Low Lying Spin Excitation in the Spin Ice, Ho$_2$Ti$_2$O$_7$

G. Ehlers and E. Mamontov
SNS, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6475, USA.
E-mail: ehlersg@ornl.gov

M. Zamponi
SNS, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6473, USA and
Jülich Center for Neutron Science, FZ Jülich, 52425 Jülich, Germany.

J. S. Gardner
Indiana University, Bloomington, IN 47408, USA and
NCNR, NIST, Gaithersburg, MD 20899-6102, USA.
E-mail: jsg@nist.gov

Abstract. The high flux and low background of the new backscattering spectrometer at the SNS combine to produce an excellent signal to noise ratio, allowing us to investigate a low lying weak excitation never seen before in the spin ice, Ho$_2$Ti$_2$O$_7$. This non-dispersive excitation has been observed at $E = 26.3 \mu$eV below 100 K but is resolution limited only below $\sim 65$ K. It is indifferent to magnetic fields below $\mu_0 H = 4.5$ T, at 1.6 K. These characteristics help us to identify the excitation as due to the nuclear spin system.

1. Introduction
When studying low temperature magnetism, especially in systems with delicately balanced and competing interactions, like for example in spin ice [1, 2], Cs$_2$CoCl$_4$ [3] or LiHoF$_4$ [4], one has to not only consider the electronic spins, but also the nuclear spins, particularly in compounds where there is a large nuclear spin in high abundance (e.g. Ho, Mn, Nd, Co etc.)

Geometrically frustrated magnets are systems where magnetic moments are placed on a lattice that is incompatible with the dominant spin-spin interactions [5]. In the rare-earth titanate pyrochlores [6], large rare-earth moments reside on a sublattice that makes up a network of corner sharing tetrahedra, and all the other elements are non magnetic. Ho$_2$Ti$_2$O$_7$ [1, 2] and Tb$_2$Ti$_2$O$_7$ [7, 8] have exchange and dipole interactions of approximately the same strength, and the single ion anisotropy gives both systems an Ising like character. However, as shown by Melko and Gingras [9], a slight change in interaction strength, albeit in sign too, can drive such a system between different ground states (spin liquid in the case of Tb$_2$Ti$_2$O$_7$ and spin ice in Ho$_2$Ti$_2$O$_7$). Another important difference between these two systems is the energy gap to the first excited state. In Tb$_2$Ti$_2$O$_7$ the gap is small ($\sim 20$ K) and reduces as the temperature is lowered. In Ho$_2$Ti$_2$O$_7$ the gap is on the order of $\sim 300$ K. These differences may or may not be the complete answer as to why the ground states are so different, but when interpreting the slow
spin dynamics at low temperature of these and other magnets, one must not forget the nuclear spin system that co-exists with the electronic spins.

The spin ice, Ho$_2$Ti$_2$O$_7$ was recently shown to be an ideal candidate for studying the nuclear spin system [10]. The slow, low temperature spin dynamics have been studied [1, 11, 12, 13, 14, 15], and it was speculated that residual fluctuations seen below 2 K are a consequence of the nuclear spins perturbing the electronic spins off their equilibrium axes causing a \textit{wobble}. In both spin ices, Ho$_2$Ti$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$ a high temperature, thermally activated process dominates the magnetic spectrum [13, 14, 15, 16, 17]. As the temperature is lowered below 30 K, the systems enter a quantum-like regime where temperature plays almost no role in the spin relaxation processes [12, 13]. This phase, which exists in Ho$_2$Ti$_2$O$_7$ between 2 K and 30 K, can be described as a slowly relaxing (≈ 20 ns) [14], concentrated spin ensemble. In Dy$_2$Ti$_2$O$_7$ the spins are significantly slower (≈ 5 ms) [13]. Recently this region has been associated with the propagation of magnetic monopoles through the system [18, 19]. Below 2 K, a unique reentrant behaviour from a quantum to a thermally activated regime has been observed in both spin ice compounds [13, 14]. The residual spin dynamics eludes the best models that describe spin ice but one possible explanation involves a coupling of the nuclear spin system to the electronic spins [12, 21].

In this paper we extend to a lower temperature the observation of a single non-dispersive excitation at $E_0 = 26.3$ µeV in Ho$_2$Ti$_2$O$_7$. This has been reported below 100 K in Ho$_2$Ti$_2$O$_7$ and is absent in isotopic $^{162}$Dy$_2$Ti$_2$O$_7$.

2. Experimental Details

Neutron experiments were performed at the new backscattering spectrometer BASIS on beam line 2 at the Spallation Neutron Source (SNS) in Oak Ridge [20]. The energy resolution of this instrument is ∼ 3.3 µeV full width at half maximum (FWHM) for our particular sample size. In one neutron experiment, a cryomagnet was used with a maximum field of $\mu_0 H = 5$ T and a base temperature of $T = 1.6$ K. In others, a $^3$He-refrigerator was used to extend the temperature range in zero field. The powders were very tightly packed in their containers to avoid reorientation of the grains in a magnetic field and to provide good thermal contact.

Natural dysprosium has two isotopes with large absorption cross sections for cold neutrons. Therefore an isotopically enriched $^{162}$Dy$_2$O$_3$ oxide was used in the preparation of the neutron sample. Thus our Dy$_2$Ti$_2$O$_7$ sample had only a very small fraction of Dy isotopes containing a nuclear spin (≤ 0.6%).

3. Results and Discussion

Our experimental findings can be summarized as follows.

The excitation is observed in Ho$_2$Ti$_2$O$_7$ in zero field and applied field below 100 K, but is absent in isotopically enriched $^{162}$Dy$_2$Ti$_2$O$_7$. It is resolution limited below 65 K. The energy of the excitation is nearly independent of temperature, with a possible small softening at the highest temperatures. The intensity is constant below 50 K and then drops to disappear at around 100 K.

The lack of a dependence on magnetic field clearly indicates that the excitation does not originate from within the electronic spins. In zero field the sample is in the spin ice state, a disordered state with short ranged magnetic correlations. In a field, on the other hand, the system is long range ordered, which is directly confirmed in our data by the presence of magnetic Bragg peaks, and the short ranged dynamic correlations are largely suppressed.

The interpretation as a transition between split nuclear states of Ho leads to an estimate of the hyperfine field of $B_{hf} = 7/2 \cdot E_0/\mu_{Ho} = (702 \pm 1)$ T, a value that is close to a previous estimate, $B_{hf} \sim 720$ T [22], and is comparable to pure Ho metal (770 T) [23]. At this magnitude of the hyperfine field, an external applied field of 5 T is negligible.
Figure 1. Top left: False colour contour plot of the inelastic spectra from Ho$_2$Ti$_2$O$_7$ at $T = 270$ mK. It is clear that the mode at $E_0 = 26.3$ $\mu$eV is independent of $Q$. Right: The energy spectra from the two spin ice compounds at $T = 1.6$ K. In Ho$_2$Ti$_2$O$_7$ the excitation can clearly be seen at 26.3 $\mu$eV with and without magnetic field, while in Dy$_2$Ti$_2$O$_7$ it is entirely absent. The temperature evolution of the mode intensity in zero field is shown in the inset for Ho$_2$Ti$_2$O$_7$. Error bars represent $\pm 1\sigma$. Bottom left: Spectra averaged over all $Q$ from the powder sample. While the nominal reading of the cold head was at 270 mK, the intensity ratio in the data between neutron energy gain and loss sides is about $\sim 1.5$, indicating that the temperature of the powder sample (by detailed balance) may be as high as $\sim 750$ mK.

Clearly, the hyperfine field has to be static on the time scale of the electronic spin fluctuations for this scenario to be valid. In other words, the Larmor frequency of the Ho nuclear moment in the hyperfine field (estimated at $\nu_L \sim 6.36$ GHz, with the gyromagnetic ratio of the Ho nucleus equal to $\gamma/2\pi = 9.06$ MHz/T) has to be slower than the electronic spin fluctuations. In the relevant temperature range, between 50 K and 100 K, the electronic spin fluctuation rate follows an Arrhenius law, $\nu = \nu_0 \cdot \exp(-\Delta/T)$, with $\nu_0 = 1.1 \cdot 10^{11}$ Hz and $\Delta = 293$ K [14], and thus equals $\nu_L$ at $T_L \sim 103$ K. Hence one expects nuclear level transition to be observable at $T \ll T_L$, and to disappear around $T \sim T_L$, in accordance with the experimental result.

There are two more arguments that make the interpretation as a nuclear excitation very plausible. (i) The published low temperature specific heat of Ho$_2$Ti$_2$O$_7$ shows a Schottky
anomaly for nuclear Ho spin ($I = 7/2$) of 0.9, and the observed level splitting of 0.3 K equals $\sim 26 \mu$eV [2]. (ii) In absolute terms, the observed scattering intensity of the excitation is very small, $\sim 500$ times smaller than the quasielastic magnetic intensity (see Fig. 1). Again, this is expected, since the incoherent scattering cross section of Ho (which is purely spin incoherent since there is only one isotope) is 0.36 bn, about $\sim 1000$ times smaller than the scattering length of an electronic magnetic moment of $\sim 10 \mu_B$.

To conclude, we have observed a low energy excitation in Ho$_2$Ti$_2$O$_7$ spin ice which is ascribed to the Ho nuclear moment. It may have a significant impact on the low temperature spin dynamics of the system for which residual traces have been found in the ice phase, and may account for the differences between the two spin ices in this regard.

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