Theory of cluster Mott insulators, and, a spinon Fermi surface spin liquid in YbMgGaO4

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Part 1. Theory of cluster Mott insulators
Outline of Part 1

• A 2D cluster magnet: LiZn$_2$Mo$_3$O$_8$

• The theory of cluster Mott insulator in 2D

• Summary
One surprising experiment on LiZn$_2$Mo$_3$O$_8$

- Why unusual? neither model works.
  1. Triangular lattice Heisenberg model
  2. Triangular lattice Hubbard model at 1/2 filling

- Further low-temperature experiments: NMR, muSR, neutron scattering, proposed as a spin liquid candidate.
Organic spin liquids?

(a) 

(b) 

\[ \kappa-(\text{BEDT-TTF})_2\text{Cu}_2(\text{CN})_3, \]
\[ \text{EtMe}_3\text{Sb}[\text{Pd(dmit)}_2]_2, \]
\[ \kappa-(\text{H}_3\text{(Cat-EDT-TTF)})_2 \quad \text{a new one!} \]

Other experiments: transport, heat capacity, optical absorption, etc. Unfortunately, no neutron scattering so far.

* No magnetic order down to 32mK
* Constant spin susceptibility at zero temperature
\[
H = -t \sum_{\langle ij \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + h.c. + U \sum_i n_{i\uparrow} n_{i\downarrow}
\]

**Fermi liquid** metal

**weak** Mott regime

**strong** Mott regime

Mott transition

- Physical mechanism for weak Mott insulator spin liquids: perturbation in t/U

\[
H_{\text{pert}} = \sum_{ij} J_{ij} S_i \cdot S_j + K \sum_{1234} (P_{1234} + P_{1234}^{-1}) + \cdots
\]

4-site ring exchange

\[
(S_1 \cdot S_2)(S_3 \cdot S_4) + (S_1 \cdot S_4)(S_2 \cdot S_3) - (S_1 \cdot S_3)(S_2 \cdot S_4)
\]
Remark (on the mechanism NOT the properties):
1. There is no sharp distinction between the charge fluctuations in the weak and strong Mott regimes.
2. Strong charge fluctuation in the weak Mott regime is a quantitative description.
3. Interesting physics occurs in the spin sector, but charge sector is completely trivial!

Question / observation (this goes beyond just spin liquid):
1. What if the change fluctuation is very strong, and in the most extreme case, the charge sector forms a quantum charge liquid Mott insulator?
2. What if the charge fluctuation leads to some structure in the charge sector? Spin sector is surely to be influenced in a non-trivial way. This would lead to a striking experimental consequence. If it is observed, it gives us confidence on the theoretical framework that we are developing.
Cluster structure of LiZn$_2$Mo$_3$O$_8$

The heat capacity as a function of temperature. Instead there is only magnetic order above that long-range magnetic order does not develop below the $T_c$.

Unambiguous determination of the ground state of LiZn to a lower symmetry. Unambiguous determination of the ground state of LiZn to a lower symmetry.

$T_c = 0.12$ K. Applied long-range order and results in low-lying magnetic excitations are indeed dynamic: at $T = 400$ K, we observe a gradual and continuous $\Delta S = 1/2$.

The magnetic entropy change of LiZn$_2$Mo$_3$O$_8$ is one-third the high-temperature value, indicating that two-thirds of the expected magnetic entropy change for a resonating valence-bond state, neutron powder diffraction data suggest that the singlets are unambiguously determined whether these singlets are static, making a resonating valence-bond solid, or dynamic, making a resonating valence-bond network and distort the lattice.

The hybrid functional produces an estimate of the on-site repulsion energy, $U = 2.06$ Å, $E = 3.01$ Å, $T = 400$ K to examine and understand the behaviour in detail.

Schottky anomaly, do not adequately describe the low-temperature changes from small magnetic fields are surprising given the large number of moments.

For Mo$_3$O$_8$, the energy gap to the next available state. The cluster shows the local coordination of each Mo atom.

$H_{text{SCHOTTKY}} = 0.12$ K; Applied field $H_{text{APPLIED}} = 1$ K. Applied field $H_{text{APPLIED}} = 1$ K: there is no sharp transition of $\Delta S = 1/2$, $T = 0$. This Curie constant is one-third the expected magnetic entropy change for a resonating valence-bond state, neutron powder diffraction data suggest that the singlets are unambiguously determined whether these singlets are static, making a resonating valence-bond solid, or dynamic, making a resonating valence-bond network and distort the lattice.

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Model

Claim: a single-band extended Hubbard model on an anisotropic Kagome lattice with 1/6 electron filling.

- Minimal model allowed by symmetry [require quantum chemistry understanding]

\[
H = \sum_{\langle i,j \rangle \in u} [-t_1(c_{i\sigma}^\dagger c_{j\sigma} + h.c.) + V_1 n_i n_j] \\
+ \sum_{\langle i,j \rangle \in d} [-t_2(c_{i\sigma}^\dagger c_{j\sigma} + h.c.) + V_2 n_i n_j] \\
+ \sum_i \frac{U}{2} (n_i - \frac{1}{2})^2,
\]

* Large U alone cannot localize the electron.
* V1 and V2 are needed: because it is 4d orbital, and also to localize the electron in the clusters.
Generic phase diagram

- A “simple” understanding:
  * Electrons are localized in one type of triangles in type-I CMI;
  * Electrons are localized in both types of triangles in type-II CMI.

Here $t_1/t_2 = 4$, no qualitative difference for different $t_1/t_2$

$V_2$ is small, $V_1$ is large snapshots of electron occupation in type-I CMI
This collective tunnelling process preserves the center of mass of 3 electrons!

\[ H_{QDM} \sim - \sum_{\text{state}} (|\text{state}\rangle \langle \text{state}| + |\text{state}\rangle \langle \text{state}|) \]
Type-II CMI: plaquette charge order via QDM

- A model study in 2001

\[ H_{QDM} = -t \sum_{i} \left( | \begin{array}{c} \downarrow \\ \uparrow \end{array} \rangle \langle \begin{array}{c} \uparrow \\ \downarrow \end{array} | + | \begin{array}{c} \downarrow \downarrow \\ \uparrow \uparrow \end{array} \rangle \langle \begin{array}{c} \uparrow \uparrow \\ \downarrow \downarrow \end{array} | + v \left( | \begin{array}{c} \downarrow \\ \downarrow \end{array} \rangle \langle \begin{array}{c} \uparrow \\ \uparrow \end{array} | + | \begin{array}{c} \downarrow \downarrow \\ \uparrow \uparrow \end{array} \rangle \langle \begin{array}{c} \uparrow \uparrow \\ \downarrow \downarrow \end{array} | \right) \right) \]

- Remarks:
  - The plaquette charge order is a local charge “RVB”.
  - One may simply view each resonating hexagon as a benzene molecule.
  - It is a collective behaviour of 3 electrons.
  - It is a quantum effect.
• High energy d.o.f. (charge) usually influences low energy d.o.f. (spin). More practically, low d.o.f serves as a probe of the physical properties of the high energy d.o.f.

• Spin state reconstruction by the charge

\[
\frac{1}{2} \otimes \frac{1}{2} \otimes \frac{1}{2} = \frac{1}{2} \oplus \frac{1}{2} \oplus \frac{3}{2}
\]

The total spin \( S_{\text{tot}} = 1/2 \);
Pseudospin \( \tau = 1/2 \), nonmagnetic

An effective Kugel-Khomskii model on the emergent triangular lattice
Explanation for fractional spin susceptibility at finite temperatures

1. Expect 1st order finite temperature transition, peak at ~100K, (was interpreted as Li freezing.) smeared out 1st transition?
2. High resolution X-ray, RIXS
3. Nuclear quadrupolar resonance: electric field gradient (suggested to me by Baskaran)
Summary: the cascade of energy scales

Below the Mott gap: usual superexchange process, new collective charge fluctuation (hallmark).
**Cluster Mott Insulator**: a new class of Mott insulators

Electrons (or bosonic particles) are localized on some cluster units instead of the lattice sites. These cluster units build the lattice.

![Triangle clusters in kagome](image1.png)  
![Tetrahedral cluster in pyrochlore](image2.png)

A large class of cluster magnets (Mott insulators)

\[
\text{Mg}_2\text{Mo}_3\text{O}_8, \text{Mn}_2\text{Mo}_3\text{O}_8, \text{Fe}_2\text{Mo}_3\text{O}_8, \text{Co}_2\text{Mo}_3\text{O}_8, \text{Ni}_2\text{Mo}_3\text{O}_8, \text{Zn}_2\text{Mo}_3\text{O}_8, \text{Cd}_2\text{Mo}_3\text{O}_8 \\
\text{LiScMo}_3\text{O}_8, \text{LiYMo}_3\text{O}_8, \text{LiInMo}_3\text{O}_8, \text{LiSmMo}_3\text{O}_8, \text{LiGdMo}_3\text{O}_8, \text{LiTbMo}_3\text{O}_8, \\
\text{LiDyMo}_3\text{O}_8, \text{LiHoMo}_3\text{O}_8, \text{LiErMo}_3\text{O}_8, \text{LiYbMo}_3\text{O}_8 \\
\text{NbO}_2, \text{Mg}_3\text{Nb}_6\text{O}_{11}, \text{Ba}_{1.14}\text{Mo}_8\text{O}_{16}, \text{NaMo}_4\text{O}_6, \text{GaTa}_4\text{Se}_8, \text{GaNb}_4\text{S}_8, \text{GaNb}_4\text{Se}_8 , \\
\text{many organic materials} \ldots .
\]

Cluster magnets can even be systematically fabricated in organic chemistry!
Further extensions

• Extension to three dimensional materials
• Extension to bosonic systems.
3D CMI as U(1) quantum charge liquid

\[ H = -t \sum_{\langle ij \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + h.c.) - \mu \sum_i n_i + V \sum_{\langle ij \rangle} n_i n_j + \frac{U}{2} \sum_i (n_i - \frac{1}{2})^2 \]

- Low-energy physics of the charge is described by an emergent (compact) quantum electrodynamics in 3+1D. Charge excitation carries 1/2 the electron charge!
- Charge ice rule

\[ \frac{q_e}{2} \]

\[ -\frac{q_e}{2} \]

two internal U(1) gauge fields here
• (Inelastic) X-ray scattering measures U(1) gauge field correlation in the charge sector

\[
\text{Im}[E_{-k,-\omega} E_{k,\omega}^\beta] \propto \left[ \delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2} \right] \omega \delta(\omega - v|k|),
\]

\[
E_{r+\frac{1}{2}e_\mu} \equiv L_{r,r+e_\mu} e_\mu |e_\mu| = (n_{r+\frac{1}{2}e_\mu} - \frac{1}{2}) e_\mu |e_\mu|
\]

\[
\langle E_{-k}^\alpha E_k^\beta \rangle \propto \delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}
\]

Pinch points in equal-time charge structure factor at \( T > \) ring hopping. “classical charge ice”

\[
I(\omega) \sim \omega
\]

emergent light in quantum charge ice!

Hermele etc 2004
N Shannon etc 2012,
L Savary etc 2012
Framework: a new parton construction

- The slave rotor construction is used to describe the conventional Mott insulator, e.g. triangular lattice Hubbard model at 1/2 filling.

\[ c_{i\sigma} = e^{-i\theta_i} f_{i\sigma} \]

one U(1) gauge field

- A new parton gauge construction is required for cluster Mott insulators to capture additional U(1) gauge structure in the charge sector.

\[ c_{j\sigma}^\dagger \sim f_{j\sigma}^\dagger \Phi_r^\dagger \Phi_{r'} e^{iA_{rr'}} \]

two U(1) gauge fields: \( U(1)_c \times U(1)_{sp} \)
2. A rare-earth triangular lattice quantum spin liquid: $\text{YbMgGaO}_4$

Experimental collaborators

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A rare-earth triangular lattice quantum spin liquid: YbMgGaO$_4$

- Recent extension to spin-orbit coupled insulators (Watanabe, Po, Vishwanath, Zaletel, PNAS 2015).
- This is the **first** strong spin-orbit coupled QSL with odd number of electrons and effective spin-1/2.
- It is the **first** clear observation of T$^{2/3}$ heat capacity. I think it is spinon Fermi surface U(1) QSL.
- Inelastic neutron scattering is consistent with spinon Fermi surface results.
- We understand the microscopic Hamiltonian and the physical mechanism.
YbMgGaO$_4$

- observation of $T^{2/3}$ heat capacity
- Entropy: effective spin-1/2 local moments

Our proposal for ground state: spinon Fermi surface U(1) QSL.
Yb$^{3+}$ ion: 4f$^{13}$ has J=7/2 due to SOC.

At $T \ll \Delta$, the only active DOF is the ground state doublet that gives rise to an effective spin-1/2.
**Advantage for neutron scattering**

**Continuum excitation**

Near T=0, but not-very-low energy excitation

Yao Shen, …Gang Chen*, Jun Zhao*  Nature
Spinon continuum

\( E = 1.5 \text{ meV} \)
\( T = 70 \text{ mK} \)

Calculation

Intensity (arb. unit)

Yao Shen, …Gang Chen*, Jun Zhao* Nature
Two Major Questions

1. Whether the continuum represents the fractionalized spinon excitation? Probably most important!
   (Our new work will appear soon.)

2. What is the physical origin of the QSL physics?
Spin-orbit coupling

4f electron is very localized, and dipolar interactions weak.

\[ \mathcal{H} = \sum_{\langle ij \rangle} \left[ J_{zz} S_i^z S_j^z + J_{\pm} (S_i^+ S_j^- + S_i^- S_j^+) \right. \\
\left. + J_{\pm} (\gamma_{ij} S_i^+ S_j^+ + \gamma_{ij}^* S_i^- S_j^-) \\
- \frac{i J_{z\pm}}{2} (\gamma_{ij}^* S_i^x S_j^x - \gamma_{ij} S_i^- S_j^z + \langle i \leftrightarrow j \rangle) \right] \]

where \( S_i^{\pm} = S_i^x \pm i S_i^y \), and the phase factor \( \gamma_{ij} = 1, e^{i 2\pi/3}, e^{-i 2\pi/3} \) for the bond \( ij \) along the \( a_1, a_2, a_3 \) direction (see Fig. 1), respectively. This generic Hamiltonian supports conventional order. (Yamamoto, etc, PRL 2014)

Ga/Mg disorder may do something too. But not very clear at this stage.
The classical spin Hamiltonian occurs at \( \theta = \frac{\pi}{3} \). Therefore, the incommensurate state can be described using orthogonal eigenvectors to construct an incommensurate order that originates from the strong spin-orbit coupling that satisfies the hard spin constraint.

Here we treat the effective spin in the XXZ model. The ground state of this XXZ model is simply that the system does not have any continuous symmetry, so the polarized phases and strong magnetic fields.

Due to the locking of the spin orientation and the ordered phases. In the region I of the phase diagram, the stripe order in region III with spins pointing along the rare earth local moments are usually very small. For the system does not have any continuous symmetry, so the spin model reduces to a XXZ model. Due to the continuous symmetry, the rare earth local moments are usually very small. For the system does not have any continuous symmetry, so the spin model reduces to a XXZ model. Due to the continuous symmetry, the rare earth local moments are usually very small.
**Parton construction and PSG classification**

\[ S_i = \sum_{\alpha, \beta} \frac{1}{2} f_{i\alpha}^\dagger \sigma_{\alpha \beta} f_{i\beta} \]

\[ H_{MF} = - \sum_{(rr')} \sum_{\alpha, \beta} [t_{rr'}, \alpha \beta f_{r\alpha}^\dagger f_{r'\beta} + h.c.] , \]

<table>
<thead>
<tr>
<th>U(1) QSL</th>
<th>( W_r^{T_1} )</th>
<th>( W_r^{T_2} )</th>
<th>( W_r^{C_2} )</th>
<th>( W_r^{C_6} )</th>
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<tbody>
<tr>
<td>U1A00</td>
<td>( I_2 \times 2 )</td>
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<tr>
<td>U1A10</td>
<td>( I_2 \times 2 )</td>
<td>( I_2 \times 2 )</td>
<td>( i\sigma^y )</td>
<td>( I_2 \times 2 )</td>
</tr>
<tr>
<td>U1A01</td>
<td>( I_2 \times 2 )</td>
<td>( I_2 \times 2 )</td>
<td>( I_2 \times 2 )</td>
<td>( i\sigma^y )</td>
</tr>
<tr>
<td>U1A11</td>
<td>( I_2 \times 2 )</td>
<td>( I_2 \times 2 )</td>
<td>( i\sigma^y )</td>
<td>( i\sigma^y )</td>
</tr>
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</table>

The U1A00 state is the spinon Fermi surface state that we proposed in Shen, et al, Nature.
The evolution of $\varpi$, ±, and $\pm$ are denoted by the two inequivalent sites in each unit cell due to their spectroscopic features for comparison. Like the $U_{1A00}$ state, $U_{1B01}$ state, and $U_{1B10}$ state, their spectroscopic features for comparison.

In the parton construction, their phenomenological treatment for the Fermi velocity and Fermi surface $U(1)$ QSL and gapless, the transition would enhance the spectral weight at the $G$ points. The polarized state is a simple product state with short-range quantum entanglement, while the unpolarized state is a simple product state with long-range quantum entanglement. Therefore, the neutron scattering profiles of the dynamic spin structure factor. We evaluate the lines from $U_{1B00}$ and $U_{1B11}$ states.

For the $U_{1B00}$ state, we consider $t'/t_1 = 0.8$, $t_2/t_1 = 0.3$. The representation is chosen to be a spinon state at $q = 0$ and consider $\pi$ wave vectors.

In Fig. 2, the dynamic spin structure factor for six free spinon mean-field states other than $U_{1A00}$. Note the $U_{1A10}$ Hamiltonian is $\mathbf{H}_{\mathbf{k}} = k_x^2 + k_y^2 + k_z^2 + \mathbf{J}^z$. The linear spin wave spectrum for the field normal to the $xy$ plane. This is partly due to the experimental resolution of the $Q$ point. For the $U_{1A00}$ state, $t'/t_1 = 0.4$, $t_2/t_1 = 0.3$. We calculate the $\mathbf{H}_{\mathbf{k}}$ and consider $\pi$ wave vectors.
Summary

1. I present a theory for cluster Mott insulator that is motivated by LiZn$_2$Mo$_3$O$_8$.

2. I review the experiments and present some recent theory progress on YbMgGaO$_4$. 