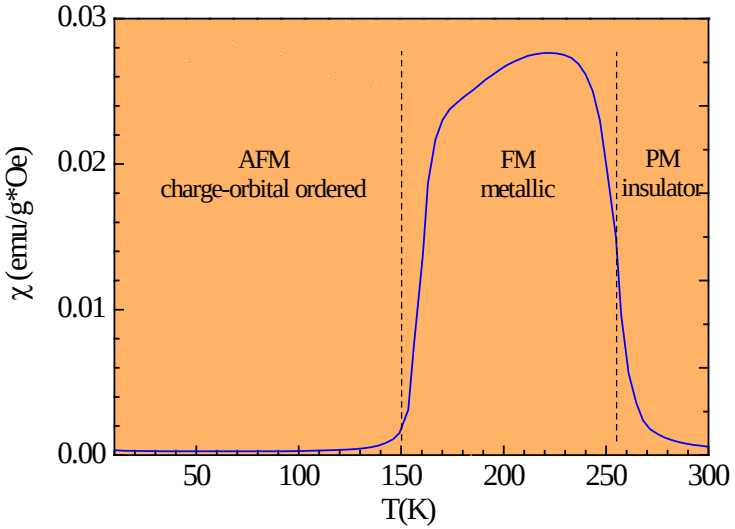
G. Subías, S. Lafuerza, J. García, J. Blasco, P. Glatzel

Temperature evolution of the Mn electronic and local structure in $Nd_{0.5}Sr_{0.5}MnO_3$

An x-ray emission and absorption spectroscopy study



XAFS
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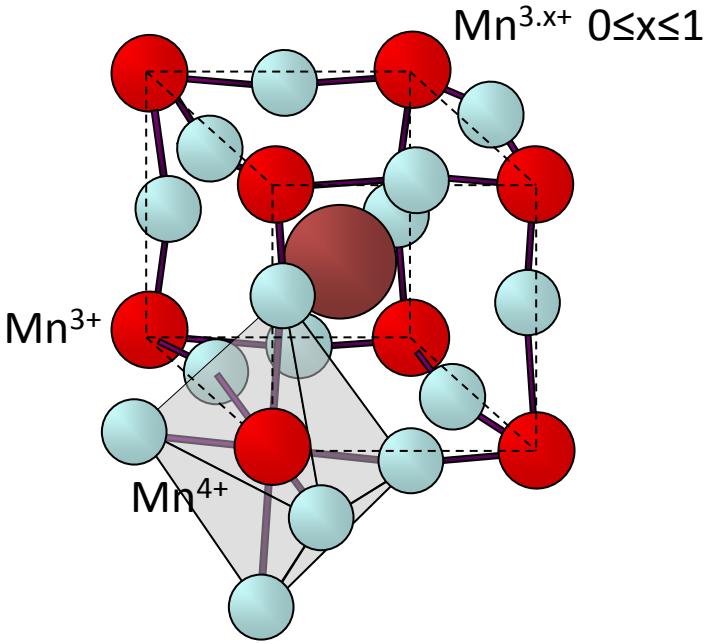
icma / Instituto de Ciencia de Materiales de Aragón
CSIC Consejo Superior de Investigaciones Científicas
Universidad Zaragoza
ESRF

Motivation

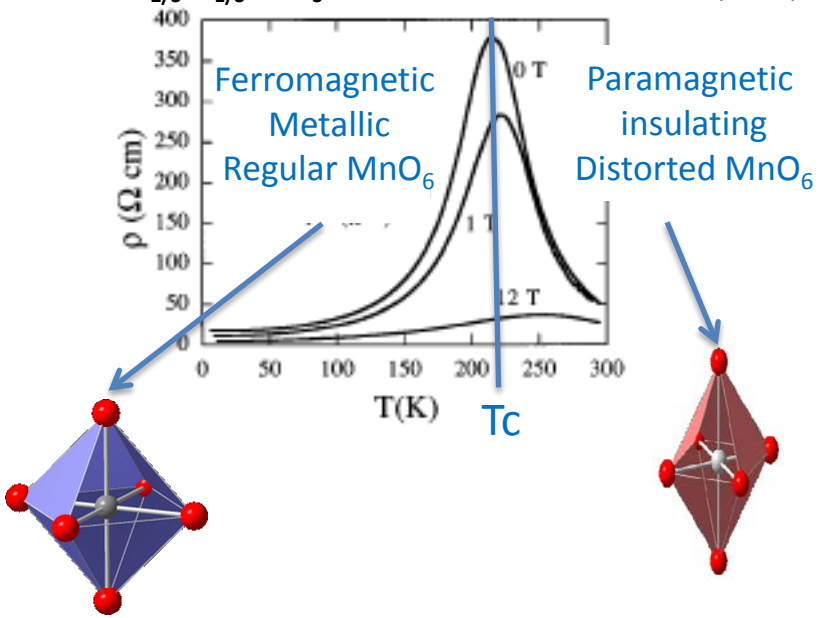
Phase diagrams of manganites ($RE^{3+}_{1-x}A^{2+}_{x}MnO_3$) are exceptionally rich -
- depending on T and x

Para-ferromagnetic, para-antiferromagnetic, insulator-metallic, charge-orbital ordered…

Nature of the Mn mixed-valence state and the local structure is a crucial ingredient for the magneto-transport properties

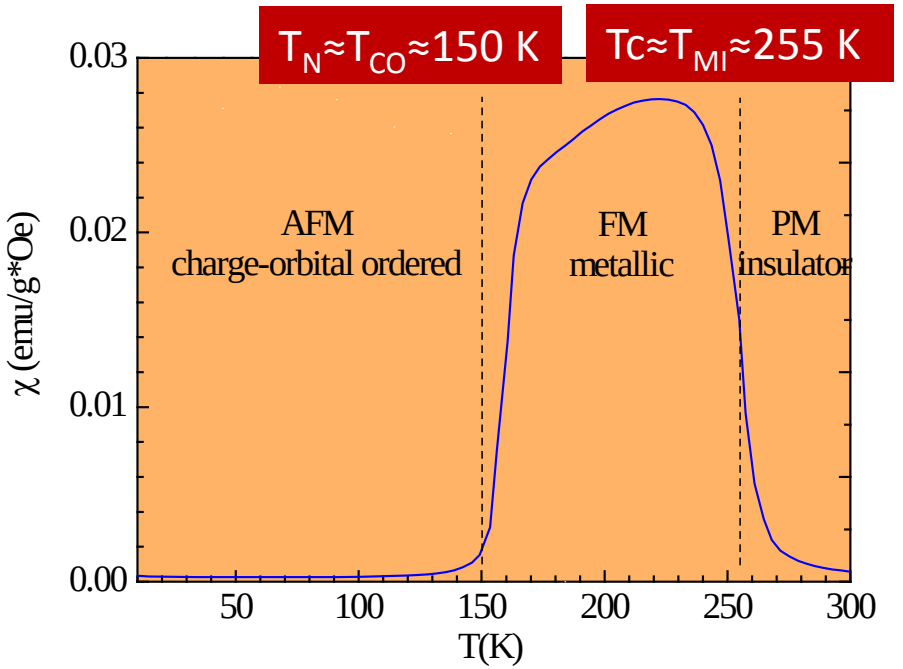


$La_{2/3}Ca_{1/3}MnO_3$ De Teresa et al. PRB 54, 1187 (1996)



Motivation

$Nd_{0.5}Sr_{0.5}MnO_3$ is a particularly interesting case…



Mechanism ← Proposed

Doped holes spatially localized at Mn sites
CO Mn^{3+} - Mn^{4+}

Doped holes highly delocalized over Mn sites

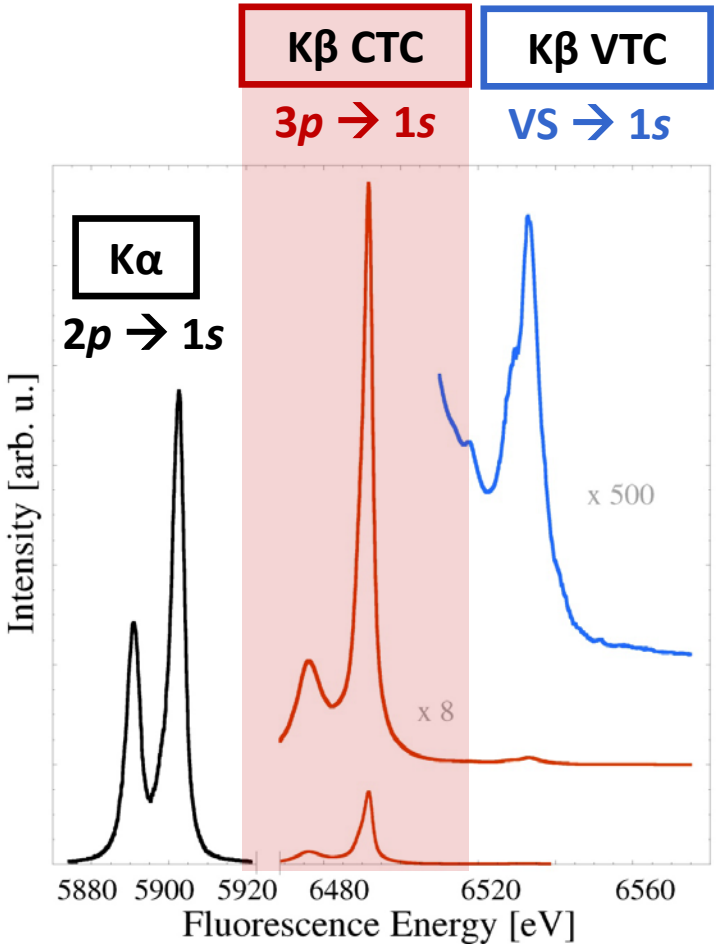
Doped holes randomly localized at Mn sites
$t_{Fluctuation} >> t_{permanence}$

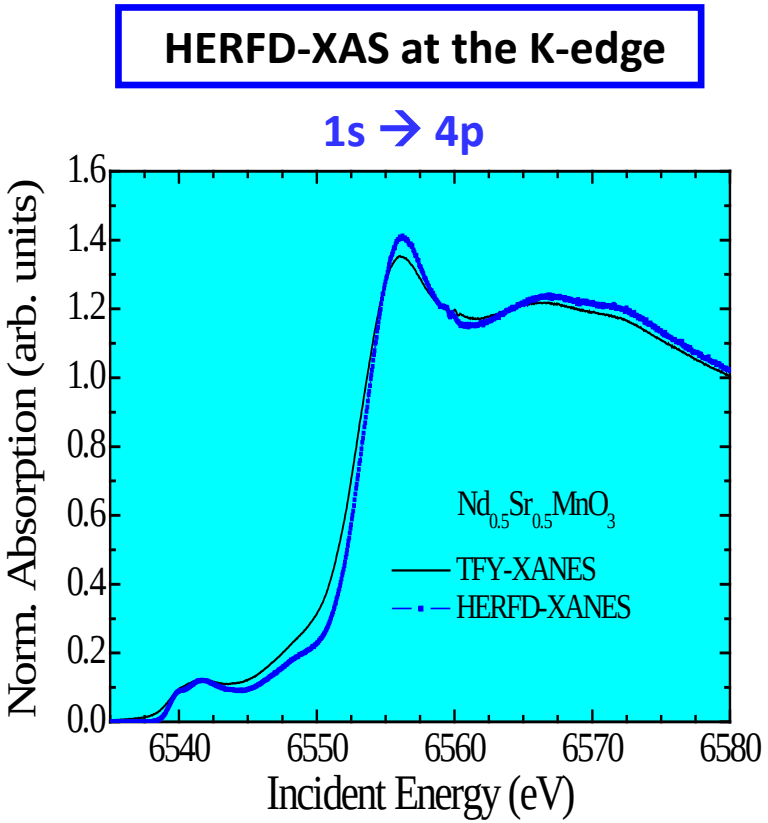
Experiment @ ID26 (ESRF)

- Kα and Kβ **X**-ray **E**mission **S**pectroscopy & **X**-ray **A**bsorption **S**pectroscopy at Mn K-edge

Occupied states **Unoccupied states**

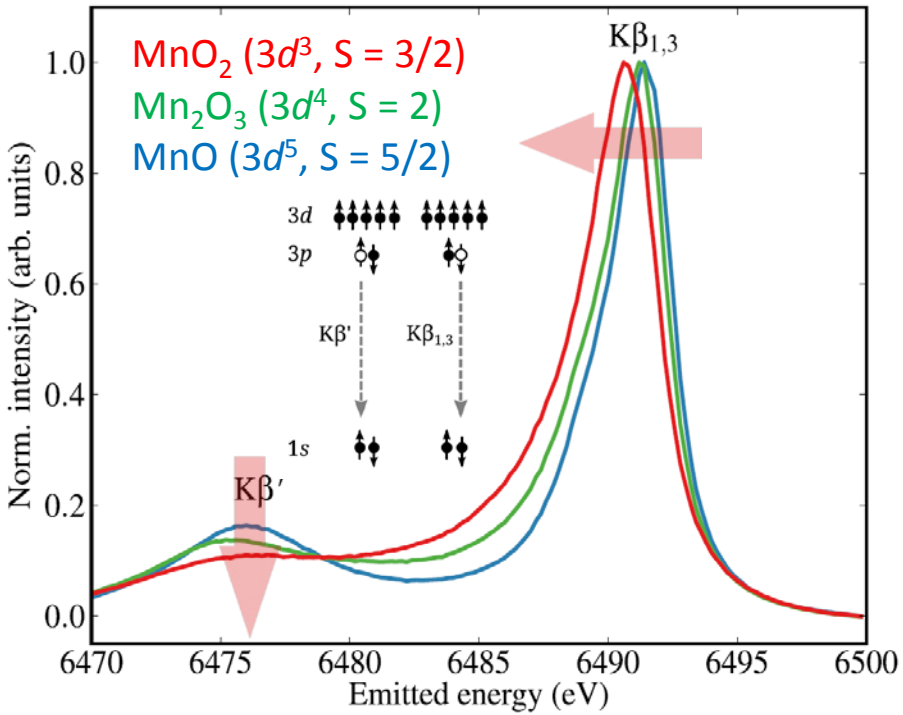
Complementary techniques to probe the electronic and local structure





ΔE (Mn Kα) ≈ 0.4 eV

- Kβ CTC XES in 3*d* transition metals: a net local spin moment probe!



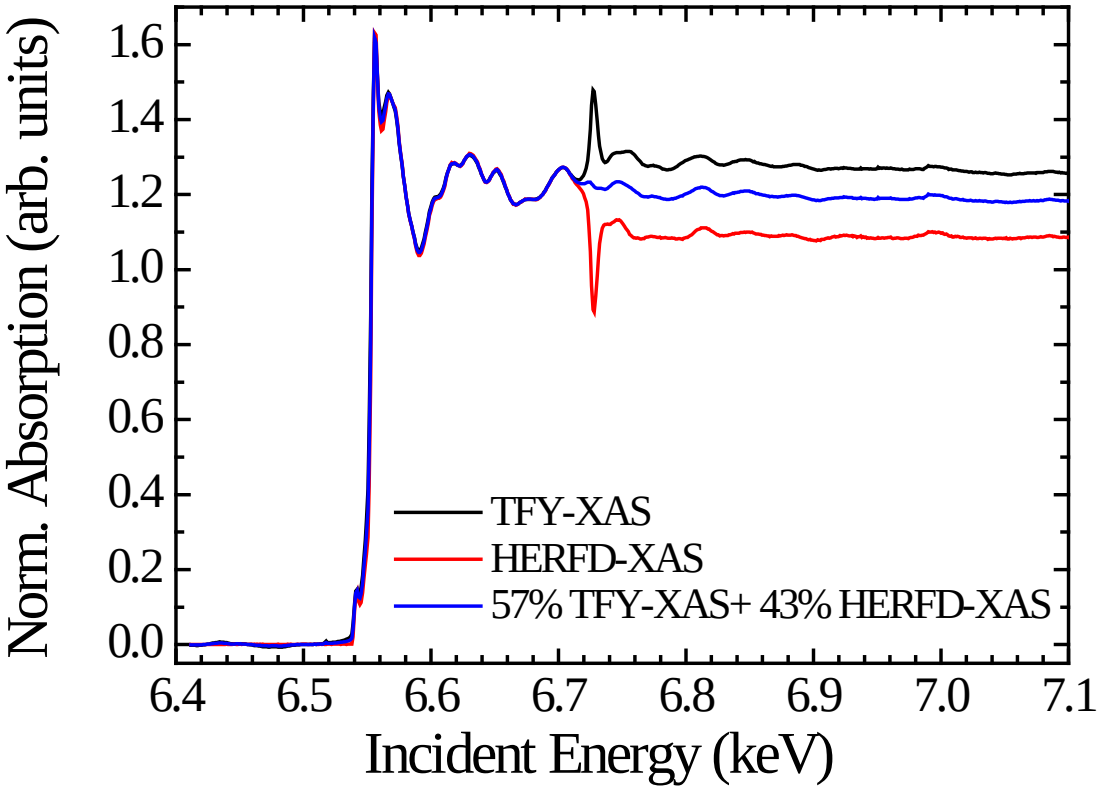
M. Rovezzi and P. Glatzel, *Semicond. Sci. Technol.* **29** 023002 (2014)

- Sensitive to the 3*d* spin due to the **intra-atomic** 3*p*-3*d* exchange interaction

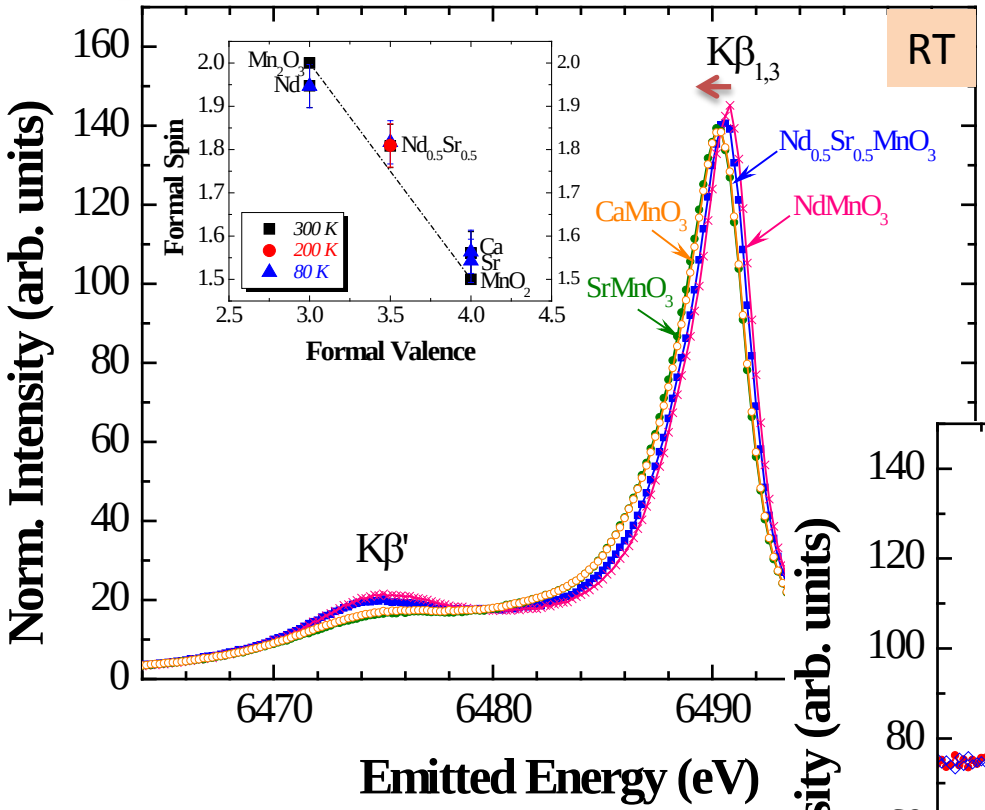
$$\Delta E = J(2S+1) \qquad I^{'}/I_{1,3} = S/(S+1)$$

Experiment @ ID26 (ESRF)

- Kα HERFD-EXAFS & TFY-EXAFS in $Nd_{0.5}Sr_{0.5}MnO_3$:
  To extract Mn K EXAFS signal free of Nd L_2 (6722 eV) self-absorption

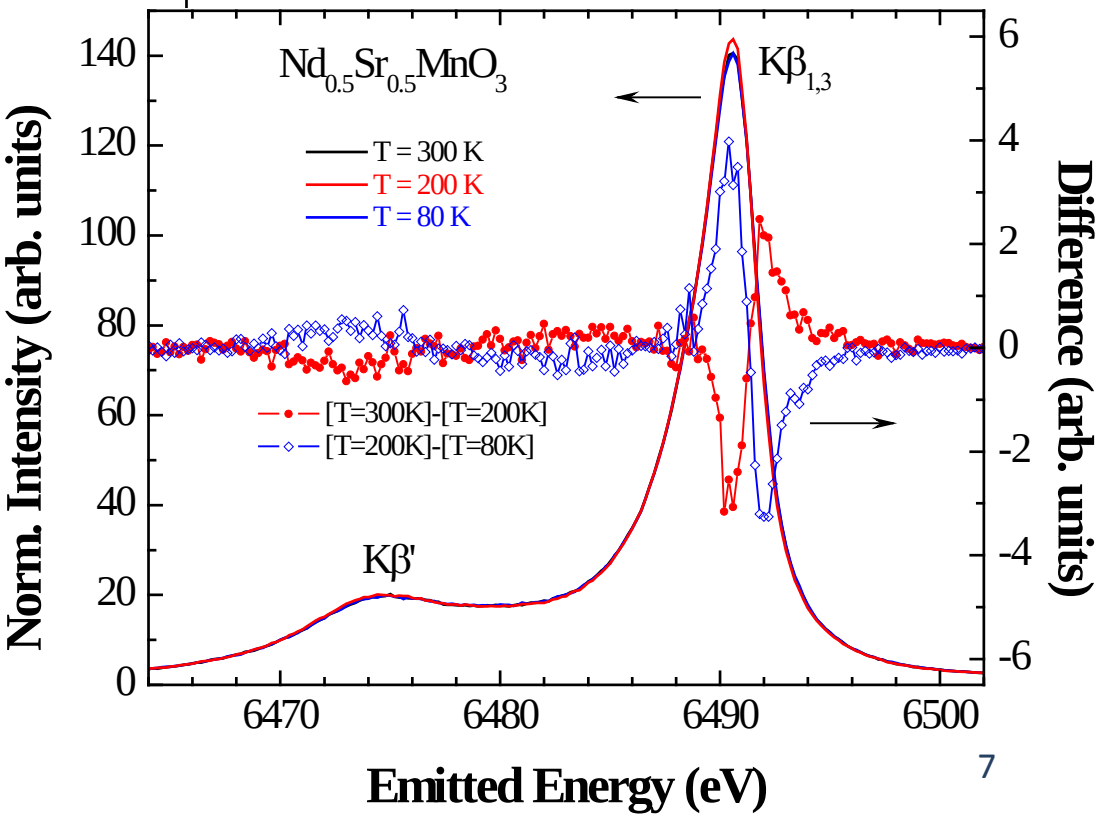


Results
Kβ CTC XES



$K\beta_{1,3}$ shifts to lower E ↔ Valence increase
Kβ' reduces Intensity

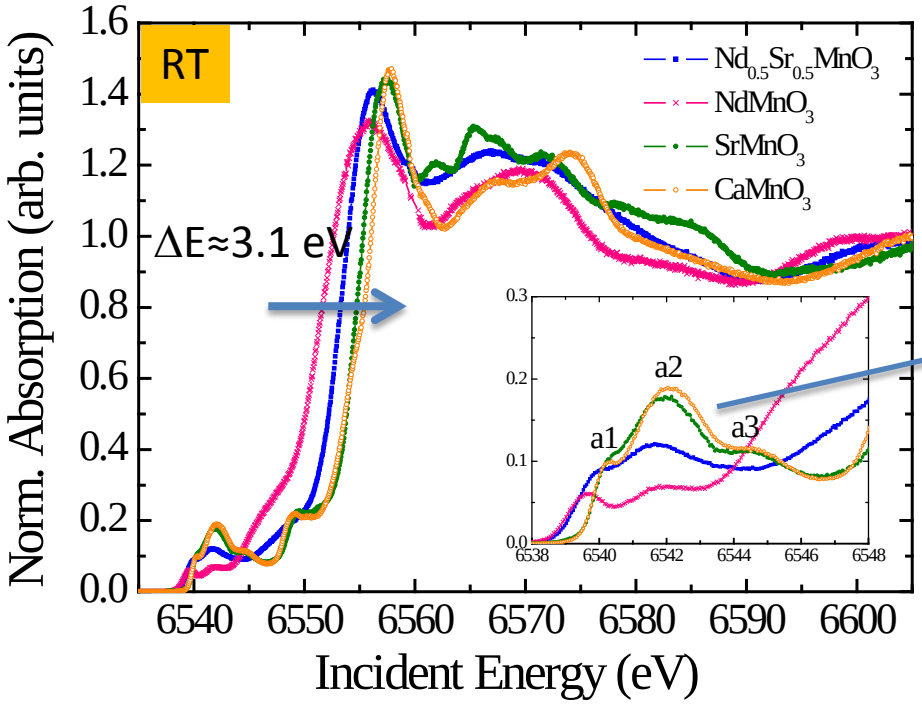
$Nd_{0.5}Sr_{0.5}MnO_3$ lies in between $NdMnO_3$ and $SrMnO_3$ ≠ 0.5:0.5



Only modest changes occurs across the magneto-electrical transitions:

- Not a Mn formal valence increase.
- Yes **a subtle decrease of the local spin density in the FMM phase.**

Results
Kα HERFD-XAS



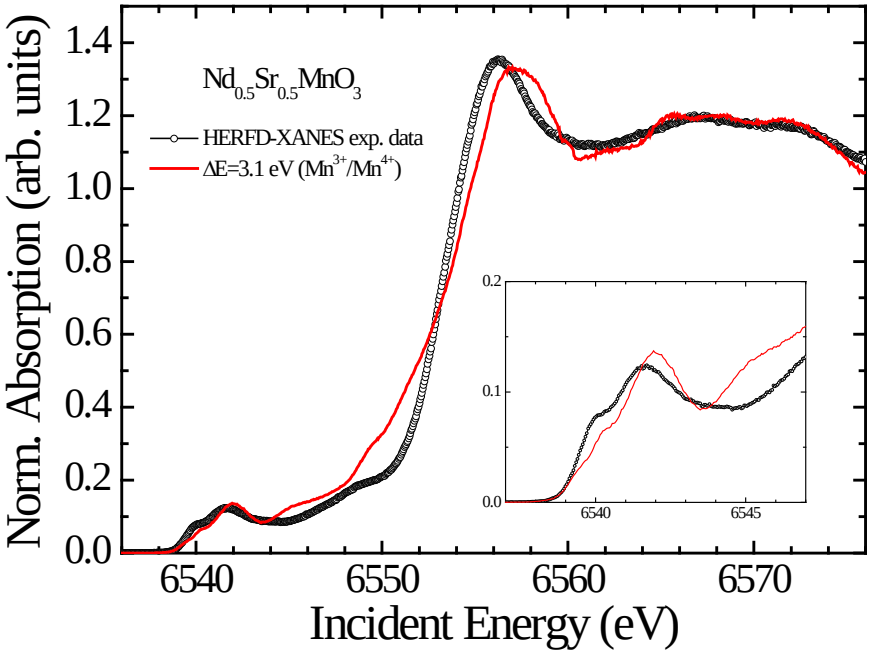
p-d hybridization

Mn in $Nd_{0.5}Sr_{0.5}MnO_3$ ≈ 50% Mn^{3+} and 50% Mn^{4+}

?

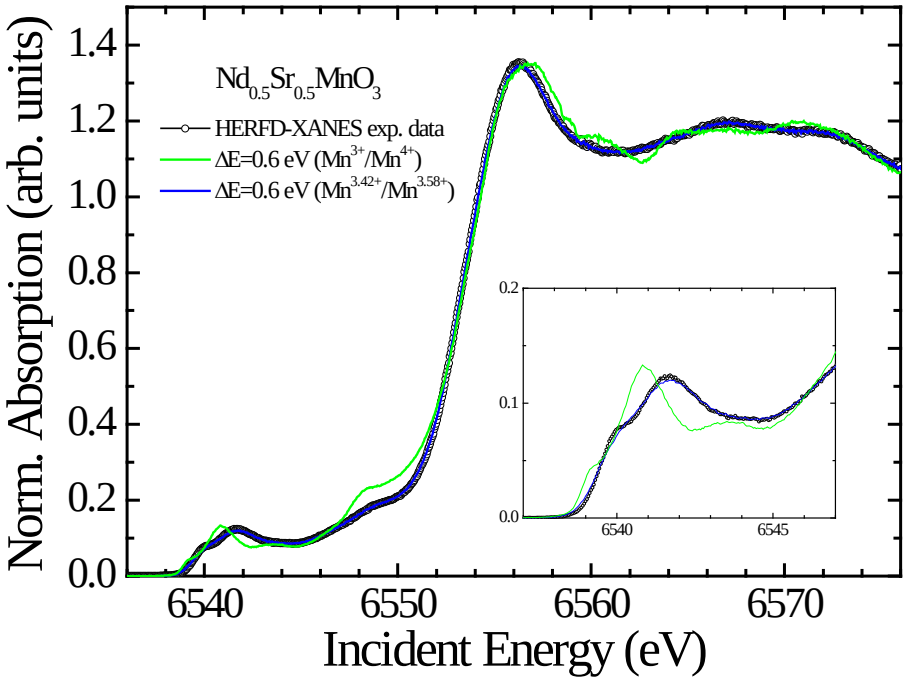
HERFD-XANES ($Nd_{0.5}Sr_{0.5}MnO_3$)≈ 0.5 HERFD-XANES ($NdMnO_3$) + 0.5 HERFD-XANES ($SrMnO_3$)

Results
Kα HERFD-XAS



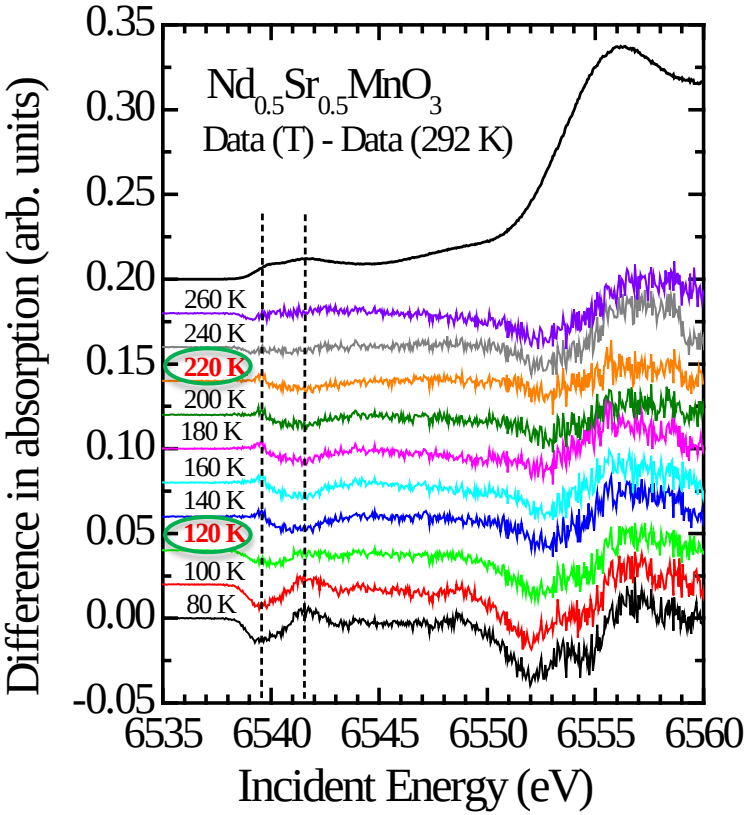
Neither spatial nor temporal distribution of Mn^{3+} - Mn^{4+} ions

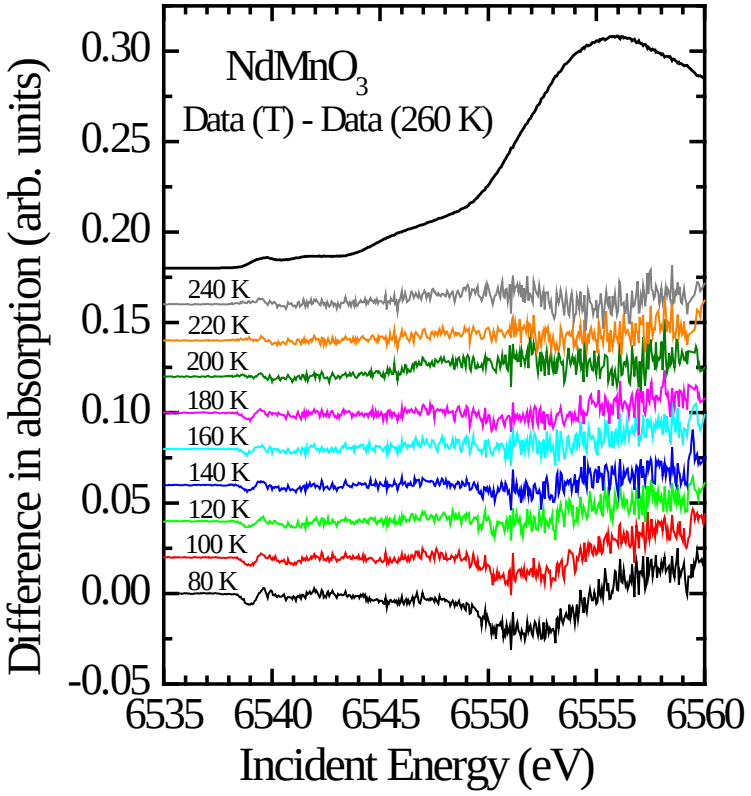
RXS experiments of the CO phase →
(J. Herrero-Martín *et al*. PRB, 70, 024408 (2004))
Two Mn sites with a charge disproportionation of 0.2 e^-



Two intermediate valence states $Mn^{3.42+}$ - $Mn^{3.58+}$

Temperature dependence

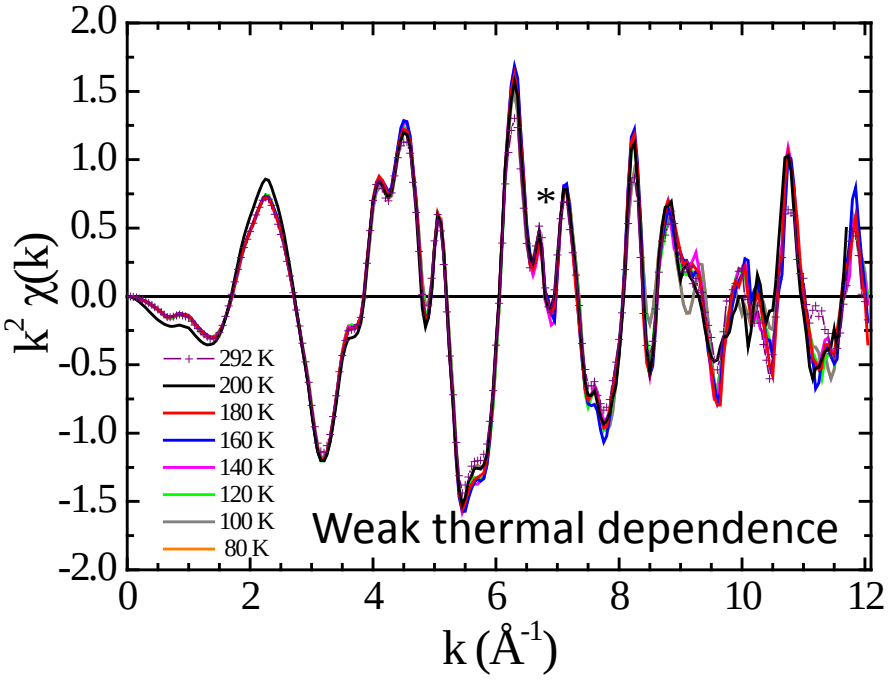


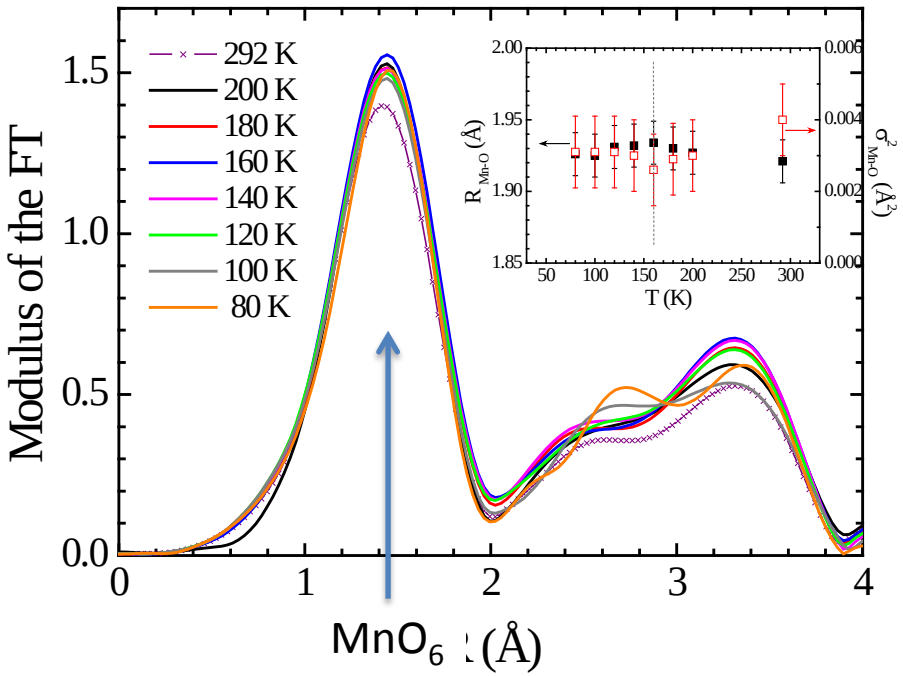


Rising edge: increase of the slope when T ↓ - freezing of thermal vibrations

Pre-edges: two changes of sign – **p-d hybridization ↑ in the FMM phase and ↓ in the AFM-CO**

EXAFS analysis of the temperature evolution of the local MnO_6 structure





- The Mn-O distance slightly increases down to the onset of the CO phase and then it remains almost constant.
- The Debye-Waller factor decreases with T ↓ showing a minimum at the onset of the CO phase, increasing again with T ↓. A high value at low T indicates a distorted MnO_6.

Conclusions

- Mn local structure and electronic state in $Nd_{0.5}Sr_{0.5}MnO_3$ hardly change across the magneto-electrical phases while clearly differ from single-valent Mn^{3+} /Mn^{4+} samples

- The main electronic structure changes relate to the Mn 3d – O 2p covalency:
  ↑ in the FMM phase connected with ↓ of the local spin moment
  (completely reversed when entering into the AFM-CO phase)

- MnO_6 octahedron:

  - PMI phase: dynamically distorted
  - FMM phase: with ↓T the system tends to stabilize by reducing the local distortion due to the long-range FM interactions
  - AFM-CO phase: the local distortion increases again and becomes T-independent instead of collapsing as for magnetoresistive manganites

- This XAS-XES study demonstrates the strong competition between the FMM and the AFM-CO phases in manganites.

S. Lafuerza et al., submitted to PRB (2016)