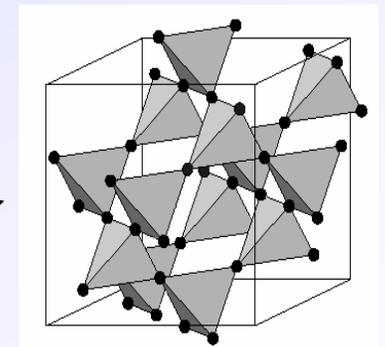
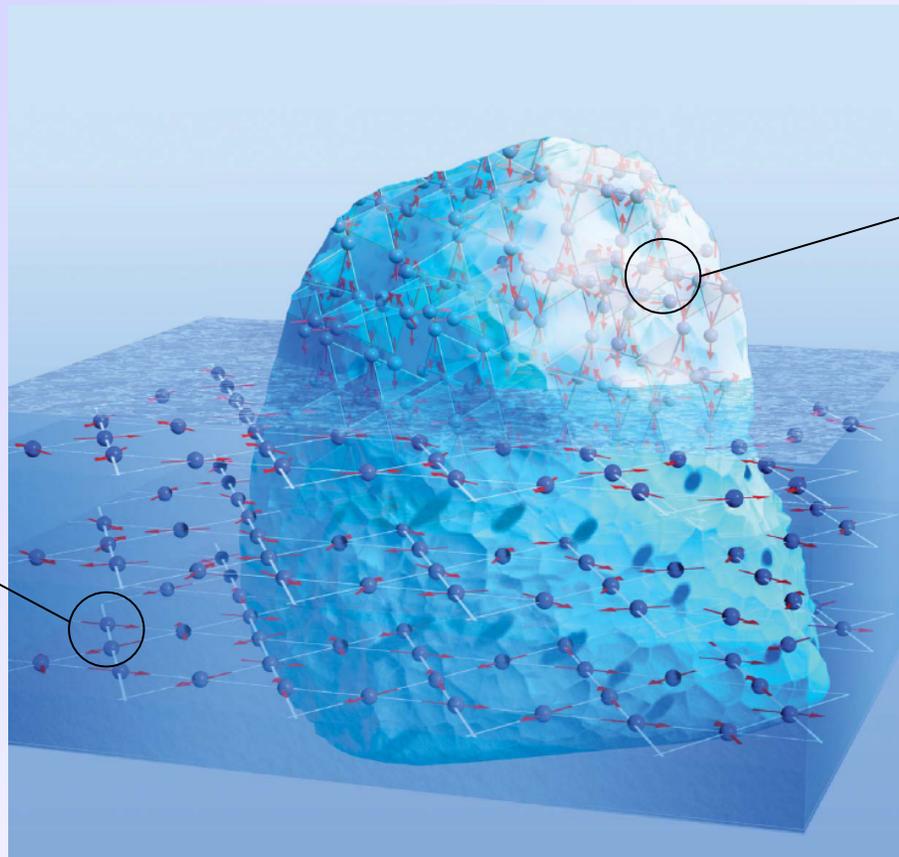
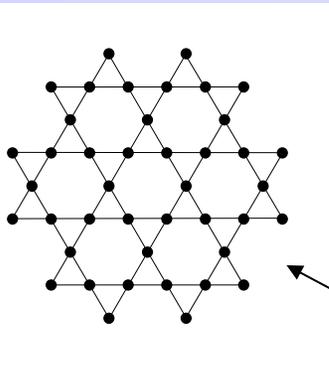
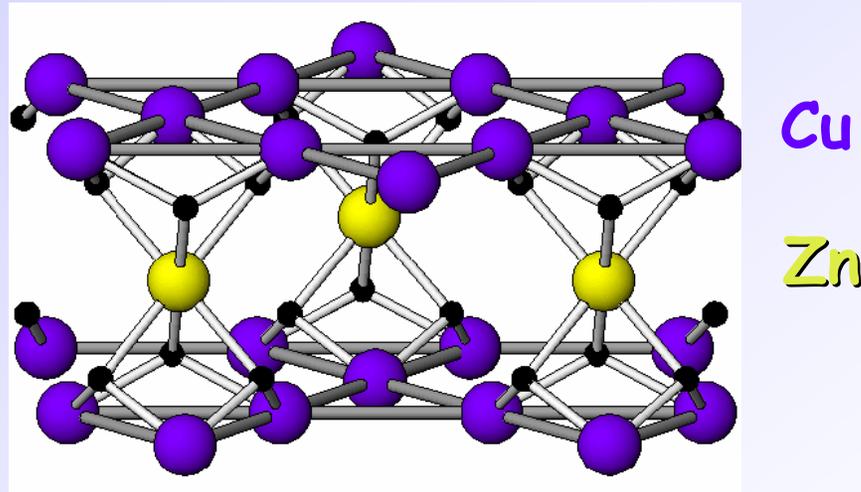


L'Herbertsmithite: un liquide de spins idéal sur réseau kagomé?



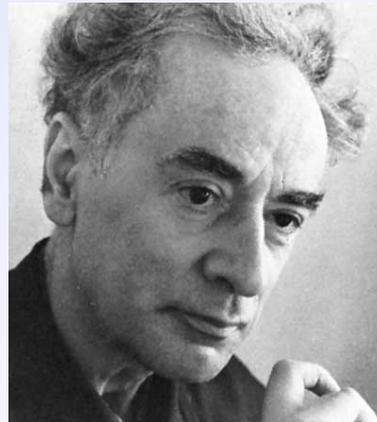
Fabrice Bert, Areta Olariu, Andrej Zorko, Philippe Mendels

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



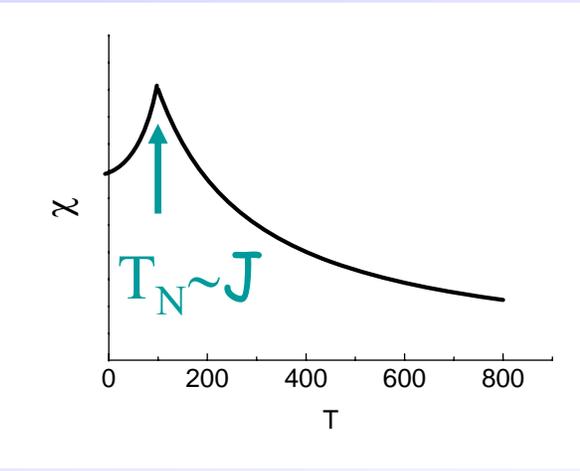
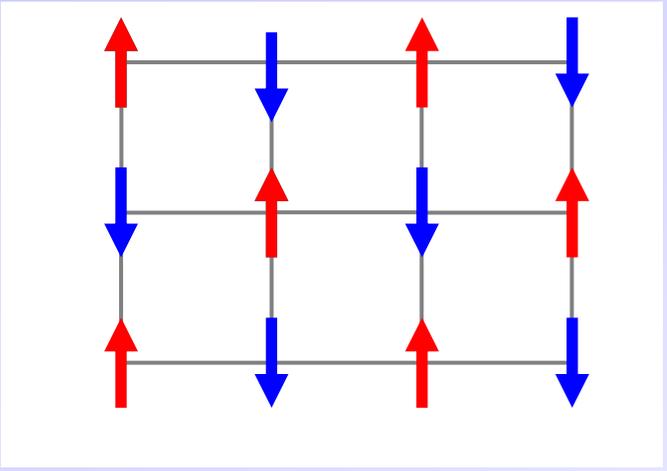
- J. C. Trombe, F. Duc, *CEMES, Toulouse, France*
- M. de Vries, G. Nilsen, A. Harrison, *Edinburgh, UK*
- P. Strobel, *Institut Néel, Grenoble*
- S. Nakamae, F. Ladieu, D. L'Hôte, P. Bonville, *CEA Saclay, France*

Néel versus Anderson



Antiferromagnétisme, Etat de Néel 'classique'

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



+

Fluctuations quantiques pour S=1/2



Antiferromagnétisme, une alternative?

RESONATING VALENCE BONDS: A NEW KIND OF INSULATOR?*

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

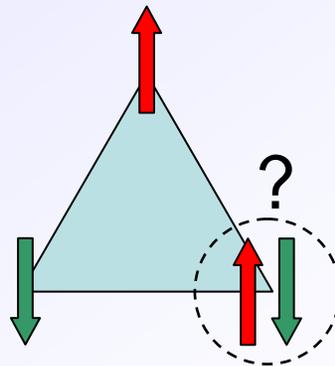
(Received December 5, 1972; Invited**)

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.



Frustration géométrique des interactions magnétiques



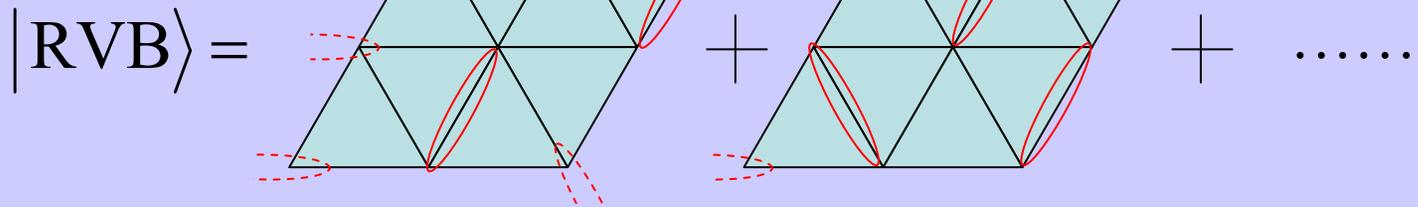
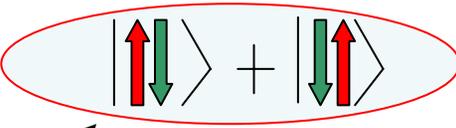
Antiferromagnétisme, une alternative?



RESONATING VALENCE BONDS: A NEW KIND OF INSULATOR?*

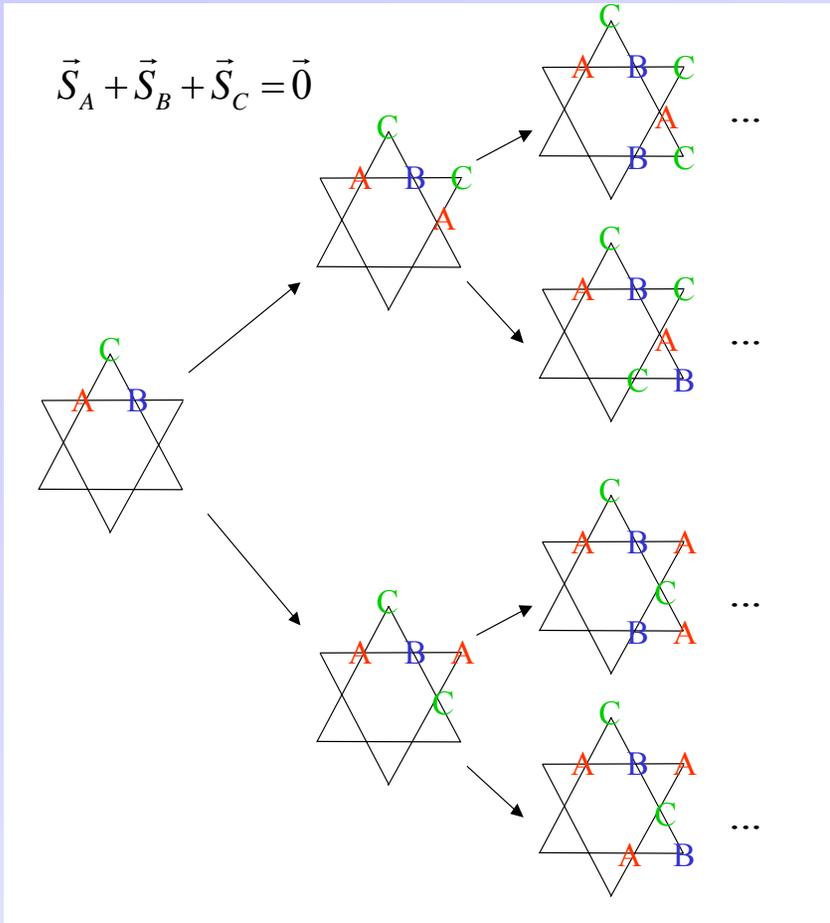
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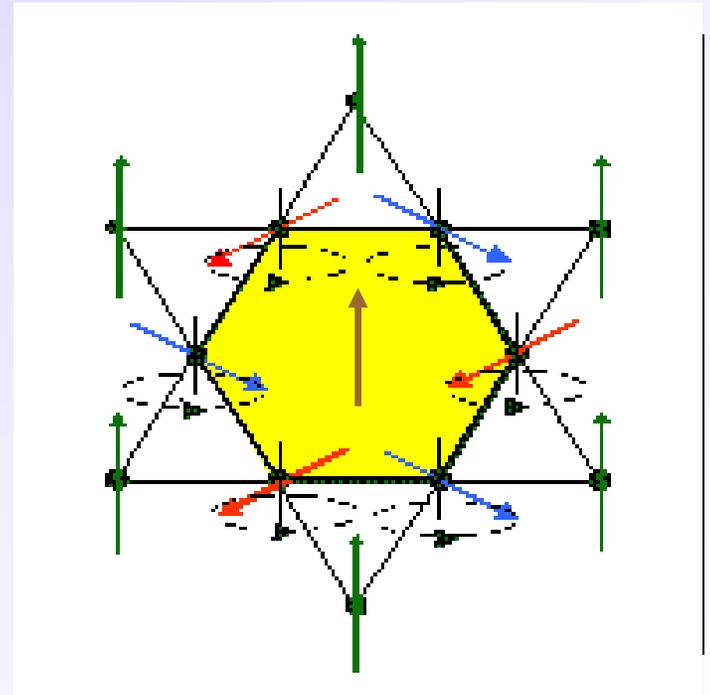


$|\text{RVB}\rangle =$

Corner sharing: kagomé lattice



Macroscopic degeneracy

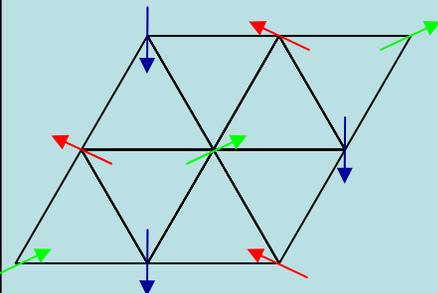


Soft modes

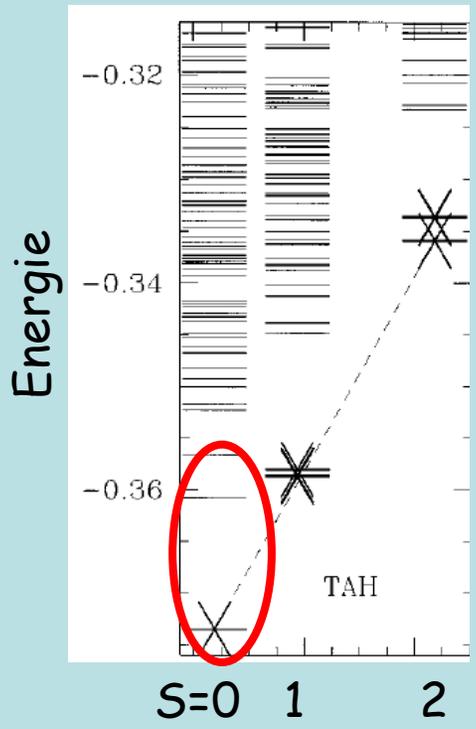
Antiferromagnétisme, une alternative?

Diagonalisations exactes
 Lecheminant, PRB **56**, 2521 (1997)
 Waldtmann, EPJB **2**, 501 (1998).

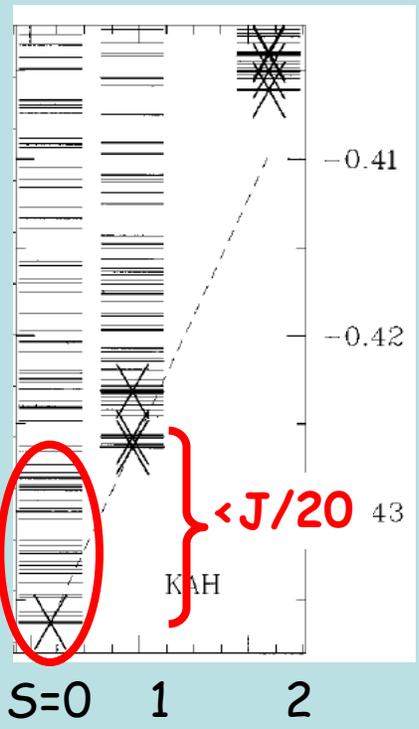
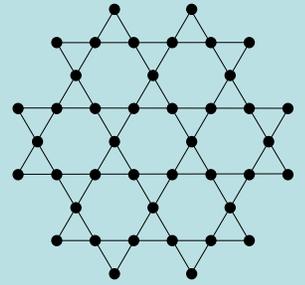
triangulaire
 Géométrie à cotés partagés



Fondamental Néel



Kagome
 Géométrie à sommets partagés



Fondamental 'liquide de spins' ≠ Néel
 RVB ? Mila, PRL **81**, 2356 (2000)

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

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

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Cambridge, Massachusetts 02139-4307*

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

L'Herbertsmithite:



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



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

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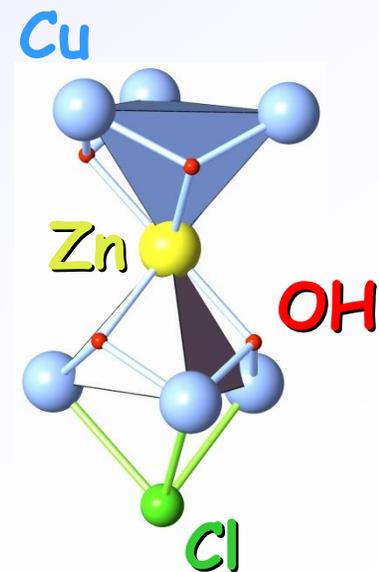
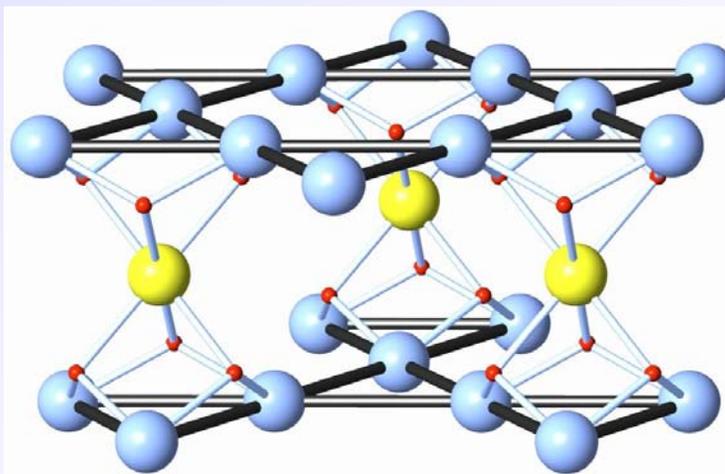
*Department of Chemistry, 6-335, Massachusetts Institute of Technology, 77 Massachusetts Avenue,
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L'Herbertsmithite:

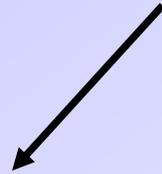


Cu^{2+} , $S=1/2$



1- $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$: famille des paratacamites $x < 1$

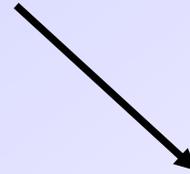
2- $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$: Herbertsmithite: kagomé idéal ?



Gap?

Mesures de χ_{local}

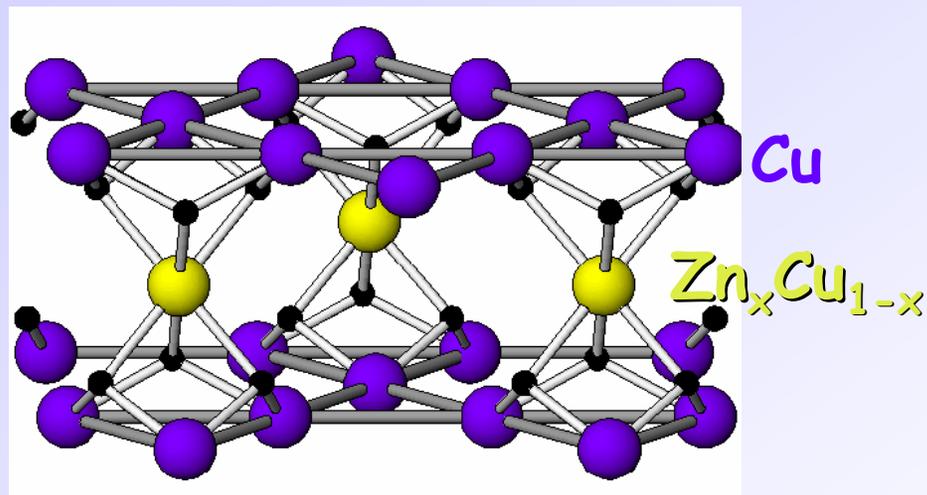
Mesures de dynamique



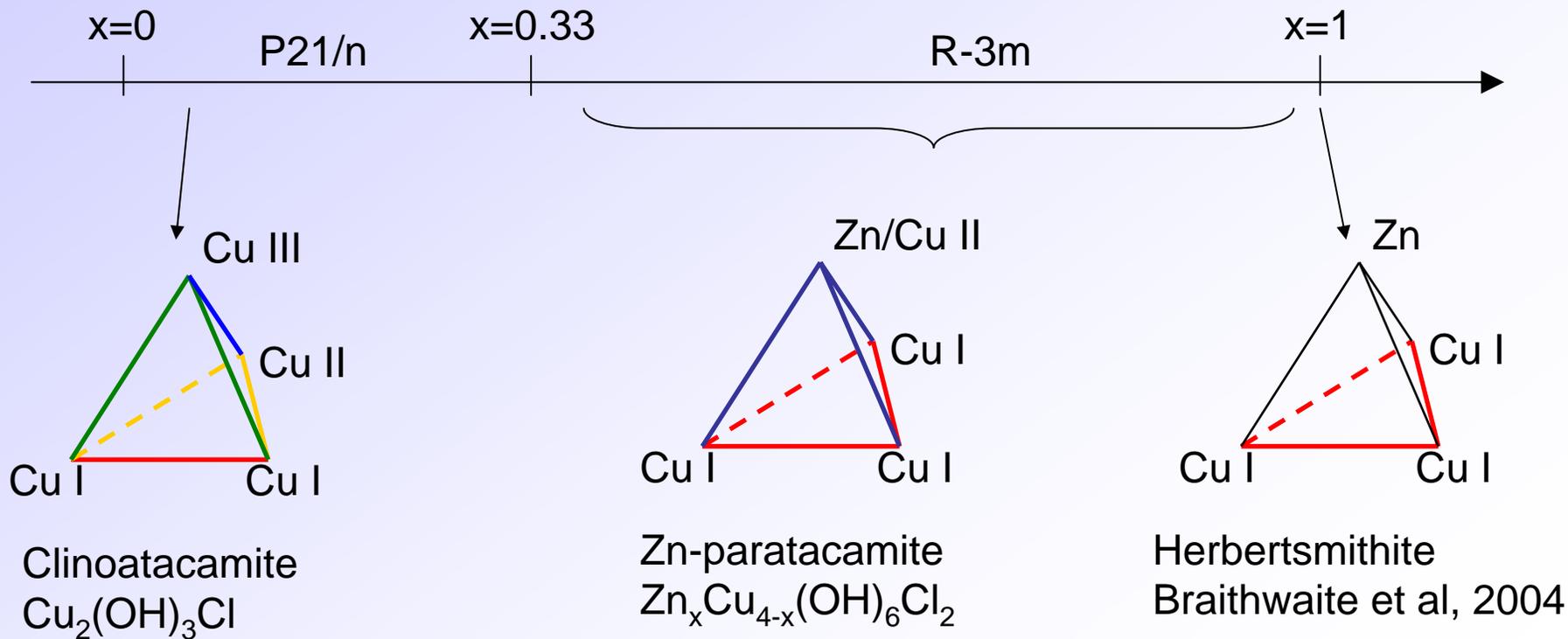
Défauts non magnétiques

Cu/Zn

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

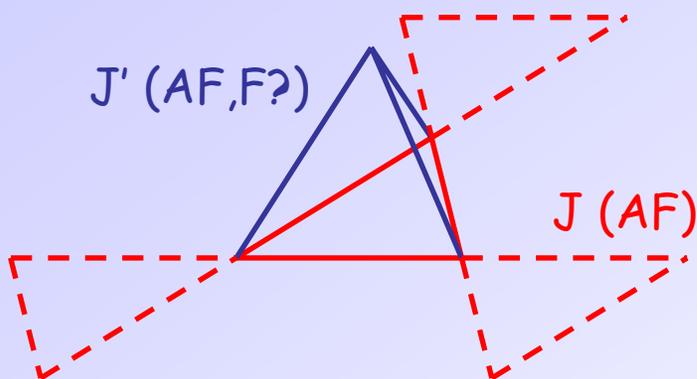


Zn/Cu substitution rate



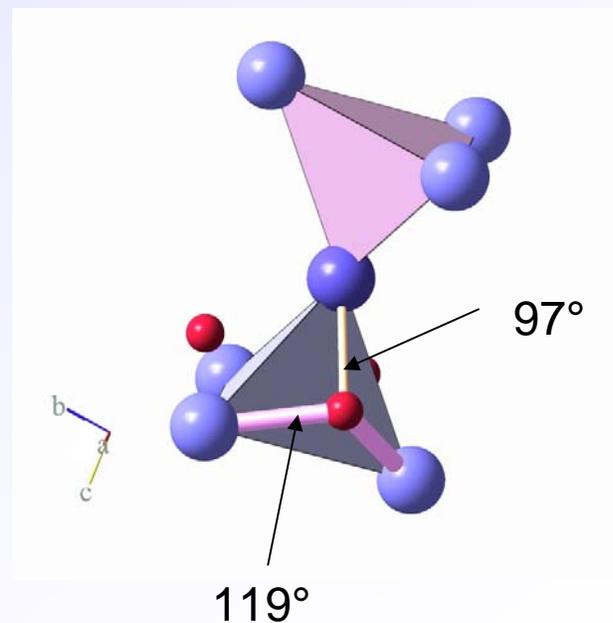
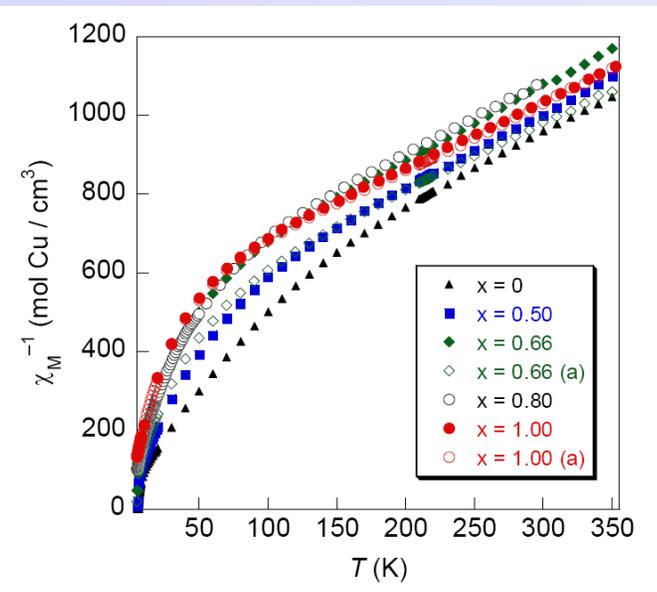


Curie Weiss behavior for all x
 → antiferromagnetic correlations



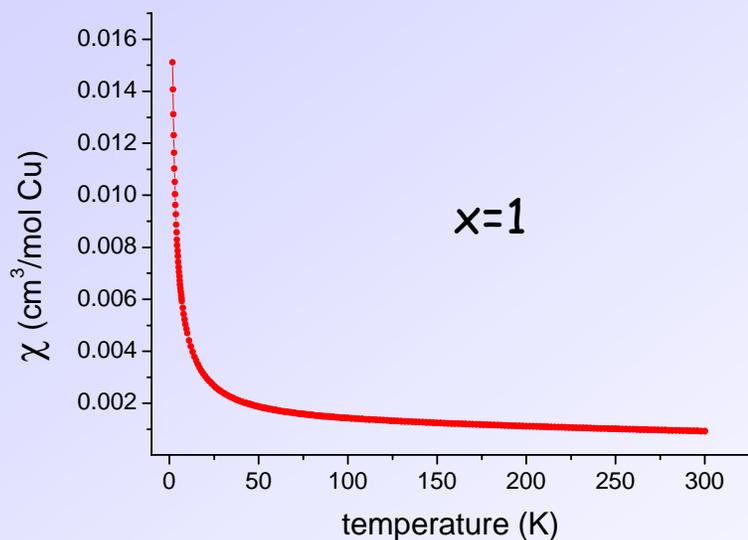
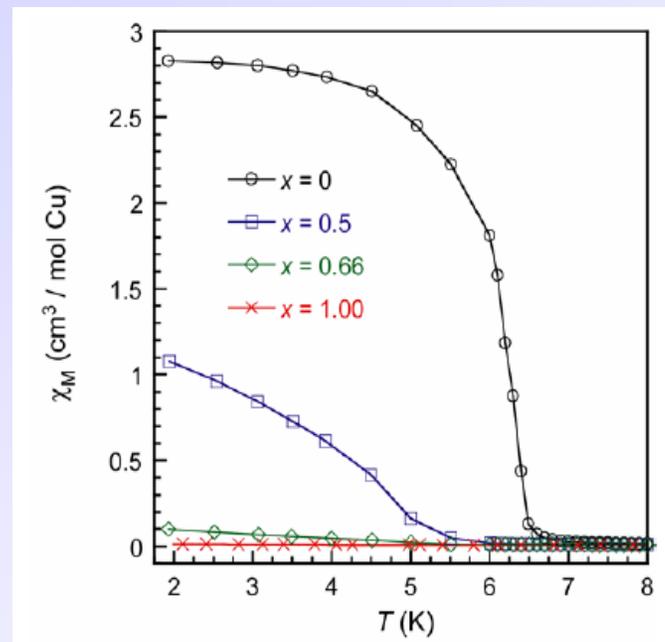
J : in-plane coupling AF ~ 175 K
 J' : inter-plane coupling small, maybe Ferro

no transition for $T \ll J$
 → highly frustrated antiferromagnets





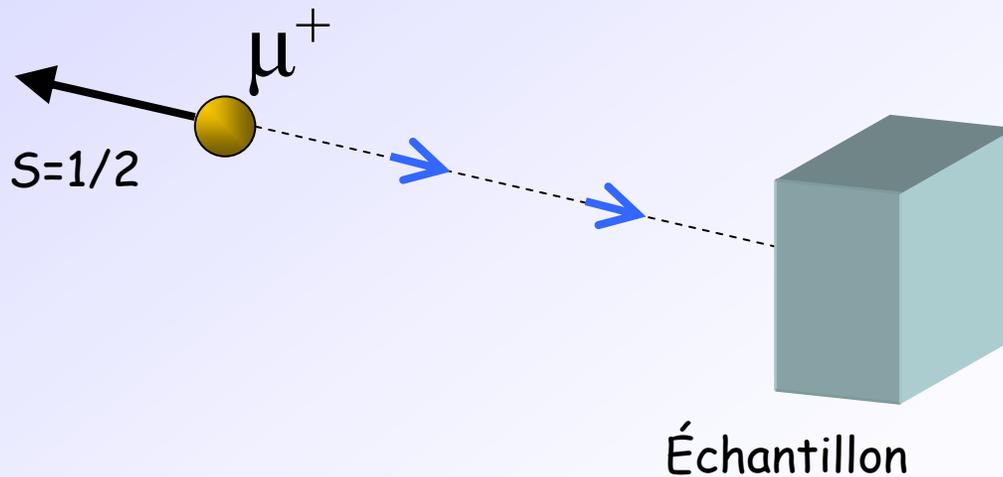
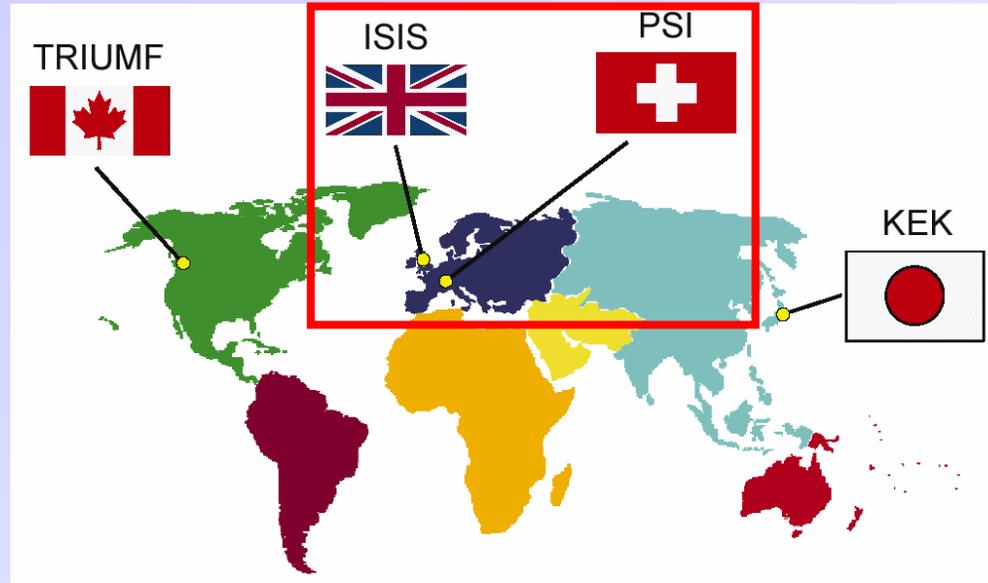
- Ferromagnetic-like transition at $T_N \sim 6\text{K}$
- Vanishes for $x \rightarrow 1$



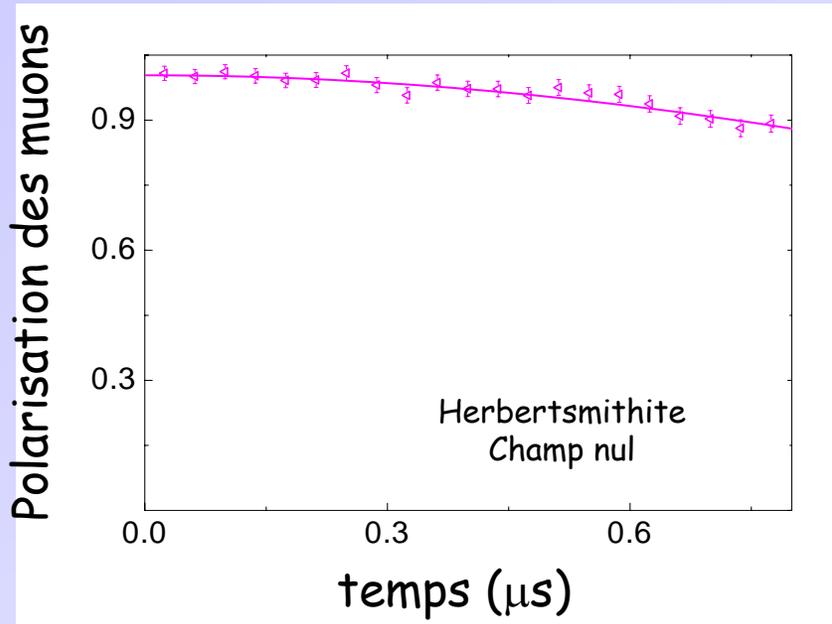
Herbersmithite $x=1$

- No sign of transition for $T > 2\text{K}$
- Low T Curie like upturn for $T < 50\text{K}$

μ SR - Relaxation des spins des muons

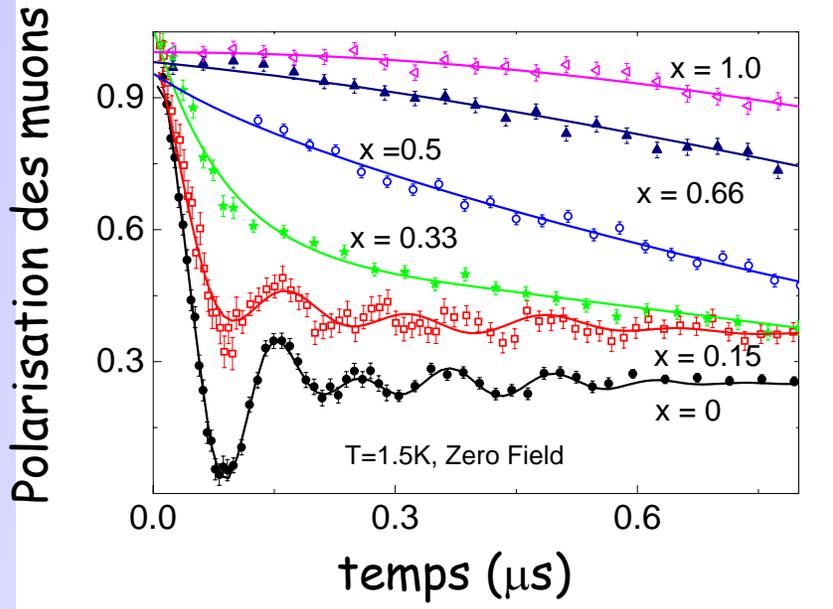
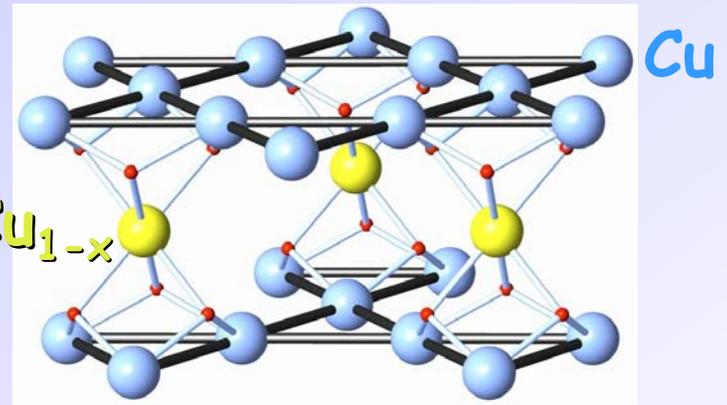


Un fondamental liquide (μ SR)



- $x=1$: jusqu'à $T=50\text{mK}$, pas
d'ordre ni de gel magnétique
($m_{\text{Cu}} < 10^{-4} \mu_{\text{B}}$)

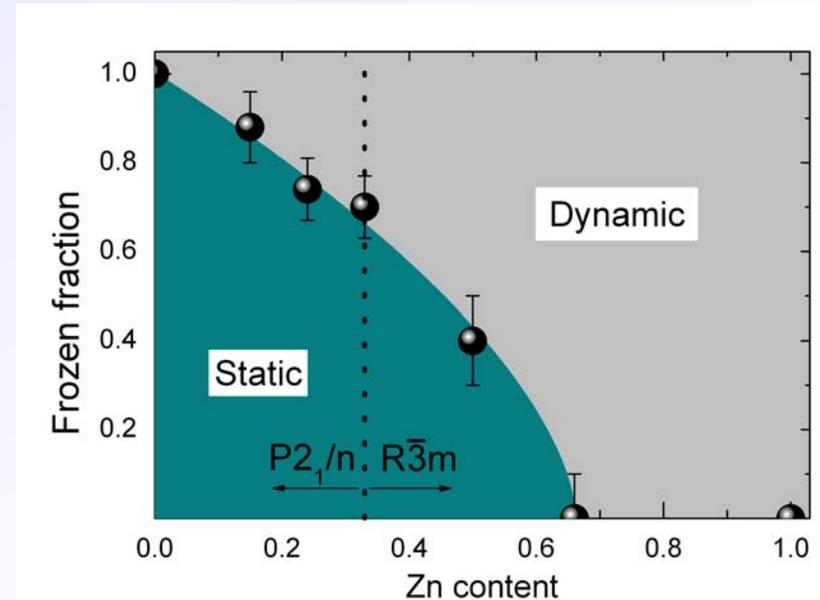
μ SR : diagramme de phase des atacamites
 $Zn_xCu_{4-x}(OH)_6Cl_2$



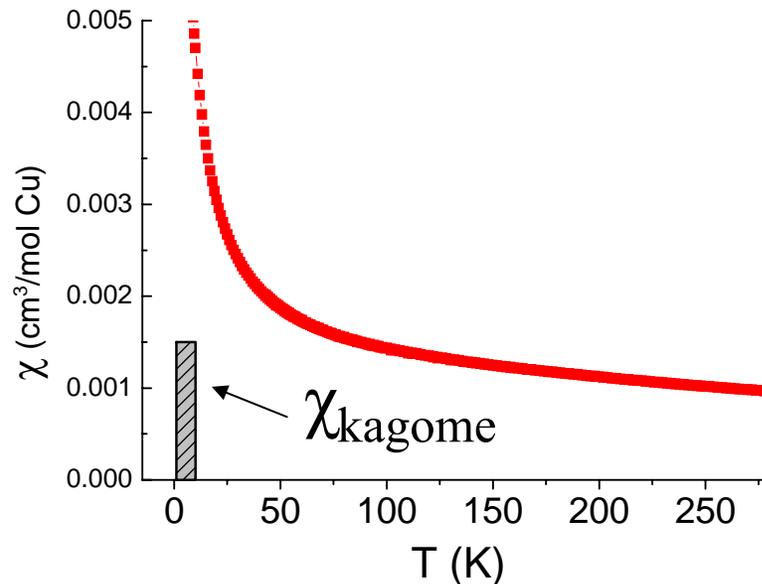
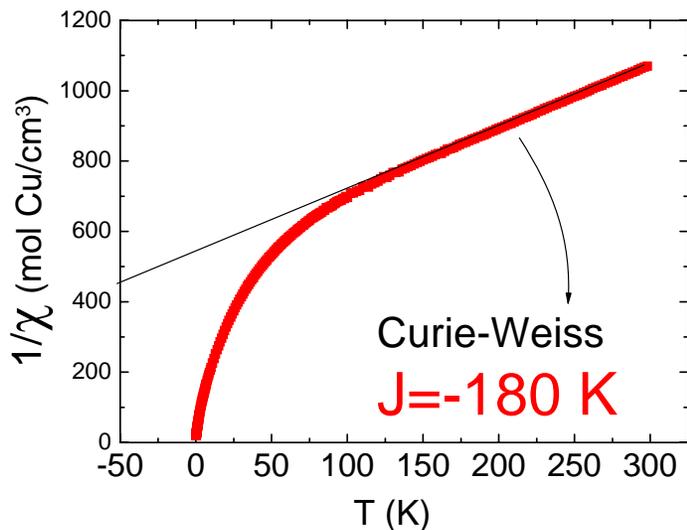
- $x=1$: jusqu'à $T=50mK$, pas d'ordre ni de gel magnétique ($m_{Cu} < 10^{-4} \mu_B$)

- $x=0$: totalement ordonné pour $T < 18K$
 X.G. Zheng et al, PRL 95, 057201 (2005)

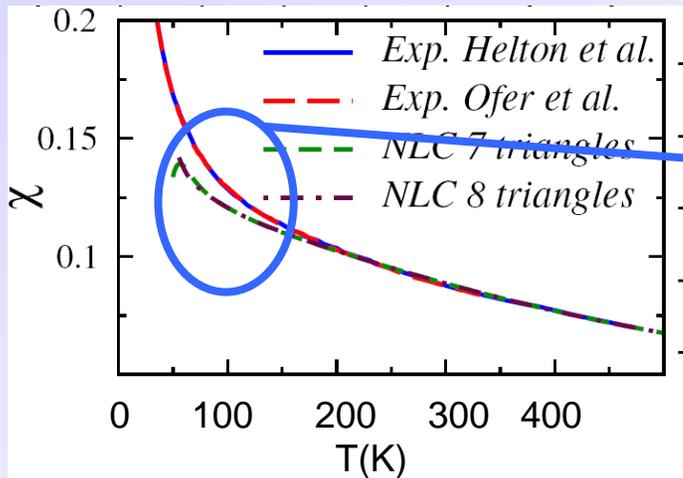
- $0 < x < 1$: disparition des oscillations + émergence d'une phase paramagnétique



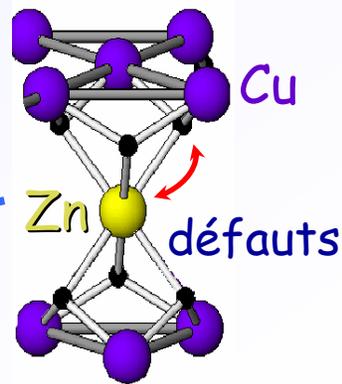
Herbertsmithite : susceptibilité macroscopique



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



Queue de Curie non reproduite dans les calculs sur kagome



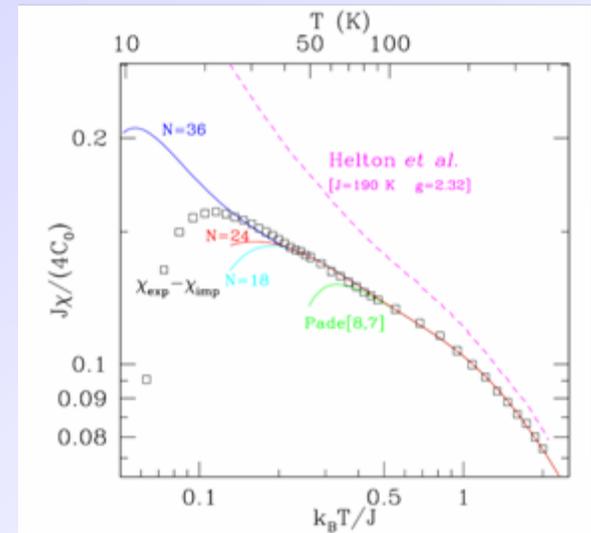
M. Rigol and R. P. Singh, PRL 98, 207204 (2007)

Magnetic defects : Zn/Cu intersite mixing

- Susceptibility fit \rightarrow $\sim 5\%$ dilution

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

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



- Low T, High Field Magnetization \rightarrow $\sim 7\%$ dilution

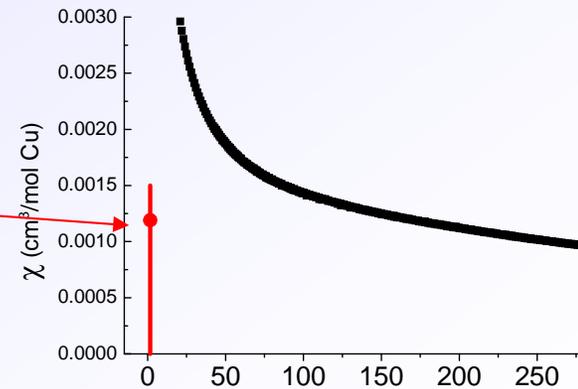
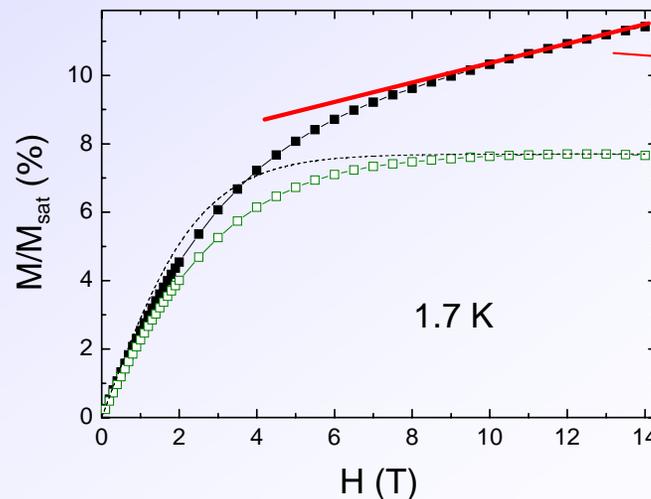
F. Bert et al, PRB 76, 132411 (2007)

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

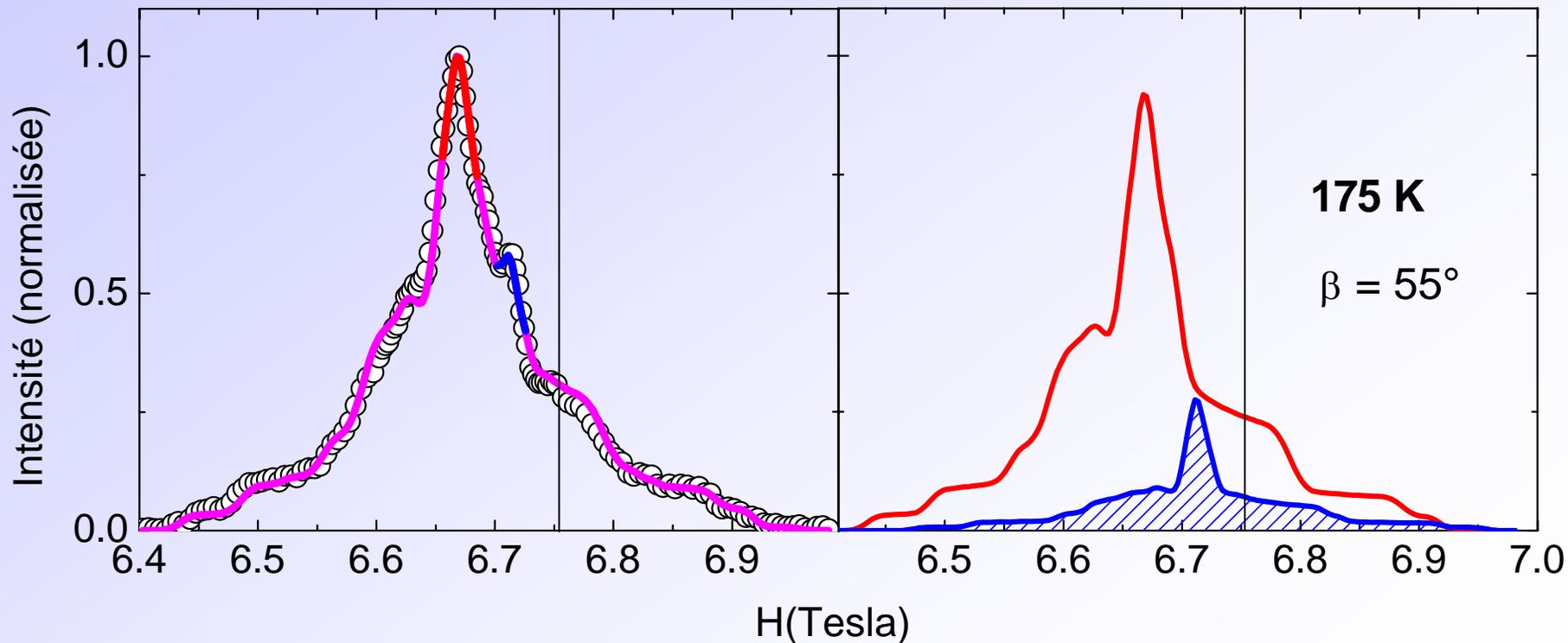
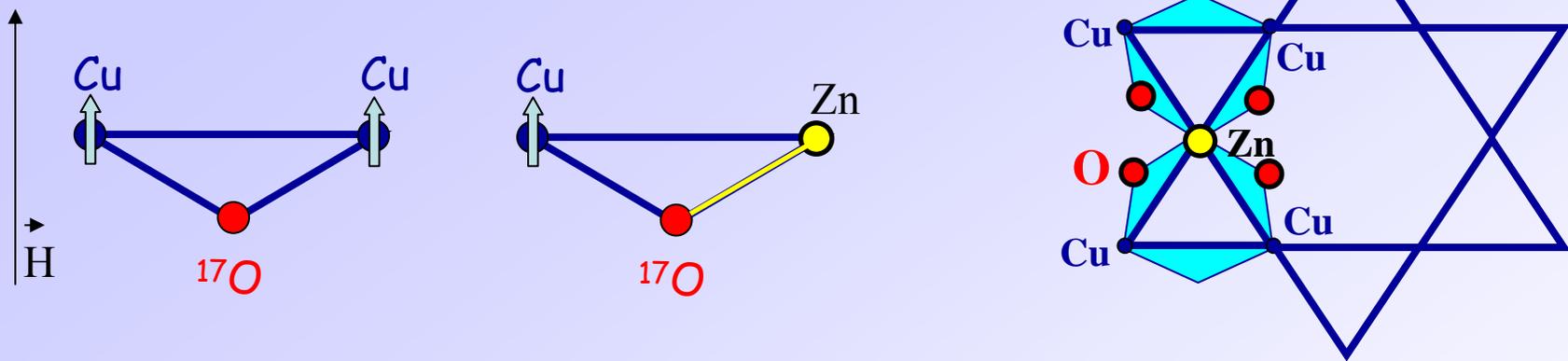
$$M_{\text{defect}} \sim \text{Brillouin}(H/T)$$

$\sim 7\%$ of interlayer Cu^{2+}

$\chi_i \ll \chi_{\text{macro}}$ at low T

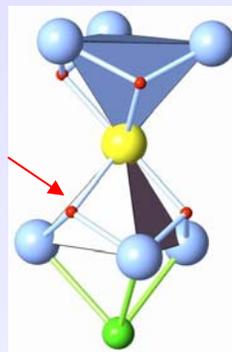
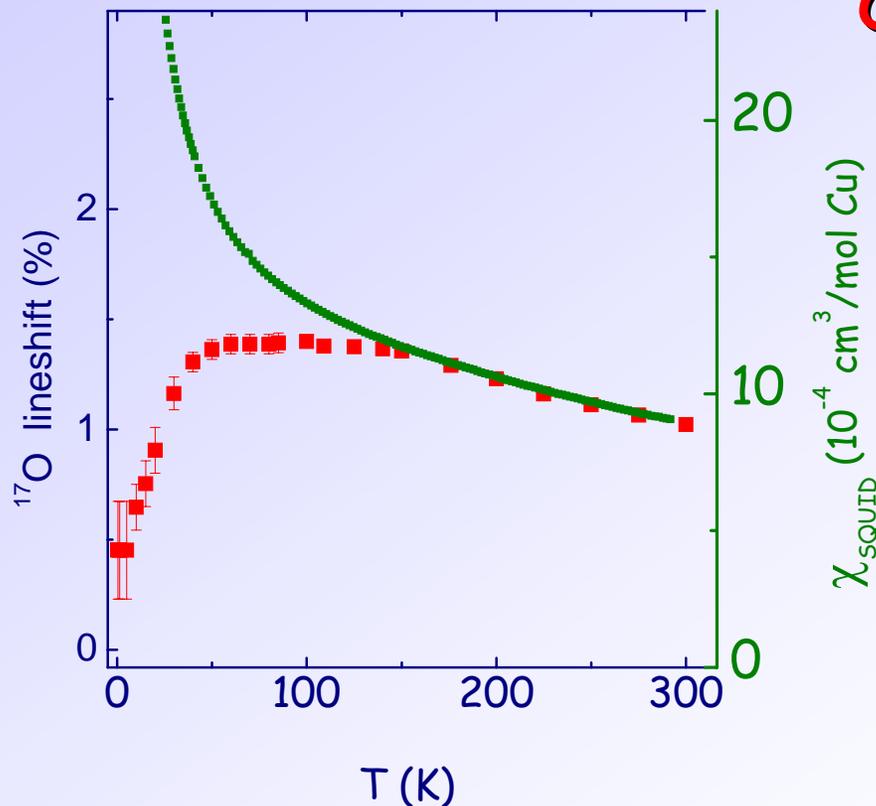
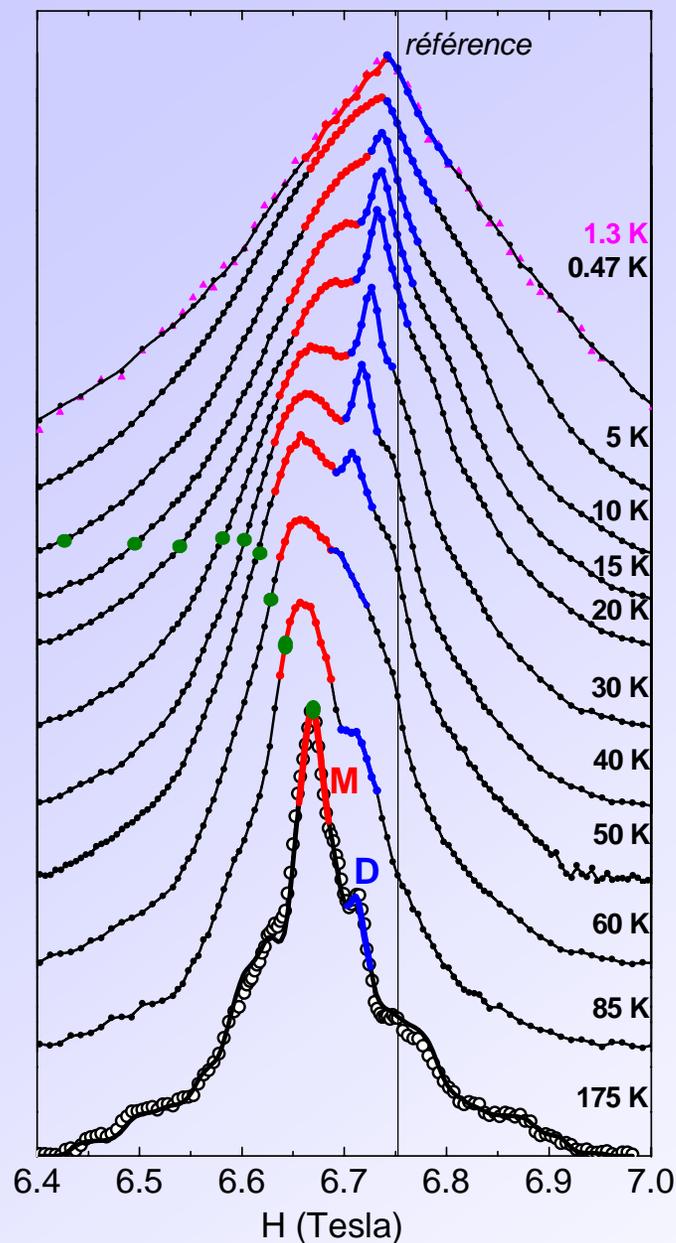


two magnetic site
O next to a Zn defect in the kagome plane



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

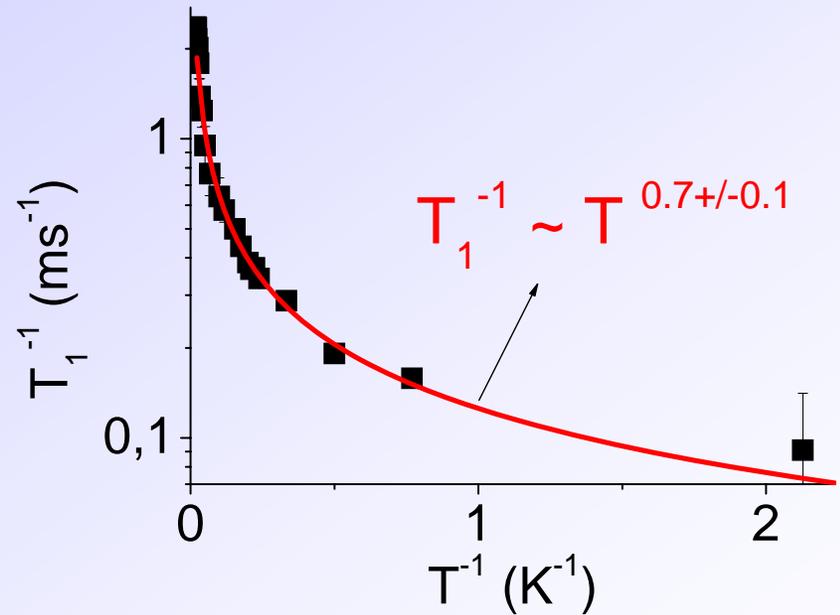
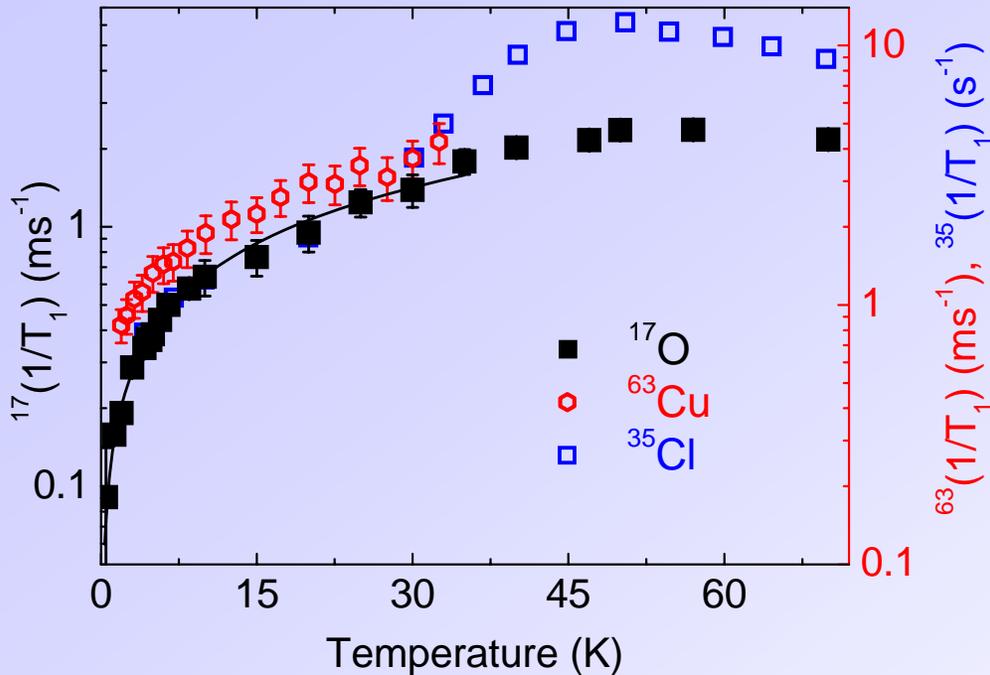
RMN de l' ^{17}O : Susceptibilité des plans kagome



- maximum de susceptibilité locale $\sim J/2$
- > renforcement des corrélations courte portée
- > émergence d'une nouvelle échelle d'énergie

-susceptibilité finie à $T \rightarrow 0$: pas de gap!

Dynamique basse température (T_1)

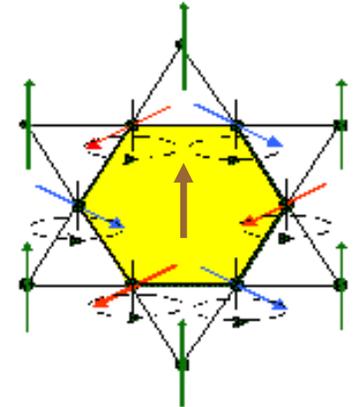


^{63}Cu et ^{35}Cl RMN : T. Imai et al, PRL 100, 077203 (2008)

-Pas de gap singulet - triplet :

-> en accord avec les mesures de shift et diffusion inélastique des neutrons

Helton et al, PRL 98 107204 (2007)



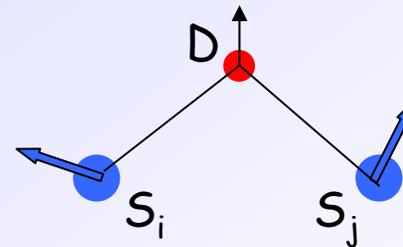
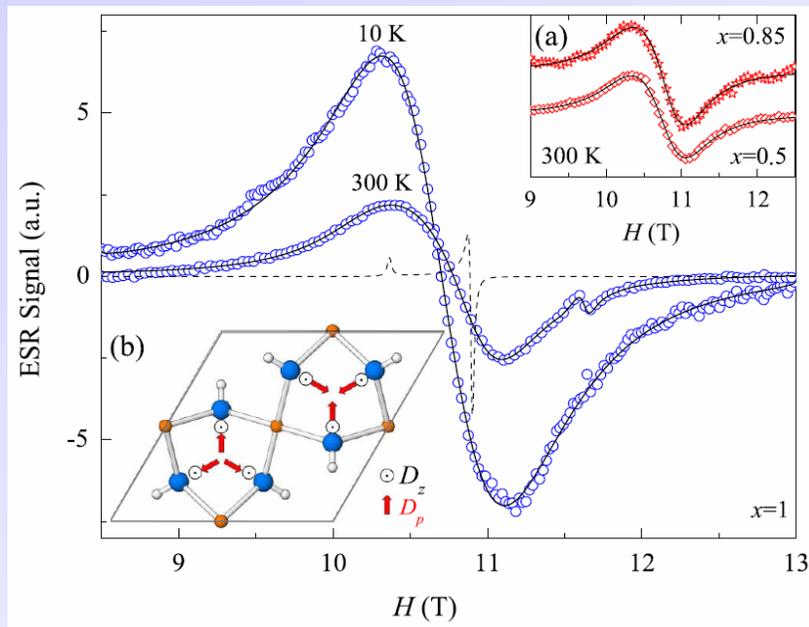
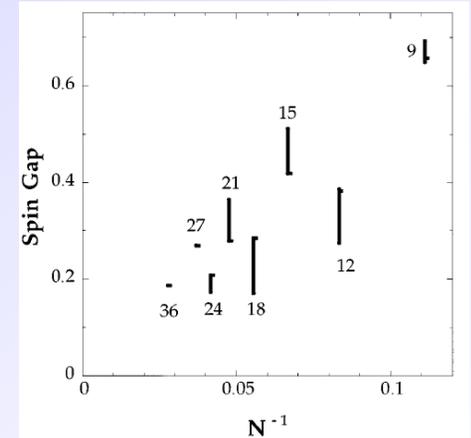
-Comportement en loi de puissance original $T_1^{-1} \propto T^{0.7 \pm 0.1}$

Absence de gap pour le modèle Heisenberg sur kagome ?

Ou

Fermeture du gap par un terme perturbatif dans l'Hamiltonien de l'Herbertsmithite ?

anisotropie Dzyaloshinskii-Moriya



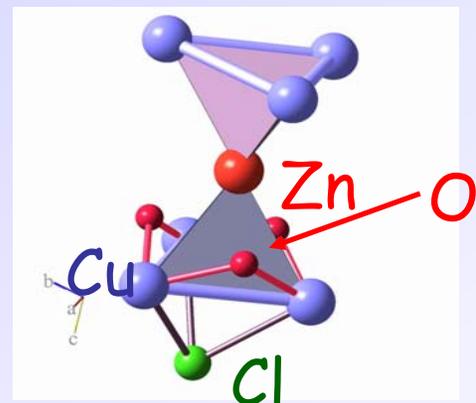
$$H_{DM} = D \cdot (S_i \wedge S_j)$$

Raie RPE très large <- anisotropie magnétique DM :

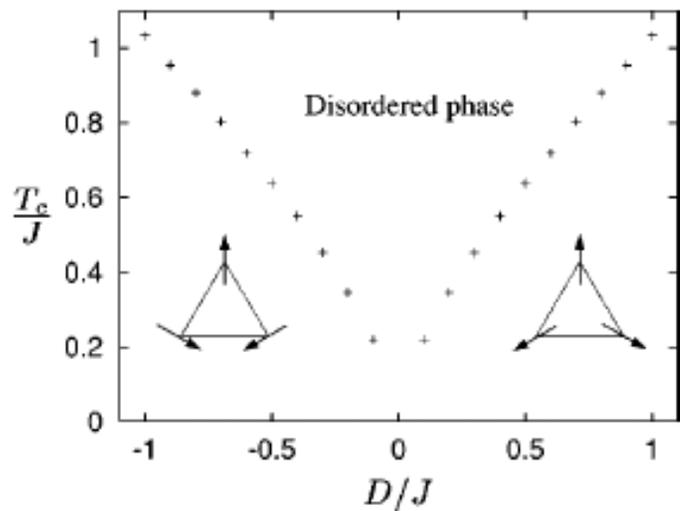
$$|D_z| = 0.08 \text{ J}, |D_p| \sim 0.01 \text{ J}$$

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

Interactions supplémentaires: Dzyaloshinskii-Moriya



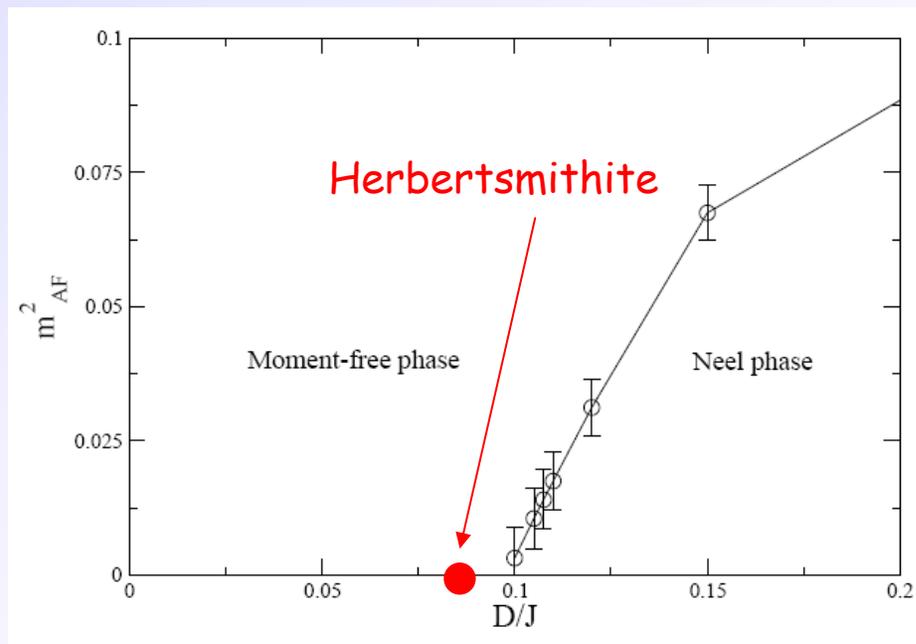
For classical spins,
DM stabilizes an order



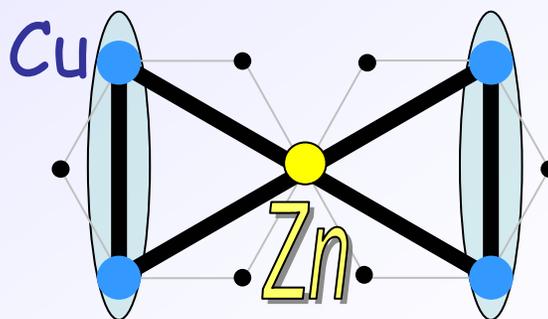
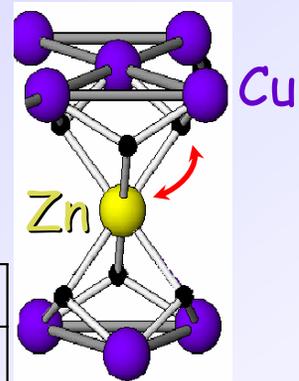
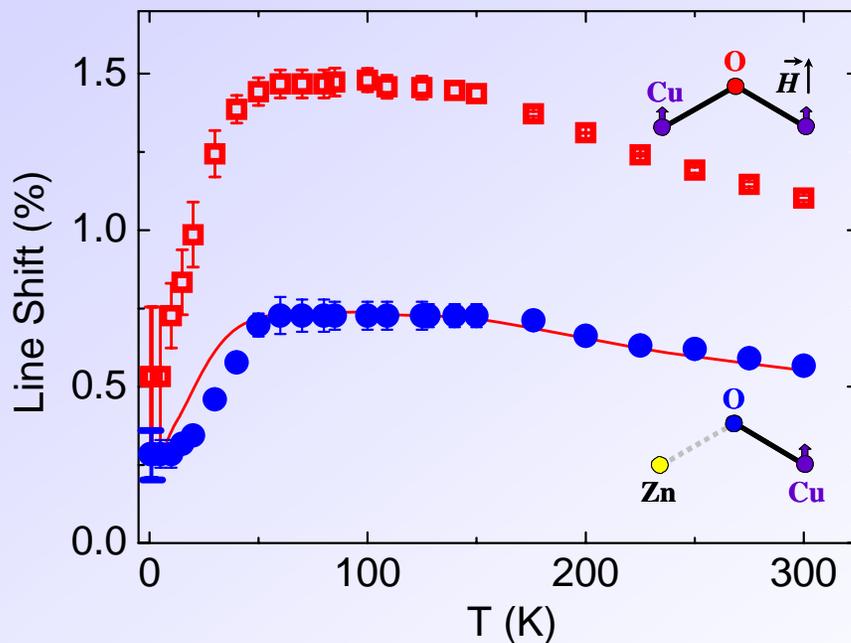
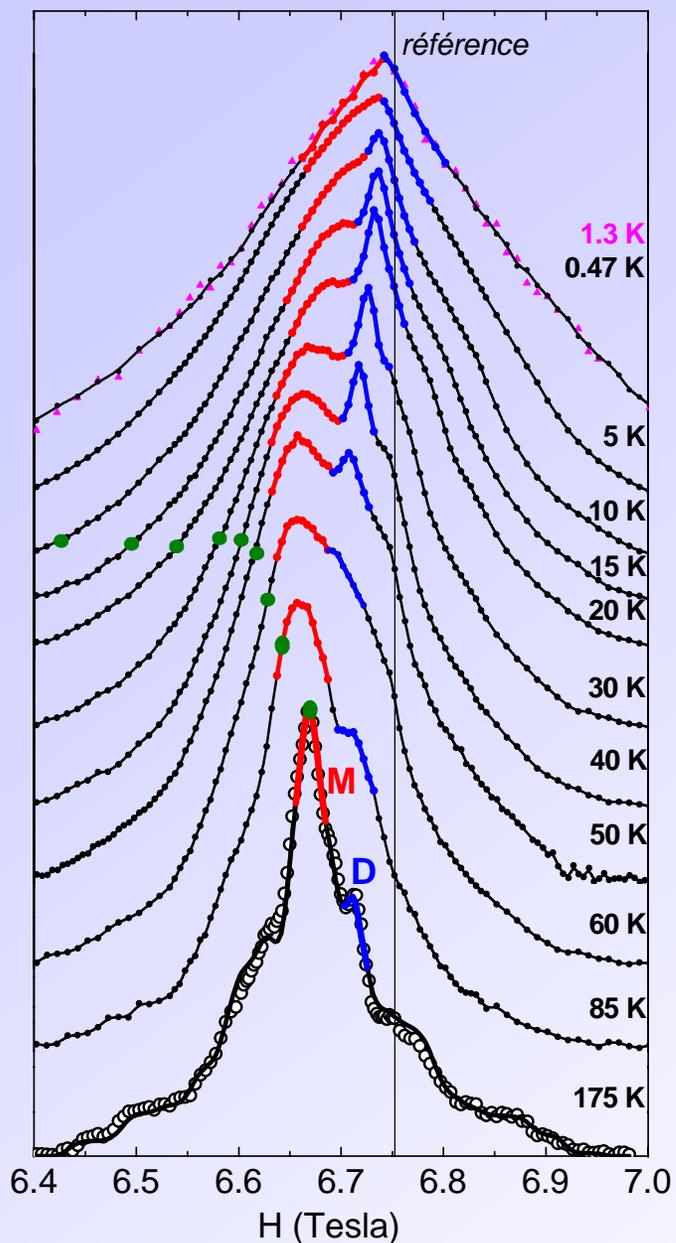
M. Elhajal et al, PRB **66**, 014422 (2002)

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

O. Cepas et al, arXiv:0806.0393v2

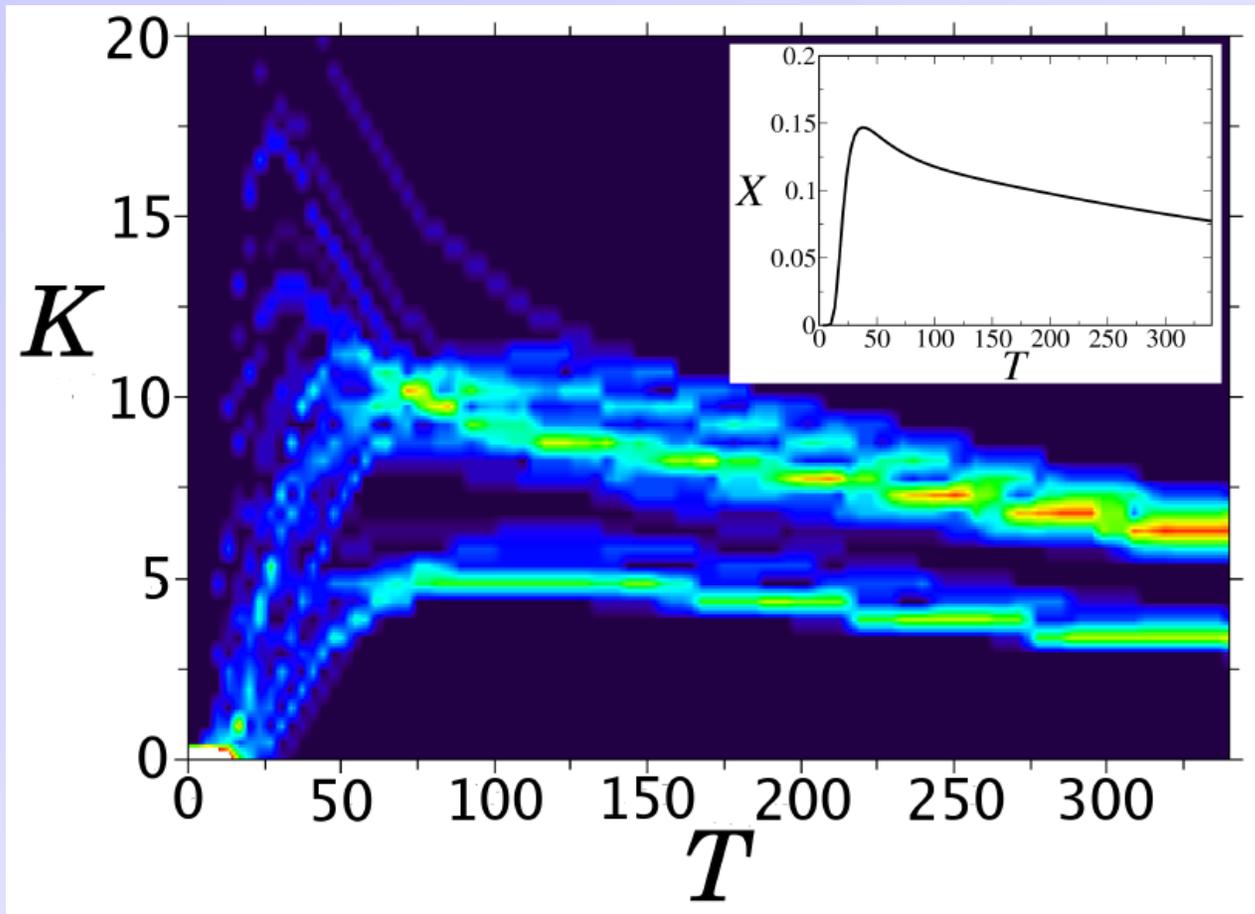


Susceptibilité au voisinage d'une lacune de spins



Stabilisation de singlets
autour de la lacune de
spin

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



Spectre RMN 'théorique' par diagonalisation exacte de clusters kagome avec 2 lacunes de spins

M.J. Rozenberg and R. Chitra, PRB 78, 132406 (2008)
R. Chitra and M.J. Rozenberg, PRB 77, 052407 (2008)

Conclusions

L' Herbertsmithite est le premier exemple d'un composé antiferromagnétique quantique

- structure kagomé parfaite
- pas de gel jusqu'à au moins $J/4000$

-> renouvelle l'intérêt pour la compréhension du fondamental kagome

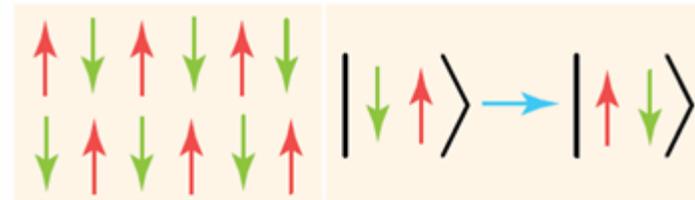
VBC : R.R.P. Singh and D.A. Huse, PRB (2007, 2008)

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.



Perspectives

Compréhension fine du fondamental :

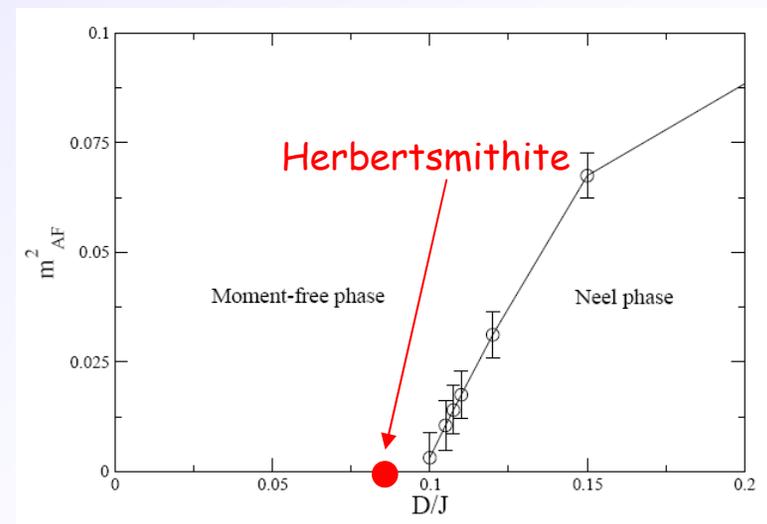
- Développements expérimentaux vers les basses T
 - > cryostat à dilution pour RMN
 - + chaleur spécifique (PPMS)
- Effet du champ magnétique sur l'état de base (RMN 14T)
- Études en lien avec la **chimie des matériaux**
 - contrôle du taux de lacunes magnétiques, orientation / **monocristaux**
 - rôle des impuretés ($x < 1$, > 1 ?) en lien avec théorie (*Mila et al*, DM+dilution)
 - retour sur volborthite (kagome anisotrope 'pur')

-exploration du diagramme de phase avec DM : Mg, Cd , pression

O. Cepas et al, arXiv:0806.0393v2, PRB 08

-nouveaux composés:

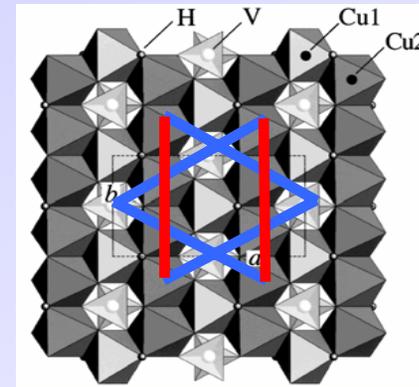
Kapellasite (coll. A. Wills), ...



Frustration et fondamentaux originaux - Collaborations

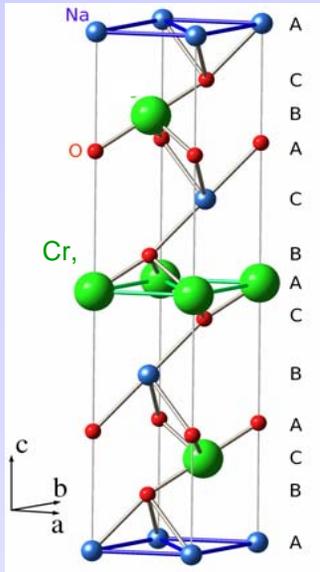
Herbertsmithite

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



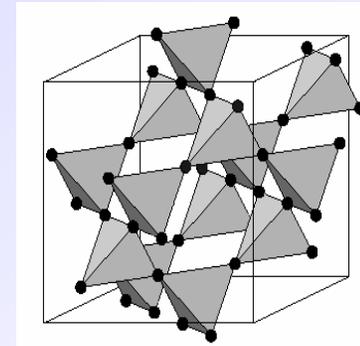
Kagome

Volborthite,
CEMES, Toulouse
Bert et al, PRL 2005



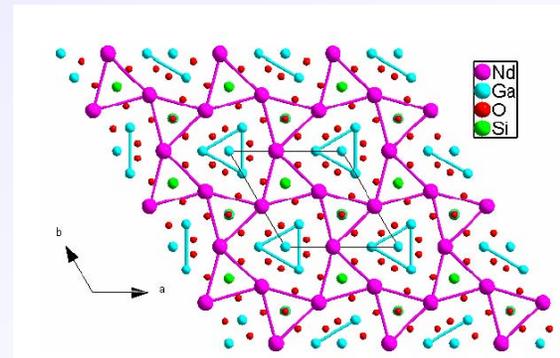
Triangulaire

NaCrO₂
R. Cava, Princeton
Olariu et al, PRL 2006



Pyrochlore

Tb₂Sn₂O₇
LLB, Saclay
Bert et al, PRL 2006

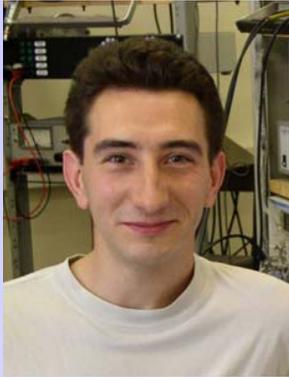


Kagome+

anisotropie de spins

Langasites
Institut Néel,
Grenoble
Zorko et al, PRL (2008)

Thanks to the MIT group for the discovery of Herbertsmithite!



F. Bert



A. Olariu

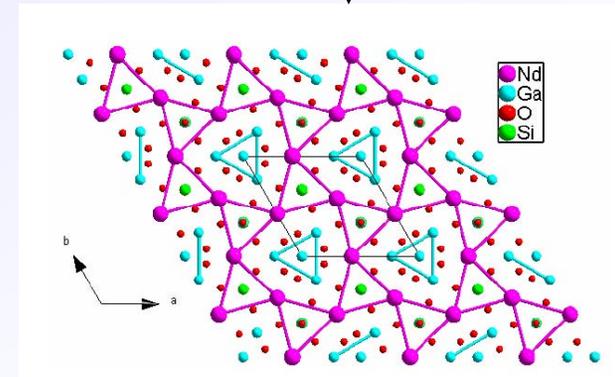


A. Zorko

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

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

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



Nd-Langasite
PRL, 2008

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