Inelastic-neutron-scattering study of excited spin multiplets and low-energy phonons in the Fe₈ nanomagnet: Implications for relaxation

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Inelastic neutron scattering is used to study excited spin multiplets and low-energy phonons in the Fe₈ nanomagnet. The energies of the three lowest-lying excited multiplets are determined. In addition, we find weakly dispersive optical phonons with energies lower than the anisotropy splitting of the ground $S=10$ spin multiplet. We show that these optical phonons may produce sharp minima in the field dependence of the relaxation time. The positions of the calculated minima agree with those that had been inferred from frequency-dependent specific heat and ac-susceptibility measurements.

I. INTRODUCTION

Molecular nanomagnets (MNMs) are clusters of strongly exchange-coupled ions. Shells of organic ligands provide magnetic separation between neighboring molecules and, at low temperature, an MNM crystal behaves as an ensemble of isolated, identical magnetic particles with fixed total spin. Single-ion and intra-cluster dipolar magnetic anisotropies hinder magnetization reversal, thus opening the possibility for information storage in single molecules.[1] In addition, it may be possible to exploit MNMs for the implementation of quantum computation algorithms.[2]

A central issue in the physics of these compounds is the role phonons play in the magnetic dynamics through the magnetoelastic interaction. Phonons provide a heat bath causing relaxation of magnetic molecular observables, which limits the possible use of MNMs as classical and quantum bits. In particular, the magnetization reversal process in MNMs such as Mn₁₂, Fe₈ or Fe₄ is usually described by assuming coupling of electron spins to Debye-like acoustic phonons.[3–6] However, because of the large number of atoms in each molecule, low-energy optical phonon modes may be expected to exist in some of these compounds. Here we report the determination by inelastic neutron scattering (INS) of the three lowest excited spin multiplet energies in Fe₈, and we show that low-energy weakly dispersive optical phonons actually exist in this prototype nanomagnet.[7] Further, by means of a master equation approach, we investigate the effect of these phonons on the relaxation of Fe₈ and we

show that their interaction with the spin degrees of freedom gives rise to new and unexpected minima in the field dependence of the magnetization relaxation-time τ. Indeed, these additional minima have been observed by frequency-dependent heat capacity and susceptibility measurements,[8,9] where they were interpreted as due to anticrossings (ACs) associated with a low-lying excited $S=9$ spin multiplet located between 0.9 and 2.5 meV. This possibility is ruled out by the present experiments, since the lowest-lying multiplet is detected at about 4.0 meV. This energy agrees with that expected on the basis of susceptibility measurements.[10]

II. MODEL AND EXPERIMENTS

Each magnetic molecule can be described by the following spin Hamiltonian:

$$H = \sum_{i>j} J_{ij}\mathbf{s}_i \cdot \mathbf{s}_j + \sum_i \sum_{k,q} b_k^q(i)O_k^q(\mathbf{s}_i)$$
$$+ \sum_{i>j} \mathbf{s}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{s}_j - \mu_B \sum_i g_i \mathbf{B} \cdot \mathbf{s}_i, \qquad (1)$$

where $\mathbf{s}_i$ are spin operators of the ith ion in the molecule. The first term is the isotropic Heisenberg exchange interaction. The second term describes the local crystal fields (CFs), with $O_k^q(\mathbf{s}_i)$ Stevens operator equivalents for the ith ion[11] and $b_k^q(i)$ CF parameters. The third term represents the dipolar anisotropic intra-cluster spin-spin interactions. The last term is the Zeeman coupling with an external field **B**. Since the Heisen-
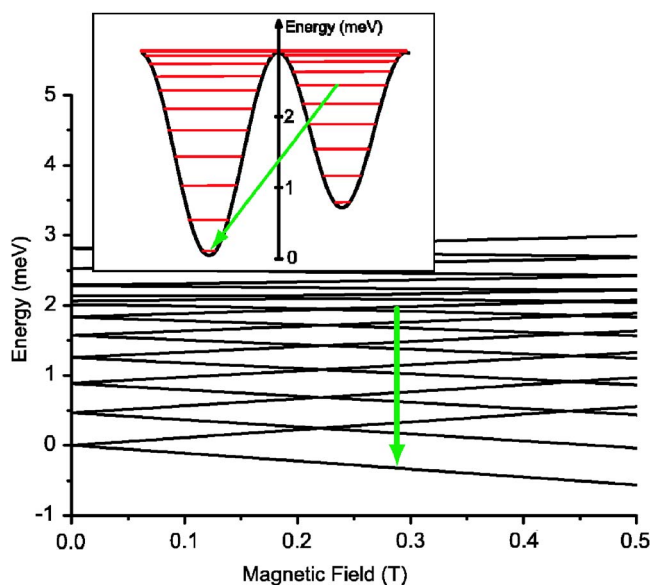
FIG. 1. (Color online) Field dependence of the $S=10$ levels in Fe$_8$ calculated from Eq. (2) with the parameters given in Ref. 7. Inset: double-well potential corresponding to the axial second-order contribution to Eq. (2). The arrow shows the transition enhanced by the 2.3 meV phonon at $B=0.29$ T (see below).

berg contribution is predominant, $|\mathbf{S}|$ is nearly conserved, and the energy spectrum of H consists of a series of level multiplets with an almost definite value of $|\mathbf{S}|$. The low-temperature and low-energy properties of MNMs are well described by projecting the Hamiltonian [Eq. (1)] onto the ground S multiplet

$$H_{sub} = \sum_{K,Q} B_K^Q O_K^Q(\mathbf{S}), \qquad (2)$$

where $\mathbf{S}$ is a vector spin operator with S equal to the total spin of the ground S multiplet. In MNMs H_{sub} is nearly easy axis, and the spectrum is close to that corresponding to a double-well potential (see Fig. 1). Relaxation of the magnetization occurs through a multi-step Orbach process in which the barrier is crossed by a series of phonon-induced transitions between spin eigenstates. If a magnetic field B is applied along the easy (z) axis, the relaxation time τ displays sharp minima at specific field values B_c at which ACs between states in different wells occur.[4,12] These ACs explain the observed steps in the magnetization hysteresis loop.[13,14] In existing calculations of $\tau(B,T)$ a smooth Debye-type density of states (DOS) is assumed for the phonon heat bath. However, if optical phonons with energy E lower than the splitting of the ground spin multiplet exist, the relaxation rate may increase at values of B for which two spin eigenstates differ in energy by E. In fact, these phonons may provide additional peak-like contributions to the phonon DOS and are in general more strongly coupled to spins than the acoustic ones. This can result in a more efficient spin-phonon energy transfer at E, producing further sharp minima in the B dependence of τ.

One possible system possessing low-E optical phonons is the Fe$_8$([Fe$_8$(tacn)$_6$(μ_3-O)$_2$(μ_2-OH)$_{12}$]Br$_7$(H$_2$O)Br·8H$_2$O,
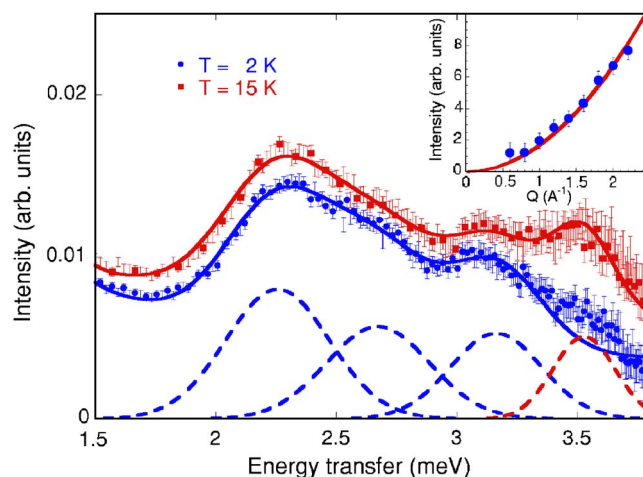

FIG. 2. (Color online) INS spectra recorded on IN6 with $\lambda=4.1$ Å for $T=2$ K (lower) and $T=15$ K (upper). The Q dependence of the peak centered at 2.3 meV is shown in the inset.

tacn$=1,4,7$-triazacyclononane) nanomagnet. Recent optical spectroscopy data show minima in the energy dependence of the transmission coefficient, two of which fall between 2 and 3 meV, i.e., in the energy window spanned by the spectrum of Eq. (2) (this is shown in Fig. 1 as a function of an applied field B). These minima may be due to either electronic transitions between the ground and the excited S multiplets or to optical phonons.[15] Using the full Hamiltonian [Eq. (1)] with exchange parameters J_{ij} estimated from susceptibility data,[10] no excited S multiplet is expected below 3 meV as the three first excited S multiplets (having $S=9$) should be found at 3.8, 5.3 and 6.2 meV. However, shoulders in the field dependence of electron paramagnetic resonance (EPR) spectra have recently been attributed to a single $S=9$ manifold located at 2.07 meV.[16] Since intermultiplet splittings cannot be directly probed by EPR, and can only be inferred indirectly by fitting the T dependence of thermally activated intra-multiplet transitions, we decided to perform INS experiments to assess the nature of the excitations observed by optical spectroscopy. In fact, the very different momentum-transfer (Q) dependence of phonon and magnetic-excitation intensities enables inter-multiplet and phonon transitions to be discriminated.

INS measurements on a deuterated Fe$_8$ sample were performed on the IN4 and IN6 time-of-flight spectrometers at the Institute Laue-Langevin in Grenoble and on the disk chopper spectrometer (DCS) of the National Institute of Standards and Technology Center for Neutron Research, Gaithersburg, MD. A polycrystalline sample (1.8 g) was sealed into an annular Al container (60 mm in height and 25 mm external radius), which was then placed inside a standard liquid-^{4}He cryostat. Data were normalized to the scattering from a vanadium sample. The energy window between 1.5 and 4 meV was carefully investigated on IN6 with an incident wavelength λ of 4.1 Å for $T=2$ and 15 K. The maximum accessible momentum transfer was 2.2 Å^{-1} for a 2.5 meV energy transfer. An excitation band around 2.5 meV (see Fig. 2) was fitted to the superposition of three Gaussians, centered at 2.26, 2.67, 3.19 meV, each having a full
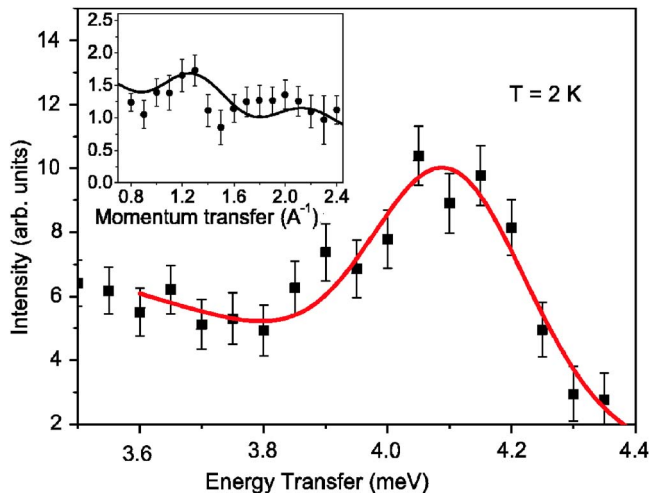
FIG. 3. (Color online) INS spectra collected on IN4 with $\lambda = 3.4$ Å and $T = 2$ K. The inset shows the Q dependence of the measured and calculated intensity for the peak at 4 meV.
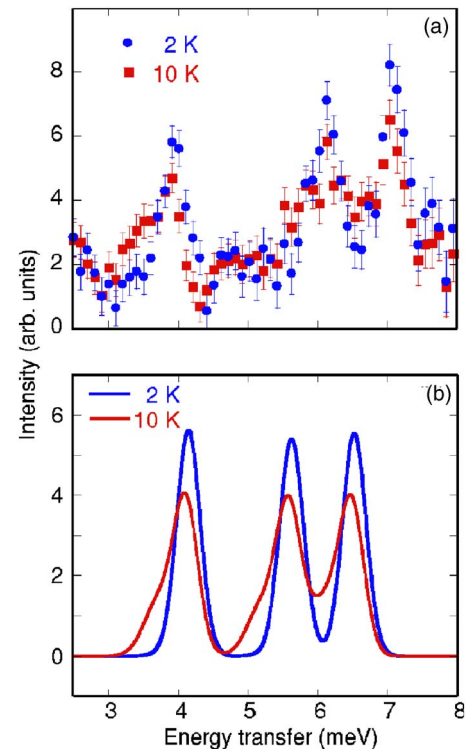

FIG. 4. (Color online) (a) DCS INS spectra of Fe_8 ($\lambda = 2.8$ Å). A spurious peak at 5.3 meV due to a Bragg reflection from the detector bank has been subtracted. (b) Calculated INS spectra at 2 and 10 K. With increasing T, the three peaks display a transfer of intensity to energies about 0.5 meV below the above values. This mainly reflects the thermal population of the first-excited quasi doublet of the ground $S = 10$ manifold (approximately given by the $M_S = \pm 9$ doublet). Correspondingly, transitions to the lowest-energy quasi doublets of the three excited $S = 9$ manifolds are activated.

width at half maximum (FWHM) of 0.5 meV. The intensity of the peak centered at 2.3 meV varies quadratically with momentum transfer as shown in the inset of Fig. 2, and the same behavior is seen for all three peaks, clearly indicating the phonon nature of these excitations. This conclusion is further substantiated by the T dependence of the peaks. If any of these corresponded to an $S = 10 \rightarrow S = 9$ transition, then its shape should change by raising T to 15 K. As a result of the thermal population of the $|10, \pm 9\rangle$ levels, a shoulder should, in fact, appear on the low-energy side of the low-T magnetic peak, at about 0.5 meV below its maximum. No change in the intensity profile is actually observed for the three excitations lying below 3.2 meV. However, a clear peak appears at about 3.5 meV when the temperature of the sample is raised to 15 K. This strongly suggests that the lowest $S = 9$ multiplet is located at about 4 meV.

In order to directly detect the lowest $S = 9$ multiplet we used the IN4 spectrometer. Data were collected at four different temperatures, i.e., $T = 1.5$, 8.0, 15.0 and 35.0 K, with $\lambda = 3.4$ Å. The spectra were recorded in the wide angle detector bank spanning a Q range at the elastic line of $0.4 \leqslant Q \leqslant 3.2$ Å^{-1}. As expected, a peak is observed at about 4 meV (see Fig. 3). The Q dependence of its intensity shows oscillatory behavior indicating the magnetic origin for this excitation. This behavior is consistent with that calculated for the lowest inter-multiplet transition using the exchange constants J_{ij} estimated from susceptibility data[10] (solid line inset Fig. 3).

If the above spectroscopic identification is correct, two further magnetic peaks should be present slightly above 4 meV, corresponding to transitions to two other $S = 9$ multiplets. To cover this range, we used the disk chopper spectrometer (DCS) with two incident neutron wavelengths, $\lambda = 2.8$ and 3.5 Å, with corresponding resolution widths for elastic scattering of 530 and 280 μeV, respectively. The angular interval spanned by the detector banks allows us to investigate a maximum momentum transfer $Q_{max} = 4.2$ Å^{-1} for $\lambda = 2.8$ Å and $Q_{max} = 3.3$ Å^{-1} for $\lambda = 3.5$ Å, at the elastic peak. The spectra recorded with $\lambda = 2.8$ Å are shown in

Fig. 4. At $T = 1.5$ K, three main features are visible, centered at about 4.0, 6.0 and 7.0 meV, respectively. Raising the temperature to 10 K, the low-energy transition at about 4 meV decreases in absolute intensity, with concurrent growth of a shoulder at about 3.5 meV, confirming the IN6 and IN4 measurements. Data taken at several temperatures (not shown) indicate that the intensity loss is due to thermal depopulation. For instance, for the integrated intensity I of the 4 meV peak, the IN4 data yield $I(8 \text{ K})/I(2 \text{ K}) \sim 0.8$ and $I(15 \text{ K})/I(2 \text{ K}) \sim 0.7$, in satisfactory agreement with the calculated values $I(8 \text{ K})/I(2 \text{ K}) = 0.8$ and $I(15 \text{ K})/I(2 \text{ K}) = 0.6$. As the $|10, 9\rangle$ level has been observed at 0.47 meV above the $|10, 10\rangle$ ground state,[7] the excitation at 3.5 meV can be attributed to the $|10, 9\rangle \rightarrow |9, 9\rangle$ transition. The peaks at higher energy transfer display a temperature behavior that can also be ascribed to a depopulation of the starting energy state of the magnetic transitions. Therefore, our results for the position of excited multiplets are consistent with what was expected from the exchange parameters deduced from susceptibility data. Indeed, these exchange parameters yield three excited S multiplets (having $S = 9$) at 3.8, 5.3 and 6.2 meV. If anisotropy is included, these energies tend to increase. For instance, by assuming the local anisotropy parameters to be the same for all eight individual Fe^{3+} spins, and such as to pro-

duce the known effective anisotropy of the $S=10$ total-spin ground manifold, INS transitions should be seen at about 4.15, 5.6 and 6.5 meV, which are close to the measured values of about 4.0, 6.0 and 7.0 meV [see Fig. 4(b)].

In Ref. 16 the EPR technique had been used to extract information on the energy of the lowest excited spin multiplet by studying thermally activated EPR transitions, which produce shoulders in the field dependence of the spectra[16] (intra-$S=10$ transitions had been studied in Refs. 17 and 18). These shoulders had been interpreted as arising from an excited $S=9$ multiplet located at 2.07 meV. However, the present INS results unambiguously indicate that the lowest excited multiplet is at about 4 meV. Therefore, the value of the exchange gap extracted from EPR data was substantially underestimated. It appears difficult to deduce unequivocal information on excited spin multiplets by studying thermally activated transitions in EPR spectra. INS measurement enables the energies of excited multiplets to be determined directly, whereas extracting these energies from EPR data requires modeling details of the field dependence and temperature dependence of line shapes. Similar disagreement between EPR spectra and INS results occurs for the other prototype nanomagnet Mn_{12}.[19–22]

III. FIELD DEPENDENCE OF THE RELAXATION RATE

In the previous section we have shown that three optical phonon branches exist in Fe_8, at about 2.3, 2.7 and 3.2 meV, and that the lowest-energy excited spin multiplet is located at about 4 meV. Hereafter, we analyze the effect of low-E phonons on the relaxation dynamics of Fe_8. The most general form for the spin-phonon coupling potential within the ground $S=10$ manifold is

$$V = \sum_{q=-2,2} \sum_{\mathbf{k}\sigma} C_q(\mathbf{k},\sigma) O_2^q(\mathbf{S})(c_{\mathbf{k}\sigma} + c_{-\mathbf{k}\sigma}^\dagger), \quad (3)$$

where $C_q(\mathbf{k},\sigma)$ is the coupling constant between the q-type quadrupole (represented by the Stevens operator $O_2^q(\mathbf{S})$[11]), and phonon modes of wave vector $\mathbf{k}$ and branch index σ. A detailed microscopic calculation of $C_q(\mathbf{k},\sigma)$ is unfeasible, nor is it possible to unequivocally deduce them from available experimental data. Therefore, for the sake of simplicity we assume $q=0,1,2$ with $C_q(\mathbf{k},\sigma)$ independent of q. We have checked that the results do not change qualitatively if different choices are made. As usual in studying relaxation in nanomagnets, we assume a Debye-type acoustic branch. Given the lack of detailed information about the nature of the observed optical phonon modes of Fe_8 and the precise form of their coupling to spins, we adopt the model requiring the minimal number of assumptions. The most straightforward way to mimic these optical phonons is to add three Einstein-like peaks to the Debye phonon DOS representing nearly nondispersive optical phonon branches. The peaks are narrow Gaussians centered at the observed energies (2.3, 2.7, and 3.2 meV).

The relaxation time $\tau(T,B)$ is obtained by calculating the inter-well transition rate $\Gamma_\downarrow$[4] through the golden rule transition probabilities associated with Eq. (3). This method is based on the existence of two very different time scales. The
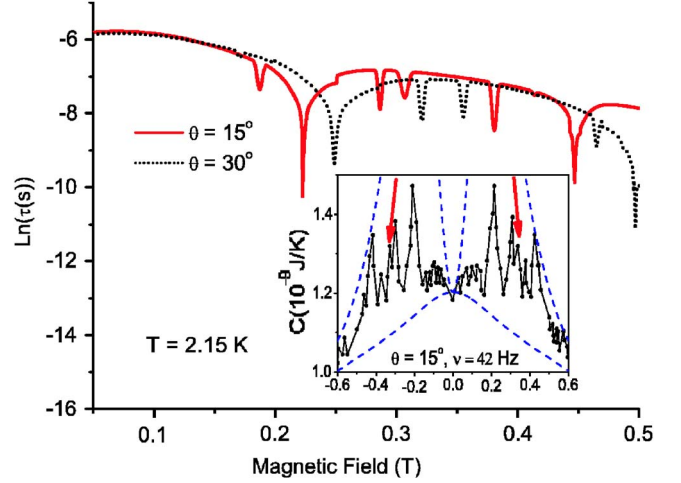

FIG. 5. (Color online) Calculated field dependence of the relaxation time τ for two different field orientations. The inset shows experimental nonequilibrium specific-heat data taken from Ref. 8.

shorter time scale represents the relaxation time within one well, involving transitions between states with the same direction of magnetization. The second and much longer time scale ($1/\Gamma_\downarrow$) involves relaxation from one well to the other, and represents the time needed to reach global thermal equilibrium. We assume the coupling constants of the quadrupoles to the three optical modes to be equal. A second free parameter quantifies the coupling to the Debye phonons.[4] Its value was obtained by a fit of the experimental (Arrhenius-like) T dependence of $\tau(B\to 0,T)$.[23] This T dependence is not affected by the optical phonon modes. Figure 5 shows the calculated $\tau(B,T=2.15$ K$)$ for two different orientations θ of the field with respect to z. The origin of the two main minima at about 0.22 and 0.45 T is well known and is the series of ACs between pairs of excited levels belonging to the two different wells (see Fig. 1). These minima are not affected by the presence of the optical phonons, whereas the latter cause new sharp minima in $\tau(B)$. In particular, three new minima are located between 0.22 and 0.45 T (see Fig. 5). The positions of these minima reflect the energy of the lowest optical phonon [the two higher-energy phonons appear to play a minor role in $\tau(B)$]. The depths and widths of the minima depend on the value of the coupling constant of the quadrupoles to this optical mode and on the width of the Gaussian assumed in the model. The mechanism causing the new minima is the increase of a specific inter-well transition probability at fields where the energy exchanged with phonons in the transition matches that of the optical phonon. For instance, the new minimum in $\tau(B)$ at about 0.29 T is associated with an increased probability for the inter-well transition shown as an arrow in Fig. 1. Since the additional minima reflect thermally activated processes, their size decreases as T is lowered. Experimental information about $\tau(B)$ in Fe_8 was obtained from measurements of the frequency-dependent specific-heat $C(\nu)$ at different applied magnetic fields.[8] The results for $\theta=15°$ and $T=2.15$ K are shown in the inset of Fig. 5. The two dashed lines represent calculated equilibrium (C_{eq}, upper) and unilateral (C_{uni}, lower) specific heats.[24] $C(\nu)$ is a nonequilibrium observable, whose value is

between C_{uni} and C_{eq}, and approaches C_{eq} as τ decreases. Indeed, maxima in $C(\nu)$ are observed at fields corresponding to the minima in $\tau(B)$. The two maxima near 0.22 and 0.45 T correspond to the increase in relaxation rate due to the acs. The three additional maxima in between 0.22 and 0.45 T (see arrow in the inset of Fig. 5) are consistent with the three minima in $\tau(B)$ due to the optical phonons. The measured C suggests, therefore, that the deepest minimum in $\tau(B)$ should be the one at $B=0.45$ T [since $C(B=0.45)$ is very close to $C_{eq}(B=0.45)$, the relaxation time is particularly short], whereas the minimum in $\tau(B)$ at 0.22 T, and the new minima between 0.22 and 0.45 T should be of comparable depth. Thus, although our model gives the right position for the minima, it probably overestimates the depth of the minimum at 0.22 T. Indeed, we have not even tried to quantitatively fit the depth and width of the minima. Fits of features more specific than the position are not unique and, therefore, of limited interest: even putting to one side the unexpected minima in $\tau(B)$ (whose depths can be varied by tuning the coupling strength to the optical phonons), quantities such as the depths of the minima at $B=0.22$ and 0.45 T or the overall slope of the $\tau(B)$ curve depend quite sensitively on details of the theoretical model. In particular, these quantities are sensitive to the precise form of the anisotropy in the spin Hamiltonian and to the precise detailed form of the magnetoelastic coupling, which is unknown and experimentally not measurable. What are important, being model independent, are the positions of the minima, on which we focus, and which are correctly reproduced.

These minima were previously attributed to additional ACs involving an $S=9$ multiplet located at about 2 meV.[8,9]

However, we have shown that the lowest excited multiplet is located at 4 meV, and it does not affect $\tau(B)$. ac-susceptibility measurements confirmed the presence of extra minima in $\tau(B)$.[9] The shift of the minima to higher field with increasing θ is also in agreement with our calculations (see Fig. 5).

IV. CONCLUSION

We have performed INS experiments on the Fe_8 nanomagnet which enabled the energies of the three lowest-lying excited multiplets to be determined (about 4, 6 and 7 meV). These energies are consistent with those expected on the basis of susceptibility measurements. In addition, we have detected optical phonons at 2.3, 2.7 and 3.2 meV. We have shown that these low-lying optical phonons may produce sharp minima in the field dependence of the relaxation time, by boosting the spin-phonon energy exchange in a narrow energy window. The positions of the calculated minima are consistent with those which have been inferred from frequency-dependent specific heat and ac-susceptibility measurements. These results show that low-energy optical phonon branches should be carefully taken into account in the modeling and design of nanomagnets.

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