Reinterpretation of the conjectured Jahn-Teller switch of MnF_6^{3-} complexes in Na_3MnF_6 under pressure

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Numerous papers have been published in the recent literature invoking the existence of Jahn-Teller switching under hydrostatic pressure in solids containing complexes of the transition metal cations Cu^{2+} (d^9 configuration) or Mn^{3+} (d^4). A significant example is the monoclinic compound Na_3MnF_6 (space group $P2_1/n$) which, at ambient pressure, contains MnF_6^{3-} complexes where the long axis corresponds to the the Mn^{3+}-F_3^- direction, close to the crystal ***c*** axis, while at 2.79 GPa the long axis is in the Mn^{3+}-F_2^- direction more or less along ***b*** axis [1].

In this work we use symmetry arguments and first-principles calculations [2] in order to show that the switch in the elongation axis of the MnF_6^{3-} complexes is not related to the Jahn-Teller effect, but rather is due to the the anisotropic response of the low symmetry lattice to hydrostatic pressure, strongly reducing the **c**-axis while the **a** and **b** axes change very little. This fact is shown to force a change of the HOMO wavefunction favoring that, at P = 2.79 G Pa, the long axis becomes the Mn^{3+}-F_2^- direction, not far from crystal ***b*** axis, after the subsequent relaxation process.

The origin of the different *d-d* transitions observed for Na_3MnF_6 and CrF_2 at ambient pressure is also discussed together with changes induced by pressure in Na_3MnF_6. The present work opens a window for understanding the pressure effects upon low symmetry insulating compounds containing d^4 or d^9 ions.

[1] S. Carlson, Y. Xu, U. Halenius, R. Norrestam, *Inorg. Chem*. **1998**, 37, 1486-1492.
[2] I. Sánchez-Movellán, D. Carrasco-Busturia, J. M. García-Lastra, P. García-Fernández, J. A. Aramburu, M. Moreno, *Chem. Eur. J.* **2022**, 28, e202200948 (1-10)