Randomness-induced quantum spin liquid behavior in the $s=1/2$ Heisenberg antiferromagnet on the pyrochlore lattice

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Quantum spin liquids now observed in many 2D frustrated magnets

RVB state  [P.W. Anderson ('73)]

* Triangular lattice  \( S=1/2 \) organic salts

\[
\kappa-(ET)_2Cu_2(CN)_3, \quad \text{EtMe}_3\text{Sb}[\text{Pd(dmit)}_2]_2, \quad \kappa-H_3(\text{Cat-EDT-TTF})_2
\]

[K. Kanoda, R. Kato, H. Mori, et al]

* Kagome lattice

herbersmithite: \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \)  

[D.G. Nocera et al]

* Honeycomb-lattice and square-lattice magnets

\[
\begin{align*}
6\text{HB- Ba}_3\text{NiSb}_2\text{O}_9 \quad (s=1) & \\
\text{Sr}_2\text{CuTe}_{1-x}\text{W}_x\text{O}_6 &
\end{align*}
\]

[J. Quilliam et al., 2016]  

[O. Mustonen et al., 2018]  

Competing interactions
Gapless QSL widely observed experimentally

**Triangular organic salt \( \kappa \)-ET**
- NMR spectrum
- NMR spectrum

**Specific heat**
- Specific heat

**Kagome herbertsmithite**
- \( \text{ZnCu}_2(\text{OH})_6\text{Cl}_2 \)
- \( \text{C/T} \)

**Square mixed-crystal AF**
- \( \text{Sr}_2\text{CuTe}_{1-x}\text{W}_x\text{O}_6 \)

**Specific heat**
- Specific heat

**\( \mu\text{SR} \)**
- \( \mu\text{SR} \)

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[S. Yamashita, 2008]
[Y. Shimizu et al., 2003]
[T. H. Han, et al., ’12]
[O. Musutone et al., 2018]
Some (many ?) of experimentally QSL might be randomness-induced ones ?

Randomness (inhomogeneity)


“RVB state”

“random singlet state”

“Anderson localization” of spin singlets ?
Origin of randomness or inhomogeneity could be either extrinsic or intrinsic

**Extrinsic randomness**
Quenched disorder
- intersite disorder: *kagome herbersmithite*
- mixed crystal: \( \text{Sr}_2\text{CuTe}_{1-x}\text{W}_x\text{O}_6 \)
- defects, impurities ...

**Intrinsic randomness**
Effective randomness for spin degrees of freedom can be self-generated even in clean systems via the coupling to other degrees of freedom in magnets, e.g., charge, lattices, etc.
- coupling to charge (dielectric) degrees of freedom: \( \kappa\)-ET & dmit salts
- coupling to protons at the hydrogen bond: Cat salt
Extrinsic randomness (quenched randomness)

**Kagome herbertsmithite:** $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$

*intersite disorder*
10~15% $\text{Zn}^{2+}$ on the triangular layer randomly replaced by $\text{Cu}^{2+}$

*bond-random modulation of the effective exchange $J$ on the kagome plane*

**Mixed crystal of square-lattice AFMs:** $\text{Sr}_2\text{CuTe}_{1-x}\text{W}_x\text{O}_6$

Random $s = 1/2 J_1 - J_2$ square-lattice Heisenberg AF

$\text{Sr}_2\text{CuTeO}_6$ ($J_2/J_1 = 0.03$, $T_N = 29K$)

and $\text{Sr}_2\text{CuWO}_6$ ($J_2/J_1 = 7.92$, $T_N = 24K$)

$\Rightarrow$ Significant quenched disorder associated with the Te/W occupation
Relevant randomness (inhomogeneity) exists in triangular organic salts?

Effective randomness is self-generated via the spin-charge coupling.
The “third” quantum spin liquid
$\kappa$-$H_3(Cat\text{-}EDT\text{-}TTF)_2$

$\pi$-electron - proton coupled triangular organic conductor

hydrogen-bonded

Proton remains delocalized

$\rightarrow$ possibly slowed down into random positions at low-$T$

$\rightarrow$ yielding random fields to $\pi$-electrons

$\rightarrow$ spatially modified random exchange coupling $J_{ij}$

$\rightarrow$ Gapless random-singlet state
Bond-random $S=1/2$ AF Heisenberg model on the triangular & kagome lattices

$$\mathcal{H} = \sum_{<i,j>} J_{ij} \hat{S}_i \cdot \hat{S}_j$$

$$(0 \leq J(1-\Delta) \leq J_{ij} \leq J(1+\Delta))$$

$\Delta$: randomness parameter $(0 \leq \Delta \leq 1)$

- $\Delta = 0$: no randomness
- $\Delta = 1$: maximal randomness

Exact diagonalization (ED) calculation performed on various 2D models, including triangular, kagome, $J_1$-$J_2$ honeycomb and square lattices

$\Rightarrow$ find a QSL-like state (random-singlet state)
ED numerical results on 2D models

**Random triangular model**

Specific heat

![Specific heat graph for random triangular model](image1)

Susceptibility

![Susceptibility graph for random triangular model](image2)

**Random kagome model**

Specific heat

![Specific heat graph for random kagome model](image3)

Dynamical spin structure factor

![Dynamical spin structure factor graph for random kagome model](image4)
Randomness-induced QSL state
--- random-singlet state ---
appear to be realized in
a variety of 2D frustrated magnets

Randomness-induced QSL state
ever possible in 3D?

e.g., pyrochlore?
Gapless QSL behavior observed in pyrochlore AF: \( \text{Lu}_2\text{Mo}_2\text{O}_5\text{N}_2 \)

\[
\begin{align*}
\text{Lu}_2\text{Mo}_2\text{O}_7 & \\
\text{Mo}^{4+} & \quad 4d^2 \quad S=1 \quad \rightarrow \quad \text{Orbital degrees of freedom} \\
\text{Apparently disorder-free system} \\
\text{Spin-glass order at } T_f = 16 \text{K} \quad (\text{similarly to } \text{Y}_2\text{Mo}_2\text{O}_7) \\
& \quad \text{due to the spin-orbital coupling}
\end{align*}
\]

\[
\begin{align*}
\text{Lu}_2\text{Mo}_2\text{O}_5\text{N}_2 & \\
\text{Random substitution of } \text{O}^{2-} \text{ by } \text{N}^{3-} \\
\text{Mo}^{5+} & \quad 4d^1 \quad S=1/2
\end{align*}
\]

\( S=1/2 \) pyrochlore Heisenberg AF with significant exchange randomness
QSL behavior of Lu$_2$Mo$_2$O$_5$N$_2$

Gapless QSL behavior with the $T$–linear specific heat and broad features in the spin structure factor

Specific heat

\[ C(\text{mag}) \propto T \]

\[ C(\text{mag}) \propto T^2 \]

Susceptibility

Magnetic neutron-scattering cross section

[Clark et al., 2014]
Model: $s = 1/2$ random-bond AF Heisenberg model on the 3D pyrochlore lattice

$$\mathcal{H} = \sum_{\langle i,j \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

- Nearest-neighbor coupling
- Periodic boundary conditions
- ED (ground state properties, $N \leq 36$) & Hams-de Raedt method (finite-temperature properties, $N = 32$)
- Averaged over 10~100 samples

* Preceding works on the regular model
  some sort of non-magnetic state $^{[1-7]}$

- Valence Bond Crystal? $^{[1-4]}$
- Chiral Spin Liquid? $^{[5,6]}$
- something else? $^{[7]}$

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Results: Ground state properties

Spin freezing parameter $q$

No magnetic order at any $\Delta$
Seems to be gapful for $\Delta < \Delta_c \sim 0.6$
but gapless for $\Delta > \Delta_c$
Gapful-gapless transition
at $\Delta = \Delta_c \sim 0.6$

Random singlet state realized
at $\Delta = \Delta_c \sim 0.6$

Spin gap

Rate of triplet ground states
Finite-temperature properties

Specific heat

Susceptibility

Lu$_2$Mo$_2$O$_5$N$_2$ (exp.)

Curie tail
Static spin correlations \((T=0)\)

Static spin structure factor \(S(q)\)

**Regular: \(\Delta = 0\)**

\((h, h, l)\)

\((h, k, 0)\)

**Random: \(\Delta = 1\)**

\((h, h, l)\)

\((h, k, 0)\)

Lu\(_2\)Mo\(_2\)O\(_5\)N\(_2\) (exp.)

Very broad spin structure factors without any peaky structure

[L. Clark et al., 2014]
Dynamical spin correlations \((T=0)\)

Dynamical spin structure factor \(S(q, \omega)\)

**Regular: \(\Delta = 0\)**

\((2, 2, 0)\)

\(\begin{align*}
\mathbf{L} & \quad \mathbf{M} \\
\mathbf{O} & \quad \mathbf{N}
\end{align*}\)

Random: \(\Delta = 1\)

\((2, 2, 0)\)

Lu\(_2\)Mo\(_2\)O\(_5\)N\(_2\) (exp.)

[L. Clark et al., 2014]
Random-singlet state in 3D looks similar to the one in 2D

**e.g., specific heat**

**3D pyrochlore**

**2D models**

- *kagome* [Kawamura et al 2014]
- *$J_1$-$J_2$ honeycomb* [Uematsu et al 2017]
- *triangular* [Watanabe et al 2014]
- *$J_1$-$J_2$ square* [Uematsu et al poster]
3D Pyrochlore

Gapped (?) QSL Random-singlet

0

$\Delta_c \sim 0.5$

$\Delta$

**triangular**

[Watanabe et al, 2014]

Neel AF Random singlet

$\Delta_c \sim 0.6$

$\Delta$

**kagome**

[Kawamura et al, 2014]

QSL Random singlet

$\Delta_c \sim 0.3$

$\Delta$

**$J_1$-$J_2$ honeycomb**

[Uematsu et al, 2017]

Gapped I Gapped II

**$J_1$-$J_2$ square**

[Uematsu et al, poster on Friday]
Summary

* Zero-$T$ and finite-$T$ properties of the bond-random $s=1/2$ AF Heisenberg model

Randomness or inhomogeneity plays a role in quantum magnetism!

* The random-singlet state in 3D is very much similar to the one in 2D, characterized by the $T$–linear low-$T$ specific heat, gapless susceptibility with a Curie-like tail, and broad features in the spin structure factor.

* The results are consistent with the recent experimental result on the pyrochlore AF Lu$_2$Mo$_2$O$_5$N$_2$ Gapped (?) QSL Random-singlet $\Delta_c\sim0.5$
Possible chiral order?

- **Scalar chirality**
- **Vector chirality**

No chiral (-glass) order both in the regular and the random cases
Origin of the $T$–linear specific heat in the random-singlet state

$T$–linear specific heat generically realized in spin glasses and molecular glasses, reflecting continuous low-energy excitations with a nonzero density of states down to zero.

[P.W. Anderson et al, ‘72]
Nature of the “random-singlet” state

Anderson-localized RVB state?

A subtle balance between the kinetic energy (resonance) and the potential energy (random $J_{ij}$)
Gapless behavior robust against $P(J_{ij})$?

Yes.

[Ex.] Discrete (binary) $J_{ij}$ distribution

Gapless behavior for larger randomness ($\delta$) even for the discrete (binary) $J_{ij}$ distribution

[T. Shimokawa et al., '15]