

Charge, Orbital and Spin Ordering in $\text{RBaFe}_2\text{O}_{5+x}$ Perovskites

Patrick M. Woodward

*Department of Chemistry
Ohio State University*

Pavel Karen

*Department of Chemistry
University of Oslo*

Charge, Orbital and Spin Ordering

Charge Ordering (T_{CO})

- $T > T_{CO} \rightarrow$ Delocalized Electrons \rightarrow Single oxidation state
- $T < T_{CO} \rightarrow$ Localized Electrons \rightarrow Distinct oxidation states

Orbital Ordering (T_{OO})

- Preferential (anisotropic) occupation of given d-orbitals
- Cooperative Jahn-Teller distortion

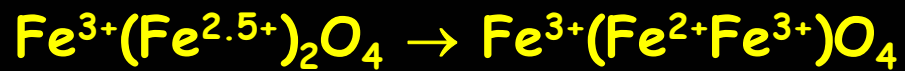
Spin Ordering (T_N or T_C)

- Long range magnetic ordering

Mixed Valency (Robin & Day Classification)

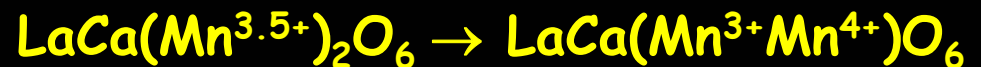
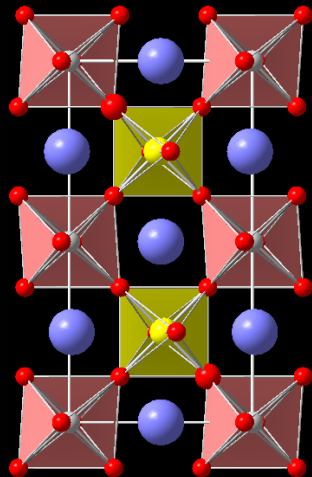
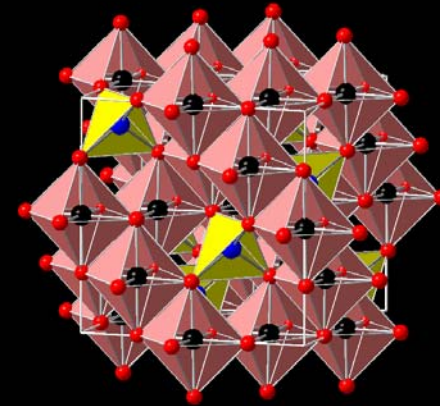
- Type III \rightarrow Metallic e^- transport \rightarrow Single oxidation state
- Type II \rightarrow Activated e^- transport \rightarrow Two oxidation states at a given instant, but CO pattern is fluctuating
- Type I \rightarrow Insulating \rightarrow Two oxidation states, with a regular (long range) CO pattern

Examples of Charge Ordering



Verwey (1939)

Double Exchange Ferromagnetism



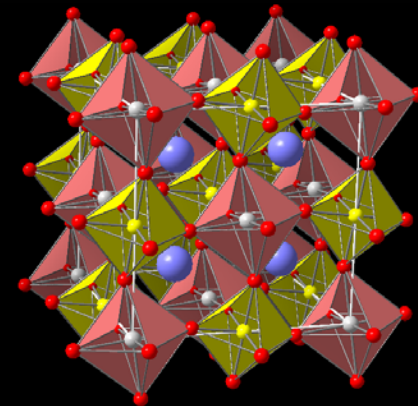
Wollan, Koehler & Goodenough (1955)

Colossal Magnetoresistance (CMR)

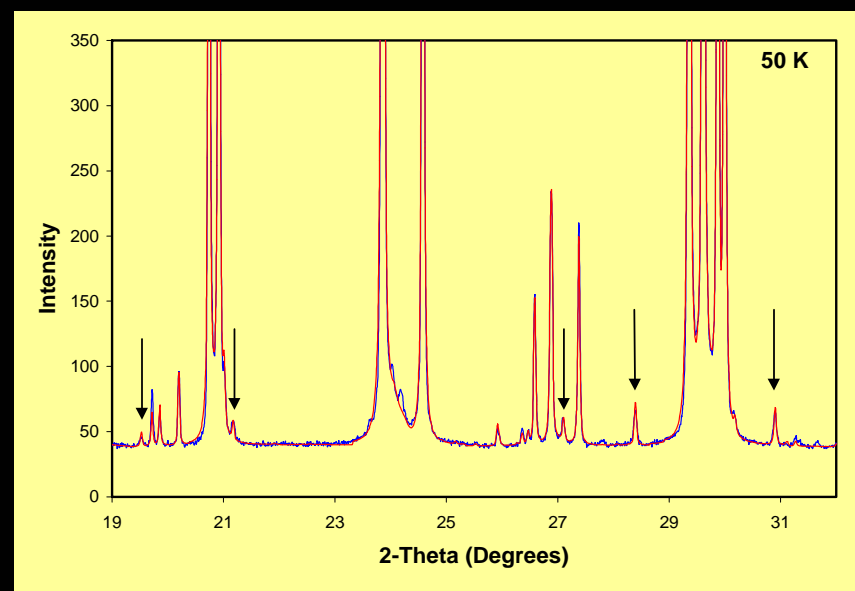
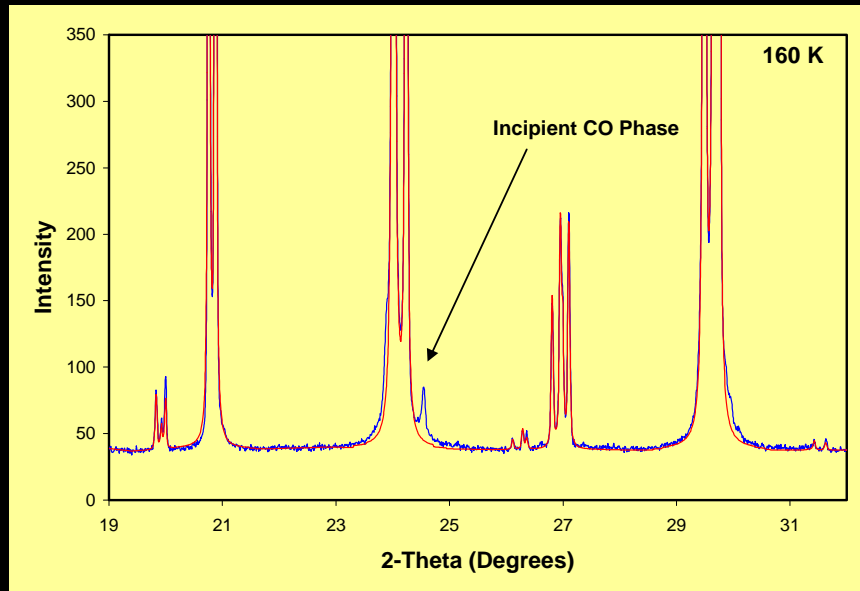


Cox & Sleight (1976)

High T_c Superconductivity in Oxides



Charge Ordering in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$



T = 160 K

Valence Mixed State

T = 60 K

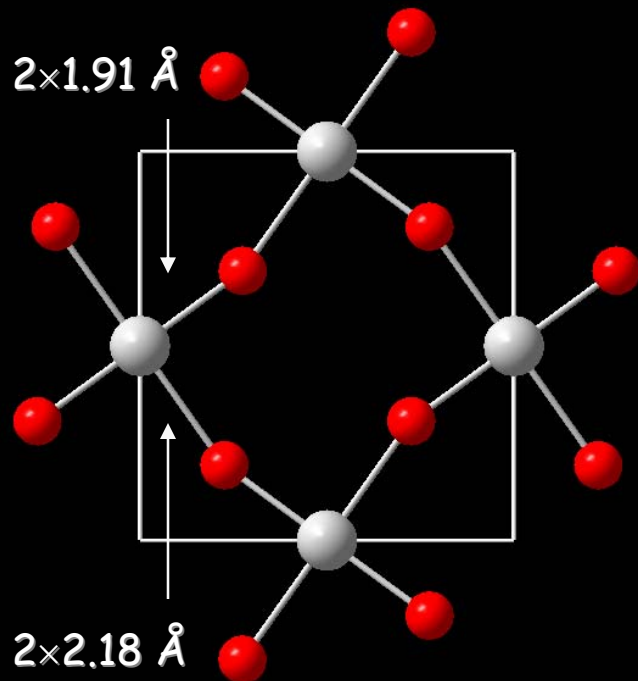
Charge Ordered State

Synchrotron X-ray Powder Diffraction Data (NSLS-X7A)

A series of weak superstructure reflections arise (1% intensity at the strongest) that indicate doubling of the a -axis.

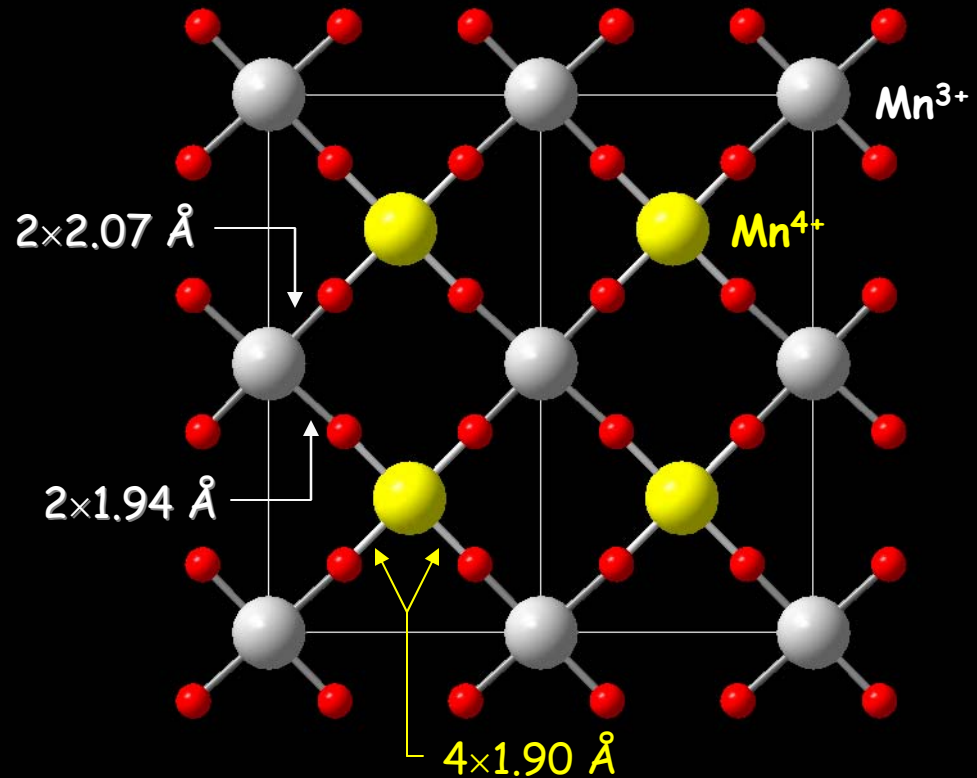
Woodward, Cox, Vogt, Rao, Cheetham, *Chem. Mater.* **11**, 3528-38 (1999).

Examples of Orbital Ordering



LaMnO_3 (298 K)

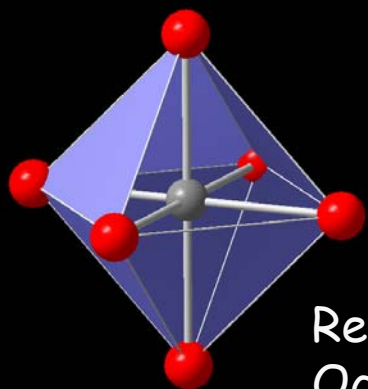
Rodriguez-Carvajal, *et al. Phys. Rev. B* 57, R3189 (1998).



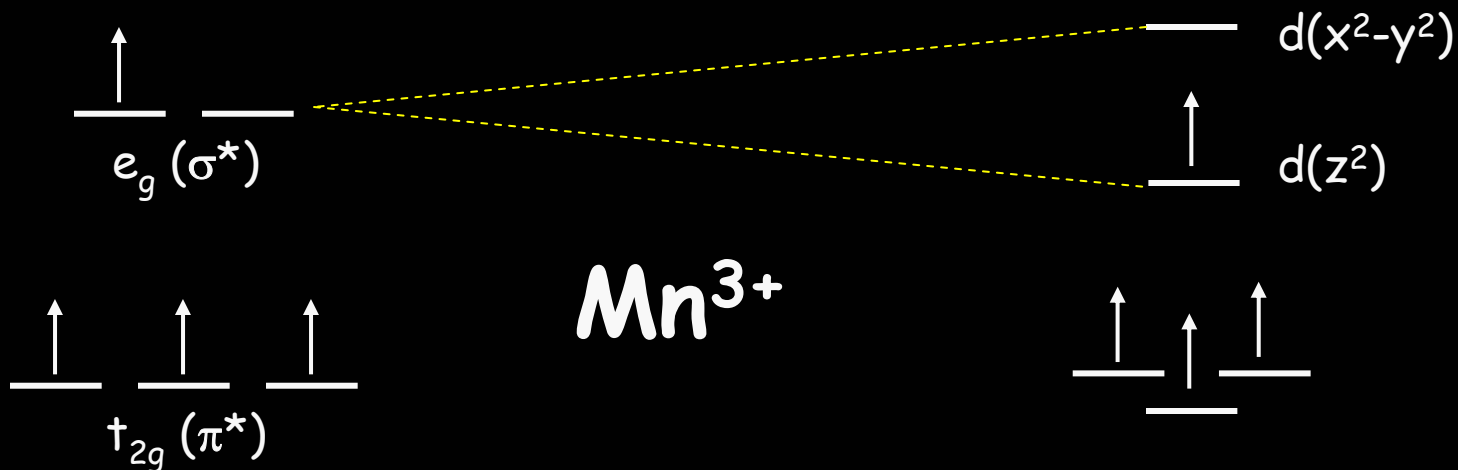
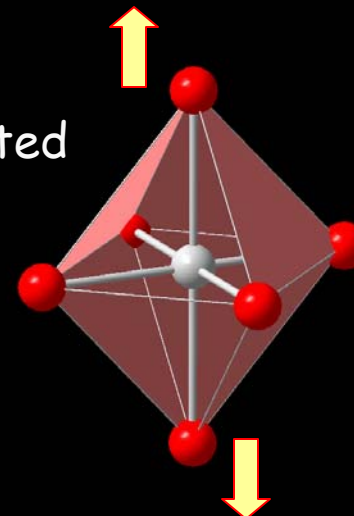
$\text{NdSrMn}_2\text{O}_6$ (50 K)

Woodward, *et al. Chem. Mater.* 11, 3528-38 (1999).

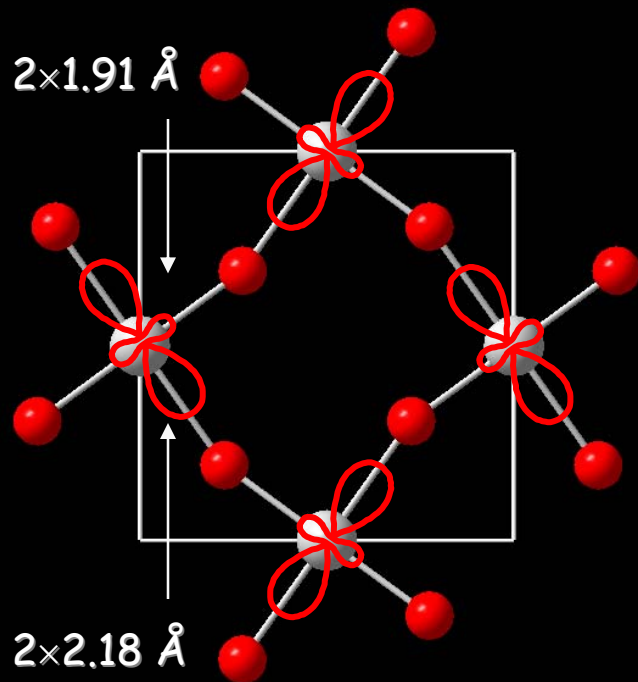
Orbital Ordering & Cooperative Jahn-Teller Distortions



Axially Elongated Octahedron

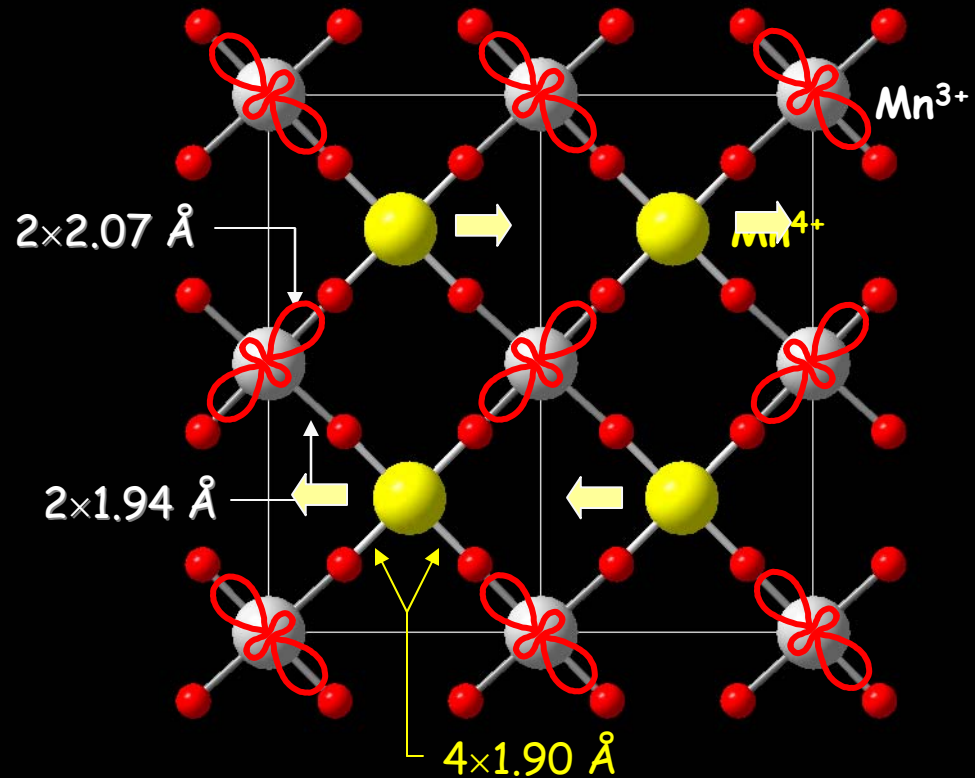


Examples of Orbital Ordering



LaMnO_3 (298 K)

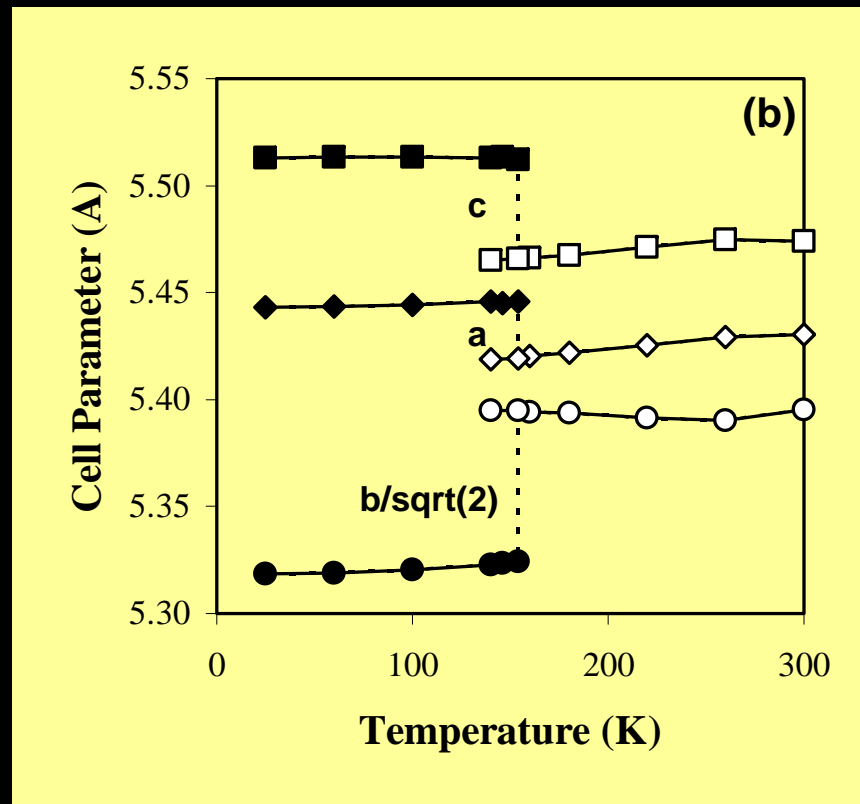
Rodriguez-Carvajal, *et al. Phys. Rev. B* 57, R3189 (1998).



$\text{NdSrMn}_2\text{O}_6$ (50 K)

Woodward, *et al. Chem. Mater.* 11, 3528-38 (1999).

Orbital Ordering in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$



Upon cooling below 150 K, the a & c -axes expand and the b -axis contracts. This is the signature of orbital ordering

Woodward, Cox, Vogt, Rao, Cheetham, *Chem. Mater.* **11**, 3528-38 (1999).

Oxygen Deficient Double Perovskites



R = Trivalent Rare Earth Ion

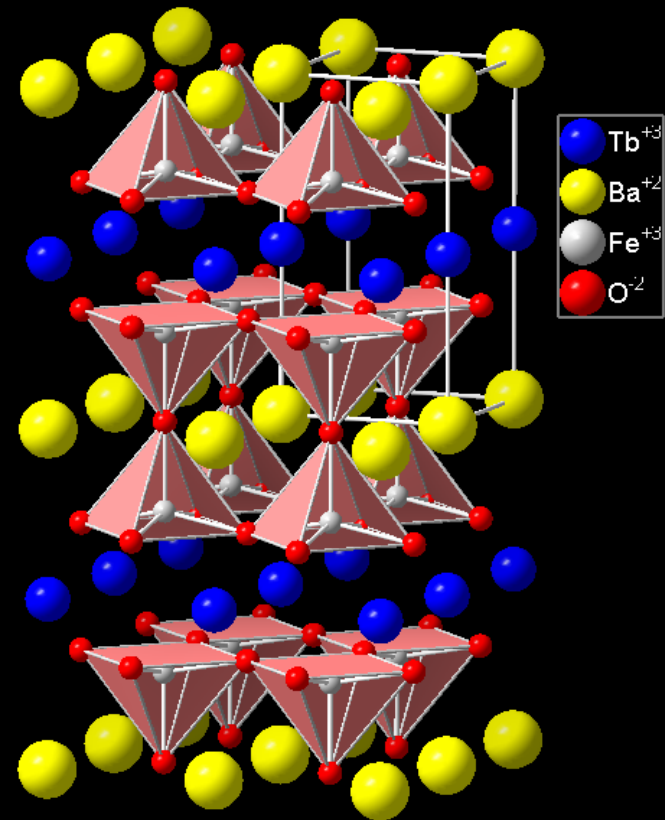
- Nd, Sm, Tb, Ho, Y
- Changing the radius of the R ion, controls the layer spacing

M = 1st row Transition Metal Ion

- V, Mn, Fe, Co, Cu
- Changing M, alters the electron count and covalency of the M-O bonds.

$0 \leq w \leq \sim 0.7$

- Excess oxygen resides in R layer
- The upper limit of w is dictated by the ionic radius of R
- $w=0 \rightarrow M^{+2.5}$, $w=0.5 \rightarrow M^{+3}$
- changes the local coordination of the transition metal ion from 5 to 6



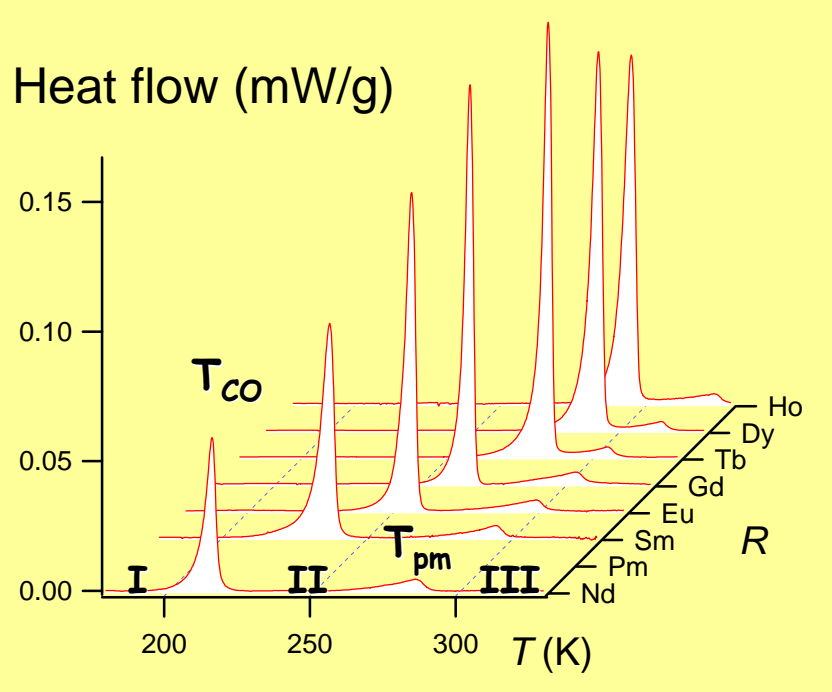
Synthesis REBaFe₂O₅



- The sample is dehydrated at ~180 °C.
- The sample is then heated at ~400 °C to drive off the organic content and produce an amorphous precursor.
- The precursor is calcined (800-900 °C) and then sintered at high temperature (1000-1150 °C) in a carefully controlled pO₂ atmosphere.
- The sintered pellets are heated at a lower temperature (600-860 °C) in a controlled atmosphere to attain the desired oxygen content.

Powder Diffraction Data Collection

- **Synchrotron X-ray Powder Diffraction**
 - NLS - X7A (Dave Cox, Tom Vogt)
 - NLS - X3B (Peter Stephens, Sylvina Pagola)
 - ESRF - BM1B (Swiss-Norwegian Beamline)
- **Neutron Powder Diffraction**
 - NIST - BT1 (Brian Toby) - YBaFe_2O_5
 - ILL - D2B (Emmanuel Suard) - $\text{HoBaFe}_2\text{O}_5$ & $\text{NdBaFe}_2\text{O}_5$
 - PSI - HRPT (Peter Fischer) - $\text{TbBaFe}_2\text{O}_5$
 - ANSTO - MRPD (Andrew Studer) - $\text{TbBaFe}_2\text{O}_5$
- **Neutron Thermodiffractometry**
 - ILL - D20 (Emmanuel Suard) - $\text{HoBaFe}_2\text{O}_5$ & $\text{NdBaFe}_2\text{O}_5$
- **Mossbauer Spectroscopy**
 - Abo Akademi (Johan Linden)

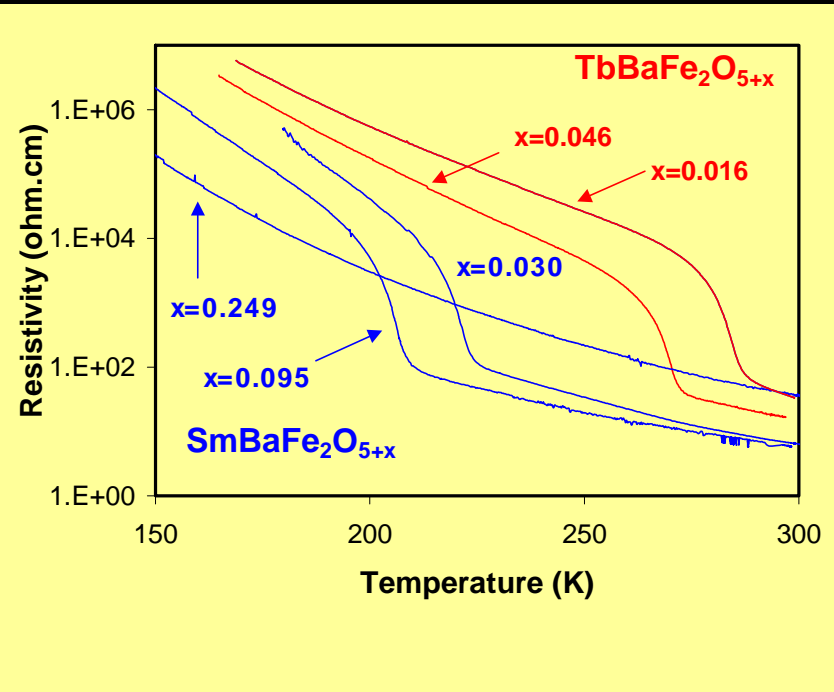


DSC

$T > T_{PM}$ Mössbauer shows one $Fe^{2.5+}$ signal (Type III MV)

$T_{PM} > T > T_{CO}$ Mössbauer signal begins to split $Fe^{2.5+x} + Fe^{2.5-x}$ (Type II MV)

$T_{CO} > T$ Mössbauer shows $Fe^{2+} + Fe^{3+}$ (Type I MV, Charge Ordered State)



Electrical Resistivity

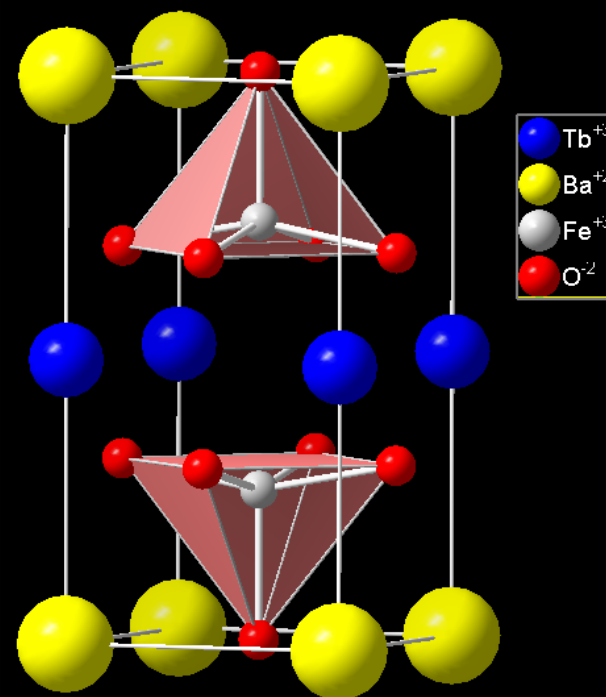
Karen, Woodward, Santhosh, Vogt, Stephens, Pagola, *J. Solid State Chem.* 167, 480 (2002).

TbBaFe₂O₅ Type III MV Structure

Temperature	350 K
Space Group	Pmmm
a	3.94453(4) Å
b	3.93331(4) Å
c	7.58655(8) Å

Bond Valences

Ba	1.98
Tb	2.88
Fe	2.52
O(x)	1.94
O(y)	1.95
O(z)	2.05

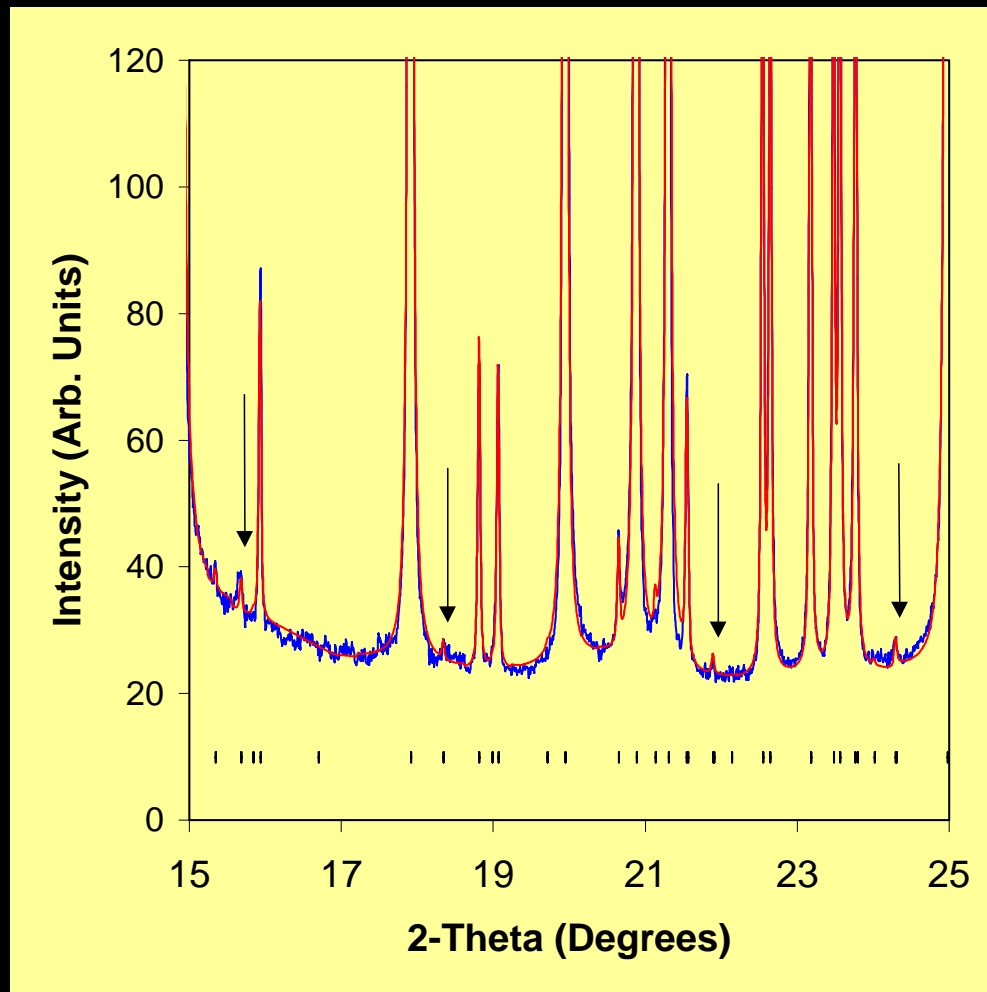


Fe-O Distances

2×2.0002(6)	[O _y]
2×2.0046(5)	[O _x]
1×1.9977(7)	[O _z]

Karen, Woodward, Linden, Vogt, Studer, Fisher, *Phys. Rev. B* 64, 214405 (2001).

TbBaFe₂O₅ Synchrotron X-ray



Superstructure
Reflections indicate a
doubled a-axis

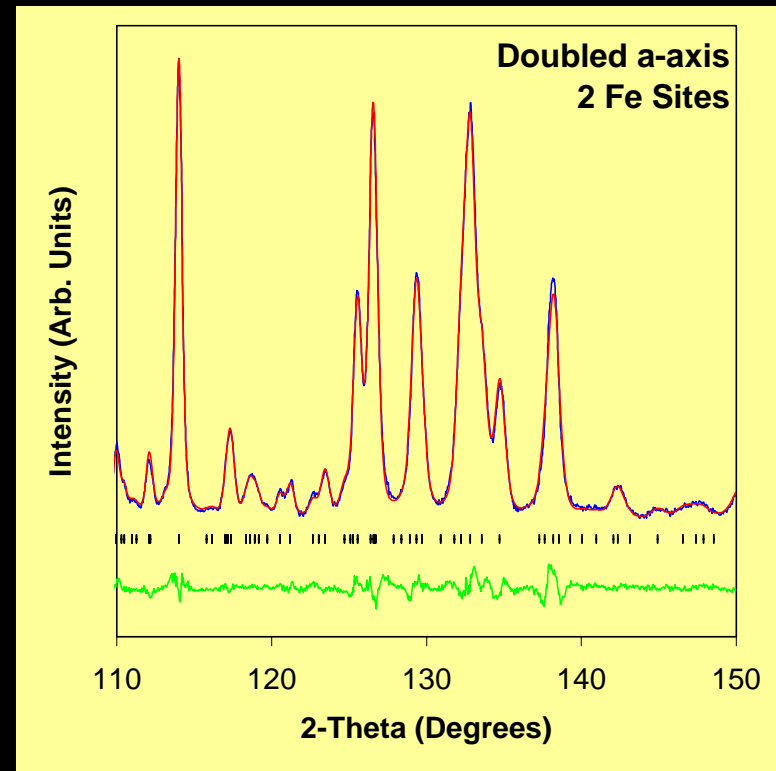
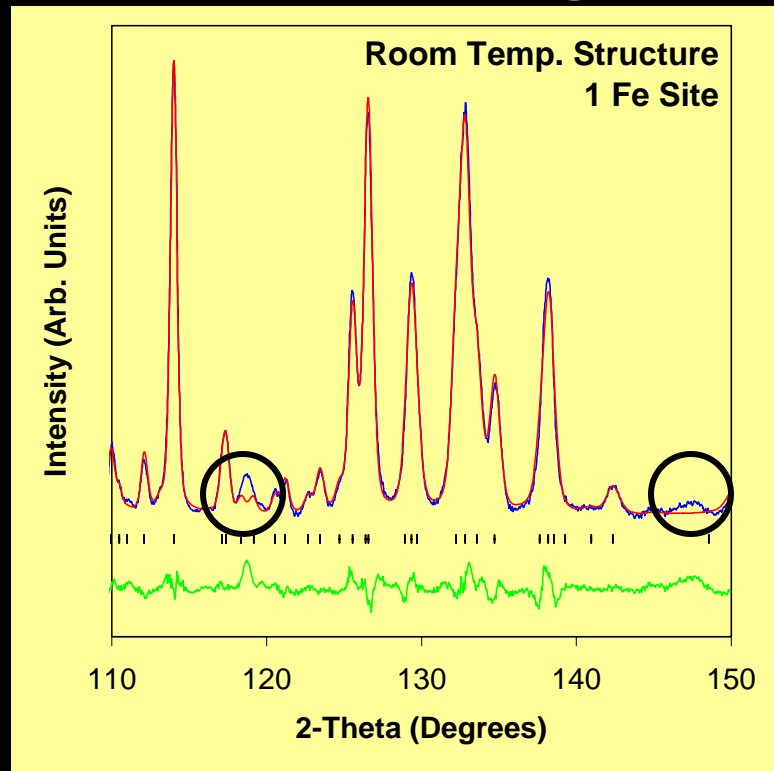
Space Group = *Pmma*

Superstructure
reflections are stronger
when $R = Nd$

Superstructure
reflections are very
difficult to observe in
neutron powder patterns

Karen, Woodward, Linden, Vogt, Studer, Fisher, *Phys. Rev. B* 64, 214405 (2001).

TbBaFe₂O₅ Neutron Diffraction



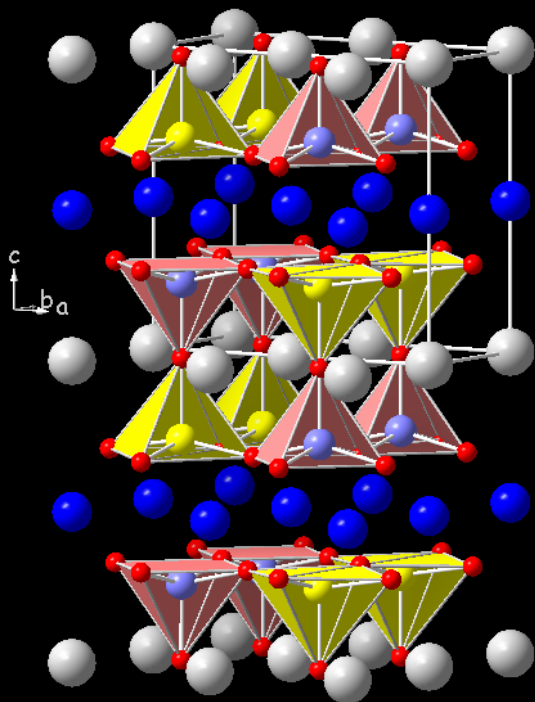
Mixed Valence Model

Charge Ordered Model

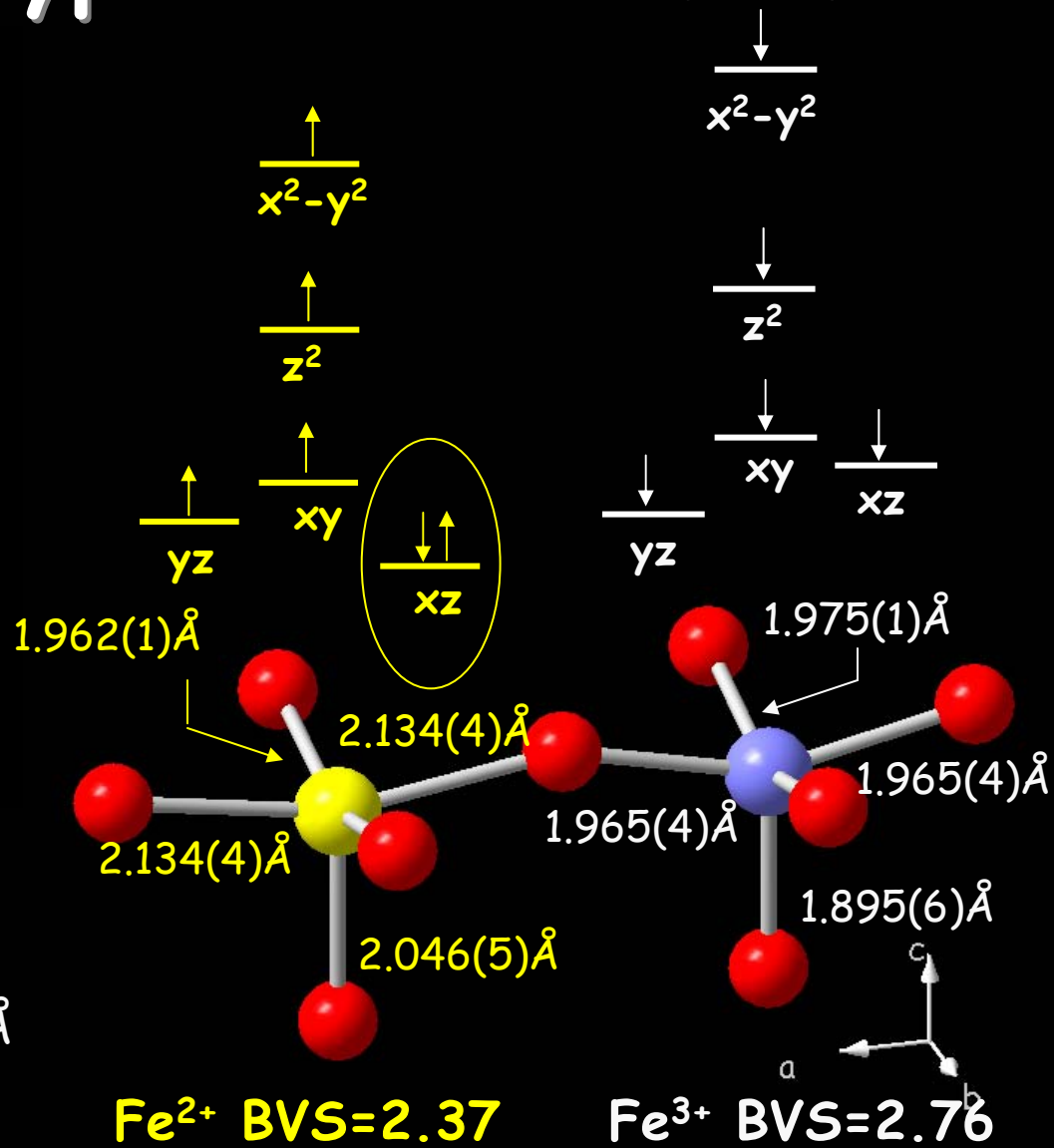
Rietveld refinements of neutron powder diffraction data confirm charge ordered structure, TbBaFe³⁺Fe²⁺O₅.

Karen, Woodward, Linden, Vogt, Studer, Fisher, *Phys. Rev. B* 64, 214405 (2001).

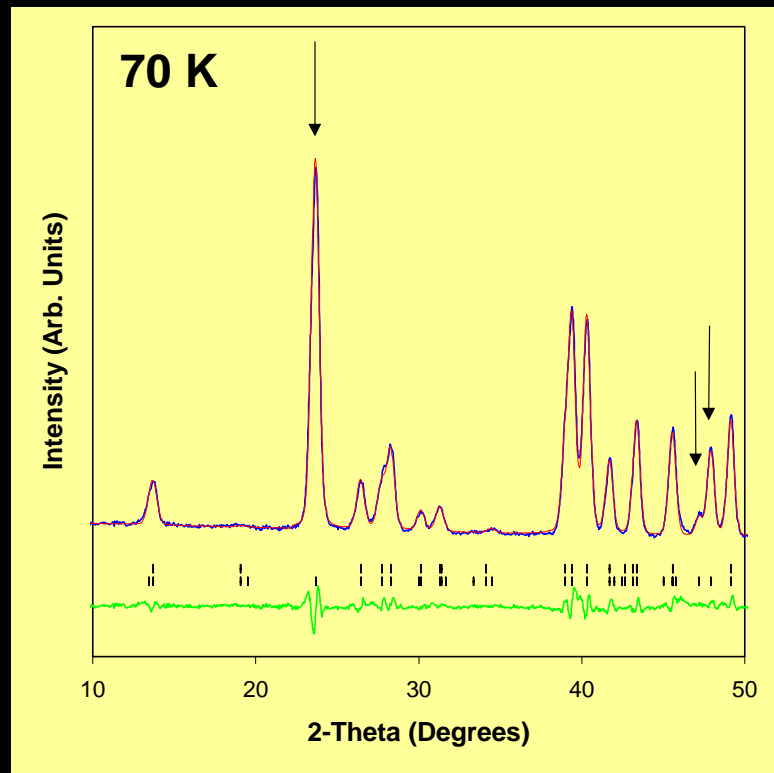
TbBaFe₂O₅ Type I CO Structure



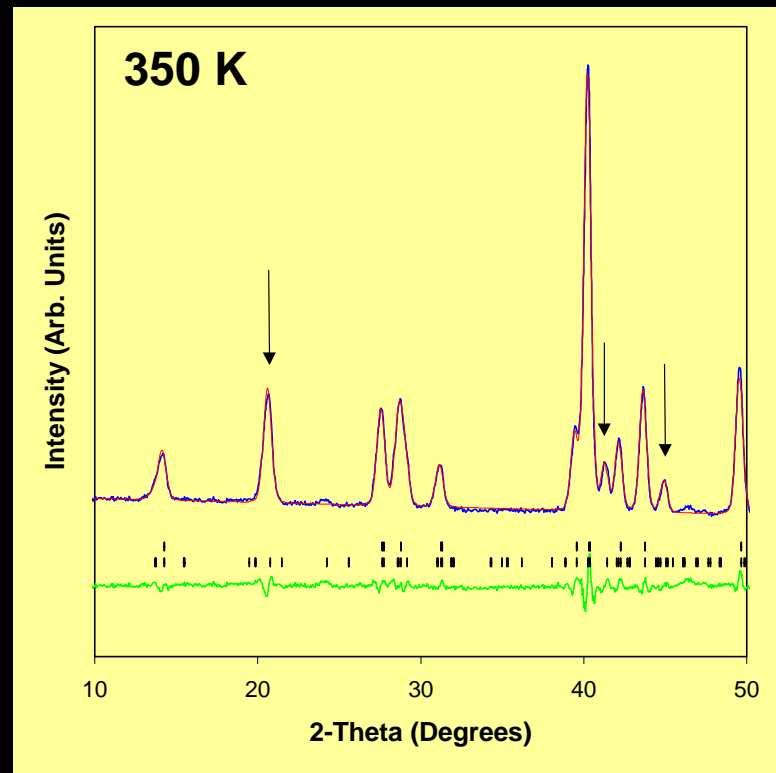
Temperature 70 K
 Space Group Pmma
 a 8.0575(2) Å
 b 3.85032(6) Å
 c 7.5526(2) Å



TbBaFe₂O₅ Magnetic Scattering



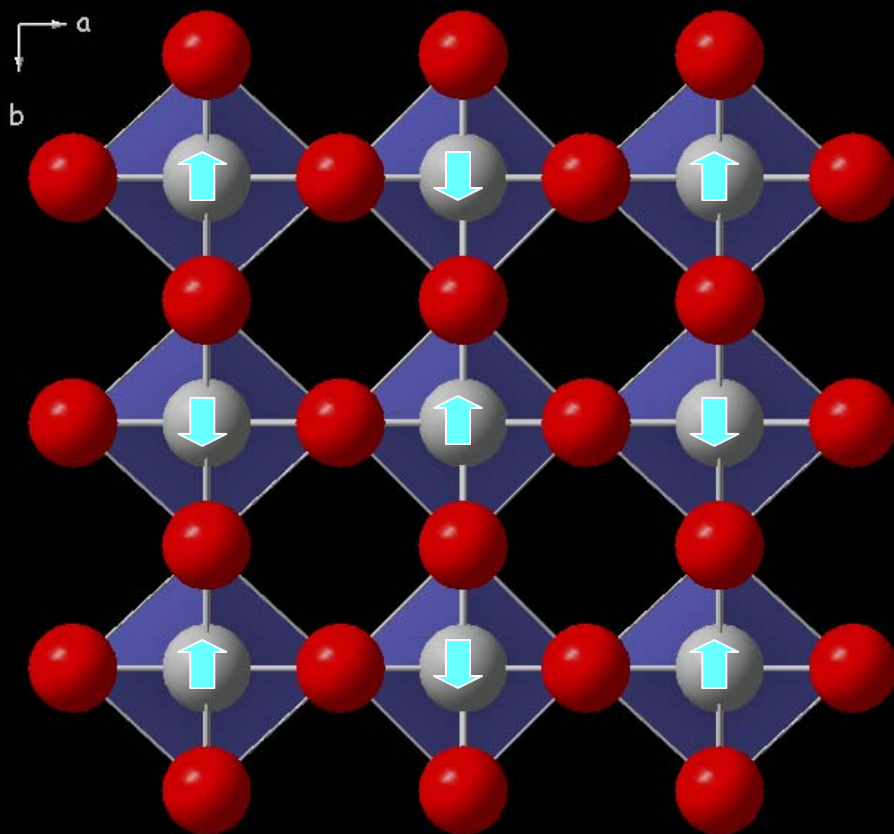
$T < T_{co}$ Magnetic Cell
 $2a \times 2b \times c$
 $8.05 \text{ \AA} \times 7.70 \text{ \AA} \times 7.55 \text{ \AA}$



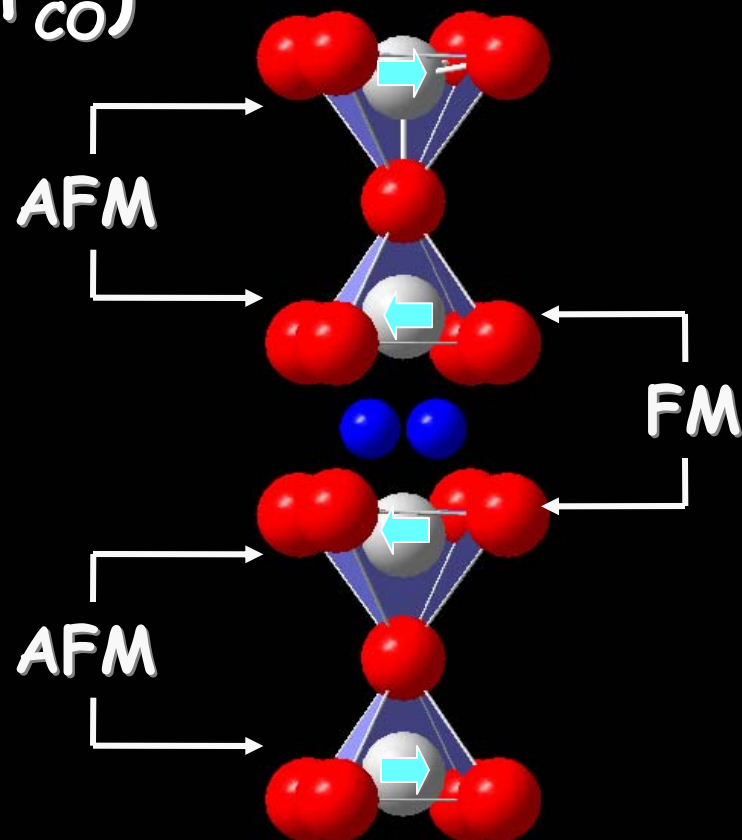
$T > T_{co}$ Magnetic Cell
 $2a \times 2b \times 2c$
 $7.88 \text{ \AA} \times 7.87 \text{ \AA} \times 15.17 \text{ \AA}$

The charge ordering induces a rearrangement of the antiferromagnetic structure!

TbBaFe₂O₅ MV State ($T > T_{co}$) Magnetic Structure

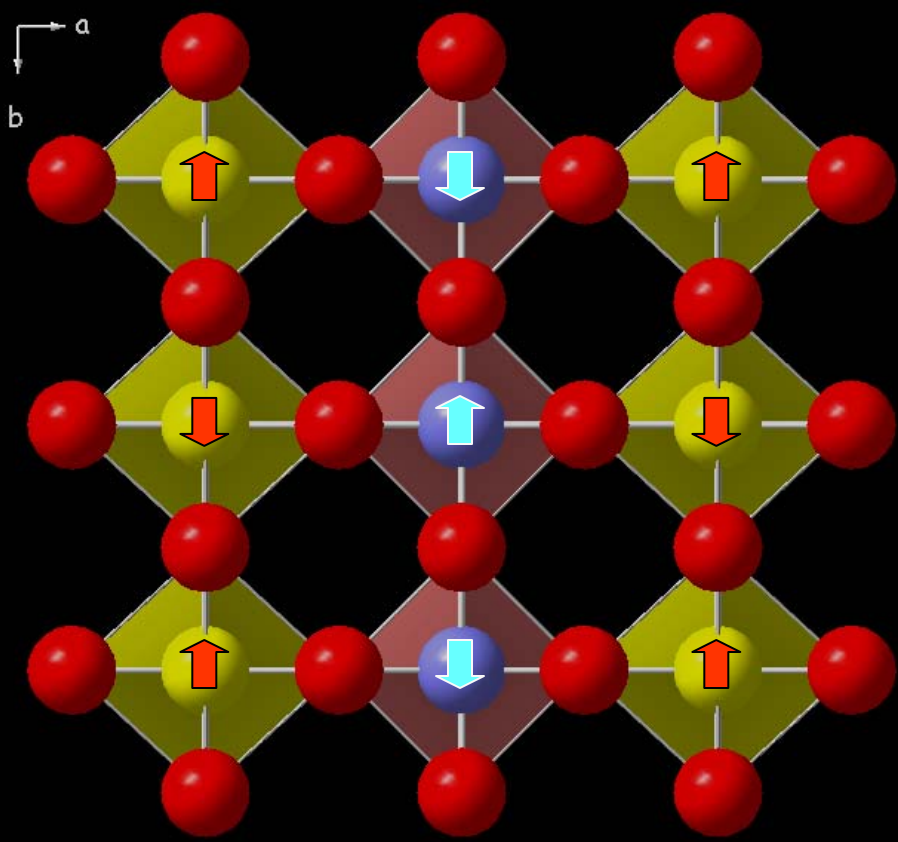


AFM Coupling in *ab* Plane

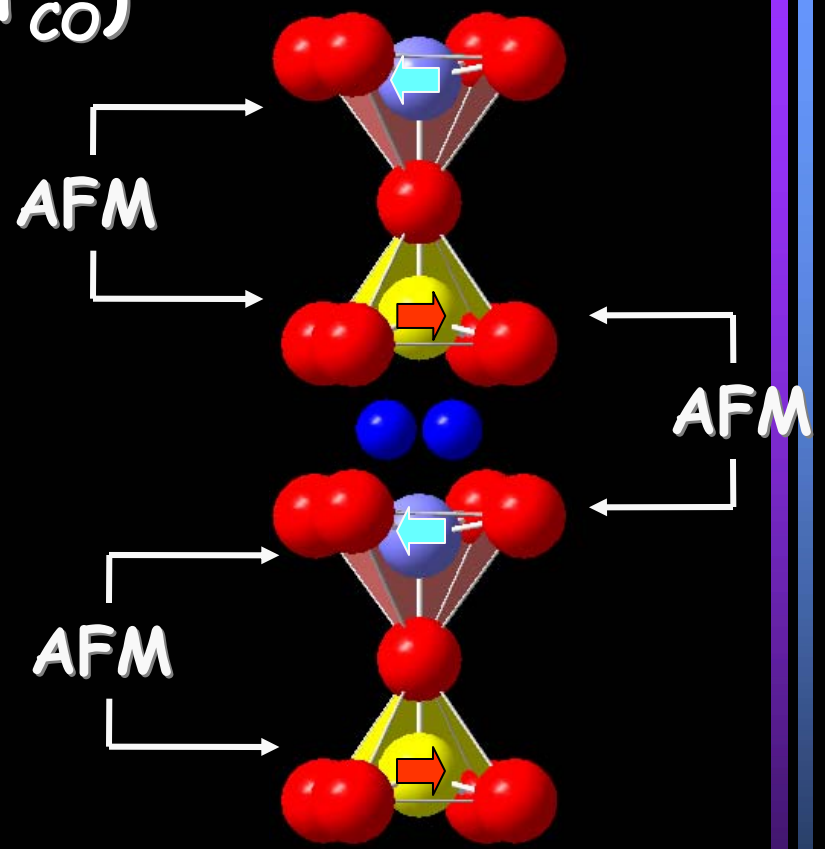


Isostructural with YBaFeCuO₅
Fe-O-Fe Superexchange AFM
Fe-Fe Direct Exchange FM

TbBaFe₂O₅ CO State ($T < T_{CO}$) Magnetic Structure

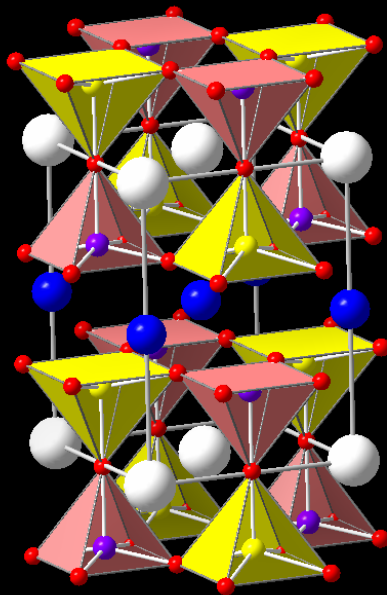


AFM Coupling in ab Plane



G-Type AFM Structure
Fe-O-Fe Superexchange AFM
Fe-Fe Direct Exchange AFM

Charge & Spin Ordering in YBaM_2O_5

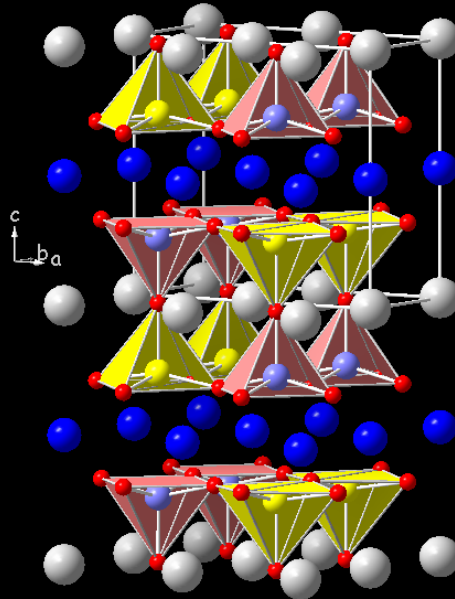


$T_{CO} > 300 \text{ K (CB)}$

$P4/nmm$

$T_C = 165 \text{ K (Ferri)}$

Millange, et al. *Mater. Res. Bull.* **1999**, 34, 1.

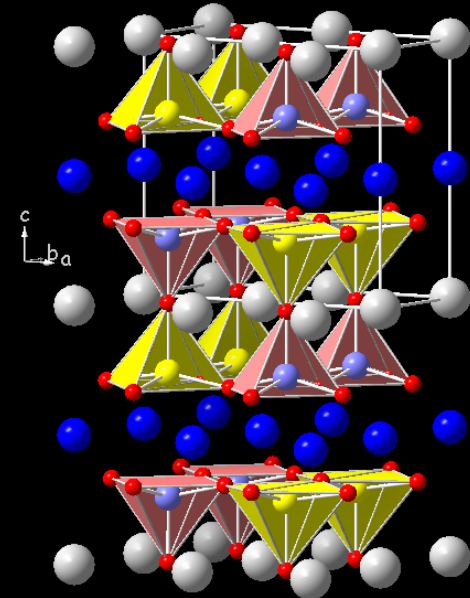


$T_{CO} > 308 \text{ K (ST)}$

$Pmma$

$T_N = 430, 308 \text{ K}$

Woodward, Karen *Inorg. Chem.* **2003**, 42, 1121.



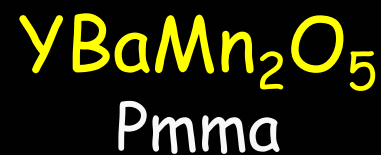
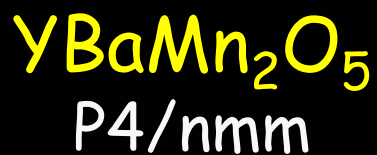
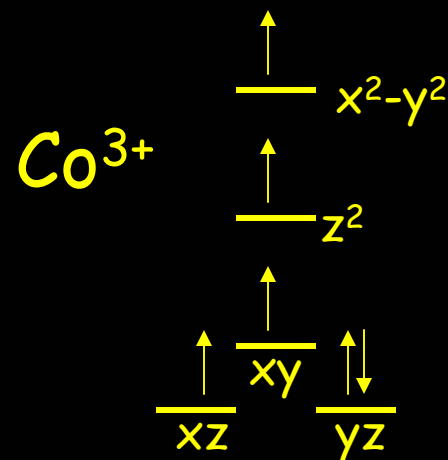
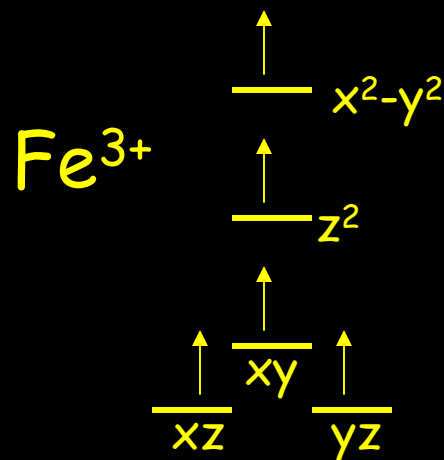
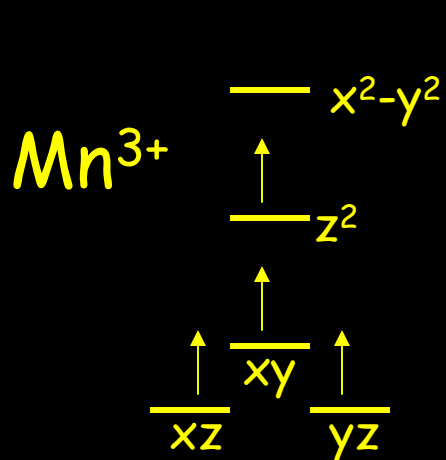
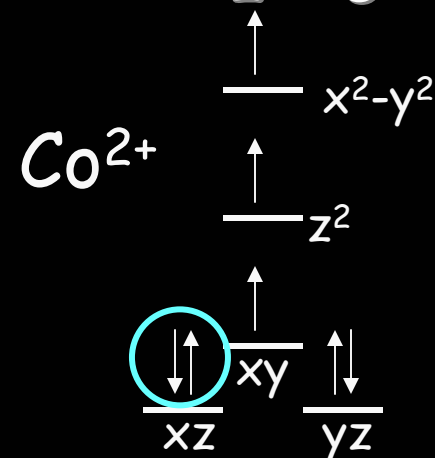
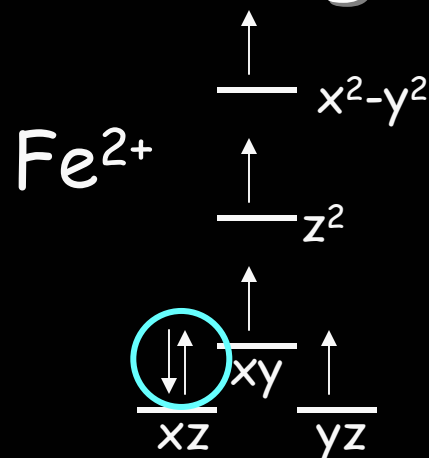
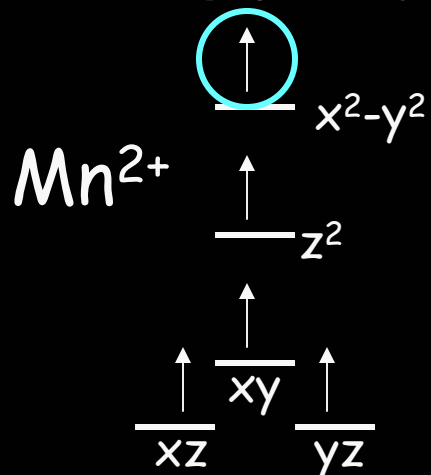
$T_{CO} > 220 \text{ K (ST)}$

$Pmma$

$T_N = 330 \text{ K}$

Vogt, et al. *PRL* **2003**, 84, 2969.

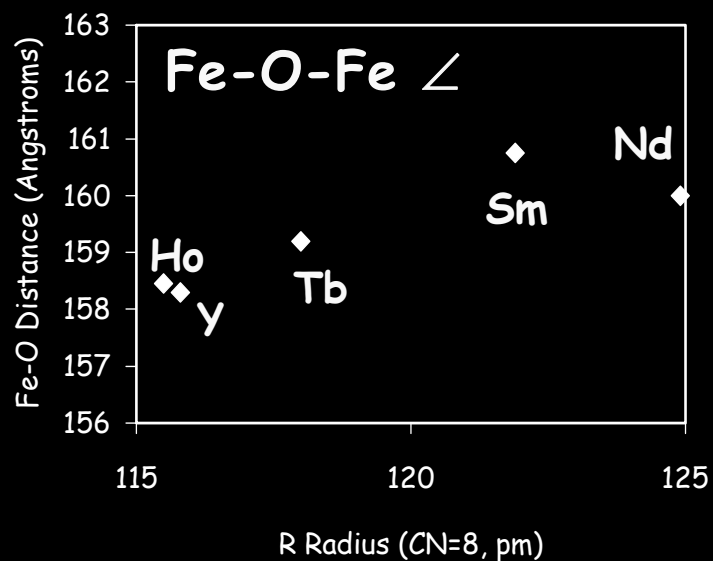
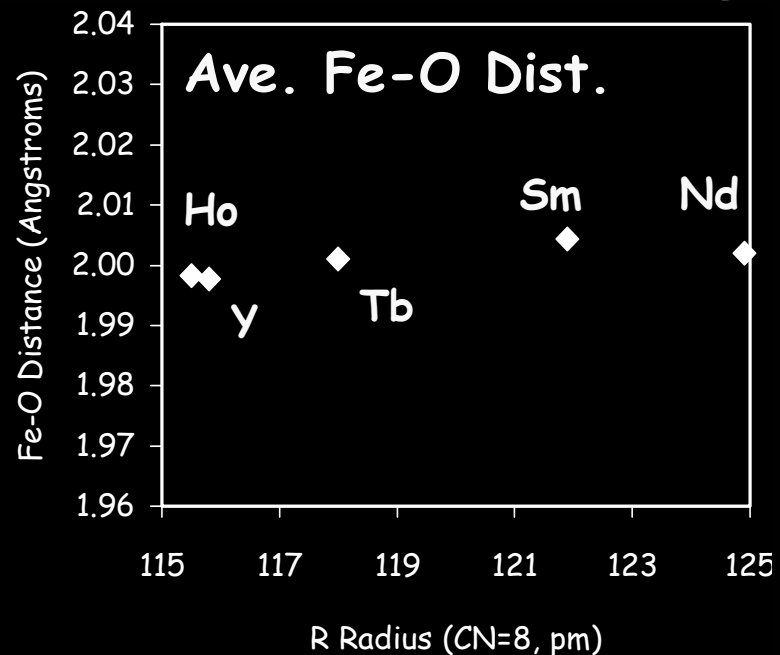
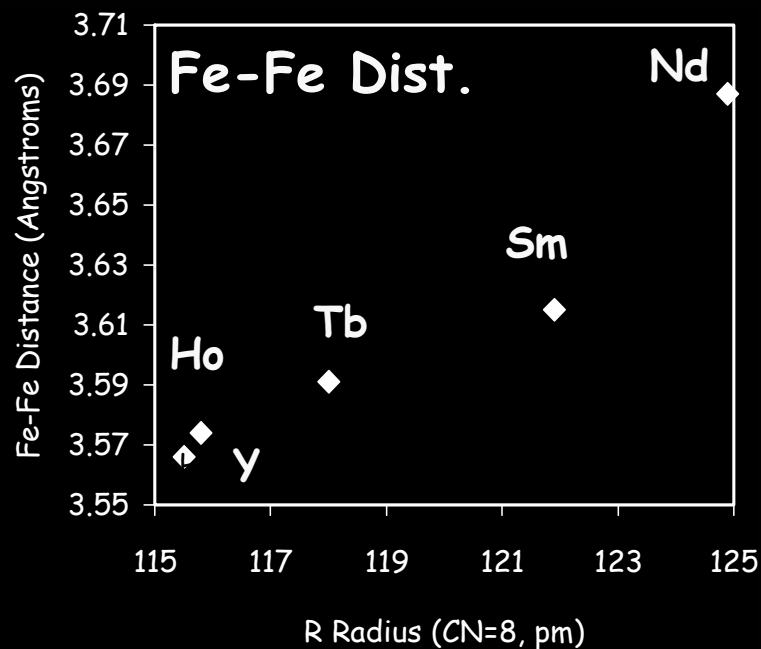
Orbital Ordering in YBaM_2O_5



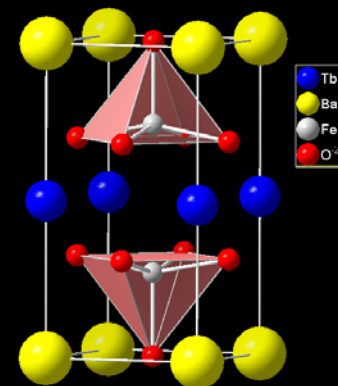
Phase Transitions - RBaFe_2O_5

- **Paramagnetic to Antiferromagnetic (430-450 K)**
 - YBaFeCuO_5 Type AFM Order
 - Small Magnetostrictive coupling leads to a subtle Tetragonal to Orthorhombic Distortion
- **Premonitory Charge Ordering (290-330 K)**
 - Subtle charge localization can be seen in DSC & Mossbauer, but not in diffraction measurements
 - Mixed valency changes from Type I to Type II
- **Long Range Charge Ordering (240-290 K)**
 - Induces a large orbital ordering transition
 - Orbital ordering stabilizes a stripe CO pattern
 - Stabilizes G-type Antiferromagnetic order (changes the sign of the Fe-Fe direct exchange)

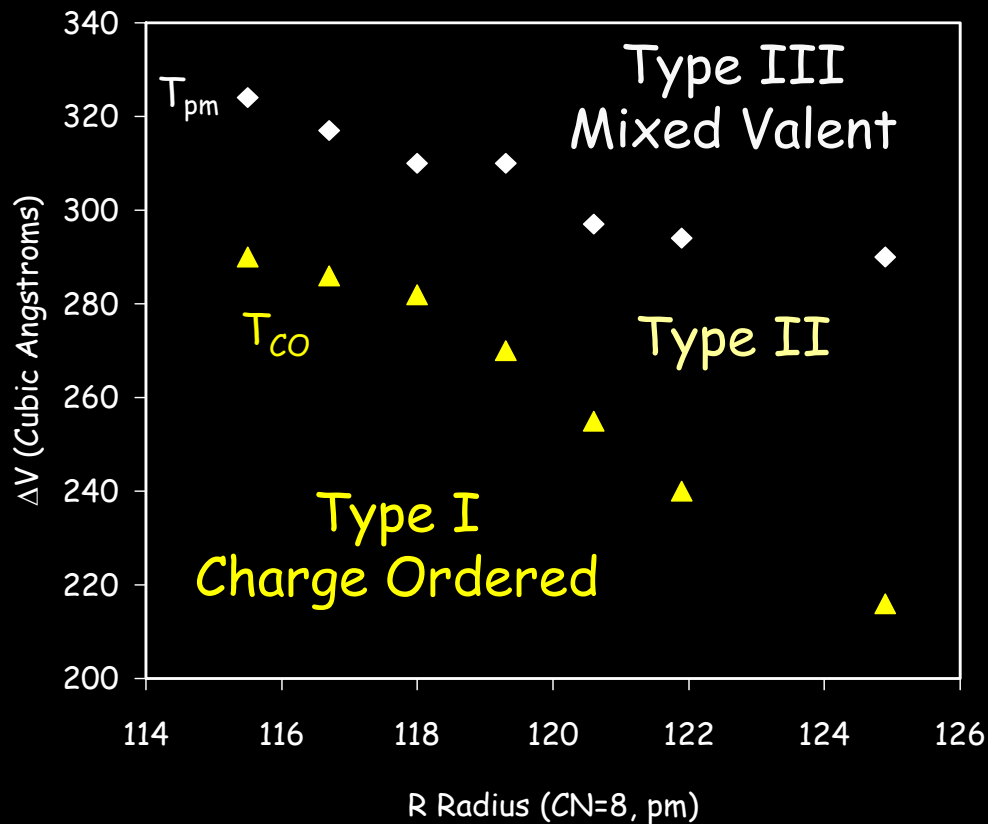
Structural Evolution: REBaFe₂O₅



Changing the size of the RE ion modifies the Fe-Fe distance.



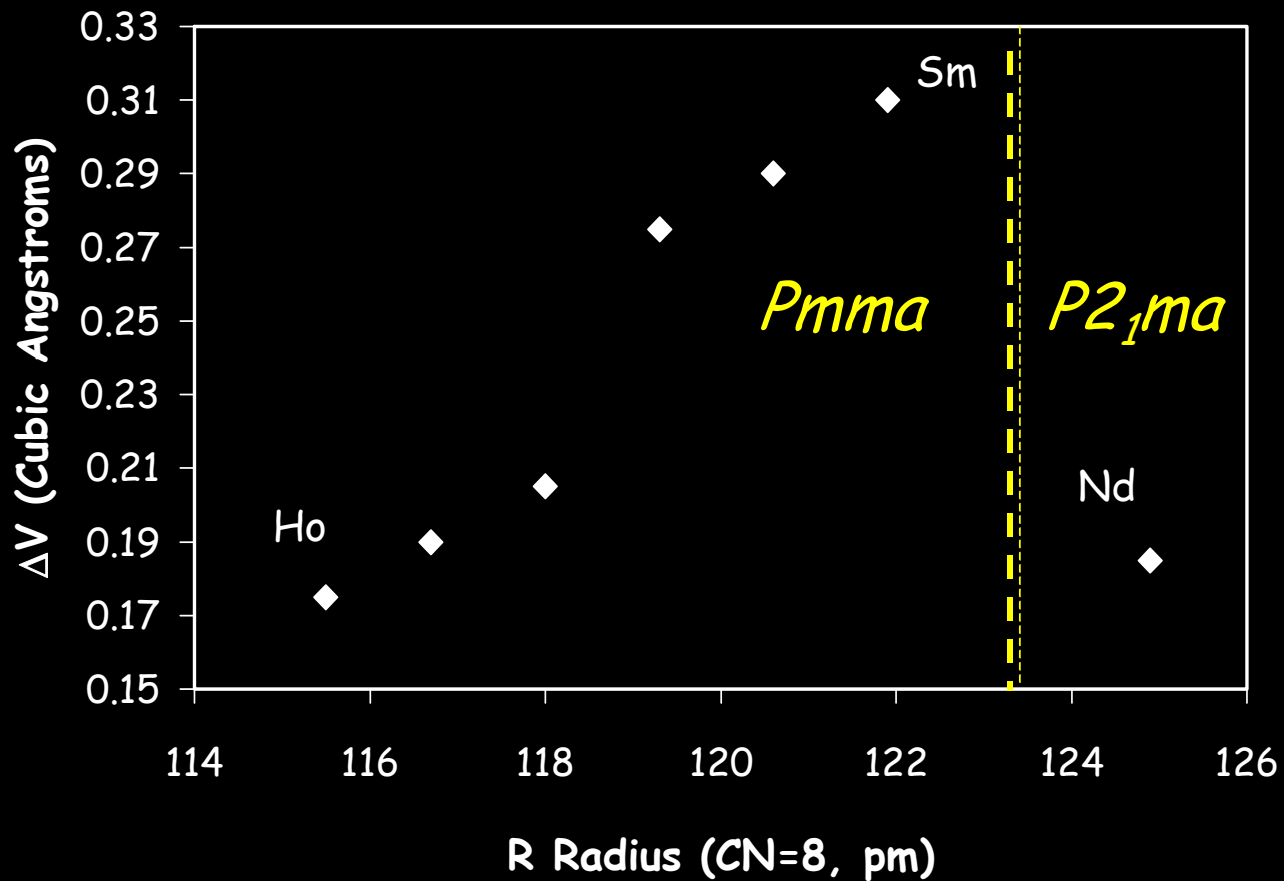
Phase Transitions vs. R size



As the radius of the R ion increases

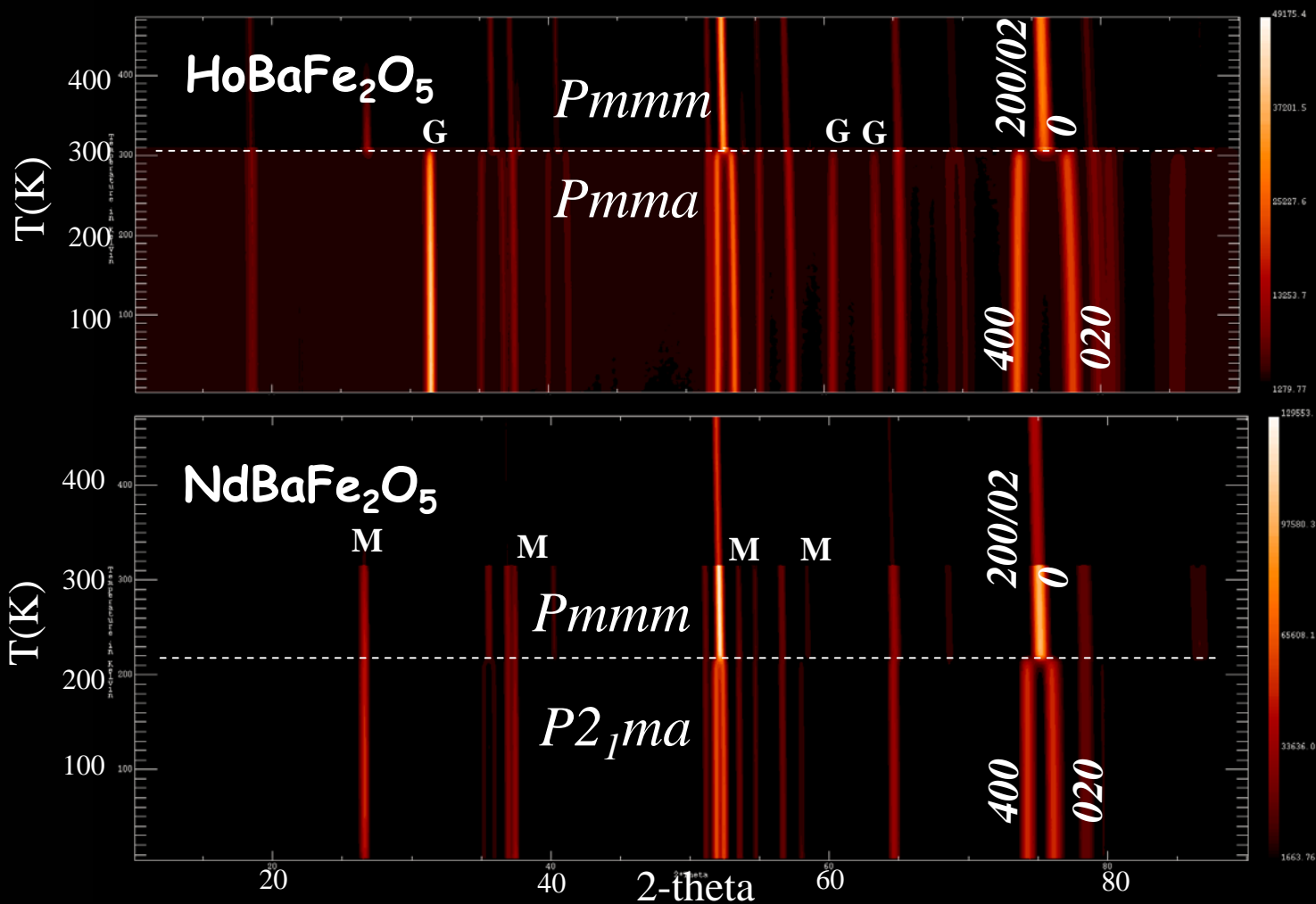
- T_{CO} (MV II \rightarrow MV I) decreases significantly.
- T_{PM} (MV III \rightarrow MV II) decreases more gradually.
- T_{N1} changes very little.

Volume Change at T_{CO}



Volume change at T_{CO} (MV II \rightarrow MV I)

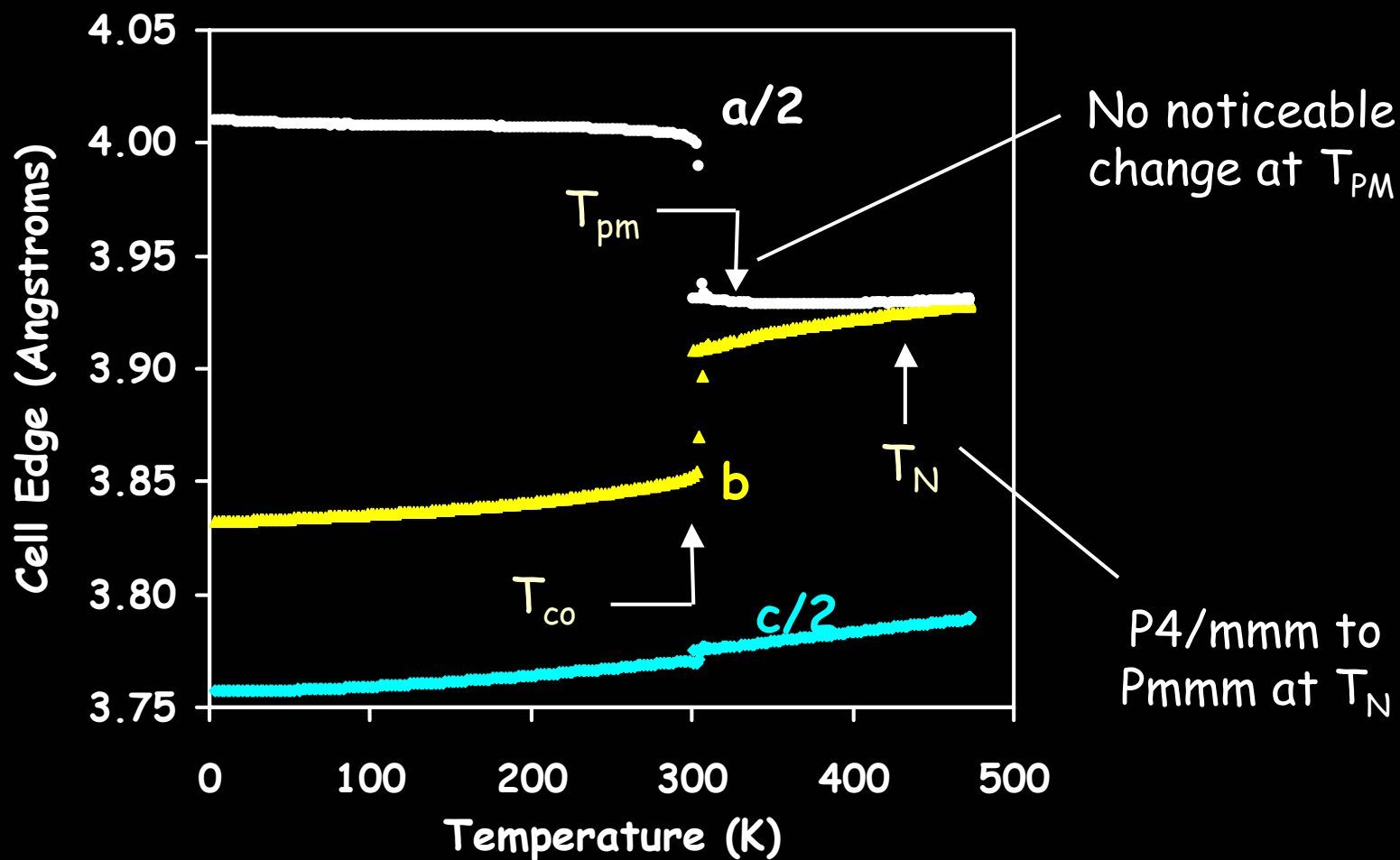
Thermodiffractometry (ILL-D20)



Woodward, Karen, Suard, *J. Amer. Chem. Soc.* 125, 8889 (2003).

HoBaFe₂O₅ Unit Cell Evolution

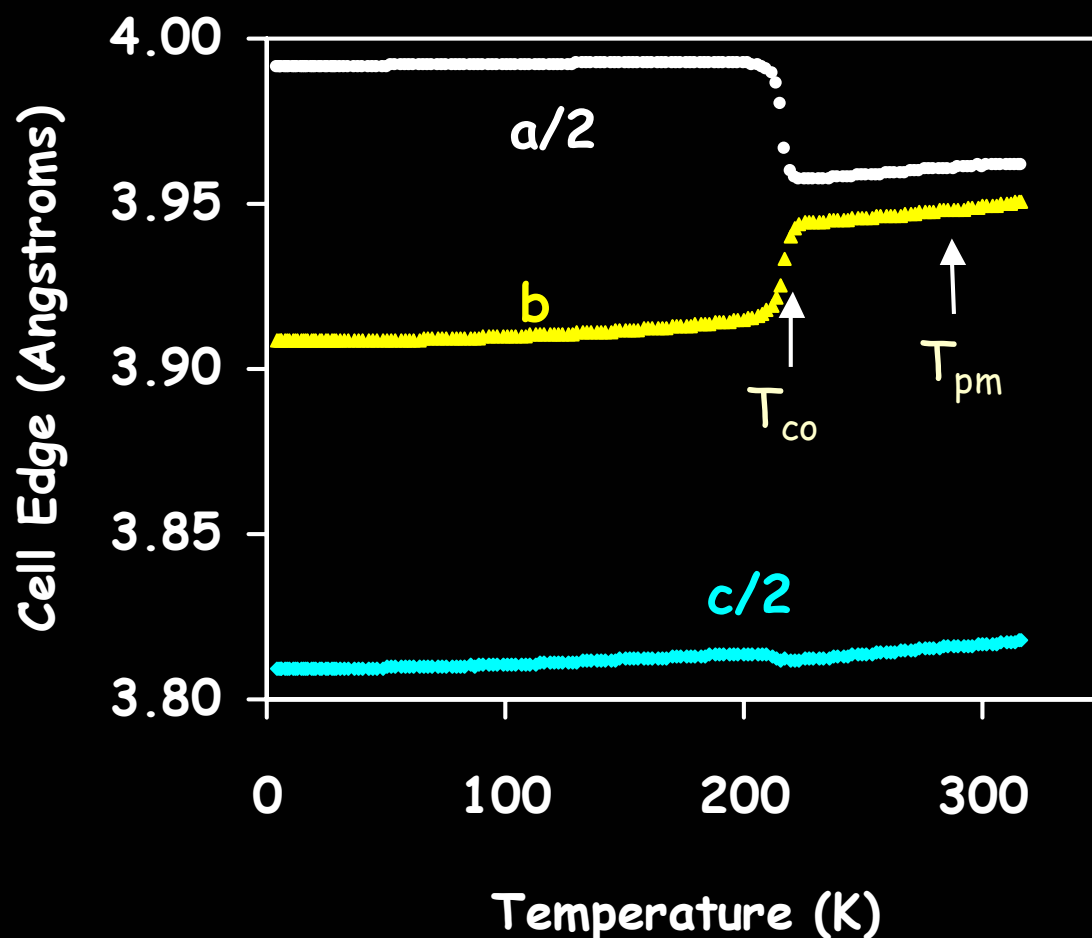
1 K Temperature grid, 1 min collection time



Woodward, Karen, Suard, *J. Amer. Chem. Soc.* 125, 8889 (2003).

NdBaFe₂O₅ Unit Cell Evolution

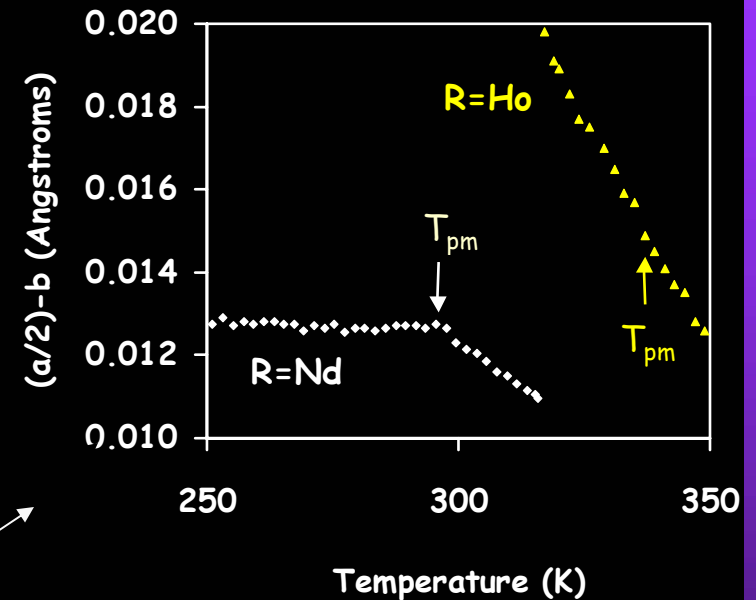
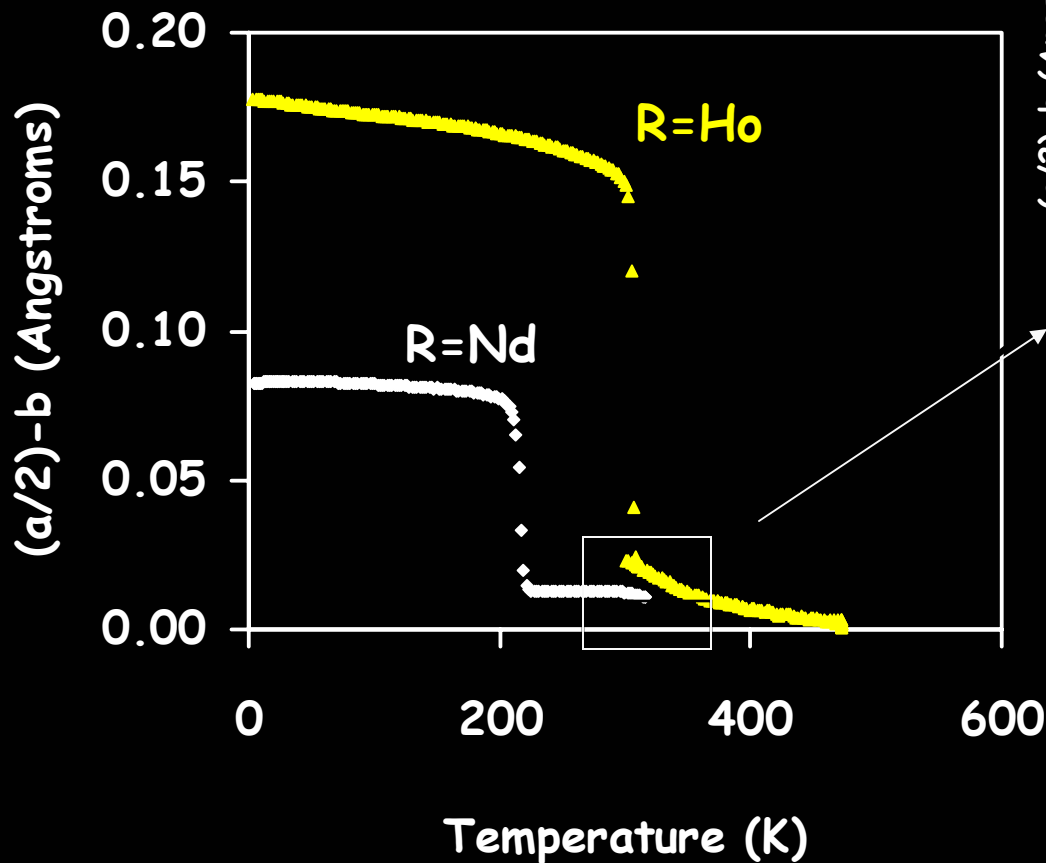
1 K Temperature grid, 1 min collection time



Woodward, Karen, Suard, *J. Amer. Chem. Soc.* 125, 8889 (2003).

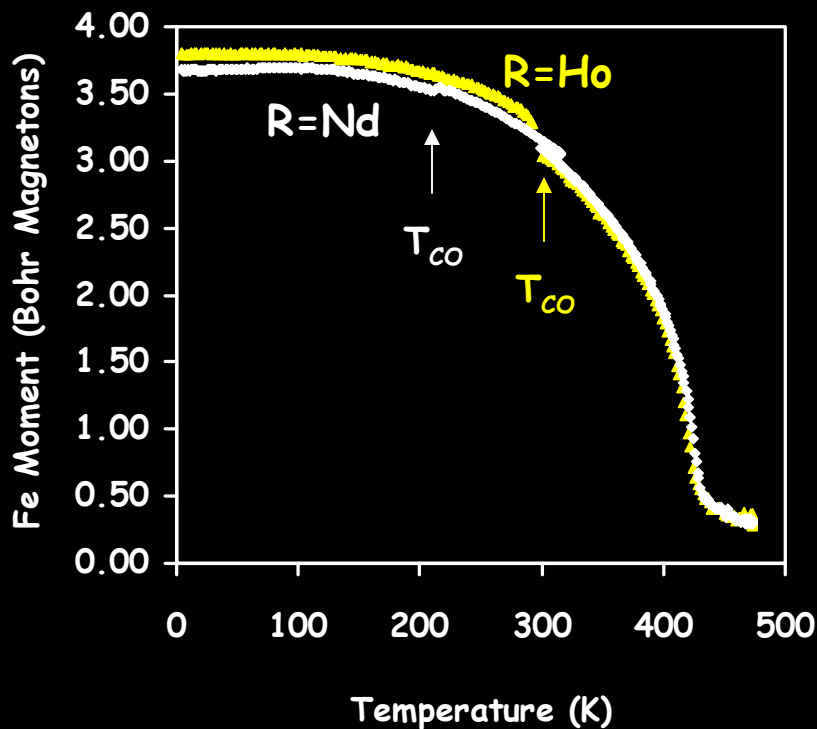
Orbital Ordering (RE = Nd, Ho)

Orthorhombic distortion increase at T_{CO} is much larger in $\text{HoBaFe}_2\text{O}_5$.



Orthorhombic distortion saturates at T_{pm} for $\text{NdBaFe}_2\text{O}_5$. Similar behavior is not observed for $\text{HoBaFe}_2\text{O}_5$

Magnetism vs. Temperature



RBaFe_2O_5 (R=Tb, Y, Ho)

YBaFeCuO_5 AFM Structure

Fe-Fe Coupling Ferromagnetic

↓ @ T_{co} ↓

G-Type AFM Structure

Fe-Fe Coupling Antiferromagnetic

$\text{NdBaFe}_2\text{O}_5$

YBaFeCuO_5 AFM Structure

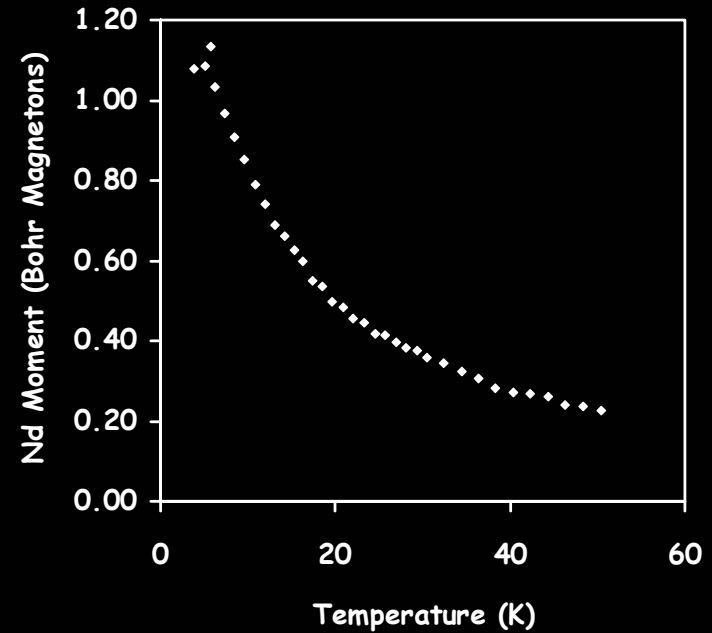
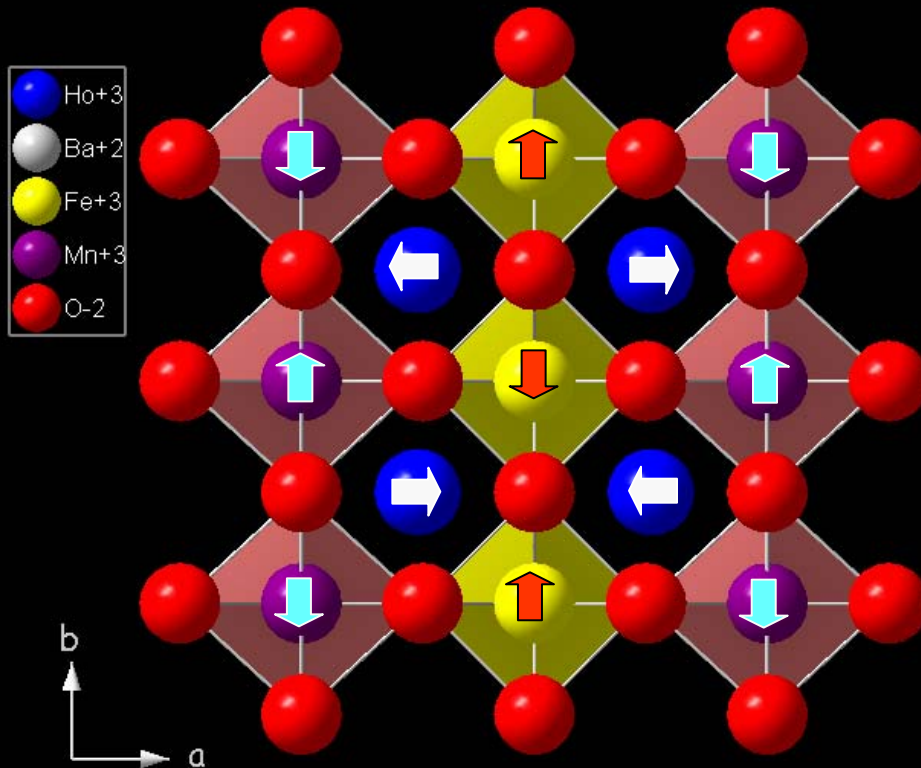
Fe-Fe Coupling Ferromagnetic

↓ @ T_{co} ↓

YBaFeCuO_5 AFM Structure

Fe-Fe Coupling Ferromagnetic

Nd Magnetism in NdBaFe₂O₅



Nd moment is $\sim 1.2 \mu_B$ at 2 K, T_N (Nd) ~ 30 K

No rare-earth magnetic order for R = Ho.

Nd magnetism is induced by Fe magnetism.

Structural Tuning in RBaFe_2O_5

As the radius of the R ion increases (R = Ho-Sm)

- The spacing across the R-layer increases
- T_{CO} decreases significantly, T_{PM} decreases more gradually
- T_{N1} changes very little
- Patterns of charge, orbital and spin order remain constant

$\text{NdBaFe}_2\text{O}_5$ The large size of Nd has several effects

- Disrupts the ideal pattern of orbital ordering
 - The CO structure has $P2_1ma$ symmetry rather than $Pmma$
 - The volume change at T_{CO} is anomalous
 - The orthorhombic distortion parameter saturates at T_{PM}
- Decouples the magnetic and charge order
 - There is no rearrangement of the magnetic structure at T_{CO}
- Destabilizes the long range charge order
 - T_{CO} is much lower than other members of the series