Two studies in two-dimensional quantum magnets: spin liquids and intertwined order

Young Lee (Stanford and SLAC)

KITP (Intertwined Order)
Order, Fluctuations, Strong Correlations Conference, August 2017

Outline

1) Quantum spin liquid on S=1/2 kagome lattice

- **spin-gap** in Herbertsmithite $ZnCu_3(OH)_6Cl_2$

2) Doped holes in S=1/2 square lattice

- spin and charge stripes $La_{2-x}Sr_xCuO_4$ and La_2CuO_{4+y} (**effects of disorder**)

Cast and Credits

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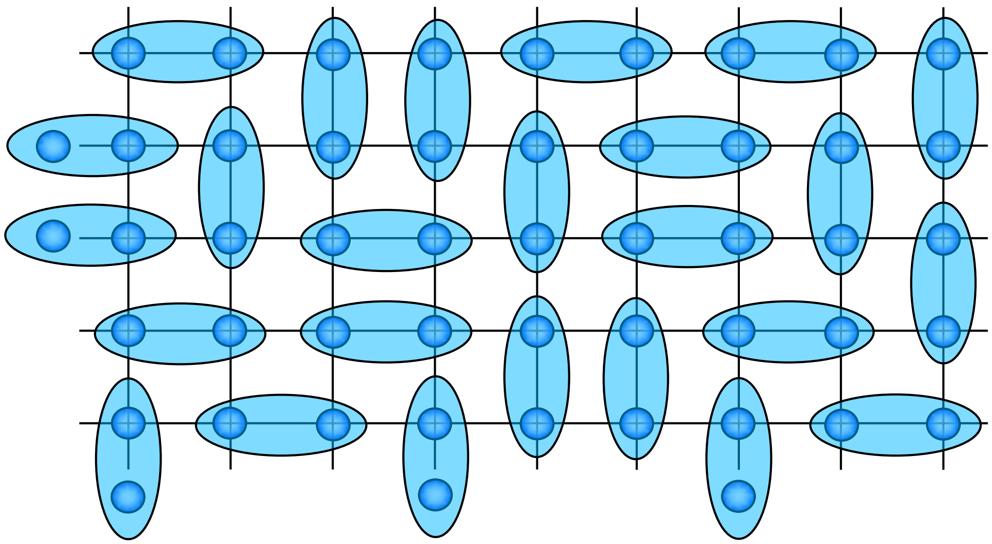
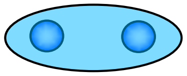
SLAC NATIONAL ACCELERATOR LABORATORY

The quantum spin-liquid:
A new state of matter in two-dimensions





$$\frac{1}{\sqrt{2}}\left(\left|\uparrow\downarrow\right\rangle - \left|\downarrow\uparrow\right\rangle\right)$$

Every spin is
hidden in a singlet

Anderson's RVB state (1973--triangular) (1987--square)

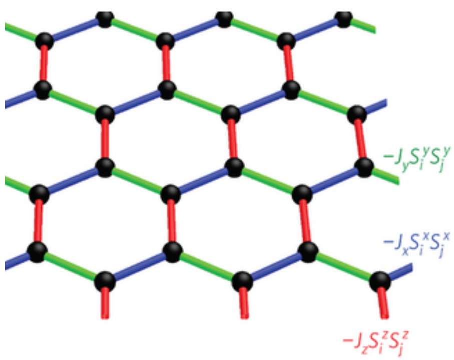
Actual wavefunction is a superposition of many configs.

The ground state does not break conventional symmetries,
it is not a crystal (no translational symmetry breaking),
and it is not an ordered magnet (no spin-rotation breaking).

List of 2D quantum spin liquid candidates continues to grow

Kitaev model

Bond-dependent int.
on honeycomb

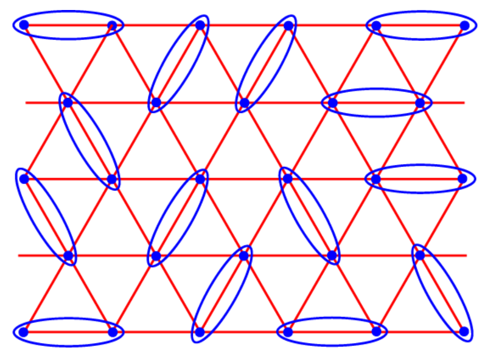


(from Moessner et al, Nature 2016)

α-$H_3LiIr_2O_6$,
α-$RuCl_3$

Triangular lattice

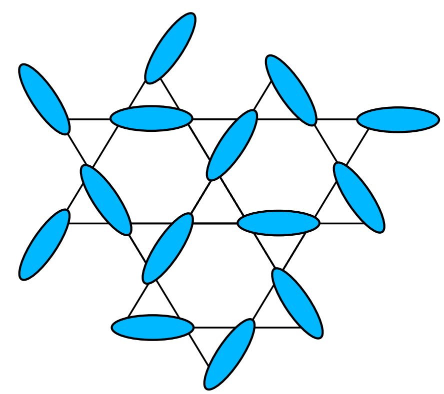
Heisenberg int.
on edge sharing



k-$(ET)_2Cu_2(CN)_3$
$EtMe_3Sb[Pd(dmit)_2]_2$
$YbMgGaO_4$

Kagome lattice

Heisenberg int.
on corner sharing

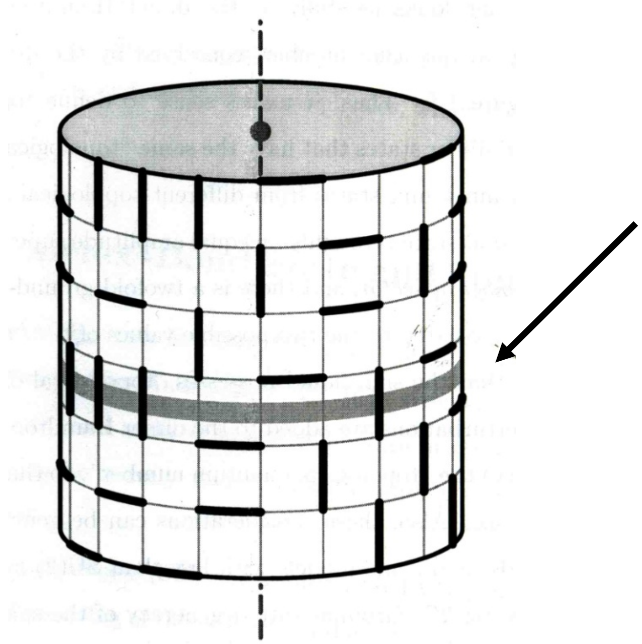


$ZnCu_3(OH)_6Cl_2$
(Herbertsmithite)

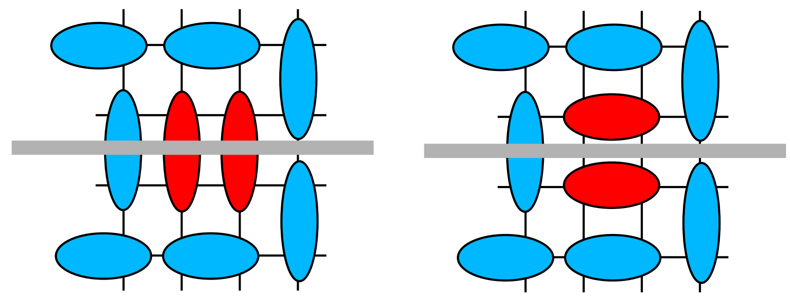
Simple and
highly frustrated

Why are quantum spin liquids (QSL) interesting?

If gapped, the QSL has “topological order”



The number of singlets cut by this reference line is odd or even (a topological invariant).



Alexei Kitaev

Xiao-Gang Wen

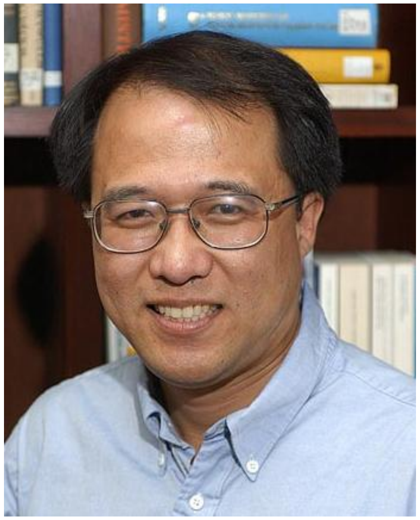
2017 Buckley Prize

"For theories of ***topological order*** and its consequences in a broad range of physical systems."

Where Kitaev-Wen meet experiment:

the quantum spin liquid

A new classification for quantum matter



Xiao-Gang Wen (MIT)

Long-range entanglement
and topological order

Examples:
1) Fractional quantum Hall effect
   - experimentally realized
2) Quantum spin liquids
   - experimentally realized (?)

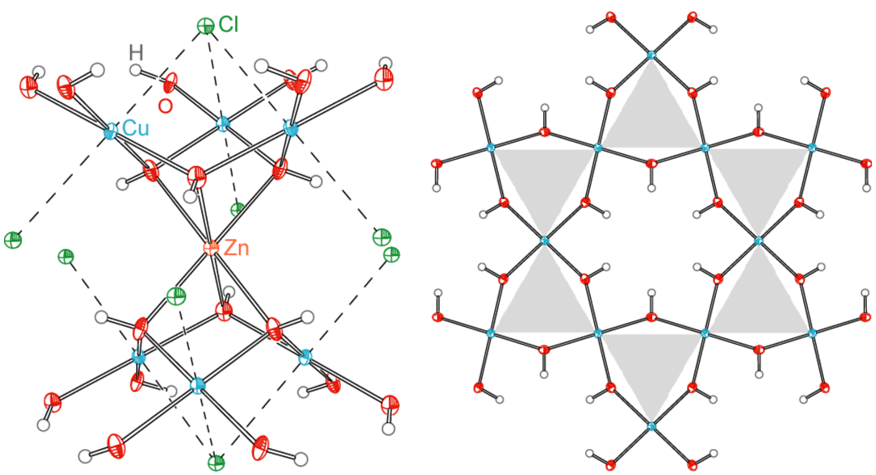
An experimental signature:
Exotic excitations with fractional quantum numbers

Quantum spin liquids on the kagome lattice

Experiment + theory : An intimate dance

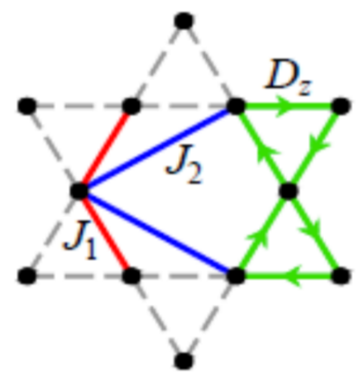
S=1/2 kagome lattice

Herbertsmithite $ZnCu_3(OH)_6Cl_2$



Theories based on Heisenberg model

$$\mathcal{H} = \sum_{\langle i,j \rangle} J_1 \vec{S_i} \cdot \vec{S_j} + J_2 \vec{S_i} \cdot \vec{S_j} + \overrightarrow{D_{ij}} \cdot (\vec{S_i} \times \vec{S_j})$$



- Large crystals
- ***Large J (17 meV)***

  (neutrons can resolve J/100)

Strong theoretical grounds for a QSL

A Zen koan:

“What QSL lives on the kagome lattice?”

“What is Herbertsmithite?”

Steps towards enlightenment

1) Seek fractionalized spin excitations
2) Understand spin Hamiltonian and phase diagram
3) Understand disorder
4) Seek evidence for a gap

What's the ground state for the **quantum spin-1/2** kagomé lattice Heisenberg model?

Theoretical consensus: <u>ground-state is not Néel ordered</u>

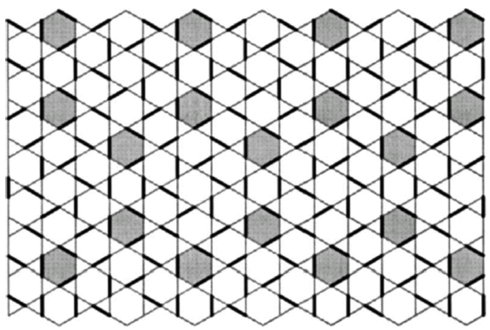
Nature of ground state?

1) Spin liquid (gapless? gapped?)

- Lee, Wen, *et al.*, PRL 98, 117205 (2007)
  → gapless Dirac fermions
- Sheng *et al.*(2008), White *et al.*(2011), Schollwock *et al.* (2012)
  → Z_2 topological order, spin-gap ~ 0.15 J

2) Valence bond crystal

Nikolic & Senthil (2003)
Singh & Huse (2008)



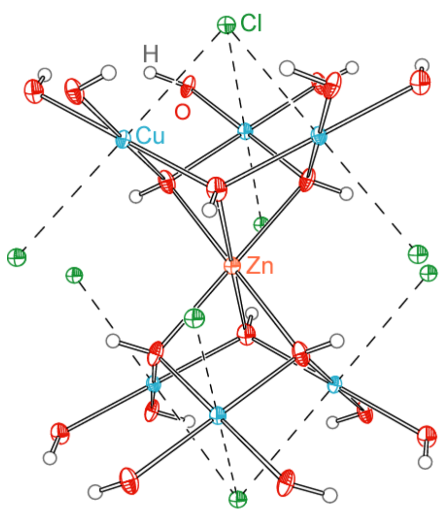
<u>Herbertsmithite</u> ($ZnCu_3(OH)_6Cl_2$): An S=1/2 kagomé lattice material

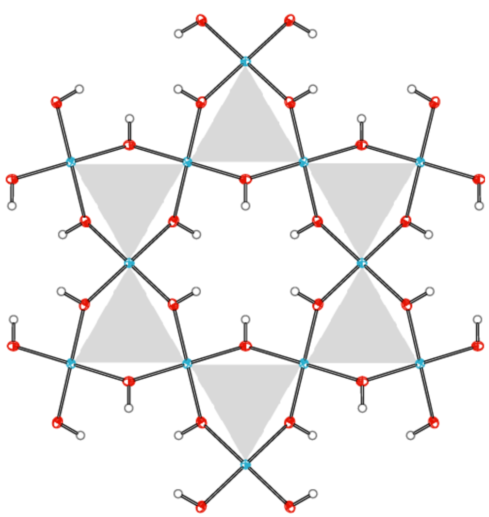
S=1/2 Cu^{2+} kagomé layers separated by non-magnetic Zn^{2+} layers

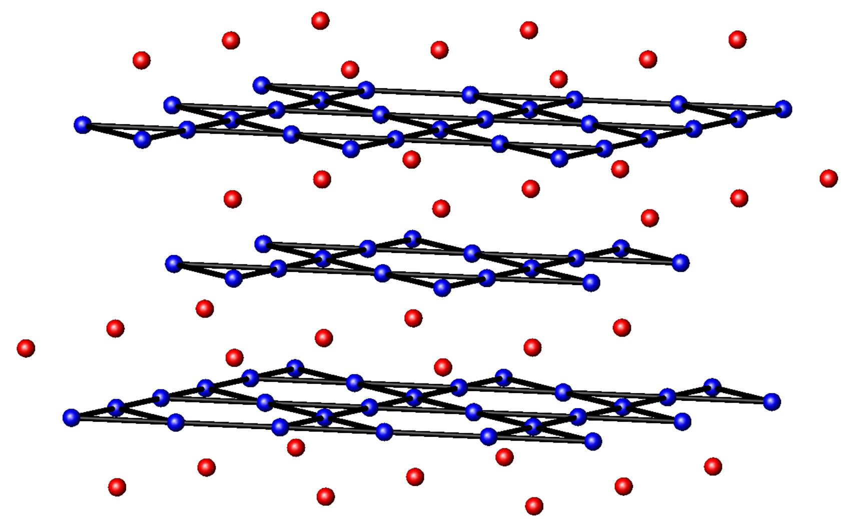
Collaboration with Dan Nocera (Harvard, Chemistry)

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

Helton *et al*, Phys. Rev. Lett., **98** (2007)







This has the ideal kagomé structure

Caveat: 15% of Zn sites (interlayer) have a S=1/2 Cu impurity

From neutron, NMR, μSR, and thermodynamic measurements on powders, we know that herbertsmithite ***is not*** :

Helton *et al*, PRL (2007), Mendels *et al*, PRL (2007)

1) It is not Néel ordered or frozen (down to T=J/3000)

2) It is not gapped (at least down to Δ=J/170)

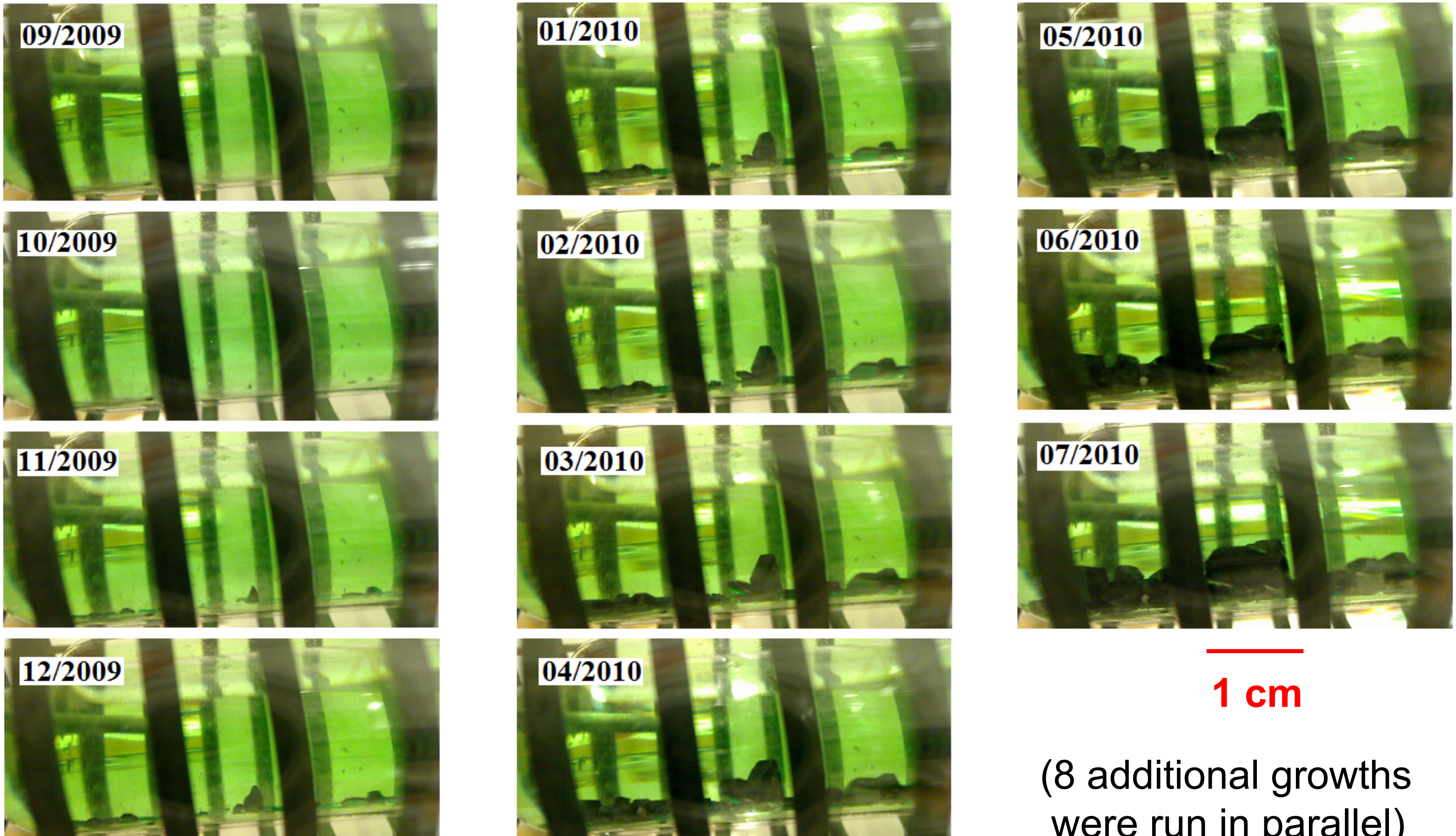
Deducing a spin liquid by ruling out other possibilities
- not completely satisfying

A better way: inelastic neutron scattering on single crystals to find deconfined spinons in a 2D magnet

Obstacles are daunting:

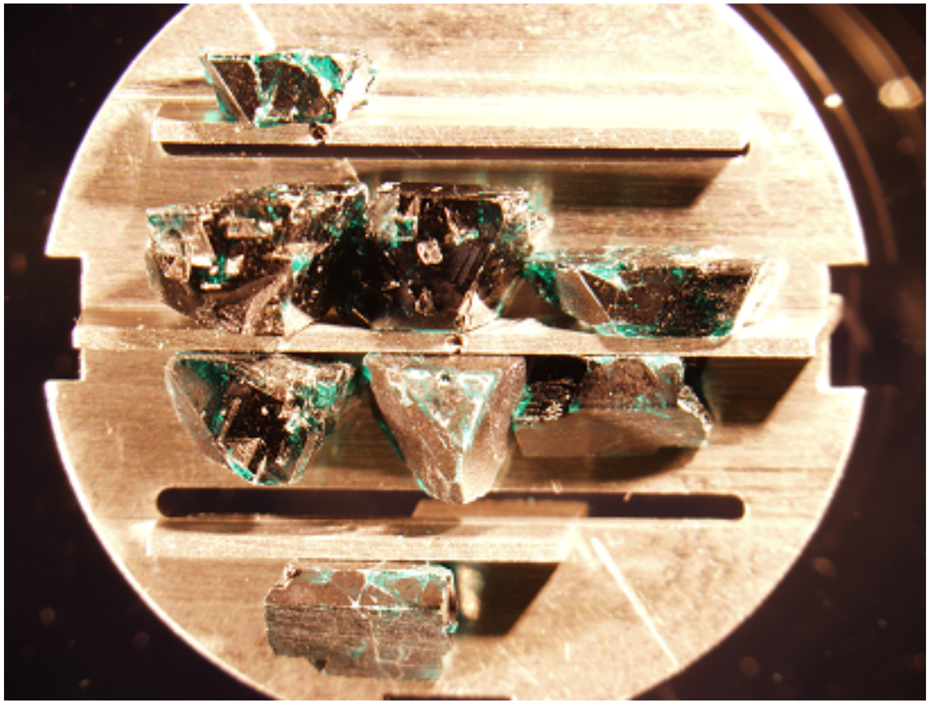
1) Small spin value S=1/2
2) No sharp peaks expected in ω or $\boldsymbol{Q}$
3) No recipe for crystals

Hydrothermal growth of large crystals: crazy thing to do... unless it works!



(8 additional growths were run in parallel)

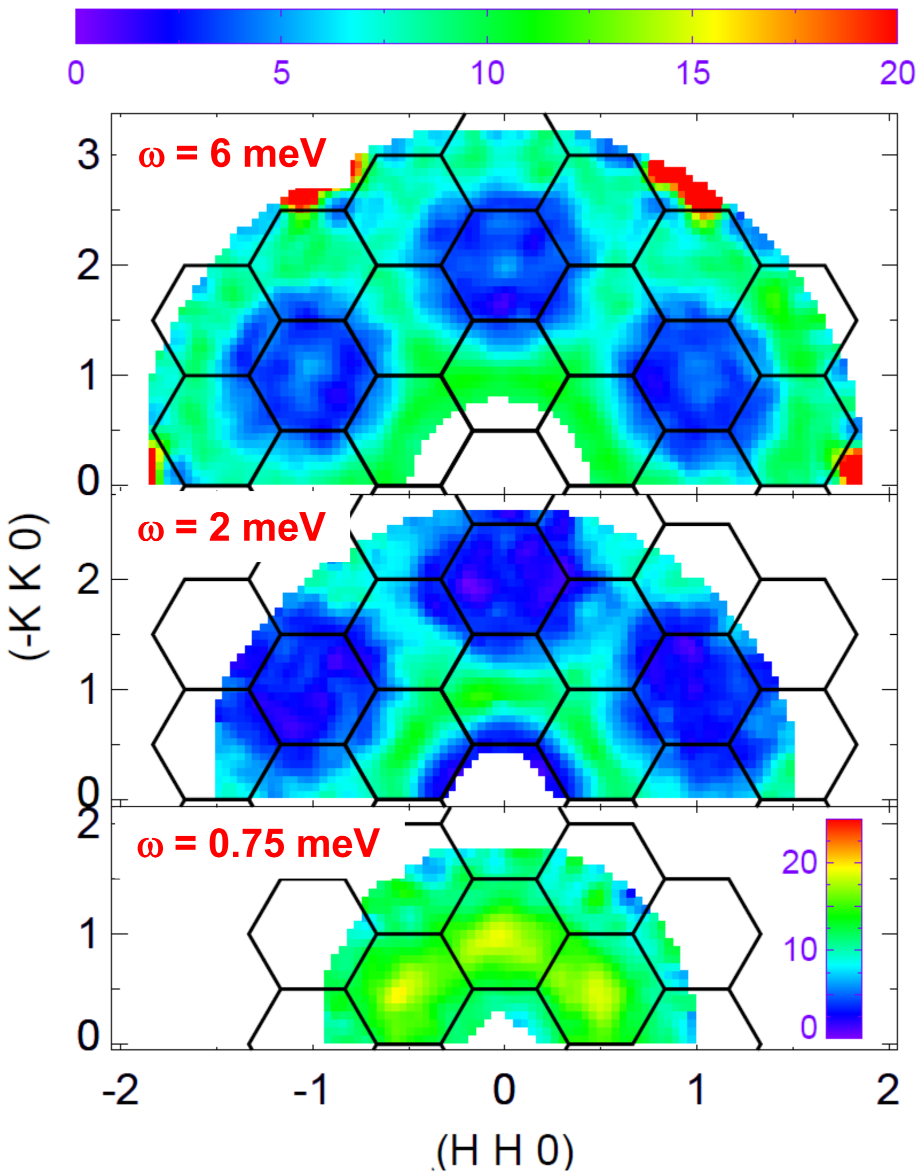
The "single" crystal for neutron scattering



← 2cm →

All crystals coaligned within 2 degrees
(the divergence of the neutron beam is ~1-2 degrees)

Spin correlations of the S=1/2 kagomé antiferromagnet



T Han, YL, et al,
Nature 492, 406 (2012)

T = 1.6 K

magnetic coupling J~17 meV

The observed scattering is:

- intrinsic to the kagomé spins
  (not just due to impurities)
- diffuse
  → no sharp dispersion surfaces !

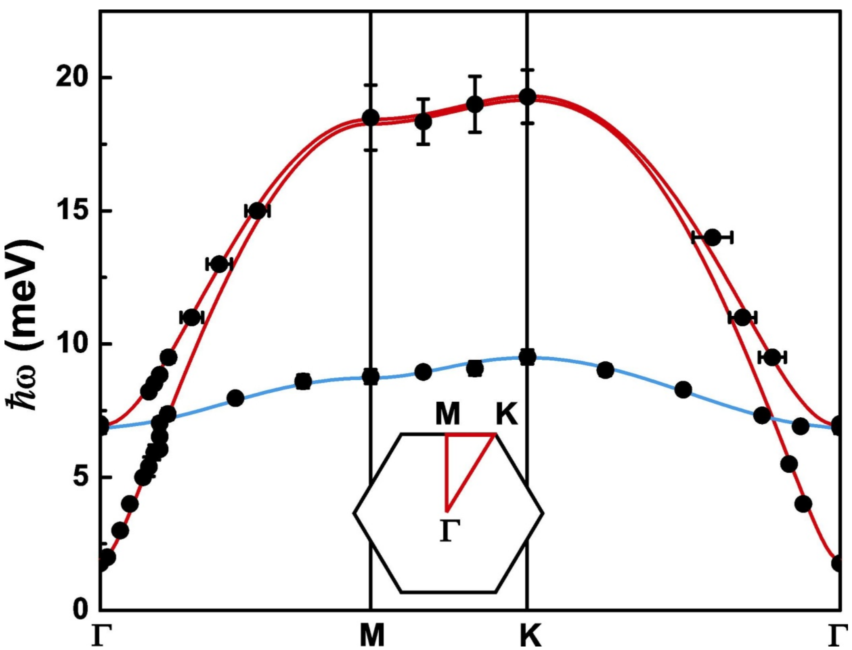
Plots of $S(\vec{Q},\omega)$ (background measured with empty sample holder and subtracted)

Contrast: a tale of two kagomé

S=5/2 $KFe_3(OH)_6(SO_4)_2$

ordered ground state

S=1 magnons

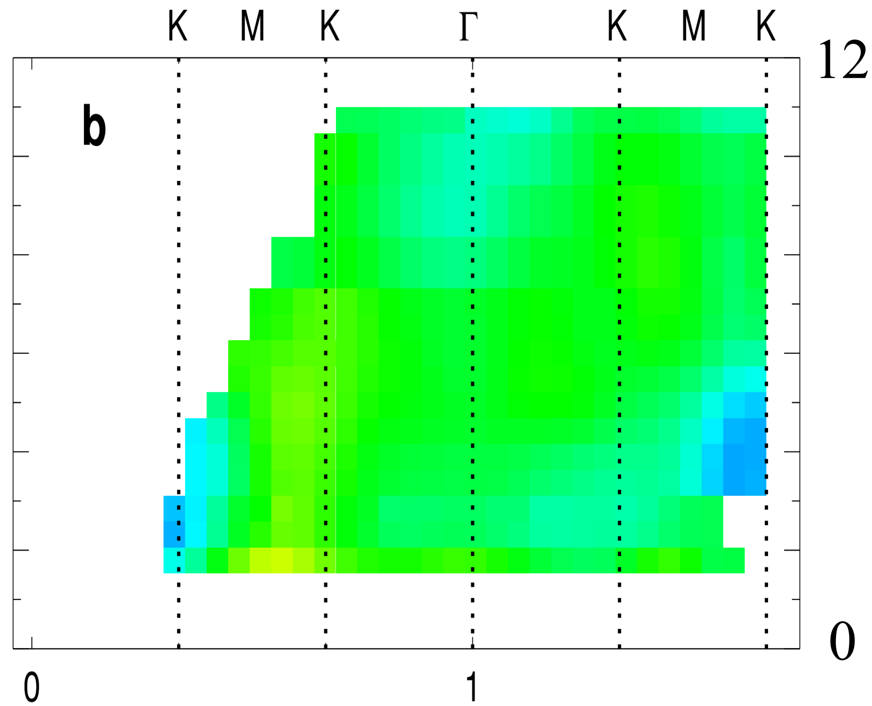


K Matan, YL, *et al.*,
PRL 96, 247201 (2006)

S=1/2 $ZnCu_3(OH)_6Cl_2$

spin liquid ground state

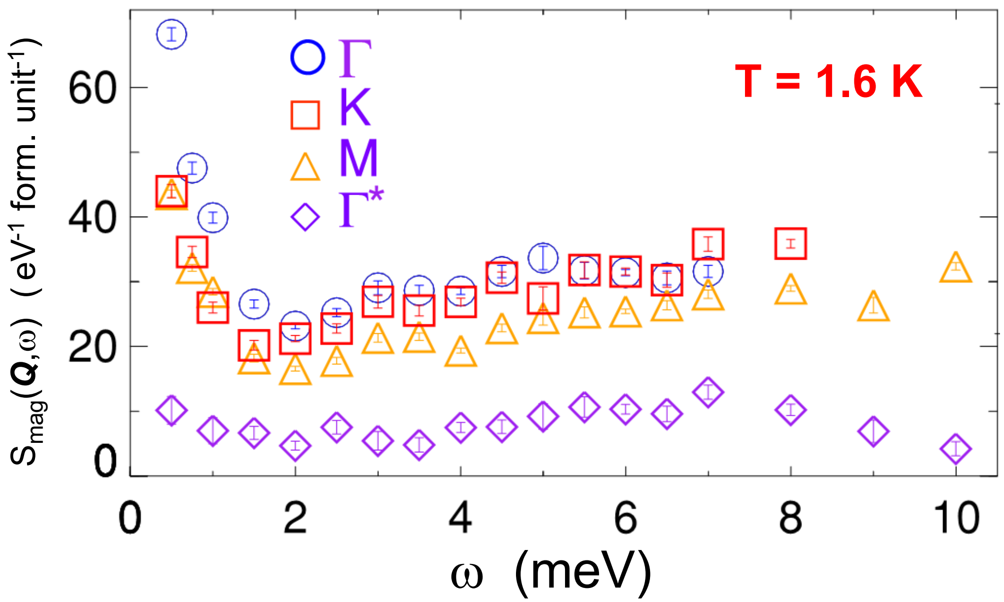
S=1/2 spinons

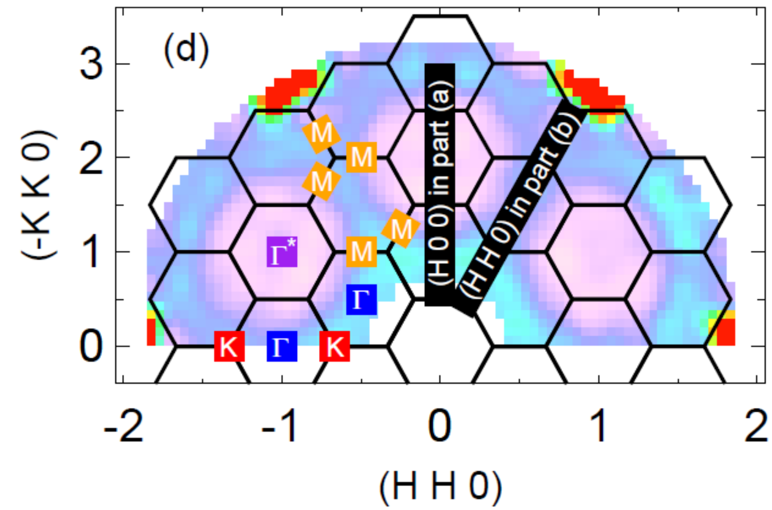


T Han, YL, et al,
Nature 492, 406 (2012)

Can we extract Hamiltonian parameters from neutron scattering?

Energy dependence at high symmetry positions





Above 2 meV: rather flat spectrum

Below 2 meV: increase in scattering at select ***Q***'s (impurity moments contribute at low ω)

<u>No spin gap observed</u> (at any ***Q*** position)

conservative statement: no gap above 2 meV (~J/10)

“To be or not to be (gapped)?”

A tennis rally between theory and experiment

< 2005: Theory early numerical work on kagome + RVB ideas
- expect **gap**

2005-2007: Experiment powder work on $ZnCu_3(OH)_6Cl_2$
- **no gap** observed

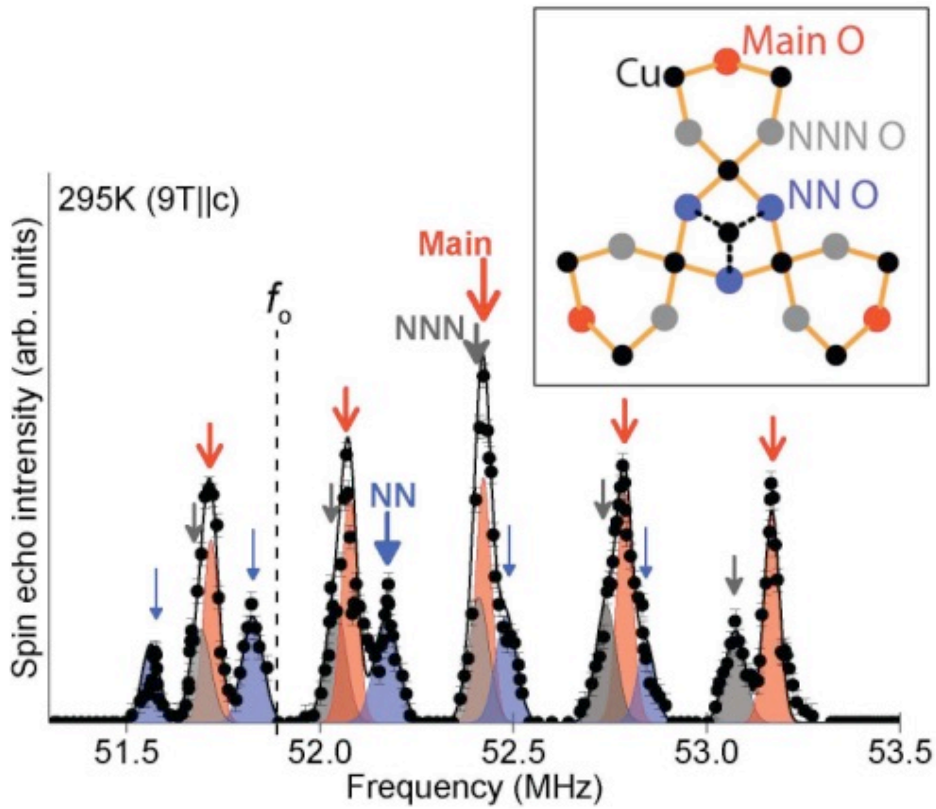
2007-2011: Theory work on spin liquids with **no gap**
(Dirac spinons)
Numerical work (DMRG) on **gapped** spin liquids
(topological Z_2 spin liquid)

2011-2014: Experiment single crystals – **no gap** (impurities?)

2016-2017: Theory Finite-size and Dirac spinons – **no gap ???**

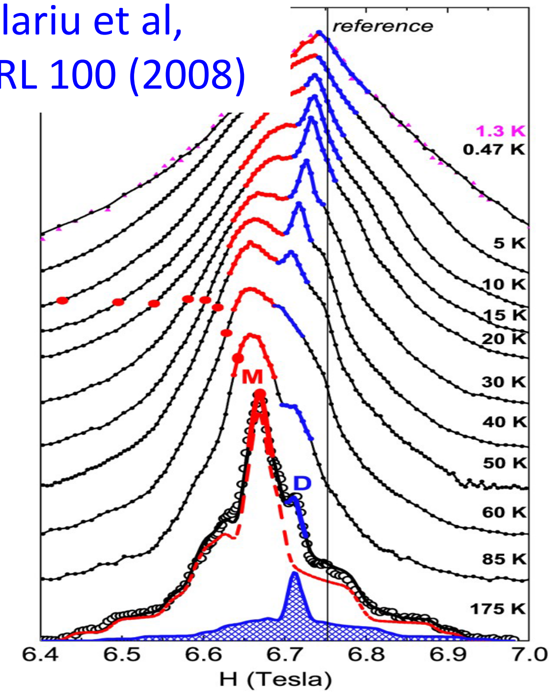
^{17}O NMR study in enriched single crystal – a local probe

Fu, Imai, Han, YL, Science 350, 655 (2015)



Compare to previous powder data:

Olariu et al, PRL 100 (2008)

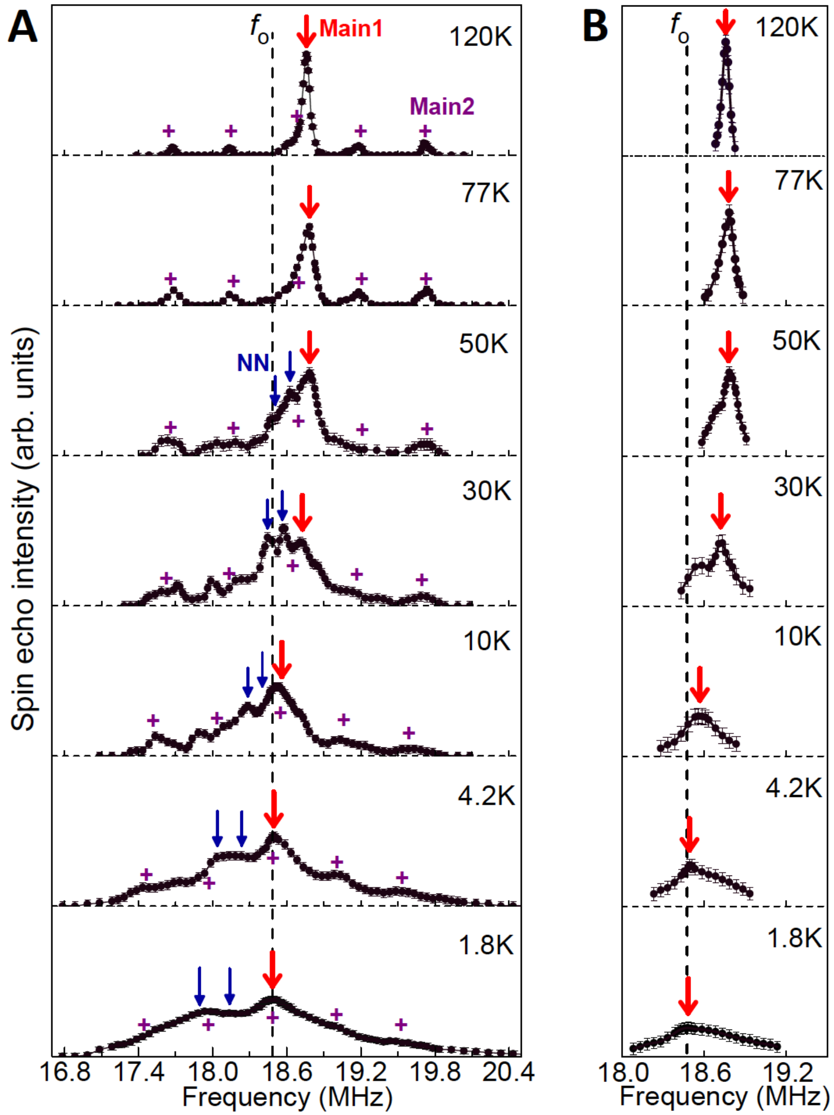


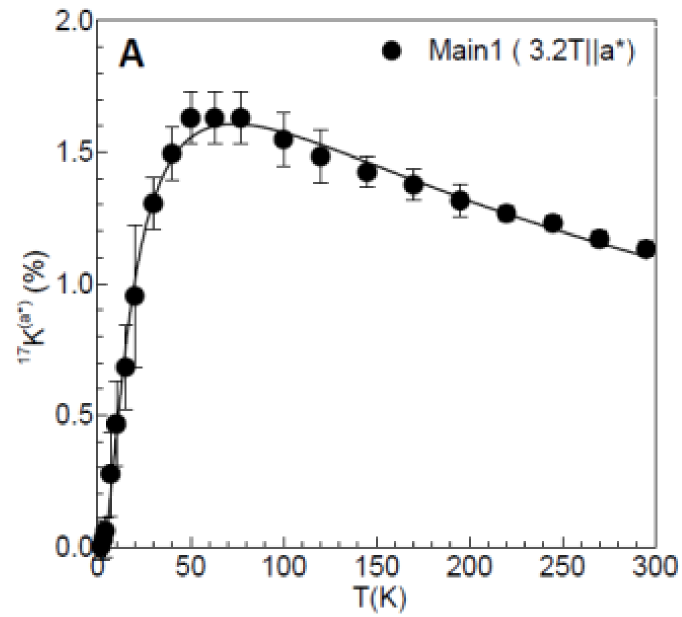
3 oxygen sites:
- A-sites (14%) -- NN of Cu^{2+} impurity
- B-sites (28%) -- NNN of Cu^{2+} impurity
- C-sites (58%) -- Main kagomé sites

NMR result #1:

Disorder is weak: impurities between kagome planes only

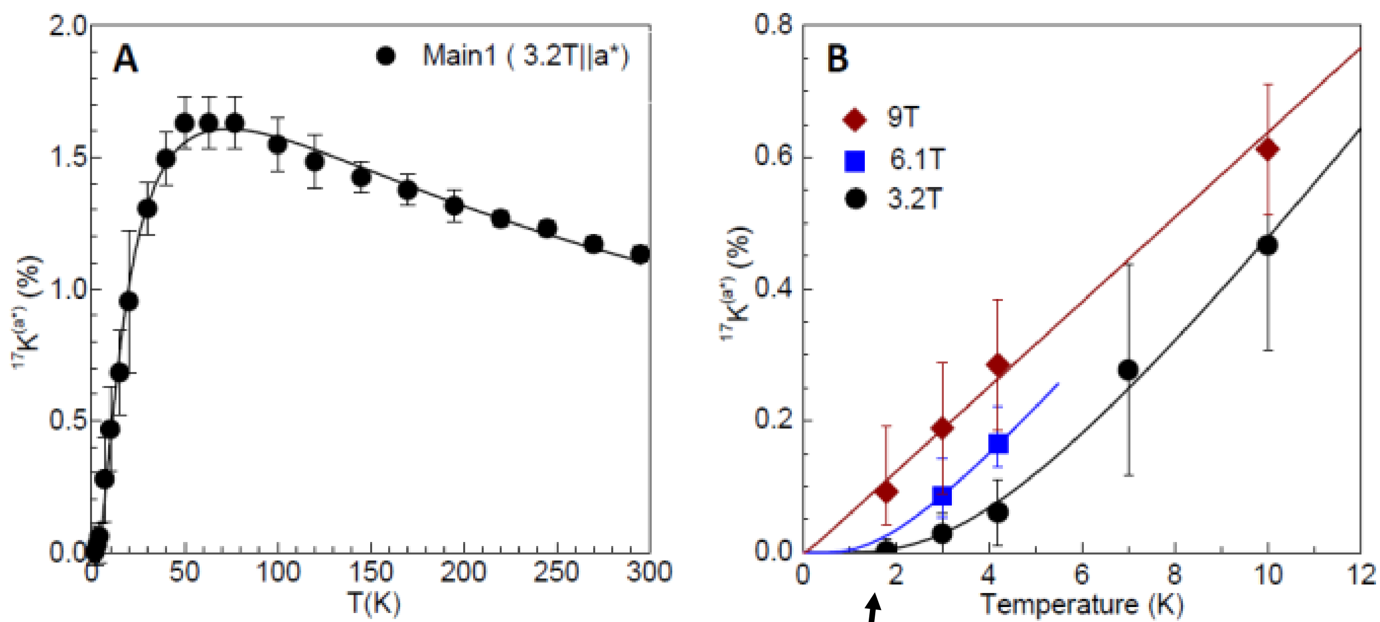
NMR result #2: the intrinsic χ_{main} reveals a spin gap!

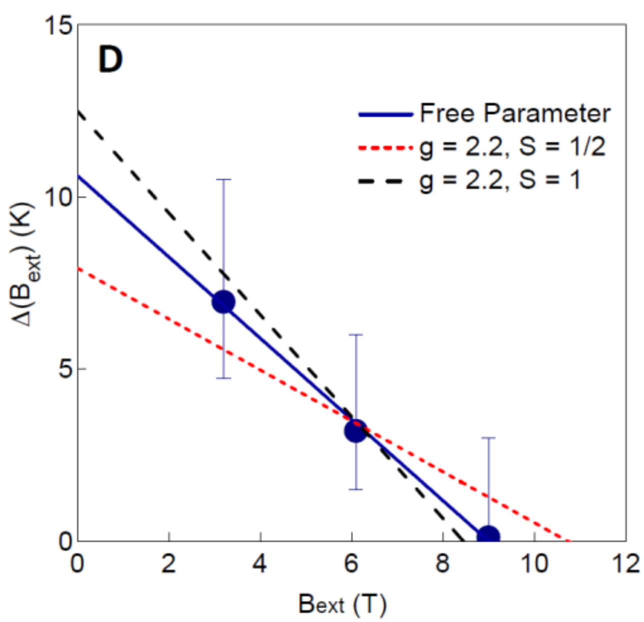




Knight shift of "Main" ^{17}O sites far from impurities

NMR result #2: the intrinsic χ_{main} reveals a spin gap!



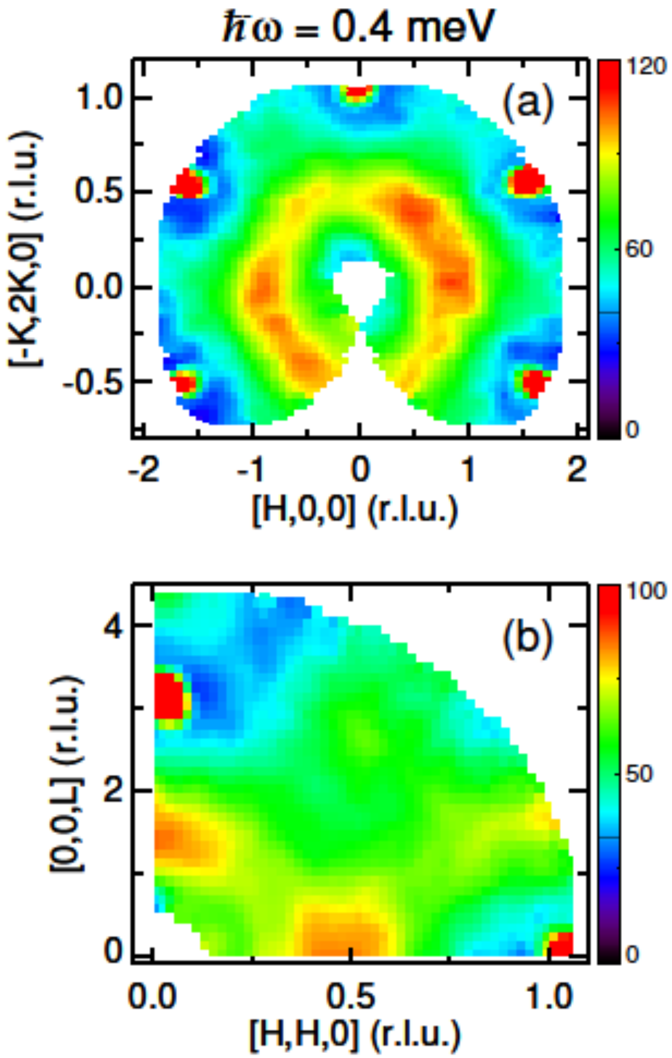


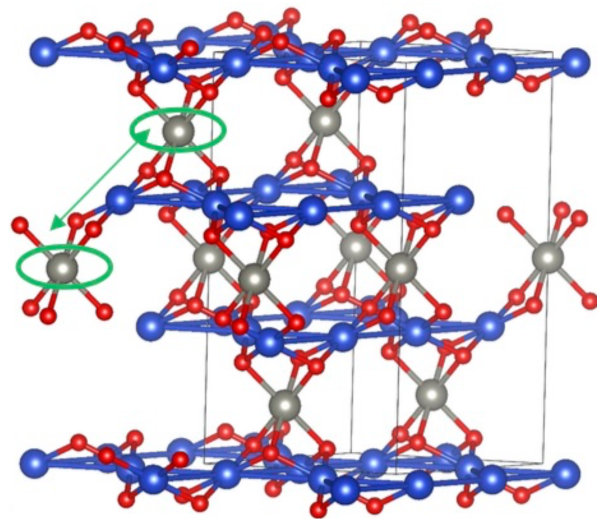
Lines are fits to ~T exp (-Δ/T)

Zero-field gap: Δ(0) ~ 10(3) K,
hence <u>Δ/J ~ 0.05</u>
(expected Δ/J = 0.10 to 0.15
for NN Heisenberg model)

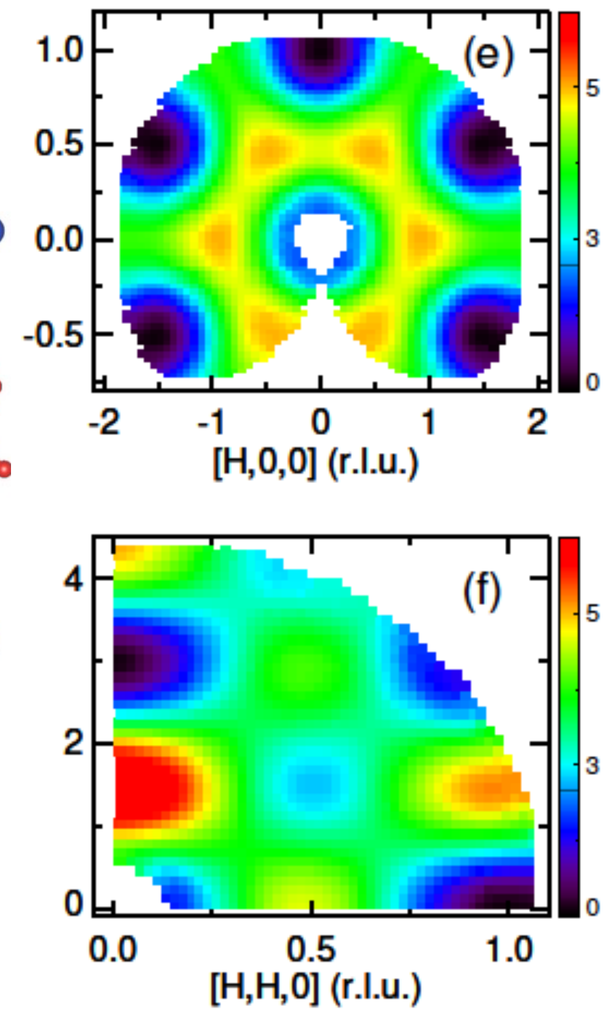
High-resolution neutron scattering on crystal (different zones)

<u>Impurity</u> scattering



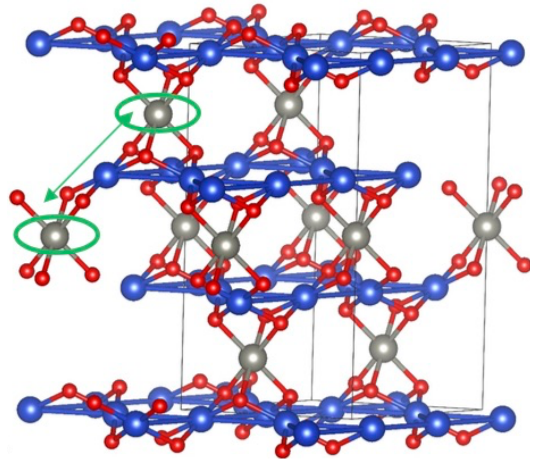


Calculation of <u>impurity</u> scattering

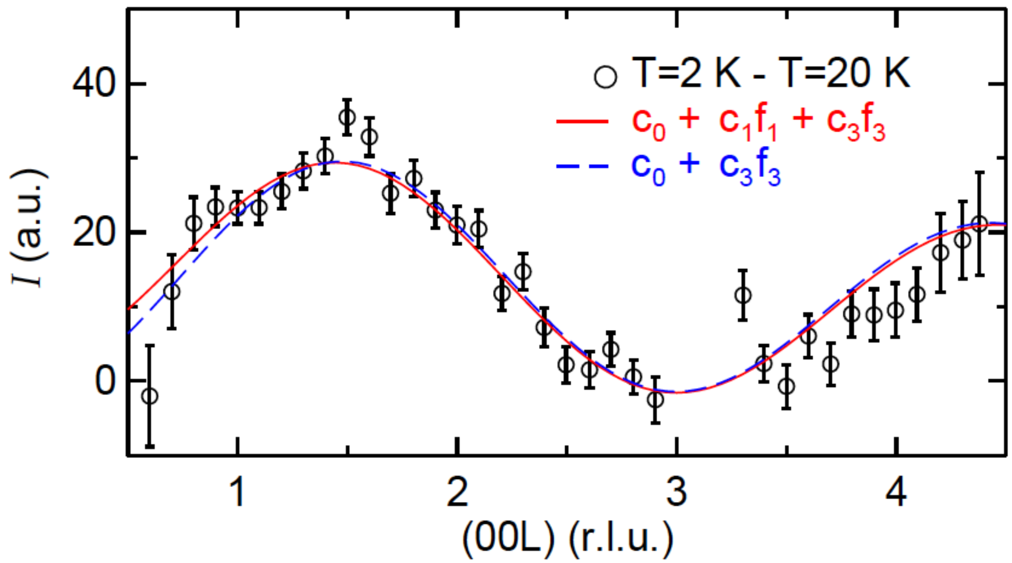


Intrinsic kagome response and impurity response are **<u>distinguishable</u> !**

Correlations between impurities and the kagome plane are small



$$\mathcal{S}(\mathbf{Q}) = N|F(Q)|^2\langle S^2\rangle(1 + \sum_n \frac{2m_n}{N} f_n(\mathbf{Q}) \frac{\langle SS'\rangle_n}{\langle S^2\rangle})$$



Deduce bound:

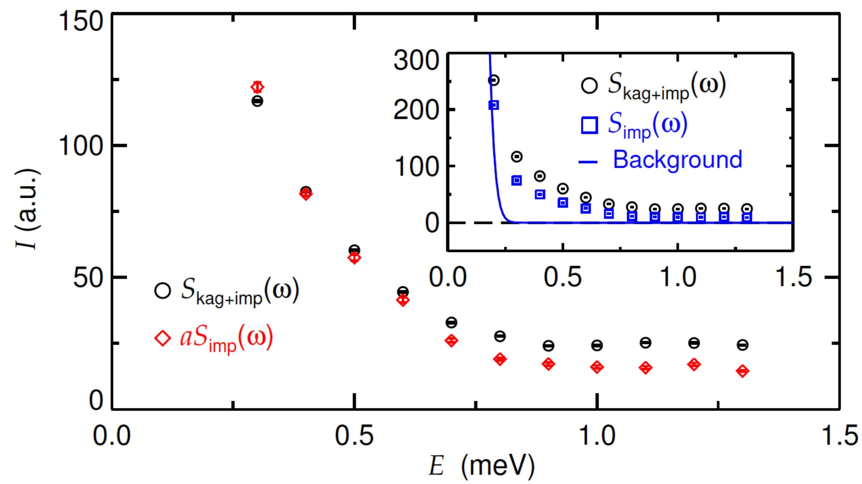
$$|\langle SS'\rangle_1 / \langle SS'\rangle_3| < 0.01$$

Impurity-impurity interaction energy scale ~ few K.

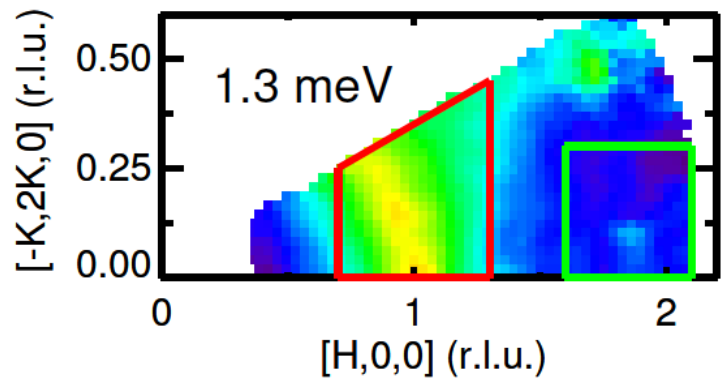
Kagome spins "protected" from locking to impurity correlations?

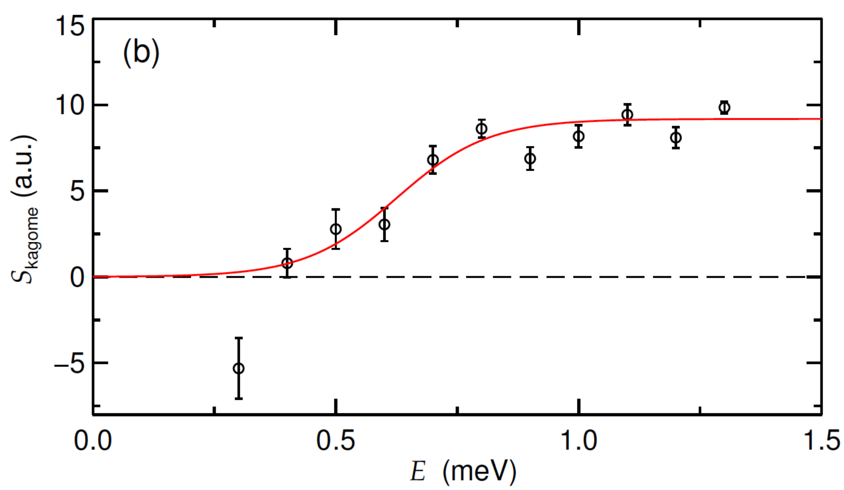
Neutrons see a spin gap !

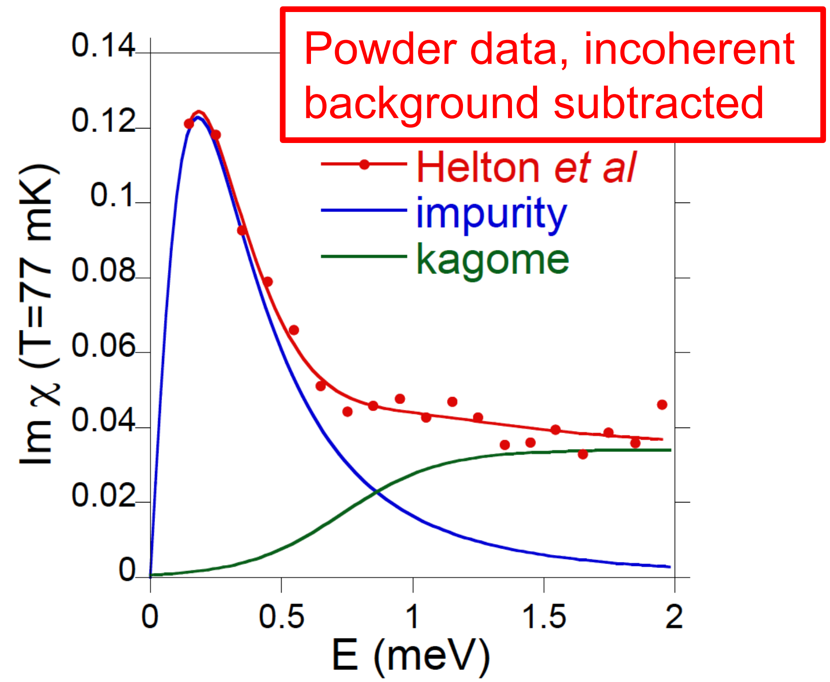
Subtract impurity response from total scattering



Han, YL, et al, Phys. Rev. B 94 (2016)







Neutrons see a 0.7 meV gap, comparable to 0.9 meV NMR gap.

What can other materials tell us?

Minerals with kagomé lattice of S=1/2 Cu^{2+} ions

<u>Herbertsmithite</u>

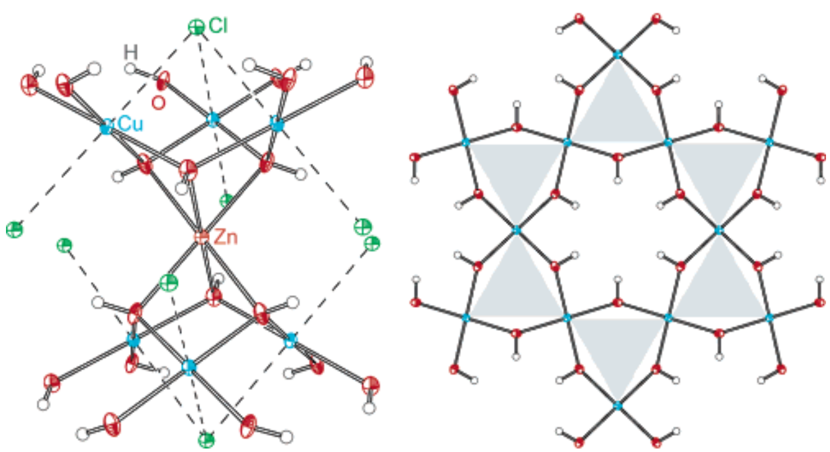
$Cu_3Zn_xCu_{1-x}(OH)_6Cl_2$

Space group $R\bar{3}m$ (#166)

No magnetic order down to 0.005K

Always some Cu on interlayer Zn site

ABC stacking sequence



Shores, M.P. et al. *JACS,* **2005**, *127*, 13462.
Han, T.-H. et al. *Nature* **2012**, *492*, 406–410.

<u>Barlowite</u>

$Cu_4(OH)_6FBr$

Space group $P6_3/mmc$ (#194)

Orders at 15 K

Cu on interlayer site

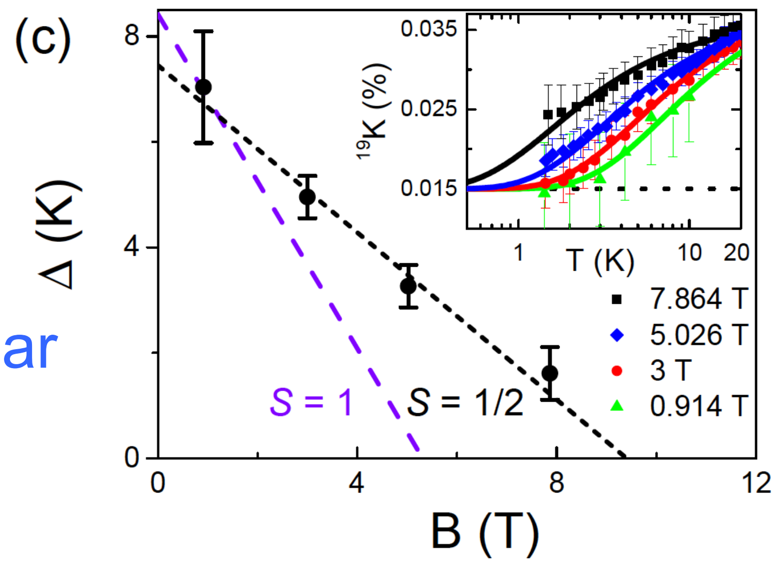
AA stacking sequence

Han, T. H. et al,. *PRL* **2014**, *113*, 227203.
Jeschke, H.O., et al, PRB **2015**, 92 094417.

New QSL candidate: Zn-barlowite

Beijing group:
Z. Feng, et al,
Chin. Phys. Lett 34 (2017)

^{19}F NMR sees spin gap, similar to that in Herbertsmithite!



Compare $\chi(T)$ between samples we made:

Shockingly similar !

Even though crystal structures are distinct:

$ZnCu_3(OH)_6Cl_2$ vs $ZnCu_3(OH)_6FBr$

Enlightenment

1) Herbertsmithite and S=1/2 kagome model are one.
   (plus perturbations at the 10% level)

2) **Spinons exist.** (Inelastic neutron scattering)

3) **Spin gap exists.** (NMR and neutron)

- due to valence bond solid?
  No, structural phase transition not seen
- impurity induced?
  No evidence.
  - impurities only weakly perturb kagome layers
  - adding many interlayer Cu yields order, not gap
  - nearby phases on phase diagram are ordered

Find harmony in a topological Z_2 QSL.

Next topic: stripes in 214 cuprates

1) Charge order in $La_{1.885}Sr_{0.115}CuO_4$

- effects of high-pulsed-field (LCLS)

2) Charge order in $La_2CuO_{4.12}$ (SSRL, NSLS-II)

- a clean 214 superconductor

Themes:

- Intertwined CDW and SDW with superconductivity
- Effects of disorder
- Coexistence, competition, phase separation

Previous: neutrons on $La_{2-x}Sr_xCuO_4$

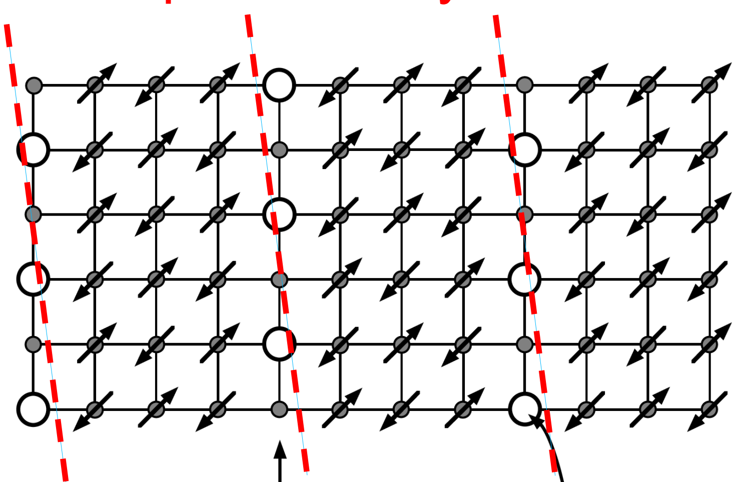
(following Tranquada et al on $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$)

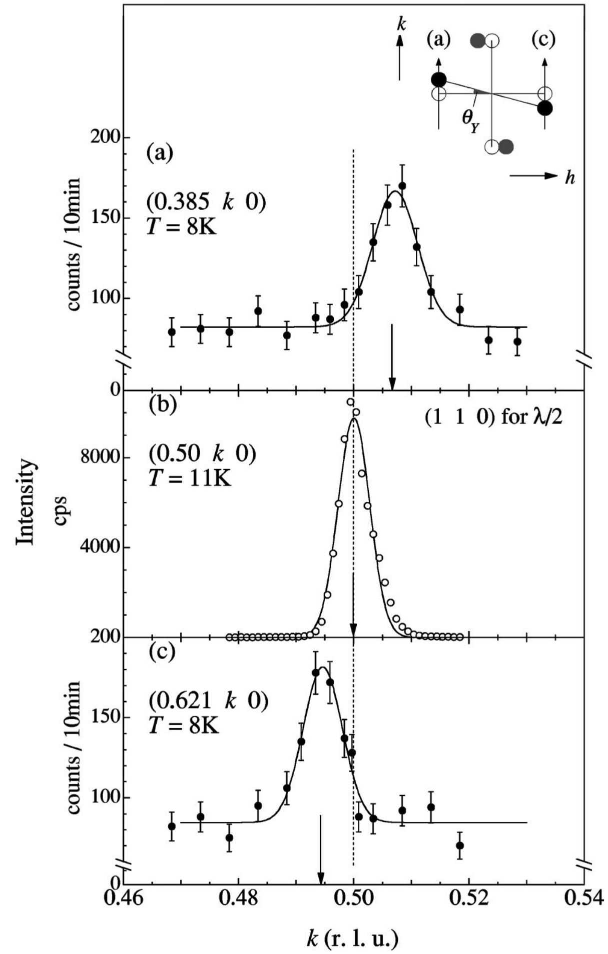
1) Spin order (SDW) for $T_{SDW}<T_C$, peaks sharpest near x=1/8

2) SDW is glassy ($T_{neutron}>T_{\mu SR}$)

3) SDW pattern is a "slanted" stripe

Stripes tilted by ~3°



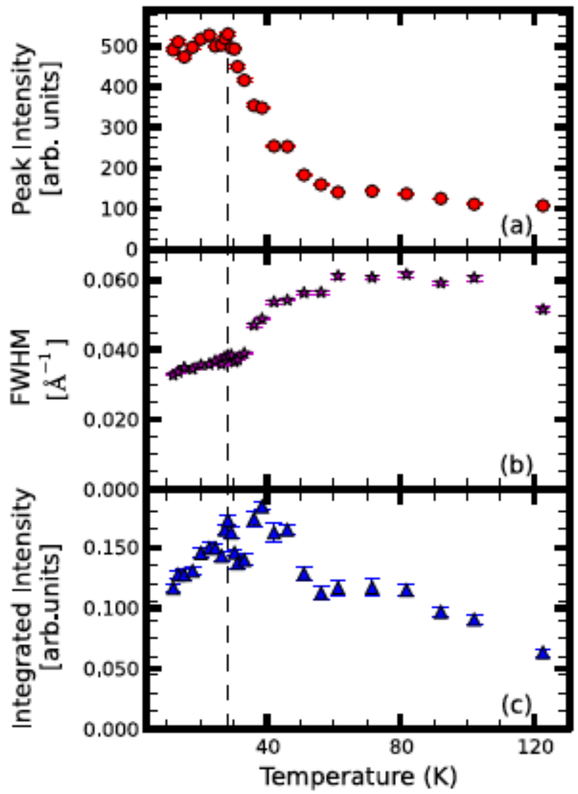


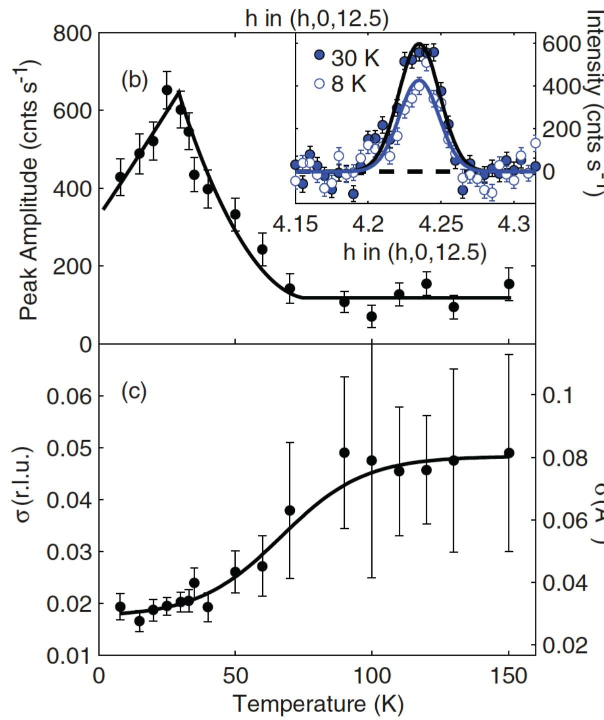
Kimura et al, PRB 61 (2000)

(called "Y-shift")

15 years later: charge order (CDW) seen with x-rays in $La_{2-x}Sr_xCuO_4$

Thampy, Dean, Hill, et al, PRB (2014)

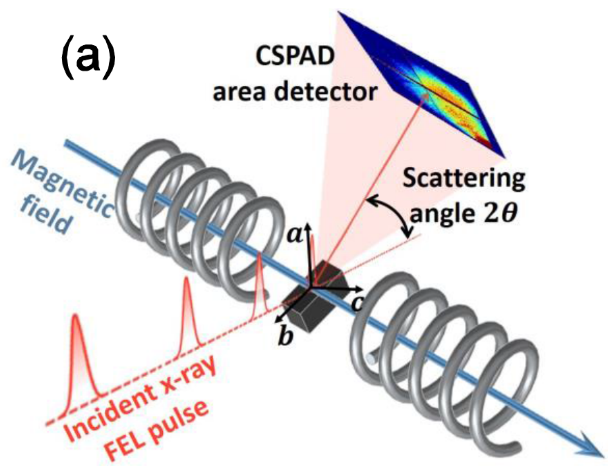


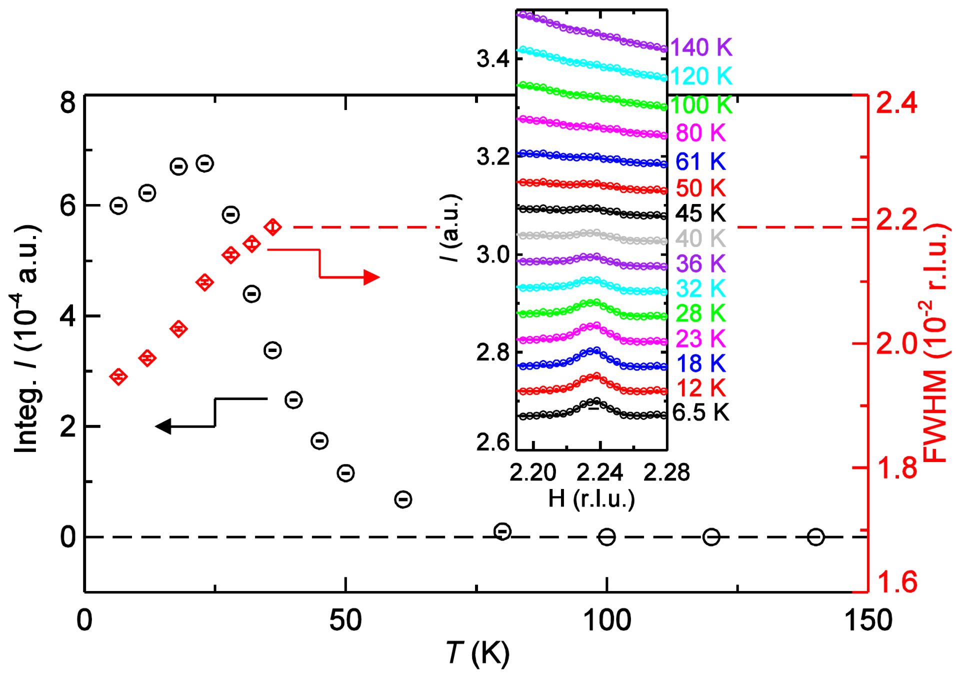


Croft, Hayden, et al, PRB (2014)

Charge and spin stripes in $La_{1.885}Sr_{0.115}CuO_4$

LCLS data on $La_{1.885}Sr_{0.115}CuO_4$

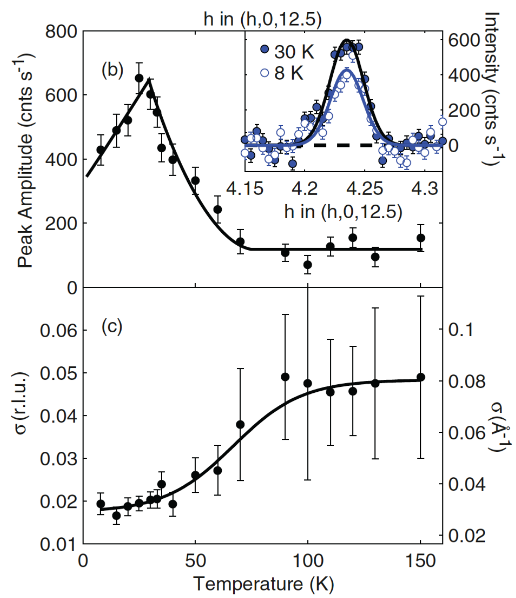




JJ Wen, JS Lee, Y Lee, et al, in prep.

Compare to prior work:

Croft, Hayden, et al, PRB (2014)



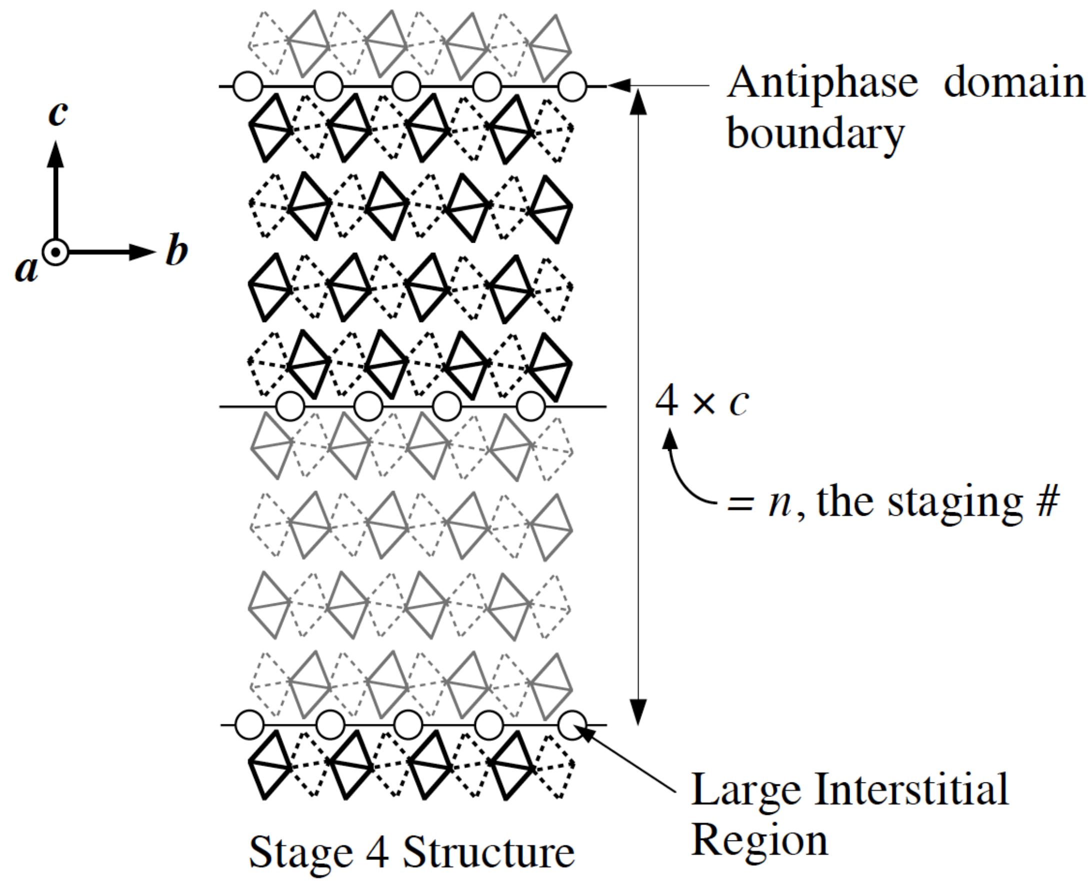
1) Onset of CDW peaks below ~75 K

2) CDW suppressed below T_C
   - but correlations continue to grow

Previous: neutrons on $La_2CuO_{4.12}$

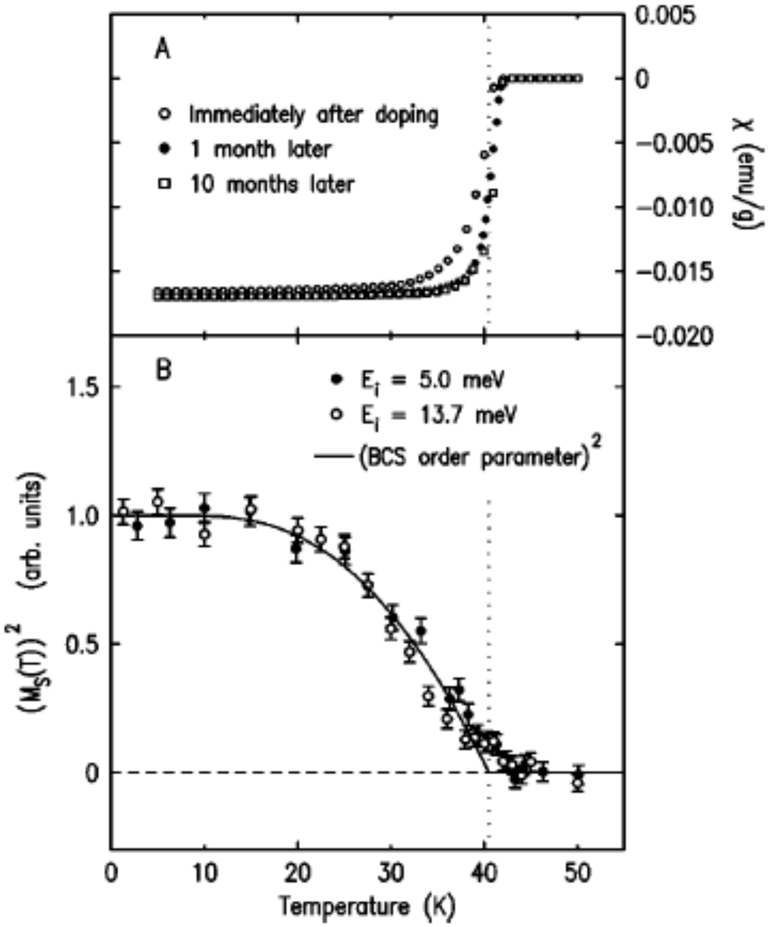
Lee et al, PRB 60 (1999) Stage-4 $La_2CuO_{4.12}$

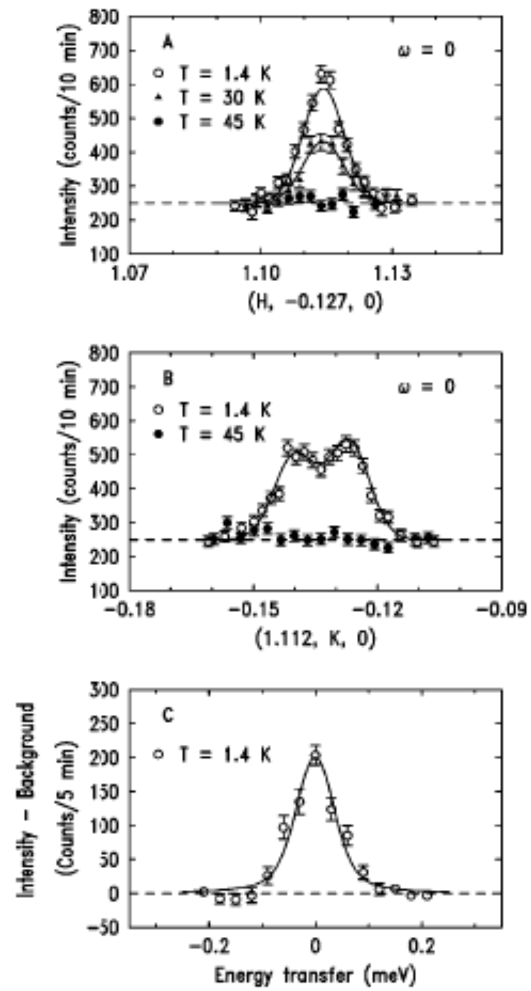
Period 4∗c tilt modulation



Previous: neutrons on $La_2CuO_{4.12}$

Lee et al, PRB 60 (1999)   Stage-4 $La_2CuO_{4.12}$





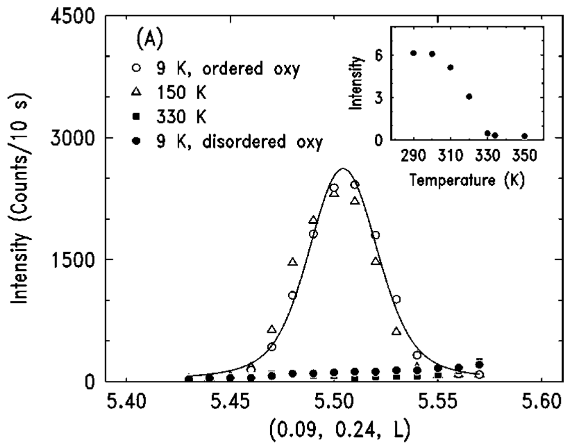
1) $T_{SDW} = T_C$!

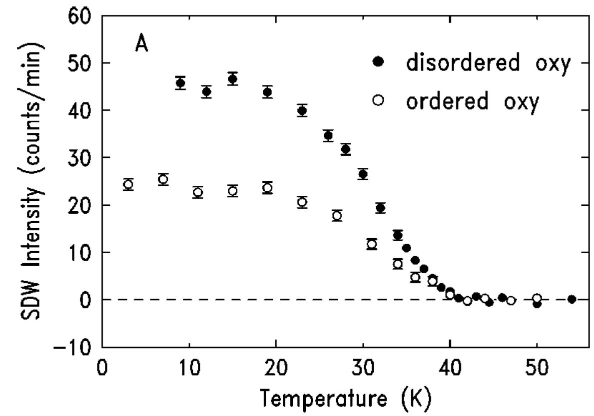
2) Static, long-range order
- $\xi > 400$ A
- $\langle s \rangle = 0.15\ \mu_B$

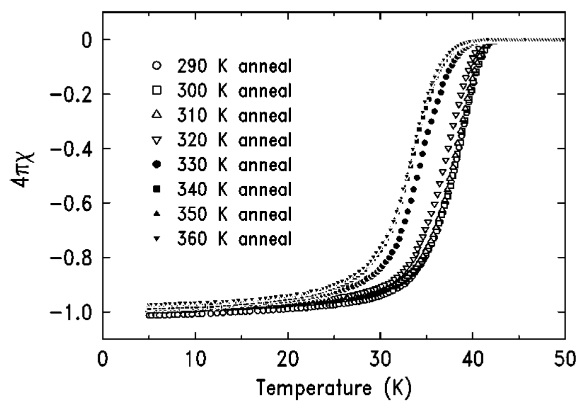
A true magnetic phase transition in an optimally doped cuprate.

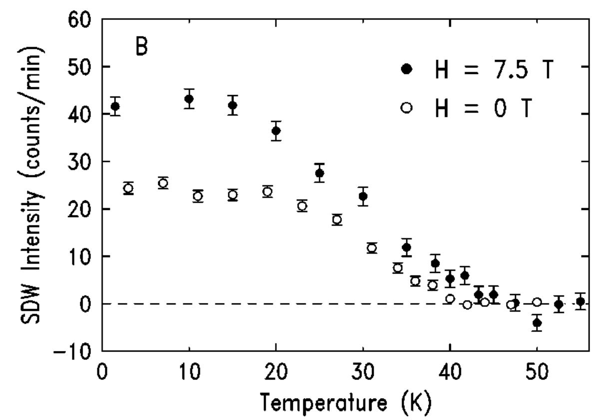
Dopant disorder in $La_2CuO_{4.12}$ is relevant

Lee et al, PRB 69 (2004)









1) Oxygen order directly tied to enhanced T_C

2) Diminished SC → enhanced SDW

Some thoughts on static order in La_2CuO_4-based cuprates

1) Intimate relation between SDW and CDW ($\delta_{CDW} = 2\ \delta_{SDW}$)
    - slanted stripes

2) Field effect: enhanced 2D CDW
    - different than YBCO

3) Dopant disorder is a relevant parameter
    - cleaner material gives more robust SDW and CDW, as well as SC with highest T_C