Applications of X-Ray Absorption Spectroscopy in Physics and Material Science.

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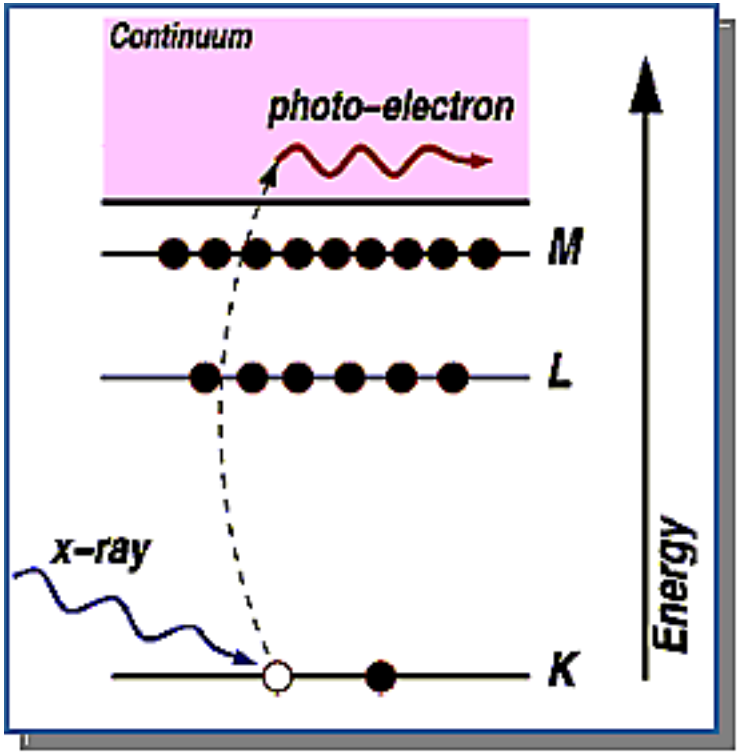
Introduction.
Experimental aspects.
Regions of the XAS spectrum. (EXAFS,XANES)
Multiple scattering description
Extended X-ray Absorption Fine Structure (EXAFS) spectra
-EXAFS formula, Fourier transform, determination of the structural parameters
Applications: Materials Science (high Tc, CMR,..), Magnetic materials,
Amorphous and liquid systems, Thin films and Surface Science. Some examples
XANES spectra (Soft and Hard X-rays)
-Information contained in XANES
-Theoretical approaches, Multiple scattering and Multiplets
- Some applications.
Related techniques
Time-resolved XAFS
Differencial EXAFS
Micro- or Nano-XAFS
X-ray magnetic circular dichroism (XMCD)
Anomalous scattering
DAFS (Diffraction anomalous Fine Structure)
Resonant X-ray scattering (RXS)

X-ray absorption process

X-rays are absorbed by all matter through the photoelectric-effect:

When the incident x-ray has an energy equal or greater than the binding energy of a core-level electron (K=1s; L_I=2s; L_{II}, L_{III}=2p, etc.), the x-ray photon is absorbed and the core electron is ejected from the atom.

The atom is left in an excited state with an empty electronic level (core hole) and any excess energy is given to the ejected photo-electron.

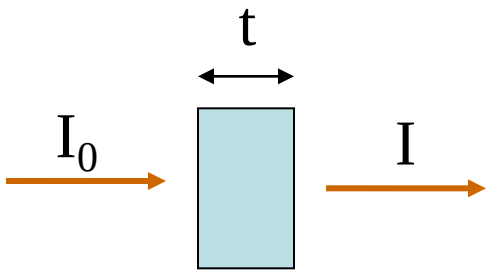


The excited core-hole will relax back to the "*ground state*" of the atom by two main mechanisms: X-ray Fluorescence, for hard x-ray regime (> 2 keV) and Auger Effect for lower energy x-ray absorption.

X-ray absorption

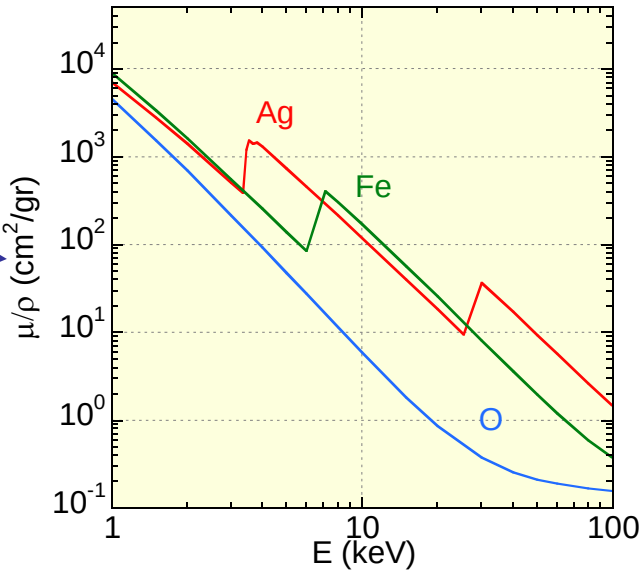
The probability that an x-ray beam passing through a material of thickness t will be absorbed is given by the *linear absorption coefficient*, μ:

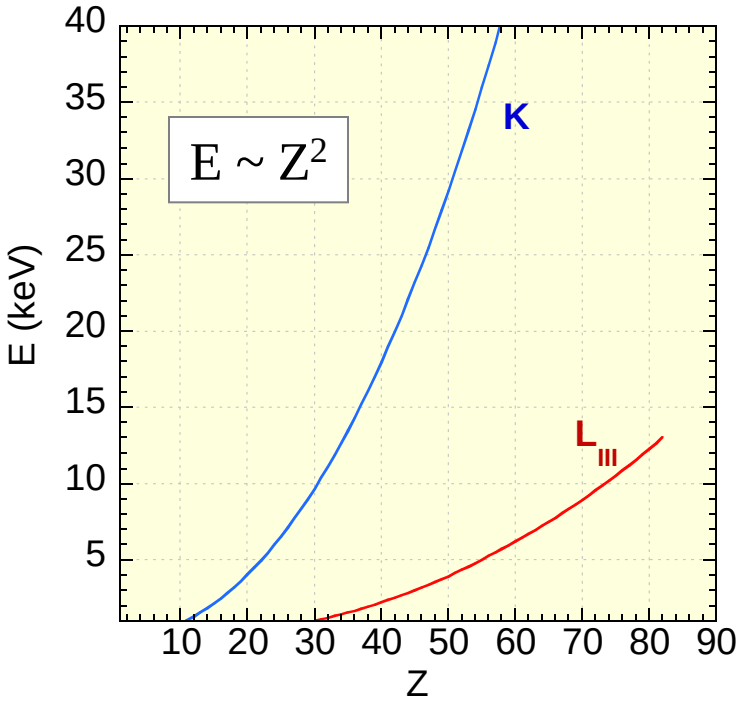
$$I = I_0 e^{-\mu t}$$



$$\mu(E) \propto Z^4 / E^3$$ +

" Absorption Edges "

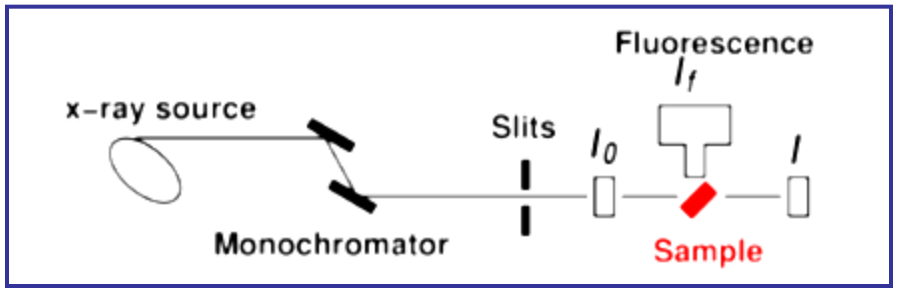


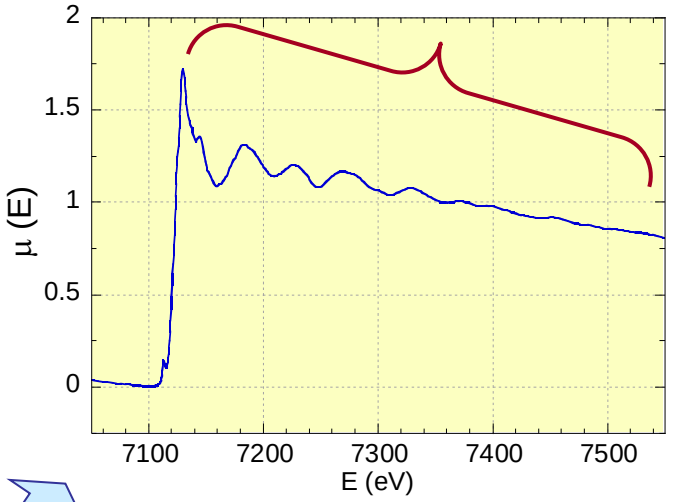


X-ray absorption measurements

XAFS measures the energy dependence of μ(E) near and above the absorption edge of a selected element.

X-ray absorption fine structure ?





Transmission: The intensity transmitted through the sample is measured (direct method)

$$\mu(E)t = \ln(I_0/I)$$

Fluorescence / Total-electron yield: The fluorescence x-ray or the electron emitted is measured (indirect methods)

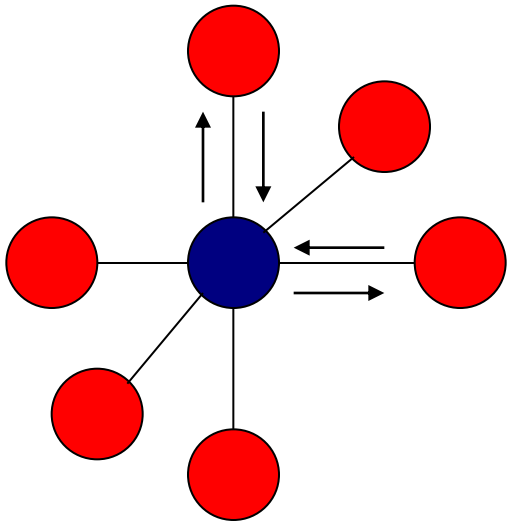
$$\mu(E) \sim I_f / I_0$$

Multiple scattering description.

Absorption coefficient can be factorized in an atomic part and a term which represents the scattering of the photoelectrons by the sourronding atoms

$$\mu(E) = \mu_0(E)\,(1 + \Sigma\, \chi_n(E))$$

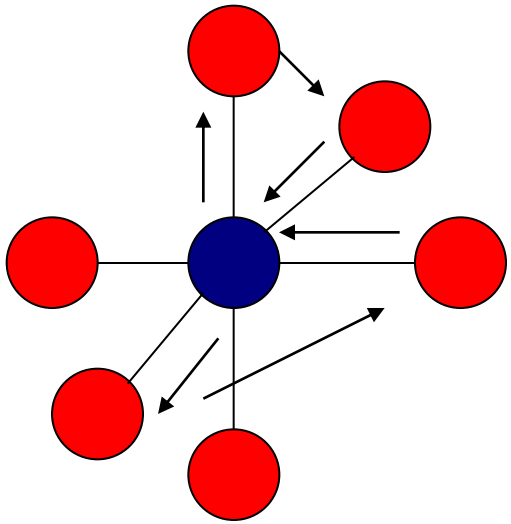
EXAFS



n= 2

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E_0)}$$

XANES

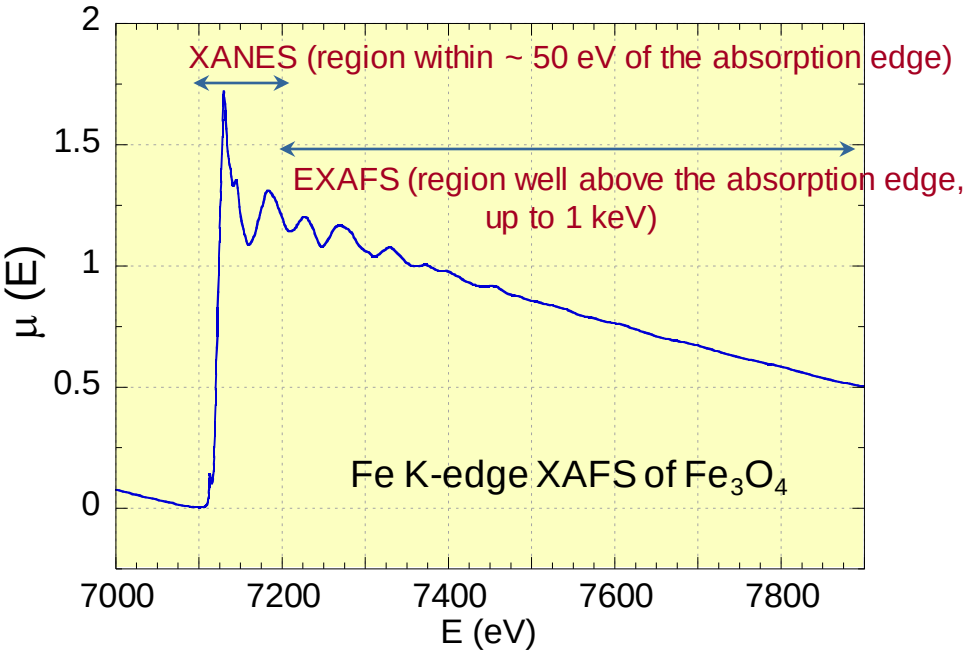


n> 2

X-ray Absorption Fine Structure (XAFS) is the modulation of an atom's x-ray absorption coefficient at energies near and above an x-ray absorption edge due to the chemical and physical state of the atom. XAFS is also referred to as X-ray Absorption Spectroscopy (XAS) and is divided into two regions:

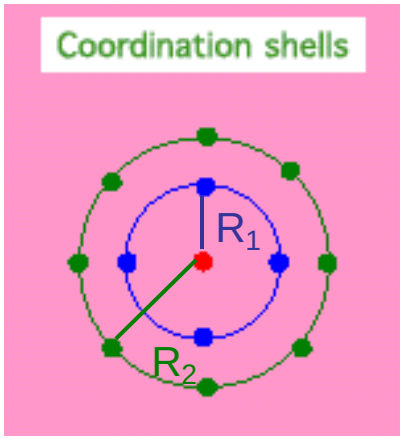
XANES	X-ray Absorption Near Edge Structure
EXAFS	Extended X-ray Absorption Fine Structure

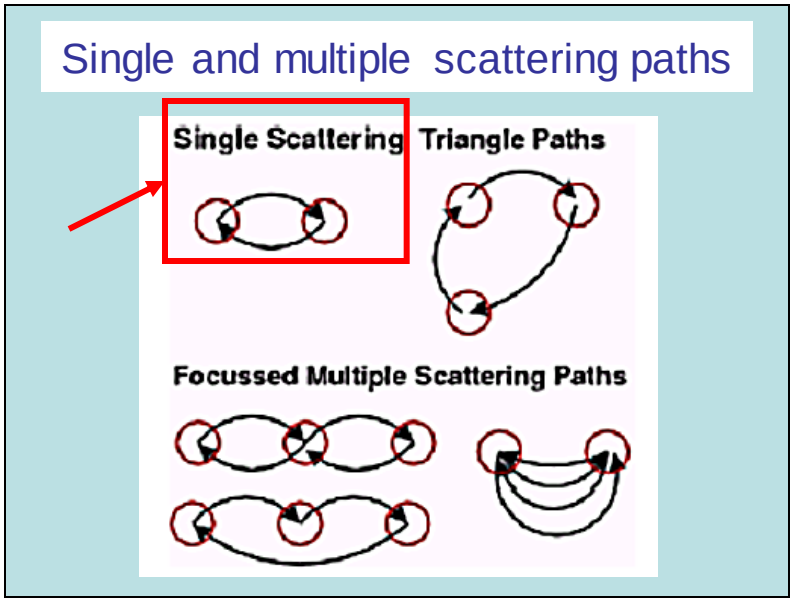
which contain related but slightly different information about the atom's local structural environment and electronic state.



XAFS Capabilities :

- local atomic probe (short-range order)
- composition/coordination
- chemical/oxidation state
- applies to any element/any phase (gas, liquid, crystalline, amorphous ...)
- minimal sample requirements (low concentrations, wide range of sample environments [T, P, H, vacuum, "in situ"...])



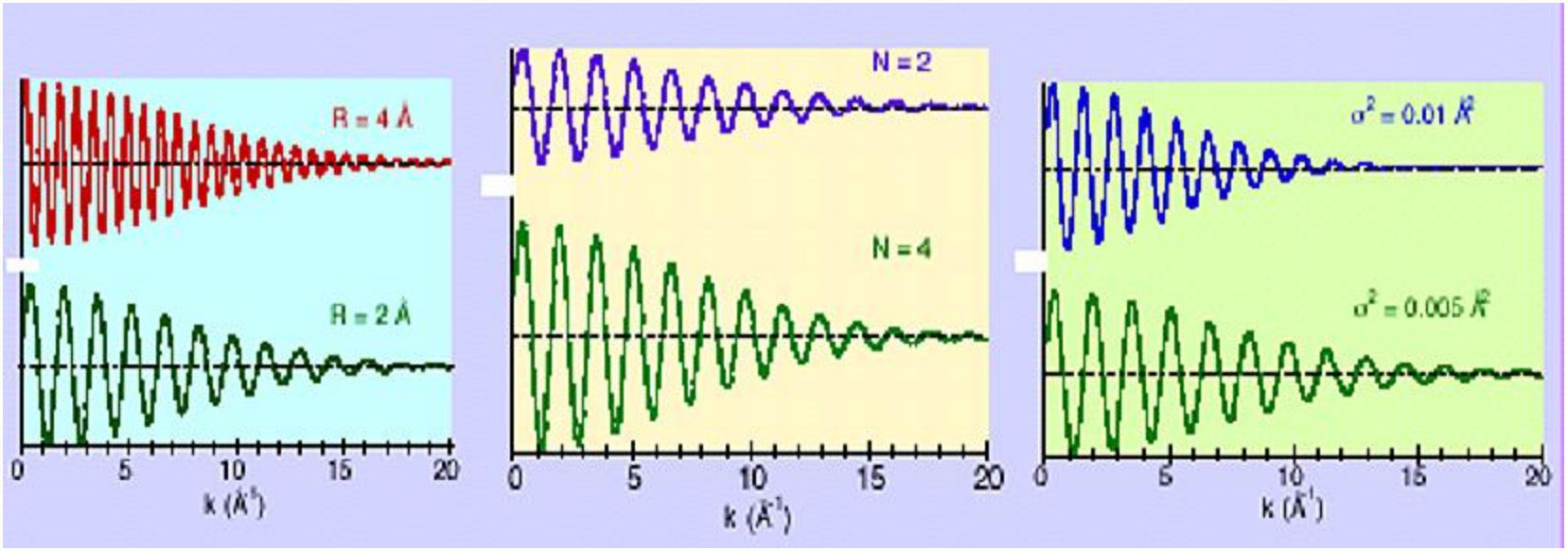


$$\chi(k) = \sum_j \frac{S_0^2 N_j f_j(k,\pi) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \sin(2kR_j + \delta_j(k))$$

Amplitude reduction term

Photo-electron mean-free path (including core-hole lifetime)

Thermal and static mean-square disorder in R

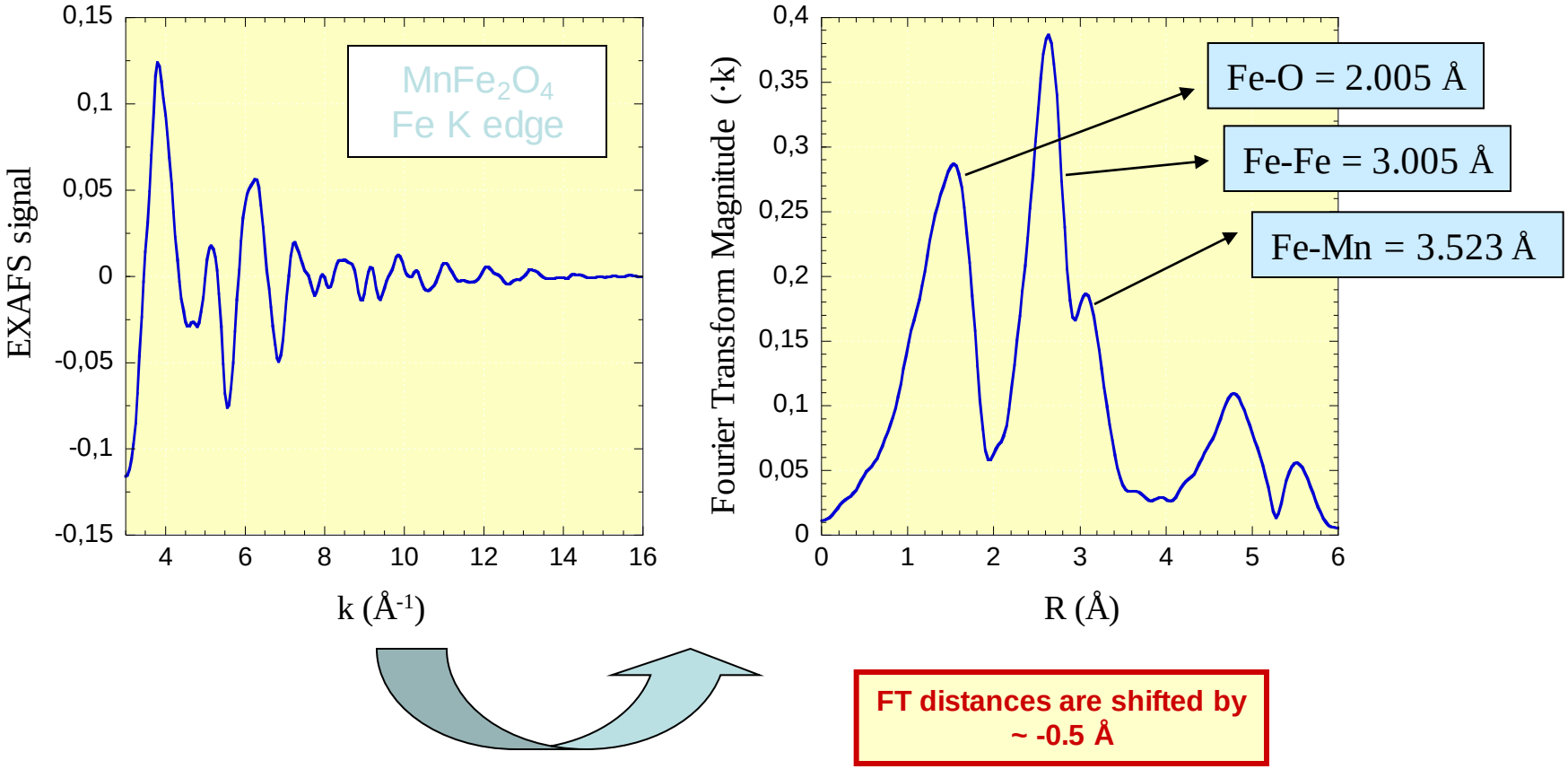


Frequency → Interatomic distance R

Amplitude → Coordinaction number N

Damping → Debye-Waller factor σ^2 (disorder)

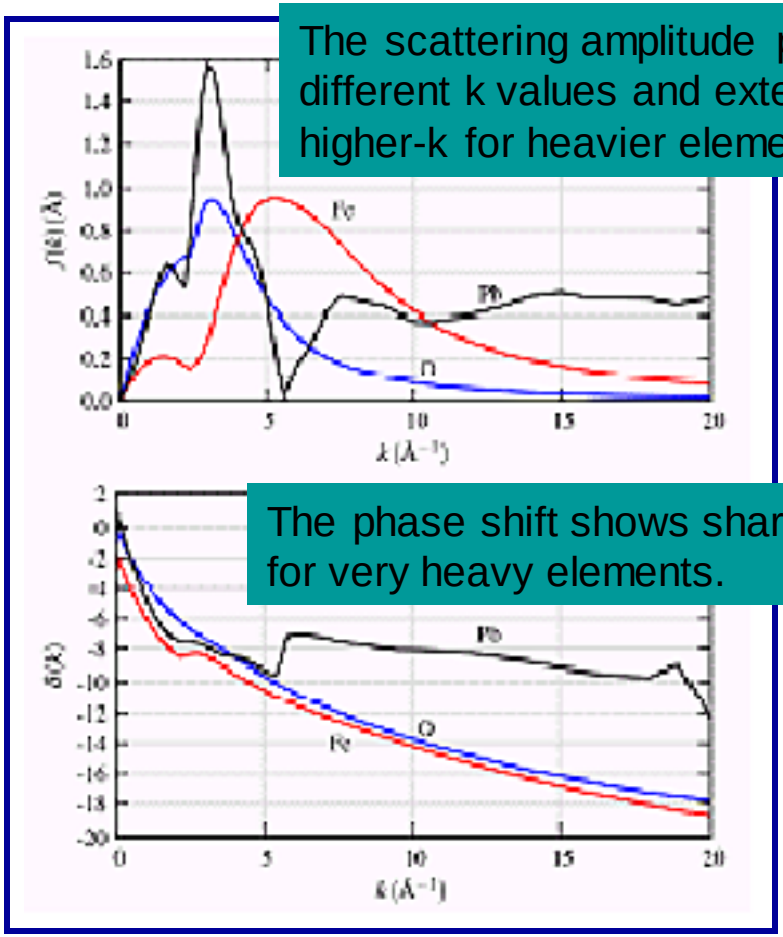
Fourier transformation can be used to descompose a frequency-space signal into its different constituent frequencies. The Fourier transform of an EXAFS spectrum gives a pseudo-radial distribution function.



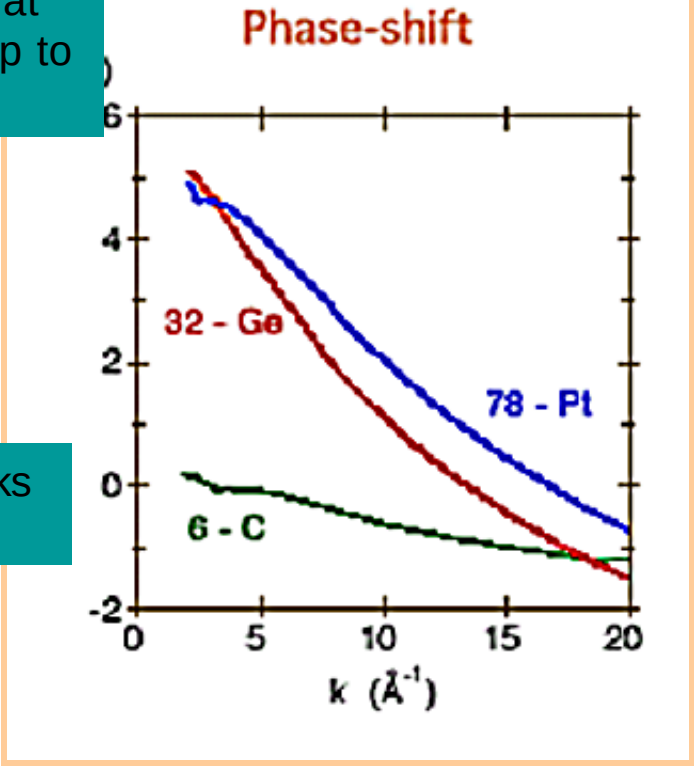
Back-scattering

Central-atom

The scattering amplitude peaks at different k values and extends up to higher-k for heavier elements.



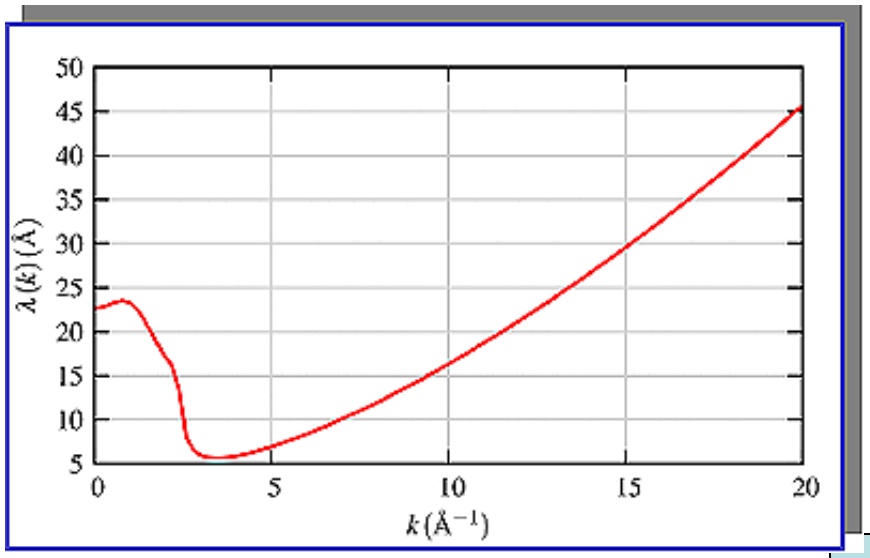
The phase shift shows sharp peaks for very heavy elements.



[Calculated by Feff 6.01]

The photo-electron mean-free path $\lambda(k)$ limites how far the photo-electron can go:

- Inelastic scattering
- Core-hole finite life-time



The mean-free path λ depends on k

λ < 25 Å for the EXAFS k-range

The term $\dfrac{e^{-2R_j/\lambda(k)}}{R_j^2}$ makes EXAFS a local atomic probe,

typically within 10 Å from the absorber

EXAFS Accuracy

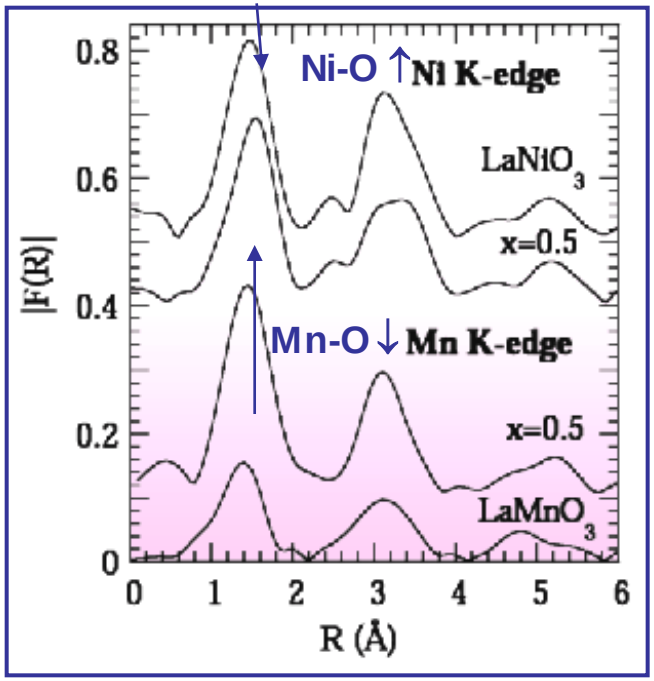
Distances	±0.01Å	The absorber–scatter distance can be measured quite accurately from the frequency of the sinusoidal oscillations.
Coordination numbers		
Debye-Waller factors	± 20-25%	High correlation between them ↔ less accurate
Scattering Atom	Z ± 1 (Z=6-17) Z ± 3 (Z=20-35)	Elements that are next to each other in the periodic table has barely distinguishable photoelectron scattering characteristics. Thus, C,N and O are impossible to distinguish and metal scattered can only be placed in the proper row of the periodic table.

Examples: Local structure in $LaNi_{1-x}Mn_xO_3$

The crystallographic structure evolves from *orthorhombic* ($LaMnO_3$) to *rhombohedral* ($LaNiO_3$)
For intermediate x, solid solution with Mn/Ni at same crystallographic site

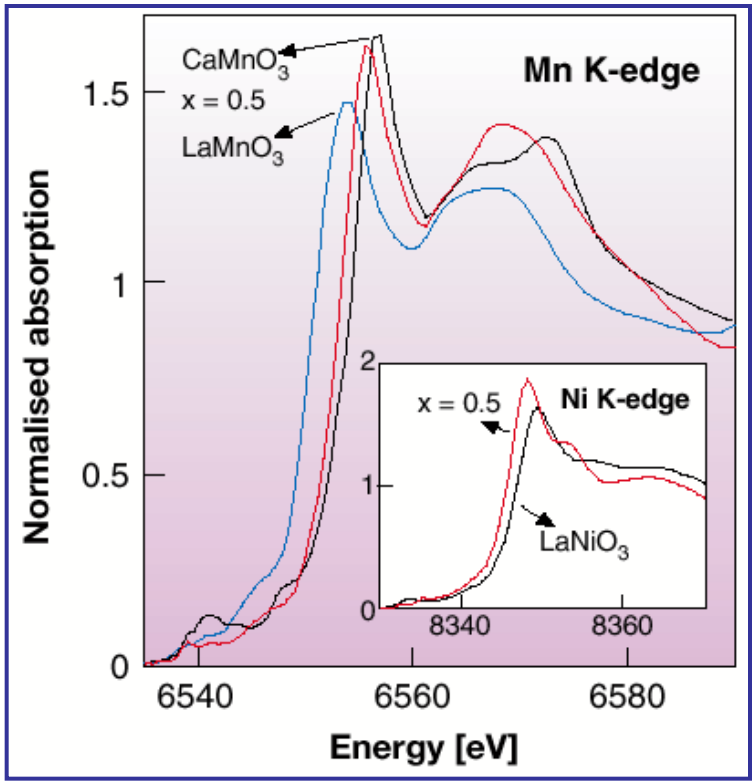
~~Diffraction~~ → XAFS ✓

(a) Local environment around each transition-metal ?



Contraction MnO_6 ⇔ Expansion NiO_6
(less distorted)

(b) Homovalent Mn^{3+}-Ni^{3+} subsitution ?



Mn^{3+} ($LaMnO_3$) ⇒ Mn^{4+} ($LaNi_{0.5}Mn_{0.5}O_3$)
Ni^{3+} ($LaNiO_3$) ⇒ Ni^{2+} ($LaNi_{0.5}Mn_{0.5}O_3$)

High-pressure EXAFS study of vitreous GeO2 up to 44 GPa

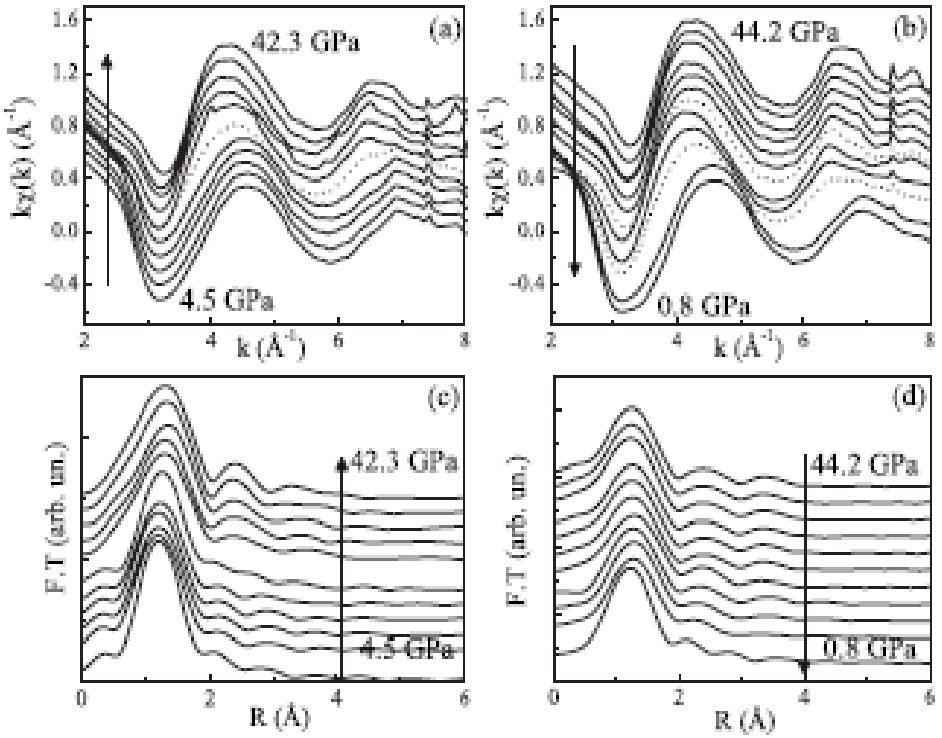


FIG. 2. Extracted $k\chi(k)$ signals (vertically shifted) for (a) compression and (b) decompression cycles. Moduli of the Fourier transform of the experimental EXAFS spectra as the pressure (c) increases and (d) decreases.

Ge-O bond lengths
Increase with pressure

1-13 GPa
Fourfold coordinated

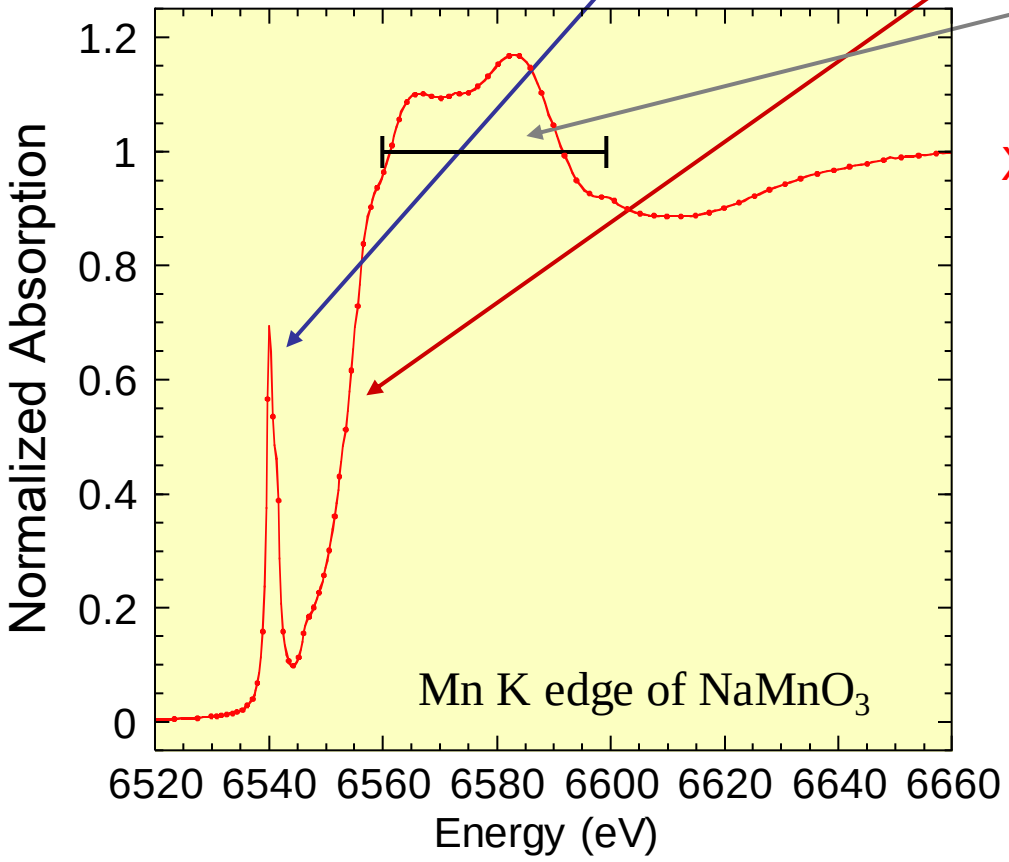
13-30 Gpa
Mixt of 4th and 5th
Coordination

>30Gpa 5th coord.

XANES Region (hard x-rays)

What is XANES ?

XANES = Pre-edge + Edge + XANES



XANES is extremely sensitive to the chemistry of the absorbing atom:

- Formal oxidation state
- Coordination environment

XANES probes the angular momentum of the unoccupied electronic states.

Why are we interested in XANES ?

Region	Transition	Information Content
Pre-edge	Electronic transitions to empty bound states (transition probability controlled by dipolar selection rules). e.g. 1s→3d, 1s→4p (1st transition series metals)	Local coordination environment around the absorbing atom. Dependence on the oxidation state and bonding.
Edge	Defines ionization threshold to continuum states.	Dependence on the oxidation state "Chemical shift": main edge (binding energy) shifts to higher energy with increasing oxidation state.
XANES	Features dominated by multiple-scattering resonances of the photoelectrons ejected at low $E_{kinetic}$.	Atomic positions of neighbours: Interatomic distances and bond angles.

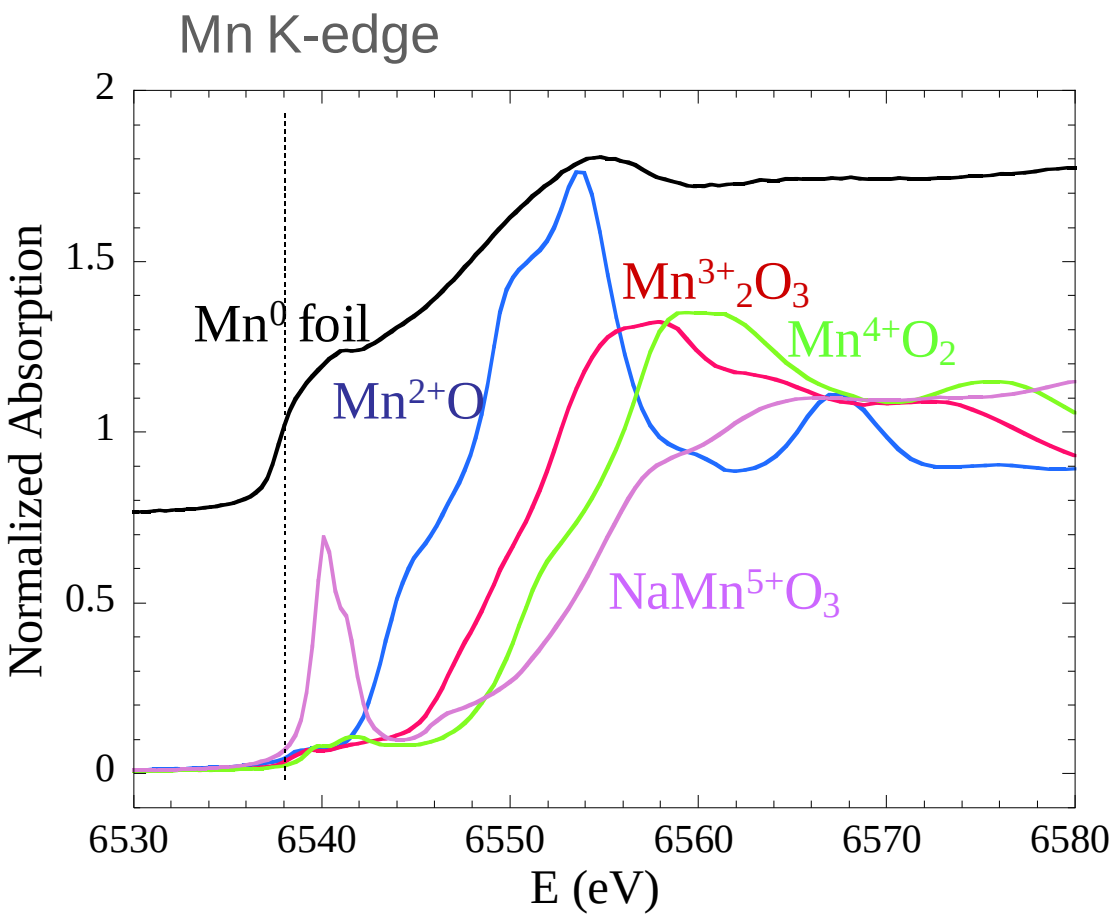
Advantages/disadvantages of XANES vs. EXAFS

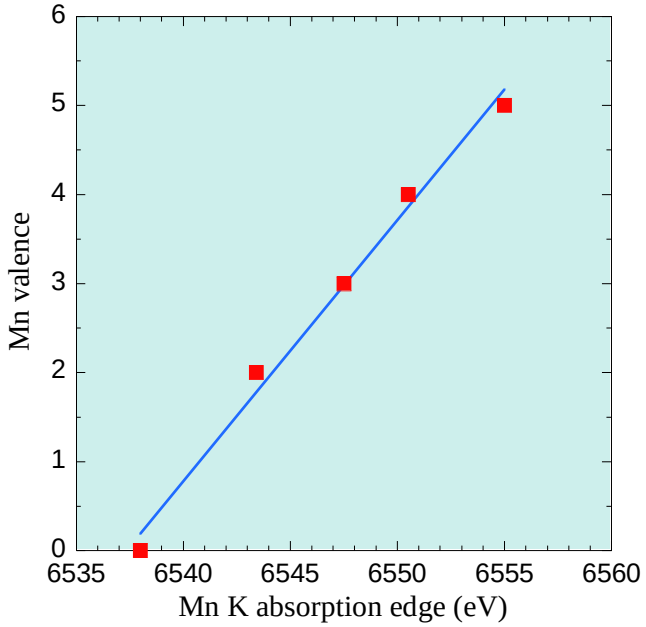
- XANES spectra are easier to measure than EXAFS spectra
  - Features more intense and in a small energy region
  - Lower concentrations and less-than-perfect sample conditions
  - The Debye-Waller damping is negligible → weak temperature dependence
    $\exp(-2 \cdot k^2\sigma^2) \sim \exp(-2 \times (0.5)^2 \times 0.005) \sim 1$
  - Faster to measure than full spectrum
- XANES is harder to fully interpret than EXAFS
  - The EXAFS equation breaks down at low-k
    Low $E_{kinetic}$ ↔ mean-free-path goes up (MS dominates when $\lambda_{photoelectron}$ > interatomic distance)
  - We don't have a simple equation but more quantitative and user-friendly analysis is improving:
    "Ab-initio" calculations with ≠ codes (Feff8, FDMNES, MXAN (XANES fit))
- Easy qualitative " fingerprint analysis " in terms of:

Coordination Chemistry :	regular or distorted, tetrahedral or octahedral, ...
Molecular orbitals :	p-d hybridization, crystal field theory
Valence state :	chemical edge shifts
Oxidation state & phases	

XANES Analysis: Oxidation state

Many absorption edges of many elements show significant binding energy shifts with oxidation state → Chemical Shift





Similar local structure:
Linear fit of Mn valence with Mn K-edge position

Can be used as fingerprint

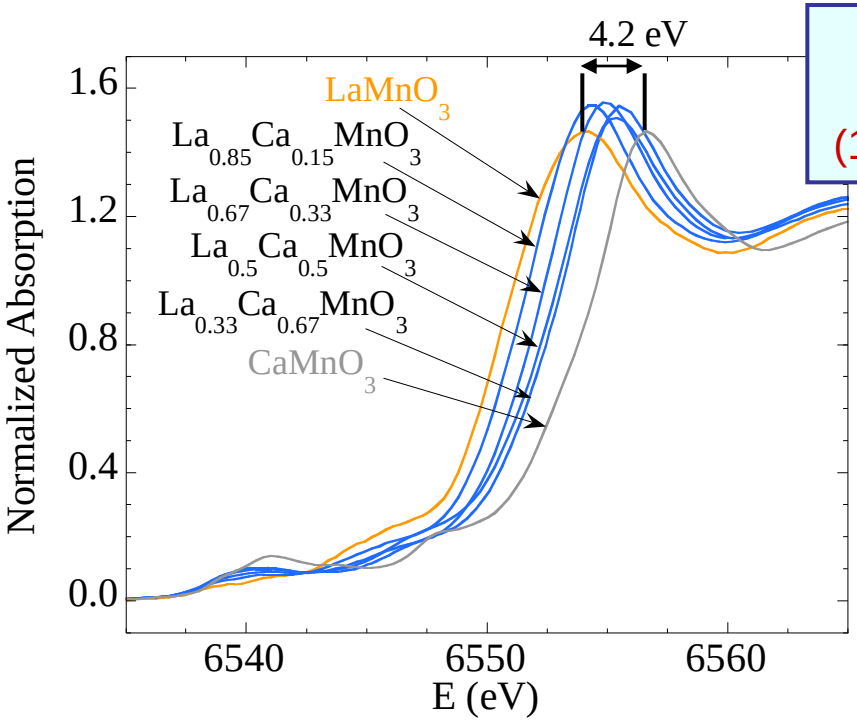
Example: Mn Mixed-valence state in $RE_{1-x}A_xMnO_3$

$La_{1-x}Ca_xMnO_3$ series: $La^{3+}Mn^{3+}O_3$ (x=0) ⟶ $Ca^{2+}Mn^{4+}O_3$ (x=1)

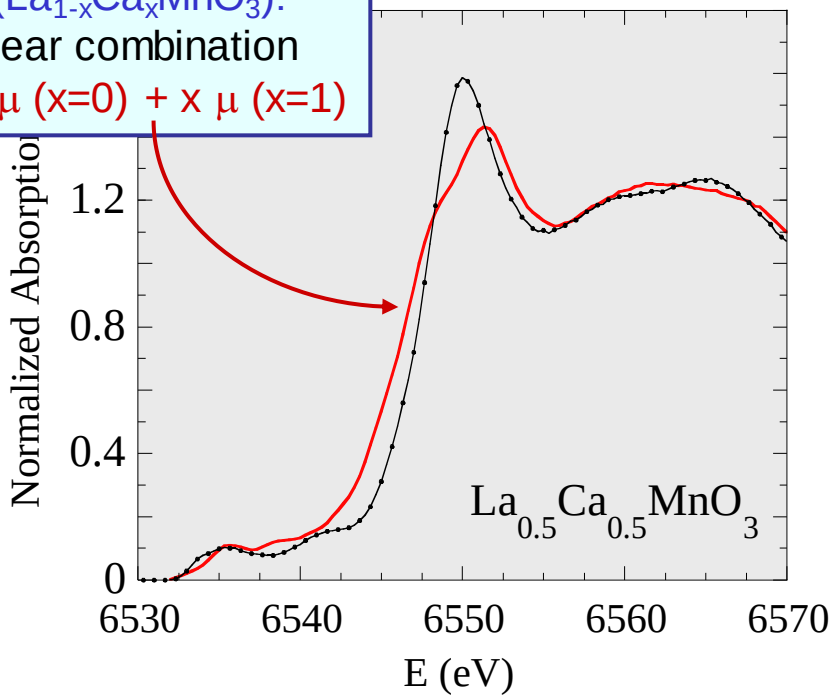
$0 < x < 1$

Mixture Mn^{3+} - Mn^{4+} or intermediate $Mn^{3.x+}$?

Mn K-edge XANES *vs.* composition x

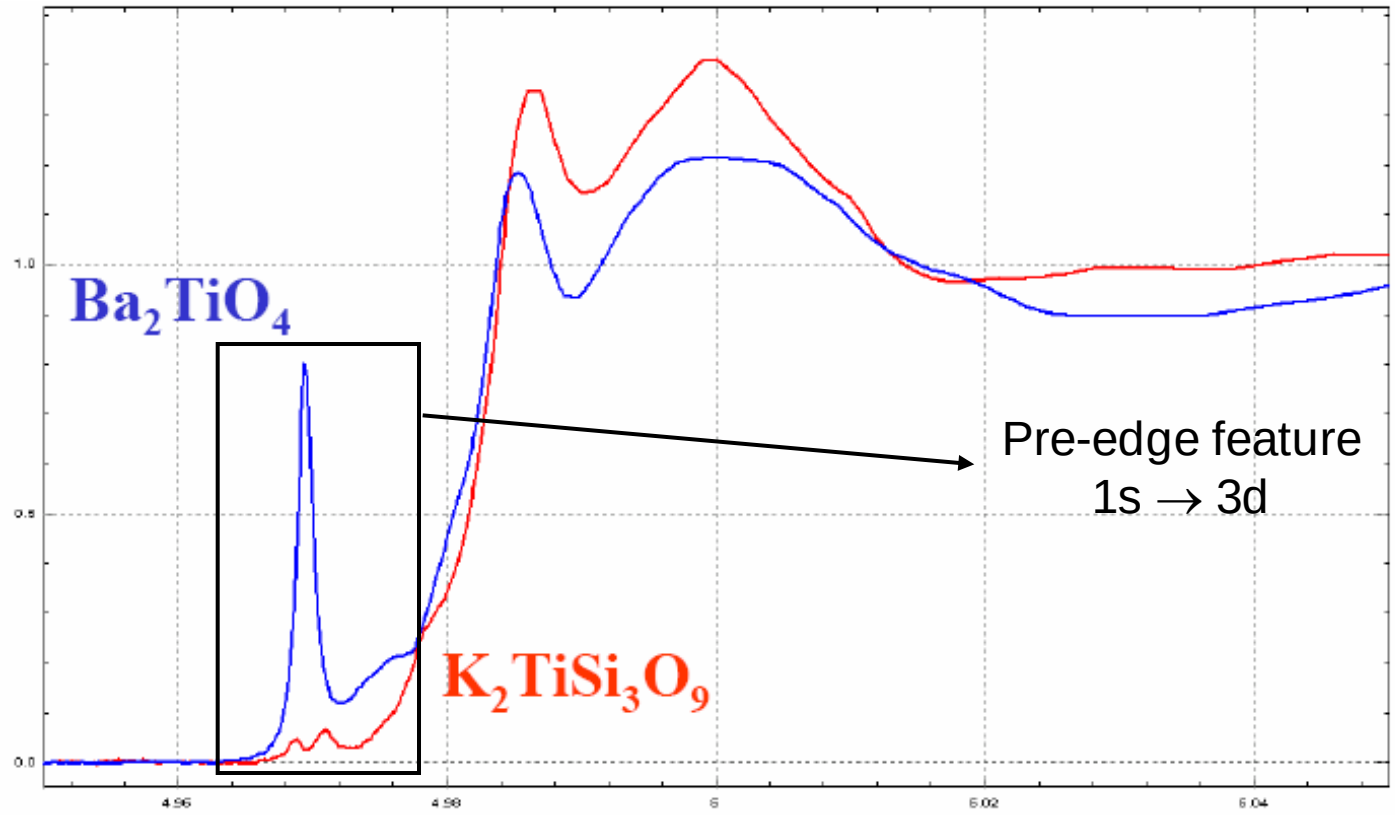


μ ($La_{1-x}Ca_xMnO_3$): Linear combination (1-x) μ (x=0) + x μ (x=1)



Mn atom does not fluctuate between two oxidation states Mn^{3+} - Mn^{4+} → Intermediate $Mn^{3.x+}$ valence state

XANES Analysis: Local coordination environment



Both Ti^{4+}

Ba_2TiO_4

$K_2TiSi_3O_9$

Ti K-edge XANES is highly dependent on the local coordination:
(1) Tetrahedral *vs*. Octahedral
(2) Different neighbors shells beyond the first O-shell

$Fe(CN)_6$ in water

"Ab initio" calculations

Codes:

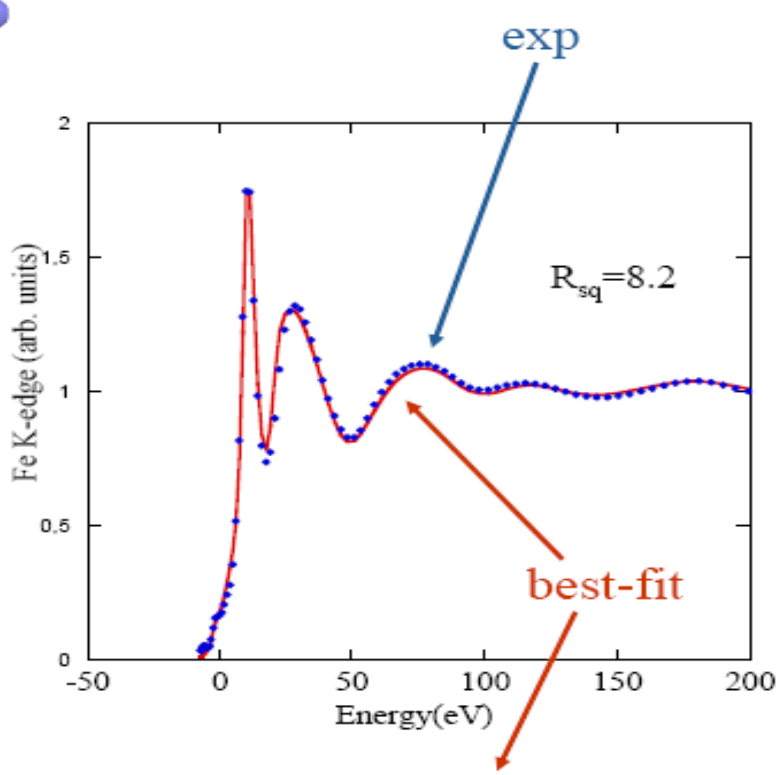
FEFF

MXAN

FDMNES

EXCURVE

MXAN



The best-fit condition corresponds to an octahedral symmetry with Fe-C distance of 1.92(0.01) Å and C-N distance of 1.21(0.01) Å

Previous GNXAS analysis (Westre et al. JACS 117 (1995)) reports Fe-C and Fe-N distances of 1.92 Å and 1.18 Å respectively

Electronic states by soft X-ray absorption spectroscopy

One electron theories are not applicable. Atomic multiplet effects needs to be considered

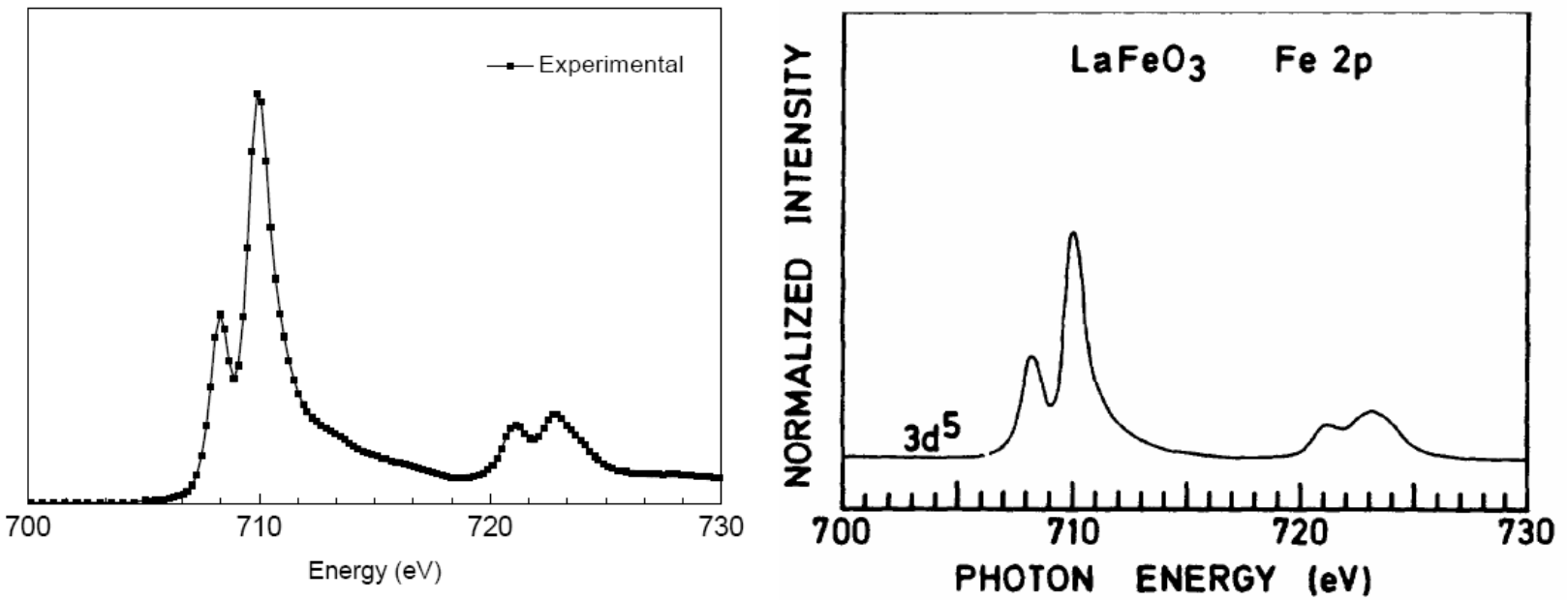


Figure 3.8. On the left side is shown our experimental Fe $L_{2,3}$ XANES spectrum for $LaFeO_3$ and at the right side we have added the theoretical calculation for the same compound by M. Abbate et al. [30] in which has been assumed a $3d^5$ ground state.

Experiments are explained in terms of mixture of electronic atomic configurations

As example a single $3d^5$ configuration. Or $3d^4L^1+3d^5$

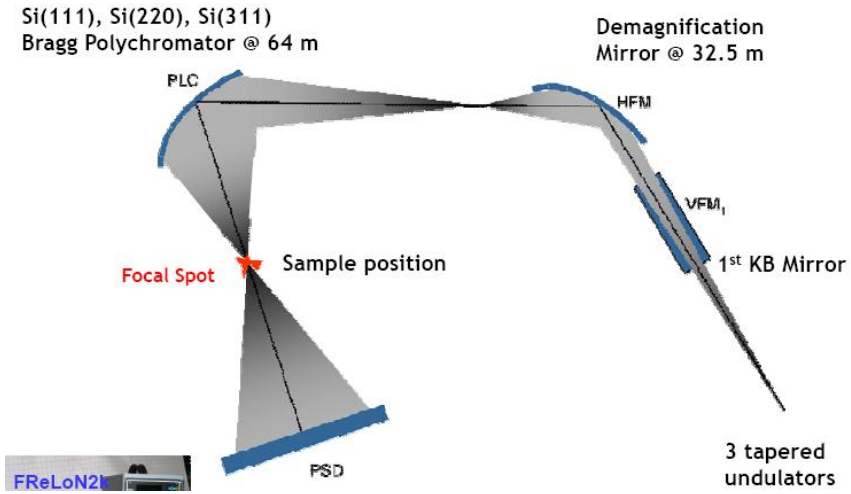
Challenge of XAFS

- ✓ Time-resolved XAFS
- ✓ Differencial EXAFS
- ✓ Micro- or Nano-XAFS
- ✓ X-ray magnetic circular dichroism (XMCD)
- ✓ Anomalous scattering
- ✓ DAFS (Diffraction anomalous Fine Structure)
- ✓ Resonant X-ray scattering (RXS)

Time-resolved XAFS

Quick EXAFS: Continuous motion of the monocromator, t= seconds

Dispersive EXAFS. $T=10^{-2}$ seconds



Pump and probe methods. 100 femtoseconds

- Electronic lifetime spectra of excited states
- Ultrafast chemical reactions, phase transitions, byological processes…

Pump-probe techniques
(fast scan, fast data acquisition, laser/X-ray sinchronization)

- Access new science in the time-domain x-ray regime

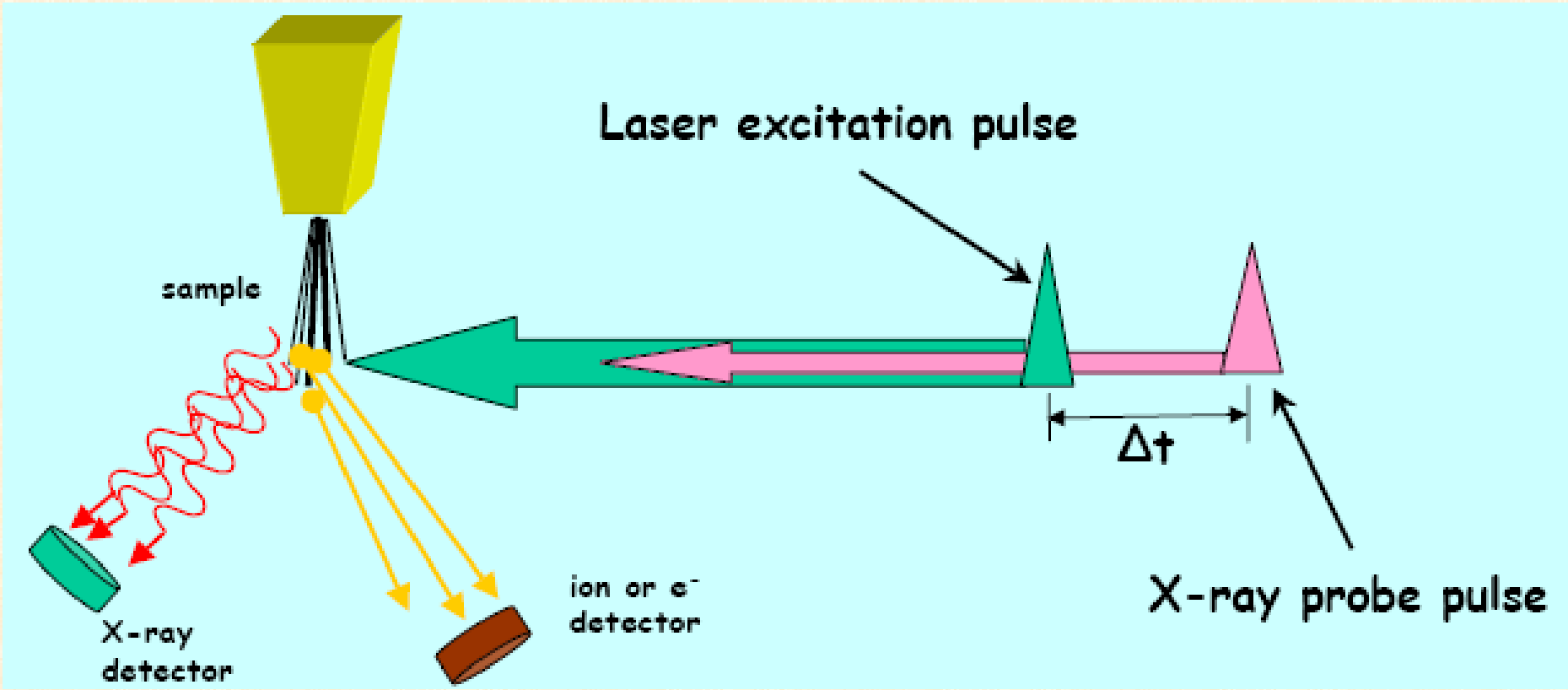
μs ⇨ ns ⇨ **ps** ⇨ fs? (free-electron laser)

1984 → 2004

Chemical reactions intermediates

Photocycles

Atomic vibrations (λ/v_s~100fs)



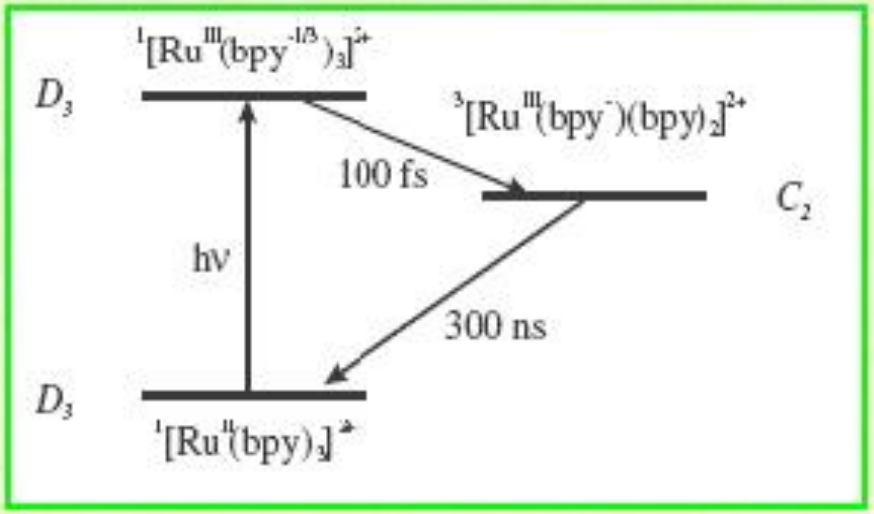
Observing Photochemical Transients by UXAFS"

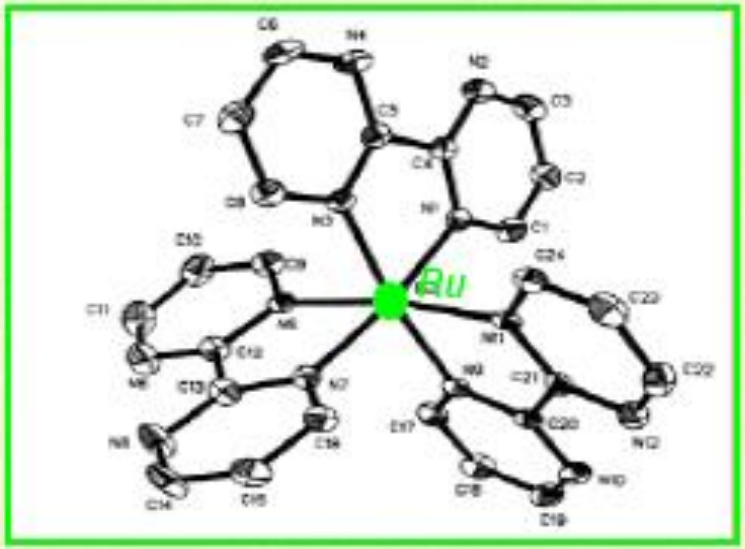
M. Saes et al., PRL, 90, 047403 (2003)

ALS, Berkeley (USA)

SLS, Villigen (CH)

Transient electronic and structural changes on the ps time-scale in XANES of Photoexcited $[RuII(bpy)_3]^{2+}$





XANES at the L_{III} edge of $[Ru^{II/III}(bpy)3]2+$ (≡2840eV)

Sample: 0.1mm free-flowing jet of 80mmol/l, in He filled chamber

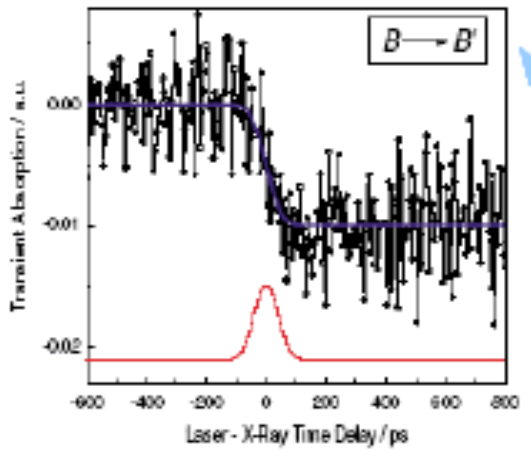
Static absorption

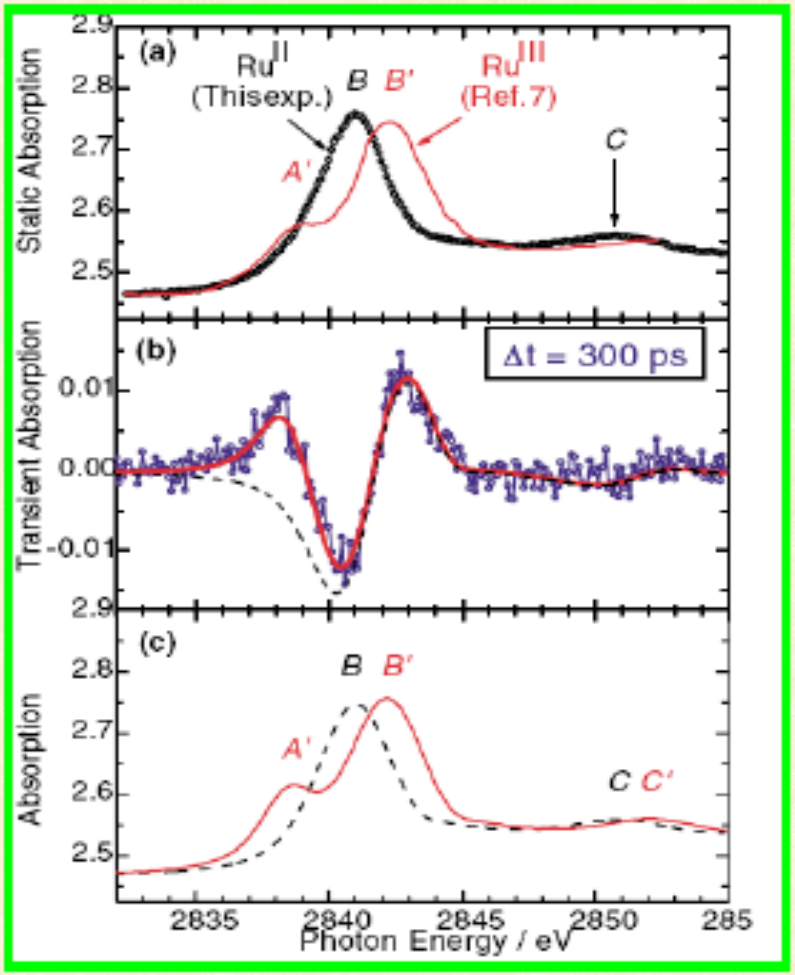
B: $2p_{3/2} \rightarrow 4d_{3/2}\ (e_g)$

A: $2p_{3/2} \rightarrow 4d_{5/2}\ (t_{2g})$

Transient absorption

Reconstr. absorption

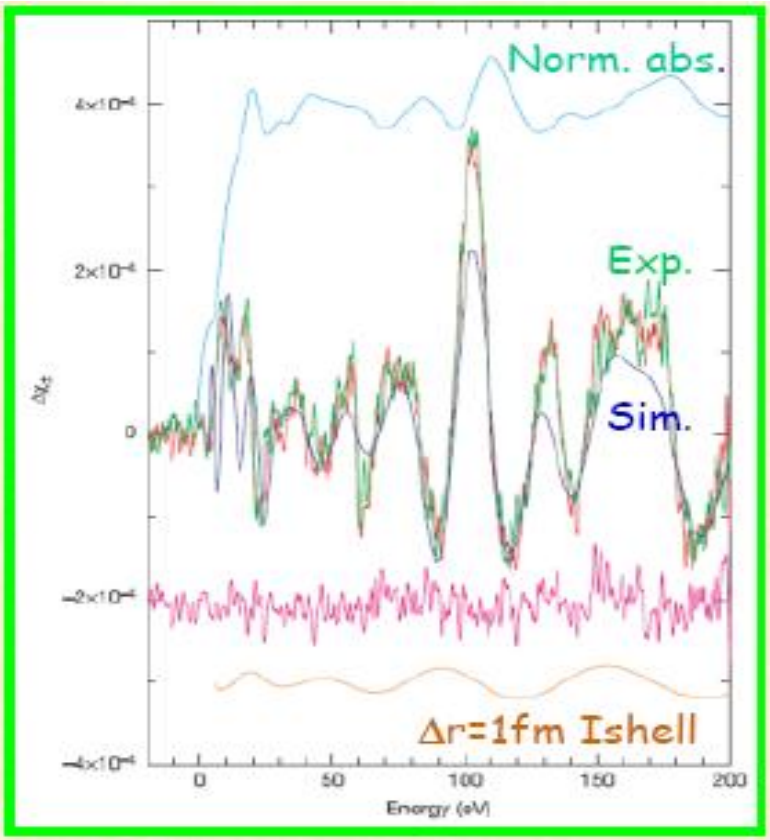




$$T(E,t) = f(t)\,[P(E,T) - R(E)]$$

ΔR (Ru-N)=0.052 ± 0.004 Å

Differencial EXAFS

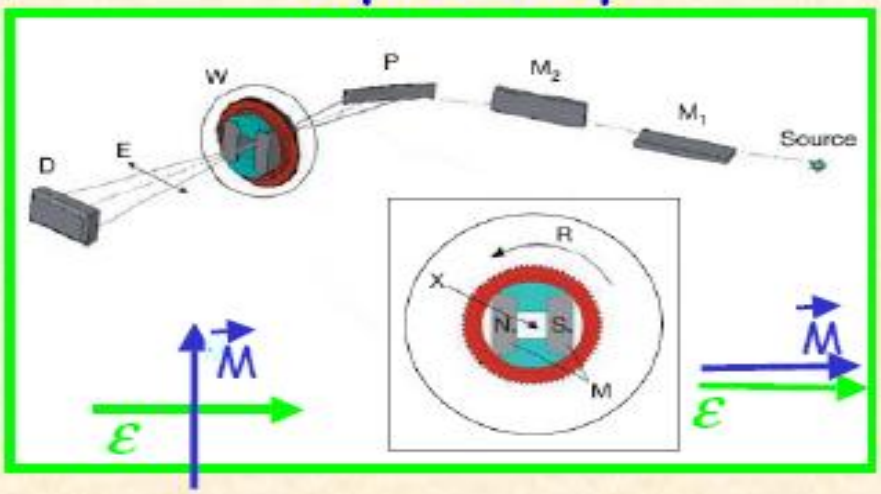


$$\chi(k) = \sum_j A_j(k)\sin\left(kS_j + \Phi_j(k)\right)$$

$$\Delta\chi = \sum_j A_j(k)\cos\left(kS_j + \Phi_j(k)\right)k\Delta S_j$$

Difference EXAFS at the **Fe K-edge** in an **FeCo** film undergoing periodic strain through **magnetostriction**

Exp. set-up



The magnets are rotated by a step motor to get M // and ⊥ to ε

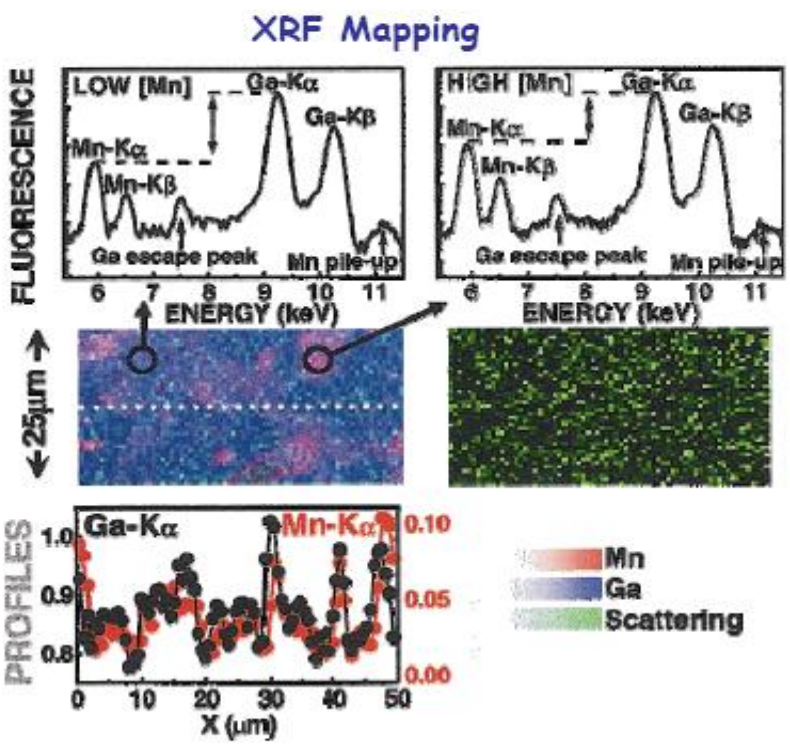
Resolution 10^{-5} Å

Micro-or Nano-XAFS

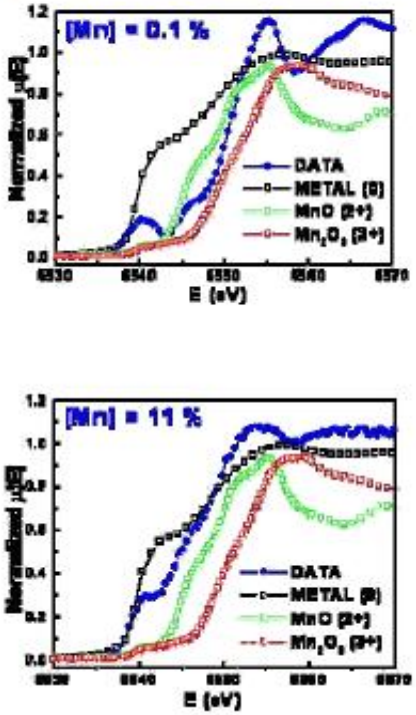
3. Material Sciences

ESRF-Universidad de Valencia

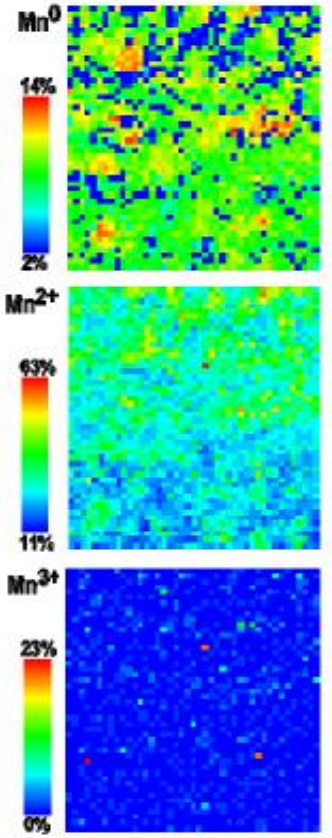
Dopant and residual impurities in GaN



Oxidation state



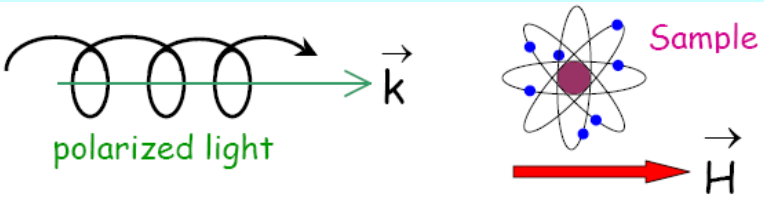
XANES Imaging

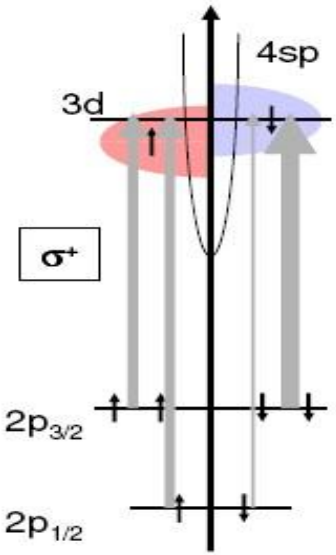


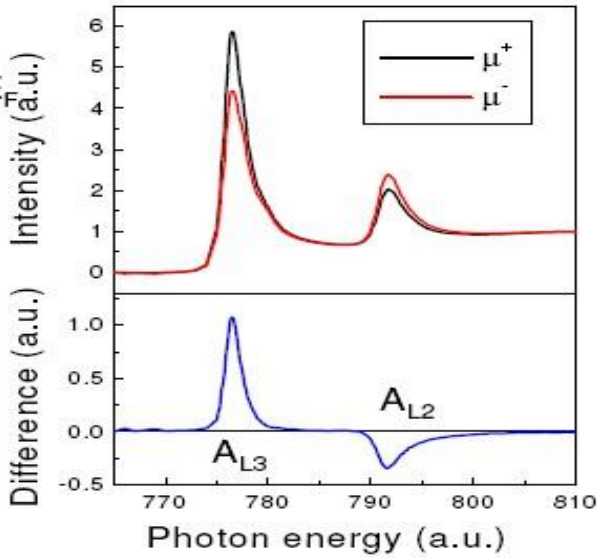
G. Martinez Criado et al., Jpn. J. Appl. Phys. 43, L697 (2004), Appl. Phys. Lett. 86, 131927 (2005)

X-Ray Magnetic Circular Dichroism

XMCD is a difference spectrum of two x-ray absorption spectra (XAS) taken in a magnetic field, one taken with left circularly polarized light, and one with right circularly polarized light. information on the spin and orbital magnetic moment.







Sum rules

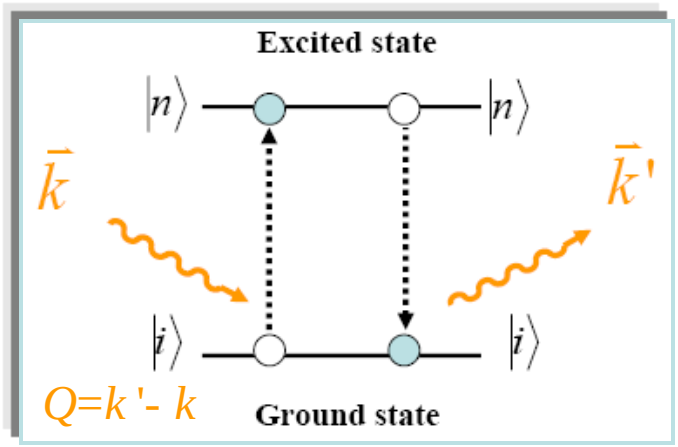
$$m_s/\mu_B \sim \frac{A_{L3} - 2A_{L2}}{A_{iso}}$$

$$m_l/\mu_B \sim \frac{A_{L3} + A_{L2}}{A_{iso}}$$

XMCD
- is very sensitive (mono-atomic layers)
- is element specific
- provides information on spin and orbital magnetizations *separately*

Anomalous X-ray scattering

photons are virtually absorbed by exciting core electrons to empty energy states, and subsequently reemitted when the excited electrons and the core holes recombine.



RXS is closely connected to real x-ray absorption but incident and emitted photons can have different polarizations

$$f(\vec{Q},E) = f_0(\vec{Q}) + f'(E) + if''(E)$$

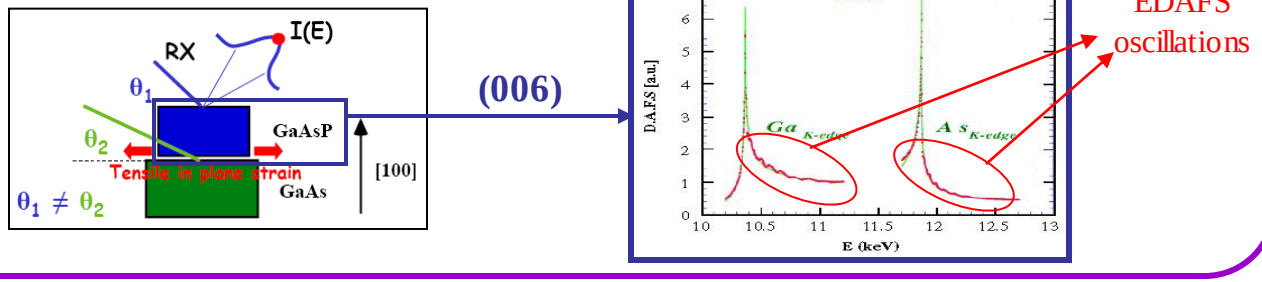
$$RXS \Leftarrow f''(\vec{Q}=0) \propto E \times \sigma_{abs}(E) \Rightarrow XAS$$

$$I = \left|F(\vec{Q},\omega)\right|^2 = \left|\sum_j e^{i\vec{Q}\cdot\vec{R}_j} f_{0j}(\vec{Q}) + \sum_j e^{i\vec{Q}\cdot\vec{R}_j}\left(f_j'(\omega) + if_j''(\omega)\right)\right|^2$$

Resonant reflections

a) $F_0(\vec{Q}) >> F(\vec{Q},\omega)$ → *DAFS* (site/spatial-selective XAS)

Example: To investigate strain accomodation in the epilayer GaAsP
(Proietti MG, Renevier H et al., PRB 59, 5479 (1999))



Special interest when ... $F_0(\vec{Q}) << F(\vec{Q},\omega)$

b1) *Superlattice* reflections ($F_0(\vec{Q}) \approx 0$): $F(\vec{Q},\omega) \propto \sum(f_{i-site} - f_{j-site})$
∃ non-equivalent sites for TM atom → *Chemical shift* (≠ local structure)
" Charge Order "

b2) *Forbidden* reflections ($F_0(\vec{Q}) = 0$): $F(\vec{Q},\omega) \propto \sum(f_{i-site} - f_{i'-site})$
∃ anisotropic local structure for TM atom at equivalent sites → *Anisotropy of ASF*
"ATS Ordering assigned to Orbital Order"

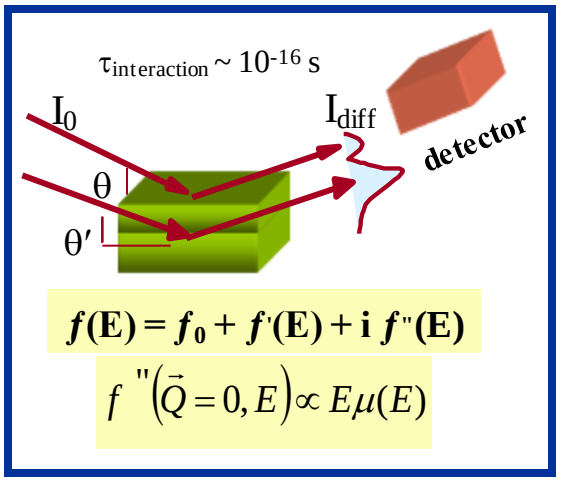
X-ray Resonant Scattering

Definition: Energy evolution of the scattered intensity near an Absorption Edge

CO reflections

↓

f is nearly scalar



$$f(E) = f_0 + f'(E) + i\, f''(E)$$

$$f''(\vec{Q}=0, E) \propto E\mu(E)$$

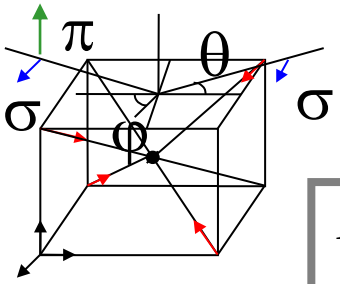
ATS reflections

↓

f is a tensor

$$f = \begin{pmatrix} f_{xx} & f_{xy} & f_{xz} \\ f_{yx} & f_{yy} & f_{yz} \\ f_{zx} & f_{zy} & f_{zz} \end{pmatrix}$$

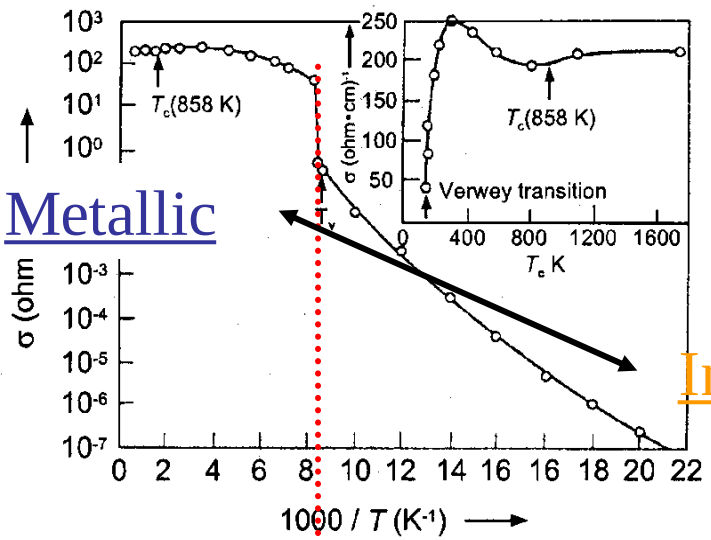
Dipolar transition



Beam polarization
σ , π

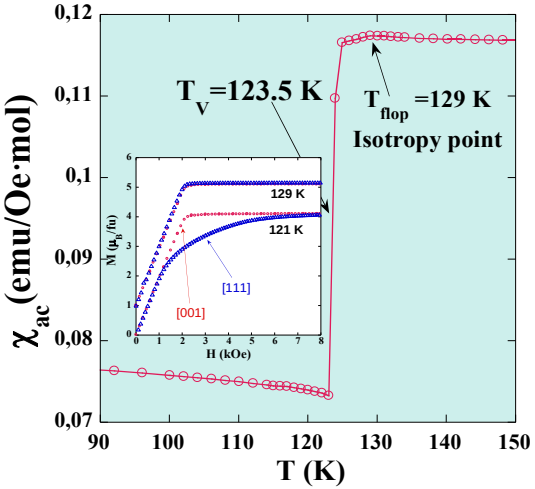
Azimuthal rotation
φ

Magnetite Fe_3O_4

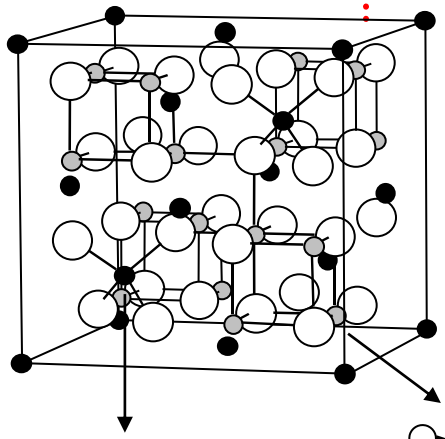


Metallic

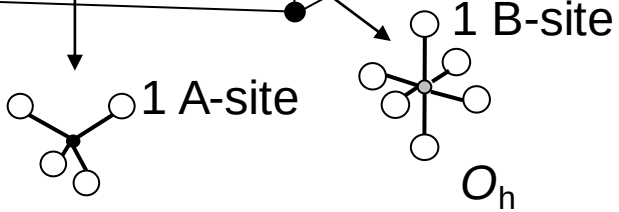
Insulating

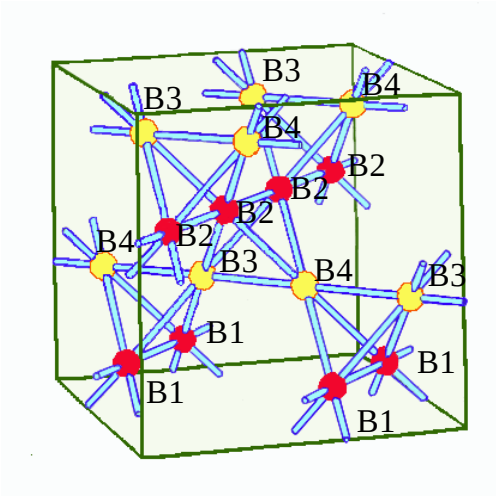


Fd-3m (a_c)



$Fe^{3+}{}_A[Fe^{2+}Fe^{3+}]_BO_4$





Magnetite

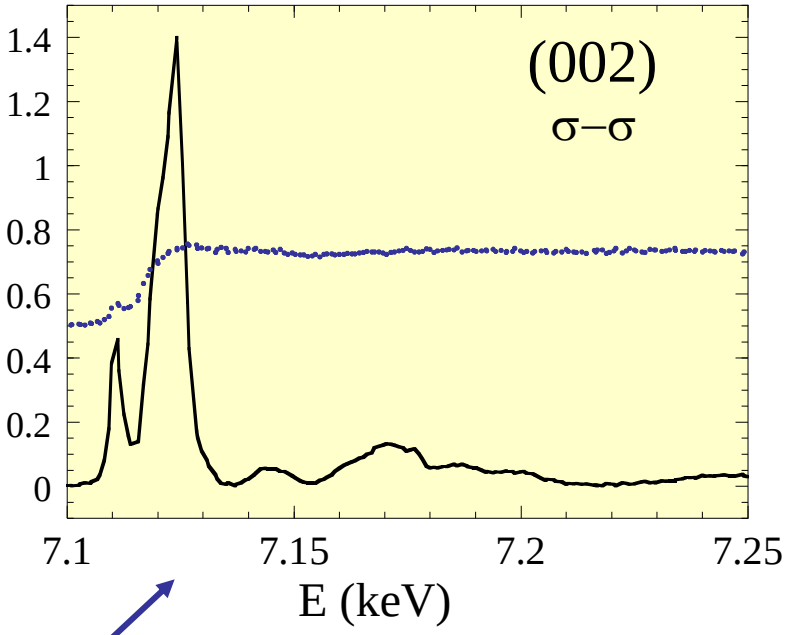
c axis

(0 0 6)

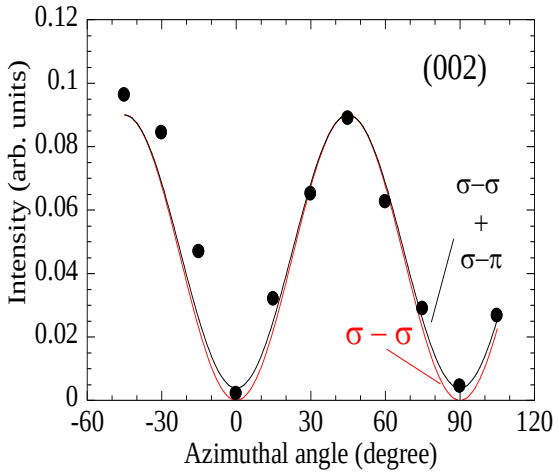
(0 0 4) Bragg

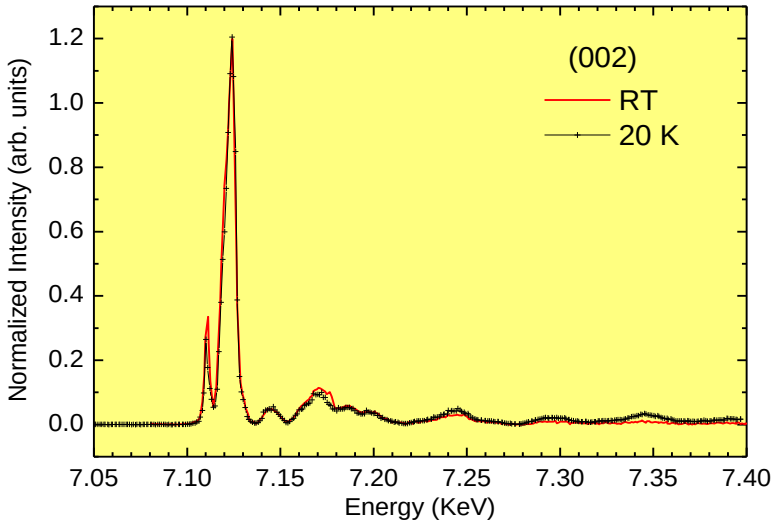
Fd-3m

(0 0 2) Bragg forbidden



$$F \propto (f_{B1} + f_{B2} - [f_{B3} + f_{B4}])$$





"ATS "

~~Verwey model~~

Books and Review Articles:

Basic Principles and Applications of EXAFS

Handbook of Synchrotron Radiation, Chapter 10, pp. 995-1014, E. A. Stern and S. M. Heald, E. E. Koch, ed., North-Holland 1983

X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES

in *Chemical Analysis* Vol. 92, D. C. Koningsberger and R. Prins, ed., John Wiley & sons, 1988

X-ray Absorption Fine Structure for Catalysis and Surfaces

World Scientific Series on Synchrotron Radiation Techniques and Applications Vol. 2, ed., Y. Iwasawa, 1996

X-ray absorption spectroscopy in coordination chemistry

J. E. Penner-Hahn, *Coordination Chemistry Reviews* 190-192, pp. 1101-1123, 1999

Tutorials and other Training Material:

http://xafs.org/Tutorials

http://gbxafs.iit.edu/training/tutorials.html Grant Bunker's tutorials

http://srs.dl.ac.uk/XRS/courses/ tutorial from Daresbury Lab, UK

Software resources:

http://xafs.org/Software

Analysis programs: *Atoms* + *Feff* + *iFeffit* (Theoretical XAFS calculations and fitting) – Univ. Chicago (USA)

Athena, Artemis (EXAFS Data Reduction and fitting

http://gnxas.unicam.it : *Gnxas* (Theoretical XAFS calculations and fitting) – Univ. Camerino (Italy)

http://www.esrf.fr/computing/scientific/xop/ *XOP* (DABAX data base, cross-section and lots of general x-ray Calculations, multipurpose data visualization and analysis)-M. Sanchez del Rio, and R. J. Dejus (ESRF, France)

http://srs.dl.ac.uk/XRS/index.html : *Excurv98* (Theoretical XAFS calculations and fitting) – Daresbury Lab (UK)