Quantum spin liquids: beyond the kagome lattice

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Quantum spin liquids: beyond the kagome lattice

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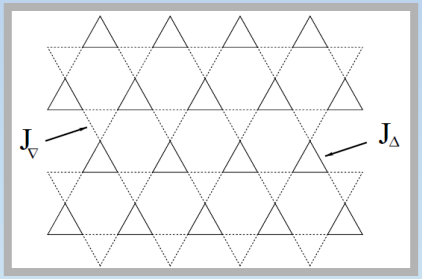
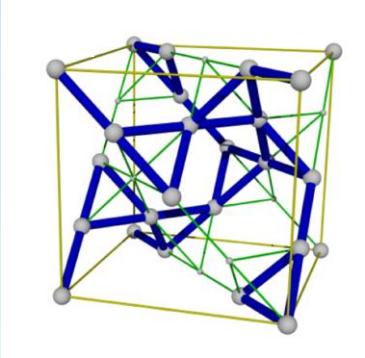
- Quantum spin liquids and frustrated magnetism

- Breathing kagome spin liquid (DQVOF)



- Hyperkagome lattice: a new player based on Cu^{2+} S=1/2 : $PbCuTe_2O_6$



Spectroscopies of Quantum Materials
P. Mendels, E. Kermarrec, V. Brouet, H. Alloul,
A. Louat (PhD), Q. Barthélemy (PhD), B. Lepennec (M2), R. Sharma (Post-doc)

J.-C. Orain
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St Andrews
P. Lightfoot
R.E. Morris
F.H. Aidoudi

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P. Attfield
M.A. de Vries
A. Harrison

L. Clark (liverpool)

B. Bernu
(LPTMC/**UPMC**)

CEA-Saclay, P. Bonville
ISIS M. Telling, J.S. Lord
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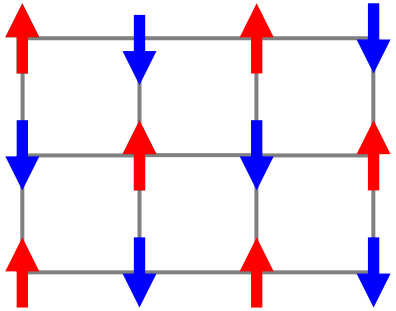
Iowa State U. : Y. Furukawa
MPI : M. Baenitz

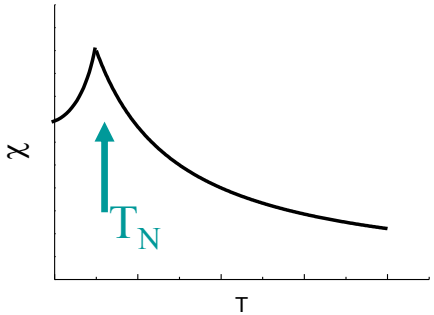
Koteswararao B.
(**IIT tirupati**)

CCMS, Taiwan F.C. Chou
Seoul U., Kee Hoon Kim

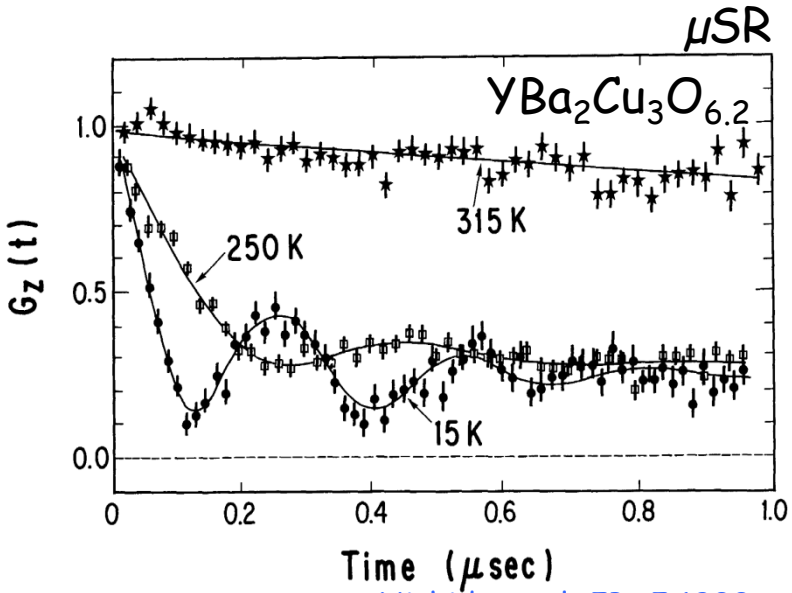
Néel state - conventional antiferromagnetism

$$\mathcal{H} = J\boldsymbol{S}_i.\boldsymbol{S}_j,\ J > 0$$

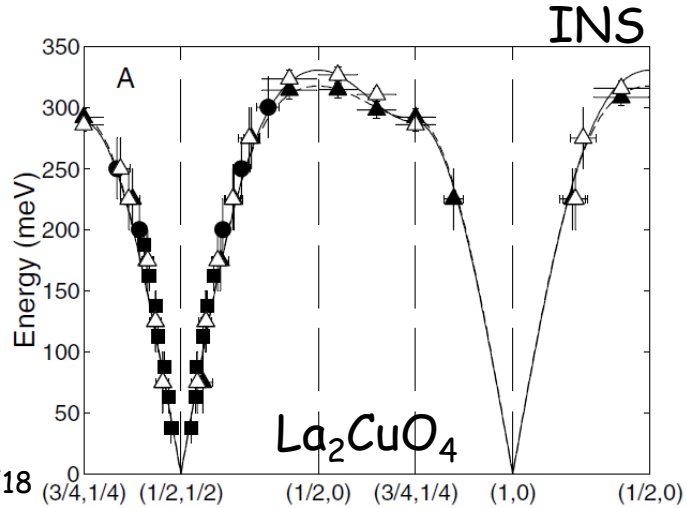




-On site static moment + LRO
  ->Spontaneous oscillations in ZF-μSR
  ->Magnetic Bragg Peaks
-Spin wave excitations



Nishida et al, JPSJ 1988



Coldea et al, PRL 2001

Frustration to destabilize Néel state

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

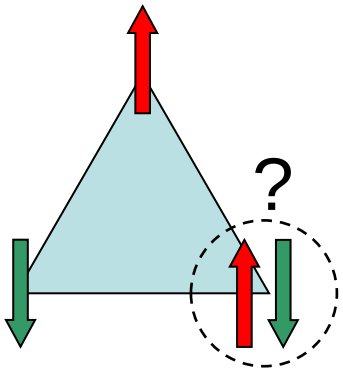
The possibility of a new kind of electronic state is pointed out, corresponding roughly to Pauling's idea of "resonating valence bonds" in metals. As observed by Pauling, a pure state of this type would be insulating; it would represent an alternative state to the Néel antiferromagnetic state for S =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

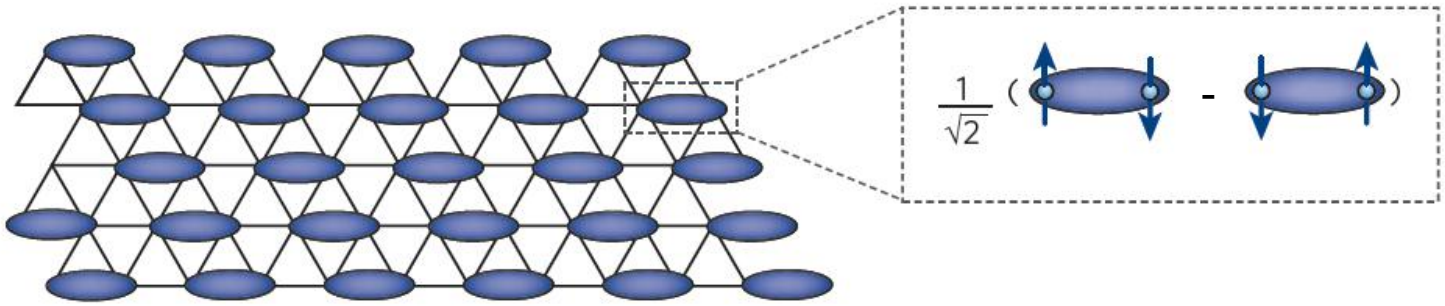
Quantum fluctuations S=1/2

$$|\psi\rangle = |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$$

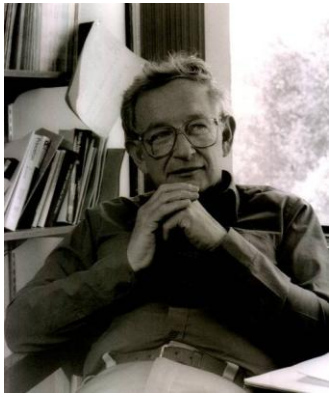
+

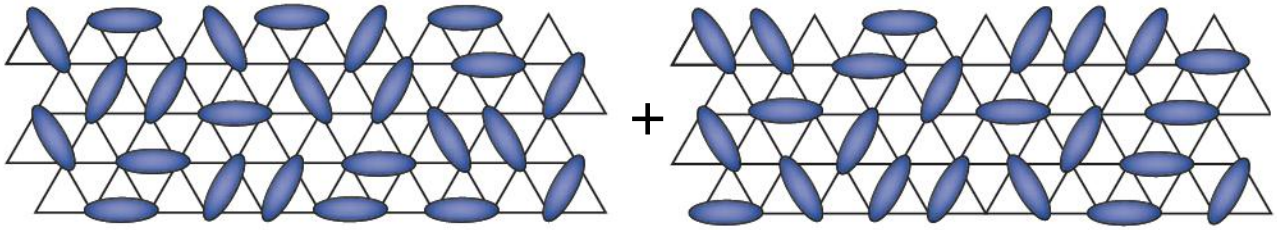
Geometric Frustration





Valence Bond Crystal



$|\mathrm{RVB}\rangle =$  $+\ldots$

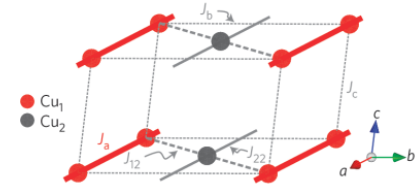
Quantum Spin Liquid:

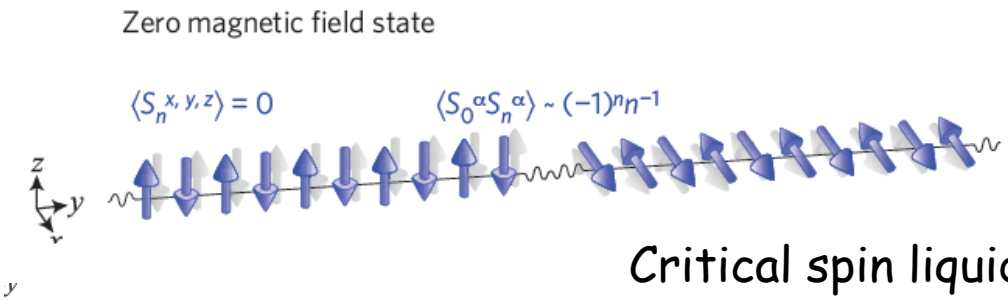
A state without any spontaneous symmetry breaking

Review L. Balents, Nature 2010

Fractional spinon excitations in the quantum state (H=0)

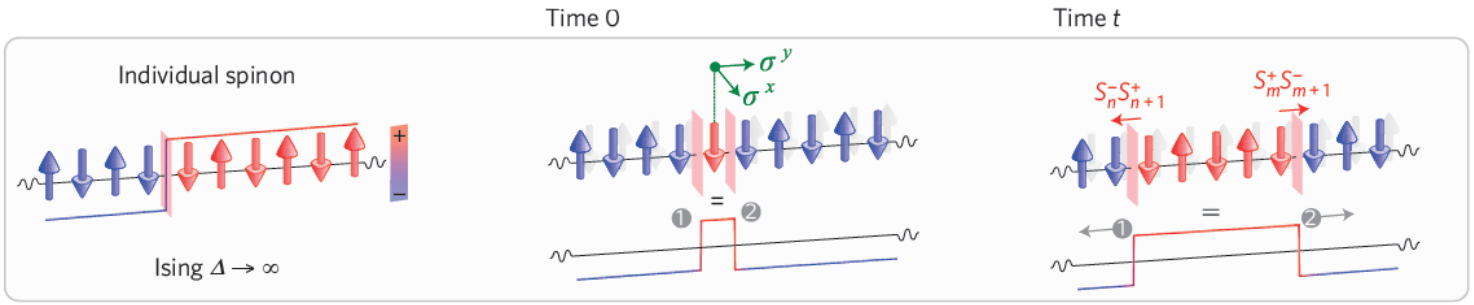
$CuSO_4.5D_2O$



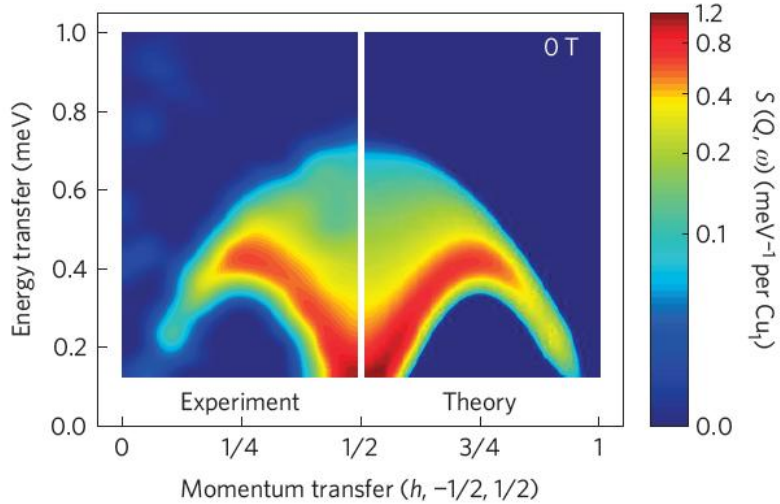


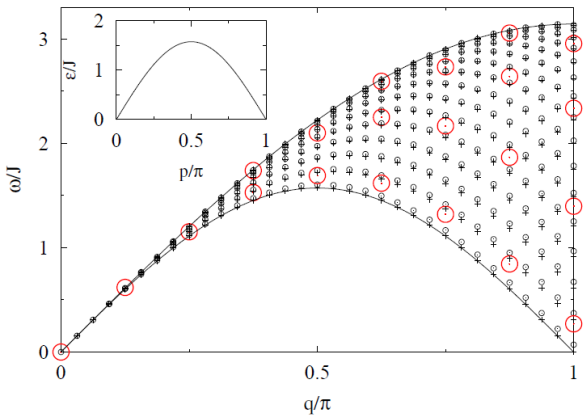
J_a=0.25meV
T_{3D}<100mK

Critical spin liquid – Bethe Ansatz



Excitations
S=1/2 spinons





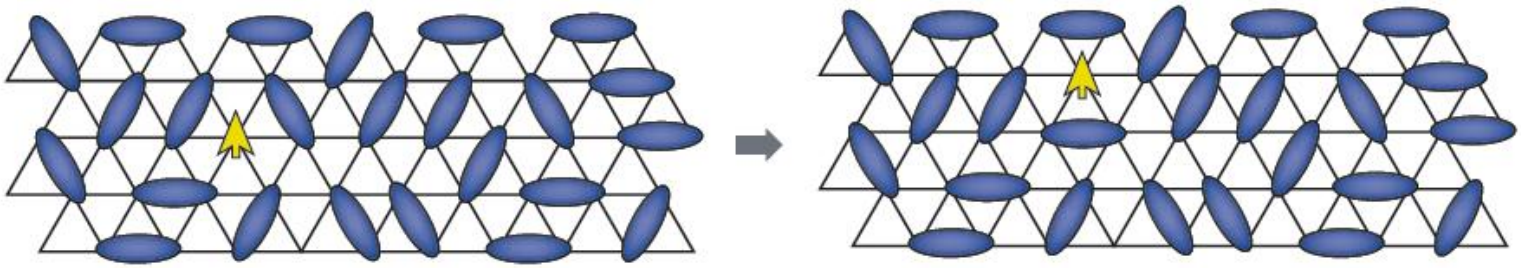
Spinon continuum

$\eta\omega = \varepsilon_1 + \varepsilon_2$

$q = p_1 + p_2$

M. Mourigal et al, Nat. Phys. 9, 435 (2013)

Fractional excitations: spinons



Excitations S=1/2 spinons (≠S=1 magnons)

- Free spinon Fermi surface QSL

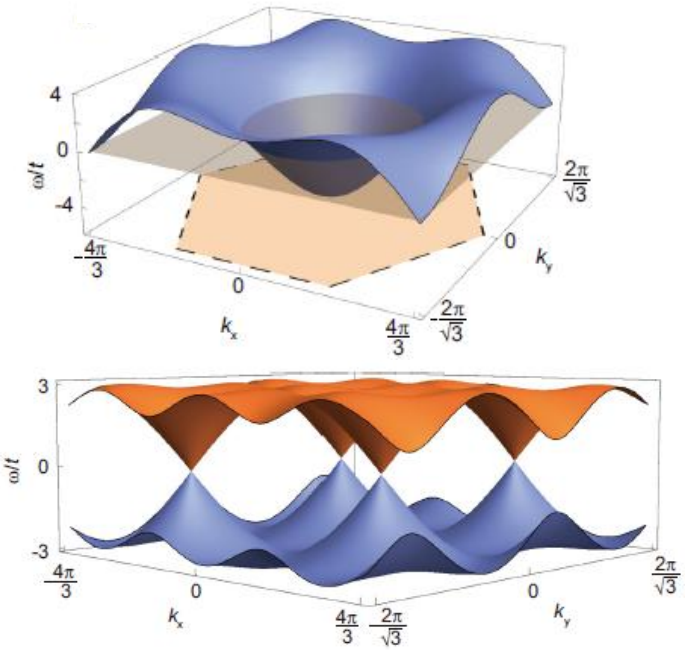
  $C_v \sim T$; Korringa $1/T_1TK^2=cste$

- … or more complex Fermi Surface

  Dirac QSL $C_v \sim T^2$; $\chi \sim T$; $1/T_1 \sim T^{\eta}$

  Partially or fully gapped

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



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

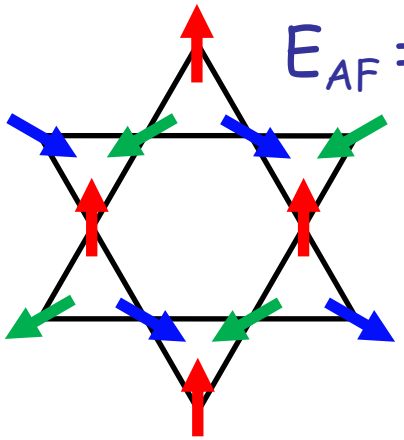
ideal material for spin liquid physics ?

- Low spin S=1/2
- geometrical frustration – triangular lattice

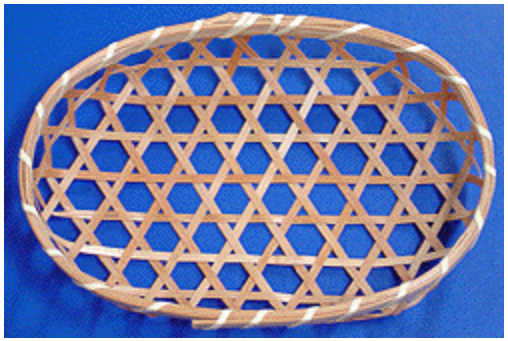
Not enough!

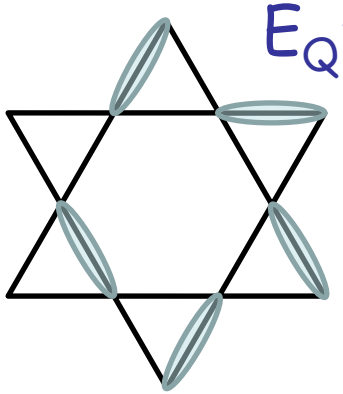
- Lecheminant, PRB **56**, 2521 (1997)
- Waldtmann *et al.*, EPJB **2**, 501 (1998).

- Lattice with low coordination number (z=4) : kagome



$E_{AF} = zJS_i.S_j/2 = -J/4$





$E_Q = -3J/8$

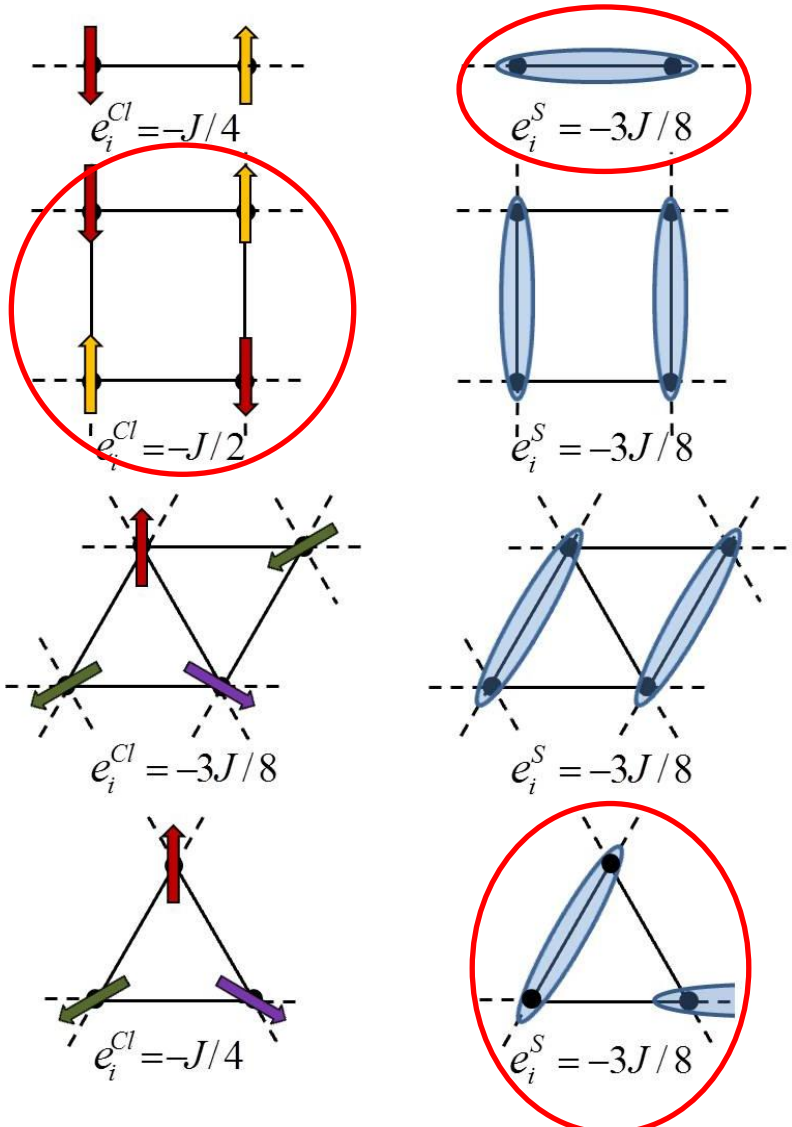
Extension to 3D, difficult because z tends to increase..
->Very few examples, none with 3d transition metals

ideal material for spin liquid physics ?

Néel state: Dimer state

1D

2D



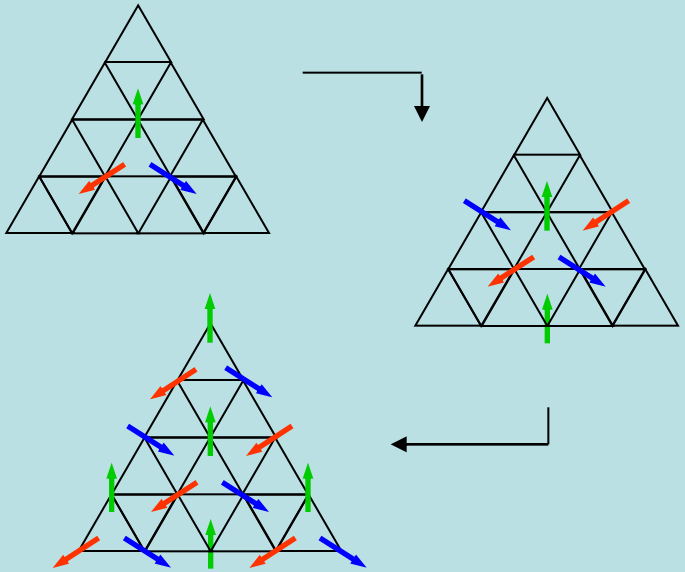
Néel state energy per site:
$zJS_i.S_j/2$

?

ideal material for spin liquid physics ?

triangular

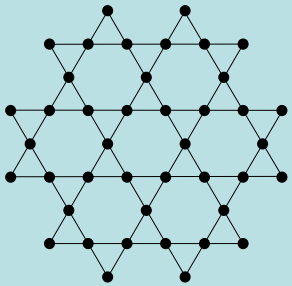
Edge sharing geometry

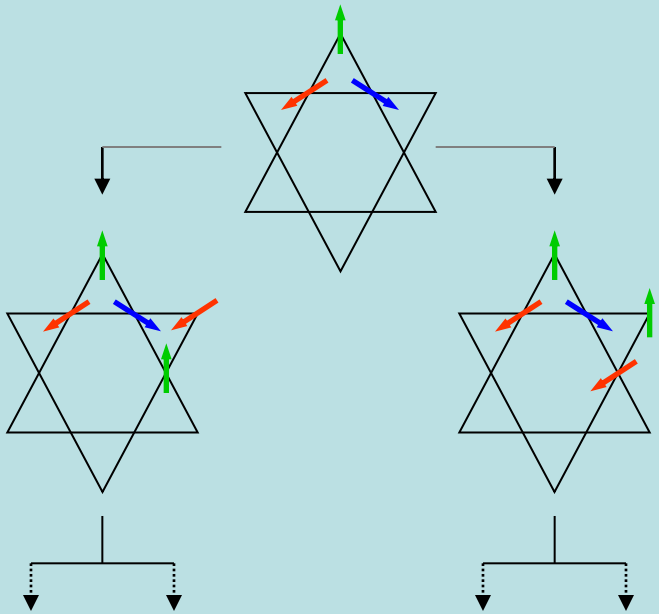


Marginal degenerecy (=2)

Kagome

Corner sharing geometry





Macroscopic degenerecy

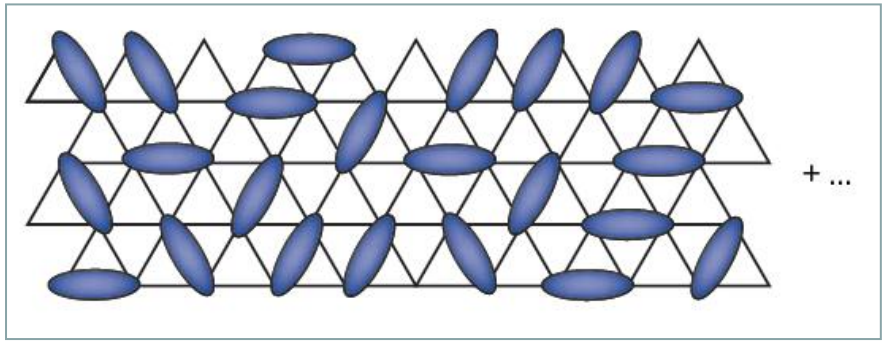
Two prototypes of quantum spin liquid

Gapped Z_2

Gapped magnetic excitations (S=1/2)

Gapped non-magnetic excitations

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



Short range RVB

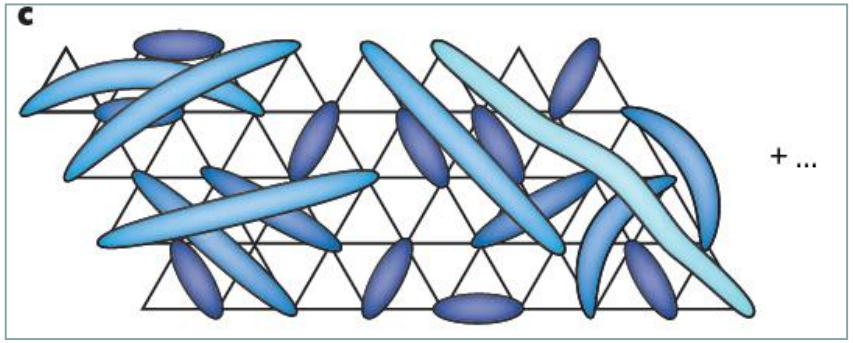
Yan et al, science 2011
S. Depenbrock et al, PRL 109, 2012

Δ =0.13(1)J

Algebraic/Critical/Dirac/U(1)

Gapless excitations

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



Long range RVB

Hastings, PRB 63, 2000
Ran et al, PRL 98, 2007
Y. Iqbal et al, PRB 87, 2013
He et al, PRX, 2017
Liao et al, PRL 118, 2017…

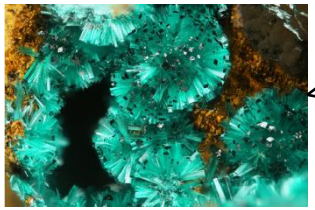
Still debated !

Materials are mostly existing minerals

all made of Cu^{2+} S=1/2

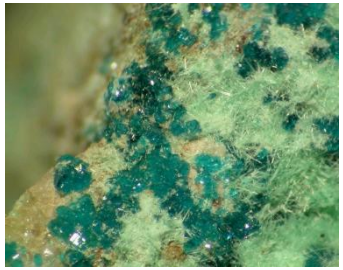
Herbertsmithite

MP Shores et al, JACS, 2005



Brochantite,

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



Haydeeite

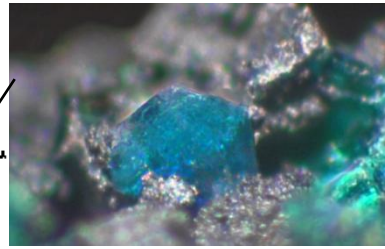
R. Colman et al, Chem. Mater. 2010

Kapellasite

R. Colman et al, Chem. Mater. 2008

Vólborthite

Z. Hiroi et al, JPSJ 2001



Barlowite

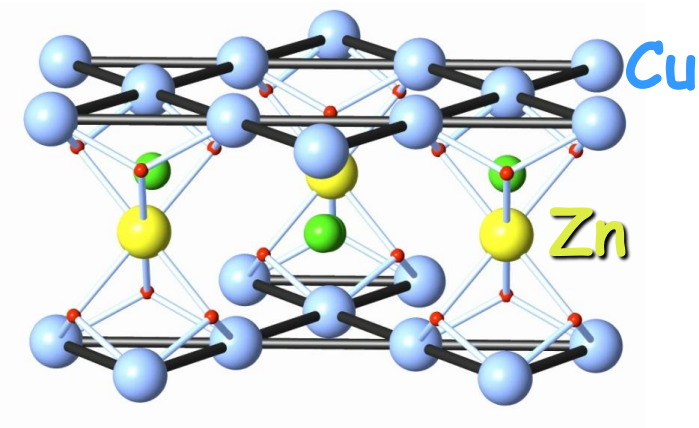
Han et al, PRL 2014

Vesignieite

Y. Okamoto et al, JPSJ 2009

Herbertsmithite:
$ZnCu_3(OH)_6Cl_2$

Cu^{2+}, S=1/2
J=180 K (AF)



Herbertsmithite remains the closest realization so far to the QKHAF with perturbations (DM, nnn J..) <J/10

Role of perturbations in real compounds?

Spin gap issue not settled mainly because of Zn/Cu disorder

P. Mendels' talk!

-> more refined experiment/analysis (SC), NMR, INS..

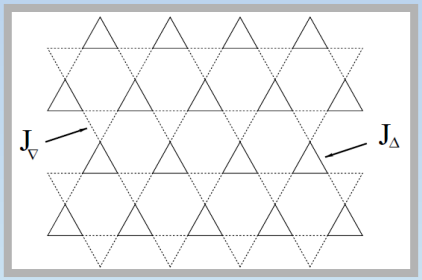
-> mastering the defects at the synthesis stage

-> **Need for other and different examples…**

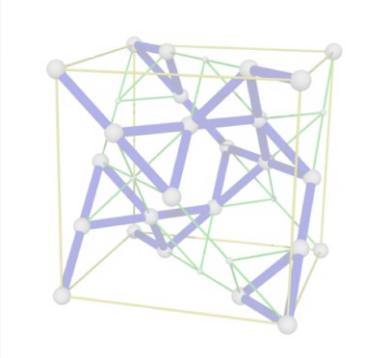
Quantum spin liquids: beyond the kagome

Fabrice Bert
Spectrosopies of Quantum Materials, LPS, Orsay

- Quantum spin liquids and frustrated magnetism
- Breathing kagome spin liquid (DQVOF)



- Hyperkagome lattice: a new player based on Cu^{2+} S=1/2 : $PbCuTe_2O_6$



Breathing kagome lattice: DQVOF

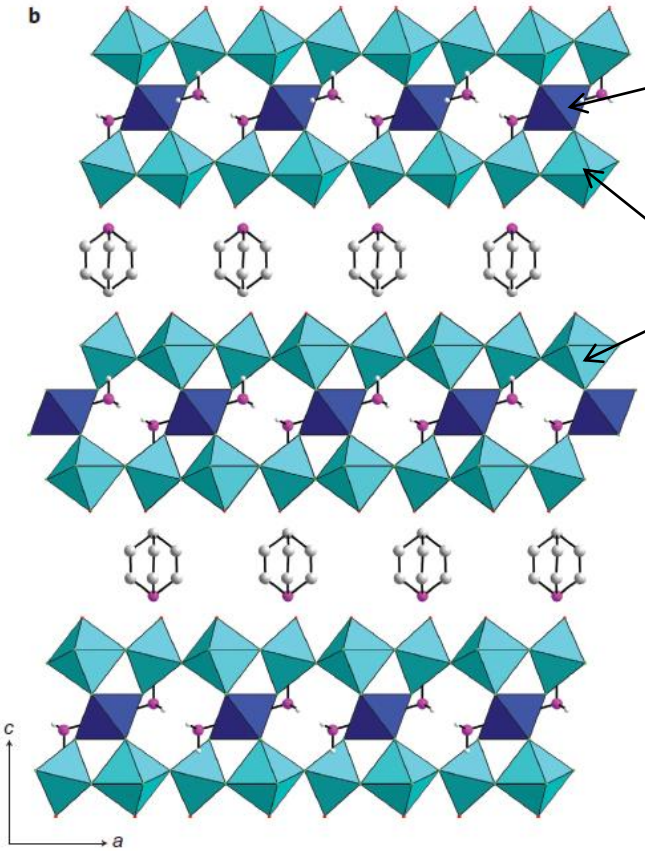
nature chemistry
ARTICLES
PUBLISHED ONLINE: 28 AUGUST 2011 | DOI: 10.1038/NCHEM.1129

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]*

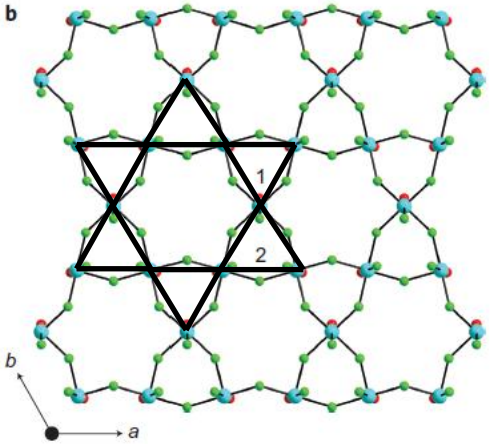
$[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$

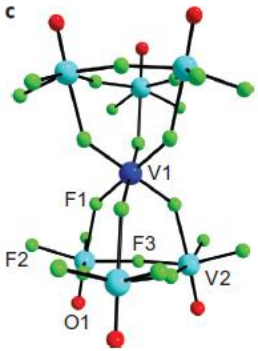
= **DQVOF**



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

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





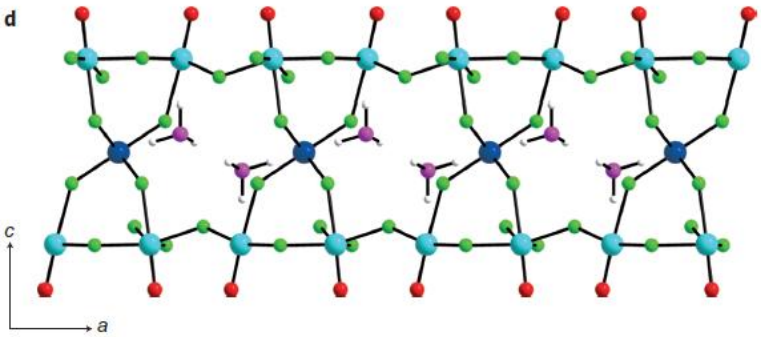
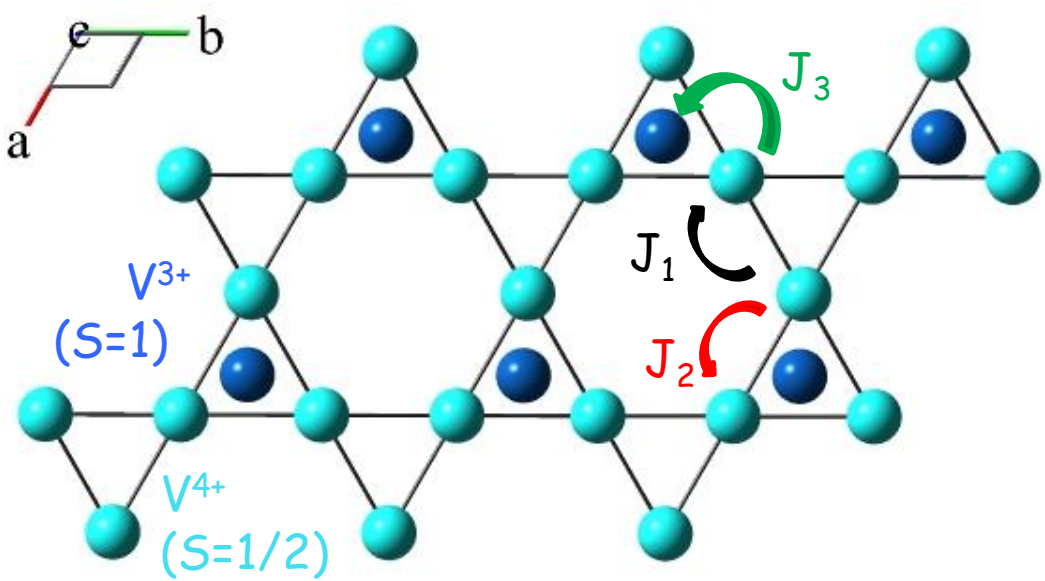
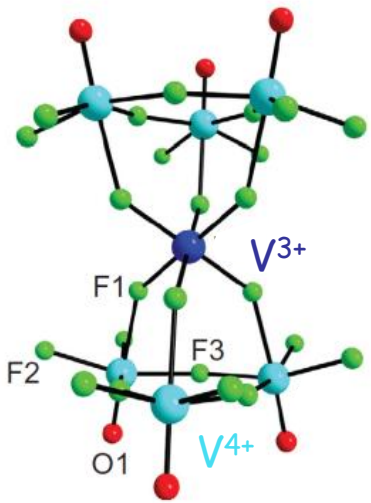


Figure 2 | Polyhedra views of the structure of $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$.

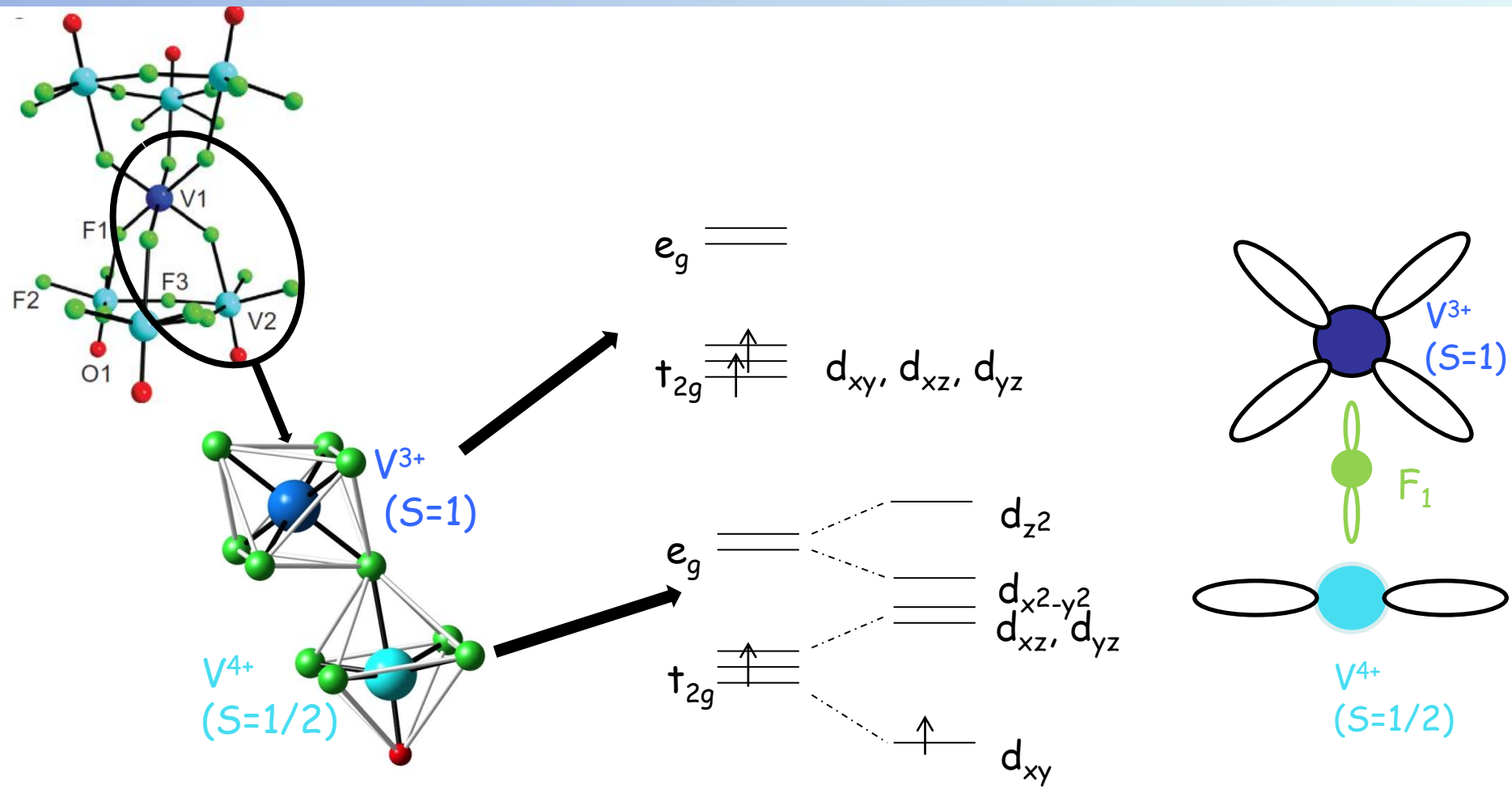




Role of spins S=1 ?

Relevance of the quantum kagome antiferromagnet model ?

DQVOF : magnetic model

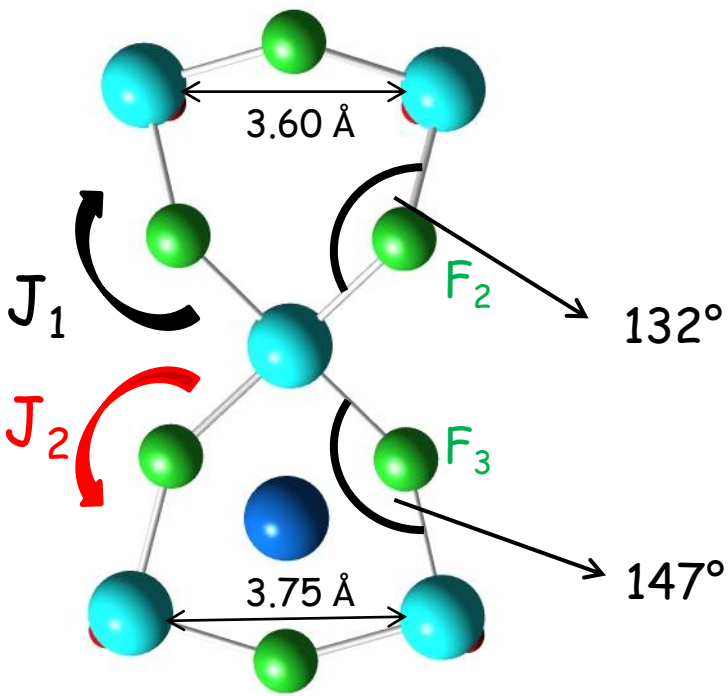


No hybridation:

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

-> kagome planes are decoupled from each others

DQVOF : magnetic model



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

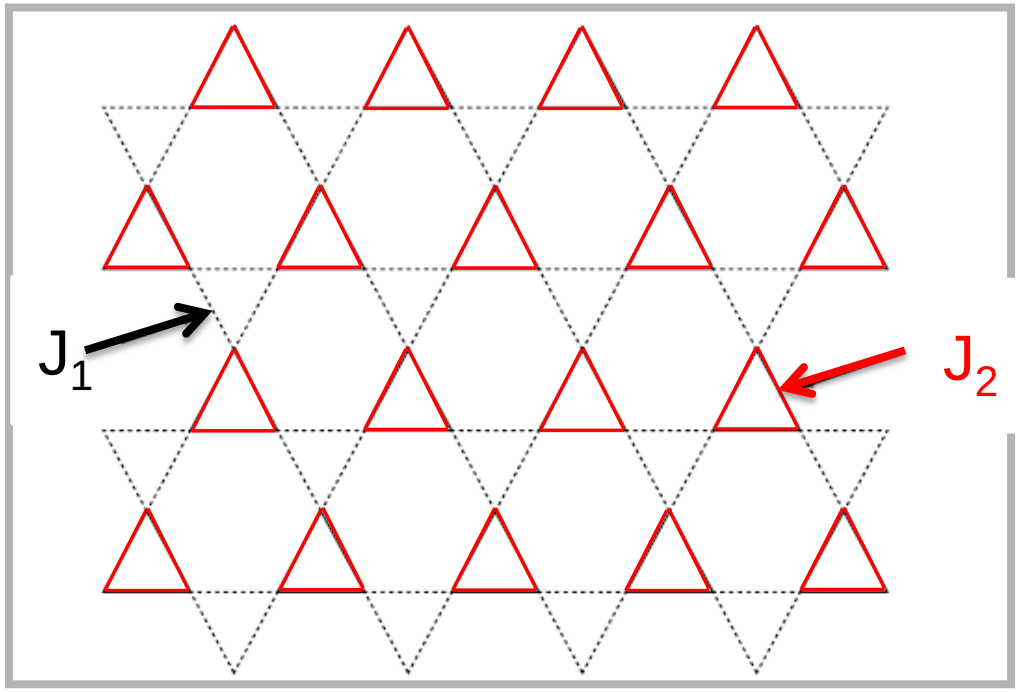
$J_1\sim47$ K
$J_2\sim73$ K

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

First experimental realisation of the trimerized/breathing kagome model.

Trimerized or breathing kagome model

Retains all the degeneracy of the isotropic kagome model (J_1=J_2)



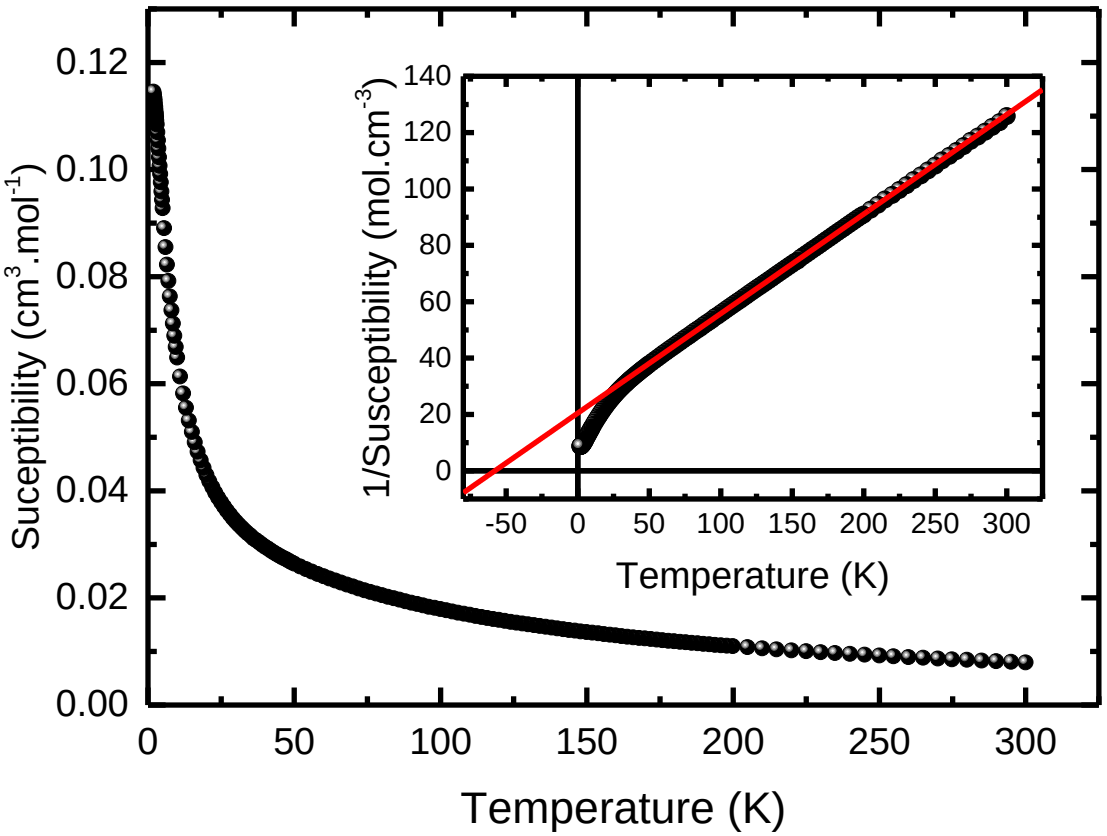
F. Mila, Phys Rev Lett 81, 2356 (1998)

M. Mambrini, F. Mila, Eur. Phys. J. B 17 (4) 651-659 (2000)

M.E Zhitomirski, Phys Rev B 71, 214413 (2005)

Highly trimerized model (J_1<<J_2) SR-RVB favored -> gapped spin liquid

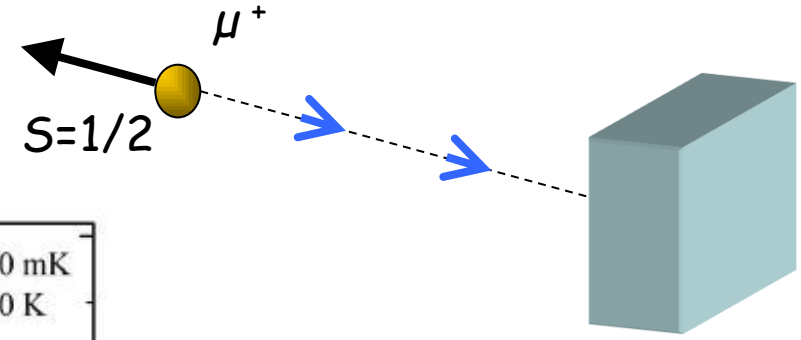
No studies since then on the J_1~J_2 limit

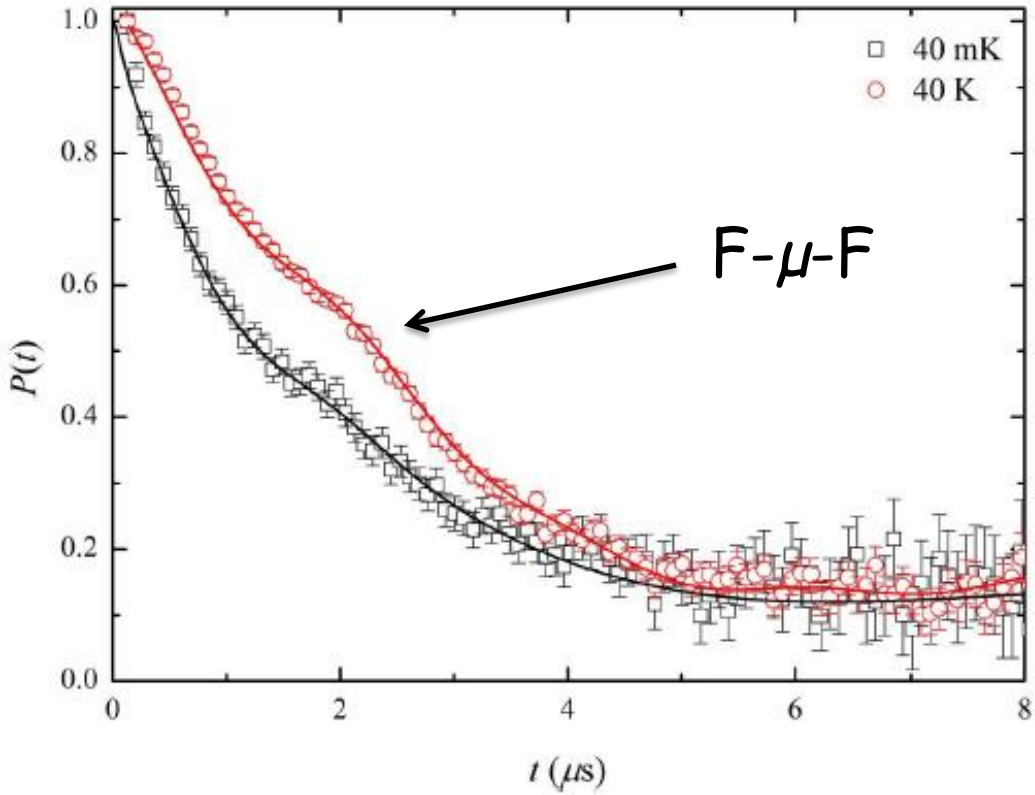


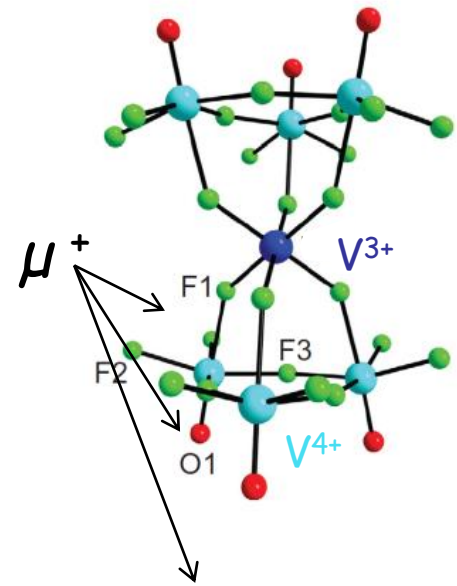
J_{Mean} = 65(6) K

AF Interaction and no sign of transition :
highly frustrated compound.

Muon spin relaxation (μSR)







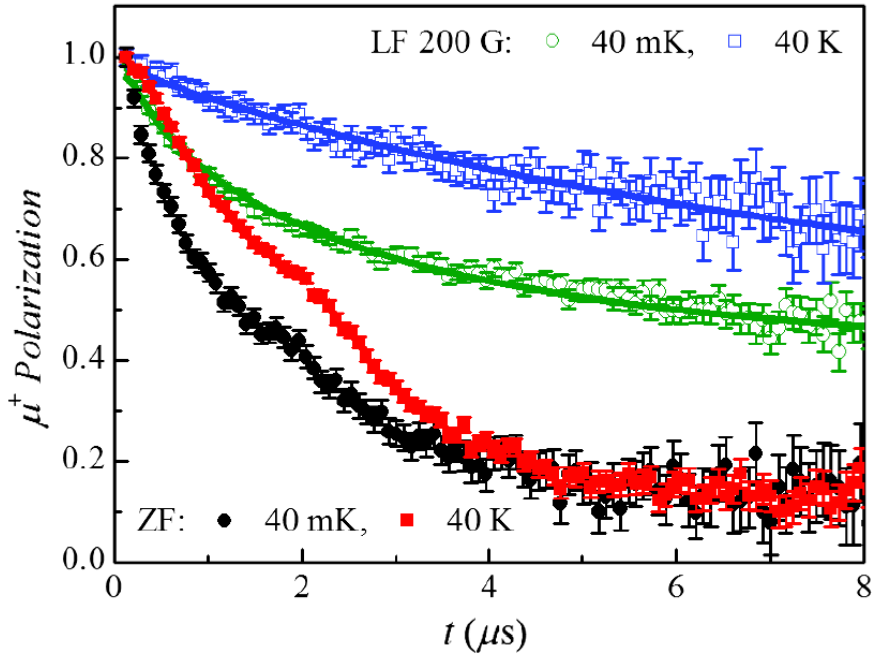
DQ ($[NH_4]_2[C_7H_{14}N]$)

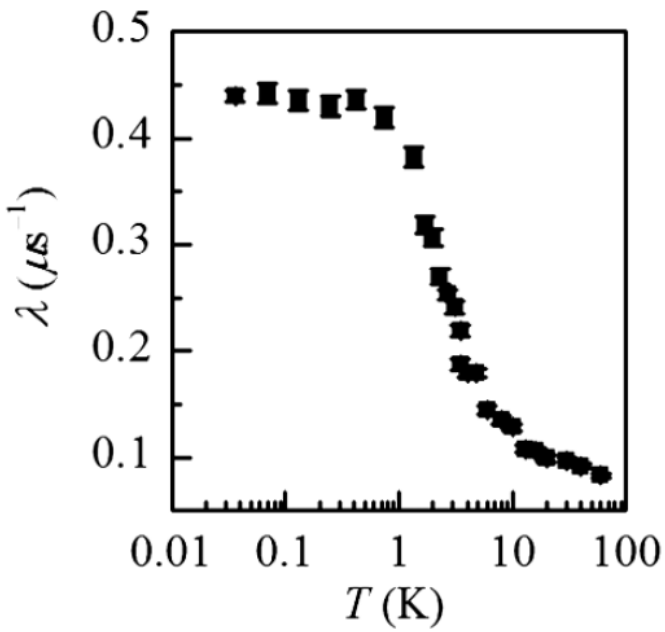
No fast relaxation, no '1/3rd tail' at low T

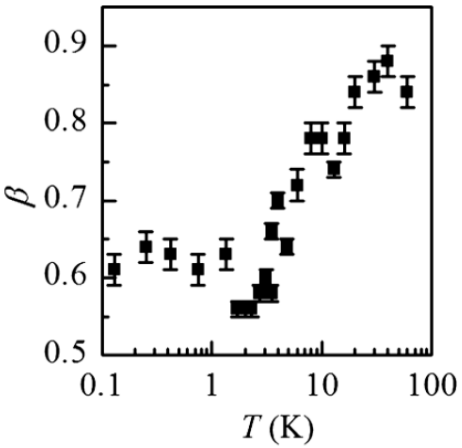
-> no spin freezing down to 40mK

L. Clark, J-C. Orain *et al*, PRL **110**, 207208 (2013).
J-C. Orain *et al*, J. Phys. Conf. Ser. **551**, 012004 (2014)

Muon spin relaxation (μSR)

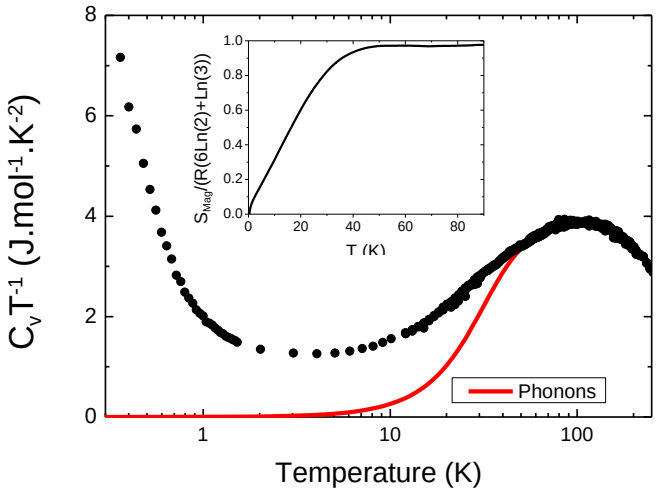






Low T spin dynamics
-> persistence of spin dynamics
-> influence of nearly free V^{3+}, S+1

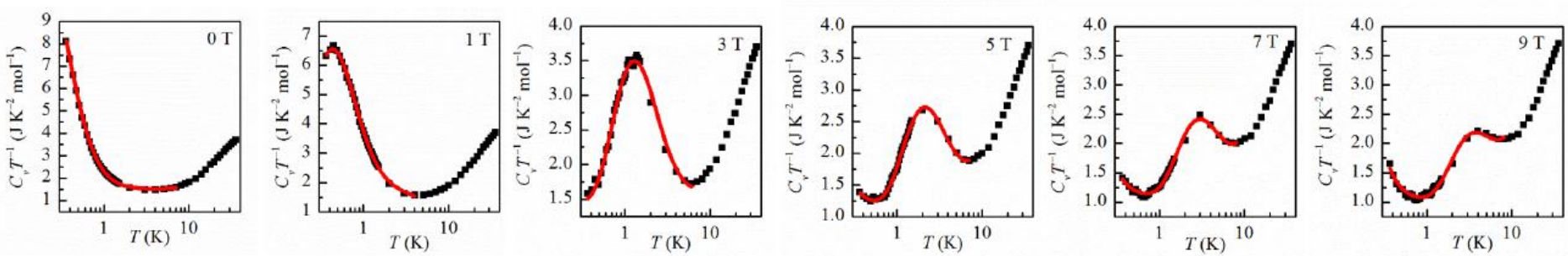
Heat capacity



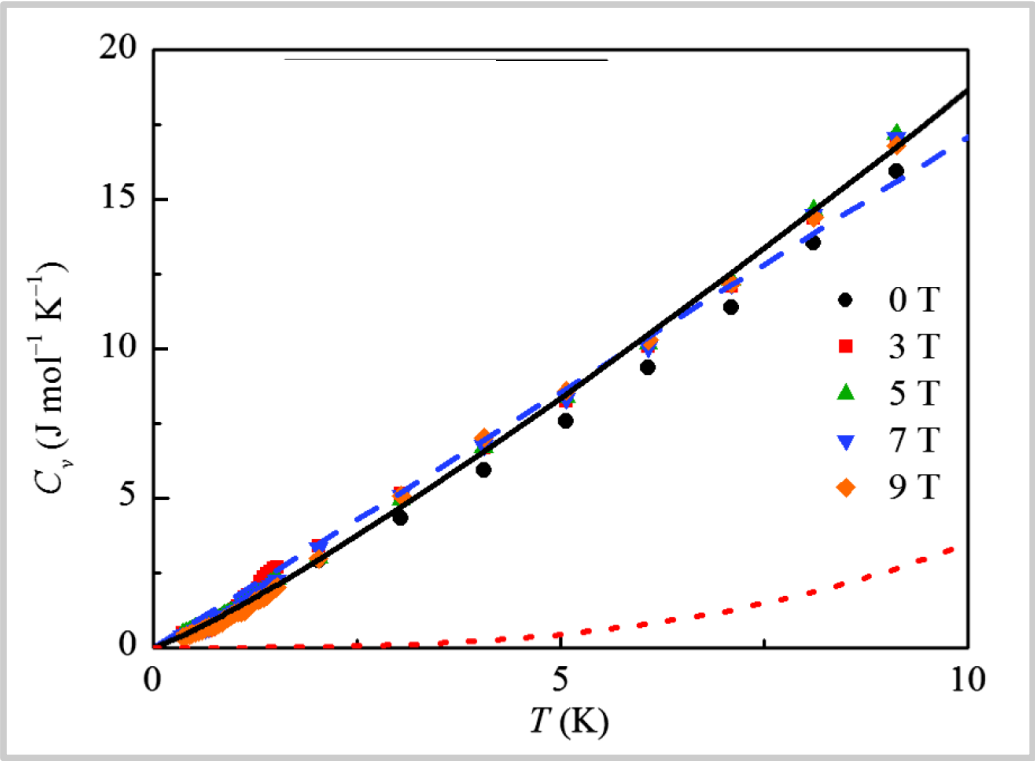
Phonons
+
V^{3+} (S=1) Schottky
+
H/F nuclear Schottky
+
kagome ?

Field dependence

✗
✓
✓
✗ ?



Heat capacity

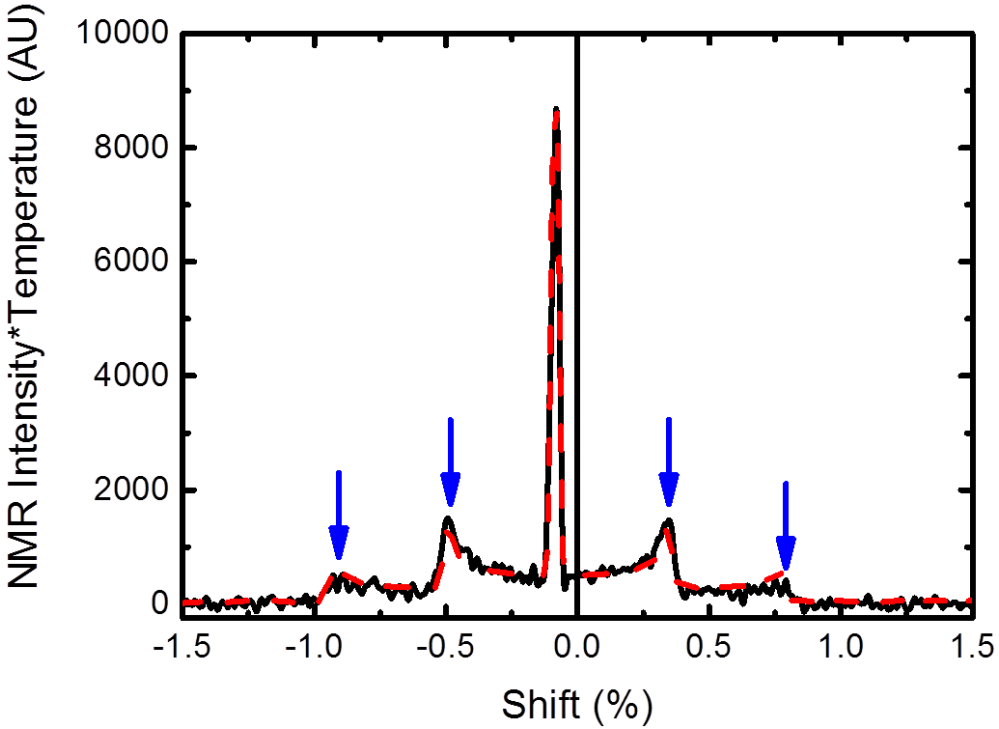


The excitation spectrum is not gapped (Δ<0.3K~J/200)

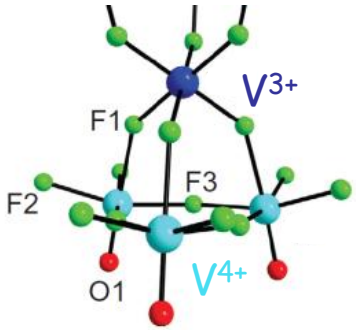
- Gapless fermionic spinon excitations, γ=0.2 J /K^2/mol V^{4+}
- Both magnetic and singlet excitations contribute

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

^{17}O NMR



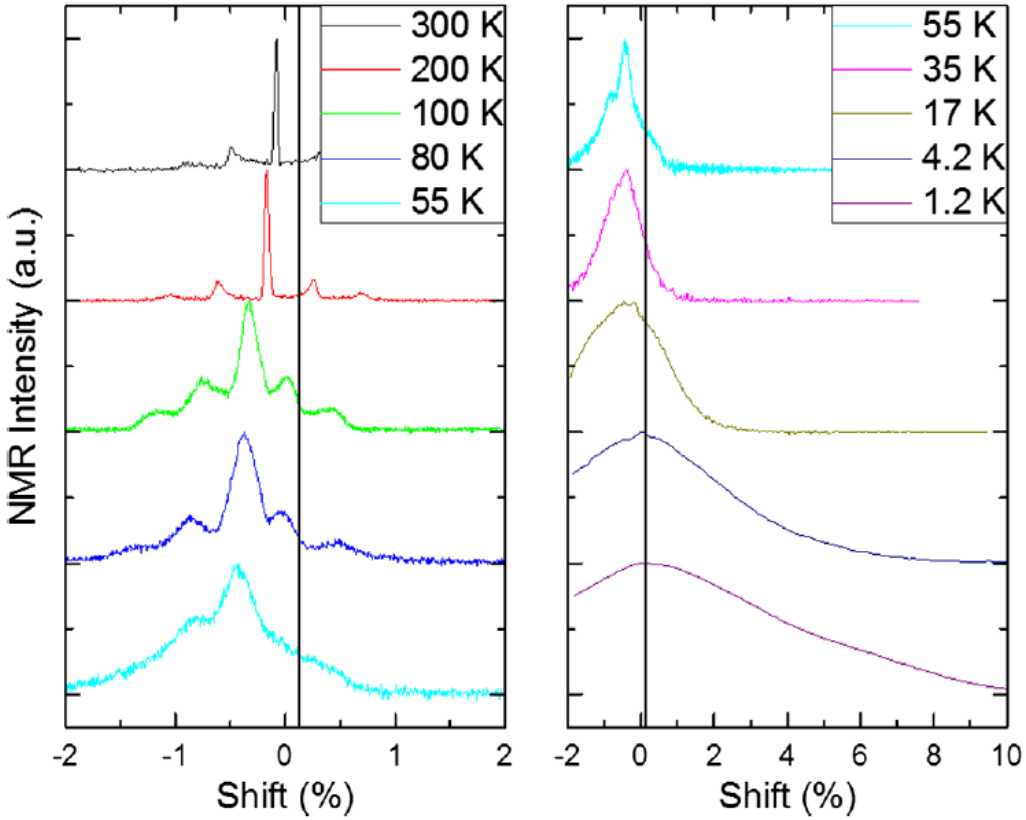
I = 5/2

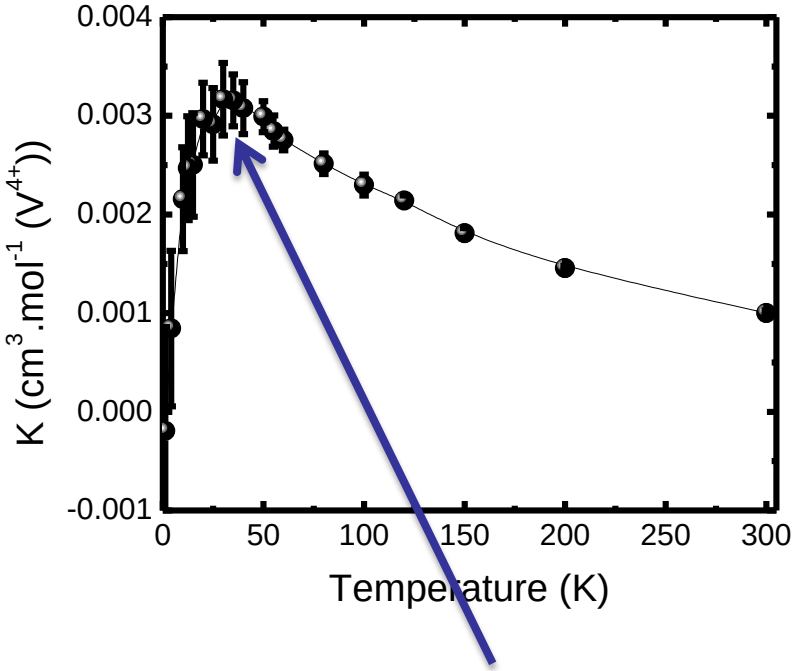


One O site (as expected): no dilution of the kagome planes

J-C. Orain *et al*, PRL **118**, 237203 (2017)

Temperature dependence: local susceptibility

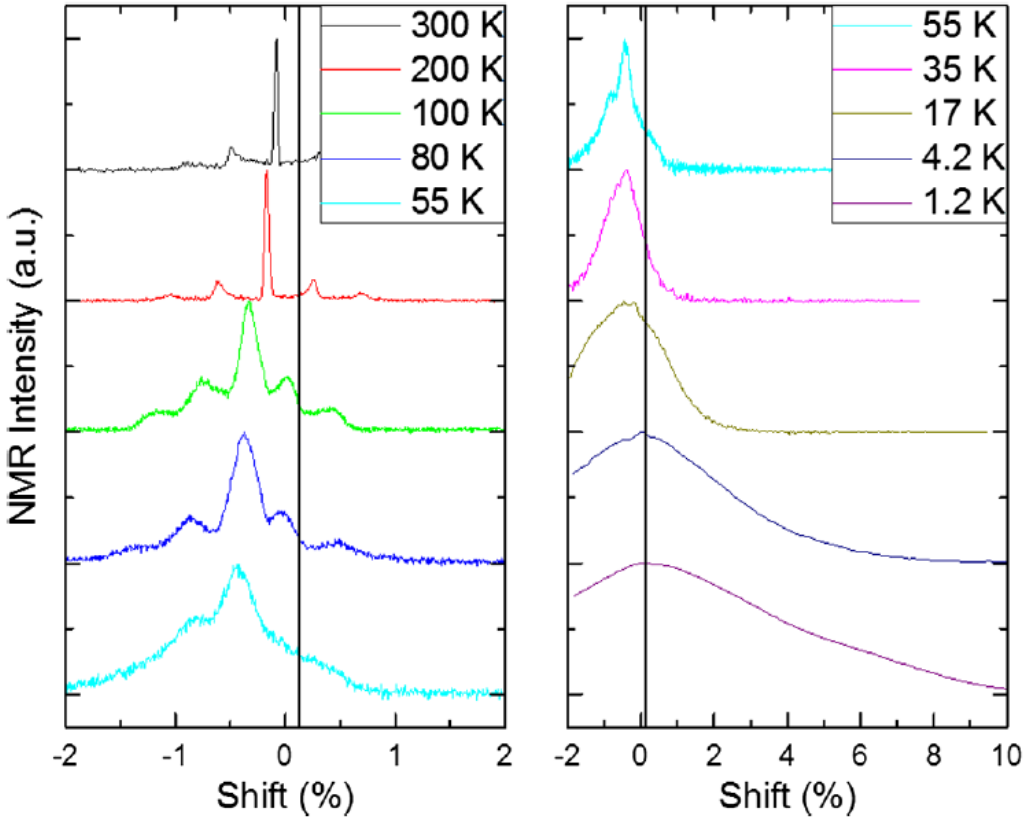


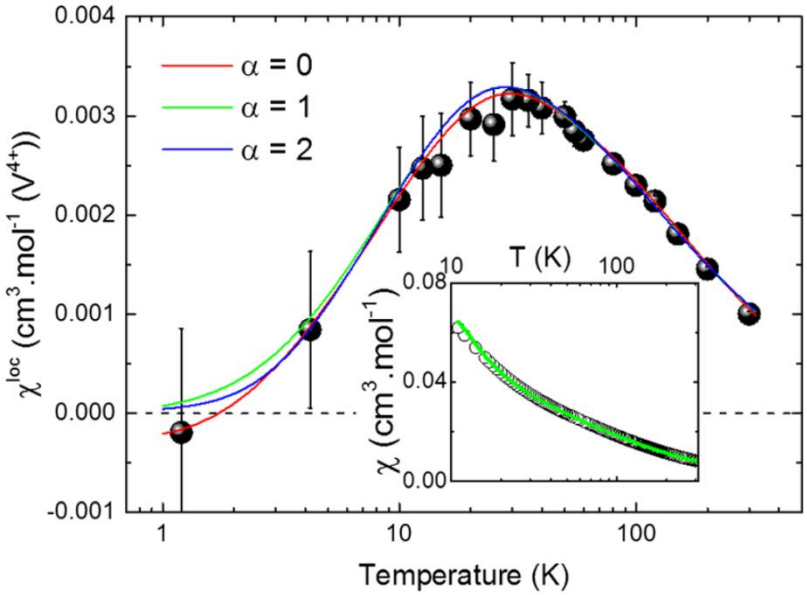


Enhancement of AF correlations at $J_{Mean}/2$
Hidden by V^{3+} contribution in squid χ

J-C. Orain *et al*, PRL **118**, 237203 (2017)

Temperature dependence: local susceptibility

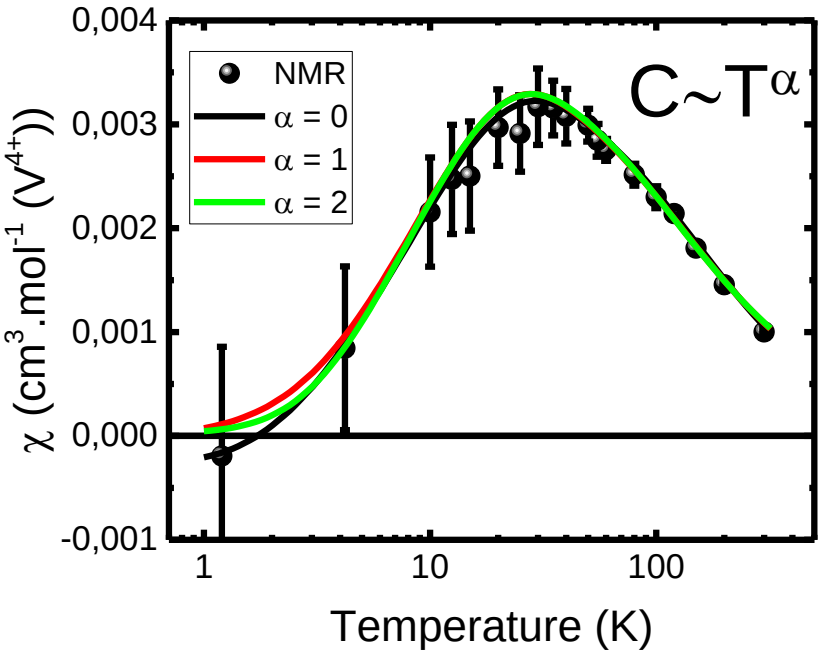




Enhancement of AF correlations at $J_{Mean}/2$
Hidden by V^{3+} contribution in squid χ

~0 susceptibility at T=0 K

Series expansion analysis of the local susceptibility



Extension of standard HTSE to full T range

approximation of s(e,H) using

-HTSE for f(T) at high energies
-a model for C(T) at low energies

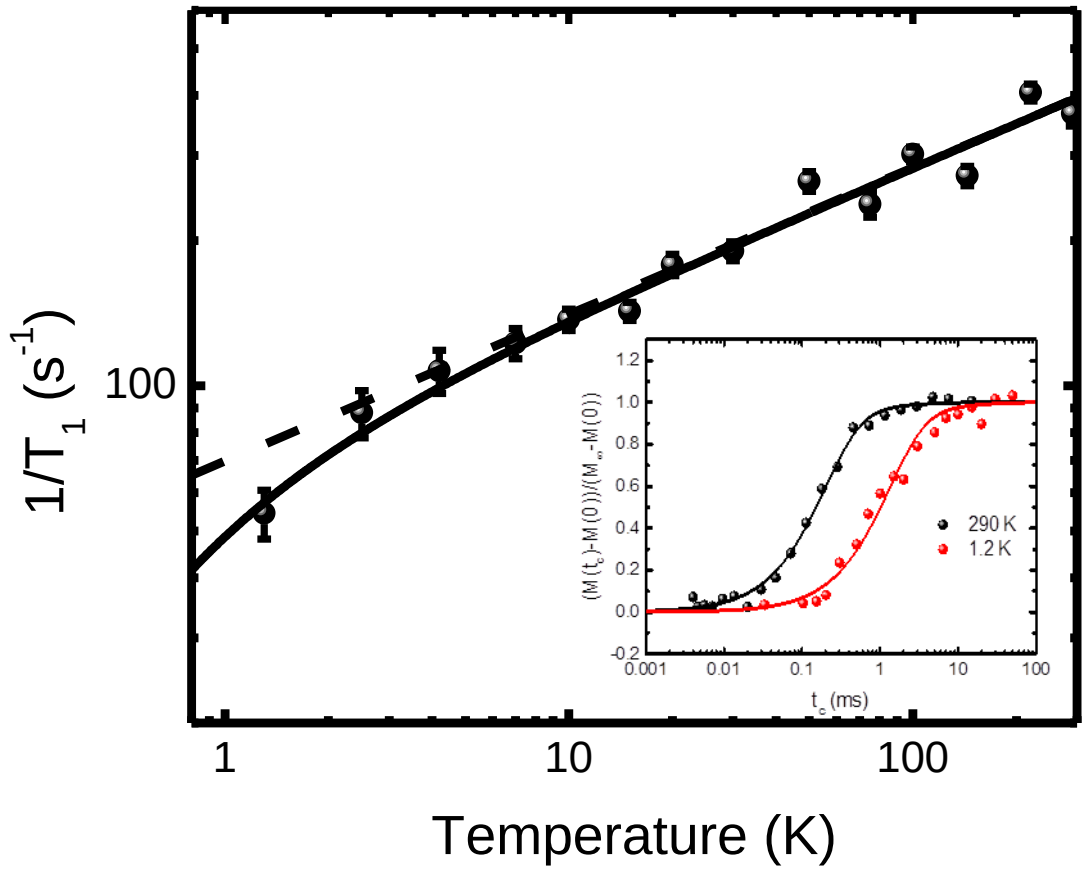
B. Bernu and C. Lhuillier, PRL 114; 057201 (2015)

Spin-gap: $0 < \Delta < 0.05(2)\ J_{mean}$

$J_1/J_2 = 0.55(4)$ $J_{mean} = 60(7)$ K

Spin Lattice Relaxation Time

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



$$\frac{1}{T_1} = AT^{\alpha} e^{-\Delta/T}$$

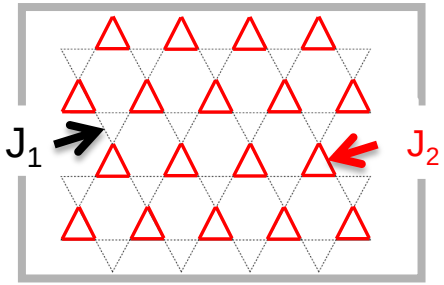
$$\alpha = 0.30(3)$$

$$\Delta = 0.4(4)\mathrm{K}$$

No spin gap (or tiny ~0.007(7) J_{mean})

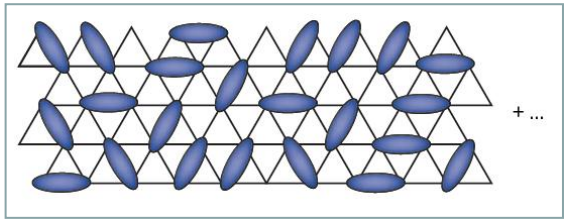
J-C. Orain *et al*, PRL **118**, 237203 (2017)

Recentent theoretical developpements



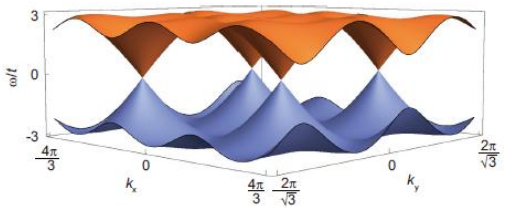
Back to theory..
beyond the highly trimerized limit ($J_1 \ll J_2$)

F. Mila, 1998
M. Mambrini, F. Mila, 2000
M.E Zhitomirski, 2005



- Schaffer et al, PRB 95, 054410 (2017)
  Variatonal Monte Carlo
  -> gapped $\mathbb{Z}_2$ SL for J_1/J_2 ~0.5

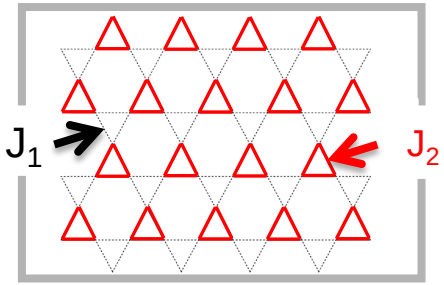
- Y. Iqbal et al, PRB 97, 115127 (2018)
  Variatonal Monte Carlo
  -> U(1) Dirac SL (gapless) for $J_1/J_2 > 0.3$



- C. Repellin et al, PRB 96 205124 (2017)
  DMRG (tubes), ED
  -> SL similar to isotropic kagome with Dirac cones signatures
  for $J_c < J_1/J_2 < 1$; $J_c < 0.1$?

  -> continuity to isotropic point
  -> existence of a nematic phase for high breathing ratio

Recentent theoretical developpements



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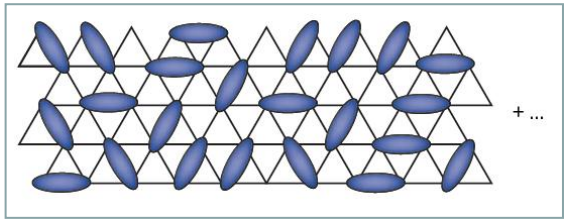

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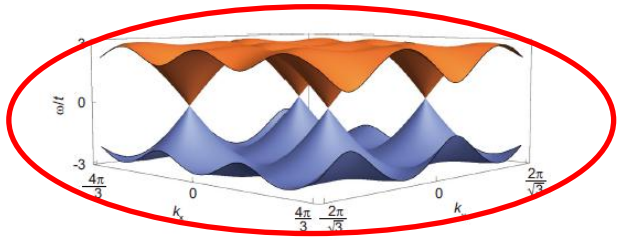

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  -> continuity to isotropic point
  -> existence of a nematic phase for strong breathing

DQVOF and Breathing kagome: conclusions

Weakly trimerized/breathing kagome (J_1/J_2=0.55(5)).
First experimental realization of this model.

DQVOF : tiny gap (Δ < 0.007(7) J_{mean}) or gapless spin liquid.

Theoretical model is likely gapless, with a ground state similar to the isotropic kagome case

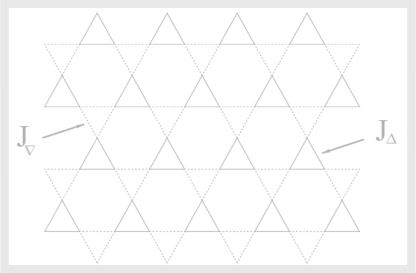
At Low T effect of the coupling between the interlayer V^{3+} and the kagome V^{4+} ?

More studies on new compounds of the VOF familly
with different organic molecules
-> different structures; S=1 kagome; …

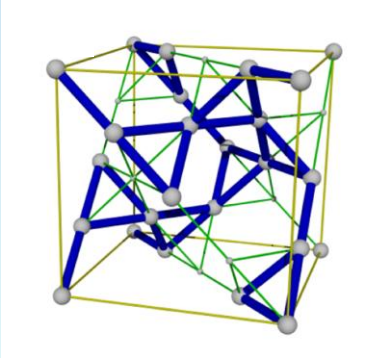
Quantum spin liquids: beyond the kagome

Fabrice Bert
Spectrosopies of Quantum Materials, LPS, Orsay

- Quantum spin liquids and frustrated magnetism
- Breathing kagome spin liquid (DQVOF)



- Hyperkagome lattice: a new player based on Cu^{2+} S=1/2 : $PbCuTe_2O_6$

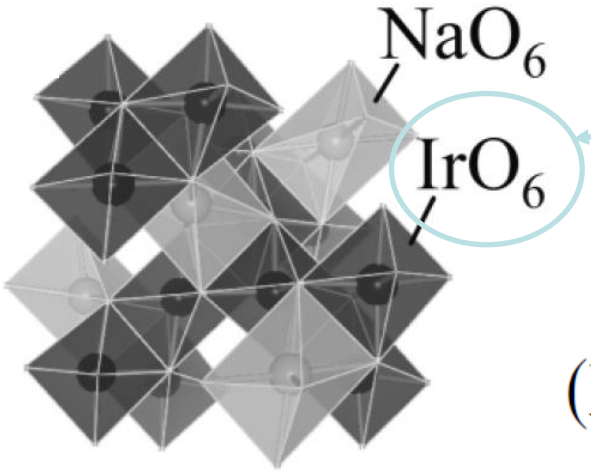


The archetypal hyperkagome: $Na_4Ir_3O_8$

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)



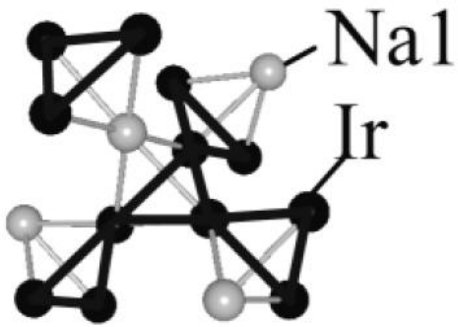
O Octahedron

Ir^{4+}: $S=1/2$ (t_{2g}^5) -> $J_{eff}=1/2$ (SOC)

B site ordered spinel

$(Na_{1.5})_1(Ir_{3/4}, Na_{1/4})_2O_4$

B site pyrochlore lattice



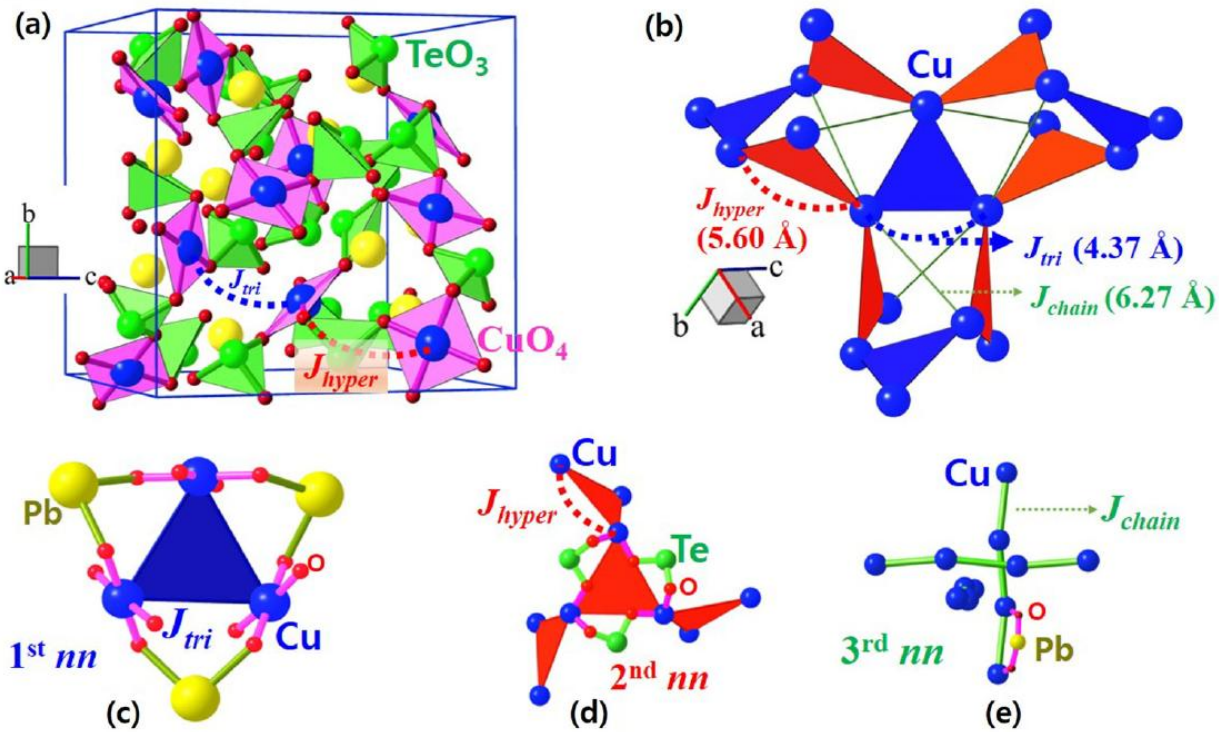
3D structure of
corner-sharing triangles (z=4)
+ $J_{eff}=1/2$ + J~300K (AF)
-> good SL candidate!

A new player: $PbCuTe_2O_6$

PHYSICAL REVIEW B **90**, 035141 (2014)

Magnetic properties and heat capacity of the three-dimensional frustrated $S = \frac{1}{2}$ antiferromagnet $PbCuTe_2O_6$

B. Koteswararao,[1,2] R. Kumar,[3] P. Khuntia,[4,*] Sayantika Bhowal,[5] S. K. Panda,[6] M. R. Rahman,[1] A. V. Mahajan,[3] I. Dasgupta,[5,6] M. Baenitz,[4] Kee Hoon Kim,[2,†] and F. C. Chou[1,‡]



3D network of Cu^{2+}
S=1/2

Strong connectivity (z=8)
>> hyperkagome (z=4)

J_{tri}/J_{hyper}=0.54 J_{hyper} J_{chain}/J_{hyper}=0.77

Cubic $P4_132$ (same as $Na_4Ir_3O_8$)

A new player: $PbCuTe_2O_6$

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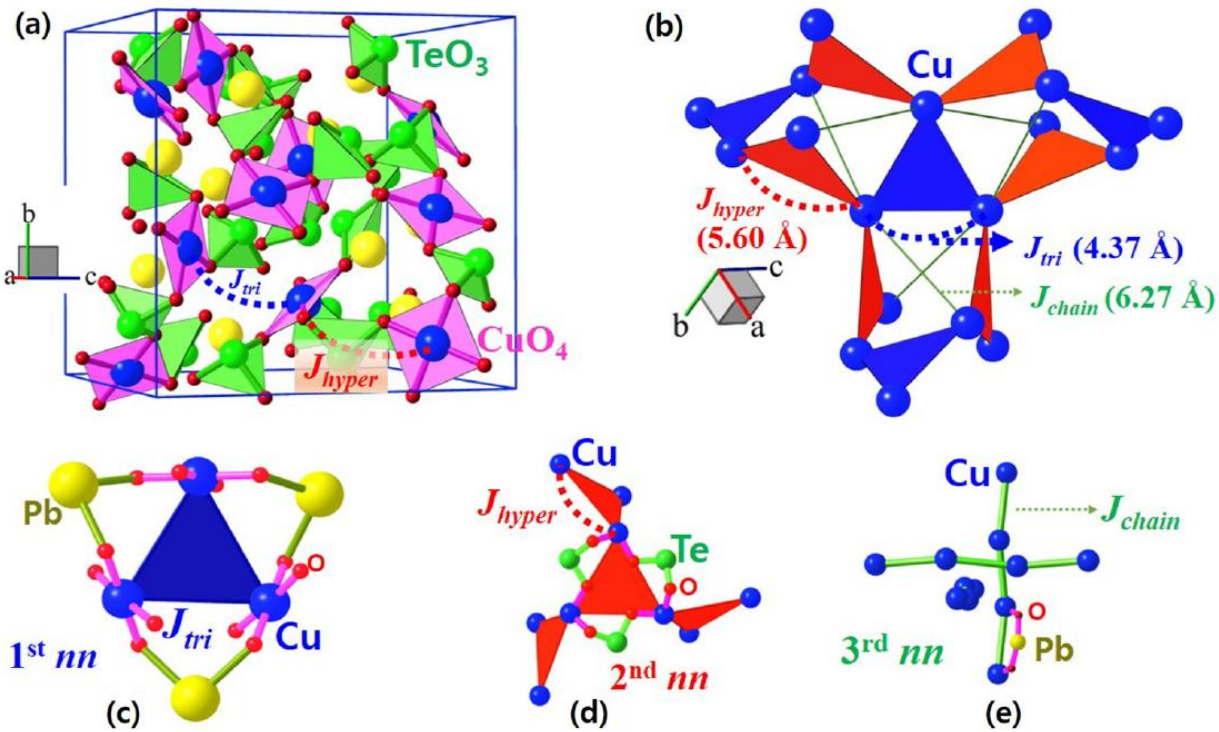


3D network of Cu^{2+}
S=1/2

Strong connectivity (z=8)
>> hyperkagome (z=4)

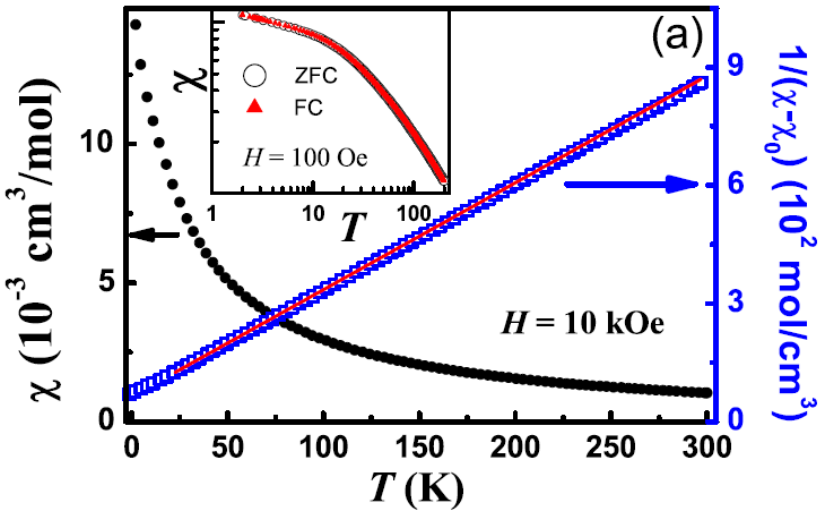
J_{tri}/J_{hyper}=0.54
=1

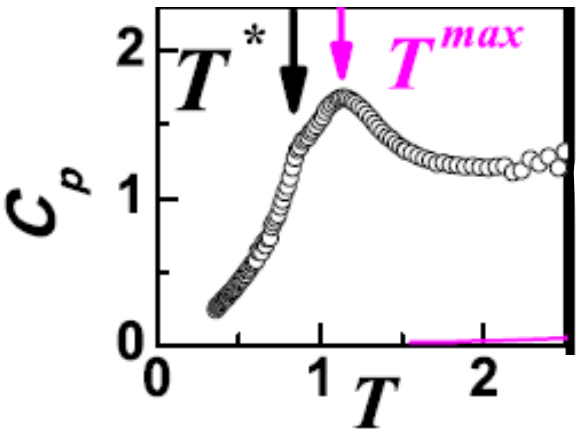
J_{hyper}

J_{chain}/J_{hyper}=0.77
=0.5

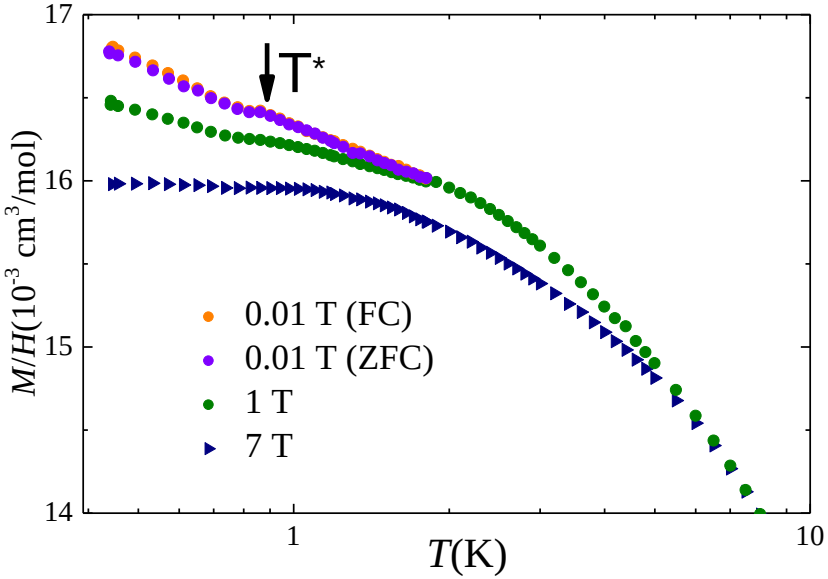
S. Chillal et al, arXiv:1712.07942

A new player: $PbCuTe_2O_6$



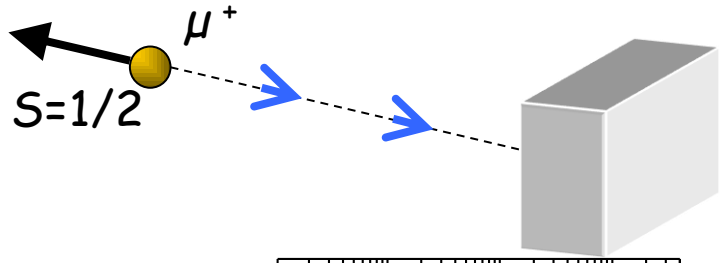


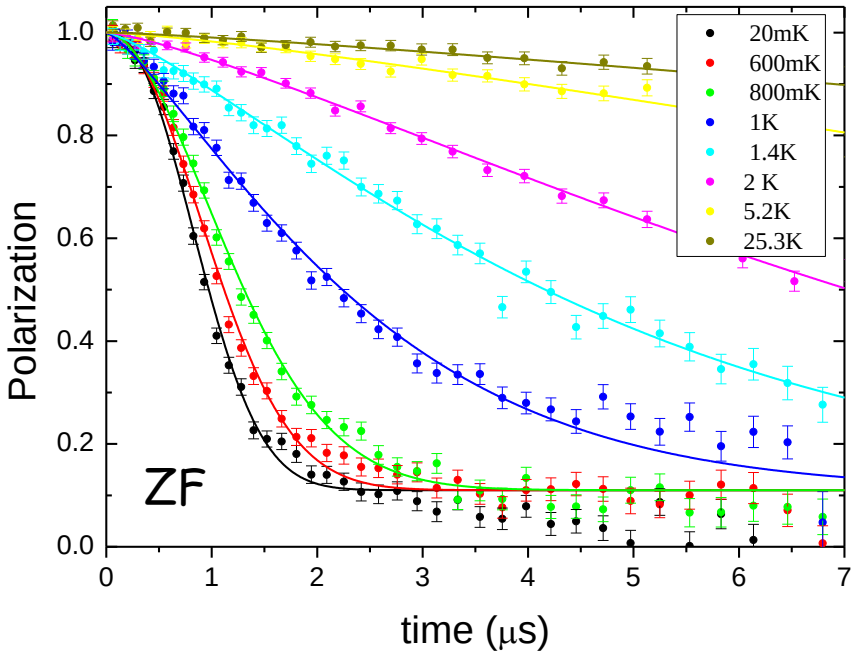
- Curie-Weiss $\theta_{CW} \approx 22$ K (AF)
- C_m/T max at 0.05 θ_{CW}
  Enhancement of short range correlations ?
- Anomaly in magnetization and heat capacity at T* =0.87 K ?
  (Vanishes at strong fields)

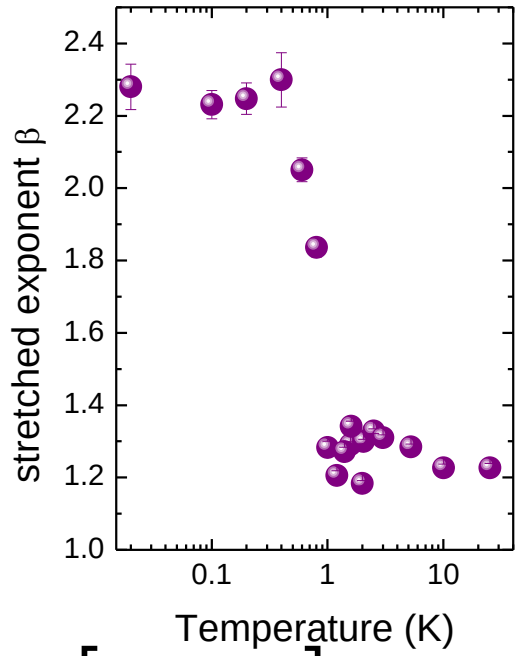


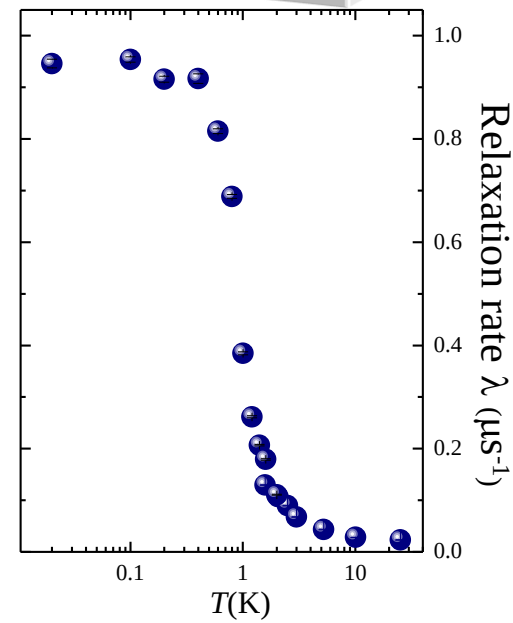
B. Koteswararao et al, PRB 2014
P. Khuntia, F. Bert et al, PRL 2016

$PbCuTe_2O_6$: Spin dynamics from μSR









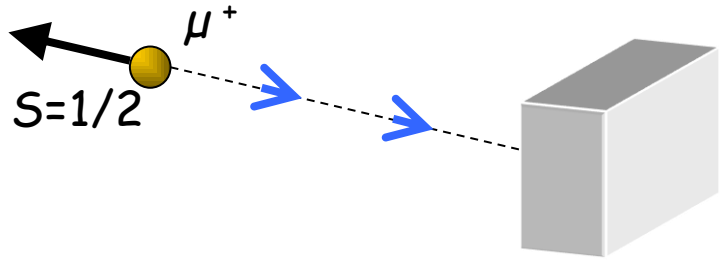
$$P(t) = \exp\left[-(\lambda t)^{\beta}\right]$$

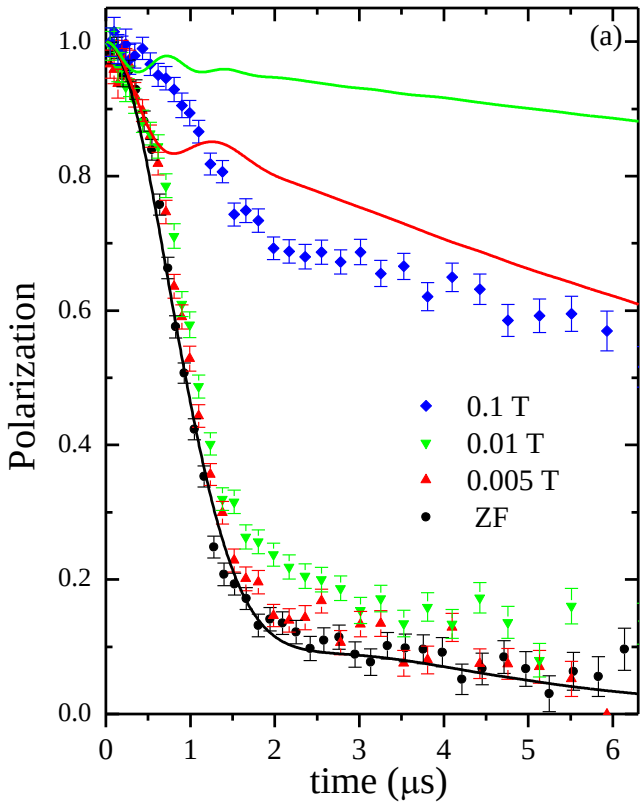
Dynamical ground state with persisting slow fluctuations

(no bulk magnetic transition at T*)

P. Khuntia, F. Bert et al, PRL 2016

Nature of the relaxation in the ground state





Zero field fits to a dynamical Kubo-Toyabe

$P_{\mathrm{DKT}}(t, \Delta H, \nu, H_{\mathrm{LF}})$ with $\Delta H = 1.1$ mT, $\nu = 0.7$ MHz

$\gamma_\mu \Delta H / \nu \sim 1.3$ close to static (~1)

-Very small internal fluctuating field

-very weak dependence on the applied field
« undecouplable gaussian shape »

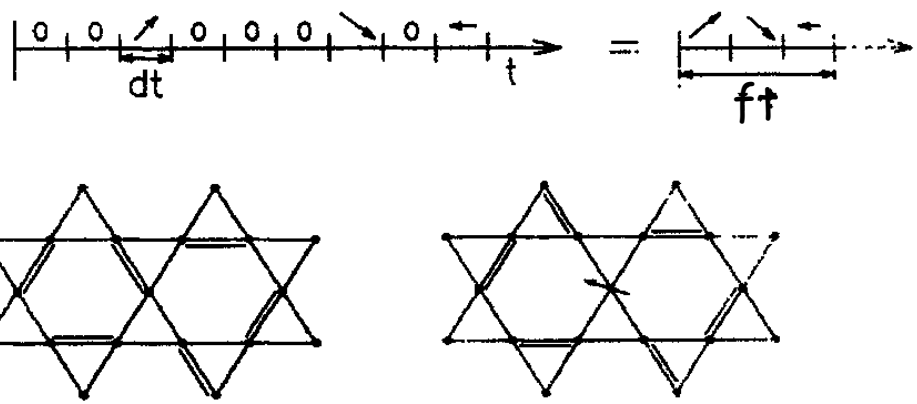
P. Khuntia, F. Bert et al, PRL 2016

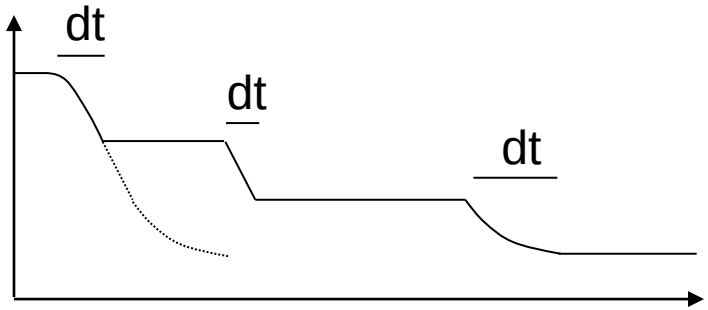
Sporadic fluctuations

VOLUME 73, NUMBER 24 PHYSICAL REVIEW LETTERS 12 DECEMBER 1994

Spin Fluctuations in Frustrated Kagomé Lattice System $SrCr_8Ga_4O_{19}$ Studied by Muon Spin Relaxation

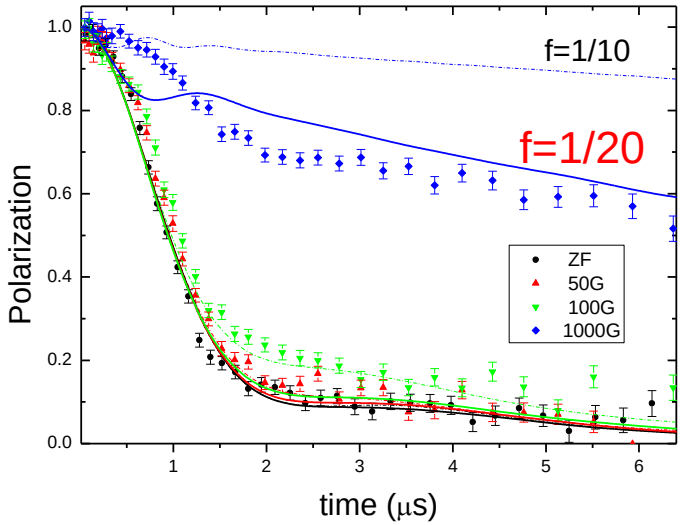
Y. J. Uemura,[1] A. Keren,[1] K. Kojima,[1] L. P. Le,[1] G. M. Luke,[1] W. D. Wu,[1] Y. Ajiro,[2] T. Asano,[2] Y. Kuriyama,[2] M. Mekata,[2] H. Kikuchi,[3] and K. Kakurai[4]



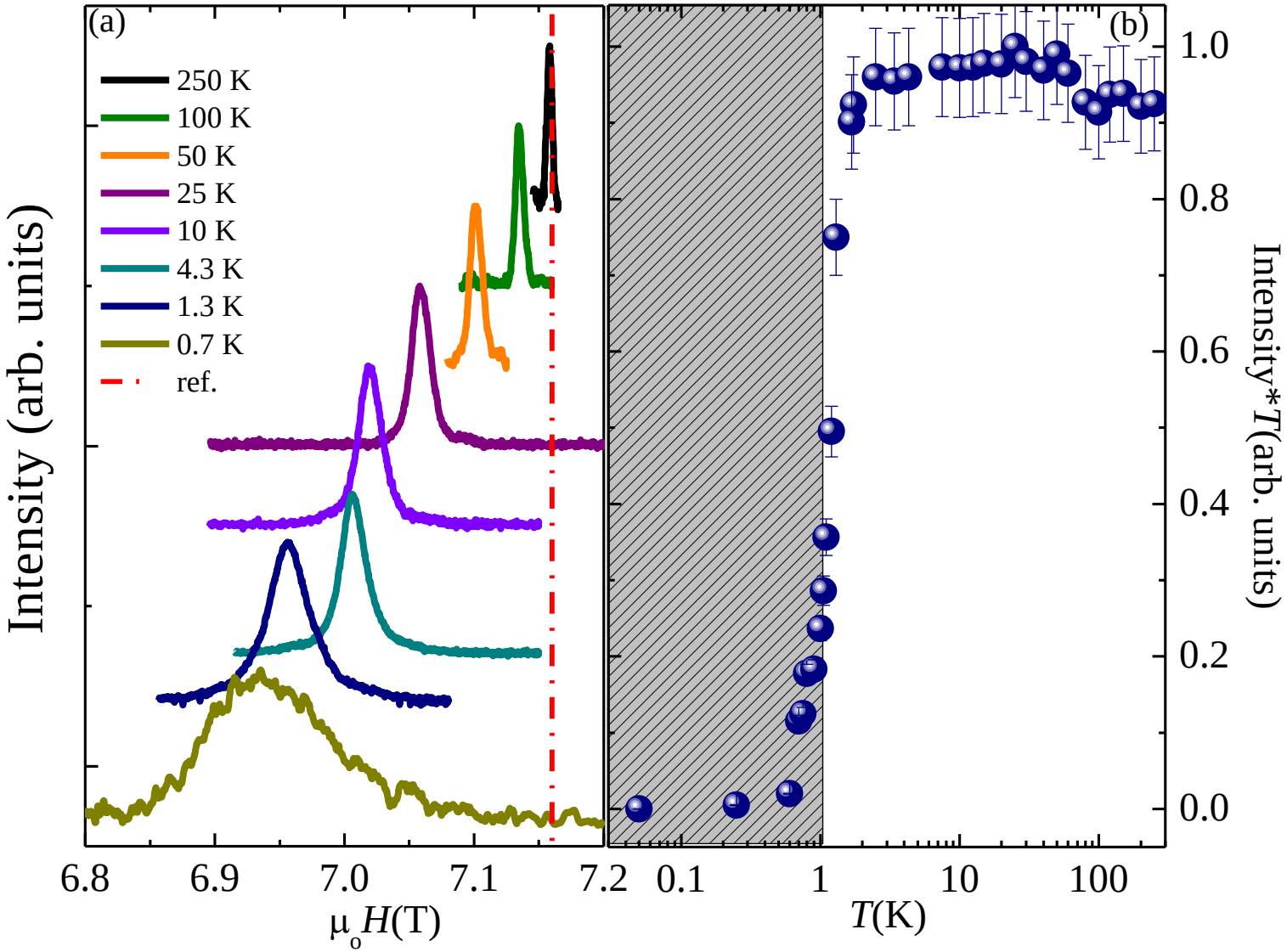


$$P(t) = P_{DKT}(ft, \Delta H, \nu, H_{LF}) = P_{DKT}(t, f\Delta H, f\nu, fH_{LF})$$

This mystery of the line shapes can be resolved if we assume that a local field of significant magnitude exists at each muon site, not persistently, but sporadically.

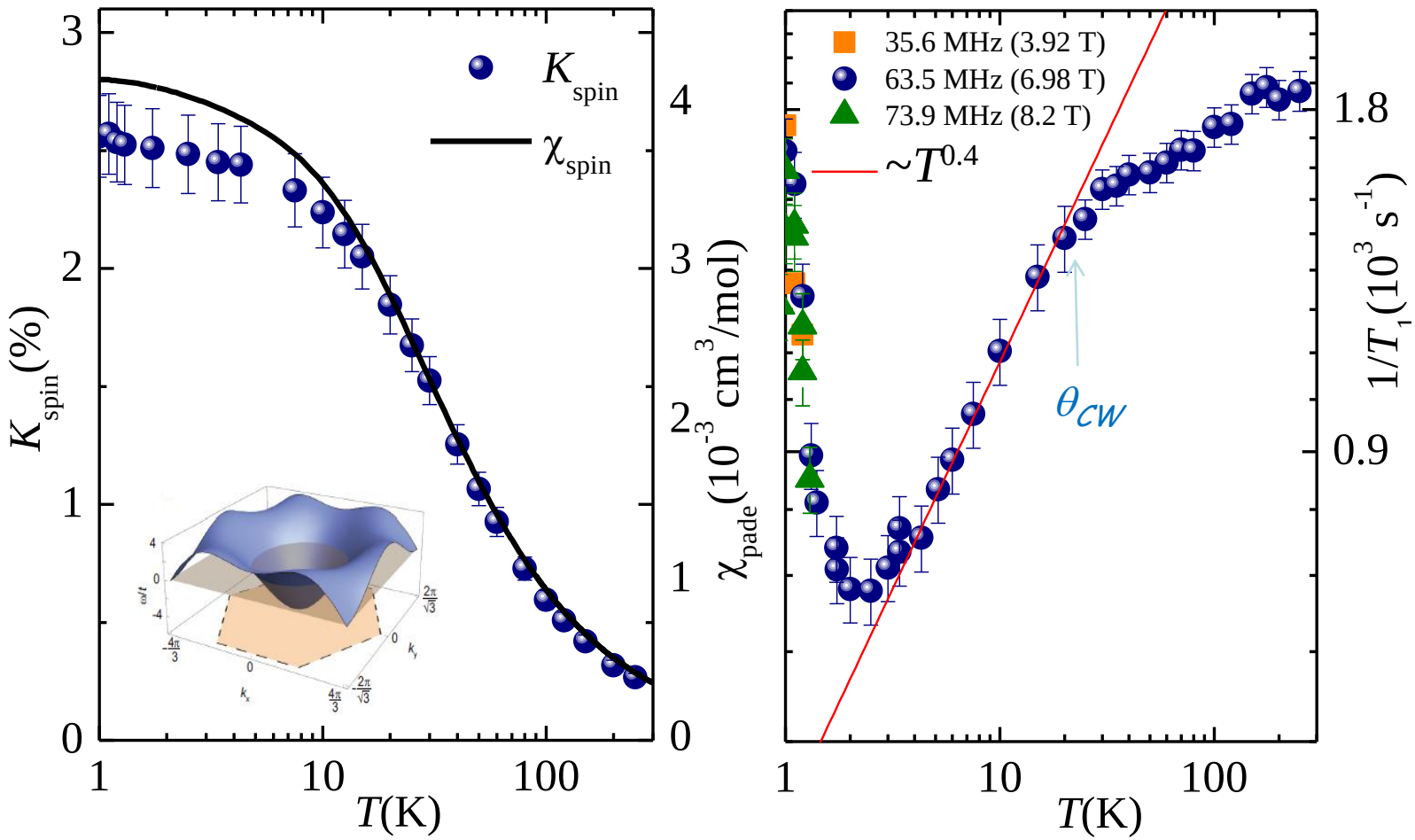


^{207}Pb NMR



Wipe out of NMR intensity below 1K
confirms persisting slow fluctuations

^{207}Pb NMR : local susceptibility and spin dynamics



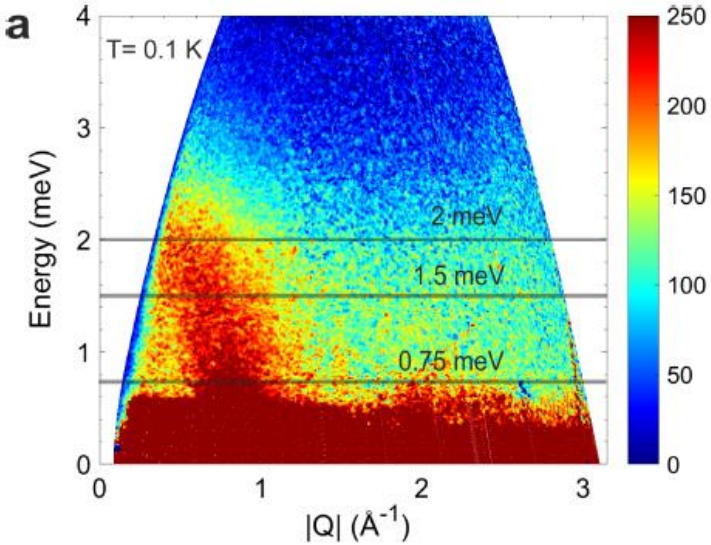
Local and squid χ are similar -> clean system (0.4(3)% orphan spin)

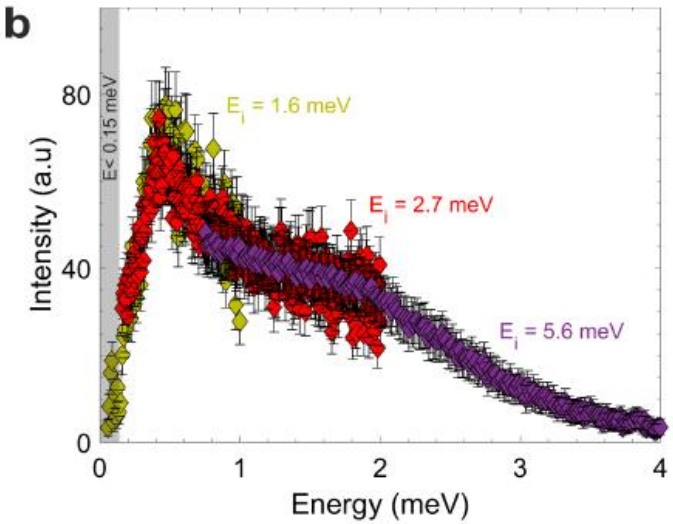
χ levels off below θ_{CW} (as in $Na_4Ir_3O_8$) -> Pauli like, SL with spion FS ?

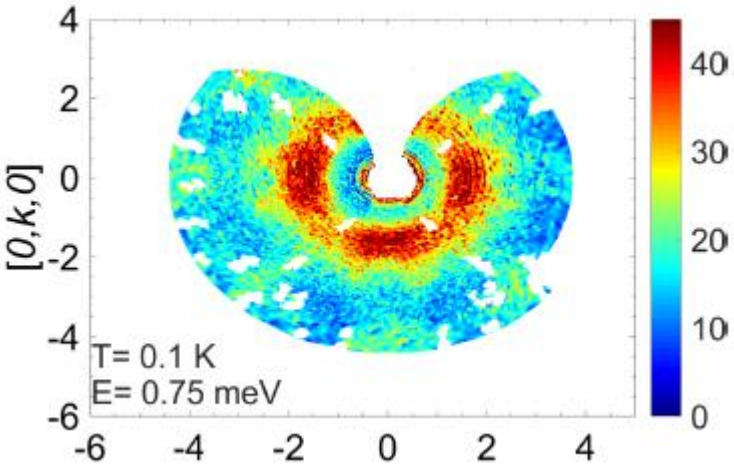
Two regime in 1/T1 above and below ~2K -> 2 spin liquid regimes ?

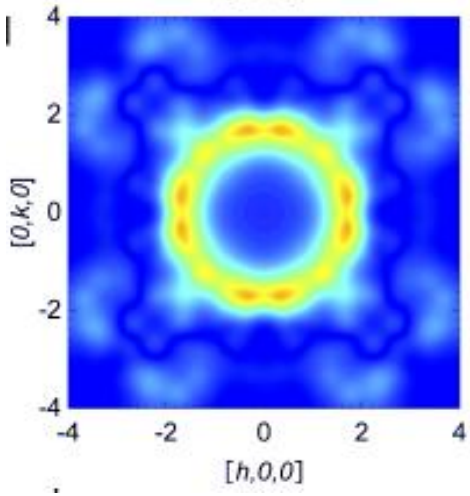
INS: continuum of spinon

S. Chillal et al, arXiv:1712.07942









No spin gap (<0.15meV)
Multi-spinons continuum of excitations

Conclusions and perspectives

-New 3D highly frustrated quantum antiferromagnet

-clean system with S=1/2 (Cu^{2+}), Heisenberg model

-Dynamical ground state, very slow fluctuations (spinons), confirmed by NMR

-NMR shifts saturates below ~J/2 (similar to $Na_4Ir_3O_8$)
Pauli-like, free spinon Fermi surface?

M.J. Lawler PRL 2008
Y. Zhou PRL 2008

-two regimes in the spin dynamics, crossover between 2 SL phases ?
Fermi-surface instability?