Spin dynamics in the frozen state of the dipolar spin ice material Dy$_2$Ti$_2$O$_7$


1Department of Physics and Astronomy and Guelph-Waterloo Physics Institute, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1
2Institute for Quantum Computing, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1
3Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, Canada L8S 4M1
4Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1
5Canadian Institute for Advanced Research, 180 Dundas Street West, Toronto, Ontario, Canada M5G 1Z8

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Low-temperature magnetic ac susceptibility measurements of single-crystal dipolar spin ice Dy$_2$Ti$_2$O$_7$ are presented. The relaxation is found to exhibit thermally activated Arrhenius behavior with an activation energy of 9.79 K ($\sim9\,J_{\text{eff}}$), which is not consistent with a simple scaling of $6\,J_{\text{eff}}$, as previously found for Ho$_2$Ti$_2$O$_7$. There are distinct quantifiable differences between Dy$_2$Ti$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$ absorption spectra. The measured dynamics does not agree with simulations based on current magnetic monopole theory nor thermal relaxation measurements, but instead freezes out at a faster rate.

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A surge of interest has surrounded the spin ice materials since the theory describing them was reformulated into a vacuum containing magnetic monopole-like excitations. Several experiments have focused on characterizing the monopole-like excitations, which include neutron scattering, specific heat, muon spin resonance, and magnetization decay. The rich physics found in spin ice originates from its inherent geometric frustration and resultant highly degenerate ground state. The monopole picture provides an elegant and intuitive way to treat the physics of the system, where excitations out of the ground state are visualized as pairs of magnetic charges. The charge pair is able to separate in an applied field and move about the lattice as individual monopoles. The chief concepts at play are the density, mobility, and the self-screening of these monopoles.

In this Rapid Communication, we present low-temperature, low-frequency ac susceptibility measurements of Dy$_2$Ti$_2$O$_7$ (DTO). Our goal is to assess if the characteristic frequency of relaxation for DTO trends toward thermally activated behavior in the low-temperature limit, and, if so, whether the energy barrier to relaxation is $6\,J_{\text{eff}}$, as is the case for Ho$_2$Ti$_2$O$_7$ (HTO). Previous work on DTO over a smaller temperature range hints at a $6\,J_{\text{eff}}$ energy barrier of relaxation, where $J_{\text{eff}}$ is the nearest-neighbor effective exchange energy. DTO has been the subject of most spin ice ac susceptibility investigations, in both polycrystalline and single-crystal forms, although HTO has also been investigated.

Here, we measure to lower frequencies and lower temperatures than in previous work. The ac magnetic field is applied along the [110] axis to facilitate comparison with previous susceptibility measurements made on HTO along the same crystal axis, using the same superconducting quantum interference device (SQUID) magnetometer.

The general dipolar spin ice model, which contains both exchange and dipolar interaction terms between the rare-earth moments, provides the most accurate representation of this system. However, consideration of only nearest-neighbor interactions within this model has provided a remarkably successful minimal description of these systems. The nearest-neighbor terms can be condensed into an effective exchange interaction, where the exchange energy is given by $J_{\text{eff}} = J_{\text{nn}} + D_{\text{nn}}$, where $D_{\text{nn}}$ is the dipole-dipole coupling, and $J_{\text{nn}}$ is the antiferromagnetic exchange. The effective exchange is weakly ferromagnetic for DTO and HTO, with $J_{\text{eff}}^\text{DTO} = 1.11\,K$ and $J_{\text{eff}}^\text{HTO} = 1.83\,K$ respectively. A monopole excitation is generated by a single spin flip out of the “vacuum” ground state, thus creating a pair of defective tetrahedra, one with the arrangement of three in, one out, and its neighbor, three out, one in. The effective magnetic dipole that is created has a positive and negative pole, each sitting at the center of their tetrahedron. The poles can move apart to neighboring tetrahedra by means of further spin flips, which have zero-energy cost in the nearest-neighbor spin ice model. In this model, the cost of a single spin flip is $4\,J_{\text{eff}}$, which means that the cost of a single monopole excitation should be $2\,J_{\text{eff}}$. The quasiplateau in relaxation time $\tau$ seen in early DTO ac susceptibility experiments by Snyder et al. from $\sim$8 to $\sim$2 K, is captured by an Arrhenius law [Eq. (1)] with a relatively small barrier energy $E_A = 2\,J_{\text{eff}}^\text{DTO}$. The quasiplateau time scale is set by microscopic tunneling time $t_0$:

$$\tau = t_0 \exp\left(\frac{E_A}{T}\right) = t_0 \exp\left(\frac{2\,J_{\text{eff}}^\text{DTO}}{T}\right).$$

However, this description does not explain the crossover to a rapid freezing out of the dynamics below $\sim$2 K, as seen by Snyder et al. This effect can be understood in terms of a failure of the nearest-neighbor spin ice model at lower temperature, where screening effects are lessened and the long-range dipolar interactions become manifest as a $\sim1/r$ Coulomb force between the monopoles. Jaubert and Holdsworth were able to reproduce this crossover using two simulation methods. The first method considers a Coulomb gas of monopoles and the dynamics of Dirac strings in spin ice, and the second method uses a dipolar spin ice model that makes no reference to monopoles. Both methods of simulation have a noted discrepancy with experimental
dynamics measured by Snyder et al. in the low-temperature limit (<1 K) (see Fig. 3). The simulated dynamics has a distinctly shorter time scale than that measured by Snyder et al. The temperature and frequency range of our experimental apparatus allows us to explore the evolution of this discrepancy to lower temperatures and frequencies.

Single-crystalline Dy$_2$Ti$_2$O$_7$ was prepared at McMaster University using a two-mirror floating-zone image furnace. It was grown in 3 atm of oxygen gas, at a growth rate of 6 mm/h. A similar growth procedure is discussed in detail in Ref. 27. Two sample geometries were studied: sample A, measuring 1.0 × 1.0 × 3.9 mm$^3$, and sample B, measuring 0.4 × 0.4 × 3.8 mm$^3$, both with the long axis along the [110] crystal direction.

ac susceptibility measurements were made by using a second-order SQUID axial gradiometer used in previous work. The magnetometer is mounted on the mixing chamber of a S.H.E. Corporation dilution refrigerator. There are three layers of magnetic shielding external to the magnetometer: a lead shield, a cryogenic μ-metal shield, and a room-temperature μ-metal shield. The long axis of the crystal was aligned parallel to the ac excitation with an orientation accuracy of ±2.$^\circ$.

The in-phase and out-of-phase components of ac susceptibility, χ′ and χ′′, respectively, are plotted for sample A in Fig. 1. All data presented here have been corrected for the demagnetization effect. The normalized χ′′ spectra are plotted in Fig. 2 as χ′′/χ′′$_{\text{max}}$ vs f/f$_{\text{max}}$. The width of the spectra has been characterized on the low- and high-frequency sides by measuring the half-width at half maximum for both, referred to as HWHM$^-$ and HWHM$^+$, respectively. We find a nearly symmetric spectral width of ~1.4–1.6 decades in f/f$_{\text{max}}$ for DTO, with some slight asymmetry and broadening developing with increasing temperatures, which is different than what was found for HTO (see the inset of Fig. 2). The DTO spectral width is larger than the theoretical width for a single relaxation mode, which is 1.14 decades.

A characteristic relaxation time τ can be extracted by taking τ = 1/2πf$_{\text{max}}$, where f$_{\text{max}}$ is the frequency at which the maximum of χ′′(f) occurs. The details of this method of analysis are presented in Ref. 14. Figure 3 contains plots of f$_{\text{max}}$ vs 1/T. In the low-temperature limit, the peak absorption frequency seems to approach an Arrhenius law, f$_{\text{max}}$ = f$_0$ exp(−E$_A$/T). The slope of the relaxation frequency in Fig. 3 determines E$_A$, the energy barrier to relaxation. Below a temperature of 850 mK, an excellent fit is obtained with a barrier energy of 9.79 K and f$_0$ = 3.92 × 10$^5$ Hz. Instead of an activation energy of 6 J DTO$_\text{eff}$, such as the 6 J HTO$_\text{eff}$ found for...
HTO, we find the activation energy corresponds to $\sim 8.9 J_{\text{eff}}^{\text{DTO}}$. This indicates that the energy barrier to relaxation of $6J_{\text{eff}}$ is not universal to dipolar spin ice.

Figure 3 shows qualitative agreement between this work and that of Snyder et al.\textsuperscript{15} The quantitative disagreement is likely due to Snyder \textit{et al.} not taking into account the demagnetization effects. Our results appear to be compatible with the relaxation frequencies found by Matsuhira \textit{et al.} on polycrystalline DTO at their lowest temperature, 1.8 K.\textsuperscript{16}

The simulations of a Coulomb monopole gas in spin ice\textsuperscript{12} and relaxation simulations of the dipolar spin ice model\textsuperscript{13} by Jaubert and Holdsworth do not agree with our work. Figure 3 shows that the measured relaxation is becoming significantly slower at a faster rate than was found in their work. Jaubert and Holdsworth scale their results to the relaxation time determined by Snyder \textit{et al.} at 4 K, which accounts for differences up to a proportionality constant between our data and Ref. 12. A rescaling of their microscopic time scale will only produce an offset on a log $y$-axis plot, not a change in slope, however. Reference 13 reports that the cost of a single spin flip, or creation of a monopole pair, is $\sim 5.8$ K in the low-temperature limit. The measured energy barrier, 9.79 K, is distinctly larger at those temperatures, and applies over a range of temperature (500–850 mK). While they propose a continuously changing energy barrier, one of the interesting differences we find is that a single barrier fits well over three decades of frequency.

The monopole density is reduced with decreasing temperature, which weakens screening. This increases the cost of defect creation, which leads to fewer monopoles. This explains why simulations exhibit the continuous slowing of dynamics at low temperatures, as the relaxation remains thermally activated.\textsuperscript{13} It is apparent from Fig. 3 that our work is still qualitatively consistent with this evaluation.

There are three key comparisons to be made between DTO and HTO. First, the microscopic tunneling time $\tau_0$, which sets the time scale of the relaxation plateau, is surprisingly similar, since the HTO relaxation frequencies\textsuperscript{14} are on the same order as DTO for all temperatures studied, contrary to prior conclusions.\textsuperscript{13} Second, it can be seen in Fig. 3 that DTO enters the spin ice regime at a slightly lower temperature than HTO, which is consistent with theory.\textsuperscript{25} Third, the energy barrier of DTO does not share the scaling of the effective exchange energy found in HTO of the same orientation, $\sim 6J_{\text{eff}}^{\text{HTO}}$ (10.70 K), but instead is $\sim 8.9 J_{\text{eff}}^{\text{DTO}}$ (9.79 K).

There is one clear difference apparent between DTO and HTO in the $\chi'$ and $\chi''$ data, as shown in the inset of Fig. 2. The absorption spectra of DTO are broader [$\log(f_{\text{FWHM}} / f_{\text{max}}) \approx 2$–2.5]. This indicates a larger spread in relaxation time scales, as compared to DTO [$\log(f_{\text{FWHM}} / f_{\text{max}}) \approx 1.5$] and to a theoretical single mode [$\log(f_{\text{FWHM}} / f_{\text{max}}) = 1.14$]. They are also significantly less symmetric over the same temperature range, exhibiting a rapidly increasing asymmetry with increasing temperature on the high-frequency side. The source of this difference is not clear, however, one distinction between the materials is the large HTO nuclear hyperfine interaction, which DTO does not possess.\textsuperscript{10}

Other techniques have extracted characteristic relaxation times for DTO at low temperatures: magnetocaloric measurements by Orendač \textit{et al.}\textsuperscript{29} and thermal relaxation measurements by Klemke \textit{et al.}\textsuperscript{5} Orendač \textit{et al.} find spin relaxation time scales consistent with both Raman or Orbach-like spin-lattice relaxation and an Arrhenius process, while Klemke \textit{et al.} see a plateau in the relaxation temperature dependence attributed to screening of defects around 500 mK, resulting in relaxation rates greater than $10^{-3}$ Hz (see the inset of Fig. 4). While both of these works use previous ac susceptibility\textsuperscript{15} to qualify their time scales, Fig. 4 clearly demonstrates the absence of relaxation in ac susceptibility corresponding to those time scales and temperatures. The disagreement between our work and these measurements may be due to the sensitivity of thermal measurements to a decoupling of the magnetic moments from the lattice at low temperatures. This decoupling is consistent with the relaxation time in Refs. 5 and 29, which appears much shorter than the freezing trend in ac susceptibility would predict. In Ref. 5, the gradual loss of charge screening should not shorten the relaxation time and is instead likely due to a departure from spin-lattice equilibrium, which we infer from Fig. 4 to be at $\sim 500$ mK, in agreement with nonequilibrium magnetization results.\textsuperscript{30}

Another approach to studying the dynamics is with time domain magnetization measurements. Giblin \textit{et al.} see two time constants in their magnetization relaxation data at 360 mK,\textsuperscript{8} which should emerge in the susceptibility absorption data as peaks at frequencies of about $10^{-2}$ Hz and about $10^{-1}$ Hz. Our measurements do not find any characteristic absorption peaks at, or close to, those frequencies below temperatures of 500 mK down to our frequency limit of $10^{-3}$ Hz (see Fig. 4). A distinction that should be made between the two measurements is that the smallest magnetic field Giblin \textit{et al.} use is 1 Oe along the [100] crystal direction, whereas the field used in our work is no greater than 6 mOe and our sample is oriented along the [110] crystal direction.
In conclusion, we have determined that the spin relaxation of Dy$_2$Ti$_2$O$_7$ exhibits a thermally activated Arrhenius character down to our low-temperature limit, as was found previously in its sister spin ice compound Ho$_2$Ti$_2$O$_7$.\textsuperscript{14} The energy barrier to relaxation was found to be $\sim$9 J$_{\text{eff}}$\textsubscript{DTO} (9.79 K) and 6 J$_{\text{eff}}$\textsubscript{HTO} (10.7 K) for Ho$_2$Ti$_2$O$_7$. There is also an obvious difference in the absorption spectra shape, in that Dy$_2$Ti$_2$O$_7$ spectra are notably narrower and more symmetric, in sharp contrast with Ho$_2$Ti$_2$O$_7$.\textsuperscript{14} The origin of the differences in the susceptibility spectra between the two materials is currently not understood. In summary, by experimentally varying $J_{\text{eff}}$, we have found that 6$J_{\text{eff}}$ is not a universal barrier to relaxation for low-temperature dipolar spin ice.

The simulations of the Coulomb monopole gas\textsuperscript{12} and dipolar spin ice model\textsuperscript{12,13} do not agree with ac susceptibility below 1 K in both a previous work\textsuperscript{15} and this work. Our measurement reveals much slower dynamics than the simulations predict, although a continuous slowing down of thermally activated dynamics, consistent with simulation, is observed. By taking into account a demagnetization correction and extending the measurement by three orders of magnitude lower in frequency from the previous experimental work,\textsuperscript{15,16} we have obtained a single-crystal sample, we have provided a benchmark for ac susceptibility on spin ice.

We see no evidence of a plateau or a speeding up of dynamics in the low-temperature relaxation as observed by magnetocaloric\textsuperscript{29} and thermal relaxation measurements.\textsuperscript{5} This is consistent with a phonon bottleneck. No modes of relaxation are observed in our experiment at 360 mK in equilibrium with the 6-mOe ac field along the [110] crystal axis, which is the temperature at which Giblin \textit{et al.}\textsuperscript{8} see two time constants. This discrepancy could be explained by the presence of nonequilibrium relaxation processes which the system accesses in response to a larger magnetic field pulse (1–5 Oe along the [100] crystal axis), or something more mundane such as poor thermometry.

With all the above points considered, this work is an expanded quantitative characterization of spin ice (and monopole) dynamics. Specifically, it points to differences between the canonical spin ice materials Ho$_2$Ti$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$, as well as to differences between the results of theoretical relaxation simulations and ac susceptibility that require reconciliation. It should help constrain theory that describes the freezing of spin ice and the dynamics of magnetic monopole excitations in these materials at low temperatures and monopole densities. Further development of the theory is required to more accurately capture the energy landscape for creation and diffusion of monopole excitations in the low-temperature limit of Dy$_2$Ti$_2$O$_7$.

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