Onset of Magnetic Correlations in LiY$_{1-x}$Ho$_x$F$_4$ with $0.002 \leq x \leq 0.05$ Studied via $\mu$SR

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Abstract. We are using $\mu$SR to probe the evolution of magnetism from single-ion to spin glass behaviour in LiY$_{1-x}$Ho$_x$F$_4$ with increasing $x$. For $x = 0.002$ the Ho spin dynamics exhibit single-ion behaviour similar to that observed in molecular magnets. Near $T \approx 10$ K, the energy gap between the Ho ground state electronic doublet and first excited singlet energy levels, we find that the longitudinal depolarization rate exhibits a peak that depends on the Larmor frequency. At temperatures $T << 10$ K we find sharp reductions in the transverse field depolarization rates in the vicinity of magnetic field induced (avoided) level crossings (ALCs) in the hyperfine-split ground state energy manifold. This is attributed to a reduction in the quasistatic magnetic disorder due to resonant Ho spin fluctuations at frequencies much larger than the muon Larmor frequency. As the Ho concentration is increased toward $x = 0.05$, magnetic correlations are observed to become significant, changing the 10 K peak into a plateau, and significantly broadening the rate changes observed at ALCs.

1. Introduction

For the Ho$^{3+}$ ion in LiYF$_4$, the axial anisotropy leads to an Ising-type ground state doublet separated from the first excited singlet by gap of 10 K (see figure 1a). This gap presents a barrier to low-temperature spin-reversal, so below 10 K the system changes from a paramagnetic state to a bistable state where quantum tunneling of the magnetization dominates the relaxation [1]. Hyperfine coupling with the Ho nuclear spin $I = 7/2$ splits this electronic ground-state doublet, and the Zeeman diagram has avoided level crossings (ALCs) where the coupled Ho electronic momentum and nuclear spin can
rotate coherently to reverse the electronic spin direction (presuming some symmetry breaking). These ALCs occur at fields $H_{\text{ALC}} = 23N \text{ mT}$, with integer $N$ and $-7 \leq N \leq 7$ (see figure 1b). Magnetization measurements show sharp steps at the resonant field values [1] due to the enhanced spin transition rate at the ALCs. Measurements of $^{19}$F nuclear magnetic resonance (NMR) spin-lattice relaxation rate $1/T_1$ [2] exhibit a peak at temperature near the gap energy, as observed in single molecule magnets [3], and also sharp peaks due to enhanced spin transition rates at magnetic field values corresponding to ALCs with $N = 4$ through 7 at 1.7 K [2]. It is advantageous to study the spin dynamics in this system because (1) the single crystal host is of high quality and presents a readily-described “environment” with which the Ho$^{3+}$ interacts, and (2) one has the ability to vary the dipolar coupling through the concentration $x$. However, the NMR technique is limited in its useful range of magnetic fields, temperatures and concentrations because of the low Larmor frequency for the lower spin resonances ($N < 4$), and the $^{19}$F $T_2$ becomes very short for very low temperatures ($T < 1$ K) or for concentrations $x > 0.003$.

Muon spin rotation/relaxation ($\mu$SR) can be used to study the spin dynamics over a wider range of temperatures, fields, and concentrations. It would be of particular interest to study the onset of magnetic correlations, as for increasing Ho concentration LiY$_{1-x}$Ho$_x$F$_4$ enters an unusual ‘anti-glass’ phase ($x = 0.05$) [4], and at higher concentrations one enters spin glass and Ising ferromagnet states [5]. It was found via zero-field $\mu$SR studies [6,7] that most of the muons form the three-body F-μ-F bound state[8], which has been used to find the muon stopping site at the four sites in the unit cell with the smallest F-F spacing (0.16 nm). The modest longitudinal fields ($B_{/ c-axis} / P_x(0)$, where $P_x(0)$ is the initial muon polarization direction) required to achieve the $N = 1$ resonance (23 mT) pin the muon spin, rendering the change in the longitudinal field spin-lattice relaxation rate, $\lambda_L$, too small for studying changes in spin dynamics at ALCs [6]. However, the transverse depolarization rate, $\lambda_T$, for which the muon precesses about the applied magnetic field, is sensitive to the presence of avoided level crossings, and can be used to study these lower resonances [9].

Here we present our preliminary report of simultaneous measurements of $\lambda_T$ and $\lambda_L$ over a range of Ho concentrations $x$ in order to probe the onset of magnetic correlations. This is facilitated by rotating the muon spin by about 50 degrees with respect to the beam (and field) direction, and monitoring the muon depolarization parallel and perpendicular to the beam direction to monitor the longitudinal and transverse depolarization rates, respectively. The longitudinal field response shows a temperature variation of the depolarization with a magnetic field-dependent peak near 10 K, as for NMR $1/T_1$ measurements. This is contrasted with zero-field and longitudinal field results for samples with $x = 0.002$ [6] and $x = 0.045$ [7], respectively, which show a depolarization rate that saturates at low temperature. We also find that the decreases in field-dependent transverse depolarization at ALCs [9] are modified by increasing Ho concentration, and are no longer measurable for $x = 0.05$.

2. Experimental

Single crystals with nominal Ho concentrations $x = 0.002, 0.005, 0.010$, and 0.050 were cut into plates with dimensions 3x8x30 mm$^3$, with the crystalline c-axis aligned along the 3mm edge. We measured the $^{19}$F $1/T_1$ as a function of magnetic field at 1.7 K for one of these plates and confirmed the presence of sharp peaks in $1/T_1$ at ALCs with $n = 5, 6, \text{ and } 7$, as reported for a different crystal in Ref. 2.

In time-differential muon spectroscopy, a spin-polarized positive muon is imbedded in a sample and decays at some later time $\tau$; the resulting positron is preferentially emitted along the muon spin polarization axis and detected. After several million independent decay events one constructs a time histogram of the detector signal asymmetry $A(t)$ [10] which is proportional to the muon depolarization function $P(t)$ in the local field at the muon stopping site. $P(t)$ is defined as the projection of the spin polarization at time $t$ along the direction parallel or perpendicular to the field direction. The $\mu$SR measurements were conducted utilizing the GPS and LTF spectrometers on the nM3 continuous beamline at the Paul Scherrer Institute (PSI). The beam momentum and external magnetic field were aligned parallel to the crystalline c-axis. Experiments were conducted in a gas flow cryostat and a dilution refrigerator so that our measurements span the range 30 mK $\leq T \leq 50$ K. We utilized the spin-rotated mode, where the muon spin is aligned at an inclination of approximately 50 degrees with
respect to the beam momentum. The longitudinal and transverse depolarization rates are simultaneously monitored with detectors oriented along lines perpendicular and parallel to the beam momentum.

![Figure 1](image1.png)  
**Figure 1.** Magnetic field variation of the (a) electronic and (b) low lying electronuclear states for the Ho$^{3+}$ ion, which exhibit avoided level crossings [1,2].

![Figure 2](image2.png)  
**Figure 2.** Evolution of the transverse depolarization rate with concentration at $T = 1.8$ K. The sharp reductions occur at the $N = 1$ (23 mT) and 3 (69 mT) resonances. Curves are offset for clarity (see text).

3. Results

3.1. Field-dependent transverse depolarization rate at low temperature

First we describe the evolution of the low temperature magnetic field dependence of the transverse depolarization rate. The results for $x = 0.002$, which are fully discussed in Ref. 9, show a pronounced decrease in $\lambda_T$ at magnetic fields of 23 and 69 mT, corresponding to the $N = 1$ and 3 avoided level crossings, respectively. These reductions result from resonant magnetic fluctuations of the Ho at rates much faster than the muon Larmor frequency, which reduce the quasi-static disorder at the muon site, thereby reducing $\lambda_T$ [9]. The $N = 2$ resonance has very small ALC splitting (see figure 1), a much lower resonant frequency, and so a very weak reduction is observed at 46 mT.

The new data presented here were analyzed as described in Ref. 9. As the Ho concentration $x$ is increased, we find that both the overall depolarization rate and the size of the reductions at the resonances are increased (see figure 2). We have estimated the broadening of these reductions by fitting them with Lorentzian lineshapes, and the results are shown in table 1. While the width of the $N = 3$ resonance is essentially unaffected by an increase in $x$, the width of the $N = 1$ resonance increases nearly linearly with $x$. Not shown are data for $x = 0.05$, for which we find no evidence for changes in $\lambda_T$ at the resonant field values. We note that the background depolarization rate has become quite high at this point ($\sim 10 \mu s^{-1}$ for $x = 0.05$, compared to 0.9 $\mu s^{-1}$, 1.5 $\mu s^{-1}$, and 2.0 $\mu s^{-1}$, for $x = 0.002, 0.005$, and 0.010, respectively), and so small changes in $\lambda_T$ become increasingly difficult to extract.
Table 1. Linewidth (in mT) for the $N = 1$ and 3 resonances at $T = 1.8$ K for three concentrations.

|       | $x = 0.002$ | $x = 0.005$ | $x = 0.010$ |
|-------|-------------|-------------|-------------|
| $N = 1$ | $3.1 \pm 0.5$ | $5.2 \pm 1.0$ | $9.1 \pm 1.4$ |
| $N = 3$ | $6.2 \pm 0.6$ | $7.3 \pm 1.2$ | $6.2 \pm 2.0$ |

3.2. Temperature-dependent longitudinal depolarization rate at intermediate temperatures

We now present the temperature dependent depolarization rate at fixed magnetic field values, and its evolution with Ho concentration. In all cases the time-dependent depolarization is adequately described by a stretched exponential function $\exp(-(\lambda_L t)^\beta)$, where the exponent $\beta$ is roughly 0.5, and with $\chi^2$ per degree of freedom less than 1.2 for all curves. At concentrations, $x \leq 0.01$, we find a field-dependent peak in $\lambda_L(T)$ near 10 K (see figure 3), which behaves in a manner similar to that observed for $1/T_1$ via $^{19}$F NMR measurements [2], and is typical for several molecular magnet systems [3]. For the $x = 0.05$ sample, however, the decrease in $\lambda_L(T)$ below 10 K and in a field of 60 mT is much weaker than for lower concentrations, and indeed, for a field of 23 mT, $\lambda_L(T)$ doesn’t decrease at all, but tends towards saturation at low temperatures (see figure 4).

![Figure 3](image3.png) ![Figure 4](image4.png)

Figure 3. Longitudinal depolarization rates versus temperature for $x = 0.01$ at two fields.

Figure 4. Longitudinal depolarization rates versus temperature for $x = 0.05$ at two fields.

4. Discussion

The broadening induced by increased Ho concentration, and the differences between the $N = 1$ and 3 resonances, are linked to the size of the ALC tunnel splitting produced by coupling of the low-lying electronuclear levels with the higher singlet states shown in figure 1(a) [9]. At present we have no qualitative explanation for why the $N = 1$ resonance is more strongly affected by the increase in Ho concentration. However, a microscopic model including which describes the magnetic susceptibility of LiY$_1-x$Ho$_x$F$_4$ [11] has been adapted to describe $^{19}$F NMR results as well [12]. We now hope to further adapt this model to describe the $\mu$SR data, and in particular to determine the role that increased Ho-Ho correlations play in determining the spin dynamics at ALCs.

The longitudinal depolarization for $x \leq 0.01$ exhibits behaviour similar to that observed in many single-molecule magnets [3]. Qualitatively, the phenomenon can be described by a temperature...
dependent lifetime broadening of the Ho energy levels, $\Gamma(T)$ [2,3] that decreases with decreasing temperature. When $\Gamma = \omega_L \gamma$ (where $\omega_L$ is the Larmor frequency of the probe particle, in this case the muon) one has a peak in $1/T_1(T)$. In contrast, the data for $x = 0.05$ in figure 4 exhibit qualitatively different behaviour. Similar results for $1/T_1(T)$ have been observed in the spin-1/2 system $V_{15}$ [13, 14] and the high spin systems $\text{CrNi}_6$ and $\text{CrMn}_6$ [15]. However, in our system the low-concentration samples do not exhibit this crossover in behaviour with magnetic field. Therefore we tentatively associate this unusual effect with a change in the level broadening $\Gamma(T)$ due to increased Ho-Ho correlations. For example, if magnetic correlations produce a significant temperature-independent contribution to $\Gamma$, this could wipe out the low-frequency (field) peak in $1/T_1(T)$, which may be recovered for higher frequencies. Again, theory similar to that developed in Ref. 12 will clarify the microscopic origins of this phenomenon.

5. Conclusion
We have observed fundamental changes in the longitudinal and transverse muon depolarization for higher concentrations of Ho that may signal the onset of magnetic correlations and the crossover to spin glass behaviour. More detailed studies, along with parallel theoretical simulations of the effects of correlations, are required to test this hypothesis.

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References
[1] Giraud R, Wernsdorfer W, Tkachuk A M, Mailly D, and Barbara B 2001 Phys. Rev. Lett. 87 057203.
[2] Graf M J, Lascialfari A, Borsa F, Tkachuk A M, and Barbara B 2006 Phys. Rev. B 73 024403.
[3] Borsa F, Lascialfari A, and Furukawa Y 2006 Novel NMR and EPR Techniques, ed. J. Dolinsek, M. Vilfan, and S. Zumer (Berlin: Springer).
[4] Ghosh S, Parthasarathy R, Rosenbaum T F, and Aeppli G 2002 Science 296 2195.
[5] Reich D H, Ellman B, Yang J, Rosenbaum T F, Aeppli G, and Belanger D P 1990 Phys. Rev. B 42 4361.
[6] Graf M J, Micotti E, Lascialfari A, Borsa F, Barbara B, and Tkachuk A M 2006 Physica B 374 – 375 9.
[7] Rodriguez J, Dunsiger S R, Kycia J B, MacDougall G J, Quilliam J A, Russo P L, Savici A T, Uemura Y J, Wiebe C R, and Luke G M 2006 Physica B 374 – 375 13.
[8] Brewer J H, Kreitzman S R, Noakes D R, Ansaldo E J, Harshman D R, and Keitel R 1986 Phys. Rev. B 33 7813.
[9] Graf M J, Lago J, Lascialfari A, Amato A, Baines C, Giblin S R, Lord J S, Tkachuk A M, and Barbara B 2007 Phys. Rev. Lett. 99 267203.
[10] See for example, Amato A 1997 Rev. Mod. Phys. 69 1199.
[11] Bertaina S, Barbara B, Giraud R, Malkin B Z, Vanyunin M V, Pominov A I, Stolov A L, and Tkachuk A M 2006 Phys.Rev. B 74 184421.
[12] Malkin B Z, Vanyunin M V, Graf M J, Lago J, Borsa F, Lascialfari A, Tkachuk A M, and Barbara B, 2008 $^{19}$F nuclear spin relaxation and spin diffusion effects in the single-ion magnet LiYF$_3$:Ho$^{3+}$ (submitted for publication, Euro. Phys. J. B).
[13] Procissi D, Lascialfari A, Micotti E, Bertassi M, Carretta P, Furukawa Y, and Kögerler P 2006 Phys. Rev. B 73 184417.
[14] Salman Z, Kiefl R F, Chow K H, MacFarlane W A, Keeler T, Parolin T, Tabbara S, and Wang D 2008 Phys. Rev. B 77 214415.
[15] Salman Z, Keren A, Mendels P, Marvaud V, Scuiller A, Verdaguer M, Lord J S, and Baines C, 2002 Phys. Rev. B 65 132403.