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Local spin dynamics at low temperature in the slowly relaxing molecular chain [Dy(hfac)₃{NIT(C₆H₄OPh)}]: A μ^+ spin relaxation study

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The spin dynamics of the molecular magnetic chain [Dy(hfac)₃{NIT(C₆H₄OPh)}] were investigated by means of the Muon Spin Relaxation (μ^+ SR) technique. This system consists of a magnetic lattice of alternating Dy(III) ions and radical spins, and exhibits single-chain-magnet behavior. The magnetic properties of [Dy(hfac)₃{NIT(C₆H₄OPh)}] have been studied by measuring the magnetization vs. temperature at different applied magnetic fields ($H = 5, 3500, \text{ and } 16500 \text{ Oe}$) and by performing μ^+ SR experiments vs. temperature in zero field and in a longitudinal applied magnetic field $H = 3500 \text{ Oe}$. The muon asymmetry $P(t)$ was fitted by the sum of three components, two stretched-exponential decays with fast and intermediate relaxation times, and a third slow exponential decay. The temperature dependence of the spin dynamics has been determined by analyzing the muon longitudinal relaxation rate $\lambda_{\text{interm}}(T)$, associated with the intermediate relaxing component. The experimental $\lambda_{\text{interm}}(T)$ data were fitted with a corrected phenomenological Bloembergen-Purcell-Pound law by using a distribution of thermally activated correlation times, which average to $\tau = \tau_0 \exp(\Delta/k_B T)$, corresponding to a distribution of energy barriers Δ . The correlation times can be associated with the spin freezing that occurs when the system condenses in the ground state. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4916024>]

I. INTRODUCTION

Experiments carried out over the last two decades on molecule-based magnetic nano-materials^{1,2} have sparked great interest in this field both from application and theoretical points of view. The possibility to tailor the magnetic properties by synthesizing systems with different spin topology and dimensionality at the molecular scale stimulated the scientific community to synthesize and investigate different classes of compounds, e.g., molecular clusters and chains, two examples of low-dimensional magnetic systems. In the field of one-dimensional (1D) magnets, extensively studied for their simplicity, several theoretical predictions were experimentally verified over the past decade or so such as the Haldane conjecture for integer-spin chains,³ the existence of the Villain mode in quasi-Ising $S = 1/2$ antiferromagnetic (AF) spin chains,⁴ and the role of solitons in the thermodynamic properties of easy-plane ferromagnetic⁵ and AF⁶ spin chains. Remarkable results were also obtained for quasi-1D magnetic chains synthesized by means of the molecular approach.^{2,7} Particularly, synthesis efforts stimulated by the peculiar properties of these systems resulted in the production of a one-dimensional system, namely, [Co(hfac)₂{NIT(C₆H₄OMe)}]⁸ (hfac = hexafluoroacetylacetonate; NIT(R):

2-(4'-R)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide), in short CoPhOMe, which exhibits superparamagnetic-like behavior. As a consequence, CoPhOMe became the prototype of a class of magnetic chains where, by changing the metal or the radical moieties, it is now possible to fine-tune the physical properties. Because of the slow relaxation of its magnetization at low temperature, CoPhOMe was classified as a single-chain magnet (SCM),^{9,10} in analogy with single-molecule magnets (SMMs).^{1,9,11} The magnetic properties of such 1D systems were theoretically predicted by Glauber in the 1960s:¹² At low temperature, the magnetization relaxes slowly with a relaxation time that follows an Arrhenius law $\tau = \tau_0 \exp(\Delta/k_B T)$, and no phase transition to three-dimensional (3D) magnetic long-range order occurs before the magnetization blockage.^{10,13}

Subsequently, several other compounds were shown to exhibit SCM behavior,^{11,14–21} with quantum effects influencing the magnetization dynamics at low temperatures.²² In particular, several works^{23–25} showed that the requirements necessary to observe Glauber dynamics—a strong Ising-like anisotropy and a very low ratio of interchain/intrachain magnetic exchange interactions—are fulfilled in [Dy(hfac)₃{NIT(C₆H₄OPh)}] (in short DyPhOPh). A previous theoretical and experimental study²⁵ demonstrated that DyPhOPh consists of two sets of non-interacting parallel chains, with projections mutually tilted by about 90°. Inside each nearly

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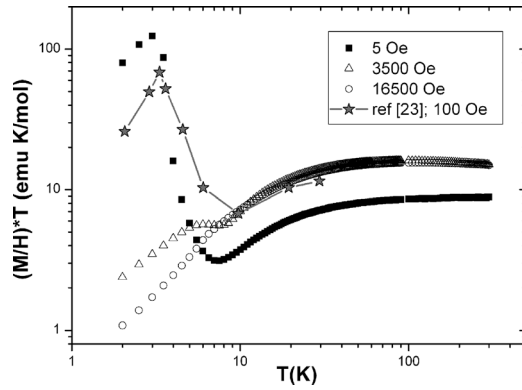


FIG. 1. $(M/H) \cdot T$ versus T plot for a powder sample of $[\text{Dy}(\text{hfac})_3\{\text{NIT}(\text{C}_6\text{H}_4\text{OPh})\}]$ at three different magnetic fields $H=5$, 3500, and 16500 Oe; for comparison, few data points collected in Ref. 23 at $H=100$ Oe are also reported.

independent chain, the magnetic behavior is determined by a strong (despite the large Dy-Dy separation) antiferromagnetic next-nearest-neighbor interaction $J \approx -24$ K between Dy^{3+} ions, while the nearest-neighbor interaction between the radicals and the Dy^{3+} ions is much weaker. Thus, a canted antiferromagnetic spin arrangement with a net magnetic moment along the chain axis is favoured.²⁵

In this paper, we report new insights into the local spin dynamics of DyPhOPh, as determined from magnetization and muon spin relaxation (μ^+ SR) experiments, that confirm the slow relaxation of the magnetization at low temperature and the Arrhenius law for the relaxation time τ .

II. EXPERIMENTAL DETAILS, RESULTS AND DISCUSSION

Microcrystalline powder samples of $[\text{Dy}(\text{hfac})_3\{\text{NIT}(\text{C}_6\text{H}_4\text{OPh})\}]$ were prepared, as described in Ref. 23. To investigate the magnetic properties of the sample, we performed magnetization measurements with a MDMS-XL7 Quantum Design magnetometer, in the temperature range of

2–300 K in constant magnetic fields of $H=5$, 3500, and 16500 Oe under field cooling (FC) conditions.

The temperature dependence of $(M/H) \cdot T$, shown in Fig. 1, confirms the results obtained in Ref. 23, where in an applied field of $H=100$ Oe a minimum at $T \sim 8.6$ K and a rounded peak at $T_{\text{peak}} \sim 3.6$ K were observed. As can be easily seen from Fig. 1, $(M/H) \cdot T$ is strongly field dependent, with the rounded peak that shifts to higher temperatures and decreases in magnitude as the magnetic field is increased, disappearing at the highest $H=16500$ Oe field value; this behaviour is typical of several 1D magnetic systems. We further observe that a relatively low field value ($H=100$ Oe) already affects the low temperature magnetic behaviour, as witnessed by the shift of the peak position from $T_{\text{peak}} = 3.6$ K at $H=100$ Oe, to $T_{\text{peak}} \sim 3$ K at $H=5$ Oe.

The μ^+ SR data were collected at the Paul Scherrer Institute (Switzerland) in the temperature range of 1.8–160 K, in zero field and in a longitudinal magnetic field (LF) $H=3500$ Oe. Figure 2 shows the time dependence of the experimental muon asymmetry (open symbols) for $H=0$ and $H=3500$ Oe at two representative temperatures of $T=13$ and 30 K. The estimated total asymmetry was $P(t) \sim 0.265$, including the non-relaxing background (about 10%) coming from the sample holder. The time dependence of the remaining $\sim 90\%$ of relaxing asymmetry suggests that the muon polarization relaxes at all temperatures through a sum of three decaying components: two stretched-exponential decays with fast and intermediate relaxation times and a slow exponential relaxation

$$P(t) = C_1 \cdot \exp(-(\lambda_{\text{fast}} t)^{\beta_1}) + C_2 \cdot \exp(-(\lambda_{\text{interm}} t)^{\beta_2}) + C_3 \cdot \exp(-\lambda_{\text{slow}} t). \quad (1)$$

Here, $P(t)$ is the muon total relaxing asymmetry, λ_{fast} , λ_{interm} , and λ_{slow} are the muon longitudinal relaxation rates of the three components; the coefficients C_1 , C_2 , and C_3 were fixed to 46%, 30%, and 23% of $P(t)$, respectively (full value estimated at high

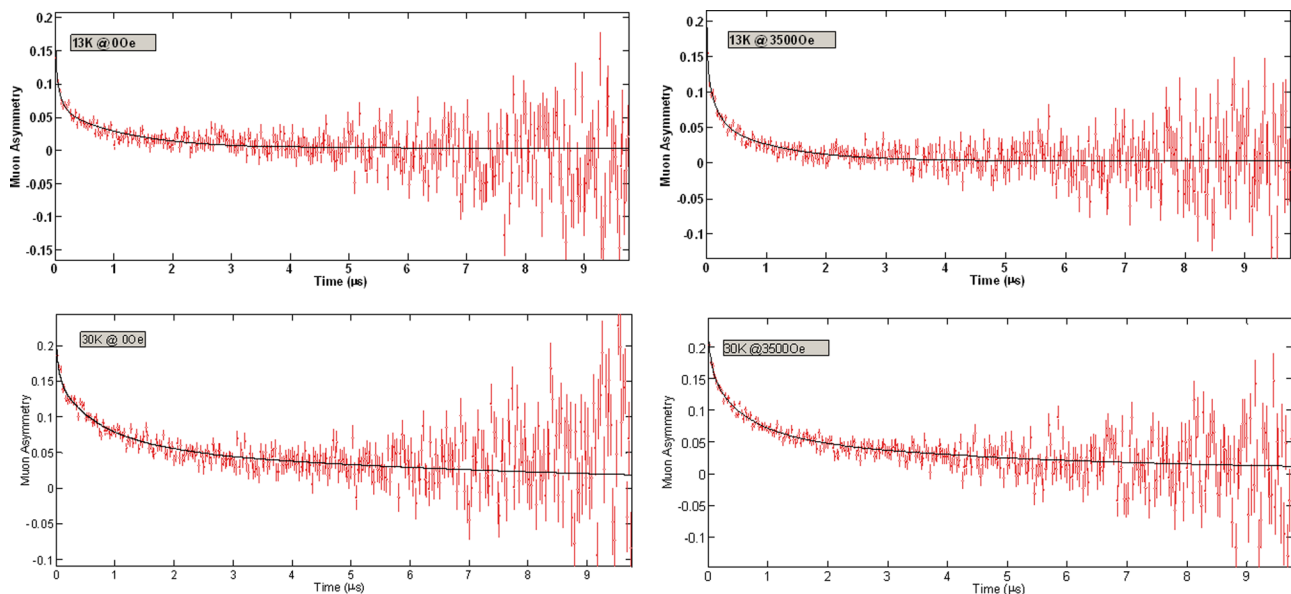


FIG. 2. Muon asymmetry decay in LF=0 and 3500 Oe at $T=13$ K and $T=30$ K. Solid lines represent the fits to Eq. (1) in the main text.

temperatures). The exponents of the two stretched exponential functions, β_1 and β_2 , were left free to vary in the range $0.5 \div 1$. The expression given in Eq. (1) for $P(t)$ is a clear mark of the presence of several muon implantation sites.

We focused our data analysis on the temperature dependence of the intermediate relaxation rate $\lambda_{\text{interm}}(T)$ obtained from the fitting curves, Eq. (1), shown in Figure 3 (solid lines). Due to the very large values of λ_{fast} for $T < 30$ K ($> 100 \mu\text{s}^{-1}$) no reliable analysis of the fast relaxing component was possible, while the qualitative behaviour of $\lambda_{\text{slow}}(T)$ is the same of $\lambda_{\text{interm}}(T)$. As can be seen from Fig. 3, the experimental relaxation rate $\lambda_{\text{interm}}(T)$ depends slightly on the temperature from 160 K down to ≈ 40 K, while for $T < 40$ K, it displays a rapid increase for both $H=0$ and $H=3500$ Oe, exhibiting a clear maximum at $T_{\text{max}} \sim 12$ K for $H=3500$ Oe. On the other hand, for $H=0$ and $T < 10$ K, the large values of λ_{interm} ($> 20 \mu\text{s}^{-1}$) did not allow us to fit properly the muon asymmetry $P(t)$, as too few sampled points are present at short times (the resulting fitting error $\pm \Delta\lambda_{\text{interm}}$ is huge), a well-known occurrence in $\mu^+\text{SR}$ experiments. Despite this difficulty, one can conclude that the temperature dependence shown in Fig. 3 is similar to that of many nanomagnets,²⁶ observed in both NMR and μSR experiments, where the maximum of the longitudinal relaxation rate displaces toward higher temperatures and assumes lower values when the field is increased. As reported in Refs. 26–28, the temperature dependence of the nuclear/muon spin-lattice relaxation rate ($1/T_1$ or λ) at different applied magnetic fields was demonstrated in some cases to depend on: the effective magnetic moment $(M/H) \cdot T$, the Larmor frequency ω_L , and an unique correlation frequency Γ , characteristic of the spin system. The correlation time $\tau_C = 1/\Gamma$ is related to the spin-phonon interaction and/or to the lifetime broadening of different discrete thermally populated molecular energy sublevels involved in the molecular transitions. However, it should be noted that, in general, the molecular magnetization dynamics, and consequently, the nuclear relaxation, are driven by a complex spectral density of the electronic spin fluctuations, where different correlation frequencies $\Gamma_i = 1/\tau_{Ci}$ may come into play.^{27–30}

To describe the temperature dependence of the muon longitudinal relaxation rate $\lambda_{\text{interm}}(T)$, we used a phenomenological

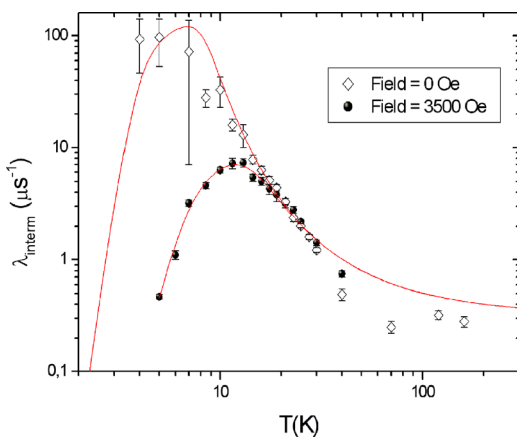


FIG. 3. Temperature dependence of the intermediate muon longitudinal relaxation rate λ_{interm} of DyPhOPH powders in LF=0 and 3500 Oe. The solid lines represent the fits of the muon longitudinal relaxation rates as determined from Eq. (5) in the text.

semiclassical model that follows from the general expression^{31,32}

$$\lambda_{\text{interm}} = \gamma_{\mu}^2/2 \int \langle h_{\pm}(t) \cdot h_{\pm}(0) \rangle \exp(-i\omega_L t) dt, \quad (2)$$

where ω_L is the muon Larmor frequency, $h_{\pm}(t)$ and $h_{\pm}(0)$ are the transverse hyperfine fields at the muon site(s), and γ_{μ} is the muon gyromagnetic ratio. By writing Eq. (2) in a weak-collision approach as a function of the different wave-vectors \mathbf{q} , one obtains^{33,34}

$$\lambda_{\text{interm}} = K(T) \times [\sum_{\mathbf{q}} \alpha_{\mathbf{q}} \chi^{+}(\mathbf{q}) J_{\mathbf{q}}^{+}(\omega_e) + \beta_{\mathbf{q}} \chi^{z}(\mathbf{q}) J_{\mathbf{q}}^{z}(\omega_L)], \quad (3)$$

where $K(T)$ is a temperature dependent parameter containing γ_{μ} , the Landè factor g , and the Bohr magneton μ_B ; $\chi^{+z}(\mathbf{q})$ are the transverse and longitudinal generalized susceptibilities (assumed to be ω -independent); ω_e is the electronic Larmor frequency; and $J_{\mathbf{q}}^{+z}(\omega_L, \omega_e)$ are the transverse and longitudinal components of the spectral density. To simplify, one can assume that $\alpha_{\mathbf{q}} \chi^{+}(\mathbf{q}) J_{\mathbf{q}}^{+}(\omega_e)$ is negligible. Moreover, the wave-vector dependence can be safely neglected because of the presence of many inequivalent muons which yields different geometrical factors $\alpha_{\mathbf{q}}$ and $\beta_{\mathbf{q}}$ at fixed \mathbf{q} , thus possibly averaging out the differences among different \mathbf{q} 's. By assuming a correlation function with exponential behaviour $f(t) = f_0 \exp(-t/\tau_C)$ and by neglecting the wave-vector dependence, one finds the Bloembergen-Purcell-Pound (BPP) law³⁵

$$\lambda_{\text{interm}}(T) = K(T) [2\tau_C(T)/(1 + \omega^2\tau_C(T)^2)]. \quad (4)$$

In Eq. (4), $\tau_C(T)$ represents a single correlation time of the electronic system. However, the data cannot be fitted with such a simple function. Thus, assuming that more than one correlation time can play a role in the magnetization dynamics,^{27–30} for the $\lambda_{\text{interm}}(T)$ data fitting we used a corrected BPP function assuming a rectangular distribution of correlation times τ_{Ci} , whose center value τ follows the Arrhenius law $\tau = \tau_0 \exp(\Delta/k_B T)$.^{29,34} This simple distribution was chosen because the corrected BPP function has a closed analytical form, and, was found to fit $\lambda_{\text{interm}}(T)$ quite well. The existence of a barrier distribution can be qualitatively attributed to different possible transitions (and as a consequence different τ_{Ci}) related the molecular energy levels involved. This same model was used for fitting the NMR and the μSR longitudinal relaxation data of another slowly relaxing chain, the above cited CoPhOMe.^{29,34–36} The resulting expression of the corrected BPP function $\lambda_{\text{interm}}(T)$ is

$$\lambda_{\text{interm}}(T) = A \cdot (M/H) \cdot T \frac{1}{2\omega_L \ln b} \times \left[\arctg(b\omega_L\tau) - \arctg\left(\frac{\omega_L\tau}{b}\right) \right], \quad (5)$$

where A is a fitting constant representing the hyperfine field fluctuations at the muon site, δ is the width of the rectangular distribution of the energy barrier Δ/k_B and $b = \exp(\delta/T)$; and $\tau = \tau_0 \exp(\Delta/k_B T)$ is the average correlation time related to the lifetime broadening of different discrete energy sublevels involved in multiplet transitions and/or to the spin-phonon

interaction.^{26–28,37} During the fitting procedure, we left free the parameters τ , Δ , and δ , while A acts as rescaling factor. Moreover, for the data with $H=0$, we took into account that at low temperatures $T \ll \Delta/k_B$, the muons are subjected to a local dipolar field H_{dip} generated by the frozen spins. Thus, the local field $H_{\text{dip}} = \omega_L/\gamma_\mu$, where γ_μ is the muon gyromagnetic ratio, was estimated by optimizing the fits. The best fitting procedure gave the values $\Delta/k_B = 45(\pm 3)$ K, $\delta = 16(\pm 3)$ K, $\tau_0 = 5.95(\pm 1.7) \times 10^{-11}$ s, $H_{\text{dip}} = 150$ Oe, and $A \approx 5.4(\pm 0.3) \times 10^{14}$ rad² Hz². One can note that (i) H_{dip} has a value in line with point-dipole calculations for some SMMs;¹ (ii) the Δ/k_B average value is consistent with the value estimated from AC magnetic susceptibility (χ_{AC}) measurements for two different activated regimes ($\Delta/k_B = 42$ K for $T < 3.5$ K and $\Delta/k_B = 69$ K for $T > 3.5$ K);²³ (iii) the value $\delta = 16$ K gives the width of the energy barrier distribution, corresponding to a distribution of correlation times; (iv) the value of the attempt time τ_0 falls in the middle of the two values $\tau_0 = 5.6 \times 10^{-10}$ s and $\tau_0 = 1.9 \times 10^{-12}$ s obtained from χ_{AC} measurements. The difference between values of τ_0 as determined by our μ^+ SR and χ_{AC} measurements is due to our fitting procedure and to the experimental (μ^+ SR) technique that uses a “local” probe to test the magnetization dynamics: a *microscopic* probe can give values of τ_0 different from those obtained from *macroscopic* experiments, like χ_{AC} ones, which measure the “bulk” response of the investigated system.

III. CONCLUSIONS

The local spin dynamics of the single chain magnet [Dy(hfac)₃{NIT(C₆H₄OPh)}] were studied by μ^+ SR. The experimental results are similar to those obtained through NMR and μ SR studies of another slowly relaxing single chain magnet CoPhOMe. By using a heuristic corrected BPP-like model that assumes a distribution of correlation times corresponding to a (rectangular) energy barrier distribution of width ≈ 16 K, the longitudinal relaxation rate $\lambda_{\text{interm}}(T)$ behaviour has been reproduced and qualitatively interpreted. The energy barrier value $\Delta/k_B = 45$ K and the attempt time $\tau_0 = 5.95 \times 10^{-11}$ s extracted from the fit agree qualitatively with the ones obtained from AC susceptibility data. Finally, the value $H_{\text{dip}} = 150$ Oe of the local dipolar field felt by muons was deduced. The presence of such dipolar field is consistent with the observed high muon zero-field longitudinal relaxation rates at low temperatures, as also observed in other magnetic molecular chains and clusters.

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