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Experimental Determination of the Weiss Temperature of Mn12-Ac and Mn12-Ac-MeOH

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Experimental determination of the Weiss temperature of Mn$_{12}$-ac and Mn$_{12}$-ac-MeOH

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We report measurements of the susceptibility in the temperature range from 3.5 to 6.0 K of a series of Mn$_{12}$-ac and Mn$_{12}$-ac-MeOH samples in the shape of rectangular prisms of length $l_a$ and square cross section of side $l_a$. The susceptibility obeys a Curie-Weiss law, $\chi = C/(T - \theta)$, where $\theta$ varies systematically with sample aspect ratio. Using published demagnetization factors, we obtain $\theta$ for an infinitely long sample corresponding to intrinsic ordering temperatures $T_c = 0.85$ K and $=0.74$ K for Mn$_{12}$-ac and Mn$_{12}$-ac-MeOH, respectively. The difference in $T_c$ for two materials that have nearly identical unit cell volumes and lattice constant ratios suggests that, in addition to dipolar interactions, there is a nondipolar (exchange) contribution to the Weiss temperature that differs in the two materials because of the difference in ligand molecules.

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II. EXPERIMENTAL PROCEDURE

Parallel studies were carried out on single crystals of the usual form of Mn$_{12}$-ac, [Mn$_{12}$O$_{12}$(O$_2$CMe)$_{16}$(H$_2$O)$_4$]-2MeCO$_2$H·4H$_2$O, and a new recently synthesized form Mn$_{12}$-ac-MeOH, [Mn$_{12}$O$_{12}$(O$_2$CMe)$_{16}$(MeOH)$_4$]-MeOH. The normal form [space group $I4$; unit-cell parameters $a=b=17.1668(3)$ Å, $c=12.2545(3)$ Å, $Z=2$, and $V=3611.39$ Å$^3$ at 83 K] (Ref. 5) and the new form [space group $I4$; unit-cell parameters $a=b=17.3500(18)$ Å, $c=11.9971(17)$ Å, $Z=2$, and $V=3611.4$ Å$^3$ at $-100$ °C] (Ref. 6) of Mn$_{12}$-ac are quite similar but they differ in the solvent molecules of crystallization that lie in between the Mn$_{12}$ molecules. In normal Mn$_{12}$-ac, each Mn$_{12}$ molecule forms O-H···O hydrogen bonds with $n$ ($n=0$–4) of the surrounding MeCO$_2$H molecules while in Mn$_{12}$-ac-MeOH, the lattice MeOH molecules form no hydrogen bonds to the Mn$_{12}$ molecules.

Sample preparations for Mn$_{12}$-ac and Mn$_{12}$-ac-MeOH are described in Refs. 7 and 6, respectively. The samples were in the form of rectangular prisms of dimensions $l_a$, $l_b$, $l_c$ ($l_c=l_a$) with $l_a$ varying from ~0.1 to ~0.4 mm. The dimensions of the samples were measured under a microscope by a small scaler. Data were taken for aspect ratios ($l_c/l_a$) varying from 0.75 to 0.97 for Mn$_{12}$-ac, and from 1.45 to 4.9 for Mn$_{12}$-ac-MeOH. The range of aspect ratios was determined by sample availability.

The magnetization was measured in a commercial Quantum Design magnetic property measurement system...
blocking temperature, slow relaxation below a sweep-rate-dependent
magnetic field. The crystals were mounted using a minimum amount of Dow Corning high vacuum grease. As the Mn$_{12}$-ac-MeOH crystals are known to degrade rapidly when removed from their mother liquor, care was taken to quickly transfer these samples into paraffin oil using a paraffin-coated stick. Hysteresis curves taken below the blocking temperature displayed the steps characteristic of tunneling in single molecule magnets, indicating the samples had not degraded significantly during handling. Care was taken to align the $c$ axis of the crystals parallel to the magnetic field.

The measured magnetization should be normalized by the volume (or mass) of each sample. In our case, the samples are so small that neither the volume, $V$, nor the mass, $m(=10^{-5}$ g), can be measured accurately. The SQUID-based magnetometer, however, provides a precise measure of the saturation magnetization, which is proportional to the volume. We therefore normalized the data for each sample by $M_{\text{sat}}$ and, noting that there are two Mn$_{12}$ molecules, each with spin $S=10$ in a (body-centered-cubic) unit cell of known volume, we applied a (calculated) conversion factor $M_{\text{sat}}=2gS/V_{\text{cell}}=102.7$ emu/cm$^3$ to obtain the magnetization and the susceptibility in cgs units.

Mn$_{12}$-ac molecules behave as nanomagnets with spin $S=10$ in crystals with strong uniaxial magnetic anisotropy along the $c$ axis of the crystals. Modeled as a double-well potential, slow relaxation below a sweep-rate-dependent blocking temperature $T_B$ gives rise to hysteresis in $M$ versus $H$, as shown in the inset of Fig. 1; the stepwise change in magnetization is typical for molecular magnets, where steps occur due to spin tunneling at values of longitudinal magnetic field where energy levels corresponding to different spin projections cross on opposite sides of the anisotropy barrier. Equilibrium measurements from which the susceptibility can be obtained therefore require sufficiently high temperatures (above blocking) and/or slow sweep rates. Reversible behavior, signaling equilibrium, was obtained in our experiments above a blocking temperature on the order of 3–4 K for the sweep rates used. As a consequence, our susceptibility measurements were limited to temperatures above 3 K.

III. EXPERIMENTAL RESULTS

As shown in Fig. 1, data for the magnetization $M$ versus $H$ were obtained in the linear regime. The susceptibility given by the slope of these straight lines, $\chi=dM/dH$ $H=0$, increases with decreasing temperature, as expected.

Figure 2 shows the inverse of the susceptibility as a function of temperature for two crystals of Mn$_{12}$-ac with aspect ratios $l_{a}/l_{c}=1.5$ and 3.3, and two samples of Mn$_{12}$-ac-MeOH with aspect ratios closely matched to those of Mn$_{12}$-ac. The straight lines demonstrate that the susceptibility obeys a Curie-Weiss law, $\chi=\xi/(T-\theta)$. The lines are approximately parallel, indicating that the Curie constant, $\xi=0.138$ for the two systems is approximately the same, as expected. For each material, (Mn$_{12}$-ac or Mn$_{12}$-ac-MeOH), the intercept $\theta$ is larger for the larger aspect ratio. A cross comparison reveals that for the same aspect ratio, the intercept is smaller for Mn$_{12}$-ac-MeOH than it is in Mn$_{12}$-ac.

The intercept $\theta$ is shown in Fig. 3 as a function of aspect ratio for Mn$_{12}$-ac and Mn$_{12}$-ac-MeOH. For each material, $\theta$ increases with increasing aspect ratio, asymptotically approaching a limiting value as the sample becomes longer and/or thinner. While the behavior as a function of aspect ratio is qualitatively similar for the two materials, it is clear that $\theta$ is smaller in Mn$_{12}$-ac-MeOH than in Mn$_{12}$-ac for every aspect ratio over the entire range of our measurements.

IV. THEORETICAL ANALYSIS

The study of demagnetization factors of homogeneous bodies has been a classical topic in magnetism. The study of demagnetization factors of homogeneous bodies has been a classical topic in magnetism. 8,9 Demagne-
The magnetometric demagnetization factor, $N_m$, was obtained for the aspect ratios of our crystals by interpolation using the published tables for bars of square cross section.\footnote{See Chen et al.\textsuperscript{9} and references therein.} We select the values listed for $\chi=0$ since the small susceptibility of our samples produces demagnetizing fields that are small compared to the applied magnetic field. The resulting curve for $N_m$ versus aspect ratio is shown in the inset of Fig. 4. Combining this with the information in Fig. 3, one obtains $\theta$ versus $N_m$ shown in the main part of the figure for $\text{Mn}_{12}$ and $\text{Mn}_{12}$-ac-MeOH.

The simplest mean-field derivation of the Curie-Weiss law incorporates the effect of interactions by postulating a “molecular field,” $H_m$. The demagnetizing field $H_d$ can be introduced in a similar way by writing $H_{tot}=H_{ext}+H_m+H_d$, from which one obtains

$$\theta = \theta_{CW} \left( \frac{C}{a} \right) - CN_m \left( \frac{1}{I_a} \right),$$

where $C$ is the Curie constant. The first term in this expression depends only on lattice properties such as $c/a$ and the local chemistry (the molecule solvent and ligand structure) and is independent of the aspect ratio while the second term depends only on the shape of the crystal and vanishes in the limit of infinite aspect ratio $l_a/l_p$. For a particular material, say, $\text{Mn}_{12}$-ac, the lattice properties such as $c/a$ and local chemistry are the same for all samples with different aspect ratios, and the value of $\theta_{CW}$ in Eq. (1) can be interpreted empirically as the intrinsic Curie-Weiss temperature $T_c$ obtained in the limit of infinite aspect ratio.\footnote{As shown in Fig. 4, $\theta$ depends linearly on $N_m$, as expected from Eq. (1), for both $\text{Mn}_{12}$-ac and $\text{Mn}_{12}$-ac-MeOH. Guided by Eq. (1), the slopes of the solid lines drawn in the figure were constrained to the value $C=0.138$ obtained from the data of Fig. 2, yielding $\theta_{CW}=T_c=0.85$ K for $\text{Mn}_{12}$-ac and $T_c=0.74$ K for $\text{Mn}_{12}$-ac-MeOH.}

Theoretical calculations\footnote{Chudnovsky and Garanin\textsuperscript{13} predicted ferromagnetic ordering of elongated crystals of $\text{Mn}_{12}$-ac below 0.8 K; Garanin\textsuperscript{14} recent investigation of elongated box-shape crystals yielded an ordering temperature $\sim 0.71$ K. Values of $J(c/a)=\theta_{CW}$ can also be obtained from the work of Millis et al.,\textsuperscript{15} who write the susceptibility as} have been carried out for $\text{Mn}_{12}$-ac based on models that consider dipolar interactions only, on the assumption that other terms (for example, direct exchange from overlap of wave functions) can be neglected. Chudnovsky and Garanin\textsuperscript{13} predicted ferromagnetic ordering of elongated crystals of $\text{Mn}_{12}$-ac below 0.8 K; Garanin\textsuperscript{14} recent investigation of elongated box-shape crystals yielded an ordering temperature $\sim 0.71$ K. Values of $J(c/a)=\theta_{CW}$ can also be obtained from the work of Millis et al.,\textsuperscript{15} who write the susceptibility as
\[
\frac{1}{\chi} = \frac{T - \theta_{\text{CW}}}{C} = \frac{T - 2E_{\text{dip}}J}{C}, \quad J = J_{\text{SR}} + 4/3.
\] (2)

Here \(E_{\text{dip}}\) is the dipolar interaction and the short-range contribution \(J_{\text{SR}}\) depends on the details of the crystal structure. For Mn\(_{12}\)-ac, with lattice constants \(a=b=17.1668(3)\) Å, \(c=12.2545(3)\) Å, one obtains \(J=5.287\) while for Mn\(_{12}\)-ac-MeOH with \(a=b=17.3500(18)\) Å, \(c=11.9971(17)\) Å, and \(J=5.514\). The strength of the dipolar interaction, \(E_{\text{dip}}\approx 0.078\) K, is essentially the same for the two materials as their unit cells have the same volume within 0.01%. This yields \(\theta_{\text{CW}}\approx 0.82\) K for Mn\(_{12}\)-ac and \(\approx 0.86\) K for Mn\(_{12}\)-ac-MeOH.

The crystal structures of Mn\(_{12}\)-ac-MeOH and Mn\(_{12}\)-ac are quite similar: the unit-cell parameters and unit volumes cell are nearly identical, and the strength of the dipolar interactions are expected to be essentially the same. These similarities are reflected by the nearly identical Curie-Weiss constants obtained experimentally for the two systems. By contrast, however, the values of the Curie-Weiss \(\theta_{\text{CW}}\)’s are clearly and consistently smaller for Mn\(_{12}\)-ac-MeOH than they are in Mn\(_{12}\)-ac, as shown in Figs. 3 and 4, implying that the magnetic interactions are weaker in Mn\(_{12}\)-ac-MeOH. We note that although the unit-cell parameters are nearly identical, the two systems have different ligands bridging the Mn\(_{12}\) molecules. A possible explanation for the different interaction strengths in the two materials may be that, in addition to the dipolar interactions, quantum-mechanical exchange derivation from wave function overlap plays a significant role. In particular, our results suggest that there is an extra direct exchange contribution of antiferromagnetic sign in Mn\(_{12}\)-ac-MeOH.

V. SUMMARY

The susceptibility of Mn\(_{12}\)-ac and Mn\(_{12}\)-ac-MeOH has been measured for a series of samples in the shape of rectangular prisms of length \(l_a\) and square cross section of side \(l_c\). Fits to a Curie-Weiss law, \(\chi=C/(T-\theta)\), yield values for \(\theta\) that vary systematically with the aspect ratio, \(l_a/l_c\). Using published values of the demagnetization factor \(3,4\), we have deduced values of \(\theta_{\text{CW}}=T_c\) that are surprisingly different for Mn\(_{12}\)-ac and Mn\(_{12}\)-ac-MeOH, two materials that have nearly identical crystal structures but different ligands bridging the Mn\(_{12}\) molecules in the crystal. This suggests that, in addition to dipolar interactions, there is a nondipolar (exchange) contribution to the Weiss temperature that is different for the different ligand molecules in the crystal.

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\cite{11} Samples of widely different size with the same aspect ratio yielded closely similar results, confirming the validity of our analysis.
\cite{12} Crystal structures have not been systematically measured as a function of temperature. In the absence of a change in phase, the lattice parameters are found to be about 1% smaller at 100 K than at room temperature, and the relative difference in \(c/a\) is expected to be much lower; we therefore assume that \(c/a\) is a constant.
\cite{14} D. A. Garanin, \textit{Phys. Rev. B} \textbf{81}, 220408 (2010); note that Garanin claims in this paper that finding the ordering temperature by linearly extrapolating the inverse susceptibility curve above the transition temperature does not provide a correct \(T_c\).