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The temperature evolution of the magnetic correlations in pure and diluted spin ice $Ho_{2-x}Y_xTi_2O_7$

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ABSTRACT

Diffuse polarized neutron scattering studies have been carried out on single crystals of pyrochlore spin ice $Ho_{2-x}Y_xTi_2O_7$ ($x=0$, 0.3, and 1) to investigate the effects of doping and anisotropy on spin correlations in the system. The crystals were aligned with the $(1\ -1\ 0)$ orientation coincident with the direction of neutron polarization. For all the samples studied the spin flip (SF) diffuse scattering (i.e. the in-plane component) reveals that the spin correlations can be described using a nearest-neighbour spin ice model (NNSM) at higher temperatures ($T=3.6$ K) and a dipolar spin ice model (DSM) as the temperature is reduced ($T=30$ mK). In the non-spin flip (NSF) channel (i.e. the out-of-plane component), the signature of strong antiferromagnetic correlations is observed for all the samples at the same temperature as the dipolar spin ice behaviour appears in the SF channel. Our studies show that the non-magnetic dopant Y does not significantly alter SF or NSF scattering for the spin ice state, even when Y doping is as high as 50%. In this paper, we focus on the experimental results of the highly doped spin ice $HoYTi_2O_7$ and compare our results with pure spin ice $Ho_2Ti_2O_7$. The crossover from a dipolar to a nearest-neighbour spin ice behaviour and the doping insensitivity in spin ices are briefly discussed.

Spin ice compounds such as $Ho_2Ti_2O_7$, $Ho_2Sn_2O_7$, $Dy_2Ti_2O_7$ and the most recently discovered $Dy_2Sn_2O_7$ exhibit an Ising-like anisotropy with an effective ferromagnetic interaction between the magnetic moments [1–6]. These compounds, with the chemical formula $A_2B_2O_7$, where A is a rare-earth ion and B is a transition-metal ion, all have a pyrochlore structure and possess a face-centred-cubic structure with a space group $Fd\bar{3}m$ with 8 formula units in a unit cell. In spin ice $Ho_2Ti_2O_7$, the Ho^{3+} ions occupy the 16d site with a local trigonal symmetry 3m and are the only magnetic ions in the specimen [7]. The organizing principles of the magnetic ground state or the "ice rules" in spin ice compounds require that two spins should point in, and two out of each elementary tetrahedron in the pyrochlore lattice. The "two in, two out" ice rule was generally believed to be the result of a delicate balance between the interaction of the large spin moments and the special geometry of the pyrochlore lattice. Heat capacity measurements and diffuse neutron scattering are two methods to characterize a spin ice compound experimentally. As in the case of water ice, spin ice has a degeneracy of energetically preferred states, which generates a residual finite entropy of $S_0=1/2\ln 3/2$ as the temperature approaches absolute zero [8]. Bramwell et al. [9] suggested that $Ho_2Ti_2O_7$ can be described using a dipolar spin ice model (DSM). However, owing to the self-screening of the dipolar interactions [10], a nearest-neighbour spin ice model (NNSM) gives a reasonable description of the magnetic correlations in spin ice and explains the residual finite entropy of the system. This feature known as "projective equivalence" between the DSM and NNSM was proposed by Isakov et al. [11]. The dipolar spin ice ground state manifold is quasi-degenerate, and the residual energy scale is expected to lead to an ordering instability at low temperatures away from $q=0$ [10,12]. However, this long-range ordered state has not yet been observed experimentally, although scattering intensities on the zone boundary have been observed for spin ice $Dy_2Ti_2O_7$ [13] in diffuse neutron scattering studies. A cluster-like correlation model was used to understand the scattering intensities on the zone boundary in spin ice as well as in spinel $ZnCr_2O_4$ [14]. On the other hand, Yavors'kii et al. [15] found that an equally satisfactory description of the spin ice data could be obtained by including the second and

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third nearest-neighbour exchange couplings in the Hamiltonian of their Monte Carlo simulations.

It has recently been proposed that excitations above the ground state manifold in the spin ice can be viewed as magnetic monopoles of opposite "charge" connected by Dirac strings [16], and these have been observed in several experiments [17–21]. Fennell et al. [17] studied magnetic correlations in $Ho_2Ti_2O_7$ in the spin flip (SF) and non-spin flip (NSF) channels via polarized neutron scattering. While a nearest-neighbour spin ice correlation pattern was clearly observed in the SF channel at 1.7 K, a faint indication of the presence of possible antiferromagnetic correlations was found in the NSF channel.

It is reasonable to expect that impurity doping would relax the local constraints imposed by the ice rules, and that significant changes would be observed experimentally in doped spin ice materials. However, relaxation measurements by neutron spin-echo and ac-susceptibility showed that the relaxation mechanism in spin ice compounds is less sensitive than expected to the concentration of dopants [22,23]. Studies on doped spin ice replacing Ho or Dy with Y, as well as stuffed spin ice materials, reveal that the spin ice state is still present even when the amount of doping is as high as 40% [8]. Here we focus on the investigation of the effects of Y doping on spin ice $Ho_2Ti_2O_7$, especially for the highly doped case of $HoYTi_2O_7$.

$Ho_{1-x}Y_xTi_2O_7$ (x=0, 0.3, and 1) single crystals were grown in an infrared double mirror image furnace [24]. Each crystal was ~0.6 cm in diameter, ~2 cm in length, and amber-red in colour. The crystals were cut and characterized by X-ray Laue diffraction. Diffuse neutron scattering incorporated with polarization analysis is a powerful technique by which one can probe short-range spin correlations as well as spatial anisotropy in highly frustrated magnets. The experiments were performed using the high-flux polarized diffuse neutron scattering spectrometer DNS, FRM-II (Garching, Germany). A ^{3}He/^{4}He dilution refrigerator insert with an Oxford Instruments cryostat was used for temperatures below 2 K, and a closed cycle cryostat was used for temperatures above 2 K. A neutron wavelength of 4.74 Å was chosen for all the experiments. The [1 –1 0] direction of each of the crystals was aligned perpendicular to the horizontal scattering plane so that the ($h\,h\,\ell$) reciprocal plane can be mapped out by rotating the samples. The neutron polarization at the sample position was aligned along the [1 –1 0] direction of the sample, i.e. z-direction of the chosen experimental coordinate system. Within this setup, the SF and NSF scattering cross sections can be derived as follows [25]:

$$\left(\frac{d\sigma}{d\Omega}\right)_z^{sf} = M^*_{\perp y}M_{\perp y} + 2/3 I_{SI},$$

$$\left(\frac{d\sigma}{d\Omega}\right)_z^{nsf} = M^*_{\perp z}M_{\perp z} + N^*N + 1/3 I_{SI},$$

where $M^*_{\perp y}M_{\perp y}$ is the component of the magnetic scattering cross section in the scattering plane (i.e. in the ($h\,h\,\ell$) reciprocal plane), $M^*_{\perp z}M_{\perp z}$ is the component of the magnetic scattering cross section perpendicular to the scattering plane, I_{SI} the total nuclear spin

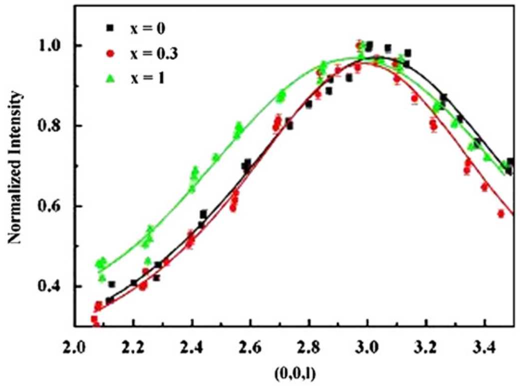

Fig. 2. Cuts across the [0 0 ℓ] NSF channels for $Ho_{2-x}Y_xTi_2O_7$ (x=0, 0.3, and 1) at 30 mK (for x=0 and 1) and 400 mK (for x=0.3). The intensities are normalized to the maximum intensity in each set of data around (0 0 3), and the lines are Gaussians fits to the data.

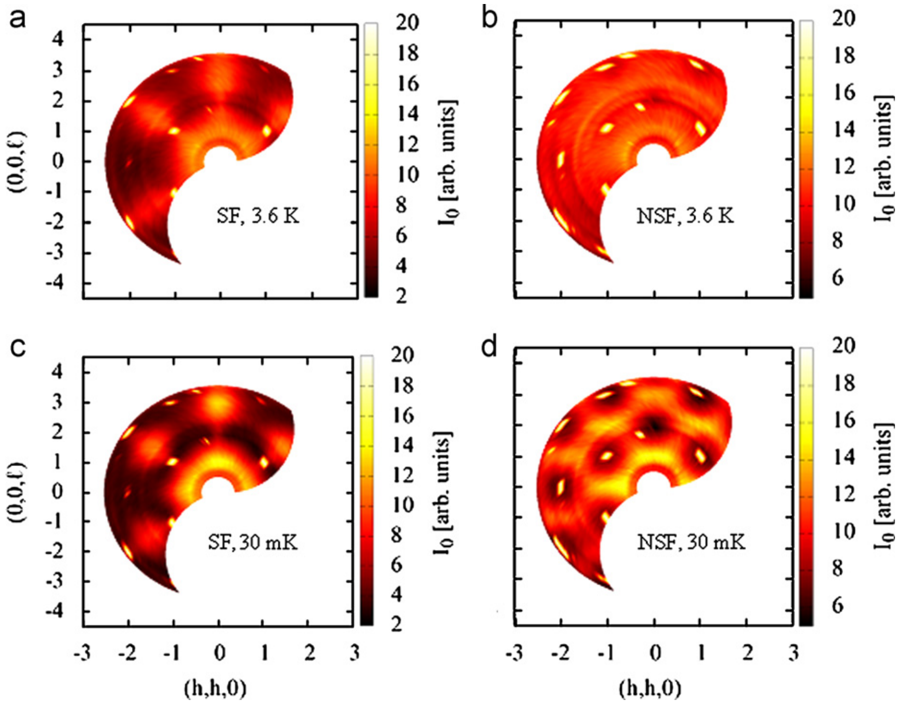

Fig. 1. Neutron polarization analysis contour plots for $HoYTi_2O_7$ for (a) SF scattering at 3.6 K, (b) NSF scattering at 3.6 K, (c) SF scattering at 30 mK, and (d) NSF scattering at 30 mK.

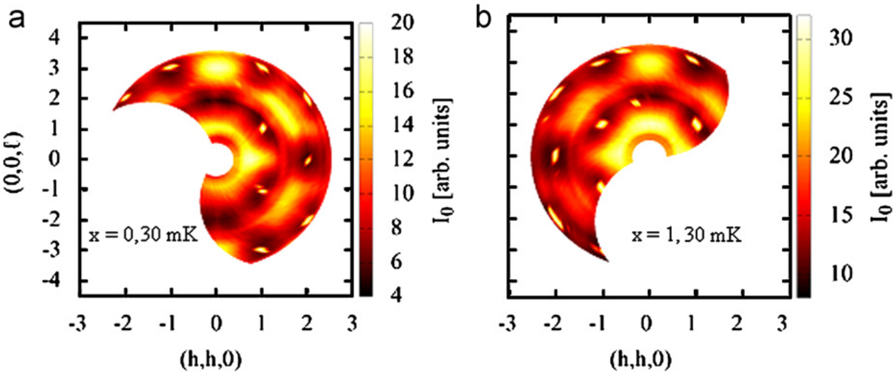

Fig. 3. Contour plots of summation of SF and NSF scatterings at 30 mK for (a) $Ho_2Ti_2O_7$ and (b) $HoYTi_2O_7$. In order to emphasize similarity of scattering patterns, colour scales used in (a) and (b) are not identical.

incoherent scattering cross section, and N^*N the nuclear coherent scattering cross section. Note that nuclear-magnetic interference and chiral scattering contributions are ignored here. The *z*-direction polarization analysis technique can thus be used in diffuse scattering experiments to separate the neutron SF magnetic scattering due to the component of the spin correlations in the plane, and the neutron NSF magnetic scattering due to the component of the spin correlations perpendicular to the plane. In general, the magnetic scatterings cross sections $M^*_{\perp y}M_{\perp y}$ and $M^*_{\perp z}M_{\perp z}$ are not identical, which can in turn provide information on the anisotropy of the magnetic correlations present in the system.

Fig. 1 shows the neutron SF (Fig. 1(a)) and NSF (Fig. 1(b)) contour maps from the *z*-direction polarization analysis of $HoYTi_2O_7$ at 3.6 K. The residual intensities at the nuclear peak positions in the SF scattering are due to finite neutron polarization of the incident neutron beam ($\sim$95% throughout the experiments). The pattern in Fig. 1(a) is similar to the NNSM correlation pattern simulated by Bramwell et al. [9]. Fig. 1(c) shows the SF diffuse pattern of $HoYTi_2O_7$ at 30 mK, which is similar to the pattern simulated using the DSM shown in Ref. [9]. The four intense regions around (0 0 0), the relative intensities of the region around (0 0 3) and (3/2 3/2 3/2), and the spread of the broad features along the diagonal in the diffuse contour maps of a DSM differentiate them from those of the NNSM. These differences in patterns have also been noted by other groups using unpolarized neutron scattering [3,9]. There is no clear pattern in the non-spin flip scattering (see Fig. 1(b))—this is similar to what has been observed by Fennell et al. [17] in $Ho_2Ti_2O_7$. The diffuse scattering pattern in Fig. 1(d) taken at a temperature of 30 mK reveals that antiferromagnetic correlations are present at the zone boundary. A similar pattern is also observed in the data for the undiluted spin ice $Ho_2Ti_2O_7$ (not shown). This indicates that these antiferromagnetic correlations are not a doping effect, but are an intrinsic part of the spin ice. Melko et al. [12] proposed the existence of an ordered state among the 6 possible ice rule ground states in spin ice. Using Monte Carlo simulations, a long-range order state has been predicted at low temperatures [10,12]. At low temperatures the residual energy scales become important and it is necessary to include the full dipolar interaction in order to account for the details of the scattering pattern. This leads to a modification in the spin flip diffuse scattering pattern, the antiferromagnetic correlations in the non-spin flip diffuse scattering pattern, and the peak appearing in heat capacity measurements [9]. Since the correlations in spin ice are long-range dipole–dipole interactions, the system is not sensitive to magnetic defects such as the Y dopants. Nevertheless, the breakdown of dipole–dipole interaction can be expected as more Y is added to the system since the magnetic moments will eventually become isolated by the non-magnetic ions. In order to investigate the effects of doping on the antiferromagnetic correlations in spin ice, a cut along [0 0 ℓ] in non-spin flip scattering is shown in Fig. 2. The intensities are normalized to the maximum intensity around the (0 0 3) position. The relative widths in the different Y compositions do not vary significantly, although the peak is clearly broader for $HoYTi_2O_7$ than for the pure $Ho_2Ti_2O_7$ sample. The non-magnetic defects do not strongly influence the long-range dipolar interactions in the ground state. Further analysis of this data is difficult due to the limited resolution of the diffuse scattering experiments.

Fig. 3 shows the summations of spin flip and non-spin flip diffuse patterns at 30 mK for $Ho_2Ti_2O_7$ (Fig. 3(a)) and $HoYTi_2O_7$ (Fig. 3(b)). No significant differences are observed between these two total diffuse scattering maps, which shows that the Y dilution in this system does not alter the scattering patterns significantly even with $x=1$, i.e. half of the Ho^{3+} spins are removed. The vacancies introduced by Y in each tetrahedron do not relax the ice rules, and thus weaken the spin ice correlations. This result agrees with previous experimental observations on diluted spin ice that the spin ice state is robust against dilution [22,23]. When the diffuse scattering patterns in Fig. 3(a) and (b) are examined closely, the intensity distributions around $\langle 2/3\ 2/3\ 2/3 \rangle$ are found to be more similar to the cluster-like model [14] than the model proposed by Yavors'kii et al. [15].

In conclusion, diffuse neutron scattering with polarization analysis has been carried out to study complex magnetic correlations in single crystals of spin ice $Ho_2Ti_2O_7$ and its Y doped derivatives. For all specimens, the observed SF diffuse neutron scattering patterns are typical of a NNSM at $T > 2$ K, and a DSM below $\sim$2 K. The emergence of a pattern typical of a DSM in the SF channel coincides with the signature of antiferromagnetic correlations along the $(h\,h\,0)$ and $(0\,0\,\ell)$ directions in the NSF scattering. These antiferromagnetic correlations may be the precursor of the predicted long-range order in the spin ice [12]. Up to 50% of non-magnetic Y doping in the spin ice $Ho_2Ti_2O_7$ does not significantly change the diffuse neutron scattering patterns for either the SF or the NSF channels. Further inelastic neutron scattering experiments to probe the residual energy scale in the quasi-degenerate manifold and the antiferromagnetic correlations in the system are under way.

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