Quantum Kagome Spin Liquids

Philippe Mendels
Laboratoire de Physique des Solides,
Université Paris-Sud, Orsay, France

Herbertsmithite $ZnCu_3(OH)_6Cl_2$ Antiferromagnet

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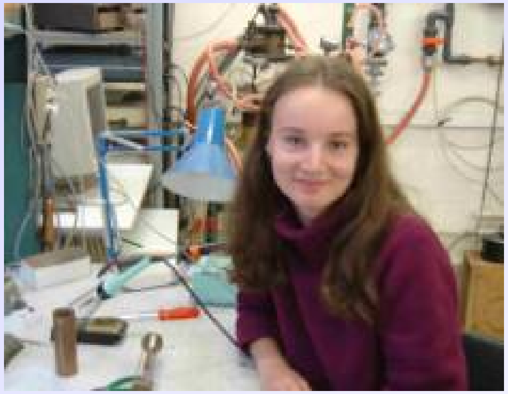
Quantum Kagome Spin Liquids: The case of Herbertsmithite

Philippe Mendels, Fabrice Bert, Areta Olariu, Andrej Zorko,

Laboratoire de Physique des Solides,

Université Paris-Sud, Orsay, France

F. Bert



A. Olariu

A. Zorko

- J. C. Trombe, F. Duc, *CEMES, Toulouse,* P. Strobel, *Grenoble , France*
- M. de Vries, G. Nilsen, A. Harrison, *Edinburgh, UK*
- S. Nakamae, F. Ladieu, D. L'Hote, P. Bonville, CEA *Saclay, France*
- *A. Mahajan's group (IIT Mumbai)*

Quantum Kagome Spin Liquids

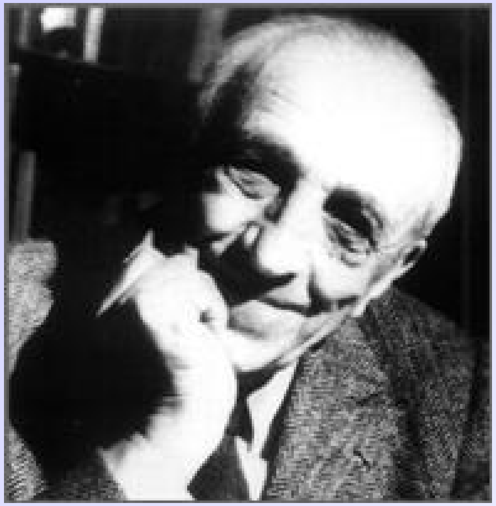
Part I

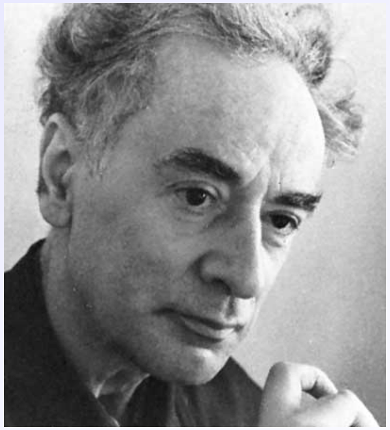
Novel states induced by frustration

Towards spin liquids

EUROPEAN SCIENCE FOUNDATION

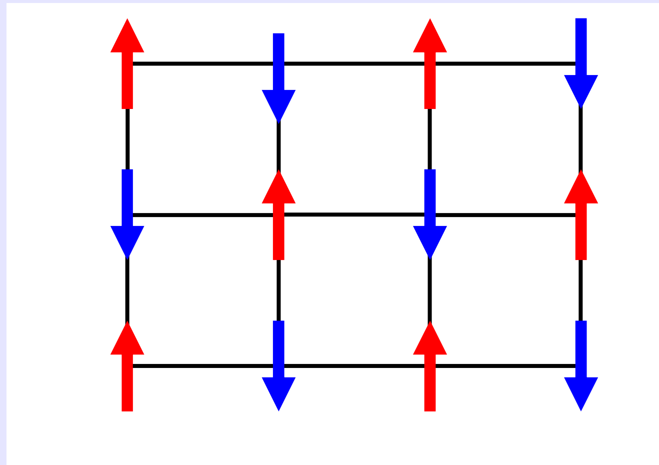
Néel versus Anderson

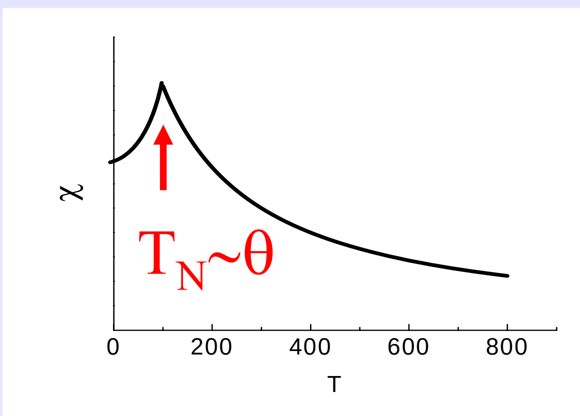


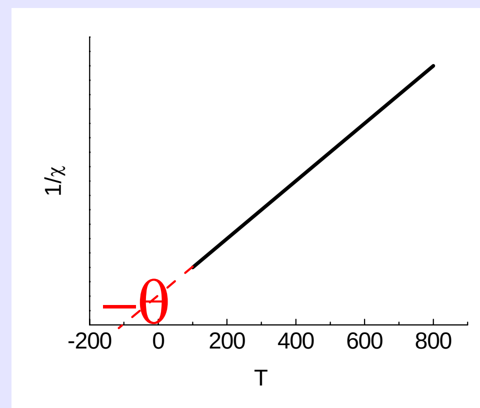


Néel State: Antiferromagn.

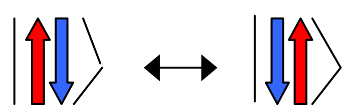
$$\mathcal{H} = -J_{ij}\vec{S}_i.\vec{S}_j\,,\; J_{ij} < 0$$



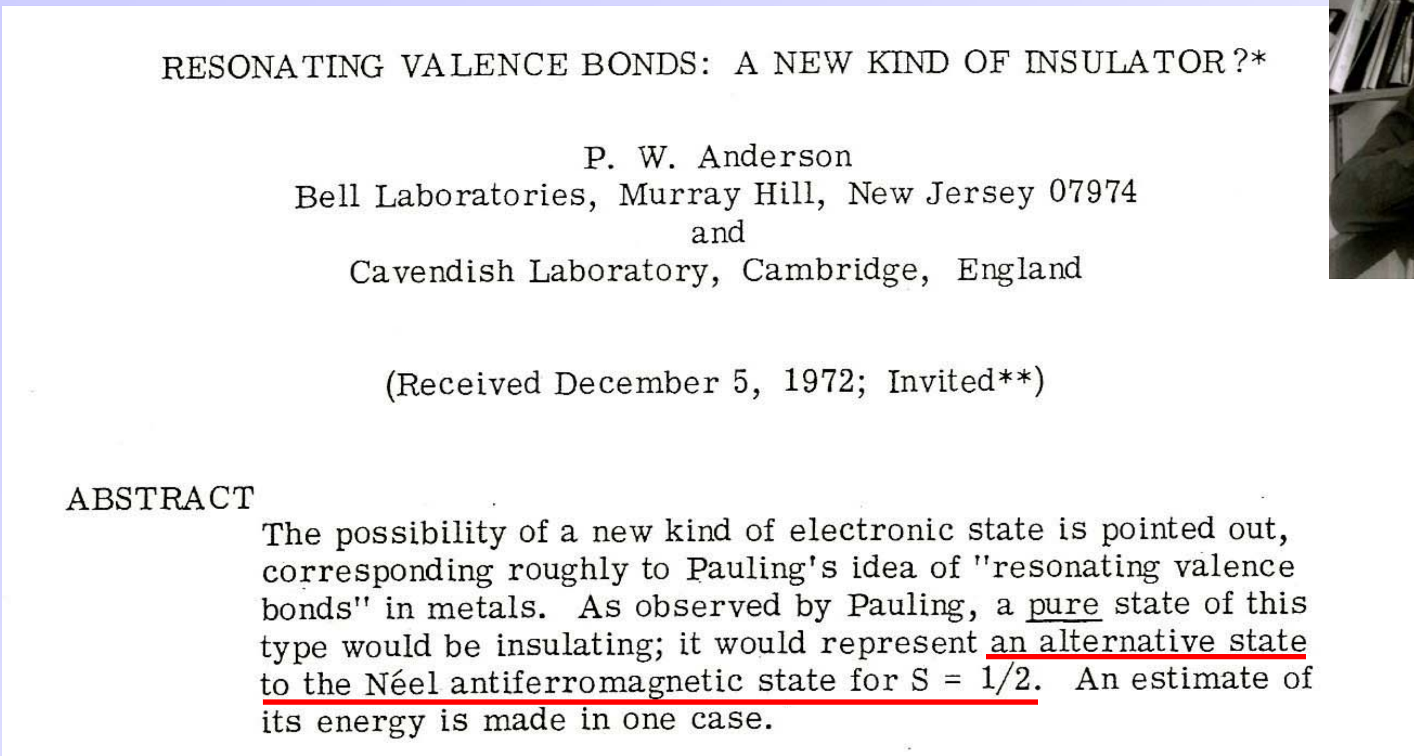




+ Quantum fluctuations for S=1/2



Antiferromagnetism, any alternative?



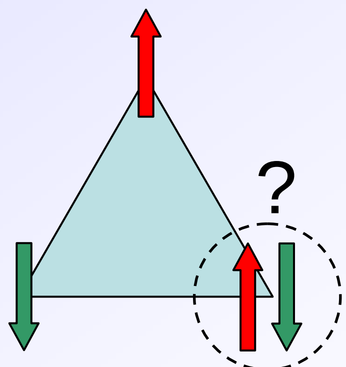
RESONATING VALENCE BONDS: A NEW KIND OF INSULATOR?*

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

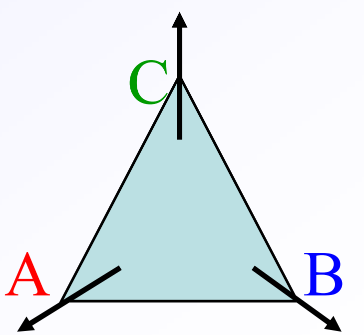
(Received December 5, 1972; Invited**)

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 of magnetic interactions

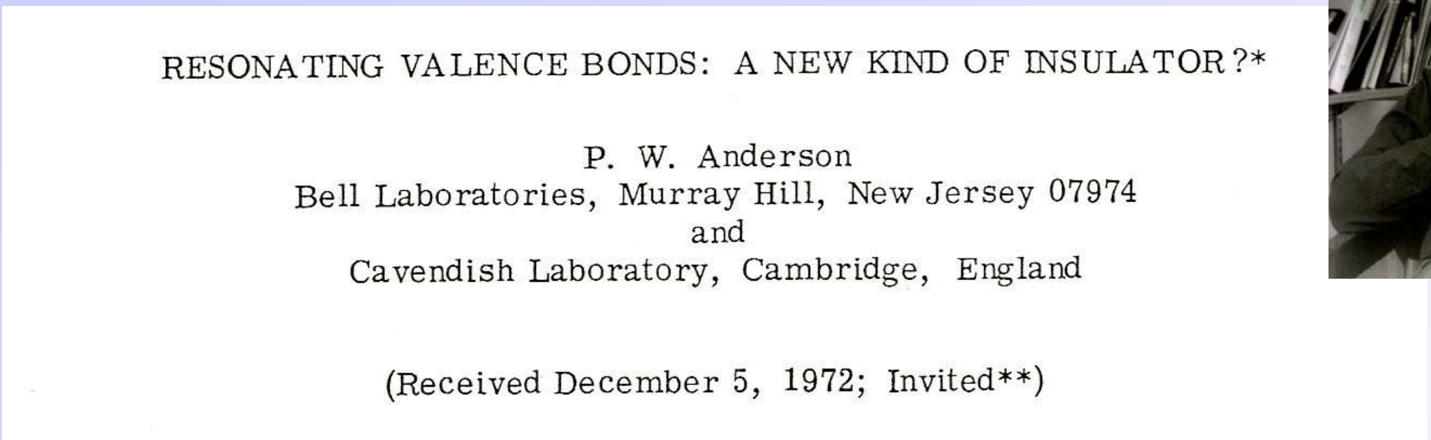


Class.



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

Antiferromagnetism, any alternative?


RESONATING VALENCE BONDS: A NEW KIND OF INSULATOR ?*

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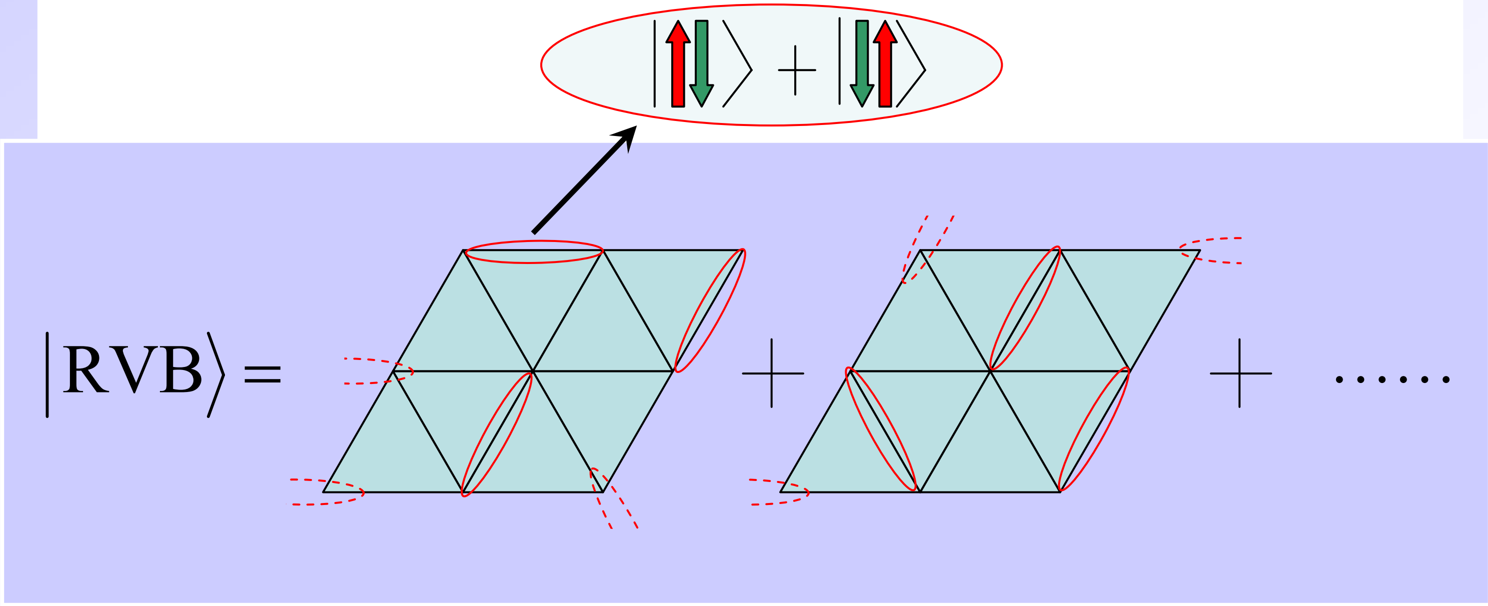
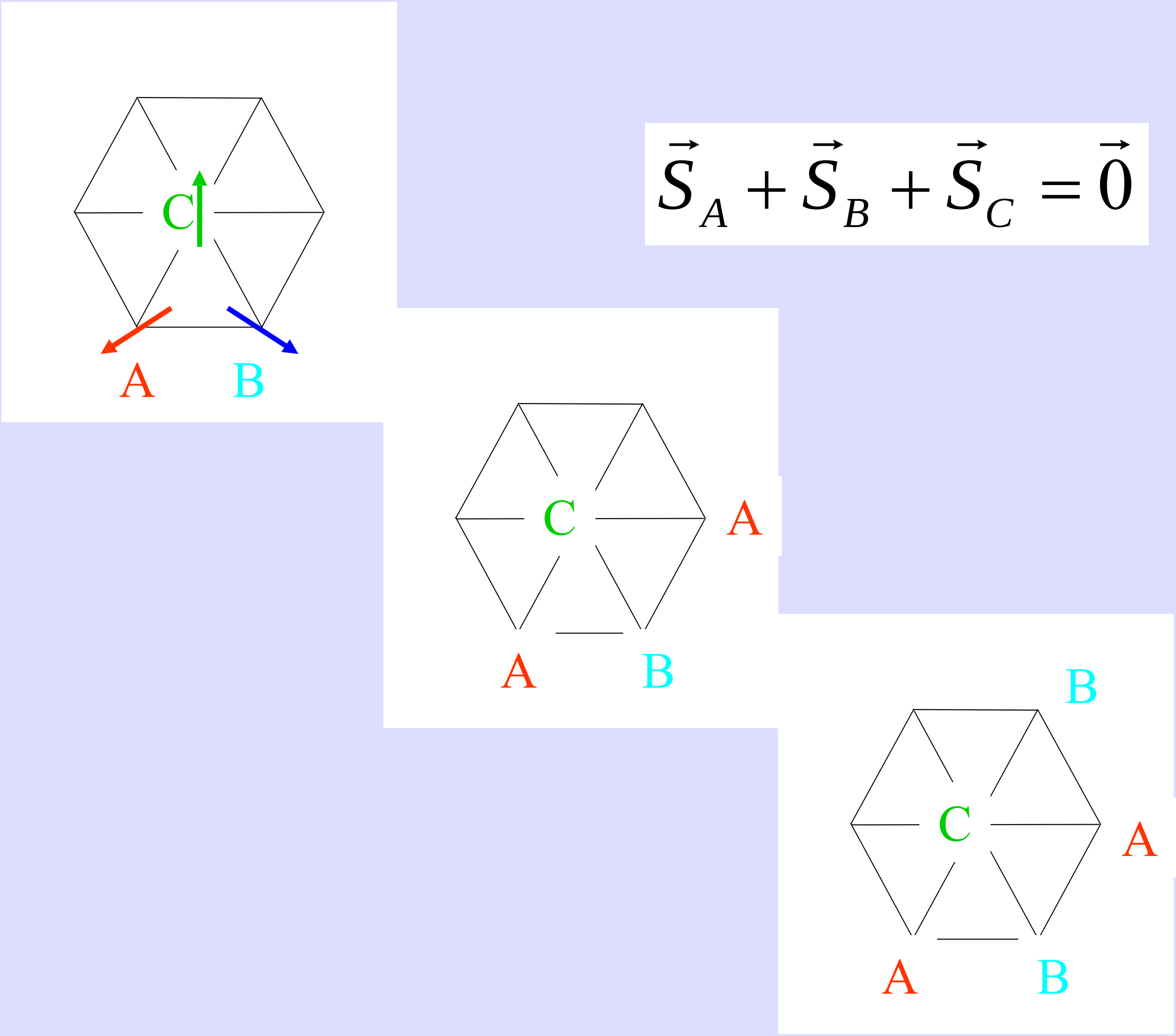


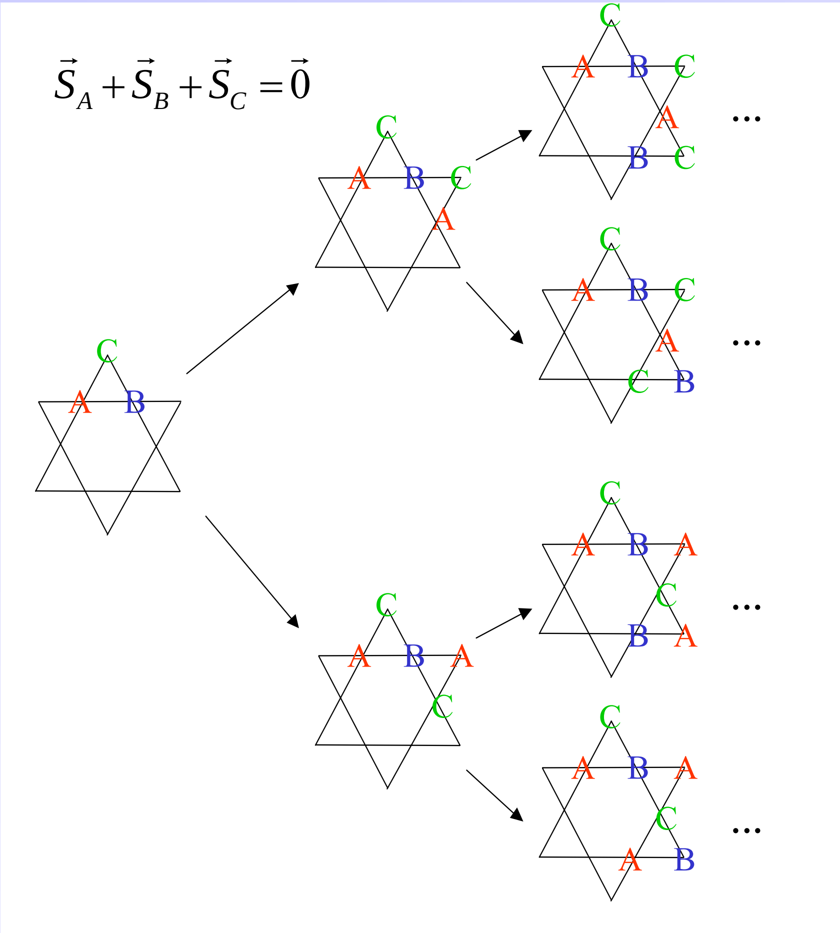
Edge sharing: triangular lattice

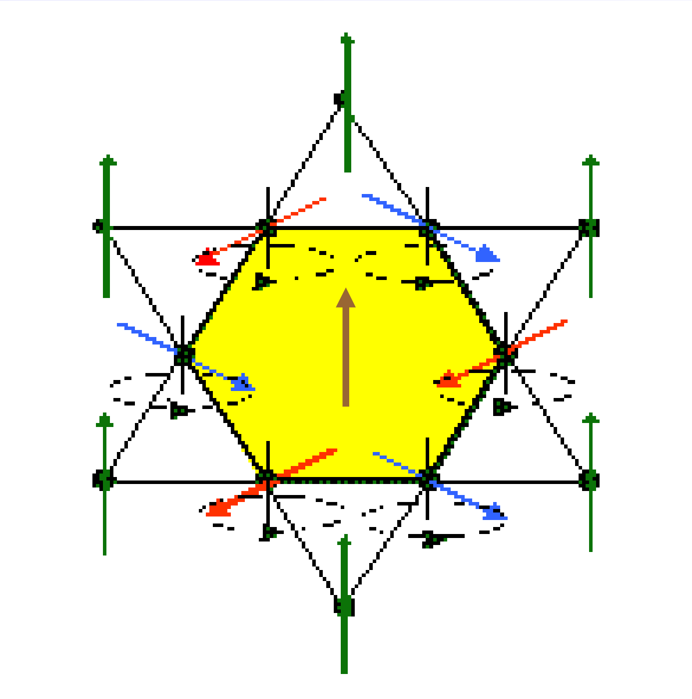


$$\vec{S}_A + \vec{S}_B + \vec{S}_C = \vec{0}$$

g = 2
(XY spins)

Corner sharing: *classical* kagomé lattice





Macroscopic degeneracy

Soft modes

Antiferromagnetism, any alternative?

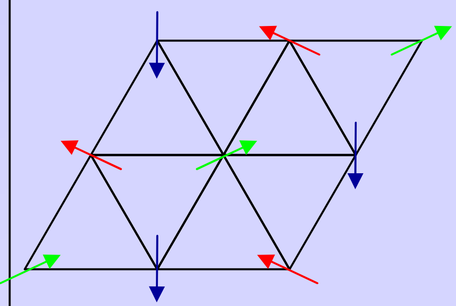
Exact diagonalizations

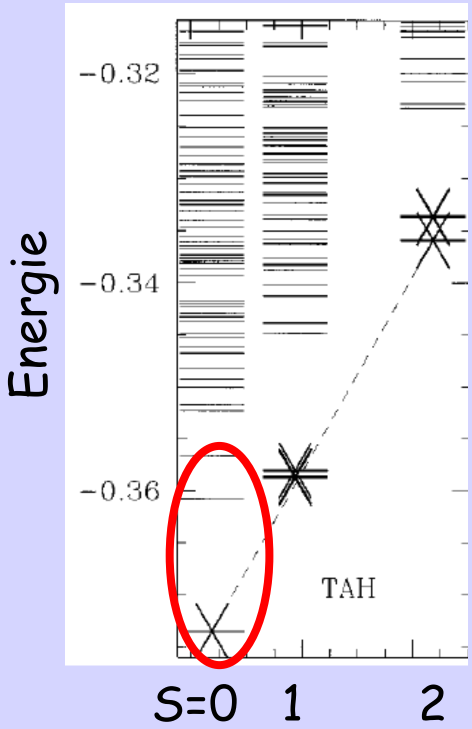
Lecheminant, PRB **56**, 2521 (1997)

Waldtmann, EPJB **2**, 501 (1998).

Triangular

Edge sharing geometry

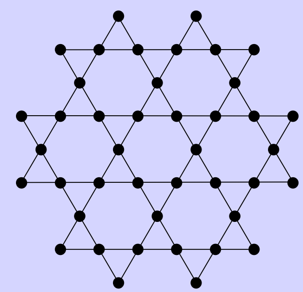




Fundamental Néel

Kagome

Corner sharing geometry

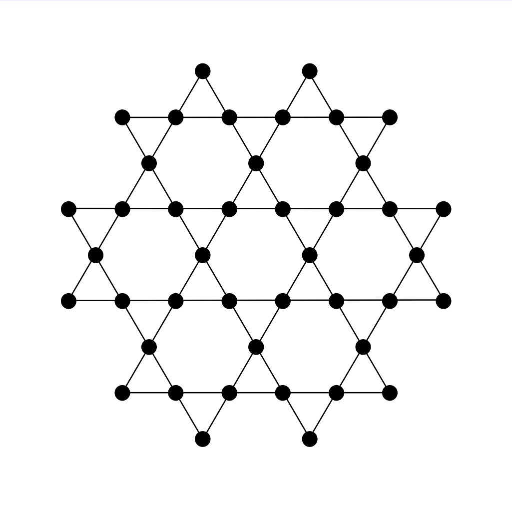


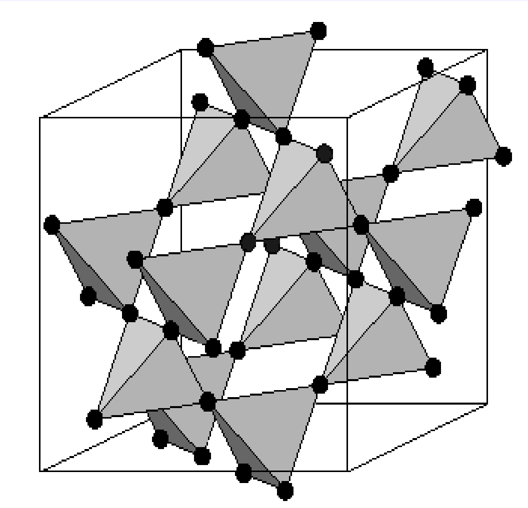
Fundamental ' spin liquid' ≠ Néel

RVB ? Mila, PRL **81**, 2356 (2000)

IDEAL Highly Frustrated Magnet

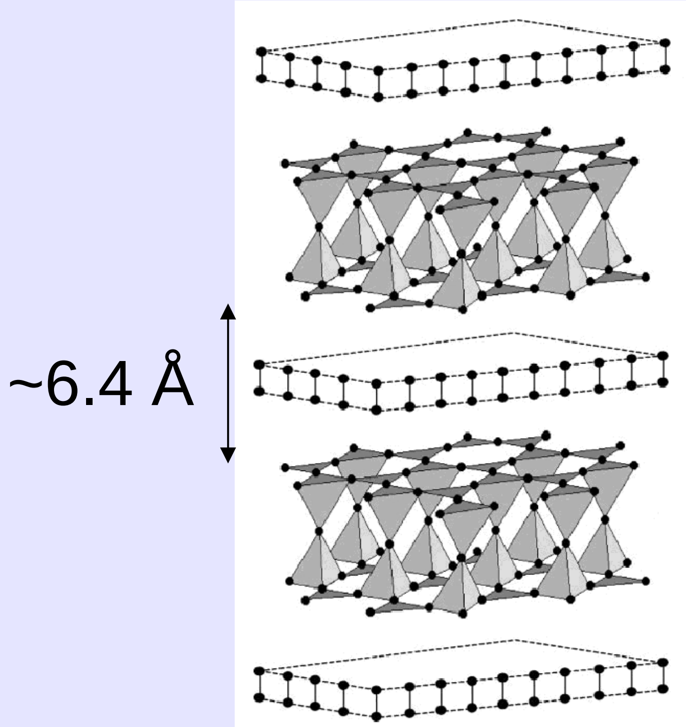
- Heisenberg spins
- S=1/2 (quantum spins)
- Corner sharing geometry: Kagomé (2D) or pyrochlore (3D) lattice
- No « perturbation » (anisotropy, dipolar interaction, n.n. interactions, *dilution*)
- For kagomé: stacking should keep the 2D kagomé planes uncoupled





Materials

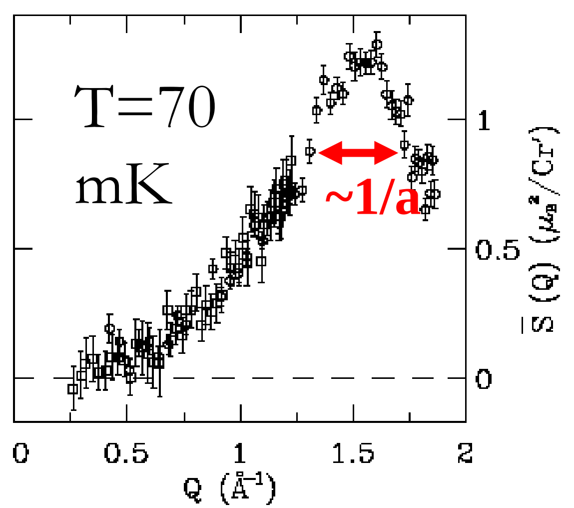
Kagomé bilayers (Cr^{3+}, S =3/2)

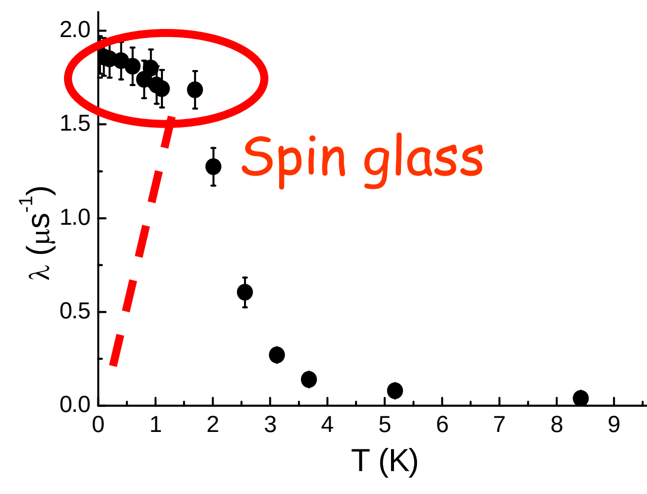


- Exotic spin glass at only low T
- High frustration ratio θ/T_g
- Fluctuations at low T
- Short correlation length
- Field independant C_v
- >3% spinless defects

?

$SrCr_{9p}Ga_{12-9p}O_{19}$
(SCGO)
Θ~500 K
T_g ~ 4 K



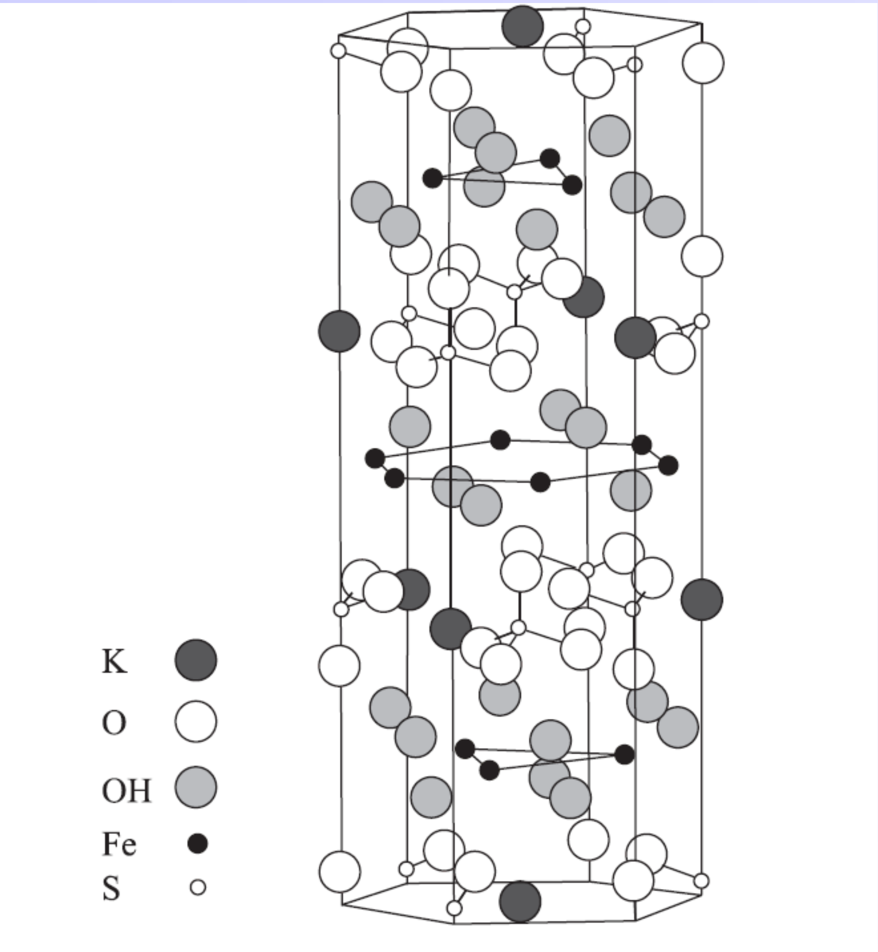


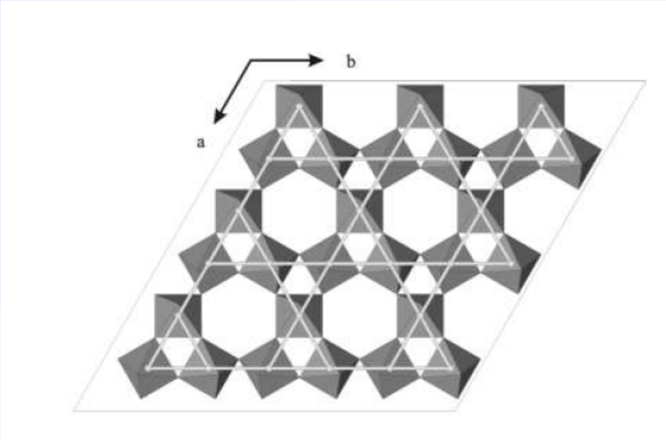
Jarosite Family

$AB_3(SO_4)_2(OH)_6$

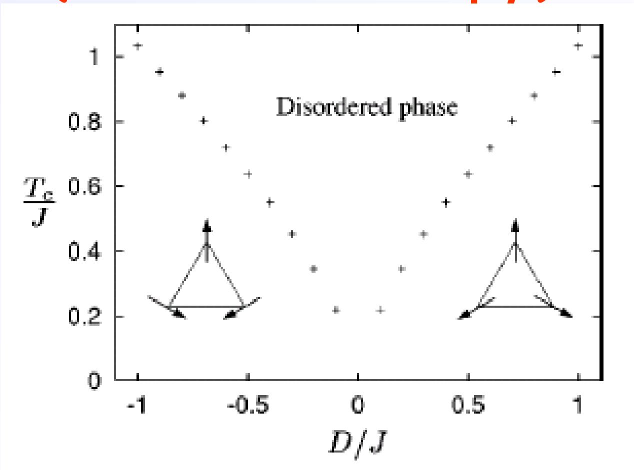
A= Na^+, K^+, Ag^+, Rb^+, H_3O^+, NH_4^+, ½ Pb^{2+}, ½ Ba^{2+}

B = Fe^{3+} (S=5/2), Cr^{3+} (S=3/2), V^{3+} (S=1)

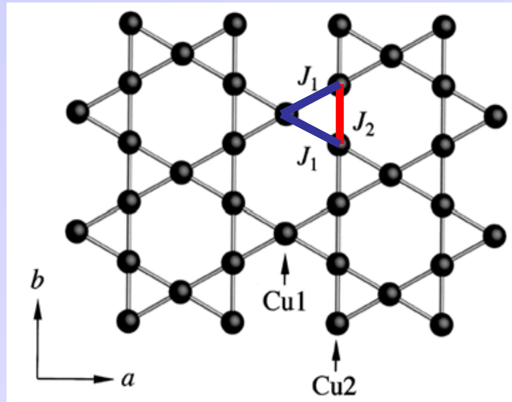




Most of Jarosites order!
(D.M. anisotropy)

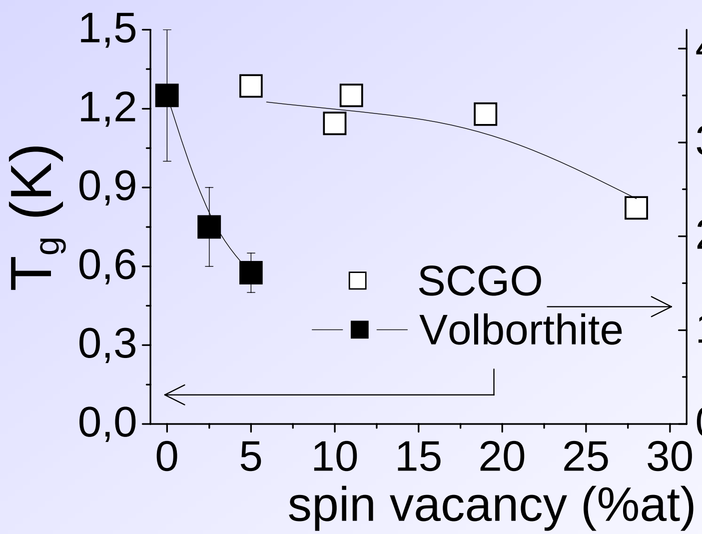


Volborthite, $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$



Z. Hiroi et al, J. Phys. Soc. Jpn 70 (2001) 3377

Another class of imperfections: J_1 and J_2



S = 1/2
High purity

But a transition

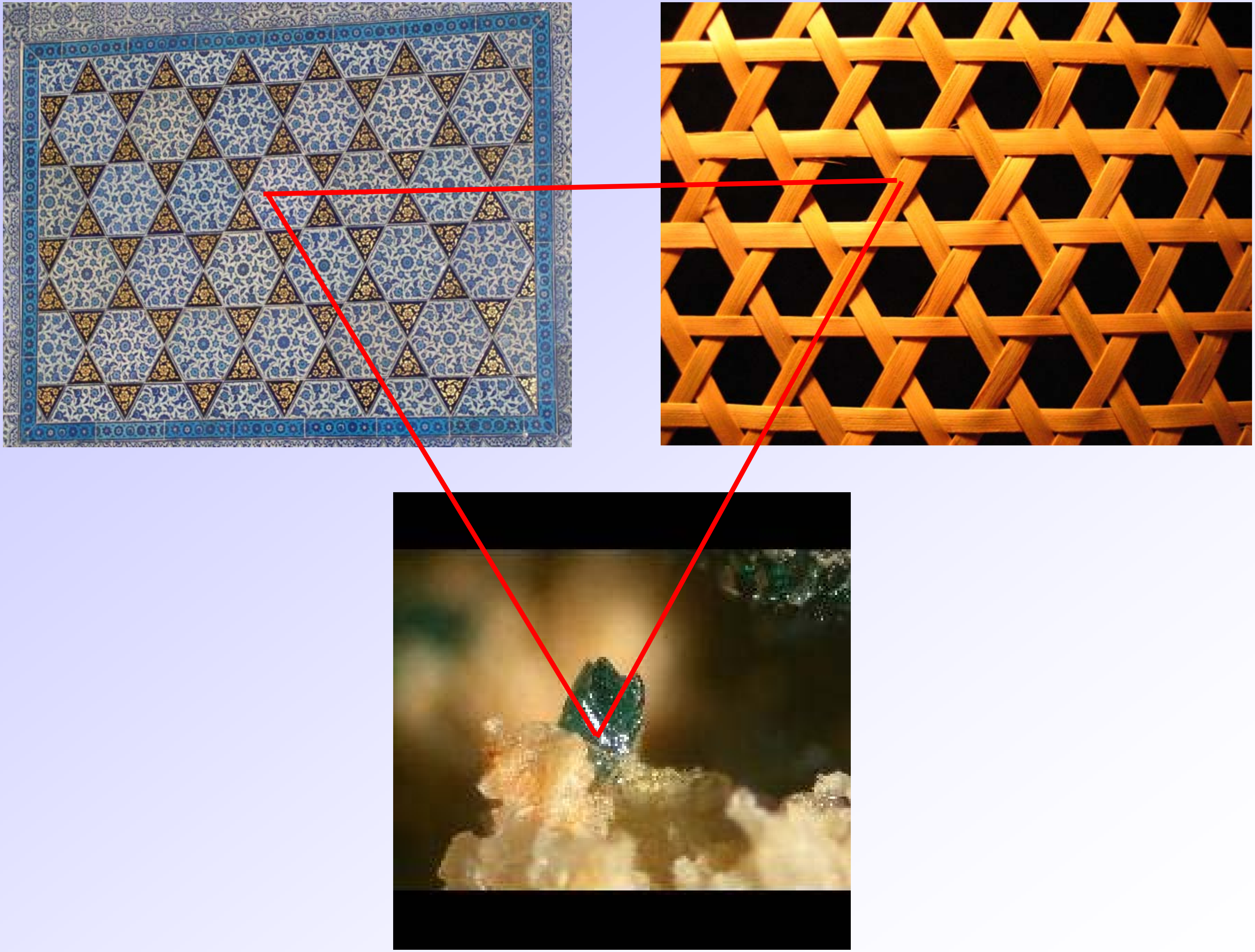
F. Bert et al, PRL, 95 (2005) 087203, Z. Hiroi, JPSJ

Quantum Kagome Spin Liquids

Part II

Novel states induced by frustration

Herbertsmithite: a true spin liquid?



JACS
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*

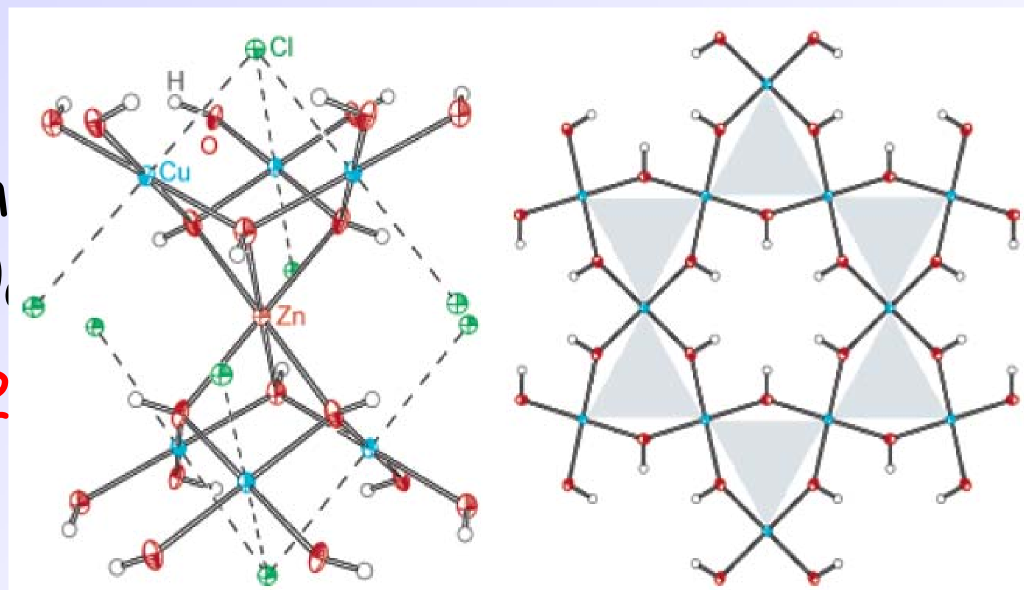
Department of Chemistry, 6-335, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139-4307

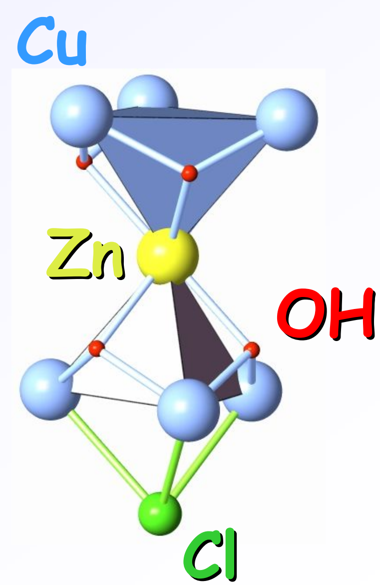
Received June 13, 2005; E-mail: nocera@mit.edu

Herbertsm

$ZnCu_3(OH)$

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





Herbertsmithite is the first example of a quantum kagome antiferromagnet

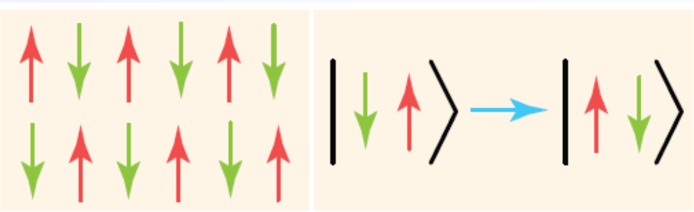
- perfect kagomé lattice
- no freezing at least down to J/4000

-> renewal ofthe search for scenarios for the kagome ground state

VBC : R.R.P. Singh and D.A. Huse, PRB (2007, 2008)

Dirac spin liquid : Y. Ran et al, PRL (2007), PRB (2008) ....

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

1- $Zn_xCu_{4-x}(OH)_6Cl_2$: paratacamite family x‹ 1

2- $ZnCu_3(OH)_6Cl_2$: Herbertsmithite: ideal kagome ?

Gap?

Measurements of χ_{local}

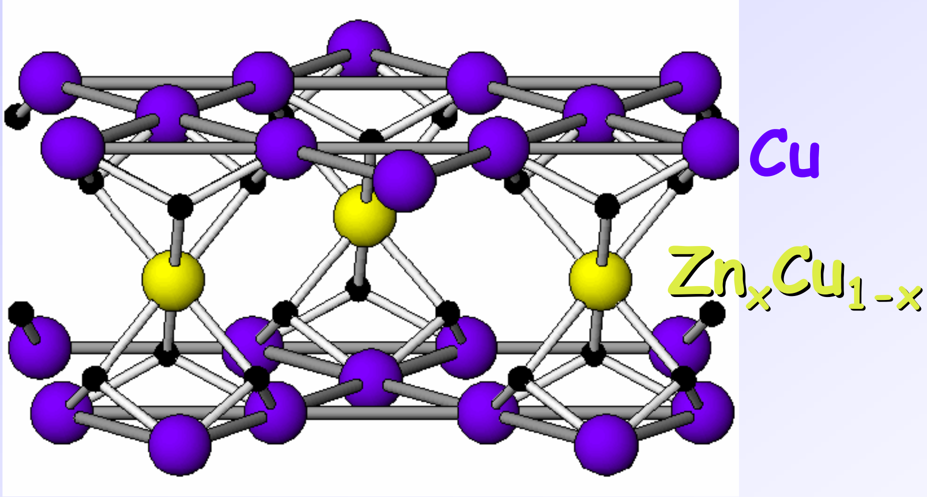
Dynamical mesurements

Non-magnetic defects

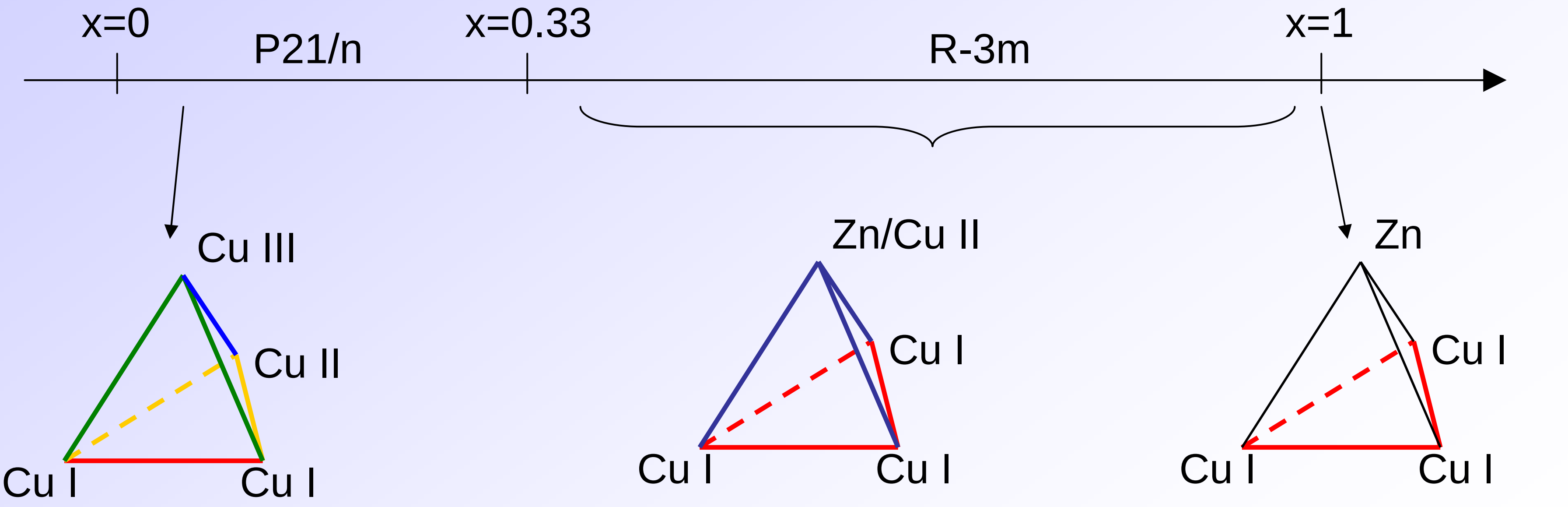
Cu/Zn

« Perturb to reveal »

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



Zn/Cu substitution rate



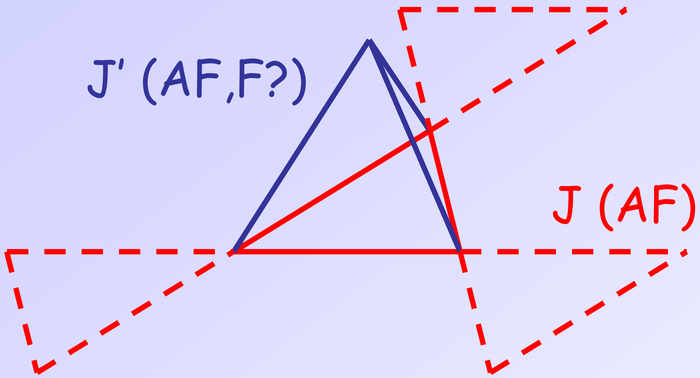
Clinoatacamite
$Cu_2(OH)_3Cl$

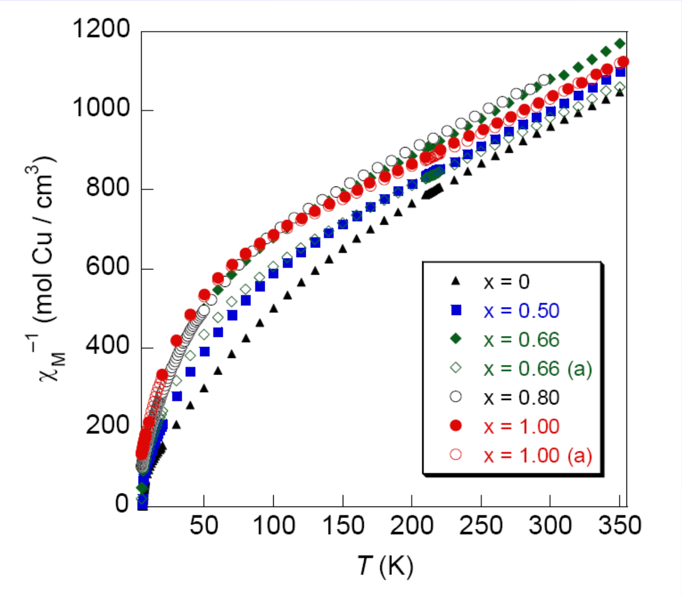
Zn-paratacamite
$Zn_xCu_{4-x}(OH)_6Cl_2$

Herbertsmithite
Braithwaite et al, 2004

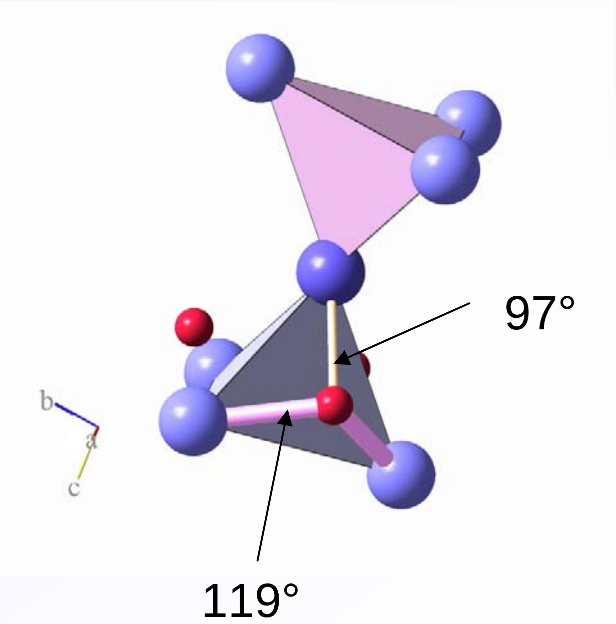
$Zn_xCu_{4-x}(OH)_6Cl_2$

Curie Weiss behavior for all x
-> antiferromagnetic correlations





J : in-plane coupling AF ~ 175 K
J': inter-plane coupling small, maybe Ferro

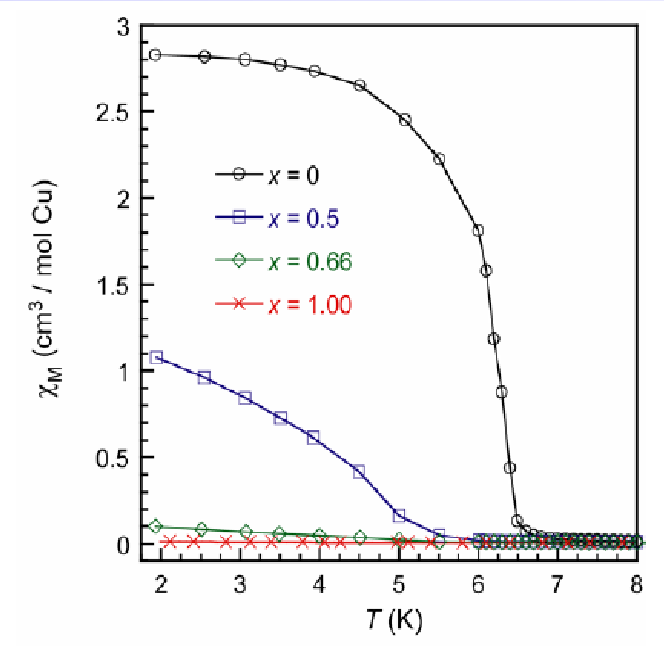


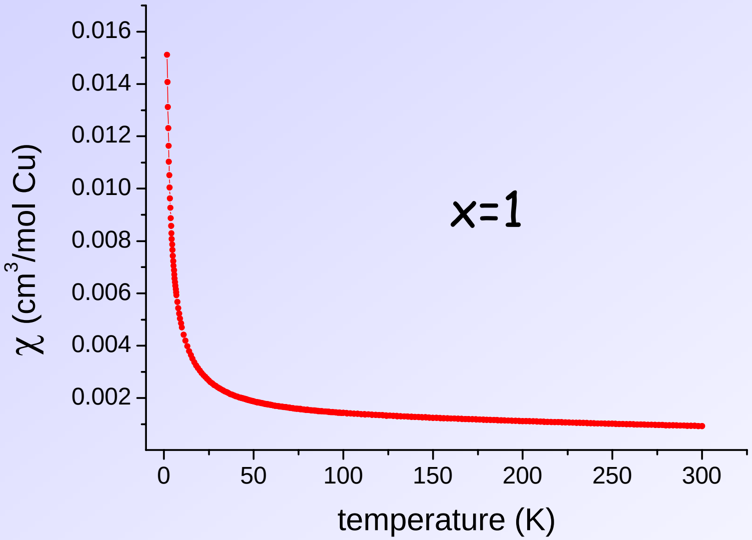
no transition for T<<J
-> highly frustrated antiferromagnets

P. Shores et al, JACS (2005)

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

- Ferromagnetic-like transition at T_N~6K
- Vanishes for x->1

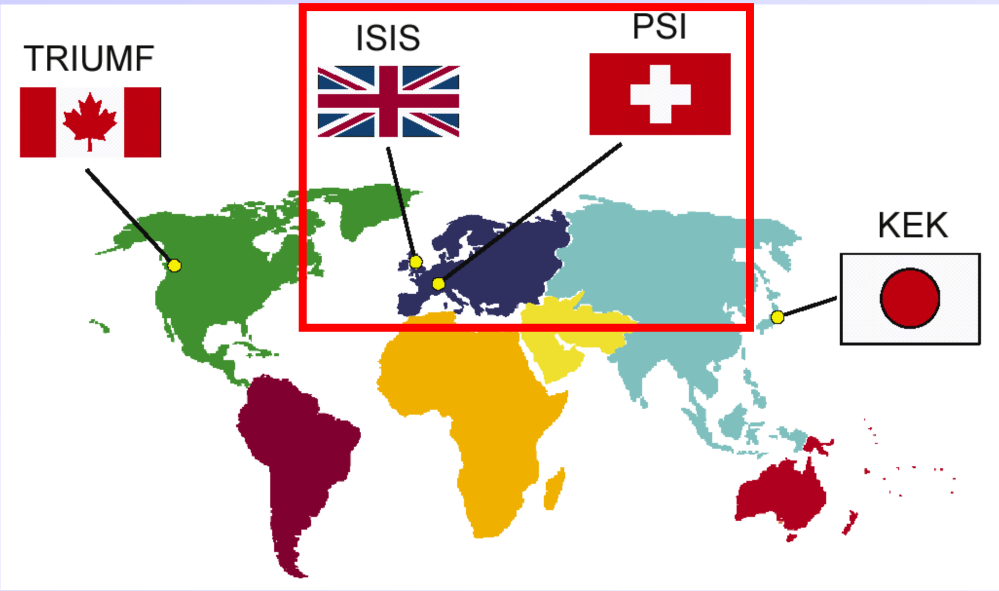


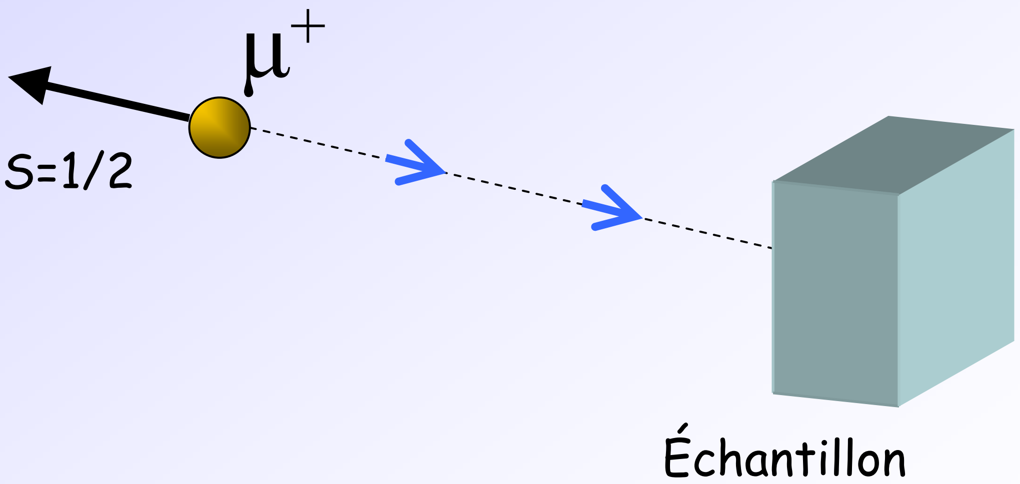


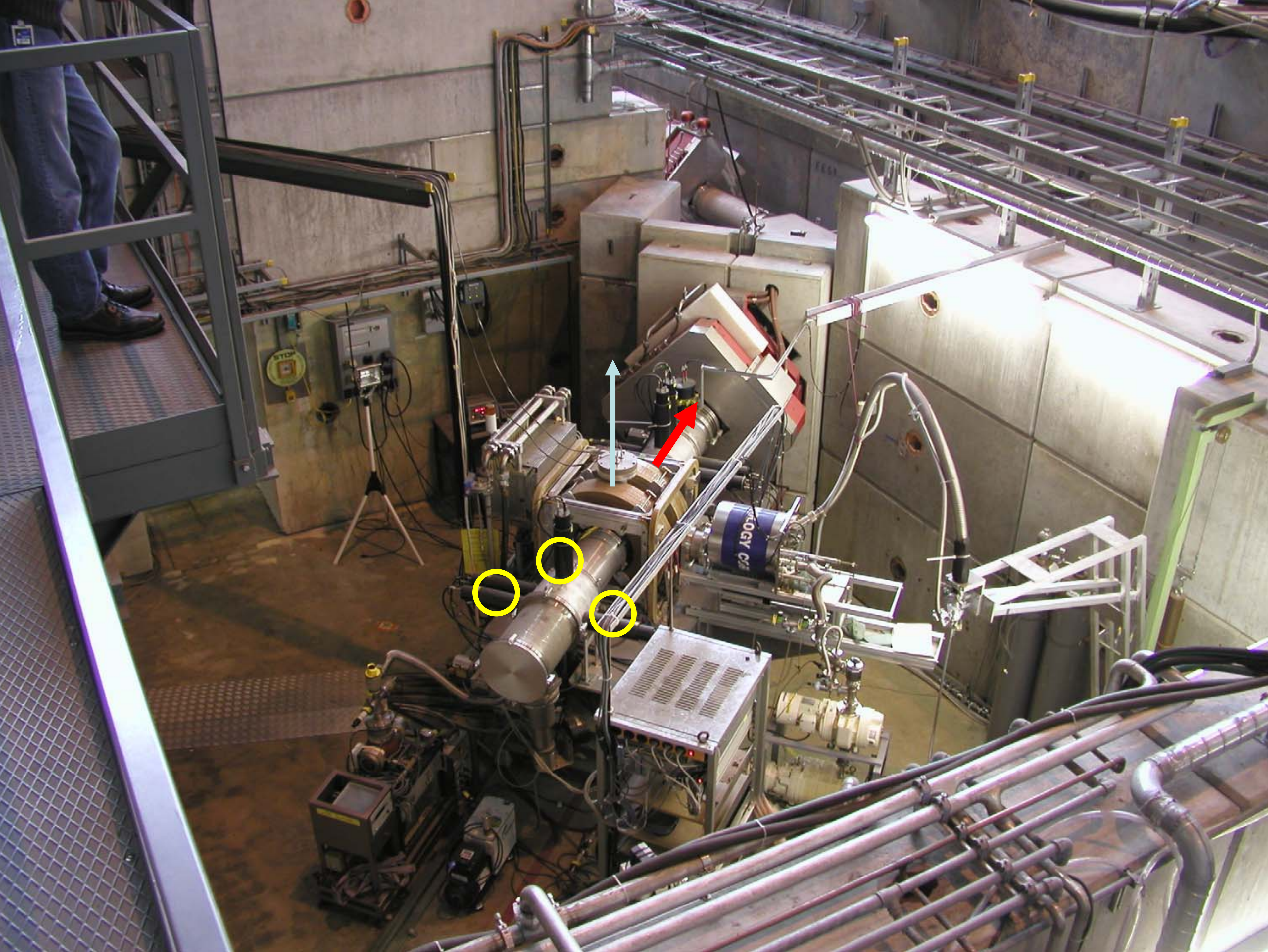
Herbersmithite x=1

-No sign of transition for T>2K
-Low T Curie like upturn for T<50K

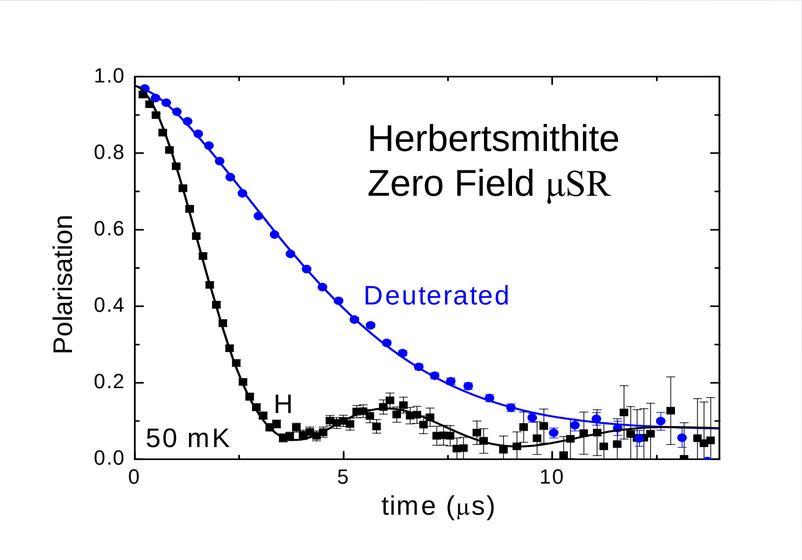
μSR - Muon spin resonance, relaxation






STOP

μSR : $ZnCu_3(OH)_6Cl_2$, x=1



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

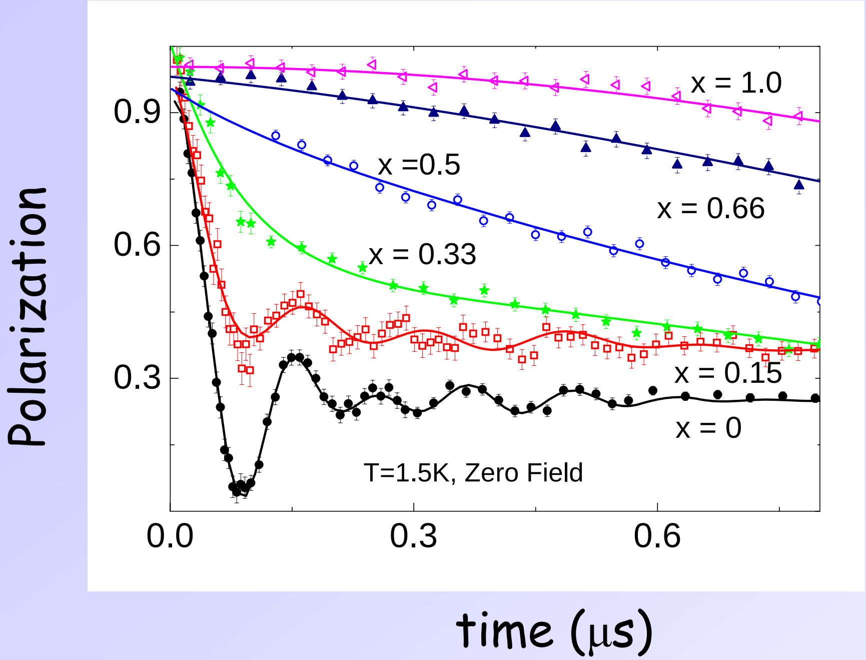
At 50mK, no sign of ordering relaxation arises from small "static" nuclear fields.

upper limit of a frozen moment for Cu^{2+}, if any : $6x10^{-4}$ μ_B

Also: ac-χ Helton et al, PRL 98 107204 (2007)
μSR O. Ofer et al, cond-mat/0610540

No order or frozen disorder down to 50 mK despite J=175 K !

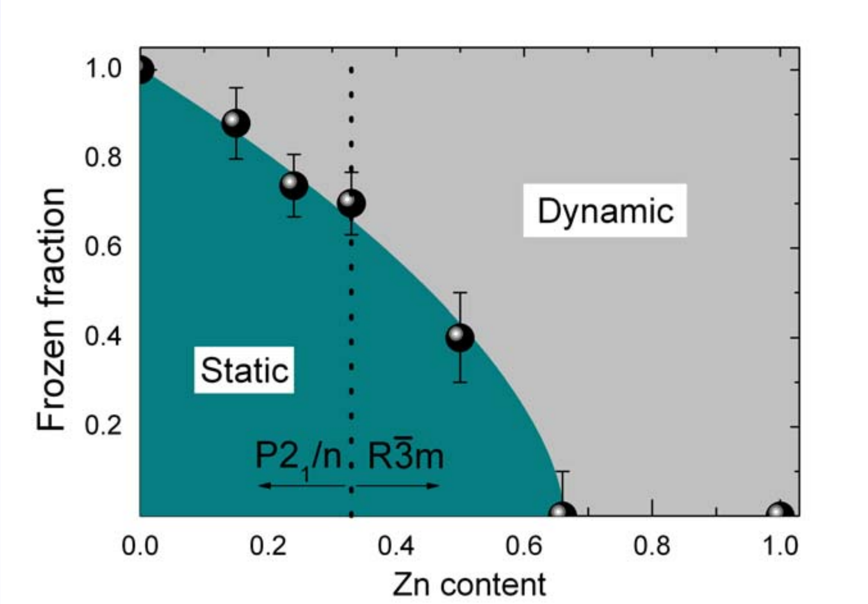
μSR : $Zn_xCu_{4-x}(OH)_6Cl_2$



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

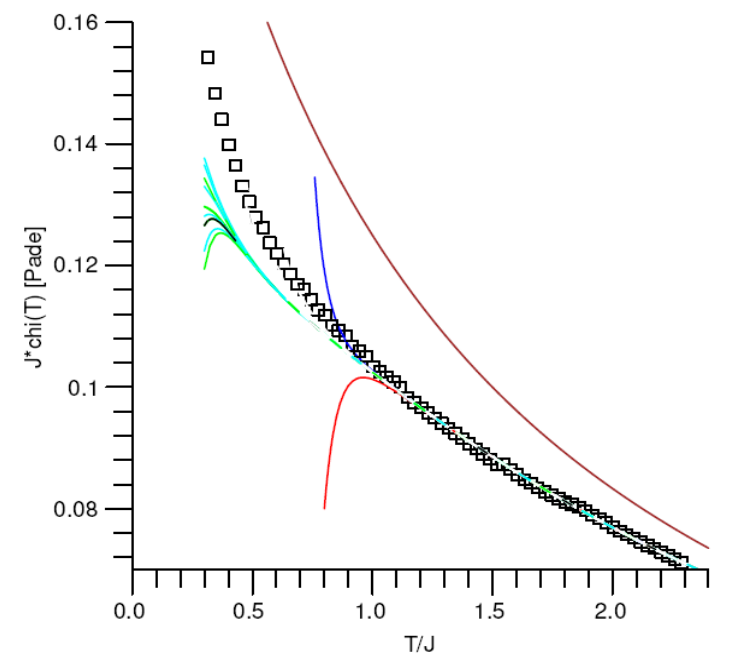
When x increases from 0 to 1 :
-Oscillations are smeared out
-A paramagnetic (x=1 type) component emerges at the expense of the frozen one

Large domain of stability 0.66<x<1 of a dynamical ground state
-> surprisingly small influence of interlayer coupling

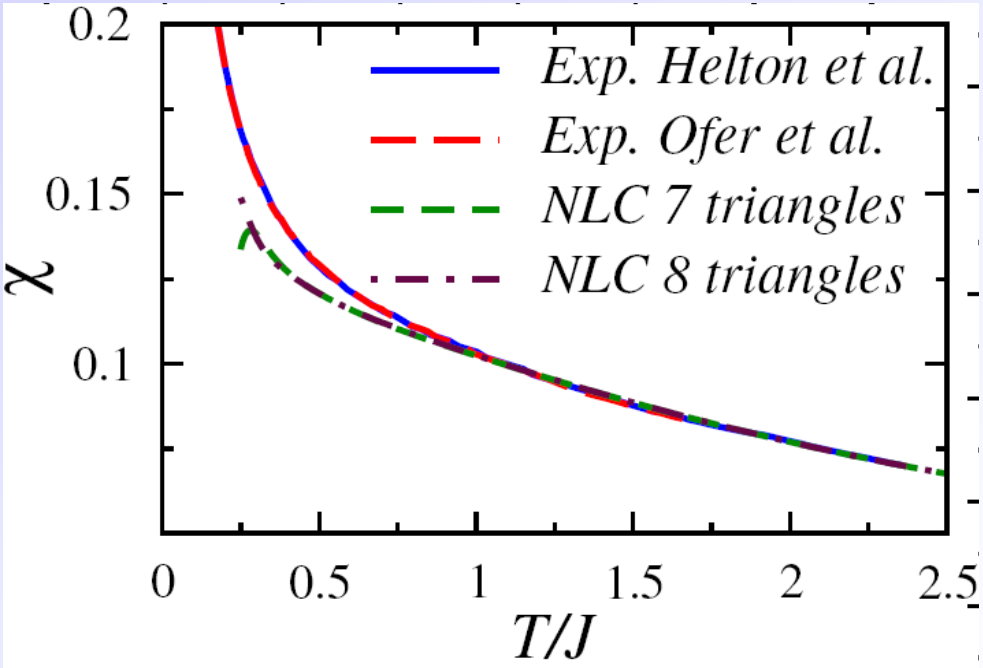


P. Mendels et al, PRL 98, 077204 (2007)

Herbertsmithite macroscopic susceptibility



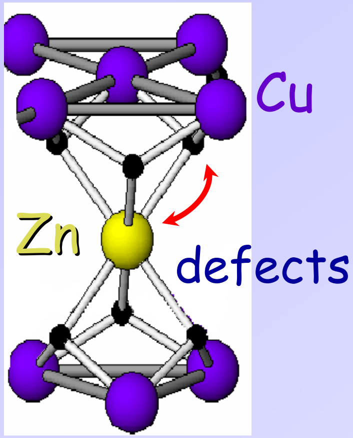
High temperature series expansion
(G. Misguish, C. Lhuillier)



M. Rigol and R. P. Singh, PRL **98**, 207204 (2007)

-> need for additional terms to the KAF Hamiltonian to account for Herbertsmithite macroscopic susceptibility

Magnetic defects : Zn/Cu intersite mixing



Cu on the Zn site
Nearly free ½ spins

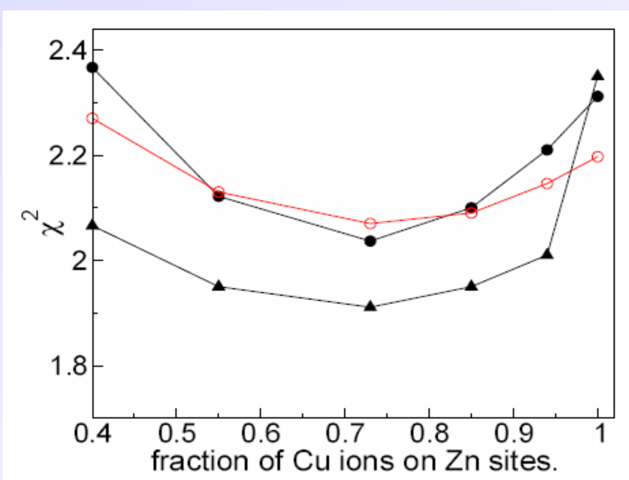
Zn in the kagome plane
-> magnetic vacancy -> staggered magnetization
-> effective paramagnetic defects (small moment?)

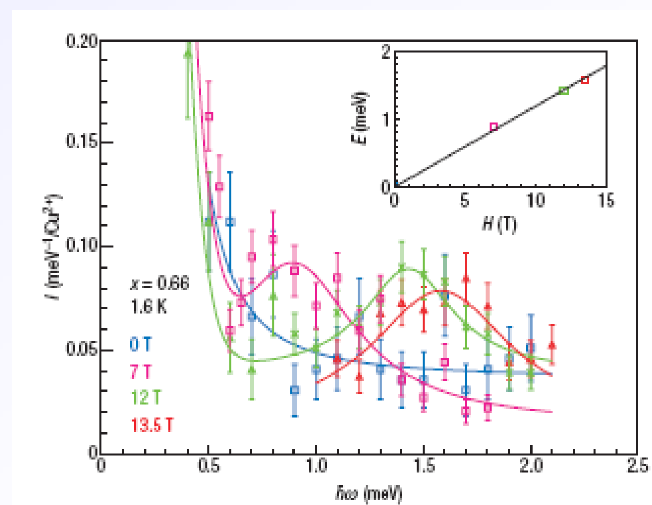
P. Mendels et al., J. Phys.: Condens. Matter 19, 145224 (2007)

- Neutron: structure refinement + H *dilution*

S.H. Lee et al, Nature Materials (2007) *-> ~10%*

M.A. de Vries et al, PRL **100**, 157205 (2008) *-> 9(2)%*



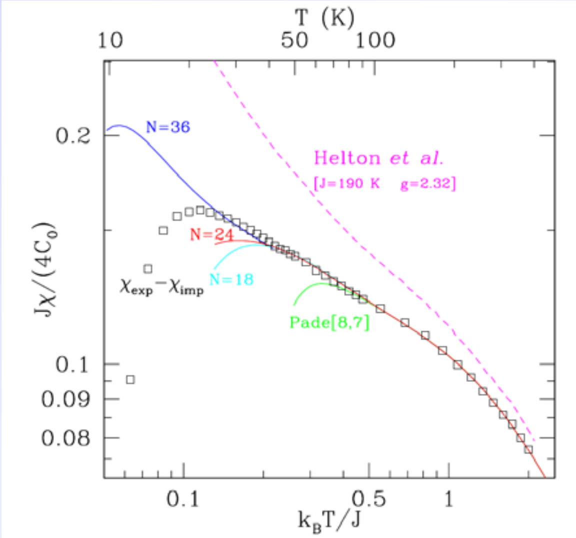


Magnetic defects : Zn/Cu intersite mixing

- Susceptibility fit -> ~5% dilution

  exact diagonalization+
  5% weakly interracting S=1/2 defects

  G. Misguich and P. Sindzingre, Eur. Phys. J. B 59, 305 (2007)



- Low T, High Field Magnetization -> ~7% dilution

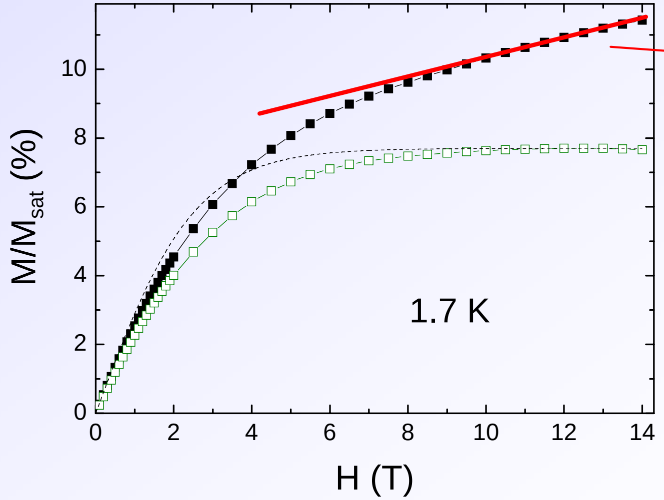
  F. Bert et al, PRB 76, 132411 (2007)

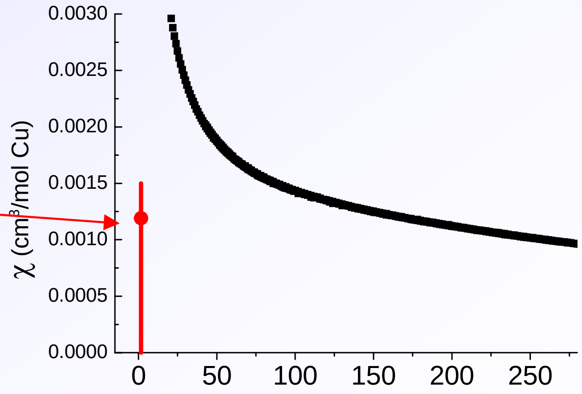
$M_{tot}=M_{defect}+\chi_i H$

M_{defect}~Brillouin(H/T)

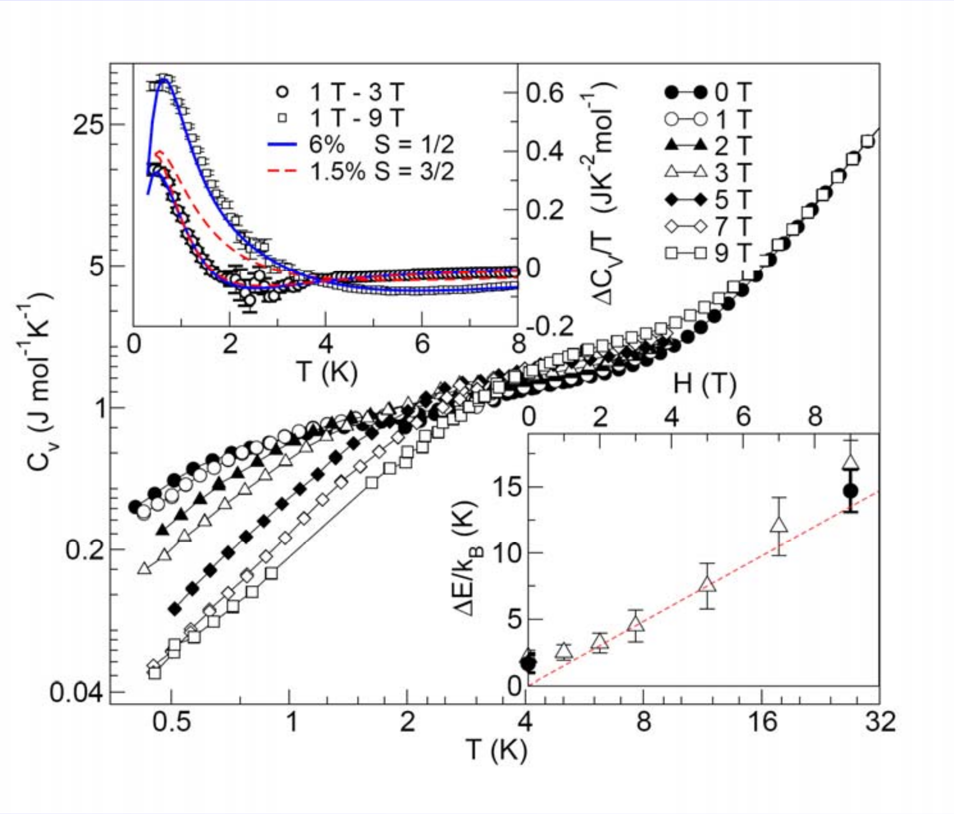
-~7% of interlayer Cu^{2+}

- $\chi_i << \chi_{macro}$ at low T





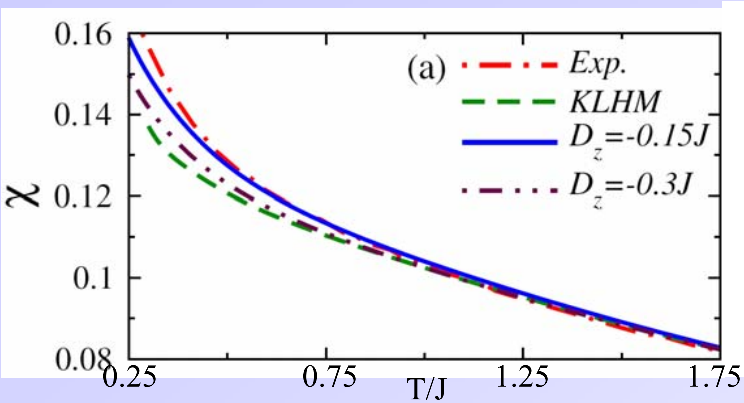
- Schottky like anomaly in heat capacity



-> Kagome lattice dilution 6.5+/-1%

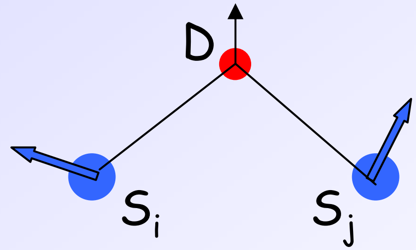
M.A. de Vries et al, PRL **100**, 157205 (2008)

Dzyaloshinskii-Moriya interactions

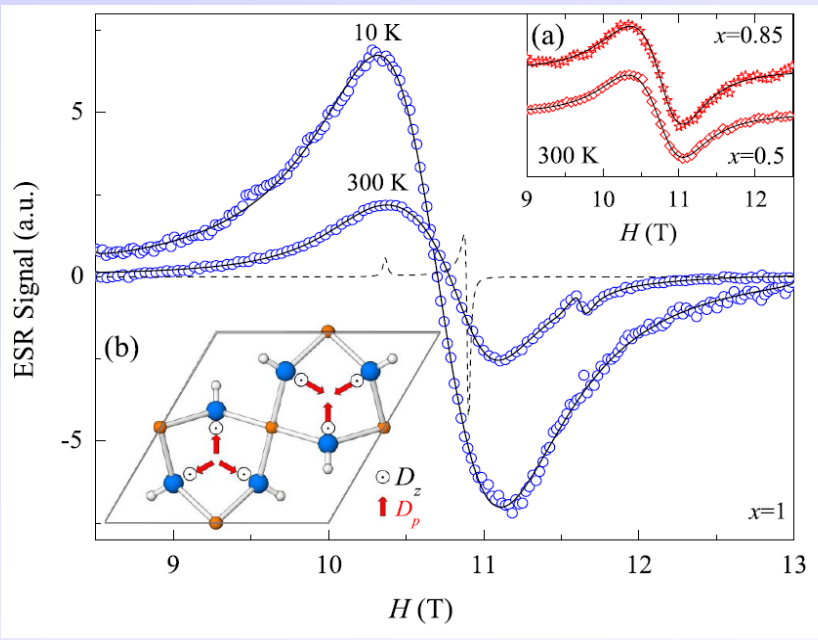


Direct fit of susceptibility (no defect contribution):
$|D_z|=0.15J$, $|Dp|=0.3J$

M. Rigol and R. P. Singh, PRL **98**, 207204 (2007)



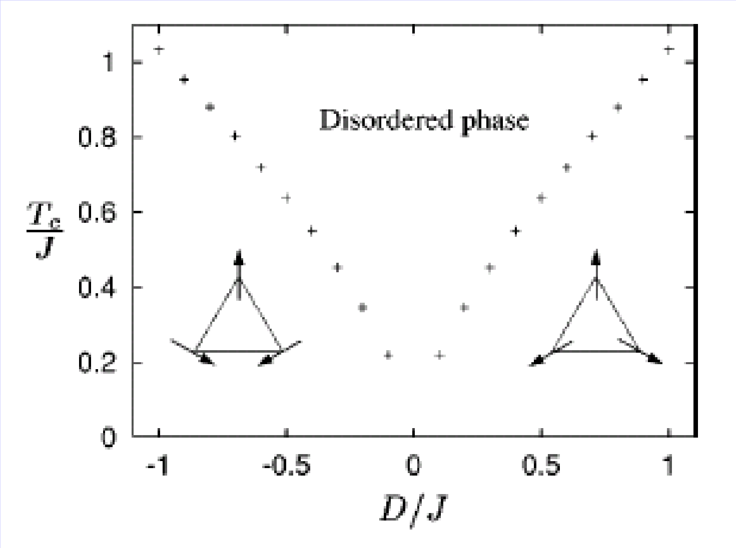
$H_{DM}=D.(S_i \wedge S_j)$



Broad room T ESR line <- magnetic anisotropy from DM
$|D_z|=0.08J$, $|D_p|$~0.01J

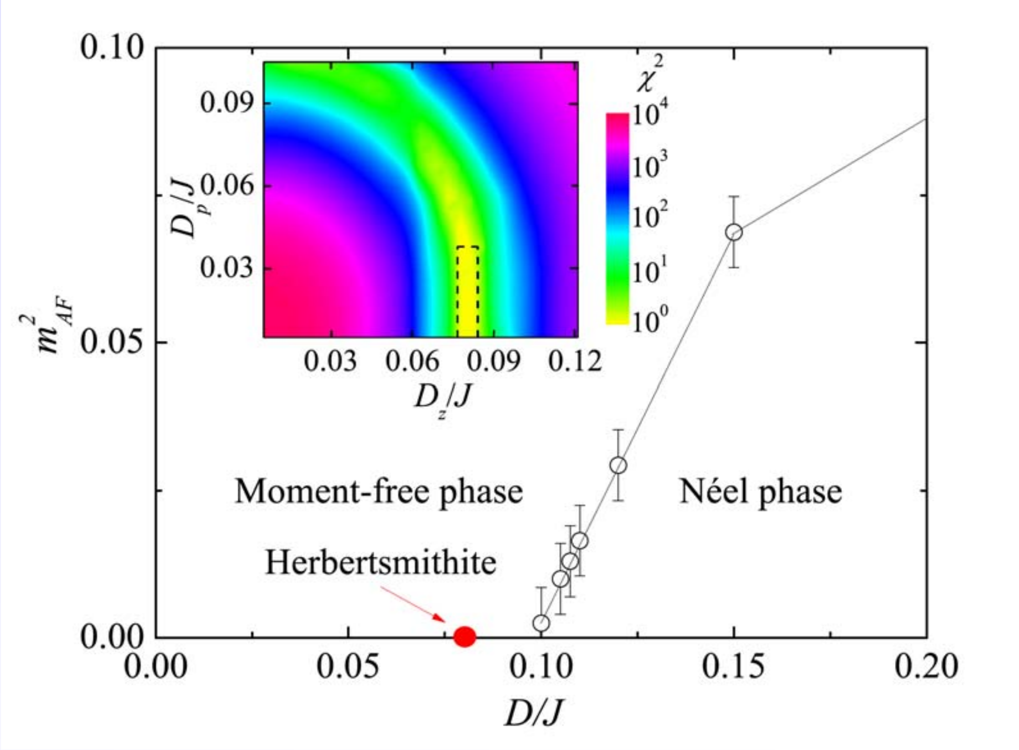
A. Zorko et al, PRL **101**, 026405 (2008)

Dzyaloshinskii-Moriya interactions



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

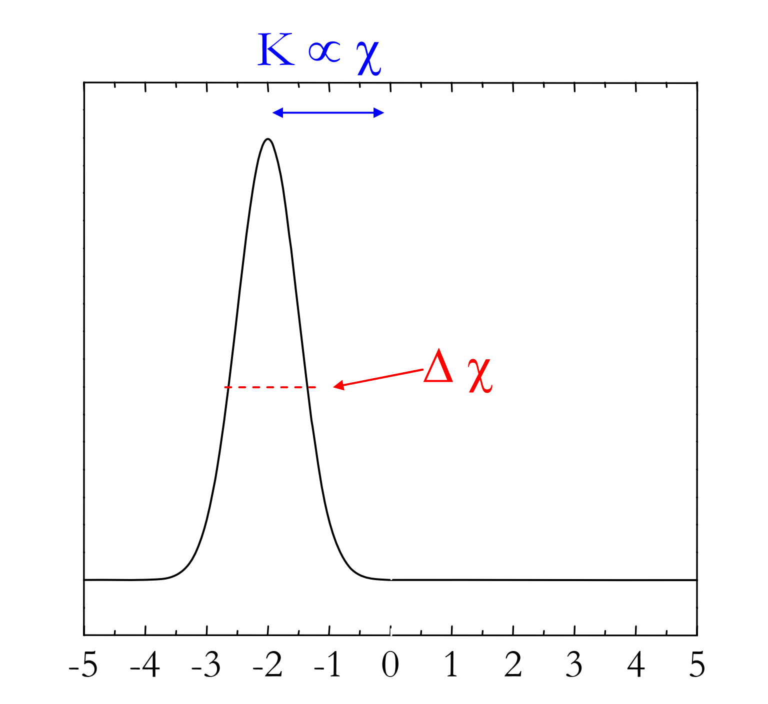
M. Elhajal et al, PRB **66**, 014422 (2002)



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

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

NMR: principles



$$H = H_Z + A\,\vec{I}.\,\vec{S}$$

Linewidth ΔH

spatially inhomogeneous susceptibility (dilution)

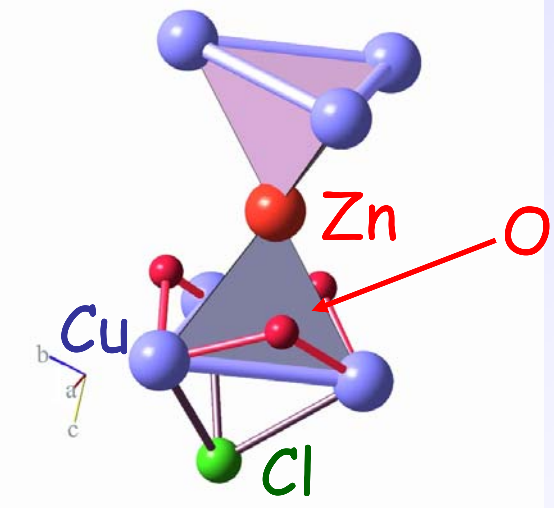
Line shift **K**

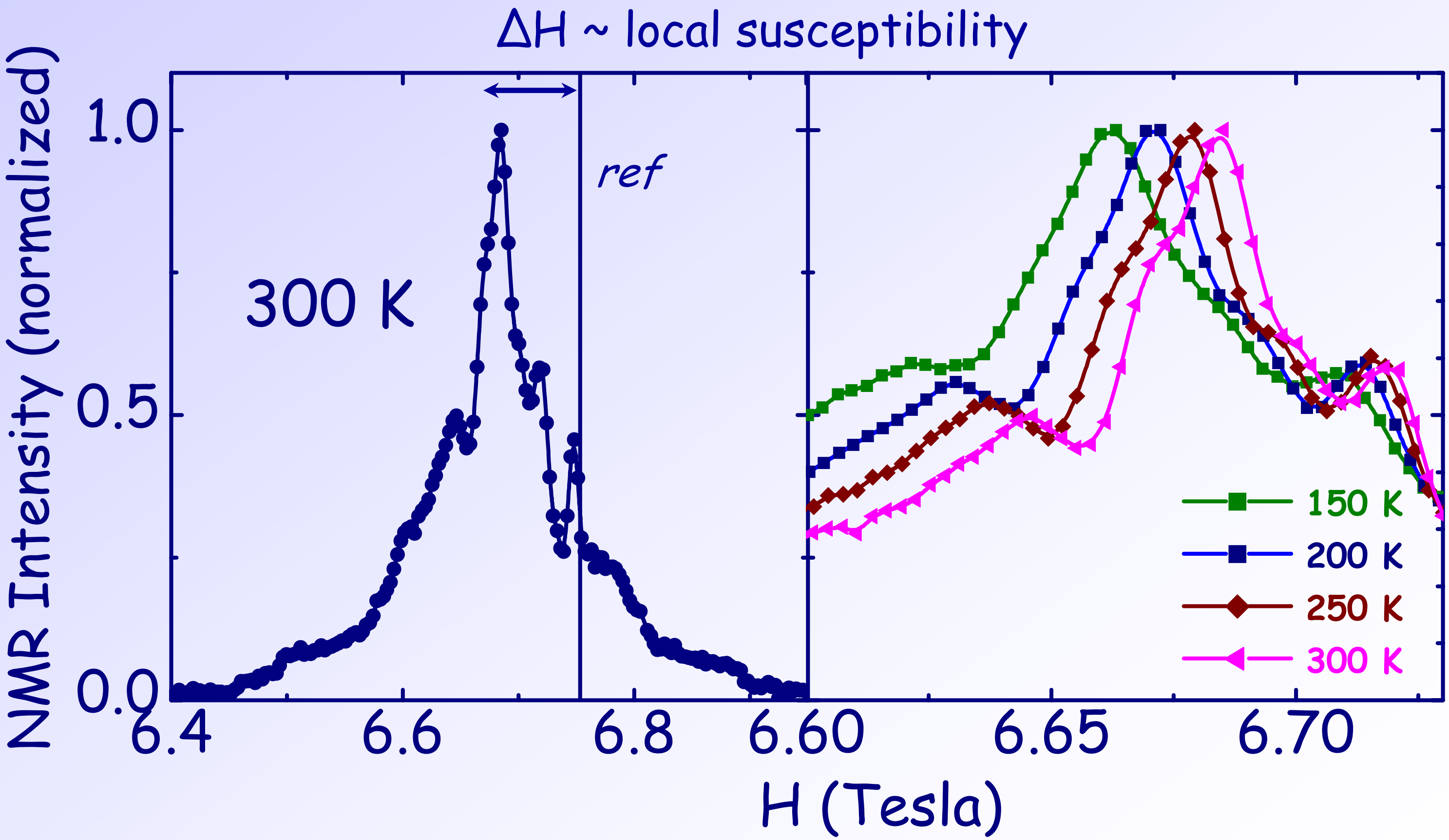
susceptibility χ_{frustr}

^{17}O NMR, local susceptibility

^{17}O: coupled to two Cu of the kagome plane

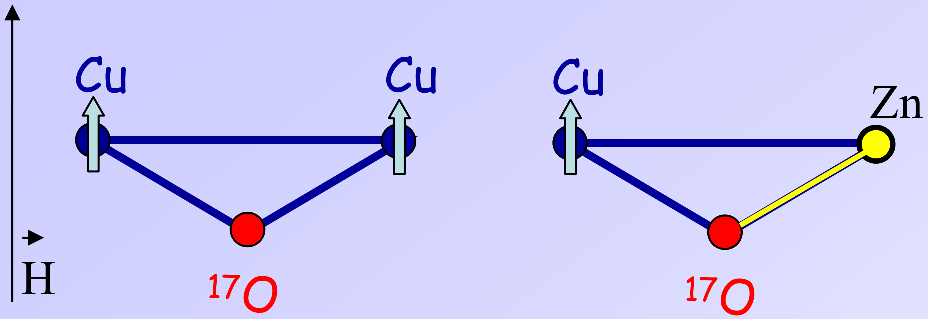
I = 5/2 → quadrupolar effects

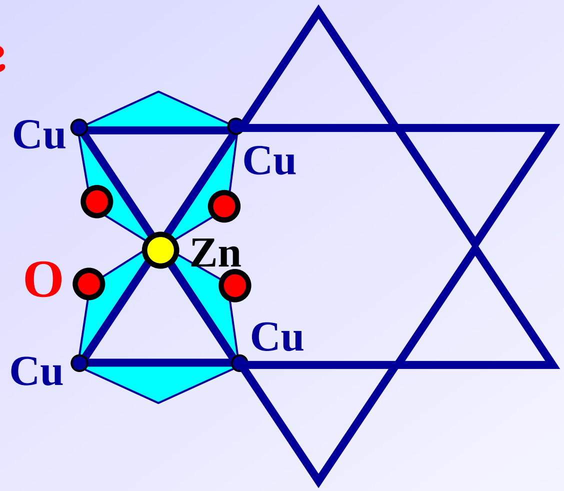


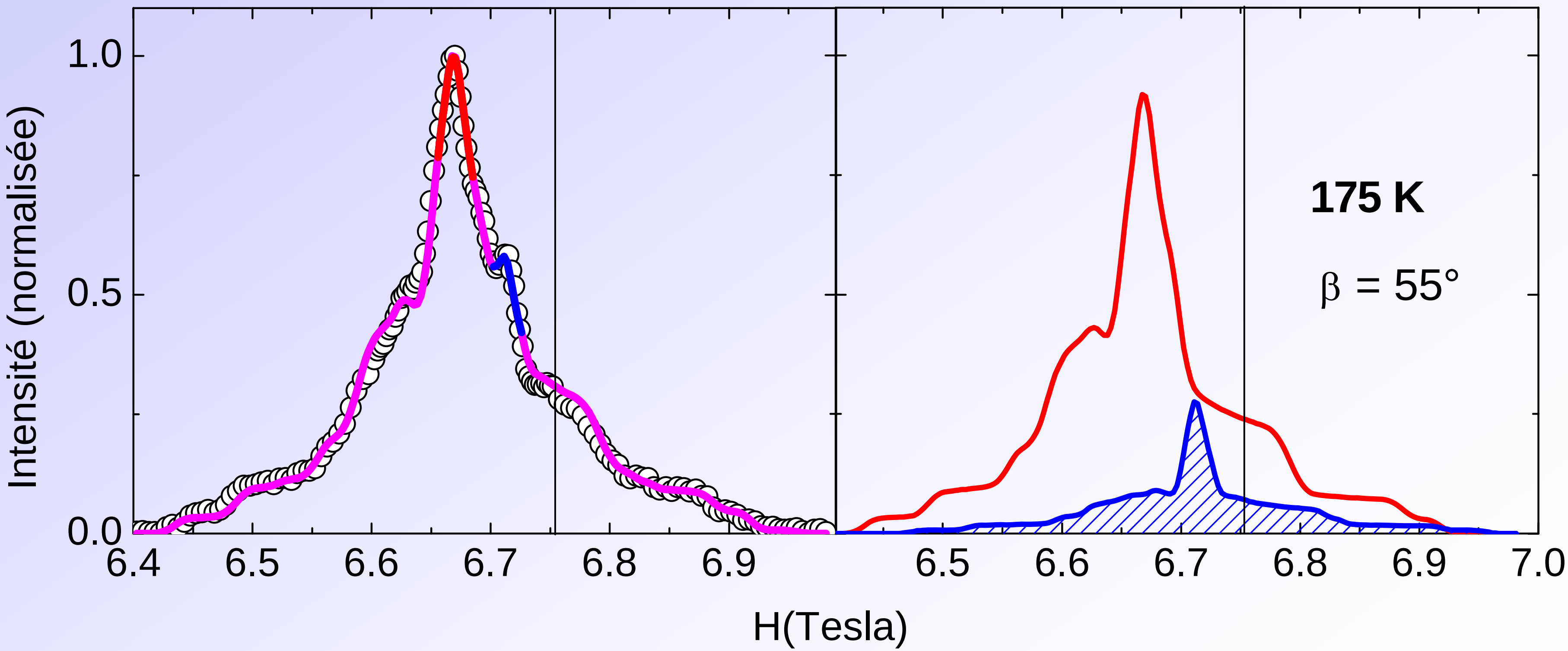


A. Olariu et al, PRL 100, 087202 (2008)

two magnetic site
O next to a Zn defect in the kagome plane

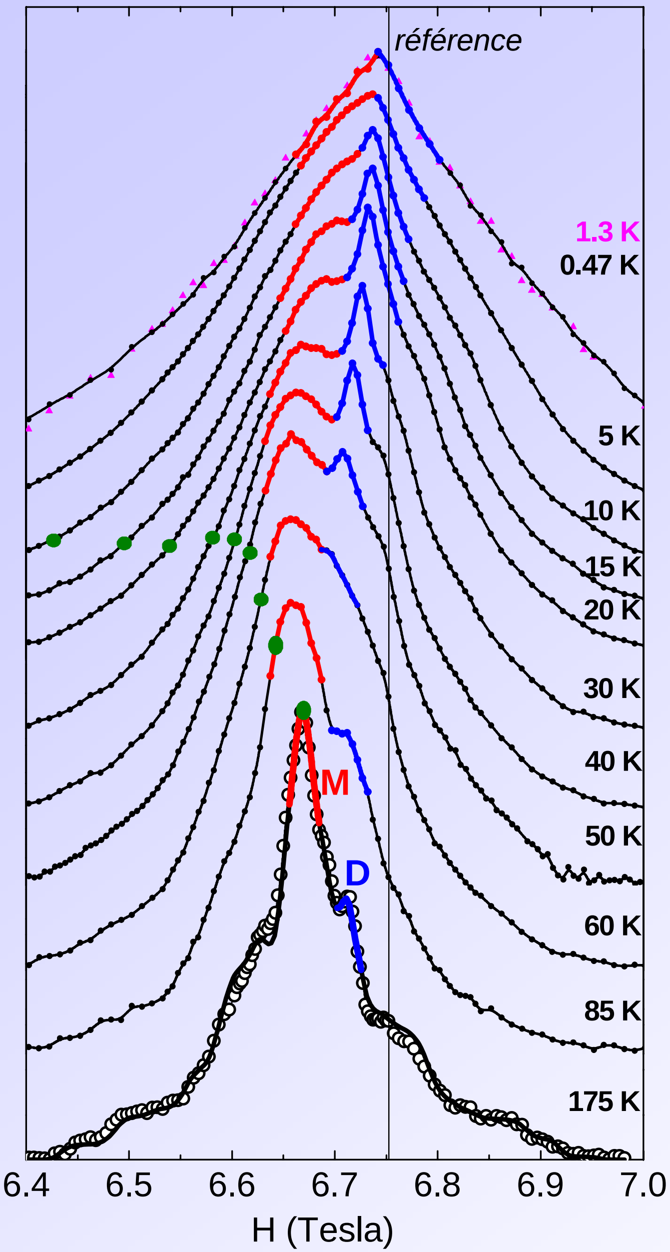


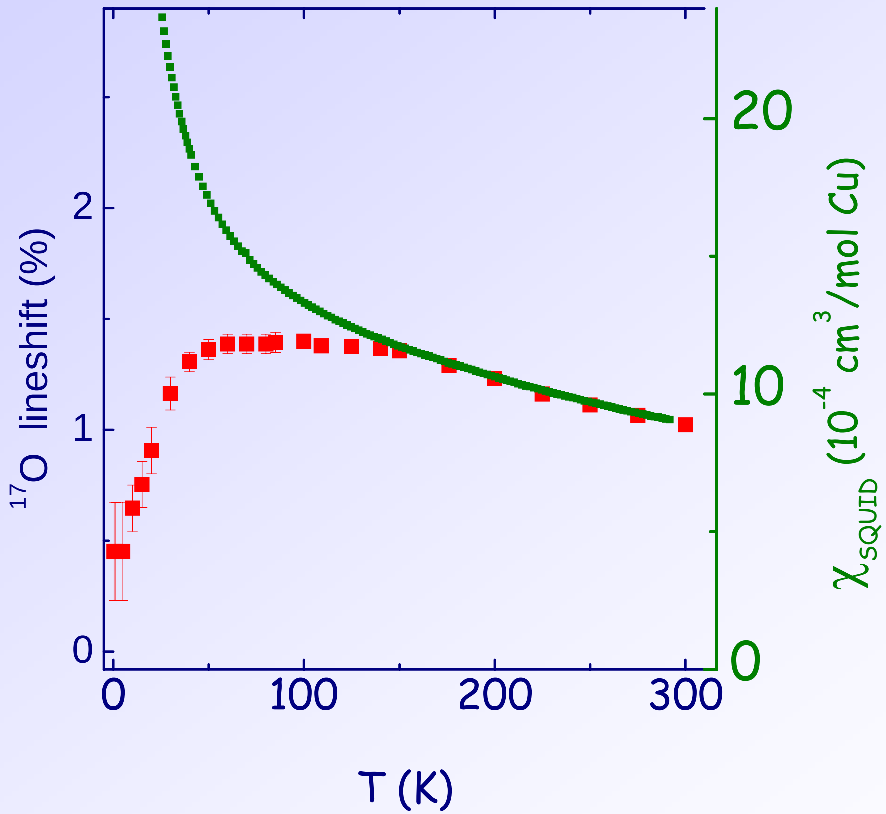




~ 20% intensity -> ~ 5% Zn/Cu defects in kagome planes

Main line, susceptibility of the kagome planes





-Susceptibility decreases below 50 K

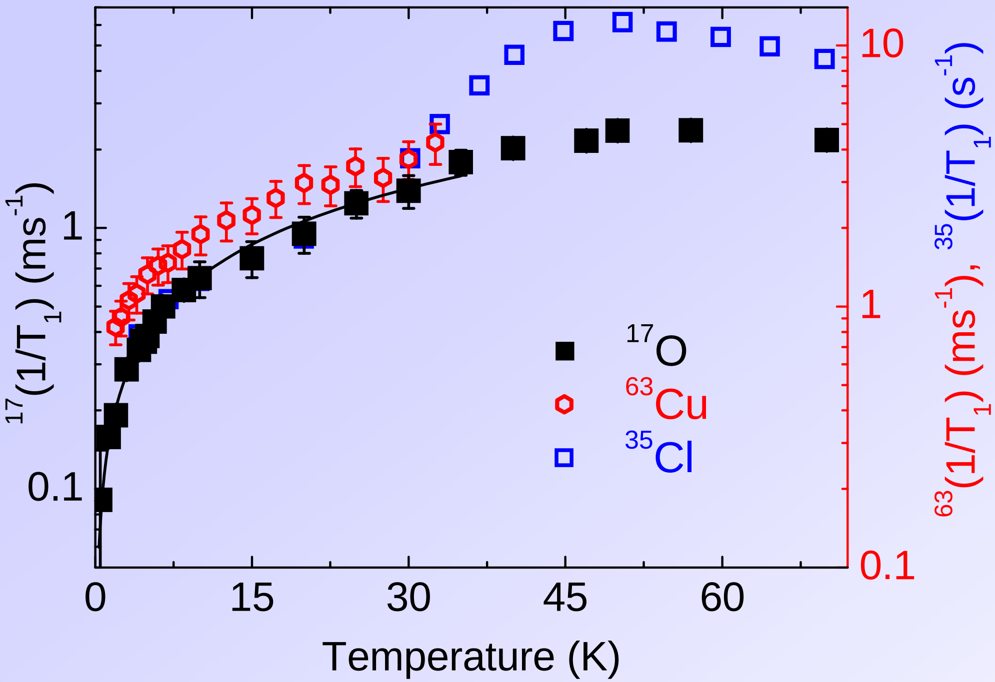
-> enhancement of short range correlations

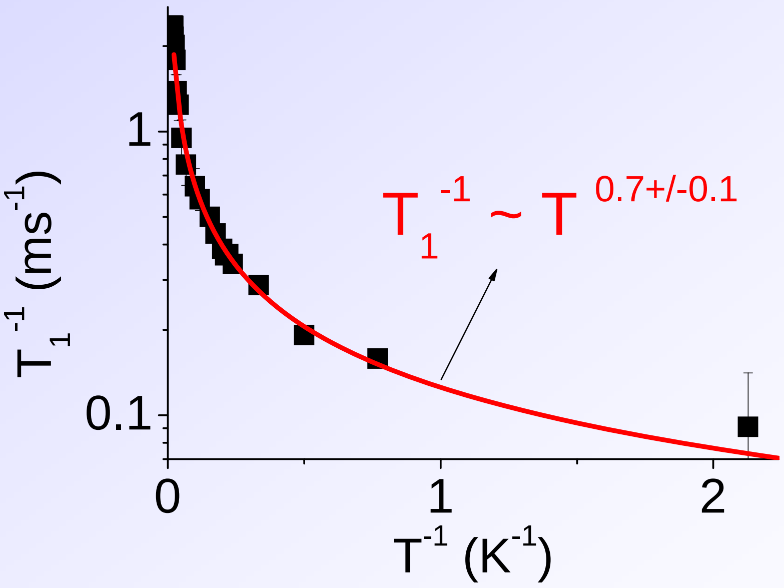
-> new energy scale

-No gap and Finite T->0 susceptibility

intrinsic or field effect, DM ?

Low T Dynamics (NMR: T_1)



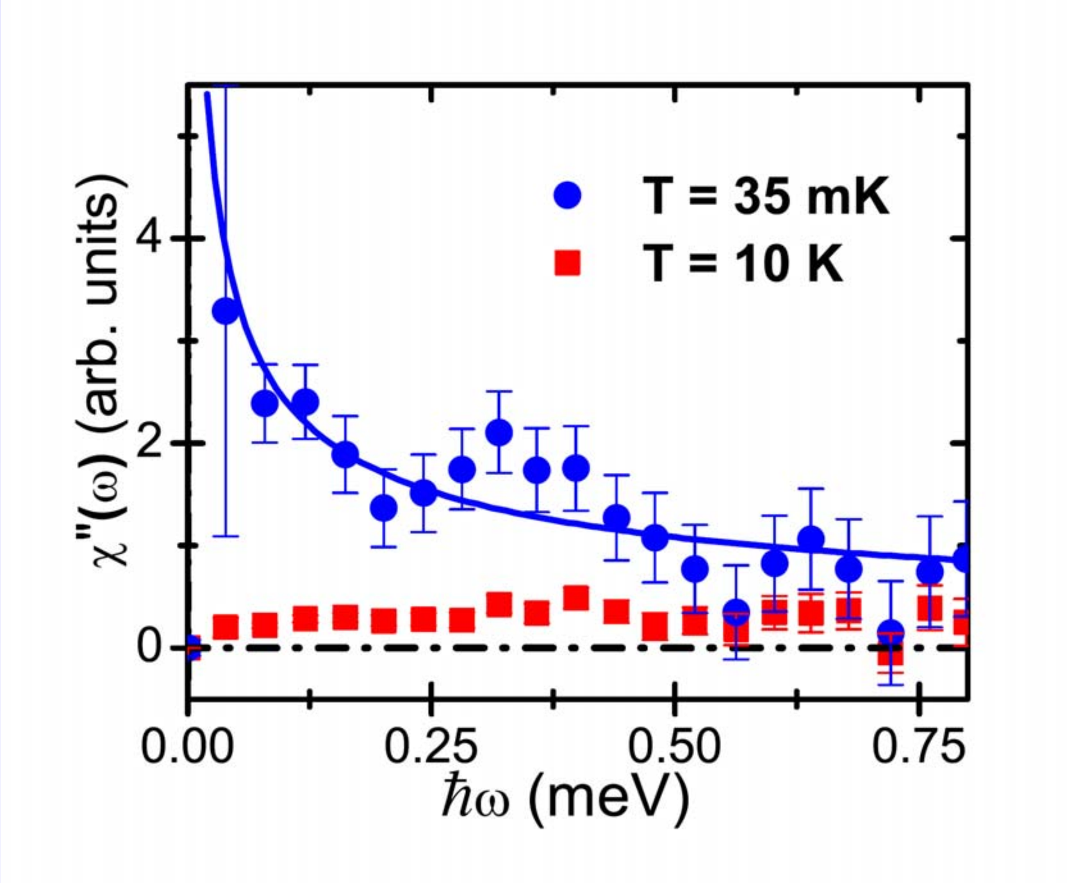


^{63}Cu and ^{35}Cl NMR from T. Imai et al, PRL 100, 077203 (2008)

- No spin gap behavior
  -> in agreement with absence of a gap>0.1meV in INS : Helton et al, PRL 98 107204 (2007)

- original sub-linear T dependence

Low T Dynamics (neutrons: χ'')



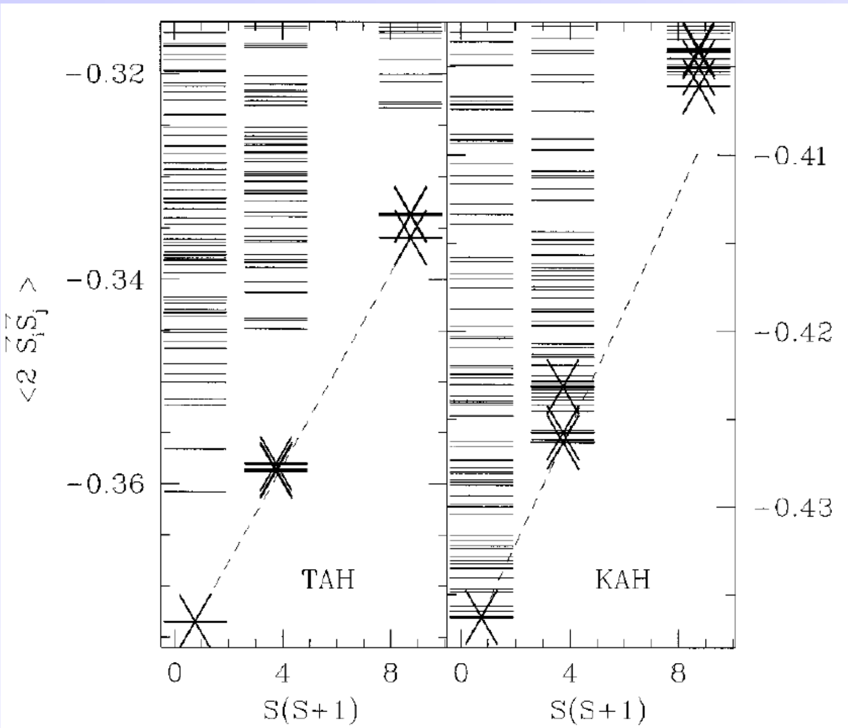
$$\chi''(\omega) \sim \omega^{-0.7(3)}$$

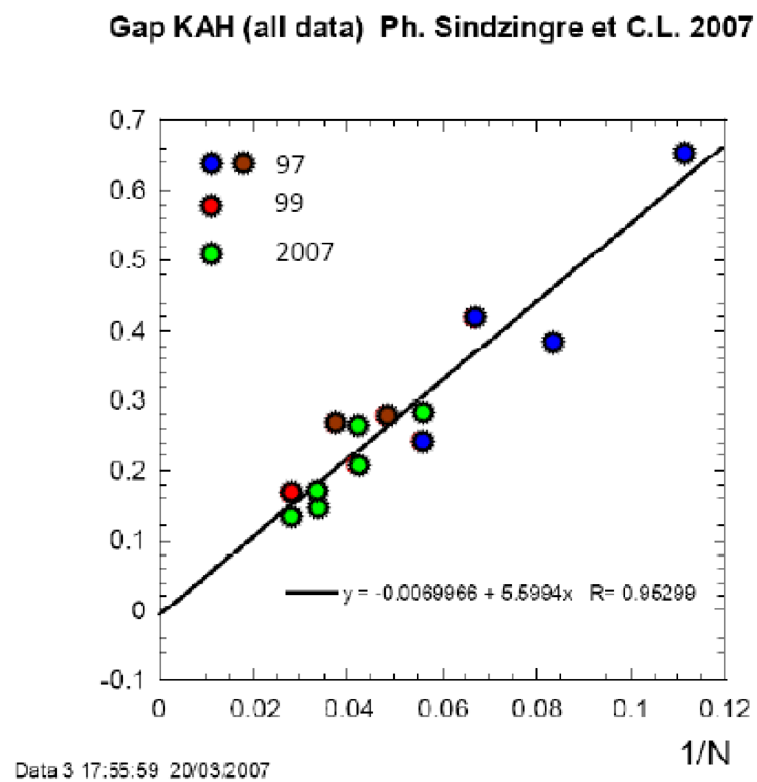
Helton et al, PRL 98 107204 (2007)

Exact Diagonalization

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

- $\Delta < J/20$ gap between singlet ground state and 1st triplet state if any…





Gap = 0 +/- 0.027

- no gap in the singlet sector.

No gap for Herbertsmithite!

- No gap (?) in exact diagonalizations (ED)
- χ(T->0) well reproduced in ED

Could be an intrinsic property

- DM interaction mixes singlet and gapped triplet and could restore a susceptibility

Could be an extrinsic property but one should also explain dynamical properties

Two classes of models

-Valence Bond Crystals with fluctuations of quantum dimers but forming an ordered pattern: a small singlet – triplet gap

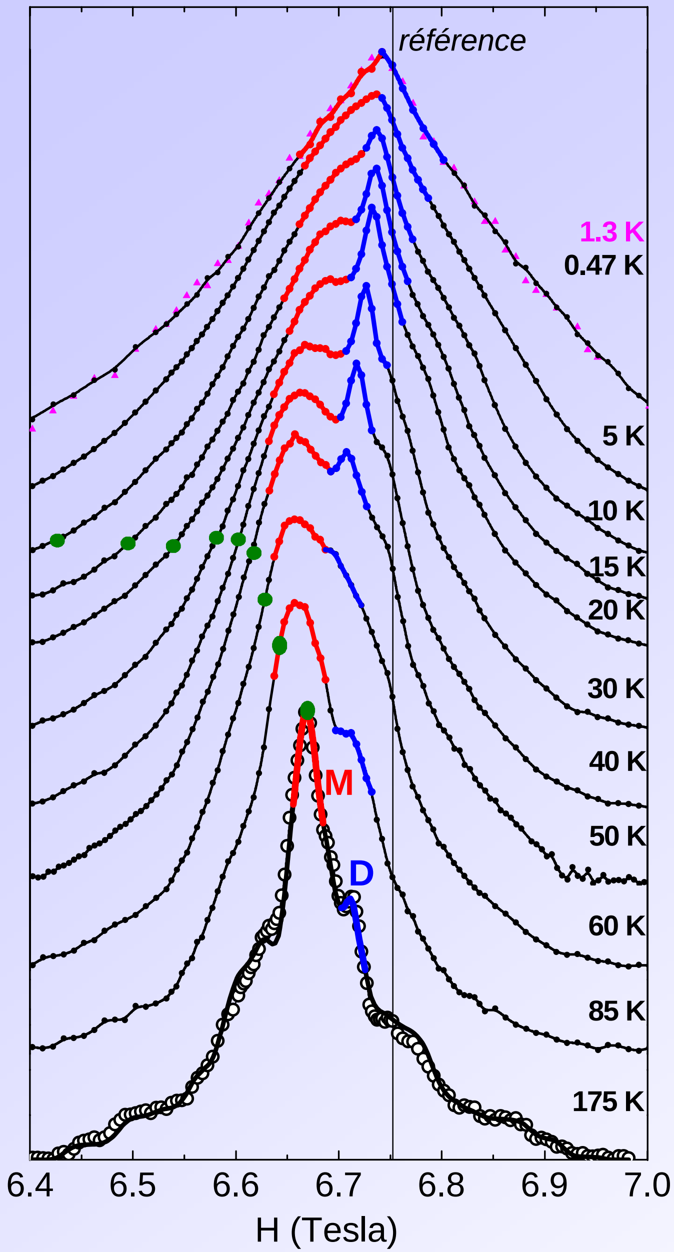
- RVB-type spin liquids: fractional excitations (spinons), e.g. algebraic spin liquids

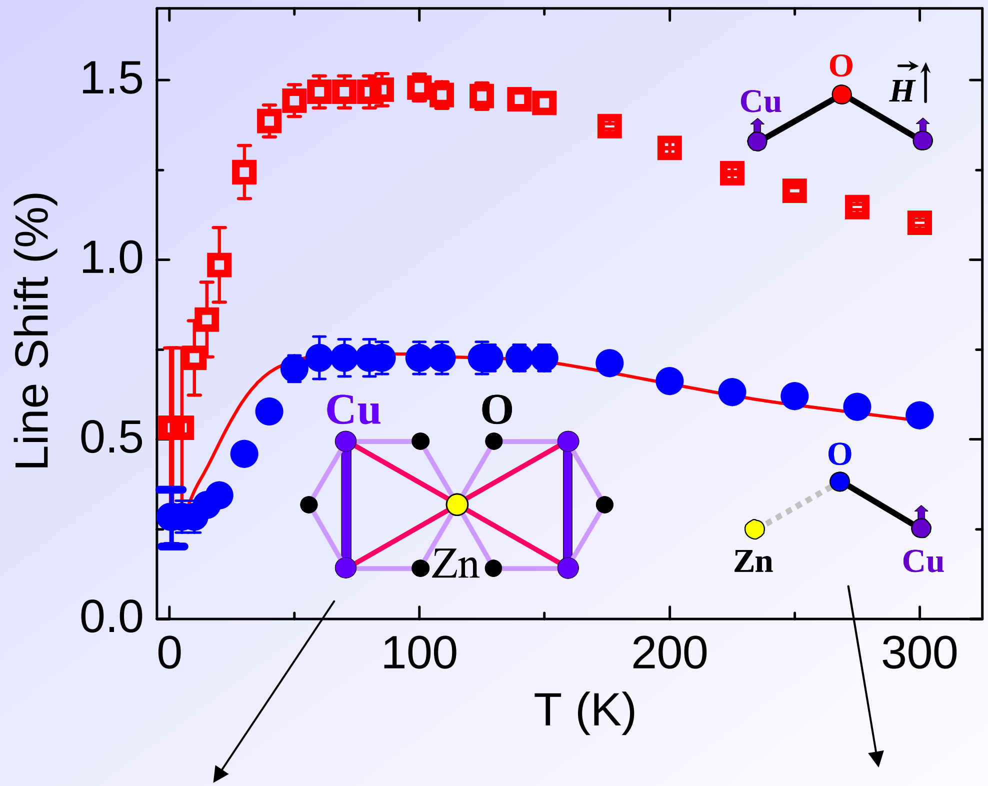
  . Algebraic decrease of correlations

  . no gap

  . Spinons are bound (singlet – spinon interact)

Defect line





~30% oxygen sites
dimer localization around
a spin vacancy

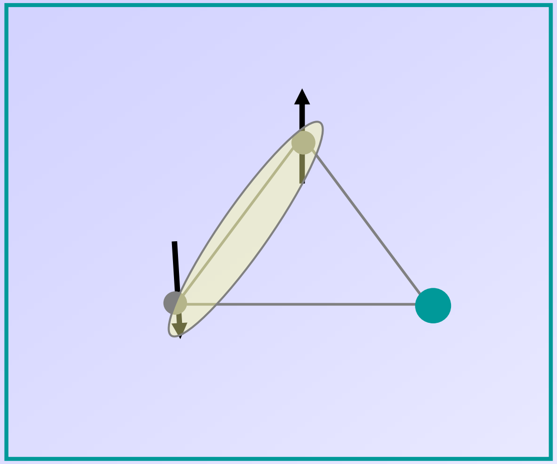
S. Dommange et al,
PRB 68 (2003) 224416

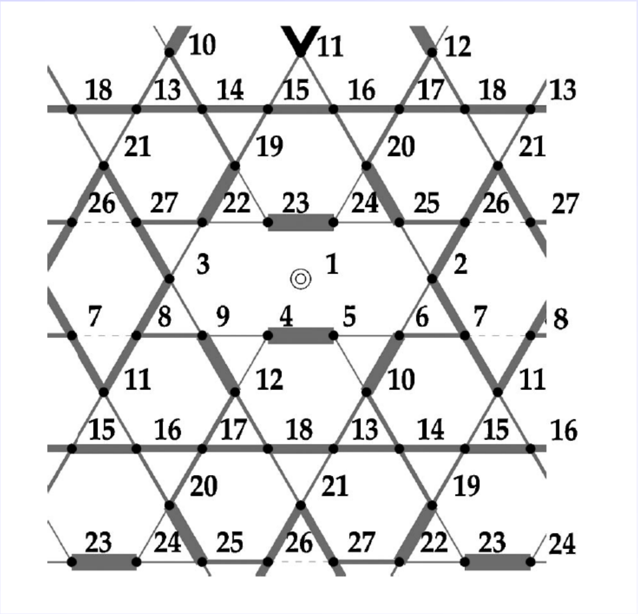
~20% oxygen sites
half shifted

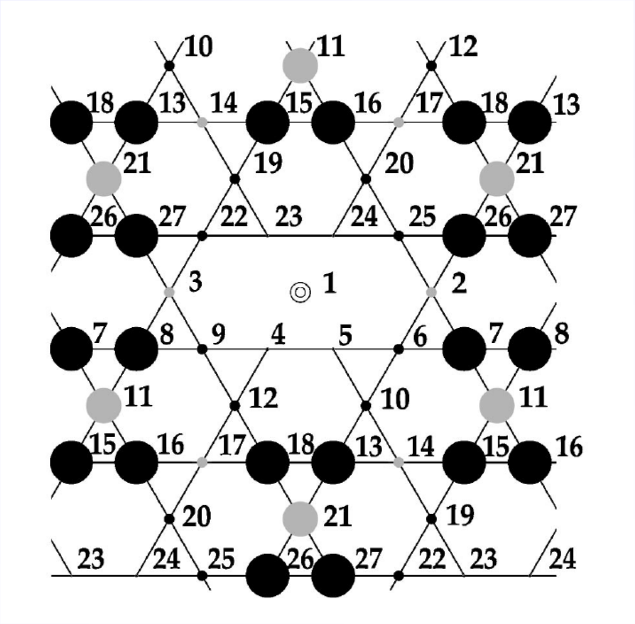
I. Rousochatzakis et al,
Phys.Rev.B 79, 214415 (2009)

-> ~5% spin vacancies in the kagome planes

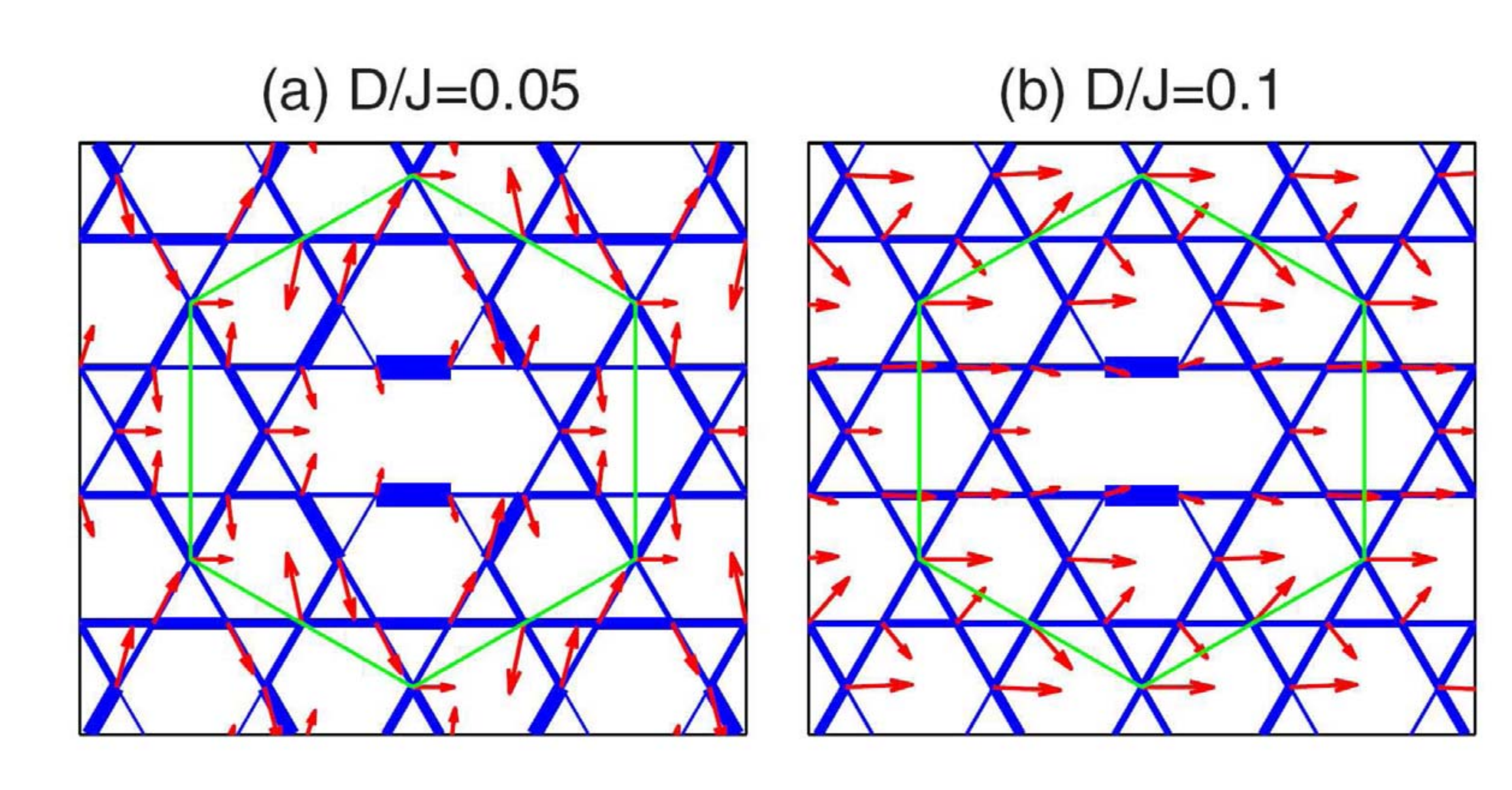
ED: one impurity







Dommange et al., PRB **68**, 224416 (2003); Lauchli et al. Phys. Rev. B 76, 144413 (2007)



-Dimers next to the impurity survive up to D~J

-DM interaction removes the singlet nature of the ground state

I. Rousochatzakis et al, Phys.Rev.B 79, 214415 (2009)

Conclusions on Herbertsmithite

- first S=1/2 antiferromagnet with perfect kagome lattice (3 fold symmetry)

- no order or frozen disorder down to 50mK despite J=175K and perturbations

Quantum spins on a perfect kagome lattice
-> allows close comparison with theory
-> renewed interest in understanding the GS

VBC : R.R.P. Singh and D.A. Huse, PRB (2007, 2008)

Dirac spin liquid : Y. Ran et al, PRL (2007), PRB (2008) ....

- magnetic defects (rather complex, in plane and out of plane) which impact the low T thermodynamic measurements
-> local probe techniques
-> second sample generation : controlled (or no) defects

- sizeable DM interaction : D/J~0.1: probe criticality: on-going

- Local susceptiblity determined from ^{17}O NMR:
ground state appears to be gap-less with a finite susceptibility
intrinsic to Heisenberg kagome model or DM interaction closes the gap ?
(no field effect)

PHFM 2010
Perspectives in Highly Frustrated Magnetism

Dresden , 19 – 23 April

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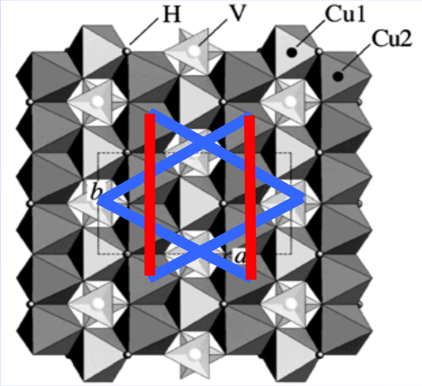
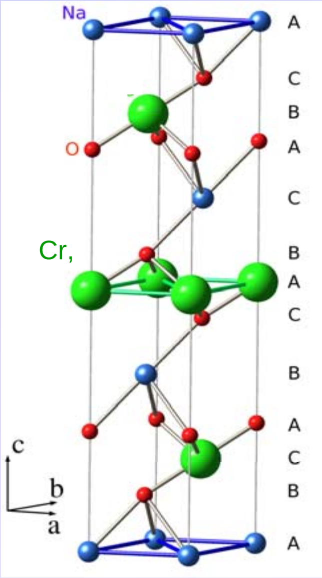
Frustration and original ground states - Collaborations

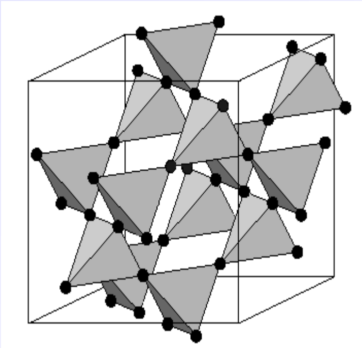
Herbertsmithite
F. Ladieux, S. Nakamae, P. Bonville
SPEC, CEA Saclay
MA de Vries, A. Harrisson, Edinburgh
F. Duc, JC Trombe CEMES, Toulouse
P. Strobel, Institut Néel, Grenoble



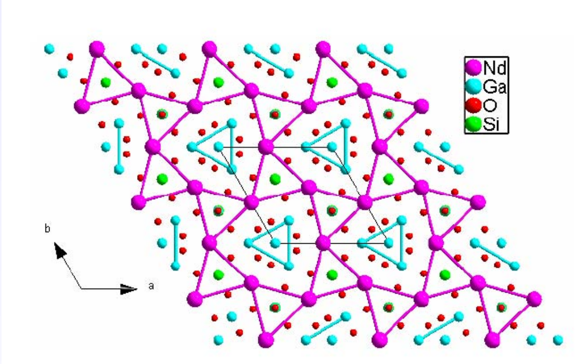
Kagome
Volborthite,
CEMES, Toulouse
Bert et al, PRL 2005



Triangular
$NaCrO_2$
R. Cava, Princeton
Olariu et al, PRL 2006



Pyrochlore
$Tb_2Sn_2O_7$
LLB, Saclay
Bert et al, PRL 2006



Kagome+
Spin anisotropy
Langasites
Institut Néel,
Grenoble
Zorko et al, PRL (2008)

Thank you!

Herbertsmithite:
$ZnCu_3(OH)_6Cl_2$

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