Frustrated Magnets (3) 
Materials Survey 

Leon Balents 
Boulder summer school, 2008
Recent Collaborators

Doron Bergman  
Gang Chen  
Sungbin Lee  
Miles Stoudenmire  
Jason Alicea  
Ryuichi Shindou  
Andreas Schnyder  
Yong-Baek Kim  
Arun Paramekanti  
Michael Lawler  
Lucile Savary

Simon Trebst  
Emmanuel Gull  
Oleg Starykh  
Masanori Kohno
What do we look for?

- Is it an insulator?
- Is it a magnet? Curie law
- Signs of frustration
  - $f \gg 1$
    - $\Theta_{CW}(\chi)$
    - $T_N$: signs of transition in $\chi$, $C_v$, ...
  - low T entropy, low energy excitations
    - $C_v$, $1/T_1$, ...
- Identify the states
  - nature of correlations?
  - ordering if it occurs
- Compare with some theoretical expectations
\( \text{AB}_2\text{X}_4 \) spinels

- One of the most common mineral structures
- Common valence:
  - \( \text{A}^{2+}, \text{B}^{3+}, \text{X}^{2-} \)
  - \( \text{X}=\text{O}, \text{S}, \text{Se} \)

![cubic Fd\bar{3}m structure](image)
Deconstructing the spinel

- A atoms: diamond lattice
- Bipartite: not geometrically frustrated
Deconstructing the spinel

- B atoms: pyrochlore
- Decorate the plaquettes of the diamond lattice
ACr$_2$O$_4$ spinels

- pyrochlore lattice
- $S=3/2$ Isotropic moment
- $X=O$ spinels: B-B distance close enough for direct overlap
- dominant AF nearest-neighbor exchange
H=0 Susceptibility

Frustration:

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Cd</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Theta_{CW}$ (K)</td>
<td>-390</td>
<td>-70</td>
<td>-32</td>
</tr>
<tr>
<td>$T_N$ (K)</td>
<td>12</td>
<td>7.8</td>
<td>5.8</td>
</tr>
<tr>
<td>$f$</td>
<td>33</td>
<td>9</td>
<td>6</td>
</tr>
</tbody>
</table>

H. Ueda et al
Degeneracy

- Heisenberg model

\[ H = \sum_{i,j} \vec{S}_i \cdot \vec{S}_j = \frac{1}{2} \sum_t \left( \sum_{i \in t} \vec{S}_i \right)^2 + \text{const.} \]

- Ground state constraint: total spin 0 per tetrahedron

- Quantum mechanically: not possible
Classical spin liquid

No LRO (Reimers)
Classical spin liquid

- No LRO (Reimers)
- Dipolar correlations
  (Youngblood+Axe,Henley, Isakov et al...)

\[ S_i^\mu = b_{ab}^\mu \]
Classical spin liquid

- No LRO (Reimers)
- Dipolar correlations

\[ S^\mu_i = b^\mu_{ab} \]
Classical spin liquid

- Unusual “ring” correlations seen in CdCr$_2$O$_4$ related
- Y$_2$Ru$_2$O$_7$: J. van Duijn et al, 2007

Broholm et al
Ordering

Many perturbations important for ordering:
- Spin-lattice coupling
- Further exchange
- Spin-orbit effects
- Quantum corrections

ZnCr$_2$O$_4$
CdCr$_2$O$_4$
HgCr$_2$O$_4$

S.H. Lee + many others

JH Chung et al, 2005
Magnetization Plateaus

Classically: $M = M_s \ H / H_s$

Plateau indicates 3:1 structure

H. Ueda et al, 2005/6
Magnetization Plateaus

Plateau mechanism:
- spin-lattice coupling favors collinearity

Order on plateau may be selected by
- spin-lattice
- quantum effects

"R" state observed in neutrons

Matsuda et al
A-site spinels

Spectrum of materials

$\text{CoRh}_2\text{O}_4$  $\text{Co}_3\text{O}_4$  $\text{MnSc}_2\text{S}_4$  $\text{FeSc}_2\text{S}_4$  $\text{MnAl}_2\text{O}_4$  $\text{CoAl}_2\text{O}_4$

$s = 5/2$  $s = 3/2$  $s = 2$

Orbital degeneracy

$T = \frac{\Theta_{\text{CW}}}{f}$

Naively unfrustrated

V. Fritsch et al. PRL 92, 116401 (2004); N. Tristan et al. PRB 72, 174404 (2005); T. Suzuki et al. (2006)
Why frustration?

- Roth, 1964: 2nd and 3rd neighbor exchange not necessarily small
- Exchange paths: A-X-B-X-B comparable
- Minimal model
- $J_1$-$J_2$ exchange
Ground state evolution

- Coplanar spirals
- Spiral surfaces:

- Neel
- \(J_2/J_1\)

- \(J_2/J_1 = 0.2\)
- \(J_2/J_1 = 0.4\)
- \(J_2/J_1 = 0.85\)
- \(J_2/J_1 = 20\)
Monte Carlo

\[ f = 11 \text{ at } J_2/J_1 = 0.85 \]

\[ \text{MnSc}_2\text{S}_4 \]
Entropy and $J_3$ compete to determine ordered state

Spiral spin liquid regime has intensity over entire spiral surface
Comparison to Expt.

- Diffuse scattering
- Ordered state
- (qq0) spiral
- Specific heat?

A. Krimmel et al., 2006

agrees with theory for FM $J_1$
**Cs$_2$CuCl$_4$**

- Spatially anisotropic triangular lattice
- Cu$^{2+}$ spin-1/2 spins

\[
H = \frac{1}{2} \sum_{i,j} \left[ J_{ij} \vec{S}_i \cdot \vec{S}_j - \vec{D}_{ij} \cdot (\vec{S}_i \times \vec{S}_j) \right]
\]

- couplings:
  - $J = 0.37 \text{meV}$
  - $J' = 0.3J$
  - $D = 0.05J$

R. Coldea et al
Neutron scattering

Coldea et al, 2001/03: a 2d spin liquid?

Very broad spectrum similar to 1d (in some directions of k space). Roughly fits power law.

Fit of “peak” dispersion to spin wave theory requires adjustment of J,J’ by 40% - in opposite directions!
Dimensional reduction?

- Frustration of interchain coupling makes it less "relevant"
- First order energy correction vanishes

Leading effects are in fact $O[(J')^4/J^3]$!
Dimensional reduction?

- Frustration of interchain coupling makes it less "relevant"
- First order energy correction vanishes.
- Numerics: $J'/J < 0.7$ is "weak"

Weng et al, 2006

Very different from spin wave theory

Very weak inter-chain correlations
Excitations

Build 2d excitations from 1d spinons

Exchange: \( \frac{J'}{2} (S_i^+ S_j^- + S_i^- S_j^+) \)

Expect spinon binding to lower inter-chain kinetic energy

Use 2-spinon Schroedinger equation
Broad lineshape: “free spinons”

- “Power law” fits well to free spinon result
- Fit determines normalization

\[ J'(k) = 0 \text{ here} \]
Bound state

Compare spectra at $J'(k)<0$ and $J'(k)>0$:

- Curves: 2-spinon theory w/ experimental resolution
- Curves: 4-spinon RPA w/ experimental resolution

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- $k'_x = -\pi/2$
- $k'_y = 2\pi$
- $J'(k)<0$

- $k'_x = -\pi/2$
- $k'_y = 4\pi$
- $J'(k)>0$

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- CVares24spinorthoRPAw/experimentalresolution
Transverse dispersion

Bound state and resonance

Solid symbols: experiment
Note peak (blue diamonds) coincides with bottom edge only for $J'(k)<0$
Spectral asymmetry

Vertical lines: $J'(k) = 0$. 
Quantum Spin Liquids
Ultimate frustration?

- Can quantum fluctuations prevent order even at T=0: f=∞?
- Many theoretical suggestions since Anderson (73)
- “Resonating Valence Bond” QSL states

\[ \Psi = \text{Diagram} + \text{Diagram} + \ldots \]
Search for QSLs

- Where do we look?
  - Spin-1/2 frustrated magnets
  - Intermediate correlation regime (near the Mott transition)
Search for QSLs

- $1/f = T_c = 0$: no ordering (magnetic or otherwise!)
- No spin freezing (hysteresis, NMR, μSR)
- Structure of low energy excitations
  - $\chi(T), C_v(T), 1/T_1$, inelastic neutrons
  - theoretical guidance helpful!
- Smoking gun?
QSL Family Tree

- **U(1) states**
  - spinons unpaired
  - strong gauge fluctuations
  - spinons must be gapless in \( d=2 \)
  - stable in \( d=3 \) at \( T=0 \) only

- **\( Z_2 \) states**
  - spinons paired
  - weak gauge fluctuations
  - stable in \( d=2 \)
  - \( T>0 \) Ising transition in \( d=3 \)
A diagnostic flowchart

Dimension?

Spin gap?

yes

Z\textsubscript{2} state

no

C\textsubscript{v}?

T\textsuperscript{2/3}

T

U(1) FS

Z\textsubscript{2} dirty Dirac

Z\textsubscript{2} Dirac

R\textsubscript{W} = 1?

yes

no

U(1) Dirac ASL
A diagnostic flowchart

- **T > 0 transition**
  - **d = 2**
  - Spin gap? yes
  - Spin gap? no
    - **U(1)** FS
    - **U(1) ??**
  - **T ln(1/T)**

- **Z₂. Spin gap?**
  - no
    - **Cᵥ?**
      - T
      - T²
    - **Z₂ FS**
    - **Z₂ line node**
  - yes
    - **Cᵥ?**

- **d = 3**
  - **U(1) FS**
  - **U(1) ??**
  - **Cᵥ?**
  - **Z₂**

- **disordered possibilities neglected**
QSL candidates

- NiGa$_2$S$_4$ - spin 1 triangular lattice
- \( \kappa-(\text{BEDT-TTF})_2\text{Cu}_2\text{(CN)}_3 \) - triangular lattice organic
- EtMe$_3$Sb[\text{Pd(dmit)}_2]$_2$ - triangular lattice organic
- Na$_4$Ir$_3$O$_8$ - hyperkagome
- ZnCu$_3$(OH)$_6$Cl$_2$ - kagome
K-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

- Organic
- $S=1/2$ triangular lattice
- Nearly isotropic Hubbard-like with $t'/t = 1.06$
  K. Kanoda group
**K-(BEDT-TTF)$_2$Cu$_2$(CN)$_3**

- Material is proximate to a Mott transition
- Non-activated transport
- Optical pseudogap

![Phase diagram](image-url)
\( \kappa-(\text{BEDT-TTF})_2 \text{Cu}_2(\text{CN})_3 \)

- Susceptibility similar to Heisenberg triangular lattice
- \( \chi(T=0) \) finite
- No ordering
$\kappa-(\text{BEDT-TTF})_2\text{Cu}_2(\text{CN})_3$

- No $^1\text{H}$ NMR line splitting down to 32 mK - no internal fields
- No ordering
$\kappa-(\text{BEDT-TTF})_2\text{Cu}_2(\text{CN})_3$

$1/T_1$ relaxation rate power law at low temperature indicating gapless excitations

Low-lying spin excitation
\( \kappa-(\text{BEDT-TTF})_2\text{Cu}_2(\text{CN})_3 \)

- Linear specific heat
- \( \gamma=15\text{mJ/K}^2\text{ mol} \)
- Field independent
- Wilson ratio \( T \propto \gamma \) is \( O(1) \)

![Graph showing heat capacity vs. temperature squared for different fields.](image-url)
Interpretation?

- Theoretical suggestion (Motrunich) – U(1) spin liquid with spinon Fermi surface
- Good variational energy for triangular lattice Hubbard model
- Large susceptibility ✔
- Linear specific heat ☹
  - theory predicts $C_V = AT^{2/3}$
- Spinon pairing?
  - features visible around $T=5K$. related?
$\kappa-(\text{BEDT-TTF})_2\text{Cu}_2(\text{CN})_3$

- $^{13}$C NMR: line broadening at low temperature in a field indicates inhomogenous AF moments induced by field.
EtMe$_3$Sb[Pd(dmit)$_2$]$_2$

another organic triangular lattice
Mott insulator!

R. Kato group
**EtMe$_3$Sb[Pd(dmit)$_2$]$_2$**

- Susceptibility very similar to κ-(ET)
- No line broadening from static moments
ZnCu$_3$(OH)$_6$Cl$_2$

Cu and Zn can "invert"

Herbertsmithite - a 2d s=1/2 kagome antiferromagnet

D. Nocera, Y.S. Lee groups
ZnCu₃(OH)₆Cl₂

- Upturn of $\chi$ below 50K, probably due to defect spins
- Curie-Weiss temperature $\Theta_{CW} \approx -240K$ from $^{35}$Cl NMR, $\Theta_{CW} \approx -300K$ from $\chi$
- No order down to $T=50mK$

T. Imai et al
**ZnCu_{3}(OH)_{6}Cl_{2}**

- Specific heat is dominated by magnetic contribution below only \( \approx 1 \text{K} \)
- This appears roughly power law \( C \sim T^{\alpha} \) with \( \alpha = 0.5-1 \)
- Indicates many low energy excitations
ZnCu$_3$(OH)$_6$Cl$_2$

- Evidence of gapless spin excitations:
  - low-energy $\chi''(E)$ in neutrons
  - Similar behavior observed in $1/T_1 \propto T \chi''(0^+,T)$
Theory

- U(1) Dirac ASL proposed (Y. Ran, M. Hermele et al)
  - Predicts $\chi \sim T$, $C_v \sim T^2$ in pure system
  - Can be reconciled to $\chi \sim \text{const}$, $C_v \sim T$ by impurities
- A large concentration of 5-10% of disorderd inverted Zn and Cu ions makes interpretation difficult
Na$_4$Ir$_3$O$_8$

- An “hyperkagome” lattice of Ir$^{4+}$ spins
- Expect S=1/2 spin state - orbital state unclear?

Ir$^{4+}$

$\uparrow \uparrow \uparrow$

$\downarrow \downarrow \downarrow$

$t_{2g}$

5d$^5$; S = 1/2

Takagi group
Na$_4$Ir$_3$O$_8$

- Susceptibility
  - Curie-Weiss temperature $\Theta_{CW} \approx -650$K
  - Large $\chi$ at low T
  - $\mu_{\text{eff}} = 1.96 \mu_B/\text{Ir} \approx 1.73 \mu_B/\text{Ir}$ (s=1/2)
- Consistent with Knight shift
- low-T upturn not seen in K: extrinsic
Na$_4$Ir$_3$O$_8$

- Specific Heat
- broad peak around 30K
- power-law (between $T$ and $T^2$)
- at low $T$ indicates many low energy excitations
\( \text{Na}_4\text{Ir}_3\text{O}_8 \)

- NMR \( 1/T_1 \) rate is power law for \( 50 < T < 200 \), suggestive of low energy excitations
**Na$_4$Ir$_3$O$_8$**

- Transport
  - Mott insulator
  - but...close to a Mott transition
- Perhaps this proximity may be important
Heavy Ir (Z=77) has strong spin-orbit
expect $j=1/2$ spin with $g=-2$
Hamiltonian may be Heisenberg plus
Dzyaloshinskii-Moriya corrections
Probably explains large $\chi(T=0)$
Large size differences between Na, Ir, O
suggests little disorder
Gapless specific heat suggests gapless
spinons
Two QSL proposals can roughly fit specific
heat but both have some difficulties
Perhaps resolved by itinerancy?
Conclusions

- Frustrated magnets provide a rich variety of phenomena including a number of promising new quantum spin liquid candidates.

- For QSLs, what is needed is a combined effort of innovative experimental and theoretical work, with attention of the latter paid to the former!