

# **X-ray Absorption spectroscopy: a precious tool for materials science**

**F. d'Acapito**

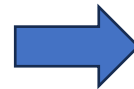
# LAYOUT

- Introduction to synchrotron radiation
- The XAS technique
- The LISA beamline @ ESRF
- Experimental examples
- Conclusions

## Synchrotron Radiation

- **D. Raoux** "Introduction to synchrotron radiation" HERCULES School book, ISBN 3-540-56561-2
- **S. Mobilio and A. Balerna**, "Introduction to the main properties of Synchrotron Radiation", SILS scuola di Pula book, ISBN 88-7438-008-9
- **P. ELLEAUME** "Insertion Devices" CERN Accelerator School Brunnen 2003, <https://cas.web.cern.ch/schools/brunnen-2003>

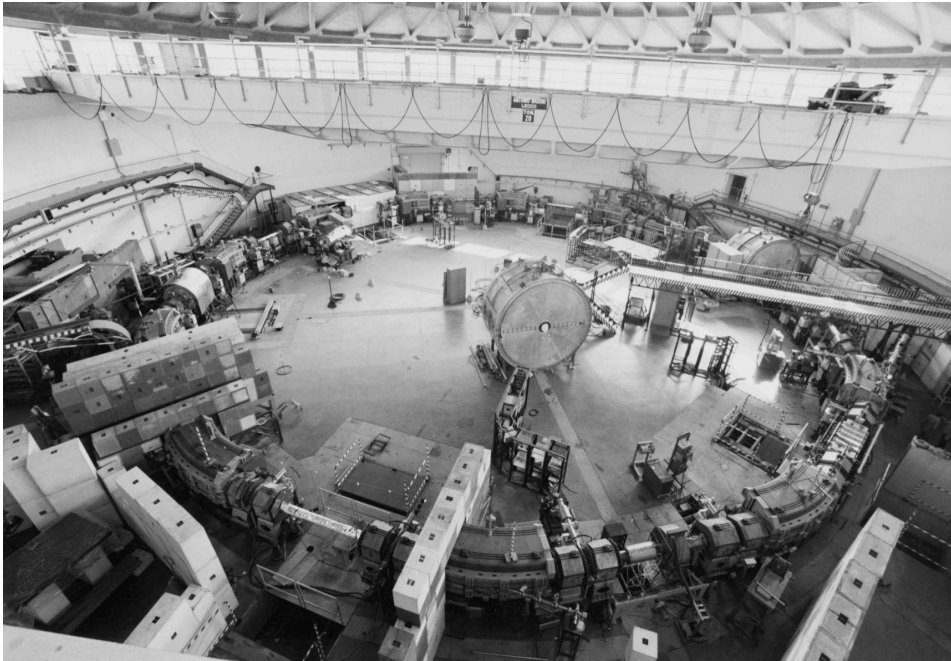
Synchrotron Radiation



The XAS technique

## Synchrotron Radiation

Emitted by *relativistic charged particles* undergoing an *acceleration* perpendicular to their velocity.



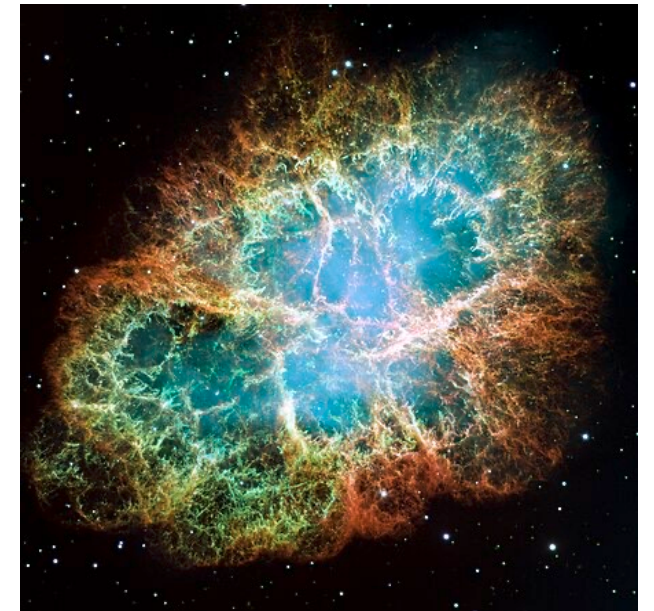
Artificial Source: the ADONE SR, Sec XX c.a.  
(w3.lnf.infn.it)



MAGNETIC DISCUSSION

F. d'Acapito BNC talk 260528

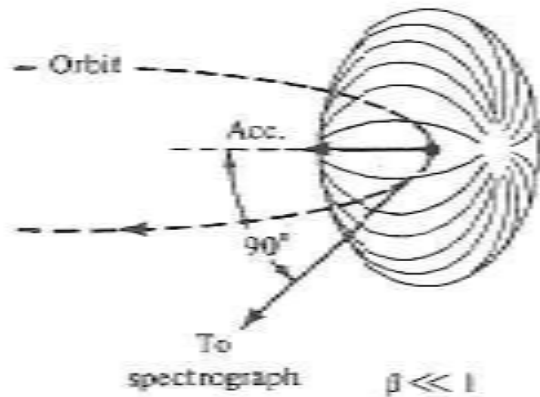
*Franco D'Acquisto*



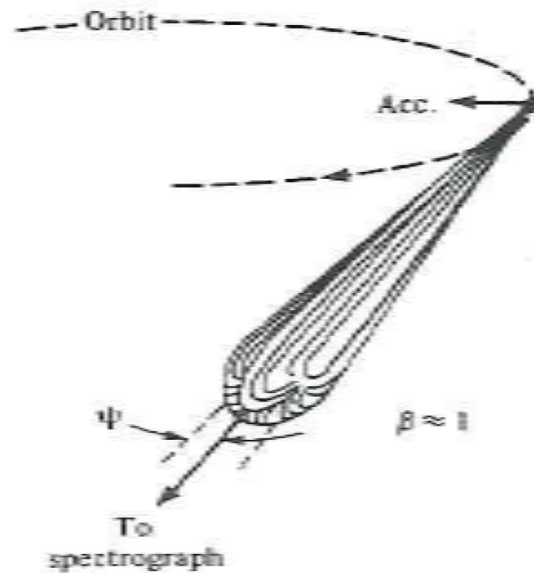
Natural Source: the Crab Nebula  
(Wikipedia)

# SYNCHROTRON LIGHT

## SR Generation



Classical particle



Relativistic particle

**Electrons** emit radiation when subject to an acceleration.

**Relativistic electrons:** radiation collimated in the orbit plane

$$E = 6 \text{ GeV}$$

$$mc^2 = 0.5 \text{ MeV}$$

$$\gamma = E/mc^2 = 12000$$

Natural divergence

$$1/\gamma = 83 \text{ } \mu\text{rad}$$

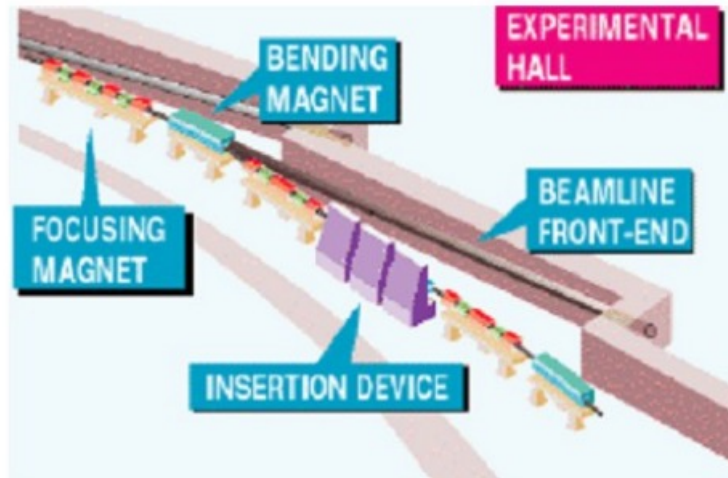
The lighter the better  
Also POSITRONS !

# SYNCHROTRON LIGHT

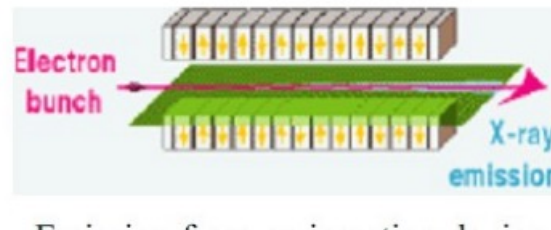
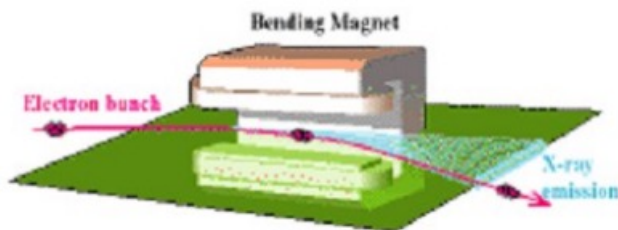
## Sources

2 kinds of sources:

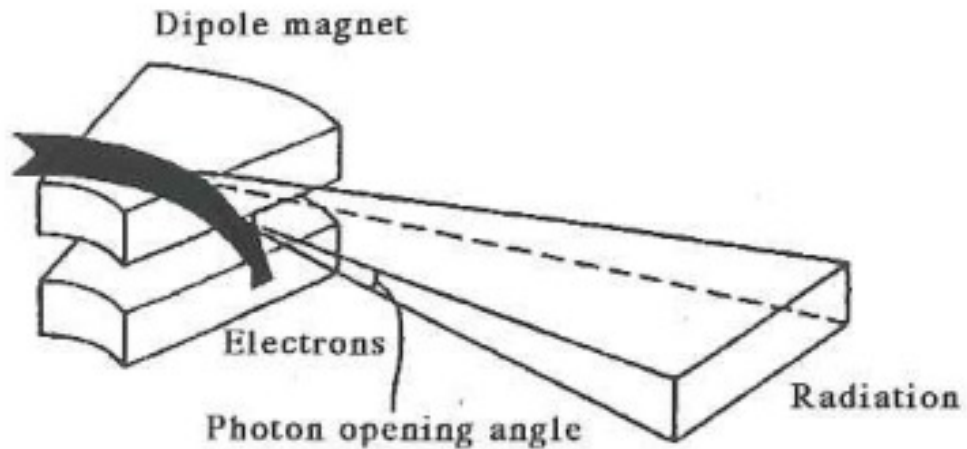
- Bending magnets (naturally occurring in a storage ring)
- Insertion devices, installed on straight sections.



Location of the different sources in the tunnel

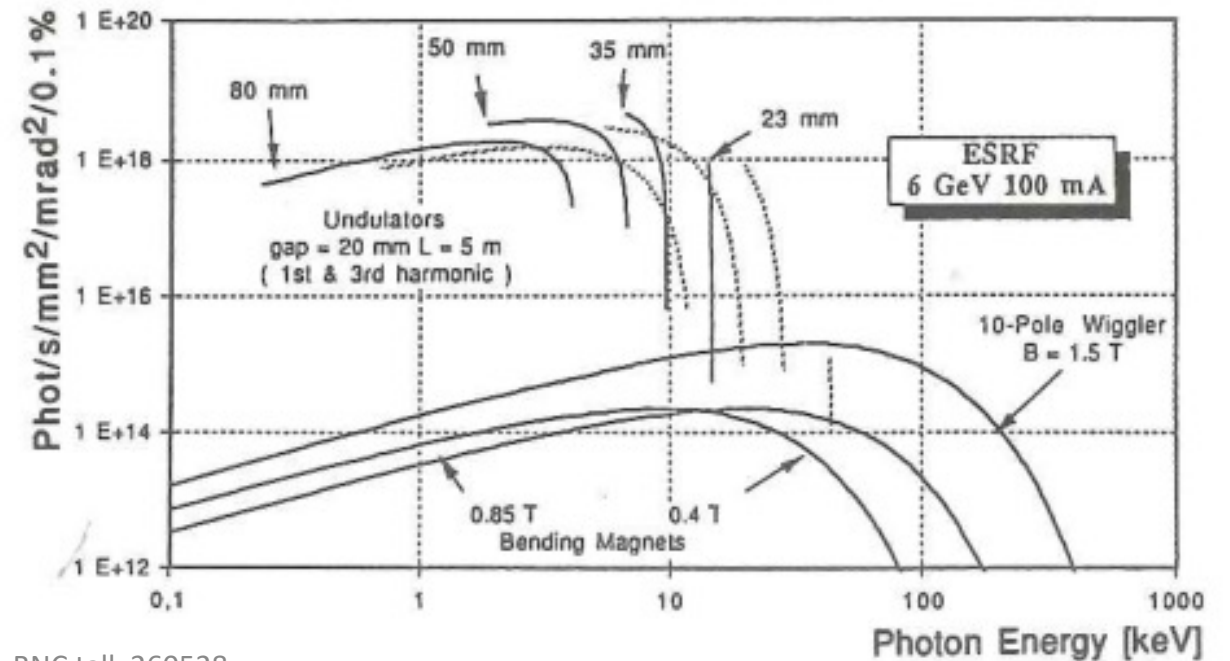


# SYNCHROTRON LIGHT

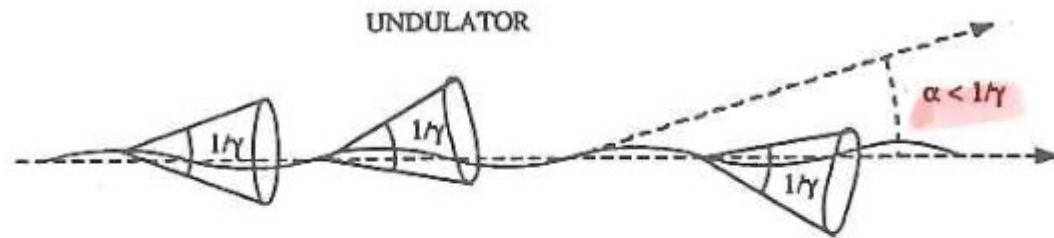


## Bending magnet

- Emission from a single curve.
- Continuous emission in energy.
- Vertically collimated emission



# SYNCHROTRON LIGHT

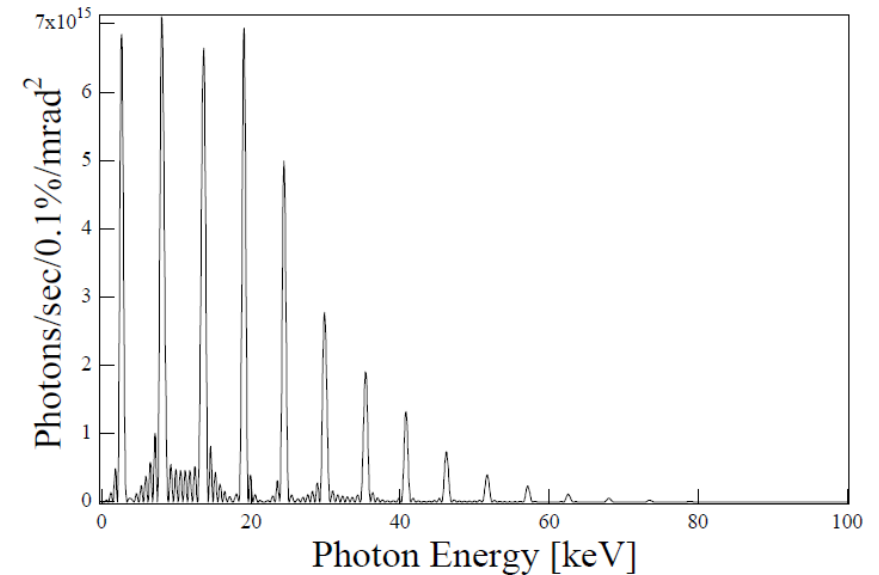
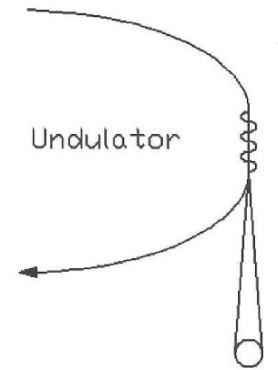


$K$  = deflection parameter.

$$K = \frac{eB_0\lambda_0}{2\pi mc} = 0.0934 B_0[T] \lambda_0[mm] \quad K/\gamma = \text{deflection}$$

## Undulators

- Small oscillations, within  $1/\gamma$
- $K < 2.5$
- Constructive interference between the emissions of the various poles.
- Vertical AND horizontal collimation
- Emission in lines



# SYNCHROTRON LIGHT

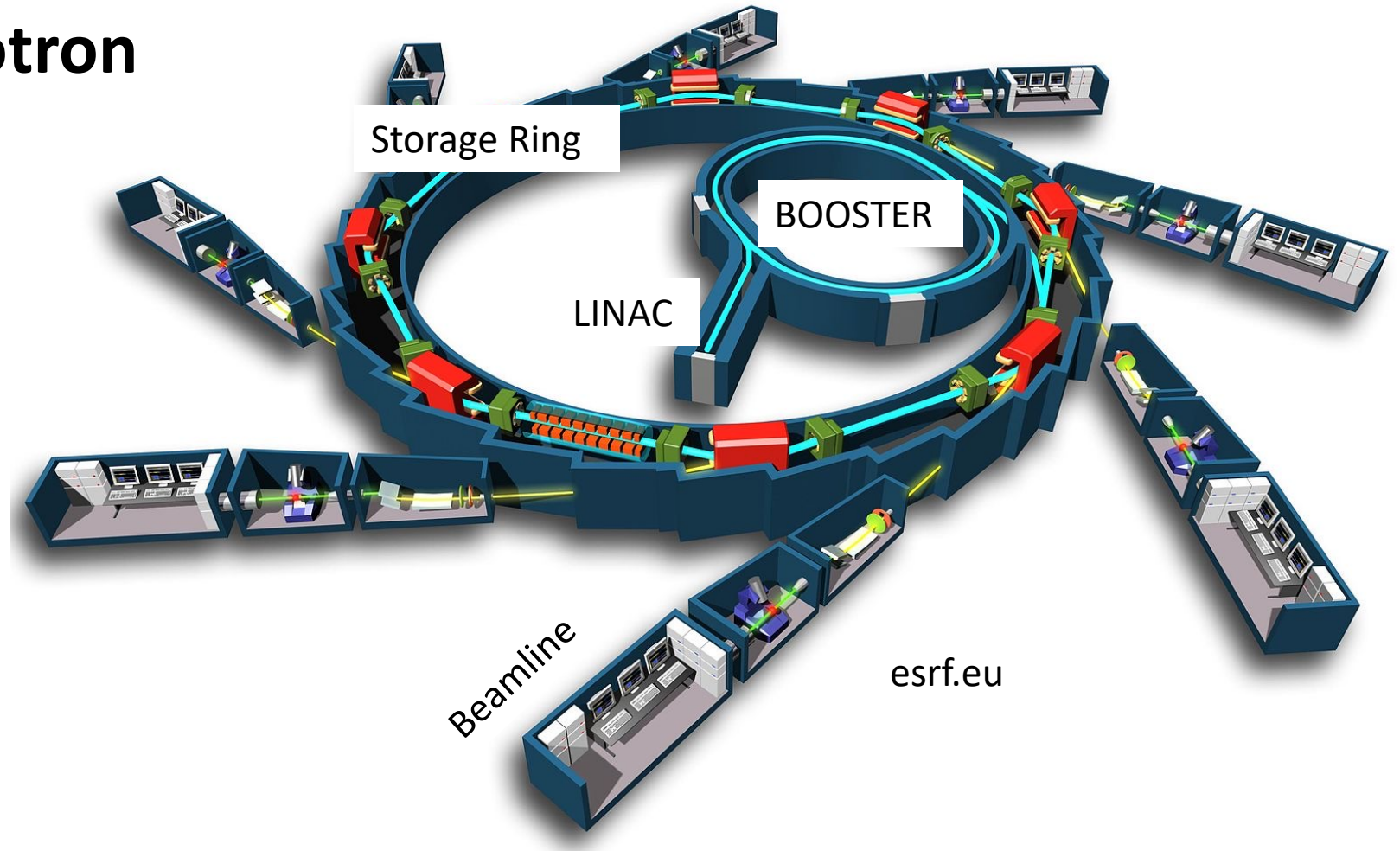
## Anatomy of a synchrotron

Electrons energy and typ.  
Length (ESRF)

LINAC  
0 - 200MeV, 30m

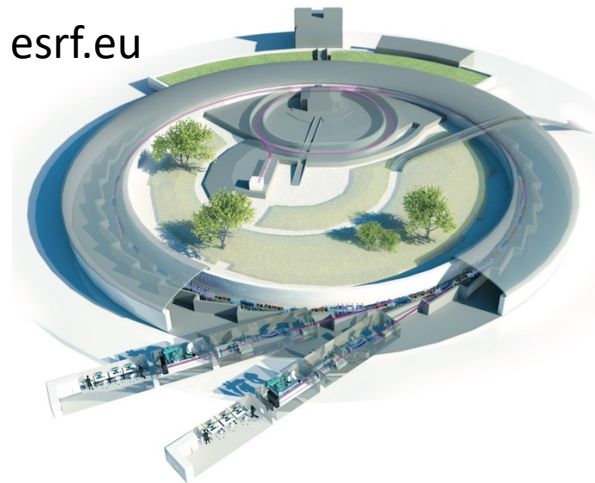
Booster:  
2MeV – 6 GeV, Diam. 95m

Storage Ring  
6 GeV, Diam. 270m

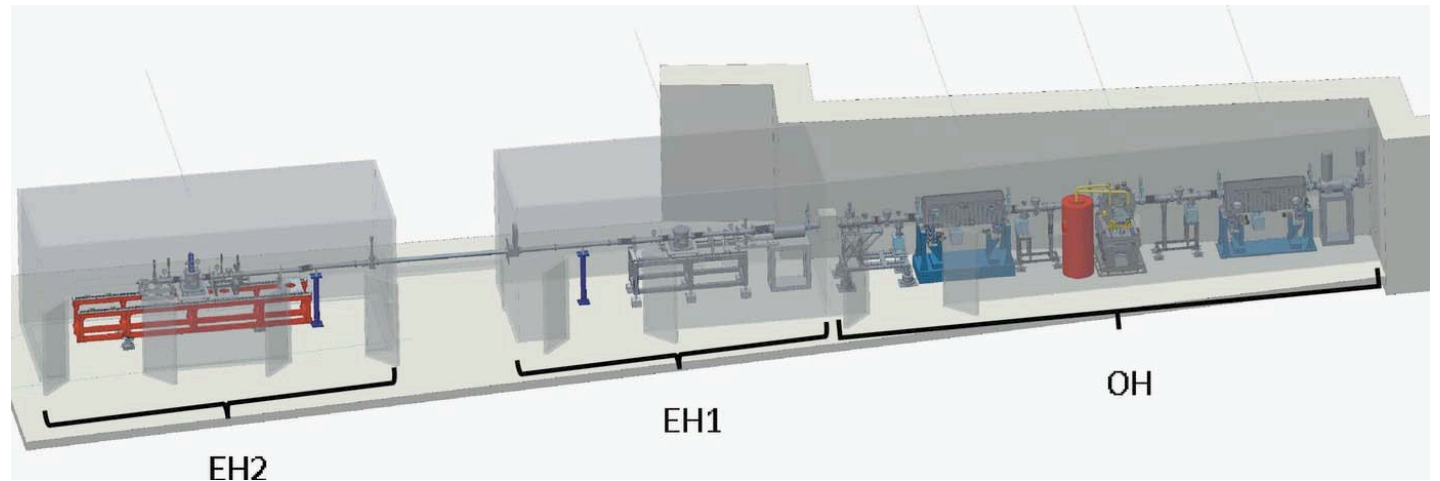


# SYNCHROTRON LIGHT

## Anatomy of a beamline



Beamlines around a SR



A beamline

OH: Optics Hutch

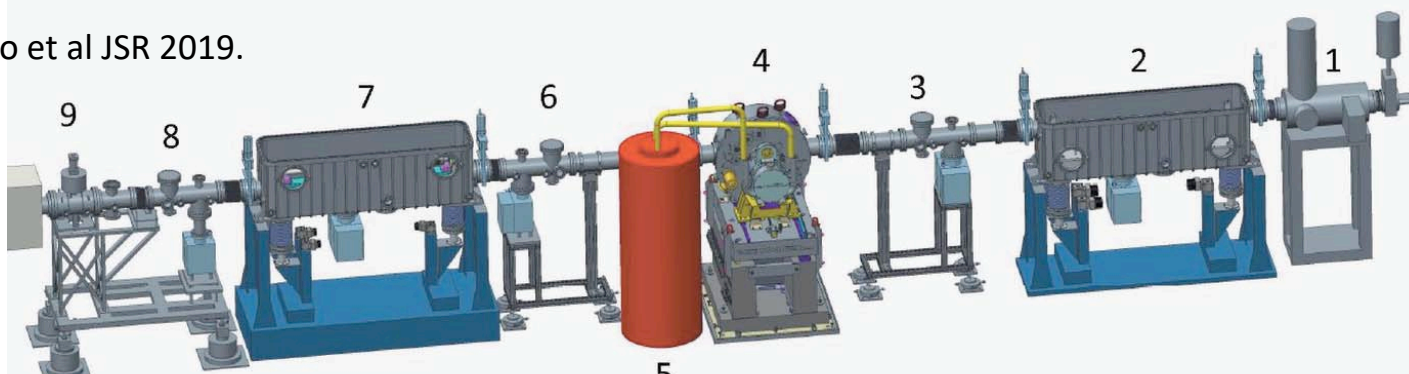
EH: Experimental Hutch

# SYNCHROTRON LIGHT

## Anatomy of a beamline

d'Acapito et al JSR 2019.

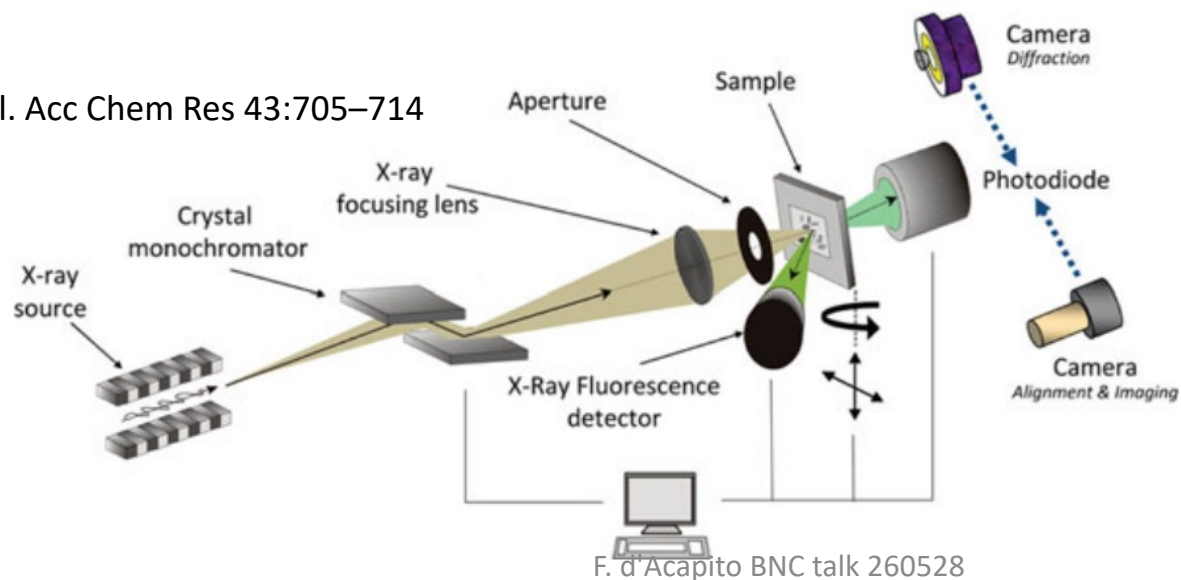
OH



- 1 = Slits & Attenuators
- 2 = Collimating mirror
- 3,6,8 = beam monitors
- 4 = monochromator
- 5 = cryocooler
- 7 = focusing mirror
- 9 = main beam shutter

Cotte et al. Acc Chem Res 43:705–714

EH



F. d'Acapito BNC talk 260528

## Access to SR

### Competitive, peer review


- 2 Calls per year
- Rolling long term, BAG projects
- Free of charge
- Peer review
- Typical acceptance rate 30-50%
- Beamtime: 6 to 9 months after acceptance

### Proprietary research

- 5k€/shift
- Fast access

Font Paragraph Styles

**EUROPEAN SYNCHROTRON RADIATION FACILITY**  
ESRF User Office  
CS 40220, F-38043 GRENOBLE Cedex 9, France  
Delivery address: 71 avenue des Martyrs, 38000 GRENOBLE, France  
Tel: +33 (0)4 7688 2552; fax: +33 (0)4 7688 2020; email: [useroff@esrf.fr](mailto:useroff@esrf.fr); web: <http://www.esrf.fr>



**Application for beam time at ESRF – Project Description**  
**Template for ESRF Standard proposals, CRG proposals, MX Rolling Crystallography, BioSAXS and SSX/TR-SSX proposals.**  
This document should consist of a **maximum of two A4 pages** (including references) with a minimal font size of 12 pt.

**Proposal Summary:**

**Scientific background:**

Help-text box to guide your writing – please remove.

**Experimental plan:**

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**Beamline(s) and beamtime requested with justification:**

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**Results expected and impact - analysis strategy and significance of the results:**

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**References**  
[1]  
[2]  
[3]

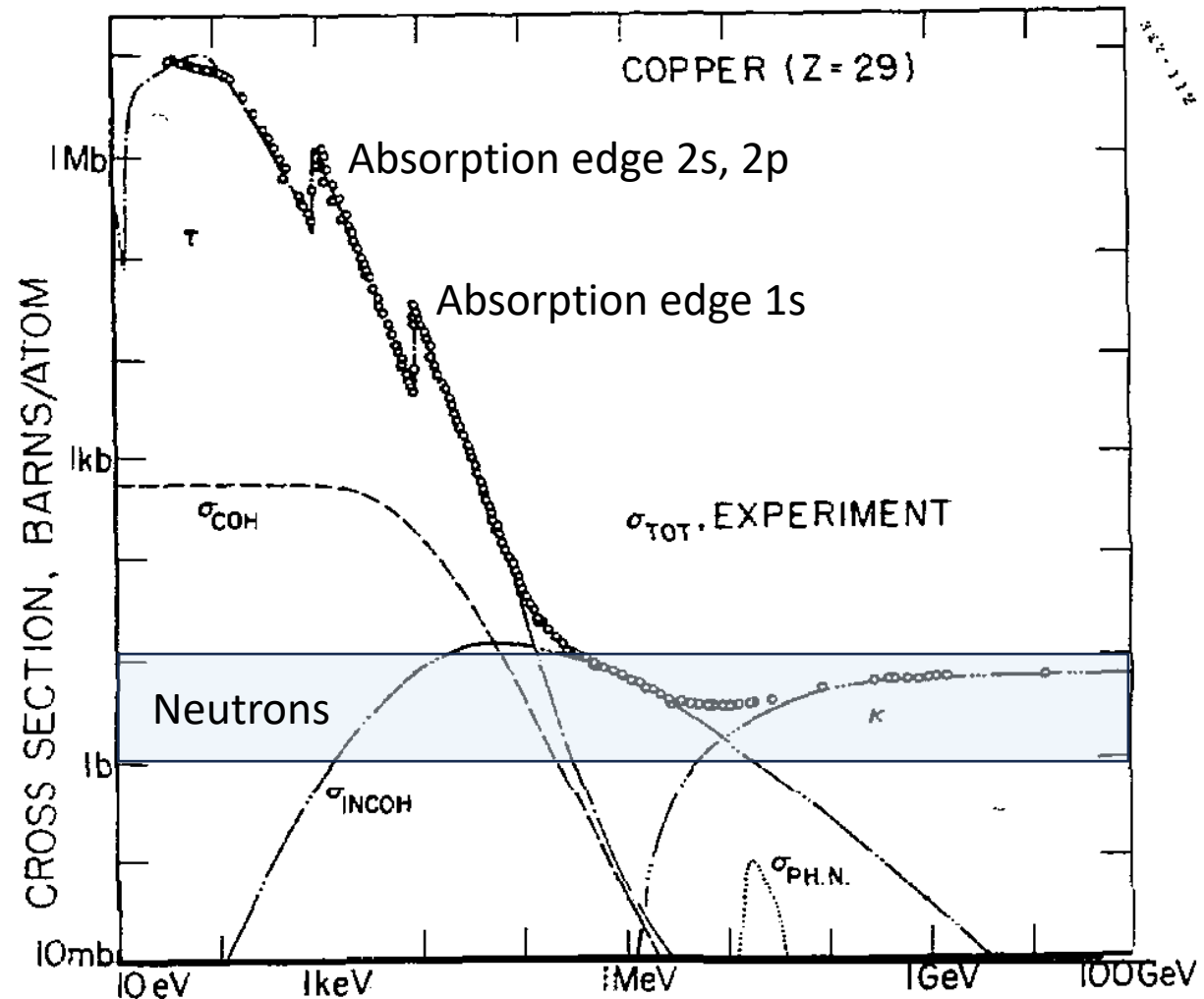
# TAKEAWAYS

- Generation of Synchrotron Radiation
  - different types of sources
- Anatomy lectures
  - of a synchrotron
  - of a beamline
- Accessing SR beamtime

# X-ray Absorption Spectroscopy



# MATTER / X-RAYS INTERACTION



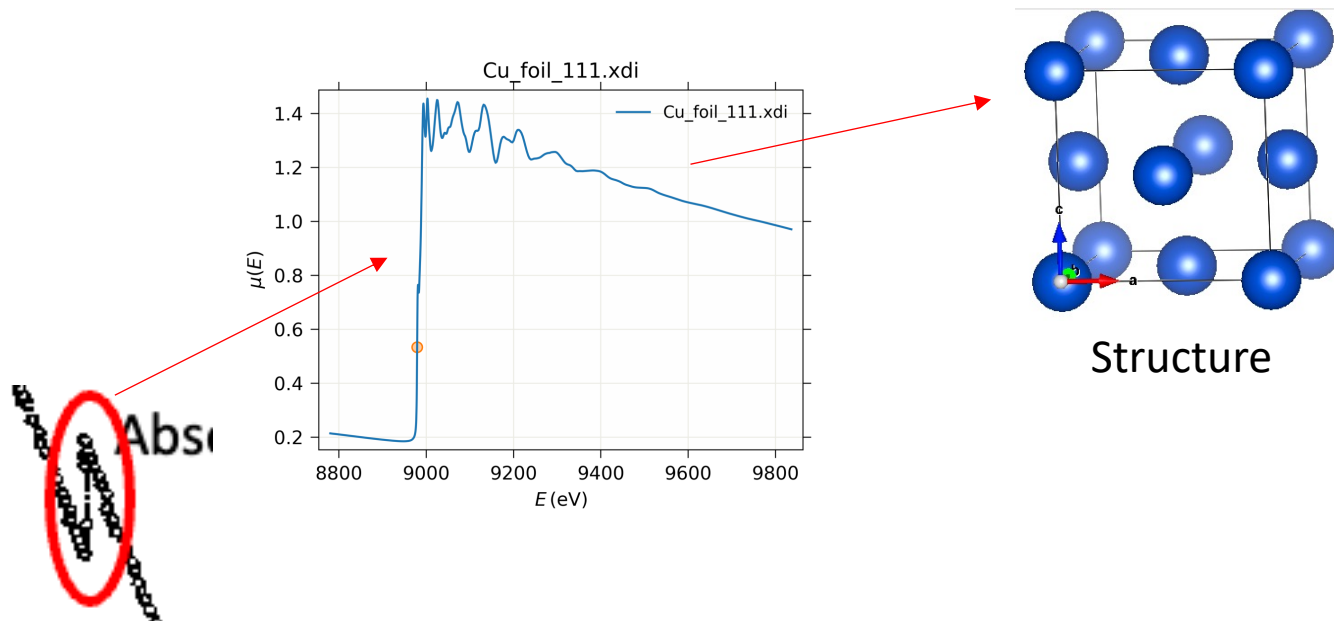
Hubbel et al. J. Phys. Chem. Ref Data **9** (1980), 1023

## General aspects

- High cross section values
- Regularly increasing with Z
- No need of fancy isotopes
- Small samples
- No activation
- Poor penetrating power
- Risk of radiation damage

# X-RAY ABSORPTION SPECTROSCOPY

The information is retrieved from the oscillations above a core level absorption edge.



## Local parameters

- Nature of ligands
- Number of ligands (10%)
- Interatomic distances (1%)
- Site symmetry
- Valence state

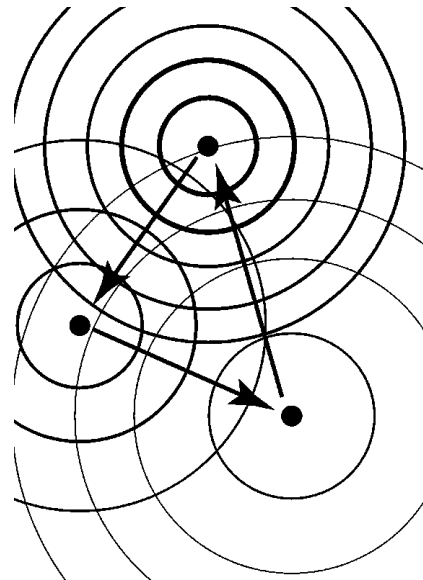
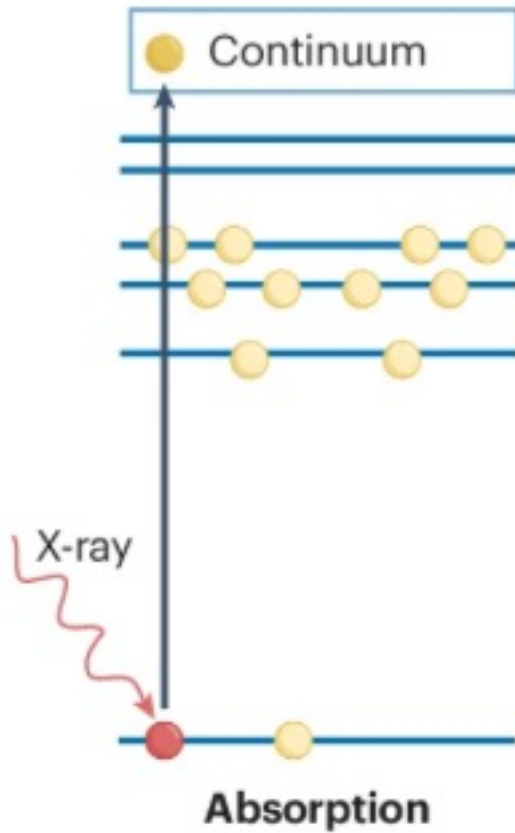
## Good News

- Applicable to most elements
- Any condition (T, P, ..)
- No need of LRO
- Bad news
  - Need a synchrotron
  - Radiation damage
  - Challenging data analysis

# X-RAY ABSORPTION SPECTROSCOPY

$$W_{if} = \frac{2\pi}{\hbar} |\langle f | \hat{H}_{Int} | i \rangle|^2 \rho(E_f) \quad \text{Transition probabilities}$$

$$\hat{H}_{Int} = i\hbar \vec{A}(\vec{r}) \cdot \vec{p} \quad \text{Electron - photon interaction Hamiltonian}$$

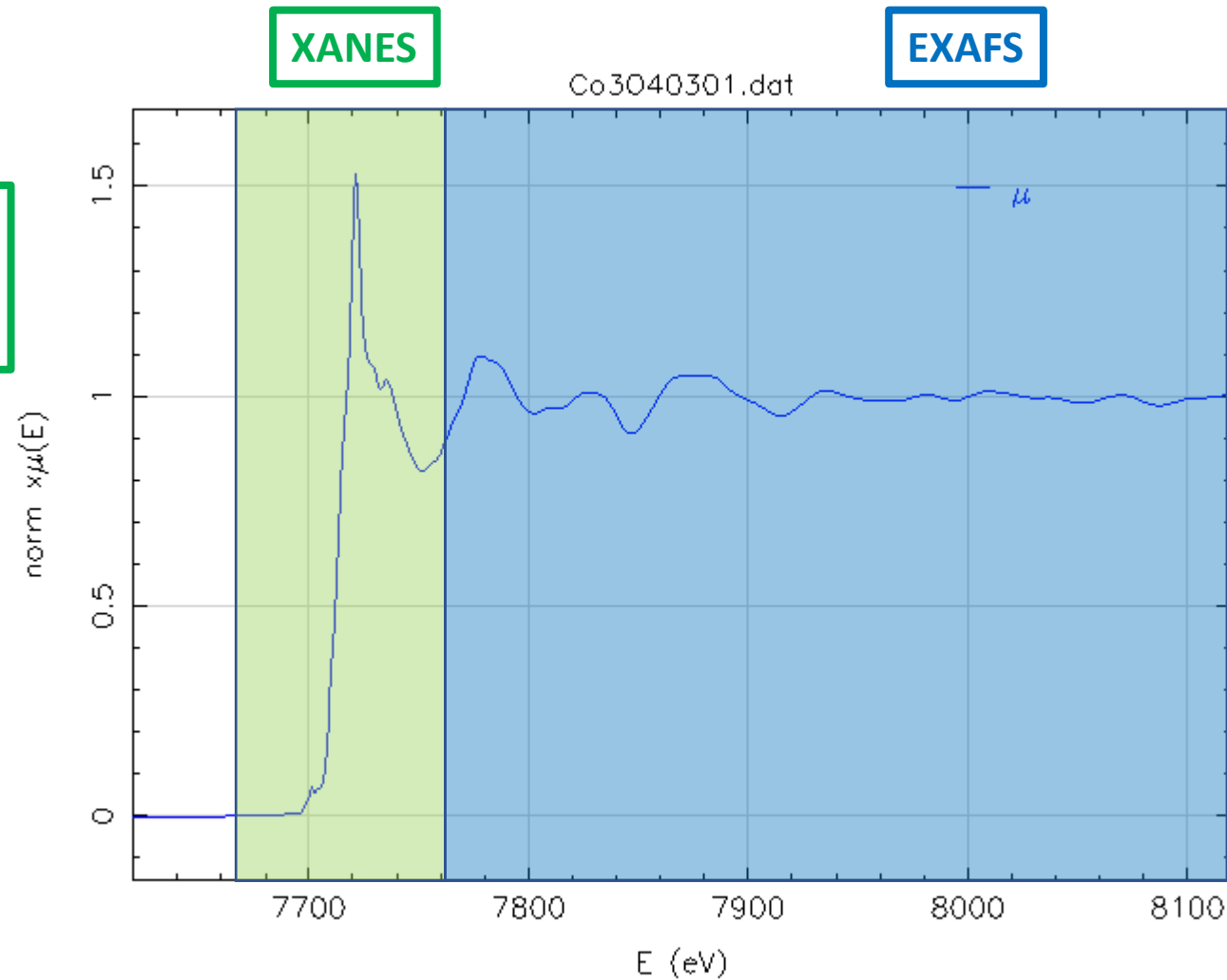


$|i\rangle$  1s, 2s 2p states, (K, L<sub>I</sub>, L<sub>II</sub>, ... edges)  
Almost a Dirac  $\delta$  function.

$\langle f|$  Outgoing spherical wave in case of isolated atom  
Sum of partially reflected waves in condensed systems

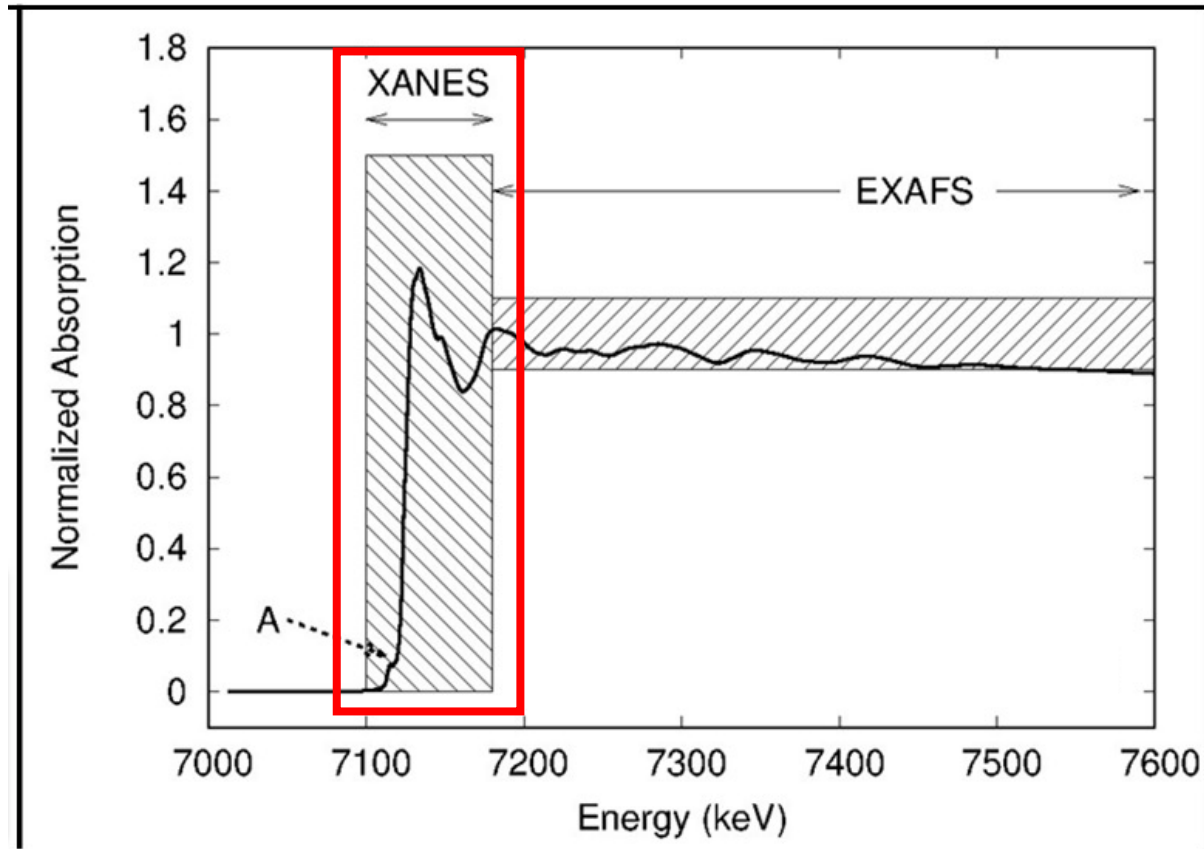
# XANES & EXAFS

**XANES**  
Low E photoelectrons  
 $\lambda_{\text{phel}} > R_{\text{interatomic}}$



**EXAFS**  
High E photoelectrons  
 $\lambda_{\text{phel}} < R_{\text{interatomic}}$

# EXAFS



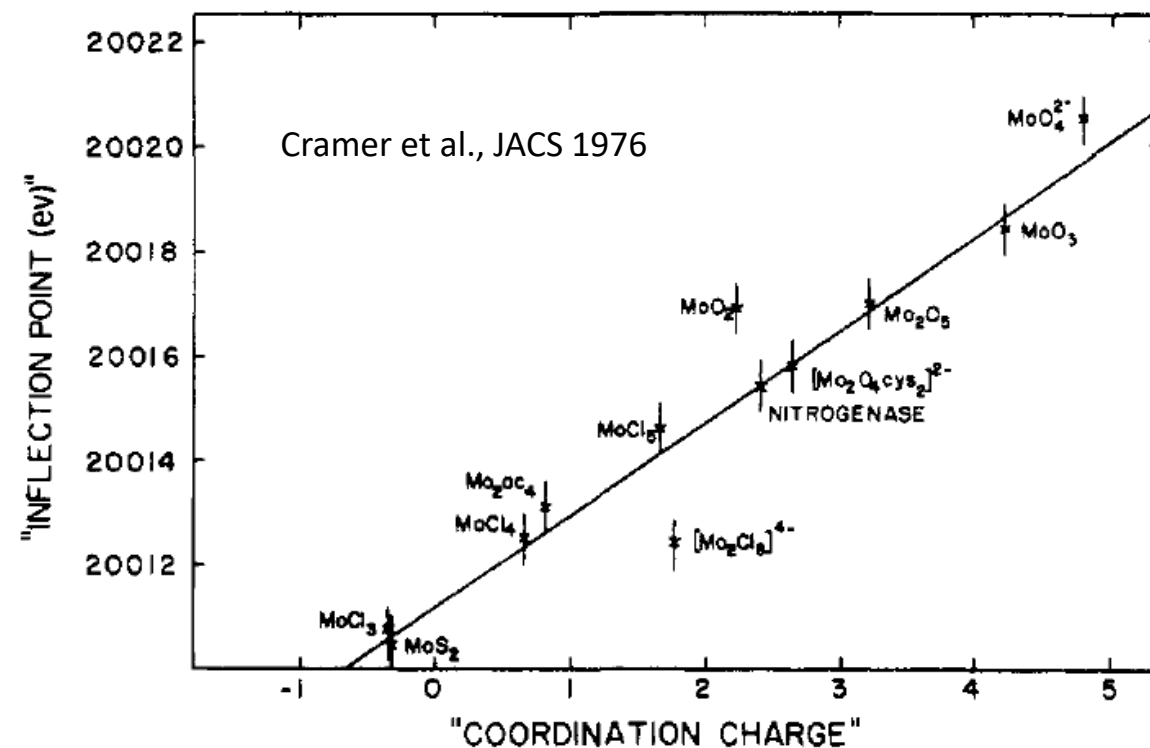
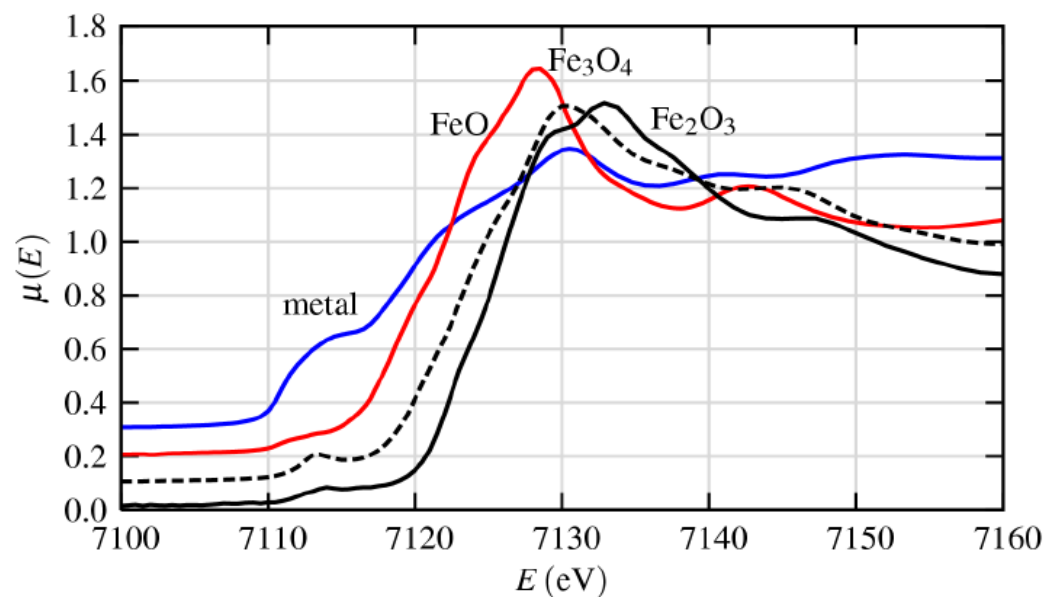
## XANES region

- Qualitative info
- Valence state
- Local symmetry
- Local electronic structure

# VALENCE STATE FROM XANES

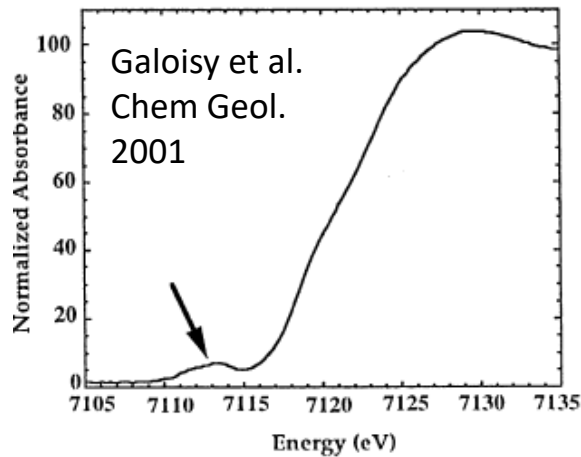
The valence state can be estimated from the edge position

M Newville "Fundamentals of XAFS"

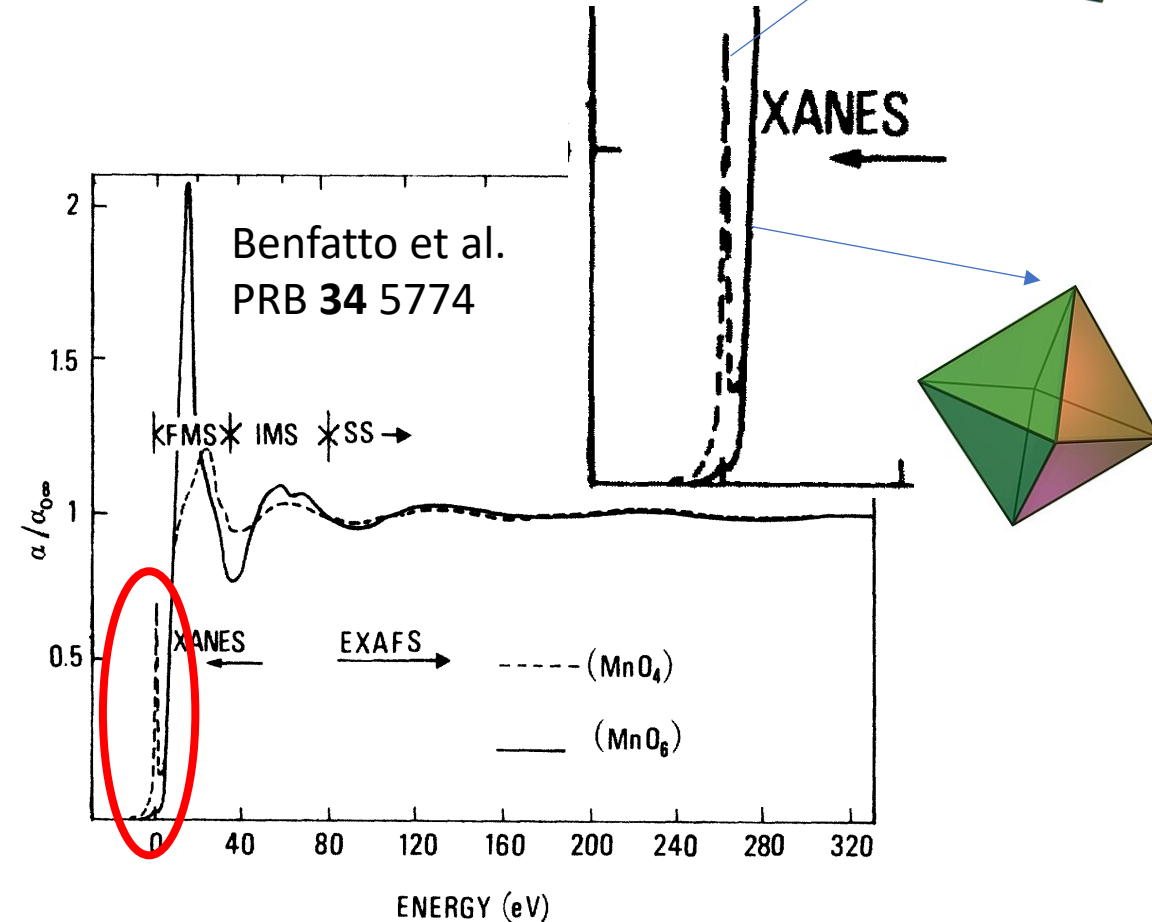


# LOCAL SYMMETRY FROM XANES

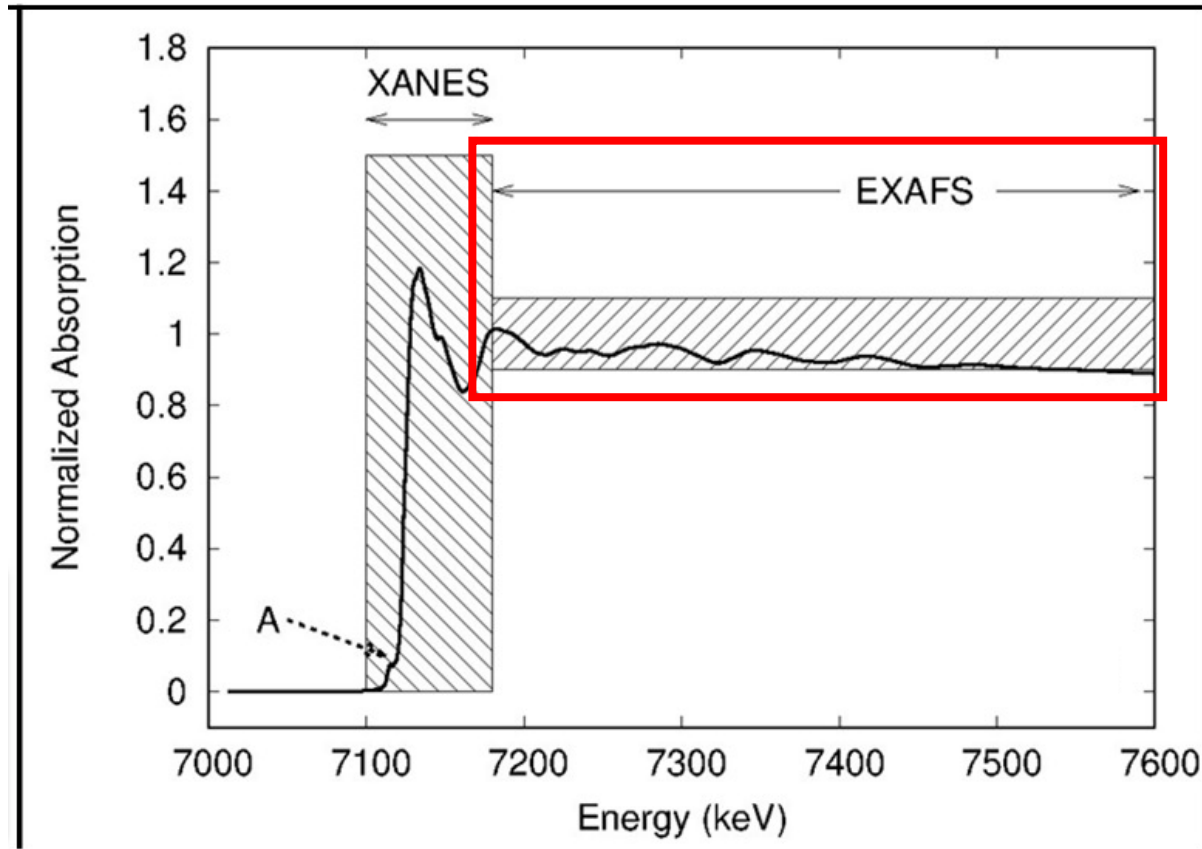
The local symmetry can be derived from the analysis of the **pre-edge peaks**



- They appear on the K edge of 3d metals
- Due to 1s-3d (semi-forbidden) transitions
- Well visible in non-centrosymmetric environments



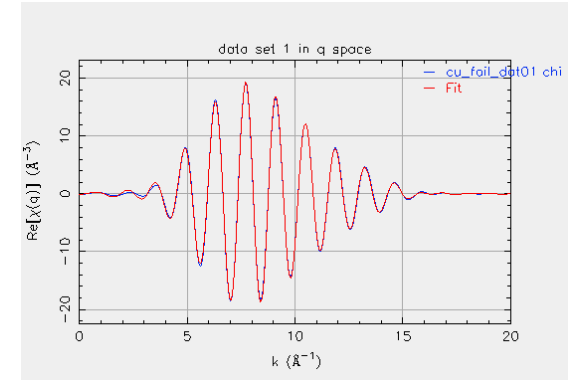
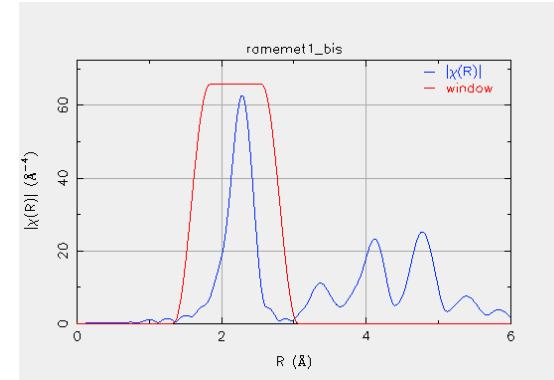
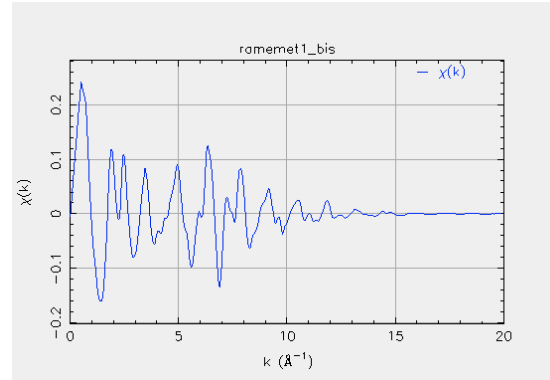
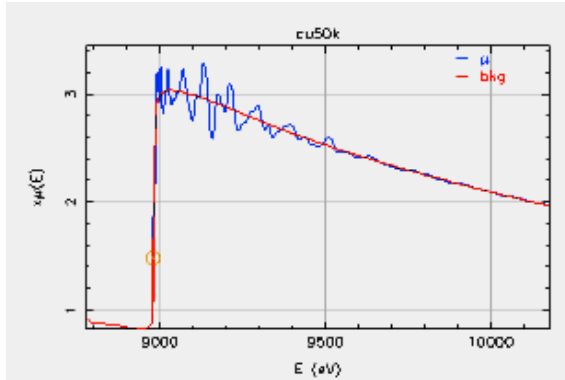
# EXAFS



## EXAFS region

- Quantitative info
- Nearest neighbours' nature (different rows of the Per. Table)
- Nearest neighbours' number ( $\pm 10\%$ )
- Interatomic distances ( $\pm 1\%$ )
- Debye-Waller factors ( $\pm 20\%$ )

# EXAFS



$$\chi(k) = S_0^2 \frac{N}{kR^2} f_{eff}(k) e^{\frac{-2R}{\lambda}} \sin(2kR + \phi_{tot}(k)) e^{-2k^2\sigma^2}$$

Structural Fitting parameters  
Functions calculated ab initio

# SUGGESTIONS FOR FURTHER READING

- C. Chantler, G. Bunker, P. d'Angelo, S. Diaz-Moreno, Nature Reviews Methods Primers 2024, 4, 89.
- P.A.Lee, P.H.Citrin, P.Eisenberger and B.M.Kincaid, Rev. Mod. Phys. **53** (1981), 769.
- C.R.Natoli, M.Benfatto, J. de Phys. Colloques **C8** (1986), C8-11.
- A. Filipponi, A di Cicco, C.R.Natoli, Phys. Rev. **B52**, (1995), 15122.
- J.J.Rehr & R.C.Albers, Phys.Rev **B41**,(1990), 8139, Rev.Mod.Phys. **72**,(2000), 621
- S.I.Zabinsky, J.J.Rehr, A.Ankudinov, R.C.Albers, M.J.Eller, Phys.Rev **B52** (1995), 2995.
- A.L.Ankudinov, B.Ravel, J.J.Rehr, S.D.Conradson, Phys.Rev. **B58** (1998), 7565.
- P.A.Lee, G.Beni, Phys.Rev. **B15** (1977), 2862.
- M. Newville, P.Livins, Y.Yacoby, J.J.Rehr, E.A.Stern, Phys. Rev. **B47** (1993), 14126.
- M. Newville, B. Ravel, D. Haskel, J. J. Rehr, E. A. Stern, and Y. Yacoby, Physica B **208&209**, p154-155 (1995).
- A. Poiarkova, J.J.Rehr Phys Rev B **59** (1999), 948.
- E. Sevillano, H.Meuth, J.J.Rehr Phys Rev B **20** (1979), 4908.
- P. Eisenberger, G.S.Brown, Solid State Commun. **29** (1979), 481.
- G. Dalba, P.Fornasini J.Synch. Rad. **4** (1997), 243.

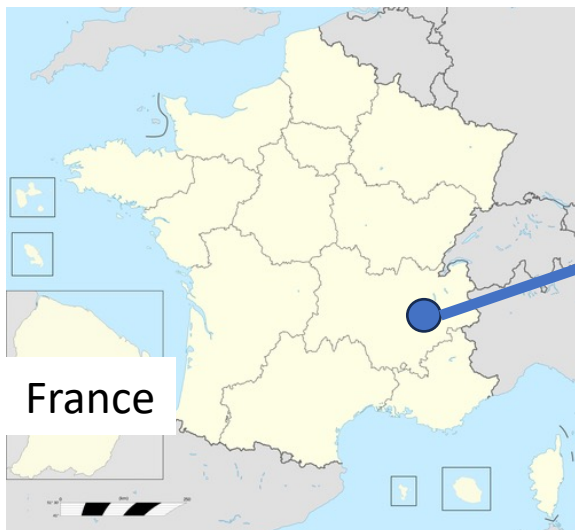
# TAKEAWAYS

- Principles of XAS
- EXAFS and XANES
- Data analysis

## The LISA beamline



# WHERE



ESRF, Grenoble



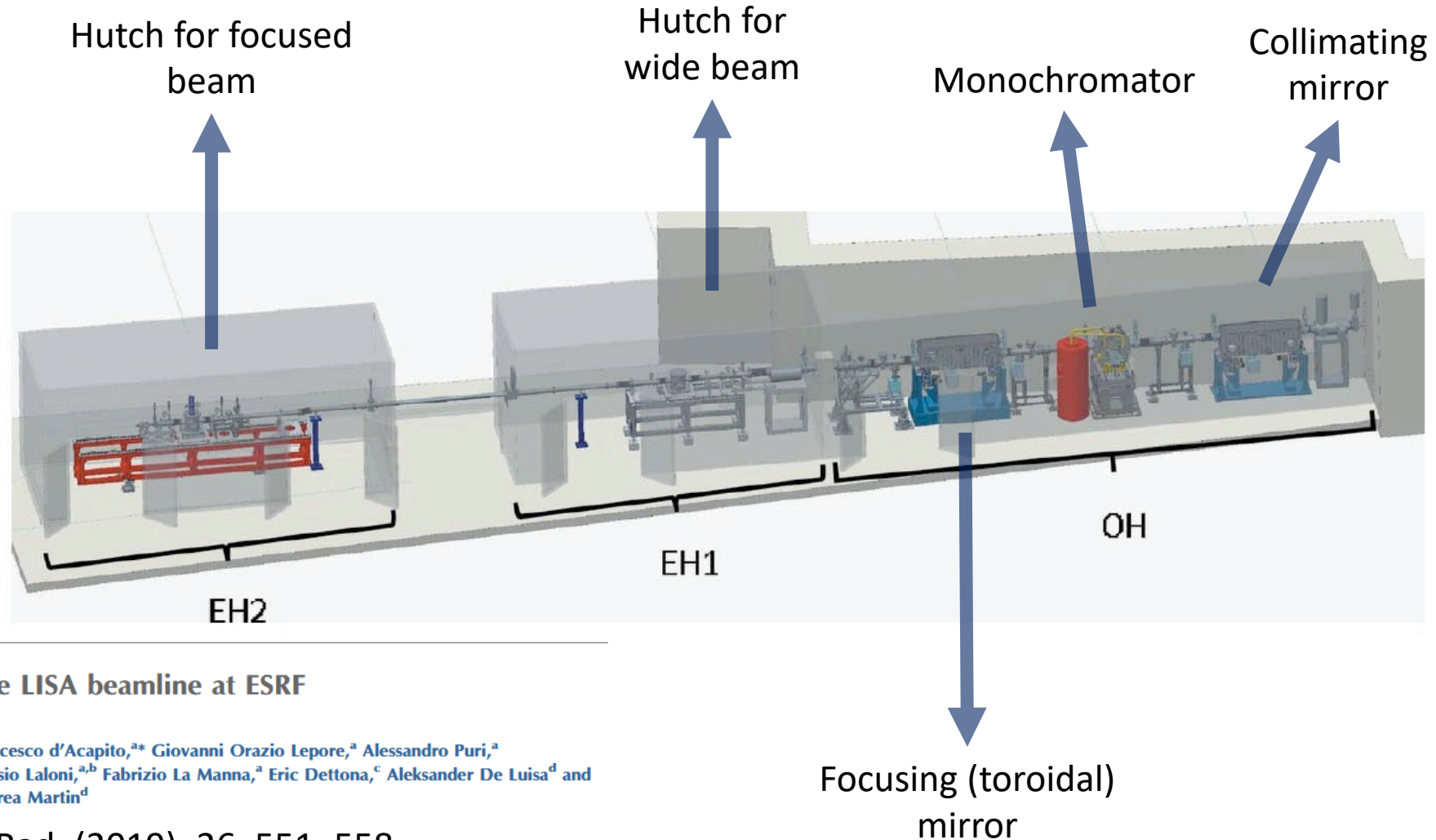
LISA



LISA is the  
italian  
beamline at  
the European  
Synchrotron



# THE LISA BEAMLINE



## The LISA beamline at ESRF

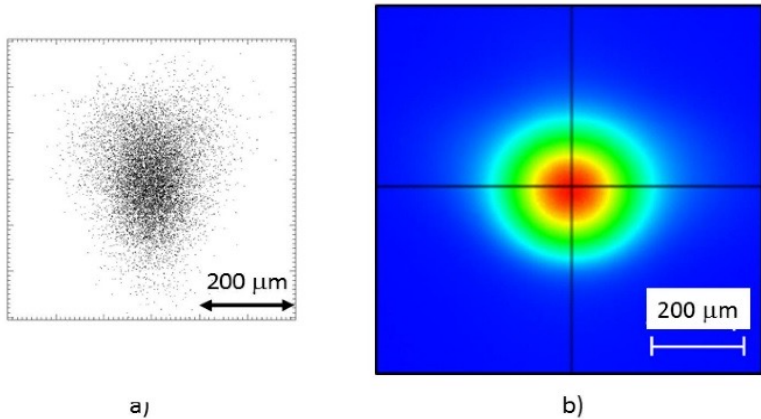
Francesco d'Acapito,<sup>a\*</sup> Giovanni Orazio Lepore,<sup>a</sup> Alessandro Puri,<sup>a</sup>  
Alessio Laloni,<sup>a,b</sup> Fabrizio La Manna,<sup>a</sup> Eric Dettona,<sup>c</sup> Aleksander De Luisa<sup>d</sup> and  
Andrea Martin<sup>d</sup>

J. Synchrotron Rad. (2019). 26, 551–558

<https://doi.org/10.1107/S160057751801843X>

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# THE LISA BEAMLINE

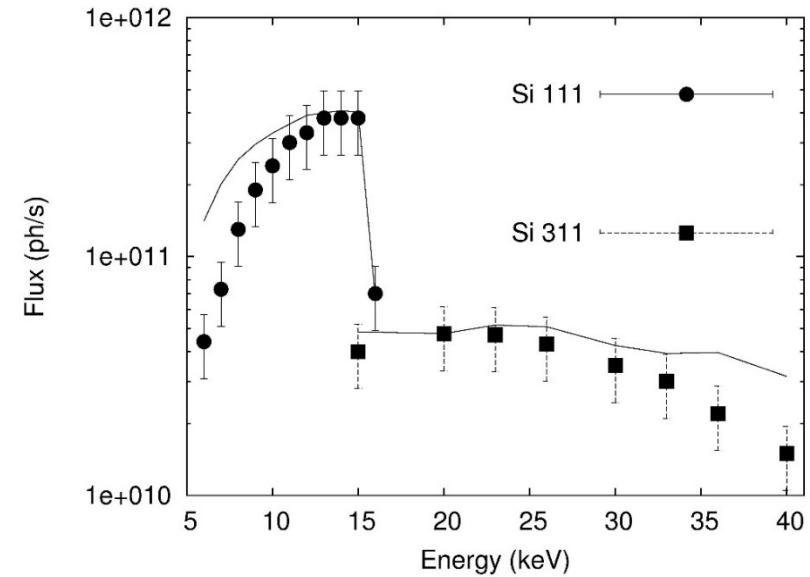


Beam shape at 10 keV , Si (111)

A] Simulation

B] Experimental data

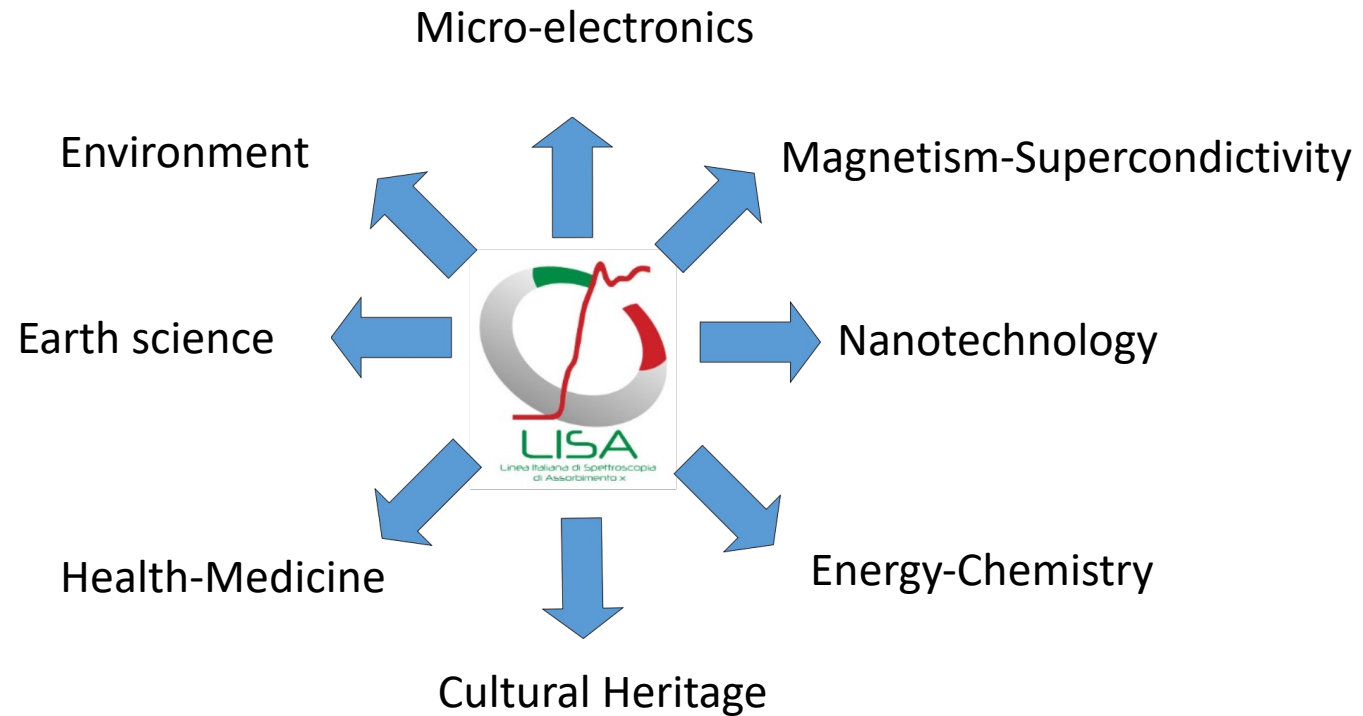
Size: 170 \* 180  $\mu\text{m}$



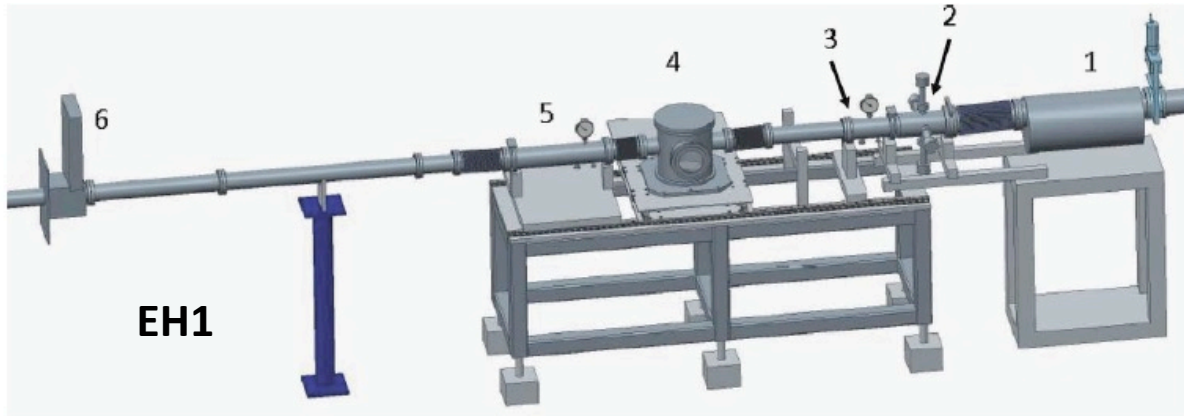
Flux on the sample in the whole energy range

(points = experiment, lines = theory)

# FIELDS OF APPLICATION



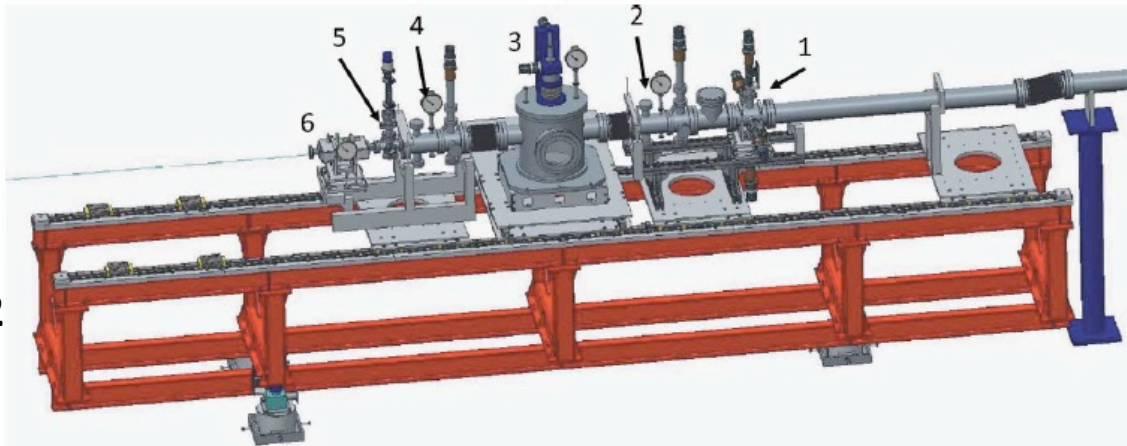
# EXPERIMENTAL HUTCHES



EH1

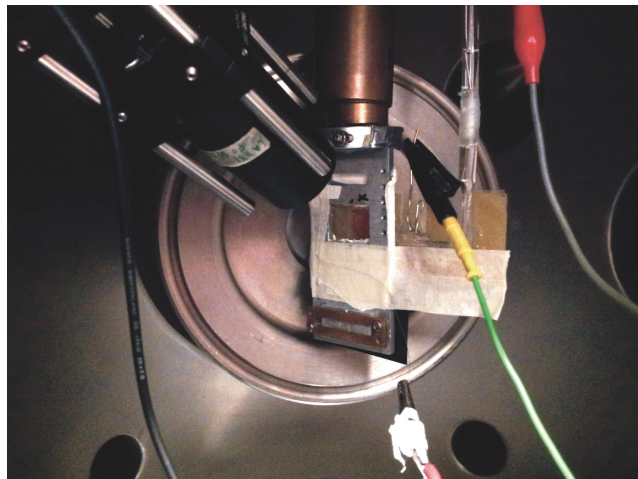
- 5m long bench
- 2 vac. chambers available
- Wide space for ancillary equipment

- Transmission mode
- Fluorescence (12elm HP-Ge + 4elm SDD)
- TEY
- ReflEXAFS
- electrochemistry
- $T$  ( $80K < T < 1000K$ )
- Controlled atmosphere
- UV pulsed source synch with machine



EH2

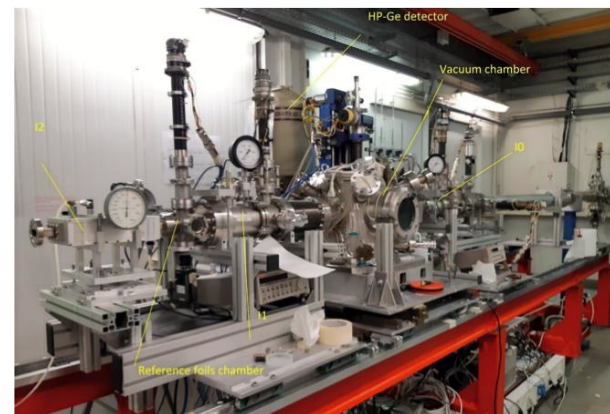
# EXPERIMENTAL APPARATA



Electrochemical cell in operando



Capillaries for liquids



Experimental bench



High Temp cell

# APPLY AT LISA

Competitive access

Peer evaluation of proposals

- ESRF quota:
  - beginning March, beginning September
  - <https://www.esrf.fr/home/UsersAndScience/Applying.html>
- CERIC quota:
  - End of march, end of september
  - <https://www.ceric-eric.eu/users/user-guide/>



# TAKEAWAYS

- Structure of the LISA beamline
- Instrumentation
- Data collection methods
- Apply for Beamtime

## Experimental examples



### Discoloration of the smalt pigment: experimental studies and *ab initio* calculations†

Ilaria Cianchetta,<sup>a</sup> Ivan Colantoni,<sup>b</sup> Fabio Talarico,<sup>\*c</sup> Francesco d'Acapito,<sup>d</sup> Angela Trapananti,<sup>d</sup> Chiara Maurizio,<sup>e</sup> Simona Fantacci<sup>f</sup> and Ivan Davoli<sup>b</sup>

Received 10th November 2011, Accepted 6th September 2012

DOI: 10.1039/c2ja30132f

**Smalt:** Co-doped potash glass (very basic).

Co<sup>II</sup> ions, blue hue

Tetrahedral environment

**Degradation** to grey color  
with time (and humidity).

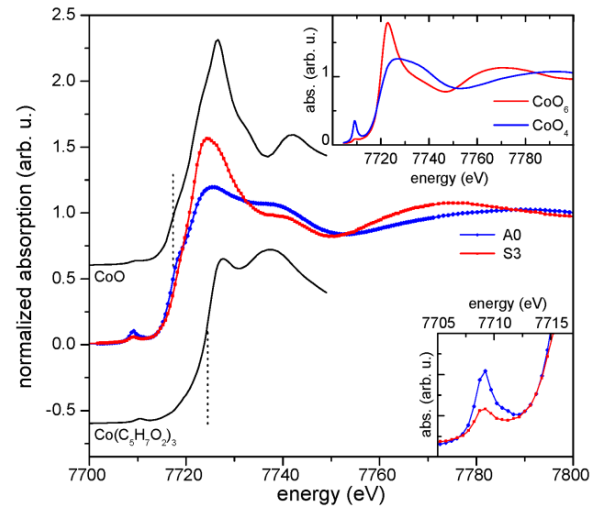
**Process:**

K moves out from the glass grains. Loosing K  
the glass becomes acidic.

More acid environment: Co switches to  
octahedral sites

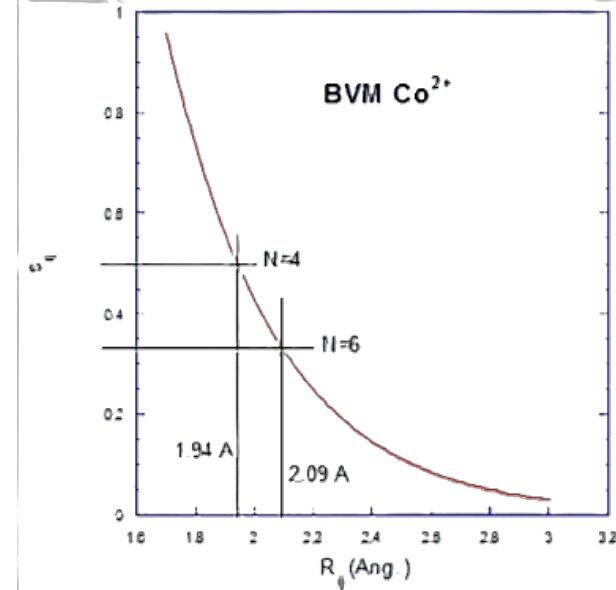
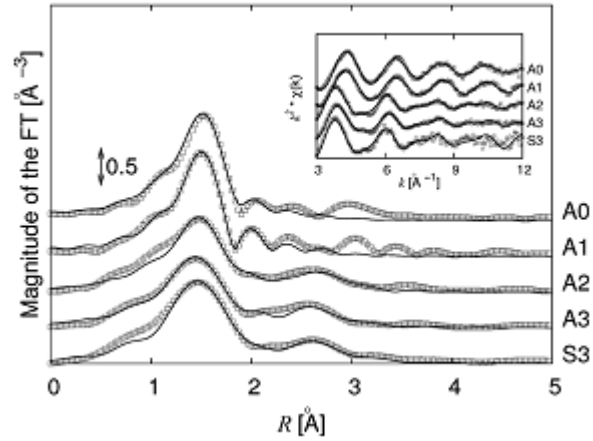


# SMALT DISCOLORATION - XAS

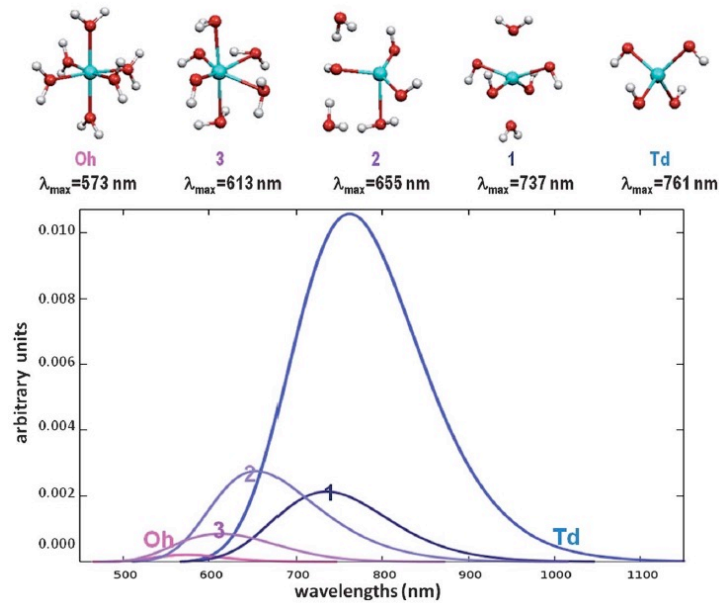


**Table 3** Results of the quantitative analysis of

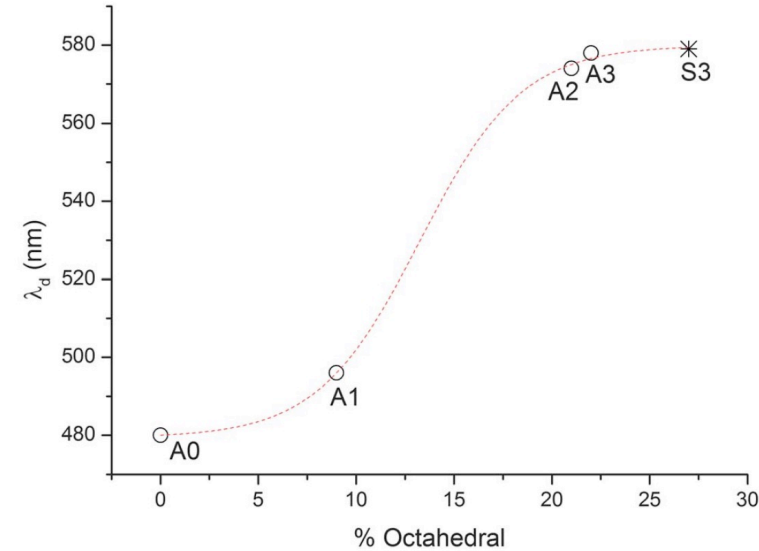
Sample	$x_{\text{oct}}$ ( $\pm 0.05$ )	$R_{\text{tet}}$ ( $\text{\AA}$ ) ( $\pm 0.02$ )	$R_{\text{oct}}$ ( $\text{\AA}$ ) ( $\pm 0.03$ )	$\sigma_{\text{O}}^2$ ( $\text{\AA}^2$ ) ( $\pm 0.00$ )
A0	0.00	1.95	—	0.004
A1	0.09	1.95	—	0.002
A2	0.21	1.97	2.14	0.003
A3	0.22	1.99	2.16	0.003
S3	0.27	1.99	2.17	0.003



# SMALT DISCOLORATION – OPTICAL RESPONSE



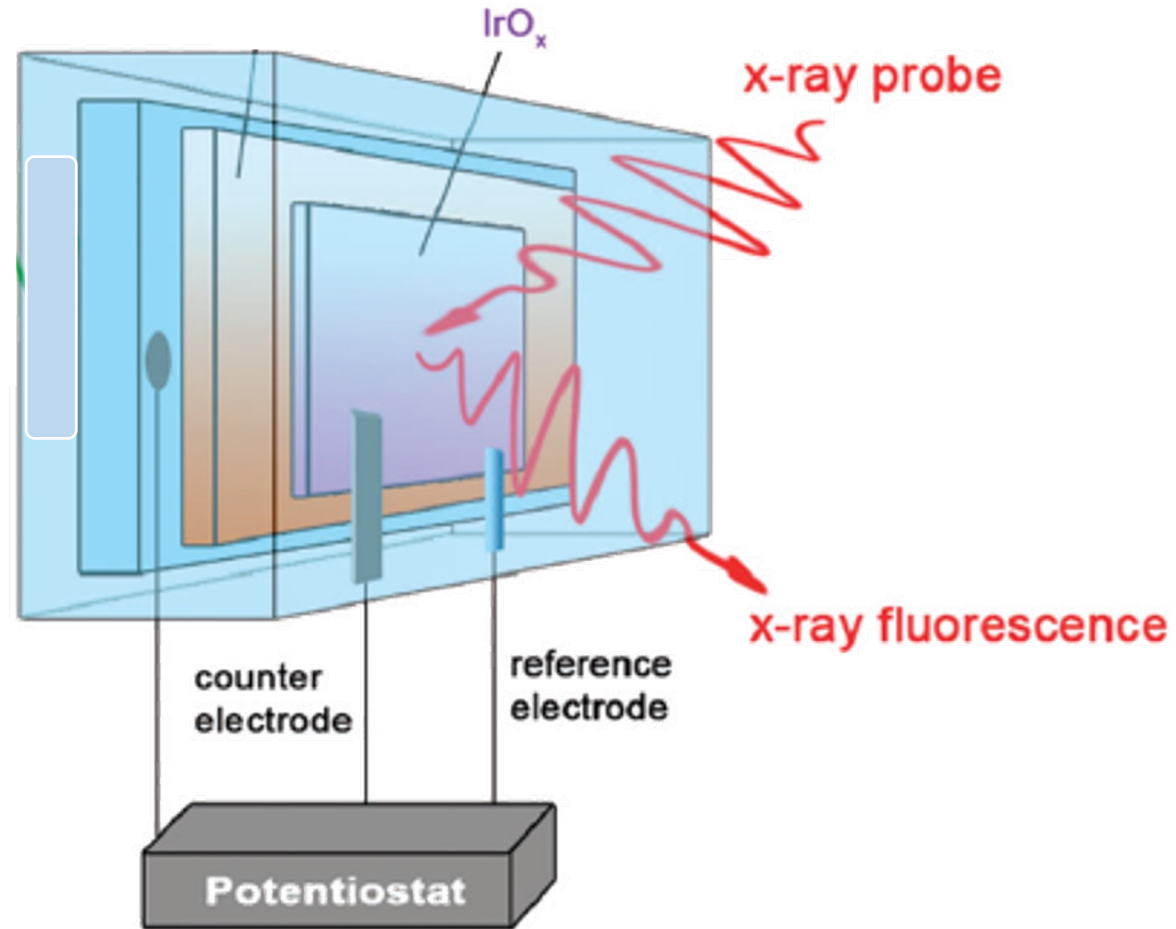
TD- DFT calculations of optical absorption spectra

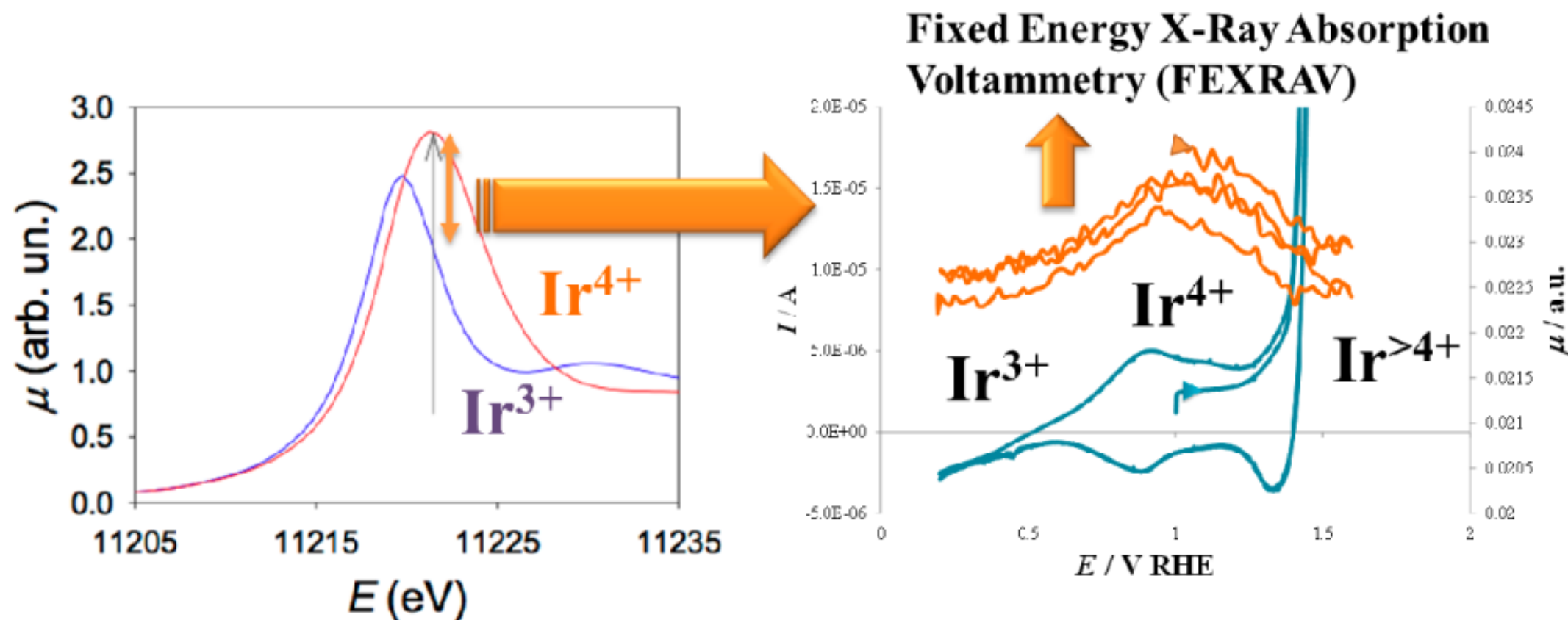


- 20% octahedral change the hue of the sample
- Absorption of pure  $O_h$  clusters too low
- Occurrence of clusters type 2 or 3.

# IRIDIUM OXIDE ELECTRODES

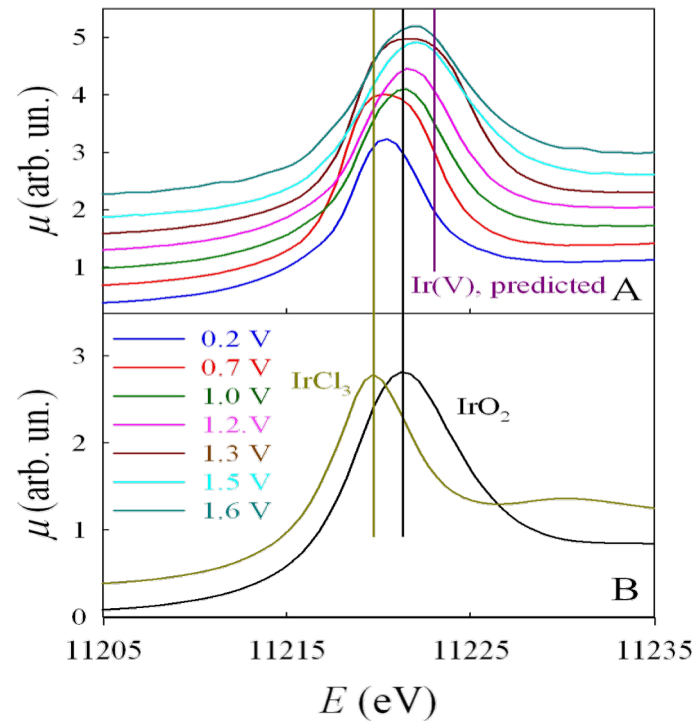
Experimental setup



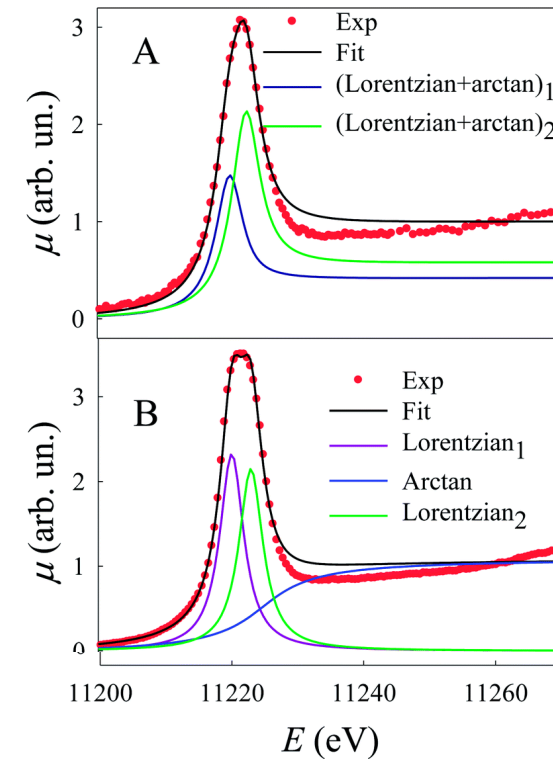


A. Minguzzi, O. Lugaresi, C. Locatelli, S. Rondinini, F. D'Acapito,  
E. Achilli, P. Ghigna, **Analytical Chemistry**, 85 (2013) 7009-7013

# XANES SPECTRA OF IR OXIDE ELECTRODES

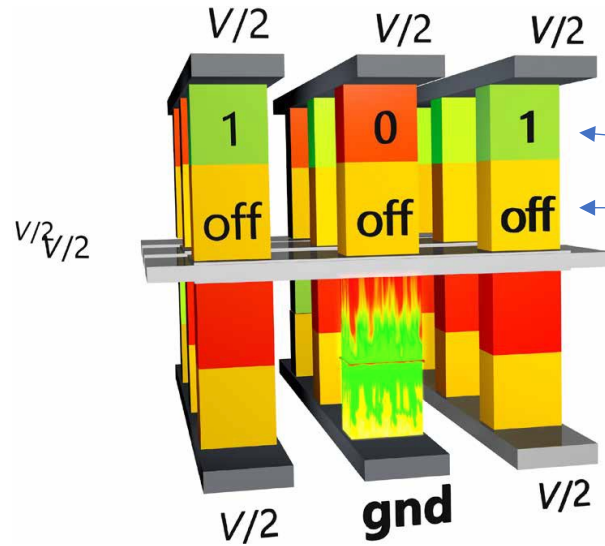


Chemical shift and broadening



Two oxidation states!

# NON VOLATILE MEMORIES

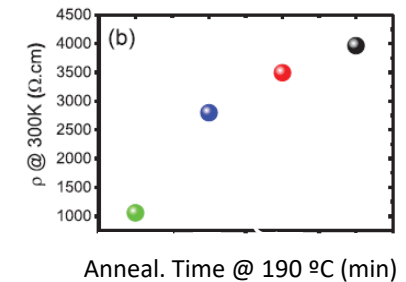
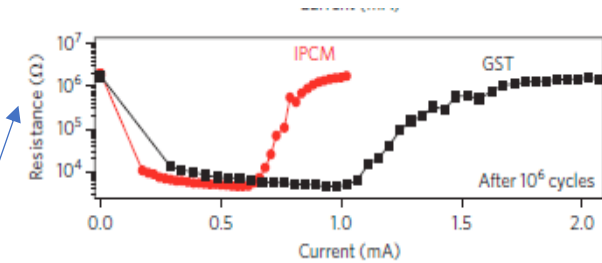


## Developing Materials for

- Non volatile memory cells
- Selectors

## Principal issues

- Set current values
- Temporal stability
- Working principles



## Goals

- Find the relation between structure, composition and best performance

# IPC-MEMORIES

IOP Publishing

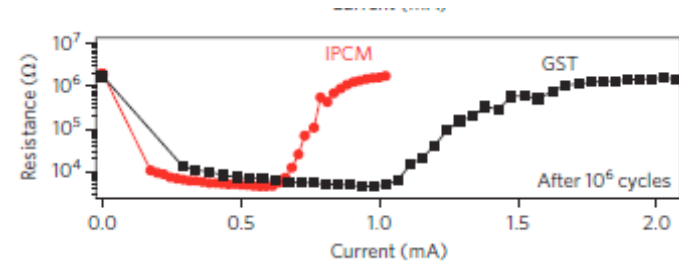
Journal of Physics D: Applied Physics

J. Phys. D: Appl. Phys. 53 (2020) 404002 (8pp)

<https://doi.org/10.1088/1361-6463/ab98c1>

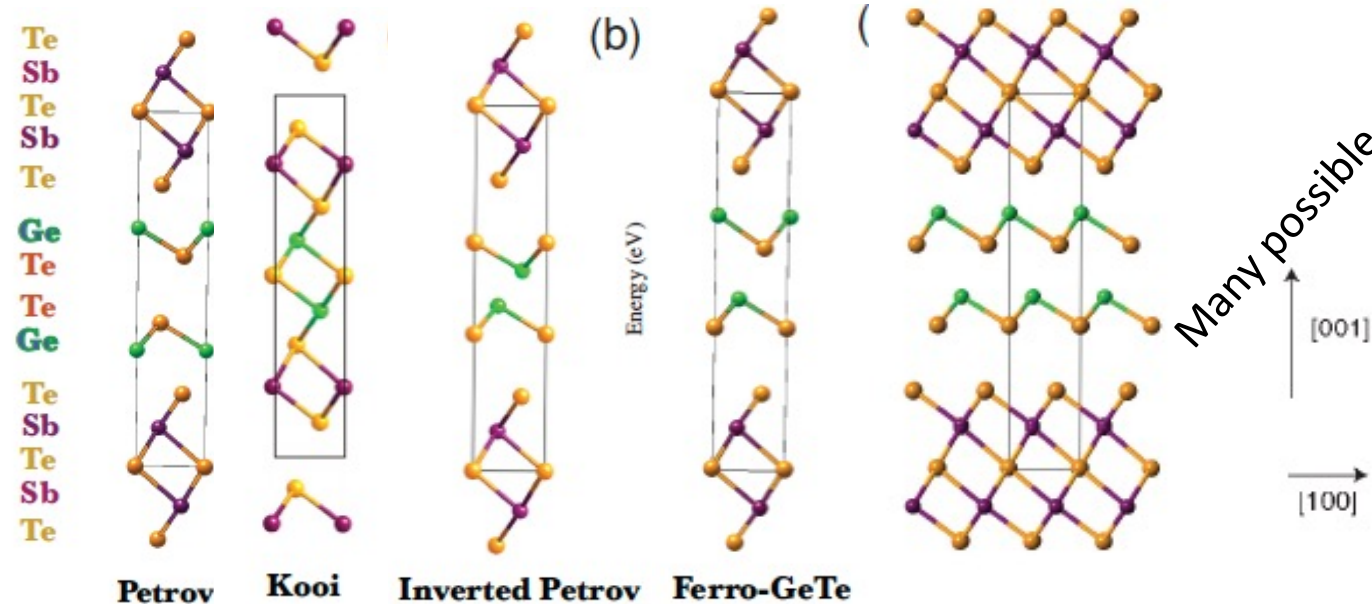
## Local structure of $[(\text{GeTe})_2/(\text{Sb}_2\text{Te}_3)_m]_n$ super-lattices by x-ray absorption spectroscopy

F d'Acapito<sup>1</sup>, P Kowalczyk<sup>2</sup>, J-Y Raty<sup>2,3</sup>, C Sabbione<sup>2</sup>, F Hippert<sup>4</sup> and P Noé<sup>2</sup>



- Promising material for PCM
- Lower switch current respect to GST

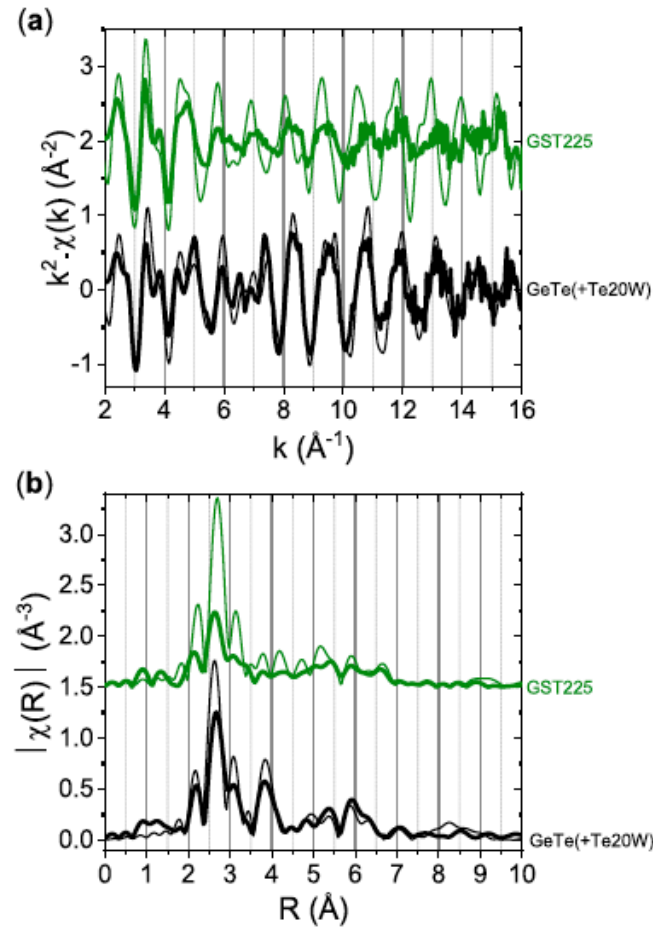
- $[(\text{GeTe})_2/(\text{Sb}_2\text{Te}_3)_m]_n$  chalcogenide super-lattices (SLs), are at the basis of interfacial Phase-Change Memory (iPCM)
- Several structural hypotheses for these materials



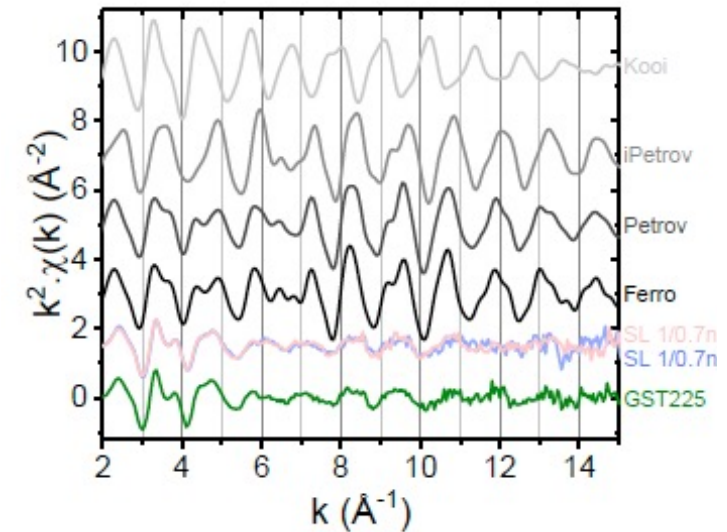
Many possible structures

# IPC-MEMORIES

- XAS Ge-K edge
- MD-DFT Ab initio simulation of XAS spectra

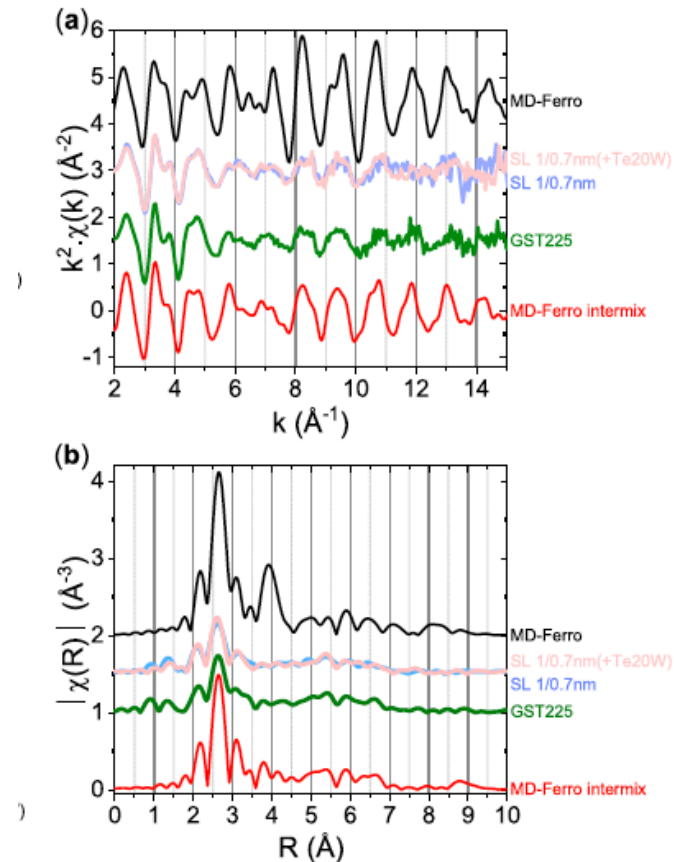


I: Comparison theoretical  
and experimental spectra  
(model compounds)



II: Comparison theoretical  
(various structures) and  
experimental spectra (samples)

# IPC-MEMORIES



II: Same as I with intermixing

## Result

- The intermixed Ferro structure is identified as that better reproducing the exp data.
- 30% GE/Sb intermixing is sufficient

# CONCLUSION

- XAS is a precious tool in materials science
  - reveals the local structure
  - nature of neighbors
  - Valence state
  - Local symmetry
- XAS applicable in many fields
  - Materials science
  - Electrochemistry
  - Cultural heritage



<https://doi.org/10.5281/zenodo.20286587>

# Thank you for your attention