Ellipsoids as a local coordination descriptor

James Cumby

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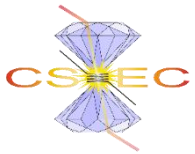

European Research Council

EPSRC Engineering and Physical Sciences Research Council

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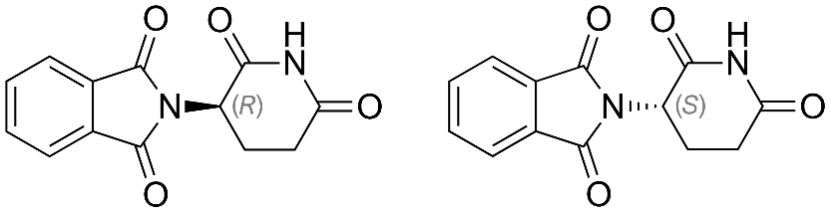
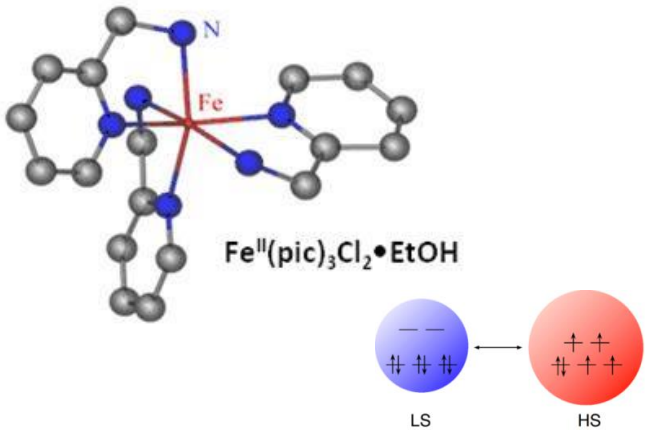
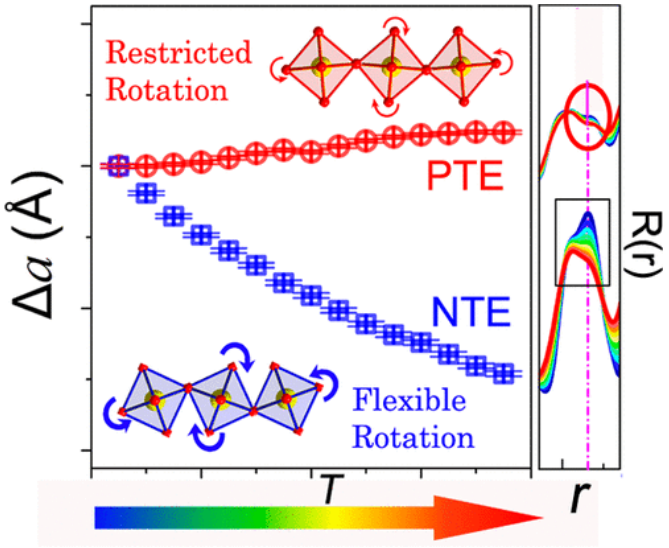
Properties often depend on *local* atomic structure



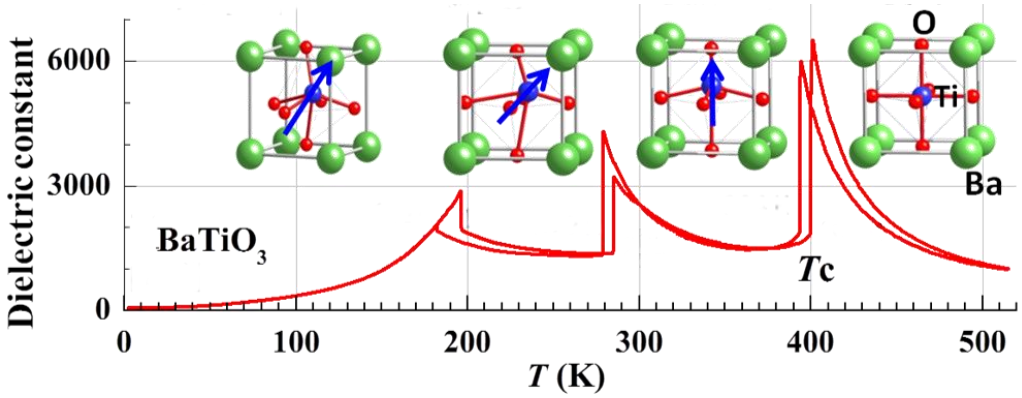
Chirality



Electronic and Magnetic behaviour

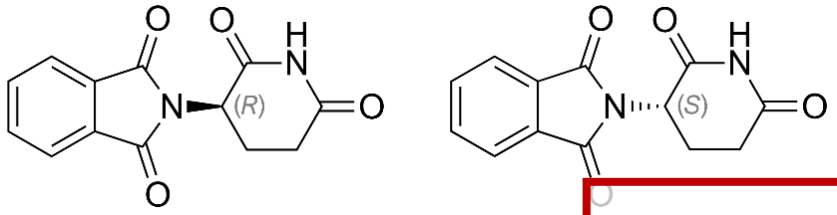


(Negative) thermal expansion



Dielectric properties

Properties often depend on *local* atomic structure



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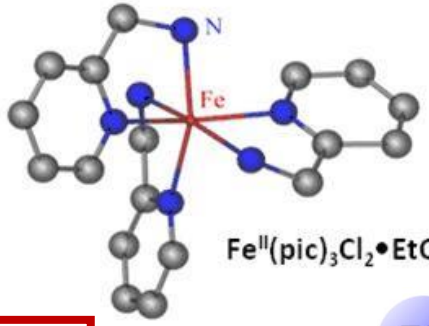

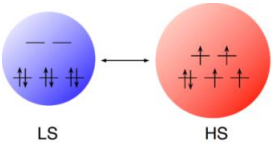

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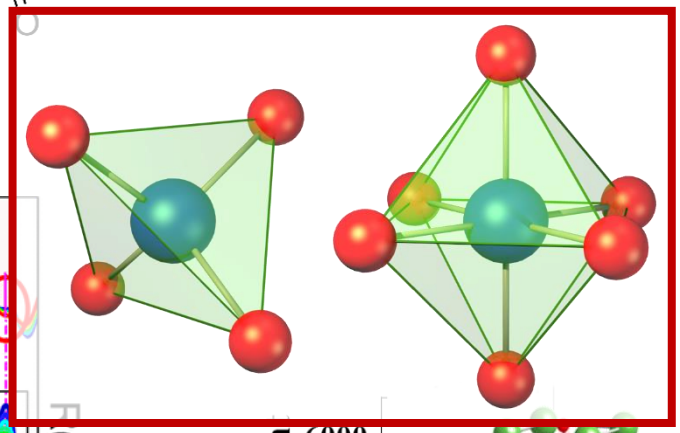

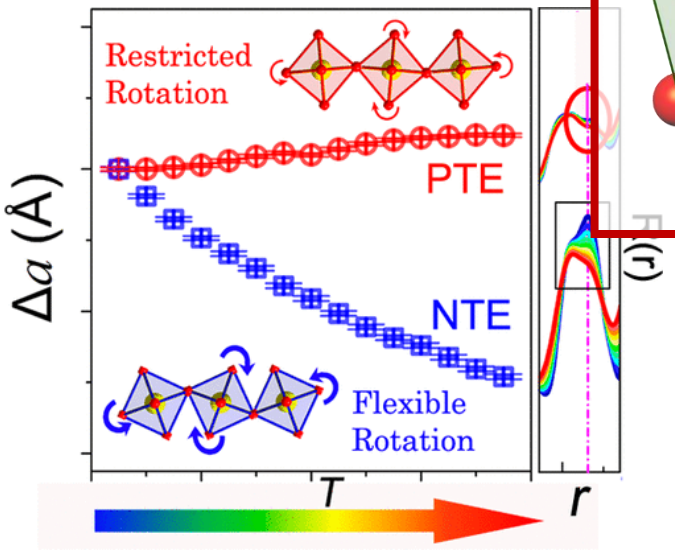

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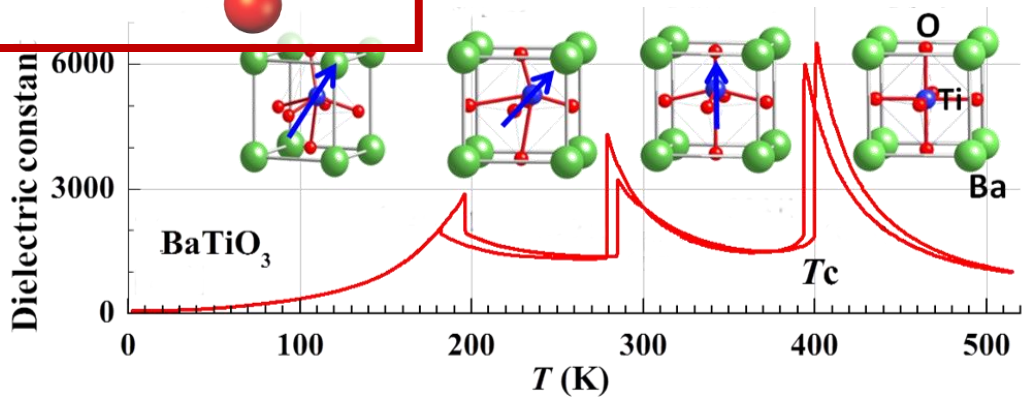
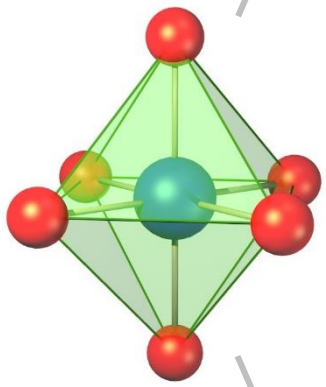
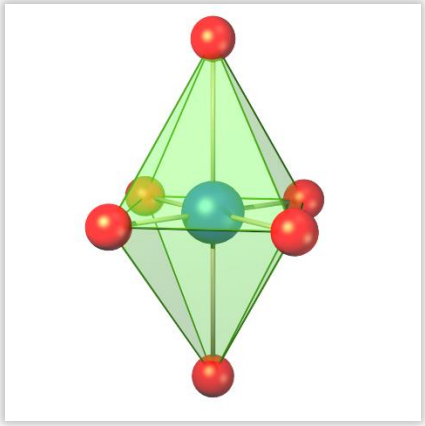


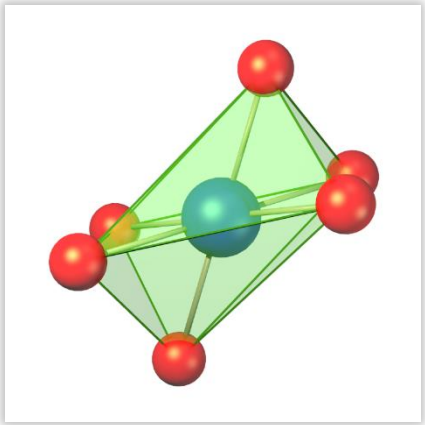
Dielectric properties

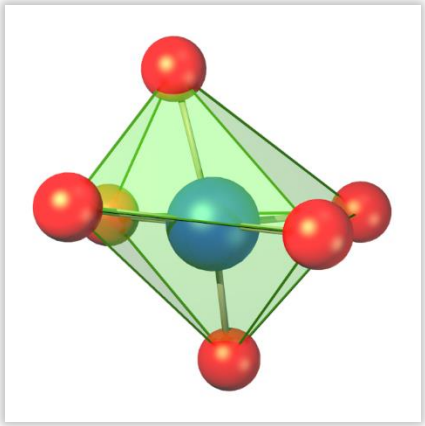
Bonding is often distorted

- Multiple origins:
  - Electronic effects
  - Connectivity
  - Strain / Pressure



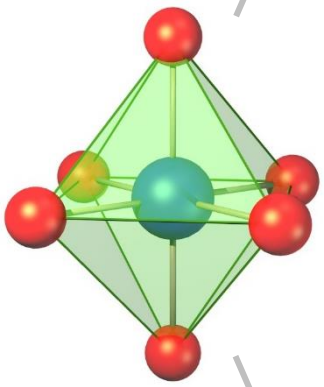


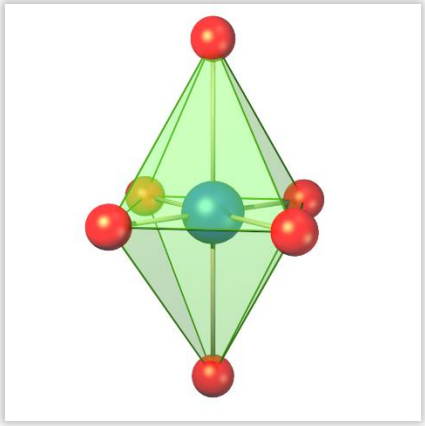


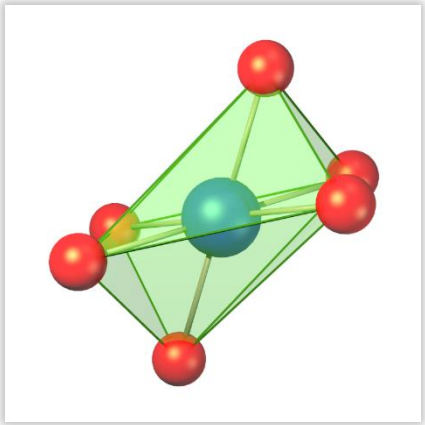


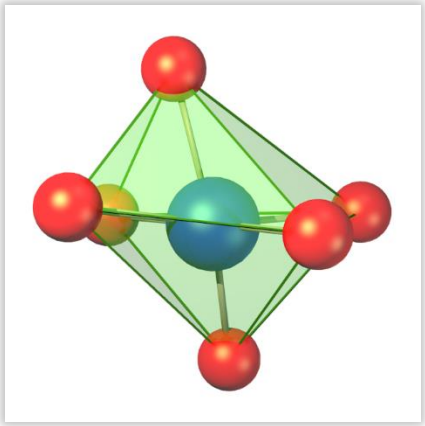
Bonding is often distorted

- Multiple origins:
  - Electronic effects
  - Connectivity
  - Strain / Pressure
- How can we describe distortion?
  - Bond lengths and angles
    - $\sigma^2(d) = \langle d^2 \rangle - \langle d \rangle^2$
    - $\sigma^2(\theta) = \langle \theta^2 \rangle - \theta_0^2$
  - Smooth Overlap of Atomic Positions (SOAP)
  - Local distortion (normal) modes
  - Continuous symmetry and shape analysis

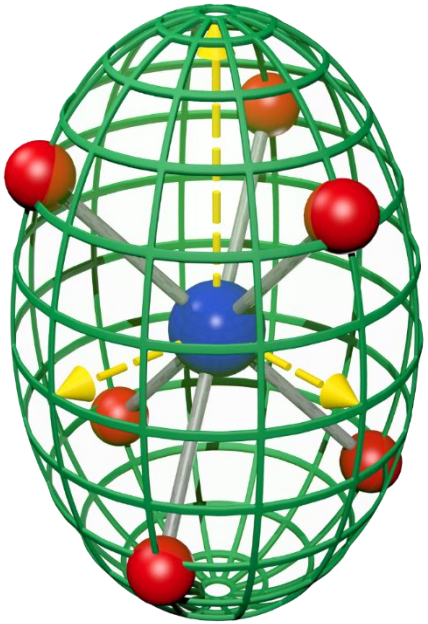








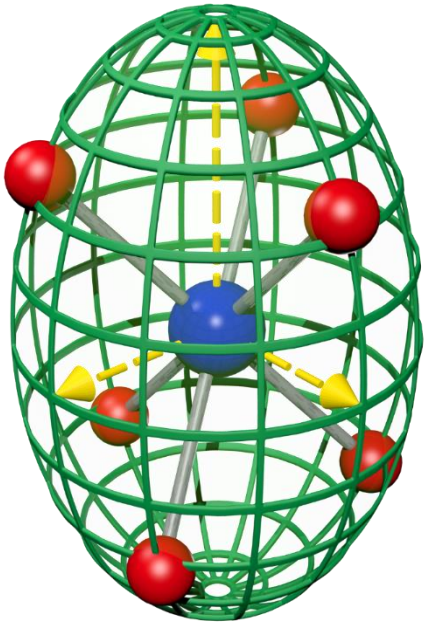
Ellipsoidal description



- Captures **angle** and **bond length** distortion

- Few parameters
  - Principal radii
    - $R_1 \geq R_2 \geq R_3$
  - Orientation
  - Central atom displacement

Ellipsoidal description



- Captures **angle** and **bond length** distortion

- Few parameters
  - Principal radii
    - $R_1 \geq R_2 \geq R_3$
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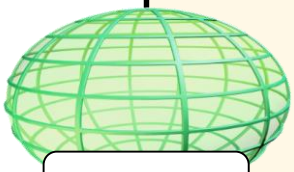
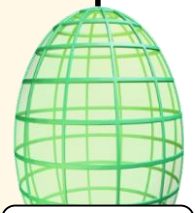
<R> → polyhedron size

σ(R) → distortion

$$S = \frac{R_3}{R_2} - \frac{R_2}{R_1}$$



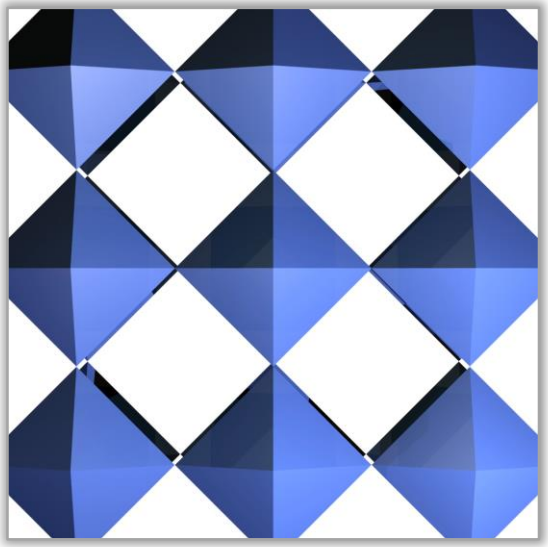
-1 ≤ S < 0

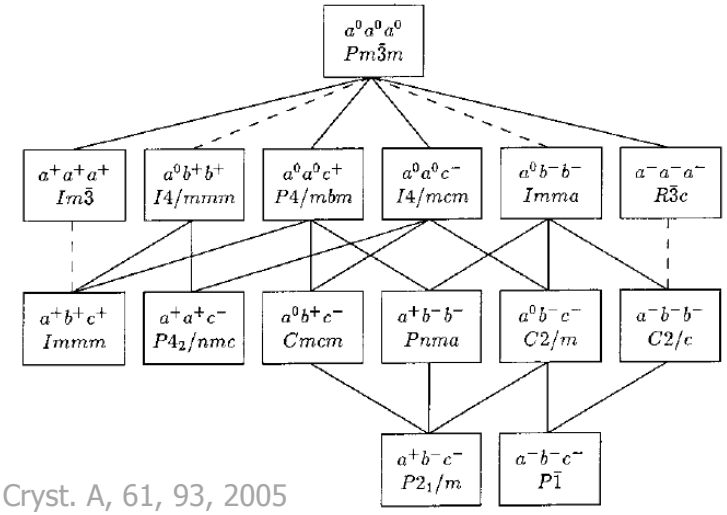


0 < S ≤ 1

Perovskite (ABO_3) phase transitions

- Cubic structure has spherical ellipsoids
- Many transform with T or P
- Occur as ordered tilts
  - 15 combinations
  - Octahedral 'tilt angle'



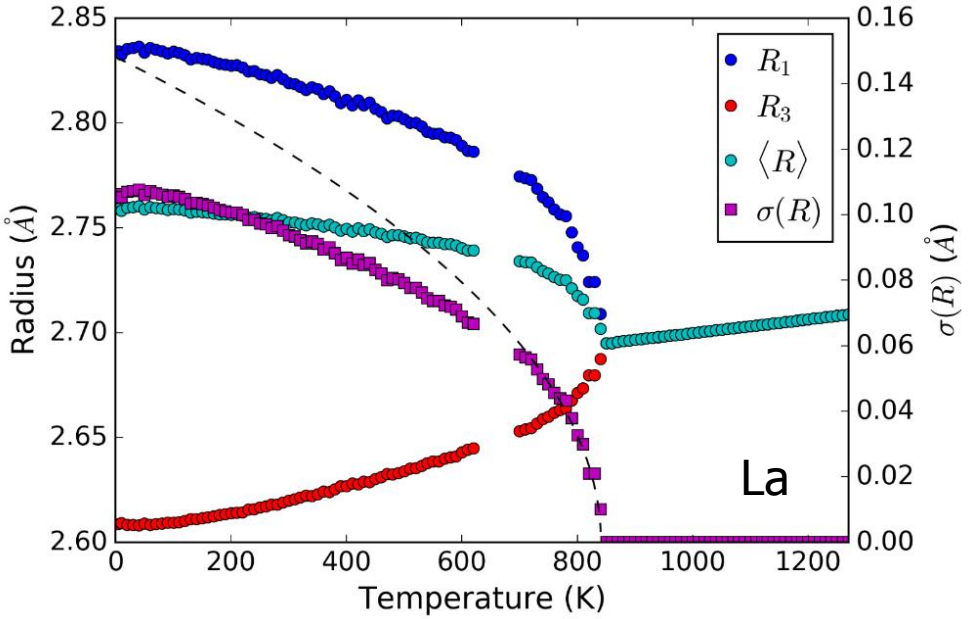


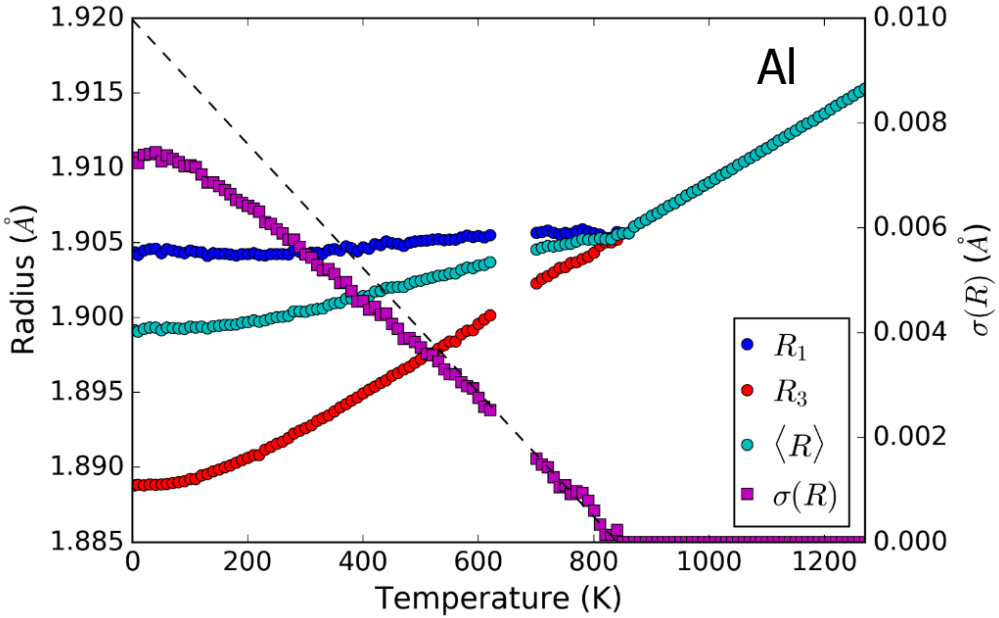
Howard & Stokes, Acta Cryst. A, 61, 93, 2005

$LaAlO_3$

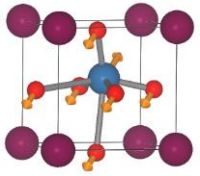
- 'Simple' transition
  - $R\bar{3}c \rightarrow Pm\bar{3}m$
- La ellipsoid reproduces order parameter
  - $\sigma(R)_{La} \propto t^{1/2}$
- Al octahedra not rigid
  - $\sigma(R)_{Al} \propto t^{1}$

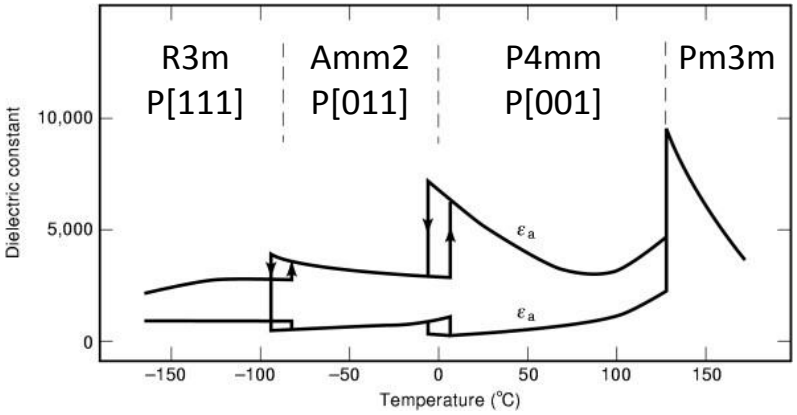
$$t = \frac{T_c - T}{T_c}$$



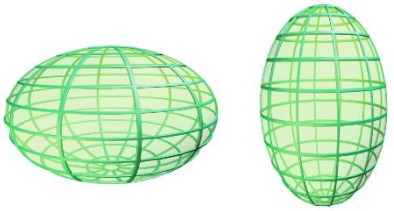


$BaTiO_3$

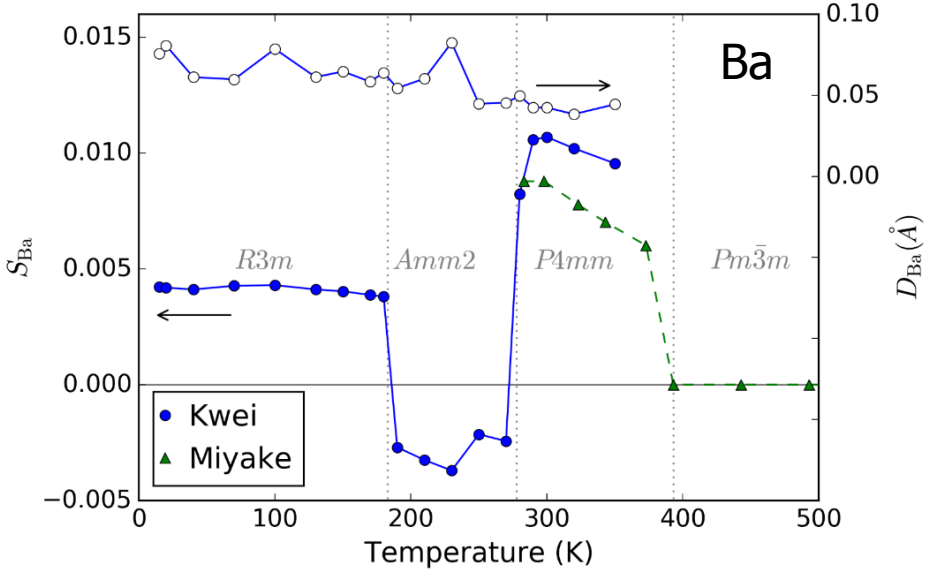


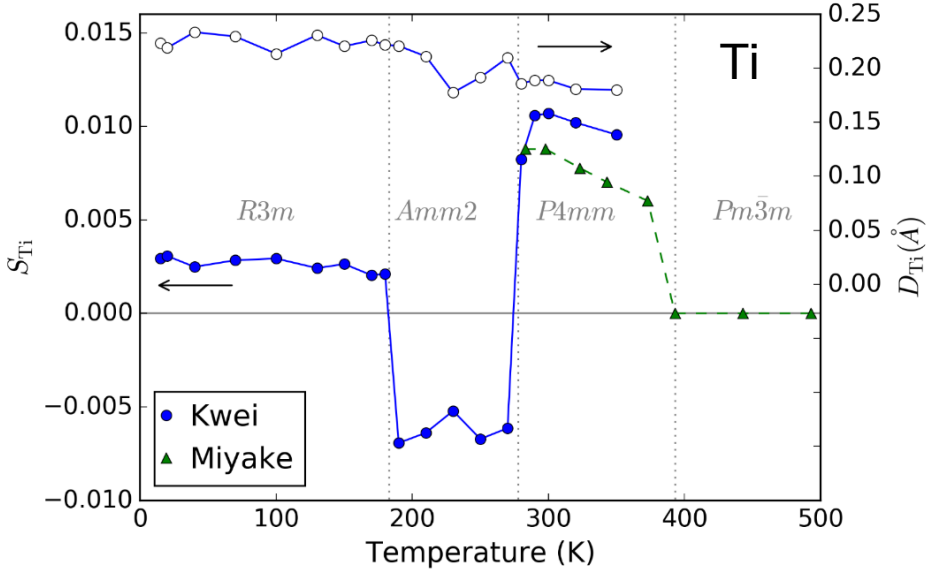


- Transitions do not follow 'simple' symmetry behaviour
  - Symmetry disallowed
- Change in sign of *S*
- Cation displacement is continuous



S < 0 S > 0

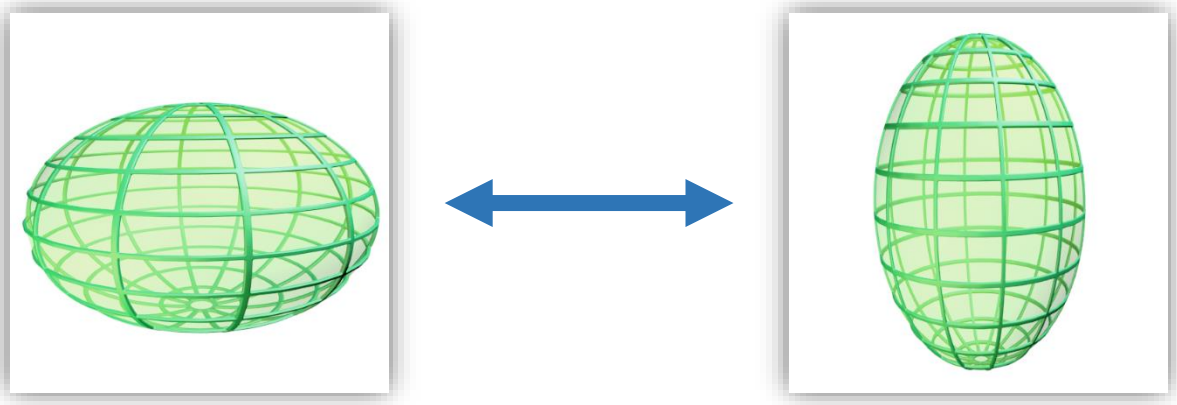




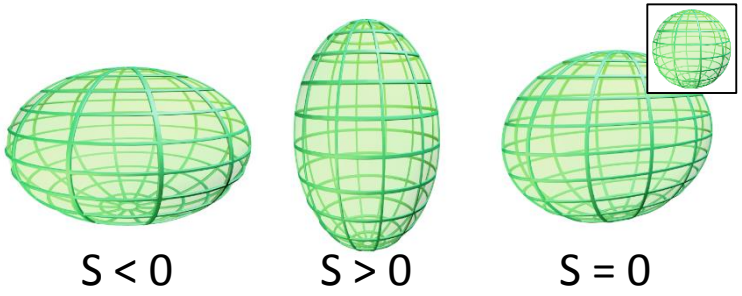
Significance of *S*

- Bistability of oblate and prolate ellipsoids
  - Competing coordinations with similar volume

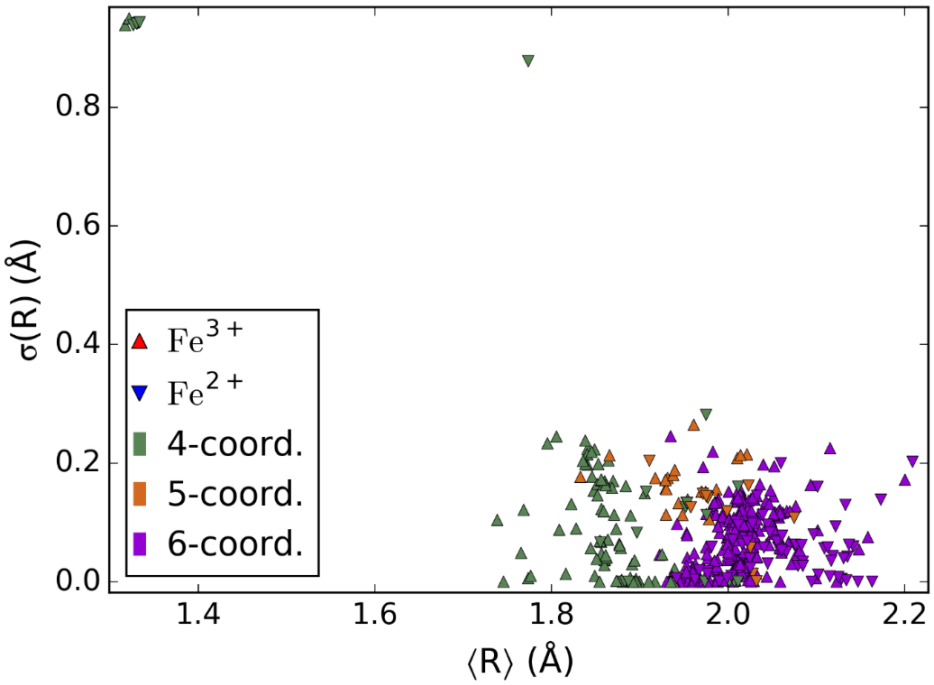
- Enhanced by electronic effects
  - Second-order Jahn-Teller effect (*e.g.* $BaTiO_3$)
  - Crystal field effects on A cation

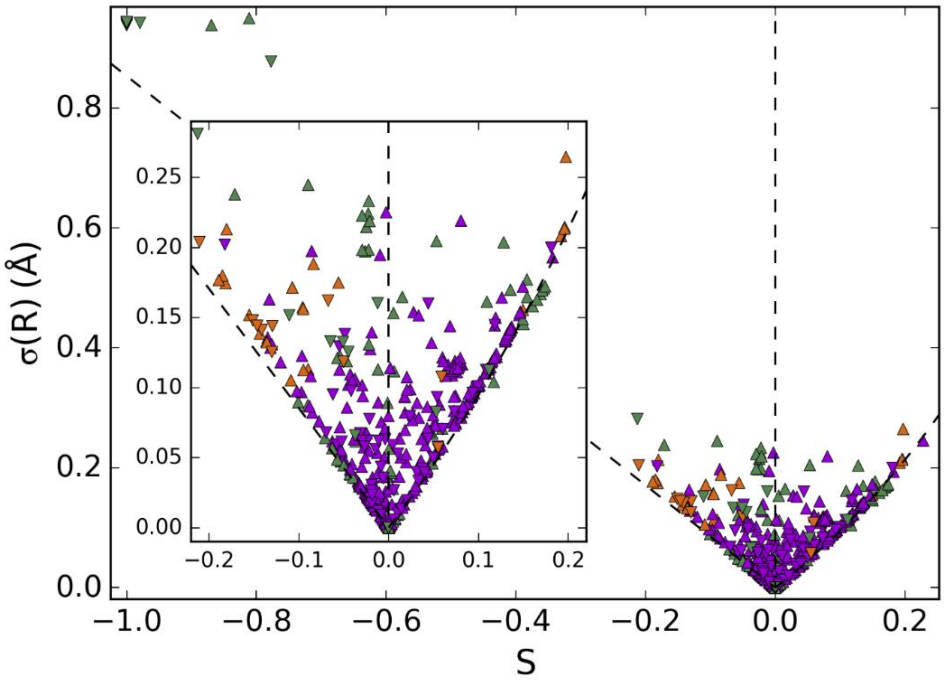


Iron oxides



- Data-mining of ICSD crystal structure database
  - 390 Structures
  - 499 Fe-O polyhedra; 98 Fe^{2+}, 401 Fe^{3+}



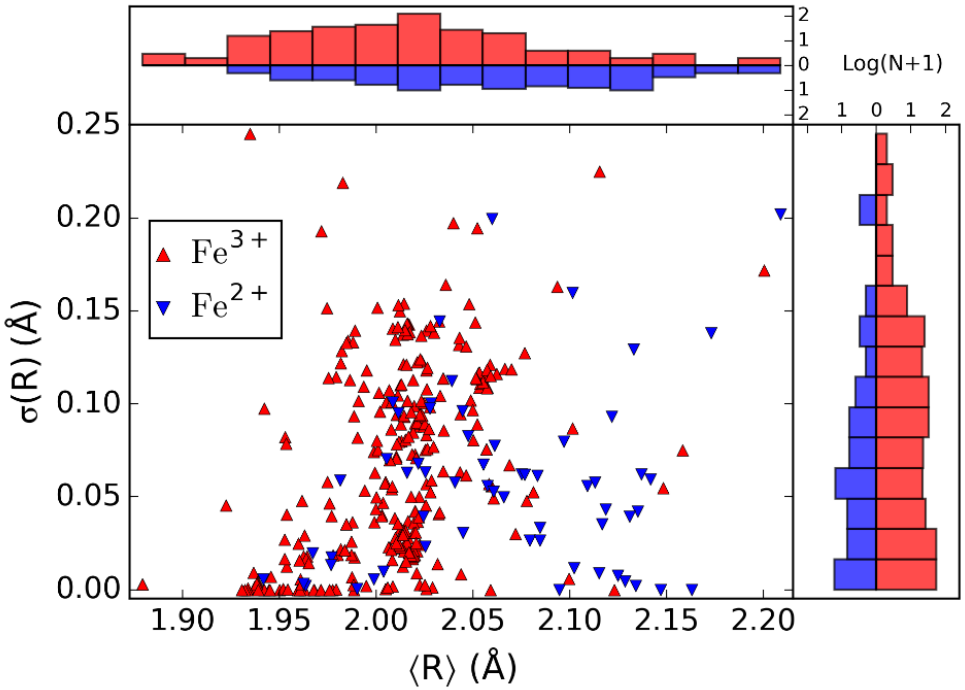


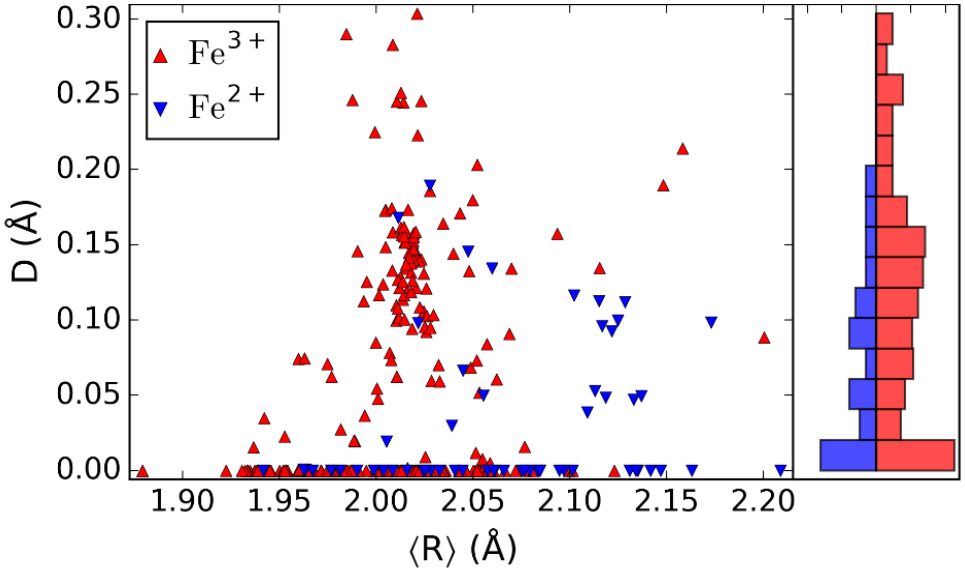
6-coordinate Fe-O

<R> : Fe-O bond lengths for Fe(II) and Fe(III)

D^{3+} peak at 0.15 Å

- "d^5 effect"





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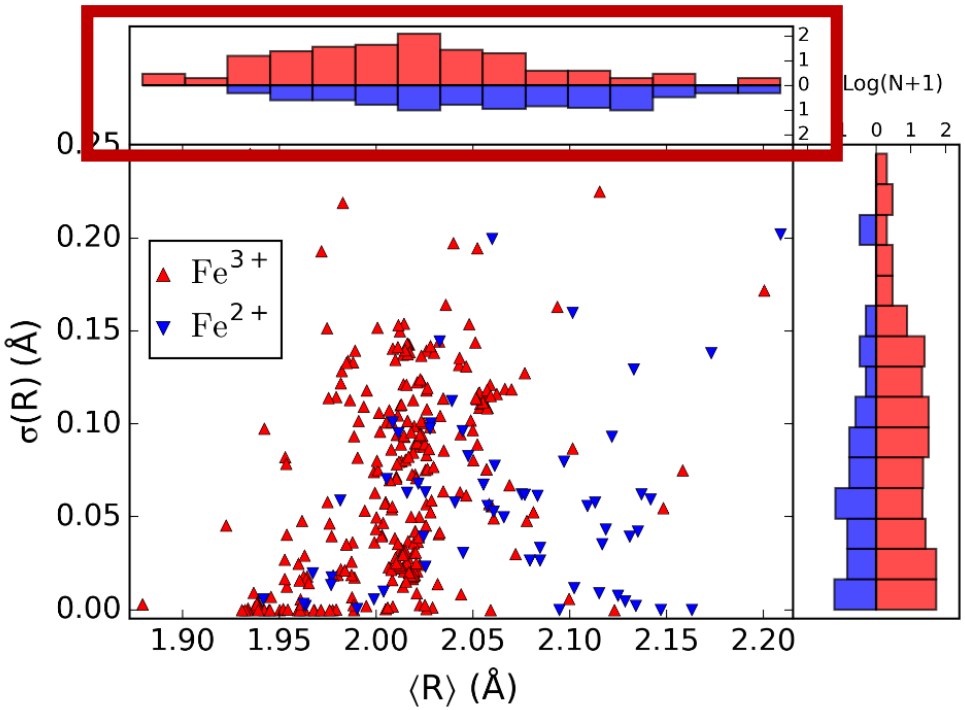

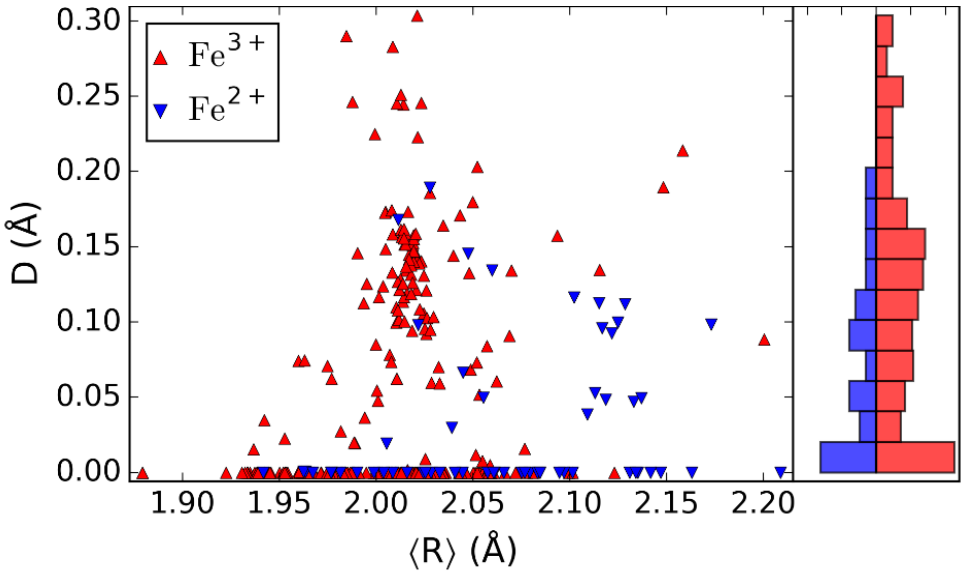

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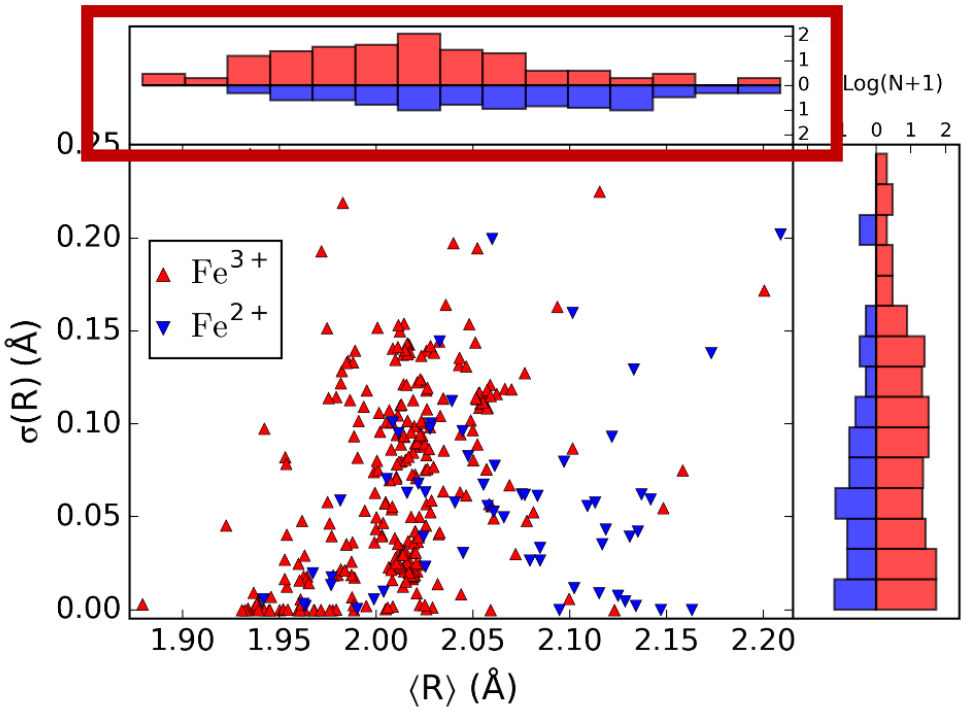
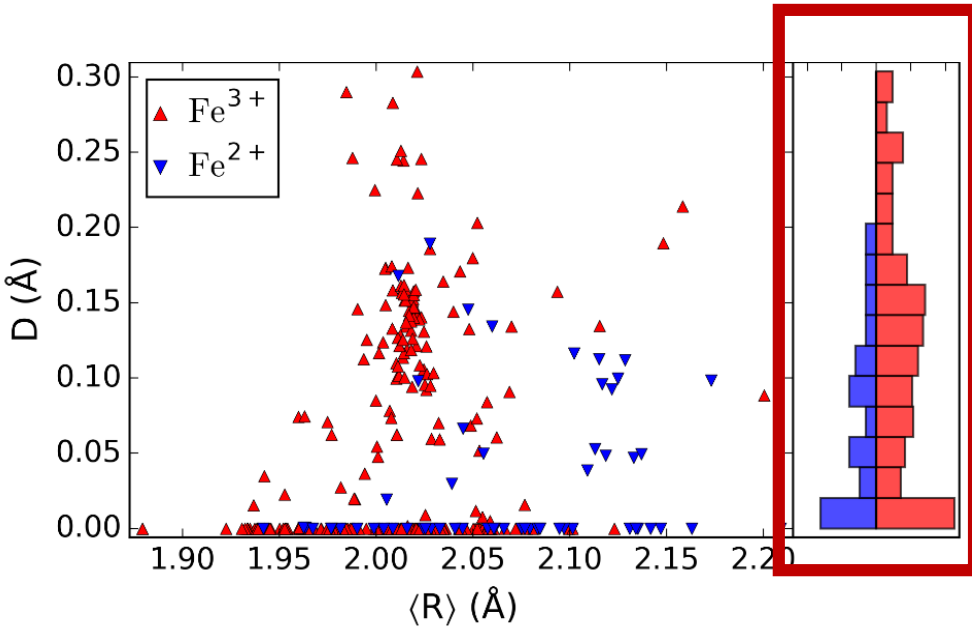
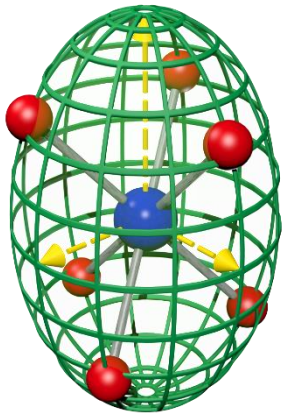
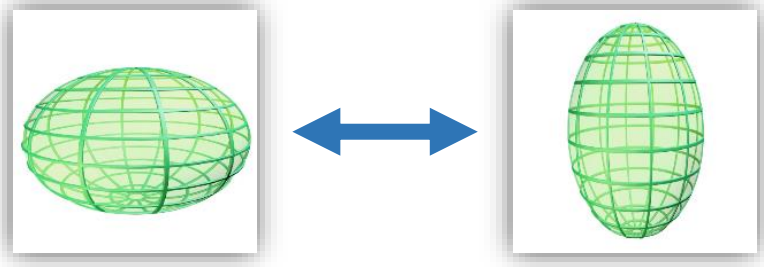




Conclusions



- Ellipsoids simplify polyhedral distortions
- Parameterise perovskite tilts
  - 'Switching' bistability
- 'd^5' effect for Fe^{3+}
  - Similar d^0 effect in *e.g.* $BaTiO_3$



- Future aim to apply ellipsoids as a machine learning descriptor

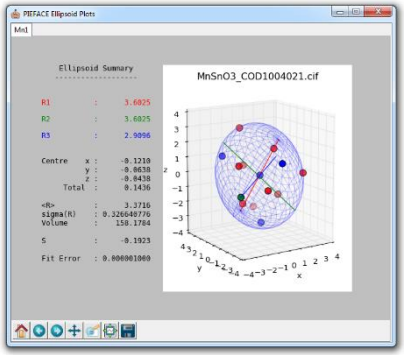
J. Cumby & J.P. Attfield, *Nature Communications*, 8, 14235, 2017.

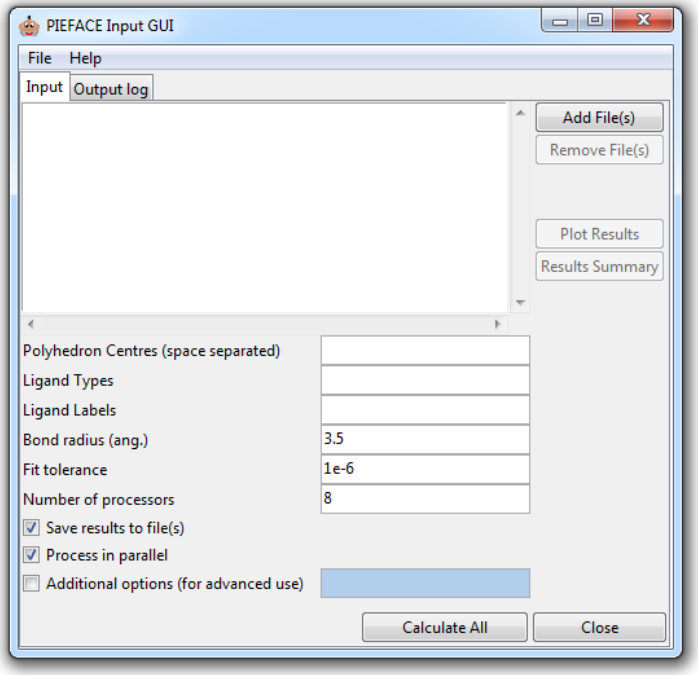
PIEFACE

Polyhedra-**I**nscribing **E**llipsoids **F**or **A**nalysing **C**oordination **E**nvironments

- Python
- Reads CIF files
- Available from GitHub and PyPI

  https://github.com/jcumby/PIEFACE





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