Half-magnetization plateaux in Cr Spinels

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Moments and Multiplets in Mott Materials

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- Riken/CREST
Guide map of “simple” spinel oxides (after Takagi)

<table>
<thead>
<tr>
<th>charge frustration</th>
<th>(d^{0.5})</th>
<th>(d^{1.5})</th>
<th>(d^{2.5})</th>
<th>(d^{3.5})</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Li(\text{Ti}_2\text{O}_4)</td>
<td>Li(\text{V}_2\text{O}_4)</td>
<td>Al(\text{V}_2\text{O}_4)</td>
<td>Li(\text{Mn}_2\text{O}_4)</td>
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<tr>
<td></td>
<td>BCS SC</td>
<td>heavy fermion</td>
<td>charge ordered insulator</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>spin frustration (insulators)</th>
<th>(d^{1})</th>
<th>(d^{2})</th>
<th>(d^{3})</th>
<th>(d^{4})</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Mg(\text{Ti}_2\text{O}_4)</td>
<td>Zn(\text{V}_2\text{O}_4)</td>
<td>Zn(\text{Cr}_2\text{O}_4)</td>
<td>Zn(\text{Mg}_2\text{O}_4)</td>
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<tr>
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<td>valence bond crystal</td>
<td>Mg(\text{V}_2\text{O}_4)</td>
<td>MgCr(\text{O}_4)</td>
<td></td>
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<tr>
<td></td>
<td>crystal</td>
<td>Cd(\text{V}_2\text{O}_4)</td>
<td>CdCr(\text{O}_4)</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>spin+orbital ordering</td>
<td>spin driven structural phase transition</td>
<td></td>
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Where does the large magnetization plateau in Cr spinel compounds come from?

H. Ueda et al., PRL 94, 047202 (2005)

H. Mitamura et al., JPSJ 76, 085001 (2007)
Experimental evidence for frustrated AF interactions

\[
\chi \text{ (emu mol}^{-1}\text{)} \quad 1/\chi \text{ (emu} \text{ mol}^{-1})
\]

\[
T \text{ (K)}
\]

\[
\Theta \text{ (K)}
\]

<table>
<thead>
<tr>
<th></th>
<th>MgCr\textsubscript{2}O\textsubscript{4}</th>
<th>ZnCr\textsubscript{2}O\textsubscript{4}</th>
<th>CdCr\textsubscript{2}O\textsubscript{4}</th>
<th>HgCr\textsubscript{2}O\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_N\text{ (K)})</td>
<td>12.5</td>
<td>12</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>(\Theta\text{ (K)})</td>
<td>-370</td>
<td>-390</td>
<td>-70</td>
<td>-32</td>
</tr>
<tr>
<td>(T_N /</td>
<td>\Theta</td>
<td>)</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

From Antiferromagnet to Ferromagnet

\[M \text{Cr}_2X_4 (M = \text{Mg, Zn, Cd, Hg, } X = \text{O, S, Se})\]
Plateau is independent of the direction of magnetic field - anisotropy negligible

(though anisotropy may be relevant to explain some fine details observed in neutron and ESR [M Yoshida JPSJ 2006] experiments )
A brief introduction to Cr spinels

spinel $\text{ACr}_2\text{X}_4$
(space group $Fd-3m$)

octahedrally coordinated magnetic Cr-site

tetrahedrally coordinated nonmagnetic A-site
A brief introduction to Cr spinels

Spinel $A\text{Cr}_2X_4$

(space group $Fd-3m$)

Octahedrally coordinated magnetic Cr-site

Tetrahedrally coordinated nonmagnetic A-site

Cr-sublattice: pyrochlore lattice
O^{2-} (2p^2)

Microscopic structure

in cubic crystal field:

\[ d \quad e_g \quad Cr^{3+} \quad t_{2g} \]

S=3/2, no orbital degrees of freedom

Typeset by FoilTEX – 2
Microscopic structure

in cubic crystal field:

\[ d \quad t_{2g} \quad Cr^{3+} \quad e_g \]

\[ S = \frac{3}{2}, \text{no orbital degrees of freedom} \]

minimal magnetic model:

\[ H = J \sum_{\langle i,j \rangle} S_i S_j \]

on pyrochlore lattice
Classical AF on pyrochlore lattice

Energy is a sum of squares:

\[ \mathcal{H} = J \sum S_i S_j \]
\[ = \frac{J}{2} (S_1 + S_2 + S_3 + S_4)^2 + \ldots \]
\[ = 4J \sum_{\text{tet.}} M^2 \]

Ground state manifold on a single tetrahedron defined by \( M = 0 \)

Due to the residual degeneracy the system remains disordered [Moessner & Chalker, (1998)].
Classical ground state manifold in applied field (T=0)

\[ H = 8J \sum_{\text{tetr.}} M^2 - 2 \sum_{\text{tetr.}} hM = 8J \sum_{\text{tetr.}} \left( M - \frac{h}{8J} \right)^2 - \sum_{\text{tetr.}} \frac{h^2}{8J} \]

GS if \( = 0 \)

For each tetrahedron, require: \( M = \frac{h}{8J} \)

Ground state degeneracy survives and magnetization is linear up to saturation.
finite $T$: order by disorder scenario does not work

Simple MC simulations of classical pyrochlore model

MC simulations of classical kagome model

[Zhitomirsky, PRL 88, 057204 (2002)]

Thermal fluctuations do not stabilize a collinear state (plateau)

What is missing?
magnetoelastic coupling: h=0

magnetic ordering accompanied with a structural transition:

![Graph showing magnetic ordering and structural transition](image)

**Figure:**
- CdCr$_2$O$_4$: $T_N = 7.8$ K
- ZrCr$_2$O$_4$: $T_N = 12.5$ K

**Sources:**
- H. Ueda et al., PRB 73, 094415 (2006)
- J-H Chung et al., PRL 95, 247204 (2005)
magnetoelastic coupling: $h > 0$

strong magnetostriction entering the plateau phase:

H. Ueda et al., PRL 94, 047202 (2005)
Coupling to lattice distortions for $h=0$


$Y_{2M_2O_7}$: Keren & Gardner PRL **87**, 177201 (2001)


In a single tetrahedron of $S=1/2$ spins ground state 2x degenerate, $E$ irrep. Coupled tetrahedra: VBS-like theory of $ZnV_2O_4$

Tchernyshyov, Moessner, & Sondhi, PRL **88**, 067203 (2002):

“Order by Distortion”

Landau-like theory of the spin-Peierls mechanism in the $E$ irrep.
How does lattice distortion affect magnetic order?

spin exchange
depends on distance:

\[ J(r) = J(r_0) + \frac{\partial J}{\partial r} \bigg|_{r_0} \delta r = J(1 + \alpha \rho) \]

Consider generalized “spin-Peierls” Hamiltonian:

\[ \mathcal{H} = \sum_{\langle i,j \rangle} \left[ J(1 - \alpha \rho_{i,j}) S_i S_j + \frac{K}{2} \rho_{i,j}^2 \right] - \hbar \sum_i S_i \]

- the elastic energy is quadratic - we can integrate it out:
- it leads to long range spin-spin effective interaction
- for realistic description we shall take realistic phonon modes
- we want to understand the basic mechanism, so we look at the simplest case (affine deformations)
Minimal symmetry breaking solution

The four-sublattice ordering does not break the translational symmetry (uniform $q=0$ distortions). The point group symmetry is broken.

The four-sublattice ordering can be stabilized e.g. by AF $J_2$ or FM $J_3$.

full point group is $O_h = T_d \times \{1,I\}$

site-factorized wave function is invariant under inversion $I$

$\Rightarrow$ only $T_d$ remains
Minimizing the energy of a tetrahedron (4LRO state)

The ground state problem is reduced to pure spin energy (assuming 4 sublattice LRO):

\[ \mathcal{H} = \sum_{\langle i,j \rangle} J \left[ S_i S_j - b(S_i S_j)^2 \right] - h \sum_i S_i \]

favours collinear spin configurations!

T=0 classical

\[ H = \sum_{\langle i,j \rangle} J \left[ S_i S_j - b(S_i S_j)^2 \right] - h \sum_i S_i \]
Irreps of tetrahedral symmetry group Td:

\[
\begin{pmatrix}
\rho_{A_1} \\
\rho_{E,1} \\
\rho_{E,2} \\
\rho_{T_2,1} \\
\rho_{T_2,2} \\
\rho_{T_2,3}
\end{pmatrix} =
\begin{pmatrix}
\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} \\
\frac{1}{\sqrt{3}} & \frac{1}{2\sqrt{3}} & \frac{1}{2\sqrt{3}} & \frac{1}{2\sqrt{3}} & \frac{1}{2\sqrt{3}} & \frac{1}{\sqrt{3}} \\
0 & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & 0 \\
0 & 0 & -1 & 1 & 0 & 0 \\
0 & -\frac{1}{\sqrt{2}} & 0 & 0 & \frac{1}{\sqrt{2}} & 0 \\
-\frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 & \frac{1}{\sqrt{2}}
\end{pmatrix}
\begin{pmatrix}
\rho_{1,2} \\
\rho_{1,3} \\
\rho_{1,4} \\
\rho_{2,3} \\
\rho_{2,4} \\
\rho_{3,4}
\end{pmatrix}
\]

\[
\begin{align*}
A_1 & \quad E & \quad T_2 \\
1 \text{ dim.} & \quad 2 \text{ dim.} & \quad 3 \text{ dim.}
\end{align*}
\]
The phase diagram

Irreps of the tetrahedral group $T_d$

cubic symmetry restored

trigonal lattice distortion

tetragonal lattice distortion

$PRL$ 93, 197203 (2004)
Why are these particular phases stable?

Irreps of tetrahedral symmetry group $Td$:

$$
\begin{pmatrix}
\Lambda_A \\
\Lambda_{E,1} \\
\Lambda_{E,2} \\
\Lambda_{T_2,1} \\
\Lambda_{T_2,2} \\
\Lambda_{T_2,3}
\end{pmatrix}
\begin{pmatrix}
\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} \\
\frac{1}{\sqrt{3}} & -1 & -1 & -1 & -1 & -1 \\
0 & \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & 2 & 2 \\
0 & 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 & 0 \\
0 & -\frac{1}{\sqrt{2}} & 0 & 0 & \frac{1}{\sqrt{2}} & 0 \\
-\frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 & \frac{1}{\sqrt{2}}
\end{pmatrix}
\begin{pmatrix}
\vec{S}_1 \cdot \vec{S}_2 \\
\vec{S}_1 \cdot \vec{S}_3 \\
\vec{S}_1 \cdot \vec{S}_4 \\
\vec{S}_2 \cdot \vec{S}_3 \\
\vec{S}_2 \cdot \vec{S}_3 \\
\vec{S}_3 \cdot \vec{S}_4
\end{pmatrix}
$$

In terms of these, the Hamiltonian reads:

$$
\mathcal{H} = 2\sqrt{6}J\Lambda_A - 2\alpha J \left(\Lambda_A \rho_A + \Lambda_E \rho_E + \Lambda_{T_2} \rho_{T_2}\right) + K \left(\rho_A^2 + \rho_E^2 + \rho_{T_2}^2\right) - 4hM
$$

Eliminating the distances:

$$
E = 2J \left(\sqrt{6}\Lambda_{A_1} - b_{A_1} \Lambda_{A_1}^2 - b_E \Lambda_{E}^2 - b_{T_2} \Lambda_{T_2}^2\right) - 4hM
$$
Why are these particular phases stable?

Surface of maximal values of second order invariants

Minimize energy as a function of $M$ and look to see which irrep wins.

\[ E = 2J \left( \sqrt{6} \Lambda_{A_1} - b_{A_1} \Lambda_{A_1}^2 - b_E \Lambda_E^2 - b_{T_2} \Lambda_{T_2}^2 \right) - 4hM \]
cusp $\Rightarrow$ stable plateau with $T_2$ symmetry

Energy as a function of magnetization:

\[ E = E_0 - 4hM \]

where $E_0 = 2J \left( \sqrt{6} \Lambda_{A_1} - b_{A_1} \Lambda_{A_1}^2 - b_E \Lambda_E^2 - b_{T_2} \Lambda_{T_2}^2 \right)$.
Local instability of collinear states

\[ E = 2J \left( \sqrt{6} \Lambda A_1 - b A_1 \Lambda^2 A_1 - b E \Lambda^2 E - b T_2 \Lambda^2 T_2 \right) - 4hM \]

\( \text{J. Phys.: Condens. Matter 19, 145267 (2007).} \)
Magnetization curve and b’s

\[ \Delta h_2 = \frac{8J}{3} (3bT_2 - b_{A_1} - 2b_E) \]

\[ \Delta h_1 = \frac{16J}{3} (b_{A_1} + b_{T_2}) \]

\[ h_u = 4J (1 + 2b_{T_2}) \]
Back to spinels

In the real material (HgCr$_2$O$_4$, Matsuda et al., Nature Physics 3, 397 (2007)), the plateau state is not a 4 sublattice, but a more complicated, 16 sublattice state.

Einstein model incorporating local site distortions can lead to 16 sublattice plateau state.

**Exchanges**: Longer range exchanges can also select the 16 sublattice state.

Magnetoelastic coupling does not lead necessarily to plateau: in ZnCr$_2$Se$_4$ magnetostriction, but M linear up to saturation (Hemberger et al., PRL 98, 147203 (2007)).
Monte Carlo Results at finite $T$
(biquadratic effective model)

half-magnetization plateau survives at finite temperatures

$m$

$b=0.1$
$J_3=-0.05$

$\chi$

$T=0$
$T=0.08$
$T=0.16$
$T=0.24$
$T=0.32$
$T=0.40$

Order Parameters - I

How to distinguish two $T_2$ phases?
nematic order parameter, measures coplanarity:

\[ Q^{x^2-y^2} = \langle S^x S^x - S^y S^y \rangle \]
\[ Q^{xy} = \langle 2S^x S^y \rangle \]
Phase Diagram at Finite $T$
Comparison with Experiments

HgCr$_2$O$_4$

H. Ueda et al., unpublished
Liquid plateau

- Liquid plateau
- T* for local order
- Tc for LRO
- gapped phase (LRO)
- pseudo gap
- T*(c)
- local T2
- Tc for LRO
- "plateau solid"
- "plateau liquid"
- magnetization plateau survives

Coulomb phase in the disordered plateau?
Phase Diagram for $J_3=0$

- 2:2 E-symmetry in each tetrahedron
- Macroscopic degeneracy
- Spin nematic order
- Power-law decay of spin correlation

- Spin nematic
- Spin-liquid plateau
- Spin pseudo-gap

- $T^*$ (crossover)
  - Broad peak of specific heat
  - No symmetry breaking

- 3up-1down $T_2$ symmetry in each tetrahedron
- Macroscopic degeneracy
- Robust plateau
Phase diagram for \( b = 0 \): order by disorder revisited

\[
\Delta \mathcal{F} \sim -\frac{T}{J_3} (S_i S_j)^2
\]

H. Kawamura and S. Miyashita, 1985

M. Zhitomirsky, 2002
Conclusions

- Coupling to lattice distortions provides a very efficient mechanism for magnetization plateaux in frustrated and degenerate AF’s.
- The phase diagram and order parameters determined.
- Plateau can survive without long range order.
- At finite $T$: order-by-disorder possible with some help.