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

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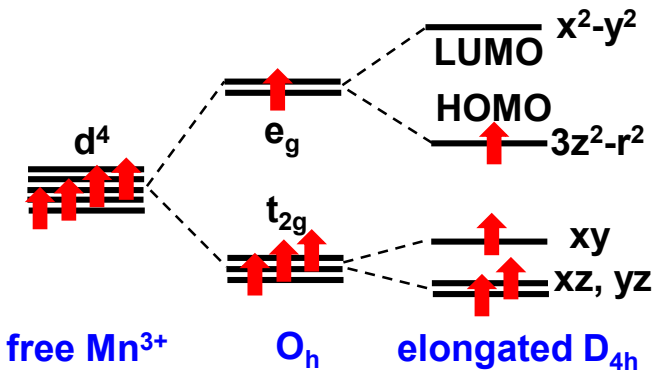
Jahn-Teller swicht under pressure

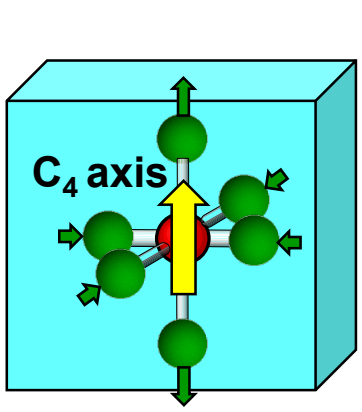
- Many works invoke the existence of a **Jahn-Teller switch under hydrostatic pressure** in solids containing complexes of transition metal cations as Cu^{2+} (d^9 configuration) or Mn^{3+} (d^4)
- **Examples: Na_3MnF_6**, $(NH_4)_2Cu(H_2O)_6(SO_4)_2$, $Cs_2Zn(ZrF_6)_2.6H_2O:Cu^{2+}$, $CuF_2(H_2O)_2(pyz)$ (pyz = pyrazine), $CuWO_4$, etc.

- **Conjetured idea:** Na_3MnF_6 → **MnF_6^{3-}** complexes (d^4, S = 2) tetragonally elongated (D_{4h}) by **Jahn-Teller effect**

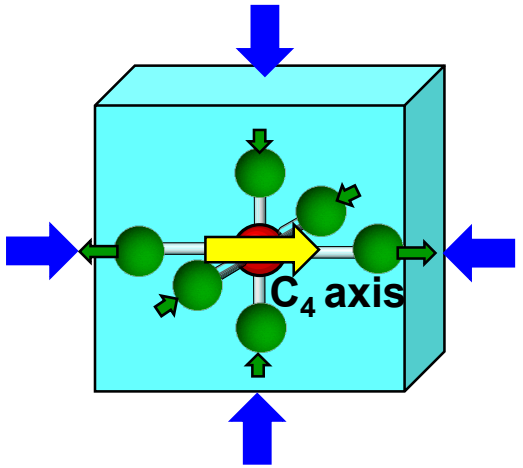
MnF_6^{3-}: Jahn-Teller view



MnF_6^{3-}: switch of the C_4 axis under P



P = 0

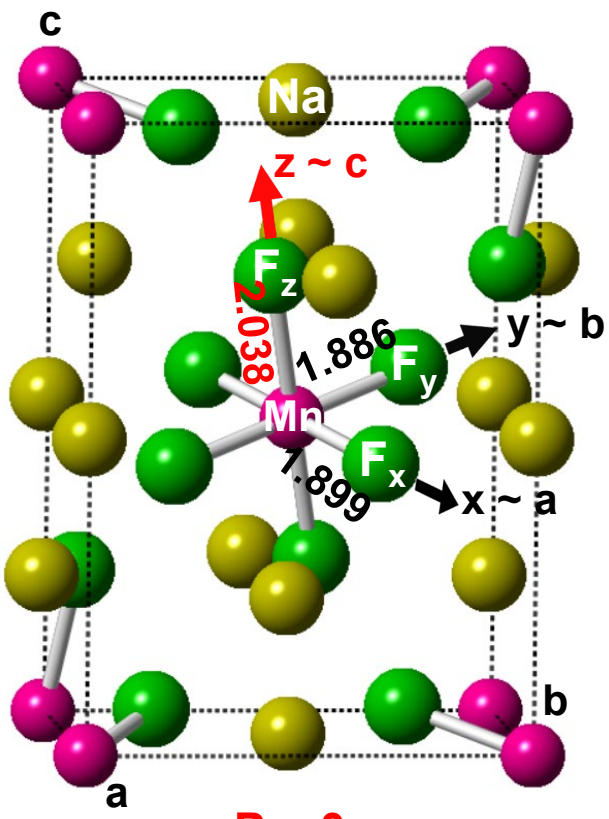


P > 1.8 GPa

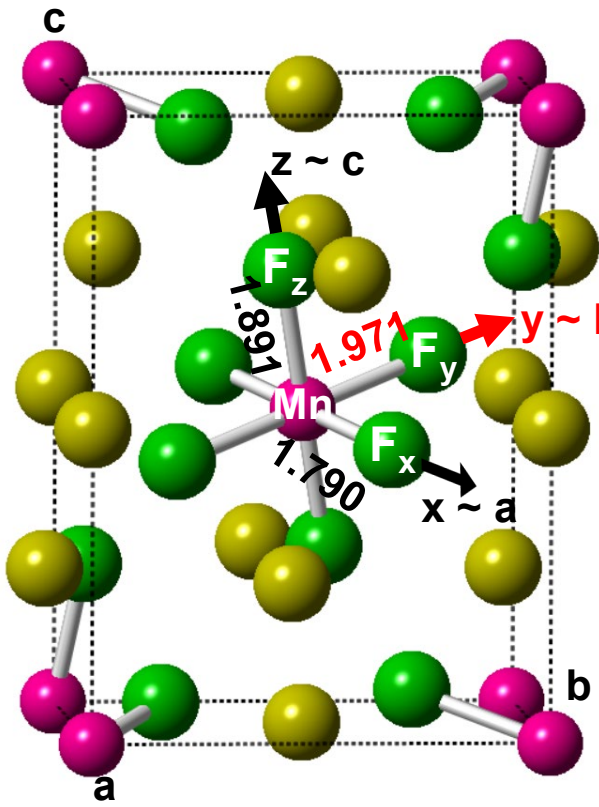
Na_3MnF_6 monoclinic $P2_1/n$ (standard $P2_1/c$)

- **Experimental data:** Carlsson et al., Inorg. Chem. 37, 1486 (1988)
- **MnF_6^{3-} complexes**: no D_{4h} elongated but **triclinic C_i**, no C_4 axis
- **Switch of the long Mn-F bond under P = 2.79 GPa: z → y**

MnF_6^{3-} C_i
R_x = 1.899 Å
R_y = 1.886 Å
R_z = 2.038 Å



P = 0
$P2_1/c$
a = 5.470, b = 5.690, c = 8.066, β = 89.1°



MnF_6^{3-} C_i
R_x = 1.790 Å
R_y = 1.971 Å
R_z = 1.891 Å

P = 2.79 GPa
$P2_1/c$
a = 5.386, b = 5.690, c = 7.783, β = 90.8°

Goals and Tools

- **3 goals**
  1. To show that **there is not a Jahn-Teller effect** in MnF_6^{3-} complexes of Na_3MnF_6 (the same for other non-cubic crystals)
  2. To show that the long axis switch is due to the **anisotropy** of the crystal
  3. To **assign the 3 observed peaks in the optical d-d spectrum**

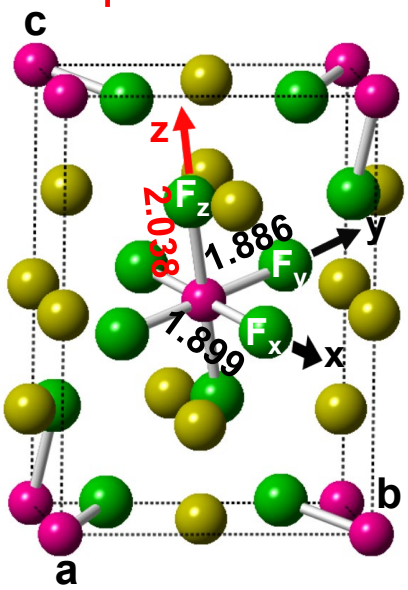
- **Basic tools**
  - First-principles DFT periodic calculations: Crystal code, hybrid XC functionals
  - First-principles DFT calculations on a MnF_6^{3-} complex with embbeding: ADF code, hybrid XC functionals
  - Symmetry

Na_3MnF_6: calculated geometry

- **Optimized geometries** for P = 0, 2.79 GPa
- Lattice parameters (a, b, c) and Mn-F distances in Å, β angle in degrees

		a	*b*	*c*	β	R_x	R_y	R_z
P = 0	Experim.	5.471	5.683	8.073	88.9	1.862	1.897	**2.018**
	Calculated	5.460	5.646	8.137	88.5	1.864	1.880	**2.069**
P = 2.79	Experim.	5.386	5.690	7.783	89.3	1.790	**1.971**	1.891
	Calculated	5.381	5.720	7.713	88.4	1.861	**2.041**	1.866
lattice variation		**-0.10** $R_x \downarrow$	**+0.01** $R_y \uparrow$	**-0.29 Å** $R_z \downarrow$				

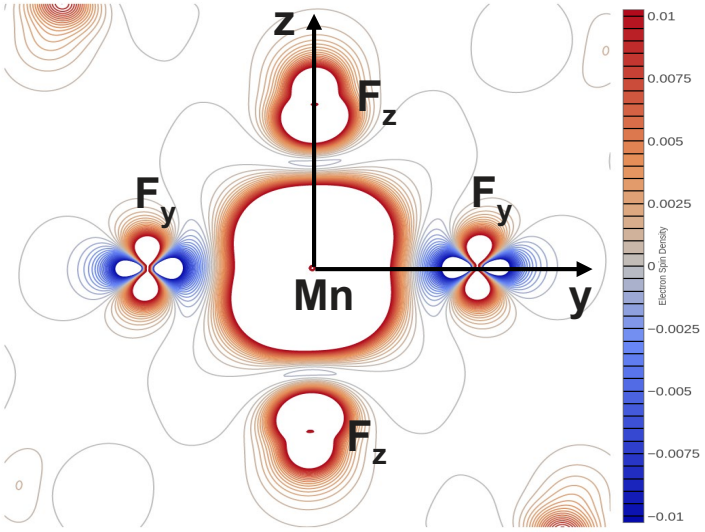
very anisotropic



- Good agreement with experimental geometries
- Calculations reproduce the switch under P

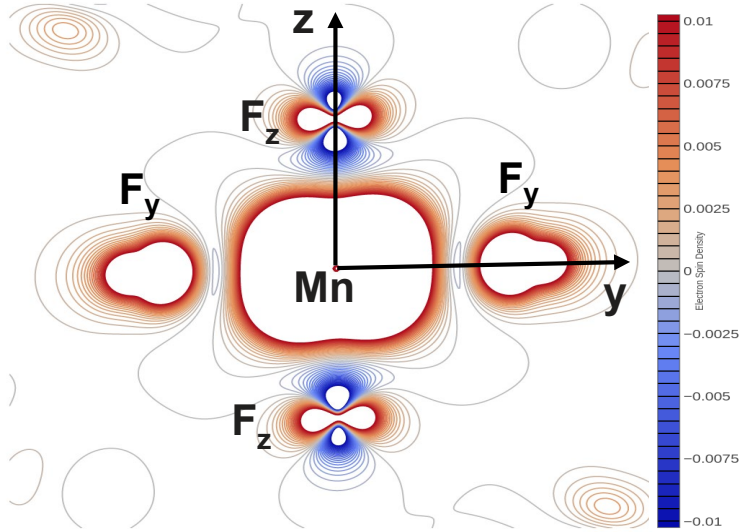
Na_3MnF_6: calculated spin density

- **Calculated spin density (up - down)** of a MnF_6^{3-} complex



P = 0

HOMO: dominant $3z^2$-r^2 character



P = 2.79 GPa

HOMO: dominant $3y^2$-r^2 character

R_x = 1.899 Å
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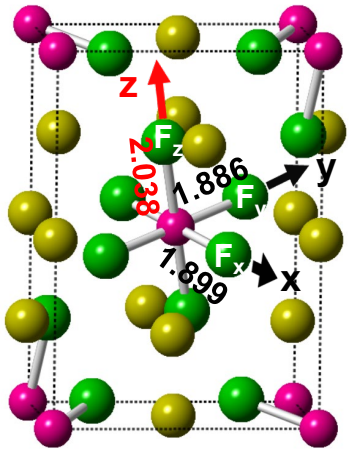

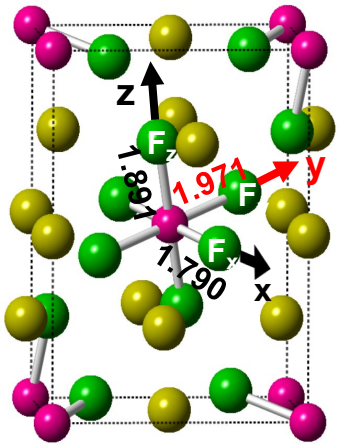

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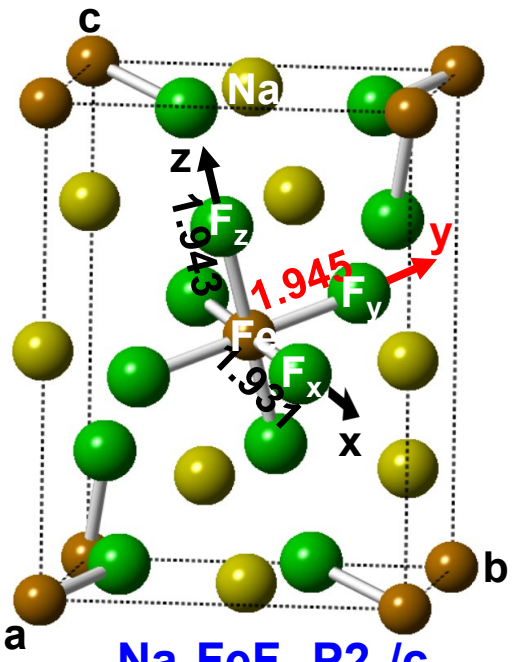
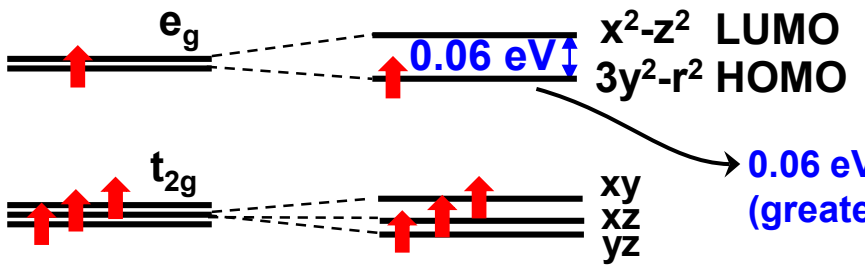
Na_3MnF_6: no Jahn-Teller effect

- Jahn-Teller effect is very restrictive: it requieres a high symmetry **parent phase where MnF_6^{3-} complexes had orbital degeneration**
- **Parent phase of Na_3MnF_6: killing any vibronic coupling**
- **Substitute all Mn^{3+}** (d^4 open shell) → **Fe^{3+}** (d^5, semiclosed shell), same ionic radii, 0.785 Å
- **Geometry optimization of Na_3FeF_6 fixing $P2_1/n$ group** ⇒ equal or greater symmetry (no lower)
- **Na_3FeF_6 parent phase no Jahn-Teller effect**
  - Same $P2_1/n$ symmetry of Na_3MnF_6
  - FeF_6^{3-} complexes: same triclinic C_i symmetry
  - Complexes elongated along y
  - Gap $(x^2-z^2) - (3y^2-r^2)$ of 0.06 eV: no degeneration



Na_3FeF_6 $P2_1/c$
R_x = 1.931 Å
R_y = 1.945 Å
R_z = 1.943 Å



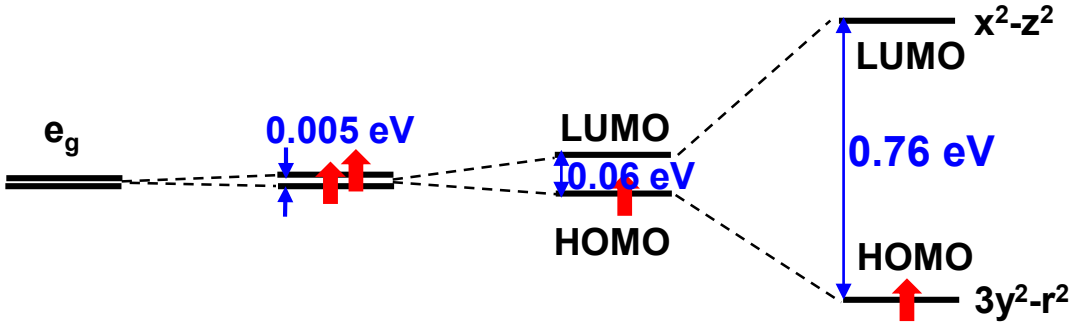
MnF_6^{3-} C_i complex in Na_3FeF_6

0.06 eV is not quasi-degeneration (greater tan Jahn-Teller barrier)

One MnF_6^{3-} complex in Na_3FeF_6

step	system	calculation	Complex	R_x (Å)	R_y (Å)	R_z (Å)	Δ (eV)
(1)	Na_3FeF_6	full optimization	FeF_6^{3-}	1.931	1.945	1.943	0.005
(2)	Na_3FeF_6:Mn^{3+}	Na_3FeF_6 param. and distances	MnF_6^{3-}	1.931	1.945	1.943	0.06
(3)	Na_3FeF_6:Mn^{3+}	Na_3FeF_6 param., optimize distances	MnF_6^{3-}	1.856	2.045	1.895	0.76
(4)	Na_3FeF_6:Mn^{3+}	increase c 1.1% optimize distances	MnF_6^{3-}	1.866	1.892	2.049	

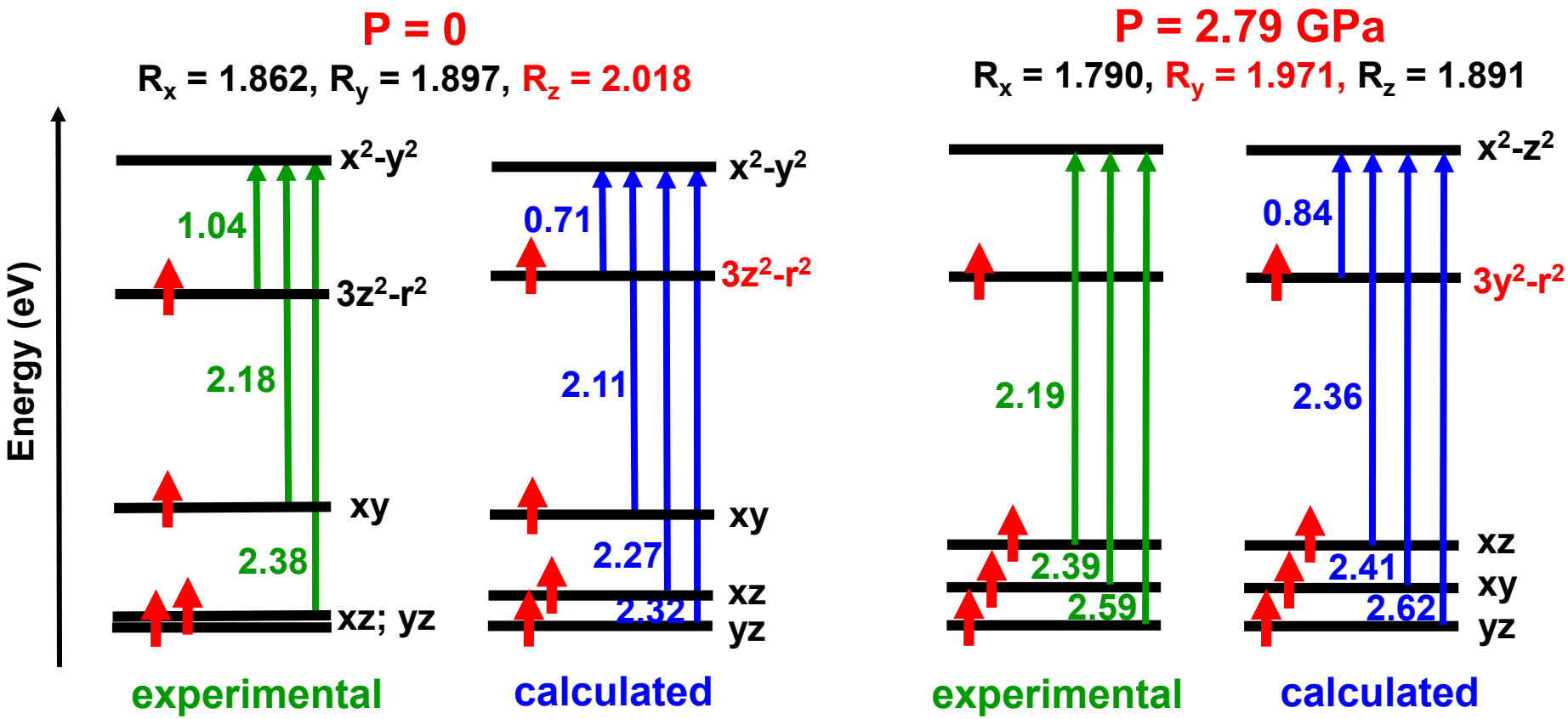
spliting Δ of e_g in a C_i complex in Na_3FeF_6



Pseudo-Jahn-Teller effect coupling HOMO-LUMO through a_g modes

MnF_6^{3-}: d-d transitions, P = 0, 2.79 GPa

- **Calculated energies (in eV)** for a C_i MnF_6^{3-} complex in Na_3MnF_6 at P = 0, 2.79 GPa
- **Experimental data:** Carlsson et al., Inorg. Chem. 37, 1486 (1988)



More information

- I. Sánchez-Movellán, D. Carrasco-Busturia, J. M. García-Lastra, J. A. Aramburu, P. Garcia-Fernández, M. Moreno, *Chem. Eur. J.* 28, e202200948 (2022)