

Effect of mechanical stress on the linewidth of single photon absorptions in Mn₁₂-acetate

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Abstract

Quantum mechanical tunneling of the magnetic moment has been observed in several single molecule magnets, including Mn₁₂-acetate, but the tunneling mechanism is not entirely understood. It has been proposed that tunneling occurs due to defects in the crystal structure. These defects can be studied through their effect on the inhomogeneous linewidth of single photon (intrawell) transitions. However, most previous studies of the linewidth have been performed on crystals that have been pressed into pellets, which may introduce additional defects into the crystal structure. We report on measurements of the linewidth of loose crystals using the method of time-domain terahertz spectroscopy. The linewidth is not significantly reduced from the measurements on pressed pellets.

Key words: single molecule magnets; Mn₁₂-acetate; linewidth; tunneling

Mn₁₂-acetate ($[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4] \cdot 2 \text{CH}_3\text{COOH} \cdot 4\text{H}_2\text{O}$) consists of a core of twelve manganese ions with spins tightly coupled via superexchange through twelve oxide ions, with a ground-state spin $S = 10$. These clusters are separated by acetate and water groups and arranged in a tetragonal body-centered lattice. The Hamiltonian for the spin clusters is approximately given by $H = -\alpha S_z^2 - \beta S_z^4 + \gamma(S_+^4 + S_-^4) - g\mu_B \mathbf{S} \cdot \mathbf{H}$, where $\alpha = 0.38 \text{ cm}^{-1}$, $\beta = 8.2 \times 10^{-4} \text{ cm}^{-1}$, $\gamma \sim \pm 2 \times 10^{-5} \text{ cm}^{-1}$, and $g \sim 2$. [1–8] In zero field, states with equal $|m|$ are degenerate. The ground states $m = \pm 10$ are separated by a barrier of approximately 66 K.

Mn₁₂-acetate has been studied intensively since 1996 when the magnetic moment was observed to tunnel quantum mechanically [9,10]. Although a mechanism for tunneling in Mn₁₂-acetate has not been definitively established, it has been proposed that tunneling occurs

due to lattice dislocations that destroy the tetragonal symmetry, permitting extra terms in the Hamiltonian that couple the two wells [11,12]. This theory helps to explain the transition linewidths that have been observed in Mn₁₂-acetate [13].

The simplest experiments that measure linewidth do so by measuring the absorption of radiation in zero applied magnetic field [7,14]. Single photons can induce transitions between adjacent levels, and the linewidth of the transitions provides information about the broadening of the levels. However, these previous experiments were performed on samples of Mn₁₂-acetate that had been pressed into pellets. The pellets are formed by applying pressure of order 10^8 Pa . It seems possible that the process of pressing a pellet might introduce additional defects into the sample that were not present in the loose crystals. Since tunneling measurements are usually performed on single crystals, it is important to determine whether mechanical stress introduced additional defects into the pellets that were not present in the loose crystals.

We use terahertz time-domain spectroscopy to mea-

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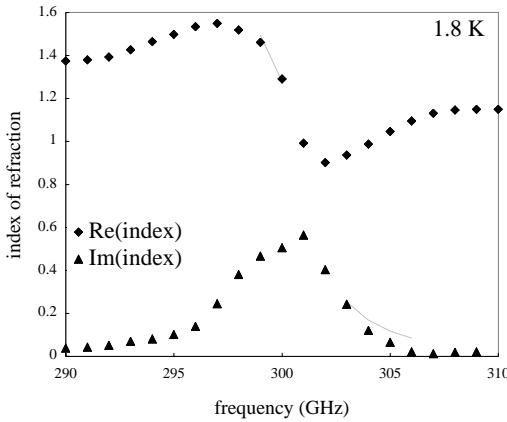


Fig. 1. Real and imaginary parts of the index of Mn₁₂ acetate. The index is calculated directly from the transmission. The line is the fit used in calculating the linewidth.

sure the linewidth of the intrawell $m = \pm 10 \rightarrow \pm 9$ transitions. The Mn₁₂-acetate was prepared according to the procedure of T. Lis [15]. The unaligned crystals were held between sheets of Mylar in a vapor flow He cryostat at 1.8 K.

In terahertz time-domain spectroscopy, a nearly single-cycle electromagnetic pulse with a length of a few picoseconds is produced and detected when optical pulses from a modelocked titanium sapphire laser gate the photoconductive generator and detector antennas. The time dependence of the transmitted electromagnetic pulse is measured by adjusting the delay between the laser pulses incident on the generator and detector. The measured electric field $E_t(t)$ is then Fourier transformed to yield $\tilde{E}_t(\omega)$, the complex frequency dependence of the transmitted field. This transmitted field can be normalized by the field measured with the sample removed from the beam path, yielding the complex transmission coefficient, $\tilde{t}(\omega)$.

In Figure 1 we focus on the absorption at 300 GHz, which corresponds to the transition from $m = \pm 10$ to ± 9 . We plot the index of refraction as a function of frequency near this absorption. The index of refraction was calculated directly from the (complex) transmission spectrum using the equations in [14]. 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 lineshape or the high and low frequency extrapolations of the response functions.

We model the absorption using the standard form for a magnetic dipole resonance [14]. The curve in Figure 1 is a fit to this form, with a linewidth of 4.5 GHz. Although we have used a standard Lorentzian lineshape with no inhomogeneous broadening to fit these data, it is likely that an equal or better fit could be achieved by

considering inhomogeneous broadening. We can measure the linewidth with some confidence, but we cannot draw any conclusions about the lineshape. However, we have argued separately that the absorption must be inhomogeneously broadened [14].

In experiments using pressed pellets, the linewidths have been measured to be 5.5 GHz [14] and 7 GHz [7]. The linewidth of 4.5 GHz measured in this experiment is not significantly different, in that all the measured values are too large to be explained by dipolar or hyperfine coupling. We conclude that mechanical stress has little effect on the linewidths, and therefore that it is likely that single crystals used in tunneling measurements have linewidths of order 5 GHz caused by inhomogeneities in the crystal lattice.

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References

- [1] A. L. Barra, D. Gatteschi, R. Sessoli, Phys. Rev. B **56** (1997) 8192.
- [2] I. Mirebeau *et al.*, Phys. Rev. Lett. **83** (1999) 628.
- [3] S. Hill *et al.*, Phys. Rev. Lett. **80** (1998) 2453.
- [4] A. Fort *et al.*, Phys. Rev. Lett. **80** (1998) 612.
- [5] F. Luis, J. Bartolomé, J. F. Fernández, Phys. Rev. B **57** (1998) 505.
- [6] W. Bao *et al.*, cond-mat/0008042.
- [7] A. A. Mukhin *et al.*, Physica B, **284-288**, 1221 (2000) and A. A. Mukhin *et al.*, Europhys. Lett. **44** (1998) 778.
- [8] Y. Zhong *et al.*, J. of Appl. Phys. **85** (1999) 5636.
- [9] J. R. Friedman, M.P. Sarachik, J. Tejada, R. Ziolo, Phys. Rev. Lett. **76** (1996) 3830.
- [10] L. Thomas *et al.*, Nature **383** (1996) 145.
- [11] E. M. Chudnovsky, D. A. Garanin, Phys. Rev. Lett. **87** (2001) 187203.
- [12] D. A. Garanin, E. M. Chudnovsky, Phys. Rev. B **65** (2002) 094423.
- [13] D. A. Garanin, E. M. Chudnovsky, cond-mat/0107586.
- [14] B. Parks, J. Loomis, E. Rumberger, D. N. Hendrickson, G. Christou, Phys. Rev. B **64** (2001) 184426.
- [15] T. Lis, Acta Crystallogr. B **36** (1980) 2042.