Unraveling the Mysteries in Complex Oxides by Neutron Scattering

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Condensed Matter Science and Neutron Scattering

Why neutron scattering is a powerful tool in CMS?
What Is Condensed Matter Science about?

- Study **Emergent phenomena** that are **collective effects** of a huge number of particles

High $T_c$ Superconductivity

! [Graph showing the relationship between temperature and hole concentration](image)

La$_{2-x}$Sr$_x$CuO$_4$

Outline

- **Introduction:**
  1. Collective phenomena in Condensed Matter Physics
  2. Magnetism and Neutron Scattering
- **Example:** Neutron scattering studies on geometrically frustrated magnets $ACr_2O_4$ ($A=$Zn, Cd)
  1. Composite spin degrees of freedom
  2. Spin-Peierls-like phase transitions
- **Summary**
Origin of Magnetism

- Unpaired electrons of ions in solids have
  1) electronic spin $\mu_S$
  2) orbital momentum $\mu_L$

Transition metals: unfilled d shells
Quenched orbital moments
Small moments

Rare earth metals: unfilled f shells
Strong spin-orbit coupling $J=S+L$
Large magnetic moments

Exchange interactions arise from the overlap of electronic orbitals of neighboring sites and the Pauli exclusion principle.

- Direct exchange arising from direct overlap of neighboring electron orbitals
- Superexchange is mediated by a diamagnetic anion such as $O^{2-}$ or $F^{-1}$
- Indirect exchange mediated by conduction electrons, RKKY interaction

Spin interactions of localized moments

$$\mathcal{H} = \sum_{ij} J_{ij} S_i S_j$$
Phase Diagram for a Three-Dimensional Ordinary Magnet

\[
F = H_{\text{mag}} - TS = - \sum J S_i S_j - TS
\]

- The Ground State is a Long range (anti)ferromagnetically ordered state.
- Low Energy Excitations can be explained by Long range linear spin waves.

Magnetic Neutron Scattering

Neutron:
- Wavelength comparable to interatomic spacing
- Penetrating \(\rightarrow\) bulk properties are measured
- has spin \(s = \frac{1}{2}\) and interacts with atomic moments

Scattering by atomic magnetic moments: \(I = (0.54)^2 S (S+1)\)

Magnetic scattering intensities can be comparable to nuclear scattering !!
Magnetic Neutron Scattering Cross Section

\[ \frac{d^2 \sigma}{d\Omega d\omega} \]

Spin-Spin Correlation Function

\[ < S_R(t) S_{R'}(0) > \]

Fourier Transform

The probability of finding a spin in a spin state \( S_R \) at position \( R \) at time \( t \) when another spin at \( R' \) at time \( t=0 \) is in a spin state \( S_{R'} \)

\[ \Gamma \sim \hbar/\tau \]

\[ \kappa \sim 1/\xi \]

\( \Gamma \): relaxation time
\( \kappa \): intrinsic linewidth

\( \tau \): lifetime
\( \xi \): correlation length

Ordered moment
Fluctuating moment

\( Q \)

\( 0 \)

\( \omega \)

Neel phase:
What kind of magnetic scattering signal in Q and \( \omega \) space would you expect?

(1) Any Elastic signal?
(2) Any Inelastic signal? If any, what kind of shape in the \( \omega \)- and Q-space?

Ferromagnet

\[ \text{Neutron intensity} \]

\[ \begin{array}{c}
\text{Antiferromagnet}
\end{array} \]

\[ \text{Neutron intensity} \]

\( 0 \)

\( 2\theta \)

\( Q \)

\( \Gamma \): relaxation time
\( \kappa \): intrinsic linewidth
Do all magnetic systems order at low temperatures?

Systems with Quantum Fluctuations at $T=0K$

Low dimensional spin systems

Frustration

Dimerization

Quantum fluctuations are important in low dimensions, systems with frustrated interactions or dimerization

Novel quantum-coherent ground states with non-conventional spin correlations
Low dimensionality suppresses magnetic long range order

Spin wave in an XY spin system \( \mathcal{H} = \sum_{ij} J_{ij} S_i S_j \)

Energy cost to create such a spin wave

a. In three-dimensions: \( E \propto L^3 \left( \frac{2\pi}{L} \right)^2 \frac{1}{L} \xrightarrow{L \to \infty} \infty \)
   presence of LRO

b. In two-dimensions: \( E \propto L^2 \left( \frac{2\pi}{L} \right)^2 \frac{1}{L} \xrightarrow{L \to \infty} \text{const} \)
   borderline case: Kosterlitz-Thouless transition

c. In one-dimension: \( E \propto L \left( \frac{2\pi}{L} \right)^2 \frac{1}{L} \xrightarrow{L \to \infty} 0 \)
   Absence of LRO

Geometrical Frustration

A simplest example: a Triangle of three antiferromagnetic Ising spins
\( H = -\sum S_i \cdot S_j \)
All exchange interactions can not be satisfied.

A tetrahedron with four isotropic spins
\( \sum S_i = 0 \)
Zero energy modes in the ground state manifold

Geometrical frustration leads to a large degeneracy in the ground state
Phase Diagram for Geometrical Frustration

\[ H = -J \sum S_i \cdot S_j \]

\[ \Theta_{CW} = \frac{J z S (S+1)}{3 k_B} \]

What is the nature of the ground state?
How are the spins correlated with each other?

Outstanding Issues

- What is the nature of spin liquid phase?
- GF vs the third law of thermodynamics, entropy \( \to 0 \) at \( T \to 0 \)?
Lattice Structure of Spinels

spinel oxides: \( AB_2O_4 \)

\( AO_4 \) tetrahedra + \( BO_6 \) octahedra

octahedra are edge-sharing

\( \rightarrow J_{NN} \) is dominant

if the B ion has \( t_{2g} \) electrons only

\( B \)-site lattice: 3D network of

corner-sharing tetrahedra = pyrochlore lattice

**strong geometrical frustration**

\( ACr_2O_4 \) can best realize the most frustrating system with

\[
H = -J \sum S_i S_j
\]

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**Bulk Susceptibility:** \( \langle M \rangle / H = \langle \Sigma S_i \rangle / H \)

\( \text{ZnCr}_2O_4 \) (3d\(^3\))

*W. Ratcliff, S-W. Cheong (2000)*

\[
\theta_{CW} = -390 \text{ K} \\
T_N = 12.5 \text{ K}
\]

\( \text{CdCr}_2O_4 \) (3d\(^3\))

*M.T. Rovers (2002); H. Ueda (2005)*

\[
\theta_{CW} = -88 \text{ K} \\
T_N = 7.8 \text{ K}
\]

1. Both systems have strong frustration: \( T_N \theta_{CW} \ll 1 \)
2. Do they have the same physics?
Nature of the Spin Liquid State in GF magnets

Emergence of Composite Spin Excitations

Spin fluctuations in the Spin liquid phase ($T > T_N$)

$\text{ZnCr}_2\text{O}_4$ (3d$^3$) and $\text{CdCr}_2\text{O}_4$ (3d$^3$) have the identical spin fluctuations in the spin liquid phase!
Composite Spin Excitations in ACr$_2$O$_4$

Spin liquid phase

$T > T_N$

The fundamental spin degree of freedom is an Antiferromagnetic hexagonal spin loop!
Nature of the **Phase Transitions** in GF magnets

**Spin-Lattice Couplings**

### Phase Transitions

**ZnCr$_2$O$_4$ (3d$^3$)**

*W. Ratcliff, S-W. Cheong (2000)*

- $\Theta_{CW} = -390$ K
- $T_N = 12.5$ K

**CdCr$_2$O$_4$ (3d$^3$)**

*M.T. Rovers (2002); H. Ueda (2005)*

- $\Theta_{CW} = -88$ K
- $T_N = 7.8$ K

1. Both systems have strong frustration: $T_N/\Theta_{CW} \ll 1$
2. Do they have the same physics?
Phase Transition due to Spin-Lattice coupling

$\text{ZnCr}_2\text{O}_4$ (3d$^3$)

$\text{W. Ratcliff, S-W. Cheong (2000)}$

$\Theta_{\text{CW}} = -390 \text{ K}$
$T_N = 12.5 \text{ K}$

**Contract**on along the c-axis ($c < a$)

**Commensurate** spin structure below $T_N$

**Spin-Peierls-like (spin-lattice) transition**

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**Why does tetragonal strain encourage Néel order?**

Edge sharing n-n exchange in $\text{ZnCr}_2\text{O}_4$ depends strongly on Cr-Cr distance, $r$:

\[
\begin{align*}
\frac{\text{d}J}{\text{d}r} &= 40 \text{ meV/Å} \\
\Delta J_\parallel &= \frac{\varepsilon_a + \varepsilon_c}{2} r_0 \frac{\text{d}J}{\text{d}r} = -0.04 \text{ meV} \\
\Delta J_\perp &= \varepsilon_a r_0 \frac{\text{d}J}{\text{d}r} = 0.06 \text{ meV}
\end{align*}
\]

The effects on a single tetrahedron is to make 4 bonds more AFM and two bonds less AFM. This relieves frustration!
Lattice distortions in CdCr$_2$O$_4$ at $T < T_N$

Single crystal diffraction
(4 0 0)$_{\text{cubic}}$

Elongation along the c-axis ($c > a$)

Phase Transitions due to Spin-Lattice Coupling

ZnCr$_2$O$_4$ (3d$^3$)

CdCr$_2$O$_4$ (3d$^3$)

Contraction along the c-axis ($c < a$)

Commensurate spin structure below $T_N$

Elongation along the c-axis ($c > a$)

Incommensurate spin structure below $T_N$
Spin Structure in the Tetragonal Phase of CdCr$_2$O$_4$

1. Incommensurate spin ordering with Q=(0,d,1)
2. Spins are lying on the ac-plane

Spin Fluctuations in the Neel Phase of CdCr$_2$O$_4$
Collaborators on $\text{ZnCr}_2\text{O}_4$, $\text{CdCr}_2\text{O}_4$

- **C. Broholm** (Johns Hopkins Univ.)
- **S-W. Cheong** (Rutgers Univ.)
- **J.-H. Chung** (NIST)
- **G. Gasparovic** (Johns Hopkins Univ.)
- **K.-P. Hong** (HANARO, KAERI, Korea)
- **Q. Huang** (NIST)
- **K. Kakurai** (JAERI, Japan)
- **T.H. Kim** (Ewha Woman’s Univ.)
- **Y.J. Kim** (University of Toronto)
- **M. Matsuda** (JAERI, Japan)
- **S. Park** (HANARO, KAERI, Korea)
- **W. Ratcliff** (Rutgers Univ., now at NIST)
- **T. Sato** (NIST, now at ISSP, U of Tokyo, Japan)
- **H. Ueda** (ISSP, U of Tokyo, Japan)

Summary

- Neutron scattering is the most powerful tool in magnetism
- Example: Neutron scattering studies on geometrically frustrated magnets $\text{ACr}_2\text{O}_4$ ($A=$Zn, Cd)
  1. Composite spin degrees of freedom
  2. Spin-Peierls-like phase transitions different in nature
- Modern neutron spectroscopy allows new science