2010

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

Christos Lampropoulos
University of North Florida, c.lampropoulos@unf.edu

Shiqi Li
Lin Bo
Bo Wen
M P. Sarachik

See next page for additional authors

Follow this and additional works at: https://digitalcommons.unf.edu/achm_facpub

Part of the Chemistry Commons

Recommended Citation
Lampropoulos, Christos; Li, Shiqi; Bo, Lin; Wen, Bo; Sarachik, M P.; Subedi, P; Kent, A D.; Yeshurun, Y; Millis, A J.; Mukherjee, S; and Christou, G, "Experimental Determination of the Weiss Temperature of Mn12-Ac and Mn12-Ac-MeOH" (2010). Chemistry Faculty Publications. 10.
https://digitalcommons.unf.edu/achm_facpub/10

This Article is brought to you for free and open access by the Department of Chemistry at UNF Digital Commons. It has been accepted for inclusion in Chemistry Faculty Publications by an authorized administrator of UNF Digital Commons. For more information, please contact Digital Projects. © 2010 All Rights Reserved
Experimental determination of the Weiss temperature of Mn$_{12}$-ac and Mn$_{12}$-ac-MeOH

Shiqi Li, Lin Bo, Bo Wen, and M. P. Sarachik
Department of Physics, City College of New York, CUNY, New York, New York 10031, USA

P. Subedi and A. D. Kent
Department of Physics, New York University, New York, New York 10003, USA

Y. Yeshurun
Department of Physics, City College of New York, CUNY, New York, New York 10031, USA; Department of Physics, New York University, New York, New York 10003, USA; and Department of Physics, Institute of Nanotechnology, Bar-Ilan University, Ramat-Gan 52900, Israel

A. J. Millis
Department of Physics, Columbia University, New York, New York 10027, USA

C. Lampropoulos, S. Mukherjee, and G. Christou
Department of Chemistry, University of Florida, Gainesville, Florida 32611, USA

Abstract

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 $l_a$, square cross section of side $l_b$, and varying aspect ratios. The susceptibility obeys a Curie-Weiss law, $\chi = C/(T - \theta)$, where $C$ is a material-specific Curie constant, $T$ is the absolute temperature, and the Weiss temperature $T_c$ is the approximate temperature below which the system is ferromagnetic or antiferromagnetic, depending on the sign of $\theta$. 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 susceptibility obeys a Curie-Weiss law, $\chi = C/(T - \theta)$, where $C$ is a material-specific Curie constant, $T$ is the absolute temperature, and the Weiss temperature $T_c$ is the approximate temperature below which the system is ferromagnetic or antiferromagnetic, depending on the sign of $\theta$. 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.

DOI: 10.1103/PhysRevB.82.174405

PACS number(s): 75.50.Xx, 75.30.Et, 75.30.Cr

I. INTRODUCTION

The magnetic susceptibility, $\chi$, is given within the mean-field approximation by the Curie-Weiss law, $\chi = C/(T - T_c)$, where $C$ is a material-specific Curie constant, $T$ is the absolute temperature, and the Weiss temperature $T_c$ is the approximate temperature below which the system is ferromagnetic or antiferromagnetic, depending on the sign of $T_c$. In order to determine the susceptibility and $T_c$ experimentally, however, the measured values need to be corrected to account for a demagnetizing field, $H_d$, which depends on sample geometry, as well as the value of the susceptibility itself.

In this paper we report measurements of the magnetization and susceptibility of a series of samples of two different variants of the molecular magnet Mn$_{12}$-ac: the usual, much-studied form referred to as Mn$_{12}$-ac and a new form abbreviated as Mn$_{12}$-ac-MeOH. The measurements were taken for a series of samples in the shape of rectangular prisms with approximately square cross section $l_b^2$ and length $l_a$. The susceptibility is found to obey the expected Curie-Weiss form, $\chi = C/(T - \theta)$, but with a Curie-Weiss $\theta$ that varies systematically with the sample aspect ratio $l_a/l_b$. Using demagnetization factors calculated by Chen, Pardo, and Sanchez, we have deduced the value of $\theta$ for an infinitely long sample, corresponding to the intrinsic ordering temperature $T_c$ for the two materials.

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$_{10}$(H$_2$O)$_{16}$]-2MeCO$_2$H·4H$_2$O, and a new recently synthesized form Mn$_{12}$-ac-MeOH, [Mn$_{12}$O$_{12}$O$_2$CMe$_{10}$(MeOH)$_{16}$]-MeOH. The normal form [space group $I4_1$; 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 $I4_1$; 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 $n$ ($n=0$ to 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 $l_a$, $l_b$, $l_c$ ($l_a=l_b$) with $l_a$ varying from $\sim 0.1$ to $\sim 0.4$ mm. The dimensions of the samples were measured under a microscope by a small scaler. Data were taken for aspect ratios ($l_a/l_b$) varying from 0.75 to 9.57 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.
(MPMS) superconducting quantum interference device (SQUID)-based magnetometer. The crystals were mounted using a minimum amount of Dow Corning high vacuum grease. As the Mn12-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 $M_{\text{sat}}=2gS\beta/V_{\text{cell}}=102.7$ 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, $\chi=C/(T-\theta)$. The lines are approximately parallel, indicating that the Curie constant, $C=0.138$ 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.$^{8,9}$ Demagn-
FIG. 3. (Color online) Temperature intercept $\theta$ as a function of aspect ratio for Mn$_{12}$-ac (triangles) and Mn$_{12}$-ac-MeOH (circles). The lines denote fits obtained as described in the text.

The susceptibility measured in our experiment, $\chi = M / H_{\text{ext}}$, is deduced from the slope of the straight lines of $M$ versus the externally applied magnetic field $H_{\text{ext}}$ shown in Fig. 1. To obtain the true susceptibility, $\chi = M / H_{\text{tot}}$, one needs to use the total magnetic field, $H_{\text{tot}} = H_{\text{ext}} + H_{d}$, where $H_{d}$ is the demagnetizing field. The demagnetizing field is opposite to and proportional to the magnetization of the sample, $H_{d} = -N_{m}M$, where $N_{m}$ depends primarily on the geometry of the sample and, to a lesser degree, the susceptibility of the material (see Chen et al.9 and references therein). Except for ellipsoidal specimens, the demagnetization factor varies from point to point and one needs to apply an averaged demagnetization factor that depends on the type of measurement, e.g., a measurement taken by a coil wound around the middle or a measurement of the entire sample. For our SQUID-based measurements of small samples, the appropriate factor is the ratio of the average demagnetizing field to the average magnetization of the entire sample, the so-called magnetometric demagnetization factor $N_{m}$.

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.3,4 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 Mn$_{12}$ and Mn$_{12}$-ac-MeOH.

The simplest mean-field derivation of the Curie-Weiss law incorporates the effects of interactions by postulating a “molecular field,” $H_{m}$. The demagnetizing field $H_{d}$ can be intro-

deuced in a similar way by writing $H_{\text{tot}} = H_{\text{ext}} + H_{m} + H_{d}$, from which one obtains

$$\theta = \theta_{\text{CW}} \left( \frac{C}{\alpha} \right) - CN_{m} \left( \frac{I_{c}}{I_{a}} \right),$$

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. For a particular material, say, 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 $\theta_{\text{CW}}$ in Eq. (1) can be interpreted empirically as the intrinsic Curie-Weiss temperature $T_{c}$ obtained in the limit of infinite aspect ratio.

As shown in Fig. 4, $\theta$ depends linearly on $N_{m}$, as expected from Eq. (1), for both Mn$_{12}$-ac and 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 $\theta_{\text{CW}} = T_{c} = 0.85$ K for Mn$_{12}$-ac and $T_{c} = 0.74$ K for Mn$_{12}$-ac-MeOH.

Theoretical calculations13–15 have been carried out for Mn$_{12}$ 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 Garanin13 predicted ferromagnetic ordering of elongated crystals of Mn$_{12}$ below 0.8 K; Garanin’s14 recent investigation of elongated box-shape crystals yielded an ordering temperature $\sim 0.71$ K. Values of $J(c/a) = \theta_{\text{CW}}$ can also be obtained from the work of Millis et al.,15 who write the susceptibility as
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 \( a=b=17.1668(3) \text{ Å}, c=12.2545(3) \text{ Å} \), one obtains \( J=5.287 \) while for Mn\(_{12}\)-ac-MeOH with \( a=b=17.3500(18) \text{ Å}, c=11.9971(17) \text{ Å} \), 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 constants observed 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 deriving 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 \( l \) and square cross section of side \( l_s \). Fits to a Curie-Weiss law, \( \chi=C/(T-\theta) \), yield values for \( \theta \) that vary systematically with the aspect ratio, \( l/l_s \). Using published values of the demagnetization factor \( ^{34} \) 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.

ACKNOWLEDGMENTS

We thank Dimitar Dimitrov for valuable technical help during the initial phases of the experiment. We acknowledge illuminating discussions with D. M. Garanin, E. M. Chudnovsky, and J. R. Friedman. Support for G.C. was provided by NSF under Grant No. CHE-0910472; A.D.K. acknowledges support by NSF under Grant No. DMR-0506946 and ARO under Grant No. W911NF-08-1-0364; A.J.M. acknowledges support of NSF under Grant No. DMR-0705847; M.P.S. acknowledges support from NSF under Grant No. DMR-0451605; Y.Y. acknowledges support of the Deutsche Forschungsgemeinschaft through a Deutsch-Israelische Projektkooperation (DIP).

11 Samples of widely different size with the same aspect ratio yielded closely similar results, confirming the validity of our analysis.
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.
14 D. A. Garanin, Phys. Rev. B 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 \( T_c \).