Charge fluctuations and spin liquids in cluster Mott Insulators

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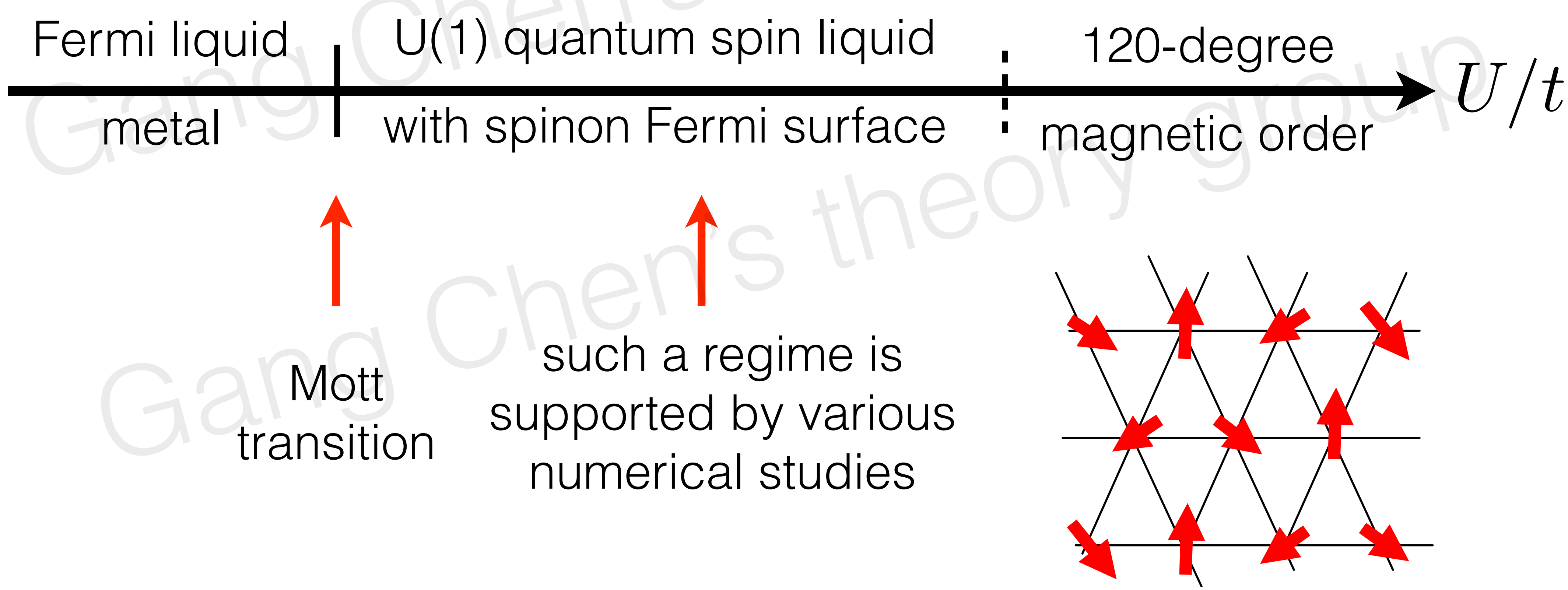
Gang Chen, Hae-Young Kee, Yong-Baek Kim, ArXiv **1402.5425**
Gang Chen, Hae-Young Kee, Yong-Baek Kim, ArXiv **1408.1963**

Outline

- Quantum spin liquid with spinon Fermi surface
- $LiZn_2Mo_3O_8$ cluster magnet
- The theory of cluster Mott insulators
- Summary

Triangular lattice Hubbard model at half filling

$$H = -t \sum_{\langle ij \rangle, \sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + h.c. + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

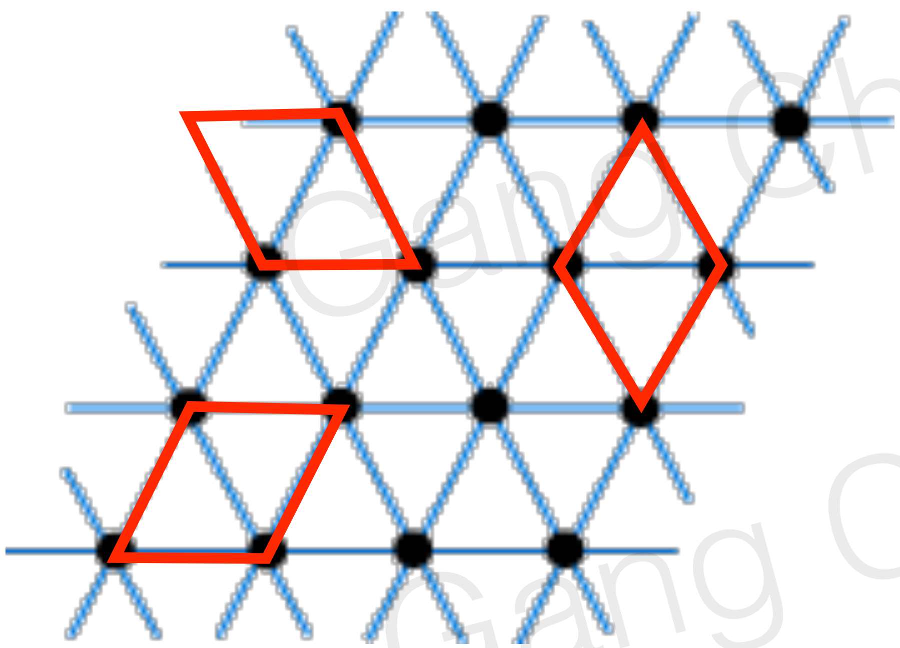


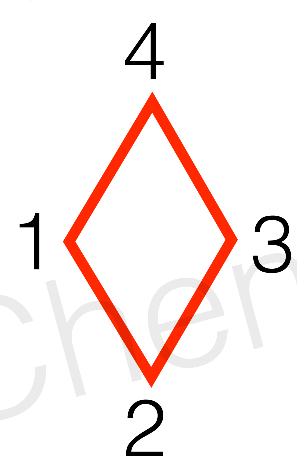
Underlying physics

- Weak Mott insulator spin liquids: perturbation theory in t/U

$$H_{\text{pert}} = \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + K \sum_{1234} (P_{1234} + P_{1234}^{-1}) + \cdots$$

4-site ring exchange





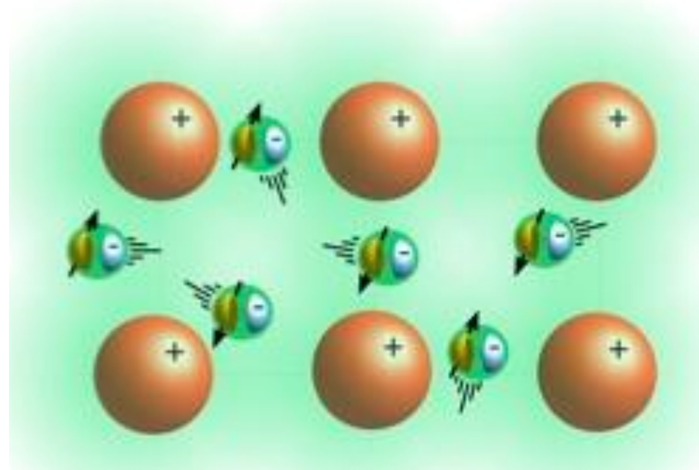
Ring exchange

$$\begin{aligned} &(\mathbf{S}_1 \cdot \mathbf{S}_2)(\mathbf{S}_3 \cdot \mathbf{S}_4) \\ +&(\mathbf{S}_1 \cdot \mathbf{S}_4)(\mathbf{S}_2 \cdot \mathbf{S}_3) \\ -&(\mathbf{S}_1 \cdot \mathbf{S}_3)(\mathbf{S}_2 \cdot \mathbf{S}_4) \end{aligned}$$

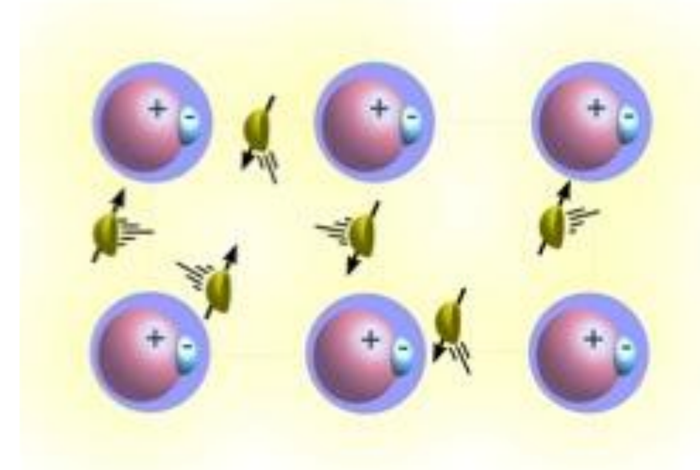
Motrunich

These are high order processes, but
are important in weak Mott regime !

Senthil



Metal in weak correlation regime



Spin-charge separation in weak Mott regime

Sung-Sik Lee

- Parton description

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

charge-q_e spinless boson

charge-neutral spin-1/2 fermion

$$n_j = \sum_{\sigma} c^{\dagger}_{j\sigma} c_{j\sigma}$$

$$[\theta_i, n_j] = i\delta_{ij}$$

Fermi liquid metal: charge rotor is condensed

QSL Mott insulator: charge rotor is gapped

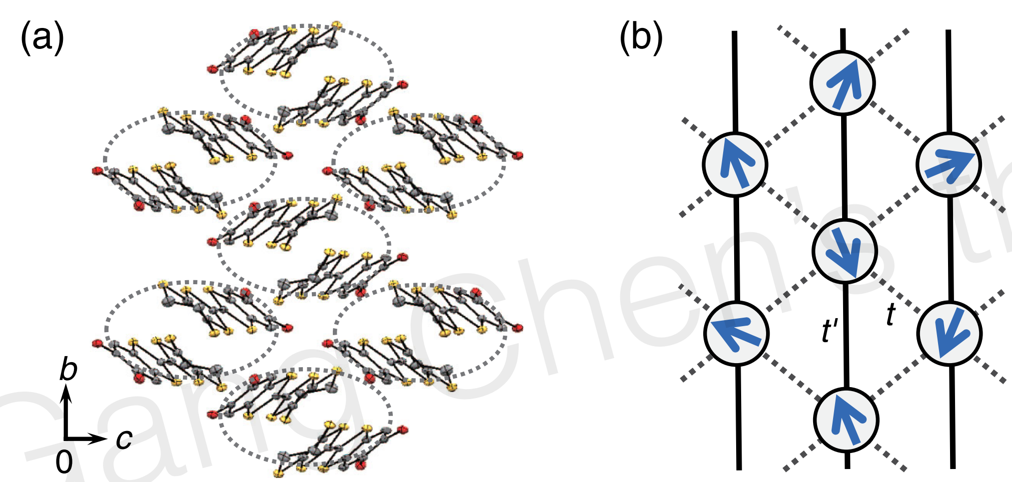
Low EFT of QSL: spinon Fermi surface coupled with a fluctuating U(1) gauge theory. It is a strong coupled theory, no controlled method !.

Many properties of spinon metal are similar to electron metal but with **subtle and important** differences !

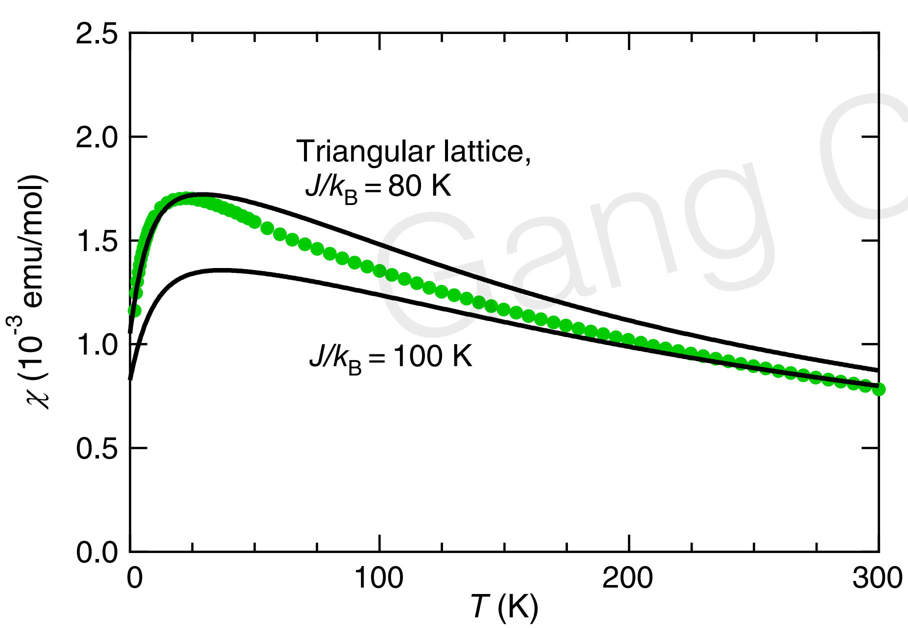
Organic triangular spin liquid ?

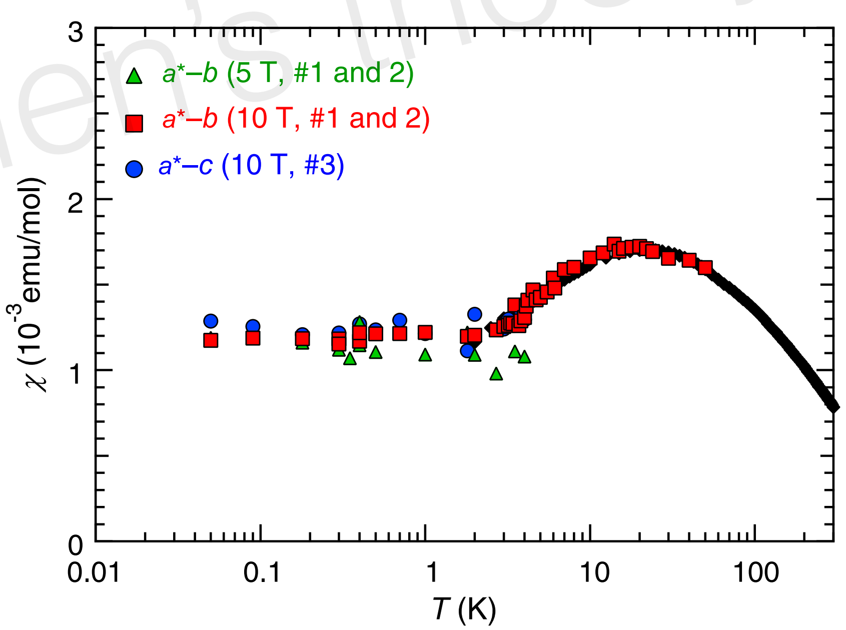
3 organic candidates: k-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, EtMe$_3$Sb[Pd(dmit)$_2$]$_2$, κ−H$_3$(Cat-EDT-TTF)$_2$

a new one!



T. Isono et al, PRL 112, 177201 (2014)





magnetic torque measurement

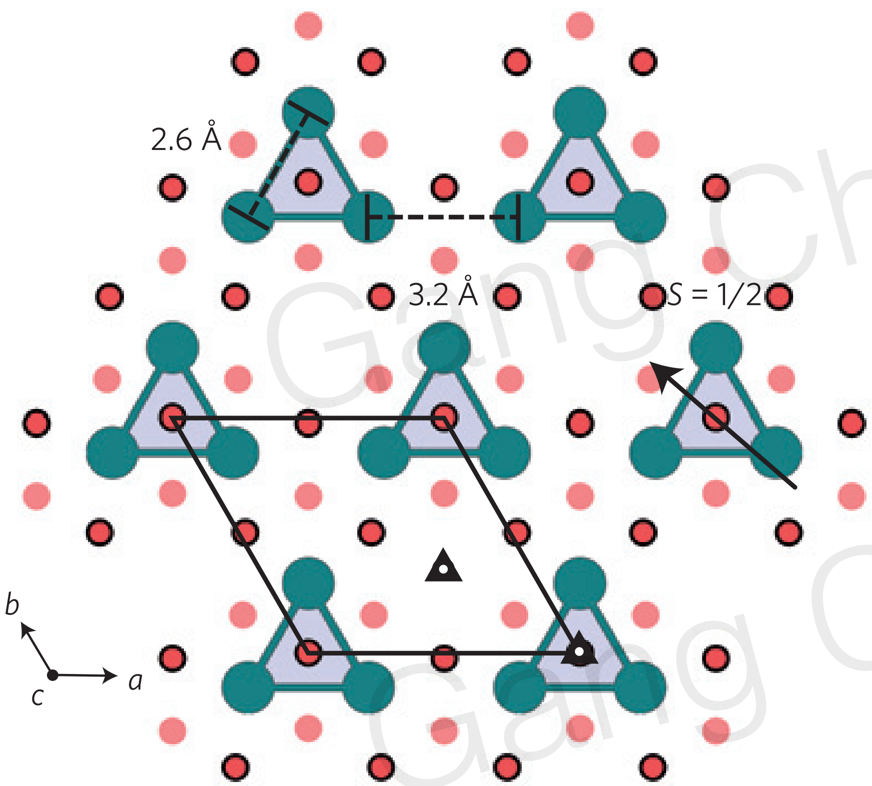
Constant Pauli-like spin susceptibility at T->0 limit

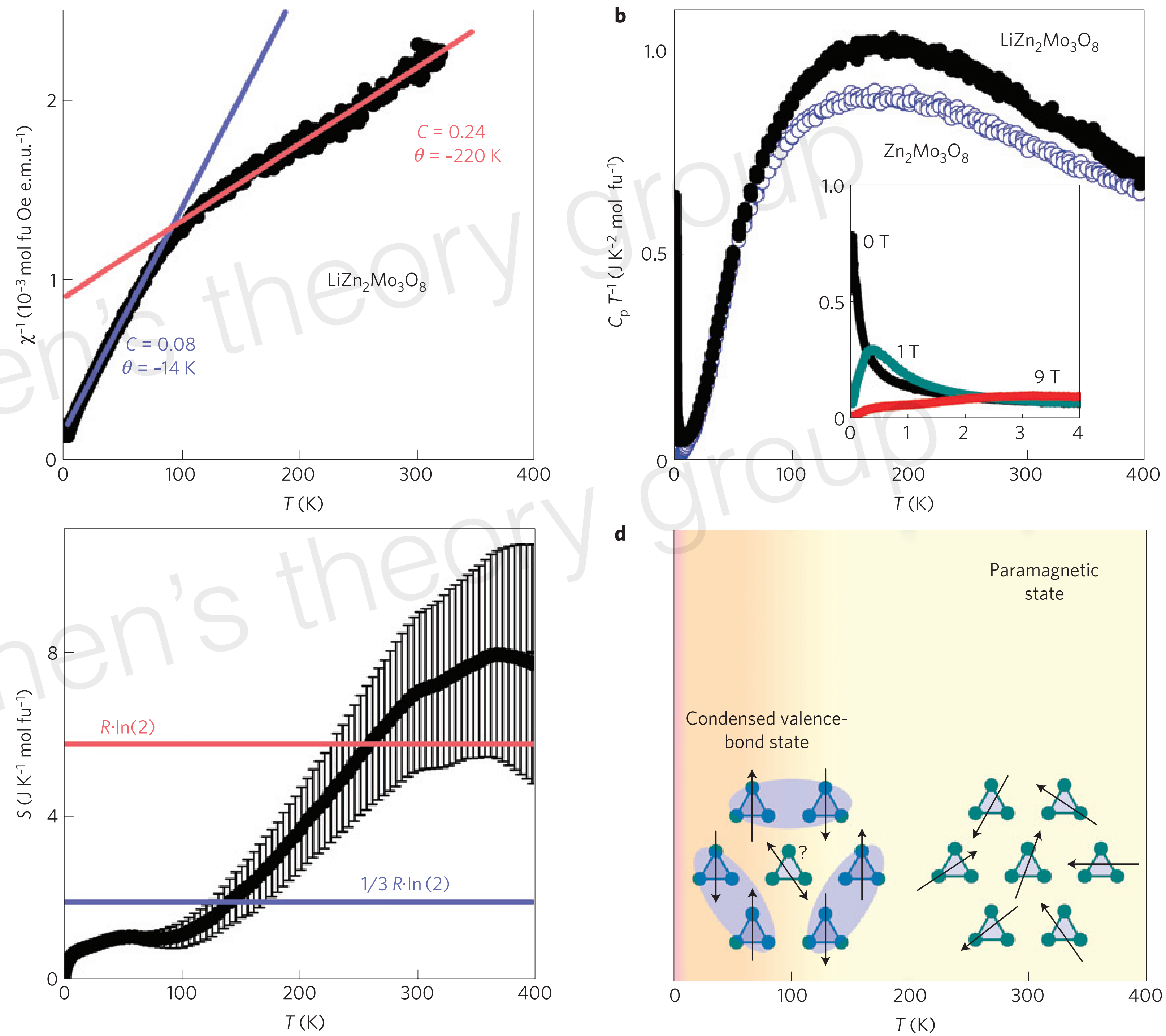
T Mcqueen

Possible valence-bond condensation in the frustrated cluster magnet $LiZn_2Mo_3O_8$

J. P. Sheckelton, J. R. Neilson, D. G. Soltan and T. M. McQueen*

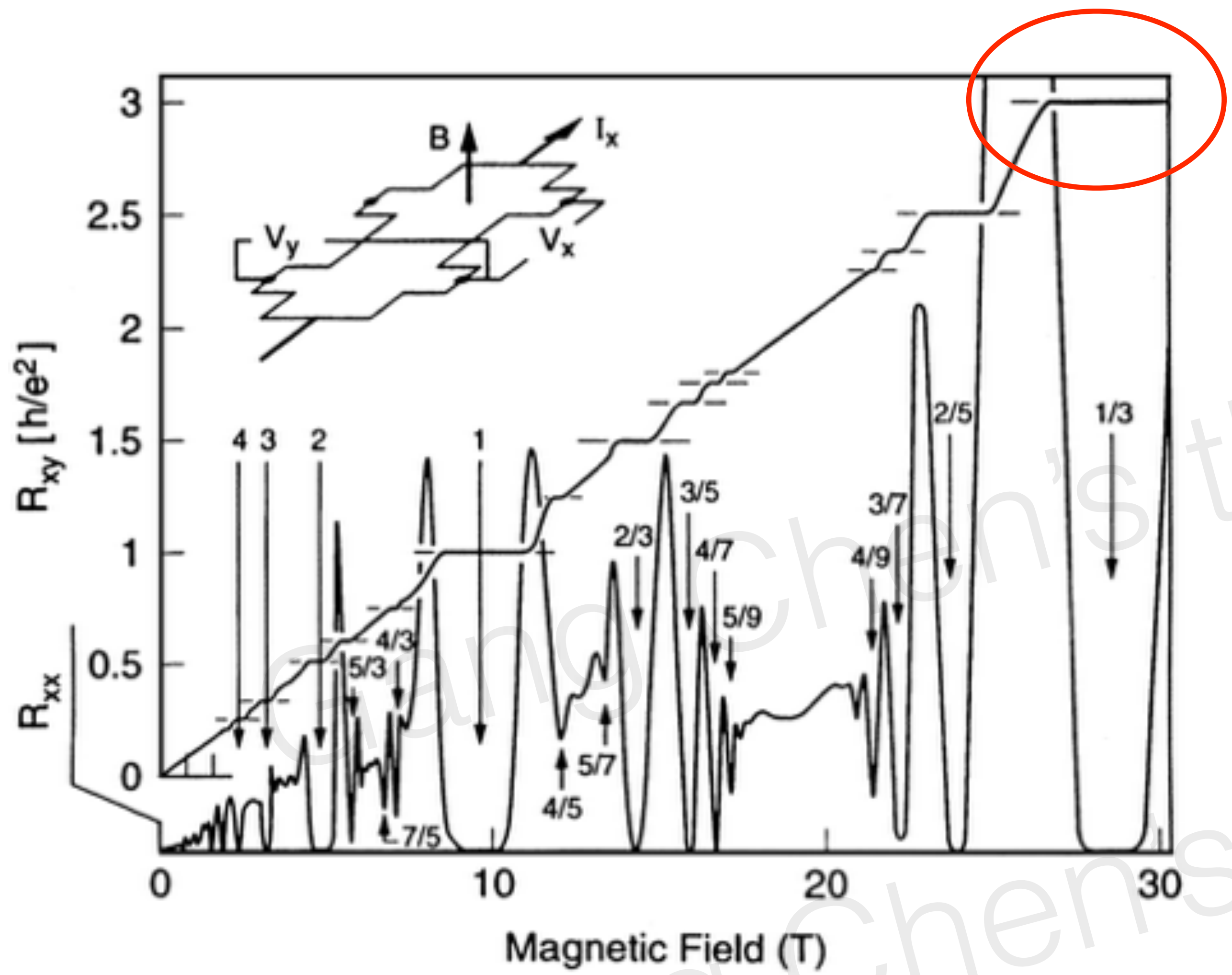
fractional spin susceptibility





FQHE (Tsui, Stormer, and Gossard)

First exotic phenomenon known to us



Laughlin

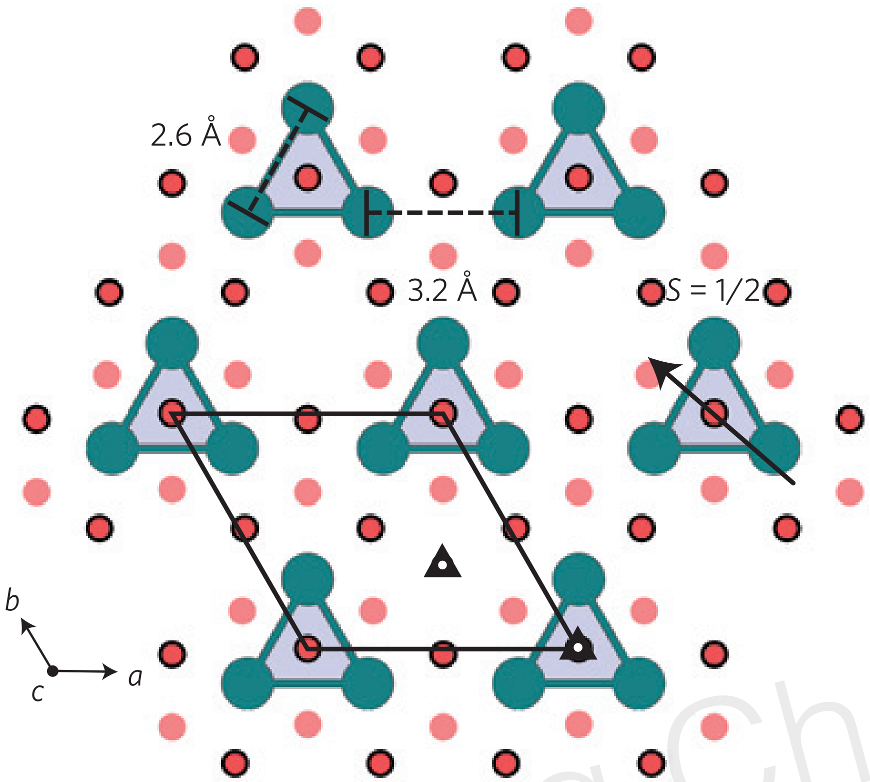
Wen

Wen: all the electrons in the Laughlin state to dance collectively.

What do electrons do in $LiZn_2Mo_3O_8$?

Any collective behaviours?

Difficulties

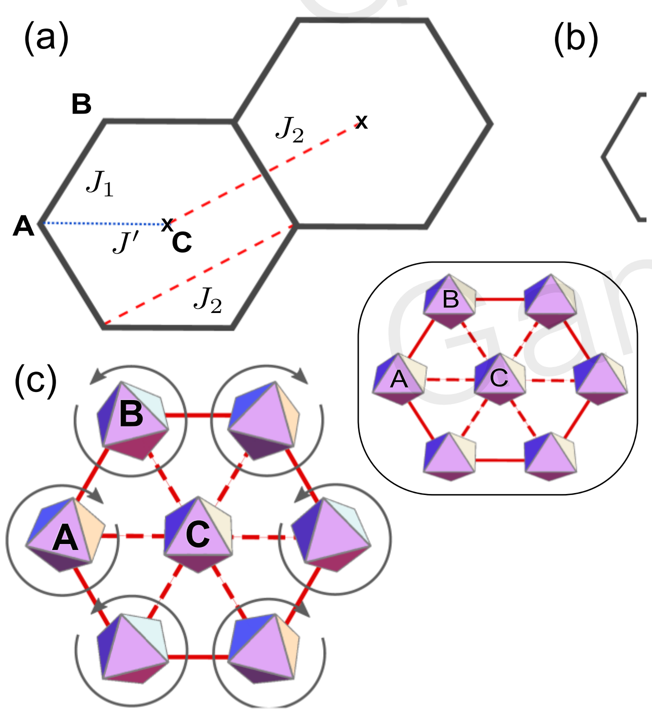


1. Triangular lattice Hubbard model at 1/2 filling
2. Triangular lattice Heisenberg model

Neither model works.

1. It requires lattice degrees of freedom to work in a *special* way to generate the honeycomb lattice.

2. It may also need a large spin gap, not seem to be supported by J1-J2 honeycomb lattice model because both the “orphan” spins and honeycomb spins contribute to the spin susceptibility.



$$\chi \sim \frac{\#_1}{T - \Theta^L_{CW}} + \#_2 e^{-\frac{\Delta}{T}}$$

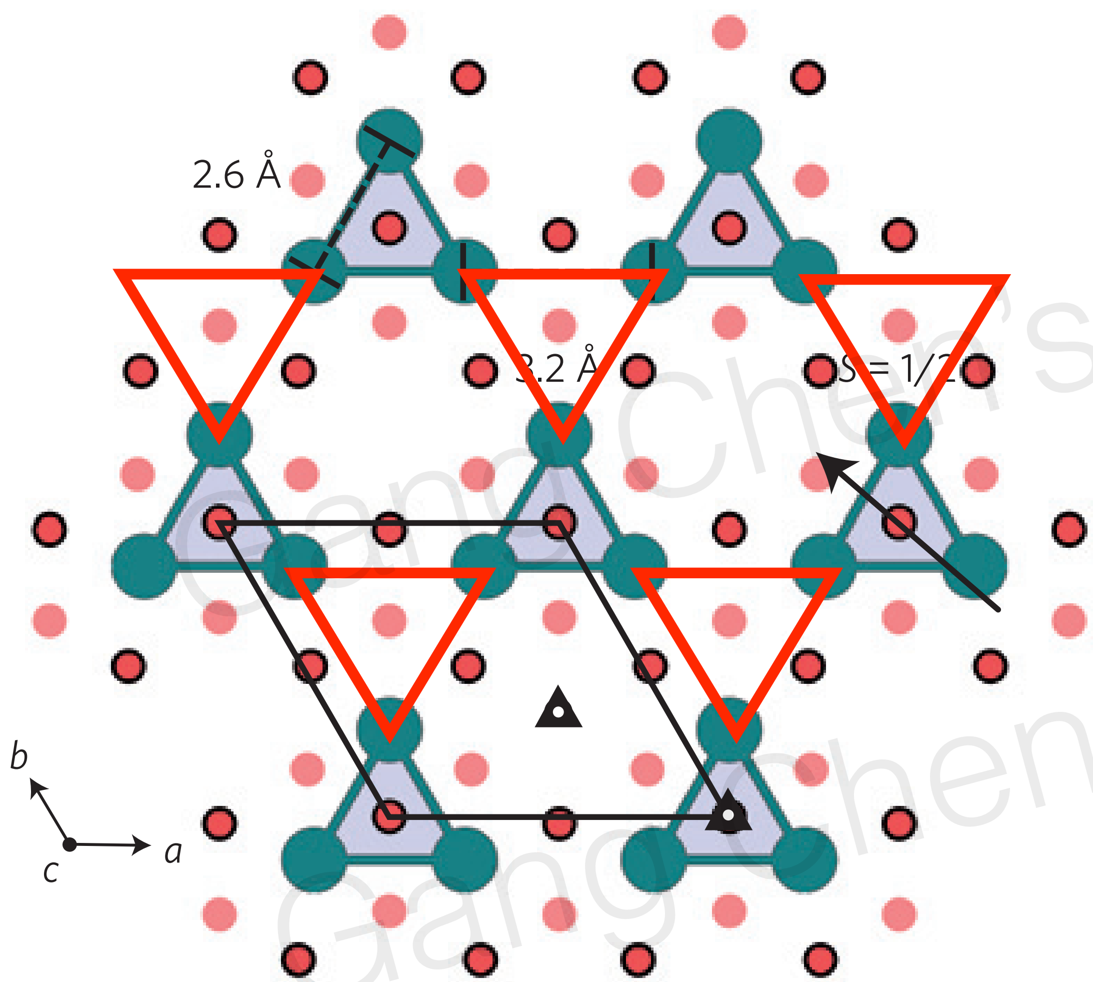
D. Sheng, L. Motrunich, M. Fisher 2012

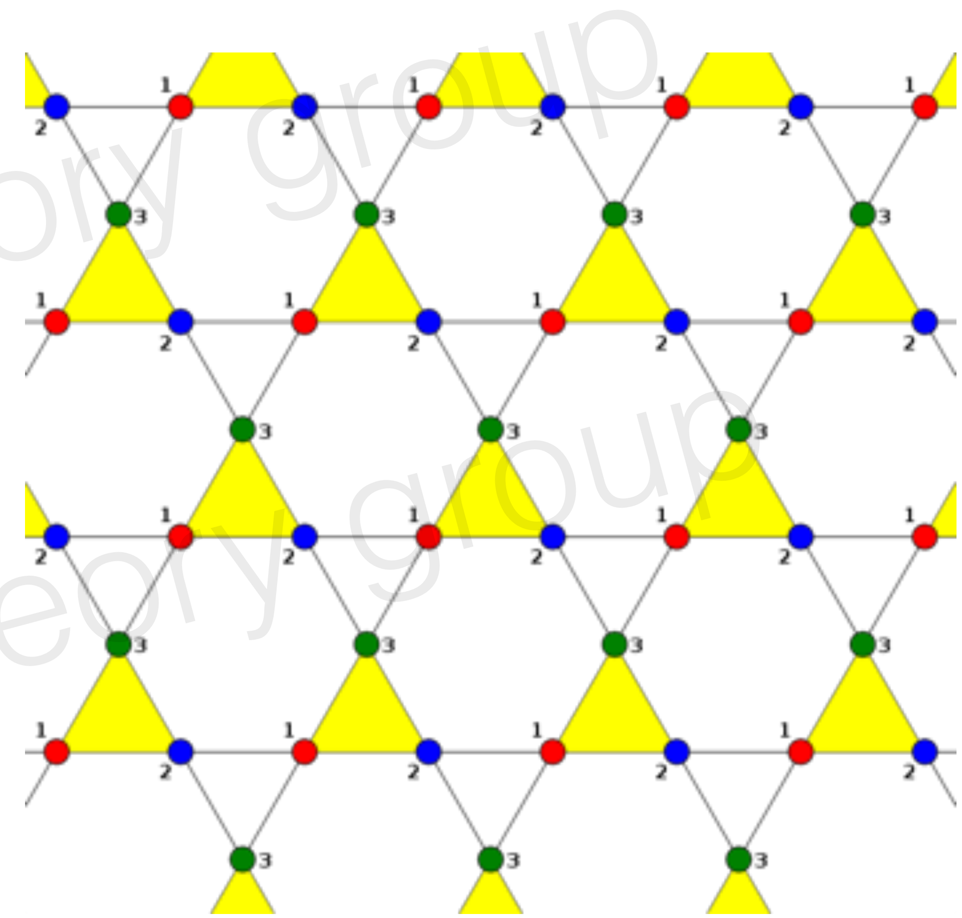
Flint, Lee 2013

Outline

- Quantum spin liquid with spinon Fermi surface
- $LiZn_2Mo_3O_8$ cluster magnet
- The theory of cluster Mott insulators: **both 2D and 3D**
- Summary

$LiZn_2Mo_3O_8$ structure

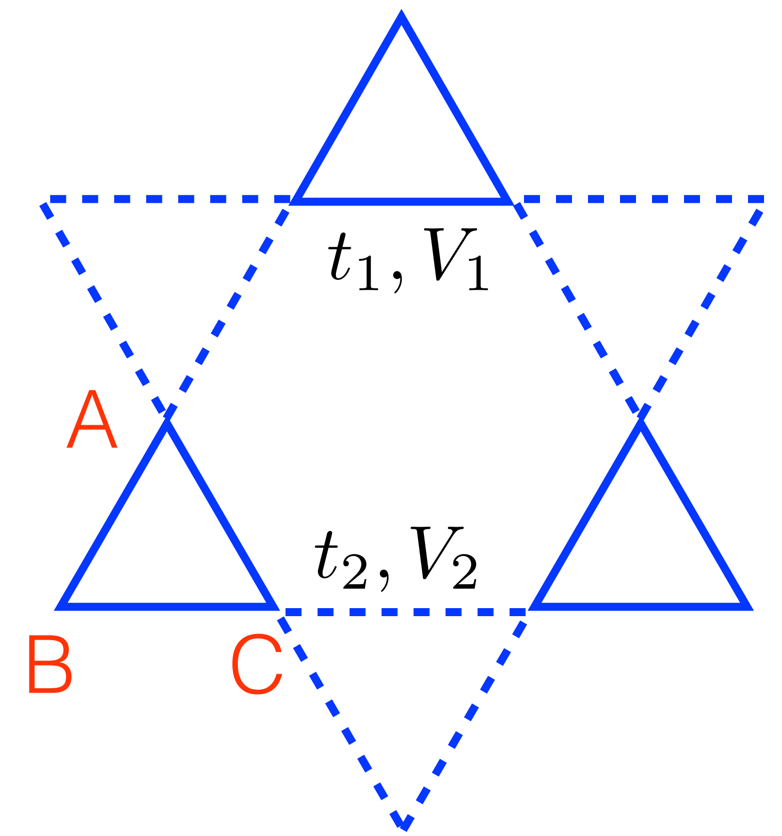




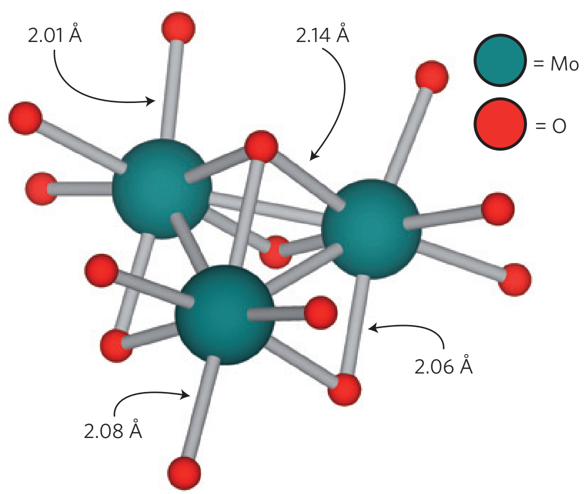
Model

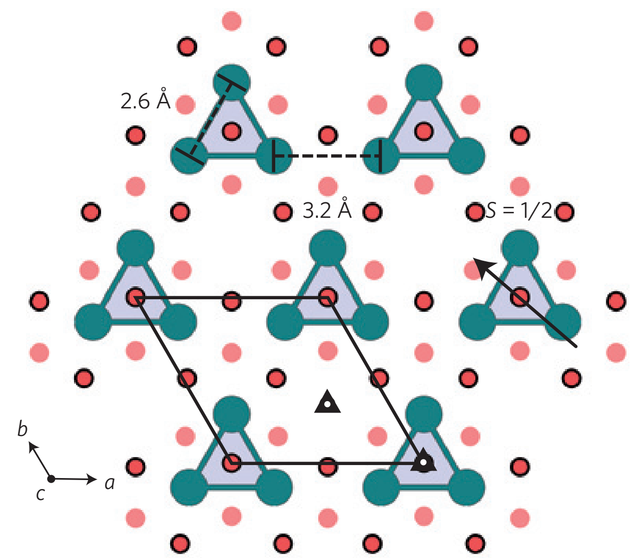
Assertion: a single-band extended Hubbard model on an anisotropic Kagome lattice with 1/6 electron filling.

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



Molecular orbitals and bands



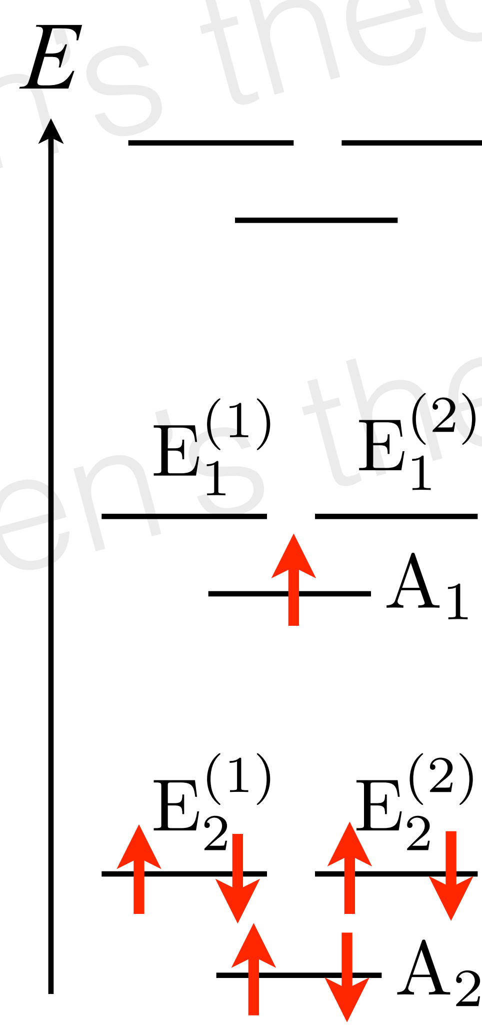


Triangular lattice of Mo_3O_{13} clusters

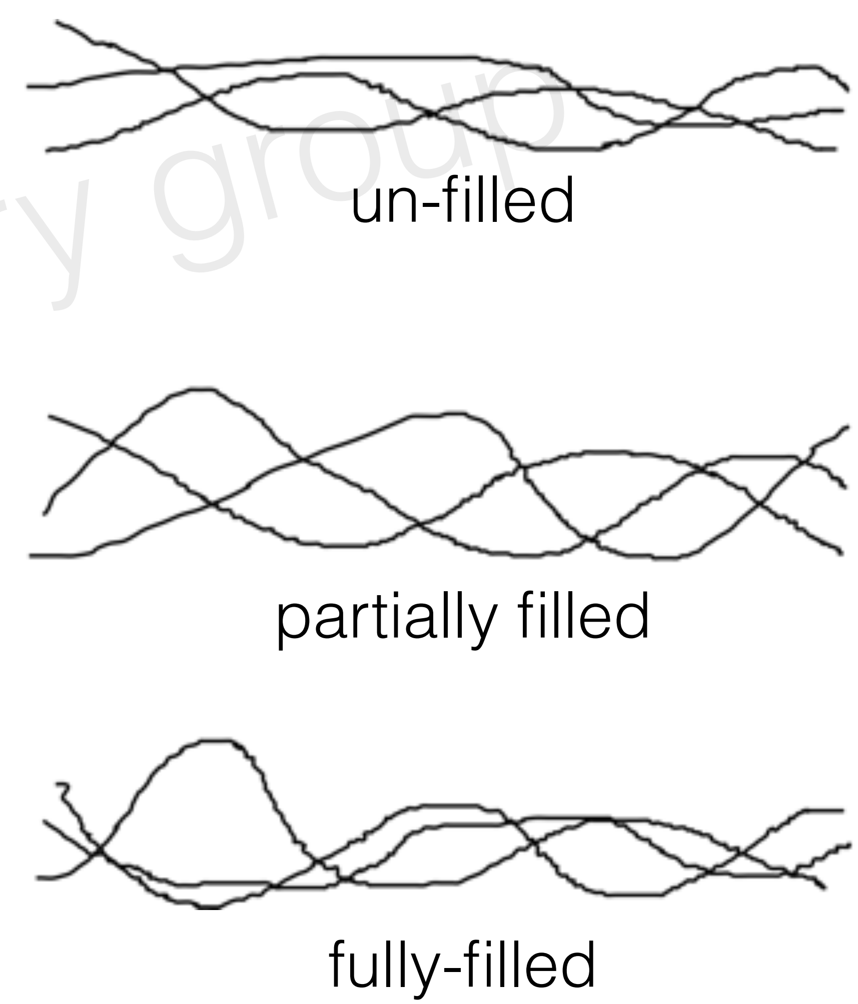
$$|\mathrm{A}_1\rangle = \frac{1}{\sqrt{3}}\left[|\psi_1\rangle_{\mathrm{A}} + |\psi_1\rangle_{\mathrm{B}} + |\psi_1\rangle_{\mathrm{C}}\right],$$

$$|\mathrm{E}_1^{(1)}\rangle = \frac{1}{\sqrt{3}}\left[|\psi_1\rangle_{\mathrm{A}} + e^{i\frac{2\pi}{3}}|\psi_1\rangle_{\mathrm{B}} + e^{-i\frac{2\pi}{3}}|\psi_1\rangle_{\mathrm{C}}\right]$$

$$|\mathrm{E}_1^{(2)}\rangle = \frac{1}{\sqrt{3}}\left[|\psi_1\rangle_{\mathrm{A}} + e^{-i\frac{2\pi}{3}}|\psi_1\rangle_{\mathrm{B}} + e^{i\frac{2\pi}{3}}|\psi_1\rangle_{\mathrm{C}}\right]$$



molecular bands

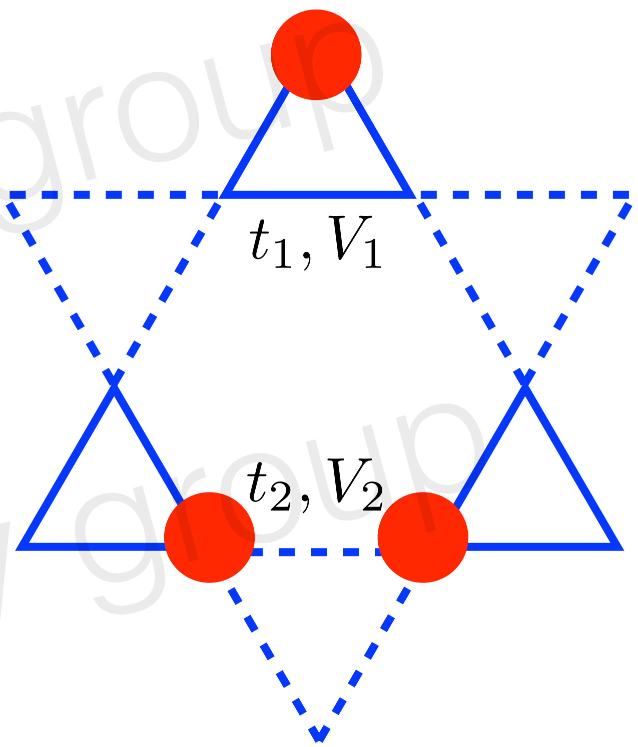


Gang Chen's theory group

Instead of a multi-molecular-band model on a triangular lattice, we go back to the atomic state on each Mo site and build an extended Hubbard model from there.

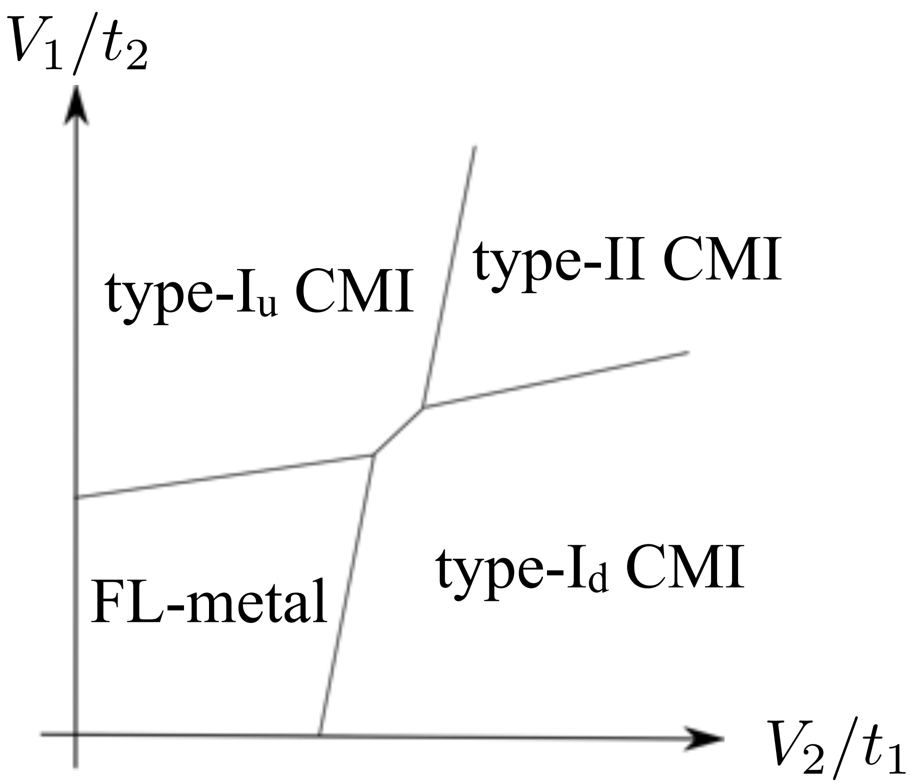
Minimal model allowed by symmetry

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



Physical meaning of electron operator,
Large U alone cannot localize the electron.
V_1 and V_2 are needed: because it is 4d orbital,
and also to localize the electron in the clusters.

Phase diagram



spin sector is spin liquid

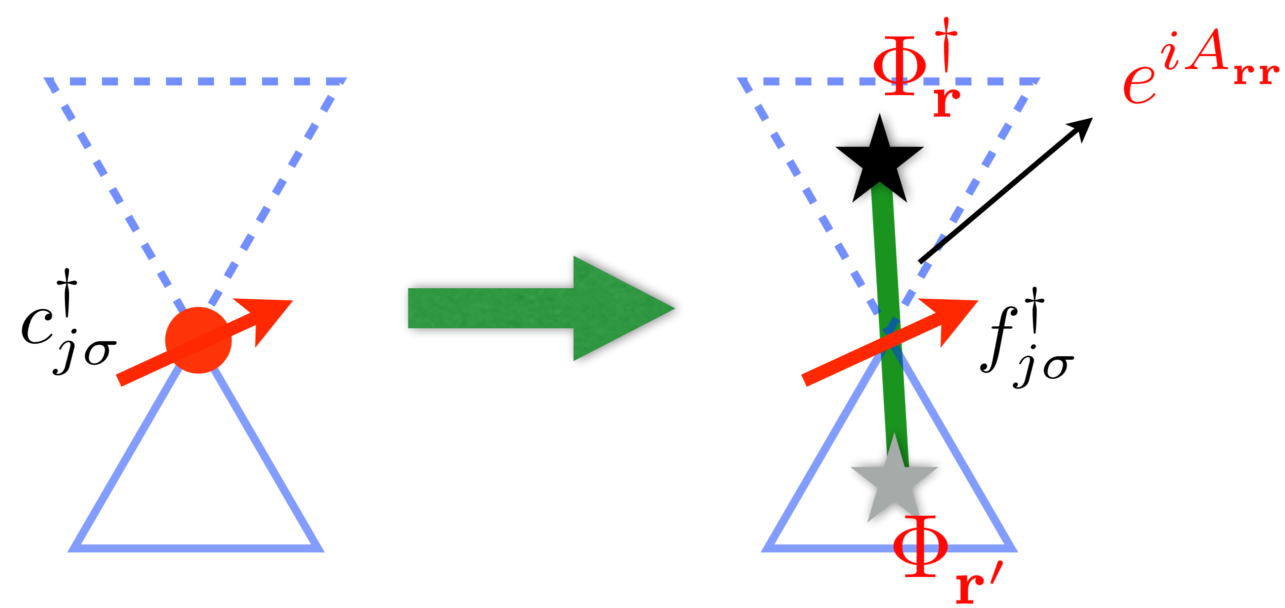
V2 is small, V1 is large

number-phase conjugation

1. FL metal: charges on ***both*** triangles are condensed;
2. Type-Iu CMI: charges on ***down*** triangles are condensed;
3. Type-Id CMI: charges on ***up*** triangles are condensed;
4. Type-II CMI: charges on both triangles are ***not condensed***.

All can be made more precise by parton-gauge construction and also the phase transition

$$c^\dagger_{j\sigma} \sim f^\dagger_{j\sigma}\Phi^\dagger_{\mathbf{r}}\Phi_{\mathbf{r}'}e^{iA_{\mathbf{r}\mathbf{r}'}}$$



A digression — two classes of gauge theories

1. A formal way of introducing spinon + gauge

$$\mathbf{S}_i = \frac{1}{2} f^\dagger_{i\alpha} \boldsymbol{\sigma}_{\alpha\beta} f_{i\beta} \qquad \text{or} \qquad \mathbf{S}_i = \frac{1}{2} b^\dagger_{i\alpha} \boldsymbol{\sigma}_{\alpha\beta} b_{i\beta}$$

and slave rotor representation

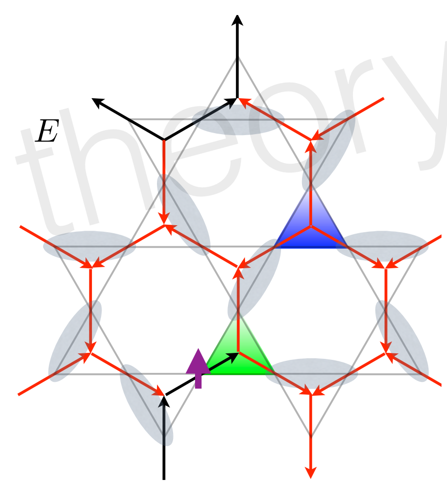
often blamed as “unjustified”, often hard to develop physical intuition


I. Affleck S. Sachdev

2. The microscopic model already looks like a gauge theory

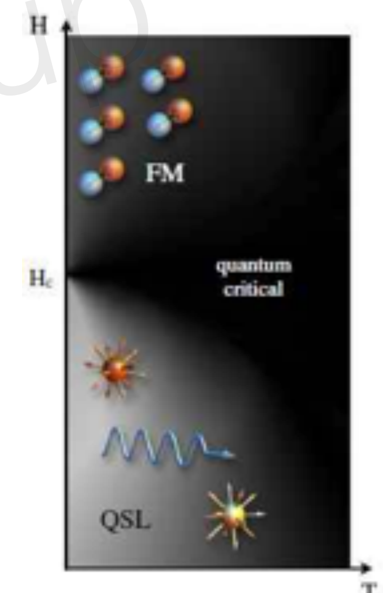

O. Tchernyshyov L. Balents

also in various contrived models (Kitaev, Senthil, Motrunich etc)



$$H = \sum_{\langle ij \rangle} \frac{E_{ij}^2}{2\epsilon} - t \sum_{\langle ij \rangle} a^\dagger_{i\sigma} e^{iA_{ij}} a_{j\sigma} - U \sum_i a^\dagger_{i\uparrow} a^\dagger_{i\downarrow} a_{i\downarrow} a_{i\uparrow}$$

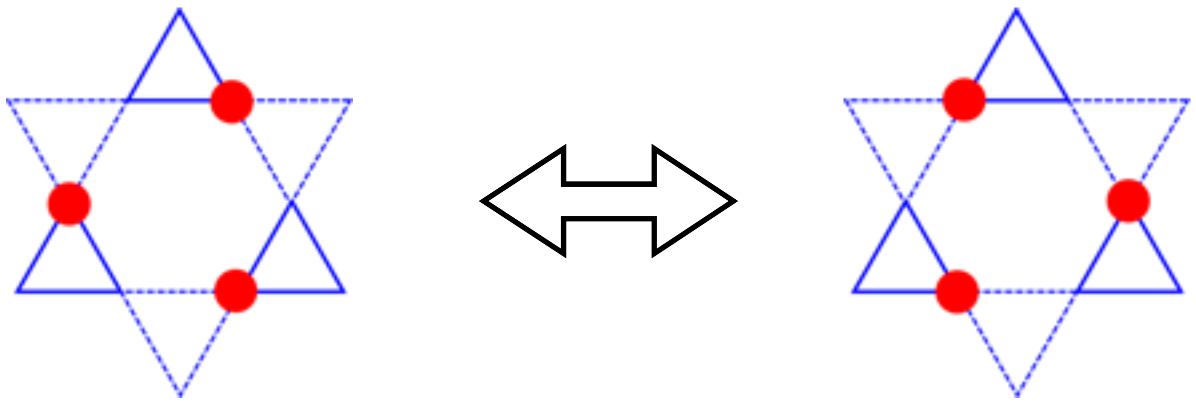
Oleg’s Kagome theory



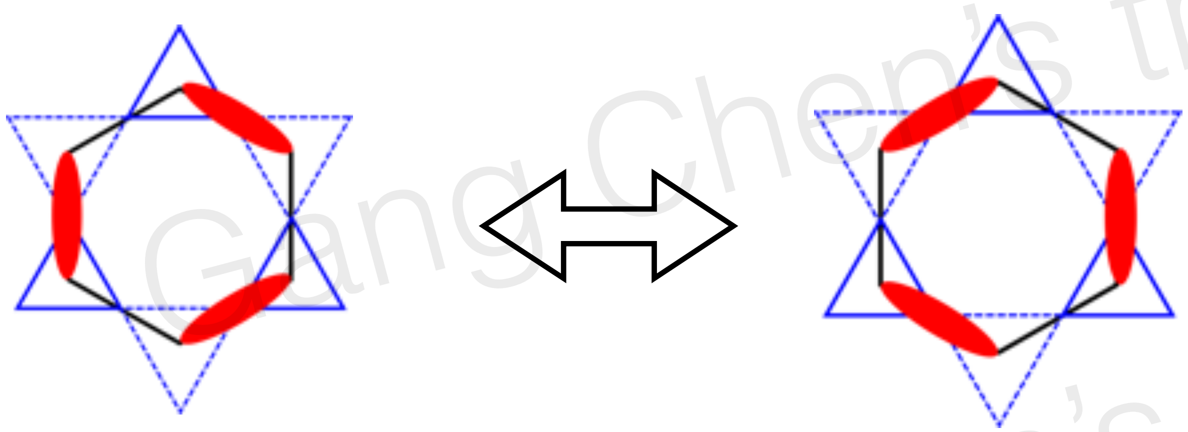
$$S_i^z = E_{ab}$$
$$S_i^\pm = e^{\pm i A_{ab}}$$

Leon’s quantum spin ice

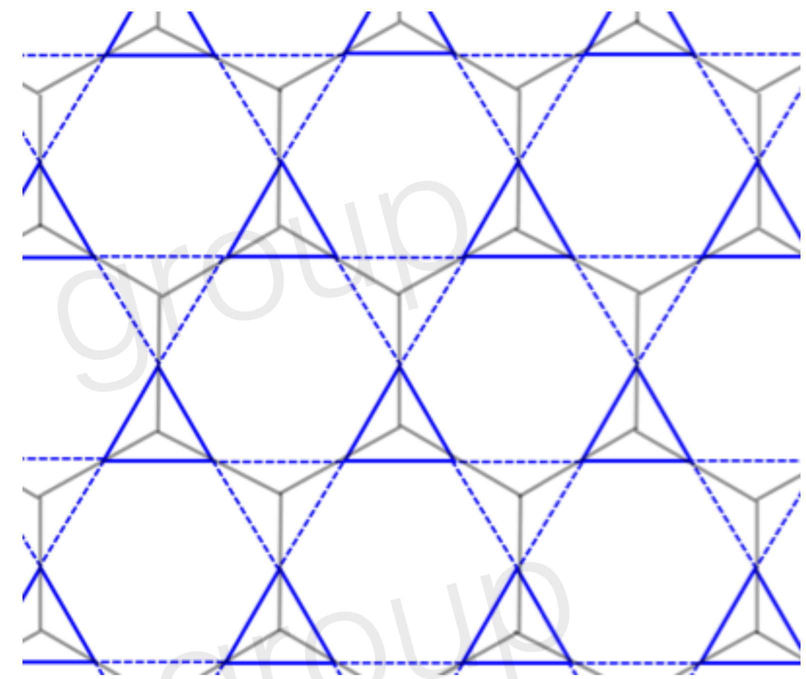
Quantum dimer model in type-II CMI



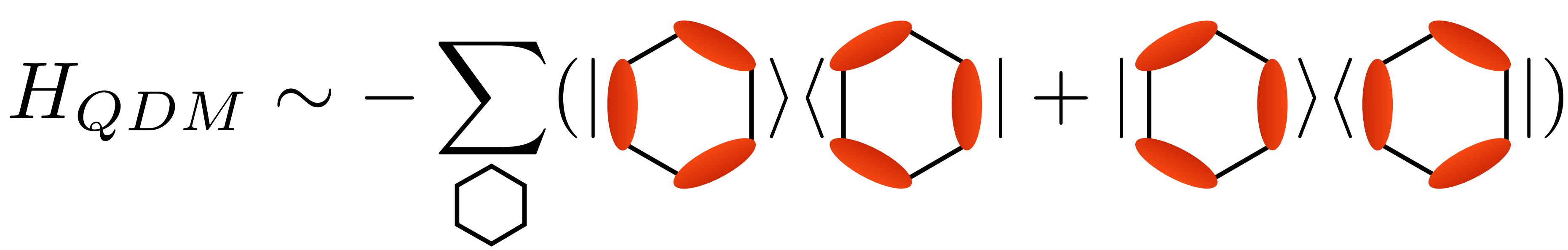
3rd order process in type-II CMI



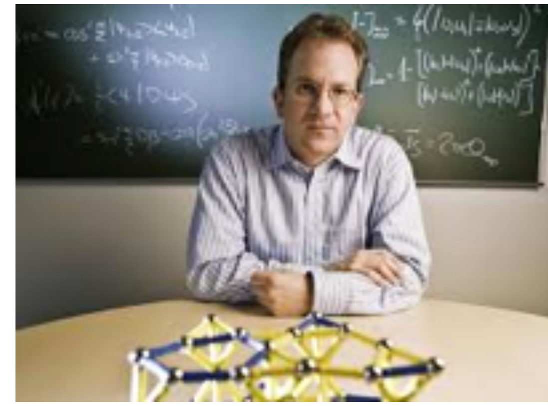
dimer resonating



dual honeycomb lattice and
Kagome lattice



Plaquette charge order via QDM



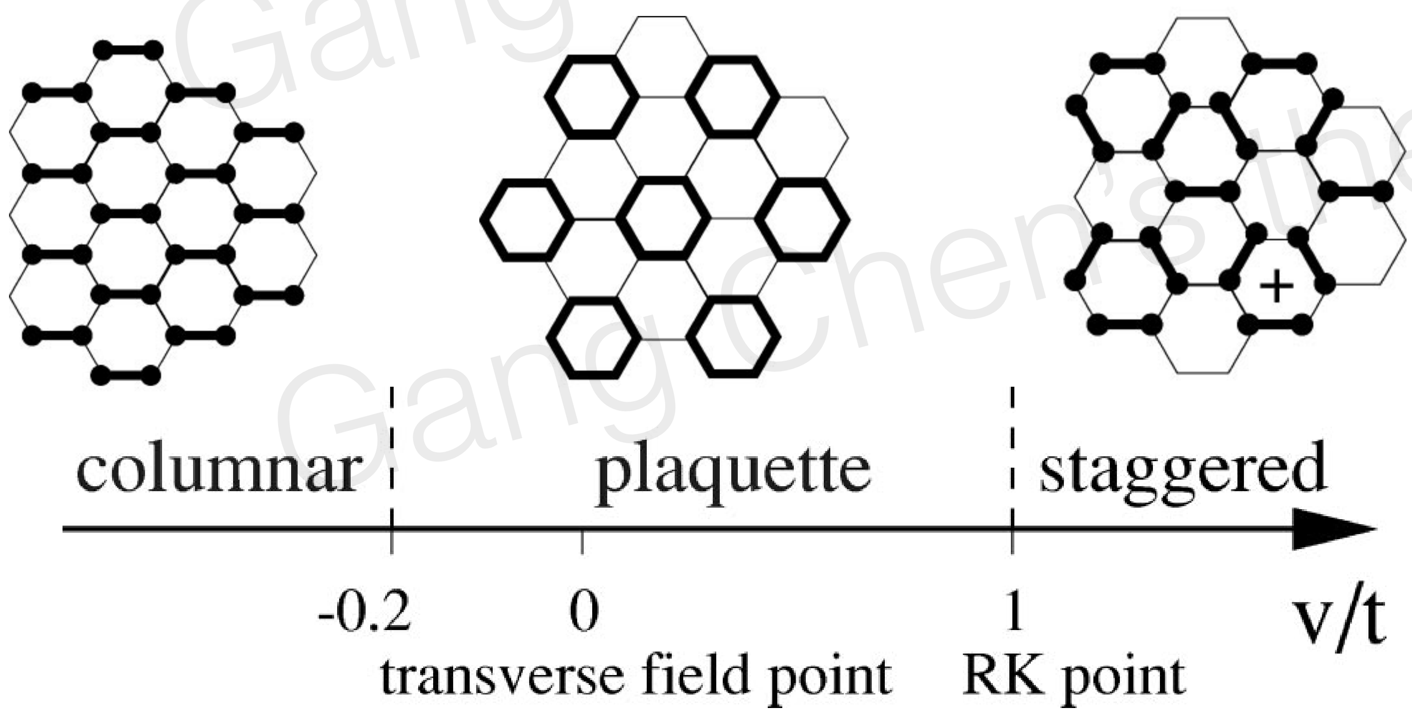
R. Moessner

S. Sondhi

P. Chandra

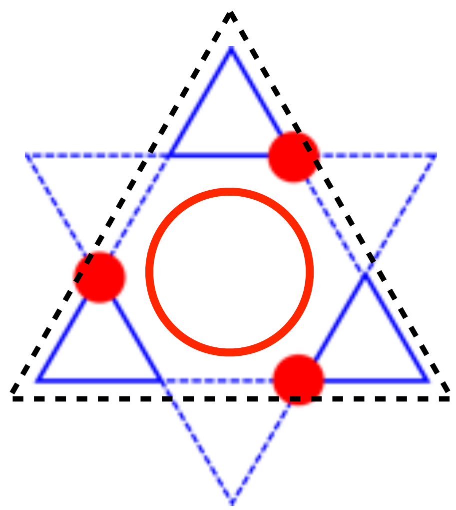
Moessner, Sondhi, Chandra 2001, also
in several other numerical works

$$H_{QDM} = -t\hat{T} + v\hat{V}$$
$$= -t\left(|\nabla\rangle\langle\triangle| + \mathrm{H.c.}\right) + v\left(|\nabla\rangle\langle\nabla| + |\triangle\rangle\langle\triangle|\right).$$

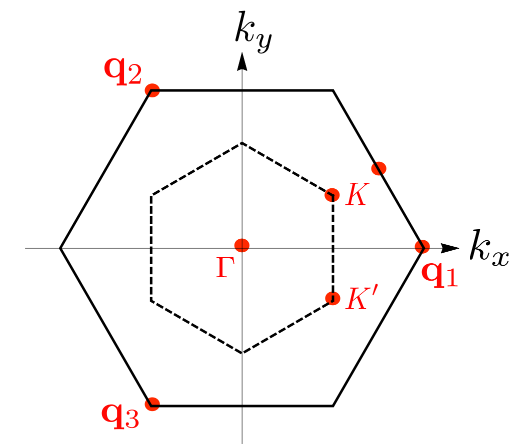


Plaquette charge order:
a local charge “RVB”,
a local collective behaviour !

Spin behaviour with weak PCO

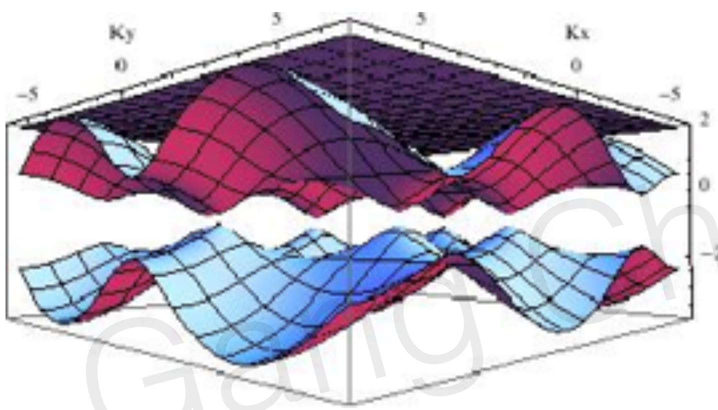


tripled unit cell,
host 3 electron

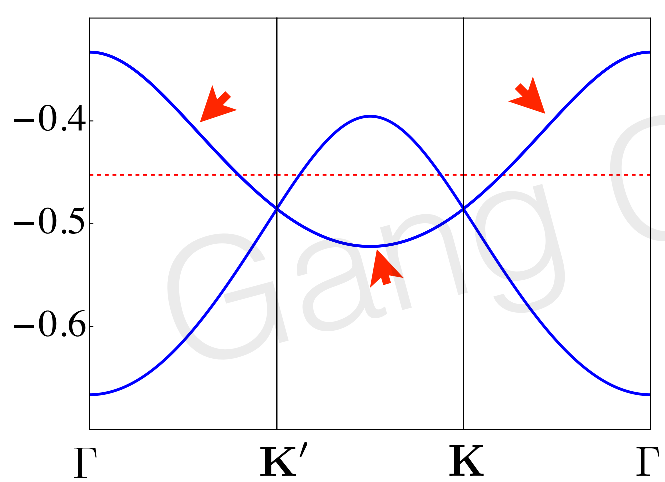


BZ of type-I & type-II CMIs

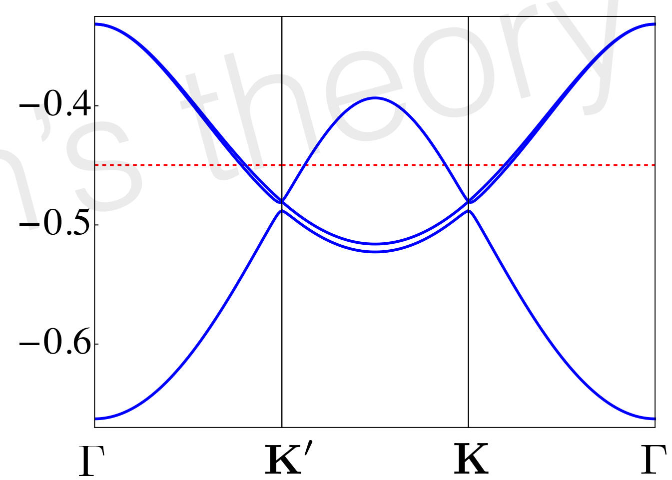
M. Hastings' theorem.

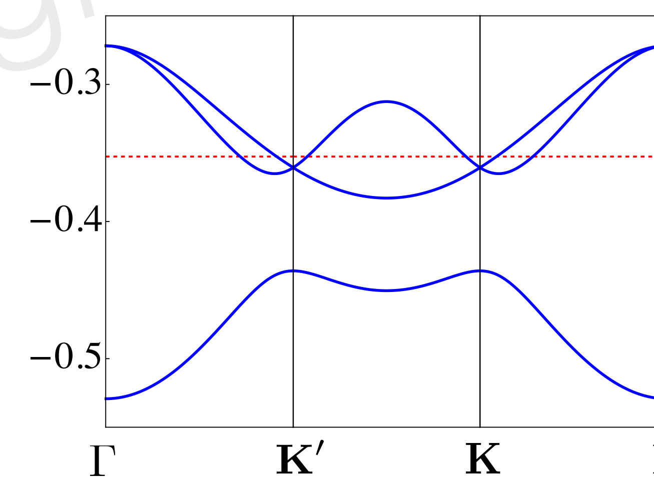


spinon band structure of type-I CMI:
fill half of the lowest spinon band



type-I CMI: no PCO
folding the lowest spinon band
onto the BZ of type-II CMI



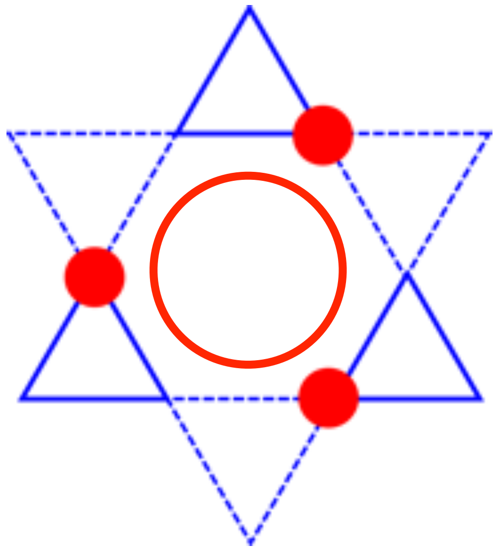


increasing PCO
in type-II CMI

Implication to susceptibility from bandwidth and filling

Gang Chen's theory group

Spin behaviour with strong PCO



a single resonating
hexagon

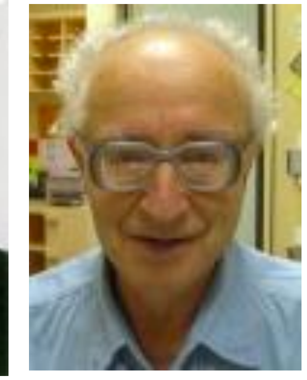
Spin state reconstruction

3 spins together act as one effective spin-1/2
and one pseudospin-1/2

$$\frac{1}{2}\otimes\frac{1}{2}\otimes\frac{1}{2}=\frac{1}{2}\oplus\frac{1}{2}\oplus\frac{3}{2}$$

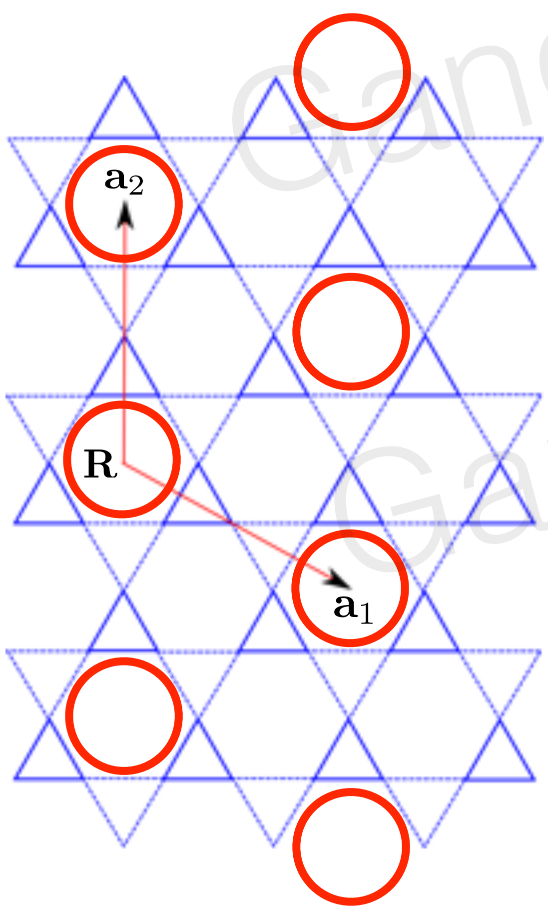
spin s=1/2, pseudospin $\mathcal{T}$=1/2, nonmagnetic

K. Kugel



D. Khomskii

An effective Kugel-Khomskii model on the **emergent triangular lattice**



$$H_{\mathrm{KK}}=\frac{J'}{9}\sum_{\mathbf{R}}\sum_{\mu=x,y,z}\left[\mathbf{s}(\mathbf{R})\cdot\mathbf{s}(\mathbf{R}+\mathbf{a}_{\mu})\right]$$
$$\times[1+4\cancel{\pi^{\mu}}(\mathbf{R})][1-2\pi^{\mu}(\cancel{\mathbf{R}}+\mathbf{a}_{\mu})]$$

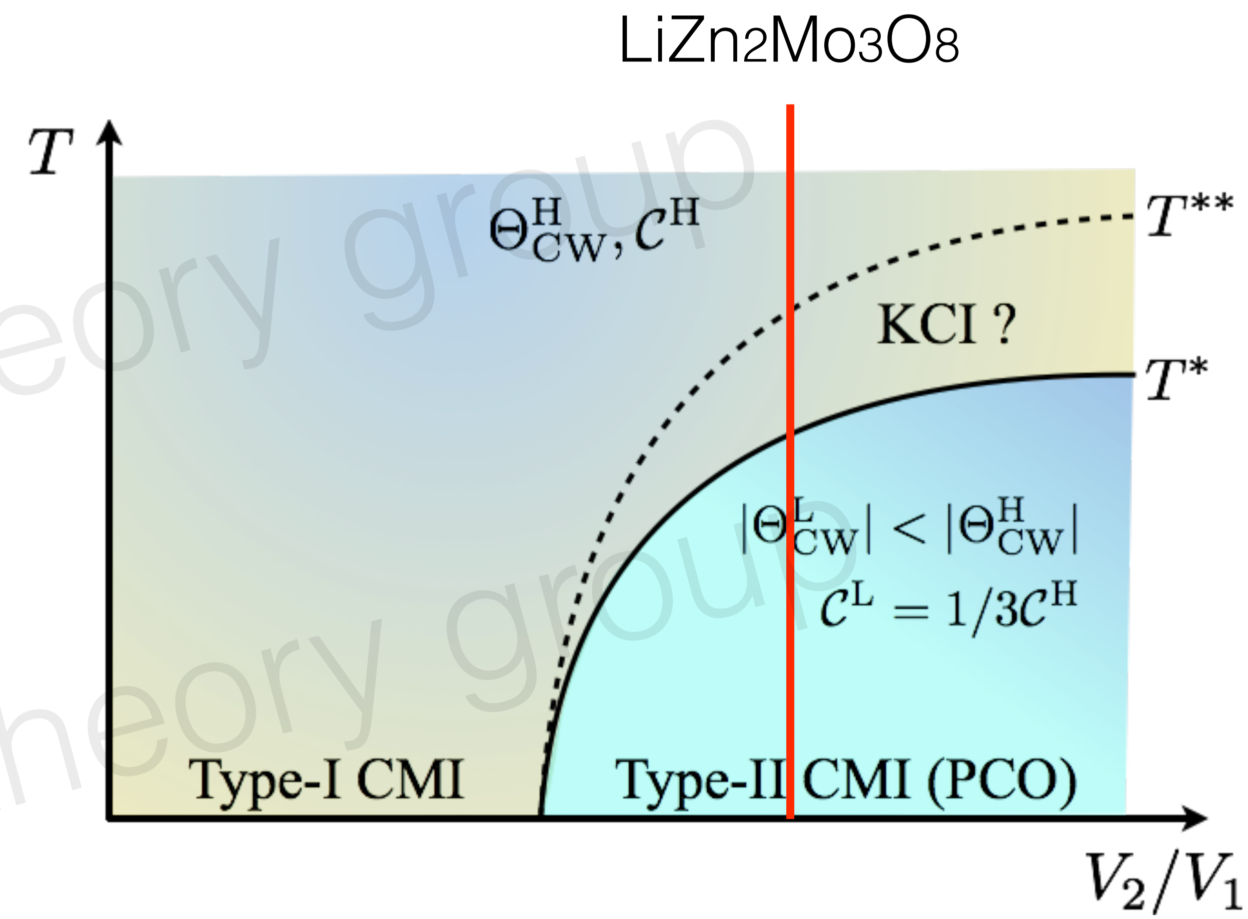
$$\Theta_{\mathrm{CW}}^{\mathrm{L}}=-\frac{z_t s(s+1)}{3}\frac{J'}{9},\quad \mathcal{C}^{\mathrm{L}}=\frac{g^2\mu_{\mathrm{B}}^2 s(s+1)}{3k_{\mathrm{B}}}\frac{N_{\Delta}}{3}$$

due to the reduced probability of spin interaction

1. very frustrated, may also support spin liquid
2. interesting ordering under a strong field

Summary about $LiZn_2Mo_3O_8$

The emergence of PCO is the driving force of the 1/3 spin susceptibility anomaly.
The ground state of the system is probably a U(1) QSL with spinon Fermi surfaces.



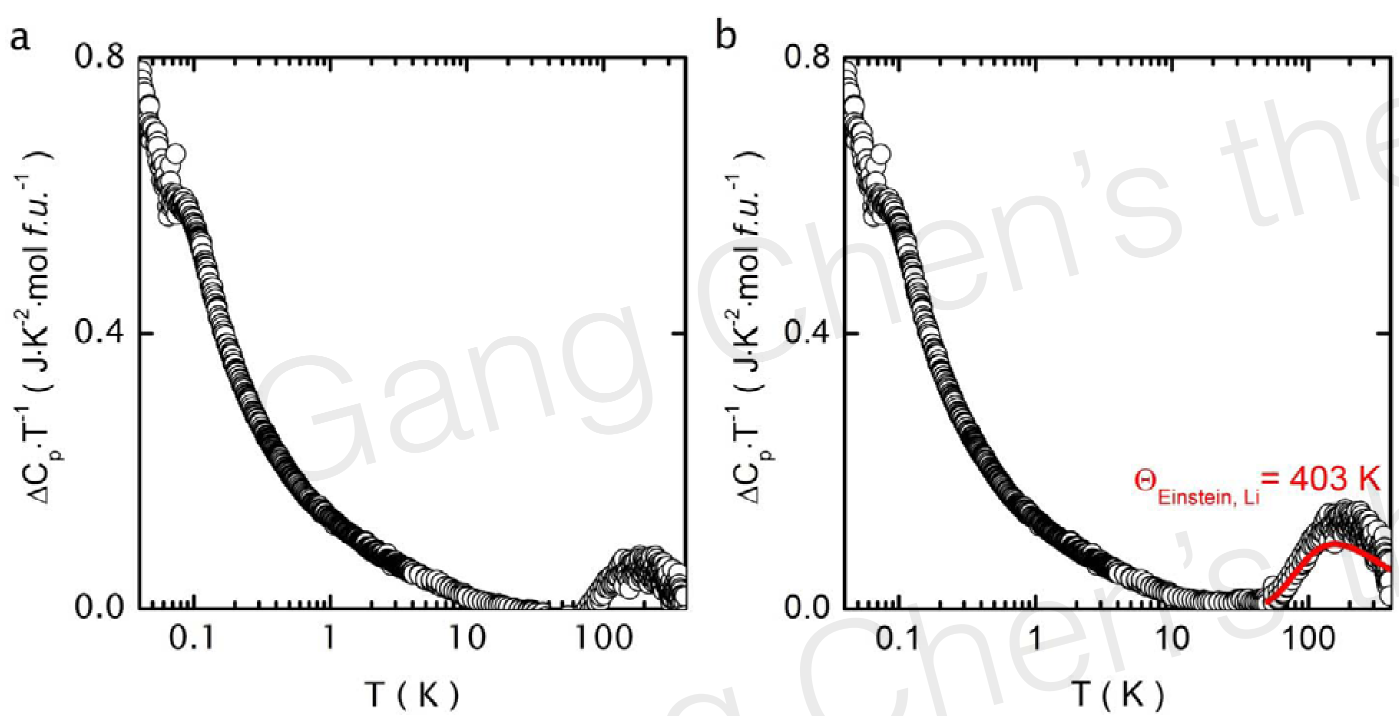
The crossover Kagome charge ice (KCI) regime is probably not sharply defined in $LiZn_2Mo_3O_8$ as it requires $V_2 >> T >$ ring hopping.

type-II CMI (PCO)

KCI: same Curie const as high-T one, slightly different Curie temperature

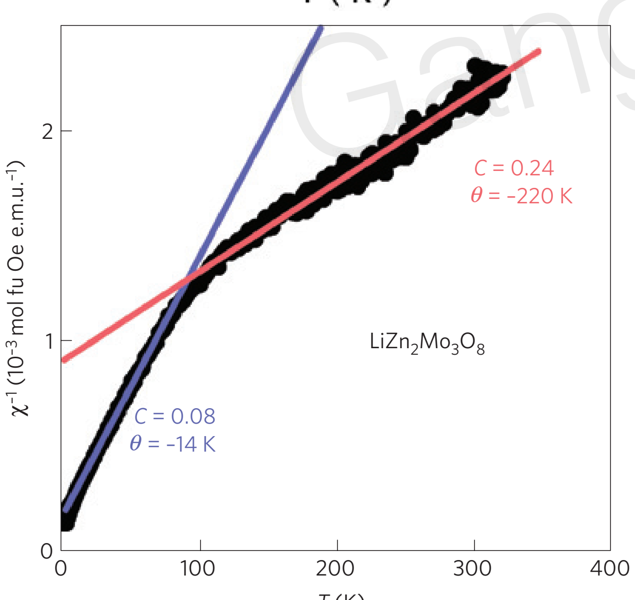
about PCO

1. Expect 1st order finite temperature transition (also in Flint-Lee's proposal) 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)



Disorders pin the charge density wave, broaden the phase transition.

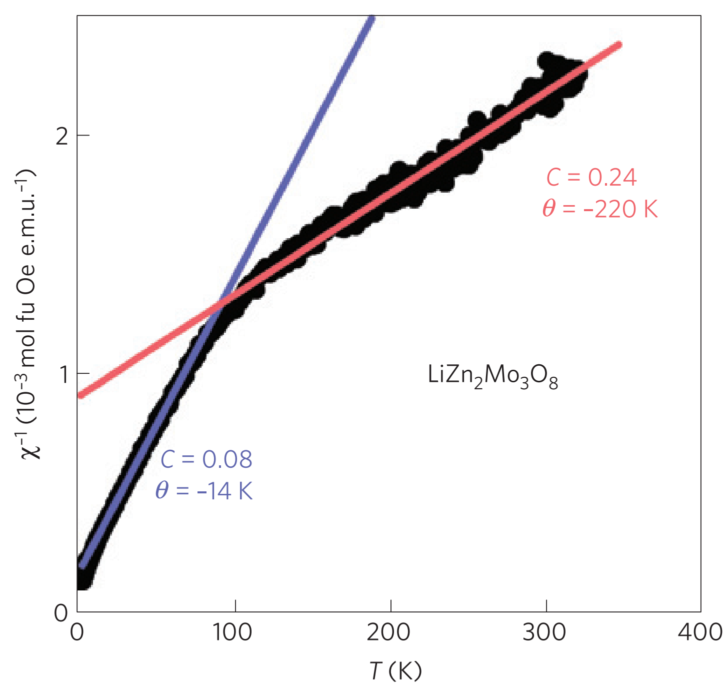
W. L. McMillan PRB 1975



coincide with susceptibility anomaly

I need to consult people here about the quality of the sample.

about low-T QSL

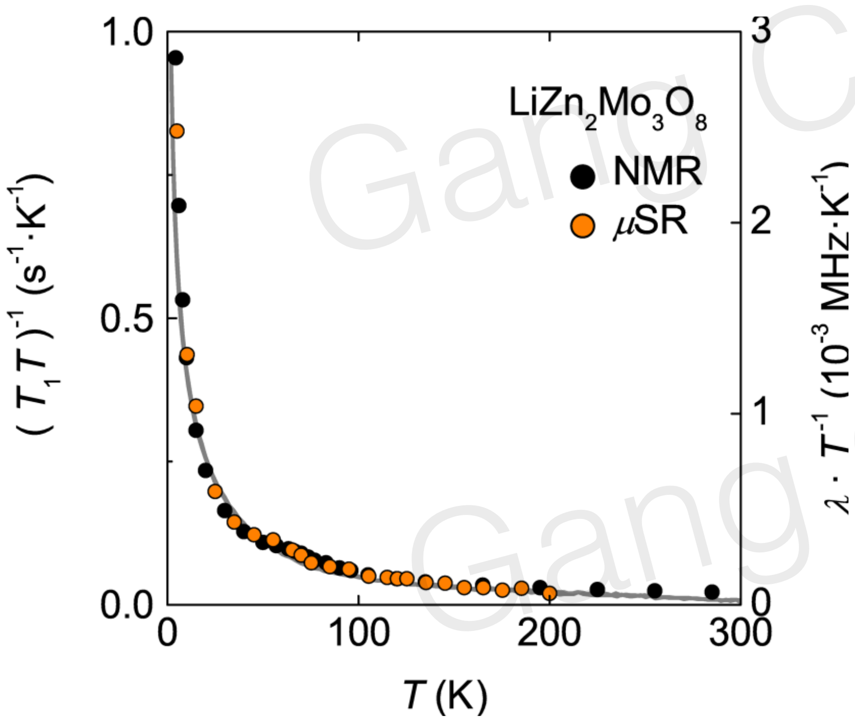


A qualitative discussion

U(1) QSL with spinon Fermi surfaces

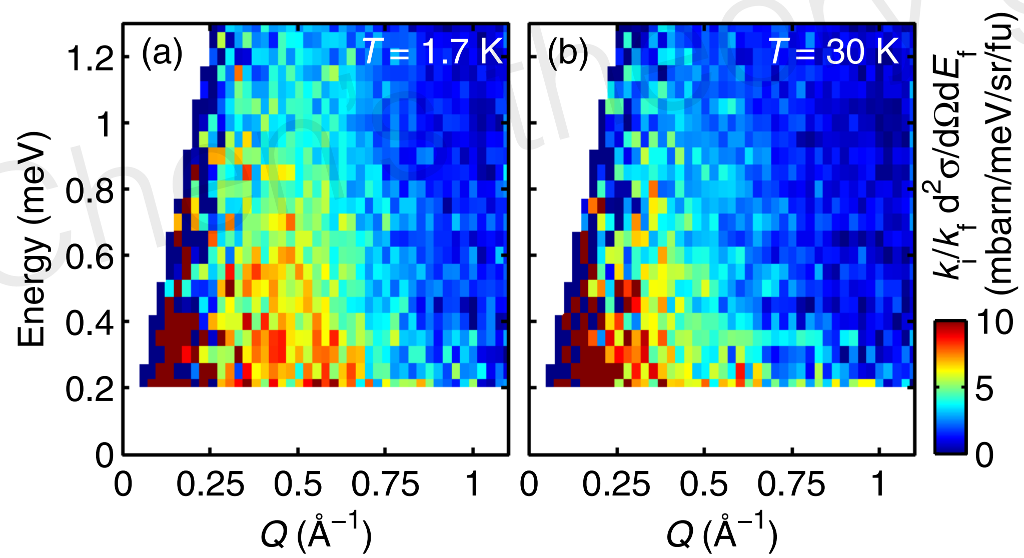
$$C_v \sim T^{2/3}, \quad \chi \sim \text{const}$$

at very low temperature (<1K), but may be hard to observe.



Large density of low-energy spin excitations

$$1/(T_1 T) \propto D(E_F)^2$$



It would be nice to compare the prediction from the spinon band structure in future work. Single crystal data are preferred.

Other Mo-based cluster magnets

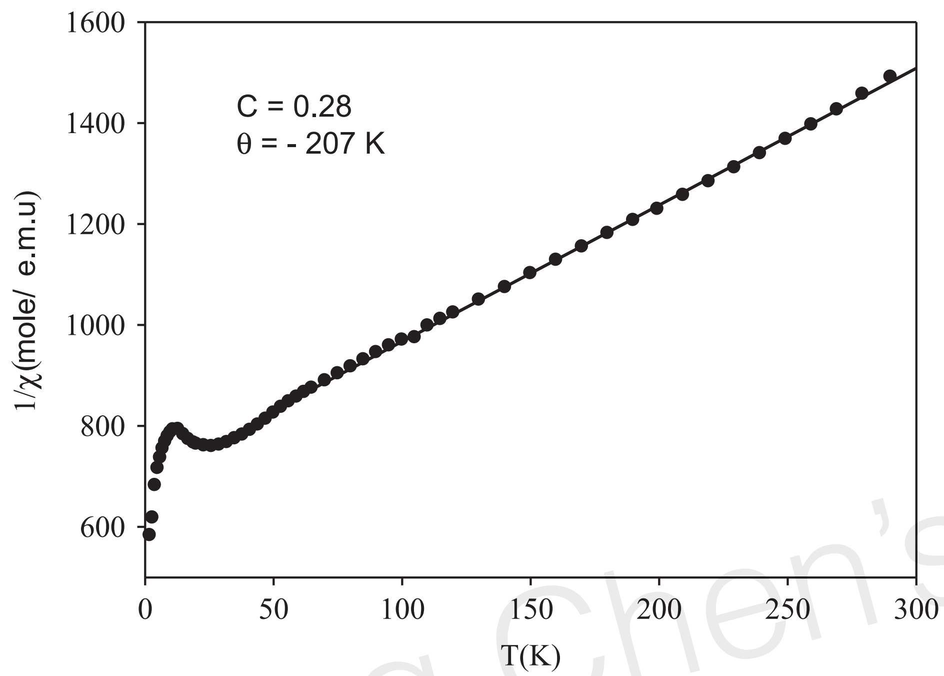
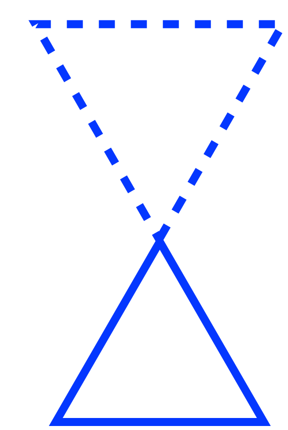


Fig. 5. Inverse magnetic susceptibility as a function of temperature for $Li_2InMo_3O_8$. Data were taken under an applied field of 5000 Oe. Curie–Weiss fit is represented by the solid line.

	$[\text{Mo-Mo}]_u$	$[\text{Mo-Mo}]_d$	λ	e^-/Mo_3
$LiZn_2Mo_3O_8$	2.6Å	3.2Å	1.23	7
$Li_2InMo_3O_8$	2.54Å	3.25Å	1.28	7
$ScZnMo_3O_8$	2.58Å	3.28Å	1.27	7

a simple phenomenological parameter



$$\lambda = \frac{[\text{Mo-Mo}]_d}{[\text{Mo-Mo}]_u}$$

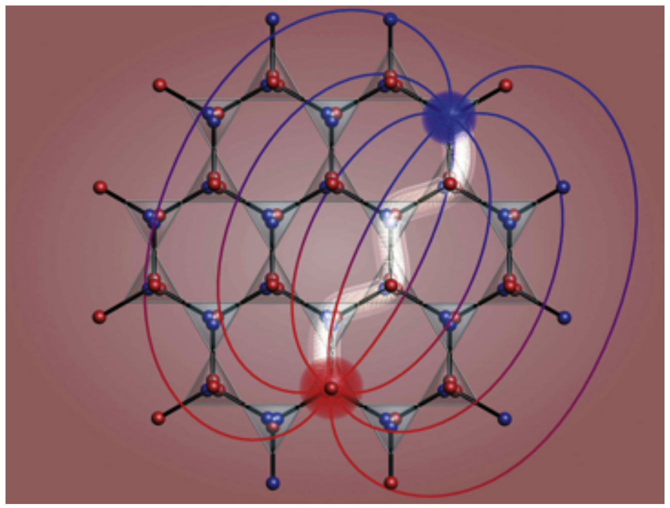
no susceptibility anomaly !

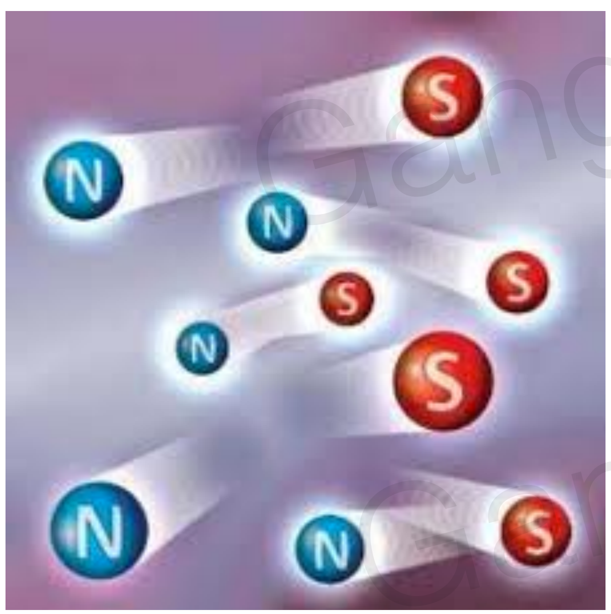
$Li_2InMo_3O_8$ as a type-I CMI ?

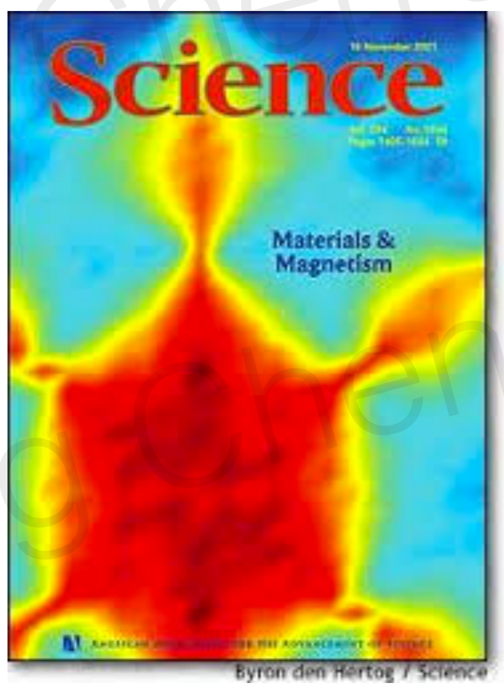
quantum spin liquid ?

type-I CMI is a triangular lattice spin liquid

ICE AGE 1: classical spin ice







M. Gingras, C. Castelnovo, R. Moessner,
S. L. Sondhi,O. Tchernyshyov, M. J. Harris,
S. T. Bramwell, D.J.P. Morris, …….

ICE AGE 2: quantum spin ice

fig from L. Balents and L. Savary

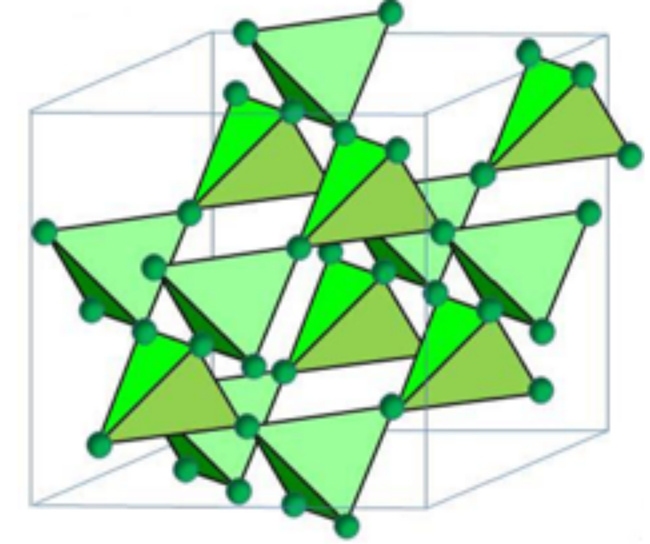
M. Hermele, L. Balents, M. Fisher,
L. Savary, S. Lee, Y. Wan, O. Tchernyshyov,
G. Chen, Y.-P. Huang, M. Gingras……..
C. Broholm, K. Ross, B. Gaulin……..

So far, not observed !
Because of very **small energy scale.**
Solution: d electrons, or others ?

ICE AGE 2.01 ? Quantum Charge Ice ?

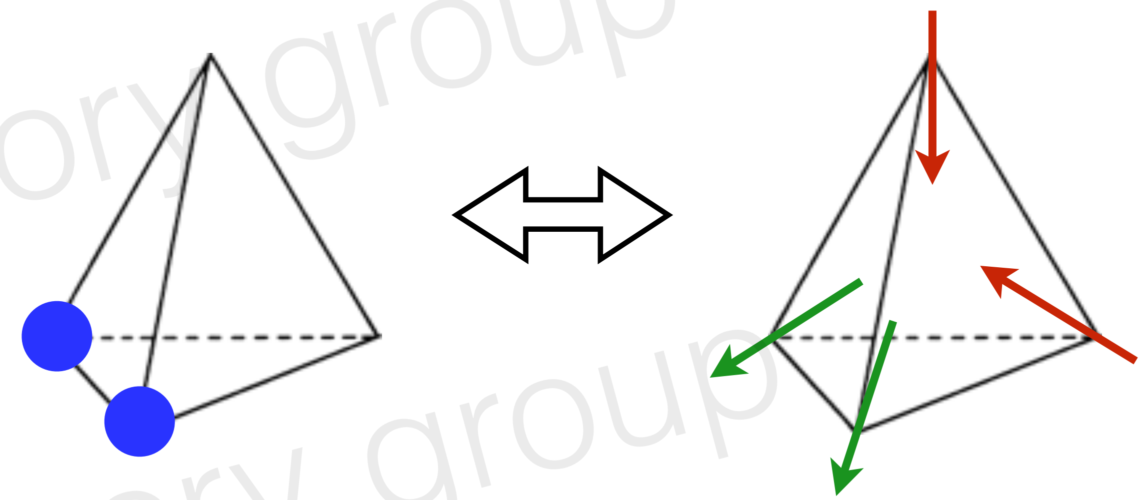
This is not a creative work,
just a suggestion to experiments.

3D cluster Mott insulator



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

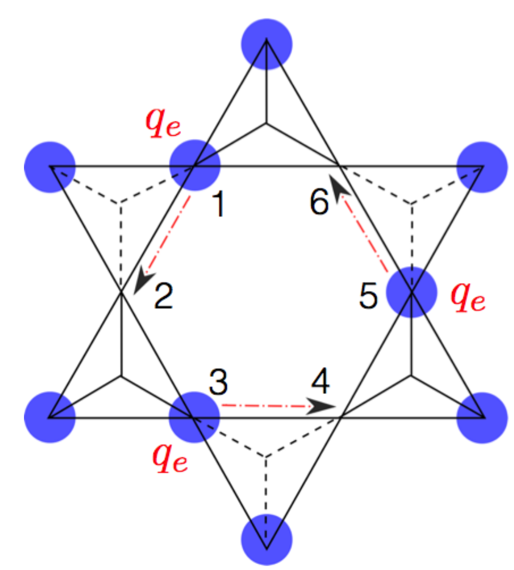
a single band Hubbard model with
1/8 or 1/4 electron filling



In large U limit, $L_i^z = \begin{cases} +\frac{1}{2}, & n_i = 1, \\ -\frac{1}{2}, & n_i = 0. \end{cases}$

When V << t, we have a Fermi liquid metal

When V >> t, we get "charge ice rule", or cluster Mott insulator.



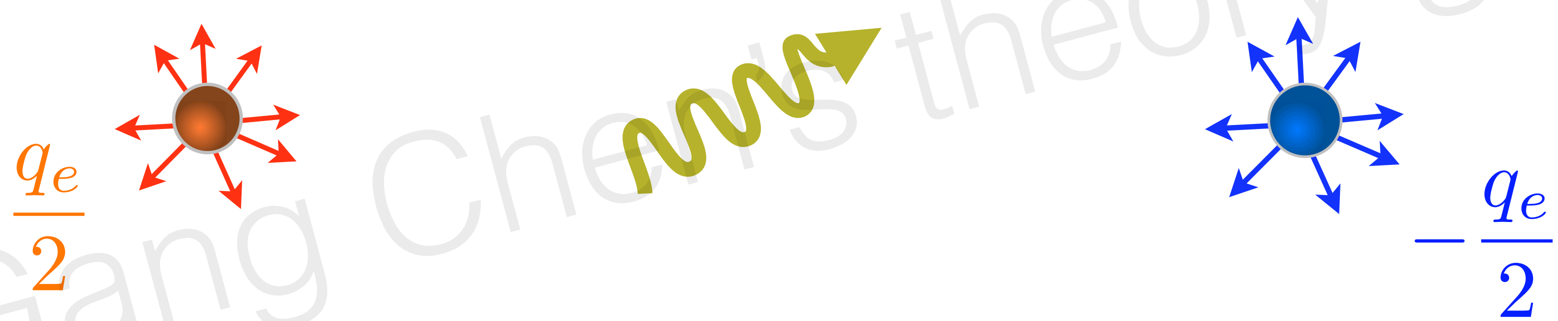
Charge sector is like a spin-1/2 XXZ model on pyrochlore lattice.

Charge fractionalization

From the properties of quantum spin ice, we can identify the corresponding properties for the charge sector !

Quantum spin ice in *L* = fractional charge liquid in charge sector

- Low-energy physics is described by an emergent (compact) quantum electrodynamics in 3+1D, indicating an **additional U(1) gauge structure** in the charge sector.

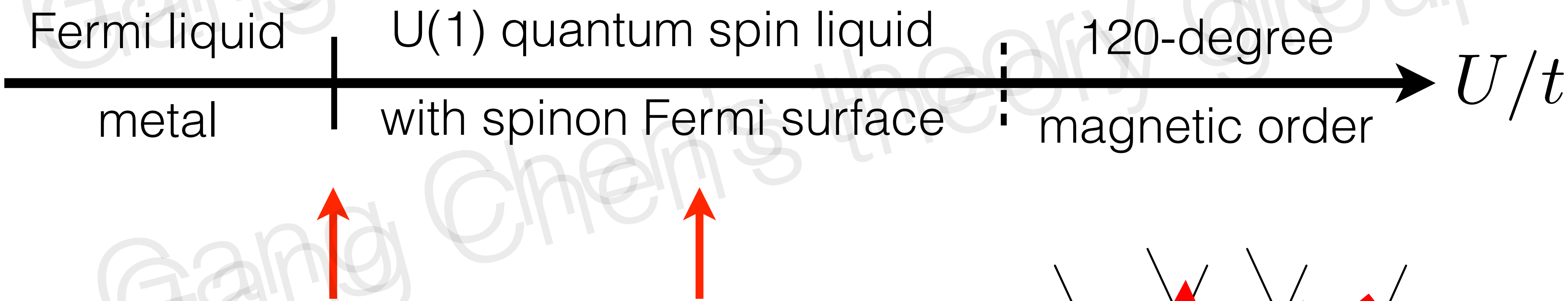


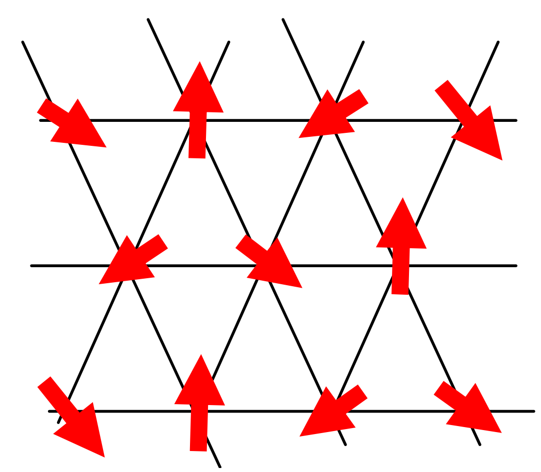
- Just as spin quantum number fractionalization in a QSI, charge excitation in FCL is also fractionalized, carrying a $q_e/2$ electric charge.

3D cluster Mott insulator as a quantum charge ice

This is a Hubbard model, energy scale is high.
Overcome the temperature obstacle of
f-electron quantum spin ice.

For the 1/2 filling case, charge sector is completely trivial !

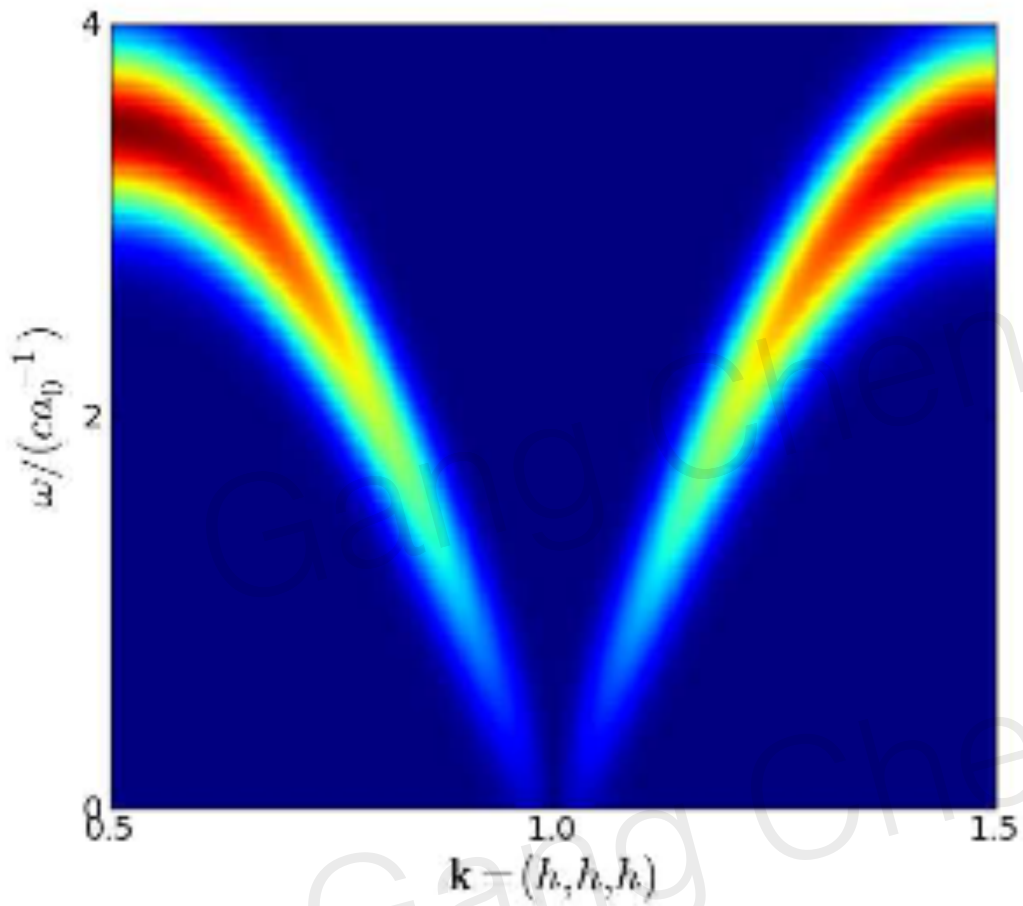




- (Inelastic) X-ray scattering measures U(1) gauge field correlation in the charge sector

$$\mathrm{Im}[E^{\alpha}_{-\mathbf{k},-\omega} E^{\beta}_{\mathbf{k},\omega}] \propto [\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{\mathbf{k}^2}]\,\omega\,\delta(\omega - v|\mathbf{k}|),$$

$$\mathbf{E}_{\mathbf{r}+\frac{1}{2}\mathbf{e}_\mu} \equiv L^z_{\mathbf{r},\mathbf{r}+\mathbf{e}_\mu} \frac{\mathbf{e}_\mu}{|\mathbf{e}_\mu|} = (n_{\mathbf{r}+\frac{1}{2}\mathbf{e}_\mu} - \tfrac{1}{2}) \frac{\mathbf{e}_\mu}{|\mathbf{e}_\mu|}$$



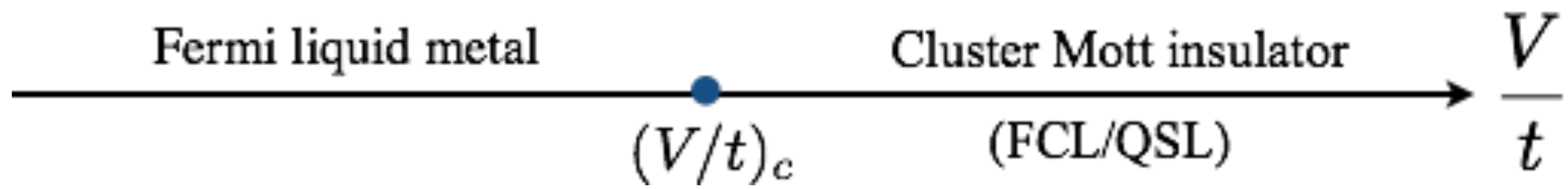
$$I(\omega) \sim \omega$$

O. Benton, et al, 2012

Byron den Hertog / Science

$$\langle E^{\alpha}_{-\mathbf{k}} E^{\beta}_{\mathbf{k}} \rangle \propto \delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{\mathbf{k}^2}$$

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



A new example of Mott transition: condensation of fractional charge excitation

When the charge bosons are condensed, the $U(1)_{ch}$ gauge field is gapped from the Higgs' mechanism. The charge fractionalization is then destroyed. The charge rotor is also condensed from which the $U(1)_{sp}$ gauge field picks up a mass. The spinon and charge rotor are then combined back into a full electron in the Fermi liquid metal phase.

Electron spectral function is a convolution of two fractionalized charge bosons and one spinon. (measure through ARPES or tunnelling spectroscopy.)

1. Activated behaviour in the cluster Mott phase: gap = 2 x boson gap

2. Pseudogap-like at Mott transition point, A(w) ~ w^4

Electric resistivity signals the z_c=1 dynamical exponent and $\rho_c = \rho_f + (\rho_I^{-1} + \rho_{II}^{-1})^{-1}$

note: the resistivity gap in the Mott regime is single boson gap.
but resistivity depends on many other things.

Gang Chen's theory group

Pyrochlore Mott insulators with fractional electron filling

usually associated with mixed valences

VOLUME 93, NUMBER 12 PHYSICAL REVIEW LETTERS week ending 17 SEPTEMBER 2004

Transition from Mott Insulator to Superconductor in $GaNb_4Se_8$ and $GaTa_4Se_8$ under High Pressure

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(Received 30 April 2004; published 16 September 2004)

$GaTa_4Se_8$ (with $Ta^{3.25+}$:$d^{1.75}$)

VOLUME 85, NUMBER 5 PHYSICAL REVIEW LETTERS 31 JULY 2000

LiV_2O_4 Spinel as a Heavy-Mass Fermi Liquid: Anomalous Transport and Role of Geometrical Frustration

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(Received 27 January 2000)

LiV_2O_4 (with $V^{3.5+}$:$d^{1.5}$)

and many others

Summary

I provide two specific examples about the physics of cluster Mott insulators.

There is a very interesting interplay between the charge and spin degrees of freedom in both 2D and 3D cluster Mott insulators.

Cluster Mott insulators are new physical systems that may host various emergent and exotic physics.