Crystal Structure Determination and physical properties of Molecule-Based Multiferroic Materials

Lidia mazzuca

All you need is neutron – season 2
General Introduction
• Multiferroics and MOFs

Previous work: $[\text{NH}_2(\text{CH}_3)_2]_n[\text{Fe}^\text{III} \text{Fe}^\text{II}(\text{HCOO})_6]_n$
• Nuclear and Magnetic structure

$[\text{NH}_2(\text{CH}_3)_2]_n[\text{Fe}^\text{III} \text{Co}^\text{II}(\text{HCOO})_6]_n$ and $[\text{NH}_2(\text{CH}_3)_2]_n[\text{Fe}^\text{III} \text{Mn}^\text{II}(\text{HCOO})_6]_n$
• X-ray and Neutron Multipattern
• Nuclear and Magnetic structure (neutron experiments)

Conclusion
What are Multiferroic materials?

Multiferroics: Compounds with more than one ferroic order in a single phase

Electric Order + Magnetic Order = Multiferroic material
Ferroelectricity and ferromagnetism have different sources and are independent.

- Weak coupling
- Different transition temperature
- High polarization (for ferroelectrics)

Multiferroics

**TYPE I**

- Ferroelectricity and ferromagnetism have different sources and are independent
- Weak coupling
- Different transition temperature
- High polarization (for ferroelectrics)

**TYPE II**

- Ferroelectricity and ferromagnetism strongly coupled
- Electric order at ‘low’ temperatures
- Low polarization (for ferroelectrics)
- Magnetic order causes ferroelectricity; magnetic (electric) moment can be changed by electric (magnetic) field
Applications

New multifunctional materials

- Ultra-sensitive solid state magnetic sensors
- Computer memory
- Storage and magnetic read/write
- .......
Multiferroic Metal Organic Framework

Classical Magnets

High Density
Close
Packed
Opaque

Molecular Magnets

Metal center

Co-ligand/cation

Low Density
Transparent
Cristalline

Organic ligand
Magnetic structures

Magnetic structures defined by:

- Propagation vector(s)
- Moment magnitude(s)
- Moment direction(s)

Nuclear Interaction: Interaction between the neutrons and the nuclei of the ions

Magnetic Interaction: Interaction between the magnetic moment of the neutron with the spin and orbital magnetic moments of the unpaired electrons in the solid
Case study

Crystal and Magnetic Structural Neutron investigation

in mixed valence:

\[ [\text{NH}_2(\text{CH}_3)_2]_n[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{HCOO})_6]_n \text{ framework} \]
$[\text{NH}_2(\text{CH}_3)_2]_n[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{HCOO})_6]_n$

Multiferroic MOF system

Crystal network: magnetic properties

Formate ligand

$P - 31c$

$a$ (Å) = 8.2550(12)

$b$ (Å) = 8.2550(12)

$c$ (Å) = 13.891(3)

Guest-molecule: electric properties, disordered at HT

Dimethylammonium counterion

L. Cañadillas-Delgado et al. JACS (2012)
Heat capacity as function of temperature

The insets show the detail of the \( \lambda \)-shaped peaks due to:

- paraelectric to antiferroelectric phase transition at 155 K
- paramagnetic to ferrimagnetic transition at 37 K
- a signal observed at 4.8 K of magnetic origin
$[\text{NH}_2(\text{CH}_3)_2]_n[\text{Fe}^{III}\text{Fe}^{II}(\text{HCOO})_6]_n$

$P\text{-}31c$

$\alpha (\text{Å}) = 8.2550(12)$

$\beta (\text{Å}) = 8.2550(12)$

$\gamma (\text{Å}) = 13.891(3)$

$\text{Room Temperature}$

---

$R\text{-}3c$

$\alpha (\text{Å}) = 14.2600(17)$

$\beta (\text{Å}) = 14.2600(17)$

$\gamma (\text{Å}) = 41.443(8)$

$\text{Low Temperature}$

$\approx 155 \text{K}$

Phase transition
\[ \text{[NH}_2\text{(CH}_3\text{)}_2\text{]}_n\text{[Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{(HCOO)}_6\text{]}_n \]

Structural phase transition

Dielectric measurement

155 K

Paraelectric

Antiferroelectric

\[ \varepsilon_3 \]

T / K

50 75 100 125 150 175 200

60 62 64 66 68 70

AFE

PE

Dielectric measurement

Structural phase transition
Magnetic measurement

D1B diffractometer

Increase of Bragg reflection (100)

Indexed with $K=(0,0,0)$

Magnetic phase transition 37 K
$[\text{NH}_2(\text{CH}_3)_2]_n[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{HCOO})_6]_n$

**Ferrimagnetic**

**Fe(II):** Component along $c$ axis + component in $ab$ plane

**Fe(III):** Strictly along $c$ axis
Case study

X-ray and Neutron Magnetic Structural investigation in mixed valence:

\[ [\text{NH}_2(\text{CH}_3)_2]_n[\text{Fe}^{\text{III}}\text{Co}^{\text{II}}(\text{HCOO})_6]_n \]

and

\[ [\text{NH}_2(\text{CH}_3)_2]_n[\text{Fe}^{\text{III}}\text{Mn}^{\text{II}}(\text{HCOO})_6]_n \]

Frameworks
Phases of our work in few steps

Replacing the divalent Fe$^{II}$ ions for Co$^{II}$ or Mn$^{II}$

Single crystal X-ray diffraction

Squid Magnetometry

Structure refinement at 45K combining X-ray and High resolution neutron diffraction using a Multipattern approach

Magnetic structures determined by difference patterns between paramagnetic and magnetically-ordered regions
X-Ray experiment at the Soleil Synchrotron facility

Data were indexed, integrated using Crysallis Pro software

The structures were solved by direct method using SHELXS

Final R indices \([I > 2\sigma(I)]\): \(R_1/wR_2 = 0.0291/0.0998\)

\[\lambda = 0.66951 \, \text{Å}\]

Co\(^{II}\)/Mn\(^{II}\)-Fe\(^{III}\)

\[a (\text{Å}) = 8.237123\]

\[b (\text{Å}) = 8.237123\]

\[c (\text{Å}) = 13.715707\]

\[T = 45 \text{K}\]
NEUTRON experiment D2B High resolution

\[ \lambda = 1.59465 \text{Å} \]

Multipattern approach using **FullProf**

Hydrogen atoms determined

\[ P - 31c \quad T = 45K \]
NO STRUCTUTRAL PHASE TRANSITION for Co(II)Fe(III) and Mn(II)Fe(III)

WHY ???

- Ordering for Fe(II) compound
- Reorientation Mn(II)/Co(II) compounds

\[
P - 31c
\]
\[
a (\text{Å}) = 8.237123
\]
\[
b (\text{Å}) = 8.237123
\]
\[
c (\text{Å}) = 13.715707
\]
Magnetometer measurements of isostructural

\[ [\text{NH}_2(\text{CH}_3)_2]_n[\text{Fe}^{\text{III}}\text{M}^{\text{II}}(\text{HCOO})_6]_n \]
NEUTRON experiment D1B High Flux

Propagation vector $\mathbf{K} = (0,0,0)$

$\lambda = 2.521 \text{ Å}$

Fe$^{II}$ Fe$^{III}$

Mn$^{II}$Fe$^{III}$

Co$^{II}$Fe$^{III}$
How to determine the MAGNETIC model?

Multipattern approach for well defined structural model - (FP)

Determine K-propagation vector - (K-Search)

Performs symmetry analysis - Baslreps (Fullprof)

Introduce and refine by LSQ the magnetic phase (FP)

and Structure solution by Sann (FP)

**INPUT**

• Peak positions of Magnetic reflections
• Cell parameters
• k vector
• Atomic positions
• Space group
• Irreducible representations
• Extracted integrated intensities
Representational analysis

BasIreps (Fullprof) → 6 possible Irreps $\Gamma_1$- $\Gamma_6$ → Possible arrangement of magnetic structure

$\Gamma_1$ to $\Gamma_4$ are real and one dimensional

$\Gamma_5$ and $\Gamma_6$ have an imaginary part and are two dimensional

BUT

Propagation vector $\mathbf{K} = (0,0,0)$ consequently the Fourier coefficients must be real

$\Gamma_1$ to $\Gamma_4$ are possible solutions

$\rho_{\Gamma 3}$
Position of atom $j$ in unit-cell $l$ is given by:

$$ R_{lj} = R_l + r_j $$

where $R_l$ is a pure lattice translation

$$ R_{lj} = R_l + r_j = l_1 a + l_2 b + l_3 c + x_j a + y_j b + z_j c $$
The magnetic moment “\( \mathbf{m}_{lj} \)” associated with the atom “\( j \)” at the unit cell with origin in \( R_l \), is determined by the Fourier series:

\[
\mathbf{m}_{lj} = \sum_{k} S_{kj} \exp\left\{-2\pi i k R_l\right\}
\]

Where \( S_{kj} \) are the Fourier components (linear combination of Basis vectors of irreps) with propagation vector \( k \) corresponding to the atom \( j \) in the zero\(^{th} \) unit cell.

For getting \( \mathbf{m}_{lj} \) as real vectors \( S_{kj}^* = S_{kj} \) should be satisfied
$[\text{NH}_2(\text{CH}_3)_2]_n[\text{Fe}^{\text{III}}\text{Co}^{\text{II}}(\text{HCOO})_6]_n$

Global AF coupling in $ab$-plane

The Co(II) magnetic moments produce a ferrimagnetic behaviour along $c$-axis
Global AF coupling in $ab$-plane

The Mn(II) magnetic moments produce a small ferromagnetic component along c-axis due to spin canting
Conclusion

From $[\text{NH}_2(\text{CH}_3)_2]_n[\text{Fe}^{\text{III}}\text{M}^{\text{II}}(\text{HCOO})_6]_n$ (where $\text{M}=$ Co(II) or Mn(II)) isostructural compounds

1. Crystal structures have been refined combining High resolution neutron diffraction with synchrotron X-ray diffraction at 45K using a multipattern approach

2. Dimethylammonium hydrogen atoms have been localized

3. We did not observe any occurrence of phase structural transition = No electric order = no multiferroic

4. Using neutron diffraction we observed that:
   i. The magnetic structure of Co(II) consist in a non compensated AFM arrangement where the magnetic moments are contained in $ab$ plane so similar to Fe(II) compound
   ii. Moreover for Mn(II) compound is almost AFM in $ab$ plane with a small spin canting together with a no compensation along $c$-axis which produce ferromagnetic order
OUTLOOK

• To investigate multiferroic materials from the same family of $[\text{NH}_2(\text{CH})_3]_n[\text{Fe}^{III}\text{M}^{II}(\text{HCOO})_6]_n$ compounds, with different metal ions and/or different co-ligands.

• In order to understand the magnetic structure observed and the role of dimethylammonium in the cavity we submitted a proposal for neutron diffraction experiments under pressure conditions.

• We are collaborating with the group of Dr. Silvia Picozzi from CNR–SPIN (Italy) in order to obtain Ab initio DFT calculation to rationalize the described magnetic structures.
THANK YOU FOR YOUR ATTENTION!
Acknowledgements and References

• Oscar Fabelo
• Alberto Rodríguez-Velamazán
• Juan Rodríguez-Carvajal