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Long axis switch in $\text{Na}_3\text{MnF}_6$ not due to the Jahn-Teller effect

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Pressure Effects on 3d<sup>n</sup> (n = 4, 9) Insulating Compounds: Long Axis Switch in Na<sub>3</sub>MnF<sub>6</sub> not Due to the Jahn-Teller Effect

Inés Sánchez-Movellán, David Carrasco-Busturia, Juan M. García-Lastra, Pablo García-Fernández, José A. Aramburu, and Miguel Moreno

Abstract: The pressure-induced switch of the long axis of MnF<sub>6</sub><sup>3−</sup> units in the monoclinic Na<sub>3</sub>MnF<sub>6</sub> compound and Mn<sup>3+</sup>-doped Na<sub>2</sub>FeF<sub>6</sub>, is explored with the help of first principles calculations. Although the switch phenomenon is usually related to the Jahn-Teller effect, we show that, due to symmetry reasons, it cannot take place in 3d<sup>n</sup> (n = 4, 9) systems displaying a static Jahn-Teller effect. By contrast, we prove that in Na<sub>3</sub>MnF<sub>6</sub> the switch arises from the anisotropic response of the low symmetry lattice to hydrostatic pressure.

Nonetheless, this explanation, though widely followed, is hard to accept first due to the restricted symmetry conditions necessary for the presence of a JT effect. Indeed, the JT effect requires the existence of an initial geometry where the ground state of the complex is actually degenerate. This condition is fulfilled under cubic or trigonal symmetry, and thus a static JT effect has been observed in cases like KZnF<sub>3</sub>: Cu<sup>2+</sup>,[11–13] d<sup>9</sup> ions (Ni<sup>2+</sup>, Cu<sup>2+</sup>, Ag<sup>2+</sup>) doped NaCl,[14–20] A-(H<sub>2</sub>O)<sub>4</sub>SiF<sub>6</sub>·Cu<sup>2+</sup> (A = Mg, Zn)[21–23] or AgF<sub>2</sub>[24,25] but not in KZnF<sub>3</sub>:Cu<sup>2+</sup>[26] where the host lattice is tetragonal. This key argument thus makes difficult to assume the existence of a JT effect in crystals like Na<sub>3</sub>MnF<sub>6</sub>, (NH<sub>2</sub>)<sub>4</sub>Cu(H<sub>2</sub>O)<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>, CuF<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(pyz)<sub>2</sub> (pyz = pyrazine) or CuWO<sub>4</sub>, and it has systematically been related[14–16] to both the existence of a static Jahn-Teller (JT) effect and a pressure-induced switch of the principal axis of the complex formed by the 3d<sup>n</sup> (n = 4, 9) cation.

Nonetheless, this explanation, though widely followed, is hard to accept first due to the restricted symmetry conditions necessary for the presence of a JT effect. Indeed, the JT effect requires the existence of an initial geometry where the ground state of the complex is actually degenerate. This condition is fulfilled under cubic or trigonal symmetry, and thus a static JT effect has been observed in cases like KZnF<sub>3</sub>: Cu<sup>2+</sup>,[11–13] d<sup>9</sup> ions (Ni<sup>2+</sup>, Cu<sup>2+</sup>, Ag<sup>2+</sup>) doped NaCl,[14–20] A-(H<sub>2</sub>O)<sub>4</sub>SiF<sub>6</sub>·Cu<sup>2+</sup> (A = Mg, Zn)[21–23] or AgF<sub>2</sub>[24,25] but not in KZnF<sub>3</sub>:Cu<sup>2+</sup>[26] where the host lattice is tetragonal. This key argument thus makes difficult to assume the existence of a JT effect in crystals like Na<sub>3</sub>MnF<sub>6</sub>, (NH<sub>2</sub>)<sub>4</sub>Cu(H<sub>2</sub>O)<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>, CuF<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(pyz), or CuWO<sub>4</sub>, whose structures are either monoclinic or triclinic.[1–8]

Furthermore, in systems displaying a static JT effect, a hydrostatic pressure can hardly switch the principal axis direction. Indeed, for a Cu<sup>2+</sup> ion in a cubic crystal like the KZnF<sub>3</sub>, perovskite,[11–13] the principal axis of the CuF<sub>6</sub><sup>4−</sup> unit can be one of the three C<sub>4</sub> axes (along X, Y, Z directions) of the lattice as a result of a static JT effect that leads to a local tetragonal symmetry. This symmetry breaking ultimately arises from the unavoidable random strains present in any real crystal, a key point firstly clarified by Ham.[9,10] Accordingly, if in a given region of the KZnF<sub>3</sub>, cubic crystal the principal axis of the CuF<sub>6</sub><sup>4−</sup> complex is forced to be Z by random strains, the X and Y axes continue to be equivalent under hydrostatic pressure, which is an isotropic stress. Thus, an applied pressure can modify the value of the tetragonal distortion and the JT stabilization energy, EJT, but not the principal direction of the CuF<sub>6</sub><sup>4−</sup> unit at a given point of the crystal. In contrast, systems that do not present a JT effect display preferential directions that, as we will show, are associated with the elastic properties of the lattice.

Acknowledged with this knowledge, gained for example using closed-shell systems that are clearly not suspect of displaying the JT...
effect, one may predict the possible change in direction of the long axis of these transition-metal complexes. This makes JT and non-JT systems quite different since in the first class there cannot be a systematic long-axis switch while in the second class this can be allowed.

Bearing these facts in mind, it has previously been shown that in low symmetry compounds like CuF$_3$, CrF$_3$, or K$_2$CuF$_4$ there is no JT effect.\footnote{28,29} Therefore, the local distortion and the ground state of involved MF$_6^{4-}$ (M = Cu, Cr) units obey to different causes that can be uncovered with the help of first principles calculations. Such an analysis stresses the importance of considering the effects of the anisotropy of the low symmetry lattice on the complex. In fact, even if the MF$_6^{4-}$ (M = Cu, Cr) complex is, in principle, octahedral the anisotropic electric field due to the rest of lattice ions generally leads to a non-degenerate ground state.\footnote{13,17,26,29} Moreover, that anisotropy makes that the six F$^-$ ligands are no longer elastically equivalent, and thus the change of the force constant due to the rest of the lattice can be different for each of the involved ligands. Both facts have been proved to play a key role in explaining the different distortion and ground state observed\footnote{30,31} for CuF$_3$ or Ni$^{2+}$ in the layered lattices K$_3$MgF$_4$ and K$_2$ZnF$_6$.\footnote{32,36}

According to the present arguments, it is now necessary to understand why in low symmetry compounds involving 3d$^n$ (n = 4, 9) cations the nature of the longest local axis of the involved complex can be switched by an applied pressure if that phenomenon is not due to a JT effect. Seeking to gain a better insight on this relevant issue, this work focuses on the monoclinic Na$_3$MnF$_6$ compound\footnote{1,6,7} where pressure effects have been investigated experimentally.\footnote{34} This compound is taken as a guide for the present study, carried out with the help of first principles calculations and an analysis of available experimental results.

The singularity of 3d$^n$ (n = 4, 9) compounds displaying a sixfold coordination just reflects that the ground state electronic density of a MX$_n$ unit (M = 3d$^3$ or 3d$^9$ ion), has not a cubic symmetry and thus, if all ligands are at the same distance, not all of them experience the same force.\footnote{10,13} However, this general behavior does not appear in high spin MX$_n$ complexes when M is a cation like Fe$^{3+}$, Mn$^{3+}$ (d$^4$) or Cr$^{3+}$ (d$^3$) whose ground state electronic density is close to spherical. For this reason, in the study of Na$_3$MnF$_6$ it is also useful to explore how the structure evolves when all Mn$^{3+}$ cations are replaced by a cation with a similar ionic radius but a more spherical electronic density, keeping the same space group. This is just the so-called parent phase previously used\footnote{24,28,29} as a good starting point for understanding the structure and ground state of compounds like AgF$_3$, CuF$_3$, CrF$_3$, or K$_2$CuF$_4$. This work is organized as follows. In section 2 we describe the crystal structure of Na$_3$MnF$_6$ as a function of pressure observed experimentally. For the sake of clarity, it is compared to that of cryolite (Na$_3$AlF$_6$) at ambient pressure.\footnote{34} The computational tools used in the present study are explained in section 3, while main results are given in section 4. Some final remarks are provided in the last section.

### Crystal structure of Na$_3$MnF$_6$ under pressure: Experimental results

According to Englich et al. the structure of Na$_3$MnF$_6$ at ambient pressure can be described\footnote{36} by the monoclinic space group P2$_1$/n, a non-standard setting more visual than the standard one, P2$_1$/c. A view of the corresponding lattice cell is displayed in Figure 1, whereas the ensemble of lattice parameters (a, b, c, and monoclinic angle, $\beta$) and Mn$^{3+}$–F$^-$ distances is reported in Table 1. When pressure increases up to 2.79 GPa, the space group of Na$_3$MnF$_6$ is unmodified,\footnote{38} being again P2$_1$/n. The structure observed experimentally at P = 2.79 GPa is also shown in Figure 1. The crystal data derived\footnote{35} by Carlson et al. at P = 0.12 GPa and P = 2.79 GPa are collected in Table 1, together with those corresponding to the cryolite compound (Na$_3$AlF$_6$) at zero pressure,\footnote{34} also displaying a P2$_1$/n space group.

![Figure 1](image-url)

**Figure 1.** Experimental unit cells of Na$_3$MnF$_6$ compound at pressures P = 0.12 and 2.79 GPa in the non-standard monoclinic P2$_1$/n setting.\footnote{35} [x,y,z] are the local axes of the MnF$_6^{4-}$ complexes, with C, point symmetry. The 3 Mn–F distances (in Angstroms) are also shown.

### Table 1. Description of the crystal structure of Na$_3$MnF$_6$ reported at P = 0 GPa by Englich et al.\footnote{36} and at P = 0.12 and 2.79 GPa by Carlson et al.\footnote{35} In addition to lattice parameters (a, b, c and monoclinic angle, $\beta$), the values of three Mn$^{3+}$–F$^-$ distances, R$_1$, R$_2$, and R$_3$, are also given. In a first approximation, it can be considered that the directions of R$_1$, R$_2$, and R$_3$ are parallel to a, b and c axes, respectively. The value of the longest metal-ligand distance is written in bold type for each structure. For comparison, the values corresponding to Na$_3$AlF$_6$\footnote{34} are also shown. All distances are in \( \text{Å} \) and the $\beta$ angle in degrees.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pressure</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>$\beta$</th>
<th>R$_1$ (Å)</th>
<th>R$_2$ (Å)</th>
<th>R$_3$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_3$MnF$_6$</td>
<td>0</td>
<td>5.471</td>
<td>5.683</td>
<td>8.073</td>
<td>88.96</td>
<td>1.862</td>
<td>1.897</td>
<td>2.018</td>
</tr>
<tr>
<td></td>
<td>0.12</td>
<td>5.402</td>
<td>5.596</td>
<td>7.756</td>
<td>90.27</td>
<td>1.804</td>
<td>1.971</td>
<td>2.038</td>
</tr>
<tr>
<td></td>
<td>2.79</td>
<td>5.386</td>
<td>5.690</td>
<td>7.783</td>
<td>90.76</td>
<td>1.891</td>
<td>1.971</td>
<td>1.891</td>
</tr>
<tr>
<td>Na$_3$AlF$_6$</td>
<td>0</td>
<td>5.402</td>
<td>5.596</td>
<td>7.756</td>
<td>90.27</td>
<td>1.804</td>
<td>1.971</td>
<td>2.038</td>
</tr>
</tbody>
</table>

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As shown in Table 1, the crystallographic data obtained at ambient pressure and at 0.12 GPa are practically identical. They reveal that the lattice cell is nearly orthorhombic with a monoclinic angle \( \beta = 89^\circ \). The \( \text{MnF}_6^{3-} \) complexes formed in \( \text{Na}_6\text{MnF}_{18} \) are practically isolated, i.e., they do not share F\(^-\) ligands and the distance between two neighbors \( \text{Mn}^{3+} \) cations is equal to 5.40 Å. As the \( F^-\text{Mn}^{3+}\text{F}^- \) angle for two F\(^-\) ions in cis position\(^1,6\) differs by about 2° from 90°, the local symmetry of a \( \text{MnF}_6^{3-} \) complex is triclinic \( \text{C} \). The \( \text{MnF}_6^{3-} \) lines (i = 1, 2, 3) in Figure 1 are not strictly parallel to the crystallographic \( a, b, \) and \( c \) axes, respectively, due to a tilting of the complex. Still, the \( \text{Mn}^3-\text{F}^- \) line is mainly oriented along the \( c \) axis and the \( \text{Mn}^-\text{F}^- \) line along the \( b \) axis. For instance, the angle between \( c \) axis and the \( \text{Mn}^2-\text{F}^- \) direction is equal to 22°. The three \( \text{Mn}^{3+} \text{F}^- \) distances are not equal: the largest one, \( R_g \), corresponds to the \( \text{Mn}^-\text{F}^- \) bond and differs from \( R \) by 0.152 Å, while \( R \) and \( R_c \) are identical within 1.5% (Table 1).

The results for \( \text{NaMnF}_3 \) at zero pressure are somewhat similar to those for \( \text{NaAlF}_3 \),\(^{24,25} \) also displayed in Table 1. Indeed, despite \( \text{Al}^{3+} \) being a closed shell cation, the three \( \text{Al}^{3+} \text{F}^- \) distances are not equal, although the differences among them are smaller than 0.01 Å. On the other hand, in the cryolite the distances are not equal, although the differences among them are smaller than 0.01 Å. On the other hand, in the cryolite the distances are not equal, although the differences among them are smaller than 0.01 Å. On the other hand, in the cryolite the distances are not equal, although the differences among them are smaller than 0.01 Å. On the other hand, in the cryolite the distances are not equal, although the differences among them (Table 1).

An increase of pressure reduces the value of lattice parameters, specially \( c \). So, on passing from \( P = 0 \) to \( P = 0.91 \) GPa the value of \( c \) decreases by 0.081 Å according to experimental data\(^1\) by Carlson et al. at the same time, the value of \( R_c \) at \( P = 0.91 \) GPa is equal only to 0.081 Å\(^1\) in comparison to \( R_g-R_c = 0.121 \) Å at ambient pressure (Table 1). As a salient feature, \( \text{NaMnF}_3 \) undergoes a phase transition\(^2\) at about 2.2 GPa, where the lattice parameter \( c \) abruptly decreases by about 2%. Moreover, it is a first-order phase transition because is isosymmetric (the space group is always \( P2_1/n \)) and involves a significant hysteresis\(^1\) of ~0.8 GPa. Despite this fact, the phase transition is characterized by a switch of the longest axis of all \( \text{MnF}_6^{3-} \) complexes. Indeed, while at ambient pressure that axis corresponds to the \( \text{Mn}^{3+}-\text{F}^- \) direction, it is the \( \text{Mn}^{2+}-\text{F}^- \) direction that becomes the longest axis after the phase transition, such as it is shown in Table 1. Furthermore, comparing the experimental results at different pressures, we can notice that, on passing from \( P = 0 \) GPa to \( P = 2.79 \) GPa the three lattice parameters evolve in a very different way: \( c \) is reduced by 0.29 Å while \( b \) is unmodified and \( a \) decreases only by 0.08 Å (Table 1).

The origin of the switch of the longest axis under pressure is discussed in Section 4 helped by the results of first principles calculations. In that analysis, particular attention is paid to exploring the electronic density changes due to pressure.

### Computational tools

First principles periodic calculations have been performed on pure \( \text{Na}_6\text{MnF}_{18} \) its parent phase \( \text{Na}_6\text{FeF}_{18} \) as well as on doped \( \text{Na}_6\text{FeF}_{18}:\text{Mn}^{3+} \) by means of the CRYSTAL17 code. This software works with linear combinations of Gaussian type functions to represent the Bloch orbitals.\(^{15} \)

All electron triple-zeta polarized basis set of high quality developed by Peitinger et al.\(^{26,27} \) were employed, together with the one-parameter hybrid functionals B1WC and PW1PW, which include 16% and 20% of Hartree-Fock exchange, respectively, and have provided accurate results for crystalline structures and properties of insulating systems containing transition metal ions.\(^{27,28} \)

First, we have optimized the geometry of the two phases that exist in \( \text{Na}_6\text{MnF}_{18} \) at ambient pressure, and at \( P = 2.79 \) GPa, at the monoclinic \( P2_1/n \) space group, obtaining that both lattice parameters and bond \( \text{Mn}^2-\text{F}^- \) distances are similar to the experimental data, with discrepancies of less than 3.5%. The sampling of reciprocal space for the numerical integration within the Brillouin zone was 8x8x8 Monkhorst-Pack grid, which represents a distance between two consecutive \( k \) points of 0.144, 0.138 and 0.072 Å\(^-1\) confirming to the three reciprocal space directions. For geometry optimizations the tolerance for energy change was 10\(^-8\) Hartree and for gradient and nuclei displacement were 0.0002 a.u.

The next step was the optimization of the parent phase structure. Regarding this calculation, all open shell \( \text{Mn}^{3+} \) ions, with \( d^6 \) electronic configuration and \( S = 2 \), were replaced by \( \text{Fe}^{3+} \) ions (\( d^5 \) electronic configuration and \( S = 5/2 \)) with spherical density (in vacuo) and equal ionic radius, \( r(\text{Mn}^{3+}) \approx r(\text{Fe}^{3+}) \approx 0.785 \) Å.\(^{39} \) The symmetry of the optimized parent phase \( \text{Na}_6\text{FeF}_{18} \) remains in the same \( P2_1/n \) space group but the complexes are less distorted, reflecting a more spherical symmetry for \( \text{Fe}^{3+} \) in \( \text{Na}_6\text{FeF}_{18} \) than for \( \text{Mn}^{3+} \) in \( \text{Na}_6\text{MnF}_{18} \). Further discussion on this issue is provided in Section 4.2.

In addition, cluster simulations on \( \text{MnF}_6^{3-} \) complexes have been performed in order to explore the relationship between the structural changes due to pressure and the variations undergone by the HOMO as well as the influence of pressure on the spin allowed \( d-d \) transitions. These calculations have been carried out by means of the Amsterdam density functional (ADF) code,\(^{40} \) which works with DFT techniques in the Kohn-Sham framework. Hybrid B3LYP functional (25% of exact exchange) combined with triple zeta polarized basis set have been employed in the simulations. The core electrons (1s-3p for \( \text{Mn}^{3+} \), 1s for \( \text{F}^- \)) were kept frozen since they do not play a relevant role in the effects we focus on. In these calculations, the \( \text{MnF}_6^{3-} \) clusters were embedded in the electrostatic potential of the rest of lattice ions,\(^{41,42} \) which was previously calculated through Ewald-Eyjen summations.\(^{43,44} \) Although the effects of this internal potential are important in systems like ruby,\(^{45-47} \) the Egyptian-blue pigment\(^{48} \) or \( \text{K}_2\text{ZnF}_4:Cu^{2+} \),\(^{7,13,25,26} \) it is not the case of \( \text{Na}_6\text{MnF}_{18} \) where only induces energy variations in the optical \( d-d \) transitions equal or smaller than 0.1 eV. Such transitions are discussed in Section 4.4. Both complex and environment were rotated in such a way that the directions \( R_i \).
R₂ and R₁ lies, approximately, along the local axes x, y and z respectively.

Understanding the long axis switch induced by pressure in Na₃MnF₆ entails the analysis of the wavefunction in the ground state at different stages since its evolution leads to the distortions observed in this system. Therefore, the HOMO wavefunction has been determined for Na₃MnF₆ at different pressures and also for Na₂FeF₆Mn⁺⁺. In the latter case, the HOMO corresponding to the MnF₆⁶⁻ unit has been derived for both the undistorted parent phase and the final equilibrium geometry. In these calculations, the wavefunction coefficients have been obtained following Mulliken population criterion.

### Results and Discussion: Na₃MnF₆

#### Results of calculations at P = 0 and P = 2.79 GPa for Na₃MnF₆

The optimized geometries for Na₃MnF₆ obtained under periodic boundary conditions working in the P₃/₁⁻/₁ space group are collected in Table 2 for P = 0 and 2.79 GPa. Such results are compared to available experimental results.¹⁶ The calculated values reasonably reproduce the experimental results. Indeed, calculated lattice parameters deviate from experimental ones less than 1% while the error on the value of the longest Mn⁺⁺--F⁻ distance is smaller than 3.5%. It is worth noting that the present calculations also lead to the long axis along the Mn⁺⁺--F₃ direction at zero pressure while it is along the Mn⁺⁺--F₃ direction for P = 2.79 GPa. Moreover, they also shed light on the nature of the ground state of the MnF₆⁶⁻ complex at both pressures.

The electronic ground state of a hypothetically octahedral (O₃ point group) MnF₆⁻ unit with S = 2 corresponds to the configuration t₂g³e_g¹. At zero pressure, the present periodic and cluster calculations on Na₃MnF₆ reveal that the unpaired electron coming from e_g has a dominant 3y²−r² character where z essentially reflects the Mn⁺⁺--F₁ direction (Figure 1). This is consistent with R₁ being the long axis while R₂ and R₃ are equal within 1.5%. Indeed, if the octahedron is elongated along the z axis and R₁ = R₂, the HOMO corresponds to a molecular orbital [3z²−r²] transforming like 3z²−r² while the LUMO corresponds to [x²−y²]. This situation is thus quite similar to that found for the low spin (S = 1/2) RhCl₆⁴⁻ complex generated by the d⁶ Rh⁺⁺ cation formed in NaCl.⁴⁵,⁵⁰

<table>
<thead>
<tr>
<th>P</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>β</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
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</thead>
<tbody>
<tr>
<td>0</td>
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<td>2.79</td>
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<td>5.646</td>
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<td>1.864</td>
<td>1.880</td>
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</tbody>
</table>

Table 2. Calculated values of lattice parameters (a, b, c and β) and the three Mn⁺⁺--F⁻ distances, R₁, R₂, R₃, for Na₃MnF₆ in the P₃/₁⁻/₁ space group at both zero pressure and P = 2.79 GPa. The results are compared to available experimental results.¹⁶ The value of the longest Mn⁺⁺--F⁻ distance is written in bold type for both pressures. All distances are in Å and the β angle in degrees.

In the study of a d⁶ (n = 4, 9) compounds it has proved to be useful to determine the actual structure once each cation is replaced by another one with a similar ionic radius but a more spherical electronic density.²⁴,²⁵,³¹,³²,³³ As during this process, giving rise to the so-called parent phase, the space group does not change, the symmetry of the parent phase is necessarily equal or higher than that of the initial dⁿ (n = 4, 9) compound. For example, for CuF₂ (monoclinic P2₁/n space group) the Cu⁺⁺ →Zn⁺⁺ substitution leads to a ZnF₂ parent phase belonging to the tetragonal P4/mmm space group.⁵¹ Accordingly, the rutile structure of ZnF₂ becomes unstable⁵¹ as far as Zn⁺⁺ ions are progressively substituted by Cu²⁺.

In the present case of Na₃MnF₆, the parent phase is obtained by substituting all Mn⁺⁺ ions by Fe⁺⁺ ions (both with the same ionic radius, 0.785 Å⁴⁹). A geometry optimization calculation performed on the Na₂FeF₆ parent phase, starting from the experimental P₂₁/n geometry of Na₃MnF₆, led to a structure displaying the same P₂₁/n space group (Table 3). Moreover, that phase actually corresponds to the experimental Na₂FeF₆ compound, whose structure at ambient pressure was firstly reported by Croft and Kestigian from X-ray diffraction in powder.²⁴ The values of lattice parameters obtained by these authors are gathered on Table 3 and compared to results of
Table 3. Experimental values of lattice parameters (a, b, c and β) derived from X-ray diffraction power data for Na₅FeF₆ at ambient pressure displaying the P₂₁/n space group.²⁹ Such values are compared to the structural information obtained from present geometry optimizations for the parent phase of Na₅MnF₆, where the three Fe³⁺–F⁻ distances have been determined. All distances are in Å and the β angle in degrees.

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>β</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
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<td>90.5</td>
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</table>

Present geometry optimization. Both sets of data are essentially coincident. However, Croft and Kestigian in their powder study did not report the values of metal-ligand distances⁵² and thus we cannot compare them to those derived from present calculations (Table 3).

The local symmetry around a Fe³⁺ cation in Na₅FeF₆ is given by the same triclinic C point group as that for Mn⁷⁺ in Na₅MnF₆. Despite this fact, it should be noticed that R₂–R₃ = 0.002 Å derived for Na₅FeF₆ is clearly smaller than R₂–R₃ = 0.180 Å determined for Na₅MnF₆ at 2.79 GPa (Table 2). This situation is thus rather similar to that found for cryolite (Table 1) where the longest Al³⁺–F⁻ distance also corresponds to R₂ and R₂–R₃ = 0.008 Å.

Particular attention has been paid to study the behavior of a single substitutional Mn⁷⁺ impurity in Na₅FeF₆. Results of the present calculations are gathered in Table 4. Although the Fe⁷⁺ → Mn⁷⁺ substitution does not modify the C₂ local symmetry, it enhances the octahedron distortion leading to a local geometry that resembles that derived for pure Na₅MnF₆ at 2.79 GPa (Table 2) with R₂–R₃ = 0.15 Å. Therefore, the Fe⁷⁺ → Mn⁷⁺ substitution does not give rise to any symmetry breaking, such as it happens in a static JT effect. Nevertheless, the increase of R₂–R₃ on passing from pure Na₅FeF₆ (R₂–R₃ = 0.002 å) to Na₅FeF₆: Mn⁷⁺ (R₂–R₃ = 0.15 Å) has to be related to the different ground state electronic density in the corresponding FeF₆³⁻ and MnF₆³⁻ units.

Table 4. Calculated values of three metal-ligand distances, R₁, R₂ and R₃, obtained for a Mn⁷⁺ impurity in the Na₅FeF₆ parent phase using two different sets of lattice parameters, those optimized for Na₅FeF₆ (second row) and other set where the value of c increases only by 1.1 % (third row). It can be noticed that in the latter case, the longest axis is along the Mn⁷⁺–F⁻ direction and not along the Mn⁷⁺–F⁻ direction. The results for pure Na₅FeF₆ (first row) are also included for comparison. In every case the longest metal-ligand distance is written in bold. All distances are in Å and the β angle in degrees.

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>β</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₅FeF₆</td>
<td>5.483</td>
<td>5.720</td>
<td>7.936</td>
<td>89.5</td>
<td>1.931</td>
<td>1.945</td>
<td>1.943</td>
</tr>
<tr>
<td>Na₅FeF₆:Mn⁷⁺</td>
<td>5.483</td>
<td>5.720</td>
<td>7.936</td>
<td>89.5</td>
<td>1.856</td>
<td>2.045</td>
<td>1.895</td>
</tr>
<tr>
<td>Na₅FeF₆:Mn⁷⁺</td>
<td>5.490</td>
<td>5.700</td>
<td>8.020</td>
<td>89.5</td>
<td>1.866</td>
<td>1.892</td>
<td>2.049</td>
</tr>
</tbody>
</table>

Let us consider an initial step where Mn⁷⁺ replaces Fe⁷⁺ in the undistorted Na₅FeF₆ lattice. We have verified that in that situation the unpaired electron coming from e_g has a dominant 3y²-z² character such as it is shown in Table 5. Indeed, the calculated function of the HOMO, |ψHOMO⟩, can shortly be written as

\[ |ψHOMO⟩ = 0.972|3y²-r²⟩ + 0.234|x²-z²⟩ \]  (1)

Table 5. Relevant data corresponding to a Mn⁷⁺ impurity in Na₅FeF₆. In the initial step, a Mn⁷⁺ ion just substitutes a Fe⁷⁺ one in the undistorted Na₅FeF₆ parent lattice, while the final step describes the equilibrium geometry of a single Mn⁷⁺ impurity in the parent phase. In both situations, the calculated wavefunction of the HOMO and the value of the HOMO-LUMO gap, Δ, are given. The relative energy of the electronic ground state (GS) derived for both situations is also reported. All distances are in Å and energies in eV.

<table>
<thead>
<tr>
<th>Step</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>HOMO</th>
<th>Δ</th>
<th>GS energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.931, 1.945, 1.94</td>
<td>0.972</td>
<td>3y²-r² &gt; + 0.234</td>
<td>x²-z² &gt;</td>
<td>0.06</td>
<td>0</td>
</tr>
<tr>
<td>Final</td>
<td>1.856, 2.045, 1.895</td>
<td>0.996</td>
<td>3y²-r² &gt; + 0.078</td>
<td>x²-z² &gt;</td>
<td>0.76</td>
<td>−0.18</td>
</tr>
</tbody>
</table>

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Here |3y²-r²⟩ just means a molecular orbital of the MnF₆⁻³⁻ unit transforming like 3y²-r². Accordingly, the LUMO is mainly made of |x²-z²⟩, and it is placed only at 0.06 eV above the HOMO just reflecting that in this initial step the local symmetry of the MnF₆⁻³⁻ unit is Cs despite the three Mn⁻¹-F⁻ distances are equal within 0.01 Å. These facts thus stress that in the initial stage the electronic ground state of the MnF₆⁻³⁻ unit is not degenerate, thus excluding the existence of a JT effect. Despite this fact, as the electron placed in the HOMO is an impurity in Na₃MnF₆, we have also investigated the influence of a small increase (1.1%) on the c lattice parameter upon both the equilibrium geometry and the electronic ground state of the MnF₆⁻³⁻ unit. The results, also displayed in Table 4, show that under that 1.1% increase on the c parameter the longest distance of the MnF₆⁻³⁻ unit changes from being R₁ to R₂ and in the final geometry the unpaired electron coming from e₉ has then a dominant 3z²-r² character.

Understanding the long axis switch induced by pressure in Na₃MnF₆

Bearing the analysis carried out in sections 4.1 and 4.2 in mind, the long axis switch in Na₃MnF₆ appears to arise from the significant anisotropic response of this compound to hydrostatic pressure. Thus, although the pressure on any crystal face is always the same, the reduction of crystal parameters is far from being isotropic. Indeed, in the pressure range 0–2 GPa the lattice parameters α and, specially, c, experience a progressive decrease, while b is nearly unmodified. This pressure reduction of c and α tends, in turn, to reduce the value of R₁ and R₂, as it is experimentally shown. For instance, at P = 0.91 GPa, R₁ = 1.978 Å and R₂ = 1.810 Å, which are clearly smaller than those reported at 0.12 GPa (Table 1). By contrast, the value R₃ = 1.897 Å measured at P = 0.91 GPa is only 0.01 Å higher than the value obtained at 0.12 GPa (Table 1).

A progressive reduction of R₁ approaches the two F₂⁻ ligands to Mn¹⁺⁻, thus increasing the energy of the |3z²-r²⟩ level, which works against having the HOMO of the MnF₆⁻³⁻ unit in Na₃MnF₆ with a dominant 3z²-r² character. For this reason, when pressure increases, it appears more favorable a change of the HOMO wavefunction in order to reach a dominant 3y²-r² character and placing the associated density along the y direction where R₁ is not reduced by pressure. Moreover, although this switch of the HOMO wavefunction involves, in principle, an energy increase there is an energy reduction in the subsequent relaxation process leading to an increase of R₁ and a decrease of R₂ (Table 2).

The main steps of this process induced by pressure in Na₃MnF₆ can quantitatively be clarified looking at Figure 3. Particular attention is paid to analyze, in each step, the shape of the HOMO wavefunction of the MnF₆⁻³⁻ unit, |ψ_HOMO⟩. In general, according to calculations, |ψ_HOMO⟩ can simply be written as follows:

\[ |ψ_HOMO⟩ = α|3z²-r²⟩ + β|x²-y²⟩ \]  

with α² + β² = 1. Four steps are considered in Figure 3. The initial step I describes the situation of a MnF₆⁻³⁻ unit in Na₃MnF₆ at ambient pressure, while step II reflects the experimental geometry and HOMO wavefunction at about P = 1.8 GPa where the longest axis is still R₂, as described by our first principles simulations. Similarly, step IV corresponds with data at P = 2.79 GPa where, the longest axis is already R₁. Step III is a virtual process where the geometry is that of step II (P = 1.8 GPa) while the HOMO wavefunction has been switched to that of the final step (P = 2.79 GPa). We describe below the process to obtain its energy.

At ambient pressure, the MnF₆⁻³⁻ unit is elongated along the z axis while R₁ and R₂ are identical within 0.03 Å. Accordingly, the HOMO wavefunction is essentially |3z²-r²⟩ (β ≈ 0). On passing from step I to step II, R₁ decreases while R₂ increases. This favors an increase of the |x²-y²⟩ component although |ψ_HOMO (II)⟩ still exhibits a dominant |3z²-r²⟩ contribution (84.2%) and is described by

\[ |ψ_HOMO (II)⟩ = 0.917|3z²-r²⟩ + 0.397|x²-y²⟩ \]  

Figure 3. Relative variation of both energy and wavefunction of the HOMO for MnF₆⁻³⁻ complexes in Na₃MnF₆ calculated at different values of metal-ligand distances, whose directions in the Na₃MnF₆ unit cell are also shown. Step I corresponds to R₁ (i = 1, 2, 3) values for zero pressure while step II reflects the experimental geometry at about 1.8 GPa and step IV that for a pressure of 2.79 GPa where the highest metal-ligand distance is already R₁ instead of R₂. Step III describes a transition state where the geometry is that of step II while the wavefunction is that of the final step IV. The increase in the HOMO energy by changing the wavefunction at the geometry corresponding to ~1.8 GPa is only 0.06 eV. By contrast, the energy decrease due to the ligand relaxation process on passing from step III to the final step is of 0.21 eV.
At the same time, on passing from step I to step II the energy of the HOMO level experiences an increase of 0.63 eV (Figure 3).

The calculated HOMO wavefunction for step IV (Figure 3)

\[|\Psi_{\text{HOMO}}(IV)\rangle = 0.738|3z^2-r^2\rangle + 0.674|x^2-y^2\rangle \]  

(4)

involves changes with respect to that of step II which are better seen written \(|\Psi_{\text{HOMO}}(IV)\rangle\) in the \(|3z^2-r^2\rangle, |x^2-y^2\rangle\) basis

\[|\Psi_{\text{HOMO}}(IV)\rangle = 0.948|3y^2-r^2\rangle + 0.302|x^2-z^2\rangle \]  

(5)

Accordingly, in \(|\Psi_{\text{HOMO}}(IV)\rangle\) there is a 90% contribution of \(|3y^2-r^2\rangle\) and thus the associated density lies mainly along the \(R_{2}\) direction.

To calculate the energy of the HOMO level in the virtual step III we have expressed the orbital wavefunction \(|\Psi_{\text{HOMO}}(IV)\rangle\) (Eq. (4)) in terms of that of the HOMO at step II, \(|\Psi_{\text{HOMO}}(II)\rangle\), and its LUMO, \(|\Psi_{\text{LUMO}}(II)\rangle\). As \(<\Psi_{\text{LUMO}}(II)|\Psi_{\text{HOMO}}(II)\rangle = 0\) and the HOMO-LUMO separation in step II is equal to 0.54 eV, this means that, on passing from step II to step III (Figure 3) which represents just a change in basis, the increase in HOMO energy can be estimated to be only 0.06 eV. This slight increase reflects the relative closeness of \(|\Psi_{\text{HOMO}}(IV)\rangle\) and \(|\Psi_{\text{HOMO}}(III)\rangle\) as \(<\Psi_{\text{HOMO}}(III)|\Psi_{\text{HOMO}}(IV)\rangle\) is equal to 0.944 from Eqs. (3) and (4). Interestingly, the 0.06 eV energy increase obtained on passing from step II to step III is widely compensated by the decrease of 0.21 eV due to the subsequent ligand relaxation involved in the transition from step III to step IV such as it is shown on Figure 3.

If the long axis switch in Na\(_3\)MnF\(_6\) is strongly influenced by the electronic ground state of the involved MnF\(_{6}^{3-}\) unit a different situation would happen in NaFeF\(_6\) where a more spherical electronic density around Fe\(^{3+}\) is expected to take place. Calculations carried out for NaFeF\(_6\) at a pressure of 2.79 GPa support this idea. Indeed, the obtained pattern of metal-ligand distances (\(R_7 = 1.922\ \text{Å}, R_8 = 1.935\ \text{Å}\) and \(R_9 = 1.932\ \text{Å}\)) is similar to that derived at zero pressure (Table 4) although all of them are reduced by \(\sim 0.01\ \text{Å}\).

It is worth noting that the switch phenomenon analyzed in Na\(_3\)MnF\(_6\) is different from that observed\(^{15,28}\) in Tutton salts like (ND\(_3\))\(_2\)Cu(D\(_3\)O\(_9\))SO\(_4\) or (ND\(_3\))\(_2\)Cu(H\(_2\)O\(_6\))SO\(_4\). As it has recently been shown\(^{17,59}\) the structure of Cu(D\(_3\)O\(_9\))\(_2\) or Cu(H\(_2\)O\(_6\))\(_2\)\(_2\) units in those salts at ambient pressure arises from a compressed geometry, with Z as principal axis and an unpaired electron in a \(|3z^2-r^2\rangle\) orbital, followed by an orthorhombic instability in the XY plane. Accordingly, the three metal-ligand distances are ordered as follows: \(R_9 > R_8 > R_7\) where \(R_7\) and \(R_8\) stand for the Cu–O\(_7\) and Cu–O\(_8\) bonds respectively while \(R_9\) corresponds to the shortest Cu–O\(_7\) bond. Interestingly, despite the orthorhombic distortion, the wavefunction of the unpaired electron at ambient pressure keeps an 82% of \(3z^2-r^2\) character.\(^{17}\)

Upon raising the applied pressure at 0.15 GPa the long axis is no longer the Cu–O\(_7\) but the Cu–O\(_8\) bond\(^{24,34}\) thus implying \(R_9 > R_8 > R_7\) with \(R_7\) being unmodified within 1%. For this reason, in the switch process corresponding to (ND\(_3\))\(_2\)Cu(D\(_3\)O\(_9\))SO\(_4\) or (ND\(_3\))\(_2\)Cu(H\(_2\)O\(_6\))SO\(_4\) the unpaired electron wavefunction main-
tains a dominant \(3z^2-r^2\) character\(^{17}\) a situation distinct to that encountered in Na\(_3\)MnF\(_6\).

Optical transitions of Na\(_3\)MnF\(_6\) at ambient and high pressure

The ground state, \(\Psi_{\text{g}}\) with \(S = 2\) and \(M_s = 2\), of a high spin \(d^4\) complex can shortly be written by the following Slater determinant

\[\Psi_0 = |xz \uparrow yz \uparrow xy \uparrow 3z^2-r^2 \uparrow | \]  

(6)

Accordingly, the spin allowed excitations involve jumps from the four orbitals appearing in \(\Psi_0\) to the empty \(|x^2-y^2\rangle\) orbital and thus they are the most intense among the \(d-d\) transitions coming from Cr\(^{2+}\) or Mn\(^{3+}\) complexes.\(^{56,57,28}\)

In the case of Na\(_3\)MnF\(_6\) at ambient pressure the values of such spin allowed transitions have been reported by Palacio and Moron\(^{15,17}\) and Carlson et al.\(^{11}\) although the last authors have not detected the lowest transition \(3z^2-r^2 \rightarrow x^2-y^2\). Experimental transition energies are collected in Table 6 and compared to the values obtained in the present calculations. The calculated \(d-d\) transitions are reasonably close to those observed experimentally at ambient pressure.

It is worth noting now that in K\(_3\)MnF\(_6\) there are two different Mn\(^{3+}\) sites\(^{58}\) and the geometry of the so-called Mn\(^{3+}\) (2) site is very close to that found in Na\(_3\)MnF\(_6\) at ambient pressure (Table 1). Indeed, the values of \(R_7\), \(R_8\), and \(R_9\) differ by less than 3%, and the value of the average metal-ligand distance, \(R\), is equal in both cases to 1.93 Å.\(^{5,58}\) The experimental \(d\)-d excitations measured in a powder K\(_3\)MnF\(_6\) for the Mn\(^{3+}\) (2) site\(^{58}\) are close to those reported for Na\(_3\)MnF\(_6\) in Table 6, the differences being smaller than 12%.

For the sake of completeness, we have compared the \(d\)-d transitions for Na\(_3\)MnF\(_6\)\(^{15,17}\) and CrF\(_3\)\(^{56}\) (involving \(3d^4\) cations, Mn\(^{3+}\) and Cr\(^{3+}\)) measured at ambient pressure. The three transitions coming from \(|xy, xz, yz\rangle\) levels are clearly higher for Na\(_3\)MnF\(_6\)\(^{5,57}\) than for CrF\(_3\).\(^{56}\) For instance, the highest \(d\)-d transition for Na\(_3\)MnF\(_6\) is found at \(\sim 2.45\) eV and only at 1.75 eV for CrF\(_3\) as shown in Table 7. This fact partially reflects the higher value of \(|R\rangle\) for CrF\(_3\) than for Na\(_3\)MnF\(_6\). For this reason, it may be surprising that the opposite happens for the lowest \(d\)-d transition (Table 7) as it is equal to 1.04 eV for Na\(_3\)MnF\(_6\)\(^{57}\) while equal to 1.22 eV for CrF\(_3\).\(^{56,28}\) Nevertheless, the CrF\(_{4}^{5+}\) unit in CrF\(_3\) is, in principle, compressed along the \(z\) direction but followed by an orthorhombic instability\(^{226}\) leading to a significant difference of final Cr\(^{2+}\)–F\(^-\) distances along \(x\) (\(R_7\)) and \(y\) (\(R_8\))

<table>
<thead>
<tr>
<th>Optical Transition</th>
<th>Calculated</th>
<th>Experim. (I)</th>
<th>Experim. (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(</td>
<td>3z^2-r^2</td>
<td>\rightarrow</td>
<td>x^2-y^2\rangle)</td>
</tr>
<tr>
<td>(</td>
<td>xy\rangle \rightarrow</td>
<td>x^2-y^2\rangle)</td>
<td>2.11 2.18</td>
</tr>
<tr>
<td>(</td>
<td>yz\rangle \rightarrow</td>
<td>x^2-y^2\rangle)</td>
<td>2.27 2.38</td>
</tr>
<tr>
<td>(</td>
<td>xz\rangle \rightarrow</td>
<td>x^2-y^2\rangle)</td>
<td>2.32 2.38</td>
</tr>
</tbody>
</table>
Table 7. Experimental values (in eV) of highest, $E_h$, and lowest, $E_L$, $d$-$d$ transitions for CrF$_2$ and Na$_2$MnF$_6$ measured at ambient pressure. The values of the average metal-ligand distance, $<R>$, and $|R_2-R_1|$ (in Å units) are also given.

|          | $E_h$  | $E_L$  | $<R>$ | $|R_2-R_1|$ |
|----------|--------|--------|-------|------------|
| CrF$_2$  | 1.75   | 1.22   | 2.14  | 0.42       |
| Na$_2$MnF$_6$ | -2.45 | 1.01   | 1.94  | 0.01       |

Directions equal to 0.416 Å (Table 7). As shown in Ref. [28], the existence of this huge orthorhombic distortion increases the value of the $x^2-y^2$ to $-3z^2-r^2$ transition in CrF$_2$ by 0.60 eV.

Concerning the influence of pressure upon $d$-$d$ excitations we have also calculated the values of four spin allowed transitions of Na$_2$MnF$_6$ at $P=2.79$ GPa. Results are depicted in Figure 4 and compared to those obtained for zero pressure. In accord with results of section 4.3, the nature of HOMO and LUMO orbitals has been modified as well as the order of three levels coming from $t_{2g}$ in O$_h$ symmetry.

Figure 4. Energies (in eV) of spin allowed $d$-$d$ transitions of Na$_2$MnF$_6$ calculated for a MnF$_6^{11}$ complex with the experimental geometries at $P=0$ and $P=2.79$ GPa. The dominant contribution for each orbital is shown, and the spin distribution corresponds to the electronic ground state ($S=2$, $M_s=2$). Note that on passing from ambient pressure to $P=2.79$ GPa, the nature of HOMO and LUMO orbitals has been modified as well as the order of three levels coming from $t_{2g}$ in O$_h$ symmetry.

Conclusions

The present results show the usefulness of the parent phase as a good starting point for understanding the behavior of low symmetry compounds containing $d^n$ ($n=4,9$) cations. In the present case, when we introduce a substitutional Mn$^{+}$ impurity in the parent Na$_2$FeF$_6$ compound, the HOMO wavefunction is already determined by the low local symmetry, which in turn, fixes the subsequent distortion due to an electron density that exerts a different force on the three kinds of ligands. Moreover, the force constant for moving a ligand is different in each type of ligands as a result of the low symmetry of the lattice. This behavior has been well studied in layered lattices like K$_3$MF$_6$ ($M=Mg, Zn$) doped with $d^7$ ions like Cu$^{2+}$ or Ni$^{2+}$.

Bearing these facts in mind, we can now envisage the differences and similarities between low symmetry and JT systems. If we place a $d^7$ cation in a cubic material with sixfold coordination, the ground state is degenerate, and thus the unpaired electron is, in general, described by a linear combination of $|3z^2-r^2|$ and $|x^2-y^2|$ molecular orbitals of the associated complex. If the unpaired electron is located in the $|3z^2-r^2|$ orbital the corresponding adiabatic minimum corresponds to a tetragonal elongated complex while it is compressed if placed in $|x^2-y^2|$. Usually for systems displaying a static JT effect the elongated conformation is preferred [9,10] with the known exception of CaO: Ni$^{2+}$ which is compressed [53], a matter discussed in Ref. [60]. Nevertheless, if the complex is tetragonal elongated, there are still three different possibilities for the electronic ground state of the complex because of the cubic symmetry. Indeed, the electron wavefunction can be either $|3z^2-r^2|$, $|3x^2-r^2|$ or $|3y^2-r^2|$. In real crystals, this equivalence is, however, often destroyed by small random strains, establishing one of the three initially degenerate options at a given point of the lattice. Once the unpaired electron is then fixed in the $|3z^2-r^2|$ orbital, the corresponding electron density does not exhibit cubic symmetry and thus, induces a tetragonal distortion [9,10]. This behavior is usually called a static JT effect [8,9,10] well observed in cases like KZn$_2$CrF$_6$ [9,10,11,12] or $d^6$ ions (Ni$^{2+}$, Cu$^{2+}$, Ag$^{+}$) in alkali halides [10,14,15,31,32]. Nevertheless, when random strains play a minor role, there is no symmetry breaking, and EPR spectra of JT systems exhibit a cubic and not a tetragonal symmetry [9,10]. This uncommon phenomenon has been observed for Cu$^{2+}$ or Ag$^{+}$-doped MgO where EPR spectra [33,34] and first principle calculations [35] prove the existence of coherent tunneling [8,9,10] among equivalent adiabatic minima thus leading to a global cubic symmetry.

According to this reasoning, if we deal with a static JT effect with $z$ as main axis, an applied hydrostatic pressure, which is an isotropic stress, cannot destroy the equivalence between $x$ and $y$ axes of a tetragonal complex and thus the nature of the principal axis is unmodified. By contrast, a different situation occurs when the $d^n$ ($n=4,9$) cation is placed in a low symmetry lattice where the corresponding complex shows at most an orthorhombic geometry such as it is found for Na$_2$MnF$_6$ and K$_3$MnF$_6$. Accordingly, in this circumstance, as the geometry does not arise from a JT effect, one can expect, after careful consideration of the elastic properties of the solid, possible...
In accord to present results, the properties of d° and d± low symmetry compounds with sixfold coordination cannot be explained by the JT framework, valid for a parent cubic symmetry, to an initial tetragonal or orthorhombic symmetry. For an initial cubic symmetry, the adiabatic minima have tetragonal symmetry well observed experimentally in cases displaying a static JT effect. Thus, when the observed local symmetry of the involved complex is orthorhombic or lower, such as it happens for Na₄MnF₆, explanations based on the JT effect are likely to be meaningless. Along this line, the existence of a switch of the JT axis recently put forward for explaining the behavior of [(CH₃)₂NH]₂Cu(HCOO)₃ under pressure is certainly doubtful due to the monoclinic symmetry of the lattice at ambient pressure. A similar situation holds for recent results on the rhombohedral CuPyr-I compound where the six ligands around Cu²⁺ are not identical (two N and four O) a fact that is already against the existence of a JT effect.

The present work stresses the importance of considering the anisotropic elastic response to pressure in low symmetry systems containing d° or d± ions. It opens a window for properly understanding the pressure effects upon insulating compounds such as CuF₂(H₂O)₆(py2)₄ (pyz = pyrazine). Further work along this line is now in progress.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: anisotropy · Jahn-Teller effect · low symmetry lattice · parent phase · pressure-induced switch
