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Tuning into Frustration: Structure and Chemistry of the Kagomé Antiferromagnet $YBaCo_4O_{7+\delta}$

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Work supported under U.S. DoE Office of Science

Outline

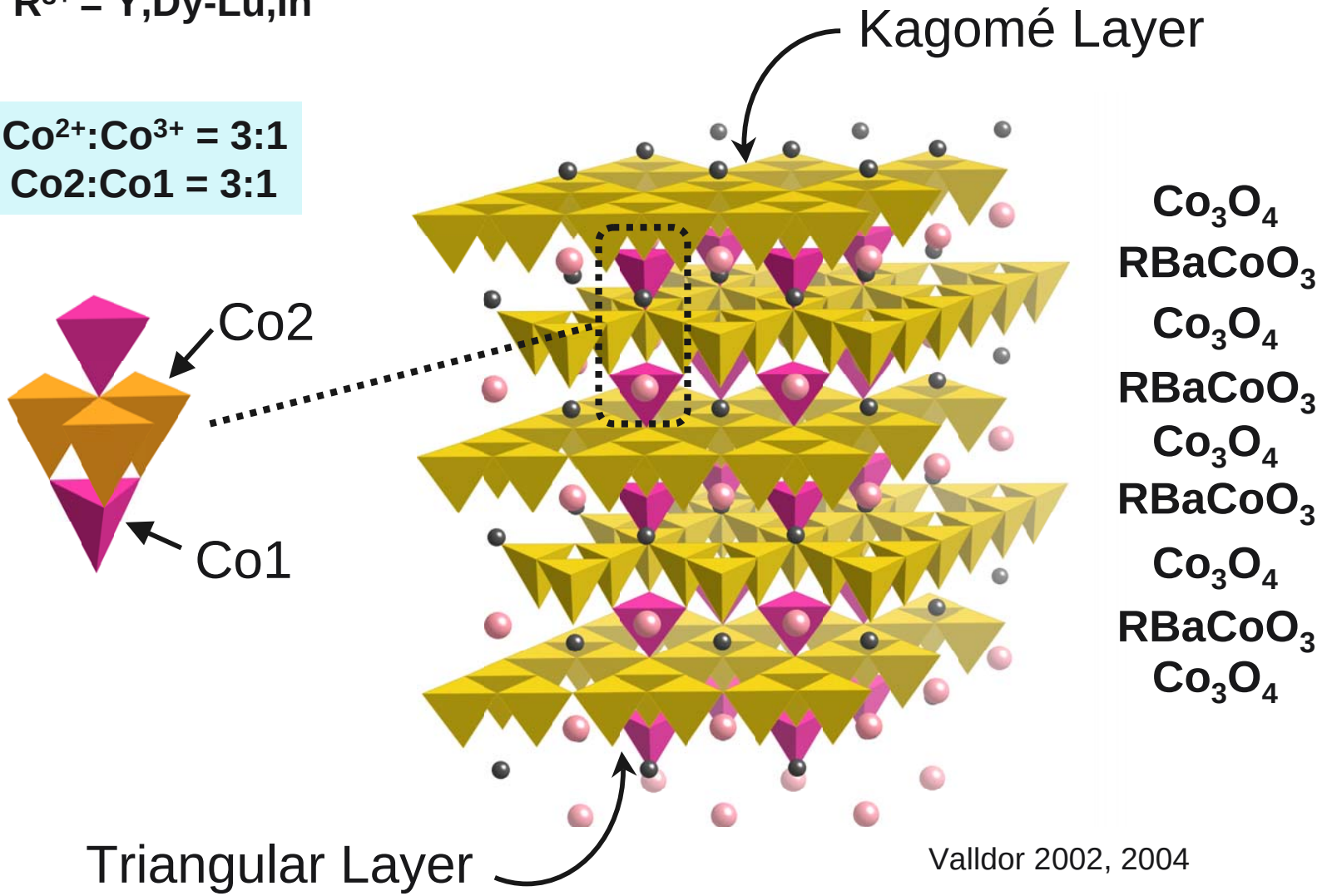
- Crystal and magnetic structure of $YBaCo_4O_{7.0}$ (Y-114)
- Oxidation I: $YBaCo_4O_8$ — A New Structure
- Oxidation II: $YBaCo_4O_{7+\delta}$ — Tuning into Frustration
- Summary

Questions/Issues will be raised along the way

Crystal Structure of $RBaCo_4O_7$

R^{3+} = Y,Dy-Lu,In

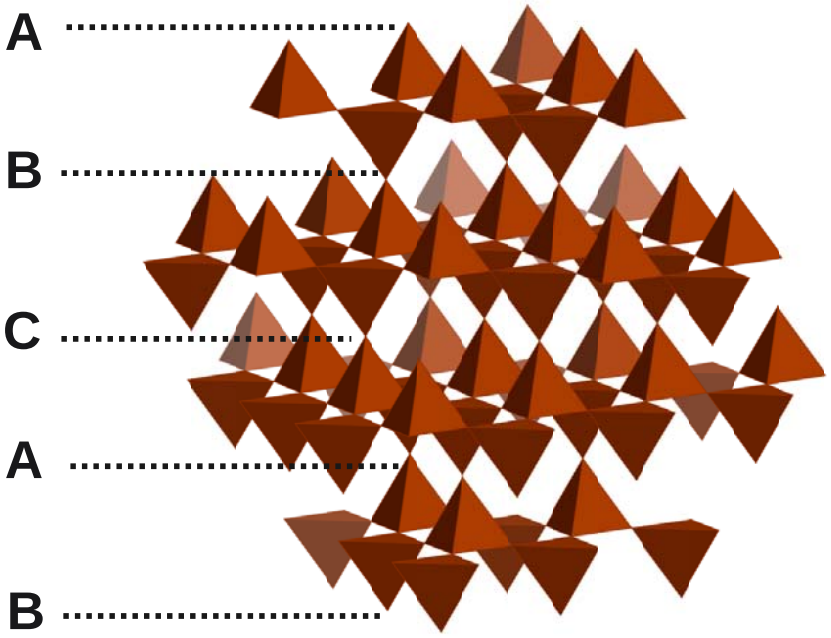
Co^{2+}:Co^{3+} = 3:1
Co2:Co1 = 3:1



Valldor 2002, 2004

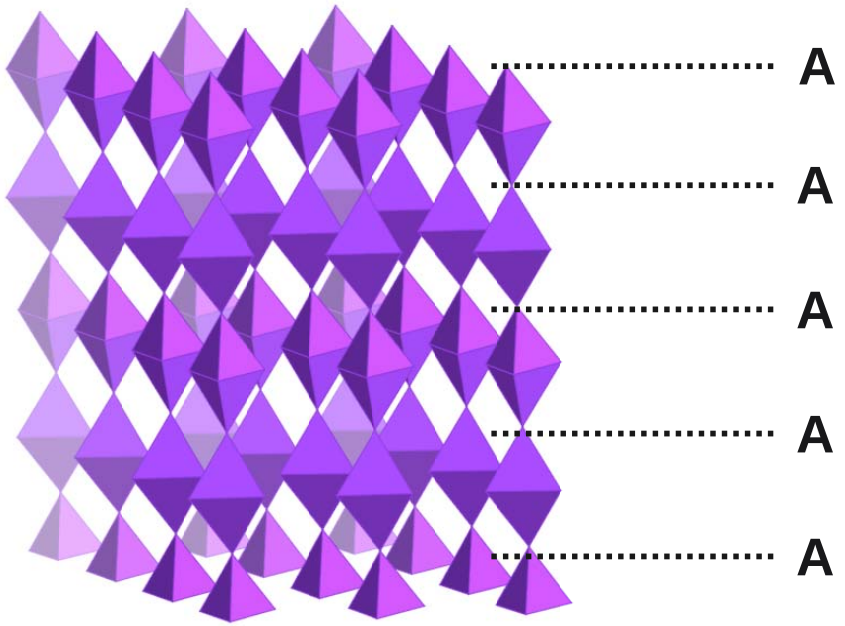
Relative of Pyrochlore

$M_2M'_2O_7$



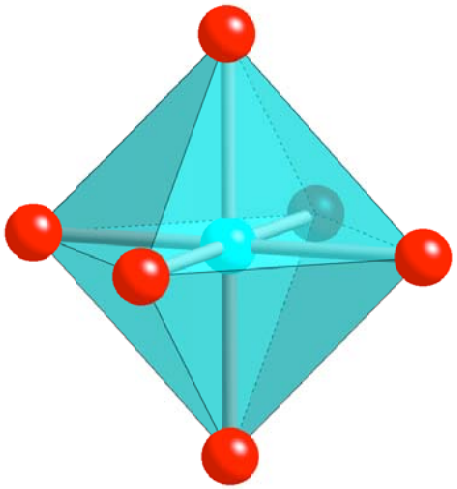
Triangular layers
•••ABCABC•••

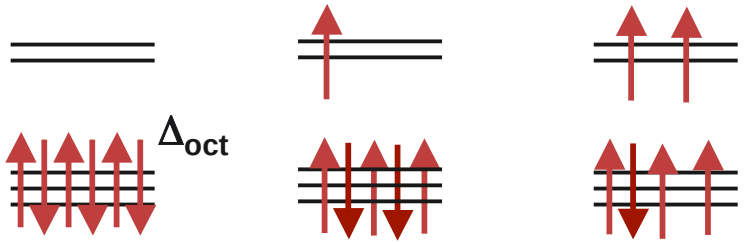
$RBaCo_4O_7$



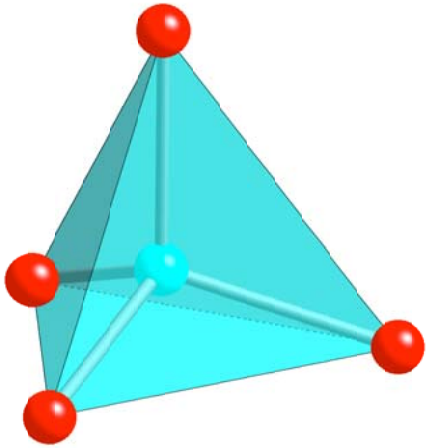
Triangular layers
•••AAAAAA•••

Probable Spin State Assignment

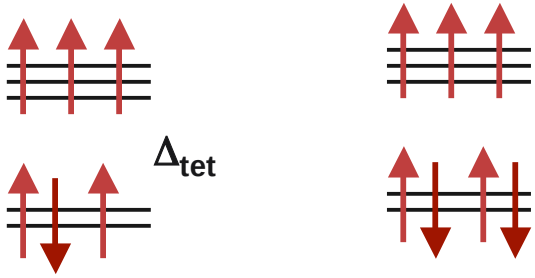




Co^{3+}, S=0 Co^{3+}, S=1 Co^{3+}, S=2

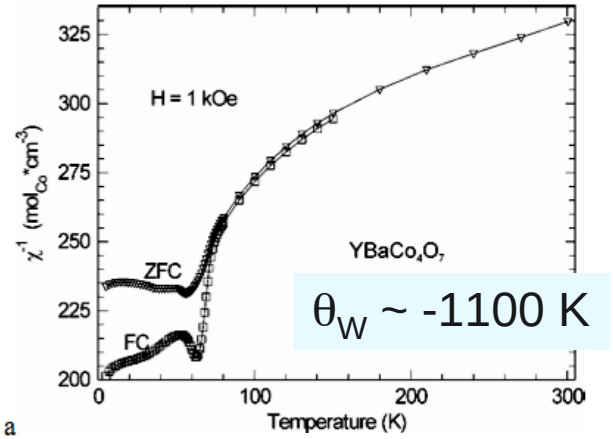


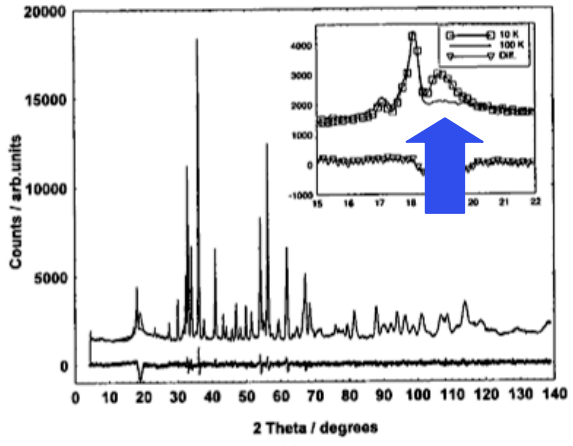
$\Delta_{tet} = 4/9\ \Delta_{oct}$ → High Spin

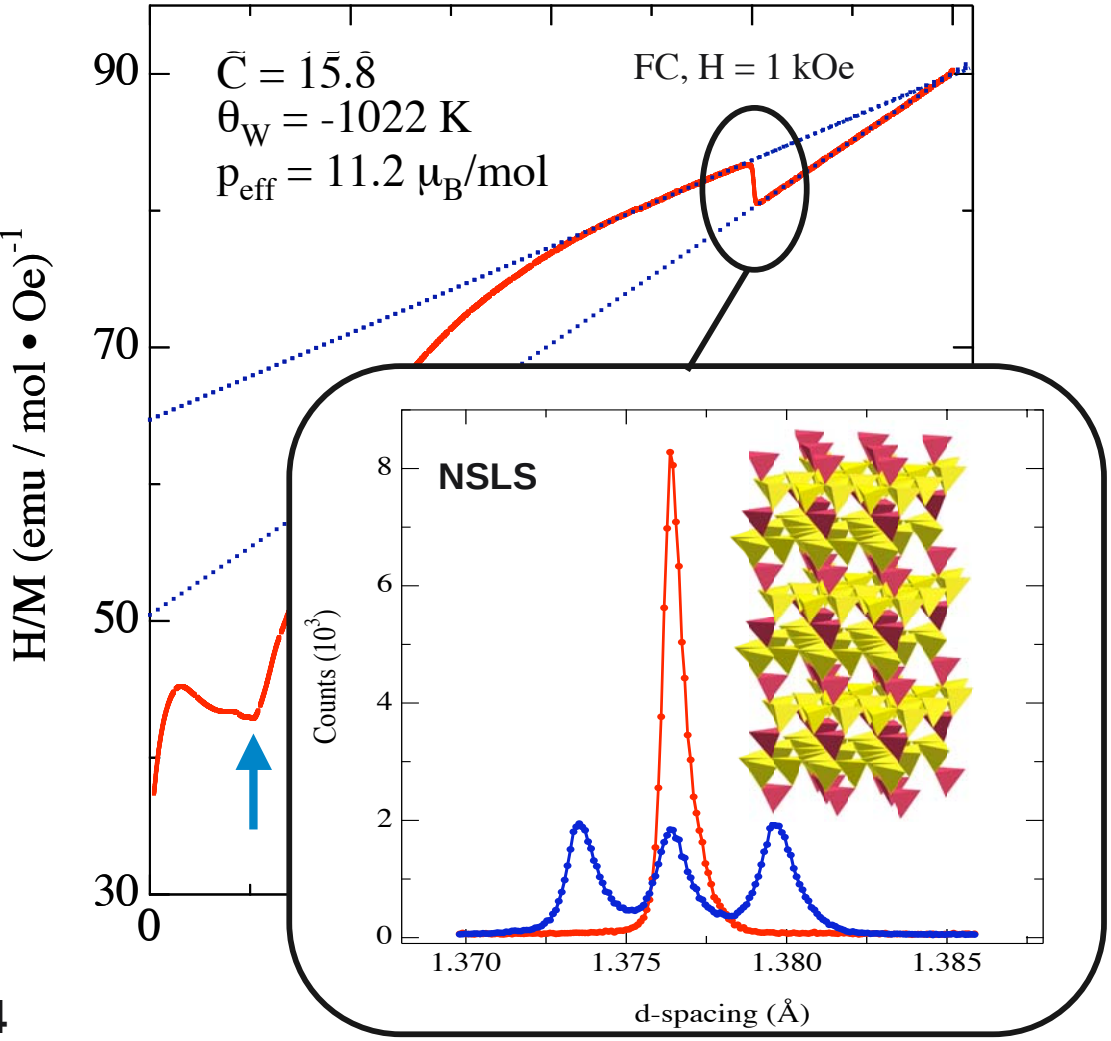


Co^{3+}, S=2 Co^{2+}, S=3/2

Magnetism: $YBaCo_4O_7$

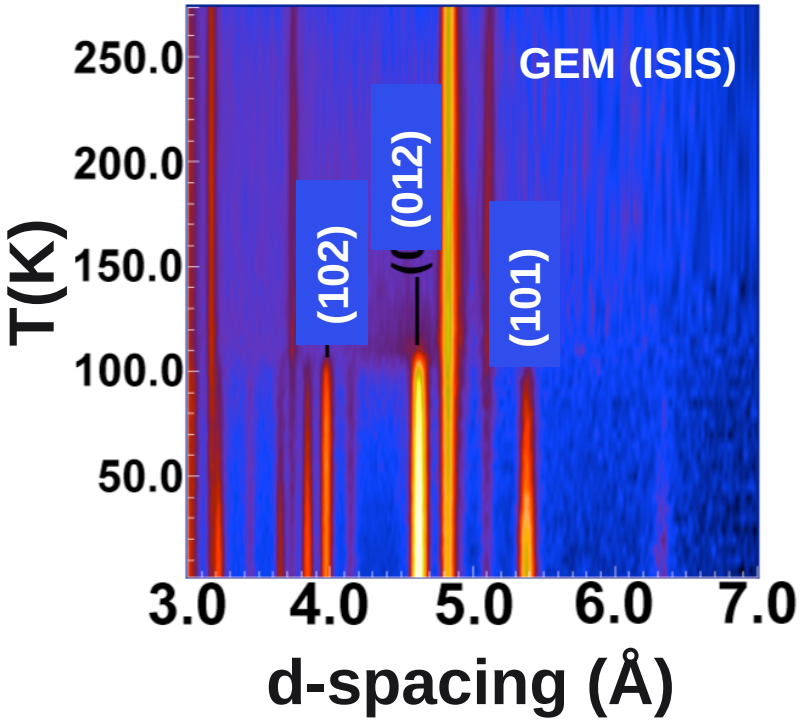


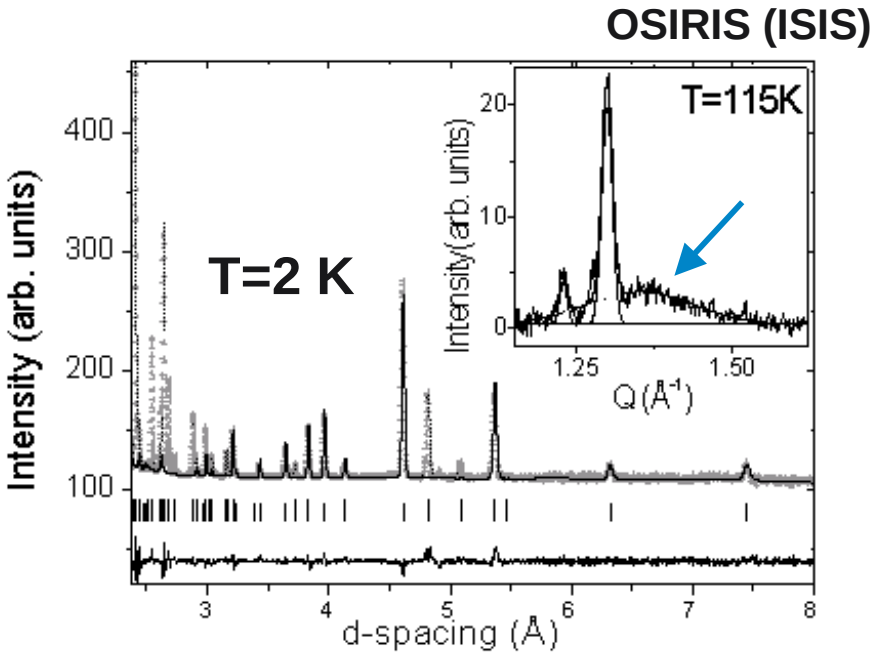




Valldor (2002): Diffuse AF peak, spin glass, $|\theta_W/T_{cusp}| \sim 14$

Low-T Magnetism: Well-Ordered Antiferromagnet





- T_N = 108 K
- *k* = 0 ordering (*Pbn2$_1$*)
- Diffuse scattering T > T_N
- $|\theta_W/T_N|$ ~ 4.5

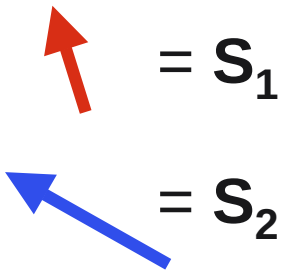
"The more we look, the less frustrated we get "

Magnetic Structure of $YBaCo_4O_7$: 120° Motif

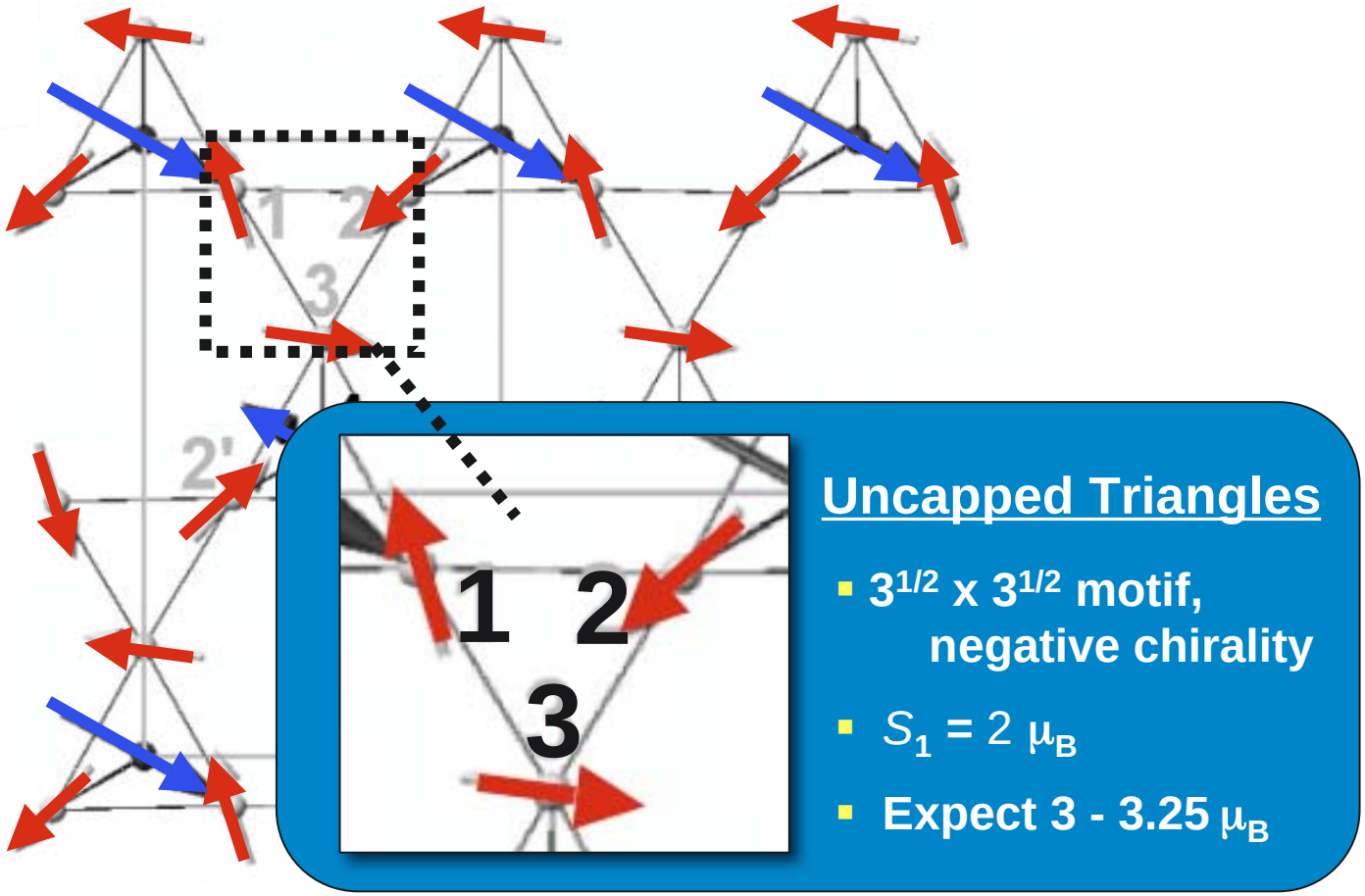
Solved by simulated annealing, Rietveld refinement (L. Chapon)

PRB 74,172401(2006)

T = 2 K
P112$_1$'
***k* = 0**
Γ_4 irrep.



$S_i \parallel ab$



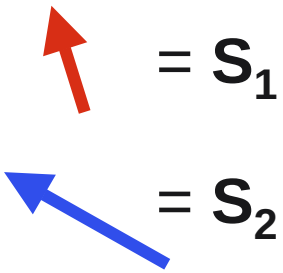
Uncapped Triangles

- $3^{1/2}$ x $3^{1/2}$ motif, negative chirality
- $S_1 = 2\ \mu_B$
- Expect 3 - 3.25 μ_B

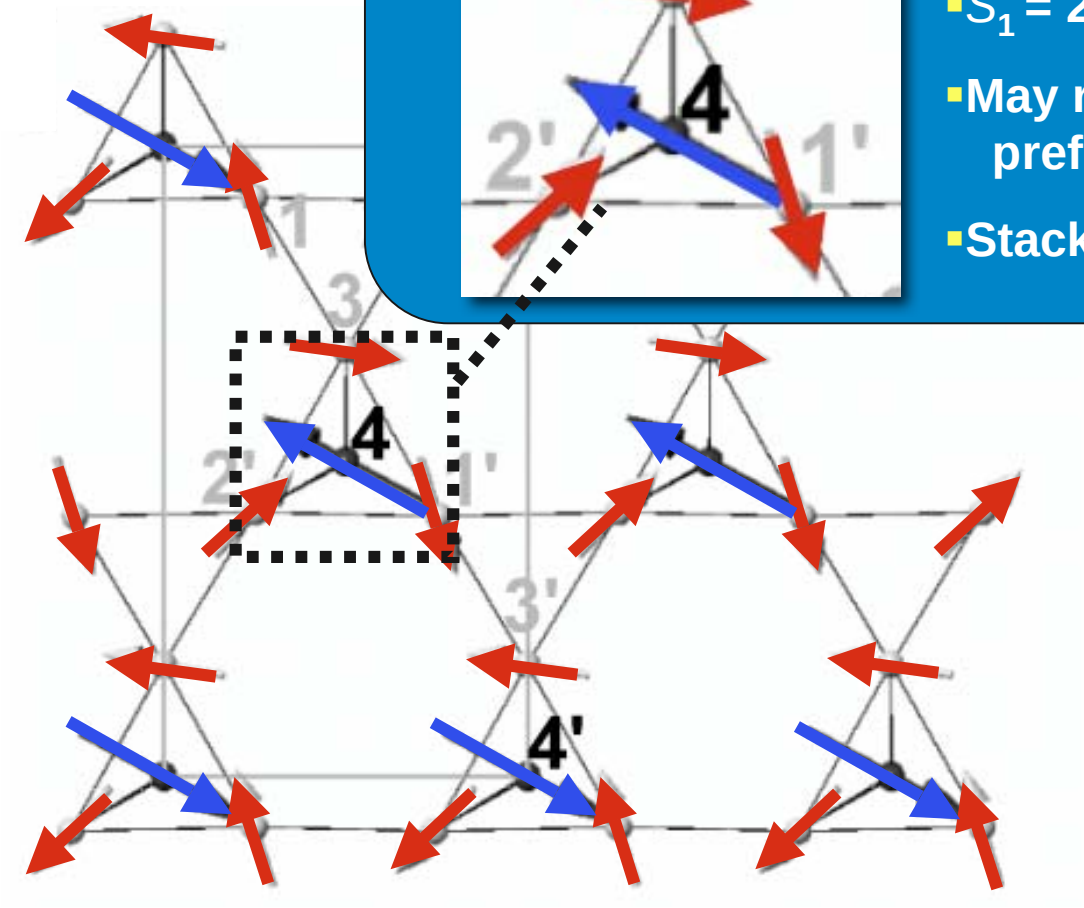
Magnetic Structure of $YBaCo_4O_7$

Solved by simulated anneali

T = 2 K
P112$_1$'
***k* = 0**
Γ_4 irrep.



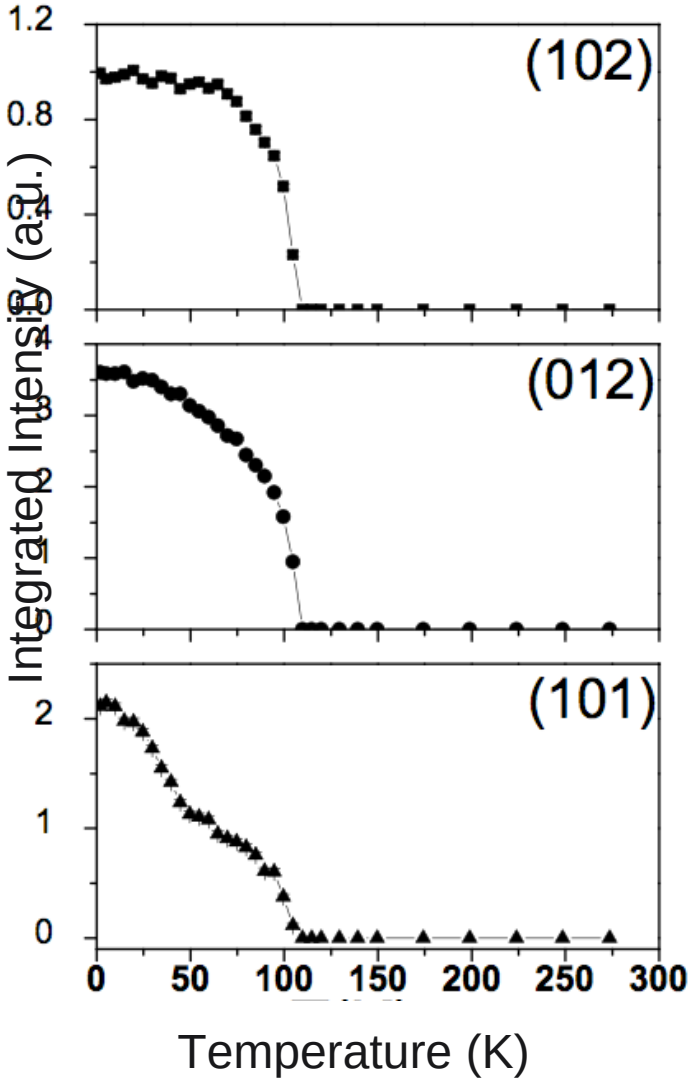
$S_i \parallel ab$

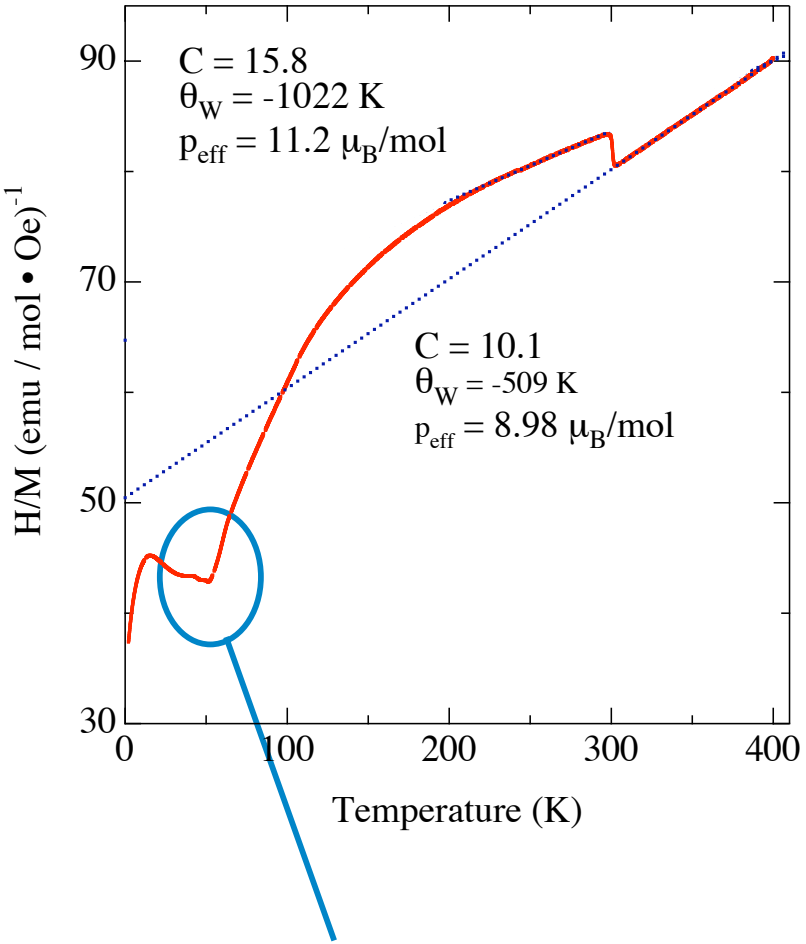


Capped Triangles

- S_1 = 2 μ_B ; S_2= 3.6 μ_B
- May reflect Co^{3+} preference (S=2)
- Stacked FM along c

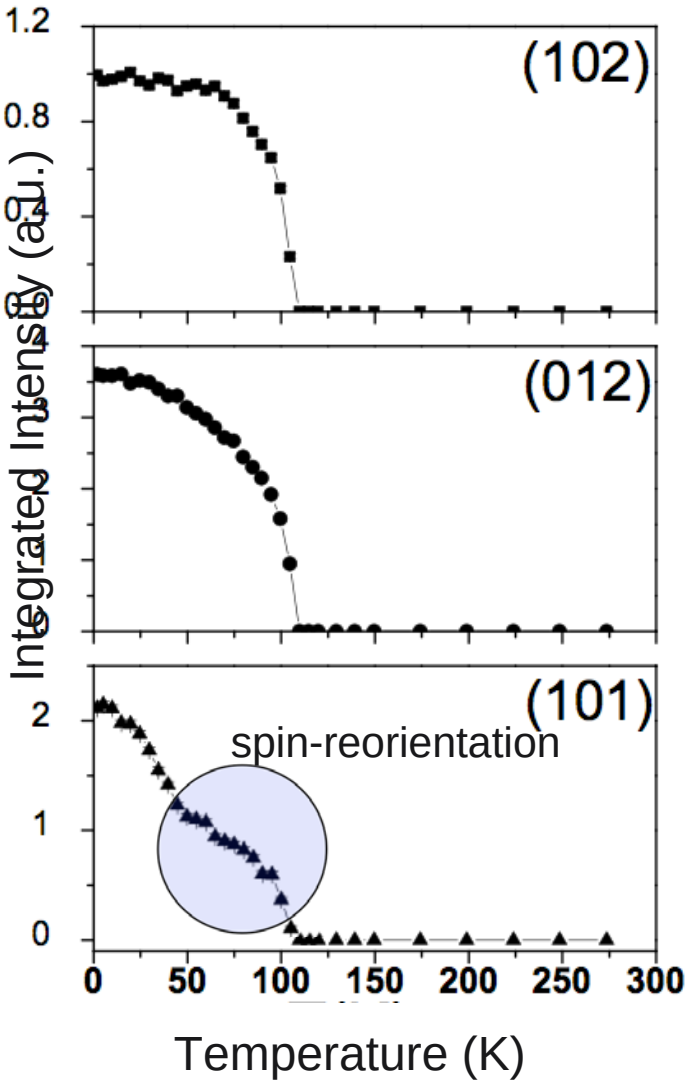
Temperature Dependence

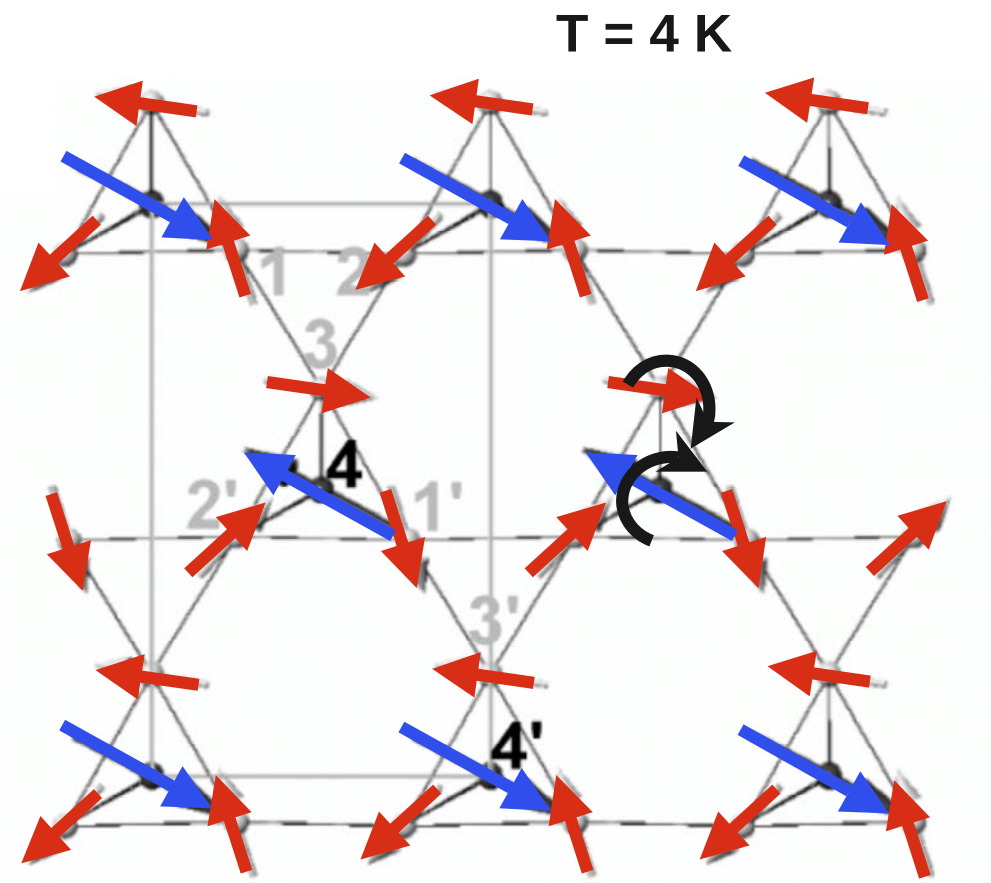




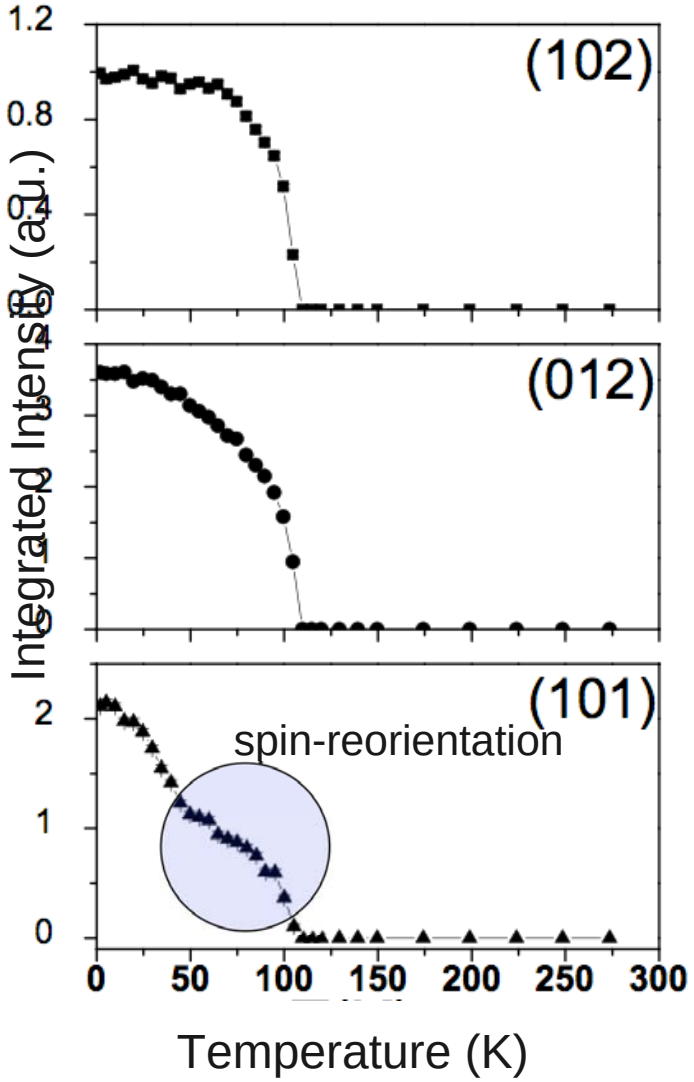
What's going on here?

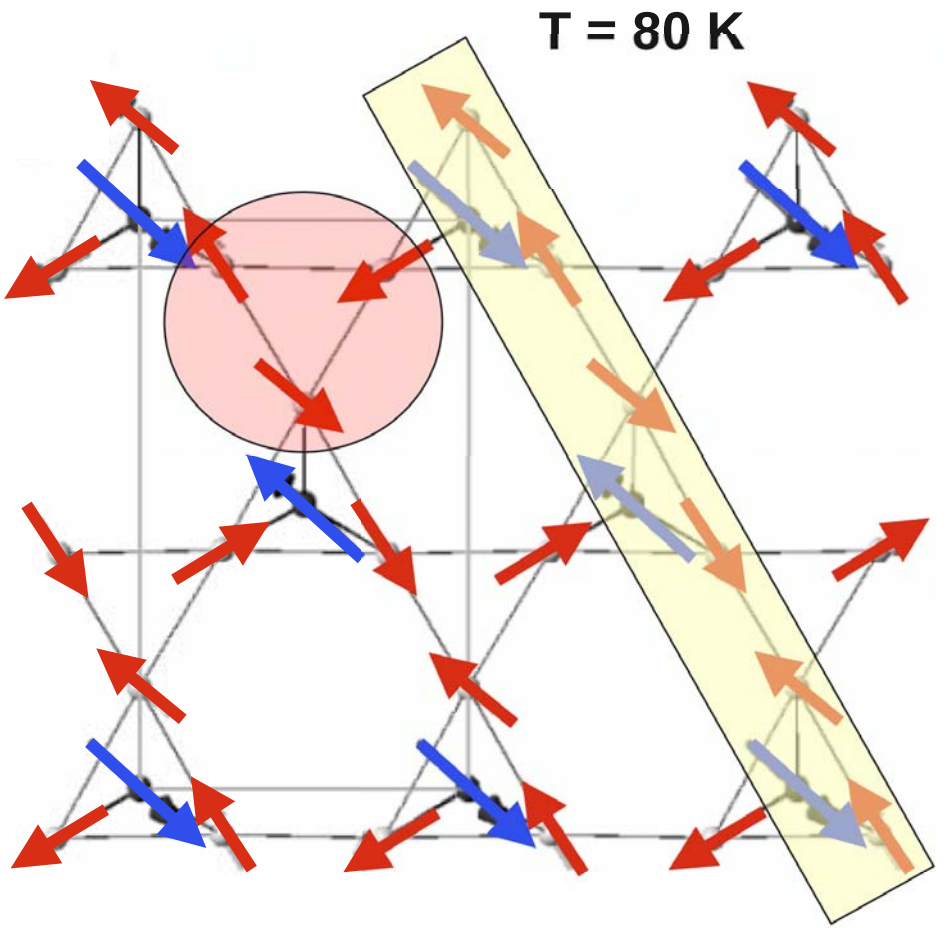
Temperature Dependence



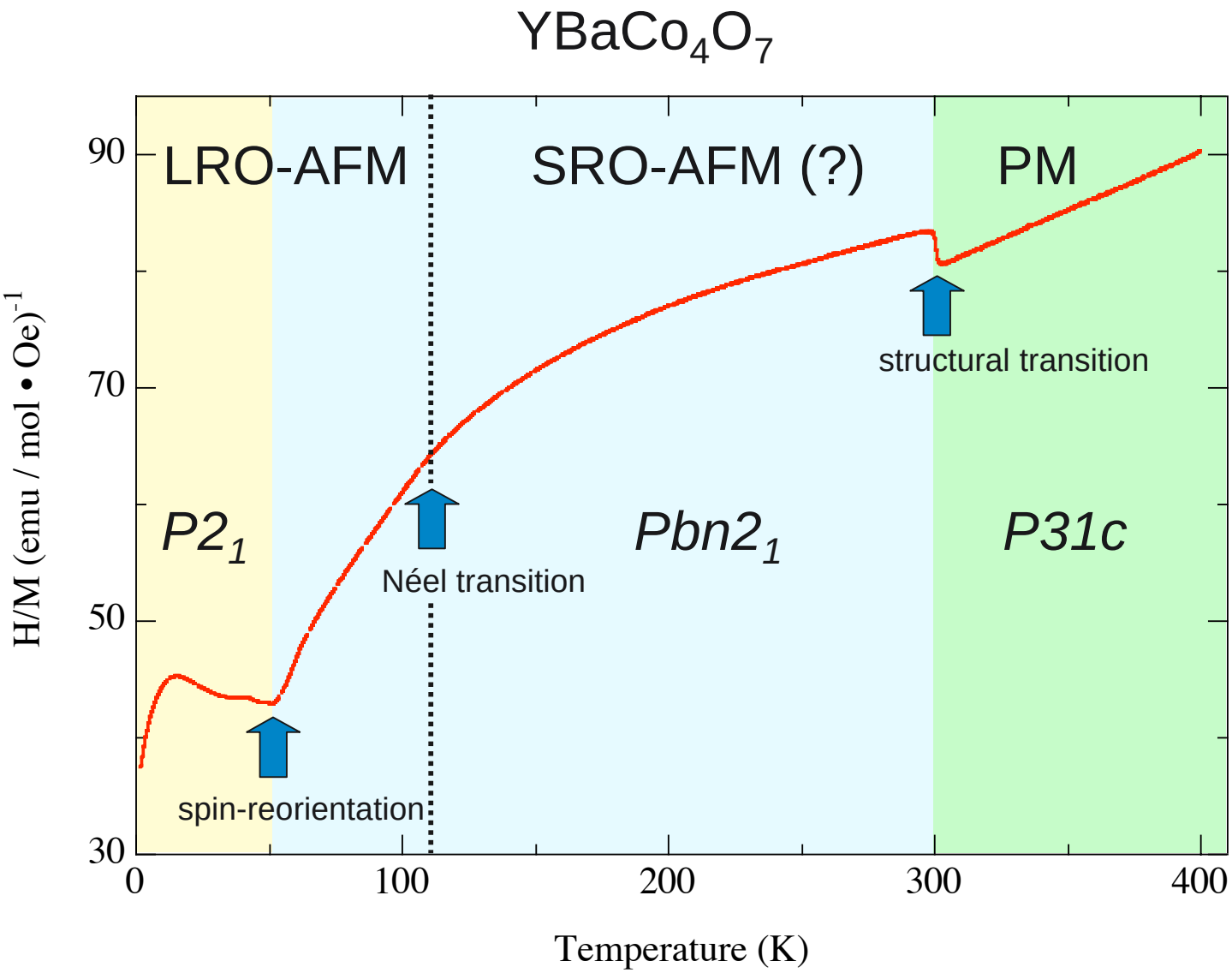


Temperature Dependence

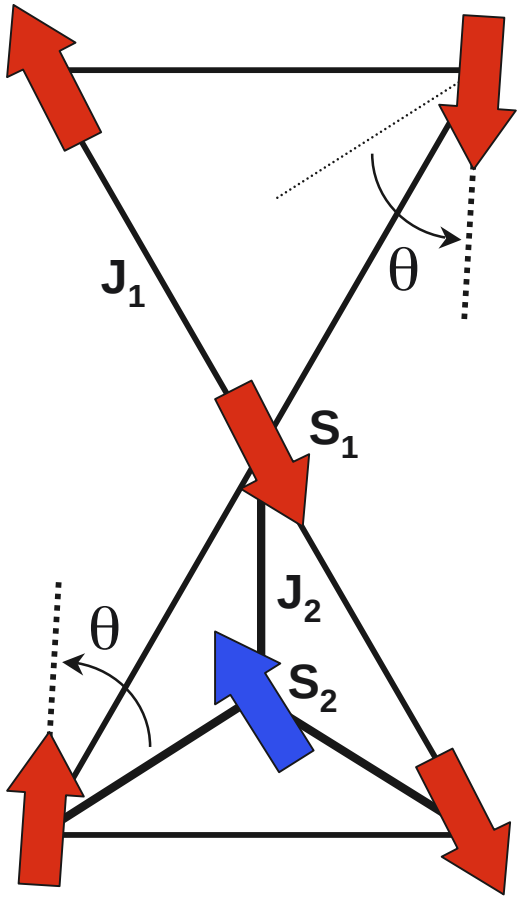




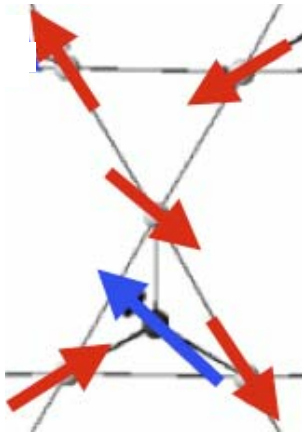
- **Uncapped triangle: S ≠ 0**
- **Capped triangle strongly collinear**
- **Implies c-axis exchange stronger**


YBaCo4O7
LRO-AFM
SRO-AFM (?)
PM
structural transition
P21
Néel transition
Pbn21
P31c
spin-reorientation
H/M (emu / mol • Oe)-1
90
70
50
30
0
100
200
300
400
Temperature (K)

Toy Model for High-T Phase



- **Experimentally: $\theta = 0$**

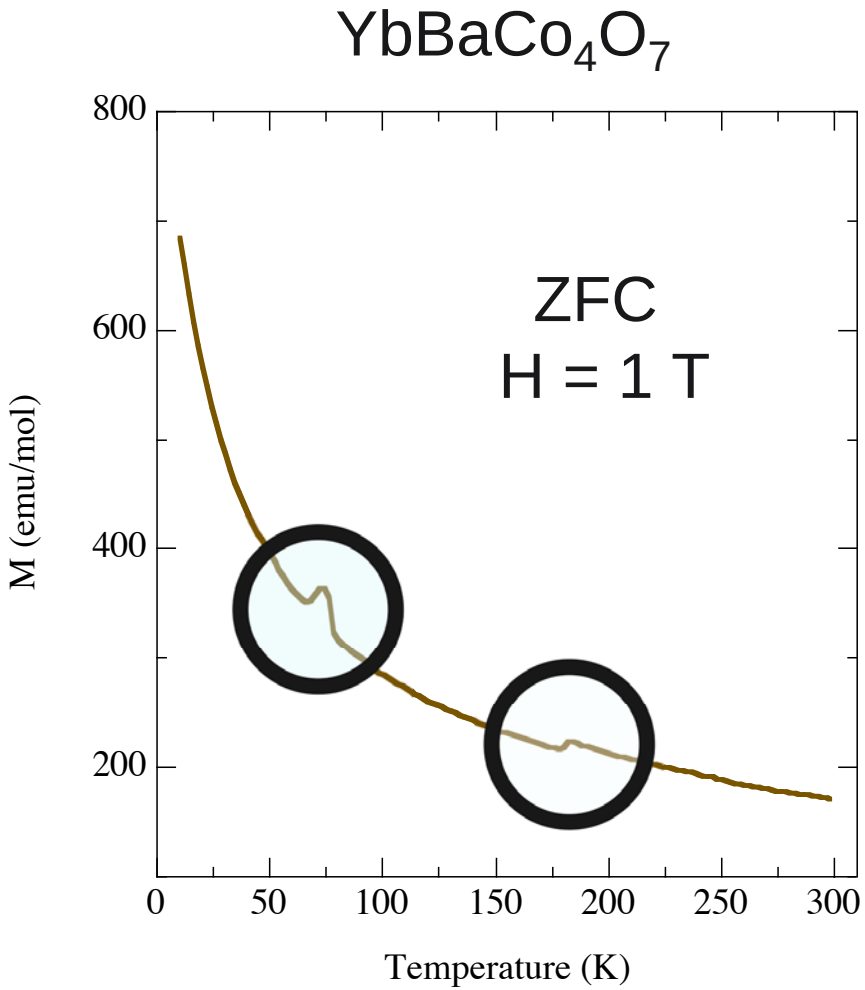


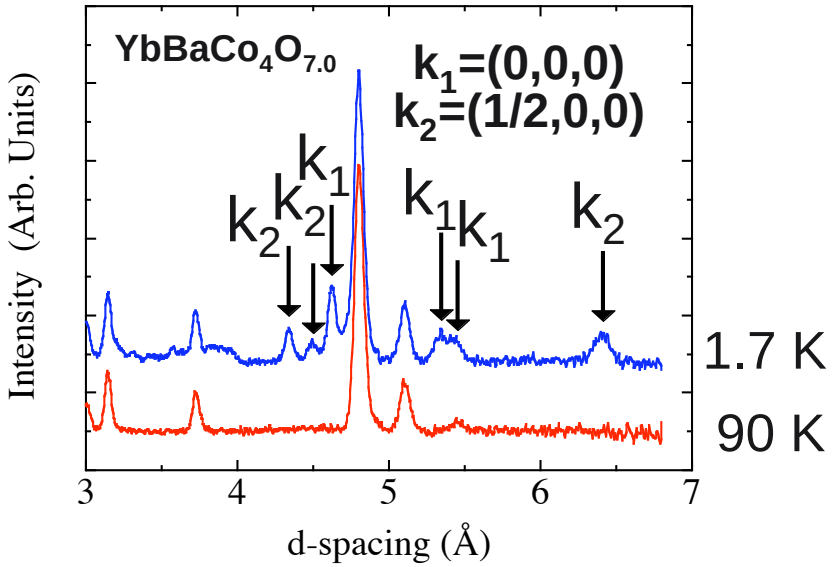
$$E(\theta) = S_1^2\left[\frac{S_2}{S_1}J_2 - 2J_1\right]\sin(\theta) - 2J_2S_1S_2$$

- **Minima at $\theta = \pm \pi/2$**
- **$J_2S_2/J_1S_1 < 2$: $\theta = \pi/2$**

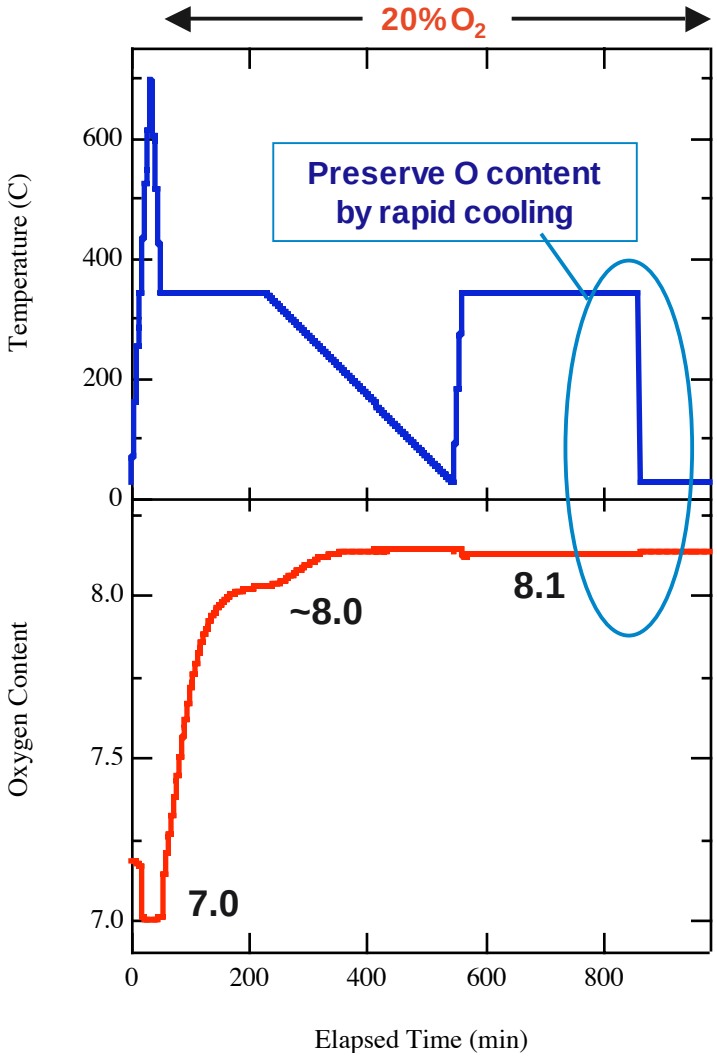
If structure right, how to explain ?

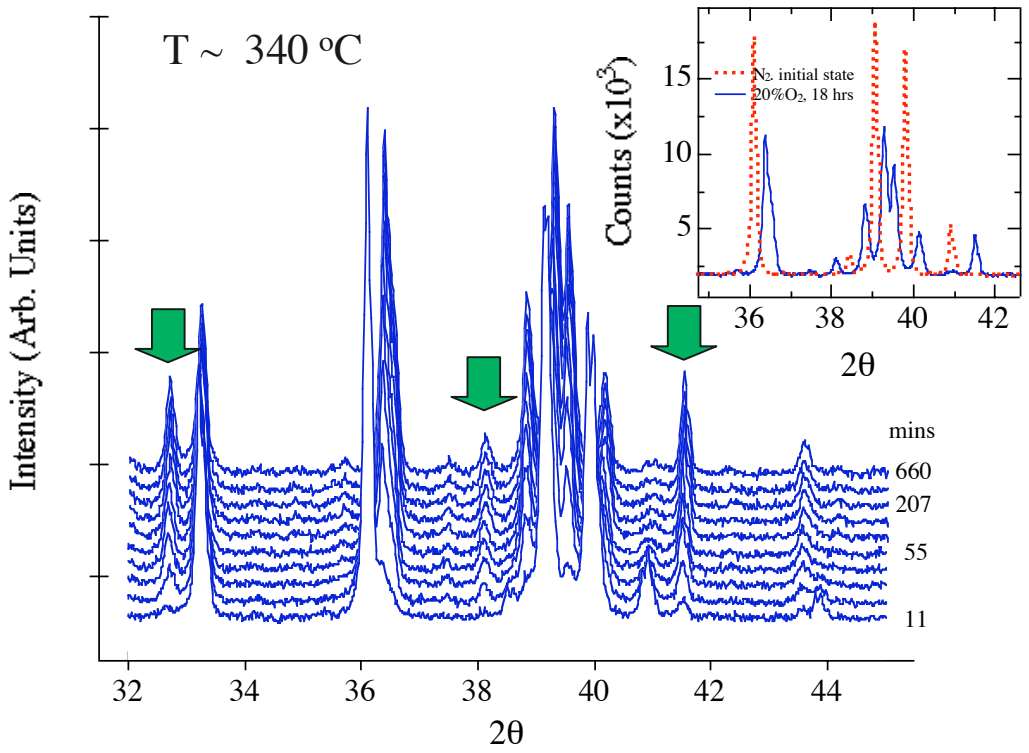
Ground State: LRO Antiferromagnet





High-Temperature Oxygenation

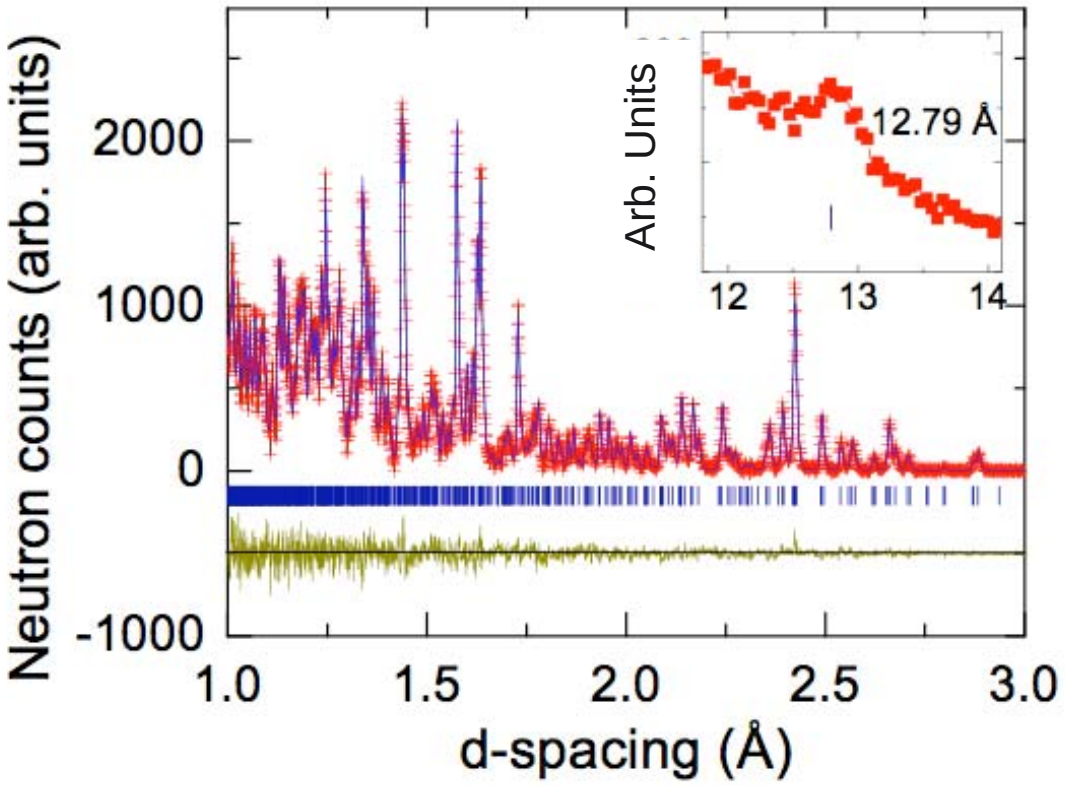


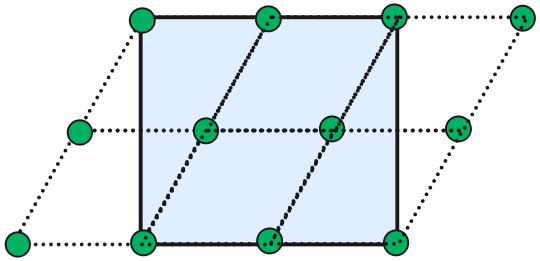


Switching from N_2 to 20%O_2 results in rapid O uptake, phase transition from trigonal to orthorhombic

Neutron Refinement

SEPD, 300 K





$a_o = 2 \cdot a_h = 12.79$ Å

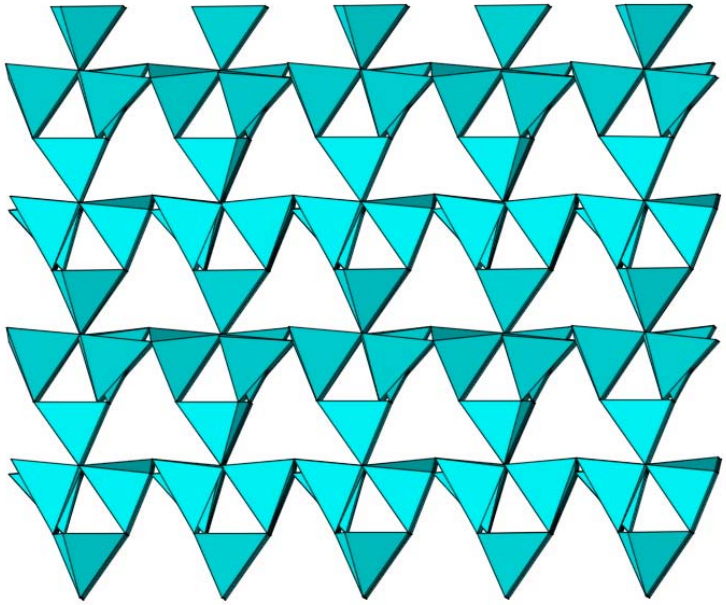
$b_o = \sqrt{3} \cdot a_h = 10.85$ Å

$c_o = c_h = 12.15$ Å

$R_p = 2.45\%$, $R_{wp} = 3.35$, $\chi^2 = 1.296$

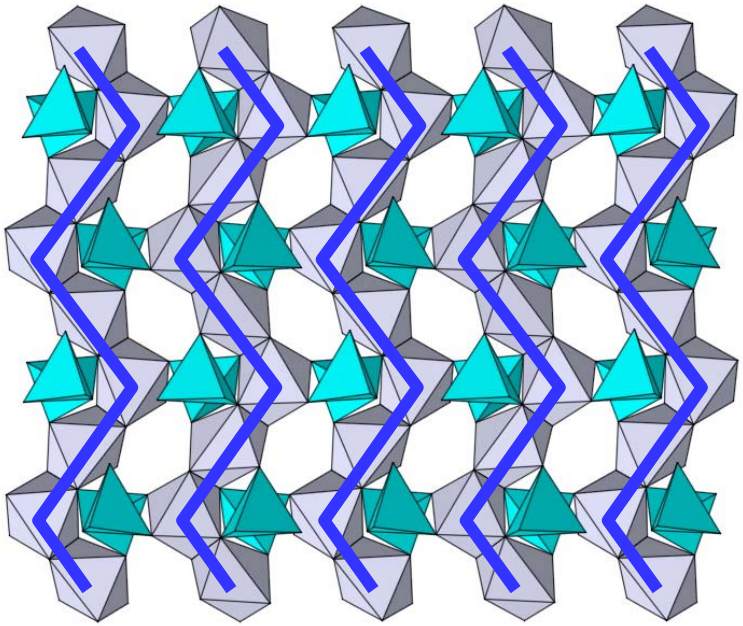
Crystal Structure of $YBaCo_4O_8$

$YBaCo_4O_7$



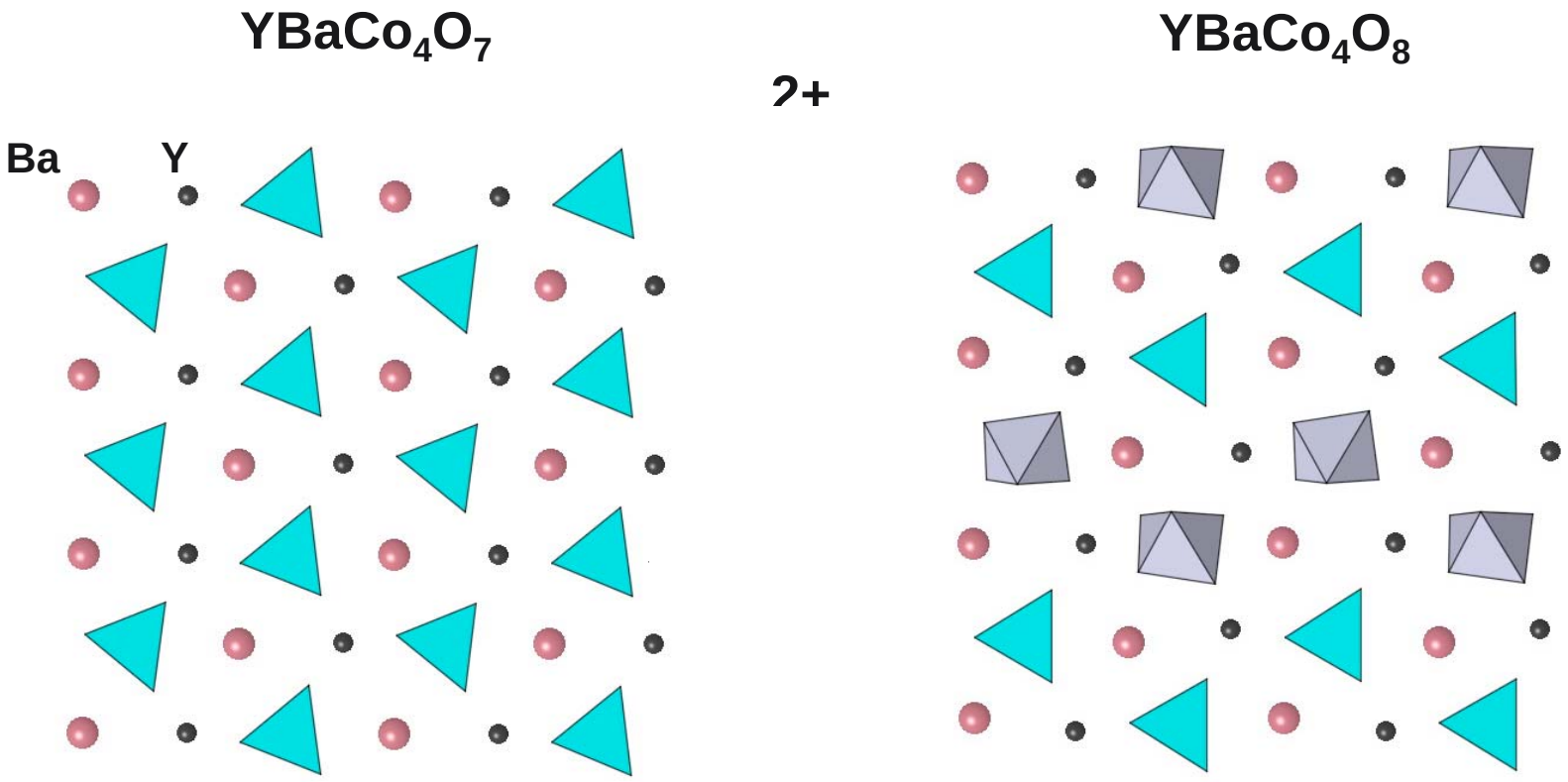
[100]

$YBaCo_4O_8$



edge-sharing, zig-zag octahedral chains along c-axis unique among mixed-metal oxides?

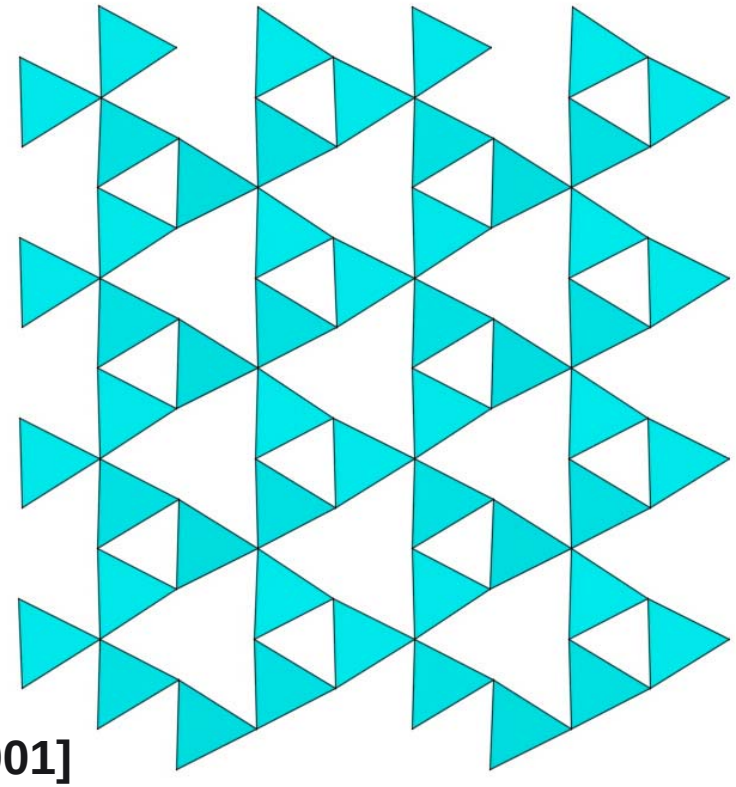
Triangular Layer Detail



- BVS: Ba = 2.03; Y = 3.01; Co(T_d) = 2.08; Co(O_h) = 2.88
- Real space ‘charge-ordering’ driven by coordination

Kagomé Layer Detail

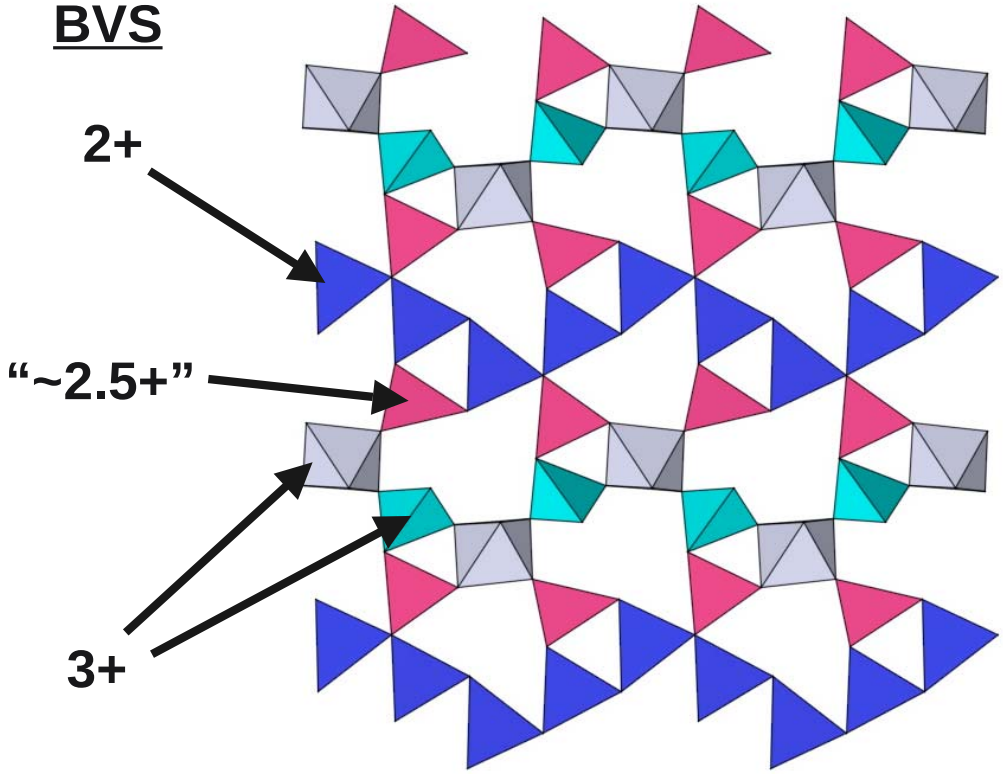
$YBaCo_4O_7$



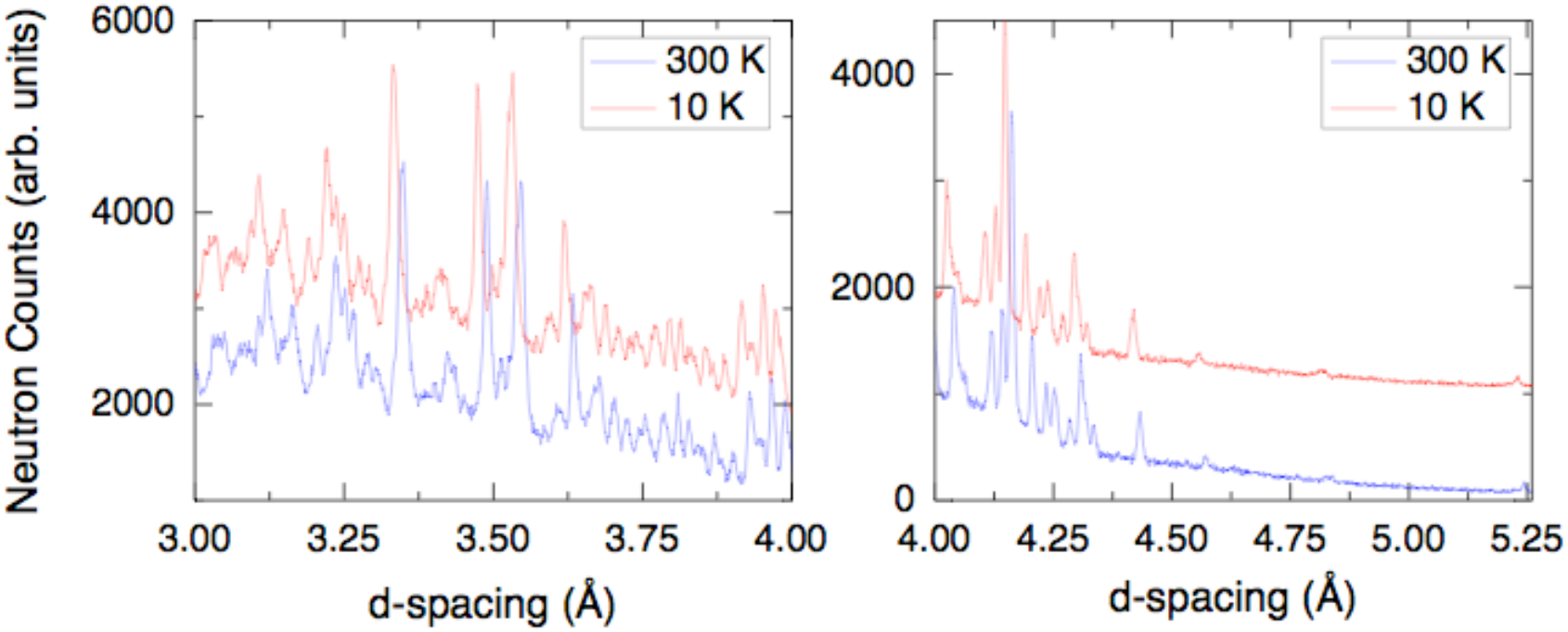
[001]

$YBaCo_4O_8$

BVS



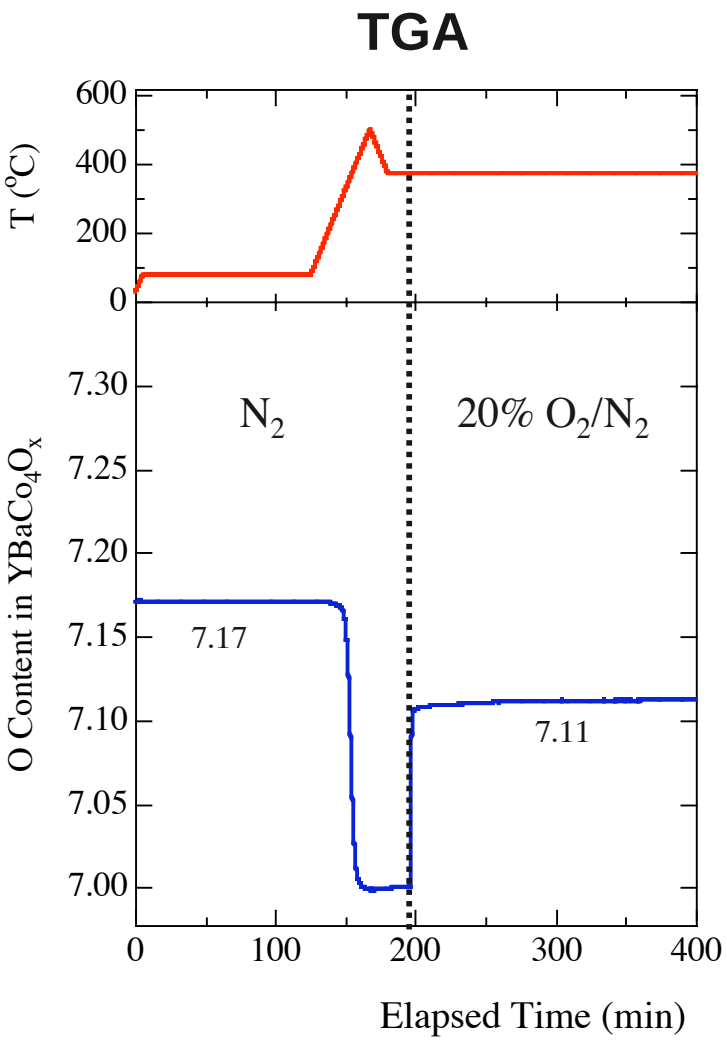
$YBaCo_4O_8$: Low Temperature Neutron Diffraction

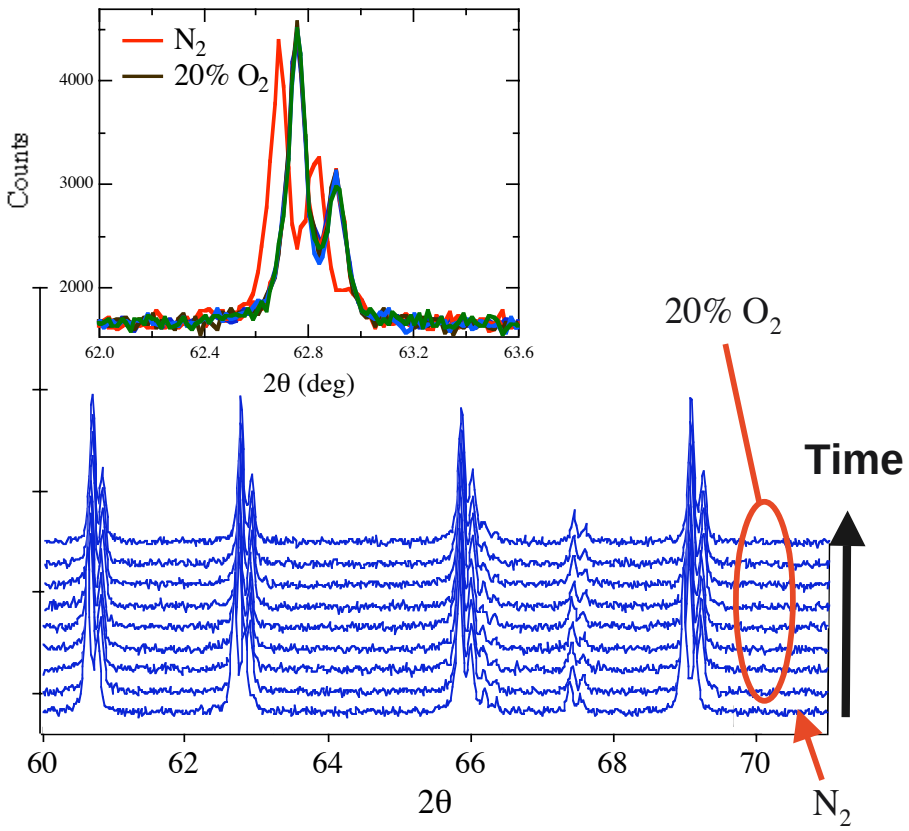


- No sign of additional magnetic reflections
- 300 K model fits 10 K data
- Question: LS Co^{3+} in O_h suppress LRO by decoupling magnetic Co^{3+} and Co^{2+} T_d ions in or between Kagomé layers?

High Temperature Oxidation: $YBaCo_4O_{7+\delta}$

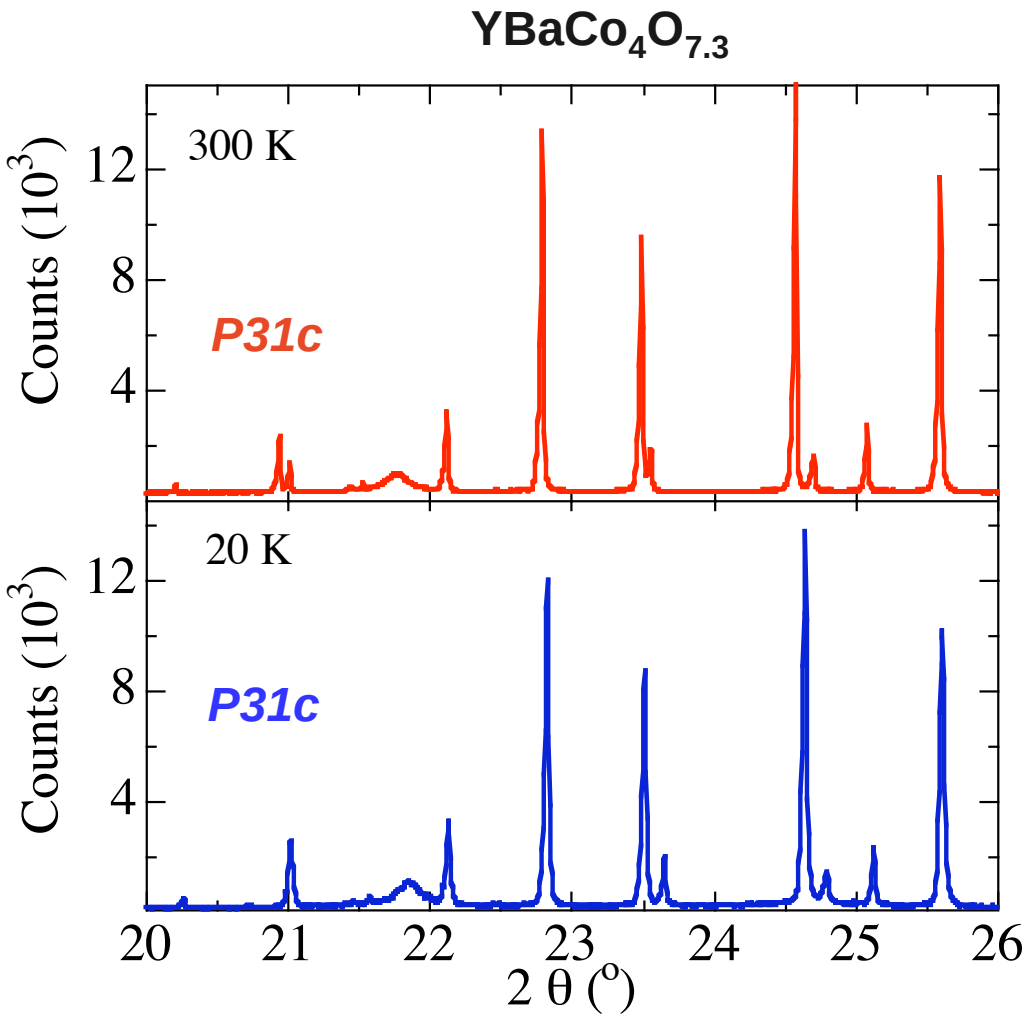
Rapid cooling: 0.2 O more added per f.u.

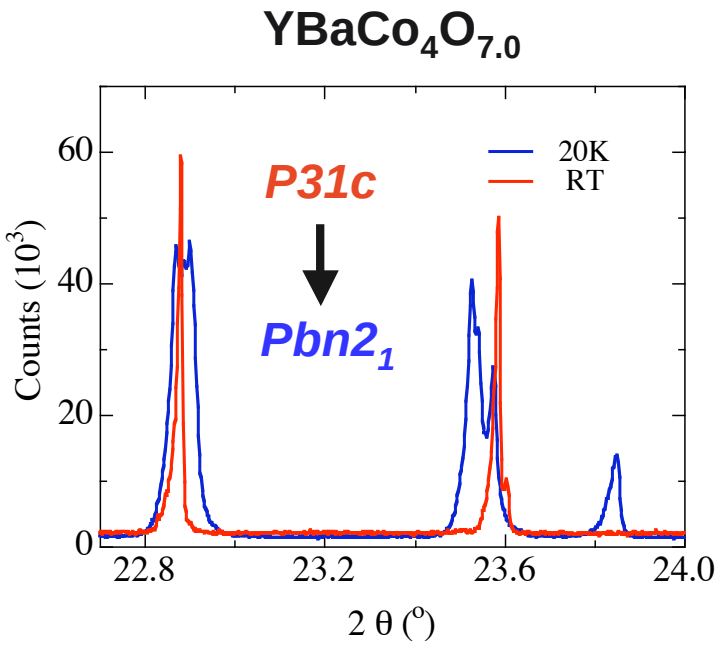




Small (δ~0.11) O uptake, symmetry remains trigonal at synthesis temperature

What Does the Extra Oxygen Do?



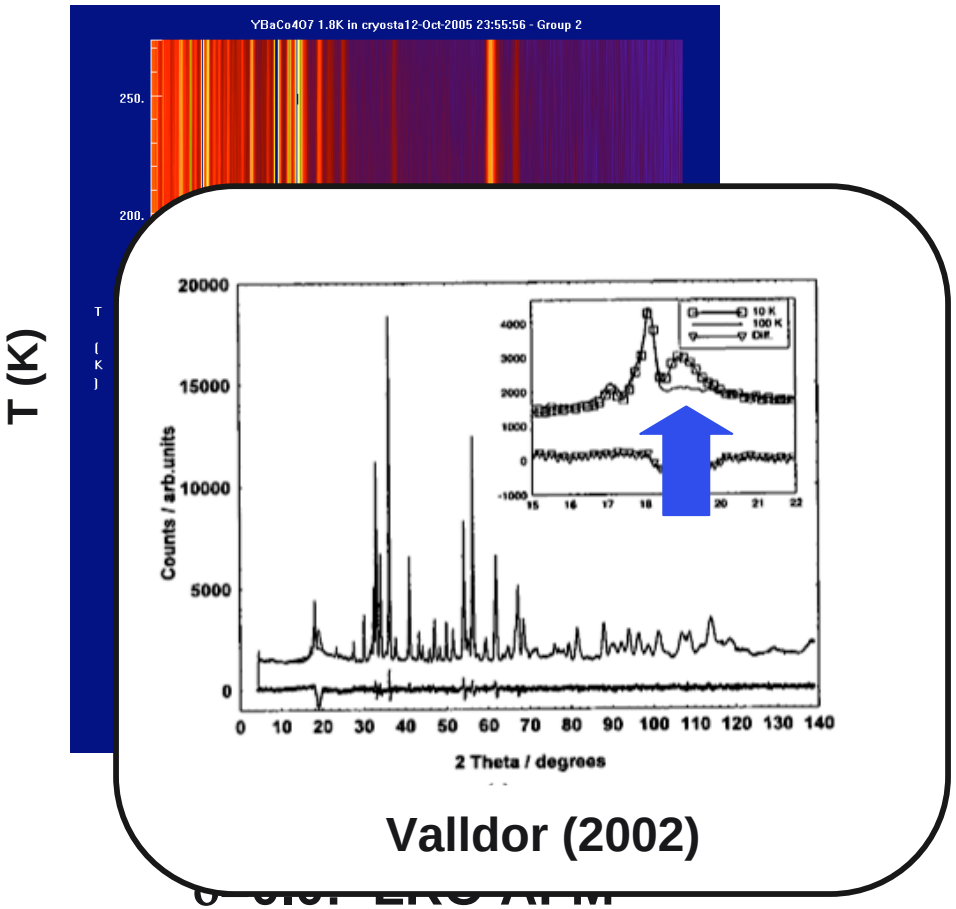


Excess O suppresses orthorhombic phase; trigonal symmetry retained

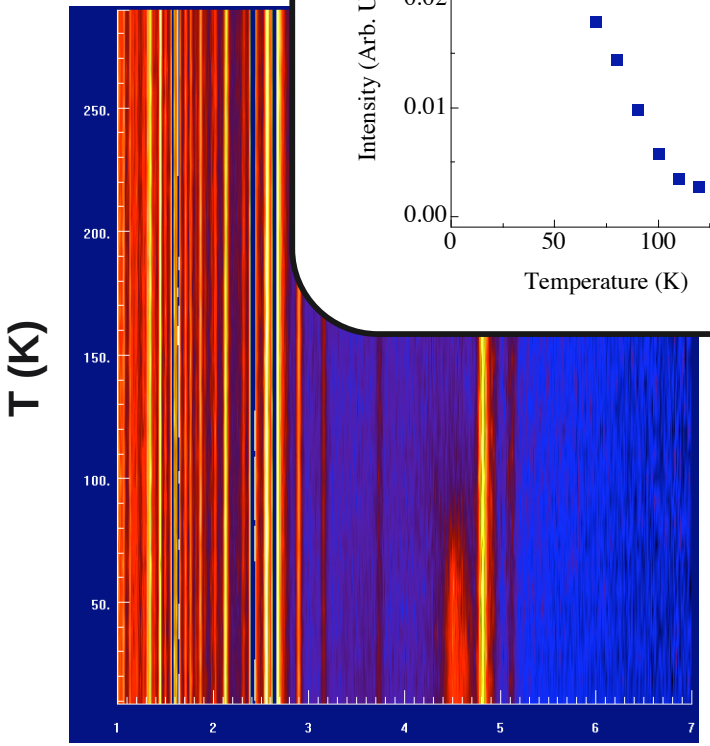
If no symmetry breaking, then . . .

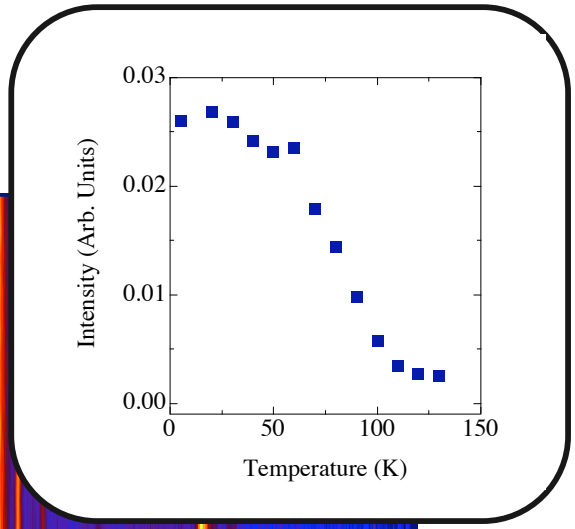
NSLS

Tuning into Frustration

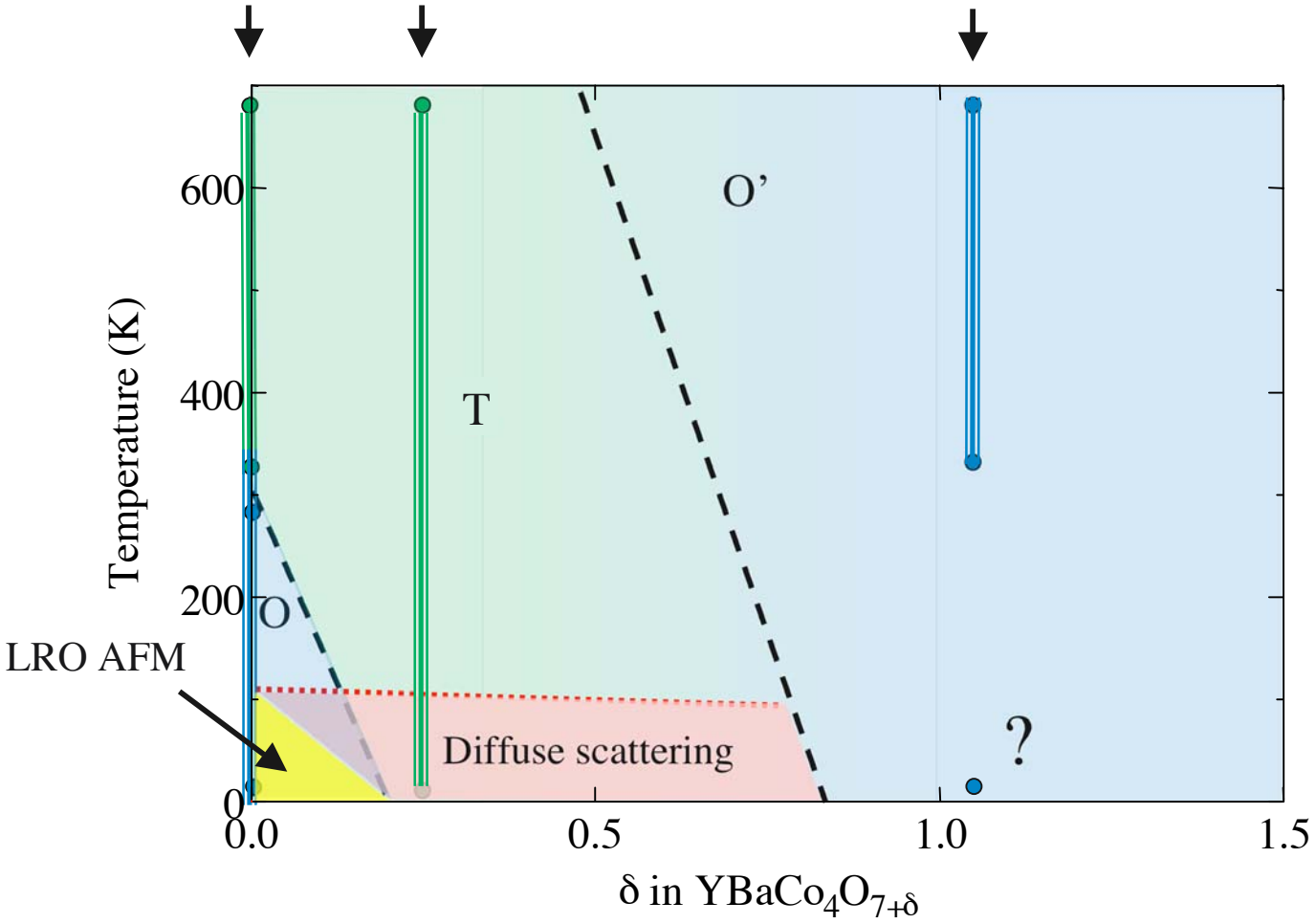


Valldor (2002)





δ=0.3: Only diffuse scattering



Most of this phase diagram is a guess !

Summary

- $YBaCo_4O_{7.0}$ — Kagomé system has long-range ordered state with unique magnetic structure
- Geometric frustration lifted by structural phase transition that improves underbonding of Ba site
- $YBaCo_4O_{7.3}$ — excess O stabilizes the geometrically frustrated state; no long-range order
- $YBaCo_4O_8$ — new structure type; zig-zag edge-sharing O_h chains
- Single crystals now grown, will be used to explore anisotropic properties, diffuse scattering, spin excitations.