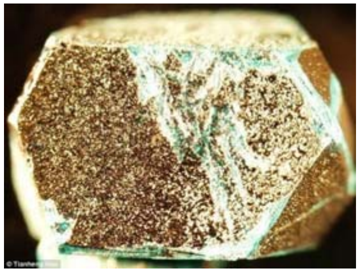
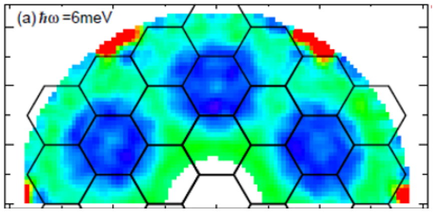
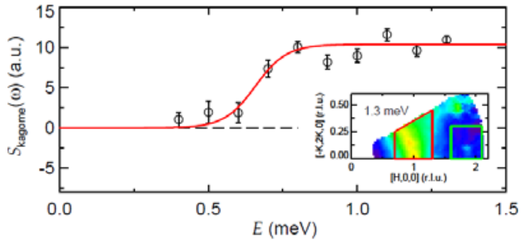
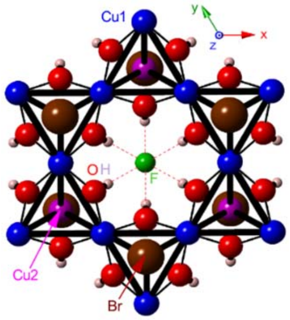
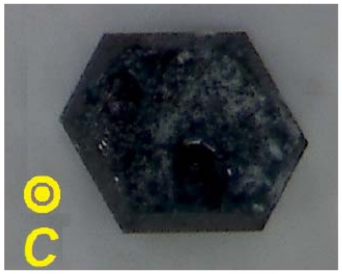
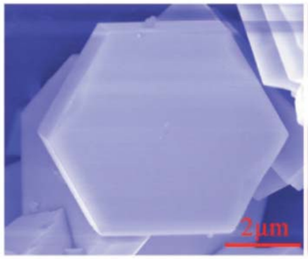
Experiments on Kagome Quantum Spin Liquids

Past, Present, Future.



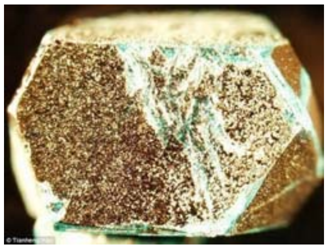


(Harry) Tian-Heng Han (韩天亨)

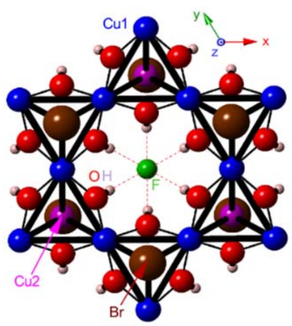
July 6, 2017 Beijing

Outline



Herbertsmithite $ZnCu_3(OH)_6Cl_2$

- Look for fractionalized spin excitations above an energy gap
- Challenges: impurity, spin Hamiltonian
- High-stakes charge doping



$Zn_xCu_{4-x}(OH)_6FBr$ (0 ≤ x ≤ 1)

- x = 0: barlowite
- x = 1: a new quantum spin-liquid candidate

PAST

Superconductivity

A condensed matter state that
most grandparents have heard of.

Heike Kamerlingh Onnes

1911

Experimental discovery

46 years

1957

BCS theory

John Bardeen

Leon Neil Cooper

John Robert Schrieffer

1986

High-temperature superconductivity

J. Georg Bednorz

K. Alexander Müller

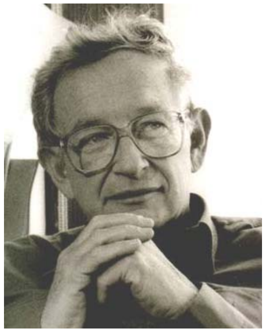
31 years + ……

Philip Warren Anderson

1987

Try my RVB state.

Quantum Spin Liquids



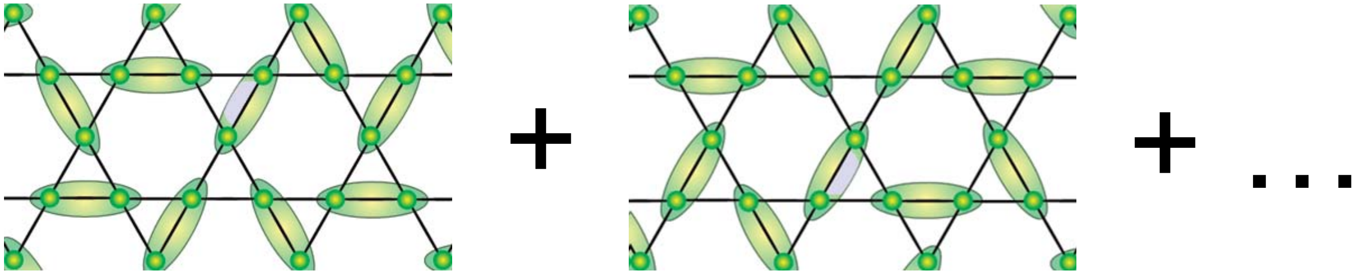
1973, Anderson

Resonating Valence Bonds

→ Superpose gazillions of spin bond configurations.

→ Spins at zero Kelvin: strong interaction, no freezing

→ Upon charge doping: spin dimers make Cooper pairs.



A kagome spin lattice covered with dimers

Full-throated proclamations from Patrick Lee, Leon Balents, and many:

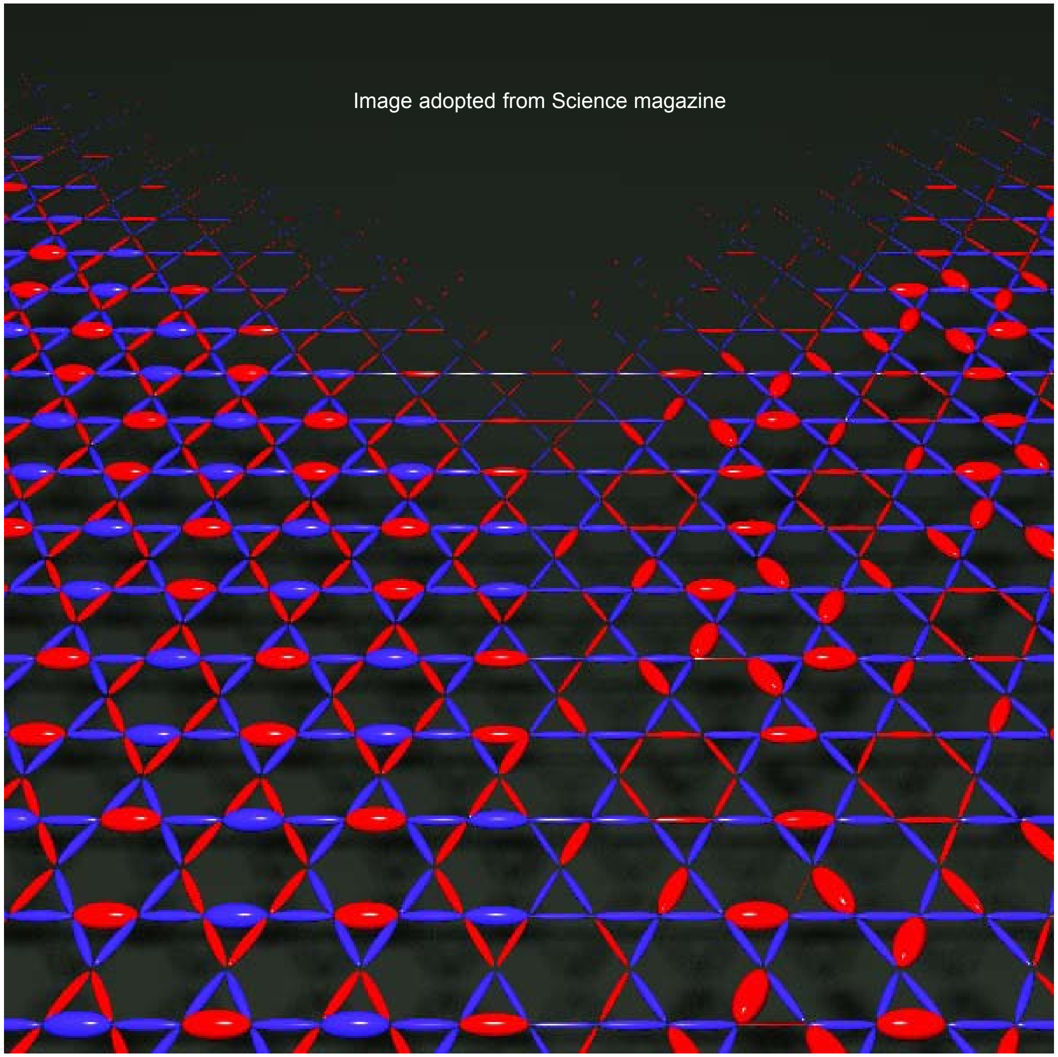
→ Lack of spin freezing is insufficient.

Can coexist with ordered moments.

→ Emergent quasi-particles, fractional statistics, and more.

We Need a Unifier.

A material which bundles spins into a large entanglement.



Quantum spin liquids can be found by 2016.

Leon Balents' prophetic prescience,
Circa 2010

Today is July 6, 2017.

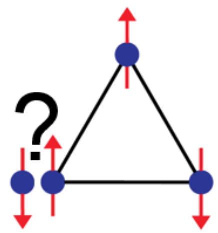
Goldbach's conjecture
Every even integer greater than 2 can be expressed as the sum of two primes.

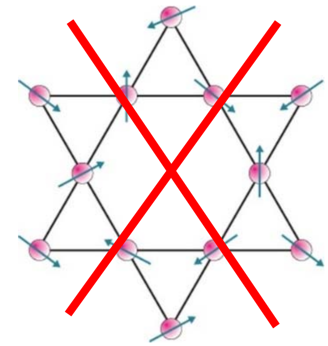
simple but not easy

***S* = 1/2 kagome Heisenberg antiferromagnet with only nearest neighbor exchanges**
What is the ground state ($H = J\, S_1 \cdot S_2$, $J > 0$)?

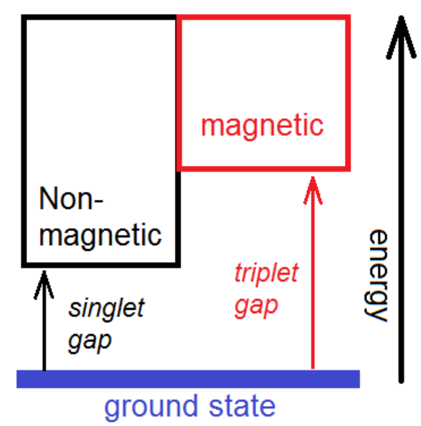
Theoretically challenging

- No analytical solution
- Consensus: no Néel order
  - → Quantum spin liquid?





fully-gapped? (Yan *et al.*, Science 2011)	singlet gap > 0	triplet gap > 0
spin-gapped? (Jiang *et al.*, PRL 2008)	singlet gap = 0	triplet gap > 0
gapless? (Ran *et al.*, PRL 2007)	singlet gap = triplet gap = 0	



  - → Valence bond solid?

Experimentally difficult to realize

- Most candidates order or freeze

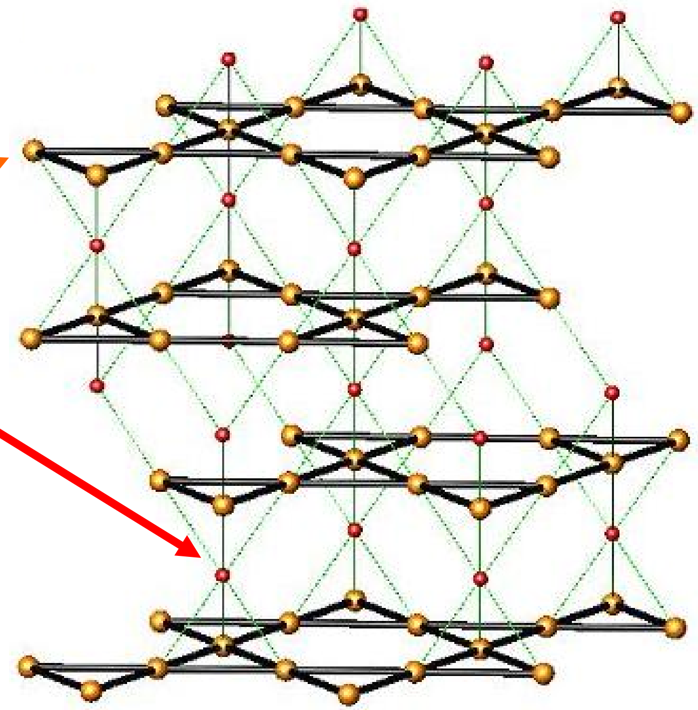
Herbertsmithite $ZnCu_3(OH)_6Cl_2$

x=1 end member of Zn-paratacamite $Zn_xCu_{4-x}(OH)_6Cl_2$ (x>1/3)

- High frustration
- Small spin
- Low dimensionality

Cu^{2+} S=1/2

Zn^{2+} S=0



Facts

- 1st realized undistorted S=1/2 kagome lattice

Matthew Shores

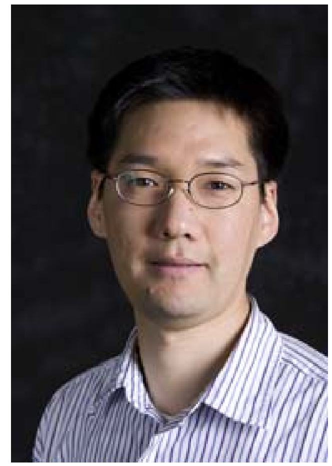
Daniel Nocera

M. Shores *et al.*, J. Am. Chem. Soc. **127**, 13462 (2005).

Pioneer studies on powder samples

Philippe Mendels

Fabrice Bert



Young Lee

Joel Helton

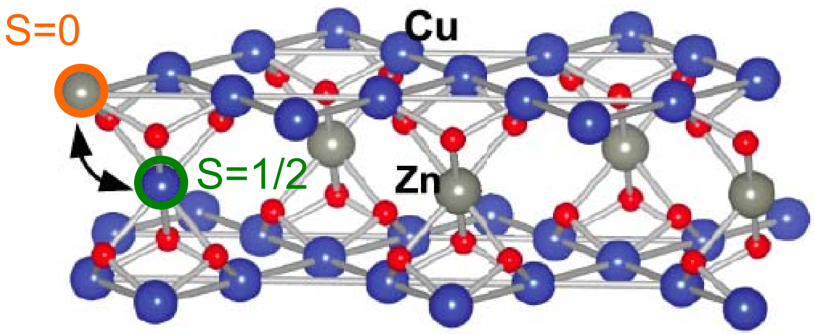
PRL **98**, 077204 (2007)
Muon Spin Rotation

PRL **98**, 107204 (2007)
Thermodynamics
Neutron Scattering

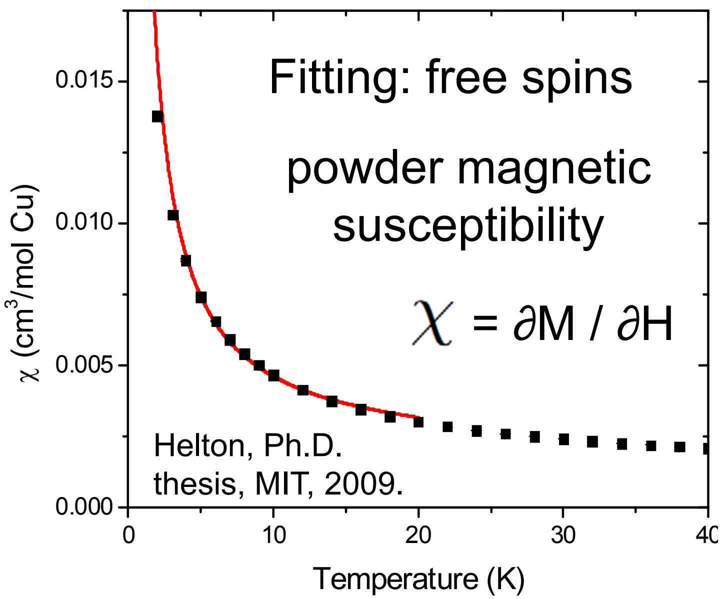
- J = 17 meV $T_{CW} = -300$ K
- No spin ordering at 50 mK
- Persistent spin dynamics at 50 mK
- Gapless magnetic excitations

The defect controversy---“Cu^{2+} and Zn^{2+} trade their positions”

Picture adopted from PRB **85**, 014422

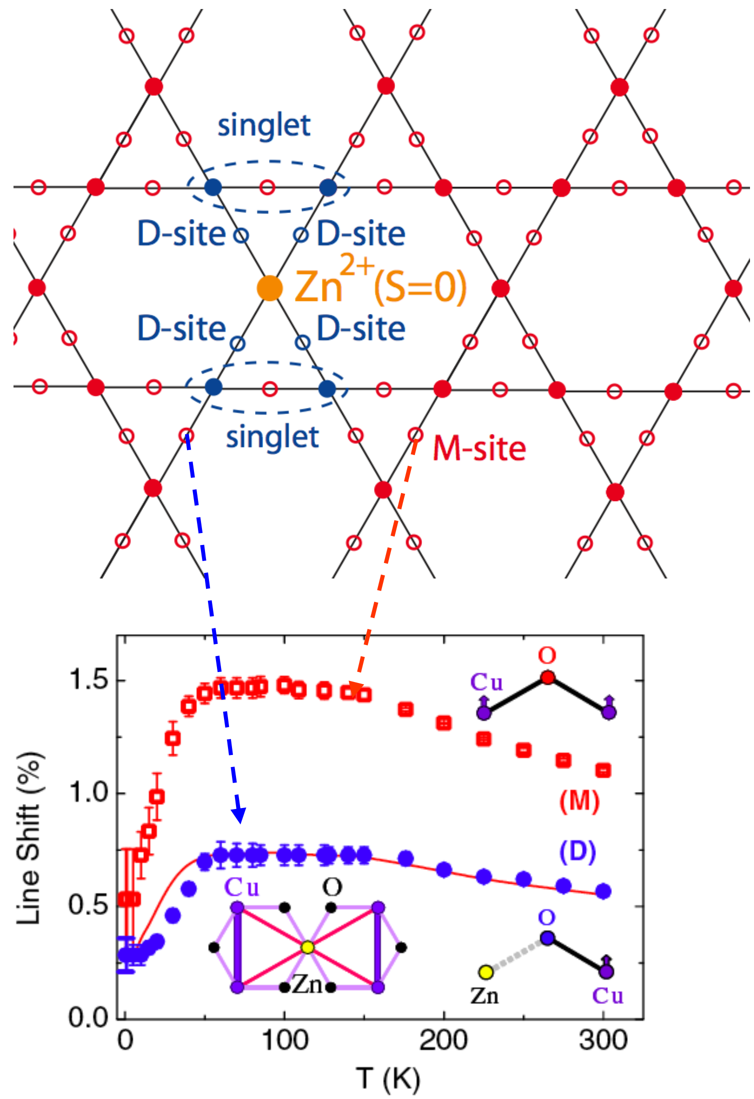


In addition to the **“Cu^{2+} in Zn^{2+}site”**defects, some **Zn^{2+} with spin *S*=0 occupy the Cu^{2+} sites** within the kagome planes, and induce singlets.



Powder ^{17}O NMR

Olariu *et al.,* PRL **100**, 087202 (2008)



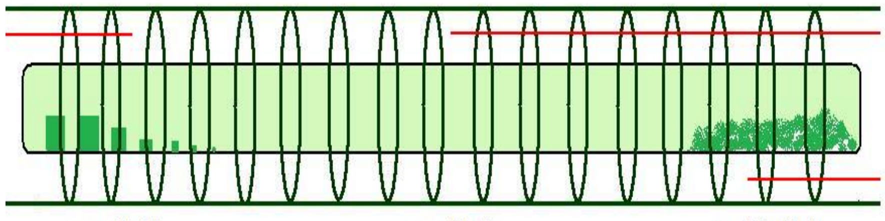
Can we have single crystal samples of herbertsmithite?

Zn^{2+} ions in kagome layers cause strong disorder.

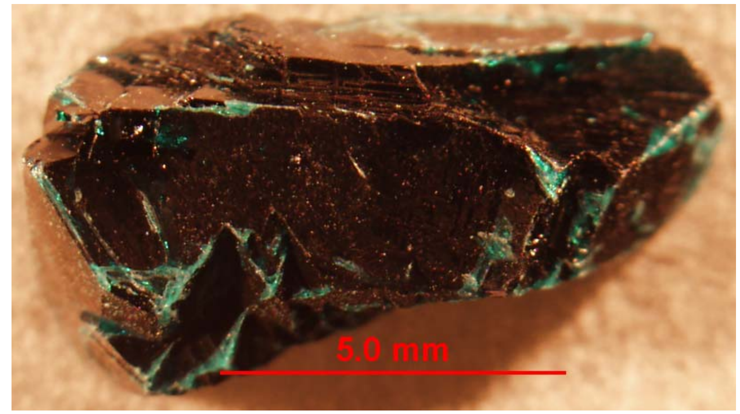
Is this real in herbertsmithite?

PRESENT

Single Crystal Era: < 2010 to present

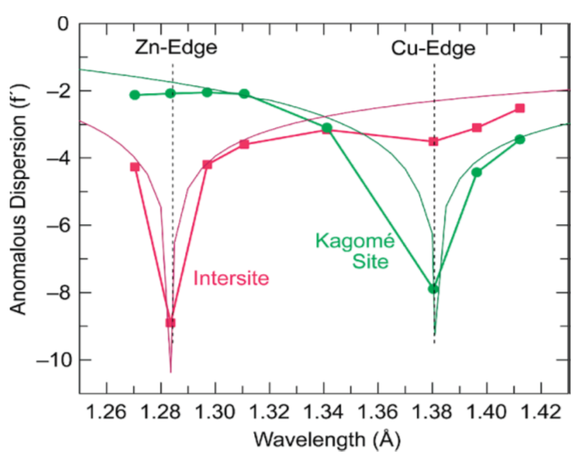


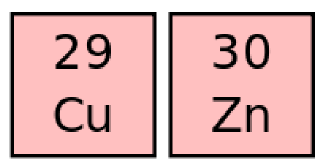
$$2CuO + ZnCl_2 \xrightarrow[T_{Max} = 180°\ C]{H_2O}$$



T. H. Han *et al.,* PRB **83**, 100402(R) (2011)

No antisite/strong disorder: anomalous x-ray diffraction on a single crystal





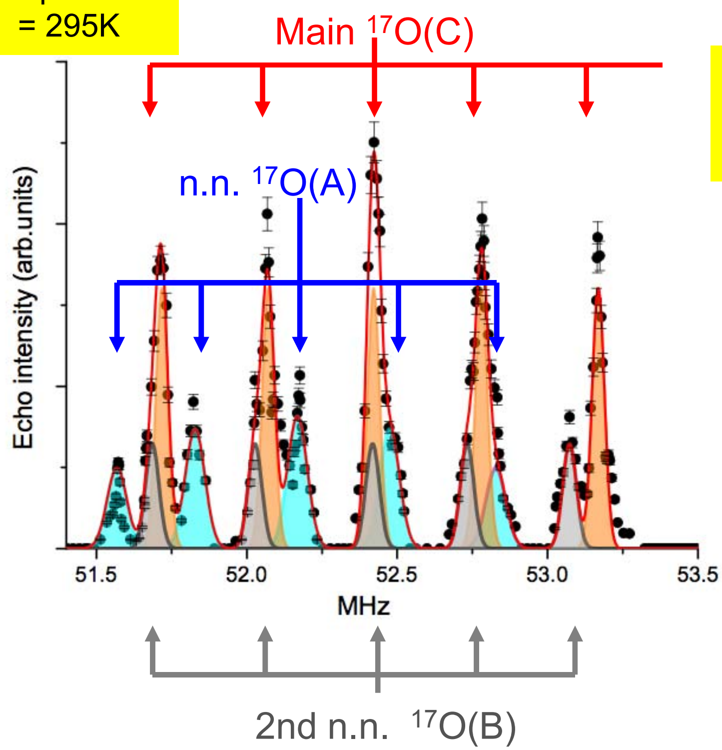
Freedman *et al.,* JACS **132**, 16185 (2010)
de Vries *et al.*, Nature **468**, 908 (2010)

Refine kagome / interlayer sites <u>separately.</u>

- Perfect kagome layers
- Zn/interlayer sites: 15% Cu^{2+}
- $(Zn_{0.85}Cu_{0.15})\ Cu_3(OH)_6Cl_2$

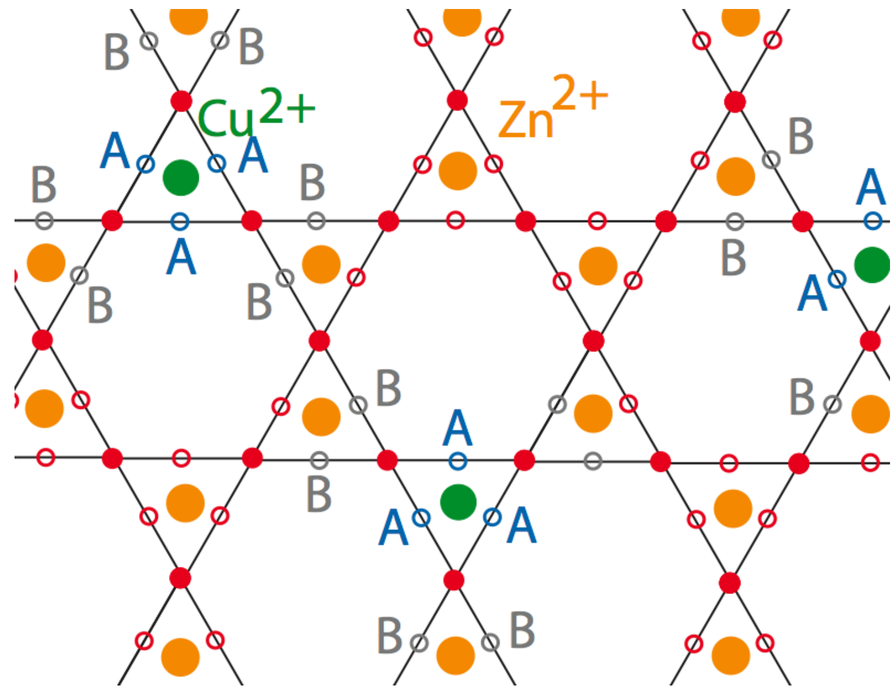
No antisite/strong disorder: ^{17}O NMR on a single crystal

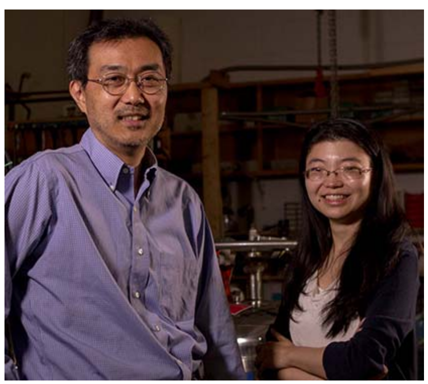
Temperature = 295K



Applied magnetic field

9T || *C*





Takashi Imai Mingxuan Fu

- Weak disorder: Cu^{2+} in Zn defect
- A-sites 13(4)% --- n.n. of Cu^{2+} in Zn defect
- B-sites 28(5)% --- 2nd n.n. of Cu^{2+} in Zn defect.
- C-sites 59(8)% --- Main kagome sites

Mission impossible for powder NMR.

Fu *et al.*, Science **350**, 655 (2015)

Refining the Spin Hamiltonian Using Single Crystals

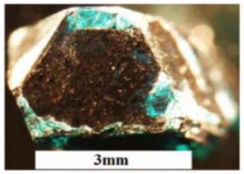
$$\mathcal{H} = J\sum_{\langle i,j\rangle} \mathbf{S}_i\mathbf{S}_j + \mathcal{H}_{DM} + \mathcal{H}_{EA}$$

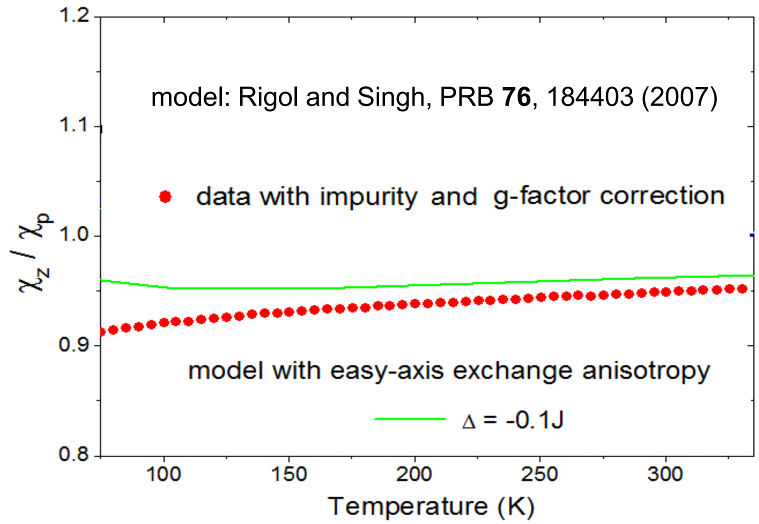
Isotropic Heisenberg >> Anisotropic exchange | Spin-orbit coupling of Cu

ESR experiment on powder sample: $\mathcal{H}_{DM} = \sum_{\langle i,j\rangle} (\mathbf{D}_{ij}\cdot\mathbf{S}_i\times\mathbf{S}_j)$ ~ 0.08 *J*. Zorko *et al.*, PRL **101**, 026405 (2008)

How about $\mathcal{H}_{EA} = \Delta\sum_{\langle i,j\rangle} (S_i^x S_j^x + S_i^y S_j^y)$?

Experiment: magnetic susceptibility on a quasi-cubic crystal





$\chi = \partial M / \partial H$

- Red data reflects the spin Hamiltonian.
- Easy-axis exchange: $\Delta \sim -0.1\,J$
- $|\Delta| \ll |J|$
- Validation of Heisenberg model approximation

T.-H. Han *et al.,* PRL **108**, 157202 (2012)

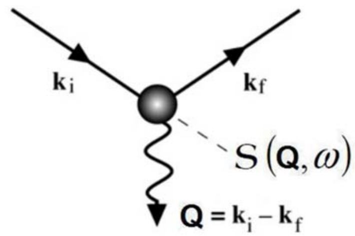
With large single crystals of herbertsmithite,

can we find direct evidence of a quantum spin-liquid

ground state?

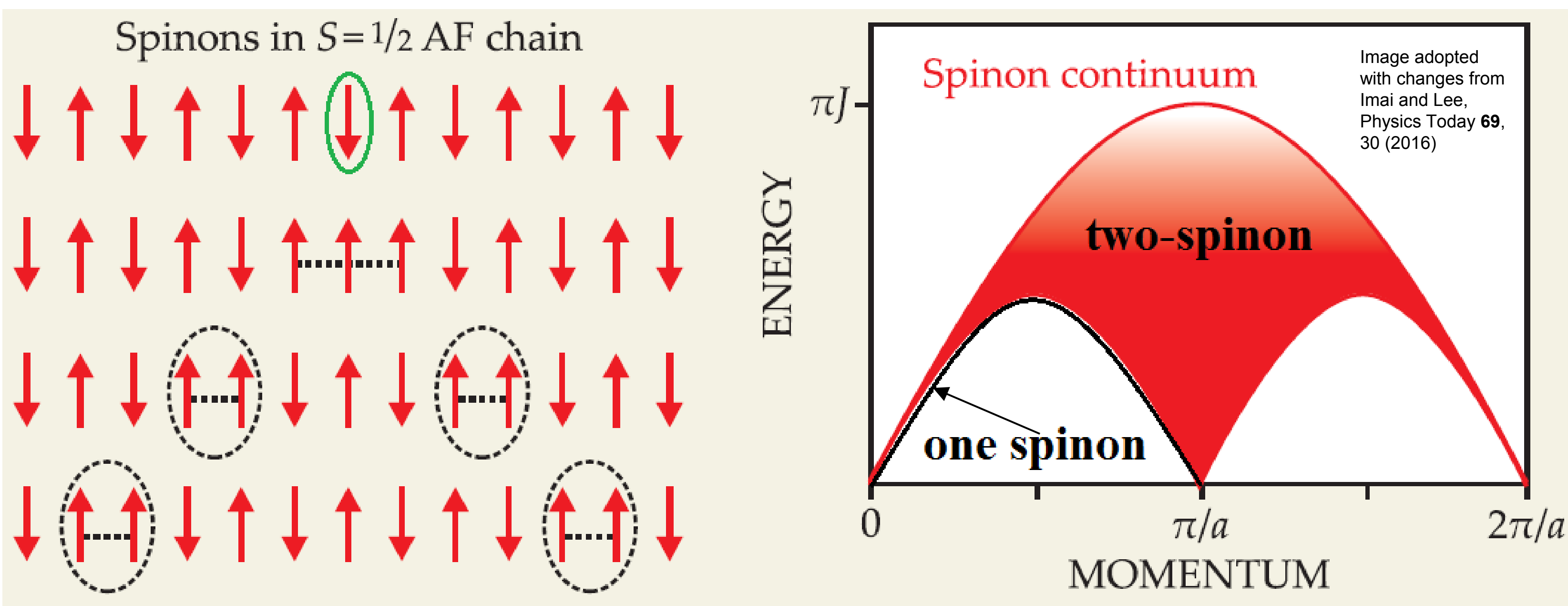
Neutron Scattering Measurement of Spin Fractionalization

- Spinons are created in pairs.
- A spinon has spin ½.
- Neutron scattering: $\Delta S_{sample} = \pm 1$.



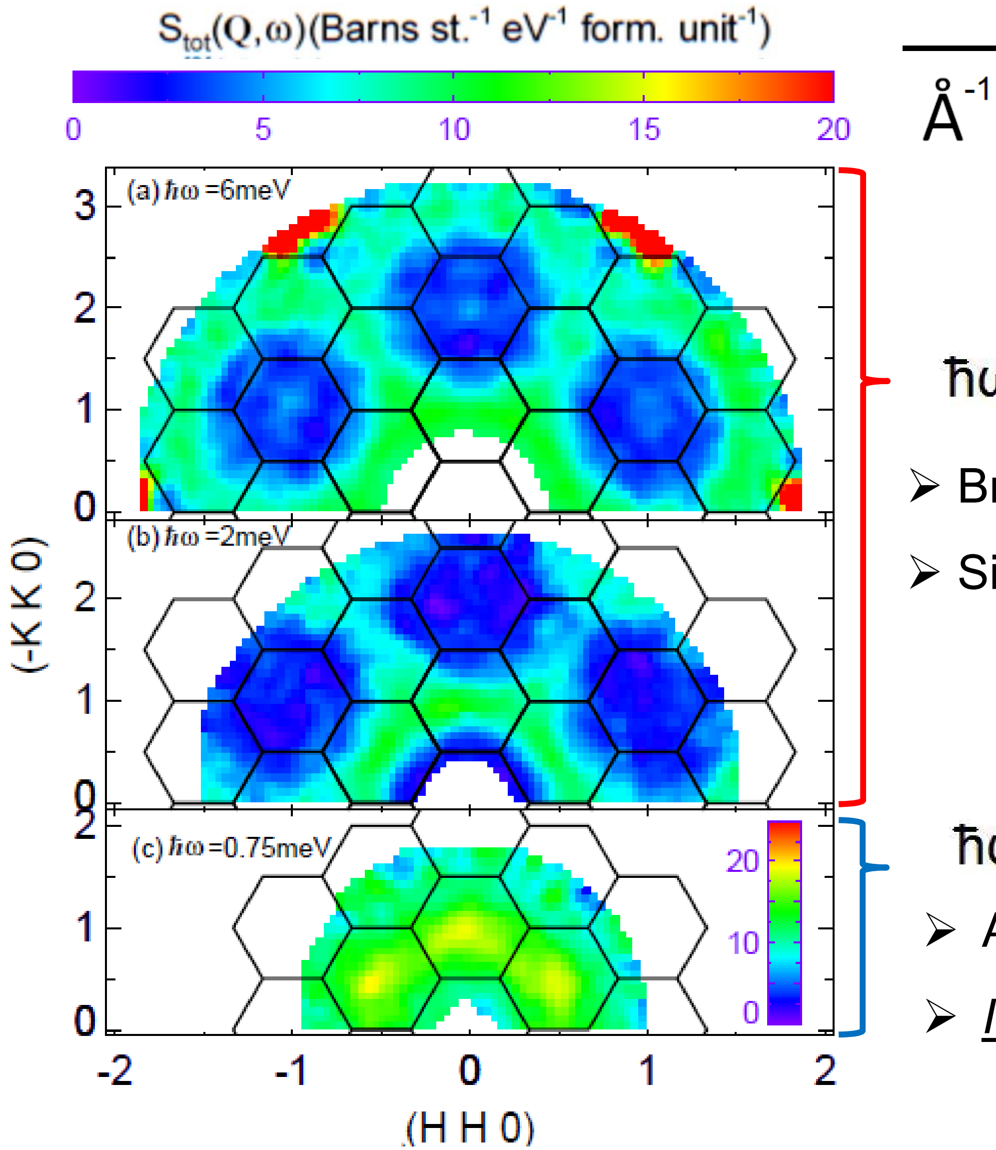
In a quantum spin liquid, a neutron detects two-spinon dispersion – a continuum in spectrum.

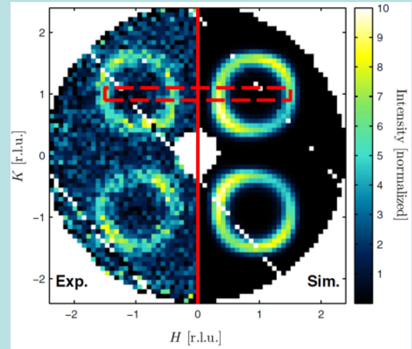
….. : a spinon / a domain boundary / an energized spin exchange



Dynamic structure factor S(Q,ω)

Temperature =1.6 K





Spin wave of $Lu_2V_2O_7$

PRL **113**, 047202

ħω > 1.5 meV: signal (green-cyan)

- Broad hexagon rings
- Similarity between 11 meV and 1.5 meV

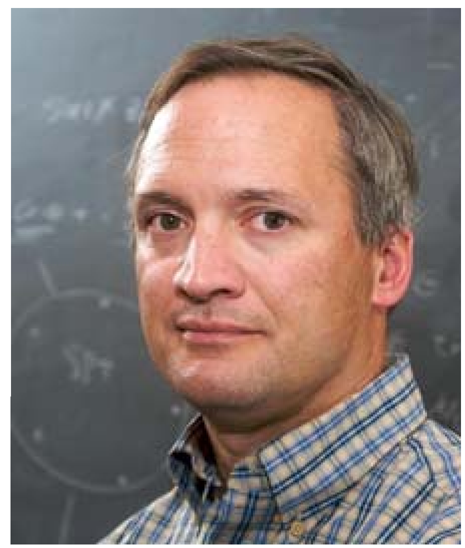
ħω < 1 meV: signal (yellow)

- A distinct pattern
- <u>*Impurity or intrinsic?*</u>

T.-H. Han *et al.,* Nature **492**, 406 (2012)

continuum ≠ featureless

Why the continuum is featureless in momentum?



Leon Balents

J_2/J_1

© Steve White

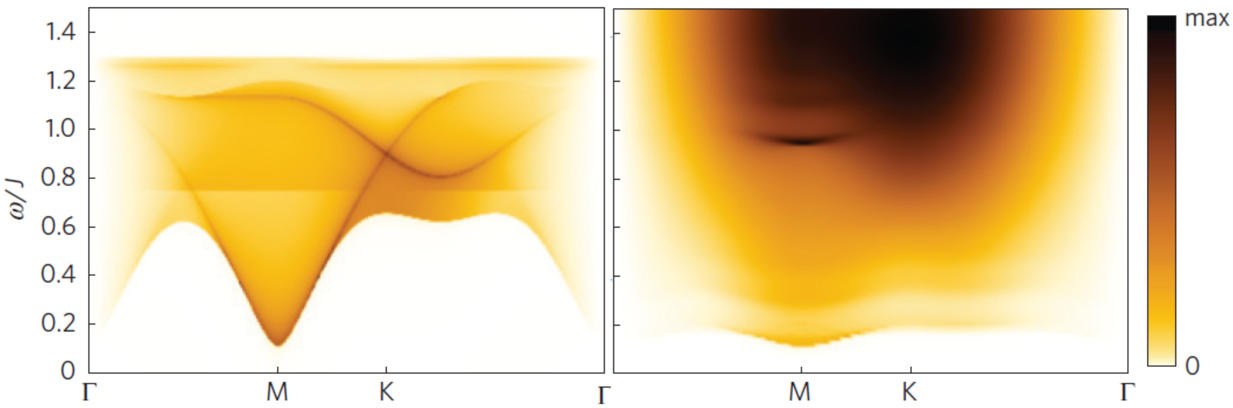
Subir Sachdev

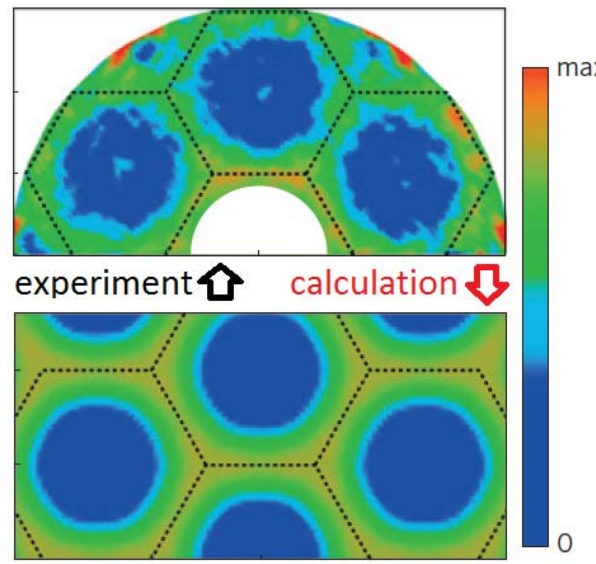
Z_2 fully-gapped QSL

Yan *et al.*, Science 2011
Depenbrock *et al.*, PRL 2012

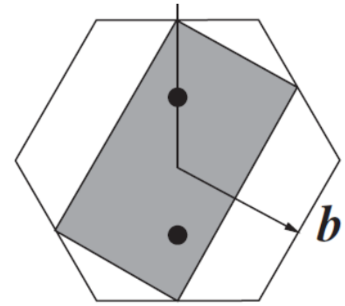
Punk, Chowdhury and Sachdev,
Nature Phys. **10**, 289 (2014)

Z_2 free spinons | Z_2 spinon-vison





At odds w/ U(1) Dirac QSL

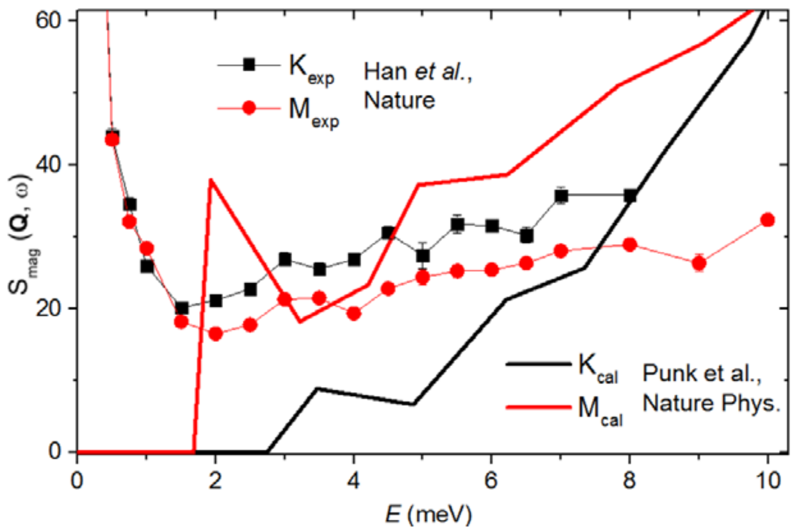


(Ran *et al.*, PRL 2007)

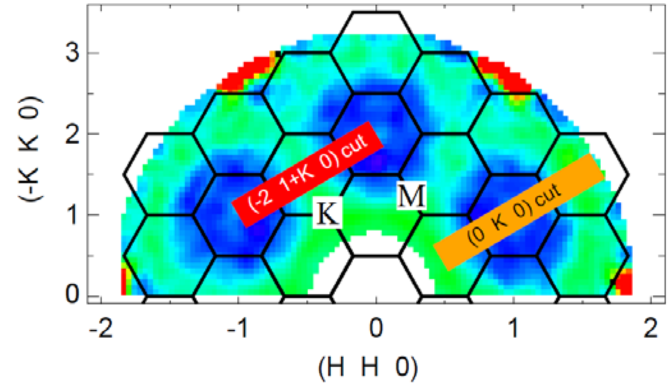
- Experiment: flat in momentum and energy.
  - → at odds with free spinons.
- Sachdev's Z_2 QSL theory: a flat vison band.
  - → momentum sink, which flattens $S(\mathbf{Q}, \omega)$.

Spin Gapped or Not ?

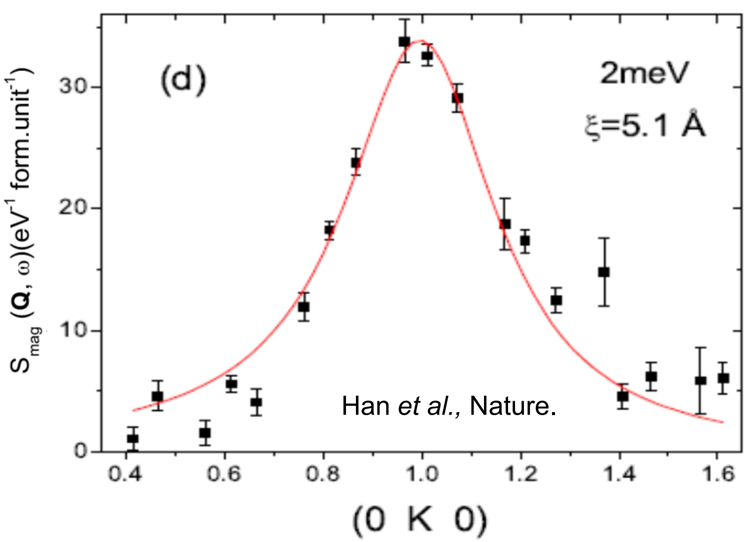
A mixed message from neutron scattering



- Experiment: gapless
- Z_2 QSL theory: gapped



Han *et al.*, Nature.

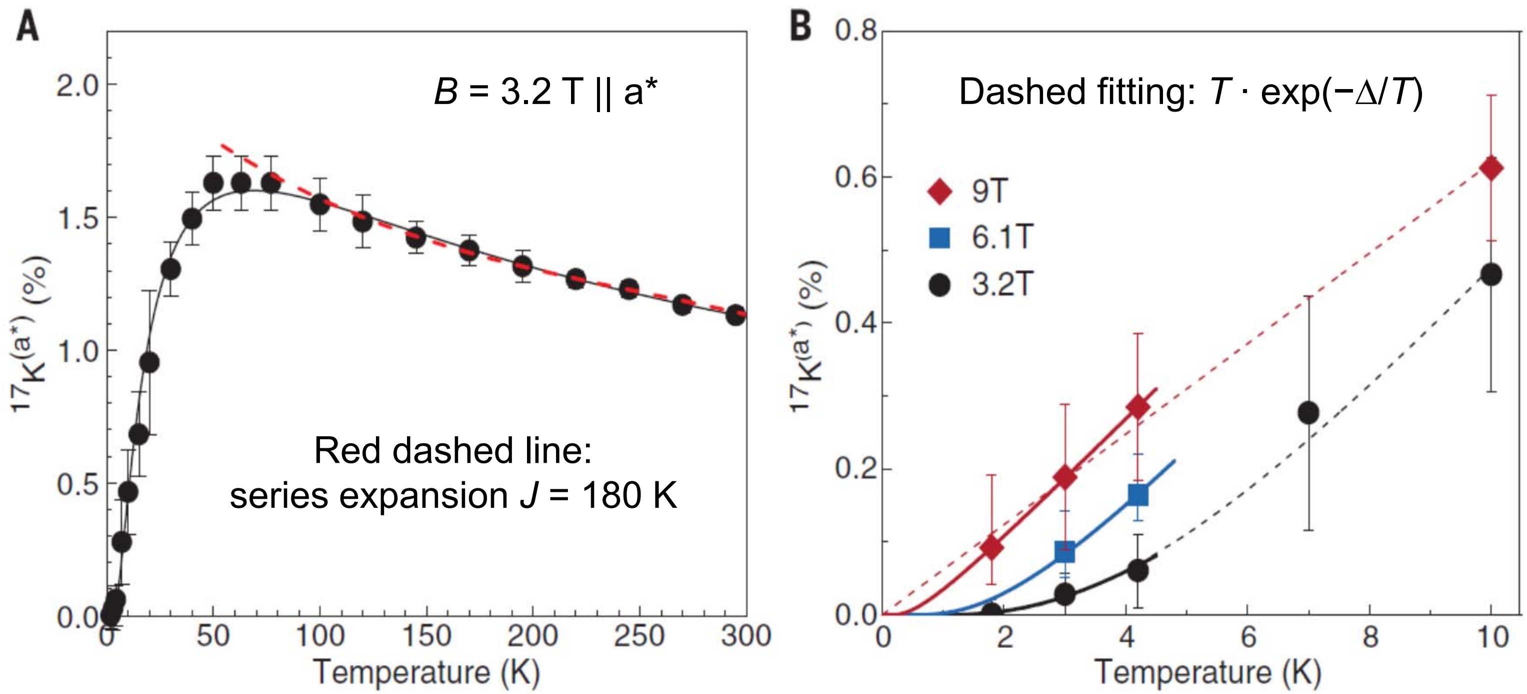


- Experiment: ξ ~ 5 Å
- DMRG w/ a gap: ξ ~ 5 Å

ξ: spin-spin correlation length

- Neutron scattering measures bulk responses.
- Gapless spin excitations exist, but they may not be kagome-intrinsic.

Local Probe: NMR evidence of a spin gap



Fu *et al.,* Science 2015

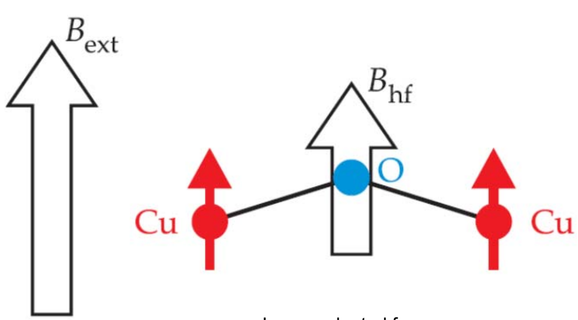
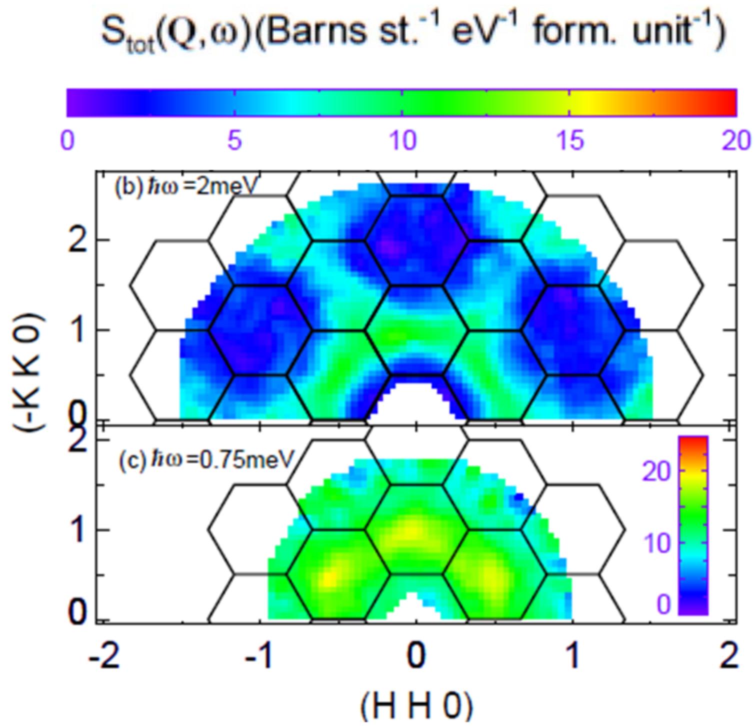


Image adopted from
Imai and Lee,
Physics Today **69**, 30 (2016)

A. Intrinsic kagome susceptibility → no curie tail

B. Spin gap Δ(0T) = 10(3) K
0.9(3) meV
0.05(2) *J*

Temperature =1.6 K



Regarding the ~1 meV spin gap,

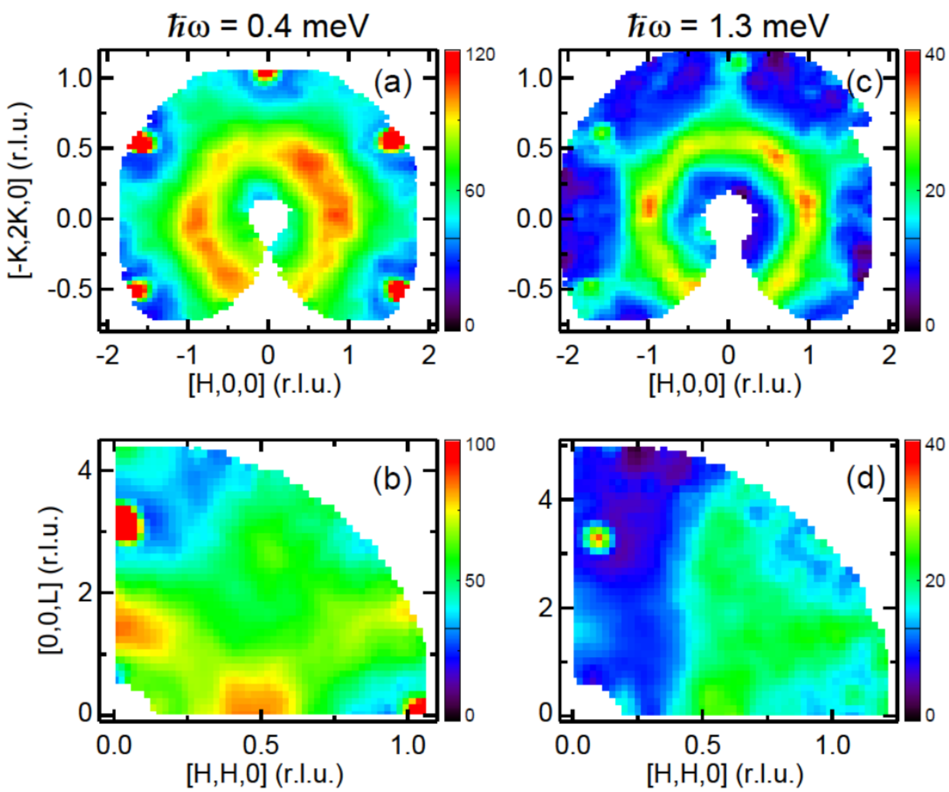
← How to understand this?

A Dichotomy of the Quantum Spin Liquid and the Correlated Impurity Spins

At T = 2 K, different **Q**-dependence below and above 0.8 meV

Top (a)(c) in [H K 0]:
- Spinon continuum at 1.3 meV
- Rotated by 30˚, more diffuse at 0.4 meV

Bottom (b)(d) in [H H L]:
- Two dimensional at 1.3 meV
- Three dimensional at 0.4 meV



MACS II: cleaner low-energy neutron scattering

T.-H. Han *et al.*, PRB **94**, 060409(R) (2016)

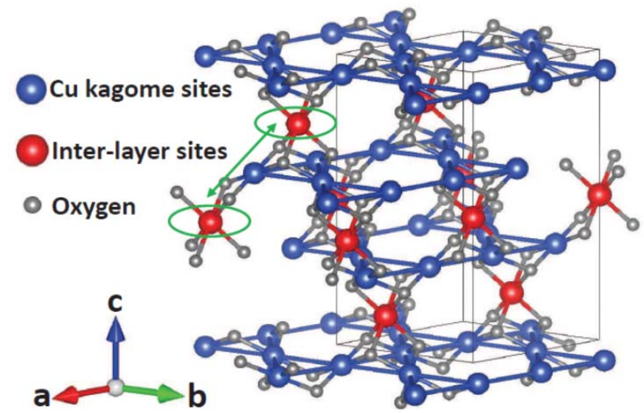
A Dichotomy of the Quantum Spin Liquid and the Correlated Impurity Spins

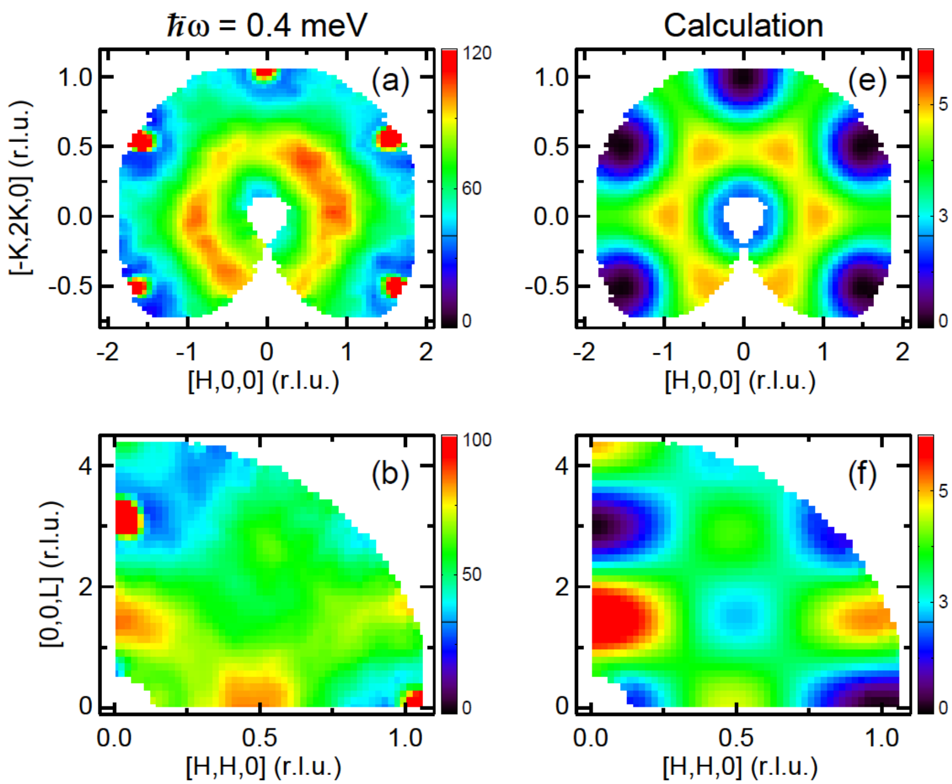
Modeling with interlayer spins for 0.4 meV data

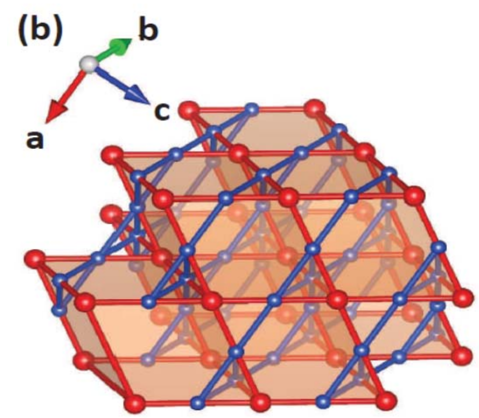
- Interlayer triangular lattice mediated by kagome spins
- Correlation: nearest trans-kagome interlayer spin pairs
- 15% of interlayer sites have Cu^{2+}

  Interlayer: $1-(1-0.15)^6$ = 62% of spins neighbor interlayer spins.

  Kagome: 0.15^2=2% are amid interlayer spins. → **weak disorder**







Interlayer spins have cubic connectivity.

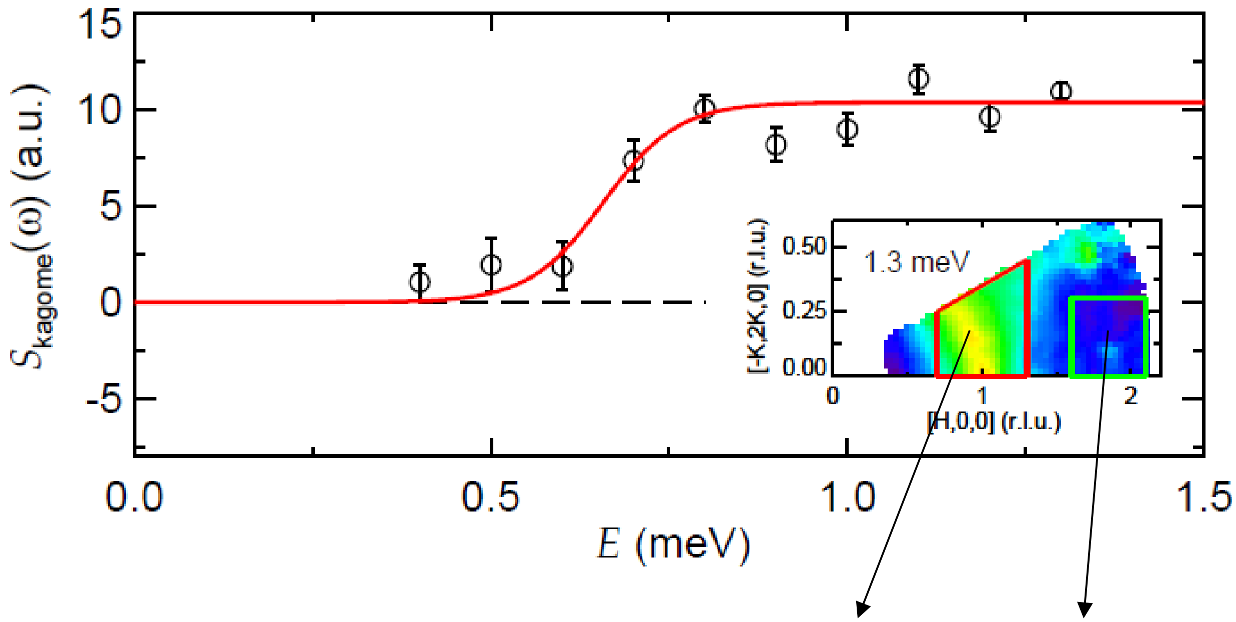
0.15 < 0.31 threshold → No ordering

Wang *et al.*, PRE **87**, 052107

T.-H. Han *et al.*, PRB **94**, 060409(R) (2016)

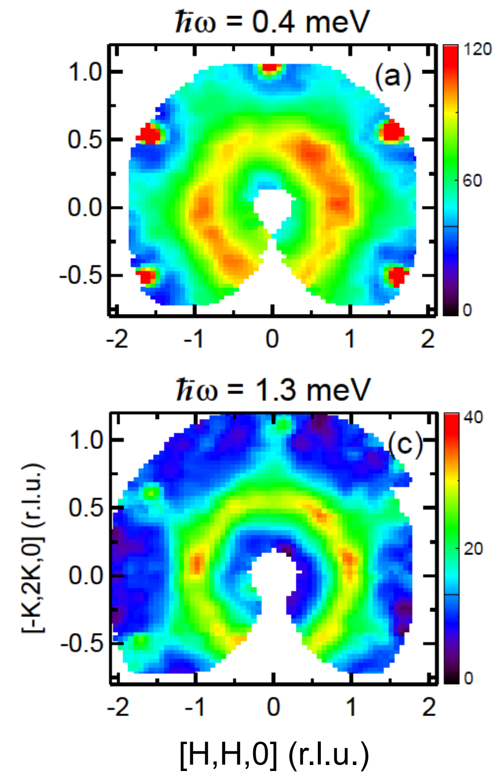
A Dichotomy of the Quantum Spin Liquid and the Correlated Impurity Spins

First neutron scattering evidence of a spin gap ≈ 0.7 meV = 0.04 J



$\mathcal{S}_{kag+imp}(\omega)$ $\mathcal{S}_{imp}(\omega)$

(1 0 0) (2 0 0)



$$\mathcal{S}_{kagome}(\omega) = \mathcal{S}_{kag+imp}(\omega) - a\ \mathcal{S}_{imp}(\omega)$$

a ≈ 1.7: → by matching scattering at 0.3 to 0.5 meV

→ consistent with calculation

Energy Resolution

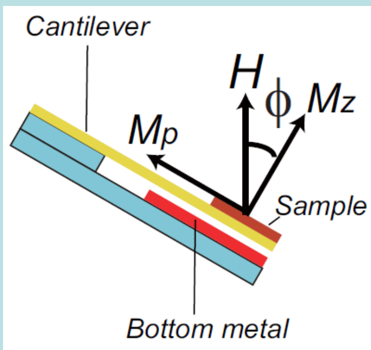
- Relative to J = 17 meV
- 0.08 meV ~ J / 200

T.-H. Han *et al.*, PRB **94**, 060409(R) (2016)

FUTURE

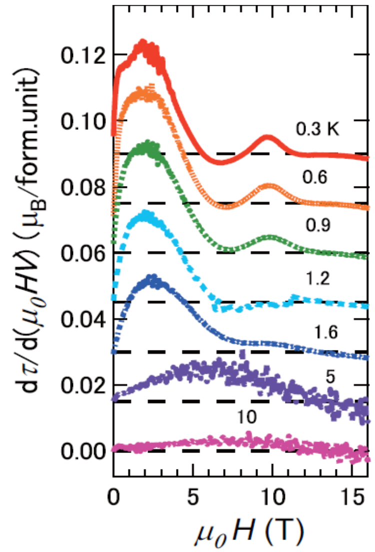
1. Advance in Magnetism: Defects and Spin Gap "Closing"

Asaba *et al.*, PRB **90**, 064417 (2014)



Torque Magnetometry

Zorko *et al.*, PRL **118**, 017202 (2017)



Lu Li

- What is at $\mu_0 H$ = 7 T ?
- Why smears at T > 1 K ?

Combined with ESR

Two types of defects

1. $\theta_{\rm CW}^{d_I} = -5.2$ K

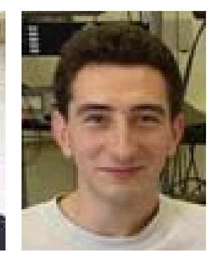
   Interlayer / impurity spins

2. $\theta_{\rm CW}^{d_{II}} \sim 0$

   Kagome: Zn^{2+} < 1%?

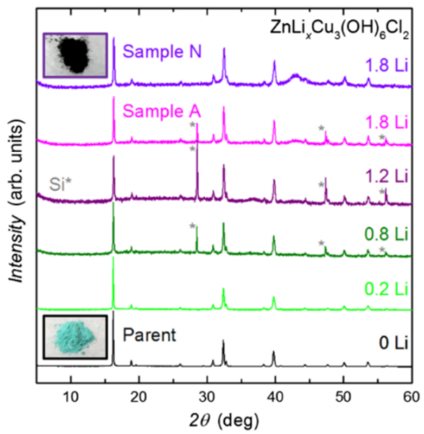
   Or, interlayer spins perturb kagome?

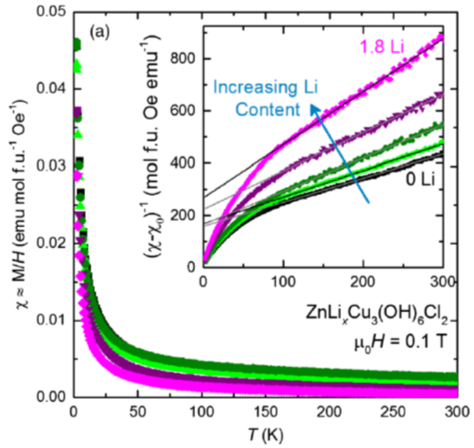
Philippe Mendels

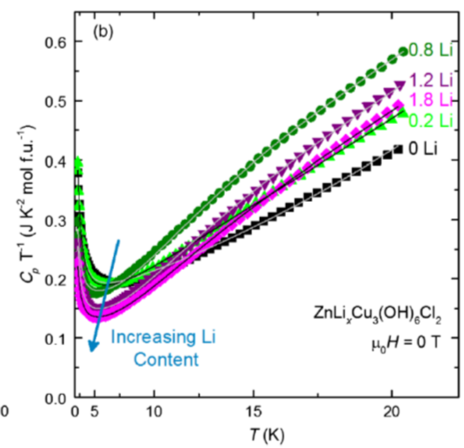


Fabrice Bert

2. Advance in Electricity: Charge Doping Herbertsmithite







Tyrel McQueen

PRX **6**, 041007 (2016)

Stable structure

- ➢ Cu^{2+} → Cu^{1+}
  kagome & interlayer

Similar magnetism

- ➢ no phase transition
- ➢ reduced spin count

Zero electric conductivity

- ➢ disorder from Li ions
- ➢ kagome connectivity

Next Steps

Neutron Scattering

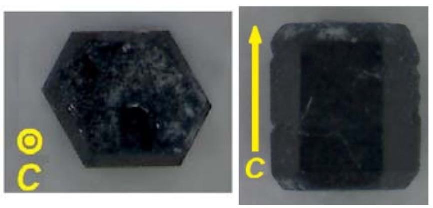
- ➢ kagome magnetism with strong disorder
  Does the spinon continuum stay?

Position Targeted Doping

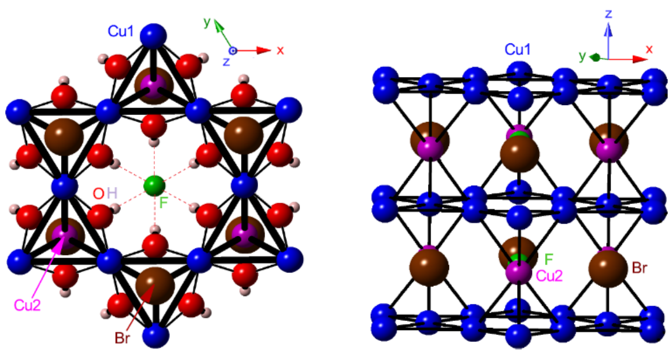
- ➢ stay away from kagome
- ➢ reduce interlayer spins

3. Advance in Materials: $Zn_xCu_{4-x}(OH)_6FBr$

Mother (x = 0): barlowite $Cu_4(OH)_6FBr$

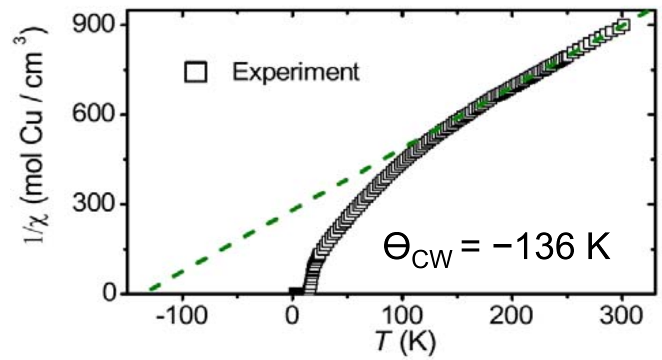


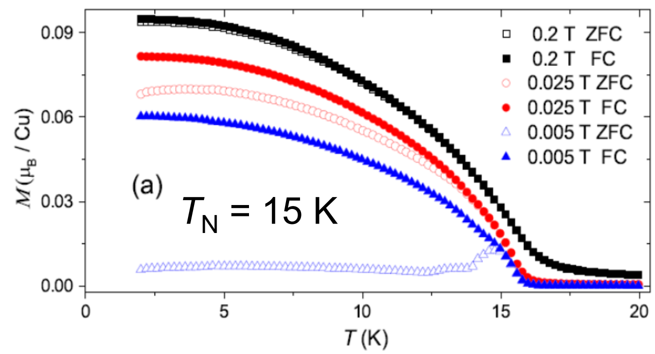
	Cu1-O-Cu1	Cu1-O-Cu2
angle	117.4°	95.8°

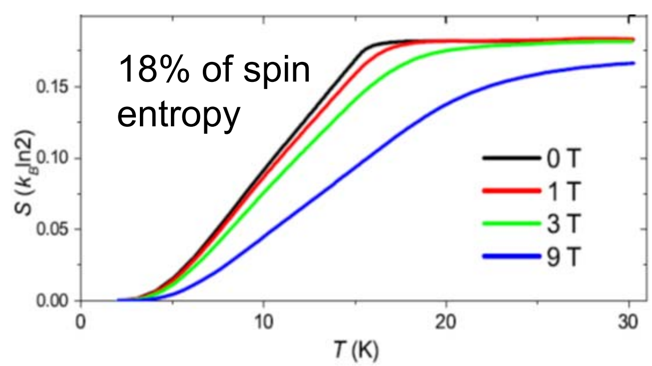


- Cu1: undistorted kagome & *J*
- Cu2: 3 equivalent positions
- AAA stacking of kagome

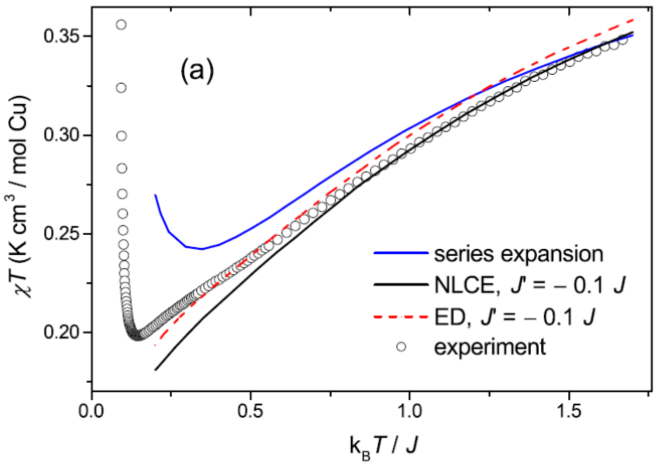
T.-H. Han *et al.,* PRL **113**, 227203 (2014)







3. Advance in Materials: $Zn_xCu_{4-x}(OH)_6FBr$



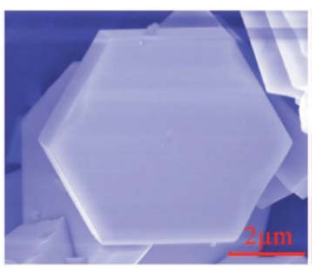
x = 0: $Cu_4(OH)_6FBr$

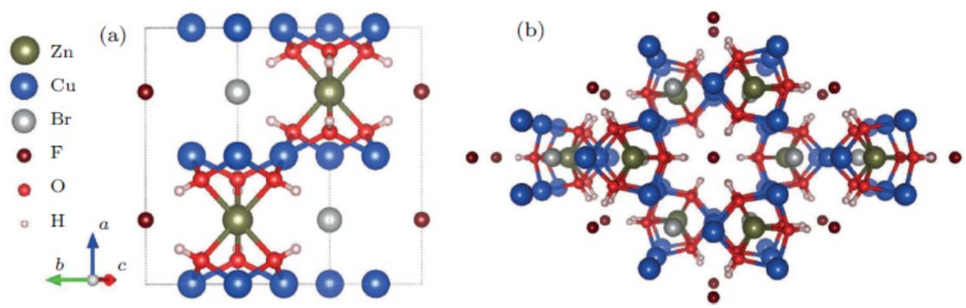
2D or not 2D? Almost 2D.

Interlayers need to be de-magnetized.

T.-H. Han *et al.*, PRB **93**, 214416 (2016)

x = 1: $ZnCu_3(OH)_6FBr$

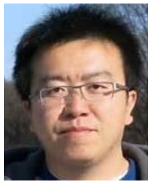




x = 0: $P6_3/mmc$; a = 6.6799(4) Å, c = 9.3063(13)Å.

x = 1: $P6_3/mmc$; a = 6.6678(2) Å, c = 9.3079(3) Å.

Guo-Qing Zheng



Zi Yang Meng

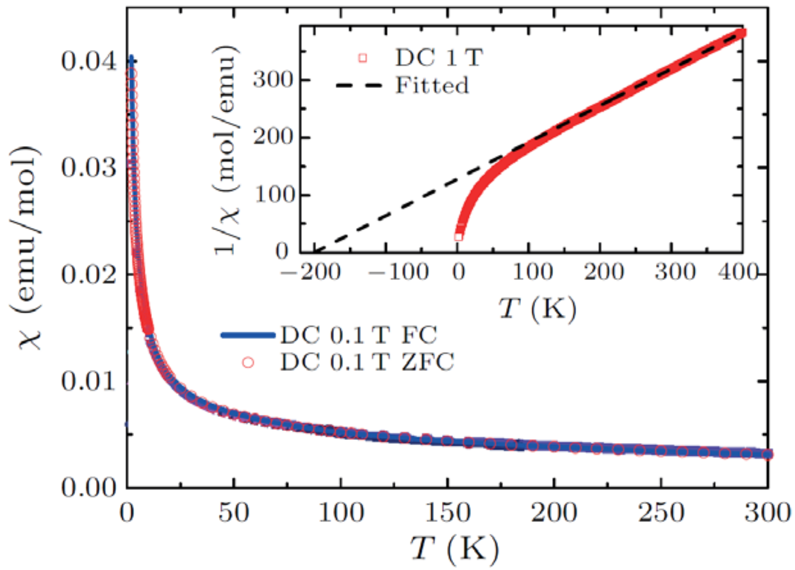
Jia-Wei Mei

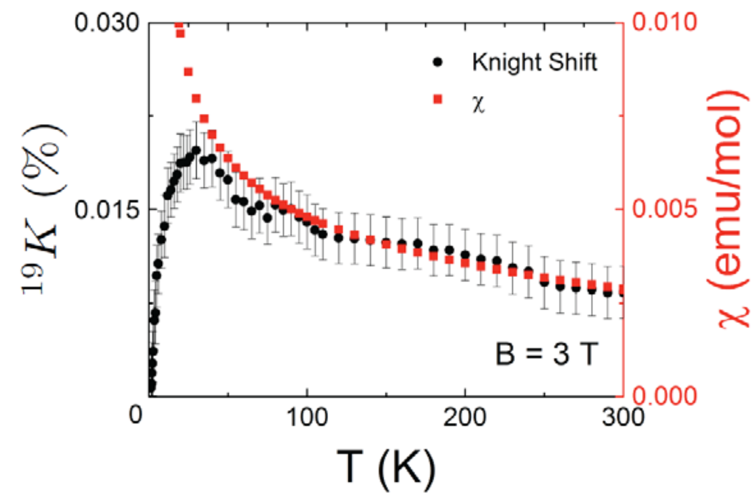
Youguo Shi

CPL **34**, 077502 (2017)

3. Advance in Materials: $Zn_xCu_{4-x}(OH)_6FBr$

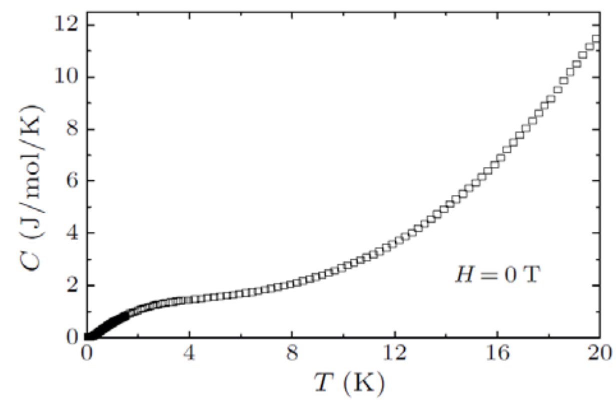
x = 1: $ZnCu_3(OH)_6FBr$ polycrystalline



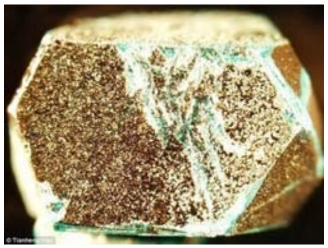


- Θ_{cw} = −200 K
- Susceptibility: no spin ordering down to 2 K.

  ZFC/FC overlap: no glassy freezing down to 2 K.
- Heat capacity: no phase transition down to 50 mK
- NMR: a spin gap ~ 7.5 K

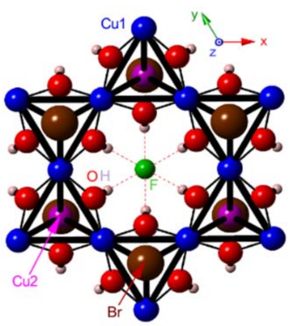


Summary



Herbertsmithite $ZnCu_3(OH)_6Cl_2$

- First observation of a spinon continuum above a ~0.05 *J* gap.
- Complications: correlated impurity, perturbations.
- Charge doping 'failure' calls for immediate follow-ups.



A new quantum spin-liquid candidate $ZnCu_3(OH)_6FBr$

- Need further measurements to compare with herbertsmithite.

Acknowledgement

Herbertsmithite

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