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 Mn_{12} 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 [Phys. Rev. B **63**, 214411 (2001)]. 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 Mn_{12} acetate. © *2002 American Institute of Physics.*
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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 Mn_{12} acetate ($[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$).[1,2] Next Fe_8 ($[Fe_8(tacn)_6O_2(OH)_{12}]Br_8\cdot 9H_2O$, where tacn is the organic ligand 1,4,7-triazacyclononane), also with spin 10, was observed to exhibit quantum tunneling.[3] 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 Mn_{12} acetate, which we have discussed more fully in a previous publication.[4] Its Hamiltonian is approximately given by $\mathcal{H}=-\alpha S_z^2-\beta S_z^4+\gamma(S_+^4+S_-^4)-g\mu_B\mathbf{S}\cdot\mathbf{H}$, where $\alpha=0.38\ \mathrm{cm}^{-1}$, $\beta=8.2\times10^{-4}\,\mathrm{cm}^{-1}$, $\gamma\sim\pm2\times10^{-5}\,\mathrm{cm}^{-1}$, and $g\sim2$.[5–12] In zero field, states with equal $|m|$ are degenerate. The ground states $m=\pm10$ 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 Mn_{12} acetate prepared according to the procedure of Lis.[13]

In Fig. 1, we focus on the absorption at 300.6 GHz, which corresponds to the transition $m=10\rightarrow9$ (and the $-10\rightarrow-9$ transition). (The absorption from $m=\pm9$ to ±8 has a similar linewidth.) We plot the index of refraction as a function of frequency near this absorption at temperature T

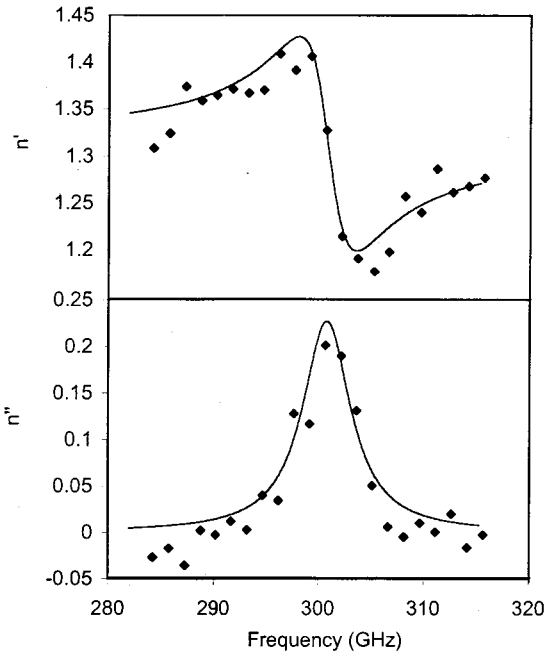

FIG. 1. Real and imaginary parts of the index of Mn_{12} acetate. The index is calculated directly from the transmission using Eq. (1). The line is a fit to the homogeneously broadened equations.

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$=2.1$ K. The index of refraction was calculated directly from the (complex) transmission spectrum using the following equation for a slab of thickness $d=1.4$ mm with complex index of refraction $\tilde{n}$:[14]

$$\tilde{t}(\omega)=\frac{4\tilde{n}}{(\tilde{n}+1)^2}\frac{e^{i\omega\tilde{n}d/c}}{1-\left(\frac{\tilde{n}-1}{\tilde{n}+1}\right)^2 e^{2i\omega\tilde{n}d/c}}. \quad (1)$$

Notice that since this is a magnetic transition, n must be correctly defined as $\sqrt{\mu\epsilon/\mu_0\epsilon_0}$, rather than approximated as $\sqrt{\epsilon/\epsilon_0}$. We stress that our measurement yields the complex index of refraction without any modeling of either the line shape or the high and low frequency extrapolations of the response functions. A fit to the data reveals a full width at half maximum (FWHM) of 5.5 GHz.

Given our limited frequency resolution, it is impossible for us to determine whether the line shape is Gaussian or Lorentzian. However, there has been another measurement of this absorption line by Mukhin *et al.*[11] Their data strongly favor a Gaussian fit to the transmission with FWHM=7 GHz.[15]

The most obvious source of this inhomogeneous broadening is local magnetic fields, which could be due to the dipolar field of neighboring clusters or the nuclear moments of the manganese atoms. The local dipolar field depends on the random orientations along the $\pm z$ directions of the magnetic moments of all the other clusters. The calculated value of the hyperfine field varies depending on the type of coupling that is assumed between the electron spins, but its maximum possible value ranges from 270 to 539 G,[16] and its FWHM has been estimated at 280–380 G.[17]

The effect of a local field would be to raise or lower the transition energy between the ± 10 and ± 9 levels, $\Delta E_{10,9}$. From the Hamiltonian, we see that $\Delta E_{10,9}(B)=\Delta E_{10,9}(B=0)\pm\mu_B g B_z$. For this material, g is very close to 2, so to explain a linewidth of 5.5 GHz requires a magnetic field distribution with width of 0.20 T.

This local field distribution seems initially to be ruled out by the measurements of the width of the tunneling peak performed by Friedman *et al.*[18] Starting with a sample cooled in zero applied field, Friedman *et al.* applied a small magnetic field parallel to the z axis and measured the relaxation rate of the magnetization toward its equilibrium value. They measured the FWHM to be 236 Oe at 2.6 K. If the local field had a FWHM of 0.20 T, as implied, then this narrow peak could never have been observed. However, it is important to remember that Friedman *et al.*[18] measured the width of the tunneling peak by fitting the tails of the exponential decay at each field, after the initial faster relaxation was complete. It is possible (albeit unlikely) that an initially broad dipole distribution is greatly narrowed once most of the spins have aligned with the applied field.

Therefore, it is useful to calculate the width of the dipolar distribution in order to check whether it could be responsible for the observed width in the intrawell transitions. This is done in Ref. 4 by considering random orientations of the 28 nearby spins that contribute the largest dipole fields. The resulting Gaussian distribution has a FWHM=520 G. The combination of this field and the hyperfine field is not sufficient 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 α. If α varied slightly ($\sim$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 variations in α, 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 α. However, we note that recent work of Chudnovsky and Garanin postulates dislocations as the source of spin tunneling and calculates the effect of these dislocations on α.[20] Finally, other experimental articles have recently presented evidence for this distribution in the anisotropy constant.[21,22]

Although such a distribution of α would have no effect on the width of the relaxation peak in zero field because all levels $\pm m$ are degenerate regardless of α, tunneling peaks at nonzero fields would be broadened, since (neglecting β) the field $H_n=-\alpha n/g\mu_B$ that brings the levels m and $-m+n$ into resonance is proportional to α. It would be difficult to observe this broadening in tunneling measurements, since the term βS_z^4 brings different levels into resonance at different 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 α.

This distribution of the anisotropy constant α 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 Fe_8, which also has a total spin of ten. However, the anisotropy constant of Fe_8 is smaller than that of Mn_{12} acetate by about a factor of three. Also, the symmetry of Fe_8 is lower—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 Fe_8, 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 $m=10\rightarrow 9$ transition. Additionally, they measured a FWHM of 9.2 GHz for the related material Fe_8 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 increasing disorder. The fact that the linewidth is larger for Fe_8 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 Mn_{12} acetate.

To confirm this conclusion, we calculated the distribution of dipole moments that would be expected due to random orientations of the 28 nearby clusters that contribute the

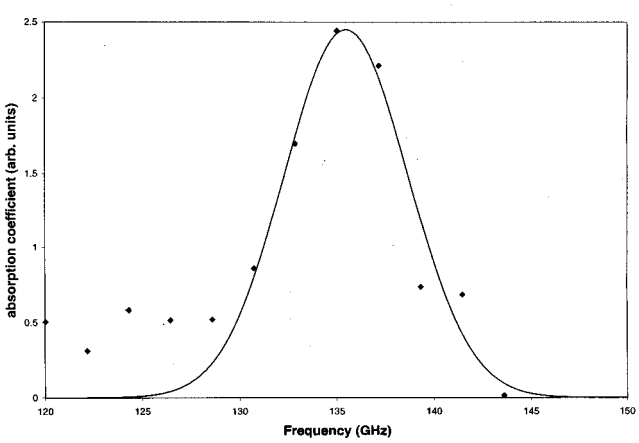

FIG. 2. Absorption coefficient of Mn_4 at 2 K. The line shows a Gaussian absorption centered on 135.5 GHz with σ=4.5 GHz.

largest dipole fields, using the same procedure as in Ref. 4. For Fe_8, 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 Fe_8 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 Fe_8, as in Mn_{12} acetate, the anisotropy constant is not uniform. However, one important difference between these systems is that in Mn_{12} acetate the defects that cause these variations in the anisotropy constant may play a role in the tunneling mechanism, while in Fe_8 the lower crystalline symmetry leads to terms in the Hamiltonian that are responsible for tunneling.

Finally, in Fig. 2, we present measurements on another molecular magnet, $[Mn_4(hmp)_6Br_2(H_2O)_2]Br_2\cdot 4H_2O$, where hmp^- is the anion of 2-hydroxymethylpyridine, which we will refer to as Mn_4. 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 $m=9\rightarrow 8$ 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 Mn_{12} acetate and Fe_8 the inhomogeneous linewidths observed in intrawell transitions can not 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, Mn_4, 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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