Quantum Liquid Produced by Geometrical Frustration in Spinel Oxides

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Collaborators

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Discussion: D. Khomskii (Koln), R. Arita (RIKEN)
Spinel oxide: $\text{AB}_2\text{O}_4$

(cubic: Fd3m) "B-sublattice"

AO$_4$ BO$_6$

Spinel oxide: AB$_2$O$_4$

corner-shared tetrahedra

S=0

More than one way to make it.

3$^+$

4$^+$

4$^+$

3$^+$

two 3$^+$

Two 4$^+$
total charge constant/tetrahedron

$\rightarrow$ geometrical frustration
Geometrical frustration in ice

$O - H - O$

$O - H - O$

H: pyrochlore lattice

O: Inside H tetrahedron

Macroscopic degeneracy remains

$S = 1/2 \ln 3/2$ per hydrogen

Pauling
What do we expect for spinel related oxides?

Strongly degenerate low lying excitations originating from geometrical frustration

- liquid state of spin, charge and (perhaps) orbital
  (liquid crystal?)

Nature always tries to suppress the degeneracy
couple with lattice, orbital, itinerant carriers

- Exotic Phase (transition)?
  how to lift the degeneracy
  self organization of spins, charges, orbitals
  sensitive to perturbation: gigantic response
Geometrically Frustrated Lattices

New candidate emerges for a quantum spin liquid

A newly synthesized mineral is perhaps the most promising material yet to realize a hypothetical state with exotic behavior.

The discovery of high-$T_c$ superconductivity renewed interest in spin liquids because copper oxide materials are antiferromagnetic insulators before they are doped to become superconductors. Anderson and others have used the concept of a resonating-valence-bond, which underlies the prediction of a spin-liquid state, to try to explain the behavior of various materials.

At MIT were able to synthesize a rare mineral known as herbertsmithite. The small amounts found in nature are not sufficiently pure. It's a member of the paratacamite family characterized by the formula $Zn_{x}Cu_{1-x}(OH)_{6}Cl_{2}$, where $x = 1$ for herbertsmithite. As pictured in figure 2 and confirmed by crystallography, the spin-$\frac{1}{2}$ copper atoms form a helical lattice.

The 3D pyrochlore lattice is one of the most studied geometrically frustrated lattices. It is a wide variety of materials, most popular oxide structure.

$\text{SrCr}_9\text{Ga}_3\text{O}_{19}$, $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$

$\text{NiGa}_2\text{S}_4$, $3\text{He}$

$\text{NaxCoO}_2$, $\text{NaTiO}_2$

$\text{Fe}_3\text{O}_4 = \text{FeFe}_2\text{O}_4$

$\text{Y}_2\text{Mo}_2\text{O}_7$

$\text{Pyrochlore}(A_2B_2O_7)$

$\text{Spinel (}AB_2O_4\text{)}$

Physics Today Feb 2007
Progress in searching for new spinel oxides and exotic spin, charge orbital states at RIKEN/Tokyo

Spin liquid ground state in Na$_4$Ir$_3$O$_8$ with hyper-Kagome lattice (ordered spinel)

new compound

PRL 99 137207 (07)

Charge frustration & heavy fermion formation in mixed valent LiV$_2$O$_4$ (1:1 V$^{3+}$ & 4+) spinel
charge analogue of spin liquid
strong electron correlations in the presence of frustration

PRL99 167402 (07)

Orbital & charge ordering in mixed valent spinel LiRh$_2$O$_4$

new compound

And more, , , , ,

LiVS$_2$, Hg$_2$Ru$_2$O$_7$
Spin liquid ground state in $\text{Na}_4\text{Ir}_3\text{O}_8$ with hyper-Kagome (ordered spinel) lattice

Okamoto, Nohara, Katori & Takagi PRL 99 137207 (07)

Searched for Ir spinel
After struggle, by chance found $\text{Na}_4\text{Ir}_3\text{O}_8$ closely related to spinel

$\text{Na}_4\text{Ir}_3\text{O}_8$: cubic $P4_132$, $a = 8.985$ Å

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$g$</th>
<th>$B(\text{Å})$</th>
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<td>Ir</td>
<td>12d</td>
<td>0.61456(7)</td>
<td>$x + 1/4$</td>
<td>5/8</td>
<td>1.00</td>
<td>0.15</td>
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<tr>
<td>Na1</td>
<td>4b</td>
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<td>7/8</td>
<td>7/8</td>
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<tr>
<td>Na2</td>
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<td>3/8</td>
<td>3/8</td>
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<tr>
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<td>0.3581(8)</td>
<td>$x + 1/4$</td>
<td>5/8</td>
<td>0.75</td>
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<td>O1</td>
<td>8c</td>
<td>0.118(11)</td>
<td>$x$</td>
<td>$x$</td>
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<tr>
<td>O2</td>
<td>24e</td>
<td>0.1348(9)</td>
<td>0.8988(8)</td>
<td>0.908(11)</td>
<td>1.00</td>
<td>0.6</td>
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</table>
**Na₄Ir₃O₈: Ir⁴⁺ oxide with hyper-kagome structure**

B-cation ordered spinel

2 \((\text{Na}^{3/2})_1 \text{(Ir}^{3/4}, \text{Na}^{1/4})_2\text{O}_4\)

Na₄Ir₃O₈: cubic \(P4_132\), \(a = 8.985\) Å

Isostructural to \(\text{Na}_4\text{Sn}_3\text{O}_8\)

B-site
\(\frac{3}{4}: \text{Ir}, \frac{1}{4}: \text{Na}\)

Cation ordering

Closely related to garnet

\(\text{Ir}^{4+}\)

"hyper-Kagome" frustration

5d⁵; \(S = 1/2\)
Hyperkagome (ordered spinel) lattice has “chirality”
**Na$_4$Ir$_3$O$_8$ S=1/2 Mott Insulator with AF interaction**

Ir$^{4+}$

$S = 1/2$

5d$^5$

<table>
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<tr>
<th>$T$ (K)</th>
<th>$\rho$ (Ωcm)</th>
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<tr>
<td>0</td>
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<tr>
<td>200</td>
<td>10$^4$</td>
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<tr>
<td>300</td>
<td>10$^3$</td>
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</table>

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\chi$ (10$^{-3}$emu/mol Ir)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>100</td>
<td>0.8</td>
</tr>
<tr>
<td>200</td>
<td>0.6</td>
</tr>
<tr>
<td>300</td>
<td>0.4</td>
</tr>
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</table>

$\mu_{\text{eff}} = 1.96 \mu_B / \text{Ir}$

$J \sim 400$K estimated

$\theta_w = -650$ K

Strong AF int. ($S = 1/2 \rightarrow 1.73 \mu_B$)

No ordering in $\chi$ down to 1.8 K << $\theta_{cw} = 650$K

Strong frustration

Spin liquid?
$^{23}\text{Na}$ NMR indicates absence of magnetic ordering down to 2 K - evidence for spin liquid

$\chi(T) \rightarrow$ constant at $T=0$ limit

gapless

Fujiyama, Kanoda
Power law decay of nuclear spin-lattice relaxation rate

S. Fujiyama, K. Kanoda

No $1/T_1$ divergence down to 2K
no ordering and freezing!

$1/T_1$ constant above
$T \sim 200K \, (\sim J/2)$

Consistent with a large $J \sim 400K$

Power low decay below 200 K

$\sim T$-linear below 10 K??
$1/T_1 T$ const
low lying spin excitation??
C(T) supports for spin liquid ground state

- No evidence for long range ordering in C(T): only broad peak
- Large entropy remains even at low T
- Magnetic field independent up to 12 T

Low E excitation originates from (large) J scale

Strongly degenerate low lying spin excitation created by J

\(<\theta_{cw} = 650K\)

\[ C_m(T) \propto T^2 \text{ down to 2K} \]

E linear DOS (gap node)
Comparison with other geometrically frustrated magnet - entropy weight down shift

Issues:
- $T^2$ specific heat in 3D?
- $-(T_1 T)^{-1}$ constant?
  
  very small $\gamma T$ term observed below 1 K

likely disorder (imp.)?

Uniqueness: 3D $S=1/2$
- Much cleaner, no evidence for freezing
Charge frustration & heavy fermion formation in LiV$_2$O$_4$ spinel probed by optical response

Jonson, Takenaka, Niitaka, Takagi, PRL99 167402 (07)
Heavy Fermion behavior in mixed valent (3+, 4+) spinel oxide LiV$_2$O$_4$

C. Urano, H. T et al. PRL 85, 1052 (00)

\[ \gamma = 380 \text{ mJ/molK}^2 \]

Li$^{1+}$V$^{3.5+}_2$O$_{2-4}$

“charge” frustration
1:1 V$^{3+}$ & V$^{4+}$ on pyrochlore lattice

want to order but cannot show any charge & spin ordering due to strong frustration

Charge analogue of spin liquid

Heavy fermion ground state results!
Evolution of quasi-particle DOS peak 4 meV above $E_F$

Only $t_{2g}$ electrons involved

A new route to heavy fermion by frustration

not Kondo

Key ingredients: close proximity to charge ordered insulator without charge/magnetic ordering due to geometrical frustration

Shin, PRL
Crystallization of heavy fermions under pressure in LiV$_2$O$_4$

HF state of LiV$_2$O$_4$ close proximity to CO  
S. Niitaka, N. Takeshita
absence of resistivity saturation (bad metal), $\log T$

analogous to TMOs near Mott(CO) transition, indicative of close proximity to CO: Mott-Hubbard physics rather than Kondo physics?

C. Urano, H. T et al PRL 85, 1052 (00)
Coherent - incoherent crossover seen in optical conductivity $\sigma(\omega)$

PRL99 167402 (07)

E scale of Spectral weight transfer?

Not $J_k \sim 20$ K But much larger

Coherent Drude marginally formed only at low T
Spectral weight transfer over eV-scale to establish coherent QP states

Mott physics dominates the QP state rather than low E Kondo physics

Close proximity to Correlation driven CO state in the presence of Frustration

“Charge” analogue of spin liquid

optical conductivity $\sigma(\omega)$
Orbital & Charge Ordering in Geometrically Frustrated LiRh$_2$O$_4$

4d 5d analogue of LiV$_2$O$_4$??

Discovered as a new compound

Two transitions to lift the degeneracy

Band JT + dimerization
New mixed valent spinel LiRh$_2$O$_4$

- Rh$^{3.5+}$: 4d$^{5.5}$ LS 0.5 hole in t$_{2g}$
- 1:1 Rh$^{3+}$ (4d$^6$) & Rh$^{4+}$ (4d$^5$)
  \[ \begin{array}{c}
  \text{non-magnetic} \\
  S=1/2
  \end{array} \]

- charge ordering (1$^{\text{st}}$ order M-I) at 170 K: Contrast to LiV$_2$O$_4$!
  “singlet molecules” in solid to suppress frustration

- Additional anomaly at 230 K (M-M)
Robust spin singlet formation indicated by Li-NMR

Activation energy ~ 3000K
Robust singlet

Waki, Takigawa
Valence bond solid (spin singlet insulator) ubiquitous in mixed valent spinel?

\( \text{CuIr}_2\text{S}_4 \) \( 1:1 \) Ir 3+ and Ir 4+
Spin singlet octomer of Ir 4+ in CO state

\( \text{AlV}_2\text{O}_4 \) \( 1:1 \) V 2+ and V 3+
Spin singlet heptamer formation in CO state

\text{CuIr}_2\text{S}_4 \)

\( T \) (K)
\( 10^3 \)
\( 10^2 \)
\( 10^1 \)
\( 10^0 \)
\( 10^{-1} \)
\( 10^{-2} \)
\( 10^{-3} \)
\( 10^{-4} \)
\( 10^{-5} \)

\text{CuIr}_2\text{S}_4 \)

\( H=12 \text{ kOe} \)
\( 1 \)
\( 0.1 \)
\( 0.01 \)
\( 0.001 \)
\( 0.0001 \)

\text{LiRh}_2\text{O}_4 \) NMR suggests singlet stabilized 3000K

P. G. Radaelli et al.,

Furubayashi et al.,

Y. Horibe, T. Katsufuji et al.
PRL 96 084606 (06)

Very large distorion of metal-metal distance
\(~10\%\) to form singlet molecule
Valence bond solid formation also in charge ordered state of LiV$_2$O$_4$?

With N. Dragoe (Orsay)

EXAFS, large V-V modulation $P>P_C$

valence bond crystal with orbital ordering

Pressure induced metal–insulator transition

PRB
How does system evolve into spin singlet insulator?

- Rh\(^{3.5+}\): 4d\(^{5.5}\) LS 0.5 hole in t\(_{2g}\)
- 1:1 Rh\(^3+\) (4d\(^6\)) & Rh\(^4+\) (4d\(^5\))

\[ \rho (\Omega \text{cm}) \]

- charge ordering (1\(^{st}\) order M-I) at 170 K:
  - “singlet molecules” in solid to suppress frustration

- Additional anomaly at 230 K (M-M)

\[ \chi (10^{-4} \text{ emu/mol Rh}) \]

\[ T (\text{K}) \]
Large (hidden) entropy change and Cubic-Tetragonal transition at M2-M1 transition

- **LiRh$_2$O$_4$**
  - $\Delta S = 5.8$ J/mol
  - $\Delta S = 1.4$ J/mol

- **Lattice constants**
  - Orthorhombic: $a = 8.29$ Å, $b = 8.36$ Å, $c = 8.67$ Å
  - Tetragonal: $a = 5.89$ Å ($\sqrt{2}a = 8.34$ Å), $c = 8.67$ Å ($c/a \approx 1.04$)
  - Cubic: $a = 8.46$ Å

- **Phase transitions**
  - Orthorhombic-tetragonal transition
  - Cubic-tetragonal transition

- **DSC data**
  - Peak at M2-M1 transition
  - ΔS ~70% of R/Rh4+
  - ΔS ~20% of R/Rh4+

- **Possible transition**
  - Likely (band) JT transition 

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**Graphical Elements**
- Line graph showing temperature vs. lattice constant
- Crystal structure diagram of LiRh$_2$O$_4$
- DSC thermogram with peaks at M2 and M1 transitions
Charge ordering - dimerization within xy chain band?

Band JT (orbital ordering) + dimerization in LiRh$_2$O$_4$

Large thermopower $\sim 100 \mu$V/K only in orbital disordered phase. Orbital enhancement of thermopower.
Other related new compound

Mott transition on frustrated lattices
Spin singlet ground state in $S=1$ Mott insulator with frustrated triangular lattice: LiVO$_2$

Suppression of spin frustration by orbital ordering

Trimer formation observed in ED

Penc, Khomskii, Sawatzky...
LiVS$_2$ : itinerant analogue of LiVO$_2$

Metal to (trimer) singlet insulator transition

Spin + orbital may not be enough for LiVO$_2$

LiVS$_2$ polycrystal

Not “new” but first investigated

LiVS$_2$  

LiVO$_2$

LiVSe$_2$

Para S=1 triangular magnet (ins.)

Para Metal

Spin singlet insulator

U/t

Spin singlet (trimer) state are so robust in the vicinity of M-I

trimer formation just like LiVO$_2$ indicated by ED in ins, phase
Metal-Insulator Transition in New Pyrochlore

Hg$_2$Ru$^{5+}$$_2$O$_7$

- Unique system
- Ru $5^+$ system not Ru $4^+ \ t_{2g}^3$
- no orbital degrees of freedom

Singlet ubiquitous even in Mott when frustrated

AF ordering found in ins. phase by Hg NMR (Takigawa) + small distortion

Itinerant analogue of ZnCr$_2$O$_4$ (spin-JT)
**Hg$_2$Ru$_2$O$_7$ vs. Tl$_2$Ru$_2$O$_7**

**No orbital**

<table>
<thead>
<tr>
<th>Hg$_2$Ru$^{5+}$$_2$O$_7$</th>
<th>t$_{2g}^3$</th>
<th>AF ins. (spin JT)</th>
</tr>
</thead>
</table>

**Orbital**

| Tl$_2$Ru$^{4+}$$_2$O$_7$ | t$_{2g}^4$ | Singlet ins. |

**Orbitals play a vital role in forming singlet**
Summary

Na$_4$Ir$_3$O$_8$

Spin liquid ground state on hyper-Kagome lattice
V shaped excitation spectrum?

LiV$_2$O$_4$

HF state realized by correlation + frustration?

LiRh$_2$O$_4$

VBS ubiquitous in mixed valent system
Band JT (orbital ordering) + dimerization
Orbital important for VBS formation

More······