Title: The importance of defects and structural flexibility in the physics of quantum spin ices

Date: Jun 07, 2017 11:15 AM

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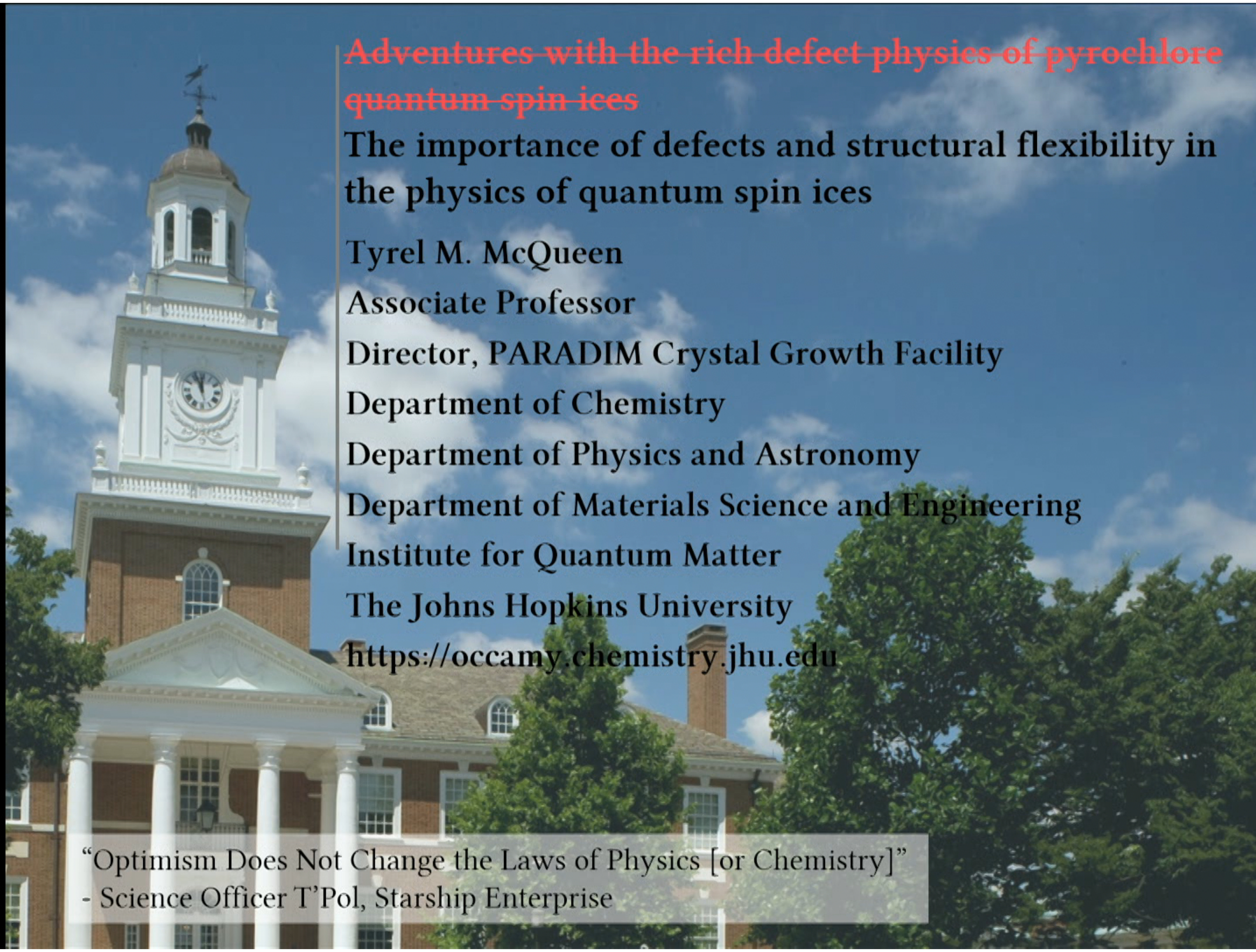
Abstract: Harboring interpenetrating lattices of corner-sharing tetrahedra, materials with the pyrochlore structure type dominate exploration of the physics of quantum spin ices. Recent synthetic advances in the control of point defects, such as in Yb2Ti2O7 and Pr2Zr2O, have demonstrated that even sub-percent changes in the type and/or number of defects radically modulates the low temperature physics of these materials. This sensitivity to disorder is driven not only by the geometrically frustrated nature of the lattice, but also by the propensity of a corner sharing tetrahedral framework to undergo displacive motions, in a manner analogous to that of beta-crystabolite (quartz), either statically, or dynamically (as soft phonons). An outlook for continued improvements in our ability to control the chemistry behind quantum spin ices will also be presented.


~~Adventures with the rich defect physics of pyrochlore quantum spin ices~~
The importance of defects and structural flexibility in the physics of quantum spin ices
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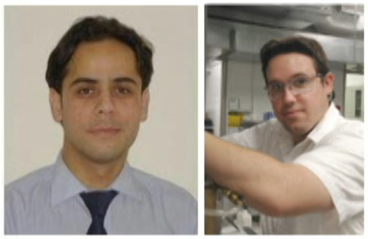
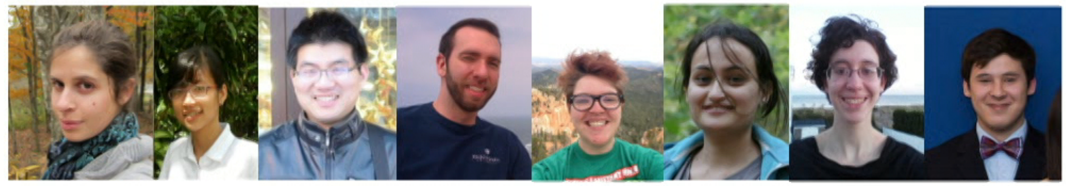
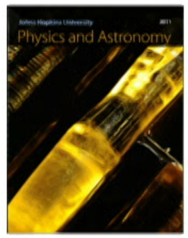
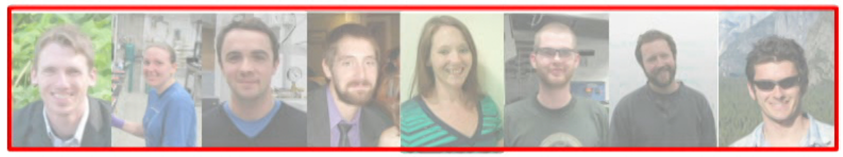
“Optimism Does Not Change the Laws of Physics [or Chemistry]”
- Science Officer T’Pol, Starship Enterprise

Acknowledgements









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<u>Collaborators</u>

- Prof. Broholm (JHU/IQM)
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- Prof. N.P. Armitage (JHU/IQM)
- Prof. Y. Li (JHU/IQM)
- Prof. A. Turner (JHU/IQM)
- Dr. Natalia Drichko (JHU)
- Dr. Jason Hodges (SNS)
- Dr. Ross McDonald (NHMFL)
- Prof. Minyea Lee (CSU)
- Prof. Takashi Imai (McMaster)
- Prof. Blundell (Oxford)
- Dr. Matthew Suchomel (APS)
- All collaborators on other projects

Outline

- Material Lifecycle and Analog Computers
- Water Ice to Quantum Spin Ice
- From Ideal to Real: Entropy (and Defects) Always Win
  - Not just point defects
- Stuffed Spin Ice: Locally Pyrochlore
- $Yb_2Ti_2O_7$: Sensitive Transitions
- $Pr_2Zr_2O_7$: Disorder for a Quantum Spin Liquid
- B-site Physics: Magnetism or Metal-Metal Bonds?
- Universal Structural Flexibility
- Wrap Up

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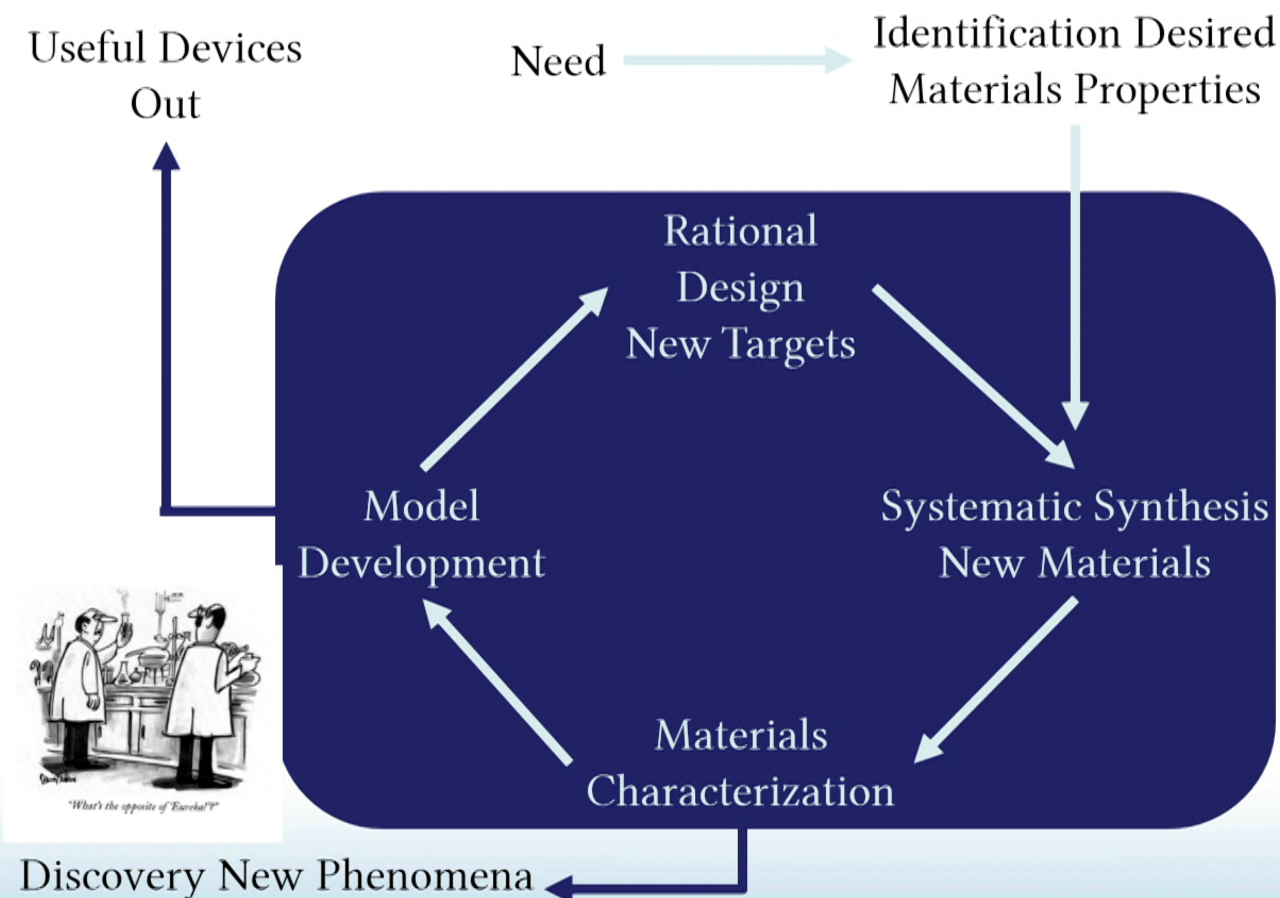
Materials Lifecycle

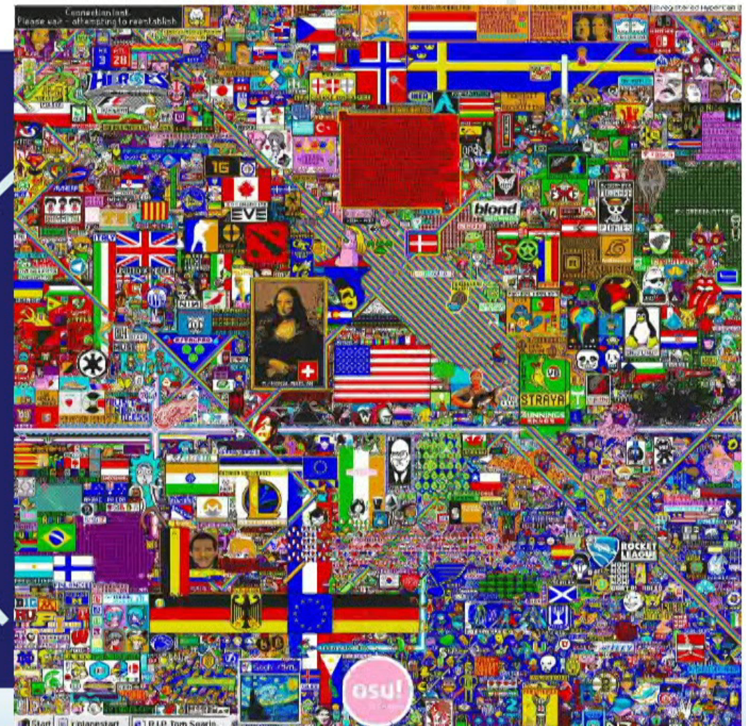


Materials Lifecycle

Useful Devices Out

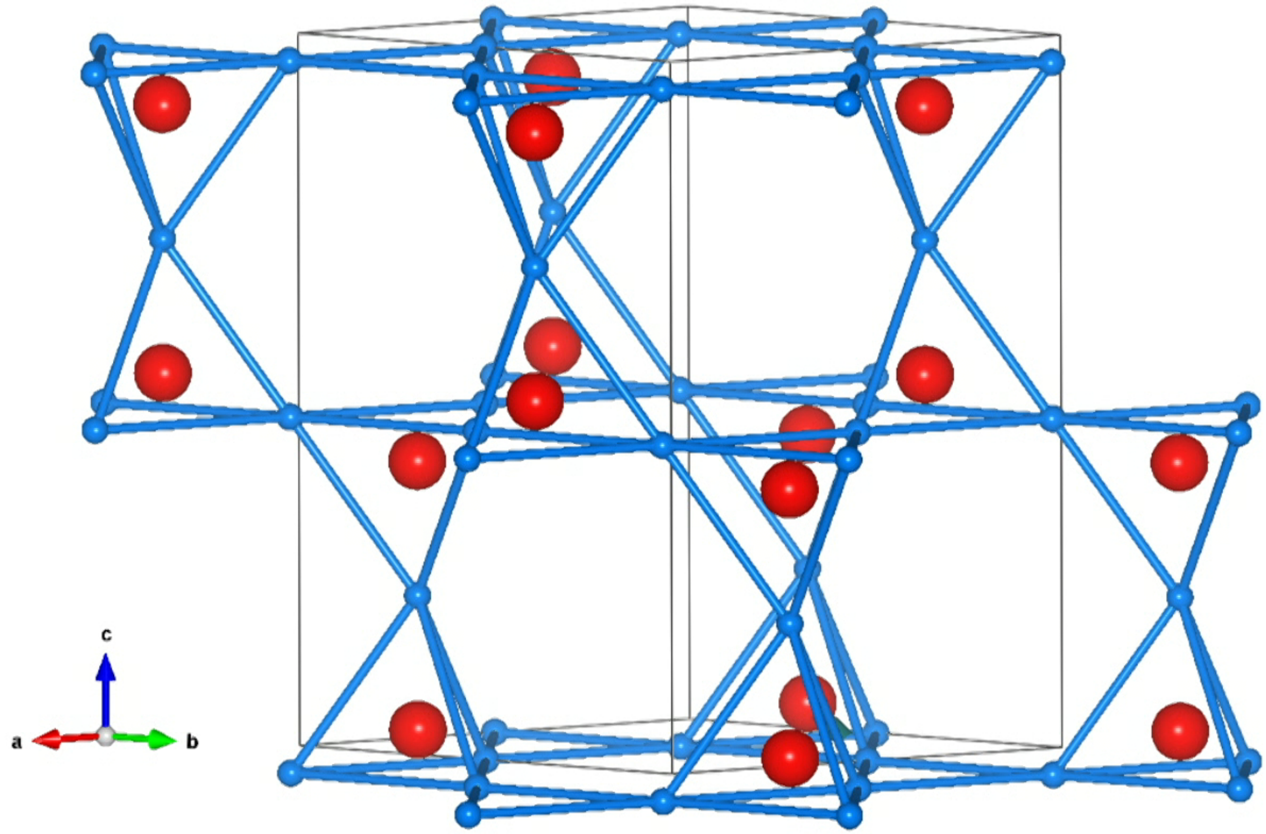
Need

Identification Desired Materials Properties



Discovery New Phenomena

Water Ice



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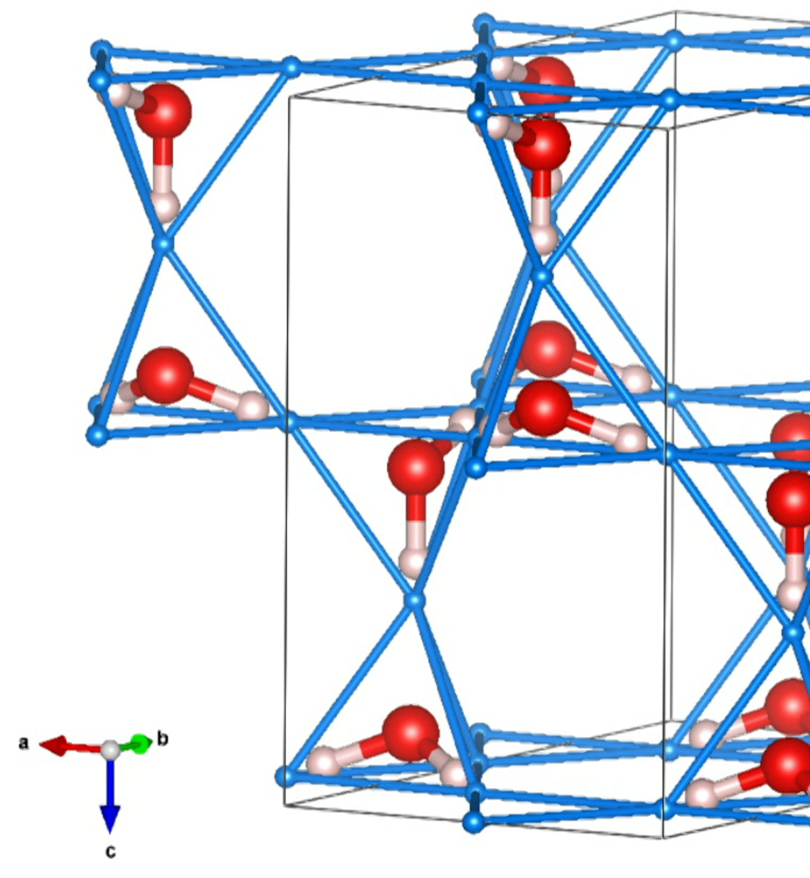
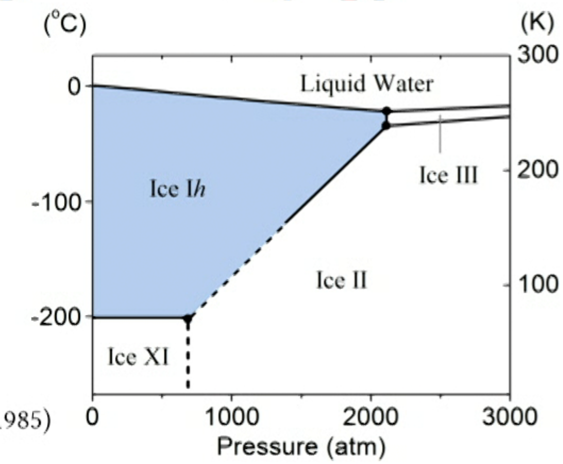
Water Ice





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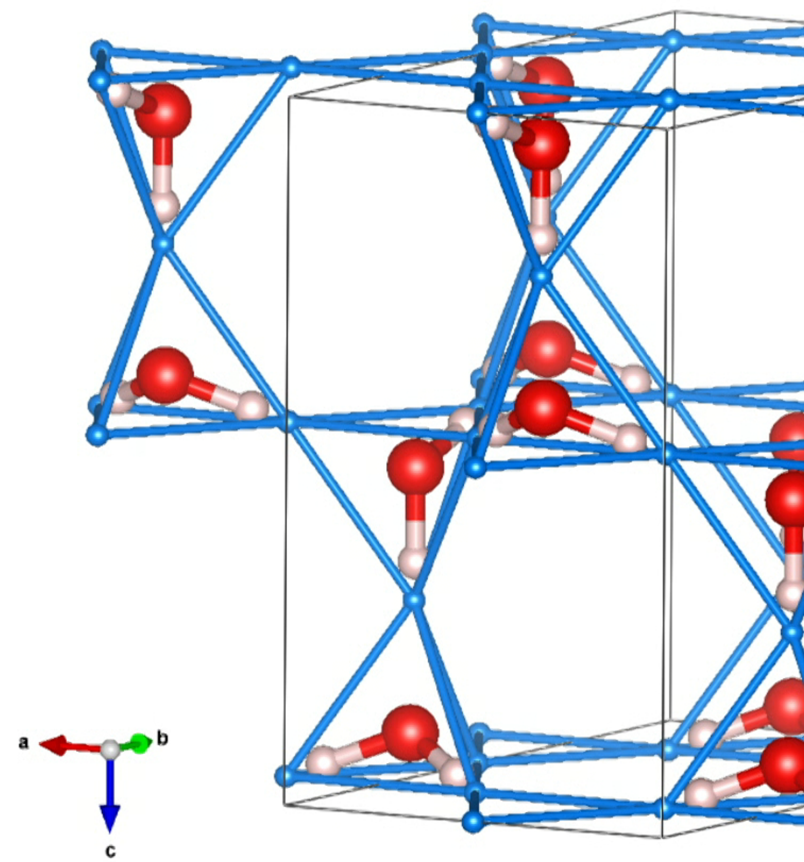
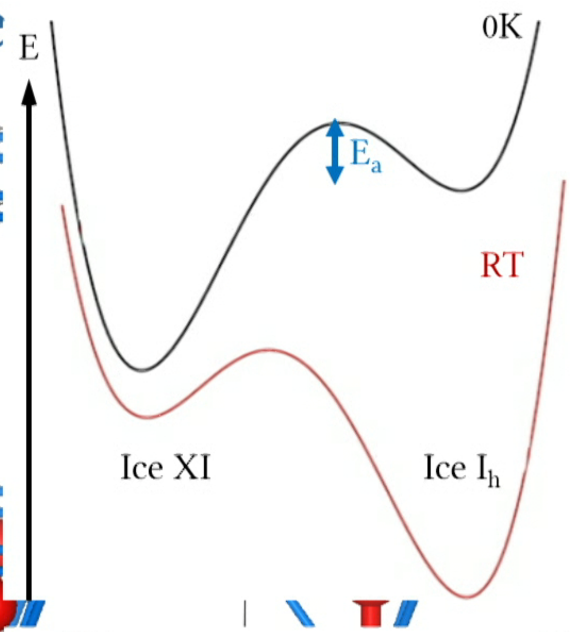
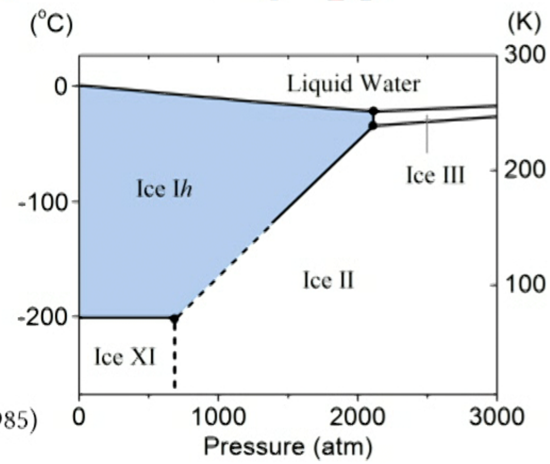
A.J. Leadbetter, et al. J. Chem. Phys. 82, 424 (1985)

Water Ice







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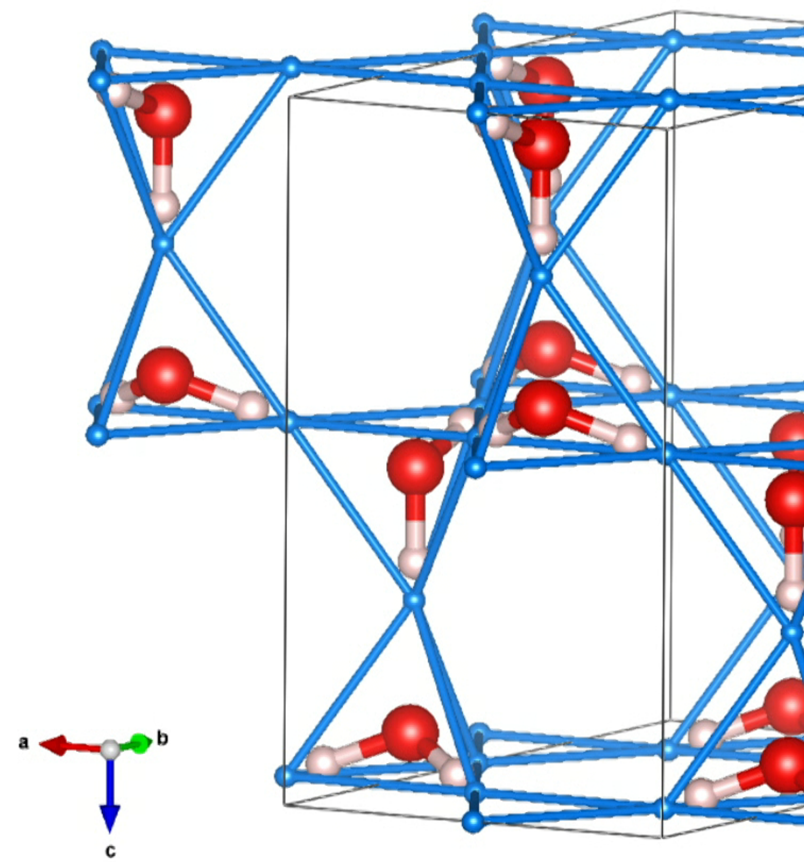

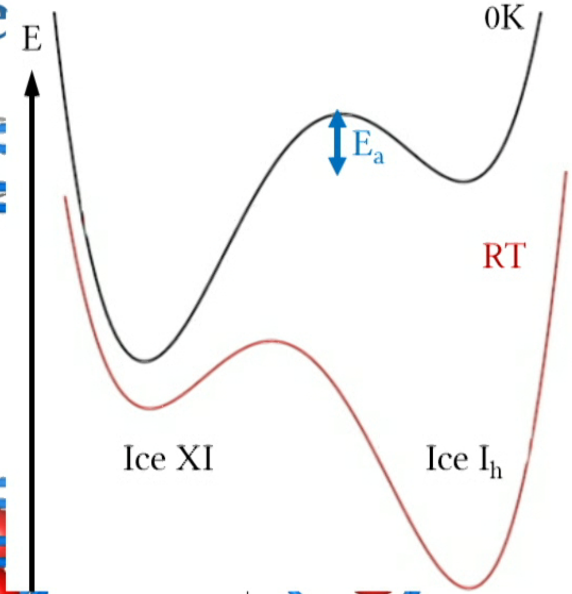

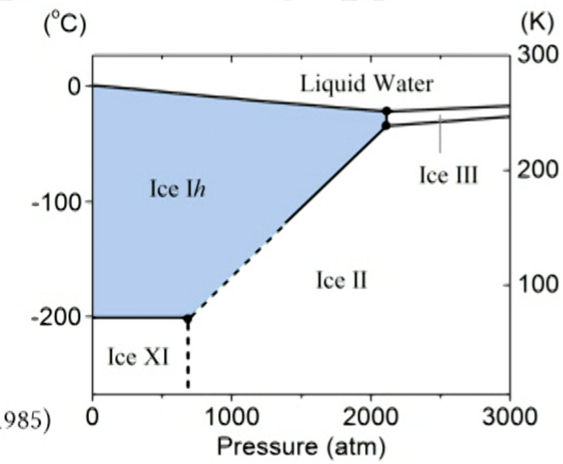

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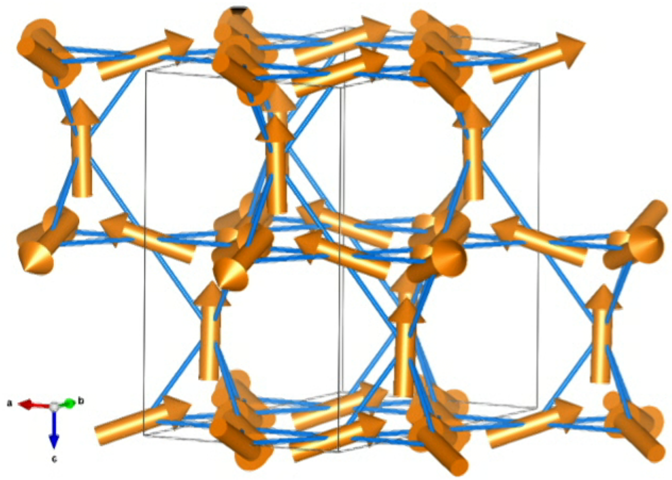
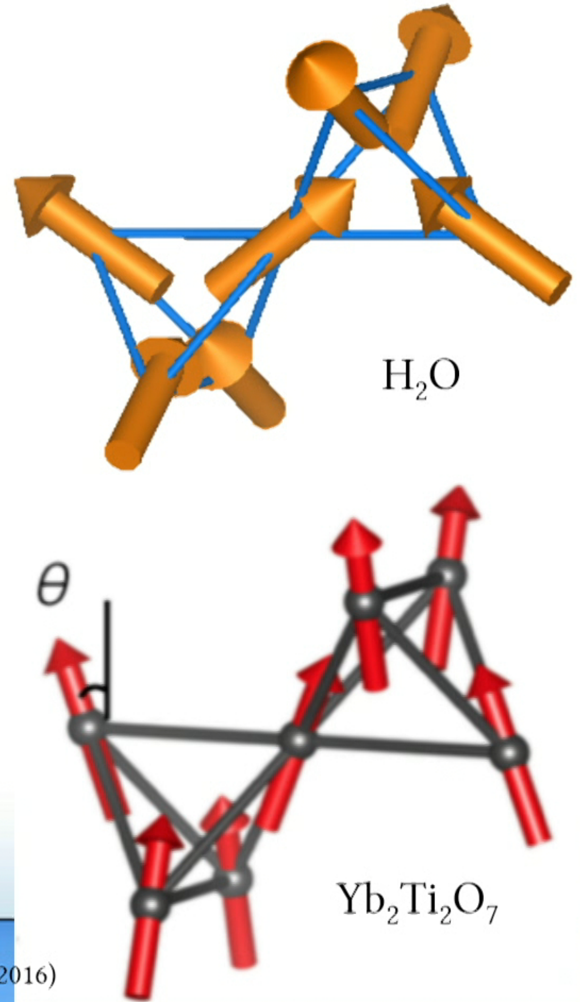
Water Ice to Quantum (?) Spin Ice





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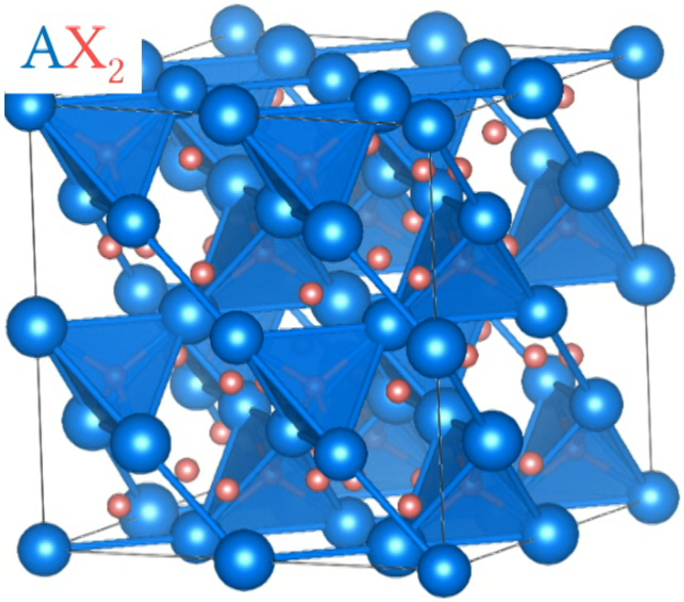
Fluorite, Pyrochlore, and Spinel



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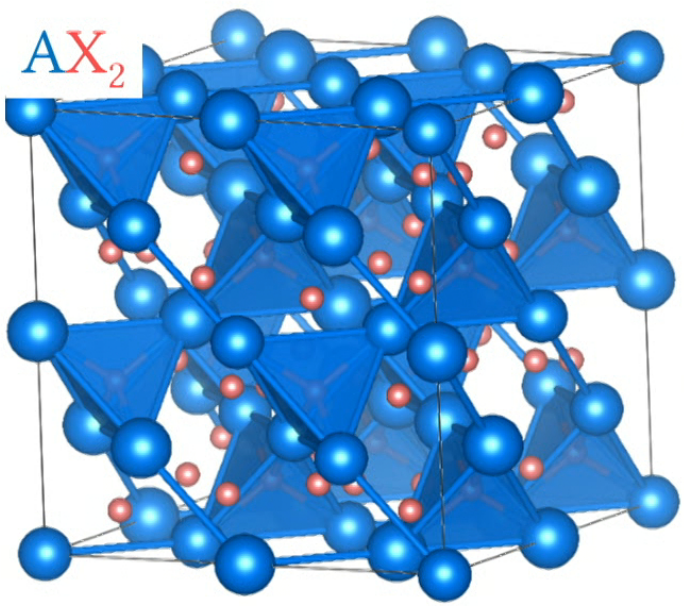

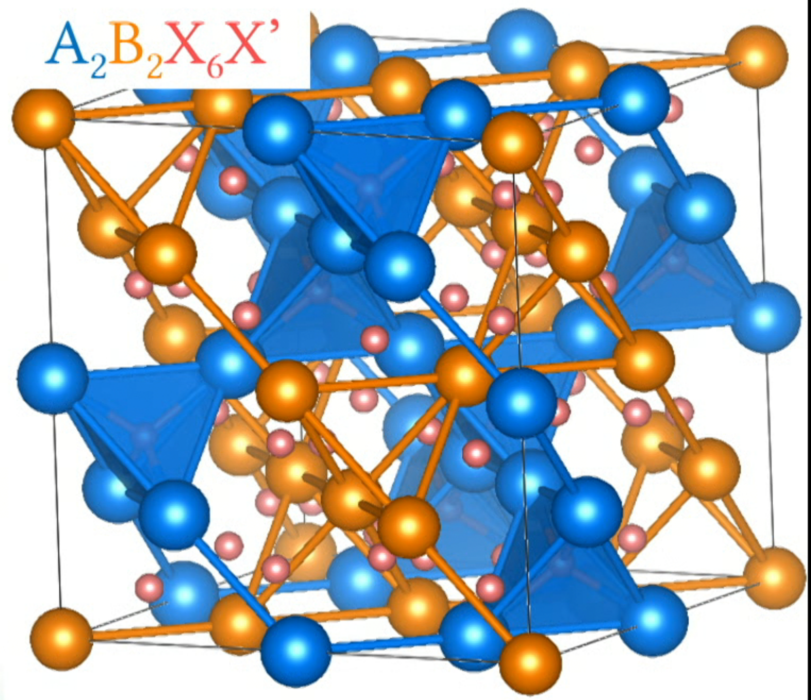

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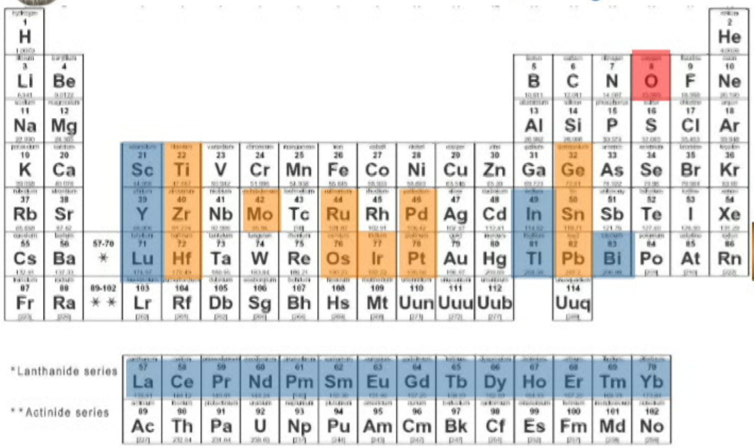

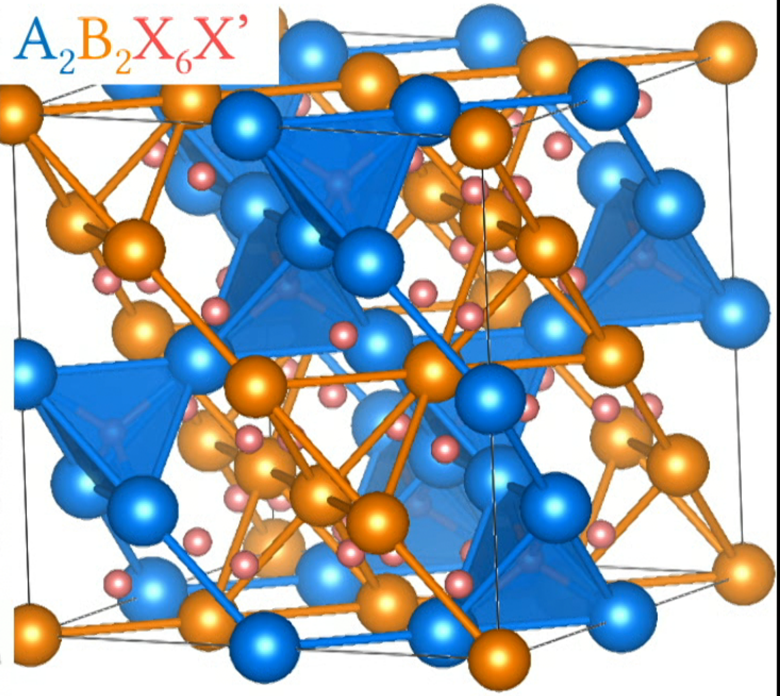

3. $A_2^{3+}B_2^{4+}O_7$ (3+,4+) PYROCHLORES

3.1. Existence and Stability Field

3.2. (3+,4+) Pyrochlores of 3d Transition Elements

3.3. (3+,4+) Pyrochlores of 4d Transition Elements

3.4. (3+,4+) Pyrochlores of 5d Transition Elements

3.5. (3+,4+) Pyrochlores of Nontransition Elements (Group IVA)

3.6. Substituted (3+,4+) Pyrochlores

3.7. Simultaneous Substitution at A and B sites in Pyrochlores

OXIDE PYROCHLORES — A REVIEW

M. A. Subramanian*, G. Aravamudan and G. V. Subba Rao
Materials Science Research Center, Indian Institute of Technology,
Madras 600 036, India

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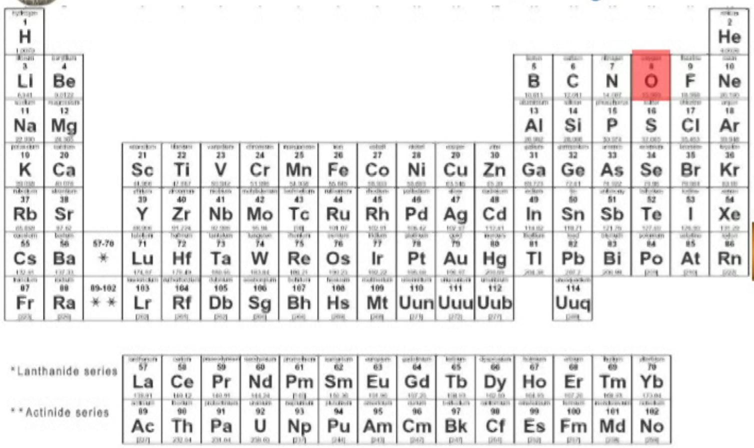

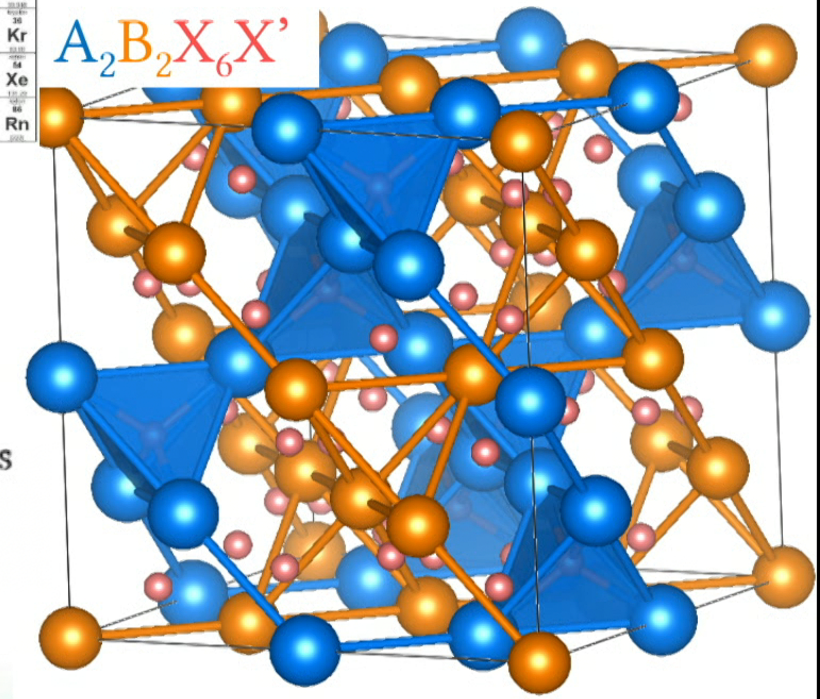

5. $A_2B_2O_6$ AND AB_2O_6 DEFECT PYROCHLORES

5.1. $A_2B_2O_6$ Pyrochlores

5.2. AB_2O_6 Pyrochlores

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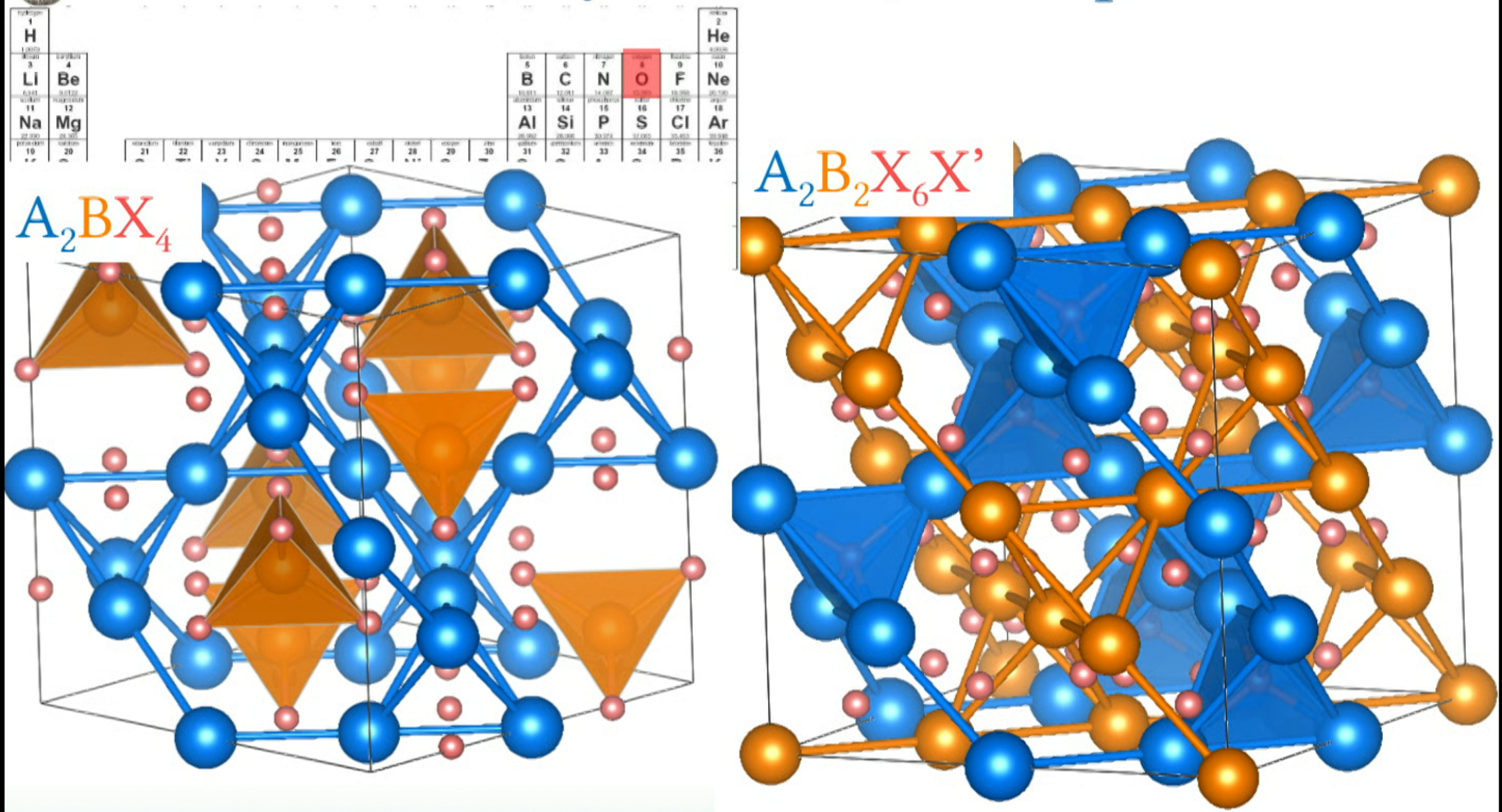

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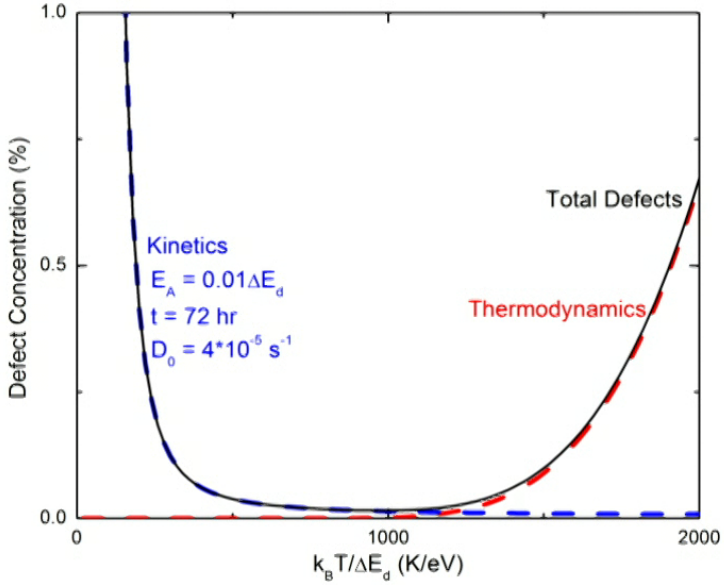
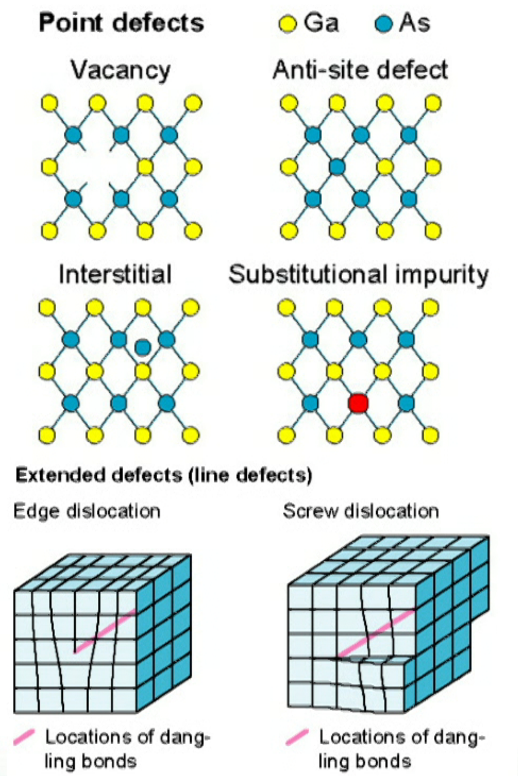
Defects Interlude





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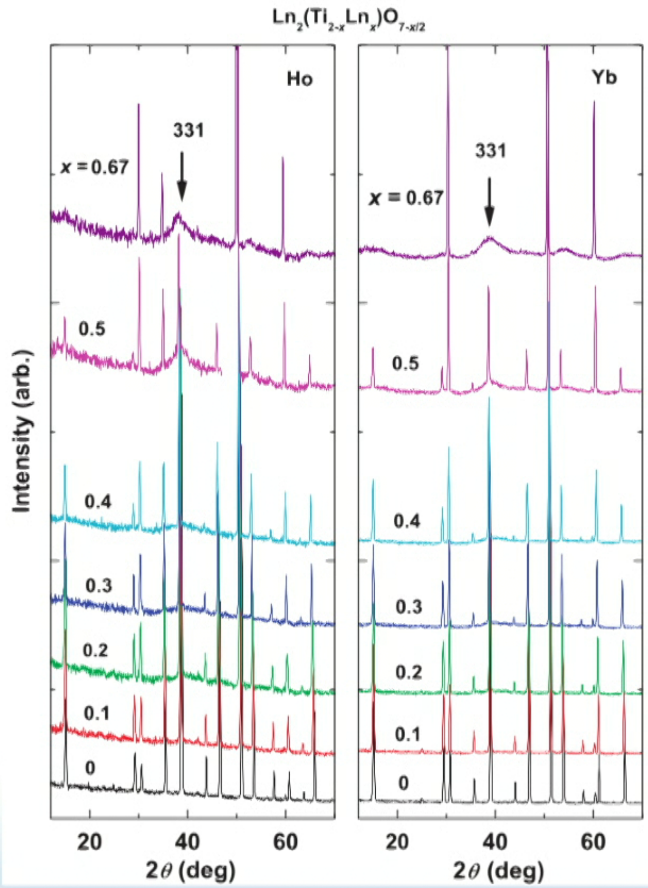
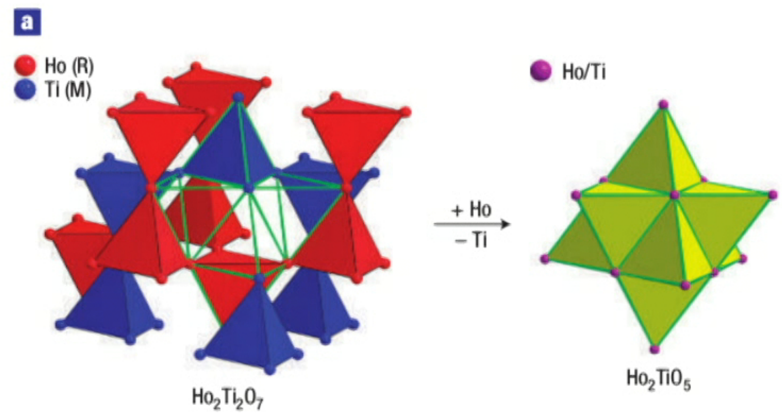
Pyrochlore Stoichiometry and 'Point' Defects





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G.C. Lau, et al. Nat. Phys. 2, 248-53 (2006)
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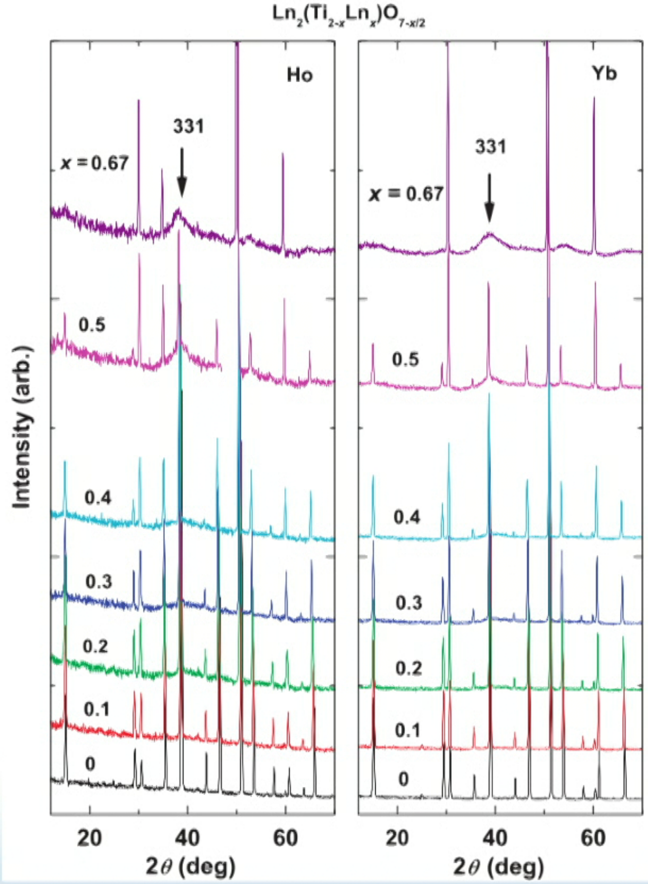
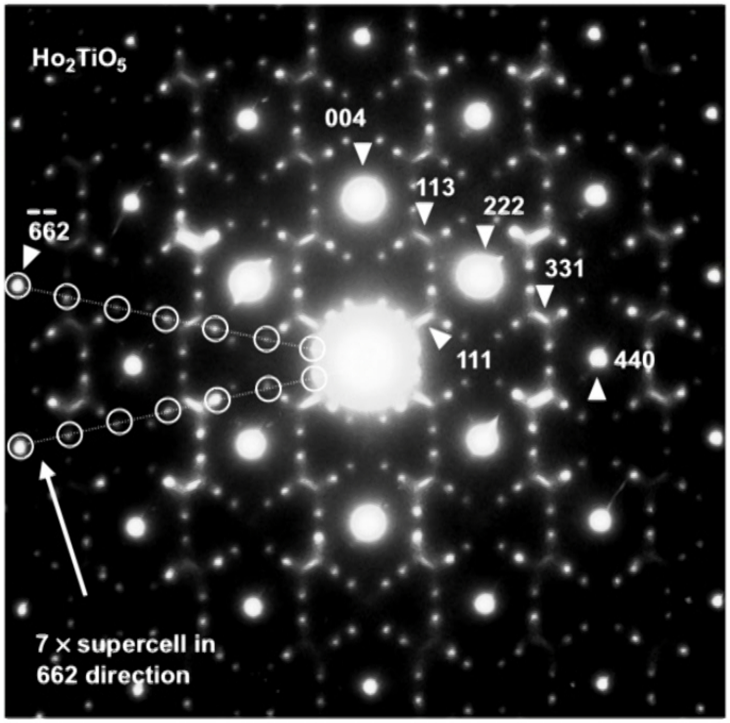
Pyrochlore Stoichiometry and 'Point' Defects





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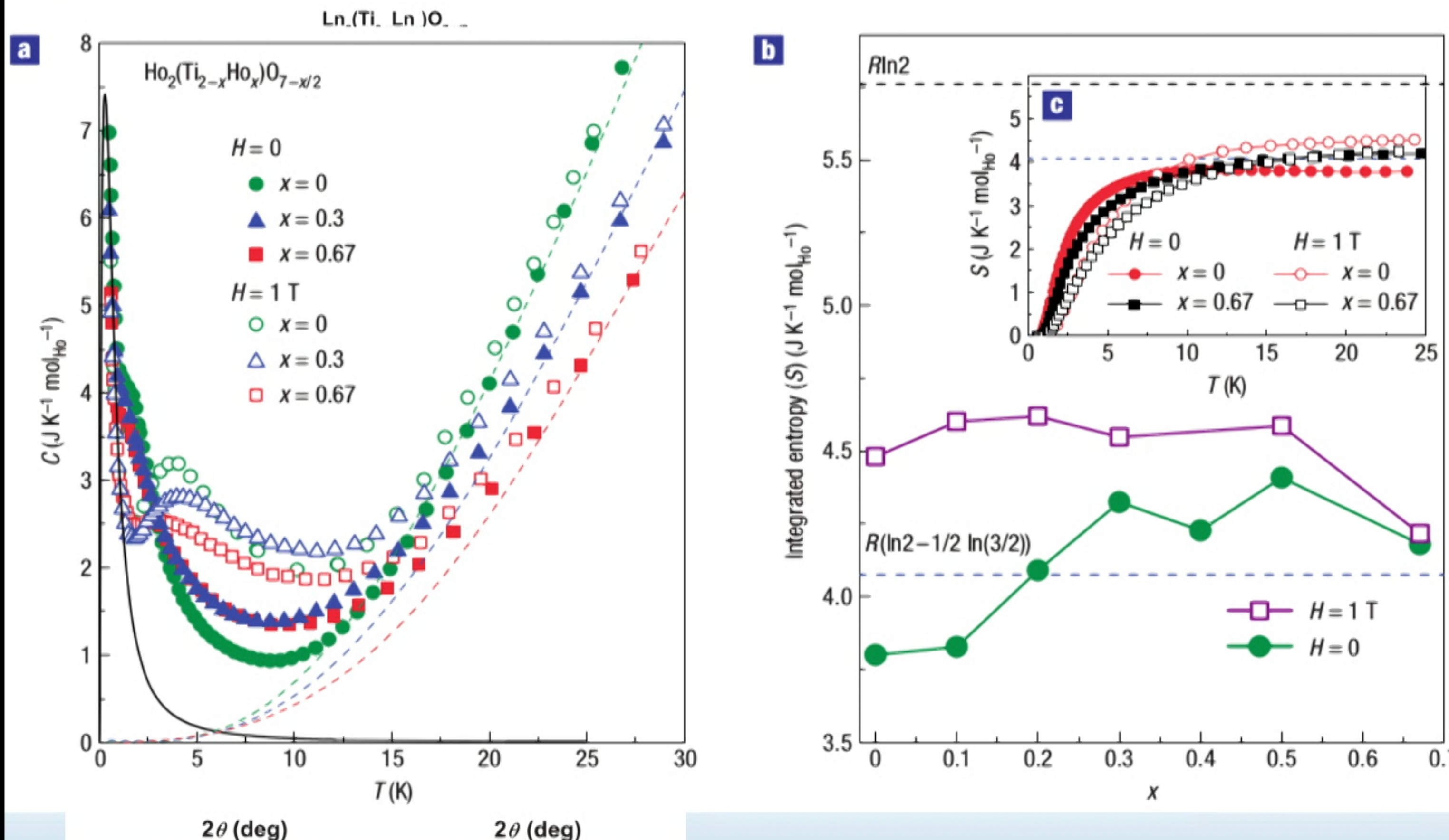

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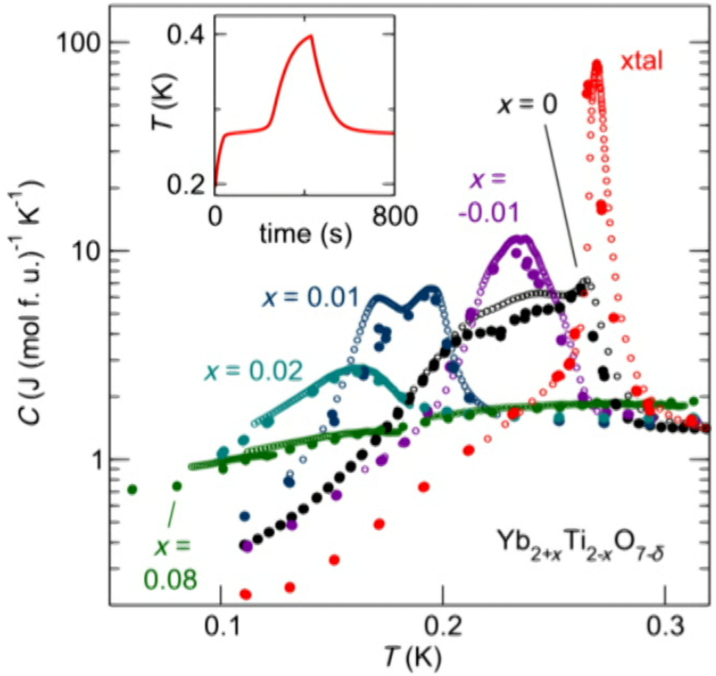
Off-Stoichiometry Continued



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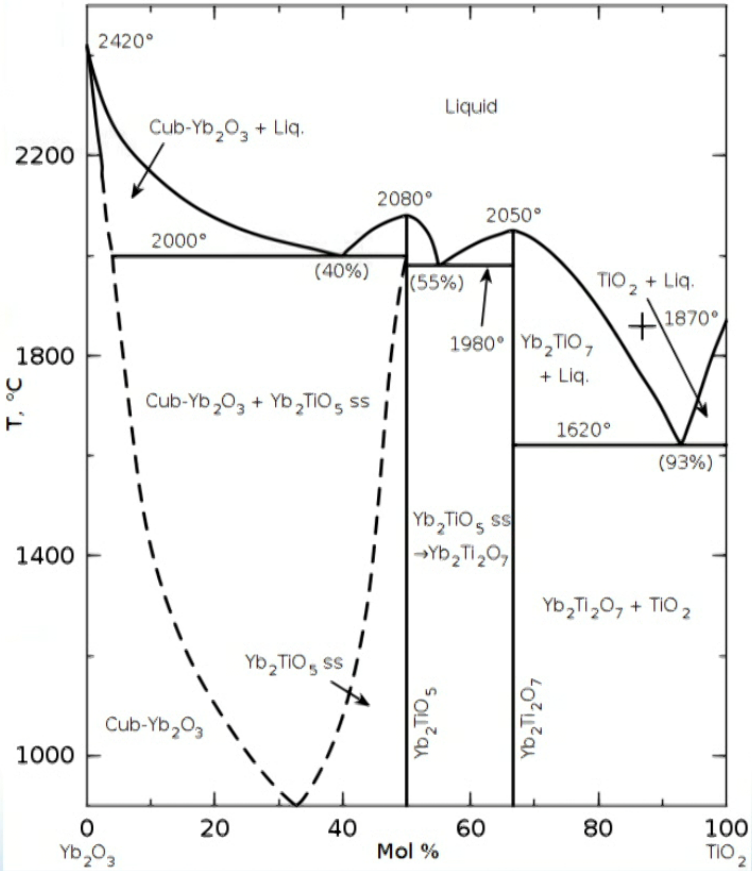
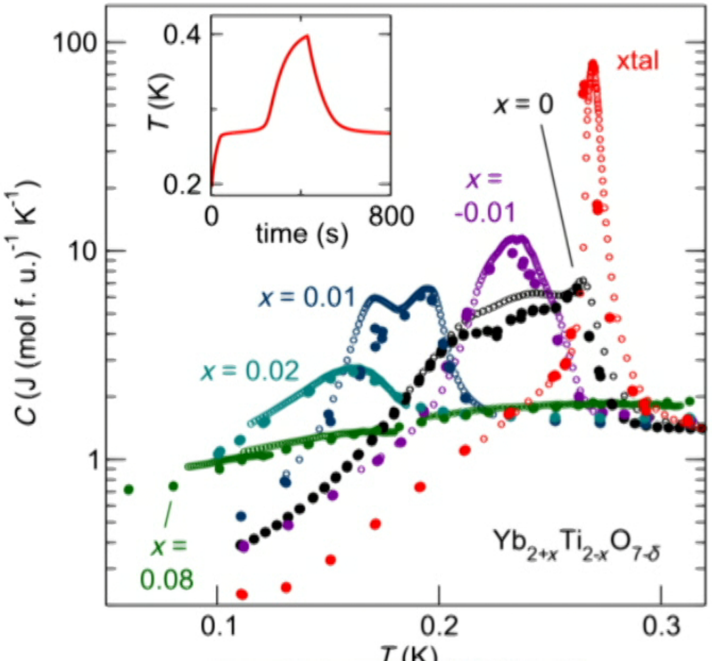
Off-Stoichiometry Continued





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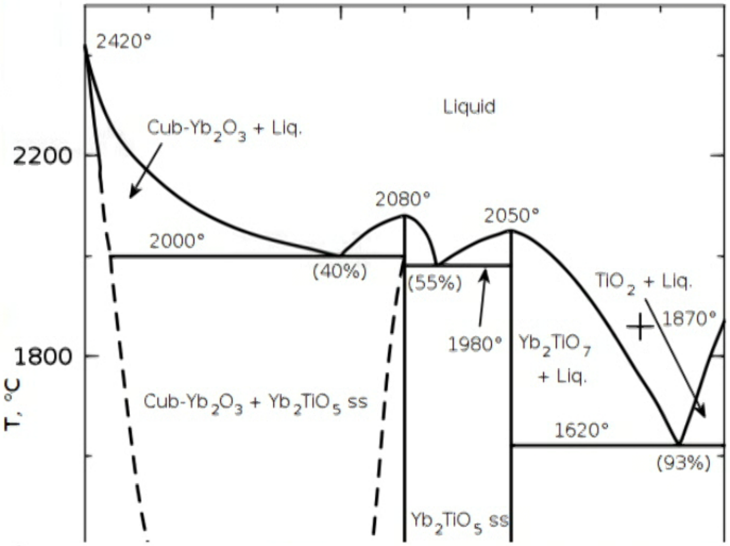
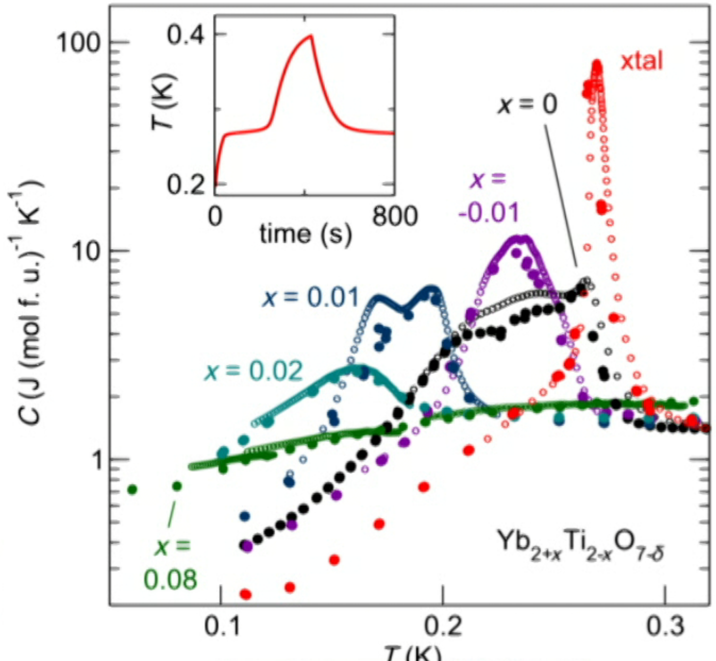
Off-Stoichiometry Continued





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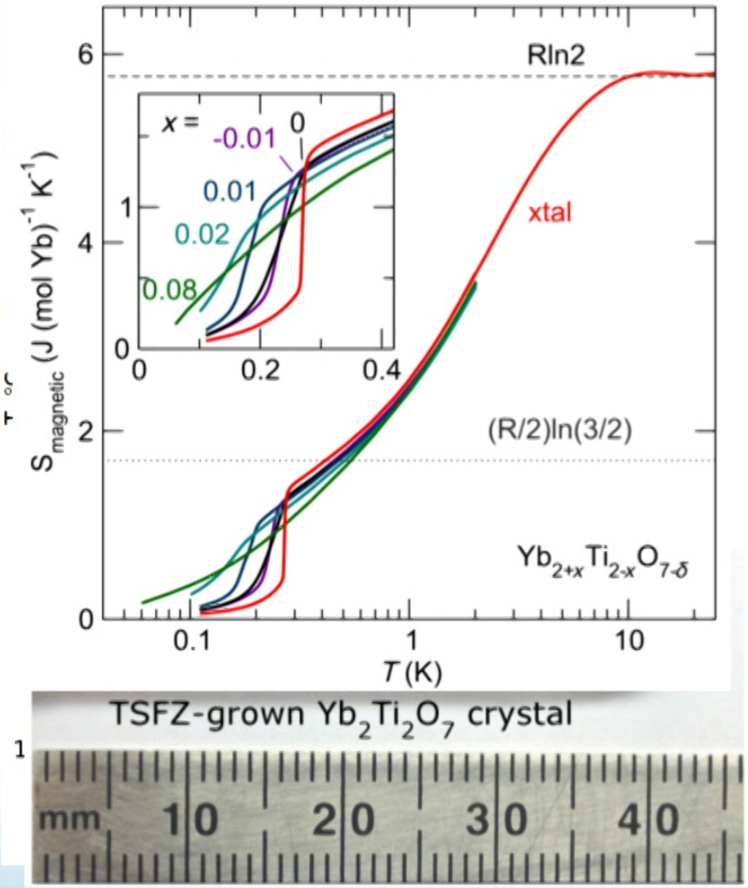

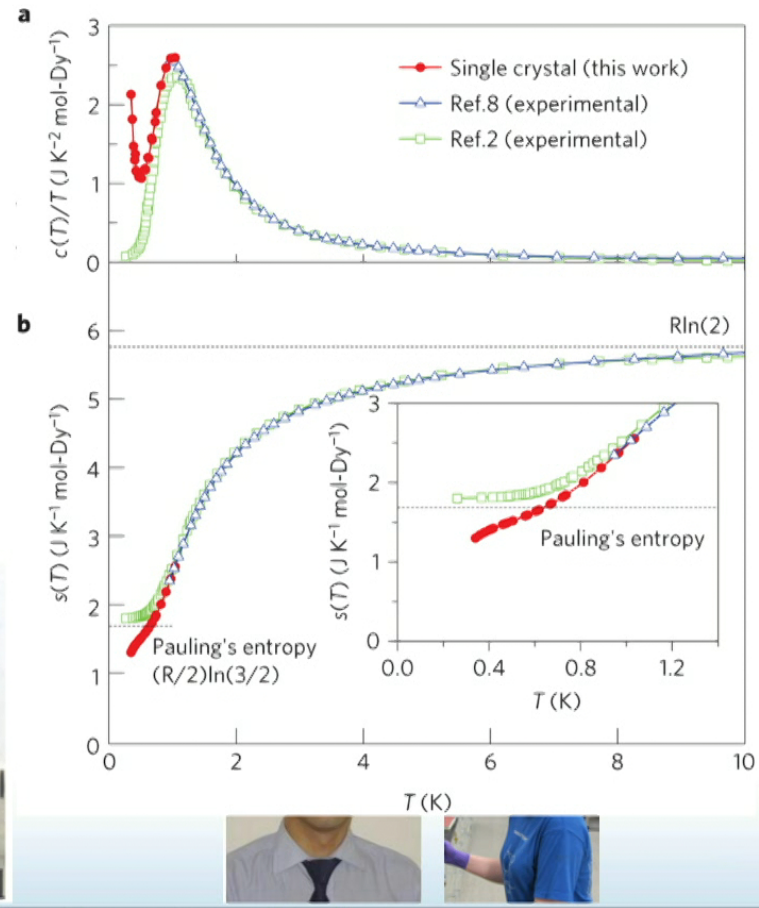

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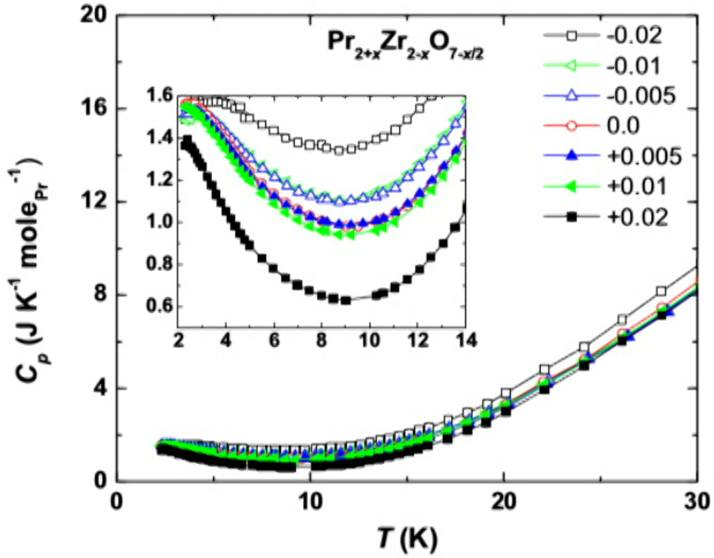
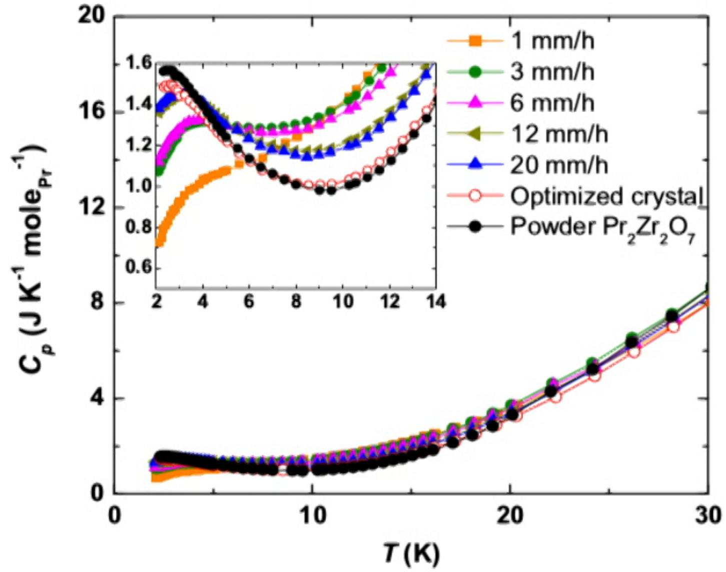
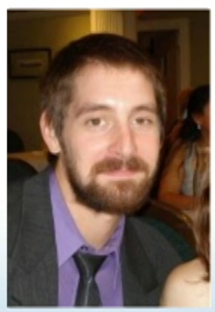
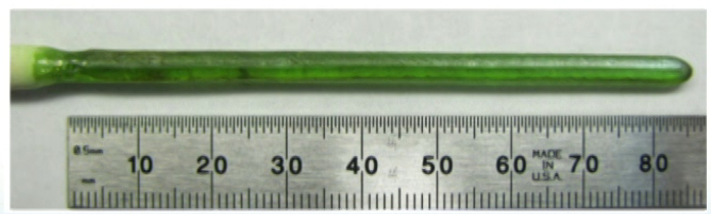
D. Pomaranski, et al. Nat. Phys. 9, 353-6 (2013)

Off-Stoichiometry Universality









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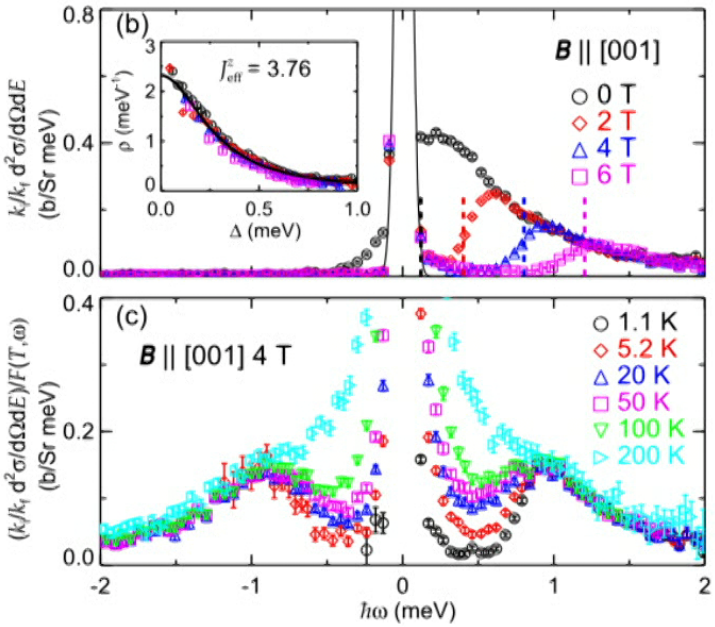
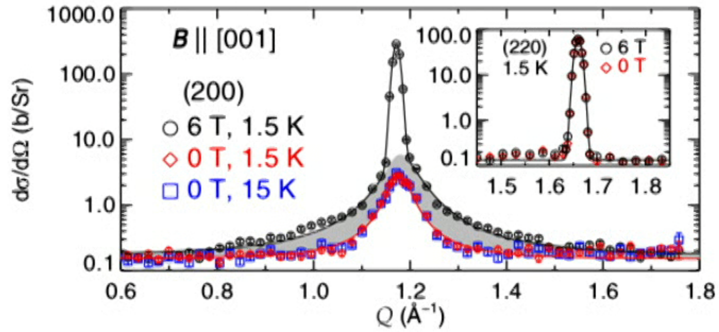
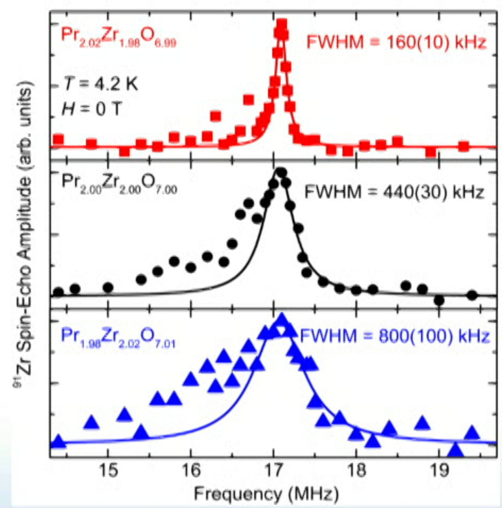
Off-Stoichiometry for Spin Liquids

$Pr_2Zr_2O_7$







See also $Tb_2Ti_2O_7$, etc.

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J.-J. Wen, et al. Phys. Rev. Lett. 118, 107206 (2017)
B.A. Trump, et al. Under Review (2017)

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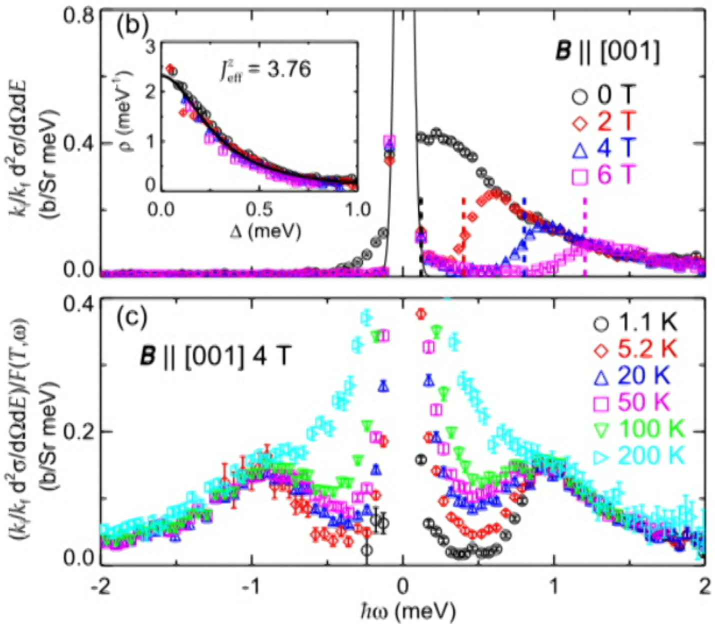

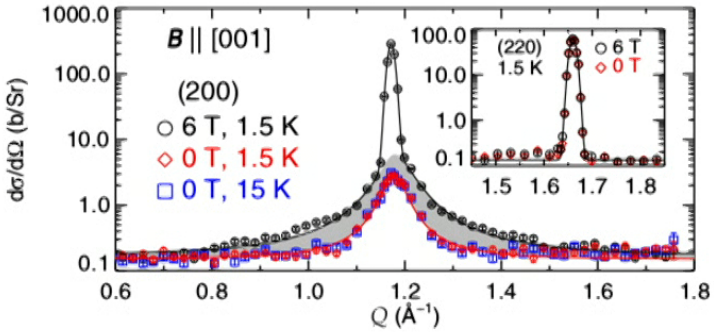

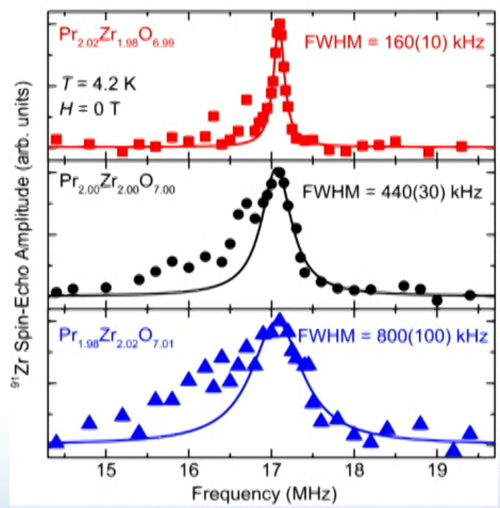

See also $Tb_2Ti_2O_7$, etc.

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J.-J. Wen, et al. Phys. Rev. Lett. 118, 107206 (2017)
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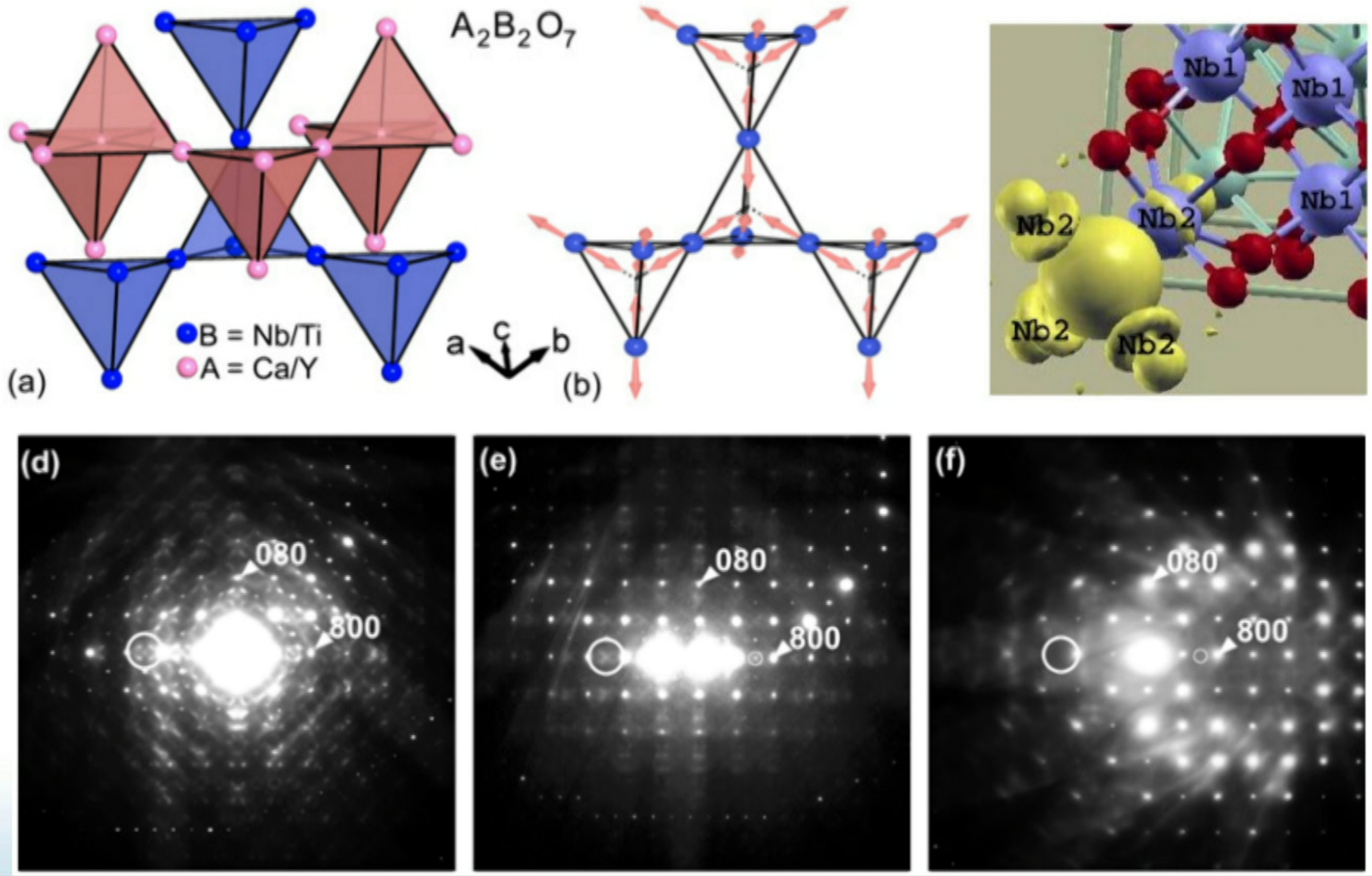
Spin Ice to Frustrated Ferroelectricity



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P. Blaha, et al. Phys. Rev. Lett. 93, 216403 (2004)
T.M. McQueen, et al. J. Phys.: Condens. Matter 20, 235210 (2008)

Here's What We Know So Far

- **Ice (and Spin-Ice) observed to have states with finite ground state degeneracy**
  - But in most (all?) cases, this is a kinetically trapped state
- **Disorder can help drive a system to a spin liquid state**
  - Or, at least, some kind of state with residual dynamics
- **Lots of evidence for local structures that are distinct from global (average/crystallographic) structures**
  - Drastic impact on the physics: why?
  - Strong composition dependence: why?

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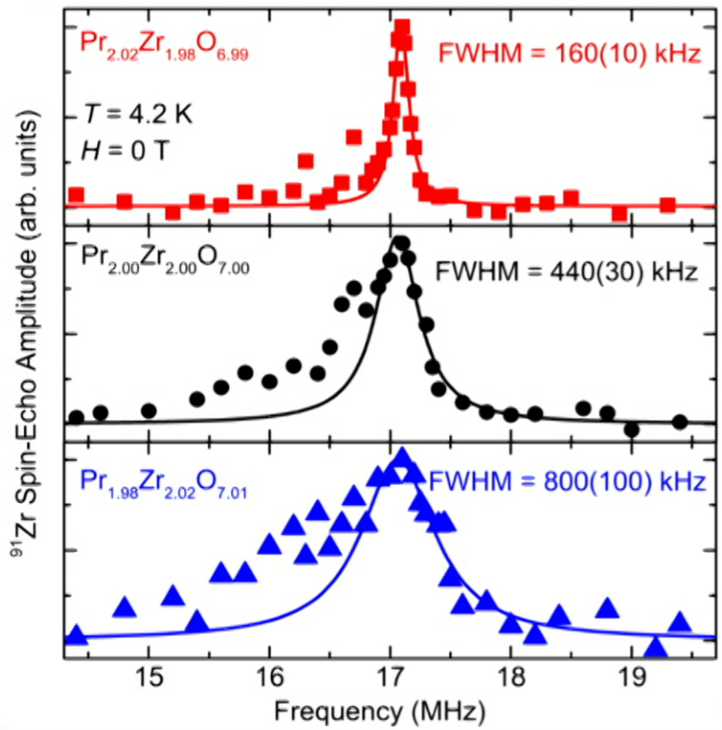
Universal Pyrochlore Flexibility



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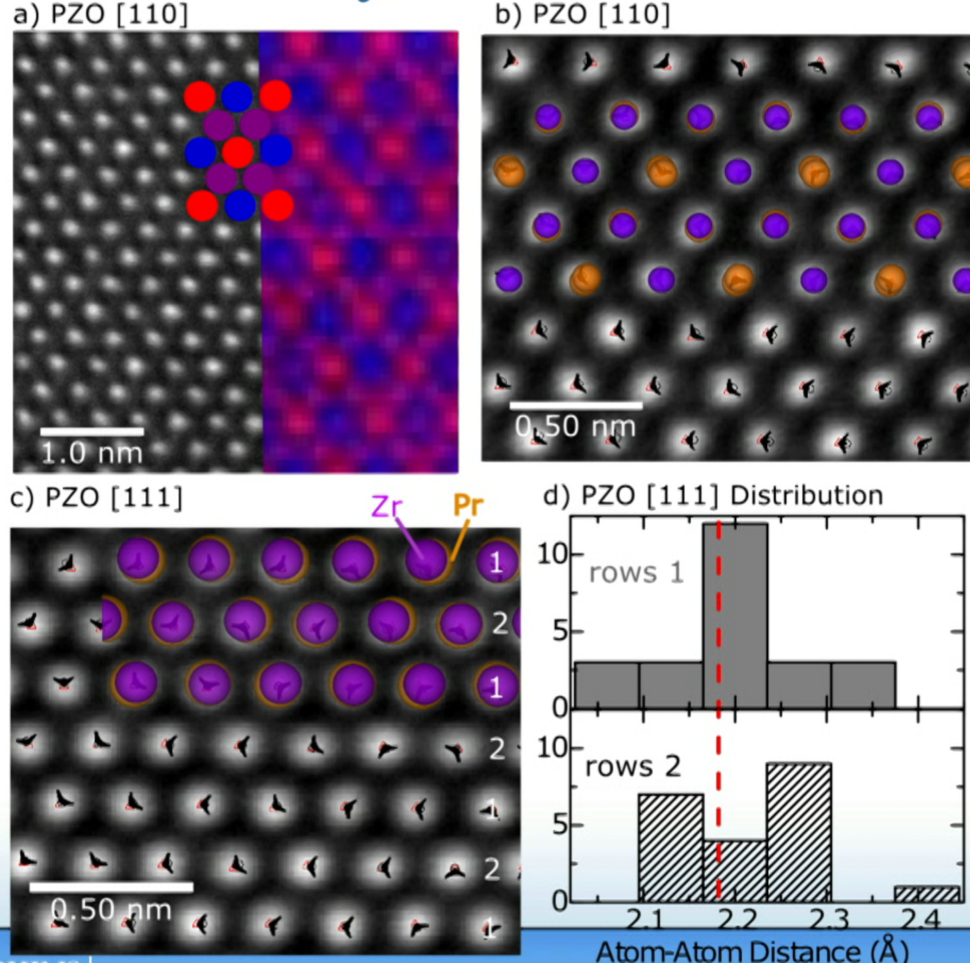

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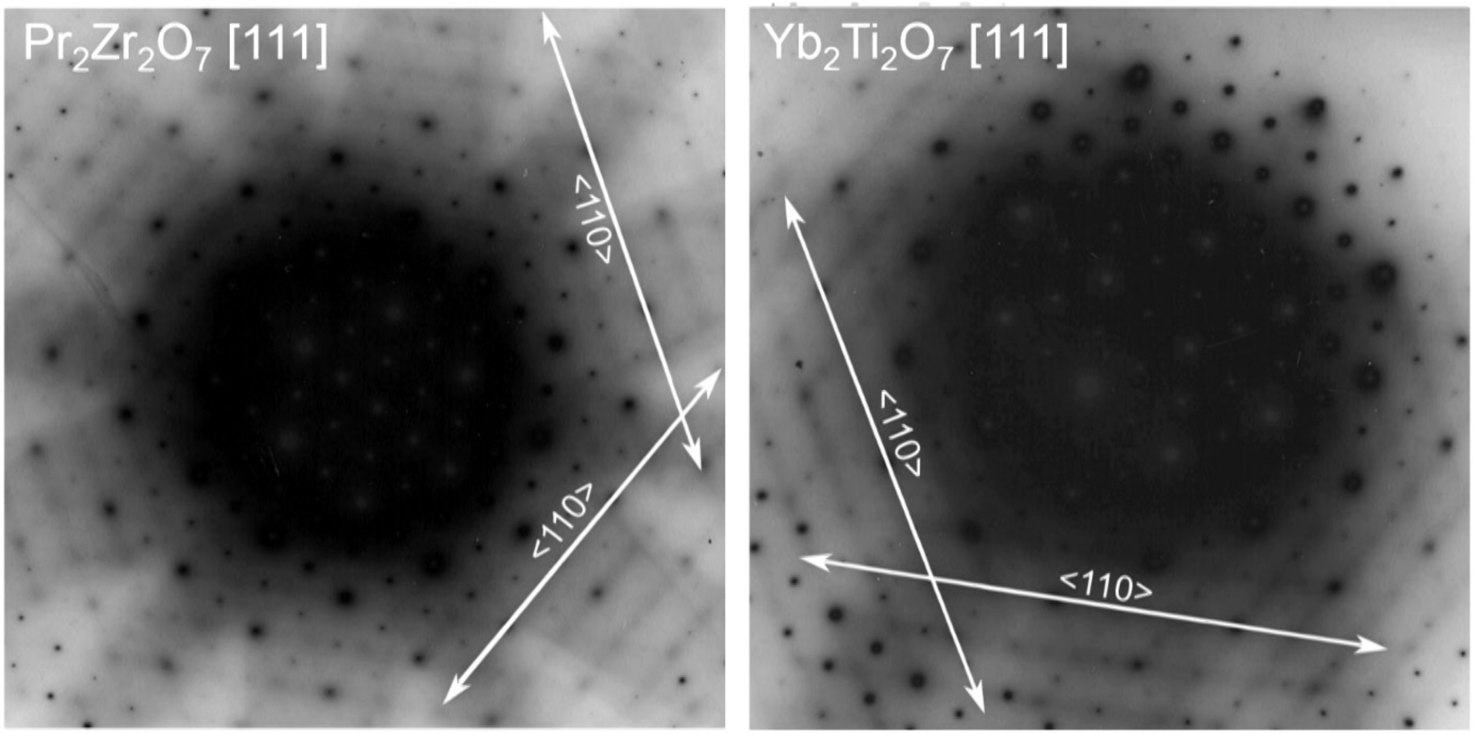
Universal Pyrochlore Flexibility



Also found in $La_2Zr_2O_7$, $Bi_2Ti_2O_7$, $Bi_2Ru_2O_7$, ...

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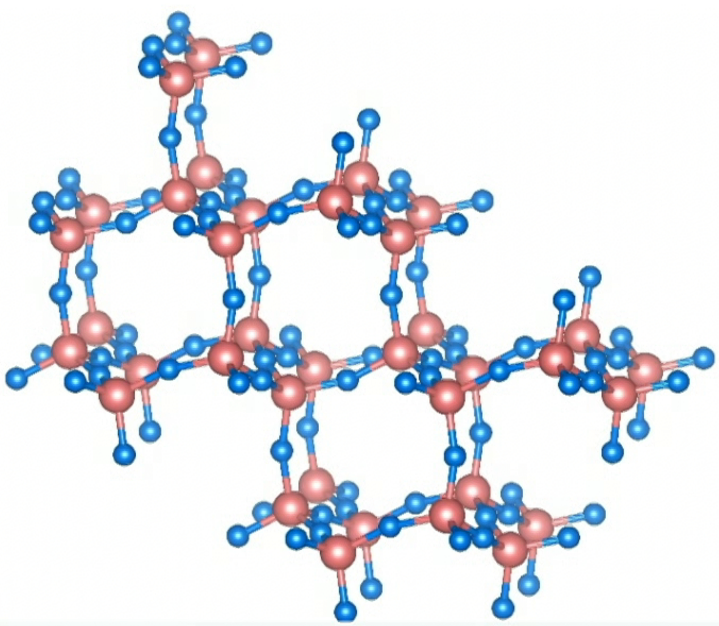
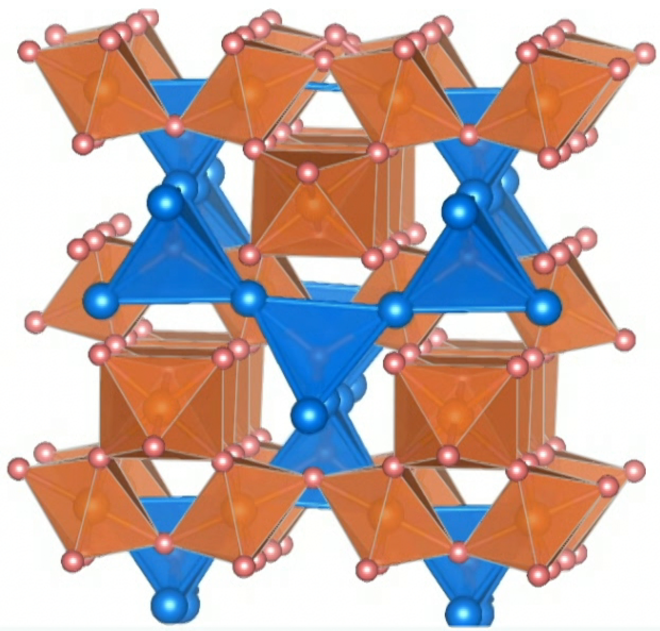
B.A. Trump, et al. Under Review (2017)

This is incipient ferroelectricity…

… just like β-SiO_2



$Pr_2Zr_2O_7$



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B.A. Trump, et al. Under Review (2017)

And means…

- **There are always low energy phonon dynamics**
  - Locally break site symmetry: at a minimum dynamically, but in many cases static (or fluctuating slower than 10's of ns)

Table 55. Character Table and Basis Functions for the Group D_{3d}

D_{3d}	E	$\bar{E}$	$2C_3$	$2\bar{C}_3$	$3C_2'$	$3\bar{C}_2'$	I	$\bar{I}$	$2S_6$	$2\bar{S}_6$	$3\sigma_d$	$3\bar{\sigma}_d$	Time Inv.	Bases
Γ_1^+	1	1	1	1	1	1	1	1	1	1	1	1	a	R
Γ_2^+	1	1	1	1	−1	−1	1	1	1	1	−1	−1	a	S_z
Γ_3^+	2	2	−1	−1	0	0	2	2	−1	−1	0	0	a	$(S_x - iS_y)$, $-(S_x + iS_y)$
Γ_1^-	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	a	zS_z
Γ_2^-	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	a	z
Γ_3^-	2	2	−1	−1	0	0	−2	−2	1	1	0	0	a	$(x - iy)$, $-(x + iy)$
Γ_4^+	2	−2	1	−1	0	0	2	−2	1	−1	0	0	c	$\phi(1/2,-1/2)$, $\phi(1/2,1/2)$
Γ_5^+	1	−1	−1	1	i	−i	1	−1	−1	1	i	−i	b	$\phi(3/2,-3/2)$ $-i\phi(3/2,3/2)$
Γ_6^+	1	−1	−1	1	−i	i	1	−1	−1	1	−i	i	b	$-(\phi(3/2,3/2)$ $-i\phi(3/2,-3/2))$
Γ_4^-	2	−2	1	−1	0	0	−2	2	−1	1	0	0	c	$\Gamma_4^+ \times \Gamma_1^-$
Γ_5^-	1	−1	−1	1	i	−i	−1	1	1	−1	−i	i	b	$\Gamma_5^+ \times \Gamma_1^-$
Γ_6^-	1	−1	−1	1	−i	i	−1	1	1	−1	i	−i	b	$\Gamma_6^+ \times \Gamma_1^-$

C_1	E	$\bar{E}$	Time Inv.
Γ_1	1	1	a
Γ_2	1	−1	a

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And means…

- **There are always low energy phonon dynamics**
  - Locally break site symmetry: at a minimum dynamically, but in many cases static (or fluctuating slower than 10's of ns)
- **Across same energy scales as CEF and magnetic interactions**
- **Even 'low' concentrations of defects can radically modulate this structural flexibility (pinning, domain generation, etc.)**

- **In other words, not negligible, and must be considered, always**
  - Is this how $Pr_2Zr_2O_7$ becomes a spin liquid, and can be tuned with small compositional changes?

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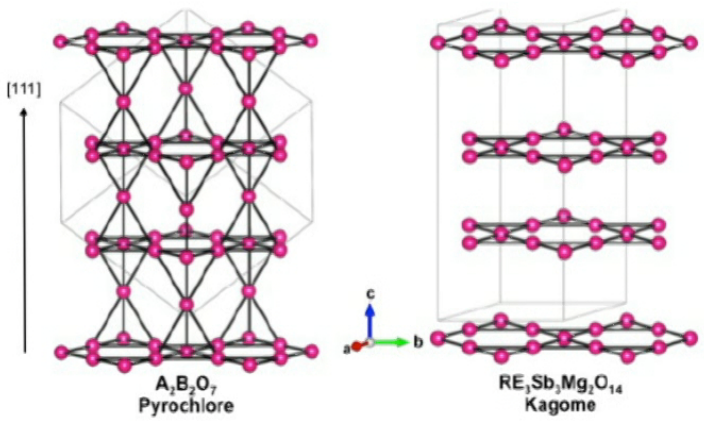
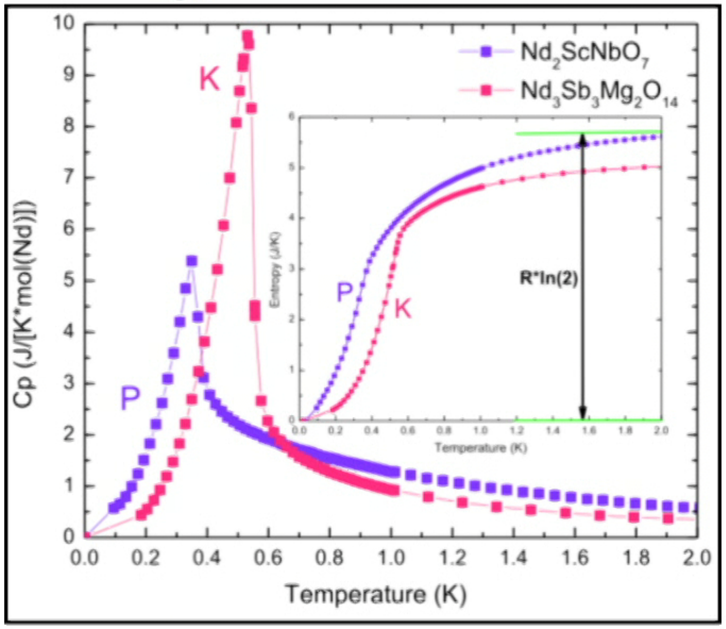
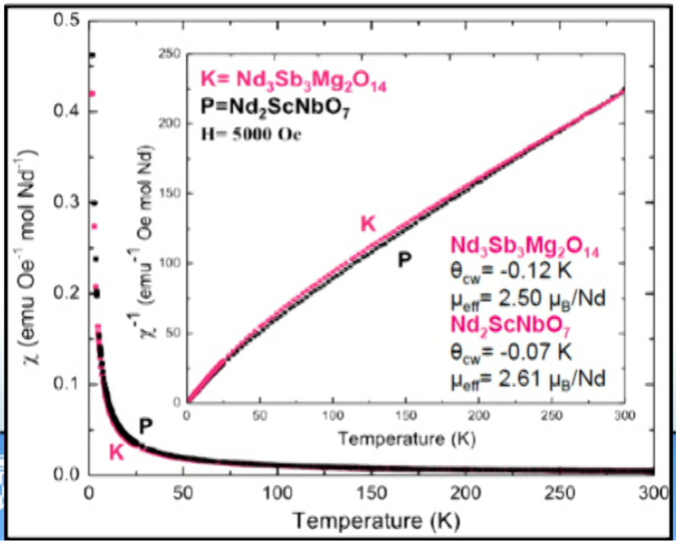
Pyrochlore to Kagomé





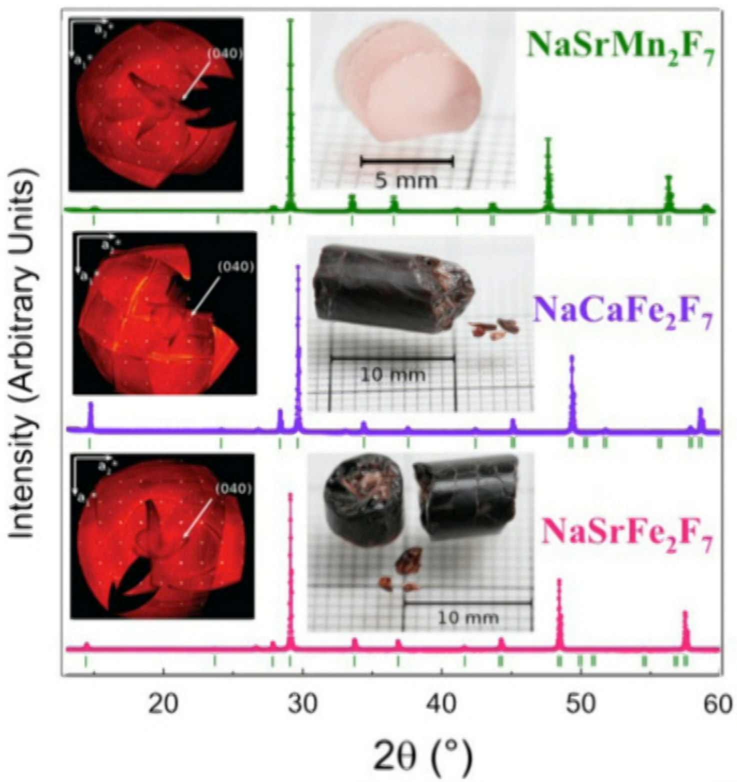


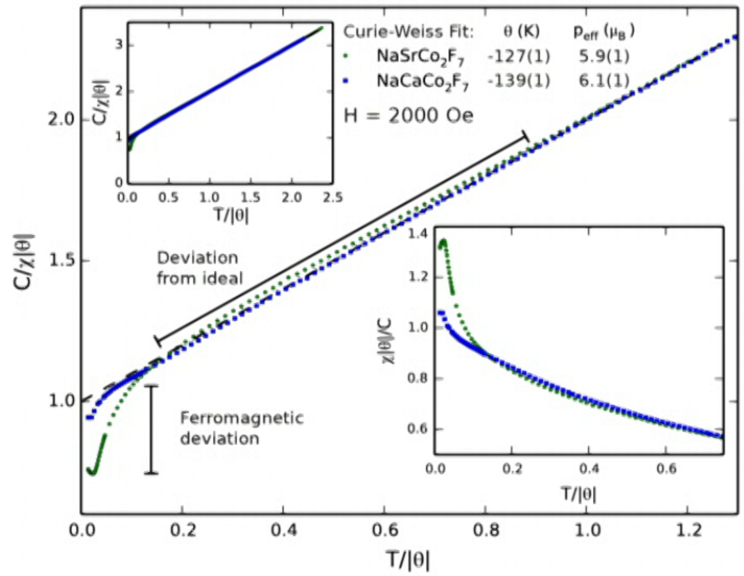
INSTITUTE FOR QUANTUM MATTER

A collaboration between JOHNS HOPKINS UNIVERSITY and PRINCETON UNIVERSITY

M. Sanders, R.J. Cava, et al. Phys. Rev. B 93, 180407 (2016)

Magnetic Transition Metal Pyrochlores





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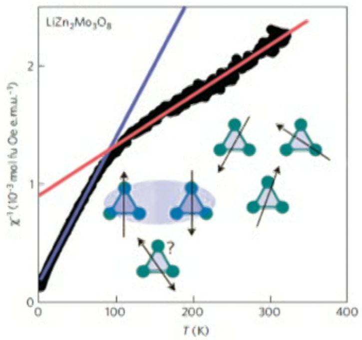
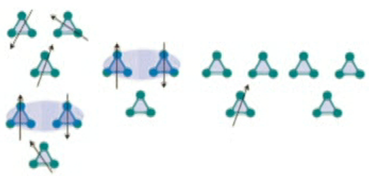
J. Krizan, R.J. Cava, et al. J. Phys.: Condens. Matter 29, 045801 (2017)

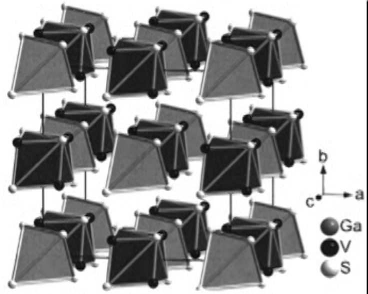
Cluster Magnet Phenomenology

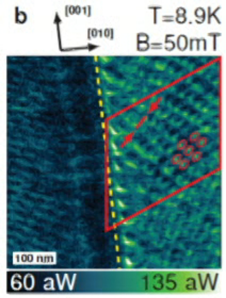




$LiZn_2Mo_3O_8$:
Valence bonds in
Triangles of Triangles

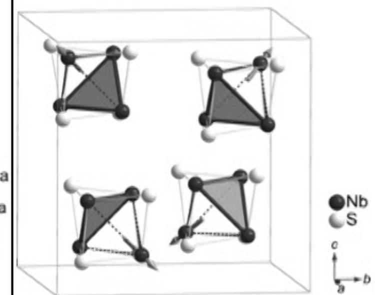
Sheckelton, et al.
Nat. Mater. 11,493-6 (2012)
Mater. Horiz. 2, 76-80 (2015)

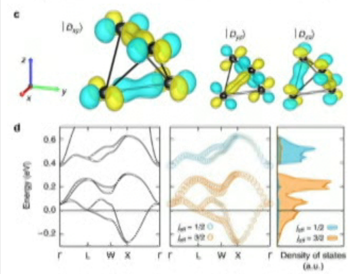




GaV_4S_8 ($1e^-/V_4$):
Ferromagnetic
Semiconductor
Skyrmions?

Pocha, et al. Chem. Mater.
12, 2882-7 (2000)
arXiv:1502.08049



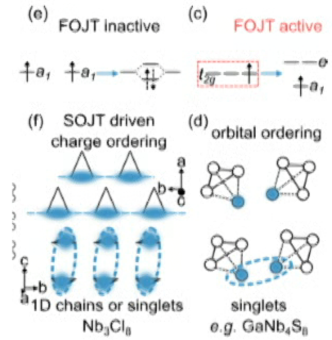


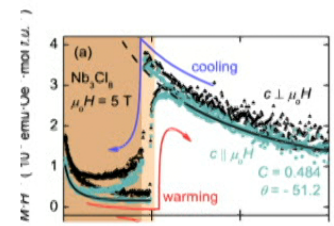
$Ga(Nb/Ta)_4(S/Se)_8$
($1e^-/(Nb/Ta)_4$):
Dimer Singlets?

Jakob, et al. J. Mater. Chem.
17, 3833-8 (2007)

$J_{eff} = \frac{1}{2}$ spin orbital?

Kim, et al. Nater. Comm.
5, 3988 (2014)





Nb_3Cl_8 ($1e^-/Nb_3$):
Avoiding
frustration via
Rearrangement of
VDW stacking

Sheckelton, et al.
doi:10.1039/C6QI00470A (2017)

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To find something new… look in new places!