The search and detection of quantum spin liquid in new materials with geometrically frustrated lattice

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Motivation:

We must learn how the astonishing properties of quantum materials can be tailored to address our most pressing technological needs, and we must dramatically improve our ability to synthesize, characterize, and control quantum materials.

Grow single crystals

Search for quantum spin liquid state candidates (NSF)

Electronically detect spin states and magnetic excitations (DOE, collaboration with Jian Liu)
Non-frustrated magnets

\[ H = - \sum_{ij} J_{ij} S_i \cdot S_j \]

\[ T_N = \frac{zS(S+1)|J|}{3k_B} \]

\[ \chi = \frac{C}{T - \theta_{CW}} \]

\[ z = 4 \text{ nearest neighbor number} \]

\[ S = 1 \]

\[ T_N \sim 2.7 \text{ } J \]
Geometrically Frustrated Lattice

Interactions between magnetic degree of freedom in a lattice are incompatible with the underlying crystal geometry —— Frustration

2D

Triangular Kagome

3D

Face centered cubic Pyrochlore
Frustration leads to degeneracy, which enhances spin fluctuations and suppresses magnetic ordering to induce *exotic magnetism*.
Spin-1/2 Triangular lattice antiferromagnet (TLAF)

Strong quantum spin fluctuations
Quantum spin liquid

Quantum spin liquid (QSL) RARE!! No long range order down to 0 K; No symmetry breaking; Long range entanglement; Fractional excitation

\[
(i,j) = \frac{1}{\sqrt{2}} (|\uparrow_i \downarrow_j\rangle - |\downarrow_i \uparrow_j\rangle).
\]

Valence-bond solid (VBS) state: a singlet dimer configuration dominates in the ground state.

Resonant valence bond (RVB) state: The valence-bond pairs in the RVB construction are dominated by short-range pairs, resulting in liquid-like states with no long-range spin order.

Gapless QSL, itinerant spin excitations, residual $k_0/T$ term

Organic molecular magnets: EtMe$_3$Sb$[$Pd(dmit)$_2]$$_2$, spin-1/2 TLAF


Very rare to observe non-zero $k_0/T$ approaching zero temperature in insulating magnets
Spin-1/2 geometrically frustrated magnets

**Cu\(^{2+}\), 3d\(^9\)**
ZnCu\(_3\)(OH)\(_6\)Cl\(_2\), Herbertsmithite, kagome lattice, QSL
Cs\(_2\)CuBr\(_4\), distorted triangular lattice, LRO with UUD

**Ir\(^{4+}\), 5d\(^5\)**
Na\(_4\)Ir\(_3\)O\(_8\), hyper-kagome, QSL
Ru\(_2\)O\(_9\) dimer
Ba\(_3\)ARu\(_2\)O\(_9\) (A = Y\(^{3+}\), In\(^{3+}\), Lu\(^{3+}\))

**Co\(^{2+}\), 3d\(^7\), effective spin 1/2**
Ba\(_3\)CoSb\(_2\)O\(_9\),
B\(_3\)CoNb\(_2\)O\(_9\),
Ba\(_8\)CoNb\(_6\)O\(_{24}\)
Mo\(_3\)O\(_{13}\) clusters
LiZn\(_2\)Mo\(_3\)O\(_8\), distorted Kagome lattice QSL
Li\(_2\)In\(_{1-x}\)Sc\(_x\)Mo\(_3\)O\(_8\)

**Yb\(^{3+}\), 4f\(^{13}\), effective spin 1/2**
Yb\(_2\)Ti\(_2\)O\(_7\), pyrochlore, QSL
Figure 1. Structure and magnetic susceptibility of Na$_2$BaCo(PO$_4$)$_2$. The crystallographic structure.

(a) The unit cell contains two Na and Ba ions in the 200 plane and two Co and P ions in the 0 plane. The c-axis is resolved. The inset shows the unit cell along the c-axis. The distances are 7.0081 Å and 5.3185 Å.

(b) The spin-1/2 triangular lattice antiferromagnet is represented by the solid lines in the figure. The changes in magnetic entropy below 4 K are calculated by integrating the susceptibility. At zero field, the recovered entropy below 200 mK (where $T < 550$ mK for $B = 0$ T and $T < 100$ mK for $B = 14$ T) is 1.6 JK$^{-1}$mol$^{-1}$, which is 28% of the theoretical entropy ($\beta$ = 1.67). This is another strong spin fluctuations above $T_{N} = 3.32$ K and a phase transition at $T_{N} = 12$ K.

The inverse of the DC susceptibility measured with 0.1 T magnetic field along the T axes is displayed. In most of this temperature region, high magnetic fields enhance the thermal conductivity. The thermal conductivity in 14 T magnetic field along the C axis is plotted in Figure 2. The obtained heat conductivity is along the a axis. The peak at 12 K is the so-called phonon peak. Also shown are the thermal conductivity and susceptibility data at 0 and 1 T, respectively. The solid lines are a linear fit to the high-magnetic field data. The measured magnetic entropy is consistent with an effective spin-1/2 triangular lattice antiferromagnet.
A single crystal is a material in which the crystal structure of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries.
**Crystallization**

*Nucleation* is the step where the solute molecules dispersed in the solvent start to gather into clusters, on the nanometer scale (elevating solute concentration in a small region).

The *crystal growth* is the subsequent growth of the nuclei that succeed in achieving the critical cluster size.
Flux growth

e.g. Rock candy

- Find the right solvent and dissolve the starting materials
- Crystallize with time and temperature

![Diagram showing the flux growth process](image)

- Crystal growth begins with the dissolution of the solute into the flux.
- The temperature is gradually increased to promote crystallization.
- Key temperatures and time points are highlighted:
  - 771-801°C (flux melting point)
  - 900°C for 10 h
- The process involves nucleation, Ostwald ripening, and crystal growth.

Cryst. Growth Des. 2018, 18, 5301−5310
Flux growth

- Reaction:
  \[ Na_2CO_3 + Ba(NO_3)_2 + (CO + (WO_4)^{2-}) + HPO_4^{2-} + Na_2 \rightarrow BaX \]

- Process:
  - RT to 950°C over 12 hours
  - 3°C/hour
  - 750°C
**Na$_2$BaCo(PO$_4$)$_2$, $T_N = 0.15$ K, field induced spin state transitions**

*N. Li., H. D. Zhou et al., Nature Communications 11, 4216 (2020).*
the UUD phase only survives for B // c, which strongly suggests its easy axis anisotropy.

\textbf{Na}_2\textbf{BaCo(PO}_4\textbf{)}_2$, magnetic phase diagram

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{phase_diagram.png}
\caption{Phase diagram of Na\textsubscript{2}BaCo(PO\textsubscript{4})\textsubscript{2}.}
\end{figure}
Na$_2$BaCo(PO$_4$)$_2$ behaves as a gapless QSL above $T_N$

\[
\frac{k_0}{T} = \frac{\pi k_B^2}{9h} \frac{l_s}{ad} = \frac{\pi}{9} \left( \frac{k_B}{\hbar} \right)^2 \frac{J}{d} \tau_s
\]

$a \sim 5.32$ Å and $d \sim 7.01$ Å are nearest-neighbor and interlayer spin distance, respectively.

From the observed $\kappa_0/T = 0.0062$ WK$^{-2}$m$^{-1}$, the $l_s$ (mean free path) is obtained as 36.6 Å, indicating that the excitations (spinons) are mobile to a distance seven times as long as the inter-spin distance without being scattered.
YbMgGaO$_4$, spin-1/2 triangular lattice antiferromagnet
Melting Growth

Bi Crystals grown in kitchen

Czochralski Crystal Growth

Crystal Pulling

Si crystal growth

Crystal Ingots

Shaping and Polishing

300 mm wafer
Image Furnaces

Two mirrors Image Furnace

2200 Celsius degree
Crystal growth, floating zone technique

- Stabilizing
- Necking
- Growth

**Stabilizing**
- Feeding: 1 mm/h
- Growth: 3 mm/h

**Necking**

**Growth**
- Feeding: 2 mm/h
- Growth: 3 mm/h
YbMgGaO$_4$, residual $k_0/T$ term

From the observed $k_0/T = 0.0058$ W K$^{-2}$m$^{-1}$, the $l_s$ (mean free path) is obtained as 78.4 Å, indicating that the excitations (spinons) are mobile to a distance 23 times as long as the inter-spin distance without being scattered.

The gapless QSL with itinerant excitations survives with Mg/Ga disorder

_X. Rao, H. D. Zhou et al., Nature Communications 12, 4949 (2021)._
YbMgGaO$_4$, field induced spin state transitions

Figure 2 Magnetic field dependence of the $a$-axis thermal conductivity of YbMgGaO$_4$. a

300 mK B // a

$C_p$ (JK$^{-1}$mol$^{-1}$)

$B_{a2}$ $B_{a3}$

$\text{d}C_p/\text{d}B$ (JK$^{-1}$mol$^{-1}$B$^{-1}$)

$0$ $0.0$ $0.2$ $0.4$ $0.6$ $0.8$ $1.0$

$B$ (T)

$0$ $2$ $4$ $6$

$0$ $0.0$ $0.2$ $0.4$ $0.6$ $0.8$ $1.0$

$B$ (T)

$0$ $2$ $4$ $6$

$0$ $0.0$ $0.2$ $0.4$ $0.6$ $0.8$ $1.0$

$B$ (T)

$0$ $2$ $4$ $6$

$0$ $0.0$ $0.2$ $0.4$ $0.6$ $0.8$ $1.0$

$B$ (T)

$0$ $2$ $4$ $6$

$0$ $0.0$ $0.2$ $0.4$ $0.6$ $0.8$ $1.0$

$B$ (T)

$0$ $2$ $4$ $6$
YbMgGaO$_4$, field induced spin state transitions

UUD phase with $B$ // $a$

UUUD phase with $B$ // $c$

Magnetization plateau feature is weak due to disorder
Pyrochlore heterostructure

To explore a new route towards “metallization of quantum magnet” or electronically detect spin states and magnetic excitations

The hypothesis of the proposed approach is that, when combined to form a heterostructure, the interfacial coupling between the magnetic degree of freedom in an insulating geometrically frustrated quantum magnet (GFQM) and the electronic degree of freedom in a spin-orbit-entangled correlated metal necessarily leads to electronic transport signatures that are characteristic of the unusual spin states and their elementary excitations.
Select Pyrochlore Dy$_2$Ti$_2$O$_7$ (DTO) as the GFQM

With applied field along the [111] axis, the spin ice (two in two out) state transforms to kagome spin ice and then three in one out state.

Select Pyrochlore Bi$_2$Ir$_2$O$_7$ (BIO) as the Correlated Metal

Paramagnetic metal BIO

Spin Ice DTO

T. F. Qi et al., J. Phys. Condens. Matter 24, 345601 (2012);
Growth (I): BIO film on DTO single crystal

A combination of optical floating zone crystal growth and pulsed laser deposition is used to synthesize the DTO/BIO heterostructures along the [111] direction.
Growth (II): Orientation, Polish, Film, Interface

AFM, $R_s \approx 1.21 \text{ Å}$

RSM, fully strained

TEM, uniform interface
Anomalous MR related to the ice-rule breaking

3 – 5 nm BIO film on DTO
$T = 50 \text{ mK}$

MR feature occurs while DTO enters the three in one out state

$H. \ Zhan, \ H.D. \ Zhou, \ J. \ Liu \ et \ al., \ arXiv:2011.09048$
Anomalous MR (II): Temperature dependence

MR feature disappears above spin ice temperature

The anomalous MR responses can be depicted with the coexistence of the two spin states in the Kagome plane perpendicular to the field.
Yb$_2$Ti$_2$O$_7$/Bi$_2$Ir$_2$O$_7$ heterostructure

Yb$_2$Ti$_2$O$_7$: a ferromagnetic ordering at 0.28 K with strong quantum spin fluctuations

Ideal system to detect quantum spin fluctuations electronically

Yb$_2$Ti$_2$O$_7$/Bi$_2$Ir$_2$O$_7$ heterostructure

MR anomalies are related to strong quantum spin fluctuations at zero field, and the field dependence of the low energy excitation.
Summary

Geometrically frustrated lattice, magnetic ordering at extremely low temperatures, disorder, and spin-1/2, are good ingredients for QSL

Demonstrate a new route to electronically probe the exotic dynamics of geometrically frustrated quantum magnets through epitaxial interfaces.

Crystals = hard work + FedEx

Thank You