Asymmetric Lineshape due to Inhomogeneous Broadening of the Crystal-Field Transitions in Mn$_{12}$ac Single Crystals

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The lineshape of crystal-field transitions in single crystals of Mn$_{12}$ac molecular magnets is determined by the magnetic history. The absorption lines are symmetric and Gaussian for the non-magnetized state obtained by zero-field cooling (zfc). In the magnetized state which is reached when the sample is cooled in a magnetic field (fc), however, they are asymmetric even in the absence of an external magnetic field. These observations are quantitatively explained by inhomogeneous symmetrical (Gaussian) broadening of the crystal-field transitions combined with a contribution of off-diagonal components of the magnetic susceptibility to the effective magnetic permeability.

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I. INTRODUCTION

The high-spin magnetic cluster of Mn$_{12}$ac (which stands for [Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$(H$_2$O)$_4$]$_2$CH$_3$COOH $\cdot$ 4H$_2$O) is the prime example of single-molecule based magnets which reveal a number of interesting phenomena like mesoscopic quantum tunneling of the magnetization and quantum phase interference$^{3,4,5,6}$. Over a wide range the properties of Mn$_{12}$ac are determined by the splitting of the crystal field (CF) of the $S = 10$ ground multiplet described by the spin Hamiltonian$^{7,8,9,10}$

$$\mathcal{H} = DS_z^2 + D_4S_x^4 + B_4^H(S_z^4 + S_y^4)/2 - g\mu_B S \cdot H$$

(1)

where the first three terms represent the crystal field and the last one the Zeeman energy in a magnetic field $H$. The large single-ion anisotropy with an energy barrier of $\sim 65$ K is produced mainly by the axial term $DS_z^2$ with $D < 0$. The magnetization $\mathbf{M}$ of the cluster is stabilized along the fourth order $C_4$ symmetry axis. At low temperatures resonant tunneling through the energy barrier is possible if the energy levels on both sides coincide$^{11,12}$. In the last years the structure of the energy levels of the ground state multiplet of Mn$_{12}$ac and the parameters of the effective spin Hamiltonian$^{11}$ were studied by EPR measurements$^{7,8}$, inelastic neutron scattering$^{2}$ and quasi-optical magnetic spectroscopy$^{10,11,12}$. Currently much attention is devoted to the shape and width of the absorption lines (CF transitions) which may provide a deeper understanding of the mechanisms of quantum tunneling in real crystals of molecular magnets. The Gaussian lineshape found at zero field$^{11,12}$ directly indicates an inhomogeneous character of the line broadening due to a distribution of intra-crystalline interactions, in particular, magneto-dipolar and crystal fields. Detailed EPR investigations$^{11,13,14}$ of various contributions to the line broadening (distribution of the crystal fields, g-factors, dipolar fields) revealed an important role of the CF distribution coming from local strains ($D$-strain). In addition, the asymmetry of the EPR lines was attributed$^{15}$ to the distribution of the easy-axis orientation. In particular, dislocations in real crystals were suggested to cause a distribution of crystal fields which strongly influences the mechanism of quantum tunneling$^{15}$. We have applied a novel type of magnetic spectroscopy to study the influence of the inhomogeneous broadening on the lineshape of magneto-dipolar transitions in Mn$_{12}$ac which allowed us to reveal new features and to advance an alternative explanation.

II. EXPERIMENTAL RESULTS

A few dozen of Mn$_{12}$ac single crystals of typically 1 to 2 mm in size were aligned to a mosaic of about 0.5 mm thickness and 7 $\times$ 7 mm$^2$ area such that the $C_4$ axes of the crystals lay in the plane of the plate and were parallel to each other (to an accuracy better than 3$^\circ$). Using a frequency-domain magnetic spectroscopy$^{12}$, we studied the magnetic absorption by measuring the optical transmission coefficient in the frequency range from 8 to 18 cm$^{-1}$. The experiments were performed at temperatures $T = 2.33$ K in a magnetic field $H$ up to 7 Tesla which was oriented perpendicular to the magnetic field vector $\mathbf{h}$ of the radiation propagating with the wavevector $\mathbf{q}$ along the $y$-direction (Voigt geometry: $\mathbf{h} \parallel x$, $\mathbf{q} \parallel y$, $H \parallel z \parallel C_4$).

The two transmission spectra plotted in Fig. 1 show the transition measured at $T = 2.33$ K with no external field present: $H = 0$; note that this corresponds to a real zero-field EPR experiment. In one case (non-magnetized, zfc state) the sample is cooled down without applied magnetic field, in the second case (magnetized, fc state) the crystals are cooled from 40 K in a field of 1 T (parallel to $C_4$) which was subsequently switched off. In fc crystals the resonance frequency is shifted up by 0.1 cm$^{-1}$ and the lineshape is significantly asymmetric, with the slope smoother on the left (low-frequency) side. Applying a magnetic field parallel to the $C_4$ axis of the fc crystals increases the transition frequency as displayed in Fig. 2; the lineshape remains asymmetric similar to the $H = 0$ case.
III. ANALYSIS

For a quantitative description of the spectra we have to consider the radiation propagating along $z$ axis through a transversely magnetized medium ($h||x, e||y$), whose optical response is determined by an effective magnetic permeability $^{20}$

$$\mu_{\text{eff}}(\nu) = \mu_{xx}(\nu) - \mu_{xy}(\nu)\mu_{yx}(\nu)/\mu_{yy}(\nu), \quad \text{(2)}$$

and thus depends on both diagonal and off-diagonal components of the magnetic permeability $\mu_{ij}(\nu)$ or susceptibility $\chi_{ik}(\nu)$ ($\mu_{ik}(\nu) = 1 + 4\pi\chi_{ik}(\nu)$), where the latter are sensitive to the magnetic state of the sample (fc or zfc).

For low temperatures only transitions from the ground state to the first excited state $|\pm 10\rangle \rightarrow |\pm 9\rangle$ contribute to the susceptibility

$$\chi_{xx,yy}(\nu) \equiv \chi_{\perp}(\nu) = \chi_{+10R_{+10}(\nu)} + \chi_{-10R_{-10}(\nu)}, \quad \text{(3)}$$

$$\chi_{xy}(\nu) = -\chi_{yx}(\nu) \quad \text{(4)}$$

where $h\nu_{\pm 10} = E_{\pm 9} - E_{\pm 10} = h\nu_{0}^{\pm 10} \pm g\mu_B H_z$ are the transition frequencies between the corresponding states on one (+) or another (-) side of an anisotropy barrier. Here $h\nu_{0}^{\pm 10} = -19[D + D_{x}(10^2 + 9^2)]$ is the zero-field frequency and $\chi_{\pm 10} = 2N(\mu\mu_B(10)S(9)) \frac{(\rho_{\pm 10} - \rho_{\pm 9})}{(h\nu_{\pm 10})}$ are the contributions to the magnetic susceptibility due to the corresponding transitions, $N$ is the particle density, and $\rho_m$ is the population of the energy levels $E_m$ which are given by the Boltzmann factor $\rho_m = \exp(-E_{m}/k_BT)/\sum\exp(-E_{m}/k_BT)$ in an equilibrium state. The lineshape functions $R_{\perp 10}(\nu) \equiv R_m(\nu)$ may be either Lorentzian $R_m(\nu) = \nu^2/\nu^2 - \nu^2 + i\nu \Delta \nu_m$, or Gaussian with the imaginary part

$$R_{m}(\nu) = (\pi/8)^{1/2}/\sigma_m \{\exp[-(\nu - \nu_m)^2/2\sigma_m^2] + \exp[-(\nu + \nu_m)^2/2\sigma_m^2]\}, \quad \text{(5)}$$

and the real one determined via the Kramers-Kronig relation $R_m'(\nu) = (2/\pi)\int_{0}^{\infty} \nu\nu_1 R_m''(\nu_1)/(\nu^2 - \nu_1^2)d\nu_1$.

In a nonmagnetized state, when the population is the same on both sides of the barrier, $\rho_{+10} \approx \rho_{-10}$, and the off-diagonal components of the susceptibility vanish $\chi_{xy,yx}(\nu) = 0$, the effective permeability is given by

$$\mu_{\text{eff}}^{\text{zfc}}(\nu) = \mu_{xx}(\nu) = 1 + 4\pi\chi_{\perp}(\nu), \quad \text{(6)}$$

where the diagonal susceptibility component $\chi_{\perp}(\nu)$ is determined by Eq. (5) for $\chi_{+10} = \chi_{-10} \equiv \chi_{10}/2$ and $R_{+10} = R_{-10}$. In a magnetized state ($\rho_{+10} \approx 1, \rho_{-10} \approx 0$)

$$\mu_{\text{eff}}^{\text{fc}}(\nu) = 1 + 4\pi\chi_{\perp}(\nu) \frac{[1 + 4\pi\chi_{\perp}(\nu)(1 - \nu^2/\nu_m^2)]}{1 + 4\pi\chi_{\perp}(\nu)} \approx 1 + \frac{4\pi\chi_{\perp}(\nu)}{1 + 4\pi\chi_{\perp}(\nu)}, \quad \text{(7)}$$

where $\chi_{\perp}(\nu) = \chi_{10}R_{+10}(\nu)$. For $H = 0$ the functions $\chi_{\perp}(\nu)$ in the Eqs. (6) and (7) coincide and the difference between zfc and fc permeability is mainly determined by the denominator $1 + 4\pi\chi_{\perp}(\nu)$ in Eq. (7).

As shown in Fig. 1 by the solid lines, we can nicely fit our experimental results for both the fc and zfc states.
by using the expressions for the transmission coefficient of a plane-parallel layer\textsuperscript{25} and a Gaussian lineshapes entering for $R_{\perp}(\nu)$ in $\chi_{\perp}(\nu)$. The main parameters, the CF resonance frequency $\nu_{10}^0 = 10.002$ cm\textsuperscript{-1}, the Gaussian linewidth $\sigma_{10}^p = 0.095$ cm\textsuperscript{-1} (corresponding full width at the half of maximum $\Delta \nu = 2\sqrt{2\ln 2} \sigma^p_{10} \approx 0.224$ cm\textsuperscript{-1}), and the contribution to the permeability $\Delta \mu_{10} = 4\pi \chi_{10} = 0.076$, were found by fitting only the zfc data\textsuperscript{26}. The calculated spectra reproduce both, the upward shift of the resonance frequency and the asymmetry of the lineshape in the fc state. The increase of the resonant frequency from the value $\nu_{10}$ in zfc state to $\nu_{10} \approx \nu_{10} \sqrt{(1 + \Delta \mu_{10})}$ in the fc state is mainly due to the change of the effective permeability since the off-diagonal term of the susceptibility becomes significant. A slight renormalization of the resonance frequency $h\nu_{10} = h\nu_{10} + g\mu_B \lambda_{||} M_0$ in the fc state is caused by the weak internal dipolar magnetic field; from our fit we obtain $\lambda_{||} M_0 \approx 265$ Oe (i.e. $g\mu_B \lambda_{||} M_0 \approx 0.024$ cm\textsuperscript{-1}), where $M_0$ is the magnetization\textsuperscript{26}. The above statement concerning the shift of the resonance frequency in the fc state is true both for Lorentzian and Gaussian lineshape. For the change of the shape, however, it is essential that the lines are inhomogeneously broadened and have to be described by Gaussian lines.

In Fig. 3 the imaginary part of the permeability spectrum $\mu''(\nu)$ (which describes the magnetic absorption) in the fc state is calculated assuming a Gaussian and a Lorentzian lineshape $R_m(\nu)$. It is clearly seen that the line becomes asymmetric only in the case of the Gaussian lineshape while for the Lorentzian case it remains symmetric. This important result is connected to the fact that for a Lorentzian lineshape $R_m(\nu)$ in the Eq. (7) only the resonant frequency and the contribution ("strength") are renormalized, while the overall frequency dependence of $\mu''(\nu)$ remains unchanged, i.e. Lorentzian\textsuperscript{26}. In the case of inhomogeneously broadened (Gaussian) lines, their shape is disturbed\textsuperscript{27}. Our approach also explains the asymmetric lineshape for finite magnetic fields, as demonstrated in Fig. 4 where the solid lines correspond to calculations using $g = 1.93$ and the aforementioned parameters.

### IV. DISCUSSION

An asymmetric EPR lineshape of Mn\textsubscript{12}2ac magneto-dipolar transitions was reported\textsuperscript{16} and was explained subsequently\textsuperscript{15} by random distributions not only of the $D$ parameter of the crystal field but also of the easy-axis orientation. In this case, however, the asymmetry should vanish in zero magnetic field which is in contradiction to our present observations. Hence, the asymmetry of the lineshape can in principle not be connected with the distribution of the easy axis but rather is determined by a distribution of the zero-field resonance frequencies. It should be noted that the experimental measurement geometry (Voigt configuration) is of crucial importance\textsuperscript{28}. Since regular EPR experiments are performed at fixed frequencies as a function of applied magnetic field – in contrast to our experiments which are conducted at fixed (finite or zero) magnetic field as a function of frequency – the smaller slope is found on the right (high-field) side relative to the resonance field as reported by Hill et al\textsuperscript{28}. Assuming that the main contribution to the observed linewidth is given by the dispersion of the crystal field $\Delta D$ and taking into account that $\sigma_{10}^p/\nu_{10} = \Delta D/(D + 181 D_4) \approx \Delta D/D$, we obtain $\Delta D \approx 0.01 D$ which is half the value estimated in\textsuperscript{26}.

Recently it was shown\textsuperscript{29} that a disorder of the acetic acids of crystallization induces different CF distortions at the Mn\textsuperscript{3+} ions positions; as a result six different isomers can be found. The estimated CF parameters $D(n)$ for the most populated isomers are -0.769 K, -0.778 K and -0.788 K for $n = 1, 2, 3$, respectively\textsuperscript{29}. The relative differences $|D(2) - D(1)|/D(2) = 0.0115$ and $|D(3) - D(2)|/D(2) = 0.0128$ agree very well with the CF distribution obtained from the linewidth. A simulation of the observed fc and zfc spectra by three narrower Gaussians lines, corresponding to the three isomers with the given concentrations, provides an excellent description of the whole lineshape (not shown). According to Cornia et al\textsuperscript{29} the CF distortions in the Mn\textsubscript{12}2ac isomers are accompanied by an appearance of a second-order transverse CF term $E(S^2 - S^2_Y)$ which is responsible for the tunnel splitting and increase of the relaxation rate. The correlation between $D$ and $E$ terms opens a possibility to observe an inhomogeneous relaxation of the spectra inside the line in a long-living non-equilibrium state created by magnetic field inversion\textsuperscript{30}.

In summary, using high-frequency magnetic spectroscopy we discovered a dependence of the frequency and lineshape of the magneto-dipolar transitions in Mn\textsubscript{12}2ac on the magnetic history of the sample.Zero-field
cooled samples show a symmetrical Gaussian lineshape of the $S = 10$ ground multiplet transition $|\pm 10\rangle \rightarrow |\pm 9\rangle$. If the sample was previously cooled in magnetic field, the line becomes asymmetric and shifts up in frequency by about 0.1 cm$^{-1}$ even for $H = 0$. These observations are explained by an inhomogeneous (Gaussian) distribution of the resonant frequencies taking into account the effective susceptibility of the transversely magnetized medium which includes off-diagonal components and the internal magnetic field. We quantitatively describe the absorption seen in the transmission spectra for both $H = 0$ and $H \neq 0$ and determined the main characteristics of interactions in the system.

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22. The linewidth agrees well with the one obtained in polycrystalline Mn$_{12}$ac [10]. The found value of $\Delta \mu_0$ is slightly smaller than the theoretical value 0.0109 obtained by $N = \rho N_A/M_{\text{Mn12}}$ using the reported density $\rho = 1.84$ g/cm$^3$ with $N_A$ the Avogadro number and $M_{\text{Mn12}}$ the mass of the Mn$_{12}$ac molecule. The reason may be the mosaic structure of the sample used in our experiments.
23. Strictly speaking, also the transverse internal dipolar fields $\sim \lambda_\perp \Delta M_{\perp}$ may become important when the magnetization deviates from the easy axis during oscillations; in general, this effect could lead to a renormalization of $\mu_{\text{eff}}(\nu)$. However, our simulation show that this effect is not relevant in our case.
24. It can be easy checked by a direct substitution of $\chi_{\perp}(\nu) = \chi_{\perp 10} R_{10}(\nu)$ in Eq. (7).
25. In Faraday geometry for a circular polarization the inhomogeneously broadened lines stays symmetric due to another kind of effective permeability. These experiments are in progress.
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