Frustration Driven Lattice Distortion in $\text{Y}_2\text{Mo}_2\text{O}_7$

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Outline

- What is frustration? Why is it interesting?
- Why $Y_2Mo_2O_7$?
- Experimental results.
- Computer simulations-no temperature.
- Computer simulations-crystal “melting”.
- Conclusions.
Geometrical Frustration

- AF Hamiltonian and triangular geometry - not all near-neighbor spin interactions can be satisfied: FRUSTRATION.

$$H = \sum_{i,j} J_{ij} S_i \cdot S_j$$
The Heisenberg Hamiltonian

\[ H = \sum_{i,j} J_{ij} S_i \cdot S_j = \frac{J}{2} \sum_{i \in \nabla} \left( \sum_{i \in \nabla} S_i \right)^2 - \frac{J}{2} \sum_{i \in \nabla} \sum_{i} (S_i)^2. \]

- The only requirement for minimum of energy: \( \sum_{i \in \nabla} S_i = 0. \)
- The frustration is “shared” among bonds.
Heisenberg Hamiltonian on the Pyrochlore Lattice

- Infinite set of mean field ground states with zero net spin on all tetrahedra.
- Each tetrahedron has an independent degree of freedom in the ground state!
- No barriers between mean field ground states.
- Infinite degeneracy, no single ground state can be selected by Heisenberg Hamiltonian- lower-order terms become significant.
Is Exchange Constant?

\[ H = \sum_{ij} J_{ij} S_i \cdot S_j \]

- \( J_{ij} \) is controlled by higher energy physics that we like to consider irrelevant at low energies.
  - Atomic spacing
  - Orbital overlap
  - Orbital occupancy
  - Localized or itinerant electronic states
- These degrees of freedom can become relevant if \( H \) produces “degenerate” state.
- The lattice might distort, changing the value of the exchange, if the cost in elastic energy is smaller than the gain in magnetic energy.
Example - the kagome lattice
Suggestion for Relief of Degeneracy-Magnetoelastic Distortion

\[
H = \sum_{i,j} \left( (J + J' \delta r_{ij}) S_i \cdot S_j + \frac{k}{2} (\delta r_{ij})^2 \right)
\]

- \(k\) models the electrostatic potential near its minimum.
- \(J'\) is the change in the exchange integral with change in interatomic distance.
Theoretical Ground State, $T=0$

$$H = \sum_{i,j} \left( (J + J' \delta r_{ij}) S_i \cdot S_j + \frac{k}{2} (\delta r_{ij})^2 \right)$$

- Find minimal value of normal vibrational coordinates in the presence of magnetoelastic term $J' \delta r_{ij} S_i \cdot S_j$.
- Arrange distorted tetrahedrons on pyrochlore lattice.
- Net zero spin on each tetrahedron.

Tchernyshyov et al., PRB 66 (2002)
The q=0 State

- The minimum energy state for a single tetrahedron can be arranged on the pyrochlore lattice in one of two q=0 configurations.
- The q=0 distortion: tetrahedrons with identical orientation distort the same way.

Tchernyshyov et al., PRB 66 (2002)
The q=0 State-Characteristics

- $\frac{2}{3}$ strong (shortened) bonds,
- $\frac{1}{3}$ weak (lengthened) bonds,
- collinear spins
- $\frac{2}{3}$ bonds with antiparallel spins, $\frac{1}{3}$ bonds with parallel spins.
Searching for Frustration Driven Distortion
How will the system behave at $T \rightarrow 0$?

<table>
<thead>
<tr>
<th>Material</th>
<th>spin type</th>
<th>spin value</th>
<th>$\Theta_{CW}$ (K)</th>
<th>$T_c$ (K)</th>
<th>Low T phase</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>MgV$_2$O$_4$</td>
<td>isotrop.</td>
<td>1</td>
<td>-750</td>
<td>45</td>
<td>LRO</td>
<td>Baltzer et al '66</td>
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<td>Ueda et al '97</td>
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<td>CdCr$_2$O$_4$</td>
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<td>-350</td>
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<td>S.-H. Lee et al '99</td>
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<td>FeF$_3$</td>
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<td>5/2</td>
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<td>20</td>
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<td>Ferey et al. '86</td>
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<tr>
<td>Y$_2$Mo$_2$O$_7$</td>
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<td>-200</td>
<td>22.5</td>
<td>spin glass</td>
<td>Gingras et al. '97</td>
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<td></td>
<td>17</td>
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<td>Reimers et al '91</td>
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<td>Tb$_2$Mo$_2$O$_7$</td>
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<td>6 and 1</td>
<td></td>
<td>25</td>
<td>spin glass</td>
<td>Greedan et al '91</td>
</tr>
<tr>
<td>Gd$_2$Ti$_2$O$_7$</td>
<td>isotrop.</td>
<td>7/2</td>
<td></td>
<td>1</td>
<td>LRO</td>
<td>Radu et al '99</td>
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<tr>
<td>Er$_2$Ti$_2$O$_7$</td>
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<td></td>
<td>-25</td>
<td>1.25</td>
<td>LRO</td>
<td>Ramirez et al '99</td>
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<tr>
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<td></td>
<td>-19</td>
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<td>spin liquid?</td>
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<td>Dy$_2$Ti$_2$O$_7$</td>
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<td>7.5 → 1/2</td>
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<td>1.2</td>
<td>spin ice</td>
<td>Ramirez et al '99</td>
</tr>
<tr>
<td>Ho$_2$Ti$_2$O$_7$</td>
<td>Ising</td>
<td>8 → 1/2</td>
<td>1.9</td>
<td></td>
<td>spin ice</td>
<td>Harris et al '97</td>
</tr>
</tbody>
</table>

- We chose Y$_2$Mo$_2$O$_7$ as a candidate to look for frustration-driven distortion, since it is a spin glass, and we want to understand the origin of the disorder in this material.
Y$_2$Mo$_2$O$_7$ Characteristics

- Cubic pyrochlore $A_2B_2O_7$
- Magnetic ion Mo$^{4+}$, spin 1
- AF interaction, $\theta_{CW}=200$K, $J=\theta_{CW}/z \sim 33$K.
- Spin-Glass transition at 22.5K
Experimental Motivation: $Y_2Mo_2O_7$

- Booth et al., XAFS: the Mo tetrahedra are in fact disordered from their ideal structure, with a relatively large amount of pair distance disorder, in the Mo-Mo pairs and perpendicular to the Y-Mo pairs (2000).

- Keren & Gardner, NMR: many nonequivalent $^{89}Y$ sites, possibly stemming from a lattice distortion (2001).
Experimental Data

- DC magnetization.
- μSR.
- High resolution neutron diffraction.
**DC magnetization**

- Measure sample magnetization with moving sample magnetometer.
- Observe phase transition to spin-glass.

![Graph showing the phase transition](image)
What is \( \mu \text{SR} \)?

- 100% spin polarized muons.
- Muon life time: 2.2\( \mu \)sec.
- Positron emitted preferentially in the muon spin direction.
- Collect positrons, obtain distribution of muon spin orientations.
\[ N(t) = Bg + N_0 e^{-t/\tau_\mu} \left[ 1 + A_0 P(t) \right] \]
Muon Relaxation Mechanisms

- Relaxation caused by dynamical field fluctuations, consists of both longitudinal relaxation caused by fluctuations in the xy plane, and dynamical transverse relaxation caused by fluctuations in the z direction.

- Static relaxation, which is reversible. It is caused by field inhomogeneities in the sample $\Delta B$ which are responsible for dephasing in the xy plane.
The $\mu$SR Experiment

- TF $\mu$SR: measure both static and dynamic relaxation.
- LF $\mu$SR: measure dynamic relaxation.
- Simultaneous TF and LF measurements, $H=6000\,G$, $20^0K<T<240^0K$.

- Subtract LF relaxation from TF relaxation - obtain relaxation from static fields only $\rightarrow$ compare to magnetization.
μSR Data

\[ A(t) = A_0 \exp\left(- \left( R_{LF}t \right)^{1/2} \right) + Bg \]

- Relaxation increases as temperature is decreased.
- TF data displayed in rotating-reference-frame, \( H = 5600 \text{G} \).
\( P_{\text{static}}(t) = P_0 e^{-(\Delta t)^{1/2}} \cos(\omega t) \)

\[ \Delta = \left( R_{TF}^{1/2} - R_{LF}^{1/2} \right)^2 \]

\[ \omega = \gamma \mu H_{TF} \]

- \( \Delta \) increases exponentially fast with increasing \( \chi \).
What Does it Mean?

- The muon’s Hamiltonian:
  \[ H = \gamma_\mu I \cdot (H_{TF} + H_{int}) \]
  \[ H_{int} = A(r)S \]

- Mean field:
  \[ \langle S \rangle = M = \chi H \]

- Relaxation function measured by \( \mu \text{SR} \):
  \[ P(t) = \int P_0 \cos \left[ \gamma_\mu (1 + A \chi)H_{TF} \right] \rho(A) dA \]
  Evolution of polarization of a single muon
  Averaging over different muons

\( A \) - magnetic coupling
\( I \) - muon spin
\( S \) - electronic spin
We want the relation between what we measure in $\mu$SR and what happens in matter:

\[ P(t) = P_0 e^{-(\Delta t)^{1/2}} \cos(\omega t) \]

\[ e^{-(\Delta t)^{1/2}} = \int \cos(A \chi \gamma \mu H_{TF} t) \rho(A) dA \]

\[ \delta A = \left| \frac{\Delta}{\chi \gamma \mu H_{TF}} \right| \]

$\delta A$ represents the width of the distribution.

As the temperature is lowered, the ratio $\frac{\Delta}{\chi}$, and therefore $\delta A$, grows, and the distribution widens.
Conclusions from Magnetic Measurements:

⇒The change in the muon environment indicates that atoms shift!

⇒However...
No evidence for periodic rearrangement of the atoms, from μSR or neutrons.

Neutron scattering data for $\text{Y}_2\text{Mo}_2\text{O}_7$ show uniform shrinking of the unit cell with decreasing temperature.
Is something wrong with theory?

- Valid only for $T=0$; we’re not there yet...
- Only first order distortional terms were taken into account.
- Assumption of zero net spin on each tetrahedron; not necessarily true in the presence of a magnetoelastic distortion.
- $q=0$ is guessed to be the ground state; the guess might be wrong...
Investigating Further - Computer Simulations

- Energy minimization at $T=0$.
- Periodic boundary conditions for the spins, open for the coordinates, to allow for non-volume-preserving change of the unit cell.
- Structure inspection by Fourier transform and virtual neutron scattering.
- Slow temperature increase from $T=0$ to inspect structure of excited states.
Structure investigation

- Fourier transform:

\[ S(q) = \left| \sum_{j} e^{iq \cdot R_j} \right| \]

Undistorted pyrochlore lattice

- Magnetic neutron scattering:

\[ S(q) = \left| \sum_{\alpha, \beta} \left( \delta_{\alpha \beta} - q_{\alpha} q_{\beta} \right) \sum_{i, j} S^i_{\alpha} S^j_{\beta} \cos(q(R_i - R_j)) \right| \]
Finite Size Effects

- Simulation lattice size $\sim 10000$ atoms $<< 10^{23}$ atoms in real crystals.
- Examine how characteristic output values of the simulation are affected by lattice size.
- Determine simulation error from finite size effects.

![Graph showing the relationship between lattice size and E_{min/spin}](image-url)
Initial Conditions

- $q=0$ state - is it stable against energy minimization, or can a lower energy state be found?
- Undistorted lattice, random spin arrangement - what minimum energy state will be achieved?
Simulation Results

- The computer could not find a state with lower energy than the $q=0$ state.
- The divergence from linearity stems from non-harmonic effects.

$$E_{theory} = -\left( J + \frac{3}{2} \frac{J'^2}{k} \right)$$
Magnetic and non-Magnetic Scattering

Conclusions

- The q=0 initial and final states exhibit scattering peaks which are shifted relative to the undistorted lattice peaks; this indicates a shrinking of the entire lattice.

- In the q=0 final state, we see a split in the peak corresponding to the kagome-triangular interplane distance, which shows that atoms have moved in and out of planes.

- The final state obtained from a random initial state does not exhibit long range spin correlations, as can be seen from the absence of magnetic scattering peaks.
Near-Neighbor Spin-Spin Correlations

- The near-neighbor spin-spin correlations are similar to those characterizing the $q=0$ state.
- Zero net spin on each tetrahedron.

SiS\(_i\) distribution—initial random spin orientations.
Temperature

- Temperature was increased slowly from $T=0.000001\text{J}$ to $T=0.1\text{J}$, starting from the $q=0$ initial state.

- Magnetoelastic term $\rightarrow$ long range spin-spin correlations, lattice distortion.

- At $T=0.001\text{J}$, splitting is no longer distinguishable, whereas magnetic correlations persist.

- Magnetic probes such as $\mu$SR and NMR are expected to be more sensitive to the presence of the magnetoelastic term than nonmagnetic probes.
Lattice distortion

Spin-spin correlations

Fourier Transform

Magnetic Neutron Scattering
Conclusions

- We looked for the ground state of the pyrochlore lattice with magnetoelastic Hamiltonian, with the aid of computer simulations. We could not find a state with lower energy than the q=0 state, for J’/k<<1.

- The computer simulation showed that for J’/k<<1 the theoretical assumptions hold: zero net spin on each tetrahedron, 2/3 strong (shortened) bonds, 1/3 weak (lengthened) bonds, 2/3 bonds with antiparallel spins, 1/3 bonds with parallel spins.

- The simulation shows that the q=0 state is not distinguishable with non-magnetic probes above T=0.001J. For Y$_2$Mo$_2$O$_7$ this means T~0.03K.