Quantum phenomena in $S_{\text{eff}} = 1/2$ pyrochlores revealed by neutron scattering

Kate A. Ross
Colorado State University

NCNR Neutron Scattering Summer School
NIST, June 22, 2017
Outline

- Geometric Frustration
- General anisotropic exchange phase diagram for pyrochlores
- Phase competition in real pyrochlores: quantitative understanding using neutrons
  - Yb$_2$Ti$_2$O$_7$, Er$_2$Ti$_2$O$_7$, and NaCaCo$_2$F$_7$
Overchoice

• Wikipedia: “Overchoice or choice overload is a cognitive process in which people have a difficult time making a decision when faced with many options.”
Overchoice = Frustration

- *Frustration* from overchoice leads to interesting excited states.
Geometric Frustration in 2D magnets

prefer ↑↓ alignment, but choice of 3rd spin direction is unclear
freedom of choice for each tetrahedron leads to a macroscopic degeneracy: **NO Long Range Order**
Local Anisotropy on the Pyrochlore Lattice

Types of Anisotropy

- Ising
- XY
- Heisenberg

- Crystal symmetry requires local axes for each sublattice
- “z” (Ising) is along local <111> (“In-to” or “out-of” tetrahedron)

Some anisotropic AFM configurations

- Ising
- XY
- Heisenberg
Example: Ising Ferromagnetic Pyrochlore

Classical Spin Ice

Ferromagnetic Ising exchange

\[
H = J_{zz} \sum_{\langle ij \rangle} \vec{S}_{zi} \cdot \vec{S}_{zj}
\]

• “Spin ice” chooses between many disordered states obeying 2-in-2-out rules
• Excitations: deconfined emergent magnetic monopoles
• Quantum spin ice: tunneling between ice like ground states, produces additional emergent excitations

Magnetic Ground States in Pyrochlores
(incomplete list!)

Spin Ice
- FM Ising
- Or
- T. Fennell, Collection SFN 13, 04001 (2014)
- Emergent magnetic monopole excitations

Quantum Spin Liquids
- FM Ising
- XY
- Or
- AFM S=1/2 Heisenberg
- "Quantum Spin Ice"
- Coulomb phase
- T. Fennell, Collection SFN 13, 04001 (2014)
Real Pyrochlores: playgrounds for frustration

$R_2Ti_2O_7$ “Rare earth titanates”

Differences in single ion anisotropy is very important

<table>
<thead>
<tr>
<th>Single Ion Anisotropy</th>
<th>Interactions</th>
<th>Ground state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho, Dy</td>
<td>Ising</td>
<td>FM</td>
</tr>
<tr>
<td>Tb</td>
<td>Ising</td>
<td>AFM</td>
</tr>
<tr>
<td>Gd</td>
<td>Heisenberg</td>
<td>AFM</td>
</tr>
<tr>
<td>Er</td>
<td>XY</td>
<td>AFM</td>
</tr>
<tr>
<td>Yb</td>
<td>XY</td>
<td>FM</td>
</tr>
</tbody>
</table>
Real Pyrochlores: playgrounds for frustration

\[(Na/A')_2M_2O_7\]
\[A' = Ca^{2+} \text{ or } Sr^{2+}\]

In 3d transition metals, usually Heisenberg — except \(Co^{2+}\)

<table>
<thead>
<tr>
<th>(M^{2+})</th>
<th>Single Ion Anisotropy</th>
<th>Interactions</th>
<th>Ground state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>XY, (S_{\text{eff}}=1/2)</td>
<td>AFM</td>
<td>spin frozen only at low effective (T)</td>
</tr>
<tr>
<td>Mn</td>
<td>Heisenberg? (S=5/2)</td>
<td>AFM</td>
<td>spin frozen</td>
</tr>
<tr>
<td>Ni</td>
<td>Heisenberg? (S=1)</td>
<td>AFM</td>
<td>spin frozen</td>
</tr>
<tr>
<td>Fe</td>
<td>Heisenberg? (S=5/2)</td>
<td>AFM</td>
<td>spin frozen</td>
</tr>
</tbody>
</table>
Origin of anisotropy in Pyrochlores

$R_2B_2O_7$ ($R^{3+} = \text{rare earth}, B^{4+} = \text{Ti, Sn, Pt, Ge}$), NaCa$\text{Co}_2F_7$, NaSr$\text{Co}_2F_7$

- **Spin orbit coupling plus crystal field** in both $\text{Co}^{2+}$ and $R^{3+}$: $J$ instead of $S$ and $L$
- **Effective $S=1/2$ doublets**
- **$g$-tensor**: describes size of single-ion magnetic moment in various directions
- **anisotropic exchange couplings**: Distinct from $g$-tensor anisotropy!

<table>
<thead>
<tr>
<th></th>
<th>$g_z$</th>
<th>$g_{xy}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Yb}_2\text{Ti}_2\text{O}_7$</td>
<td>1.85</td>
<td>3.62</td>
</tr>
<tr>
<td>$\text{NaCaCo}_2\text{F}_7$</td>
<td>1.87</td>
<td>6.08</td>
</tr>
</tbody>
</table>

Gaudet et al, PRB 92, 134420 (2015)
Ross et al, PRB 95, 144414 (2017)
General Anisotropic Exchange

Tensor with 4 unique elements:

\[ J_2 S^x_1 S^x_2 + J_1 (S^y_1 S^y_2 + S^z_1 S^z_2) + J_3 (S^y_1 S^z_2 + S^z_1 S^y_2) + \ldots \]

\[
H = \frac{1}{2} \sum_{ij} J_{ij} S_i^{\mu} S_j^{\nu}
\]

\[
J_{01} = \begin{pmatrix}
J_2 & J_4 & J_4 \\
-J_4 & J_1 & J_3 \\
-J_4 & J_3 & J_1
\end{pmatrix}
\]

Classical phase diagram:
Types of Long Range Order (for \(J_4 = 0\))

Yan et al, “General theory of anisotropic exchange on the pyrochlore lattice”, PRB 95, 094422 (2017)
General Anisotropic Exchange

Tensor with 4 unique elements:

\[ J_2 S_x^1 S_x^2 + J_1 (S_y^1 S_y^2 + S_z^1 S_z^2) + J_3 (S_y^1 S_z^2 + S_z^1 S_y^2) + \ldots \]

\[
H = \frac{1}{2} \sum_{ij} J_{ij}^{\mu\nu} S_i^\mu S_j^\nu
\]

\[
J_{01} = \begin{pmatrix}
J_2 & J_4 & J_4 \\
-J_4 & J_1 & J_3 \\
-J_4 & J_3 & J_1
\end{pmatrix}
\]

White regions: quantum fluctuations destroy conventional LRO

Yan et al, “General theory of anisotropic exchange on the pyrochlore lattice”, PRB 95, 094422 (2017)
Determining exchange interactions from field polarized states

Can extract quantitative values for $J_1$-$J_4$
Linear Spin Wave Theory + Neutron Scattering

Unusual ground state
(Quantum effects from effective $S=1/2$)

Field polarized
(Semi-Classical)

H || [110]

H = 0

Paramagnetic

Bruce Gaulin

Leon Balents

Lucile Savary
“Time of Flight” Inelastic Neutron Scattering

“Disk Chopper Spectrometer” (DCS)

@ NIST Center for Neutron Research

Single Crystal Yb$_2$Ti$_2$O$_7$

7.5 cm
“Time of Flight” Inelastic Neutron Scattering

“Disk Chopper Spectrometer” (DCS)

@ NIST Center for Neutron Research

Single Crystal Yb$_2$Ti$_2$O$_7$

7.5 cm
Volume of “Time of Flight” Data

Can slice through this volume in several directions
Volume of “Time of Flight” Data

Can slice through this volume in several directions
Volume of “Time of Flight” Data

Can slice through this volume in several directions.
Determining exchange interactions with spin waves from field polarized state

### Yb$_2$Ti$_2$O$_7$


<table>
<thead>
<tr>
<th></th>
<th>Yb$_2$Ti$_2$O$_7$</th>
<th>Er$_2$Ti$_2$O$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>J1</td>
<td>-0.09</td>
<td>0.11</td>
</tr>
<tr>
<td>J2</td>
<td>-0.22</td>
<td>-0.06</td>
</tr>
<tr>
<td>J3</td>
<td>-0.29</td>
<td>-0.10</td>
</tr>
<tr>
<td>J4</td>
<td>0.01</td>
<td>0.00</td>
</tr>
</tbody>
</table>

### Er$_2$Ti$_2$O$_7$

Determining exchange interactions with spin waves from field polarized state

**Yb$_2$Ti$_2$O$_7$**


![Graphs and images showing data and fit for Yb$_2$Ti$_2$O$_7$](image1)

![Table showing exchange parameters for Yb$_2$Ti$_2$O$_7$ and Er$_2$Ti$_2$O$_7$](table1)

**Er$_2$Ti$_2$O$_7$**


![Graphs and images showing data and fit for Er$_2$Ti$_2$O$_7$](image2)

- $J_1$: -0.09, 0.11
- $J_2$: -0.22, -0.06
- $J_3$: -0.29, -0.10
- $J_4$: 0.01, 0.00

Params lead to phase competition, and possible Quantum Spin Ice
**Yb$_2$Ti$_2$O$_7$: splayed ferromagnet with gapless “continuum” excitations**

- Heat capacity anomaly at low temperatures, with some sample dependence
- **“Best” samples** (usually powders) show Ice-like splayed ferromagnetic order at 265 mK
- Despite this, excitations are relatively unstructured below $T_c$ - **unlike conventional magnons**

---

**Graph and Diagrams**

- Heat capacity vs. temperature graph
- “Spin Ice-Like” (2-in 2-out) Splaying
- Powder: elastic
- Powder: inelastic

---

Compare zero field spin waves to Linear Spin Wave Theory

Calculated zero-field spin waves

Using Exchange parameters from Ross et al, Phys. Rev. X 1, 021002 (2011)

Measured Yb$_2$Ti$_2$O$_7$ 100 mK

Time-of-Flight Spectrometer (DCS)
Yb$_2$Ti$_2$O$_7$ on phase diagram

- Modified parameters from other groups$^{[1,2]}$ suggest Yb$_2$Ti$_2$O$_7$ is right on the edge of AFM order
- Do quantum fluctuations arise from proximity to AFM state, i.e. competing orders?
- **What role does the known sample dependence play?**

All proposed parameters put Yb$_2$Ti$_2$O$_7$ close to a classical phase boundary with AFM order

$J_1 = -0.09, J_2 = -0.22, J_3 = -0.29, J_4 = 0.01$


$J_1 = -0.03, J_2 = -0.32, J_3 = -0.28, J_4 = 0.02$

Determining exchange interactions with spin waves from field polarized state

**Yb\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}**


- \( J_1 = -0.09 \)
- \( J_2 = -0.22 \)
- \( J_3 = -0.29 \)
- \( J_4 = 0.01 \)

**Er\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}**


- \( J_1 = 0.11 \)
- \( J_2 = -0.06 \)
- \( J_3 = -0.10 \)
- \( J_4 = 0.00 \)
Determining exchange interactions with spin waves from field polarized state

Yb$_2$Ti$_2$O$_7$  Er$_2$Ti$_2$O$_7$

<table>
<thead>
<tr>
<th></th>
<th>Yb$_2$Ti$_2$O$_7$</th>
<th>Er$_2$Ti$_2$O$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>J1</td>
<td>-0.09</td>
<td>0.11</td>
</tr>
<tr>
<td>J2</td>
<td>-0.22</td>
<td>-0.06</td>
</tr>
<tr>
<td>J3</td>
<td>-0.29</td>
<td>-0.10</td>
</tr>
<tr>
<td>J4</td>
<td>0.01</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Params lead to “Order by Disorder”

Determining exchange interactions with spin waves from field polarized state

Yb$_2$Ti$_2$O$_7$

| H || to [1-10] |

Er$_2$Ti$_2$O$_7$


| H || to [111] |

| Params lead to “Order by Disorder” |

<table>
<thead>
<tr>
<th></th>
<th>Yb$_2$Ti$_2$O$_7$</th>
<th>Er$_2$Ti$_2$O$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>J1</td>
<td>-0.09</td>
<td>0.11</td>
</tr>
<tr>
<td>J2</td>
<td>-0.22</td>
<td>-0.06</td>
</tr>
<tr>
<td>J3</td>
<td>-0.29</td>
<td>-0.10</td>
</tr>
<tr>
<td>J4</td>
<td>0.01</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Determining exchange interactions with spin waves from field polarized state

$\Gamma_5$ manifold:

Accidentally Degenerate

$\psi_2$ basis state selected by thermal and quantum fluctuations

<table>
<thead>
<tr>
<th></th>
<th>Yb$_2$Ti$_2$O$_7$</th>
<th>Er$_2$Ti$_2$O$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>J1</td>
<td>-0.09</td>
<td>0.11</td>
</tr>
<tr>
<td>J2</td>
<td>-0.22</td>
<td>-0.06</td>
</tr>
<tr>
<td>J3</td>
<td>-0.29</td>
<td>-0.10</td>
</tr>
<tr>
<td>J4</td>
<td>0.01</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Params lead to “Order by Disorder”


Er$_2$Ti$_2$O$_7$

data, H=3T

fit
Er$_2$Ti$_2$O$_7$ on phase diagram

- Classical Monte Carlo agrees and puts Er$_2$Ti$_2$O$_7$ squarely inside $\psi_2$

- Not as close to the phase boundary
  - But remember, thermal (and quantum) fluctuations put it there

- Helps to explain why no sample dependence has been observed over the 12 years it’s been studied! (despite similar synthesis as Yb$_2$Ti$_2$O$_7$)

NaCaCo$_2$F$_7$ and NaSrCo$_2$F$_7$

$A_2B_2X_7$: $A = \text{Na/(Ca,Sr)}, \ B = \text{Co}, \ X = \text{F}$

Co$^{2+}$

high spin $S = 3/2, \ L = 3$

CEF + SOC

$S_{\text{eff}} = 1/2$

Na$^+$/Ca$^{2+}$ or Sr$^{2+}$

non-magnetic, disordered site

J.W. Krizan, R.J. Cava, PRB 89, 214401 (2014)
XY AFM pyrochlores with $S_{\text{eff}} = 1/2$

**Strong AFM interactions**

$1/\chi$ (mol-Co·Oe/emu) vs $T$ (K)

- Measured: blue circles
- Calculated: orange line

CEF + SOC model

$NaCaCo_2F_7$

- $\mu_{\text{eff}} = 6.1 \mu_B$
- $\Theta_{\text{cw}} = -139$ K

**Broad feature in $C_p$**

- Releases $R \ln(2)$ entropy
- Spin freezing at $T_F = 2.4$ K

**Single ion analysis:**
K.A. Ross, et al,
PRB 95 (2017)

**Crystal growth and thermodynamics:**
J.W. Krizan, R.J. Cava,
PRB 89, (2014)

**Spin freezing below $T_F = 2.4$ K**

- Heat capacity $C_p$ vs $T$
- Magnetic susceptibility $\chi'$ vs $T$
- Inset: $\ln(2F^+/F^-)$ vs $T$

$NaCaCo_2F_7$

- $H = 20$ Oe $|| [111]$
- $H = 200$ Oe $|| [110]$
- [110] FC
- [110] ZFC
Neutron scattering from frozen state

zig-zag pattern persists to finite energies

It is telling us about the **low energy fluctuations** in the thermal spin liquid state

- With **MACS**, we build up $S(Q,\omega)$ using constant energy slices
- Can we interpret the $Q$ dependence of finite energy slices?
- **Fourier components of spin fluctuations** away from static configuration

$$S^{\alpha\beta}(Q,\omega) \equiv \frac{1}{2\pi \hbar} \int dt e^{-i\omega t} \frac{1}{N} \sum_{\mathbf{r}_r} e^{iQ(\mathbf{r}_r)} \langle S_\alpha^{\mathbf{r}_r}(0) S_\beta^{\mathbf{r}_r}(t) \rangle$$

$T = 1.7K$
Inelastic scattering in frozen state

Same manifold of states as $\text{Er}_2\text{Ti}_2\text{O}_7$!

MACS spectrometer NCNR

Inelastic scattering in frozen state

Same manifold of states as Er$_2$Ti$_2$O$_7$!

MACS spectrometer NCNR

Inelastic scattering in frozen state

Same manifold of states as $\text{Er}_2\text{Ti}_2\text{O}_7$!

MACS spectrometer NCNR

Damped Spin Excitations

- XY clusters relax slowly: explore the continuous manifold

- Crossover to Heisenberg local mode at 5.5 meV

Damped Spin Excitations

- XY clusters relax slowly: explore the continuous manifold

- Crossover to Heisenberg local mode at 5.5 meV

Damped Spin Excitations

- XY clusters relax slowly: explore the continuous manifold
- Crossover to Heisenberg local mode at 5.5 meV

Above $T_F$, thermal spin liquid

- **Broad excitations** consistent with strongly correlated paramagnet
- Above $T_F$, Thermal spin liquid over range of nearly 140 K
- **Highly frustrated:**
  - $f = \theta_{CW}/T_F = 58$ in NaCaCo$_2$F$_7$
  - compared to $f = 18$ in Er$_2$Ti$_2$O$_7$
Above $T_F$, thermal spin liquid

- **Broad excitations** consistent with strongly correlated paramagnet
- Above $T_F$, Thermal spin liquid over range of nearly 140 K
- **Highly frustrated:**
  - $f = \theta_{CW}/T_F = 58$ in NaCaCo$_2$F$_7$
  - compared to $f = 18$ in Er$_2$Ti$_2$O$_7$

![Graphs and images showing magnetic properties]
Above $T_F$, thermal spin liquid

- **Broad excitations** consistent with strongly correlated paramagnet
- Above $T_F$, Thermal spin liquid over range of nearly 140 K
- **Highly frustrated:**
  - $f = \theta_{CW}/T_F = 58$ in NaCaCo$_2$F$_7$
  - compared to $f = 18$ in Er$_2$Ti$_2$O$_7$

![Graphs and diagrams showing energy levels and heat capacity plots.](image-url)
Comparison to Effective-Spin 1/2 Hamiltonian

\[ S_{\text{eff}} = \frac{1}{2} \text{ with XY anisotropic exchange} \]

\[
\begin{align*}
    J_1 &= 0.11 \\
    J_2 &= 0.06 \\
    J_3 &= -0.1 \\
    J_4 &= 0
\end{align*}
\]

Yan et al., arXiv:1603.09466 (2016)

Yan et al., PRB 95, 094422 (2017)
Summary

- Frustrated pyrochlore materials based on $R^{3+}$ earths and Co$^{2+}$ act as **effective $S=1/2$** - the “most quantum” they can be.

- The same **spin orbit coupling** effects responsible for establishing $S_{\text{eff}}=1/2$ also lead to **anisotropic exchange**.

- A general 4-parameter anisotropic exchange model can be used to describe $S_{\text{eff}}=1/2$ pyrochlores.

- **Neutron scattering** allows us to probe the diffuse magnetic scattering and field-polarized spin waves, to extract parameters for real pyrochlores, and understand spin correlations.

- **Amazing diversity of ground states** can be understood from the deduced relative positions in the **unified phase diagram**.

- **MACS, DCS, SPINS** - cold neutron spectrometers used for these studies.
Thanks to...

Collaborators

- Bruce Gaulin
- Edwin Kermarrec
- Jonathan Gaudet
- Lucile Savary
- Leon Balents
- Collin Broholm
- Bob Cava
- Jason Krizan
- Steve Nagler
- Matt Stone
- Jan Kycia
- Jeff Quilliam
- Jan Kycia
- Jeff Quilliam
- Juscelino Leao
- Jose Rodriguez
- Nick Butch
- Leland Harriger
- Yiming Qiu

Funding

- NSERC (McMaster)
- Department of Energy (JHU, Princeton, SNS)
- NSF (CHRNS)
- Colorado State University (startup)