

# Direct Evidence of $\text{Fe}^{2+}/\text{Fe}^{3+}$ Charge Ordering in Ferrimagnetic $\text{Fe}_{1.35}\text{Ti}_{0.65}\text{O}_{3-\delta}$ Thin Films

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# Functional Complex Metal Oxides

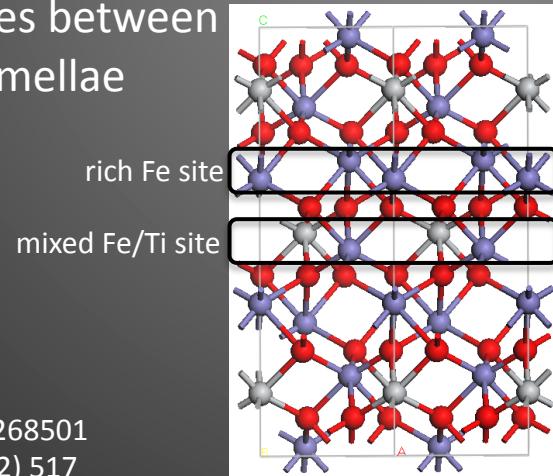
- Strong interplay between lattice, charge, orbitals and spin degrees of freedom  
A **real driving force** controlling electronic and magnetic interactions
- Mixed valence-states of **3d** elements and **oxygen** content variation

## ► Hematite-ilmenite system: $\text{Fe}_{2-x}\text{Ti}_x\text{O}_{3-\delta}$

### Geomagnetism

atomic scale spinodal decomposition

→ coherent interfaces between  
 $\text{Fe}_2\text{O}_3/\text{FeTiO}_3$  lamellae



Harrison R. J. et al. PRL **95** (2005) 268501  
Robinson P. et al. Nature **418** (2002) 517

### Spintronic

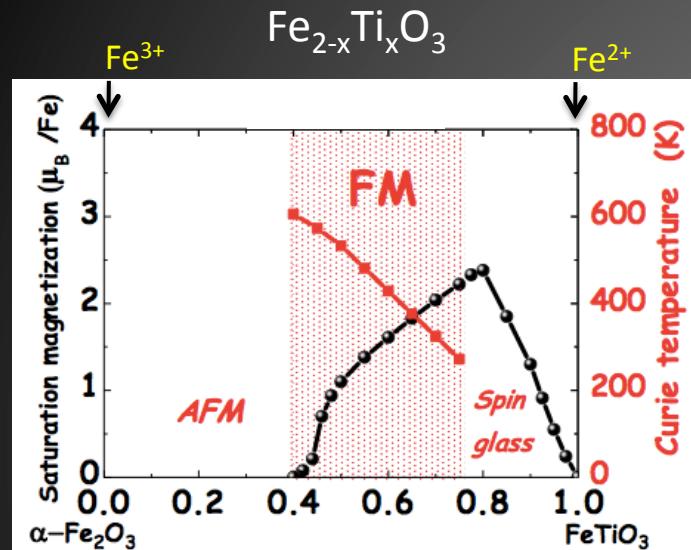
spin polarisation theoretical predictions

→ with delocalized electronic states at  $E_F$   
→ more localized ones depending  
on the electronic correlations

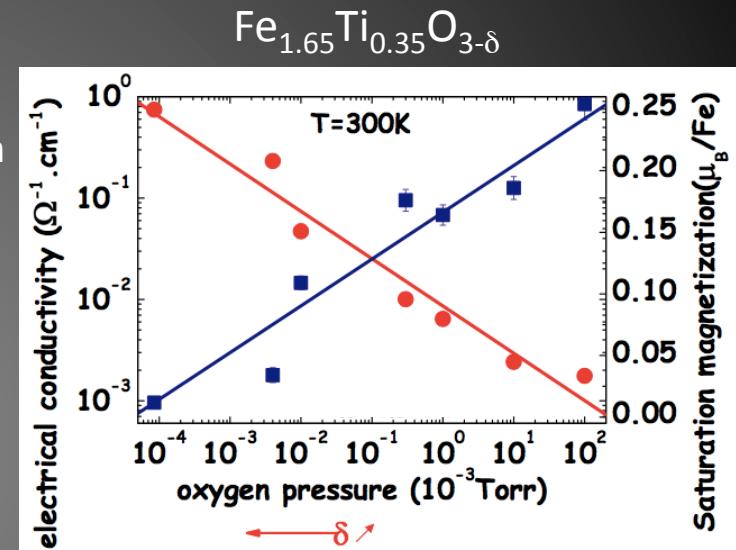
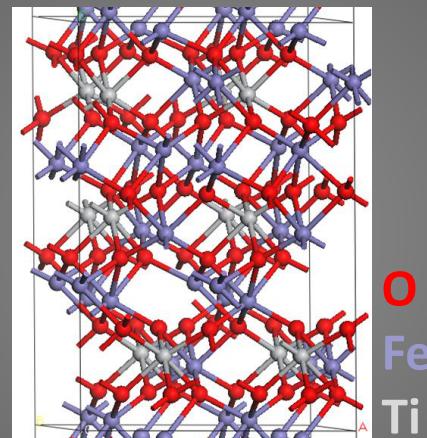
Pencheva R et al. PRB **77** (2008) 172405

# Magnetic semiconductor $\text{Fe}_{2-x}\text{Ti}_x\text{O}_{3-\delta}$ (FTO)

► A complex structure-property relationship



$\text{Fe}_{1.5}\text{Ti}_{0.5}\text{O}_3$  model system  
R-3 ordered structure



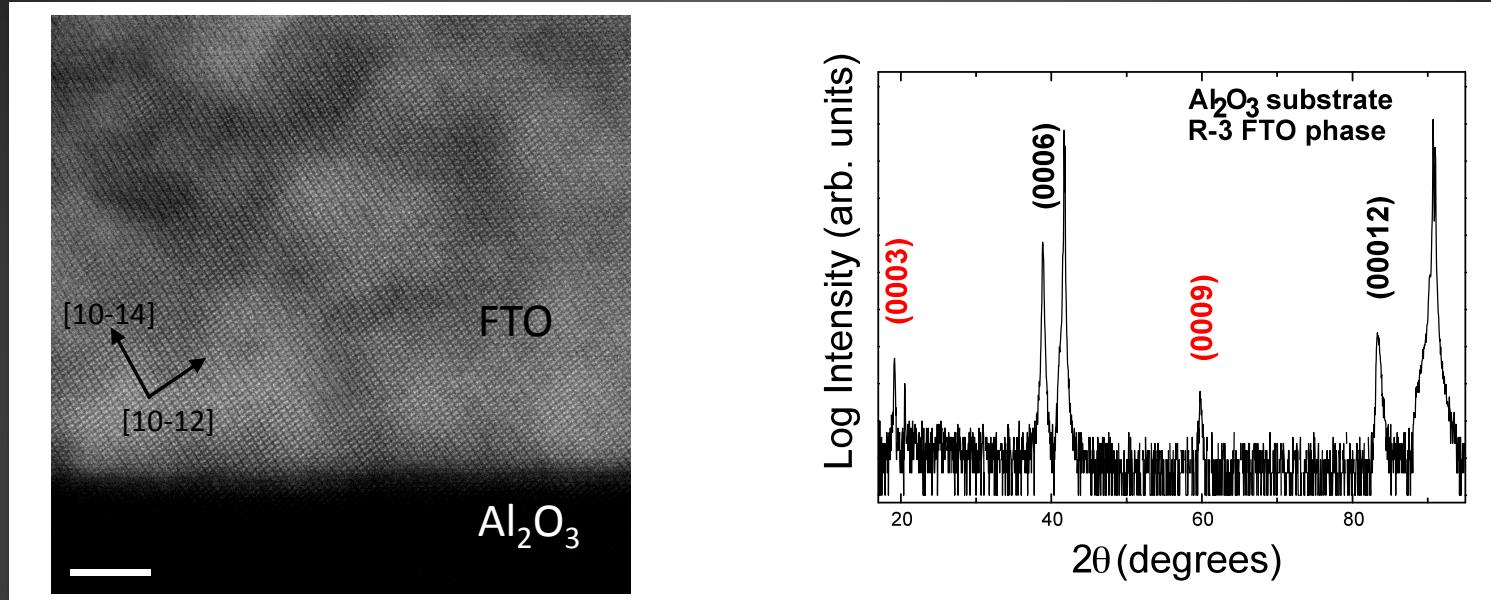
Influence of the → cation order/disorder?

→ oxygen vacancies?

→ mixed valence-states:  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and/or  $\text{Ti}^{3+}/\text{Ti}^{4+}$

...a possible charge ordering???

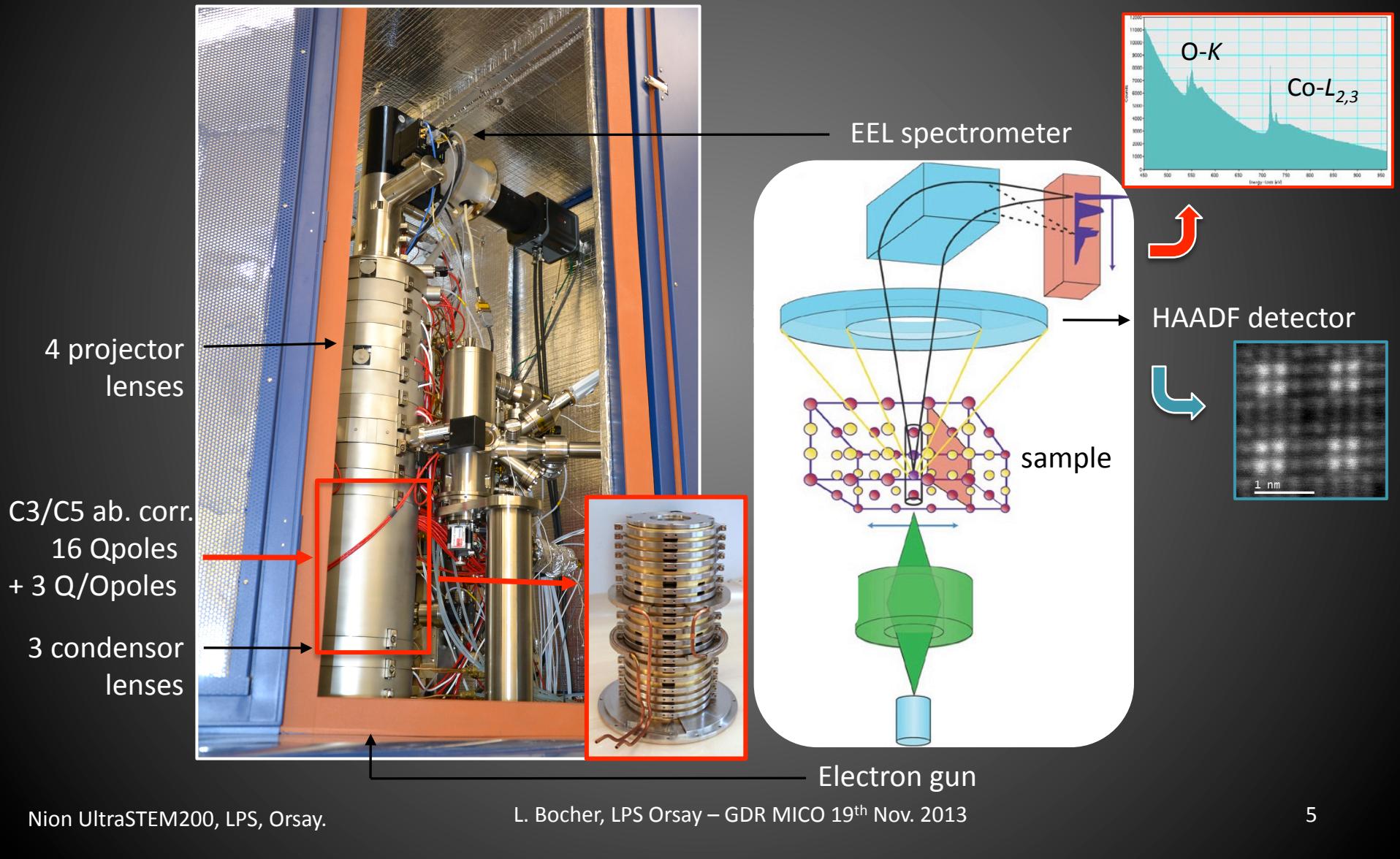
# $\text{Fe}_{1.35}\text{TiO}_{0.65}\text{O}_{3-\delta}$ thin films



- Epitaxially grown on  $\alpha\text{-Al}_2\text{O}_3$  by PLD technique
- Presence of the  $(0, 0, 0, 2n+1)$  Bragg reflexions characteristic of the **R-3 symmetry**  
→ at the macroscopic scale : **cation ordering** along the [0001] zone axis / the *c*-axis
  - ▶ What's going on down to the atomic scale?

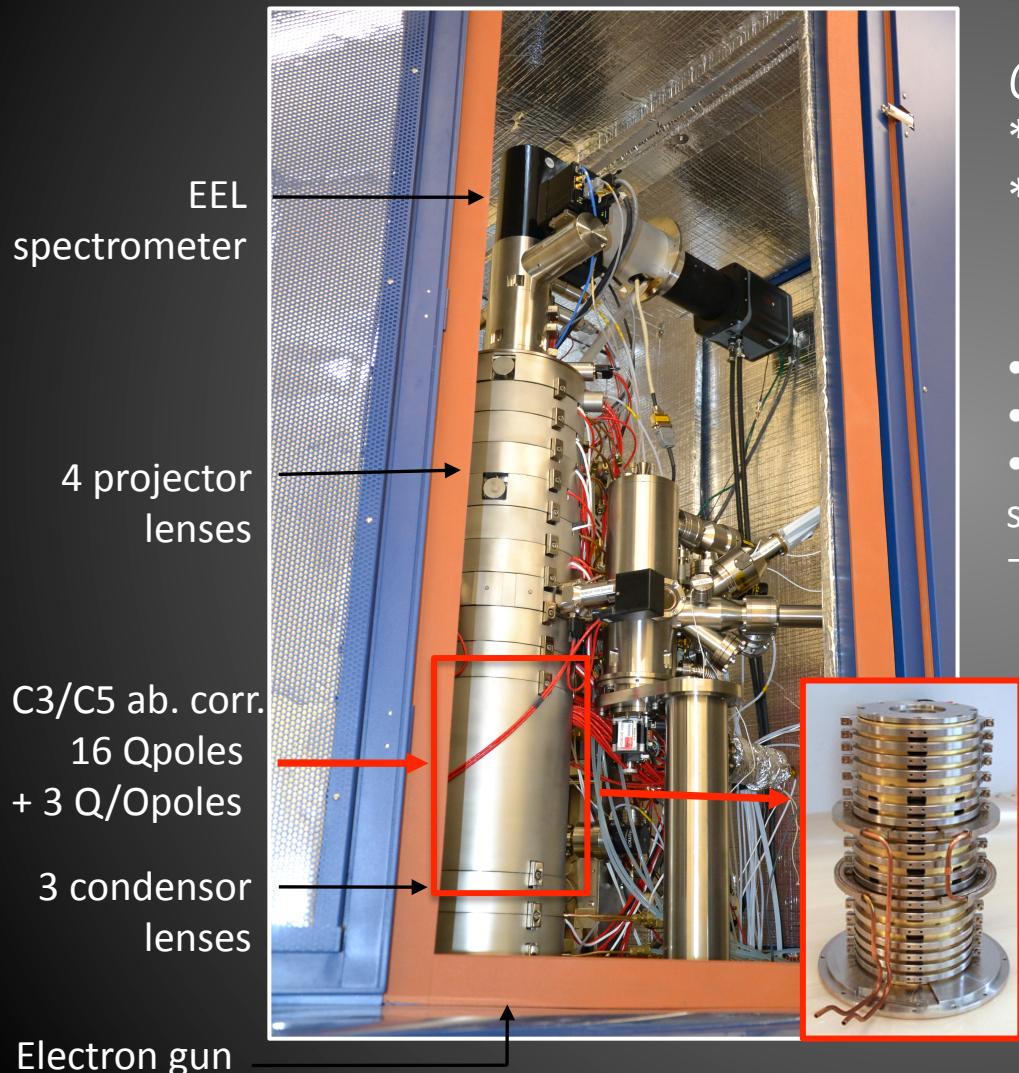
# Aberration-corrected NION UltraSTEM 200

→ Resolving the **atomic and electronic structures** of low dimensional systems



# Aberration-corrected NION UltraSTEM 200

→ Resolving the **atomic and electronic structures** of low dimensional systems



@ 100 keV

\* probe size : 0.8 Å

\* energy resolution : 350 meV (core-loss region)

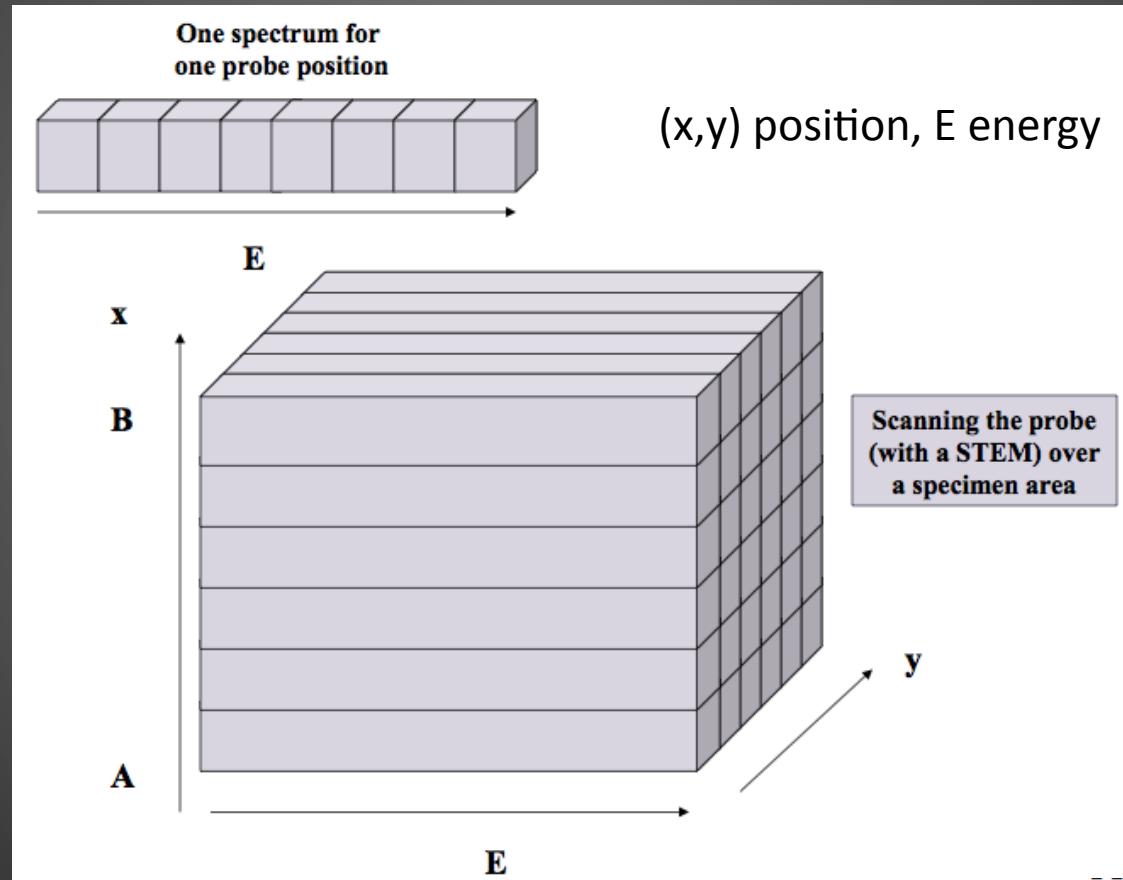
- NION 40 – 200 keV CFEG
- C3/C5 aberration STEM
- Enfina spectrometer fitted with very high sensitivity fast CCD camera  
→ Orsay's optic coupling system® (M. Tencé)

Nion UltraSTEM200, LPS, Orsay.

# Spectrum-Imaging (SPIM) mode – 3D data cube\*

► Multi-dimensional spectro-microscopy technique

→ spatially-resolved information down to the atomic scale



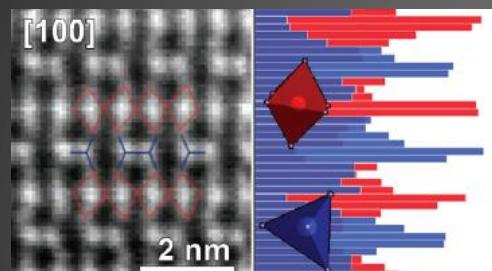
\* C. Jeanguillaume & C. Colliex – Ultram. **28** (1989) 252

# Advanced STEM/EELS on Functional Oxides

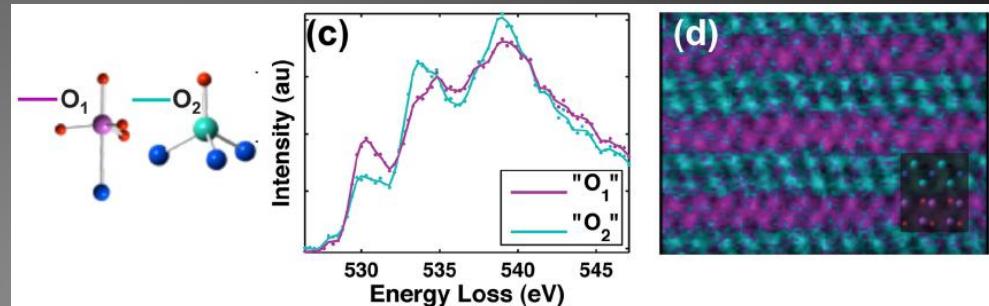
Beyond « looking at » atoms

→ probing local bonding environment & electronic structure by mapping the:

- coordination / hybridization geometries

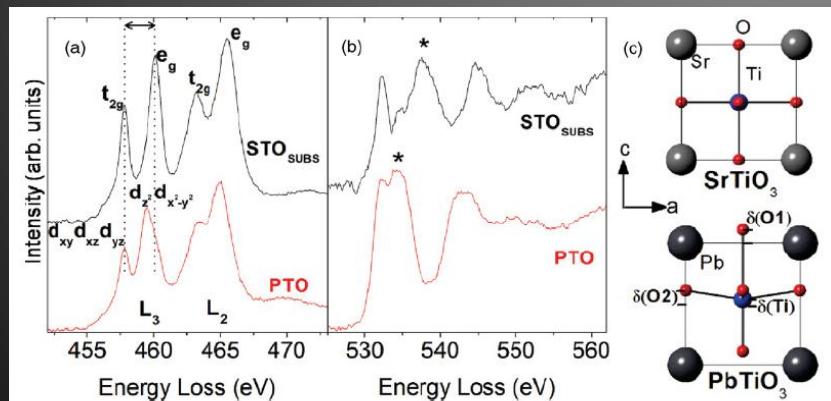


<sup>1</sup> Turner S. et al. Chem. Mat. **24** (2012) 1904



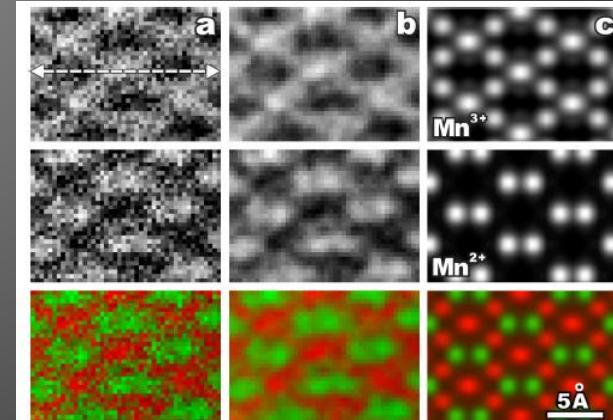
<sup>2</sup> Mundy J.A. et al. APL, **101** (2012) 042907

- structural distortions



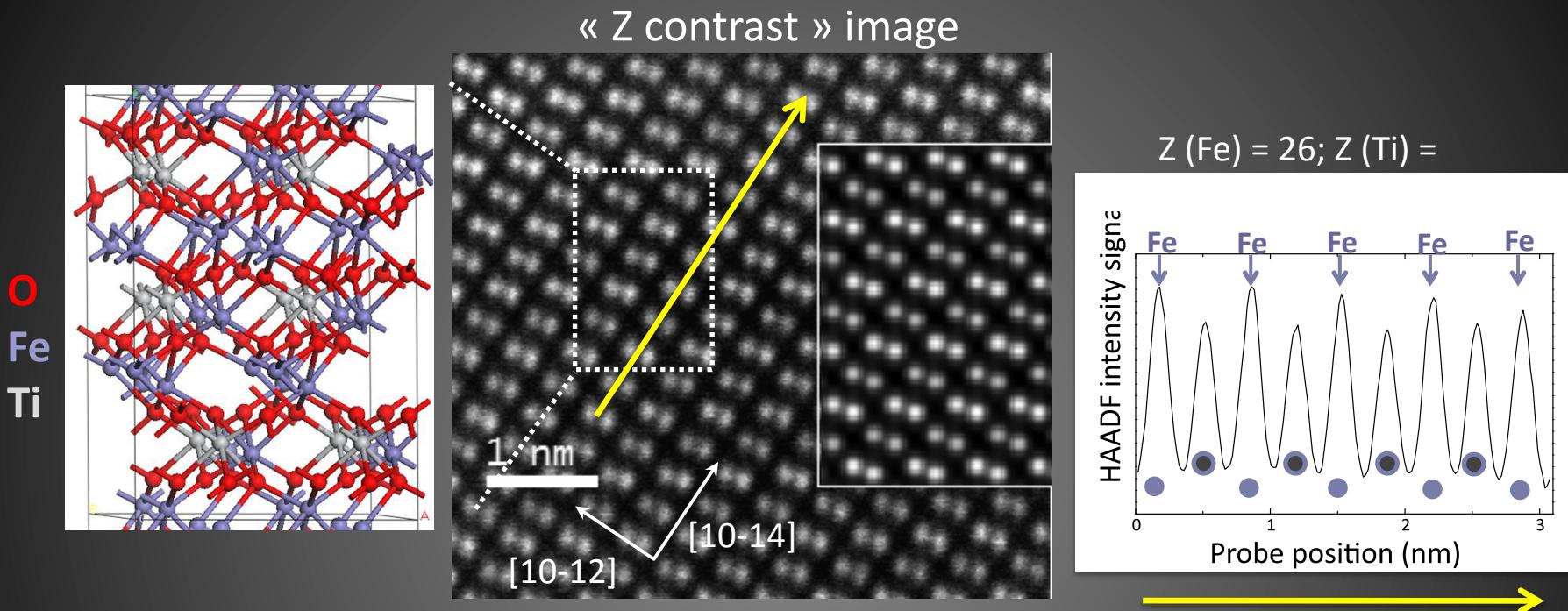
<sup>3</sup> Torres-Pardo A. et al. PRB, **84** (2011) 220102

- valence state distribution



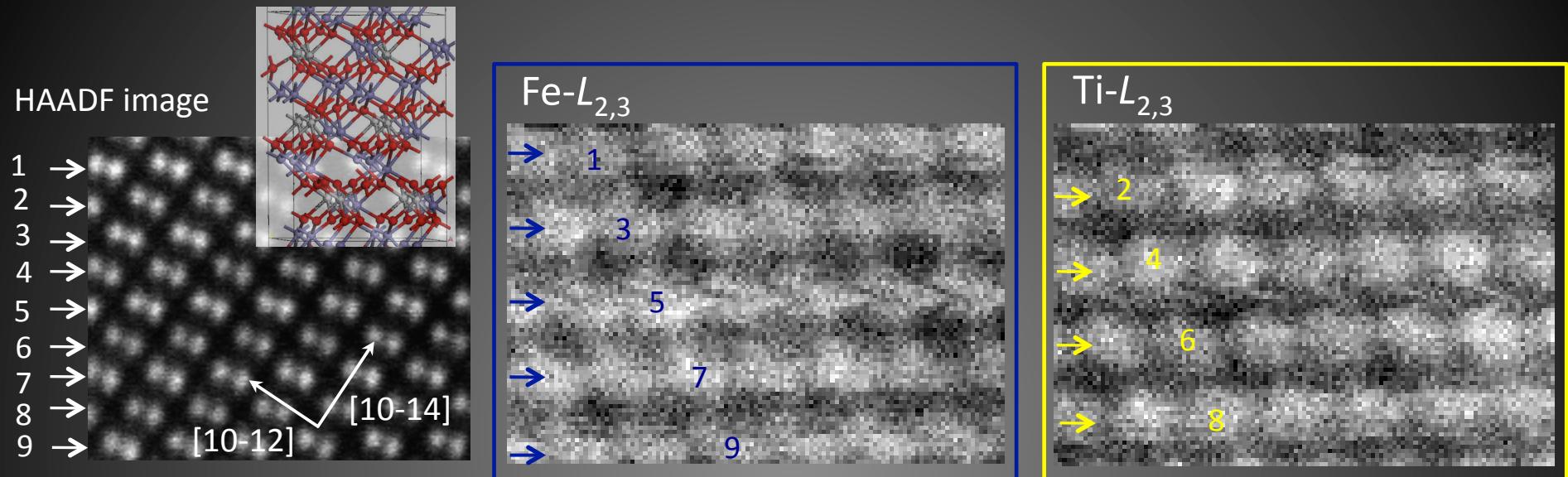
<sup>4</sup> Tan H. T. et al. PRL **107** (2011) 107602

# Imaging the cation modulation



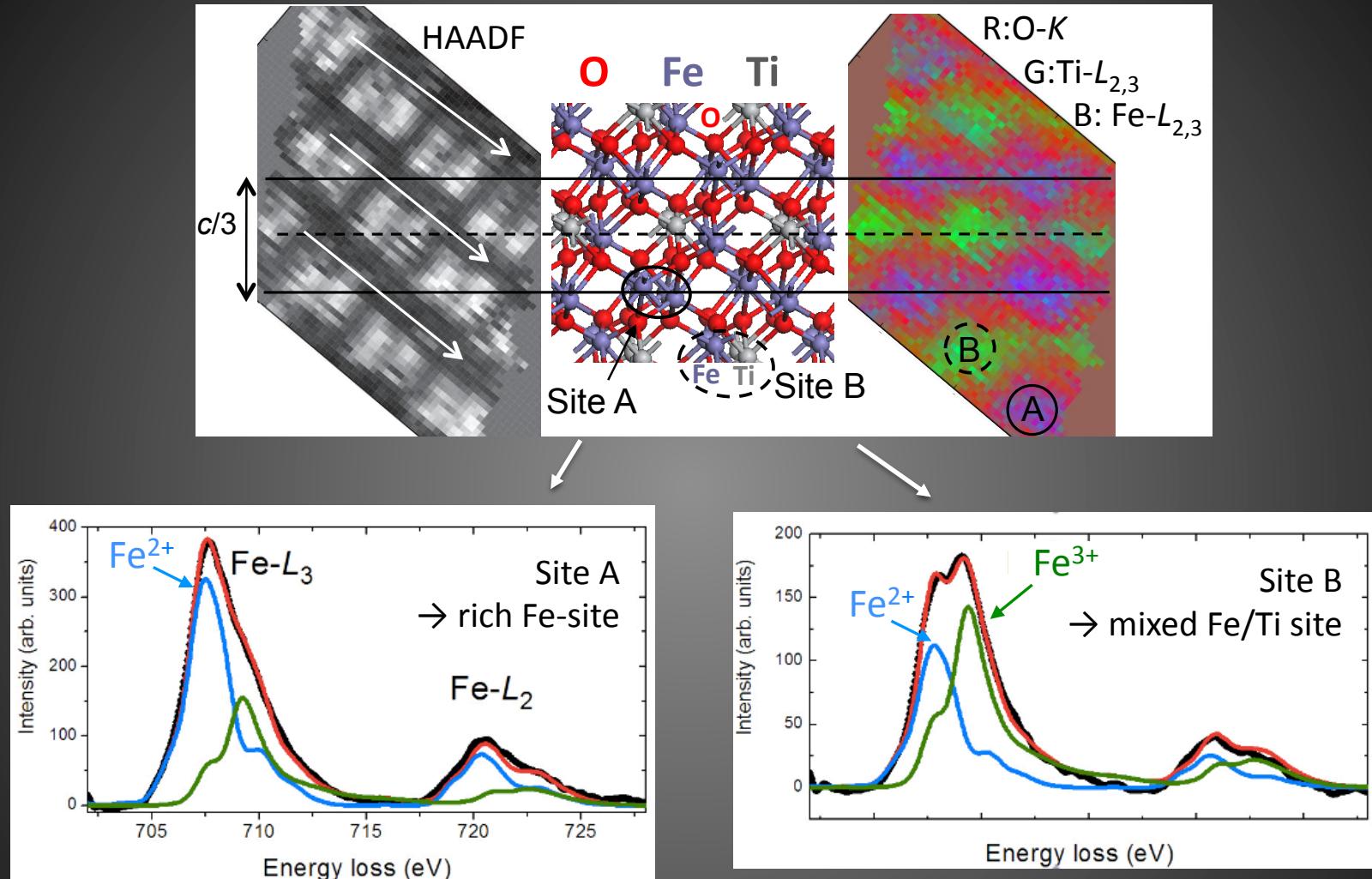
- Clear visualization of the **cation dumbbells**
- Contrast variation along the *c*-axis
- Modulation confirmed by HAADF image simulation  
→ **Cation arrangement** at the atomic scale

# Mapping the cation modulation



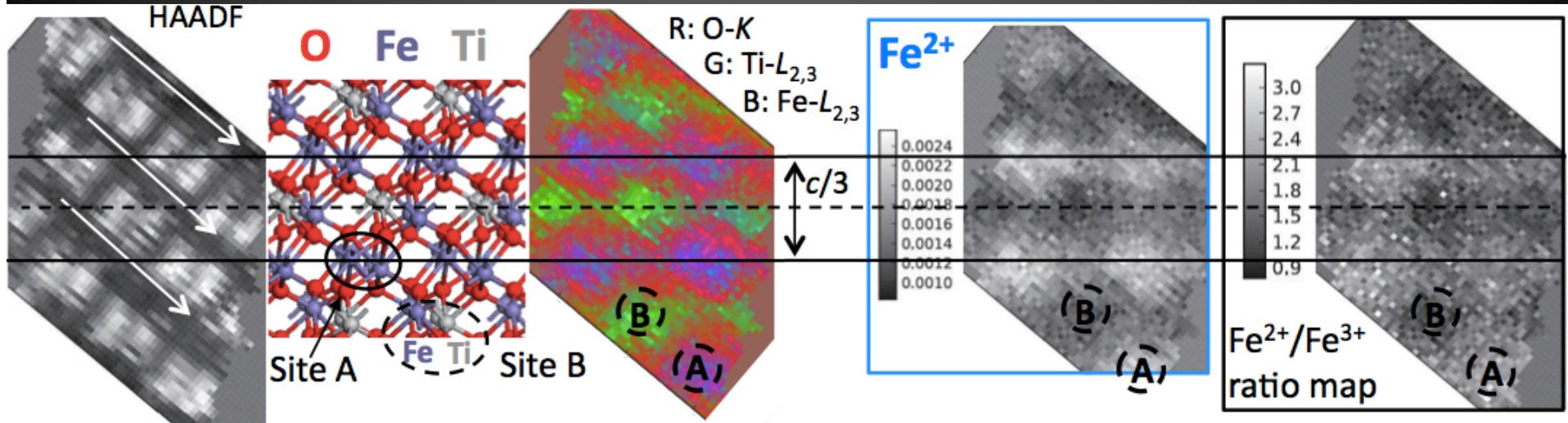
- R-3 FTO phase consists of rich Fe columns alternating with mixed Fe/Ti ones
- Evidence of a cation ordering at the atomic scale

# Toward higher energy resolution...



► Multiplet features characteristics of  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  contributions

# Real-space valence mapping



→ Fe<sup>2+</sup> distribution **strongly modulated** on the Fe-rich site

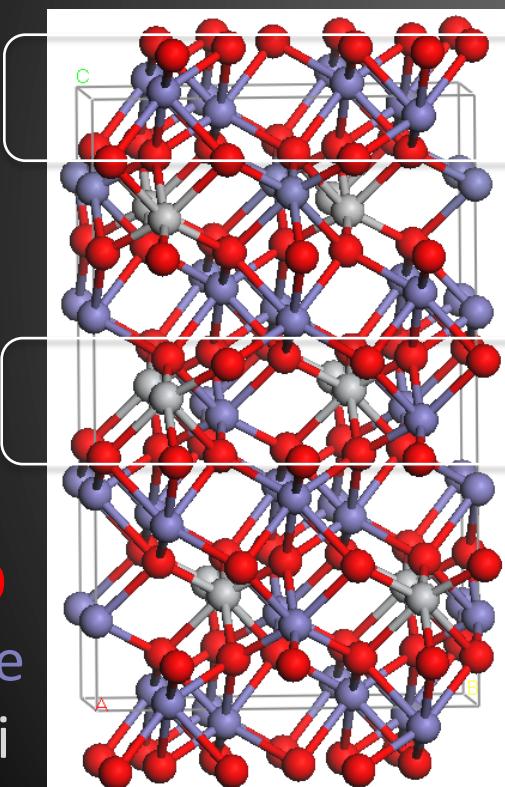
- Fe-rich site:  $\text{Fe}^{2+}/\text{Fe}^{3+} \approx 3/1$
- mixed Fe/Ti site:  $\text{Fe}^{2+}/\text{Fe}^{3+} \approx 1$  and solely Ti<sup>4+</sup>

► Direct experimental evidence of Fe<sup>2+</sup>/Fe<sup>3+</sup> charge ordering

# Back to the structural model

*Ab initio* theoretical calculations: DFT + U formalism  
VASP code using PAW potentials

$\text{Fe}_{1.5}\text{Ti}_{0.5}\text{O}_3$  model system  
→ R-3 ordered structure

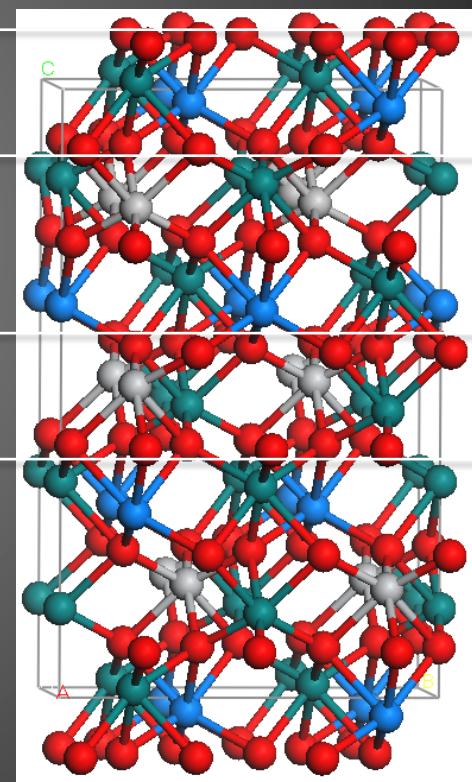


rich-Fe planes  
→ mixed  $\text{Fe}^{2+}/\text{Fe}^{3+}$

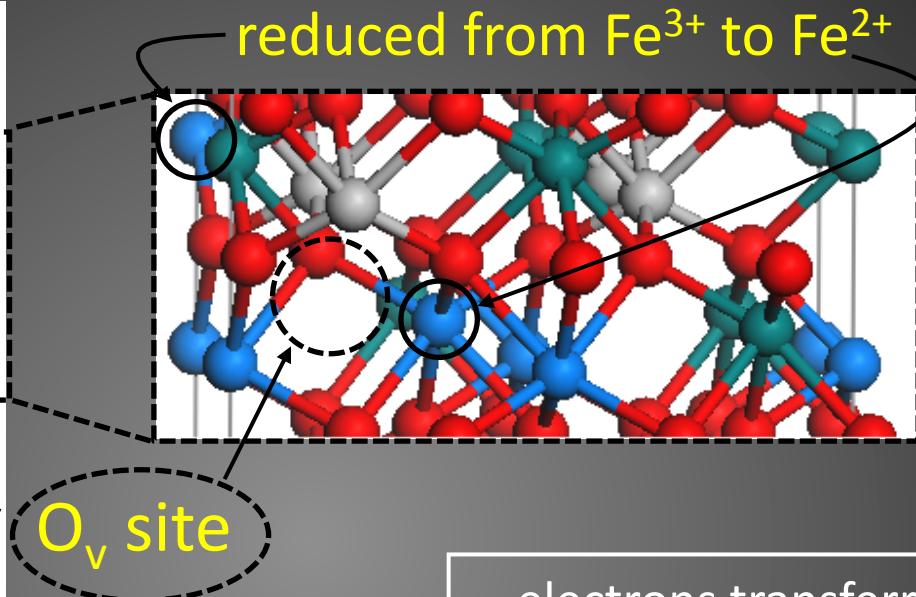
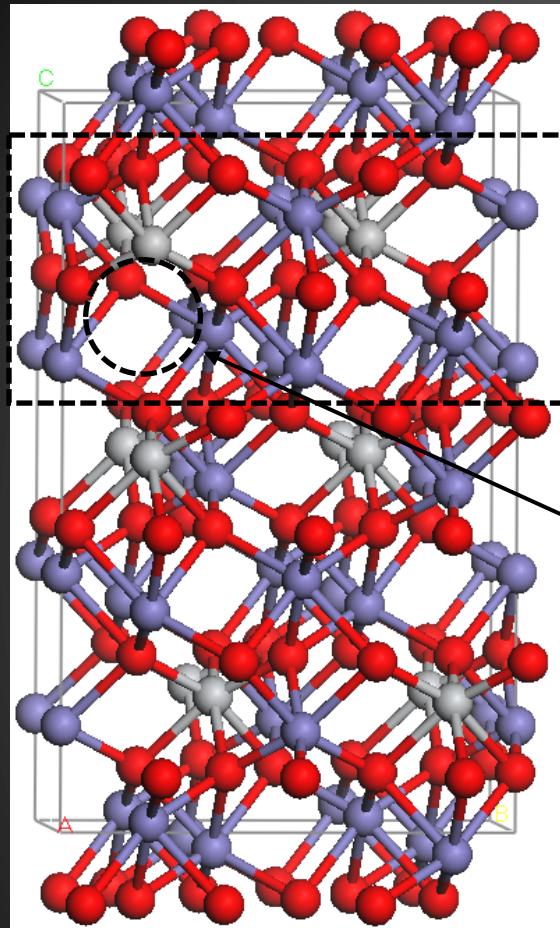
mixed Fe/Ti planes  
→ mixed  $\text{Fe}^{3+}$  &  $\text{Ti}^{4+}$

- but experimentally:
- rich-Fe site:  $\text{Fe}^{2+}-\text{Fe}^{3+}$
  - mixed Fe/Ti site:  $\text{Fe}^{2+}-\text{Fe}^{3+}-\text{Ti}^{4+}$

resulting from DFT calculations



# Introducing oxygen vacancies

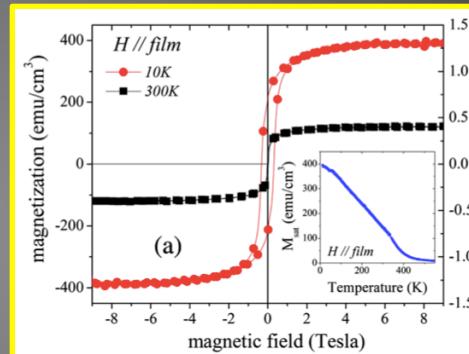
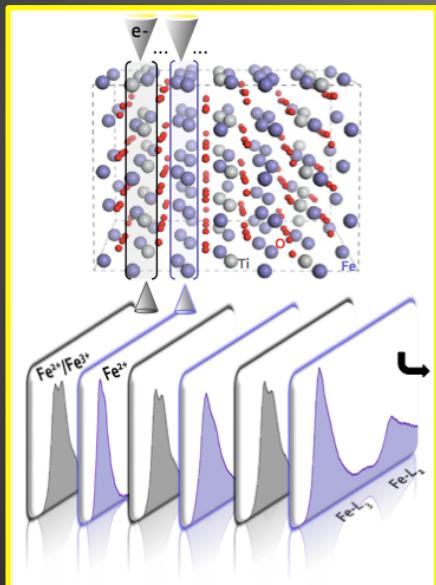


... electrons transferred to  
→ either Ti reducing  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$   
→ or Fe reducing  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$

► charge and cation orderings  
...  $2\text{Fe}^{3+} - 6\text{Fe}^{2+}$  /  $2\text{Fe}^{3+} - 2\text{Fe}^{2+} - 4\text{Ti}^{4+}$  ...

# Conclusions

- ▶ evidence of solely mixed  $\text{Fe}^{2+}/\text{Fe}^{3+}$  valence states
- ▶ real-space technique revealing  $\text{Fe}^{2+}$  localized on Fe-rich sites
- ▶ key-role of oxygen vacancies on the charge modulation



▶ On a real system

