Reinterpretation of the conjectured Jahn-Teller switch of MnF$_6^{3-}$ complexes in Na$_3$MnF$_6$ under pressure

I. Sánchez-Movellán$^1$, D. Carrasco-Busturia$^2$, J. M. García-Lastra$^2$, P. García-Fernández$^1$, J. A. Aramburu$^1$, M. Moreno$^1$

$^1$Departament CITIMAC, University of Cantabria, Santander, Spain
$^2$Department of Energy Conversion and Storage, Technical University of Denmark, Lyngby, Denmark

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$_3$MnF$_6$ (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 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$_3$MnF$_6$ and CrF$_2$ at ambient pressure is also discussed together with changes induced by pressure in Na$_3$MnF$_6$. The present work opens a window for understanding the pressure effects upon low symmetry insulating compounds containing d$^4$ or d$^9$ ions.