

Probing the magnetic ground state of the molecular dysprosium triangle with muon spin relaxation

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We present zero field muon spin lattice relaxation measurements of a Dysprosium triangle molecular magnet. The local magnetic fields sensed by the implanted muons indicate the coexistence of static and dynamic internal magnetic fields below $T^* \sim 35$ K. Bulk magnetization and heat capacity measurements show no indication of magnetic ordering below this temperature. We attribute the static fields to the slow relaxation of the magnetization in the ground state of Dy_3 . The fluctuation time of the dynamic part of the field is estimated to be ~ 0.55 μ s at low temperatures.

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I. INTRODUCTION

Recent development in the field of molecular magnetism has produced idealized model systems that allow the investigation of quantum phenomena in nanomagnets.¹ Examples include slow relaxation in high spin molecules,² quantum tunneling of the magnetization,^{3,4} topological quantum phase interference,^{5,6} and quantum coherence.⁷⁻⁹ Within these systems, antiferromagnetic clusters, rings or triangles,^{9,10} have been considered for possible use in quantum computation, due to longer decoherence time as a result of weaker intercluster dipolar interactions.⁸ Here we investigate a recently synthesized trinuclear cluster $[Dy_3(\mu_3-OH)_2L_3Cl(H_2O)_5]Cl_3$ (where L is the anion of orthovanillin),¹¹ hereafter abbreviated as Dy_3 (see Fig. 1). This compound exhibits two important properties; a system with a nonmagnetic ground state as well as slow relaxation of the magnetization which is typical of some high spin clusters.¹² Magnetization measurements have been explained using a model of three Dy^{3+} moments arranged on a triangle, each with a large Ising anisotropy axis in the plane rotated by 120° relative to its neighbors (see Fig. 1). A small antiferromagnetic interaction (~ 0.2 K) between Dy^{3+} results in a nonmagnetic, $S=0$, ground state characterized by a vortex spin-chirality.

In this paper we present a zero field (ZF) muon spin relaxation (μ SR) study of Dy_3 . In this technique polarized muons are used as local spin probes of the microscopic magnetic structure of the individual Dy_3 molecules. We find that below $T^* \sim 35$ K the local magnetic field experienced by the muons has two components, dynamic and static. The static component is direct evidence of the slow relaxation of the magnetization in the ground state of Dy_3 , while the dynamic component is used to measure the fluctuations time of the Dy_3 ground spin state directly. This is possible due to the unique local perspective of the muon.

II. EXPERIMENTAL

The μ SR experiments were performed on the DOLLY spectrometer at the Paul Scherrer Institute, Switzerland. In

these experiments 100 % polarized (along the beam direction, z) positive muons are implanted in the sample. Each implanted muon decays (lifetime $\tau_\mu = 2.2$ μ s) emitting a positron preferentially in the direction of its polarization at the time of decay. Using appropriately positioned detectors, one measures the asymmetry of the muon beta decay along z as a function of time $A(t)$, which is proportional to the time evolution of the muon spin polarization. $A(t)$ depends on the distribution of internal magnetic fields and their temporal fluctuations. Further details on the μ SR technique may be found in Ref. 13.

The composition and structure of Dy_3 sample was confirmed using X-ray diffraction and magnetization measurements. The powder sample was placed in a 4He gas flow cryostat to measure the muon spin relaxation in the temperature range between 1.6 and 300 K. Heat capacity measurements at ZF and in the temperature range between 2 and 100 K were performed on the same sample using a quantum design physical properties measurement system. Additionally, magnetization measurements in the same temperature range were performed using a quantum design magnetic properties measurement system.

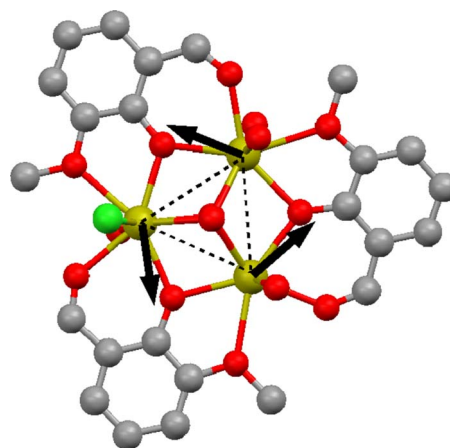


FIG. 1. (Color online) The magnetic core of the Dy_3 molecules. The yellow, red, green and gray balls represent the Dy, O, Cl, and C atoms, respectively.

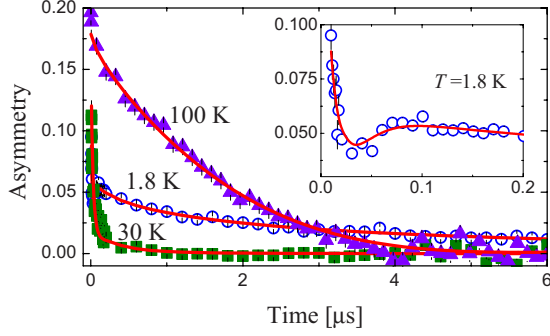


FIG. 2. (Color online) The asymmetry as a function of time at three different temperatures. The inset shows the asymmetry at very short times, where the dip is clear evidence for a static local field experienced by the muons. The solid lines are fits to Eq. (2).

III. RESULTS

Example muon spin relaxation curves measured in ZF are presented in Fig. 2. Note that at low temperatures, the asymmetry exhibits a dip at early times (inset of Fig. 2), followed by a recovery and then relaxation at longer times. In contrast, at high temperature the asymmetry relaxes almost exponentially from its initial value to zero. The low temperature relaxation curves are evidence that the internal magnetic field experienced by the implanted muons in Dy_3 contains two contributions; a static (time independent) component and a fluctuating component. As we discuss below, the static component is direct evidence of the slow relaxation of the individual Dy_3 (or Dy^{3+}) magnetic moments. Generally, when muons experience a distribution of static magnetic fields $\rho(\mathbf{B}-\mathbf{B}_s, \Delta)$, where \mathbf{B}_s is the average static field and Δ is the root mean square of the field distribution, then the asymmetry follows a static Kubo-Toyabe function:

$$A_{\text{KT}}(t) = A_0 \int \rho(\mathbf{B}-\mathbf{B}_s, \Delta) G_z(t) d^3B, \quad (1)$$

$$G_z(t) = \cos^2 \theta + \sin^2 \theta \cos(\gamma B t). \quad (1)$$

Here $\gamma = 135.5 \text{ MHz/T}$ is the muon gyromagnetic ratio, θ is the angle between the initial muon spin and the local static magnetic field \mathbf{B} which is averaged over a powder sample. For example, if $\mathbf{B}_s = 0$ then the asymmetry is at its maximum value at $t=0$, it exhibits a dip at $t \sim 1/\Delta$ and recovers to $\sim 1/3$ its initial value at long times. Depending on the form of ρ , e.g., Gaussian or Lorentzian, the relaxation follows a Gaussian Kubo-Toyabe (GKT), A_{GKT} , or a Lorentzian Kubo-Toyabe (LKT), A_{LKT} , respectively. However, if in addition to the static field component a small fluctuating field $B_d(t)$ is present, then the $1/3$ tail continues to relax to zero.¹⁴⁻¹⁶ In this case the relaxation can be described by a phenomenological function: a LKT or GKT multiplied by a suitable dynamic relaxation function.¹⁷

In our case, the asymmetry measured in Dy_3 at all temperatures was found to fit best to LKT multiplied by a square root exponential relaxation,

$$A(t) = A_{\text{LKT}}(t) e^{-\sqrt{\lambda} t}. \quad (2)$$

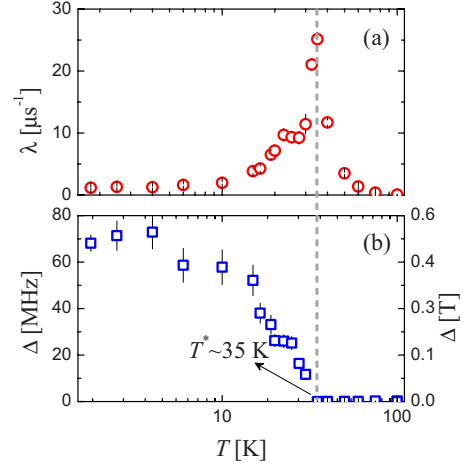


FIG. 3. (Color online) The values of (a) λ and (b) Δ obtained from fits of the relaxation curves as a function of temperature.

where λ is the relaxation rate, containing information regarding the dynamics of the local field. In particular, at low temperatures where $\Delta > \lambda$, $A(t)$ is almost identical to the well known dynamic LKT function and hence $\lambda = 2/3\tau$,^{14,15} where τ is the fluctuation time of the local magnetic field.¹⁸ The square root exponential relaxation reflects the averaging of the relaxation behavior of muons stopping in multiple inequivalent sites.^{15,19-22}

The parameters λ and Δ obtained from the fits are shown in Figs. 3(a) and 3(b), respectively. Note that at high temperatures λ is small and $\Delta \approx 0$. As the temperature is decreased λ increases sharply while Δ remains zero. At $T^* \sim 35 \text{ K}$, λ peaks and Δ becomes nonzero. Finally, at lower temperatures λ decreases again while Δ saturates at $\sim 70 \text{ MHz}$, corresponding to a width in field of $\sim 0.45 \text{ T}$ [right side axis of Fig. 3(b)]. These temperature dependencies are commonly seen in materials undergoing magnetic ordering at $T_c = T^*$.²³ In such cases the increase of λ above T_c is attributed to a critical slowing down of the fluctuations and Δ is proportional to the order parameter (local magnetization).^{23,24} This behavior is quite unusual, and exhibits a sharp transition from a paramagnetic to an ordered/static regime, or the sudden appearance of static magnetic fields in the system. Such static fields are rarely observed in SMMs studied by μSR .²²

Triggered by these findings we measured the magnetization and heat capacity to confirm that there is no evidence of long range magnetic ordering in the Dy_3 system. As can be seen in Fig. 4, bulk magnetization measurements in 50 mT show no indication of ordering at $\sim 35 \text{ K}$.^{11,12} Similarly, heat capacity measurements in ZF show no anomalies around this temperature. Therefore, the observed static fields can be associated with either (I) an ordering only on the *local scale*, e.g., the freezing (or slowing down) of the fluctuations of the individual Dy^{3+} magnetic moments, or (II) a magnetic ground state where the Dy^{3+} moments order is such a way that they do not cancel each other, resulting in a ground state with a nonvanishing magnetic moment. The latter possibility is ruled out by bulk magnetization measurements which confirm a nonmagnetic ground state in Dy_3 molecules.^{11,12}

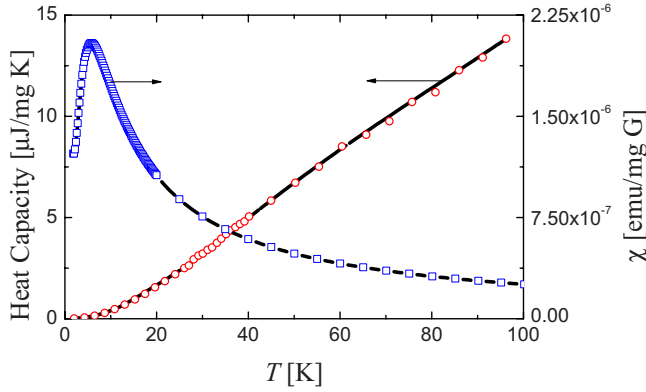


FIG. 4. (Color online) The heat capacity measured in ZF (circles, left axes) and susceptibility measured in 50 mT (squares, right axes) of Dy₃ as a function of temperature. There is no evidence for any anomaly at 35 K. The solid lines are a guide for the eyes.

IV. DISCUSSION

We start by discussing the local static field contribution and its origin. Assuming that the muons occupy sites which are relatively far from the Dy₃ magnetic core (i.e., at a distance much larger than the distance between different Dy ions in the molecule), one expects that the static dipolar field experienced by the muons will decrease and vanish as the magnetic moment of Dy₃ decreases at low temperature. However, since muons sense a strong nonvanishing static field at low temperatures (up to Δ₀ ~ 0.45 T), we conclude that the muons occupy sites which are close to the magnetic core, and therefore are sensitive to the microscopic magnetic structure of the molecules. One such possibility is a site near the Cl ion shown in Fig. 1. This site is negatively charged and therefore may attract the positively charged implanted muons. On this site, the dipolar fields from the three individual Dy ions do not cancel each other even if the Dy³⁺ moments are arranged in a nonmagnetic ground state configuration. Instead, the Dy³⁺ closest to the Cl contributes mostly to the magnetic field experienced by the muon (roughly 20 times larger). For example, assuming Δ₀ is due to a dipolar field of a single Dy³⁺ moment we expect that the distance between this moment and its neighboring muon is roughly ~5 Å. This distance is similar to that between the Cl mentioned above and its neighboring Dy³⁺ (~2.7 Å). Therefore, we conclude that this static field is direct evidence of the slow relaxation of individual Dy₃ moments, which can be associated with single Dy³⁺ ion anisotropy.¹²

These measurements exhibits the power of a local probe measurement and its advantages over conventional bulk magnetization measurements in resolving the magnetic properties of individual magnetic molecules, and the microscopic magnetic structure in general. Moreover, the observed local static magnetic fields, despite the nonmagnetic ground state, reflect the peculiar nature of the spin vortex arrangement and the Ising/classical type interactions between the spins which give a nonmagnetic doublet, i.e., two distinct magnetic states. Although muons cannot detect the sense of chirality of the ground state, they provide evidence of its static magnetic nature.

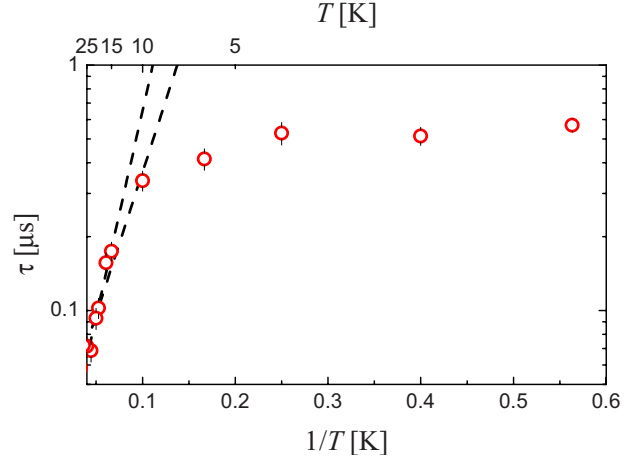


FIG. 5. (Color online) The fluctuation time of the local field experienced by muons as a function of temperature. The dashed lines indicate the range of parameters for fits to Arrhenius law.

Next, we investigate the dynamic properties of the local field experienced by the implanted muons. As we mentioned earlier, the low temperature relaxation λ can be used to extract the fluctuation time τ of the local field. In Fig. 5 we plot τ as a function of temperatures (below ~25 K where Δ > λ). We find that τ ~ 0.1 μs at ~20 K, increases gradually as the temperature is decreased and saturates at ~0.55 μs below ~4 K. These fluctuations are due to fluctuations of the Dy³⁺ magnetic moments near the stopping site of the muon. In a very simplified picture, muons are sensitive to τ only when it is shorter than the muon’s lifetime (τ_μ = 2.2 μs). When τ ≥ τ_μ we expect the muon to experience a static field component. This is consistent with the extracted values of τ, in the range of a fraction of a μs. In contrast to this scale of dynamics, ac susceptibility measurements of the relaxation time of the magnetization at zero applied field have shown that it follows an Arrhenius law¹²

$$\tau_m = \tau_m^0 \exp(U_m/T), \tag{3}$$

where τ_m⁰ = 2.5(5) × 10⁻⁷ s and U_m = 36(2) K. The similarity between the temperature dependence of our results and those extracted from ac susceptibility is striking. However, the low temperature saturation value of the fluctuation time is an order of magnitude longer in the ac susceptibility measurements. For comparison, fits of τ in the range 10–25 K to Eq. (3) yield an activation barrier U = 27–39 K and attempt time τ⁰ = (1.4–2.5) × 10⁻⁸ s (dashed lines in Fig. 5). This discrepancy indicates that although both μSR and ac susceptibility measurements confirm the slow relaxation of the magnetization, the techniques do not measure the same scale of dynamics. However, given that these techniques and their temporal sensitivities are different, there are two possible explanations of the discrepancy. One possibility is that while the dynamics measured with ac susceptibility are those of collective bulk magnetization, μSR measures fluctuations of individual molecules or Dy³⁺ moments within it. For example, studies in Ni₁₀ magnetic molecules have shown that while ac susceptibility exhibits slow relaxation of bulk magnetization, nuclear magnetic resonance (NMR) measurements confirm the pres-

ence of fast single molecule dynamics.^{25,26} This was interpreted as slowing down of the bulk magnetization due to a resonant phonon trapping mechanism which prevents thermalization of the bulk magnetization but allows fast spin flipping of the individual molecular moments.²⁶ Another possibility is that each techniques is sensitive to a different dynamic process, which may not be even related. The dynamics of the bulk magnetization was associated to fluctuations of the Dy₃ magnetization in the plane of the Dy³⁺ triangle. However, fluctuations out of the plane cannot be ruled out. This type of fluctuations may be faster, and therefore more effective in causing muon spin lattice relaxation. We believe that NMR measurements in Dy₃ should be sensitive to both scales of dynamics, and therefore would provide valuable information that could clarify the discrepancy between bulk magnetization measurements and μ SR.

V. CONCLUSIONS

In conclusion, we find that muons implanted in Dy₃ observe a fluctuating field at high temperatures. Below ~ 35 K the local field has two components, static and dynamic. Bulk magnetization and heat capacity measurements rule out the existence of long range ordering associated with the observed temperature dependence of the local field. Instead, the observed static local magnetic field is direct evidence of the

slow relaxation of the magnetization. Our measurements exhibit that in spite of the peculiar nature of the Dy³⁺ spins vortex arrangement which produces a nonmagnetic doublet, a local probe such as muons can detect their static magnetic nature. Therefore, although no net magnetic moment is present, they can be used, in principle, to store magnetic information (sense of chirality) with the advantage of long coherence time due to the small intermolecular dipolar couplings. Finally, we find that the time scale of low temperature dynamics detected with μ SR is an order of magnitude shorter than that extracted from ac susceptibility measurements. The different time scale of dynamics could be due to the sensitivity of the different techniques to different relaxation processes or a difference between fluctuations of collective and individual moments.

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