Inelastic neutron scattering study of Mn_{12}–acetate

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We report zero-field inelastic neutron scattering experiments on a deuterated powder sample of Mn_{12}–acetate consisting of a large number of nominally identical spin-10 magnetic clusters. Our resolution enables us to see a series of peaks corresponding to transitions between the anisotropy levels within the spin-10 manifold. A fit to the spin Hamiltonian $H=-DS_z^2-\mu_B\mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S}-AS_z^4+C(S_+^4+S_-^4)$ yields an anisotropy constant $D=(0.54\pm0.02)$ K and a fourth-order diagonal anisotropy coefficient $A=(1.2\pm0.1)\times10^{-3}$ K (the other terms being negligible). Performed in the absence of a magnetic field, our experiments do not involve the g values as fitting parameters, thereby yielding particularly reliable values of D and A. © *1999 American Institute of Physics.* [S0021-8979(99)65508-6]

INTRODUCTION

High-spin molecular magnets provide a unique laboratory for the study of quantum tunneling of magnetization (QTM). To date, the most intensively studied system of this type is Mn_{12}–acetate, $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot2CH_3COOH\cdot4H_2O$ (hereafter referred to as Mn_{12}–Ac). First synthesized by Lis,[1] it consists of Avogadro's number of weakly interacting,[2] chemically identical Mn_{12}–Ac molecules residing on a body-centered tetragonal lattice. The magnetic core of each molecule contains four Mn^{4+} ($S=3/2$) and eight Mn^{3+} ($S=2$) ions which form an $S=10$ ground state at low temperatures.[3] A strong magnetocrystalline anisotropy results in a double-well potential with each molecule's $(2S+1)=21$ states yielding two degenerate ground states $m=\pm10$, and a set of doubly degenerate excited states $m=\pm9,\pm8....$ (except for $m=0$).[3,4] Below the blocking temperature of ≈3 K, a remarkable series of steps were found in the hysteresis loops of oriented-powder samples at regular intervals of magnetic field, steps which were interpreted as a manifestation of QTM.[5] Experimental confirmation of these steps was provided soon thereafter in studies of single crystals.[6]

Other experimental evidence supports this interpretation[7,8] but there is no general agreement on the mechanism responsible for the QTM in Mn_{12}–Ac. Up to fourth-order terms, the spin Hamiltonian of the system can be written as:

$$H=-DS_z^2-\mu_B\mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S}-AS_z^4+C(S_+^4+S_-^4)=H_0+H', \tag{1}$$

where D is the anisotropy constant, the second term represents the Zeeman energy, and the remaining are higher-order terms in the crystalline anisotropy. $H_0=-DS_z^2-g_{\text{para}}\mu_BB_zS_z-AS_z^4$ includes all terms that commute with S_z and do not give rise to tunneling; $H'=-g_{\text{perp}}\mu_BB_xS_x+C(S_+^4+S_-^4)$ represents symmetry-breaking terms that could give rise to tunneling, associated with a transverse magnetic field and transverse fourth-order anisotropy terms. Major efforts are currently underway to determine the relative importance of magnetic fields and crystalline anisotropy in accounting for the relaxation rates observed in Mn_{12}–Ac.[9–11] Accurate, reliable experimental determinations of the spin Hamiltonian, Eq. (1), thus provide crucial information.

Electron paramagnetic resonance (EPR) measurements performed recently in Mn_{12}–Ac have yielded two different sets of values for the coefficients D and A of Eq. (1). Barra *et al.*[12] measured high-field EPR spectra at frequencies ranging from 150 to 525 GHz in magnetic fields up to 25 T on a polycrystalline powder sample, yielding $g_\parallel=(1.93\pm0.01)$, $g_\perp=(1.96\pm0.01)$, $D=(0.56\pm0.04)$ K, and $A=(1.1\pm0.1)\times10^{-3}$ K. Using high-sensitivity EPR techniques in the frequency range between 35 and 115 GHz, Hill *et al.*[13] studied a submillimeter single crystal; their results imply $D=0.59$ K and $A=0.88\times10^{-3}$ K[14] with $g_\parallel$ ranging from 1.97 to 2.08 and $g_\perp=1.9$.

EPR measurements are normally done in a magnetic field and the g values, generally unknown, are treated as

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(additional) fitting parameters. In contrast, neutron scattering experiments are normally performed in the absence of external magnetic fields, and yield a more direct determination of the coefficients A and D. An inelastic neutron scattering study by Hennion *et al.*[15] of partially deuterated Mn_{12}–Ac found a well-defined peak around 0.3 THz (1.24 meV) which was attributed to excitations from $m=\pm 10$ to ± 9. The peak broadens on its low energy side as the temperature increases, but these authors were unable to resolve any detailed structure.

In the present study, we have performed zero-field inelastic neutron scattering experiments on fully deuterated Mn_{12}–Ac. The excitation spectra were measured with relatively uniform and high resolution at finite neutron energy transfer up to 20 meV, covering the excitation energies of the spin-10 manifold of Mn_{12}–Ac. Since g factors do not enter the problem in the absence of a magnetic field, this method allows a more accurate determination of the spin Hamiltonian.

EXPERIMENTS AND RESULTS

A 14 g deuterated Mn_{12}–Ac powder sample was prepared for the inelastic neutron scattering experiments. The sample was characterized following the method of Ref. 5 and steps at the same values of magnetic field were seen in its hysteresis loops. We used the PHAROS chopper spectrometer[16] at the LANSCE spallation neutron source at Los Alamos, covering energy transfers between 0 and 20 meV with resolutions of 0.4 and 0.8 meV full-width at half-maximum (FWHM) at two different incident energies (12 and 20 meV), and temperatures between 1.4 and 77 K. We also used QENS,[17] an inverse geometry crystal analyzer spectrometer at the Intense Pulsed Neutron Source at Argonne National Laboratory with final neutron energy of 3.63 meV at five different temperatures ranging from 1.4 to 30 K. Its energy resolution is $\approx 100\ \mu$eV FWHM.

Data taken at temperatures of 1.4, 10, 17, and 30 K are shown in Fig. 1. The large maximum centered about zero energy is due to elastic scattering. At 1.4 K, a single sharp peak is observed at 1.24 meV, we attribute this to excitations from spin states $m=\pm 10$ to $m=\pm 9$. We note that at 1.4 K, the overwhelming majority of spins are in the ground states $m=\pm 10$. As the temperature is raised and some of the spins are thermally activated to higher energy states, new peaks develop on the low energy side of the 1.24 meV peak; we attribute these to transitions from $m=\pm 9$ to ± 8, ± 8 to ± 7, etc. Transitions such as those between $m=\pm 9$ and ± 7 are forbidden by neutron scattering selection rules, $\Delta S=0,\ \pm 1$, $\Delta m=0,\ \pm 1$. Due to the increased population of higher energy levels at higher temperature, peaks also appear that are symmetrically placed with respect to $E=0$ on the neutron energy-gain side. No maxima appear above 1.24 meV up to ≈ 3 meV, where further excitations occur that are possibly associated with transitions between different spin manifolds;[15] this confirms that the peak at 1.24 meV corresponds to transitions between the ground and first excited states of the spin-10 manifold. The maxima are labeled by the index m, which denotes the level from which each excitation occurs; thus, the 1.24 meV peak is labeled 10, the adjacent peak, 9, and so on. As shown below, the positions of these peaks contain key information regarding the spin Hamiltonian of Mn_{12}–Ac.

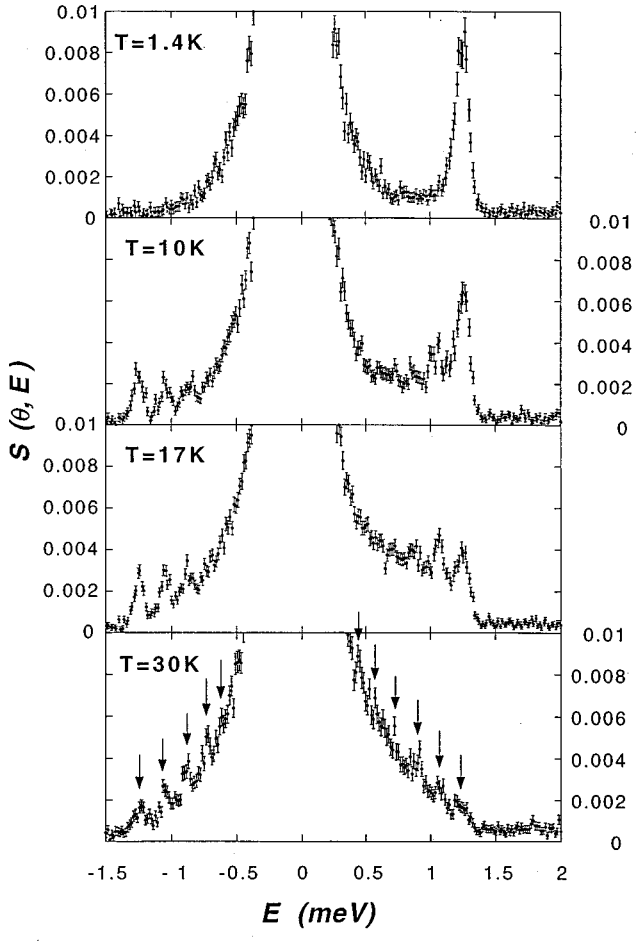

FIG. 1. Neutron scattered intensity vs energy at temperatures of 1.4, 10, 17, and 30 K. The spectra shown in this figure were obtained at different scattering angles. The arrows denote the positions of peaks deduced from data taken at all temperatures and scattering angles.

Since there is no externally applied magnetic field in our experiments, and the Zeeman energy due to the internal magnetic field of Mn_{12}–Ac (estimated to be several hundred Oe[18]) is at least two orders of magnitude smaller than the anisotropy energy, the term $-\mu_B \mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S}$ in spin Hamiltonian (1) can be safely neglected. Furthermore, the fourth-order transverse anisotropy term $C(S_+^4+S_-^4)$ has little effect on the Eigen energies of the states with large $|m|$. The energy of the states probed in our experiments near the bottom of the anisotropy wells can thus be approximated by $E_m=-Dm^2-Am^4$, and the energy of excitation from levels $\pm m$ to $\pm(m-1)$ will be

$$\Delta E_m = E_{m-1}-E_m = D(2m-1)+A[m^4-(m-1)^4]. \quad (2)$$

In Fig. 2, six excitation energies are plotted as a function of the index m. The deviation from linear dependence clearly indicates the importance of including a diagonal fourth-order term. A two-parameter fit to Eq. (2) gives $D=(4.67\pm 0.18)\times 10^{-2}$ meV $=(0.54\pm 0.02)$ K and $A=(1.04\pm 0.10)$

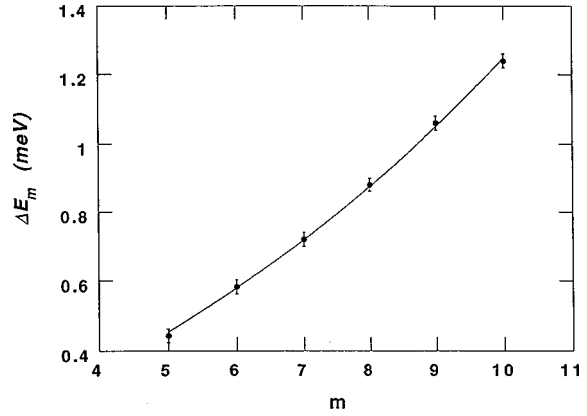

FIG. 2. Energies of the peaks of Fig. 1 plotted as a function of index m (m denotes initial states for energy loss and final states for energy gain).

$\times 10^{-4}$ meV$=(1.2\pm 0.1)\times 10^{-3}$ K. These values are very close to the EPR results obtained by Barra *et al.*: $D=(0.56\pm 0.04)$ K, $A=(1.1\pm 0.1)\times 10^{-3}$ K.

DISCUSSION

For our values of D and A, the full height of the anisotropy barrier (defined as the energy difference between $m=0$ and 10) is calculated to be (66 ± 3) K. The ratio $|Am^4/Dm^2|\approx 0.2$ for $m=10$. Since A and D have the same sign, the level spacings near the bottom of the anisotropy wells are relatively sparser, and the distribution of levels near the top of the barrier denser. Due to the presence of a fourth-order term, the energy levels will not come into resonance simultaneously for a given field applied along the anisotropy axis. Since two levels of different quantum numbers m and m' are degenerate when $H=-(m+m')[D+A(m^2+m'^2)]/(g_{\text{para}}\mu_B)$, all pairs of states $m'=-m$ come into resonance simultaneously only in zero magnetic field. Moreover, the spacing between steps in the hysteresis loops will not be constant. Detailed comparison of the magnetic fields at which maxima in the relaxation rate occur with the calculated level crossings using the parameters given above can, in principle, allow a determination of the specific levels near the top of the barrier that participate in the tunneling.

In summary, we have used zero-field inelastic neutron scattering to probe the excitation spectrum of Mn_{12}–Ac. Our resolution enables us to observe a series of peaks within the range from 0 to 1.24 meV; we attribute these peaks to transitions within the $S=10$ manifold. A two-parameter fit yields values for the anisotropy constant D and the coefficient of the fourth-order diagonal anisotropy A that are inconsistent with those deduced from EPR experiments of Hill *et al.* and agree well with results of Barra *et al.*[12]

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