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Dynamic spin correlations in stuffed spin ice $\mathbf{Ho_{2+x}Ti_{2-x}O_{7-\delta}}$

G. Ehlers,[1,*] J. S. Gardner,[2,3] Y. Qiu,[3] P. Fouquet,[4] C. R. Wiebe,[5,6] L. Balicas,[5] and H. D. Zhou[5]
[1]*Spallation Neutron Source, Oak Ridge National Laboratory, Building 8600, Oak Ridge, Tennessee 37831-6475, USA*
[2]*Indiana University, 2401 Milo B. Sampson Lane, Bloomington, Indiana 47408, USA*
[3]*NIST Center for Neutron Research, NIST, Gaithersburg, Maryland 20899-8562, USA*
[4]*Institut Laue-Langevin, 6 rue Jules Horowitz, Boîte Postale 156, 38042 Grenoble Cedex 9, France*
[5]*Department of Physics, Florida State University, Tallahassee, Florida 32306-3016, USA*
[6]*National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32306-4005, USA*
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The magnetic correlations in "stuffed" spin ice $Ho_{2+x}Ti_{2-x}O_{7-\delta}$ have been characterized using quasielastic neutron scattering. At temperatures above 1 K, these correlations are short ranged in nature and dynamic on a picosecond to nanosecond time scale. As for the case of pure spin ice $Ho_2Ti_2O_7$, one can identify, above the freezing temperature, a quantum relaxation regime which is enhanced as it persists to even higher temperatures, $T \sim 30-40$ K, than in the parent compound.

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Geometrical frustration is an important theme in current condensed matter physics, as it allows the possibility of exotic ground states.[1] In the context of magnetism, this refers to the inability to form a ground state with long range order at sufficiently low temperature. Often, it is the spatial arrangement of the magnetic ions in the particular lattice which is in some way incompatible with near neighbor couplings, as, for example, in the case of an antiferromagnet on a quasi-two-dimensional triangular or *kagome* lattice.[2,3] Frustration is not exclusive to magnetism, and therefore, this phenomenon attracts the interest from a much broader scientific community.[4,5]

Ternary pyrochlore oxides of general composition $R_2T_2O_7$, where R is a rare earth metal and T is a transition metal, display a particularly rich variety of unusual phenomena at low temperature which are related to frustration effects. Earlier studies have found partially ordered states in $Gd_2Ti_2O_7$ and $Tb_2Sn_2O_7$,[6–8] order by disorder in $Er_2Ti_2O_7$,[9] cooperative paramagnetism in $Tb_2Ti_2O_7$,[10] a unique dynamic phase transition in $Yb_2Ti_2O_7$,[11] spin glass states with very little positional disorder in $Y_2Mo_2O_7$ and $Tb_2Mo_2O_7$,[12,13] and spin ice behavior in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$.[14,15] The spin ices stand out as unique examples for frustrated systems with effective *ferromagnetic* interactions and consequently have been studied extensively.[14–31]

Apart from thermodynamic variables, such as temperature and magnetic field, the chemical composition of the systems may be altered to study the relationship of structural and magnetic properties. Following along this avenue, "stuffed" spin ice materials with the general formula $Ho_{2+x}Ti_{2-x}O_{7-\delta}$ have been synthesized recently, in which additional magnetic ions replace the nonmagnetic Ti^{4+} ions ($\delta > 0$, as the oxygen content needs to be adjusted for charge balance).[32–34] Due to the way the Ho and Ti sublattices penetrate each other [both are identical pyrochlore lattices displaced by a $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ vector], one creates for some Ho sites additional close neighbors, the nearest being at a distance of $(a/4)\sqrt{2} \sim 3.6$ Å which is the length of an edge of the tetrahedra (a denotes the cubic lattice constant). The additional magnetic exchange pathways represent a major disturbance of the system, introducing positional disorder, but surprisingly it has been found that the stuffed spin ice systems have the same entropy per spin at low temperature as the "unstuffed" spin ice.[32–34] In this paper, we present the results of quasielastic neutron scattering and neutron spin echo experiments which reveal the nature of the spin correlations in these new systems.

Powder samples with composition parameters $x=0.10$, $x=0.25$, and $x=0.30$ have been prepared and characterized using procedures described elsewhere.[34] All samples were single phase with the cubic pyrochlore structure (space group $Fd\bar{3}m$).

The quasielastic neutron scattering measurements were performed by the time-of-flight technique at the Disk Chopper Spectrometer[35] (DCS) at the NIST Center for Neutron Research with an incident wavelength of 1.8 Å, giving an energy resolution of ~ 2 meV full width at half maximum. The sample was mounted in a dilution refrigerator and cooled to base temperature, $T \sim 50$ mK. The scattering patterns were appropriately corrected for sample transmission, background, and detector efficiency using measurements of an empty container and a vanadium reference sample.

The neutron spin echo[36] (NSE) experiments were performed at NG5 at NIST and at IN11 at the Institut Laue-Langevin (ILL) in Grenoble, France. At NIST, a wavelength of 6 Å was chosen (bandwidth of 20%), giving a time range of 40 ps $\leq t \leq$ 10 ns, and two values for the momentum transfer Q, $Q=0.4$ Å^{-1} and $Q=0.7$ Å^{-1}. At ILL, the NSE experiments were performed on the multidetector instrument IN11C using a wavelength of 5.5 Å (bandwidth of 15%), giving a dynamic range of 5 ps $\leq t \leq$ 1.5 ns and simultaneous access to a Q range of 0.5 Å$^{-1} \leq Q \leq$ 1.1 Å^{-1}. The instrument resolution was measured in both cases with a $Ho_{0.7}Y_{1.3}Ti_2O_7$ sample that is known to be elastic in the NSE time window at a temperature around $T \sim 5$ K.[37] NSE has been used successfully for studies of frustrated magnets[38] for mainly two reasons. First, the use of a polarized neutron beam allows for a separation of magnetic, nuclear coherent, and nuclear spin-incoherent scattering contributions. Second, NSE is uniquely sensitive to slow fluctuations on the nanosecond time scale,

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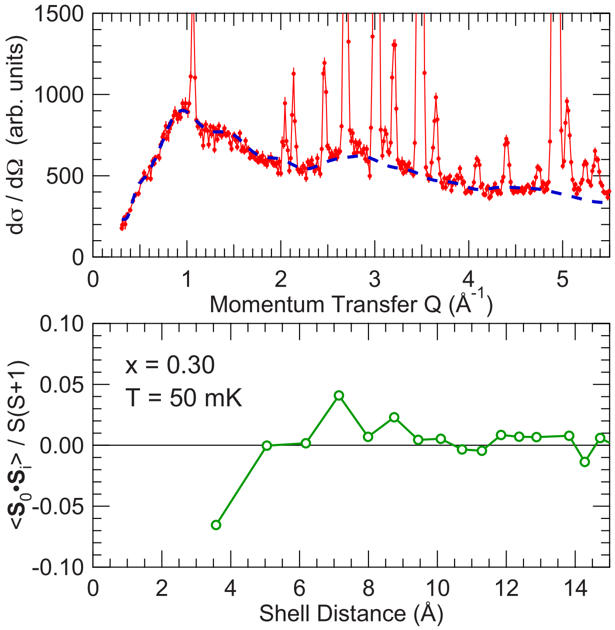

FIG. 1. (Color online) Upper panel: the quasielastic scattering, as measured at DCS after integration over the energy transfer range between ±1 meV, is shown by the data points; the fit to the diffuse scattering resulting from reverse Monte Carlo simulation is shown by the dashed line. Lower panel: the time averaged spin correlation for near neighbor shells is shown.

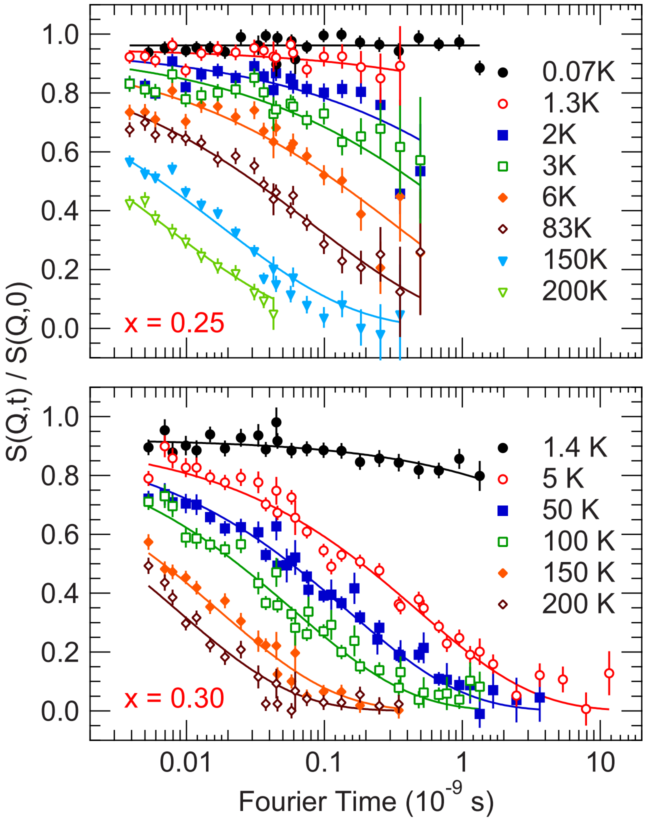

FIG. 2. (Color online) NSE spectra of the $x=0.25$ (upper panel) and $x=0.30$ (lower panel) samples. Error bars represent ±1 standard deviation arising from counting statistics. The lines are fits to a stretched exponential relaxation function (see text).

which is essential because in many frustrated systems, one finds a significant spectral weight of low energy excitations.

Figure 1 shows the quasielastic scattering of the $x=0.30$ sample as measured at DCS after integration over energy transfer between ±1 meV (upper panel). The short ranged nature of the spin correlations is revealed by intense diffuse scattering in the $Q \lesssim 2$ Å^{-1} range. The NSE experiment, using polarization analysis, confirmed the almost exclusively magnetic origin, ~90%, of this scattering. Comparing to the parent compound $Ho_2Ti_2O_7$, the maximum of the first correlation peak is shifted to significantly higher Q, from $Q \sim 0.6$ Å^{-1} (Ref. 39) to $Q \sim 1$ Å^{-1}.

In order to better understand this observation and the spin correlations, the diffuse scattering was analyzed by means of a reverse Monte Carlo technique. A cube of $n \times n \times n$ cubic unit cells, $n=6$, was considered with magnetic moments situated at all 16d sites and 15% of the 16c sites which were chosen randomly. On the 16d sites, individual moments were constrained to be parallel to a local $\langle 111 \rangle$ axis, to point to the center of a tetrahedron. Without *a priori* knowledge of the spin anisotropy on the 16c sites, runs were performed with or without the same constraint for the 16c site. This made no significant difference to the results of the fit, indicating that the measurement at the given precision is not sensitive enough to determine the spin anisotropy on the 16c site. Starting with an arbitrary spin configuration, ~100 spins were randomly chosen and flipped in one step of the simulation. A powder average of the cross section $d\sigma/d\Omega$ was then computed using

$$\frac{d\sigma}{d\Omega} = \text{const}\, F^2(Q) \sum_{m,n} \frac{\sin Qr_{m,n}}{Qr_{m,n}} \frac{\langle \boldsymbol{S}_m \cdot \boldsymbol{S}_n \rangle}{S(S+1)},$$

where m,n run through the cube, S denotes the moment on a site, $r_{m,n}$ is the distance between two sites, and $F(Q)$ is the magnetic form factor. The Monte Carlo (MC) step was accepted if the fit to the measured intensity was improved, and repeated if not. The fit involved a scale factor since the measurement did not yield the scattering cross section in absolute units. Since the function to be optimized has many local minima in its parameter space, 48 MC runs were performed until convergence, and then linearly combined in a last step to produce the final best fit. The fit to $d\sigma/d\Omega$ resulting from the reverse Monte Carlo simulation is also shown in the upper panel of Fig. 1 and the resulting time averaged spin correlations for near neighbor shells are shown in the lower panel. The results suggest that even for nearest neighbors, these correlations are very small, $\langle \boldsymbol{S}_m \cdot \boldsymbol{S}_n \rangle / S(S+1) \sim -0.07$, in the nearest neighbor shell. In subsequent shells, the correlations then appear either quenched or slightly ferromagnetic and do not extend beyond ~15 Å.

Figure 2 shows NSE spectra for the $x=0.25$ and $x=0.30$ samples. These results show that the spin dynamics is significantly altered in the stuffed samples when compared to the parent compound $Ho_2Ti_2O_7$.[26] The relaxation is clearly

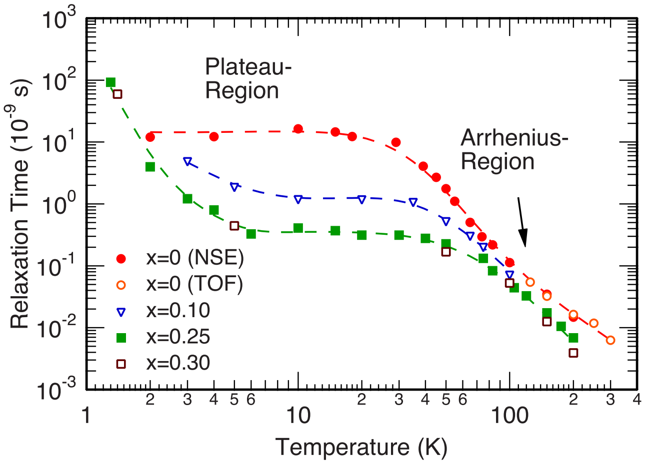

FIG. 3. (Color online) Temperature dependence of observed relaxation times. The $x=0$ curves are for the pure spin ice (see Ref. 27). The lines are guides to the eye.

not a single exponential in time, rather the data are consistent with a stretched exponential,

$$\frac{S(Q,t)}{S(Q,0)} = A \exp\left[-\left(\frac{t}{\tau(T)}\right)^{\beta}\right],$$

where $A \sim 1$ and $\beta \sim 1/2$. In the ranges studied, β appears independent of composition and temperature. The stretched nature of the spin relaxation function can be interpreted in different ways, e.g., in terms of hierarchical cascades of relaxing clusters,[40,41] or with the presence of a distribution of single exponential relaxation channels,[42] originating from the different magnetic environments that the individual spins experience. Based on the data at hand, it is not possible to clearly rule out either scenario, and the observed absence of a noticeable Q dependence of the dynamics seems to be consistent with both, indicating that the dynamics is primarily single ion as in the pure spin ice.

For the present discussion of the temperature dependence, one global relaxation time was fitted for each spectrum with the stretched exponential lineshape. Figure 3 shows the fitted relaxation times for all samples investigated here and for pure spin ice. For all samples, one observes an Arrhenius law at high temperature, indicating thermal activation of the spin flips. As indicated by the slope in the figure at high temperature, the energy barrier is the same as in pure $Ho_2Ti_2O_7$, $\Delta \sim 290$ K. On cooling, the systems enter a plateau region where the dynamics becomes virtually independent of temperature. In pure spin ice, this plateau has been associated with the quantum relaxation regime,[26] and one may postulate that in the stuffed systems, the same crossover from thermally activated to quantum relaxation takes place. The transition temperature is $T_0 \sim 15$ K in pure $Ho_2Ti_2O_7$ and even higher in the stuffed systems, for example, $T_0 \sim 30-40$ K in the $x=0.30$ system. On the other hand, the mean spin relaxation time in the plateau is decidedly much shorter, 1–2 orders of magnitude, indicating that the additional near neighbors assist in the relaxation. On further cooling, the systems freeze eventually and leave the plateau, i.e., the relaxation times diverge. This has been observed by means of ac susceptibility measurements in the pure spin ices and also in diluted systems.[19,23,43,44] In the stuffed spin ices, the freezing temperature appears higher, by a few kelvins, than in the pure systems when probed with an $\sim 10^9$ Hz frequency typical for neutron scattering.

In pure spin ice $Ho_2Ti_2O_7$, there is virtually no positional disorder as all magnetic Ho^{3+} ions are residing in equivalent sites at the 16*d* position. When the lattice is stuffed with Ho^{3+} ions on the Ti site (which itself also constitutes a pyrochlore lattice), this situation changes as one introduces, for some individual ions, additional magnetic near neighbors at a distance of $(a/4)\sqrt{2} \sim 3.6$ Å. One also creates a distribution of ions that have 1, 2, etc., additional such neighbors. The next nearest neighbor shell in stuffed spin ice is at a distance of $a/2$, while in pure spin ice, it is at $a\sqrt{3/8}$.

With a certain degree of positional disorder, one may expect the system to turn into a hybrid of a spin ice and a spin glass. In stuffed spin ice, one finds a stretched exponential spin relaxation that resembles spin glass behavior but the similarity seems rather superficial. Spin glasses show a gradual freezing and a change of $S(Q,t)$ to a power law below T_g, but no plateau region where the dynamics becomes independent of temperature. It thus appears, at this level of stuffing, that the systems retain the basic characteristics of spin ice. At low temperature, the stuffed systems also freeze, but in the quantum dynamics regime, they are much more dynamic than pure spin ice.

Future research on stuffed spin ice compounds, including Dy based systems, will have to address the open questions of spin anisotropy, the crystal field, and why the nature of the ground state seems so different from diluted spin ice systems. It will also be relevant to study the quantum dynamics regime at a higher degree of stuffing, where the systems gradually adopt a fluorite structure.[32,33]

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*Corresponding author; ehlersg@ornl.gov

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