

Signatures of orbital order and disorder in fluoroperovskites with t_{2g} electronic degeneracies

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A detailed high-resolution, variable temperature powder diffraction study of the fluoro-perovskites NaFeF_3 and NaCoF_3 is performed to probe their orbital ordering transitions. Through analysis of the symmetry adapted macrostrains and atomic distortions, we show that NaFeF_3 undergoes a C-type orbital order transition associated with the t_{2g}^4 states of Fe^{2+} . Counterintuitively, the phase transition leading to the orbital order appears second-order-like, which contradicts the thermodynamic requirements for electronic and isosymmetric phase transitions, implying that there must be an associated hidden symmetry breaking. On the other hand, for NaCoF_3 , consideration of the symmetry adapted strains allows us to confidently rule out the occurrence of any long-range orbital orders down to 4 K. Since NaCoF_3 is an insulator with quenched orbital angular momentum at this temperature, our findings point towards a novel kind of orbital disorder associated to the t_{2g}^5 electronic degeneracy.

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I. INTRODUCTION

For decades oxide-based perovskites, ABX_3 , have been subject to thorough investigation regarding their extensive structural phase transitions and subsequent properties [1]. The occurrence of symmetry-lowering phase transitions with decreasing temperature can be driven by a multitude of mechanisms, including the onset of various ordering schemes such as magnetic order or charge ordering, or by the variation and/or onset of octahedral rotations related to the tolerance factor (i.e., the relationship between the size of the A and B site cations and the anion, X). Structural transitions may also be electronically driven depending on the cations present and result in changes to the coordination environments of these cations. A well-studied phenomenon is the Jahn-Teller (JT) distortion that results from the lifting of degeneracy of the e_g orbitals that have an unpaired spin [Fig. 1(a)]. This drives the divergence of bond lengths within an MX_6 octahedron which results in either a compression or elongation [Figs. 1(c) and 1(d)]. Over a periodic structure, a long-range orbital ordering (OO) of cooperative JT distortions can manifest to reduce the coulombic repulsion between neighboring atoms and reduce the total energy of the system [2,3]. Where degeneracy has been lifted from the e_g orbital (e.g., Cu^{2+} or Mn^{3+}) an ordering of the d_{z^2} orbital along various x , y , and z axes can occur [Fig. 1(e)]. Orbital order arising from cooperative JT

distortions has been observed in both oxide (LaMnO_3) [4] and fluoride (NaCuF_3 [5] and KCuF_3 [6]) perovskites. When considering an aristotype, cubic perovskite cell, ordering of the $e_g d_{z^2}$ orbitals results in a symmetry-lowering expansion of the unit cell [denoted by the dashed line in Fig. 1(e)] leading to the observation of supercell reflections in diffraction data. In C-type OO, the orbitals order within layers along a specified axis, for example in the case of LaMnO_3 , when crystallising in space group $Pnma$, the orbitals are ordered in the ac plane, with no alternating orbital order along b . This can be observed crystallographically by the alternating directions of the elongation of the MnO_6 octahedra evidenced by variations in the bond lengths. In LaMnO_3 and A-site substituted LaMnO_3 perovskites, at the onset of orbital order, the resistivity of the material drops in a metal-to-insulator transition [7,8], meaning the study of compositionally simple perovskites may provide further insight and implications for the tuning of functional properties such as colossal magnetoresistance which is directly related to orbital order and disorder.

JT distortions arising from electronic degeneracies in the t_{2g} orbitals in perovskites are also possible, though have not been studied to the same extent as JT distortions of the e_g orbitals [9]. Typically, distortions arising from the e_g orbitals result in bond length variations whereas local distortion modes exist that can remove the degeneracy of the t_{2g} orbitals [Fig. 1(b)] via bond angle shearing of the octahedra. In practice, similar bond length distortions, although of much smaller magnitudes compared to those arising from e_g degeneracy, are also found to be associated with the removal of t_{2g} orbital degeneracy and long-range OO in these systems. In the LnVO_3 series (Ln = lanthanoid), V^{3+} (d^2) undergoes various orbital ordering transitions depending on the size of the lanthanoid ion. For all Ln cations, the VO_6 arrangement undergoes a G-type OO transition from $Pnma$ to $P2_1/b11$, and those where $\text{Ln} = \text{Dy}$ to Lu and Y , have a further transition

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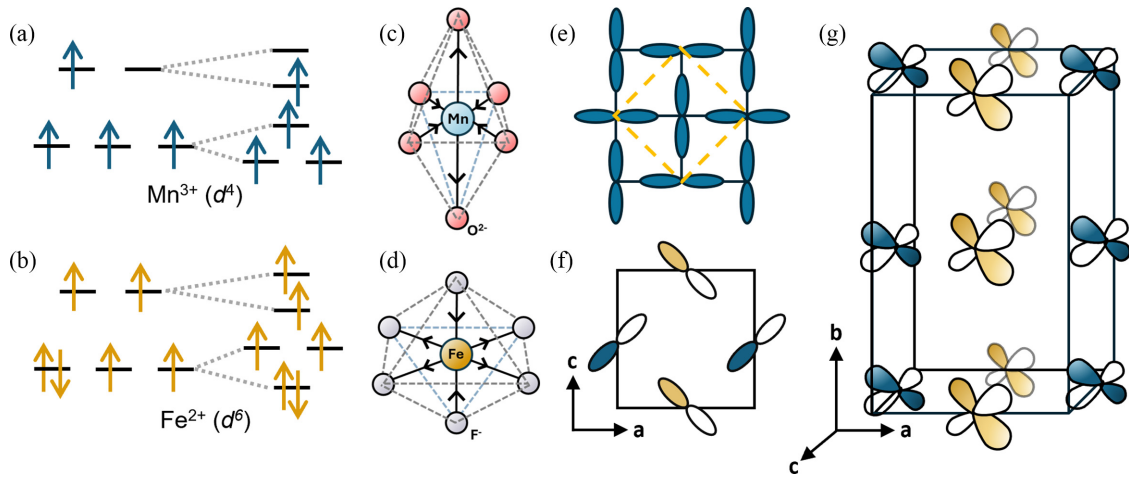


FIG. 1. Crystal field splitting diagrams showing the removal of degeneracy of the (a) e_g and (b) t_{2g} orbitals. These distortions manifest as (c) an elongation (MnO_6) and (d) compression (FeF_6) of the MF_6 octahedra, respectively. (e) Schematic showing orbital order of the d_{z^2} orbitals in a 2×2 primitive cubic cell. Dashed lines denote the new unit cell to describe the OO. [(f) and (g)] C-type orbital order of the d_{xy} orbitals in $Pnma$.

back to $Pnma$ which has a C-type orbital order [10–12]. This series of phase transitions has also been observed in TmVO_3 [13]. The magnitude of JT distortions of the t_{2g} orbitals are far smaller than those of the e_g orbitals, and so care must be taken not to mistake the additional degrees of freedom afforded by the symmetry lowering in orthorhombic perovskites (i.e., octahedral rotations) for those arising from electronic effects. With this in mind one might look to the other transition-metal (TM) cations that may have t_{2g} JT activity, such as Co^{3+} and Fe^{2+} (d^6), Ni^{3+} (d^7). However, the LnCoO_3 (d^6) generally remains in the low spin state with all t_{2g} orbitals doubly occupied and no long-range Co magnetic order is observed [14]; and LnNiO_3 (d^7) may charge disproportionate to Ni^{2+} and Ni^{4+} , where the charge ordering directly competes with and interrupts any long-range OO. Additionally, many $\text{AFe}^{2+}\text{X}_3$ materials do not have the perovskite structure but rather form isolated 1D edge-sharing chains of octahedra (KFeCl_3 , KFeBr_3 [15]) or face-sharing chains (CsFeCl_3 [16], CsFeBr_3 [17]) with no evidence of JT distortions.

Switching the anion from oxide to fluoride, provides an opportunity to study the late d -block transition metals in their 2+ oxidation state with electron configurations that would result in electronic degeneracies of the t_{2g} rather than e_g orbitals. With this in mind, we have synthesised NaCoF_3 (d^7) and NaFeF_3 (d^6). At room temperature, both compositions crystallize in the GdFeO_3 archetype, $Pnma$ space group. A recent study on NaFeF_3 determined the magnetic structure but did not resolve the existence of orbital order [18]. Here we seek to compare the behavior between NaFeF_3 and NaCoF_3 , where a naïve interpretation of the t_{2g} occupancies would lead to an expectation of JT distortions characterised by different patterns of bond length compressions [Fe, Fig. 1(b)] and elongations [Co, equivalent splitting to Mn^{3+} Fig. 1(a)] in the two compounds. Our study aims to deconvolute the bond length distortions that arise from JT distortions and those that are intrinsic to the $Pnma$ perovskite system by comparing the magnitude of structural distortions with two further examples, NaMF_3 ($M = \text{Mn}, \text{Ni}$) which are expected to be JT-inactive.

II. METHODS

NaF (Acros Organics, 97%), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (VWR, analytical grade), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Thermo Scientific, 99 + %), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Thermo Scientific, 99.9 + %), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, 99%) and ethylene glycol (Fisher, $\geq 99\%$) were all used as received without further purification. Polycrystalline powder samples were synthesised using a solvothermal method, whereby 0.060 mol NaF (2.519 g) and 0.020 mol $\text{MCl}_2 \cdot x\text{H}_2\text{O}$ ($M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) were heated in 100 ml of ethylene glycol in a sealed 200 ml autoclave at 120°C for 120 hours. The samples were filtered and dried at 70°C overnight to give approximately 2.5 g of perovskite. If initial powder diffraction showed unreacted NaF was present, the samples were stirred in 10 mL distilled water for 24 hours before being re-filtered and again dried at 70°C overnight (this was not done for NaFeF_3 , to prevent oxidation to Na_3FeF_6). The powders were initially characterised by powder x-ray diffraction (PXRD) on a Panalytical Empyrean diffractometer with a $\text{Cu K}\alpha_{1,2}$ ($\lambda = 1.5406 \text{ \AA}$, $1.5444 \text{ \AA}$) source to confirm phase purity.

Magnetometry measurements were performed on a Quantum Design MPMS-5S SQUID magnetometer. Around 20 mg of accurately weighed powdered sample was loaded into a gel capsule, encased within a plastic straw. Zero-field cooled (ZFC) and field cooled (FC) DC magnetic susceptibility measurements were taken in the range of 2–300 K with an applied field of 1000 Oe.

High-resolution synchrotron PXRD measurements were performed at beamline ID22 ($\lambda = 0.35433788(8) \text{ \AA}$) at the European Synchrotron Radiation Facility (ESRF) between 4–300 K using a Dynaflo ESRF cryostat [19]. Further variable temperature PXRD data were collected between 100 to 500 K at beamline I11 ($\lambda = 0.825257(7) \text{ \AA}$) at Diamond Light Source (DLS). Powder neutron diffraction (PND) data for NaCoF_3 were collected on the high-resolution diffractometer, D2B ($\lambda = 1.595 \text{ \AA}$) at the Institut Laue Langevin (ILL) with samples loaded into a 9 mm cylindrical vanadium can.

Data were analysed by the Rietveld method using TOPAS Academic, version 7 [20] with an incorporated jEdit text editor. All Rietveld refinements of the nuclear structure were carried out on the synchrotron x-ray data collected at ID22 (ESRF) and I11 (DLS). For both ID22 and I11 data the zero error, wavelength and peak profiles were determined from refinement against a NIST silicon standard and fixed. Peak broadening was modeled with Gaussian and Lorentzian contributions to crystallite size and microstrain, which were allowed to refine. Thompson-Cox peak profiles were used for the I11 data, and for ID22 data, peak profiles were modeled with a convolution of Gaussian and Lorentzian contributions using macros defined in TOPAS. Isotropic thermal displacement parameters for each site and scale factors for each phase were allowed to refine freely. Using files generated by ISODISTORT [21–24], a symmetry-based approach was used to investigate structural distortions. With this approach, lattice parameters were determined through refining symmetry-adapted strain modes, and atomic coordinates were determined through refining the irreducible representations corresponding to different structural distortions with respect to a $Pm\bar{3}m$ perovskite with the B -site cation at the center of the unit cell, and lattice parameter, $a_{\text{cubic}} = (\frac{abc}{4})^{1/3}$ where a , b , and c are the $Pnma$ lattice parameters at 300 K for each composition. All strain and distortion mode parameters were allowed to refine freely. It should be noted that there are minor discontinuities in the data at 100 and 300 K due to the use of different datasets. Crystallographic information files (CIF) were visualised using the structure viewing software, VESTA [25]. The PYTHON package, VANVLECKCALCULATOR [26] was used to aid the analysis of Van Vleck distortion modes quantifying the distortion of the B -site octahedra. Details on set up of the octahedral axes are provided in S2 [27]. The magnetic structure of NaCoF_3 was determined from a combined refinement with both x-ray and neutron data to ensure consistency of structural distortions across both datasets.

III. RESULTS AND DISCUSSION

Initial PXRD measurements at room temperature confirmed phase formation for all NaMF_3 perovskites with only minor NaF impurities present. Rietveld models at 10 K using data collected at ID22 are provided in Figs. S3–S6 [27]. Magnetometry results (provided in S6 [27]) for all materials show bulk antiferromagnetic (AFM) transitions accompanied by a weak ferromagnetic (FM) component as evidenced by the splitting of the FC and ZFC measurements. Curie-Weiss fitting of the paramagnetic region for $M = \text{Fe}$ and Co yielded values that were indicative of both transition metals being in their high-spin electron configuration, in line with previous reports [18]. This is important to establish when comparing NaFeF_3 to LnCoO_3 , since while both are d^6 , Co^{3+} tends to form the low spin [14], t_{2g}^6 electron configuration which is neither JT active nor magnetic.

Rietveld refinements carried out against the synchrotron x-ray data (both ID22 and I11) show that all NaMF_3 crystallize in $Pnma$ between 4 to 500 K [Fig. 2(a)]. By performing distortion mode refinements generated using ISODISTORT, it is possible to extract further information on the symmetry lowering structural distortions away from the aristotype

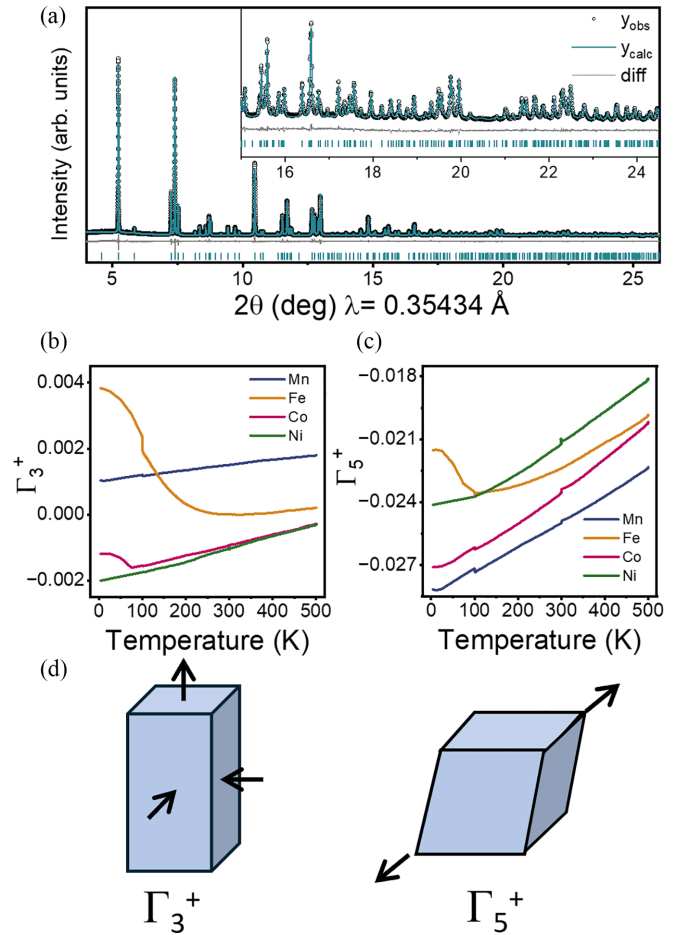


FIG. 2. (a) Rietveld refinement of NaFeF_3 in $Pnma$ using XRD data collected at ID22 [$\lambda = 0.35433788(8) \text{ \AA}$] at 4 K. (b) Γ_3^+ and (c) Γ_5^+ strain modes determined from symmetry mode refinements for NaMF_3 . (d) schematic depictions of the Γ_3^+ and Γ_5^+ strain modes.

$Pm\bar{3}m$ perovskite via irreducible representation (irrep) analysis. Within this formalism the symmetry breaking strain modes, related to the refined lattice parameters transform as irreps Γ_3^+ and Γ_5^+ [Figs. 2(b)–2(d)]. Symmetrized strains for $M = \text{Co}$ and Fe show a deviation from the expected trend at lower temperatures hinting at possible phase transitions, when compared to $M = \text{Ni}$ and Mn where no OO is expected. While the smaller deviation in Γ_3^+ in Co is concomitant with its AFM transition temperature, T_N [78(1) K] and therefore likely related to magnetostriction, the deviation in Γ_3^+ for Fe [$T_N = 89(1) \text{ K}$] occurs far above this, at nearer 300 K [Fig. 2(b)], and is significantly larger in magnitude suggesting it is not of magnetostrictive origin. In the basis of the $Pnma$ crystal structure, this has a pronounced effect in the b lattice parameter (Fig. S1 [27]) which shows a clear negative thermal expansion below 160 K, and plateaus below T_N . Bernal *et al.* observed similar behavior in the lattice parameter trends for NaFeF_3 , however they ascribed this to magnetostriction based on the observation of a diffuse magnetic peak occurring below 120 K [18]. This is well below the onset of the rapid increase of Γ_3^+ strain shown in Fig. 2(b) but may be related to the small anomaly we see in Γ_5^+ at this temperature [Fig. 2(c)],

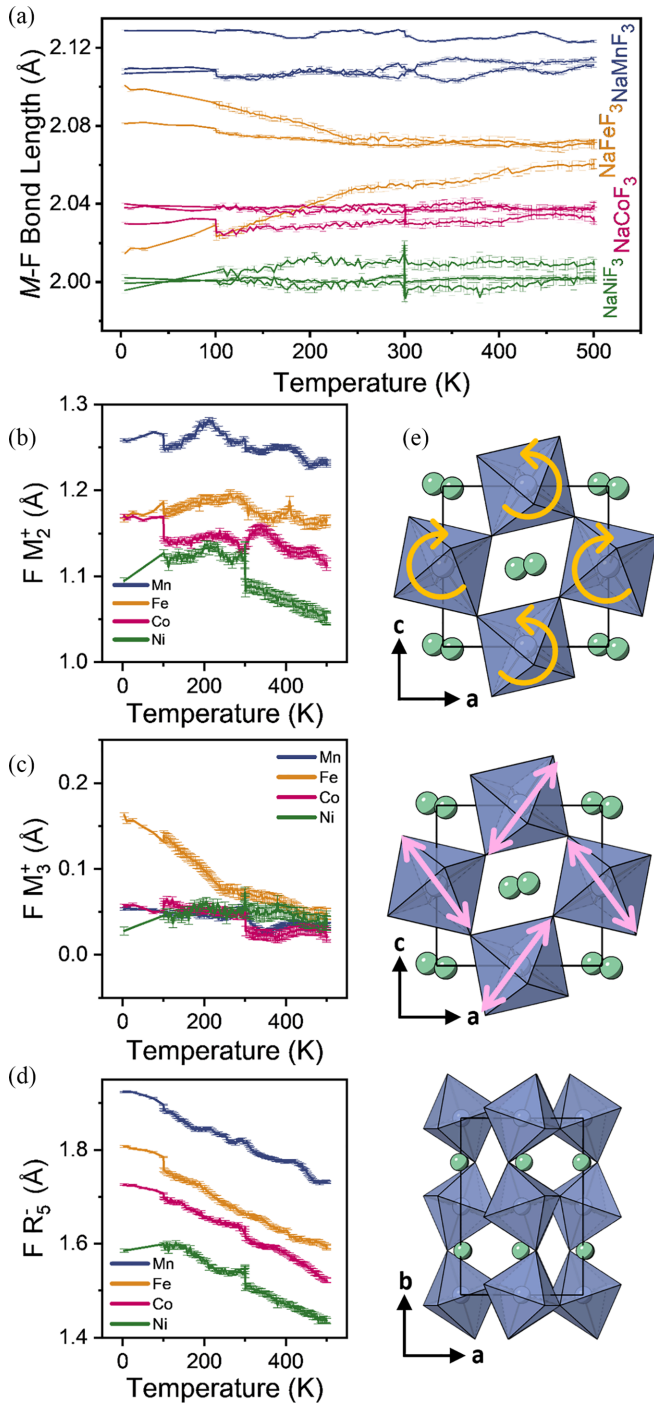


FIG. 3. (a) M -F bond lengths versus temperature highlighting the octahedral compression in NaFeF₃ compared to Mn, Co, and Ni. Variations in the; (b) M_2^+ , (c) M_3^+ , and (d) R_5^- distortion modes with temperature, determined from symmetry mode refinements. (e) depictions of the (top to bottom) M_2^+ , M_3^+ , and R_5^- distortion modes.

highlighting the benefit of working in this symmetry-adapted basis.

Figure 3(a) shows the M -F bond lengths with decreasing temperature. While it is noted that in $Pnma$, there is an allowed deviation of the bond lengths from each other, the deviation observed in NaFeF₃ is far greater than any other

in the series and becomes more pronounced with decreasing temperature. It also shows the four long, two short arrangement as expected when considering the crystal field splitting in Fig. 1(b).

As well as providing an orthogonal basis in which to view the evolution of the structural degrees of freedom, when using symmetry mode analysis, in many cases the irreps have a fortuitous direct correspondence with physically intuitive origins such as octahedral tilting, bond length distortions and antipolar displacements [28].¹ The M_2^+ and R_5^- distortion modes describe the in-phase and out-of-phase tilting of the B -site octahedra respectively, whereas M_3^+ describes B -X bond length distortions associated with a JT elongation/compression of the octahedra which are shown in Fig. 3(c). The trends [Figs. 3(b) and 3(d)] in NaFeF₃ for the M_2^+ and R_5^- mode amplitudes follow those of the other transition metals, however, the M_3^+ mode which controls the octahedral compression/elongation drastically increases with decreasing temperature to be over three times as large at 4 K than for the other transition metals. All additional distortion modes are provided in Fig. S2 [27].

To further understand the underpinning distortions, the Van Vleck distortion modes (Q modes) [29] for the MX_6 octahedra were calculated. Q_2 and Q_3 describe bond length distortions, and were calculated using bond lengths whereas Q_{4-6} describe bond angle distortions (Fig. S9 [27]). To calculate Q_{4-6} , the PYTHON package, VANVLECKCALCULATOR [26] was used. This method allows the Q modes to be extracted without disregarding any angular distortion resulting from shearing of the octahedra; a point we consider important to investigate since in principle, these shearings provide an alternative mechanism for removing the degeneracy of the local t_{2g} electronic state. Q_1 is a breathing mode, and $Q_{2,3}$ have transformational E_g symmetry, whereas Q_{4-6} distortions are of T_{2g} symmetry [29]. Thus these Q modes form a natural basis by which to investigate the local OO. The Q_2 mode character reflects a 2 long, 2 medium, 2 short planar rhombic distortion, and Q_3 as a Jahn-Teller 2:4 tetragonal elongation or compression. Q_{4-6} do not appear to have significant variations with temperature (see Fig. S8 [27]) however clearly Q_2 and Q_3 appear to behave like an order parameter in NaFeF₃. This is in stark contrast to the behavior of M_3^+ mode amplitudes and Q_2/Q_3 distortions in $M = \text{Mn, Co or Ni}$ which have small, temperature independent values.

Since the symmetry breaking distortions that lead to these local $Q_{2,3}$ distortions are formally allowed through improper couplings with octahedral rotations that give rise to the observed $Pnma$ symmetry in these perovskites, it is important to untangle those contributions from that intrinsically driven by the electronic ordering. Here, a comparison of different compositions with similar tolerance factors but varying electronic degeneracies enable these two factors to be unpicked. To do this, the Jahn-Teller parameters ϕ and ρ_0 were calculated; $\phi = \arctan(Q_2/Q_3)$ and $\rho_0 = (Q_2^2 + Q_3^2)^{1/2}$. ϕ and ρ_0 [Figs. 4(a) and 4(b)] describe the angle and vector magnitude of JT distortion respectively within the Q_2 - Q_3 distortion

¹All irrep labels are given with respect to a $Pm\bar{3}m$ unit cell with the A site at the origin.

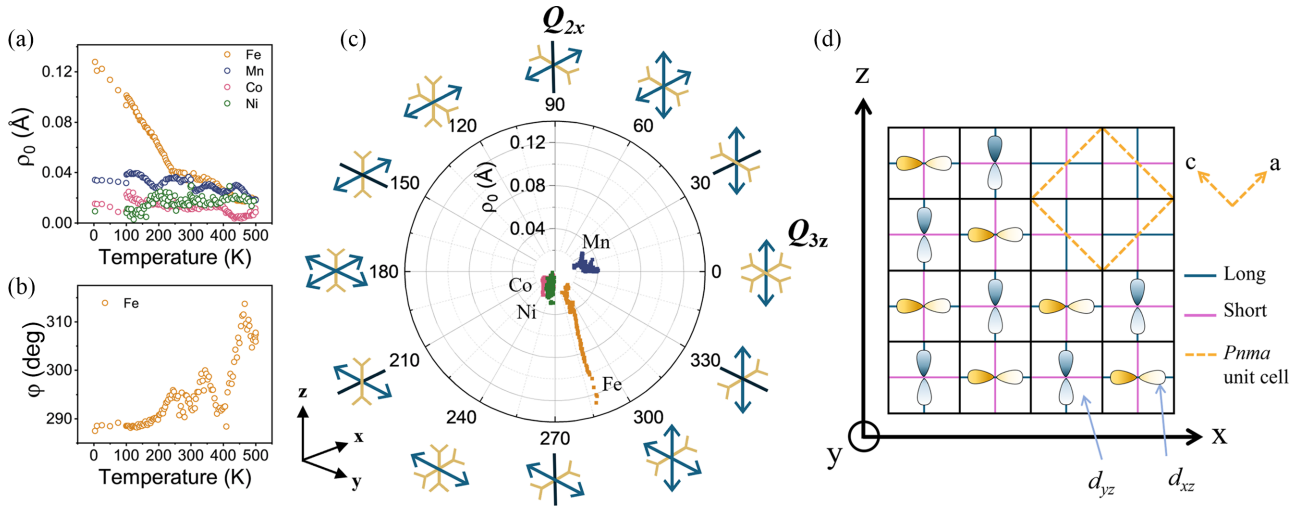


FIG. 4. (a) ρ_0 vs temperature for NaMF₃. (b) ϕ vs temperature for NaFeF₃. (c) Polar figure drawn following the convention used in Ref. [35] showing the Q_2 - Q_3 distortion space with the magnitudes of NaMF₃ shown. The axes in the bottom left corner depict the axes of the octahedron. (d) A schematic highlighting the ordering of the doubly filled d_{xz} and d_{yz} orbitals.

space, used to describe octahedral distortions occurring due to the lifting of degeneracy within the e_g orbitals. Whilst Fe²⁺ has degeneracy within the t_{2g} orbitals, the resulting octahedral deformations also cause a splitting of the e_g orbitals, meaning that there may be signatures of these distortions within the e_g phase space. A polar plot of the Q_2 - Q_3 phase space is shown in Fig. 4(c) which describes the octahedral configuration along different octahedral directions [30,31]. The magnitude of the distortion observed in Fe²⁺ is far greater than the other transition metals, clearly indicating the presence of the JT distortion [see Fig. 4(a)]. As anticipated the tetragonal compression occurs along x , with an elongation along y and z , indicative of the fully occupied, stabilized d_{yz} orbital which would be consistent with the expected splitting for a d^6 high spin cation. A 90° rotation of the octahedra on the neighboring B site corresponds to a swapping of the long and short bond lengths along x and z , resulting in a ϕ angle where the compression occurs along y meaning a stabilization of the d_{xz} orbital (Fig. S10 [27]). This relationship is imposed by the $Pnma$ symmetry and is a form of C-type orbital order. It should be noted that the ϕ values for NaFeF₃ lie somewhere between that of a pure Q_3 or Q_2 . This is a similar intermediate situation as observed in LaMnO₃ which has a ϕ of 107°, i.e., somewhere between 90° (pure Q_2) and 120° (pure Q_3) [4,30]. Additionally, there is no abrupt change in the magnitude of ρ_0 [Fig. 4(a)] which gradually increases with decreasing temperature, indicative of a second-order phase transition. This creates an apparent contradiction since an isosymmetric phase transition (i.e., a phase transition with no space group symmetry lowering) should be first order [32]. This is true for all processes involving an instantaneous transfer of electrons between states, for example, the phase transition from orbital ordered to disordered state in LaMnO₃ at around 750 K is accompanied by a sharp discontinuity in the volume [33,34]. This contradiction would be resolved if there was some hidden symmetry breaking associated with this transition that we are not sensitive to see with the diffraction methods used to probe the phase transition. The microstrain of our sample $\epsilon_0 \approx 0.06\%$, as determined from our high-resolution powder

diffraction data collected on ID22, sets an upper limit on any such coupling to macrostrain such further symmetry breaking could impose. This is approximately an order of magnitude lower than the excess strain associated with the coupling of Γ_3^+ to the OO.

As mentioned above, on cooling, NaFeF₃ shows no signs of long-range symmetry lowering by diffraction and is fitted well to $Pnma$ at all temperatures. This does not exclude the presence of Jahn-Teller distortions with a C-type orbital ordering (Fig. 4(d)), as allowed by symmetry in $Pnma$ perovskites and is observed in LnTiO₃ (t_{2g}^1) [9,36]. However, identifying the onset of OO becomes more complex since $Pnma$ has an intrinsic distortion of the MF_6 bond lengths that transforms as the M_3^+ irreducible representation and forms a secondary order parameter to the in-phase (M_2^+) and out-of-phase (R_5^-) octahedral tiltings, and results in a 2 long, 2 medium, 2 short M -F bond lengths, as evident in $M = Ni$ and Mn [Fig. 3(a)]. By comparing $M = Fe$ to $M = Ni$ and Mn we can disentangle the bond length distortions arising simply due to the coupling with the primary order parameter (octahedral tilting and rotations, see Fig. S4 [27]), and those distortions which are driven by the orbital order itself (see Fig. S11 [27]). Taking the excess Γ_3^+ strain due to OO as proxy for the order parameter [37], this allows us to estimate a second-order phase transition temperature $T_{OO} = 240.1$ (8) K. There is additionally a higher temperature region with $T_{JT} = 457.8$ (10) K which may be related to the onset of JT distortion of the octahedra and the presence of short-to-mid-range cooperative motions (Fig. S12 [27]). Details of the fitting are provided in Ref. [27]. The merit in this analysis is that the strain can be determined very precisely when using data approaching a resolution of 10^{-5} (i.e., the high-resolution ID22 data), whereas distortion modes typically have a high degree of uncertainty associated with them on account of correlations and systematic errors.

By looking at the ordering of individual bond lengths within the structure [Fig. 4(d)], there are alternating short and long Fe-F bonds perpendicular to b , and a second long bond is aligned along b . This results in a compressed octahedron with an alternating compression along the [101] and [10 $\bar{1}$]

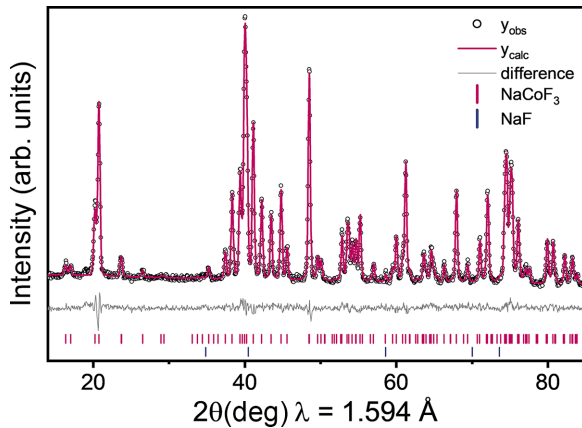


FIG. 5. (a) Rietveld refinement of NaCoF₃ in *Pnma*.1 (BNS number 62.441) using neutron diffraction data collected at D2B ($\lambda = 1.594$ Å) at 4 K. An NaF impurity is present corresponding to a phase fraction of 0.37%.

directions between neighboring octahedra in the *ac* plane. This occurs due to the 90° rotation of the symmetry equivalent, corner-sharing octahedra, that may be assigned to have an alternation of the doubly occupied t_{2g} orbital: the d_{xz} and d_{yz} . Since there is no alternating of bond lengths along *b* and rather “columns” of octahedra elongated along one direction (*b*) occur, the OO pattern is described as C-type OO. Figure 4(d) depicts the alternating ordering of the d_{xz} and d_{yz} orbitals through a schematic representation.

The absence of any deviation in $M = \text{Co}$ from the general trend in Γ_3^+ observed, allows us to rule out the presence of any C-type orbital ordering in this compound down to 4 K. Additionally no monoclinic distortions or supercell reflections were observed in the diffraction data, which would have indicated the presence of any symmetry lowering. Given that NaCoF₃ is an AFM insulator with a fully saturated magnetic moment of 2.89(2) μ_B/Co , this implies it has an orbitally disordered ground state in which any orbital angular momentum is fully quenched, rather than a high spin - low spin (t_{2g}^6) transition or adopting a fully delocalized metallic state. (See magnetic susceptibility indicating high spin Co²⁺, and magnetic structure in Fig. S13(b) and S13(d) [27] determined by refinement against neutron diffraction data (Fig. 5).) It is interesting to compare NaCoF₃ with the LnVO₃ series since one might expect them to have strong similarities in the JT distortions associated with t_{2g}^5 and t_{2g}^2 degeneracies and hence the nature of the orbital order. As stated in the introduction, LnVO₃ have G-type OO transitions, with the smaller Ln hosting a further lower temperature reentrant C-type OO transition (*Pnma*) [10,12,38]. In YVO₃ the C-type OO phase transition temperature to *Pnma* symmetry from one that has G-type orbital order [39] occurs below approximately 60 K, and above 220 K the G-type orbital order disappears. In comparison NaCoF₃ shows no evidence of symmetry lowering to a G-type OO phase or ordering of bond lengths to a C-type OO in *Pnma*.

Since the tolerance factor for both YVO₃ ($\tau = 0.836$) and NaCoF₃ ($\tau = 0.842$) are similar and their structures would be assumed to have similar degrees of octahedral tilting it may be surprising in their apparent discrepancy between the adopted

ground states. Comparing the structures at room temperature, above any orbital ordering, we find YVO₃ has negative Γ_3^+ (−0.016) indicating a tetragonal compression. NaCoF₃ on the other hand has a value that is much closer to zero (0.001). This intrinsic strain biases the LnVO₃ to form G-type OO below the ordering temperature [39] and hence offers a reason why a similar form of OO is absent in NaCoF₃.

IV. CONCLUSIONS

Our studies have shown the presence of t_{2g} orbital order in fluoride perovskites by analysis of the octahedral distortions. We show that Jahn-Teller distortions are present in NaFeF₃, and manifest as an ordering of a fully occupied d_{xz} and d_{yz} orbital in a C-type ordered fashion as allowed in *Pnma*.

We further show that NaFeF₃, undergoes a C-type orbital order transition that is driven by the electronic degeneracy of the local t_{2g}^4 states of Fe²⁺, producing a Jahn-Teller distortion with 2 short, 4 long bonds in accordance with expectations based on crystal field arguments. Surprisingly, the apparently isosymmetric phase transition is second-order like, inconsistent with thermodynamic requirements and thus imply there must be an associated hidden symmetry breaking. On the other hand, the careful consideration of the temperature evolution of the symmetry adapted strain in NaCoF₃ allows us to confidently rule out the occurrence of any long-range orbital orders. Since NaCoF₃ is an insulator in which orbital angular momentum is evidently fully quenched below T_N , our findings point towards a novel orbital disorder associated to the t_{2g}^5 electronic degeneracy. Our findings should motivate further investigations into the factors that can control and tune the cross-over from orbital order to disorder, with implications for technologically relevant properties.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [40], embargo periods may apply.

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