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Direct Identification of the Minority and Majority Species in the Single-Molecule Magnet Mn_{12}-Acetate by Inelastic Neutron Scattering

Oliver Waldmann,* Graham Carver, Chris Dobe, Andreas Sieber, Hans U. Güdel, and Hannu Mutka

Department of Chemistry and Biochemistry, University of Bern, CH-3012 Bern, Switzerland, and
Institut Laue-Langevin, 6 rue Jules Horowitz, BP 156, 38042 Grenoble Cedex 9, France

Received November 22, 2006; E-mail: waldmann@iac.unibe.ch

Single-molecule magnets (SMMs), such as the compound $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot2CH_3COOH\cdot4H_2O$ (Mn_{12}-acetate), have attracted enormous attention recently.[1] At low temperatures, below a blocking temperature T_B, they exhibit slow relaxation of the magnetization, and each molecule in principle may function as a data-storage unit. It has been recognized that large molecular ground-state spins S and easy-axis anisotropy parameters D have to be realized in order to achieve high blocking temperatures, $T_B \propto |D|S^2$. Hence, much effort is directed into the understanding and control of these two parameters (for Mn_{12}-acetate, $T_B \approx 3.5$ K, $S = 10$, $D = -0.057$ meV). While impressive progress toward larger spin-ground states has been made,[2] the simultaneous control of the easy-axis anisotropy is still a challenge, and Mn_{12}-acetate is still the SMM with the highest known blocking temperature. Understanding the structural origin of D in Mn_{12}-acetate in particular is thus of interest.

Crystals of Mn_{12}-acetate contain the normal slow-relaxing (SR) molecules, but also about 5% of a fast-relaxing (FR) species, which is believed to be related to a Jahn−Teller isomer where the Jahn−Teller axis of one or more of the Mn(III) ions is tilted, with the result that D and hence T_B is reduced.[3] Inelastic neutron scattering (INS)[4] is the right experimental tool to determine D of the FR species, since its spectroscopic resolution allows one to characterize individual species. Indeed, in a recent pressure-dependent INS study the anisotropy splitting of two species, called majority and minority species, were observed and carefully characterized.[5] In particular, the D values were determined. The majority species is obviously related to the SR species of Mn_{12}-acetate. Concerning the minority species it is natural to relate it to the FR species, but there exists no direct experimental evidence for this association so far.

In this Communication, this gap in the logic of the argument is closed. A sophisticated INS experiment is presented, which directly demonstrates that the minority species in the INS spectrum is a FR species (and that the majority species is a SR species). This point is of some importance because with that the D value of the FR species is known precisely, enabling attempts toward its structural rationalization.

Single crystals of nondeuterated Mn_{12}-acetate (typical dimensions $5 \times 0.5 \times 0.5$ mm^3 and mass ~2 mg) were synthesized as in ref 6. An oriented array of about 500 single crystals was obtained by positioning the needle-shaped tetragonal crystals in grooves milled into aluminum platelets, such that the anisotropy axes z (= needle axes) are oriented along the grooves. INS measurements were performed on the time-of-flight spectrometer IN5 at the Institute Laue-Langevin in Grenoble, France. The sample was inserted into an orange cryostat with a 2.5 T vertical-field magnet, and aligned with the z axes of the crystals parallel to the magnetic field. The initial neutron wavelength was 5.9 Å, and the resolution at the elastic line was 60 μeV. The efficiency of the detectors was calibrated using a vanadium standard. The spectra shown here correspond to the sum over all the scattering angles. For further details of the experimental procedure, see ref 7.

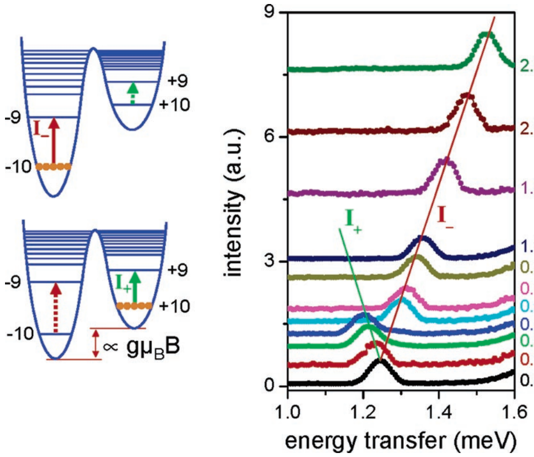

Figure 1. Left: Schematic representation of the state of the Mn_{12}-acetate molecules for fields below (bottom) and above (top) 0.45 T after initialization with a negative magnetic field. Because of the Zeeman splitting in an applied magnetic field, the double-well potential for magnetization reversal is tilted such that the $M = +10$ level is raised with respect to the $M = -10$ level. For fields below 0.45 T, the $M = +10$ level is populated and transition I_+ (green) is observed; for fields above 0.45 T, the $M = -10$ level is populated instead and transition I_- (red) is observed. Right: Neutron energy-loss spectra at 1.5 K for various magnetic fields after initialization with a negative field. For clarity, curves are vertically offset proportionally to the field. Solid lines indicate the field dependence of the peaks, which correspond to the transitions I_+ and I_- of the majority species for fields below and above 0.45 T, respectively.

The following set of experiments was conducted. At a temperature of 1.5 K, the magnetic field was first set to −0.85 T, such that all molecules populate the $M = +10$ level on the right side of the double-well potential reflecting the easy-axis anisotropy (Figure 1). Then the magnetic field was swept to a positive magnetic field $\mathbf{B}_0$, and the INS spectrum recorded. This procedure was repeated for several different values of $\mathbf{B}_0$ in the range from 0 to 2.5 T, see Figure 1. At zero field, the INS spectrum exhibits a strong feature at around 1.24 meV, and a much weaker feature at around 0.9 meV, corresponding to the above-mentioned majority and minority species, respectively (Figure 2).

For the majority species the experimental findings are as follows. At fields below 0.45 T the chosen temperature of 1.5 K is much lower than the blocking temperature of Mn_{12}-acetate, and the relaxation time for magnetization reversal can be considered infinite for the time scale of the experiment (at 2 K the relaxation time is already about 2 months at zero field[1]). Hence, all molecules stay in the $M = +10$ level, that is, right side of the potential well, even though this state is above the $M = -10$ ground state owing to the Zeeman energy, which is $E_z(M) = g\mu_B\mathbf{B}_0M$ (μ_B is the Bohr magneton). This gives rise to an INS transition from the $M = +10$

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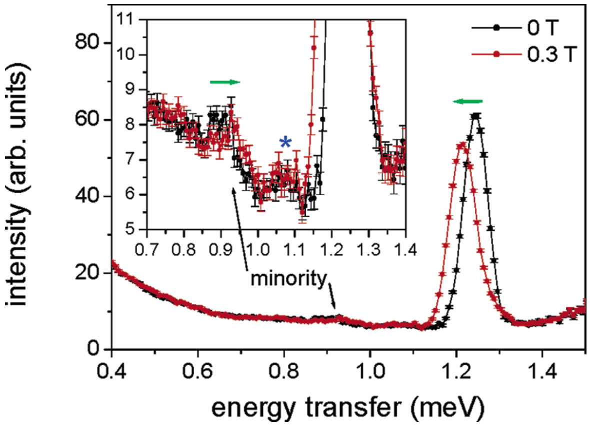

Figure 2. Neutron energy-loss spectra at 1.5 K in a magnetic field of 0 and 0.3 T after initialization with a negative field. The peak of the majority species at around 1.24 meV is shifted to lower energy transfer by the magnetic field, while the peak of the minority species at around 0.9 meV is shifted to higher energy transfer. These shifts are indicated by the green arrows. The inset shows the minority peak in more detail. The blue asterisk indicates a spurios feature.

to $M = +9$ level (green transition I_+ in Figure 1). The transition $M = -10 \rightarrow -9$ (red transition I_-), which is also allowed by the INS selection rules, is not observed because the $M = -10$ level is not populated. Accordingly, one peak corresponding to transition I_+ at the energy $E_+ = E_0 + E_z(9) - E_z(10) = E_0 - g\mu_B\mathbf{B}_0$ is observed in the INS spectrum, see Figure 1 (E_0 is the energy gap between the $M = \pm10$ and $\pm$ 9 levels in zero field).

For fields $\mathbf{B}_0$ larger than 0.45 T, the $M = +10$ level crosses the $M = -9$ level on the other side of the double-well potential during the field reversal from -0.85 T to $\mathbf{B}_0$, which opens an efficient relaxation path, and the molecules relax quickly to the $M = -10$ ground state. Hence, only the peak due to the transition I_- is now observed in the INS spectrum, at an energy of $E_- = E_0 + E_z(-9) - E_z(-10) = E_0 + g\mu_B\mathbf{B}_0$ (see Figure 1).

Hence, for a SR molecule the peak in the INS spectrum shifts to *lower* energy, while for a FR molecule the peak shifts to *higher* energy with *increasing* field.

The behavior of the minority species is presented in Figure 2 for the fields of 0 and 0.3 T. Clearly, for the minority species the INS peak is shifted to higher energies with increasing magnetic field, as shown in the inset of Figure 2. Accordingly, the minority species is a FR species, which is the main conclusion of this Communication. Figure 2 clearly demonstrates the opposite shifts (green arrows) of the FR minority and SR majority species in a small magnetic field.

Figure 3 summarizes the experimental findings of the present work. The open circles represent the peak positions of the observed INS transitions as function of field, and the solid lines correspond to best-fit curves. For the majority species $E_0 = 1.245(1)$ meV, and $g = 1.950(2)$ is obtained, in perfect agreement with previous estimates.[1,8] For the minority species $E_0 = 0.904(3)$ meV, and $g = 1.89(9)$ is obtained. The smaller value of E_0 corresponds to a smaller D value in this species, and hence the fast magnetic relaxation.

In conclusion, our field-dependent inelastic neutron scattering experiment on an array of oriented single crystals of Mn_{12}-acetate provides unambiguous evidence that the minority species observed in the INS spectra indeed is the fast-relaxing species observed, for instance, in AC-susceptibility measurements. Together with the previous pressure-dependent INS experiment,[5] the anisotropy parameters of the fast-relaxing species of Mn_{12}-acetate are now known precisely: $D = -0.0360(1)$ meV and $B^0_4 = -4(1) \times 10^{-6}$ meV. This should enable a better understanding of the structural origin of the easy-axis anisotropy parameter D and the slow magnetic relaxation in the prototypical SMM Mn_{12}-acetate in the future.

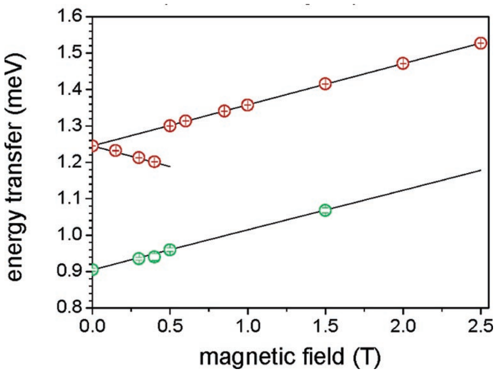

Figure 3. Field dependence of the INS peaks of the majority (red) and minority (green) species. The solid lines correspond to best-fit curves with parameters given in the text.

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