

Evidence of Spin Glass Dynamics in Dilute $\text{LiHo}_x\text{Y}_{1-x}\text{F}_4$

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ac susceptibility measurements are presented on the dilute, dipolar coupled, Ising magnet $\text{LiHo}_x\text{Y}_{1-x}\text{F}_4$ for a concentration $x = 0.045$. The frequency and temperature dependences of the susceptibility show characteristic glassy relaxation. The absorption spectrum is found to broaden with decreasing temperature suggesting that the material is behaving as a spin glass and not as an exotic spin liquid as was previously observed. A dynamical scaling analysis suggests a spin glass transition temperature of 43 ± 2 mK with an exponent $z\nu = 7.8 \pm 0.2$.

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Spin glass behavior is an effect resulting from quenched disorder that has been extensively studied for many years and is largely well understood. It was therefore surprising that the system $\text{LiHo}_x\text{Y}_{1-x}\text{F}_4$, a seemingly ideal dilute, dipolar coupled Ising magnet, would exhibit an unusual spin liquid state at a low concentration of magnetic ions, $x = 0.045$ [1,2]. This spin liquid, or “antiglass,” phase was most notably characterized by a narrowing of the absorption spectrum $\chi''(\omega)$ as temperature was lowered. This was found in stark contrast to a higher concentration ($x = 0.167$) spin glass state where the absorption spectrum broadens [2,3] and with theoretical predictions that the spin glass state should persist to 0 concentration in such a system with long-range interactions [4].

Later publications found numerous interesting effects at $x = 0.045$ including unusually narrow absorption spectra with strong asymmetry, ringing magnetization oscillations, sharp features in the specific heat, and a $T^{-0.75}$ power law in the dc limit of the susceptibility [5,6]. Recently there has been a large amount of activity on this series of materials, both theoretical and experimental. The dilution of the Ho moments and the competing ferromagnetic and antiferromagnetic dipolar interactions provide the necessary ingredients for glassiness: randomness and frustration, respectively. Nevertheless there is an ongoing debate on the existence of a spin glass transition at any value of x in the $\text{LiHo}_x\text{Y}_{1-x}\text{F}_4$ series [7–10]. Much research has also taken place attempting to understand the effects of transverse magnetic field on the purported spin glass state (see, for example, [3,11,12]).

In this Letter we will focus on the low-concentration limit of these materials ($x = 0.045$) in zero field. We have measured the ac magnetic susceptibility of this stoichiometry in the hope of reproducing the exotic physics that was observed previously. We will show that, in fact, the susceptibility of this material behaves much more like that of a spin glass and that we are unable to reproduce the unusual antiglass phenomenology.

For this work, a magnetometer based on a dc superconducting quantum interference device (SQUID) and a

superconducting flux transformer was developed, chosen for its sensitivity and flat frequency response at very low frequencies, as compared to a conventional inductive pickup coil where the signal is proportional to frequency. The magnetometer consists of a NbTi primary coil wrapped on a phenolic form surrounding a niobium, 2nd-order gradiometer. The SQUID [13] and magnetometer apparatus are contained within superconducting lead shields and the cryostat is surrounded by two μ -metal shields.

Measurements were performed on a single crystal sample of $\text{LiHo}_x\text{Y}_{1-x}\text{F}_4$ with $x = 0.045$, glued to a sapphire rod which was heat sunk to the dilution refrigerator. Previously, the specific heat of a sample from the same crystal was measured and it was characterized with various x-ray scattering techniques as discussed in Ref. [14]. For most measurements, the sample was cut to be needle shaped (dimensions $0.57 \times 0.77 \times 7.7$ mm³) to reduce demagnetization effects with the long dimension along the c axis (also the direction of the applied field). The resulting demagnetization factor is $4\pi N = 0.49$ [15]. Some measurements were reproduced using the same sample cut to a different aspect ratio ($0.57 \times 0.77 \times 3.31$ mm³) with demagnetization factor $4\pi N = 1.10$. Matching the results for two differently shaped samples allowed us to calibrate our magnetometer and confidently determine the correct demagnetization correction.

Both frequency scans at constant temperature and temperature scans at constant frequency were obtained. It was carefully checked that the sample was in equilibrium for all measurements by waiting several hours before measurement at a given temperature and also by taking multiple spectra to check for reproducibility. The applied ac magnetic field was kept below 20 mOe at all times to ensure that there was no appreciable heating of the sample. A range of fields around this value was tested and did not indicate any heating effect. Measurements in the frequency range 0.001 Hz–2 kHz are presented here. The accessible frequency window of these experiments was limited at the high end by frequency dependent background signals and phase shifts, and the SQUID feedback electronics. It is

fairly impractical to perform any measurements appreciably below 1 mHz.

The measured frequency scans of the complex ac susceptibility are typical of glassy relaxation, showing broad peaks in $\chi''(\omega)$ and suppression of $\chi'(\omega)$ at higher frequencies as shown in Fig. 1. The characteristic time constants of relaxation, which may be parametrized by the peak frequencies in χ'' , f_{\max} , are shifted to lower frequency with decreasing temperature as thermal fluctuations become weaker and are unable to excite the system over energy barriers. Several studies of the $\chi(\omega)$ spectra of spin glasses have been performed previously including work on the $\text{LiHo}_x\text{Y}_{1-x}\text{F}_4$ series [2] and on other materials [16,17]. Despite being quite broad, the absorption spectra measured here are in fact narrow when compared to some other spin glass measurements [2,16].

Normalizing $\chi''(\omega)$ by the peak height χ''_{\max} and dividing the frequency by the peak frequency f_{\max} superimposes the absorption spectra. The result is a clear broadening of the spectra with decreasing temperature as seen in Fig. 2. The full width at half maximum (FWHM) of the spectra appears to level off at ~ 1.4 decades at higher temperatures, as seen in the inset of Fig. 2. Though we have not shown higher frequency scans here, an 8% sample also showed broadening of the absorption spectra with decreasing temperature. This behavior is qualitatively similar to that of a higher concentration, $x = 0.167$, material in this series [2].

At the higher temperatures studied, the absorption spectra show low and high frequency limiting behavior of $\chi'' \sim \omega^1$ and $\chi'' \sim \omega^{-0.75}$, respectively. This is not consistent with the Debye model with a single time constant where the limits are ω^1 and ω^{-1} . As the temperature is reduced and the curves become broader, the tails of the spectrum become less steep. At the lowest temperatures studied here, the high frequency limit can be seen to be as shallow as

$\chi'' \sim \omega^{-0.63}$. Several standard fitting functions including the Debye model, the Davidson-Cole form, and the Havriliak-Negami form [18] were considered but were not able to fit the full frequency range studied.

An important aspect of glassy systems is the critical slowing of dynamics or a divergence of the characteristic time constant of the system τ . The most robust way of determining τ would be to take the limit of $\chi''/\omega\chi'$ as $\omega \rightarrow 0$ [19], but such a limit is only achievable in a very small temperature window due to the broadness of the spectra and experimental time limitations. Thus, in this work, we have chosen to parametrize the dynamics of the system with $\tau_{\max} = 1/2\pi f_{\max}$.

At first glance, these peak positions appear to roughly follow an Arrhenius law, $\tau_{\max}(T) = \tau_{0A} \exp(-E_A/k_B T)$, at least at higher temperatures, as shown in Fig. 3(a), giving $E_A = 1.57$ K and $\tau_{0A} = 0.32$ μs . Such an Arrhenius law is often attributed to superparamagnetic behavior such as that seen in $\text{Eu}_x\text{Sr}_{1-x}\text{S}$ in the low-concentration, dipolar regime below its percolation threshold [20].

On closer inspection, $\text{LiHo}_x\text{Y}_{1-x}\text{F}_4$ shows a noticeable deviation from the Arrhenius law at low T shown in Fig. 3(a) and the fit is only able to accommodate the higher temperature data points. A likely scenario at lower T is a dynamical scaling law of the form $\tau_{\max} = \tau_0(T/T_g - 1)^{-z\nu}$, that is predicted to apply to spin glasses [19]. Such a fit, plotted in Fig. 3(b), is quite successful for the data below ~ 200 mK giving a transition temperature $T_g = 43 \pm 2$ mK and an exponent of $z\nu = 7.8 \pm 0.2$, very near the exponent 7.9 obtained in Monte Carlo simulations [19]. Above 200 mK, as we move further from T_g and out of the critical regime, the power law behavior breaks down and appears to give way to an Arrhenius law.

The overall intrinsic time scale of this material, $\tau_0 = 16 \pm 7$ s, extracted from the power law fit, is extremely long (in $\text{Eu}_{0.4}\text{Sr}_{0.6}\text{S}$, for example, $\tau_0 \approx 2 \times 10^{-7}$ s [21])

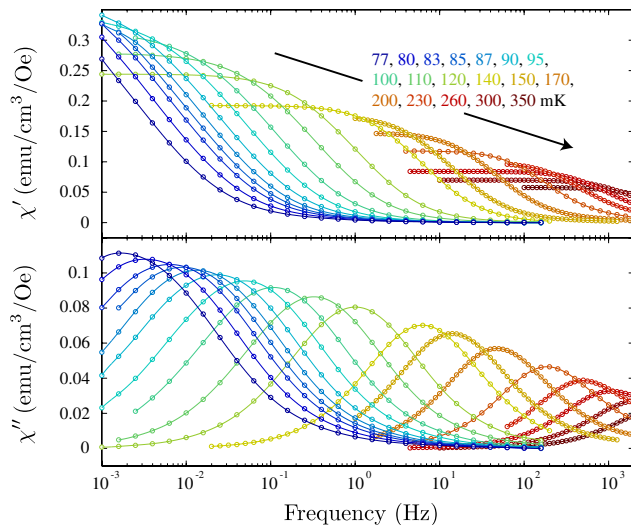


FIG. 1 (color online). In-phase $\chi'(f)$ and out-of-phase $\chi''(f)$ spectra obtained at temperatures from 77 mK (blue, left) to 350 mK (red, right).

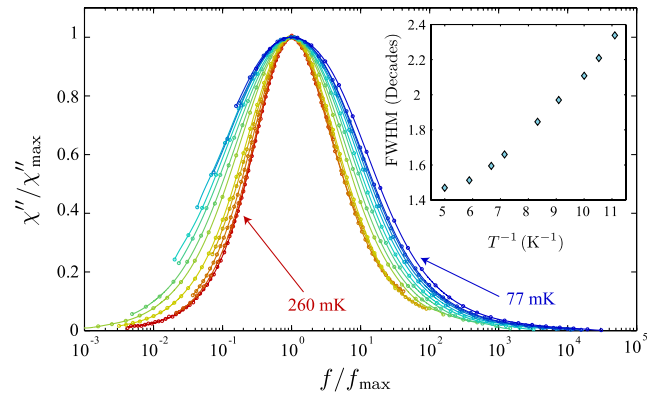


FIG. 2 (color online). Frequency scans of χ'' for various temperatures normalized by the peak height χ''_{\max} on the vertical axis and by the peak frequency f_{\max} on the horizontal axis. A clear broadening of the absorption spectra can be seen as the temperature is lowered. The FWHM in decades (where obtainable) is shown in the inset as a function of T^{-1} .

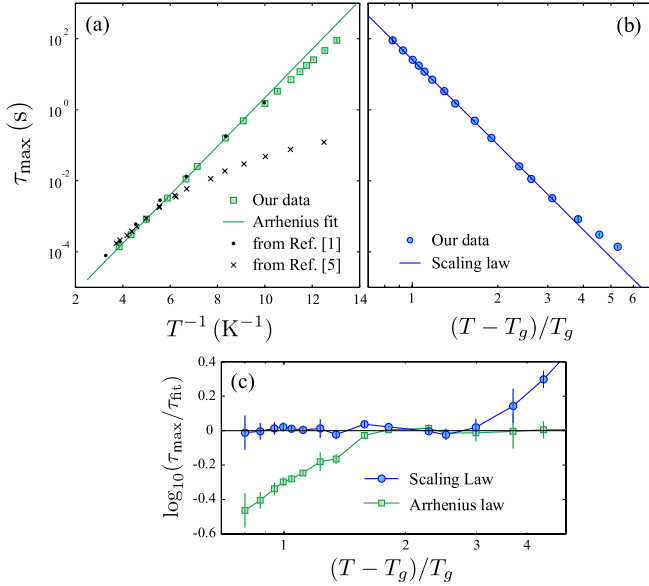


FIG. 3 (color online). Different scenarios for scaling of the time constants obtained from the peak frequencies of the absorption spectra, $\tau_{\max}(T)$. (a) Data from this work fitted by an Arrhenius law at high T (straight line). Also shown are the time constants τ_{\max} from Ref. [1] (dots) and Ref. [5] (crosses). (b) Data from this work (circles) fitted by a dynamical scaling law at low T . (c) Residuals and estimated error bars for the Arrhenius and scaling law fits.

and explains why obtaining equilibrium data anywhere close to the transition temperature becomes completely impractical. For example, measurements with a frequency of $\sim 3 \times 10^{-5}$ Hz would be required to properly study even $T = 1.5T_g$. This difficulty would also apply to other measurements such as nonlinear susceptibility and field-cooled versus zero-field-cooled magnetization. For most spin glasses, a measurement frequency of 1 mHz could be regarded as probing the dc limit of the material, but in this system that is not the case even well above the transition. The near-Arrhenius law that is observed is likely due to measuring at temperatures far above T_g .

Temperature scans of χ' at constant frequencies are shown in Fig. 4. Predictably, one sees an increase in χ' with lower temperature until the frequency of relaxation of the sample becomes slower than the probe frequency. At higher temperatures, where the sample's time constant is fast, the measurements shown can be considered to be in the limit of static susceptibility. However, below approximately 90 mK, the sample's relaxation is so slow that even 1 mHz cannot be considered to be in the dc limit and there is a downturn in χ' .

Comparison of these results with those obtained by Reich *et al.* [1,2] shows a fair bit of agreement in certain respects. In both cases the peak frequencies roughly follow an Arrhenius law and match quantitatively as shown in Fig. 3(a). The static limit of the magnetic susceptibility shows somewhat similar behavior as a function of tem-

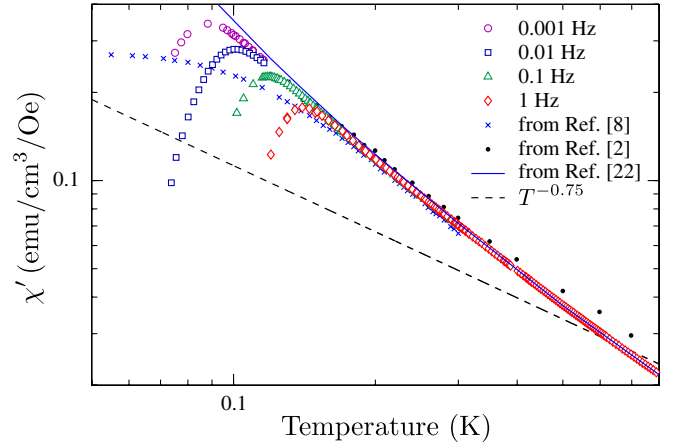


FIG. 4 (color online). $\chi'(T)$ at four different excitation frequencies. Experimental and theoretical results from other research groups are shown for comparison: the dc limit of χ from Ref. [2] (as published), χ' taken with a linear field sweep from Ref. [8] (after correcting for demagnetization), Monte Carlo simulations [22] (arbitrary units, scaled to match at high T), and a $T^{-0.75}$ power law that was proposed in Ref. [6].

perature (see Fig. 4). However, our results show that the widths of the absorption spectra do not narrow but rather broaden with lower temperature, a result more consistent with a spin glass. In other words, we do not see ‘‘antiglass’’ physics reported in Refs. [1,2,5,6].

Papers published more recently [5,6] show results that differ strongly both from work by the same research group [1,2] and from our results presented here. The shape and width of the absorption spectra are qualitatively different in Ref. [5] from the results in this work. The peak frequencies also do not match with Refs. [1,2] and clearly do not follow an Arrhenius law, as shown in Fig. 3(a). Additionally, Ref. [6] states that the static susceptibility obeys a power law $T^{-\alpha}$ with an unusual $\alpha = 0.75$, a much shallower temperature dependence from that seen in this work and by Reich *et al.* [1,2] (see Fig. 4). Previous work by the authors of this Letter [14], measuring the specific heat at several values of x , found consistent, smooth features also in disagreement with Refs. [2,6] where unusual, sharp features were seen.

The susceptibility of $\text{LiHo}_{0.045}\text{Y}_{0.955}\text{F}_4$ was also measured recently by a third research group [8] and a third, distinct temperature dependence is observed. At higher temperatures, where the response is fast, Ref. [8] matches well with our results here. At lower temperatures, the discrepancy is likely a result of the magnetic field sweep rates used in Ref. [8] corresponding to frequencies of measurement that are too fast to be considered in the static limit and leading to an apparent reduction of χ (see Fig. 4). The nonlinear susceptibility measured in Ref. [8] should also be vulnerable to such dynamical effects.

We also compare our results to very recent Monte Carlo simulations of this material [22] and find that there is indeed very close agreement with the static limit of the

susceptibility as a function of temperature (Fig. 4). There is also qualitative agreement between the specific heat measured in Ref. [14] and that calculated in the simulations [22]. These and other recent Monte Carlo simulations [7,22,23] find no divergence of the spin glass susceptibility suggesting that there is no finite temperature spin glass transition even if this system is viewed as a perfect Ising model.

However, classically, the mean-field theory of Aharony and Stephen [4] would lead us to believe that there should be a spin glass transition all the way down to $x = 0$. It has been suggested by Ghosh *et al.* [6] that off-diagonal terms inherent in the dipolar interaction can introduce quantum fluctuations, leading to a spin liquid state. Recent theoretical work [12] analyzing a more detailed model incorporating random fields resulting from the hyperfine interaction and off-diagonal dipolar coupling maintains that quantum effects are not strong enough to stabilize a spin liquid state and that the system should therefore undergo a spin glass transition. They estimate a T_g of roughly 35 mK, quite close to the 43 mK that we have determined in this work. Additionally, Ref. [12] predicts a significant slowing of the dynamics as the concentration x is lowered to 4.5% as a result of the hyperfine coupling to the holmium $S = 7/2$ nuclear moments.

In superspin glasses, disordered collections of nanomagnets, τ_0 is often longer than that seen in atomic spin glasses [24]. This system may represent an extreme example of such an effect. The hyperfine coupling may create significant energy barriers to spin flips, in essence causing the individual holmium moments to behave as large superspins with slow internal time constants.

In conclusion, our measurements of $\text{LiHo}_x\text{Y}_{1-x}\text{F}_4$ have not shown the exotic antiglass physics that was observed previously [1,2,5,6]. Instead, the absorption spectrum broadens with lower temperature, consistent with behavior expected of a spin glass or a superparamagnet. The temperature dependence of τ_{max} , obtained from the maxima in χ'' , follows a near-Arrhenius behavior which could suggest that this system is a superparamagnet or a spin glass far above its transition temperature. Nonetheless, there is a discernible deviation from the Arrhenius law at lower temperatures and a dynamical scaling analysis provides compelling evidence for the existence of a spin glass transition around $T_g = 43$ mK, a conclusion which is supported by the theoretical work of Ref. [12].

A surprisingly slow response of the system has also been observed and illustrates clearly the need for very low frequency measurements when studying dilute $\text{LiHo}_x\text{Y}_{1-x}\text{F}_4$ and other similar systems. Other tests such as nonlinear susceptibility, aging, and memory experiments would be useful to verify the existence of a spin glass state, though interpretation of the results must simi-

larly take into account the long τ_0 of the material. The ongoing debate [7–10] on the existence of a spin glass transition at higher concentration in $\text{LiHo}_{0.167}\text{Y}_{0.833}\text{F}_4$ could likely be resolved through more careful attention to the diverging time scales involved.

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