Hard Condensed Matter Science with Neutrons

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Outline

• Neutrons as a probe for structure and dynamics in condensed matter
  • what neutrons probe, and why they are great at it
  • breadth of techniques ↔ diversity of scientific questions

• Examples
  • Spin resonance in High $T_c$ Superconductors
  • Skyrmion lattices
  • “Quantum spin liquids” - a brief look at our neutron work on Yb$_2$Ti$_2$O$_7$, spanning a decade of research — NIST Center for Neutron Research (NBSR)
Neutron Scattering in Condensed Matter

- Using neutrons for diffraction and spectroscopy
  - $\lambda = 2d \sin(\theta)$
  - $E = \frac{h^2}{2m\lambda^2} = \frac{1}{2}mv^2$
- for thermal neutrons,
  - $\lambda \sim 2\text{Å}, E \sim 20\text{ meV}$
- Well suited to probe lattice structure and dynamics in condensed matter
- Neutrons have a magnetic dipole moment: Magnetic diffraction and spectroscopy possible

Phonons from FeSi
ARCS instrument at SNS
The measured intensity is the “Dynamic Structure Factor” $S(Q, \omega)$

$$S(Q, \omega) = \frac{1}{2\pi \hbar} \int \int G(r, t) e^{iQ \cdot r} e^{-i\omega t} d^3r dt$$

Pairwise Correlations in Space and Time

- Can measure **structural** and **magnetic** correlations
- Spatial information comes from measuring “Q”, i.e., momentum transfer
- Dynamic information comes from measuring “$\omega$”, aka $E$ (energy transfer).
“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

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

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Volume of “Time of Flight” Data
Volume of “Time of Flight” Data

Elastic Static Correlations
Volume of “Time of Flight” Data

Elastic:
- Static Correlations

Inelastic:
- Dynamic Correlations
MACS: multiplexed “triple axis” spectrometer

With MACS, build up $S(Q,\omega)$ using constant energy slices

MACS has huge flux of cold neutrons — proximity to reactor core + double-focusing monochromator

Great for small samples, low signal applications — big discoveries in exotic magnetism

Magnetic Scattering from new frustrated magnet NaCaCo$_2$F$_7$ at MACS
# Neutrons in hard condensed matter

## Scientific Questions

- **Crystal structures:** Metal Organic Frameworks (MOFs), functional metastable structures, batteries, photovoltaics, etc.

- **Magnetic structures:** High $T_c$ superconductors parent compounds, Skyrmion lattices, multiferroics, magnetic nanoparticles, etc.

- **Phonons:** Thermoelectrics, piezoelectrics, superconductors, etc.

- **Spin excitations:** Unconventional superconductors, frustrated and quantum magnetism, multiferroics, etc.

## Neutron Techniques

- **Diffraction**
  - BT-1 (NCNR)
  - HB-2A, HB-3A (HFIR)
  - POWGEN, Topaz, CORELLI (SNS)

- **Small Angle Neutron Scattering**
  - 4 x SANS (NCNR)
  - GPSANS, BIO-SANS (HFIR)
  - EQ-SANS, USANS (SNS)

- **Reflectometry**
  - 2 x reflectometers (SNS)
  - 4 x reflectometers (NCNR)

- **Time-of-flight spectrometry (TOF)**
  - DCS (NCNR)
  - 4 x TOF (SNS)

- **Triple axis spectrometry (TAX)**
  - 5 x TAX (NCNR)
  - 4 x TAX (HFIR)

- **Backscattering**
  - HFBS (NCNR)
  - BASIS (SNS)
Example: Spin Resonance in Unconventional Superconductors

- **Unconventional superconductivity**: Does not follow the standard “BCS” theory of phonon mediated pairing of electrons - *what is pairing mechanism?*

- Many show similar phase diagrams - *proximity to magnetic order*, determined by neutron diffraction.

- **Spin resonance** observed using *inelastic neutron scattering* gives important clues. Parametric studies important.

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Some materials with helical order host topological spin textures called **Skyrmions**.

Topological nature means they are **stable once created**, and relatively large size means they are not pinned easily.

Skyrmions proposed as carriers for low dissipation, high density magnetic information storage technology.

**Skyrmion lattices** form as stable phases, stabilized by thermal fluctuations, identified in several compounds by **Small Angle Neutron Scattering (SANS)**.
My favorite application of neutrons in hard condensed matter:
Frustrated and Quantum Magnetism

- Solve complicated magnetic structures
- Measure and model magnetic diffuse neutron scattering (short range correlations)
- Measure spin wave dispersions to determine Hamiltonian parameters
- Look for exotic emergent excitations in spin liquids
My favorite application of neutrons in hard condensed matter: Frustrated and Quantum Magnetism

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Geometric Frustration in 2D

prefer $\uparrow \downarrow$ alignment, but choice of 3rd spin direction is unclear

"Extensive degeneracy" of ground states
Quantum Entanglement in frustrated magnetic materials

Instead of spins fighting… let’s make spin singlet friends!

Locally entangled spins forming a Valence Bond Crystal (VBC)

Breaks translational symmetry


$S = 0$, singlet state
Valence Bond Crystal: Excitations

L. Balents, *Spin Liquids in Frustrated Magnets.*

*Nature* 464, 199-208 (11 March 2010)

- Excited state is the $S=1$ triplet (measurable with neutrons)! Three degenerate energy levels, can be split by a magnetic field

\[ S = 1 \text{ triplet} \]

\[ = \left[ \begin{array}{c} \uparrow \uparrow \\ \downarrow \downarrow \\ \uparrow \downarrow + \downarrow \uparrow \end{array} \right] \]

\[ Sz=+1 \]

\[ Sz=-1 \]

\[ Sz= 0 \]

Use neutrons to see these e.g. $\text{SrCu}_2(\text{BO}_3)_2$

- Magnetic Field
- Energy

- $Sz=-1$
- $Sz= 0$
- $Sz=+1$
Quantum Spin Liquid

- **non-extensive degeneracy!** Quantum ground state is a superposition state of disordered configurations.
- Absence of long range order, **not even “singlets” are ordered**
- now **global entanglement** emerges
- Fractionalized excitations (“spinons”), potentially useful in quantum information
- Example: Resonating Valence Bond (RVB) state shown below

L. Balents, *Spin Liquids in Frustrated Magnets*.  
*Nature* 464, 199-208 (11 March 2010)
Fractionalized Excitations in a Quantum Spin Liquid

RVB: delocalization of spin degrees of freedom in an insulator

Pair of “spinons” are deconfined and fractionalized
spin = 1/2, charge = 0
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Fractionalized Excitations in a Quantum Spin Liquid

RVB:
delocalization of \text{spin} degrees of freedom in an insulator

Pair of “spinons” are \textit{deconfined} and \textit{fractionalized}

\text{spin} = \frac{1}{2}, \text{charge} = 0
Pair of “spinons” are deconfined and fractionalized
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RVB: delocalization of spin degrees of freedom in an insulator
Pair of “spinons” are *deconfined* and *fractionalized*.

**spin = 1/2, charge = 0**

**RVB:**

delocalization of *spin* degrees of freedom in an insulator.
How to prove you have a quantum spin liquid?

Generally, you first show what it isn’t

- Not fully magnetically long range ordered
- Not “quantum ordered” in a valence bond crystal phase

**Unusual excitations** *(continuum of scattering)*

**Neutron scattering is needed to identify these types of spectra**

e.g., CuSO$_4$·5D$_2$O: spin 1/2 Chain

freedom of choice for each tetrahedron leads to a macroscopic degeneracy: **NO Long Range Order**
Broad range of exotic behavior due to frustration

<table>
<thead>
<tr>
<th>Single Ion Anisotropy</th>
<th>Interactions</th>
<th>Ground state</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ho, Dy</strong></td>
<td>Ising</td>
<td>FM</td>
</tr>
<tr>
<td></td>
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<td>Heisenberg</td>
<td>AFM</td>
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<tr>
<td></td>
<td>partial order</td>
<td></td>
</tr>
<tr>
<td><strong>Er</strong></td>
<td>XY</td>
<td>AFM</td>
</tr>
<tr>
<td></td>
<td>“order by disorder”</td>
<td></td>
</tr>
<tr>
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<td>FM</td>
</tr>
<tr>
<td></td>
<td>Quantum spin liquid?</td>
<td></td>
</tr>
</tbody>
</table>
**Example: Ising Ferromagnetic Pyrochlore**

**“Classical” Spin Ice**

Ferromagnetic Ising exchange gives “Ice Rules”: Two-in Two-out

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

- Spin ice chooses between many disordered states obeying 2-in-2-out rules
- No tunneling allowed
- Excitations: *deconfined emergent magnetic monopoles*

“Quantum” Spin Ice?

- Can tunnel between ice rules states
- Introduces fluctuations in the gauge field
  - **Electric monopoles** — coherent, propagating wavepacket of changing ice configurations
  - **Magnetic monopoles** — violate ice rules, i.e. 3-in 1-out
  - **Photons** — gapless transverse fluctuations of spins

\[ \vec{\nabla} \cdot \vec{B} = 4\pi \rho_m \]
\[ \vec{\nabla} \times \vec{E} = -\frac{1}{c} \frac{\partial \vec{B}}{\partial t} - \frac{4\pi}{c} \vec{j}_m \]

\[ H = \sum_{\langle ij \rangle} \{ J_{zz} S_i^z S_j^z - J_{\pm} (S_i^+ S_j^- + S_i^- S_j^+) \} \]

Now we also have \( \mathbf{E}! \)
Full Emergent Electrodynamics

\[ r \times \mathbf{E} = \frac{1}{c} \partial \mathbf{B} \]
\[ 4 \pi \mathbf{J}_m \]


\[ \text{small XY terms} \]


\[ \mathbf{E} \]
\[ \text{Full Emergent Electrodynamics} \]

\[ r \times \mathbf{E} = \frac{1}{c} \partial \mathbf{B} \]
\[ 4 \pi \mathbf{J}_m \]

Predicted Neutron Scattering Pattern from **Photons** in quantum spin ice

Energy Transfer
Momentum Transfer
General Pyrochlore Exchange Hamiltonian

\[ H = \sum_{\langle ij \rangle} \left\{ J_{zz} S_i^z S_j^z - J_{\pm} (S_i^+ S_j^- + S_i^- S_j^+) + J_{++} \left[ \gamma_{ij} S_i^+ S_j^+ + \gamma_{ij}^* S_i^- S_j^- \right] \right\} + J_{z\pm} \left[ S_i^z (\zeta_{ij} S_j^+ + \zeta_{ij}^* S_j^-) + i \leftrightarrow j \right] \]
Yb$_2$Ti$_2$O$_7$: a puzzling pyrochlore

Specific Heat vs. Temperature

Spin Fluctuation Rate (µSR)


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

250 mK

Ferromagnet with gapless “continuum” excitations

- Heat capacity anomaly at low temperatures
- “Best” samples (usually powders) show Ice-like splayed ferromagnetic order at 265 mK
- Despite this, excitations are relatively unstructured at low $T$: \textit{gapless continuum, no magnons}??

Ferromagnet with gapless “continuum” excitations

- Heat capacity anomaly at low temperatures
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~250 mK

FM Order? QSL?

Correlated, quantum coherent?

splayed ferromagnetic order

powder: elastic magnetic

powder: inelastic magnetic

Evolution of $S(Q, \omega)$ in Single Crystals

Broad scattering develops into sharp magnons with increasing field ($H \parallel [1,-1,0]$)

K. A. Ross et al, PRL 103 227202 (2009)
“Quantum Spin Ice” Exchange Parameters for Yb$_2$Ti$_2$O$_7$

H along [110] \( g_z = 1.8, \ g_{xy} = 4.32 \)

![Data and fit plots](image)

Spin Ice plus quantum fluctuations

[Parameters written in local basis]

\[
\begin{align*}
J_{zz} &= 0.17 \pm 0.04, \\
J_\pm &= 0.05 \pm 0.01, \\
J_{\pm\pm} &= 0.05 \pm 0.01, \\
J_{z\pm} &= -0.14 \pm 0.01 
\end{align*}
\] (meV)

"Quantum Spin Ice" Exchange Parameters for Yb$_2$Ti$_2$O$_7$

$H$ along $[1\overline{1}0]$ \hspace{1cm} $g_z = 1.8, \ g_{xy} = 4.32$

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$J_{zz} = 0.17 \pm 0.04, \ J_\pm = 0.05 \pm 0.01, \ J_{\pm\pm} = 0.05 \pm 0.01, \ J_{z\pm} = -0.14 \pm 0.01$ (meV)

What is the ground state?

Exchange parameters for $\text{Yb}_2\text{Ti}_2\text{O}_7$ compared to theoretical phase diagram

- $\text{Yb}_2\text{Ti}_2\text{O}_7$ “close to” the boundary with exotic phases of matter?
  - **Quantum Spin Liquid** (QSL)
    - supports emergent electrodynamics
    - Monopoles, Photons, Electrons
  - **Coulomb Ferromagnet** (CFM)
    - partially polarized phase
    - supports emergent electrodynamics

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Phase competition in Yb$_2$Ti$_2$O$_7$

[Parameters written in *global* basis]

- Our parameters, as well as recently proposed 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?

\[\text{Parameters written in global basis}\]

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

\[J_1 = -0.09, J_2 = -0.22, J_3 = -0.29, J_4 = 0.01\]


\[J_1 = -0.03, J_2 = -0.32, J_3 = -0.28, J_4 = 0.02\]

Other examples …

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


- Data, $H=5T$
- Fit

![Graph showing data and fit for Yb$_2$Ti$_2$O$_7$](image)

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


- Data, $H=3T$
- Fit

![Graph showing data and fit for Er$_2$Ti$_2$O$_7$](image)

**Table: Swap Energies**

<table>
<thead>
<tr>
<th></th>
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<th>Er$_2$Ti$_2$O$_7$</th>
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<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>
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<td>-0.10</td>
</tr>
<tr>
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Other examples …

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

![Data and fit for Yb$_2$Ti$_2$O$_7$](image)

![Table of parameters](table)

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

![Data and fit for Er$_2$Ti$_2$O$_7$](image)

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<tr>
<td>J4</td>
<td>0.01</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Params lead to "Order by Disorder"
**NaCaCo$_2$F$_7$ — MACS**

NEW single crystal pyrochlores:
Constant energy slices compared to models

**NaCaCo$_2$F$_7$ — MACS, SEQUOIA**

$S_{\text{eff}} = 1/2$ with $XY$ anisotropic exchange

$J_1 = 0.11$

$J_2 = 0.06$

$J_3 = -0.1$

$J_4 = 0$


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Summary

- Neutrons provide a means to understand structure and dynamics of hard condensed matter.
- A vast range of topical scientific questions can be addressed with neutron scattering - availability of diverse neutron techniques is crucial.
- The search for novel quantum phases of matter, (potentially paradigm shifting) such as “Quantum Spin Liquids” relies heavily on neutrons.
- New discoveries in quantum frustrated magnets are presently rapid due to access to neutron measurements of magnetic correlations, unusual spectra.
- Precise and quantitative comparisons to theory are afforded by the simplicity of the neutron cross section.

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