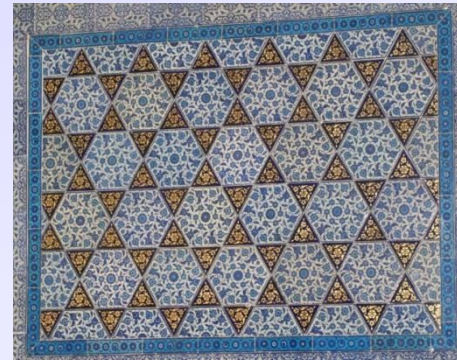
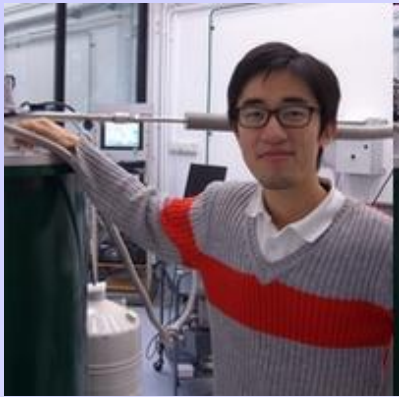


Kagome quantum spin liquids: some recent experimental developments

M. Jeong, F. Bert, E. Kermarrec, J. Quilliam, P. Mendels
*Laboratoire de Physique des Solides,
Université Paris-Sud, Orsay, France*





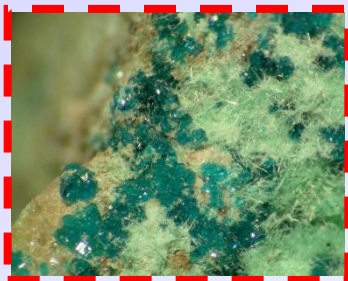
Materials are all existing minerals !



Herbertsmithite



Volborthite



Haydeeite



Kapellasite



Vesignieite

Kagome Physics vs time (exp^{al}) :

- SrCrGaO (SCGO) Cr³⁺ (S=3/2)

90'

- kagome bilayers
- spin-glass freezing but **large density of low energy excitations**
- **Spin textures** (A.Sen et al. Phys. Rev. Lett. **106**, 127203)

- Jarosites (classical spins)

90'

- Neel transitions
- **importance of DM interactions**

- Volborthite

2001

- First **S=1/2** kagome compound (1st nn interactions)
- ordering, fluctuations(μ SR), distorted lattice, **field induced transitions**

- Expansion of the quantum kagome universe

2005

- **Discovery of Herbertsmithite (2005)**
- **No freezing (2007): a spin liquid state**
- Many cuprates : Kapellasite, Vesigneite, Haydeite
- Also Hyperkagome (Na₃Ir₄O₈)

M.I.T., 2005

J|A|C|S
COMMUNICATIONS

Published on Web 09/09/2005

A Structurally Perfect $S = 1/2$ Kagomé Antiferromagnet

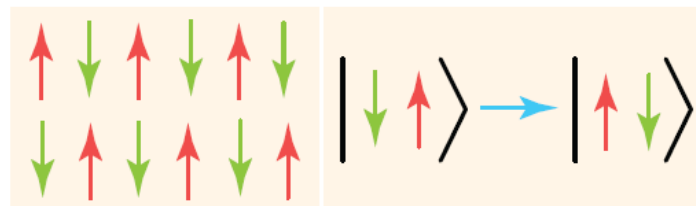
Matthew P. Shores, Emily A. Nytko, Bart M. Bartlett, and Daniel G. Nocera*

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

An End to the Drought of Quantum Spin Liquids

Patrick A. Lee

After decades of searching, several promising examples of a new quantum state of matter have now emerged.



Sciences, perspectives sept 2008

Outline

- Zn and Mg Herbertsmithite $\text{Cu}_3(\text{Zn,Mg})(\text{OH})_6\text{Cl}_2$
 - a gapless quantum spin liquid (summary)
 - field induced solidification of the QSL
- Vesignieite $\text{Cu}_3\text{Ba}(\text{VO}_5\text{H})_2$
 - local susceptibility (NMR)
 - ~~heterogeneous~~ frozen ground state ($\mu\text{SR}+\text{NMR}$)
- Kapellasite, Haydeite $\text{Cu}_3(\text{Zn,Mg})(\text{OH})_6\text{Cl}_2$
 - competing exchange interactions
 - A new QSL, cuboc-2 type

Quantum criticality
Dzyaloshinsky-Moriya interactions

J1-J2 model on kagome lattice
Novel spin liquid?

Zn and Mg Herbertsmithite $\text{Cu}_3(\text{Zn,Mg})(\text{OH})_6\text{Cl}_2$

- discussion about defects
- Mg-Herbertsmithite
- a gapless quantum spin liquid (summary)
- field induced solidification of the QSL

Collaborations

Samples

Ross H Colman, David Boldrin, Andrew S Wills, *UCL, UK*
P. Strobel, Institut Neel, *Grenoble, France*
J. C. Trombe, F. Duc, *CEMES, Toulouse, France*
M. de Vries, A. Harrison, *Edinburgh, UK*

ESR

A. Zorko, Inst J. Stefan, *Slovenia*

Magnetization

P. Bonville, CEA Saclay (*France*)

μSR

PSI (A. Amato, C. Baines); ISIS (A. Hillier, J. Lord)

M.I.T., 2005

J|A|C|S
COMMUNICATIONS

Published on Web 09/09/2005

A Structurally Perfect $S = 1/2$ Kagomé Antiferromagnet

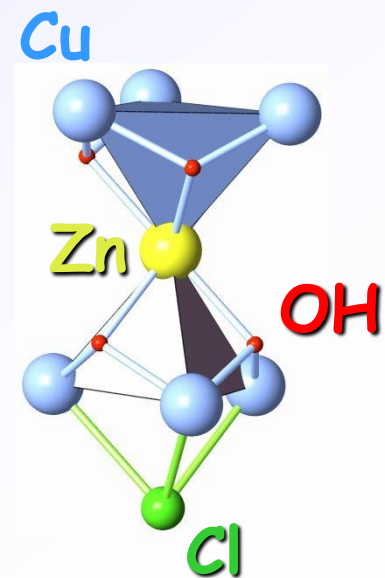
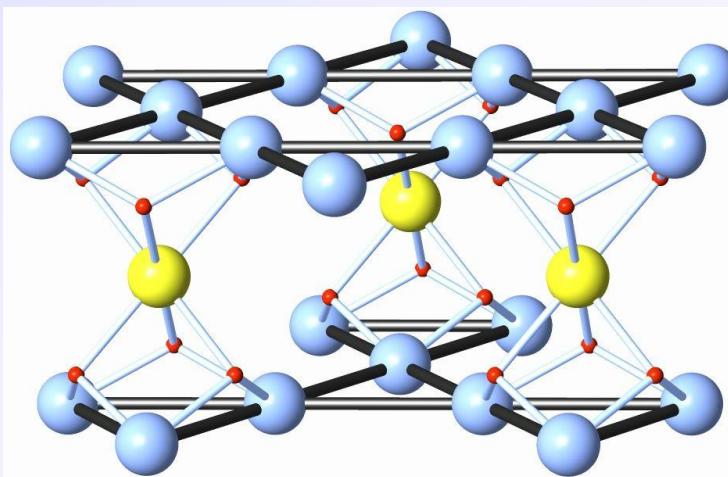
Matthew P. Shores, Emily A. Nytko, Bart M. Bartlett, and Daniel G. Nocera*

*Department of Chemistry, 6-335, Massachusetts Institute of Technology, 77 Massachusetts Avenue,
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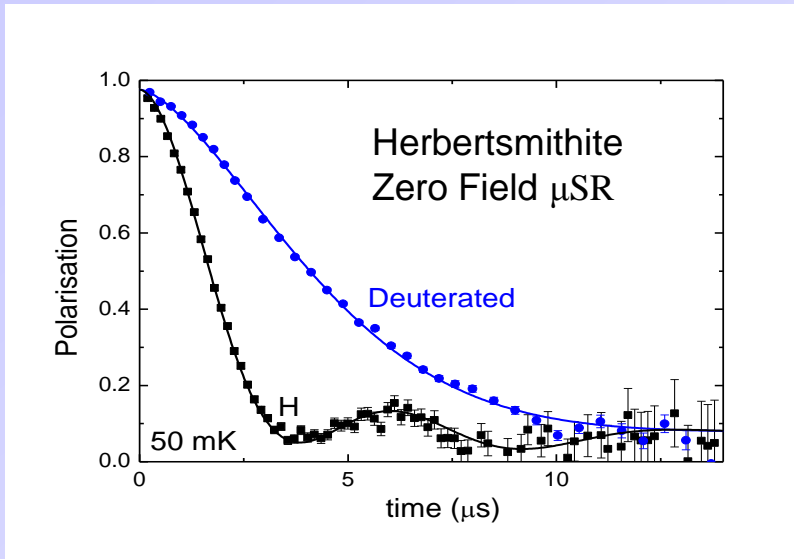
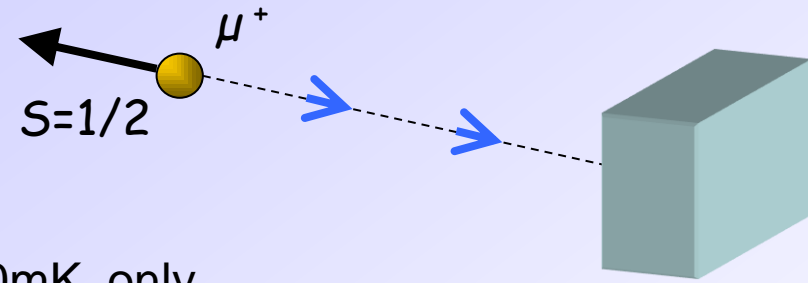
Herbertsmithite:



Cu^{2+} , $S=1/2$



Muon spin relaxation (μ SR)



P. Mendels et al, PRL 98, 077204 (2007)

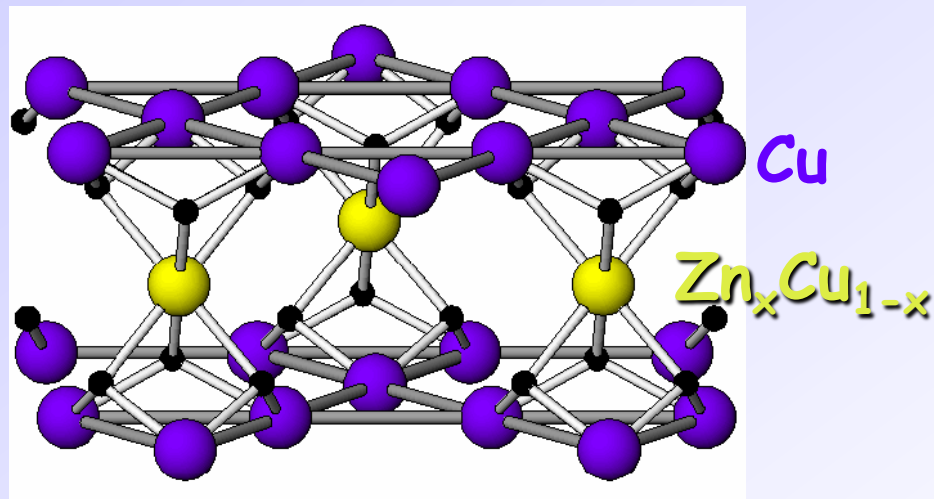
At 50mK, only small “static” nuclear fields.

upper limit of a frozen moment for Cu^{2+} , if any : $6 \times 10^{-4} \mu_B$

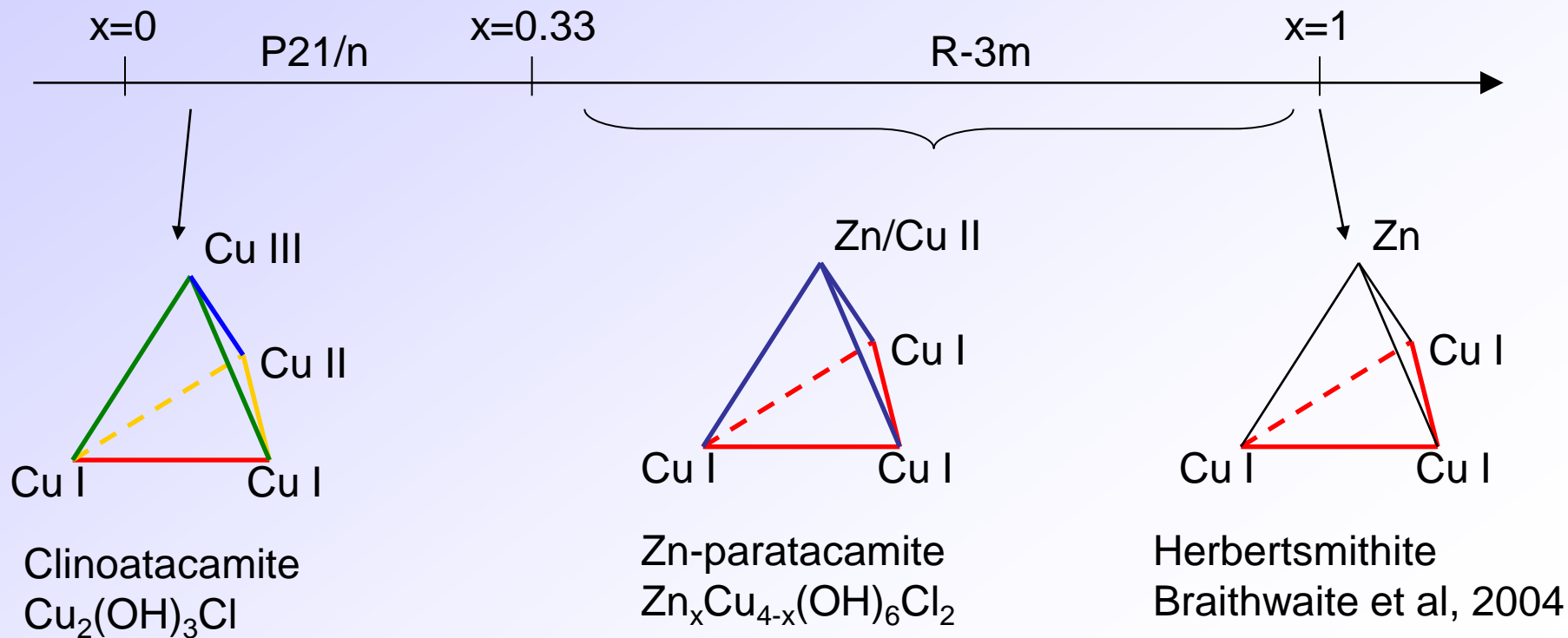
Also: ac- χ , Neutron Scattering Helton et al, PRL 98 107204 (2007)

No order or frozen disorder down to 20 mK ($\sim 10^{-4}$ J)
despite $J=180$ K !

$Zn_xCu_{4-x}(OH)_6Cl_2$
atacamite family



Zn/Cu substitution rate

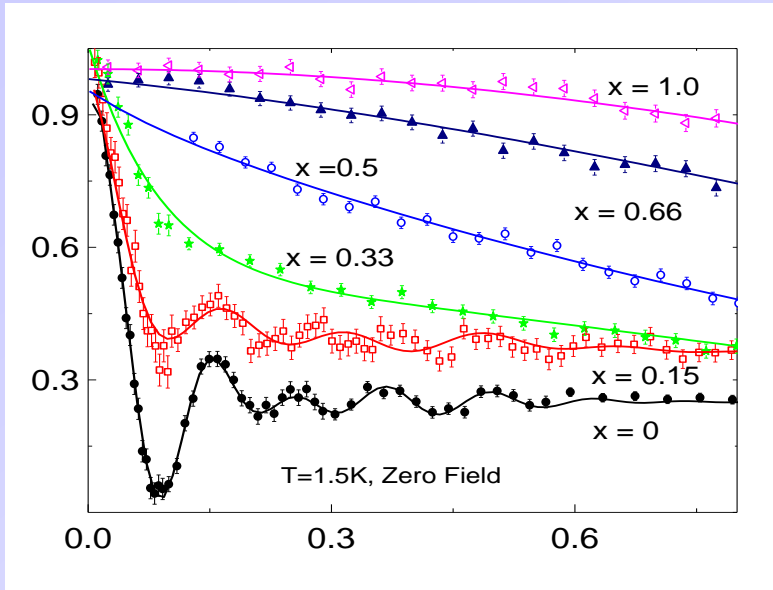


μ SR : Zn atacamites $Zn_xCu_{4-x}(OH)_6Cl_2$

-x=0 : fully ordered below ~18K
X.G. Zheng et al, PRL 95, 057201 (2005)

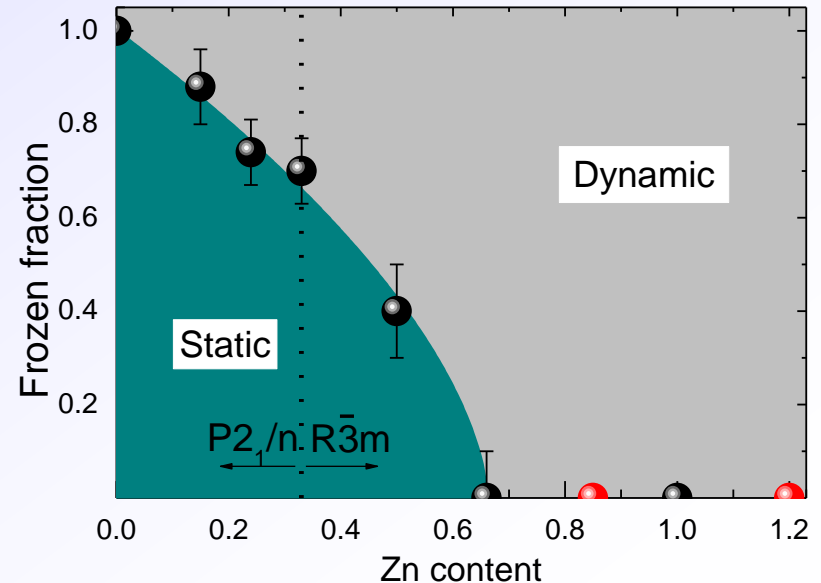
When x increases from 0 to 1 :
-Oscillations are smeared out
-A paramagnetic (x=1 type) component emerges at the expense of the frozen one

Polarization

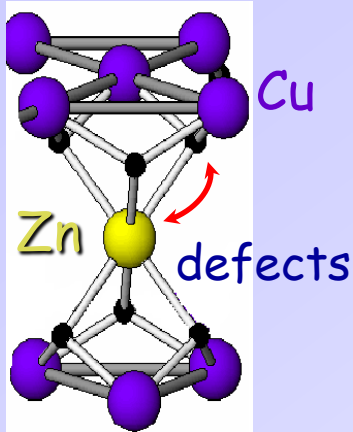


time (μ s)

Large domain of stability $0.66 < x < 1.2$ of a dynamical ground state



Magnetic defects : Zn/Cu intersite mixing



Cu on the Zn site
Nearly free $\frac{1}{2}$ spins

(~ 15-25 %)

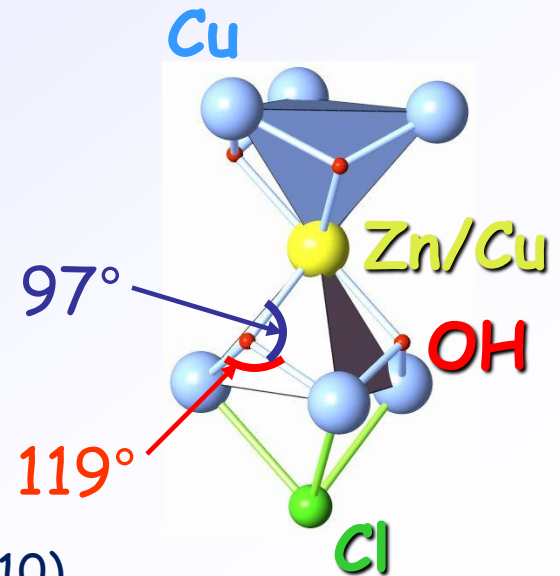
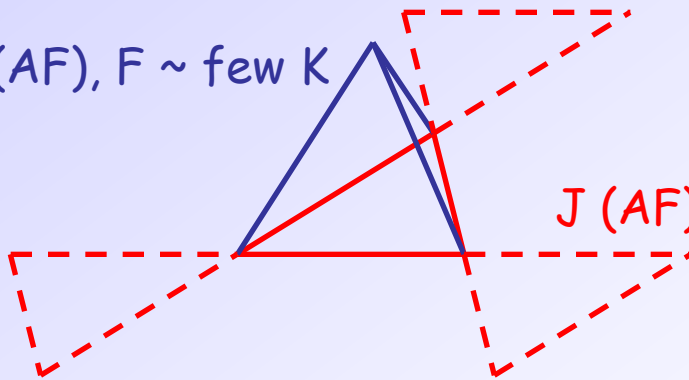
Freedman et al, JACS, 132 (2010)

Zn in the kagome plane
-> magnetic vacancy

(~ 1 - 7%)

?

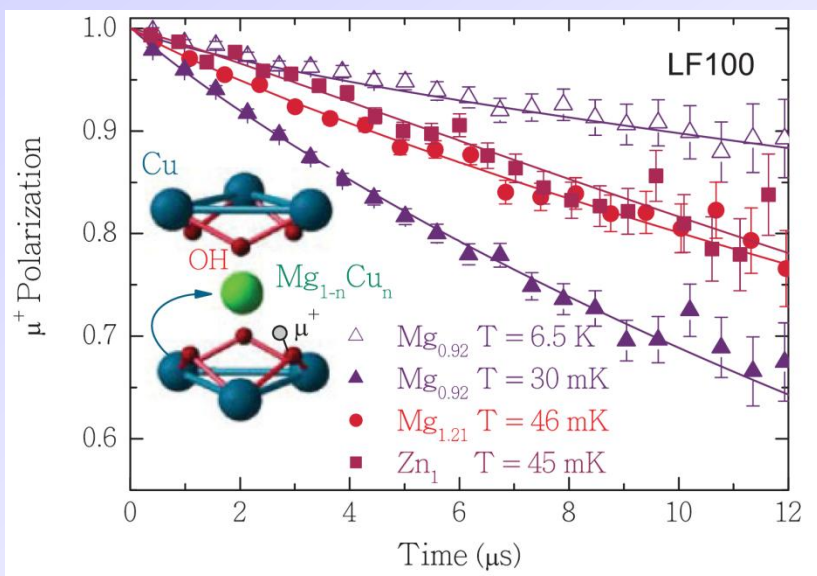
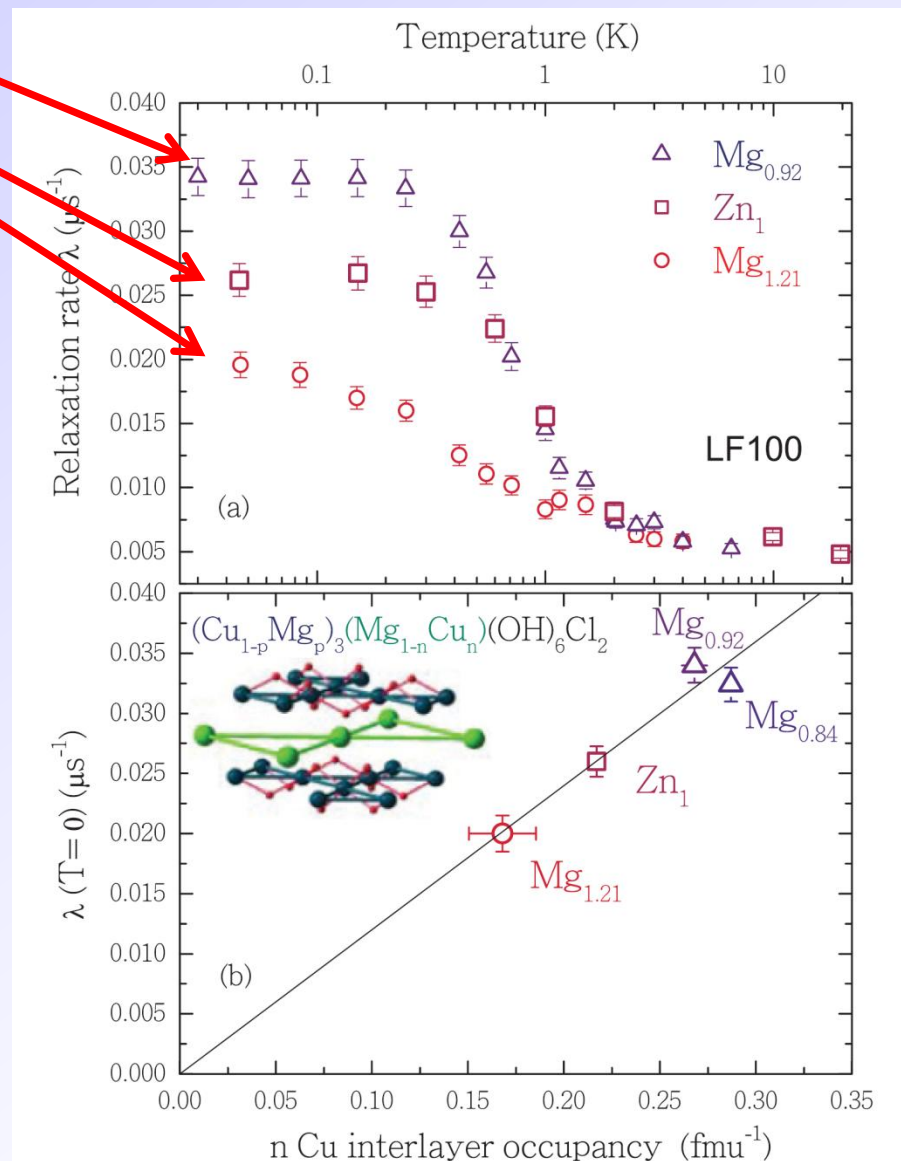
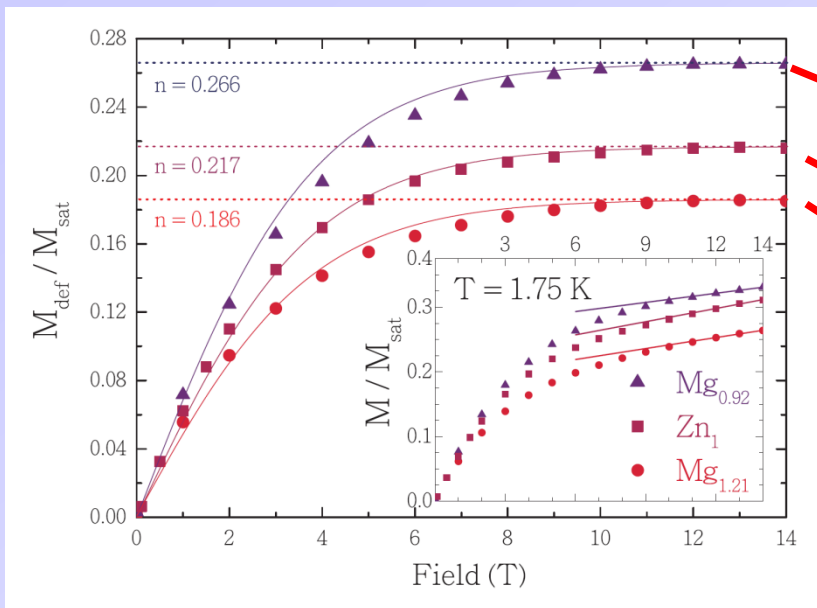
J' (AF), $F \sim$ few K

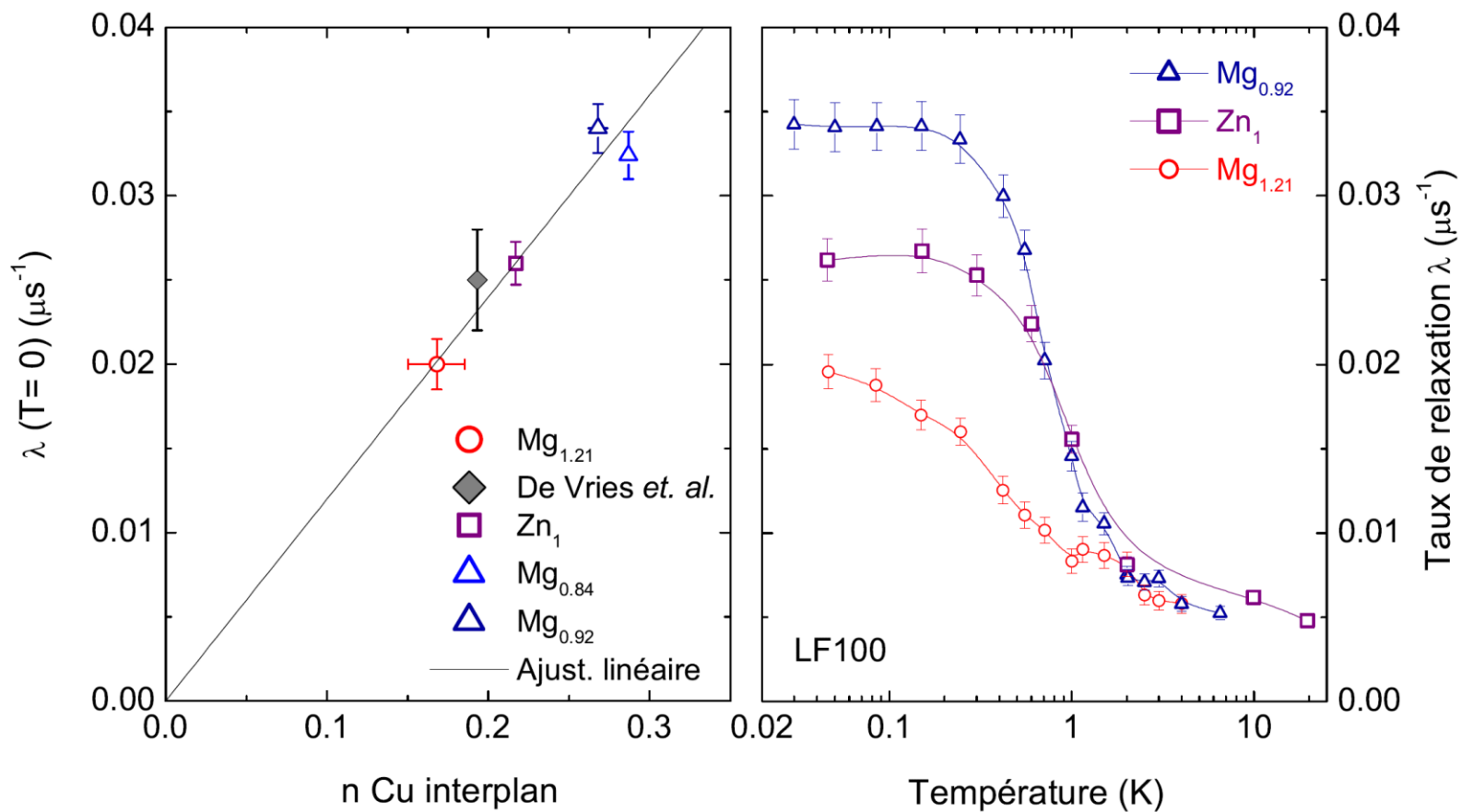


For a review and discussion, see

P. Mendels and F. Bert, J. Phys. Soc. Jpn 79 011001 (2010)
J. Phys. Conf. Series (2011)

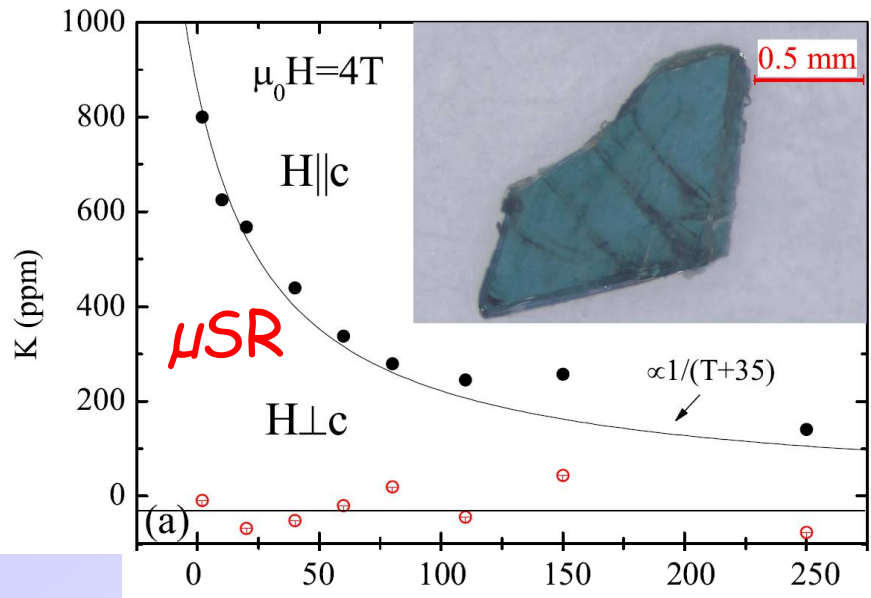
Mg- Herbertsmithite: control of *inter-site* defects



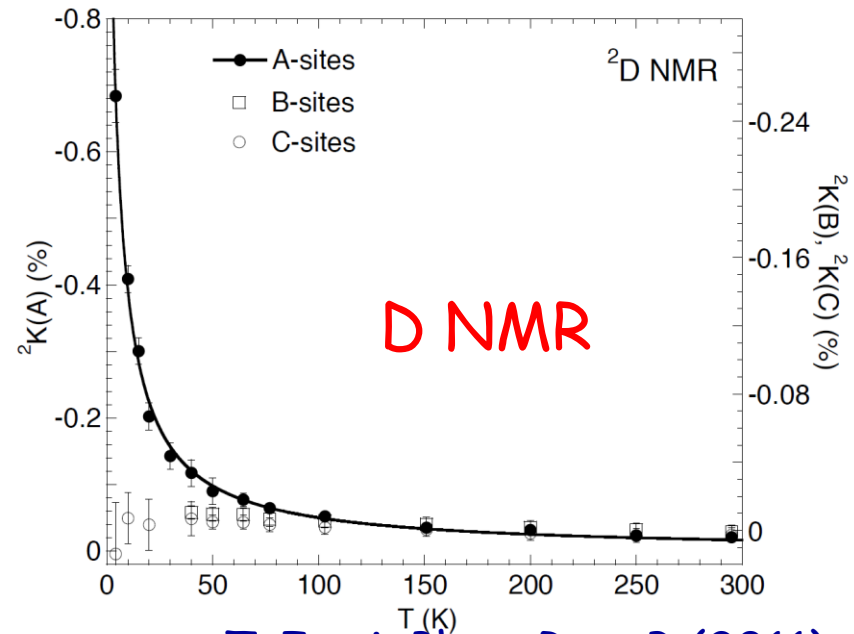


- Indirect coupling between inter-site defects (through Kagme planes?)
- Dynamics of inter-site defects governed by the kagome planes physics?

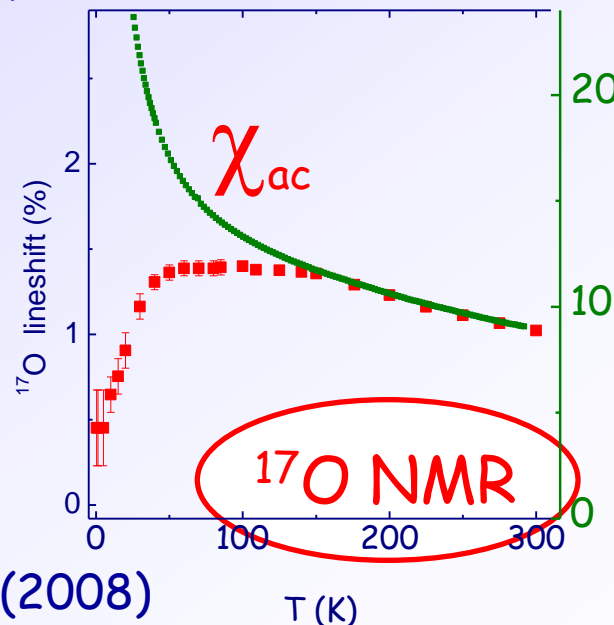
Susceptibility: χ muons, D NMR vs ^{17}O NMR (*intrinsic, defects*)



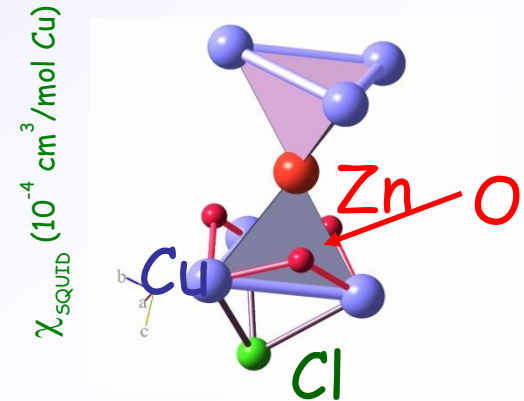
O. Ofer et al., ArXiv (2010)



T. Imai, Phys. Rev. B (2011)



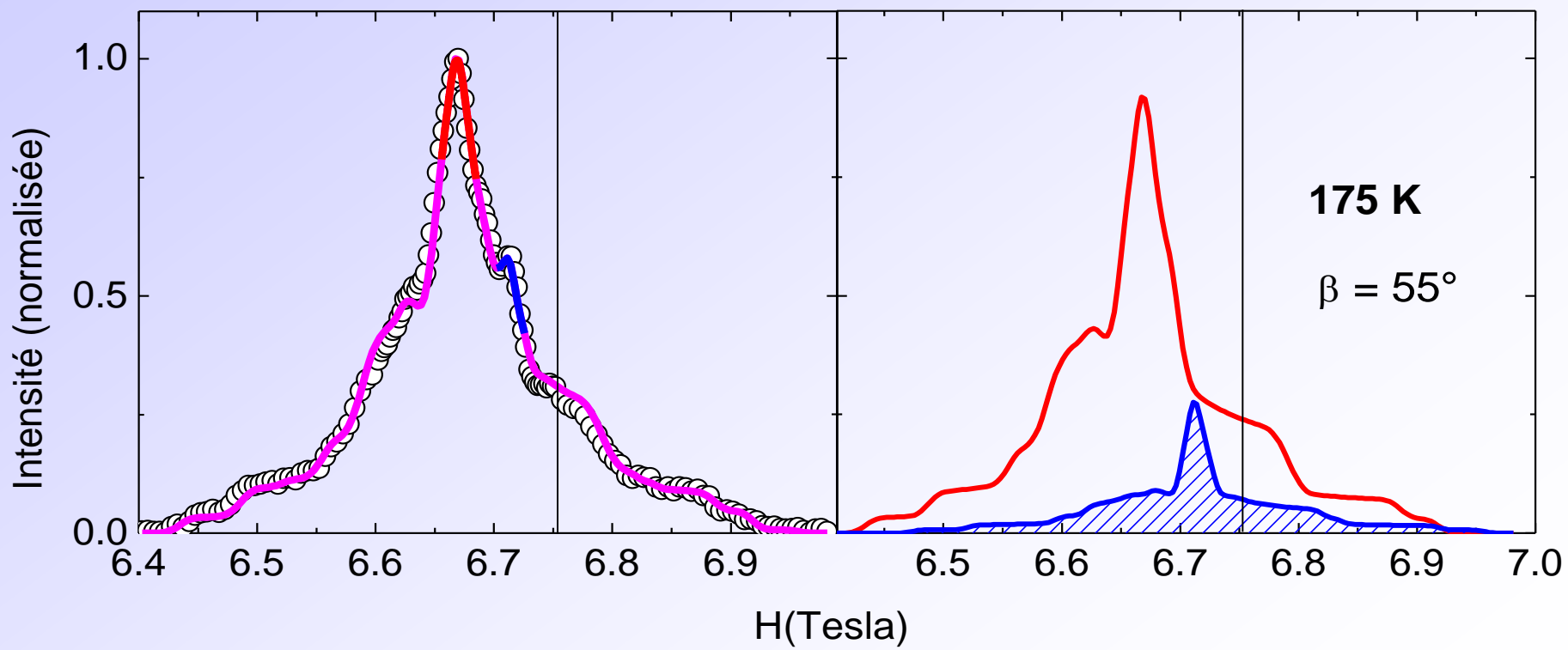
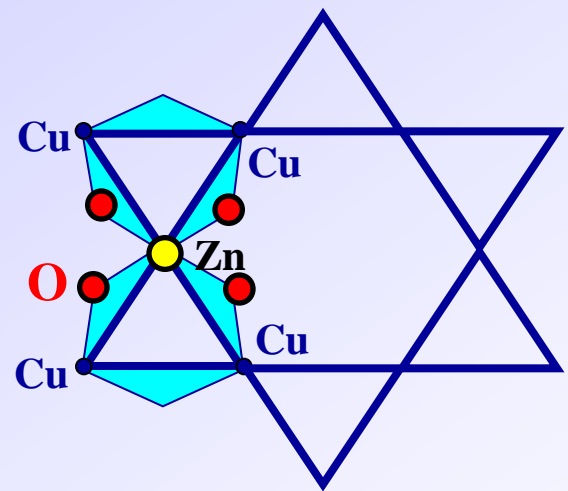
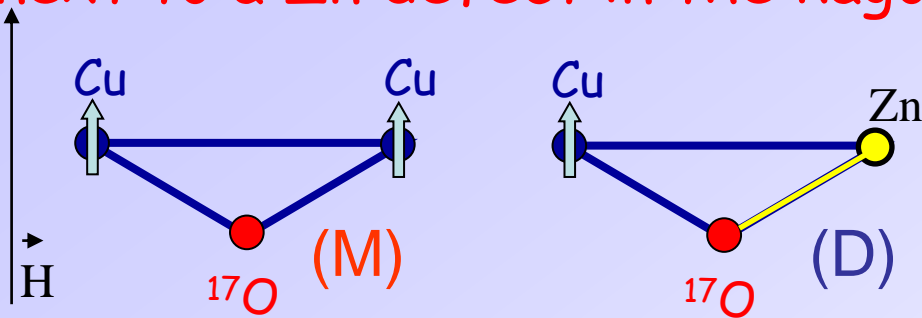
A. Olariu et al., Phys. Rev. Lett (2008)



Local

Two O sites

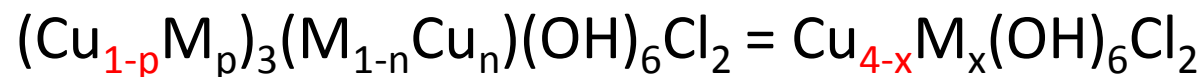
O next to a Zn defect in the kagome plane



~ 20% intensity \rightarrow ~ 5% Zn/Cu defects in kagome planes

ICP, diffraction, ^{17}O NMR (*intrinsic, defects*)

n = inter- plane Cu^{2+} defect $\leftrightarrow M(\text{H})$; diffraction (Mg case)
 p = intra-plane dilution (%) $\leftrightarrow ^{17}\text{O}$; diffraction (Mg case)
 x = total Mg (Zn) content per f.u. \leftrightarrow ICP



Composé	ICP	Diffraction ^a			$M(\text{H})$	RMN ^{17}O
$x = 3p - n + 1$	x	x	n	p	n	p
Mg 0.55	-	0.55	0.45	0	0.5(1)	-
Mg 0.84	0.84(1)	0.83 ^b	0.287(4)	0.041(1)	-	-
Zn 0.85	0.85(3)	-	-	-	0.297(4)	-
Mg 0.92	0.92(1)	0.91 ^b	0.266(3)	0.063(1)	0.266(4)	-
Mg 0.93	-	-	-	-	0.282(4)	0.07(2)
Zn 1	1.00(7)	1.0(1)	0.27(6)	0.09(2)	0.217(5)	-
Mg 1.21	1.25(3)	1.21(4)	0.15(1)	0.12(1)	0.186(4)	-
Mg 1.2	-	1.2	?	?	0.182(4)	0.12(2)

With Mg- Herbertsmithite, we check the overall consistency of the three methods to determine the amount of substitution on each site.

Conclusion about "defects"

- Intersite defects: Cu^{2+} on Zn sites

fair agreement between all methods: neutrons, M, specific heat,...

- Intraplane defects: Zn^{2+} on Cu sites: spin vacancies

Pro: ^{17}O NMR

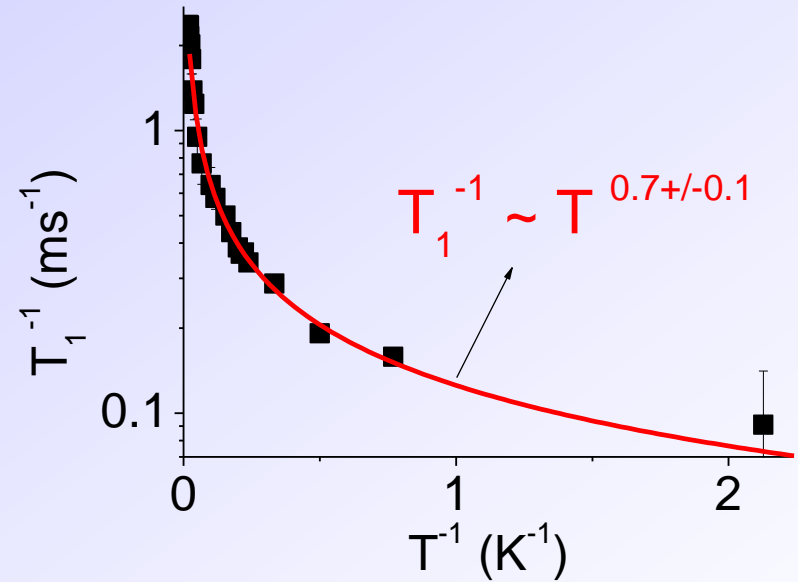
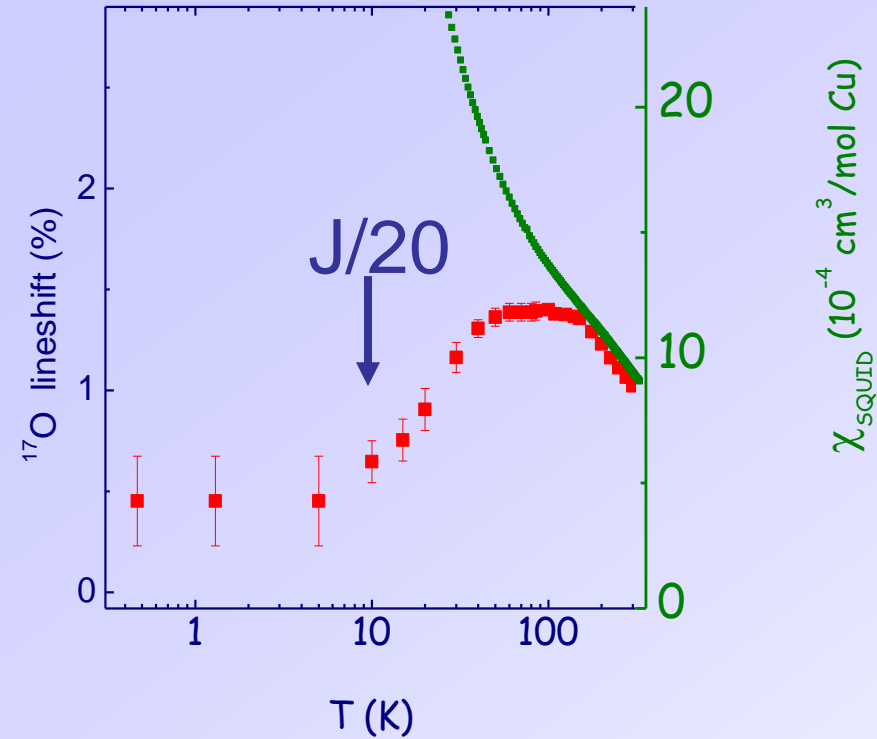
ICP constrain \oplus number of intersite defects

Contra: anomalous diffraction \oplus no better refinement
skepticism about ICP (if not, hard to reconcile the two measurements)

Question: Can intersite defects induce a response in the planes? If not then NMR linewidth not interpreted in the contra scenario

Issue: Different samples? « MIT » crystals vs « Orsay » powders

Gapless spin liquid



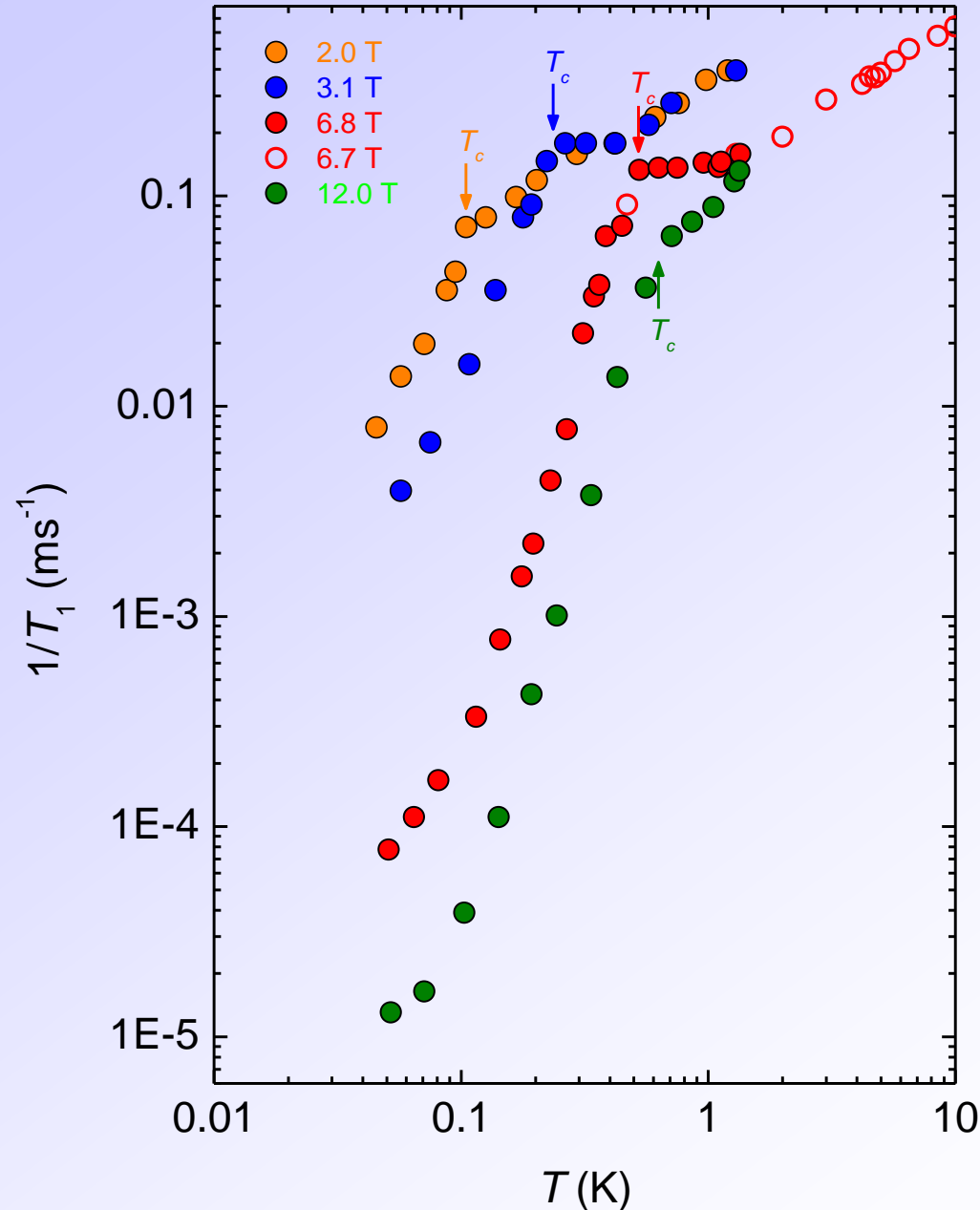
Olariu et al, PRL 100, 087202 (2008)

See also Imai et al, PRL 100, 077208 (2008)

Inelastic Neutron scattering: Helton et al, PRL 98 107204 (2007)

$$\chi'' \sim \omega^{-0.7}$$

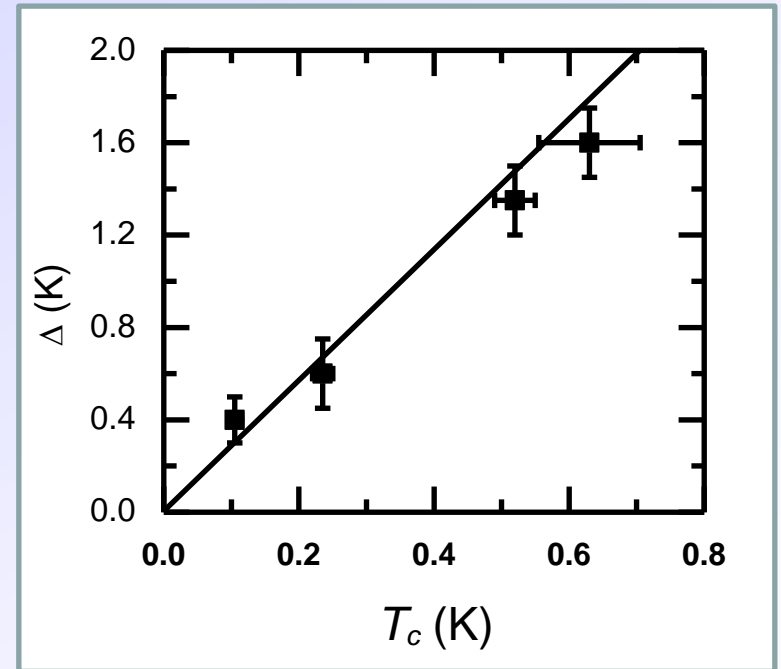
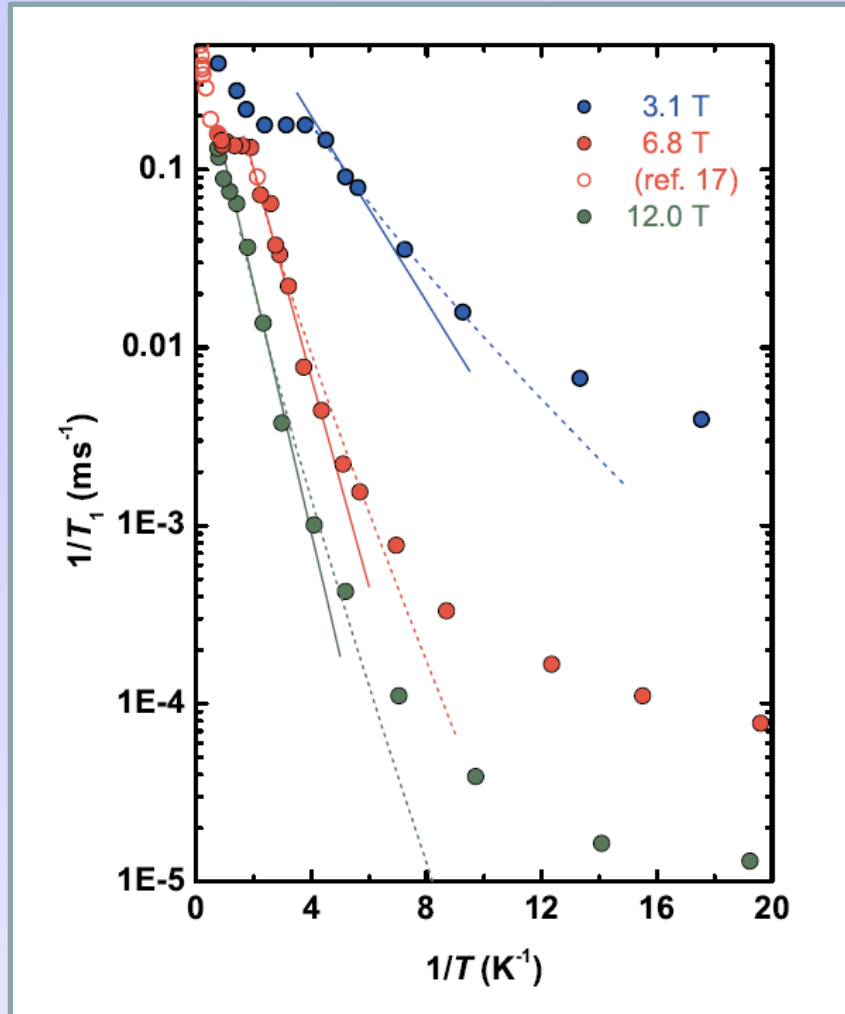
Very Low T Spin Dynamics: freezing under a field



M. Jeong et al,
Phys. Rev. Lett **107** (2011)

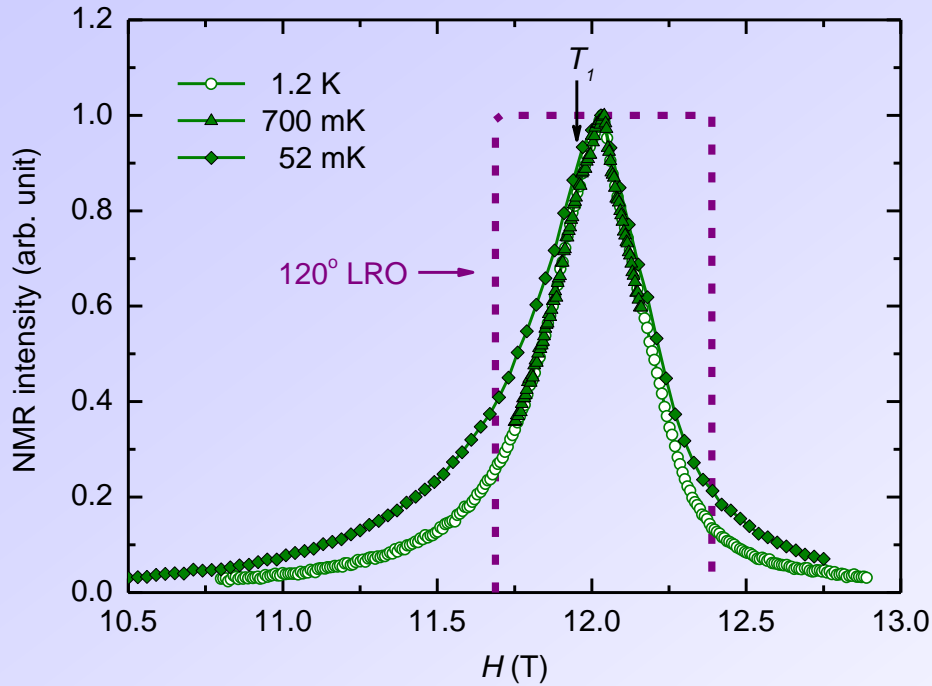
T_c increases with H

Field induced spin-gap

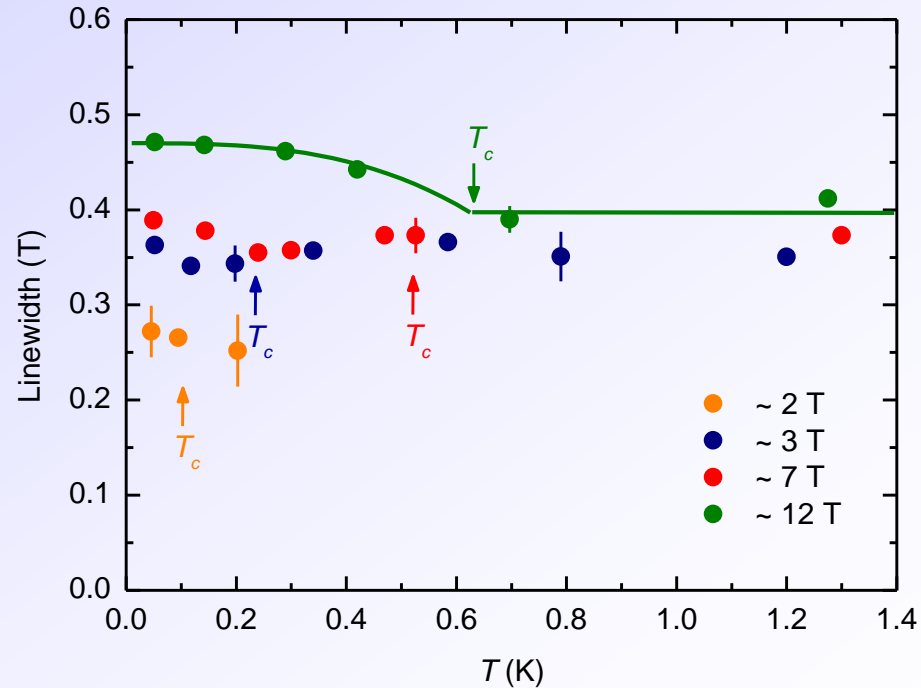


$$\Delta \sim 2.3 k_B T_c$$

Very Small frozen moment



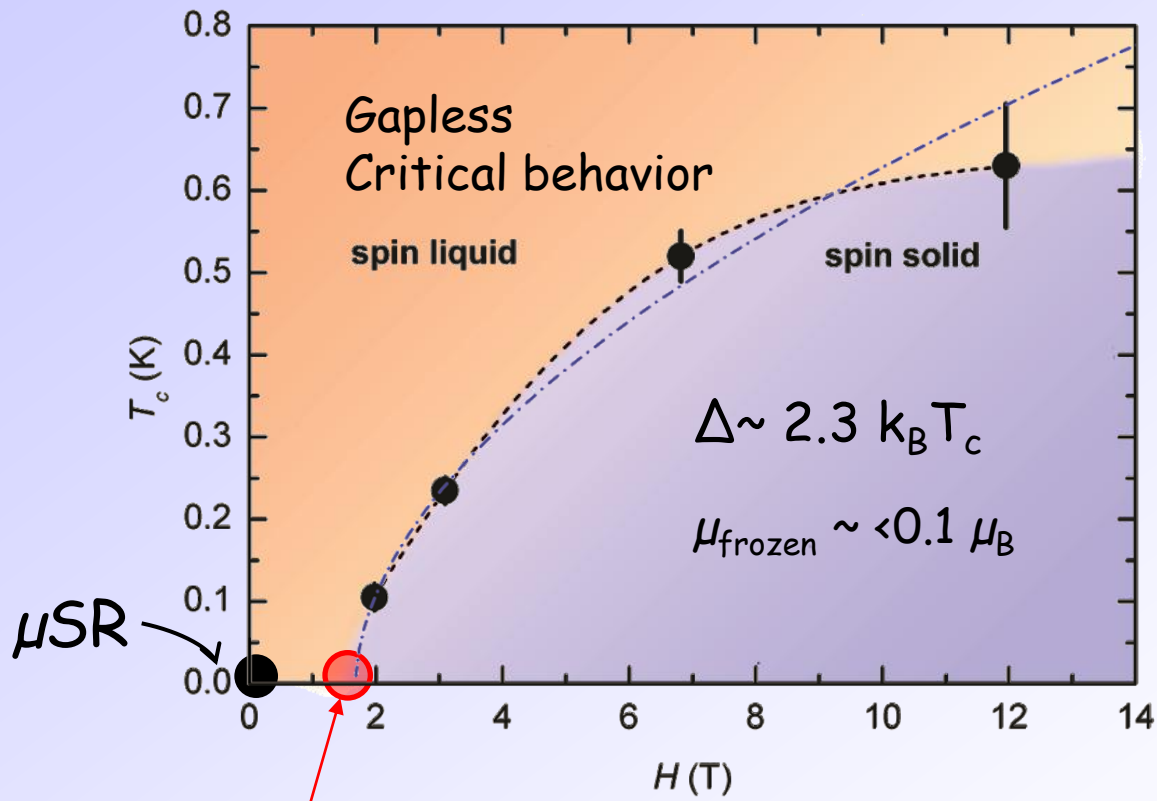
No ordered structure



Hyperfine constant: $3.5 \text{ T}/\mu_B$

$\mu_{\text{frozen}} \sim 0.1 \mu_B$ @ 12 T
 μ_{frozen} smaller for $H \searrow$

A Quantum Critical Point ?



$$\begin{aligned} T_c &\sim (H - H_c)^{0.65} \\ H_c &= 1.55(25) \text{ T} \\ \mu_B H_c &\sim J/180 \end{aligned}$$

Comparison to theories

○ Algebraic critical spin liquid - U(1)

Ran et al, PRL **98**, 117205 (2007)

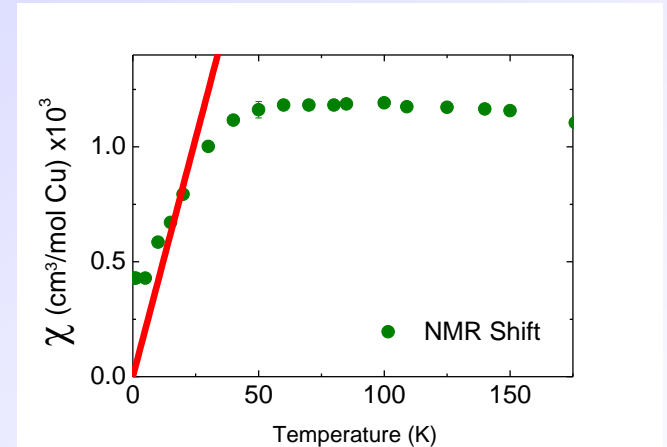
Hermele et al, PRB **77**, 224413 (2008)

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

$$\frac{1}{T_1} \propto T^\eta$$

-Gapless

-Critical behavior



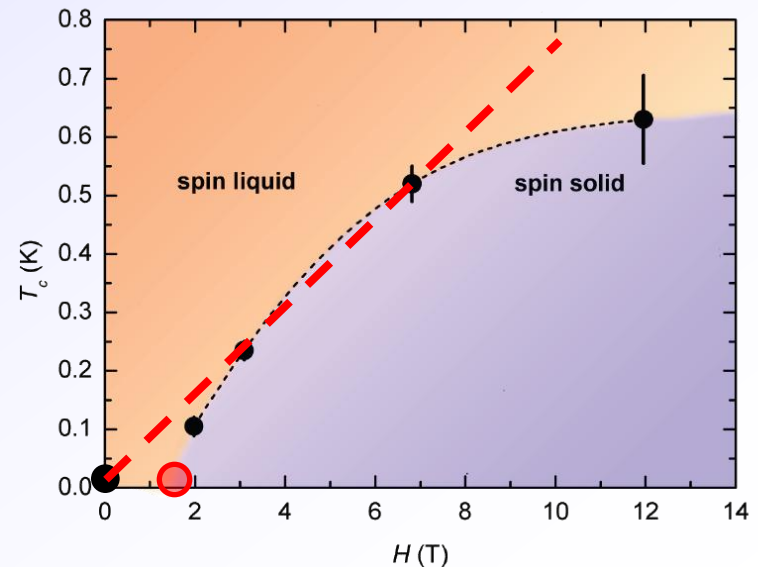
-Instability ($H \neq 0$) $M \sim H^\alpha$ but $T_c \sim H$

Ran et al, PRL **102** 117205 (2009)

-Unstable to anisotropy

DM interaction \rightarrow L.R.O.

Hermele et al, PRB **77**, 224413 (2008)



Comparison to theories

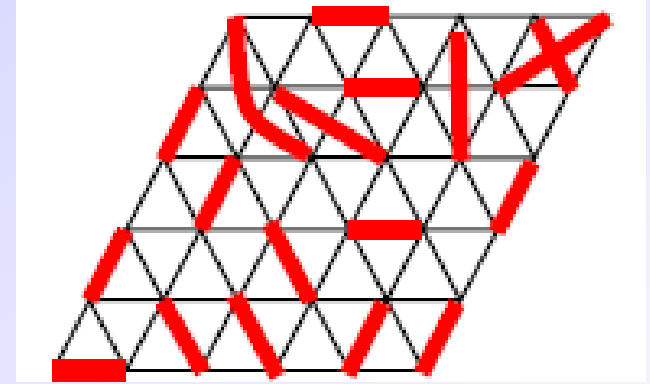
- Z_2 spin liquid

Yan et al, Science (2011)

Gapped magnetic excitations ($S=1/2$)

Gapped non-magnetic excitations

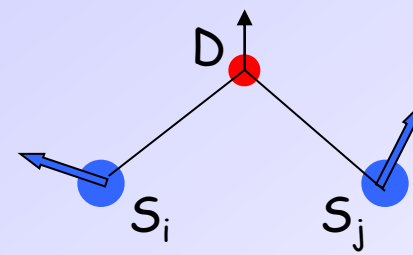
$$C_v \sim e^{-\Delta/T} ; \chi \sim e^{-\Delta'/T}$$



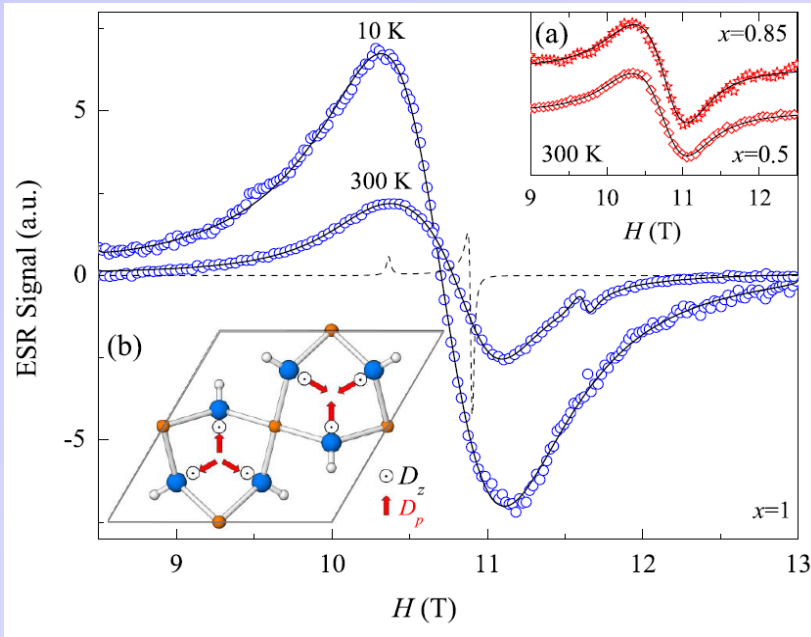
Short range RVB

Need to restore
ground state susceptibility
and some criticality...

Dzyaloshinskii-Moriya interactions



$$H_{DM} = D \cdot (S_i \wedge S_j)$$



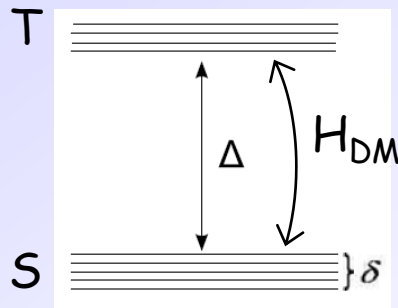
Broad room T ESR line \leftarrow magnetic anisotropy from DM

$$|D_z| = 0.08 \text{ J}, |D_p| \sim 0.01 \text{ J}$$

A. Zorko et al, PRL **101**, 026405 (2008)

S. El Shawish et al, PRB **81**, 224421 (2010)

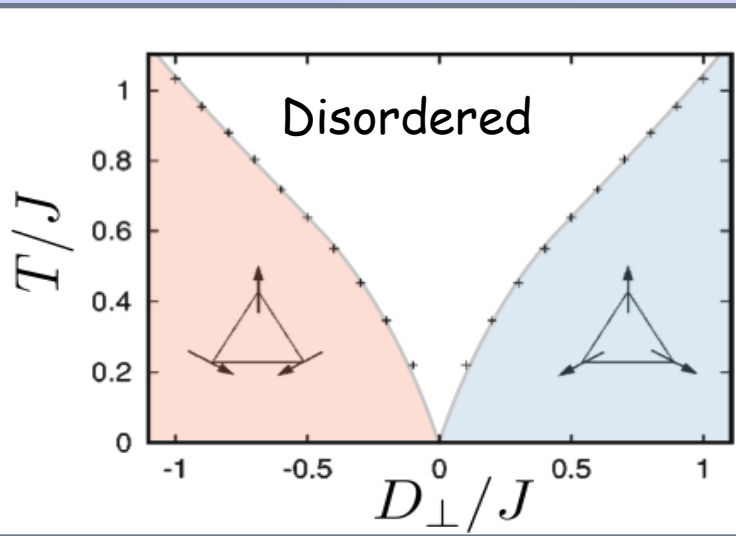
- DM interaction mixes singlet and triplet which restores a susceptibility at $T=0$



Miyahara et al. PRB **75**, 184407 (2007)

Tovar et al, PRB **79**, 024405 (2009)

Dzyaloshinskii-Moriya interactions: quantum criticality

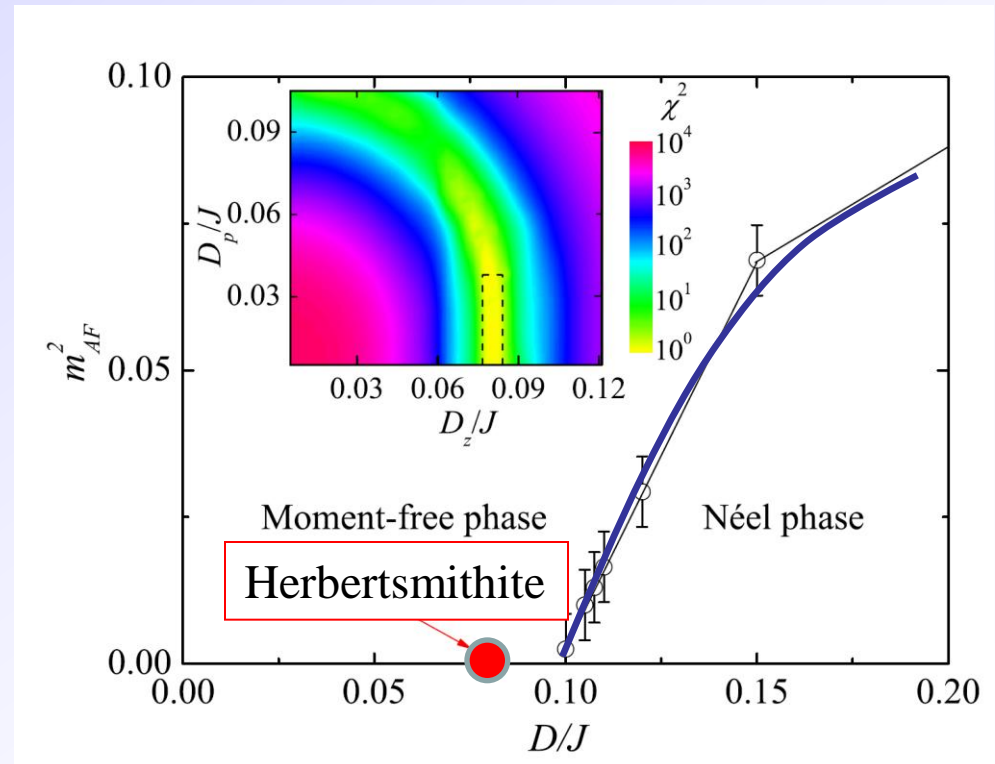


For **classical** spins, DM stabilizes ordered phases (cf jarosites)

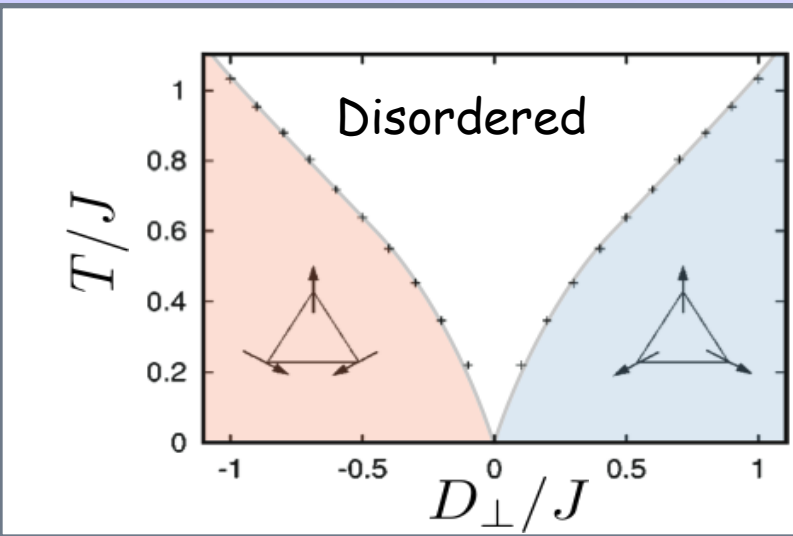
M. Elhajal et al, PRB **66**, 014422 (2002)

In the quantum case,
a moment free phase
survives up to $D/J \sim 0.1$

O. Cepas et al, PRB **78**, 140405 (R) (2008)
Y. Huh et al, PRB **81**, 144432 (2010)
L. Messio et al, PRB **81**, 064428 (2010)



Dzyaloshinskii-Moriya interactions: quantum criticality



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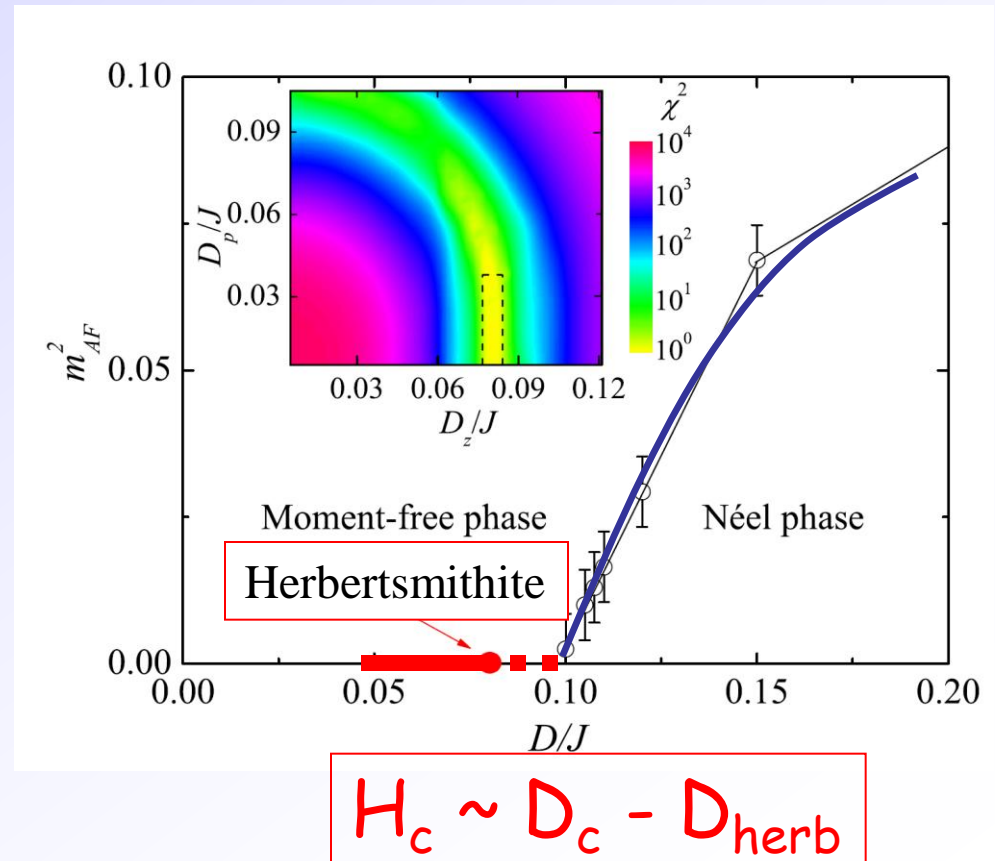
ESR: A. Zorko et al., PRL **101** (2008)

O. Cepas et al, PRB **78**, 140405 (R) (2008)

Y. Huh et al, PRB **81**, 144432 (2010)

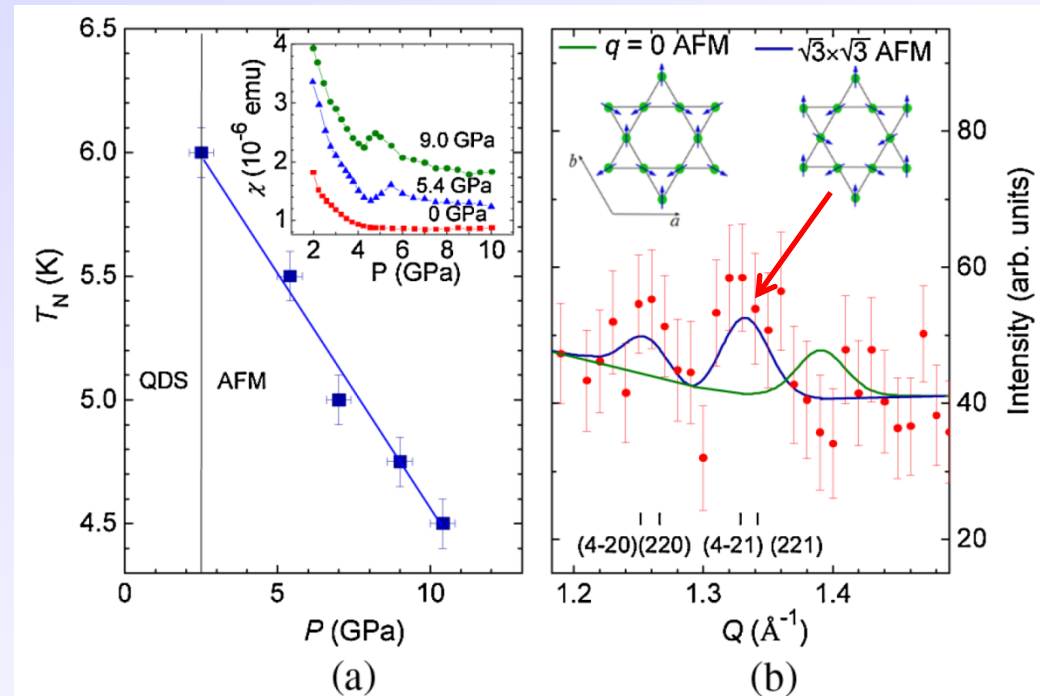
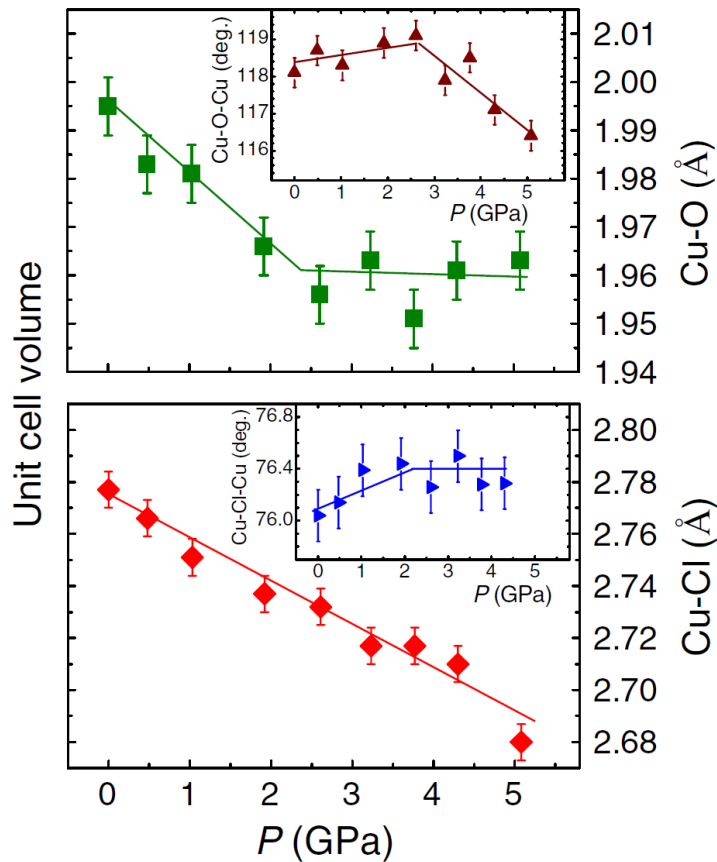
L. Messio et al, PRB **81**, 064428 (2010)

S. El Shawish et al, PRB **81**, 224421 (2010)



Pressure effects: order restored

- μ SR: no effect up to 2 Gpa (Orsay, unpublished)
- **Neutrons:** D.P. Kozlenko et al., PRL **108**, 187207 (2012)



Crystal symmetry $R\bar{3}m$; Changes in DM: No
Local disymmetry of the exchanges paths \sim clinoatacamite?

Outline

- Zn and Mg Herbertsmithite $\text{Cu}_3(\text{Zn,Mg})(\text{OH})_6\text{Cl}_2$
 - a gapless quantum spin liquid (summary)
 - field induced solidification of the QSL

- Vesignieite $\text{Cu}_3\text{Ba}(\text{VO}_5\text{H})_2$
 - local susceptibility (NMR)
 - heterogeneous frozen ground state (μSR +NMR)

Quantum criticality
Dzyaloshinsky-Moriya interactions

- Kapellasite $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$
 - competing exchange interactions

Collaborations

Samples:

Ross H Colman, David Boldrin, Andrew S Wills, UCL, UK

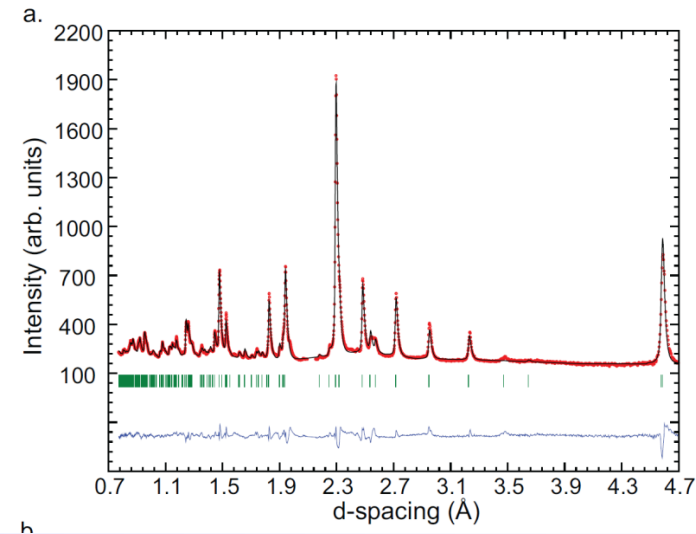
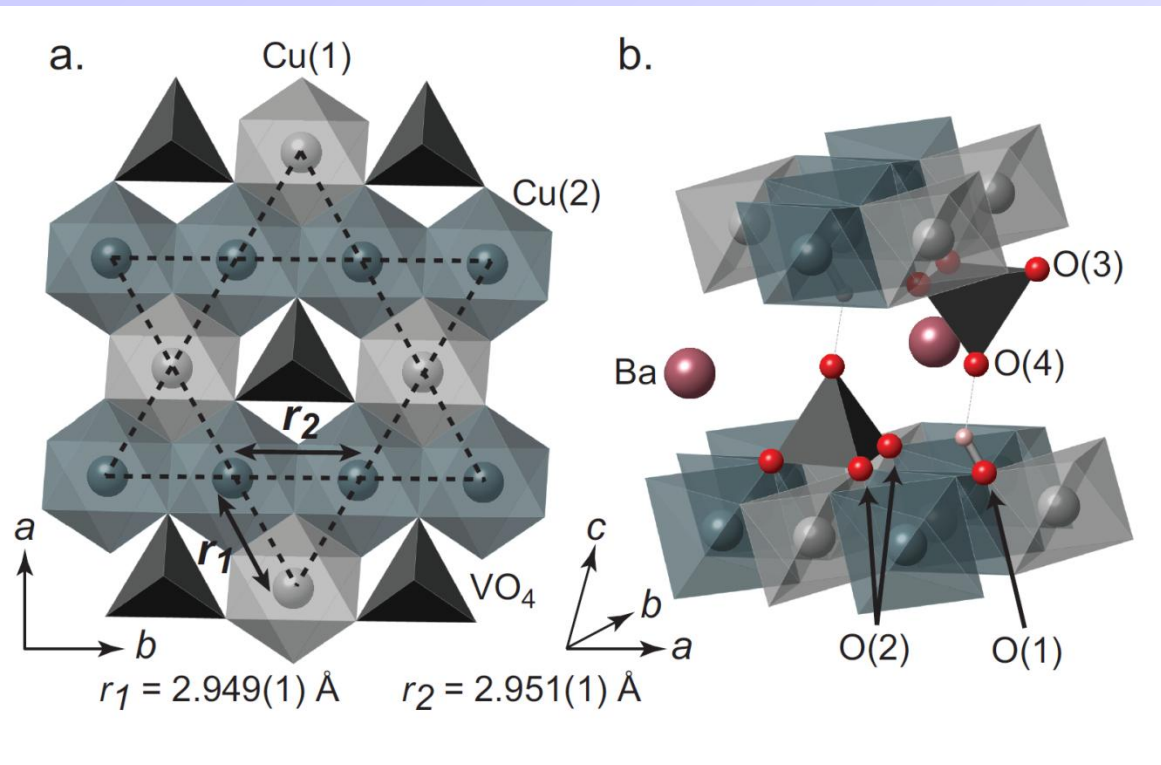
μSR :

- C. Baines, A. Amato, PSI, Switzerland
- J. Lord, A.D. Hillier, ISIS, UK

Vesignieite

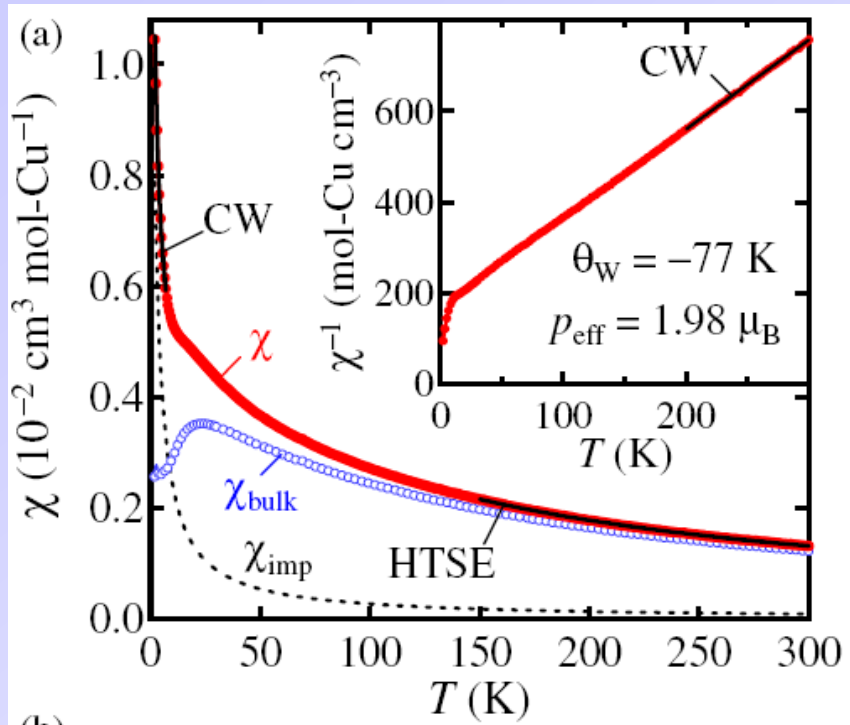


Y. Okamoto et al, JPSJ **78**, 33701 (2009)

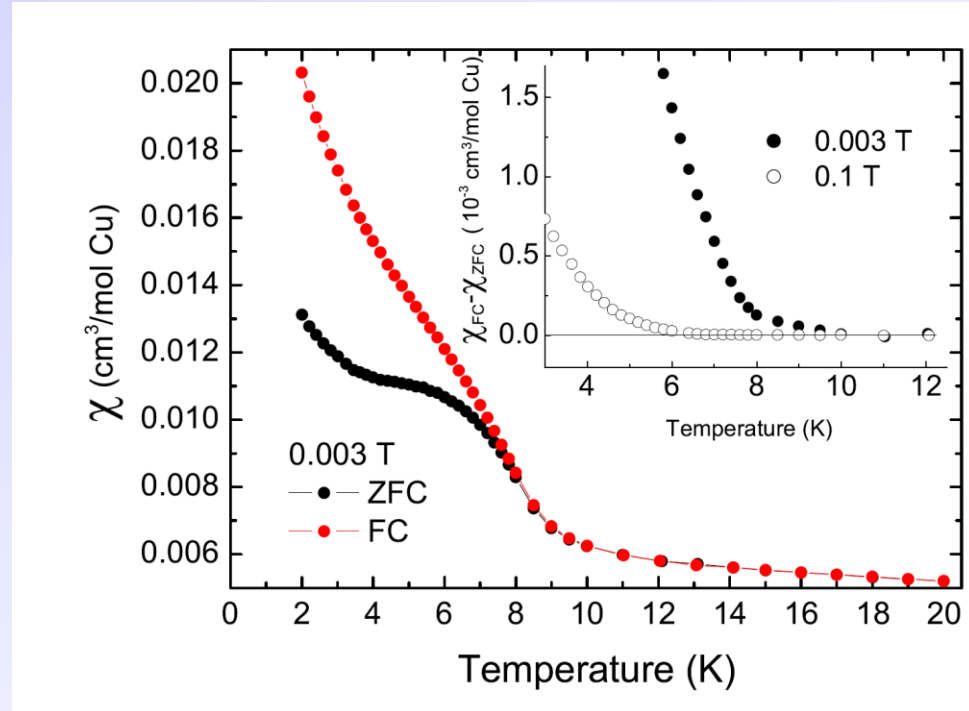


a weakly distorted kagome lattice 0.1 %
(Volborthite : 3%)

Vesignieite susceptibility



Y. Okamoto et al (2009)



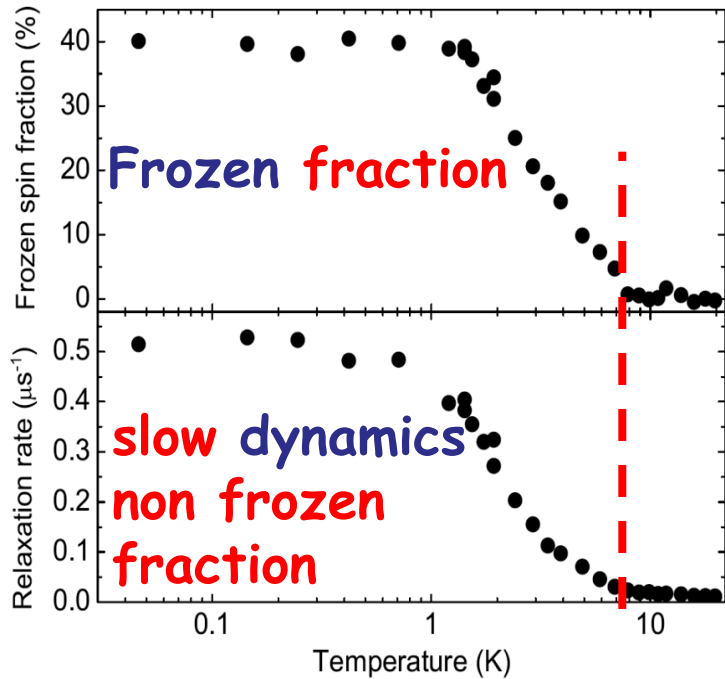
R.C. Colman et al (2011)

- $J \sim 54$ K
- Curie tail = $\sim 7\%$ $S=1/2$
- Kink + FC/ZFC at $T \sim 9$ K $\sim J/6$

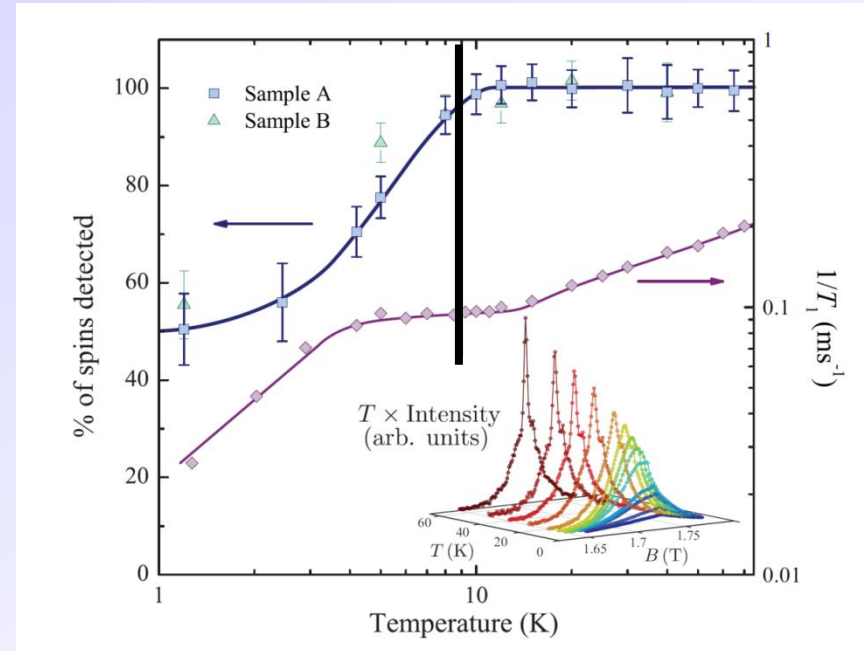
Ground state: two components

μ SR

NMR



Coupled

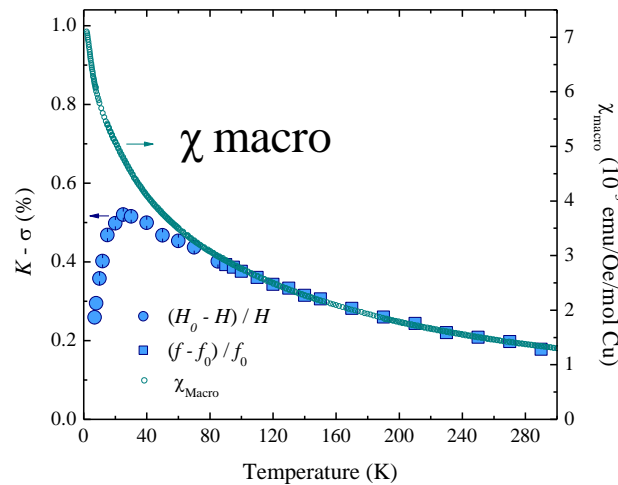
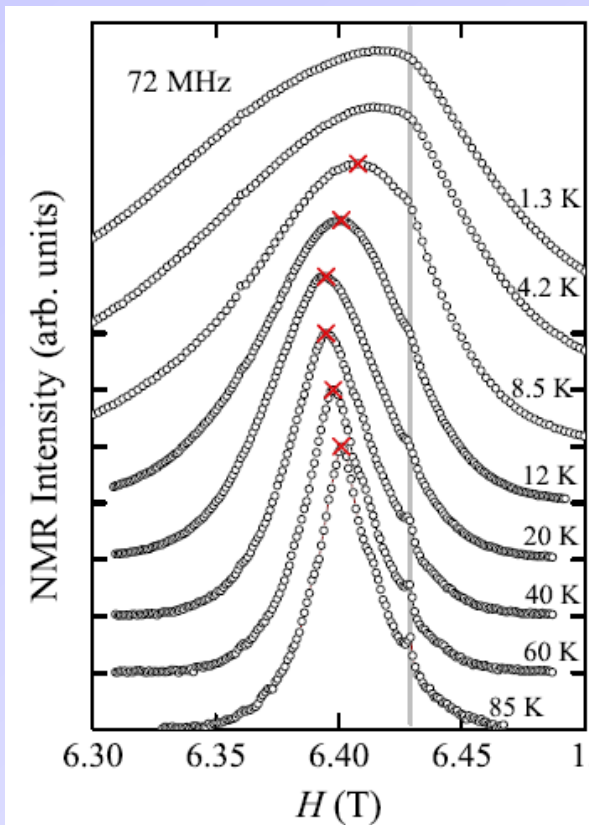


- No macroscopic phase separation.
- Spin dynamics of all Cu^{2+} suppressed down to spin freezing for 40%.

Vesignieite

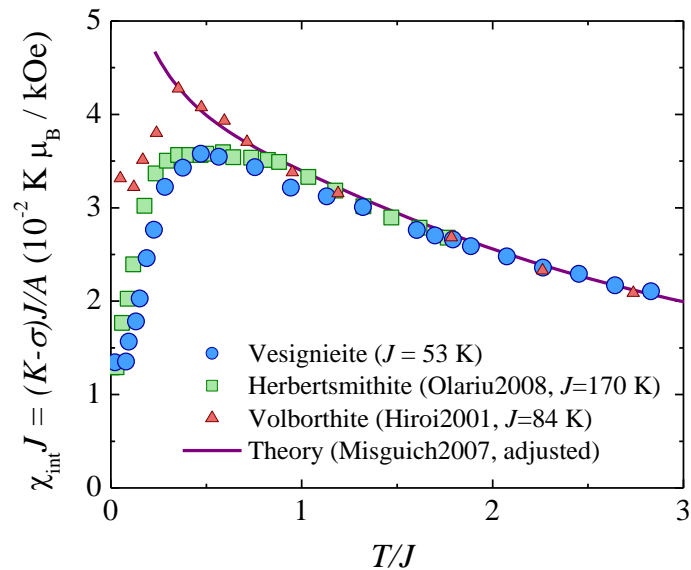
V NMR ($T > 9\text{K}$)

V @ Cu hexagon



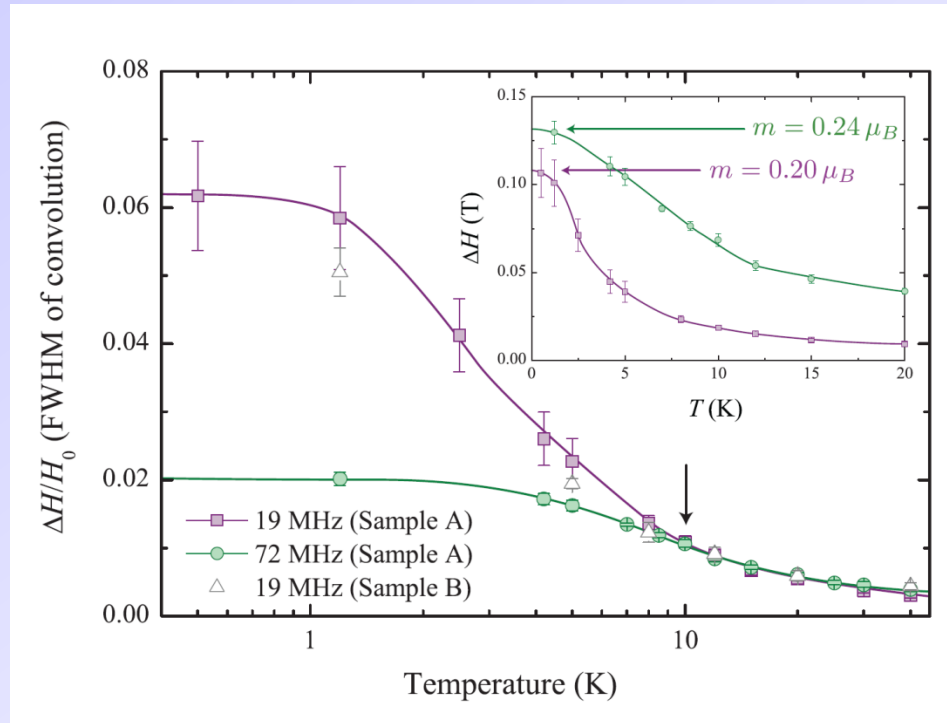
Shift \equiv Herbertsmithite

J. Quilliam et al, PRB (R) 2011



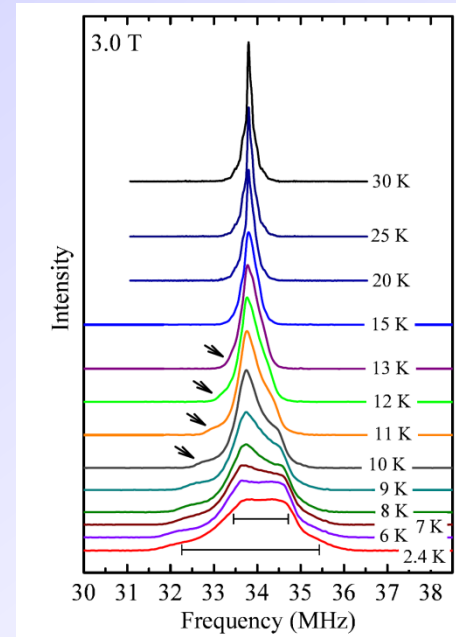
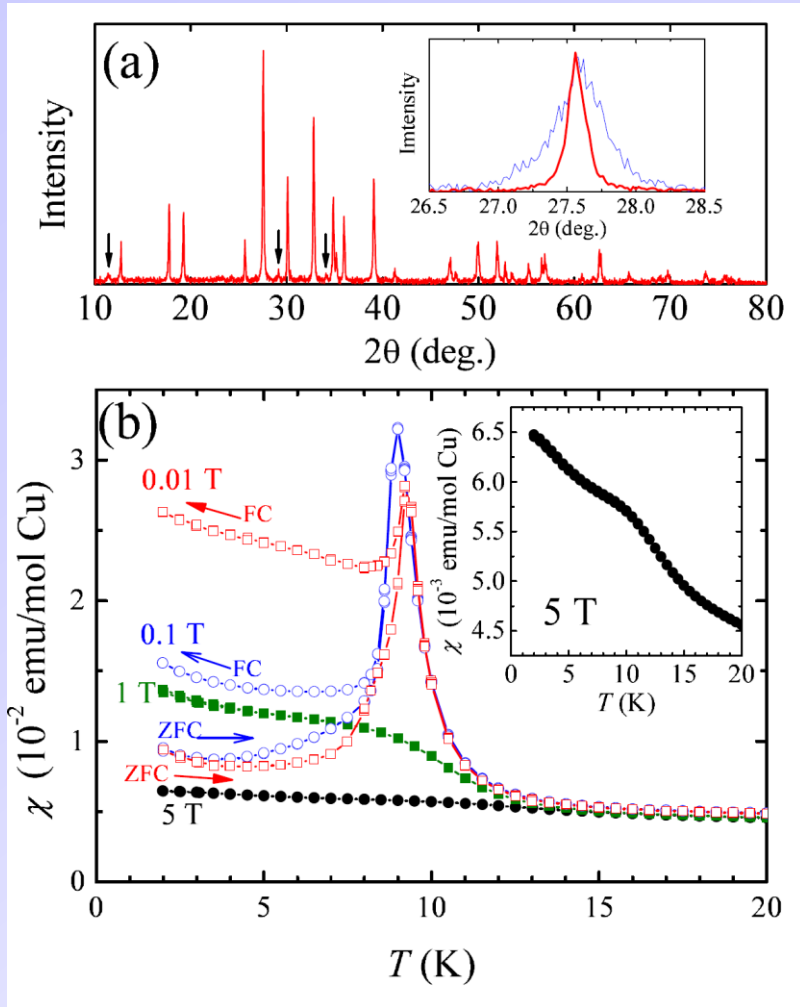
Vesignieite

^{51}V NMR ($T < 9\text{K}$)

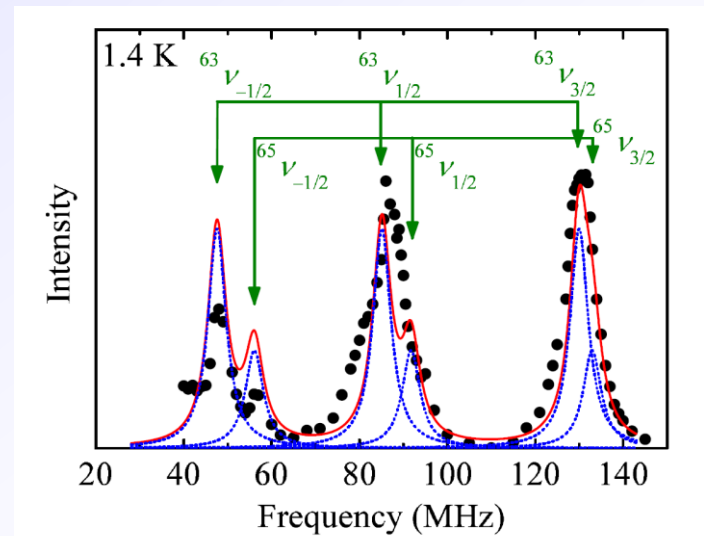


Static component below 9 K $\sim 0.2 \mu_B$

Vesignieite: more recent NMR results



V NMR



Cu
ZFNMR

Q = 0 structure

- Quilliam et al.

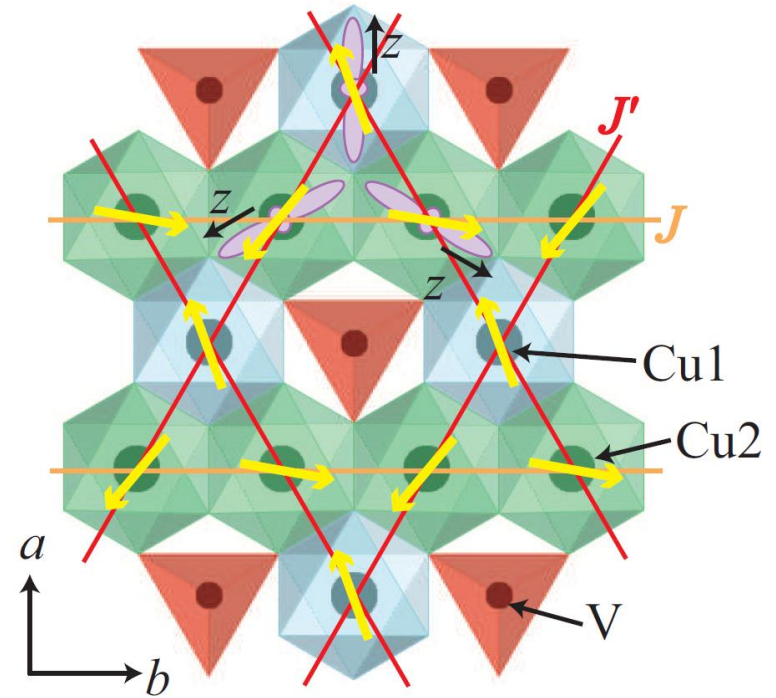
Disordered freezing at 9 K
Moment from V NMR $0.2 \mu_B$

- Yoshida et al.

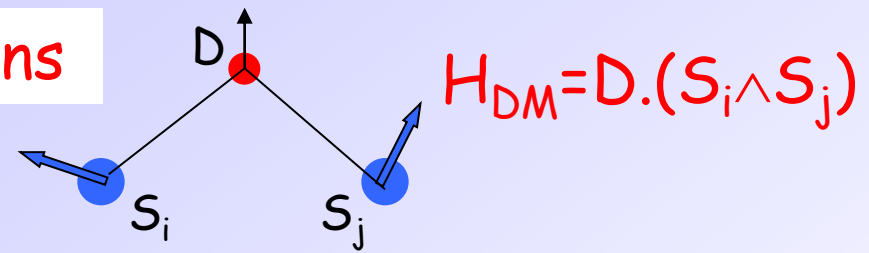
Q=0 order (120°)

$\mu_{//}$ from Cu NMR $0.6 \mu_B$

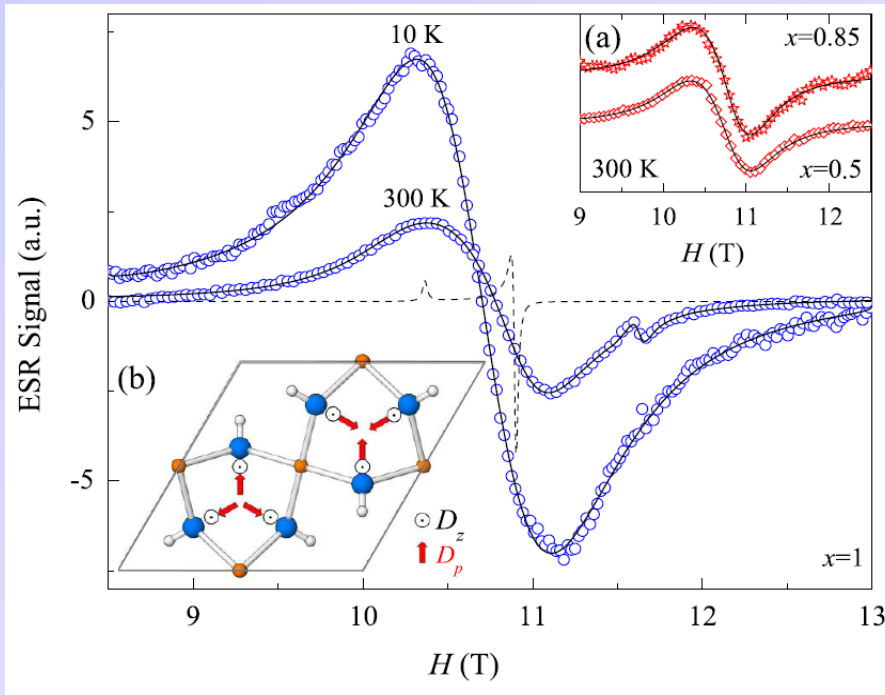
μ_{\perp} from V NMR $0.1 \mu_B$



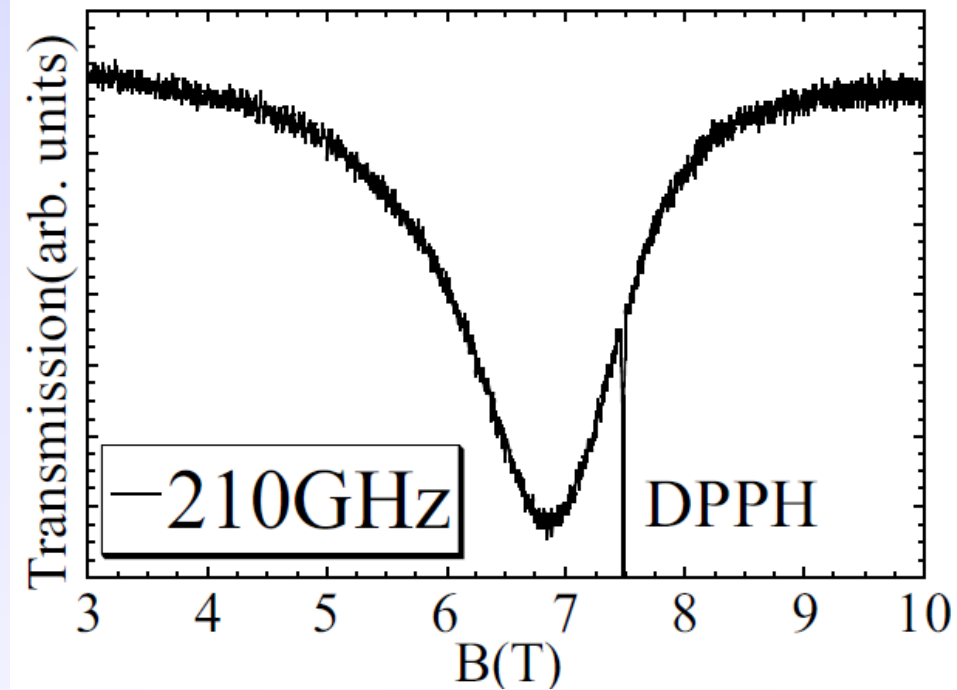
Dzyaloshinskii-Moriya interactions



Herbertsmithite



Vesignieite



$$|D_z| = 0.08 \text{ J}, |D_p| \sim 0.01 \text{ J}$$

$$J_{\text{vesi}} \sim J_{\text{herb}}/3; \Delta H_{\text{vesi}} \sim \Delta H_{\text{volb}}$$

$$\text{ESR: } \Delta H \sim D^2/J$$

$$D/J_{\text{vesi}} \sim 1.7 D/J_{\text{herb}} \sim 0.14 D_c/J$$

Summary (II)

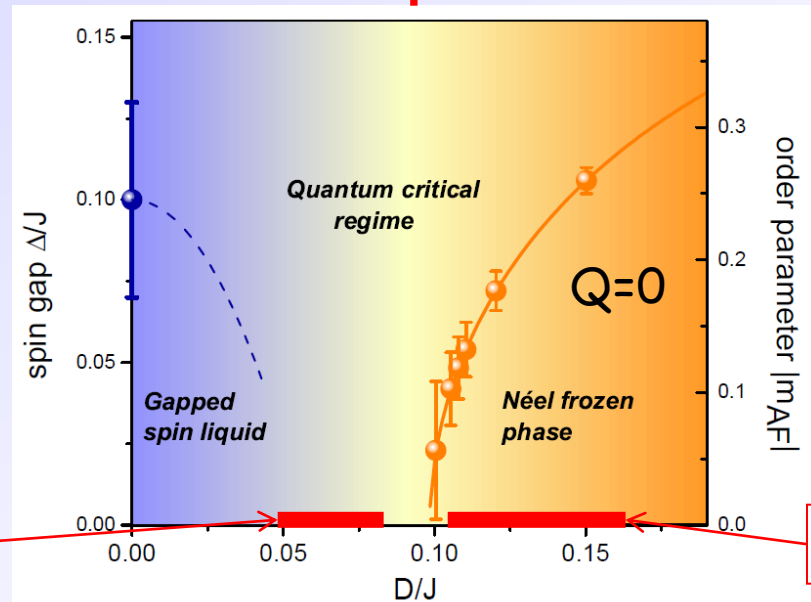
Herbertsmithite

- Perfect kagome
- No freezing at $H=0$
- $0.44 < D/J < 0.08 < D_c$
- **Field induced freezing**

Vesignieite

- Close to perfect kagome
- **$Q=0$** ordered state @ $J/6$
- $D_c < 0.1 < D/J < 0.17$
- Moment $0.6 \mu_B$ close to max

QCP



Herbertsmithite

Vesignieite

Outline

- Zn and Mg Herbertsmithite $\text{Cu}_3(\text{Zn,Mg})(\text{OH})_6\text{Cl}_2$
 - a gapless quantum spin liquid (summary)
 - field induced solidification of the QSL
- Vesignieite $\text{Cu}_3\text{Ba}(\text{VO}_5\text{H})_2$
 - local susceptibility (NMR)
 - heterogeneous frozen ground state ($\mu\text{SR}+\text{NMR}$)
- Kapellasite $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$
 - competing exchange interactions

Quantum criticality
Dzyaloshinsky-Moriya interactions

Collaborations

Samples: Ross H Colman, David Boldrin, Andrew S Wills, UCL, UK
Neutrons: B. Fak, CENG, Grenoble, France
Magnetization: P. Bonville, CEA Saclay
Theory: L. Messio, C. Lhuillier, B. Bernu, Paris, France

Quantum Kagome Antiferromagnets $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$

PRL **101**, 106403 (2008)

PHYSICAL REVIEW LETTERS

week ending
5 SEPTEMBER 2008

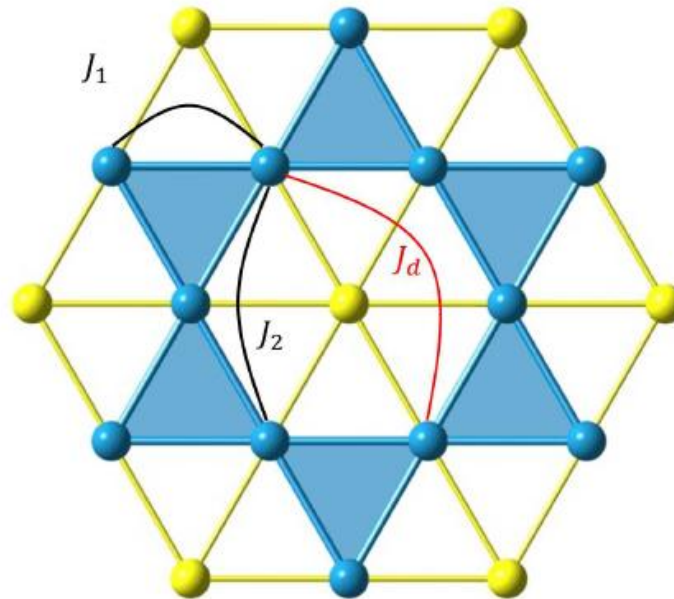
Modified Kagome Physics in the Natural Spin-1/2 Kagome Lattice Systems: **Kapellasite** $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$ and Haydeeite $\text{Cu}_3\text{Mg}(\text{OH})_6\text{Cl}_2$

O. Janson,¹ J. Richter,² and H. Rosner^{1,*}

¹Max-Planck-Institut für Chemische Physik fester Stoffe, D-01187 Dresden, Germany

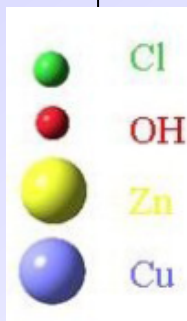
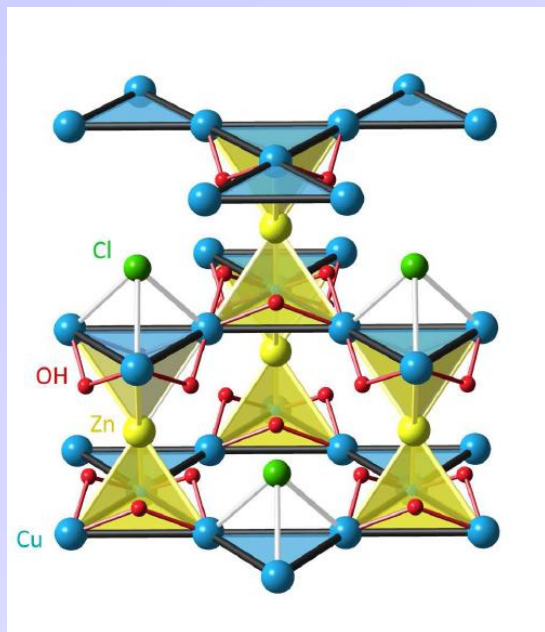
²Institut für Theoretische Physik, Universität Magdeburg, D-39016 Magdeburg, Germany

(Received 26 May 2008; published 3 September 2008)

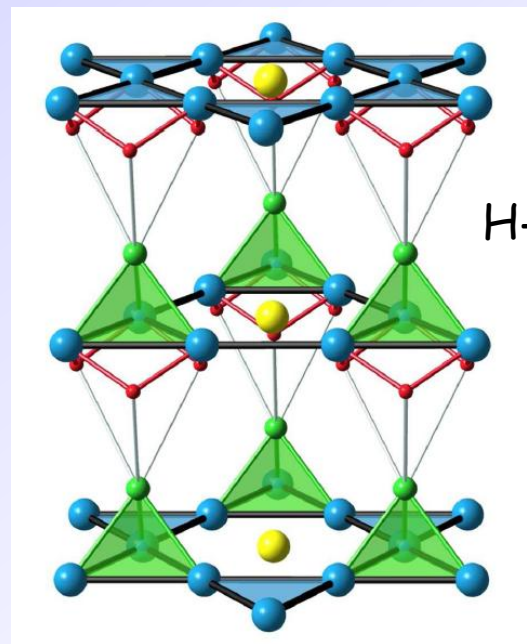


Kapellasite : a polymorph of Herbertsmithite

Herbertsmithite

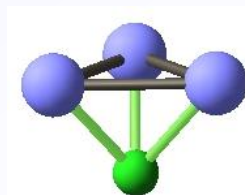


Kapellasite

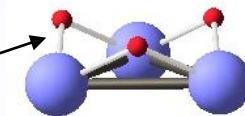


Weak
H-Cl bonds

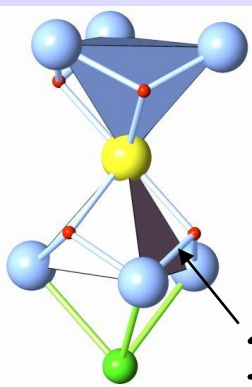
$P\bar{3}m1$



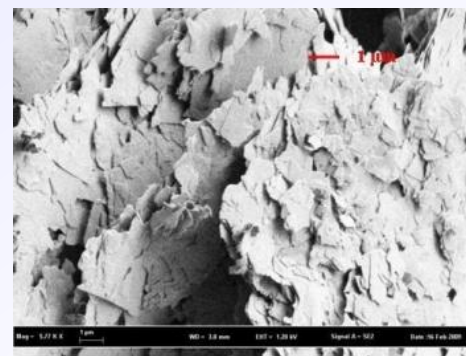
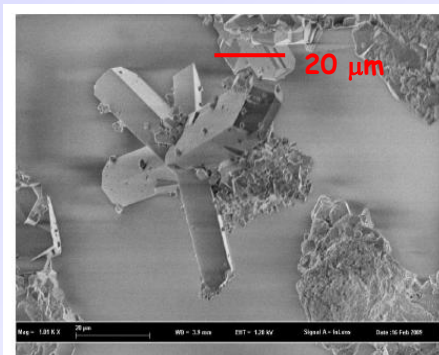
105°



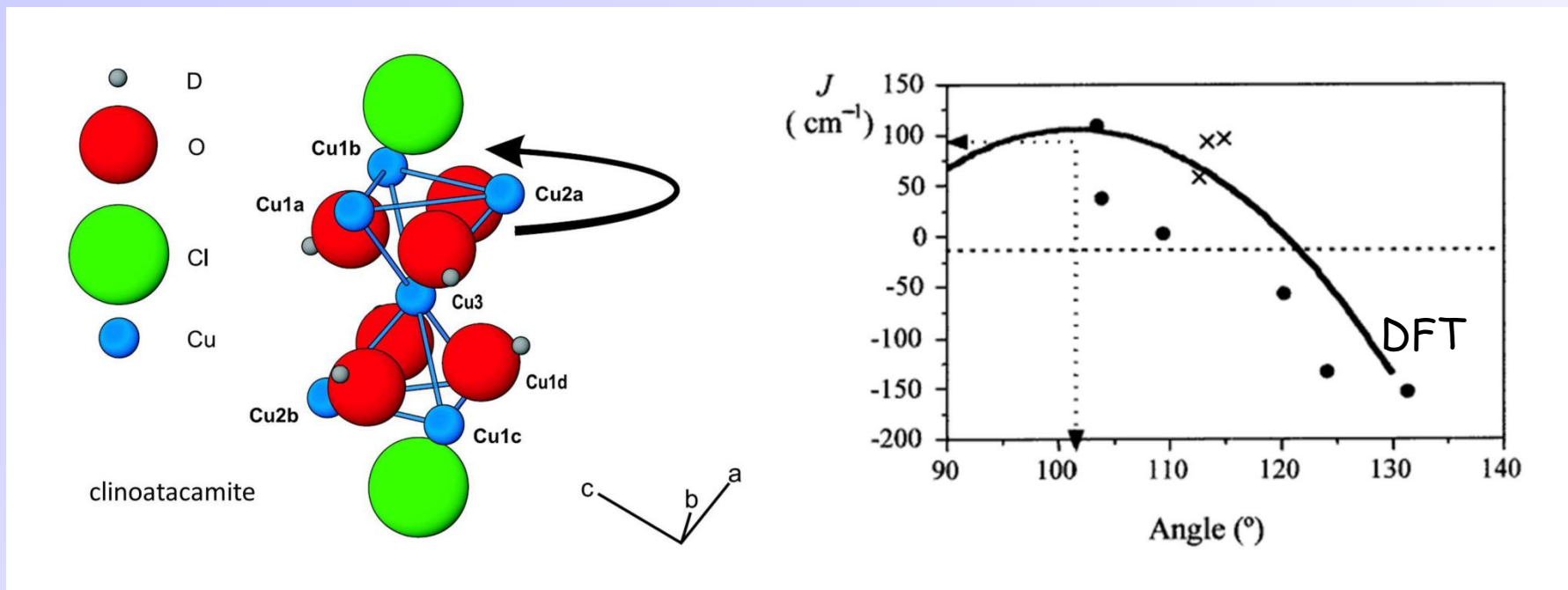
$R\bar{3}m$



119°



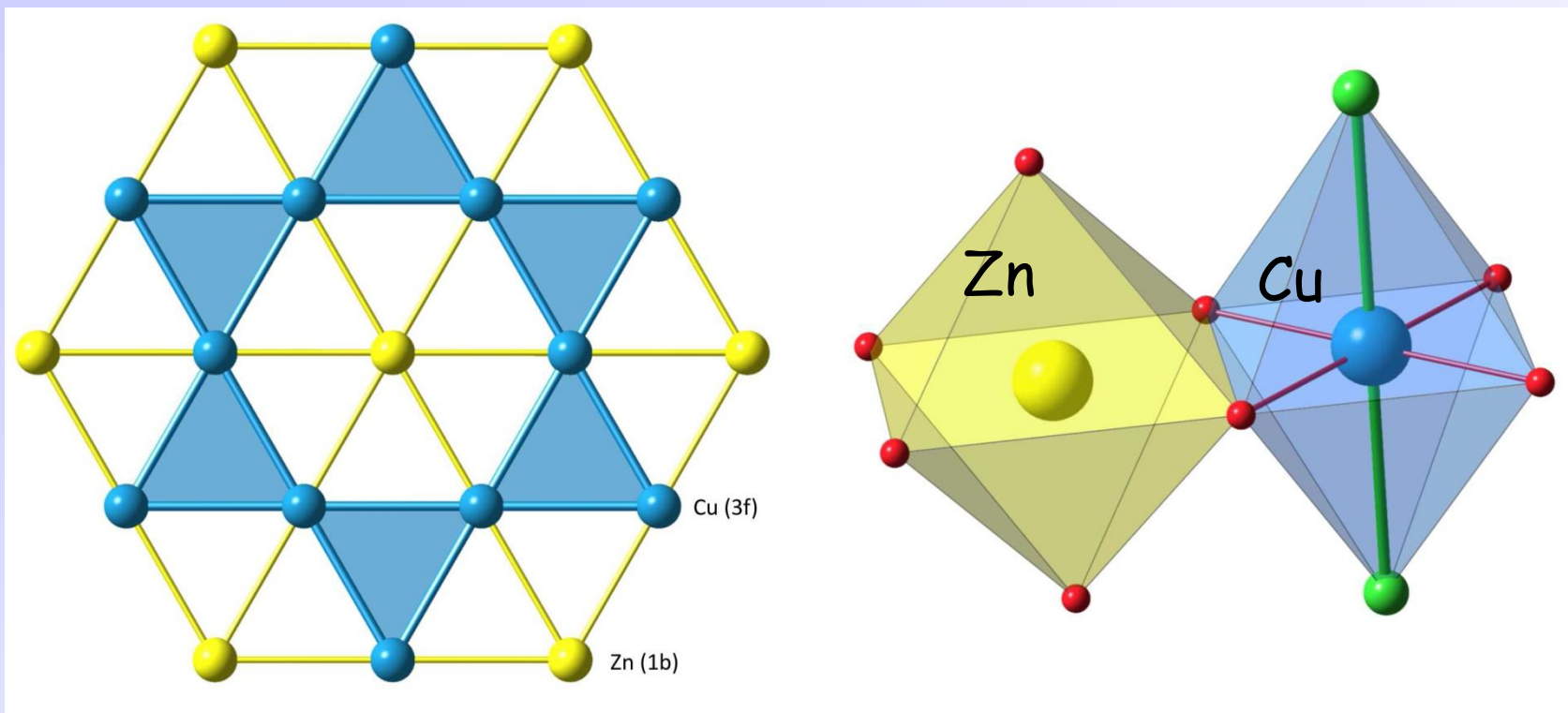
Smallness of interactions Cu-O-Cu angle



Janson et al. *Phys. Rev. Lett.* (2008)

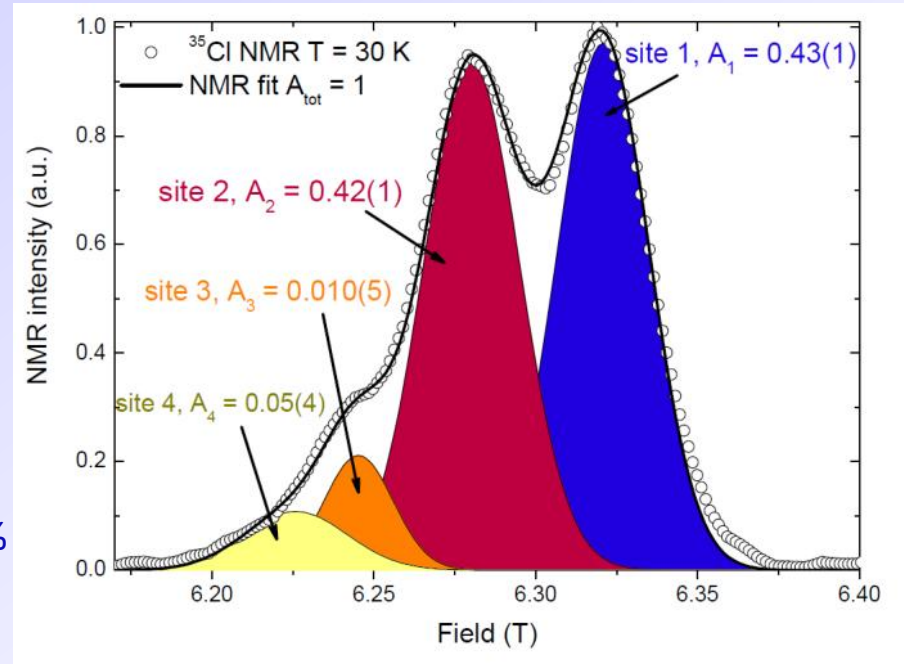
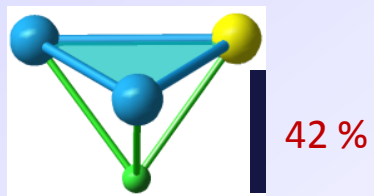
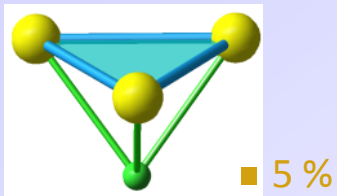
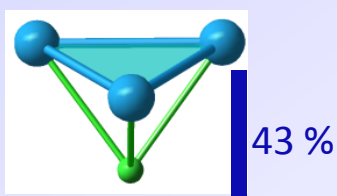
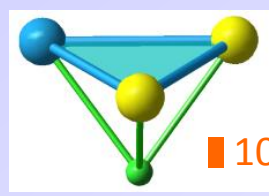
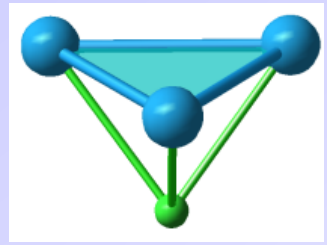
Gutierrez L. et al., *Eur. J. Inorg. Chem.* 2094 (2002)

Two different crystallographic sites in the triangular plane

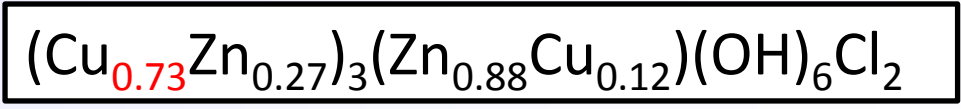


^{35}Cl NMR (oriented powders) \rightarrow Diluted kagome plane

One Cl site expected in NMR

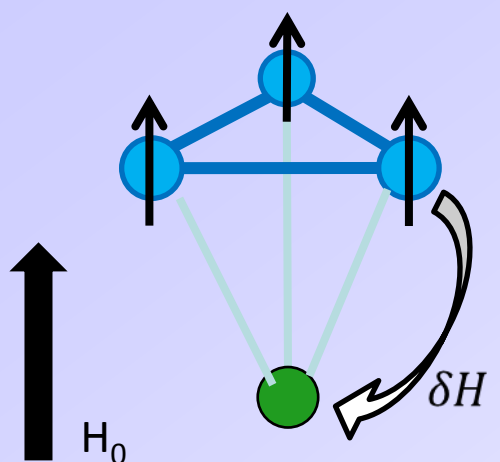


ICP
Neutrons
NMR



Kagome site occupancy $p = 0.73 > p_c \approx 0.652\dots$

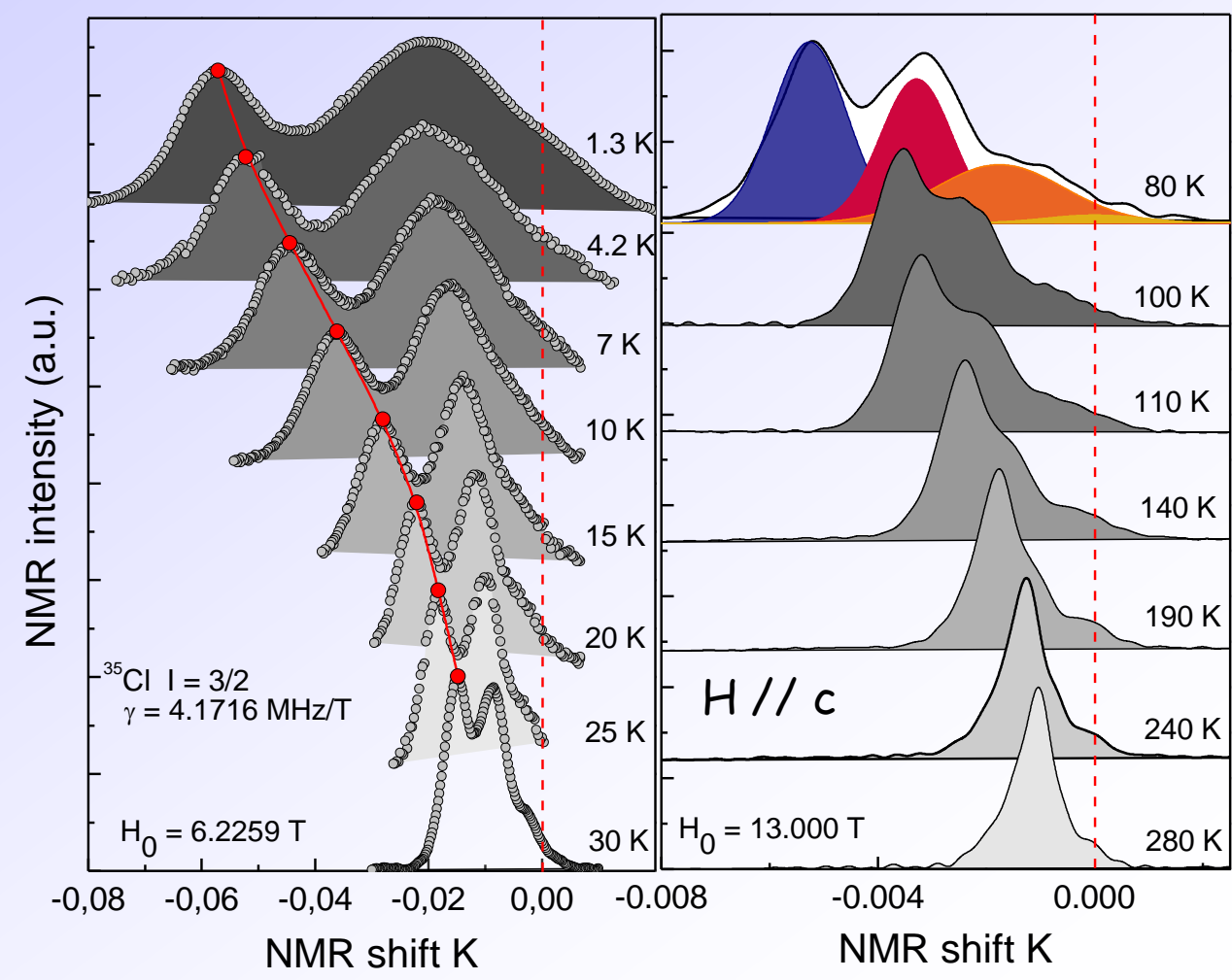
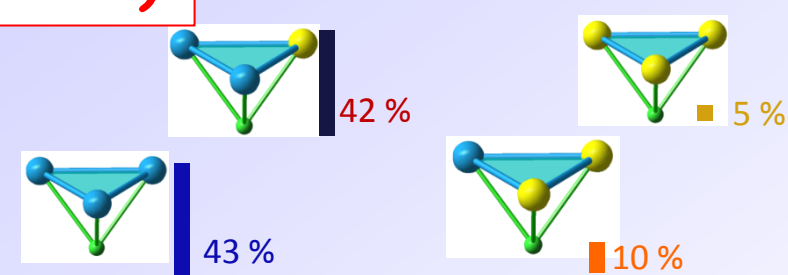
³⁵Cl NMR: oriented powders (>85%)



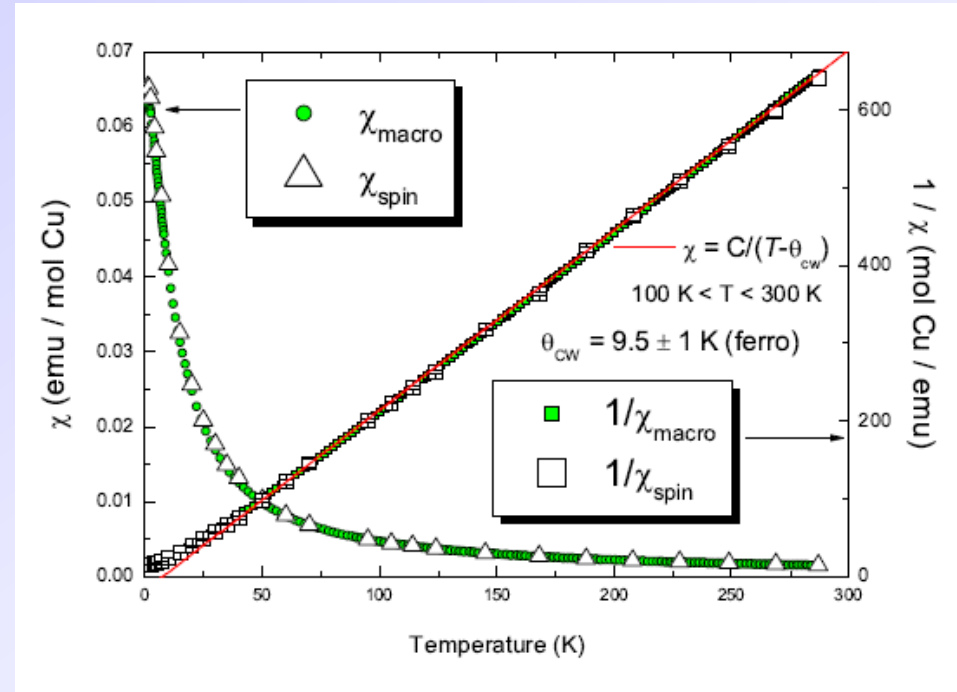
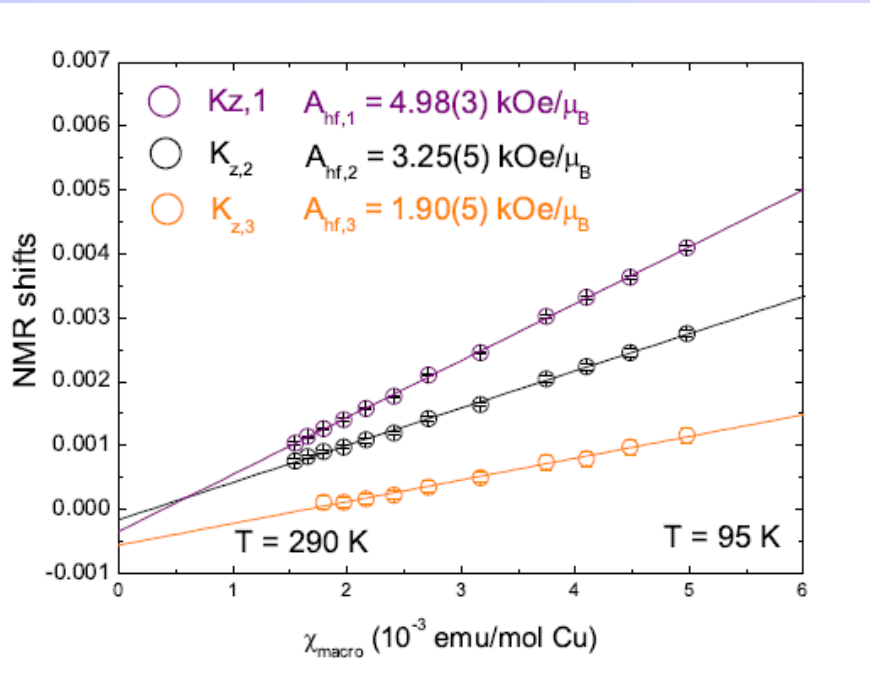
$$H_{res} = H_0 + \delta H$$

$$\delta H = KH_0$$

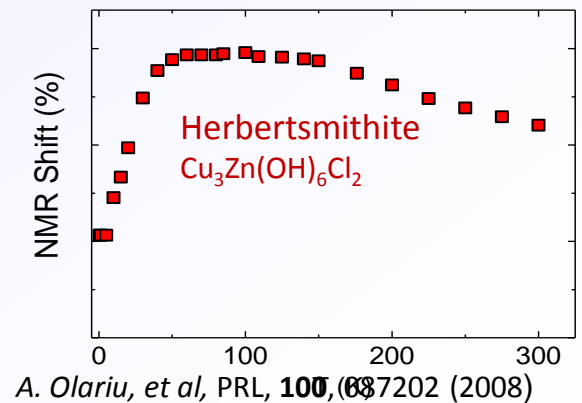
$$K(T) = \frac{A_{hf}}{N_A \mu_B} \chi_{spin}(T)$$



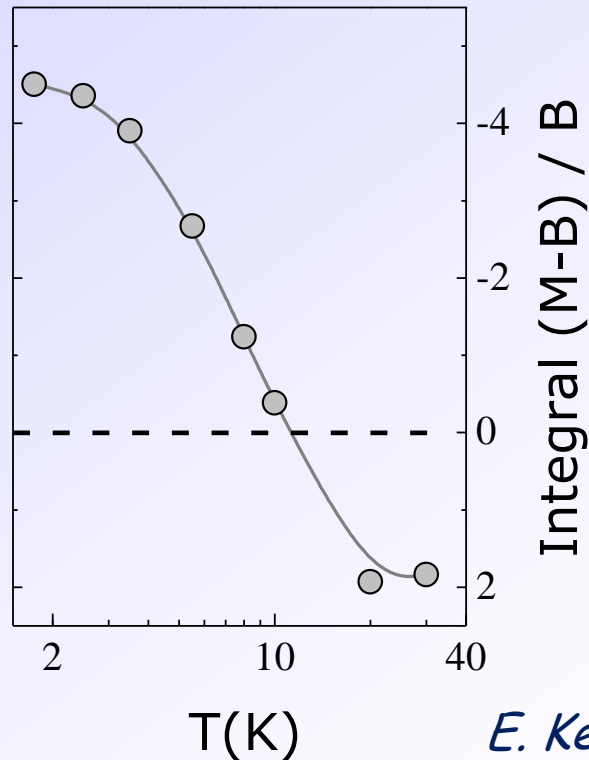
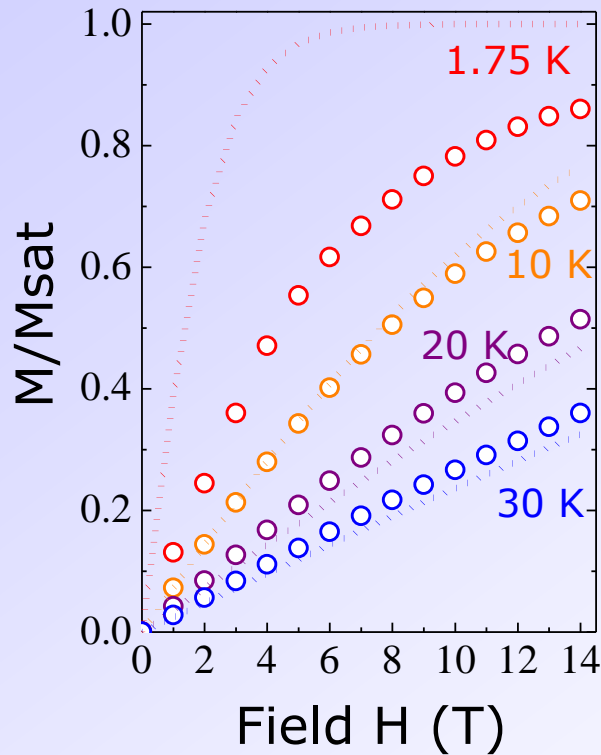
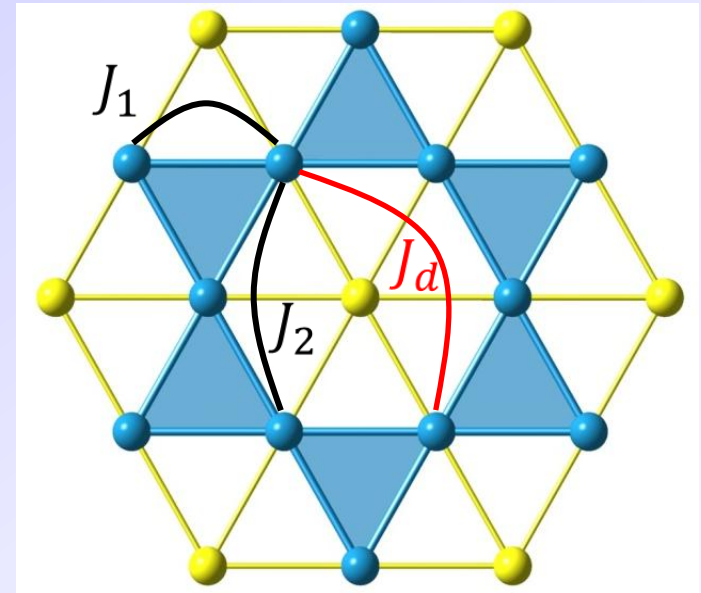
^{35}Cl NMR: local susceptibility



B. Fak, E. Kermarrec et al., Phys. Rev. Lett. 109, 037208 (2012)

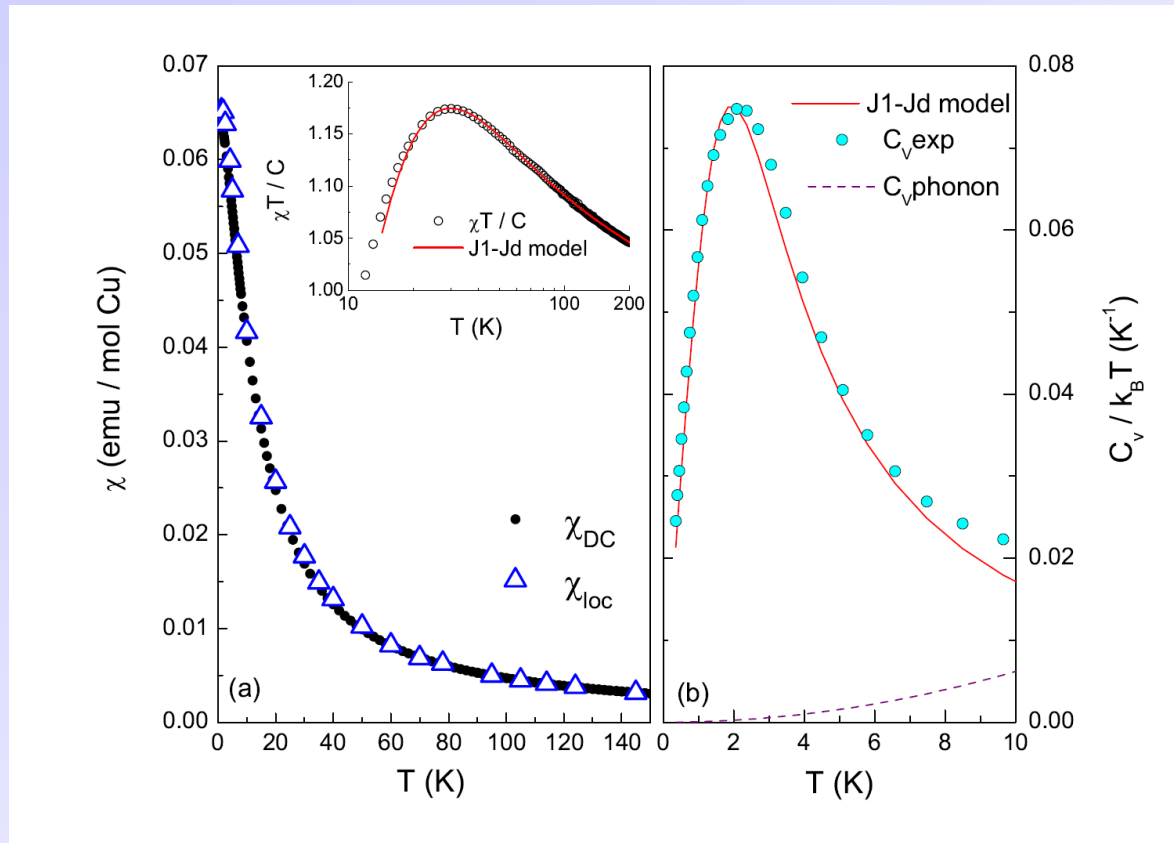


Magnetization measurements



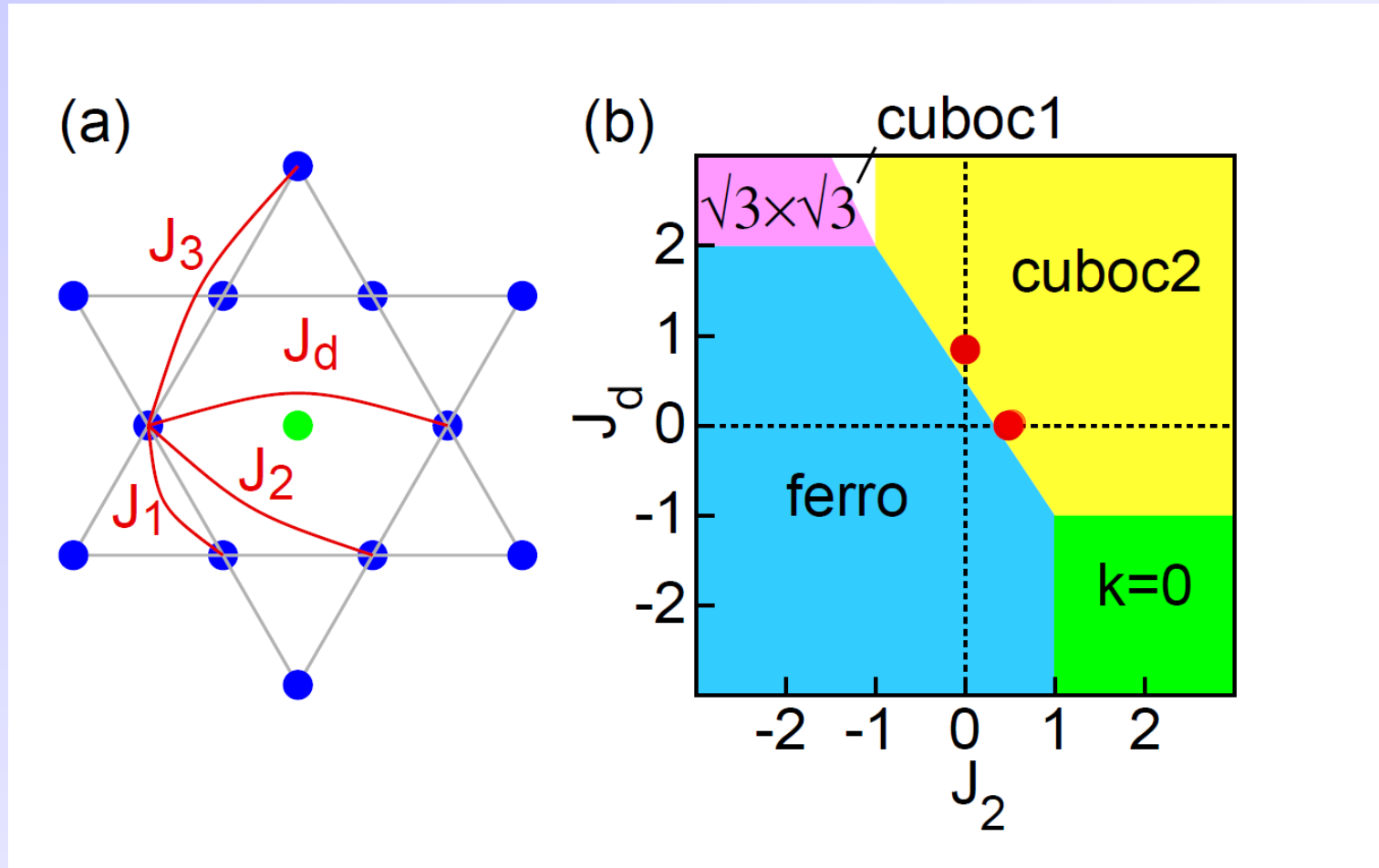
E. Kermarrec et al., in preparation

High-Temperature series expansion analysis



J_1 ferro -15 K ~ further neighbor J_d 13 K

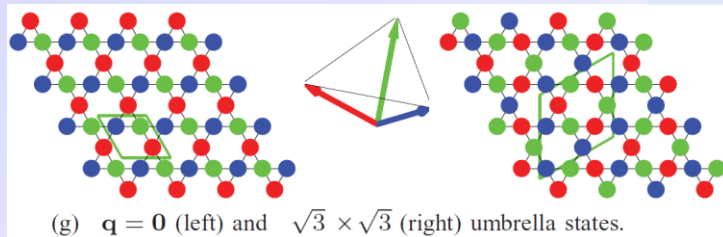
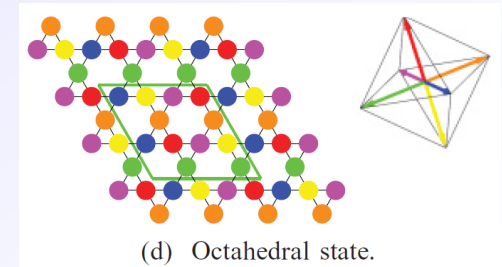
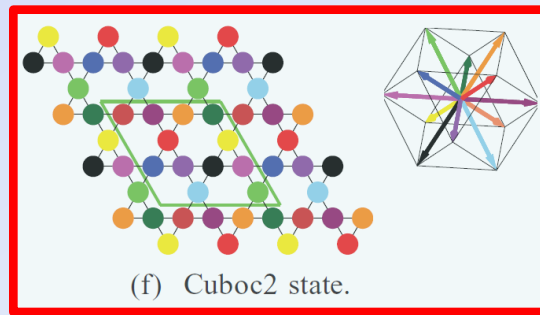
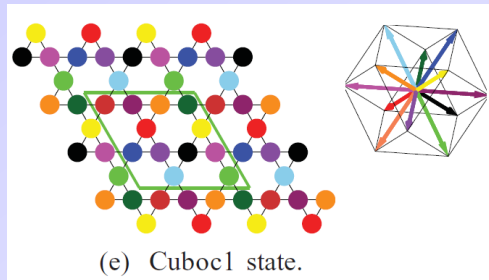
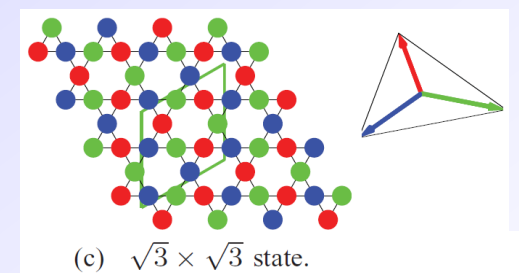
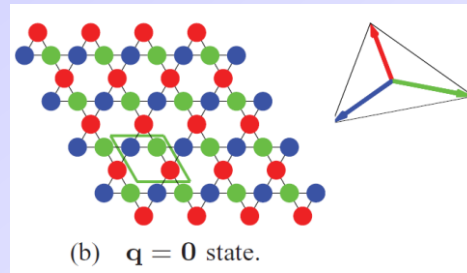
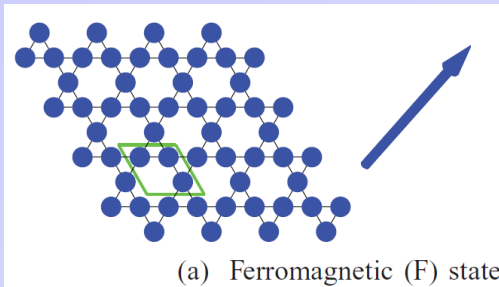
Interactions scheme



Classical ordered states on the Kagome lattice

L. Messio, C. Lhuillier, G. Misguich, LPTMC Paris, CEA

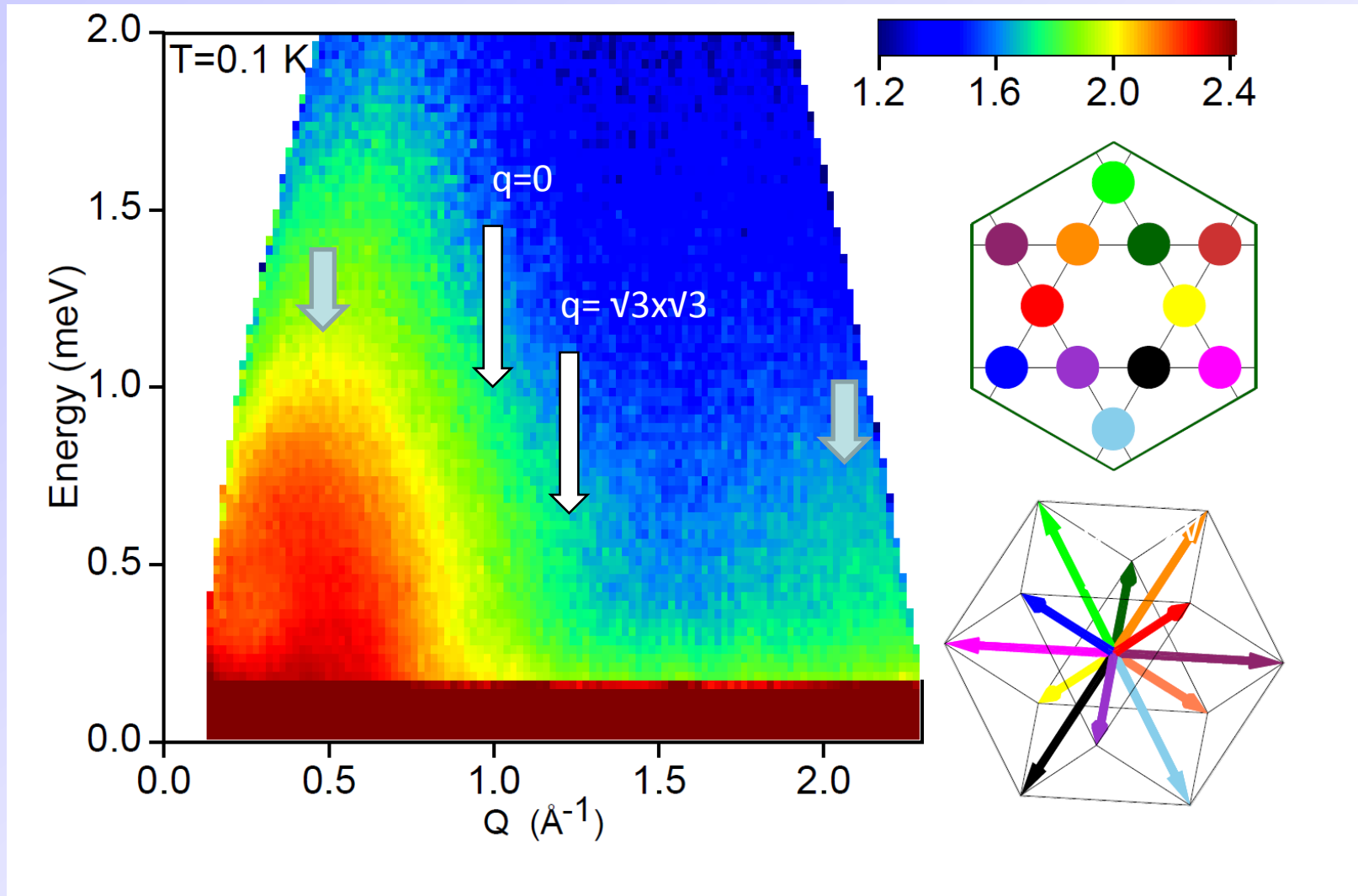
8 Classical long-range ordered states allowed by symmetries



Non coplanar state

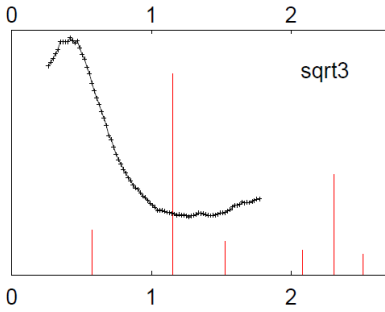
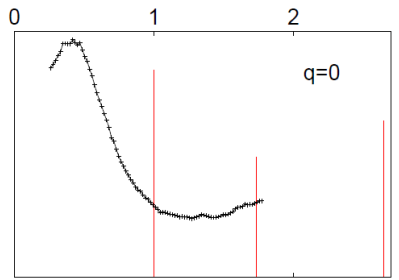
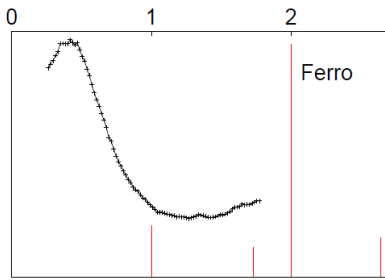
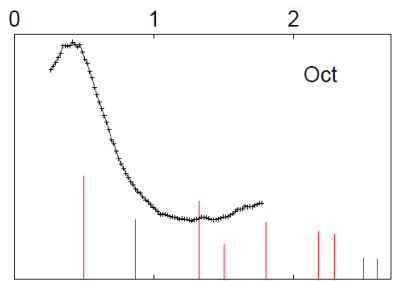
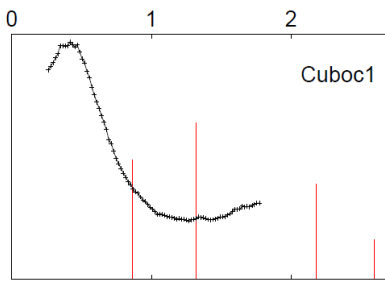
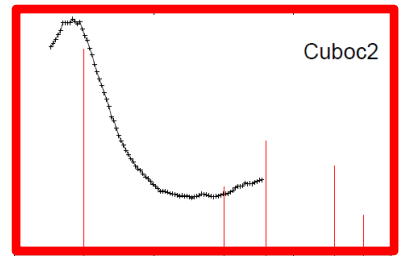
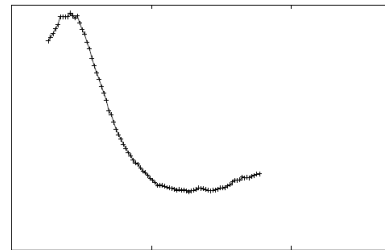
- 12 sublattice spins order : « cuboc2 »
- Neutrons experiment shows correlations reminiscent of this peculiar state

Neutron scattering (B. Fak, ILL)

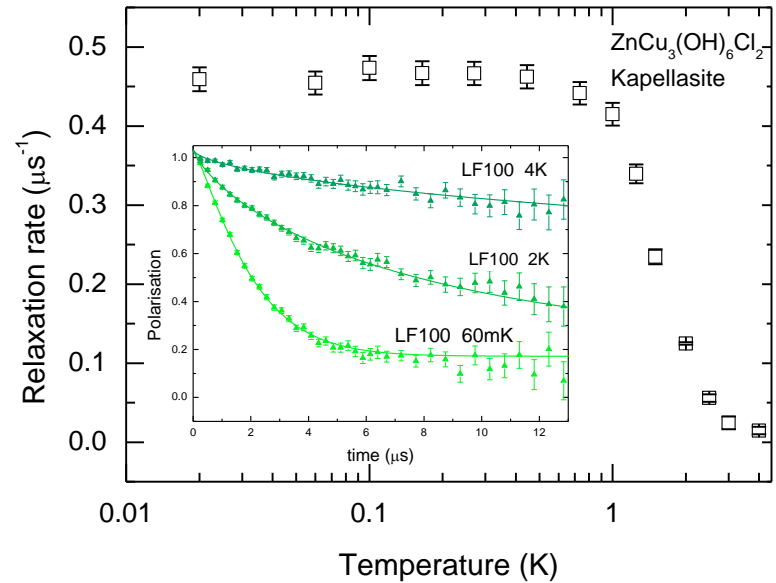
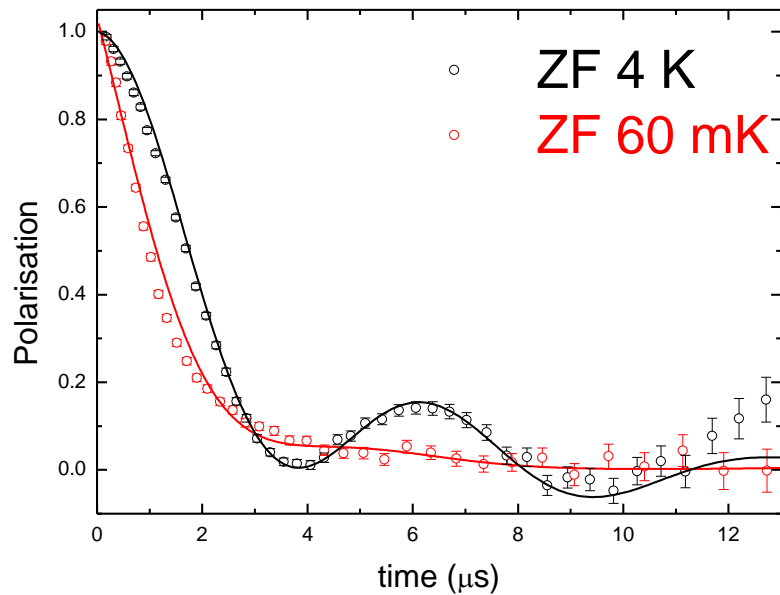


Cuboc-2 correlations survive up to 100 K (also specific heat)

B. Fak, E. Kermarrec et al., Phys. Rev. Lett. 109, 037208 (2012)

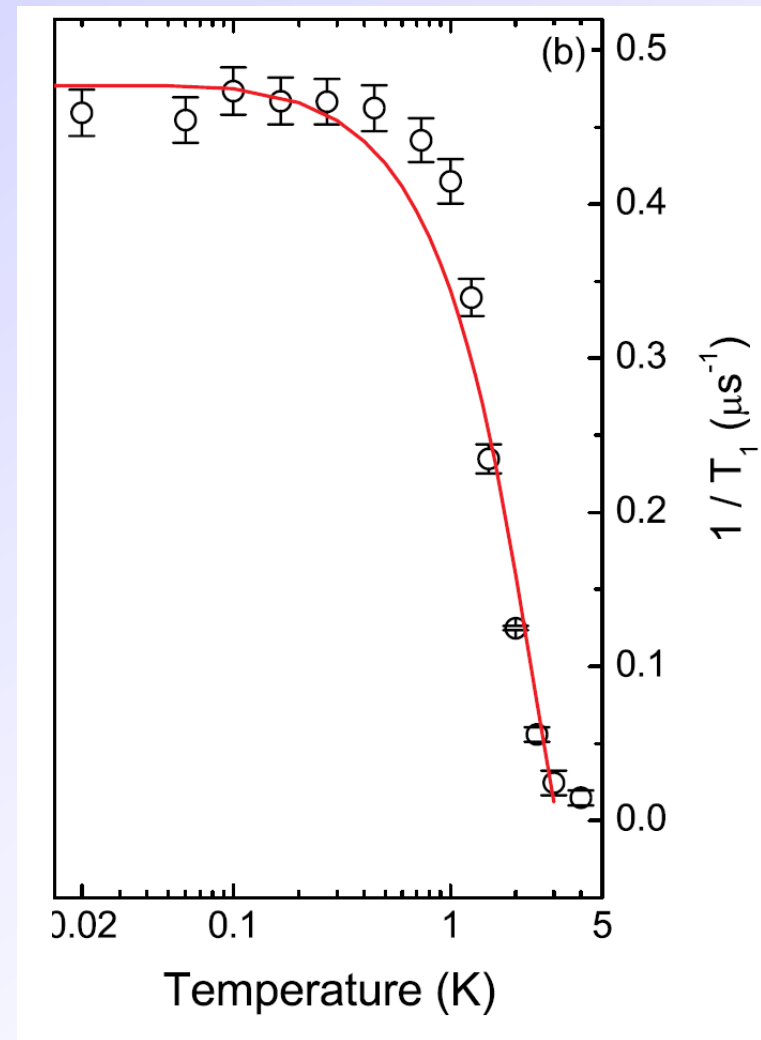
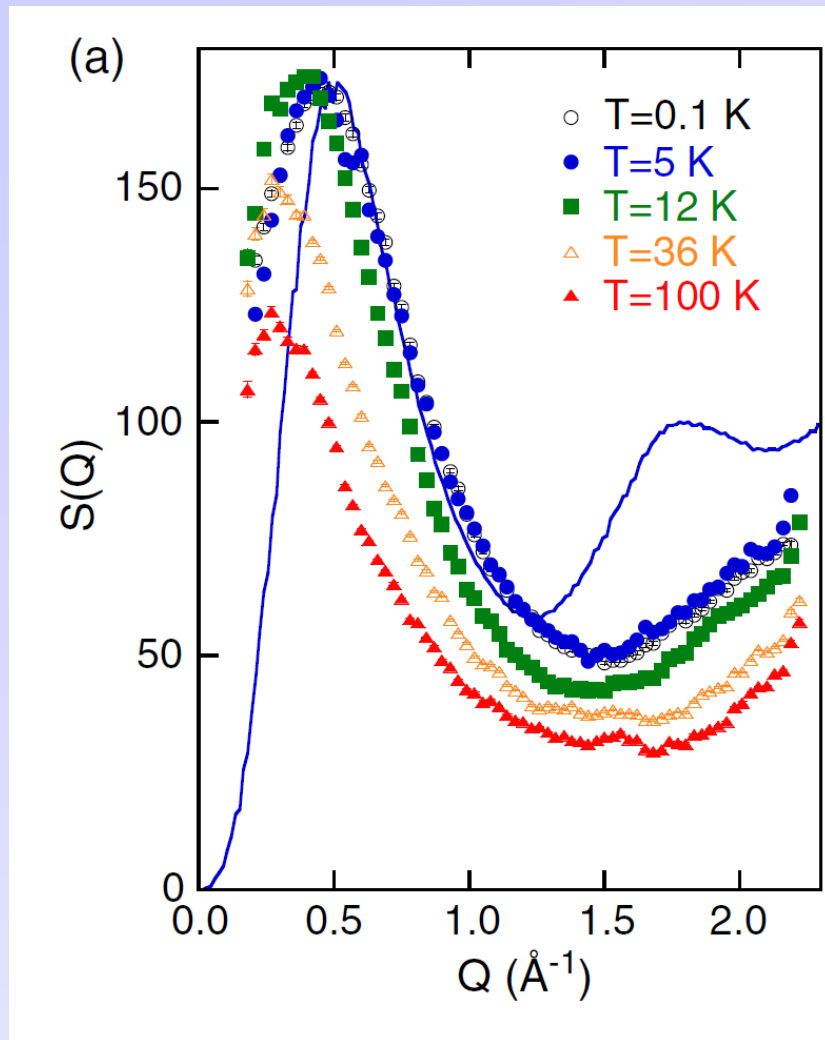


μ SR: dynamical study



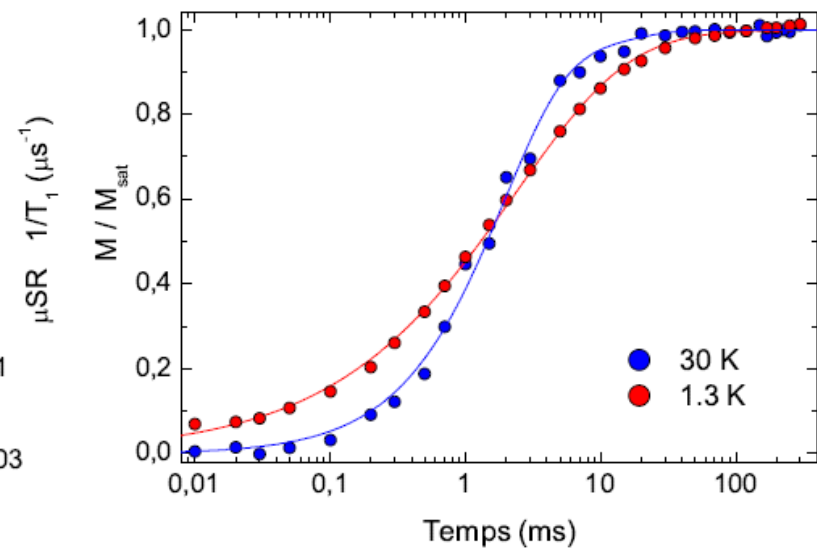
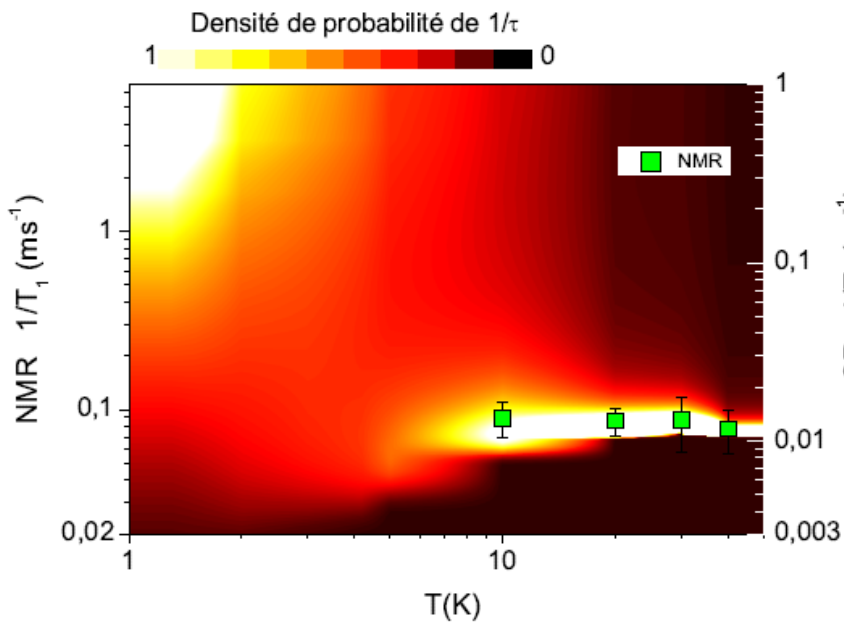
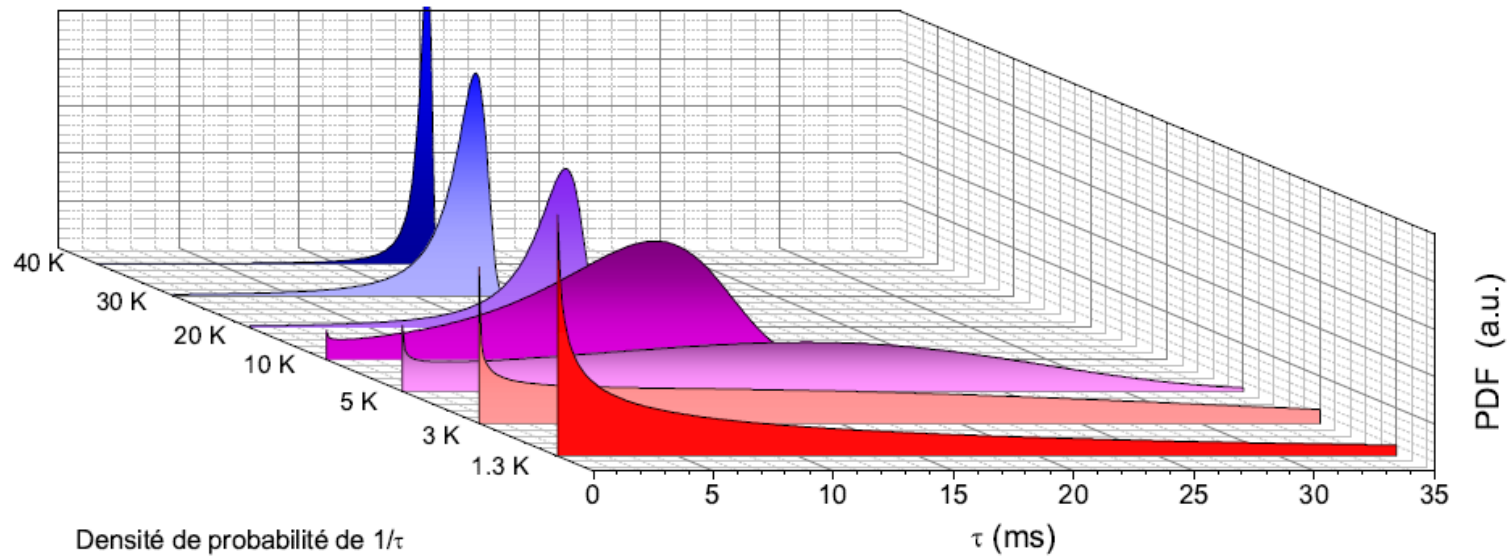
- no freezing
- Persistent slow fluctuations

Schwinger boson MFT: captures $S(Q)$, low energy scale

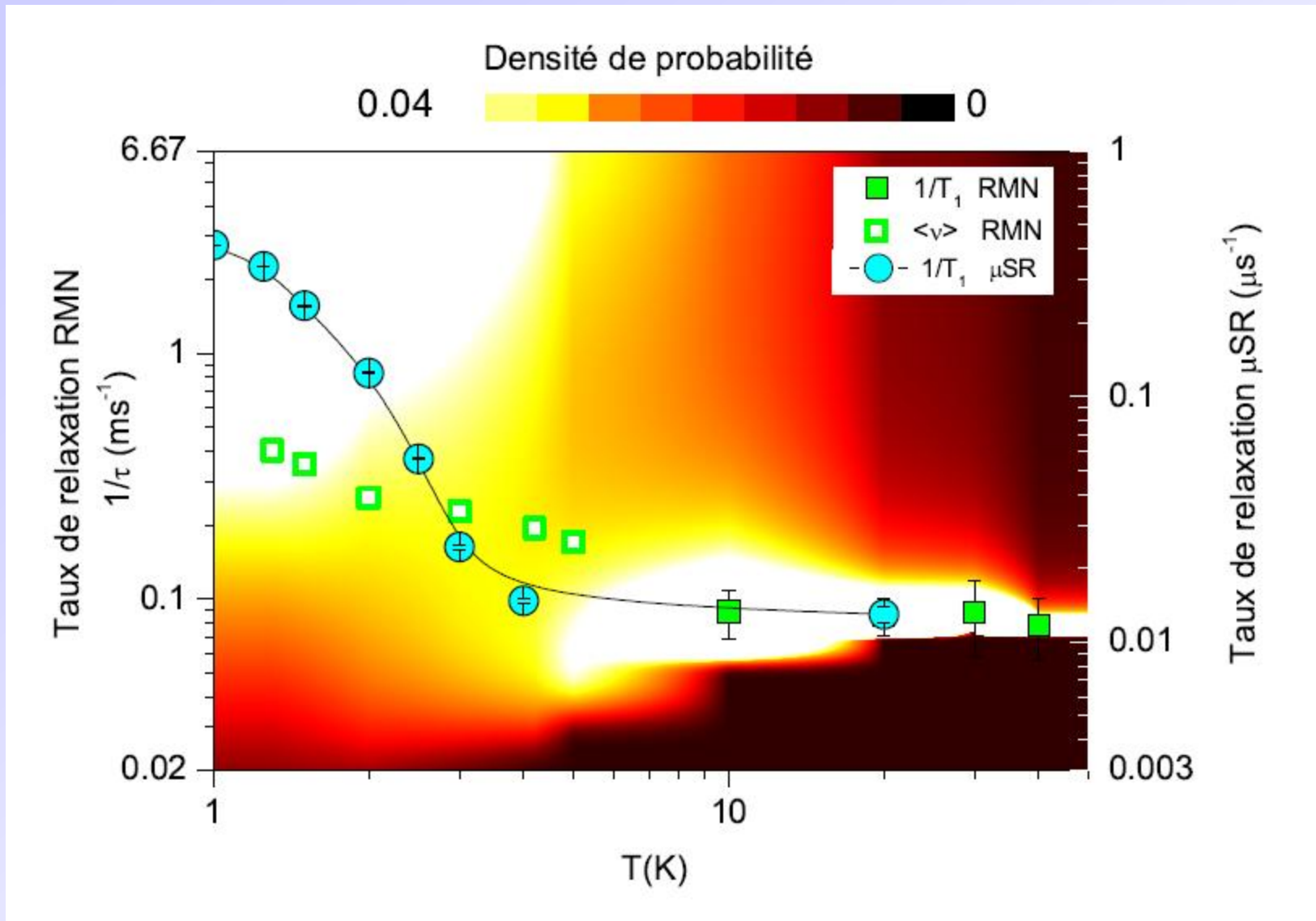


but SBMFT: predicts order at $T=0$, spin wave-like excitations

NMR: dynamical study



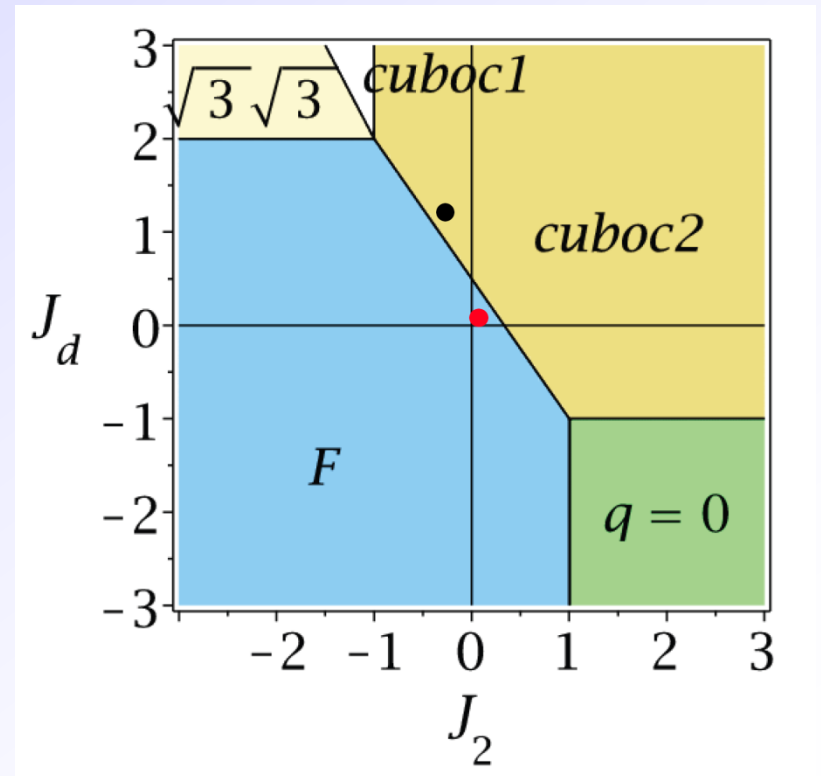
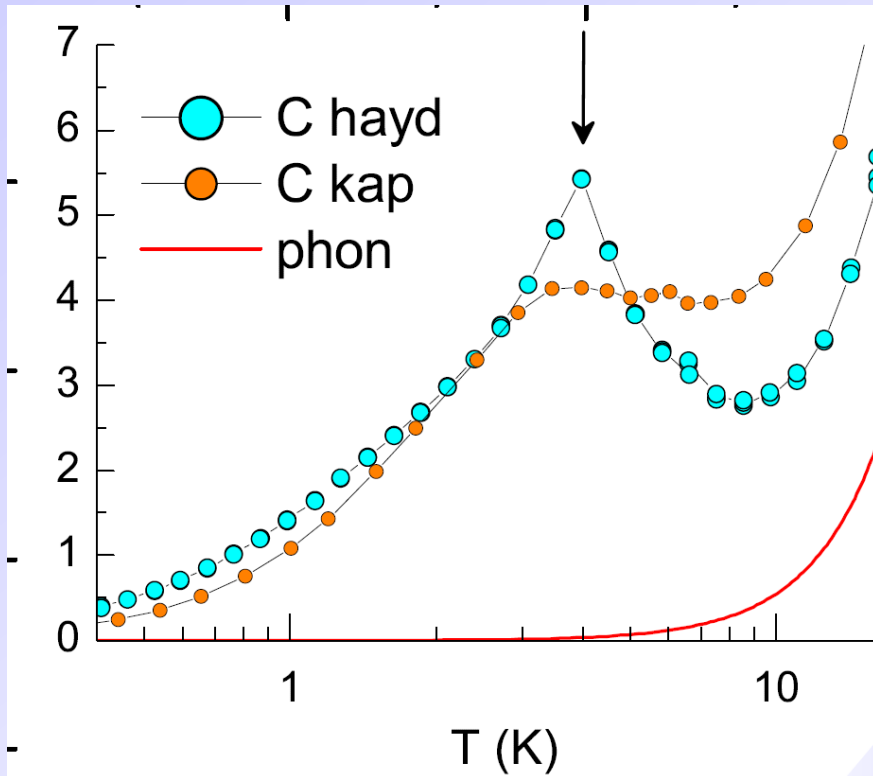
NMR: dynamical study



NMR: more local than μSR : more inhomogeneous?

Haydeite = Mg-Kapellasite

- 55% freezing @ $T = 4\text{K}$
- Peak in specific heat
- KT series $J_1 = 12.4\text{K}$, $J_d = -2.1\text{K}$, $J_2 = -1.2\text{K}$



B. Bernu, E. Kermarrec et al., unpublished

Summary III and open issues (kapellasite)

✓ Experimentally:

a new quantum spin liquid: quantum cuboc-2 phase

✓ Theoretically:

• Schwinger Boson MFT captures low energy physics

$$S(Q,E), 1/T_1)_{\mu\text{SR}}$$

• SBMFT predicts spin waves around 0.5 mEV for $T < 3\text{K}$
(not observed)

• Fermionic chiral approach (C. Lhuillier, L. Messio, B. Bernu)

• Disorder?

Thank you!



Last but not least: some (personal) feeling

- ✓ Kagome lattice dilution: does not impact much the physics
(SCGO, Herbertsmithite, Vesignieite?)
- ✓ Non-equivalent interactions matters
(Volborthite)
- ✓ Low symmetry lattices → DM