Kagome Quantum Spin Liquids: the case of herbertsmithite (and beyond?)

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Spectroscopies of Quantum Materials
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Université Paris-Saclay, France

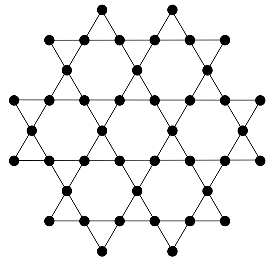
Kagome materials: QSL candidates

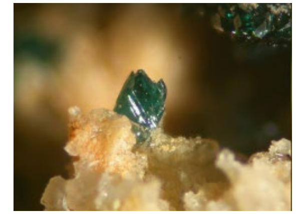
Kagome materials (Heisenberg, Quantum)

- Good realizations (+ small perturbations)

herbertsmithite $ZnCu_3(OH)_6Cl_2$

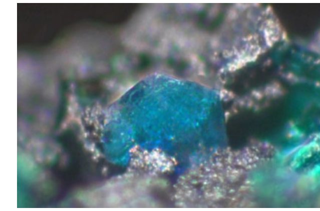
Zn-barlowite $ZnCu_3(OH)_6FBr$





Herbertsmithite

Shores et al, JACS, 2005



Barlowite

Han et al, PRL 2014

-> Signature of QSL : no LRO, continuum of excitations …

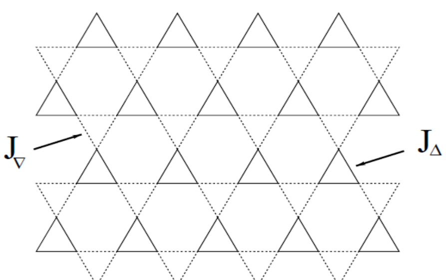
-> Type of QSL (gapped, gapless..), nature of the excitations remains challenging

- Modified kagome lattice : a side view, extending the phase diagram

-> new (quantum) states

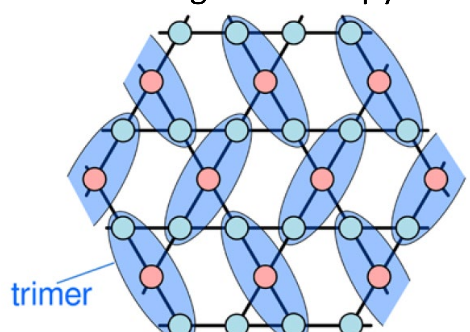
-> feedback on the kagome problem ?

Breathing kagome



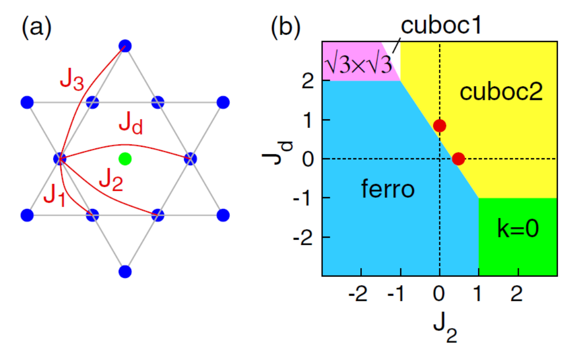
$[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$: Orain, PRL (2017)
Repellin, PRB (2017); Iqbal PRB (2018) ..

Exchange anisotropy



Volborthite $Cu_3V_2O_7(OH)_2{\cdot}2H_2O$: Hiroi, JPSJ (2001)
Janson PRL (2016), Yoshida PRB (2017)..

Competing exchange interactions



Zn-Kapellasite $ZnCu_3(OH)_6Cl_2$: Fak, PRL (2012)
Bieri, PRB (2016)…

Herbertsmithite, a spin liquid: no order, which is it?

M.R. Norman, RMP (2016)
Exp Reviews
C. Broholm et al. Science (2020)

J|A|C|S
COMMUNICATIONS

Published on Web 09/09/2005

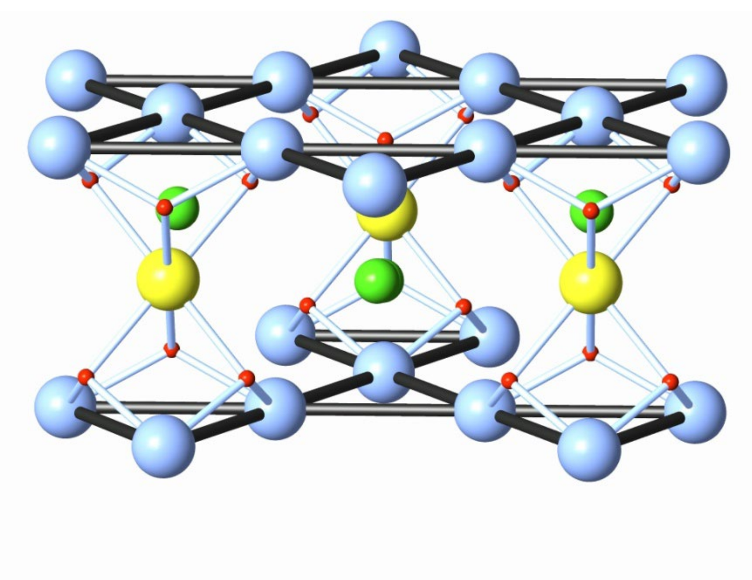
A Structurally Perfect $S = {}^{1}/_{2}$ Kagomé Antiferromagnet

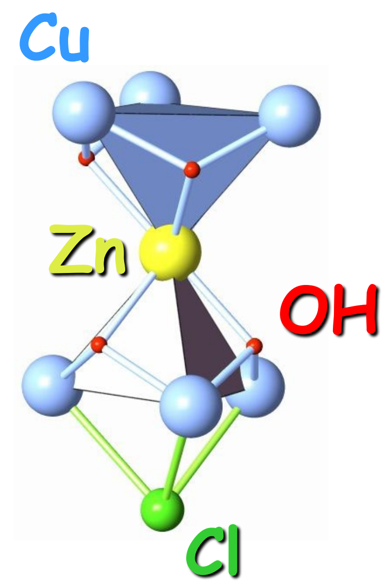
Matthew P. Shores, Emily A. Nytko, Bart M. Bartlett, and Daniel G. Nocera*

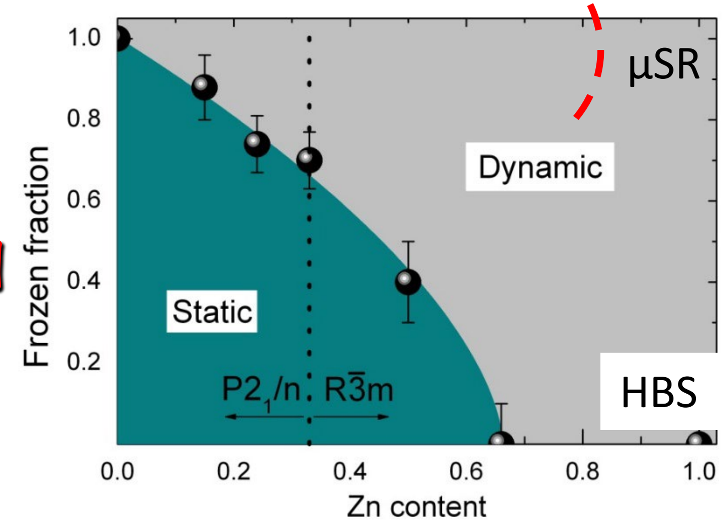
Department of Chemistry, 6-335, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139-4307

Herbertsmithite (HS): $ZnCu_3(OH)_6Cl_2$ Cu^{2+}, S=1/2; J=190 K (AF)

No freezing (at +/- 6×10^{-4} μ_B) down to 20 mK (J/9000) !







P. Mendels et al, PRL 98 (2007)

Interlayer, n.n. 2nd , 3rd n.n. couplings < 5 K (H. Jeschke, Phys. Rev. B 2013)

A spin liquid: no order. 15 years later: which is it?

M.R. Norman, RMP (2016)
Exp Reviews
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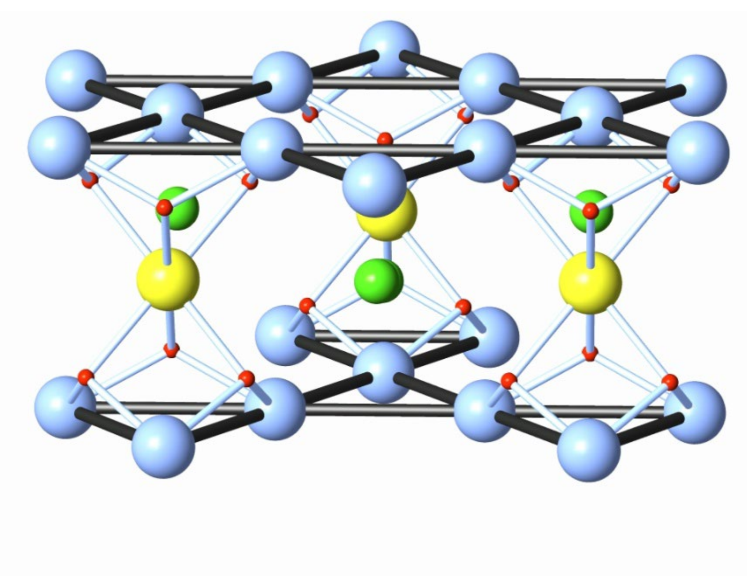
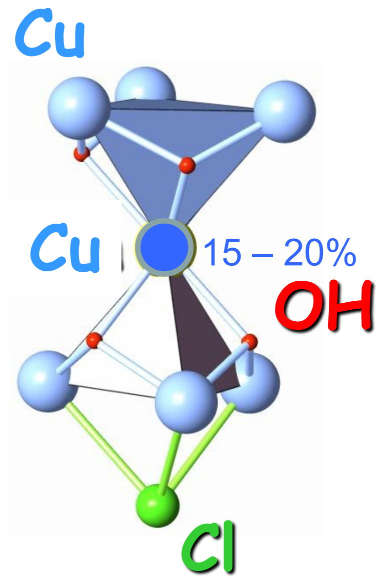
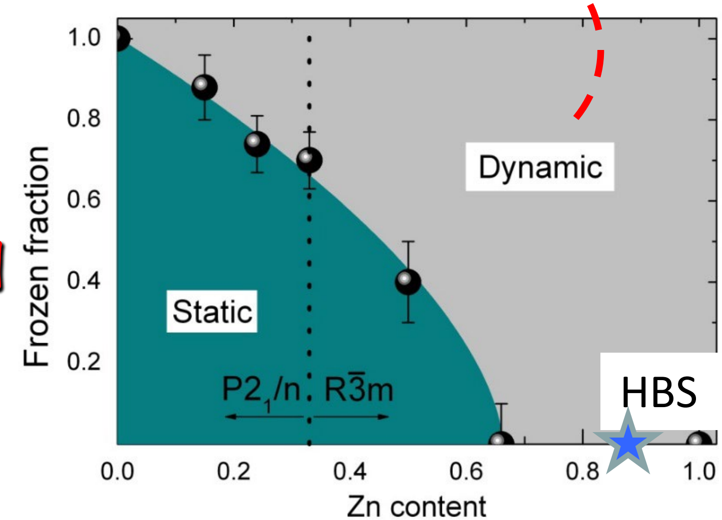




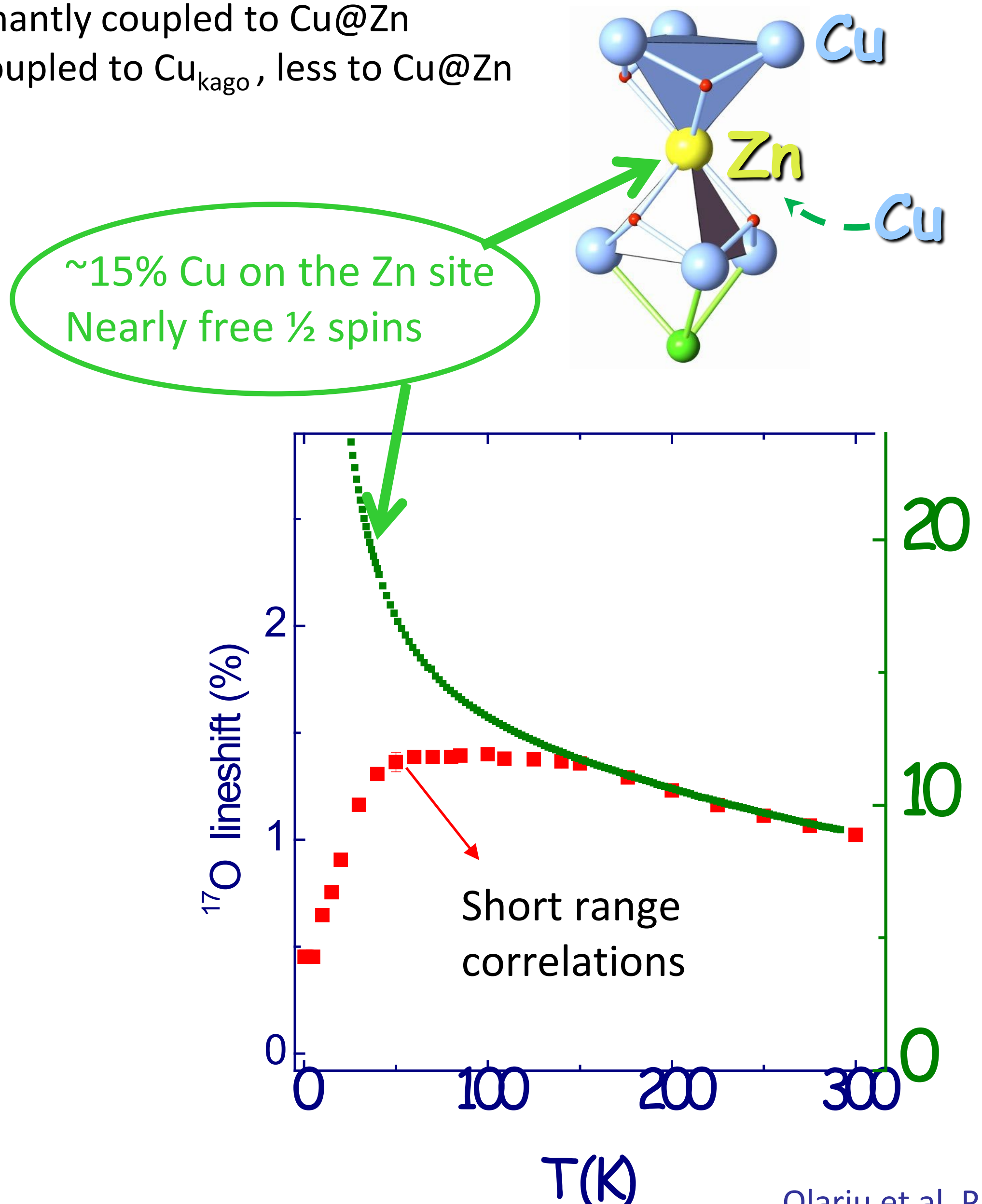


P. Mendels et al, PRL 98 (2007)

No Zn on kagome site (Smaha, Phys. Rev. Materials 2020)

Site selective spectroscopy: ^{17}O NMR

Nuclei:
- Cl, H, D are dominantly coupled to Cu@Zn
- O dominantly coupled to Cu_{kago} , less to Cu@Zn



Olariu et al, PRL 100, 087202 (2008)

Low-T NMR and C_p investigations of kagome herbertsmithite crystals

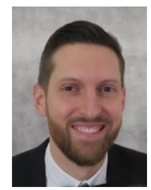
Nature Physics 16, 469-474 (2020)
Phys Rev X, 12, 011014 (2022)

P. Mendels, Lab. Physique des Solides, Univ. Paris-Saclay
Spectrocopies of Quantum Materials

P. Khuntia, F. Bert, E. Kermarrec, Q. Barthélemy

Now IIT Madras

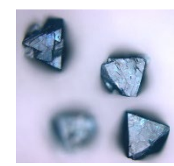
Post-doc



PhD

Now IQ Sherbrooke

- ✓ M. Velazquez (crystals): ICMCB, INP Grenoble (France)



- ✓ A. DeMuer, C. Marcenat, T. Klein (C_p): LNCMI & Néel (Grenoble)

- ✓ B. Bernu, L. Messio (Theory): LPTMC, (Paris)

A spin liquid : yes, but gapped or gapless?

SCIENCE sciencemag.org

FRUSTRATED MAGNETISM

Imai's group

Evidence for a gapped spin-liquid ground state in a kagome Heisenberg antiferromagnet

2015

Mingxuan Fu,[1] Takashi Imai,[1,2*] Tian-Heng Han,[3,4] Young S. Lee[5,6]

nature physics ARTICLES
https://doi.org/10.1038/s41567-020-0792-1
Check for updates

Mendels' group

Gapless ground state in the archetypal quantum kagome antiferromagnet $ZnCu_3(OH)_6Cl_2$

2020

P. Khuntia[1,2], M. Velazquez[3,4], Q. Barthélemy[1], F. Bert[1], E. Kermarrec[1], A. Legros[1], B. Bernu[5], L. Messio[5,6], A. Zorko[7,8] and P. Mendels[1]✉

nature physics LETTERS
https://doi.org/10.1038/s41567-021-01310-3
Check for updates

Imai's group

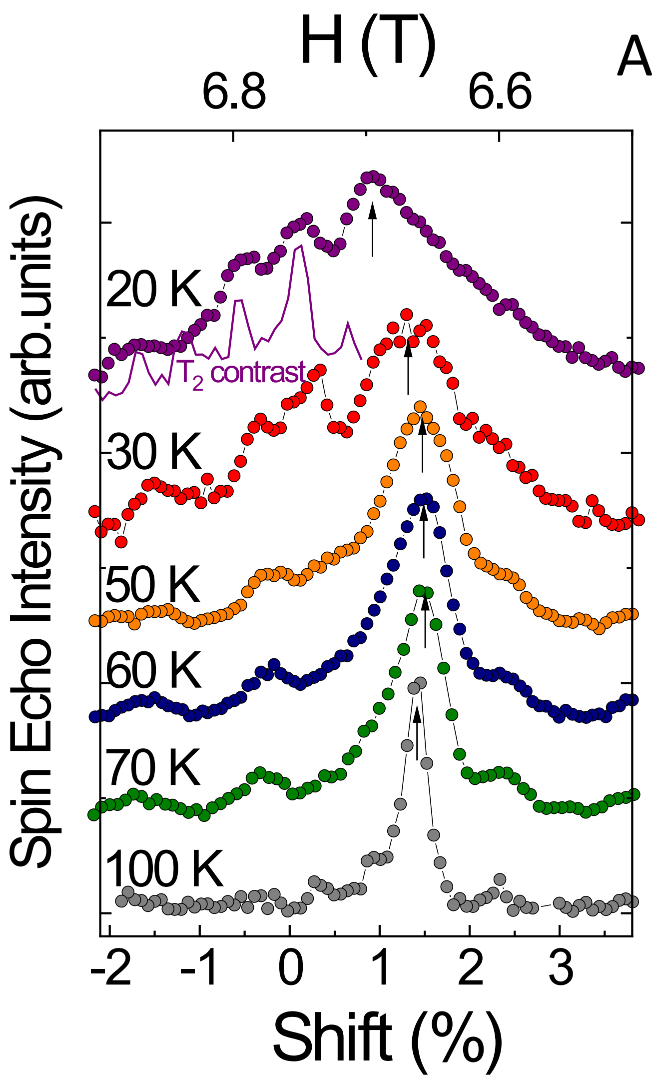
Emergence of spin singlets with inhomogeneous gaps in the kagome lattice Heisenberg antiferromagnets Zn-barlowite and herbertsmithite

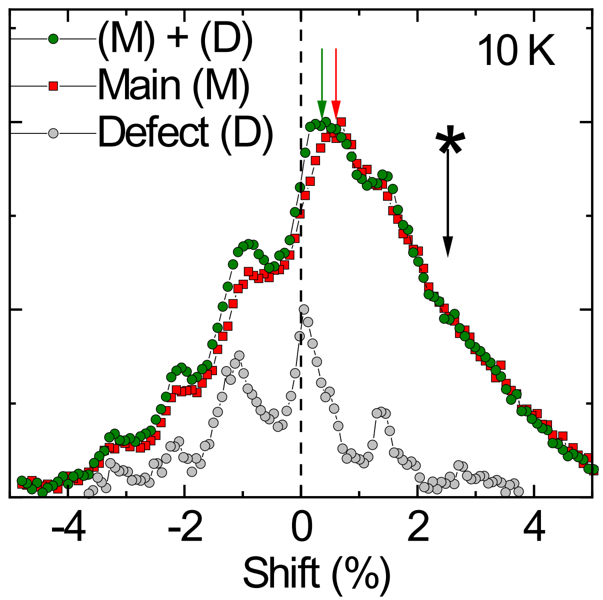
2021

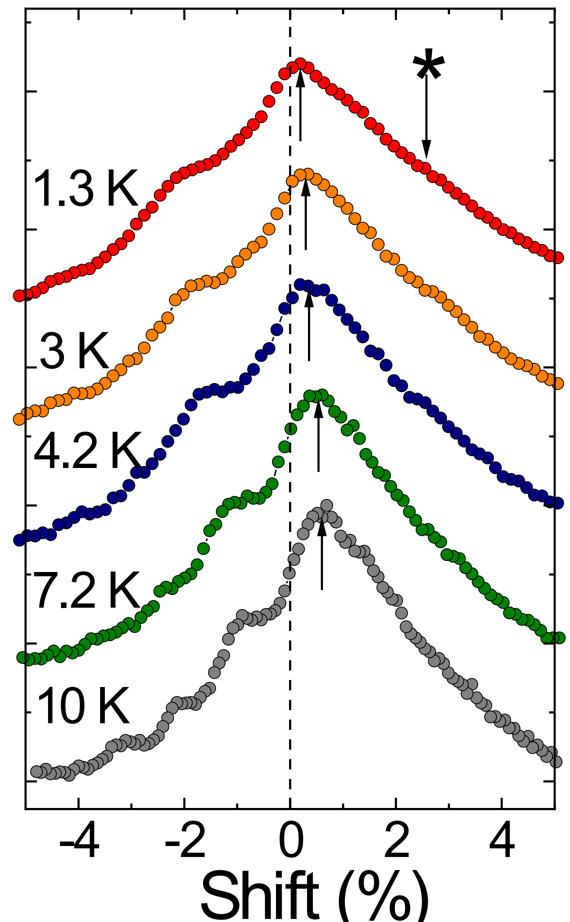
Jiaming Wang[1], Weishi Yuan[1], Philip M. Singer[2], Rebecca W. Smaha[3,4], Wei He[3,5], Jiajia Wen[3], Young S. Lee[3,6] and Takashi Imai[1,7]✉

Two (or more) spectral components → deconvolution

Applied field // a^* (McMaster)







No contrast

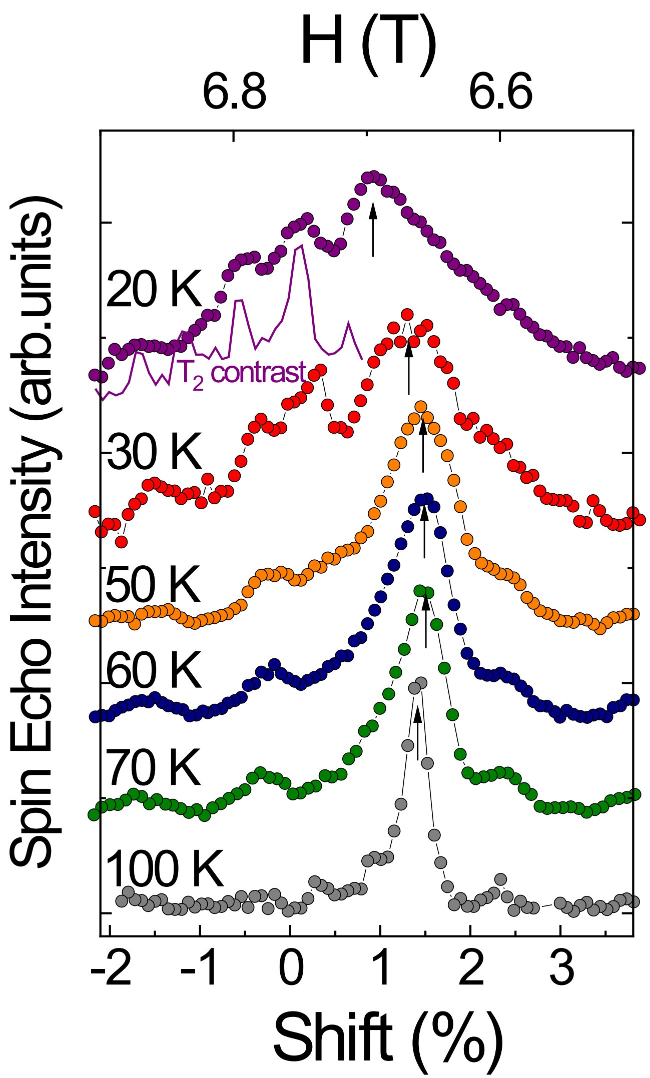
T_2 contrast

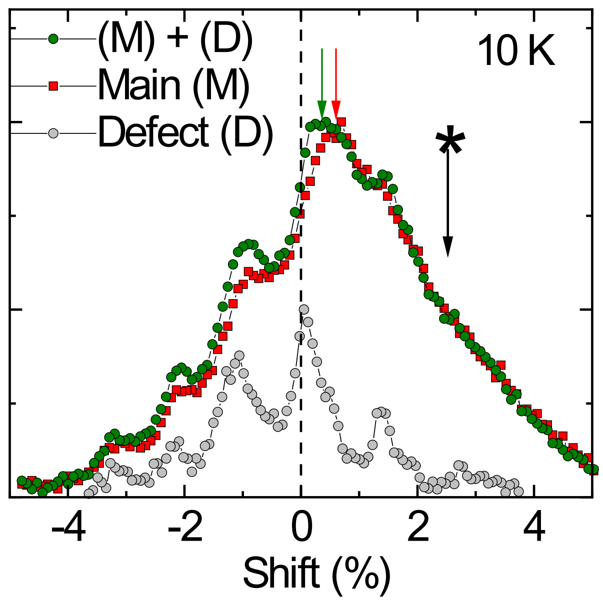
T_1 contrast

T=1.2 K

From long T_2, short T_2 component & spectral integration ~ 45% (D) weight)
From smoothing out singularities of (M) + (D) spectrum ~ 39(4)% (D) weight

A New T-scale : T < 30 K





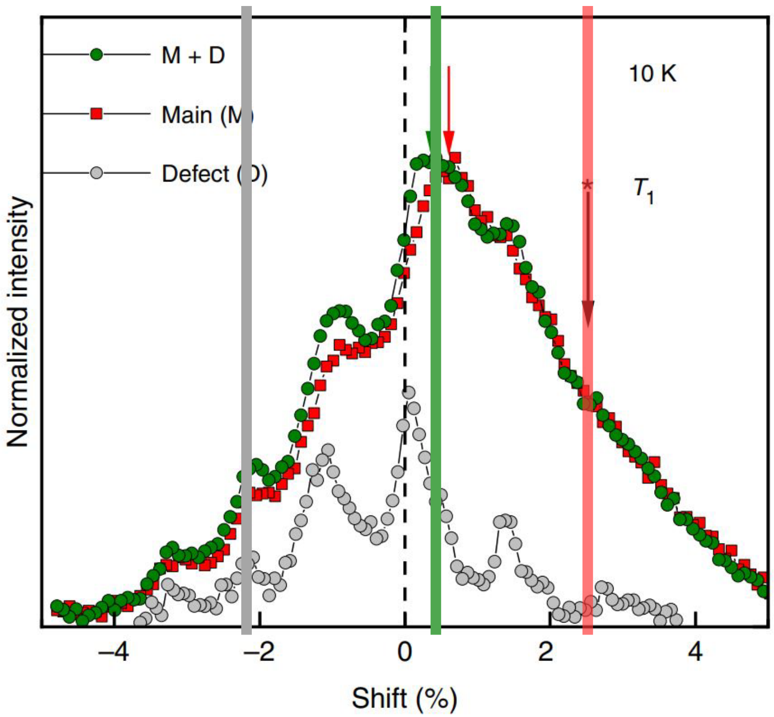
Spectrum with narrower peaks only resolved below 30 K

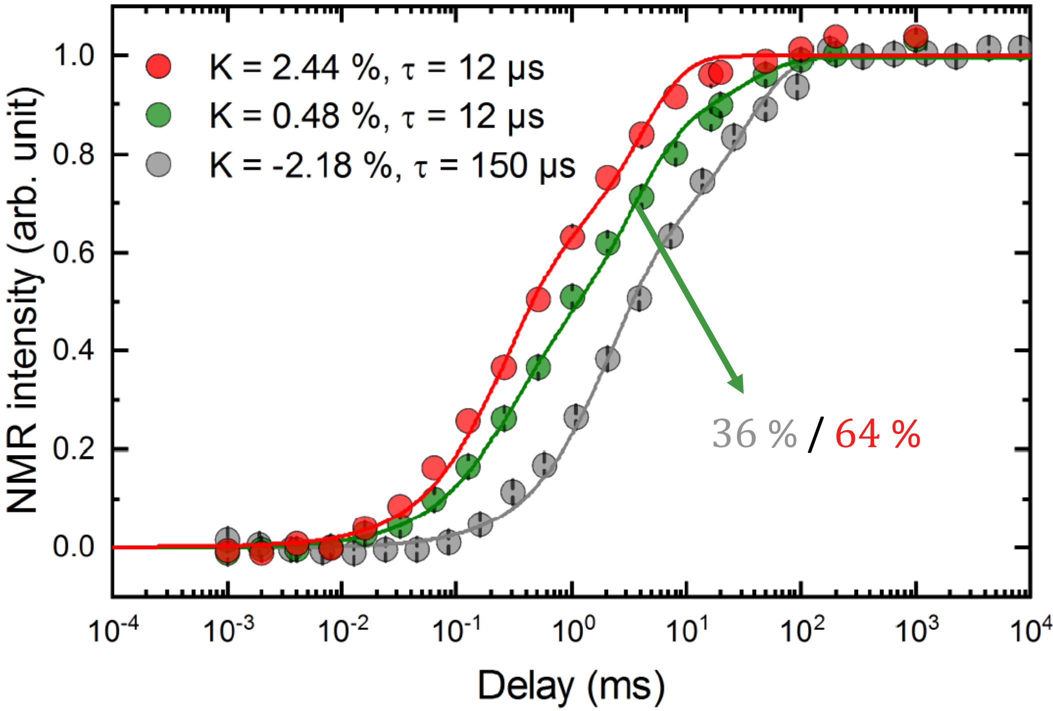
Typical of the spin liquid state?

Low-T Spin Dynamics T_1 : 2 components spectrally resolved

B//a* 6.6 T

$$\frac{1}{T_1} = \frac{1}{\hbar^2} \frac{k_B T}{(g\mu_B)^2} \sum_q |A(q)|^2 \frac{\chi_t''(q,\omega_n)}{\omega_n}$$





P. Khuntia et al. Nat. Phys. 2020

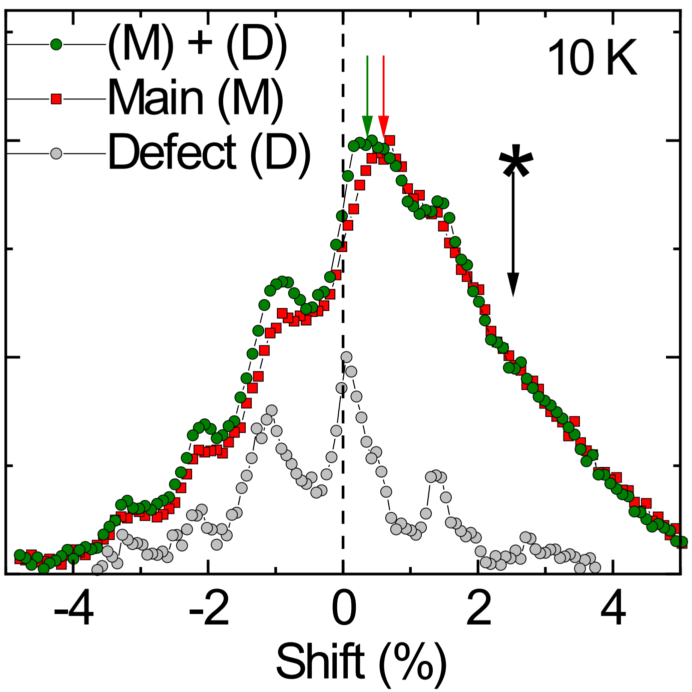
dominantly gapless

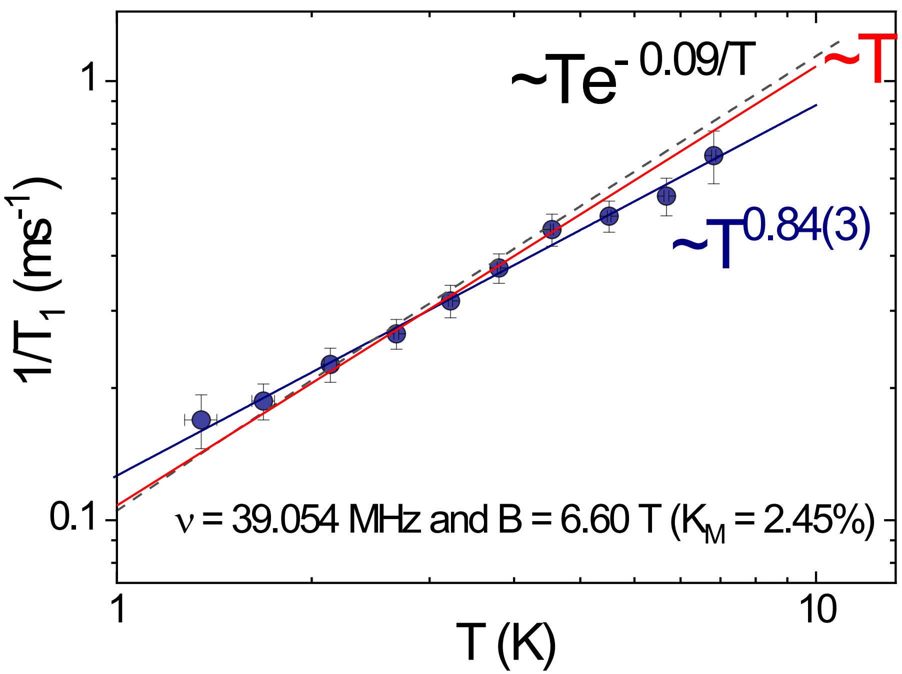
From long T_2, short T_2 component & spectral integration ~ 45% (D) weight
From smoothing out singularities of (M) + (D) spectrum ~ 39(4) % (D) weight
From T1 (amplitude) ~ 36% (D) weight

Low-T Spin Dynamics T_1

B//a* 6.6 T

$$\frac{1}{T_1} \sim \int_{-\infty}^{\infty} < B_L^+(t) B_L^-(0) > \exp(-i\omega_{RMN}\, t)\, dt$$



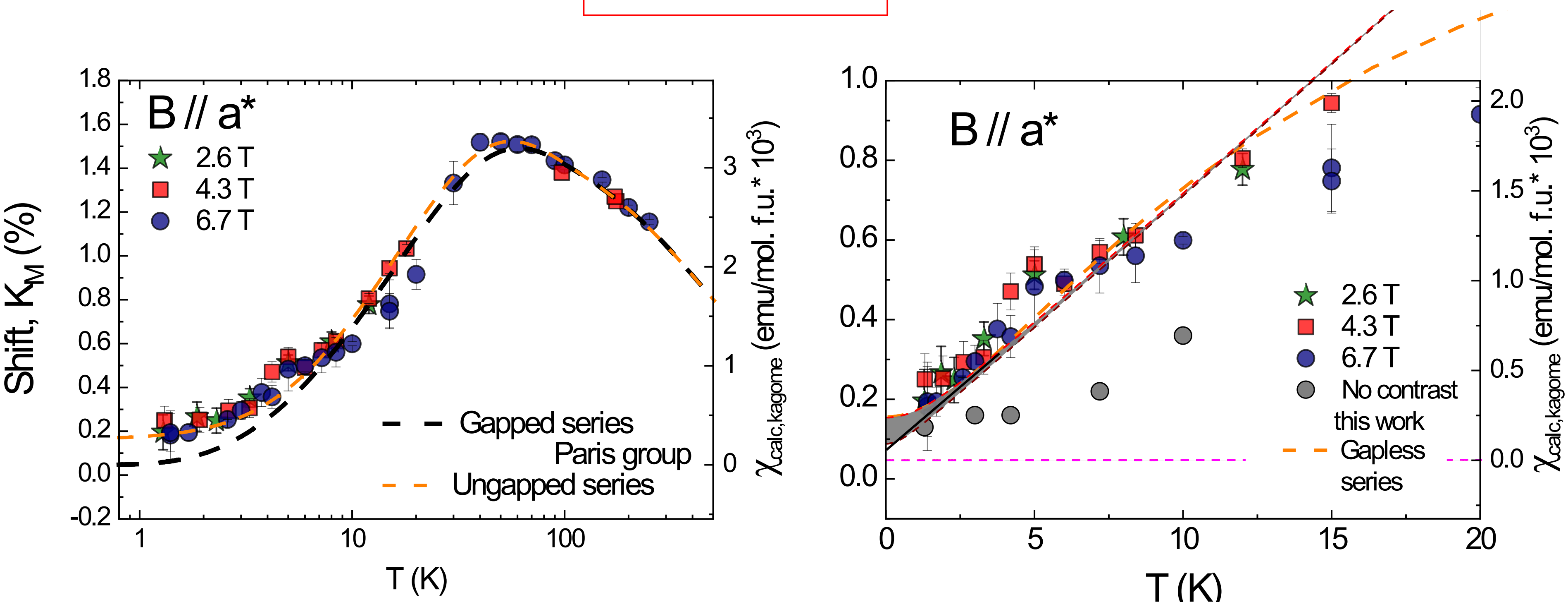


P. Khuntia et al. Nat. Phys. 2020
Q. Barthélemy, PhD :3.1 Tesla

- No spin gap behavior (conservative < 0.02 J)
- power law dependence $1/T_1 \sim T^{0.84(3)}$
- defect : 10 times lower relaxation rate (no gap)

Shift of the main line (intrinsic)

J = 190 K



- ✓ Fu et al (Science 2015) : gap ~ 9K (closing with applied field)
  P. Khuntia et al (Nat. Phys. 2019) : no gap, χ~T, field independent

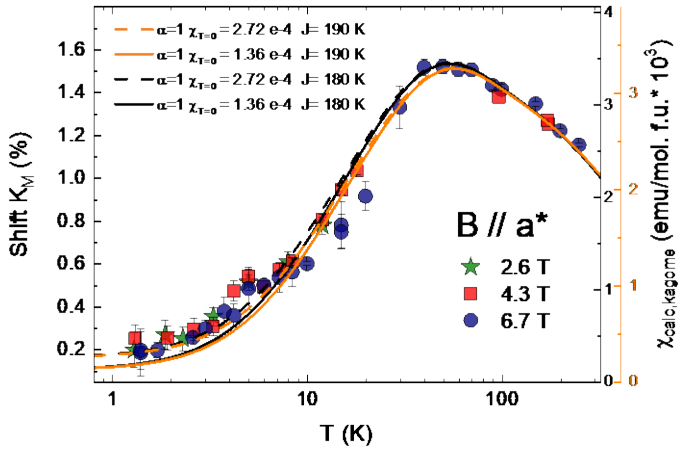
- ✓ Series expansion for the kagome susceptibility
  Expansion of S(E) + assume asymptotic behavior of C and χ(T=0) gapped or gapless
  Two boundary conditions: e_0 ground state energy and high T expansions

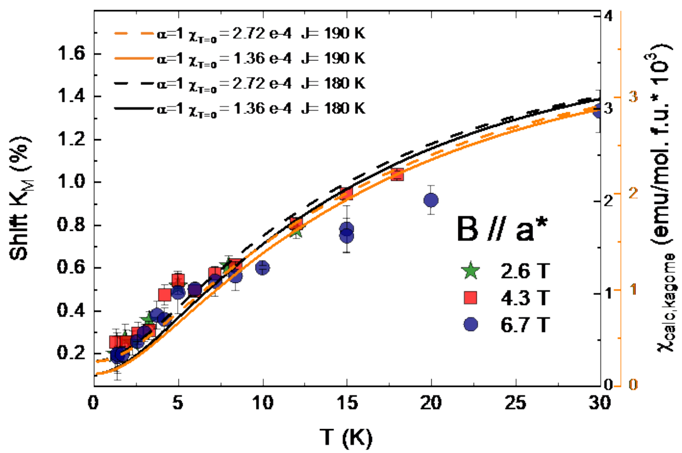
B. Bernu C. Lhuillier, PRL 114 (2015). B. Bernu et al. PRB 101, 140403 (R) (2020)

Comparison to series

(b) $K_{chem}(T=0) = 0.05\%$ $C \sim T$

(Also compatible with $C \sim T^2$)





- ✓ Series expansion for the kagome susceptibility

  Expansion of S(E) + assume asymptotic behavior of C and $\chi(T=0)$ gapped or gapless

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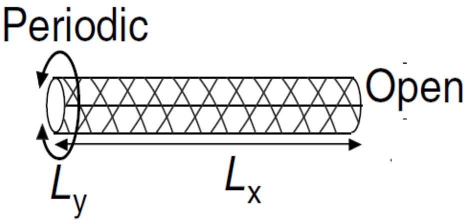
A gapless Dirac model ?

Gapped

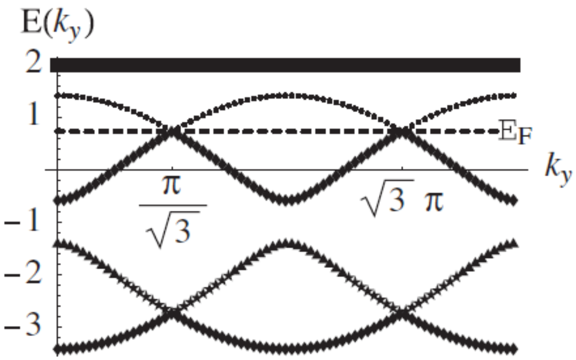
The ground-state of QKHA would be a gapped spin-liquid (short-range RVB)



Yan et al Science (2011): first DMRG, Depenbrock et al PRL (2012)

. Z_2 from correlations

. Gap 0.13 J $\rightarrow$ 0.05 J



Gapless

He et al, PRX (2017) DMRG (revisited)

. DMRG in infinite system: a Dirac SL woud be gapped

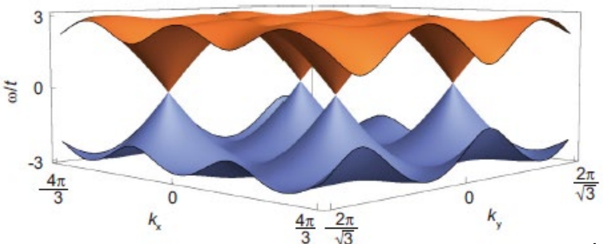
. Momentum dependent excitation spectrum

$\Rightarrow$ Dirac Spin Liquid favoured

Iqbal, Poilblanc, Becca (2011 – 2015) Variational MC

Hotta et al, PRB (2018) Exact Diagonalization (+SSD) ….

Liao et al, PRL (2017) Tensor network states



A gapless Dirac model ?

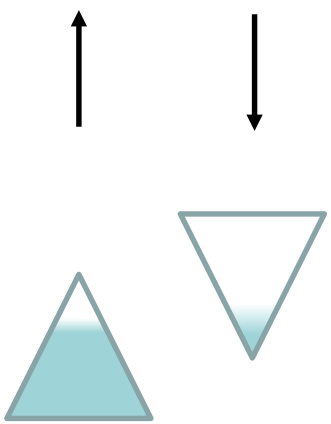
Two energy scales: kT vs $\mu_B B$

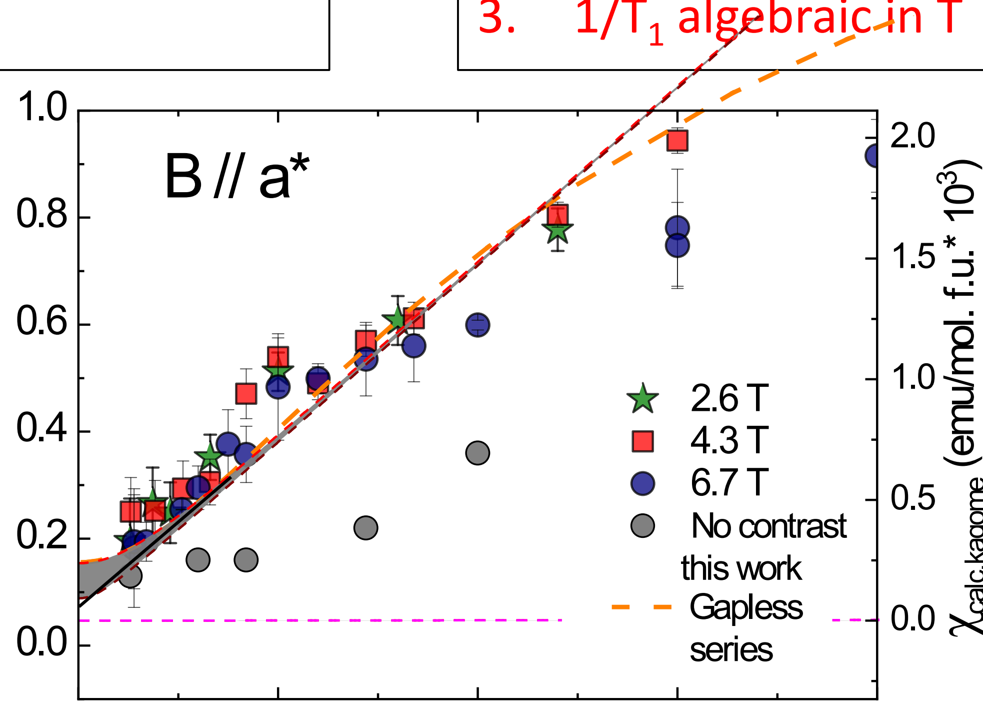
$kT \ll \mu_B B$ (spinon pockets)

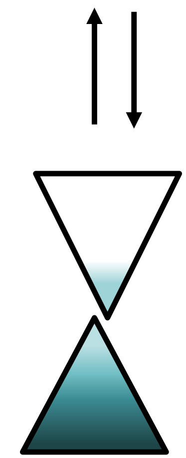
1. finite $\chi \sim B$ at T=0
2. $C \sim T$ for $T \to 0$
3. $1/T_1$ algebraic in T

$kT \gg \mu_B B$ (Dirac cones)

1. Susceptibility : χ linear in T
2. Specific heat ~T^2
3. $1/T_1$ algebraic in T







A gapless Dirac model ?

Two energy scales: kT vs $\mu_B B$

kT □ $\mu_B B$ (spinon pockets)	kT >> $\mu_B B$ (Dirac cones)
1. finite □□ B at T=0	1. Susceptibility : χ linear in T
2. C □ T for T $\rightarrow$ 0	2. Specific heat ~T^2
3. $1/T_1$ algebraic in T	3. $1/T_1$ algebraic in T

Ran et al, PRL 98, 2007; Hermele et al. PRB 2008 ; Ran et al PRL 2009

1. Yes $\chi(T) = \frac{3.2\mu_B^2}{J^2}(k_B T)$

(Slope)$^{0.5}$ ~ v_F = 4.8 x 10^3 m/s <-> only factor 1.2 off

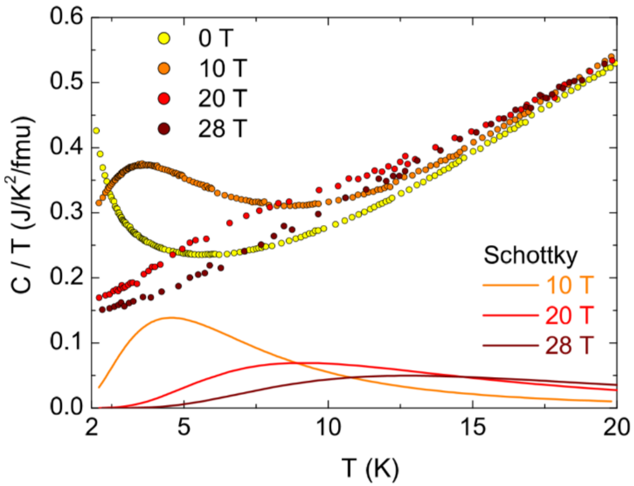
2. Yes, Series consistent with C (T $\rightarrow$ 0) ~T… valid for $\mu_B B$ >> kT or C (T $\rightarrow$ 0) ~T^2

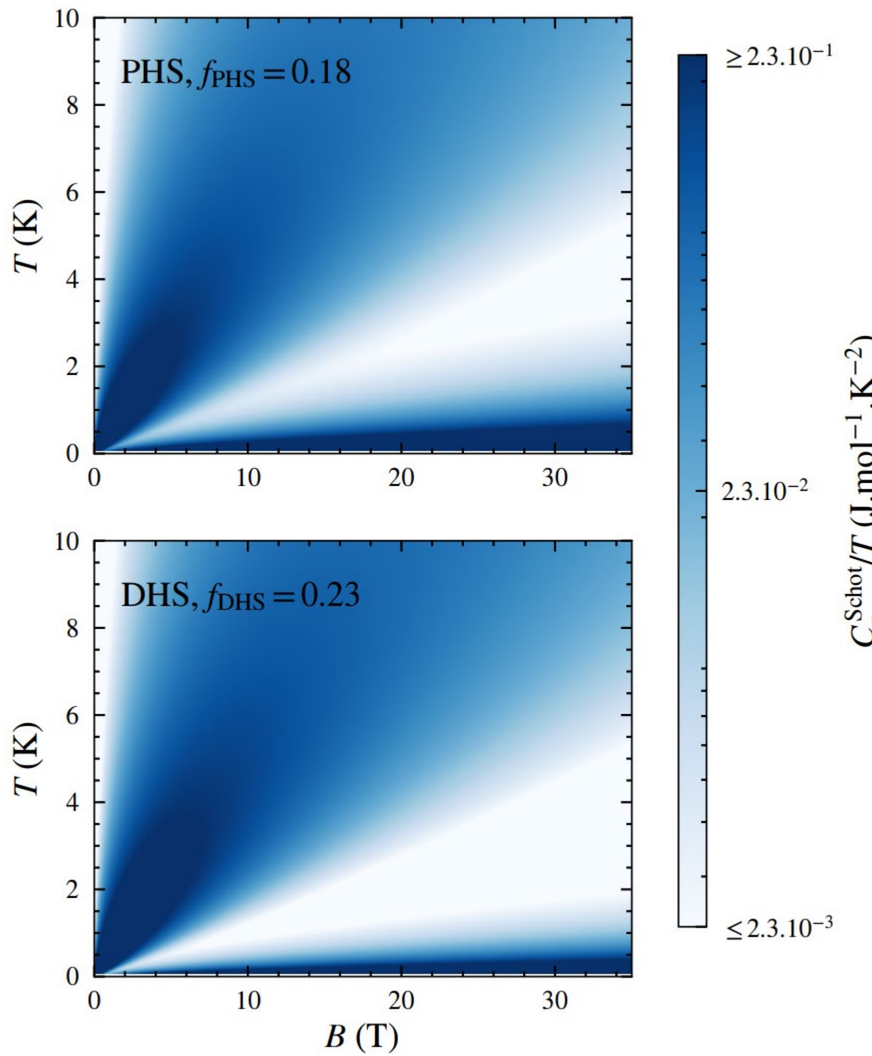
3. Yes

Consistency with Dirac cone of spinon excitations
but
U(1) Dirac spin liquid is unstable (anisotropy DM, field) any similar model stable???
High Field specific heat data invalidate the Dirac cone model
Q. Barthélemy et al., Phys. Rev. X (2022)

High-Field, Low-T specific heat: not a Dirac SL

Q. Barthélemy et al., Phys. Rev. X (2022)





$C_p = C_p^{\mathrm{kago}} + C_p^{\mathrm{imp}} + C_p^{\mathrm{phon}}$, where $C_p^{\mathrm{imp}} \approx C_p^{\mathrm{Schot}}$.

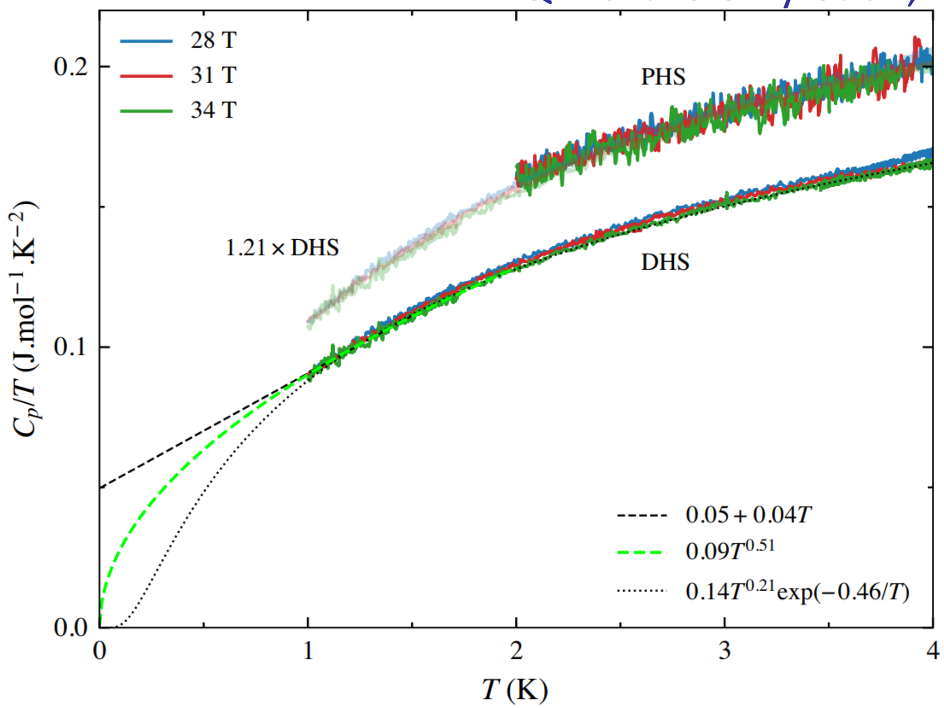
$$C_p^{\mathrm{Schot}}(T,\Delta) = \boxed{f} \frac{N_A k_B \Delta^2 \exp(\Delta/T)}{T^2[1+\exp(\Delta/T)]^2},$$

with

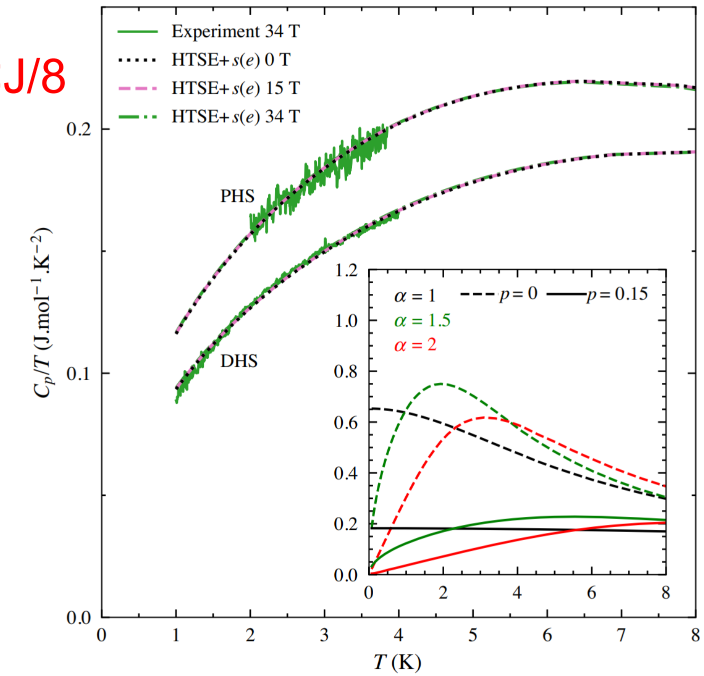
$\Delta = g\mu_B B/k_B$ (Zeeman gap, $g \approx 2.2$).

High-Field, Low-T specific heat: not a Dirac SL

Q. Barthélemy et al., Phys. Rev. X (2022)

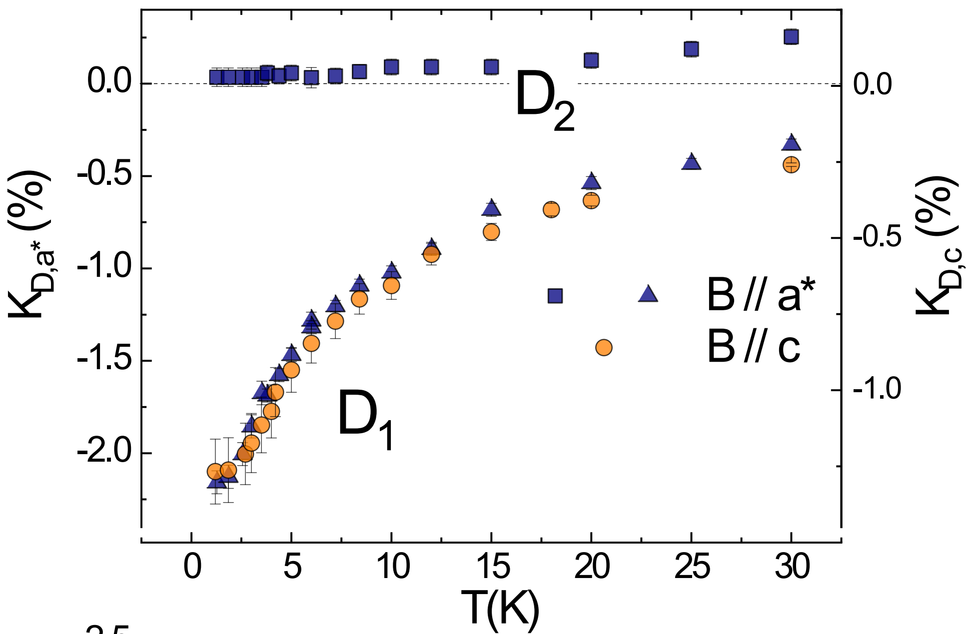


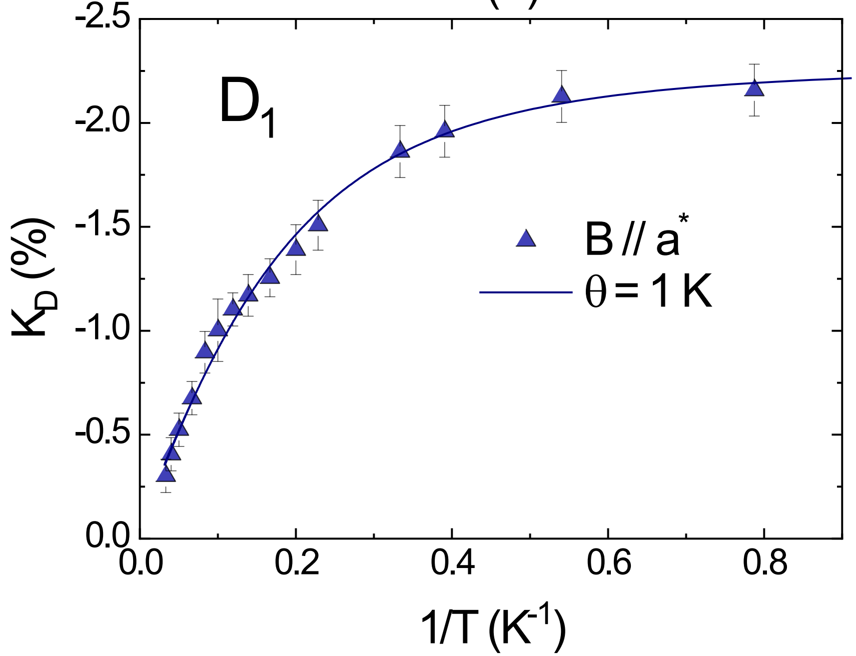
μ_B B <J/8

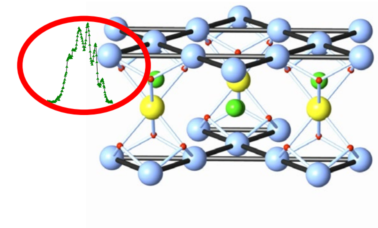


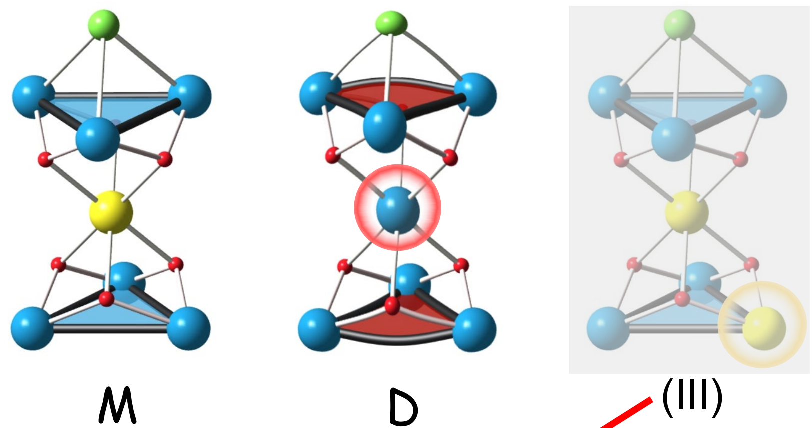
- ✓ Field independent C_p for $1 \leq T \leq 4$ K and $28 \leq B \leq 34$ T: not a Dirac SL.
- ✓ Spinon: v_F from NMR too small to explain the magnitude of C_p
- ✓ If any gap, it would be less than J/500 (models give $\Delta > J/20$)
- ✓ Power law: $C_p \sim T^{1.51}$
- ✓ Fit to series are severely constrained → effective dilution of kagome planes 11% to 13.5%. → $C_p \sim T^{1.5}$
- ✓ Consistency of $C_p \sim T^{1.5}$ with low-field data + Schottky → field-invariant down to $B \to 0$.

Shift of the defect lines









Dommange et al, PRB (2003)
Rousochatzakis et al., PRB (2009)

Cu NQR (T<30 K): McMaster's group

nature physics

LETTERS

https://doi.org/10.1038/s41567-021-01310-3

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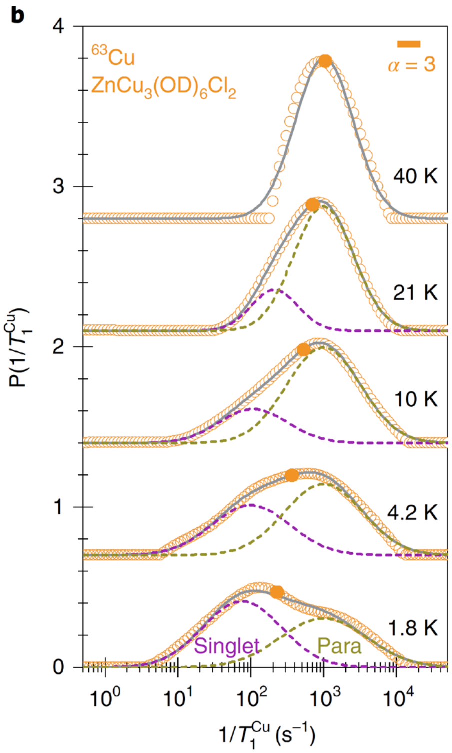
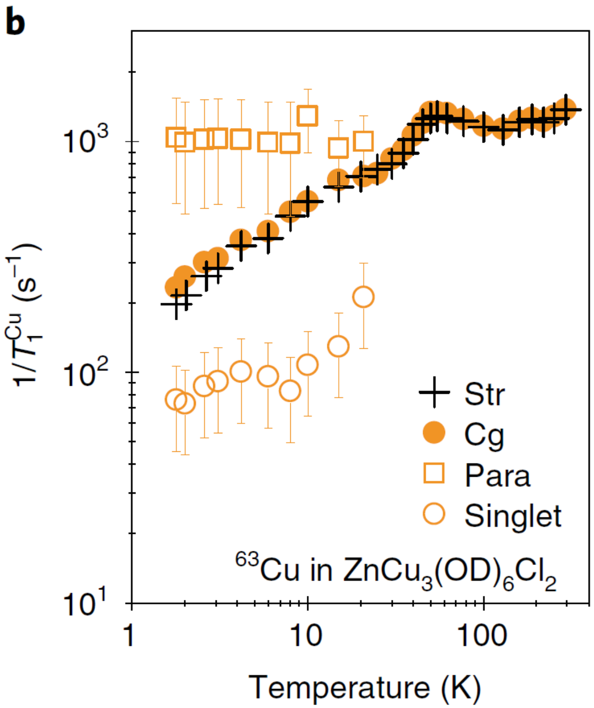
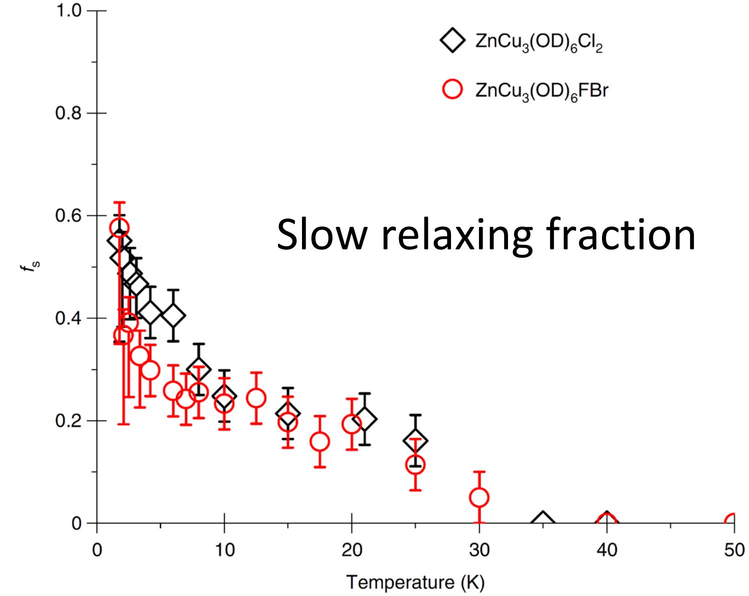
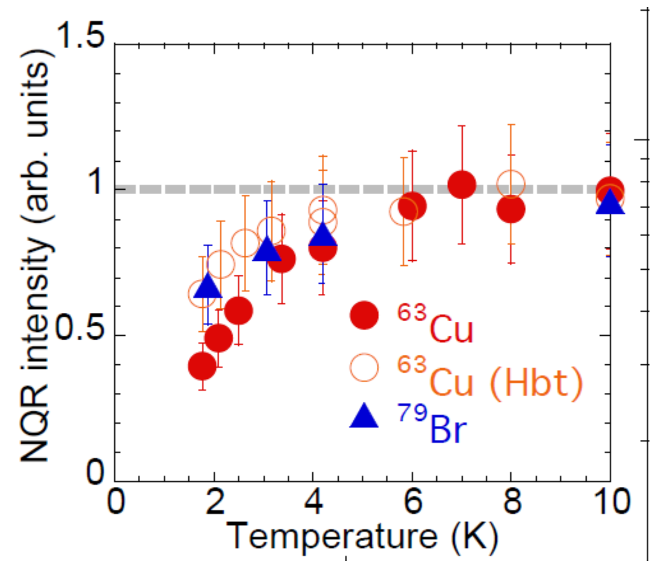
Emergence of spin singlets with inhomogeneous gaps in the kagome lattice Heisenberg antiferromagnets Zn-barlowite and herbertsmithite









J. Wang et al., Nat. Phys (2021)

Comparison ^{17}O NMR and Cu NQR (T<30 K)

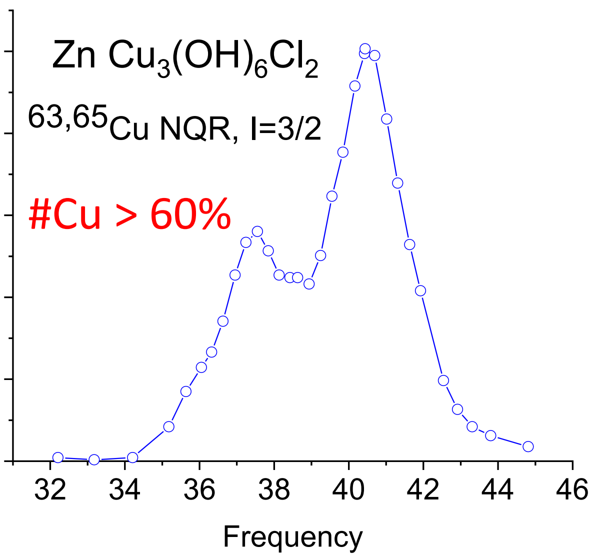
^{17}O NMR T = 1.2 K

P. Khuntia et al. Nat. Phys. (2019)

(M) Line
Weight 60%
No gap
« Fast » relaxing site

(D) Lines
Weight 40%
« Slow » relaxing sites

P. Khuntia et al. Nat. Phys. 2020



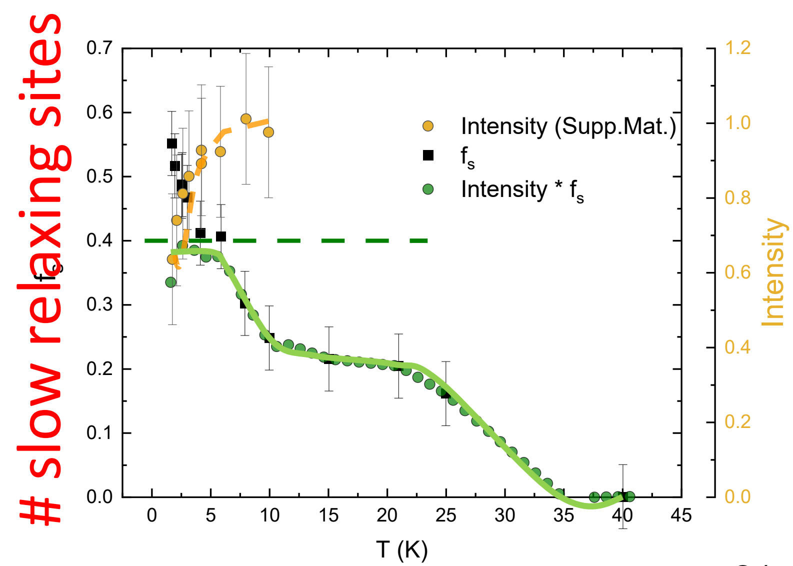
P. Mendels, unpublished

Cu NQR, T decreasing

J. Wang et al. Nat. Phys. (2021)

Two components of T1
Fast, Slow
Fraction Slow / Fast ↑
Intensity ↓
Fast/Slow ~ 60%/40% ?

J. Wang et al., Nat. Phys (2021)

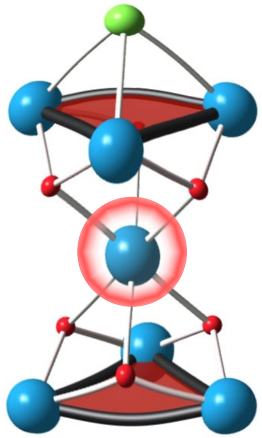


Adapted from J. Wang et al.

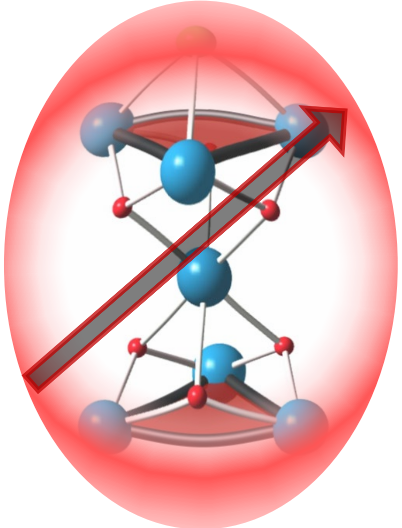
Nature of the defect : Two scenarios ?

In-plane spin-texture: indirectly induced by out of plane defects

$J_\perp = 0$ (?? many rivals)



$J_\perp$ sizeable



$S_{eff} = 1/2$

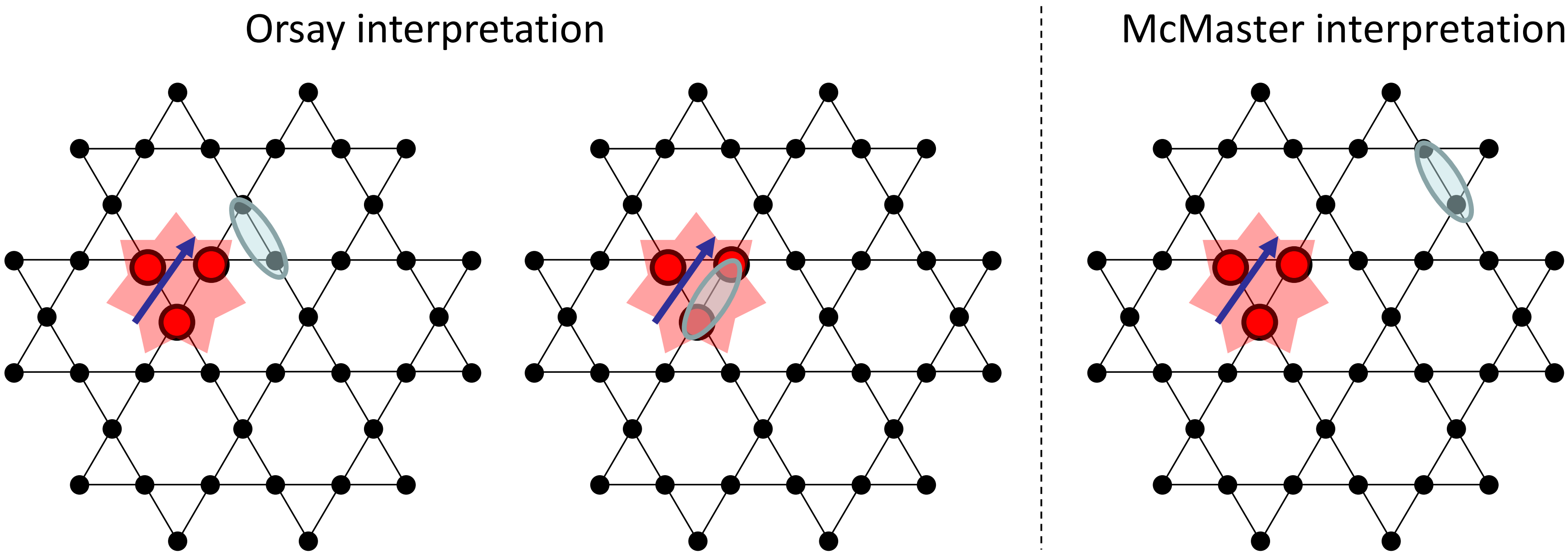
Structural distortion around interlayer Cu
→ Impacts adjacent Cu's triangles @ kagome
→ Effective in-plane defect
→ Local and long-distance response

Coupling of inter-and intra- layer Cu spins
→ Effective spin ½ defect
→ Coupling to the kagome plane
→ Local and long-distance response

⇓ Our proposal

- ✓ NN O to a « defect »: not feeling the long distance response (Sachdev, Mila,….)
- ✓ Spin texture around the defect: staggered response (M line progressively broadening)
- ✓ Quenching of the dynamics for NN O to a « defect »: release of frustration

Which picture for the low-T « defect-induced physics »?



- ✓ 40 % slow relaxing of very specific sites
  (*well resolved, protected, quenching of dynamics*)
- ✓ Spin texture for 60% fast relaxing, gapless sites

Need for understanding the nature of the defect induced by Cu on interlayer site: $J_{interlayer}$

Summary for NMR and C_p

- ✓ Herbertsmithite is clearly an ABCA-stacked QSL kagome antiferromagnet , with the largest amount of data available to-date and a clean equilateral geometry.
- ✓ Not all excitation channels are gapped : T1, shift, specific heat (conservative)
- ✓ $T < J/10$: gapless susceptibility for main site : zero or finite $\chi_0 < 0.07\ \chi_{max}$
- ✓ Relaxing components
  - $1/T_1 \sim T^{0.84\,(3)}$ for fast relaxing component ~60% of total
  - Two slow relaxing components, protected against disorder singled out below 30 K: an energy scale for the spin liquid phase?

Huang et al., Phys. Rev. Lett. 127 (2021)

- ✓ $C_p \sim T^{1.5}$, field independent up to J/12; thermal conductivity: no deconfined spinon

Murayama et al., arXiv 2106.07223 (2021)

- ✓ Theoretical scenario still open for herbertsmithite and for the pure KHAF

We know what it is not: not Z2 short range RVB, “not just a soup of featureless singlets: a large number of possible Q many body states (Lauchli et al PRB 2019)”, Dirac in the pure case ? But not with defects, <u>another kind of defect-induced QSL</u>?

Collaboration

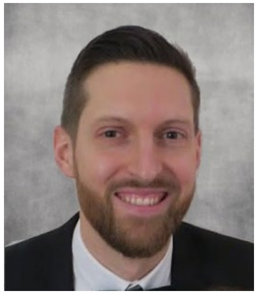
$Y_3Cu_9(OH)_{19}Cl_8$

P. Puphal
MPI Stuttgart

Q. Barthélemy
U. Sherbrooke

D. Chatterjee
phD SQM/LPS

F. Bert
SQM/LPS



E. Kermarrec
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M. Parzer, A. Riss, F. Garmroudi, A. Pustogow
K.M. Zoch, C. Krellner
Sylvain Petit,
J. Willwater, S. Süllow
C. Baines
E. Ressouches, J. Ollivier

NEUTRONS FOR SOCIETY

PAUL SCHERRER INSTITUT PSI

Theory:
M. Hering, J. Reuther
F. Ferrari, A. Razpopov,, R. Valentí,
H.O. Jeschke
I. Mazin

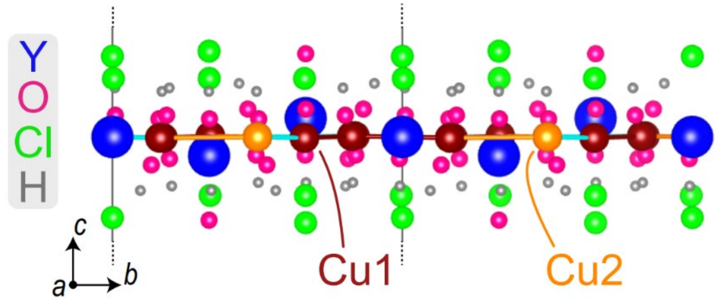
Chatterjee et al, PRB 107, 125156 (2023)

Y-Kapellasite, a new distorted kagome model

$Y_3Cu_9(OH)_{19}Cl_8$

Charge doping herbertmithite Zn^{2+} <-> Y^{3+} ? fails ☹

-> new (anisotropic) kagome $Y_3Cu_9(OH)_{19}Cl_8$ ☺



$R\bar{3}$

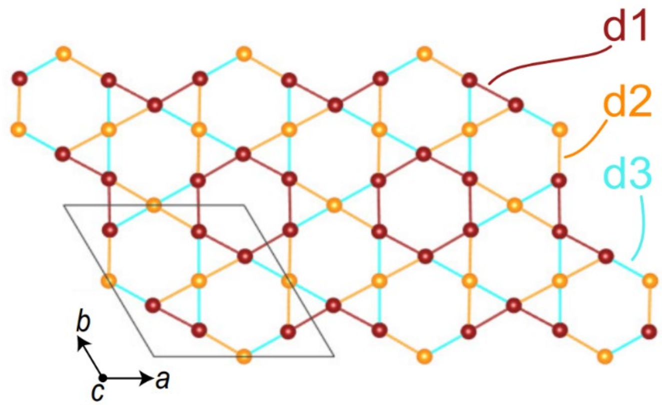
kapellasite-like AA stacking

No Cu^{2+} <-> Y^{3+} intersite mixing

Anisotropic kagome:

2 Cu sites

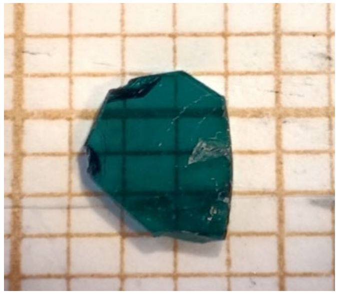
9 times larger unit cell



Puphal, J.Mat.Chem C (2017)

Sun, PRM (2021)

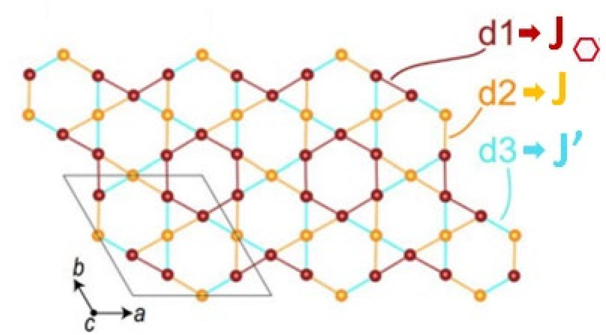
Barthélemy PRM (2019)



Chatterjee et al, PRB 107, 125156 (2023)

Y-Kapellasite, a new distorted kagome model

$Y_3Cu_9(OH)_{19}Cl_8$



d_1=3.353(8) $(Cu_1$-O_2-$Cu_1)$=117.7°

d_2=3.328(11) $(Cu_2$-O_4-$Cu_1)$=116.6°

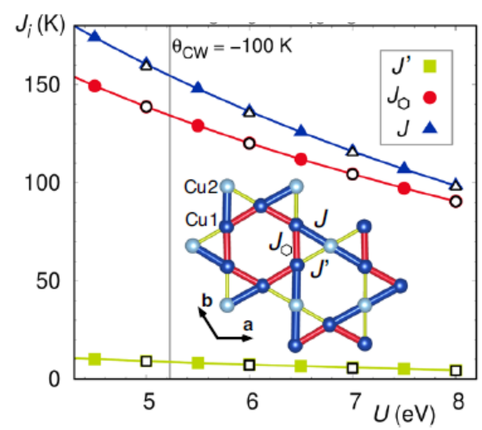
d_3=3.314(8) $(Cu_1$-O_3-$Cu_2)$=113.1°

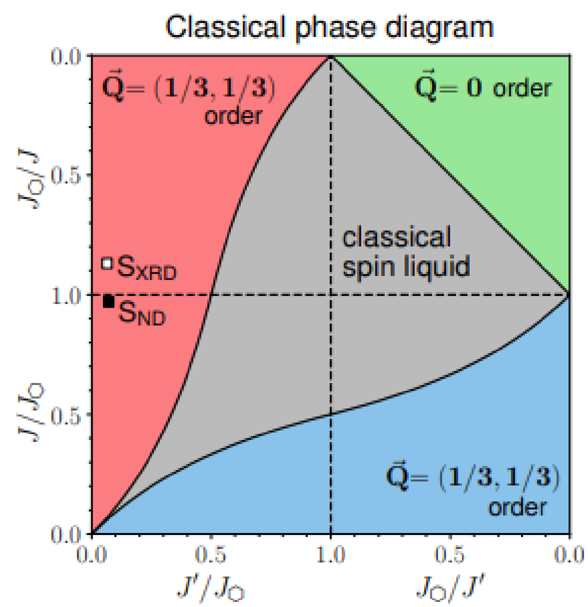
(In Zn-Kapellasite 105° -> J=-15K)

Phase diagram of a distorted kagome antiferromagnet and application to Y-kapellasite

Max Hering[1,2], Francesco Ferrari[3], Aleksandar Razpopov[3], Igor I. Mazin[4], Roser Valentí[3], Harald O. Jeschke[5] and Johannes Reuther[1,2]

npj Computational Materials 2022





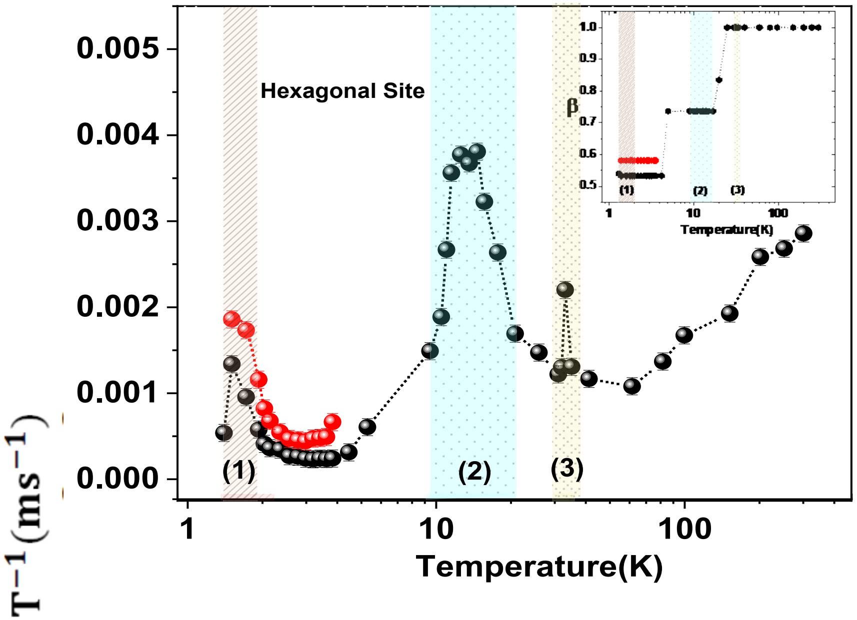
All other J_i<J⬡/50

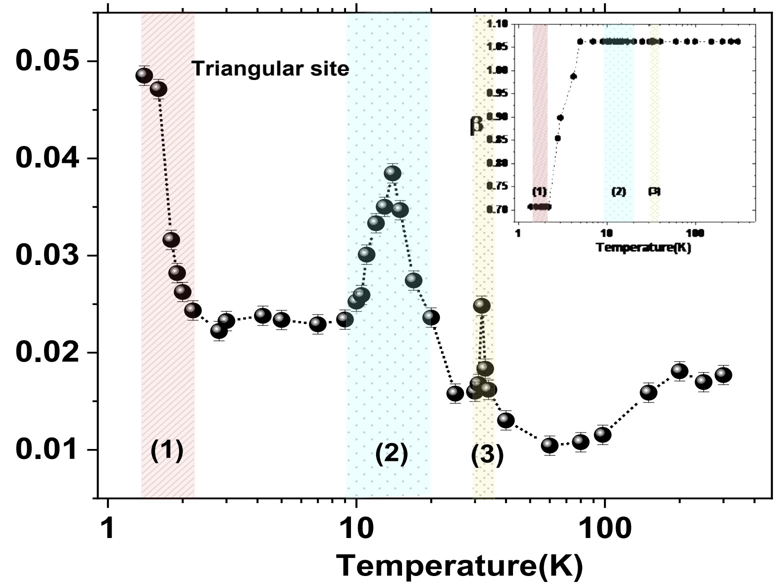
-1st nn model

-strongly 2D

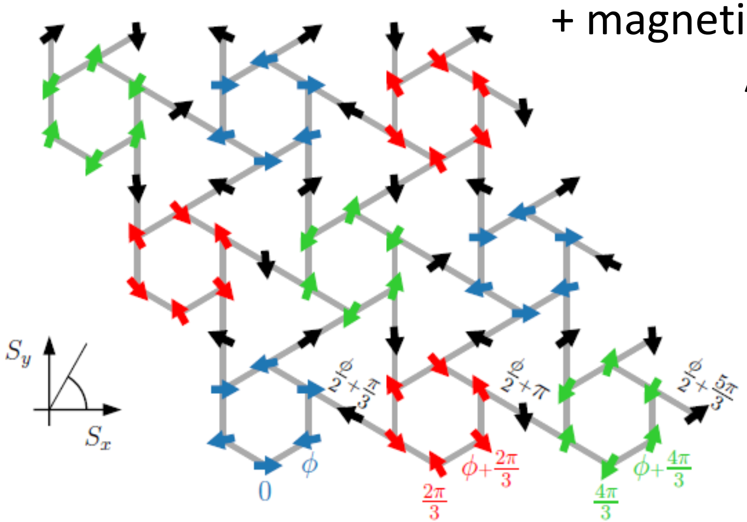
-retains 6 fold rotation symmetry

Transitions from Cl NMR relaxation





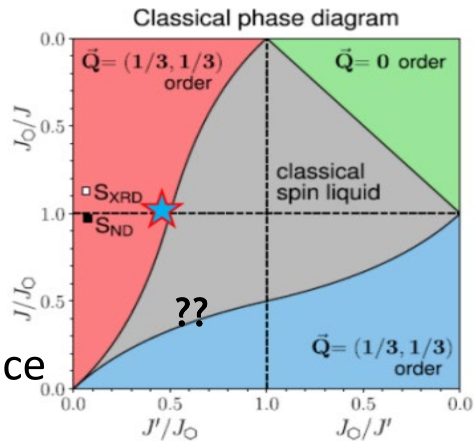
Structural transitions at 33K and around 12K
+ magnetic transition below 2K (also from μSR)
All detected at both Cl sites

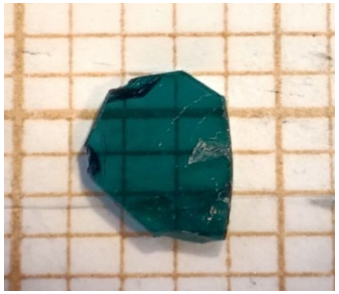


100% transition from μSR
NMR onsistent with predicted Q=1/3,1/3) order
Small moment 1/30 μ_B
Fit of spin waves -> new estimate of the couplings

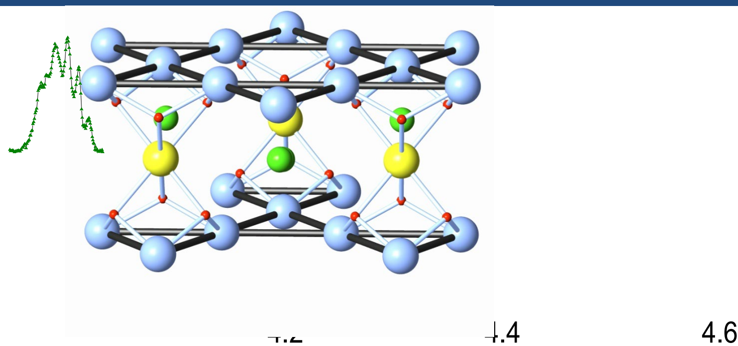
Conclusion Y-Kapellasite (single crystal)

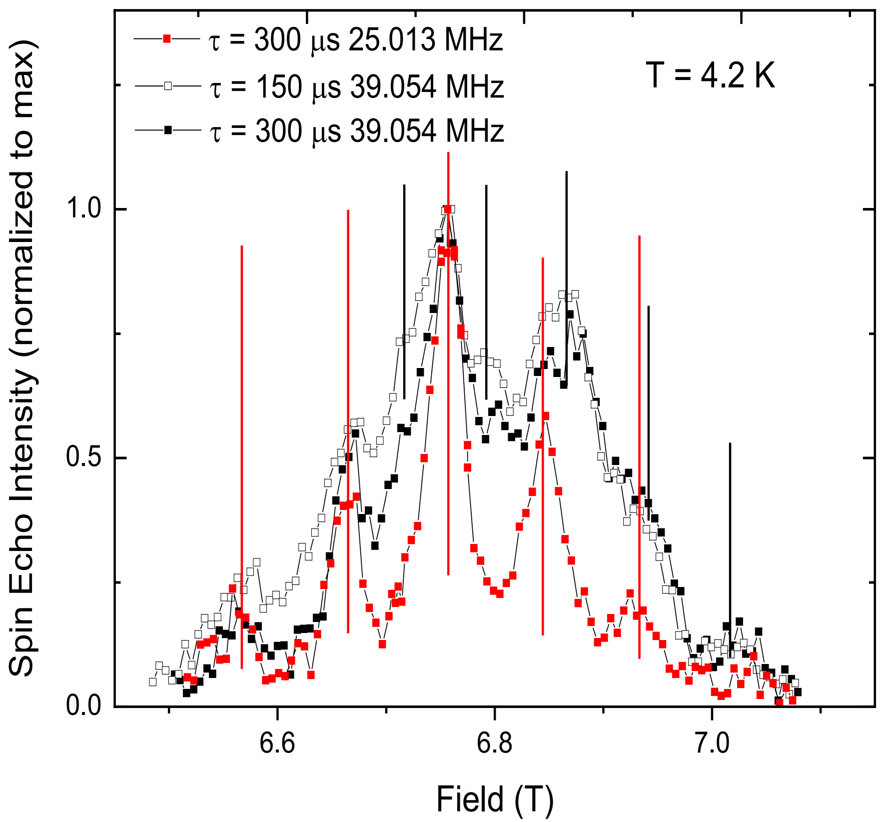
- Y-Kapellasite features a new interesting magnetic model
- Long ranged magnetic (1/3,1/3) ordering at 2.1 K
  + Spin texture compatible with theory
  but $J' \sim 0.45 J_{\hexagon}$ and distributed,
  locating Y-Kapellasite close to the 'classical spin liquid' phase
- Low value of magnetic moment < 0.1 μ_B
- Role of 'disorder'/perturbation
  - 2 structural transitions (33K, 13K), not affecting the magnetic lattice
  - anisotropy DM ? (large in x=0)
- Strain releases frustration (J. Wang et al, arXiv:2209.08613)
- Spanning phase diagram $Y_3Cu_9(OH)_{19}Br_8$ (Zengh et al PRB 2022) ?
- Classical spin liquid phase? (Jammed SL, Bilitewski et al, PRL 2017)
  Quantum fluctuations close to CSL phase (or in)?

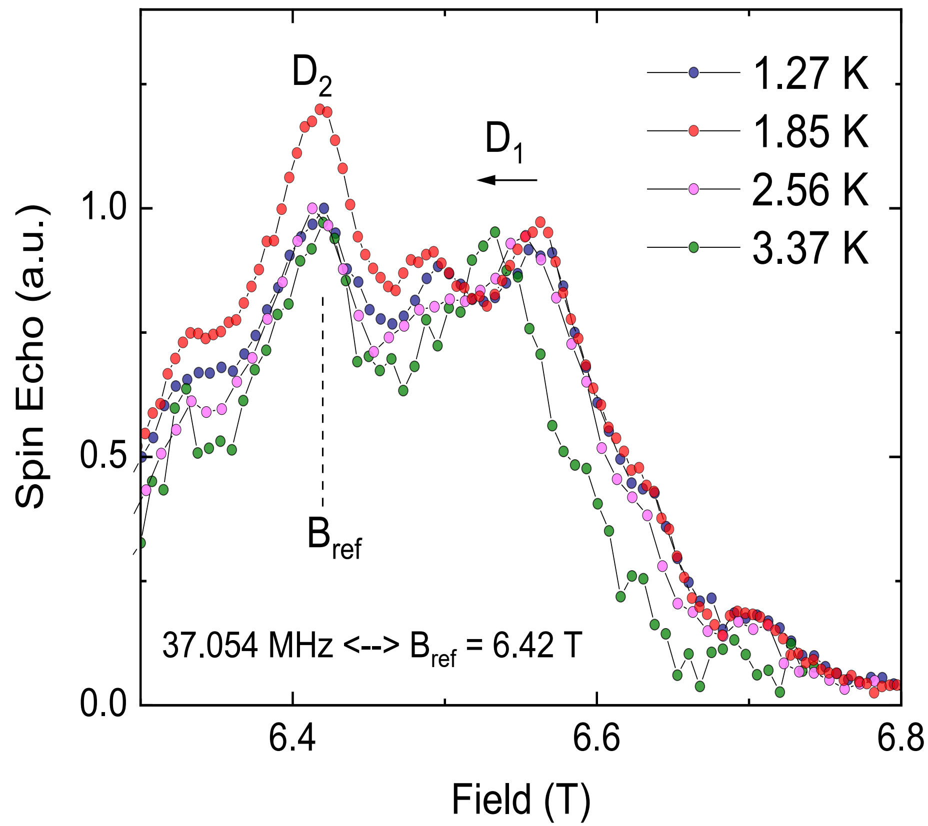




Two O sites -> two types of defects; T_2 contrast







Exchange constants: n.n. Heisenberg model

First-principles determination of Heisenberg Hamiltonian parameters for the spin-1/2 kagomé antiferromagnet $ZnCu_3(OH)_6Cl_2$

Harald O. Jeschke,* Francesc Salvat-Pujol, and Roser Valentí
Institut für Theoretische Physik, Goethe-Universität Frankfurt, Max-von-Laue-Strasse 1, 60438 Frankfurt am Main, Germany
(Dated: February 5, 2018)

TABLE V: Exchange coupling constants for $ZnCu_3(OH)_6Cl_2$ (herbertsmithite) determined from total energies of nine different spin configurations. Energies were calculated with GGA+U functionals at $J = 1$ eV with different values of U and with atomic limit double counting correction.

name	d_{Cu-Cu}	type	J_i (K) $U=6$ eV	J_i (K) $U=7$ eV	J_i (K) $U=8$ eV
		kagomé layer couplings			
J_1	3.4171	kagomé nn	182.4	155.4	131.8
J_3	5.91859	kagomé 2nd nn	3.4	2.9	2.3
J_5	6.8342	kagomé 3rd nn	−0.4	−0.5	−0.4
		interlayer couplings			
J_2	5.07638	interlayer 1st nn	5.3	4.5	3.7
J_4	6.11933	interlayer 2nd nn	−1.5	−1.1	−0.8
J_6	7.00876	interlayer 3rd nn	−6.4	−5.4	−4.4
J_7	8.51328	interlayer 4th nn	3.0	2.5	2.1
J_9	9.17347	interlayer 6th nn	2.5	2.1	1.7

Materials are mostly existing minerals

all based on Cu^{2+} S=1/2

Herbertsmithite

$ZnCu_3(OH)_6Cl_2$

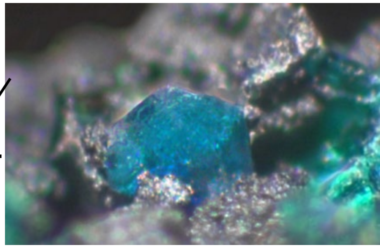
MP Shores et al, JACS, 2005

Vólborthite

Z. Hiroi et al, JPSJ 2001

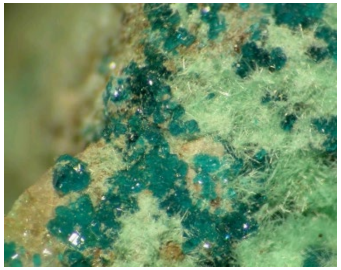
Brochantite,

Y. Li et al, New J. Phys. 2014



Barlowite

Han et al, PRL 2014



Haydeeite

R. Colman et al, Chem. Mater. 2010

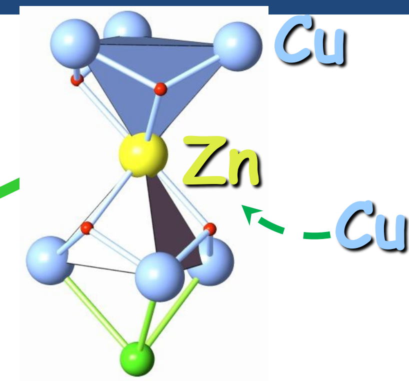
Kapellasite

R. Colman et al, Chem. Mater. 2008

Vesignieite

Y. Okamoto et al, JPSJ 2009

Site selective spectroscopy: ^{17}O NMR



- ✓ Low-T NMR ($7\ 10^{-3}$ J – 0.1 J):

$K_{spin}=A_{hf}\,\chi_{loc}(q=0,\omega=0)$

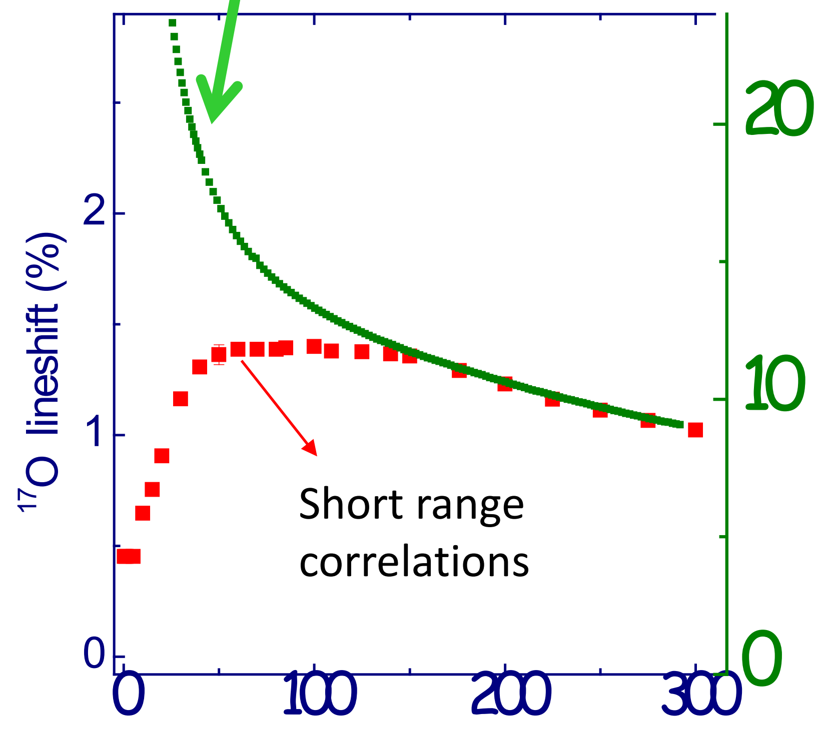
$K\to\chi$ defect contribution
intrinsic contribution: analysis

T_1 dynamics

~15% Cu on the Zn site
Nearly free ½ spins

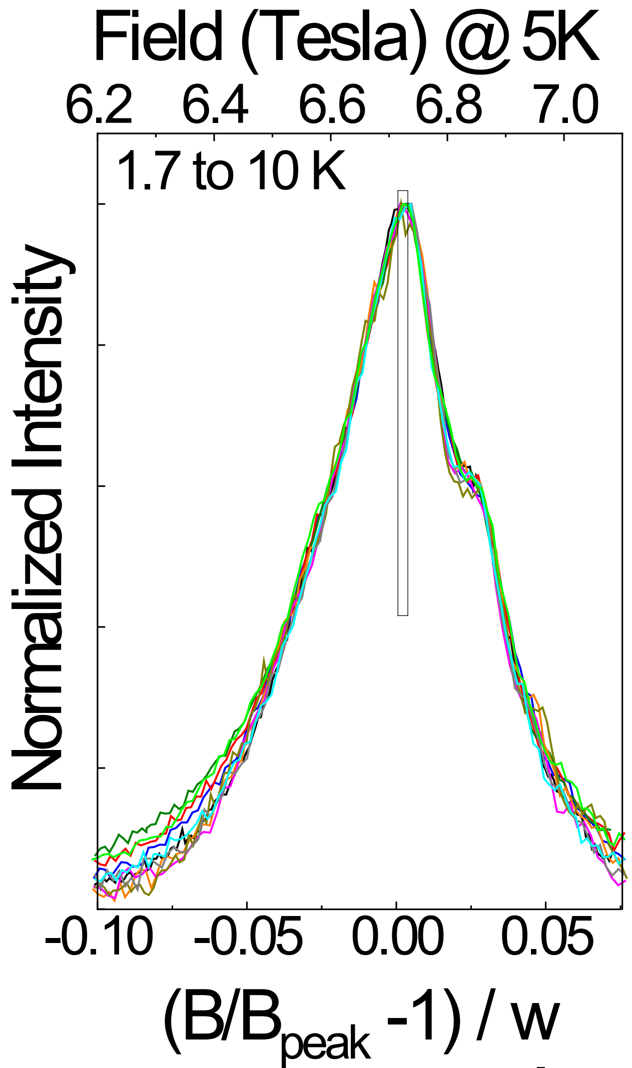
$$\frac{1}{T_1}=\frac{1}{\hbar^2}\frac{k_B T}{(g\mu_B)^2}\sum_q |A(q)|^2\,\frac{\chi_t''(q,\omega_n)}{\omega_n}$$

- ✓ Issue: what is the so-called « defect »
- ✓ What is the « defect » impact on the pure kagome physics



Olariu et al, PRL 100, 087202 (2008)

Shift: T1 contrast and scaling



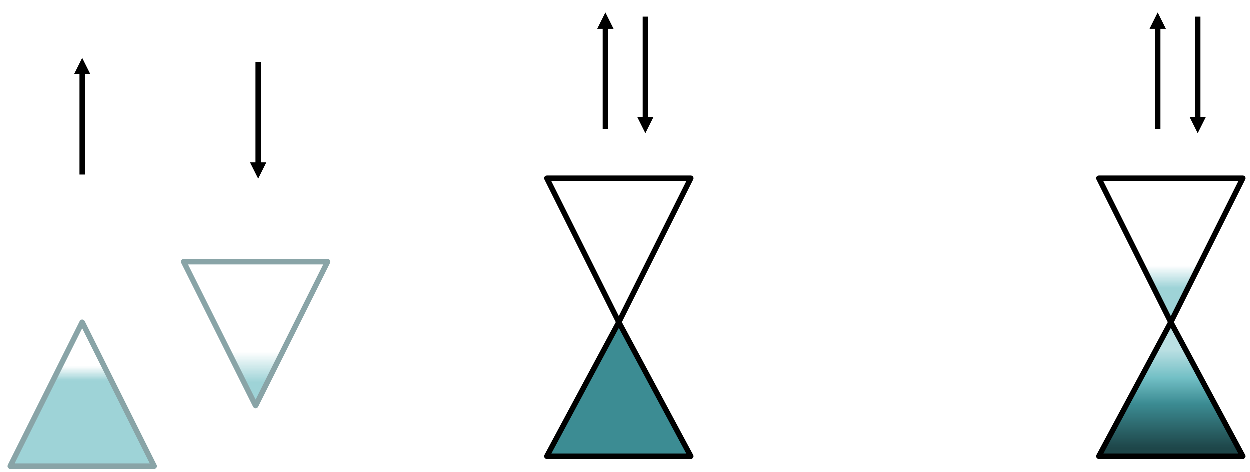
Bref/Bpeak=1+K

Width

A gapless Dirac model ?

Two energy scales: kT vs $\mu_B B$

kT □ $\mu_B B$ (spinon pockets)	kT □ $\mu_B B$ (Dirac cones)
1. finite □□ B at T=0	1. Susceptibility : χ linear in T
2. C □ T for T $\rightarrow$ 0	2. Specific heat ~T^2
3. $1/T_1$ algebraic in T	3. $1/T_1$ algebraic in T



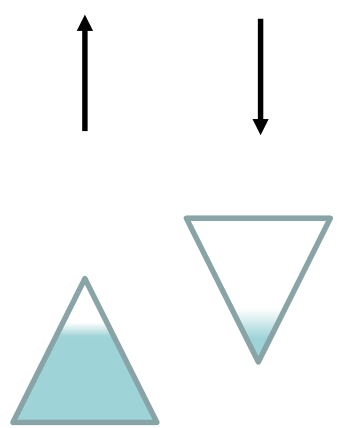
T = 0 and B =0

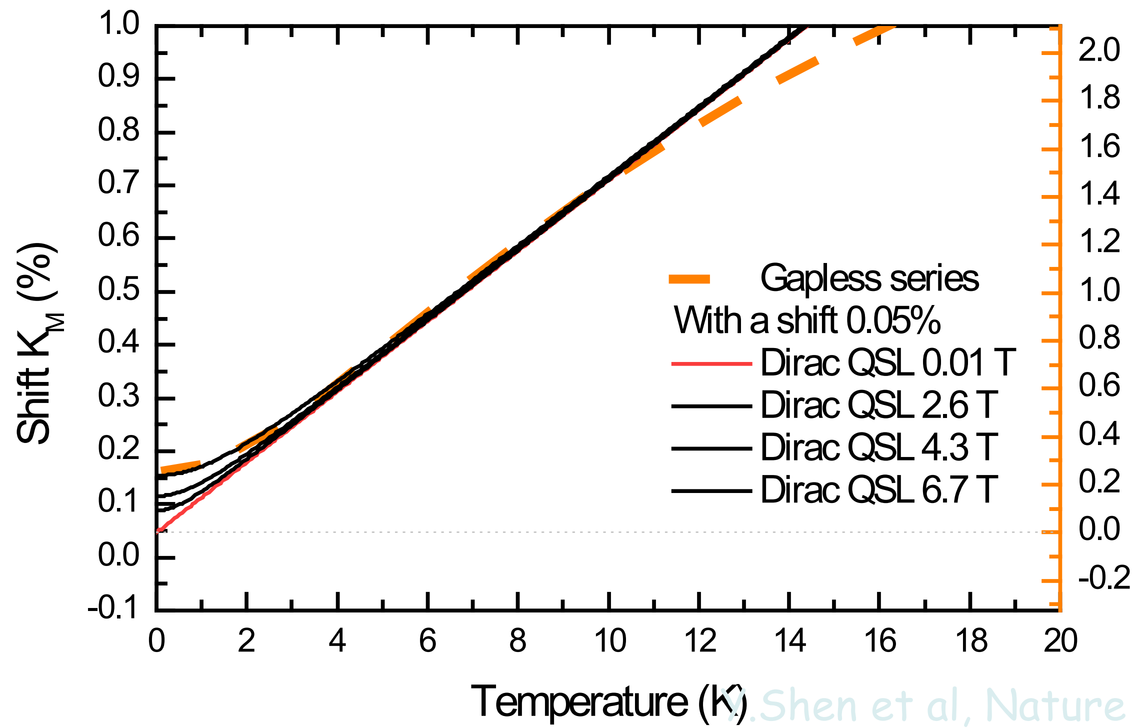
P. Khuntia et al., Nature Physics 16, 469 (2020)

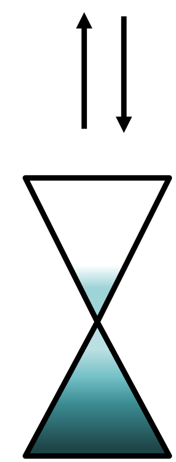
A gapless Dirac model ?

Two energy scales: kT vs $\mu_B B$

kT □ $\mu_B B$ (spinon pockets)	$kT >> \mu_B B$ (Dirac cones)
1. finite □□ B at T=0	1. Susceptibility : χ linear in T
2. C □ T for T $\rightarrow$ 0	2. Specific heat ~T^2
3. $1/T_1$ algebraic in T	3. $1/T_1$ algebraic in T

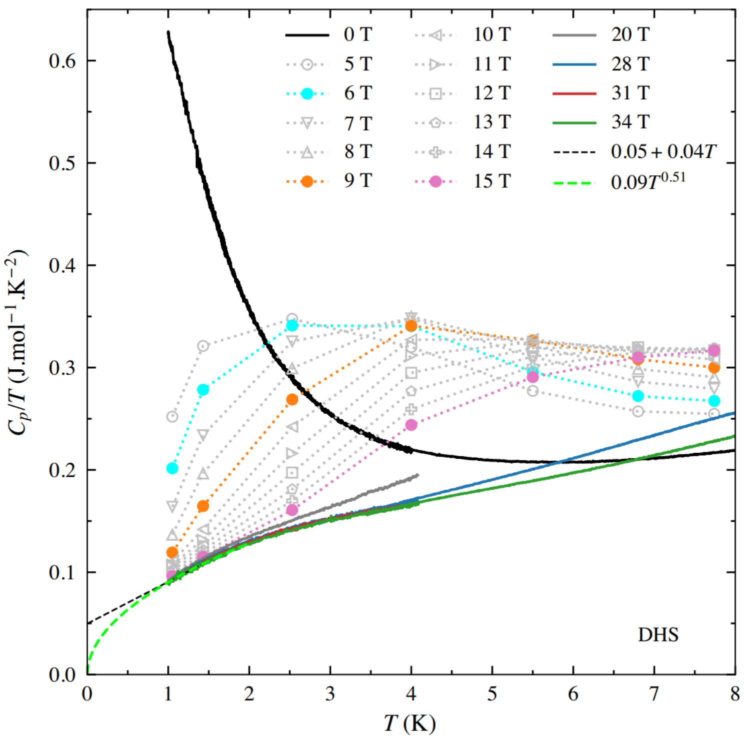






Y.Shen et al, Nature 540, 559 (2016)

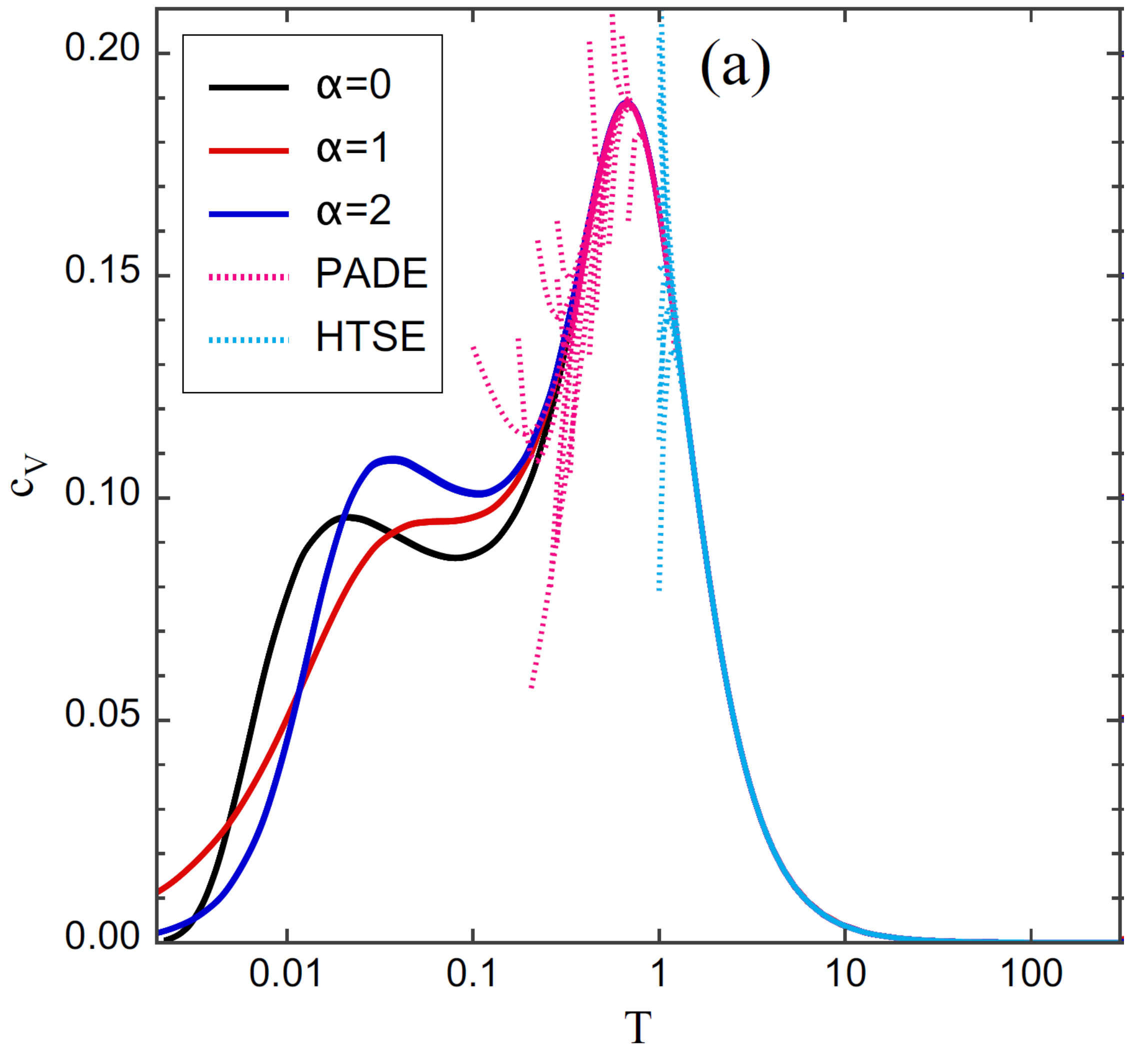
Direct measurement of C^{kago}



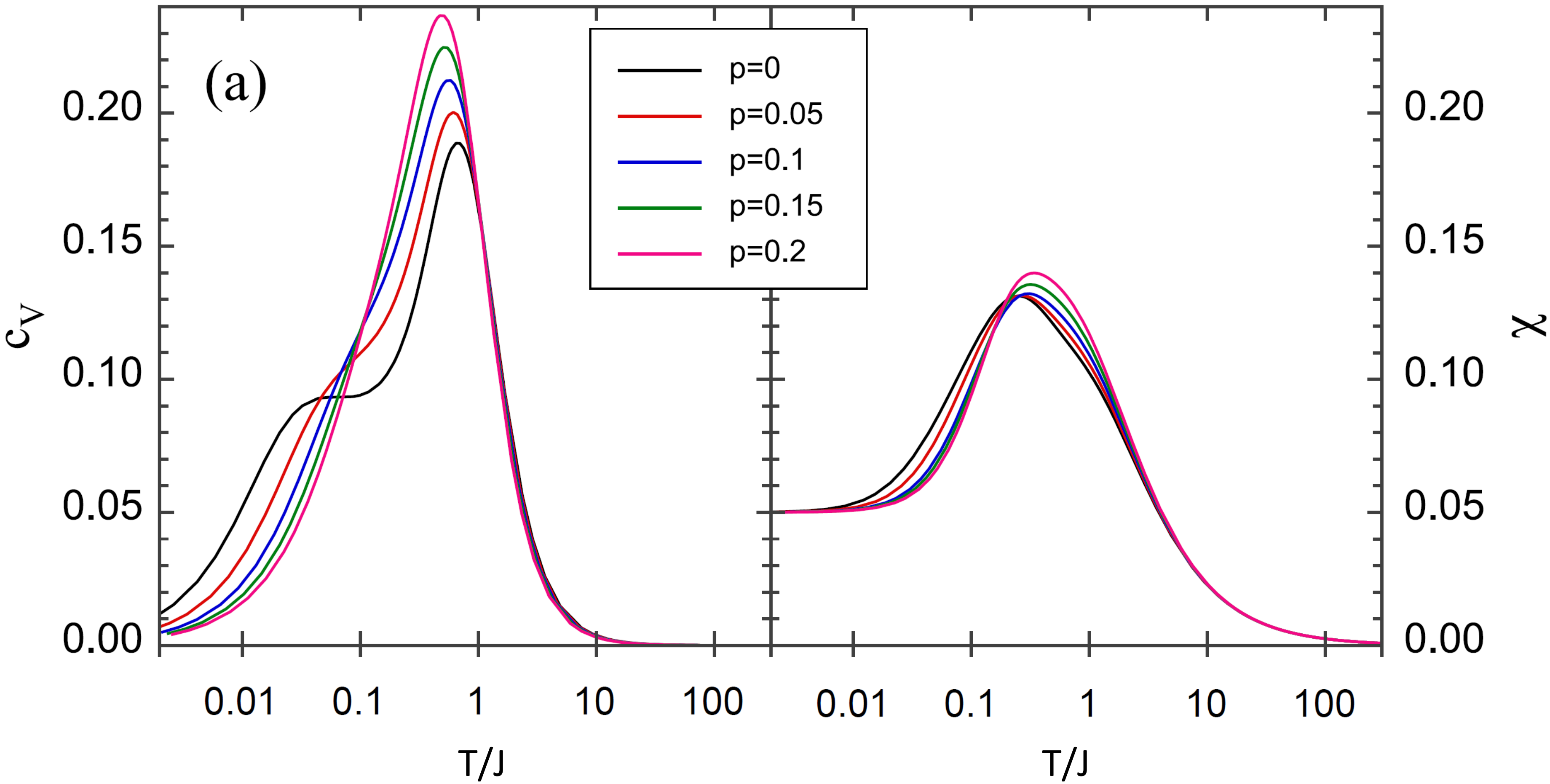
Field-independent for $1 \leq T \leq 4$ K and $28 \leq B \leq 34$ T

$1.21 \sim q = 1.3(1)$: effective (impurity-induced) dilution of the kagome planes

Tentative extrapolation: unusual power law $C_p(T \to 0) \propto T^{\alpha}$ with $\alpha \sim 1.5$



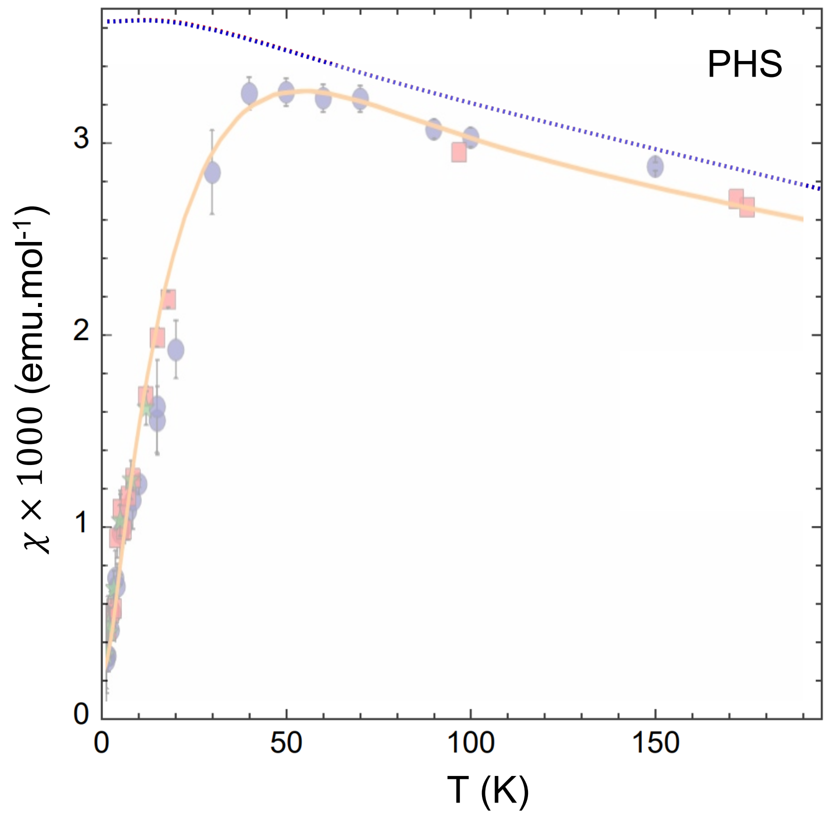
B. Bernu et al. PRB 101, 140403 (R) (2020)



B. Bernu, L. Messio et al. PRB 101, 140403 (R) (2020)

Fitting series for C_p does not match NMR susceptibility

Q. Barthélemy et al., Phys. Rev. X (2022)



- ✓ Susceptibility deduced from series inconsistent with NMR (too large / more dependent on B)
- ✓ But susceptibility deduced from ^{17}O NMR is for 60% of the fast relaxing sites «far from defects»

Analysis with the HTSE+$s(e)$ Method

Khuntia et al., Nat. Phys. 16 (2020)
Bernu et al., Phys. Rev. B 101 (2020)
Barthélemy et al., Phys. Rev. X 12 (2022)

B. Bernu
LPTMC Paris

L. Messio
LPTMC Paris

HTSE+$s(e)$:
extrapolations of high-T series expansions with the entropy method.

→ **The HTSE+$s(e)$ computations fit the experimental data <u>if and only if</u>:**

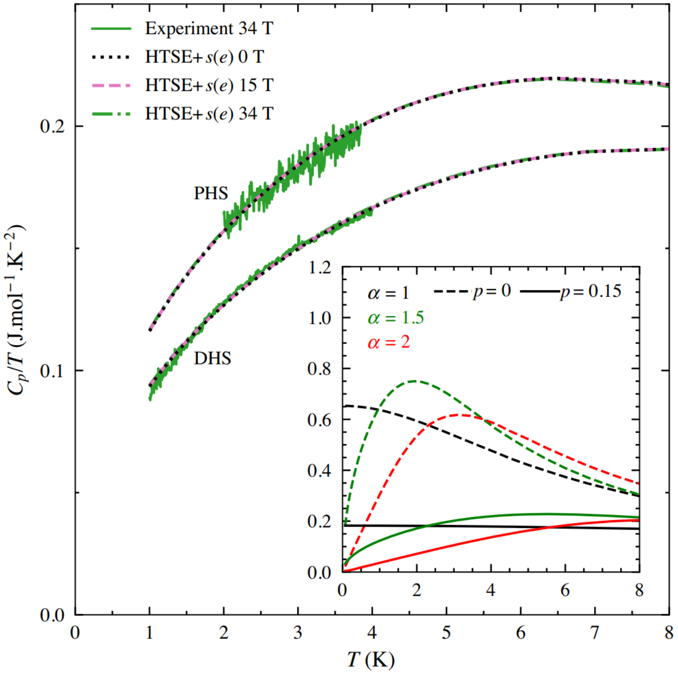
1. We set a **nontrivial power law** $C_p(T \longrightarrow 0) \propto T^{\alpha}$ with $\boldsymbol{\alpha \approx 1.45}$.

2. We set a **dilution of the kagome planes**: random vacancies with concentration p. $p \sim 13.5$ % for DHS and $p \sim 11$ % for PHS. <u>Note that the p ratio matches the low-T Curie constants ratio $q = 1.3(1)$.</u>

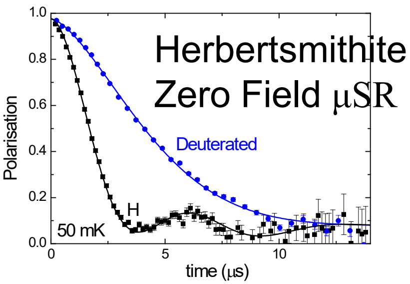
→ The optimized ground state energy follows $\boldsymbol{e_0(B,p) = e_{00}(p) - A(p)B^2}$.

→ The optimized C_p is **field-independent** on a large field range up to about 150 T.

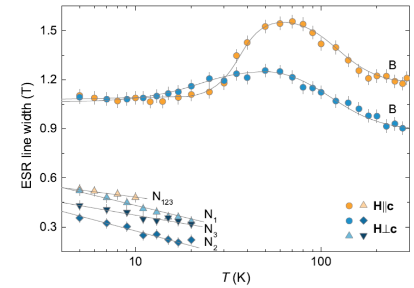
→ With the C_p parameters, the optimized χ_0 is about **10 times larger than the NMR χ_0**.



Energy scales (J = 190 K)



Exchange anisotropy



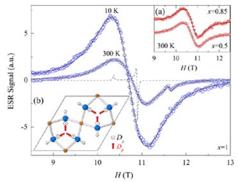
J/100 J/10 J

μSR

D_p

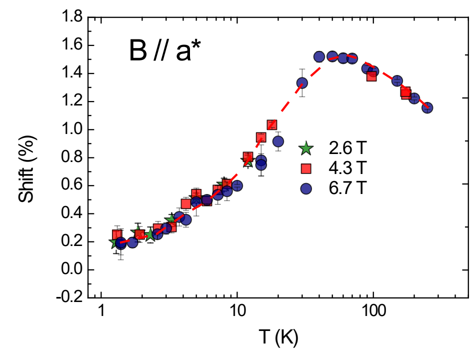
D_z

0.06 J

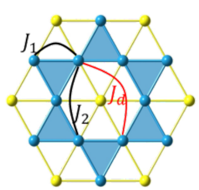


χ max

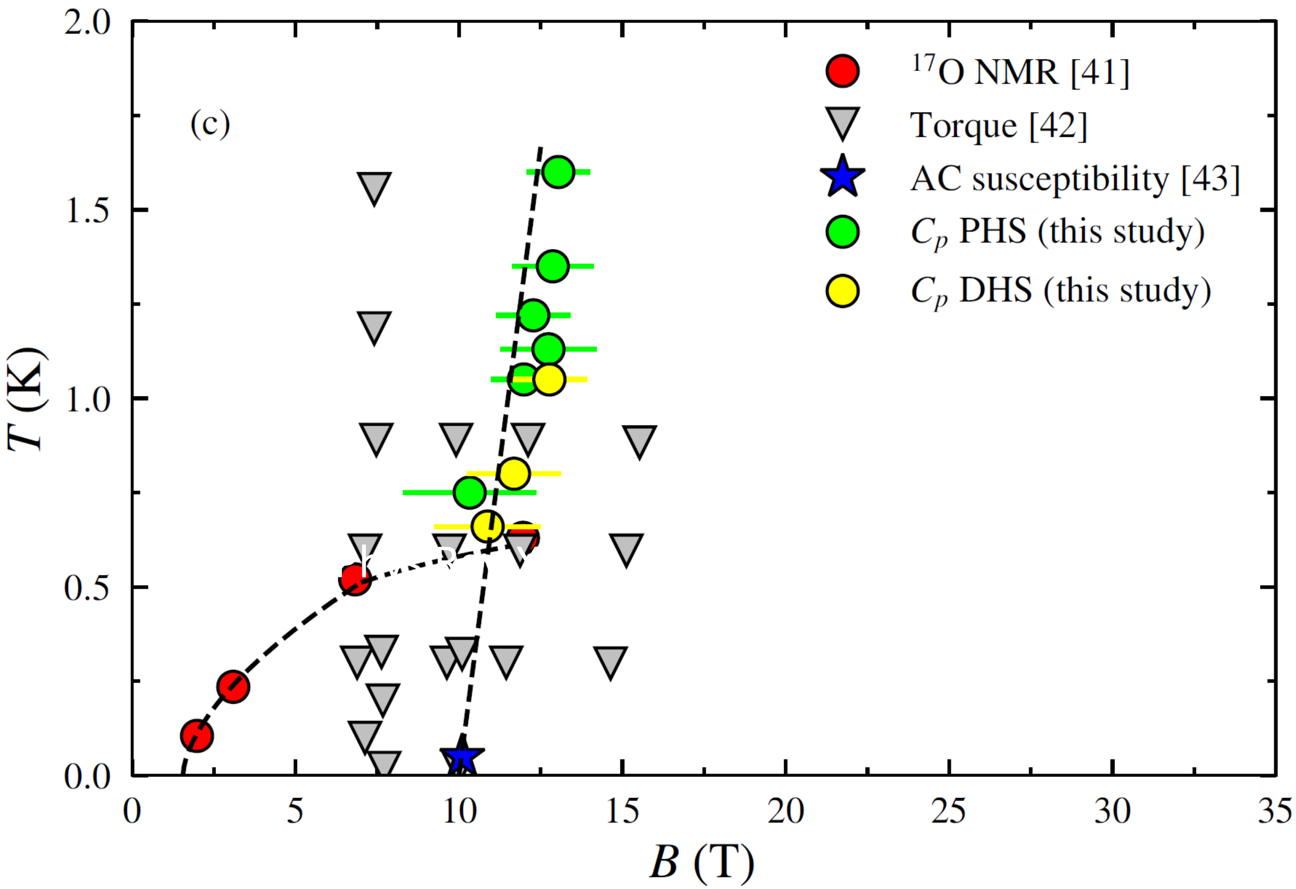
J/3



Further neighbors



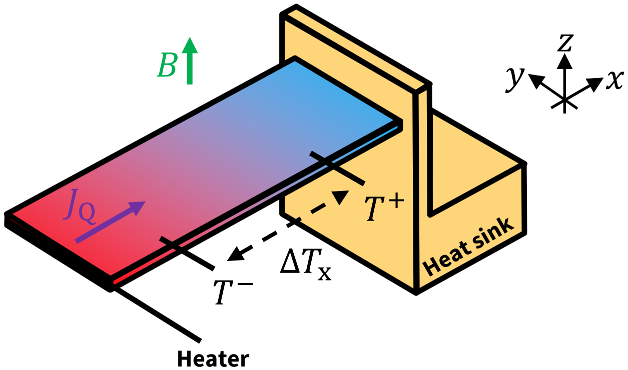
Field- induced crossover from QSL to ???



- M. Jeong et al, PRL 107, 237201 (2011): frozen moments ~0.1 μ_B
- T. Asaba et al, PRB 90, 64417 (2014)
- J. Helton, PhD (2009)
- Q. Barthélemy, PRX (2022)

(No?) Mobile Spin Excitations

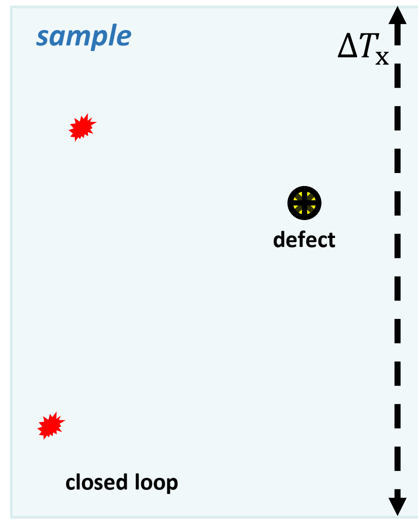
Huang et al., Phys. Rev. Lett. 127 (2021)
Murayama et al., arXiv 2106.07223 (2021)

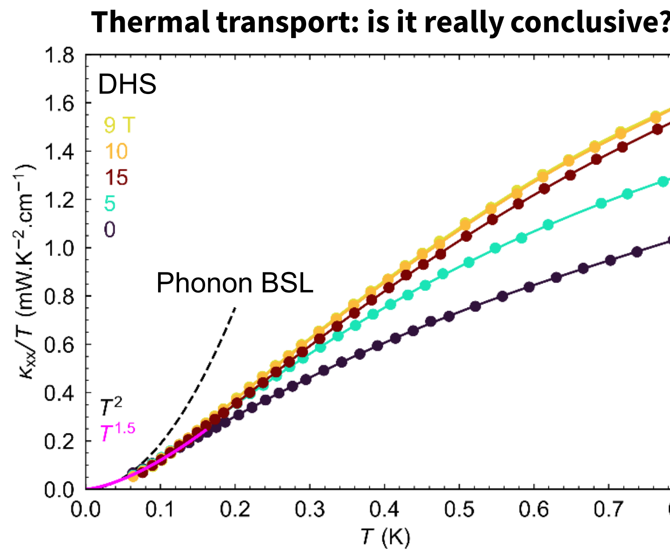


<u>*Longitudinal thermal conductivity:*</u>

$$\kappa_{xx} \propto \frac{J_Q}{\Delta T_x}$$

It probes the **mobile heat carriers**: phonons + …



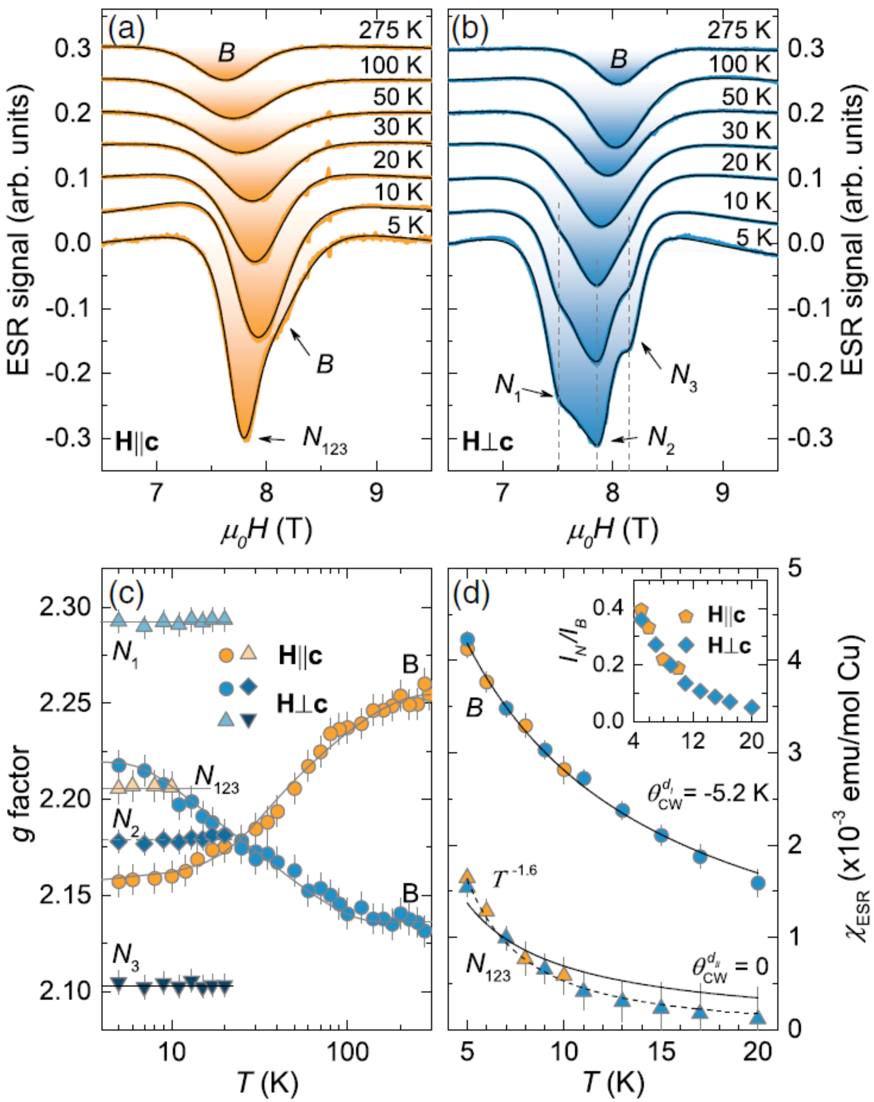


→ In zero field, **no sizeable residual term** in the $T \to 0$ limit ⟹ **phonons are the main heat carriers**. Compatible with recent reports.

→ **Low magnitude** & **field dependence** ⟹ phonons are **strongly scattered by some magnetic degrees of freedom**.

→ Scattering centers: **the (localized?) QSL excitations** and the **defects**.

ESR at low T, dominated by defects: 2 types



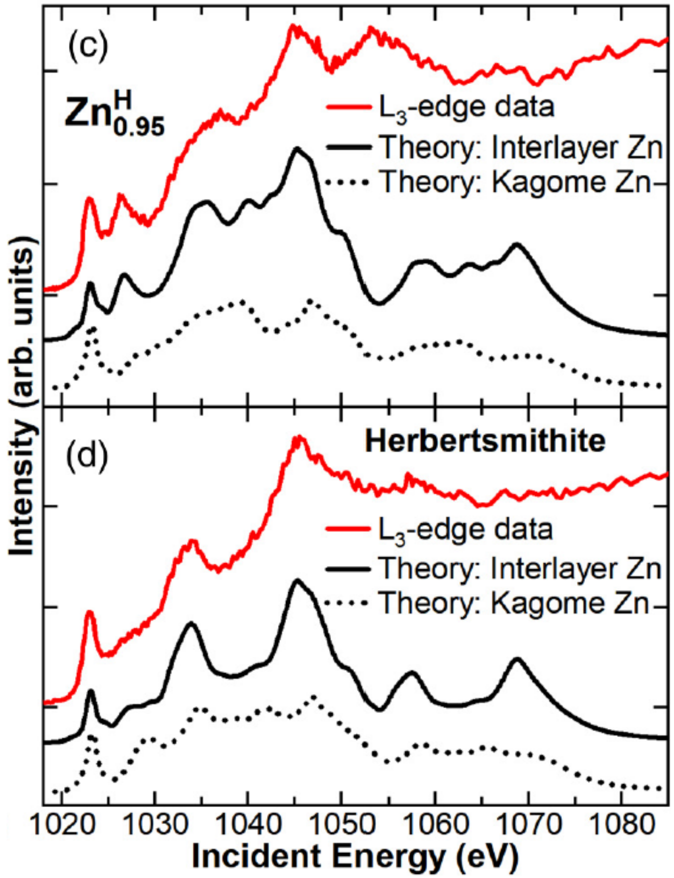
(B) Coupled defect to kagome
(N) weakly coupled defects,
In plane defect or induced effect in the plane!

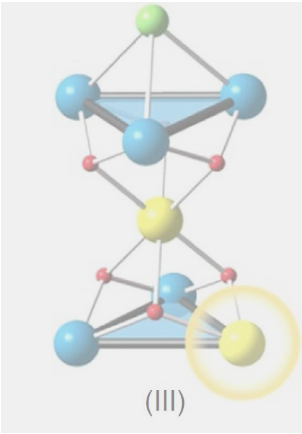
Lowering of symmetry: tiny effect

ESR, Torque, Zorko et al., PRL (2017)
^{17}O NMR, M. Fu et al., Science (2015)
2nd harmonic, N.J. Laurita, ArXiv (2019)
Cl NMR ?, T. Imai et al., PRL (2008)
Infrared, A.B. Sushkov, JPCM (2017)

A. Zorko et al., PRL (2008, 2017)

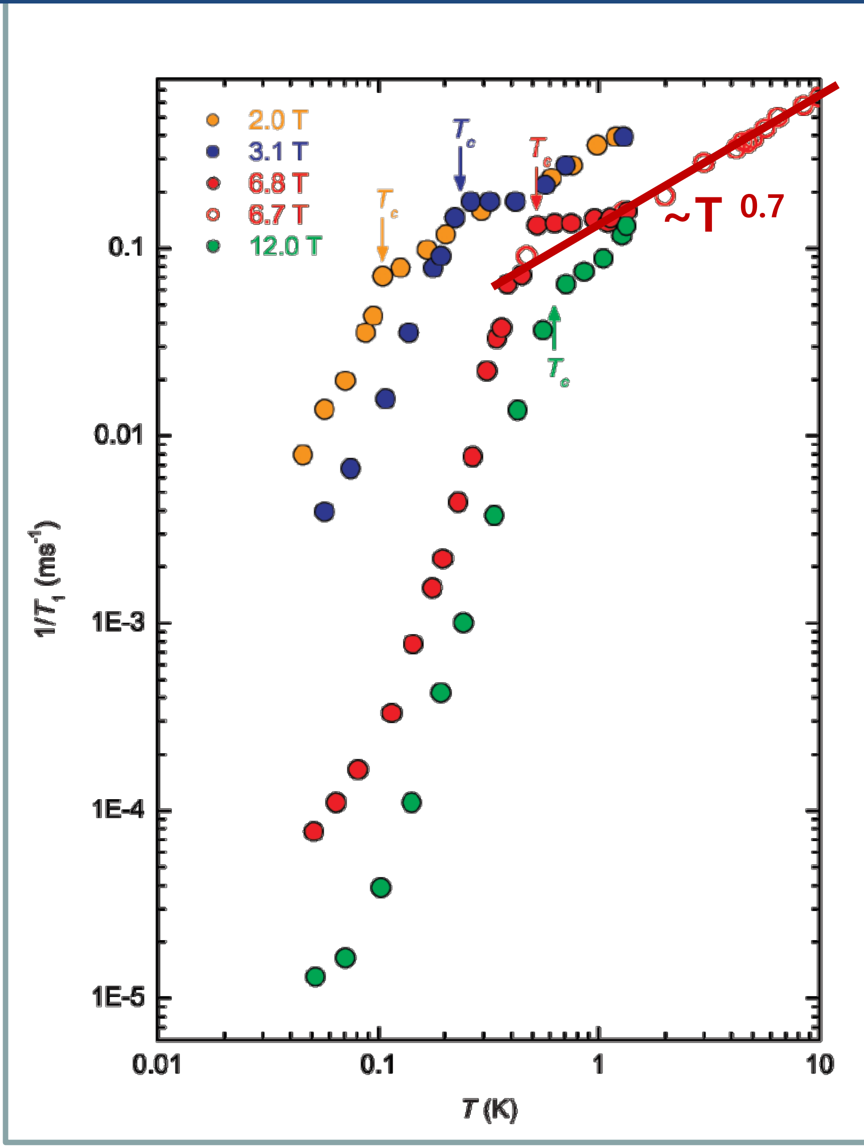
X-ray absorption near edge spectroscopy

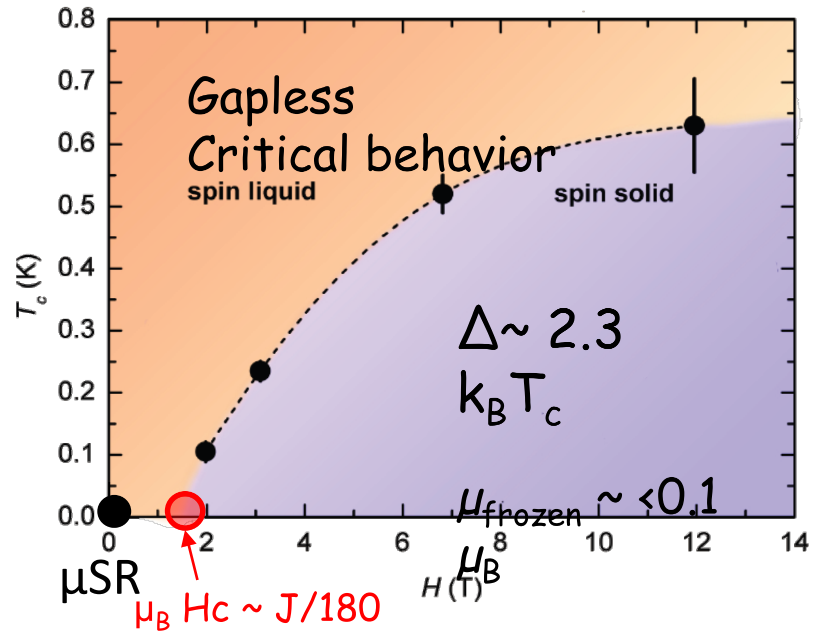


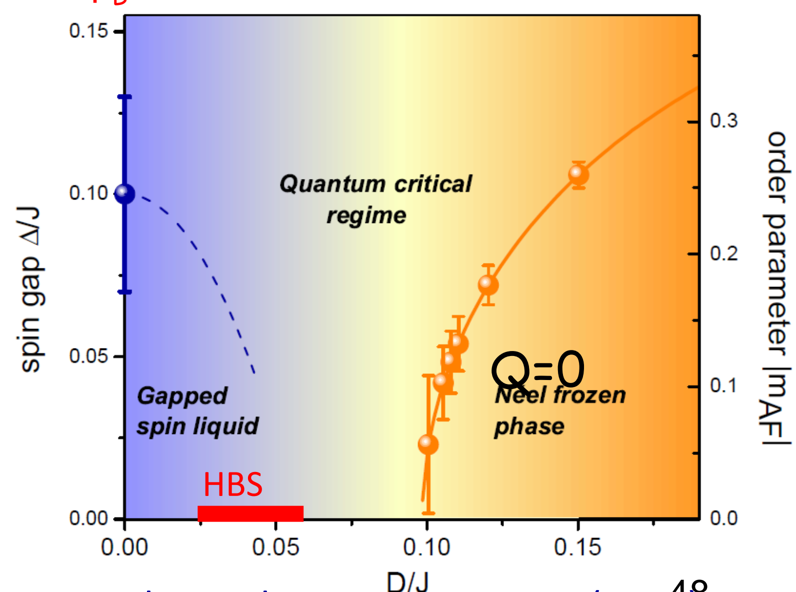


Smaha et al. PhysRevMaterials.4.124406

Evading the QSL phase : T ~1K under applied field



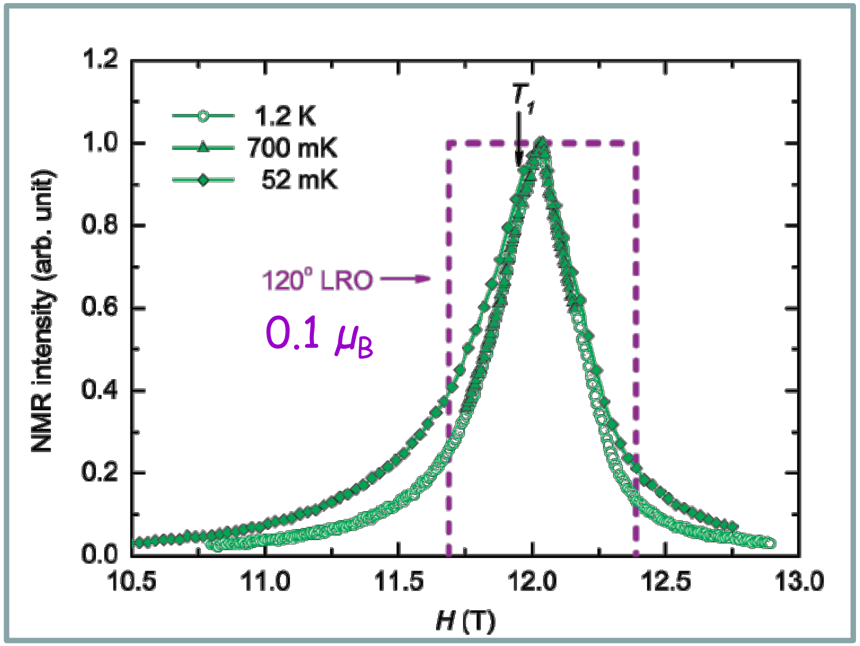


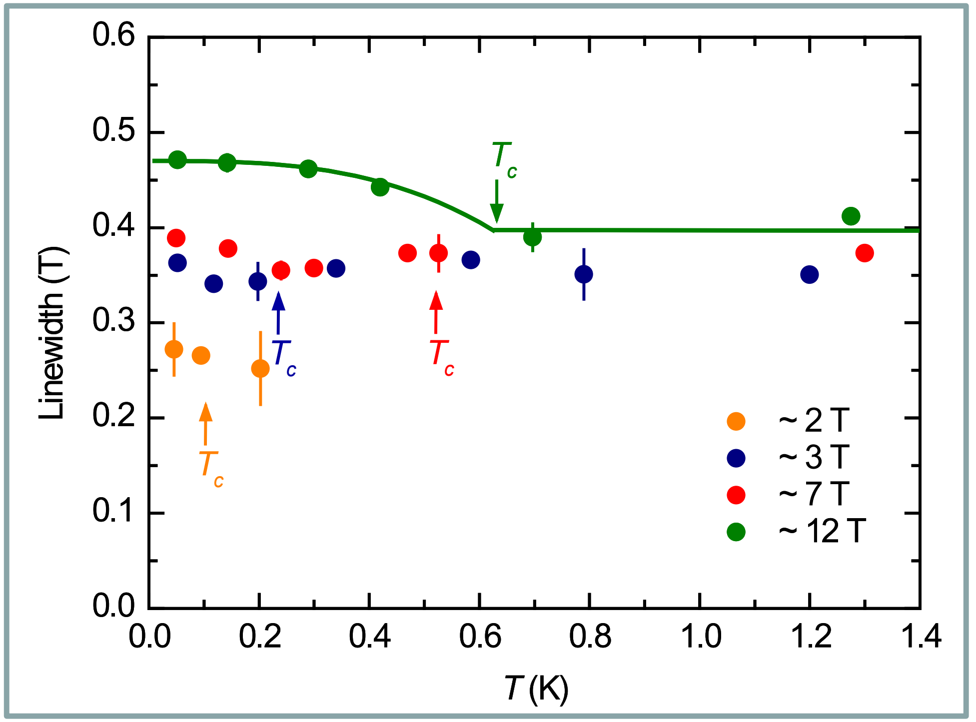


M. Jeong et al, PRL 107, 237201 (2011)
Q. Barthélemy, PhD

A. Zorko et al, PRL 101, 026405 (2008)
S. El Shawish et al, PRB 81, 224421 (2010)

Very Small frozen moment





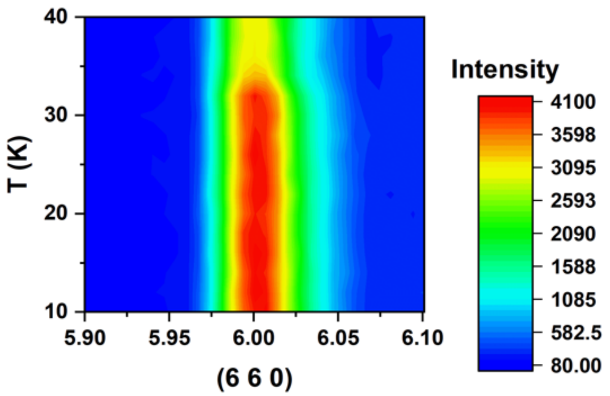
-No long range order but frozen state

-Hyperfine constant: 3.5 T/μ_B

μ_{frozen} ~ 0.1 μ_B @ 12 T

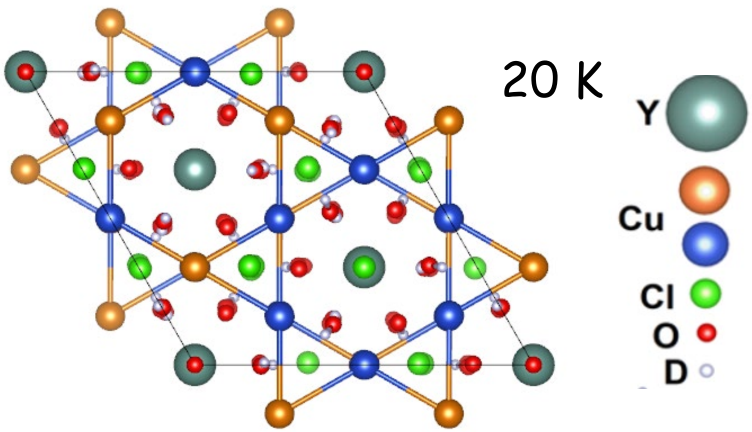
μ_{frozen} even smaller for smaller H

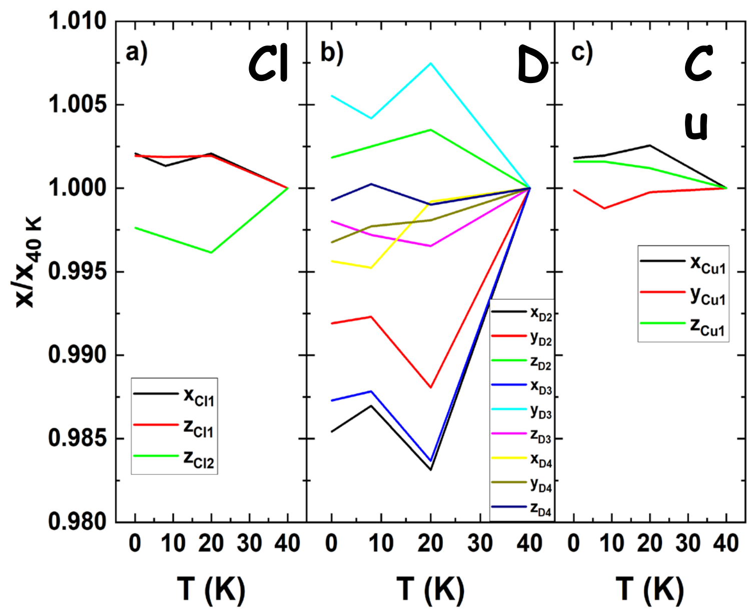
Neutron diffraction measurements



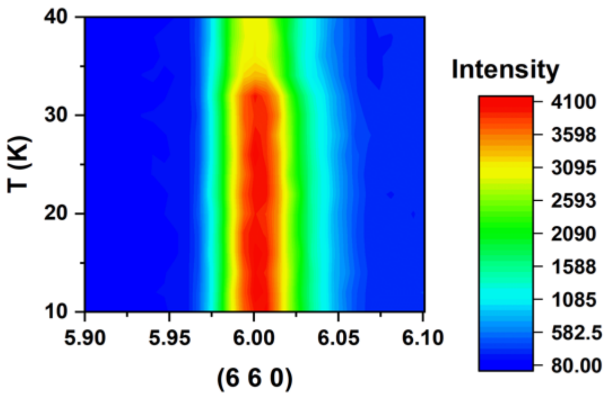
No additional Bragg peaks down to 65mK
but intensities change at **33 K**

Transition preserves the crystal symmetry (on average)
involves mostly small changes in the hydrogen positions.





Neutron diffraction measurements



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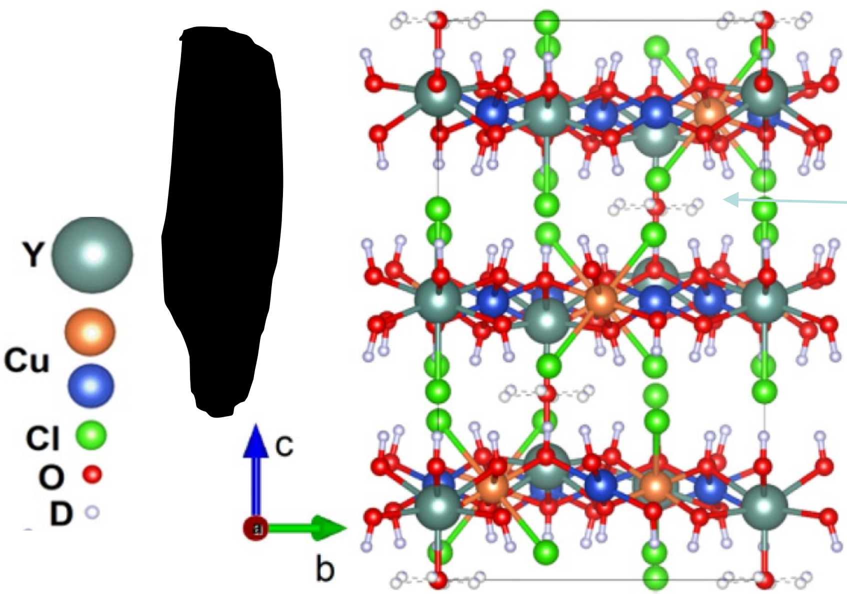
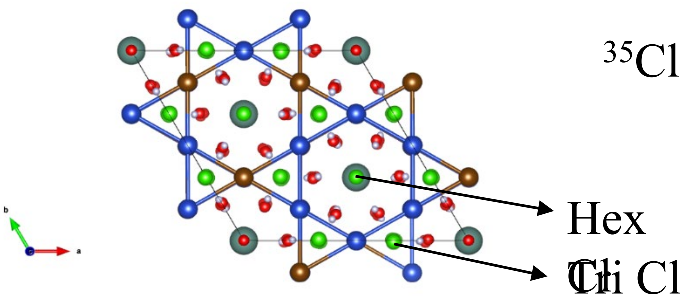
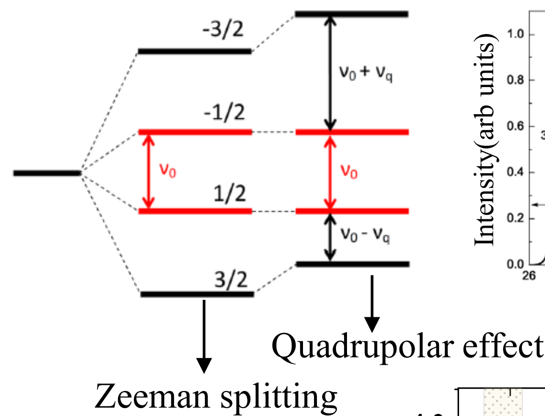


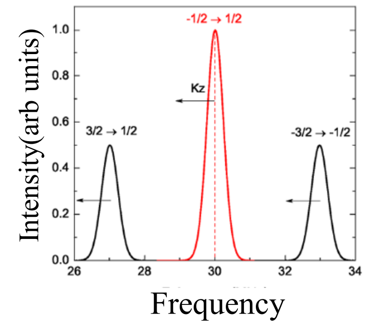
freezing of H1 on 1 of the 6 allowed positions

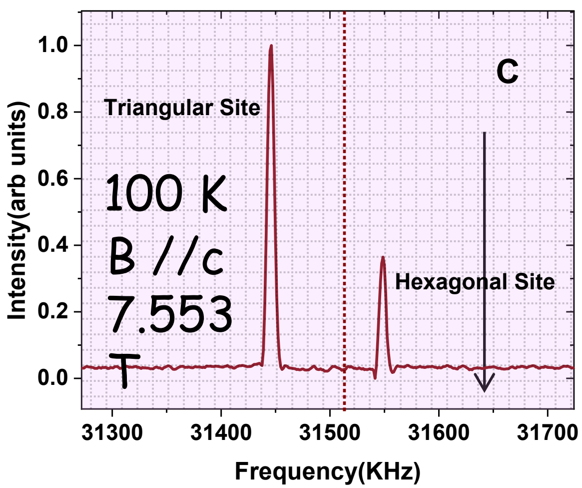
^{35}Cl NMR in structurally distorted kagome lattice



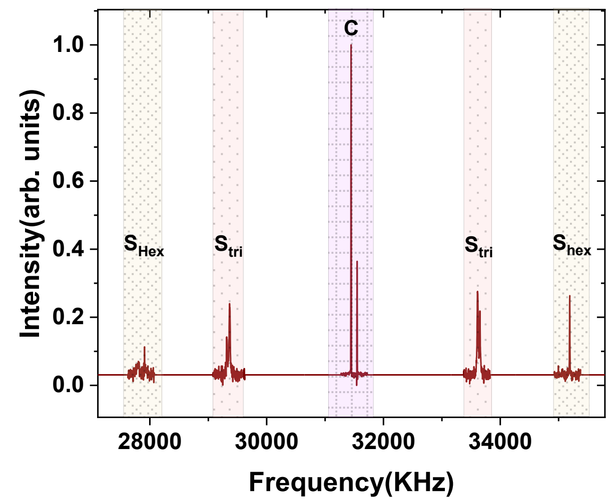
^{35}Cl I=3/2



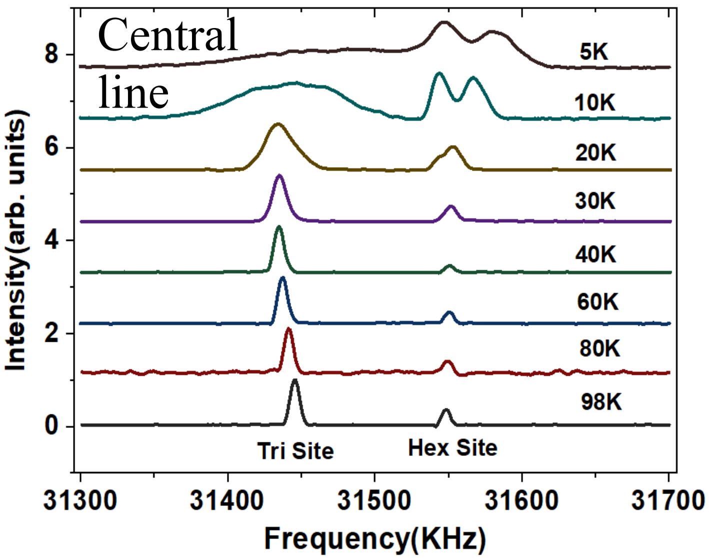


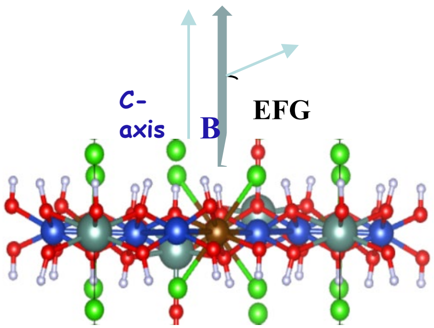


2 sites ✓
Intensity ratio 3:1 ✓

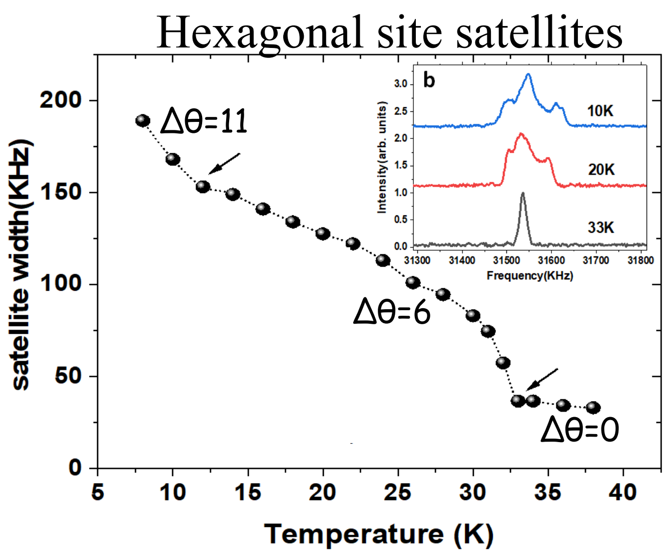


Structural transition from NMR local probe



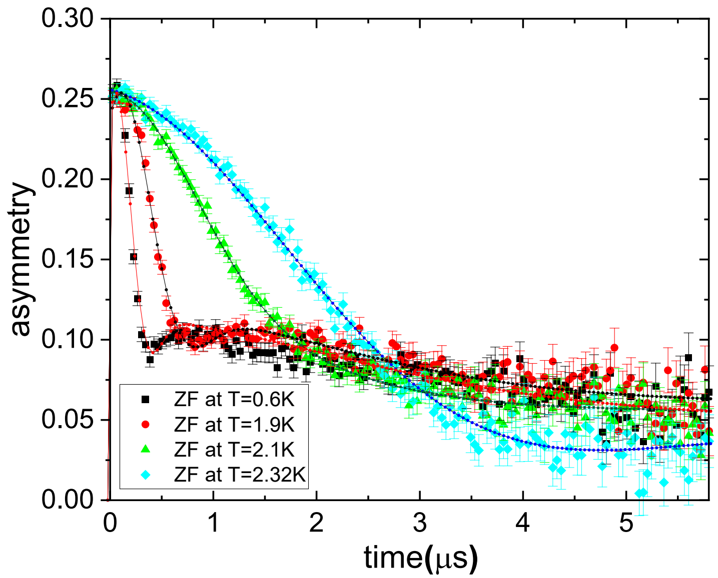


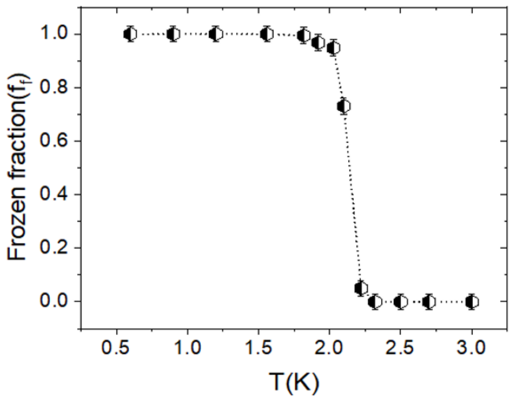
Δθ ~ 5° at 20 K and around ~ 10° at 10 K

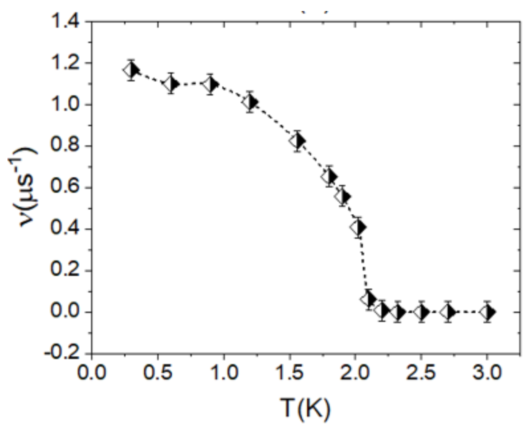


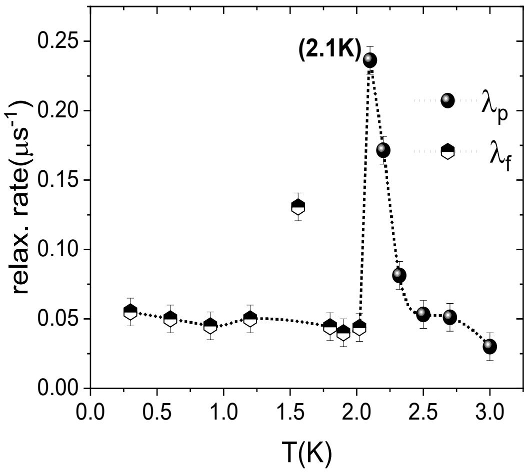
Marked changes at 33K and around 12K
Multiple Cl sites with rotated local EFG
≠ average structure from neutron

Muon spin relaxation measurements







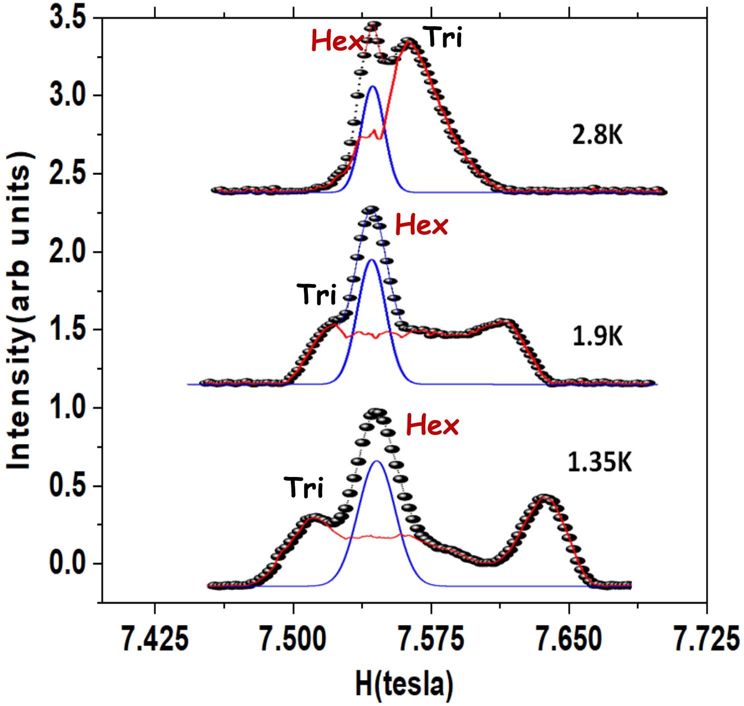


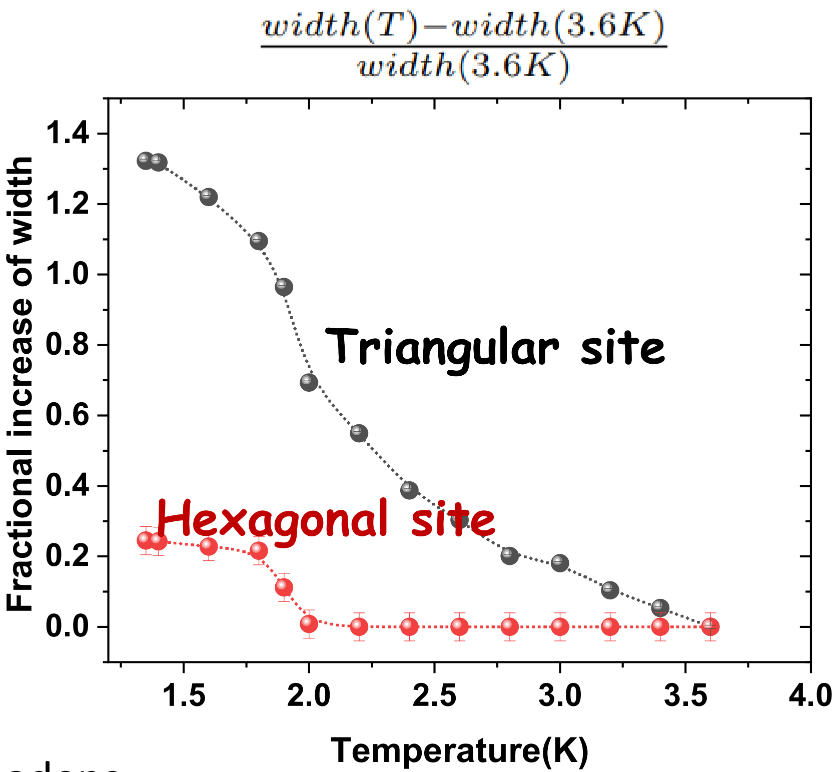
Complete transition at 2.1 K

Frozen moment ~ 0.03 μ_B

Strongly damped oscillations, SRO //c?, multiple stopping sites…)

Magnetic ordering at low temperature

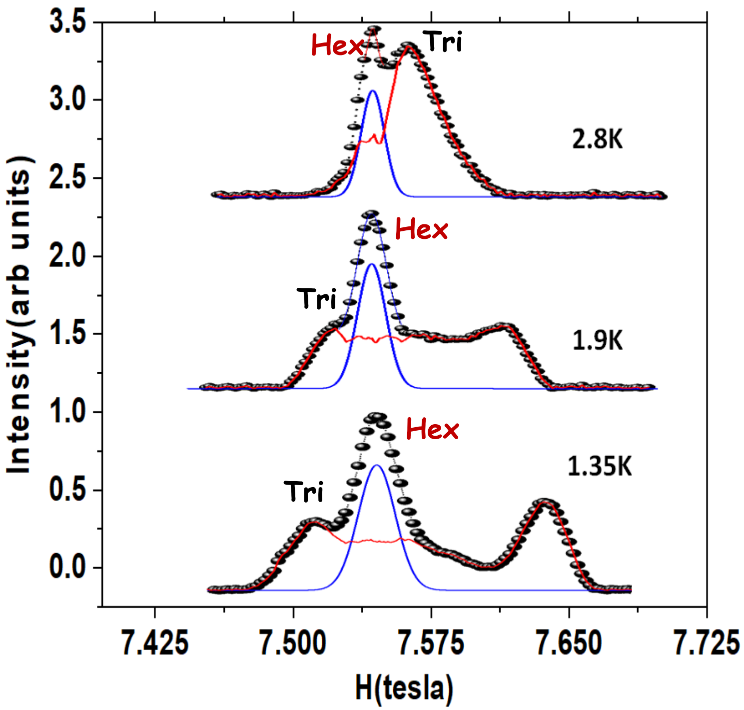




Hexagonal Cl hardly broadens

Triangular Cl line broadens/splits at the magnetic transition

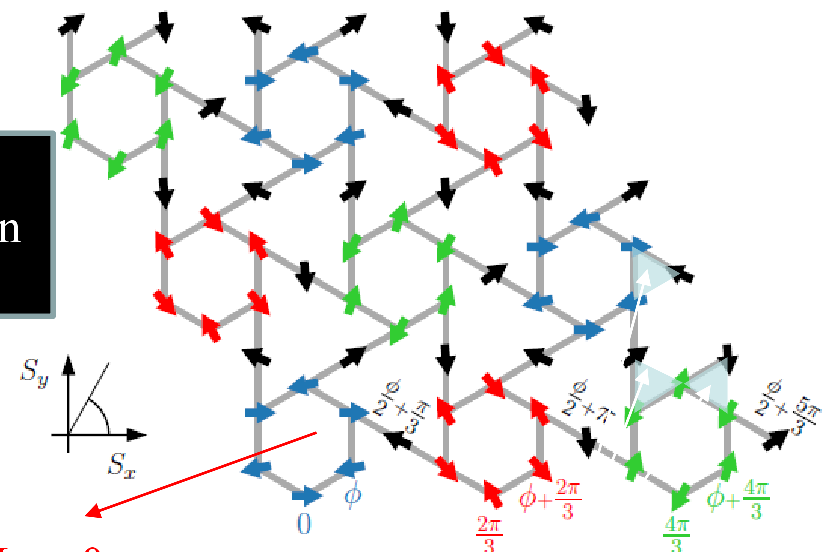
Magnetic ordering at low temperature



in line with proposed spin texture…

Proposed (1/3,1/3) ordering

Hering et al, npj Comput Mater 8, 10 (2022)



$H_{int} \sim 0$

Finite H_{int}, 3 configurations

Hexagonal Cl hardly broadens

Triangular Cl line broadens/splits at the magnetic transition

PHYSICAL REVIEW MATERIALS **5**, 064401 (2021)

Magnetic ordering of the distorted kagome antiferromagnet $Y_3Cu_9(OH)_{18}[Cl_8(OH)]$ prepared via optimal synthesis

W. Sun,[1] T. Arh,[2,3] M. Gomilšek,[2] P. Koželj,[2,3] S. Vrtnik,[2] M. Herak,[4] J.-X. Mi,[1] and A. Zorko[2,3,*]

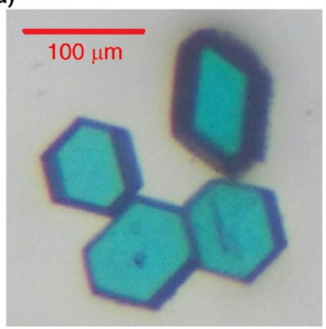
[1]*Fujian Provincial Key Laboratory of Advanced Materials, Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, Fujian Province, People's Republic of China*

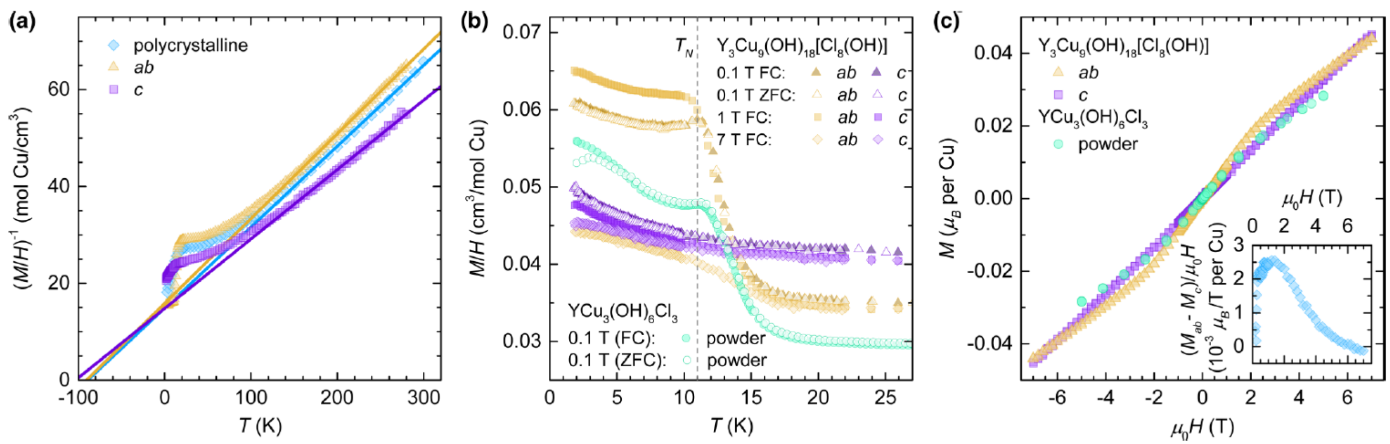
[2]*Jožef Stefan Institute, Jamova cesta 39, SI-1000 Ljubljana, Slovenia*

[3]*Faculty of Mathematics and Physics, University of Ljubljana, Jadranska ulica 19, SI-1000 Ljubljana, Slovenia*

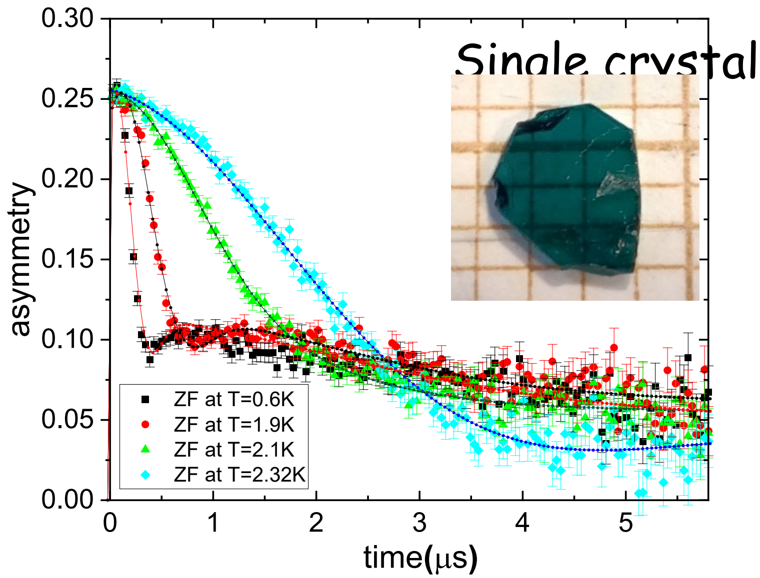
[4]*Institute of Physics, Bijenička cesta 46, HR-10000 Zagreb, Croatia*

(a)



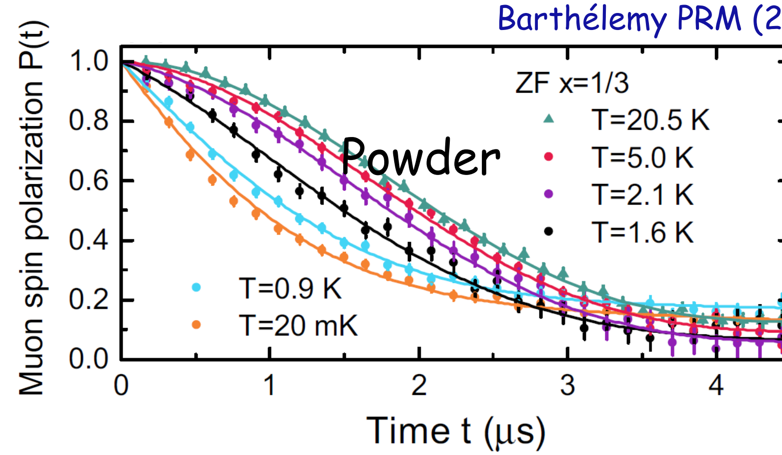


Muon spin relaxation measurements



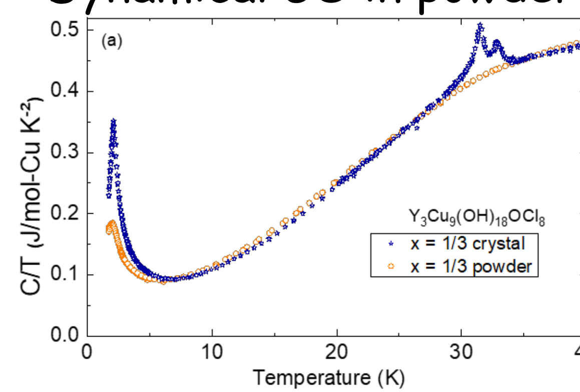
≠

Barthélemy PRM (2019)

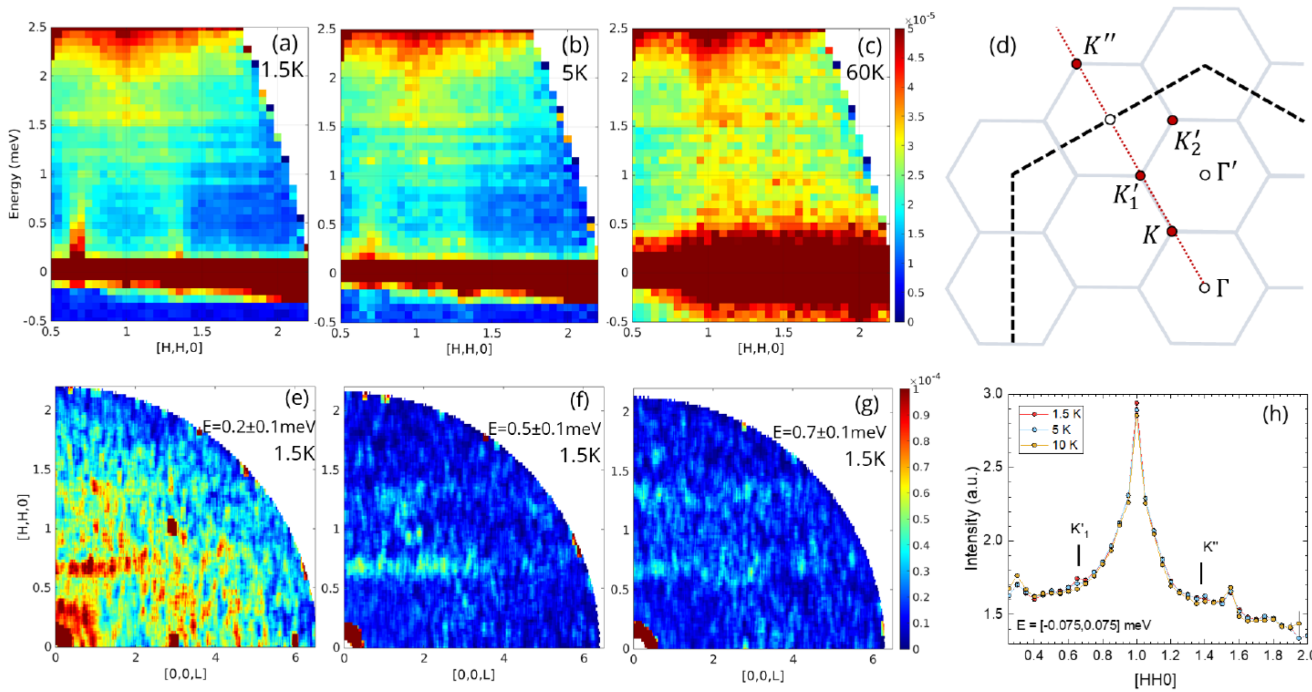


Complete transition at 2.1 K
Frozen moment <~$0.1\mu_B$

Dynamical GS in powder sample



Long range magnetic order (INS)



Spin waves dispersion emerging from K points at 1.5K inline with (1/3,1/3) LR

No dispersion along (00L), strongly 2D

Very weak static moment