Abstract: I will present our results on two hafnium-based pyrochlores. Firstly, I will summarize our findings on Tb2Hf2O7, where a sizeable gap isolates a non-Kramers ground state doublet with Ising-like anisotropy at low temperature. Long-range magnetic order is avoided down to the lowest temperatures, where Tb2Hf2O has correlations typical of a Coulomb phase. A large density of anion Frenkel defects leads to quenched random crystal fields, making this material relevant to theories of disorder-induced quantum entanglement in spin ices. Secondly, I will present our results on another non-Kramers pyrochlore with Ising-like moments, Pr2Hf2O, which displays macroscopic signatures that are consistent with spin ice-like correlations. Using the results of neutron scattering experiments I will demonstrate that Pr2Hf2O conforms to the predictions of the quantum-coherent regime of a QSI, where pinch-points are suppressed. Our result allows an estimate for the speed of light associated with magnetic photon excitations.
A summary of our results on $\text{Tb}_2\text{Hf}_2\text{O}_7$ and $\text{Pr}_2\text{Hf}_2\text{O}_7$
Quantum spin liquid and spin ice states in new pyrochlores

Outline

• \(\text{Tb}_2\text{Hf}_2\text{O}_7\): Coulomb (Quantum?) Spin Liquid in anion-disordered pyrochlore
  R. Sibille et al. *arXiv:1610.08714*

• \(\text{Pr}_2\text{Hf}_2\text{O}_7\): Quantum Spin Ice
  + other recent results...

• \(\text{Ce}_2\text{Sn}_2\text{O}_7\): QSL from dipole-octupole doublets in a Kramers pyrochlore
  + other recent results...
My thanks go to

- M. Kenzelmann (PSI)
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- E. Lhotel (Institut Néel)
- N. Shannon (OIST)
- N. Gauthier (PSI) & H. Yan (OIST)
- M. Ciomaga Hatnean & G. Balakrishnan (Warwick)

+ many instrument scientists:
  A. Amato (PSI), A. Cervellino (PSI), G. Ehlers (SNS), M. Frontzek (HFIR),
  D. Keen (ISIS), H. Luetkens (PSI), G. Nilsen (ISIS), J. Ollivier (ILL), T. Perring (ISIS),
  V. Pomjakushin (PSI), E. Ressouche (ILL), B. Winn (SNS), O. Zaharko (PSI), ...
Coulomb spin liquid in anion-disordered $\text{Tb}_2\text{Hf}_2\text{O}_7$

$\text{A}^{3+}_2\text{B}^{4+}_2\text{O}_7$ pyrochlore oxides

- Crystal chemistry

Defective fluorite

Pyrochlore

Order – Disorder transition:
- antisite cation defects (lowest energy)
- anion Frenkel pair defects
Coulomb spin liquid in anion-disordered $\text{Tb}_2\text{Hf}_2\text{O}_7$

$\text{A}^{3+}_2\text{B}^{4+}_2\text{O}_7$ pyrochlore oxides

- **Stability field:** $\approx$ governed by $R_A/R_B$ + chemical bonding

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Coulomb spin liquid in anion-disordered $\text{Tb}_2\text{Hf}_2\text{O}_7$

Crystal chemistry of $\text{Tb}_2\text{Hf}_2\text{O}_7$

- An open question
  poor Tb/Hf constrat

- Increased contrast at $L_3$ Tb absorption edge
  joint refinement resonant X-rays + Neutrons
Coulomb spin liquid in anion-disordered Tb$_2$Hf$_2$O$_7$

**Crystal chemistry of Tb$_2$Hf$_2$O$_7**

- **An open question**
  - poor Tb/Hf constrat

- **Increased contrast at L$_3$ Tb absorption edge**
  - joint refinement resonant X-rays + Neutrons

**Result:** NO cation antosite disorder,
but oxygen Frenkel defects

$O_{48f} \approx 8\%$ depleted  $\equiv$  $O_{8a} \approx 50\%$ filled
Coulomb spin liquid in anion-disordered $\text{Tb}_2\text{Hf}_2\text{O}_7$

Crystal chemistry of $\text{Tb}_2\text{Hf}_2\text{O}_7$

- Symmetry breaking around $\text{Tb}^{3+}$ ions

$O_{48f} \approx 8\%$ depleted $\equiv O_{8a} \approx 50\%$ filled
Coulomb spin liquid in anion-disordered \( \text{Tb}_2\text{Hf}_2\text{O}_7 \)

Crystal chemistry of \( \text{Tb}_2\text{Hf}_2\text{O}_7 \)

- Symmetry breaking around \( \text{Tb}^{3+} \) ions

\[
\text{O}_{48f} \approx 8\% \text{ depleted } \equiv \text{O}_{8a} \approx 50\% \text{ filled}
\]

Pair Distribution Function (Fourier transform of the experimental normalized total structure factor \( S(Q) \))

→ Large local distortions around \( \text{Tb}^{3+} \) (order 0.1 Å)
Coulomb spin liquid in anion-disordered $\text{Tb}_2\text{Hf}_2\text{O}_7$

Crystal growth of $\text{Tb}_2\text{Hf}_2\text{O}_7$

- **Challenge:** order-disorder transition $T_{O-D} \approx 2150^\circ\text{C} < T_{\text{melting}} \approx 2650^\circ\text{C}$
Coulomb spin liquid in anion-disordered $\text{Tb}_2\text{Hf}_2\text{O}_7$

**Crystal growth of $\text{Tb}_2\text{Hf}_2\text{O}_7$**

- **Challenge:** order-disorder transition $T_{O-D} \approx 2150^\circ C < T_{\text{melting}} \approx 2650^\circ C$

![Diagram showing crystal growth process](image)

**Remark:** possibility to control the concentration of those defects!
Coulomb spin liquid in anion-disordered $\text{Tb}_2\text{Hf}_2\text{O}_7$

Crystal field states of $\text{Tb}_2\text{Hf}_2\text{O}_7$

- Distribution of states, gap to 1st excited level, preserved Ising moments

Magnetic down to low temperature

Strongly Ising

Energy scales:
- CEF gap: $\approx 50$ K
- Doublet splitting estimate: $\approx 0.5$ K
Coulomb spin liquid in anion-disordered Tb$_2$Hf$_2$O$_7$

Spin Liquid state of Tb$_2$Hf$_2$O$_7$

- Elastic magnetic scattering

Coulomb spin liquid in anion-disordered $\text{Tb}_2\text{Hf}_2\text{O}_7$

Spin Liquid state of $\text{Tb}_2\text{Hf}_2\text{O}_7$

- Elastic magnetic scattering

Coulomb spin liquid in anion-disordered $\text{Tb}_2\text{Hf}_2\text{O}_7$

Spin Liquid state of $\text{Tb}_2\text{Hf}_2\text{O}_7$

- Elastic magnetic scattering

red line/calculated pattern: single tetrahedron, AF-correlated, isotropic spin model  

Spin liquid, despite non-magnetic disorder in non-Kramers spin ice

Savary & Balents  
*Phys. Rev. Lett.* 2017

- splits the ground state doublet
- Ising-pyrochlore: quenched random transverse field Ising model
- Quantum Spin Liquid (QSL) phases induced by disorder
Spin Liquid state of Tb$_2$Hf$_2$O$_7$

- **Polarization analysis** ($T = 0.07$ K)

Map reciprocal space in two polarization channels, $z$ (non-spin flip) and $z'$ (spin-flip)

→ distinguish correlations among spin components $||$ or $\perp$ ($h,h,l$)

Power-law correlations

→ magnetic Coulomb phase
Defect-induced frozen magnetic degrees of freedom

- Ac susceptibility

→ spin glass transition at $T_{SG} = 0.8$ K, inside Coulomb phase!
Crystal chemistry and crystal growth of $\text{Pr}_2\text{Hf}_2\text{O}_7$

- “Perfect” pyrochlore phase

- Xe-lamps floating zone ($T_{\text{melting}} \approx 2470^\circ\text{C}$) in Ar

Quantum Spin Ice $\text{Pr}_2\text{Hf}_2\text{O}_7$

Single-ion physics in $\text{Pr}_2\text{Hf}_2\text{O}_7$

- **Crystal field**: $4f^2$ ion in $D_{3d}$ symmetry (91 states in $|^{2S+1}L_J, M_J\rangle$ basis)

\[
\Gamma_{3}^{+} = 0.83|^{3}H_{4}, \pm 4\rangle \pm 0.51|^{3}H_{4}, \pm 1\rangle - 0.12|^{3}H_{4}, \mp 2\rangle \\
+ 0.14|^{1}G_{4}, \pm 4\rangle \pm 0.09|^{1}G_{4}, \pm 1\rangle \\
\mp 0.06|^{3}H_{5}, \pm 4\rangle \pm 0.05|^{3}H_{5}, \mp 2\rangle
\]

- Non-Kramers ground doublet with **Ising** anisotropy (gap of $\sim 9$ meV: $\chi_{//}/\chi_{\perp} \sim 24$ at 10 K)
- $\mu = 2.43\ \mu_{\text{B}}/\text{Pr}^{3+}$
- Admixture of **quadrupolar terms** $|M_J \neq \pm J\rangle$
Quantum Spin Ice \( \text{Pr}_2\text{Hf}_2\text{O}_7 \)

**Magnetism in \( \text{Pr}_2\text{Hf}_2\text{O}_7 \)**

- Temperature dependence

→ Change of regime below 0.5 K
Quantum Spin Ice Pr$_2$Hf$_2$O$_7$

Magnetism in Pr$_2$Hf$_2$O$_7$

- Macroscopic behavior at $T < 0.5$ K

Ferromagnetic spin ice-like correlations

Estimate of exchange $E_{\text{eff}} = \frac{1}{3} \mu_0 \mu_{\text{eff}} H_C / k_B \approx 1.2$ K
Magnetism in Pr$_2$Hf$_2$O$_7$

- Macroscopic behavior at $T < 0.5$ K

Ferromagnetic spin ice-like correlations

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Quantum Spin Ice $\text{Pr}_2\text{Hf}_2\text{O}_7$

**Magnetism in $\text{Pr}_2\text{Hf}_2\text{O}_7$**

- Magnetic correlations at $T < 0.5$ K

**IN5 – ILL**

![Graph showing magnetism in $\text{Pr}_2\text{Hf}_2\text{O}_7$](image)
Quantum Spin Ice $\text{Pr}_2\text{Hf}_2\text{O}_7$

Magnetism in $\text{Pr}_2\text{Hf}_2\text{O}_7$
- Magnetic correlations at $T < 0.5$ K

IN5 – ILL

QSI lattice field theory
Benton, Sikora & Shannon
*Phys. Rev. B* 2012

Suppressed pinch-points (c.f. Shannon et al. *Phys. Rev. Lett.* 2012); Speed of light: $c \approx 3.6$ m/s for $T = 0.05$ K
Quantum Spin Ice $\text{Pr}_2\text{Hf}_2\text{O}_7$

Magnetism in $\text{Pr}_2\text{Hf}_2\text{O}_7$

- Magnetic excitations at $T < 0.5$ K
Quantum Spin Ice Pr$_2$Hf$_2$O$_7$

Magnetism in Pr$_2$Hf$_2$O$_7$

- Magnetic excitations at $T < 0.5$ K

- Inelastic response appears to have two major contributions

- AFQ spinons? bandwidth $\approx 10$ times $J \approx 0.1$ meV
  

- Reminiscent of QMC calculations incl. spinons
  

- Overall results rather different from Pr$_2$Zr$_2$O$_7$
  
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  R. Sibille et al. *arXiv:1610.08714*

• \( \text{Pr}_2\text{Hf}_2\text{O}_7 \): Quantum Spin Ice  

**Suppressed pinch-points & Continuum of excitations** \( \rightarrow \) strong case that \( \text{Pr}_2\text{Hf}_2\text{O}_7 \) is a QSI

• \( \text{Ce}_2\text{Sn}_2\text{O}_7 \): QSL from dipole-octupole doublets in a Kramers pyrochlore  
  + other recent results...
Quantum Spin Liquid candidate Ce$_2$Sn$_2$O$_7$

**Magnetism in Ce$_2$Sn$_2$O$_7$**

- Low-temperature correlated state

Quantum Spin Liquid candidate Ce$_2$Sn$_2$O$_7$

Magnetism in Ce$_2$Sn$_2$O$_7$

• Follow-up theory:

PHYSICAL REVIEW B 95, 041106(R) (2017)

Symmetry enriched U(1) topological orders for dipole-octupole doublets on a pyrochlore lattice

Yao-Dong Li$^1$ and Gang Chen$^{1,2,*}$

![Diagram]

FIG. 1. The electron configuration and the D$_{3d}$ crystal electric field (CEF) splitting of the Ce$^{3+}$ ion in Ce$_2$Sn$_2$O$_7$. The CEF ground state wave functions are combinations of $J^z = \pm 3/2$ states [14], thus the CEF ground state is a DO doublet. $\Delta$ is the CEF gap and was fitted to be $\Delta = 50 \pm 5$ meV [14].
Quantum Spin Liquid candidate Ce$_2$Sn$_2$O$_7$

Magnetism in Ce$_2$Sn$_2$O$_7$

- **Crystal field**: $4f$ ion in $D_{3d}$ symmetry (14 states in $|^{2S+1}L_J, M_J\rangle$ basis)

[Graphs and data plots]

$$|\pm\rangle = 0.92|^{2}F_{5/2}, \pm 3/2\rangle \pm 0.35|^{2}F_{5/2}, \mp 3/2\rangle$$

$$\mp 0.15|^{2}F_{7/2}, \mp 3/2\rangle \pm 0.02|^{2}F_{7/2}, \pm 3/2\rangle.$$  

Ce$_2$Sn$_2$O$_7$ has Dipole-Octupole Kramers doublets, nature of the correlated ground state to be determined: dipolar or octupolar U(1) QSL?
My thanks go to

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