Structural disorder and magnetic properties of geometrically frustrated magnets

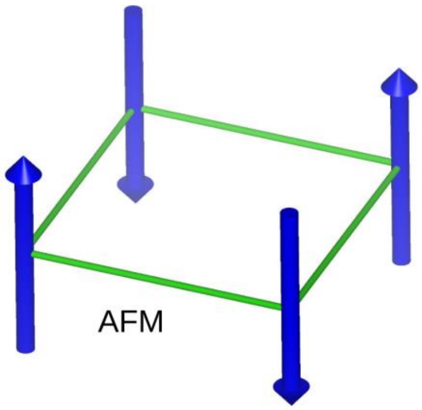
Rafael Sá de Freitas

Dep. Física dos Materiais e Mecânica

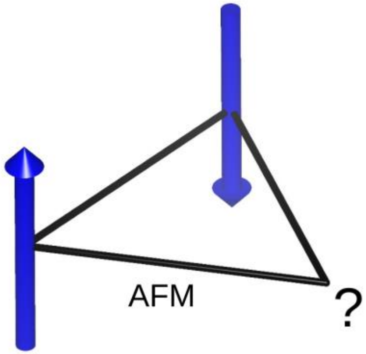
IF - USP

Magnetic Frustration

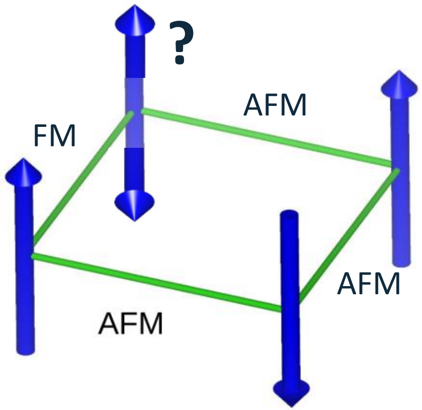
No Frustration



Geometrical Frustration

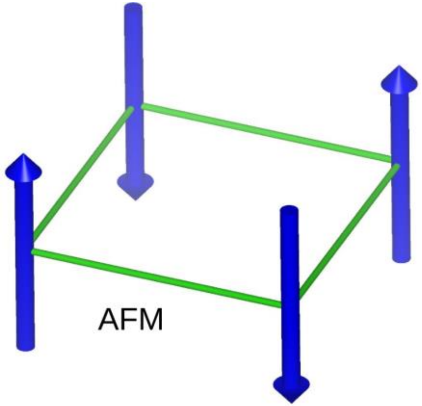


Bond Frustration

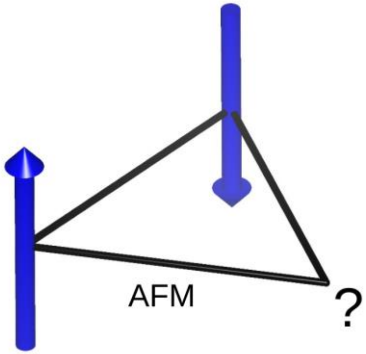


Magnetic Frustration

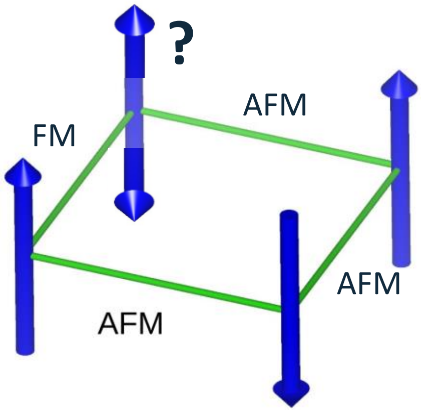
No Frustration



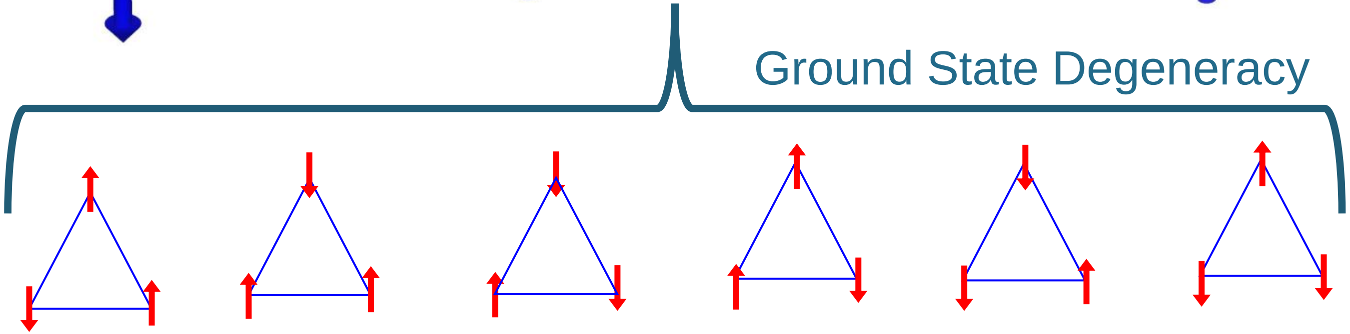
Geometrical Frustration



Bond Frustration

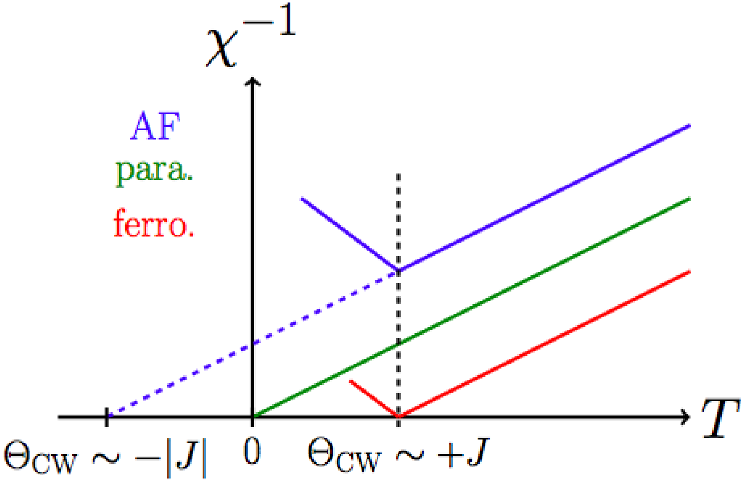


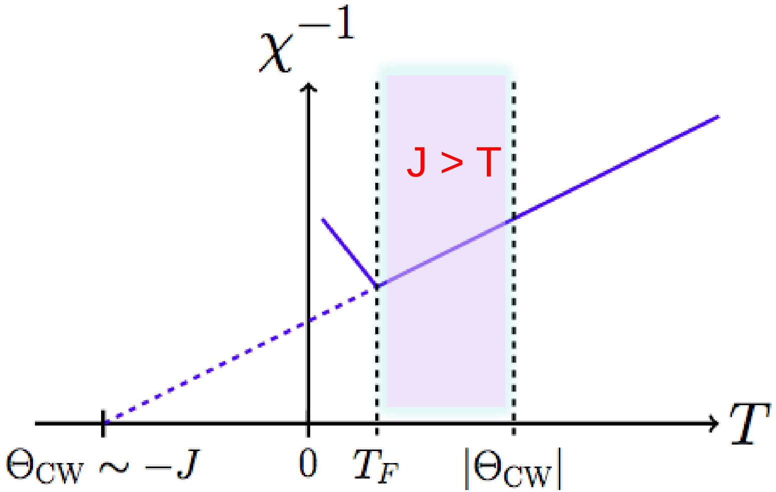
Ground State Degeneracy



Magnetic Frustration

Curie-Weiss Law: $\chi^{-1} = \frac{T - \Theta_{CW}}{C}$, $T >> \Theta_{CW}$

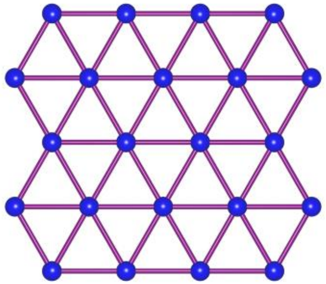




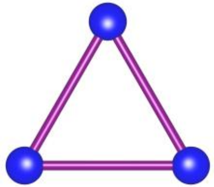
No Frustration → LRO at Θ_{CW}

Frustration index: $f = |\Theta_{CW}| / T_F$

Frustrated Lattices

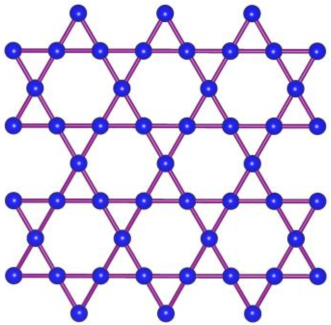


Triangular

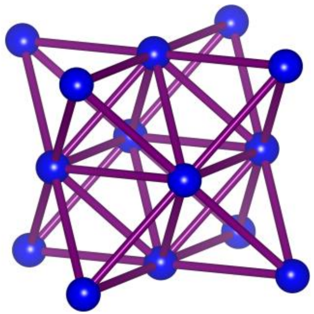


2D Unit

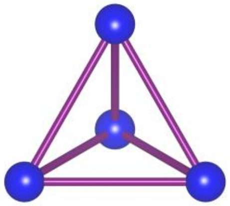
Kagome



Edge-Sharing



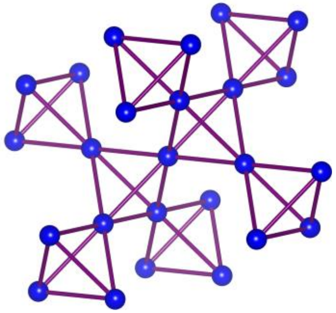
FCC



3D Unit

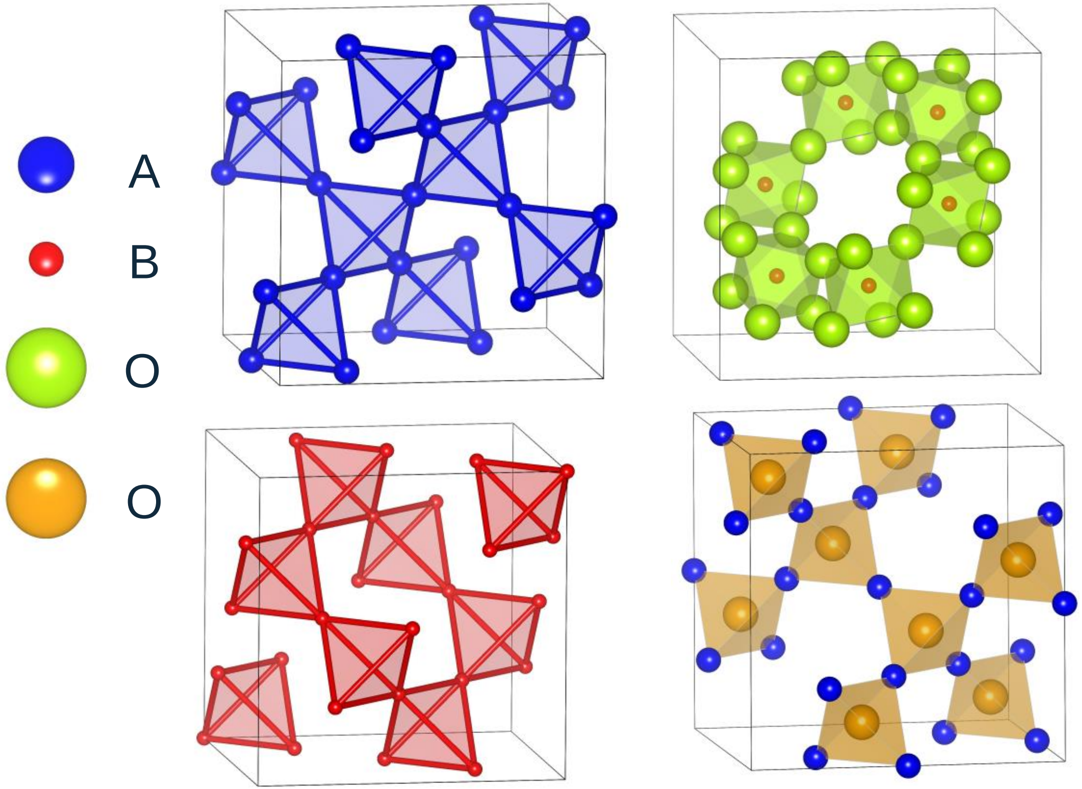
Vertex-Sharing

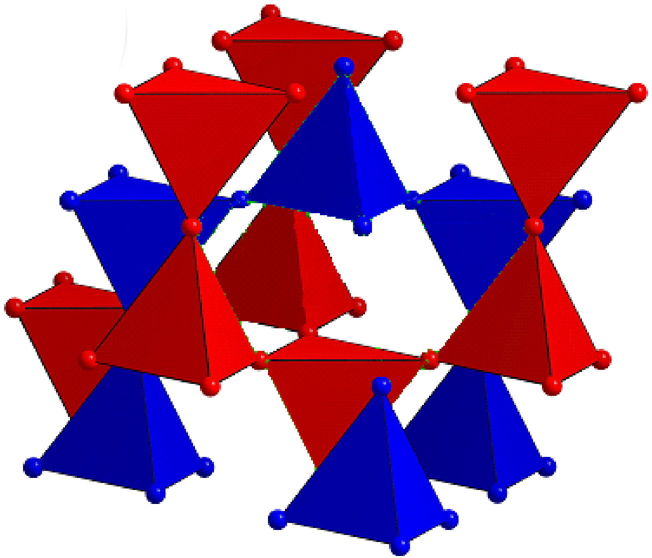
Pyrochlore



Pyrochlore Lattice

$A_2B_2O_7$





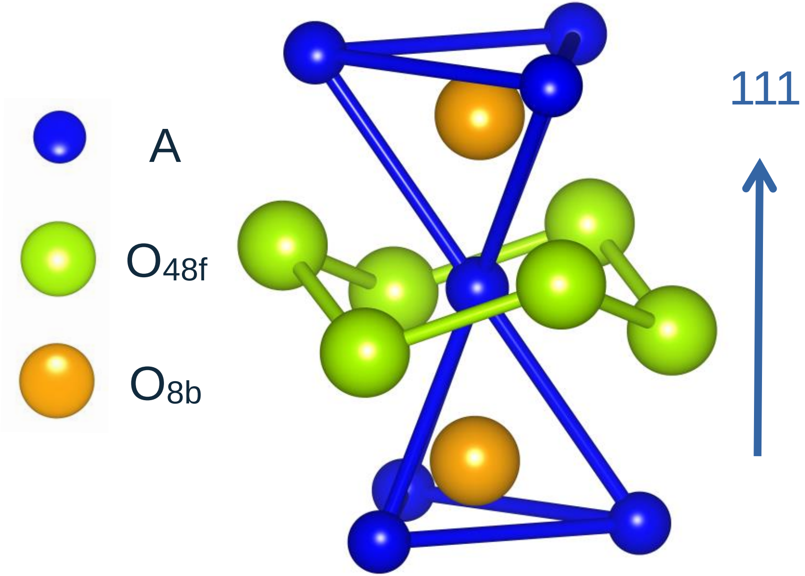
Pyrochlore Oxides

$A_2B_2O_7$

Pyrochlore Oxides

$A_2B_2O_7$

Pyrochlore Magnetism



$A_2Ti_2O_7$

CEF ANISOTROPY

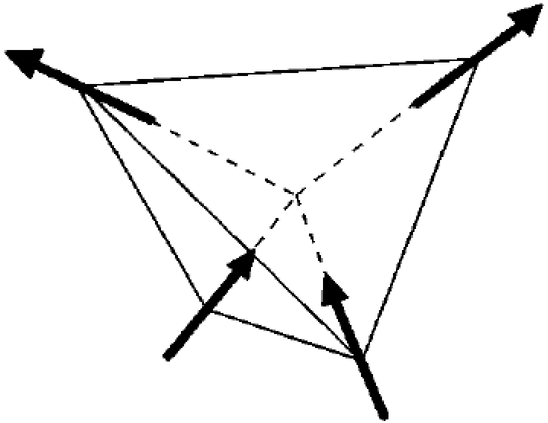
$$\begin{aligned} \text{Gd} &\longrightarrow \text{isotropic (Heisenberg)} \\ \text{Tb, Ho, Dy} &\longrightarrow \text{easy-axis (Ising)} \\ \text{Er, Yb} &\longrightarrow \text{easy-plane (xy)} \end{aligned}$$

Spin Ice

Strong Anisotropy

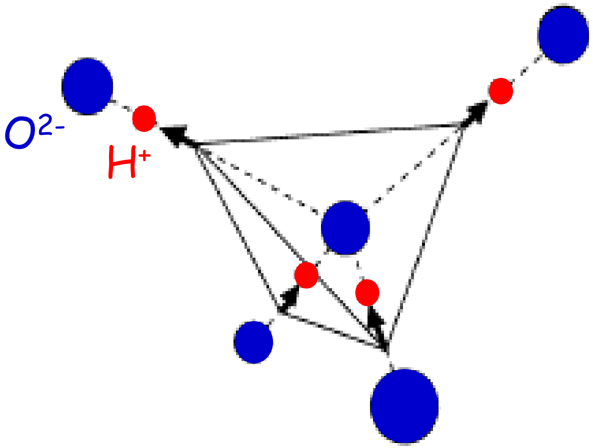
Ferromagnetic Interaction $J_{FM} \sim 2K$

Spin Ices: $Dy_2Ti_2O_7$, $Ho_2Ti_2O_7$



"2 in-2 out" Ice Rules

Water Ice

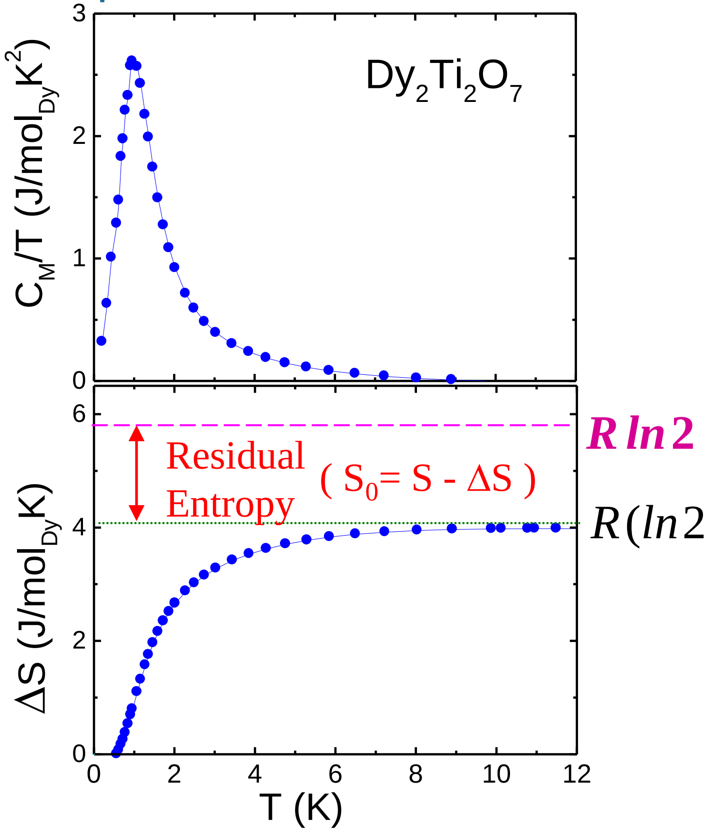


M. J. Harris et al. Phys. Rev. Lett. 79, 2554 (1997)

J. D. Bernal and R. H. Fowler J. Chem. Phys. 1, 515 (1933)

Spin Ice

Specific Heat



$R(ln2$ - **$0.5\,ln1.5$**$)$

A.P. Ramirez et al., Nature 399, 333 (1999)

Pauling's estimation for ice:

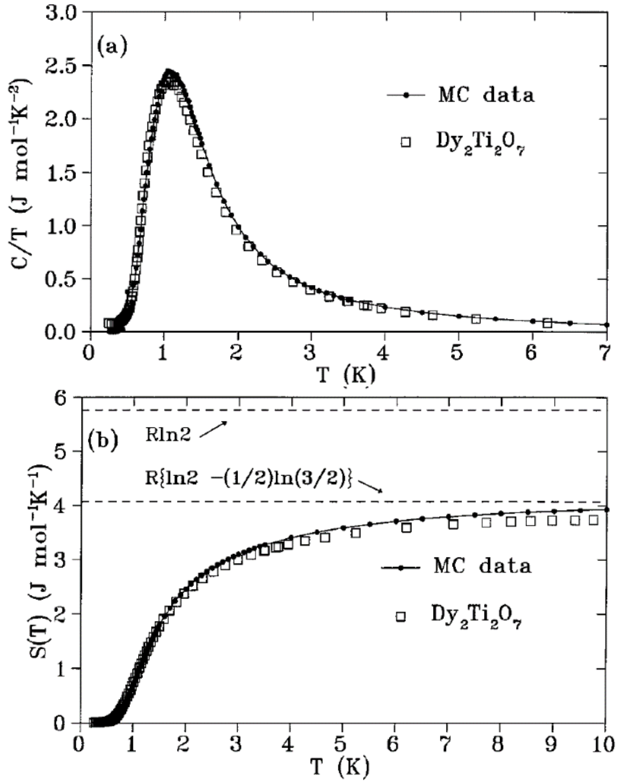
$$S_0 = K_B \ln\left\{2^N \left(\frac{6}{16}\right)^{N/2}\right\}$$

$$S_0 = 0.5\, R \ln 1.5$$

L. Pauling, *J. Am. Chem. Soc.* **57**, 2680 (1935).

Dipolar Spin Ice Model

Specific heat $Dy_2Ti_2O_7$

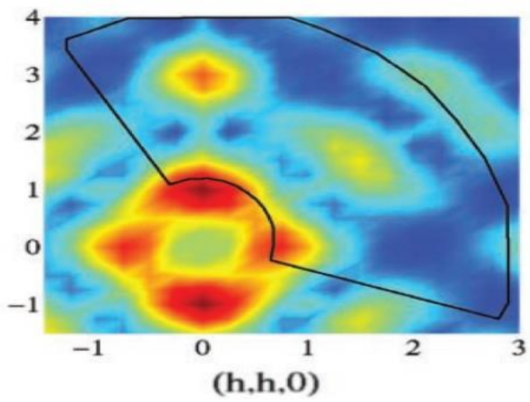


B.C. den Hertog et al. Phys. Rev. Lett. (2000)

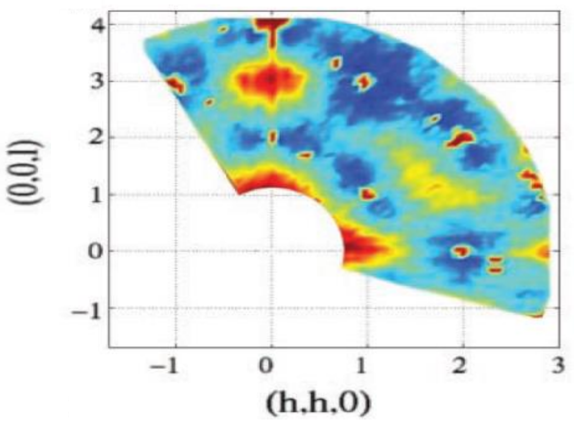
$$\mathcal{H} = -\mathrm{J}\sum_{(ij)} \boldsymbol{S}_i \cdot \boldsymbol{S}_j + \mathrm{D}r_{\mathrm{nn}}^3 \sum_{i>j}\left[\frac{\boldsymbol{S}_i \cdot \boldsymbol{S}_j}{|\boldsymbol{r}_{ij}|^3} - \frac{3(\boldsymbol{S}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{S}_j \cdot \boldsymbol{r}_{ij})}{|\boldsymbol{r}_{ij}|^5}\right]$$

Neutron Scattering $Ho_2Ti_2O_7$

Theory



Experiment

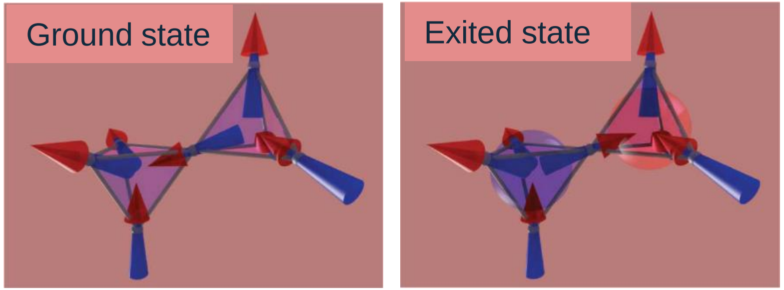


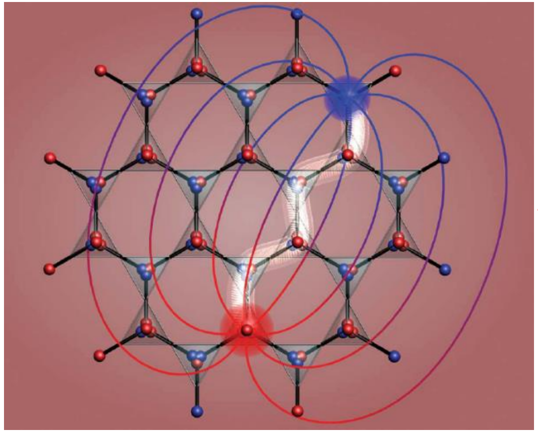
S. T. Bramwell et al. Phys. Rev. Lett. (2001)

T. Yavors'kii et al. Phys. Rev. Lett. (2008)

Spin Ice: A Coulomb Spin Liquid (or glass)

Monopole pair creation





Magnetic Coulomb Interaction

$$V(r_{ij}) = \frac{\mu_0}{4\pi} \frac{q_i q_j}{r_{ij}}$$

C. Castelnovo et al., Nature 451, 42 (2008)

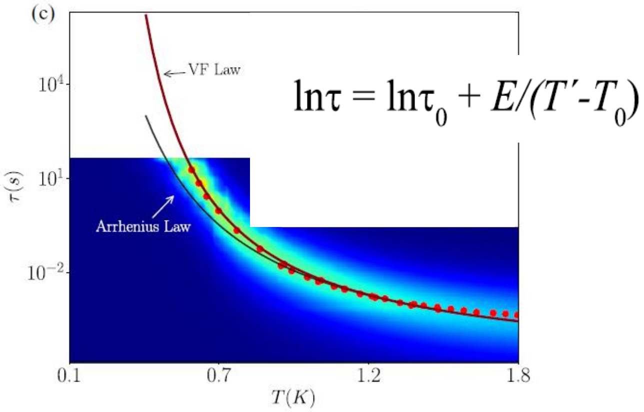
Spin Dynamics ➡ Motion of Monopoles

Monopoles increasingly sparse upon cooling.

Cooperative and Memory Effects

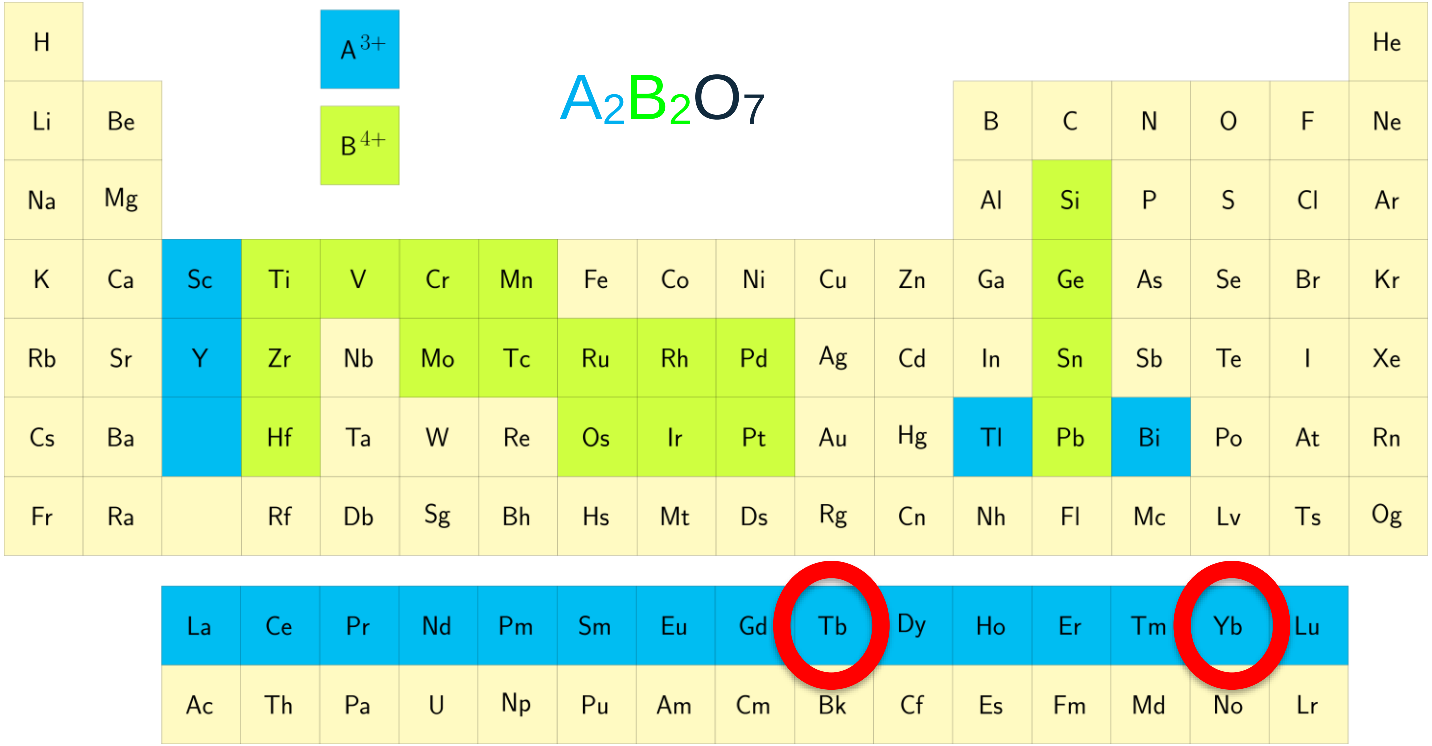
No Evident Intrinsic Disorder

Structural magnetic glass



DOI: 10.1103/PhysRevResearch.4.033159 - PNAS 119, e2117453119 (2022)

Pyrochlore Oxides

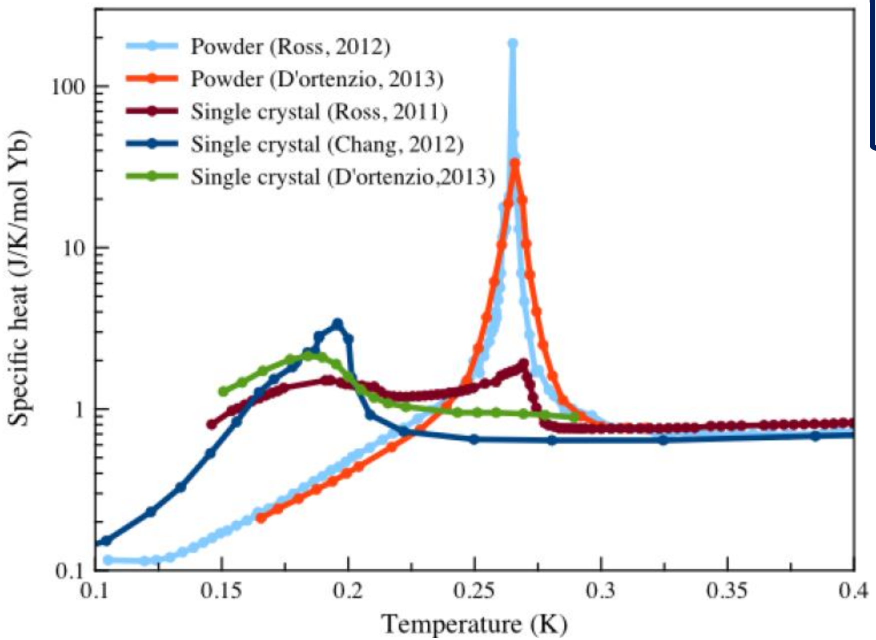


$Yb_2Ti_2O_7$

Signature of spin liquid physics

Continuum of spin excitations which condense into sharp coherent spin waves in a small applied magnetic field

Conventional magnetic order not found in many neutrons experiments

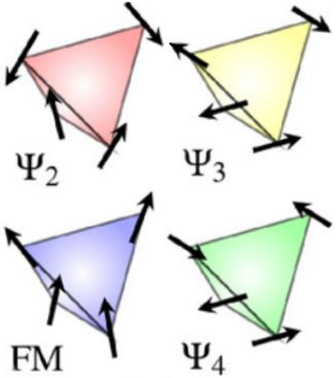


Extreme sensitivity to small amounts of disorder due to variation on 1% level in stoichiometry

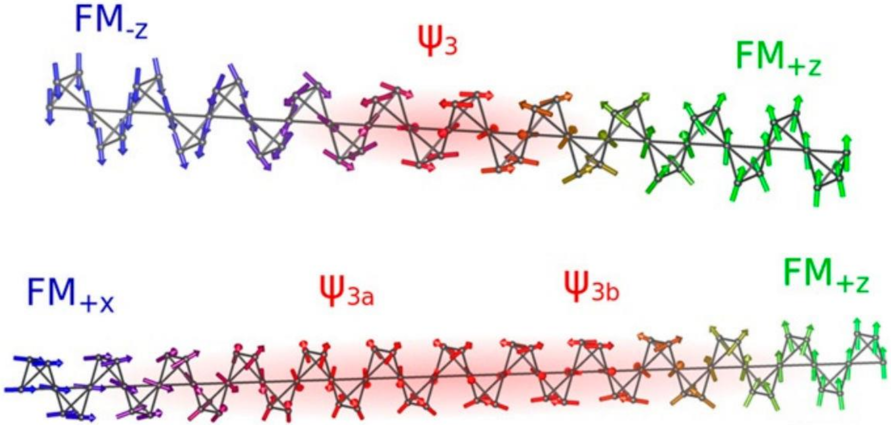
$Yb_2Ti_2O_7$

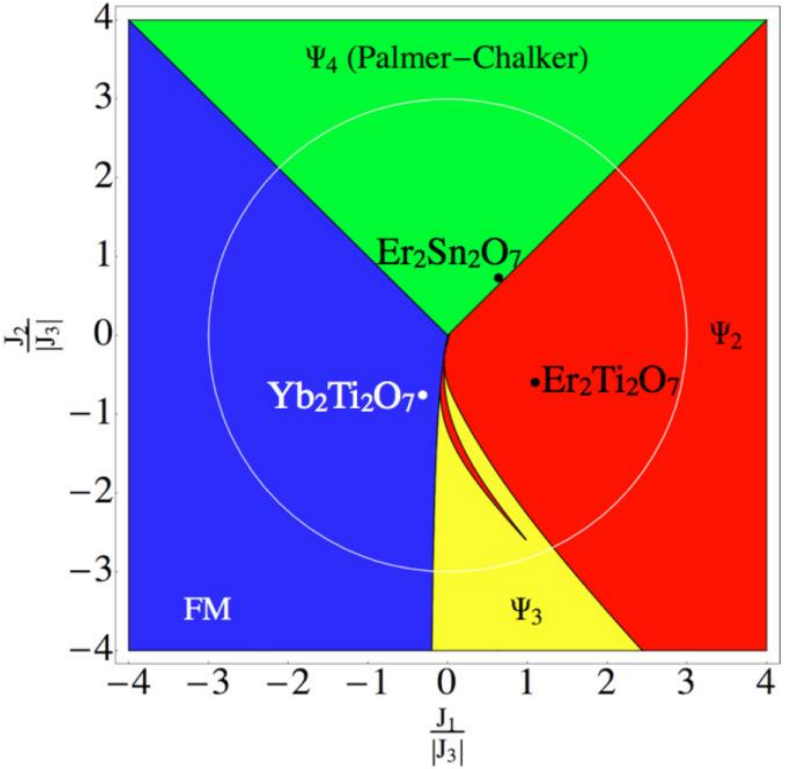
$$H = \sum_{\langle i,j \rangle} \mathbf{S}_i^T \mathbf{J}_{ij} \mathbf{S}_j$$

$$\mathbf{J}_{ij} = \begin{bmatrix} J_2 & J_4 & J_4 \\ -J_4 & J_1 & J_3 \\ -J_4 & J_3 & J_1 \end{bmatrix}$$



$T_C \approx 260\text{mK}$





Physical Review X, 1(2):021002, 2011

PRB 95, 094422. DOI:10.1103/PhysRevB.95.094422

PNAS 117 (44) 27245-27254. DOI:10.1073/pnas.2008791117

Synthesis of $Yb_2Zr_xTi_{2-x}O_7$

Why Zr?

$$r_{\mathrm{Ti}} = 0.61\text{Å}$$

$$r_{\mathrm{Zr}} = 0.72\text{Å}$$

Sc	Ti	V
Y	Zr	Nb
	Hf	Ta

Papers on magnetism

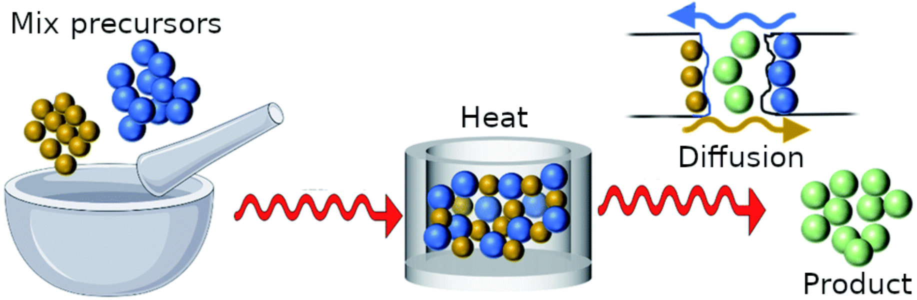
$Yb_2Ti_2O_7$: 50+

$Yb_2Zr_2O_7$: 0

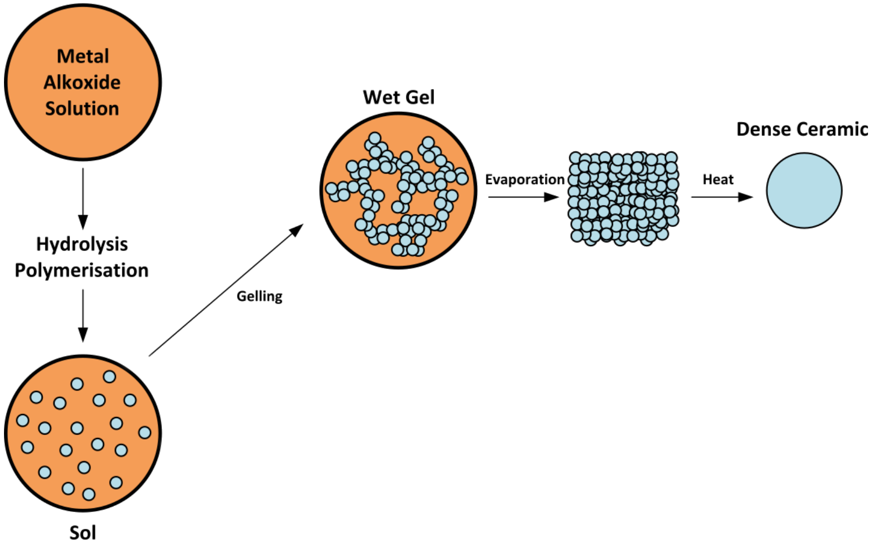
Chemical composition x is analogous to pressure, can be used to tune material properties

Synthesis of $Yb_2Zr_xTi_{2-x}O_7$

Solid-State Reaction



Sol-Gel Method

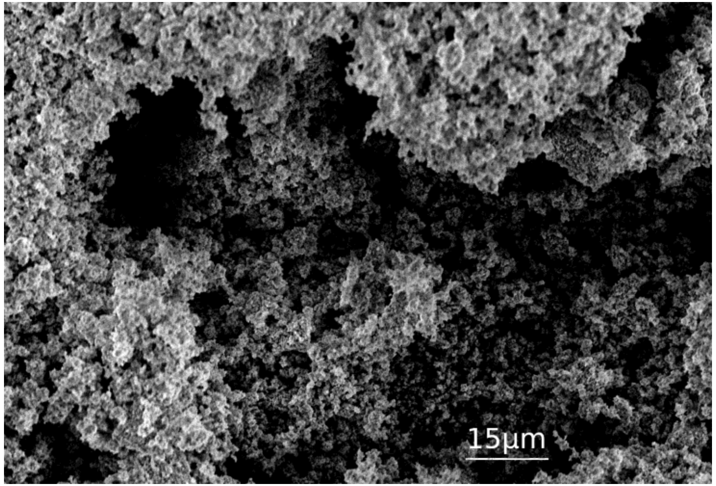


Adapted from DOI: 10.1039/D0RA07884K

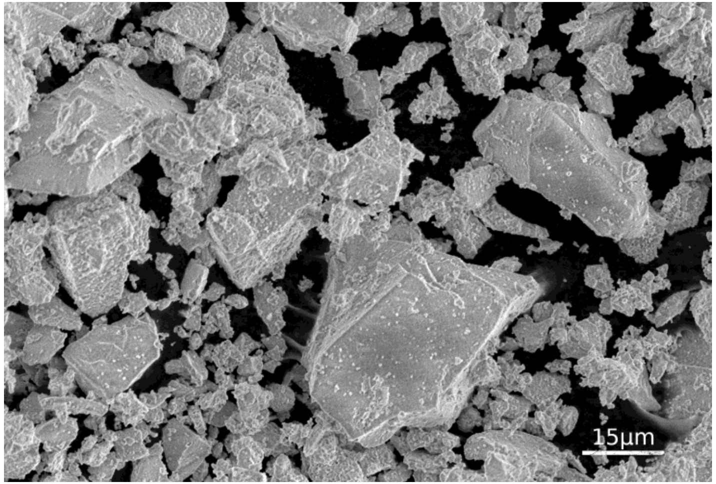
Adapted from DOI:10.1016/j.petlm.2017.03.001

$Yb_2Zr_xTi_{2-x}O_7$ Morphology

x = 1.5 (1500°C)



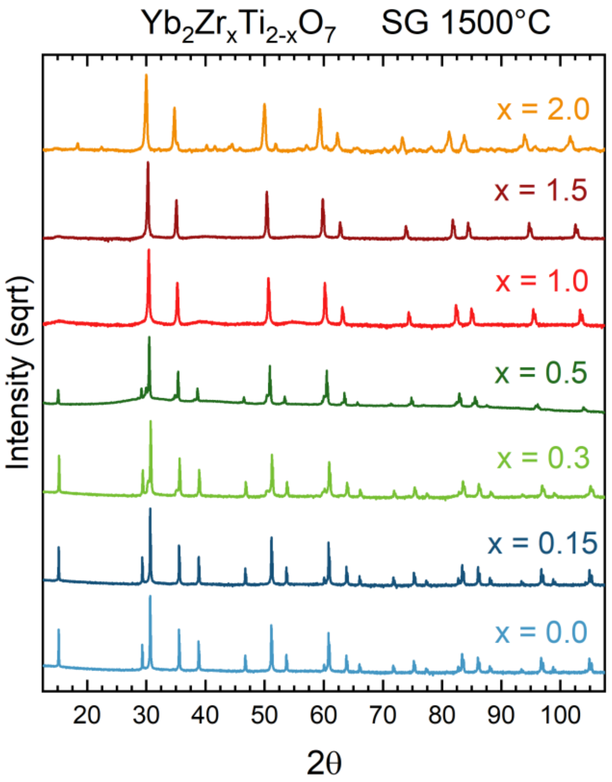
x = 2.0 (1500°C)



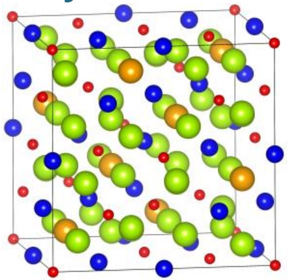
Mixed Zr/Ti → increased porosity

End members (x=0 and x=2) → more crystalline

X-Ray Diffraction



Pyrochlore

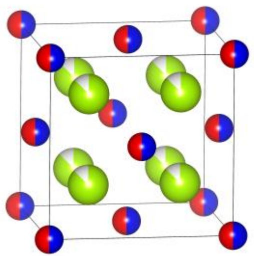


$$\alpha = \beta = \gamma = 90^\circ$$

$$a = b = c \approx 10\text{Å}$$

$$Fd\bar{3}m$$

Defect Fluorite

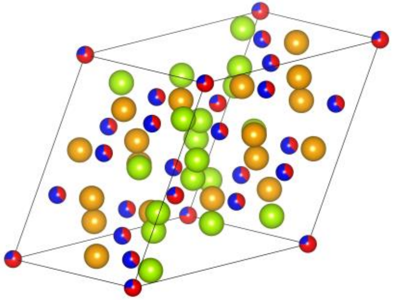


$$\alpha = \beta = \gamma = 90^\circ$$

$$a = b = c \approx 5\text{Å}$$

$$Fm\bar{3}m$$

δ-Phase



$$\alpha = \beta = 90^\circ$$

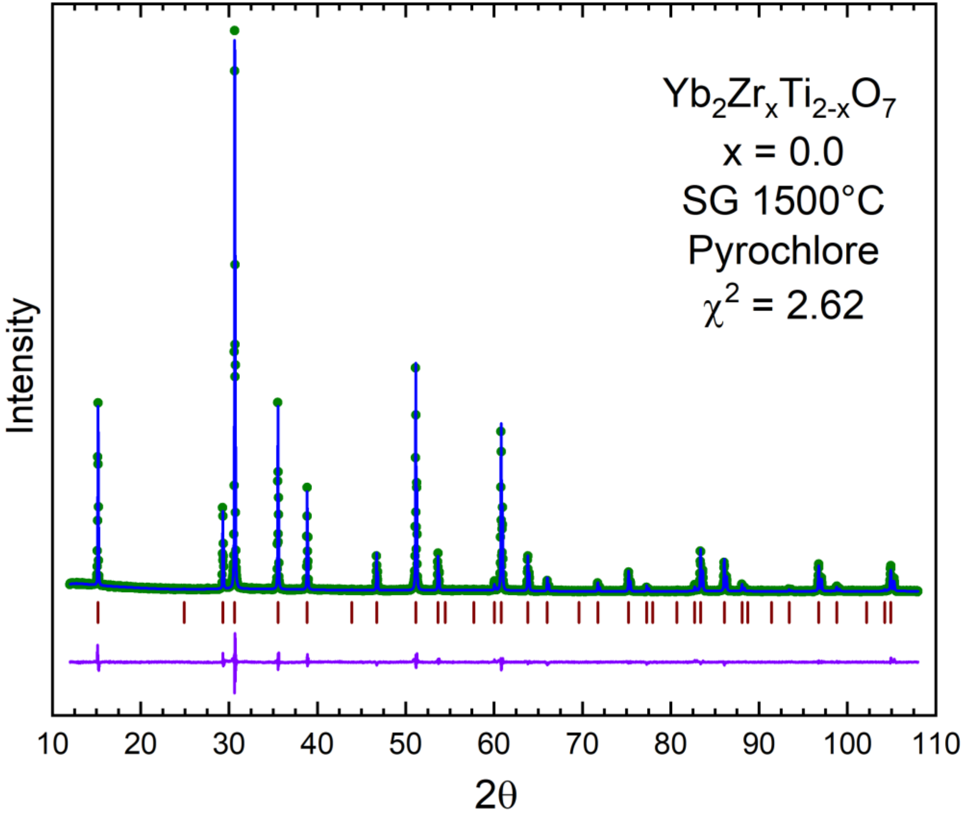
$$\gamma = 120^\circ$$

$$a = b \approx 9.5\text{Å}$$

$$c \approx 9\text{Å}$$

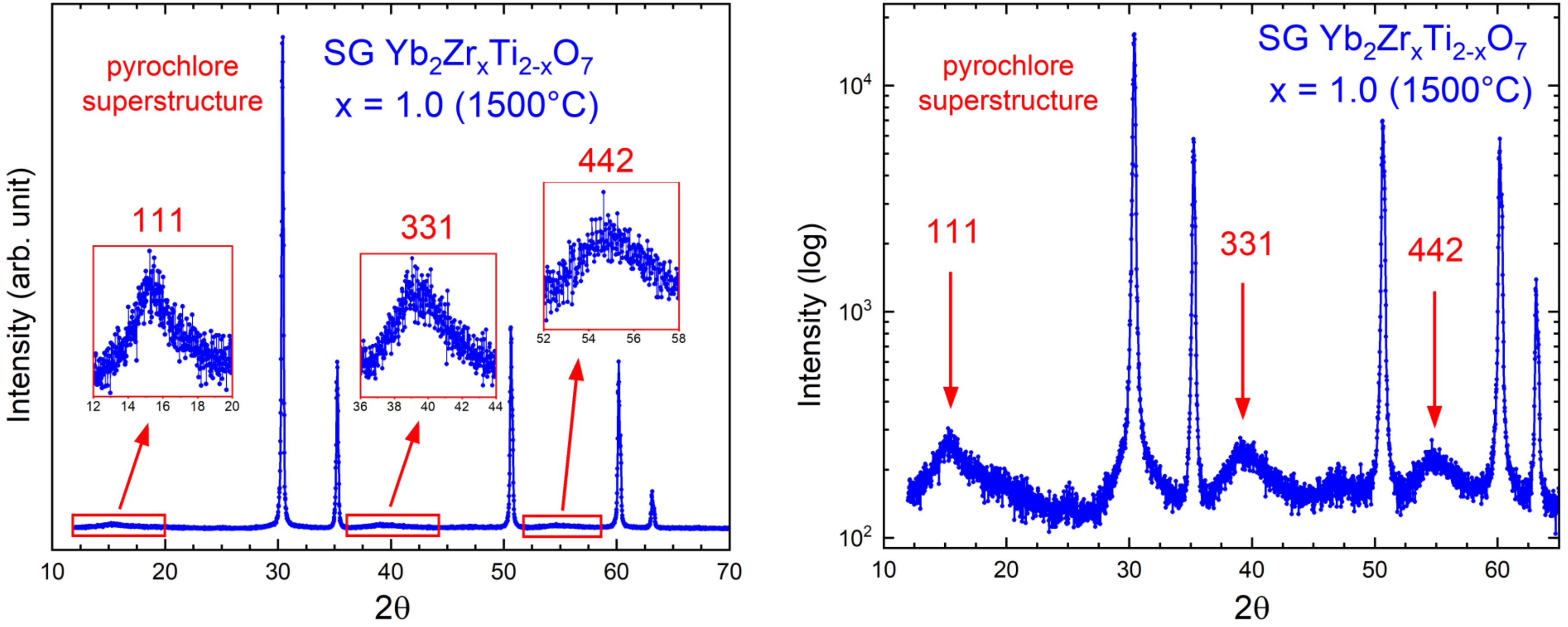
$$R\bar{3}$$

Rietveld Refinement: $Yb_2Zr_xTi_{2-x}O_7$

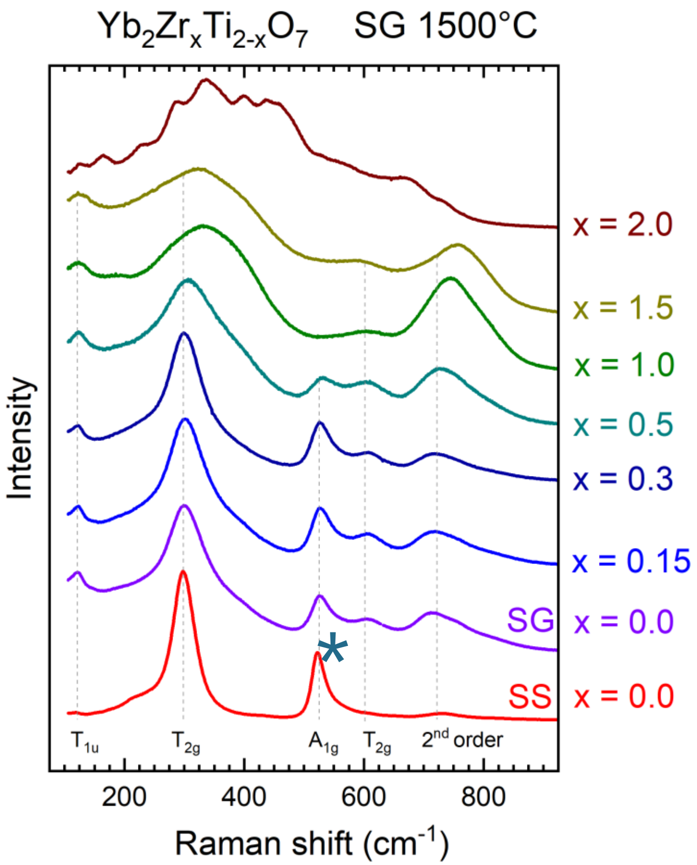


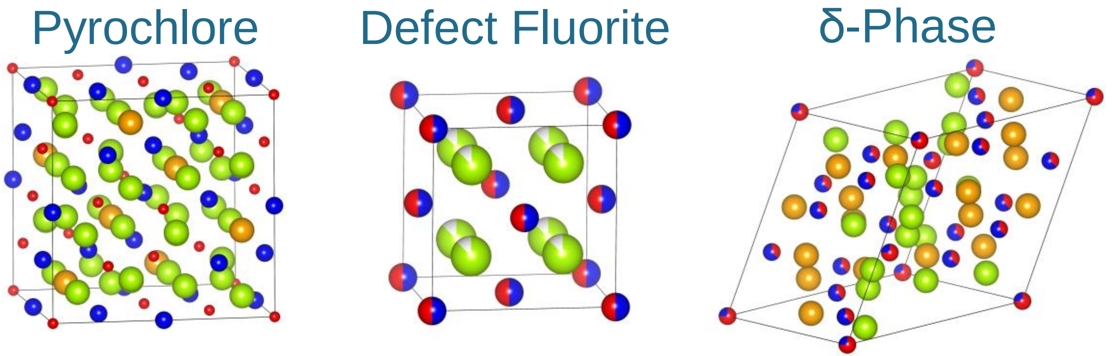
Parameter	Symbol	Refined value	Unit	Occupation
lattice parameter	a	10.09501	Å	
crystallite size	μ	1859	nm	
microstrain	ϵ	640	10^{-6}	
oxygen coordinate	x_{48f}	0.3327		
isotropic	U_{iso} (Yb_{16d})	0.02526		0.987
atomic	U_{iso} (Ti_{16c})	0.01517	$Å^2$	1.012
displacement	U_{iso} (O_{8b})	0.02965		0.962
parameters	U_{iso} (O_{48f})	0.05890		1.008

Long-Range vs Local Order



Raman Spectroscopy





Pyrochlore

$\alpha = \beta = \gamma = 90^\circ$

$a = b = c \approx 10\text{Å}$

$Fd\bar{3}m$

Defect Fluorite

$\alpha = \beta = \gamma = 90^\circ$

$a = b = c \approx 5\text{Å}$

$Fm\bar{3}m$

δ-Phase

$\alpha = \beta = 90^\circ$

$\gamma = 120^\circ$

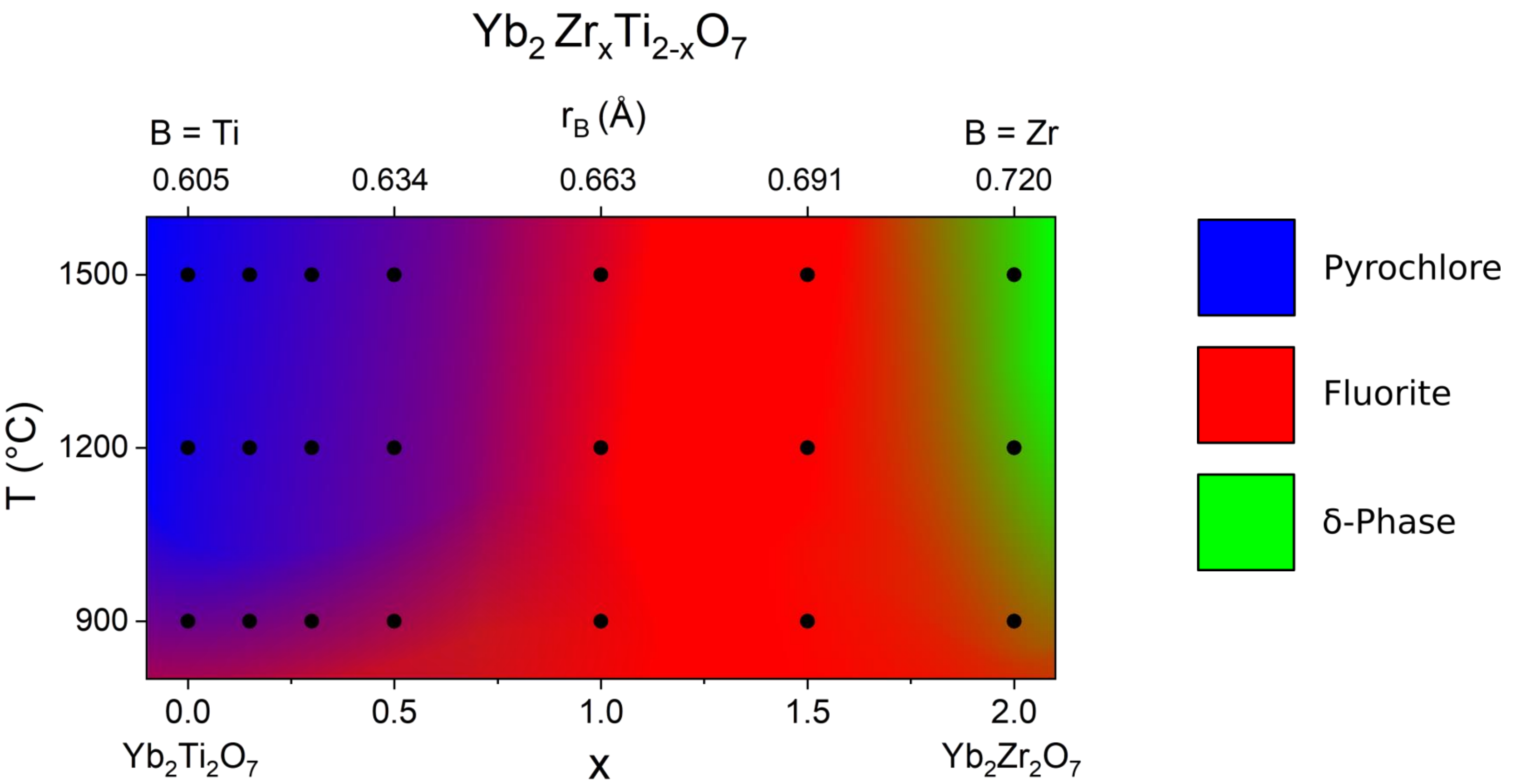
$a = b \approx 9.5\text{Å}$

$c \approx 9\text{Å}$

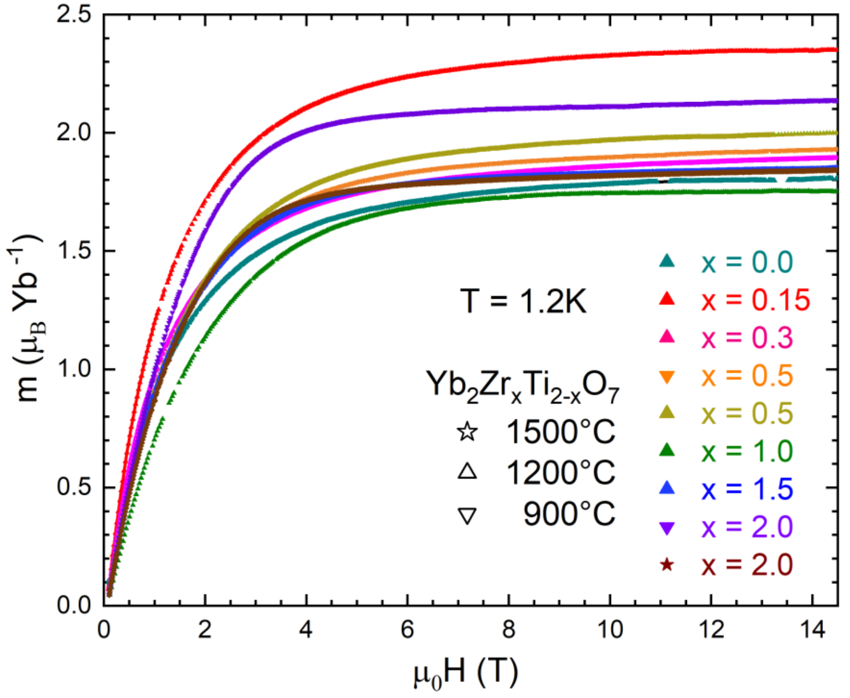
$R\bar{3}$

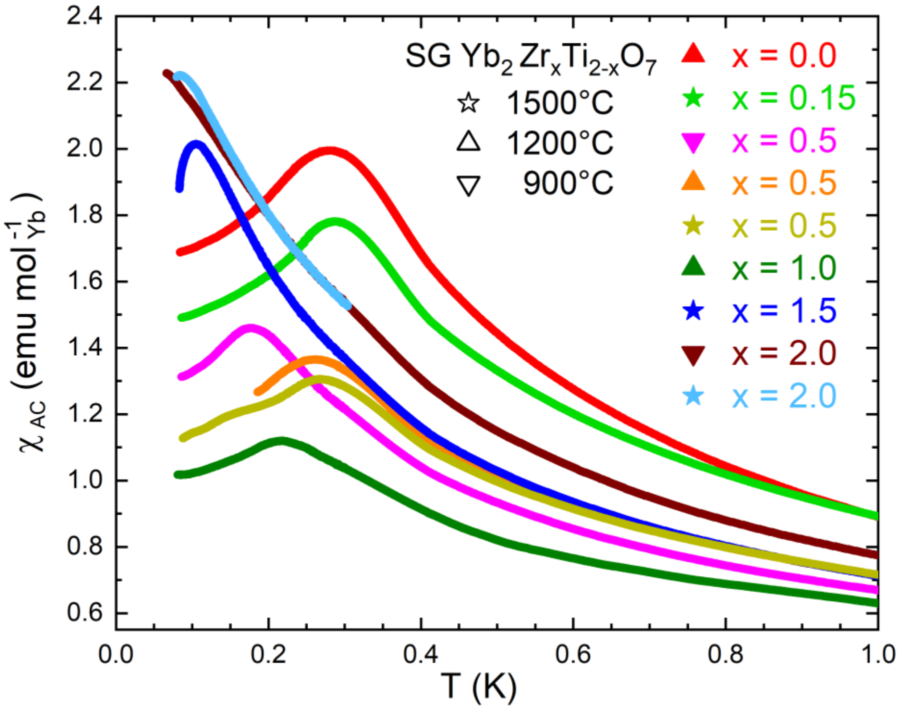
*Pyrochlore

Phase Diagram

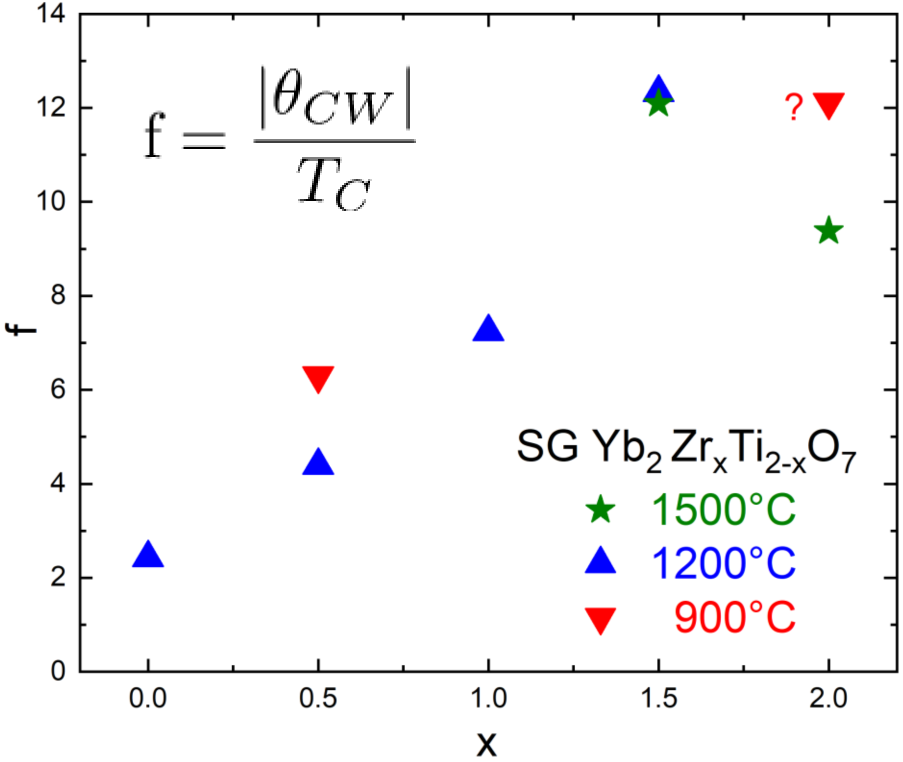


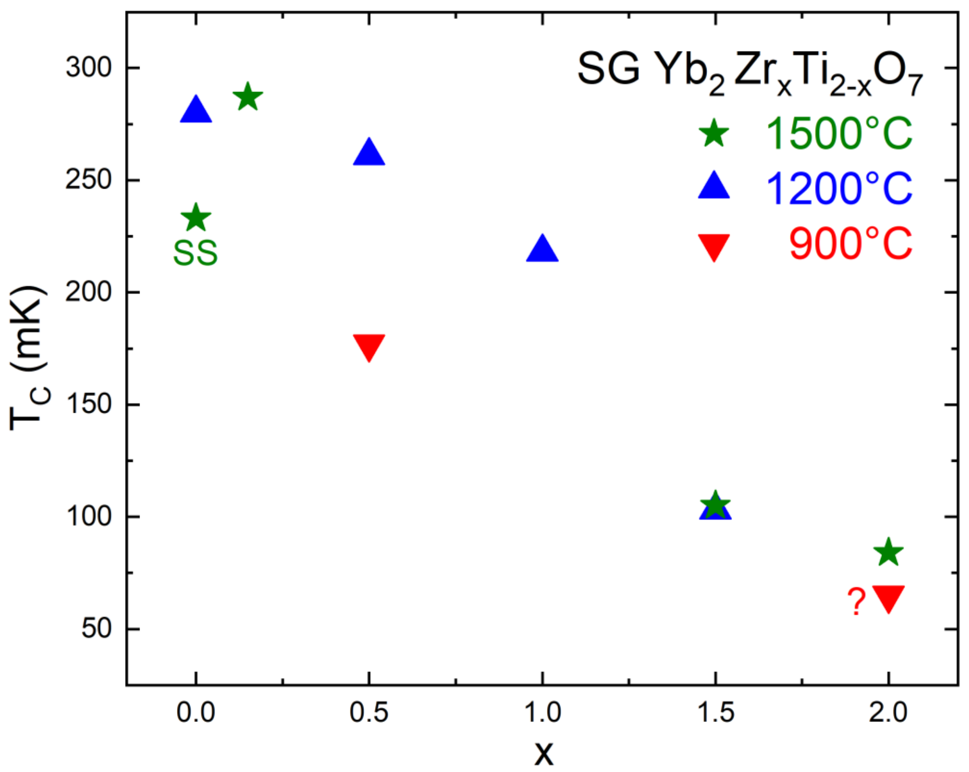
Magnetic Data





AC Magnetic Susceptibility





$Tb_2Ti_2O_7$

Antiferromagnetic correlations

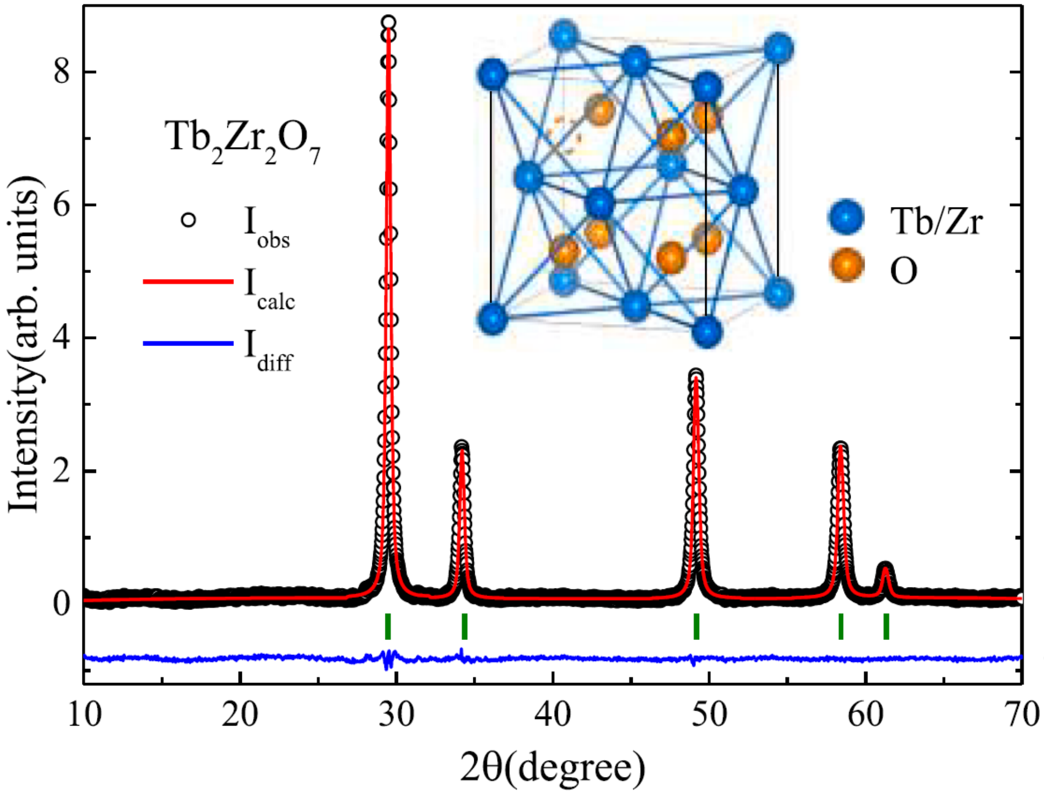
Fluctuating ground state → No long-range order down to 50 mK (Θ_{CW} = -19 K)

Possible spin-liquid ground state

Pyrochlore → Defect Fluorite

$Tb_2Ti_2O_7$ → $Tb_2Zr_2O_7$

X-Ray Diffraction

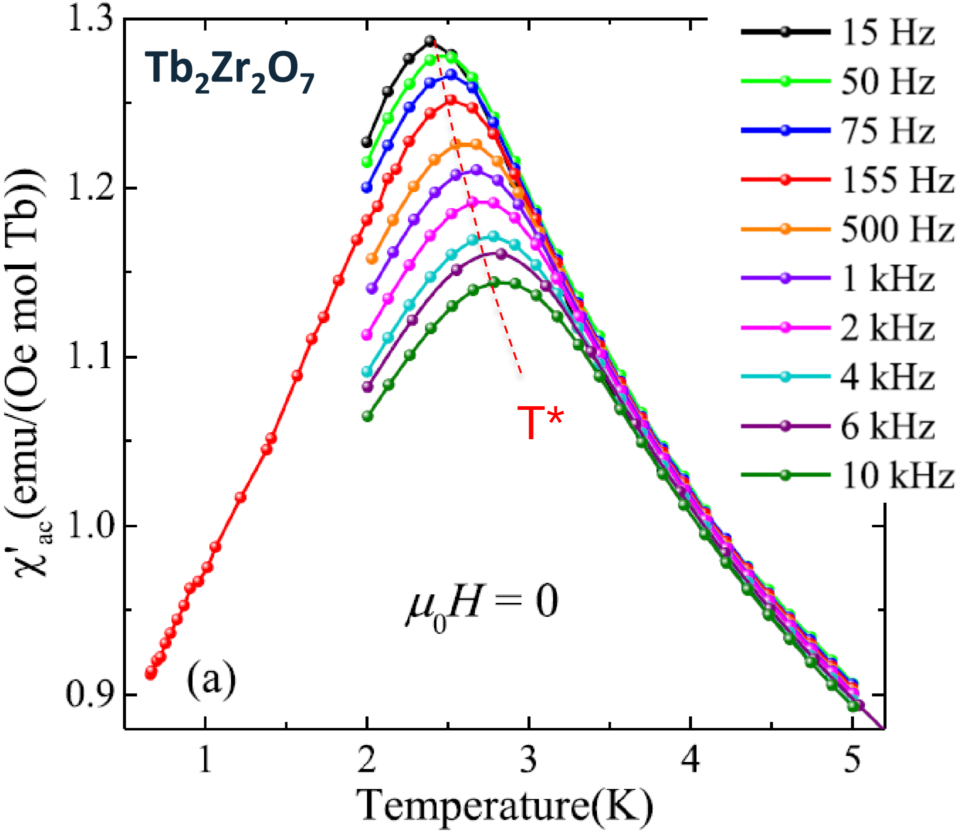


Sol-gel sample
Defect Fluorite Structure

Refined crystallographic parameters for $Tb_2Zr_2O_7$.

Crystal system	Cubic
Space Group	$Fm\bar{3}m$
a (Å)	5.233(2)
Tb	4a (0,0,0)
Occupancy	0.499(4)
Zr	4a (0,0,0)
Occupancy	0.499(5)
O	8c (0.25,0.25,0.25)
Occupancy	0.92(2)
Number of variables	21
R_{wp} (%)	14.3
R_{exp} (%)	6.6
χ^2	4.6

AC Magnetic Susceptibility



$Tb_2Zr_2O_7$

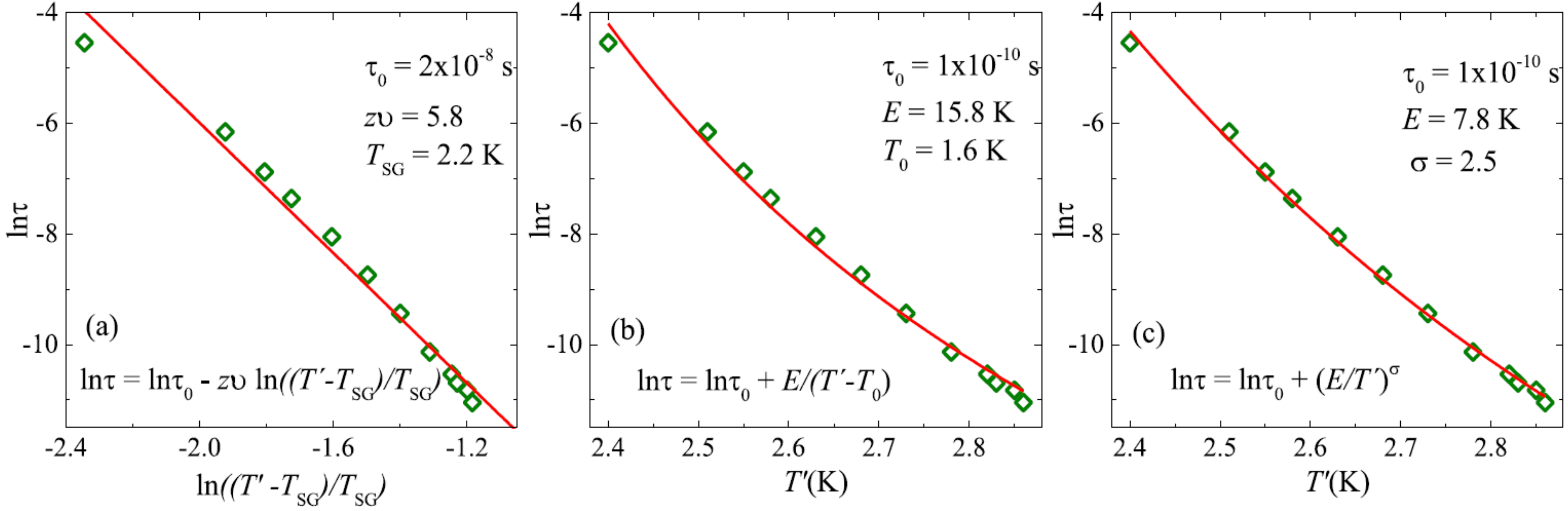
$\Delta T^*/(T^* \Delta \log f) = 0.064$

$Tb_2Ti_2O_7$ (T*=0.25 K)
$Tb_2Hf_2O_7$ (T*=0.75 K)
} 0.06

Canonical spin glasses : 0.005 - 0.01

JMMM - doi.org/10.1016/j.jmmm.2022.170215

Spin glasses models



Dynamic scaling law

Vogel-Fulcher law

Power law of Arrhenius

Canonical SG ($z\upsilon$ = 4–12)

T0 ≠T*= 2.5 K

$Tb_2Zr_2O_7$

(τ_0 = 1.1 × 10^{-9} s, E = 0.91)

Concluding remarks

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- Structural disorder increases with Zr content
- Pyrochlore → Defect Fluorite → δ-Phase
- Magnetic ordering suppressed by structural disorder
- Increase disorder/frustration → possible spin liquid in $Yb_2Zr_2O_7$
- Spin-glass-like transition in $Tb_2Zr_2O_7$
- Considerabe spin dynamics remains down to 100 mK

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