# The theory of cluster Mott insulators: charge fluctuations and quantum spin liquids

GANG CHEN (Univ of Toronto)

ArXiv 1402.5425 **(PRL 2014),** 1408.1963 **(unpublished).** 

Collaborators: Hae-Young Kee, Yong-Baek Kim

## Outline

- Motivation and introduction
- Cluster Mott insulator in 2D: theory and experiments
- Cluster Mott insulator in 3D: theory and experiments
- Summary



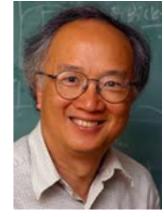


Sung-Sik Lee

T Senthil

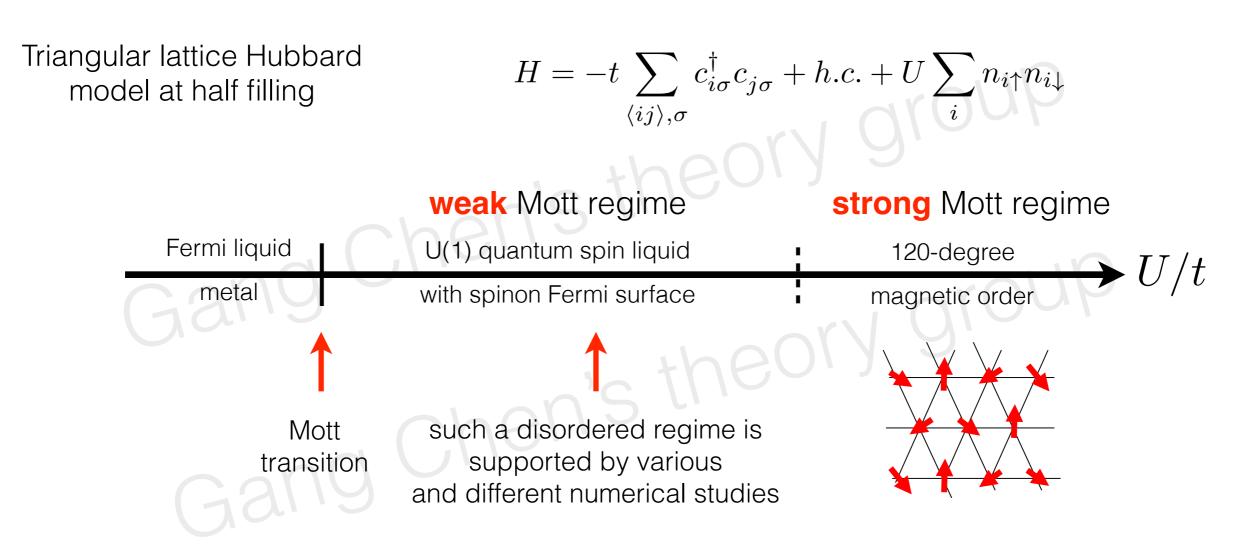
#### Mott insulator and Mott transition "Conventional"





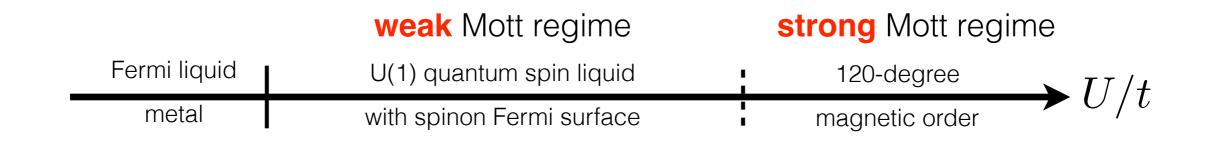
O Motrunich

P Lee



Low EFT of QSL: spinon Fermi surface coupled with a fluctuating U(1) gauge field. 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 !



#### **Remark (on the mechanism NOT the properties of QSL)**:

- 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.

#### **Question / observation:**

- What if the change fluctuation is very strong, and in the most extreme case, the charge sector forms a quantum charge liquid? Spin sector is even more likely to be in a QSL.
- 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 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.

## My Goal Of This Talk

- 1. Introduce the notion of cluster Mott insulator (they are interesting and they exist in nature, actually quite a lot, not studied)
- 2. Develop a **new theoretical framework** to understand the **novel charge fluctuation** and spin fluctuation
- 3. Apply to illustrative examples and explain the puzzling experiments.

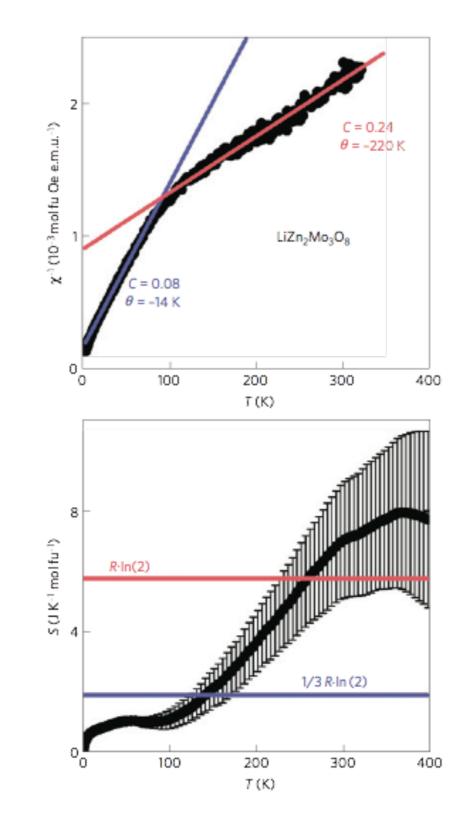
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T. McQueen @ JHU

#### One striking experiment on LiZn2Mo3O8



#### Why striking and difficult?

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

Neither model works.

Nature Materials 2012



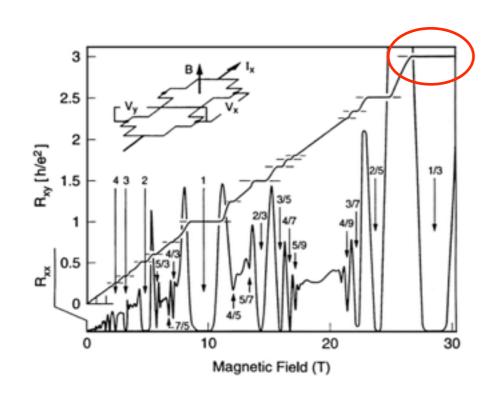
Laughlin

FQHE (Tsui, Stormer, and Gossard)

First exotic phenomenon known to us



Wen

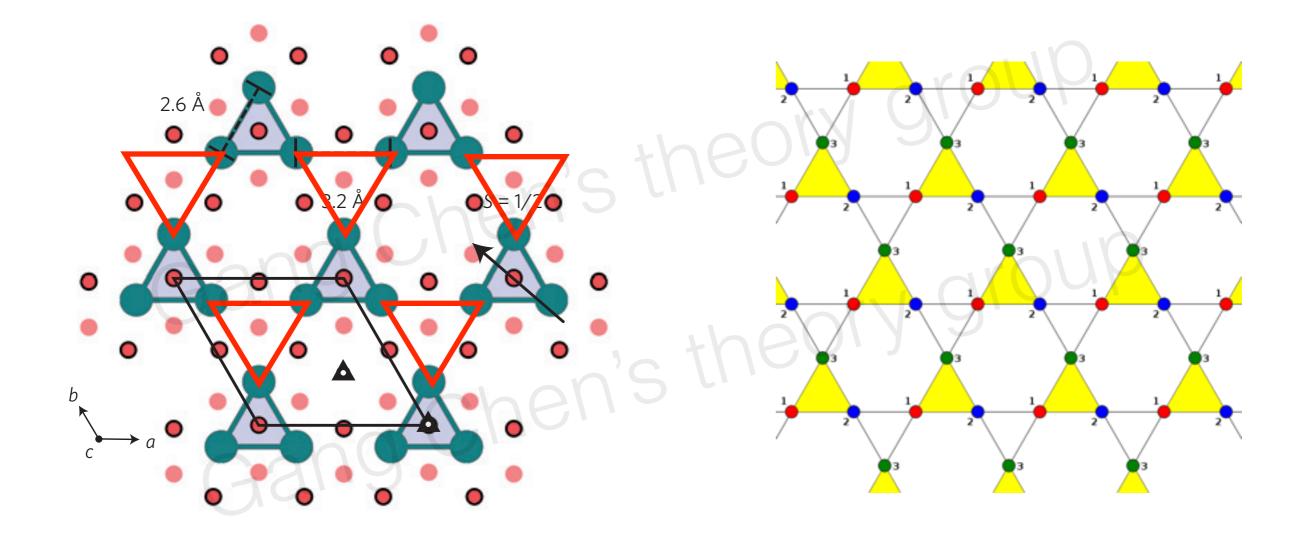




Wen: all the electrons in the Laughlin state dance collectively.

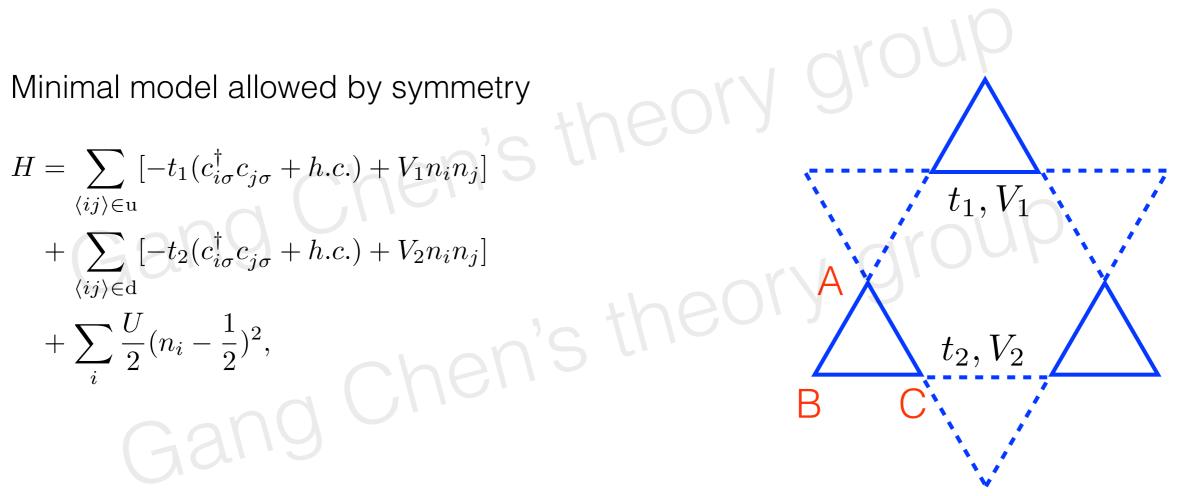
What do electrons do in LiZn2Mo3O8 ? Collective behaviours? Actually there are similarities.

### LiZn<sub>2</sub>Mo<sub>3</sub>O<sub>8</sub> structure



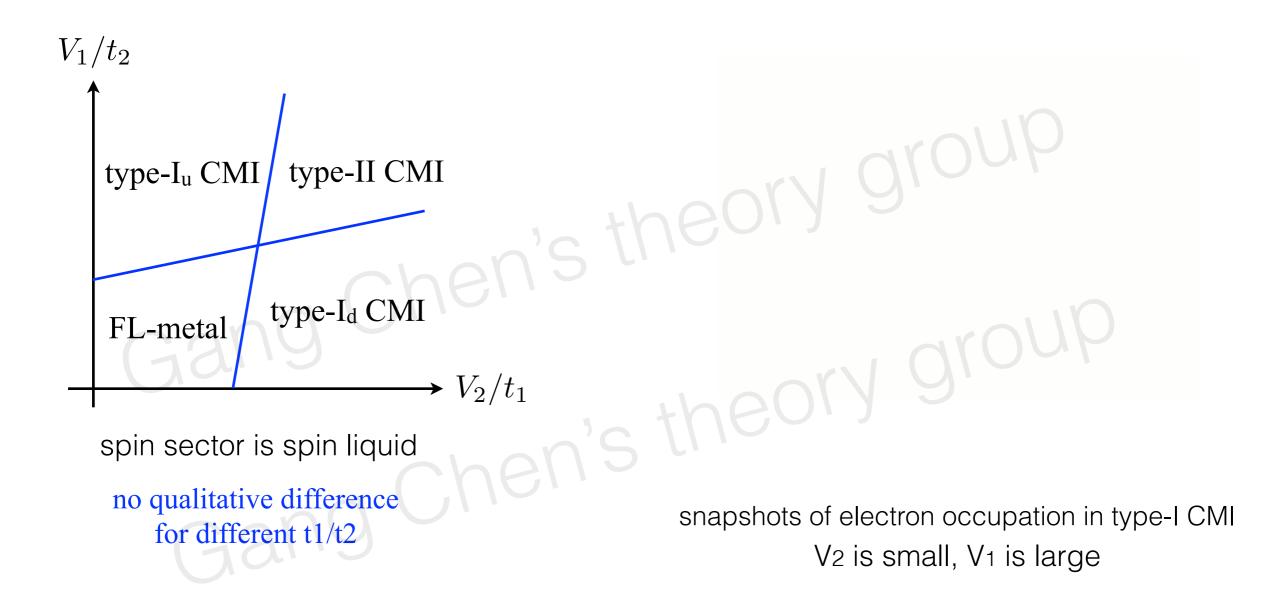
#### Model

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



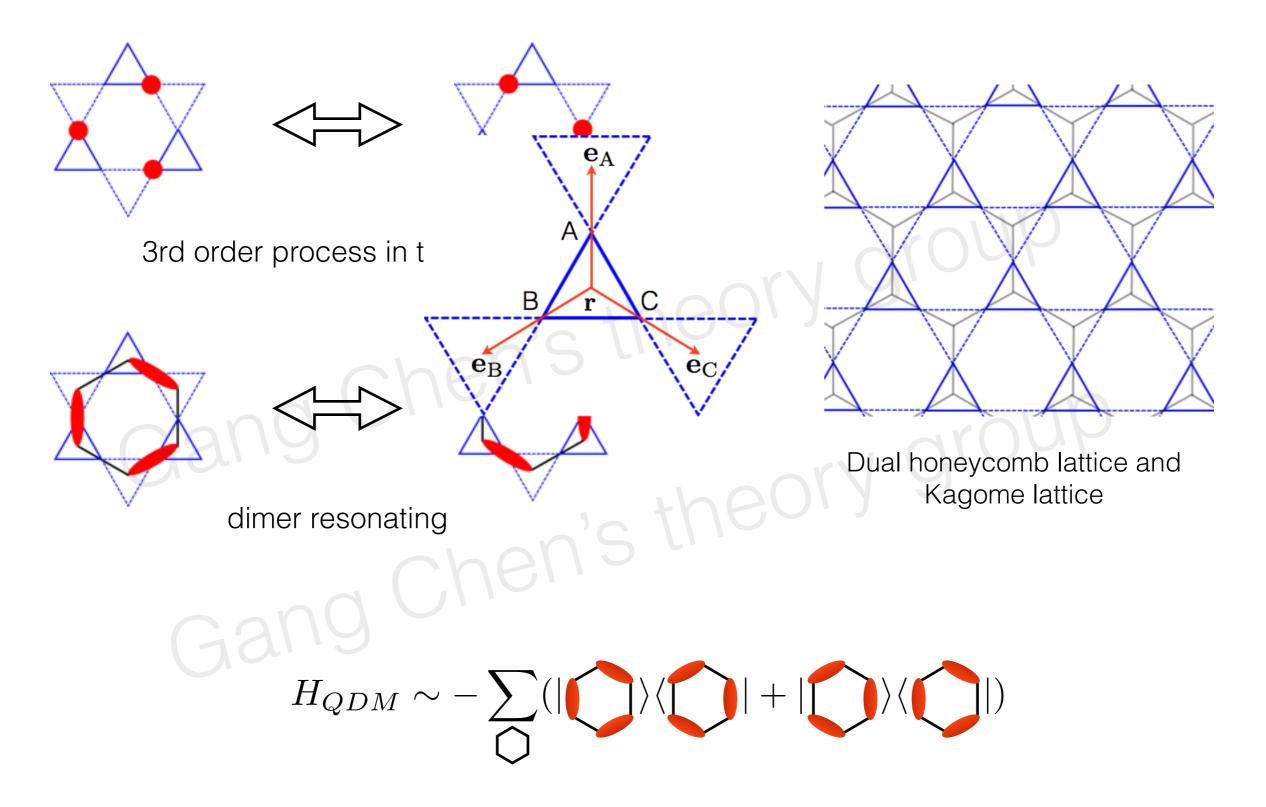
Large U alone **cannot** localize the electron. V1 and V2 are needed: because it is 4d orbital, and also to localize the electron in the clusters.

#### Generic phase diagram



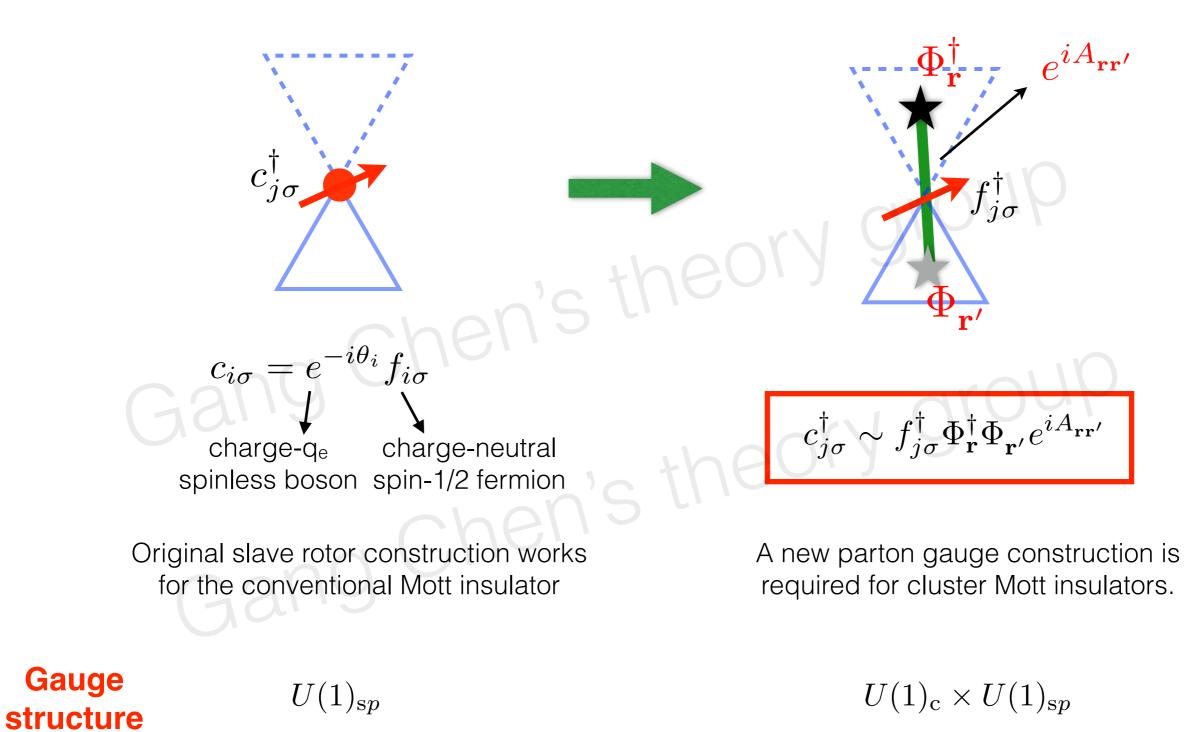
A "simple" understanding: electrons are localized in **one** type of triangles in type-I CMI; electrons are localized in **both** types of triangles in type-II CMI.

#### type-II CMI: correlated electron motion



Charge sector is described by a compact U(1) gauge theory on the dual honeycomb lattice.

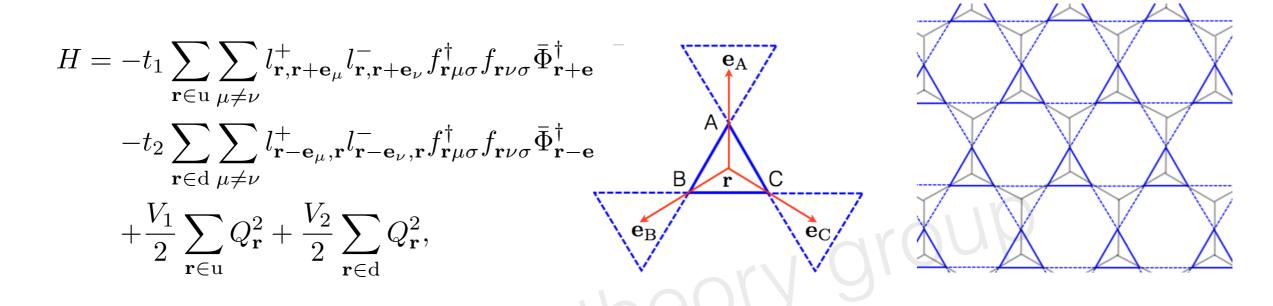
#### A new parton gauge construction



one U(1) gauge field

two U(1) gauge fields

#### A formalism



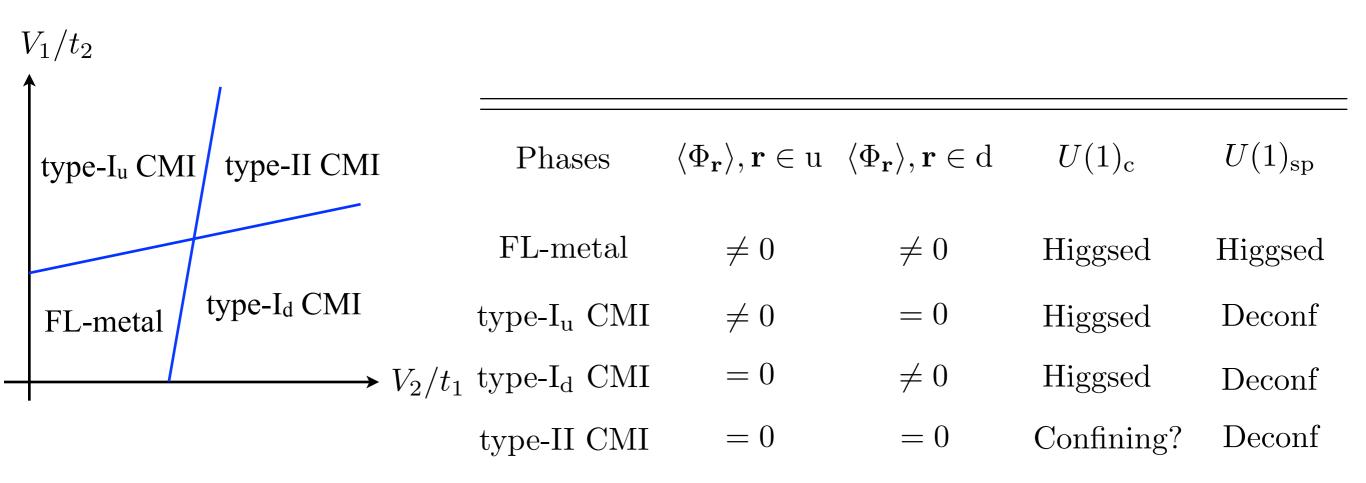
#### Self-consistent mean field theory: charge, spin, gauge sectors

$$\begin{split} H_{\rm ch}^{\rm u} &= -\bar{J}_1 \sum_{\mathbf{r} \in \mathrm{d}} \sum_{\mu \neq \nu} \bar{\Phi}_{\mathbf{r} - \mathbf{e}_{\mu}}^{\dagger} \bar{\Phi}_{\mathbf{r} - \mathbf{e}_{\nu}} + \frac{V_1}{2} \sum_{\mathbf{r} \in \mathrm{u}} Q_{\mathbf{r}}^2, \\ H_{\rm ch}^{\rm d} &= -\bar{J}_2 \sum_{\mathbf{r} \in \mathrm{u}} \sum_{\mu \neq \nu} \bar{\Phi}_{\mathbf{r} + \mathbf{e}_{\mu}}^{\dagger} \bar{\Phi}_{\mathbf{r} + \mathbf{e}_{\nu}} + \frac{V_2}{2} \sum_{\mathbf{r} \in \mathrm{d}} Q_{\mathbf{r}}^2, \\ H_{\rm sp} &= -\sum_{\mu \neq \nu} [\bar{t}_1 \sum_{\mathbf{r} \in \mathrm{u}} f_{\mathbf{r}\mu\sigma}^{\dagger} f_{\mathbf{r}\nu\sigma} + \bar{t}_2 \sum_{\mathbf{r} \in \mathrm{d}} f_{\mathbf{r}\mu\sigma}^{\dagger} f_{\mathbf{r}\nu\sigma}], \\ H_A &= -\sum_{\mu \neq \nu} \left[ \bar{K}_1 \sum_{\mathbf{r} \in \mathrm{u}} l_{\mathbf{r},\mathbf{r} + \mathbf{e}_{\mu}}^{+} l_{\mathbf{r},\mathbf{r} + \mathbf{e}_{\nu}}^{-} \\ &+ \bar{K}_2 \sum_{\mathbf{r} \in \mathrm{d}} l_{\mathbf{r} - \mathbf{e}_{\mu},\mathbf{r}}^{+} l_{\mathbf{r} - \mathbf{e}_{\nu},\mathbf{r}}^{-} \right], \end{split}$$

$$\begin{split} \bar{J}_{1} &= t_{2} \langle l_{\mathbf{r}-\mathbf{e}_{\mu},\mathbf{r}}^{+} \rangle \langle l_{\mathbf{r}-\mathbf{e}_{\nu},\mathbf{r}}^{-} \rangle \sum_{\sigma} \langle f_{\mathbf{r}\mu\sigma}^{\dagger} f_{\mathbf{r}\nu\sigma} \rangle, \quad \mathbf{r} \in \mathbf{d}, \\ \bar{J}_{2} &= t_{1} \langle l_{\mathbf{r},\mathbf{r}+\mathbf{e}_{\mu}}^{+} \rangle \langle l_{\mathbf{r},\mathbf{r}+\mathbf{e}_{\nu}}^{-} \rangle \sum_{\sigma} \langle f_{\mathbf{r}\mu\sigma}^{\dagger} f_{\mathbf{r}\nu\sigma} \rangle, \quad \mathbf{r} \in \mathbf{u}, \\ \bar{t}_{1} &= t_{1} \langle l_{\mathbf{r},\mathbf{r}+\mathbf{e}_{\mu}}^{+} \rangle \langle l_{\mathbf{r},\mathbf{r}+\mathbf{e}_{\nu}}^{-} \rangle \langle \bar{\Phi}_{\mathbf{r}+\mathbf{e}_{\mu}}^{\dagger} \bar{\Phi}_{\mathbf{r}+\mathbf{e}_{\nu}} \rangle, \quad \mathbf{r} \in \mathbf{u}, \\ \bar{t}_{2} &= t_{2} \langle l_{\mathbf{r}-\mathbf{e}_{\mu},\mathbf{r}}^{+} \rangle \langle l_{\mathbf{r}-\mathbf{e}_{\nu},\mathbf{r}}^{-} \rangle \langle \bar{\Phi}_{\mathbf{r}-\mathbf{e}_{\mu}}^{\dagger} \bar{\Phi}_{\mathbf{r}-\mathbf{e}_{\nu}} \rangle, \quad \mathbf{r} \in \mathbf{d}, \\ \bar{K}_{1} &= t_{1} \sum_{\sigma} \langle f_{\mathbf{r}\mu\sigma}^{\dagger} f_{\mathbf{r}\nu\sigma} \rangle \langle \bar{\Phi}_{\mathbf{r}+\mathbf{e}_{\mu}}^{\dagger} \bar{\Phi}_{\mathbf{r}+\mathbf{e}_{\nu}} \rangle, \quad \mathbf{r} \in \mathbf{u}, \\ \bar{K}_{2} &= t_{2} \sum_{\sigma} \langle f_{\mathbf{r}\mu\sigma}^{\dagger} f_{\mathbf{r}\nu\sigma} \rangle \langle \bar{\Phi}_{\mathbf{r}-\mathbf{e}_{\mu}}^{\dagger} \bar{\Phi}_{\mathbf{r}-\mathbf{e}_{\nu}} \rangle, \quad \mathbf{r} \in \mathbf{d}. \end{split}$$

 $\sigma$ 

#### Generic phase diagram from gauge theory of charge sector

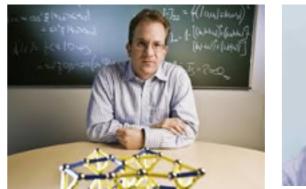


type-II CMI: plaquette charge order via QDM

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

 $H_{QDM} = -t\hat{T} + v\hat{V}$ 

 $= -t\left(|\nabla\rangle\langle\Delta| + \text{H.c.}\right) + v\left(|\nabla\rangle\langle\nabla| + |\Delta\rangle\langle\Delta|\right).$ 



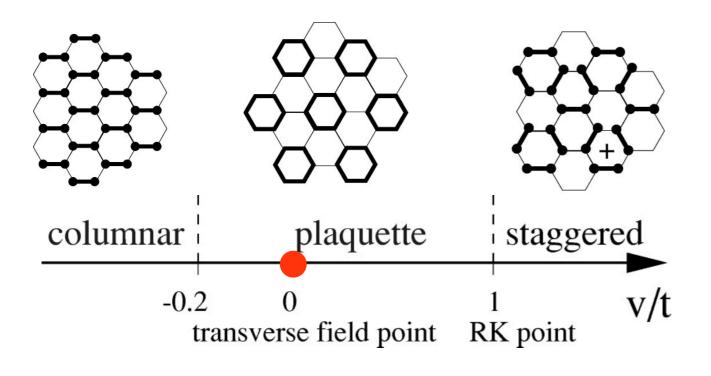




R. Moessner

S. Sondhi

P. Chandra

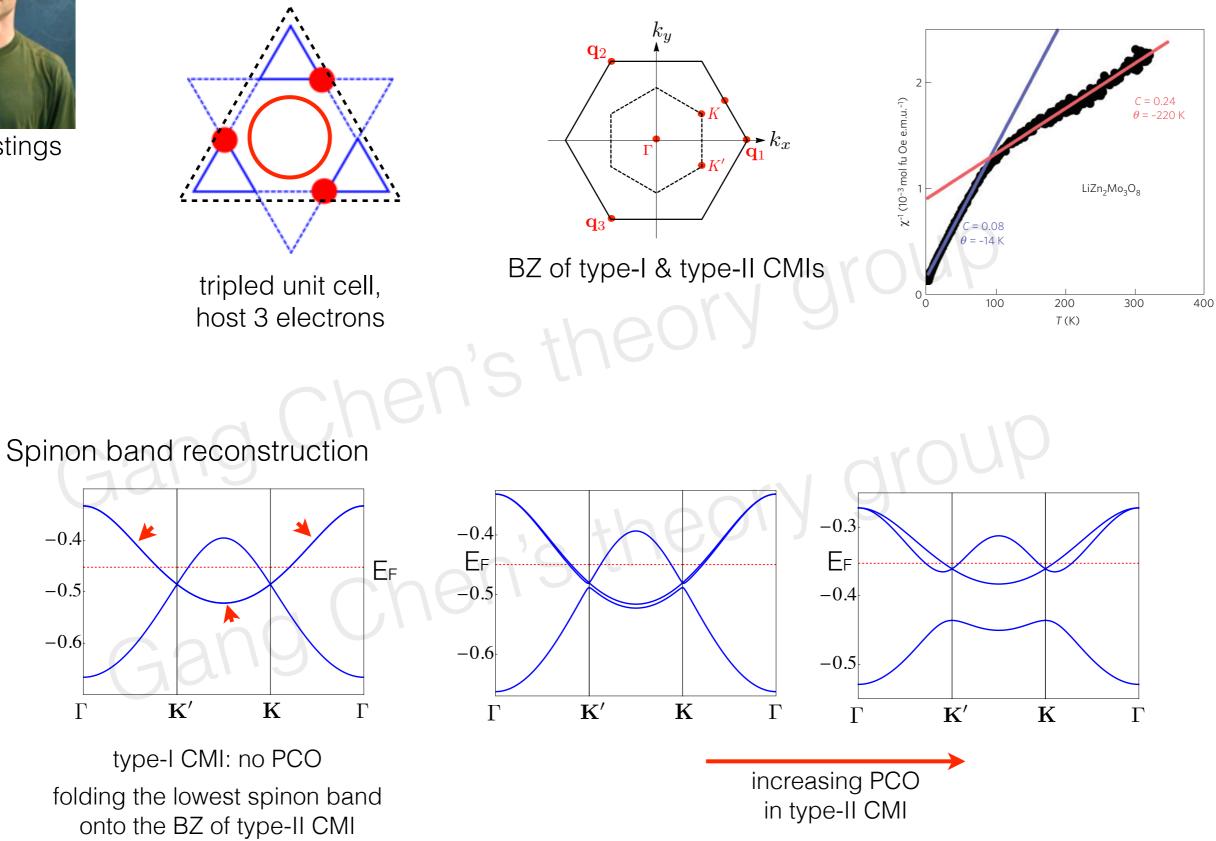


Plaquette charge order: a local **charge "RVB"**, a local collective behaviour ! It is a quantum effect.

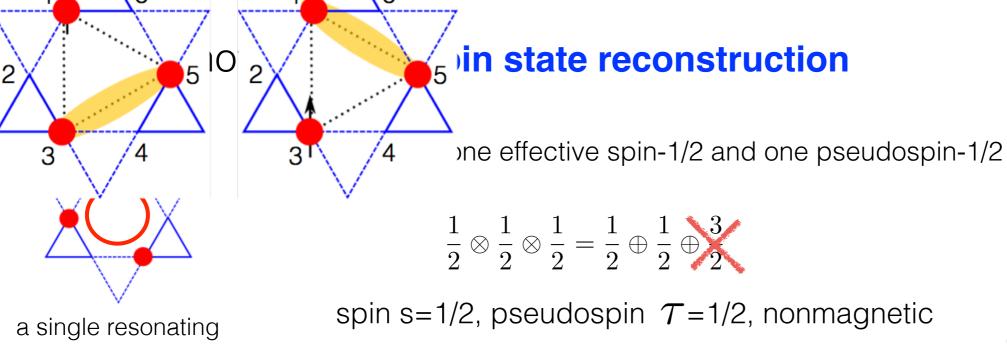


M. Hastings

Lieb-Schultz-Mattis-Oshikawa-Hastings' theorem: apply to type-II CMI



Implication to susceptibility from bandwidth and filling



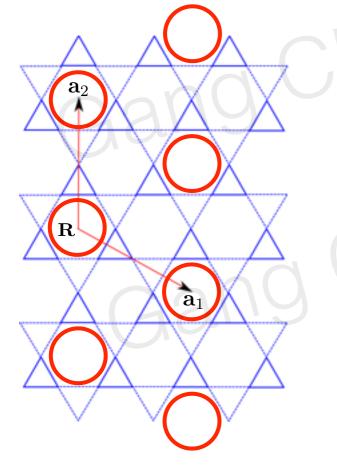




K. Kugel

D. Khomskii

hexagon



An effective Kugel-Khomskii model on the emergent triangular lattice

$$H_{\rm KK} = \frac{J'}{9} \sum_{\mathbf{R}} \sum_{\mu=x,y,z} \left[ \mathbf{s}(\mathbf{R}) \cdot \mathbf{s}(\mathbf{R} + \mathbf{a}_{\mu}) \right] \\ \times \left[ 1 + 4\pi^{\mu}(\mathbf{R}) \right] \left[ 1 - 2\pi^{\mu}(\mathbf{R} + \mathbf{a}_{\mu}) \right] \\ \Theta_{\rm CW}^{\rm L} = -\frac{z_t s(s+1)}{3} \left( \frac{J'}{9} \right) \, \mathcal{C}^{\rm L} = \frac{g^2 \mu_{\rm B}^2 s(s+1) N_{\Delta}}{3k_{\rm B}} \frac{N_{\Delta}}{3}$$

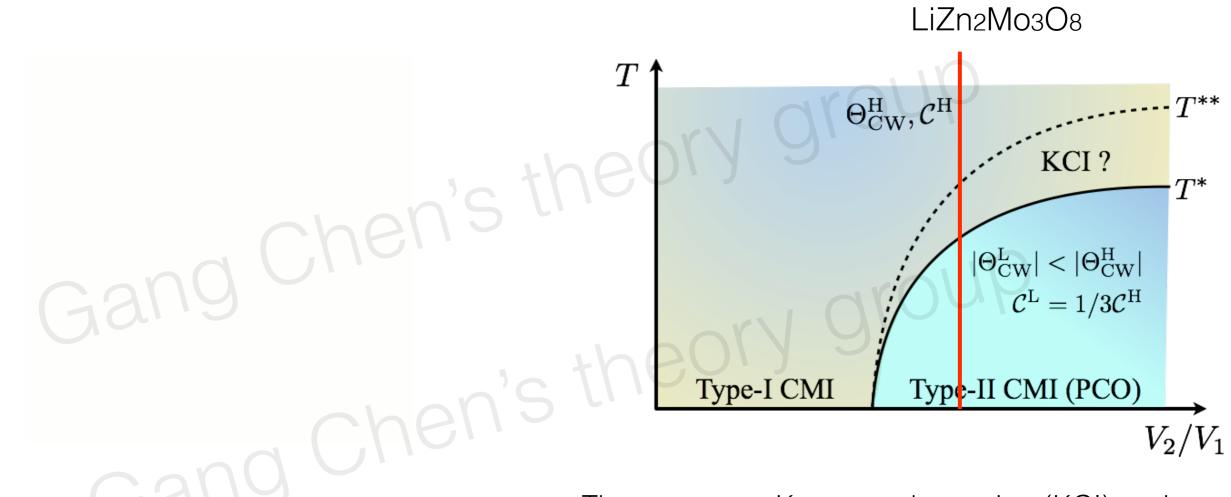
due to the reduced probability of spin interaction

1. very frustrated, may also support spin liquid

interesting ordering under a strong field 2.

#### Summary about LiZn<sub>2</sub>Mo<sub>3</sub>O<sub>8</sub>

The emergence of PCO is the driving force of the 1/3 susceptibility anomaly. —> "**Short-range quantum entanglement**" The spin GS of the system is probably a U(1) QSL with spinon Fermi surfaces.—>"**Long-range quantum entanglement**"



type-II CMI (PCO)

The crossover Kagome charge ice (KCI) regime is probably not sharply defined in LiZn<sub>2</sub>Mo<sub>3</sub>O<sub>8</sub> as it requires V<sub>2</sub> >> T > ring hopping.

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

#### **Prediction A :** charge sector

Einstein (or Debye) oscillator mode (fit shown in red).

- Expect 1st order finite temperature transition, peak at ~100K, (was interpreted as Li freezing.) smeared out 1st transition? Both methods give similar insights into the magnetic behav
- High resolution X-ray, RIXS 2.

100

200

T (K)

300

400

Nuclear quadrupolar resonance: electric field gradient (suggested to me by Baskaran) gives a larger feature at  $T \ge 100$  K, which must (at least particular resonance) which must (at least particular resonance) and the second З.

vibrational modes from Li in LiZn<sub>2</sub>Mo<sub>3</sub>O<sub>8</sub>. Figure S3(b) show

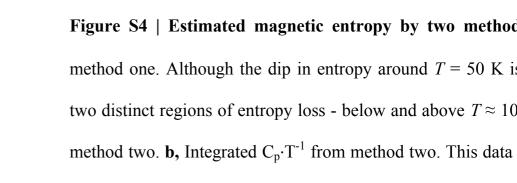
oscillator mode, with an Einstein temperature  $\Theta = 403$  K (

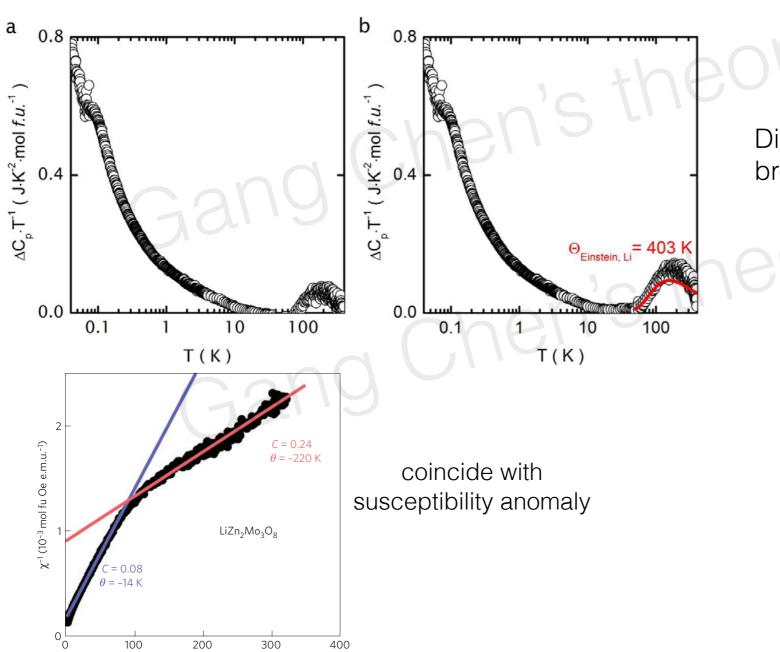
which was subtracted to leave the magnetic contribution. In bo

then extracted by computing  $S(T) = \int_0^T \frac{C}{T} dT$ . A comparison of

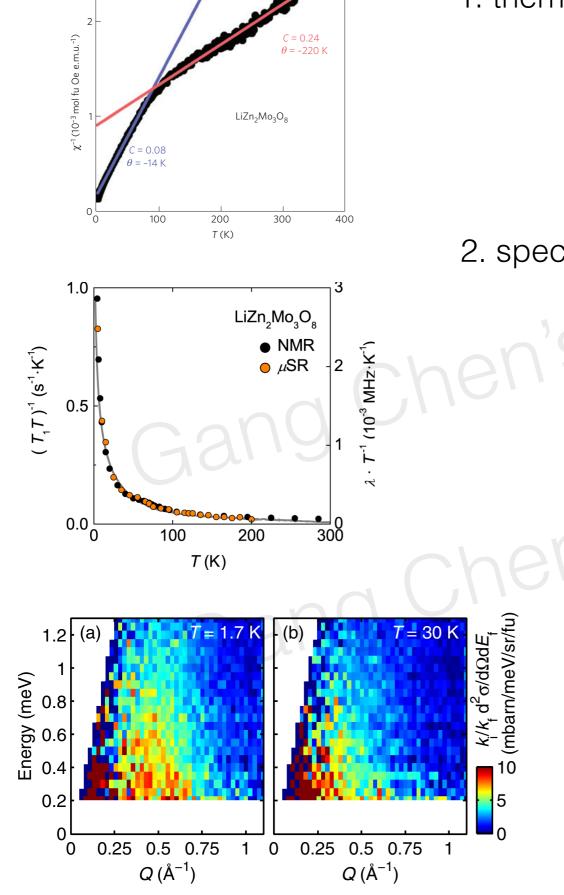
Disorders pin the charge density wave, broaden the phase transition.

W. L. McMillan PRB 1975





#### Further **prediction B**: low-T QSL



1. thermodynamics

U(1) QSL with spinon Fermi surfaces

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

at very low temperature (<1K).

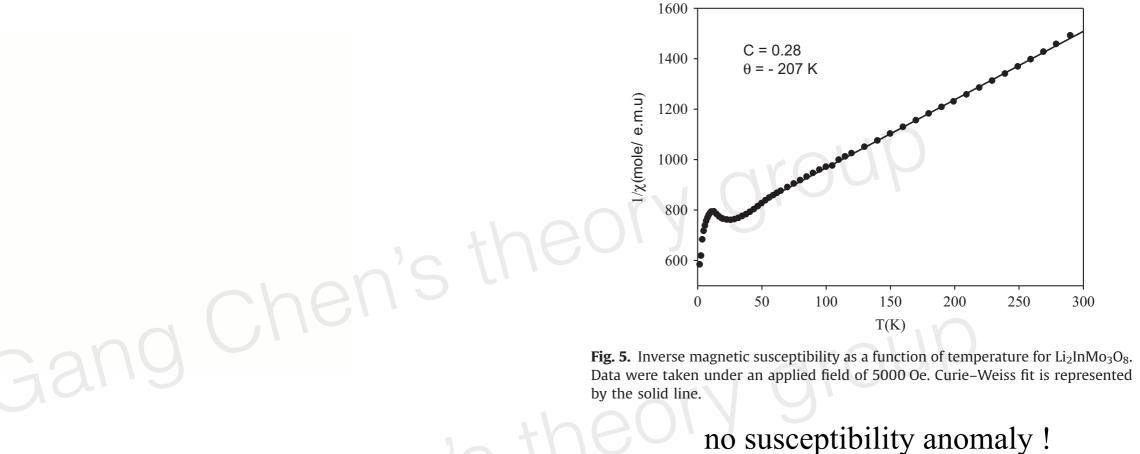
2. spectroscopic

NMR: large density of low-energy spin excitations because of the reduced bandwidth

 $1/(T_1T) \propto D(E_F)^2$ 

Neutron scattering: it would be nice to compare the prediction from the spinon band structure in future work. Single crystal data and better resolution are preferred.

#### What is type-I CMI?



Li2InMo3O8 as a type-I CMI ? quantum spin liquid ? type-I CMI is a triangular lattice spin liquid

P Gall, etc, J Solid State Chem. 2013

M2Mo3O8 (M=Mg,Mn,Fe,Co,Ni,Zn,Cd),

LiRMo3O8 (R=Sc,Y,In,Sm,Gd,Tb,Dy,Ho,Er,Yb) and many others.

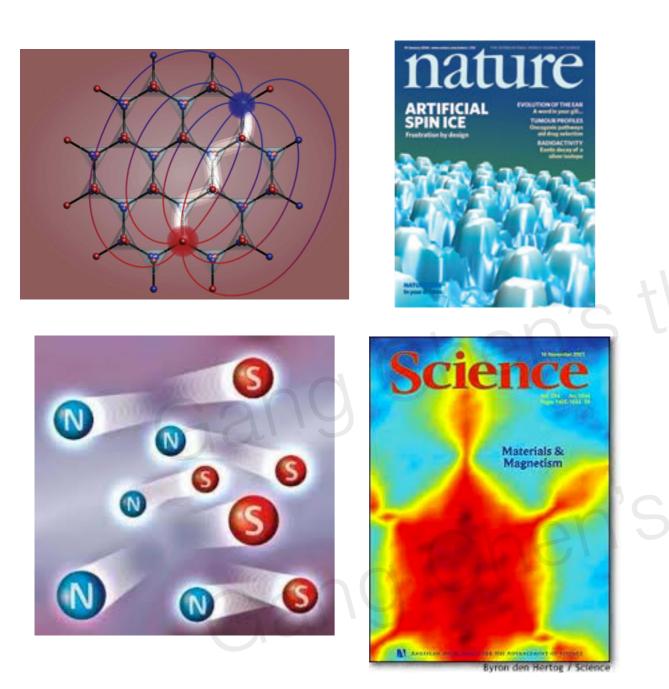
Many materials mean many opportunities to discover new physics there.

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### nfonopolessical spin ice

#### ICE AGE 2: quantum spin ice



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



stolen from L. Balents and L. Savary

M. Gingras, R. Melko, M Hermele, L. Balents,

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

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

#### lots of materials

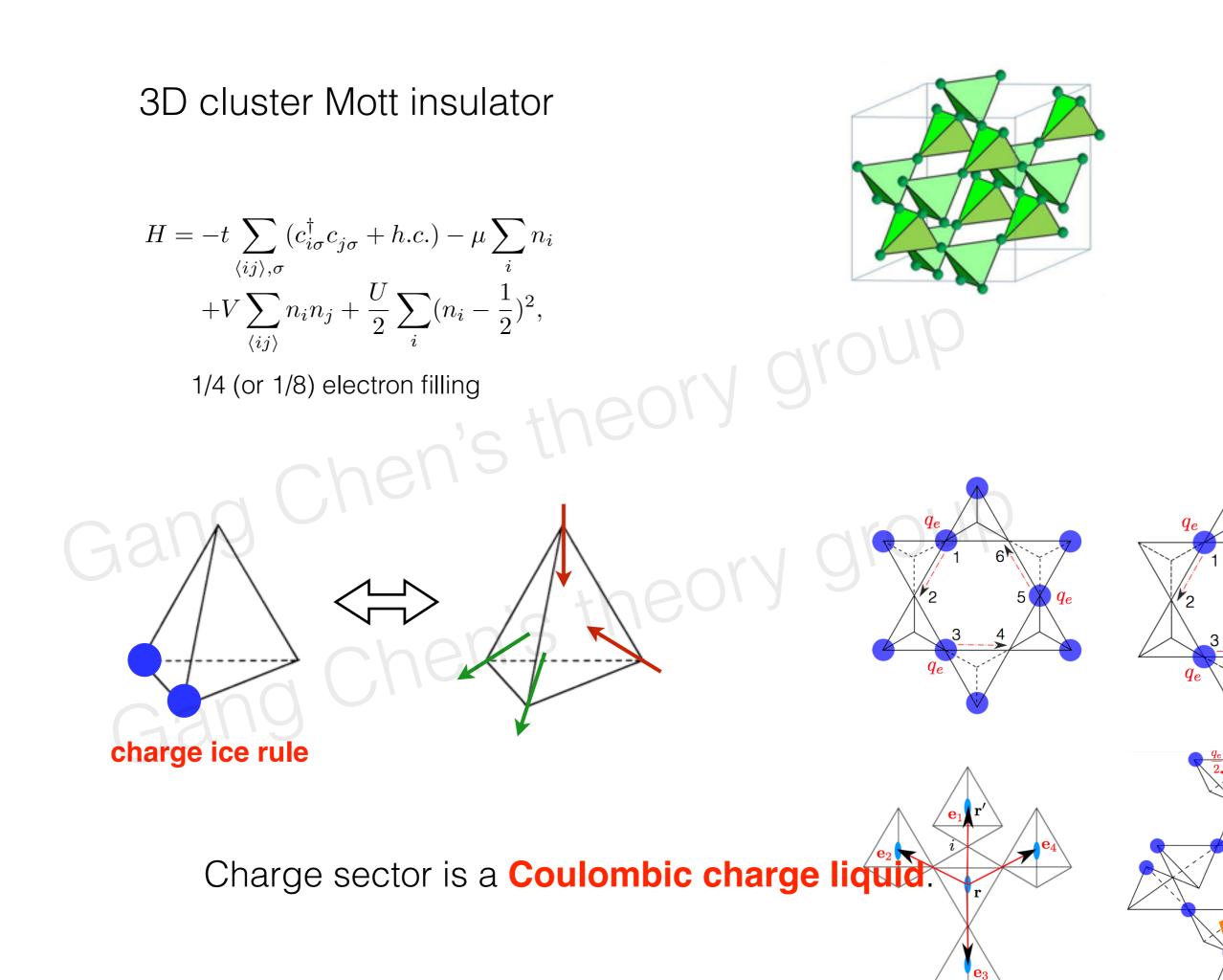
A little more about the motivation

1. Can we use other degrees of freedom to reveal quantum spin ice physics?

electron = spin + charge + orbital (for **condensed matter physicists only!**)

quantum spin ice (most famous !) quantum charge ice (the rest of the talk) quantum orbital ice (Gang Chen, unpublished)

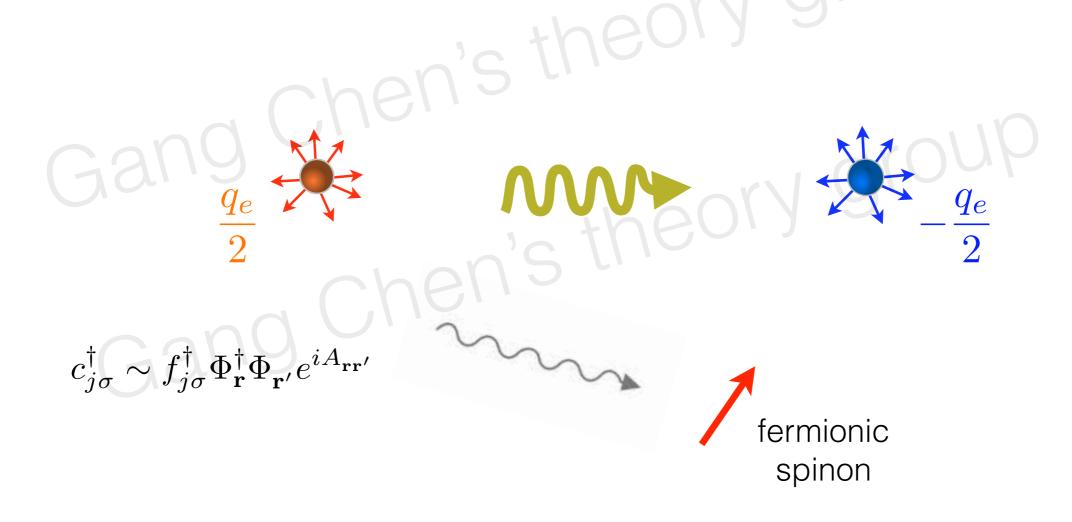
2. Any other physical observables that do not have strong temperature constraint but still manifest the intrinsic properties of quantum spin ice? Not trivial ! (Gang Chen, working in progress !)



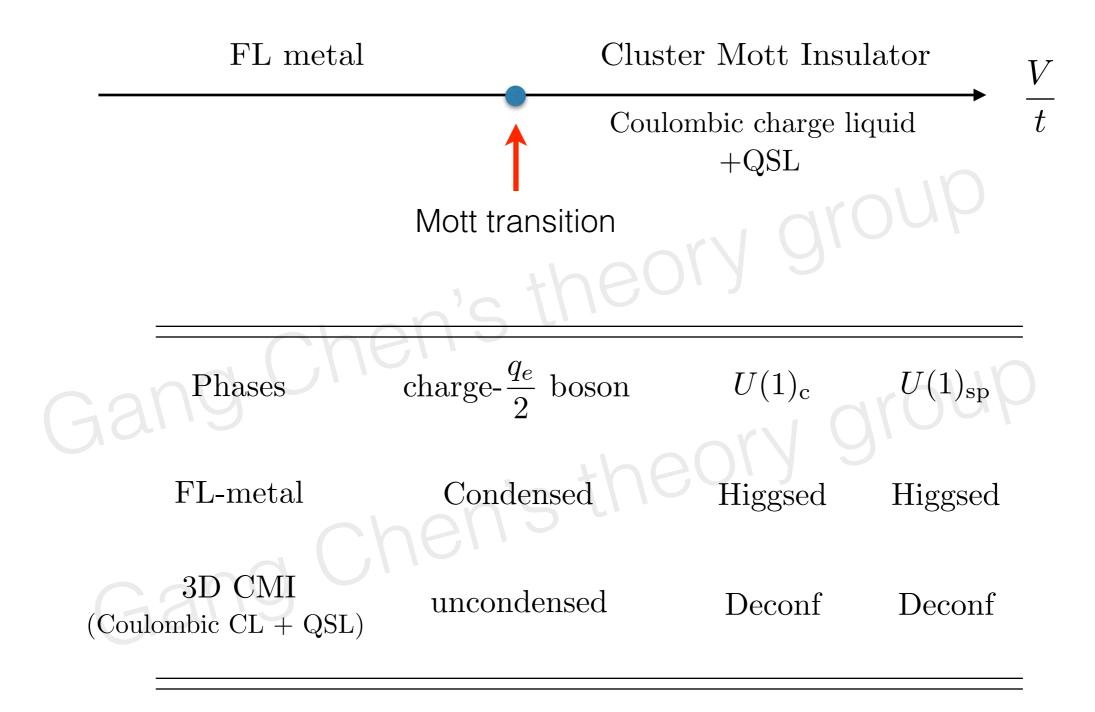
### 

Charge fractionalization of the Coulombic charge liquid

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

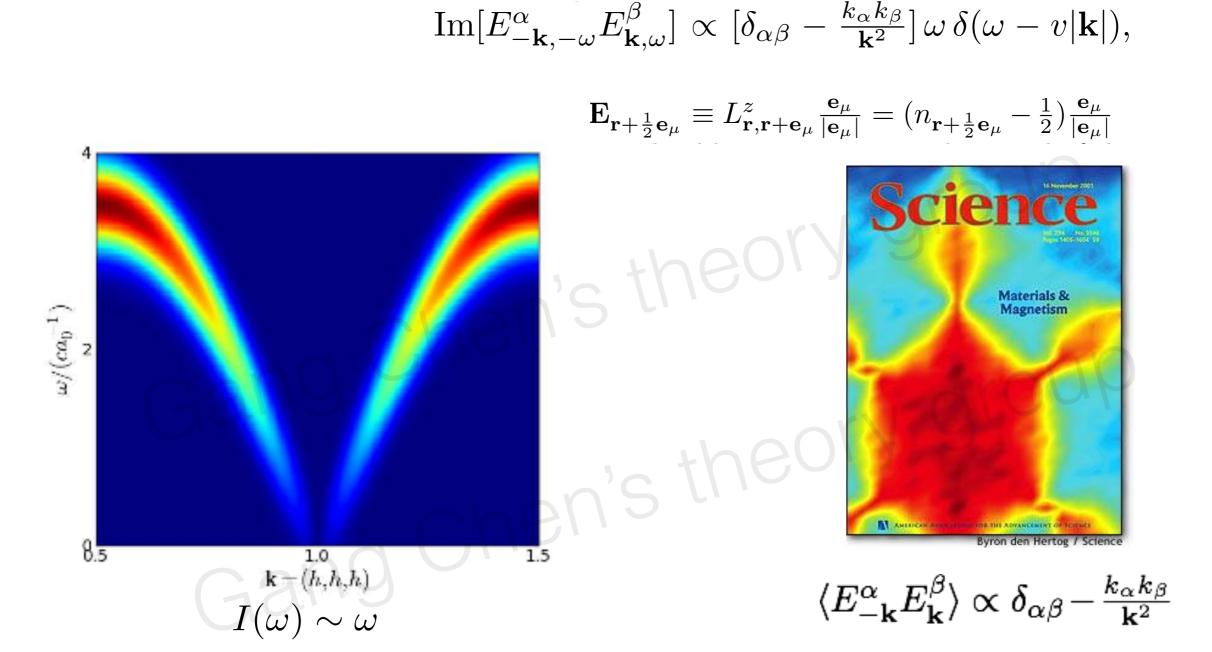


#### Phase diagram and gauge description



Here charge boson carries both  $U(1)_c$  and  $U(1)_{sp}$  gauge charge.

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



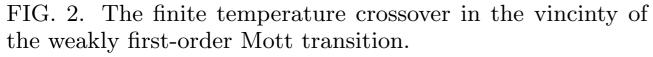
emergent light in quantum charge ice !

N Shannon etc 2012, L Savary etc 2012, Gingras etc, 2007-now Pinch points in equal-time charge structure factor at T > ring hopping. "classical charge ice"

#### Mott transition: low-energy field theory

$$\mathcal{L} = \mathcal{L}_{\Phi} + \mathcal{L}_{f} + \mathcal{L}_{A} + \mathcal{L}_{a} + \mathcal{L}_{bf}$$
(6)  

$$\mathcal{L}_{\Phi} = \left| [\partial_{\mu} - i(\mathcal{A}_{\mu} - \frac{a_{\mu}}{2})] \Phi_{I} \right|^{2} + \left| [\partial_{\mu} - i(\mathcal{A}_{\mu} + \frac{a_{\mu}}{2})] \Phi_{II} \right|^{2}$$
$$+ m^{2} [|\Phi_{I}|^{2} + |\Phi_{II}|^{2}] + u[|\Phi_{I}|^{4} + |\Phi_{II}|^{4}] + v|\Phi_{I}|^{2} |\Phi_{II}|^{2}$$
$$\mathcal{L}_{f} = \psi_{\sigma}^{\dagger} (\partial_{\tau} - ia_{0} - \mu_{f}) \psi_{\sigma} + \frac{1}{2m_{f}} |(\nabla - i\mathbf{a})\psi_{\sigma}|^{2}$$
$$\mathcal{L}_{A} = \frac{1}{4g_{A}^{2}} (\partial_{\mu}\mathcal{A}_{\nu} - \partial_{\nu}\mathcal{A}_{\mu})^{2}, \quad \mathcal{L}_{a} = \frac{1}{4g_{a}^{2}} (\partial_{\mu}a_{\nu} - \partial_{\nu}a_{\mu})^{2}$$
$$\mathcal{L}_{f\Phi} = \lambda |\psi_{\sigma}|^{2} (|\Phi_{I}|^{2} + |\Phi_{II}|^{2}).$$
  
T/t 
$$T'_{T} = \frac{T}{(V_{f})_{c}} = \frac{V_{f}}{(V/t)_{c}} + \frac{V_{f}}{V/t}$$
spin sector  $T^{s}$  crossover  $T^{s}$  crossover  $T^{s}$  crossover  $Zc=1, Zs=3$   
different dynamical scalings for spin and charge  $Zc=1, Zs=3$ 



Crossover in heat capacity and electric conductivity

1. Heat capacity crossover signals the  $z_s=3$  dynamical exponent Spinon-U(1)<sub>sp</sub> gauge sector controls/dominates the thermodynamics

 $C \approx \begin{cases} T \ln \ln 1/T & T > |V - V_c|^{3/2} & \text{critical regime} \\ \gamma_1 T \ln 1/T & T < (V - V_c)^{3/2} & \text{U(1) QSL} \\ \gamma_2 T & T < (V_c - V)^{3/2} & \text{FL metal} \end{cases}$ 

2. Electric resistivity signals the zc=1 dynamical exponent

In the left of th

note: the resistivity gap in the Mott regime is single boson gap.

Mott transition itself is insulating. Crossover to metal in the metallic side.

#### Pyrochlore Mott insulators with fractional electron filling

usually associated with mixed valences

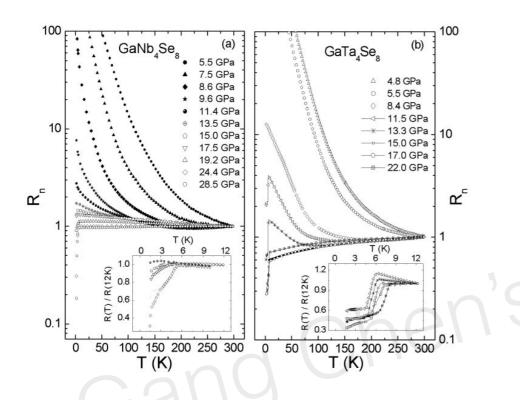


FIG. 2. Temperature dependence of the normalized electrical resistance  $R_n = [R(T)/R(297 \text{ K})]$  of GaNb<sub>4</sub>Se<sub>8</sub> (a) and GaTa<sub>4</sub>Se<sub>8</sub> (b) at different pressures up to 28.5 GPa. The insets show the drop of  $R_n$  at high pressures and low temperatures.

Metal-insulator transition: but **superconductivity** intervenes!

M.M.Abd-Elmeguid etc, PRL 2004

Superconductivity is actually interesting!

Both  $U(1)_c$  and  $U(1)_{sp}$  gauge fields can be higgsed down to Z<sub>2</sub> gauge fields.

The resulting CMI is **Z2 QCL + Z2 QSL** Gang Chen, YB Kim, HY Kee, working in progress!

#### **Question / observation:**

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- 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 striking experimental consequence. If it is observed, it gives us confidence on the theoretical framework that we are developing. Gang Chen's

# Summary of grou

- 1. I provide two specific examples about the physics of cluster Mott insulators.
- 2. There is a very interesting interplay between the charge and spin degrees of freedom in both 2D and 3D cluster Mott insulators.
- 3. Cluster Mott insulators are new physical systems that may host various emergent and exotic physics.