Magnetic field – temperature phase diagram of multiferroic \((\text{NH}_4)_2\text{FeCl}_5\cdot\text{H}_2\text{O}\)

A. J. Clune, K. D. Hughey, A. L. Blockmon, **J. L. Musfeldt** (UT); J. Nam, M. Lee, J. H. Lee (UNIST); W. Tian, R. S. Fishman (ORNL); J. Fernandez-Baca (ORNL & UT); J. Singleton, M. Lee, V Zapf (LANL)

Objectives:

- explore molecule-based multiferroic \((\text{NH}_4)_2\text{FeCl}_5\cdot\text{H}_2\text{O}\) in high magnetic fields
- reveal complex \(B-T\) phase diagram
- enable new types of property investigations

image of a single crystal
Multifunctional material vs. multiferroics?

Multifunctional: must combine >1 interesting functionalities

Multiferroics: must have >1 primary ferroic order parameter

What are they?

- ferroelectricity
- ferroelasticity
- ferromagnetism
- ferrotoroidicity

Extending this definition to include non-primary order parameters…

- ferrimagnetism
- antiferromagnetism

Appear in different forms…

- single phase
- heterostructures
- composites
- nanoparticles

Cross-coupling gives rise to rich phase diagrams!

Schmidt (1996); Spaldin + Fiebig, Science (2005)
why molecule-based multiferroics?

- molecule-based multiferroics
  - low energy scales
  - flexible architecture
  - chemical substitution
  - experimentally accessible fields!

- field-induced transitions to fully-saturated state under-explored
- how to fix this?
  - develop phase diagrams!
  - reveal properties

A. Clune, et al., PRB (2017)

\[
[(\text{CH}_3)_2\text{NH}_2]\text{Mn(HCOO)}_3
\]
Erythrosiderite \((\text{NH}_4)_2\text{FeCl}_5\cdot\text{H}_2\text{O}\)

- space group: \textit{Pnma}
- \(\text{Fe}^{+3} = \frac{5}{2}\)
- \(T_{\text{O/D}} = 79 \text{ K}\)
- \(T_N = 7.25 \text{ K}\)
- \(T_{\text{FE}} = 6.9 \text{ K}\)
- \textit{multiferroic}!
- mechanism is curious

image of a single crystal
oh, the places you will go!

exotic properties emerge when phases compete!
Erythrosiderite $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$

but what about the high field behavior?
Competition between exchange pathways

\[ J_1 = -2.51 \text{ K} \]

\[ J_2 = -1.55 \text{ K} \]

\[ J_3 = -0.27 \text{ K} \]

\[ J_4 = -1.25 \text{ K} \]

\[ J_5 = -0.71 \text{ K} \]

Distance between Fe•••Fe (Å)

Frustration!
Driving to the fully saturated state

- two sets of transitions
  - $B_{\text{low field}} < 6$ T
  - $B_{\text{Sat}} \approx 30$ T
- shape consistent with 3D materials
Derivatives to reveal magnetic transitions

Hydrogenated, Deuterated

Magnetic Field (T)

Magnetic field \( \frac{\partial M}{\partial B} \)

Distance between Fe...Fe (Å)

Series of P and M flops

Series of magnetic transitions \( B_{Sat} \)
Developing the phase diagram
(hydrogenated $B \parallel c$)

$(\text{NH}_4)_2\text{FeCl}_5\cdot\text{H}_2\text{O}$… the full view

electric polarization across the magnetic quantum phase transition?

Pulsed fields = very low noise!

Pulse up to 65 T
electric polarization across the magnetic quantum phase transition

consequences of Type II multiferroic:

ferroelectricity derives from magnetic order
spin-lattice interactions in multiferroics

\[(\text{CH}_3)_2\text{NH}_2\text{Mn(HCOO)}_3\]

\[(\text{NH}_4)_2\text{FeCl}_5\cdot\text{H}_2\text{O}\]

phonon mode links ferroicities!

\[J_{\text{AFM}} \sim \frac{t^2}{U}\]

Spin-phonon coupling in Ruby?

Absorption ($10^3$ cm$^{-1}$)

- $\Delta\alpha = \alpha(35 \text{ T}) - \alpha(0 \text{ T})$
- $H = 35 \text{ T}$
- $H = 0 \text{ T}$

NH$_4$ and H$_2$O librations

NH$_4$ and H$_2$O librations

Fe-Cl stretch

NH$_4$ breathing

NH$_4$ twist

Fe-O stretch

Fe-OH$_2$ rocking

(b)

NH$_4$ libration

NH$_4$ breathing

Fe-O stretch

Fe-OH$_2$ rocking

(c)

$M(H) M_{\text{sat}} |\Delta\alpha(0 \text{ T})|$

$[M(H)]^2$

$H_c = 30 \text{ T}$
Table 1: Summary of the coupling processes in $(\text{NH}_4)_2[\text{FeCl}_5\cdot(\text{H}_2\text{O})]$ along with the overall size of each effect and mechanisms. Here, $\alpha$ and $\lambda$ are the magnetoelastic and spin-phonon coupling constants, respectively.

<table>
<thead>
<tr>
<th>Type of coupling</th>
<th>Overall size</th>
<th>Coupling mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic field-induced electric polarization change</td>
<td>$8.83 \ \mu\text{C/cm}^2$ (1.5 K, 4 T, $P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\alpha = 0.025 \ \text{nC/cm}^2\cdot\text{T}$ (0 - 5 T)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$11.1 \ \mu\text{C/cm}^2$ (1.5 K, 26 T, $P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\alpha = 0.048 \ \text{nC/cm}^2\cdot\text{T}$ (5 - 26 T)</td>
<td></td>
</tr>
<tr>
<td>Spin-lattice interaction</td>
<td>$\lambda = 0.30$ for Fe-O stretch</td>
<td>Spin-phonon coupling $\omega = \omega_0 + \lambda \langle S_i \cdot S_j \rangle$</td>
</tr>
<tr>
<td></td>
<td>$\lambda = 0.34$ for Fe-OH$_2$ rocking</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\lambda = 0.04$ NH$_4$ for twist</td>
<td></td>
</tr>
</tbody>
</table>
What we learned…

- able to drive molecular multiferroics into the fully saturated state at realizable fields
- generated a rich + complex $B$-$T$ phase diagram
- opens door to exploring high field properties

We thank NSF and NHMFL for support of this work!