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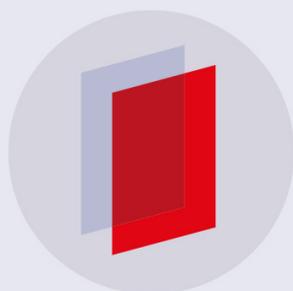
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## Ice rule correlations in stuffed spin ice

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**Abstract.** Stuffed spin ice is a chemical variation of a spin ice material like  $\text{Ho}_2\text{Ti}_2\text{O}_7$  in which extra magnetic ions are inserted into the crystal structure. Previous studies have shown that the degree of stuffing has very little effect on the residual entropy in the system, which takes a value very close to the spin ice entropy. We argue, however, that the observation of this entropy does not imply long range coherence of the ice rules, that determine the local spin configurations. We have characterized deviations from the ice rules by means of a polarized neutron diffraction study of a single crystal of  $\text{Ho}_{2+\delta}\text{Ti}_{2-\delta}\text{O}_{7-\delta/2}$

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with  $\delta = 0.3$ . Our results demonstrate that the ice rules in stuffed spin ice are strictly valid only over a relatively short range, and that at longer range stuffed spin ice exhibits some characteristics of a ‘cluster glass’, with a tendency to more conventional ferromagnetic correlations.

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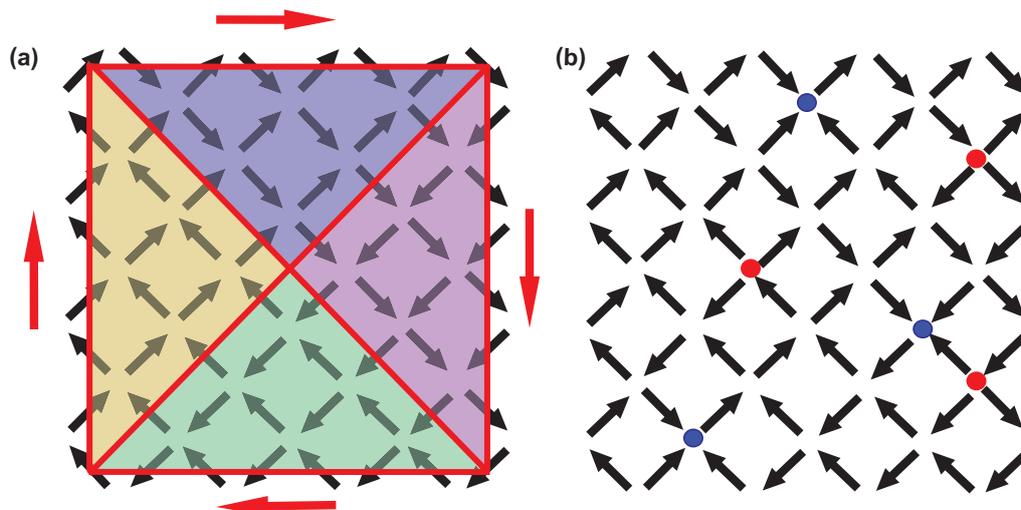
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## 1. Introduction

In the spin ice materials,  $R_2Ti_2O_7$  where  $R = Ho$  or  $Dy$  [1, 2] the rare earth magnetic moments or ‘spins’ populate the pyrochlore lattice of corner-sharing tetrahedra and are orientated along the local  $\langle 111 \rangle$  axes that connect the centres of neighbouring tetrahedra. Effectively ferromagnetic spin–spin interactions, of a largely dipolar nature, stabilize a state in which two spins point into and two point out of any given tetrahedron [1]. This is equivalent to the ice rule that determines proton configurations in water ice, and hence spin ice and water ice both share the Pauling configurational entropy,  $S = R \ln(3/2)$  per mole tetrahedron [2, 3]. Spin ice has proved to be an excellent laboratory for investigating new phenomena such as emergent clustering [4], the Kasteleyn transition [5, 6], magnetic monopoles [7–10] and magnetic current [11].

Stuffed spin ice is a partially disordered variation of pristine spin ice, in which non-magnetic  $Ti^{4+}$  ions are substituted by extra rare earth ions  $R^{3+}$ , with loss of oxide ions for charge balance [12]. Stuffed holmium titanate therefore has the general formula  $Ho_{2+\delta}Ti_{2-\delta}O_{7-\delta/2}$ . Bulk measurements on this material have indicated that the degree of ‘stuffing’ ( $\delta$ ) has surprisingly little effect on the residual entropy in the system [13] which maintains a value very close to the ice entropy [2]. Here we investigate the adherence to the ice rules in a particular realization of stuffed spin ice with  $\delta = 0.3$ , with a view to contrasting it with the pristine system ( $\delta = 0$ ).

Although the ice rules are a local constraint, operating at the length scale of a single tetrahedron, they produce long-ranged correlations with a  $1/r^3$  form [14]. However, it is first worth pointing out that the observation of the characteristic residual entropy does not necessarily imply long-range correlation of the ice rules. It is easy to show by counting the possible two-in, two-out states on small pyrochlore lattices that the majority of the characteristic Pauling entropy is contained in relatively short range correlations. Thus correlation over a single tetrahedron already reduces the paramagnetic spin entropy from  $R \ln(4)$  to  $R \ln(2.4)$  per mole tetrahedron and this decays gradually to the Pauling entropy  $R \ln(1.5)$  as ice rule correlations are extended towards a much longer range. A modification to the ice rule state, such as that caused by ‘stuffing’ can either increase or decrease this component. Hence the entropy is a relatively insensitive measure of long range correlation in the ice rules. Nevertheless, there is a method of characterizing the long-range ice rule correlations using neutron scattering [8, 9, 15]. Using this method, pristine  $Ho_2Ti_2O_7$  spin ice has been shown to exhibit ice rule correlations over many unit cells at low temperature ( $T < 2$  K) [8]. An ice rules correlation length  $\xi_{ice}$  was estimated as the inverse width of a ‘pinch-point’ in the quasistatic neutron scattering function, near to the

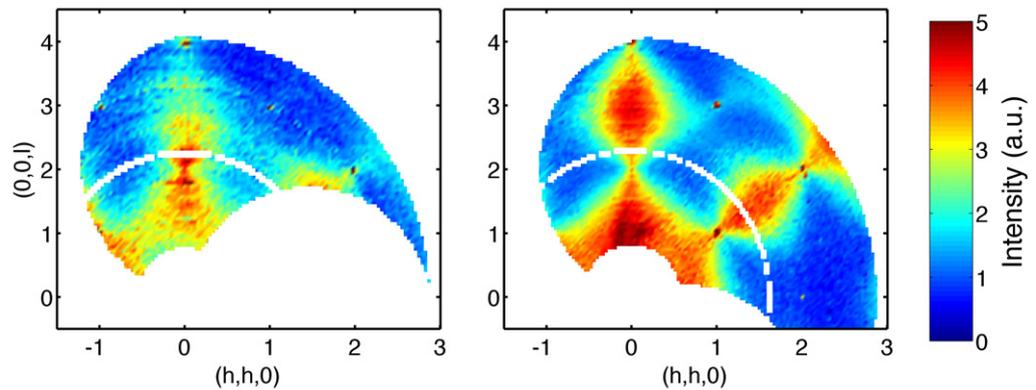


**Figure 1.** A schematic illustrating two types of magnetization fluctuation in spin ice: (a) shows domains (transverse fluctuations) that do not violate the ice rules, while (b) shows ice rule defects (longitudinal fluctuations) or effective ‘magnetic monopoles’.

Brillouin zone centre. The  $(0, 0, 2)$  zone centre was used in order to exploit the perfect systematic absence of nuclear Bragg intensity at that point (which was demonstrated in [8]). In a pyrochlore with chemical disorder, this systematic absence may be violated, making measurement of a very sharp pinch point more difficult, but still possible using polarized neutron scattering [8].

Owing to the partly random and complex nature of chemical substitution in stuffed spin ice, we suggest that a microscopic approach to the problem of ice rule correlations in this material is less likely to be successful than a thermodynamic approach. In work on ferroelectrics Youngblood and Axe [16] proposed a parametrized free energy function, that, when applied to magnetism, effectively interpolates between a pure ice rules system and a conventional ferromagnet in its paramagnetic phase. The parameters essentially tune the free energy cost of transverse and longitudinal fluctuations. Transverse features are interpreted as a domain wall-like fluctuation between ice rule obeying regions which do not necessarily entail an ice rule violation and as such cost little or no energy. A long range ( $q \rightarrow 0$ ) quasi-domain wall for an ideal ice rule system is illustrated in figure 1(a) showing that it can be envisaged as a fluctuation away from a  $q = 0$  ice rules state. Longitudinal defects are instances of non-ice rule obeying vertices [7] as shown in figure 1(b).

We have found the Youngblood–Axe approach to be useful for describing neutron scattering patterns in stuffed spin ice, as described further below. We believe that this represents the first application of Youngblood and Axe’s idea to a magnetic system, and hence stuffed spin ice may be treated as a test case. Our experiments were performed at (bath) temperatures down to 60 mK, and it should be noted that slow spin dynamics are expected at such temperatures, which might raise questions about the validity of a thermodynamic approach. Thus in the case of pristine spin ice, slow spin dynamics are observed below 500 mK, and it is not yet fully understood which degrees of freedom are equilibrated with the thermal bath and which remain out of equilibrium [17–19]. However, lack of perfect equilibrium does not preclude use of the Youngblood–Axe scattering function to analyse and interpret the experimental data: it only calls



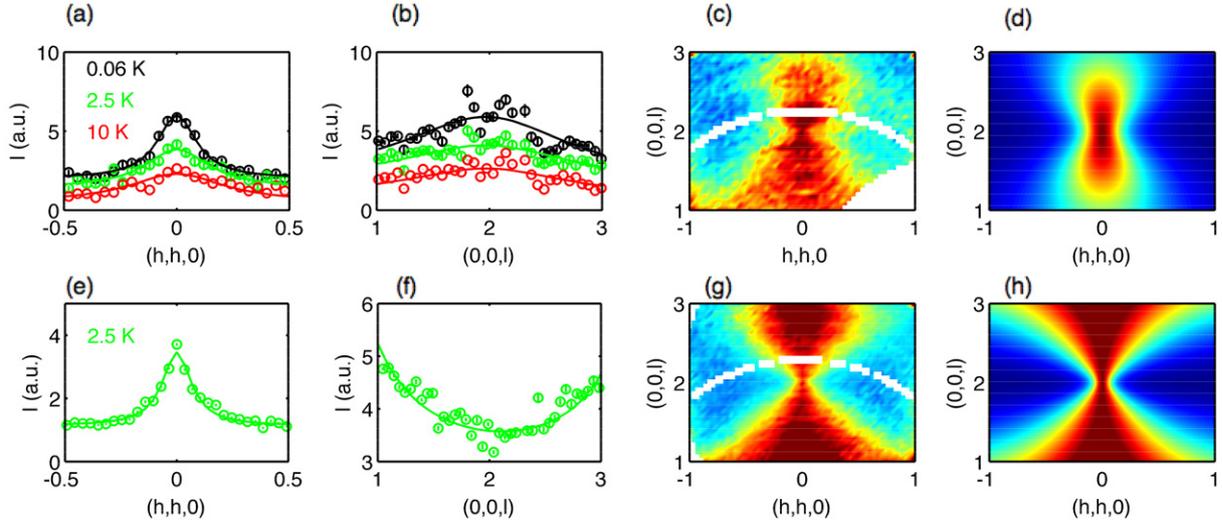
**Figure 2.** Spin-flip scattering datasets at 2.5 K in zero applied field, showing the  $(h, h, l)$  planes in (left) stuffed spin ice and (right) spin ice.

into question whether any derived parameters at the lowest applied temperatures may be treated as equilibrium parameters or not. We return to this point below.

## 2. Results

We have conducted a neutron scattering study of a  $64.1 \text{ mm}^3$  single crystal of  $\text{Ho}_{2.3}\text{Ti}_{1.7}\text{O}_{6.85}$  prepared via the floating zone method with crystallinity checked by Laue x-ray scattering [20]. The crystal structure [12] was confirmed with neutrons at room temperature using the CEA-CRG diffractometer D23, at the Institut Laue–Langevin (ILL), Grenoble. Diffuse magnetic scattering was measured using polarized neutron scattering on the polarization analysis spectrometer D7 [21]. The crystal was aligned such that  $(h, h, l)$  wavevectors formed the scattering plane. The sample was cooled to a base temperature of 0.06 K using a dilution refrigerator. A  $360^\circ$  map of reciprocal space was measured at 0.06 K over approximately 24 h. Polarized neutron scattering was conducted using scans in which the crystal was rotated around its vertical axis by approximately  $90^\circ$  in total. As in [8], only the  $z$  or  $[1, \bar{1}, 0]$  polarization axis was used. This separates the scattering into *spin-flip* and *non-spin-flip* scattering. The spin-flip channel is dominated by magnetic scattering. We found the non-spin-flip diffuse scattering to be featureless, and so we only discuss our results for the spin-flip scattering. We believe that the static approximation was met in our experiment, as a survey of excitations in our samples has not revealed any below 2 meV ( $\delta E \leq 100 \mu\text{eV}$ , not shown). This contrast to the result of Zhou *et al* [22], who found low energy excitations in a powder sample of stuffed spin ice. Scattering maps were taken at 0.06, 0.5, 0.85, 1.7, 2.5, 3.75, 5, 10 and 20 K. Above 0.06 K the scans covered  $90^\circ$  in approximately 5 h with a few minutes between scans. Standard corrections for instrumental background, polarization efficiency and detector efficiency were applied (measurements of an empty cryostat and sample holder, amorphous silica and vanadium foil respectively). The data was corrected for absorption effects arising from the irregular crystal shape, using the method of Busing and Levy [23].

A comparison of spin ice and stuffed spin ice (spin-flip) scattering maps at 2.5 K is shown in figure 2. In particular, both patterns share a ‘six-armed star’ motif that is easily shown to be a consequence of a near-neighbour ice rule correlation on a single tetrahedron, consistent with the observed entropy. The most striking difference is in the scattering at  $(0, 0, 2)$ . In pristine spin



**Figure 3.** Comparison of pinch points and related features in stuffed spin ice (upper row) and spin ice (lower row). Panels (a) and (b) show cuts along  $(h, h, 2)$  and  $(0, 0, l)$ , where the lines represent fits to the data from the theory at 0.06 K (black), 2.5 K (green) and 10 K (red), offset each by 1 unit; panel (c) shows the experimental scattering, while panel (d) shows the scattering calculated using extracted parameters  $C = 1.5 \text{ \AA}^2$  and  $D = 26 \text{ \AA}^2$  for stuffed spin ice at 2.5 K. Panels (e)–(h) show corresponding results for spin ice fitted with  $C = -0.4 \text{ \AA}^2$  and  $D = 121 \text{ \AA}^2$ .

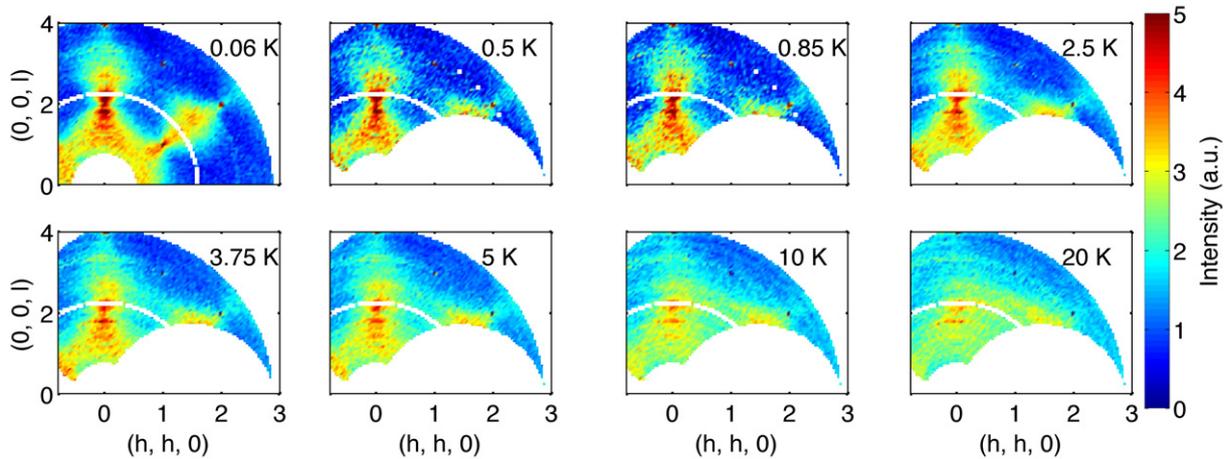
ice this marks a narrow pinch point feature with very small scattering width across  $(h, h, 2)$  while in stuffed spin ice the corresponding feature has a relatively broad width and an enhanced amplitude compared to pristine spin ice.

These data have been fitted to the following function for scattering vectors  $(h, h, 2)$  and  $(0, 0, l)$ :

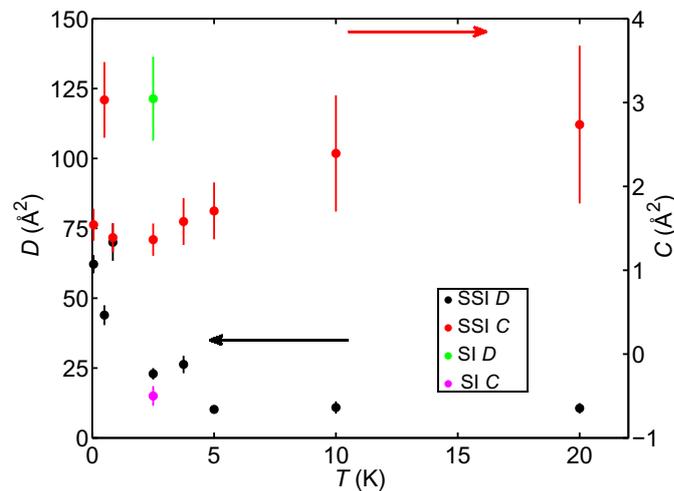
$$S_{yy}(q_x, q_y) \propto \frac{1 + 2(Dq_x^2 + Cq_y^2)}{1 + 2(Dq_x^2 + Cq_y^2) + 2(Cq_x^2 + Dq_y^2) + 4DCq^4}, \quad (1)$$

where  $y$  is perpendicular to the scattering vector ( $x$ ) and polarization ( $z$ ) directions, and  $\mathbf{q} = 0$  refers to the centre of the pinch point (i.e.  $(0, 0, 2)$  in this case). Following Youngblood and Axe [16], the parameters  $C$  and  $D$  are introduced to take into account fluctuations away from the pure ice rules state. One term,  $D[\mathbf{q} \cdot \mathbf{M}(\mathbf{q})]^2$ , accounts for longitudinal defects. It is proportional to  $(\nabla \cdot \mathbf{M})^2$  (where  $M$  is magnetization) and is representative of the energy cost of ice rule violations. The parameter  $D$  is therefore inversely proportional to the density of monopoles:  $D = \infty$  corresponds to a perfect ice rules state. Transverse features are represented by the term  $C[\mathbf{q} \times \mathbf{M}(\mathbf{q})]^2$ . A pure ice rules system has  $C = 0$ , or alternatively fluctuations of this type out of a  $q = 0$  cost zero energy. The two terms dependent on  $D \neq \infty$  and  $C \neq 0$  change the shape of the scattering in different ways. With  $D < \infty$  the scattering is broadened across the narrow axis of the pinch point while for  $C > 0$  the scattering is boosted in the area around the centre of the pinch point, along the broad axis.

Fits to the above scattering function are shown in figure 3. Referring to the figure, the scattering pattern of stuffed spin ice is seen to differ markedly from the spin ice pattern in the



**Figure 4.** Stuffed spin ice:  $(h, h, l)$  scattering plane at 0.1, 0.5, 0.85, 2.5, 3.75, 5, 10 and 20 K. The scattering around  $(0, 0, 2)$  reduces as temperature rises.



**Figure 5.** The values of the extracted quantities as a function of temperature with the stuffed spin ice  $C$  and  $D$  in red and black respectively. The spin ice values of  $C$  and  $D$  obtained using D7 data at 2.5 K are  $-0.4 \text{ \AA}^2$  (magenta) and  $121 \text{ \AA}^2$  (green) respectively.

region near to  $(0, 0, 2)$ . In particular for pristine spin ice  $(0, 0, 2)$  marks a low, narrow saddle point, whereas for stuffed spin ice it marks a peak on a low broad ridge. The temperature dependence of the scattering pattern of stuffed spin ice is shown in figure 4. It can be seen that any remnant pinch point at higher temperature becomes difficult to distinguish as isotropic scattering increases. The increasing width of the ridge with increasing temperature is presumably an increase in the longitudinal defect population [8].

Fitted values of  $C$  and  $D$  for stuffed spin ice as a function of temperature are shown in figure 5, where they are compared to those for pristine spin ice at 2.4 K. In stuffed spin ice the broadening of the pattern at small  $\mathbf{q}$  is represented by the finite values of  $C$  and  $D$ , whereas in pristine spin ice the value of  $D$  is large, and that of  $C$  is close to zero. The value of  $D$  of stuffed

spin ice is less than that of pristine spin ice, showing that long range ice rule correlation is broken up by stuffing. The value of  $C$  for stuffed spin ice is quite large and positive, showing a tendency to ferromagnetic correlations, whereas that for pristine spin ice is small and negative, showing a preference for short range transverse correlations, which may be interpreted as six-spin loops in the spin ice structure.

In general for stuffed spin ice, the finite  $C$  and  $D$  confirm that the long-range ice rule correlations are strongly violated, increasingly so at higher temperatures, and that there is a tendency to more conventional ferromagnetic correlations (i.e.  $C \approx D$ ). Thus a picture of stuffed spin ice emerges as being ice-like at very short range and more like a ‘cluster glass’ at slightly longer range (i.e. a system consisting of frozen ferromagnetic clusters [24]). Nevertheless it should be emphasized that the tendency to ferromagnetic spin correlations in stuffed spin ice is a weak one, and there is no evidence of any long characteristic length scale in this system.

### 3. Discussion and conclusion

While it is probably inaccurate to speak of magnetic monopoles in stuffed spin ice, we may conclude that the presence of monopole-like defects increases as temperature is increased, as reflected in the decrease of  $D$ . It is possible that there is an upper limit on  $D$  corresponding to the fixed separation of extra magnetic moments in stuffed spin ice but we cannot be certain of this. The domain wall population as measured by the  $C$  parameter also appears to reduce as  $T$  is increased (within the caveat of large error bars). However  $C$  is undeniably positive, in contrast to that of pristine spin ice which adopts small negative values upon fitting. This strongly implies that stuffed spin ice is constrained to have many small domains, each of which may locally obey the ice rules, while spin ice is not constrained in this way. This effect in stuffed spin ice may be related to the presence of both long and short ranged pyrochlore ordered regions in the crystal structure [25]. It is possible that the extra magnetic moments in the material exert a local mean field which favours local order, which then terminates at a transverse domain wall. This could be the reason that the  $C$  parameter takes a finite value in this material.

The relatively large value of  $D$  for the spin ice system is expected due to its long-range ice rule behaviour though even the value measured here is probably systematically reduced from its true value [8] owing to the relatively poor instrumental resolution of D7. When  $C = 0$ ,  $\sqrt{2D}$  acts as a defect separation length like  $\xi_{\text{ice}}$  in [8]. Taking the spin ice value of  $121 \text{ \AA}^2$  we find a monopole separation length of  $16 \text{ \AA}$  which is similar to that found by Fennell *et al.* Note that for consistency the ice rule correlation length of [8] must be divided by  $2\pi$  [26] and is thus approximately  $19 \text{ \AA}$ . The continual evolution of  $C$  and  $D$  with temperature implies that the spins are not entirely frozen on experimental time scales down to the lowest temperatures. However this thermal evolution does not necessarily imply thermal equilibrium. Hence at the lowest temperatures our fitted parameters  $C$  and  $D$  may not correspond to equilibrium values.

In previous neutron scattering work on stuffed spin ice Zhou *et al* [22] have found experimental evidence of spin dynamics. Our studies did not reveal these features, but we see no contradiction, as different samples could easily have different properties, and a very detailed comparison of the samples has not been performed. It has been shown conclusively that in fully-doped stuffed spin ice samples of  $\text{Ho}_2\text{TiO}_5$  the rate of reducing the temperature after preparation at high temperature had some effect on the magnetic properties [25] and this could lead to sample-dependent properties. We therefore present our results as a study of a sample produced via the method described in [20].

Our findings contrast with the properties of diamagnetically diluted spin ice, as reported by Chang *et al* [27]. These authors found very little change in the pinch point width upon diamagnetic dilution of spin ice at millikelvin temperatures, but a significant broadening at higher temperature. In contrast we find that in stuffed spin ice broadening extends down to the lowest achievable temperatures and that there is a weak diffuse peak in the scattering along  $(0, 0, 2)$ . This implies qualitatively that the perfect ice rules state is disrupted to a greater degree by ‘stuffing’ than by dilution. This is perhaps not surprising as stuffed spin ice is the more severe modification to spin ice due to both the addition of extra magnetic moments and the disruption of the oxygen lattice. We cannot separate these effects, but it might be possible to do so by doping with niobium to ensure the full complement of oxide ions, as has been achieved for  $\text{Tb}_{2+x}\text{Ti}_{2-2x}\text{Nb}_x\text{O}_7$  [28]. An investigation into the relaxation processes in stuffed spin ice has also been reported [29] which found that it exhibited similar relaxation regimes as a function of temperature to pristine spin ice.

Finally we note that recent work by Benton *et al* [30] has emphasized the importance of the pinch point feature in reflecting possible quantum dynamics in spin ice. In particular the quantum-mechanical flipping of six-spin loops tends to suppress the pinch point. As noted in [30], the neutron structure factor in pristine spin ice is consistent with some degree of quantum dynamics. In fact the negative  $C$  is evidence that short loops are favoured over long ones. In stuffed spin ice the finite  $C$  means short loops are disfavoured, which might be interpreted as a suppression of quantum fluctuations, although there may also be less exotic interpretations [4].

In conclusion, the result of interest in our study of stuffed spin ice is that stuffing clearly alters the nature of the long-range ice rule-correlations. The thermodynamic approach we have adopted here provides a highly consistent picture of spin correlations and entropy in stuffed spin ice. The system obeys the ice rules at short range only, and more closely resembles a cluster glass at long range. It would be interesting to apply these ideas to other disordered spin ices and frustrated magnets obeying the ice rules.

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