

**NaCaNi<sub>2</sub>F<sub>7</sub>: A frustrated high-temperature pyrochlore antiferromagnet with  $S = 1$  Ni<sup>2+</sup>**

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NaCaNi<sub>2</sub>F<sub>7</sub> is an insulating, frustrated A<sub>2</sub>B<sub>2</sub>F<sub>7</sub> pyrochlore with magnetic  $S = 1$  Ni<sup>2+</sup> on the pyrochlore B site. Nonmagnetic Na and Ca are disordered on the A site. Magnetic susceptibility measurements made on an oriented single crystal, grown in a floating zone furnace, show isotropic behavior at temperatures between 5 and 300 K, with an effective moment of 3.7  $\mu_B$ /Ni. Despite displaying a large Curie-Weiss theta (−129 K), spin-ordering-related features are not seen in the susceptibility or specific heat until a spin glass transition at 3.6 K. This yields an empirical frustration index of  $f = -\theta_{CW}/T_f \approx 36$ . The spin glass behavior is substantiated by a shift of the freezing temperature with frequency in the ac susceptibility, bifurcation in the dc susceptibility, and by a broad maximum in the magnetic specific heat. The observations as made on large single crystals suggest that NaCaNi<sub>2</sub>F<sub>7</sub> is likely a realization of a frustrated spin 1 pyrochlore antiferromagnet with weak bond disorder.

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**I. INTRODUCTION**

The lattice of corner-sharing metal atom tetrahedra in pyrochlores is one of the well-known magnetic motifs where nearest neighbor antiferromagnetic interactions cannot be strictly satisfied, and as a result, rare earth (*R*) pyrochlores have been intensely studied as model geometrically frustrated magnets. Research has focused on those with Ti and Sn on the nonmagnetic sites and especially on the R<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> pyrochlores due to the availability of large single crystals grown by the floating zone method. These oxide pyrochlores host different low-temperature phenomena such as long range ordered spin ice, spin glass, and spin liquid ground states [1,2]. The low magnetic coupling strengths in *R* pyrochlores add complexity to the modeling and measurements, as small perturbations in structural characteristics can often have significant effects on the magnetic ground states, which manifest at low temperatures. Using the R<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> pyrochlores as inspiration, we seek analogous systems based on magnetic transition elements due to their potentially larger magnetic interactions. This has motivated us to resurrect the little known fluoride pyrochlores of the A<sup>+</sup>A<sup>2+</sup>B<sub>2</sub><sup>2-</sup>F<sub>7</sub> type; very few fully fluorine-based pyrochlores are known [3,4], and fewer still have been grown as single crystals and characterized [4,5].

The experimentally determined frustration index ( $f$ ) is expressed as  $f = -\theta_{CW}/T_f$ , where  $\theta_{CW}$  is the Weiss temperature and  $T_f$  is the temperature where an ordering-related feature is observed by susceptibility or specific heat. The frustration index is frequently employed as an empirical one-parameter indication of the degree of magnetic frustration in a system [6]. Here we report our characterization of cm-scale NaCaNi<sub>2</sub>F<sub>7</sub> single crystals, which show a large moment of 3.7  $\mu_B$ /Ni, a high Curie-Weiss theta (−129 K), and no spin freezing until 3.6 K, yielding a frustration index of 36. While the moment is large, it is still well below what would be possible if the full orbital contribution for Ni<sup>2+</sup> is present (5.59  $\mu_B$ /Ni). Specific heat measurements show that a substantial amount of the spin entropy is released at the 3.6 K transition, indicating a large majority or all of the spins participate in the spin glass ordering.

Structurally, Na and Ca are found to be fully disordered on the A site of the pyrochlore with the Ni and F sublattices fully ordered. The magnetic properties observed for NaCaNi<sub>2</sub>F<sub>7</sub> suggest that the A site disorder likely induces weak bond disorder in the Ni-Ni interactions. This type of bond disorder has been described theoretically and is expected to precipitate a spin glass state under the circumstances found in NaCaNi<sub>2</sub>F<sub>7</sub> [7–9]. Bond disorder has similarly been proposed to explain the enigmatic properties of the nominally structurally ordered 4d metal oxide pyrochlore Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> [10]. In the fluoride systems, the origin of the bond disorder (the Ca/Na mixing) appears to be far clearer.

In many other materials commonly referred to as pyrochlores, the “pyrochlore network” designation refers to the arrangement of the magnetic cations only, with the remainder of the structure quite different from that of a traditional pyrochlore—thus these compounds are not ideally analogous to the R<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> materials or the fluorides studied here [11,12]. While single crystals are available of Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>, other transition-metal-based traditional oxide pyrochlores, many of which show antiferromagnetic interactions and exhibit glassy behavior, are not available as large single crystals and do not show the same level of frustration as the fluorides [10,13–15]. There is theoretical interest in the FeF<sub>3</sub> pyrochlore, but unfortunately the methods employed for its synthesis likely preclude the growth of this material as large single crystals [14,16,17]. In contrast, the  $S = 1$  NaCaNi<sub>2</sub>F<sub>7</sub>,  $S = 3/2$  NaCaCo<sub>2</sub>F<sub>7</sub>, and NaSrCo<sub>2</sub>F<sub>7</sub> fluoride pyrochlores have now been grown as centimeter-scale single crystals, suggesting that transition metal fluorides have the potential to develop into a significant and readily accessible new family of geometrically frustrated magnets [4,5].

**II. EXPERIMENTAL**

Large single crystals of NaCaNi<sub>2</sub>F<sub>7</sub> were grown by a modified Bridgman-Stockbarger method [18,19] in an optical floating zone furnace. Elemental fluorides were prereacted in a custom-built alloy 400 reactor in an atmosphere of anhydrous HF and argon. Throughout the synthetic procedure, air and moisture were rigorously excluded due to the hygroscopic nature of NiF<sub>2</sub>. The structural characterization of NaCaNi<sub>2</sub>F<sub>7</sub>

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was carried out at 100 K by single crystal x-ray diffraction. See Supplemental Material [20] for additional details regarding the growth of single crystals, single crystal structure determination, and tabulated structural parameters [21–24]. Temperature dependent dc susceptibility measurements were carried out in a superconducting quantum interference device (SQUID) equipped Quantum Design Magnetic Property Measurement System (Model MPMS XL-5). Field dependent dc susceptibility measurements, ac susceptibility measurements, and heat capacity measurements were made in a Quantum Design Physical Property Measurement System (PPMS). All magnetization measurements used the same oriented single crystal. The heat capacity was extracted by the heat relaxation method on a 7.1 mg single crystal. The crystal platelet used was mounted with Apiezon-N grease on a nonmagnetic sapphire stage. Low-temperature heat capacity measurements utilized the Quantum Design  $^3\text{He}$  insert. The heat capacity of nonmagnetic  $\text{NaCaZn}_2\text{F}_7$  [5] was subtracted from that of  $\text{NaCaNi}_2\text{F}_7$  to estimate the magnetic heat capacity.

### III. RESULTS AND DISCUSSION

An image of the single crystal that was sectioned and employed in this study is shown in Fig. 1; its light green color is characteristic of insulating  $\text{Ni}^{2+}$  compounds. Figure 1 also shows the  $0kl$  plane of the  $Fd-3m$  reciprocal lattice of a  $\text{NaCaNi}_2\text{F}_7$  crystal obtained at 100 K, which is fully consistent with what is expected for the classical pyrochlore structure; the observed reflections indicate that there is no long-range

ordering of Na and Ca on the A site. The quantitative structure refinements indicated that the stoichiometry was within error of the expected  $\text{NaCaNi}_2\text{F}_7$  and no A-B site mixing (i.e., stuffing or antistuffing) was detectable within an error of 1%. The only variable structural parameter in the pyrochlore structure describes the position of the framework fluorine ion. This parameter,  $x = 0.3303(2)$  for  $\text{NaCaNi}_2\text{F}_7$ , reflects  $\text{NiF}_6$  octahedra with six equal Ni-F bond lengths of 2.0 Å with F-Ni-F bond angles, 83.2° and 96.8°, that deviate somewhat from the ideal 90° value. In the lower panel of Fig. 1, a powder-diffraction pattern from a ground single crystal shows a characteristic pyrochlore pattern, in excellent agreement with a calculated pattern from the structural model determined by single-crystal x-ray diffraction. Diffraction experiments on finely ground powders from the single crystals exposed to laboratory air for a few days (not shown) indicate changes in diffracted peak intensity, suggesting decomposition of the samples on exposure to moisture in the air. No degradation was detected in the single crystals over the course of months, however, it was likely due to their small surface to volume ratio. As a precaution, crystals were stored in a desiccator.

The temperature dependent bulk dc susceptibility of  $\text{NaCaNi}_2\text{F}_7$  is presented in Fig. 2. The applied field ( $H$ )-dependent magnetization ( $M$ ) at 2 K (upper inset) shows a linear response up to  $\mu_0 H = 9$  T with no signs of saturation. The susceptibility was therefore defined as  $M/H$  for  $\mu_0 H = 0.2$  T. The lower inset shows the susceptibility data of a single crystal with the field applied in the [100], [110], and [111] directions. The observed susceptibilities are equal, within

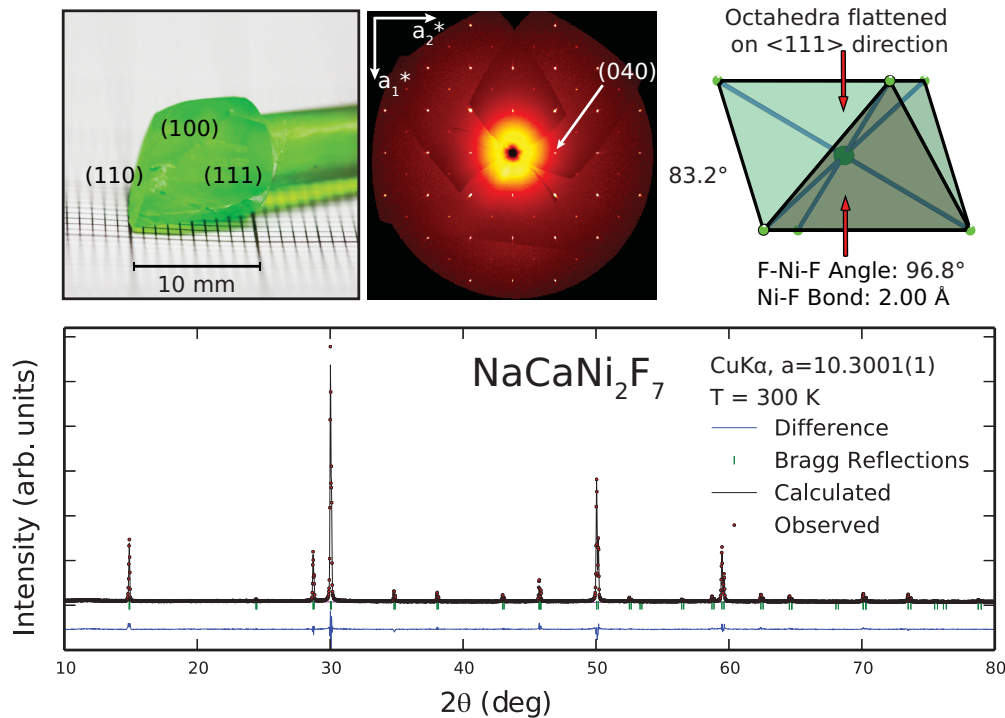


FIG. 1. (Color online) Top left panel: Oriented single-crystal boule of  $\text{NaCaNi}_2\text{F}_7$  used in this paper, with the indexed faces labeled. Top middle panel: Single-crystal precession image of the  $(0kl)$  reciprocal lattice plane for  $\text{NaCaNi}_2\text{F}_7$  at 100 K. No superlattice reflections are seen, indicating the absence of Na-Ca long-range ordering. Top right panel:  $\text{NiF}_6$  octahedra in  $\text{NaCaNi}_2\text{F}_7$  are slightly distorted along  $(111)$ , with equivalent bond lengths of 2.0 Å but F-Ni-F bond angles of 83.2° and 96.8°. Bottom panel: Powder-diffraction data showing that the bulk material of the crystal boule is an  $\text{A}_2\text{B}_2\text{F}_7$  pyrochlore. The pattern fits the calculated pattern from the structure model determined by single crystal diffraction. The unit cell is 10.3001(1) Å at 300 K. Green ticks show the expected peak positions.

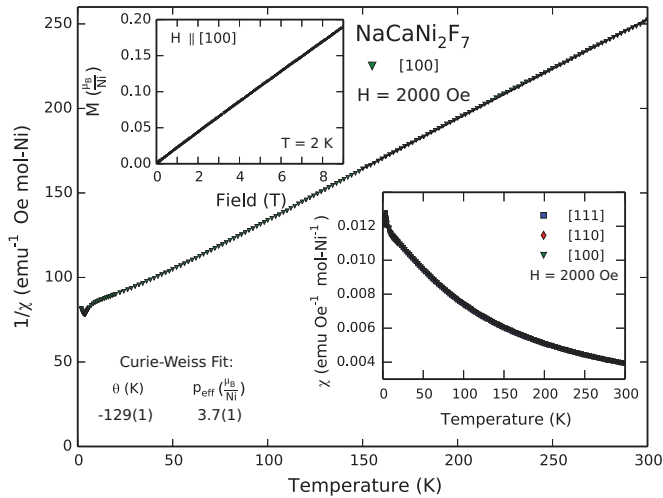


FIG. 2. (Color online) Top inset: Field-dependent dc susceptibility at 2 K with the field applied along the [100] crystallographic direction. The magnetization was measured with both increasing and decreasing field, and no hysteresis was observed. Bottom inset: Temperature-dependent dc susceptibility with a field of 2000 Oe applied parallel to the [100], [110], and [111] crystallographic directions, indicating isotropic behavior. Main panel: Inverse susceptibility and Curie-Weiss fit to the [100] data. Despite the large  $\theta_{\text{CW}} = -129$  K, no spin freezing is seen until 3.6 K.

experimental error, as is expected for a second rank tensor property in this space group. For the sake of clarity, the inverse susceptibility of only the [100] direction is therefore given in the main panel. The Curie-Weiss law ( $\chi = C/T - \theta$ ) is fit from 150 to 300 K. The fit shows a large effective moment,  $p_{\text{eff}} = 3.7$ , for  $S=1$  Ni<sup>2+</sup>, indicating the presence of a significant, but not maximum, orbital contribution [25]. The Curie-Weiss temperature of  $-129$  K indicates strong antiferromagnetic interactions, but no features are seen in the susceptibility until roughly 3.6 K. This yields a frustration index of 36.

By rearranging the Curie-Weiss law ( $\chi = C/T - \theta$ ) to  $C/(\chi|\theta|) = T/|\theta| - 1$ , it is possible to create a normalized, dimensionless plot that is useful for comparing the magnetic behavior of related materials [26]. In Fig. 3, ideal antiferromagnets would follow the line  $y = x + 1$  (shown as a dashed line), with indications of magnetic ordering on the order of  $T/|\theta| \approx 1$ . Using this representation, the magnetic behavior of NaCaNi<sub>2</sub>F<sub>7</sub> is compared to NaCaCo<sub>2</sub>F<sub>7</sub> [5]. The results of the Curie-Weiss fits are given in the upper left for reference. Looking at the middle of the main panel, it is evident that both materials follow ideal Curie-Weiss behavior (dashed line) very closely at higher temperatures. NaCaNi<sub>2</sub>F<sub>7</sub> may show a very slight ferromagnetic deviation from Curie Weiss behavior between 0.5 and 1.0 ( $T/|\theta|$ ). As highlighted in the inset, both materials deviate from Curie Weiss behavior at temperatures below 0.25 ( $T/|\theta|$ ) but in opposite directions. This difference suggests that at temperatures just above the spin glass ordering, the low-temperature magnetic behavior for the  $S = 1$  Ni pyrochlore is significantly different from that of the  $S = 3/2$  Co<sup>2+</sup> pyrochlores, despite the other similarities of the Ni and the Co  $S = 3/2$  fluoride pyrochlore systems.

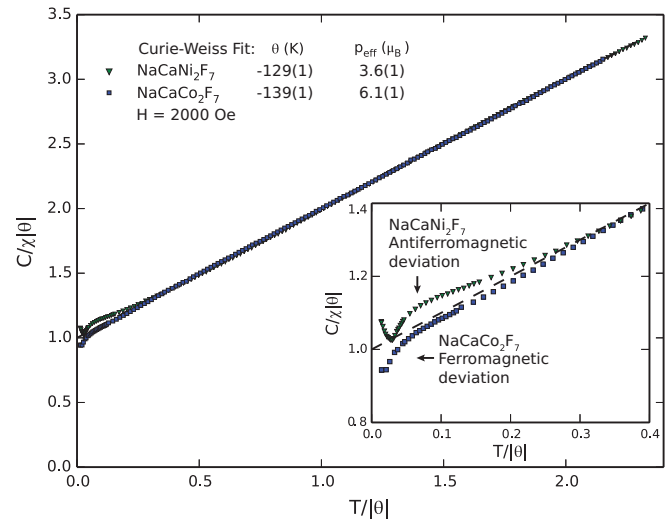


FIG. 3. (Color online) A dimensionless, normalized plot of the magnetization to compare the behavior of NaCaNi<sub>2</sub>F<sub>7</sub> to NaCaCo<sub>2</sub>F<sub>7</sub> (Ref. [5]) based on the normalized Curie-Weiss behavior,  $C/(\chi|\theta|) = T/|\theta| - 1$ . The main panel shows that both materials follow Curie Weiss behavior to low temperatures. The inset highlights the low  $T/|\theta|$  region near the transitions. Here NaCaNi<sub>2</sub>F<sub>7</sub> shows an antiferromagnetic deviation from ideal behavior, and NaCaCo<sub>2</sub>F<sub>7</sub> shows a smaller ferromagnetic deviation from ideal behavior.

To further characterize the behavior of NaCaNi<sub>2</sub>F<sub>7</sub>, it is helpful to look in more detail at the low-temperature susceptibility, shown in Fig. 4. The upper panel shows the temperature-dependent ac susceptibility under an applied field of 20 Oe and a variety of excitation frequencies (10 and 50 Hz omitted for clarity). No additional features were observed in the ac susceptibility between 5 and 300 K (not shown). A systematic upward temperature shift in the spin freezing is seen with increasing frequency ( $\omega$ ). This, in conjunction with the dc susceptibility shown in the middle panel, is a strong indication of the presence of a glassy transition in the magnetic system.

The dc susceptibility shows significant bifurcation between the zero-field-cooled and field-cooled data with an applied field of 200 Oe. This 3.6 K maximum in the dc susceptibility is an estimate of the freezing temperature ( $T_f$ ) and is used to calculate the frustration index mentioned above. From the AC susceptibility measurements, the expression  $\frac{\Delta T_f}{T_f \Delta \log \omega}$  is useful for characterizing the spin glass (and can be used for spin-glasslike materials [27–29]). A value of 0.024 is obtained for NaCaNi<sub>2</sub>F<sub>7</sub>, which, like the Co<sup>2+</sup> fluoride pyrochlores, falls into the range expected for an insulating spin glass [27,28]. The value for the current material is slightly lower than 0.029 (NaCaNi<sub>2</sub>F<sub>7</sub>) and 0.027 (NaSrCo<sub>2</sub>F<sub>7</sub>) [4,5]. Despite the presence of different magnetic ions, all three are very close. The spin glass behavior can be further parameterized by fitting the shift in the ac susceptibility to the Vogel-Fulcher law,  $T_f = T_0 - \frac{E_a}{k_b} \frac{1}{\ln(\tau_0 f)}$ , which relates the freezing temperature and frequency to the intrinsic relaxation time ( $\tau_0$ ), the activation energy of the process ( $E_a$ ), and the ideal glass temperature ( $T_0$ ) [27,30,31]. The NaCaNi<sub>2</sub>F<sub>7</sub> fit is compared to that of NaCaCo<sub>2</sub>F<sub>7</sub> in the bottom panel of Fig. 4 [5].  $T_f$

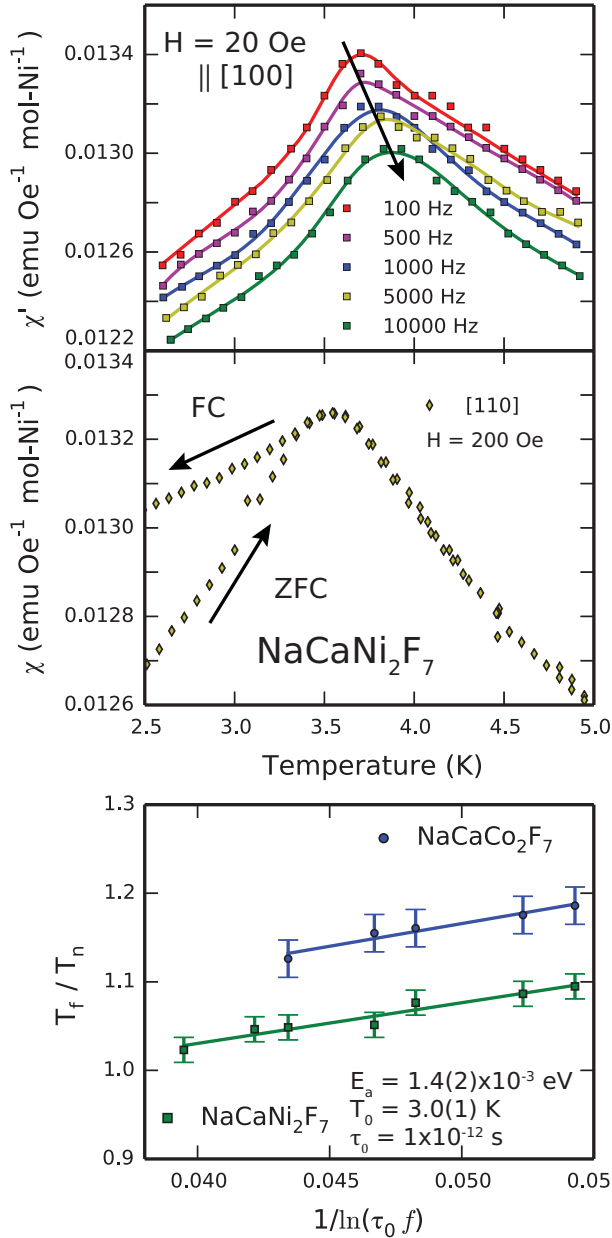


FIG. 4. (Color online) Top panel: Frequency dependence of the AC susceptibility in an applied field of 20 Oe. Lines are a guide to the eye. Middle panel: Bifurcation in the DC susceptibility with an applied field of 200 Oe between the zero-field-cooled and field-cooled data. Bottom panel: Parameterization of the shift in the AC susceptibility by fitting the frequency-dependent freezing temperature to the Vogel-Fulcher law. The fit is also shown for NaCaCo<sub>2</sub>F<sub>7</sub> (Ref. [5]). To aid in comparison, the y axis is scaled by the freezing temperature, as determined by the maximum in the DC susceptibility.

on the y axis is scaled by the freezing temperature found from the DC susceptibility in order to compare the materials on the same scale. Given the very small temperature shift and the limited number of data points, a meaningful fit to all three parameters could not be obtained for NaCaNi<sub>2</sub>F<sub>7</sub>. Thus,  $\tau_0$  was set to a physically meaningful value of  $1 \times 10^{-12}$  s for direct comparison to NaCaCo<sub>2</sub>F<sub>7</sub> and  $1.4(2) \times 10^{-3}$  eV [4,5]. Values of  $1.4(2) \times 10^{-3}$  eV and 3.0(1) K were found for  $E_a$  and  $T_0$ ,

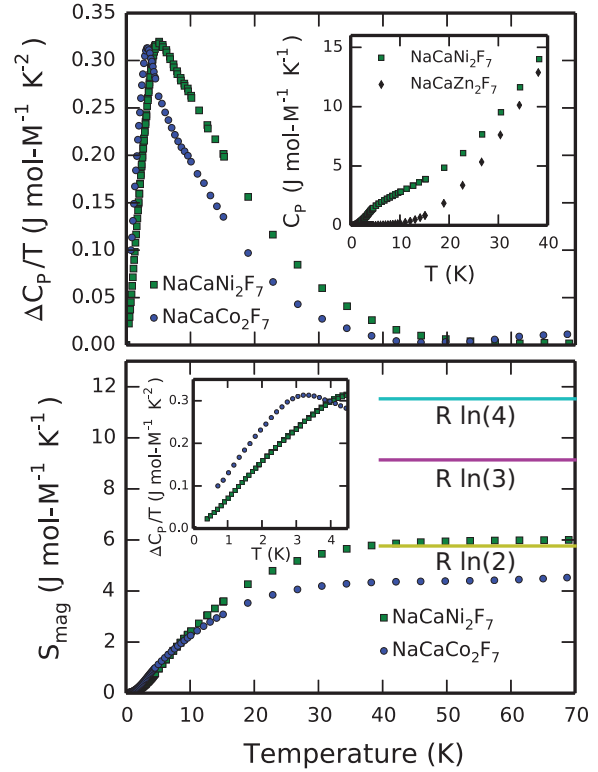


FIG. 5. (Color online) The heat capacity, scaled per mol of the B site cation ( $M$ ). The inset to the top panel shows the raw heat capacity of NaCaNi<sub>2</sub>F<sub>7</sub> and the nonmagnetic analog NaCaZn<sub>2</sub>F<sub>7</sub> (Ref. [5]) (scaled, used for subtraction to yield the magnetic heat capacity). Middle panel: Compares NaCaNi<sub>2</sub>F<sub>7</sub> to NaCaCo<sub>2</sub>F<sub>7</sub> (Ref. [5]). In the bottom panel, the entropy from the magnetic heat capacity is compared to the two state [ $R \ln(2)$ ] and Heisenberg [ $R \ln(2S + 1)$ ] limits. Inset: Temperature dependence of the heat capacity below the spin-freezing transition shows roughly  $C(T) \propto T^2$  behavior for NaCaNi<sub>2</sub>F<sub>7</sub> and curvature in the heat capacity of NaCaCo<sub>2</sub>F<sub>7</sub>.

respectively. The activation energy is very close to the other reported fluoride pyrochlores, and, as expected, the ideal glass temperature is slightly lower than the temperature observed in the dc susceptibility [27]. A visual comparison of the fits shows the similarity of the materials. NaCaNi<sub>2</sub>F<sub>7</sub> has a slightly higher activation energy, and on a relative scale of  $T_0/T_N$ , the ideal glass temperature is lower. More precise measurements and further characterization are required to more accurately understand these subtle differences.

The magnetic heat capacity of NaCaNi<sub>2</sub>F<sub>7</sub> yields further insight. The inset of the top panel of Fig. 5 shows the raw heat capacity of NaCaNi<sub>2</sub>F<sub>7</sub> and the previously reported nonmagnetic analog NaCaZn<sub>2</sub>F<sub>7</sub> [5]. The nonmagnetic analog was scaled down by 10.5%, which is more than for the Co analogs, to approximate the phonon contribution of NaCaNi<sub>2</sub>F<sub>7</sub>. The raw heat capacity shows that NaCaNi<sub>2</sub>F<sub>7</sub> diverges significantly from the nonmagnetic analog near the spin freezing transition. Through subtraction, this difference translates to the magnetic heat capacity peak in the top panel of Fig. 5. There are no additional features at high temperature, and so this information was omitted for clarity. The figure shows that the heat capacities at the peaks in NaCaCo<sub>2</sub>F<sub>7</sub> and

NaCaNi<sub>2</sub>F<sub>7</sub> are roughly equivalent, but the peak in the latter is significantly broader and extends to higher temperatures [5]. Both materials show a saturation of the magnetic heat capacity by roughly 40 K. Integrating  $C_p/T$  yields an estimate of the magnetic entropy freezing out in the transition (lower panel). The value for NaCaNi<sub>2</sub>F<sub>7</sub> is close to that expected for a two-state magnetic system. As can be inferred from the top panel, there is more entropy released in NaCaNi<sub>2</sub>F<sub>7</sub> than in NaCaCo<sub>2</sub>F<sub>7</sub> in this temperature range, which we believe is beyond the experimental error [5]. With no other apparent features, it is also possible that a fraction of the spins remains fluctuating at the low-temperature measurement limit. Further work is necessary to elucidate the nature of the observed heat capacities. While it is surprising that NaCaNi<sub>2</sub>F<sub>7</sub> ( $S = 1$ ) releases more entropy than the more magnetic Co( $S = 3/2$ ) analog, NaCaNi<sub>2</sub>F<sub>7</sub> appears to be slightly less frustrated, which may cause more spins to freeze out at accessible temperatures and shift more entropy into the available temperature measurement window.

The shape of the heat capacity below the freezing transition can sometimes give information regarding the elementary spin excitations in the material. The inset of the lower panel shows that the heat capacity below the spin glass transition is linear on a  $C(T) \propto T^2$  scale. For a spin glass, it is expected that the heat capacity is linear on a  $C(T) \propto T$  scale, arising from a distribution of two level systems linear in energy [6]. Despite the other magnetic behavior observed for NaCaNi<sub>2</sub>F<sub>7</sub>, consistent with a classical spin glass, linear behavior of the heat capacity is not observed. The behavior observed,  $C(T) \propto T^2$ , is expected for spin waves in a quasi-two-dimensional (2D) antiferromagnet, and while it is unusual for a spin glass, this behavior is not entirely unprecedented for geometrically frustrated spin glasses [32]. Further research is required to better understand this behavior. At temperatures lower than those measured here, similar behavior was observed in the Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> pyrochlore and was attributed to the presence of a large density of states at low energy [33]. There is some curvature still present in NaCaCo<sub>2</sub>F<sub>7</sub> on these scales, so no conclusion was obtained regarding the excitations [5].

#### IV. CONCLUSION

Despite the Curie-Weiss fit suggesting the presence of strong antiferromagnetic interactions on the order of 130 K,

spin freezing does not occur until 3.6 K in NaCaNi<sub>2</sub>F<sub>7</sub>. This difference indicates that this material is a highly frustrated  $S = 1$  Ni<sup>2+</sup> pyrochlore. The crystal structure determination shows that Na and Ca are completely disordered over the A site, and the unit cell dimension is in good agreement with the previous report [3]. Disorder results in a lowering of symmetry in the local environment around the B-site magnetic cation, as has been seen in other pyrochlores [5,34,35]. It is reasonable to assume that some short range Na-Ca ordering is present to maintain local charge balance; measurements of the diffuse x-ray or neutron scattering, pair distribution function (PDF), or solid-state nuclear magnetic resonance spectroscopy (NMR) may help to clarify the nature of the local B site environments. Theoretical studies of the Heisenberg antiferromagnet on the pyrochlore lattice indicate that weak randomness in the exchange interactions (i.e., magnetic bond disorder) can precipitate a spin glass ground state, with the spin glass temperature set by the strength of the bond disorder [7–9]. While the properties presented here do not provide a full understanding of the magnetic ground states, we propose that the bond disorder induced by the A site mixing is responsible for the spin glass ground state. Further neutron scattering experiments probing the magnetic excitations are necessary to elucidate nature of the magnetic anisotropy. The robustness and similarity seen in the transition metal fluoride pyrochlores offers an opportunity to explore the structure property relationships in a comparatively unexplored class of materials. The similarity in magnetic behavior of the Co<sup>2+</sup>(3d<sup>7</sup>)Co<sup>2+</sup>(3d<sup>7</sup>) and Ni<sup>2+</sup>(3d<sup>8</sup>)-based fluoride pyrochlores is surprising, as these two ions do not typically behave similarly in solids. Further experiments to probe the magnetic properties are necessary and will be facilitated by the availability of large single crystals and readily accessible temperature range. Neutron scattering measurements on single crystals of these materials would allow significantly more detailed characterization of their magnetic interactions and comparison to current theoretical models for the pyrochlore antiferromagnet.

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- [1] J. S. Gardner, M. J. P. Gingras, and J. E. Greedan, *Rev. Mod. Phys.* **82**, 53 (2010).
  - [2] M. A. Subramanian, G. Aravamudan, and G. V. Subba Rao, *Prog. Solid St. Chem.* **15**, 55 (1983).
  - [3] R. Hänsler and W. Rüdorff, *Z. Naturforsch. B* **25**, 1306 (1970).
  - [4] J. W. Krizan and R. J. Cava, *J. Phys.: Condens. Matter* **27**, 296002 (2015).
  - [5] J. W. Krizan and R. J. Cava, *Phys. Rev. B* **89**, 214401 (2014).
  - [6] A. P. Ramirez, *Annu. Rev. Mater. Sci.* **24**, 453 (1994).
  - [7] T. E. Saunders and J. T. Chalker, *Phys. Rev. Lett.* **98**, 157201 (2007).
  - [8] A. Andreev, J. T. Chalker, T. E. Saunders, and D. Sherrington, *Phys. Rev. B* **81**, 014406 (2010).
  - [9] H. Shinaoka, Y. Tomita, and Y. Motome, *Phys. Rev. Lett.* **107**, 047204 (2011).
  - [10] H. J. Silverstein, K. Fritsch, F. Flicker, A. M. Hallas, J. S. Gardner, Y. Qiu, G. Ehlers, A. T. Savici, Z. Yamani, K. A. Ross, B. D. Gaulin, M. J. P. Gingras, J. A. M. Paddison, K. Foyevtsova, R. Valenti, F. Hawthorne, C. R. Wiebe, and H. D. Zhou, *Phys. Rev. B* **89**, 054433 (2014).
  - [11] Y. Zheng, A. Ellern, and P. Kögerler, *Acta Crystallogr. C* **67**, i56 (2011).

- [12] Z. Fu, Y. Zheng, Y. Xiao, S. Bedanta, A. Senyshyn, G. G. Simeoni, Y. Su, U. Rücker, P. Kögerler, and T. Brückel, *Phys. Rev. B* **87**, 214406 (2013).
- [13] H. D. Zhou, C. R. Wiebe, J. A. Janik, B. Vogt, A. Harter, N. S. Dalal, and J. S. Gardner, *J. Solid State Chem.* **183**, 890 (2010).
- [14] J. N. Reimers, J. E. Greedan, C. V. Stager, M. Bjorgvinnsen, and M. A. Subramanian, *Phys. Rev. B* **43**, 5692 (1991).
- [15] K.-M. Tam, A. J. Hitchcock, and M. J. P. Gingras, [arXiv:1009.1272](https://arxiv.org/abs/1009.1272).
- [16] R. De Pape and G. Ferey, *Mater. Res. Bull.* **21**, 971 (1986).
- [17] A. Sadeghi, M. Alaei, F. Shahbazi, and M. J. P. Gingras, *Phys. Rev. B* **91**, 140407 (2015).
- [18] D. C. Stockbarger, *Rev. Sci. Instrum.* **7**, 133 (1936).
- [19] P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **60**, 305 (1925).
- [20] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.92.014406> regarding the growth of single crystals, single crystal structure determination, and tabulated structural parameters.
- [21] Bruker, Bruker AXS, Inc. Madison, WI, USA (2008).
- [22] G. M. Sheldrick, *Acta Crystallogr. A* **64**, 112 (2007).
- [23] L. J. Farrugia, *J. Appl. Crystallogr.* **45**, 849 (2012).
- [24] J. Rodríguez-Carvajal, *Newsl. Comm. Powder Diffr.* **26**, 12 (2001).
- [25] S. Blundell, *Magnetism in Condensed Matter*, 1st ed. (Oxford University Press, USA, 2001).
- [26] S. E. Dutton, E. D. Hanson, C. L. Broholm, J. S. Slusky, and R. J. Cava, *J. Phys.: Condens. Matter* **23**, 386001 (2011).
- [27] J. A. Mydosh, *Spin Glasses: An Experimental Introduction* (Taylor & Francis, London, 1993).
- [28] K. Miyoshi, Y. Nishimura, K. Honda, K. Fujiwara, and J. Takeuchi, *J. Phys. Soc. Jpn.* **69**, 3517 (2000).
- [29] T. Klimczuk, H. W. Zandbergen, Q. Huang, T. M. McQueen, F. Ronning, B. Kusz, J. D. Thompson, and R. J. Cava, *J. Phys.: Condens. Matter* **21**, 105801 (2009).
- [30] J. L. Tholence, *Solid State Commun.* **35**, 113 (1980).
- [31] Y. Yeshurun, J. L. Tholence, J. K. Kjems, and B. Wanklyn, *J. Phys. C: Solid State Phys.* **18**, L483 (1985).
- [32] A. P. Ramirez, B. Hesse, and M. Winklemann, *Phys. Rev. Lett.* **84**, 2957 (2000).
- [33] A. Yaouanc, P. Dalmas de Réotier, V. Glazkov, C. Marin, P. Bonville, J. A. Hodges, P. C. M. Gubbens, S. Sakarya, and C. Baines, *Phys. Rev. Lett.* **95**, 047203 (2005).
- [34] E. A. Oliveira, I. Guedes, A. P. Ayala, J.-Y. Gesland, J. Ellena, R. L. Moreira, and M. Grimsditch, *J. Solid State Chem.* **177**, 2943 (2004).
- [35] A. P. Ayala, C. W. A. Paschoal, I. Guedes, W. Paraguassu, P. T. C. Freire, J. Mendes Filho, R. L. Moreira, and J.-Y. Gesland, *Phys. Rev. B* **66**, 214105 (2002).