NMR Evidence for a gapped spin-liquid ground state
in a kagome Heisenberg antiferromagnet (herbertsmithite $ZnCu_3(OH)_6Cl_2$)

Takashi Imai

McMaster University
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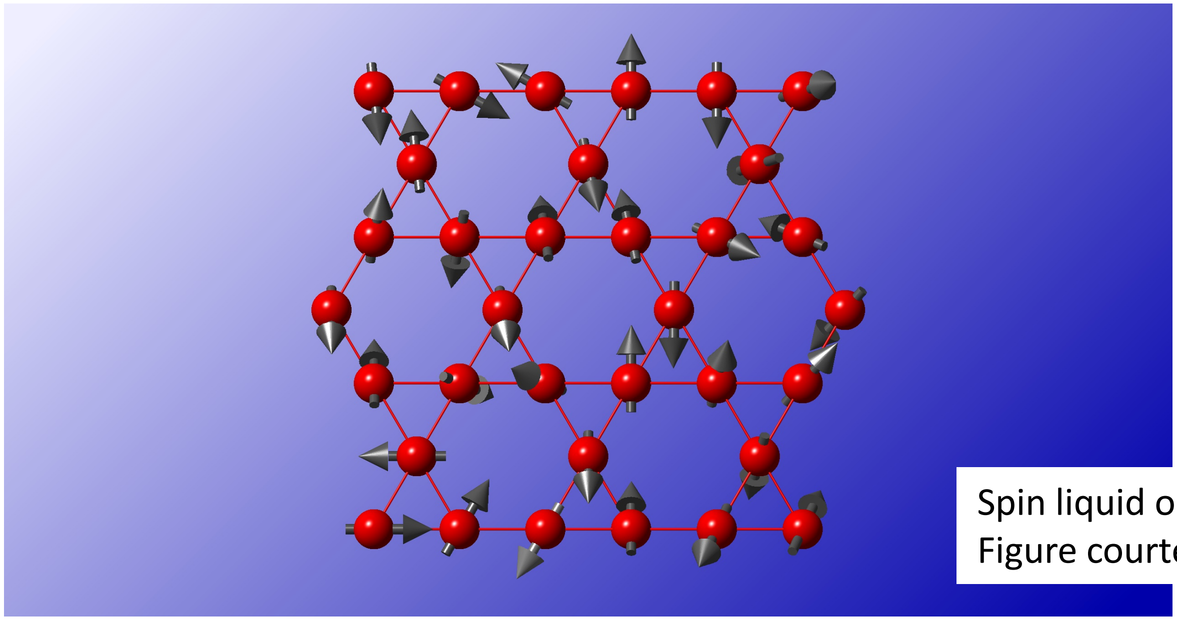


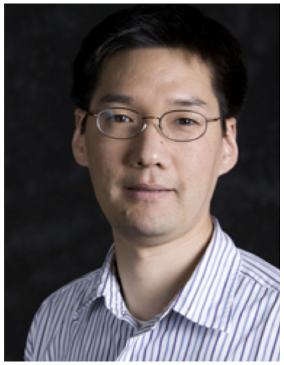
Spin liquid on “Kagome lattice”
Figure courtesy of Sean Takahashi

McMaster University

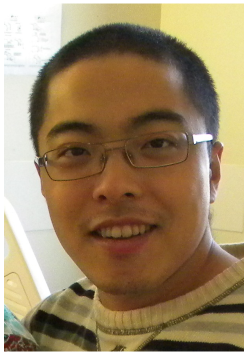
CIFAR
CANADIAN INSTITUTE
for ADVANCED RESEARCH

A Short List of Recent Collaborators

Dr. Mingxuan Fu
McMaster
→PDF at Johns Hopkins
→NSERC PDF at Univ. of Toronto



Prof. Y.S. Lee
M.I.T.→ Stanford
(Neutron / X'tal growth)



Dr. T. H. Han
M.I.T.→ Chicago/Argonne Nat. Lab.
(Neutron / X'tal growth)

Prof. R.R.P. Singh
U.C. Davis
(Series expansion)

N.E. Sherman
U.C. Davis
(Series expansion)

Outline

1. Introduction: kagome lattice in herbertsmithite, and why NMR is useful

   T. Imai and Y.S. Lee., Physics Today, p-30, August (2016).

2. First generation ^{35}Cl, ^{1}H, and ^{63}Cu powder NMR measurements

   T. Imai *et al*., PRL 100 (2008) 077203

3. Second generation single crystal ^{2}D NMR measurements on $ZnCu_3(OD)_6Cl_2$

   T. Imai *et al*., PRB 83(2011) 020411 (Rapid).

4. Third generation single crystal ^{17}O NMR measurements on $ZnCu_3(OH)_6Cl_2$

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

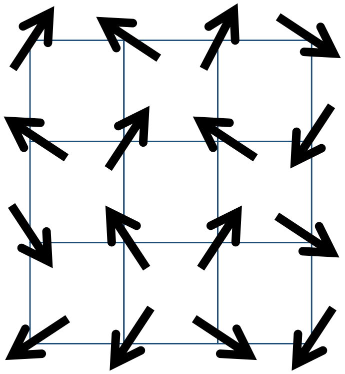
   N. Sherman, T.I., R.R.P. Singh, PRB 94 (2016) 140405. [Series expansion.]

5. Summary

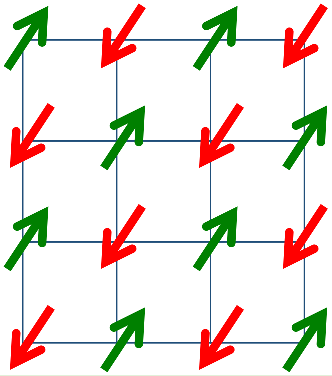
Paramagnetic ground state vs. antiferromagnetic phases

Antiferromagnetic “Heisenberg model” (model Hamiltonian)

$$\boxed{\hat{H} = J \sum_{<i,j>} \hat{S}_i \cdot \hat{S}_j} \qquad (J > 0)$$



Higher temperatures



$T \leq T_N$
(Neel temperature)

Paramagnetic state with randomly oriented spins

Neel state : usually, spins are antiferromagnetically ordered with a regular pattern (T_N=0 for square-lattice)

In analogy with……….

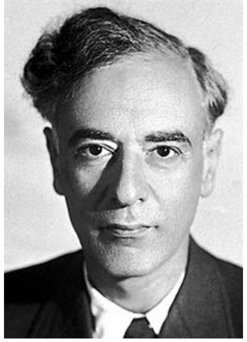
Liquid water

Solid ice
T < 273 K

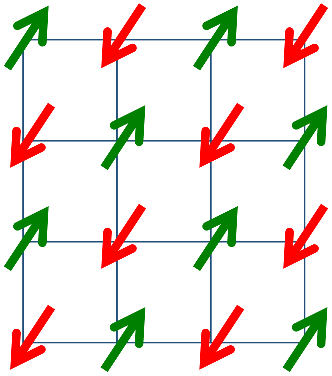
Old controversy: Antiferromagnetically ordered state vs. Landau's superposed singlets

Antiferromagnetic "Heisenberg model"
(model Hamiltonian)

$$\boxed{\hat{H} = J \sum_{<i,j>} \hat{S}_i \cdot \hat{S}_j} \qquad (J > 0)$$



"Neel state" is not an eigenstate of the Hamiltonian.



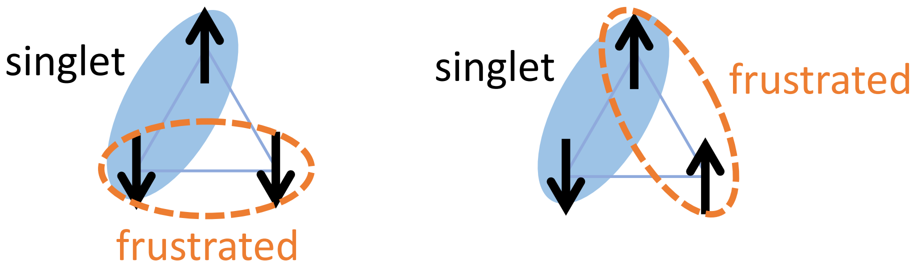
Landau (1962 Nobel Physics) thought *there is no such a thing as antiferromagnetically ordered state; Instead, superposed* singlet states must be realized.

$$|\downarrow\uparrow\rangle \rightarrow |\uparrow\downarrow\rangle$$

Mostly forgotten idea for decades, because antiferromagnets do exist after all.

Cf. P.A. Lee, Science <u>321</u> (2008) 1306

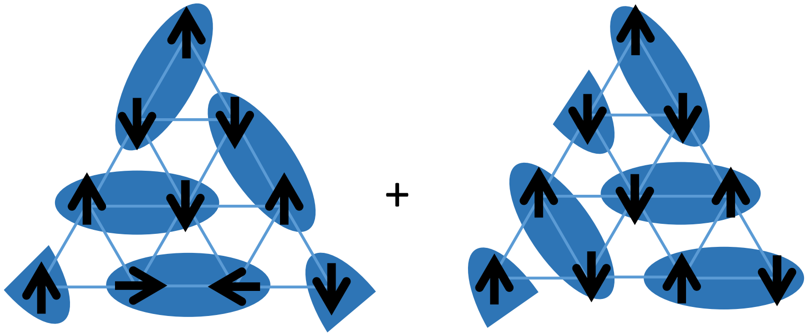
Geometrical frustration effects of spins on the triangular-lattice Heisenberg model and the RVB "spin liquid" (P.W. Anderson 1973)



Frustration effects arise from love-and-hate relationship between S=1/2 spins on a triangle

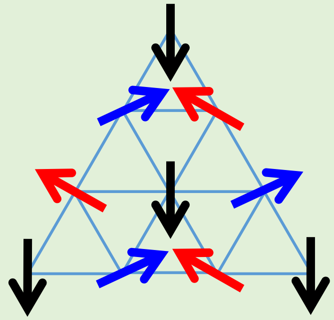
P.W. Anderson (Nobel physics 1977)

$|RVB\rangle$ =



+ .... (superposition of many other states)

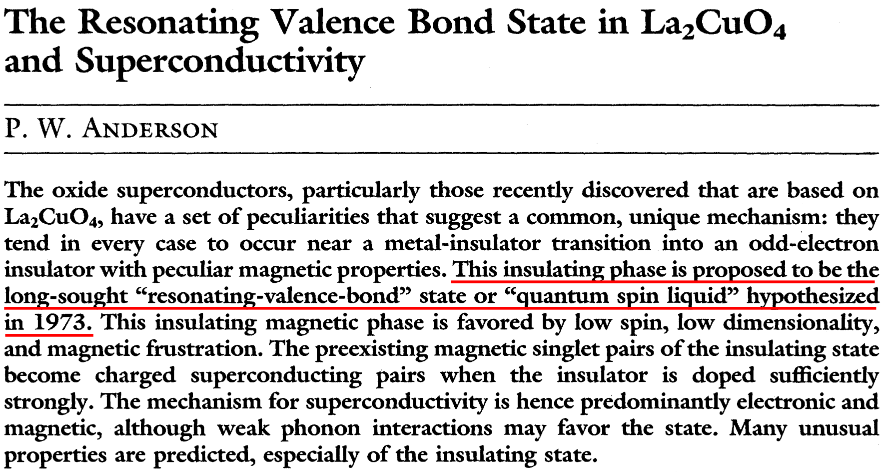
"Resonating Valence Bond (RVB)"



In reality, spins usually compromise by forming a 120-degree ordered state (favored classically)

Resurrection of the old RVB idea in the context of undoped square-lattice Heisenberg antiferromagnet La_2CuO_4 (Parent phase of Copper-oxide high T_c superconductors)

P.W. Anderson, Science 235 (1987) 1196



The Resonating Valence Bond State in La_2CuO_4 and Superconductivity

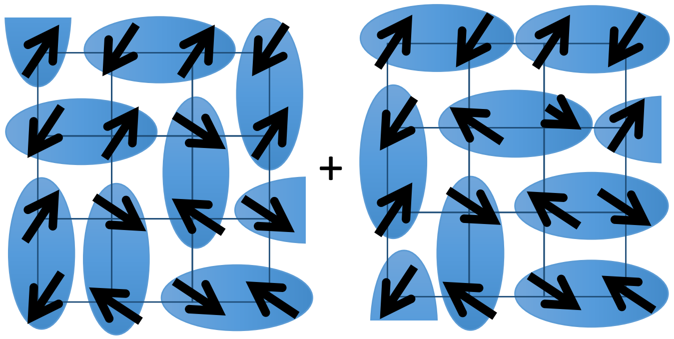
P. W. ANDERSON

The oxide superconductors, particularly those recently discovered that are based on La_2CuO_4, have a set of peculiarities that suggest a common, unique mechanism: they tend in every case to occur near a metal-insulator transition into an odd-electron insulator with peculiar magnetic properties. This insulating phase is proposed to be the long-sought "resonating-valence-bond" state or "quantum spin liquid" hypothesized in 1973. This insulating magnetic phase is favored by low spin, low dimensionality, and magnetic frustration. The preexisting magnetic singlet pairs of the insulating state become charged superconducting pairs when the insulator is doped sufficiently strongly. The mechanism for superconductivity is hence predominantly electronic and magnetic, although weak phonon interactions may favor the state. Many unusual properties are predicted, especially of the insulating state.

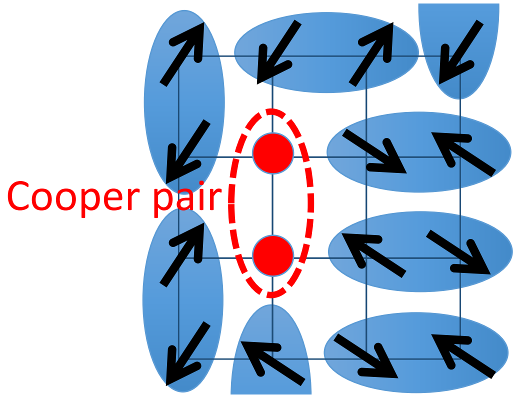
Anderson's proposition:
High temperature superconductivity emerges when we remove ~15% of spins

Cu^{2+} ion ($S=1/2$) at each corner

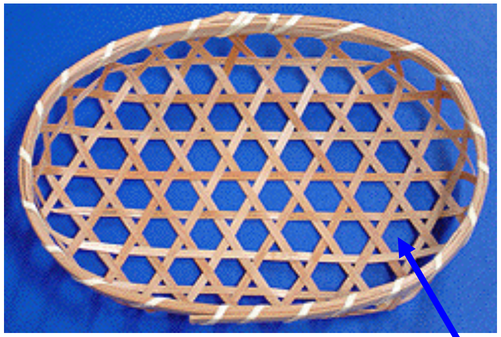
$|RVB\rangle$ =



+ ....



Where should we look for a quantum spin liquid?
"Kagome" 籠目 : "Basket pattern" composed of corner-sharing triangles



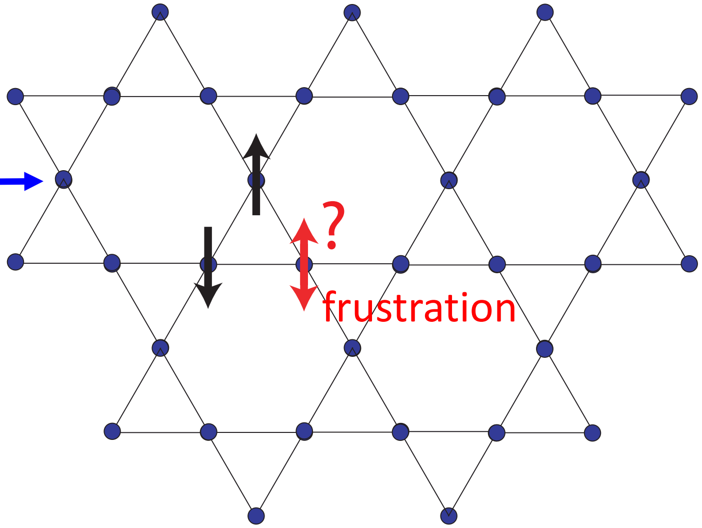
"Basket pattern"

(kago) (me)

籠 目

Japanese "Kagome Tomato Ketchup"

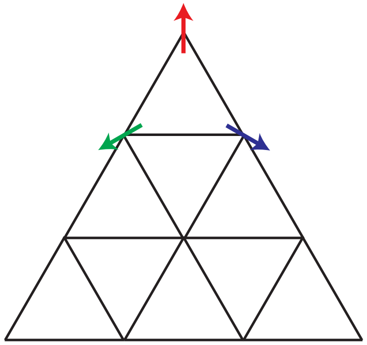
Corner-sharing triangles



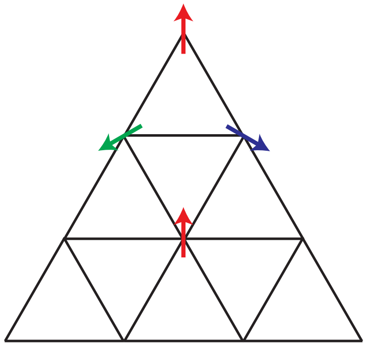
Advantage of the kagome Heisenberg antiferromagnet = (strong degeneracy).
Favors a quantum spin liquid ground state

Edge-sharing triangular lattice

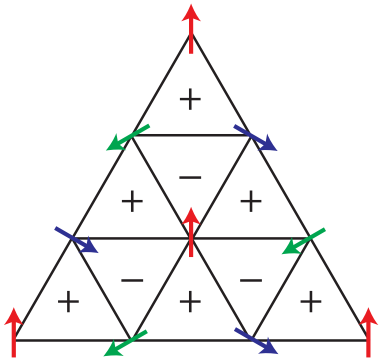
120 degree arrangement on a triangle minimizes the energy (classically)



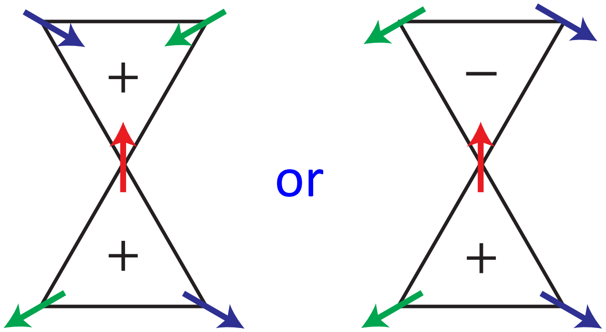
…. and constrains another spin



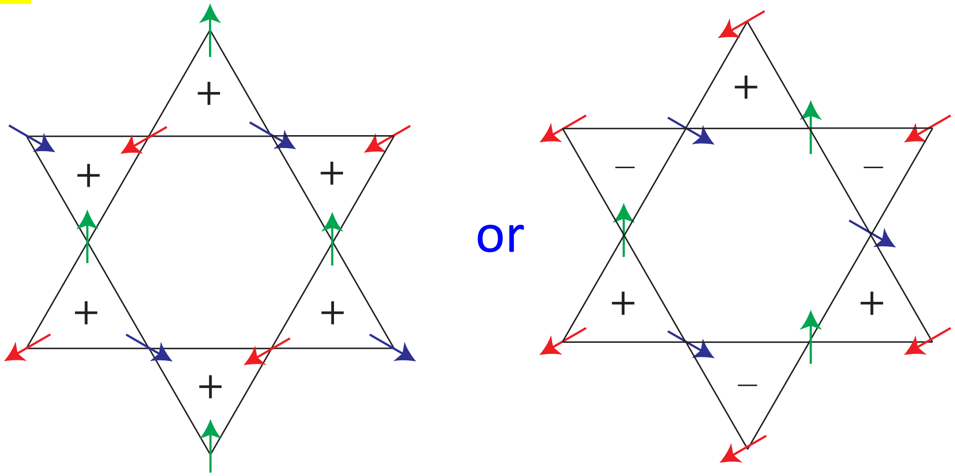
…. and all spins



Corner-sharing triangular lattice (kagome)

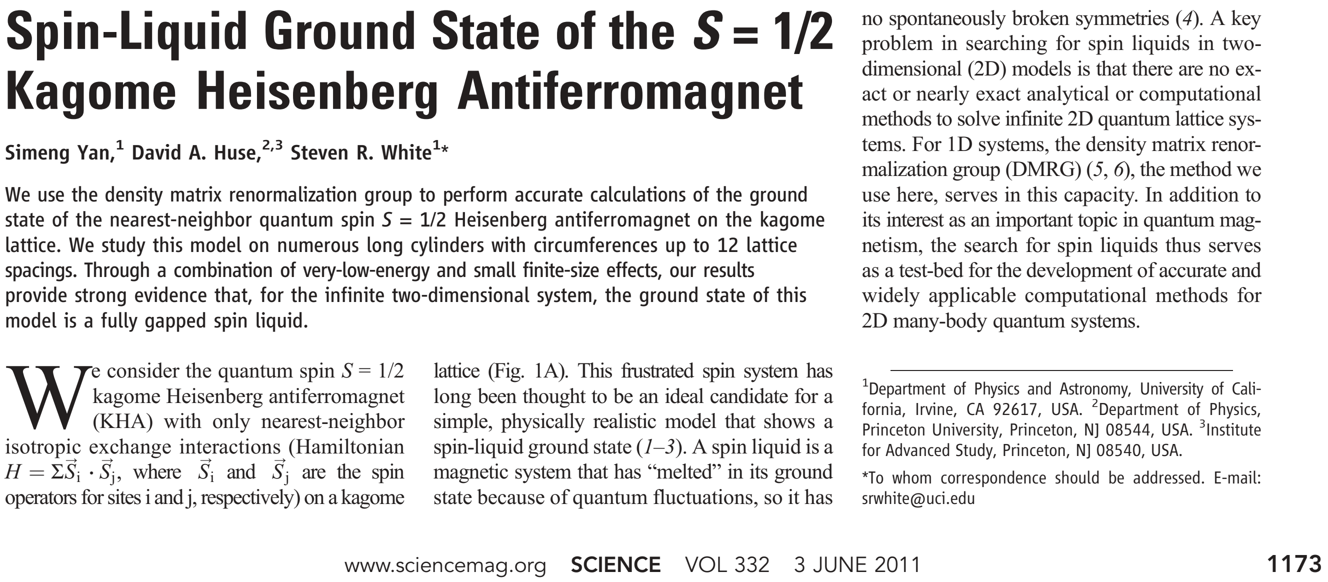


One triangle does not constrain the arrangement of the adjacent triangle



Spins have a hard time to choose ordering pattern!

“The ground state of the kagome Heisenberg antiferromagnet is a gapped Z_2 spin liquid”



Spin-Liquid Ground State of the $S = 1/2$ Kagome Heisenberg Antiferromagnet

Simeng Yan,[1] David A. Huse,[2,3] Steven R. White[1]*

We use the density matrix renormalization group to perform accurate calculations of the ground state of the nearest-neighbor quantum spin $S = 1/2$ Heisenberg antiferromagnet on the kagome lattice. We study this model on numerous long cylinders with circumferences up to 12 lattice spacings. Through a combination of very-low-energy and small finite-size effects, our results provide strong evidence that, for the infinite two-dimensional system, the ground state of this model is a fully gapped spin liquid.

We consider the quantum spin $S = 1/2$ kagome Heisenberg antiferromagnet (KHA) with only nearest-neighbor isotropic exchange interactions (Hamiltonian $H = \Sigma \vec{S}_i \cdot \vec{S}_j$, where $\vec{S}_i$ and $\vec{S}_j$ are the spin operators for sites i and j, respectively) on a kagome lattice (Fig. 1A). This frustrated spin system has long been thought to be an ideal candidate for a simple, physically realistic model that shows a spin-liquid ground state (*1*–*3*). A spin liquid is a magnetic system that has “melted” in its ground state because of quantum fluctuations, so it has no spontaneously broken symmetries (*4*). A key problem in searching for spin liquids in two-dimensional (2D) models is that there are no exact or nearly exact analytical or computational methods to solve infinite 2D quantum lattice systems. For 1D systems, the density matrix renormalization group (DMRG) (*5*, *6*), the method we use here, serves in this capacity. In addition to its interest as an important topic in quantum magnetism, the search for spin liquids thus serves as a test-bed for the development of accurate and widely applicable computational methods for 2D many-body quantum systems.

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www.sciencemag.org SCIENCE VOL 332 3 JUNE 2011 1173

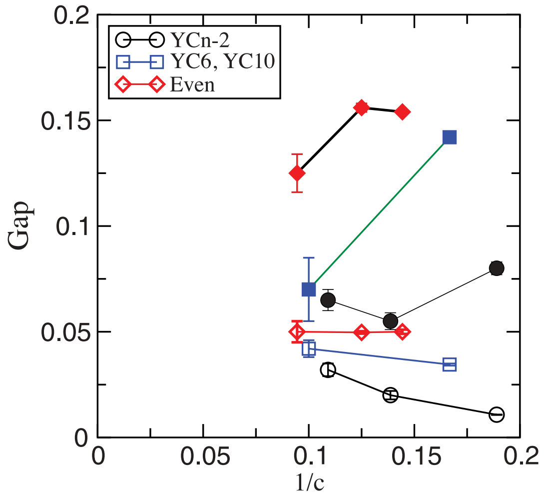


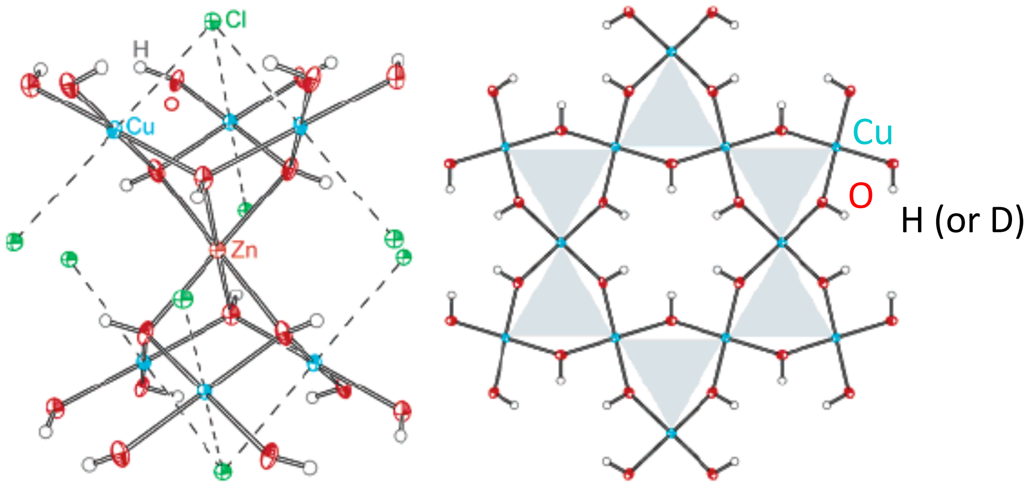
Fig. 4. Spin triplet (solid symbols) and singlet (hollow symbols) gaps for various cylinders with circumferences *c*. The type of cylinder (*15*) is indicated in the key (inset).

Large scale DMRG (Density Matrix Renormalization Group) calculations

Yan, Huse, and White, Science <u>332</u> (2011) 1173.
Also see Jiang *et al.*, PRL 101 (2008) 117203;
Deepenblock *et al.*, 109 (2011) 067201;
Liao *et al.*, PRL 118 (2017) 137202.

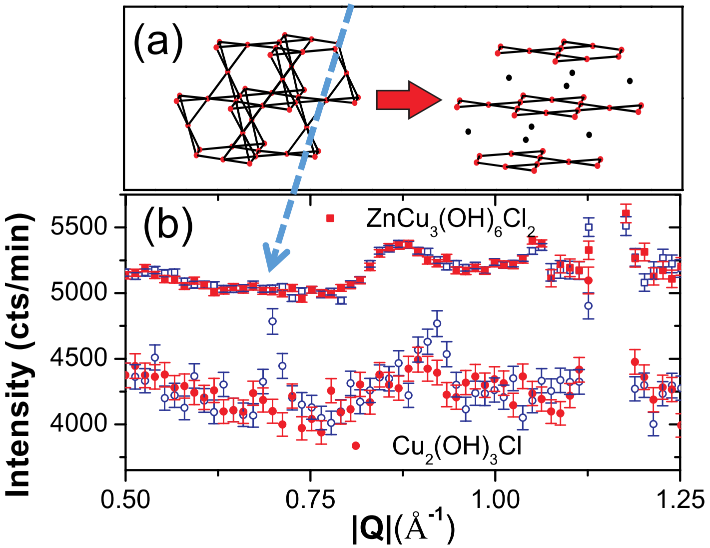
Successful laboratory-synthesis of the structurally ideal kagome lattice Herbertsmithite $ZnCu_3(OH)_6Cl_2$

M.P. Shores, D. Nocera *et al*.   (M.I.T. Chemistry)
J. Amer. Chem. Soc. **127**, (2005) 13462



- Cu^{2+} ions (S = ½) form a perfect kagome lattice
- Cu-Cu super-exchange interaction *J* ~ 200 K

No magnetic Bragg peak



Paramagnetic down to ~50 mK

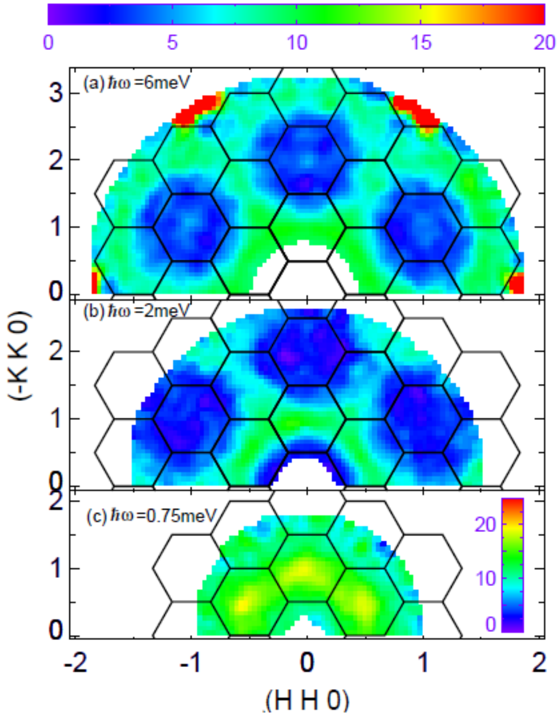
Helton *et al*. PRL 98 (2007) 107204.

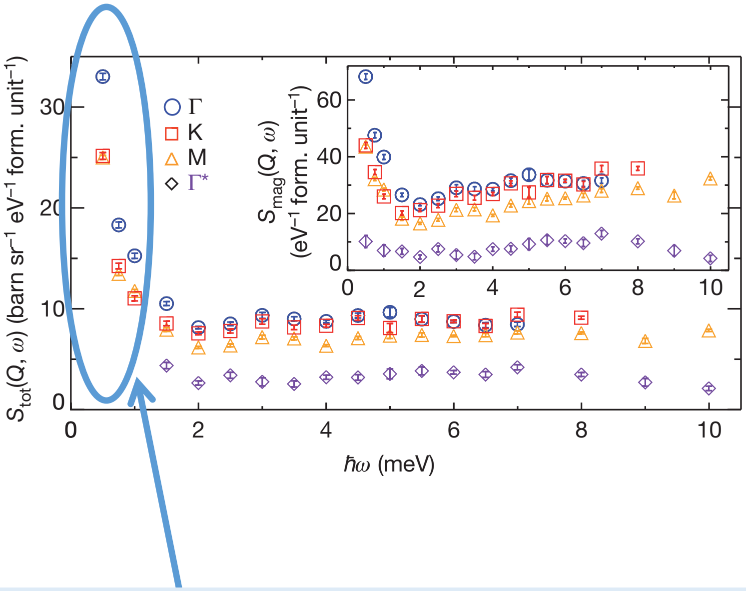
Also by μSR, see Mendels *et al*., PRL 98 (2007) 077204.

Absence of conventional magnon excitations in $ZnCu_3(OH)_6Cl_2$ in inelastic neutron scattering

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

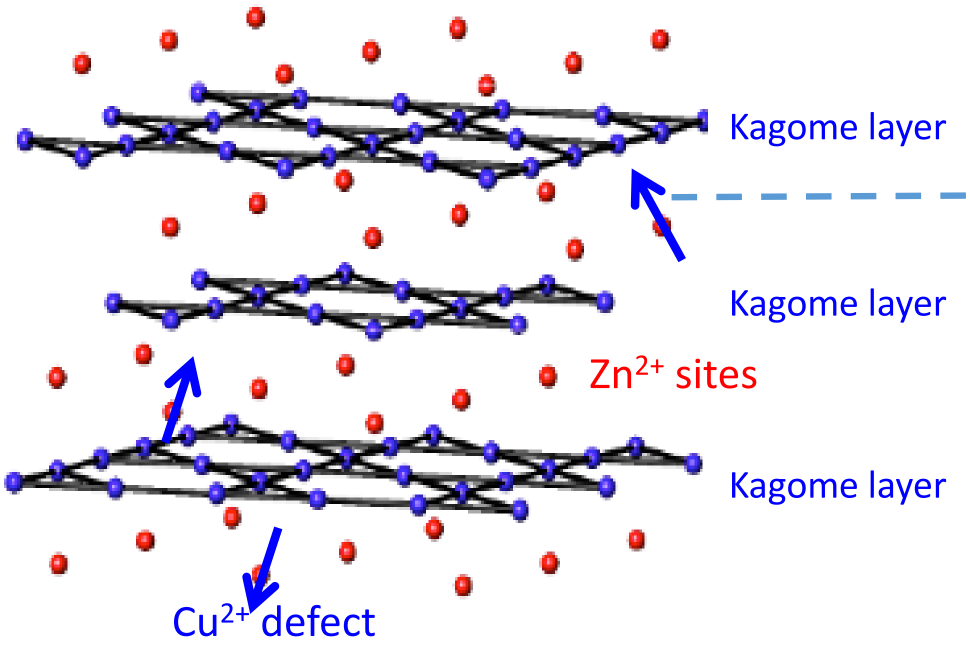
Good news: Spinon Continuum (rather than conventional magnon dispersion); Consistent with continuous S=1/2 spin excitations from a spin-liquid ground state

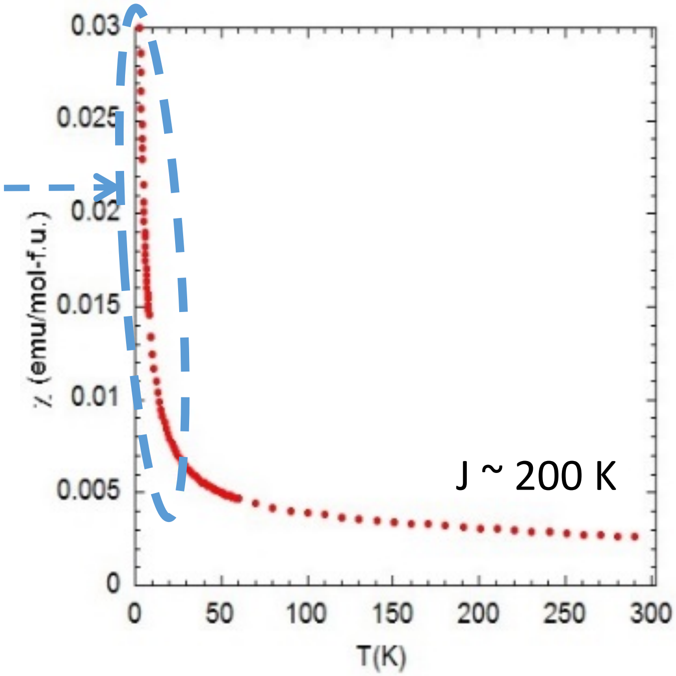




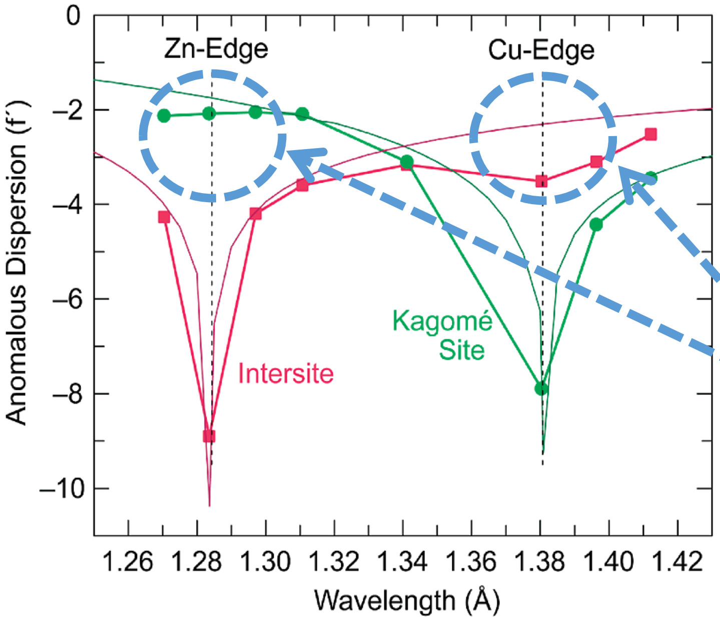
Bad news: Defect spins dominate the low energy part of spin excitations; unable to study the ground state, including the possibility of a small gap

Complications : Defect Cu^{2+} spins occupy the non-magnetic Zn^{2+} sites with 15% probability → actual composition is $(Zn_{0.85}Cu_{0.15})Cu_3(OH)_6Cl_2$





Cu^{2+} defect spins dominate χ (and all *bulk-averaged* thermodynamic data) at low tempertures



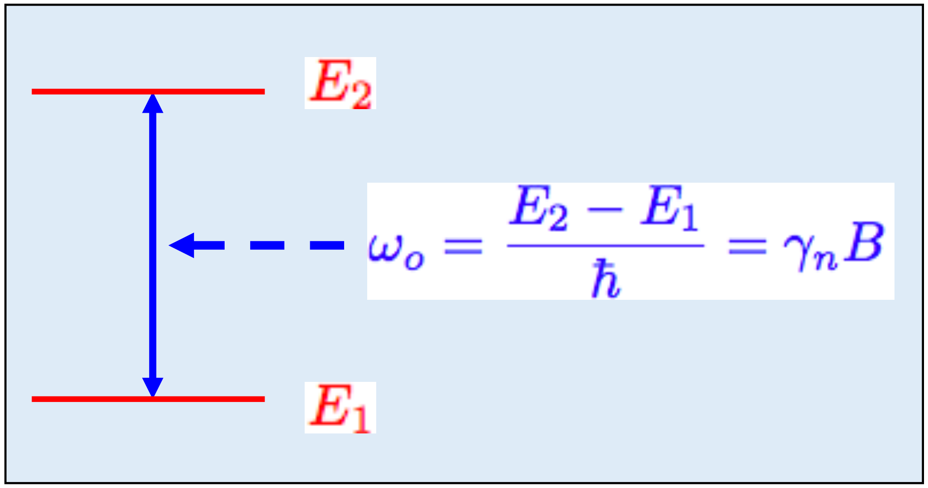
Anomalous X-ray diffraction experiments on single crystal:

- 15% of Zn^{2+} sites are occupied by Cu^{2+} defect spins
- No Zn^{2+} occupy Cu^{2+} kagome sites (*i.e*. no anti-site defects)

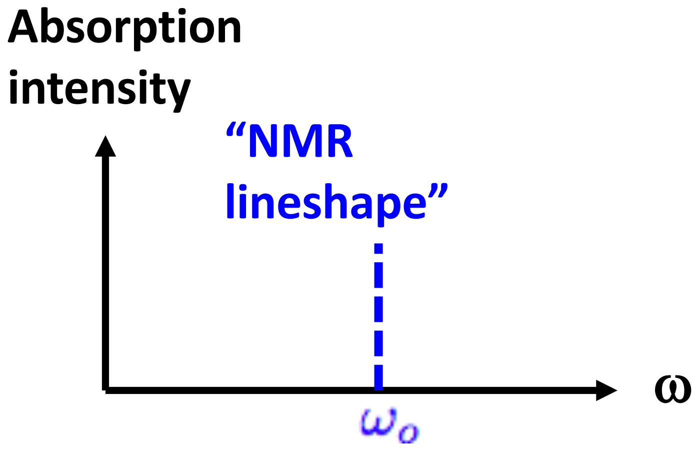
Freedman *et al*, JACS 132 (2010) 16185.

How shall we probe the properties of the kagome layers separately from the defects?

Answer: NMR



$$\omega_o = \frac{E_2 - E_1}{\hbar} = \gamma_n B$$



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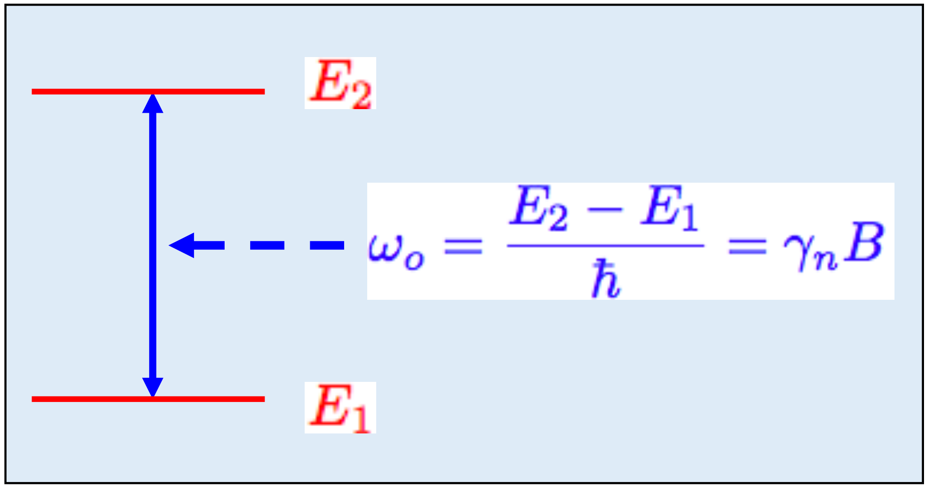

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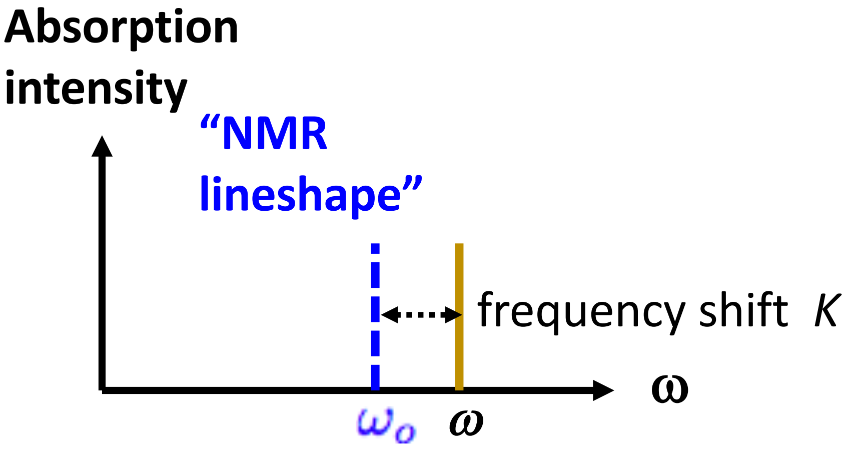
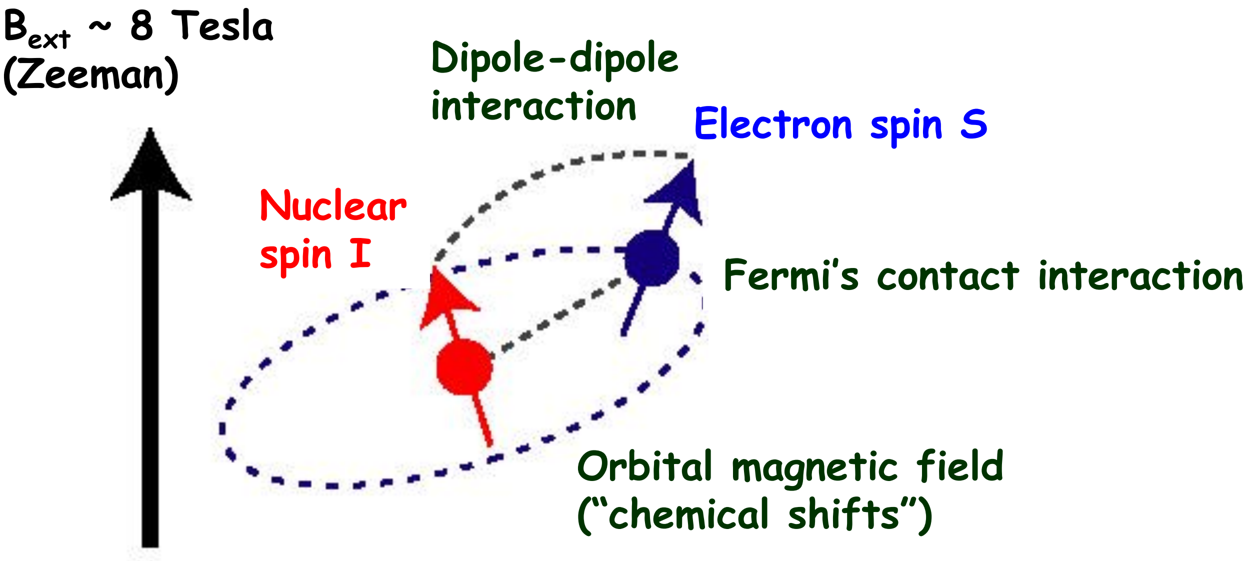


Influence of electron spins via hyperfine interactions



NMR frequency shifts to

$$\omega = \gamma_n (B_{ext} + B_{hf})$$

$$= \omega_o (1 + K)$$

$$K = \frac{A_{hf}}{N_A \mu_B} \chi_{spin} + K_{chem}$$

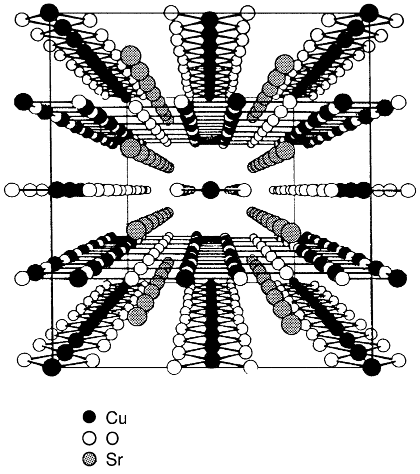
where

A_{hf} : "Hyperfine coupling"

$|K_{chem}|$ ~ 0.02(%) << K_{spin}

^{17}O NMR successfully probed a spin liquid state in the two-leg ladder layers of $A_{14}Cu_{24}O_{41}$ although the bulk spin susceptibility is dominated by chain layers !

T. Imai et al., PRL 81 (1998) 220.



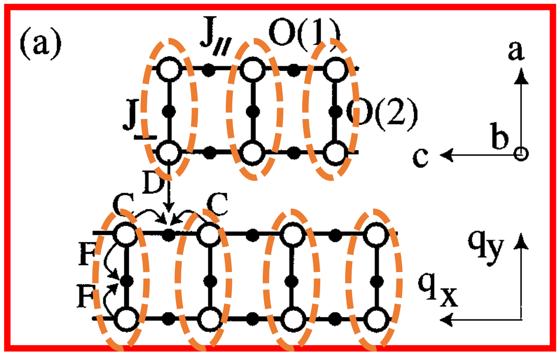
Chain

Ladder

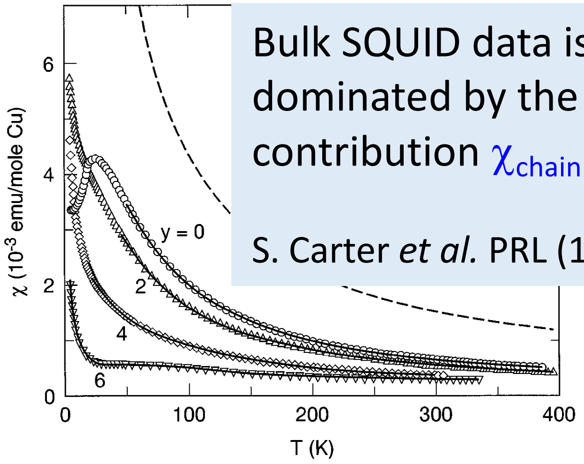
Chain

Ladder

Chain



Spin liquid on two-leg ladder layer



Bulk SQUID data is dominated by the chain contribution χ_{chain}

S. Carter *et al.* PRL (1996)

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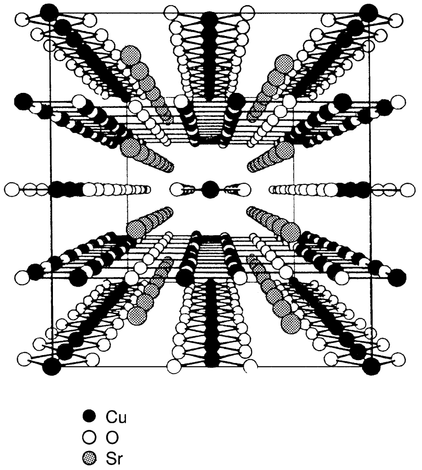


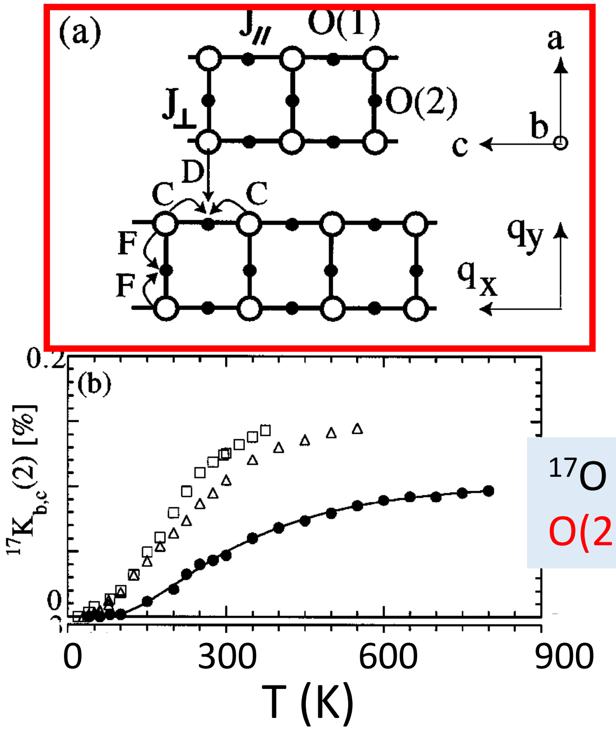
Chain

Ladder

Chain

Ladder

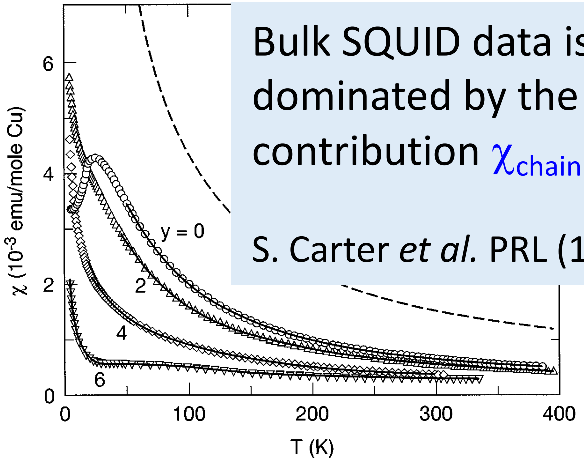
Chain



Spin liquid on two-leg ladder layer

^{17}O NMR Knight shift at O(2) sites reflects χ_{Ladder}

^{17}O nuclear spins at O(1) and O(2) sites couple mostly with Cu electron spins in the ladder layers



Bulk SQUID data is dominated by the chain contribution χ_{chain}

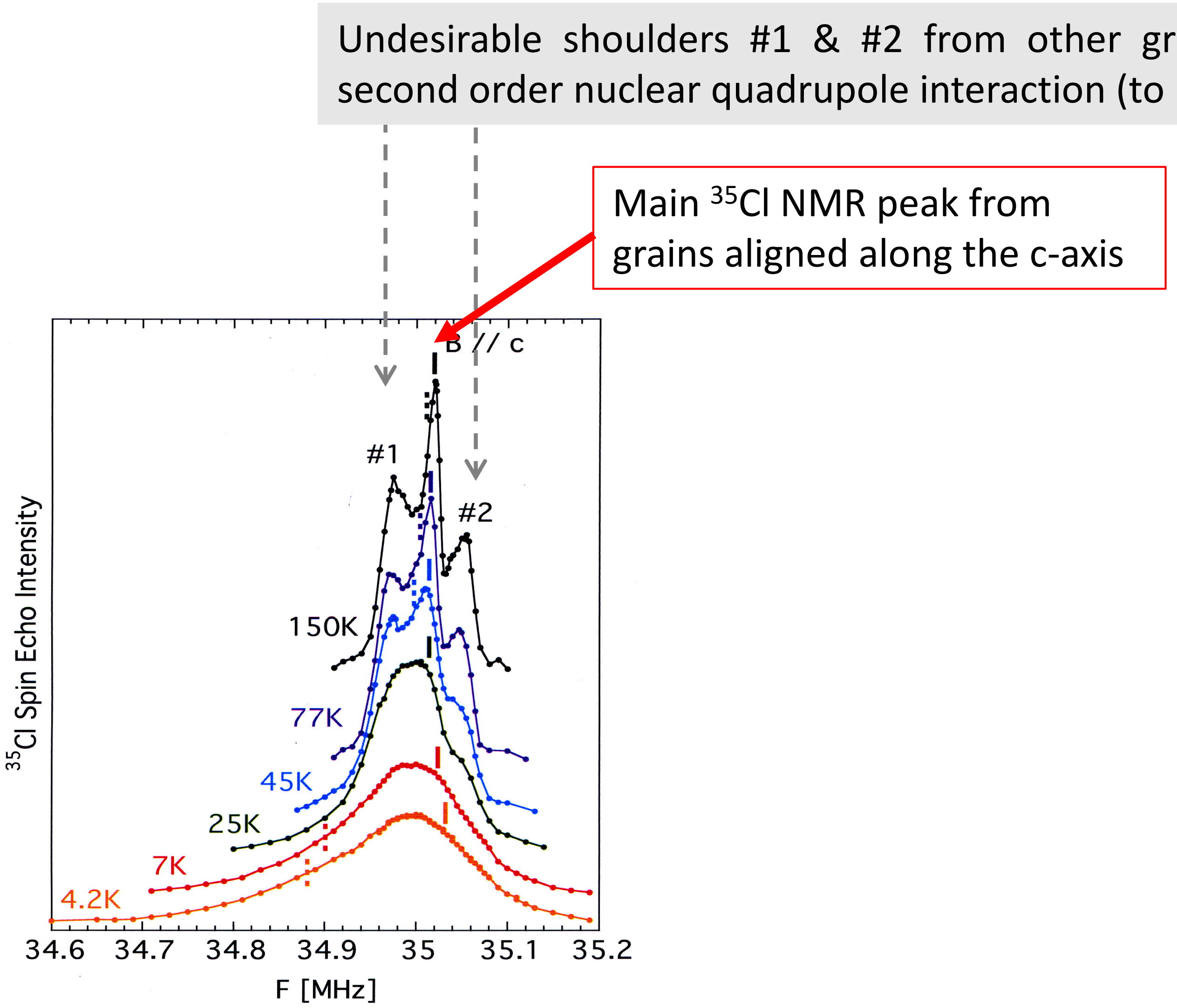
S. Carter *et al.* PRL (1996)

First generation ^{63}Cu, ^{1}H and ^{35}Cl, NMR in partially aligned powder sample of $ZnCu_3(OH)_6Cl_2$

T. I. *et al*., PRL 100 (2008) 077203

^{63,65}Cu NMR : Direct but inconvenient probe (nuclear quadrupole interaction too large).
^{1}H NMR : hyperfine coupling is too small, compared with line broadening induced by defect spins

^{35}Cl nuclear spin has decent strength of *negative* hyperfine coupling with Cu electron spins.



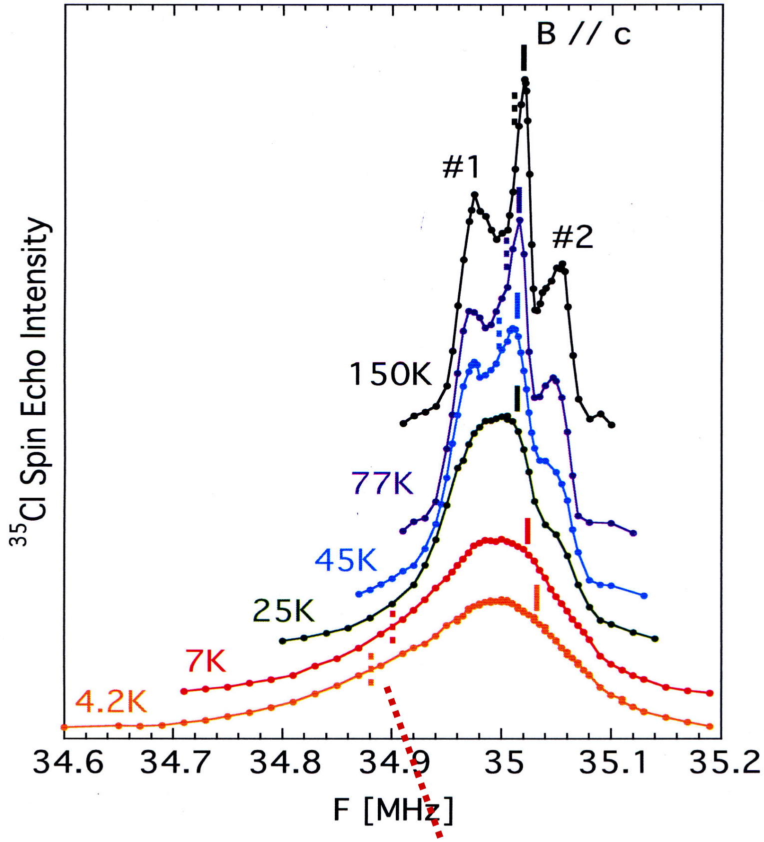
Undesirable shoulders #1 & #2 from other grains split by second order nuclear quadrupole interaction (to be ignored)

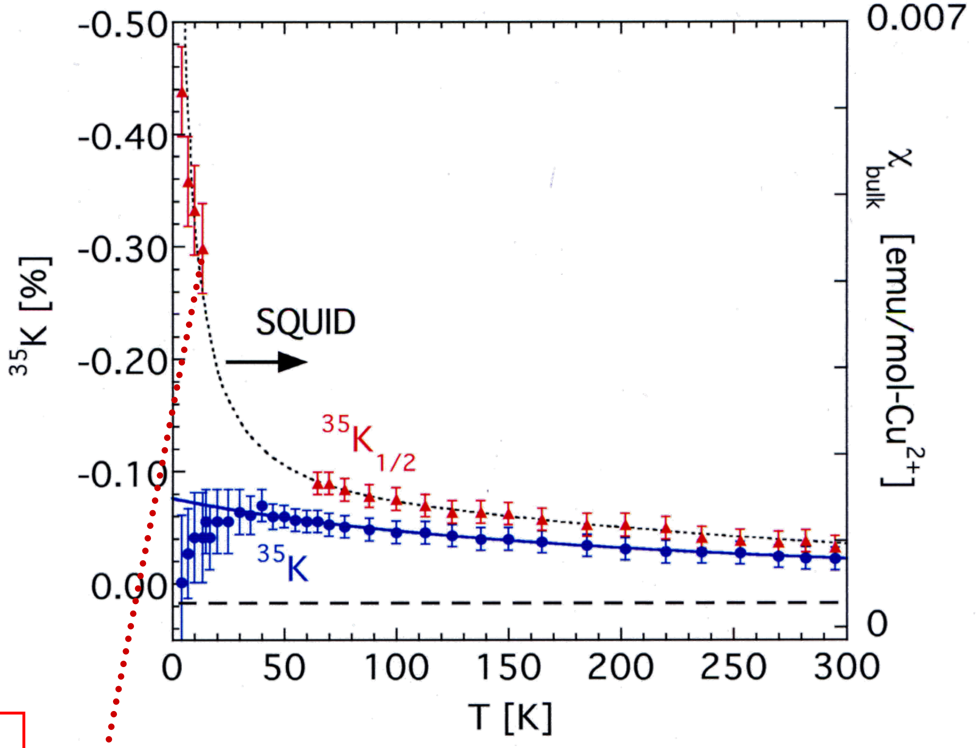
Main ^{35}Cl NMR peak from grains aligned along the c-axis

^{35}Cl NMR in partially aligned powder sample of $ZnCu_3(OH)_6Cl_2$

T. I. *et al.*, PRL 100 (2008) 077203

Larger spin susceptibility



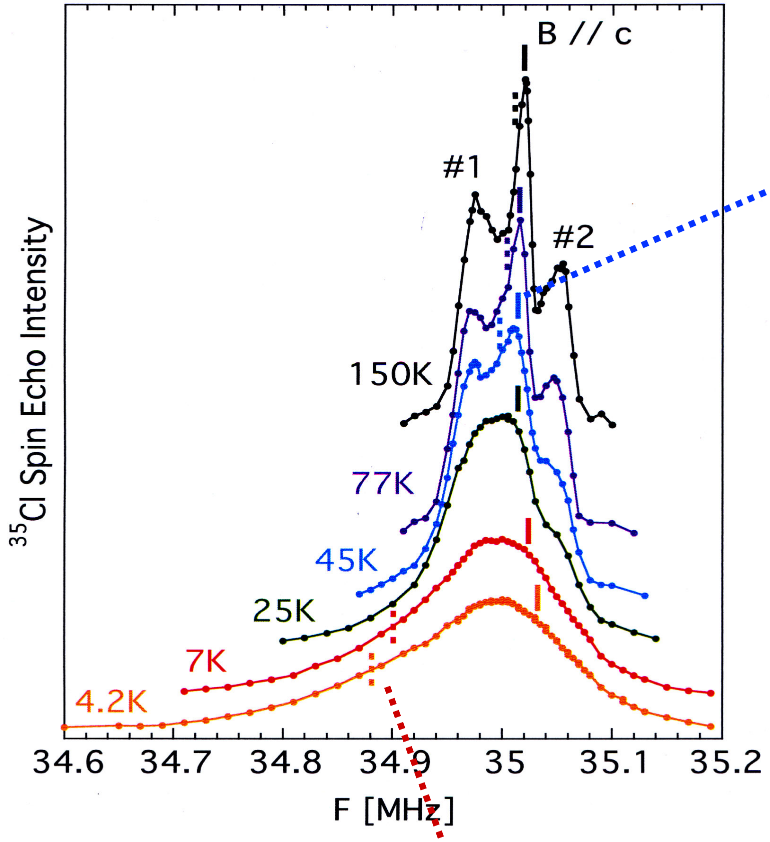


Asymmetrically broadened. Low frequency tail reflects large Curie-Weiss defect susceptibility.

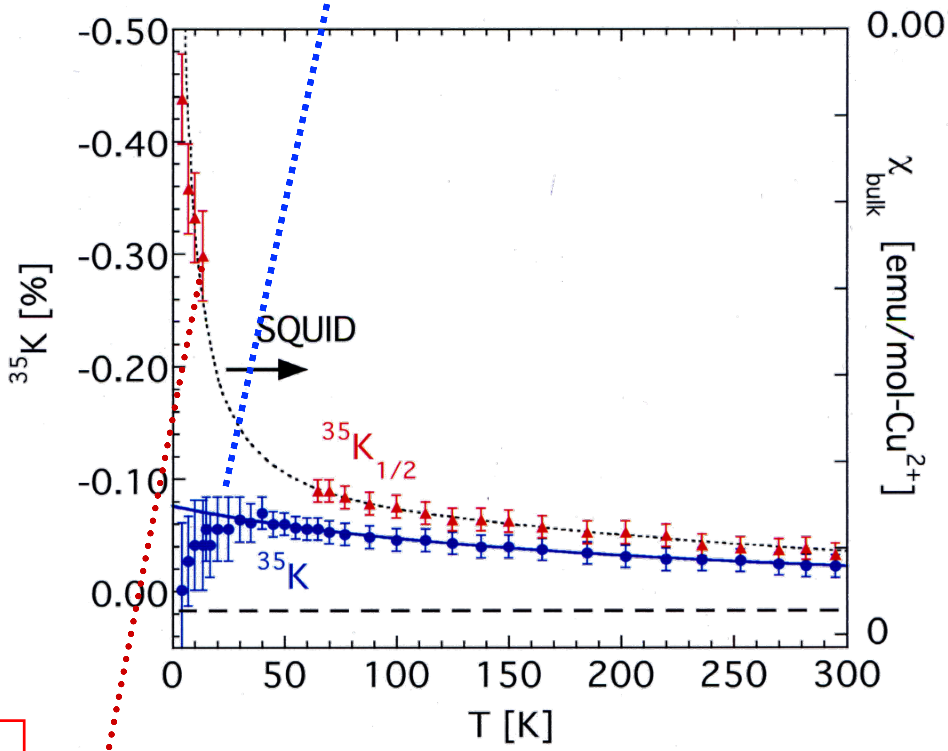
^{35}Cl NMR in partially aligned powder sample of $ZnCu_3(OH)_6Cl_2$

T. I. *et al.*, PRL 100 (2008) 077203

Larger spin susceptibility

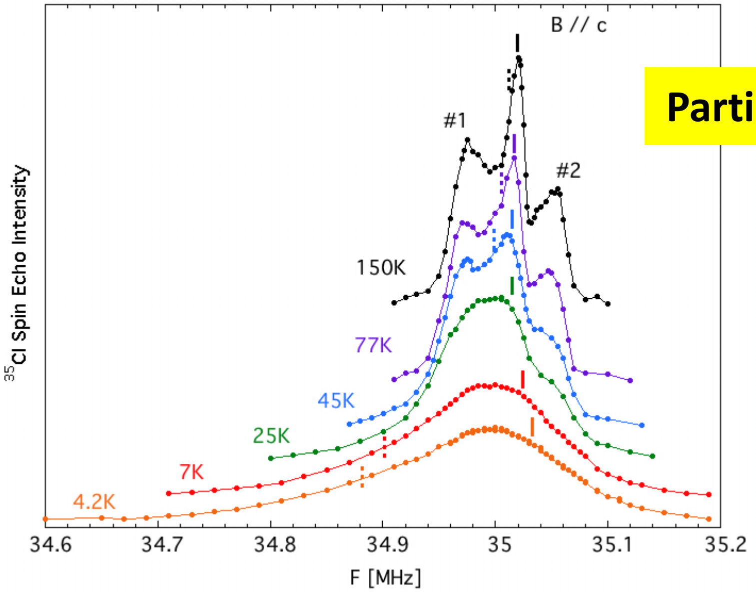


Main peak seems to suggest $\chi_{kagome} \rightarrow 0$ at $T = 0$, but inconclusive

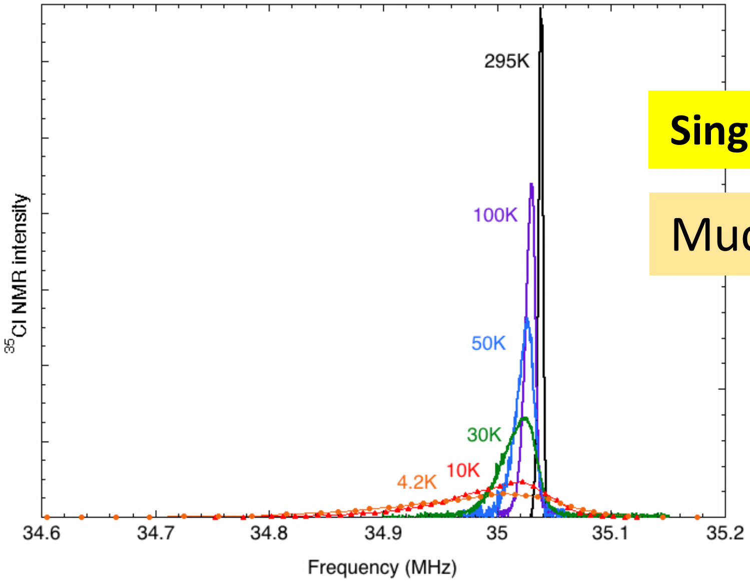


Asymmetrically broadened. Low frequency tail reflects large Curie-Weiss defect susceptibility.

Advantages of single crystal NMR of $ZnCu_3(OH)_6Cl_2$



Partially aligned powder



Single crystal (B || c)

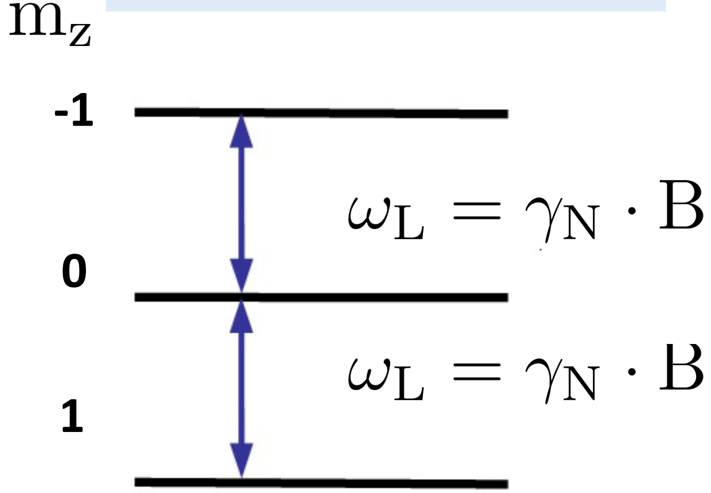
Much higher resolutions!

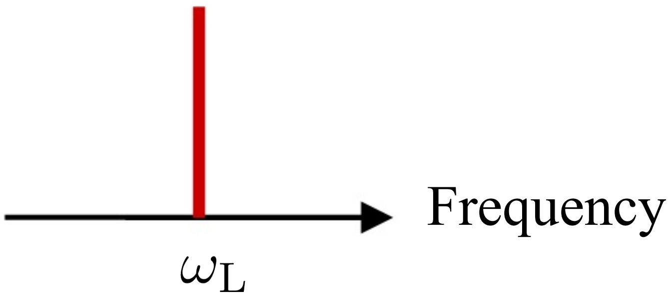
Second generation ^{2}D (nuclear spin I = 1) NMR in $ZnCu_3(OD)_6Cl_2$ deuterated singe crystal

T. I. *et al.*, PRB 83(2011) 020411 (Rapid).

$$H = -\gamma_n \hbar \mathbf{B} \cdot \mathbf{I}$$

Zeeman interaction only





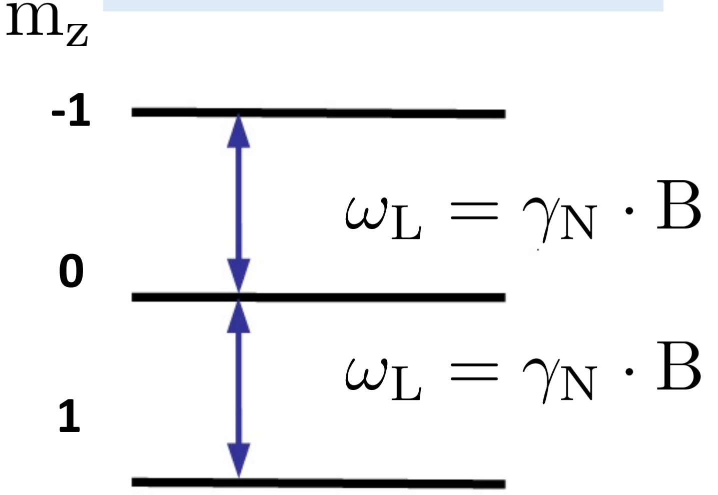
Second generation ^{2}D (nuclear spin $I = 1$) NMR in $ZnCu_3(OD)_6Cl_2$ deuterated singe crystal

T. I. *et al.*, PRB <u>83</u>(2011) 020411 (Rapid).

$$H = -\gamma_n \hbar \mathbf{B} \cdot \mathbf{I} + \boxed{\frac{\hbar\nu_Q^Z}{6}\{3I_Z^2 - I(I+1) + \eta(I_x^2 - I_y^2)\}}$$

Zeeman interaction only

Nuclear quadrupole interaction with charge/lattice



$$\omega_L = \gamma_N \cdot B$$

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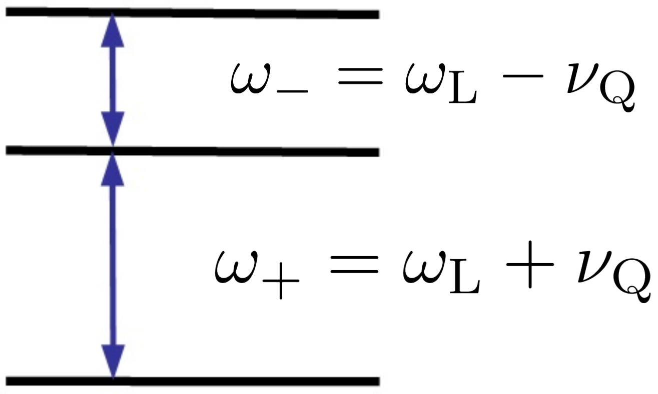
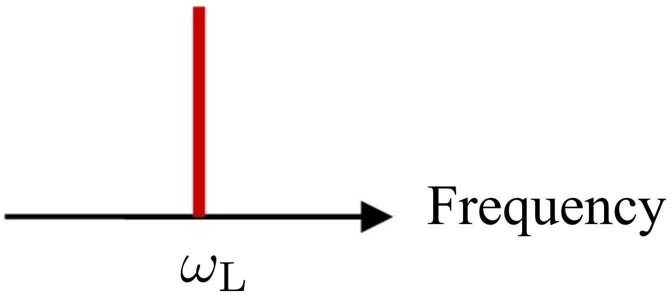
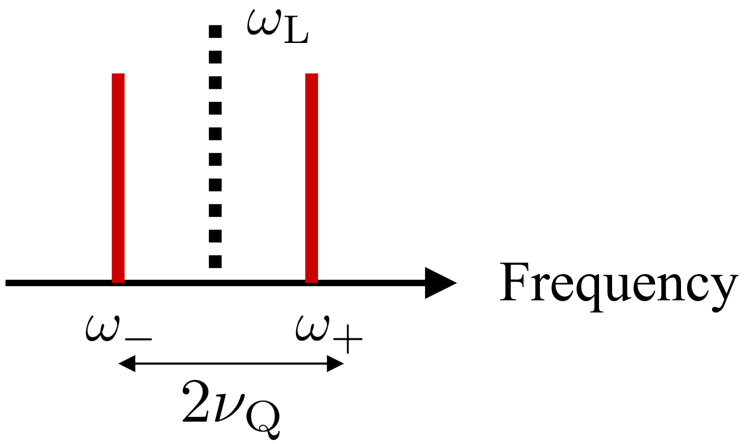


$$\omega_- = \omega_L - \nu_Q$$

$$\omega_+ = \omega_L + \nu_Q$$

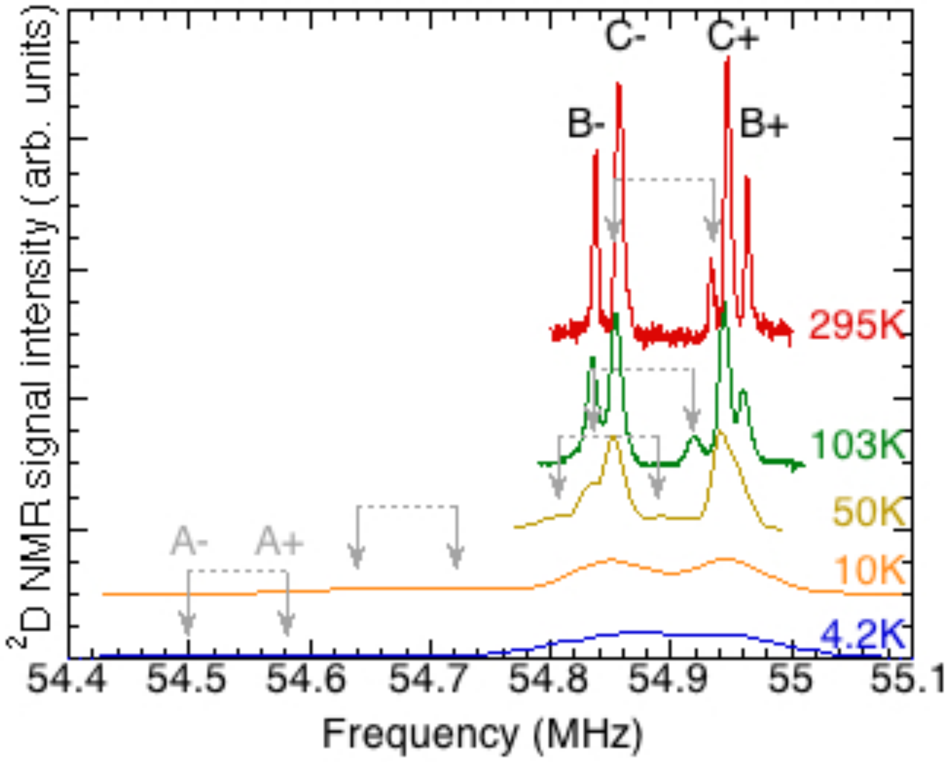




^{2}D single crystal NMR reveled 14% Zn^{2+} sites are occupied by Cu^{2+} defects in $ZnCu_3(OD)_6Cl_2$

3 pairs of ^{2}D NMR signals from 3 inequivalent ^{2}D sites

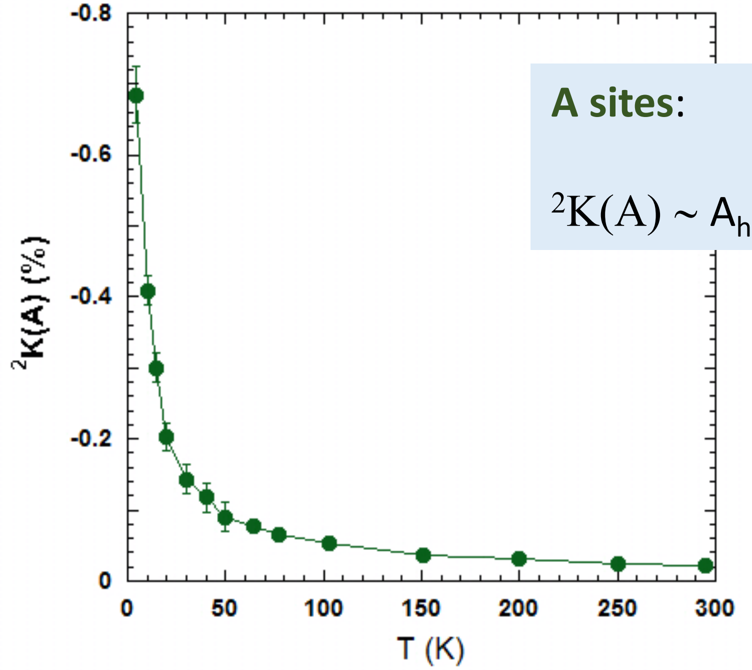
A sites (~14% population) : **NN of Cu^{2+} defects** occupying Zn^{2+} non-magnetic sites.
B sites (~28% population) : **NNN of Cu^{2+} defects** occupying Zn^{2+} non-magnetic sites
C sites (~58% population) : **No defects nearby**



Consistent with $Zn_{0.86}Cu_{3.14}(OD)_6Cl_2$; ~14% of Zn^{2+} sites are occupied by Cu^{2+} defect spins

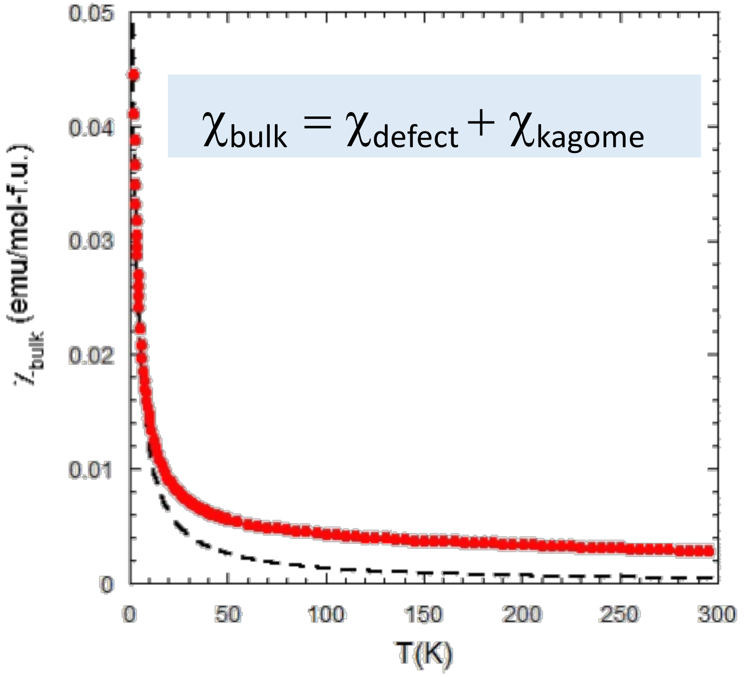
No evidence for anti-site Zn^{2+} defects occupying Cu^{2+} sites

Defect spin susceptibility probed by ^2D A sites in $ZnCu_3(OD)_6Cl_2$

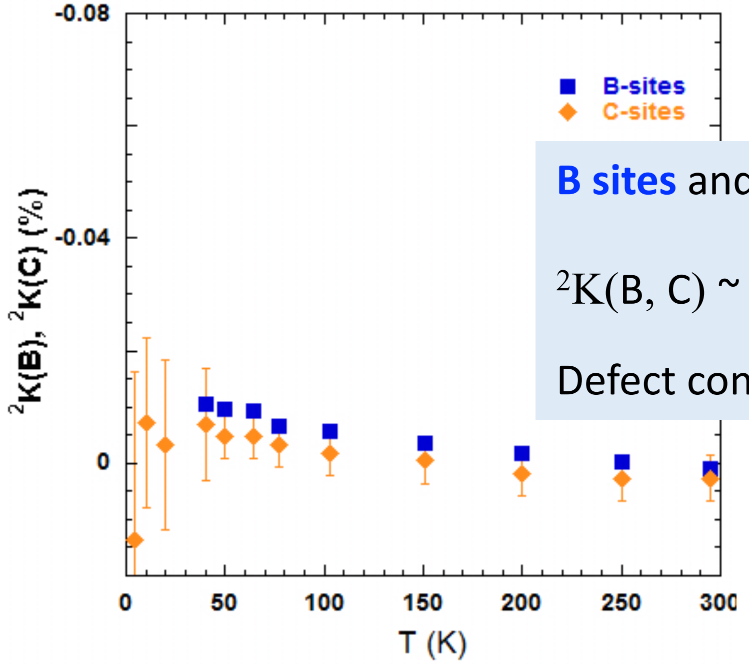


A sites:

$^2K(A) \sim A_{hf}^{defect}\ \chi_{defect}$



$$\chi_{bulk} = \chi_{defect} + \chi_{kagome}$$

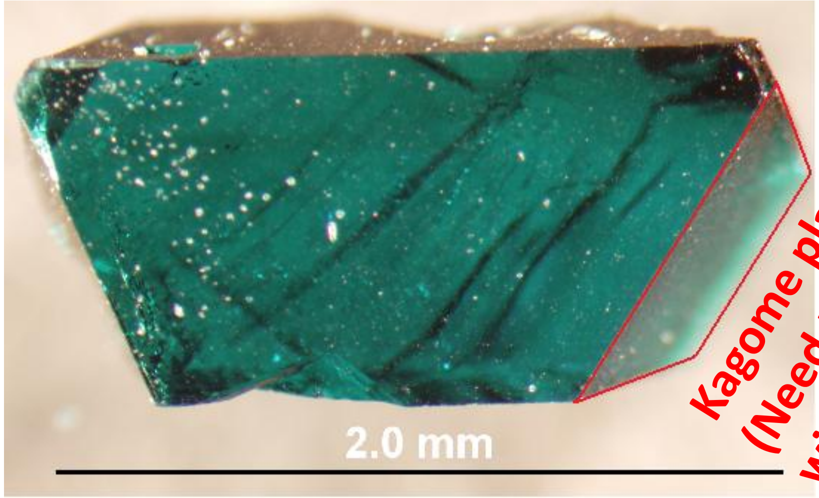


B sites and **C sites**

$^2K(B, C) \sim A_{hf}^{kagome}\ \chi_{kagome} + A_{hf}^{defect}\ \chi_{defect}$

Defect contribution obscures the intrinsic term

Change of strategy: angle-dependent ^{17}O (nuclear spin $I = 5/2$) NMR for isotope-enriched single crystal



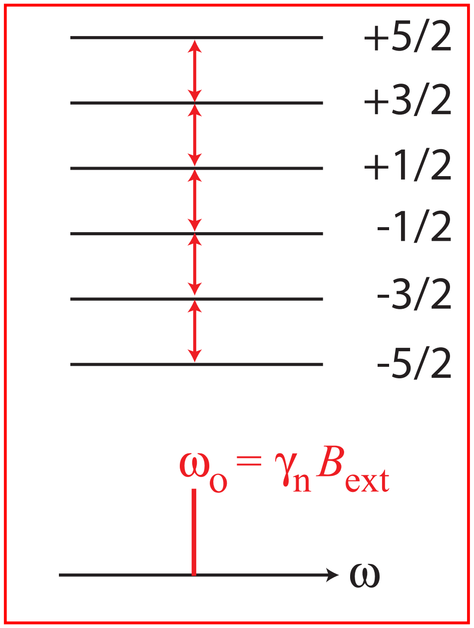
Kagome plane
(Need to be aligned
with magnetic field)

Single crystal courtesy of T.-H. Han & Y.S. Lee

Compact goniometer for NMR & X-ray designed by M. Fu

Nuclear spin Hamiltonian for ^{17}O (nuclear spin I = 5/2) and resonant peak(s)

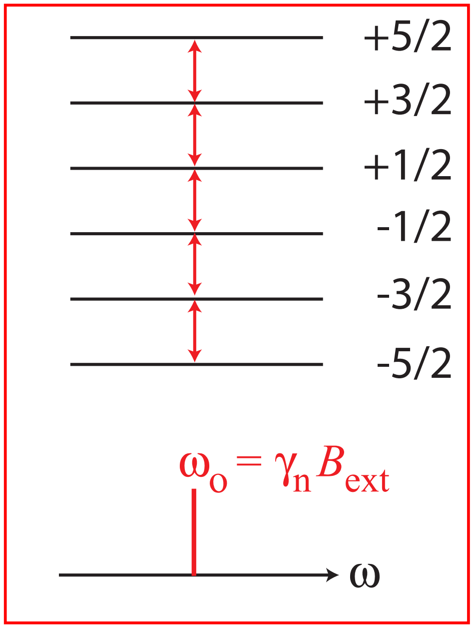
$$\hat{H} = \boxed{\gamma_n \vec{B}_{ext} \bullet \vec{I}}$$

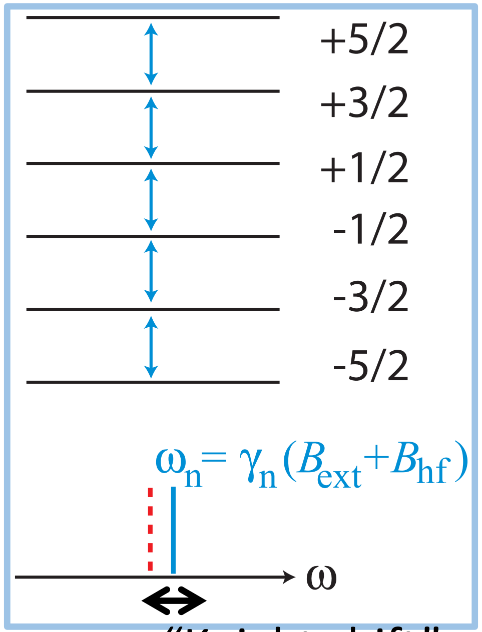


Zeeman only

Nuclear spin Hamiltonian for ^{17}O (nuclear spin I = 5/2) and resonant peak(s)

$$\hat{H} = \boxed{\gamma_n \vec{B}_{ext} \bullet \vec{I}} + \boxed{\gamma_n \vec{B}_{hf} \bullet \vec{I}}$$





"Knight shift"

Zeeman only

Zeeman + hyperfine

NMR frequency shifts to

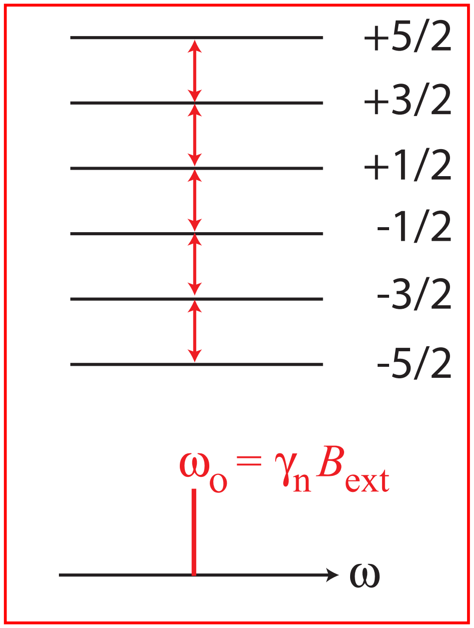
$\omega_n = \omega_o(1 + K)$

where $K = \dfrac{A_{hf}}{N_A \mu_B} \chi_{spin} + K_{chem}$

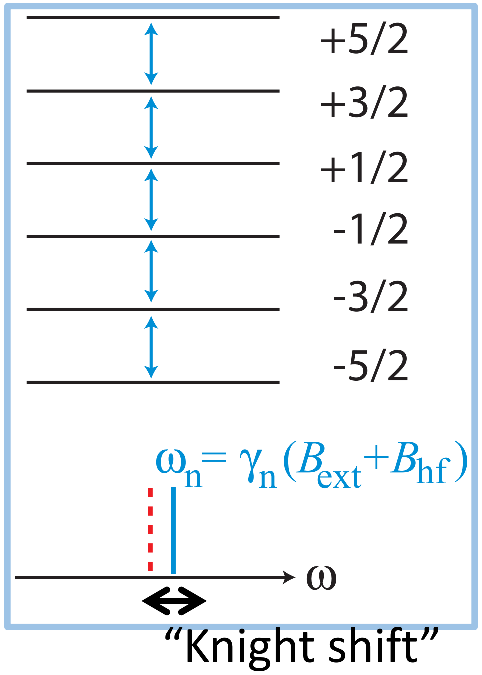
and $|K_{chem}| \sim 0.02(\%) << K_{spin}$

Nuclear spin Hamiltonian for ^{17}O (nuclear spin I = 5/2) and resonant peak(s)

$$\hat{H} = \boxed{\gamma_n \vec{B}_{ext} \bullet \vec{I}} + \boxed{\gamma_n \vec{B}_{hf} \bullet \vec{I}} + \boxed{\frac{\nu_Q}{2} \hat{I}_z^2} + \ldots\ldots\ldots$$



Zeeman only



Zeeman + hyperfine

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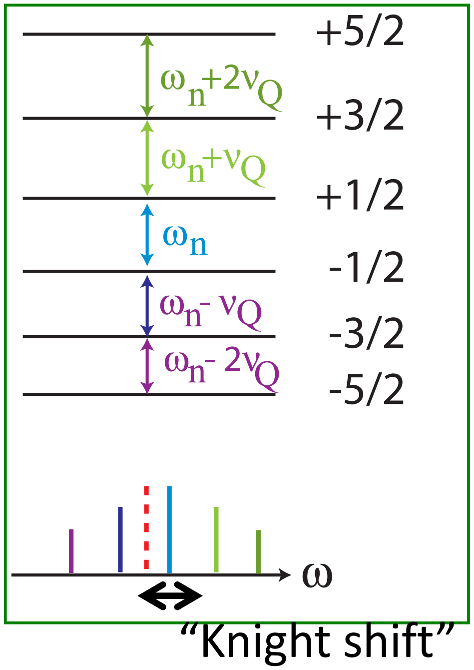
$$\omega_n = \omega_o(1 + K)$$

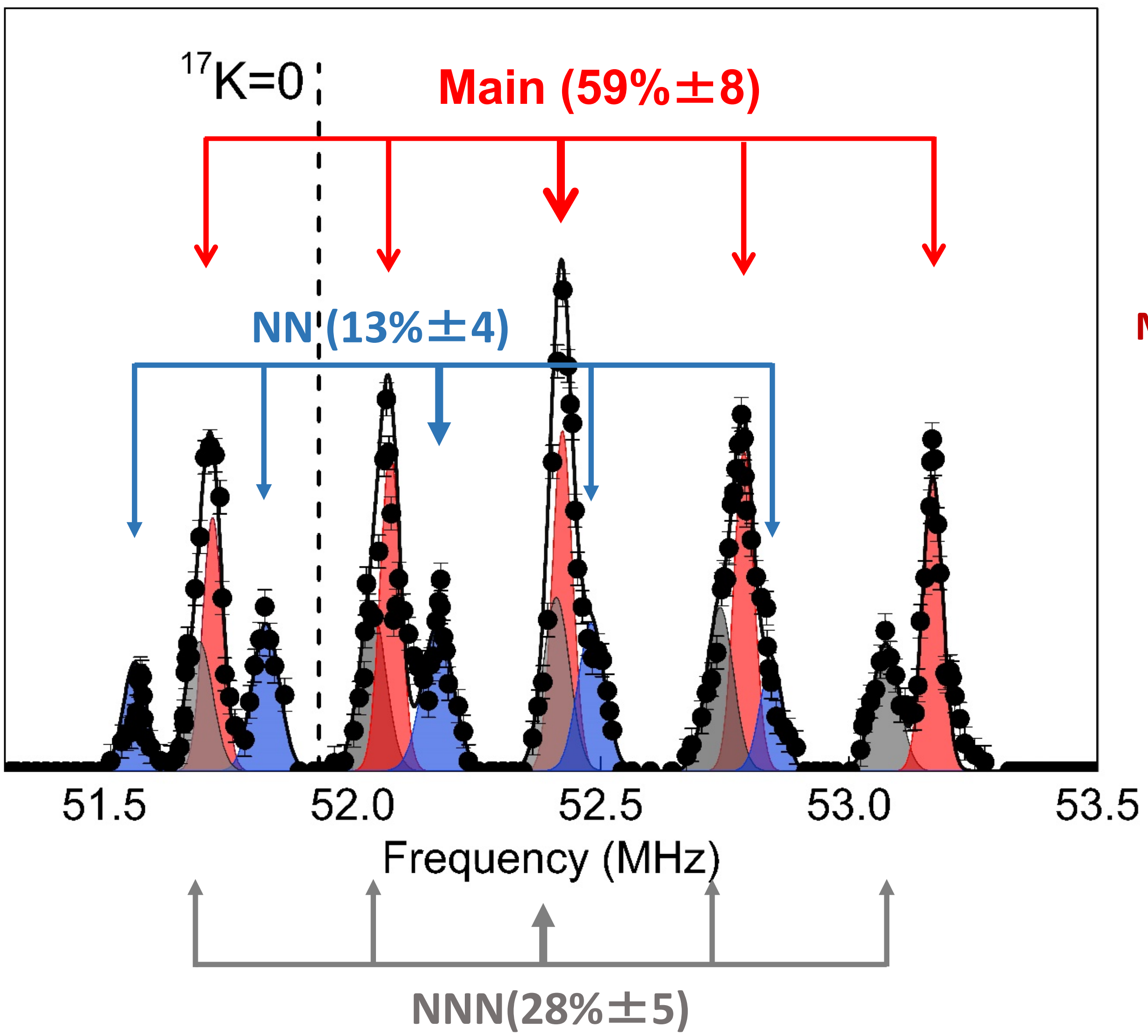
where $K = \dfrac{A_{hf}}{N_A \mu_B} \chi_{spin} + K_{chem}$

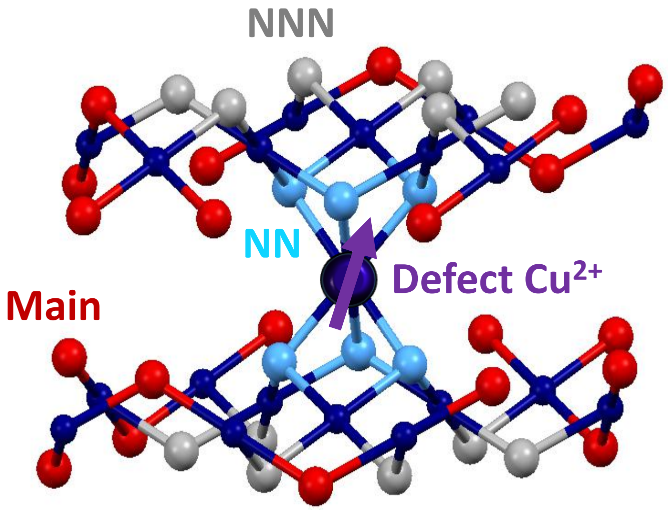
and $|K_{chem}| \sim 0.02(\%) \ll K_{spin}$



Zeeman + hyperfine + quadrupole interaction

^{17}O NMR lineshape of $ZnCu_3(OH)_6Cl_2$ single crystal in B_{ext} || c

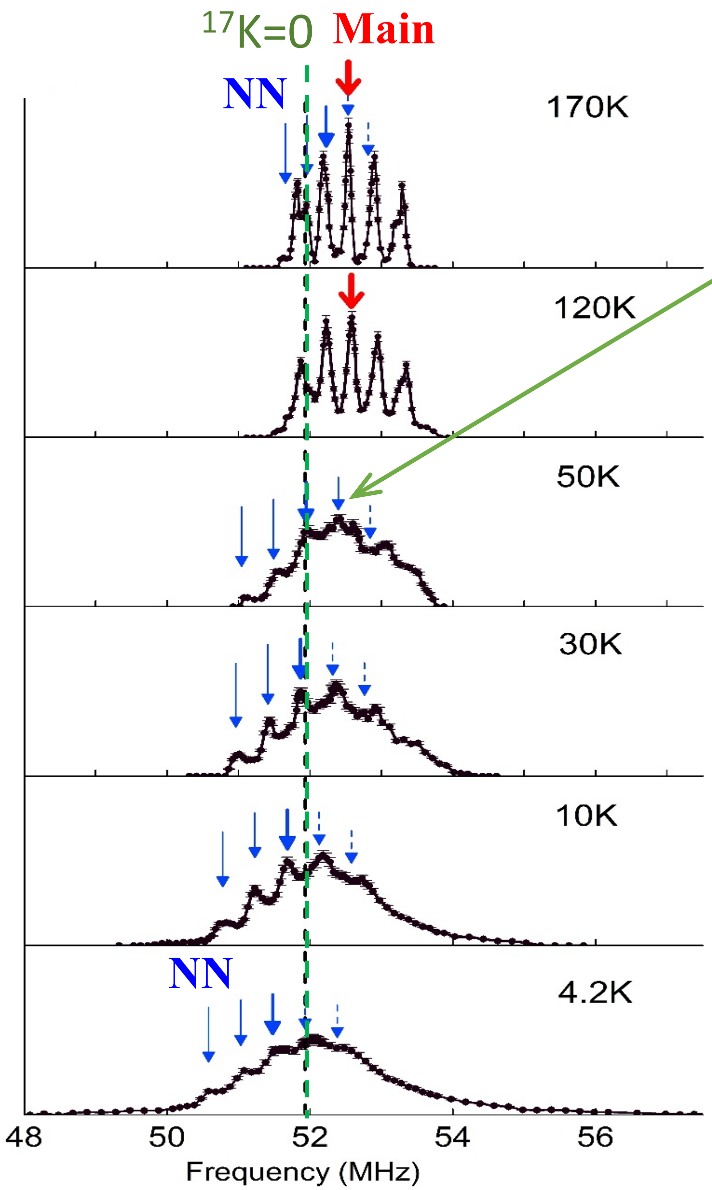




Temperature dependence of ^{17}O NMR lineshapes in B_{ext} || c

M Fu *et al*. Science (2015)

We cannot resolve the crucial center peak of the Main sites below ~50K



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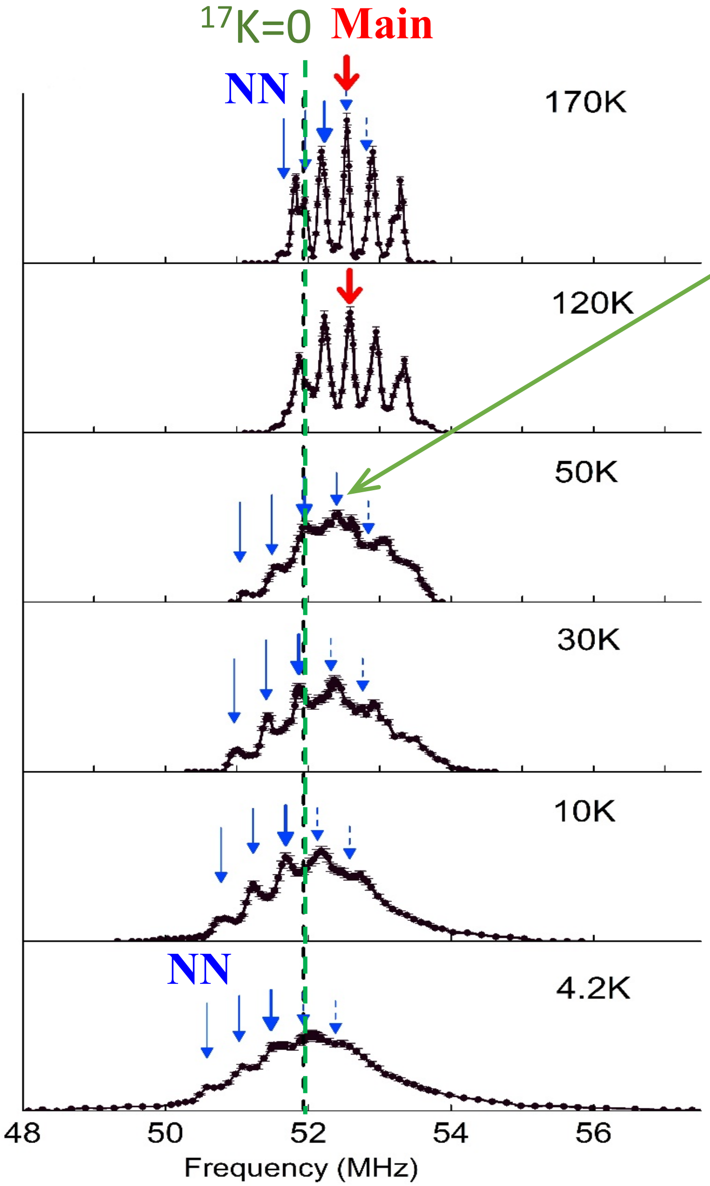

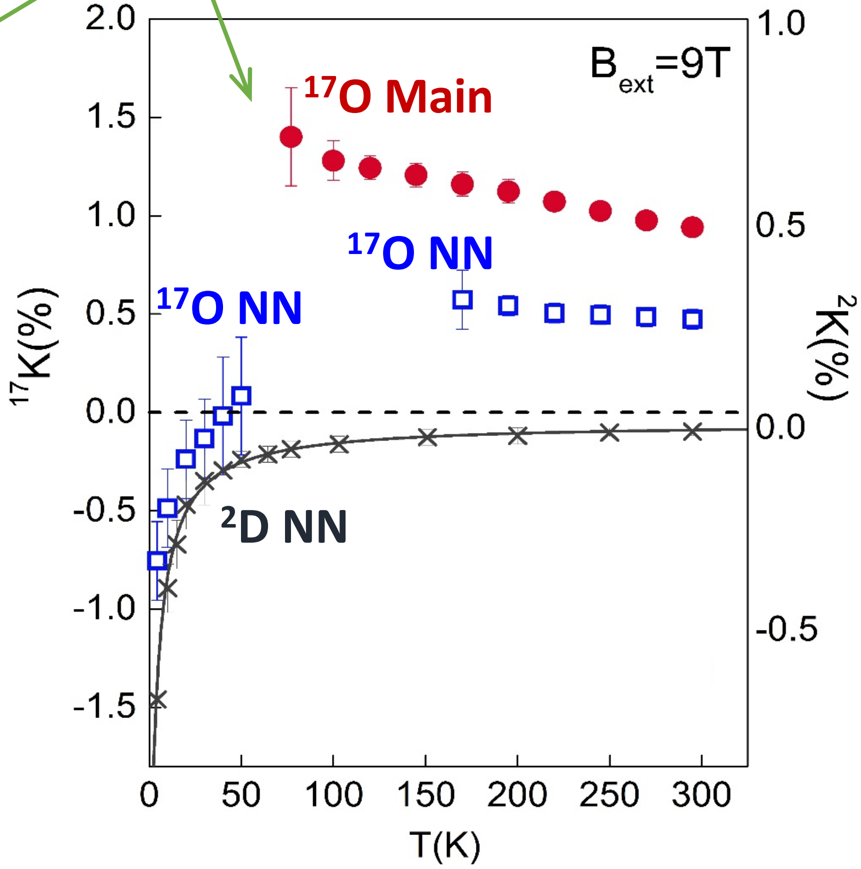

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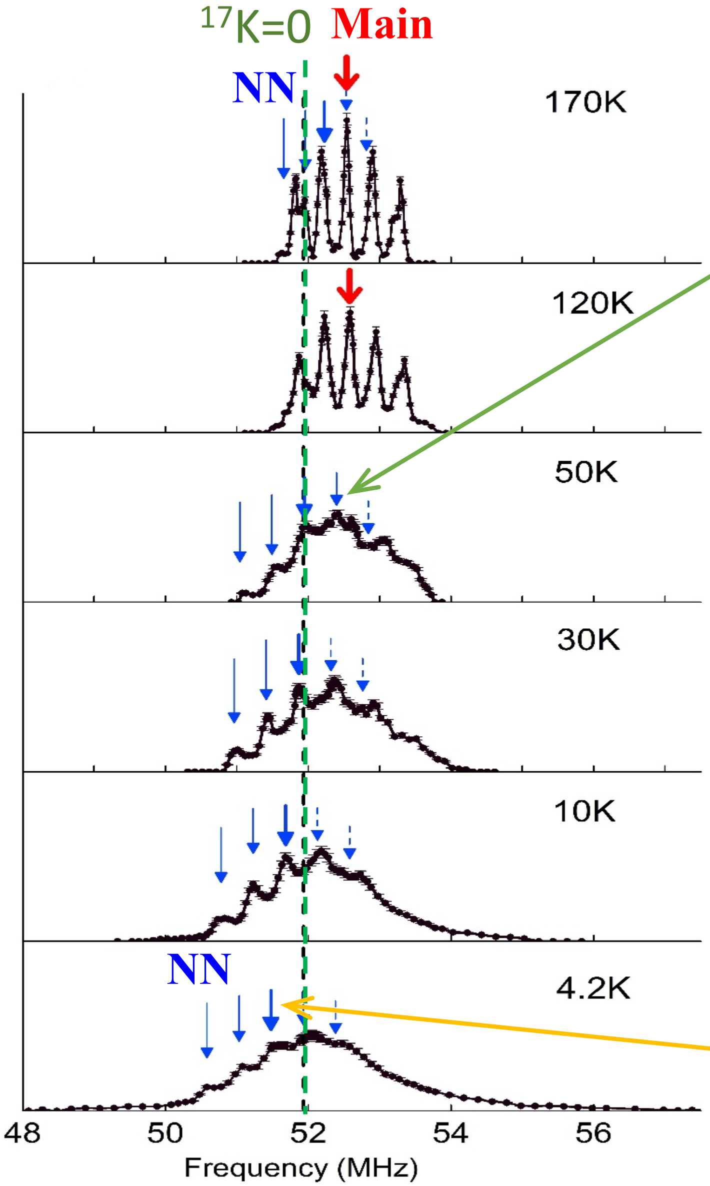
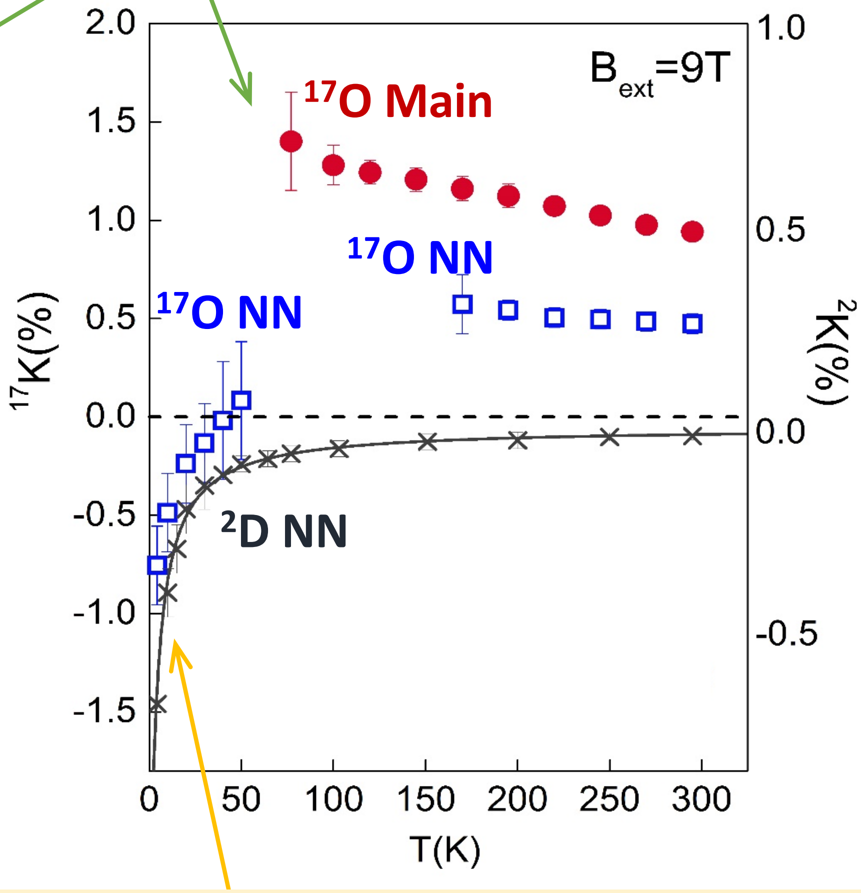




Low T behavior at ^{17}O and ^{2}D *NN* sites is dominated by a large Curie - Weiss contribution,

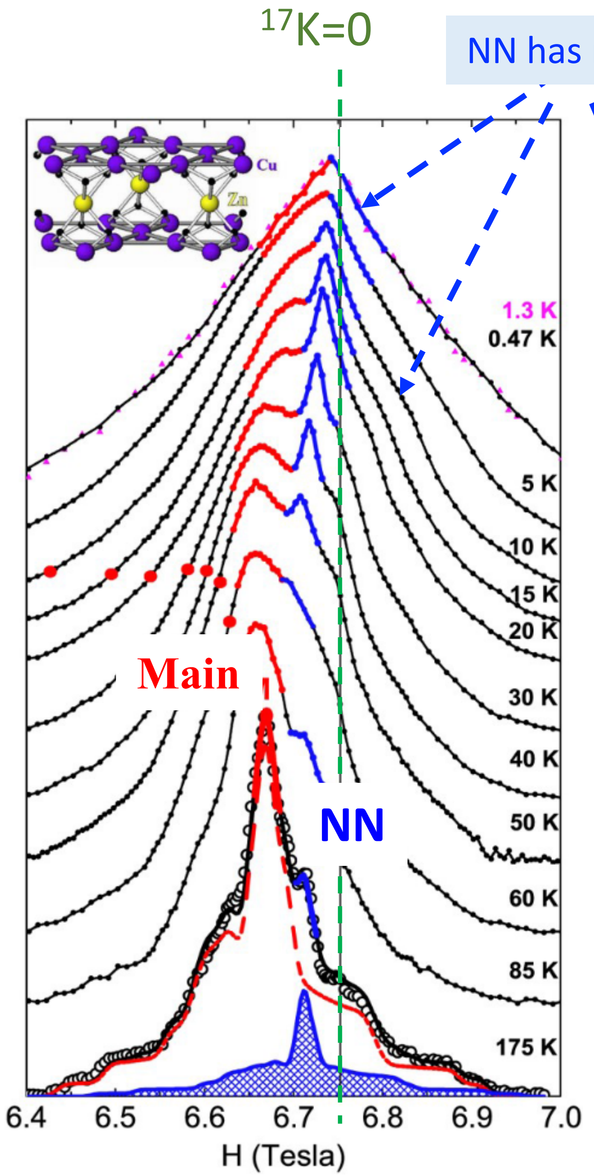
$$\chi_{defect} \sim \frac{C}{T+\theta}$$

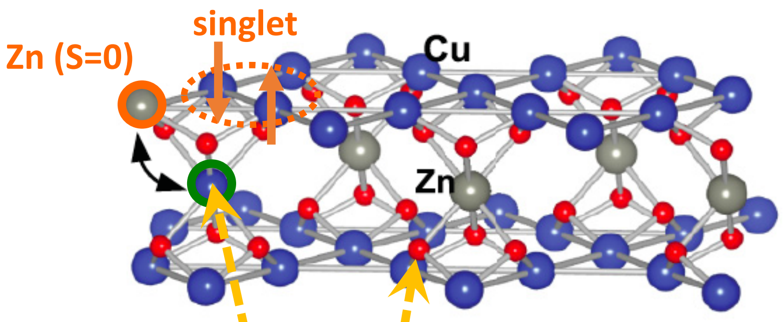
with θ ~1 K and negative hyperfine coupling $A_{hf} < 0$

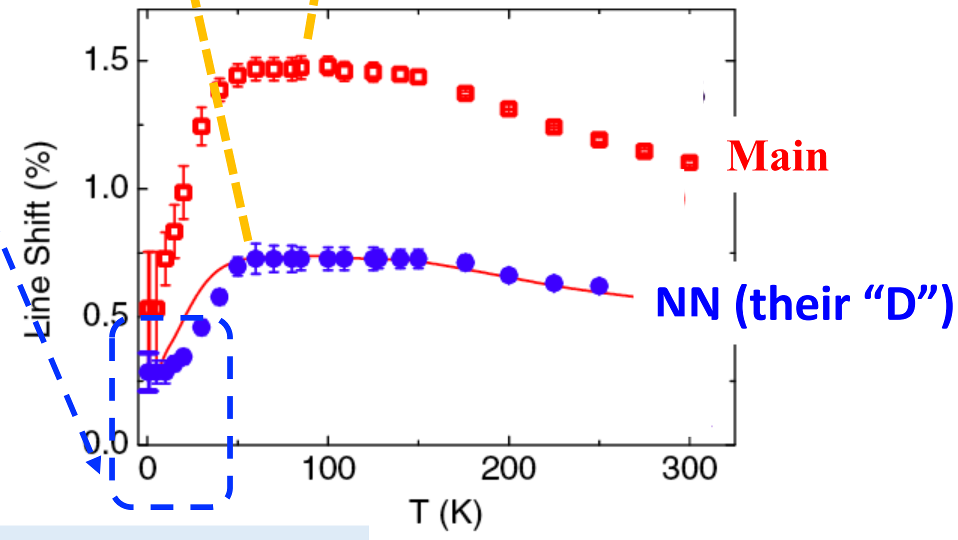
(Side) Earlier powder ^{17}O results are consistent with our data (NOT a proof of anti-site defects)

Olariu, Mendels *et al.*, PRL <u>100</u> (2008) 087202

NN has negative shifts at low T





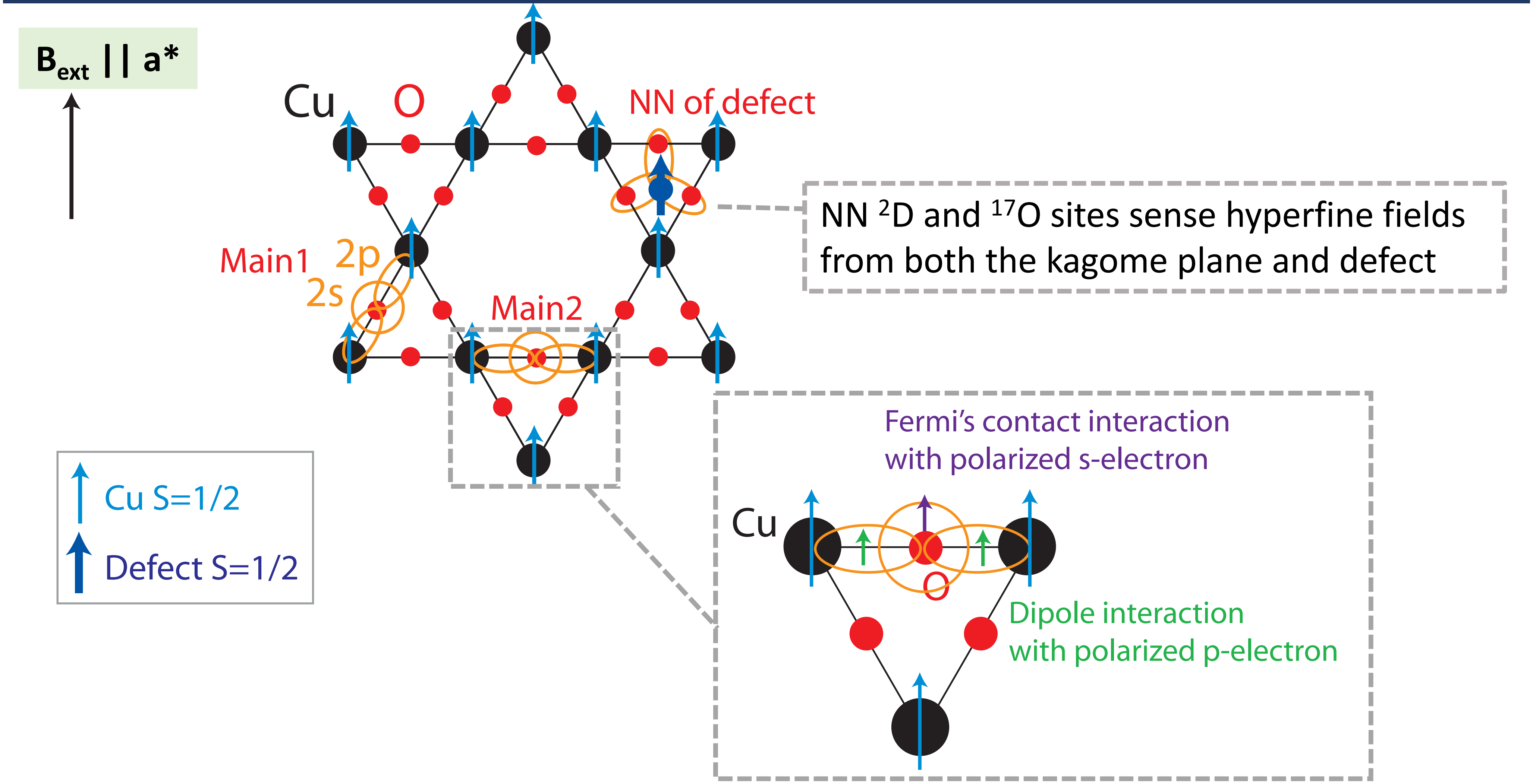


NN data points should have been negative

Positive shift (in field swept mode)

Try a different field geometry : B_{ext} || a*

(which we initially thought would be hopelessly complicated)



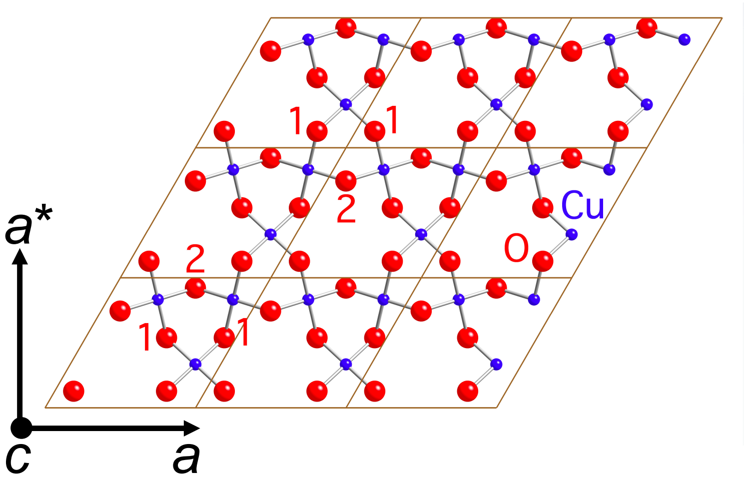
NN ^{2}D and ^{17}O sites sense hyperfine fields from both the kagome plane and defect

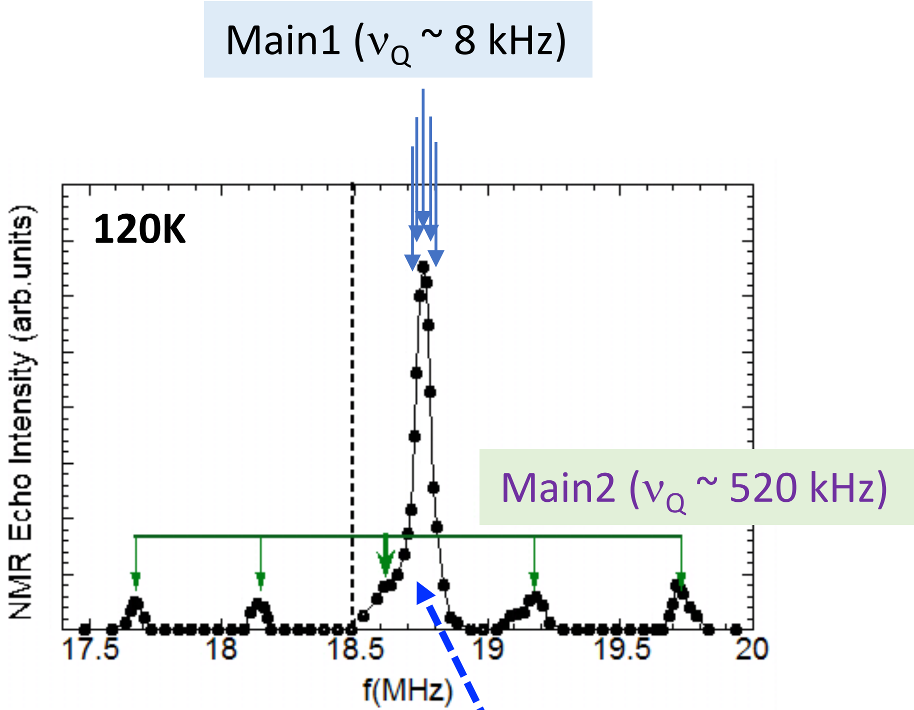
Fermi's contact interaction with polarized s-electron

Dipole interaction with polarized p-electron

- Hybridization between O 2s & 2p orbitals and Cu 3d orbital(s) transfers spin polarization to O sites.
- The latter interacts with the ^{17}O nuclear spin.
- *Main1, Main2, NN sites have different hyperfine fields from Cu sites, hence each of 5 NMR transitions split*

Intrinsic susceptibility χ_{kagome} of the kagome plane as determined from the ^{17}O Knight shift in B = 3.2 T || a*



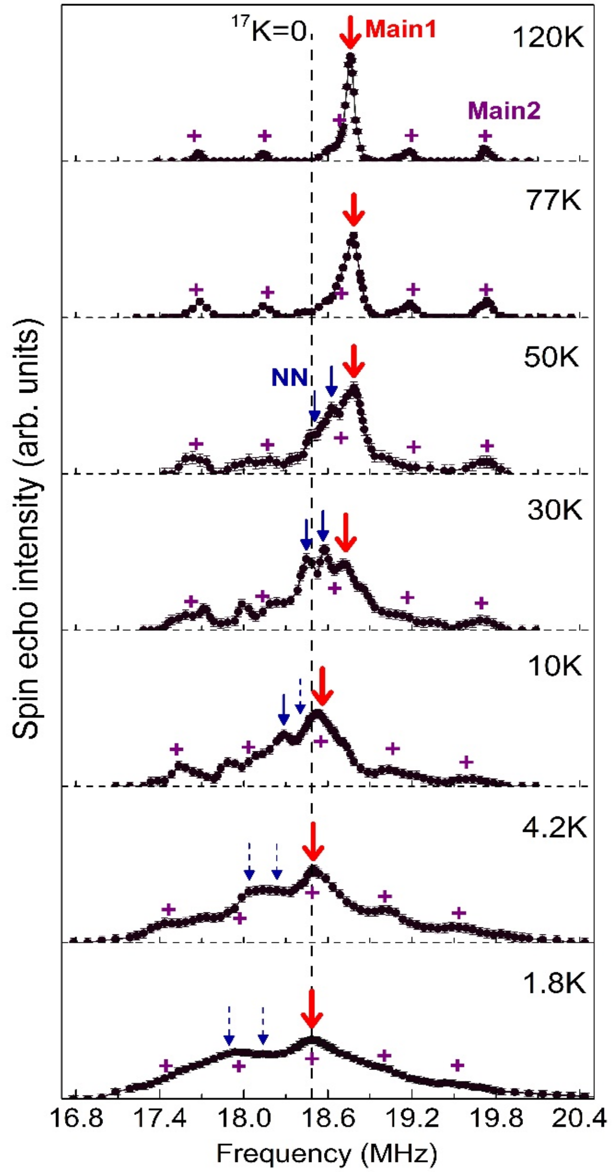


Hyperfine tensors depend on the relative orientation
of the magnetic field B with respect to the Cu-O-Cu bond axis.

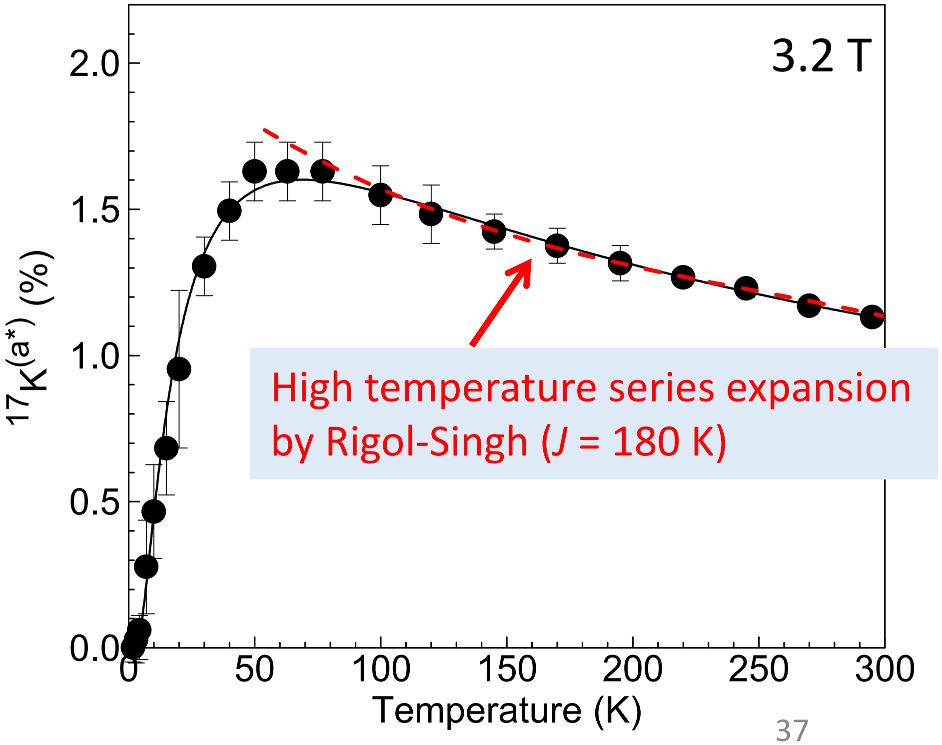
^{17}O NMR signals at **"Main1"** and "Main2" sites appear
separately with the intensity ratio ~ 2 : 1.

"Main1" sites happen to have ν_Q ~ 0 for B || a*. All 5 transitions appear together as a gigantic peak!!

Intrinsic susceptibility χ_{kagome} of the kagome plane as determined from the ^{17}O Knight shift at the main sites measured with B = 3.2 T || a*

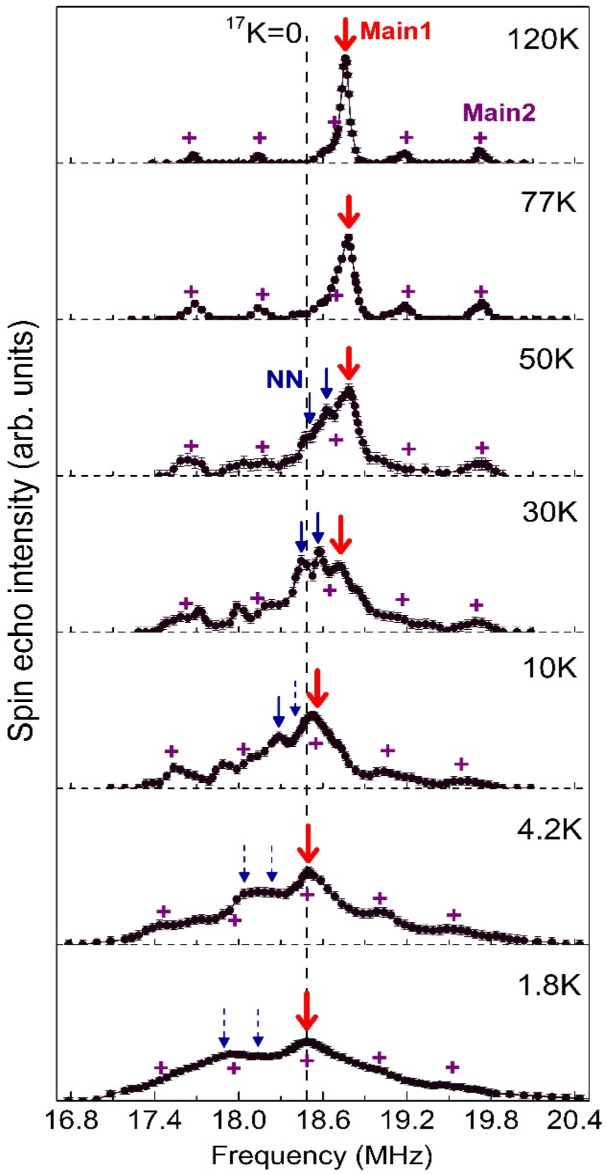


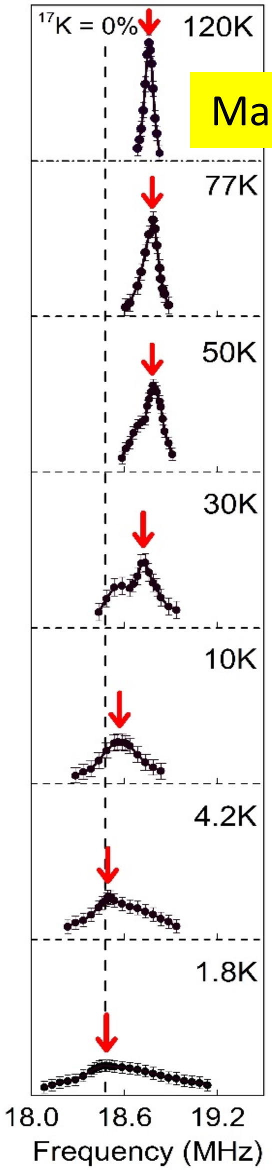
Larger frequency shift
Larger ^{17}K and χ_{kagome}



High temperature series expansion by Rigol-Singh (*J* = 180 K)

Intrinsic susceptibility χ_{kagome} of the kagome plane as determined from the ^{17}O Knight shift at the main sites measured with B = 3.2 T || a*

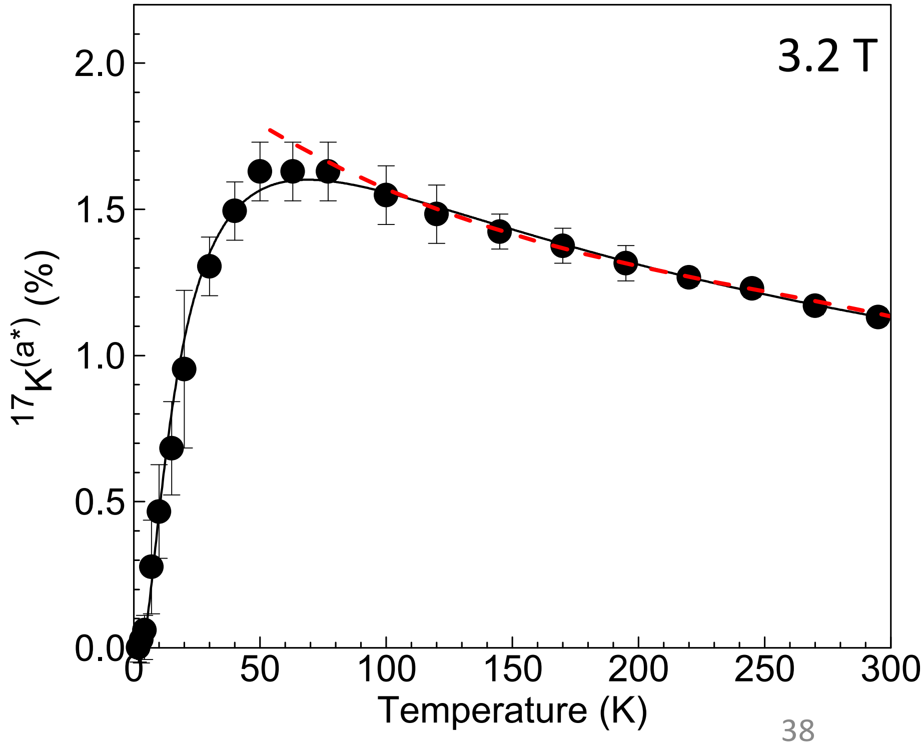




Main1 only (measured with long RF pulses)

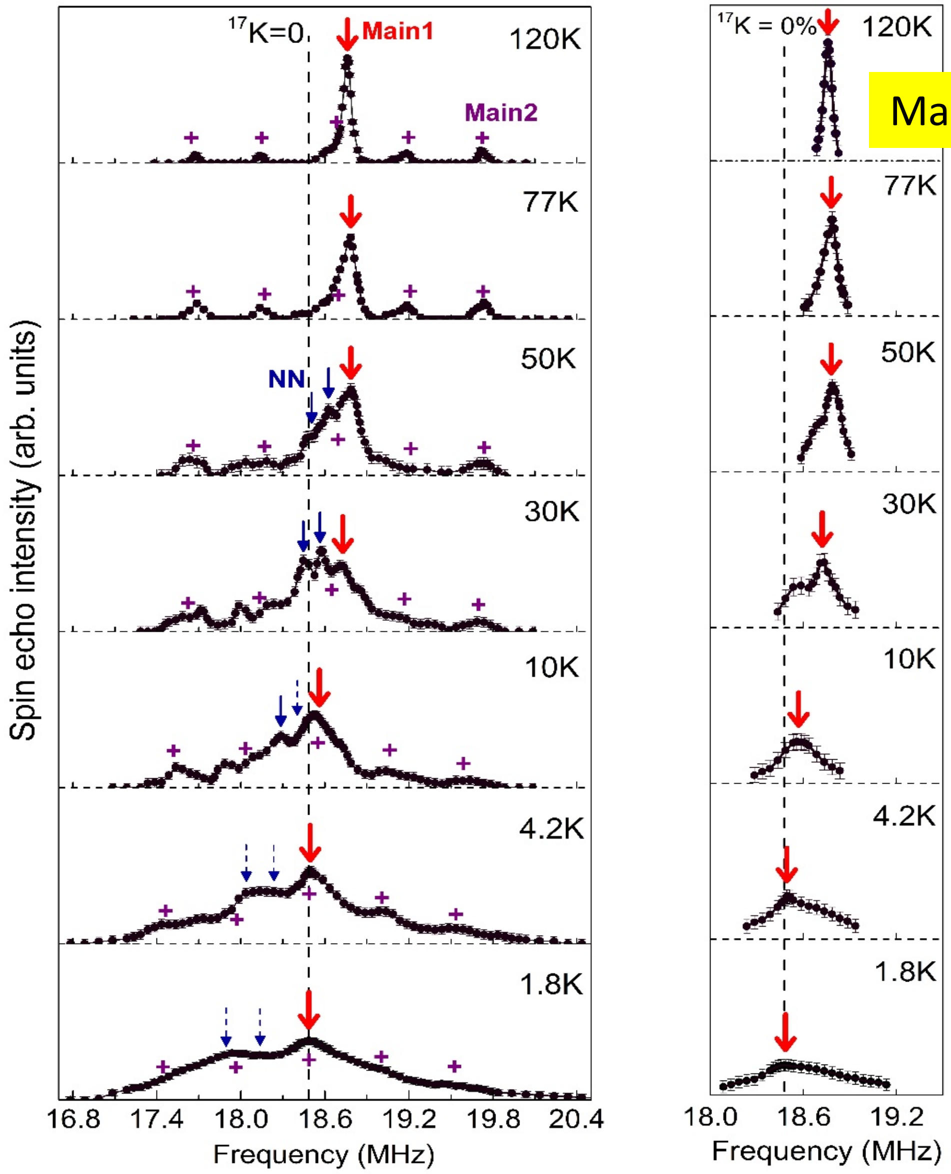
The optimal RF pulse width for Main1 is factor 2 ~ 3 times broader (because we flip all 5 transitions at the same time).

We can measure Main1 peak **selectively**, and observed the same results for ^{17}K.



Larger frequency shift
Larger ^{17}K and χ_{kagome}

Intrinsic susceptibility χ_{kagome} of the kagome plane as determined from the ^{17}O Knight shift at the main sites measured with B = 3.2 T || a*



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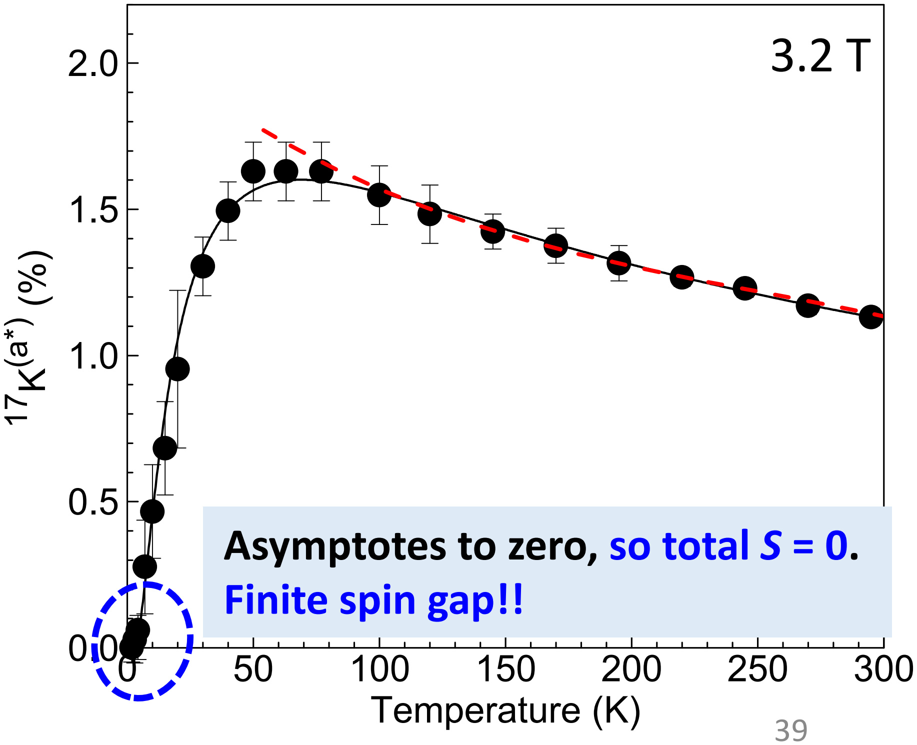
Larger frequency shift

Larger ^{17}K and χ_{kagome}

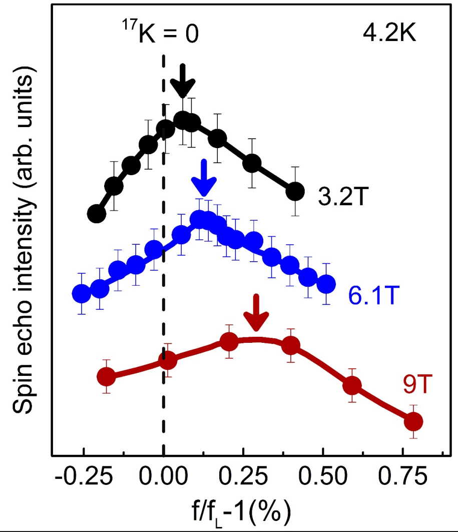


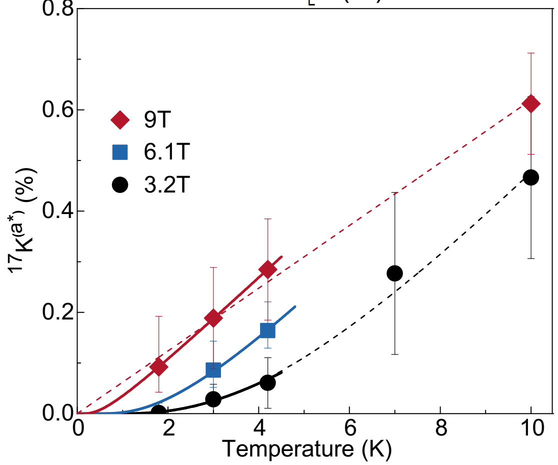
Asymptotes to zero, so total $S = 0$.

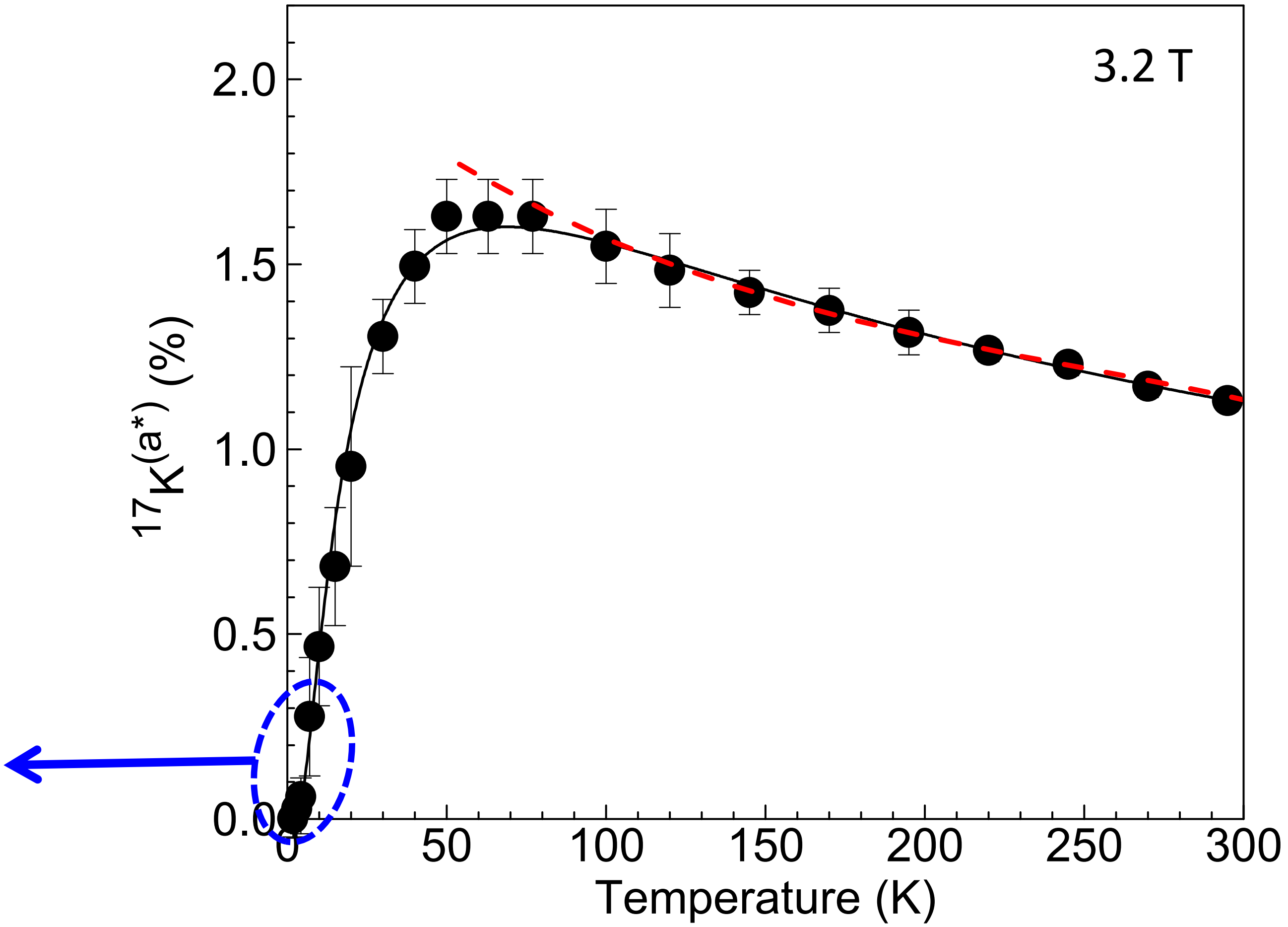
Finite spin gap!!

Magnetic field dependence of the gap

$^{17}K^{(a^*)}$ depends on |B| below ~10K



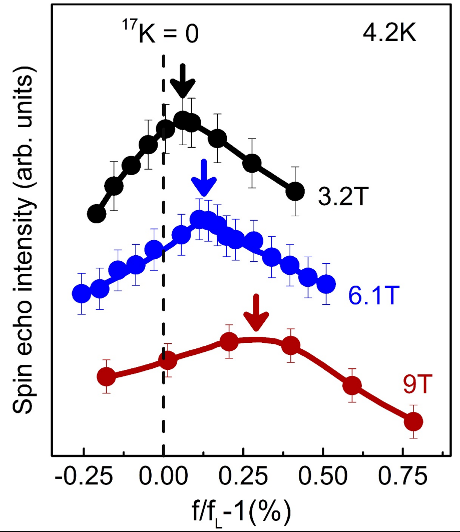


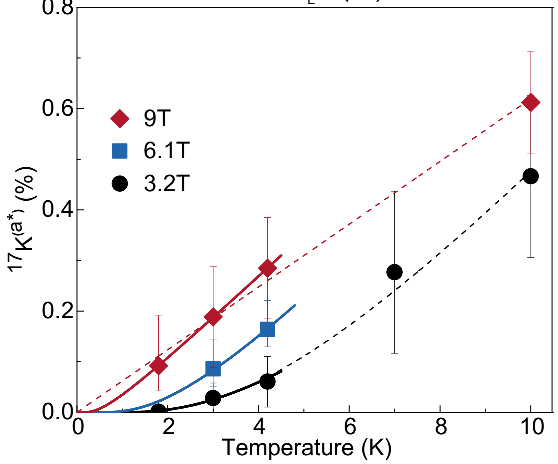


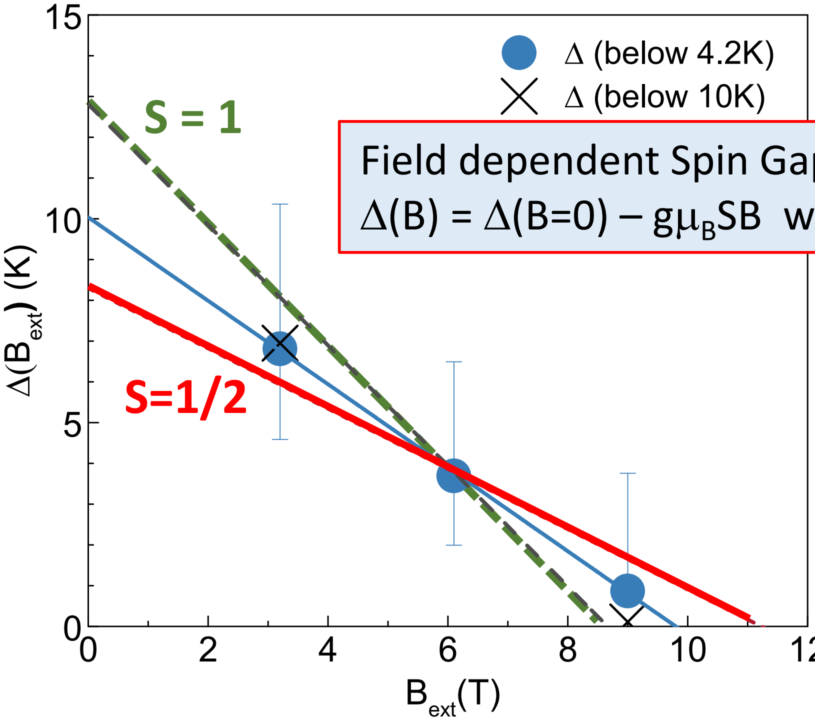
Solid (dashed) lines:
best fit to $^{17}K^{(a^*)} \sim T * \exp(-\Delta/T)$ below 4.2 K (10 K).
Pre-factor T: to account for the expected decrease caused by SRO
(also arises in Dirac Fermion Model, P.A. Lee, private communications).

Magnetic field dependence of the gap: $\Delta(B_{ext} \rightarrow 0) \sim 0.05J$

$^{17}K^{(a*)}$ depends on |B| below ~10K







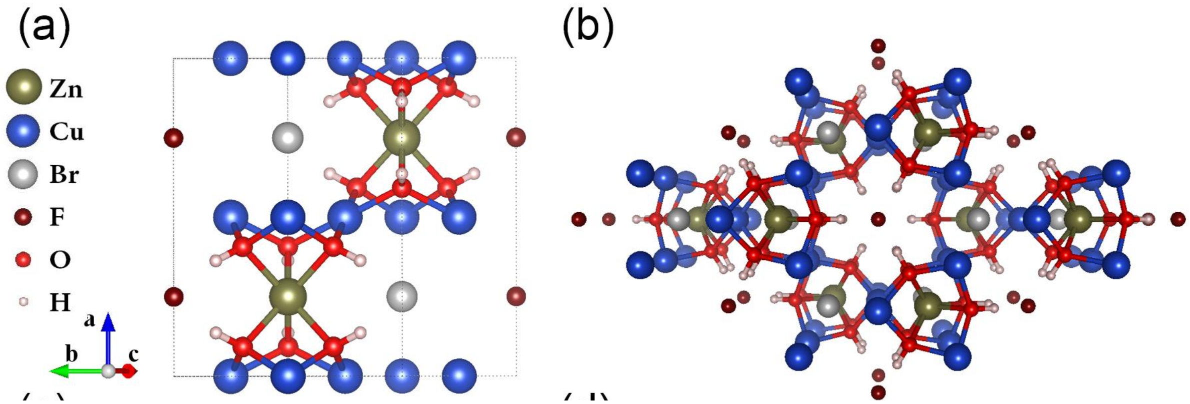
Field dependent Spin Gap:
$\Delta(B) = \Delta(B{=}0) - g\mu_B SB$ with **S=1/2 spinons**

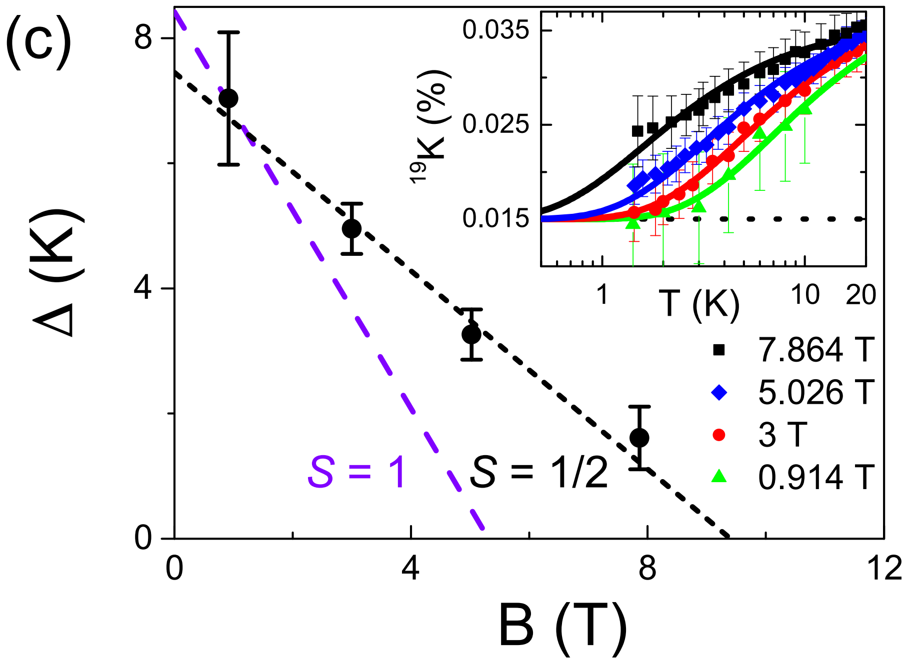
Δ(0) ~ 10 K, hence Δ(0) ~ 0.05 J
Consistent with DMRG calculations, Yan *et al.*, *Science* (2011)
Note: we cannot entirely rule out **S = 1** excitations.

Solid (dashed) lines:
best fit to $^{17}K^{(a^*)} \sim T * \exp(-\Delta/T)$ below 4.2 K (10 K).
Pre-factor T: to account for the expected decrease caused by SRO
(also arises in Dirac Fermion Model, P.A. Lee, private communications).

Spin ½ excitations in Barlowite $Cu_3Zn(OH)_6FBr$ from 19-F NMR (?)

Z. Feng, G.-q. Zheng et al.
arXiv:1702.01658





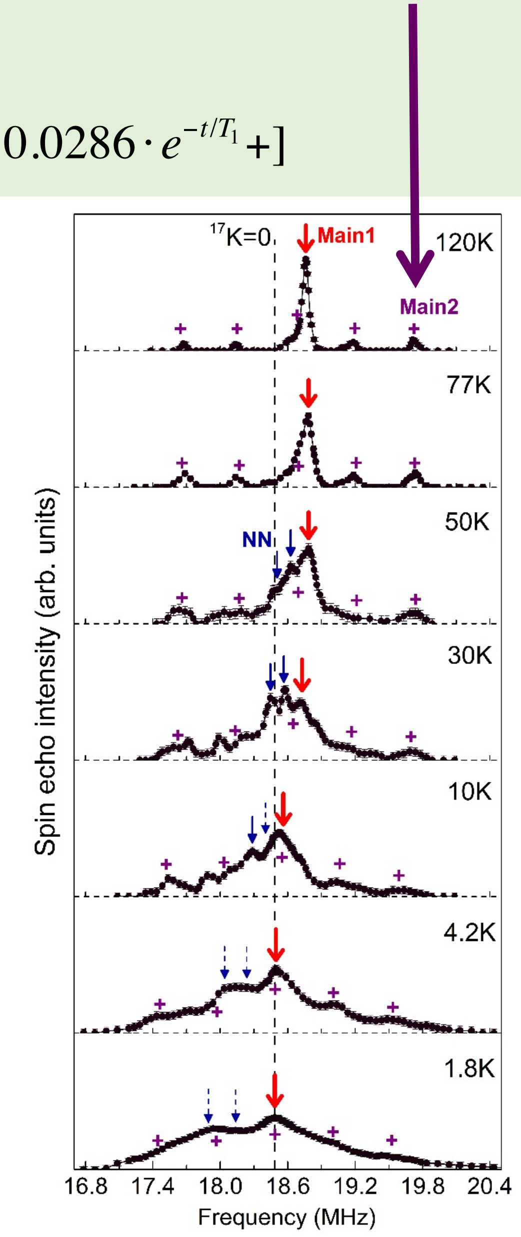
Additional evidence for a finite gap Δ based on low-frequency spin dynamics

^{17}O nuclear spin-lattice relaxation rate $1/T_1$ at Main2 sites

We measured $1/T_1$ in B = 3.2 or 9 T using the isolated, clean, upper-most Main2 satellite peak for the I_z = 3/2 to 5/2 transition to obtain reliable results.

$$\frac{M(t)}{M(\infty)} = 1 - [0.0714 \cdot e^{-15t/T_1} + 0.2857 \cdot e^{-10t/T_1} + 0.4 \cdot e^{-6t/T_1} + 0.2143 \cdot e^{-3t/T_1} + 0.0286 \cdot e^{-t/T_1} +]$$

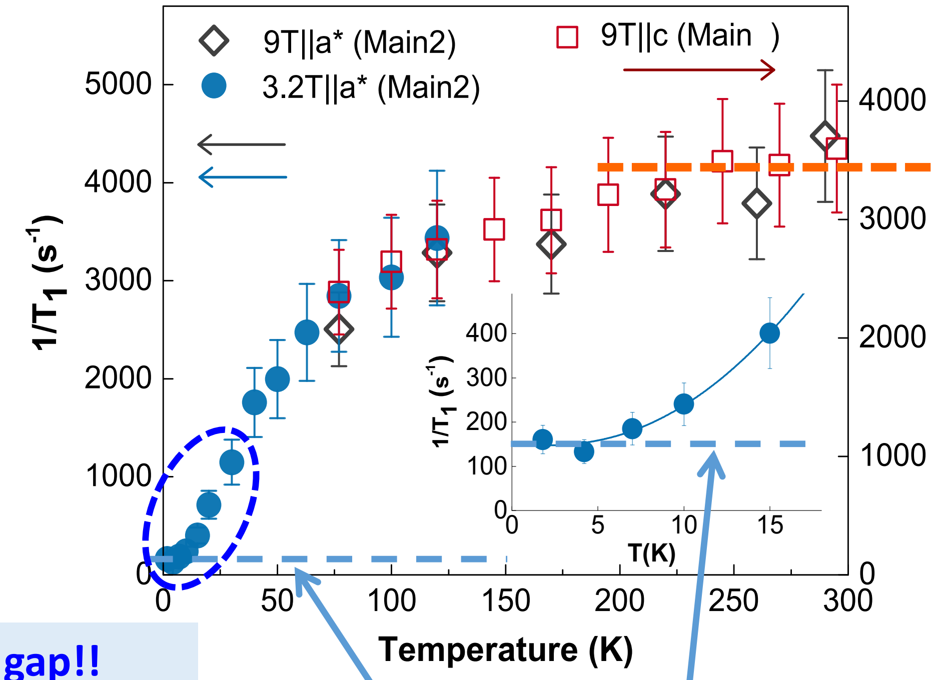
Note: this is the only way to measure $1/T_1$ accurately at the ^{17}O sites, even though the signal intensity is miserably small!



Additional evidence for a finite gap Δ based on low-frequency spin dynamics

^{17}O nuclear spin-lattice relaxation rate $1/T_1$ at the Main site

$$\frac{1}{T_1} \propto T \cdot \sum_{\vec{q}} |A_{hf}(\vec{q})|^2 \frac{\chi''(\vec{q}, f_{NMR})}{f_{NMR}} \sim \sum_{\vec{q}} |A_{hf}(\vec{q})|^2 S(\vec{q}, f_{NMR})$$



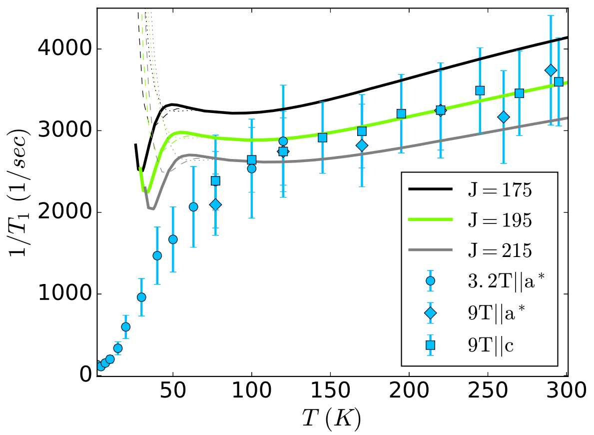
$$(1/T_1)_\infty \sim \frac{A_{hf}^2}{J} \sim 3{,}300 \quad \text{sec}^{-1}$$

Parameter-free theoretical estimation in the high temperature limit ($T >> J$) based on Moriya's Gaussian approximation applied to kagome Heisenberg model (J = 180 K)

Spin gap!!

Δ ~ 7 K in 3.2T

Defect contribution (in-gap excitations)



N.Sherman, T.I., R.R.P. Singh
PRB 94 (2016) 140415(R).

A comparable gap Δ deduced from inelastic neutron scattering

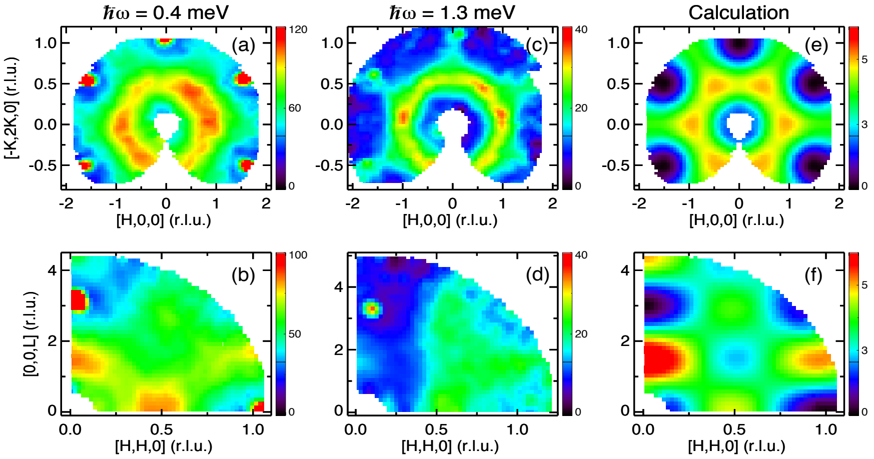
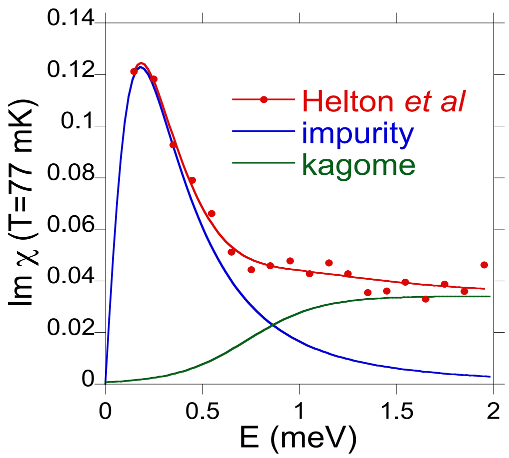


FIG. 12 (Color online) Momentum structure of the INS data at 0.4 meV and 1.3 meV for single crystal herbertsmithite at 2 K in the (HK0) scattering plane (top row) and (HHL) scattering plane (bottom row) (Han *et al.*, 2015). The plots in the right column are the calculated structure factor for near neighbor AF correlations between copper defects on the zinc sites, taking into account the copper form factor. These correspond to correlations between the brown and the gray sites of Fig. 1, which sit in successive triangular planes.

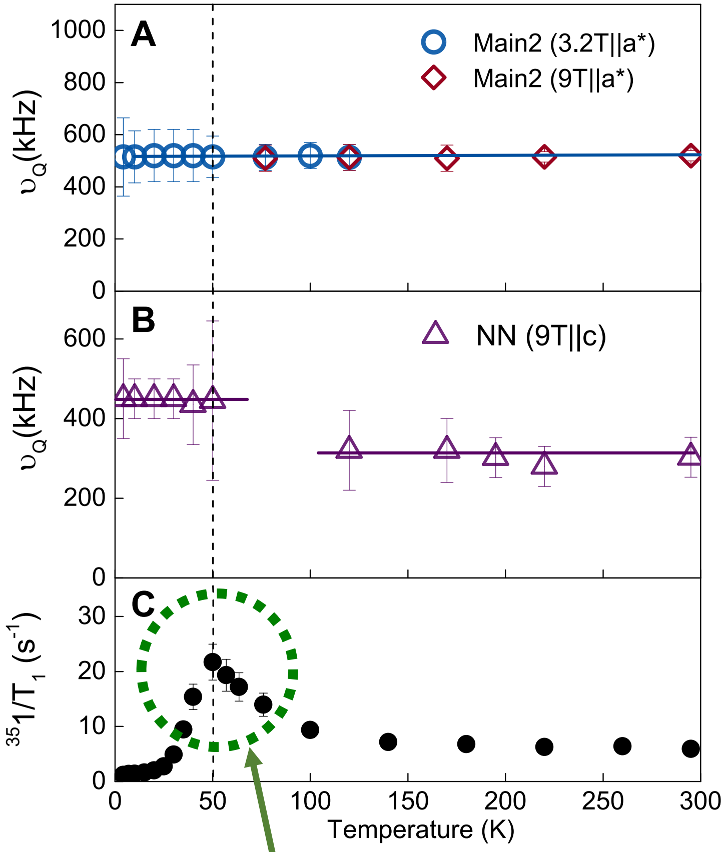


Magnitude of gap comparable to NMR results

T.-H. Han, M. Norman, Y.S. Lee *et al.*
PRB (2016). Arxiv:1604.03048

Additional complications caused by defects

Supplementary Materials, Science (2015) Fu, *T.I. et al*

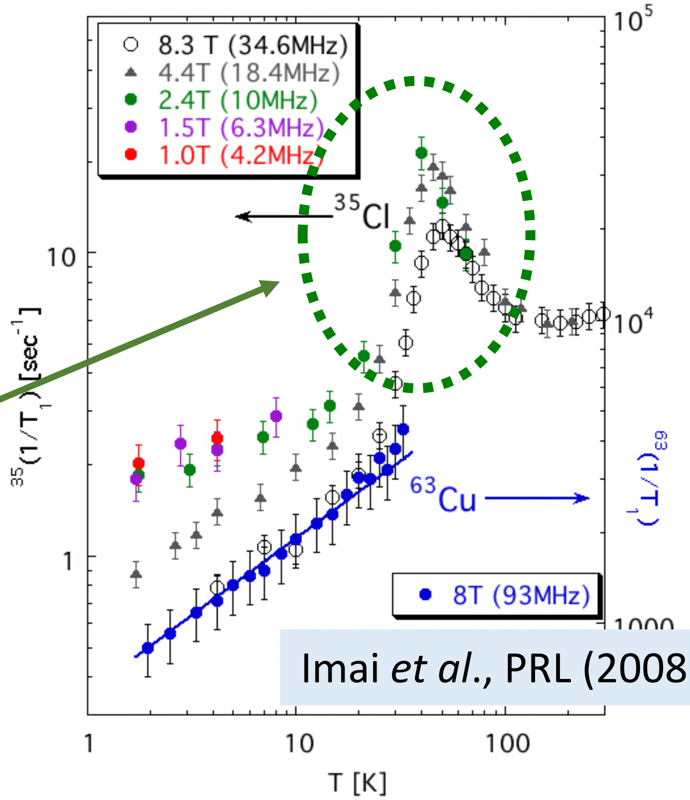


ν_Q stays constant for the Main^{17}O sites

Average structure of the kagome plain remains unchanged

ν_Q changes for the NN ^{17}O sites

Local structure deforms near the defects.



Imai *et al.*, PRL (2008)

Bump of $1/T_1$ at ^{35}Cl sites; depends on frequency.

Something is slowly freezing below 50K.

Key Conclusions

- Cu^{2+} defect spins occupy the Zn sites with ~15% probability; $(Zn_{0.85}Cu_{0.15})Cu_3(OH)_6Cl_2$.

- Defect spins exhibits Curie-Weiss behavior: $\chi_{defect} \sim C/(T + \theta)$ with $\theta \sim +1$ K.

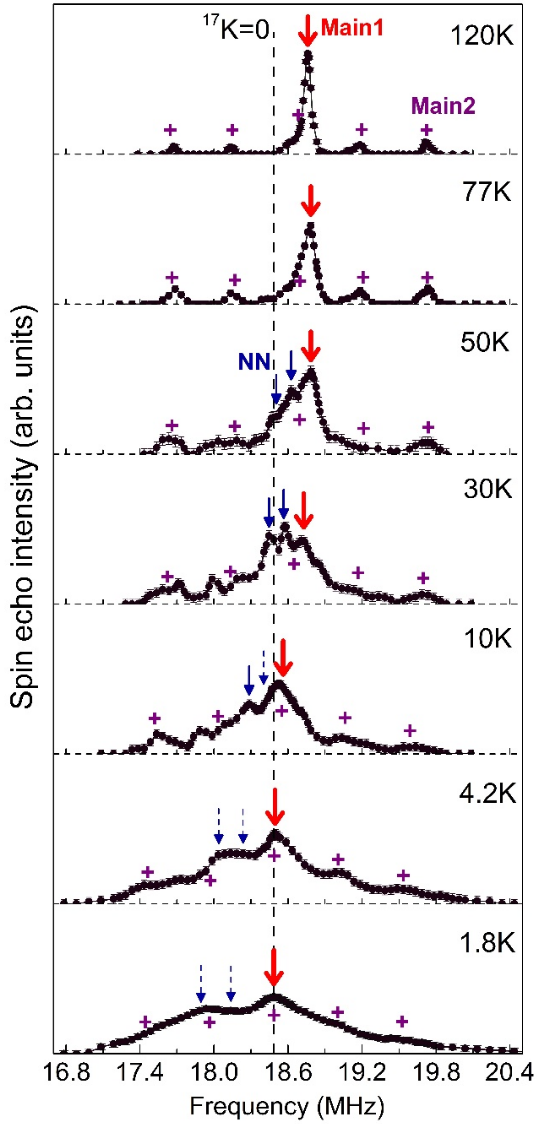
- No evidence for Zn anti-site defects at the kagome Cu sites in anomalous X-ray, powder Rietveld refinement, ^{2}D single-crystal NMR, nor ^{17}O single crystal NMR.

- kagome spin susceptibility $\chi_{kagome} \rightarrow 0$ at $T = 0$ with a small, field-dependent gap; $\Delta \sim 0.05J$.

- Lattice deformation freezes in the immediate vicinity of defects below ~50 K;
(Open question) effects on the overall magnetism of the kagome planes?

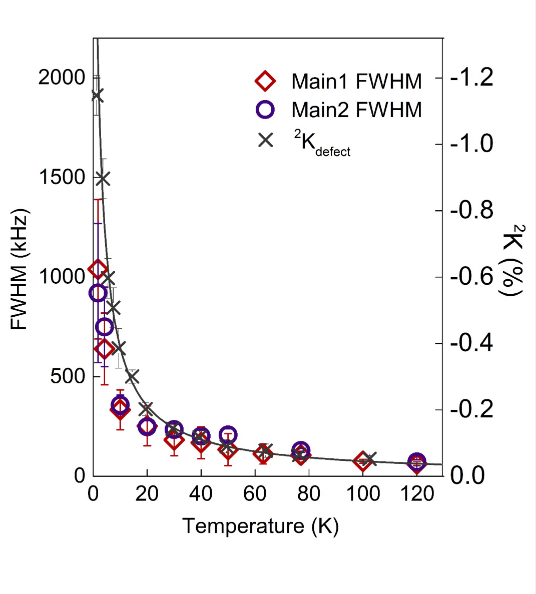
Thank you for your attention!

Intrinsic susceptibility χ_{kagome} of the kagome plane as determined from the ^{17}O Knight shift at the main sites measured with B = 3.2 T || a*



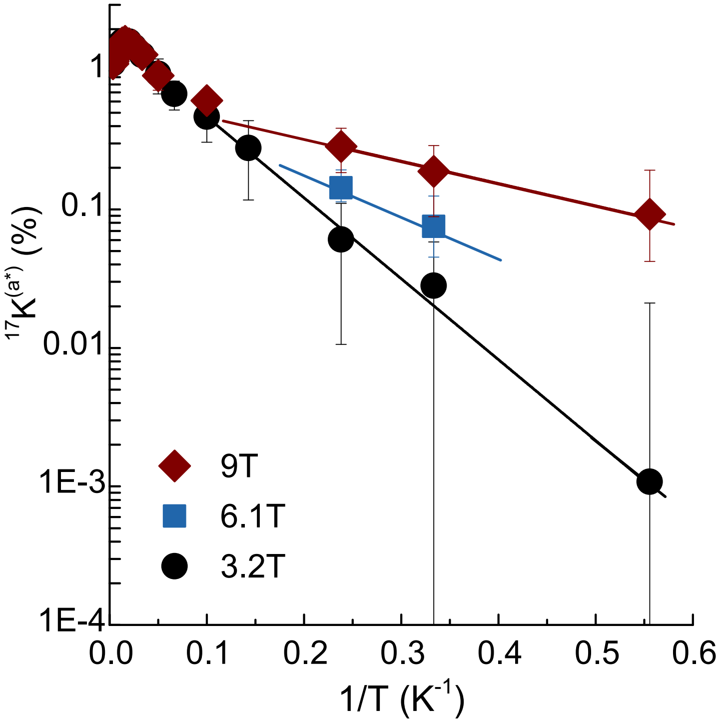
Larger frequency shift
Larger ^{17}K
Larger χ_{kagome}

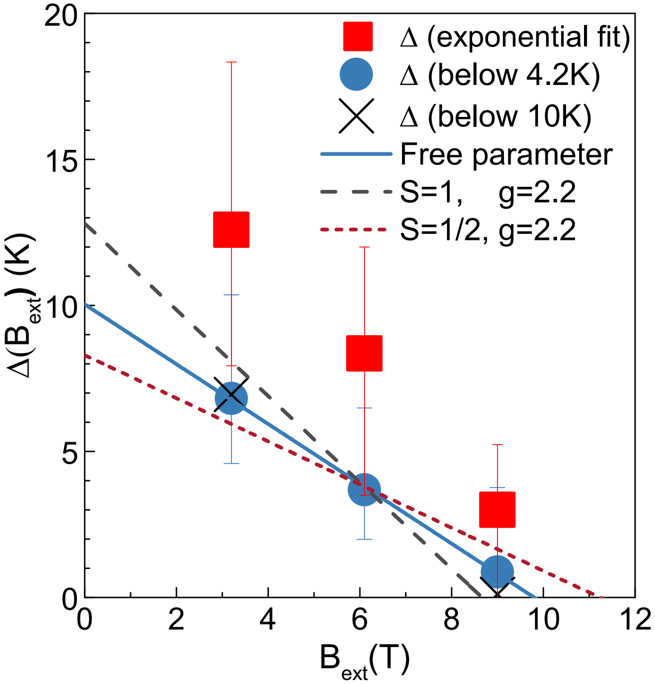
- All NMR lines broaden in proportion to χ_{defect}.



- But we can trace the Main1 peak down to 1.8 K (~0.01J), because it is singularly larger than all other peaks.
- Main1 peak frequency reaches a maximum at ~60K, then **shifts back to the zero Knight shift position at low temperatures.**
- We cannot resolve the central peak of Main2, but its uppermost satellite peak displays qualitatively the same trend.

Magnetic field dependence of the gap --- alternate fits with a simple exponential function





Semi-quantitatively the same results for Δ