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# Effect of mechanical stress on the line width of single photon absorptions in $Mn_{12}$-acetate

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**Abstract**

Quantum mechanical tunneling of the magnetic moment has been observed in several single-molecule magnets, including $Mn_{12}$-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 line width of single photon (intrawell) transitions. However, most previous studies of the line width 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 line width of loose crystals using the method of time-domain terahertz spectroscopy. The line width is not significantly reduced from the measurements on pressed pellets.


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$Mn_{12}$-acetate ($[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$) consists of a core of 12 manganese ions with spins tightly coupled via superexchange through 12 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 $\alpha=0.38\ \mathrm{cm}^{-1}$, $\beta=8.2\times 10^{-4}\ \mathrm{cm}^{-1}$, $\gamma\sim\pm 2\times 10^{-5}\ \mathrm{cm}^{-1}$, 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.

$Mn_{12}$-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 $Mn_{12}$-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 line widths that have been observed in $Mn_{12}$-acetate [13].

The simplest experiments that measure line width 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 line width of the transitions provides information about the broadening of the levels. However, these previous experiments were performed on samples of $Mn_{12}$-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

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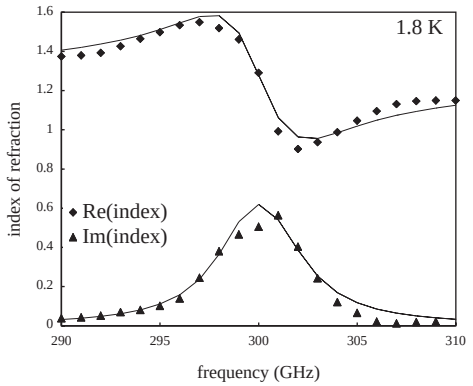


Fig. 1. Real and imaginary parts of the index of $Mn_{12}$ acetate. The index is calculated directly from the transmission. The line is the fit used in calculating the line width.

introduced additional defects into the pellets that were not present in the loose crystals.

We use terahertz time-domain spectroscopy to measure the line width of the intrawell $m = \pm 10 \rightarrow \pm 9$ transitions. The $Mn_{12}$-acetate was prepared according to the procedure of 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 mode-locked 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 Fig. 1 we focus on the absorption at 300 GHz, which corresponds to the transition from $m = \pm 10$ to $\pm 9$. 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 Ref. [14]. Notice that since this is a magnetic transition, $n$ must be correctly defined as $\sqrt{\mu\varepsilon/\mu_0\varepsilon_0}$, rather than approximated as $\sqrt{\varepsilon/\varepsilon_0}$. 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.

We model the absorption using the standard form for a magnetic dipole resonance [14]. The curve in Fig. 1 is a fit to this form, with a line width of 4.5 GHz. Although we have used a standard Lorentzian line shape 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 line width with some confidence, but we cannot draw any conclusions about the line shape. However, we have argued separately that the absorption must be inhomogeneously broadened [14].

In experiments using pressed pellets, the line widths have been measured to be 5.5 [14] and 7 GHz [7]. The line width 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 line widths, and therefore that it is likely that single crystals used in tunneling measurements have line widths of order 5 GHz caused by inhomogeneities in the crystal lattice.

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