In the limit of weak disorder including a distribution of exchange interactions spanning HAFM pyrochlore has been studied in the past by in-is predicted to select a coplanar LRO state in the same rochlore Er
thus a rich field of study, with many possible outcomes...induced LRO state of the coplanar
XY spin clusters in a pyrochlore antiferromagnet

K.A. Ross,1,2 J.W. Krizan,3 J.A. Rodriguez-Rivera,2,4 R.J. Cava,3 and C.L. Broholm1,2,5
1Institute for Quantum Matter and Department of Physics and Astronomy, Johns Hopkins University, Baltimore, Maryland 21218, USA
2NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
3Institute for Quantum Matter, Princeton University, Princeton, New Jersey 08544, USA
4Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA
5Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
(Dated: March 17, 2015)

A single crystal of NaCaCoF7 was studied using elastic and inelastic neutron scattering. NaCaCoF7 is a newly synthesized A2B2X7 type pyrochlore, hosting magnetic Co2+ ions on the B-site and mixed non-magnetic Na+/Ca2+ ions on the a A-site. Fluctuating magnetic correlations are present at temperatures well below the antiferromagnetic interaction strength (θCw = -140 K). The Q-dependence of the inelastic intensity indicates local XY-like antiferromagnetic clusters at energies below ~ 2.5 meV, and fluctuating collinear antiferromagnetic clusters above this energy. Below the freezing transition at Tf = 2.4 K, diffuse elastic scattering develops that is consistent with short range XY antiferromagnetism with a correlation length of ~ 16 Å. The relevant XY states arise from a continuously deformable manifold of states. Contrary to well-known models that produce the same continuous manifold, order-by-disorder does not select an ordered state in NaCaCoF7. Instead, we argue that the weak exchange disorder expected to arise from the heterovalent A-site causes the spin system to freeze into short range ordered clusters that explore this manifold spatially and dynamically on long time scales.

The spin liquid state of the Heisenberg antiferromagnet (HAFM) on the pyrochlore lattice supports fluctuations amongst an extensively degenerate ground state manifold consisting of correlated yet disordered spin configurations. This beautiful state of matter arises from a perfect frustration of antiferromagnetic (AFM) interactions on the corner sharing tetrahedra that comprise the pyrochlore lattice. However, the spin liquid is extremely susceptible to small perturbations that can reduce the ground state degeneracy and lower the free energy. The manner in which this spin liquid is modified in real materials with deviations from ideal Heisenberg exchange is thus a rich field of study, with many possible outcomes depending on the relevant perturbations. In particular, the role of fluctuations in selecting subsets of the ground state manifold must often be considered. Thermal and quantum fluctuations that are softer for certain spin configurations can, in some cases, select long range ordered (LRO) states; this phenomenon is called order-by-disorder.

Quenched fluctuations in the strength of the spin-spin interactions can also play a role, and can sometimes compete with thermal fluctuations in selecting low energy spin configurations. For example, thermal and quantum order-by-disorder have been argued to select the non-coplanar LRO state of the XY antiferromagnetic pyrochlore Er2Ti2O7 [3 11 12], while quenched disorder is predicted to select a coplanar LRO state in the same material [4 13]. The role of quenched disorder for the HAFM pyrochlore has been studied in the past by including a distribution of exchange interactions spanning J ± ∆ in the HAFM Hamiltonian, H = ∑ij Jij Si · Sj. In the limit of weak disorder, ∆ << J, where J is the mean exchange interaction, the spins are expected to form locally collinear antiferromagnetic correlations and the system eventually freezes at temperature Tf ≈ ∆ [14]. This model has been discussed in the context of the unconventional spin glass pyrochlore material Y2Mo2O7, where subtle local distortions are argued to create weak exchange disorder [17]. However, the nature of the spin correlations in this system is nebulous even though single crystals having sufficient quality for their detailed study have recently been produced.

Here we report on the nature of static and dynamic spin correlations in the newly discovered pyrochlo
FIG. 2. Temperature dependence of a) elastic ($E = 0.00 \pm 0.25$ meV), and b) energy-integrated ($E < 5.20$ meV) scattering at the (111) Bragg peak. Comparison of the two panels reveals that significant diffuse inelastic scattering exists above $T_f$, which condenses into the elastic window as the temperature is lowered below 5 K. c) Line shape analysis of the lowest temperature data shown in a). The line scan along the [H,H,2H] direction at 1.7 K (scan direction illustrated in the upper left inset, dotted white line) can be fit by the sum of a Gaussian and Lorentzian function. The fitting parameters for the Gaussian were fixed to their values at 14 K. The area and full width at half maximum (FWHM) of the Lorentzian are shown in the upper right inset. The error bars represent one standard deviation.

equally occupied by disordered Na$^+$ and Ca$^{2+}$ ions [20]. Thermodynamic magnetic properties of NaCaCo$_2$F$_7$ [19], point to a spin-freezing transition at $T_f \approx 2.4$ K. The low freezing temperature indicates NaCaCo$_2$F$_7$ is in the limit of weak exchange disorder assuming that $T_f \approx \Delta$, as in the models of [14, 15], and $J \sim 20$ K based on the Curie-Weiss temperature and assuming $S = 3/2$. The effective moment determined from Curie-Weiss analysis at high temperatures is $6.1 \mu_B$; this unusually large moment indicates a high spin state ($S = 3/2$) for Co$^{2+}$ combined with almost the full orbital contribution of the free ion ($\mu_{\text{eff}} = 6.6 \mu_B$ in free Co$^{2+}$). Nonetheless, the change in entropy at low temperatures reported in Ref. 19 approaches $R \ln 2$, suggesting a spin-orbit coupled ground state Kramers doublet with $j_{\text{eff}} = 1/2$, as is often relevant to Co$^{2+}$ materials [21-24]. The degree of anisotropy of the effective moments in NaCaCo$_2$F$_7$ is not yet determined, but magnetization measurements from $T = 2$ to 40 K reveal isotropic behavior up to $\mu_B H = 9$ T [19, 25].

We have studied a 0.87 gram single crystal of NaCaCo$_2$F$_7$ using the MACS II spectrometer at the NIST Center for Neutron Research [26]. The dynamic structure factor, $S(Q, E)$, was measured in the [HHL] reciprocal lattice plane. MACS II is equipped with both a spectroscopic and diffraction detector in each of its 20 channels, allowing the simultaneous collection of energy-analyzed and energy-integrated signals. Two configurations were used for spectroscopic measurements; for low energy transfer scans, neutrons with a final energy $E_f = 3.7$ meV were selected post-sample using vertically focussed pyrolytic graphite analyzers, and BeO filters post-sample were used to remove higher harmonic contamination. For incident energies below (above) $E_i = 5.2$ meV, a Be filter (open channel) preceded the sample. For energy transfers above $E = 8.2$ meV, a fixed $E_f = 5.0$ meV was used with Be filters post-sample and an open channel pre-sample. In all figures, measurements made in these various configurations have been normalized to the same intensity units using a vanadium standard. The energy resolution was $\delta E = 0.25$ meV at the elastic line for $E_f = 3.7$ meV and $\delta E = 0.43$ meV for $E_f = 5.0$ meV.

Below $T_f$, the elastic magnetic scattering is indicative of static short range AFM spin correlations. The subtraction of 14 K from 1.7 K data reveals strong magnetic diffuse scattering [Fig. 3 a)]. The finite energy resolution means that the elastic scans probe spins fluctuating slower than $1.6 \times 10^{-11}$ s. There are two components to the this diffuse scattering; quasi-Bragg peaks (not resolution limited in $Q$, as will be discussed below), in addition to diffuse scattering taking the shape of a zig-zag pattern underlying the peaks. The zig-zag diffuse pattern persists at finite energy transfer; Fig. 3 b) shows the dynamic structure factor at $E = 1.25 \pm 0.25$ meV, and Fig. 4 b) shows that this diffuse pattern persists to approximately 2.5 meV. Above 2.5 meV the diffuse pattern broadens considerably and intensity is shifted to
FIG. 3. Comparison of measured scattering at $T = 1.7\,\text{K}$ (a,b,c) to simulated patterns involving $XY$ and collinear AFM static spin configurations (d,e,f). Measurements show diffuse scattering at $a)\ E = 0.00 \pm 0.25\,\text{meV}$ [nuclear scattering at 14K subtracted, see also Fig. 1], b) $E = 1.25 \pm 0.25\,\text{meV}$, c) $E = 8.25 \pm 0.43\,\text{meV}$. Calculations of magnetic scattering from d) short range correlated cluster of $XY$ AFM order with symmetry $\Gamma_5$ and correlation length 16 Å, e) independent tetrahedron model of 47% $\Gamma_5$ states (α randomly chosen for each tetrahedron) plus 52 % collinear AFM spin configurations (collinear direction randomly chosen for each tetrahedron), and f) independent tetrahedron collinear AFM model.

The quasi-Bragg peaks arise at the $(111), (220)$, and $(113)$ zone centers, but importantly not at $(000), (002)$, or $(222)$ [25]. These absences strongly constrain the frozen spin configuration. Although a short range structure based on collinear antiferromagnetic moments might be expected based on the weak disorder HAFM model, the absence of the $(002)$ quasi-Bragg peak rules out this scenario. The observed magnetic peaks are instead consistent with $XY$ spin configurations, specifically those transforming as the $\Gamma_5$ irreducible representation (IR) of the tetrahedral point group. The $\Gamma_5$ IR admits a continuously deformable manifold of states parameterized by a single angular parameter, $\alpha$, which rotates the spin on each sublattice around its local $<111>$ axis (see Eqn. 4 of the supplementary information [25]).

Above $T_f$, the frozen short range spin configuration melts into a fluctuating, correlated state, i.e. a cooperative paramagnet or thermal spin liquid. This is demonstrated by following the temperature dependence of a scan transverse to the $[111]$ position as a function of temperature (Fig. 2). The elastic scattering (Fig. 2 a) appears at 14 K as a sharp Bragg peak with Gaussian lineshape; this peak arises from the lattice structure and can be taken as a measure of the instrumental $Q$-resolution. Upon cooling, a broad Lorentzian component gradually appears and is well-developed by $T_f$ [27]. The FWHM gradually decreases with decreasing temperature (Fig. 2 c), saturating at 0.1214(8) Å$^{-1}$ which implies a correlation length of 16.10(1) Å. Comparison of the elastic scattering to energy-integrated scattering (Fig. 2 b) shows this broad Lorentzian component is present at $T > T_f$, but resides fully at finite energy transfers. The correlated paramagnetic fluctuations in this cooperative paramagnetic state resemble the low energy fluctuations in the frozen state which are discussed next [25].

Below $T_f$, spin fluctuations can be excited from the frozen configuration. The spectrum of these fluctuations is gapless to within $\delta E = 0.25\,\text{meV}$, and spans all energies up to at least $11\,\text{meV}$ (Fig. 4). The $Q$ dependence of constant $E$ is of interest, as it represents the spatial Fourier transform of spin correlations with a characteristic fluctuation frequency of $\omega = E/\hbar$. The same zig-zag pattern of diffuse scattering which is present under the quasi-Bragg peaks on the elastic line persists to finite energy transfers [Fig. 3 b]. Notably, this entire pattern is gapless; the lowest energy excitations have intensity at wave vectors away from Brillouin zone centers.

This zig-zag pattern appears to be related to rotations between equivalent $XY$ spin configurations in the $\Gamma_5$ manifold; we have compared a constant energy slice at 1.25 meV to the calculated neutron scattering intensity from a spatial average of independent $XY$ tetrahedra in the Supplementary Information [25]. In this approximation, the lattice is conceptually divided into isolated tetrahedral units. On each tetrahedron, one value of $\alpha$ is chosen from the continuous $\Gamma_5$ manifold. While the agreement is not perfect, this independent $XY$ tetrahedra model captures the lack of intensity near the $(002)$ position [25]. A better agreement is obtained, however, when collinear AFM spin components are added to each $XY$ tetrahedron on the level of $\sim 50\%$ [Fig. 3 e)]. This observation indicates that while the frozen state is fully $XY$-like, the low energy (slow) spin fluctuations have both Heisenberg and $XY$ character. At higher energies (fast spin fluctuations), the constant energy slices are best reproduced by fully collinear AFM configurations on independent tetrahedra [Fig. 1 b) and Fig. 3 f)]. An important difference between the simple models proposed here and the real system is that the independent tetrahedra approximation does not appear to be valid at low energies; the widths of the diffuse scattering indicate a correlation length of 3.95 Å (i.e. a correlated region of diameter $\sim 8$ Å) for the slow spin fluctuations
occurs near 2.5 meV. (Integration ranges: a) between the (002) dominated and (111) dominated scattering. The inelastic intensity near (002) decreases as $E_{\text{diffuse}}$ gapless to within $\delta E_{\text{Fermi}}$. 

FIG. 4. Energy vs. $Q$ scattering at $T=1.7$ K. Excitations are diffuse, gapless to within $\delta E \pm 0.25$ meV, and non-dispersive. The inelastic intensity near (002) decreases as $E$ approaches zero (a), while that at (111) increases (b). c) the crossover between the (002) dominated and (111) dominated scattering occurs near 2.5 meV. (Integration ranges: a) [H0H0]: $-0.1 < H < 0.1$ b) [HH0]: $0.0 < H < 1.1$ c) ±0.1 r.l.u. in $H$ and $L$. Errorbars represent one standard deviation.

at 1.25 meV, and even at $T = 14$ K the inverse correlation length of the inelastic scattering is approximately half of that expected for independent tetrahedra. 

The change in the character of spin correlations occurs at a characteristic energy scale of $\sim 2.5$ meV, as revealed by $E$ vs. $Q$ slices in the frozen state (Fig. 4). Intensity at (002) and (111) can be taken as measures of the collinear and $XY$ nature, respectively; the intensity near (002) strongly decreases as energy approaches zero, while that at (111) increases [Fig. 4c]. No dispersive features are observed in the inelastic scattering, which instead retains diffusive character over the entire energy range.

The $\Gamma_5$ IR can be decomposed into two basis vectors which have commonly been called $\psi_2$ (non-coplanar) and $\psi_3$ (coplanar) [25]. The $\Gamma_5$ states are known to be selected in the HAFM model by the inclusion of “indirect” Dzyaloshinskii-Moriya (DM) interactions [7], where an accidental ground state degeneracy admitting all values of $\alpha$ occurs at the mean field level. The same continuously degenerate manifold is also present at the mean field level for the $XY$ AFM pyrochlore model [6, 30], and the $XY$-like anisotropic exchange model proposed for $Er_2Ti_2O_7$ [2, 4, 13]. In all of these models, the degeneracy is lifted by fluctuations, and an ordered ground state is selected; fluctuations can be thermal, quantum, or quenched (i.e. bond disorder). However, in NaCaCo$_2$F$_7$, despite a clear mechanism for bond disorder, the $\Gamma_5$ degeneracy is apparently retained and explored by the system on short length scales and long time scales. In this case, disorder does not lead to order, but instead to a preservation of the continuous $\Gamma_5$ manifold through freezing.

The microscopic reason for the development of $XY$ configurations in NaCaCo$_2$F$_7$ is not yet clear. In $Er_2Ti_2O_7$, $XY$ anisotropy arises directly from the single-ion properties and strong spin orbit coupling. Similarly, the spin orbit coupled $j_{eff} = 1/2$ state expected for Co$^{2+}$ in a distorted octahedral environment could lead to $XY$ anisotropy, either in the $g$-tensor or the exchange interactions, or both. Based on two observations it can be inferred that NaCaCo$_2$F$_7$ is unlikely to have strict $XY$ anisotropy: 1) the magnetization is isotropic up to 9 T [15] [25], and 2) we have shown that the spin fluctuations contain sizable collinear components which would violate perfect $XY$ anisotropy. Indeed, at high enough energies (above 2.5 meV), a crossover to fully collinear fluctuations occurs. This crossover may result from an energy scale at which $XY$ configurations are selected.

The nature of the single-ion magnetism in NaCaCo$_2$F$_7$ is not yet fully understood and should be explored in more detail. Open questions, aside from determining the level of single ion anisotropy, include whether orbital and lattice degrees of freedom are relevant as was shown to be the case in the related spinel compound GeCo$_2$O$_4$ [31].

In summary, NaCaCo$_2$F$_7$ is the first example of a new class of pyrochlore materials based on a spatially uniform sublattice of magnetic transition metal cations surrounded by fluorine anions. The disordered non-magnetic $A$-site is expected to lead to weak disorder in the strong AFM interactions ($\theta_{CW} = -140$ K), an inference supported by the presence of a low temperature freezing transition at $T_f = 2.4$ K. We have observed $XY$ spin configurations forming a short range ordered state below $T_f$ with a correlation length 16 Å, approximately one and a half unit cells. The low energy fluctuations away from this frozen state are gapless to within the energy resolution of our measurement (0.25 meV) and take on a distinctive diffuse pattern that suggests the possibility of zero-energy fluctuations between $XY$ clusters within the continuous manifold of $\Gamma_5$ states. At energies above 2.5 meV, the spin correlations become more like collinear antiferromagnetic tetrahedral fluctuations, indicating a term in the microscopic Hamiltonian which selects $XY$ states below an energy scale of $\sim 30$ K.

The $XY$ spin configurations in NaCaCo$_2$F$_7$ are the same as those selected by various types of order-by-disorder in models relevant to $Er_2Ti_2O_7$ as well as by DM interactions in the HAFM model on the pyrochlore lattice. However, unlike the aforementioned cases, disor-
order in NaCaCo$_2$F$_7$ does not lead to the selection of an ordered state, but instead produces a freezing of the spin system which explores the manifold both spatially and temporally on long time scales. NaCaCo$_2$F$_7$ thus offers a new example to explore the effects of weak disorder, DM interactions, and order-by-disorder on the thermal spin liquid state of the Heisenberg antiferromagnetic pyrochlore lattice.

The authors gratefully acknowledge enlightening discussions with O. Tchernyshyov, J.T. Chalker, and J.W. Lynn. KAR acknowledges the hospitality of the Chemistry and Physics Departments at Colorado State University during the writing of this manuscript. The bulk of the work was supported by the US Department of Energy, office of Basic Energy Sciences, Division of Material Sciences and Engineering under grant DE-FG02-08ER46544. In particular this included the crystal growth activities and neutron scattering experiments. This work utilized facilities supported in part by the National Science Foundation under Agreement No. DMR-0944772. KAR was partially supported by NSERC of Canada.

* Current Address: Colorado State University, Fort Collins, Colorado, 80523

[1] R. Moessner and J. T. Chalker, Physical Review B 58, 12049 (1998).
[2] R. Moessner and J. T. Chalker, Physical Review Letters 80, 2929 (1998).
[3] C. Lacroix, P. Mendels, and F. Mila, *Introduction to Frustrated Magnetism: Materials, Experiments, Theory*, Vol. 164 (Springer, 2011).
[4] J. S. Gardner, M. J. P. Gingras, and J. E. Greedan, Reviews of Modern Physics 82, 53 (2010).
[5] J. D. M. Champion, M. J. Harris, P. C. W. Holdsworth, A. S. Wills, G. Balakrishnan, S. T. Bramwell, E. Čížmár, T. Fennell, J. S. Gardner, J. Lago, et al., Physical Review B 68, 020401 (2003).
[6] M. E. Zhitomirsky, M. V. Gvozdikova, P. C. W. Holdsworth, and R. Moessner, Physical review letters 109, 077204 (2012).
[7] L. Savary, K. A. Ross, B. D. Gaulin, J. P. Ruff, and L. Balents, Physical Review Letters 109, 167201 (2012).
[8] V. S. Maryasin and M. E. Zhitomirsky, Physical Review B 90, 094412 (2014).
[9] A. W. C. Wong, Z. Hao, and M. J. P. Gingras, Physical Review B 88, 144402 (2013).
[10] P. A. McClarty, P. Stasiak, and M. J. P. Gingras, Physical Review B 89, 024425 (2014).
[11] J. Ottmaa, R. R. P. Singh, B. Javanparast, A. G. R. Day, B. V. Bagheri, and M. J. P. Gingras, Physical Review B 88, 220404 (2013).
[12] Though order-by-disorder definitely selects the ground state in the particular bilinear pseudo-spin 1/2 models studied for Er$_2$Ti$_2$O$_7$, there is still some debate as to whether alternative models including the effects of higher CEF levels is more appropriate to this material [32], which select the ground state energetically.
[13] A. Andreanov and P. A. McClarty, arXiv preprint arXiv:1408.7119 (2014).
[14] T. E. Saunders and J. T. Chalker, Physical Review Letters 98, 157201 (2007).
[15] A. Andreanov, J. T. Chalker, T. E. Saunders, and D. Sherrington, Physical Review B 81, 014406 (2010).
[16] L. Bellier-Castella, M. J. P. Gingras, P. C. W. Holdsworth, and R. Moessner, Canadian Journal of Physics 79, 1365 (2001).
[17] J. E. Greedan, D. Gout, A. D. Lozano-Gorrin, S. Derakhshan, T. Proffen, H.-J. Kim, E. Bozin, and S. J. Billinge, Physical Review B 79, 014427 (2009).
[18] H. J. Silverstein, K. Fritsch, F. Flicker, A. M. Hallas, J. Gardner, Y. Qiu, G. Ehlers, A. T. Savici, Z. Yamani, K. A. Ross, et al., Physical Review B 89, 054433 (2014).
[19] J. W. Krizan and R. J. Cava, Physical Review B 89, 214401 (2014).
[20] It is possible that the heterovalent charged species on the A-site could form a correlated “ionic ice” arrangement with pseudo-dipolar correlations, rather than being distributed completely randomly. Such a scenario would have interesting consequences for the magnetic exchange disorder. A similar idea has been explored in the context of mixed magnetic cations on the pyrochlore lattice [33].
[21] I. Maartense, I. Yaeger, and B. M. Wanklyn, Solid State Communications 21, 93 (1977).
[22] L. P. Regnault, P. Burlet, and J. Rossat-Mignod, Physica B 86, 660 (1977).
[23] H. D. Zhou, C. Xu, A. M. Hallas, H. J. Silverstein, C. Wiebe, I. Umegaki, J. Q. Yan, T. P. Murphy, J.-H. Park, Y. Qiu, et al., Physical Review Letters 109, 267206 (2012).
[24] M. Kenzelmann, R. Coldea, D. A. Tennant, D. Visser, M. Hofmann, P. Smeibidl, and Z. Tylczynsky, Physical Review B 65, 144432 (2002).
[25] K. A. Ross, J. W. Krizan, J. A. Rodriguez, R. J. Cava, and C. L. Broholm, Supplementary Information (2015).
[26] J. A. Rodriguez, D. M. Adler, P. C. Brand, C. Broholm, J. C. Cook, C. Brocker, R. Hammond, Z. Huang, P. Hundertmark, J. W. Lynn, et al., Measurement Science and Technology 19, 034023 (2008).
[27] The apparent freezing temperature of a spin glass depends on the timescale of the measurement and we therefore expect the Lorentzian (magnetic) elastic component to develop at $T > T_f$, as observed, since $T_f$ was determined by low frequency ac susceptibility.
[28] The labels for the basis vectors of $\Gamma_5$ are not standardized. For example, in some works these are called $\psi_1$ (coplanar) and $\psi_2$ (non-coplanar), as in Ref. [1].
[29] M. Elhajal, B. Canals, R. Sunyer, and C. Lacroix, Physical Review B 71, 094420 (2005).
[30] J. D. M. Champion and P. C. W. Holdsworth, Journal of Physics: Condensed Matter 16, S665 (2004).
[31] K. Tomiyasu, M. K. Crawford, D. T. Adroja, P. Manuel, A. Tominaga, S. Hara, H. Sato, T. Watanabe, S. I. Ikeda, J. W. Lynn, et al., Physical Review B 84, 054405 (2011).
[32] S. Petit, J. Robert, S. Guitteny, P. Bonville, C. Decorse, J. Ollivier, H. Mutka, M. J. Gingras, and I. Mirebeau, Supplementary Information (2015).
Supplemental Materials: \(XY\) spin clusters in a pyrochlore antiferromagnet

DEFINITION OF STATES IN THE \(\Gamma_5\) MANIFOLD

The sublattices of the pyrochlore lattice are assigned in fractional coordinates as follows:

\[
\begin{align*}
R_0 &= \left( \frac{3}{8}, \frac{3}{8}, \frac{3}{8} \right), & R_1 &= \left( \frac{3}{8}, \frac{1}{8}, \frac{1}{8} \right), \\
R_2 &= \left( \frac{1}{8}, \frac{3}{8}, \frac{1}{8} \right), & R_3 &= \left( \frac{1}{8}, \frac{1}{8}, \frac{3}{8} \right).
\end{align*}
\]

(S1)

(S2)

The moments (vectors) forming the \(\psi_2\) and \(\psi_3\) bases of the \(\Gamma_5\) representation are assigned to these sublattices as:

\[
\begin{align*}
\hat{s}_0 &= (1, 1, 2)/\sqrt{6}, & \hat{s}_0 &= (1, 1, 0)/\sqrt{2} \\
\hat{s}_1 &= (1, 1, 2)/\sqrt{6}, & \hat{s}_1 &= (1, 1, 0)/\sqrt{2} \\
\hat{s}_2 &= (\bar{1}, 1, 2)/\sqrt{6}, & \hat{s}_2 &= (\bar{1}, 1, 0)/\sqrt{2} \\
\hat{s}_3 &= (\bar{1}, \bar{1}, 2)/\sqrt{6}, & \hat{s}_3 &= (\bar{1}, 1, 0)/\sqrt{2}
\end{align*}
\]

(S3)

A general tetrahedral state with the symmetry of \(\Gamma_5\) can be written as a linear combination of these sets,

\[
\vec{\chi}(\alpha) = \cos \alpha \cdot \vec{\psi}_2 + \sin \alpha \cdot \vec{\psi}_3
\]

(S4)

Assigning each “up” tetrahedron in the pyrochlore lattice a state \(\chi\) with a random value of \(\alpha\) constitutes the independent tetrahedron \(XY\) AFM state that is modeled in Figure S2 e). \(\chi(\alpha)\) spans a continuously deformable manifold of \(XY\) states. These are the relevant ground states at the mean field level for the case of \(Er_2Ti_2O_7\) [S1] [S6] or the HAFM model with “indirect” DM interactions [S7].

\[\text{FIG. S1. Basis states of the } \Gamma_5 \text{ IR (Eqn. S3)}\]

\[\text{FIG. S2. Comparison of measured diffuse scattering (a,b,c) to calculations involving } XY \text{ (d,e,f), collinear AFM (j,k,l), and a mixture of the two types (g,h,i) of spin configurations. Diffuse scattering at a) } E = 0.00 \pm 0.25 \text{ meV, b) } E = 1.25 \pm 0.25 \text{ meV, c) } E = 8.25 \pm 0.43 \text{ meV. d),e),f) calculations of magnetic scattering for short range correlated cluster of } \Gamma_5 \text{ } XY \text{ AFM with correlation length } 16 \text{ Å (d) and independent } XY \text{ tetrahedra (e,f). g),h),i) calculations involving tetrahedra with } 50\% \text{ } XY \text{ and } 50\% \text{ collinear AFM components [g] SRO with } 16\text{Å, h}) \text{ independent tetrahedra. j),k),l) calculations involving collinear AFM configurations. Intensities and } Q\text{-ranges in f), i) and l) are rescaled from e), h), and k) to compare to panel c). For the independent tetrahedra models, each diffuse scattering pattern is computed using 50 instances of a } 7 \times 7 \times 7 \text{ unit cell lattice (68600 tetrahedra in total).} \]

SUPPORTING NEUTRON SCATTERING DATA

Here we present additional information obtained from neutron scattering from NaCaCo2F7. Figure S2 shows a more detailed comparison to three choices of models; short range ordered states with 16 Å correlation lengths, and single tetrahedron states with \(XY\) or locally collinear character, or a mixture of these. Fig. S3 a) shows the widths of diffuse features as compared to the independent tetrahedra model, as well as both lower temperature (100 mK) and higher temperature (14 K) inelastic scans. The low energy diffuse inelastic scattering corresponds to a correlated region (∼8 Å) much larger than a single tetrahedron (3.5 Å), at all temperatures measured, from 100 mK to 14 K. Figure S4 a) shows an elastic scan taken with \(E_i = E_f = 13.5 \text{ meV at } T = 1.7 \text{ K (subtracting 14 K scan), revealing diffuse magnetic scattering throughout a larger range of } Q\). Note in particular the absence of a diffuse feature at (222). Figure S3 b) also shows that the inelastic scattering takes on the same pattern in the thermal spin liquid phase (14 K) as it does in the frozen phase (100 mK) (“empty can” background subtractions made in both panels). In Fig. S4 b and c) we show raw elastic scattering data (no subtraction) at \(T = 1.7 \text{ K and } T = 14 \text{ K.} \]
MAGNETIZATION DATA

In order to investigate the possibility of an anisotropic \( g \)-tensor in NaCaCo\(_2\)F\(_7\), magnetization measurements were performed at temperatures above the freezing transition \( (T > 2.4 \text{ K}) \), using the extraction magnetometry technique in a commercial physical properties measurement system. Measurements with the field applied along three different crystallographic axes were compared. The data taken at \( T = 40 \text{ K} \) are shown in Fig. S5 a) and b). Only slight deviations from isotropic behavior are observed at the highest field strengths \( (\sim 9 \text{ T}) \), and these could easily be due to demagnetization effects for crystals having slightly different shapes for the different field orientations. Furthermore, the deviation from isotropic magnetization does not correspond to the expected hierarchy for either \( XY \)-like \([|M_{(110)}| > |M_{(111)}| > |M_{(100)}|]\) or Ising-like \([|M_{(100)}| > |M_{(111)}| > |M_{(110)}|]\) \( g \)-tensors. For example, the magnetization of an ideal pyrochlore paramagnet with an \( XY \)-like \( g \)-tensor is shown in Fig. S5 c), using the equation,

\[
M_\text{\( \alpha \)}(H,T) = g_\text{\( \alpha \)}J_\mu B_\mu (g_\text{\( \alpha \)}\mu B/|H|k_B T),
\]  

where \( H \) is the applied magnetic field, \( g_\text{\( \alpha \)} \) is the average projection of the \( g \)-tensor onto the field direction (averaged over the four sites on the tetrahedron), \( J \) is the effective angular momentum, here taken to be 1/2 since we may assume a spin-orbit coupled Kramers doublet ground state for Co\(^{2+}\), and \( B_\mu \) is the Brillouin function. In Fig. S5 c) an \( XY \)-like \( g \)-tensor was assumed, with \( g_{xy} = 3.6 \) and \( g_z = 3.0 \). Although this equation is not expected to be valid at \( T = 40 \text{ K} \) for NaCaCo\(_2\)F\(_7\), since \( T < \theta_{\text{CW}} \), one may expect the same hierarchy of magnetization strengths to be observed, even in such a correlated paramagnetic regime. Thus, at least to within the demagnetization effects in these measurements, the \( g \)-tensor anisotropy in NaCaCo\(_2\)F\(_7\) is shown to be small on average.

---

[S1] J. D. M. Champion, M. J. Harris, P. C. W. Holdsworth, A. S. Wills, G. Balakrishnan, S. T. Bramwell, E. Čížmár, T. Fennell, J. S. Gardner, J. Lago, et al., Physical Review B 71, 094420 (2005).
[S2] M. E. Zhitomirsky, M. V. Gvozdikova, P. C. W. Holdsworth, and R. Moessner, Physical review letters 109, 077204 (2012).
[S3] L. Savary, K. A. Ross, B. D. Gaulin, J. P. Ruff, and L. Balents, Physical Review Letters 109, 167201 (2012).
[S4] V. S. Maryasin and M. E. Zhitomirsky, Physical Review B 90, 094412 (2014).
[S5] A. W. C. Wong, Z. Hao, and M. J. P. Gingras, Physical Review B 88, 144402 (2013).
[S6] P. A. McClarty, P. Stasiak, and M. J. P. Gingras, Physical Review B 89, 024425 (2014).
[S7] M. Elhajal, B. Canals, R. Sunyer, and C. Lacroix, Physical Review B 71, 094420 (2005).
FIG. S4. a) Elastic scattering at 1.7 K (14 K subtracted) taken with \( E_i = E_f = 13.5 \) meV. Pyrolytic graphite filters were used before and after the sample. Rings are due to an imperfect subtraction of the aluminum powder lines arising from the sample mount. b) Raw elastic data at 1.7 K (no subtraction) using \( E_f = 3.7 \) meV c) raw elastic data at 14K using \( E_f = 3.7 \) meV.

FIG. S5. Magnetization vs. magnetic field applied along three crystallographic directions. a), b) Magnetization data for a single crystal of NaCaCo\(_2\)F\(_7\) at \( T = 40 \) K. b) Slight differences in magnetization for the three directions can be seen high fields, but the hierarchy of magnetization does not correspond to the expectations for XY-like or Ising-like g-tensors. c) Calculation for an ideal pyrochlore paramagnet (Eqn. S5) with \( g_{xy} = 3.6 \), \( g_z = 3.0 \), \( J = 1/2 \), and \( T = 40 \) K.