Order by Chemical Disorder: Destruction of Moment Fragmentation by Charge Disorder in Nd$_3$ScNbO$_7$

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The question of structural disorder and its effects on magnetism is relevant to a number of spin liquid candidate materials. Although commonly thought of as a route to spin glass behavior, here we describe a system in which the structural disorder destroys a disordered moment fragmentation system resulting in long-range antiferromagnetic order due to local symmetry breaking. Nd$_3$ScNbO$_7$ is shown to have traces of moment fragmentation behavior through polarized and inelastic neutron scattering. However this is shown to only occur on 14.0(2) % of the neodymium ions. The remaining magnetic species order completely into the all-in all-out Ising antiferromagnetic structure. This can be seen as a result of local symmetry breaking due disordered Sc$^{+3}$ and Nb$^{+5}$ ions about the A-site. As the moment fragmentation phenomenon is closely linked to the D$_5$h symmetry, it is proposed that only systems retaining this symmetry, or the reduced D$_3$ symmetry exhibit moment fragmentation. However, the phenomenon of moment fragmentation in magnetic pyrochlore lattices is very robust with respect to chemical structural disorder.

Magnetic disorder induced by structural disorder has been an increasingly important issue in the search for quantum spin liquids. One of the open questions in this field concerns the role that chemical disorder plays in the low temperature magnetic properties of frustrated magnets which can lead to effects that mimic spin liquid behaviour. Naively, one would expect that adding chemical disorder would lead to trivial spin glass behaviour, but even this issue has not been resolved.$^{11}$ Over the last few years, there have been a number of key studies of chemical disorder in quantum spin liquid candidates such as the kagome based Herbstsmithite $^{2,9}$, the triangular lattice YbMgGaO$_4$ $^{4,5}$ and a variety of pyrochlore materials with tetrahedral magnetic sublattices $^{6-8}$. In the latter case, the pyrochlores with mixed nonmagnetic sites are beginning to see a significant amount of investigation, which include the $\text{A}^{+1}\text{A}^{+2}\text{B}_2\text{F}_7$ transition metal pyrochlores $^9$ where A an alkali metal and B is a magnetic transition metal, and the $\text{Ln}_2\text{B}_{+3}\text{B}_{+5}\text{O}_7$ rare earth pyrochlores $^{10,11}$ where B is a transition metal and Ln is a Lanthanide. One of the crucial issues which has not been resolved has been the effect of non-magnetic cation disorder upon the magnetic cations in tetrahedral lattices. This is important not only for the case of the quantum spin liquid, but also for other exotic low temperature ground states such as the quantum spin ice.

The role of chemical disorder in moment fragmentation systems such as Nd$_2$Zr$_2$O$_7$ $^{12}$ and Nd$_3$Hf$_3$O$_7$ $^{13}$ is particularly topical as chemical disorder has been widely studied in these pyrochlores $^{14,15}$. The chemical robustness of this unusual low temperature state in these pyrochlores, in which a large portion of the total moment remains in a gapped dynamic spin ice-like state, $^{16}$ has never been studied until now. This is important not only in the identification of monopole crystallization, which may be nucleated by magnetic defects, but also in unraveling the spectroscopic signature of moment fragmentation - the coexistence of a divergencefull ordering in the elastic portion of the spectrum, and a divergence free part, which remains fluctuating with a dispersionless gap in the spectrum. To address the issue of chemical disorder on the moment fragmentation ground state, we have prepared the mixed B-site pyrochlore Nd$_3$ScNbO$_7$. In this system, the rare earth neodymium fully occupies the 16c site but the 16d site contains a solid solution of Sc$^{+3}$ and Nb$^{+5}$, with no evidence of long-range charge order. Remarkably, we find that even in the limit of severe chemical disorder on the B-site the system shows key signatures of moment fragmentation. Therefore, in the case of moment fragmentation in Kramers doublet systems which allow the dipolar and octupolar components of the moment to transform independently, we show here that chemical
disorder does not play a strong role in the underlying physics at low temperatures. Instead the maintenance of symmetry is required for retaining moment fragmentation, and the destruction of that symmetry, even by next-nearest neighbors, destroys moment fragmentation.

We have prepared the mixed B-site pyrochlore Nd$_2$ScNbO$_7$ through standard solid state synthesis methods. Rietveld refinement of the x-ray powder diffraction patterns have been used to investigate 16c-16d site mixing, with an upper limit of 0.1%. Single crystals were prepared by the optical floating zone method under flowing air. This yields large single crystals (approximately 3 g) of an ideal neodymium pyrochlore sublattice with respect to the A-site and oxygen sites, with a charge disordered non-magnetic B-site. All errors reported herein are reported as one standard deviation unless otherwise stated.

Neutron crystal electric field (CEF) spectroscopy was performed at SEQUOIA (ORNL) on a powder sample of Nd$_2$ScNbO$_7$. To remove phonon interference the non-magnetic structural analog La$_2$ScNbO$_7$ was used as a background subtraction (Fig 1). It is immediately obvious that the crystal fields are not well defined, which is a natural consequence of the heterogeneous local distortions imposed by the charge disorder. A broad inelastic excitation centered around 25 meV energy transfer follows the magnetic form factor (supplemental material) and is assumed to be the result of the 3 very broad excited crystal field doublets overlapping within the region (Fig 1). Another well-developed crystal field doublet appears at 108 meV energy transfer (supplemental material). On top of this large, broad crystal field excitation, four discrete excitations are observed. The excitation labeled $p_1$ is an optical phonon visible in La$_2$ScNbO$_7$ that is not perfectly subtracted (the remainder $e_0$ are crystal fields). The four observable CEF excitations are fit to the $J = 9/2$ ground state manifold for Nd under an assumed hexagonal local symmetry ($D_{3d}$ or $D_d$) which require six crystal field parameters. The crystal field scheme was fit using the Spectre crystal field analysis package. Using the Wybourne description of the crystal field for a hexagonally symmetric system ($D_3$ or $D_{3d}$):

$$H_{CEF} = B_2^0 C_2^0 + B_4^0 C_4^0 + B_6^0 C_6^0 + B_2^3 C_2^3 + B_4^3 C_4^3 + B_6^3 C_6^3$$

The set of parameters were refined to $B_2^0 = -36.36$ meV, $B_4^0 = 442.4$ meV, $B_6^0 = 186.2$ meV, $B_2^3 = 173.7$ meV, $B_4^3 = -66.75$ meV, and $B_6^3 = 118.8$ meV. This results in the crystal field scheme presented in Table 1, which gives a completely Ising moment of 2.0 $\mu_B$.

This idealized crystal field scheme does not account for the large broad crystal field excitation labeled $e_0$ (Fig 1). Comparing the spectral weight of the broad and discrete excitations shows that the discrete crystal fields only comprises 14(2)% of the spectral weight.

![FIG. 1. Electronic excitation spectrum of Nd$_2$ScNbO$_7$ using La$_2$ScNbO$_7$ as a phonon correction, integrated over Q from 2.5-4 Å$^{-1}$. Discrete crystal electric fields are labeled $e_i$ with the broad anomaly labeled $e_0$, $p_1$ is an imperfectly subtracted phonon.](image)

![FIG. 2. Possible local environments of Sc$^{+3}$ and Nb$^{+5}$ that retain a C$_4$ rotation centre, of the possible 2$^4$ configurations. The D3d configurations maintain the crystallographic site symmetry, whereas the D$_3$ configurations have lost inversion. The configuration in the bottom right is enlarged to accommodate labelling that applies to all configurations.](image)
tations originated from the $D_{3d}$ double group of the $D_{3d}$ retaining configurations, which exists for two possible arrangements of Sc$^{3+}$ and Nb$^{5+}$ next nearest neighbor configurations (Fig 2), in which all Sc or all Nb form a hexagon about the A-site. We could assume a statistical distribution of Sc and Nb on the B-site we would expect $1/32$ ($3\%$) of the magnetic ions to retain $D_{3d}$ symmetry; however the two configurations would likely split the CEF excitations. Additionally, grouping of the Sc and Nb ions seems unlikely due to charge repulsion. If, for example, we assume that each tetrahedron has an average +4 charge (two Sc$^{3+}$ and two Nb$^{5+}$) only 0.4 $\%$ of magnetic ions should retain $D_{3d}$ symmetry.

Instead what is likely being observed as discrete excitations in the CEF spectrum are the $D_3$ systems (Fig 2). Under $D_3$ symmetry equation 1 still holds and we should still expect a similar crystal field spectrum to other Nd pyrochlores. The fact that the discrete $e_i$ excitations stand out against the background of Nd ions with various local environments suggests that these discrete excitations originate from the most probable local configuration of ions about Nd.

The $D_3$ configurations appearing well above the statistical expectation of a fully disordered system, is due to the charge repulsion of Sc and Nb ions, as this configuration will provide the least charge repulsion, or potentially the least local strain due to ionic size discrepancies. This demonstrates that there are strong short-range correlations between Sc and Nb ions. If we assume the charge ice rule of two Sc$^{3+}$ and two Nb$^{5+}$ per B-site tetrahedron, giving each tetrahedron a net +4 charge per ion, 17.6 $\%$ of our Nd environments should have the $D_3$ configuration. With 14(2) $\%$ of the Nd ions containing this local environment, it suggests that the system does not have perfect charge ice behaviour but strong correlations approaching charge ice.

The general ice configuration appears in many types of frustrated systems that exist on corner shared tetrahedra. Frustration from bond disorder (covalent or hydrogen bonding) leads to the ice rules within water ice with two bonding and two non-bonding hydrogens on each tetrahedron. Ising ferromagnetic interactions gives rise to the ice rule in spin ice, with two spins pointing into each tetrahedron and two out. Another charge ice system Cd(CN)$_2$ has distortions of the cyanide tetrahedrons toward or away from Cd centres [20]. We believe Nd$_2$ScNbO$_7$ is the first observed case of a solid solution of cations ordering within the ice rules, with two Sc$^{3+}$ and two Nb$^{5+}$ occupying each tetrahedron, albeit with a significant number of defects.

To determine the effect this crystal field level imposes on the magnetic ordering of the system, polarized neutron diffraction was performed on the Diffuse Neutron Spectrometer (DNS) at FRMII. Magnetic Bragg peaks associated with Ising antiferromagnetic order were observed along with a weak signal of diffuse scattering along the (HHH) and (00L) directions consistent with the spin ice structure factor [21]. The moment associated with the Ising antiferromagnetic structure was refined from the total scattering of two equivalent (113) reflections using the SARAh representational analysis [22] and FullProf Suite [23] software packages. The refined moment shows 1.6(2) $\mu_B$ contributing to the antiferromagnetic state, just slightly less than the 2.0 $\mu_B$ available within the crystal field manifold. Even ignoring the crystal field argument due to the disorder present potentially changing the possible moment within the disordered crystal fields, Nd$^{3+}$ has a maximum moment in the ground state J multiplet of 3.27 $\mu_B$. This clearly shows that the antiferromagnetic moment comprises much more than the 0.8 $\mu_B$ of the total 2.5 $\mu_B$ moment seen in Nd$_2$Zr$_2$O$_7$ [24], or the 0.6 $\mu_B$ of the total 2.5 $\mu_B$ seen in Nd$_2$Hf$_2$O$_7$ [25]. Although some reports have reported larger moments [20] this moment of 1.6 $\mu_B$ out of 2.0 $\mu_B$ remains anomalously high.

### Table I. Crystal electric field results for Nd$_2$ScNbO$_7$

| $E_{obs}$ (meV) | $I_{obs}$ | $E_{fit}$ (meV) | $I_{fit}$ | $\pm\frac{1}{2}$ | $\pm\frac{1}{2}$ | $\pm\frac{1}{2}$ | $\pm\frac{1}{2}$ | $\pm\frac{1}{2}$ |
|----------------|----------|----------------|----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0.0            | 0        | 0              | 0        | 0               | 0               | 0               | 0               | 0               |
| 14.6(1)        | 1        | 13.52          | 1        | 0.77            | 0.63            | 0.01            | 0               | 0               |
| 19.9(1)        | 0.5(1)   | 20.92          | 0.46     | 0.85            | 0               | 0               | 0.50            | 0               |
| 27.7(1)        | 0.4(2)   | 28.23          | 0.5      | 0.55            | 0.66            | 0.47            | 0               | 0               |
| 106.5(1)       | -        | 104.86         | -        | 0.30            | 0.38            | 0.86            | 0               | 0               |

FIG. 3. Spin Flip difference scattering with polarization in the [H,-H,0] plane shown on two intensity scales (left and right). The temperature dependance of an antiferromagnetic Bragg peak (220) and the spin ice like diffuse scattering (3/2,3/2,3/2) (bottom left). Spin Flip difference scattering with polarization in the [H,-H,0] plane above the Néel order (bottom right).
Contradicting the nearly fully ordered moment, some evidence of moment fragmentation is clearly seen in the coexisting spin ice like scattering (Fig 3). There exists clear diffuse scattering along the [HHH] and [00L] directions associated with spin ice scattering. True pinch points at (111), and (002) are not observed but this is likely due to the fact that this is an energy integrated spectrum and this scattering is not solely elastic in nature. This scattering feature is also qualitatively much too weak to be comprised of the majority of the total moment, in agreement with the large moment observed on the Bragg peaks.

To confirm the existence of moment fragmentation, energy resolved measurements of the spin ice like scattering are required [12], the Disk Chopper Spectrometer (DCS) [27] at the NCNR was used to obtain low energy inelastic measurements in the [HHL] plane. Powder averaging over a wide [HHH] direction withing the [HHL] plane, the data shows a dispersionless gap (figure 4) characteristic of moment fragmentation. While this feature should contain the spin ice structure factor, the statistics were too poor to resolve the Q dependence completely within the scattering plane. However this is almost certainly the same feature observed with DNS. Integration over [HH0], [HHH] and [00L] high symmetry directions confirm that the scattering is anisotropic, and consistent with spin ice scattering (see supplemental material). Again the weak scattering here is not consistent with a majority fraction of the total moment, but with a much smaller component. The magnon spectrum seen in other fragmentation systems was not observed here, potentially due to the disorder preventing the long-range propagation of magnons.

Considering that moment fragmentation is a direct result of $m_3 = \{0, \frac{2}{3}, \frac{1}{3}\}$ within the $D_{3d}$ double group, it is likely that a break in the local symmetry due to non-magnetic ion disorder can destroy this state, stabilizing a fully ordered Ising antiferromagnet. However our observation of a weak signal due to moment fragmentation demonstrates that some Nd$^{3+}$ ions still undergo moment fragmentation. From the CEF measurements some of the Nd$^{3+}$ ions retain $D_3$ symmetry. As far as we are aware there have not been any reports in the literature discussing dipole-octupole magnetic states under $D_3$ symmetry. However under the symmetry argument presented by Huang [28] it appears that the removal of inversion symmetry should maintain the dipole-octupole symmetry required for fragmentation. The fundamental symmetry requirement of moment fragmentation is that the $x$ and $z$ components of the moment transform like magnetic dipoles and the $y$ component transforms like a magnetic octupole. This provides the two unique exchange components in the magnetic Hamiltonian. This is the case under $D_{3d}$ symmetry with the ground state crystal field doublet having a $m_y$ of $3n/2$ where $n$ is an odd integer. This yields a doublet of $\Gamma^+_5$ and $\Gamma^+_6$. Under these conditions the dipole-octupole doublet transforms like

$$C_3: \tau^{x,y,z} \Rightarrow \tau^{x,y,z}$$
$$\sigma_d: \tau^{x,y} \Rightarrow -\tau^{x,y}, \tau^y \Rightarrow \tau^y$$
$$I: \tau^{x,y,z} \Rightarrow \tau^{x,y,z}$$

as described by Y.P. Huang (2014) [28], and consequently

$$C_2: \tau^{x,z} \Rightarrow -\tau^{x,z}, \tau^y \Rightarrow \tau^y$$

as

$$C_2 = I \otimes \perp \sigma_d$$

An important consequence of these transformation is that $\tau^{x}$ and $\tau^z$ transform dipoles and $\tau^y$ an octupole creating the dipole-octupole doublet and allowing for the moment fragmentation phenomenon. In Nd$_2$ScNbO$_7$, the local B environments that retain $D_{3d}$ symmetry are likely exceedingly rare. Instead a local environment of alternating Sc and Nb ions are proposed as showing moment fragmentation. This causes a symmetry reduction to $D_3$, removing inversion symmetry. However under this symmetry reduction $\Gamma^+_5 \Rightarrow \Gamma_5$ and $\Gamma^+_6 \Rightarrow \Gamma_6$ retain the same symmetry, excluding inversion. With $C_3$ and $C_2$ retained we maintain the distinction of $\tau^y$ as an octupole and $\tau^{x,z}$ as dipoles. Therefore the reduction to $D_3$ symmetry should not prohibit the existence of moment fragmentation.

Following this analysis, this system should nominally exhibit moment fragmentation. However, local distortions induced by the solid state solution of non-magnetic cations break the symmetry requirements for a dipole-octupole ground state which is evidenced by the fact that 1.6(2) $\mu_B$ orders into an Ising antiferromagnet. By CEF spectroscopy we can observe that 14(2) % of Nd ions do in fact retain $D_3$ symmetry. This small fraction of Nd ions are still able to show signatures of moment fragmentation, resulting in a gapped state with a spin ice structure factor, which can be weakly observed in our polarized and time of flight neutron scattering measurements. This moment agrees reasonably well with the moment missing from

FIG. 4. Inelastic spectroscopy at 100 mK with an incident wavelength of 8 Å, obtained along [H,H,H] integrating over ± 0.25 r.l.u along [-2H,H,H] (left), shown also as a cut along energy using $|Q|$ [0,2,1] (right).
the antiferromagnetic Bragg peaks compared to the total crystal electric field moment.

Structural disorder is well known to cause magnetic disorder, such as in spin glasses. Nd$_2$ScNbO$_7$ presents an interesting case where in the case of severe structural disorder, a remnant of the moment fragmentation state still exists at low temperatures. While Nd$_2$ScNbO$_7$ is an extreme example of disorder among the rare earth pyrochlores, this system provides insight into the effect of chemical disorder on disordered magnetic states. Many studies of disorder focus on the missing occupation of magnetic ions from the A-site or addition of magnetic cations to the B-site \[2, 29, 31\]. Equally important are studies of structural distortions that break or maintain symmetry \[3\], and magnetic disorder can be robust against large structural perturbations assuming an appropriate symmetry is maintained. Additionally this study provides insight into the symmetry requirements of moment fragmentation. Fragmentation may occur in systems of $D_3$ symmetry on the pyrochlore lattice, with broken inversion symmetry, the destruction of the local $C_3$ axis allows the system to order into a static Ising antiferromagnet, and these two states may coexist. Additionally our spectroscopic data suggests that Nd$_2$ScNbO$_7$, and likely other charge disordered pyrochlores have charge ice short-range correlations, adding ionic charge ice to the varied types of systems that exhibit ice-like correlations.

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