisenberg and DM exchanges leads to an unusual state in which order and disorder seem to coexist.

We should note that, although very similar, these three compounds do not have completely identical magnetic properties. For instance, there are some slight differences in the exchange constants and g values, in the saturation magnetization and coercive fields, etc. These differences are likely related to the slight structural differences within the layers between the three systems.[40]

Also, although there is a general consistence of some of the results of the scaling analyses, some puzzling questions persist. One is related to the unusually large values of the critical exponent β. A second question is related to the different values of the critical temperature obtained through the various scaling analyses. The relatively large error bars in T_c (estimated generally to $\sim 10\%$) show that the different values are within the accuracy of our data and of our fitting procedures. The values that we believe best describe the transition in these systems are the ones obtained through the Kouvel-Fisher analysis. In that case the estimated errors were at a minimum, despite the fact that the fitting procedure required taking the derivative of the susceptibility data.

It has been known, that in real compounds, there usually exist either symmetry-reducing lattice distortions[63] or additional interactions,[9] which relieve frustration and allow the system to order at a temperature determined by the dominant interaction strength. In the case of our compounds we propose, based on both structural information and magnetic data, that the additional DM interaction (whose strength was estimated to 5 K, about ten times smaller than the Heisenberg exchange) is the cause of the anisotropy leading at low temperatures to 2D Ising-like behavior.

The spin-glass-like behavior seen in these compounds has features similar to typical spin glasses [the relative variation of the T_p in χ_1' per decade of frequency, $(\Delta T_p/T_p)/\Delta(\log_{10}f)$, as well as the dynamical critical exponents] but the evidence for canted antiferromagnetic ordering shows that these systems cannot be simple spin glasses.

In the case of triangular Heisenberg AF's with Ising-like anisotropy it was suggested that site dilution produces a random anisotropy field that leads to low-temperature properties similar to a 2D-Ising spin glass.[64] Numerical studies considering the appropriate amount of impurities lead to good agreement with experimental specific heat data[65] confirming the initial suggestion that the glassiness in that system was due to site disorder.[66] A spin wave analysis of the triangular quantum Heisenberg AF with vacancies found that frustration remains the dominant influence even in the presence of defects and, also, that the magnetic properties depend on the

relative position of the vacancies and not simply on their distance of separation.[67]

It is questionable that the glassy behavior in our compounds could be attributed solely to the existence of frustration, especially as the degeneracy of the ground state of a classical THAF is not macroscopic. It is unlikely that such degeneracy can lead to a disordered state. More likely, it is the interplay between the Heisenberg and DM exchanges (the former causing frustration, the latter causing anisotropy in the spin orientation) that might lead to a rough free-energy landscape responsible for the glassiness observed in these systems. If the frustration caused by the Heisenberg exchange could be released, in the absence of other interactions, by a $120°$ noncollinear spin configuration, the spin canting favored by the additional DM interaction may oppose such tendencies and lead to spin freezing along anisotropy directions. The influence of DM interaction in metallic spin-glasses and re-entrant spin-glasses has been discussed in the past and it was shown that the DM exchange seems to play a role in the observed macroscopic irreversibility in such systems.[68]

It is difficult to address the role of structural disorder on the magnetic behavior of our compounds because of the limited structural information available at this time.[37,40] The x-ray powder diffraction revealed the layered structure and the presence of crystallites, while the TEM micrographs showed interference patterns usually seen in structurally ordered systems.[41] It is possible to have some site defects and dislocations in the lattice, which, along with possible surface effects, might also play some role in causing some of the glassy behavior. However, given the strength of the interactions involved ($2J \sim 60$ K and $D \sim 5$ K) we speculate that any effects due to possible structural disorder are in fact hidden (as it was proposed for some nominally disorder-free geometrically frustrated compounds[19]) by the more important ones caused by the two major interactions.

Quantum fluctuations are very important at low temperatures, even though it is still debated whether they could be strong enough to prevent the pure TQHAF from achieving zero temperature noncollinear magnetic LRO.[27] Given the relatively high temperature where the transition occurs (~ 20 K) and the strength of the additional DM interaction it is unlikely that quantum fluctuations play the crucial role, even though their contribution cannot be ruled out.

The interlayer interaction (superexchange or dipole-dipole interaction), expected to be negligible based on the structural data, do not affect the magnetic behavior in the range of temperatures probed, as all three compounds have very similar behavior despite the large differences in interlayer separation. If 3D behavior could be seen in these compounds, it should be at temperatures much lower than 20 K and probably less than 1 K (based on specific heat data).

Given the mixture of canted antiferromagnetism and spin-glass-like characteristics in the low temperature behavior of these compounds we are lead to two possible explanations. One is based on the coexistence of antiferromagnetic short-range order and spin-glass long-range order predicted for the diluted fcc AF,[69] while the other is "partial order" proposed for the bcc Heisenberg AF.[6] In the absence of clear evidence for structural disorder the first possibility seems less likely. Moreover, given the nonuniform but periodic magnetic lattice it is conceivable that some of the spins will be interacting more strongly than others, (in particular the absence of DM interaction between spins on particular sites might give extra freedom) such that ordered and disordered sublattices might be formed. Therefore we are lead to speculate that the low temperature state might be partially ordered. The possibility of partial order in these compounds is, however, an open question and deserves further consideration. A deeper understanding of this apparent coexistence of canted antiferromagnetic and spin-glass-like characteristics awaits theoretical studies of systems with both Heisenberg and DM interactions.

V. CONCLUSION

We reported extensive 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.

We proposed that the unusual behavior of these three TQHAF systems is determined by the interplay between the Heisenberg exchange, causing geometrical frustration, and the DM exchange, leading to spin canting. Instead of choosing between the resonant valence bond or noncollinear Néel ground states, we proposed that these systems evolve, due to the additional DM interaction, toward a finite temperature 2D Ising-like canted antiferromagnetic state. Geometrical frustration, together with the anisotropy caused by the additional DM interaction, proves to be strong enough to cause some kind of spin freezing, slow relaxation processes, and glassiness. The interplay of Heisenberg and DM exchanges leads to an unusual state in which order and disorder appear to coexist.

We also speculated that the effects of structural disorder, quantum fluctuations and interlayer interactions are likely to be hidden at the relatively high temperature of the transition due to the strength of the main two interactions. We suggested that glassiness in our systems is different from that found in typical spin glasses. Based on structural information we proposed that these systems are candidates for studying partial order as the interactions are nonuniform but periodic, with possibilities for making distinctions between the various sublattices.

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