

Pressure-induced orbital reordering in Na_2CuF_4

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The high-pressure behavior of Na_2CuF_4 is explored by powder neutron diffraction and density functional theory (DFT) calculations. A first-order phase transition is observed to take place between 2.4 and 2.9 GPa, involving a reorientation of the Jahn-Teller (JT) long axes of the $[\text{CuF}_6]$ octahedra (and therefore the d_{z^2} Cu orbitals), in agreement with our DFT calculations which suggest a transition at ~ 2.8 GPa. The transition can be described as being between a state of ferro-orbital order and one of A-type antiferro-orbital order, reflecting a shift in the associated electronic instability from being in the zone center to zone boundary of the first Brillouin zone of the parent structure. This change results in a decoupling of magnitude of the associated Jahn-Teller distortion of the Cu-F bond lengths from the lattice strain. This scenario is supported by our observations that the compressibility of the pretransition phase is highly anisotropic, while in the posttransition phase it becomes almost isotropic, and that we observed no further decrease of the magnitude the JT distortion up to 5 GPa, or melting of the orbital ordering in our DFT calculations up to at least 5 GPa.

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I. INTRODUCTION

The degenerate electronic ground state of Cu^{2+} (d^9) in an octahedral crystal field makes it Jahn-Teller (JT) active, which is manifested as a distortion of the Cu local environment. Many crystalline phases with infinitely connected structures containing Cu^{2+} display a cooperative JT effect, i.e., an ordering of the Cu d orbitals, leading to a lowering of the structure's symmetry relative to its aristotype. For example, while the majority of the fluoride perovskites (general formula AMF_3) are considered to be cubic at room temperature, KCuF_3 adopts a tetragonal [1–4] (or orthorhombic [5]) structure due to an elongation of the c axis, yielding one-dimensional $S = 1/2$ antiferromagnetism [6], and similarly cuprospinel (CuFe_2O_4) has a tetragonal structure that is a distorted variant of the spinel structure [7]. The cooperative JT effect has been suggested as the underlying cause of a variety of unusual electronic phenomena such as superconductivity in cuprates [8] and colossal magnetoresistance in manganites [9].

Although the (doped) copper oxide $n = 1$ Ruddlesden-Popper (RP) phases are the eponymous high- T_c superconduct-

ing materials [10], the phenomenon appears to be absent in RP copper fluorides (general formula A_2CuF_4). Despite being isostructural and isoelectronic, the magnetic interactions are completely different: La_2CuO_4 displays antiferromagnetic order [11–13] while A_2CuF_4 ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) all display two-dimensional ferromagnetism in the ab plane [14,15]. This is possibly on account of a small structural distortion present in La_2CuO_4 consisting of tilting of the $[\text{CuO}_6]$ octahedra caused by the large difference in ionic radii between A^+ and La^{3+} (e.g., nine-coordinate $r_{\text{K}} = 1.55 \text{ \AA}$ compared to $r_{\text{La}} = 1.216 \text{ \AA}$ [16]), leading to significant differences in the electronic structure.

While Na_2CuF_4 has the RP stoichiometry, and $r_{\text{Na}} = 1.24 \text{ \AA}$ is very close to that of r_{La} , it adopts a monoclinic structure ($P2_1/c$) consisting of one-dimensional chains of edge-sharing $[\text{CuF}_6]$ octahedra [17,18]. A similar structure is adopted by several other $3d$ metal fluorides which have been considered analogues of the silicate Mg_2SiO_4 , thought to be found at extremely high-pressures [19] and identified as possible Na-ion battery cathode materials [20]. A recent study on Na_2CuF_4 observed several phase transitions up to 30 GPa by Raman spectroscopy in a diamond anvil cell [19], with the first occurring at 4 GPa, but direct characterization of the structure and symmetry of these phases is missing in the literature. Motivated by this, and the prospect of transforming Na_2CuF_4 to the denser RP structural type, we have conducted variable-pressure neutron powder diffraction (which is particularly sensitive to sodium and fluoride ions) up to 5 GPa revealing a structural phase transition driven by orbital reordering.

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II. EXPERIMENTAL TECHNIQUES

NaF (Acros Organics, 97%) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Honeywell, $\geq 99.0\%$) and ethylene glycol (Fisher, $\geq 99\%$) were all used as received without further purification. Polycrystalline samples were synthesized using a solvothermal method. 1.705 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.01 mol) and 1.260 g NaF (0.03 mol) were added to 100 ml ethylene glycol. The resulting solution was added to a 200 ml Teflon-lined steel autoclave and heated to 120 °C for 120 h. After cooling, the sample was filtered and rinsed with a small additional quantity of ethylene glycol and subsequently allowed to dry at 70 °C overnight (1.145 g yield).

The sample was initially characterized by laboratory x-ray powder diffraction (XRD) using a Panalytical Empyrean diffractometer with $\text{Cu K}\alpha_{1,2}$ (1.5406 Å, 1.5444 Å) source. Refinements against laboratory XRD data showed a small (0.78(14) wt. %) impurity of NaF, as well as some unidentified even weaker peaks (Fig. S1 [21]). No attempt was made to remove the NaF by washing with water, since it was found in preliminary experiments that Na_2CuF_4 readily reacts with water to form $\text{Cu}(\text{OH})\text{F}$.

Time-of-flight variable-pressure neutron diffraction measurements [22] were carried out using the PEARL diffractometer [23] at the ISIS Neutron and Muon Facility. A small amount of sample (~ 0.2 g) was encapsulated in a TiZr gasket with a Pb pressure marker and deuterated 4 : 1 methanol and ethanol mixture as pressure transmitting medium. The gasket was sealed between a pair of single-toroidal profiled anvils machined from zirconia-toughened alumina (ZTA) and the assembly was loaded into a V3 Paris-Edinburgh press. An initial load of 4 tons was applied, and then increased in 2 ton increments (~ 0.2 GPa) up to 20 tons (with a resulting pressure of ~ 2 GPa), followed by 5 ton increments (~ 0.5 GPa) up to 60 tons (with a resulting pressure of ~ 5 GPa). The applied load was then decreased to 5 tons and then 0 tons. Resulting diffraction patterns showed peaks from the ZTA anvils (ZrO_2 , Al_2O_3) and the Pb pressure marker, which were included as phases in Rietveld refinement models. All structural refinements were carried out against powder diffraction data using TOPAS version 6 [24] (further details of Rietveld refinements against variable-pressure neutron diffraction data are included in Results and Discussion). The contribution of the secondary phases [NaF and an unidentified phase that was visible by XRD (see above)] to the variable-pressure neutron diffraction patterns collected using PEARL with lower signal : noise from reasonable collection times is minimal: the diffraction peaks from NaF were not observed and only weak unidentified diffraction peaks were visible at $Q = 2.75 \text{ \AA}^{-1}$ and $2.85 \text{ \AA}^{-1}$ (Fig. S2 [21]). To simplify the model, these additional peaks were not accounted for in Rietveld refinements against variable-pressure powder neutron patterns and were treated as part of the background. The applied pressure at the sample was determined from the refined Pb lattice volume using the Birch-Murnaghan equation of state [25] (Eq. S1 [21]) for Pb [26].

The structural models of the high-pressure phase and the aristrotypes were generated using functions within the ISOTROPY suite [27] (further details form part of the Results and Discussion). The software PASCAL [28] was used

to calculate the principal compressibilities and carry out a Birch-Murnaghan equation of state fit against the refined cell volume of Na_2CuF_4 .

First-principles calculations were performed within the DFT framework as implemented in the VASP code [29,30], version 6.3.2. Perdew-Burke-Ernzerhof (PBE) sol variant of the generalized gradient approximation was used as the exchange-correlation functional, which is known for its accuracy in describing bulk structural properties [31]. Projector-augmented-wave pseudopotentials (PBE, potpaw.64) [32,33] with the following valence configurations were employed: $2s^2 2p^6 3s^1$ (Na), $3p^6 4s^1 3d^{10}$ (Cu), and $2s^2 2p^5$ (F). Convergence tests performed on a 14-atom unit cell of the ambient-pressure monoclinic structure revealed that a plane wave energy cutoff of 900 eV and a k -mesh grid of $9 \times 3 \times 5$ were necessary to resolve the total energy within 0.002 meV/f.u. The energy convergence criterion was set to 10^{-9} eV and performed full relaxations until the Hellmann-Feynman forces on each atom converged to 1 meV/Å. Correlation effects of the 3d electrons of Cu were included using $U = 7.5$ eV and $J = 1.0$ eV [19,34–36] within the DFT+ U approach introduced by Dudarev *et al.* [37].

III. RESULTS AND DISCUSSION

Rietveld refinement against powder neutron diffraction data at $p = 0.193(4)$ GPa shows good agreement with the monoclinic ($P 1 2_1/c 1$) structure of Na_2CuF_4 determined by single crystal x-ray diffraction [18] [Fig. 1(a), Table I], named herein as Na_2CuF_4 -I. Upon application of pressure, the onset of a phase transition is observed at $p = 2.44(2)$ GPa which is not complete until 3.39(3) GPa [Fig. 1(b)]. This coexistence of both the initial and new phases is indicative of a first-order phase transition. No further phase transitions were observed up to $p = 5.05(7)$ GPa, and upon depressurization to ambient pressure the material returns to the Na_2CuF_4 -I structure (Fig. S3 [21]).

While the Na_2CuF_4 -I ($P 1 2_1/c 1$) model provides an approximate fit to the high-pressure diffraction data; it does not capture all features with some peaks poorly fitted (Fig. S4b, Table S1 [21]). None of the previously calculated structures proposed by Upadhyay *et al.* [19] provided a satisfactory fit to our high-pressure diffraction data, nor did the related orthorhombic structure adopted by Na_2FeF_4 [20] (see Fig. S4, Table S1 [21]). An orthorhombic ($Ammm$) [38] structural aristotype [$a = 3.2621 \text{ \AA}$, $b = 9.3607 \text{ \AA}$, $c = 5.6066 \text{ \AA}$, $\text{Cu}1(0,0,0)$, $\text{F}1(1/2,0,1/4)$, $\text{F}2(0,1/4,0)$, $\text{Na}(1/2,1/4,1/4)$] was identified using the FINDSYM software [39] and permitted subgroups were identified by ISODISTORT [39], both of which are part of the ISOTROPY software suite [26]. The $Ammm$ aristotype consists of one-dimensional chains of edge-sharing $[\text{CuF}_6]$ octahedra extending along the a -axis direction, separated by Na ions [Fig. 2(b)]. The space group symmetry confines all Cu–F1 bonds (which form the edge-sharing network) to have the same length, precluding any kind of long-range orbital ordering driven by JT distortions along the chains. Additionally, the chains can display no rotation around the chain axis (equivalent to the crystallographic a axis).

Octahedral rotation around the chain axis (Y_2^+ distortion mode, where the rotation direction alternates between

TABLE I. Refined parameters for Na₂CuF₄ polymorphs from Rietveld refinements to neutron powder diffraction at $p = 0.194(3)$ GPa and 5.05(7) GPa.

	Na ₂ CuF ₄ -I	Na ₂ CuF ₄ -II
Pressure / GPa	0.194(3)	5.05(7)
R_{wp} / %	3.03	3.68
Space group	$P 1 2_1/c 1$	$P 1 1 2_1/b$
a / Å	3.26249(11)	3.1695(2)
b / Å	9.3613(3)	9.0986(5)
c / Å	5.6071(3)	5.4685(4)
Unique angle / °	β , 92.441(2)	γ , 90.777(6)
V / Å ³	171.091(12)	157.686(19)
Cu1, 2a		0, 0, 0
Na1, 4e	0.5217(17), 0.1858(7), 0.4136(8)	0.499(2), 0.1830(9), 0.4193(9)
F1, 4e	0.5692(9), 0.4502(4), 0.2689(7)	0.5799(14), 0.4522(5), 0.2628(7)
F2, 4e	0.0109(12), 0.1861(5), 0.1268(7)	0.0131(15), 0.1929(6), 0.1294(7)
B_{iso}	0.79(5)	0.19(5)

neighboring chains) lowers the symmetry to $Pmcb$ [Fig. 2(c)]. From $Pmcb$, applying either the Y_4^+ or Y_3^+ distortion modes lead to either Na₂CuF₄-I ($P 1 2_1/c 1$) or to a structure with the space group $P 1 1 2_1/b$ (Na₂CuF₄-II), respectively [Fig. 2(a)], that provides a very good fit to the high-pressure neutron powder diffraction data at 5.05(7) GPa [Fig. 1(c)]. While both distortions lead to a monoclinic cell, each has an additional degree of freedom (that transform at the Γ_3^+ and Γ_4^+ irreducible representations (irreps), respectively), and lead to a different unique axis. The Y_4^+ (in Na₂CuF₄-I) and Γ_4^+ (in Na₂CuF₄-II) distortion modes displace the “apical” (i.e., not part of the edge-sharing network) F2 site along the a axis from the aristotypical site. On the other hand, the Γ_3^+ (as in Na₂CuF₄-I) and Y_3^+ (as in Na₂CuF₄-II) modes correspond to x -direction displacement of the F1 site which allows for two Cu–F1 bond distances, allowing the JT elongated (l) Cu–F bond to lie within the edge-sharing network in both phases. The key structural difference between Na₂CuF₄-I and Na₂CuF₄-II lies in the orientation of the l Cu–F bonds. In Na₂CuF₄-I, the Γ_3^+ distortion leads to l Cu–F bonds being parallel within the chains and pseudo-parallel (i.e., parallel if the Y_2^+ chain rotation is disregarded) to those of the nearest neighboring chain [Fig. 2(d)]. In Na₂CuF₄-II, the Y_3^+ distortion still yields parallel interchain l Cu–F bonds, but the intrachain l Cu–F bonds are now pseudoperpendicular [Fig. 2(e)]. Since one of these distortions may be viewed as transforming as a zone center and the other as a zone-boundary irrep of $Ammm$, the transition can be considered as going from ferro-orbital (Na₂CuF₄-I) to A-type antiferro-orbital (Na₂CuF₄-II, with ferro-orbital ordering in one-dimension, and antiferro-orbital ordering between nearest neighbors in two dimensions [40]) ordering. The relative energies of each structure at ambient pressure were calculated by DFT, and it was found that Na₂CuF₄-II is only ~ 2 meV/f.u. less stable than Na₂CuF₄-I [Figs. 2(b)–2(e)], compared to the intermediate symmetry phase ($Pmcb$), which is over 50 meV/f.u. higher. With the exception of the $Ammm$ aristotype, the structures were all predicted to have A-type antiferromagnetic ground states (Fig. S5, Table S2 [21]).

The structures of Na₂CuF₄-I and Na₂CuF₄-II allow a good fit to the data at all pressure points studied [up to $p = 5.05(7)$

GPa, Fig. 1(c)]. Rietveld fits against each dataset were carried out using (in addition to phases arising from the sample environment and pressure marker): only Na₂CuF₄-I from $p = 0.193(4)$ GPa to $p = 1.963(12)$ GPa; both Na₂CuF₄-I and Na₂CuF₄-II at $p = 2.44(2)$ GPa, $p = 2.91(2)$ GPa and 3.39(3) GPa; and only Na₂CuF₄-II from $p = 3.93(3)$ GPa to $p = 5.05(7)$ GPa. In the pressure region in which both phases coexist, the refined relative mass fraction is shown in Fig. S6 [21]. When significant quantities of the two phases are present [at $p = 2.44(2)$ GPa and 2.91(2) GPa], strong peak overlap made refined crystallographic atomic parameters extremely correlated and unreliable. In the data measured at $p = 3.39(3)$ GPa, the fraction of Na₂CuF₄-I was sufficiently low (9.8(5) wt. %) that parameters for Na₂CuF₄-II could be extracted. To minimize the number of refined parameters, a single atomic displacement parameter was refined across all sites, which was found to decrease as a function of pressure; at 5.05(7) GPa it was around 25% of the ambient pressure value (Table I), broadly in line with other high-pressure studies which ascribe this to reduced atomic vibrations due to closer atomic packing [41,42]. Plots of refined lattice parameters as a function of pressure are available in Figs. S7a–c [21].

In Na₂CuF₄-I, β tends towards 90° as the pressure increases from 92.441(2)° at $p = 0.193(12)$ GPa to 91.65(2)° at $p = 2.91(2)$ GPa. However, in Na₂CuF₄-II the oblique angle γ is largely invariant with pressure at $\sim 90.8^\circ$ between $p = 2.44(2)$ GPa and $p = 5.05(7)$ GPa [Fig. 3(a)]. In both phases the change in cell lengths remain continuous and the oblique angle’s proximity to 90° means its variability has a small influence on cell volume, V , leading to no significant discontinuity in V . To demonstrate this, a single third order Birch-Murnaghan equation of state [25] (Eq. S1 [21]) was fitted to V of both Na₂CuF₄-I and Na₂CuF₄-II as a function of pressure using PASCAL [Fig. 3b, Table II] [28], with a bulk modulus, B_0 , of 46.1(4) GPa. In the absence of a significant decrease in V , it is not immediately obvious what is driving this subtle pressure-induced phase transition, since the local bonding environments of each atom is essentially unchanged (Figs. S7d–f [21]).

The Γ_1^+ distortion mode (that transforms as a breathing mode of the [CuF₆] octahedron) which has the same variation

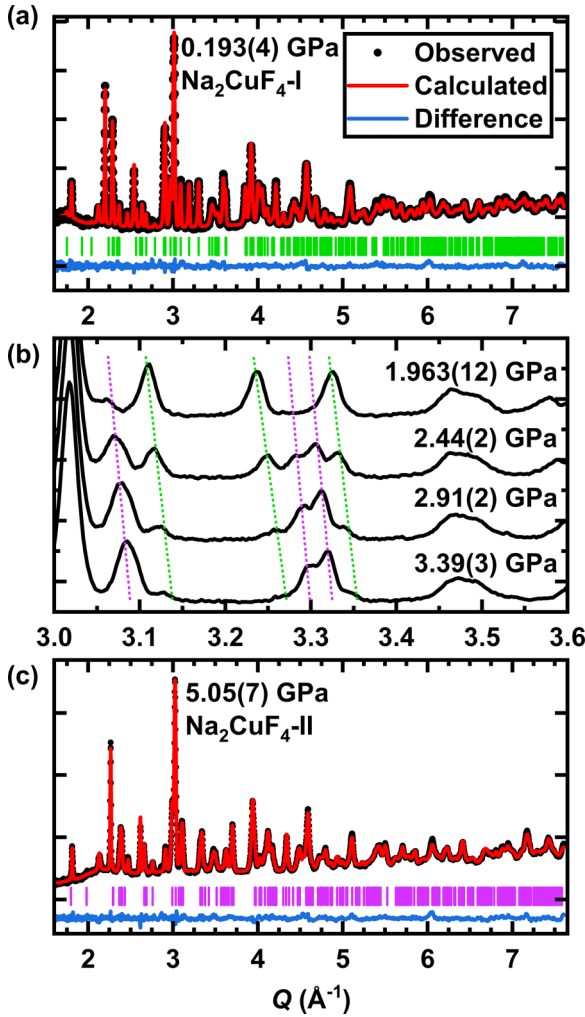


FIG. 1. Variable-pressure neutron powder diffraction data measured at PEARL plotted in scattering vector, Q ($=2\pi/d$). (a) Rietveld refinement of the $\text{Na}_2\text{CuF}_4\text{-I}$ ($P 1\ 2_1/c\ 1$) structure against data measured at $p = 0.193(4)$ GPa. (b) Diffraction patterns measured around the phase transition with an incremental offset for clarity. As a guide for the eye, colored lines track the approximate positions of diffraction peaks of the $\text{Na}_2\text{CuF}_4\text{-I}$ (green) and $\text{Na}_2\text{CuF}_4\text{-II}$ (purple) phases. (c) Rietveld refinement of the $\text{Na}_2\text{CuF}_4\text{-II}$ ($P 1\ 1\ 2_1/b$) structure to data measured at $p = 5.05(7)$ GPa. Tick marks in (a) and (c) are only for the Na_2CuF_4 phase with tick marks from the sample environment and pressure marker phases omitted for clarity.

with pressure as the cell volume (Fig. S8a [21]). The distortion mode Y_2^+ [transforming as the rotation of the octahedra around the chain axis, Fig. 2(c)] remains almost constant as a function of pressure, even between the two phases (Fig. S8b [21]). This results in chains of octahedra that are rotated by $\sim 45^\circ$ relative to those in their neighboring chain (determined by measurement of the angle between the apical Cu–F bond directions in neighboring chains) in both phases at all pressures measured. The Y_4^+ and Γ_4^+ modes (relating to x displacement of the apical F2 site relative to the aristotype) in $\text{Na}_2\text{CuF}_4\text{-I}$ and $\text{Na}_2\text{CuF}_4\text{-II}$, respectively, are small but show a systematic decrease with pressure in $\text{Na}_2\text{CuF}_4\text{-I}$ with little variation as a function of pressure in $\text{Na}_2\text{CuF}_4\text{-II}$ [Fig. 3(c)].

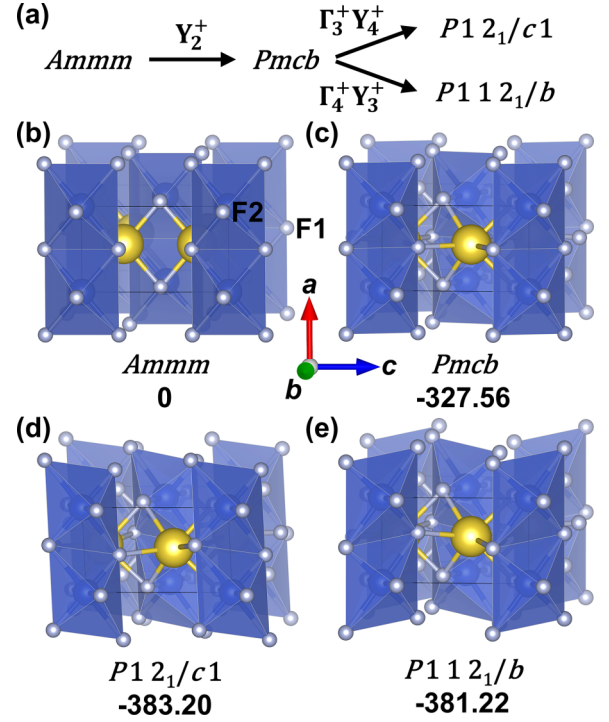


FIG. 2. (a) Space group relationship showing the derivation of the $\text{Na}_2\text{CuF}_4\text{-I}$ ($P 1\ 2_1/c\ 1$) and $\text{Na}_2\text{CuF}_4\text{-II}$ ($P 1\ 1\ 2_1/b$) structures from the aristotype (Ammm) via an orthorhombic intermediate (Pmcb). (b)–(e) the crystal structures of the aristotypes and observed phases with DFT calculated energies of the relaxed structures (in meV/f.u.), relative to the aristotype at ambient pressure. Sodium atoms are shown in yellow with blue $[\text{CuF}_6]$ octahedra. The same cell directions are used throughout (N.B. the monoclinic structures have unique angle $\approx 90^\circ$).

The Γ_3^+ and Y_3^+ modes, which correspond to F1 x -displacement in $\text{Na}_2\text{CuF}_4\text{-I}$ and $\text{Na}_2\text{CuF}_4\text{-II}$, respectively, also display little dependence on pressure but have a much greater magnitude than the modes affecting the F2 site [Fig. 3(c)]. The deviation of the β and γ angles from 90° can be represented as symmetry breaking strain modes Γ_3^+ / Γ_4^+ (respectively) which are proportional to the amplitudes of the atomic displacements transforming as the same irreps (Fig. S9 [21]).

The distortion of the $[\text{CuF}_6]$ octahedron, ρ_0 , is quantified using Van Vleck Q_2 and Q_3 distortion modes (Eqs. S2–5 [21]) [43]. As a function of p , ρ_0 in the $\text{Na}_2\text{CuF}_4\text{-I}$ decreases linearly, i.e., the octahedron is becoming less distorted as pressure increases, concordant with other Cu phases [Fig. 3(d)] [44,45]. Around the phase transition ρ_0 in $\text{Na}_2\text{CuF}_4\text{-II}$ at 3.39(3) GPa is unchanged (within one standard deviation) compared to ρ_0 in $\text{Na}_2\text{CuF}_4\text{-I}$ at 1.963(12) GPa, and thereafter remains approximately constant upon the application of increasing pressure, indicating $\text{Na}_2\text{CuF}_4\text{-II}$ is better able to retain the remaining JT distortion upon the application of pressure (up to at least 5.05(7) GPa). A polar plot ($\varphi = \tan^{-1}(Q_2/Q_3)$) shows that the character of the JT distortion remains unchanged with pressure and corresponds to an almost pure Q_3 2-long bond: 4-short bond distortion, as is typically observed for Cu^{2+} compounds [46] (Fig. S10 [21]). Thus, it appears both the character and magnitude of the JT

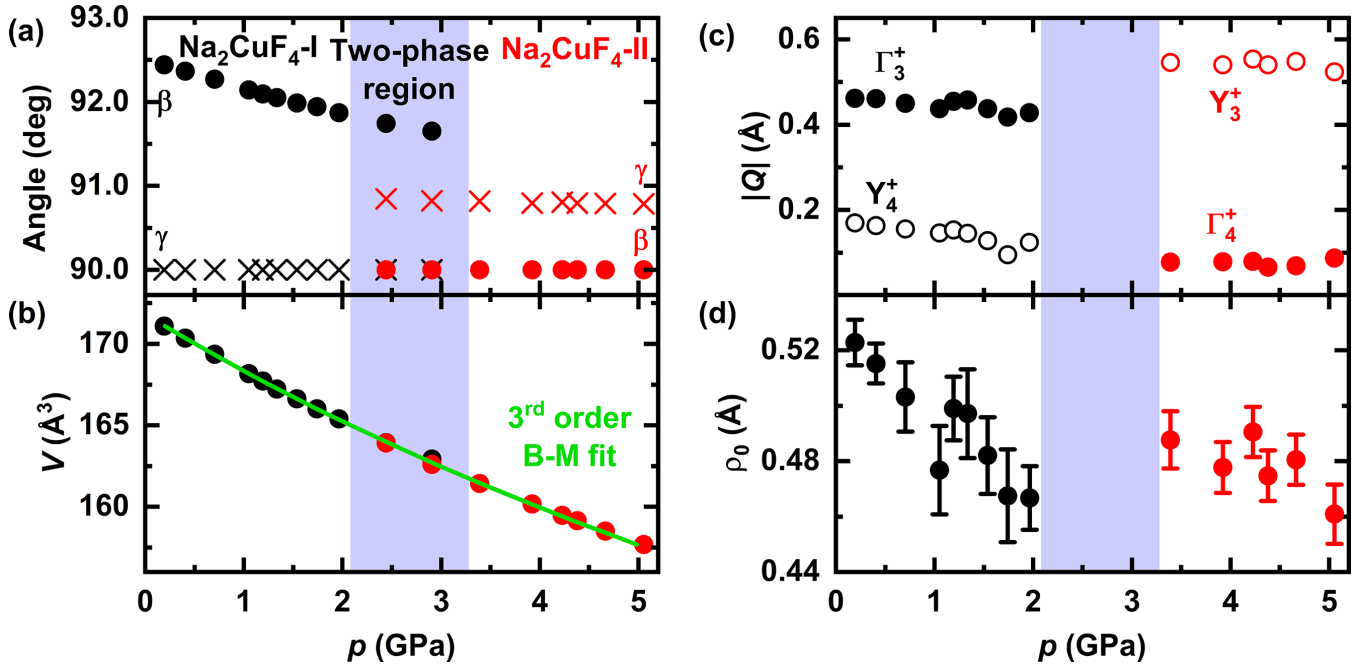


FIG. 3. Structural parameters from Rietveld fits against variable-pressure neutron powder diffraction data. Where not shown, error bars are smaller than data points. (a) Unique angles in $\text{Na}_2\text{CuF}_4\text{-I}$ ($P 1\ 2_1/c\ 1$, black) and $\text{Na}_2\text{CuF}_4\text{-II}$ ($P 1\ 1\ 2_1/b$, red) phases. γ and β in $\text{Na}_2\text{CuF}_4\text{-I}$ and $\text{Na}_2\text{CuF}_4\text{-II}$, respectively are also shown. (b) Cell volume, V , with third order Birch-Murnaghan equation of state fit to V in both phases shown in green. (c) Distortion mode amplitudes, $|Q|$, for modes related to distortion of $[\text{CuF}_6]$ octahedra. (d) Octahedral distortion, ρ_0 . In (c) and (d), the values obtained in the two-phase region were highly correlated due to peak overlap and have been omitted.

distortion is robust to the application of hydrostatic pressure in $\text{Na}_2\text{CuF}_4\text{-II}$. This is in marked contrast to what is observed in canonical JT distorted fluoride KCuF_3 (and to a lesser extent, $\text{Na}_2\text{CuF}_4\text{-I}$) which shows a gradual suppression of ρ_0 upon compression over the same pressure range [46], see Fig. S10 [21]. It would therefore appear the phase transition to $\text{Na}_2\text{CuF}_4\text{-II}$ acts to relieve the melting of the orbital ordering in $\text{Na}_2\text{CuF}_4\text{-I}$.

To investigate this point further, the compressibility of Na_2CuF_4 was calculated using the software PASCAL [28]. It was necessary to calculate the compressibilities of $\text{Na}_2\text{CuF}_4\text{-I}$ and $\text{Na}_2\text{CuF}_4\text{-II}$ separately, with the former studied up to 1.963(12) GPa and the latter studied from 2.44(2) GPa. PASCAL first calculated a set of orthogonalized principal axes for each phase with principal directions denoted X_i and X'_i for $\text{Na}_2\text{CuF}_4\text{-I}$ and $\text{Na}_2\text{CuF}_4\text{-II}$ respectively [Fig. 4(a)–4(c)]. X_2 aligns precisely along the crystallographic b axis, while X_1 and X_3 lie within the ac plane at approximately 45° to the a and c axes. X'_3 lies precisely on the c axis, while X'_1 and X'_2 align approximately along a and b axes, respectively. The relative change in principal axes' lengths, ℓ_i , for both phases show good agreement with empirical fits, with $R^2 > 0.999$ for

all axes [Fig. 4(d)]. From these empirical fits, the principal compressibilities, K_i and K'_i (for $\text{Na}_2\text{CuF}_4\text{-I}$ and $\text{Na}_2\text{CuF}_4\text{-II}$, respectively) can be calculated as a function of pressure [Fig. 4(e)]. In $\text{Na}_2\text{CuF}_4\text{-I}$, X_1 , which approximately aligns with the direction of the l Cu–F bond [(Fig. 4(b)], is the most compressible direction, suggesting that the l bond undergoes the most compression, corresponding to the decrease in the octahedral distortion, ρ_0 of the Cu in the ambient pressure phase as a function of pressure Fig. 3(d)]. X_3 , which is approximately aligned with the short Cu–F1 bond, is the least compressible. In $\text{Na}_2\text{CuF}_4\text{-II}$, the compressibilities are much more isotropic, explaining the relative invariance of ρ_0 to pressure in this phase. Notably, K'_1 demonstrates a small increase in compressibility as a function of pressure (i.e., the structure becomes softer along the chain direction as the pressure increases). In $\text{Na}_2\text{CuF}_4\text{-II}$ the l Cu–F bonds [Fig. 4(c)] are (pseudo)-perpendicular, meaning they are no longer all aligned along a single principal axis, but alternate in the $X'_1X'_3$ plane. The phase transition thus acts to decouple the orbital ordering from the hydrostatic pressure-induced compression of the unit cell by shifting the electronic instability from the Brillouin zone center to a zone boundary.

The energy of $\text{Na}_2\text{CuF}_4\text{-II}$ relative to $\text{Na}_2\text{CuF}_4\text{-I}$ was computed as a function of pressure using DFT in steps of 0.5 GPa from 0 to 5 GPa. At each pressure, the structure was allowed to relax, yielding minimized structures with unit cell volumes within 2.5% of those experimentally determined (Fig. S11 [21]). The energy difference, ΔE , at each pressure is shown in Fig. 5. $\text{Na}_2\text{CuF}_4\text{-II}$ is initially higher in energy than $\text{Na}_2\text{CuF}_4\text{-I}$, but becomes more stable as the pressure increases, with a calculated critical pressure, p_c , of ~ 2.8 GPa, compared to the observed p_c of 2.4 GPa–2.9 GPa.

TABLE II. Birch-Murnaghan equation of state (Equation S1 [21]) parameters for Na_2CuF_4 (both polymorphs) for a third order fit from PASCAL. B_0 is bulk modulus, V_0 is the unit cell volume at zero pressure and B' is the pressure derivative of the modulus.

B_0 (GPa)	V_0 ($\text{\AA}^3$)	B'	R^2
46.1(4)	171.82(2)	5.4(3)	0.9998

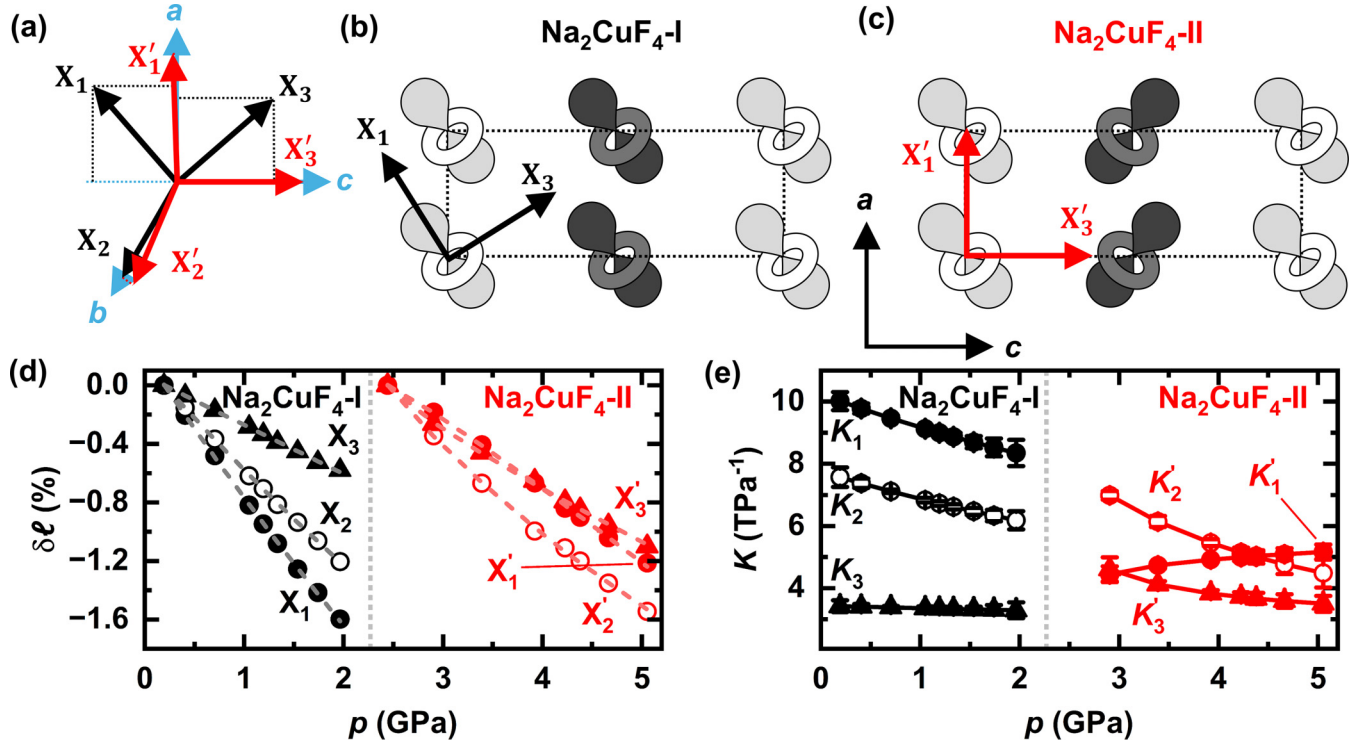


FIG. 4. (a) The orthogonalized principal axes of $\text{Na}_2\text{CuF}_4\text{-I}$ (X_i , black) and $\text{Na}_2\text{CuF}_4\text{-II}$ (X'_i , red) overlaid onto the approximate crystallographic axes (blue). Note, only X_2 and X'_3 are precisely aligned to a crystallographic axis. Exact principal axis vectors are given in Tables S3 and S4 [21]. (b), (c) Schematic of $\text{Na}_2\text{CuF}_4\text{-I}$ and $\text{Na}_2\text{CuF}_4\text{-II}$ (respectively) $\text{Cu } d_{z^2}$ orbital ordering viewed (approximately) along the b axis, with principal axis directions overlaid. Light-shaded orbitals are from Cu atoms on the cell origin while darker-shaded are from Cu atoms with a y fractional coordinate of 0.5. (d) The % change in principal axes' lengths $\delta\ell$ as a function of pressure (relative to their initial lengths at 0.193(4) GPa and 2.44(2) GPa for X_i and X'_i , respectively) with empirical fits (dashed lines, parameters given in Tables S3 and S4 [21]). (e) The derived principal compressibilities, K , (data points are joined by solid lines for clarity).

There are other Cu-containing crystal structures that display orbital reordering under pressure. For example, in the hybrid perovskite $[(\text{CH}_3)_2\text{NH}_2]\text{Cu}(\text{HCOO})_3$, a reordering occurs at 5.2 GPa, caused by a change in the degree of octahedral tilting [47]. High-pressure structural studies of copper fluoride RP phases have found that in $(\text{K}, \text{Rb})_2\text{CuF}_4$ an orbital reordering occurs at ~ 9 GPa such that the JT elongated Cu–F bonds realign from along the c axis to along the a axis disrupting the ambient pressure ferromagnetic structure [48,49], while at 2.2 GPa Cs_2CuF_4 begins to display

antiferromagnetic next-nearest-neighbor intralayer ordering while retaining its interlayer ferromagnetism [50], suggesting a change in the orbital ordering. In Na_2CuF_4 , the magnetic interactions are unlikely to be drastically different in the two polymorphs, since the one-dimensional edge-sharing $[\text{CuF}_6]$ chains that constitute the strongest magnetic superexchange pathways are essentially unchanged. Furthermore, the quasi-one-dimensionality of both structures suppresses their magnetic order [51], making elucidation of these interactions extremely difficult. The high-pressure behavior of Na_2CuF_4 reported here is relatively unusual because the magnitude of the orbital ordering instability remains approximately constant, while the point at which it occurs is switching from the Brillouin zone center to a zone boundary, leading to a transition from ferro- to A-type antiferro-orbital ordering.

IV. CONCLUSIONS

The crystal structure of Na_2CuF_4 as a function of pressure has been studied by powder neutron diffraction up to 5 GPa. At 2.4–2.8 GPa a first-order phase transition occurs from $P 1 2_1/c 1$ to $P 1 1 2_1/b$, consisting of a reorientation of half the Cu–F JT long (l) bonds to give interchain pseudoperpendicular l bonds, compared to pseudoparallel l bonds seen in $\text{Na}_2\text{CuF}_4\text{-I}$, i.e., a transition from ferro-orbital to A-type antiferro-orbital ordering. We find this transition is driven by the ability of $\text{Na}_2\text{CuF}_4\text{-II}$ to accommodate JT l Cu–F bonds at

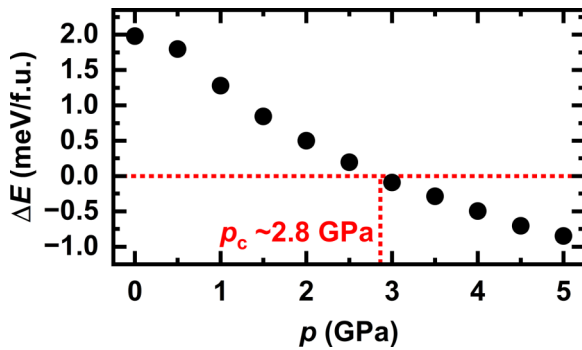


FIG. 5. Energy of the high-pressure $\text{Na}_2\text{CuF}_4\text{-II}$ phase relative to the ambient-pressure $\text{Na}_2\text{CuF}_4\text{-I}$ phase (ΔE) as a function of pressure, p , with the calculated p_c indicated.

high pressure, as evidenced by a constant octahedral distortion factor (ρ_0). The transition can be viewed as a switch in the point at which an instability arises in the Brillouin zone, from the zone center to a zone boundary. DFT calculations show that Na_2CuF_4 -II becomes more stable at $p_c \sim 2.8$ GPa, in agreement with the experimental observations. In combination with the compositional analogs A_2CuF_4 ($A = \text{K}, \text{Rb}, \text{Cs}$), we demonstrate that copper fluorides undergo a diverse range of orbital reorderings under pressure. This work highlights the need for further structural studies at pressures up to 40 GPa to elucidate the nature of high-pressure phase transitions observed by Raman spectroscopy [19].

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DATA AVAILABILITY

The data that support the findings of this article are openly available [22].

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