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Asymmetric lineshape due to inhomogeneous broadening of the crystal-field transitions in Mn_{12} acetate single crystals

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The lineshape of crystal-field transitions in oriented single crystals of Mn_{12} acetate molecular magnets is determined by the magnetic history. The absorption lines are symmetric and Gaussian for the nonmagnetized state obtained by zero-field cooling. In the magnetized state which is reached when the sample is cooled in a magnetic field, 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. This can be qualitatively understood as a redistribution of the interacting modes superposed in the total inhomogeneously broadened line which dynamically occurs via the magnetic medium, i.e., via different components of its susceptibility depending on the magnetic state.

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I. INTRODUCTION

The high-spin magnetic cluster of Mn_{12} acetate (which stands for $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH \cdot 4H_2O$) is the prime example of single-molecule based magnets which reveal a number of interesting phenomena such as mesoscopic quantum tunneling of the magnetization and quantum phase interference.[1–6] Over a wide range the properties of Mn_{12} acetate are determined by the splitting in the crystal field (CF) of the $S=10$ ground multiplet described by the spin Hamiltonian[7–10]

$$\mathcal{H}=DS_z^2+D_4S_z^4+B_4^4(S_+^4+S_-^4)/2-g\mu_B\mathbf{S}\cdot\mathbf{H}, \tag{1}$$

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 ~ 65 K is produced mainly by the axial term DS_z^2 with $D<0$. The magnetization **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.[3,5,4]

In the last years the structure of the energy levels of the ground-state multiplet of Mn_{12} acetate and the parameters of the effective spin Hamiltonian (1) were studied by electron-paramagnetic-resonance (EPR) measurements,[7,8] inelastic neutron scattering,[9] and quasioptical magnetic spectroscopy.[10–12] 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 intracrystalline interactions, in particular, magnetodipolar and crystal fields. Detailed EPR investigations[13–16] 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[17] 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.[18] The environmental effects determined by internal magnetodipolar and hyperfine fields and their distributions also become clearly apparent in resonance quantum tunneling.[19,20] They result in a dependence of the tunneling resonances on the magnetic state[4] and in a strong effect of the time-dependent internal field on the relaxation law predicted in Ref. 21 (see also the recent review by Tupitsyn and Barbara[22]).

Applying a different type of frequency-domain magnetic spectroscopy we have studied the influence of the inhomogeneous broadening and magnetic state on the lineshape of magnetodipolar transitions in Mn_{12} acetate which allowed us to reveal and explain a remarkable dependence of the lineshape on the magnetic history of the sample: i.e., field-cooled (fc) and in contrast to zero-field-cooled (zfc) states.

II. EXPERIMENTAL RESULTS

A few dozen of Mn_{12} acetate single crystals of typically 1–2 mm in size were aligned to a mosaic of about 0.5 mm thickness and 7×7 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°). Using a frequency-domain magnetic spectroscopy,[23,24] 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 temperature $T=2.33$ K in a magnetic field **H** up to 7 T which was oriented perpendicular to the magnetic-field vector **h** of the radiation propagating (with the wave vector **q**) along the y direction (Voigt geometry: $\mathbf{h}\|x$, $\mathbf{q}\|y$, $\mathbf{H}\|z\|C_4$).

The two transmission spectra plotted in Fig. 1 show the $|\pm 10\rangle\rightarrow|\pm 9\rangle$ 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 (nonmagnetized, zfc

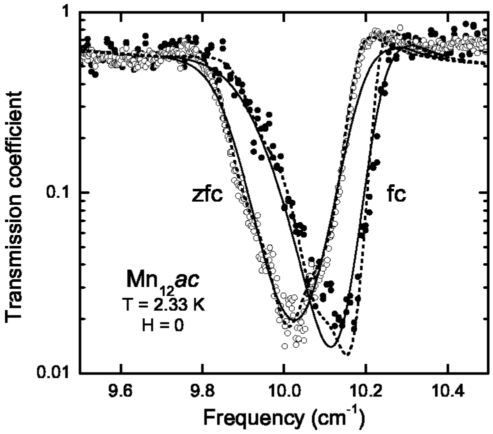

FIG. 1. Magnetic absorption due to the $|\pm 10\rangle \rightarrow |\pm 9\rangle$ crystal-field transition in the transmission coefficient spectra (dots) of Mn$_{12}$ acetate single crystals measured at $T=2.33$ K without external magnetic field. In the first case (zfc) the sample is cooled down without applied magnetic field, in the second case (fc) the sample is cooled in a field of 1 T which was subsequently switched off. The solids lines represent the calculations using a single Gaussian line and an effective susceptibility as described in the text. The dashed lines show calculations with three Gaussians corresponding to the most populated isomers with distorted CF which arise from the random distribution of the acetic acids; the parameters are given in the text.

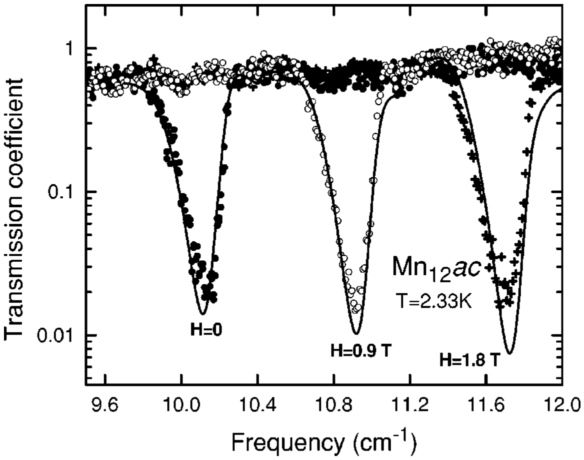

FIG. 2. Absorption of the $|\pm 10\rangle \rightarrow |\pm 9\rangle$ crystal-field transition in Mn$_{12}$ acetate single crystals at $T=2.33$ K measured by transmission at different magnetic fields. The lines represent the calculations using a single Gaussian term and an effective susceptibility.

state) the sample is cooled down without applied magnetic field, in the second case (magnetized, fc state) the crystals are cooled from 20 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 y axis through a transversely magnetized medium $(\mathbf{h}\|x,\mathbf{e}\|z)$, whose optical response is determined by an effective magnetic permeability[25]

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

and thus depends on both diagonal and off-diagonal components of the magnetic permeability $\mu_{ij}(\nu)$ where the latter are sensitive to the magnetic state of the sample (fc or zfc). The magnetic susceptibility $\chi_{ik}(\nu)$ is related to the permeability via $\mu_{ik}(\nu)=\delta_{ij}+4\pi\chi_{ik}(\nu)$ with the Kronecker symbol δ_{ij}. 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

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

$$\chi_{xy}(\nu)=-\chi_{yx}(\nu)=i\nu[\chi_{+10}R_{+10}(\nu)/\nu_{+10} - \chi_{-10}R_{-10}(\nu)/\nu_{-10}], \tag{3b}$$

where $h\nu_{\pm 10}=E_{\pm 9}-E_{\pm 10}=h\nu_{10}^{0}\pm g\mu_B H_z$ are the transition frequencies between the corresponding states on one $(+)$ or another $(-)$ side of an anisotropy barrier. Here $h\nu_{10}^{0}=-19[D+D_4(10^2+9^2)]$ is the zero-field energy and $\chi_{\pm 10}=2N(g\mu_B\langle 10|S_x|9\rangle)^2(\rho_{\pm 10}-\rho_{\pm 9})/h\nu_{\pm 10}$ are the contributions to the magnetic susceptibility due to the corresponding transitions, N is the particle density, and ρ_m is the population of the energy levels E_m which are given by the Boltzmann factor $\rho_m=\exp\{-E_m/k_BT\}/\Sigma\exp\{-E_n/k_BT\}$ in an equilibrium state.

The lineshape functions $R_{\pm 10}(\nu)\equiv R_m(\nu)$ may be either Lorentzian,

$$R_m(\nu)=\frac{\nu_m^2}{\nu_m^2-\nu^2+i\nu\Delta\nu_m}, \tag{4}$$

or Gaussian[11] with the imaginary part

$$R_m''(\nu)=(\pi/8)^{1/2}(\nu/\sigma_m)[\exp\{-(\nu-\nu_m)^2/2\sigma_m^2\} + \exp\{-(\nu+\nu_m)^2/2\sigma_m^2\}], \tag{5a}$$

and the real one determined via the Kramers-Kronig relation

$$R_m'(\nu)=(2/\pi)\int_0^{\infty}\frac{\nu_1 R_m''(\nu_1)}{\nu_1^2-\nu^2}d\nu_1. \tag{5b}$$

However, we cannot exclude more complicated lineshapes related to a superposition of several CF transitions due to different isomers in real crystals[19,28,27] (see subsequent section).

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

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

where the diagonal susceptibility component $\chi_{\perp}(\nu)$ is determined by Eq. (3a) for $\chi_{+10}=\chi_{-10}\equiv\chi_{10}/2$ and $R_{+10}=R_{-10}$. In a magnetized state $(\rho_{+10}\approx 1, \rho_{-10}\approx 0)$

$$\begin{aligned}\mu_{\mathrm{eff}}^{\mathrm{fc}}(\nu)&=1+\frac{4\pi\chi_{\perp}(\nu)[1+4\pi\chi_{\perp}(\nu)(1-\nu^2/\nu_{+}^2)]}{1+4\pi\chi_{\perp}(\nu)}\\&\approx 1+\frac{4\pi\chi_{\perp}(\nu)}{1+4\pi\chi_{\perp}(\nu)},\end{aligned} \tag{7}$$

where $\chi_{\perp}(\nu)=\chi_{+10}R_{+10}(\nu)$. For $H=0$ the functions $\chi_{\perp}(\nu)$ in 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[26] and a Gaussian lineshape entering for $R_{\pm}(\nu)$ in $\chi_{\perp}(\nu)$. The main parameters, the CF resonance frequency $\nu_{10}^{0}=10.002\ \mathrm{cm}^{-1}$, the Gaussian linewidth $\sigma_{10}^{\pm}=0.095\ \mathrm{cm}^{-1}$ [corresponding full width at half maximum (FWHM) $\Delta\nu_{10}^{\pm}=2\sqrt{2\ln 2}\sigma_{10}^{\pm}\approx 0.224\ \mathrm{cm}^{-1}$], and the contribution to the permeability $\Delta\mu_{10}=4\pi\chi_{10}=0.076$, were found by fitting only the zfc data.[29] 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 ν_{10} in zfc state to approximately $\tilde{\nu}_{10}\sqrt{(1+\Delta\mu_{10})}$ 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 $h\tilde{\nu}_{10}=h\nu_{10}+g\mu_{B}\lambda_{\parallel}M_{0}$ in the fc state is caused by the weak internal dipolar magnetic field; from our fit we obtain $\lambda_{\parallel}M_{0}\approx 265$ Oe (i.e., $g\mu_{B}\lambda_{\parallel}M_{0}\approx 0.024\ \mathrm{cm}^{-1}$), where M_0 is the magnetization. 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 $\mu_{\mathrm{eff}}(\nu)$. However, our simulations show that this effect is not relevant in our case. 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 inhomogeneous by broadened and have to be described by Gaussian lines.

In Fig. 3 the imaginary part of the permeability spectrum $\mu_{\mathrm{eff}}''(\nu)$ (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 Eq. (7) only the resonant frequency and the contribution ("strength") are renormalized, while the overall frequency dependence of $\mu_{\mathrm{eff}}(\nu)$ remains unchanged, i.e., Lorentzian. It can be easily checked by a direct substitution of $\chi_{\perp}(\nu)=\chi_{+10}R_{+10}(\nu)$ in Eq. (7). In the case of inhomogeneously broadened (Gaussian) lines, their shape is disturbed.[31] Qualitatively the findings can be understood in the following manner. An inhomogeneously broadened line can be represented as a superposition of a (finite or infinite) number of homogeneous, i.e., Lorentzian, narrow lines (modes). For the zfc state they can be considered as independent, while in the fc state the modes are coupled via the nondiagonal $\mu_{xy,yx}$ components resulting in a shift of the superposing modes, which is not carried out uniformly: the low-frequency part of the superposed line (left side) shifts less than the high-frequency part (right side). A redistribution of the spectral weight is directly coupled to the shift of the modes. It can be considered as a dynamic interaction of the composing modes via a magnetized media which changes their frequency positions and intensities which cause the asymmetrical shift of the spectral weight of the integrated line. A direct simulation of the total line by a finite number of Lorentzian oscillations has confirmed this picture.

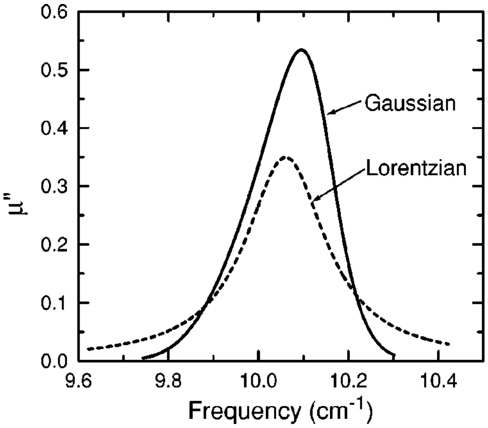

FIG. 3. Magnetic absorption spectra μ'' at zero magnetic field $(H=0)$ for the field-cooled (fc) state of Mn_{12} acetate. The calculation compare Gaussian with Lorentzian lineshapes of the $|\pm 10\rangle\rightarrow|\pm 9\rangle$ crystal-field transition.

Our approach also explains the asymmetric lineshape for finite magnetic fields, as demonstrated in Fig. 2 where the solid lines correspond to calculations using $g=1.93$ and the aforementioned parameters. The less perfect description of the line at $H=1.8$ T as compare to the one at $H=0.9$ T can be explained by distortions of the spectrum due to standing waves in the cryostat. The high-field spectra are more susceptible to the alignment.

IV. DISCUSSION

There are several contributions to the inhomogeneous broadening of the CF transitions related to the random distribution of magnetodipolar fields (H^{dip}),[4,14–16,22] hyperfine fields (H^{hyp}),[4,19,22] tilting of the easy axis of a single Mn_{12} acetate molecule from the c axis,[17] local variations of the CF parameters (D strains),[15,16,18] etc. By adding the corresponding amendments into the Hamiltonian (1), the frequency of the $|\pm m\rangle \rightarrow |\pm(m-1)\rangle$ CF transitions ($m=1,\ldots,9,10$) can be expressed as $\tilde{\nu}_{\pm m}=\nu_{\pm m}+\Delta\nu^{(2)}_{\pm m}$. Here $h\nu_{\pm m}=-(2m-1)[D+D_4(m^2+(m-1)^2)]\pm g\mu_B H_c^{\mathrm{eff}}\cos\theta$ correspond to the unperturbed frequencies determined by the CF splitting and projection of the effective field $\mathbf{H}^{\mathrm{eff}}=\mathbf{H}+\mathbf{H}^{\mathrm{dip}}+\mathbf{H}^{\mathrm{hyp}}$, which is parallel to the crystallographic c axis, onto the local easy axis (z) of a molecule which is weakly tilted from the c axis by the angle θ. The terms $\Delta\nu^{(2)}_{\pm m}\propto(H_c^{\mathrm{eff}}\sin\theta)^2$ are the second-order perturbation-theory contributions due to components of the effective magnetic field H^{eff} perpendicular to the local easy axis (see Ref. 17). In particular, for $m=10$ the energy shifts by $h\Delta\nu^{(2)}_{+10}=[g\mu_B H_c^{\mathrm{eff}}\sin\theta]^2[10/(h\nu_{+10})-19/(2h\nu_{+9})]$.

An asymmetrical EPR lineshape of Mn_{12} acetate magnetodipolar transitions was reported by Hill *et al.*[16] and was explained subsequently[17] 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 practically vanish in zero external magnetic field and for typical internal dipolar field $H^{\mathrm{dip}}\sim 300-500$ Oe and standard deviation $\sigma_\theta=6°-10°$ which obviously is in contrast to our present observations.[30] Hence, the observed asymmetry of the lineshape cannot be connected with the distribution of the easy axis but rather is determined by a distribution of the zero-field resonance frequencies combined with a contribution of off-diagonal components of the magnetic susceptibility to the effective magnetic permeability. It should be noted that the experimental measurement geometry (Voigt configuration) is of crucial importance.[31] 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.[16]

Assuming that the random magnetodipolar, hyperfine, and CF fields are independent and Gaussian distributed with a standard deviations, respectively, σ_H^{dip}, σ_H^{hyp}, and σ_D, the total Gaussian linewidth can be expressed as $\sigma_m^2=g^2\mu_B^2[(\sigma_H^{\mathrm{dip}})^2+(\sigma_H^{\mathrm{hyp}})^2+(2m-1)^2\sigma_D^2]$. According to calculations of Parks *et al.*[14] $\sigma_H^{\mathrm{dip}}\approx 220$ Oe (the corresponding FWHM is of 520 Oe) in the demagnetized state of the Mn_{12} acetate. The hyperfine standard deviation is of the same order, $\sigma_H^{\mathrm{hyp}}=50$–70 Oe (the FWHM is of 120–160 Oe).[4,19] However, their total contribution to the linewidth, $\sim 0.02\ \mathrm{cm}^{-1}$, is much less then the observed value $\sigma_{10}\approx 0.1\ \mathrm{cm}^{-1}$ which basically does not depend on the magnetic state (fc or zfc), too. This implies that the main contribution to the observed linewidth comes from the dispersion of the crystal field σ_D with the dependence on the state number m observed in Ref. 16. Taking into account that $\sigma_{10}^{\pm}/\nu_{10}=\sigma_D/(D+181D_4)\approx\sigma_D/D$, we obtain $\sigma_D\approx 0.01D$ which is half the value estimated by Hill *et al.*[16]

Above we have considered the simplest Gaussian type of inhomogeneous broadening. In real crystals the character of the broadening can be more complicated due to existence of various defects, such as dislocations[18] as well as different isomer forms within the same single crystal.[19,28] Recently it was shown[27] that a disorder of the acetic acids during the crystallization induces different CF distortions at the Mn^{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 $n=1,2$, and 3, respectively.[27] 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 width of the CF distribution obtained from the linewidth.

To elucidate the sensitivity of the above description of the lineshape to the CF distribution we have carried out a simulation of the observed fc and zfc spectra by three narrower Gaussians lines, corresponding to the three isomers with the given concentrations. The results shown by the dashed lines in Fig. 1 demonstrate an excellent description of the total lineshape and its weak sensitivity to details of the distribution. The resonance frequencies 9.9014, 9.9988, and 10.0954 cm^{-1} of the superposed modes were taken in accordance to the variations of the axial CF parameters in the corresponding isomers;[27] their linewidths $\sigma_{10}(n)\approx 0.045\ \mathrm{cm}^{-1}$ were taken equal. The broadening of the contributing modes could be due to additional CF distributions caused by dislocations,[18] hyperfine fields,[21] or inhomogeneous magnetodipolar fields.

According to Cornia *et al.*[27] the CF distortions in the Mn_{12} acetate isomers are accompanied by the appearance of a second-order transverse CF term $E(S_x^2-S_y^2)$ which is responsible for the tunnel splitting and the 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 nonequilibrium state created by magnetic-field inversion.[32]

V. CONCLUSION

In summary, using high-frequency magnetic spectroscopy we discovered a dependence of the frequency and lineshape of the magnetodipolar transitions in Mn_{12} acetate 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 $H=0$. The linewidth in the both cases remains, practically, the same. These observations are explained by an inhomogeneous (Gaussian) distribution of the resonant frequencies with equal fc and zfc widths, taking into account the effective susceptibility of the transversely magnetized medium which includes off-diagonal components and the internal magnetic field. The both factors play a key role and allow us to explain the observations qualitatively as a result of a redistribution of the interacting modes superposed in the total inhomogeneously broadened line which occurs dynamically via magnetic media (i.e., via different components of its susceptibility depending on the magnetic state). 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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[1] R. Sessoli, D. Gatteschi, A. Caneschi, and H.A. Novak, Nature (London) **356**, 141 (1993).

[2] D. Gatteschi, A. Caneschi, L. Pardi, and R. Sessoli, Science **265**, 1054 (1994).

[3] J.R. Friedman, M.P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996).

[4] B. Barbara, L. Thomas, F. Lionti, I. Chioresu, and A. Sulpice, J. Magn. Magn. Mater. **200**, 167 (1999).

[5] A. Caneschi, D. Gatteschi, C. Sangregorio, R. Sessoli, L. Sorace, A. Corina, M.N. Novak, C. Paulsen, and W. Wernsdorfer, J. Magn. Magn. Mater. **200**, 182 (1999).

[6] W. Wernsdorfer and R. Sessoli, Science **284**, 133 (1999).

[7] A.L. Barra, D. Gatteschi, and R. Sessoli, Phys. Rev. B **56**, 8192 (1997).

[8] S. Hill, J.A.A.J. Perenboom, N.S. Dalal, T. Hathaway, T. Stalcup, and J.S. Brooks, Phys. Rev. Lett. **80**, 2453 (1997).

[9] M. Hennion, L. Pardi, I. Mirebeau, E. Suard, R. Sessoli, and A. Caneschi, Phys. Rev. B **56**, 8819 (1997); I. Mirebeau, M. Hennion, H. Casalta, H. Andres, H.U. Gudel, A. V Irodova, and A. Caneschi, Phys. Rev. Lett. **83**, 628 (1999).

[10] A.A. Mukhin, V.D. Travkin, A.K. Zvezdin, S.P. Lebedev, A. Caneschi, and D. Gatteschi, Europhys. Lett. **44**, 778 (1998).

[11] A.A. Mukhin, B. Gorshunov, M. Dressel, C. Sangregorio, and D. Gatteschi, Phys. Rev. B **63**, 214411 (2001).

[12] A.A. Mukhin, A.S. Prokhorov, B. Gorshunov, A.K. Zvezdin, V.D. Travkin, and M. Dressel, Phys. Usp. **34**, 1306 (2002).

[13] S. Hill, R.S. Edwards, S.I. Jones, N.S. Dalal, and J.M. North, Phys. Rev. Lett. **90**, 217204 (2003).

[14] B. Parks, J. Loomis, E. Rumberger, D.N. Hendrickson, and G. Christou, Phys. Rev. B **64**, 184426 (2001).

[15] K. Park, M.A. Novotny, N.S. Dalal, S. Hill, and P.A. Rikvold, Phys. Rev. B **65**, 014426 (2002).

[16] S. Hill, S. Maccagnano, K. Park, R.M. Achey, J.M. North, and N.S. Dalal, Phys. Rev. B **65**, 224410 (2002).

[17] K. Park, M.A. Novotny, N.S. Dalal, and P.A. Rikvold, J. Appl. Phys. **91**, 7167 (2002); K. Park, M.A. Novotny, and N.S. Dalal, J. Chem. Phys. **117**, 11 292 (2002).

[18] E.M. Chudnovsky and D.A. Garanin, Phys. Rev. Lett. **87**, 187203 (2001); D.A. Garanin and E.M. Chudnovsky, Phys. Rev. B **65**, 094423 (2002); F. Torres, J.M. Hernandez, E. Molins, A. Garica-Santiago, and J. Tejada, cond-mat/0110538 (unpublished).

[19] W. Wernsdorfer, R. Sessoli, and D. Gatteschi, Europhys. Lett. **47**, 254 (1999).

[20] W. Wernsdorfer, T. Ohm, C. Sangregorio, R. Sessoli, D. Mailly, and C. Paulsen, Phys. Rev. Lett. **82**, 3903 (1999).

[21] N.V. Prokofev and P.C.E. Stamm, Phys. Rev. Lett. **80**, 5794 (1998).

[22] I. Tupitsyn and B. Barbara, in *Magnetism: Molecules to Materials III*, edited by J. S. Miller and M. Drillon (Wiley-VCH, Weinhein, 2002), p. 109.

[23] G. V. Kozlov and A. A. Volkov, *Millimeter and Submillimeter Wave Spectroscopy of Solids*, edited by G. Grüner (Springer, Berlin, 1998), p. 51.

[24] J. van Slageren, S. Vongtragool, B. Gorshunov, A.A. Mukhin, N. Karl, J. Krzystek, J. Telser, A. Müller, C. Sangregorio, D. Gatteschi, and M. Dressel, Phys. Chem. Chem. Phys. **5**, 3837 (2003).

[25] See, for example, B. Lax and K. J. Button, *Microwave Ferrites and Ferrimagnets* (McGraw-Hill, New York, 1962).

[26] M. Dressel and G. Grüner, *Electrodynamics of Solids* (Cambridge University Press, Cambridge, 2002).

[27] A. Cornia, R. Sessoli, L. Sorace, D. Gatteschi, A.L. Barra, and C. Daiguebonne, Phys. Rev. Lett. **89**, 257201 (2002).

[28] S.M.J. Aubin, Z. Sun, I.A. Guzei, A.L. Rheingold, G. Chrisou, and D.N. Hendrickson, Chem. Commun. (Cambridge) **1997**, 2239 (1997); S.M.J. Aubin, Z. Sun, H.J. Eppley, E.M. Rumberger, I.A. Guzei, K. Folting, P.K. Gantzel, A.L. Rheingold, G. Chrisou, and D.N. Hendrickson, Inorg. Chem. **40**, 2127 (2001).

[29] The linewidth agrees well with the one obtained in polycrystalline Mn_{12} acetate.[10–12] The found value of $\Delta\mu_{10}$ is slightly smaller than the theoretical value 0.0109 obtained by $N=\rho N_A/M_{\mathrm{Mn12}}$ using the reported density $\rho=1.84\mathrm{g/cm}^3$ with N_A the Avogadro number and M_{Mn12} the mass of the Mn_{12} acetate molecule. The reason may be the mosaic structure of the sample used in our experiments.

[30] This conclusion is based on our calculations (similar to ones of Ref. 17) of the probability distribution function (i.e., lineshape function) for the given resonance frequencies $\tilde{\nu}_{\pm m}$.

[31] In Faraday geometry for a circular polarization the inhomogeneously broadened lines stay symmetric due to another kind of effective permeability. These experiments are in progress.

[32] M. Dressel, B. Gorshunov, K. Rajagopal, S. Vongtragool, and A.A. Mukhin, Phys. Rev. B **67**, 060405(R) (2003).