Quantum kagome spin liquids

Philippe Mendels - Univ Paris-Sud Orsa

The discovery of Herbertsmithite, $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$, which features a perfect kagome geometry, has been coined as the "end to the drought of spin liquids" [1,2]. It has triggered an intense activity on new kagome materials and related theories for the ground state of the quantum kagome Heisenberg antiferromagnet which has eluded any definitive conclusion for the last twenty years.

This is indeed the first experimental example of a kagome lattice where no order has been found at any temperature well below $J$ through all experimental techniques, among which $\mu$SR [3] has been by far the most accurate. This illustrates the power of the association of an enhancement of quantum fluctuations for $S=1/2$ spins with the frustration of antiferromagnetic interactions on the loosely connected kagome lattice to stabilize novel ground states of magnetic matter, namely quantum spin liquids.

I will review and discuss our contribution to this field through $\mu$SR, in connection with our NMR work. Through the various $\text{Cu}^{2+}$ $S=1/2$ materials which we have studied, I’ll illustrate some of the research thrusts in tracking down quantum spin liquid physics. This will encompass Zn and Mg-paratacamites, ($\text{Zn,Mg})_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$), their polymorphs kapellasite [4] and haydeite, vesigneite [5] as well as the recently discovered triangular-based lattice $\text{Ba}_3\text{CuSb}_2\text{O}_9$[6] compound.

Quantum Spin liquids

F. Bert, E. Kermarrec, A. Olariu, J. Quilliam, M. Jeong, A. Zorko
Laboratoire de Physique des Solides,
Université Paris-Sud, Orsay, France
Antiferromagnetism, Classical state ‘à la Néel’

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

-exitations = magnons (S=1)

- 1/S quantum corrections (fluctuations) → moments reduction

\[ \langle \vec{S}_i \cdot \vec{S}_j \rangle = e^{-|\vec{r}_i - \vec{r}_j|/\xi} , \quad \xi \rightarrow +\infty \]
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.
Néel AF 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**)
Corner sharing: classical kagomé lattice

\[ \vec{S}_A + \vec{S}_B + \vec{S}_C = 0 \]

Macroscopic degeneracy

Soft modes
Corner sharing: classical vs quantum kagomé lattice

Classical soft modes

Triangular $\neq$ Kagome

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

Back to 90’s

• Lecheminant, PRB 56, 2521 (1997)
Other stream: can one stabilize a spin liquid in dimension >1?

Spinon continuum

Spin waves branches « Fractional excitations fractionnaires » ($\Delta S \neq 1$)
The IDEAL Highly Frustrated Magnet
- Heisenberg or Ising spins
- $S=1/2$ (quantum spins)
- Corner sharing geometry:
  Kagomé (2D), hyperkagome or pyrochlore (3D) lattice
- No « perturbation » (anisotropy, dipolar interaction, n.n. interactions, dilution)
- For kagome: stacking should keep the 2D kagome planes uncoupled
Kagome Heisenberg antiferromagnet, a model of geometrically "frustrated " magnetism
Kagome Heisenberg antiferromagnet, a model of geometrically "frustrated" magnetism


Chiral spin liquid
Messio et al., PRL 2012

diamond-pattern valence bond crystal

honeycomb valence bond crystal
Kagome ground state?

- Quantum spin liquid?

A state without any spontaneously broken symmetry

$Z_2$ QSL
Gapped magnetic excitations ($S=1/2$)
Gapped non-magnetic excitations

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

Algebraic/Critical/Dirac/U(1) QSL
Gapless excitations

\[ C_v \sim T^2; \chi \sim T \]

Yan et al, science (2011)

Hastings, PRB 63, 2000
Ran et al, PRL 98, 2007
Ryu et al, PRB 75, 2007
The ground-state of QKHA would be a gapped spin-liquid (short-range RVB)

S. Yan et al, Science 332 (2011)
The Cu\(^{2+}\) world (S=1/2, \sim Heisenberg)
Materials are all existing minerals!

$\text{Cu}^{2+} \ S=1/2$

Ross H Colman, David Boldrin, Andrew S Wills, UCL, UK
A Structurally Perfect $S = \frac{1}{2}$ 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

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.
From C. Broholm (2010)
**FRUSTRATION**: unsatisfied pairwise interactions

- **Disorder**: Spin glasses (e.g. CuMn)
- **No disorder**: Geometric Frustration

**NETWORK GEOMETRY**:
- Triangular based lattice
- AF coupling

**INTERACTIONS GEOMETRY**:
- Disorder: Spin glasses (e.g. CuMn)
- No disorder: Geometric Frustration

\[ J_2 / J_1 = 0.5, \ J_1 (AF) \]

(Carretta; Geibel)
Outline

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

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

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

**Collaborations** (Herbertsmithite, Vesigneite, Kapellasite)

samples

Ross H Colman, David Boldrin, Andrew S Wills, UCL, UK
P. Strobel, Institut Neel, Grenoble, France
A. Harrisson, M. de Vries, Edinburgh, UK
F. Duc, Toulouse

Quantum criticality
Dzyaloshinky-Moriya interactions

$\mu$SR @ ISIS, PSI $\oplus$ NMR

J1-J2 model on kagome lattice
Novel spin liquid?
Herbertsmithite: $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$

$\text{Cu}^{2+}$, $S=1/2$
µSR: ZnCu₃(OH)₆Cl₂: zero field

OH-μ : 85%
Cl⁻ : 15%

upper limit of a frozen moment for Cu²⁺, if any : 6x10⁻⁴ μₜ

No order or frozen disorder down to 50 mK despite J=190 K!
Liquid down to J/4000 under ZF


Also: ac-χ Helton et al, PRL 98 107204 (2007)
µSR O. Ofer et al, cond-mat/0610540
μSR: phase diagram of paratacamites $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$

- Paramagnetic ($x=1$ type) component
- Oscillations smeared out
- $x=0$: fully ordered below ~18K

Large dynamical domain $0.66 < x < 1$

- $x=0$: fully ordered below ~18K

Susceptibility: $\chi$muons, D NMR vs $^{17}$O NMR (intrinsic, defects)

O. Ofer et al., ArXiv (2010)
**Gapless spin liquid**

\[ \chi'' \sim \omega^{-0.7} \]

\[ T_1^{-1} \sim T^{0.7 \pm 0.1} \]

\[ T \text{ (K)} \]

\[ \chi \text{ (SQUID)} (10^{-4} \text{ cm}^3/\text{mol Cu}) \]

\[ J/20 \]

\[ ^{17}\text{O line shift (\%)} \]

Olariu et al, PRL 100, 087202 (2008)

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

Very Low T Spin Dynamics


\[
\frac{1}{T_1} \text{ (ms}^{-1})
\]

\[
0.01 \quad 0.1 \quad 1 \quad 10
\]

\[
1E-5 \quad 1E-4 \quad 1E-3
\]

\[
T (K)
\]
Very Low T Spin Dynamics: freezing under a field

Small frozen moment $\sim 0.1\mu_B$
A Quantum Critical Point?

Algebraic critical spin liquid?

- No gap ($H = 0$)
- Instability ($H \neq 0$) $M \sim H^\alpha$ but $T_c \sim H$
- DM interaction $\rightarrow$ L.R.O.

Ran et al, PRL 98 117205 (2007)

$T_c \sim (H-H_c)^{0.65}$

$H_c = 1.5$ T

$\Delta \sim 2.3 k_B T_c$

$\mu_B H_c \sim J/180$
Ideally…

Zn/Cu local environments

Cu distorted octahedron

… Nobody is perfect
Magnetic defects: Zn/Cu intersite mixing

- Zn in the kagome plane -> magnetic vacancy (~ 1 - 7%)
- Cu on the Zn site
  - Nearly free $\frac{1}{2}$ spins (~ 15 - 25%)

For a review and discussion, see
Freedman et al, JACS, 132 (2010)
Out-of-plane (?) defects (2)

Electronic spin signal

Dynamical relaxation ($T_1$ process)

\[ P = \exp(-\lambda t) \]
\[ \lambda = 2\gamma_\mu H_\mu^2 / \nu \]

- $H_\mu \sim 20$ G very small
- relaxation involves few Cu$^{2+}$ (defects?)

- Weak decrease of the electronic spin fluctuation rate when $T \to 0$

- "Dynamical plateau" vanishes when $x \uparrow$

$\text{ZnCu}_3(\text{OH})_6\text{Cl}_2 : x=1$

Energy scale $\sim 1$K in the defect channel
Mg- Herbertsmithite: control of inter-site defects

Dzyaloshinskii-Moriya interactions: quantum criticality

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

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

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

M. Elhajal et al., PRB 66, 014422 (2002)
Dzyaloshinskii-Moriya interactions: quantum criticality

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


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ESR: A. Zorko et al., PRL 101 (2008)
O. Cepas et al, PRB 78, 140405 (R) (2008)
Y. Huh et al, PRB 81, 144432 (2010)
L. Messio et al, PRB 81, 064428 (2010)
S. El Shawish et al, PRB 81, 224421 (2010)

$H_c \sim D_c - D_{\text{herb}}$
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  - competing exchange interactions

Collaborations

Ross H Colman, David Boldrin, Andrew S Wills, UCL, UK
L. Messio, C. Lhuillier, B. Bernu, Paris, France
B. Fak, CENG, Grenoble, France
Vesignieite

\[
\text{Cu}_3\text{Ba(VO}_5\text{H)}_2
\]

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

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


Coll. UCL London
V NMR (T>9K)

\[ \chi_{int} = (K-\sigma J/A) \frac{J}{k_B} \frac{1}{T} \]

Herbertsmithite (Olariu 2008, \( J = 170 \) K)
Volborthite (Hiroi 2001, \( J = 84 \) K)
Theory (Misguich 2007, adjusted)

**susceptibility**

- \( J \sim 50 \) K
- Curie tail \( \sim 7\% \) \( S=1/2 \)
- Kink at \( T \sim 9K \)

R.C. Colman et al (2011)

Shift \equiv Herbertsmithite

J. Quilliam et al, arXiv:1105.4338
Vesignieite  \( \mu SR: \) two components
One static – disordered- one dynamical

\[ P(t) = f_f P_f(t) + (1-f_f)P_{para}(t) \]
\[ T < 9K \text{ decoupling} \quad \mu_{\text{stat}} \sim 0.1 \mu_B \]

Coll. UCL London
Vesignieite  \( \mu SR: \) two components

- No macroscopic phase separation.
- Spin dynamics of all Cu\(^{2+}\) suppressed down to spin freezing for 40%.
Vesignieite  V NMR  T<9K

Static component below 9 K ~ 0.2 \( \mu_B \)

J. Quilliam et al, PRB (R), 2011
Vesigneite

NMR -> two components
Static + dynamic (lost)

Lost in NMR

Good agreement

Coll. Orsay / UCL London

J. Quilliam et al.

NMR

μSR

R.C. Colman et al
Dzyaloshinskii-Moriya induced quantum criticality

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

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

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

$D/J_{vesi} \sim 0.1 - 0.17$


W. Zhang, H. Ohta et al., JSPJ (2010)
Conclusions

Herbertsmithite

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

Vesignieite

• Close to perfect kagome
• Partial freezing @ $J/6$
• $D/J > 0.1$
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L. Messio, C. Lhuillier, B. Bernu, Paris, France
B. Fak, CENG, Grenoble, France
Modified Kagome Physics in the Natural Spin-1/2 Kagome Lattice Systems: Kapellasite $\text{Cu}_3\text{Zn(OH)}_6\text{Cl}_2$ and Haydeeite $\text{Cu}_3\text{Mg(OH)}_6\text{Cl}_2$

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(Received 26 May 2008; published 3 September 2008)

B. Fak, E. Kermarrec et al, PRL, 2012
Kapellasite: a polymorph of Herbertsmithite

Herbertsmithite

$\text{Cu}_3\text{Zn(OH)}_6\text{Cl}_2$

Kapellasite

$R-3m$

$P\overline{3}m1$
$^{35}$Cl NMR

Chemical analysis (ICP) $\text{Cu}_{2.3}\text{Zn}_{1.7}(\text{OH})_6\text{Cl}_2$

Neutron diffraction $\left(\text{Cu}_{0.73}\text{Zn}_{0.27}\right)_3\left(\text{Zn}_{0.88}\text{Cu}_{0.12}\right)(\text{OH})_6\text{Cl}_2$

Kagome site $p_c = 0.65$
High-Temperature series expansion analysis

$J_1$ ferro -15 K  ~ further neighbor $J_{2,d}$ 13 K

B. Fak, E. Kermarrec et al, PRL, 2012
Interactions scheme

L. Messio, et. al, PRB 83, 184401 (2011)
Classical ordered states on the Kagome lattice

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

8 Classical long-range ordered states allowed by symmetries

(a) Ferromagnetic (F) state
(b) $q = 0$ state.
(c) $\sqrt{3} \times \sqrt{3}$ state.
(d) Octahedral state.
(e) Cuboc1 state.
(f) Cuboc2 state.
(g) $q = 0$ (left) and $\sqrt{3} \times \sqrt{3}$ (right) umbrella states.

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

L. Messio, et. al, PRB 83, 184401 (2011)
Kagome pattern: colors mean different spin direction

12 spins pointing to cuboctahedron vertices
μSR

-no freezing (no decoupling)
-Persistent slow fluctuations
Cuboc-2 correlations survive up to 100 K (also specific heat)
µSR vs NMR
Conclusions

✓ Experimentally:
  two quantum spin liquids on the kagome lattice: Heisenberg + anisotropy and J1-J2

✓ Fragility of the QSL:
  • Defects: no
  • Anisotropy, field: yes

✓ Is the gapless behavior intrinsic or not?

✓ Can we achieve a better understanding of the relaxation plateaus?

✓ Other materials: S=1/2 Vanadates

Thank you to ISIS team!