Structural and magnetic characterization of the elusive Jahn-Teller active NaCrF₃

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We report the structural and magnetic characterization of the elusive Jahn-Teller active compound NaCrF₃. The crystal structure of NaCrF₃ is initially described from a DFT model which serves as basis for indexing and structure determination confirmed by high-resolution synchrotron X-ray diffraction experiments. NaCrF₃ adopts the triclinic space group P1 (isostuctural with NaCuF₃). Magnetometry studies at low temperature show that NaCrF₃ is a weak antiferromagnet, Curie temperature $\theta = -4$ K. The Néel temperature is $T_N = 21.3$ K and magnetic moment $\mu = 4.47 \mu_B$ in accordance with the theoretical $S = 2$. Field-dependent measurements between 2 and 12 K unveil the onset of metamagnetic behavior. Our experiments revealed a canted $A$-type magnetic structure observed by neutron powder diffraction, with a magnetic propagation vector $(1/2, 1/2, 0)$ and a magnetic moment of $3.51 \mu_B$ at 1.5 K. Our results shed further light on the Jahn-Teller effects and strong correlations as a function of $A$-ion size in the family $ACrF₃$.

I. INTRODUCTION

The cooperative Jahn-Teller [1] (JT) effect is the common name given to the structural distortions caused by the coupling between electronically degenerate orbital states of transition metal ions and their normal modes of vibration. This coupling results in reduction of the symmetry of the bonding around the JT ion to give more stable structures. JT-active perovskite-type materials are at the center of intensive research within the material science community for their wide range of physical properties and structural diversity. Superconductivity, colossal magnetoresistance (CMR) and polaron confinement are known for these compounds, giving applications in information storage and spintronics [2-4]. Perovskites have the chemical formula $ABX₃$. JT-active ions such as $\text{Mn}^{3+}$, $\text{Cr}^{2+}$ and $\text{Cu}^{2+}$ (with electronic structure $3d^4$ and $3d^5$, respectively) can occupy the octahedral $B$-site (e.g., $[\text{MnO}_6]$). The octahedra are linked by their vertices forming a $B$-$X$-$B$ bond angle $\xi$ (defined here as the perovskite angle). The electron-phonon coupling (i.e., $E \otimes \epsilon$) causes octahedral distortion which favor the occupation of one of the degenerate orbital states. At the same time, the choice of orbital state induces an orbital ordering (OO).

The best known JT-active oxide perovskite is lanthanum manganite LaMnO₃, a precursor of several crystalline compounds exhibiting CMR. An essential feature of the manganites is the role played by the atom occupying the $A$-site in influencing JT-structural distortions, leading to a rich diversity of spin, orbital and charge orderings. In fluorides JT-ions have shown also interesting phenomena under external stimuli. Alkali ternary manganese (III) fluorides with formula $A_x\text{MnF}_{3+x}$ (with $A =$Na, K, Cs) show significant structural diversity, adopting 0-, 1- and 2-dimensional vertex-sharing arrangements of the octahedral units depending on the value of $x$. [5,6].

3-dimensional compounds of transition metals with the high spin $3d^4$ electronic configuration can form perovskite-type fluoride structures (fluoroperovskites). These include ternary chromium (II) fluoroperovskites with formula ACrF₃ (where $A =$ alkali metals). KCrF₃ has two structural-phase transitions at elevated temperatures: $I112/m \rightarrow I4/mcm$ and $I4/mcm \rightarrow Pm3m$ between 250 and 973 K [7,8], and theoretical studies have associated the metal to insulator transition with the onset of the tetragonal-to-cubic phase transition [9]. In addition, KCrF₃ displays a rich magnetic phase diagram at low temperatures: an incommensurate antiferromagnetic ordering at 79.5 K, an incommensurate-to-commensurate antiferromagnetic transition at 45.8 K, and below 9.5 K a canted ferromagnetic ordering with weak ferromagnetic interactions [10]. Further studies of the role played by the
FIG. 1. (a) Final observed (black dots), calculated (red line) and difference (blue line) synchrotron X-ray powder diffraction profiles ($\lambda = 0.4501 \text{ Å}$) for NaCrF$_3$ at 298 K ($a = 5.51515(2) \text{ Å}$, $b = 5.68817(3) \text{ Å}$, $c = 8.18349(3) \text{ Å}$, $\alpha = 90.5039(3)^{\circ}$, $\beta = 92.2554(3)^{\circ}$, $\gamma = 86.0599(2)^{\circ}$). $R_{wp} = 11.52\%$; $R_{exp} = 5.53\%$. Inset, close up of the high angle region of the refinement. (b) Structure of NaCrF$_3$ viewed in the (110) direction.

A–site in ACrF$_3$ are currently lacking despite the interesting phase diagram of KCrF$_3$. The main reason for this is the lack of proper synthetic protocols for the reactions of Cr$^{2+}$ compounds with fluorides. The synthesis of NaCrF$_3$ has until now proved extremely problematic due to the sensitivity of Cr$^{2+}$ to oxidation. None of the synthesis routes described by Deyrup and Earnshaw et al. resulted in NaCrF$_3$[12, 13]. To the best of our knowledge, the only evidence of the preparation of NaCrF$_3$ was given by the work of Vollmer and UV-vis spectroscopy studies performed by Kruger[14, 15]. A reliable synthetic protocol for NaCrF$_3$ opens up further possibilities for
analogous materials for information storage technologies, richer states of matter and novel physical phenomena by further stoichiometric and non-stoichiometric modification of the $A$- and $B$ sites in the $ACrF_3$ family. We report for the first time the crystal and magnetic structure of the elusive JT- active compound, NaCrF$_3$ prepared by a novel wet-chemistry method. These results are complemented by magnetometry studies.

II. EXPERIMENTAL AND COMPUTATION SECTION

A. Synthesis of NaCrF$_3$

Chromium (II) acetate dihydrate (Cr$_2$OAc$_4$) (0.5 g 1.33 mmol) and 2 mL of degassed water is loaded into a 85 mL polycarbonate (PC) vial closed with a septum under a constant flow of Ar. NaHF$_2$ (0.45 g 5.45 mmol) is dissolved in 10 mL deoxygenated water in a second PC vial under Ar by heating to above 50°C. The hot-solution of NaHF$_2$ is carefully and quickly injected into the vial containing Cr$_2$OAc$_4$ under vigorous stirring. NaCrF$_3$ precipitates after few seconds. The supernatant is decanted off and the solid product is washed once with 2 mL 50:50 deoxygenated water and methanol solution, and subsequently with 5 mL deoxygenated methanol. Finally, the product is vacuum-dried overnight to yield air-stable NaCrF$_3$.

B. Computational simulations

For the structural phase model of NaCrF$_3$, density functional theory (DFT) was applied using the Vienna $Ab$ initio Simulation Package (VASP) [16, 17], with the PBE general gradient approximation (GGA) [18]. The cutoff energy of the plane wave basis set expansion was set to at least 450 eV. The density of states in the plane wave basis set expansion was determined by magnetometry studies.

C. Synchrotron X-ray diffraction

High-resolution synchrotron powder X-ray diffraction (HR-SPXRD) experiments were conducted at ID22 beamline of the European Synchrotron (ESRF), Grenoble, France where the diffraction patterns were recorded using a wavelength of $\lambda = 0.40013$ Å at room temperature. The crystal structure of NaCrF$_3$ has been refined using TOPAS v5 (Bruker AXS) [19]. The initial model was obtained by DFT minimisation of a symmetry free (space group $P1$) triclinic model based on the crystal structure of NaCuF$_3$ [14, 20] with Cr replacing Cu. This model was refined against the HR-PXRD data to obtain the correct lattice parameters and crystallite size peak broadening. The model was then processed using the ADDSYMM routine in PLATON [21] to determine the crystallographic symmetry. The new model, now in space group $P1$, was refined against the HR-SPXRD data. Scale, lattice parameters, 13 term Chebyshev polynomial background function, Gaussian crystallite size and strain and Lorentzian strain broadening terms (fundamental parameters peak shape) and all Na and F atomic coordinates and isotropic temperature factors were refined. Atoms of the same type (Na, Cr and F) were constrained to have the same isotropic thermal parameters.

D. Magnetic characterization

Magnetometry experiments were performed on a Quantum Design 14 T Physical Property Measurement System (PPMS). Temperature dependent DC magnetic susceptibility $\chi(T)$ measurements were conducted between 4-300 K following a zero-field-cooled field-cooled (ZFC-FC) modes. The magnetic susceptibility is calculated by $\chi = M/H$ where $M$ is the magnetization given in emu mol$^{-1}$Oe$^{-1}$ and the magnetic field $H = 1$ T. Isothermal field dependent measurements ($M(H)$) were collected at 2 K, and half-loop isothermal measurements at 4, 12 and 23 K up to 14 kOe.

E. Neutron Powder Diffraction

Neutron powder diffraction (NPD) patterns were collected at ISIS Neutron and Muon Source (UK) by using the WISH long-wavelength diffractometer [22]. The sample was placed in thin wall vanadium container (7 mm in diameter) and cooled down to 1.5 K. The measurements were performed while heating from 1.5 K up to 127 K at several temperature steps. The raw data was integrated by using the Mantid suite [23] and analysed using Jana2006 software [24]. The structure refinement was performed using data from the 4 detector banks with highest resolution. The lowest resolution bank was discarded as the it contained no information not present in the other detector banks. The background (10 term Chebyshev polynomial), peak-shape, isotropic thermal displacement parameters for each element type, lattice parameters and angles, and scale parameters were refined. The superspace formalism for commensurate magnetic moment modulation was used for the magnetic structure description. The magnetic form factor of Cr$^{2+}$ was employed in the refinements. Spherical coordinates were used to refine the magnetic moments. The four Cr$^{2+}$ sites were constrained to have a single magnetic moment magnitude. Polar angles ($\varphi_1$ and $\varphi_2$) were refined for Cr$_1$ and Cr$_3$, with the polar angles of Cr$_2$ and Cr$_4$ constrained to values of 180$^\circ$-$\varphi_1$ and 180$^\circ$-$\varphi_3$ respectively. Independent azimuthal angles were refined for all Cr sites. These constraints are summarised in Table IV. At 17 and 19 K, the azimuthal angle of Cr$_1$ and Cr$_3$,
TABLE I. Structural parameters from Rietveld refinement of HR-SPXRD dataset of NaCrF$_3$ at ambient conditions. $l$, $m$ and $s$ are long, medium and short bond distances, respectively.

| Space Group:          | $P\overline{1}$ |
|-----------------------|------------------|
| $a$                   | 5.51515(2) Å     |
| $b$                   | 5.68817(3) Å     |
| $c$                   | 8.18349(3) Å     |
| $\alpha$              | 90.5039(3)°      |
| $\beta$               | 92.2554(3)°      |
| $\gamma$              | 86.0599(2)°      |
| $V$                   | 255.915(2) Å     |
| $R_{wp}, R_{wp-bkg}$  | 11.516, 21.573   |
| $R_{exp}, R_{exp-bkg}$| 5.5252, 10.3500 |
| $N^0$ of independent parameters | 53 |
| Restrains, constrains | 0, 3             |
| Rigid bodies          | 0                |
| $Z$                   | 4                |

Octahedral distortions:

- $\Delta d_{\text{Cr}1} = 78.37 \times 10^{-4}$ Å
- $\Delta d_{\text{Cr}2} = 59.01 \times 10^{-4}$ Å
- $\Delta d_{\text{Cr}3} = 72.35 \times 10^{-4}$ Å
- $\Delta d_{\text{Cr}4} = 76.86 \times 10^{-4}$ Å

Selected Bond Distances

| Bond Type | Cr1-F | Cr2-F | Cr3-F | Cr4-F |
|-----------|-------|-------|-------|-------|
| $l \times 2$ | 2.383(6) Å | 2.289(5) Å | 2.346(5) Å | 2.371(5) Å |
| $m \times 2$ | 2.028(5) Å | 2.045(5) Å | 2.019(5) Å | 2.022(5) Å |
| $s \times 2$ | 1.987(5) Å | 1.976(5) Å | 1.986(5) Å | 1.986(5) Å |

III. RESULTS

A. Crystal structure determination

To the best of our knowledge, no reliable synthesis protocol for NaCrF$_3$ has previously been described, and the crystal structure of the compound has not been described in detail. The air-sensitivity of Cr$^{2+}$ is intrinsically difficult to combine with fluorine chemistry. Conventional solid-state methods are therefore unsuitable, so we developed our own wet-chemistry protocol. Using this we can work under conditions where Cr$^{2+}$ is stable and obtain pure, single phase NaCrF$_3$ in large quantities. We expect that other fluorides can be prepared using the same approach. Results of the Rietveld refinement against HR-PXRD data are shown in Figure 1 and Table I. The plot, fitting statistics and bond lengths and angles obtained indicate that the model is an excellent representation of the real structure. Table II and Table III SI show the structural parameters and atomic coordinates, respectively after Rietveld refinement.

The Cr$^{2+}$ cations occupy four inequivalent crystallographic sites. Although the structure is triclinic, the cell edges and angles are close to those of a tetragonal unit cell. The corresponding approximate tetragonal distortion, $c/a = 1.48$, corresponds to the (stretching) normal mode $Q_2$ of the octahedral units Cr$^{2+}$F$_6$. Figure 1(b) shows the crystal structure of NaCrF$_3$ where the octahedral units (blue) are vertex shared with Na$^+$ ions (red). We calculate the octahedral distortion according to the equation $\Delta d = 1/6 \sum_{i=1}^{6} |l_i - l_{av}|/l_{av}$ where $l_i$ are the bond distances of the octahedral unit, and $l_{av}$ is the average bond distance. Figure 1(b) shows the $l$ and $s$ bonds building a tilted $ls$-motif connected through the Cr-F-Cr angles $\xi$. Figure 1(b) shows the $ls$- motif stacking along [110]-direction, with the bonding-motif rotating 90° (represented here as blue and red planes to indicate the 90° rotation), whereas the $m$ bonds propagate above and below the [001]-plane in the [110]-direction. The four CrF$_6^{2-}$ distortions can be found in Table III The octahedra are sharply tilted, corresponding to the Glazer notation $a^−b−c^−$ [25].

B. Magnetic characterization and Neutron diffraction studies

DC temperature dependent magnetic susceptibility experiments on a polycrystalline sample of NaCrF$_3$ between 4 and 300 K show a kink corresponding to the onset of long-range antiferromagnetic ordering on reaching the Néel temperature at $T_N = 21.3$ K, Figure 3(a). Furthermore, an upswing at around 9 K reveals the emergence
of a weak ferromagnetic component at lower temperature. The Curie - Weiss (CW) law was applicable for the temperature range from 300 - 24 K. The fit to the inverse susceptibility curves $1/\chi$ show a linear behaviour where the calculated magnetic moment of $\mu_{eff} = 4.47 \mu_B$ is in good agreement with the theoretical value of the spin-only configuration $S = 2$ for Cr$^{2+}$. The Curie temperature is $\theta = -4$ K measured under 1 T indicating weak antiferromagnetic interactions. This contrasts with KCrF$_3$ which displays weak ferromagnetic interactions $\theta = 2.7(1)$ K at 1 T. This suggests that reduction of the ion size at the A-site is of paramount importance in tuning the magnetic exchange interactions.

Magnetic field dependent isothermal $M(H)$ half-loops (forward and reverse field application) for NaCrF$_3$ are presented in Figure 3 (b). These loops were measured at 2, 4, 12 and 23 K in applied magnetic fields up to 14 kOe. At 23 K the half-loop shows linear behaviour with a small hysteresis indicating the presence of ferromagnetic interactions without saturation at 14 kOe. The half-loop at 12 K retains the hysteresis with additional signatures of metamagnetic transitions identified by the S-shape between 6 and 8 kOe.

The metamagnetic transition becomes more pronounced with decreasing temperature as observed at 4 and 2 K. At 4 K the hysteresis is at its widest. The path difference between forward and reverse field application is non-zero. The inset in Figure 3 (b) shows the complete isothermal loop at 2 K. The symmetry of the complete loop with a magnetic moment of $0.73 \mu_B$/Cr at 14 T indicates that there is no longer hysteresis at 2 K. This means that the ferromagnetic components are suppressed by temperature. In order to identify the point of metamagnetic transition we calculated the first derivative $dM/dH$ of the magnetization $M$ with respect to applied field $H$ as shown in 4. The behaviour above $T_N$ suggest no change in the magnetic moment. An emergent peak at 8 kOe is observed below $T_N$ with well-defined singularity at 4 and 2 K.

Our synthesis protocol makes it possible to prepare...
Magnetic moments in the [11\bar{1}]-direction. The canted A-structure where chromium have a saturated magnetic moment of \( \mu = 3.5197(55) \mu_B \) at 1.5 K, Figure 5(b). The magnetic moments of chromium couples antiferromagnetic along the [110]-direction and ferromagnetic along the [110]- and [001]-directions. This configuration gives rise to ferromagnetic layers stacked alternating along the [110]-direction. In the triclinic structure, the magnetic moments of chromium point almost directly through the middle of the edge between the equatorial and axial fluorine atoms of the JT distorted CrF\(_6\) octahedra. Consequently, the magnetic moments are directed towards the second adjacent octahedra, thus forming chains of magnetic moments in the [111]-direction. The canted A-type antiferromagnetic structure is in agreement with the structural ls-motif corresponding to ferromagnetic interactions in the (110)-plane and antiferromagnetic interactions perpendicular to it. However, the canting effect reduces the strength of the magnetic interactions as the extent of adjacent orbital overlap is diminished by the \( \alpha-b-c \) tilt in the presence of Na\(^+\) ions.

When the direction of the magnetic moments of the four chromium sites were constrained to be either parallel or anti-parallel, several weaker reflections originating from magnetic ordering at i.e. \( d = 5.64 \) and 5.86 Å were not correctly accounted for. Therefore, we applied a slightly more complex set of constraints to the magnetic moment components. Table IV presents the minimal set of magnetic structure parameters and the constraints applied for the refinement. The presence of the two reflections (at \( d = 5.64 \) and 5.86) clearly shows that the four chromium sites have slightly different tilt of the magnetic moments. These subtle aspects of the magnetic structure could only be described due the high resolution and low signal to noise ratio of the neutron diffraction data obtained from the WISH instrument at ISIS (UK). The magnetic structure of NaCrF\(_3\) is accurately described at 1.5 K, and details are given in Table IV.

Using the magnetic structure determined above, we studied its evolution below the Néel temperature (\( T_N = 21.3 \) K). In accordance with the spin only approximation (\( \mu_{eff} = 4.47 \mu_B \), see above), the magnetic moment of chromium is stabilized at 3.5196(56)\( \mu_B \) at 1.5 K. The slightly lower experimental value compared to the theoretical value is attributed to some degree of covalency in the chemical bonding which effectively reduces the number of electrons contributing to the magnetic moment. The magnetic moment of chromium steadily decreases with increasing temperature up to the Néel temperature at 21 K where the magnetic ordering disappears (see Fig. 6(b)).

The polar angle difference between the magnetic moments of Cr1 and Cr3 is fairly constant, with a possible small tendency of divergence for temperatures closer to the Néel temperature (see Fig. 6(b,c)). The two pairs of azimuthal angles (Cr1, Cr3) and (Cr2, Cr4) show similar values, but cannot be constrained to be equal without worsening the fit. However, at 17 and 19 K the azimuthal angle \( \theta \) of Cr1 and Cr3, and Cr2 and Cr4 were constrained. Also at 19 K all angle values were frozen at 17 K due to fit instability. The antiferromagnetic ordering at the Néel temperature is also associated with a change in the rate of lattice contraction with cooling. The rate of unit cell volume and lattice parameter contraction increases significantly at the Néel temperature Figure 7. At the same temperature changes in the behavior of the perovskite angles are observed. These observations are attributed to the onset of the antiferromagnetic ordering, with an associated change in the structural features.

![Graph](image-url)  
**FIG. 4.** First derivative \( dM/dH \) of the isothermal half-loops at 2, 4, 12, and 23 K. The upswing is represented with connected line-guides and the down-swing with dashed-lines. A metamagnetic transition occurs at 8 T in the half-loops at 2 and 4 K. Up and downswing data are emphasised by arrows for the 4 T data.
IV. DISCUSSION

The reliable new synthesis route for NaCrF$_3$ has allowed us to undertake a detailed study of its structure and magnetic properties for the first time. The JT-active ions Cr$^{2+}$ of NaCrF$_3$ occupy four independent crystallographic sites with different octahedral distortions. Our results further demonstrate the importance of the ion size at the A-site in tuning the properties of systems containing JT-active ions. A-site dependent physical phenomena have previously been observed in the isoelectronic low-dimensional manganese (III) fluoroperovskites, where the A-site ion size tunes diverse and interesting phase diagrams under external stimuli.

The most significant feature of NaCrF$_3$ comes from its metamagnetic signatures below $T_N$ under field dependent measurements in addition to the residual ferromagnetic interactions at 23 K. The presence of the metamagnetism in NaCrF$_3$ in some aspects resembles other known systems with exotic properties (See Ref. [26], [27], [28]). We believe that this behavior is related to correlations established between the orbital structure and magnetic ordering as studied by Kugel and Khomskii [29]. The temperature dependent NPD data reveals a smooth decrease in the unit cell volume and $\gamma$ angle above $T_N$, with a rapid collapse at lower temperatures Figure 7 (a). We expected that the $\xi$ angle would reduce for all four Cr$^{2+}$ sites, however, they follow independent patterns as shown in Figure 7 (b). $\xi_0^o$ displays a slight decrease upon cooling while $\xi_1^o$ increases. Perovskite angle reduction further decreases the orbital overlap, weakening the magnetic interactions while reinforcing Cr-to-Cr interactions. The refined magnetic moments of Cr$^{2+}$ ions in NaCrF$_3$ are in agreement with NPD studies on KCrF$_3$ by Xiao et al. [11]. Compared to other sodium transition metal fluoroperovskites, NaCrF$_3$ deviates from the family trend by displaying a canted A$-$type magnetic ordering compared to the G-types found in NaNiF$_3$ and NaCoF$_3$ [30] [31].

To further investigate the role of the A-site in ACrF$_3$...
with magnetic characterization studies to compare the change takes place.

\[ \gamma (\text{deg}) \]

\[ \text{Temperature dependence of the unit cell lattice parameters \( a \), \( b \), \( c \), \( \gamma \)} \]

Vertical dashed line at \( \text{Cr}_2 \).

\[ \xi \]

Temperature dependence of the unit cell volume and \( \gamma \) angles showing same decreasing pattern. (b) Temperature dependence of the unit cell lattice parameters (c) Perovskite angles composing the canted \( ls \)-motif \( \text{NaCrF}_3 \) as function of temperature: \( \xi_1 = \text{Cr}_1 - \text{F}_1 - \text{Cr}_2 \), \( \xi_2 = \text{Cr}_2 - \text{F}_6 - \text{Cr}_4 \), \( \xi_3 = \text{Cr}_4 - \text{F}_3 - \text{Cr}_3 \), \( \xi_4 = \text{Cr}_3 - \text{F}_5 - \text{Cr}_1 \). Vertical dashed line at \( T_N \) to emphasize the place where the change takes place.

we report elsewhere the use of UV-vis spectroscopy along with magnetic characterization studies to compare the local electronic structure of the JT-systems \( \text{KCrF}_3 \) and \( \text{NaCrF}_3 \) as a function of temperature and magnetic field. Such experiments could provide more detailed information about the strength of the JT-distortions and be used to assess OO-melting points in other JT-active fluorides.

\[ \text{FIG. 7. (a) Temperature dependence of unit cells and volume, and } \gamma \text{ angles showing same decreasing pattern. (b) Temperature dependence of the unit cell lattice parameters (c) Perovskite angles composing the canted } ls \text{-motif } \text{NaCrF}_3 \text{ as function of temperature: } \xi_1 = \text{Cr}_1 - \text{F}_1 - \text{Cr}_2 \text{, } \xi_2 = \text{Cr}_2 - \text{F}_6 - \text{Cr}_4 \text{, } \xi_3 = \text{Cr}_4 - \text{F}_3 - \text{Cr}_3 \text{, } \xi_4 = \text{Cr}_3 - \text{F}_5 - \text{Cr}_1 \text{. Vertical dashed line at } T_N \text{ to emphasize the place where the change takes place.} \]

V. CONCLUSIONS

This work provides compelling evidence of the existence of the JT-active compound \( \text{NaCrF}_3 \), and describes its structural and magnetic properties. By developing a reliable, reproducible synthesis route we have shed further light on the properties of the \( A\text{CrF}_3 \) family, one which has previously proved elusive owing to the air-sensitive chemistry of \( \text{Cr}^{2+} \). \( \text{NaCrF}_3 \) does not display the structural and magnetic phase diversity observed for \( \text{KCrF}_3 \) at low temperature. This is due to the smaller \( A \)-ion size causing the structure to adopt the low symmetry space group \( P1 \) at relatively high temperature. The low symmetry structure is responsible for the unusual metamagnetic behavior of \( \text{NaCrF}_3 \), which can be clearly linked to variations in both the crystal structure (perovskite angles and lattice parameters) and the magnetic structure (polar and azimuthal angles of the magnetic moments), observed in the variable temperature NPD data. The new synthesis protocol also opens up the possibility of preparing numerous novel stoichiometric compounds by tuning the \( A \) and \( B \) sites (e.g., \( A_1^{1+}A_2^{2+}\text{CrF}_3 \) and \( A_1^3\text{Cr}^{2+}B_2^{2+}\text{F}_3 \)) which may reveal further new and interesting physical properties.

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TABLE III. Atomic positions of NaCrF$_3$ from HR-SPXRD Rietveld refinement. See Table I for crystal structure details.

| Atom | Multiplicity | x               | y               | z               | Occ | B$_{iso}$ |
|------|--------------|-----------------|-----------------|-----------------|-----|---------|
| Na1  | 2            | 0.5062(8)       | 0.5511(7)       | 0.2370(5)       | 1   | 1.53(7) |
| Na2  | 2            | 0.9765(8)       | 0.0563(7)       | 0.2603(5)       | 1   | 1.53(7) |
| Cr1  | 1            | 0.5             | 0               | 0               | 1   | 0.79(3) |
| Cr2  | 1            | 0               | 0.5             | 0               | 1   | 0.79(3) |
| Cr3  | 1            | 0.5             | 0               | 0.5             | 1   | 0.79(3) |
| Cr4  | 1            | 0               | 0.5             | 0.5             | 1   | 0.79(3) |
| F1   | 2            | 0.6788(9)       | 0.2832(9)       | 0.0558(6)       | 1   | 0.98(5) |
| F2   | 2            | 0.2019(9)       | 0.2062(8)       | 0.9260(6)       | 1   | 0.98(5) |
| F3   | 2            | 0.7153(9)       | 0.3238(8)       | 0.4292(6)       | 1   | 0.98(5) |
| F4   | 2            | 0.1887(10)      | 0.1902(9)       | 0.5503(7)       | 1   | 0.98(5) |
| F5   | 2            | 0.3801(9)       | 0.9405(8)       | 0.2724(7)       | 1   | 0.98(5) |
| F6   | 2            | 0.1204(9)       | 0.4380(8)       | 0.2272(7)       | 1   | 0.98(5) |

TABLE IV. Selected bond angels in NaCrF$_3$ from HR-SPXRD Rietveld refinements

| F$_i$-Cr-F$_j$ | Cr1 $(i=2,5,5;j=1,2,1)$ | Cr2 $(i=2,1,1;j=6,2,6)$ | Cr3 $(i=4,3,3;j=5,4,5)$ | Cr4 $(i=4,6,6;j=3,4,5)$ |
|---------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 90.8(2)       | 89.1(2)                  | 88.5(2)                  | 89.2(2)                  |
| 96.17(19)     | 91.72(19)                | 95.72(19)                | 94.00(19)                |
| 94.61(19)     | 92.95(19)                | 94.19(19)                | 84.50(19)                |
| 180.00(6)     | 179.999(7)               | 180.00(7)                | 180.00(9)                |

TABLE V. Structural parameters from Rietveld refinement of NPD dataset of NaCrF$_3$ at 1.5 K. $l, m$ and $s$ are long, medium and short bond distances, respectively.

| Space Group: | $P\bar{1}$ | Octahedral distortions: |
|--------------|------------|--------------------------|
| $a$          | 5.48428(11) Å | $\Delta d_{Cr1} = 79.90 \times 10^{-4}$ Å |
| $b$          | 5.67072(12) Å | $\Delta d_{Cr2} = 54.68 \times 10^{-4}$ Å |
| $c$          | 8.13620(15) Å | $\Delta d_{Cr3} = 71.39 \times 10^{-4}$ Å |
| $\alpha$    | 90.3860(10)$^\circ$ | $\Delta d_{Cr4} = 75.07 \times 10^{-4}$ Å |
| $\beta$     | 92.2816(8)$^\circ$ | $\Delta d_{Cr4} = 75.07 \times 10^{-4}$ Å |
| $\gamma$    | 86.3255(8)$^\circ$ | $\Delta d_{Cr4} = 75.07 \times 10^{-4}$ Å |
| $V$          | 252.312(9) Å$^3$ | $\Delta d_{Cr4} = 75.07 \times 10^{-4}$ Å |

| $R_{wp}$ | 2.37 | $R_p$ | 1.72 |
|-----------|------|-------|------|
| N$^*$ of independent parameters | 111 |
| Restrains, constrains | 0, 5 |
| Rigid bodies | 0 |
| Z | 4 |

Selected Bond Distances

| $l \times 2$ | Cr1-F | Cr2-F | Cr3-F | Cr4-F |
|--------------|-------|-------|-------|-------|
| 2.3807(19) Å | 2.2835(18) Å | 2.3480(17) Å | 2.3489(18) Å |

| $m \times 2$ | Cr1-F | Cr2-F | Cr3-F | Cr4-F |
|--------------|-------|-------|-------|-------|
| 2.0243(16) Å | 2.0550(16) Å | 2.0332(18) Å | 2.0131(17) Å |

| $s \times 2$ | Cr1-F | Cr2-F | Cr3-F | Cr4-F |
|--------------|-------|-------|-------|-------|
| 1.9727(17) Å | 1.9931(18) Å | 1.9808(18) Å | 1.9714(17) Å |
TABLE VI. Atomic positions of NaCrF$_3$ from NPD Rietveld refinements at 1.5 K. See Table V for crystal structure details.

| Atom | Multiplicity | x     | y     | z     | Occ | $U_{iso}$ |
|------|--------------|-------|-------|-------|-----|-----------|
| Na1  | 2            | 0.5084(5) | 0.5551(4) | 0.2358(3) | 1   | 0.0181(4) |
| Na2  | 2            | 0.9718(5) | 0.0597(4) | 0.2621(3) | 1   | 0.0181(4) |
| Cr1  | 1            | 0.5     | 0     | 0     | 1   | 0.0085(4) |
| Cr2  | 1            | 0      | 0.5   | 0     | 1   | 0.0085(4) |
| Cr3  | 1            | 0.5    | 0     | 0.5   | 1   | 0.0085(4) |
| Cr4  | 1            | 0      | 0.5   | 0.5   | 1   | 0.0085(4) |
| F1   | 2            | 0.6791(3) | 0.2814(3) | 0.0585(2) | 1   | 0.0151(3) |
| F2   | 2            | 0.2023(3) | 0.2052(3) | 0.9229(2) | 1   | 0.0151(3) |
| F3   | 2            | 0.7161(3) | 0.3249(3) | 0.4261(2) | 1   | 0.0151(3) |
| F4   | 2            | 0.1854(4) | 0.1900(3) | 0.5525(2) | 1   | 0.0151(3) |
| F5   | 2            | 0.3750(3) | 0.9405(2) | 0.2727(2) | 1   | 0.0151(3) |
| F6   | 2            | 0.1252(3) | 0.4358(3) | 0.2297(2) | 1   | 0.0151(3) |

TABLE VII. Magnetic parameters of Cr$^{2+}$ ions in NaCrF$_3$ from Rietveld refinements of PND as function of temperature.

| Temperature | M     | $\varphi$(Cr1) | $\vartheta$(Cr1) | $\varphi$(Cr2) | $\vartheta$(Cr2) | $\varphi$(Cr3) | $\vartheta$(Cr3) | $\varphi$(Cr4) | $\vartheta$(Cr4) |
|-------------|-------|----------------|------------------|----------------|------------------|----------------|------------------|----------------|-----------------|
| 1.5         | 3.51969 | -136.9916   | 38.94935        | 43.00841       | 129.5479       | -151.1129     | 56.12197        | 28.88715       | 136.5042        |
| 5           | 3.46608 | -137.1359   | 39.5289         | 42.86414       | 129.5129       | -149.6677     | 55.52545        | 30.33231        | 136.3085        |
| 7           | 3.40534 | -136.6089   | 38.33702        | 43.39112       | 128.9114       | -149.7235     | 54.45972        | 30.27652        | 134.9575        |
| 9           | 3.29101 | -136.7846   | 39.77436        | 43.21539       | 133.1239       | -149.2775     | 55.90062        | 30.72252        | 136.6471        |
| 11          | 3.12823 | -135.8486   | 42.12699        | 44.15142       | 134.918        | -150.2494     | 57.66518        | 29.75058        | 139.0407        |
| 13          | 2.9001  | -133.409    | 36.74886        | 46.591         | 130.0525       | -151.4175     | 52.1276         | 28.58247        | 134.7129        |
| 15          | 2.57635 | -131.5435   | 40.35261        | 48.4565        | 133.1635       | -154.1384     | 53.42544        | 25.86157        | 136.7845        |
| 17          | 2.02352 | -129.6754   | 49.17003        | 50.32455       | 137.5972       | -158.6962     | 49.17003        | 21.30376        | 137.5972        |
| 19          | 0.6124  | -129.6754   | 49.17003        | 50.32456       | 137.5972       | -158.6962     | 49.17001        | 21.30381        | 137.5972        |