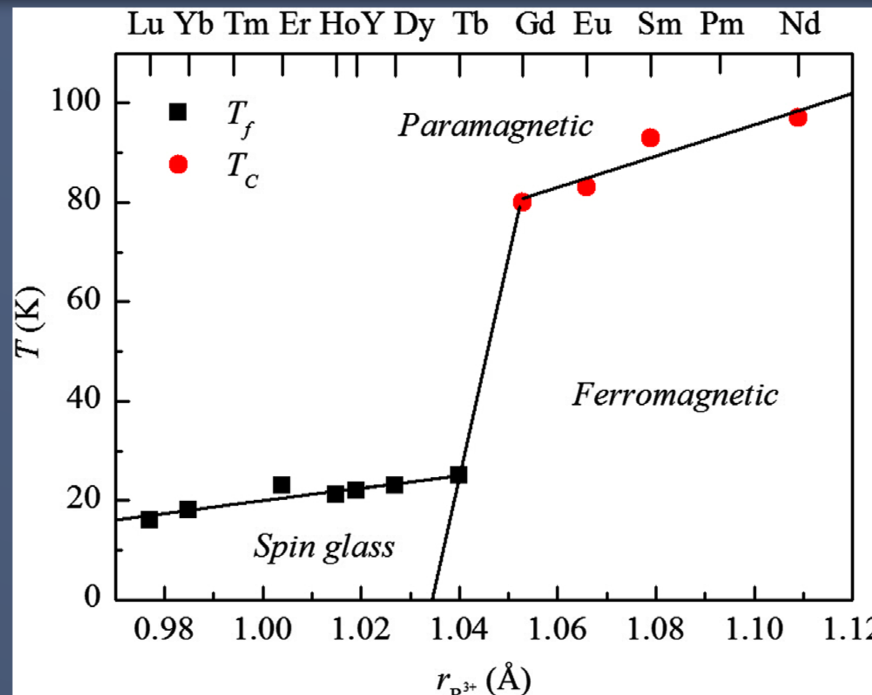
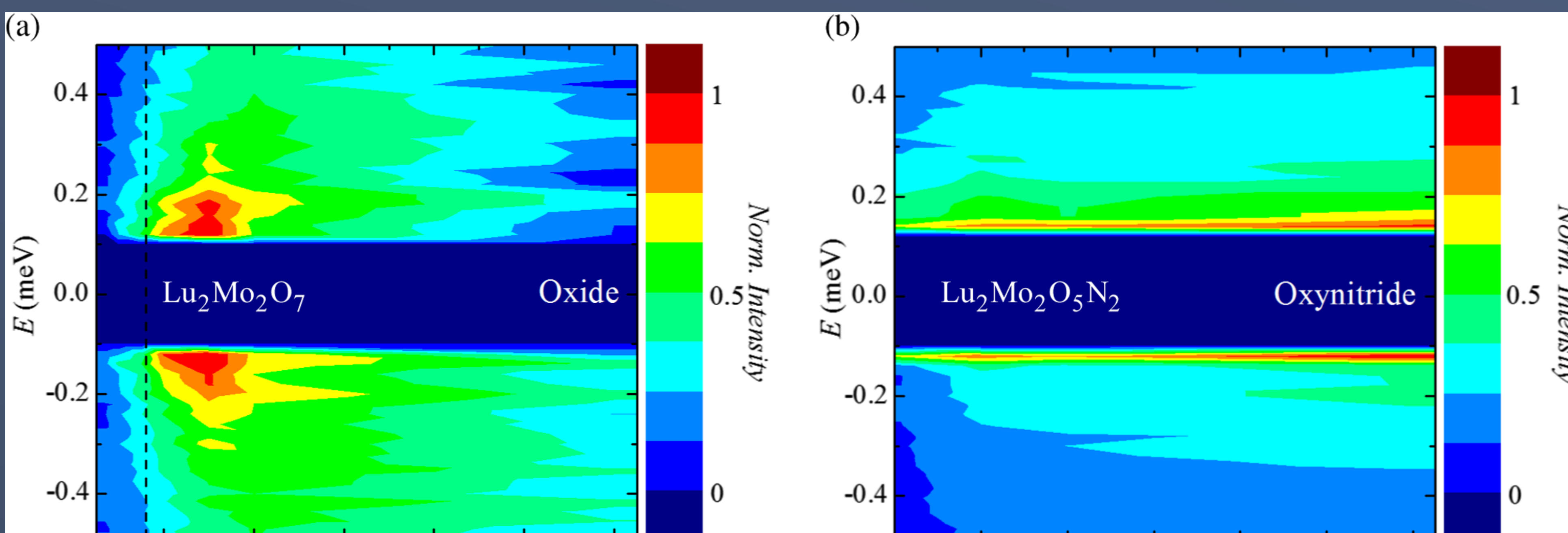
From Spin Glass to Spin Liquid Ground States in Molybdate Pyrochlores





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J. P. Attfield [6]
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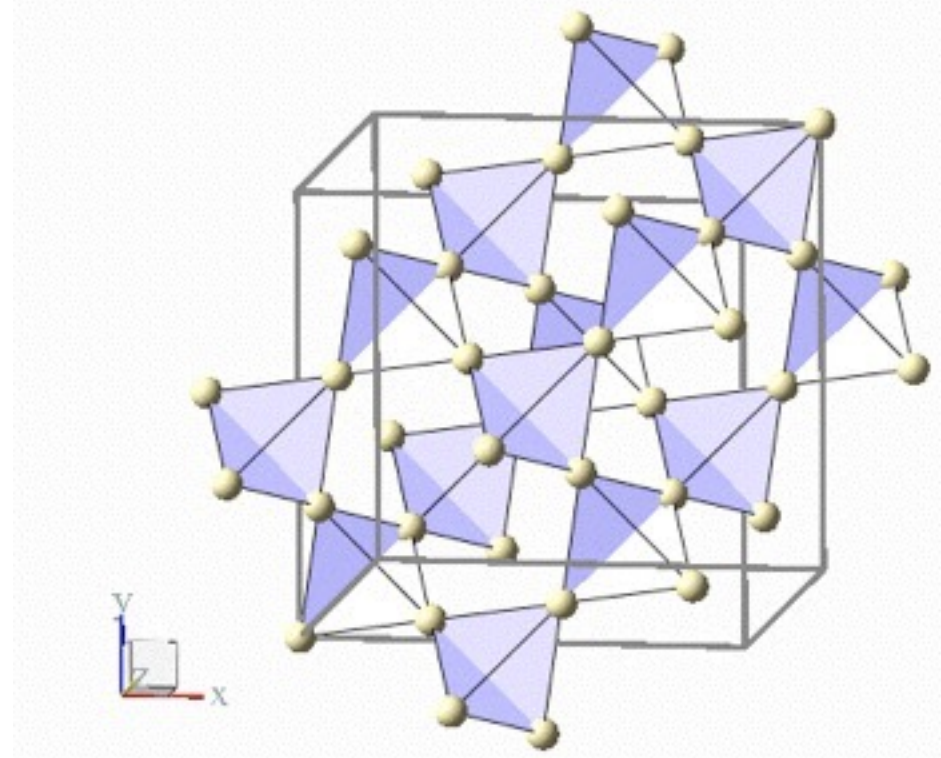
Geometric Frustration from Tetrahedra

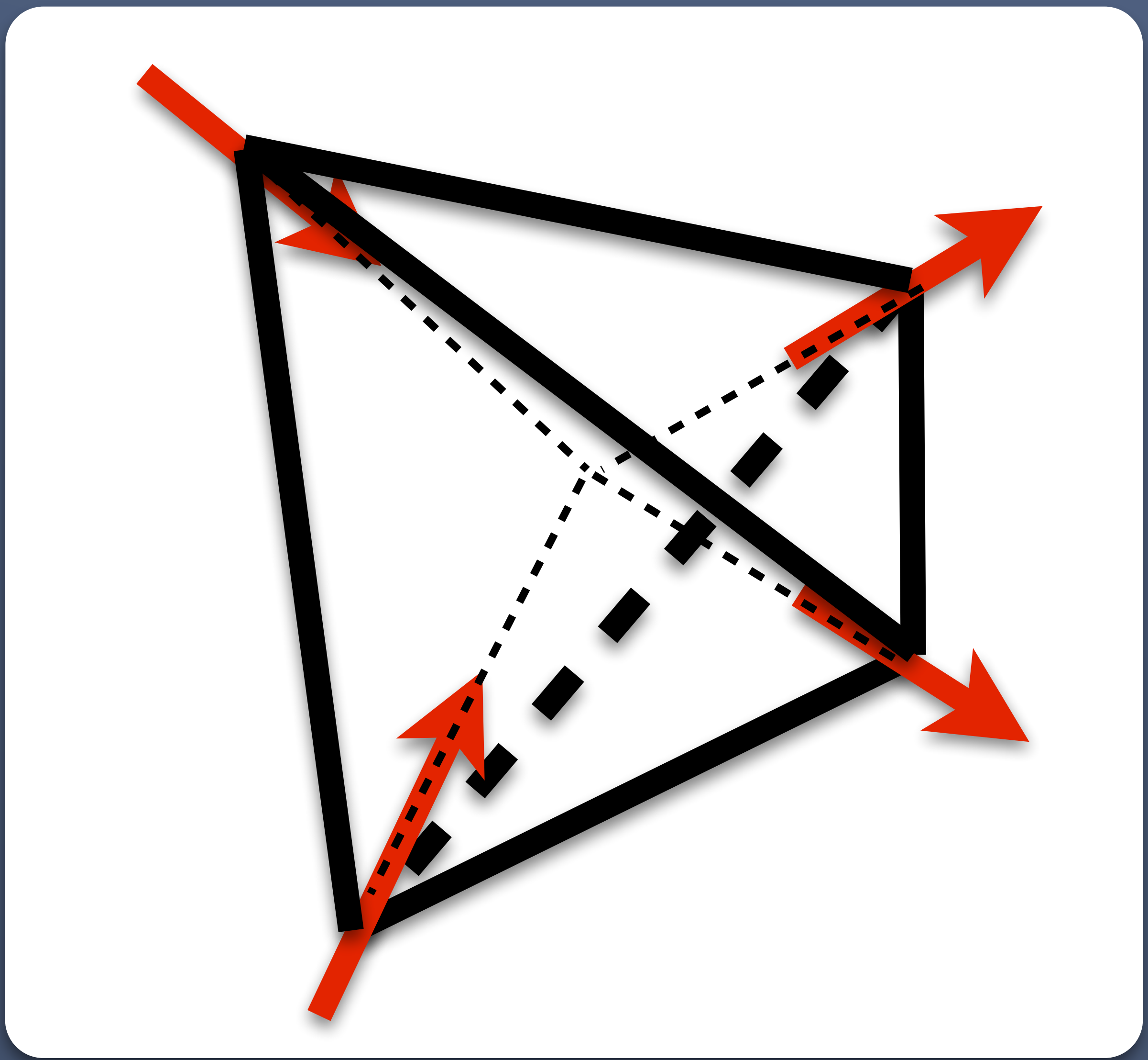


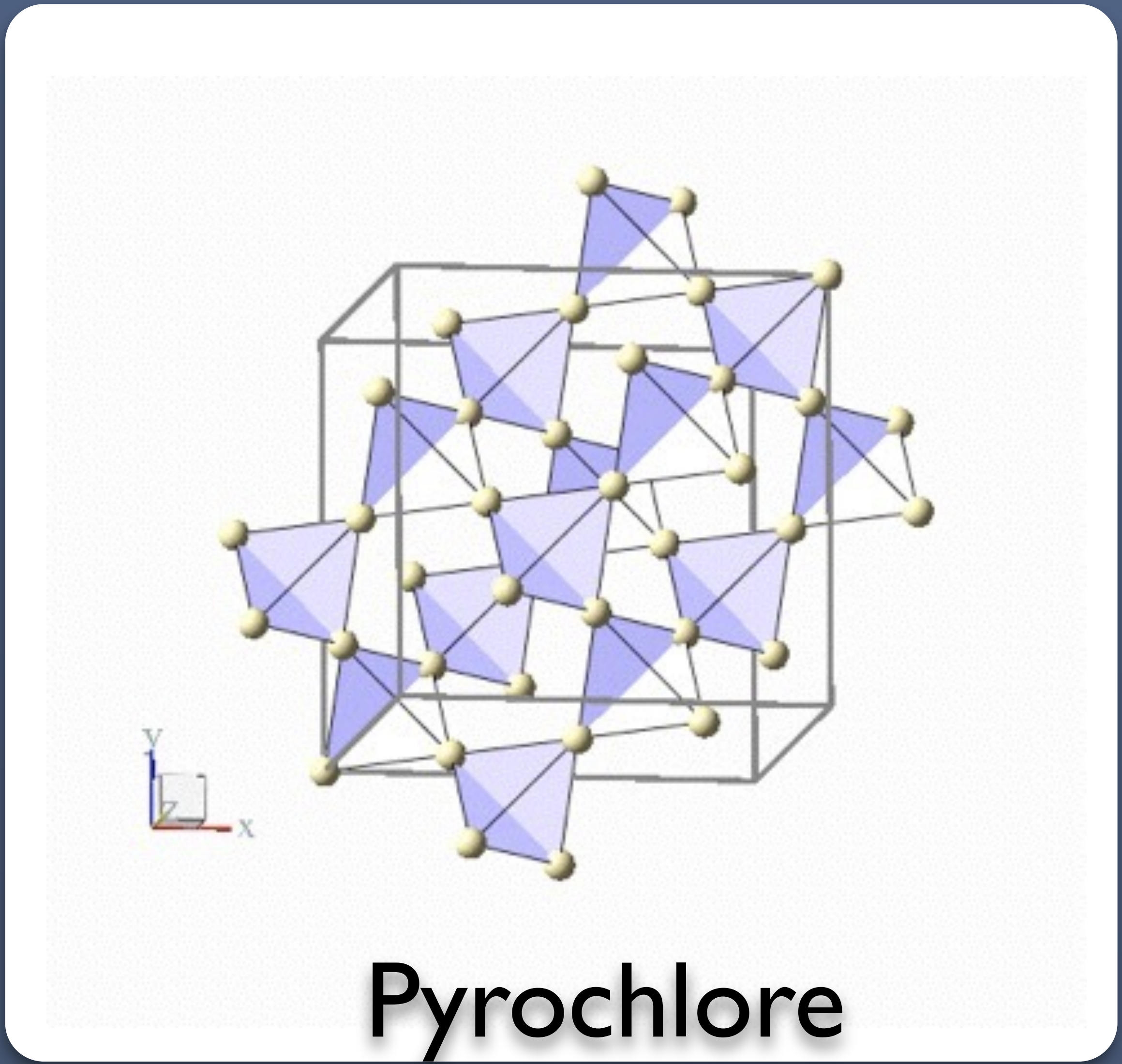
Pyrochlore

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.

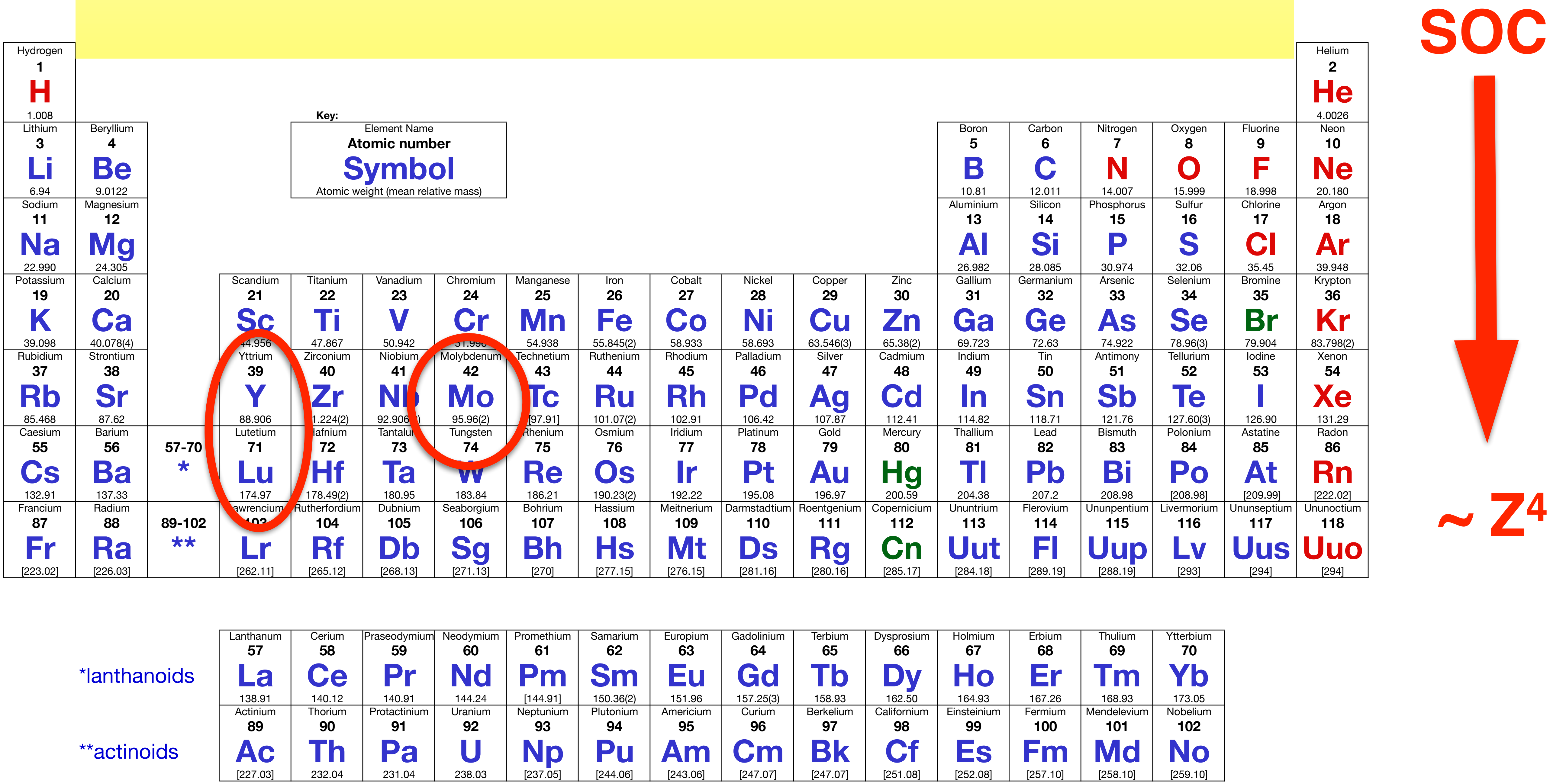
Macroscopic degeneracy for network of corner-sharing tetrahedra.

Cubic Pyrochlores: $A_2B_2O_7$

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

$Lu_2Mo_2O_7$: Mo^{4+} $4d^2$

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



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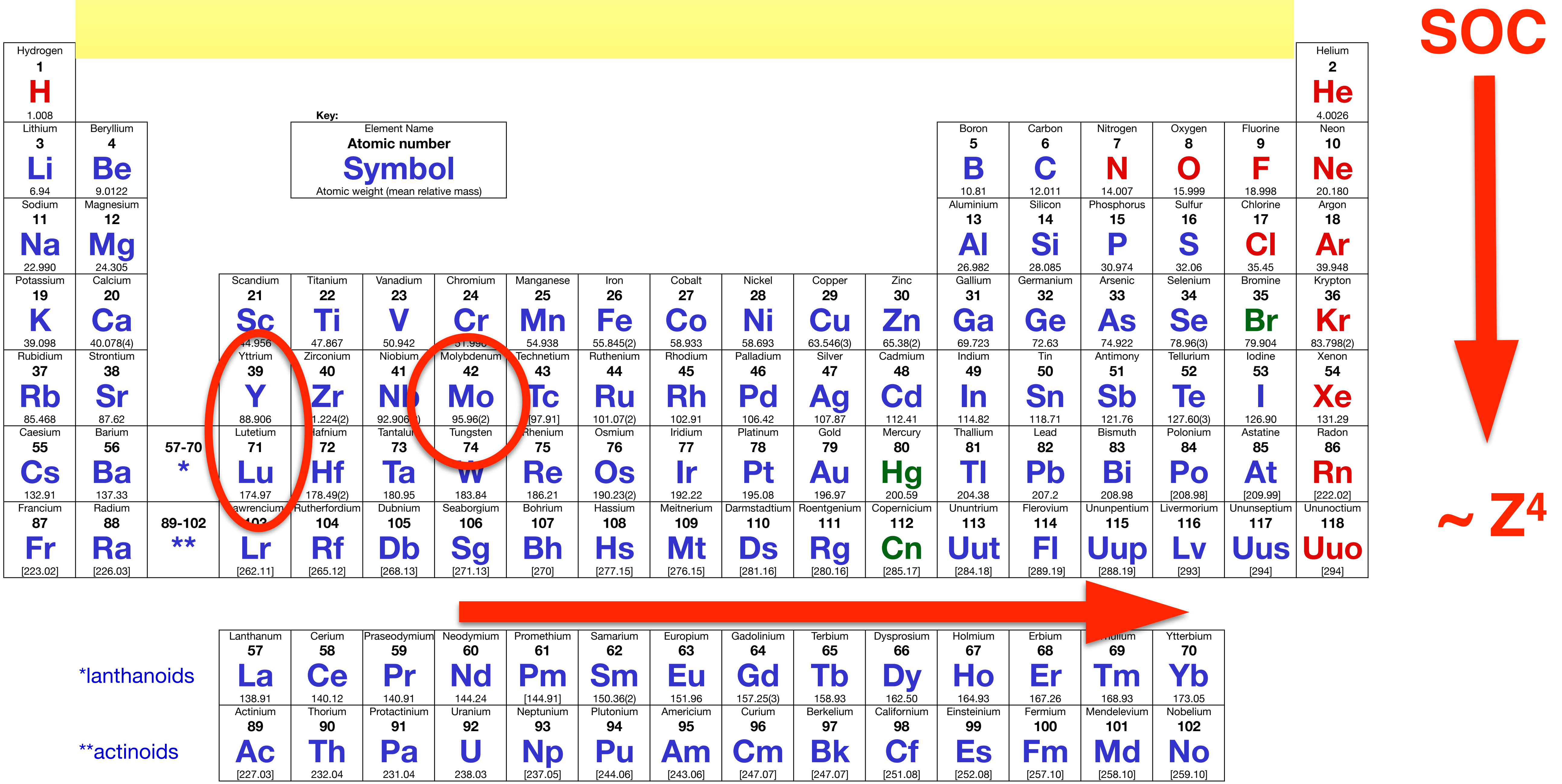

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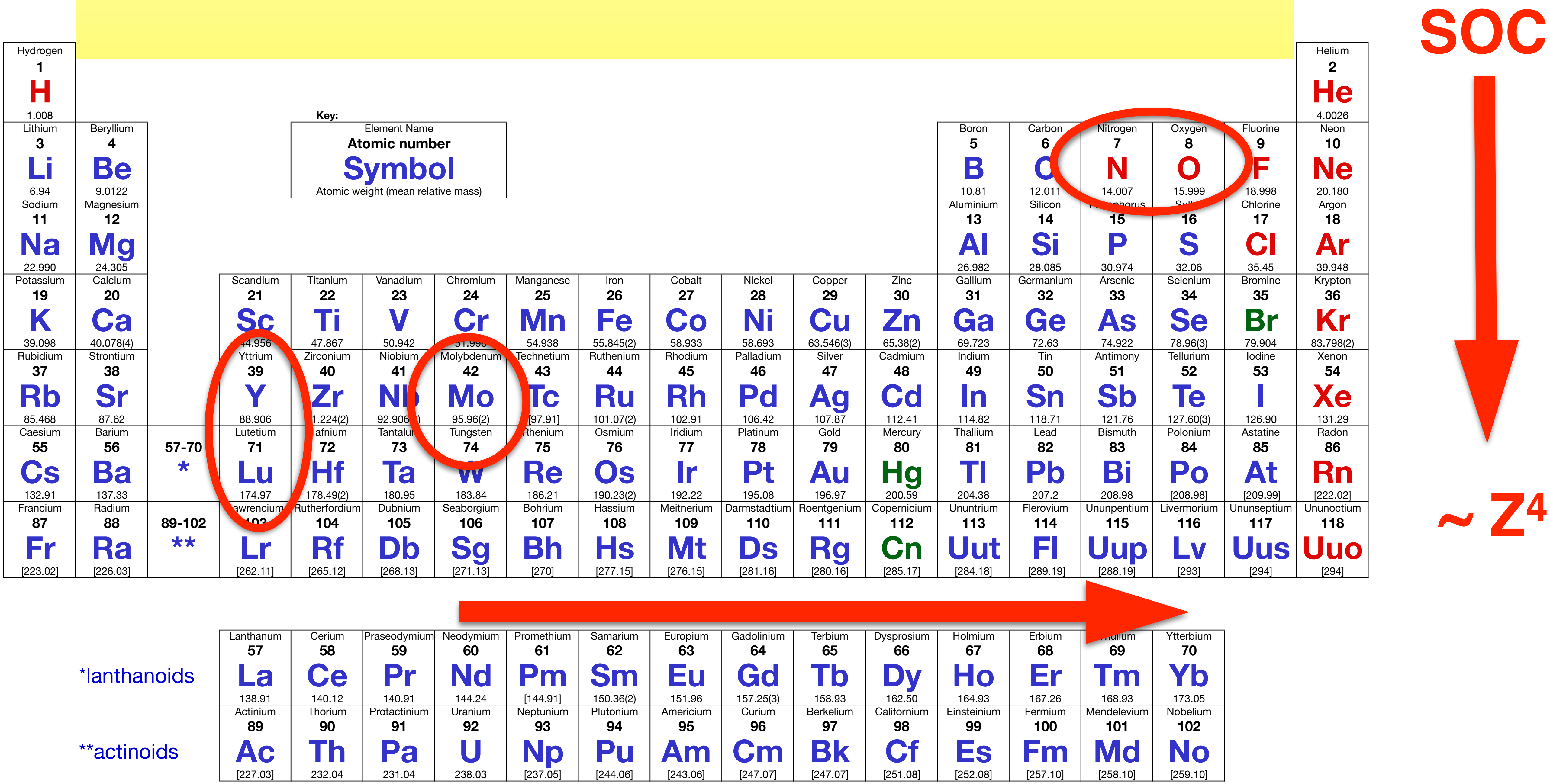
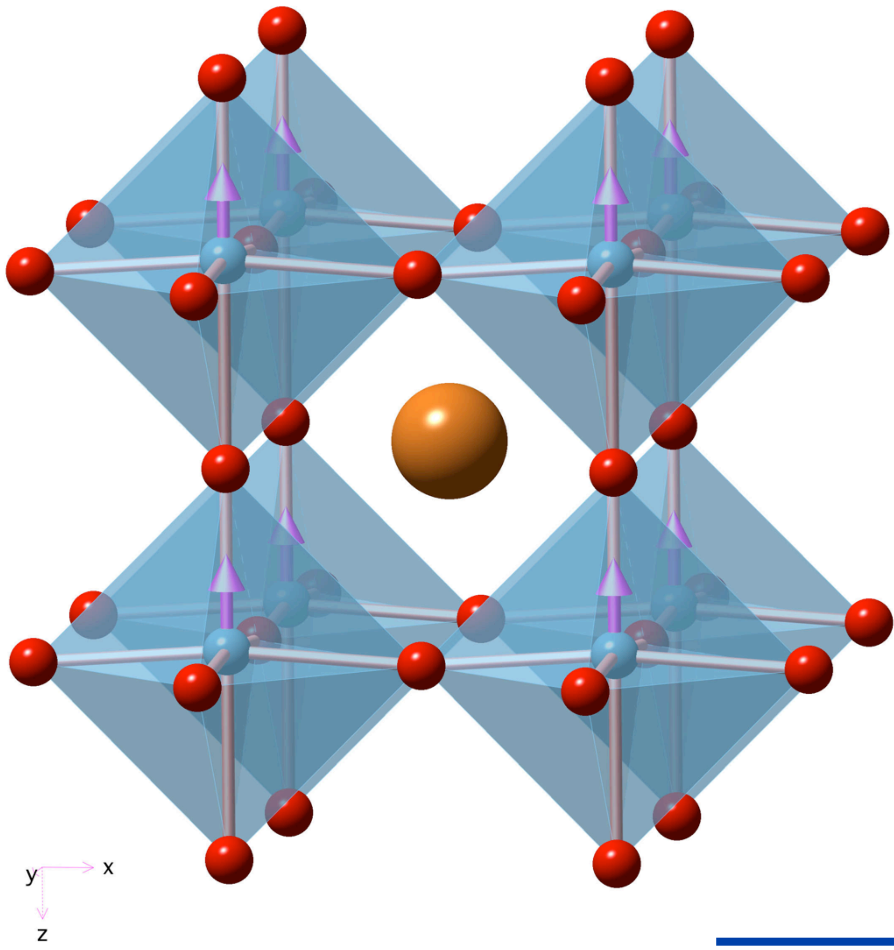
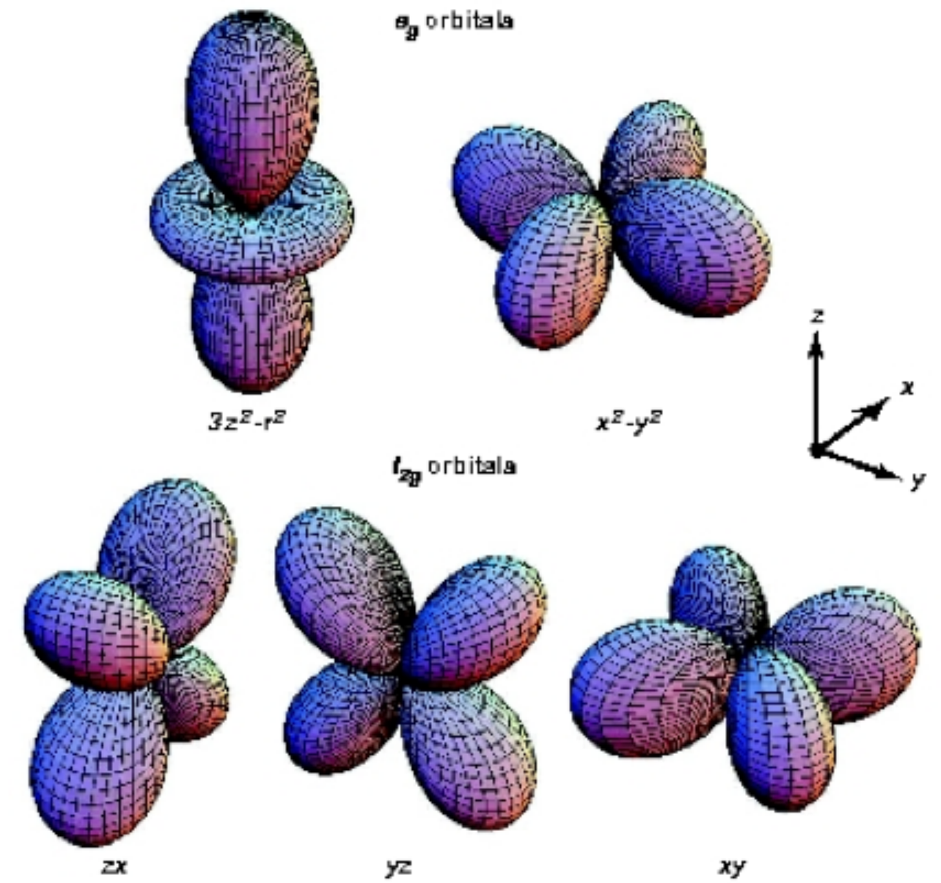






e_g

Octahedral CEF

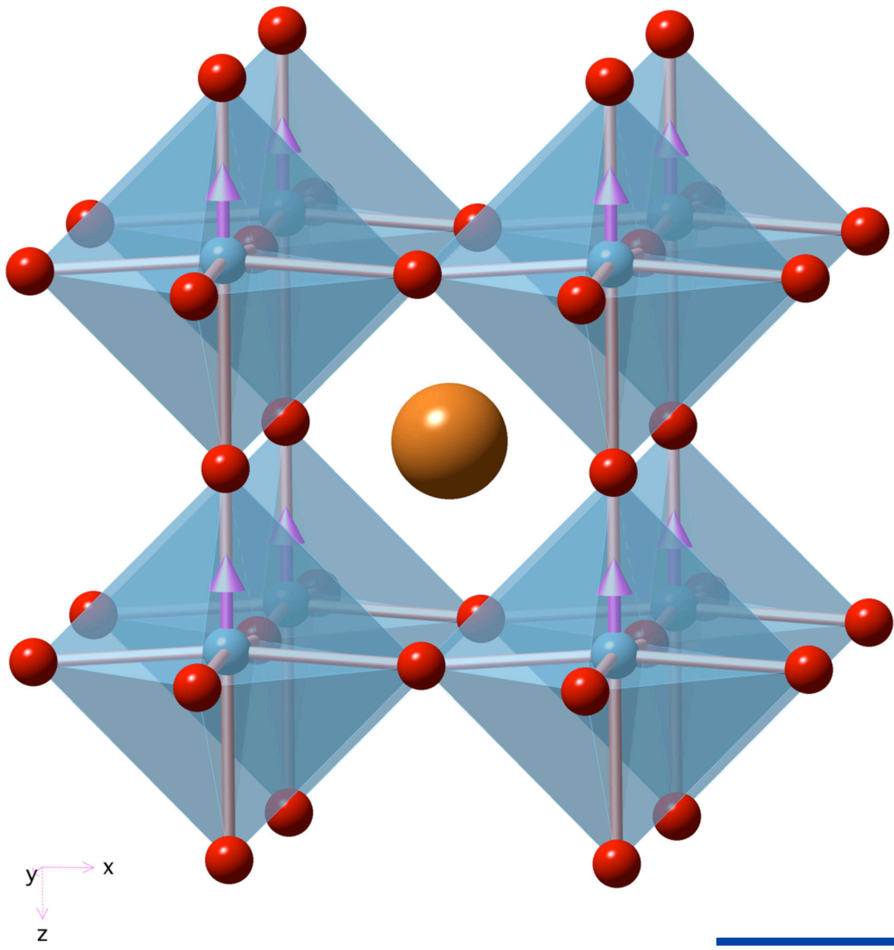
t_{2g}

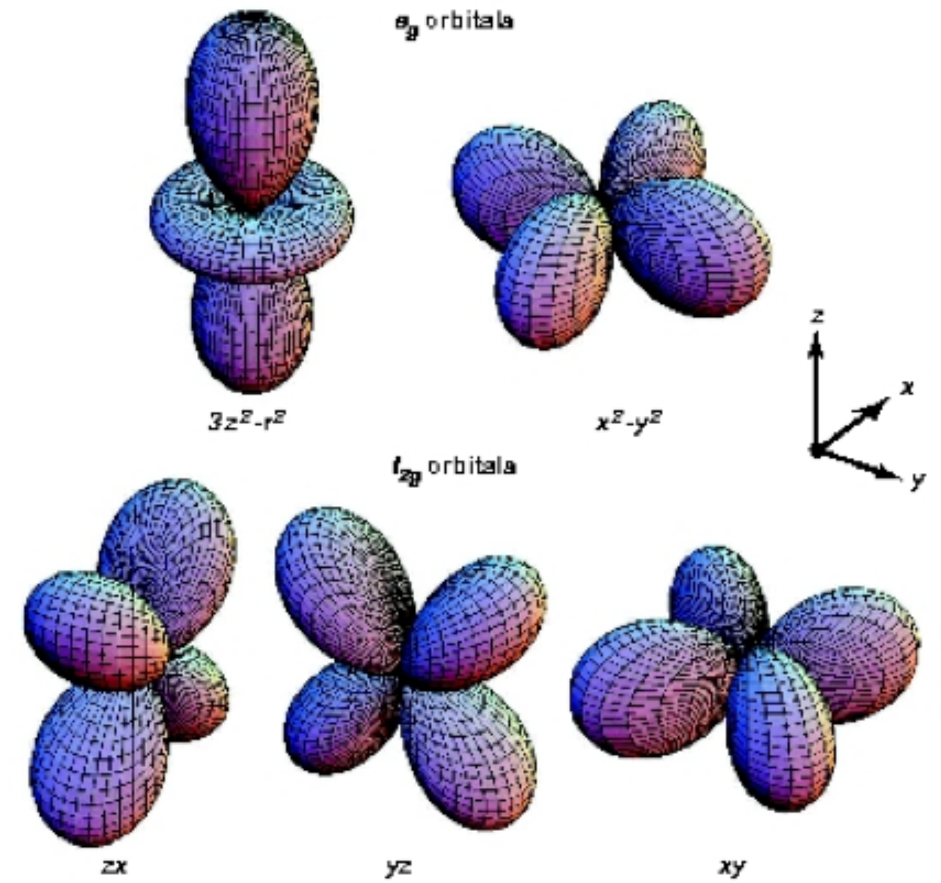
$j_{eff}=1/2$

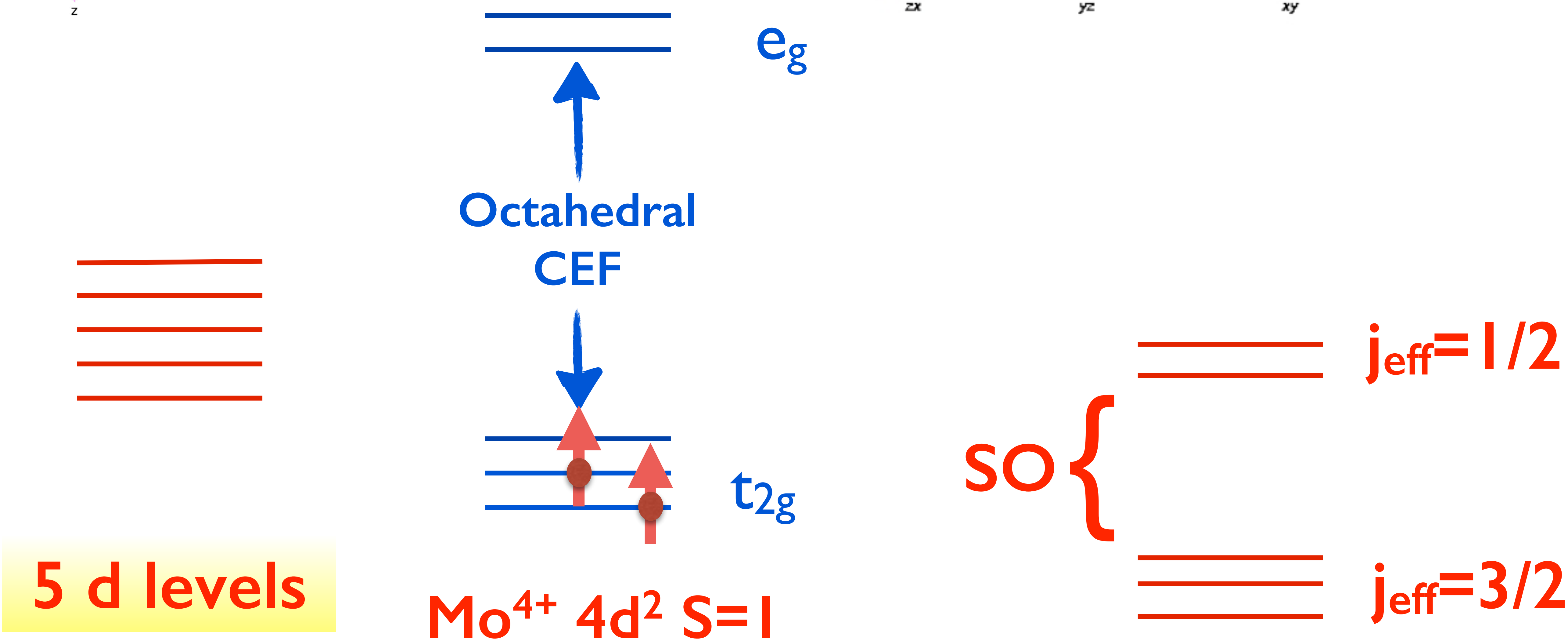
SO

$j_{eff}=3/2$

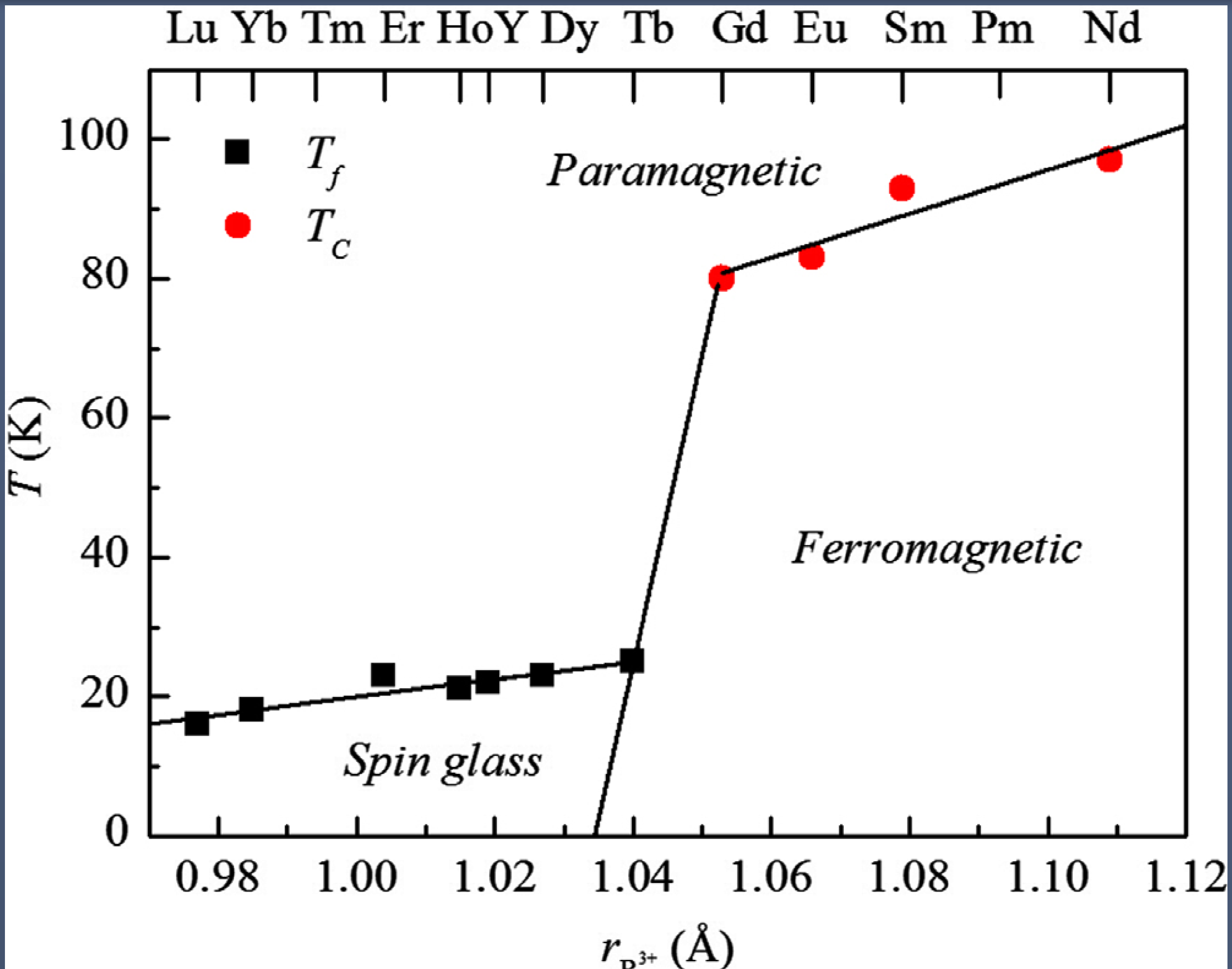
5 d levels


y
x
z


e_g orbitals
$3z^2-r^2$
x^2-y^2
t_{2g} orbitals
zx
yz
xy
z
x
y

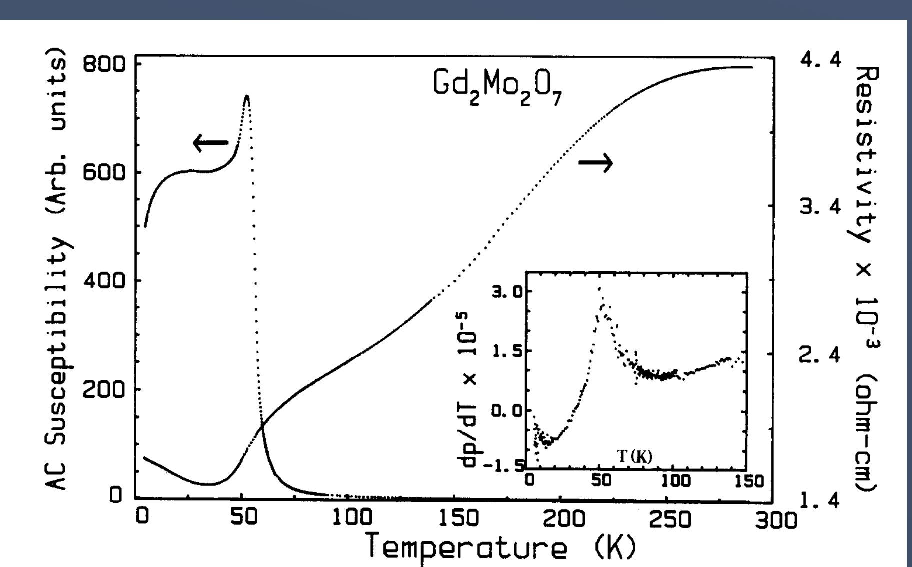

e_g
Octahedral
CEF
t_{2g}
5 d levels
Mo^{4+} $4d^2$ S=1
SO
$j_{eff}=1/2$
$j_{eff}=3/2$

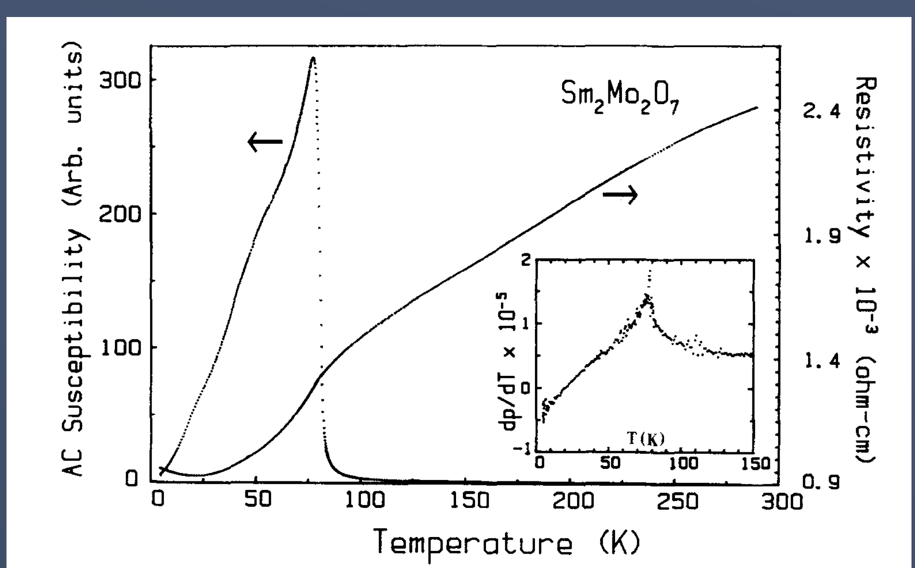
MIT in Rare Earth Molybdate Pyrochlores

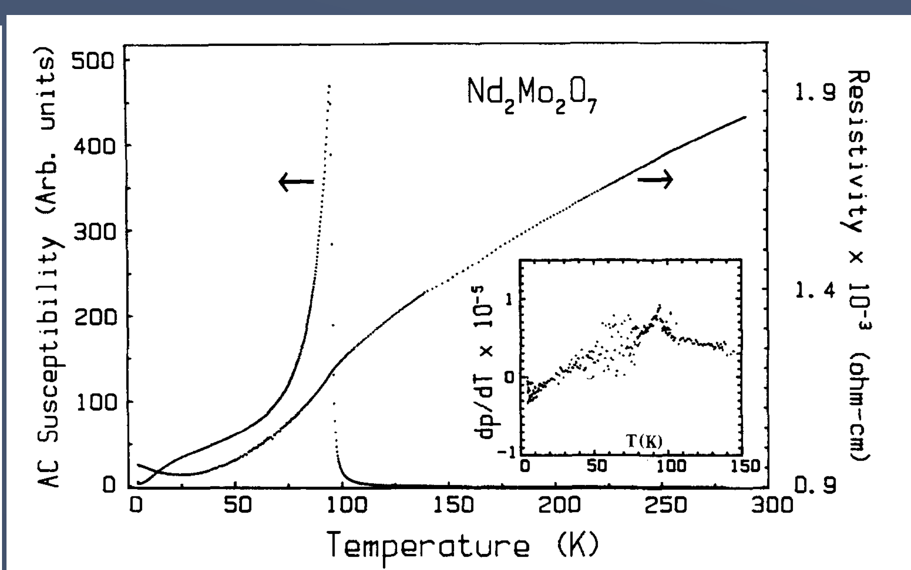


L. Clark et al., J. Sol. State Chem, 203, 199, 2013

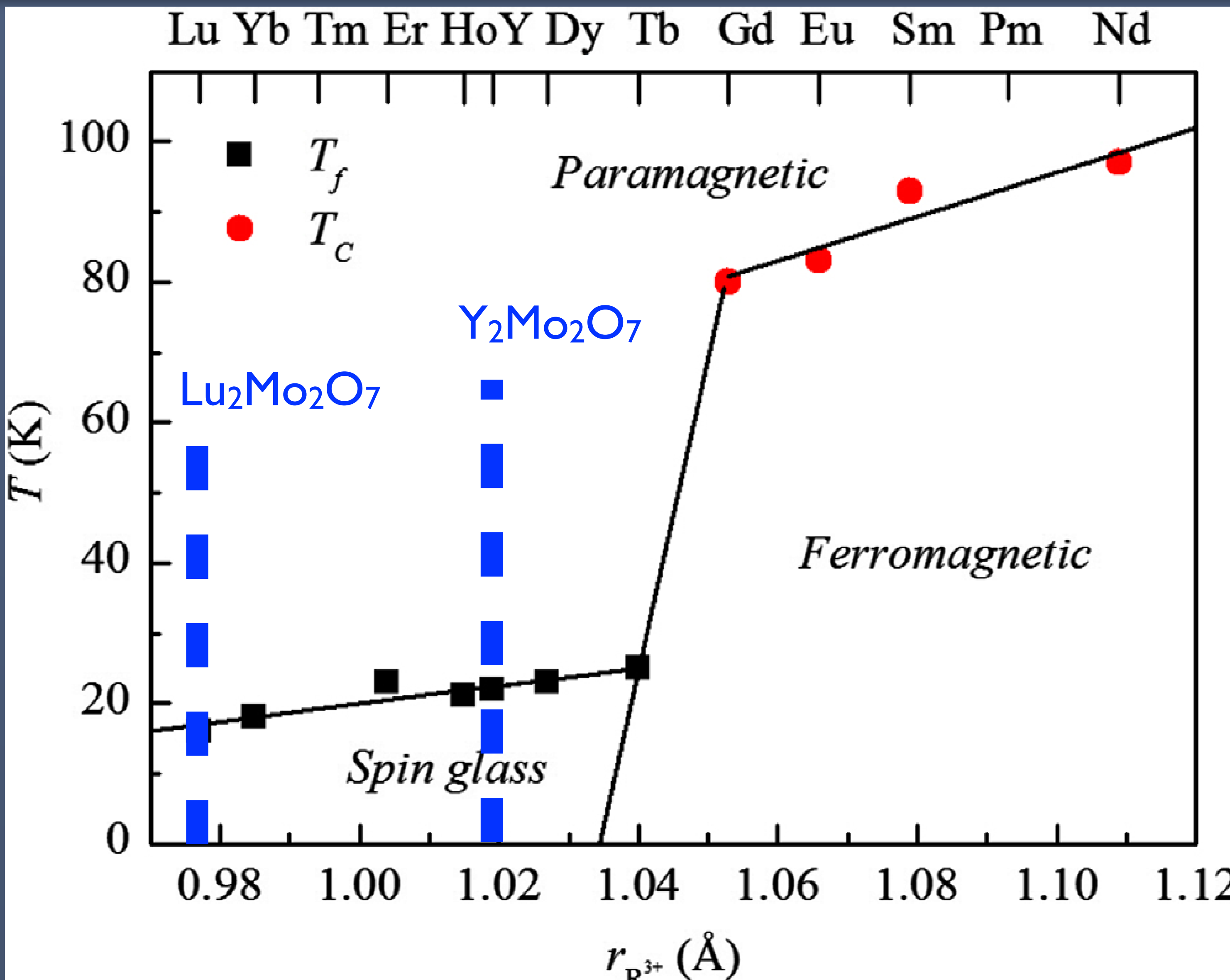
N. Ali et al., J. Sol. State Chem, 83, 178, 1989





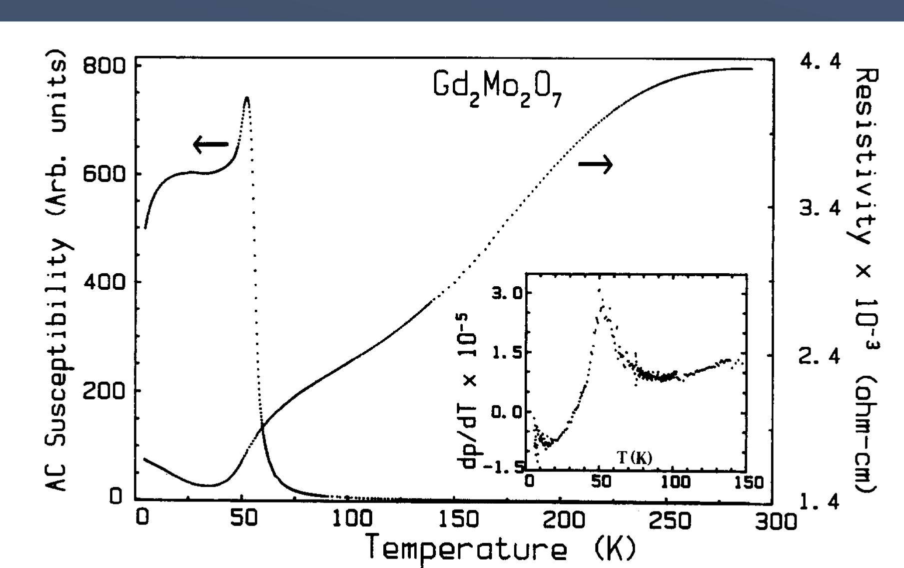


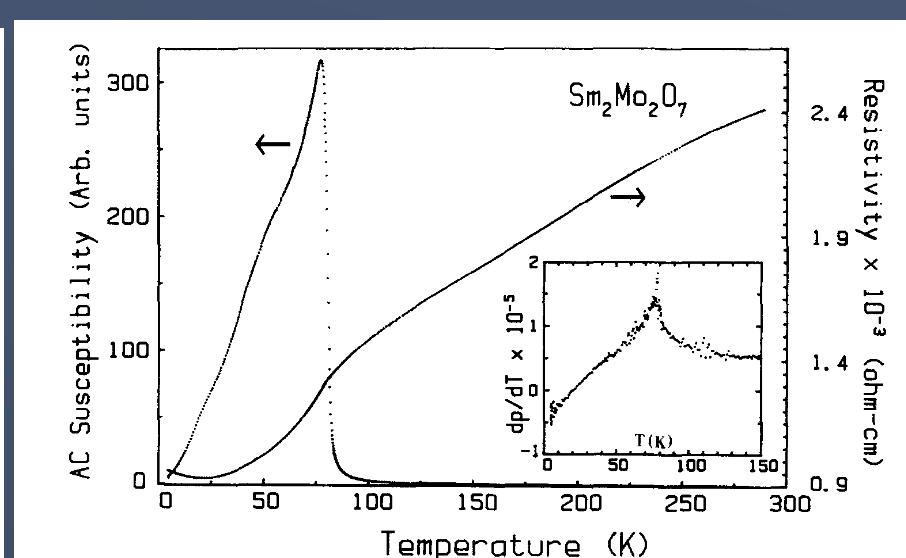
MIT in Rare Earth Molybdate Pyrochlores

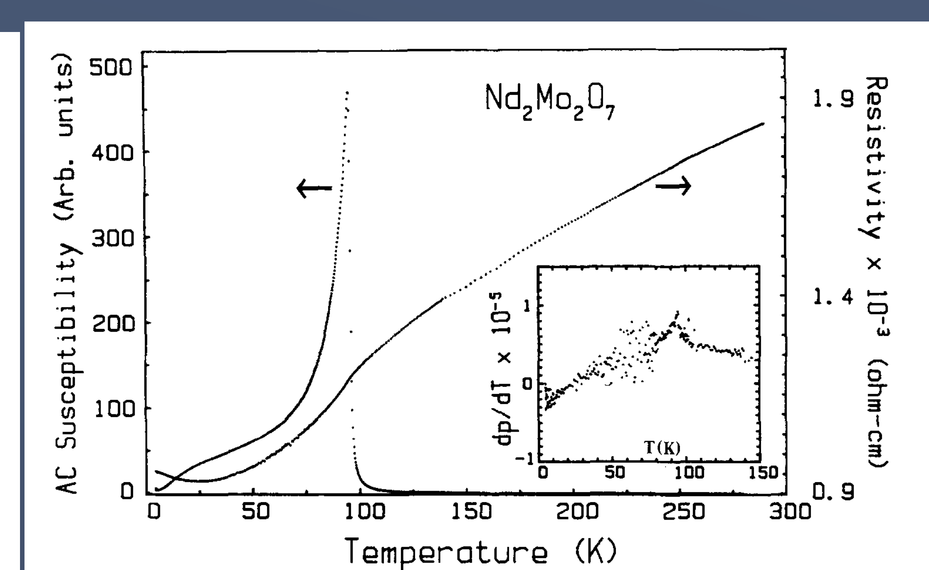


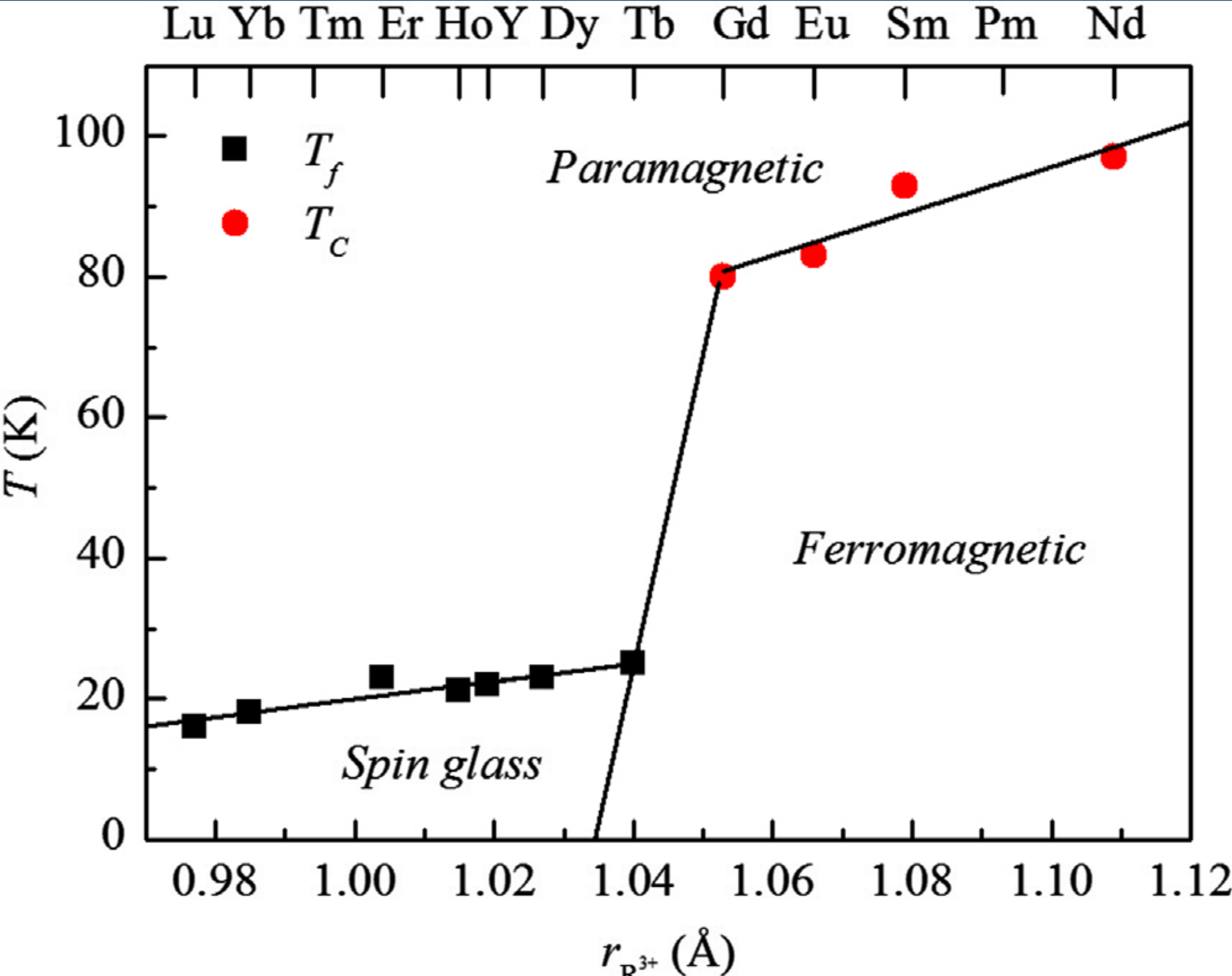
L. Clark et al.,
J. Sol. State Chem, 203, 199, 2013

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



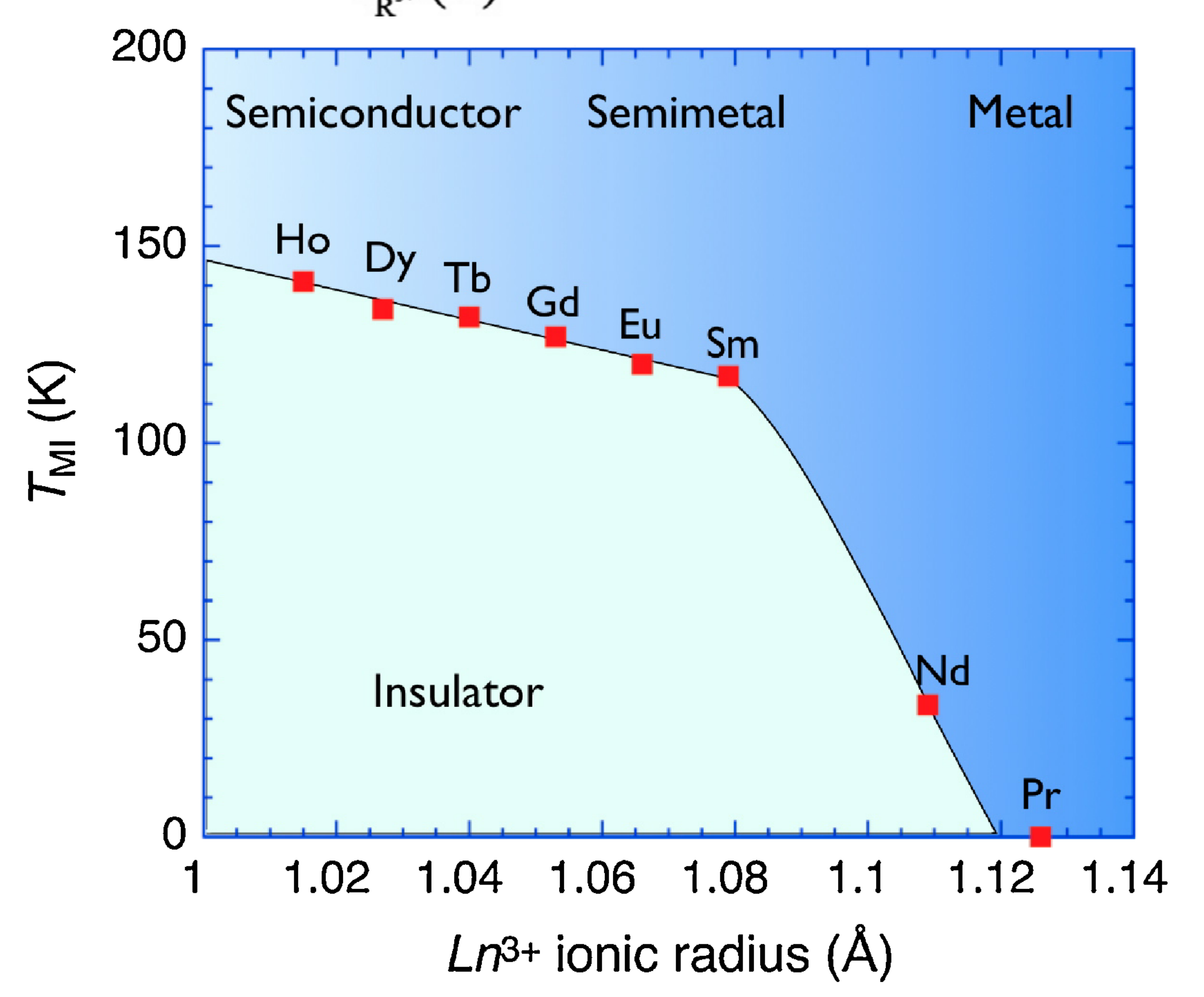




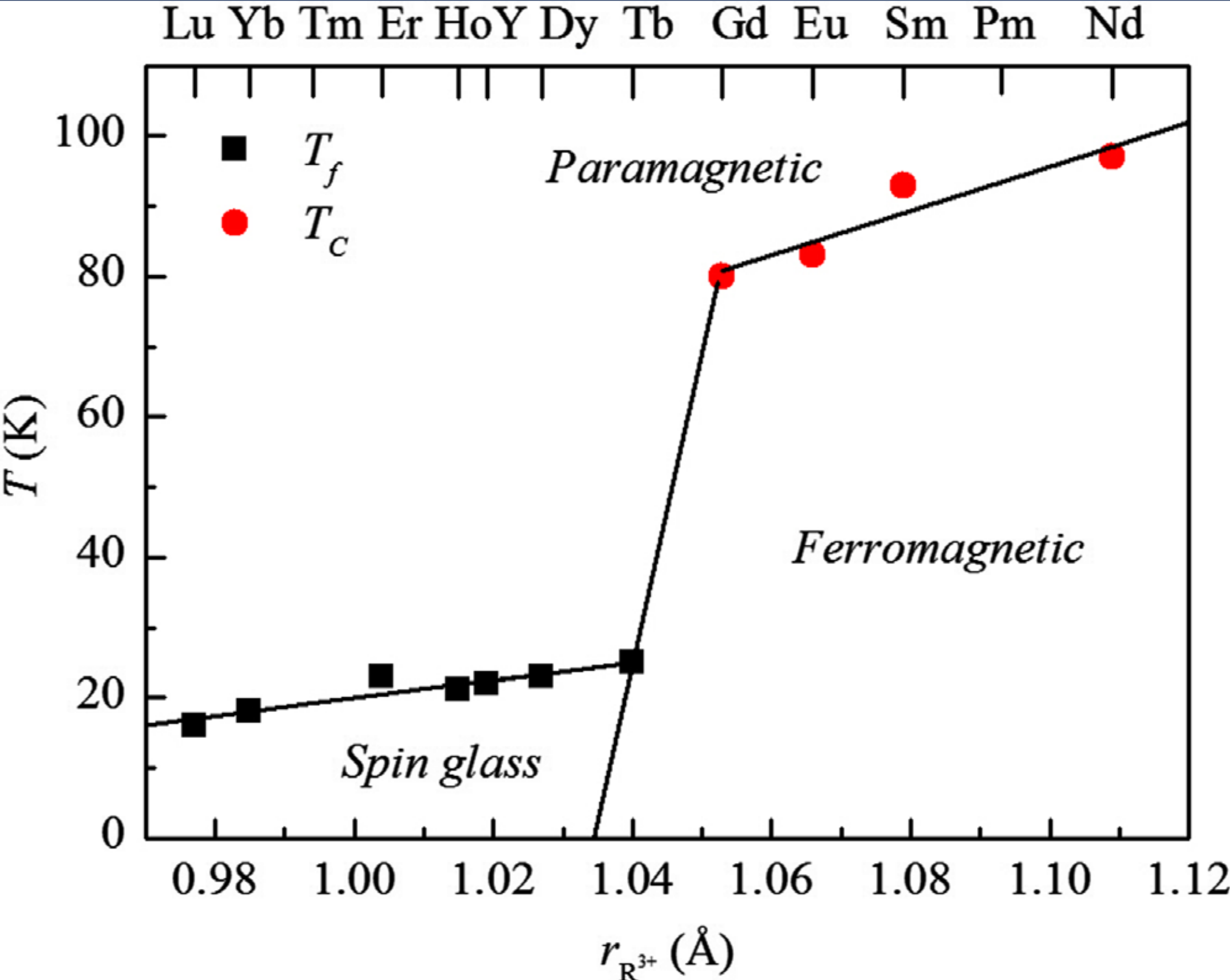


Rare Earth Molybdates
$4d^2$

Comparing Cubic Pyrochlore Molybdates and Iridates



Rare Earth Iridates
$5d^5$



Rare Earth Molybdates
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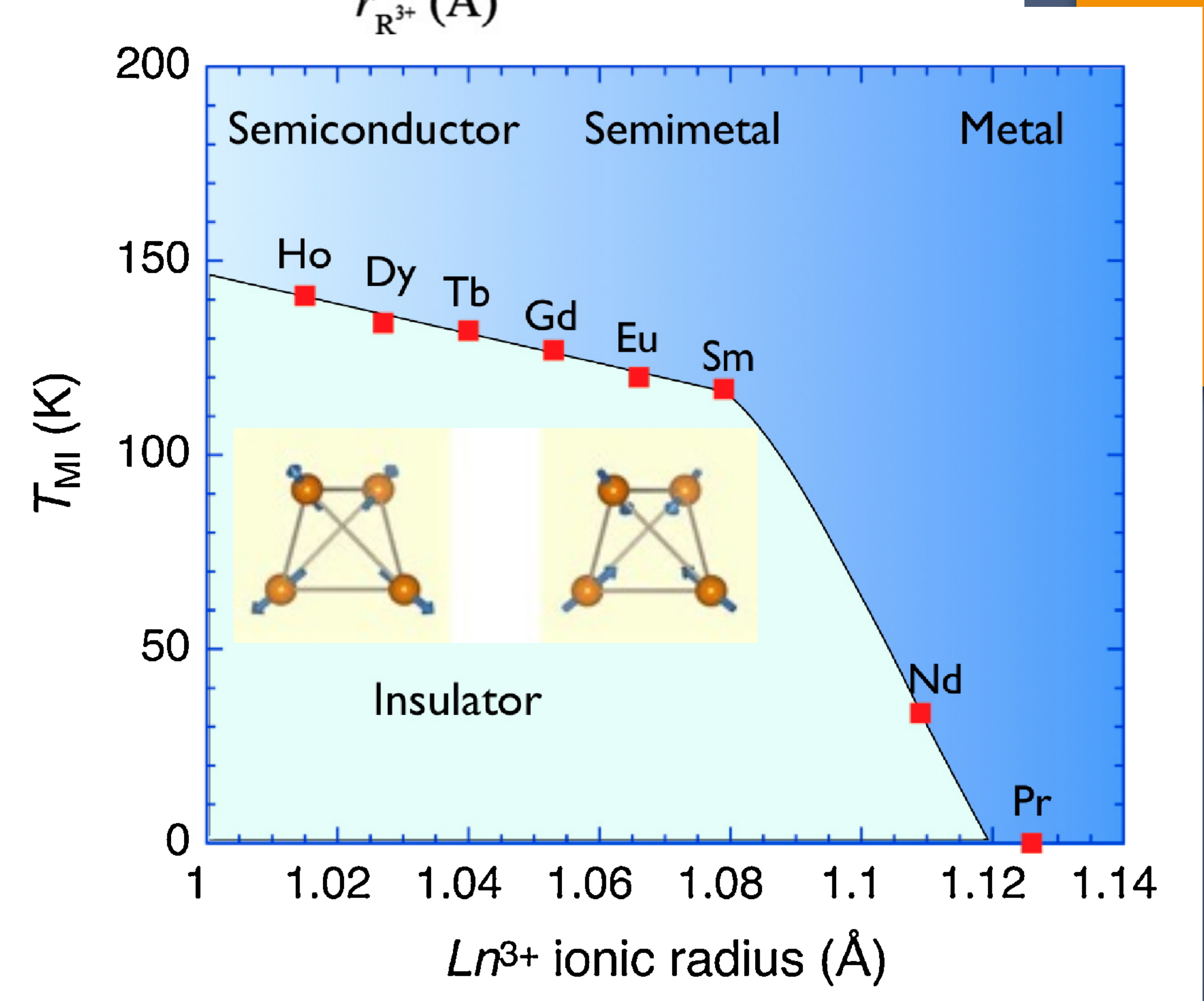
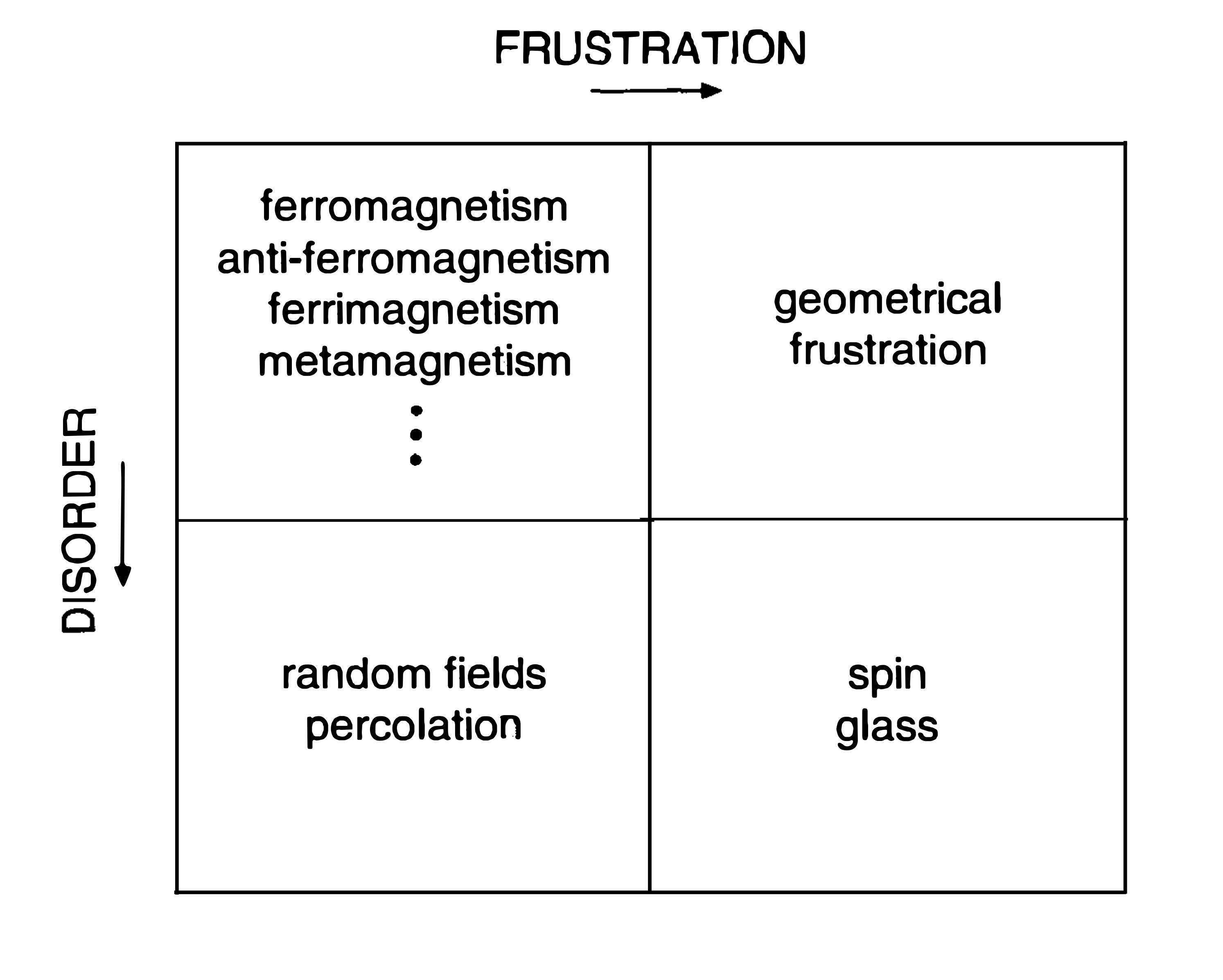


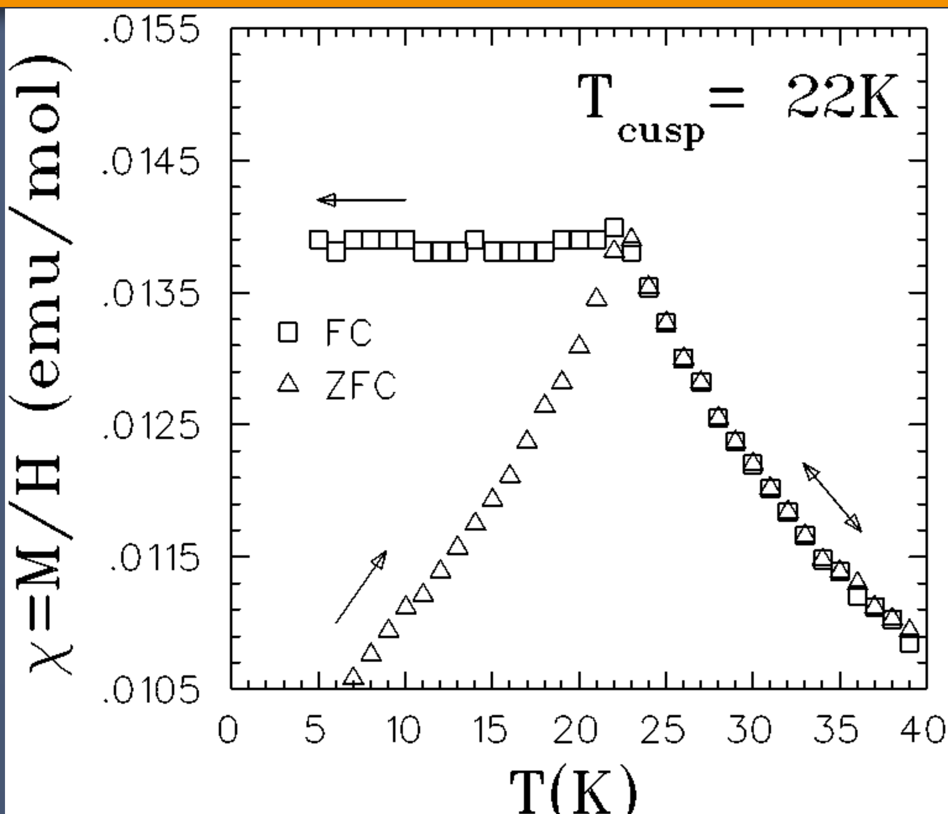
Rare Earth Iridates
$5d^5$

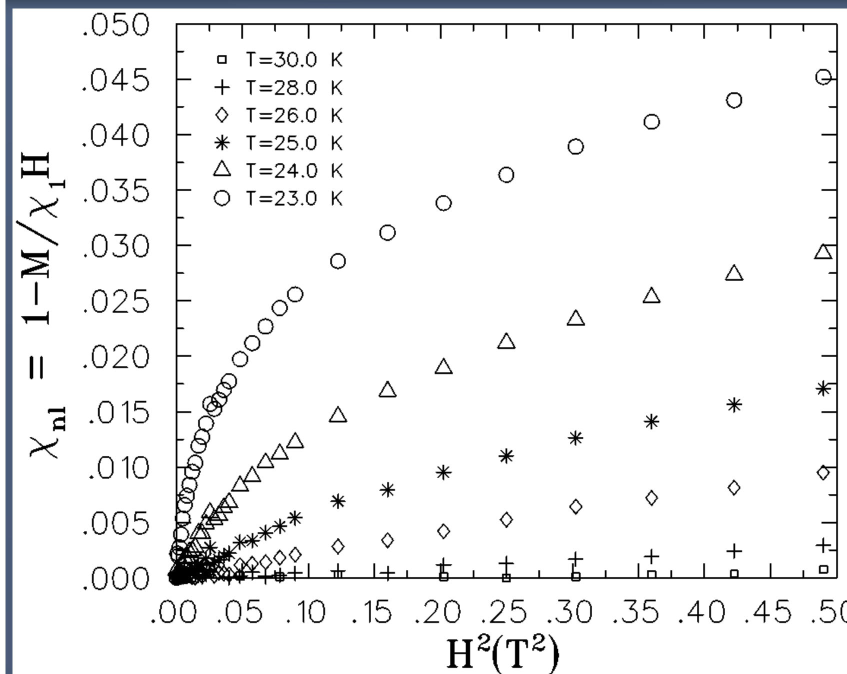
Conventional View of Magnetic Ground States Selected by Frustration and Disorder



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

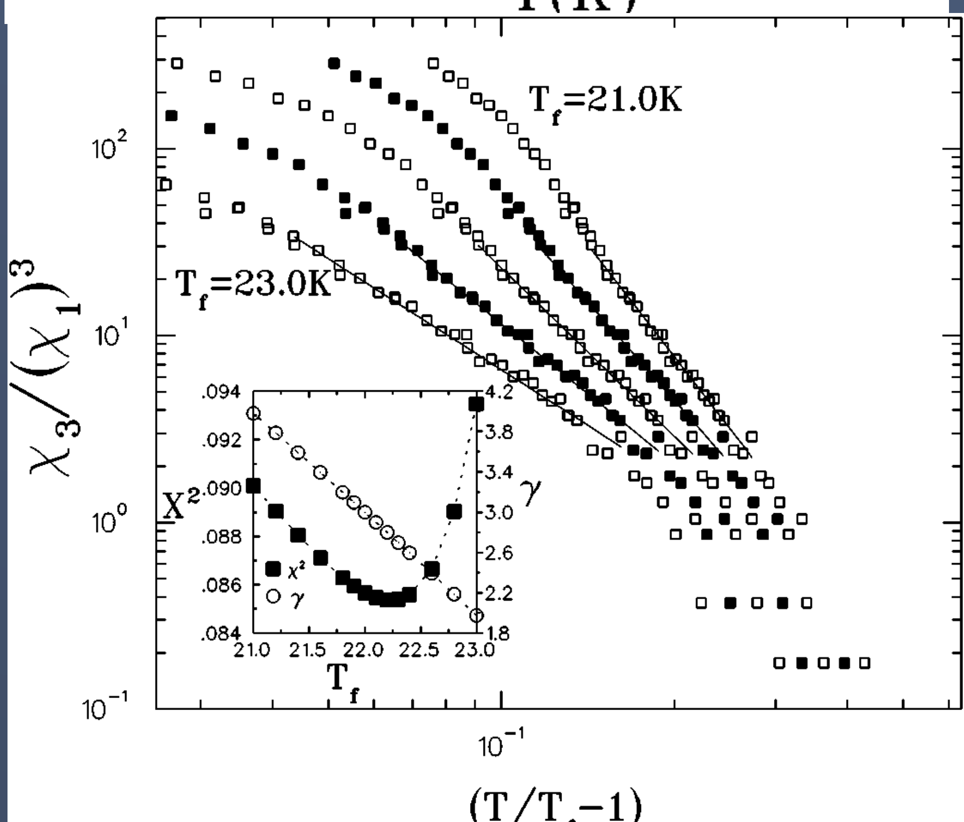
Spin Glass Transition at T_f ~ 22 K in $Y_2Mo_2O_7$





Thermodynamic phase transition at T_f ~ 22 K

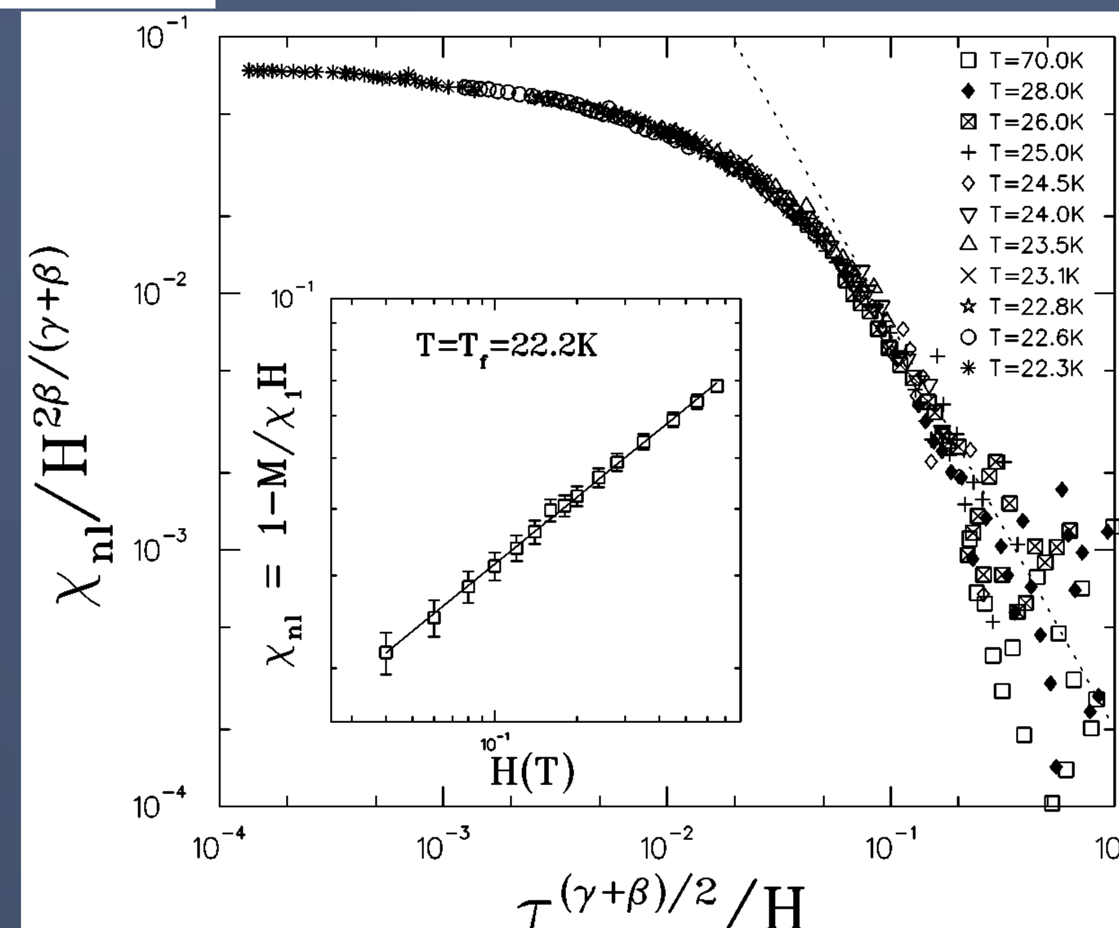
Criticality typical of random spin glasses



T_{CW} ~ -200 K

mu_{eff} ~ 2.5 mu_B

S=1 mu_{eff} = 2.83 mu_B



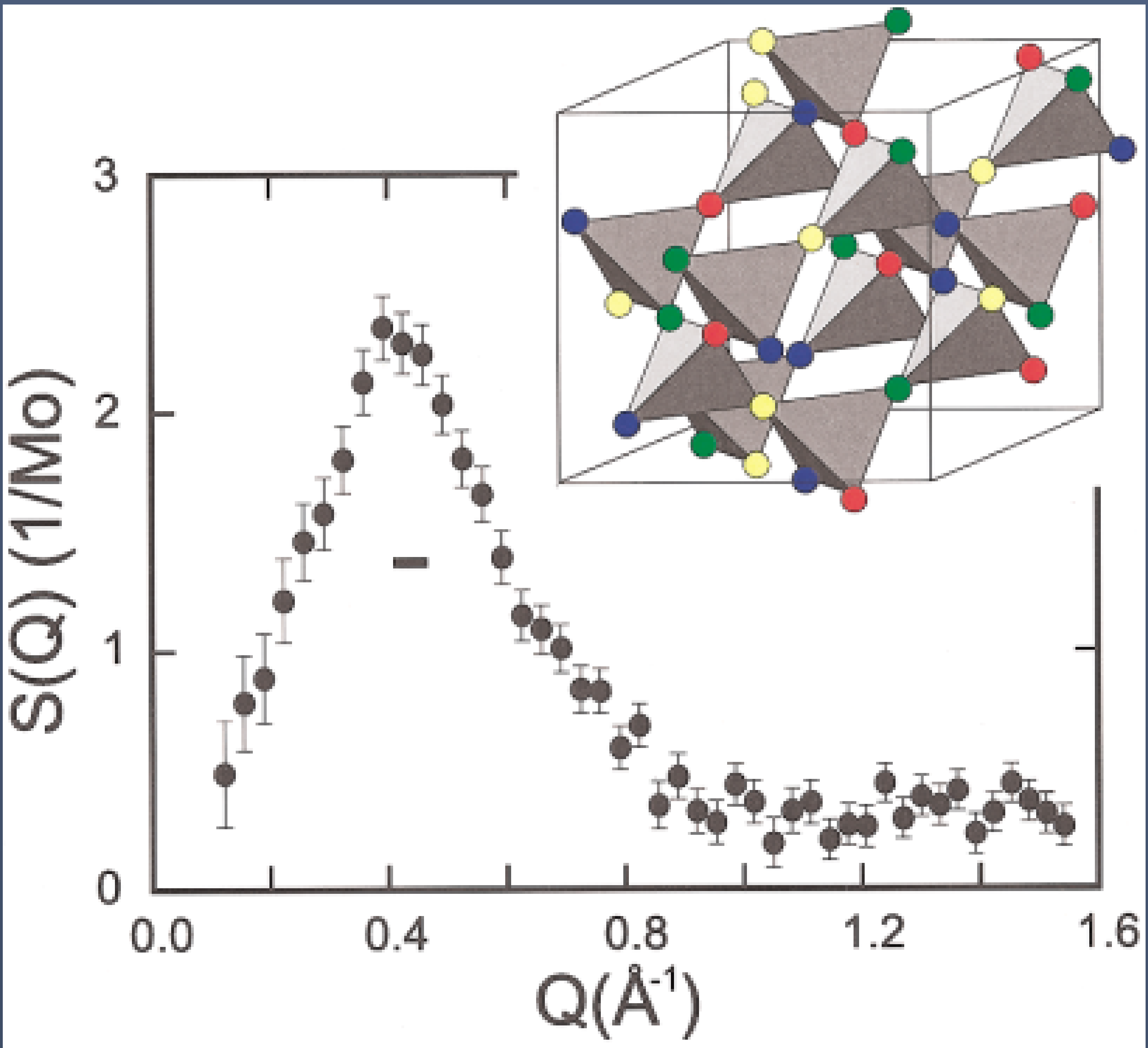
$T_f = 22$ K, $\gamma = 2.8$, and $\beta = 0.75$.

$\delta = 4.73$

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

Elastic Neutron Scattering from $Y_2Mo_2O_7$

"Cluster Glass" with Qmax ~ 0.44 A^{-1}

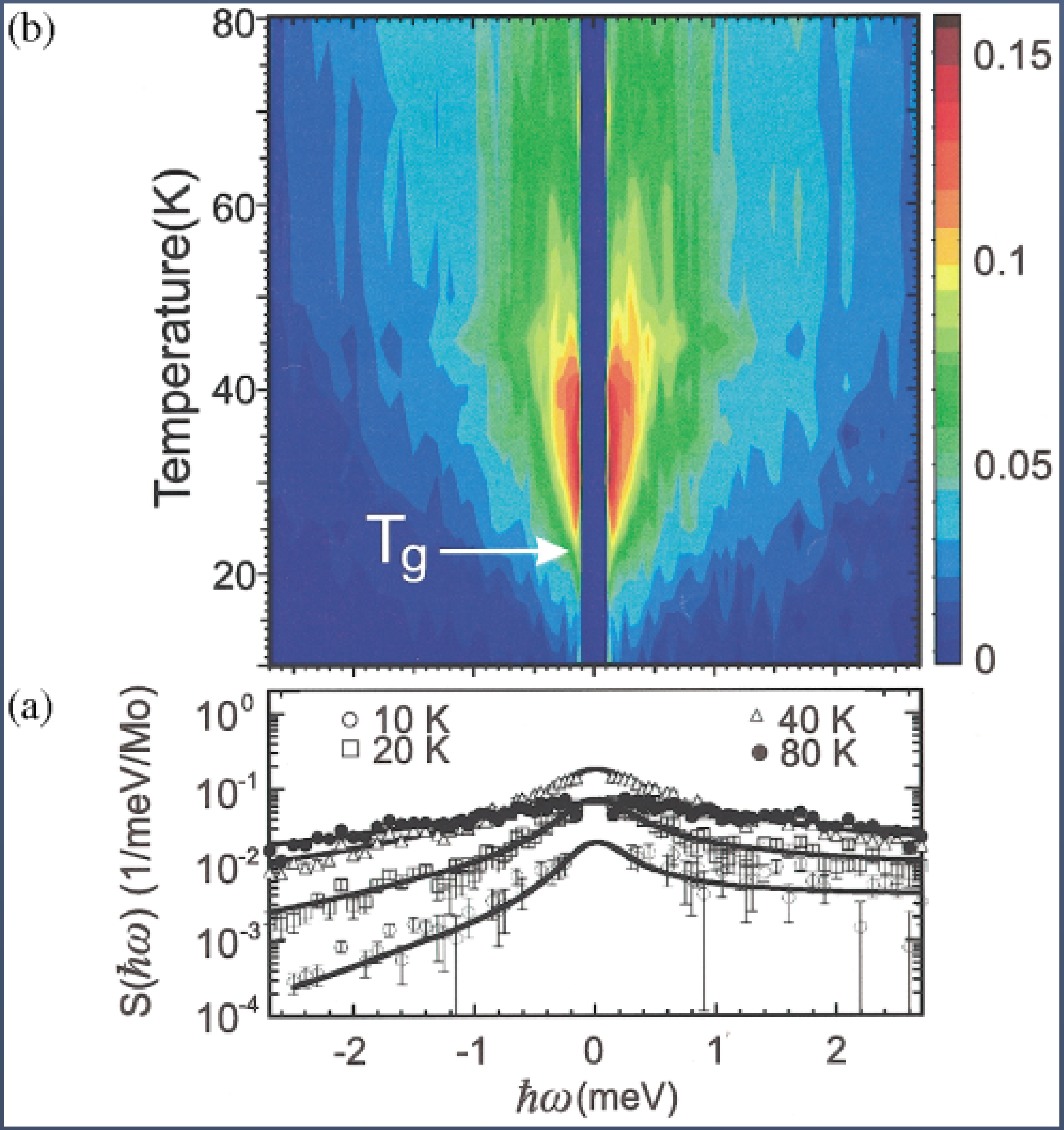


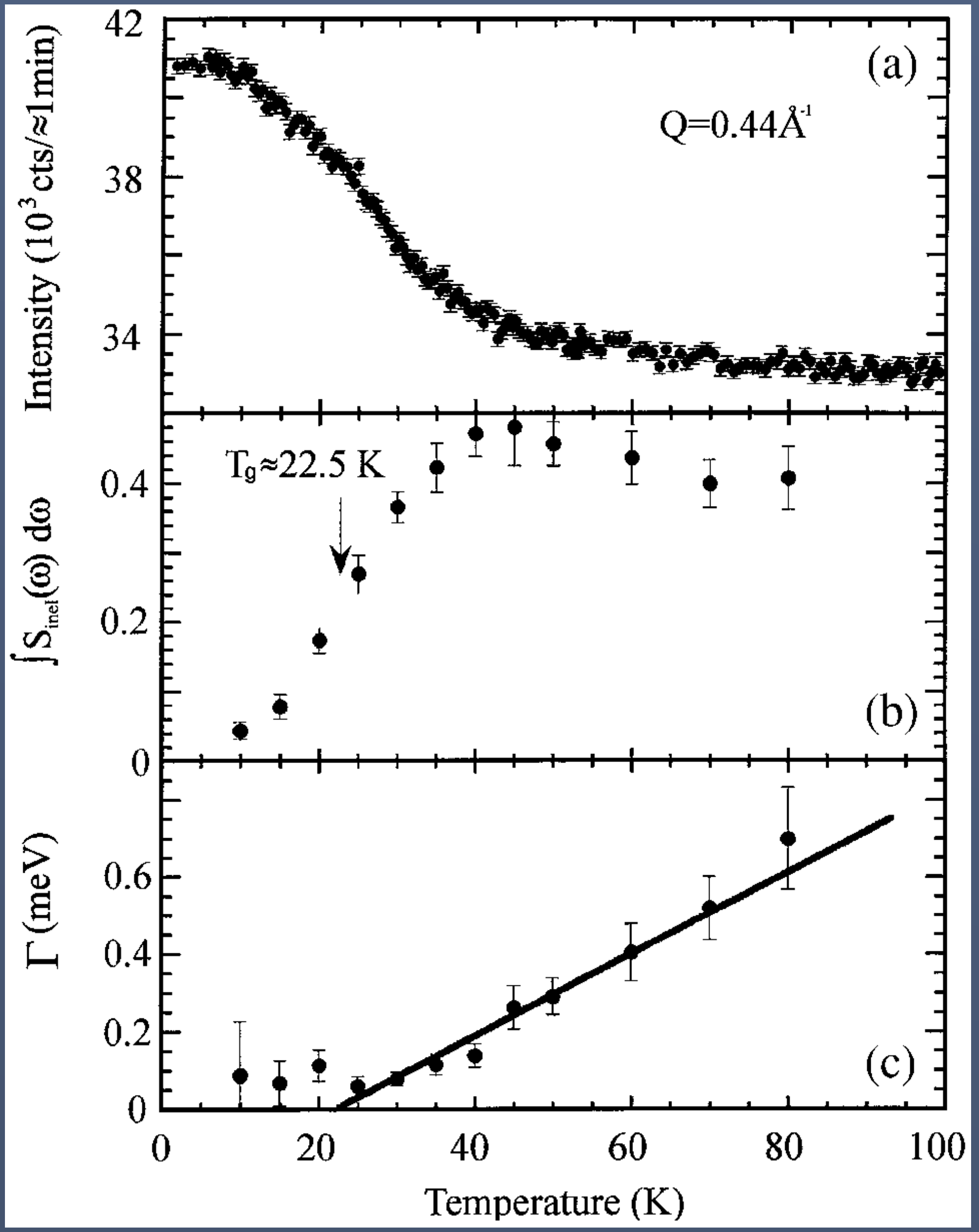
T=1.4 K - 50 K

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

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

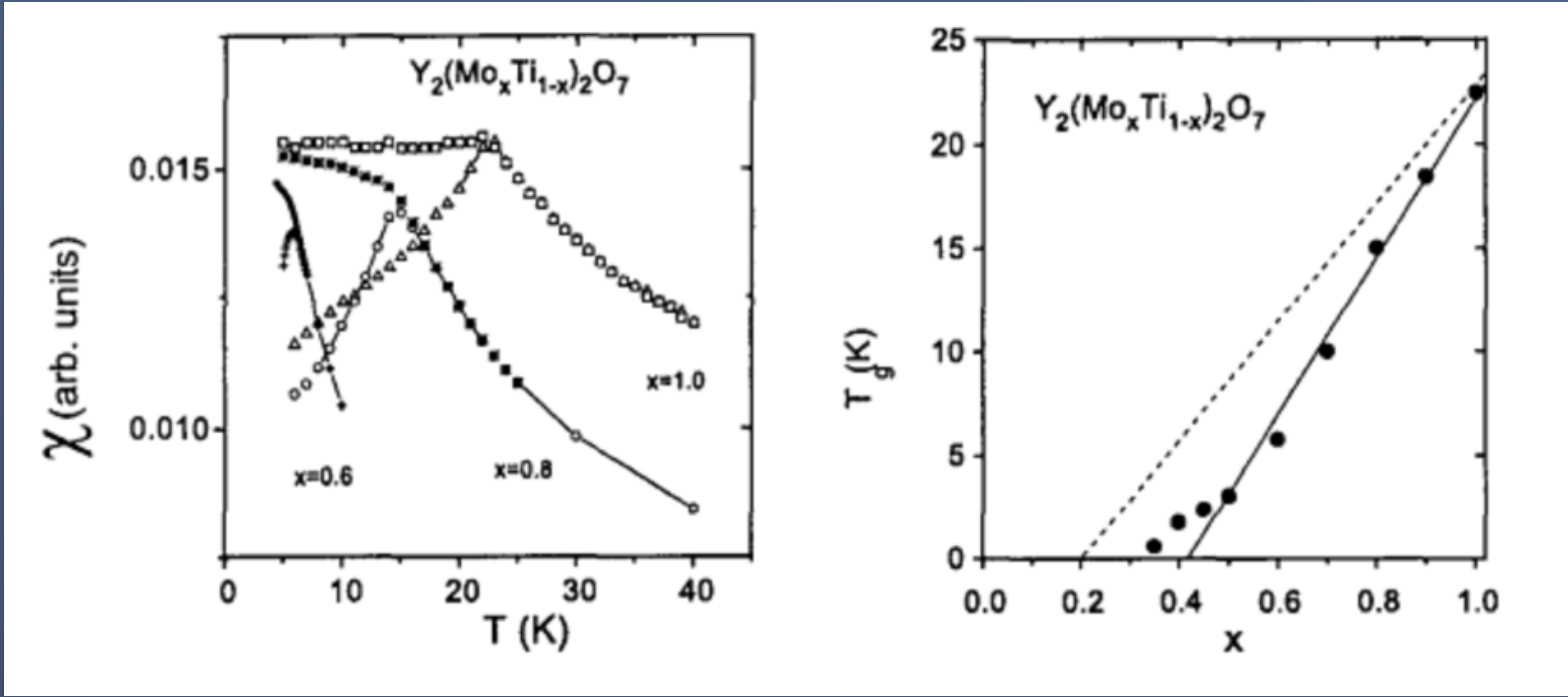
Inelastic Neutron Scattering from $Y_2Mo_2O_7$





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

3D Percolation: Just another ordered state?



Site substitution with non-magnetic Ti^{4+}

Structural Disorder in $Y_2Mo_2O_7$

definitely low, but is it measurable?

PHYSICAL REVIEW B **79**, 014427 (2009)

Local and average structures of the spin-glass pyrochlore $Y_2Mo_2O_7$ from neutron diffraction and neutron pair distribution function analysis

J. E. Greedan,[1] Delphine Gout,[2] A. D. Lozano-Gorrin,[1] Shahab Derahkshan,[1] Th. Proffen,[3] H.-J. Kim,[3] E. Božin,[4] and S. J. L. Billinge[4]

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 $Y_2Mo_2O_7$

C. H. Booth,[1,2] J. S. Gardner,[2] G. H. Kwei,[2] R. H. Heffner,[2] F. Bridges,[3] and M. A. Subramanian[4]

XAFS

- Weak Mo-Mo disorder

VOLUME 87, NUMBER 17 PHYSICAL REVIEW LETTERS 22 OCTOBER 2001

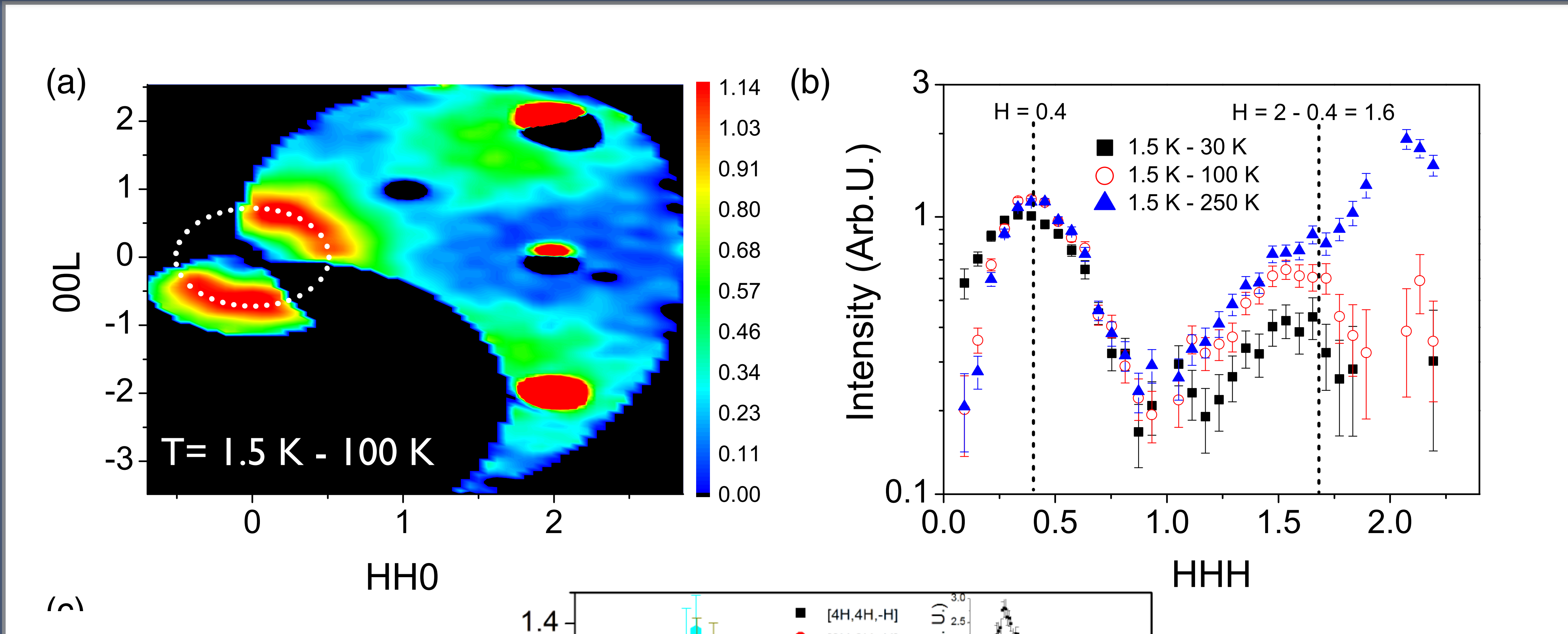
Frustration Driven Lattice Distortion: An NMR Investigation of $Y_2Mo_2O_7$

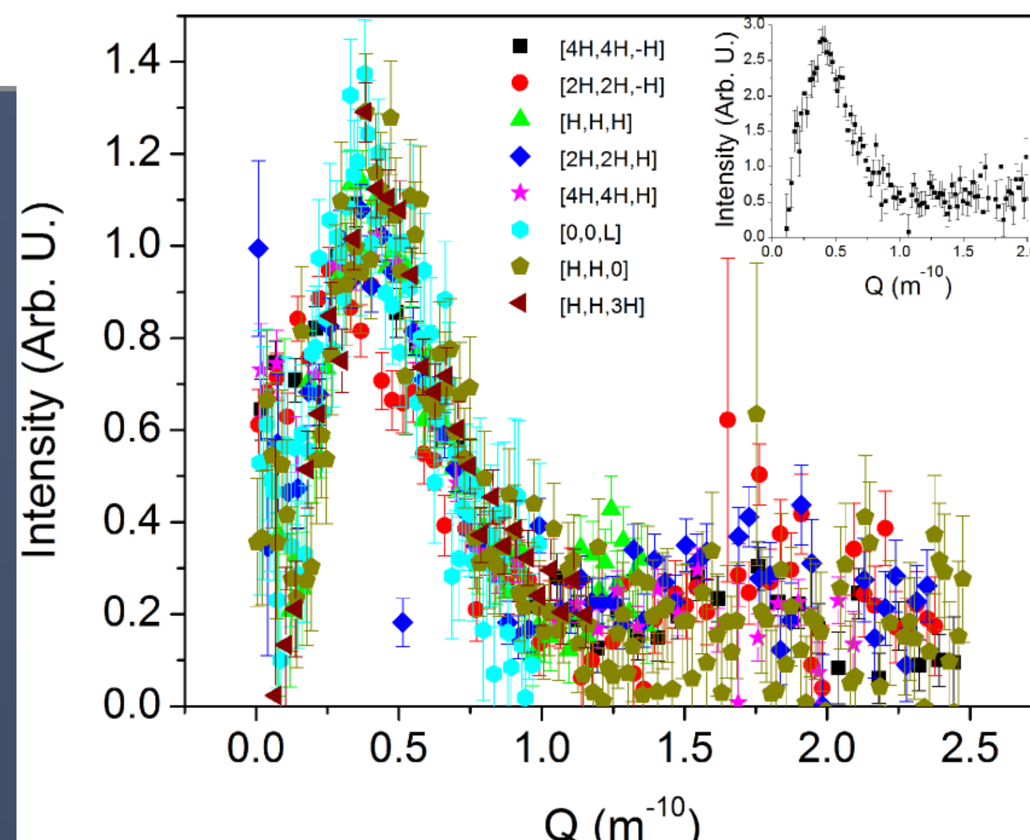
Amit Keren[1] and Jason S. Gardner[2]

^{89}Y NMR

- Weak Mo-Mo disorder

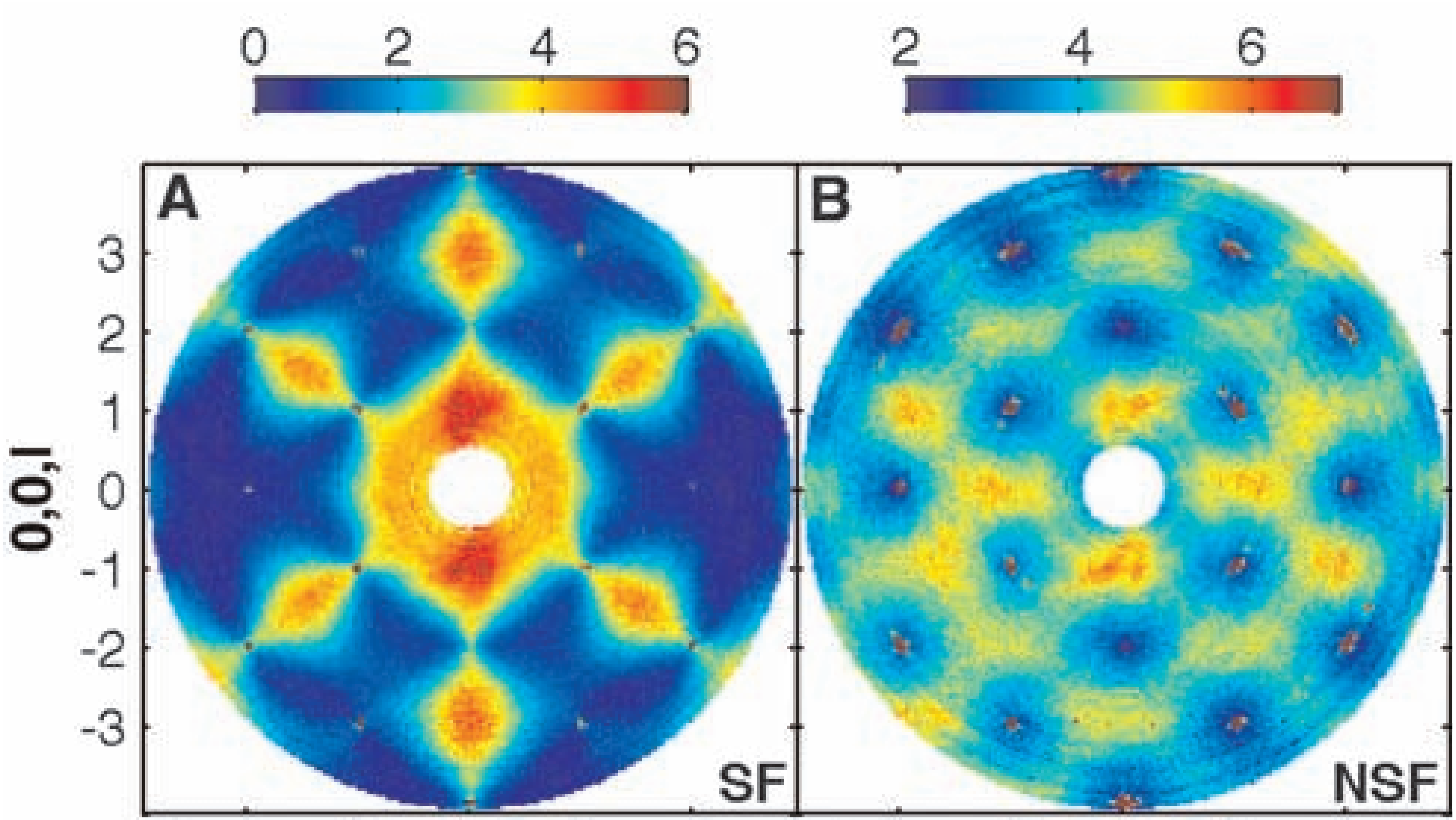
Single Crystal Samples: Real Liquid Correlations!





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

Spin Ice Ground State in $Ho_2Ti_2O_7$



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

Oxygen miscibility gap in $Lu_2Mo_2O_7$

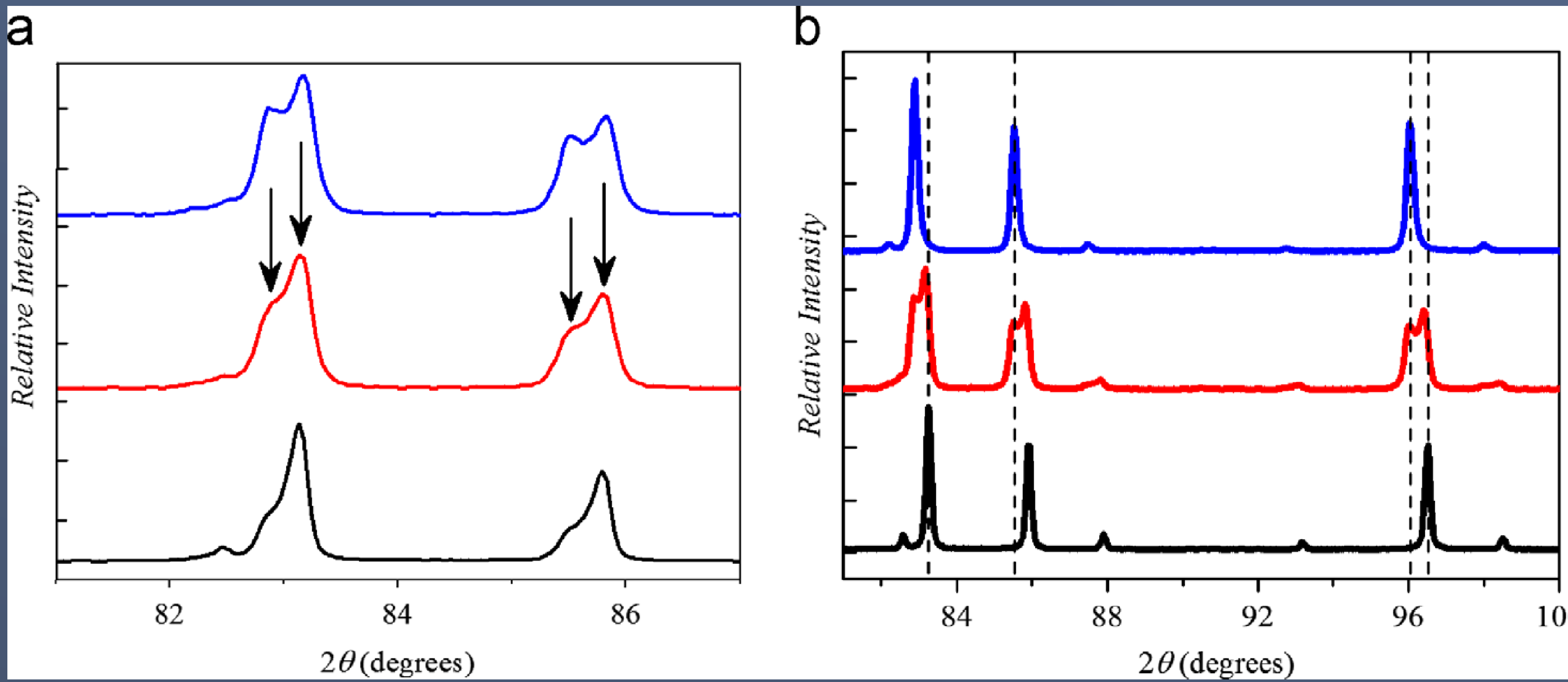
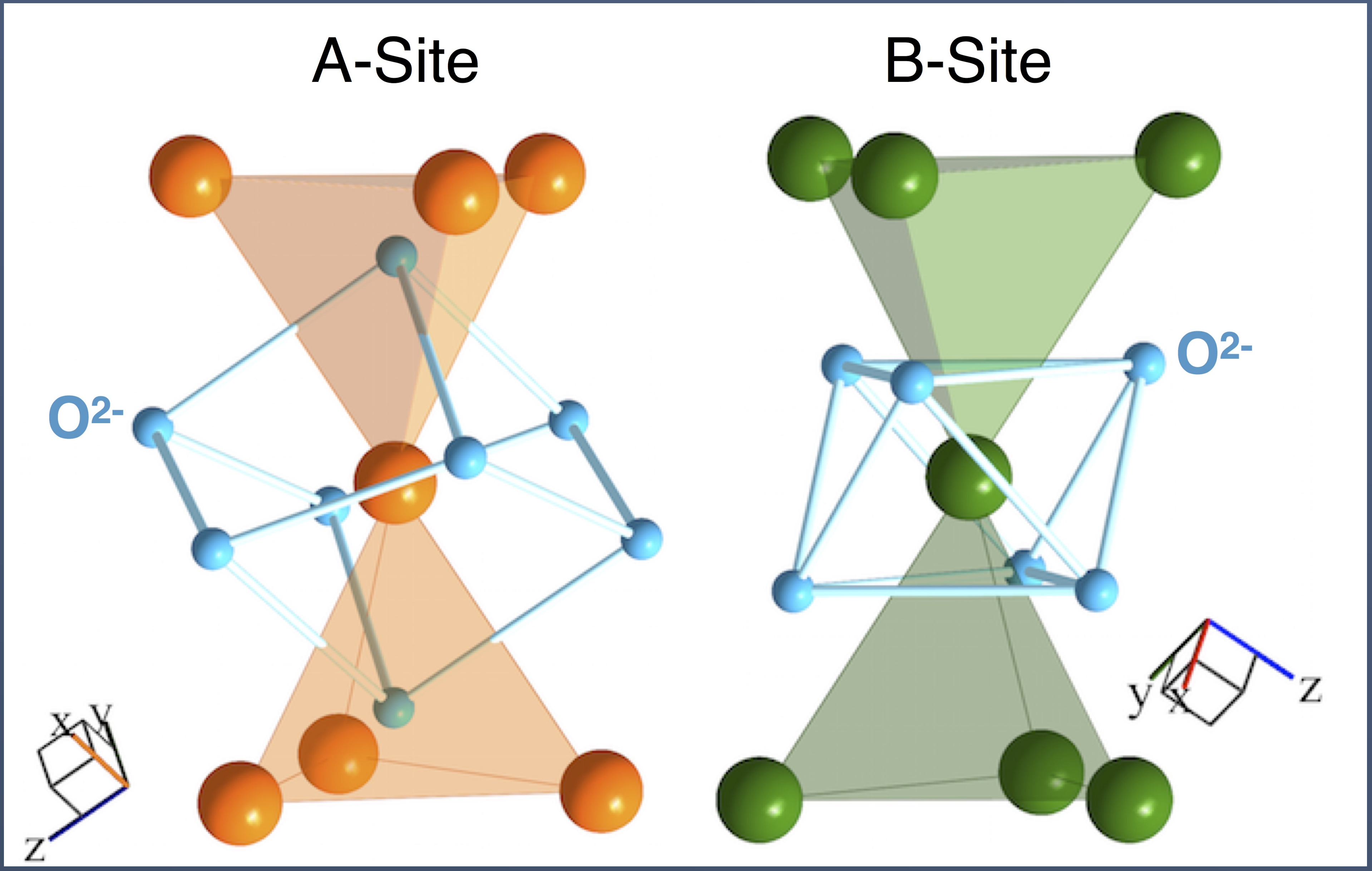


Table 1
Refined atomic coordinates and occupancies for $Lu_2Mo_2O_7$ ($a = 10.1478(1)$ Å) and (lower values where different) for $Lu_2Mo_2O_{6.69(6)}$ ($a = 10.1789(1)$ Å). Isotropic U-factors were 0.0091(2) $Å^2$ for metal cations and 0.0152(3) $Å^2$ for oxygen sites. Residuals for the combined refinement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

Atom	Site	*x*	*y*	*z*	Occupancy
Lu	16*d*	0.5	0.5	0.5	1.0
Mo	16*c*	0.0	0.0	0.0	1.0
O	48*f*	0.3417(1) 0.3477(1)	0.125	0.125	1.0 0.97(1)
O'	8*b*	0.375	0.375	0.375	1.0 0.87(2)

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

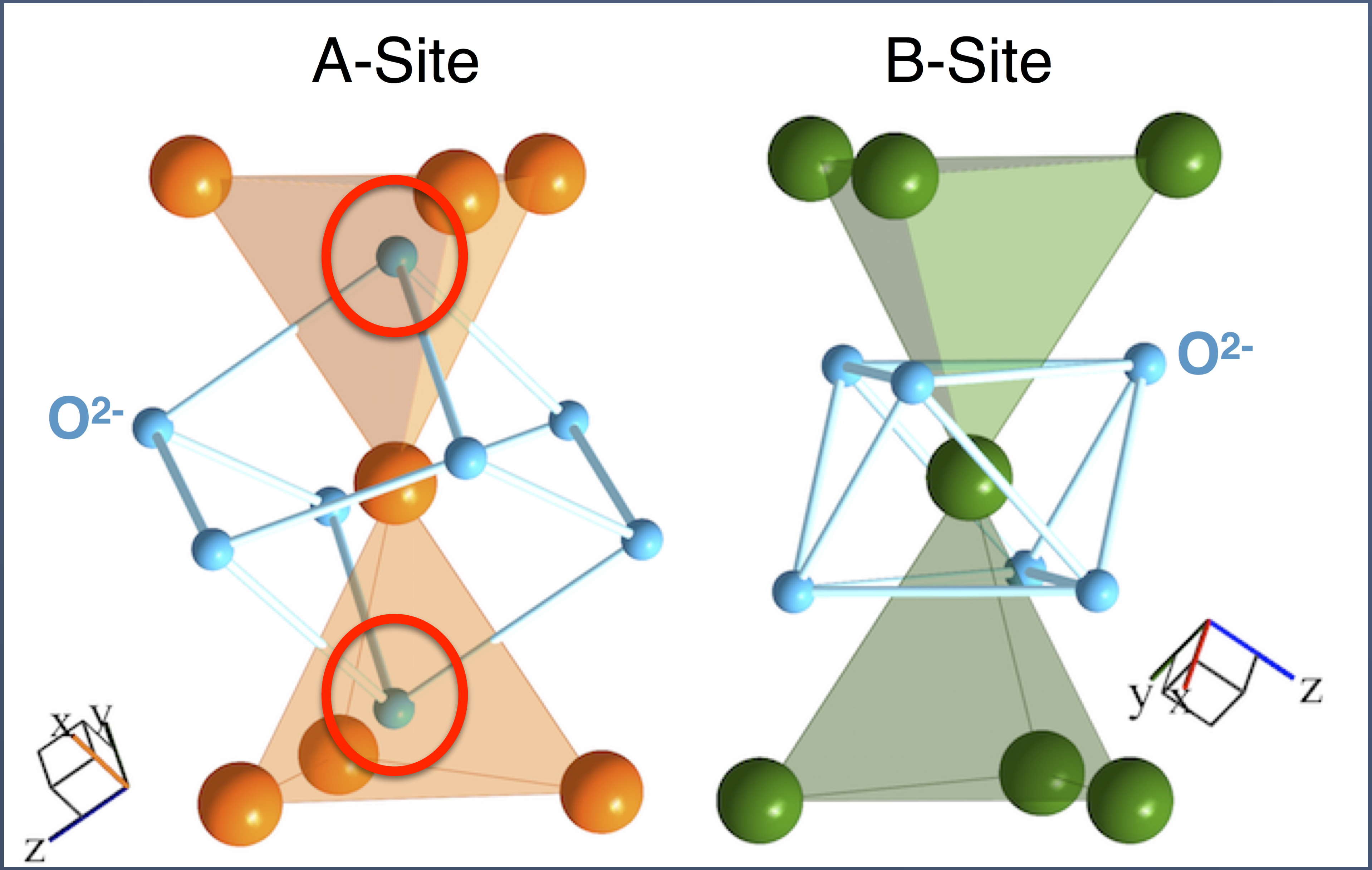
Local environments at the A^{3+} and B^{4+} sites:



Rare earth site **Mo site**

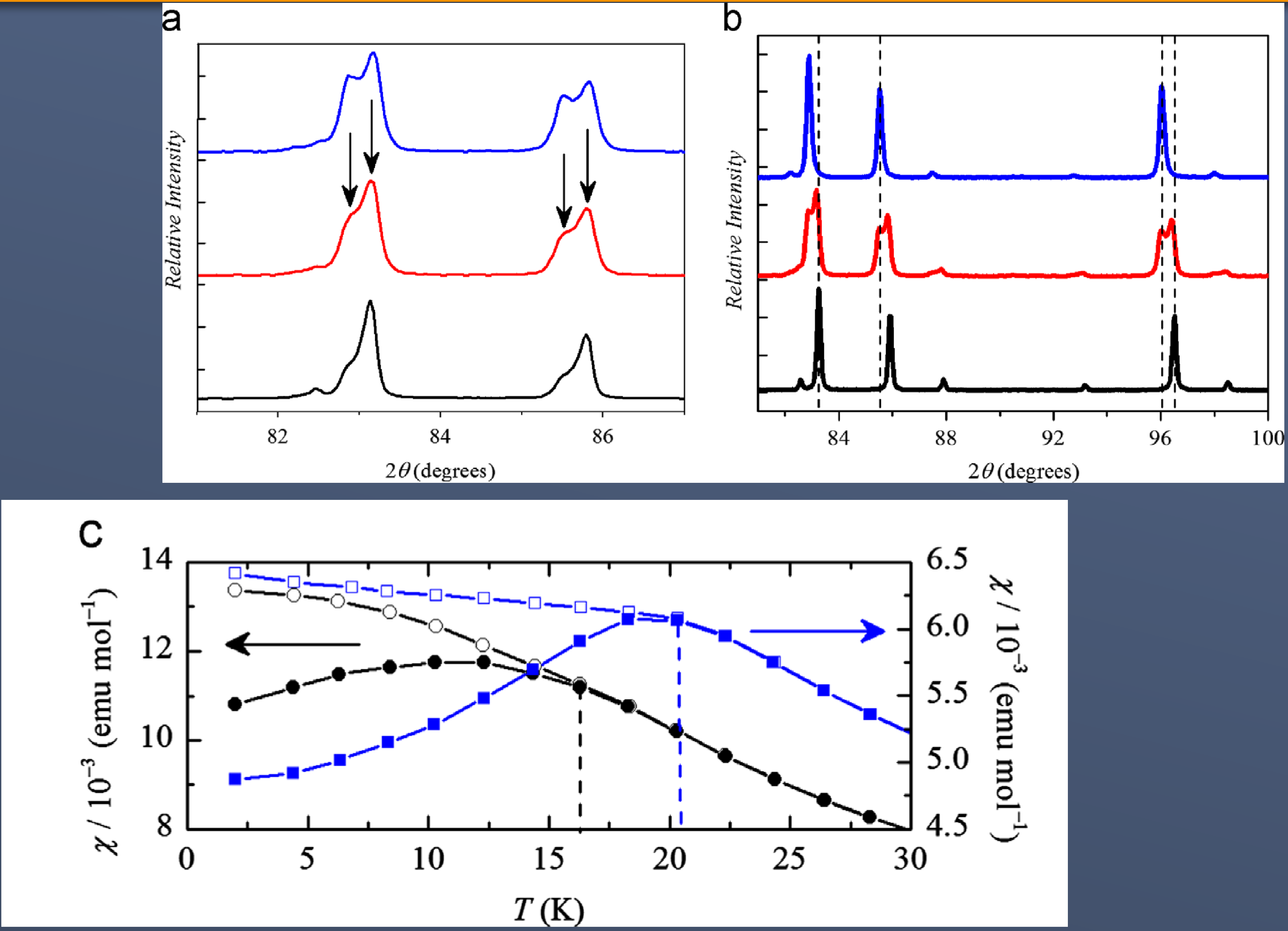
Local environments at the A^{3+} and B^{4+} sites:

$Lu_2Mo_2O_{6.7}$ oxygen deficiency is primarily at the O' site

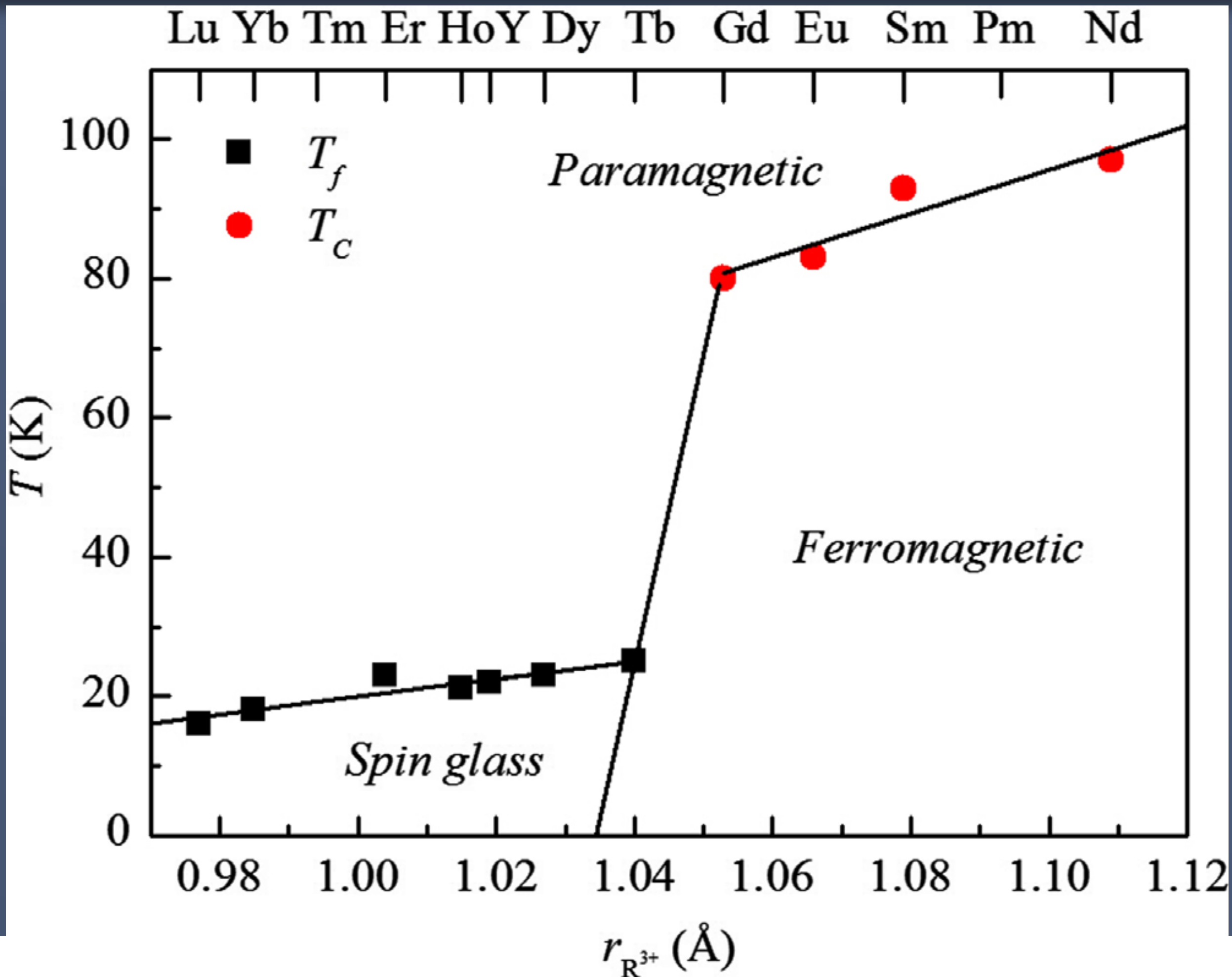


Rare earth site **Mo site**

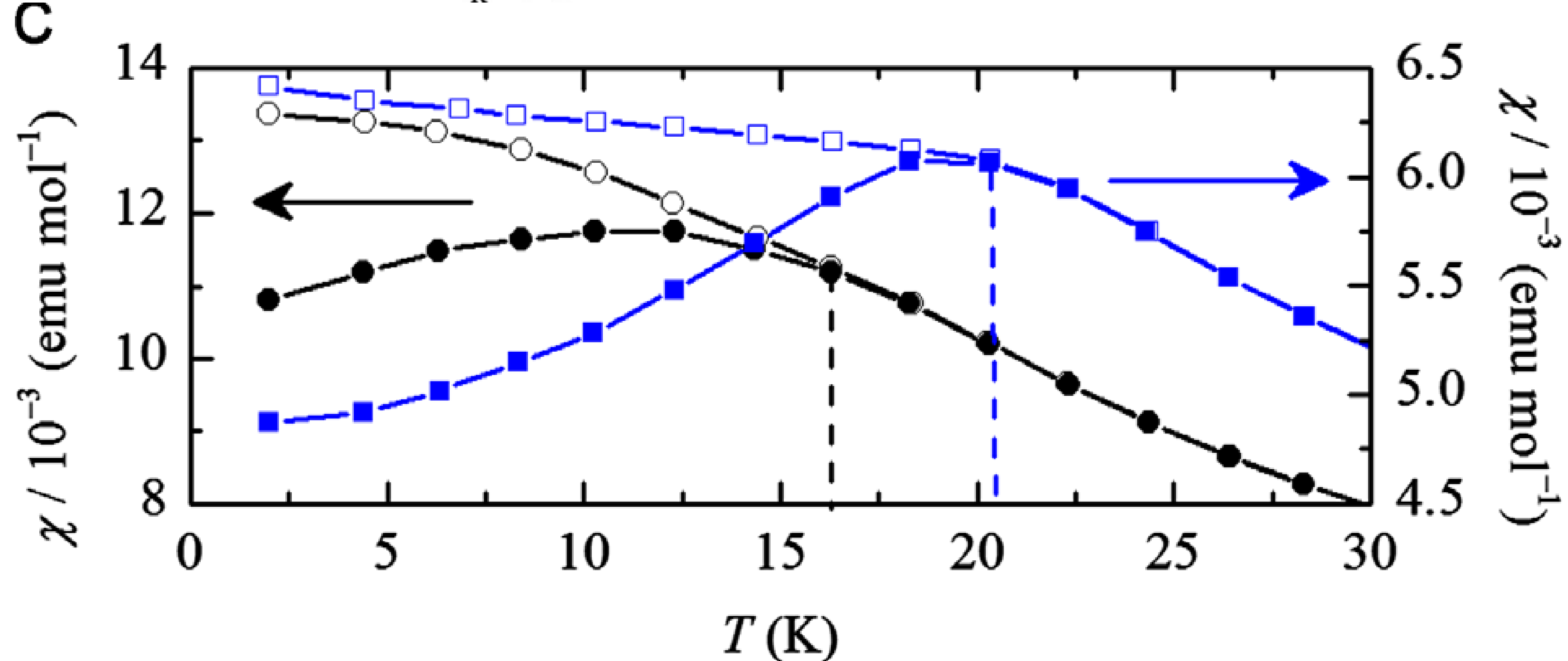
Synthesize either $Lu_2Mo_2O_7$ or $Lu_2Mo_2O_{6.7}$



$Lu_2Mo_2O_7$ vs $Lu_2Mo_2O_{6.7}$



Increase in T_f due in part to expansion of the lattice



Topochemical nitration of $Lu_2Mo_2O_7$

$$Lu_2Mo_2O_7\ (Mo^{4+},\ 4d^2,\ S=1) \xrightarrow[\text{24 hrs, 600 °C}]{NH_3\text{ (g), 250 cm}^3\text{ min}^{-1}} Lu_2Mo_2O_5N_2\ (Mo^{5+},\ 4d^1,\ S=½)$$

a = 10.1452(8) Å → a = 10.1499(1) Å

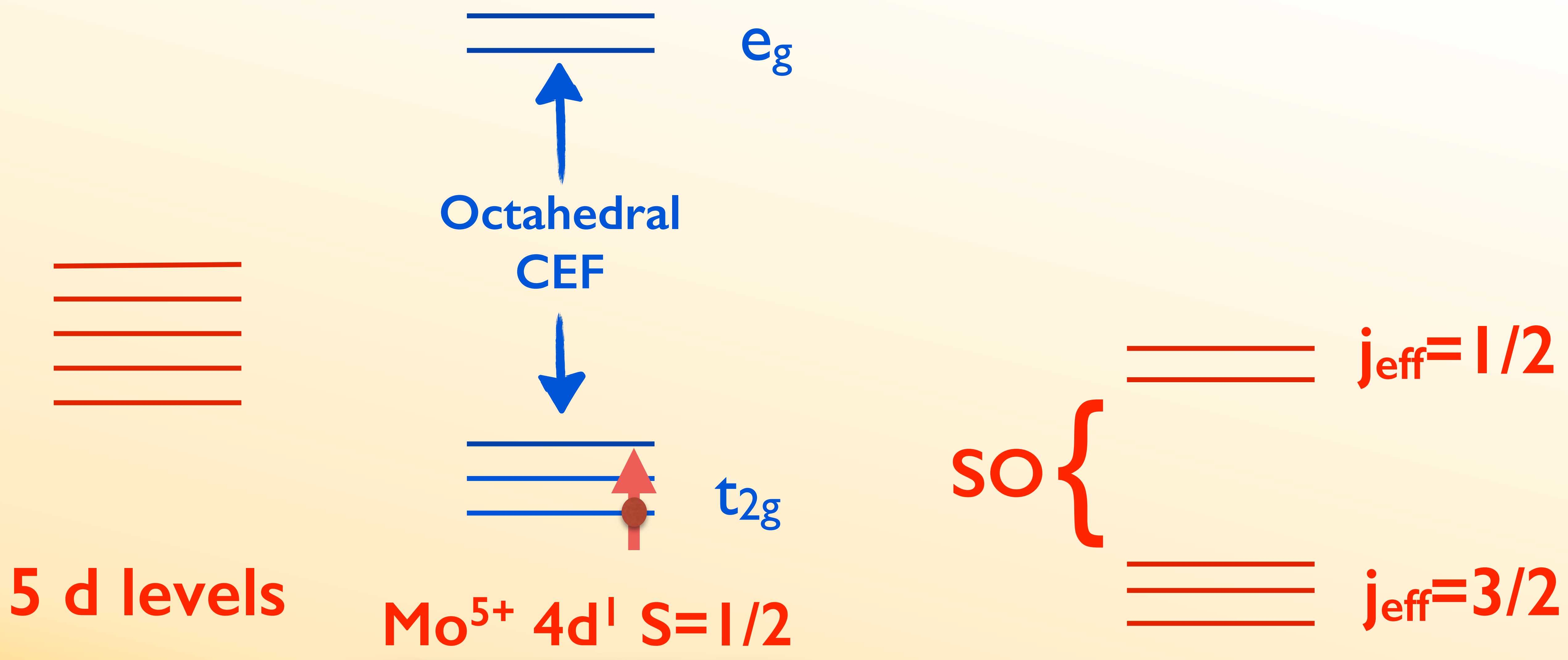


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TABLE I. Refined atomic coordinates and occupancies for $Lu_2Mo_2O_{4.8}N_{1.7}$ ($a = 10.1428(2)$ Å). Isotropic thermal parameters were 0.0337(6) Å^2 for metal cations and 0.0398(6) Å^2 for anion sites. Total $R_{wp} = 2.21$ %, $\chi^2 = 14.58$ for 64 variables.

Atom	Site	x	y	z	Occupancy
Lu	16d	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1.0
Mo	16c	0	0	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

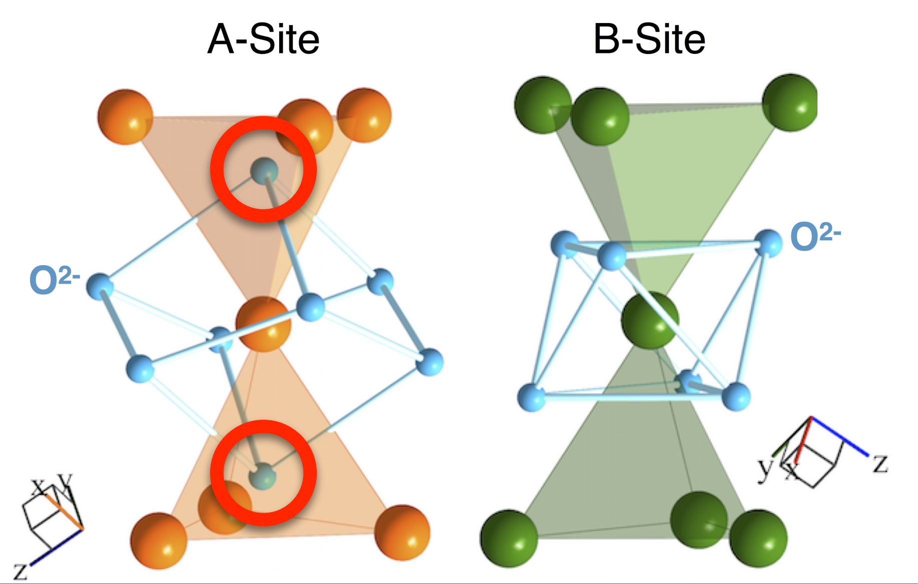


TABLE II. Results from the Curie Weiss fit to magnetic susceptibilities of the oxide and oxynitride pyrochlores.

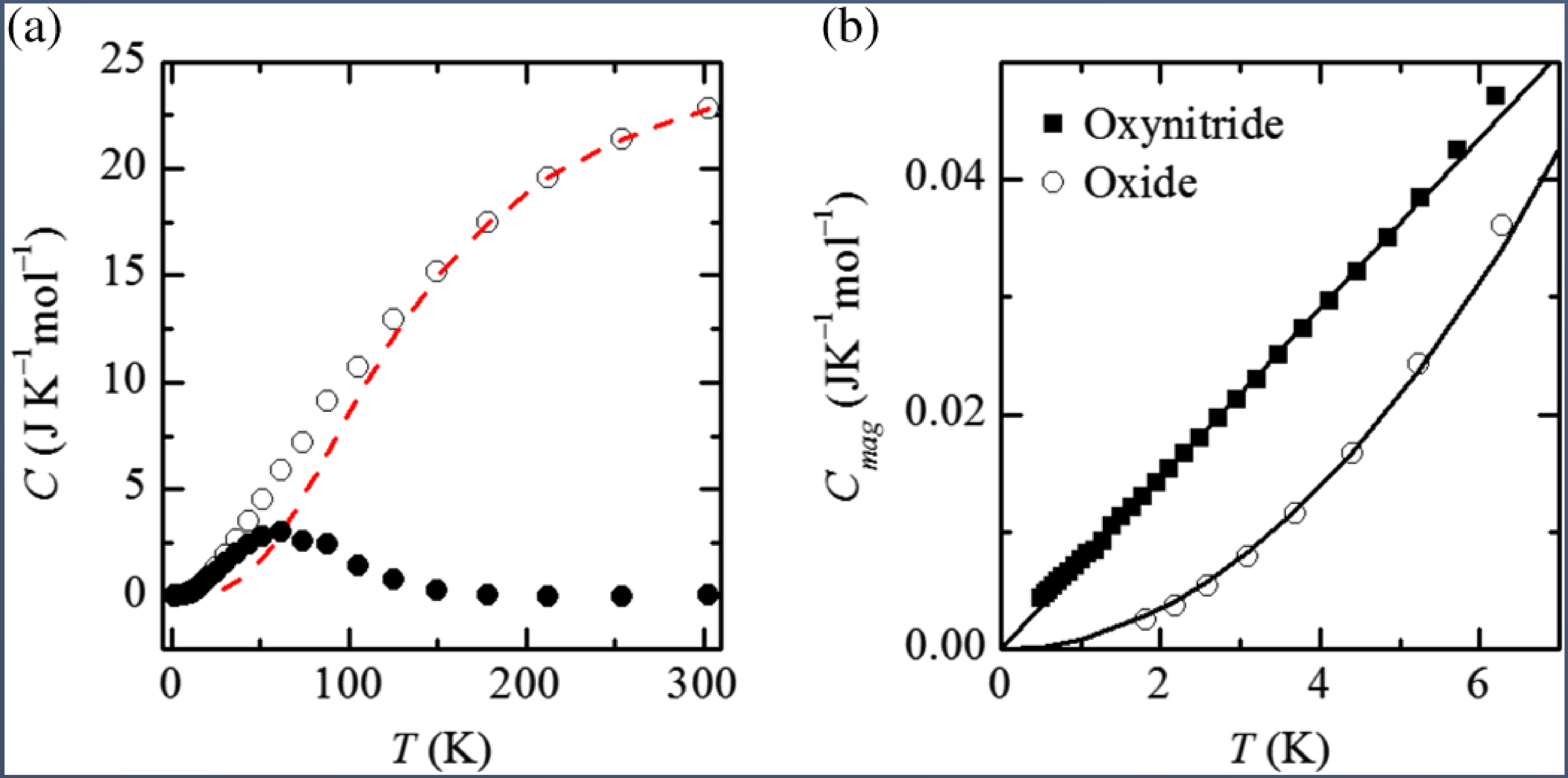
Sample	Fit region / K	$-\theta$ / K	μ_{eff} / μ_B
$Lu_2Mo_2O_7$	150 – 300	158(1)	1.89(1)
	200 – 300	171(1)	1.92(1)
	250 – 300	184(2)	1.85(1)
$Lu_2Mo_2O_5N_2$	150 – 300	121(1)	1.11(1)
	200 – 300	135(1)	1.13(1)
	250 – 300	152(2)	1.16(1)

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

Topochemical nitration of $Lu_2Mo_2O_7$

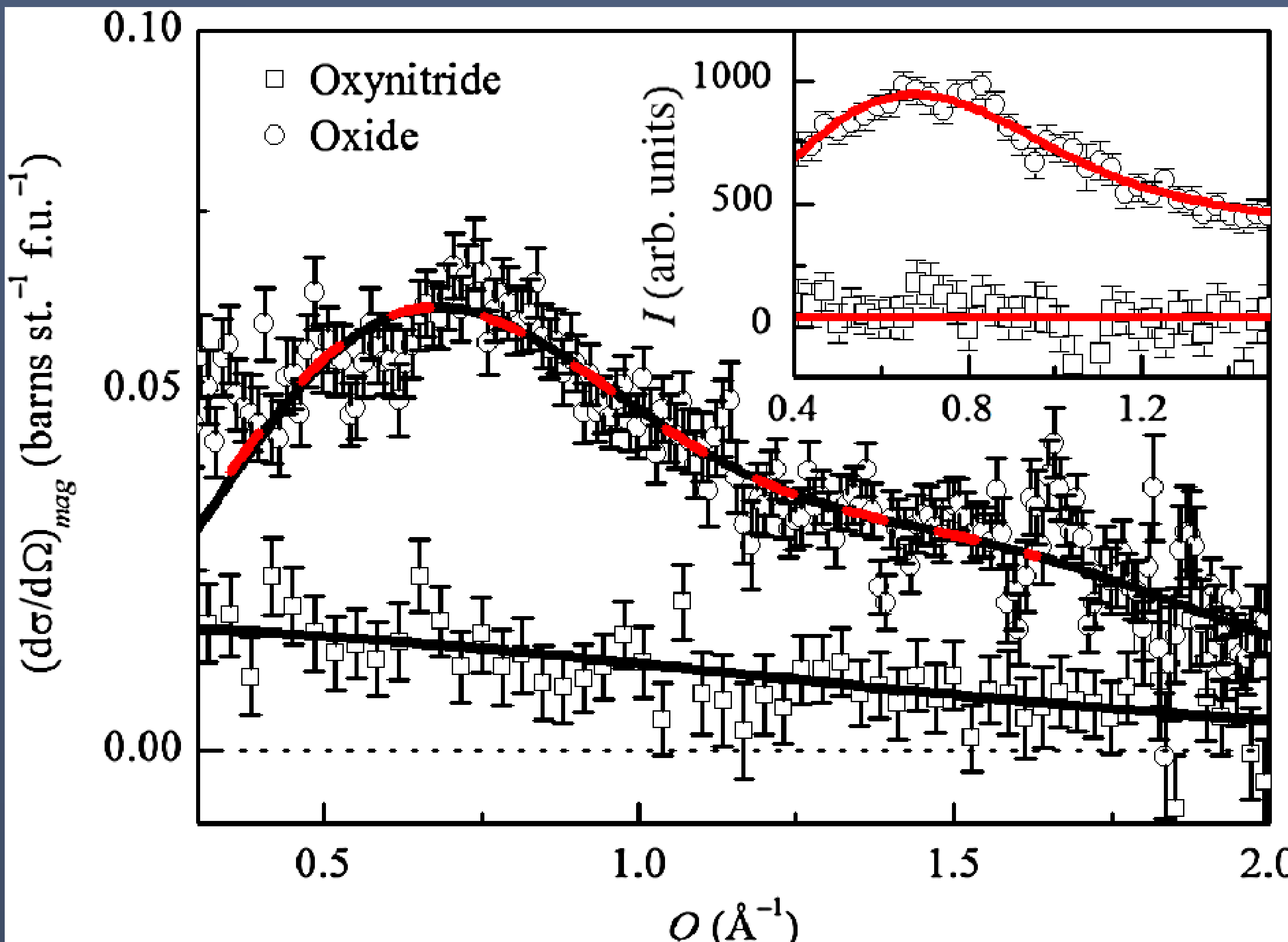
$$Lu_2Mo_2O_7\ (Mo^{4+},\ 4d^2,\ S = 1) \xrightarrow[\text{24 hrs, 600 °C}]{NH_3\text{ (g), 250 cm}^3\text{ min}^{-1}} Lu_2Mo_2O_5N_2\ (Mo^{5+},\ 4d^1,\ S = ½)$$

$a = 10.1452(8)$ Å → $a = 10.1499(1)$ Å



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

Elastic Neutron Scattering: $Lu_2Mo_2O_7$ vs $Lu_2Mo_2O_5N_2$

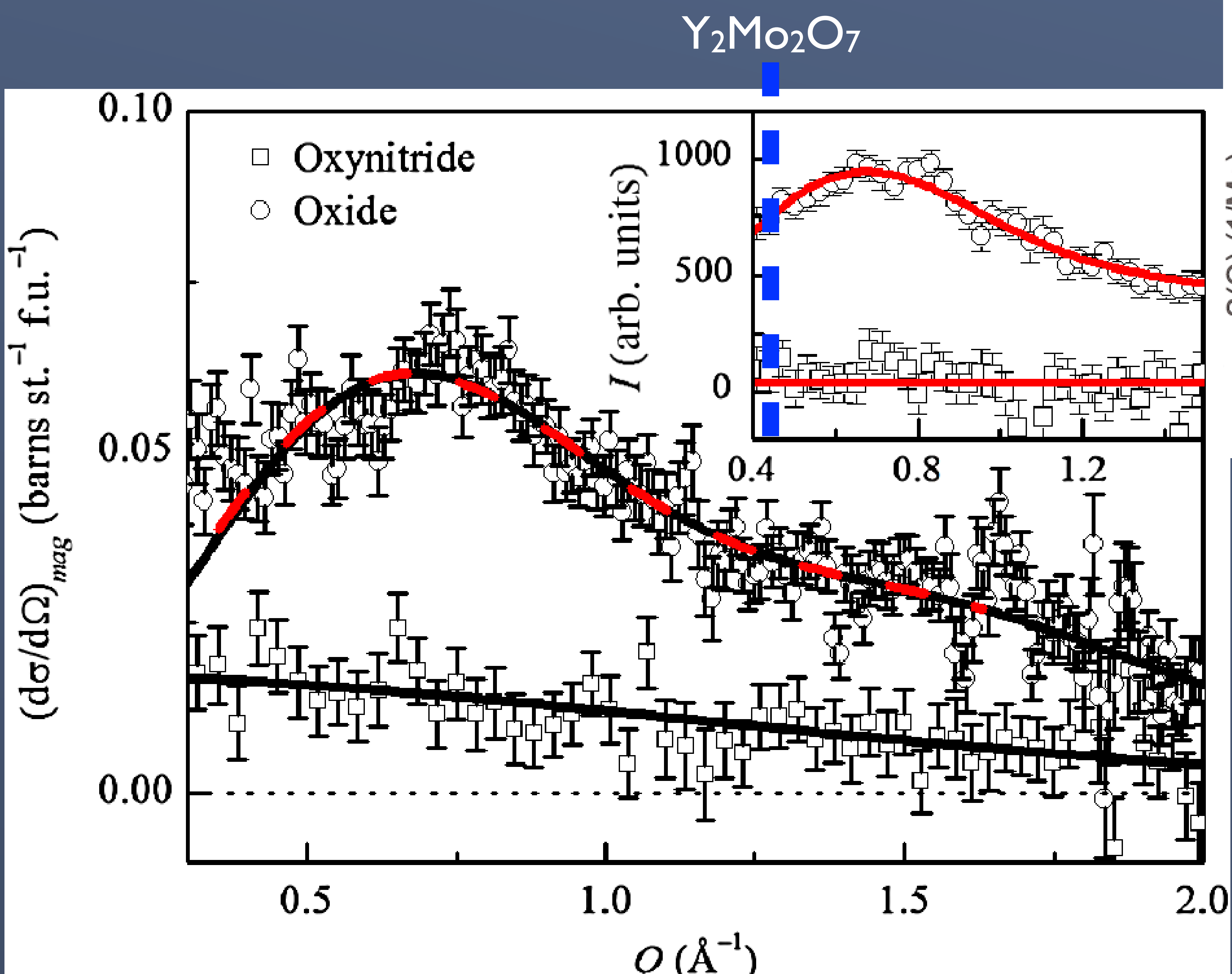


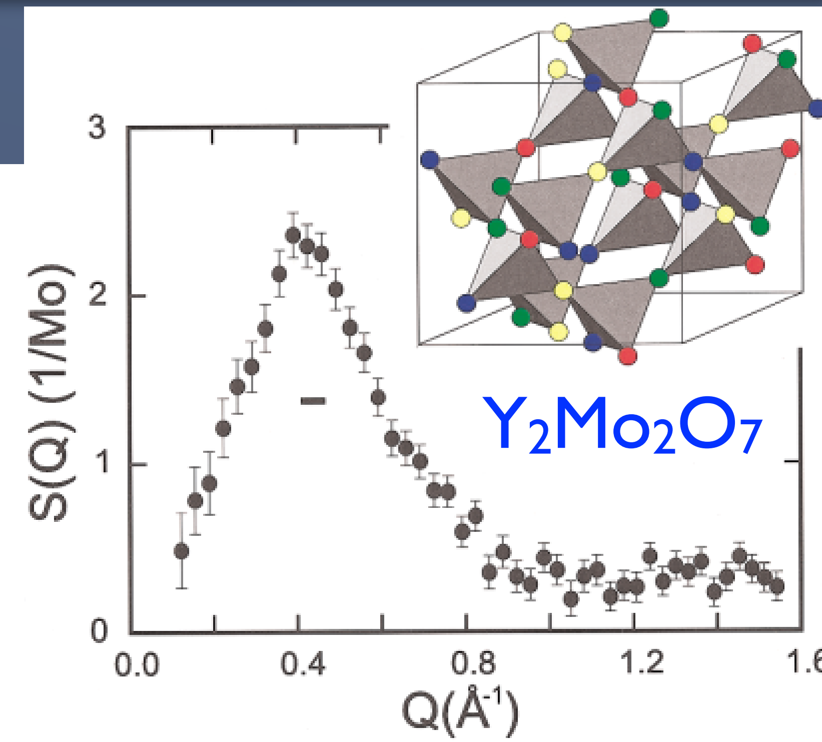
High resolution inelastic scattering res +/- 0.1 meV

Polarized Neutron Diffraction

T=1.5 K

Elastic Neutron Scattering: $Lu_2Mo_2O_7$ vs $Y_2Mo_2O_7$ vs $Lu_2Mo_2O_5N_2$

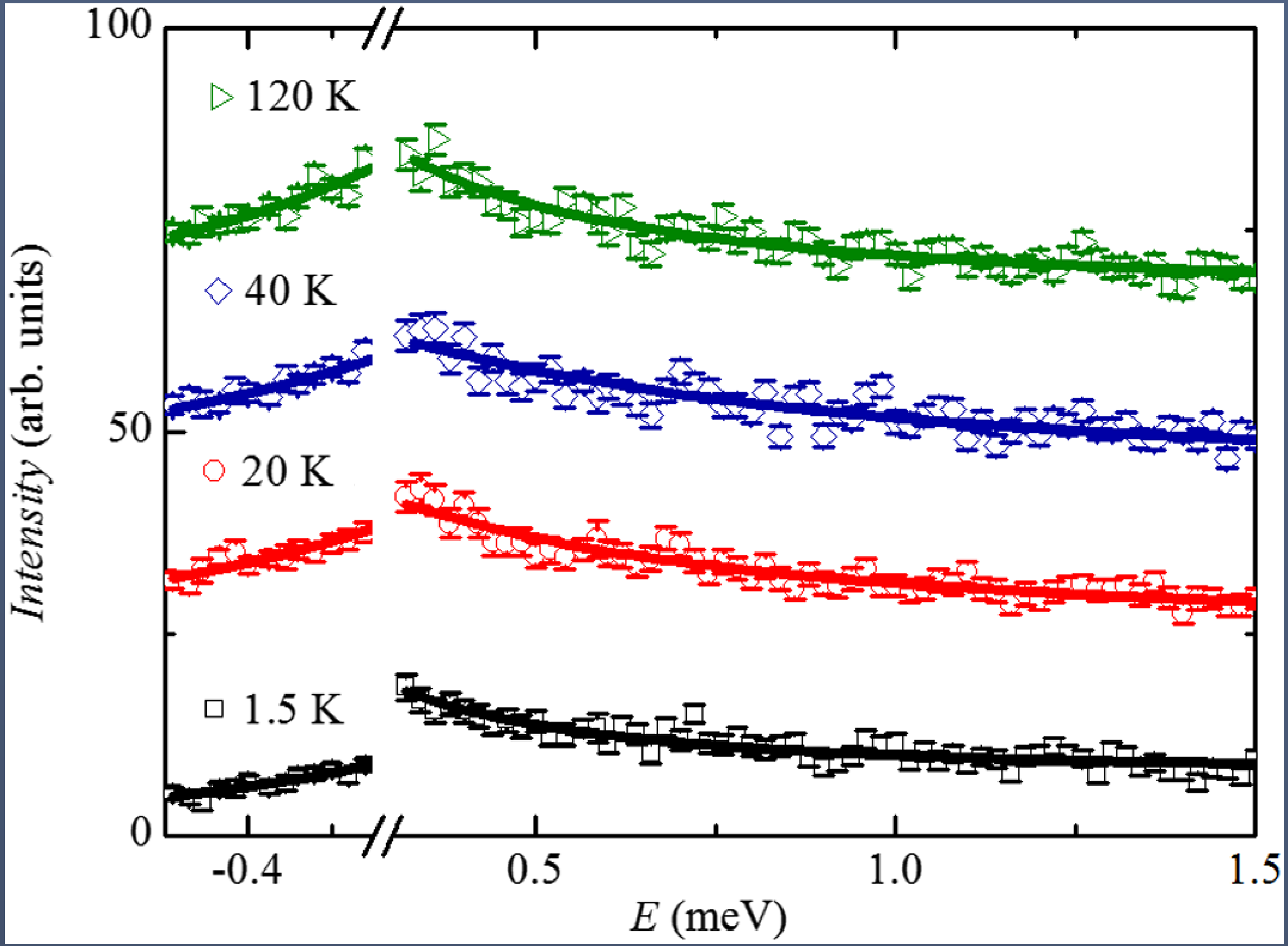




Polarized Neutron Diffraction

T=1.5 K

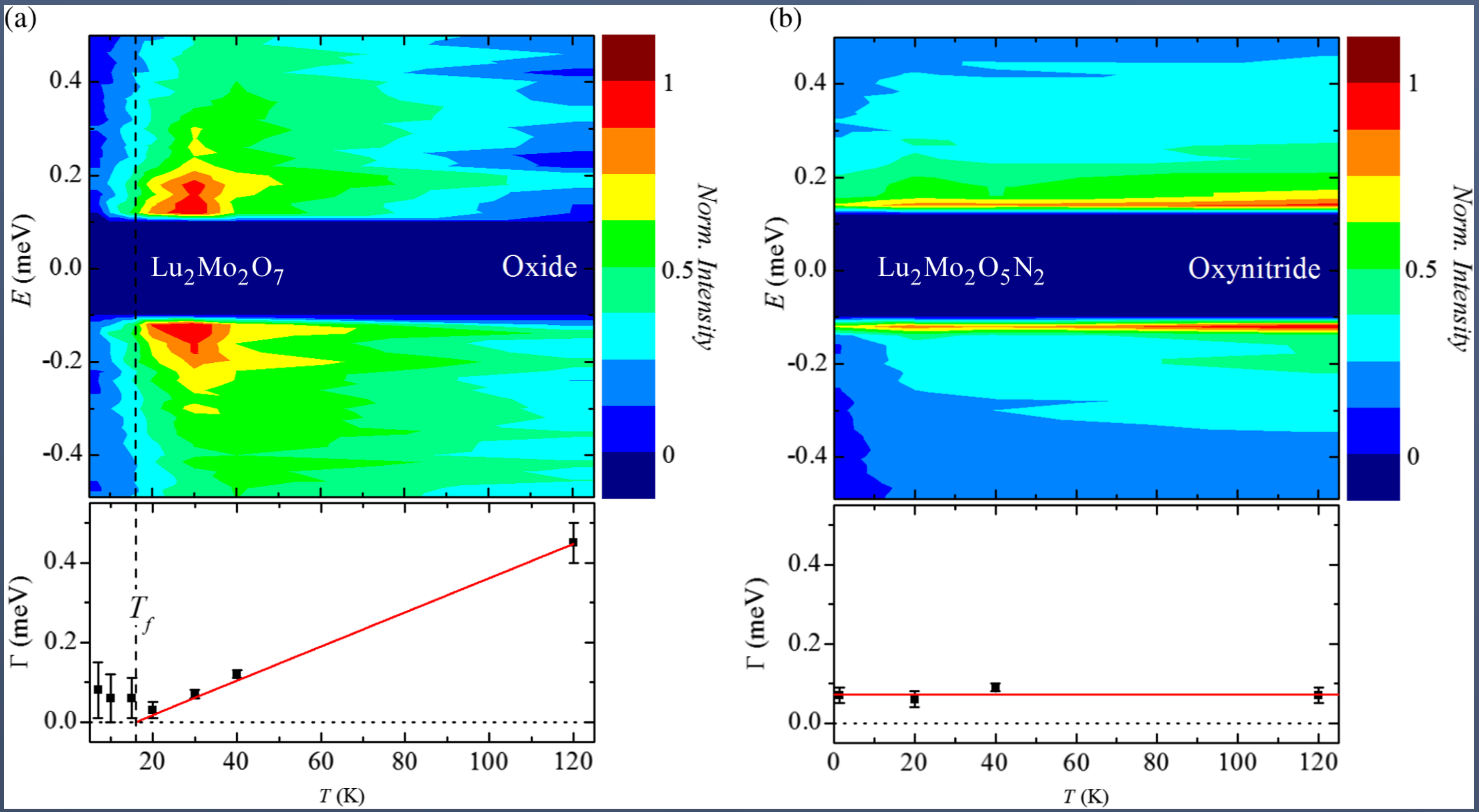
Modeling the inelastic scattering



$Lu_2Mo_2O_5N_2$

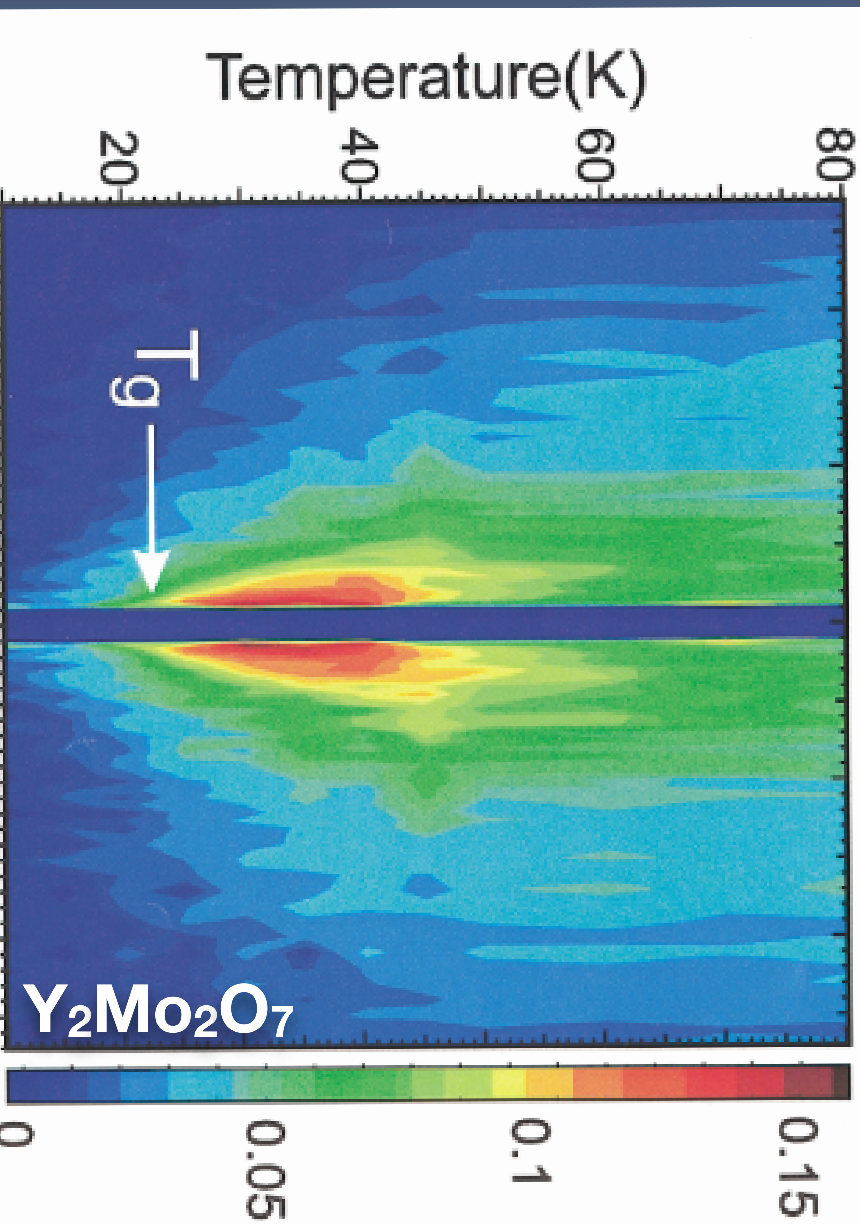
$$S(E) = \frac{1}{\pi}\chi''(E)[1 + n(E)], \quad \chi''(E) = \chi_0 \arctan\left(\frac{E}{\Gamma}\right)$$

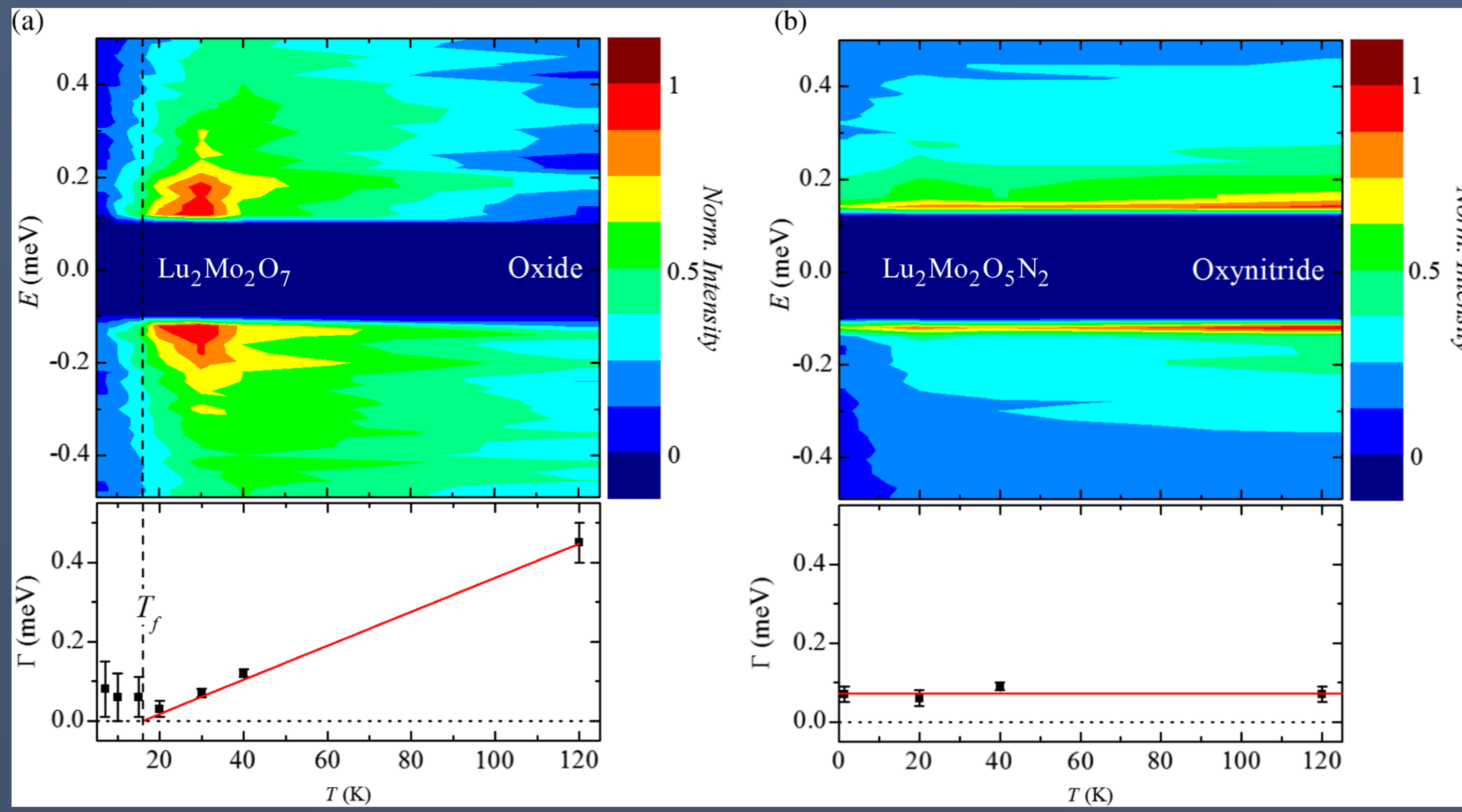
Inelastic Neutron Scattering: $Lu_2Mo_2O_7$ vs $Lu_2Mo_2O_5N_2$



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

Inelastic Neutron Scattering: $Y_2Mo_2O_7$ vs $Lu_2Mo_2O_7$ vs $Lu_2Mo_2O_5N_2$

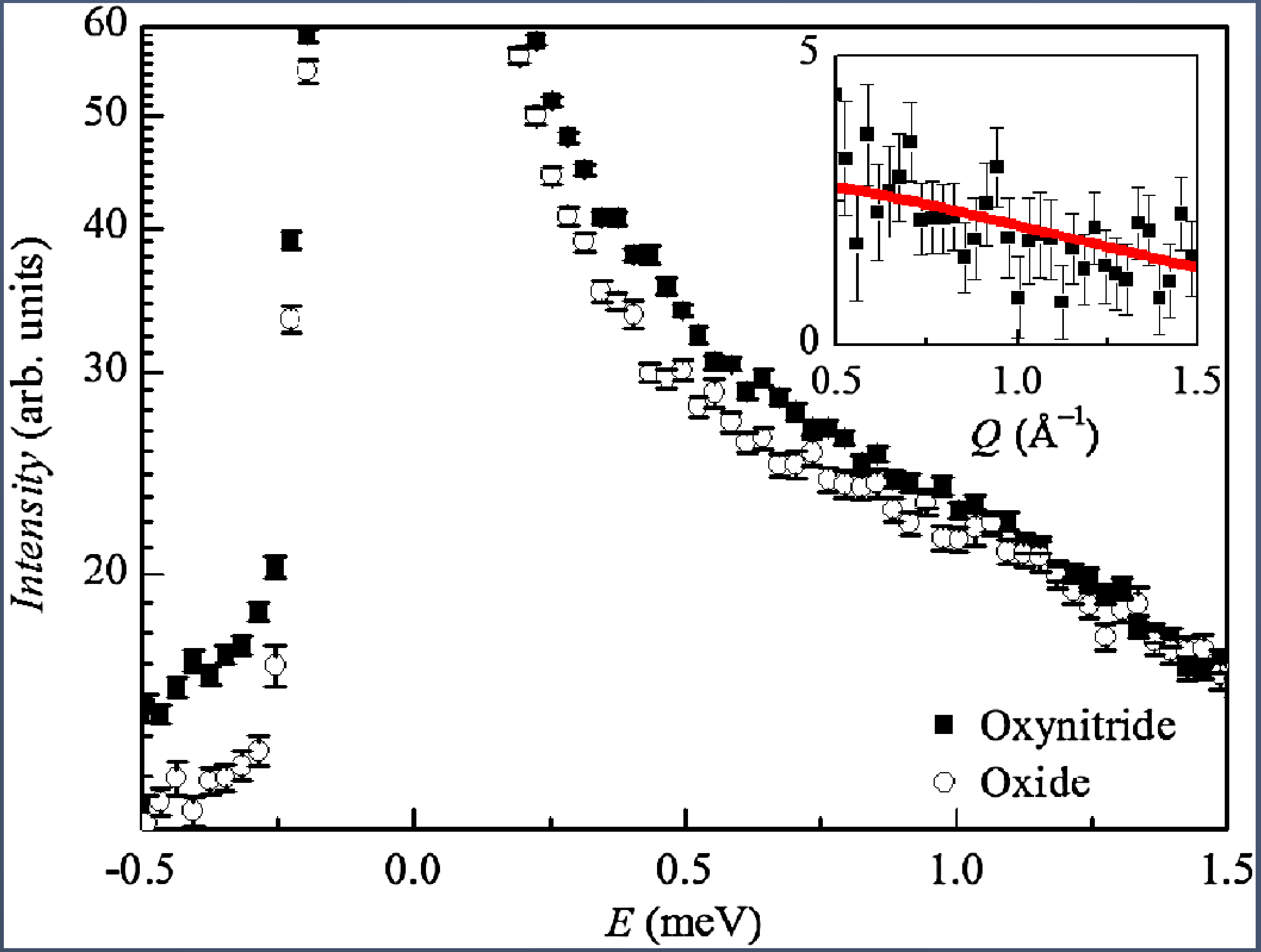




S=1 Moly Oxides freeze at T_f ~ 20 K

S=1/2 Oxynitride doesn't freeze!

Inelastic Neutron Scattering: $Lu_2Mo_2O_7$ vs $Lu_2Mo_2O_5N_2$



S=1/2 degrees of freedom are strongly fluctuating at T=1.5 K ~ 0.012 T_{CW}

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 ~ 20 K*

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

- *Topochemical nitration of $Lu_2Mo_2O_7$ yields $Lu_2Mo_2O_5N_2$*
  Variation of S=1/2 pyrochlore antiferromagnet?
  Gapless, strongly fluctuating ground state - no freezing!

Collaboration: