Inhomogeneous broadening of single photon transitions in molecular magnets

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Single photon transitions in molecular magnets provide valuable probes of the widths of energy levels. We use time-domain terahertz spectroscopy to measure the width of the transition from the ground state to the first excited state in Mn12 acetate in zero applied field. The width of this transition, approximately 5.5 GHz full width at half maximum, is too large to be caused by local magnetic fields. Experiments by Mukhin et al. rule out homogeneous broadening as the source of the linewidth. The linewidth can be explained if the anisotropy constant in the spin Hamiltonian is not uniform due to crystal defects such as dislocations. Since similar linewidths are observed in several other materials, we conclude that whatever disorder causes this broadening is not limited to Mn12 acetate. © 2002 American Institute of Physics. DOI: 10.1063/1.1450789

In recent years high-spin molecular clusters have been the focus of much investigation because they have been shown to exhibit quantum tunneling of the magnetic moment. The first to be shown to exhibit quantum tunneling and the most heavily studied is Mn12 acetate (\(\text{Mn}_{12}O_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4\cdot 2\text{CH}_3\text{COOH}\cdot 4\text{H}_2\text{O}\)). Next Fe8 (\(\text{Fe}_8(\text{tacn})_{6}\text{O}_2\text{OH})_{12}\cdot \text{Br}_8\cdot 9\text{H}_2\text{O}\), where tacn is the organic ligand 1,4,7-triazacyclononane) is also with spin 10, was observed to exhibit quantum tunneling. In the following years, many other such molecules have been discovered.

One particularly interesting area of investigation is the interaction of the spins with their environment, as reflected in the linewidth of the energy levels. In some cases, the measured linewidth of transitions provides information about the intrinsic properties of the clusters (homogeneous broadening), while in others it seems to be due to variations in the local environments of clusters (heterogeneous broadening). Careful analysis of the linewidths observed under different conditions leads us to conclude that the presence of defects leads to variations in the anisotropy constant in these materials.

We first review the case of Mn12 acetate, which we have discussed more fully in a previous publication. Its Hamiltonian is approximately given by \(\mathcal{H} = -\alpha S_z^2 - \beta S_z^4 + \gamma (S_+^4 + S_-^4) - g\mu_B S \cdot H\), where \(\alpha = 0.38 \text{ cm}^{-1}\), \(\beta = 8.2 \times 10^{-3}\text{ cm}^{-1}\), \(\gamma = \pm 2 \times 10^{-5}\text{ cm}^{-1}\), and \(g = 2.5\). In zero field, states with equal \(|m|\) are degenerate. The ground states \(m = \pm 10\) are separated by a barrier of approximately 66 K.

We have measured the linewidth of intrawell transitions using time-domain terahertz spectroscopy. The measurements were made on a pellet pressed from small unaligned crystals of Mn12 acetate prepared according to the procedure of Lis.

In Fig. 1, we focus on the absorption at 300.6 GHz, which corresponds to the transition \(m = 10 \rightarrow 9\) (and the \(-10 \rightarrow -9\) transition). (The absorption from \(m = \pm 9\) to \(\pm 8\) has a similar linewidth.) We plot the index of refraction as a function of frequency near this absorption at temperature \(T\).
narrow peak could never have been observed. However, it is
local field had a FWHM of 0.20 T, as implied, then this
They measured the FWHM to be 236 Oe at 2.6 K. If the
ation rate of the magnetization toward its equilibrium value.
FWHM has been estimated at 280–380 G. 17
From the Hamiltonian, we see that
Lorentzian. However, there has been another measurement of
for us to determine whether the line shape is Gaussian or
explain a linewidth of 5.5 GHz requires a magnetic field
magnetic field parallel to the
axis and measured the relax-
relaxation experiments would be sensitive to variations in
a, but the width seen in the zero-field tunneling experiments
would be due to homogeneous broadening mechanisms, either due to the tunneling time itself or the
interactions with phonons, as proposed in Ref. 19.
These experiments are unable to determine the nature of the
defects that cause the variations in a. However, we note that recent work of Chudnovsky and Garanin postulates dis-
locations as the source of spin tunneling and calculates the
effect of these dislocations on a. 20 Finally, other experi-
tmental articles have recently presented evidence for this distrib-
ution in the anisotropy constant. 21,22
Although such a distribution of a would have no effect on the width of the relaxation peak in zero field because all
levels ±m are degenerate regardless of a, tunneling peaks at
nonzero fields would be broadened, since (neglecting β) the
field
Hn = − an / gμB
that brings the levels m and −m+n into resonance is proportional to a. It would be difficult to observe this broadening in tunneling measurements, since the term βS4 a brings different levels into resonance at differ-
ent fields, so that if more than one level m is involved in the
thermally assisted tunneling, the relaxation peak will be
broadened. However, we note that the width of the relaxation
peaks in nonzero fields observed in Ref. 23 is sufficiently
large to accommodate the required distribution of a.
This distribution of the anisotropy constant a seems to be a feature of other high-spin molecules, as well. The other
commonly studied molecule that exhibits quantum tunneling
of the spin is Fe₈, which also has a total spin of ten. How-
ever, the anisotropy constant of Fe₈ is smaller than that of
Mn₁₂ acetate by about a factor of three. Also, the symmetry
of Fe₈ is lower—and its crystal structure is triclinic rather than
tetragonal—so there are lower order terms in its Hamiltonian
that allow tunneling.
While we have not made any measurements on Fe₈,
Mukhin et al. 15 have measured the intrawell transitions in
this material. They observed a Gaussian line shape with a
FWHM=4.6 GHz for the m = 10→9 transition. Additionally,
they measured a FWHM of 9.2 GHz for the related material
Fe₈ PCL. In this material, perchlor ions are substituted for
some of the bromine ions, which increases the intercluster
distance, thereby decreasing the dipole coupling while in-
creasing disorder. The fact that the linewidth is larger for Fe₈
PCL even though the intercluster distance is larger suggests
that, in contrast to the conclusions of Ref. 15, the linewidth
is not caused by a distribution of dipolar magnetic fields, but
rather by a distribution of the anisotropy constant as in Mn₁₂
acetate.
To confirm this conclusion, we calculated the distribu-
tion of dipole moments that would be expected due to ran-
don orientations of the 28 nearby clusters that contribute the
combination of this field and the hyperfine field is not suffi-
cient to explain the width observed in our spectroscopy.
Since local magnetic fields cannot be the cause of the
observed inhomogeneous broadening, it seems most likely to
be caused by variations in the anisotropy constant a. If a
varied slightly (~1%) between clusters due to defects, then
this variation would be seen in the linewidth of the photon-
induced transition, but not in the zero-field tunneling. The
photon absorption experiments would be sensitive to vari-
ations in a, but the width seen in the zero-field tunneling
experiments would be due to homogeneous broadening
mechanisms, either due to the tunneling time itself or the
interactions with phonons, as proposed in Ref. 19.
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acetate.
To confirm this conclusion, we calculated the distribu-
tion of dipole moments that would be expected due to ran-
don orientations of the 28 nearby clusters that contribute the
largest dipole fields, using the same procedure as in Ref. 4. For Fe₈, the FWHM of the distribution was 740 G, which is not sufficient to explain the observed linewidth. However, this dipole width is in fairly good agreement with the width of 600 G measured by Wernsdorfer et al. for samples quenched in zero applied field.²⁴

The observed width of 4.6 GHz in Fe₈ could be explained by local magnetic fields only if the width of the magnetic field distribution were 0.16 T. Since both calculations and experiments yield a width that is much smaller than this, we conclude that in Fe₈, as in Mn₁₂acetate, the anisotropy constant is not uniform. However, one important difference between these systems is that in Mn₁₂acetate the defects that cause these variations in the anisotropy constant may play a role in the tunneling mechanism, while in Fe₈ the lower crystalline symmetry leads to terms in the Hamiltonian that are responsible for tunneling.²⁵

Finally, in Fig. 2, we present measurements on another molecular magnet, [Mn₃(hmp)₄Br₂(H₂O)₂]Br₂·4H₂O, where hmp⁻ is the anion of 2-hydroxymethylpyridine, which we will refer to as Mn₄. This molecule has S = 9, and electron paramagnetic resonance measurements indicate an anisotropy constant of −0.498 K with some uncertainty due to fitting of the rather complicated signal.²⁵ We measure the absorption from m = 9 → 8 to occur at 135 GHz, implying that the anisotropy constant is closer to 0.38 K. We also measure a FWHM on the order of 11 GHz, similar to the other molecules that have been studied.

In conclusion, we observe that in Mn₁₂acetate and Fe₈ the inhomogeneous linewidths observed in intrawall transitions cannot be explained by variations in local magnetic fields, and are therefore probably due to variations in the anisotropy constant. The similar transition width observed in another single molecule magnet, Mn₄, suggests that the type of disorder responsible for the variations in the anisotropy constant is probably a feature of many other single molecule magnets.

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FIG. 2. Absorption coefficient of Mn₄ at 2 K. The line shows a Gaussian absorption centered on 135.5 GHz with σ=4.5 GHz.