Quantum kagome spin liquids and beyond : a local investigation

Pompidou Museum in Metz (France)

Quantum kagome spin liquids and beyond : a local investigation

Néel state, any alternative?

RESONATING VALENCE BONDS: A NEW KIND OF INSULATOR?*

P. W. Anderson
Bell Laboratories, Murray Hill, New Jersey 07974
and
Cavendish Laboratory, Cambridge, England

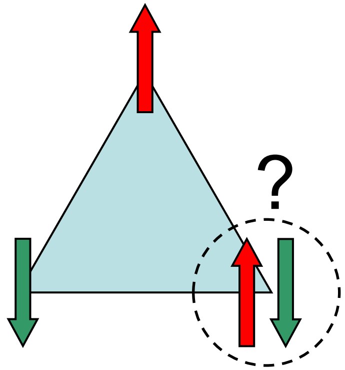
1972

(Received December 5, 1972; Invited**)

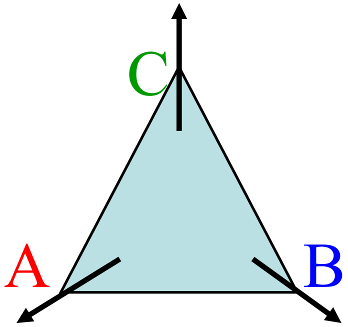
ABSTRACT

The possibility of a new kind of electronic state is pointed out, corresponding roughly to Pauling's idea of "resonating valence bonds" in metals. As observed by Pauling, a pure state of this type would be insulating; it would represent an alternative state to the Néel antiferromagnetic state for S = 1/2. An estimate of its energy is made in one case.

Geometrical Frustration of magnetic interactions

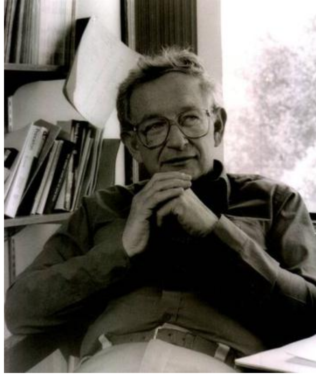


Class. →



$$\vec{S}_A + \vec{S}_B + \vec{S}_C = \vec{0}$$

Néel state, any alternative?



RESONATING VALENCE BONDS: A NEW KIND OF INSULATOR?*

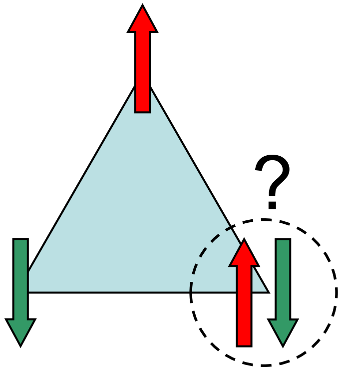
P. W. Anderson
Bell Laboratories, Murray Hill, New Jersey 07974
and
Cavendish Laboratory, Cambridge, England

(Received December 5, 1972; Invited**)

ABSTRACT

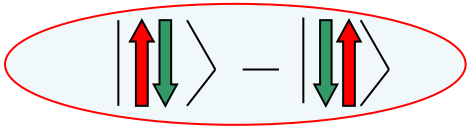
The possibility of a new kind of electronic state is pointed out, corresponding roughly to Pauling's idea of "resonating valence bonds" in metals. As observed by Pauling, a pure state of this type would be insulating; it would represent an alternative state to the Néel antiferromagnetic state for S = 1/2. An estimate of its energy is made in one case.

Geometrical Frustration



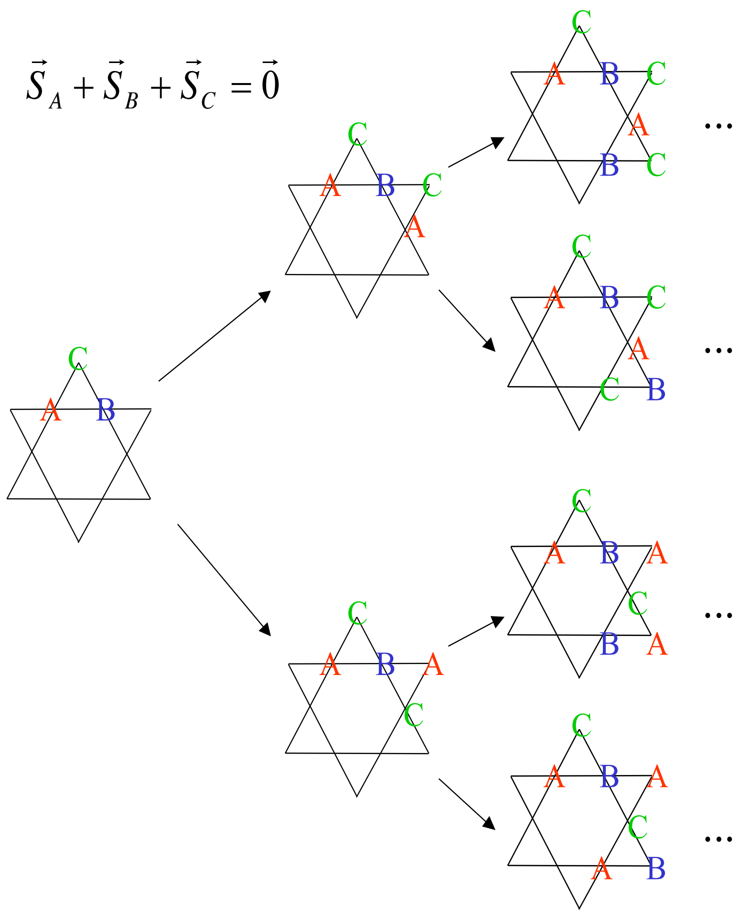
+

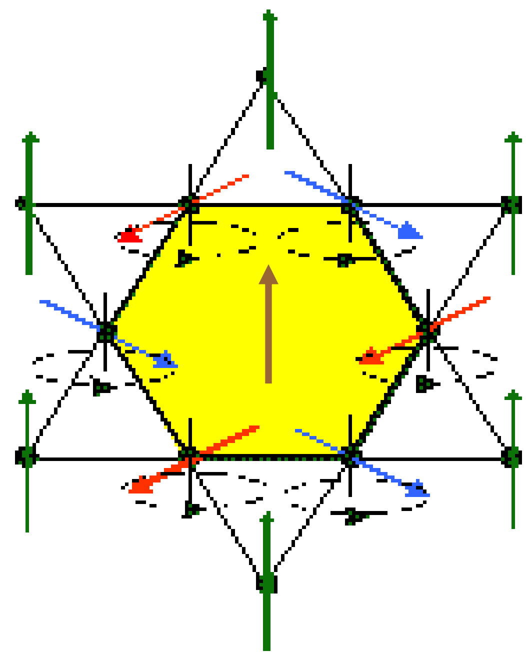
Quantum fluctuations S=1/2



Corner sharing: *classical* kagomé lattice

$$\vec{S}_A + \vec{S}_B + \vec{S}_C = \vec{0}$$



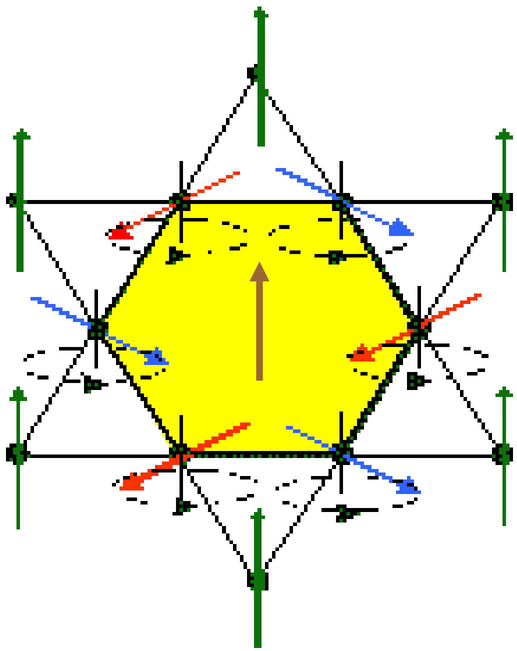


Macroscopic degeneracy

Soft modes

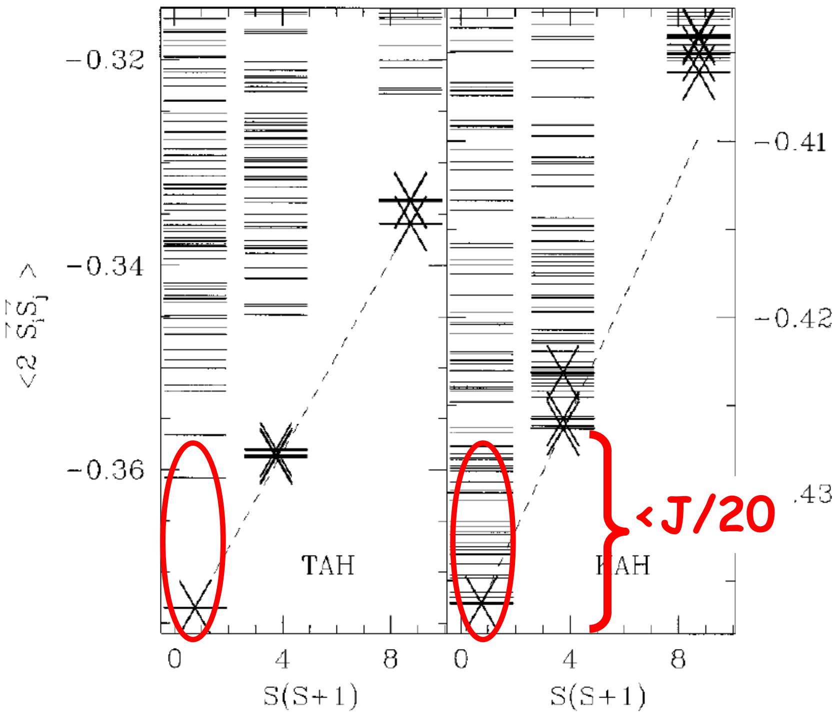
Corner sharing: *classical* vs quantum kagomé lattice

Classical soft modes



Back to 90's

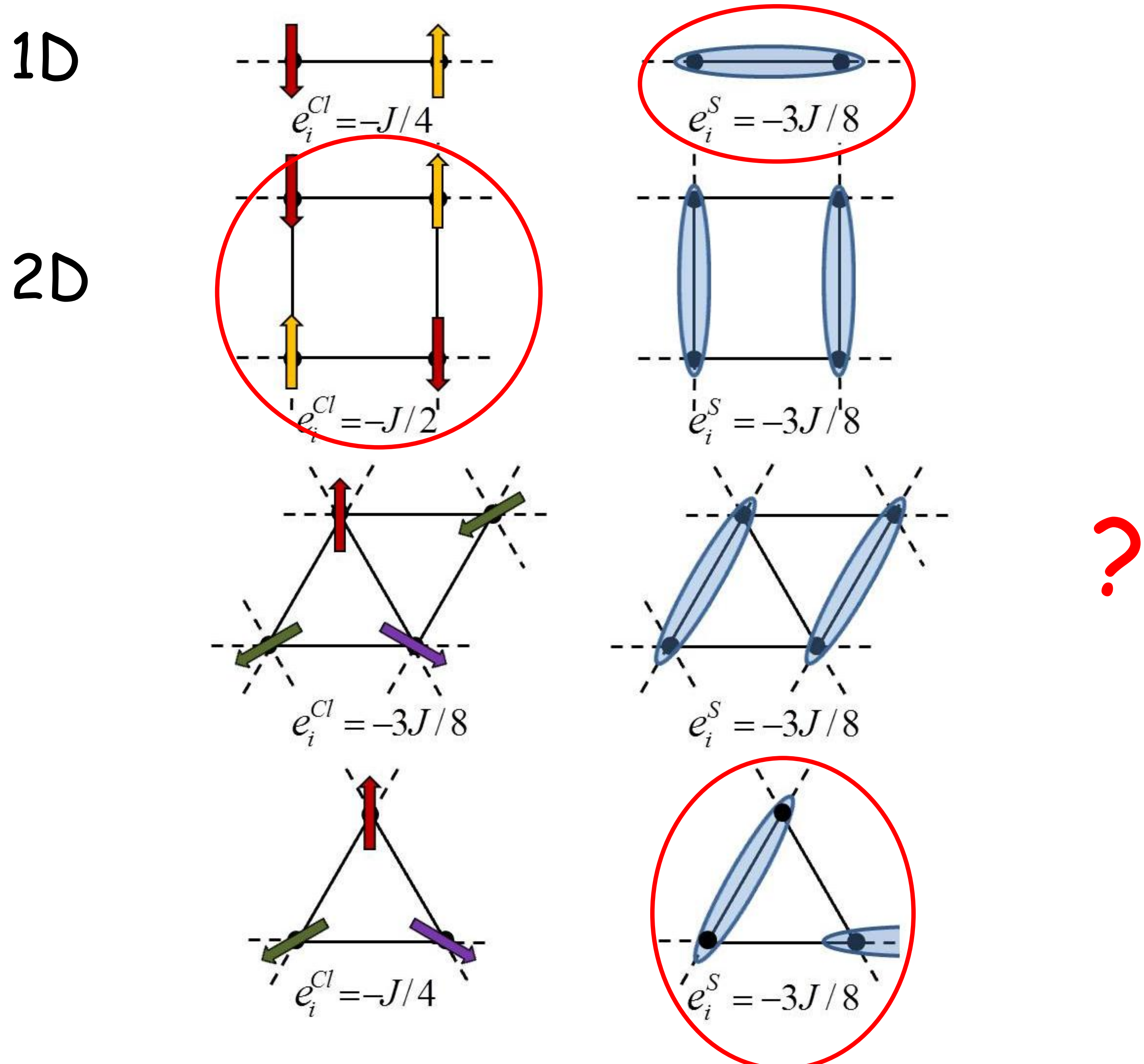
Triangular ≠ Kagome



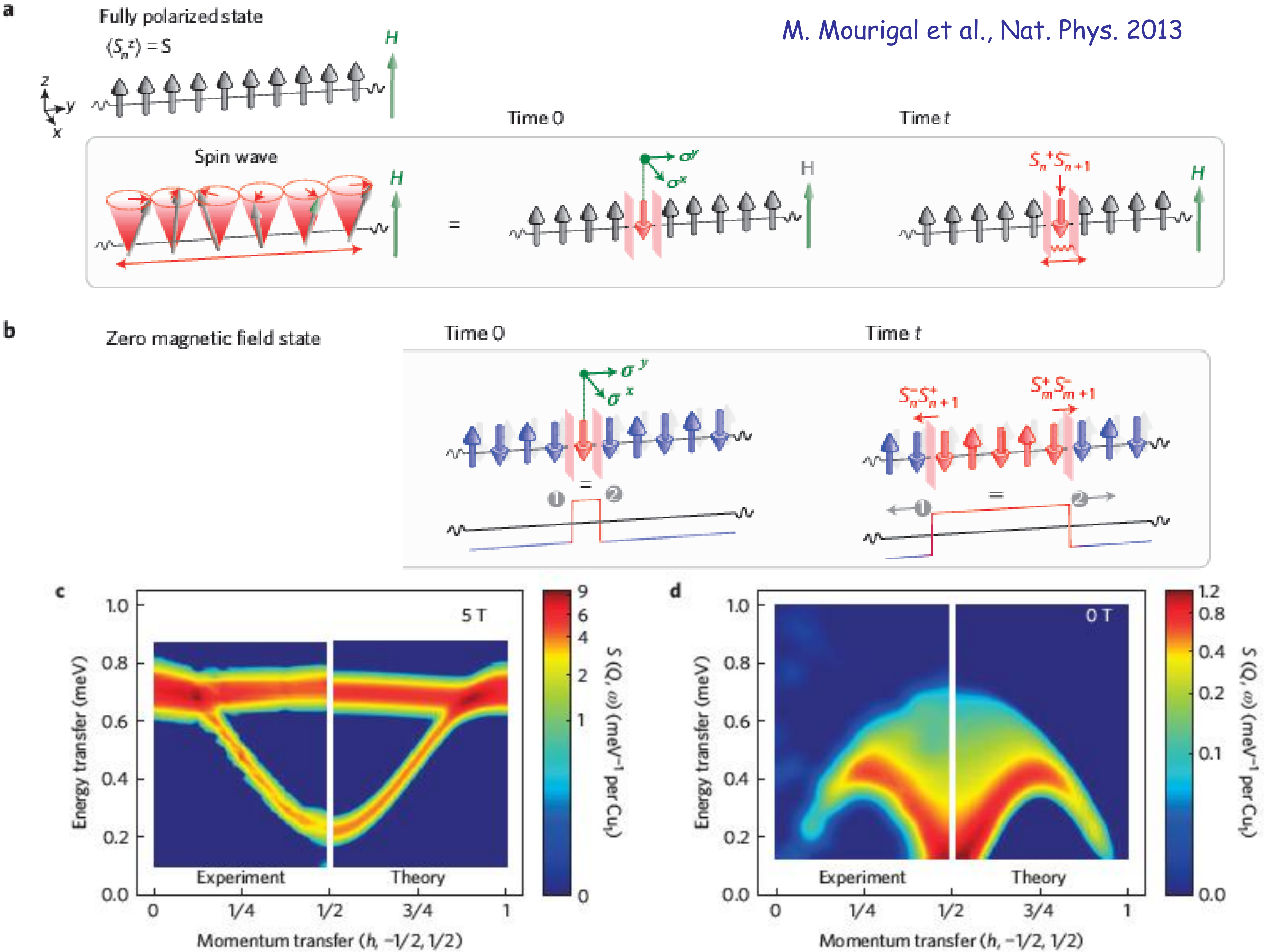
- $\Delta < J/20$
- No gap in the singlet sector

•Lecheminant, PRB **56**, 2521 (1997)
•Waldtmann *et al.*, EPJB **2**, 501 (1998).

Néel state Dimer state

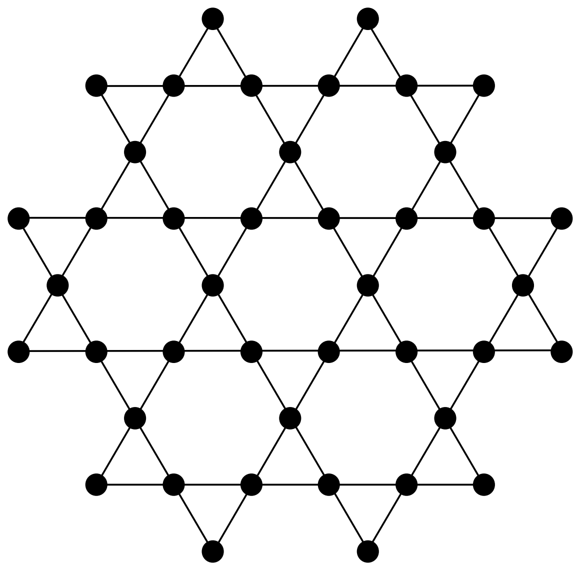


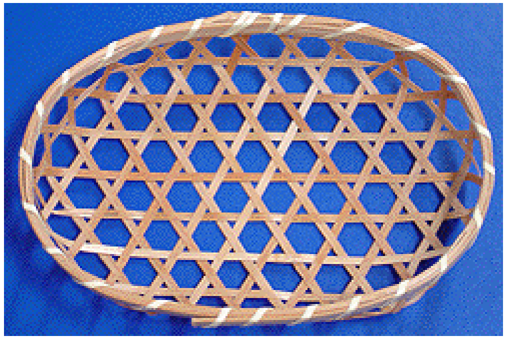
M. Mourigal et al., Nat. Phys. 2013

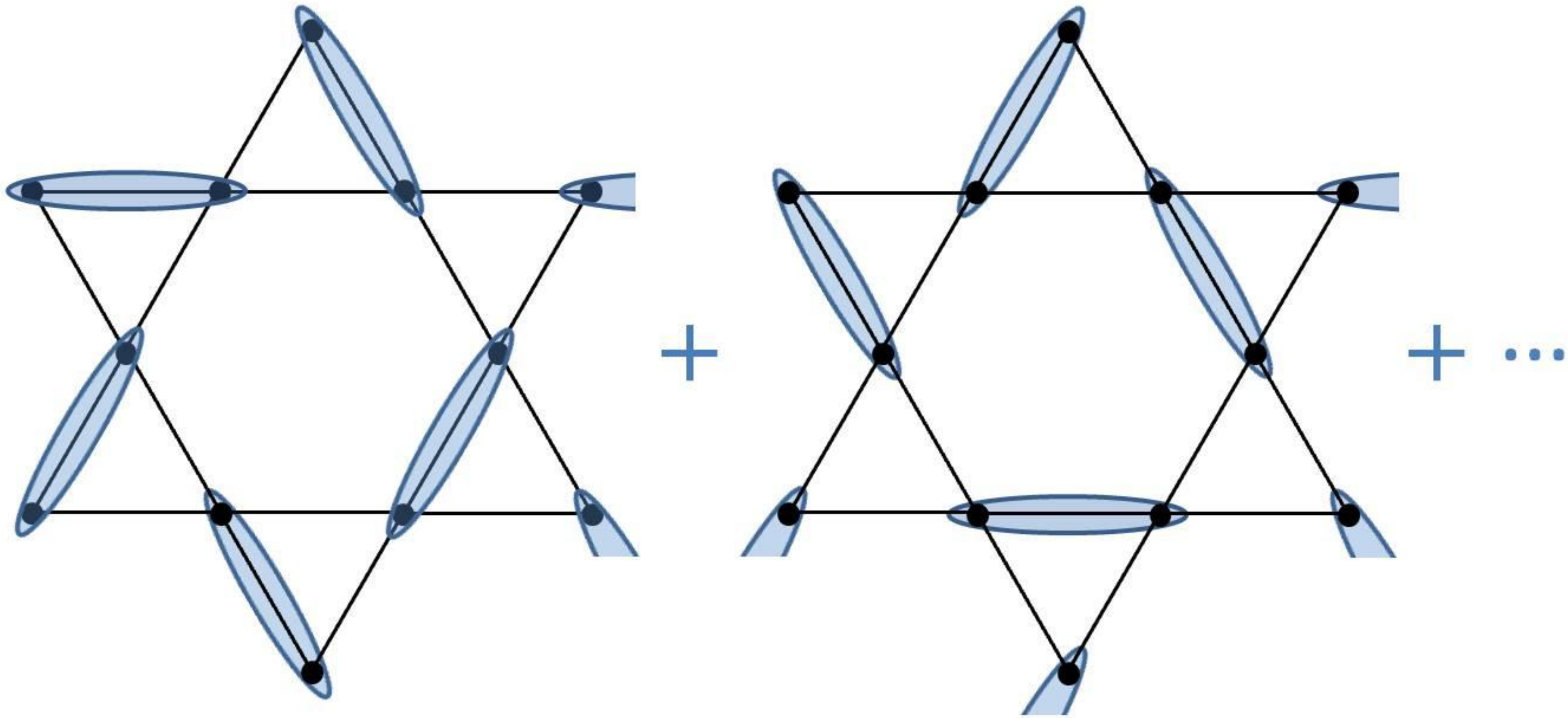


Quantum kagome antiferromagnet:
ideal playground for spin liquid physics

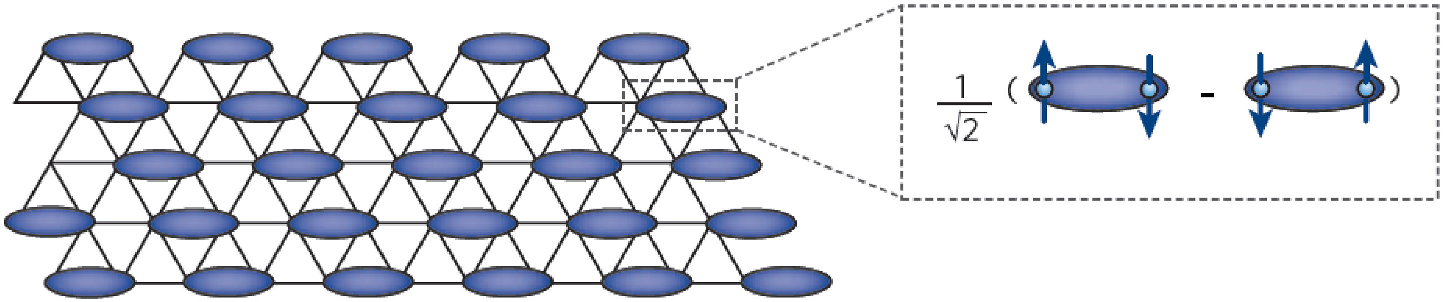
- Low spin S=1/2
- High geometrical frustration: corner-sharing geometry
- Lattice with low coordination number (z=4)

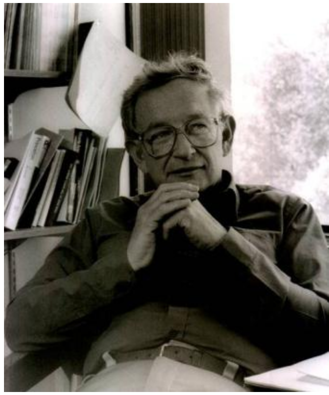


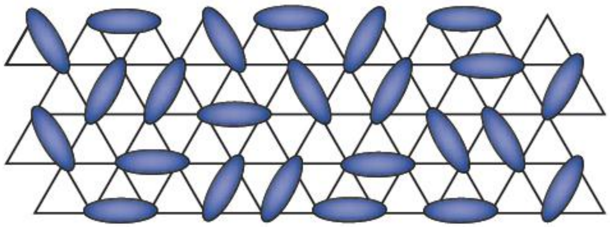
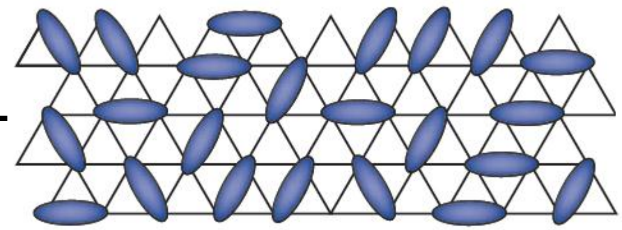




Quantum states





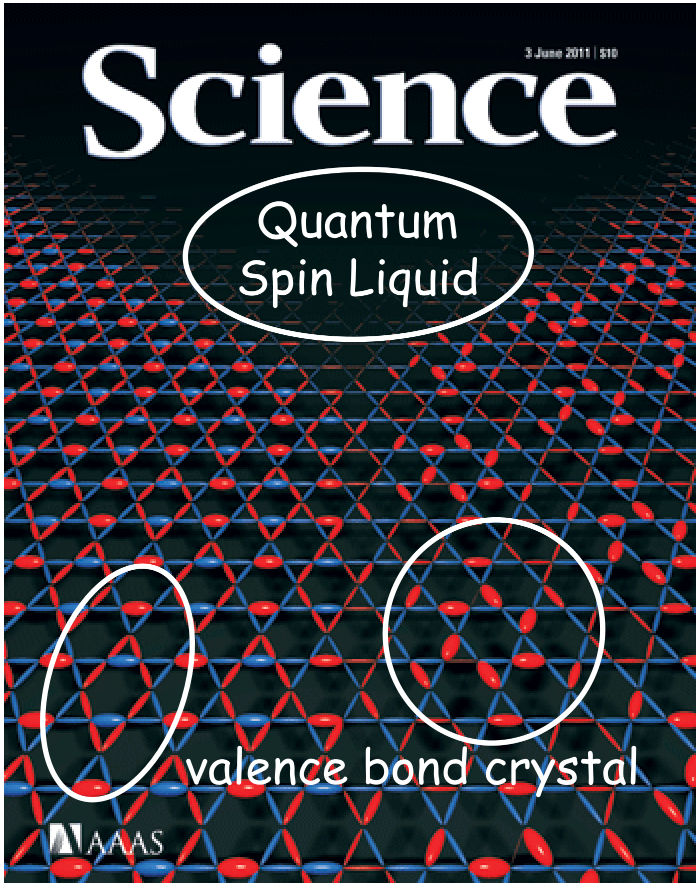
$|\mathrm{RVB}\rangle =$  +  +…

quantum spin liquid:

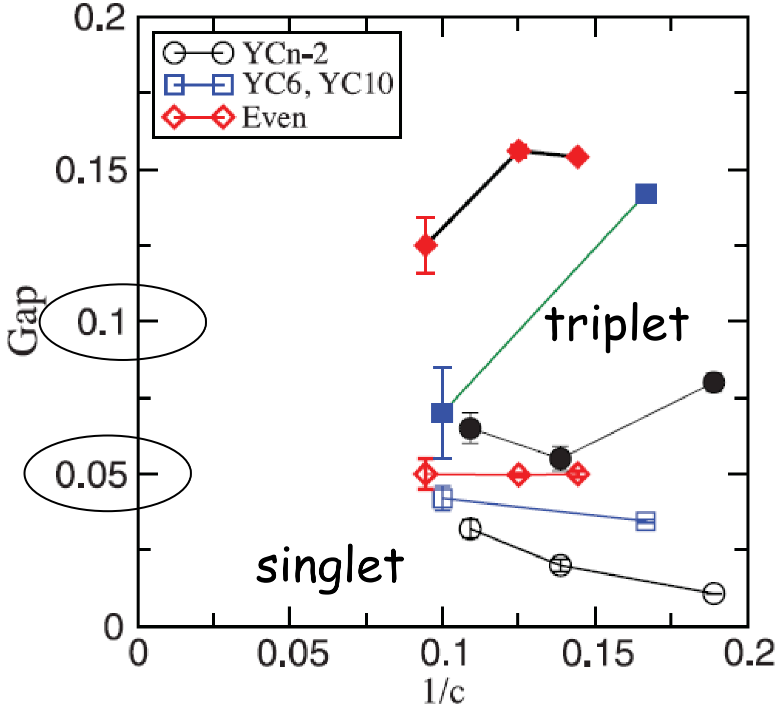
A state without any spontaneous symmetry breaking

Review L. Balents, Nature 2010

On the theoretical front: Large size numerical study (DMRG)



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



S. Yan et al, Science **332** (2011)

S. Depenbrock et al, PRL **109**, 067201 (2012) : $\Delta = 0.13(1)$ J

S. Nishimoto et al, Nature Com, (2013) $\Delta = 0.05(2)$ J

Quantum Kagome ground state? The lowest energy!!!

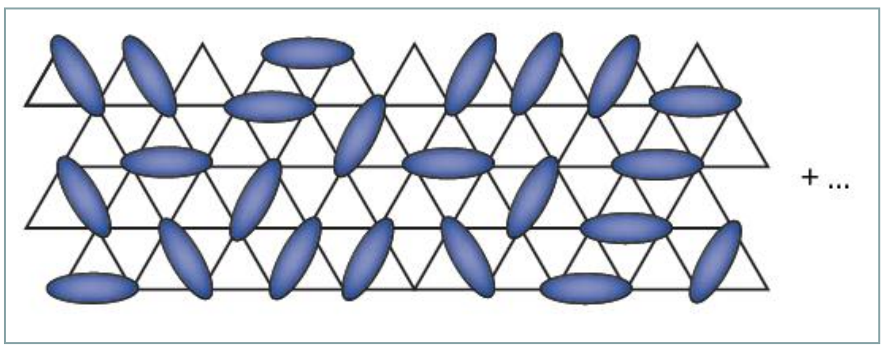
Two prototypes of quantum spin liquid

Z_2 QSL

Gapped magnetic excitations (S=1/2)

Gapped non-magnetic excitations

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



Short range RVB

Yan et al, science 2011

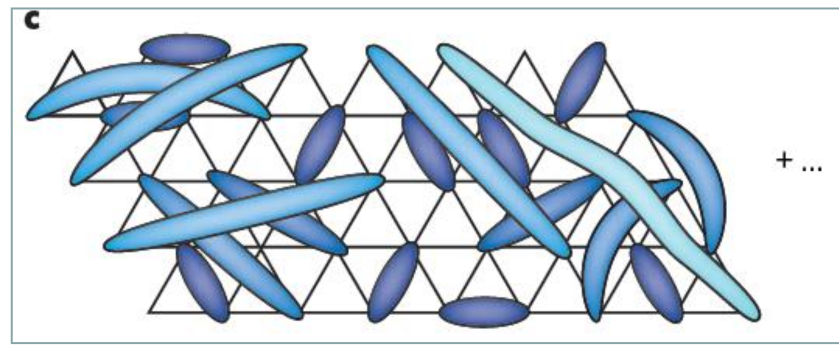
S. Depenbrock et al, PRL 109, 2012

Δ =0.13(1)J→ 0.05 (2) J

Algebraic/Critical/Dirac/U(1) QSL

Gapless excitations

$C_v \sim T^2$; $\chi \sim T$



Long range RVB

Hastings, PRB 63, 2000

Ran et al, PRL 98, 2007

Ryu et al, PRB 75, 2007

Outline

- ✓ Herbertsmithite $Cu_3Zn(OH)_6Cl_2$

  gapless spin liquid

  relevance of perturbations

- ✓ Vanadium based kagome $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$

  Magnetic model – « trimerized kagome »

  Gapless excitation spectrum (heat capacity)

  gapped magnetic excitations (NMR)

- ✓ Hyperkagome $Na_4Ir_3O_8$

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*

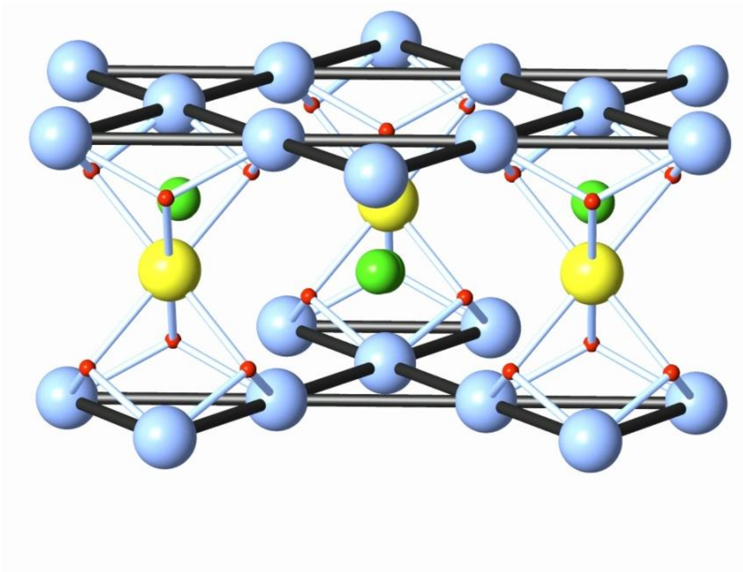
Department of Chemistry, 6-335, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139-4307

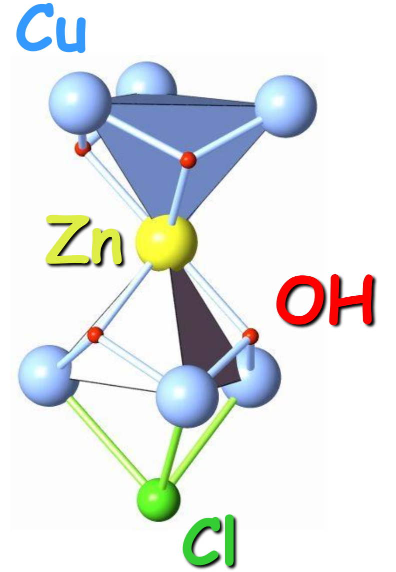
Received June 13, 2005; E-mail: nocera@mit.edu

Herbertsmithite:
$ZnCu_3(OH)_6Cl_2$

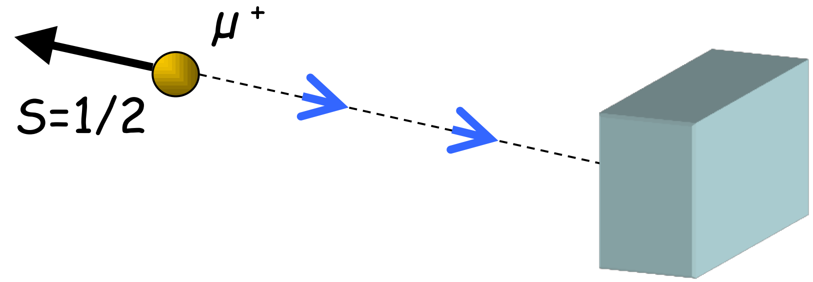
Cu^{2+}, S=1/2

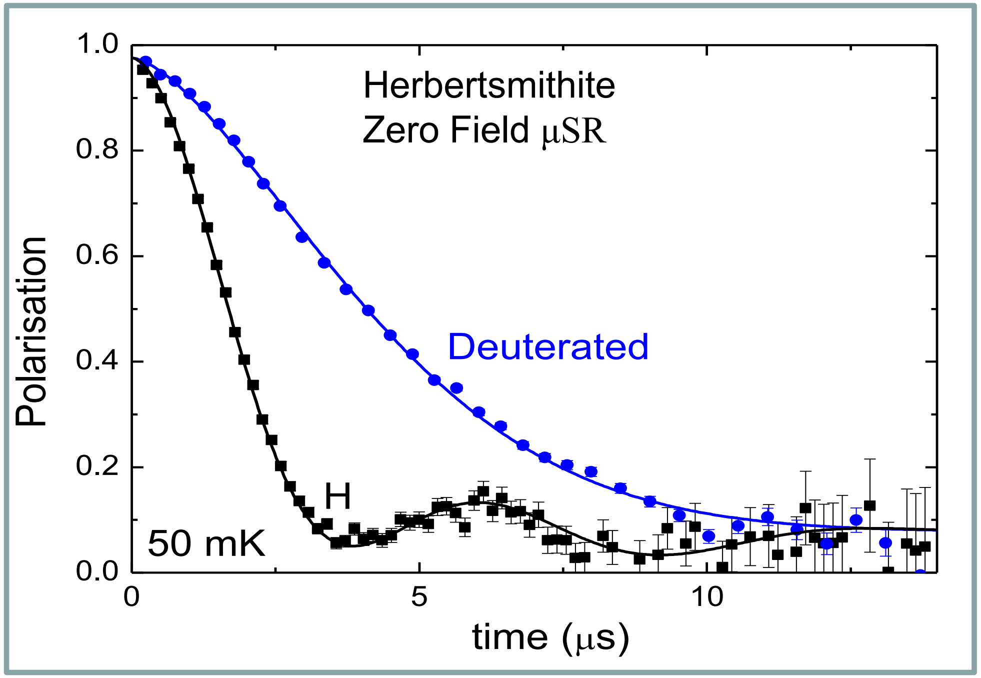
J=180 K (AF)





Muon spin relaxation (μSR)



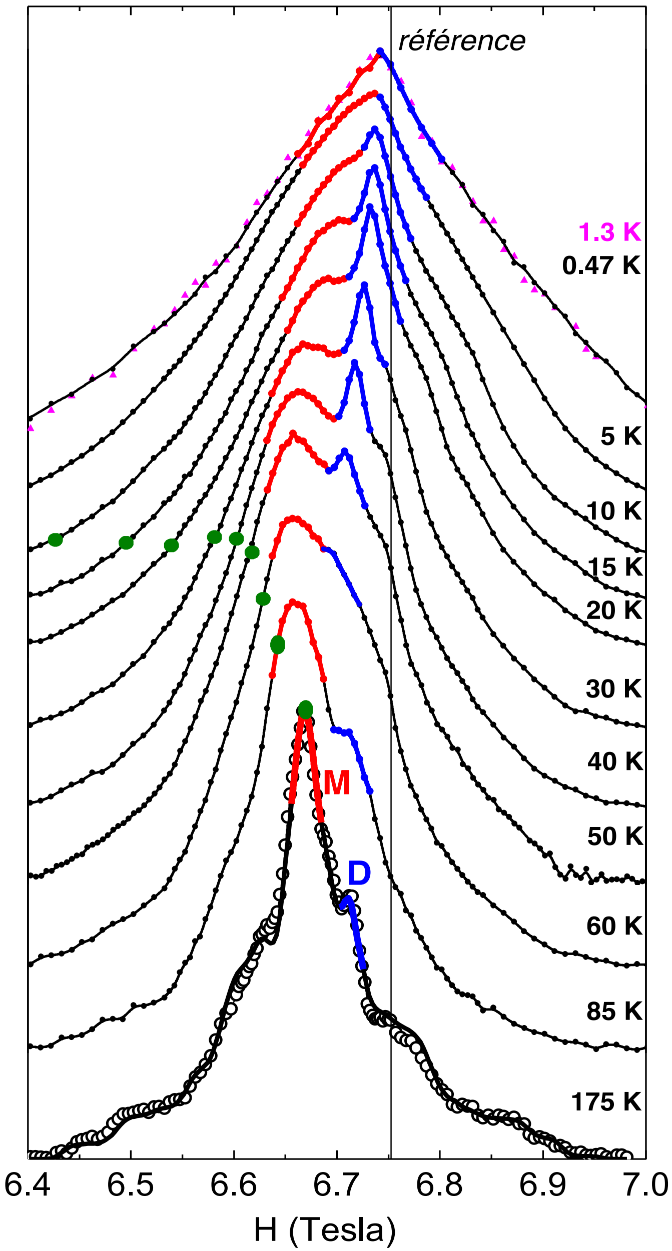


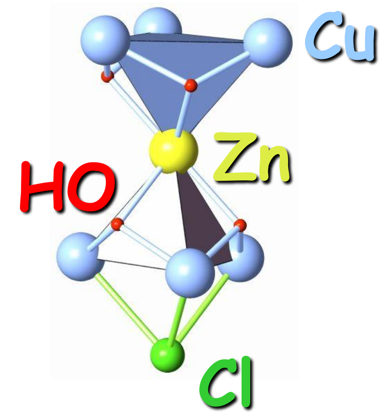
-relaxation from "static" nuclear fields.
-upper limit of a frozen moment for Cu^{2+}, if any : 6×10^{-4} μ_B

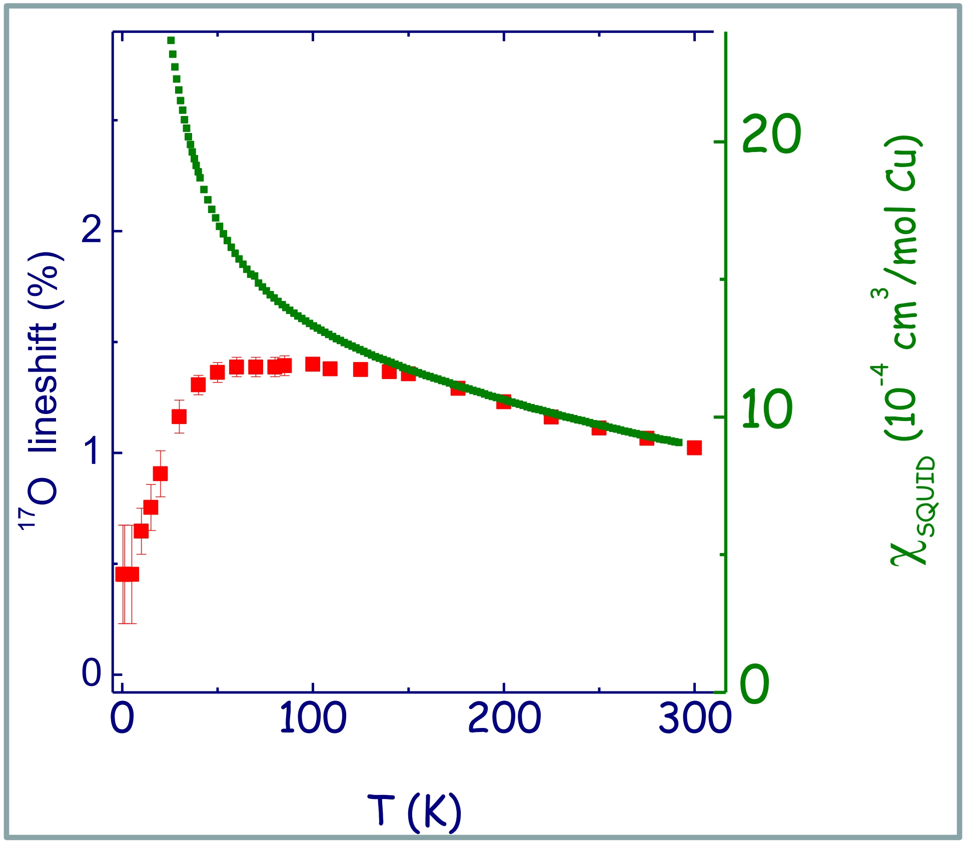
No order or frozen disorder down to 20 mK (J/8000) !

P. Mendels et al, PRL 98, 077204 (2007)
PSI : Amato, C. Baines - ISIS : A.D. Hillier, J. Lord

^{17}O NMR :
Local susceptibility of the kagome planes

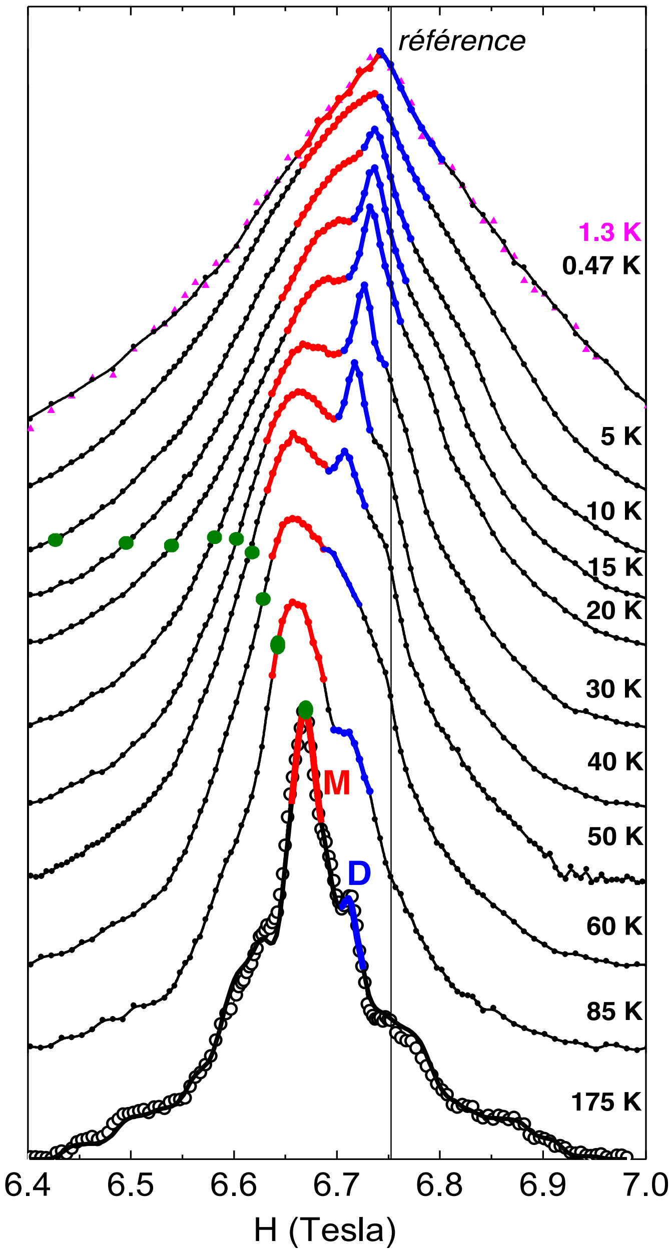


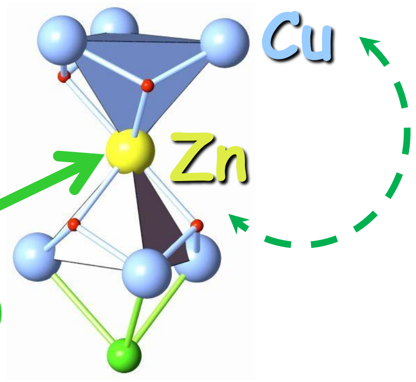




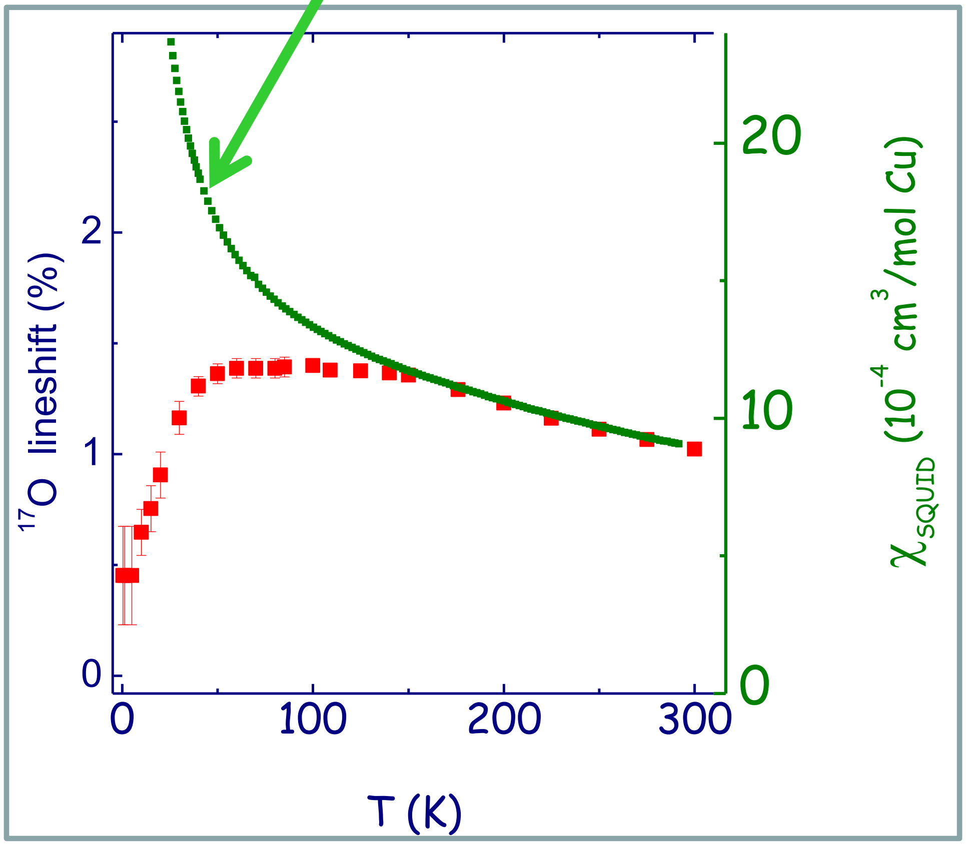
Olariu et al, PRL 100, 087202 (2008)

^{17}O NMR :
Local susceptibility of the kagome planes



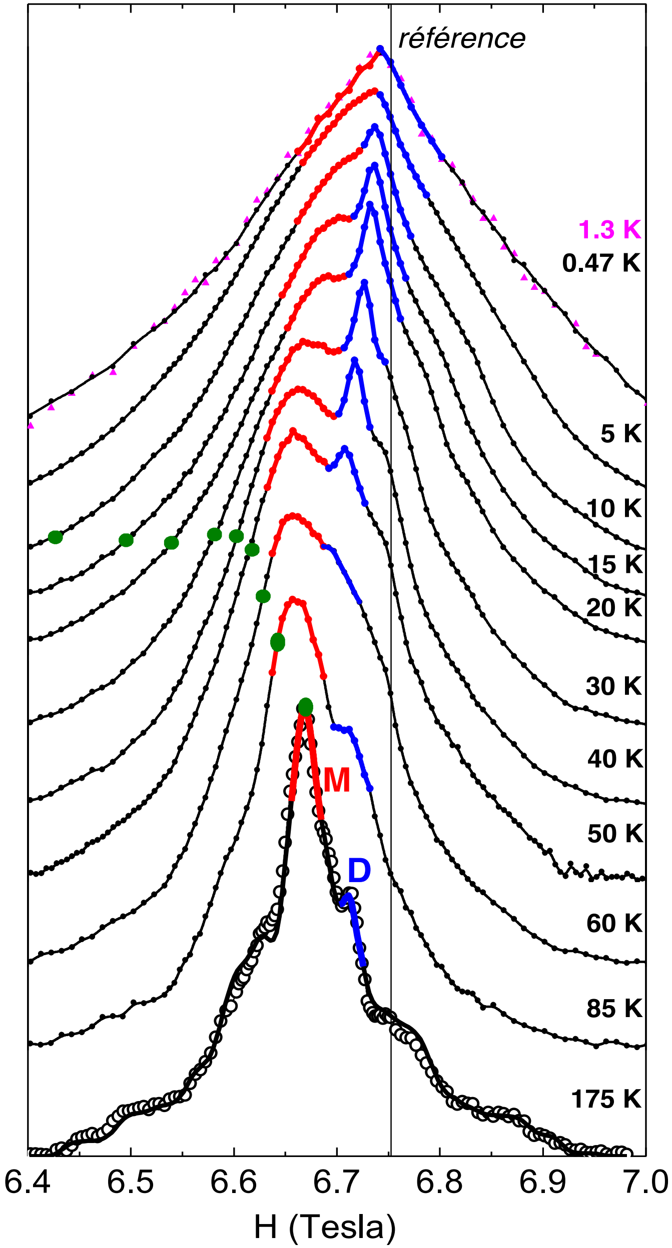


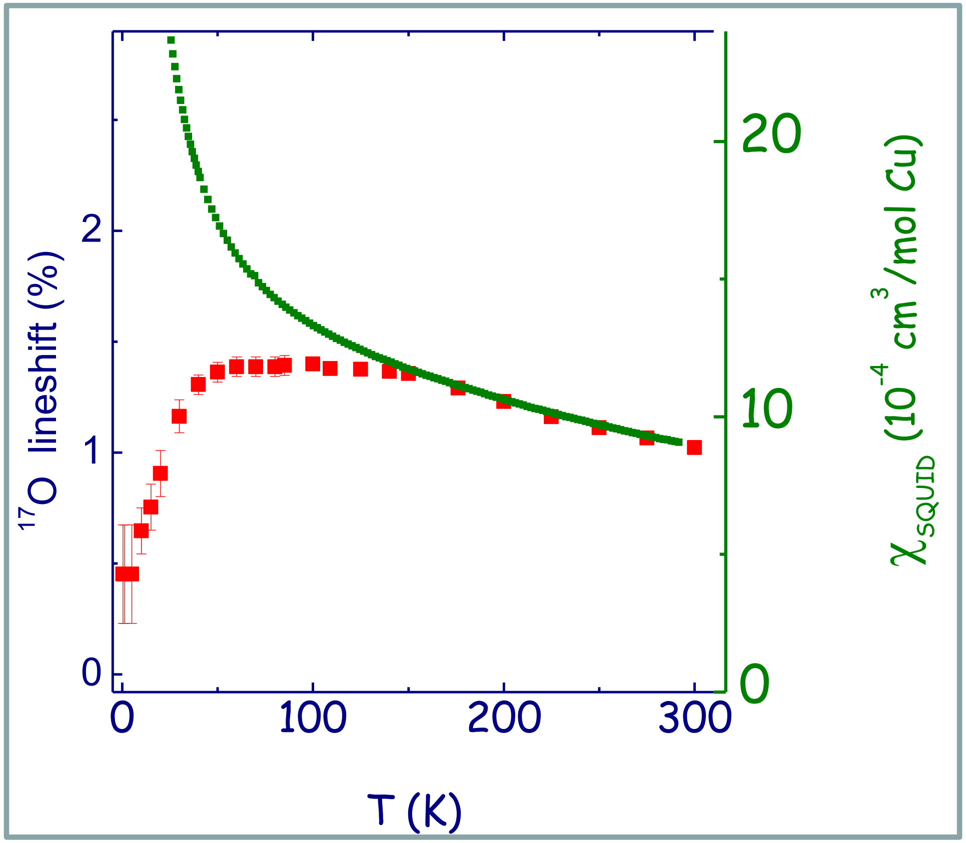
~5% Cu on the Zn site
Nearly free ½ spins



Olariu et al, PRL 100, 087202 (2008)

^{17}O NMR :
Local susceptibility of the kagome planes

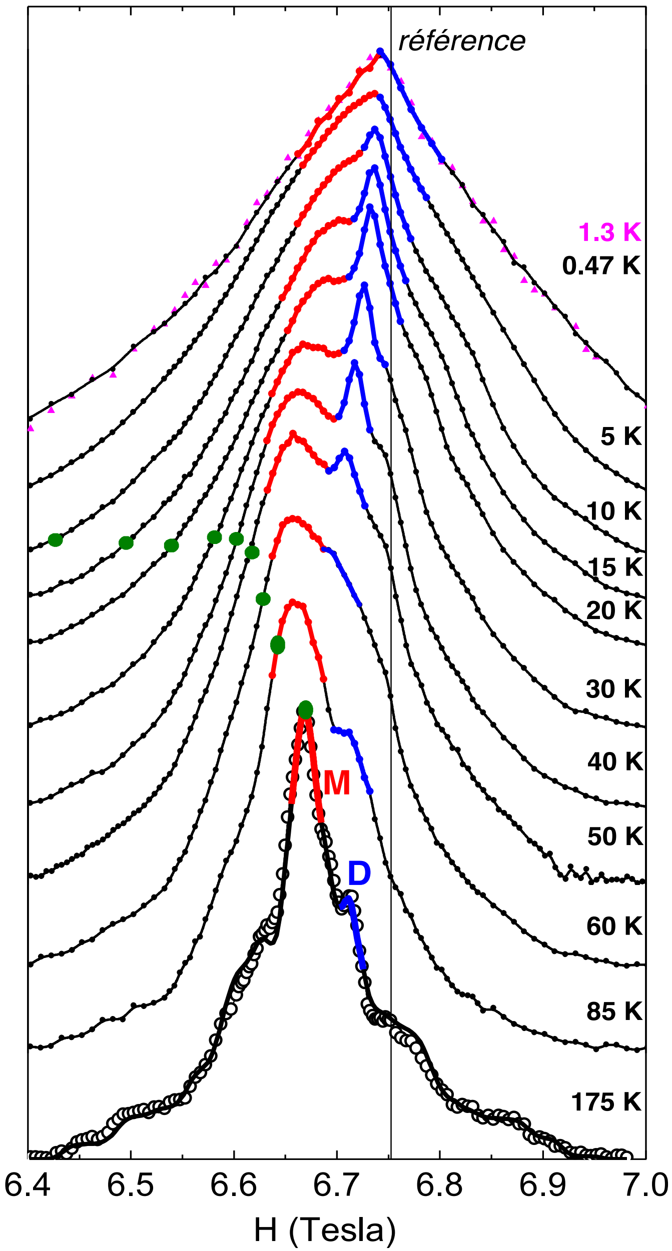


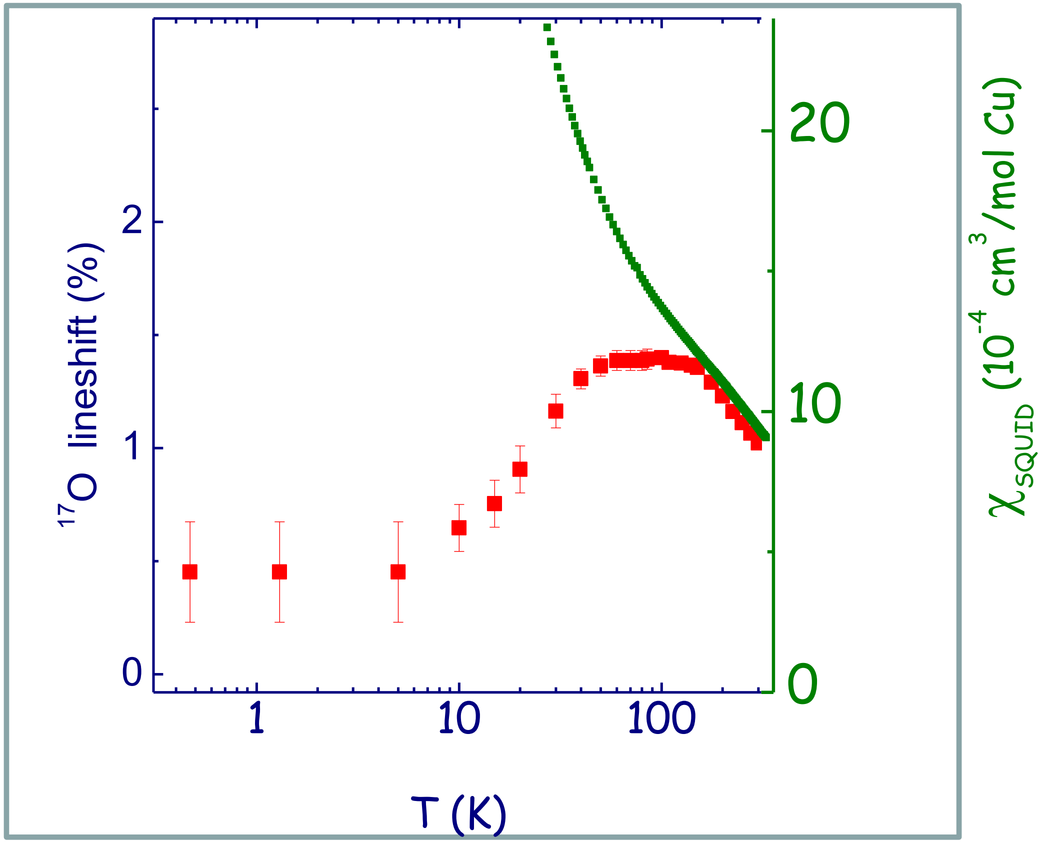


-Enhancement of short range AF correlations at ~J/3

Olariu et al, PRL 100, 087202 (2008)

^{17}O NMR : Local susceptibility of the kagome planes



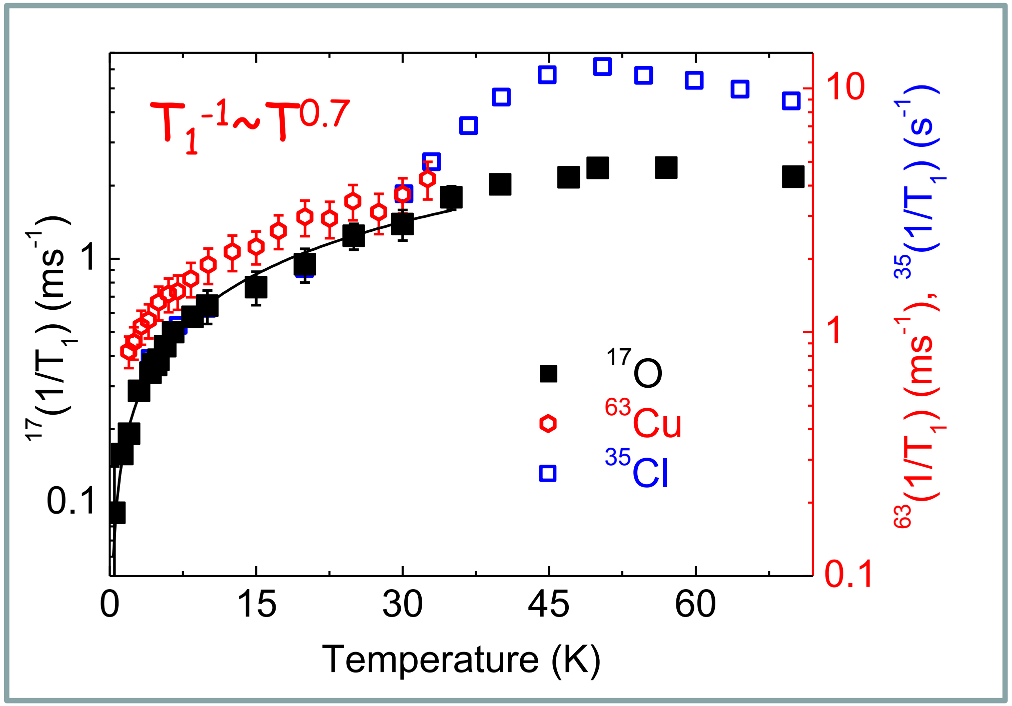


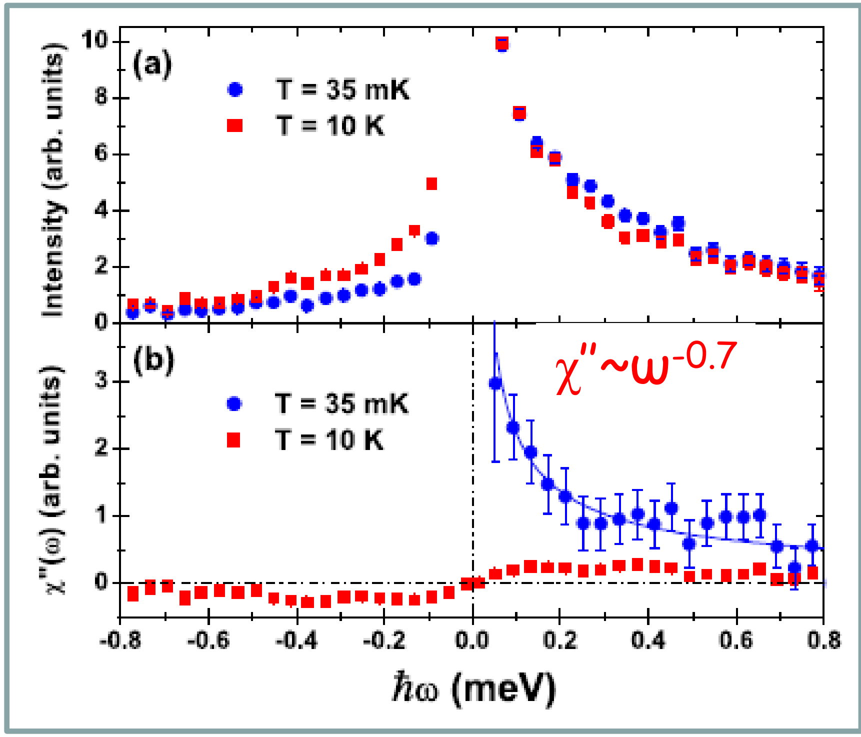
-Enhancement of short range AF correlations at ~J/3

-Finte T->0 susceptibility : no spin gap

Olariu et al, PRL 100, 087202 (2008)

Low T Spin Dynamics





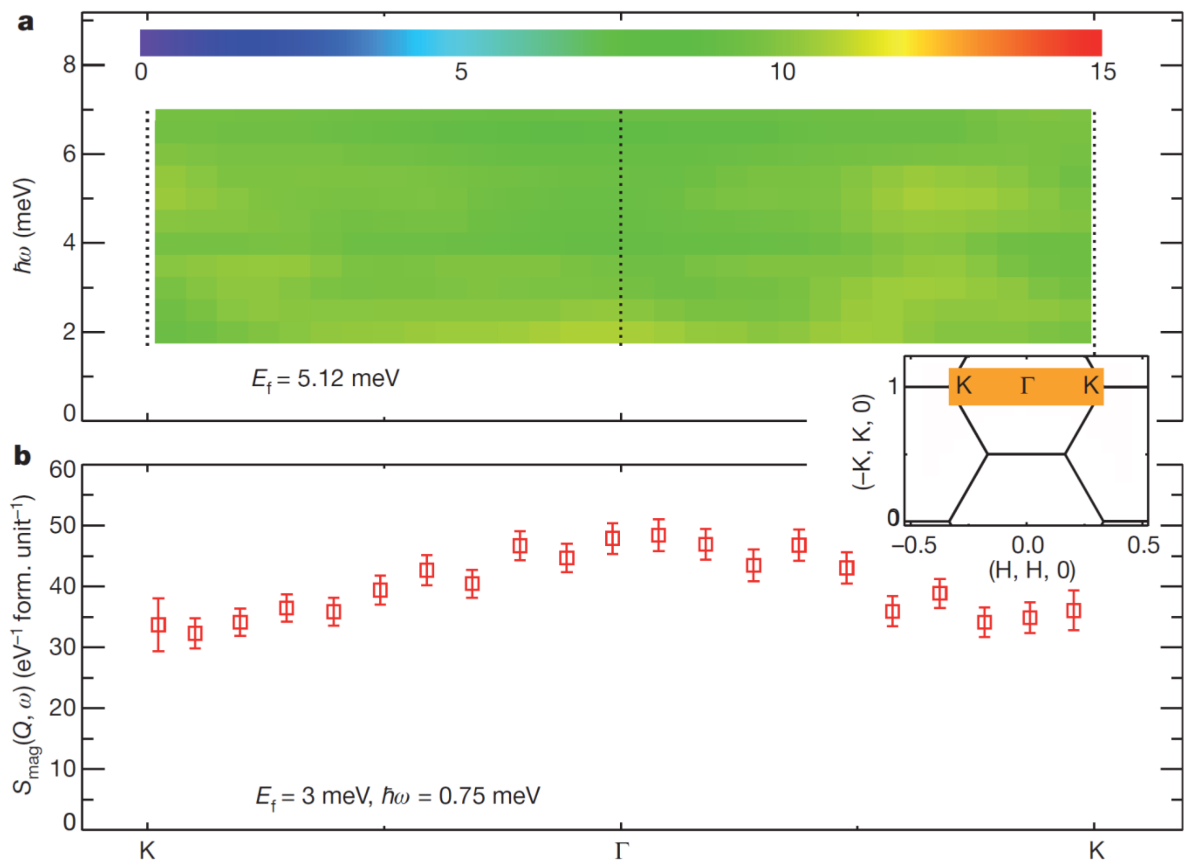
Olariu et al, PRL 100, 087202 (2008)
Imai, PRL 100, 077208 (2008)

Helton et al, PRL 98 107204 (2007)

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

- No spin gap behavior
- power law dependence, criticality?

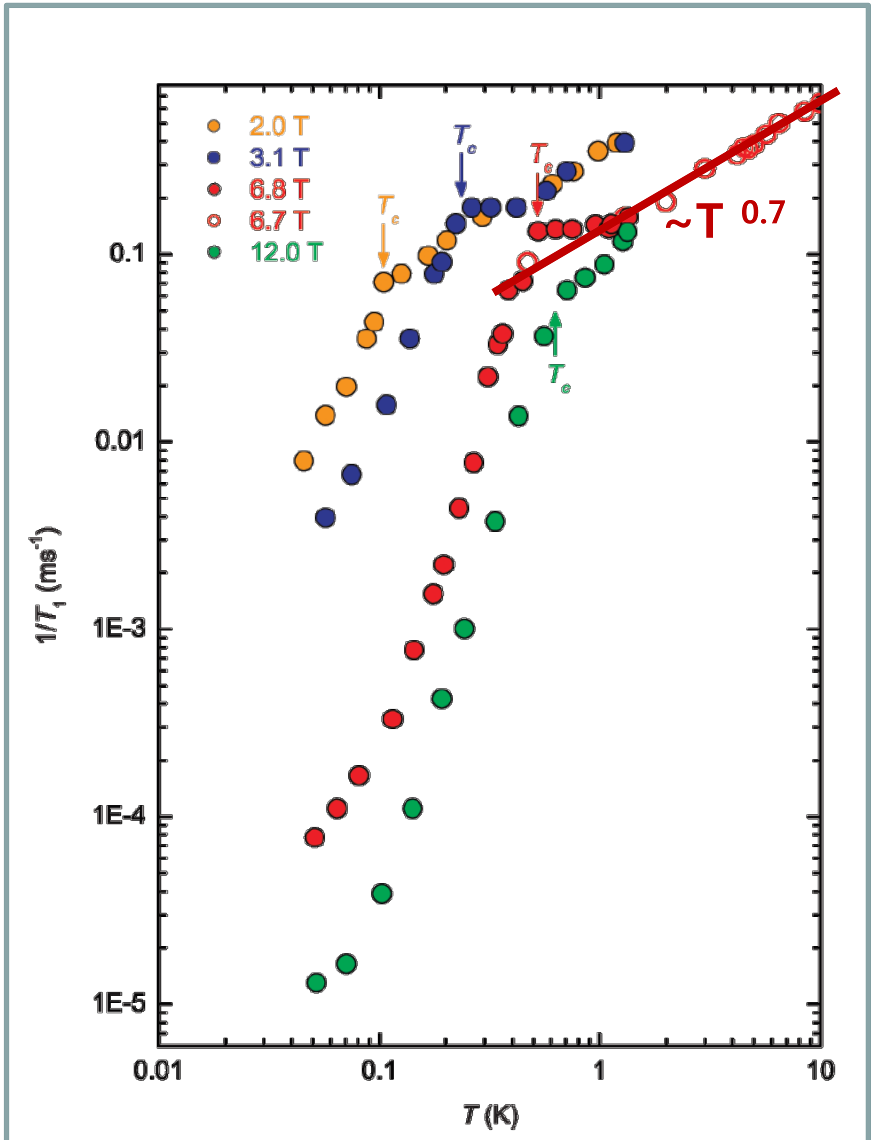
Neutrons on single crystals

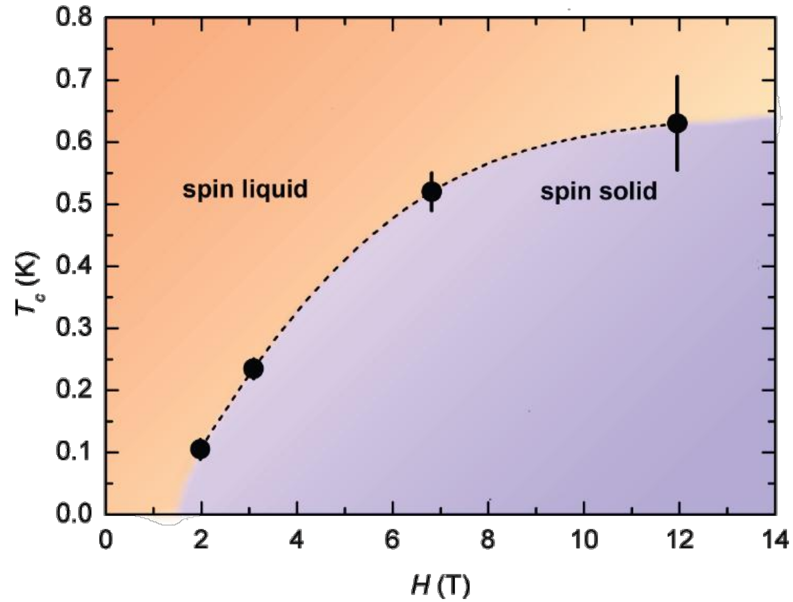


- Gapless: $\Delta < 0.1\,J$
- Continuum of excitations
- No n.n. dimer correlation

Han et al, Nature 492, 406 (2012)

Very Low T Spin Dynamics: field induced freezing



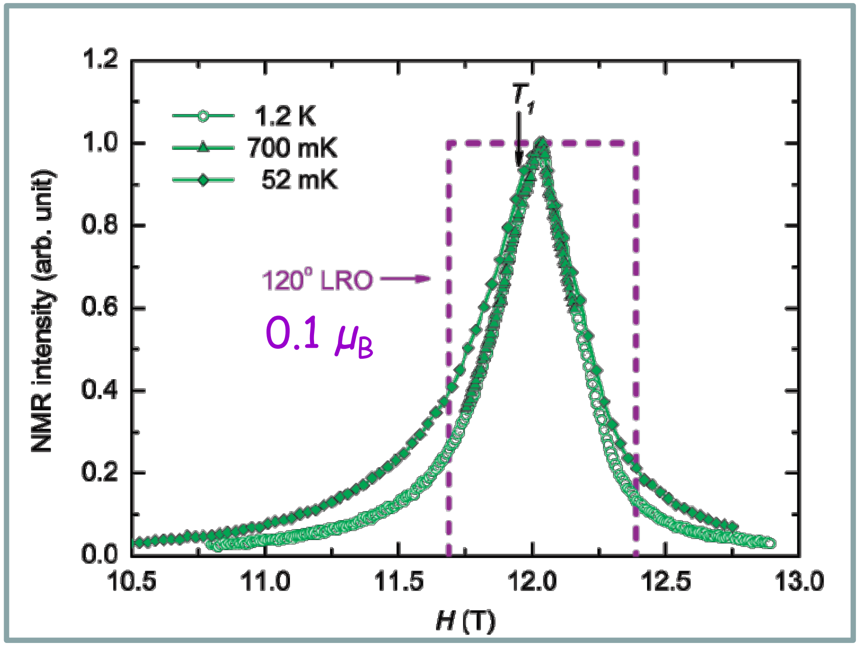


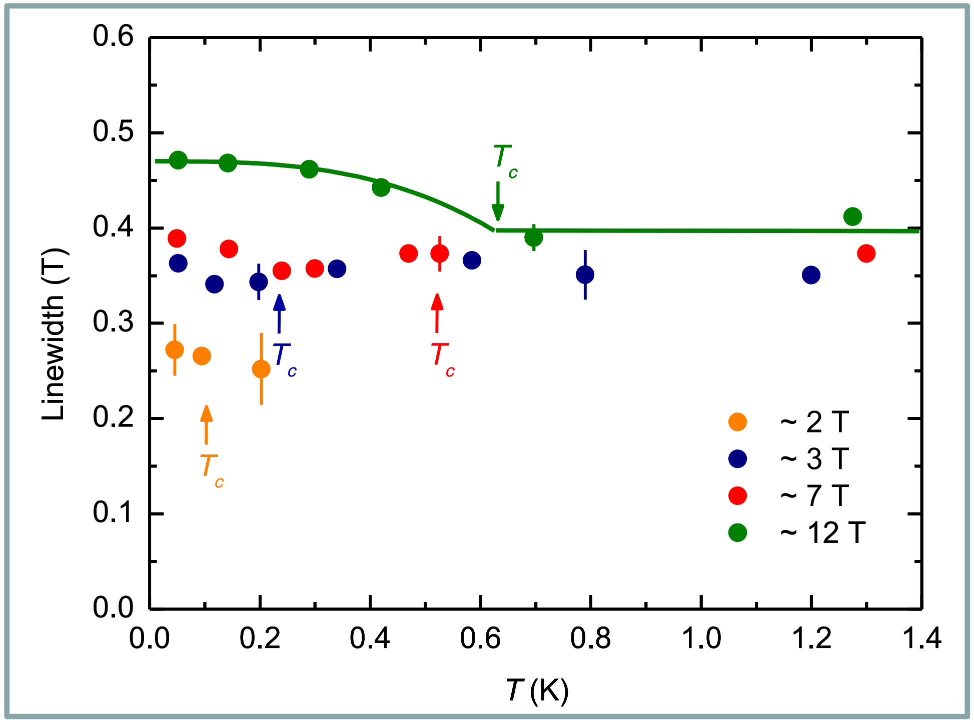
- $T>T_c$: gapless, spin-liquid behavior
- $T<T_c$: drastic suppression of spin dynamics
  spin-solid (?)

- No peak at Tc, no critical slowing down

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

Very Small frozen moment





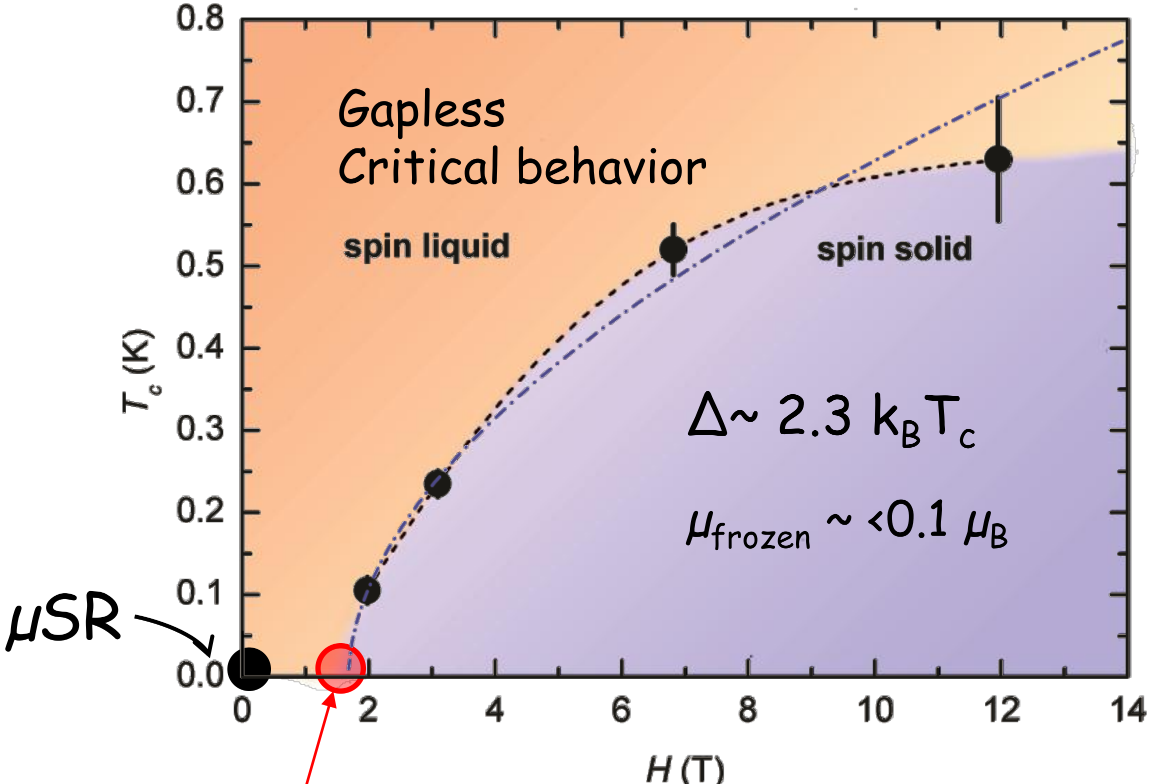
-No long range order but frozen state

-Hyperfine constant: 3.5 T/μ_B

μ_{frozen} ~ 0.1 μ_B @ 12 T

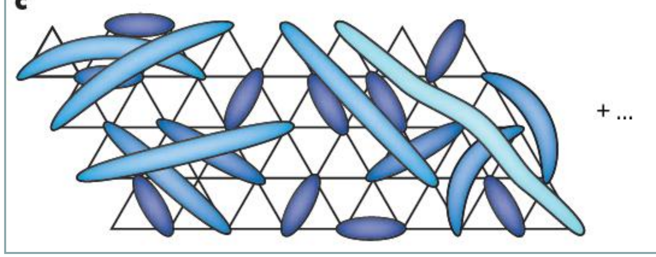
μ_{frozen} even smaller for smaller H

A Quantum Critical Point ?



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

Comparison to theories

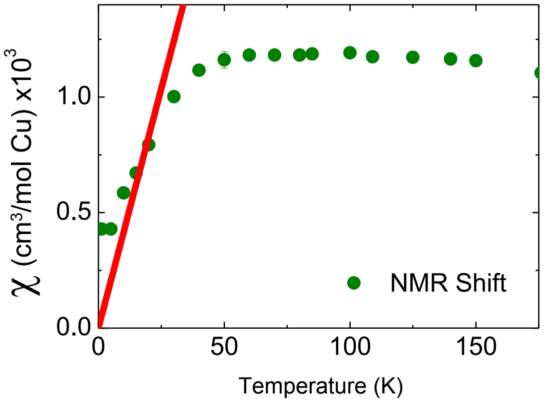


- Algebraic critical spin liquid - U(1)

  Ran et al, PRL **98**, 117205 (2007)
  Hermele et al, PRB **77**, 224413 (2008)

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

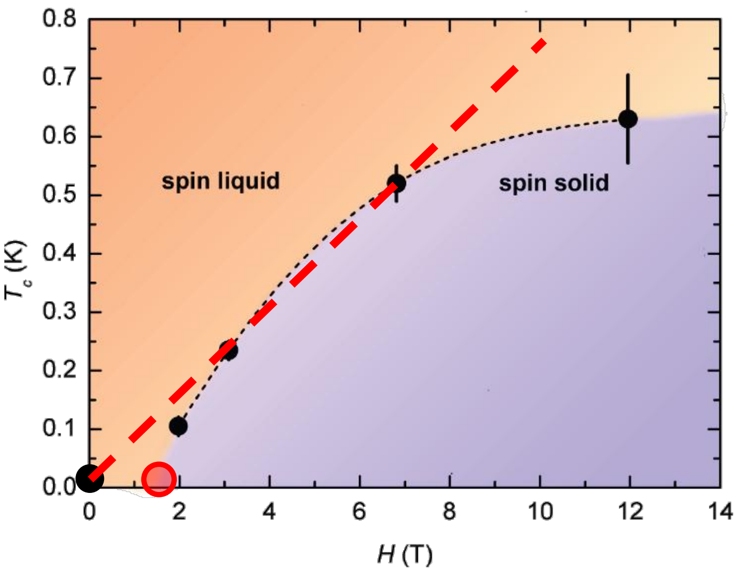
$$\frac{1}{T_1} \propto T^\eta$$



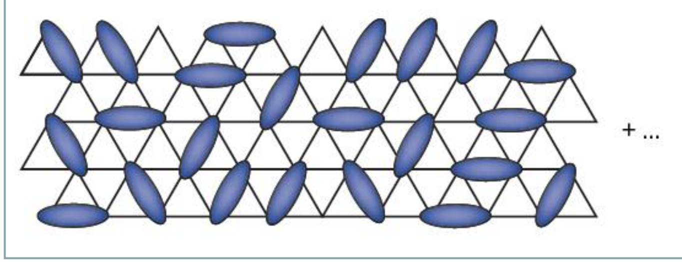
-Gapless
-Critical behavior

-Instability (H≠ 0) M ~ H^α but Tc ~ H
Ran et al, PRL **102** 117205 (2009)

-Unstable to anisotropy
DM interaction -> L.R.O.
Hermele et al, PRB **77**, 224413 (2008)



Comparison to theories



- gapped spin liquid

  Yan et al, Science (2011)

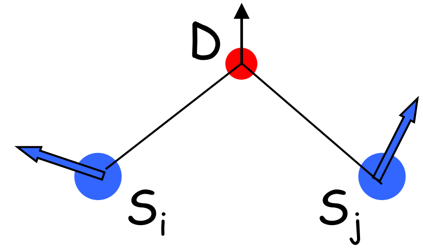
  Gapped magnetic excitations (S=1/2)

  Gapped non-magnetic excitations

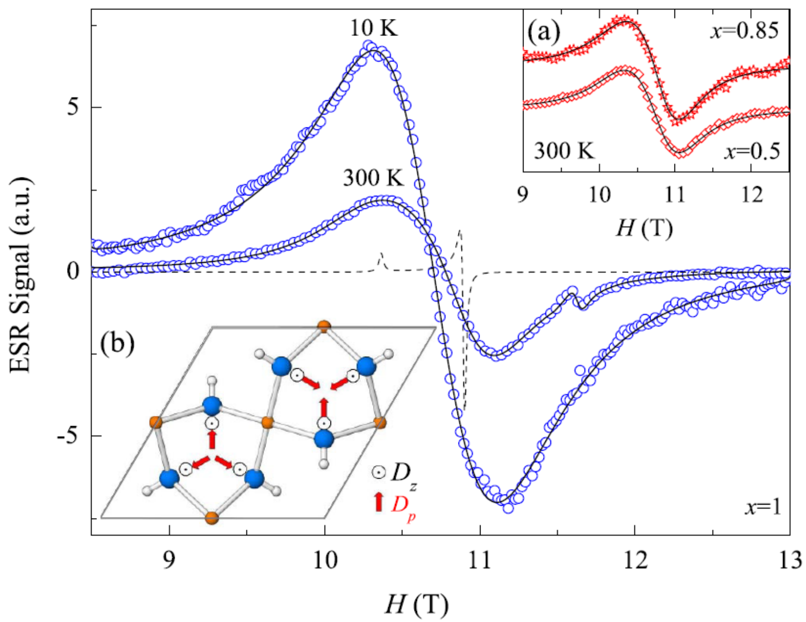
$$C_v \sim e^{-\Delta/T} \; ; \; \chi \sim e^{-\Delta'/T}$$

Need to restore
ground state susceptibility
and some criticality…

Dzyaloshinskii-Moriya interactions



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



Broad room T ESR line <- magnetic anisotropy from DM

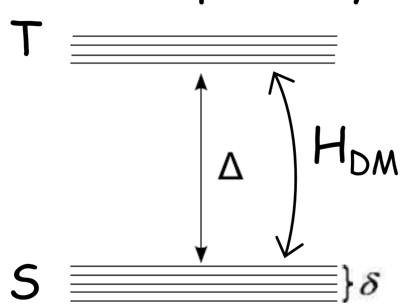
$|D_z|=0.08J, |D_p|\sim 0.01J$

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

$0.045J < |Dz| < 0.08J$

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

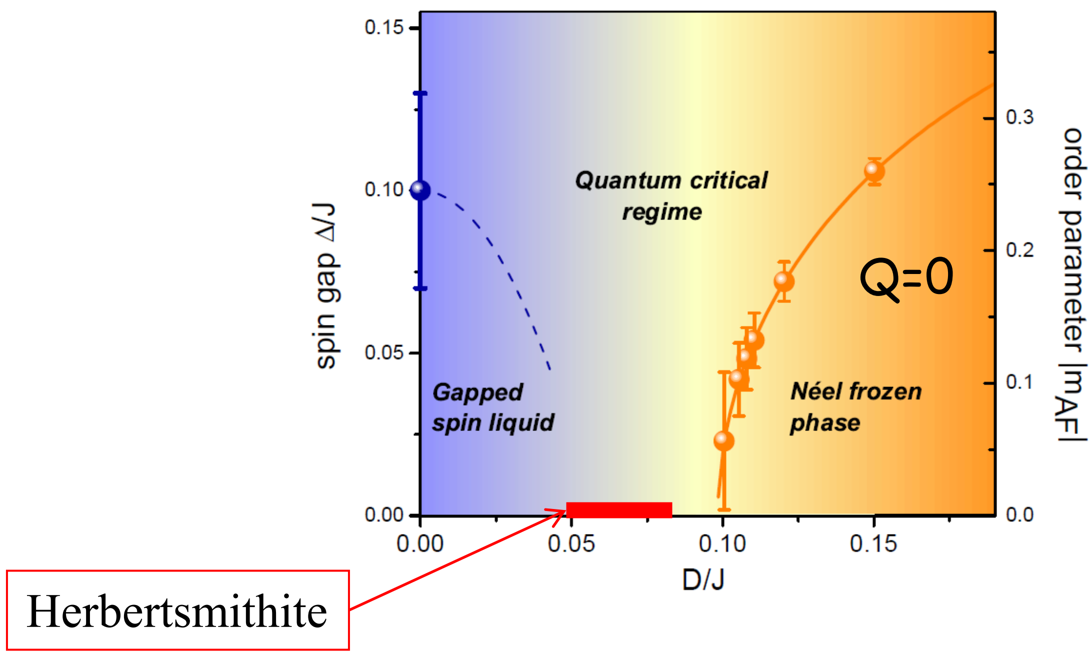
- DM interaction mixes singlet and triplet and could restore a susceptibility at T=0



Miyahara et al. PRB **75**, 184407 (2007)
Tovar et al, PRB **79**, 024405 (2009)

quantum criticality sustained by DM

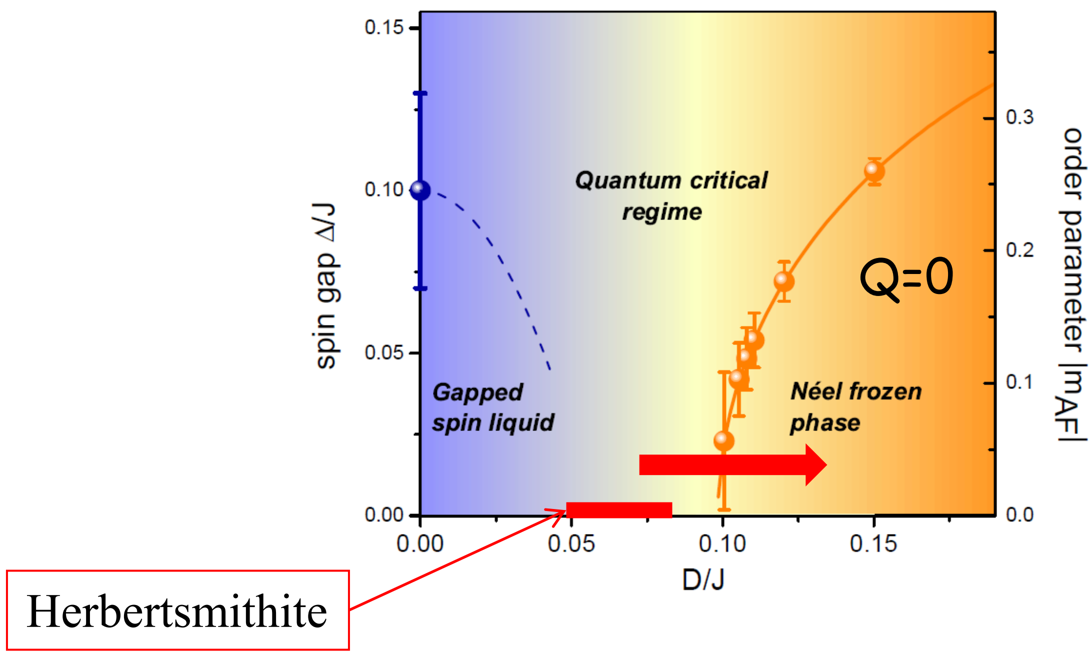
O. Cepas et al, PRB **78**, 140405 (R) (2008)
Y. Huh et al, PRB **81**, 144432 (2010)
L. Messio et al, PRB **81** , 064428 (2010)



- H=0 Spin liquid (some kind), finite T=0 susceptibility and hints of criticality (T_1, INS) due to proximity of QCP

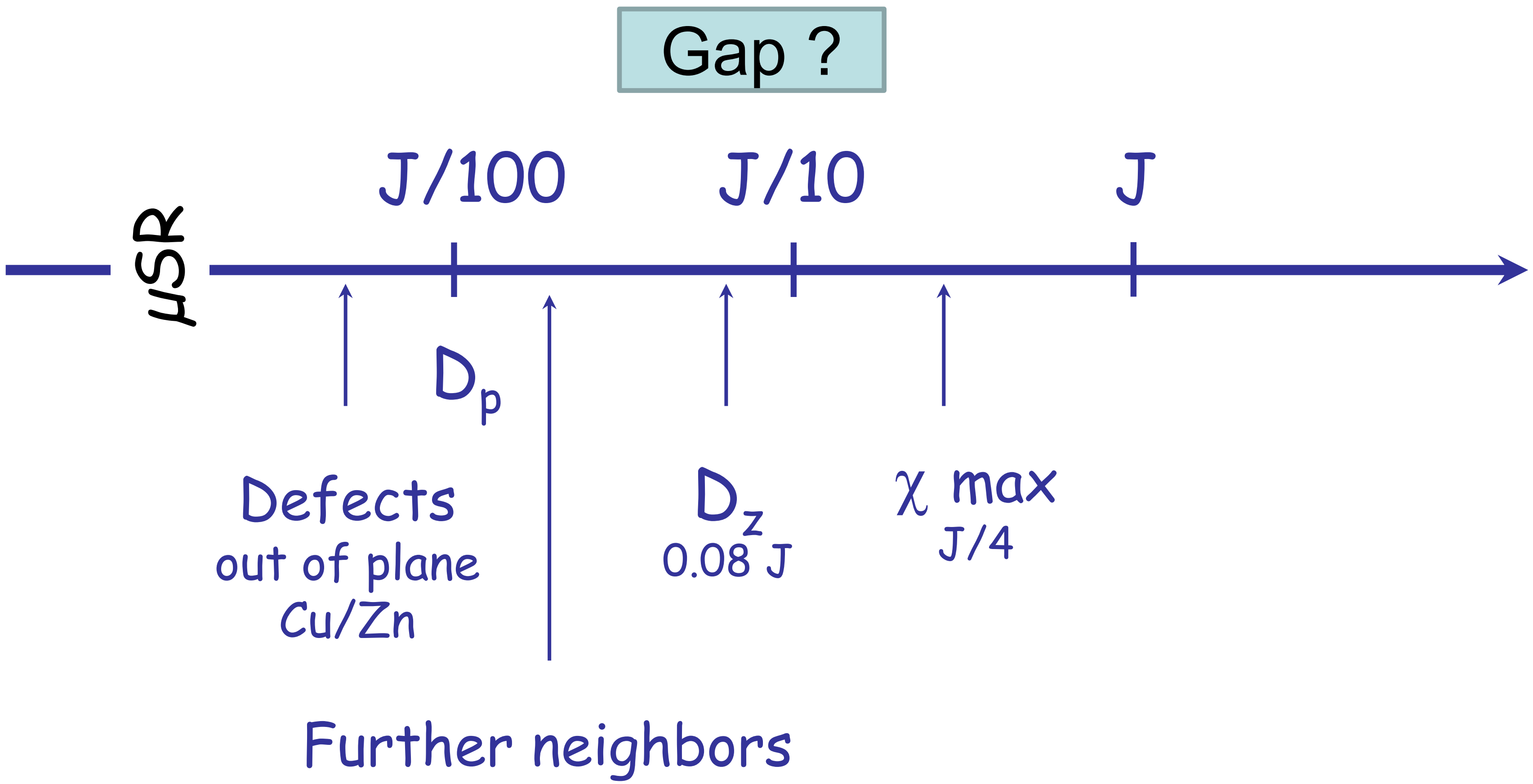
quantum criticality sustained by DM

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)



- H=0 Spin liquid (some kind), finite T=0 susceptibility and hints of criticality (T_1, INS) due to proximity of QCP
- H<>0 Field induced transition for $H_c \sim D_c - D_{herb}$

Energy scales (J = 180 K)



Conclusion (1)

The spin liquid state is quite elusive experimentally

-> « perturb to reveal » strategy

- Magnetic Field and/or DM

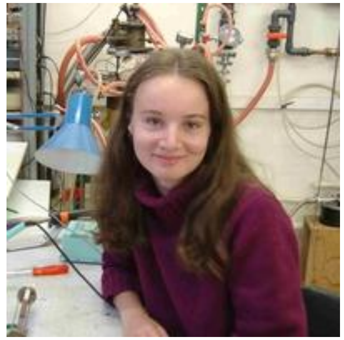
- Pressure
  D. P. Kozlenko et al, Phys. Rev. Lett. 108, 187207 (2012)

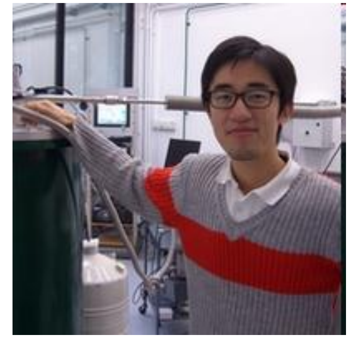
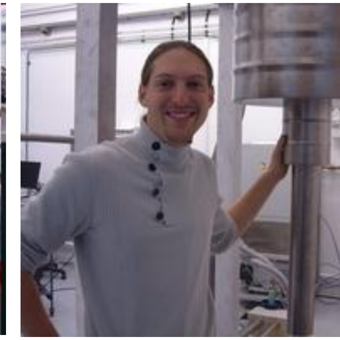
- Response to (non magnetic) defects
  Olariu et al, PRL 100, 087202 (2008)
  I. Rousochatzakis et al, PRB 79, 214415 (2009)

Collaborations

@ LPS

F. Bert, A. Olariu (phD), A. Zorko (post doc), M. Jeong (post doc), E. Kermarrec (phD)

Samples

- J. C. Trombe, F. Duc, *CEMES, Toulouse, France*
-M. de Vries, G. Nilsen, A. Harrison, *Edinburgh, UK*
-P. Strobel, Institut Néél, *Grenoble, France*
-R. Colman, A. Wills
-M. Velazquez, ICMCB Bordeaux

Low T/ High field magnetization

S. Nakamae, F. Ladieu, D. L'Hote, P. Bonville, CEA *Saclay, France*

μSR

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

High field NMR

M. Horvatic, S. Kraemer, LNCMI Grenoble

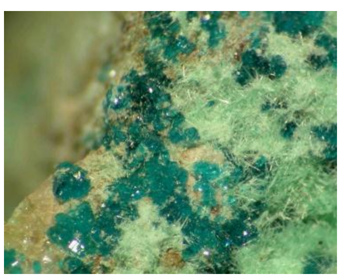
Materials are mostly existing minerals all made of Cu^{2+} S=1/2

Herbertsmithite

MP Shores et al, JACS, 2005

Volborthite

Z. Hiroi et al, JPSJ 2001



Haydeeite

R. Colman et al, Chem. Mater. 2010

Kapellasite

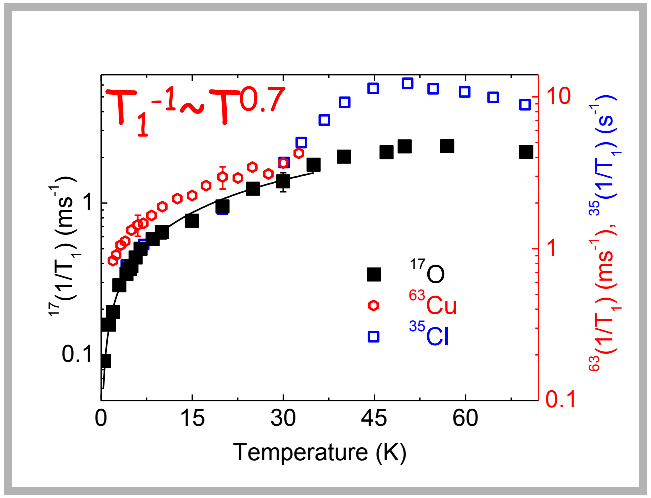
R. Colman et al, Chem. Mater. 2008

Vesignieite

Y. Okamoto et al, JPSJ 2009

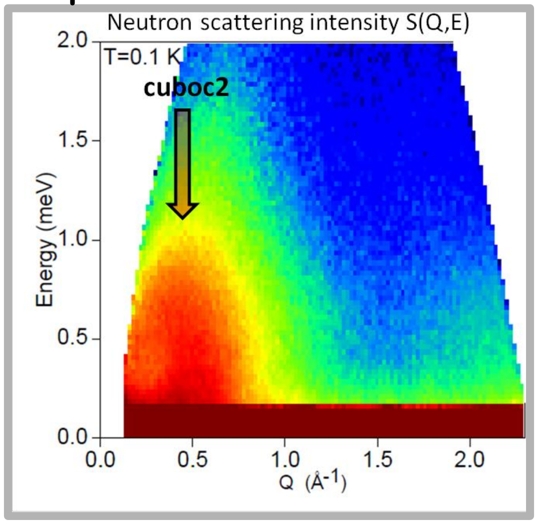
Gapped or gapless spin liquids…

Herbertsmithite



Olariu et al, PRL 100, 087202 (2008)
Imai, PRL 100, 077208 (2008)

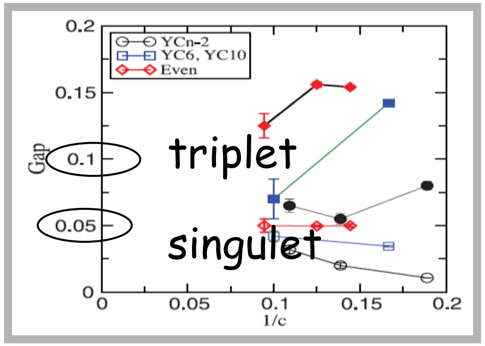
kapellasite



B. Fak et al, PRL 109, 037208 (2012)

DMRG : gapped excitation spectrum

S. Yan et al, Science **332** (2011)
S. Depenbrock et al, PRL **109**, 067201 (2012) : Δ =0.13(1)J



Role of perturbations in real compounds?
Need for other and different examples…

Spin liquid state in the vanadium based kagome compound $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$

L. Clark, J.-C. Orain, F. Bert et al, PRL 110, 207208 (2013)

nature chemistry
ARTICLES
PUBLISHED ONLINE: 28 AUGUST 2011 | DOI: 10.1038/NCHEM.1129

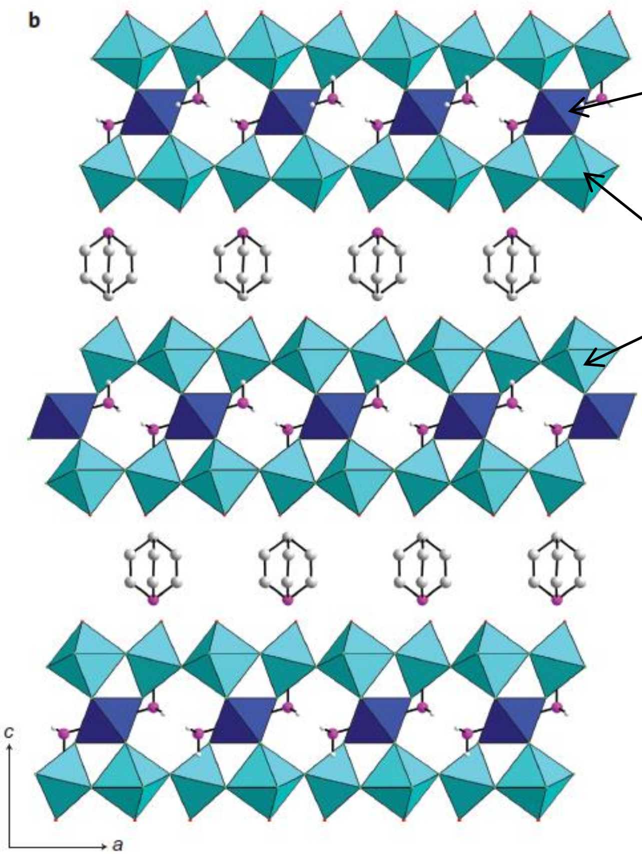
$[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$

= DQVOF

An ionothermally prepared $S = 1/2$ vanadium oxyfluoride kagome lattice

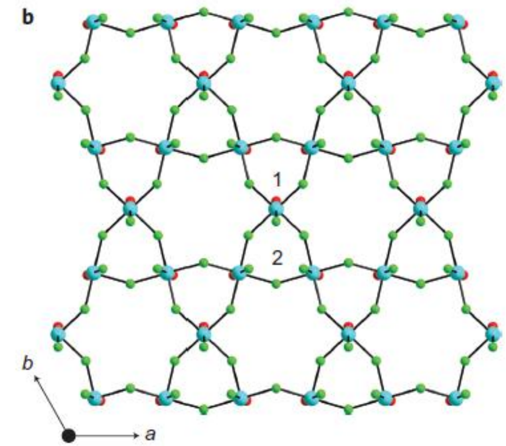
Farida H. Aidoudi[1], David W. Aldous[1], Richard J. Goff[1], Alexandra M. Z. Slawin[1], J. Paul Attfield[2], Russell E. Morris[1] and Philip Lightfoot[1]*

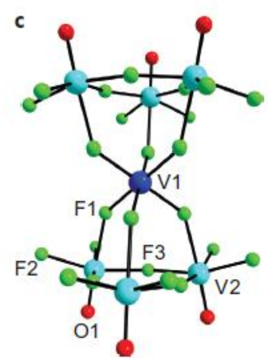
θ_{AF}~60 K



V^{3+} $(3d^2)$ S=1

V^{4+} $(3d^1)$ S=1/2





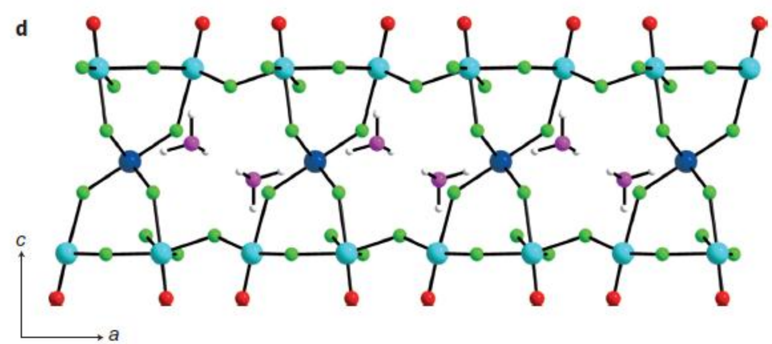
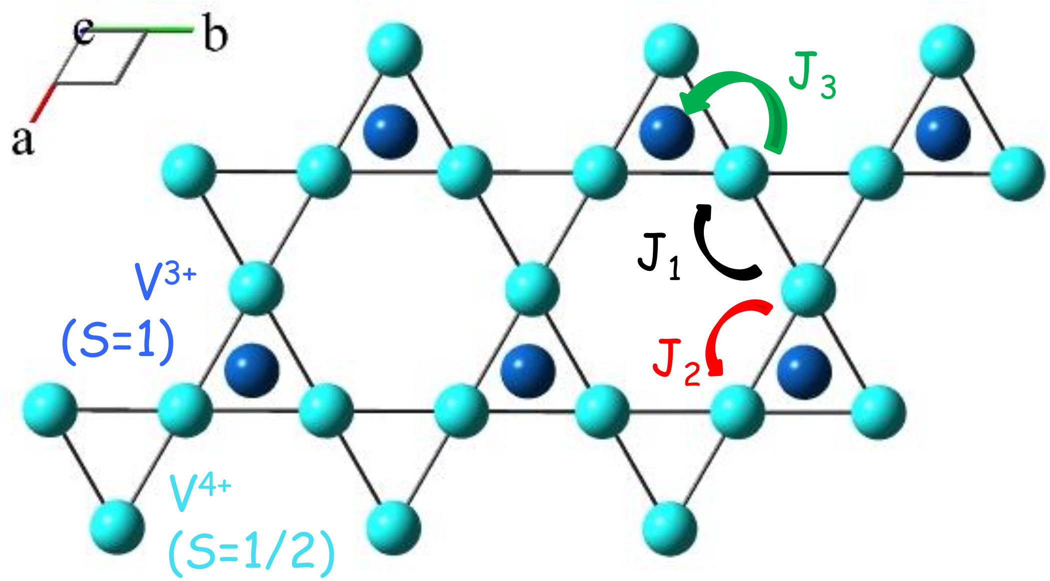
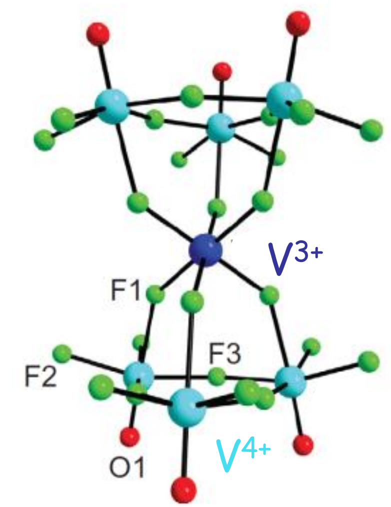


Figure 2 | Polyhedra views of the structure of $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$.

Magnetic model for DQVOF

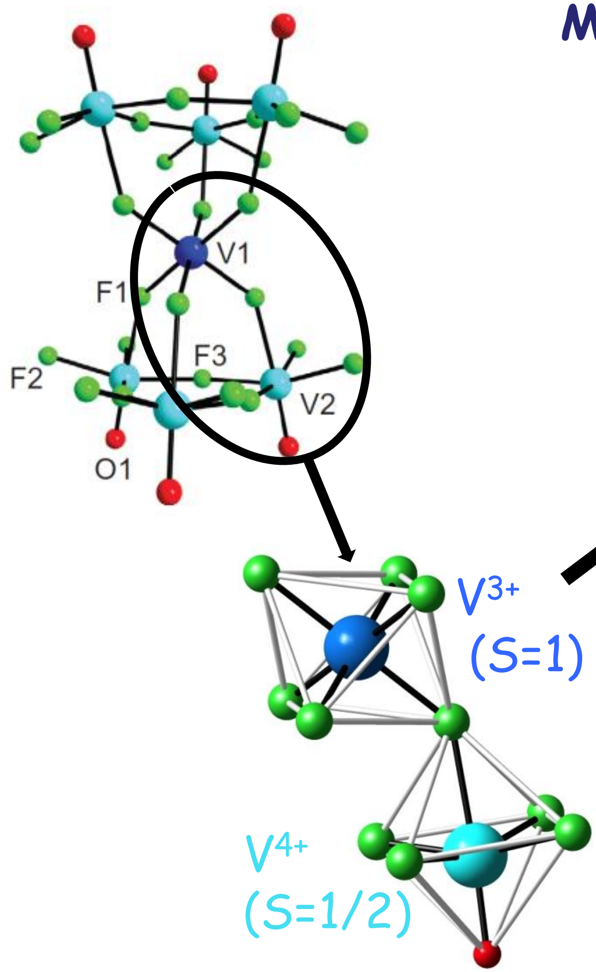


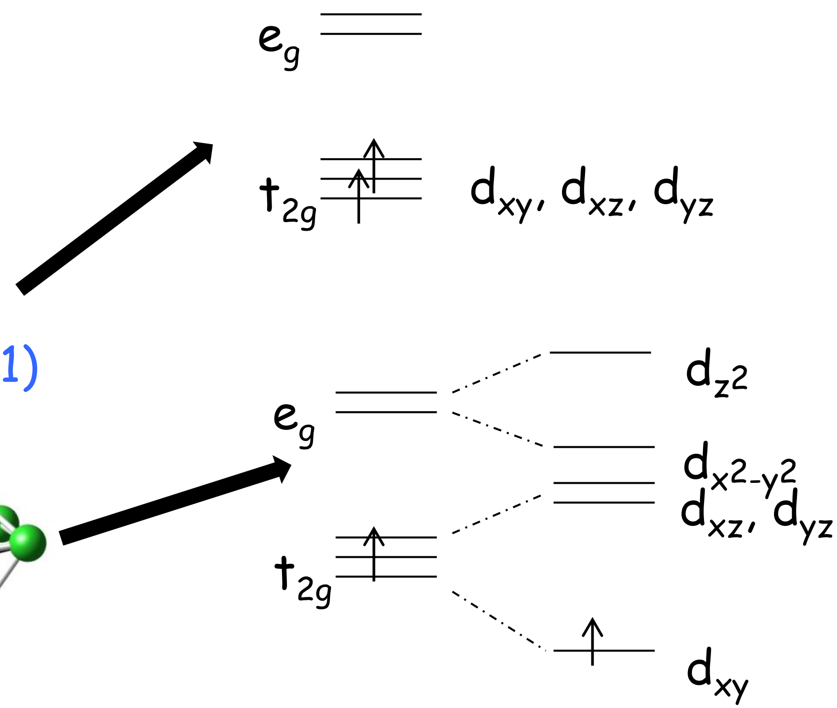


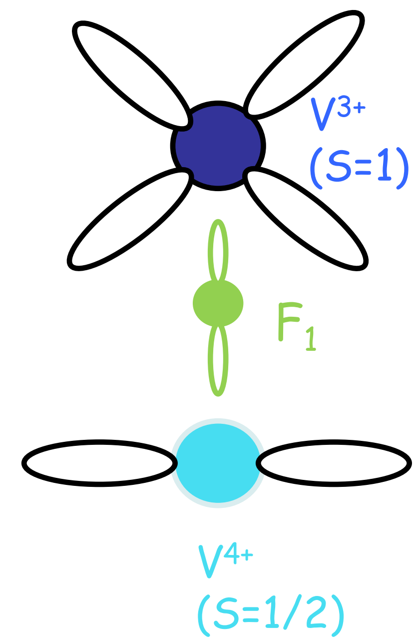
Role of spins S=1 ?

Relevance of the quantum kagome antiferromagnet model ?

Magnetic model for DQVOF





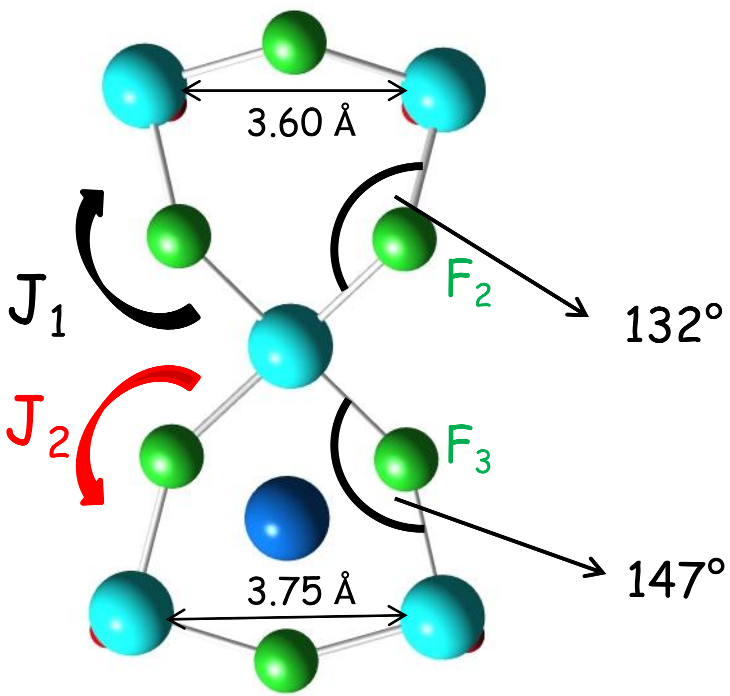


No hybridation:

J_3~0 ->interplane V^{3+} are decoupled from kagome planes

-> kagome planes are decoupled from each others

Magnetic model for DQVOF

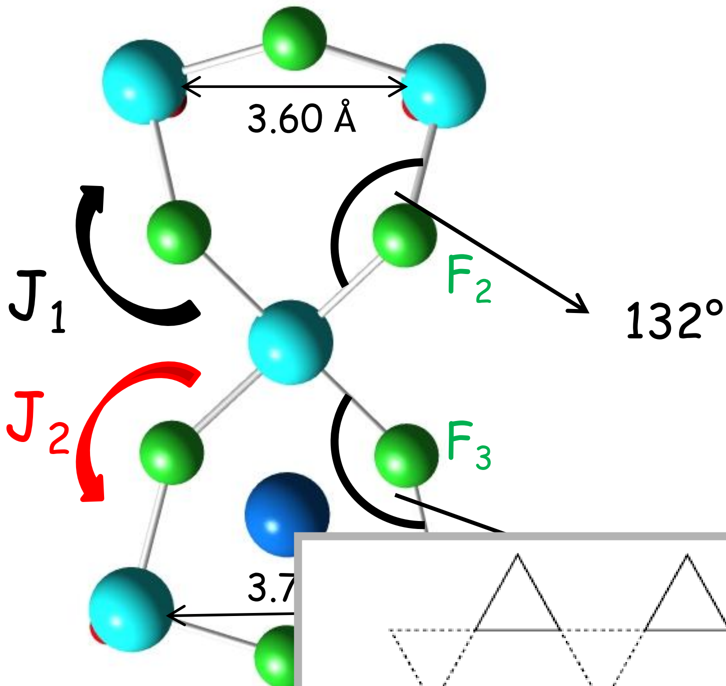


- Curie Weiss $\theta=(J_1+J_2)/2\sim60$ K
- $J\sim \cos^2\theta$ -> $J_1/J_2=0.64$

$J_1\sim47$ K $J_2\sim73$ K

DFT (O. Janson et al S10107) :
$J_1/J_2=0.75$

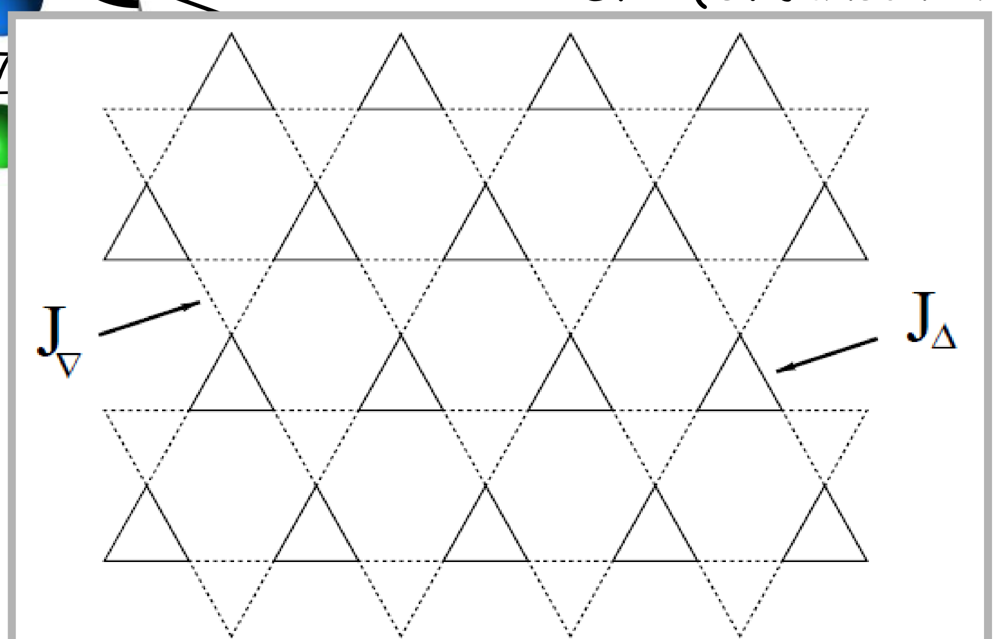
Magnetic model for DQVOF



- Curie Weiss $\theta=(J_1+J_2)/2 \sim 60$ K
- $J \sim \cos^2 \theta$ -> $J_1/J_2=0.64$

$J_1 \sim 47$ K
$J_2 \sim 73$ K

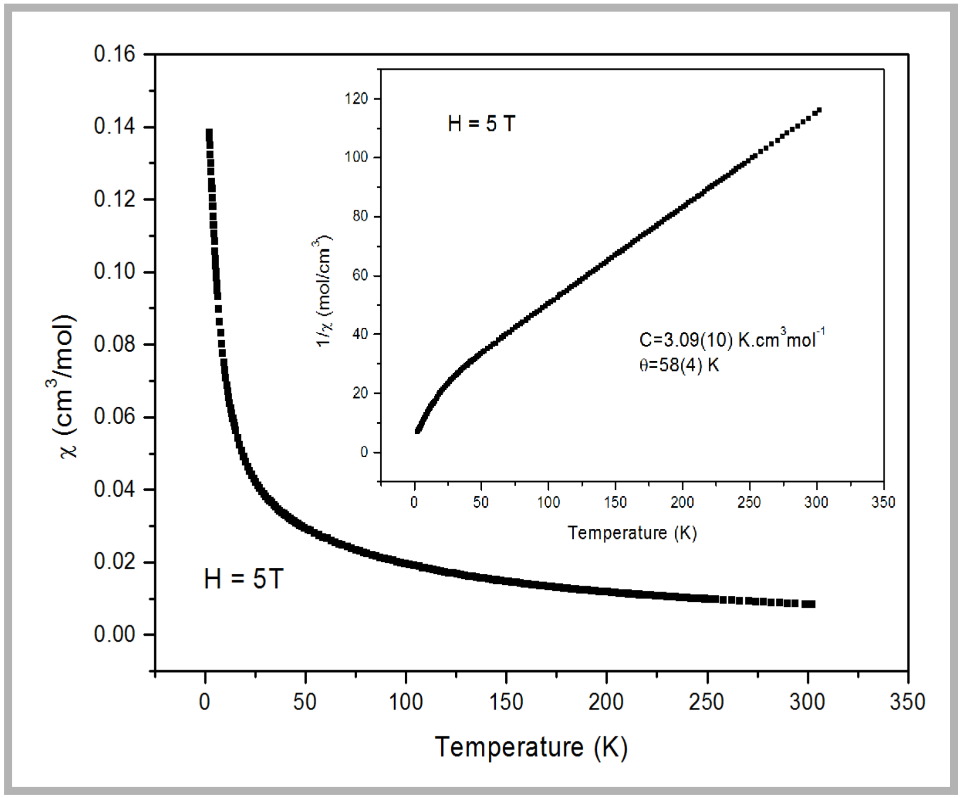
DFT (O. Janson et al S10107) :



« Trimerized kagome lattice »

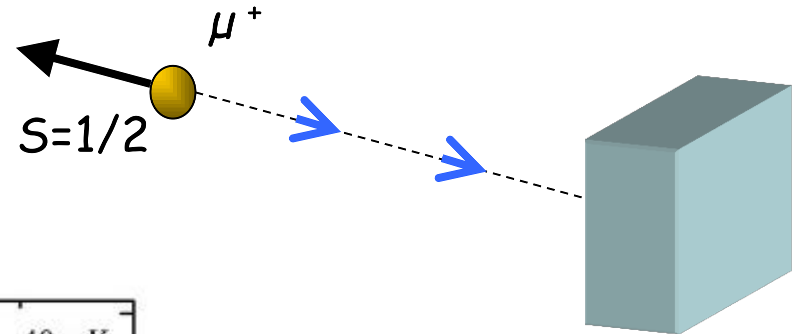
F. Mila 98,
M. Mambrini et al 00
M. Zhitomirsky 05

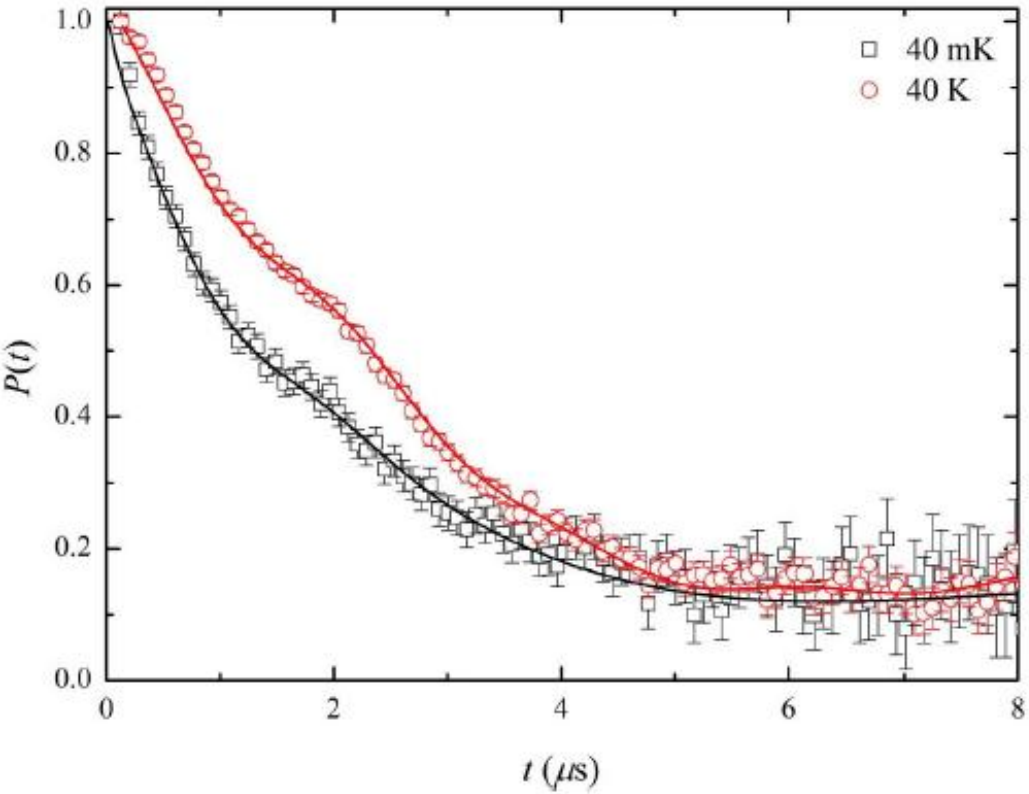
Susceptibility

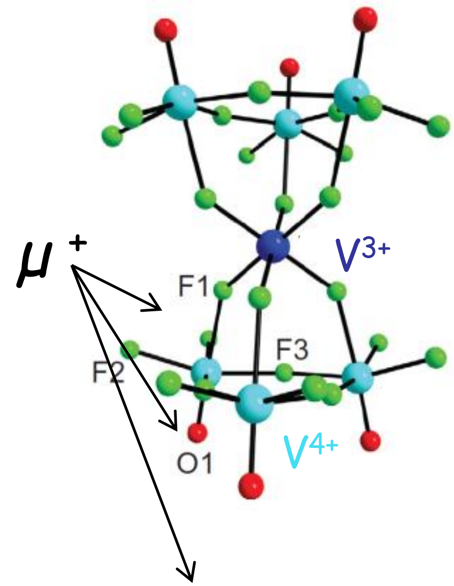


AF interactions, no sign of transition down to 2K -> frustration
Large curie tail C/T at low T <- nearly free S=1 (V^{3+})

Muon spin relaxation (μSR)





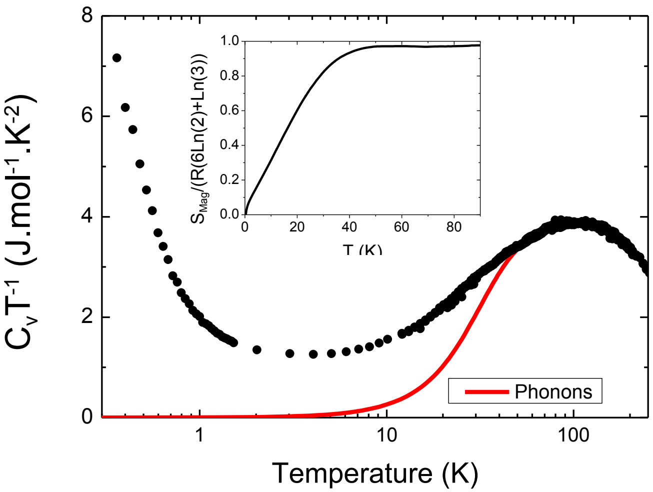


DQ $([NH_4]_2[C_7H_{14}N])$

No fast relaxation, no '1/3rd tail' at low T

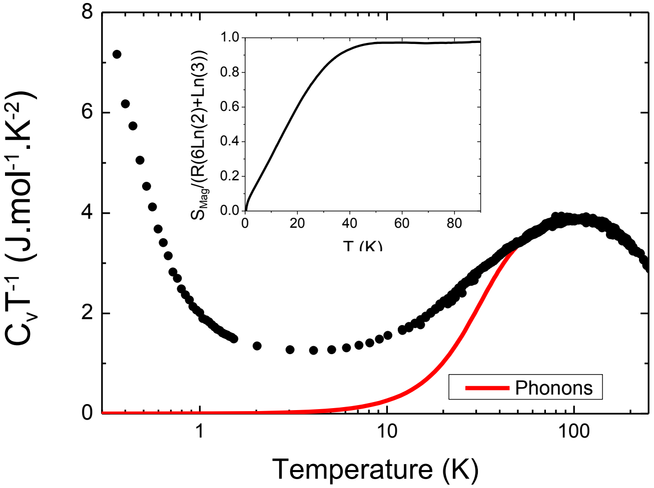
-> no spin freezing down to 40mK

Heat capacity

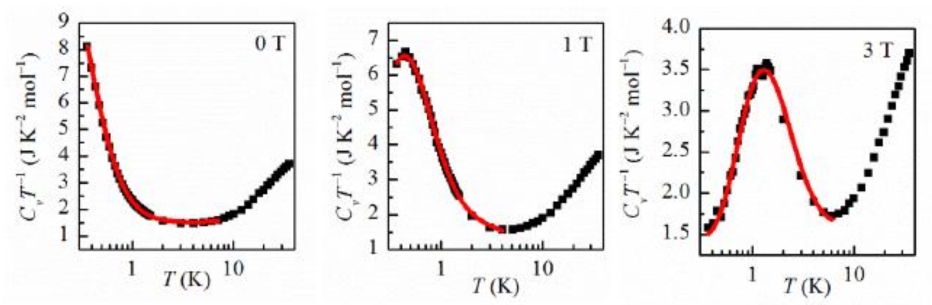


Phonons

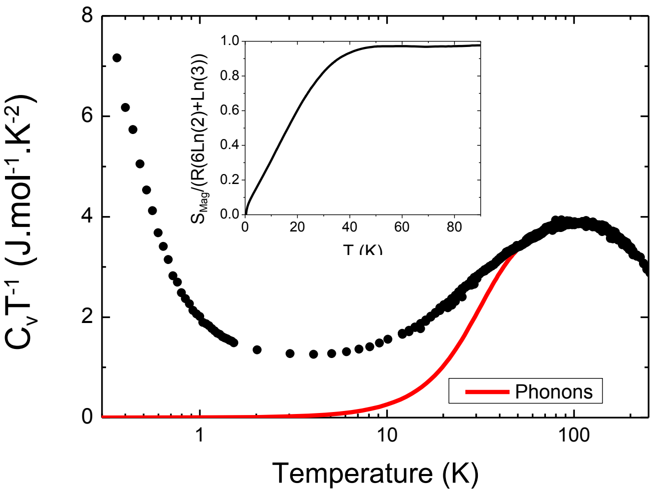
Heat capacity



Phonons
+
V^{3+} (S=1) Schottky



Heat capacity



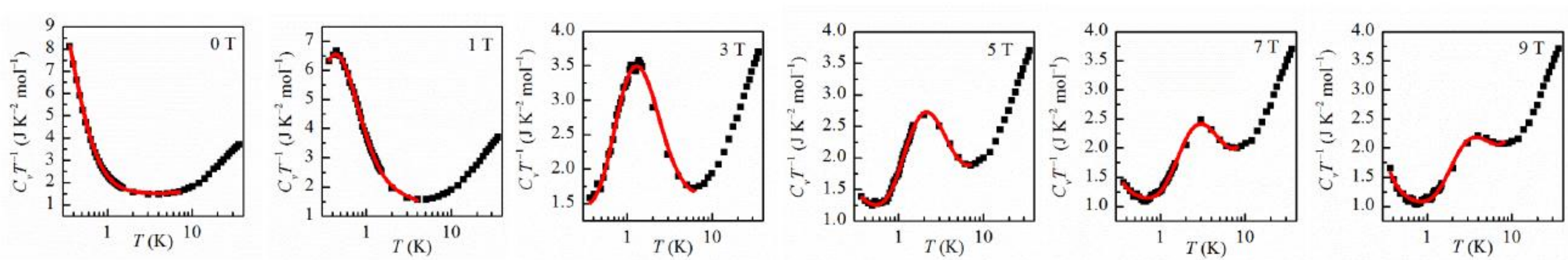
Phonons

+

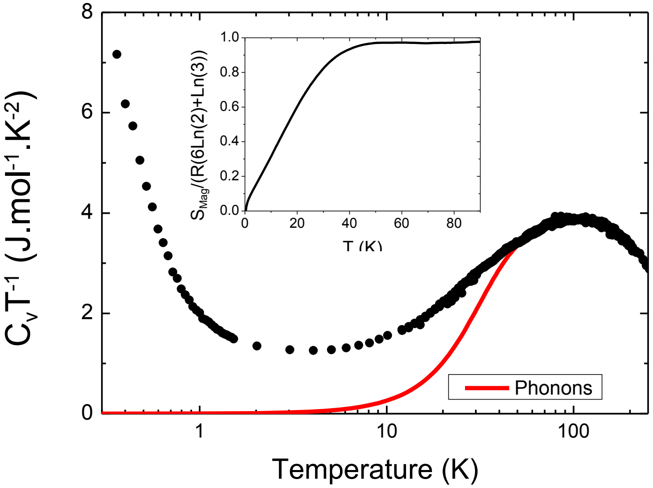
V^{3+} (S=1) Schottky

+

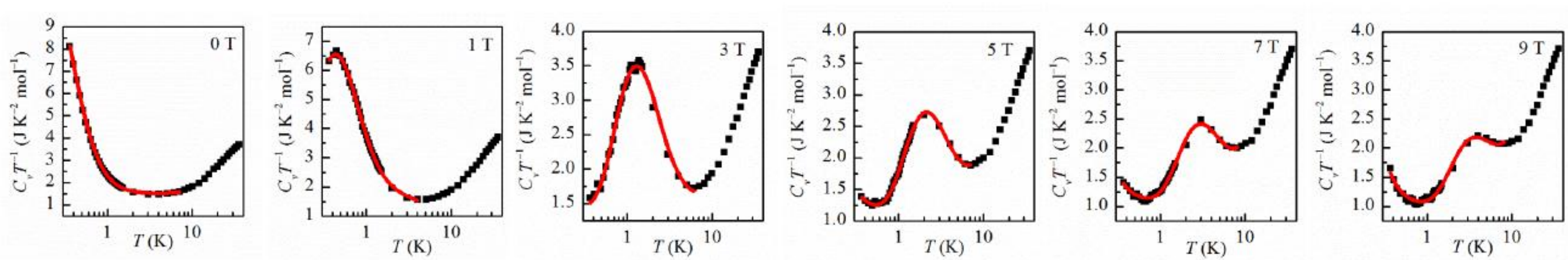
H/F nuclear Schottky



Heat capacity



Phonons
\+
V^{3+} (S=1) Schottky
\+
H/F nuclear Schottky
\+
kagome ?



Heat capacity

Phonons

+

V^{3+} (S=1) Schottky

+

H/F nuclear Schottky

+

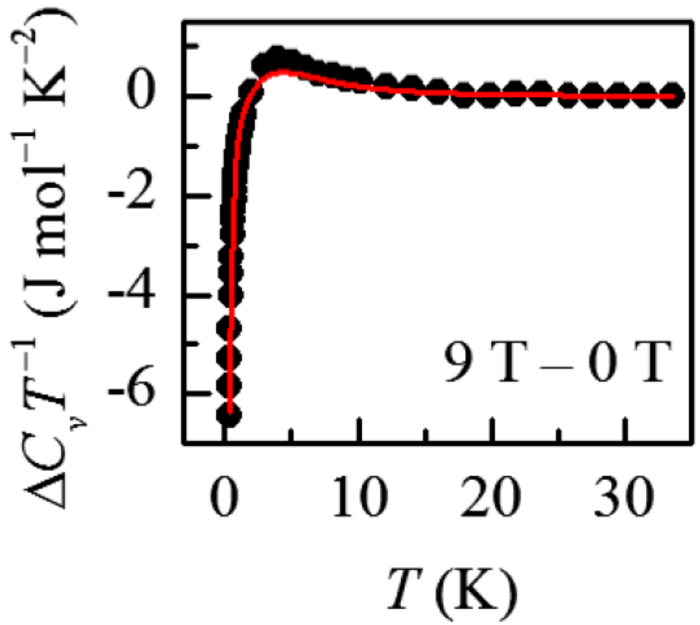
kagome ?

Heat capacity

	Field dependence
Phonons	✗
+	
V^{3+} (S=1) Schottky	✓
+	
H/F nuclear Schottky	✓
+	
kagome ?	✗

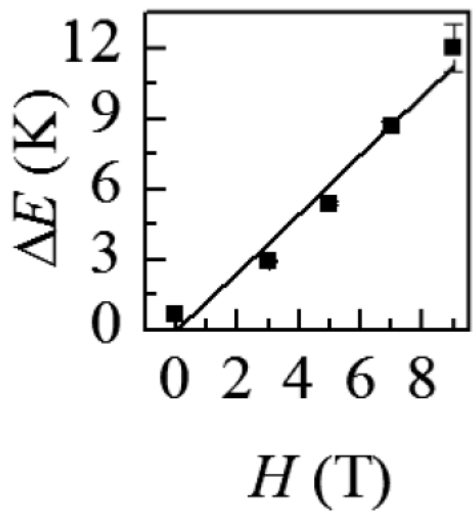
Heat capacity

	Field dependence
Phonons	✗
+ V^{3+} (S=1) Schottky	✓
+ H/F nuclear Schottky	✓
+ **kagome ?**	✗

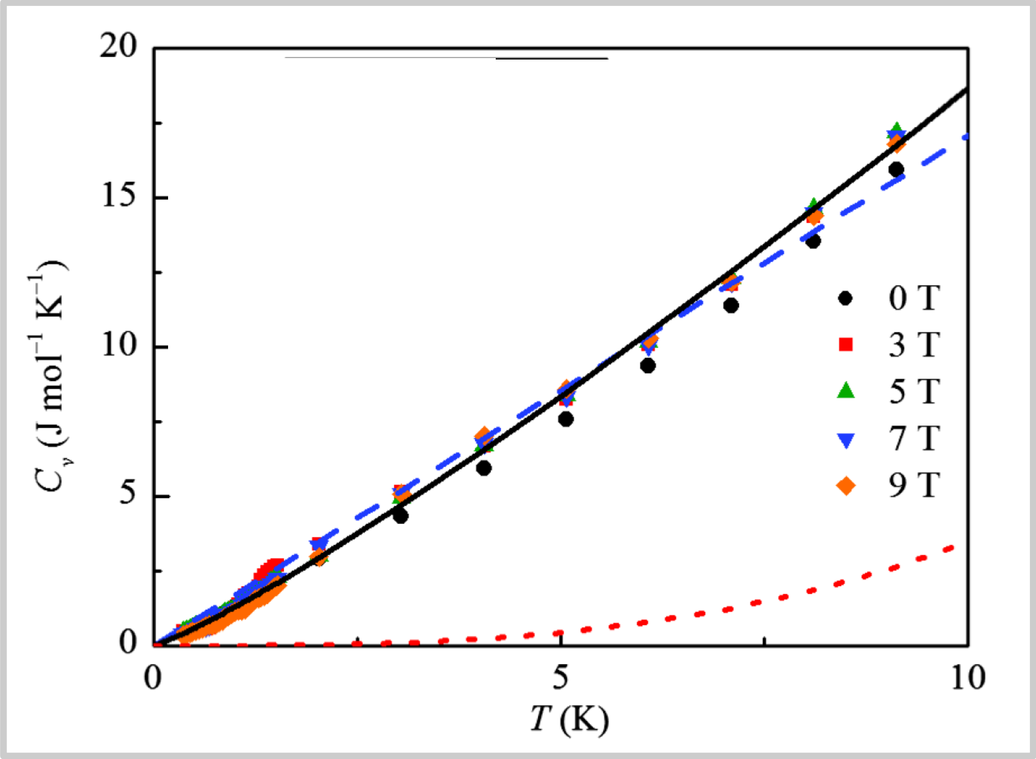


$\Delta E = g\mu_B S$

-> g=1.8 (V^{3+})



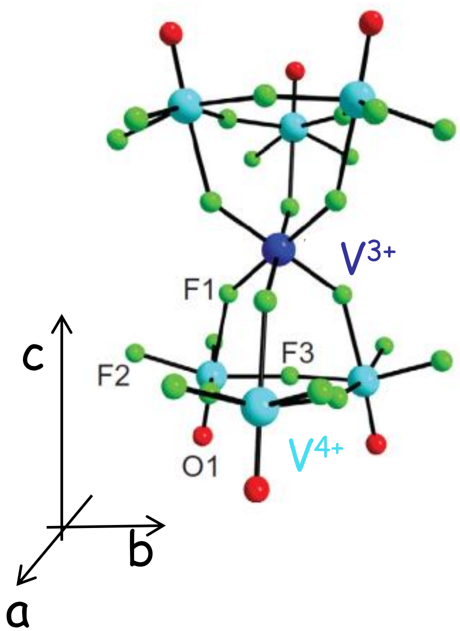
Heat capacity



The full excitation spectrum is not gapped (Δ<0.3K~J/200)

- Gapless fermionic spinon excitations, γ=0.2 J /K^2/mol V^{4+}
- Gapless continuum of non-magnetic excitations?

F NMR



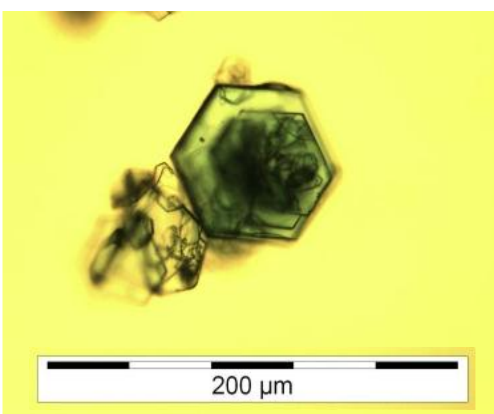
Fluorine nuclear magnetic resonance (I=1/2)

-> F participate in superexchange
-> good local probe of magnetism

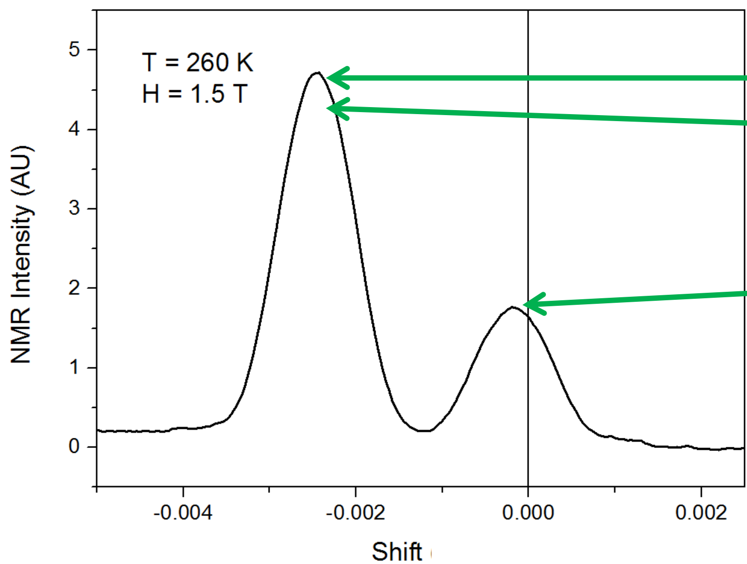
Sample : powder
(powder distribution-> broad spectra)

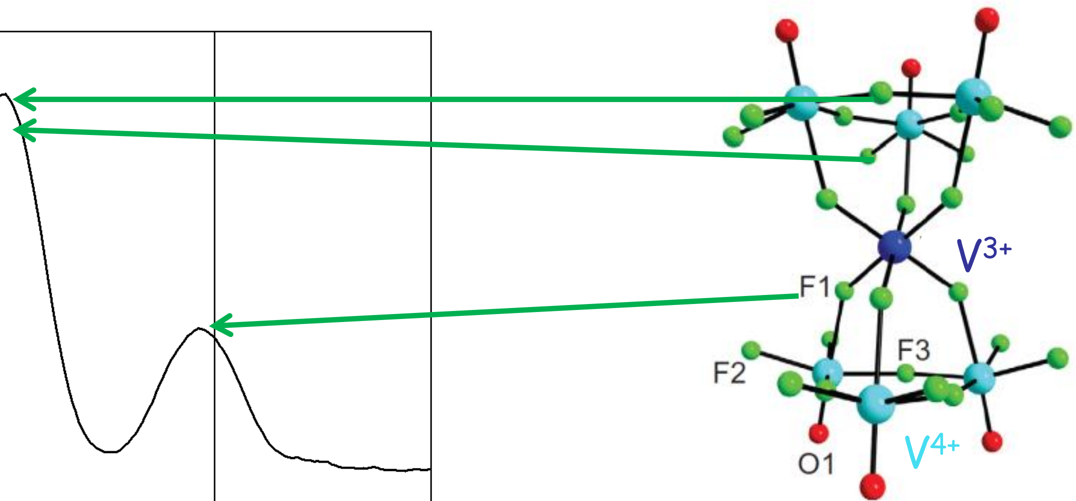
100% oriented powder

c//B
a,b random

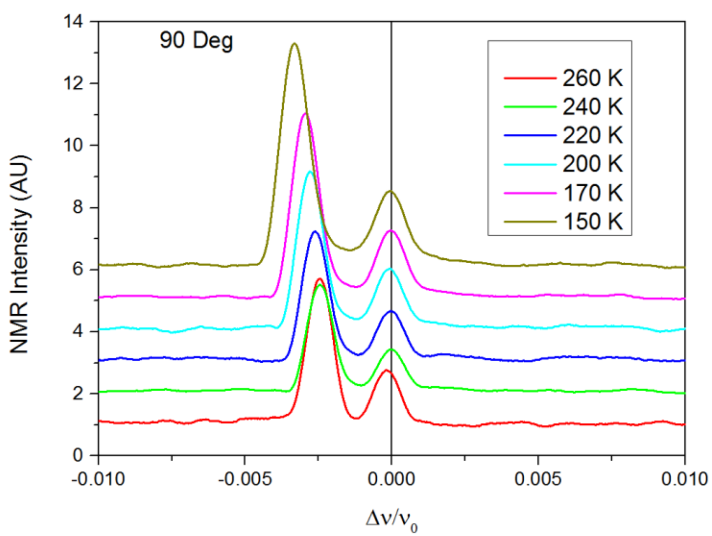


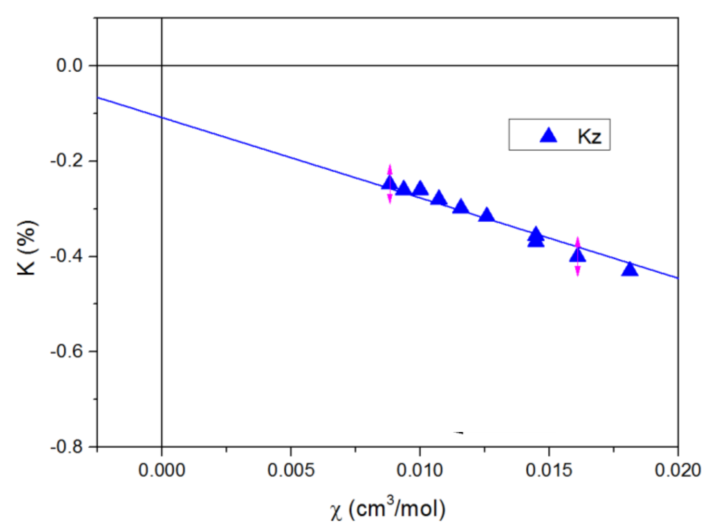
F NMR – local susceptibility



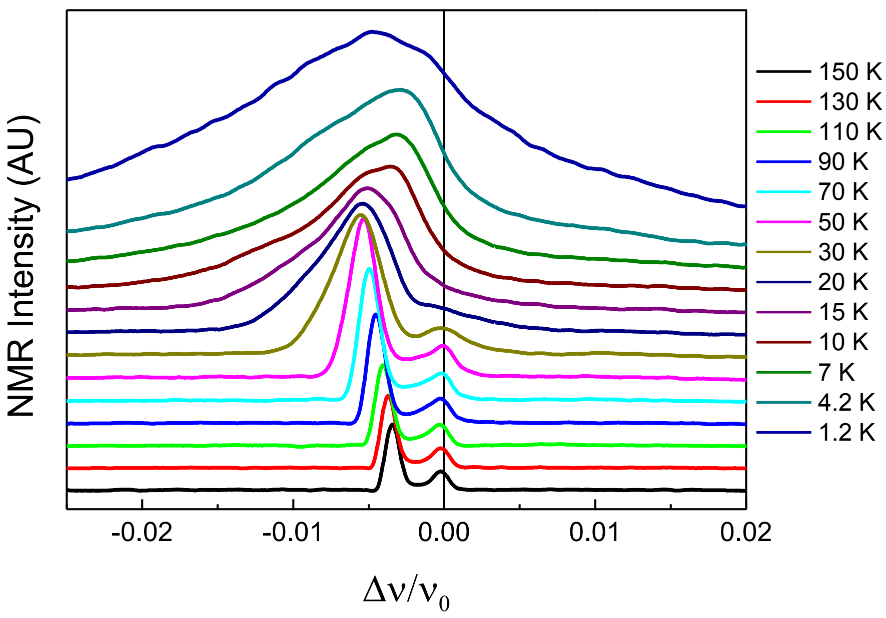


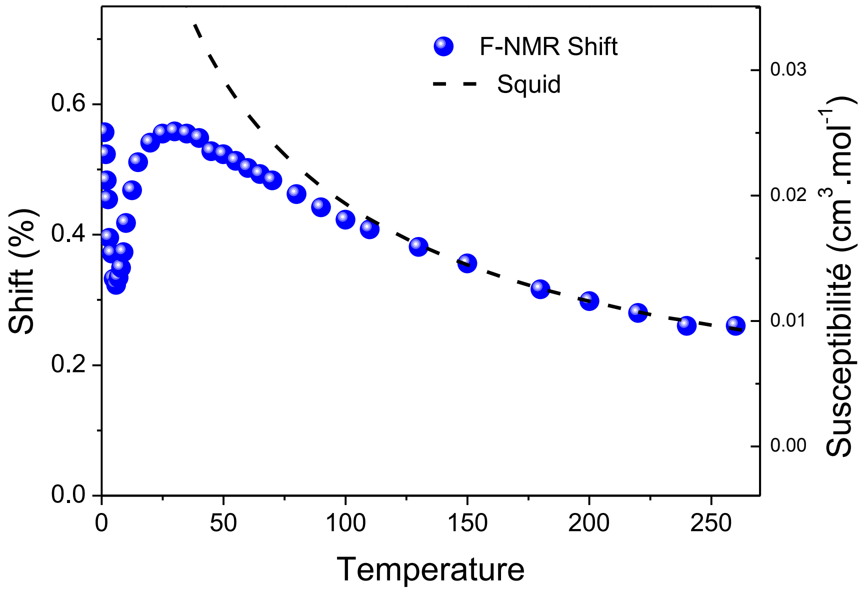
Oriented samples H//c





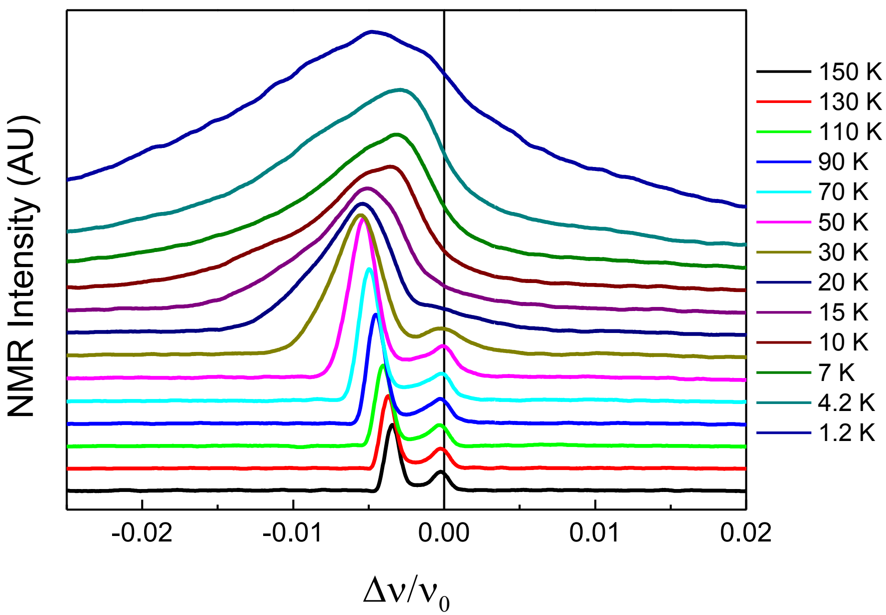
F NMR – local susceptibility

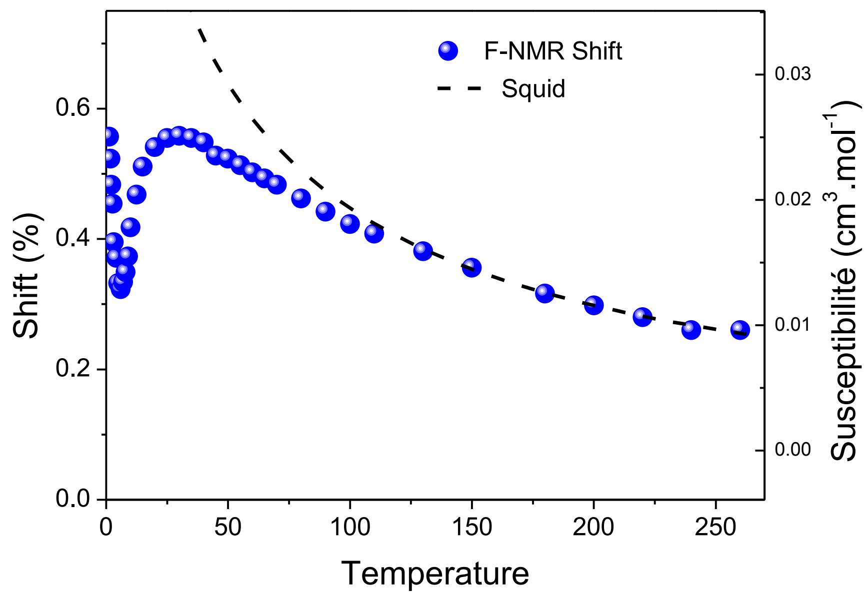




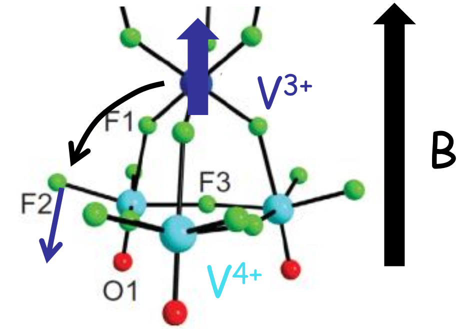
- F-NMR probes the local kagome susceptibility $\neq \chi_{SQUID}$
- Enhancement of short range AF correlations at T~J/2

F NMR – local susceptibility

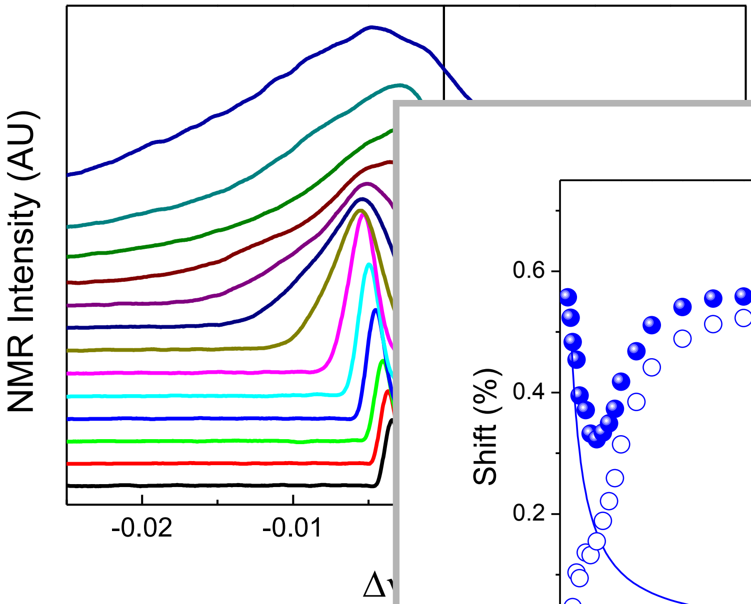


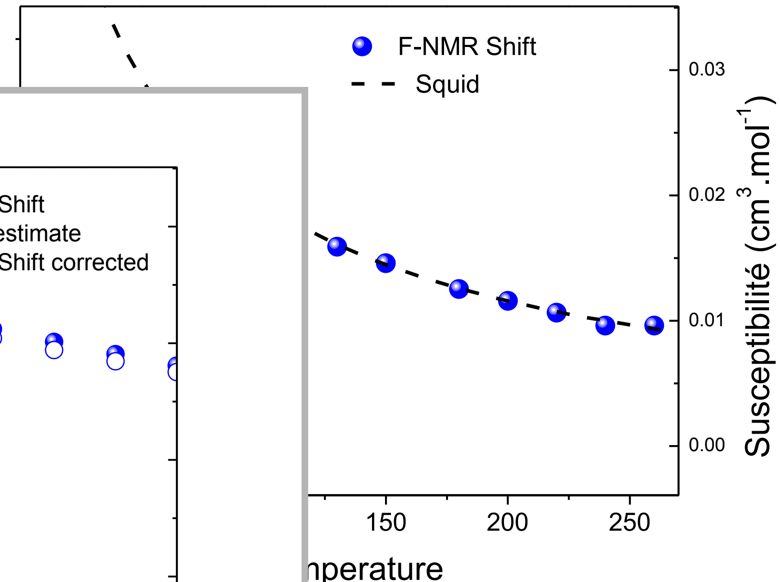


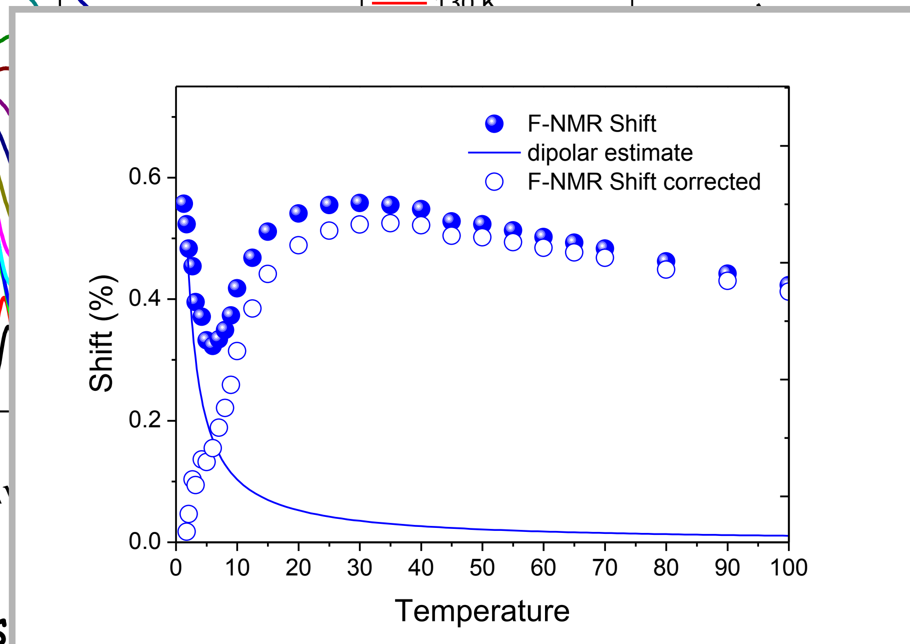
- F-NMR probes the local kagome susceptibility $\neq \chi_{SQUID}$
- Enhancement of short range AF correlations at T~J/2
- At low T, influence of V^{3+} dipolar field



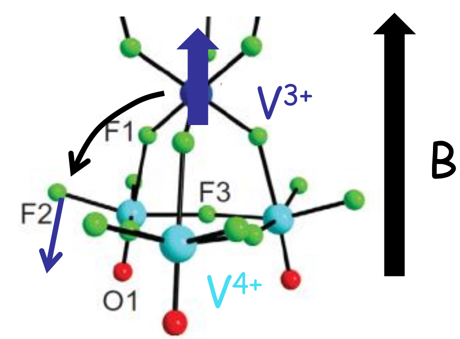
F NMR – local susceptibility



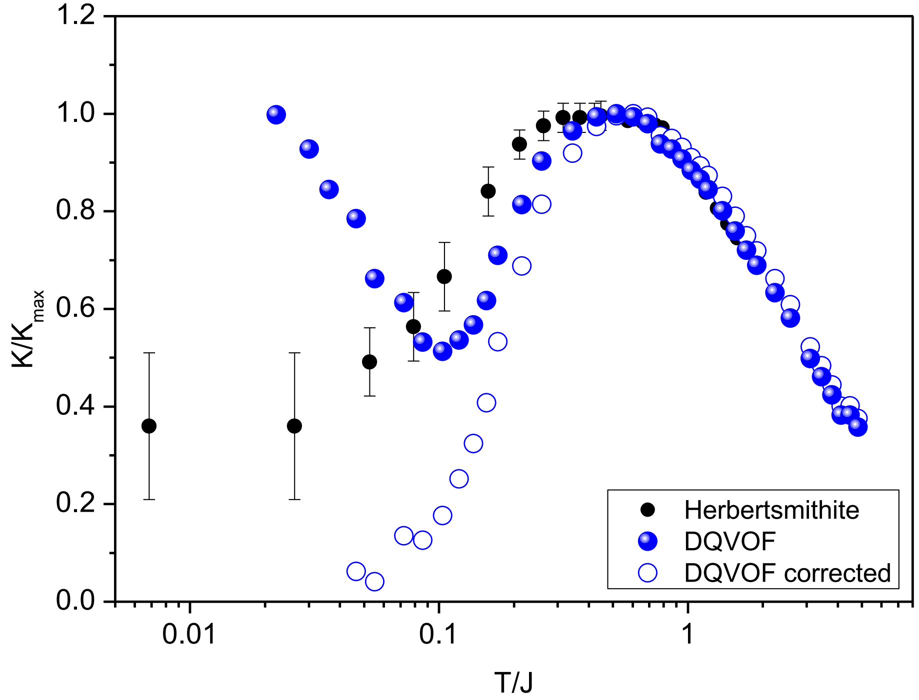




- F-NMR probes
- Enhancement of short range AF correlations at T~J/2
- At low T, influence of V^{3+} dipolar field
- At T->0, local susceptibility is very small if not 0

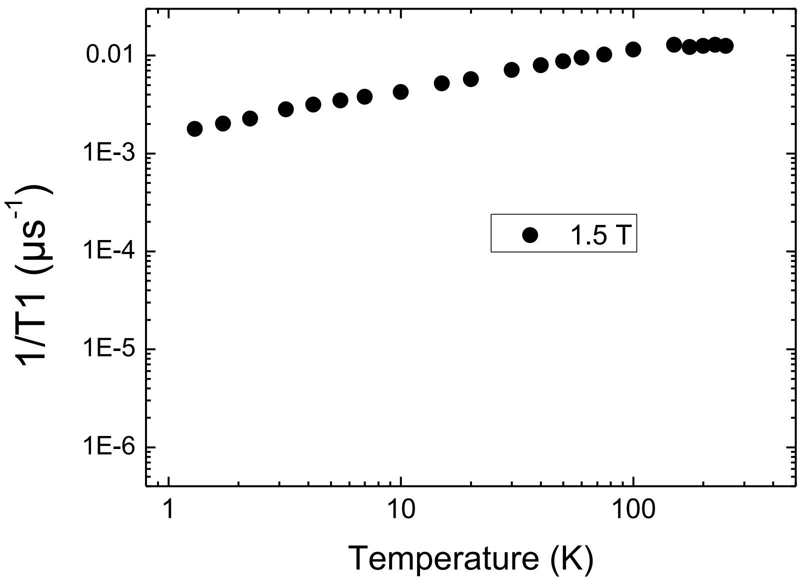


F NMR – local susceptibility

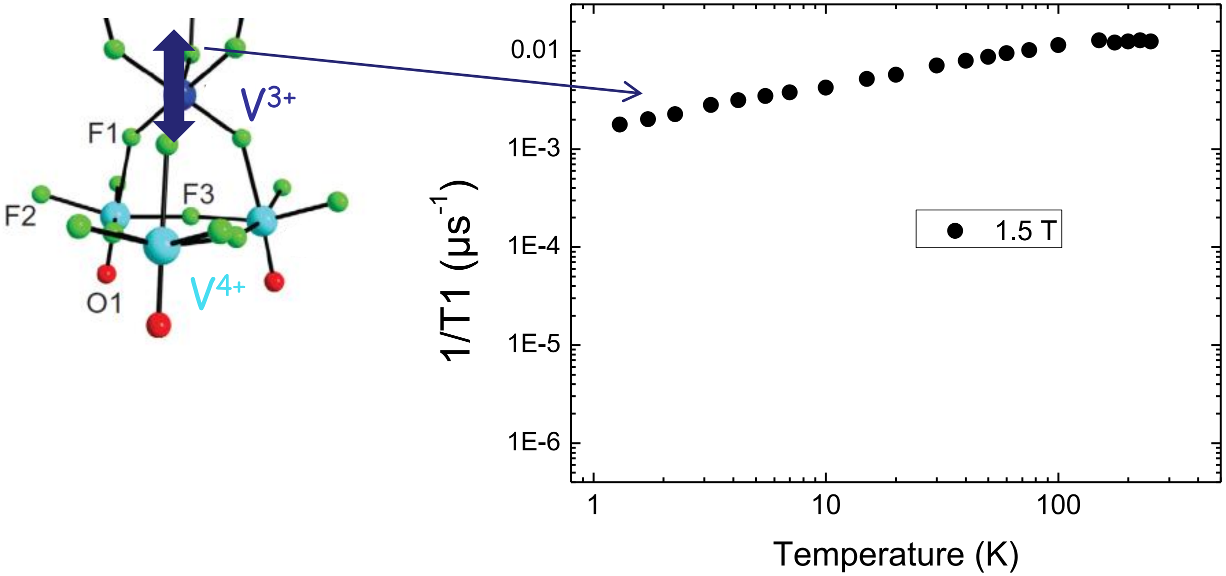


- Faster drop of the susceptibility than in gapless Herbertsmithite

F NMR – spin dynamics

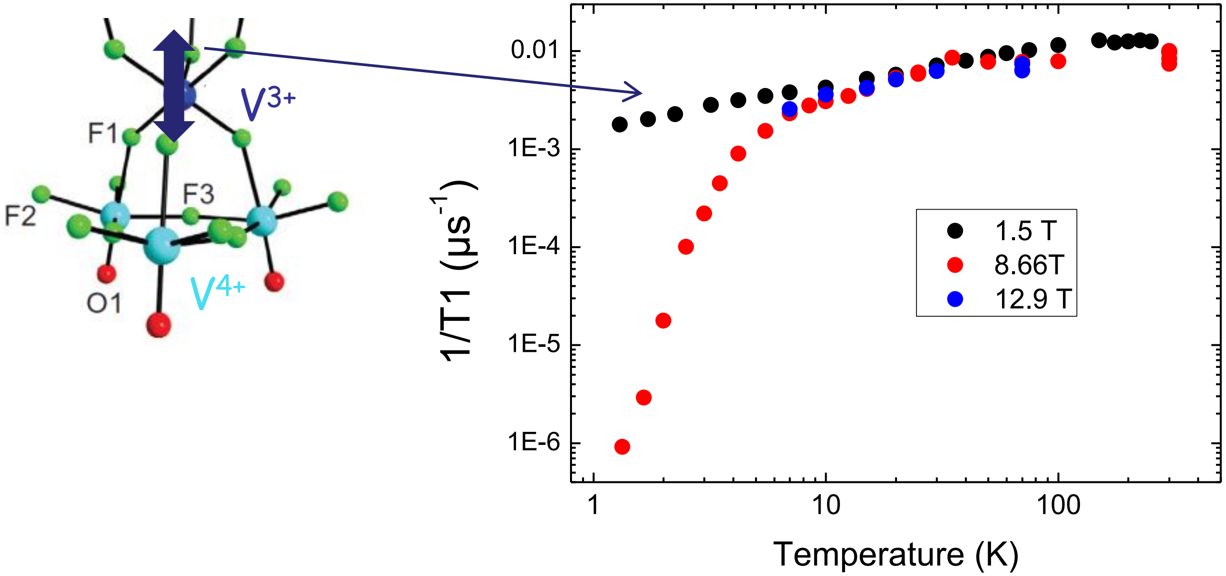


F NMR – spin dynamics



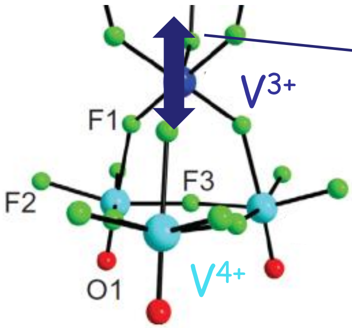
- At low field, low T, V^{3+} S=1 fluctuations dominate

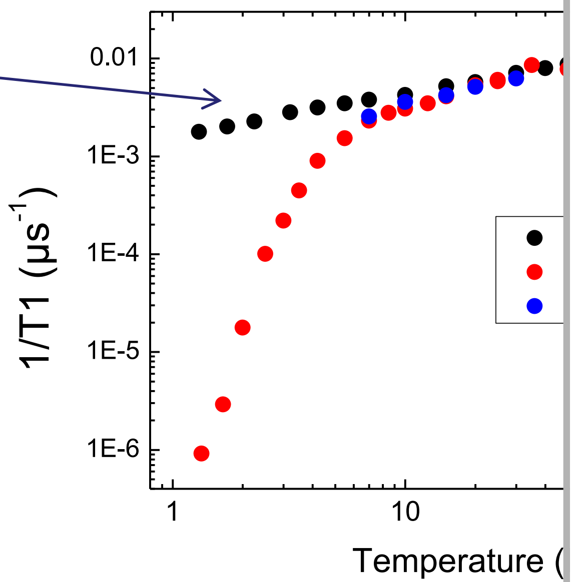
F NMR – spin dynamics



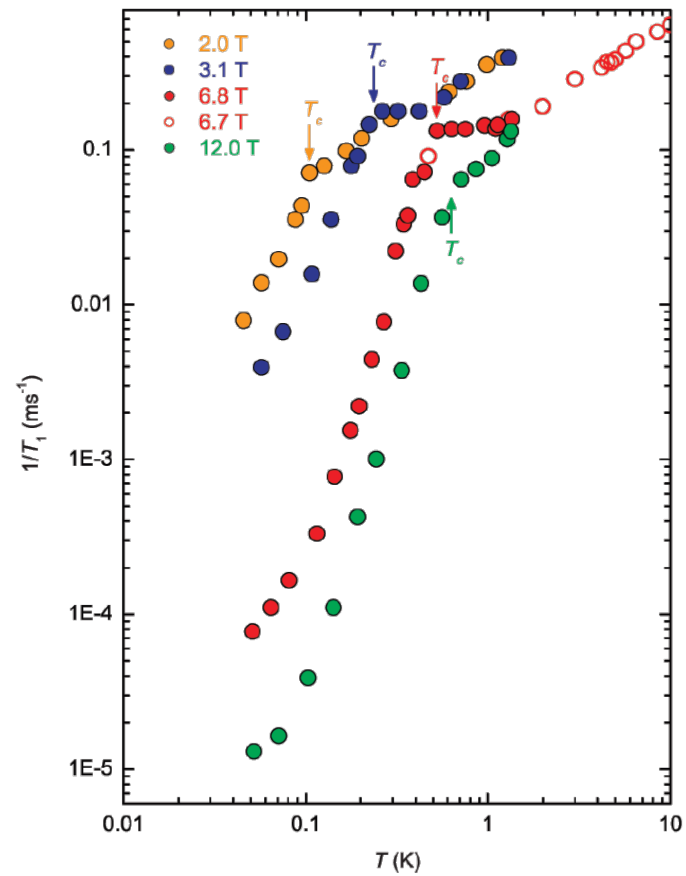
- At low field, low T, V^{3+} S=1 fluctuations dominate
- At large field, low T, fast drop of $1/T_1$
  - Saturation of S=1 spins (brillouin) : probably no

F NMR – spin dynamics



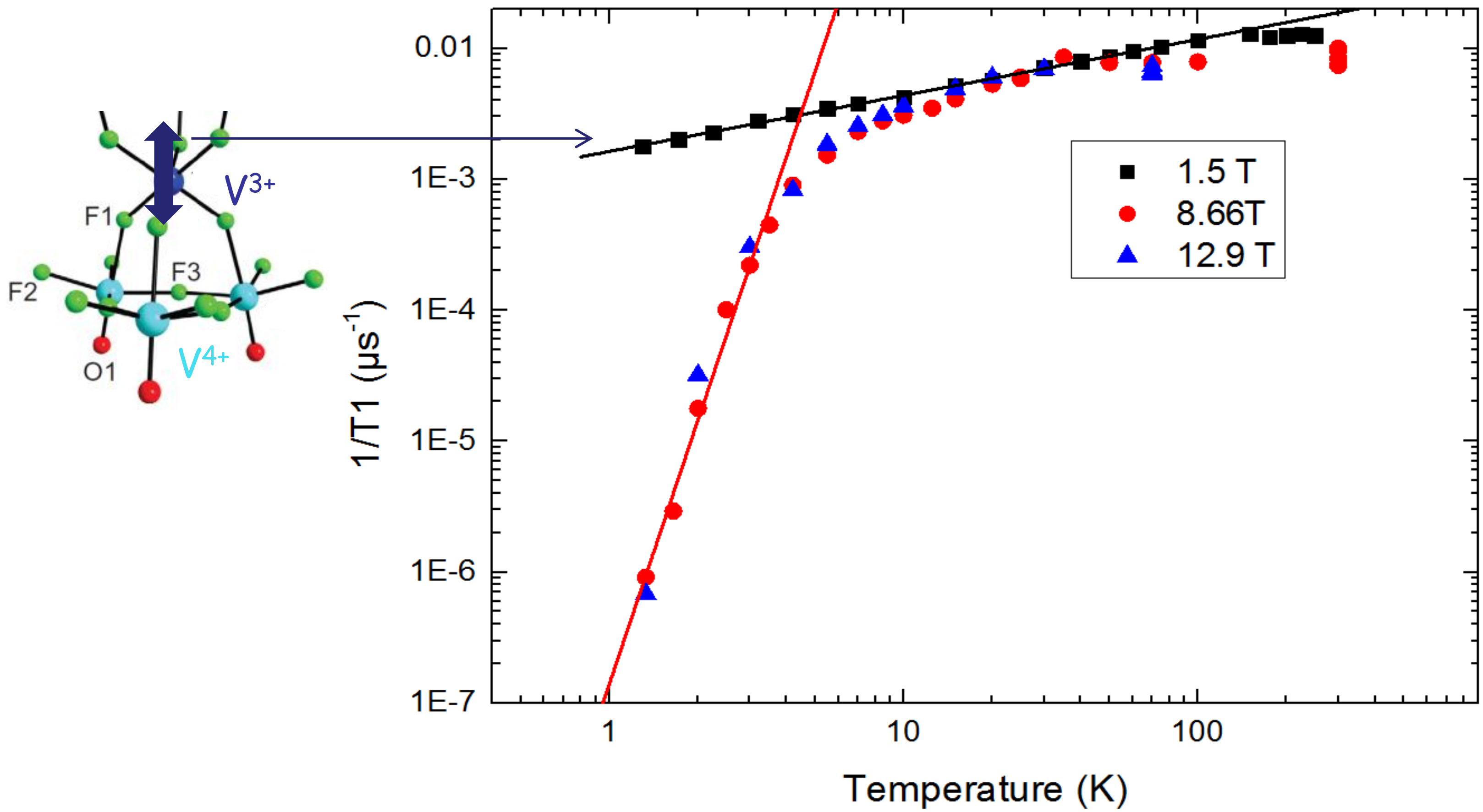


M. Jeong et al, PRL 107, 237201 (2011)



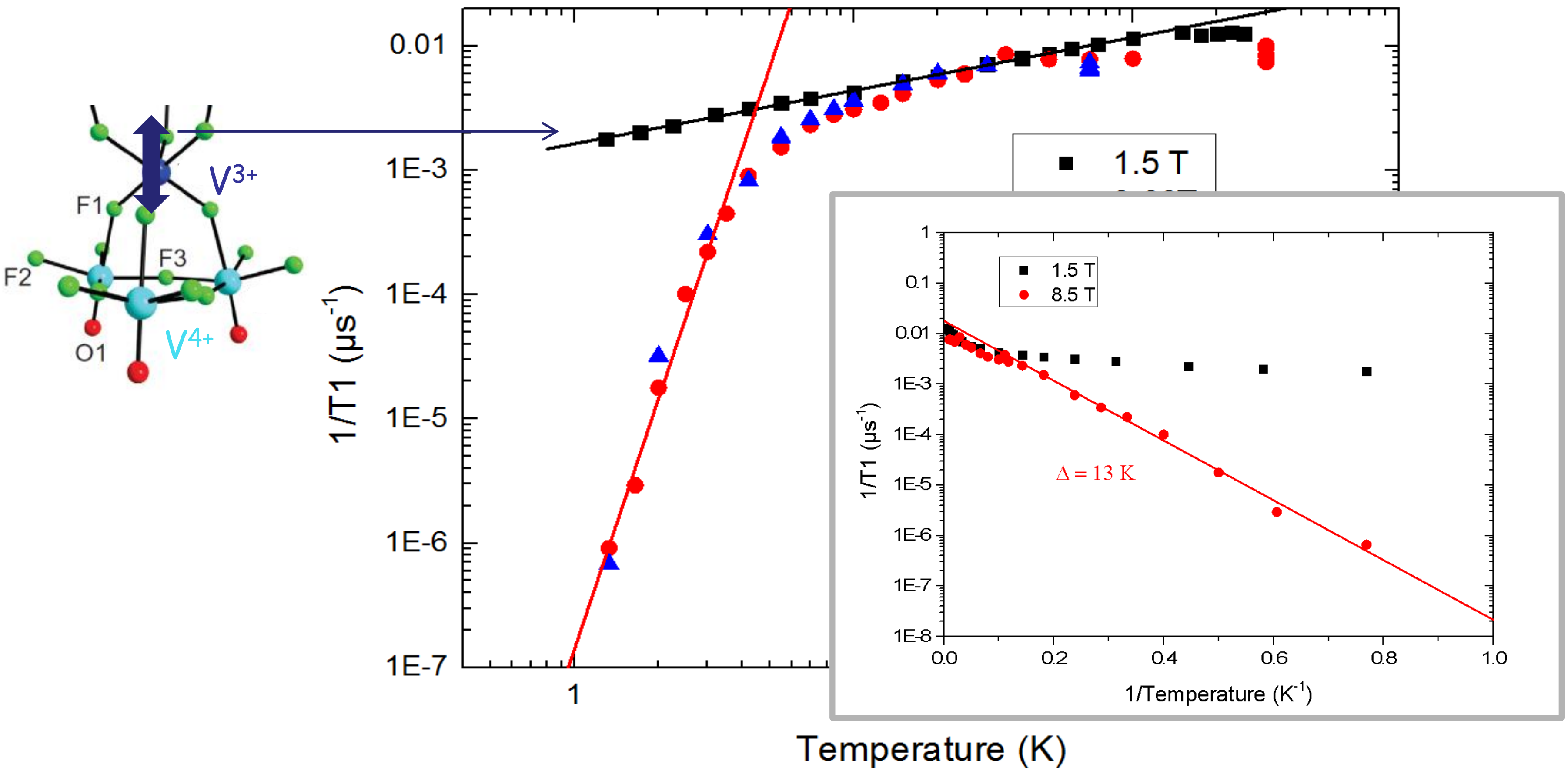
- At low field, low T, V^{3+} S=1 fluctuations
- At large field, low T, fast drop of $1/T_1$
  - Saturation of S=1 spins (brillouin) : probably no
  - Field induced transition : probably no

F NMR – spin dynamics



- At low field, low T, V^{3+} S=1 fluctuations dominate
- At large field, low T, fast drop of $1/T_1$

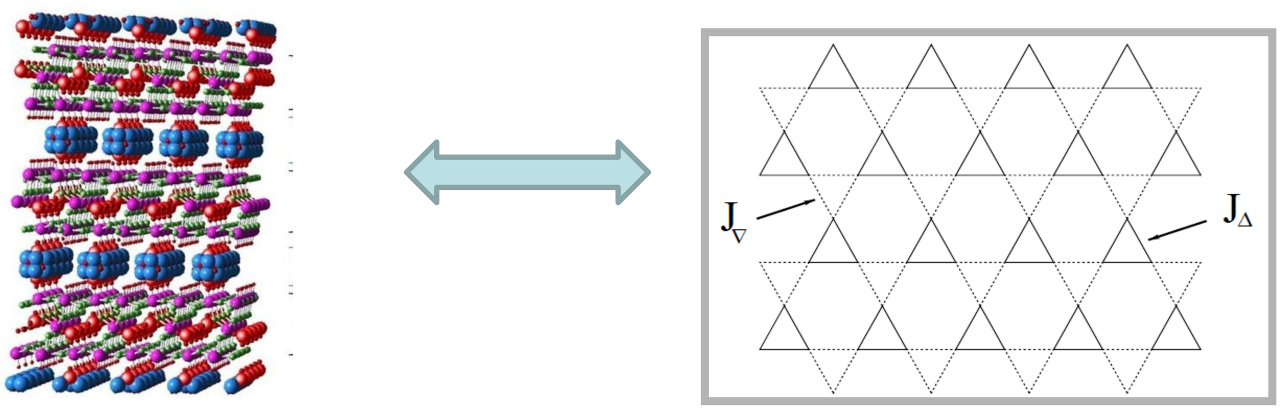
F NMR – spin dynamics



- At low field, low T, V^{3+} S=1 fluctuations dominate
- At large field, low T, fast drop of $1/T_1$
  - Spin gap $\Delta \sim 13$ K$=0.27J_1$

Conclusion (2)

- DQVOF is a new highly frustrated quantum material based on vanadium
- Gapless excitation spectrum / gapped magnetic excitation
- complex structure but eventually rather simple and unique realization of trimerized kagome



- Relevant to the issue of the proliferation of singlets in the SRRVB picture

Collaborators - DQVOF

Université Paris-Sud
F. Bert

J.-C. Orain phD

University of St Andrews
P. Lightfoot,
R.E. Morris;
F.H. Aidoudi

L. Clark

University of Edinburgh
P. Attfield,
M.A. de Vries,
A. Harrison

ISIS
M.T.F. Telling
J.S. Lord

PSI
A. Amato,
C. Baines

CEA - Saclay
P. Bonville

Hyperkagome: a 3D S=1/2 frustrated lattice

PRL **99,** 137207 (2007) PHYSICAL REVIEW LETTERS week ending 28 SEPTEMBER 2007

Spin-Liquid State in the $S = 1/2$ Hyperkagome Antiferromagnet $Na_4Ir_3O_8$

Yoshihiko Okamoto,[1,*] Minoru Nohara,[2] Hiroko Aruga-Katori,[1] and Hidenori Takagi[1,2]

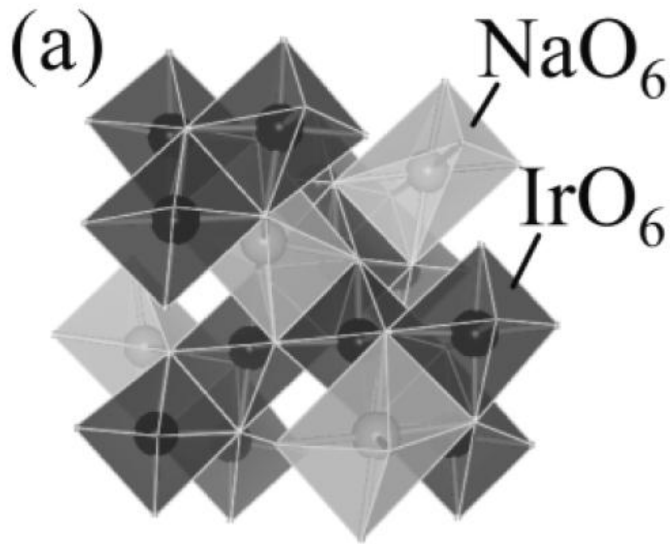
[1]*RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*

[2]*Department of Advanced Materials, University of Tokyo and CREST-JST, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan*

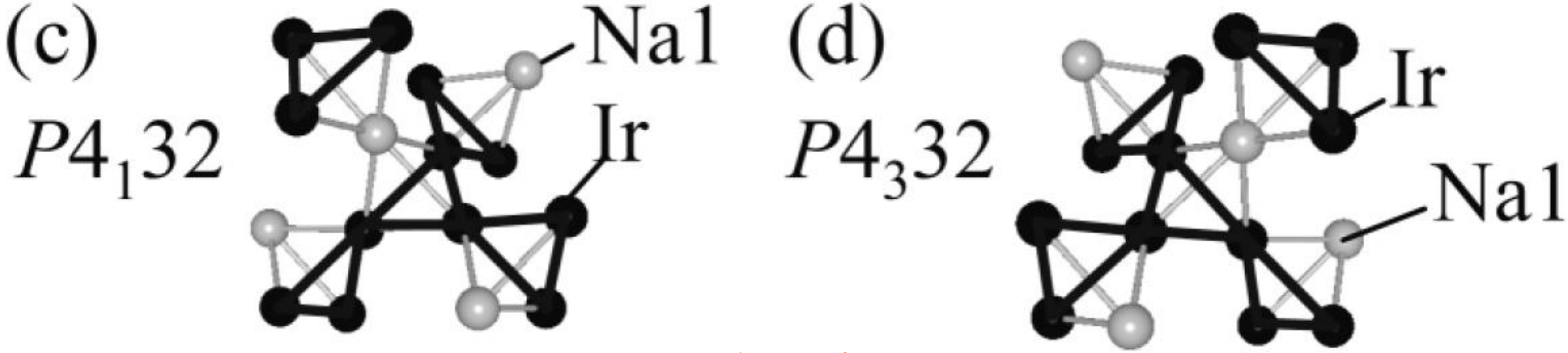
(Received 19 May 2007; revised manuscript received 24 July 2007; published 27 September 2007)

A spinel related oxide, $Na_4Ir_3O_8$, was found to have a three dimensional network of corner shared Ir^{4+} ($t_{2g}{}^5$) triangles. This gives rise to an antiferromagnetically coupled $S = 1/2$ spin system formed on a geometrically frustrated hyperkagome lattice. Magnetization M and magnetic specific heat C_m data

Hyperkagome structure: corner sharing



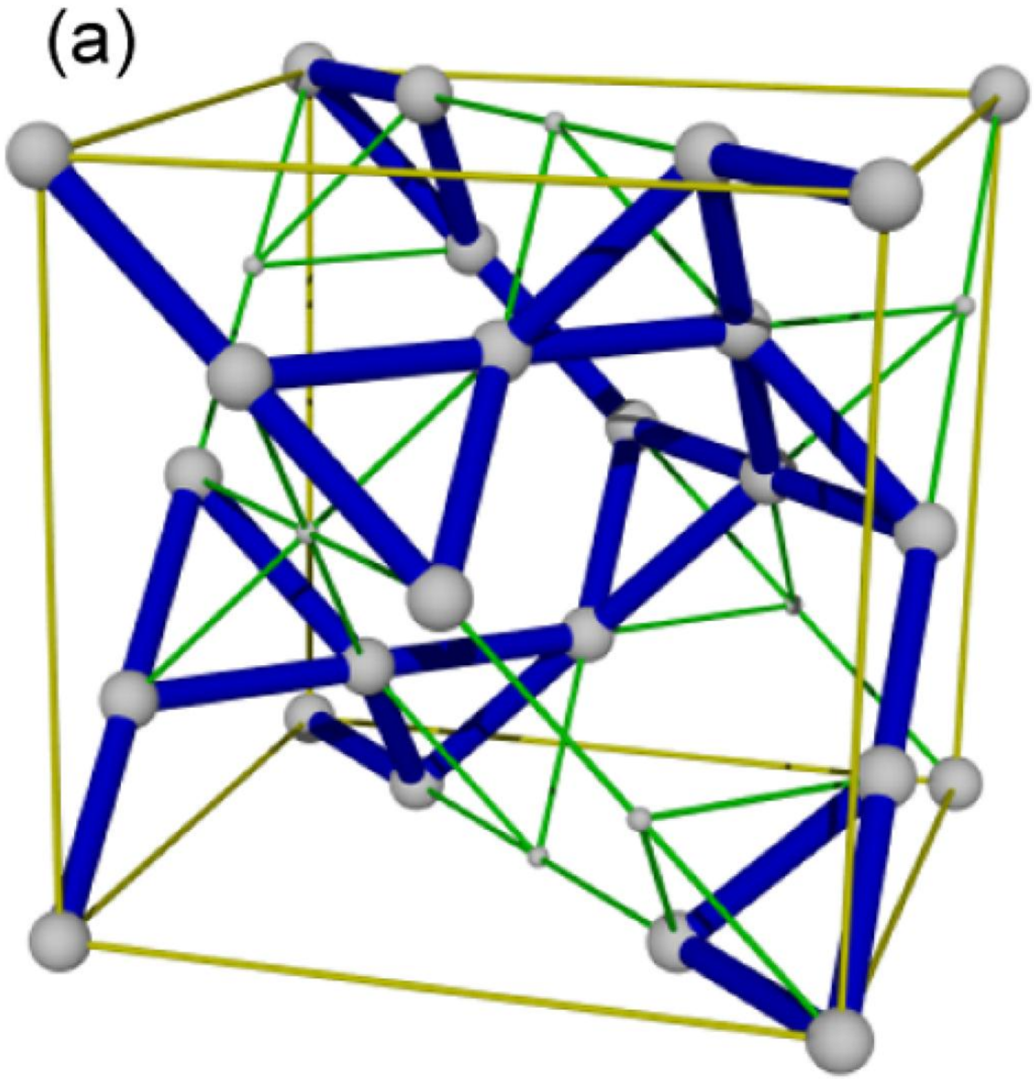
Effective spin
Ir^{4+}: $J=1/2$ (t_{2g}^5)



Two chiralities

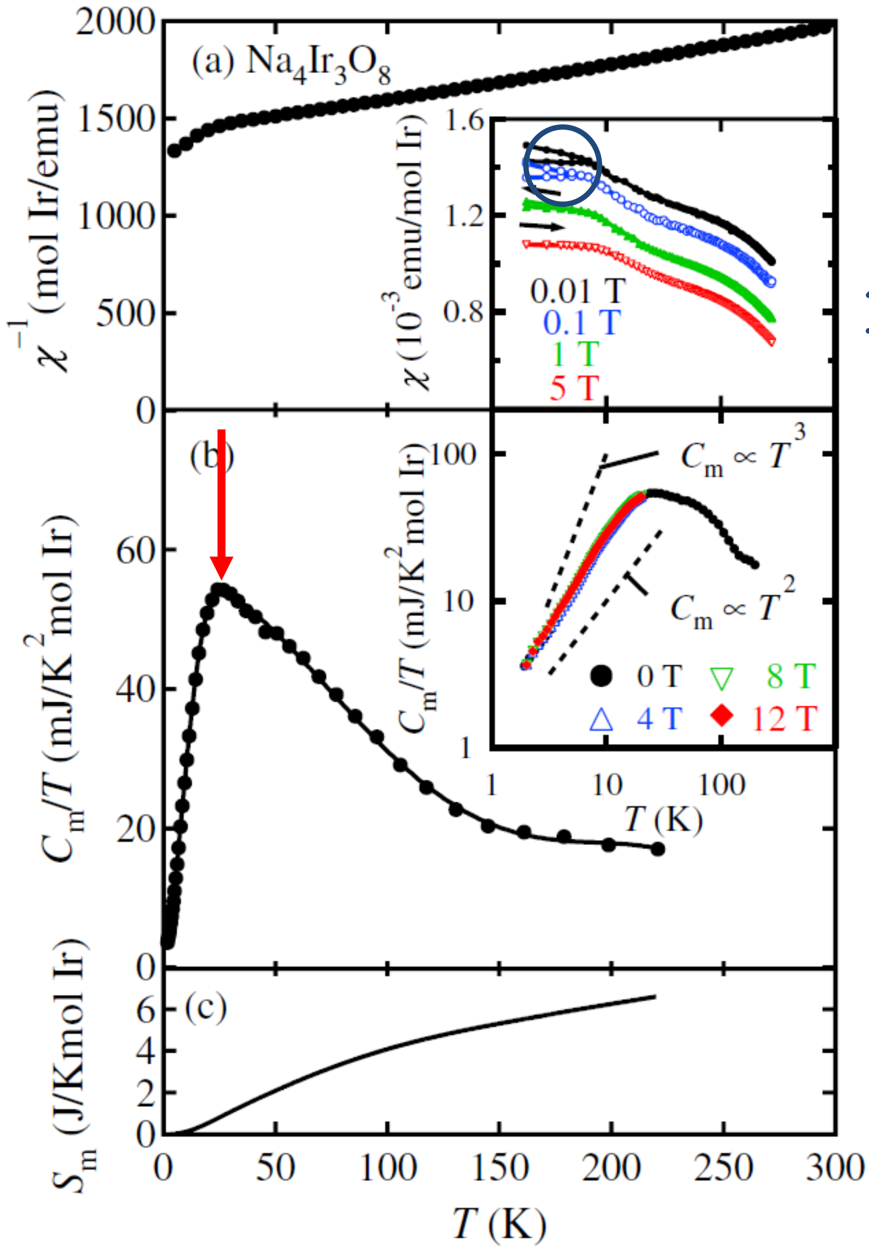
Y. Okamoto et al, PRL 98, 2007

Hyperkagome structure: corner sharing



Ir^{4+} only

Thermodynamic measurements: gapless spin liquid



Θ_{CW} ~500 - 600 K

HTSE: J ~300 K

1% impurities (J=1/2)?

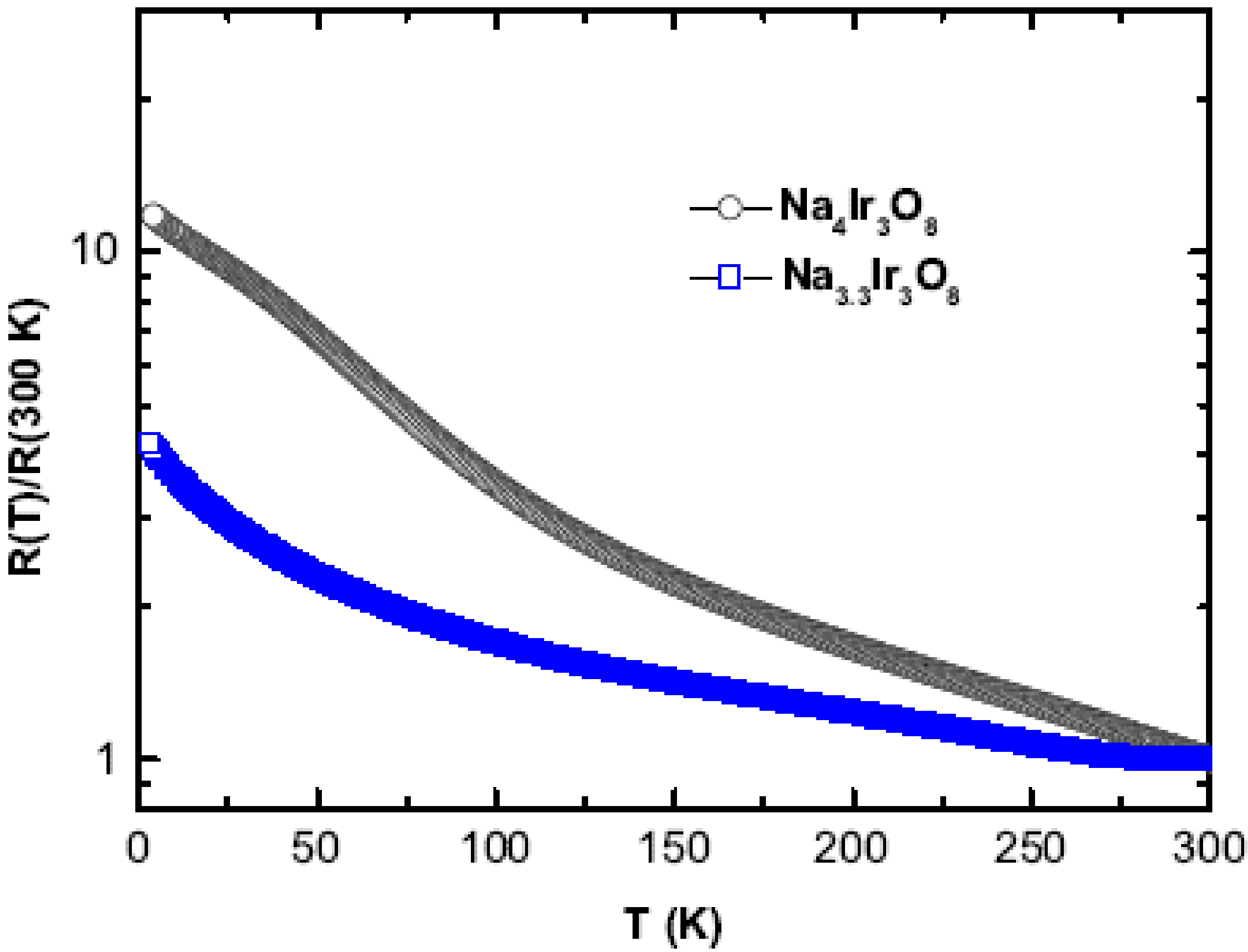
✓ χ levels off

✓ Low-T $C \sim T^{2.4}$

No gap
Max C/T ~ 24 K

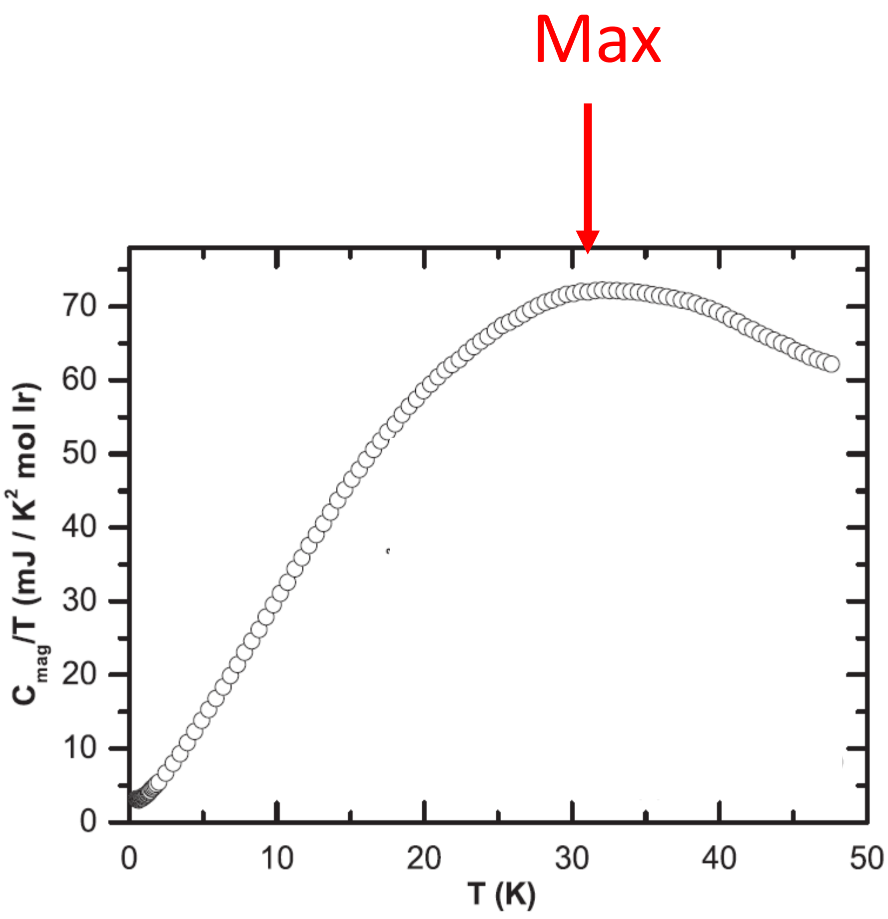
Y. Okamoto et al, PRL 98, 2007
R. Singh, J.Oitmaa, PRB 2012

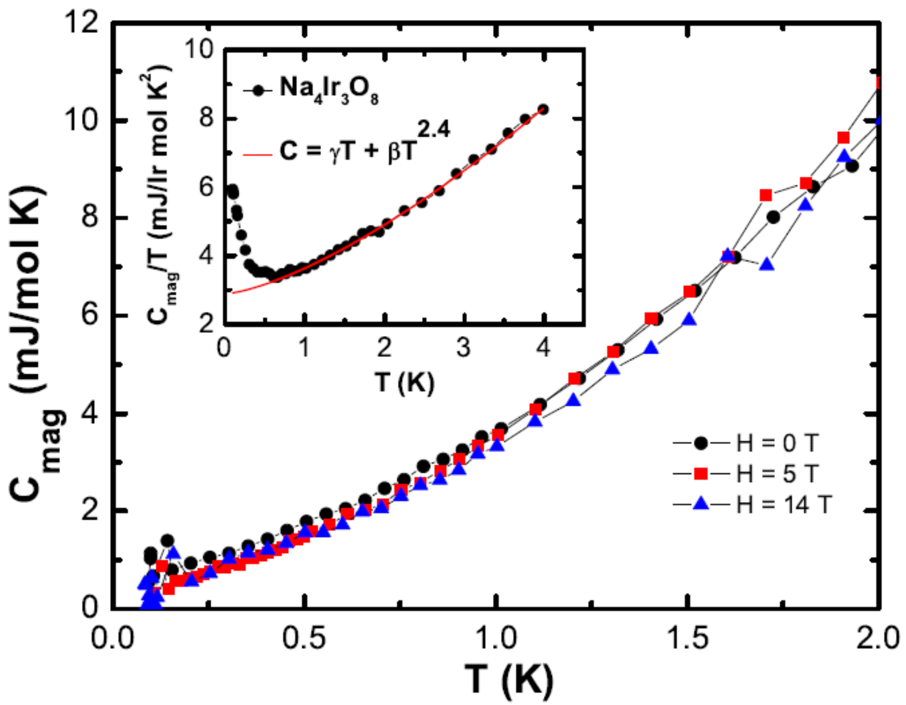
Doping is possible -> even more excitement



Balodhi et al. ArXiv 2014
See also Takayama et al, Nature (2014)

Low-T specific heat: extension to low-T





Y. Singh et al. PRB 2014

Balodhi et al. ArXiv 2014

Models (spin liquid)

✓ Fermionic approach: spinon Fermi Surface

Max C/T: crossover from Z2to U(1) SL
Paired spinons with line nodes in the gap
Susceptibility Pauli-like: mixing singlet and triplet state

✓ Mottness

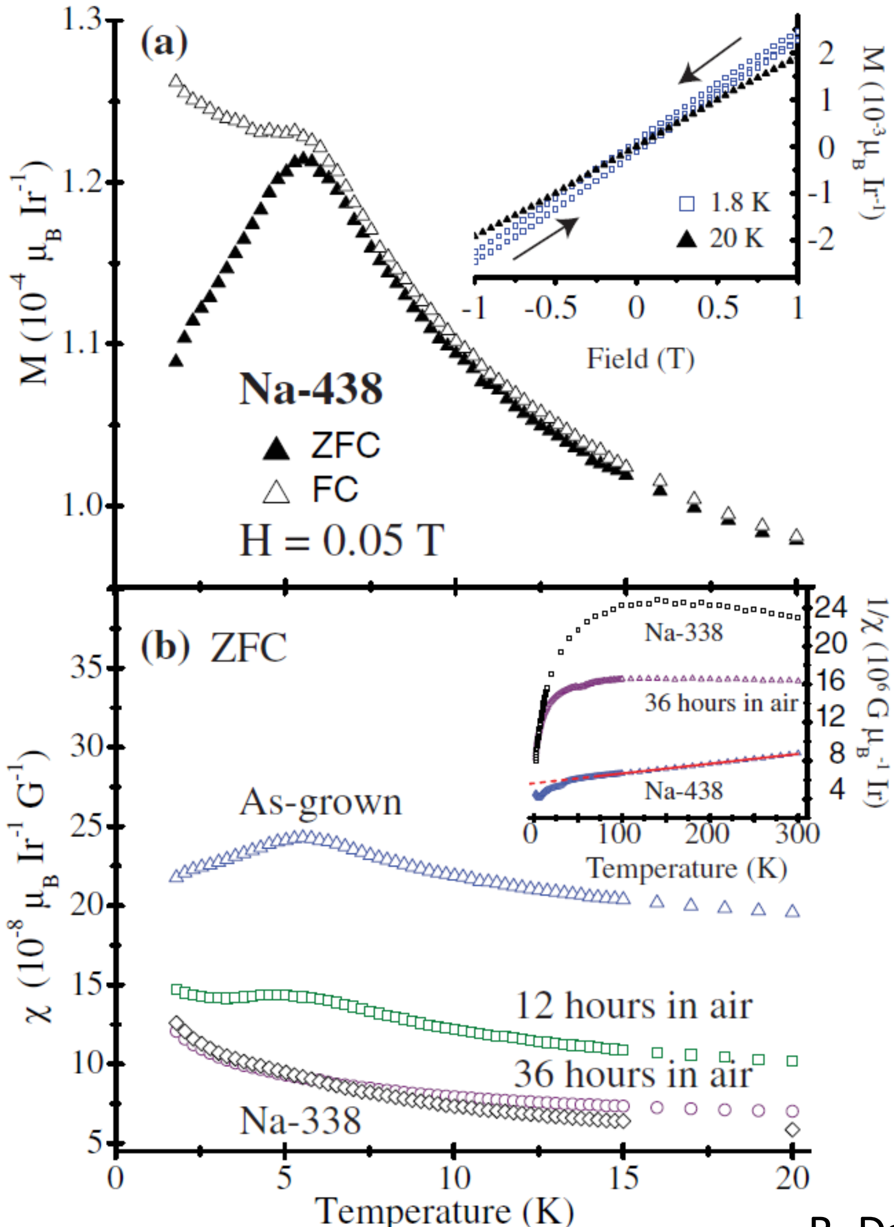
Proximity to a metal-insulator transition
Quantum criticality
Susceptibility and specific heat: right trend
Wilson ratio: little variation of specific heat, large variation of susceptibility

✓ Valence Bond Crystal: 72 sites

Gap of the order of J

Y. Zhou et al. PRL (2008)
D. Podolsky et al., PRL (2009); PRB (2011)
E. Bergholtz et al. PRL (2010)
…

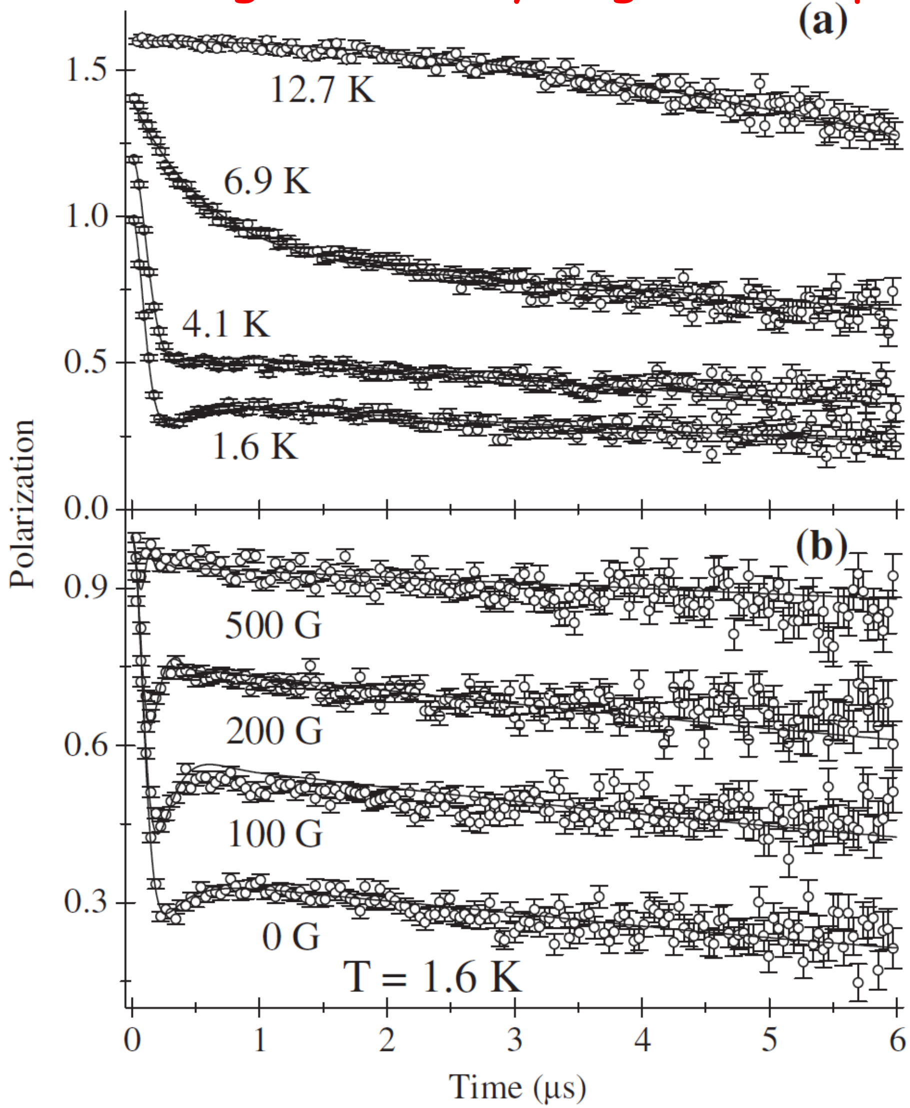
Degradation of sample with time!!!



R. Dally et al, PRL 113, 2014

μSR: freezing CDFO

CDFO = configurationnaly degenerate phases with fluctuating order

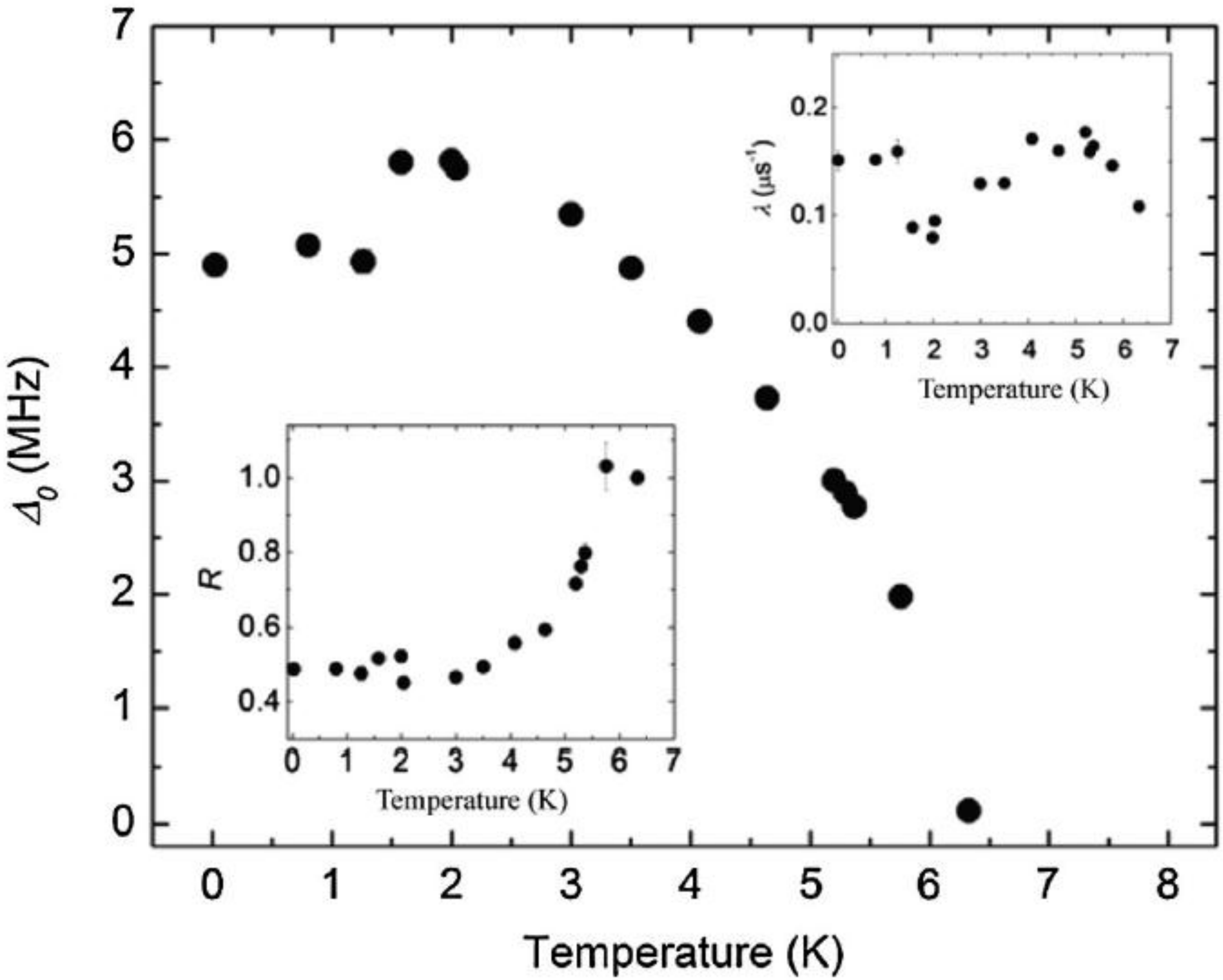


Quasistatic magnetic field distribution dressed with slow fluctuations

R. Dally et al, PRL 113, 2014

μSR: freezing: order parameter and relaxation

Order parameter



R. Dally et al, PRL 113, 2014

Our study: ^{17}O and ^{23}Na NMR

Université Paris-Sud
F. Bert

A. Shockley

J.C. Orain

U. Nagoya (Japan), ISSP
Y. Okamoto

université PARIS-SACLAY

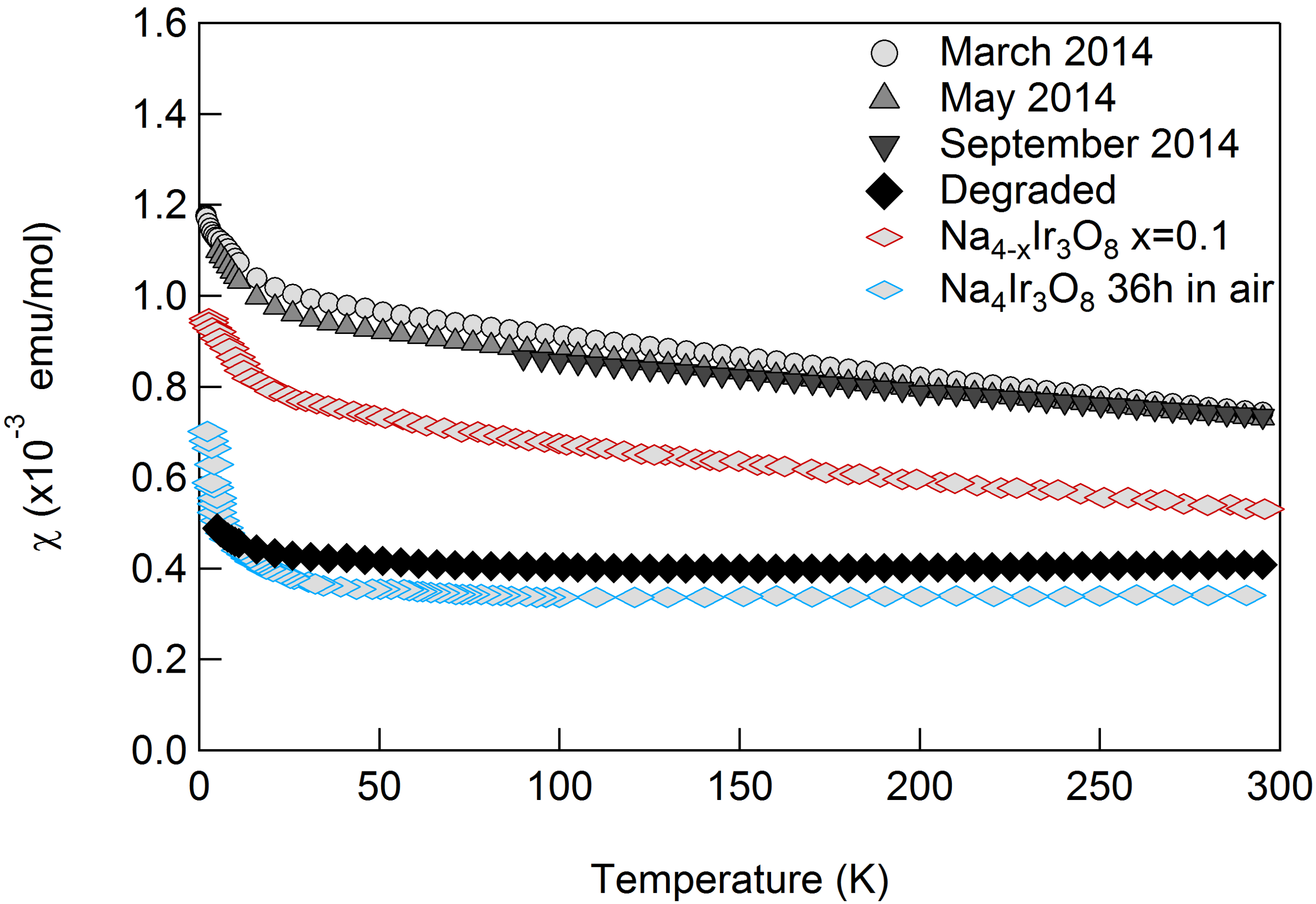
UNIVERSITÉ PARIS SUD

cnrs

OxyMORE

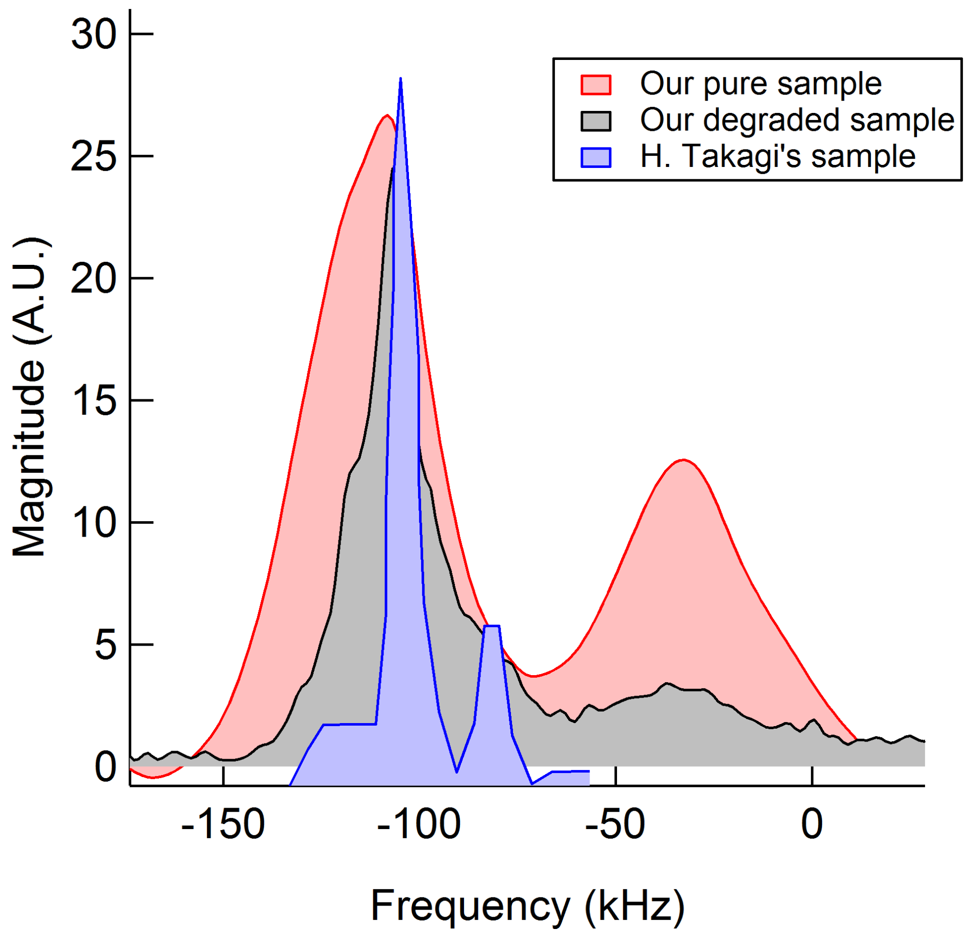
AGENCE NATIONALE DE LA RECHERCHE ANR

No degradation

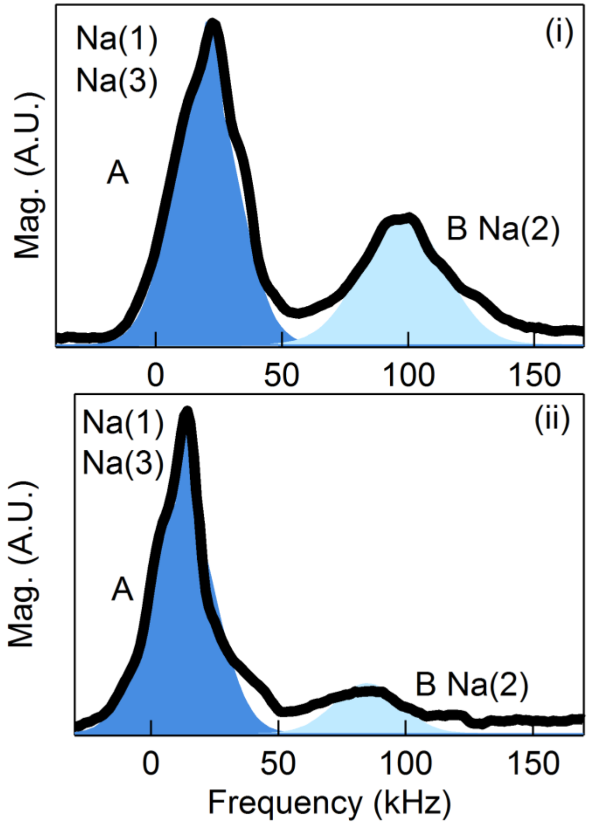


Balodhi et al,
Arxiv 2014

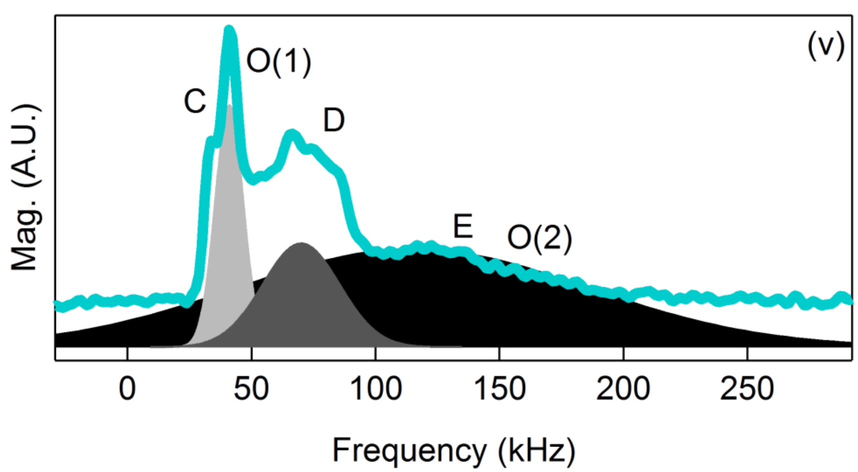
Typical degradation from ^{23}Na NMR

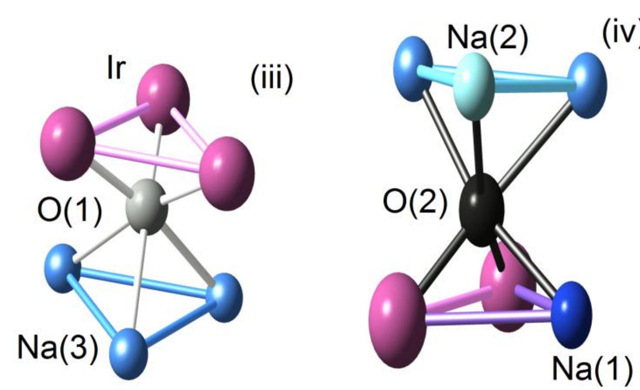


^{17}O and ^{23}Na NMR: site assignment

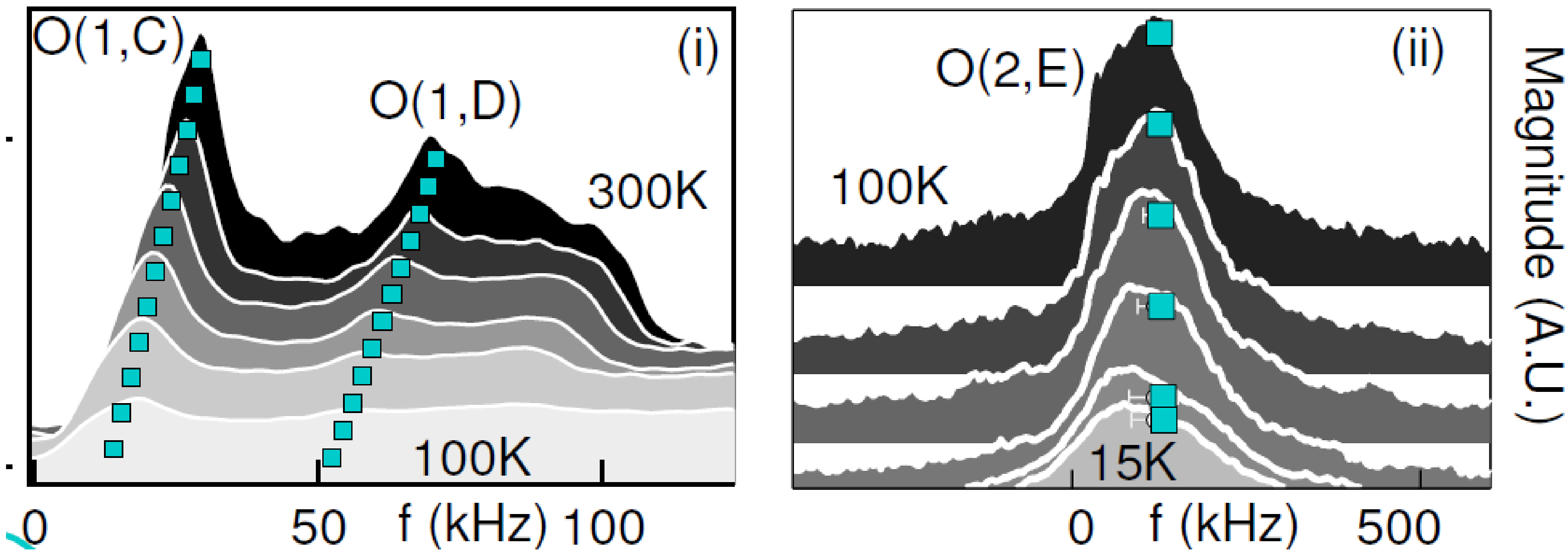


75% occupation of Na(2,3) sites

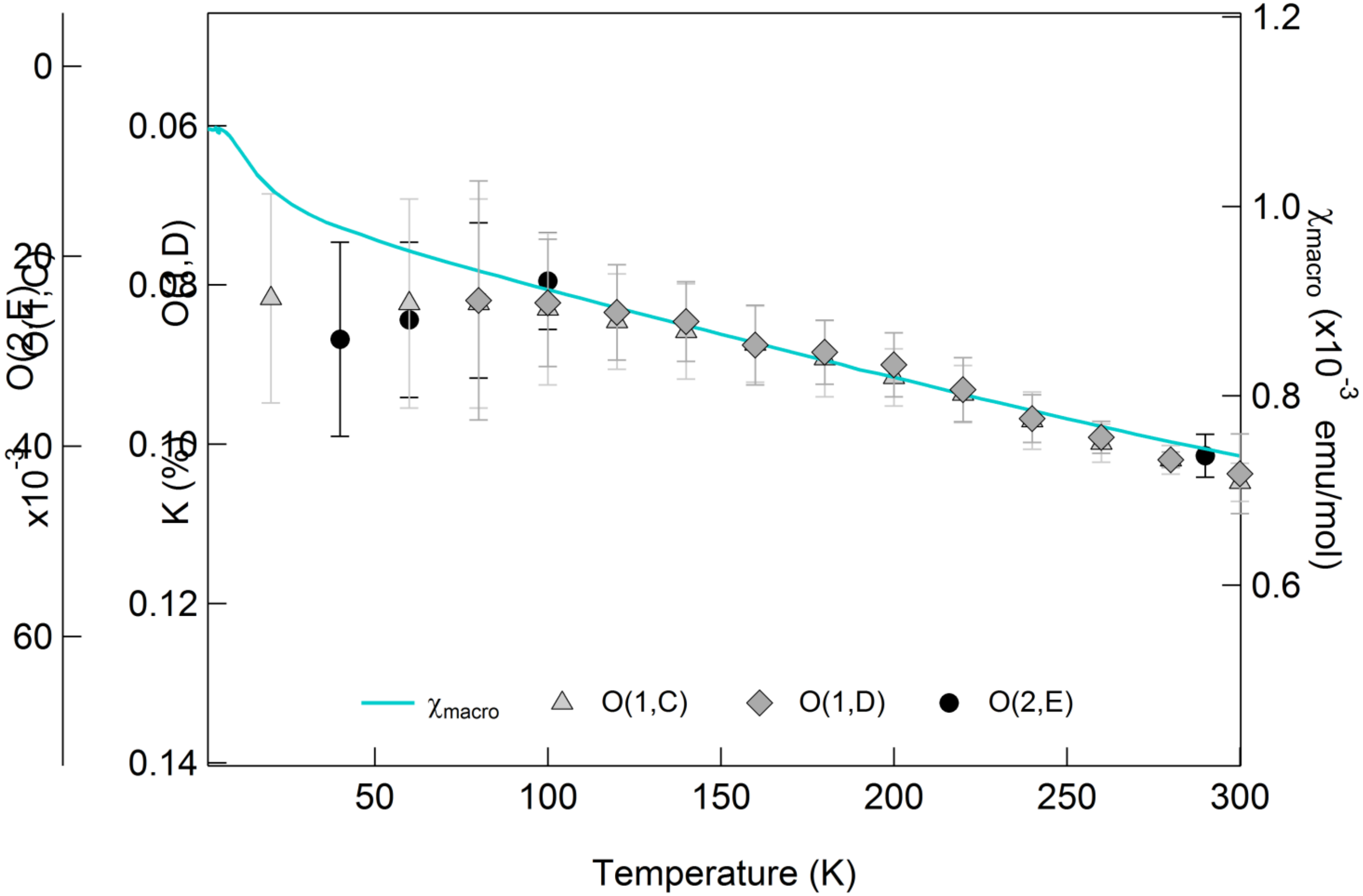




$^{17}O(1)$ NMR: shift

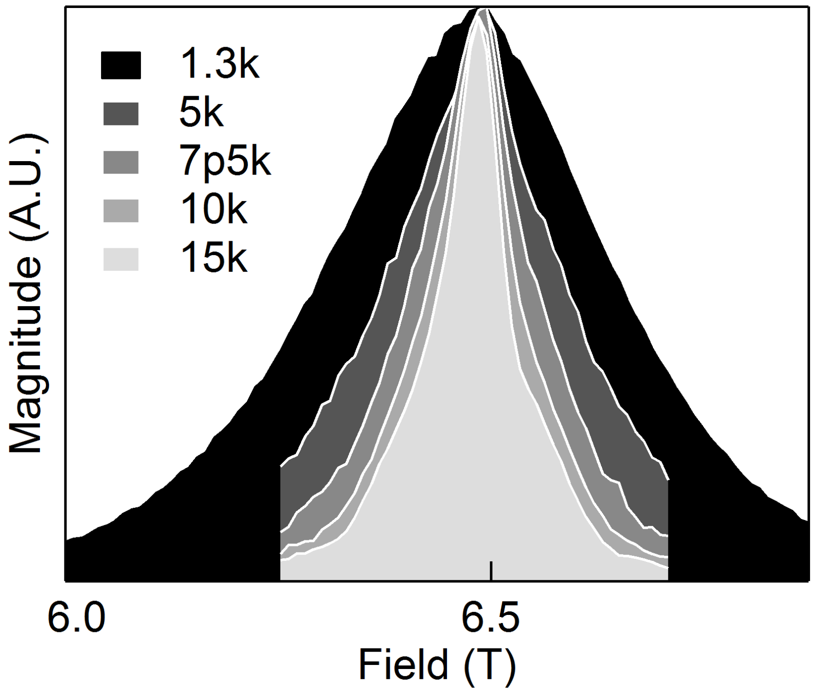


^{17}O NMR: shift



Susceptibility levels off: no gap

Low temperatures: 17O NMR

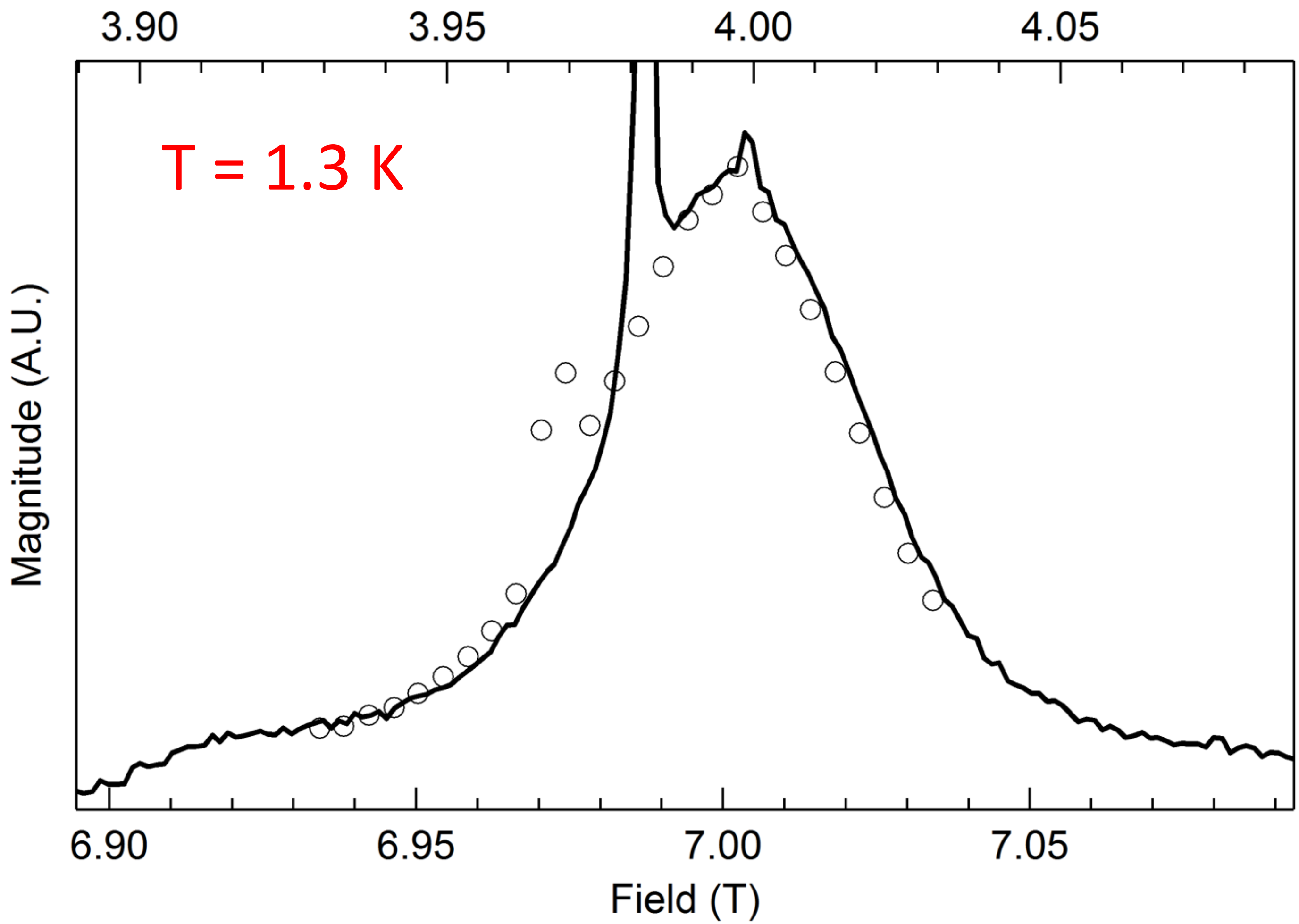


Line broadening

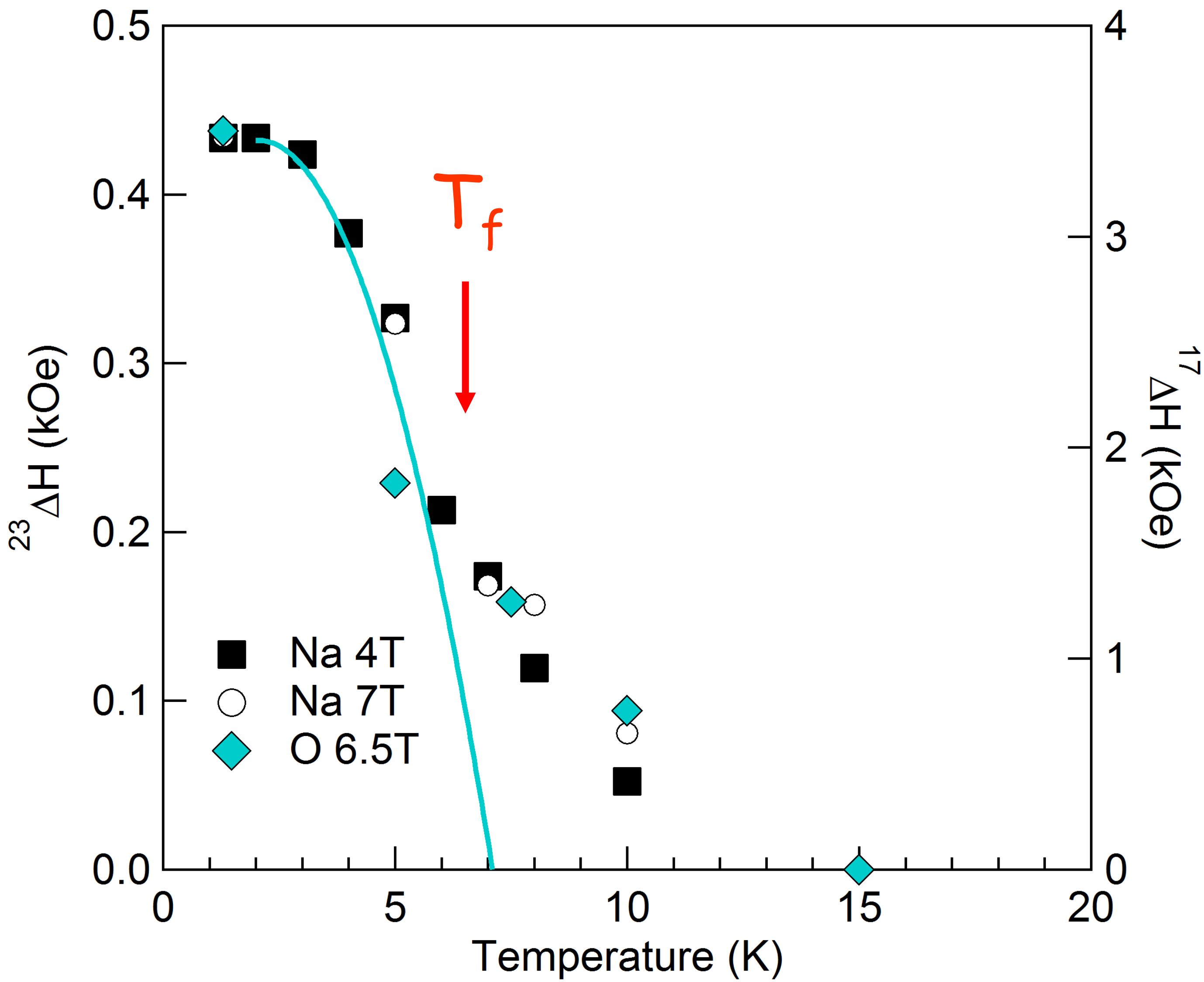
T_f ~7.5 K

Width saturates at low T

Low temperatures: width independent of field



Low temperatures



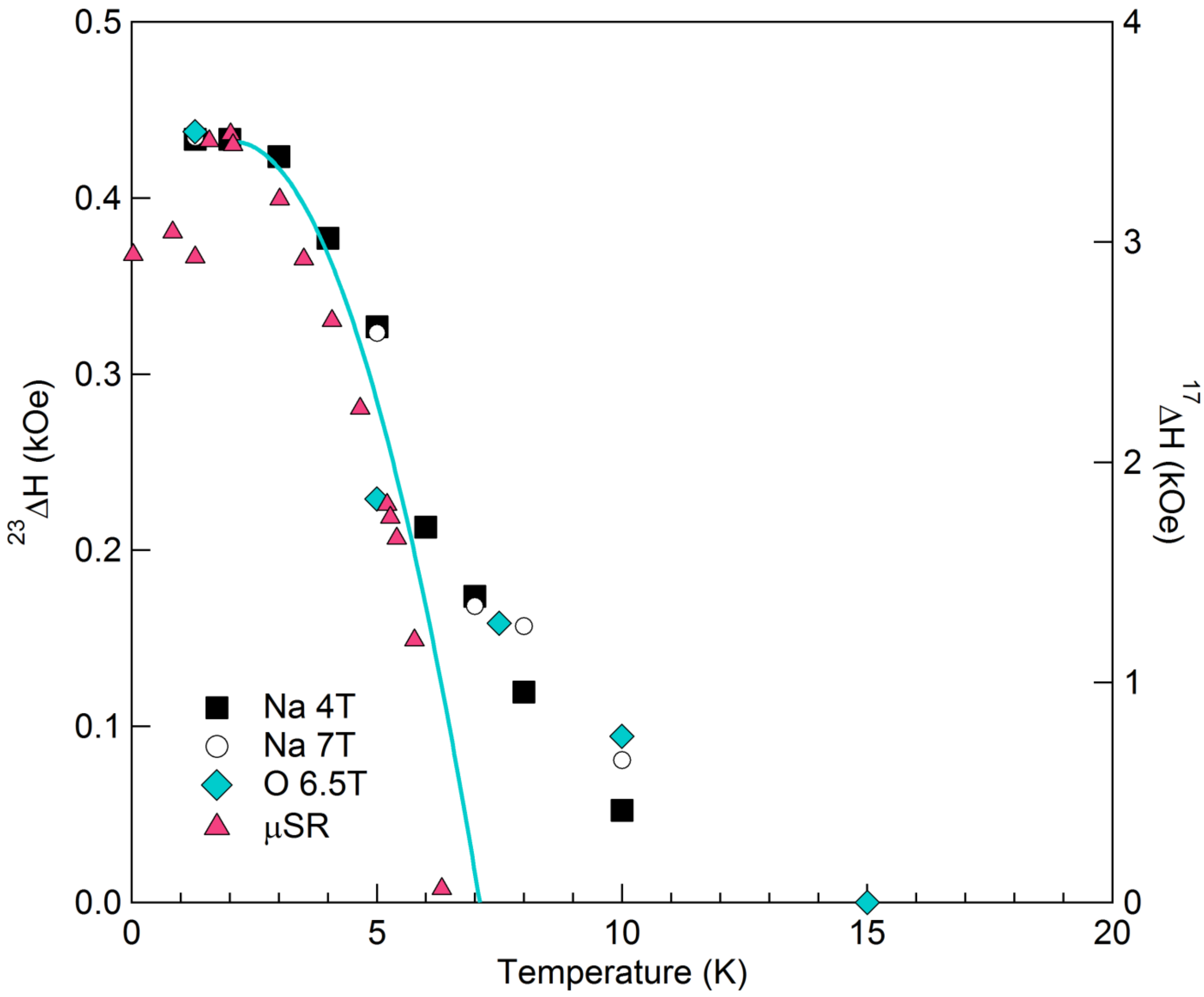
Bulk freezing
- Static
- Disordered

T_f ~7.5 K

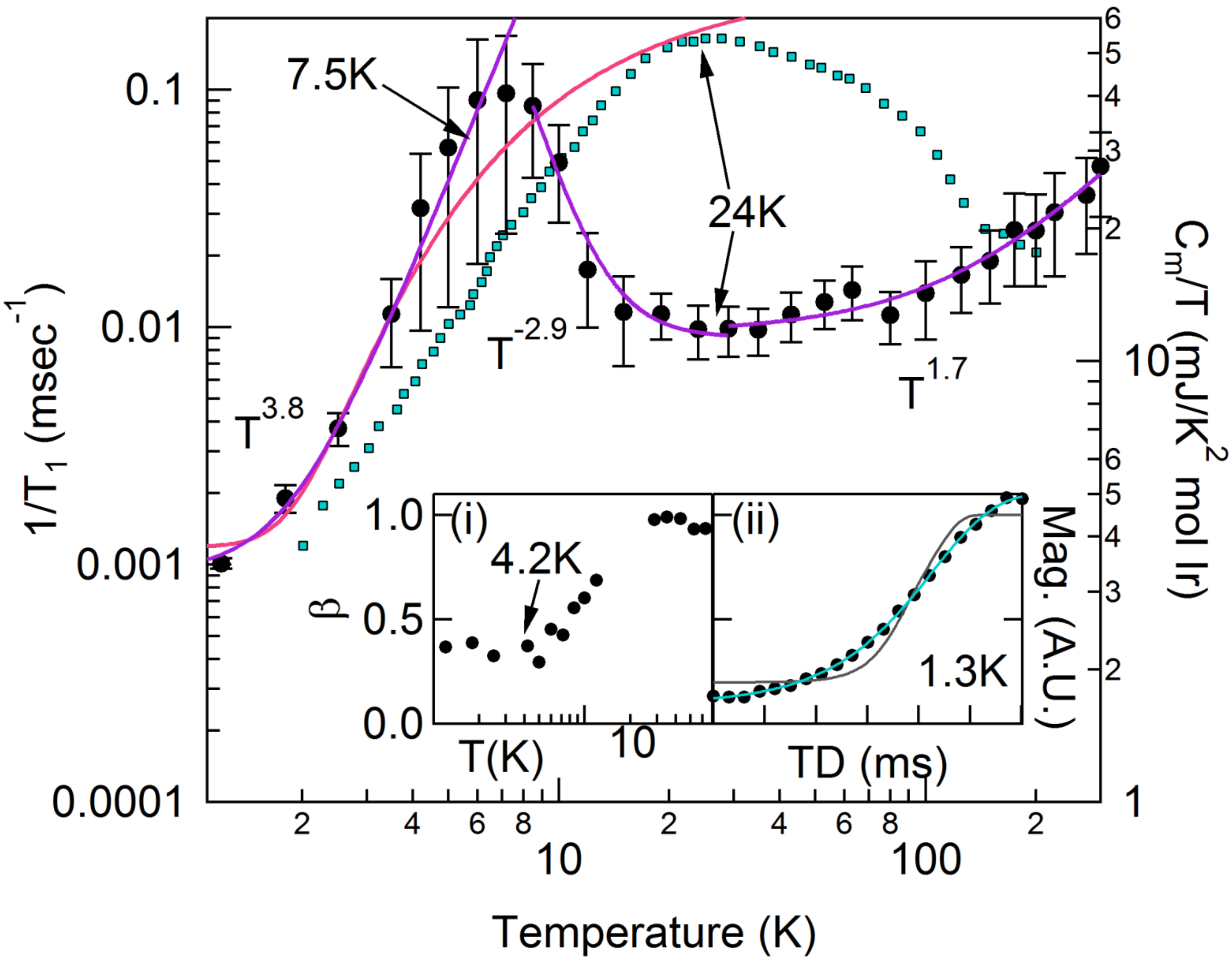
(Kink of susceptibility)

$\mu \sim 0.27(4)\ \mu_B$

Low temperatures: NMR vs μSR

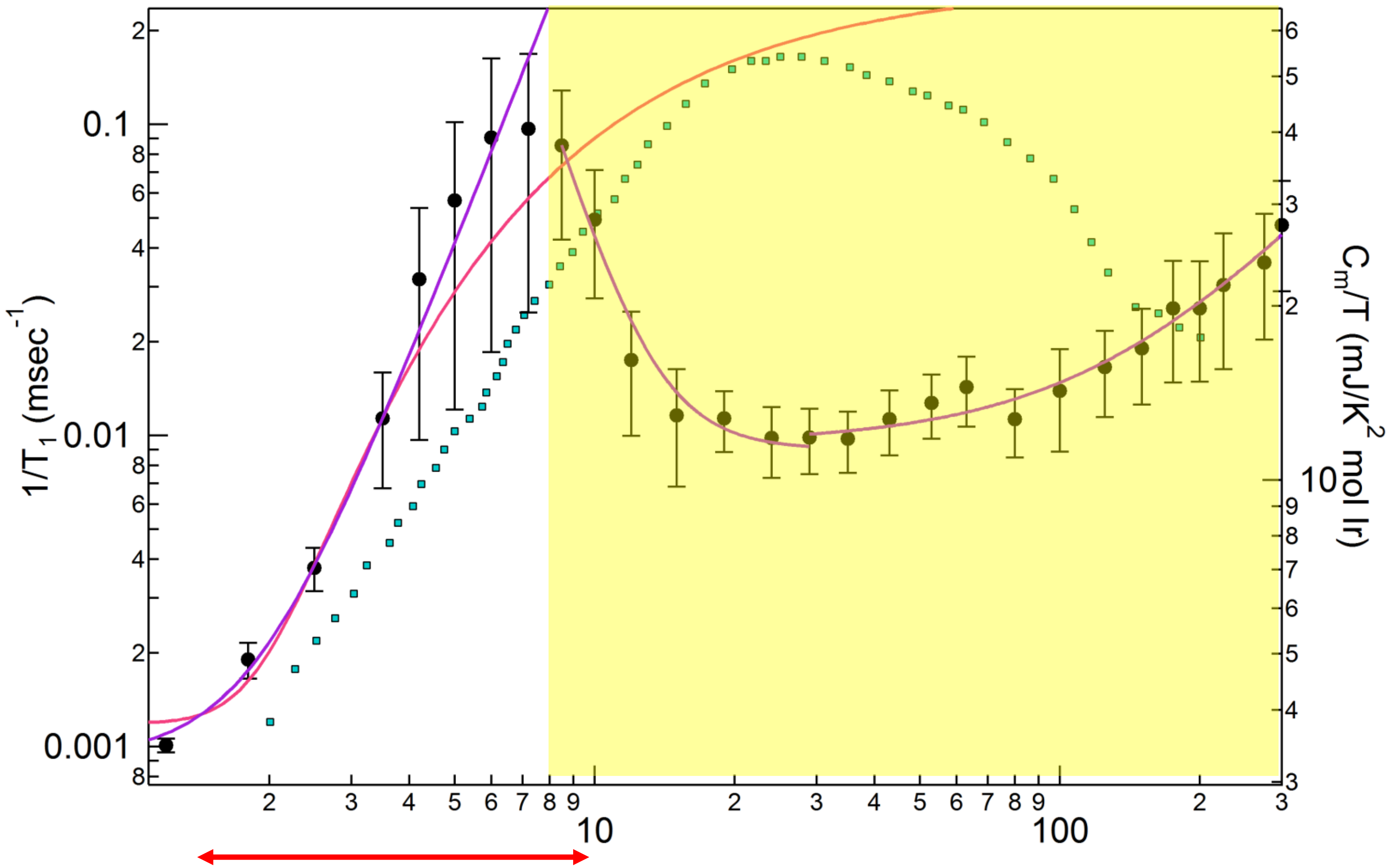


Relaxation



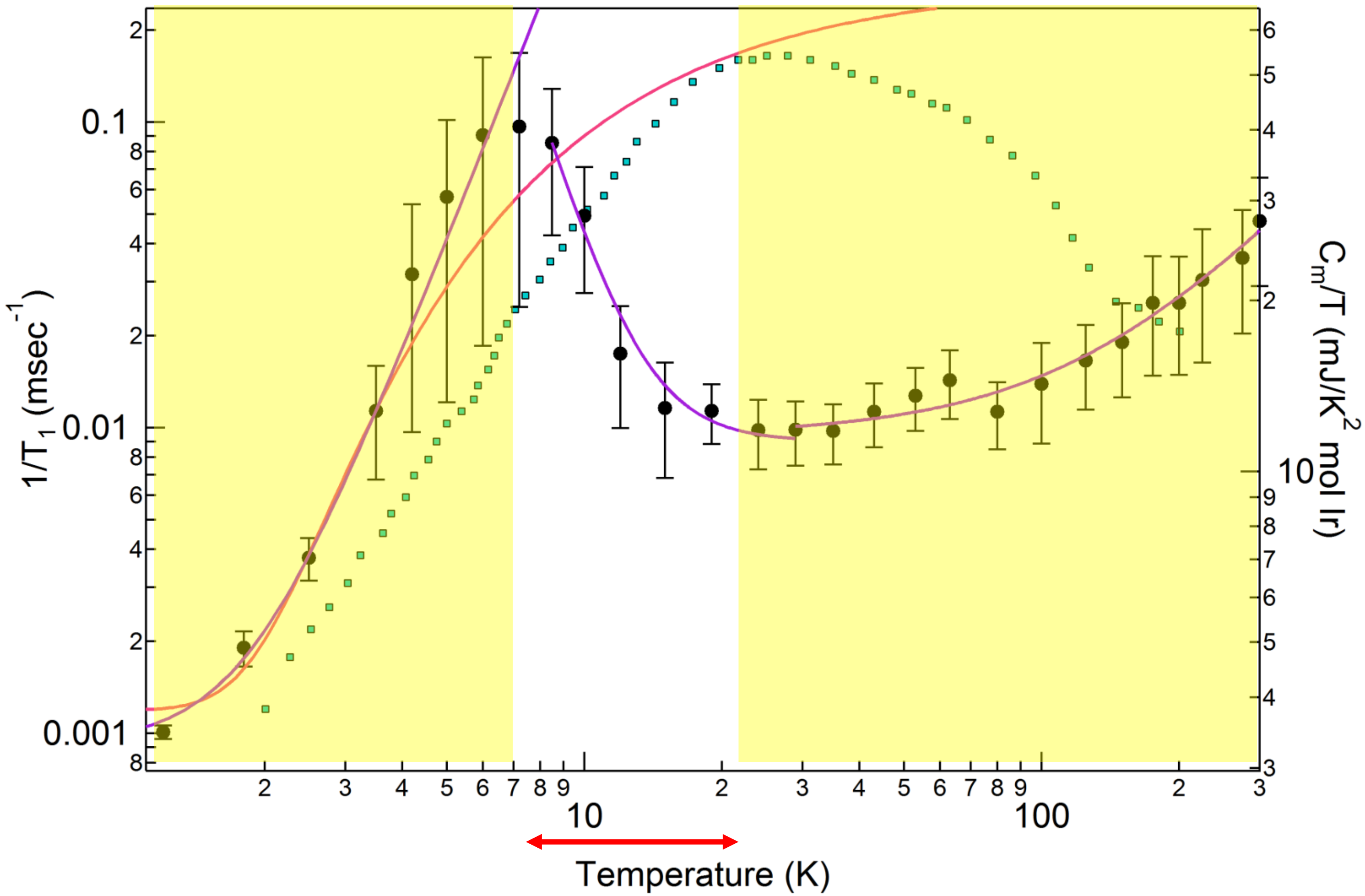
0.1
0.01
0.001
0.0001
1/T1 (msec-1)
7.5K
24K
T-2.9
T1.7
T3.8
Cm/T (mJ/K2 mol Ir)
(i)
(ii)
4.2K
1.3K
β
T(K)
TD (ms)
Mag. (A.U.)
Temperature (K)

3 T-ranges



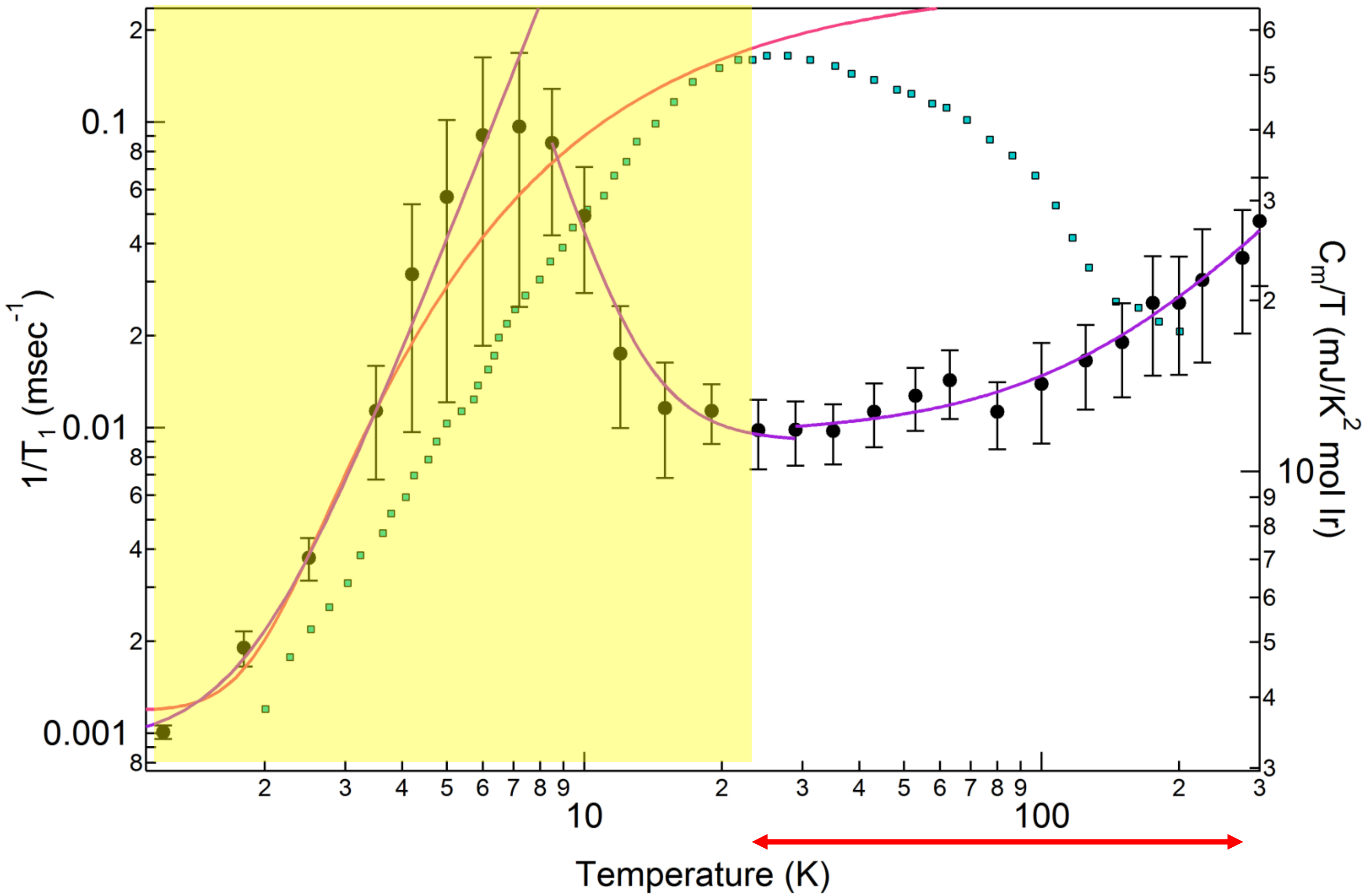
Frozen phase
Slowing down of dynamics
C typical of frozen phase

3 T-ranges



Critical fluctuations
Crossover typical of hyperkagome

3 T-ranges



T1 ~T$^{1.7}$

χ ~cte

Back to models (spin liquid)

✓ Fermionic approach: spinon Fermi Surface

Max C/T: crossover from Z2to U(1) SL

Paired spinons with line nodes in the gap: contradiction with T_1?

Susceptibility Pauli-like: mixing singlet and triplet state

~Korringa law T_1TK^2 ~ cte

✓ Mottness

Proximity to a metal-insulator transition

Quantum criticality

Susceptibility and specific heat: right trend

Wilson ratio: little variation of specific heat, large variation of susceptibility

T_1 could be a test for models

✓ Valence Bond ~~Crystal~~ Glass

Downward shift of the transition?

C typical of a valence bond glass?

Summary (hyperkagome)

✓ Low-T state dominated by disorder: static

$C/T \sim \gamma + b\,T^{1.4}$ (not a spinglass)

$1/T1 \sim T^4$

Valence bond crystal -> valence bond glass?

Downward shift of the transition $J \rightarrow T_f$

✓ Intermediate T-region

If crossover region, not towards a gapped regime

Or

Broad critical regime (disorder)

✓ $2\,T_f = J/20 < T < J/3$? : intrinsic spin liq properties

Max of $C/T \sim 3T_f$

$T_1 \sim T^{1.7}$

χ constante

Summary

✓ Spin $\frac{1}{2}$ $\oplus$ Corner sharing geometry $\oplus$ frustration

✓ Equilateral triangles are a must!

✓ More work: track the deviations to the Heisenberg Hamiltonian ~ J/20 - J/10

✓ Disorder plays a role at low T (only)

✓ Avenues:

- control of defects: perturb to reveal
- Iridates: spin orbit interaction
- …