Dual nature of improper ferroelectricity in a magnetoelectric multiferroic

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Introduction on Bulk Multiferroics

.....But: “d⁰-ness”: standard ferroelectrics show an empty d-shell ($\text{Ti}^{4+}$, $\text{Nb}^{5+}$) whereas magnetism requires partially filled d-shells .... 😞

... One needs new mechanisms....

“Multiferroic”

Our approach:
looking at “improper ferroelectricity” in magnets
(i.e. where polarization appears as a consequence or concomitantly with some other kind of orderings)
How can we induce ferroelectricity in magnets?

For ferroelectricity, we need to break inversion symmetry.

How to do that in magnets via electronic degrees of freedom?

1. **Spin** degree of freedom:
   - Spirals (see talk by M. Mostovoy)
   - Some kinds of anti-ferromagnetism (see for example AFM-E)
How can we induce ferroelectricity in magnets?

For ferroelectricity, we need to break inversion symmetry.

How to do that in magnets via the electronic degrees of freedom?

1. Spin degree of freedom:
2. Charge degree of freedom:

- LuFe$_2$O$_4$

  *N. Ikeda et al., Nature 436, 1136 (2005)*
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For ferroelectricity, we need to break inversion symmetry.

How to do that in magnets via the electronic degrees of freedom?

1. **Spin** degree of freedom:
2. **Charge** degree of freedom:

- **LuFe$_2$O$_4$$**

- Intermediate bond- and site-centered ordering in **PrCaMnO$_3$$**
How can we induce ferroelectricity in magnets?

For ferroelectricity, we need to break inversion symmetry. How to do that in magnets via the electronic degrees of freedom?

1. **Spin** degree of freedom:
2. **Charge** degree of freedom:
3. **Orbital** degree of freedom:

Bilayer manganite $\text{Pr(Sr}_{0.1}\text{Ca}_{0.9})_2\text{Mn}_2\text{O}_7$

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1. Spin degree of freedom:
2. Charge degree of freedom:
3. Orbital degree of freedom:

So far:
Is antiferromagnetism enough to induce ferroelectricity and how big?
Let’s look at AFM-E HoMnO$_3$
Starting point: the AFM-E spin configuration

1. Distorted ortho-manganites: Jahn-Teller and GdFeO$_3$-like tilting
2. $Pnma$ space group
3. Double along $a$ and form zig-zag FM spin chains AFM coupled with respect to neighboring chains

When does the AFM-E occur?

- Transition from AFM-A to AFM-E with octahedral GdFeO$_3$-like distortions$^1$
- AFM-E: expts in HoMnO$_3$ + model-hamiltonian-studies$^2$

### Magnetic Ordering

**AFM-E as ground state in distorted RMnO$_3$**

Table: energy difference (in meV/Mn) with respect to FM

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In-plane spin ordering for AFM-E and AFM-E* (with AFM and FM interplanar stacking, resp.)

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Outline/Questions on Ferroelectricity AND Magnetism

AFM-E ortho-HoMnO$_3$: is this a novel multiferroic?
First-principles density-functional calculations

- Electric polarization from “displacement” mechanism: is it effective?

- Ferroelectric switching path: how can we achieve it?

- Which is the mechanism for polarization induced by AFM-E magnetic ordering?

- Conclusions
Computational details

- VASP\textsuperscript{1} simulations with Projector Augmented Wave pseudopotentials
- Generalized Gradient Approx. (PBE exch.-corr.)
- Ho pseudopotential: 4f not-pseudized
- Monkhorst-Pack shell: [3,4,6]
- Hubbard potential\textsuperscript{2} on Mn d: GGA +U (for various U and J = 0.15*U)
- Berry phase approach to polarization\textsuperscript{3}
- Non-collinear magnetism\textsuperscript{4}
- Spin-orbit neglected


Structural details

- Experimental lattice constants for paramagnetic HoMnO\textsubscript{3}
- Extremely high GdFeO\textsubscript{3}-like distortions
- Internal atomic positions fully relaxed (forces < 0.01 meV/Å)
Polarization from “Displacement” mechanism *

Simple model:
- start from centro-symmetric atomic positions
- only O atoms can move and they are forced in the MnO$_2$ planes

In total: O center of mass move “right”: Polarization directed along c axis

Polarization from “Displacement” mechanism

Simple model:
- start from centro-symmetric atomic positions
- only O atoms can move and they are forced in the MnO$_2$ planes

... But.... actually the displacement pattern is not so simple (also Mns move), but the polarization is indeed directed along c
Does the Mn-O-Mn angle depend on Mn-Mn spin configuration?

In-plane FM (AFM) interactions ↔ Larger (Smaller) angles

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$ ($^\circ$)</th>
<th>$d_l$ (Å)</th>
<th>$d_s$ (Å)</th>
</tr>
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<tbody>
<tr>
<td>FM</td>
<td>143.9</td>
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<td>AFM-G</td>
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“long” Mn-O bond = $d_l$
“short” Mn-O bond = $d_s$
NB: Zig-zag chains and symmetry reduction:

- 2 different Mn-O-Mn angles (FM and AFM)
- 2 different Mn-O “long” bond lengths
- 2 different Mn-O “short” bond lengths

<table>
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<tr>
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<th>$\alpha^p$</th>
<th>$\alpha^{ap}$</th>
<th>$d^l_1$</th>
<th>$d^l_2$</th>
<th>$d^s_1$</th>
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<td>145.3</td>
<td>141.9</td>
<td>2.25</td>
<td>2.18</td>
<td>1.92</td>
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Very different Mn-O-Mn $\alpha$ and Mn-O $d_l$: displacement mechanism active!
Ferroelectric switching

Sergienko et al.¹:
- Model calculations using Landau theory
- two E-phase domains differing for orientation of half of the Mn spins and giving opposite P


How to go from $E_1$ to $E_2$?

- Via progressive rotation of “central” spins
- Non collinear VASP calculations constraining the direction of local moments
Structural changes along the switching path
Ferroelectric switching

Depth of the well
\~ 8 meV/f.u.

(cfr 18 meV/f.u. in BaTiO₃)
Insulating character along the switching path

Band structure along the main symmetry lines for relaxed AFM-E1

NB: the DOS look pretty much unaltered along the path: no drastic charge rearrangement…
What about polarization?

Electrical control of AFM domains

P much higher than other multiferroic manganites (in TbMnO$_3$ P~0.1 $\mu$C/cm$^2$)

$P_{\text{PCM}}$ not reliable! Need for fully quantum approach: electronic effects at play!
What about polarization?

Take centro-symmetric positions from $\perp$ and switch the AFM-E1 or AFM-E2 spin-configurations: $P \sim 3 \, \mu\text{C/cm}^2$ (with opposite sign):

Magnetism breaks the symmetry and gives $P$ !!!
Model study:
Landau theory of phase transitions

\[ P_c = \chi_z (c_{xz} \sin \phi - c_0 \cos \phi) \]
\[ P_a = c'_{xz} \chi_x \sin \phi \]
\[ P_b = 0 \]

\[ \chi_z (\chi_x) = z (x) \text{ component of dielectric susceptibility} \]
\[ \phi = \text{rotation angle of the central spins} \]

NB: \( c_{xz} \) and \( c'_{xz} \) originate from coupling of \( P \) to the product of the \( a \) and \( c \) components of the magnetic moments (relativistic origin)

No SOC => Only \( c \) component of \( P \) left:
\[ P_c = - \chi_z c_0 \cos \phi \]

Excellent agreement!
Symmetry-breaking induced by magnetic ordering

- “Centro-symmetric positions” with AFM-E₁ ordering
- Plot charge density for Mn $e_g$ + O $p$ orbitals

- O atom bonded to AFM Mn is different from O bonded to two FM spins
- More charge on the “short” compared to the “long” bond:
  relevance of magnetic ordering, Jahn-Teller and GdFeO₃ tilting
In-plane Mn and O Born effective charges

\[ Z^*_{\kappa,\alpha\beta} = \Omega \frac{(\Delta P)_\alpha}{|e|u_{\kappa,\beta}} \]

- \((\Delta P)_\alpha\) = change of polarization along direction \(\alpha\)
- \(u_{\kappa,\beta}\) = displacement of atom \(\kappa\) in direction \(\beta\)
- \(\Omega\) = unit cell volume
- NB: calc. only the \((3,3)\) comp. of the \(Z^*\) tensor

\[
\begin{array}{|c|c|c|c|}
\hline
 & Mn & O^{ap} & Op \\
\hline
"\perp" & 3.9 e & -3.1 e & -3.1 e \\
AFM-E & 3.8 e & -2.6 e & -3.5 e \\
\hline
\end{array}
\]

- \(Z^*\) values not so "anomalous" : rather "ionic" picture
- Polarization in centrosymmetric structure comes from inequivalency of the oxygens
How about correlations? “GGA+U”

- Difference between Mn-O-Mn angles for FM and AFM Mn decreases with U
- The two “short” Mn-O bond lengths are very similar
- The two “large” Mn-O bond lengths become closer with U

Smaller distortions!
What about P vs U?

- P follows the displacement trend and decreases with U. It makes sense: 
  \( U = \text{energy penalty paid for adding an extra-}e \text{ on Mn} \) 
  If U increases, hopping is less favourable, therefore \( \alpha_p - \alpha_{ap} \) (and eventually P) decreases

- However, P > 0.5 \( \mu \text{C/cm}^2 \) in the whole U range
Polarization from integrating pyroelectric current on HoMnO$_3$ poly-cristalline samples (single crystals not available)

- P small (although it is a lower bound…)
- P increases at ordering temperature of Ho spins!

1. Expt: Make better samples ??? Deposit thin films ???
2. Theory: Make better simulations ??? Ho 4f spins ???

* B. Lorenz, YQ. Wang and C.W.Chu, cond-mat/0608195
Summary

AFM-E ortho-HoMnO$_3$: is this a novel multiferroic?
First-principles density-functional calculations

- **Electric polarization from “displacement” mechanism**
  
  Largest $P$ predicted so far for an “improper magnetic ferroelectric” (IMF)

- **Ferroelectric switching path**
  
  Via spin-rotations: Electrical control of AFM domains

- **Polarization induced by AFM-E magnetic ordering**
  
  1. **Dual nature of $P$**: both of “ionic” and “electronic/magnetic” origin. This solves controversy in model Hamiltonian studies + we believe it is rather general in the class of IMF
  
  2. It is possible to achieve “large” $P$ (i.e. few $\mu$C/cm$^2$) with centrosymmetric positions

# S.Picozzi, K.Yamauchi, B.Sanyal, I.A.Sergienko and E.Dagotto, arXiv/0704.3578
• Both in-plane and out-of-plane Mn-O-Mn angles decrease with the R ionic radius (IR): agreement with expts.
Work in progress: what happens for other rare-earth manganites?

• Both in-plane and out-of-plane Mn-O-Mn angles decrease with the R ionic radius: agreement with expts.
• Broad maximum of I (and s) around Gd-Tb
Work in progress: what happens for other rare-earth manganites?

- In-plane 1st nearest neighbour $J_{||}^{(1)}$ decreases with IR: "less FM"
Work in progress: what happens for other rare-earth manganites?

- In-plane 1\textsuperscript{st} nearest neighbour $J_{||}(1)$ decreases with IR: “less FM”
- In-plane 2\textsuperscript{nd} nearest neighbour $J_{||}(2)$ (AFM) becomes important

![Graph showing exchange constants vs IR](graph.png)

**Exchange constants vs IR**
Work in progress: what happens for other rare-earth manganites?

- In-plane 1\textsuperscript{st} nearest neighbour $J_{\parallel}^{(1)}$ decreases with IR: “less FM”
- In-plane 2\textsuperscript{nd} nearest neighbour $J_{\parallel}^{(2)}$ (AFM) becomes important
- Out-of-plane 1\textsuperscript{st} nearest neighbour $J_{\perp}^{(1)}$ (AFM) increases for large IR but then stays almost constant
Work in progress: what happens for other rare-earth manganites?

Region I: predominance of $J_{\parallel}^{(1)} \implies$ AFM-A

Region II: Spin frustration and non-coll.

Region III: both $J_{\parallel}^{(1)}$ and $J_{\parallel}^{(2)} \implies$ AFM-E is solution
Work in progress: what happens for other rare-earth manganites?

Ferroelectric Polarization (forcing the AFM-E spin configuration)

- P goes up to 12 μC/cm², but on the “wrong” side (AFM-E is stable for small Mn-O-Mn angles)!
- Very large electronic effects in LaMnO₃: orbital ordering involved? Hopping terms?
How can we induce ferroelectricity in magnets?

For ferroelectricity, we need to break inversion symmetry. How to do that in magnets via the electronic degrees of freedom?

1. Spin degree of freedom
2. Charge degree of freedom
3. Orbital degree of freedom

Any good candidates?

Take-home message:

“Dual nature” of P in real compounds:
- displacements of ions
- electronic/magnetic effects can both sizably contribute to P
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“Dual nature” of $P$ in real compounds:
- displacements of ions
- and
- electronic/magnetic effects can both contribute to $P$

Any good candidates?

Thanks for your attention!
### Magnetic ordering: Auxiliary “artificial” structures

#### Change Tb 4f core polarizat.: 4↑, 4↓

#### Table: energy difference (in meV/Mn) with respect to FM

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**Legenda:**
- • = Ground state
- (7↑,1↓): Tb 4f frozen “open core” (7 up, 1 down)