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Origin of octahedral tilting in the perovskites

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Introduction
Perovskite crystals present a large variety of properties
  Electrical: Conducting, insulators, superconductors
  Magnetic: Ferro, antiferro, diamagnetic
  Dielectric: Ferroelectricity, ...
Many properties are sensitive to external influence
  Temperature, pressure, strain, applied fields...
Changes associated to structural phase transitions!
The simple perovskite ABX$_3$ structure is cubic Pm3m

Three main types of distortion
  - Jahn-Teller effect in BX$_6$ octahedra  electronic
  - Ferroelectric distortions  electronic
  - Tilting of the BX$_6$ octahedra  steric

Is tilting unrelated to the Pseudo Jahn-Teller?

**Introduction**

Perovskite structure is formed of alternating \( AX \) and \( BX_2 \) planes.

Tilting is associated with the rotation of \( BX_6 \) octahedra.

Two triply degenerate modes associated to them.

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**Origin of octahedral tilting in the perovskites**
Steric models

Tiltings appear due to the misfit size of the A cation

How do the atoms fit inside the perfect cubic lattice if they are considered hard spheres?

\[ a = 2R(B) + 2R(X) \]

\[ a = \frac{2}{\sqrt{2}} R(A) + \frac{2}{\sqrt{2}} R(X) \]

Goldschmidt ratio

\[ \tau = \frac{1}{\sqrt{2}} \left( \frac{R(A) + R(X)}{R(B) + R(X)} \right) \]

- The origin of ferroelectricity is not steric
- Why does A not move off-center when small?
- Ionic radii are empiric parameters depending on:
  - Ion charge
  - Ion coordination
  - Magnetic state
  - Reasonable
  - Born-Mayer

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Steric models

The origin of ferroelectricity is not steric

The origin of octahedral tilting in the perovskites

Goldschmidt ratio

\[ \tau = \frac{1}{\sqrt{2}} \frac{R(A)+R(X)}{R(B)+R(X)} \]

- The origin of ferroelectricity is not steric
- Why does A not move off-center when small?
- Ionic radii are empiric parameters depending on:
  - Ion charge
  - Ion coordination
  - Magnetic state

\( \tau < 1 \) tilting
\( \tau \sim 1 \) cubic
\( \tau > 1 \) Ferroelectric (B site)

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Steric models

How does it perform?

\[ \tau = \frac{1}{\sqrt{2}} \frac{R(A)+R(X)}{R(B)+R(X)} \]

- \( \tau \approx 1 \) cubic
- \( \tau < 1 \) tilting

<table>
<thead>
<tr>
<th>0 tilt</th>
<th>1 tilt</th>
<th>3 tilt</th>
</tr>
</thead>
<tbody>
<tr>
<td>KMgF(_3)</td>
<td>1.032</td>
<td>KAgF(_3)</td>
</tr>
<tr>
<td>BaNbO(_3)</td>
<td>1.031</td>
<td>SrZrO(_3)</td>
</tr>
<tr>
<td>KZnF(_3)</td>
<td>1.021</td>
<td>CaTiO(_3)</td>
</tr>
<tr>
<td>KNiF(_3)</td>
<td>1.014</td>
<td>SrRuO(_3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CaMnO(_3)</td>
</tr>
</tbody>
</table>

It usually works well enough to predict tendencies

It has problems in a system-by-system basis

Reasonable due to the small energy scale (100-500K) typical of these phase transitions

More advanced theories (bond-valence, etc.) with same background are supposed to overcome some of these problems

How are tiltings connected to the crystal’s electronic properties?


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Magnetic properties

The magnetic phase is dependent on the tiltings

Consider: Superexchange interaction

Antiferromagnetic phases are common for no or low tiltings
Ferromagnetic phases are common for large rotations

\[
\begin{align*}
\text{no tilting} & \quad \text{strong } \sigma\text{-bonding!} \\
\text{large tilting} & \quad \text{weak } \sigma\text{-bonding!}
\end{align*}
\]

\[
\begin{align*}
\text{metal (3d)} & \quad \begin{cases} \uparrow & \uparrow \\
\text{ligand (2p)} & \quad \begin{cases} \downarrow & \downarrow \\
\end{cases}
\end{cases} \\
\text{antiferromagnetic} & \\
\text{metal (3d)} & \quad \begin{cases} \uparrow & \uparrow \\
\text{ligand (2p)} & \quad \begin{cases} \downarrow & \downarrow \\
\end{cases}
\end{cases} \\
\text{ferromagnetic}
\end{align*}
\]

d-orbital energy is sensitive to distortion and covalency

Strong similarity to Pseudo Jahn-Teller?

P. Jeffrey Hay et al., J. Am. Chem. Soc. 97, 4884 (1975)
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Local view of the distortion

Locally, tilting is similar to bending in a linear molecule

Bending in molecules is related to the presence of empty d(xy,xz,yz)-orbitals on the metal

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgF$_2$</td>
<td>linear</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>bent</td>
</tr>
<tr>
<td>SrF$_2$</td>
<td>bent</td>
</tr>
<tr>
<td>BaF$_2$</td>
<td>bent</td>
</tr>
</tbody>
</table>

Similarly KMgF$_3$ does not present tilting, KCaF$_3$ presents tilting

Is tilting associated to d(xy,xz,yz) orbitals?


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Method

We have studied the presence of tilting in the ionic series:

\[ \text{KMF}_3 \quad \text{M=Ca, Sc, \ldots, Zn} \]

where the population of d-orbitals increases along the row

What is the effect of population on \( t_{2g}(xy, xz, yz) \) and \( e_g(3z^2-r^2, x^2-y^2) \)?

low-spin \( t_{2g} \) and \( e_g \) high-spin

\[ \text{Origin of octahedral tilting in the perovskites} \]
Computational details

We have performed full geometry optimization of the cell following \(R_{3z}^+\) and \(M_{3z}^+\) modes

We have employed Hartree-Fock and Density-Functional-Theory
- LDA
- B3LYP (Hybrid Functional)

Exact-exchange is necessary to correctly simulate magnetic states

k-space sampling: 8x8x8

All electron localized gaussian basis set
- DZP quality

Tight convergence parameters

All calculations carried out with CRYSTAL06 package

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Results

With the previous method accurate results can be obtained

- Lattice parameters within 1% of experimental results
- Angles within 1º of experimental results
- Correct magnetic states for the lattice (AFM)

Is the population of the $t_{2g}$ orbital relevant to tilting?

High spin configuration $\rightarrow$ Larger rotation

less $t_{2g}$ electrons

low-spin high-spin

Energy cross-section

It is interesting to study the energy cross-section for different cases

Comparing Ni$^{2+}$ and Zn$^{2+}$ radii

\[ R(\text{Ni}^{2+}) > R(\text{Zn}^{2+}) \]

83pm > 74pm

We would expect KZnF$_3$ to be even more stable than KNiF$_3$

KZnF$_3$ is almost unstable!

KZnF$_3$ tends to tilting due to low-lying Zn 4s-orbitals → extra PJT contributions

Different crystals have different covalent bonding patterns and different tilting tendency

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Covalency

Let us visualize the rotation in a $BX_2$ plane
Covalency

Let us visualize the rotation in a $\text{BX}_2$ plane

Tilting breaks $\sigma$-bonding
The overlap variation is quadratic
Covalency

Let us visualize the rotation in a $\text{BX}_2$ plane.

Tilting allows new overlaps.

The effect is linear.

Tilting breaks $\sigma$-bonding.

The overlap variation is quadratic.

Tilting allows new overlaps.

The effect is linear.
Covalency
Pseudo Jahn-Teller is associated with new covalencies

Where is charge concentrating? Compare KMnF$_3$ cases

Density difference diagram with respect to spheric ions

- electron concentration
- electron defect

High-spin system shows increased $\pi$-covalency
**Covalency**

Steric interactions $\rightarrow$ lower electron-electron repulsion

PJT $\rightarrow$ new covalencies $\rightarrow$ higher electron-nuclei interaction

high-spin KMnF$_3$ vs low-spin KMnF$_3$

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**Total energy variation**

Energy (eV)

0 200

0 100

0 50

0 0

-50

-100

$\theta$ (degree)

0 2 4 6 8 10 12

**Variation difference (high-low)**

Energy (eV)

0 0.4

0 0.3

0 0.2

0 0.1

-0.1

-0.2

$\theta$ (degree)

0 2 4 6 8 10 12

---

V$_{en}$

V$_{nn}$

V$_{ee}$

---

Trends seem to agree with steric interpretation but:

It is impossible to distinguish high and low spin KMnF$_3$

Energy scale is much higher than that of the transition (55K)

High spin shows increased covalency with respect to low spin

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Are there no steric effects in the perovskites?
The force constant of a system can be written:

\[ K = K_0 + K_v = K_0 - \frac{F^2}{\Delta} \]

- elastic term
  - positive (against distortion)
- steric terms
  - smaller A ions may favor distortion but never produce it
- vibronic term
  - negative (favors distortion)
  - describes the change in electron density

PJT theorem (Bersuker, 1980)

NaMgF\(_3\) shows extra covalency vs KMgF\(_3\)

NaMgF\(_3\) shows extra covalency vs KMgF\(_3\)

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14/16
Oxides

Let us consider the spin-lattice coupling

In some systems the vibrational frequencies associated to different magnetic states are different

Calculation of the tilting frequencies for FM and AFM states:

<table>
<thead>
<tr>
<th></th>
<th>KMnF$_3$</th>
<th>SrMnO$_3$</th>
<th>CaMnO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>antiferromagnetic</td>
<td>22i</td>
<td>10</td>
<td>193i</td>
</tr>
<tr>
<td>ferromagnetic</td>
<td>39i</td>
<td>202i</td>
<td>250i</td>
</tr>
</tbody>
</table>

Steric models are clearly incorrect to describe this behavior

However, the effect is dependent on the fine details of the electronic structure and can only be explained by PJT

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Conclusions

• Tiltings have traditionally been attributed to steric effects, however, this approach contains many problems.
  • Cannot explain tiltings in a system-by-system basis
  • Leads to unphysical results in WO$_3$
  • Clearly unable to explain spin-lattice coupling

• The Pseudo Jahn-Teller model solves many of these inconsistencies
• Allows to establish bridges between electronic properties and structure
• When the B-ion is a transition metal the population of the $t_{2g}$ orbitals is of great importance in the rotation.


Thank you for your attention!
**Covalency**

From a local point the main effects of tilting on electronic structure can be depicted in an orbital diagram:

Does the change of electronic structure influence any property?

Unusual localization of electrons in $d^1$ transition metal containing perovskites

PJT increases gap which is associated to localization

---

Oxides

Let us study a special system: \( \text{WO}_3 \)

Its structure is that of a perovskite with its A ion removed

Minimum tolerance factor possible!

Large tiltings!

Does it make sense?

In steric models the energy is gained by getting the anions closer to the A cation

Attraction

Repulsion

However, in \( \text{WO}_3 \) rigid rotations only increase the energy that way!

The energy gain must come from covalency!
Oxides

Let us compare two typical oxides:

<table>
<thead>
<tr>
<th></th>
<th>$\tau$</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaTiO$_3$</td>
<td>0.97</td>
<td>Tilting</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>1.07</td>
<td>No tilting</td>
</tr>
<tr>
<td>KMgF$_3$</td>
<td>1.03</td>
<td>No tilting</td>
</tr>
</tbody>
</table>

BaTiO$_3$ does not rotate, as expected by large tolerance factor
What happens when we apply pressure? Is this general?

Some authors explain these effects by ion site compressibility using more empirical parameters!

The overlap due to distortion increases fast with pressure!

small PJT constant  
large PJT constant
Introduction

Perovskite structure is formed of alternating AX and BX₂ planes

A
B
X (F⁻, O²⁻)

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Two triply degenerate modes associated to them