Wilson Ratio enhancement in a quantum spin liquid candidate: $\text{Na}_4\text{Ir}_3\text{O}_8$ (hyperkagome)

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Acknowledge Dr. Perry and Prof. Takagi for sharing their experimental results

KITP conference 2012
Quantum spin liquid candidates

Triangle

\[ \kappa - (ET)_2Cu_2(CN)_3, EtMe_3Sb[Pd(dmit)_2]_2, \]
\[ LiZn_2Mo_3O_8 \]
\[ He - 3 on graphite layer \]

Kagome

\[ Cu_3Zn(OH)_6Cl_2 (kapellasite), \]
\[ BaCu_3V_2O_8(OH)_2 (vesignieite), \]
\[ ZnCu_3(OH)_6Cl_2 (herbertsmithite) \]

FCC

\[ Ba_2YM_0O_6 \]

Pyrochlore

some \[ R_2TM_2O_7 \]
\[ R= \text{rare earth, } TM= \text{transition metal} \]

Hyperkagome

\[ Na_4Ir_3O_8 \]

Quantum spin ice
# Quantum spin liquid candidates

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triangle</td>
<td>( \kappa - (ET)_2Cu_2(CN)_3, EtMe_3Sb[Pd(dmit)_2]_2, LiZn_2Mo_3O_8 )</td>
</tr>
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<td>Kagome</td>
<td>( Cu_3Zn(OH)_6Cl_2 ) (kapellasite), ( BaCu_3V_2O_8(OH)_2 ) (vesignieite), ( ZnCu_3(OH)_6Cl_2 ) (herbertsmithite)</td>
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<td>( Na_4Ir_3O_8 )</td>
</tr>
</tbody>
</table>

4d, 5d and f electrons: Spin-orbit coupling is expected to be important, and may lead to some new physics.
Outline

Part 1. Review experiments and current theories

Part 2. Present a possible explanation for the experiments
Na$_4$Ir$_3$O$_8$: a hyperkagome Ir sublattice

- Na$_4$Ir$_3$O$_8$
- hyperkagome
- pyrochlore

Na$_4$Ir$_3$O$_8$ has a hyperkagome sublattice of Ir ions.

Ir$_3$: regular triangle
5d: 5
LS: $\frac{1}{2}$

Ir$^{4+}$

Na$_4$Ir$_3$O$_8$: a hyperkagome Ir sublattice

- hyperkagome
- kagome

12 sites per unit cell
3 sites per unit cell

Y. Okamoto, et al, H. Takagi
Polycrystal sample

From Prof. Takagi’s talk

Curie-Weiss fit:

\[ \mu_{\text{eff}} = 1.96 \mu_B \quad \text{close to spin-1/2} \]

\[ \Theta_{\text{CW}} = -650 \text{K} \]

No indication of ordering down to 2K from \( C_v \) and \( \chi \) NMR measurement confirms the absence of magnetic ordering. (See Prof. Takagi’s talk on Monday)

\[ \chi|_{T \to 0} = \text{constant} \]

\[ C_v/T|_{T \to 0} = \text{constant} \]

Very large Wilson Ratio, 35!

Y. Okamoto, et al, H. Takagi
Wilson Ratios of some QSL candidates

Table 1 | Some experimental materials studied in the search for QSLs

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice</th>
<th>S</th>
<th>$\Theta_{CW}$ (K)</th>
<th>$R^*$</th>
<th>Status or explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$</td>
<td>Triangular†</td>
<td>½</td>
<td>$-375\ddagger$</td>
<td>1.8</td>
<td>Possible QSL</td>
</tr>
<tr>
<td>EtMe$_2$Sb[Pd(dmit)$_2$]$_2$</td>
<td>Triangular†</td>
<td>½</td>
<td>$(375-325)\ddagger$</td>
<td>? ~1.0-3.0</td>
<td>Possible QSL</td>
</tr>
<tr>
<td>Cu$_3$V$_2$O$_7$(OH)$_2$$\cdot$2H$_2$O (volborthite)</td>
<td>Kagomé†</td>
<td>½</td>
<td>$-115$</td>
<td>6</td>
<td>Magnetic</td>
</tr>
<tr>
<td>ZnCu$_3$(OH)$_2$Cl$_2$ (herbertsmithite)</td>
<td>Kagomé</td>
<td>½</td>
<td>$-241$</td>
<td>?</td>
<td>Possible QSL</td>
</tr>
<tr>
<td>BaCu$_3$V$_2$O$_6$(OH)$_2$ (vesignieite)</td>
<td>Kagomé†</td>
<td>½</td>
<td>$-77$</td>
<td>4</td>
<td>Possible QSL</td>
</tr>
<tr>
<td>Na$_4$Ir$_3$O$_8$</td>
<td>Hyperkagomé</td>
<td>½</td>
<td>$-650$</td>
<td>70 30-40</td>
<td>Possible QSL</td>
</tr>
<tr>
<td>Cs$_2$CuCl$_4$</td>
<td>Triangular†</td>
<td>½</td>
<td>$-4$</td>
<td>0</td>
<td>Dimensional reduction</td>
</tr>
<tr>
<td>FeS$_2$S$_4$</td>
<td>Diamond</td>
<td>2</td>
<td>$-45$</td>
<td>230</td>
<td>Quantum criticality</td>
</tr>
</tbody>
</table>

BEDT-TTF, bis(ethylenedithio)-tetrathiafulvalene; dmit, 1,3-dithiole-2-thione-4,5-ditholate; Et, ethyl; Me, methyl. *$R$ is the Wilson ratio, which is defined in equation (1) in the main text. For EtMe$_2$Sb[Pd(dmit)$_2$]$_2$ and ZnCu$_3$(OH)$_2$Cl$_2$, experimental data for the intrinsic low-temperature specific heat are not available, hence $R$ is not determined. †Some degree of spatial anisotropy is present, implying that $J' \neq J$ in Fig. 1a. ‡A theoretical Curie–Weiss temperature ($\Theta_{CW}$) calculated from the high-temperature expansion for an $S = ½$ triangular lattice; $\Theta_{CW} = 3J/2k_B$ using the $J$ fitted to experiment.

Wilson Ratio quantifies spin fluctuations that enhance the susceptibility.

Basic physics in Na$_4$Ir$_3$O$_8$

Fermi gas
He-3 (almost localized fermi liquid) $W = 1$
Fe-Superconductor (Fe$_{1.04}$Te$_{0.67}$Se$_{0.33}$) $W = 4$
Fe-Superconductor (Fe$_{1.04}$Te$_{0.67}$Se$_{0.33}$) $W = 5.7$

- Strong spin-orbit coupling (Z=77)
- Multi-orbital bands, 3 t2g orbitals
- Close to metal-insulator transition (true for almost all iridates under current investigation)

With SOC, spin-rotational symmetry is broken, large Wilson Ratio is certainly possible, e.g. ordered AFMagnet with gapped spin-wave excitations $W = \infty$
New data: schematic plots

- Single-crystal metallic sample (*R. Perry*, et al, unpublished, Prof. Takagi’s group)

Small change (~18%) in linear-$T$ heat capacity

Large enhancement of magnetic susceptibility. Susceptibility increases with resistivity (several other single-crystal samples)
Summary of the experiments: schematic plots

\[ \gamma \equiv \frac{C_v}{T} \bigg|_{T \to 0} \]

Control parameter: carrier concentration? chemical pressure? etc?

Wilson Ratio

\[ W = \frac{\pi^2 \chi/\mu_B^2}{3 \gamma/k_B^2} \]

Q1: Why is \( W \) (or \( \chi \)) enhanced in the insulating phase?
Q2: Why is \( W \) (or \( \chi \)) so sensitive to Mott transition?
Current theoretical work on Na$_4$Ir$_3$O$_8$

**U(1) QSL**
M. Lawler, et al  

**Z$_2$ QSL**
M. Lawler, et al  
Y. Zhou, et al  

**VBS**
E. J. Bergholtz, et al  

Other works focus on various other things

John M. Hopkinson, et al  

**G. Chen**, et al  
D. Podolsky, et al  
T. Micklitz, et al  
M. R. Norman, et al  
D. Podolsky, et al  

Formation of local moment in the strong Mott regime

$\begin{align*}
\text{IrO}_6 & \\
\text{e}_g & \quad \text{crystal field splitting} \\
\text{t}_{2g} &  \\
xy, xz, yz & \quad \text{SOC}
\end{align*}$
Theoretical proposals


Spinon fermi surface: (nearly) linear-T $C_v$, constant $\chi$ (Heisenberg model)

If other interactions are included to break spin-rotational symmetry, large $W$ might be obtained for this state.


Suppress $C_v$ by spinon pairing to enhance $W$ (interesting)

Explain the susceptibility remaining constant by large SOC $\lambda \gg \Delta$

Expect suppressed $C_v$ from metal to QSL, and also superconductivity in metallic side just like kappa-ET organics


Similar series expansion like Huse+Singh’s work on kagome

Complicated ground state: 72 sites in one cell

a bit hard to explain power-law $C_v$ and constant $\chi$ over a large temperature range
Extended Hubbard Model

\[ \mathcal{H} = \mathcal{H}_{\text{hop}} + \mathcal{H}_{\text{soc}} + \mathcal{H}_{\text{ion}} + \mathcal{H}_{\text{int}} \]

- **\( \mathcal{H}_{\text{hop}} \)**: Tight-binding model
- **\( \mathcal{H}_{\text{soc}} \)**: Atomic spin-orbit coupling
- **\( \mathcal{H}_{\text{ion}} \)**: Single-ion (crystal field) term due to IrO\(_6\) distortion (drive transition from TBI to metal in 227 iridates)
- **\( \mathcal{H}_{\text{int}} \)**: Multiorbital interactions

Tight-binding model

- **\( \sigma \)-bonding**
- **\( \pi \)-bonding**
- Indirect hop through oxygen

\[ t_\sigma = 1, \quad t_\pi = 0.2, \quad t_2 = 0.5 \]

No band insulator

\[ \text{Na}_4\text{Ir}_3\text{O}_8 \]

\[ \text{IrO}_6 \text{ (slightly distorted)} \]

\[ \text{Na} \]

\[ \text{Ir} \]

\[ \text{O} \]

\[ t_\sigma \]

\[ t_\pi \]

\[ t_2 \]

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T. Micklitz, et al


M. R. Norman, et al

Wilson ratio for the non-interacting case

\[ \mathcal{H}_0 = \mathcal{H}_{\text{hop}} + \mathcal{H}_{\text{soc}} + \mathcal{H}_{\text{ion}} \]

\[ t_\sigma = 1, t_\pi = 0.2, t_2 = 0.5 \]

\[ W = 1, \lambda/t_\sigma \]

Two anisotropic parameters

- \( D = 0 \)
- \( D = 0.4 \)

Same reason why Heisenberg model is relevant for \( \text{Sr}_2\text{IrO}_4 \)

\[ \mathbf{M}_i \equiv \mu_B(\mathbf{L}_i + 2\mathbf{S}_i) \]

\( W \neq 1 \) is because of the hybridization of different orbitals

Multi-orbital interactions

\[ H_{\text{int}} = U \sum_{i,m} \hat{n}_{i,m,\uparrow} \hat{n}_{i,m,\downarrow} + \frac{U'}{2} \sum_{i,m \neq m'} \hat{n}_{i,m} \hat{n}_{i,m'} + \frac{J}{2} \sum_{i,m \neq m'} d_{im\sigma}^\dagger d_{im'\sigma'}^\dagger d_{im'\sigma} d_{im\sigma} + \frac{J'}{2} \sum_{i,m \neq m'} d_{im\uparrow}^\dagger d_{im\downarrow}^\dagger d_{im'\downarrow} d_{im'\uparrow} \]

\[ i \text{ is a position index.} \]
\[ m \text{ is an orbital index.} \]

In atomic limit,

\[ U = U' + J + J' \]
\[ J = J' \]

Rewrite interaction,

\[ H_{\text{int}} = H_{\text{c-int}} + H_{\text{ex-int}} \]
\[ H_{\text{c-int}} = \frac{U}{2} \sum_i (\hat{n}_i - 5)^2 \]
\[ H_{\text{ex-int}} = -J \sum_{i,m \neq m'} \hat{n}_{i,m} \hat{n}_{i,m'} + \frac{J}{2} \sum_{i,m \neq m'} d_{im\sigma}^\dagger d_{im'\sigma'}^\dagger d_{im'\sigma} d_{im\sigma} + \frac{J'}{2} \sum_{i,m \neq m'} d_{im\uparrow}^\dagger d_{im\downarrow}^\dagger d_{im'\downarrow} d_{im'\uparrow} \]

U is the energy scale for excessive electron/charge occupation.

J is the energy scale for electron distribution among different spin and orbital states.

\( H_{\text{ex-int}} \) is like an onsite exchange interaction in the Kugel-Khomskii picture.

Strong coupling mean field: slave-rotor theory

\[ \mathcal{H} = \mathcal{H}_{\text{hop}} + \mathcal{H}_{\text{soc}} + \mathcal{H}_{\text{ion}} + \mathcal{H}_{\text{c-int}} \]

Original electron Hamiltonian

\[ H_{\text{hop}} = \sum_{R_{i}i'm'} t_{mm'}^{ii'} d_{im\sigma}^{\dagger}(R)d_{im'\sigma}(R') + h.c. \]

\[ H_{\text{c-int}} = \frac{U}{2} \sum_{R_{i}} \left( \sum_{m,\alpha} d_{im\alpha}^{\dagger}(R)d_{im\alpha}(R) - 5 \right)^2 \]

\[ H_{\text{ion}} = D \sum_{R_{i}\alpha} (L_{i}^{\mu})_{mn}^{2} d_{im\alpha}^{\dagger}(R)d_{im\alpha}(R) \]

\[ H_{\text{soc}} = \frac{\lambda}{2} \sum_{R_{i}} \mathbf{L}_{mn} \cdot \sigma_{\alpha\beta} d_{im\alpha}^{\dagger}(R)d_{in\beta}(R) \]

Slave-rotor approach to obtain fermionic spinons

(see Prof. Senthil's talk)

\[ d_{im\alpha} = e^{-i\theta_{i}} f_{im\alpha} \]

\[ L_{i}(R) = \sum_{m\sigma} f_{im\sigma}(R)f_{im\sigma}(R) - 5 \]

\[ [\theta_{i}, L_{i}] = i \]

Slave-rotor mean field Hamiltonian

\[ H_{f} = Q_{f} \sum_{R_{i}i'm'} (t_{mm'}^{ii'} f_{im\sigma}^{\dagger}(R)f_{im'\sigma}(R') + h.c.) \]

\[ + \frac{\lambda}{2} \sum_{R_{i}} \mathbf{L}_{mn} \cdot \sigma_{\alpha\beta} f_{im\alpha}^{\dagger}(R)f_{in\beta}(R) + D \sum_{R_{i}\alpha} (L_{i}^{\mu})_{mn}^{2} f_{im\alpha}^{\dagger}(R)f_{im\alpha}(R) \]

\[ H_{L} = \frac{U}{2} \sum_{R_{i}} L_{i}^{2}(R) + \sum_{R_{i}} (hL_{i}(R) + 5h) + Q_{r} \sum_{R_{i},R'i'} e^{i\theta_{i}(R) - i\theta_{i'}(R')} + h.c. \]

\[ Q_{f} \equiv \langle e^{i\theta_{i}(R) - i\theta_{i'}(R')} \rangle_{\theta} \]

\[ Q_{r} \equiv \sum_{mm'} t_{mm'} \langle f_{im\sigma}^{\dagger} f_{im'\sigma}(R) \rangle_{f} \]

Slave-rotor phase diagram

\[ \langle e^{-i\theta_i} \rangle \neq 0, \; Z \neq 0, \; \text{spin and charge are confined, we have a “correlated FL”}. \]

\[ \langle e^{-i\theta_i} \rangle = 0, \; Z = 0, \; \text{we have a “U(1) QSL”}. \]

From left to right, the single-ion anisotropies are

\[ D = 0.8t_\sigma \]
\[ D = 0.4t_\sigma \]
\[ D = 0.2t_\sigma \]
\[ D = 0 \]

Three energy scales: SOC, correlation, bandwidth

Two observations (also see Prof. Balents’ talk):

1. SOC enhances correlation effects. Strong correlation physics may be seen in 4d/5d electron system

2. Correlation effects enhance SOC. SOC may be also important even in 3d electron system in certain cases: FeSc$_2$S$_4$, ZnV$_2$O$_4$, etc

Onsite exchange interaction

We put the onsite exchange interaction in the spinon mean field hamiltonian.


\[
H_{\text{ex-int}} = \sum_i \left[ -J \sum_{m \neq m'} f_{im\sigma}^\dagger f_{im\sigma} f_{im'\sigma'}^\dagger f_{im'\sigma'} + \frac{J}{2} \sum_{m \neq m'} f_{im\sigma}^\dagger f_{im'\sigma}^\dagger f_{im\sigma'} f_{im'\sigma'} 
+ \frac{J}{2} \sum_{m \neq m'} f_{im\uparrow}^\dagger f_{im\downarrow}^\dagger f_{im'\downarrow} f_{im'\uparrow} \right]
\]

\[
H_f \rightarrow H_f + H_{\text{ex-int}}
\]

Study Wilson ratio along the dashed line

\[ M_i \equiv \mu_B (L_i + 2S_i) \]

Correlated FL with SOC

U(1) QSL

\[
\lambda/t_\sigma
\]

\[
M_i \equiv \mu_B (L_i + 2S_i)
\]

Study Wilson ratio along the dashed line

\[
\frac{\lambda}{t_\sigma}
\]
Both “effective mass” and fermi surfaces are changed due to SOC

\[ J \lesssim 0.1 U_c \]

From bottom to top,\n\[ \begin{align*}
J &= 0 \\
J &= 0.2 t_\sigma \\
J &= 0.3 t_\sigma \\
J &= 0.4 t_\sigma
\end{align*} \]

relevant energy scales: \( J \) and bandwidth
Summary

Na₄Ir₃O₈ is likely to be a U(1) quantum spin liquid with spinon fermi surfaces.
The large Wilson ratio might arise from the combined effect of spin-orbit coupling, correlation and onsite spin-orbital exchange.
(other possible explanation, gauge fluctuations?)

For experiments,

Other experiments: resonant inelastic x-ray scattering (planned), thermal conductivity (seems like a metal), quantum oscillations (too soft gauge field? O. Motrunich, PRB 2005)

Can similar physics be observed in related materials?
e.g. nonmagnetic R₂Ir₂O₇, Os-compounds, etc