SPICE-Workshop on "Computational Quantum Magnetism", Mainz – May 2015





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Collaborators

Er₂Ti₂O₇:

- Zhihao Hao (UW)
- Paul McClarty
- Pawel Stasiak
- Behnam Javanparast (UW)
- Alex Day
- Jaan Oitmaa
- Rajiv Singh
- Behnaz Bagheri
- Anson Wong

Yb₂**Ti**₂**O**₇:

- Ludovic Jaubert (OIST)
- Zhihao Hao (UW)
- Jeff Rau (UW)
- Owen Benton
- Nic Shannon
- Rajiv Singh
- Jaan Oitmaa
- Robert Hayre
- Ryan Applegate
- Taoran Lin
- Anson Wong
- Alex Day

<u>Outline</u>

- 1. Rare-earth pyrochlore oxides
- 2. Order-by-disorder (ObD) in $Er_2Ti_2O_7$
- 3. Why should one care about ObD?
- 4. $Yb_2Ti_2O_7$: what is the hidden order?
- 5. Conclusion

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Message of Talk

- 1. Order-by-disorder (ObD) appears quite likely in $\text{Er}_2\text{Ti}_2\text{O}_7$
- 2. $Yb_2Ti_2O_7$ is puzzling:
 - Some form of hidden order in $Yb_2Ti_2O_7$?
 - Are (i) competing orders and (ii) the consequential ObD the missing links in $Yb_2Ti_2O_7$?























$R_2Ti_2O_7$ R=Gd, Tb, Dy, Ho, Er, Yb









statistical mechanics of "conventional" (i.e. nonfrustrated) magnets – <u>what happens in frustrated ones?</u>

Effective Hamiltonian Method

$$H = H_{\text{cef}} + H_{\text{int}} \qquad H_{\text{int}} = \sum_{i>j} \sum_{K,K',Q,Q'} I^{QQ'}_{KK'}O^Q_K(J_i)O^{Q'}_{K'}(J_j)$$

$$H_{\text{eff}} = PH_{\text{int}}P + PH_{\text{int}}QH_{\text{int}}P + \cdots$$

$$\mathbf{P} = \sum_{\alpha \in \mathbf{P}} |\alpha\rangle \langle \alpha|$$

Large (CEF gap Δ) denominator compared to the energy scale of H_{int}



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$$\mathbf{P} = \sum_{\alpha \in \mathbf{P}} |\alpha\rangle \langle \alpha|$$

Large (CEF gap Δ) denominator compared to the energy scale of H_{int}



Note: Fine for Dy, Ho, Er, Yb; not Tb



$$H_{\text{eff}} = J_{zz} \sum_{\langle i,j \rangle} S_{i}^{z} S_{j}^{z} - J_{\pm} \sum_{\langle i,j \rangle} \left(S_{i}^{+} S_{j}^{-} + S_{i}^{-} S_{j}^{+} \right) \text{ For } \Delta J_{zz} > 1, \text{ ground doublet projection is good enough}$$
$$+ J_{z\pm} \sum_{\langle i,j \rangle} \left[S_{i}^{z} \left(\zeta_{ij} S_{j}^{+} + \zeta_{ij}^{*} S_{j}^{-} \right) + i \leftrightarrow j \right] + J_{\pm\pm} \sum_{\langle i,j \rangle} \left(\gamma_{ij} S_{i}^{+} S_{j}^{+} + \gamma_{ij}^{*} S_{i}^{-} S_{j}^{-} \right) S = \frac{1}{2} \text{ operator}$$
$$\text{K.A. Ross, L. Savary, B.D. Gaulin, and L. Balents; PRX 1, 021002 (2011)}$$
$$H_{\text{eff}} = J_{\text{Ising}} \sum_{\langle i,j \rangle} S_{i}^{z_{i}} S_{j}^{z_{j}} + J_{\text{iso}} \sum_{\langle i,j \rangle} \overline{S}_{i} \bullet \overline{S}_{j} + J_{\text{DM}} \sum_{\langle i,j \rangle} \overline{d}_{ij} \bullet \overline{S}_{i} \times \overline{S}_{j}$$
$$+ J_{\text{pd}} \sum_{\langle i,j \rangle} \left(\overline{S}_{i} \bullet \overline{S}_{j} - 3\overline{S}_{i} \bullet \widehat{r}_{ij} \widehat{r}_{ij} \bullet \overline{S}_{j} \right)$$
$$P.A. McClarty, S.H. Curnoe, and M J.P. Gingras,$$



P.A. McClarty, S.H. Curnoe, and M J.P. Gingras, J. Phys.: Conf. Ser. **145**, 012032 (2009)

J.D. Thompson et al. Phys. Rev. Lett. 106, 187202 (2011)

Frustrated Rare-earth Pyrochlore Oxides

Examples of phenomena

- $(Ho,Dy)_2(Ti,Sn,Ge)_2O_7$
- $Yb_2Ti_2O_7$
- $Tb_2Ti_2O_7$
- Gd₂Ti₂O₇
- Er₂Ti₂O₇

- : spin ice
 - : quantum spin ice ?
 - : spin liquid / QSI?
 - : multiple transitions
 - : order-by-disorder

J.S. Gardner, M.J.P. Gingras, and J.E. Greedan, *Magnetic Pyrochlore Oxides*, Rev. Mod. Phys. **82**, 53 (2010)





QSI is expected to be a U(1) quantum spin liquid

Gingras & McClarty, Rep. Prog. Phys. 77, 056501 (2014)

There is an ongoing search for quantum spin ice materials

PRL 98, 157204 (2007) PHYSICAL REVIEW LETTERS	week endin 13 APRIL 20	¹ g 207		
Dynamically Induced Frustration as a Route to a Quantum Spin Ice State in Tb ₂ Ti ₂ O ₇ via Virtual Crystal Field Excitations and Quantum Many-Body Effects Hamid R. Molavian. ¹ Michel J. P. Gingras. ^{1,2} and Benjamin Canals ^{1,3}		natur	PRICATIONS	
PRL 101, 227204 (2008) PHYSICAL REVIEW LETTERS	week ending 28 NOVEMBER 2008	ARTICL Received 20 Quar K. Kimura ¹	E Sep 2012 Accepted 18 Apr 2013 Published 17 Jun 2013 Published 18	-like Pr ₂ Zr ₂ O ₇ Iishibori ⁶ & H. Sawa ⁶
Dynamic Spin Ice: Pr ₂ Sn ₂ O ₇ H. D. Zhou, ^{1,2} C. R. Wiebe, ^{1,2,*} J. A. Janik, ^{1,2} L. Balicas, ² Y. J. Yo, ² Y. Qiu, ^{3,4} J. R. D. Copley, ³	and J. S. Gardner ^{3,5}			
		PHYS	ICAL REVIEW X 1, 021002 (2011)	
PRL 110, 127207 (2013) PHYSICAL REVIEW LETTERS Dynamical Splayed Ferromagnetic Ground State in the Quantum Spin A. Yaouanc. ^{1,*} P. Dalmas de Réotier. ¹ P. Bonville. ² J. A. Hodges. ² V. Glazkov. ^{1,3} L. Kelle	Kate A. R 22 MARCH 2013 Ice Yb ₂ Sn ₂ O ₇ er. ⁴ V. Sikolenko. ⁴	Quantun	n Excitations in Quantum Spin Ice le Savary, ² Bruce D. Gaulin, ^{1,3,4} and Leon Bal	ents ^{5,*}
M. Bartkowiak, ⁵ A. Amato, ⁶ C. Baines, ⁶ P. J. C. King, ⁷ P. C. M. Gubbens, ⁸ and A	PRL 109, 09720.	5 (2012)	PHYSICAL REVIEW LETTERS	week ending 31 AUGUST 2012
PHYSICAL REVIEW X 4, 041037 (2014)		Vindicatio Applegate, ¹ N.	on of Yb ₂ Ti ₂ O ₇ as a Model Exchange Quantum S R. Hayre, ¹ R. R. P. Singh, ¹ T. Lin, ² A. G. R. Day, ^{2,3} and M. J.	pin Ice P. Gingras ^{1,2,4}
Quantum Spin-Ice and Dimer Models with Rydberg Atoms				week ending
A. W. Glaetzle, *** M. Dalmonte, ** R. Nath, **** I. Rousochatzakis, * R. Moessner, * and P. Zoller***	PRL 105, 047201 (2010) Quantum M Condense	elting of Sp	Din Ice: Emergent Cooperative Quadrupole and Shigeki Onoda and Yoichi Tanaka y Laboratory, RIKEN, 2-1, Hirosawa, Wako 351-0198, Saitama,	23 JULY 2010 1 Chirality , Japan

Frustrated Rare-earth Pyrochlore Oxides

Examples of phenomena

- $(Ho,Dy)_2(Ti,Sn,Ge)_2O_7$
- \rightarrow Yb₂Ti₂O₇ (XY)
- $Tb_2Ti_2O_7$
- $Gd_2Ti_2O_7$
- \rightarrow Er₂Ti₂O₇ (XY)

- : spin ice
- : quantum spin ice ?
- : spin liquid / QSI?
- : multiple transitions
- : order-by-disorder

J.S. Gardner, M.J.P. Gingras, and J.E. Greedan, *Magnetic Pyrochlore Oxides*, Rev. Mod. Phys. **82**, 53 (2010)



Rare- earth pyrochlore oxides
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Order-by-disorder

ObD is a phenomenon via which thermal fluctuations and/or quantum fluctuations lift an <u>accidental</u> classical *T*=0 ground state degeneracy by

 (i) selecting the subset of states of the degenerate around which the system <u>fluctuate the most</u>
 which

(ii) then "allows" for a spontaneous symmetry breaking and long-range order



Order-by-disorder – does it "occur"?

The concept of (thermal/quantum) *order-bydisorder* (ObD) is compelling (and presumably correct) for a number of theoretical models described by some minimal Hamiltonian.

→But does it really occur in nature, in real materials?

Sevidence for ObD is strong in $Er_2Ti_2O_7$

The problem of order in XY-like Er₂Ti₂O₇



Z

 ψ_3



Champion *et al.* found in a classical pyrochlore *XY* antiferromagnet toymodel a selection of ψ₂ proceeding via <u>thermal</u> order-by-disorder (ObD)
 They further speculated that quantum fluctuations could proceed similarly and that a ψ₂ ground state could be stabilized via <u>quantum</u> ObD

Degeneracy of Classical Ground State



Degeneracy of Classical Ground State



"No bilinear spin-spin interaction of arbitrary range and anisotropy can lift the classical degeneracy of the ψ_2/ψ_3 manifold"

Savary, Ross, Gaulin, Ruff, and Balents; Phys. Rev. Lett. 109, 167201 (2012).

Proposed Solution to the Er₂Ti₂O₇ Problem

Order by Quantum Disorder in $Er_2Ti_2O_7$

L. Savary, K.A. Ross, B.D. Gaulin, J.P.C. Ruff, and L. Balents; Phys. Rev. Lett. **109**, 167201 (Published 15 October 2012)

 $H = J_{zz} \sum_{\langle i,j \rangle} S_i^z S_j^z - J_{\pm} \sum_{\langle i,j \rangle} \left(S_i^+ S_j^- + S_i^- S_j^+ \right)$ + $J_{z\pm} \sum_{\langle i,j \rangle} \left[S_i^z \left(\zeta_{ij} S_j^+ + \zeta_{ij}^* S_j^- \right) + i \leftrightarrow j \right] + J_{\pm\pm} \sum_{\langle i,j \rangle} \left(\gamma_{ij} S_i^+ S_j^+ + \gamma_{ij}^* S_i^- S_j^- \right) \quad S = \frac{1}{2} \text{ operator}$



FIG. 1 (color). The measured $S(\mathbf{Q}, \omega)$ at T = 30 mK, H = 3 T sliced along several directions. The first five columns show $S(\mathbf{Q}, \omega)$ in the *HHL* plane, with the field along [110], while the last two columns show $S(\mathbf{Q}, \omega)$ for the field along [111]. Top row: measured $S(\mathbf{Q}, \omega)$. Bottom row: calculated $S(\mathbf{Q}, \omega)$, based on an anisotropic exchange model with six free parameters (see text) that were extracted by fitting to the measured dispersions.

What are (classical) long-range ordered phases?









More about the splayed-ferromagnet phase



- Canted spin ice ("2-in/2-out")
- Splayed ferromagnet (SF)
- Net magnetization along <100>

Stability of ψ_2 for Er₂Ti₂O₇ against long-range dipolar interaction



Ground state phase diagram of generic XY pyrochlore magnets with quantum fluctuations; Anson W.C. Wong, Zhihao Hao, and M.J.P. Gingras, Phys. Rev. B **88**, 144402 (2013)

"Phase Transition and Thermal Order-by-Disorder in the Pyrochlore Quantum Antiferromagnet $Er_2Ti_2O_7$: a High-Temperature Series Expansion Study"; J. Oitmaa, R.P. Singh, A.G.R. Day, B.V. Bagheri, M.J.P. Gingras; Phys. Rev. B (RC) **88**, 220404 (2013).



→ "demonstration" of thermal ObD operating at T_c in H_{Savary}



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PHYSICAL REVIEW X 1, 021002 (2011)

Quantum Excitations in Quantum Spin Ice

Kate A. Ross,¹ Lucile Savary,² Bruce D. Gaulin,^{1,3,4} and Leon Balents^{5,*}

$$\left| H = J_{zz} \sum_{\langle i,j \rangle} S_i^z S_j^z - J_{\pm} \sum_{\langle i,j \rangle} \left(S_i^+ S_j^- + S_i^- S_j^+ \right) + J_{z\pm} \sum_{\langle i,j \rangle} \left[S_i^z \left(\zeta_{ij} S_j^+ + \zeta_{ij}^* S_j^- \right) + i \leftrightarrow j \right] + J_{\pm\pm} \sum_{\langle i,j \rangle} \left(\gamma_{ij} S_i^+ S_j^+ + \gamma_{ij}^* S_i^- S_j^- \right) \right] \right| = J_{zz} \sum_{\langle i,j \rangle} \left[S_i^z \left(\zeta_{ij} S_j^+ + \zeta_{ij}^* S_j^- \right) + i \leftrightarrow j \right] + J_{\pm\pm} \sum_{\langle i,j \rangle} \left(\gamma_{ij} S_i^+ S_j^+ + \gamma_{ij}^* S_i^- S_j^- \right) \right]$$





Where is $Yb_2Ti_2O_7$?



Ground state phase diagram of generic XY pyrochlore magnets with quantum fluctuations; Anson W.C. Wong, Zhihao Hao, and M.J.P. Gingras, Phys. Rev. B **88**, 144402 (2013)

Yasui et al., J.Phys. Soc. Jpn 72, 3014 (2003)



- q=0 peaks + ferromag.-like bulk at $0.03 \text{K} < T_c \sim 0.24 \text{K}$
- But not confirmed by neutron depolarization experiment [Gardner *et al.*, Phys. Rev. B **70**, 180404 (2004).

Chang *et al.*, Nature Communications | 3:992 | DOI: 10.1038/ncomms1989











Crucial hint: Lhotel et al. Physical Review B 89, 224419 (2014)



Summary of Yb₂Ti₂O₇ Experiments

- Large sensitivity to sample preparation (powders vs single crystals)
- Clear tendency towards ferromagnetic-like state
- A few (powder and single crystal) samples show a 5-25% difference in rise of magnetization vs highest-temperature magnetic specific heat peak

→ Suggests that the material is in the vicinity of a ferromagnetic-like state and a competing order

Jaubert, Benton, Rau, Oitmaa, Singh, Shannon, Gingras; *"Are multiphase competition & order-by-disorder the keys to understanding Yb*₂ Ti_2O_7 ?"; arXiv:1505.05499

By combining:

- Classical Monte Carlo
- Classical and quantum spin wave calculations
- Exact diagonalization
- Cluster mean-field theory
- Numerical linked-cluster expansion
- High-temperature series expansion
- Given the uncertainty on the exchange parameters determined by Ross, Savary, Gaulin and Balents; Phys. Rev. X 1, 021002 (2011)
- and the computed quantum shift/renormalization of the SFM-AF boundary

→ We found that $Yb_2Ti_2O_7$ is very close to the SFM-AF boundary, and ...









Message of Talk

- 1. Order-by-disorder (ObD) appears quite likely in $\text{Er}_2\text{Ti}_2\text{O}_7$
- 2. $Yb_2Ti_2O_7$ is puzzling:

The competition of energetically versus entropically stabilized orders are likely (the) essential missing ingredients to understand $Yb_2Ti_2O_7$.



Alighiero Fabrizio Boetti, 1940-1994