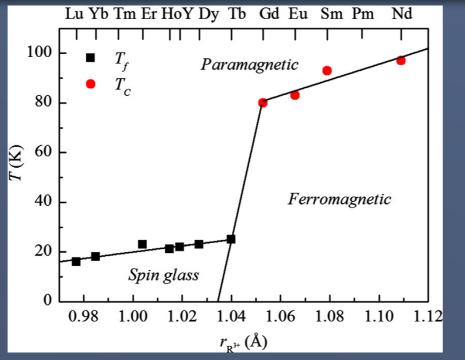
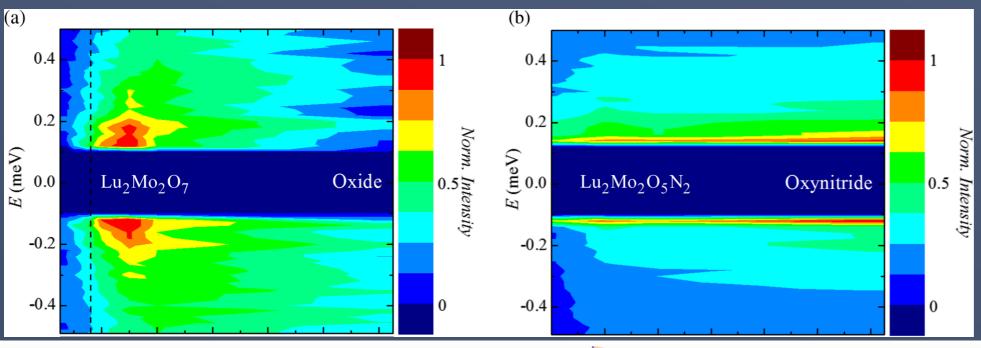
## From Spin Glass to Spin Liquid Ground States in Molybdate Pyrochlores





L. Clark <sup>1, 2</sup>
E. Kermarrec <sup>1, 3</sup>
K. Fritsch <sup>1, 4</sup>
G. J. Nilsen <sup>5</sup>
J. P. Attfield <sup>6</sup>
A. Harrison <sup>5, 6</sup>
H. J. Silverstein <sup>7, 8</sup>
C. R. Wiebe <sup>7</sup>
H. Zhou <sup>9</sup>
J. S. Gardner <sup>10</sup>
M. J. P. Gingras <sup>11</sup>
J. E. Greedan <sup>1</sup>

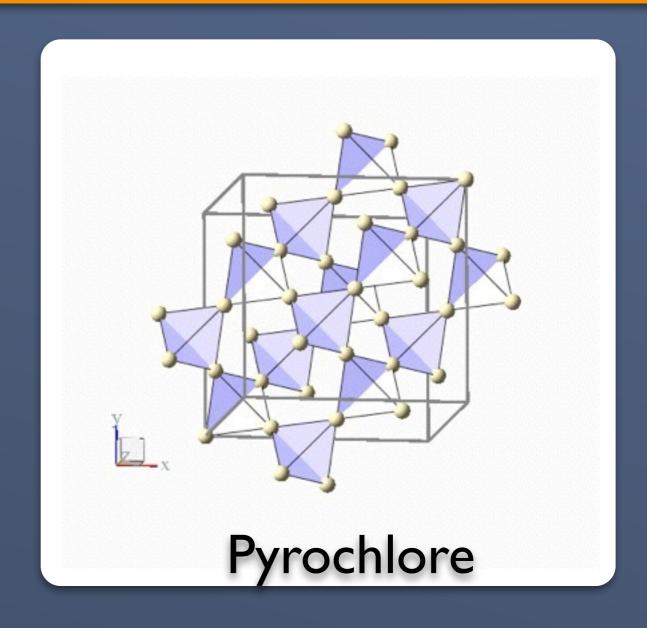
- <sup>1</sup> McMaster University
- <sup>2</sup> St. Andrew's University
- <sup>3</sup> Universite Paris-Sud
- <sup>4</sup> Hemlholz Zentrum Berlin
- Institut Laue LangevinEdinburgh University
- <sup>7</sup> University of Winnipeg
- 8 Stanford University
- <sup>9</sup> University of Tennessee <sup>10</sup> NSRRC Taiwan
- <sup>10</sup> NSRRC, Taiwan
- <sup>11</sup> University of Waterloo

Bruce D. Gaulin McMaster University



**Brockhouse Institute** for **Materials Research** 

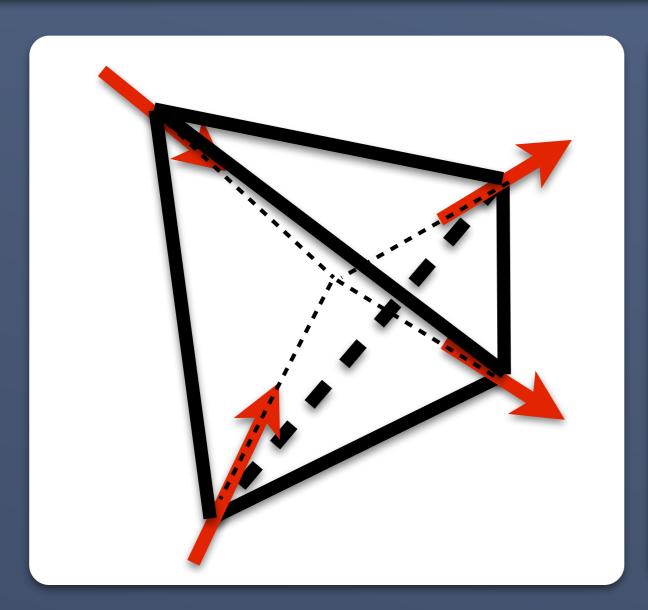
# Geometric Frustration from Tetrahedra

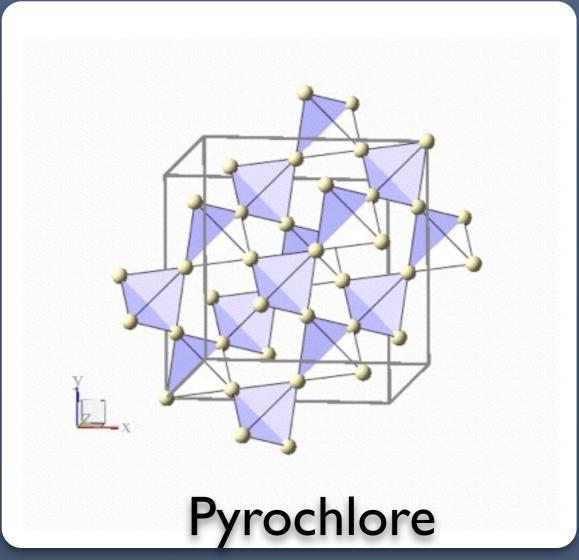


Spin Ice: FM near-neighbour coupling + local Ising anisotropy leads to 6-fold degenerate "ice states" for a single tetrahedron.

Macroscopic degeneracy for network of corner-sharing tetrahedra.

# Geometric Frustration from Tetrahedra





Spin Ice: FM near-neighbour coupling + local Ising anisotropy leads to 6-fold degenerate "ice states" for a single tetrahedron.

Macroscopic degeneracy for network of corner-sharing tetrahedra.

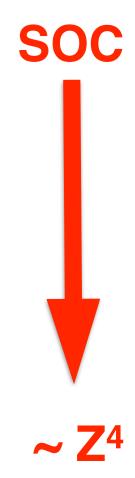
#### Cubic Pyrochlores: A<sub>2</sub>B<sub>2</sub>O<sub>7</sub>

 $Y_2Mo_2O_7: Mo^{4+} 4d^2$ 

Lu<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>: Mo<sup>4+</sup> 4d<sup>2</sup>

 $Lu_2Mo_2O_5N_2 : Mo^{5+} 4d^{1}$ 

Hydrogen																		Helium
1																		2
ш																		Ц۵
																		Не
1.008			_	Key:														4.0026
Lithium	Beryllium				Element Name								Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon
3	4			At	omic numb	per							5	6	7	8	9	10
Li	Be			S	ymb	ol							В	C	N	0	F	Ne
6.94	9.0122			Atomic we	eight (mean rela	tive mass)							10.81	12.011	14.007	15.999	18.998	20.180
Sodium	Magnesium												Aluminium	Silicon	Phosphorus	Sulfur	Chlorine	Argon
11	12												13	14	15	16	17	18
Na	Mg												Al	Si	P	S	CI	Ar
22.990	24.305												26.982	28.085	30.974	32.06	35.45	39.948
Potassium	Calcium		Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine	Krypton
19	20		21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.098	40.078(4)		44.956	47.867	50.942	o1.990	54.938	55.845(2)	58.933	58.693	63.546(3)	65.38(2)	69.723	72.63	74.922	78.96(3)	79.904	83.798(2)
Rubidium	Strontium		Yttrium	Zirconium	Niobium	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium	Indium	Tin	Antimony	Tellurium	lodine	Xenon
37	38		39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr		Y	Zr	N	Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te		Xe
85.468	87.62		88.906	1.224(2)	92.906	95.96(2)	[97.91]	101.07(2)	102.91	106.42	107.87	112.41	114.82	118.71	121.76	127.60(3)	126.90	131.29
Caesium	Barium	F7 70	Lutetium	lafnium	Tantalui	Tungsten	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury	Thallium	Lead	Bismuth	Polonium	Astatine	Radon
55	56	57-70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	*	Lu	Hf	Ta	VV	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
132.91	137.33		174.97	178.49(2)	180.95	183.84	186.21	190.23(2)	192.22	195.08	196.97	200.59	204.38	207.2	208.98	[208.98]	[209.99]	[222.02]
Francium <b>87</b>	Radium <b>88</b>	89-102	awrencium	Rutherfordium 104	Dubnium <b>105</b>	Seaborgium 106	Bohrium 107	Hassium 108	Meitnerium 109	Darmstadtium 110	Roentgenium 111	Copernicium 112	Ununtrium 113	Flerovium 114	Ununpentium 115	Livermorium 116	Ununseptium 117	Ununoctium 118
												_		l				
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	FI	Uup	Lv	Uus	Uuo
[223.02]	[226.03]		[262.11]	[265.12]	[268.13]	[271.13]	[270]	[277.15]	[276.15]	[281.16]	[280.16]	[285.17]	[284.18]	[289.19]	[288.19]	[293]	[294]	[294]



\*lanthanoids

70 Pr Sm Tb Dy Er Ce Nd Eu Gd Ho Yb La Pm Tm 144.24 [144.91] 150.36(2) 158.93 167.26 173.05 138.91 140.91 157.25(3) 168.93 100 102 Bk U Es No Ac Np Fm Am Cm

\*\*actinoids

#### Cubic Pyrochlores: A<sub>2</sub>B<sub>2</sub>O<sub>7</sub>

 $Y_2Mo_2O_7: Mo^{4+} 4d^2$ 

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Hydrogen																		Helium
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Н																		He
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Lithium	Beryllium		[		Element Name								Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon
3	4			At	omic numb	oer							5	6	7	8	9	10
Li	Be			S	ymb	ol							В	C	N	0	F	Ne
6.94	9.0122		L	Atomic we	eight (mean rela	ative mass)							10.81	12.011	14.007	15.999	18.998	20.180
Sodium	Magnesium												Aluminium	Silicon	Phosphorus	Sulfur	Chlorine	Argon
11	12												13	14	15	16	17	18
Na	Mg												Al	Si	P	S	CI	Ar
22.990	24.305	ı	0	T9 1	Maria Para			1	0.111	Nr.L.I	0	7'	26.982	28.085	30.974	32.06	35.45	39.948
Potassium 19	Calcium <b>20</b>		Scandium 21	Titanium <b>22</b>	Vanadium <b>23</b>	Chromium <b>24</b>	Manganese <b>25</b>	Iron <b>26</b>	Cobalt 27	Nickel 28	Copper <b>29</b>	Zinc <b>30</b>	Gallium <b>31</b>	Germanium <b>32</b>	Arsenic 33	Selenium <b>34</b>	Bromine <b>35</b>	Krypton <b>36</b>
	_		_		23			_	_									
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.098 Rubidium	40.078(4) Strontium		44.956 Yttrium	47.867 Zirconium	50.942 Niobium	Molybdenum	54.938 Technetium	55.845(2) Ruthenium	58.933 Rhodium	58.693 Palladium	63.546(3) Silver	65.38(2) Cadmium	69.723 Indium	72.63 Tin	74.922	78.96(3) Tellurium	79.904 lodine	83.798(2)
<b>37</b>	<b>38</b>		39	40	41	42	43	44	45	46	47	48	49	50	Antimony <b>51</b>	<b>52</b>	53	Xenon <b>54</b>
			39	40							_			_			33	
Rb	Sr		Y	Zr	N	Mo	TC	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	400.00	Xe
85.468 Caesium	87.62 Barium	-	88.906 Lutetium	1.224(2) lafnium	92.906 ) Tantalui	95.96(2) Tungsten	[97.91] Rhenium	101.07(2) Osmium	102.91 Iridium	106.42 Platinum	107.87 Gold	112.41 Mercury	114.82 Thallium	118.71 Lead	121.76 Bismuth	127.60(3) Polonium	126.90 Astatine	131.29 Radon
<b>55</b>	56	57-70	71	72	73	74	75	76	77	78	<b>79</b>	80	81	82	83	84	85	86
		*		_					_		_				1			
Cs	Ba	^	Lu	Hf	Ta	VV	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
132.91	137.33		174.97	178.49(2)	180.95	183.84	186.21	190.23(2)	192.22	195.08	196.97	200.59	204.38	207.2	208.98	[208.98]	[209.99]	[222.02]
Francium	Radium	90 400	awrencium	Rutherfordium	Dubnium	Seaborgium	Bohrium	Hassium	Meitnerium	Darmstadtium	Roentgenium	Copernicium	Ununtrium	Flerovium	Ununpentium	Livermorium	Ununseptium	Ununoctium
87	88	89-102		104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	FI	Uup	Lv	Uus	Uuo
[223.02]	[226.03]		[262.11]	[265.12]	[268.13]	[271.13]	[270]	[277.15]	[276.15]	[281.16]	[280.16]	[285.17]	[284.18]	[289.19]	[288.19]	[293]	[294]	[294]

SOC

\*lanthanoids

70 Pr Sm Tb Dy Er Ce Nd Eu Gd Ho Yb La Pm [144.91] 150.36(2) 158.93 164.93 138.91 140.91 144.24 157.25(3) 167.26 173.05 100 102 Bk U Es No Ac Np Fm Am Cm

\*\*actinoids

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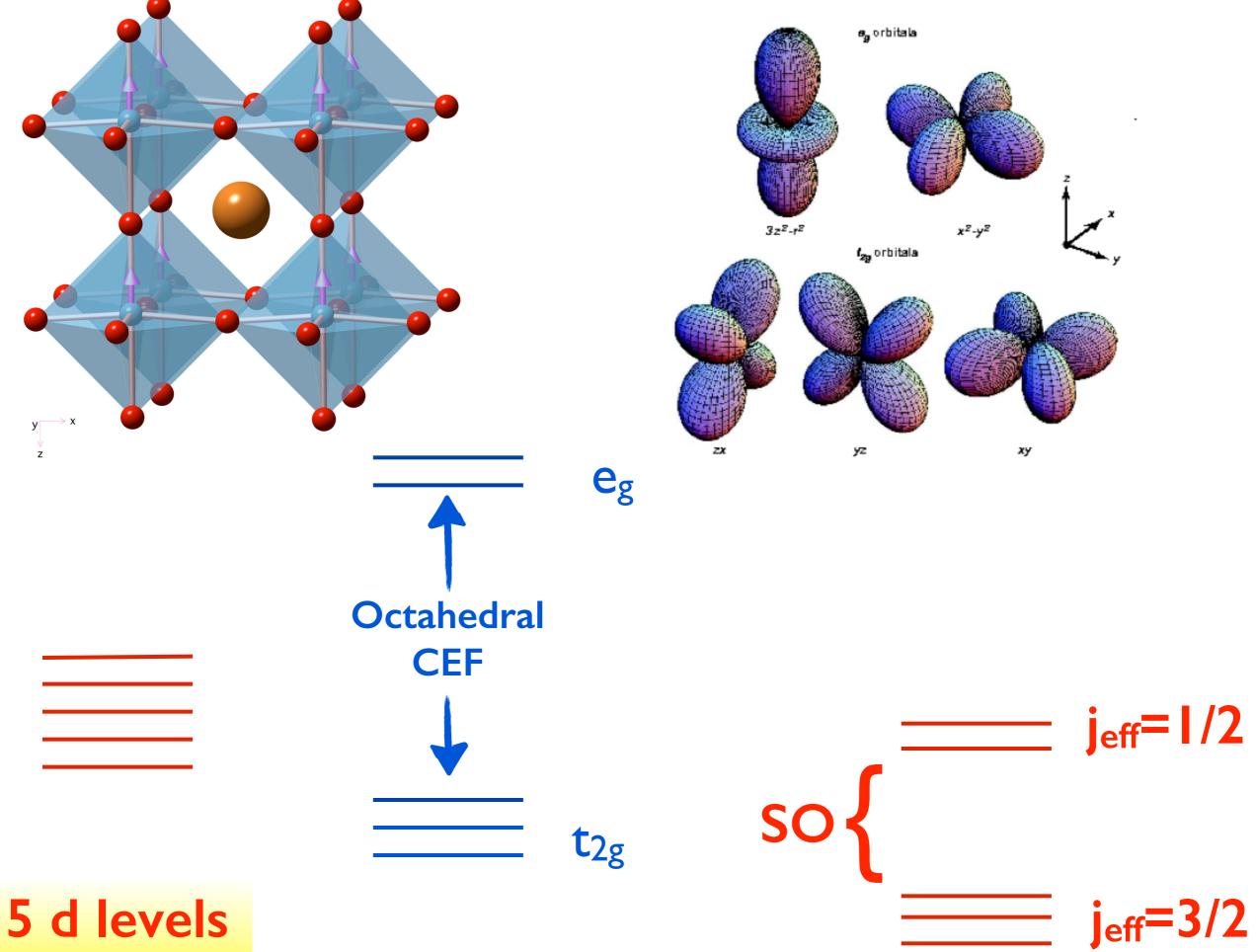
Hydrogen																		Helium
1 1																		2
																		L
																		Не
1.008				Key:														4.0026
Lithium	Beryllium				Element Name								Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon
3	4			Ate	omic numb	er							5	6	7	8	9	10
1 1 1	Da			C	voo b	~ I							D		N.I.			NIa
	Be			3	ymbo								В	<b>U</b>	N	O		Ne
6.94	9.0122			Atomic we	eight (mean rela	tive mass)							10.81	12.011	14.007	15.999	18.998	20.180
Sodium	Magnesium												Aluminium	Silicon	phorus	Sule	Chlorine	Argon
11	12												13	14	15	16	17	18
Na	Ma												Al	Si	P	S	CI	۸r
Na	Mg												Al	<b>3</b> 1		3		Ar
22.990	24.305												26.982	28.085	30.974	32.06	35.45	39.948
Potassium	Calcium		Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine	Krypton
19	20		21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
, n					V	OI								l	1		I	
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Rubidium	Strontium		Yttrium	Zirconium	Niobium	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium	Indium	Tin	Antimony	Tellurium	lodine	Xenon
37	38		39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr			<b>\7</b> r	NI	Mo	TC	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te		Xe
	l I										79			l				
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55	<b>56</b>	57-70	71	<b>72</b>	73	74	75	<b>76</b>	77	78	79	80	81	<b>82</b>	83	84	85	<b>86</b>
_			_''	_		74		70			19			l	1			
Cs	Ba	*	Lu	Hf	Ta	VV	Re	Os	l Ir	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
132.91	137.33		174.97	178.49(2)	180.95	183.84	186.21	190.23(2)	192.22	195.08	196.97	200.59	204.38	207.2	208.98	[208.98]	[209.99]	[222.02]
Francium	Radium			Rutherfordium	Dubnium	Seaborgium	Bohrium	Hassium	Meitnerium	Darmstadtium	Roentgenium	Copernicium	Ununtrium	Flerovium	Ununpentium	Livermorium	Ununseptium	Ununoctium
87	88	89-102	102	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
		**					_					_		l				
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	FI	Uup	LV	Uus	Uuo
[223.02]	[226.03]		[262.11]	[265.12]	[268.13]	[271.13]	[270]	[277.15]	[276.15]	[281.16]	[280.16]	[285.17]	[284.18]	[289.19]	[288.19]	[293]	[294]	[294]
[]																		

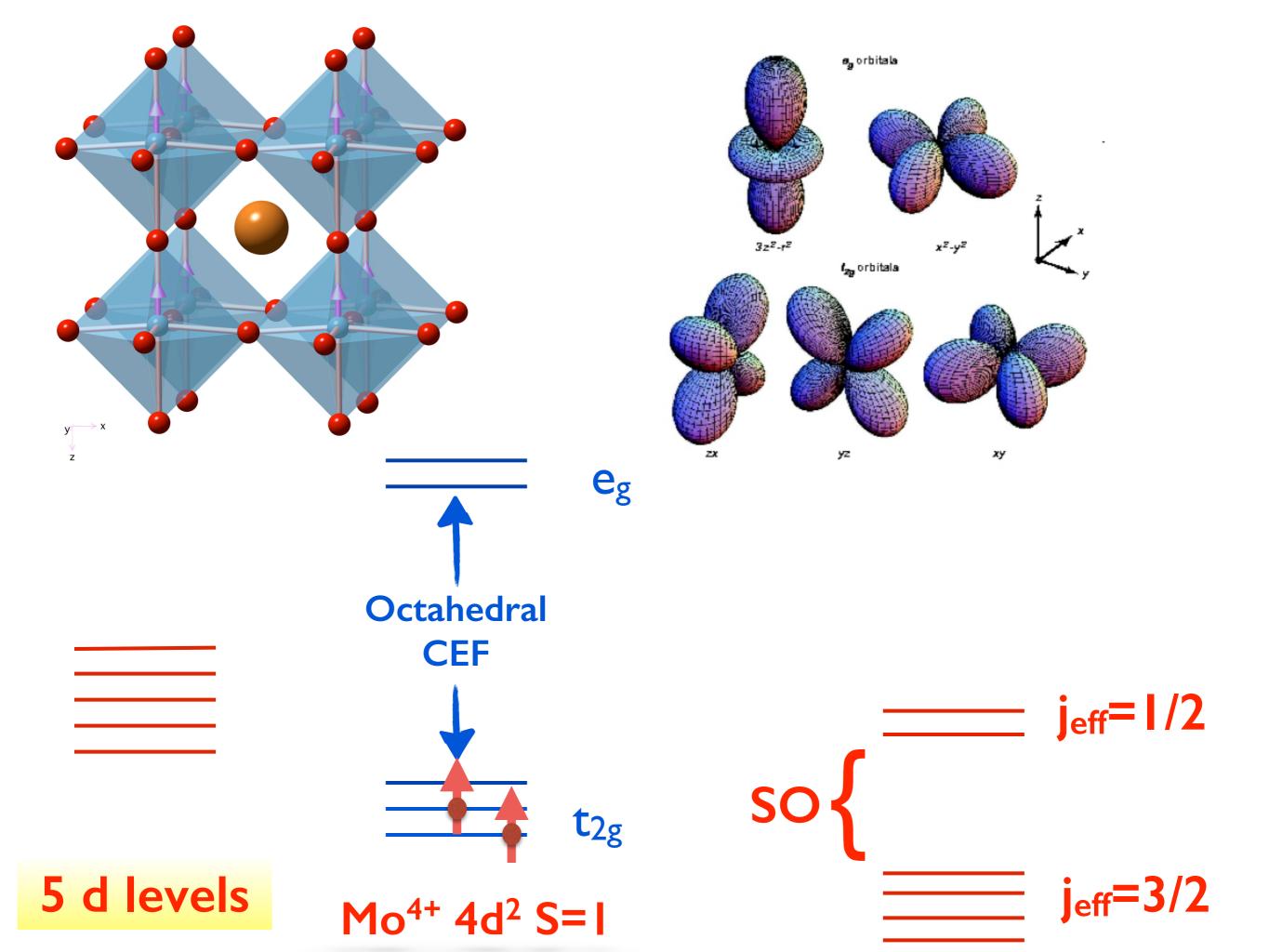
**SOC**- 74

\*lanthanoids

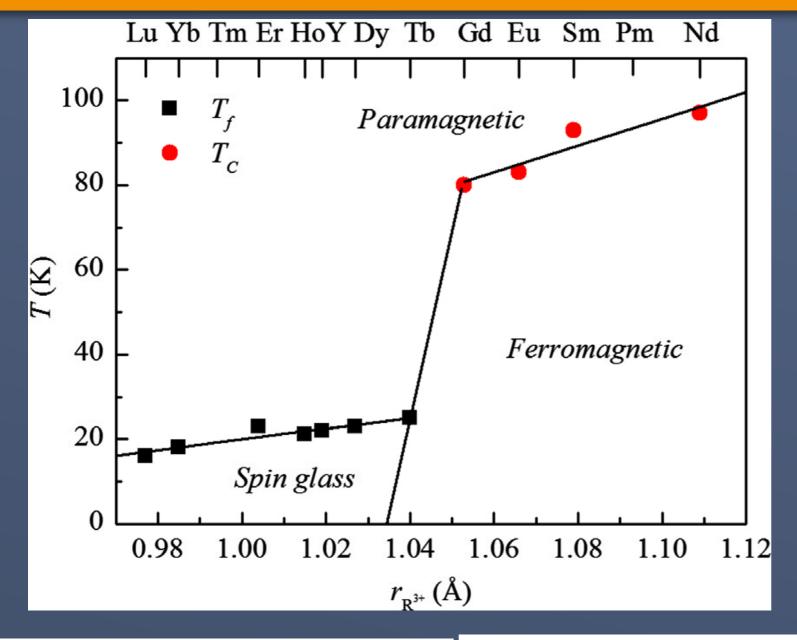
70 Pr Sm Tb Dy Er Ce Nd Eu Gd Ho Yb La Pm [144.91] 150.36(2) 158.93 138.91 140.91 144.24 157.25(3) 167.26 173.05 100 102 Bk U Es Md No Ac Np Fm Am Cm

\*\*actinoids





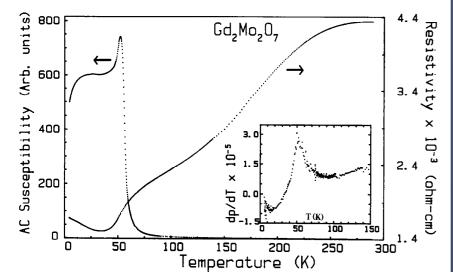
#### MIT in Rare Earth Molybdate Pyrochlores

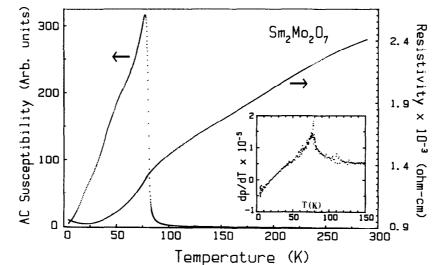


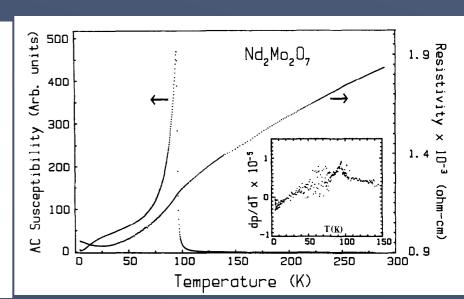
L. Clark et al., J. Sol. State Chem, 203, 199, 2013

> N. Ali et al., J. Sol. State Chem, 83, 178, 1989

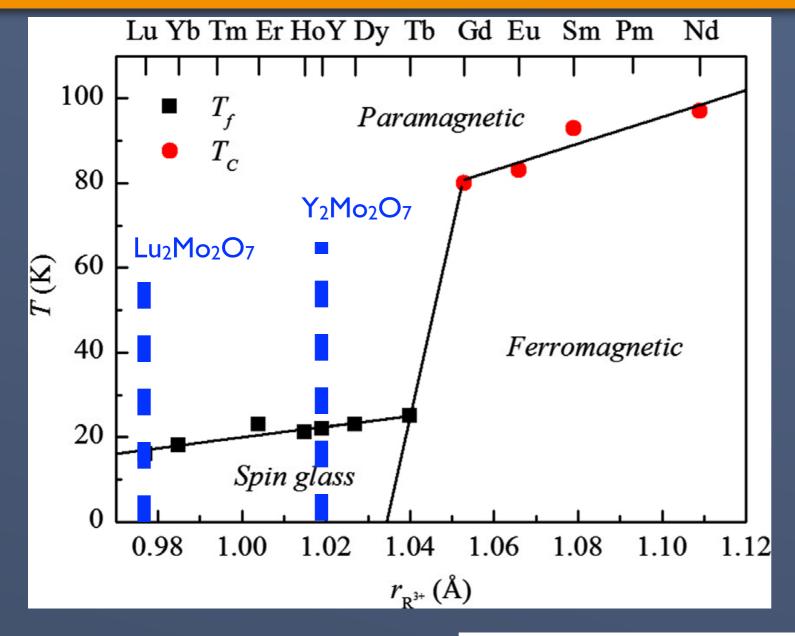








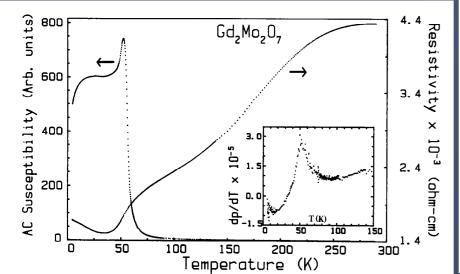
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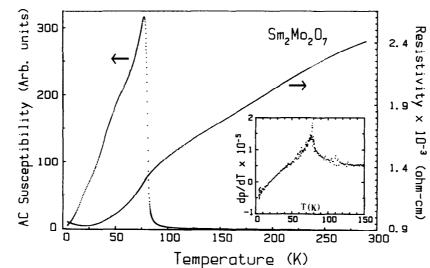


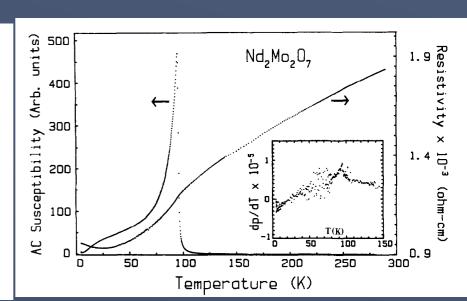
L. Clark et al., J. Sol. State Chem, 203, 199, 2013

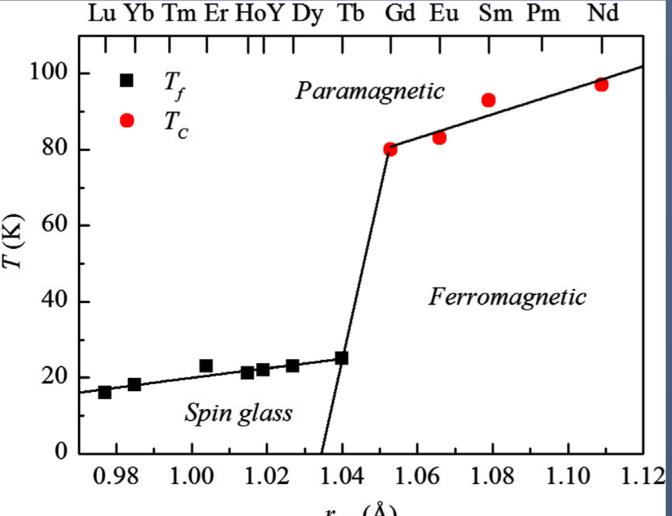
> N. Ali et al., J. Sol. State Chem, 83, 178, 1989











0

1.02

1.04

1.06

1.08

*Ln*<sup>3+</sup> ionic radius (Å)

# 8 1.00 1.02 1.04 1.06 1.08 1.10 1.12 $r_{R^{3+}}(\text{Å})$ Semiconductor Semimetal Metal 150 Ho Dy Tb Gd Eu Sm Semiconductor Semimetal Metal

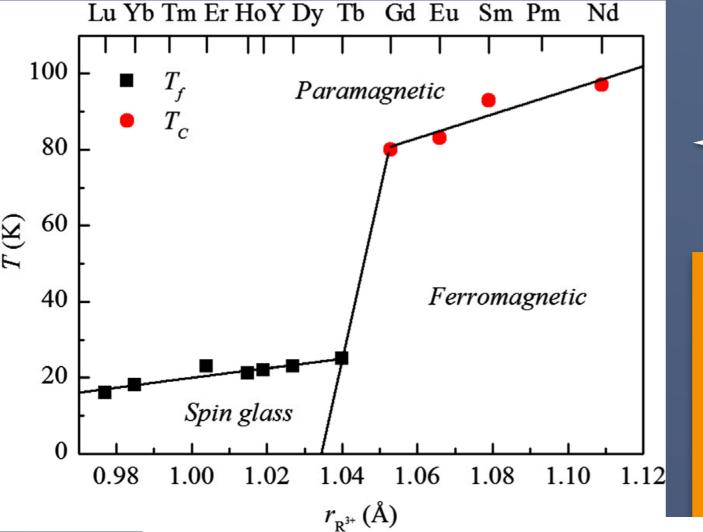
1.12 1.14

## Rare Earth Molybdates 4d<sup>2</sup>

# Comparing Cubic Pyrochlore Molybdates and Iridates

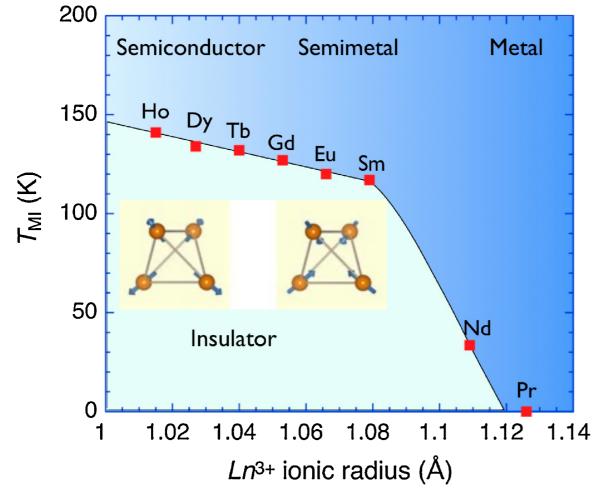
Rare Earth Iridates

5d<sup>5</sup>



## Rare Earth Molybdates 4d<sup>2</sup>

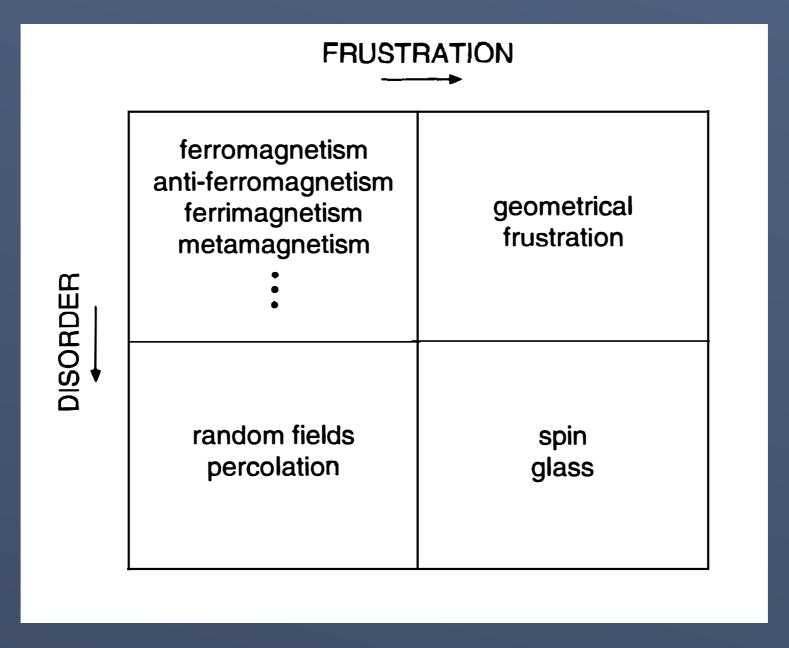
# Comparing Cubic Pyrochlore Molybdates and Iridates



Rare Earth Iridates

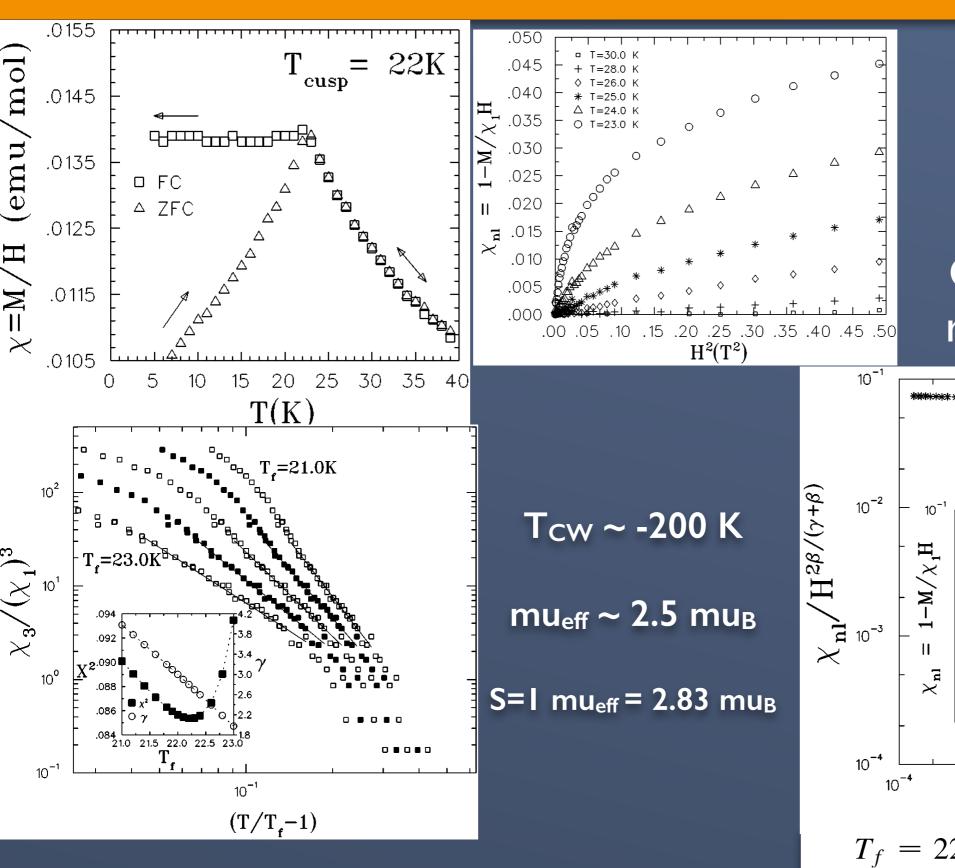
5d<sup>5</sup>

#### Conventional View of Magnetic Ground States Selected by Frustration and Disorder



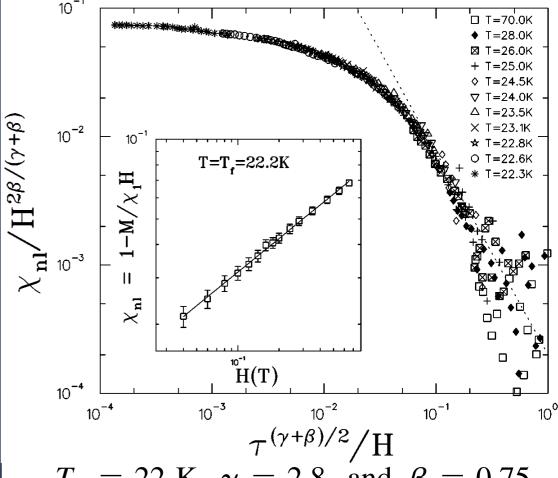
A.P. Ramirez, Ann. Rev. Mat. Sci., 1994

#### Spin Glass Transition at T<sub>f</sub> ~ 22 K in Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>



Thermodynamic phase transition at  $T_f \sim 22 \text{ K}$ 

Criticality typical of random spin glasses

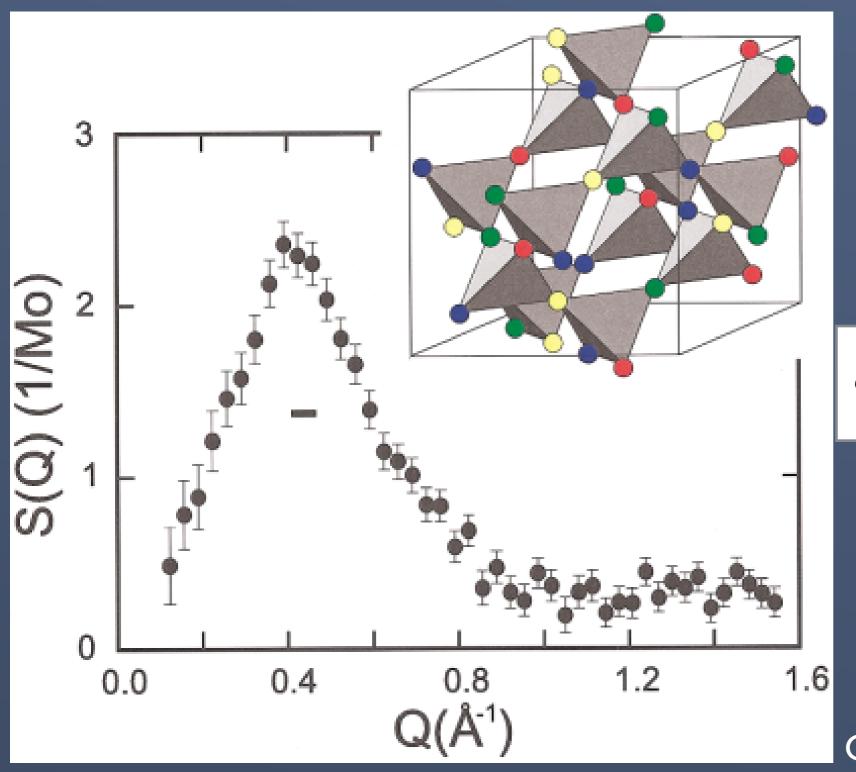


 $T_f = 22 \text{ K}, \ \gamma = 2.8, \ \text{and} \ \beta = 0.75.$   $\delta = 4.73$ 

Gingras et al., PRL, 78, 947, 1997

#### Elastic Neutron Scattering from Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>

"Cluster Glass" with Qmax ~ 0.44 A<sup>-1</sup>

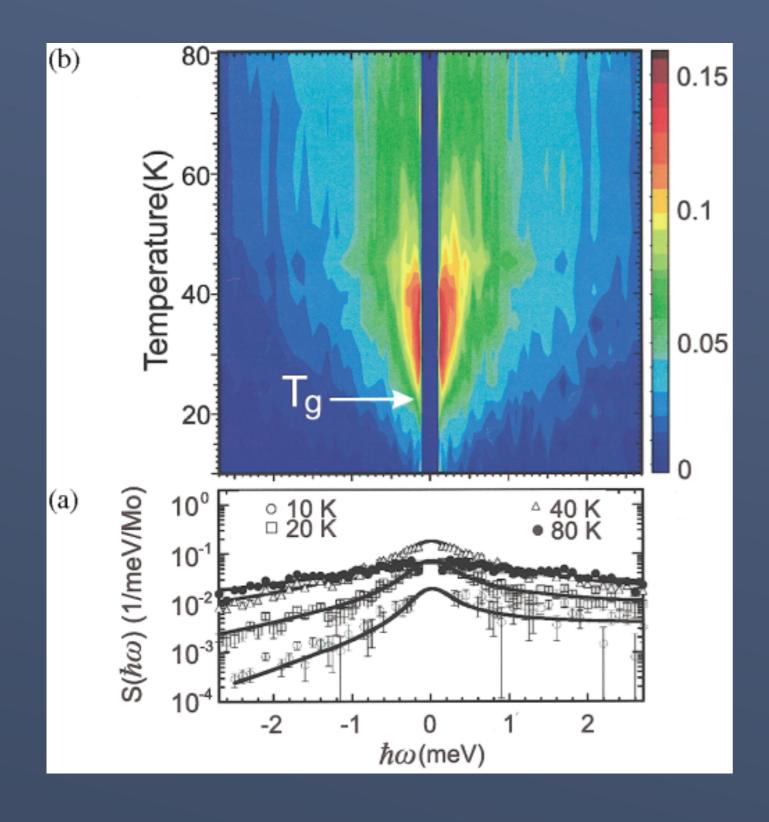


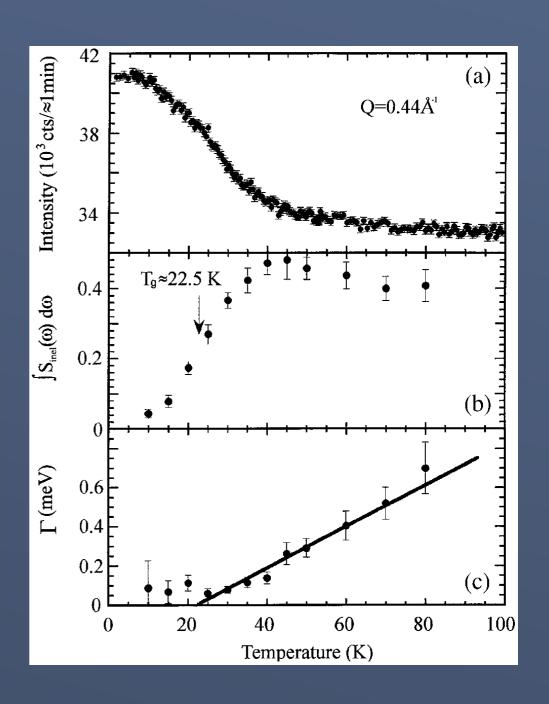
T=1.4 K - 50 K

 $\xi \approx 1/\text{HWHM} \approx 5 \text{ Å},$ 

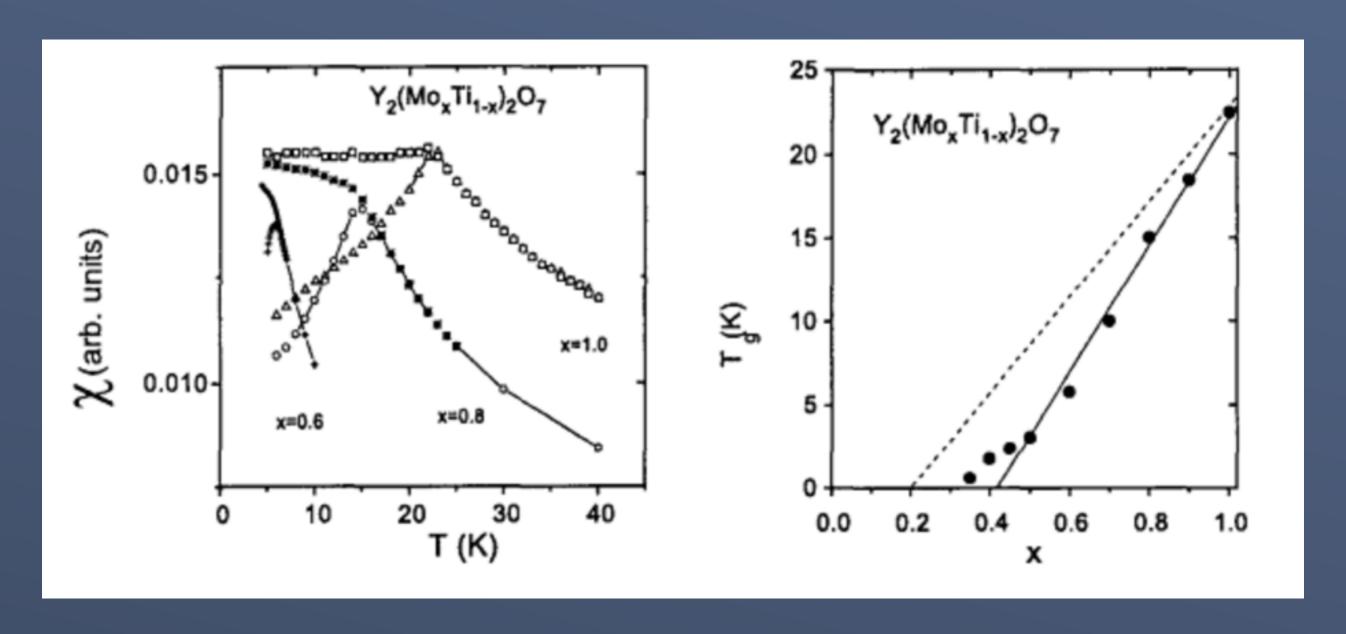
Gardner et al., PRL, 83, 211, 1999

#### Inelastic Neutron Scattering from Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>





#### 3D Percolation: Just another ordered state?



Site substitution with non-magnetic Ti<sup>4+</sup>

## Structural Disorder in Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> definitely low, but is it measurable?

PHYSICAL REVIEW B 79, 014427 (2009)



Local and average structures of the spin-glass pyrochlore Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> from neutron diffraction and neutron pair distribution function analysis

J. E. Greedan, Delphine Gout, A. D. Lozano-Gorrin, Shahab Derahkshan, Th. Proffen, H.-J. Kim, E. Božin, and S. J. L. Billinge

#### Neutron PDF

- Weak Y-O' disorder
- No Mo-Mo disorder

RAPID COMMUNICA

PHYSICAL REVIEW B

VOLUME 62, NUMBER 2

1 JULY 2000-II

Local lattice disorder in the geometrically frustrated spin-glass pyrochlore Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>

C. H. Booth, <sup>1,2</sup> J. S. Gardner, <sup>2</sup> G. H. Kwei, <sup>2</sup> R. H. Heffner, <sup>2</sup> F. Bridges, <sup>3</sup> and M. A. Subramanian <sup>4</sup>

**XAFS** 

Weak Mo-Mo disorder

VOLUME 87, NUMBER 17

PHYSICAL REVIEW LETTERS

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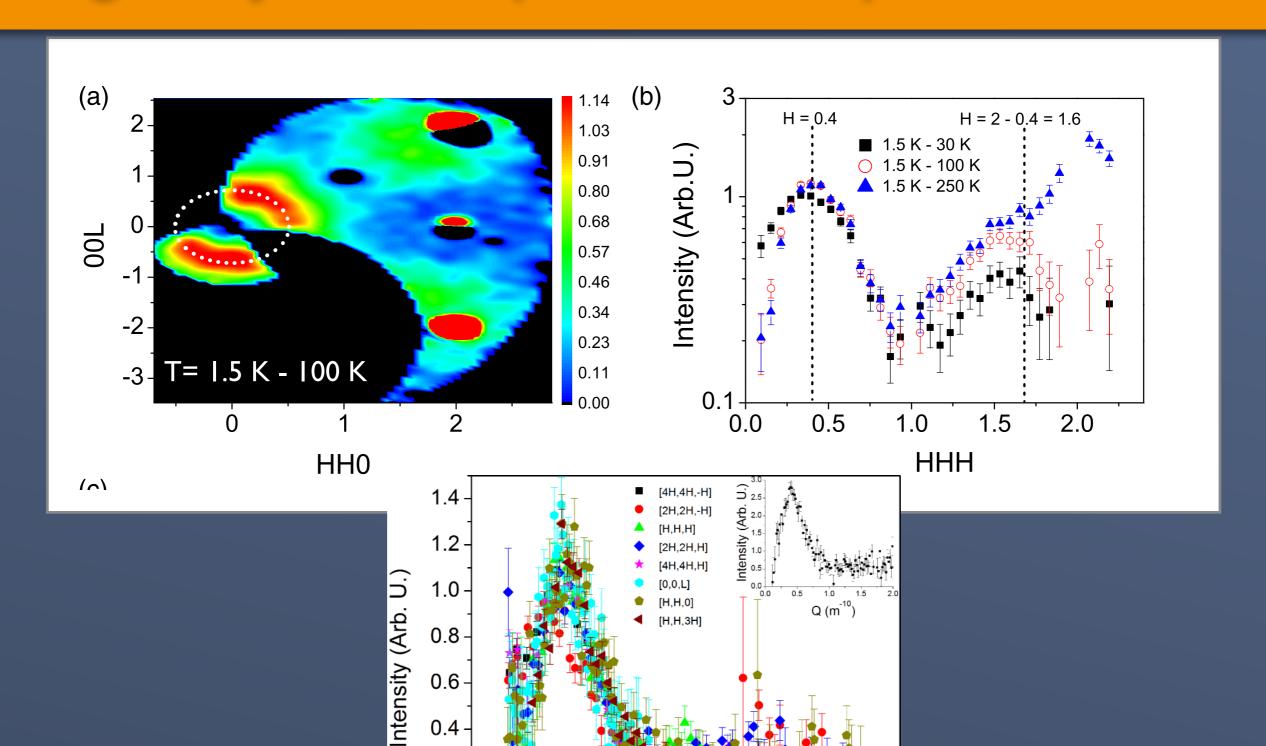
Frustration Driven Lattice Distortion: An NMR Investigation of Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>

Amit Keren<sup>1</sup> and Jason S. Gardner<sup>2</sup>

89Y NMR

Weak Mo-Mo disorder

#### Single Crystal Samples: Real Liquid Correlations!



0.4

0.2

0.0

0.0

0.5

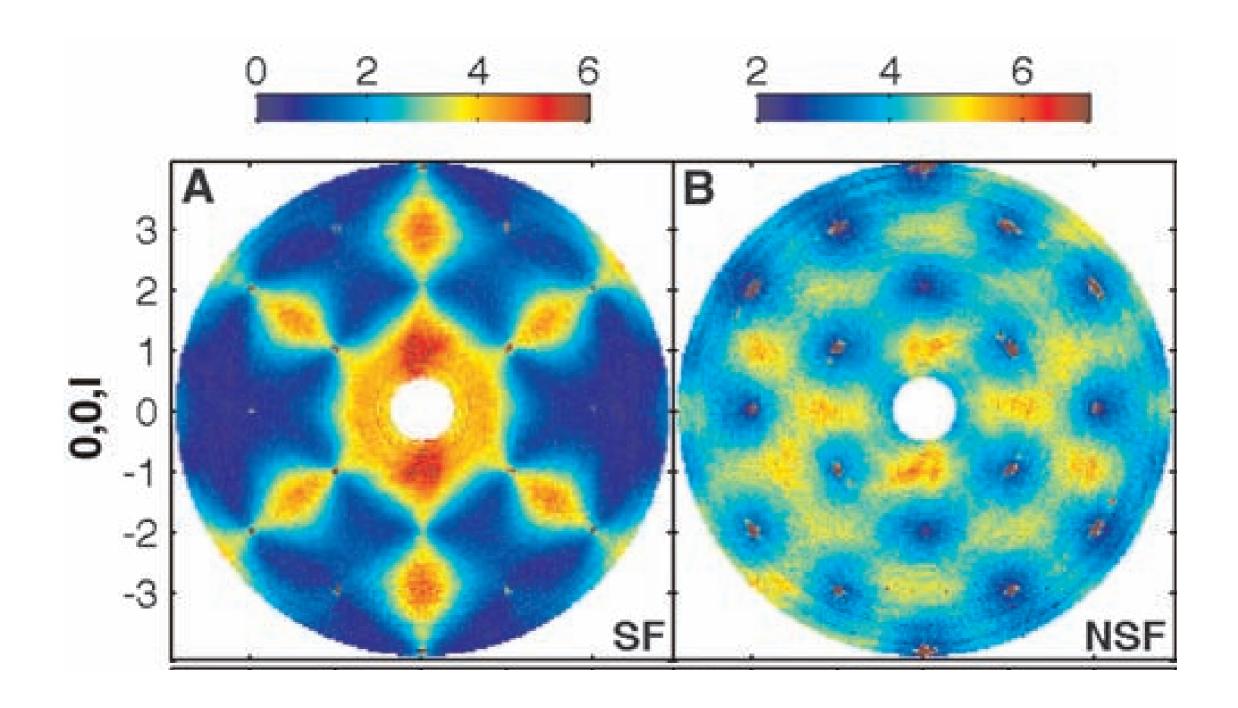
2.0

Q (m<sup>-10</sup>)

2.5

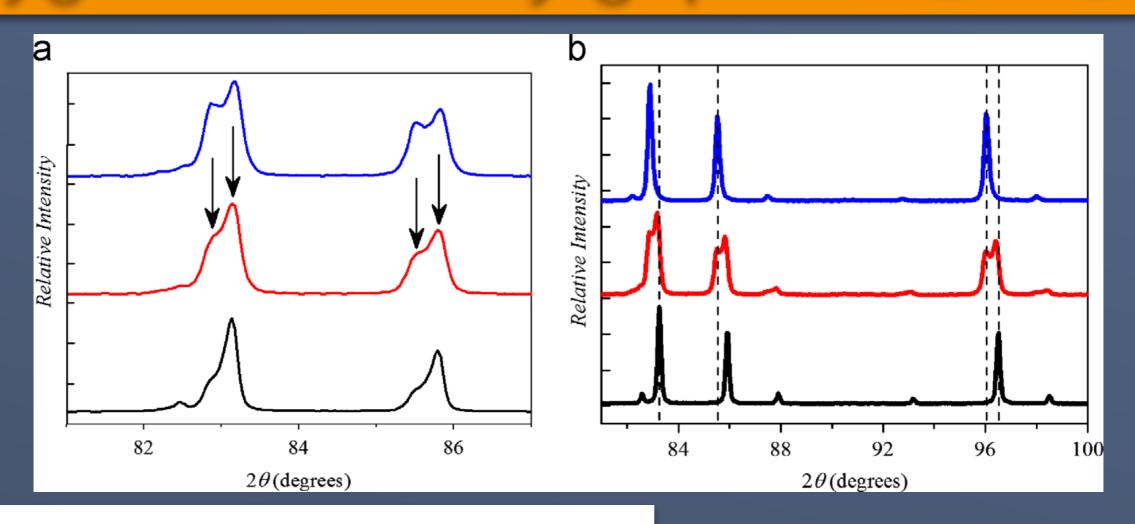
Silverstein et al., PRB, 89, 054433, 2014

#### Spin Ice Ground State in Ho<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>



T. Fennell et al., Science, 326 (5951): 415-417 (2009)

## Oxygen miscibility gap in Lu<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>

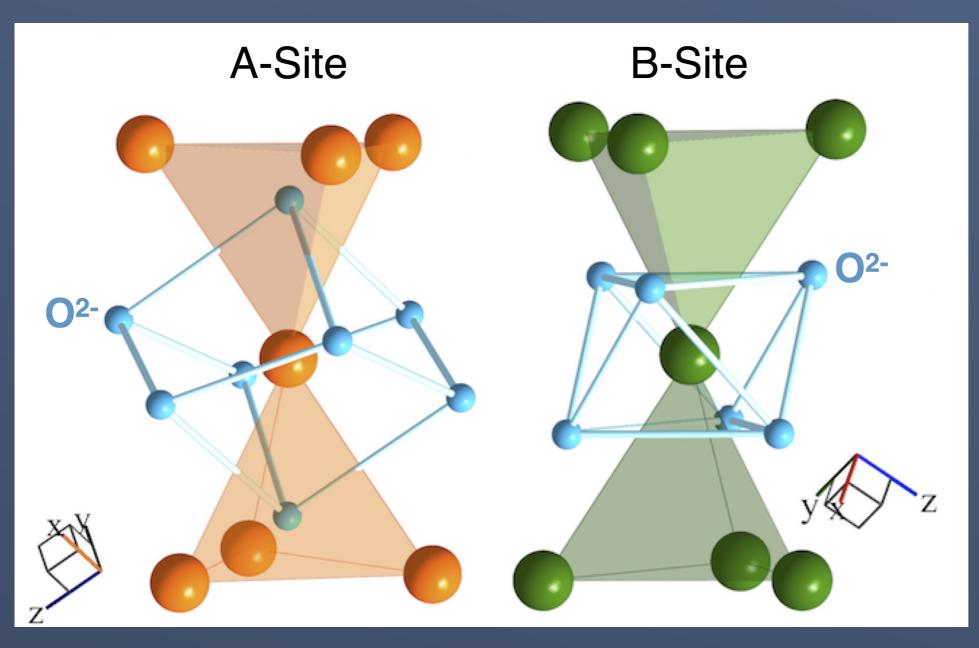


**Table 1** Refined atomic coordinates and occupancies for  $Lu_2Mo_2O_7$  (a=10.1478(1) Å) and (lower values where different) for  $Lu_2Mo_2O_{6.69(6)}$  (a=10.1789(1) Å). Isotropic U-factors were 0.0091(2) Å<sup>2</sup> for metal cations and 0.0152(3) Å<sup>2</sup> for oxygen sites. Residuals for the combined refinement were  $R_{wp}=5.83\%$ , and  $\chi^2=6.9$ .

Atom	Site	X	У	Z	Occupancy
Lu Mo O	16d 16c 48f 8b	0.5 0.0 0.3417(1) 0.3477(1) 0.375	0.5 0.0 0.125 0.375	0.5 0.0 0.125 0.375	1.0 1.0 1.0 0.97(1) 1.0 0.87(2)

L. Clark et al., J. Sol. State Chem, 203, 199, 2013

#### Local environments at the A<sup>3+</sup> and B<sup>4+</sup> sites:

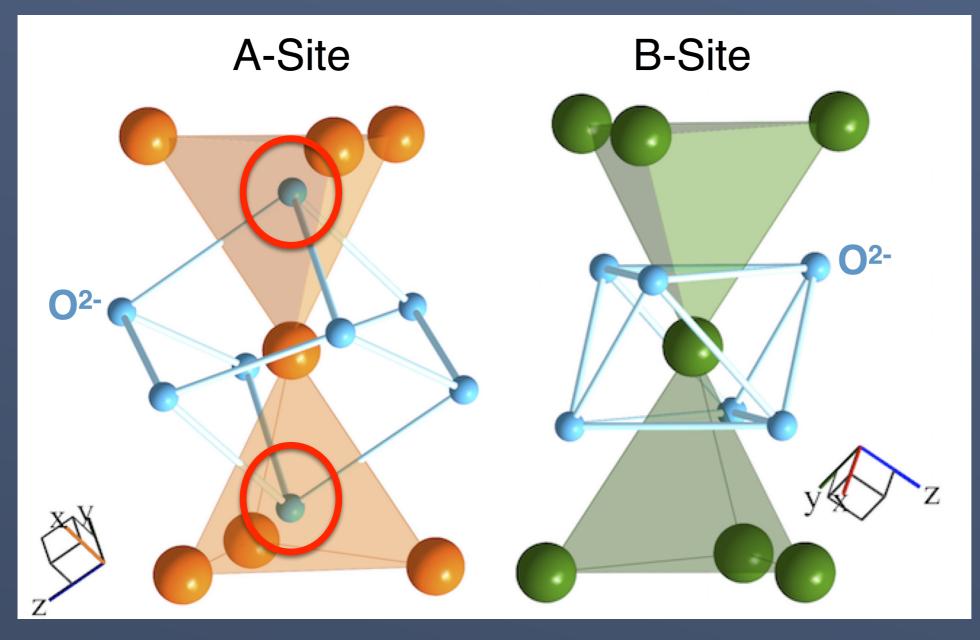


Rare earth site

Mo site

#### Local environments at the A<sup>3+</sup> and B<sup>4+</sup> sites:

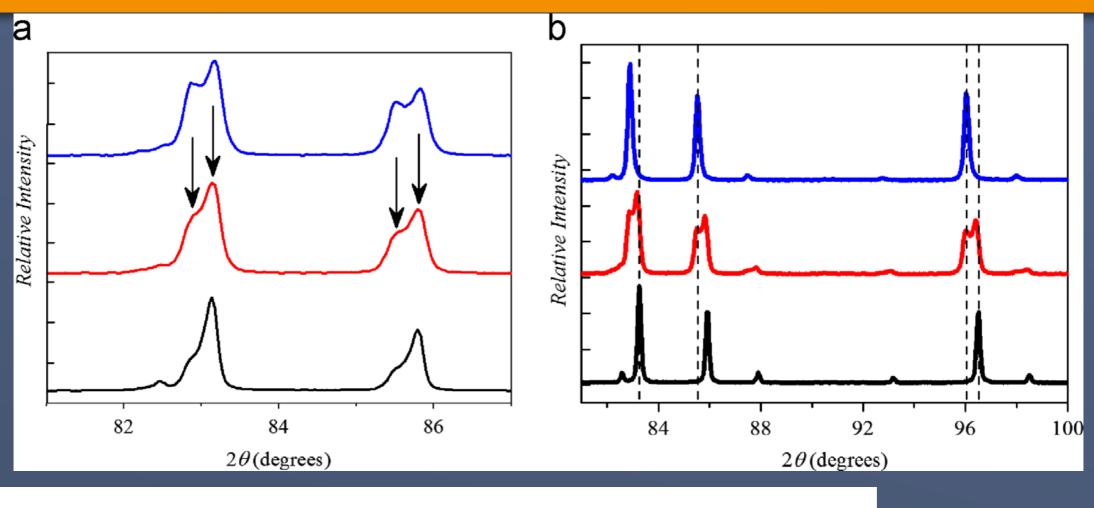
Lu<sub>2</sub>Mo<sub>2</sub>O<sub>6.7</sub> oxygen deficiency is primarily at the O' site

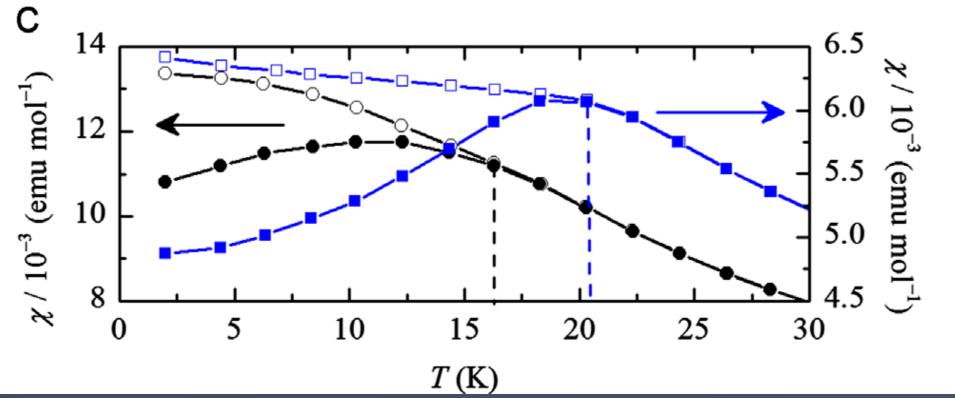


Rare earth site

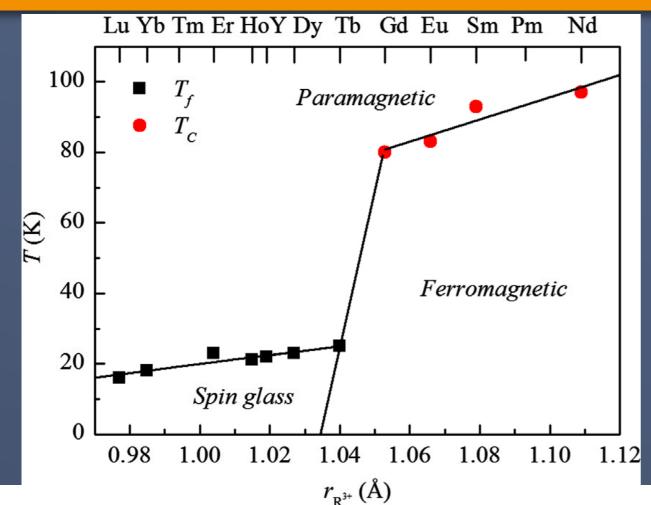
Mo site

#### Synthesize either Lu<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> or Lu<sub>2</sub>Mo<sub>2</sub>O<sub>6.7</sub>

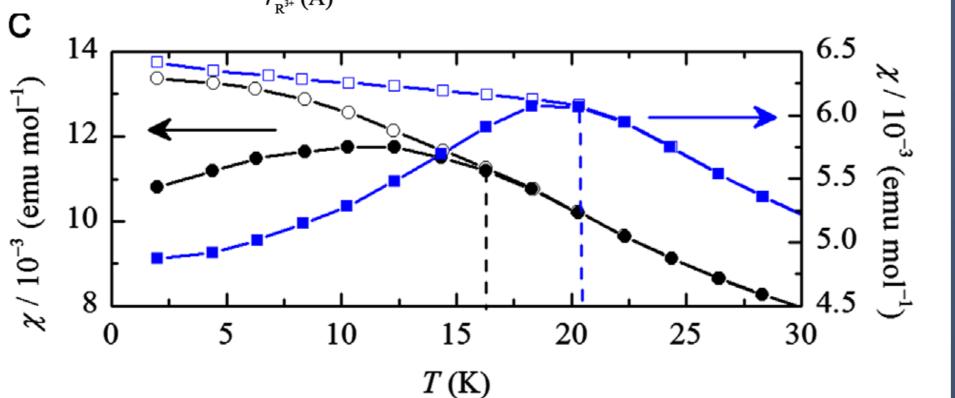




#### Lu<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> vs Lu<sub>2</sub>Mo<sub>2</sub>O<sub>6.7</sub>



Increase in  $T_f$  due in part to expansion of the lattice

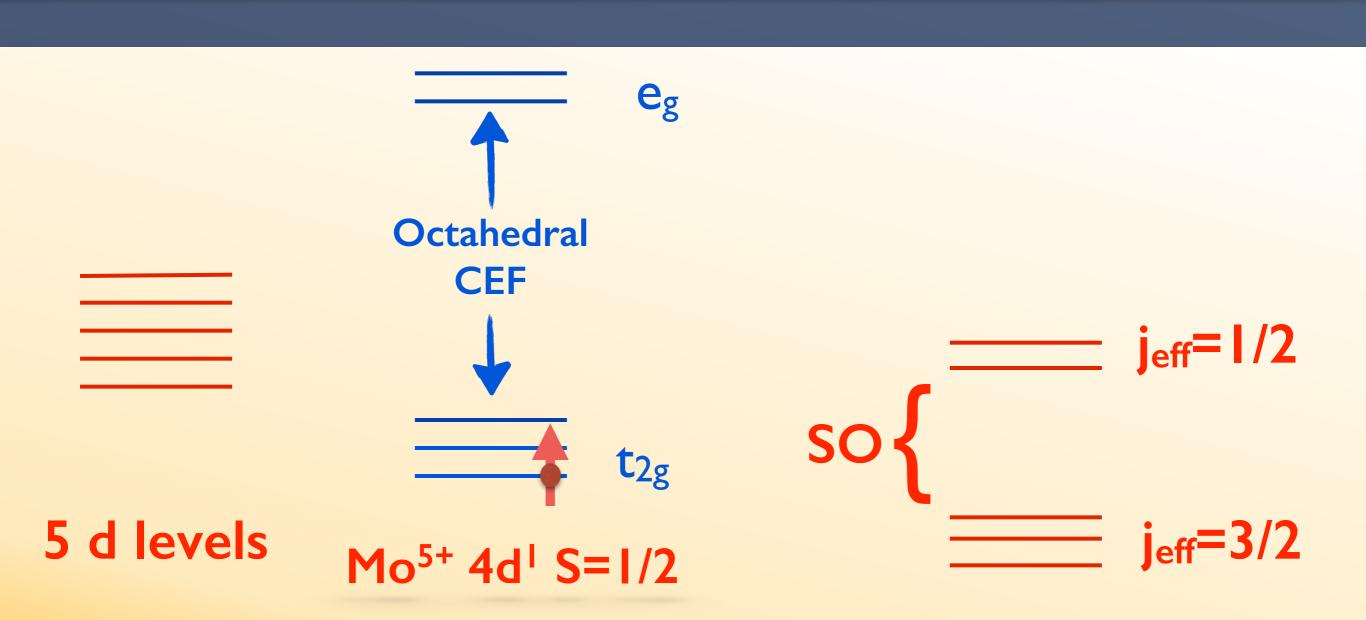


## Topochemical nitration of Lu<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>

$$Lu_{2}Mo_{2}O_{7} (Mo^{4+}, 4d^{2}, S = 1) \xrightarrow{NH_{3}(g), 250 \text{ cm}^{3} \text{ min}^{-1}} Lu_{2}Mo_{2}O_{5}N_{2} (Mo^{5+}, 4d^{1}, S = \frac{1}{2})$$

$$a = 10.1452(8) \text{ Å}$$

$$a = 10.1499(1) \text{ Å}$$



## Topochemical nitration of Lu<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>

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$$a = 10.1499(1) \text{ Å}$$

TABLE I. Refined atomic coordinates and occupancies for  $\text{Lu}_2\text{Mo}_2\text{O}_{4.8}\text{N}_{1.7}$  (a=10.1428(2) Å). Isotropic thermal parameters were 0.0337(6) Å<sup>2</sup> for metal cations and 0.0398(6) Å<sup>2</sup> for anion sites. Total  $R_{wp}=2.21$  %,  $\chi^2=14.58$  for 64 variables.

Atom	Site	x	$\overline{y}$	z	Occupancy
Lu	16d	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1.0
Mo	16c	$ar{0}$	$\bar{0}$	$\bar{0}$	1.0
O/N	48f	0.3477(1)	$\frac{1}{8}$	$\frac{1}{8}$	0.663(2)/0.257
O'/N'	8b	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	0.831/0.169

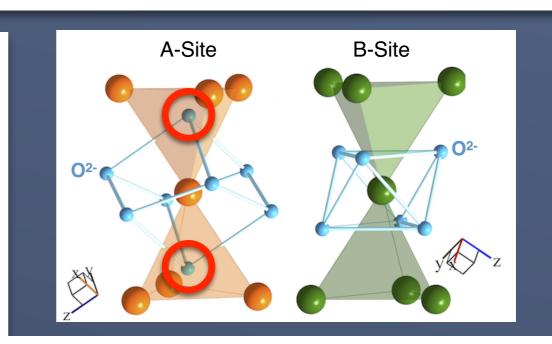


TABLE II. Results from the Curie Weiss fit to magnetic susceptibilities of the oxide and oxynitride pyrochlores.

Sample	Fit region / K	$\theta / K$	$\mu_{eff} / \mu_B$
	150 - 300	158(1)	1.89(1)
$Lu_2Mo_2O_7$	200 - 300	171(1)	1.92(1)
	250 - 300	184(2)	1.85(1)
	150 - 300	121(1)	1.11(1)
$Lu_2Mo_2O_5N_2$	200 - 300	135(1)	1.13(1)
	250 - 300	152(2)	1.16(1)

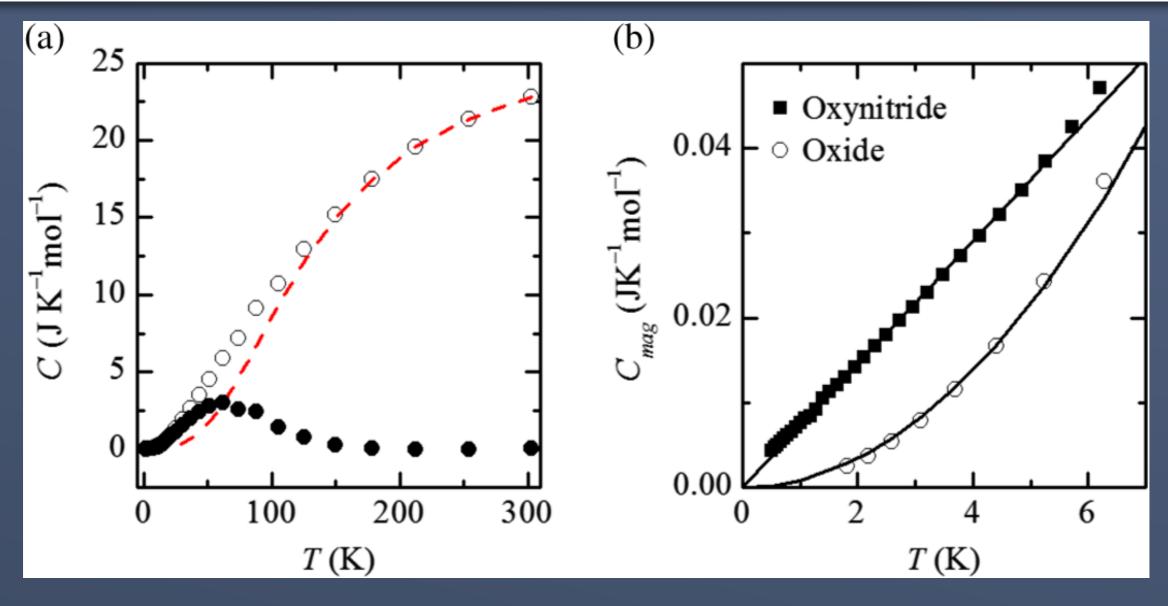
L. Clark et al., PRL, 113 117201, 2014

### Topochemical nitration of Lu<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>

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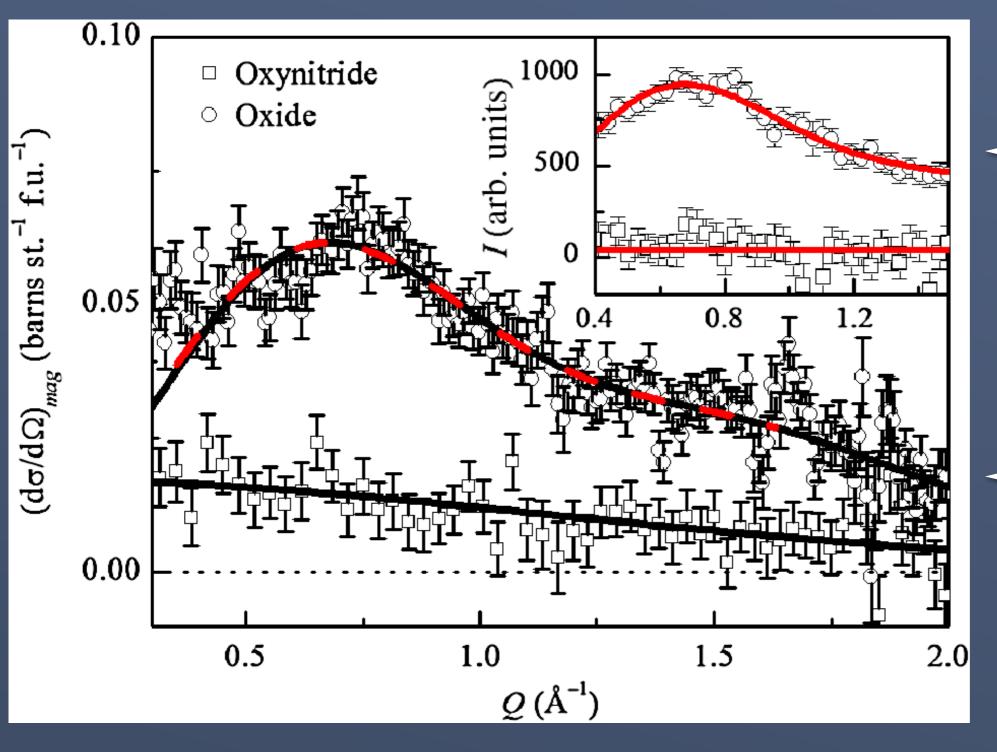
$$a = 10.1452(8) \text{ Å}$$

$$a = 10.1499(1) \text{ Å}$$



L. Clark et al., PRL, 113 117201, 2014

# Elastic Neutron Scattering: Lu<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> vs Lu<sub>2</sub>Mo<sub>2</sub>O<sub>5</sub>N<sub>2</sub>

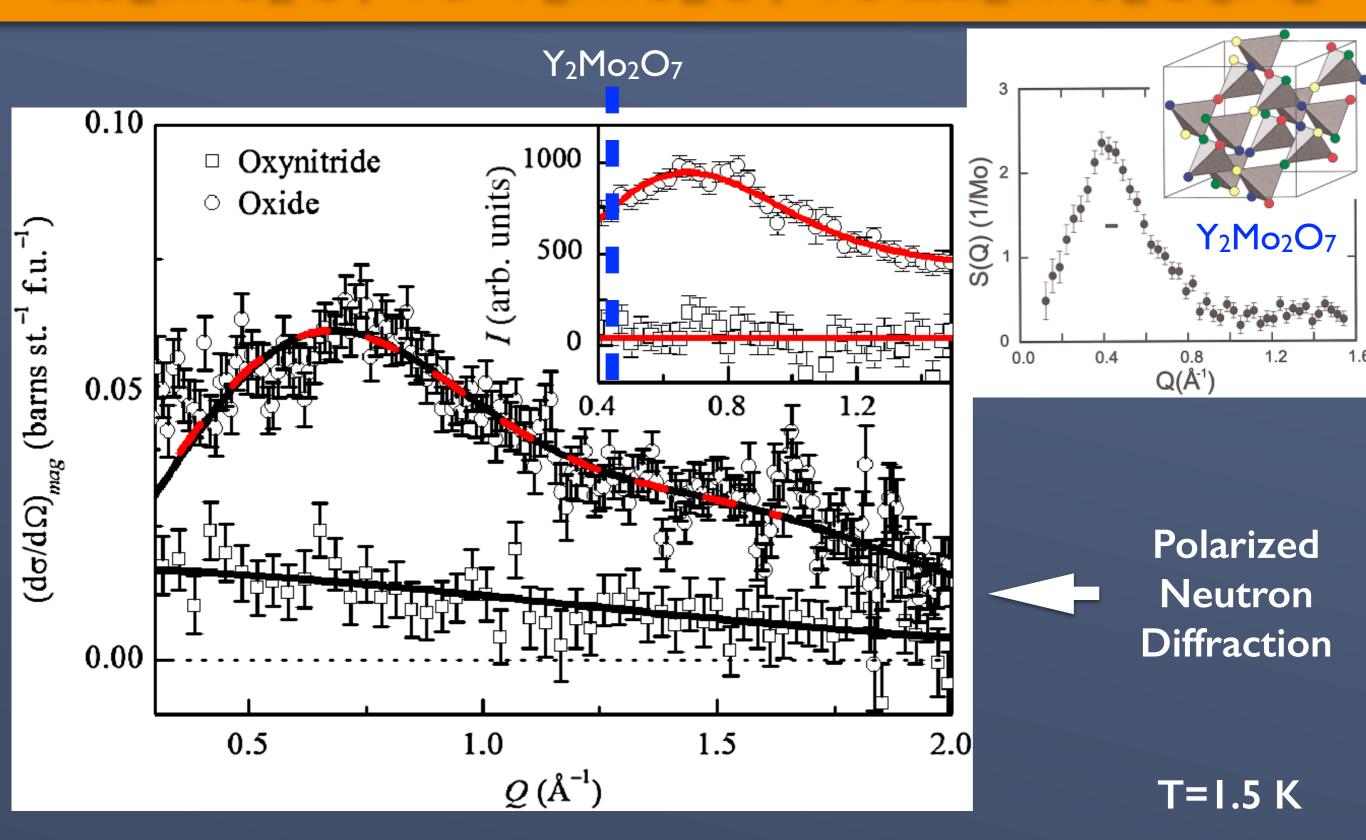


High
resolution
inelastic
scattering
res +/- 0.1 meV

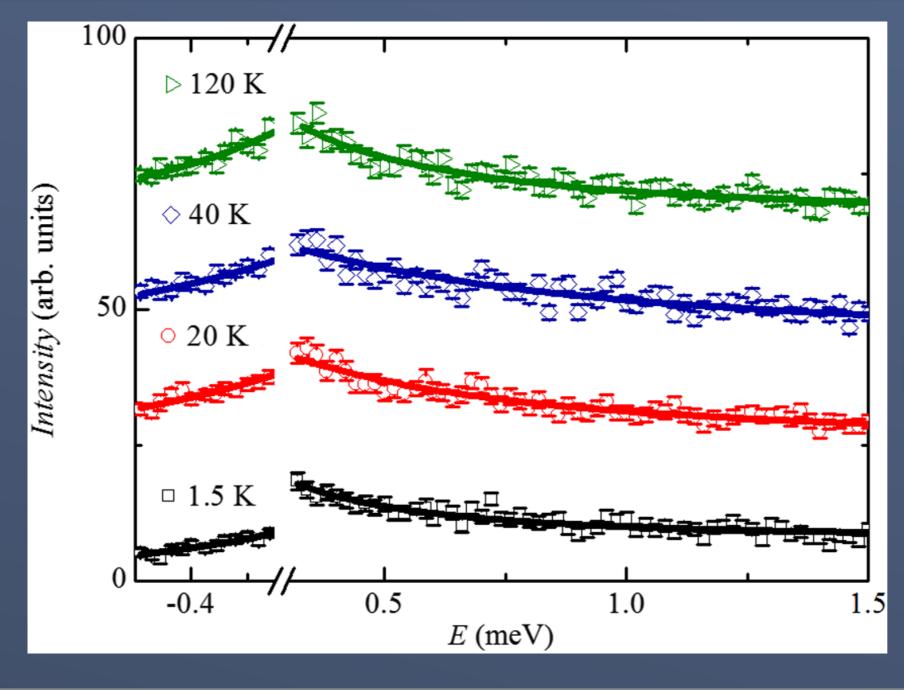


Polarized Neutron Diffraction

## Elastic Neutron Scattering: Lu<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> vs Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> vs Lu<sub>2</sub>Mo<sub>2</sub>O<sub>5</sub>N<sub>2</sub>



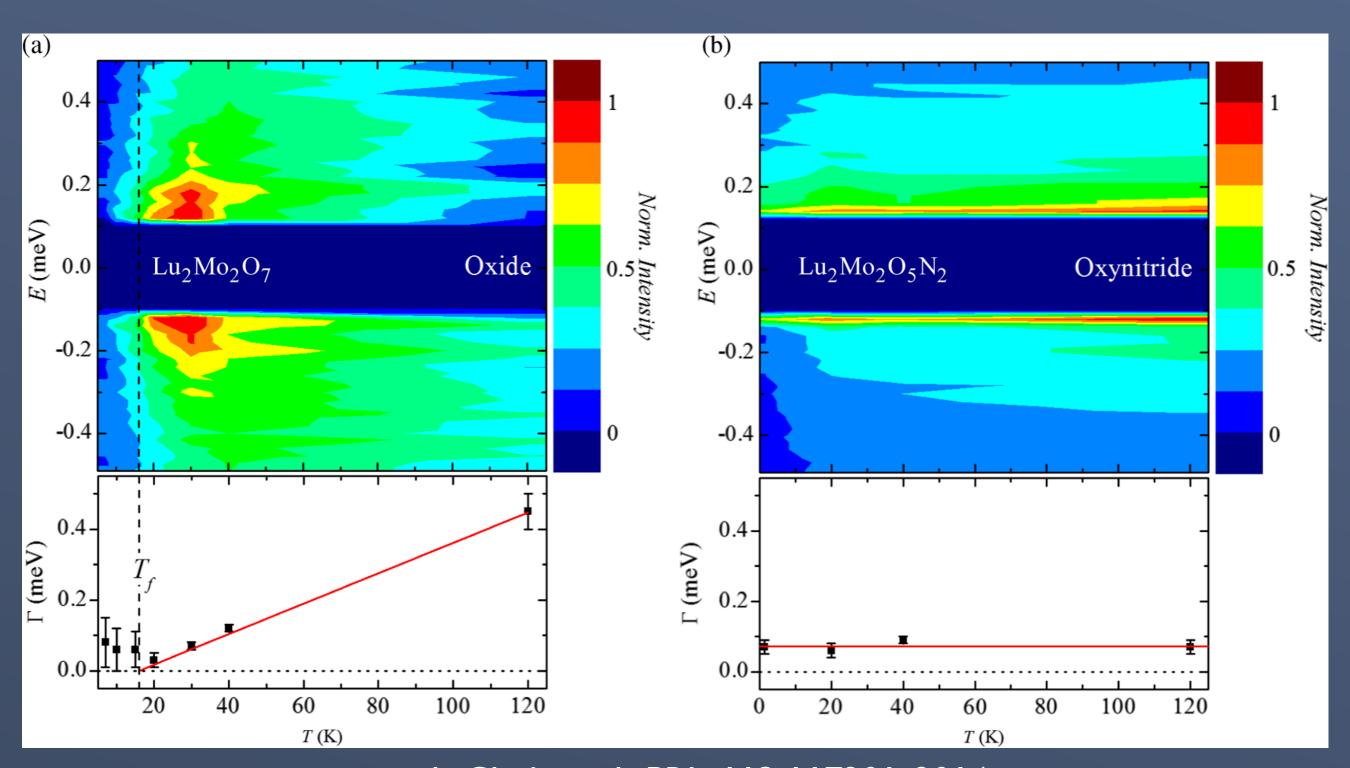
### Modeling the inelastic scattering



Lu<sub>2</sub>Mo<sub>2</sub>O<sub>5</sub>N<sub>2</sub>

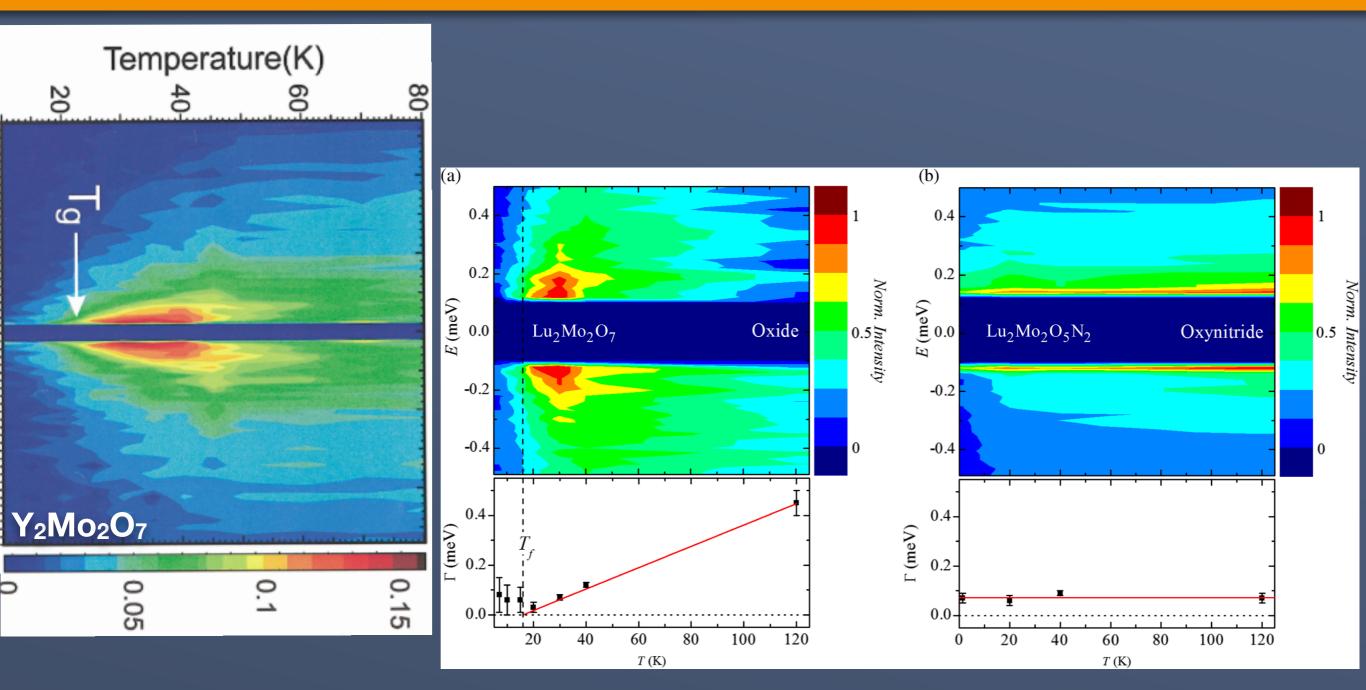
$$S(E) = \frac{1}{\pi} \chi''(E) [1 + n(E)], \quad \chi''(E) = \chi_0 \arctan\left(\frac{E}{\Gamma}\right)$$

# Inelastic Neutron Scattering: Lu<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> vs Lu<sub>2</sub>Mo<sub>2</sub>O<sub>5</sub>N<sub>2</sub>



L. Clark et al., PRL, 113 117201, 2014

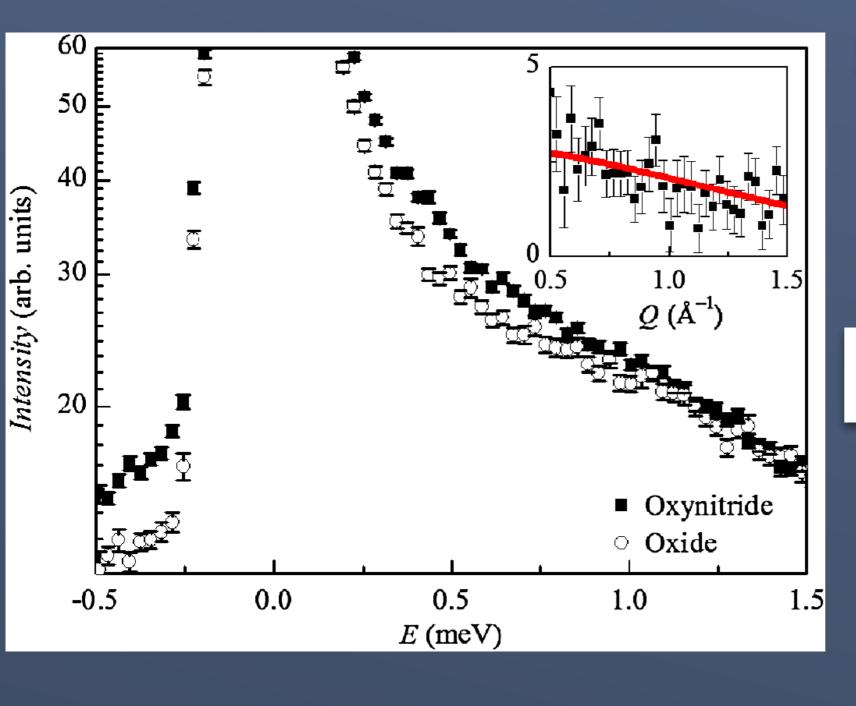
# Inelastic Neutron Scattering: Y<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> vs Lu<sub>2</sub>Mo<sub>2</sub>O<sub>5</sub>N<sub>2</sub>



S=1 Moly Oxides freeze at  $T_f \sim 20 \text{ K}$ 

S=1/2 Oxynitride doesn't freeze!

# Inelastic Neutron Scattering: Lu<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> vs Lu<sub>2</sub>Mo<sub>2</sub>O<sub>5</sub>N<sub>2</sub>



S=1/2 degrees of freedom are strongly fluctuating at T=1.5 K ~ 0.012 T<sub>CW</sub>

Gapless - with gap <

 $\Delta \sim 0.05 \text{ meV or } \Delta/|\theta| \sim 0.004$ 

Scattering follows  $F(Q)^2$  for  $Mo^{5+}$  only

#### Conclusions:

• TOF neutron techniques have made great recent advances, and are well suited to exotic magnetism as they measure very effectively across wide dynamic range in Q and energy

•  $R_2Mo_2O_7$  with heavy  $R^{3+}$  displays robust spin glass phase below  $\sim 20~K$ 

Disorder-free glassiness or role of weak disorder? Isotropic static, short range correlations at low T - why?

• Topochemical nitration of Lu<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> yields Lu<sub>2</sub>Mo<sub>2</sub>O<sub>5</sub>N<sub>2</sub> Variation of S=1/2 pyrochlore antiferromagnet? Gapless, strongly fluctuating ground state - no freezing!

## Collaboration:

