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Transverse anisotropy in the mixed-valent Mn$_2^{II}$Mn$_4^{III}$Mn$_3^{IV}$ single-molecule magnet

Saiti Datta, Constantinos J. Milios, Euan Brechin, and Stephen Hill

Department of Physics, University of Florida, Gainesville, Florida 32611, USA
School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, United Kingdom

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High-frequency electron paramagnetic resonance measurements have been performed on a single-crystal sample of a recently discovered mixed-valent Mn$_2^{II}$Mn$_4^{III}$Mn$_3^{IV}$ single-molecule magnet, with a spin S=17/2 ground state. Frequency, temperature and field-orientation dependent studies confirm previously reported axial magnetic anisotropy parameters and also provide clear evidence for higher order (fourth and sixth) transverse terms that are responsible for the magnetic quantum tunneling observed in this system.

INTRODUCTION

Mixed-valent manganese clusters are considered ideal candidates for single-molecule magnets (SMMs) as they often (a) exhibit large spin ground states and (b) possess Jahn–Teller distorted Mn$^{III}$ ions which contribute to a large easy-axis-type magnetic anisotropy. These nanosized magnetic materials display magnetization hysteresis and quantum tunneling of magnetization suggesting that they may one day find applications in information storage and possibly quantum computation.

Here, we present single-crystal high-frequency electron paramagnetic resonance (HF-EPR) studies of a mixed-valent Mn$_2^{II}$Mn$_4^{III}$Mn$_3^{IV}$ complex [hereafter Mn$_9$ (Ref. 4)], confirming the main findings of previous magnetic measurements and inelastic neutron scattering (INS) studies, which showed that Mn$_9$ has a spin ground state of S=17/2, a dominant axial anisotropy parameterized by a D of value ~0.24 cm$^{-1}$, together with a fourth-order axial zero-field splitting (ZFS) term $B_4^{II}$=+6.68×10$^{-6}$ cm$^{-1}$. Crucially, the present study provides clear evidence for higher-order (fourth and even sixth order) transverse anisotropy terms, which will clearly influence the tunneling.

EXPERIMENTAL

The [Mn$_9$O$_4$(O$_2$CCH$_3$)$_{11}$(thme)(py)$_4$(H$_2$O)$_2$] complex was prepared as reported previously. Good sized black crystals were obtained for single-crystal HF-EPR measurements. The metallic skeleton of the complex can be thought to comprise two rings: a smaller [Mn$^{IV}$O]$_{10}^{10+}$ triangle within a [Mn$^{III}$Mn$^{II}$O$_6$]$_{16}^{16+}$ hexagon (the charge is compensated by the ligands). At first sight, the magnetic core appears to have a pseudothreefold topology. However, closer inspection of the Mn valence states on the outer hexagon reveal a much lower symmetry. All of the Mn ions are in distorted octahedral geometries with the Jahn–Teller elongation of the Mn$^{IV}$ ions lying almost perpendicular to the plane of the [Mn$^{III}$Mn$^{II}$O$_6$]$_{16}^{16+}$ hexagon. The complex crystallizes such that there are two symmetry-equivalent, but differently oriented molecules in the unit cell whose magnetic easy axes are approximately perpendicular to each other.

HF-EPR experiments were performed on a single crystal at various temperatures and frequencies from 50 to 200 GHz with the dc magnetic field applied along different crystallographic directions. The spectra were obtained at fixed frequencies and temperatures while varying the strength of the dc magnetic field. Details of the experimental technique can be found elsewhere.

DATA AND DISCUSSION

Single-axis rotation studies were first performed to roughly determine the orientation of the crystal in the magnetic field. Figure 1 shows temperature dependent spectra obtained at 120 GHz, with the field oriented reasonably close (30°) to the easy axis associated with one of the two sites in the unit cell. The intensities of the lowest field peaks decrease upon increasing the temperature. This can be ex-
plained assuming a negative uniaxial anisotropy ($D < 0$). The appearance of two sets of peaks in Fig. 1 indicates that, in addition to the two different molecular orientations, there exist inequivalent Mn$_5$ species with slightly different ZFS parameters. We label the stronger peaks A and the weaker ones B. Peaks 1, 2, 3, 4, and 5 correspond to the following axial parameters: $D = -0.247$ cm$^{-1}$, $B_3^0 = 4.6(1)$ $10^{-6}$ cm$^{-1}$ and $g_z = 1.98$. It is well documented that low-field data (especially extrapolations to $B = 0$) obtained for fields close to the easy axis are insensitive to transverse anisotropy terms. As can be seen from Table I, the obtained axial parameters agree very well with previous magnetic and spectroscopic measurements.

Rotation about a single axis guarantees field-alignment in the hard plane, although the orientation of the field within the hard plane is not known. Detailed studies (not shown) allow identification of one or other of the hard plane orientations from the angle dependence of the peak positions (see Ref. 9). Figure 3(a) displays temperature dependent 52 GHz spectra for one of these hard-plane orientations. The A and B peaks are again observed, corresponding to the two species. The reversed ordering of A and B (see Fig. 1) is consistent with Eq. (1). Peaks labeled A$1'$, A$3'$, and A$5'$ (likewise for the B peaks) correspond to the following fine-structure transitions: $m_3 = -\frac{17}{2} \rightarrow -\frac{11}{2}$, $-\frac{15}{2} \rightarrow -\frac{9}{2}$, and $-\frac{7}{2} \rightarrow -\frac{3}{2}$, respectively, where $m_3$ represents the spin projection along the easy ($z$) axis of the crystal.

The simulations assume $S = \frac{17}{2}$, and best overall agreement with the data is obtained with $D = -0.24$ cm$^{-1}$ ($D = -0.25$ cm$^{-1}$) for species A (species B), $B_3^0 = +6.68 \times 10^{-6}$ cm$^{-1}$ and $g_z = 1.98$. It is well documented that low-field data (especially extrapolations to $B = 0$) obtained for fields close to the easy axis are insensitive to transverse anisotropy terms. As can be seen from Table I, the obtained axial parameters agree very well with previous magnetic and spectroscopic measurements.

Rotation about a single axis guarantees field-alignment in the hard plane, although the orientation of the field within the hard plane is not known. Detailed studies (not shown) allow identification of one or other of the hard plane orientations from the angle dependence of the peak positions (see Ref. 9). Figure 3(a) displays temperature dependent 52 GHz spectra for one of these hard-plane orientations. The A and B peaks are again observed, corresponding to the two species. The reversed ordering of A and B (see Fig. 1) is consistent with Eq. (1). Peaks labeled A$1'$, A$3'$, and A$5'$ (likewise for the B peaks) correspond to the following fine-structure transitions: $m_3 = -\frac{17}{2} \rightarrow -\frac{11}{2}$, $-\frac{15}{2} \rightarrow -\frac{9}{2}$, and $-\frac{7}{2} \rightarrow -\frac{3}{2}$, respectively, where $m_3$ represents the spin projection along the (high) magnetic field quantization axis. The low field portion of the figure (fields below A$5'$) is complicated by absorptions due to the other molecular orientation.

We now argue that fourth and higher-order transverse ZFS interactions are necessary in order to account for these spectra. It is well documented that HFPR measurements

![FIG. 2. Frequency dependence of the peak positions (□) associated with the two species: (a) A and (b) B. Data were obtained at 5 K for the same field orientation as in Fig. 1. The solid lines are simulations based on Eq. (1), using the parameters given in the main text.](image)

![FIG. 3. (Color online) (a) Temperature dependent EPR spectra obtained at 52 GHz with the field in the hard plane of one of the molecular orientations. The fine structure splitting (A and B peaks) can again be clearly seen (refer to main text for explanation of numbering). At the highest temperature, additional peaks appear (labeled X) which we attribute to excited spin multiplets. (b) Frequency dependence of the 7 K hard plane peak positions (○) associated with species A [the dashed curve corresponds to the data in (a)]. The orientation of the field within the hard plane is not known. The curves correspond to various simulations based on Eq. (1) with the inclusion of a rhombic term $[E(\mathbf{S}_z^2 - \mathbf{S}_x^2)]$. See main text for explanation.](image)

<table>
<thead>
<tr>
<th>ZFS (cm$^{-1}$)</th>
<th>FDMRS</th>
<th>INS</th>
<th>Magnetization</th>
<th>$\mu$-SQUID</th>
<th>DFT</th>
<th>EPR (A)</th>
<th>EPR (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>$-0.247(5)$</td>
<td>$-0.249(5)$</td>
<td>$-0.29(3)$</td>
<td>$-0.258$</td>
<td>$-0.235$</td>
<td>$-0.24$</td>
<td>$-0.25$</td>
</tr>
<tr>
<td>$B_3^0/10^{-6}$</td>
<td>$4.6(1)$</td>
<td>$7(4)$</td>
<td></td>
<td></td>
<td></td>
<td>$6.7$</td>
<td>$6.7$</td>
</tr>
</tbody>
</table>
find that it is impossible to obtain agreement between our
=0.035 cm−1, E curves were generated with the following parameters:
for extremely weak transverse second order anisotropy
peaks are reasonably close to the positions one would expect
Here, the goal was to achieve agreement with the A3
order transverse terms, as illustrated in Fig.4. In fact, one
obtain anything approaching agreement with more than one
impossible. The coeffi-
clearly visible to the naked eye down to low fields. This
suggests that a B^2.O^2 interaction would cause very fast tunnel-
ing in this Mn9 complex, which is not found experiment-
tally and, therefore, seems to be unphysical. Again, this hints
at the importance of multiple high-order transverse ZFS in-
teractions that can account for both the EPR data presented
here and the slow magnetization dynamics in the quantum
regime. We also note that internal dipolar and hyperfine
fields must be important for zero-field QTM in these half
integer SMMs.

CONCLUSIONS
Multi-high frequency and field orientation dependent
EPR studies have enabled a detailed characterization of the
spin Hamiltonian of a mixed valent Mn9 complex. These
measurements hint at the importance of high- (fourth and
sixth) order transverse anisotropy terms in the low tempera-
ture quantum dynamics.

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with B ⊥ c provide information concerning transverse terms.8
In the following analysis, we constrain the axial terms (D
and B^2) on the basis of the simulations in Fig. 2. Density
functional theory (DFT) calculations predict that Mn9
possesses a rhombohedral ZFS parameter E=0.035 cm−1.5 We
find that it is impossible to obtain agreement between our
results and simulations including only this interaction [E(S^2
−S_y^2)], as demonstrated in Fig. 3(b). The black curves
were generated for two different E values and field orientations
relative to the hard axis (within the hard plane): E
=0.035 cm−1, φ=25°; and E=0.015 cm−1, φ=0° (i.e., B∥x).
These parameters were chosen in order to obtain agreement
between the simulations and the A1’ peak. However, as can
be seen, agreement with A3’ is not good. Conversely, the red
curves were generated with the following parameters: E
=0.035 cm−1, φ=40° and E=0.015 cm−1, φ=38° (i.e., B∥x).
Here, the goal was to achieve agreement with the A3’ peak.
g_x and g_y were set to 2.00 for all of these simulations, as well
as those in Fig. 4. The main result is that it is impossible to
obtain anything approaching agreement with more than one
of these peaks using only an E parameter.

It turns out that, with the exception of A1’, all EPR
peaks are reasonably close to the positions one would expect
for extremely weak transverse second order anisotropy (or
φ=45°). In contrast, A1’ is shifted considerably to higher
fields. It is only possible to mimic its behavior using higher
order transverse terms, as illustrated in Fig. 4. In fact, one
can obtain good agreement with the hard-plane spectra for
several different parameter sets. Examples are displayed in
Fig. 4 involving purely B^2.O^2 (a) and B^2.O^2 (b). The coefficients
are given in the captions. Interestingly, B^2.O^2 gives
excellent agreement, whereas terms that one might expect to
work well, such as B^2.O^2, do not give good agreement. In
reality, it is likely that the transverse Hamiltonian involves
admixtures of all of these interactions, reflecting the pseudo
treefold,5 albeit low symmetry of the molecule. Only detailed
multihigh-frequency measurements performed as a function
of the field orientation within the hard plane can resolve
this issue, which would be greatly complicated by the
multiple species, orientations, and the overall low sym-
metry of this complex. Nevertheless, the present measure-
ments serve a useful purpose, hinting at the significant fourth
and higher-order anisotropy that likely results as a conse-
quence of S mixing brought about by low-lying excited spin
states.10 Indeed, the spectra in Fig. 3(a) clearly show features
(labeled X) associated with the population of low-lying S
< S/2 spin states.

One final point to note from Fig. 4(a) is the huge tunnel
splitting of the lowest-lying m_s=± S/2 doublet, which is
clearly visible to the naked eye down to low fields. This
suggests that a B^2.O^2 interaction would cause very fast tun-
neling in this Mn9 complex, which is not found experiment-
tally and, therefore, seems to be unphysical. Again, this hints
at the importance of multiple high-order transverse ZFS in-
teractions that can account for both the EPR data presented
here and the slow magnetization dynamics in the quantum
regime. We also note that internal dipolar and hyperfine
fields must be important for zero-field QTM in these half
integer SMMs.

FIG. 4. (Color online) Hard-plane data (from Fig. 3) and simulations based
on Eq. (1), with the additional inclusion of the higher-order transverse in-
teractions (a) B^2.O^2 and (b) B^2.O^2 (actual functions given in the figures). Both
simulations agree reasonably well with the experimental data using the axial
ZFS parameters determined from the simulations in Fig. 2, along with the
following parameters: (a) B^2=8.4×10^{-5} cm^{-1}, B^2=8.4×10^{-7} cm^{-1}, and
φ=0 for both (a) and (b). See main text for detailed explanation. The blue
colors correspond to the splitting in the ground state m_s=± S/2 doublet.