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**Microscopic origin of pressure-induced isosymmetric transitions in fluoromanganate cryolites**

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I. INTRODUCTION

Perovskite transition metal compounds with ABX₃ stoichiometry, where X is either oxygen or fluorine, have been extensively studied owing to their ability to support a rich set of physical phenomena ranging from multiferroism to superconductivity. Many of these properties are a direct consequence of structural phase transitions and symmetry reductions, which alter chemical bonding pathways and electronic properties through distortions and rotations of BX₆ octahedra through strong electron-lattice coupling. Indeed, the physical properties of perovskites can be tailored by changing the bonding environments by manipulating the BX₆ size, shape, and connectivity using chemical pressure or epitaxial strain. Thus, for electronic function engineering purposes it is useful to understand the tendency of a perovskite to distort, or undergo a structural transitions, which can be estimated using the Goldschmidt tolerance factor.

The tremendous success of perovskites has sparked interest in a closely related set of materials, the A₂BB'X₆ double perovskites with multiple cations that order among various planes in a periodic fashion. The additional degree of freedom from compositional ordering not found in simple perovskites can be used to obtain desirable ferroic responses, and explore correlated electron properties. It is important to note that while there are a multitude of studies on perovskites and double perovskites, most of the materials physics literature is keenly focused on X=O transition metal oxides. Fluoride compounds, however, also show an affinity for functional electronic behavior, including multiferroicity, ionic conductivity. Yet these ternary fluorides have received considerably less attention than their oxide counterparts although they are ferroelastic and exhibit polymorphism. As such, their properties are structure and symmetry dependent, albeit they tend to adopt the ideal undistorted structure more frequently.

For the case of rock salt ordered double perovskites with two possible B cations (B and B'), with X = F (fluorine), these compounds are generally referred to by one of the two prototypes illustrated in Fig. 1. The first class being cryolite, after the compound Na₃AlF₆. This family contains compounds with 12-coordinate A sites, whereby the same cation on the A site is chemically identical to one at the octahedrally coordinated B site (A = B), while the B' cation remains unique. This results in the stoichiometry A₃B'B₆ for cryolite, and as a result the B cation interactions are ‘interrupted’ by the A cation occupying the B sublattice. The other prototype is elpasolite, which is named for the mineral K₂NaAlF₆. It also refers to structures with 12-fold coordinated A cations, but unlike cryolite, the two octahedrally coordinated B sites are chemically distinct species (B and B'). Thus the stoichiometry for elpasolite is A₂BB'F₆.

Here we focus on the cryolite Na₃MnF₆ (tolerance factor of 0.89), which possesses a strong first-order active Jahn-Teller d⁴ Mn³⁺ cation and exhibits a distorted monoclinic P2₁/n (space group 14) structure with both in-phase and out-of-phase MnF₆ octahedral rotations in its ground state. It is ferroelastic and experimentally undergoes an isostuctural first-order monoclinic-to-monoclinic phase transition with hydrostatic pressure. Such isosctructural/isosymmetric phase transitions (IPT) without symmetry reductions infrequently occur in inorganic condensed matter phases—displacive transitions are much more common. Microscopic origins for such transitions include spin-state transitions, electronic or magnetic polarization rotation, or from bond reconfigurations due to mechanical epitaxial strain constraints. For example, IPTs in Mn-based complex oxides have been reported to be induced by chemical pressure, surface effects in nanoparticles, and thermal cycling by melting an orbitally ordered state. In such cases, the driving force is either a reduction in an electric polarization (YMnO₃)
or due to the removal of the Jahn-Teller distortion altogether.

The IPT in Na$_3$MnF$_6$ is experimentally found to be reversible while showing characteristic first order hysteric behavior. Above and below the critical pressure value for the phase transition, the authors of Ref. 31 identified that the short and long Mn–F bond lengths, which are signatures of the Jahn-Teller distortion, persisted across the transition. Unlike the related oxides, the bond distortions remain and only the relative orientation of the distorted bond pairs with respect to the monoclinic axes switch. What are the atomic and electronic features responsible for the phase transition: is it due to spontaneous strain, the Mn electronic degrees of freedom, or strong electron–lattice interactions? We are unaware of a theory that captures the microscopic origin of this IPT in Na$_3$MnF$_6$ or related manganites where the Jahn-Teller distortion is not removed across the isosymmetric transition.

Herein, we use density functional theory calculations to identify the microscopic origin of the pressure-induced IPT in the fluoromanganate Na$_3$MnF$_6$. We find that the ground state monoclinic structure is stabilized through a combination of energy lowering MnF$_6$ octahedral rotations and Jahn-Teller (JT) bond elongations; the latter arise to remove the orbital degeneracy owing to electron occupation of the majority spin $e^1_g$-manifold presented by a cubic crystal field. These combined effects produce a crystal structure at ambient pressure that exhibits elongated Mn–F bonds along the long, crystallographic $c$ axis depicted in Fig. 2(b), and is common for manganates with axial ratios $c/a > 1$.44,45

Upon application of hydrostatic pressure, we find a re-orientation of the long JT Mn–F bond occurs for unit cell volumes of 240±0.1Å$^3$, corresponding to an experimental pressure between 2.10 GPa and 2.15 GPa in agreement with Ref. 31. At the electronic structure level, we find that the low-pressure fluoromanganate phases have fully occupied $d_{x^2-r^2}$ orbitals, whereas in the high-pressure phase, the occupancy reverses to be predominately of $d_{x^2-r^2}$ orbital character. Unlike previously reported IPTs in manganites, the Jahn-Teller mode is always present and the strong orbital-lattice coupling facilitates the electronic transition, which is marked by a giant (70%) change in the orbital polarization of the Mn $e_g$ manifold through a renormalization of the mode stiffness of the Jahn-Teller distortion. Uncovering the microscopic origins of the transition sheds light on the effect of stress on the magnetic, electronic and structural degrees of freedom in Na$_3$MnF$_6$, but more broadly it reveals the Jahn-Teller distortion need not be removed across such transitions and hence well-defined orbitally ordered state may exists across such phase boundaries in related phases.

II. COMPUTATIONAL & SIMULATION DETAILS

We performed density functional theory calculations with the general gradient approximation (GGA) of Perdew-Burke-Ernzerhof revised for solids40 (PBEsol) as implemented in the Vienna Ab initio Simulation Package (VASP)47,48 with the projector augmented wave (PAW) method49 to treat the core and valence electrons using the following valence configurations: 2$p^63s^1$ for Na, 3$p^64s^13d^6$ for Mn, and 2$s^22p^5$ for F. We used a $7 \times 7 \times 7$ Monkhorst-Pack $k$-point mesh50 with Gaussian smearing (0.1 eV width) for the Brillouin zone (BZ) integrations and a 600 eV plane wave cutoff. Spin-polarized structural relaxations were performed until the Hellmann-Feynman forces were less than 1 meV Å$^{-1}$ for each atom position.
**Magnetic Order.** The long-range spin order for Na$_3$MnF$_6$ has not been previously reported. Therefore, prior to carrying out the pressure study, we explored the energetics for A-type antiferromagnetic order (in-plane ferromagnetic coupling between Mn sites, with out-of-plane antiferromagnetic coupling) and ferromagnetic order on the monoclinic $P2_1/n$ (ambient) structure with the JT Mn–F bond directed along the c axis. These two magnetic configurations are compatible with the 20 atom unit cell used in all calculations. From our total energy calculations of the fully relaxed phases, we find that the ferromagnetic configuration is essentially degenerate with the antiferromagnetic configuration: There is less than 0.1% difference in cell volume and an energy difference of 0.4 meV per formula unit (f.u.). These small differences between the magnetic variants also persist for calculations performed at elevated pressures. Owing to the strong ionic character of the fluoride and the fact that there appears to be very weak spin–lattice coupling, we use structures with ferromagnetic (FM) order throughout to perform the hydrostatic pressure simulations. As described below, the FM order yields excellent agreement with experimental structural data.

**Application of Hydrostatic Pressure.** We computationally mimic the experimental hydrostatic pressure study by imposing the lattice constants and monoclinic angles reported in Ref. 30 while allowing the internal coordinates to fully relax to obtain the total energies for both the low-pressure ([21/n]$_1$) and high-pressure ([21/n]$_2$) phases. Throughout we distinguish between the two phases by using the space group label with an additional index, 1 or 2, appended to the end to indicate if it is the low-pressure (phase 1) or high-pressure (phase 2) Na$_3$MnF$_6$ structure. The starting atomic configuration for the [21/n]$_1$ phases employ the positions obtained from our fully relaxed zero pressure DFT-PBEsol simulations, whereas for the [21/n]$_2$ structural relaxations, we initialize the atomic positions to those reported experimentally. 30

### III. RESULTS

#### A. Na$_3$MnF$_6$ Equilibrium Structure

Before performing the hydrostatic pressure study on Na$_3$MnF$_6$, we first determine the equilibrium structure at zero pressure with ferromagnetic spin order. Consistent with experiments, we find a distorted monoclinic structure with in-phase MnF$_6$ octahedral rotations about the c axis and out-of-phase tilts. The combination of rotations and tilts gives the $a\bar{a}c$ tilt pattern as described within Glazer notation. Table I shows that the PBEsol functional provides an accurate description of the structural parameters of Na$_3$MnF$_6$ when compared to experiment. The error in the cell volume is $\sim$0.05%, under the constraint that the PBEsol structure has the same monoclinic angle as that reported in Ref. 30.

| Atom | WP | PBEsol | Experiment | a (Å) | b (Å) | c (Å) |
|------|-----|--------|------------|-------|-------|-------|
| Na(2) | 4e | x | 0.510 | 0.509 | 5.472 | 5.471 |
| y | 0.058 | 0.555 | 5.471 | 5.472 | 0.724 | 0.721 |
| z | 0.750 | 0.750 | 0.068 | 0.067 | 5.684 | 5.683 |
| F(1) | 4e | x | 0.122 | 0.115 | 0.828 | 0.829 |
| y | -0.063 | -0.058 | 0.829 | 0.828 | -0.058 | -0.053 |
| z | 0.761 | 0.767 | 0.724 | 0.721 | 0.750 | 0.750 |
| F(2) | 4e | x | 0.722 | 0.719 | 0.724 | 0.721 |
| y | 0.828 | 0.829 | 0.750 | 0.750 | 0.750 |
| z | -0.058 | -0.053 | 0.750 | 0.750 | 0.750 |
| F(3) | 4e | x | 0.162 | 0.163 | 0.068 | 0.067 |
| y | 0.724 | 0.721 | 0.068 | 0.067 | 5.675 | 5.673 |
| z | 0.724 | 0.721 | 0.724 | 0.721 | 0.750 | 0.750 |

To understand the complex atomic distortions in the monoclinic phase, we first recognize that a group-subgroup relationship exists between the ideal high-symmetry cubic structure without octahedral distortions or rotations, $Fm3m$, and the $P2_1/n$ structure. 52 Mode crystallographic analysis then enables us to determine the full set of unique symmetry-adapted mode displacements active in the $Fm3m \rightarrow P2_1/n$ transition (see Fig. 3 for schematic illustrations), described as irreducible representation (irreps) of $Fm3m$. We find that the cubic-to-monoclinic symmetry reduction requires a combination of at least two of these modes; based on the physical character (Fig. 3) and distortion mode amplitudes (Table SI of the Supplementary Material available in Ref. 25) of the modes present in the ground state structure, we deduce that the symmetry reduction is driven by out-of-phase octahedral rotations about the b axis and in-phase rotations about c-axis, i.e., $\Gamma_4^+ \otimes X_4^-$. 55

B. Hydrostatic Pressure-induced Isosymmetric Transition

We investigate phase stability of the monoclinic Na$_3$MnF$_6$ by computing the total energy at various volumes for both the [21/n]$_1$ and [21/n]$_2$ structures. Fig. 4 shows that the energy of both monoclinic phases increases with increasing pressure (decreasing cell volume).
At low-pressure $[P2_1/n]_1$, exhibiting the Jahn-Teller bond axis oriented along the $c$ axis, is more stable than $[P2_1/n]_2$ (JT bond axis in the $ab$ plane) by $\sim 20$ meV. This energetic stability remains until near the unit cell volume of 240 Å, where we find that both monoclinic structures are stable within our simulations. Upon further increase in pressure, $[P2_1/n]_2$ is stabilized relative to $[P2_1/n]_1$ by nearly the same energetic difference. From our mode crystallographic analyses, we find that the $Q_3$ irrep has the largest response at the transition, exhibiting both a discontinuity and sign change [Fig. 4 (inset)]. (We explore the energetics of this mode in more detail below.) We observe no change in space group symmetry or occupied Wyckoff positions for all volumes computed, consistent with available experimental results, which makes this transition isosymmetric.

We now explore changes in the internal atomic positions with pressure, focusing on the cooperative behavior of the Mn–F octahedra. We first examine the changes in the Mn–F bond lengths. Rather than using the symmetry-mode description, we parameterize the structural distortions to the MnF$_6$ octahedra in terms of first-order Jahn-Teller (JT) elongations $Q_2$ and $Q_3$. This allows us to describe the JT modes by the position of the surrounding ligands in an octahedral field whose normal coordinates are associated with the vibrational mode that leads to a flattening of the MnF$_6$ octahedra. Note that the Na(2) cations are excluded for clarity throughout, and broken lines indicate atomic displacements in the layer below.

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![FIG. 3. Illustration of symmetry-adapted mode displacements which appear in monoclinic Na$_3$MnF$_6$ labeled according to irreps of the undistorted (a) $Fm\bar{3}m$ structure: (b) $\Gamma^+_1$: the $Q_1$ Jahn-Teller (JT) mode commonly referred to as the breathing distortion. (c) $\Gamma^+_3$: the $Q_3$ (two out–four in) JT vibrational mode. (d) $\Gamma^+_4$: the out-of-phase tilting distortion. (e) $\Gamma^+_3$: scissors mode. (f) $X^+_2$: Jahn-Teller distortions. (g) $X^+_3$: in-phase rotations of the octahedra about the $b$ axis. The tilt angle is measured as $(180^\circ - \phi)/2$. (e) $\Gamma^+_3$: “scissors” mode which brings equatorial F anions in the MnF$_6$ octahedra closer together and reducing the intra-octahedral F–Mn–F bond angle from the ideal 90°. (f) $X^+_2$: the $Q_2$ (two in–two out) bond stretching mode in the $ab$ plane. (g) $X^+_3$: in-phase rotations of the octahedra about the $c$ axis. The rotation angle is measured as $(90^\circ - \theta)/2$. (h) $X^+_5$: octahedral flattening.](image-url)
present in the stable monoclinic low- and high-pressure variants as a function of hydrostatic pressure by computing the magnitude of the Jahn-Teller normal modes as follows:

\[
Q_2 = \frac{2}{\sqrt{2}}[F(3) - F(2)],
\]

\[
Q_3 = \frac{2}{\sqrt{6}}[2F(1) - F(2) - F(3)],
\]

where, \(F(1), F(2),\) and \(F(3)\) are the Mn-F bond lengths directed along the \(c, a,\) and \(b\) axes, respectively. The JT phase is defined by \(\Theta = \tan^{-1}Q_2/Q_3.\) Within this formalism, \(\Theta = 0^\circ\) represents a JT distortion of octahedra stretched along the \(c\) axis. Angles of \(\Theta = \pm 120^\circ\) correspond to JT distortions along the \(b\) and \(a\) axes, respectively.\(^{44,45,57}\)

![FIG. 5. Phase stability of \([P2_1/n]_1\) and \([P2_1/n]_2\) represented in the \(Q_2-Q_3\) plane of the Jahn-Teller lattice distortions. The red, green, and gray wedges illustrate the stability regions for \([P2_1/n]_1, [P2_1/n]_2,\) and the transition region, revealing each structure is characterized by a dominant \(Q_2\) or \(Q_3\) mode.](image)

C. Jahn-Teller Electronic Effects

We now investigate the electronic structure evolution across the IPT to understand the coupling between the electron and lattice degrees of freedom in \(Na_3MnF_6.\) Here, Mn(III) is found in a high-spin \(d^4\) configuration with one electron in the \(e_g\) manifold, which appears as a strong Jahn-Teller distortion in the octahedra.\(^{58-60}\) Thus, we anticipate that hydrostatic pressure directly affects the value of \(\Theta\) in the \(Q_2-Q_3\) subspace. Importantly, the value of \(\Theta\) also provides a measure of the average character of the occupied molecular orbital state \(\langle \Theta \rangle\) of the Jahn-Teller ion for a given static cooperative JT distortion as an arbitrary superposition of the \(e_g\) orbitals wave functions.\(^{44,61}\) It can be approximated for a system at absolute zero as\(^{57}\)

\[
\langle \Theta \rangle = \cos(\Theta/2) |d_{z^2-r^2}| + \sin(\Theta/2) |d_{x^2-y^2}|.
\]

We now use Maximally Localized Wannier Functions (MLWF)\(^{62,63}\) to transform our periodic wave functions forming the valence band (VB) and conduction band (CB) edges into a local real-space representation of the \(e_g\) \((d_{z^2-r^2}\) and \(d_{x^2-y^2}\)) orbitals. The subspace is spanned by these atomic-like orbitals for the two Mn cations in the unit cell to evaluate the percent character of each orbital contributing to \(\langle \Theta \rangle\).

![FIG. 6. Low energy electronic band structure about the Fermi level (horizontal line at 0 eV) with the projected \(e_g\) orbital character for \(Na_3MnF_6\) at (a) \([P2_1/n]_1\) (0.0 GPa), and (b) \([P2_1/n]_2\) (2.5 GPa). The MLWF for the occupied molecular orbital for the (c) \([P2_1/n]_1\) and (d) \([P2_1/n]_2\).](image)
TABLE II. Symmetry-adapted mode amplitudes (in Å) 

| Mode      | Space group (number) | DFT-PBEsol |
|-----------|----------------------|------------|
| $\Gamma^+_1$ | $Fm\bar{3}m$ (225)  | 0.119      |
| $\Gamma^+_2$ | $I4/mmm$ (139)      | 0.103      |
| $\Gamma^+_3$ | $C2/m (12)$         | 1.465      |
| $\Gamma^+_4$ | $C2/m (12)$         | 0.219      |
| $X^+_1$    | $P4_2/nmm$ (136)    | 0.083      |
| $X^+_2$    | $P4/nnc$ (128)      | 0.892      |
| $X^+_3$    | $Pnnm$ (58)         | 0.786      |

orbital directed along the long JT-bond to reduce the Coulombic repulsion induced by the F 2p electron cloud.

Fig. 6(b) depicts the electronic structure for [P21]/n1 at 2.50 GPa. From the projection onto the MLWFs, we observe in the high pressure phase that the VB and CB adopt mixed $e_g$-orbital character throughout the BZ. The occupied orbital, although dominated by atomic $d_{x^2-y^2}$ character, has an admixture of $d_{z^2}$ [Fig. 6(d)]. At 2.50 GPa, $\Theta = 114.2^\circ$ in [P21]/n2 and this angle predicts a wavefunction with 29.5% $d_{x^2-y^2}$ orbital character—a 70% change in the orbital polarization. The mixed $e_g$ molecular orbital state is typical for manganates with a $Q_2$-like JT distortion, i.e., the long-JT bond axis is oriented in the $ab$ plane.\(^{45,64,65}\)

We now examine the energetics associated with the changes in $\Theta$ by computing the $Q_2 - Q_3$ energy surface (Fig. 7). We achieve this by incrementally increasing the $Q_2$ ($X^+_2$) and $Q_3$ ($\Gamma^+_1$) symmetry-adapted mode amplitudes in the [P21]/n1 phase at ambient pressure\(^{25}\) and [P21]/n2 at 2.50 GPa (Table II) with respect to the undistorted reference structures.\(^{66}\) In Fig. 7, mode amplitudes of $Q_3 > 0$ represent a JT distortion which elongates the Mn–F(3) bond and shortens the Mn–F(2) bonds in the $ab$ plane, while $Q_3 < 0$ shortens Mn–F(3) and elongates Mn–F(2). Similarly, $Q_3 > 0$ mode amplitudes corresponds to a two-out–four-in JT distortion, which stretches the apical Mn–F(1) while shortening the Mn–F(2) and Mn–F(3) equatorial bonds. Conversely, $Q_3 < 0$ gives the four-out–two-in JT bonding environment that elongates bonds in the $ab$ plane [Mn–F(2) and Mn–F(3)] and shortens the Mn–F(1) bond.

Considering only JT modes in the equilibrium volume of [P21]/n1 at ambient pressure, we find a single energy minimum at $Q_3 \approx 0.11$ and $Q_2 = 0$ [Fig. 7(a)]. In this phase, a two-out–four-in Q3 JT vibrational mode stabilizes Na3MnF6 at ambient pressure by approximately 38.6 meV/f.u. over the undistorted phase, which is consistent with the structural and electronic investigations already described. Despite having a small finite amplitude of $Q_3$ ($X^+_2$) present in the equilibrium structure,\(^{25}\) Fig. 7(a) indicates that in the absence of other distortions any nonzero amplitude of $Q_2$ leads to an energetic penalty in [P21]/n1. Thus, an asymmetric Mn–F bond stretching in the $ab$ plane is an unfavorable distortion at ambient conditions without the presence of another distortion.

From Fig. 7(b), we observe that our two-dimensional energy surface predicts a single energy minimum for [P21]/n2 at 2.50 GPa. Here, the minimum is located at $Q_3 \approx -0.048$ and $Q_2 = 0$. In the stable [P21]/n2 phase it is noteworthy that the stability regime for the $Q_3$ vibrational mode is in a negative range. This indicates that unlike the [P21]/n1 phase, at high pressures beyond the IPT a four-out–two-in $Q_3$ and not a two-out–four-in Mn–F distortion is required to stabilize the structure. According to the JT theory, a $d^4$ cation with $Q_3 < 0$ distortion splits the $e_g$ degeneracy by occupying the $d_{x^2-y^2}$ orbital. Thus, the change in sign of the $Q_3$ mode is in accord with the $d_{x^2-y^2}$ state forming the valence band edge as observed in our calculations (Fig. 6). However, since $Q_2 = 0$ in the absence of any other distortion, at high pressure Na3MnF6 would exhibit four equivalent equatorial bonds, i.e., Mn–F(2) = Mn–F(3), in the reduced subspace. The latter is in contrast to the fully relaxed atomic and electronic structure of the [P21]/n2 phase. The MnF6 octahedra exhibit multiple distortions with an approximately $Q_2 > 0$-like JT bonding environment. Indeed, the symmetry-adapted mode amplitudes for Na3MnF6 at 2.50 GPa (Table II) indicate that the $Q_2$ mode ($X^+_2$) is finite and larger in amplitude ($Q_2 = 0.083$) than at ambient pressure ($Q_2 = 0.056$).

We now seek to identify which other structural distortion (non-Jahn-Teller) acts to stabilize nonzero $Q_2$ mode amplitudes in the equilibrium structures. From the mode decomposition analysis at ambient and elevated pressure, we observe that the largest contribution to the equilibrium structures arise from the tilt ($\Gamma^+_1$) and rotation ($X^+_2$) of the MnF6 units. To understand the nature of the tilt–$Q_2$ and rotation–$Q_2$ coupling, we incrementally increase the mode amplitude of $Q_2$ at finite amplitudes of the tilt and rotation (0%, 50%, 80%, 90% and 100% of their maximum) with respect to the undistorted reference structure.
Fig. 8 shows that both the tilt and rotation modes couple to $Q_2$ and give a net energy gain in the total energy in both pressure regimes at finite amplitude. From Fig. 8(a) we observe that as the amplitude of tilt distortion increases in $|P_{21}/n_1\rangle$, the curvature of the $Q_2$ free energy evolves from a positive parabola with a single minimum at the $Q_2 = 0$ to a double-well potential with negative curvature about the origin and minima at finite $Q_2$ for tilt amplitudes $> 80\%$. This signifies a continuous softening of the $Q_2$ phonon mode induced by large amplitudes of the tilt mode ($T^+_{1}$ irrep), which effectively stabilizes the finite value of the asymmetric stretching observed in the ground state through a fourth-order biquadratic anharmonic interaction that renormalizes the mode stiffness of the quadratic $Q^2_2$ mode. The behavior of the MnF$_6$ rotation–$Q_2$ coupling in Fig. 8(b) shows that there is a large energetic gain associated with increasing amplitudes of the rotation mode. The single minima of the parabolic energy curves indicate, however, that while this coupling contributes to the total energy it does not soften the $Q_2$ mode frequency, but rather shifts the mode amplitude of $Q_2$ to a non-zero value through a linear-quadratic interaction.

In the high pressure phase (2.50 GPa) phase [Fig. 8(c) and (d)], we observe that the $Q_2$ irrep is unstable with a small energy gain $< 1$ meV at both 0\% tilt and rotation amplitudes. Fig. 8(c) shows that increasing the amplitude of the tilt distortion in $|P_{21}/n_2\rangle$ leads to an enhanced energy stabilization, which ultimately promotes a larger $Q_2$ distortion in the high pressure phase. In contrast, increasing the contribution of the rotational mode hardens the $Q_2$ mode, the negative curvature at the origin is lost as shown in [Fig. 8(d)], and leads to a smaller amplitude of $Q_2$ through the coupled $Q^2_2Q_{X^+}$ interaction.

**IV. DISCUSSION**

Our calculations and structural analysis indicate that the IPT is due to the spontaneous redistribution of the electronic charge density among the $e_g$ orbitals of the strong JT Mn cation. There is a giant change in orbital occupation between the two isostructural variants owing to the persistent JT distortion across the transition. Specifically, we find that at low values of hydrostatic pressure the system is stabilized with the long bond along the $c$ axis with a filled $d_{z^2-r^2}$ orbital which is characteristic of a $Q_3 > 0$ JT where $c/a > 1^{44,45}$. Mode crystallographic analysis coupled with phenomenological Landau investigations of the JT Mn–F bond distortions reveals that the lattice strain induced by hydrostatic pressure renormalizes the mode stiffness of the JT vibrational modes across the transition. The leading coefficient of the harmonic $Q^2_3$ term of Hamiltonian changes sign under hydrostatic pressure.

Most significantly, we observe that across the transition the $Q_3$ JT irrep switches from a two-out-four-in $(Q_3 > 0)$ in $|P_{21}/n_1\rangle$ to a four-out-two-in $(Q_3 < 0)$ in the $|P_{21}/n_2\rangle$. While the key structural signature defining $|P_{21}/n_2\rangle$ is a $Q_2$-like Mn–F bonding arrangement, we contend that the primary factor in the stabilization of the high pressure phase in Na$_3$MnF$_6$ is the change in sign of the $Q_3$ distortion mediated by the $Q_2$–MnF$_6$ tilt interaction. Table SI and Table II clearly show that the rotation amplitude is unchanged under pressure. Our electronic and phenomenological investigations indicate that at high pressure, it is more favorable for the charge to localize in the $d_{z^2-r^2}$-like orbital. Thus, the characteristic $Q_2$-like Mn–F$_6$ bonding distortion that differentiates the $|P_{21}/n_2\rangle$ and $|P_{21}/n_1\rangle$ phases is stabilized by second order effects. We show that a strong coupling exists between the tilt and $Q_2$ lattice degrees of freedom owing to an anharmonic interaction that stabilizes finite amplitudes of $Q_2$ in the equilibrium structures. The importance of this secondary effect is highlighted by comparing [Fig. 8(a) and (c)], as the energetic gain produced by the tilt–$Q_2$ coupling is increased approximately 20X in the $|P_{21}/n_2\rangle$ phase at equilibrium over the ambient case.

In addition, our electronic structure calculations show that hydrostatic pressure has an effect on the crystal field splitting in the stable phases of Na$_3$MnF$_6$. We observe that energy gap between the filled $d_{z^2-r^2}$ and the unoccupied $d_{z^2-r^2}$ is reduced from 0.43 eV at ambient pressure to 0.34 eV at the transition. Across the critical pressure for the transition, the band gap is 0.37 eV at 2.20 GPa.
The continued application of hydrostatic pressure in the high pressure phase further decreases the band gap at approximately 0.02 eV/GPa which allows us to predict an insulator-to-metal transition around ~20 GPa.

Based on this understanding, we performed a similar set of calculations for the \( d^9 \) compound Na\(_3\)ScF\(_6\), which also crystallizes with \( P2_1/n \) symmetry and for which experimental structural data under hydrostatic pressure exists.\(^{67}\) We find there is no discontinuity in either the total energies (Fig. 9) or in the evolution of the Sc–F bond lengths up to a pressure of 6.82 GPa, which indicates that no isosymmetric transitions occur up to a pressure that is approximately 4.7 GPa higher than required for the fluoromanganate. Indeed, Fig. 9 shows the partial charge density for Na\(_3\)ScF\(_6\) obtained by integrating over a finite region from -2 eV to \( E_F \) is highly uniform at both ambient Fig. 9(a) and high pressure Fig. 9(b). The absence of both a JT instability and an anisotropic bonding environment is consistent with the experimental findings and the proposed electronic origin for the IPT in Na\(_3\)MnF\(_6\), highlighting the importance of the JT-active Mn(III).

V. CONCLUSION

We used first principles density functional calculations to study the electronic and atomic origins of the first-order pressure induced phase transition in Na\(_3\)MnF\(_6\). We identified that the isosymmetric transition originates from two key features present in the fluoromanganate: (i) a Jahn-Teller active Mn(III) ion with an \( e_g \) orbital degeneracy, and (ii) the strong coupling of the cooperative Mn–F bond distortions with hydrostatic pressure. We observe that while simple structural arguments may identify the \([P2_1/n]_1\) phase of Na\(_3\)MnF\(_6\) as being dominated by a \( Q_3 \)-type JT distortion and the \([P2_1/n]_2\) phase as \( Q_2 \)-type, the combined effect of both distortions with collective MnF\(_6\) tilts are essential to describing the stability of the structure at ambient and hydrostatic pressures.

In the \([P2_1/n]_1\) structures the \( Q_3 > 0 \) JT distortion splits the \( e_g \) manifold into atomic-like occupied \( d_z^2-r^2 \) and an unoccupied \( d_x^2-y^2 \) orbitals owing to an elongated JT Mn–F bond aligned along the crystallographic \( c \)-axis. After the transition to the high pressure phase \([P2_1/n]_2\), the JT-bond axis reorients into the \( ab \) plane with the structure largely characterized by a \( Q_2 \)-type bonding arrangement. The transition above 2.15 GPa is arguably driven by a spontaneous renormalization of the \( Q_3 \) vibrational mode, \( i.e. \ Q_3 < 0 \). The equilibrium structure of the \([P2_1/n]_2\) phase is stabilized by secondary lattice effects which couple the tilt and \( Q_2 \) JT phonon modes to give the Mn–F(3) > Mn–F(1) > Mn–F(2) which is the signature of the high pressure phase of Na\(_3\)MnF\(_6\).

This mechanism for the IPT drives a giant orbital reconstruction within the occupied 3d manifold of Mn\(^{3+}\), whereby the JT distortion is always present in the structure. While it is understood that fluctuations in the orbital occupancy of the \( d \) orbitals can alter physical properties and drive structural transitions,\(^{68}\) this study presents an interesting case were the orbital degrees of freedom are highly sensitive to the mechanical boundary conditions owing to the cryolite structure. Finding materials where it is possible to induce large changes in orbital polarization is an active area of research, because even small changes in orbital occupations particularly in thin films at surfaces and interfaces\(^{69–72}\) can produce drastic variations in magnetic and transport properties. Given the extreme nature of the orbital reconstruction we observe with hydrostatic pressure, we anticipate our study will motivate new synthetic efforts focused on exploring Na\(_3\)MnF\(_6\) and related magnetic cryolites in thin film form. Electronic structure calculations focused on evaluating the feasibility of epitaxial strain to induced the IPT are in progress.

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The undistorted structures are constructed to have cell volumes and monoclinic angles that correspond to the pressure being studied with all mode amplitudes equal to zero relative to the DFT-PBEsol relaxed monoclinic structures. The energy maps are obtained from 225 self-consistent total energy calculations and then fitting these points to a polynomial expansion in orders of $Q^2$ and $Q^3$. 

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