Soft X-Ray Synchrotron Techniques at CELLS-ALBA

Eric Pellegrin

on behalf of the
"Electronic and Magnetic Structure of Matter" Section

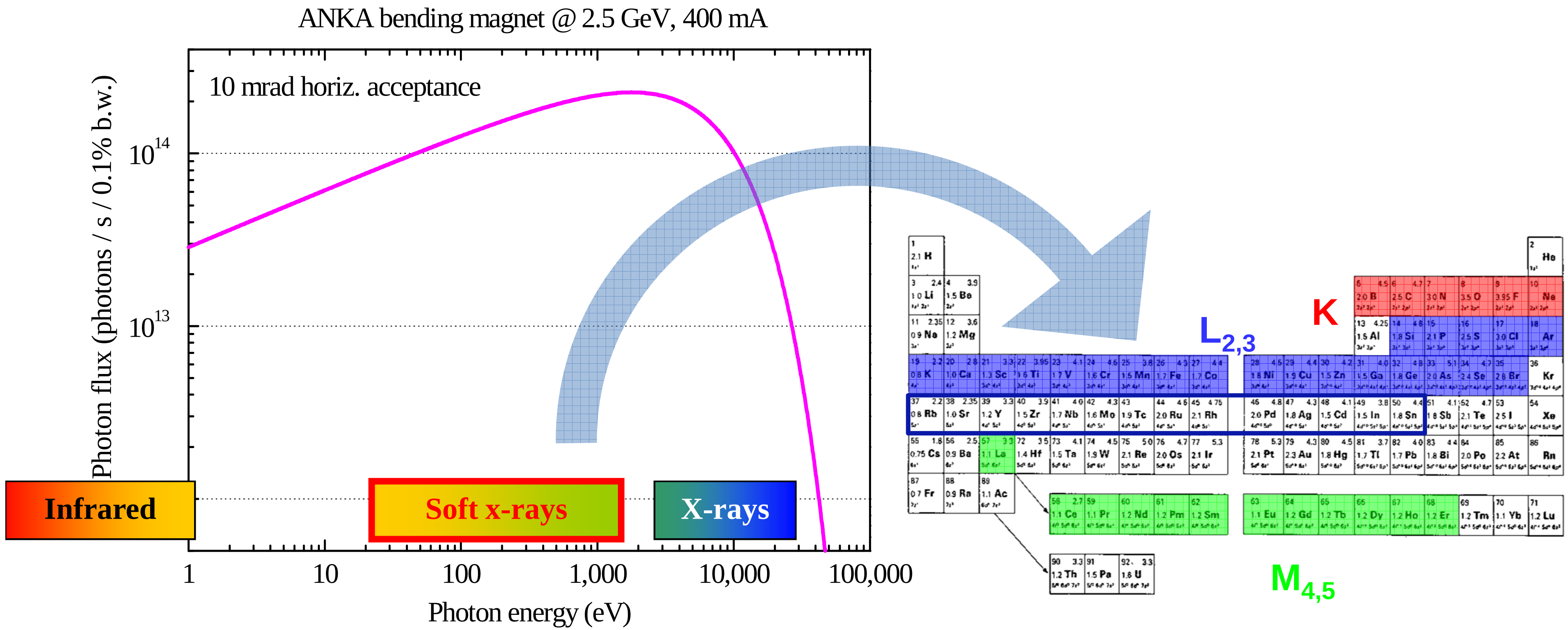
Contents:

- ***Some basics on soft x-ray spectroscopies***
- ***Some standard XAS & XMCD examples***
- ***A few recent examples:***
  - ***Strain effects on LSMO/STO thin films***
  - ***"Breathing chemistry" of FePc on Au(111)***
  - ***PEEM on $SrTiO_3$ surfaces***

Overview ALBA Phase I Beamlines

Beamline	Beamline use	Field of activity	Light source
MSPD BL	**M**aterial **S**cience and **P**owder **D**iffraction	Materials science	Superconducting wiggler
NCD BL	**N**on-**C**rystalline **D**iffraction	Life sciences, Materials science	In-vacuum undulator
XALOC BL	Macromolecular Crystallography	Life sciences	In-vacuum undulator
CLAESS BL	X-Ray Absorption Spectroscopy	Materials science	Wiggler
CIRCE BL	Photoemission spectroscopy and microscopy	Polarized electron spectroscopies	Helical undulator (Apple II type)
BOREAS BL	Soft X-Ray Magnetic Circular Dichroism	Polarized electron spectroscopies	Helical undulator (Apple II type)
MISTRAL BL	Soft X-Ray Microscopy beamline	Life sciences, Materials science	Bending magnet

The Soft X-Ray Photon Energy Range



Soft x-ray photon energy range 20 – 1600 eV **(ALBA: 80–4000 eV)**
- the classic domain for investigating electronic structure of matter

e. g., with soft x-ray absorption spectroscopy
light elements; 3d transition metals; lanthanides; ***4d transition metals***

Experimental Tools in the Soft X-Ray Range

Classical (e. g., non laterally-resolved) techniques:

- NEXAFS: **Unoccupied** electronic density of states (DOS)
- SXMCD: Element-specific spin and orbital magnetic moments
- Photoemission – PES, valence-band PES, core-level XPS: **Occupied** electronic DOS

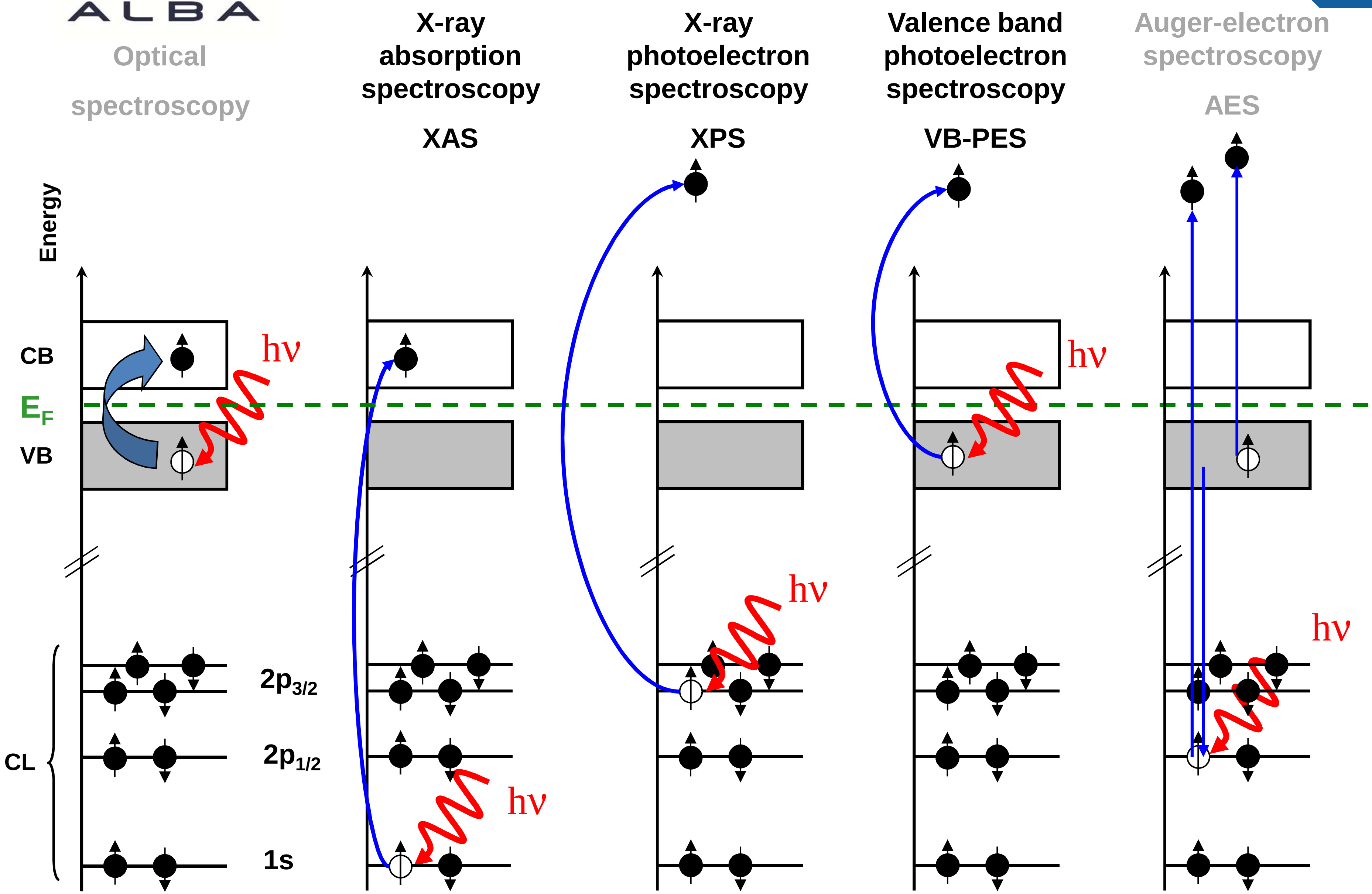
Laterally resolved techniques:

- Photoemission electron microscopy - PEEM
- Scanning transmission x-ray microscopy - STXM
- Transmission x-ray microscopy - TXM

Recent developments:

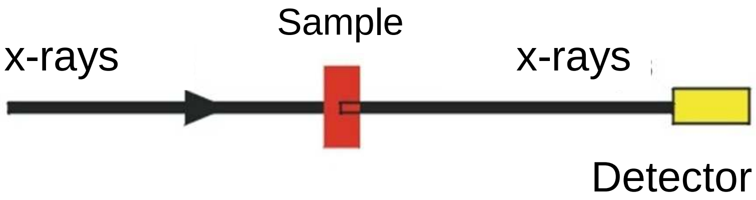
- Soft x-ray holography
- Resonant inelastic soft x-ray scattering - RIXS
- Magnetic speckle
- High-energy photoemission (using x-rays)

Some Electron Spectroscopy Techniques



X-Ray Absorption Detection Techniques

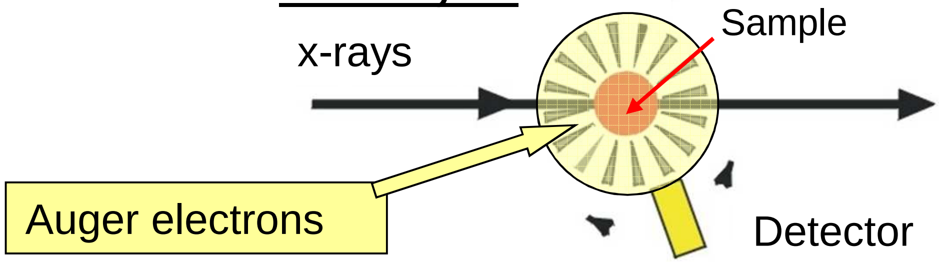
Absorption via Transmission



Bulk sensitive

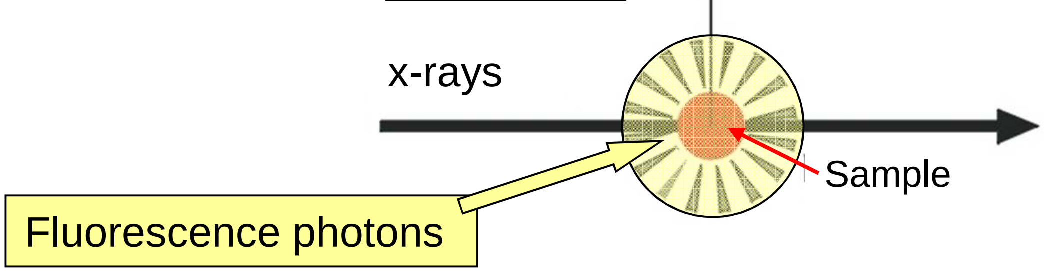
(sample thickness <0.1 µm)

Absorption via electron yield



Bulk & surface sensitive (tunable)

Absorption via Fluorescence



Bulk sensitive

Fermi's Golden Rule

Fermi's Golden Rule
in one-electron approximation: $\sigma(E) \propto \sum_{f}^{E_f > E_F} \left| \langle f | H_{\text{int}} | i \rangle \right|^2 \delta(E - E_f + E_i)$

$|i\rangle$ is an initial deep core state (e.g., Cu2p),

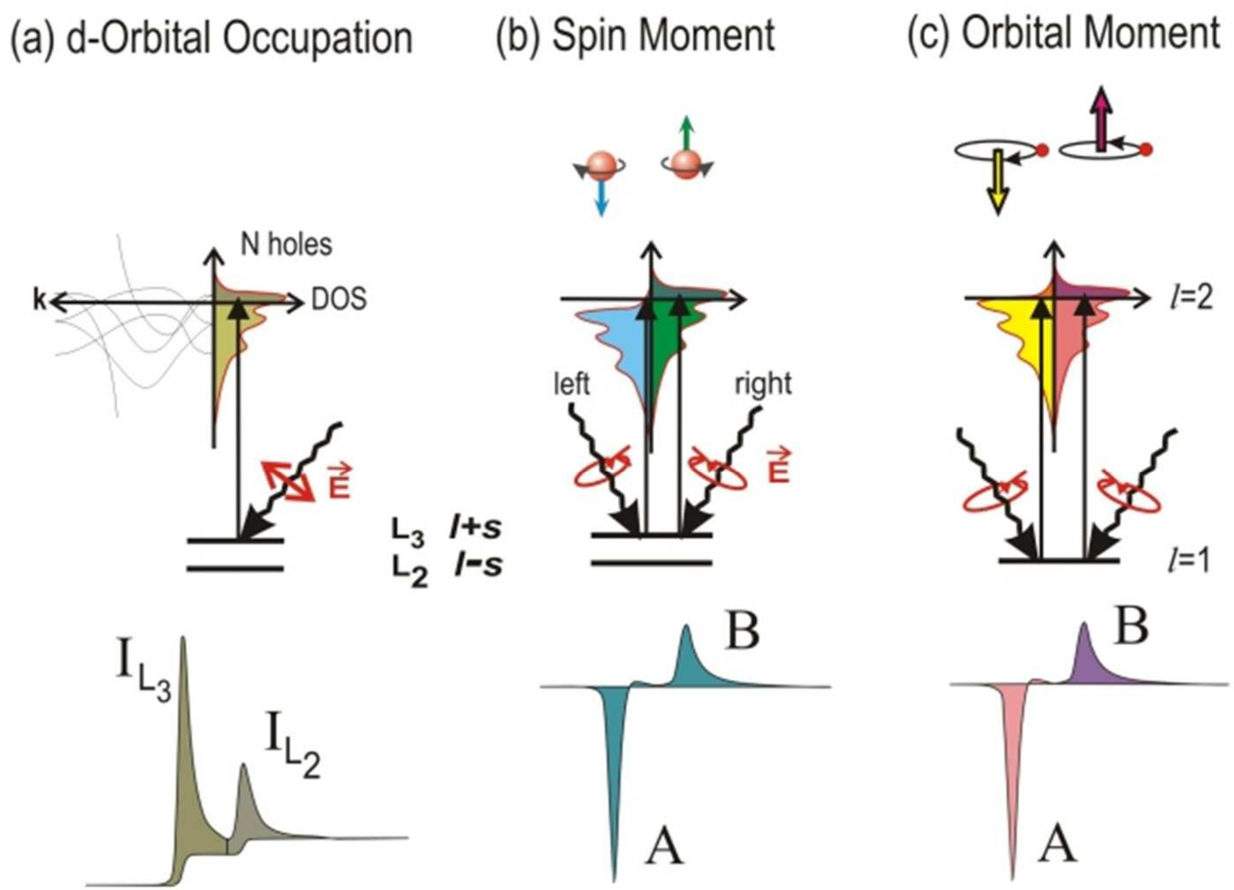
$\langle f|$ is an unoccupied state (e.g., Cu3d) in the presence of a core hole,

H_{int} is the electron transition dipole operator ($\sim \mathbf{r} \cdot \boldsymbol{e}$).

Dipole transition rules apply (in general, $\Delta \ell = \pm 1$):

$\rightarrow$ Allowed transitions: 1s $\rightarrow$ 2p, 2p $\rightarrow$ 3d, 3d $\rightarrow$ 4f etc.

NEXAFS and XMCD Sum Rules



NEXAFS:

- **Unoccupied local electronic density of states**
- **Atom-specific**
- **Mapping out unoc. states with TM 3d character**

XMCD:

$$m_{spin} \sim \frac{A - 2B}{I_{ISO}}$$

$$m_{orbital} \sim \frac{A + B}{I_{ISO}}$$

A little Intermezzo….

- XAS is ***element-specific*** since the photon energy is tuned to a specific absorption edge.

- Due to the selection rules, the ***orbital character*** of the empty final states can be selected (by selecting the absorption edge)

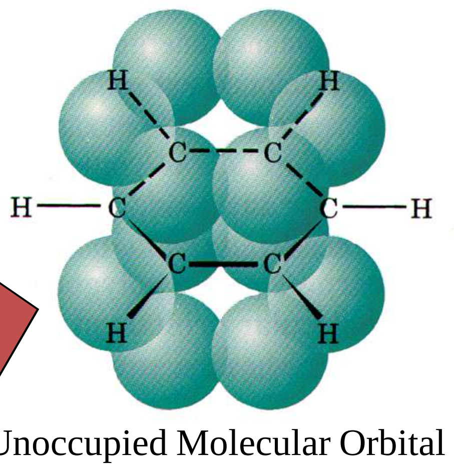
- XAS is a ***local*** probe due to the limited extent of the core hole wave function (site-sensitivity).

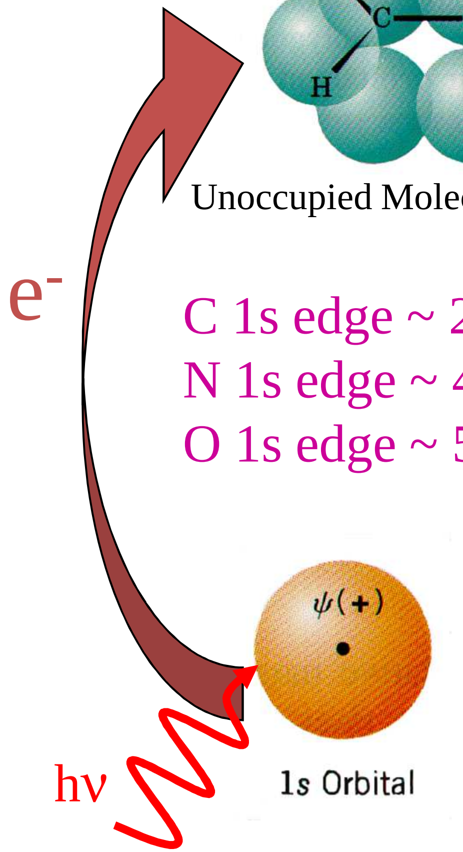
- XAS is sensitive to the filling of the final state bands, i.e., it is sensitive to the ***valence*** of chemical species.

- The product $\mathbf{r} \cdot \boldsymbol{e}$ equals sensitivity with respect to ***anisotropic properties*** of the electronic structure of a solid.

XANES:
Atomic Site Selectivity
via
Tunable Photon Energies

NEXAFS/XANES on C1s edges

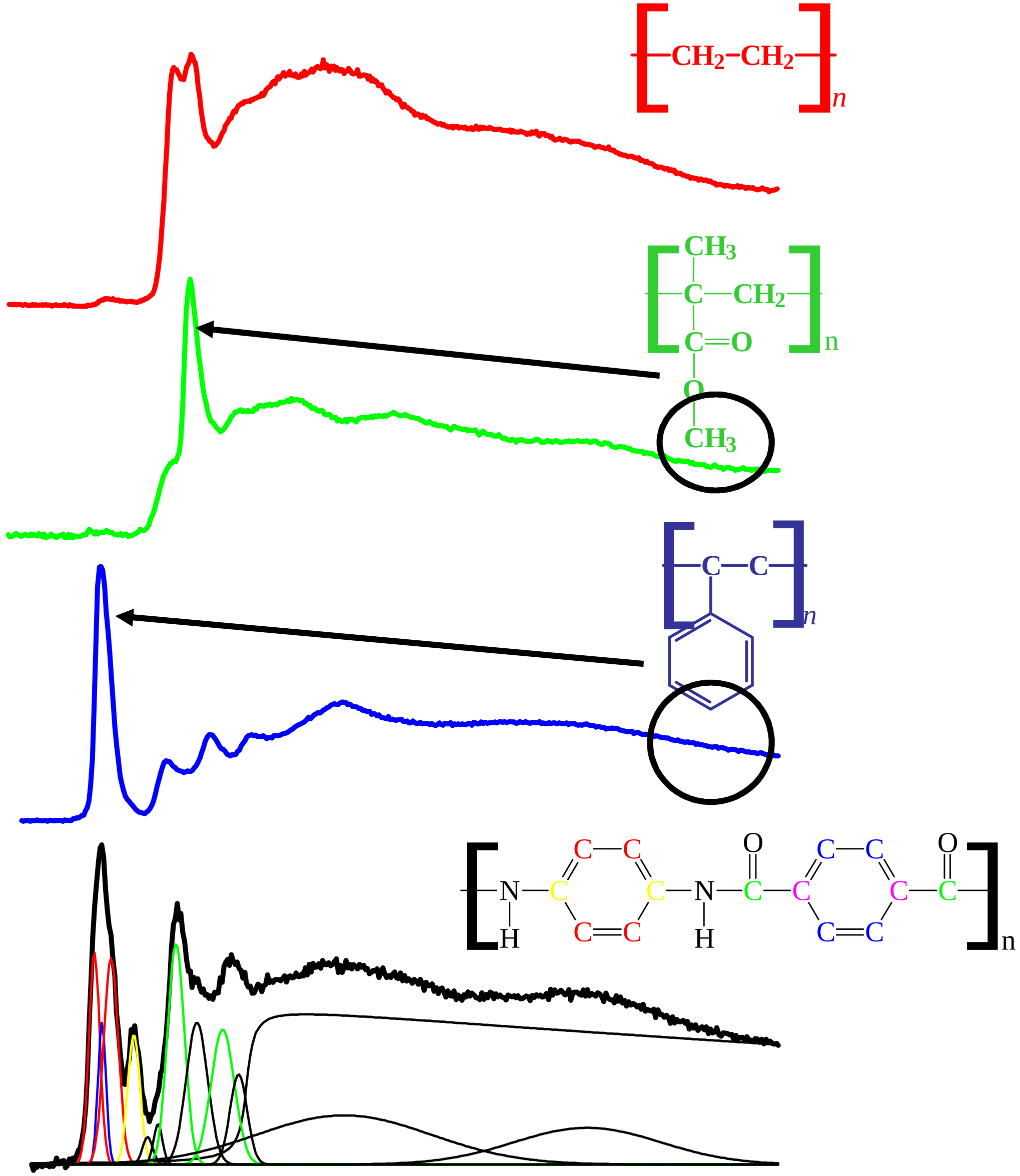




C 1s edge ~ 290 eV

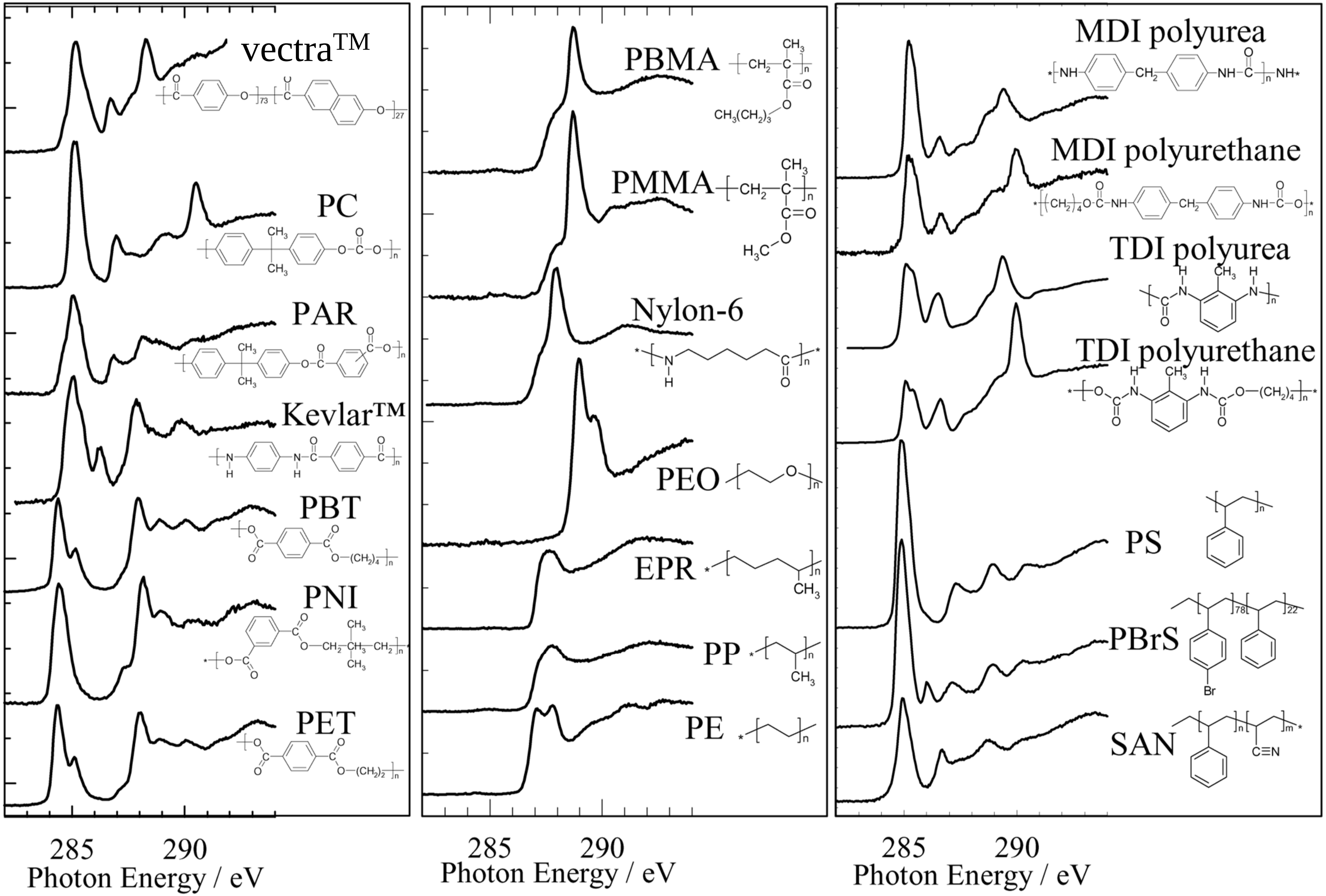
N 1s edge ~ 405 eV

O 1s edge ~ 540 eV



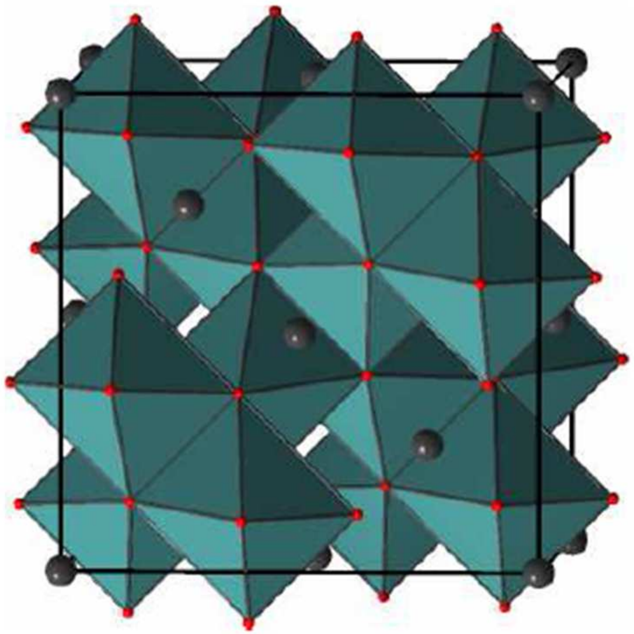
Some Polymer NEXAFS Spectra

Dhez, Ade, and Urquhart
J. Electron Spectrosc. 128, 85 (2003)



XANES:
Atomic Site Selectivity
and
Magnetic Properties
via
Tunable Circular Polarization

A few Basics on Magnetite (Fe_3O_4)



- Red: oxygen
- Hidden inside octahedra:

Fe^{3+} and Fe^{2+} octahedral B sites

- Grey: Fe^{3+} tetrahedral A sites

More precisely: $Fe^{3+}_A\ [Fe^{3+}Fe^{2+}]_B O^{2-}_4$

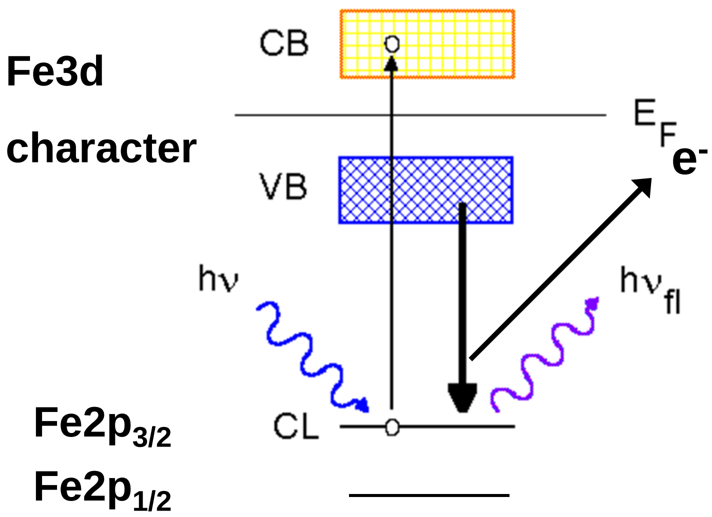
- Inverse spinel structure
- Tetrahedral A sites: Fe^{3+} ($3d^5$), S=5/2
- Octahedral B sites: Fe^{2+} ($3d^6$), S=2

  Fe^{3+} ($3d^5$), S=5/2
- Ferromagn. coupling between A sites
- Ferromagn. coupling between B sites
- Antiferromagn. coupling between A & B

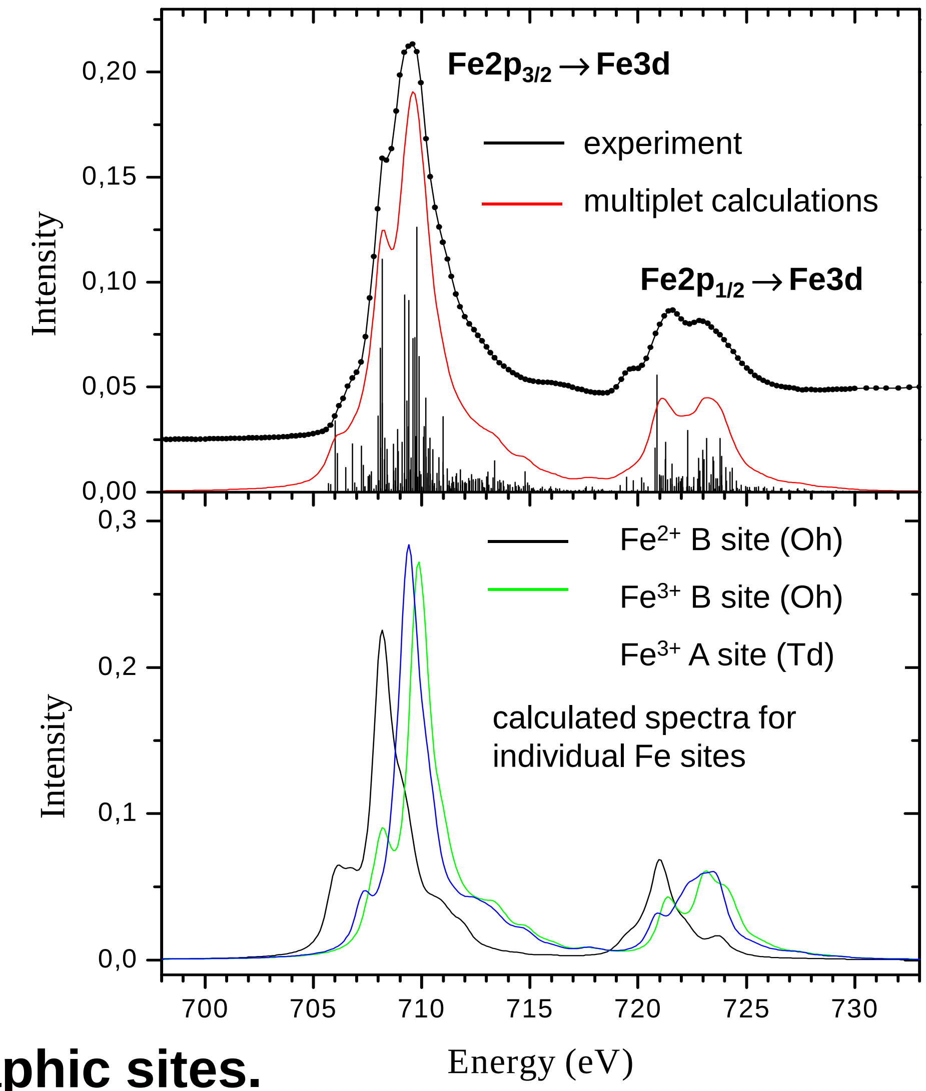
$\Rightarrow$ Magnetite is a ferrimagnet

- Curie temperature T_C = 858 K
- Verwey temperature T_V = 120 K

Linear Polarized Fe2*p* XAS of Fe_3O_4



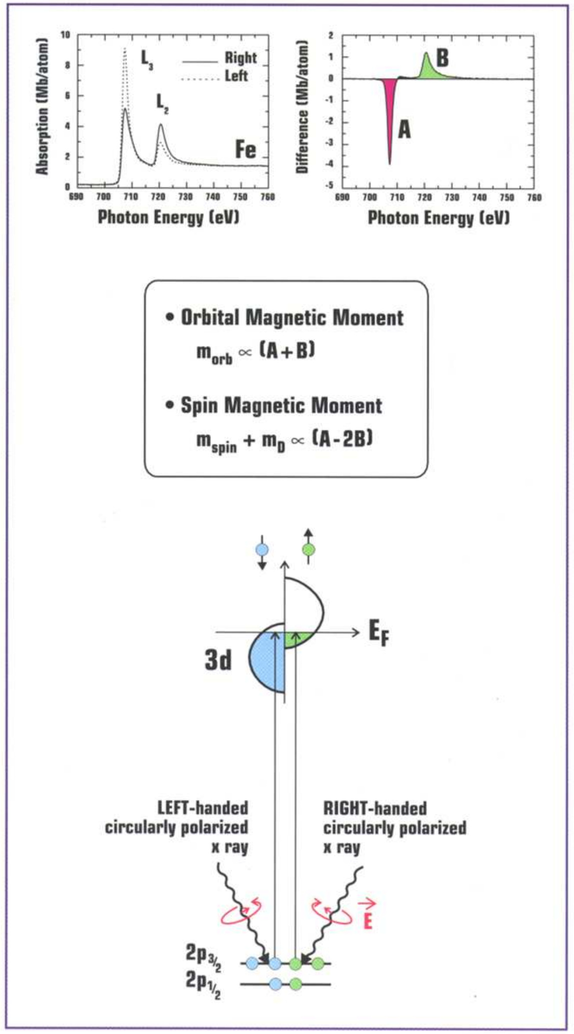
$Fe^{3+}_A [Fe^{3+}Fe^{2+}]_B O^{2-}_4$, 44 ML film, 200 K



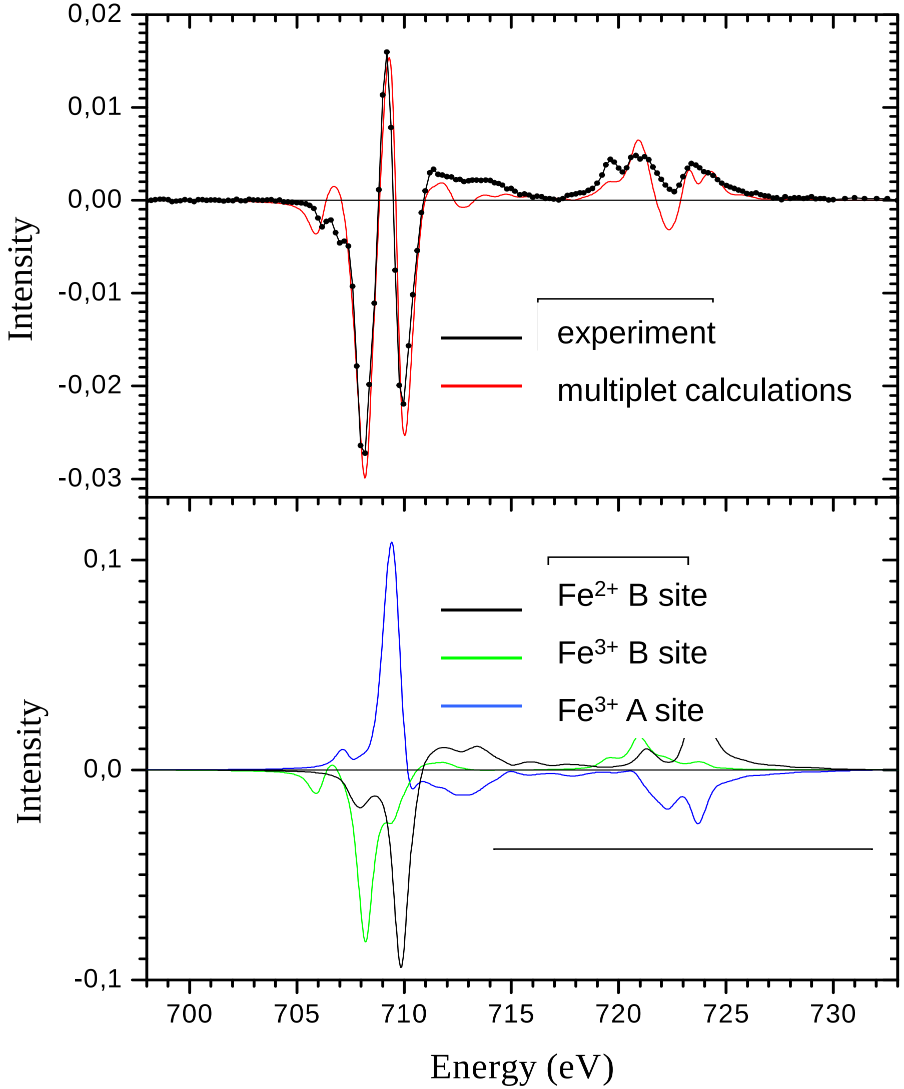
2 different Fe valencies

distributed over 3 crystallographic sites.

Fe2*p* XMCD of Fe_3O_4



$Fe^{3+}{}_A\,[Fe^{3+}Fe^{2+}]_B O^{2-}{}_4$, 44 ML film, 200 K



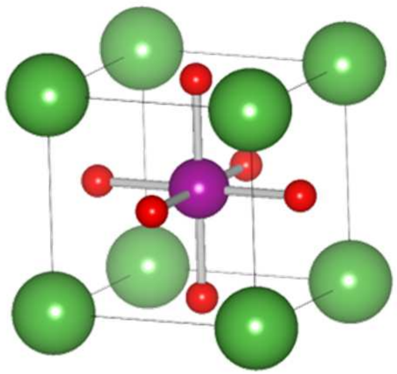
XANES:

Rotatable Linear Polarization

Hector End Station / Boreas Beamline:

Surface symmetry-breaking & strain effects

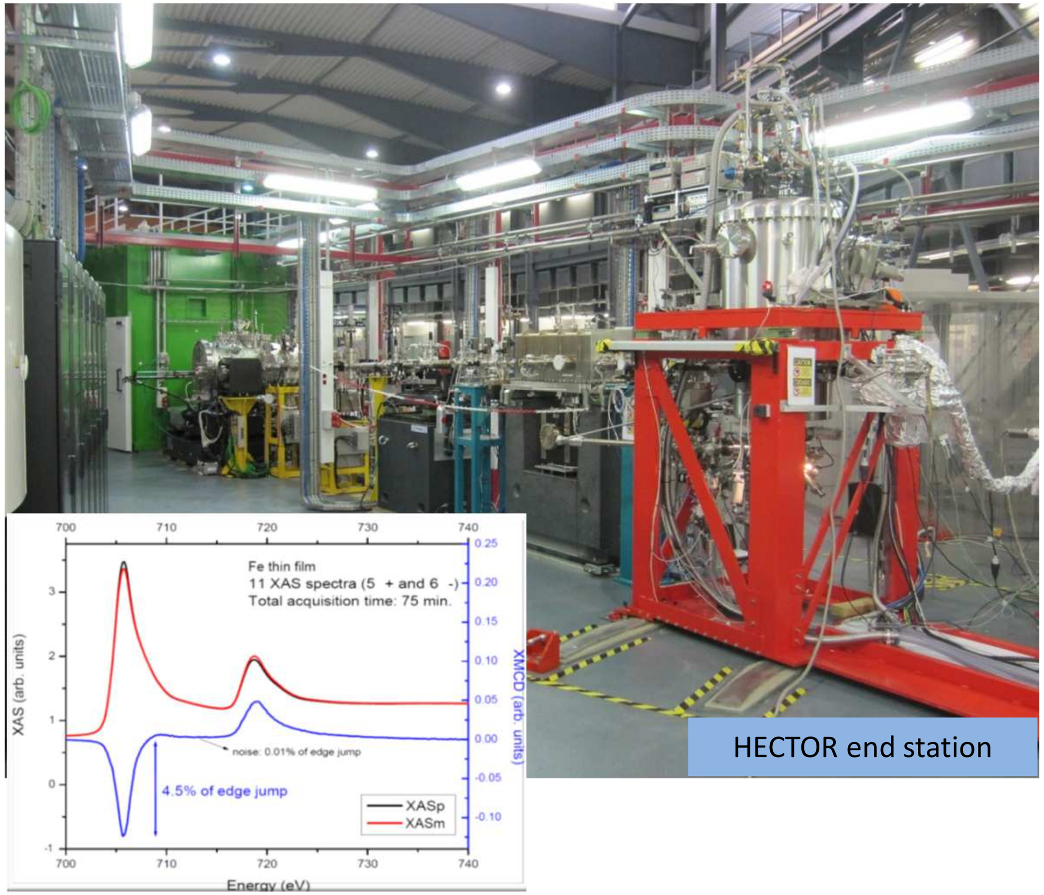
on orbital occupancy in LSMO/STO thin films



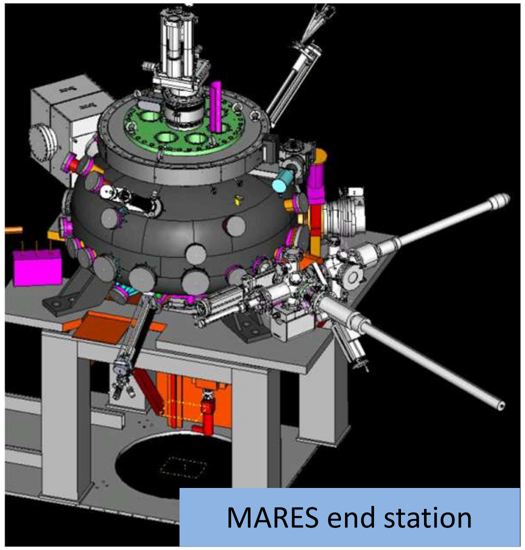
D. Pesquera et al.

Cooperation ICMAB / Elettra / CELLS-ALBA

BL29 BOREAS – Resonant Absorption & Scattering



HECTOR end station



MARES end station

- ***Dedicated to polarization-dependent spectroscopies of advanced materials.***
- ***Two cutting edge end stations:***
  - ✓ ***HECTOR vector magnet (up to 2 / 6 Tesla) for absorption methods***
  - ✓ ***MARES UHV reflectometer for soft x-ray scattering & reflection***
- ***Photon energy range: 80 to 4000 eV***

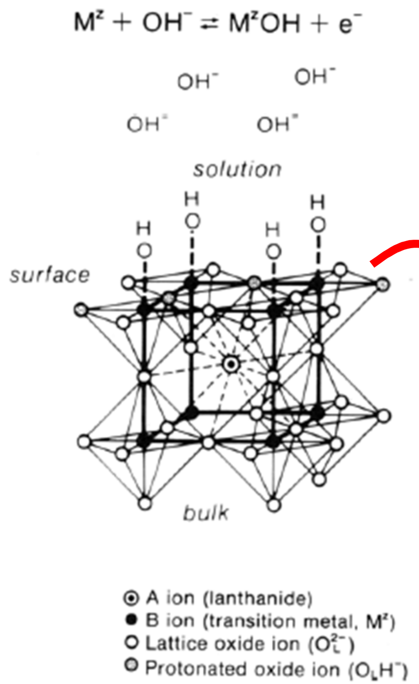
Interest in Catalysis Applications

T. Wolfram, Phys.Rev.Lett. 30, 1214-1217 (1973)

J. Bockris, J. Electrochem. Soc. ,131, 290-302 (1984)

J. Suntivich, Nat. chem. 3, 546–550 (2011)

J. Suntivich, Science, 334, 1383–1385 (2011)



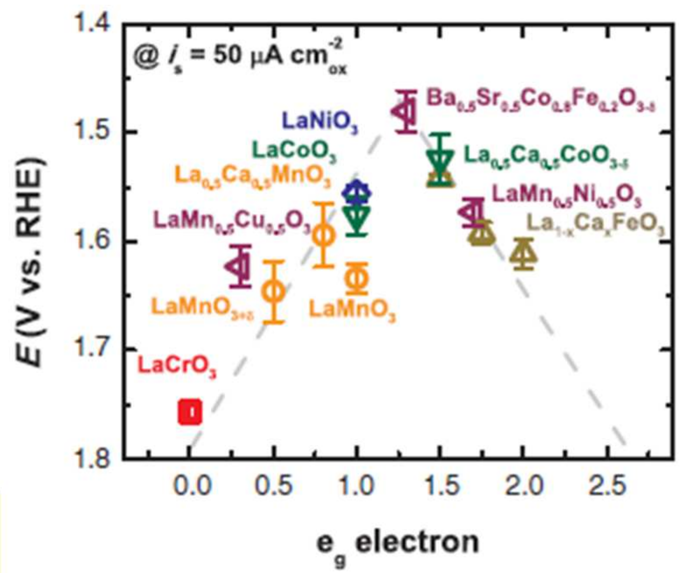
Catalysts have the role to provide occupied surface states of the correct symmetry to allow the reaction to proceed with symmetry conservation.

Active reaction surface

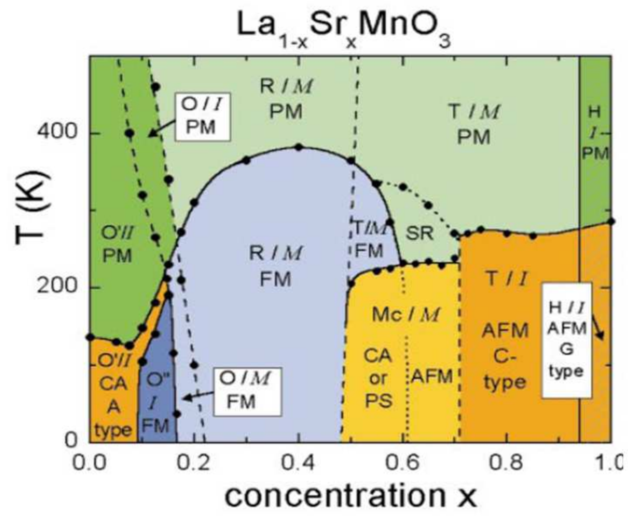
This implies the existence of occupied surface states whose symmetry permits a net positive overlap to occur between surface states and antibonding orbitals of the gaseous reactant

***ORR** activity as a function of $\mathbf{e_g}$ filling*

***O**xygen **R**eduction **R**eaction activity of transition metal oxide catalysts*



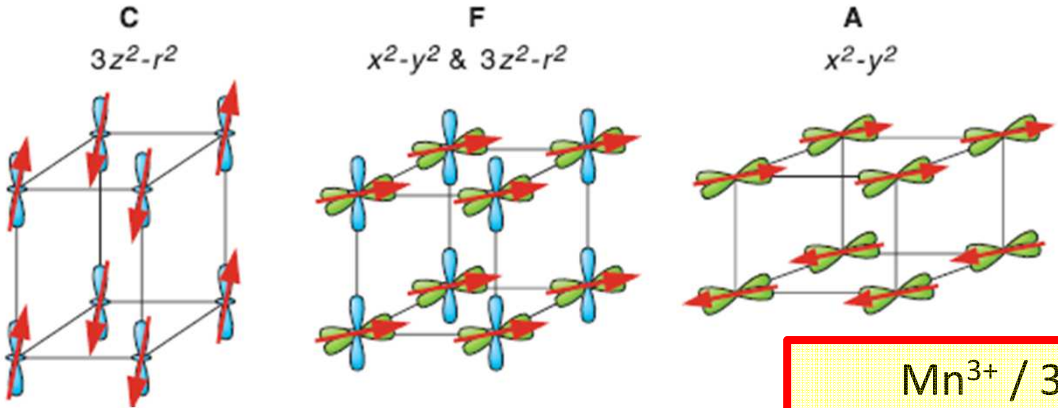
Orbital Physics in Transition Metal Oxides

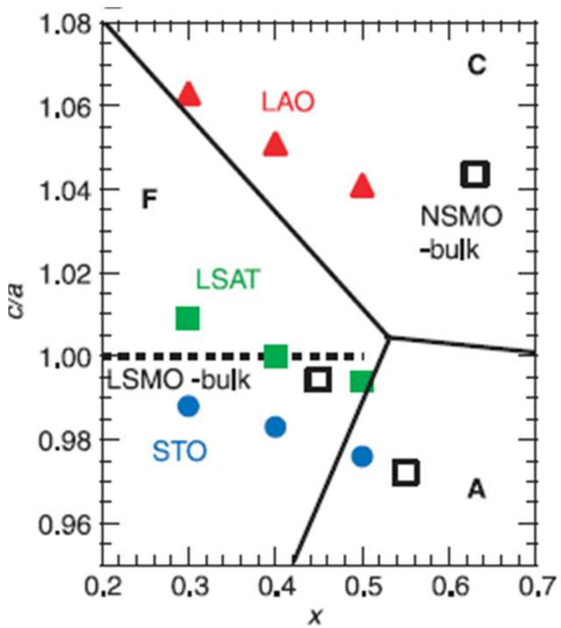


Y. Tokura, Science, 288, 462–468 (2000)

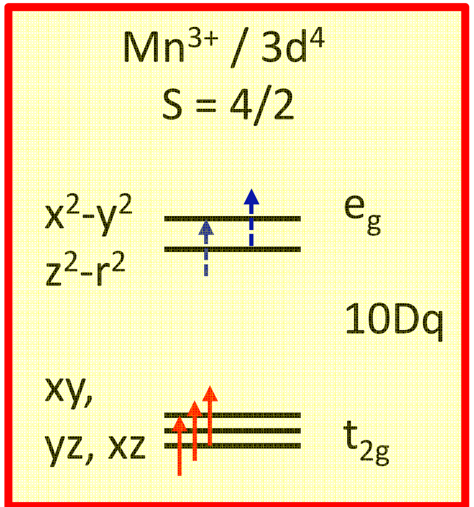
Z.Fang, Phys. Rev. Lett. 84, 3169–3172 (2000)

Change of orbital (magnetic) configuration with hole ***doping***



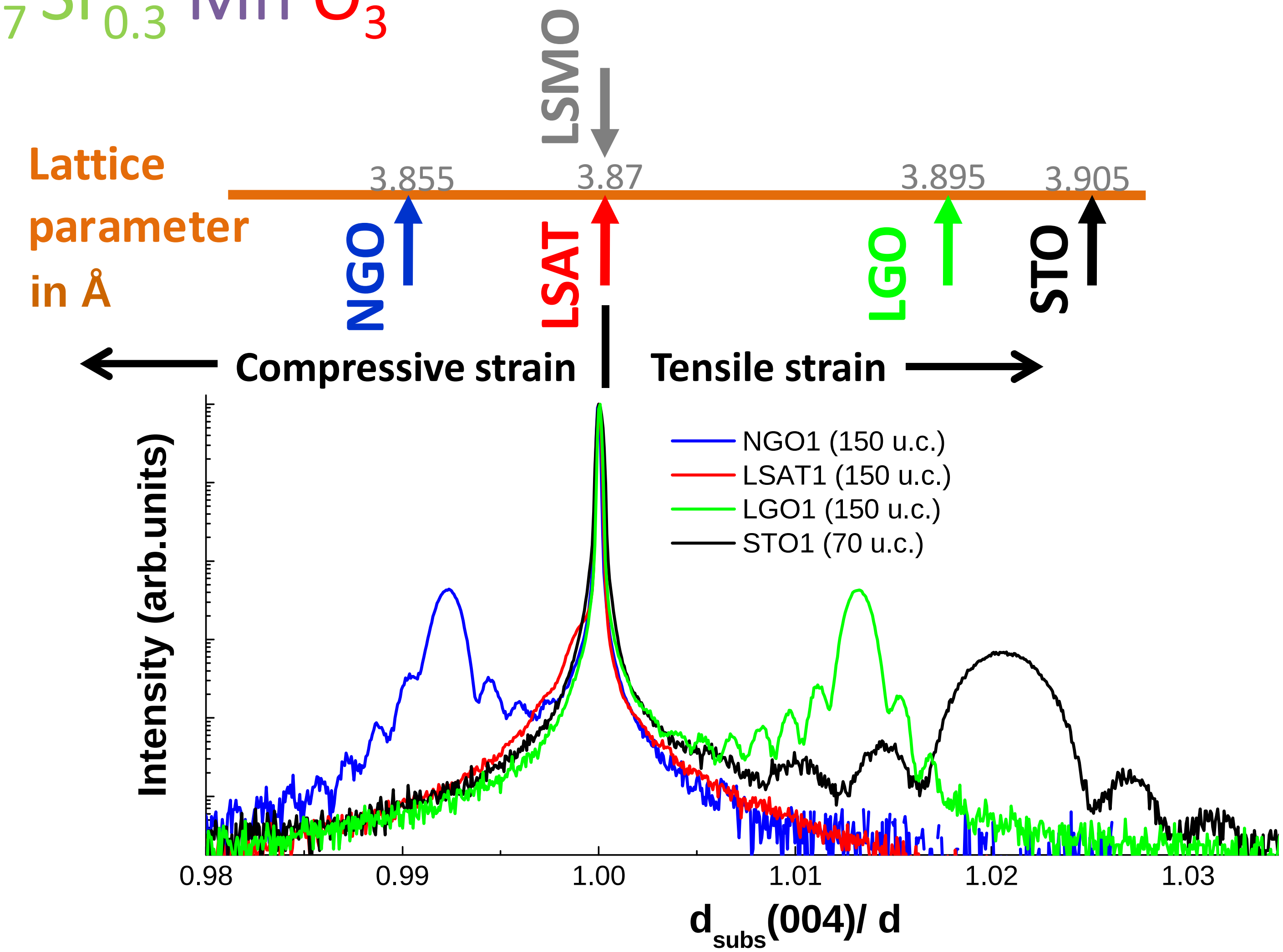


Change of orbital (magnetic) configuration with ***strain***



Tuning Strain in LSMO Films

$La_{0.7}Sr_{0.3}MnO_3$

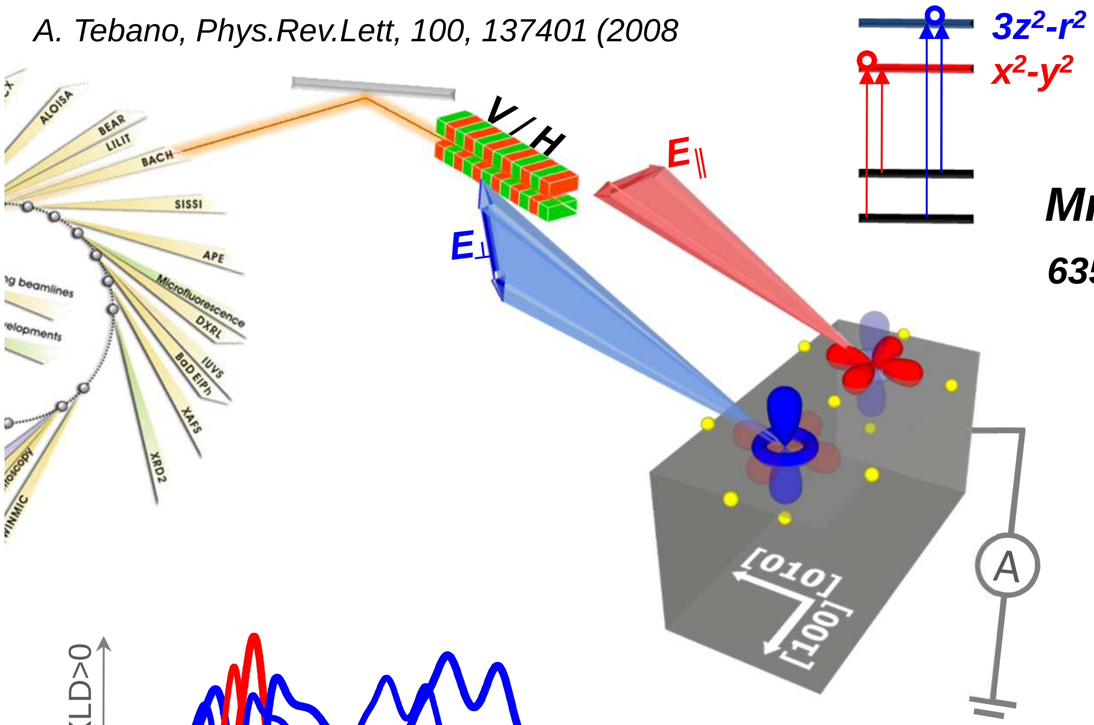


Exploring Electronic Structure with

X-Ray Linear Dichroism (XLD)

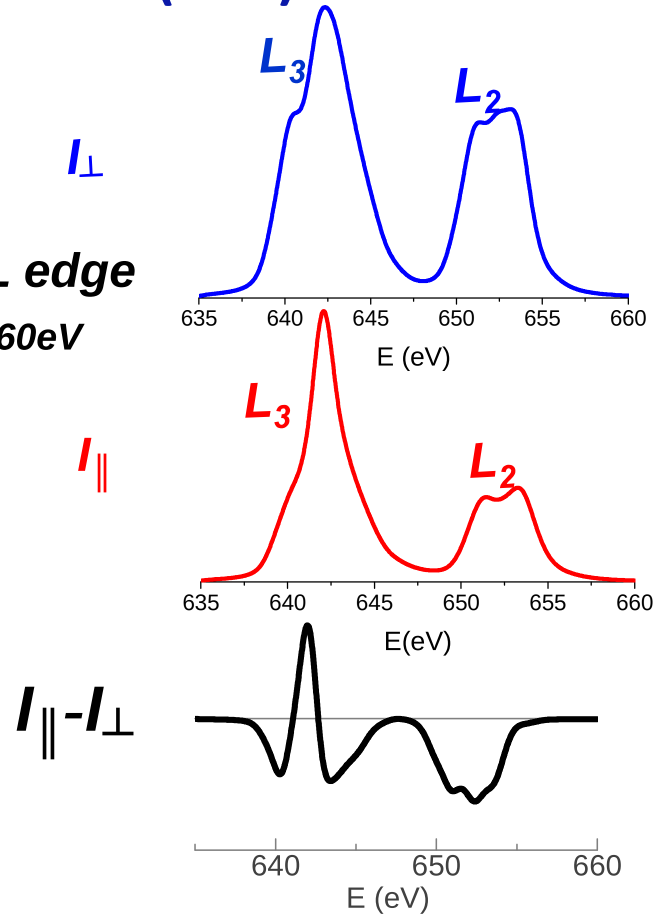
E.Stavitski, Micron 1993, 687–694 (2010)

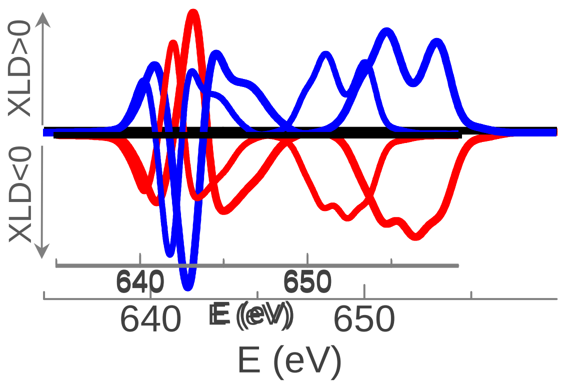
A. Tebano, Phys.Rev.Lett, 100, 137401 (2008

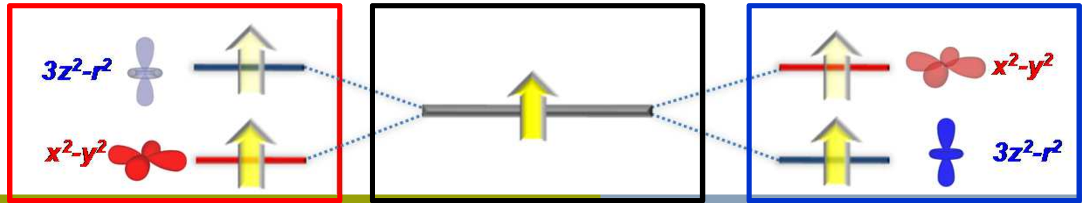


Mn-L edge

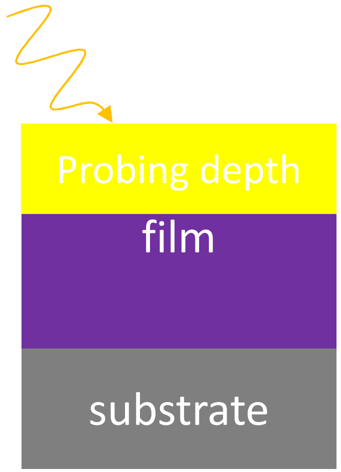
635-660eV

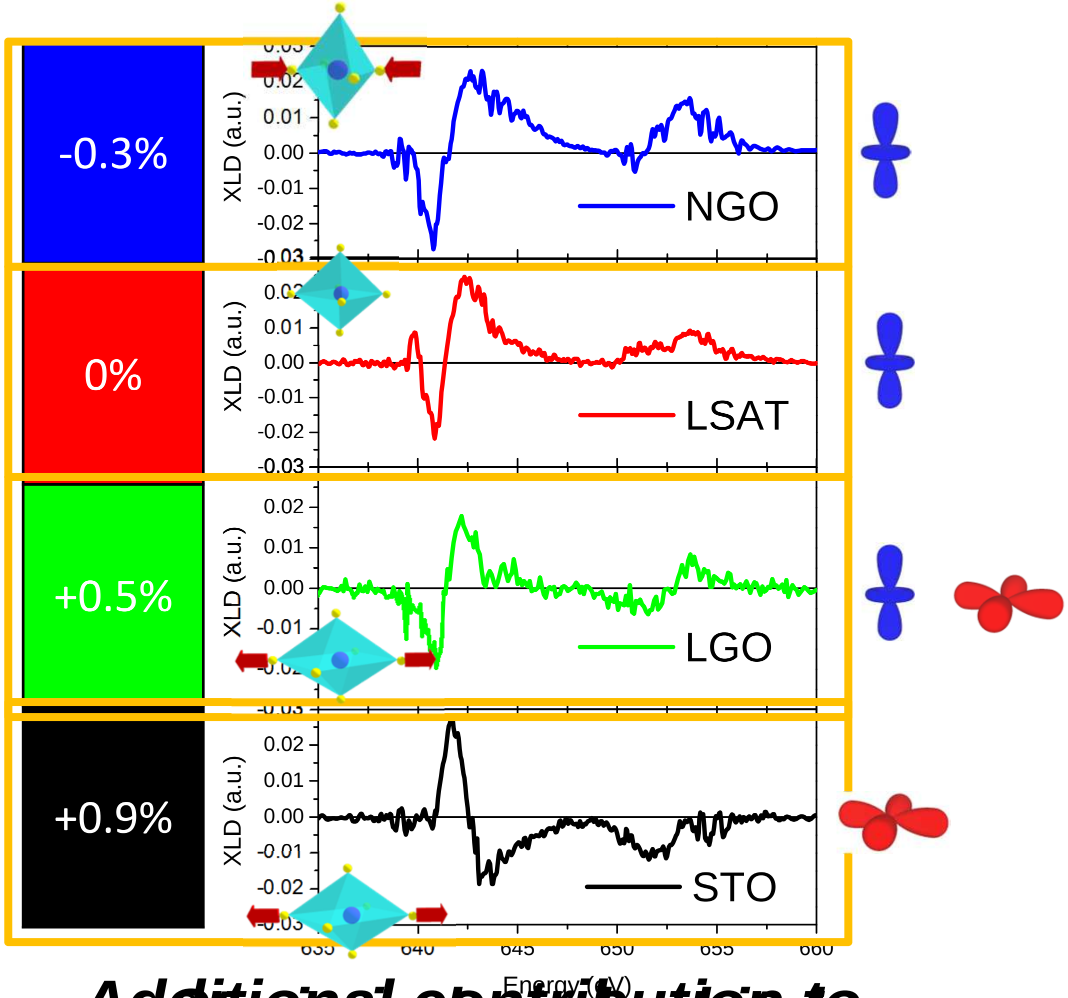






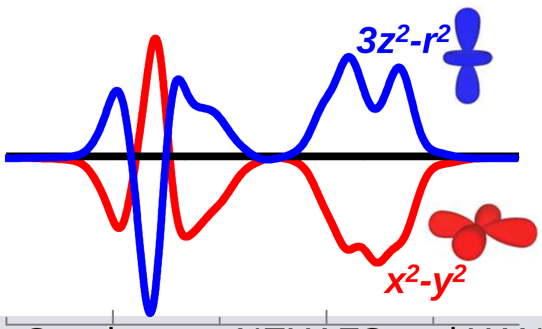
Orbital Occupancy in LSMO Films





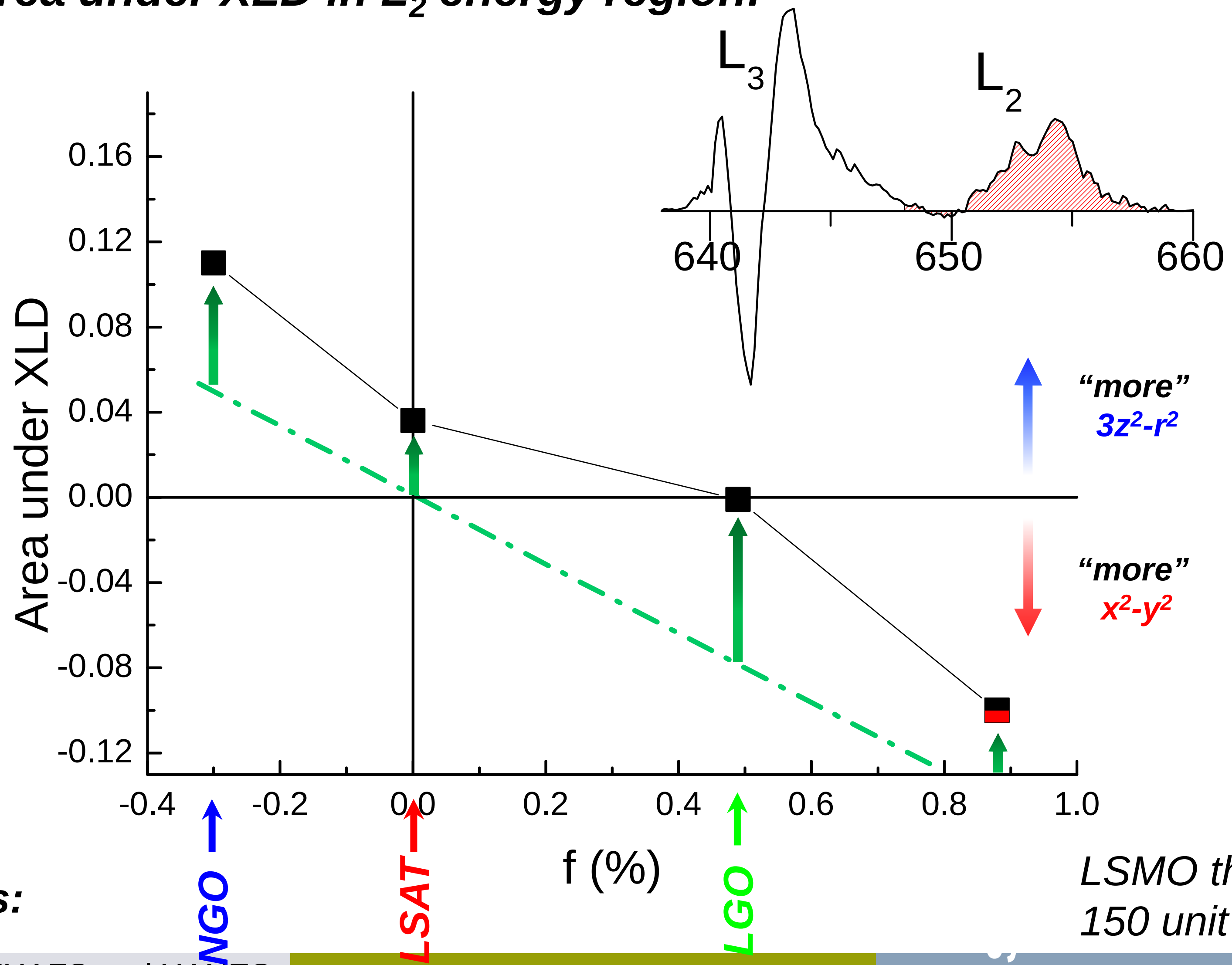
Additional contribution to orbital occupancy

Strain induced orbital occupancy



Orbital occupancy in LSMO films

Integral area under XLD in L_2 energy region:



Substrates:

LSMO thickness: 150 unit cells

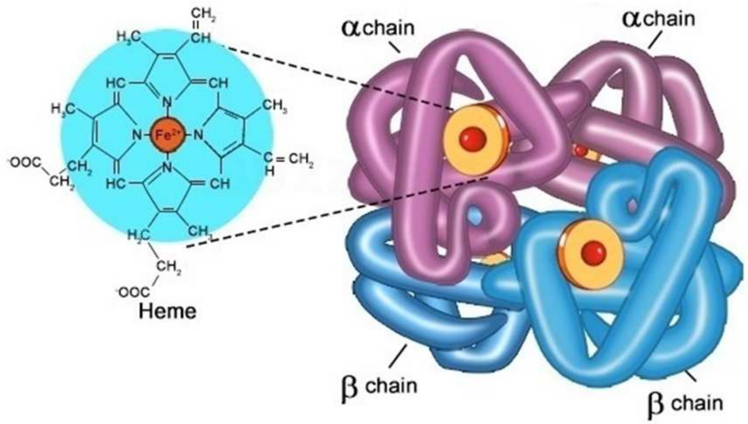
XPS-NAPP:
Surface-Gas Interactions

NAPP End Station / Circe beamline:

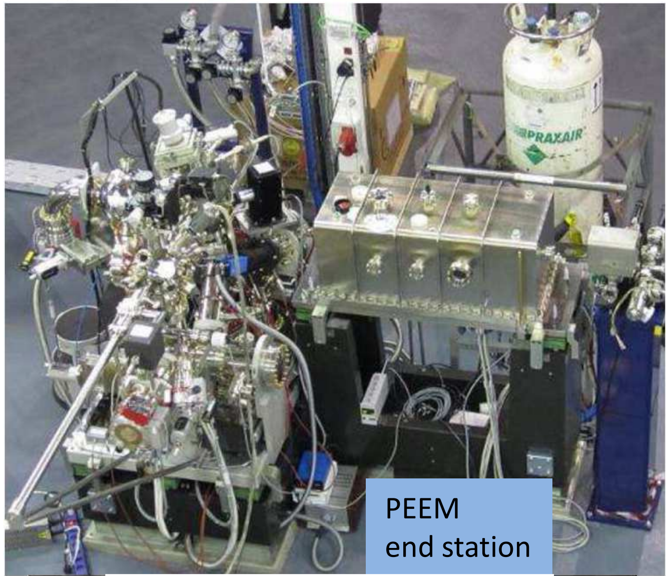
"Breathing Chemistry" in FePc

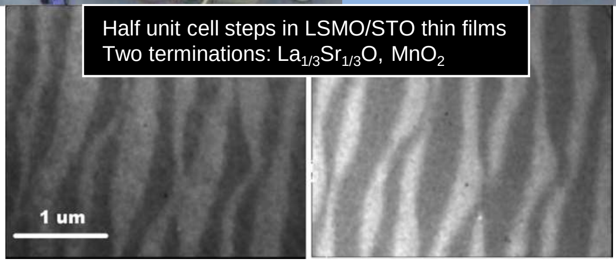
C. Rogero et al.

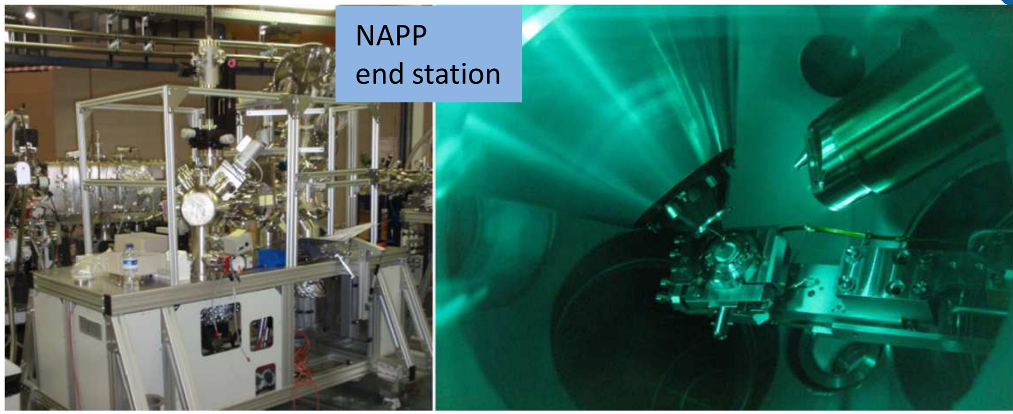
Cooperation CSIC-UPV/EHU / CELLS-ALBA



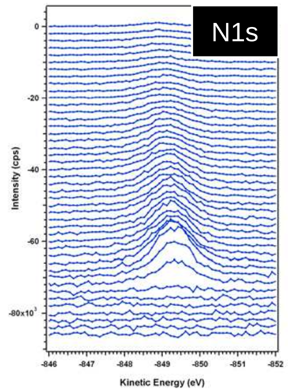
BL24 CIRCE – Photoemission Microscopy & Spectroscopy

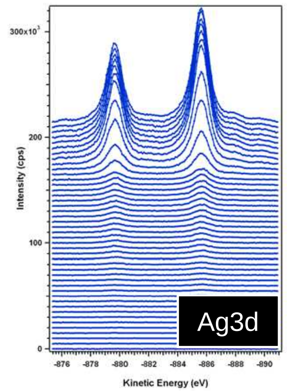






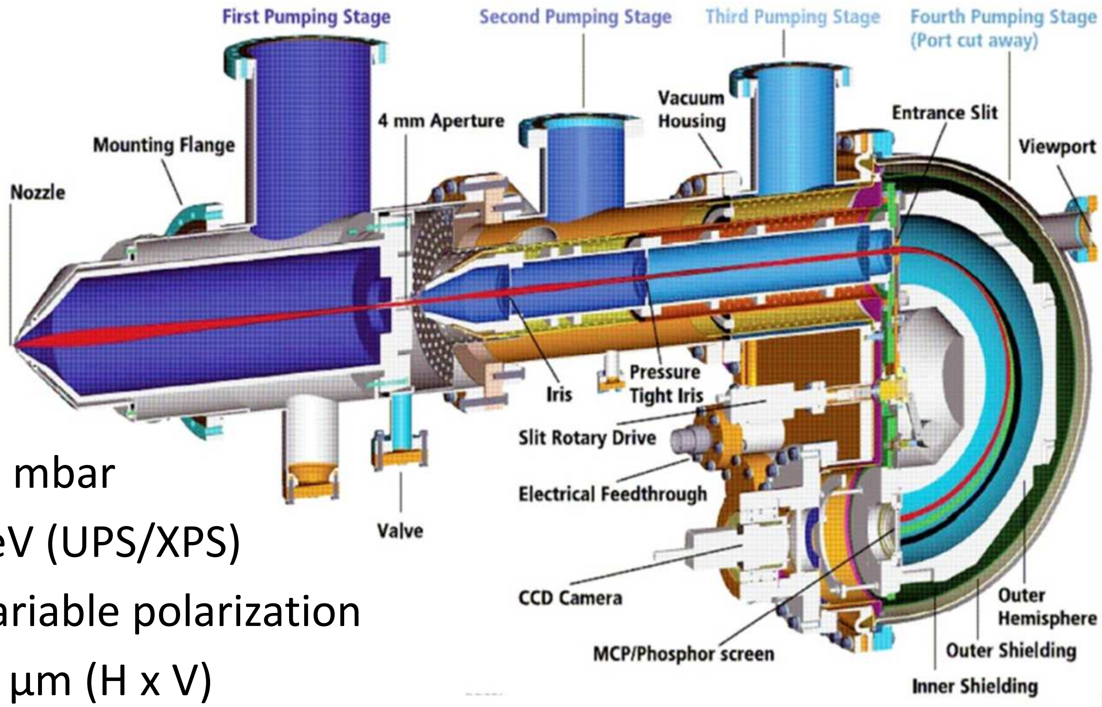
NAPP XPS
Ag sample/Mg Kα
From UHV (top) to
25 mbar N_2 (bottom)





- Variable polarization BL dedicated to advanced photoemission microscopy and spectroscopy.
- Two branches with dedicated state-of-the-art end stations:
  - ✓ PEEM (photoemission electron microscopy)
  - ✓ NAPP (near ambient pressure photoemission).
- Photon energy range: 100 - 2000 eV

Near Ambient Pressure Photoemission

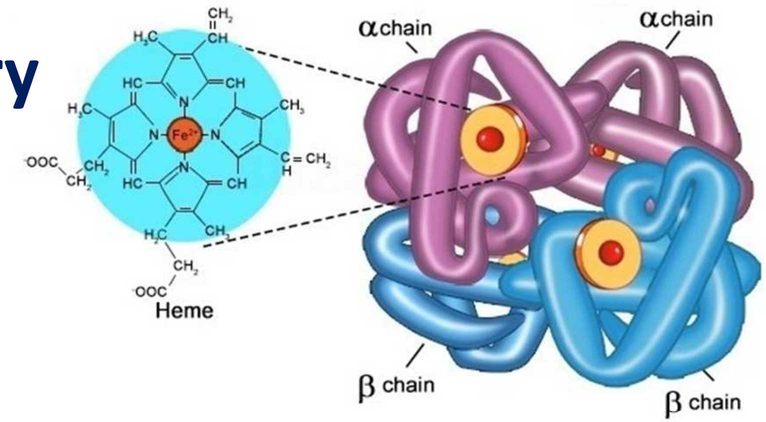


- Maximum pressure at the sample ≈20 mbar
- Analyzer energy resolution ~ 5/10 meV (UPS/XPS)
- Variable beam incidence angle and variable polarization
- Beam size at the sample 100 µm x 30 µm (H x V)
- Infrared laser heating & Peltier cooling -30 °C < T_{sample} < 1200 °C
- Residual gas analyzer to monitor reaction products
- Sample in horizontal position with fully horizontal transfer
- Ultrapure gases inlet manifold with three lines
- Liquids vaporizer (Bronkhorst CEM)
- Surface science preparation chamber

SPECS™ Innovation in Surface Spectroscopy and Microscopy Systems

Breathing chemistry

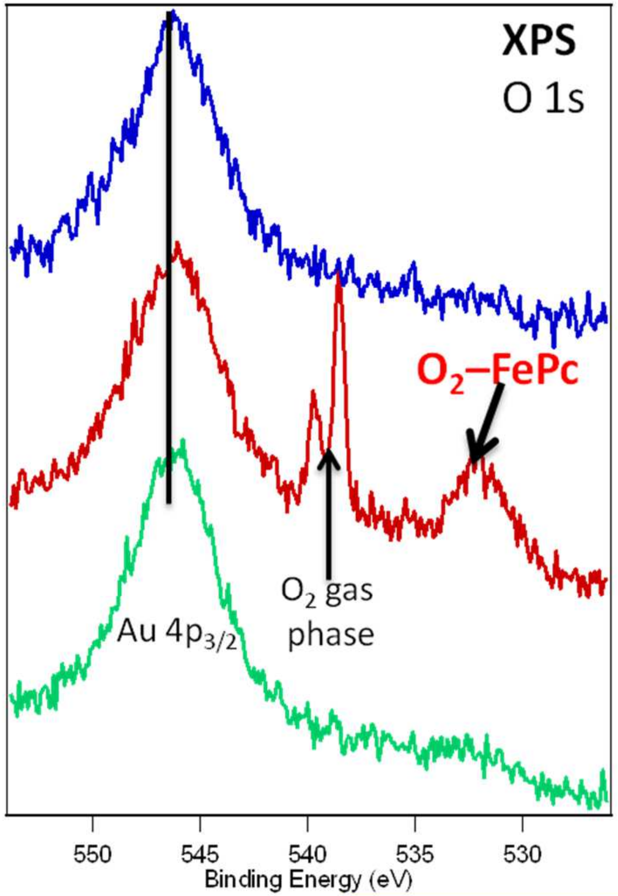
By courtesy of Dr. Celia Rogero (CSIC-UPV/EHU)

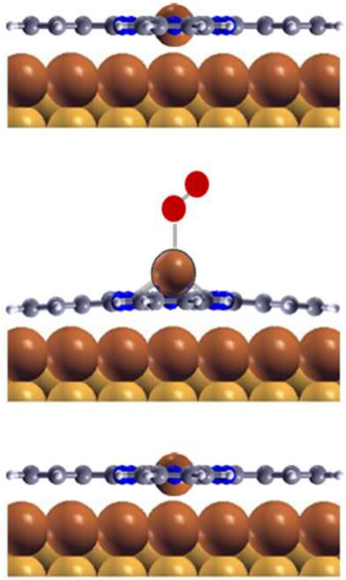


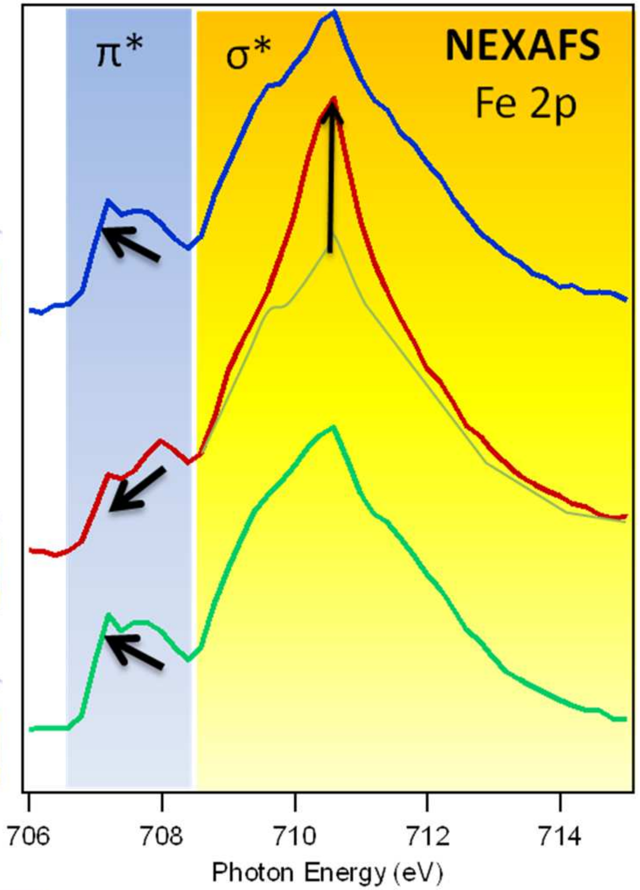
UHV

0.01 mbar O_2

UHV







PEEM End Station / Circe Beamline:

Surface Re-Structuring in STO(001),

Electrical switching of magnetization in $La_{2/3}Sr_{1/3}MnO_3$

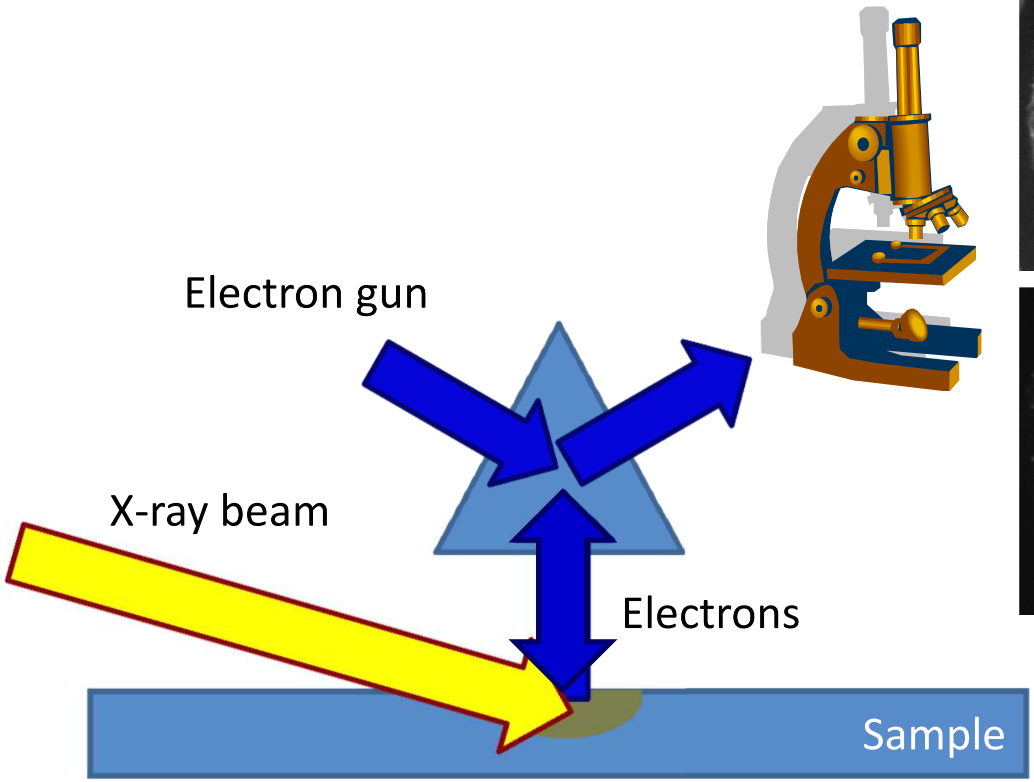
L. Aballe et al.

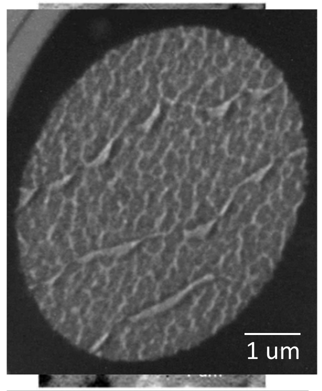
Cooperation ICMAB / CELLS-ALBA

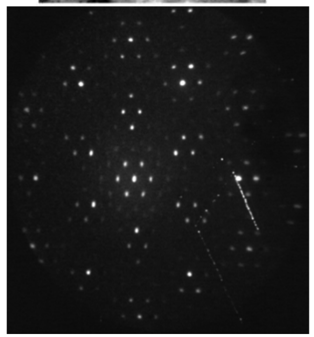
X-PEEM, LEEM, and LEED

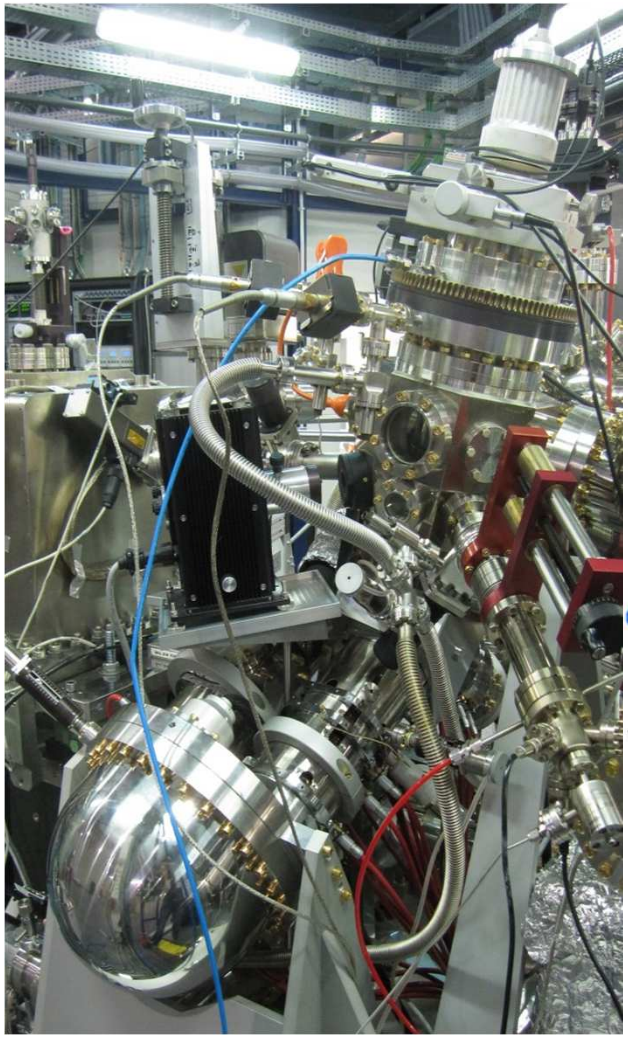
X ay
P hoto
E emission
E lectron
M icroscopy

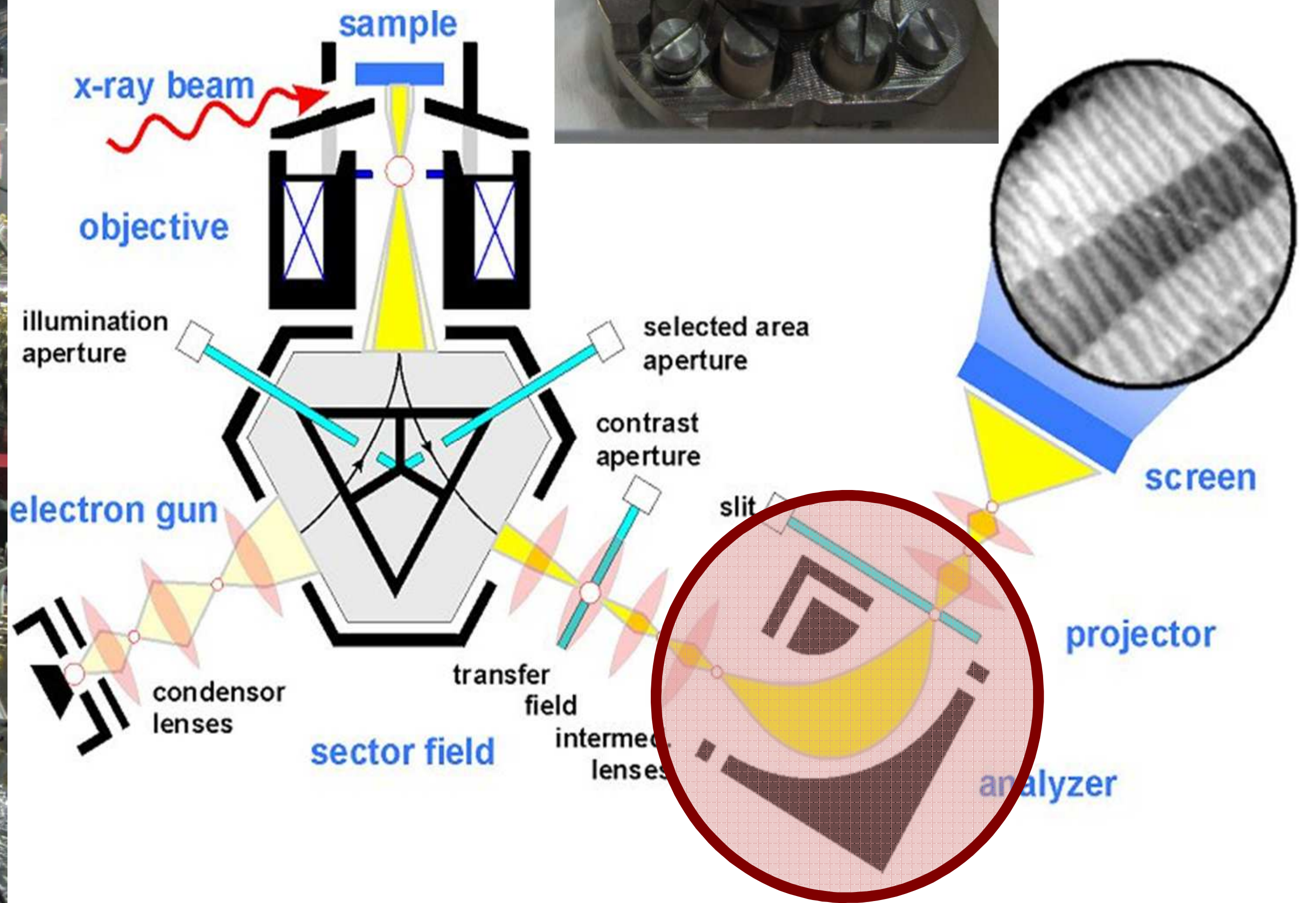
L ow
E nergy
E lectron
M icroscopy/**D**iffraction







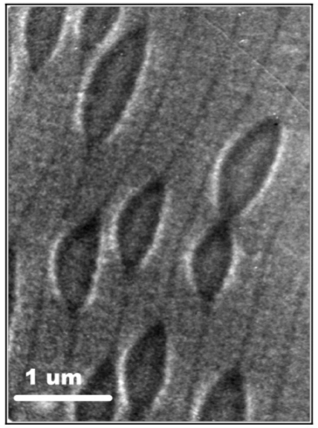




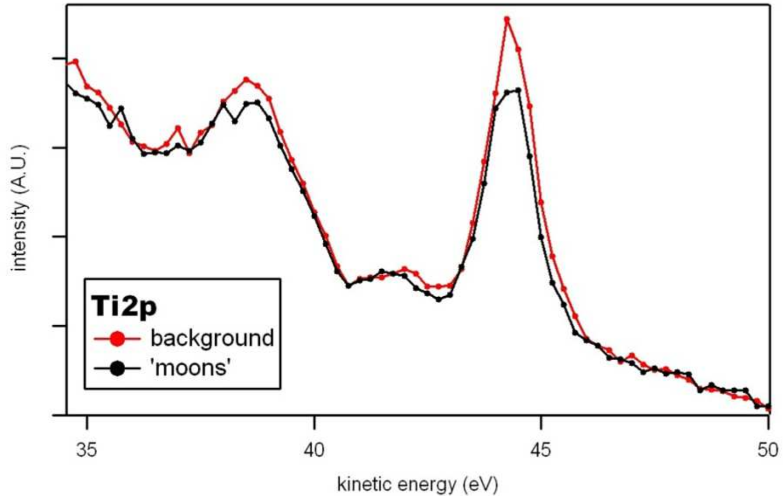
Th. Schmidt et al,
Surf. Rev. and Lett. 5 (1998)

XPEEM & LEEM

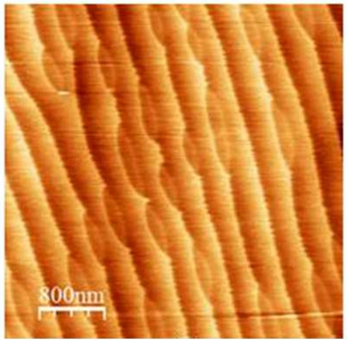
Self assembled distinct termination areas on $SrTiO_3(100)$

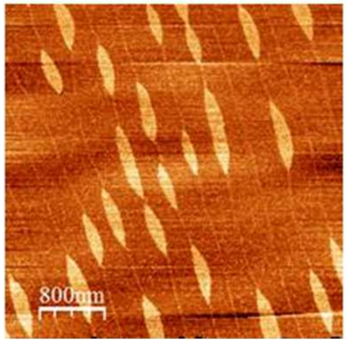


MEM image:
- SrO/TiO_2 areas
- steps

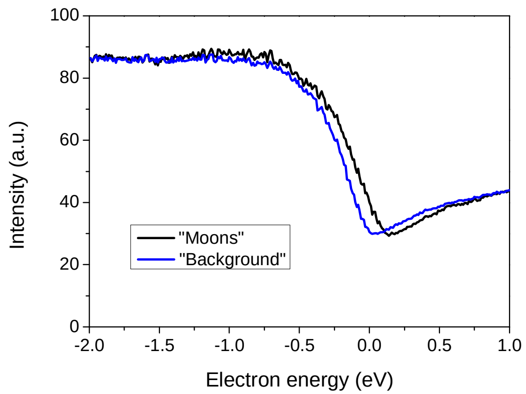


XPEEM spectromicroscopy at minimum electron escape depth confirms surface SrO vs TiO_2





AFM: topography (left) & lateral force (right)

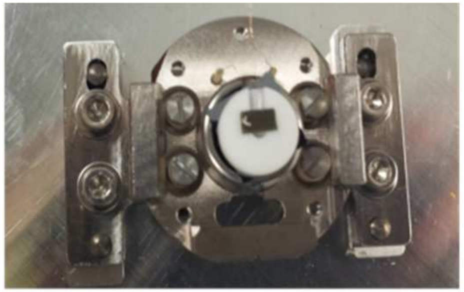


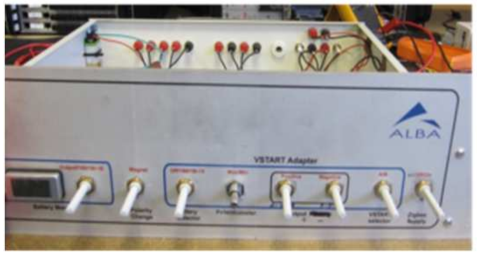
Work function difference from MEM-LEEM transition shift < 70 meV

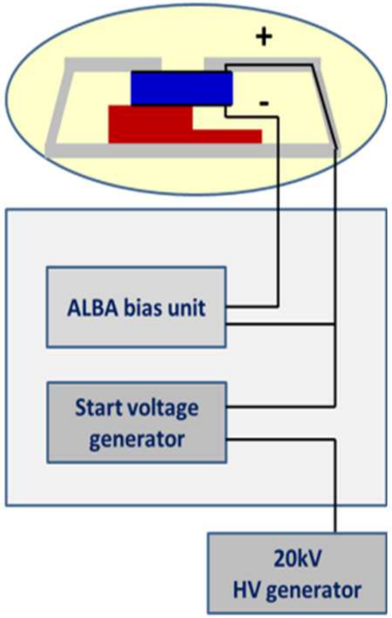
C. Ocal, E. Barrena, S. Matencio, J. Fontcuberta (ICMAB-CSIC)

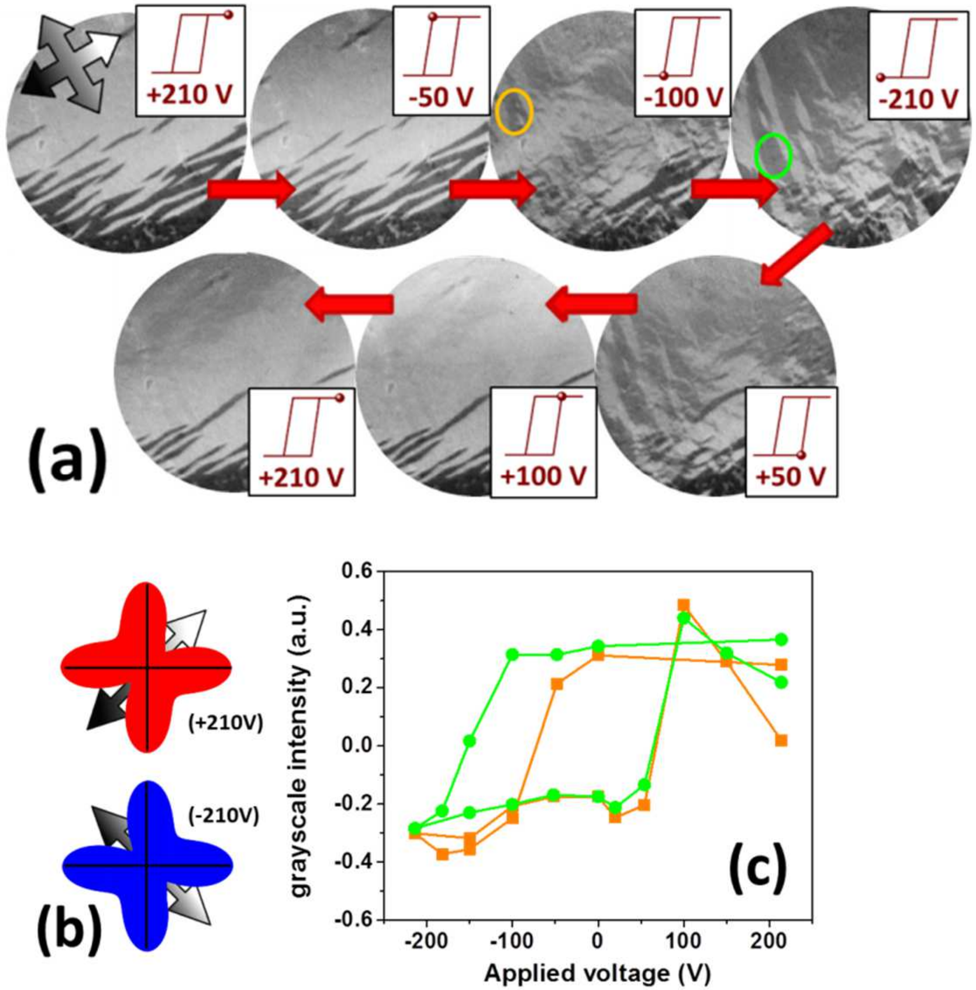
Electrical switching of magnetization

$La_{2/3}Sr_{1/3}MnO_3$//PMN-PT (100) with OOP electrical poling at RT









D. Pesquera, B. Casals, G. Herranz, J. Fontcuberta (ICMAB-CSIC)

Soft X-Ray Caveats

So what can we & can't we do for you?

Topic	Soft X-Ray Techniques			X-Ray Techniques
	XAS	NAPP	PEEM	EXAFS & XANES
XANES in transmission	😐	-	-	☺
Surface sensitivity	☺	☺	☺	😐
Bulk sensitivity	😐	☹	☹	☺
Gas sample environment	not yet	☺ $\leq$20 mbar	☹ $\leq 10^{-6}$ mbar	☺ up to several bars
Liquid samples	not yet	not yet	☹	☺
Humid samples	😐	☺	☹	☺

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Surface re-structuring in $SrTiO_3$ surfaces:

- ***C. Ocal, E. Berena F. Sanchez, J. Fontcuberta – ICMAB Barcelona***
- ***L. Aballe, M. Foerster – ALBA Circe beamline (PEEM)***

Electrical switching of magnetization in LSMO thin films:

- ***D. Pesquera, G. Herranz, F. Sanchez, J. Fontcuberta – ICMAB Barcelona***
- ***L. Aballe, M. Foerster – ALBA Circe beamline (PEEM)***

"Breathing chemistry":

- ***C. Rogero – CSIC-UPV/EHU***
- ***V. Perez, C. Escudero – ALBA Circe beamline (NAPP)***

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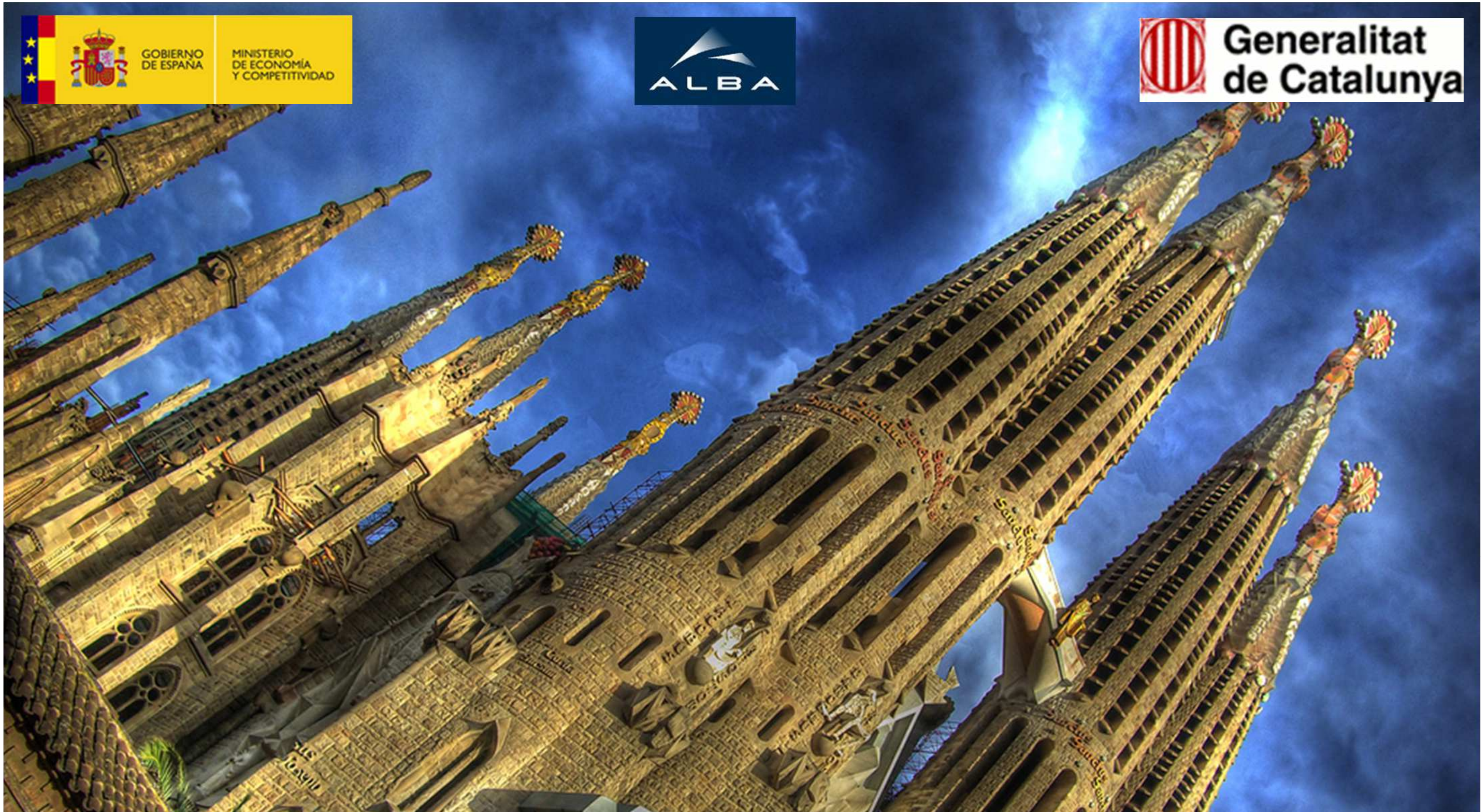

Thank you for your time & attention