Muon spin relaxation investigation of tetranuclear iron(III) $Fe_4(OCH_3)_6(dpm)_6$ molecular cluster

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We present a study of the spin dynamics of $Fe_4(OCH_3)_6(dpm)_6$ single molecule magnet by means of SQUID magnetization and muon relaxation (μ^+SR) measurements. In longitudinal field μ^+SR experiments performed at magnetic fields $H=200$, 1000 Oe, the muon asymmetry $P(t)$ could be fitted by means of three components, the first constant, the second fast relaxing through a quasiexponential decay, and the third, the slowest relaxing, showing an exponential decay. The slowest muon relaxation rate λ studied as a function of temperature T displayed two structures, a broad peak at $T\sim 15/20$ K and a shoulder at $T<5$ K, both decreasing in amplitude and displacing toward higher temperatures as the field is increased. To mimic qualitatively the temperature behavior $\lambda(T)$ at the investigated fields, we used a function expressed as the sum of two Bloembergen-Purcell-Pound (BPP)-like laws, reproducing the mechanism of relaxation. The exponential data resulted well fitted by means of a heuristic model which takes into account two correlation times τ' and τ, related to the ground-state multiplet barrier ($\Delta'/k_B=7.25$ K) and to the intermultiplet separation ($\Delta/k_B=86.4$ K) between S=5 and S=4.

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I. INTRODUCTION

The study of magnetic clusters of transition-metal ions has attracted much interest after the discovery of single molecule magnet (SMM) behavior. At low temperatures, SMMs exhibit magnetic bistability at the level of a single molecule due to the slow relaxation of the magnetization, which occurs via thermal activation over an anisotropy barrier and, at very low T, by a quantum tunneling mechanism.[1–3] SMMs are often clusters of exchange-coupled transition-metal ions and the height of the magnetic anisotropy barrier is mainly associated with the total spin value in the ground state and with the sum of single-ion anisotropies, which in turn are dependent on the nature of the ligands and their arrangement around the metal centers. Dipole-dipole interactions and mixing of states with different total spin can also play an important role[4] and must usually be taken into account. After the first observation of magnetic bistability in a Mn_{12} cluster[5] considerable efforts have been made to increase the barrier height and, consequently, the blocking temperature in order to make real applications viable. In addition, many fundamental studies have been devoted to quantum-size effects, as evidenced by the thermodynamic properties,[6] and to the situation of near degeneracy of two magnetic levels, where quantum phenomena such as tunneling can occur. These effects have been explored in the high-spin molecules Mn_{12} and Fe_8, two systems characterized by a peculiar steplike magnetic hysteresis cycle, and a very slow relaxation of the magnetization at low temperature.[1,3,7]

Here we present a muon spin-relaxation (μSR) investigation of a tetrairon(III) SMM having a formula $Fe_4(OCH_3)_6(dpm)_6$, in the following Fe_4 (where Hdpm =dipivaloylmethane). Its molecular structure is shown in Fig. 1. The four iron atoms lie exactly in a plane, the inner Fe atom being in the center of an isosceles triangle. The molecule has a twofold symmetry due to the presence of a crystallographic C_2 axis passing through Fe1 and Fe2 (for more details see Ref. 8). Although Fe_4 has a smaller anisotropy with respect to Mn_{12} or Fe_8 and, as a consequence, a lower

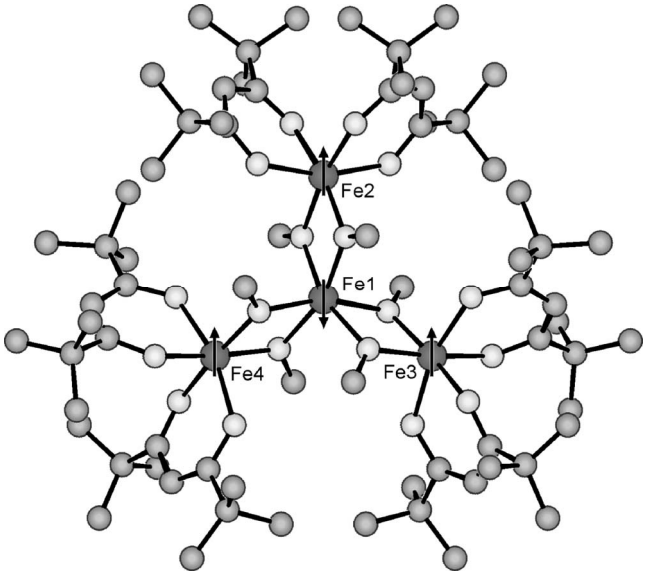

FIG. 1. Molecular structure of $Fe_4(OCH_3)_6(dpm)_6$. The four iron(III) ions are represented as dark-gray spheres while the oxygen and carbon atoms are drawn as light gray and medium-gray spheres, respectively. Hydrogen atoms are omitted for clarity. The arrows provide the spin configuration in the ground $S_T=5$ state.

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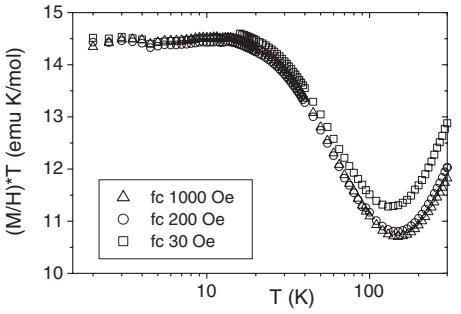

FIG. 2. $(M/H)\cdot T$ versus T plot for a powder sample of $Fe_4(OCH_3)_6(dpm)_6$ at three different fields.

blocking temperature, it is attractive for an investigation of the spin dynamics due to its simple structure. The main findings about this molecule are reported in Refs. 9 and 10. Fe_4 has a $S_T=5$ ground state and shows slow relaxation of the magnetization below 1 K.[9] The first-excited level, $S_T=4$ is separated from the ground state by approximately 86.4 K. High-frequency electron paramagnetic resonance spectroscopy on a powder sample[10] revealed that the system has an essentially uniaxial magnetic anisotropy resulting in a spin Hamiltonian $\mathcal{H}=-DS_z^2+g\mu_B HM_s$, where the last term represents the Zeeman interaction; from Ref. 10 results $D=-0.20$ $cm^{-1}=-0.29$ K. The sign of D and the unresolved rhombicity of the spectra are consistent with the expected single-ion anisotropies based on the angular overlap model and with the estimated intramolecular dipole-dipole contributions.[11] Thus the anisotropy barrier calculated as the difference between the $M_S=0$ and the $M_S=\pm 5$ levels at zero applied field is $\Delta'/k_B \cong 7.25$ K.[11,12] The magnetization overcomes the barrier with a reversal time τ' that follows the Arrhenius law $\tau'=\tau_0' \exp(\Delta'/k_BT)$.

We will show that qualitatively the muon longitudinal relaxation-rate data versus temperature are reproduced by using a heuristic model based on a function expressed as a sum of two Bloembergen-Purcell-Pound (BPP)-like laws[13,14] that takes into account two spin-spin correlation times related, respectively, to the ground-state multiplet barrier and to the intermultiplet $(S_T=4/S_T=5)$ separation. This finding suggests that the μSR technique is suitable for detecting the spin dynamics related to intermultiplet molecular transitions.

II. EXPERIMENTAL DETAILS, RESULTS, AND DISCUSSION

Microcrystalline powder samples of $Fe_4(OCH_3)_6(dpm)_6$ were prepared as described in Ref. 8. In order to characterize the magnetic properties of the sample, we performed magnetization measurements with a MDMS-XL7 Quantum Design magnetometer by using the standard extraction technique, in the temperature range 2–300 K at different constant magnetic fields $H=30$, 200, and 1000 Oe, in field cooling conditions (see Fig. 2). As can be seen from Fig. 2, $(M/H)\cdot T$ data do not depend much on applied fields.

The μ^+SR data were collected at the ISIS facility, Rutherford Appleton Laboratory (U.K.), in the temperature range 1.5–210 K, in longitudinal magnetic fields (LF) $H=200$ and

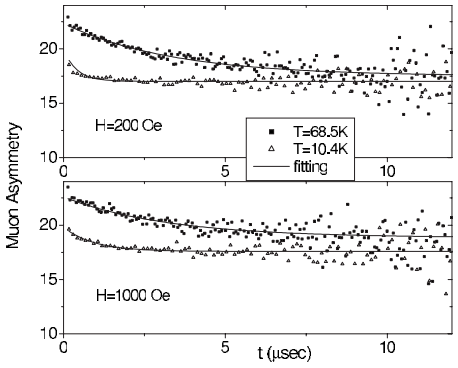

FIG. 3. Temperature dependence of the μ^+ polarization decay in LF=200 and 1000 Oe. Solid lines represent the fits to Eq. (1) in the main text.

1000 Oe. Zero-field data were collected too but due to the contribution of nuclei to the muon asymmetry decay, no good fit of data was possible. The total asymmetry estimated was ~0.24, the nonrelaxing asymmetry being about 2/3 of the total one. Taking into account that the (not relaxing) background coming from the sample holder can be estimated around 10–15 % of the total asymmetry, approximately half of muons implanted in the sample do not relax at any temperature. These muons possibly stop very far from the magnetic core also in intermolecular interstitials. The remaining 1/3 of muon asymmetry shows that the muon spin relaxes at any temperature through two exponentially decaying components. As the first component presents very fast relaxation rate, a reliable fitting of its decay was not possible because of the few sampled points ($\lambda > 20$ μsec^{-1}); so we decided to fit the slowest relaxing component using an exponential function, in the range $t > 0.5$ μsec. This means that we have been able to obtain information only about the spin dynamics felt by muons implanted in one of three, at least, different sites.

For the slowest component we fitted the data by the function

$$P(t) = C \exp(-\lambda t), \tag{1}$$

where λ is the muon longitudinal relaxation rate. Figure 3 shows the time dependence of the muon asymmetry for LF =200, 1000 Oe at two representative temperatures.

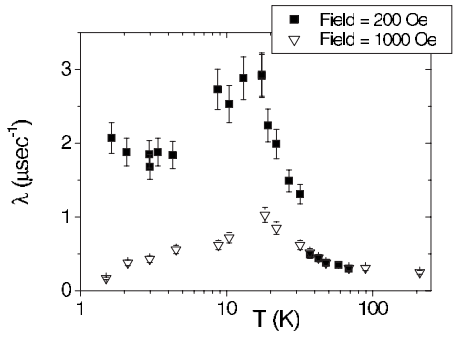

FIG. 4. Temperature dependence of the muon longitudinal relaxation rates λ on $Fe_4(OCH_3)_6(dpm)_6$ powder in LF=200 and 1000 Oe.

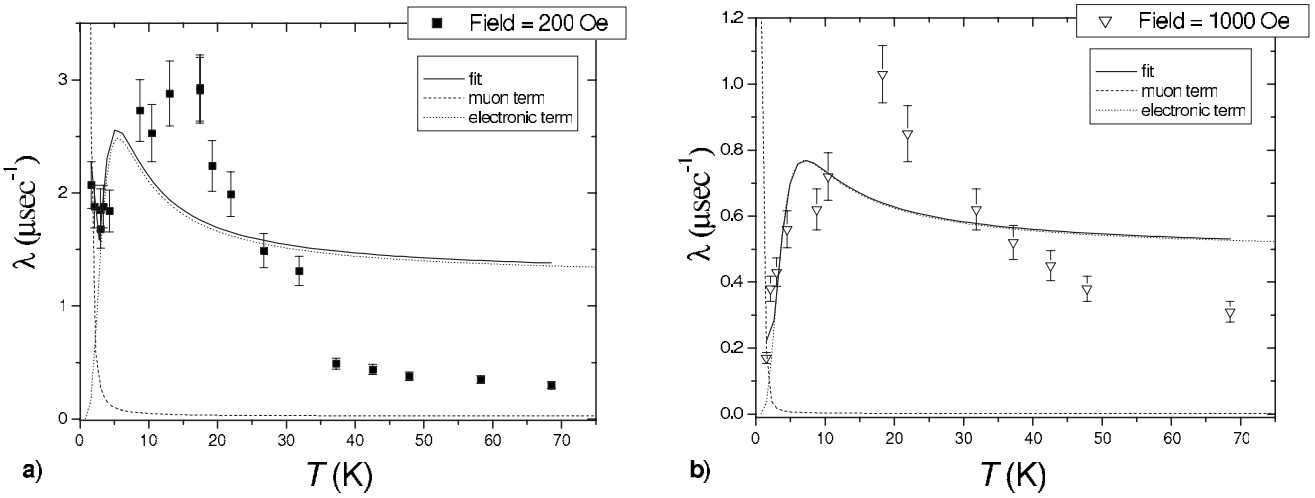

FIG. 5. Fits (solid lines) of the muon longitudinal relaxation rates λ on $Fe_4(OCH_3)_6(dpm)_6$ powder in (a) LF=200 and (b) 1000 Oe by means of Eq. (3); contributions at muon Larmor frequency ω_L (dashed lines) and at electronic Larmor frequency (dotted lines) are also shown.

The temperature dependence of the μ^+ relaxation rate obtained from fits to Eq. (1) is shown in Fig. 4. The relaxation remains slow and slightly temperature dependent down to ≈35 K while a broad peak with a maximum at about 15/20 K (depending on the field) and a shoulder at low temperatures (below $T\sim 5$ K) are evident. These two structures decrease in amplitude and displace toward higher temperatures by increasing the field.

The presence of a low-temperature maximum in the longitudinal relaxation rate vs temperature, is a feature typical of many molecular nanomagnets,[15–24] in both NMR and μSR experiments. By means of an accurate data analysis,[15,19–21] it was shown that the nuclear/muon spin-lattice relaxation rate $(1/T_1)$ behavior versus temperature at different applied magnetic fields, follows the universal law

$$\frac{1}{T_1} = K\left(\frac{M}{H}\right)T\frac{\Gamma(T)}{\Gamma^2(T)+\omega_L^2}, \tag{2}$$

where K is a constant, ω_L is the Larmor frequency, and Γ is a characteristic frequency of the system having a power law[17,21] or an exponential-like[18] behavior. The inverse of Γ, τ_C, represents an average of the lifetime broadenings of different discrete molecular energy sublevels, thermally populated, involved in the transitions responsible for the nuclear relaxation. It should be noticed that the validity of an universal law, Eq. (2), implies that in most cases the spin dynamics can be driven by a unique effective correlation time $\tau_C = 1/\Gamma$, a result somewhat surprising in presence of many differently populated levels.[18] However, one must note also that in NMR experiments on high-spin clusters, included Fe_4, the wipeout effect often prevents an accurate analysis of the $1/T_1$ versus T data as the ^1H fastest relaxing nuclei give no signal for $T<60/80$ K.[12,21]

On the other hand the μSR data for molecular clusters, such as V_{15} and Fe_{30} show[19,20] that the relaxation rate behavior can be explained by Eq. (2) at high and intermediate temperatures while at low temperatures a flattening is observed (the relaxation remains fast until $T<1$ K). This flattening, possibly due to quantum effects, has been observed also in other molecular clusters.[22,23] Differently, the presently investigated Fe_4 shows a behavior similar to Mn_{12} and Fe_8.[15,24] In Mn_{12} the BPP-like behavior was explained by a heuristic model invoking the fine structure of the energy levels of the $S_T=10$ ground state, taking into account the lifetime of each M_S sublevel.[16] A qualitative fit of NMR data was possible with a single τ_C.[21] In the present Fe_4 case, Eq. (2) does not account properly of the T behavior of λ at different investigated fields, mainly because of the presence of two structures, as clearly evidenced in Fig. 4.

To reproduce the experimental data, we implemented a model based on a single dominant correlation time, where the muon probes the spectrum of the electronic spin fluctuation at two different frequencies, the muon (ω_L) and the electronic (ω_e) Larmor frequencies. This is the typical result valid also in NMR case that follows essentially from Moriya's weak-collision theory.[25] In Moriya's theory the local probe (muon/nucleus) is shown to experience a longitudinal relaxation rate proportional to the sum of two spectral densities of the electronic spin fluctuations calculated at ω_L and ω_e, i.e., $\frac{1}{T_1}\propto A\cdot J(\omega_L)+B\cdot J(\omega_e)$. If the time-correlation function $G(t)$ has an exponential decay [namely, $G(t)\propto\exp(-t/\tau)$], the expression of $\frac{1}{T_1}$ can be written

$$\frac{1}{T_1} = A\frac{\Gamma(T)}{\Gamma^2(T)+\omega_L^2} + A'\frac{\Gamma(T)}{\Gamma^2(T)+\omega_e^2}. \tag{3}$$

With this model we were able to fit the experimental data well enough only for temperatures $T<10$ K while the broad peak with a maximum at 15/20 K as well as the data at high temperatures are not reproduced. In Fig. 5 the fitting curves obtained, respectively, at (a) 200 Oe and (b) 1000 Oe fields and the different contributions to the fit of the muon and electronic frequencies are reported.

From the analysis of the two contributions is evident that the muon Larmor frequency dominates at very low tempera-

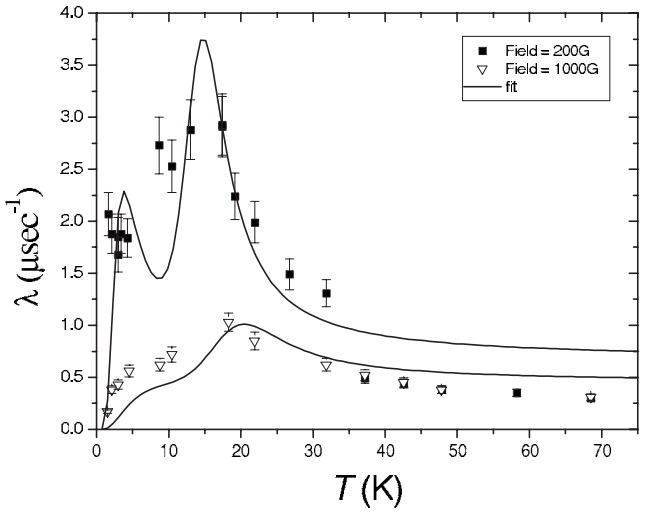

FIG. 6. Fits (solid lines) of the muon longitudinal relaxation rates λ on $Fe_4(OCH_3)_6(dpm)_6$ powder in LF=200 and 1000 Oe by means of the Eq. (4).

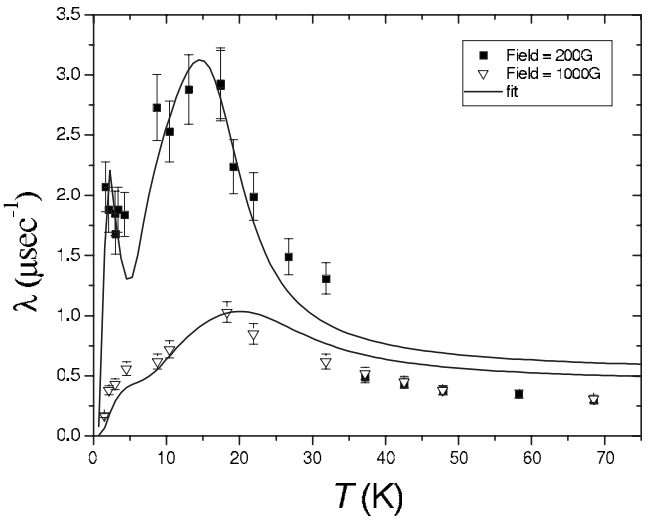

FIG. 7. Fits (solid lines) of the muon longitudinal relaxation rates λ on $Fe_4(OCH_3)_6(dpm)_6$ powder in LF=200 and 1000 Oe by means of Eq. (5) with five free parameters. The rectangular distribution width for the energy barrier Δ of the intermultiplet transition is δ=34.5 K.

ture ($T<1.5$ K) while at temperatures >5 K only the electronic term is present for both magnetic fields. These evidences indicate that by using a single correlation time we did not reproduce satisfactorily the data.

As a consequence, we tried to fit our data using a modified model of Eq. (2), introducing two typical correlation times (or frequencies) $\tau \equiv 1/\Gamma$ and $\tau' \equiv 1/\Gamma'$ to explain the presence of both structures, the peak and the shoulder. The corresponding new equation includes two Lorentzian BPP terms

$$\frac{1}{T_1} = A\frac{\tau}{1+\tau^2\omega_L^2} + A'\frac{\tau'}{1+\tau'^2\omega_L^2}. \tag{4}$$

For both τ and τ' an exponential Arrhenius law $\tau = \tau_0 \exp(\Delta/k_BT)$ [or $\tau' = \tau'_0 \exp(\Delta'/k_BT)$] was assumed. The corresponding energy barriers Δ and Δ′ were chosen as the S_T=5 ground-state multiplet barrier (Δ'/k_B=7.25 K) and the intermultiplet S_T=5 to S_T=4 average distance (Δ/k_B =86.4 K). The quality of the fitting reported in Fig. 6 remains clearly poor also by using Eq. (4) that takes into account of two correlation times. For H=1000 Oe this model fails in the whole temperature range and for H=200 Oe the data at high temperature ($T>20$ K) are not well fitted and the increase at about 5 K is shifted with respect to the data.

By looking at Fig. 4 one can evince that the fitting of the data is complicated by the too large width of the high-temperature peak, possibly related to intermultiplet transitions occurring at high and intermediate temperatures $T>10/15$ K. To overcome this problem we assumed a distribution for the intermultiplet distance Δ. The shape of the distribution was assumed to be rectangular because in this case the BPP-like $1/T_1$ law has an analytical expression. The existence of a barrier distribution can be qualitatively attributed to different possible transitions related to different gaps among the molecular energy levels involved. Furthermore, as the $(M/H)\cdot T$ effective moment in the range $2 \le T \le 70$ K varies slightly and is almost independent of H, we assumed $(M/H)\cdot T$=constant.

The modified fitting equation includes two BPP-like laws (one of which distributed in energy) resulting in

$$\frac{1}{T_1} = A\frac{1}{2\omega_L \ln b}\left[\text{arc}tg(b\omega_L\tau) - \text{arc}tg\left(\frac{\omega_L\tau}{b}\right)\right] + A'\frac{\tau'}{1+\tau'^2\omega_L^2}, \tag{5}$$

where A and A' are fitting constants independent of both H and T, and represent the hyperfine field fluctuations at the muon site, ω_L is the muon Larmor frequency, $b=\exp(\delta/T)$ with δ width of the rectangular distribution of the energy barrier Δ/k_B, $\tau=\tau_0 \exp(\Delta/k_BT)$ is the average lifetime broadening of different discrete energy sublevels involved in intermultiplet transitions and/or in spin-phonons interaction[15,17,18] and $\tau' = \tau'_0 \exp(\Delta'/k_BT)$ is the intramultiplet average lifetime of the energy sublevels of the ground state.[12]

As a first tentative with Eq. (5) instead of using data found in literature, we left free all the varying parameters τ, τ'_0, Δ, Δ′, and δ while A and A' act as rescaling factors. The best fitting procedure has given the values Δ=69 K, Δ′ =4.75 K, and δ=34.5 K; we note that Δ and Δ′ assumed values different from those reported in literature and that the parameter δ was forced to be less than half of the intermultiplet separation Δ, a higher value being difficult to have physical meaning. Despite the fitting curve reproduces better the experimental data as can be seen from Fig. 7, the fit remains unsatisfactory for both magnetic fields at $T>25$ K and at the higher field also below $T\sim 10$ K.

As the above presented fits were not fully satisfactory, we decided to perform a final fit by fixing the values of the ground-state barrier Δ'/k_B=7.25 K and of the intermultiplet barrier Δ/k_B=86.4 K, i.e., the ones reported in literature.[9–12] Moreover we fixed δ=43 K (again at about $\frac{1}{2}$ of the energy

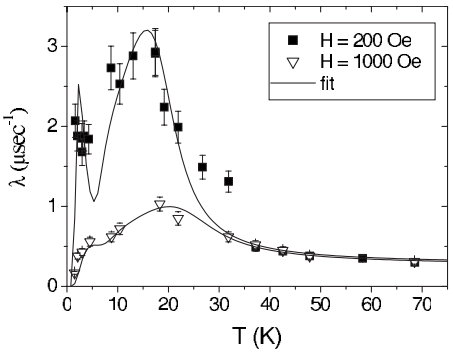

FIG. 8. Fits (solid lines) of the muon longitudinal relaxation rates λ on $Fe_4(OCH_3)_6(dpm)_6$ powder in LF=200 and 1000 Oe by means of the heuristic model, Eq. (5), with $\Delta'/k_B=7.25$ K, $\Delta/k_B=86.4$ K, and $\delta=43$ K.

gap among the center of $S_T=5$ and $S_T=4$ multiplets). Using these parameters in Eq. (5), we have been able to qualitatively reproduce the data (see Fig. 8) confirming: (1) the presence of the broad peak that decreases and displaces toward higher temperatures by increasing the applied field and (2) the presence of a second anomaly below ~5 K. In our final fitting procedure the free parameters are τ_0 and τ_0', Δ/k_B, Δ'/k_B and δ are fixed as reported above while A and A' act as rescaling factors. Estimated values of the fitting parameters are $\tau_0=9.2\times10^{-11}$ sec, $\tau_0'=2.9\times10^{-9}$ sec, $A=1.9\times10^{14}$ rad^2 Hz^2, and $A'=8.7\times10^{13}$ rad^2 Hz^2. The value of τ_0' is not far from the values obtained with different techniques;[9,10] it should be remarked that its value has been demonstrated to depend on the experimental technique of investigation in several SMMs because of the different experimental measurement conditions and because of the different sensitivity to local/macroscopic spin dynamics.[1]

III. CONCLUSIONS

A qualitative explanation of the local spin dynamics versus temperature was provided for the Fe_4 high-spin ($S_T=5$) SMM, as revealed by the muon longitudinal relaxation rate λ in applied longitudinal fields $H=200$ and 1000 Oe. By using a heuristic BPP-like model where two correlation times $\tau'=\tau_0'\exp(\Delta'/k_BT)$ and $\tau=\tau_0\exp(\Delta/k_BT)$, are taken into account, the $\lambda(T)$ data can be reproduced and qualitatively interpreted. In this model we assumed an anisotropy ground-state ($S_T=5$) energy barrier of $\Delta'/k_B=7.25$ K (from previous works[12,13]) and interpreted τ' as an average correlation time of the intramultiplet ground-state transitions. For the energy separation between the center of $S_T=5$ and $S_T=4$ molecular energy multiplets, we used the value $\Delta/k_B=86.4$ K, as deduced from neutron-scattering experimental data.[4,11] By taking into account that the $S_T=4$ and $S_T=5$ multiplets have a finite width in energy (due to M_S degeneration), we assumed that their energy separation has a distribution of values centered at $\Delta/k_B=86.4$ K, with average width $\delta=43$ K. In this case τ represents an average correlation time related to different intermultiplet transitions. These results suggest that μSR is a good technique to investigate and to obtain information on the intermultiplet separation and molecular transitions in the single molecule magnet Fe_4.

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