X-ray Absorption Fine Structure Spectroscopy

François Farges
Dept. of Environmental and Geological Sciences
Stanford University - Univ. of Marne la Vallée, France

farges@pangea.stanford.edu

Interactive lecture (Quicktime 7) at http://pangea.stanford.edu/~farges/SB2005

Plan :

I. Introduction

- history
- general principles : absorption coefficients, electronic mechanisms
- synchrotron sources : principles, available facilities
- data collection outlook: transmission, fluorescence, dispersive…

II. Analysis and data reduction in real

- pre-edge region : electronic transitions
- edge region : Fermi level and redox
- interference region : XANES/EXAFS

- more complicated: multiple-scattering, disorder,
  multi-electronic excitations
- data reduction stategies, softwares comparison

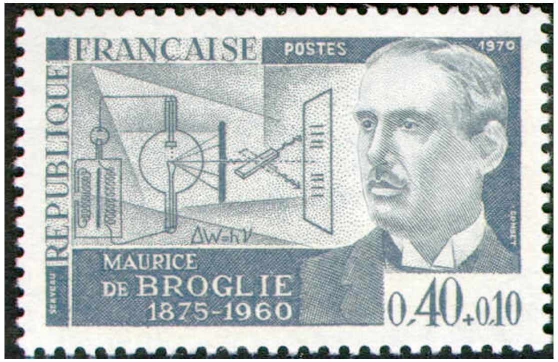
III. Some examples : glasses, mineral surfaces

IV. Prospectives…

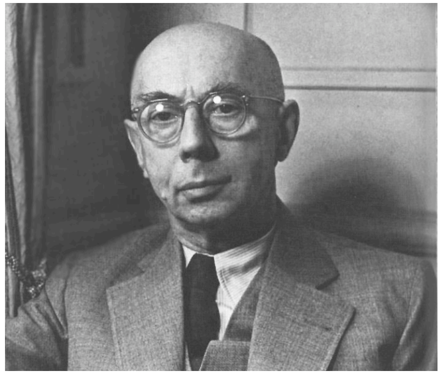
I. Introduction

One upon a time *(brief summary)*

1895 : Röntgen discovered x-rays



1913 : Maurice de Broglie measured the first absorption edge



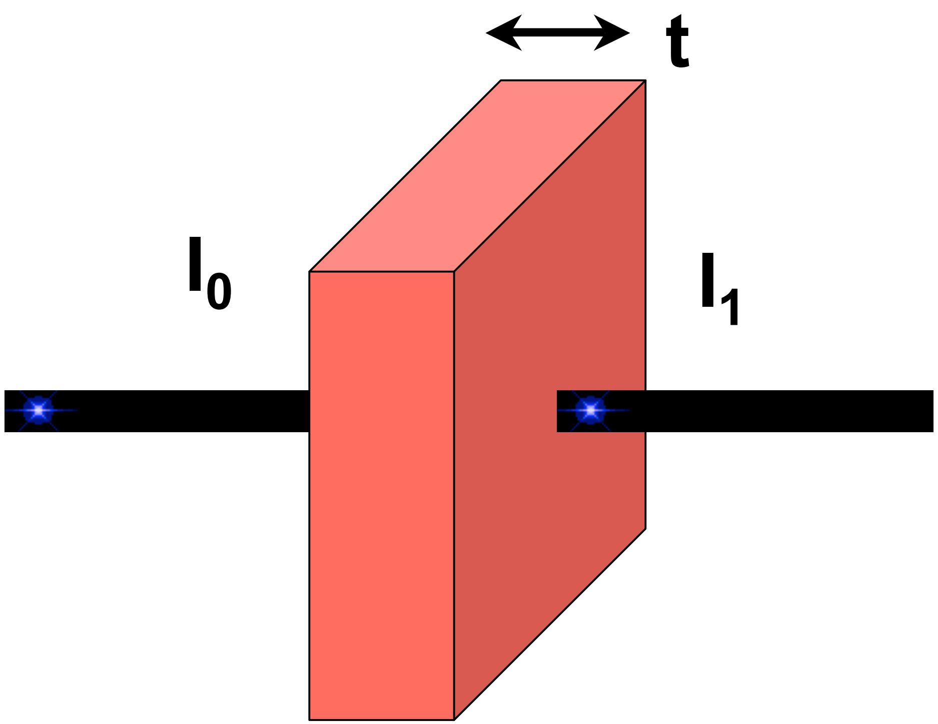
1920 : Fricke and Hertz (*shown*) reported the first fine structures

1931 : Kronig wrote the first theory of EXAFS

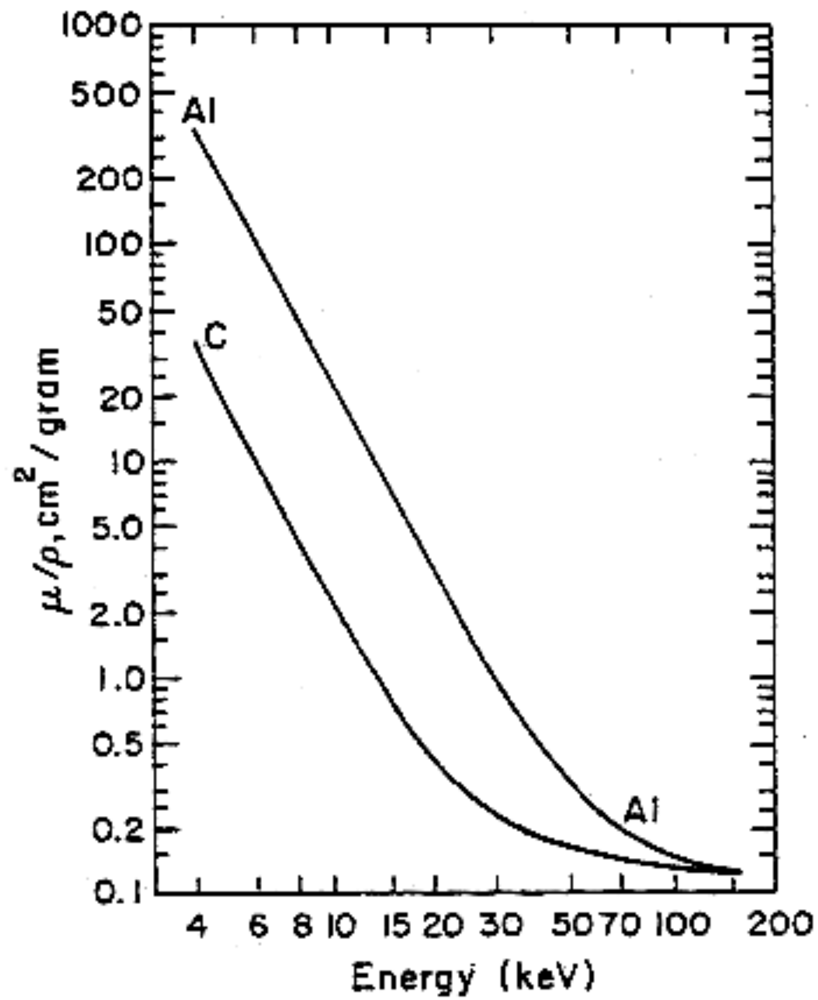
1971 : Stern, Sayers and Lytle introduced the most of the current theory, incl. Fourier transform of EXAFS

More ? See http://www.exafsco.com/techpapers/

The (x-ray) photon intensity (I_1) that passes through a sample of thickness t is function of the absorption coefficient, μ :



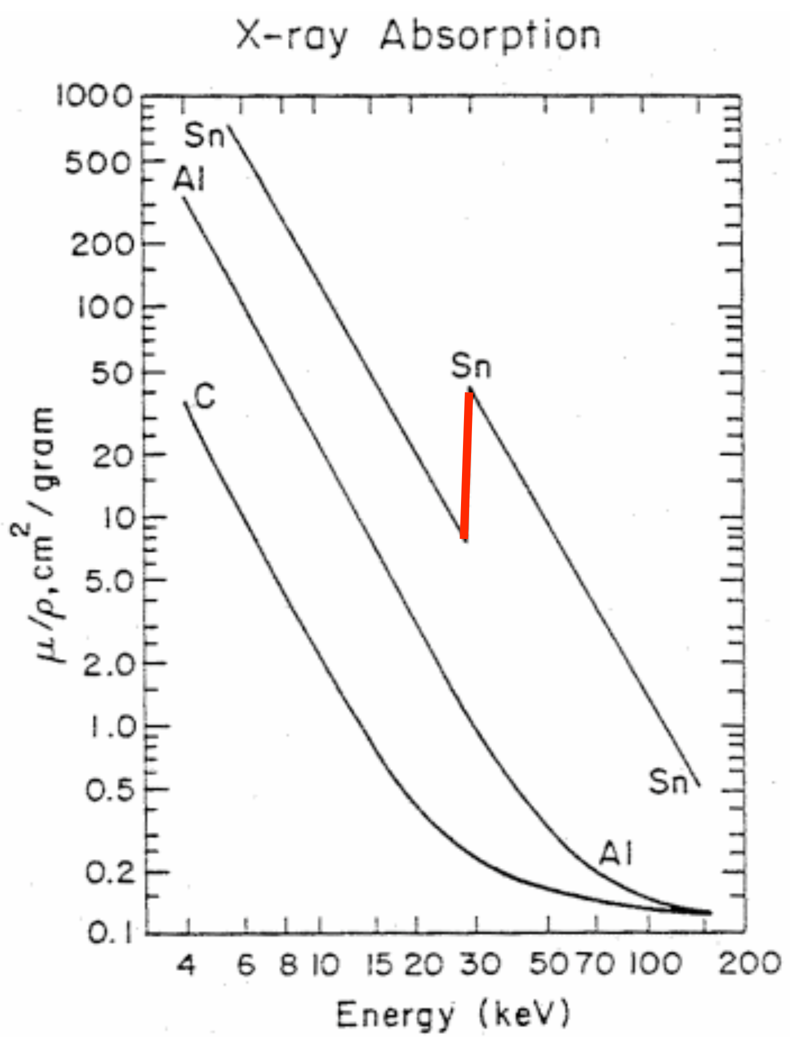
$$I_1 = I_0 e^{-\mu t}$$



μ is function of Z, density (ρ) and photon energy ~ $\rho Z^4/AE^3$

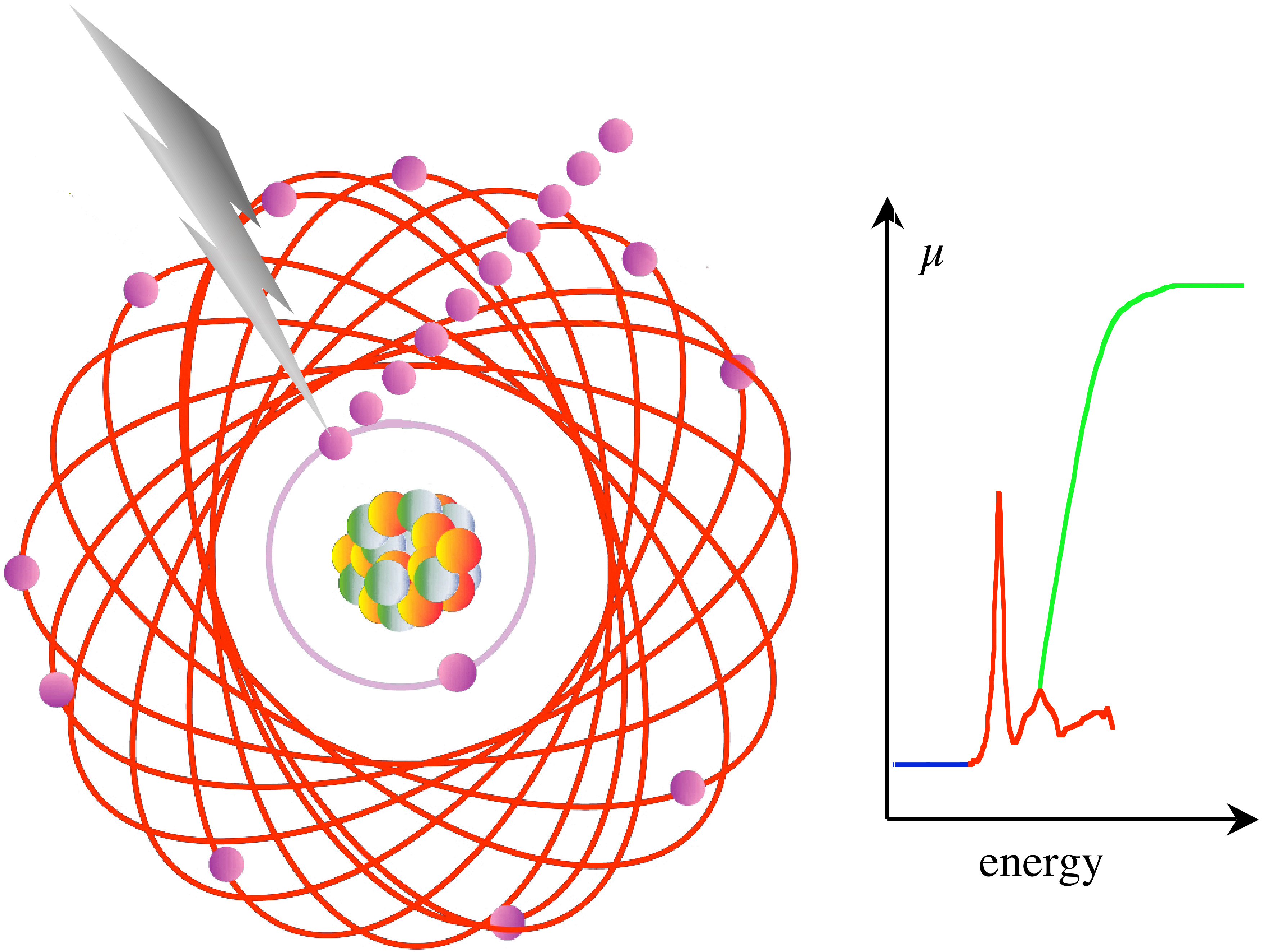
(A is the atomic mass)

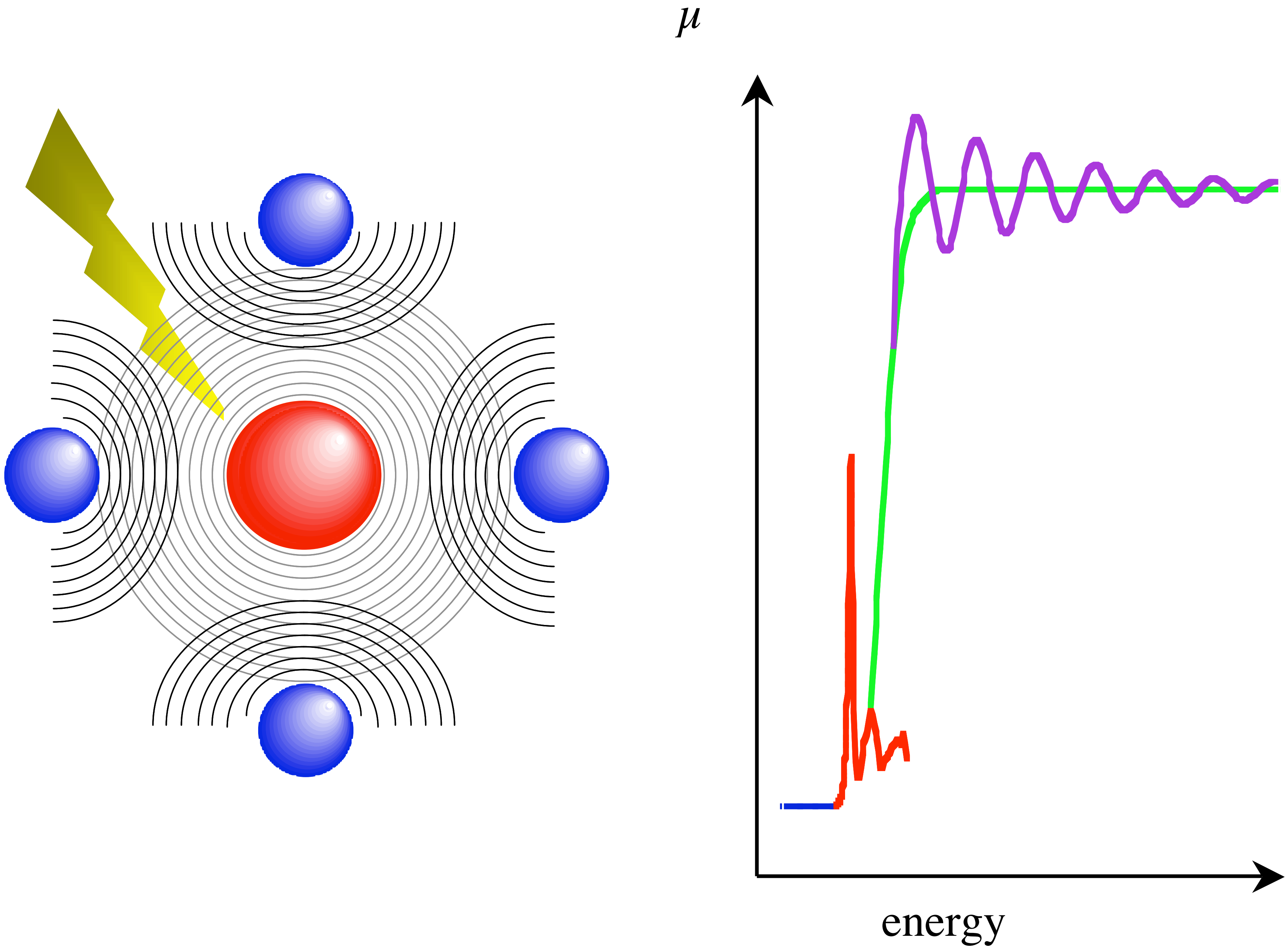
Discontinuities in μ = *f* (E) are observed,
called absorption edges
and related to the excitation of core electrons



element	1s (K-edge)	2p (L edges)
H	13.6	…
Si	1840	149 - 99
Zn	9657	1194 - 1020
Sn	29200	4465 - 3929
U	115606	21755 - 17166

available on synchrotron


μ
energy


μ
energy

example

$Fe_2Al_9Si_4O_{22}(OH)_2$ (staurolite) at the iron K-edge

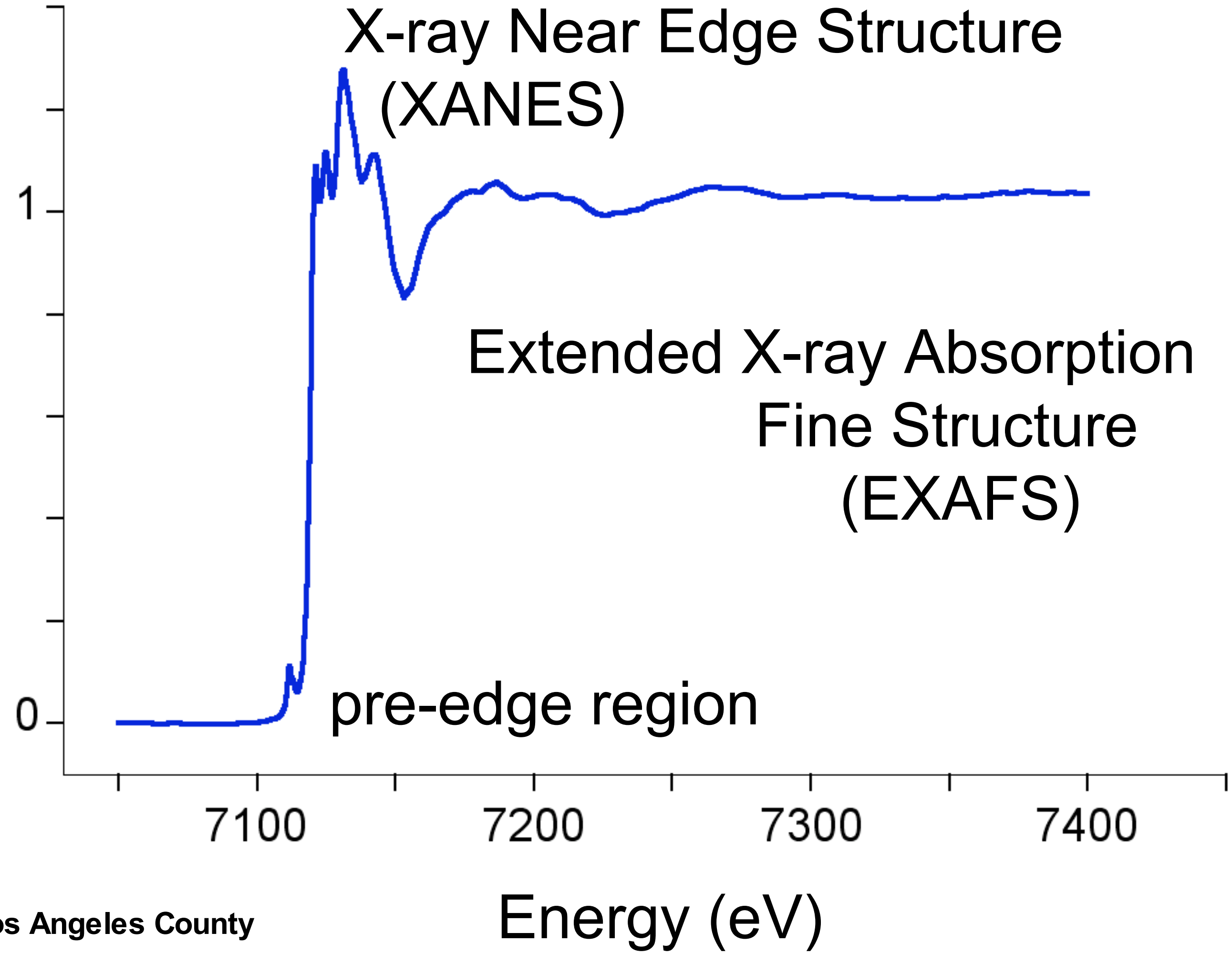
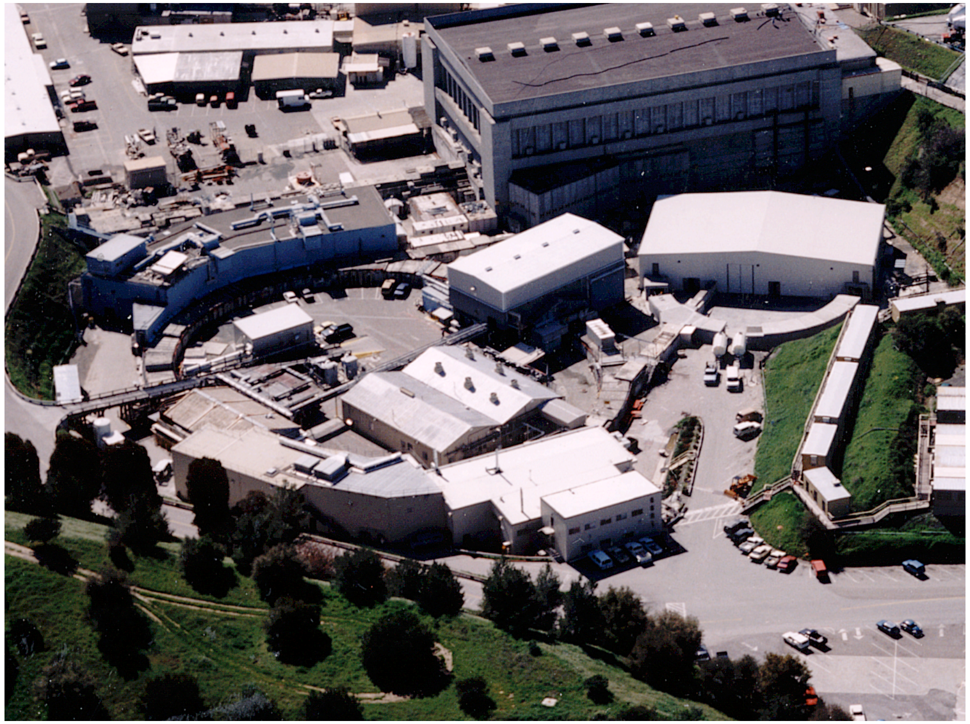


Image: National History Museum of Los Angeles County
http://www.nhm.org/~gmc/images/50746.gif

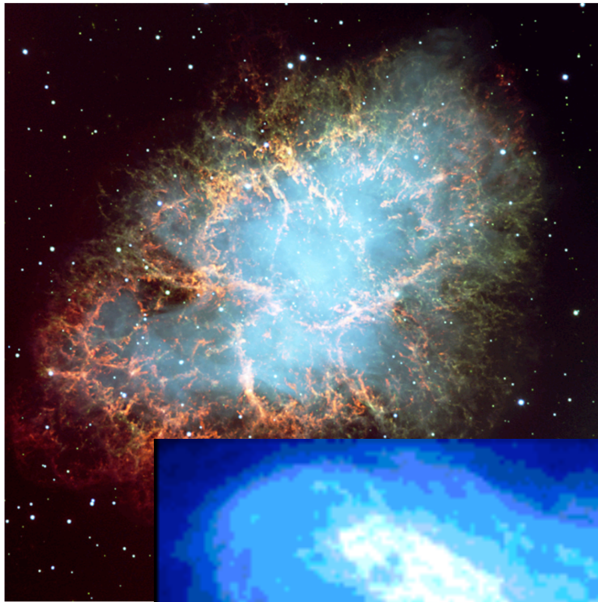
- chemically selective
- available from boron ‘till actinides
- sensibility as down as ppm (in the best cases)
- sensitive to redox, speciation (incl. Its distorsions)
- detect “medium-range environnement” (3-5 Å)
- works with “amorphous” matter, organic, wet, iron-rich matter
- OK with any natural/industriel “real” samples
- sample preparation usually minimal
- fewer beam/matter interactions (precious samples OK)
- very active community : theoreticians, sources, applications

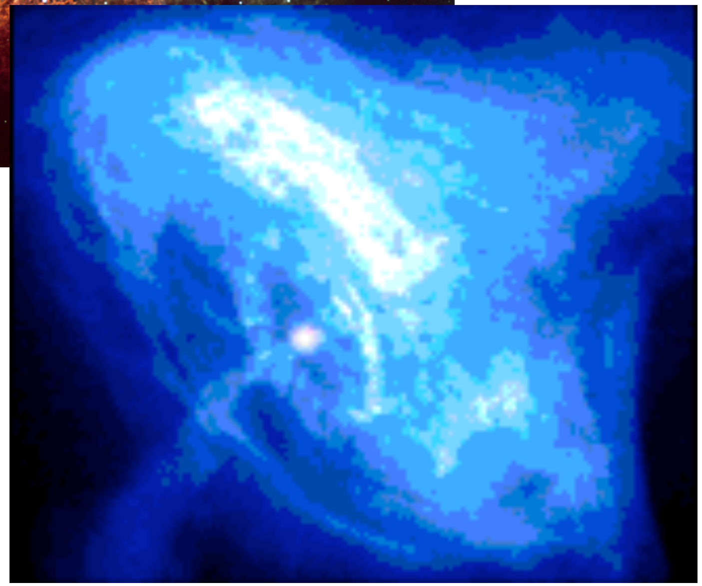
- not sensitive anymore when disorder is too high
- not sensitive to neighboring ions with close Z-numbers
- access to large instruments is tough and highly competitive
- only a few beamtime days a year
- must be ready for experiment - no improvisation
- expensive, centralized - writing proposals and activity reports
- interface with theoricians not always easy
- spectrometers are often “home-made”, not standardized
- must read Phys Rev, Amer Min, JACS, GCA and many others

synchrotron = coherent source of x rays (among others), directional and intense



SSRL

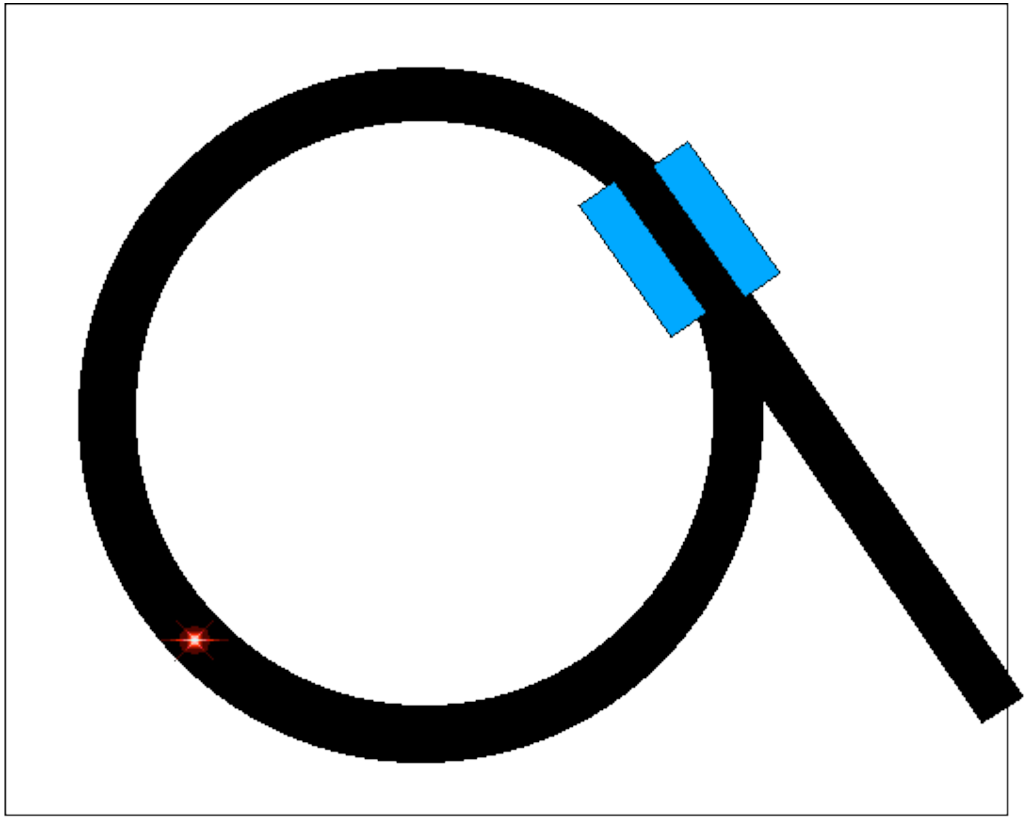


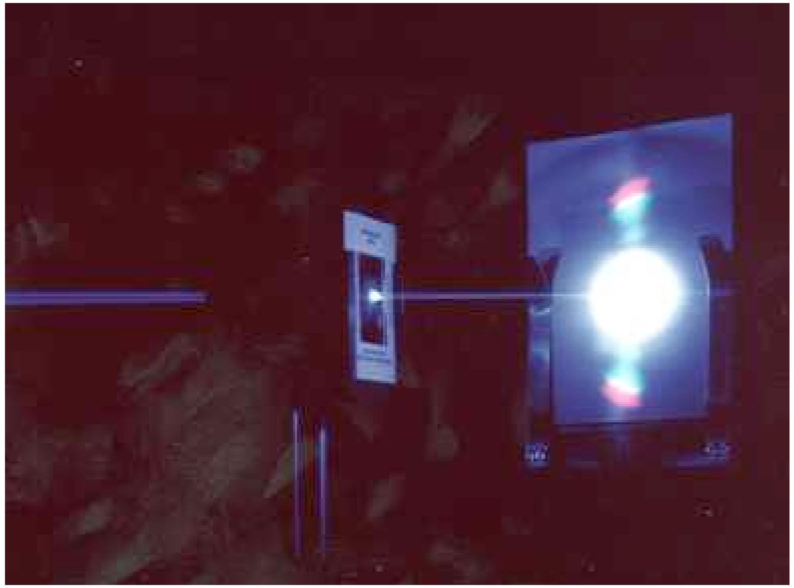


pulsar of the
Crab nebulae
(supernova of 1054)

principle :

Particle (positon) field = electrostatic field + radiative field





under a magnetic field,
the radiative field dissociate from the electrostatic field
of the accelerated particule

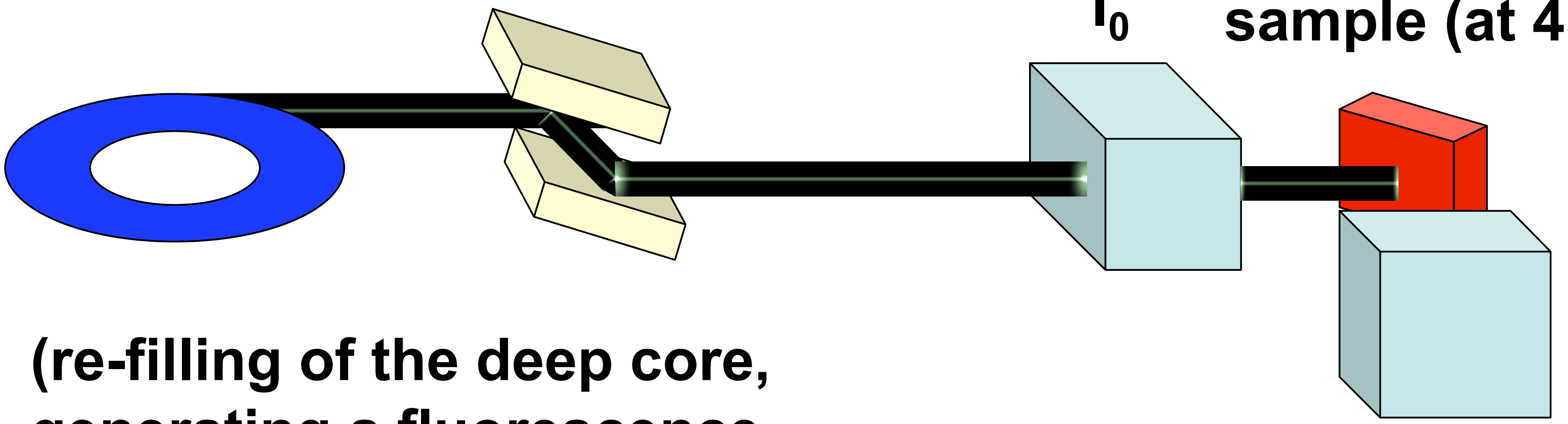
a world of synchrotrons…

Spectra are collected in :

- the transmission mode

$\mu(E) = \log (I_0 / I_1)$

- the fluorescence mode



(re-filling of the deep core, generating a fluorescence, proportional to absorption)

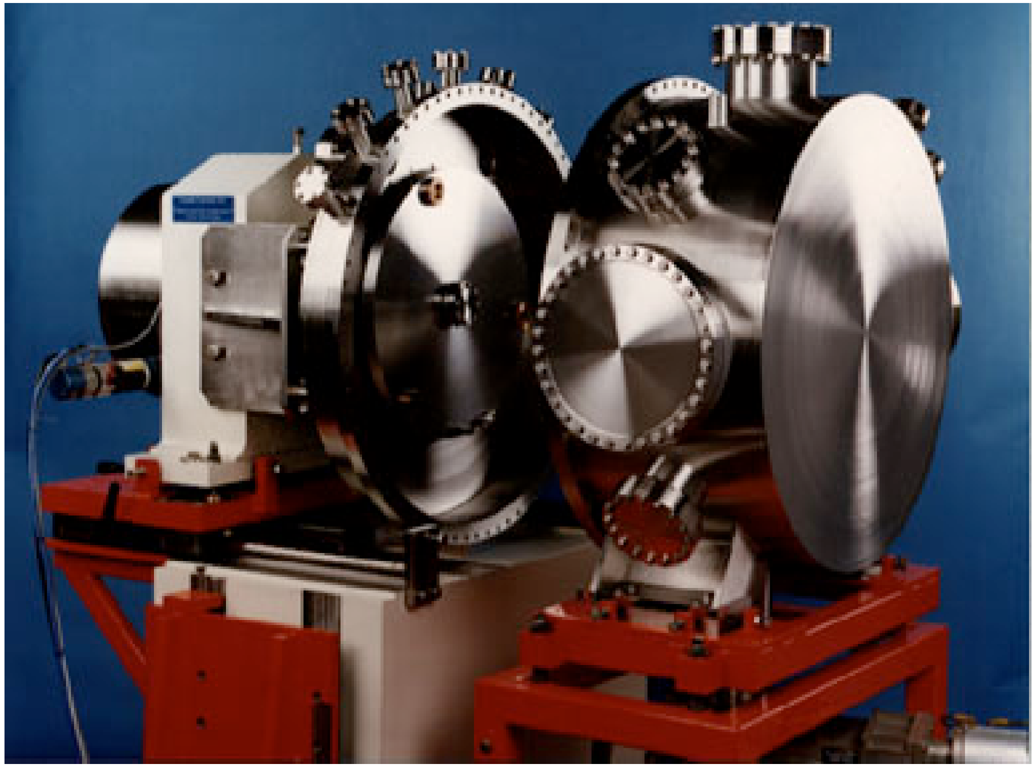
$\mu(E) \sim I_f / I_0$

Monochromators :

Bragg's law

to select one (±ΔE) energy

from a continuum of radiations from the ring



gratings (100-2000 l/mm)

beryl
YB_{66}
KTP
Quartz

Si (111)
Si (220)
Si (311)
Si (511)

Monochromators :

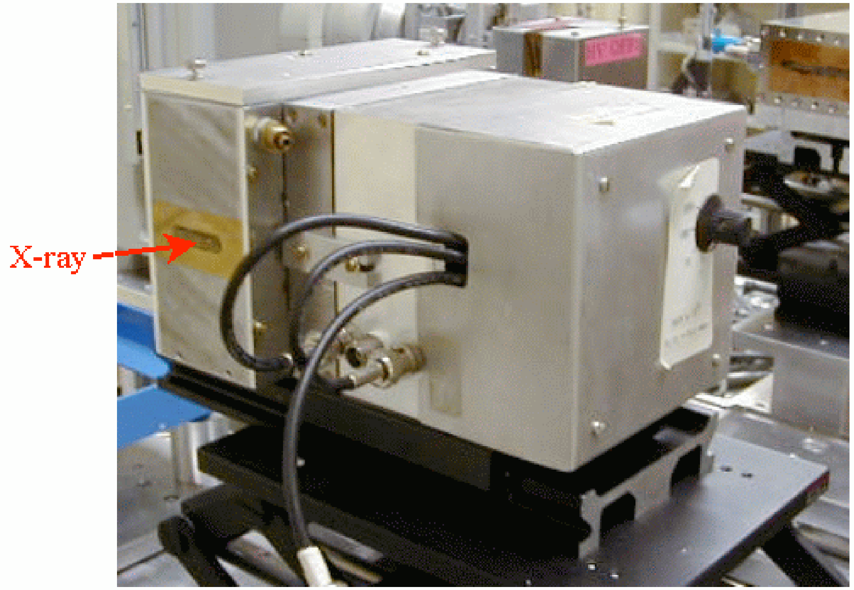
www.accel.de

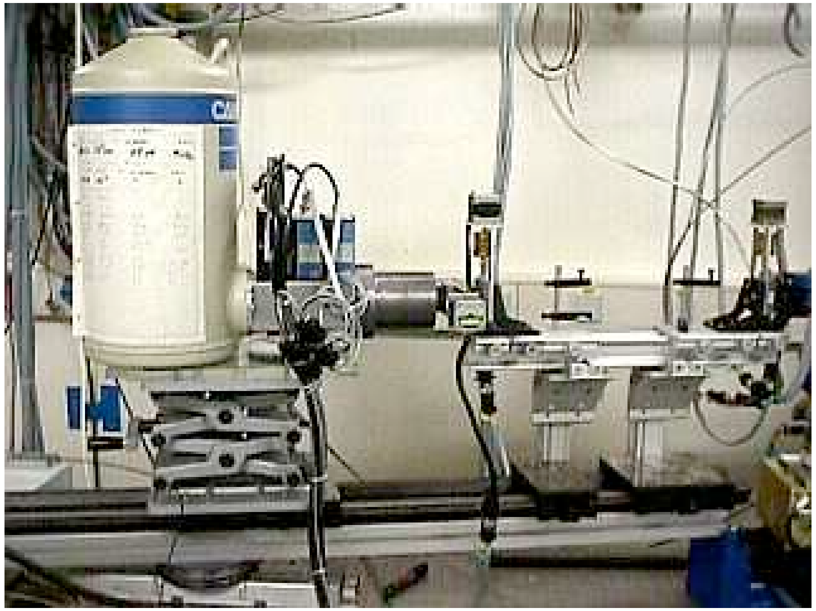
flux resolution

(111) (220) (311) (511)

Detectors :

Gaz chambers : ***flexible, easy***

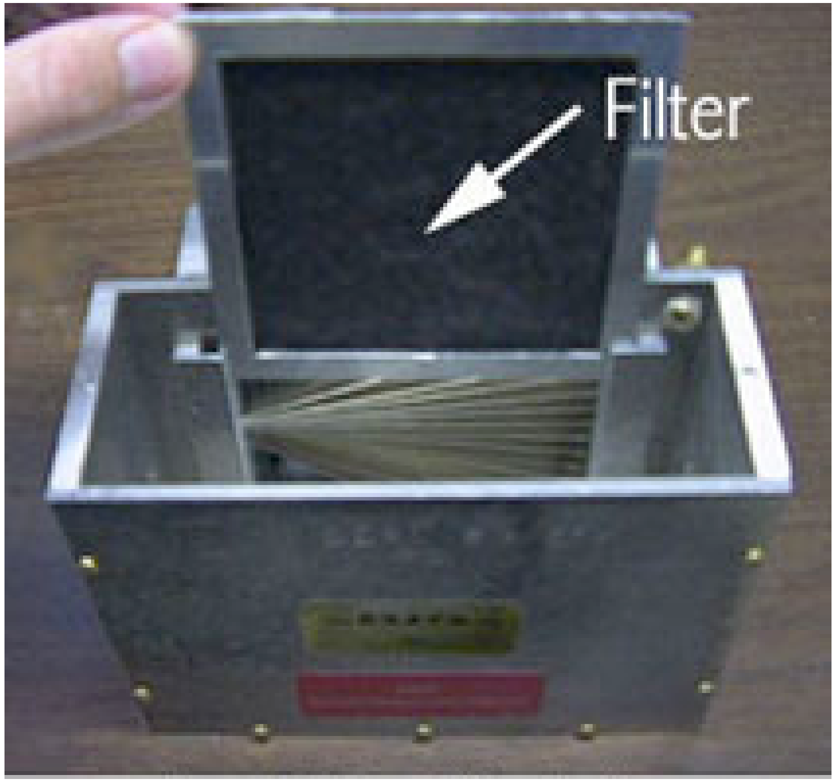


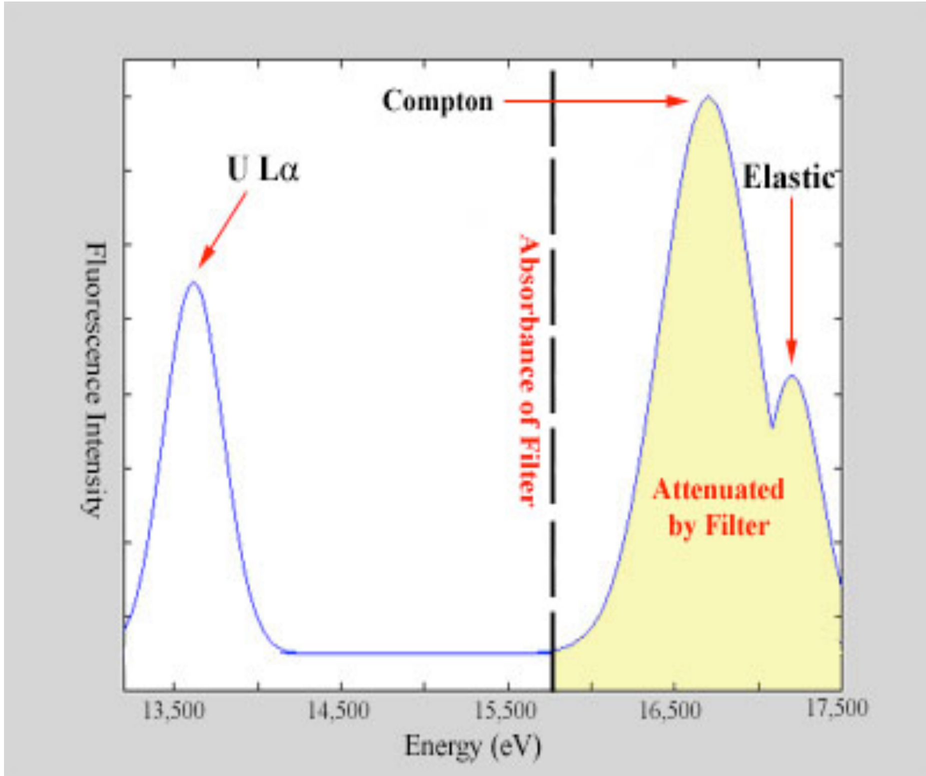


Solid state detectors :
more sensitive, expensive

Si-strips : ***the future, all in one***
(no cooling)

• **data collection "in fluorescence" ("through the fluo"):**





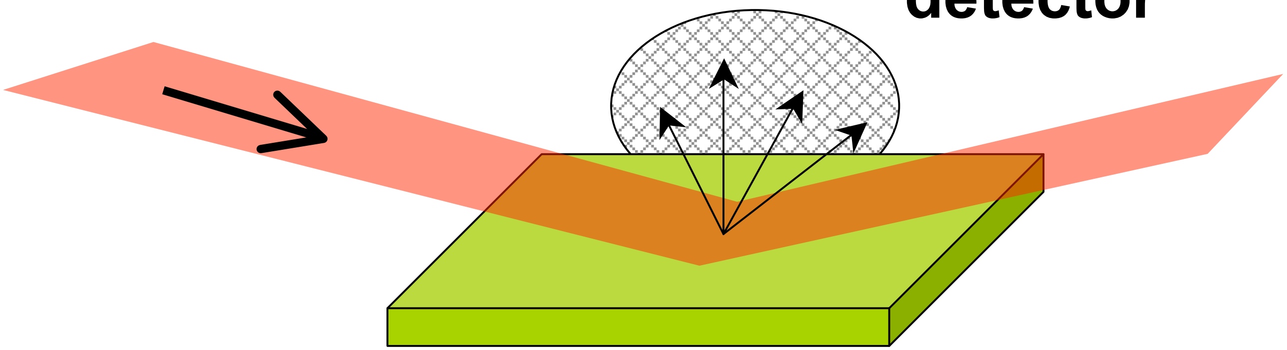
MES 11-2 SSRL beamline documents

• **intensity of the fluo. is proportional to the absorbed x-rays**

• **use a filter to cut unwanted "elastic scattering"**

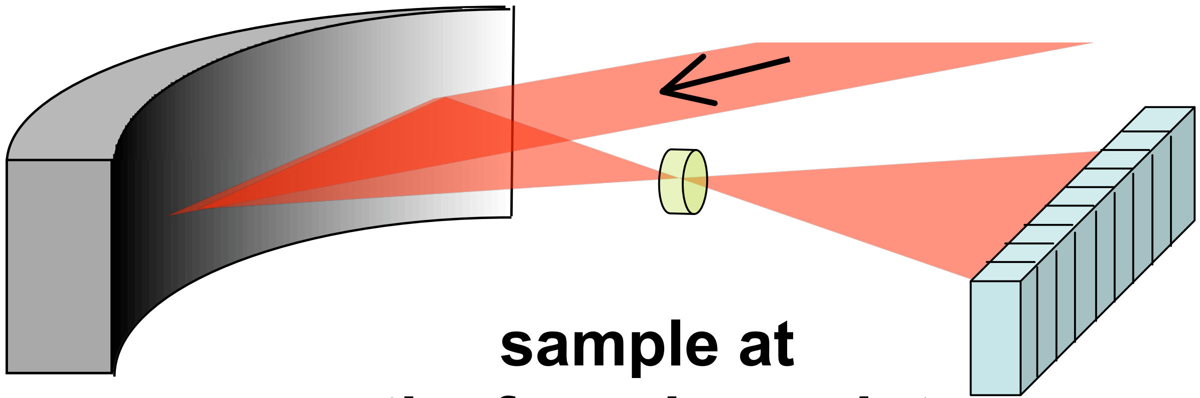
OTHER MODES :

- **REFLEXAFS (SEXAFS / GI-EXAFS) :**



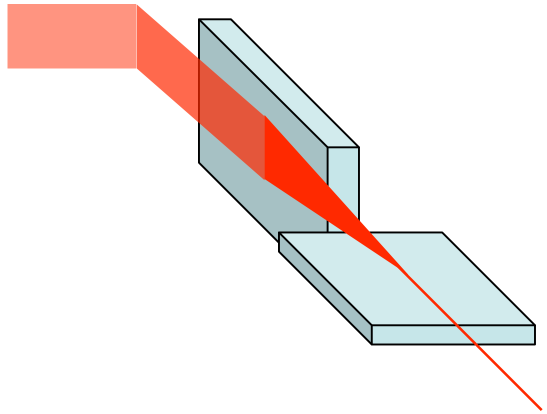
FLUO

- **DISPERSIVE EXAFS :**



TRANS

top : microXAFS (and nanoXAFS…)



- various focusing devices :
  - Kirckpatrick-Baez (“KB”) mirrors
  - capillaries
  - Fresnel zone plates

- advantages
  - lateral resolution down to the µm
  - coupling chemical mapping / speciation
  - 3D XAFS tomography

- problems
  - auto-absorption at the point of impact (corrigible)
  - baseline distorsions (corrigible)
  - high quality EXAFS is harder to get
  - local concentration rather high (> 0.1 wt. %)

II. Analysis & data reduction in real

I) corrections
II) pre-edge
III) edge
IV) EXAFS

(1) Deadtime corrections

(in fluorescence, using solid state detectors)

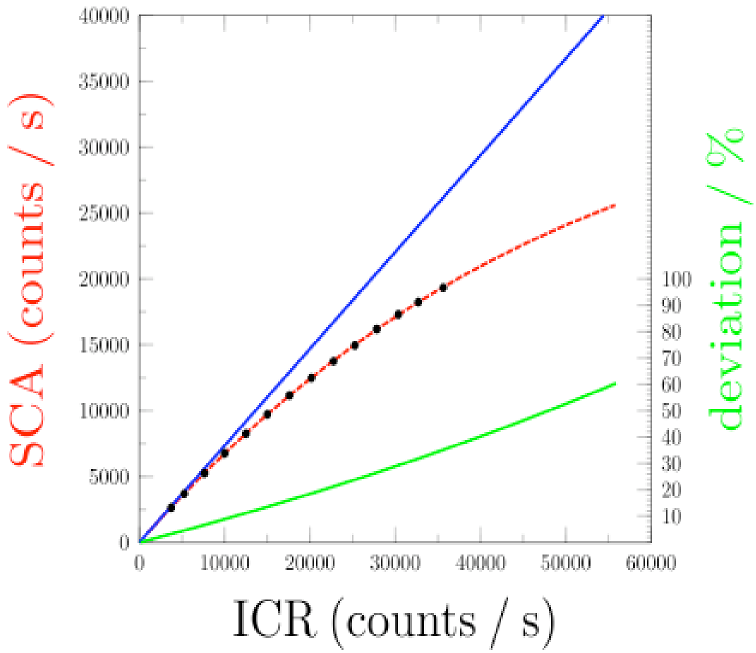
It is a fluorescence correction factor, measured for each energy available on the spectrometer used

Minor but important intensity corrections

Can significantly reduce noise in your data

Specific to each beamline, often negligible (negliged), sometimes really worth to consider !

Ask your beamline scientist about that (even if he/she hates…)



Konarev et al. (*1999)*
Hasylab-Desy

2) non-linear baselines :

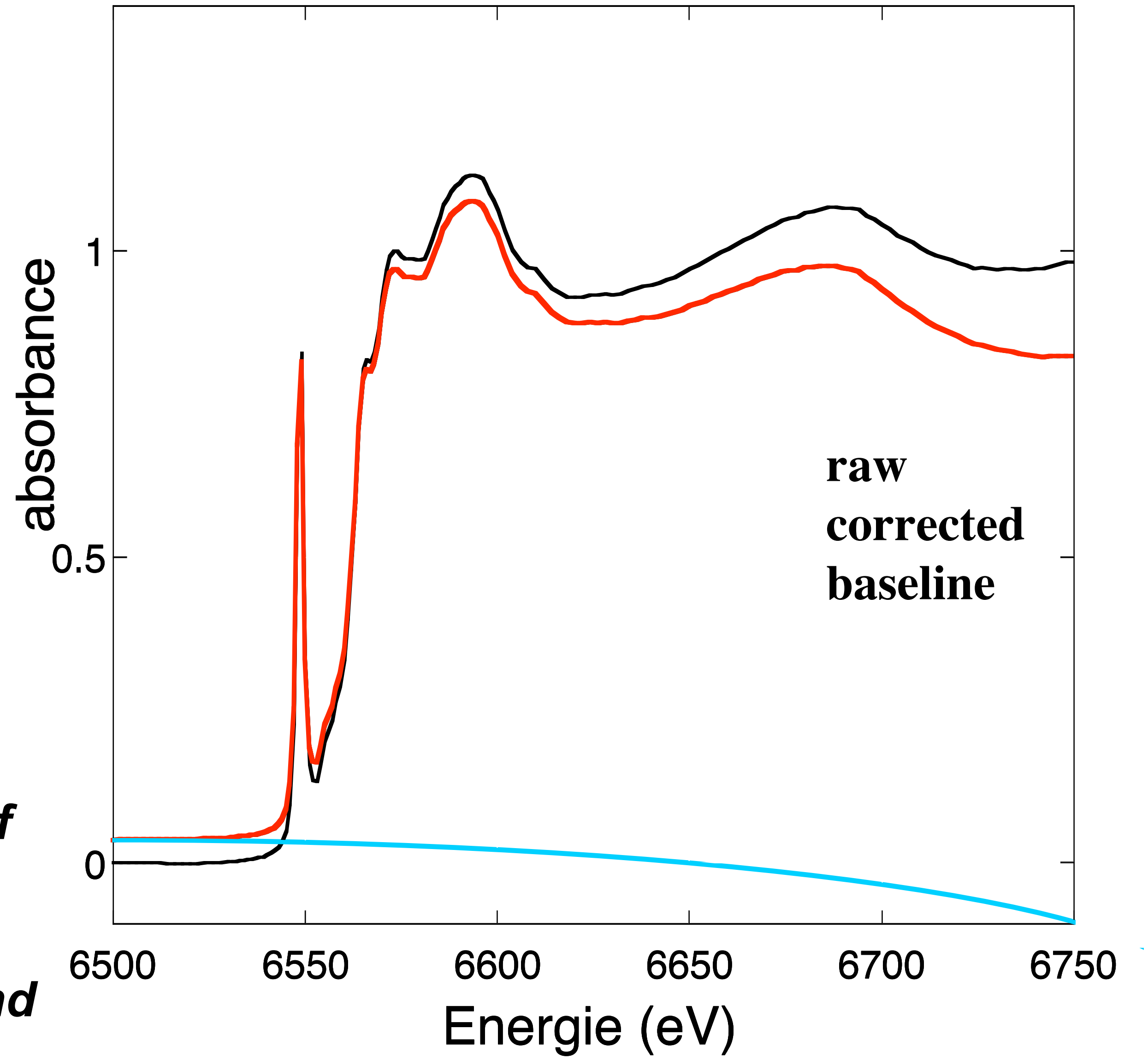
- *μ-XAFS*

- *use of solid state detectors in some cases*

self-made code

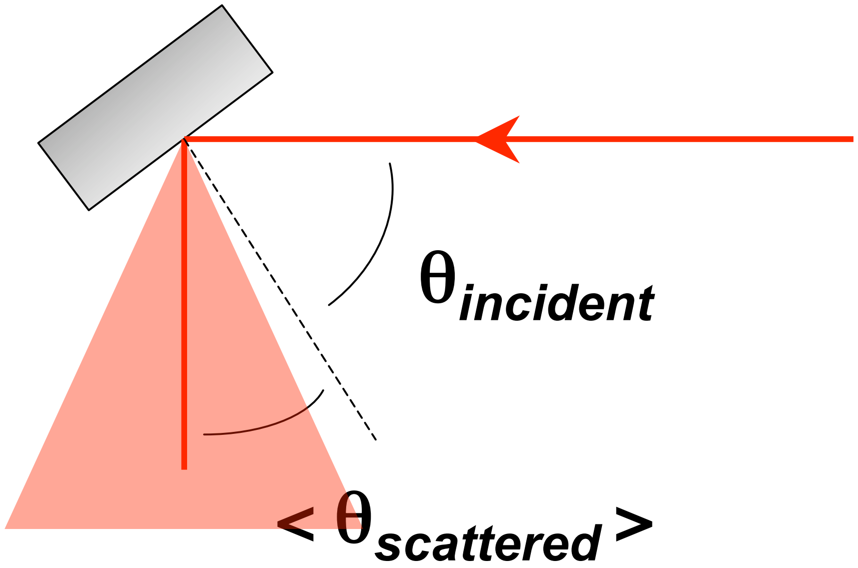
using combination of polynomials

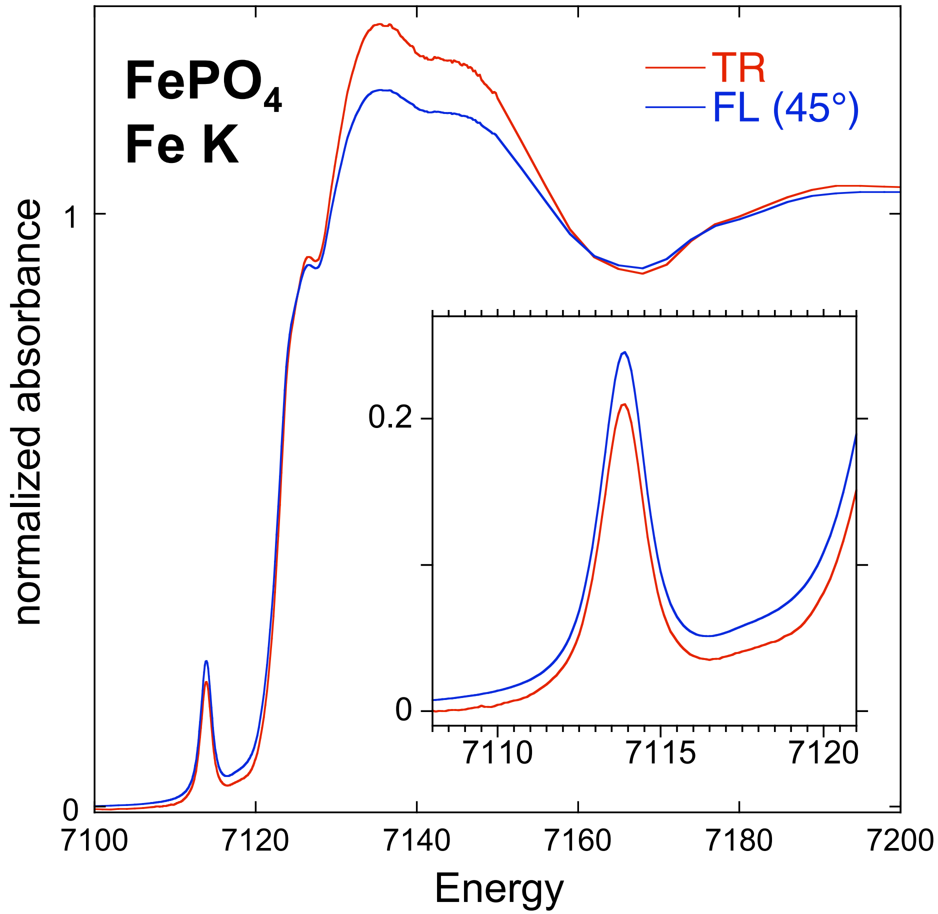
to "flatten" before and after the edge



3) Self-absorption corrections

(in fluorescence)





Haskel et al., 1999 :

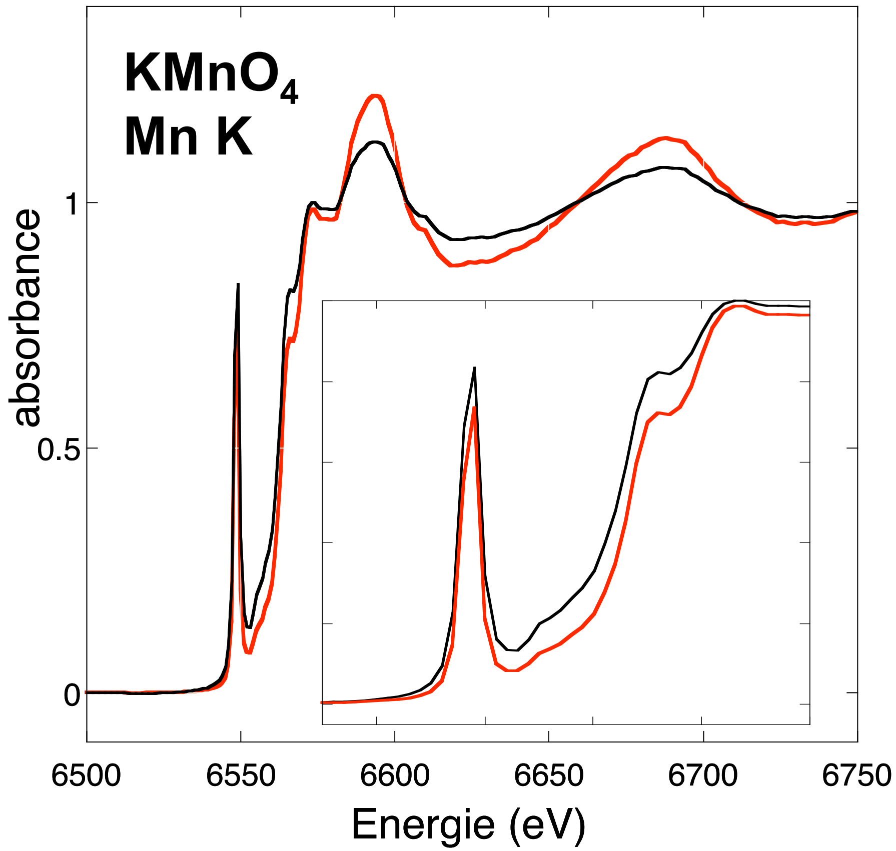
$$\frac{I_f(\omega)}{I_0(\omega)} = \varepsilon_f(\omega)\,\frac{\Omega}{4\pi}\,\frac{\mu_e(\omega)}{\mu_t(\omega) + \mu_t(\omega_f)\,\dfrac{\sin\theta_{incident}}{\sin\theta_{diffusé}}}$$

S.A. occurs when :

45° geometry

+

Absorbing atom is more than (±) 20 mol.% in sample on the sample surface illuminated

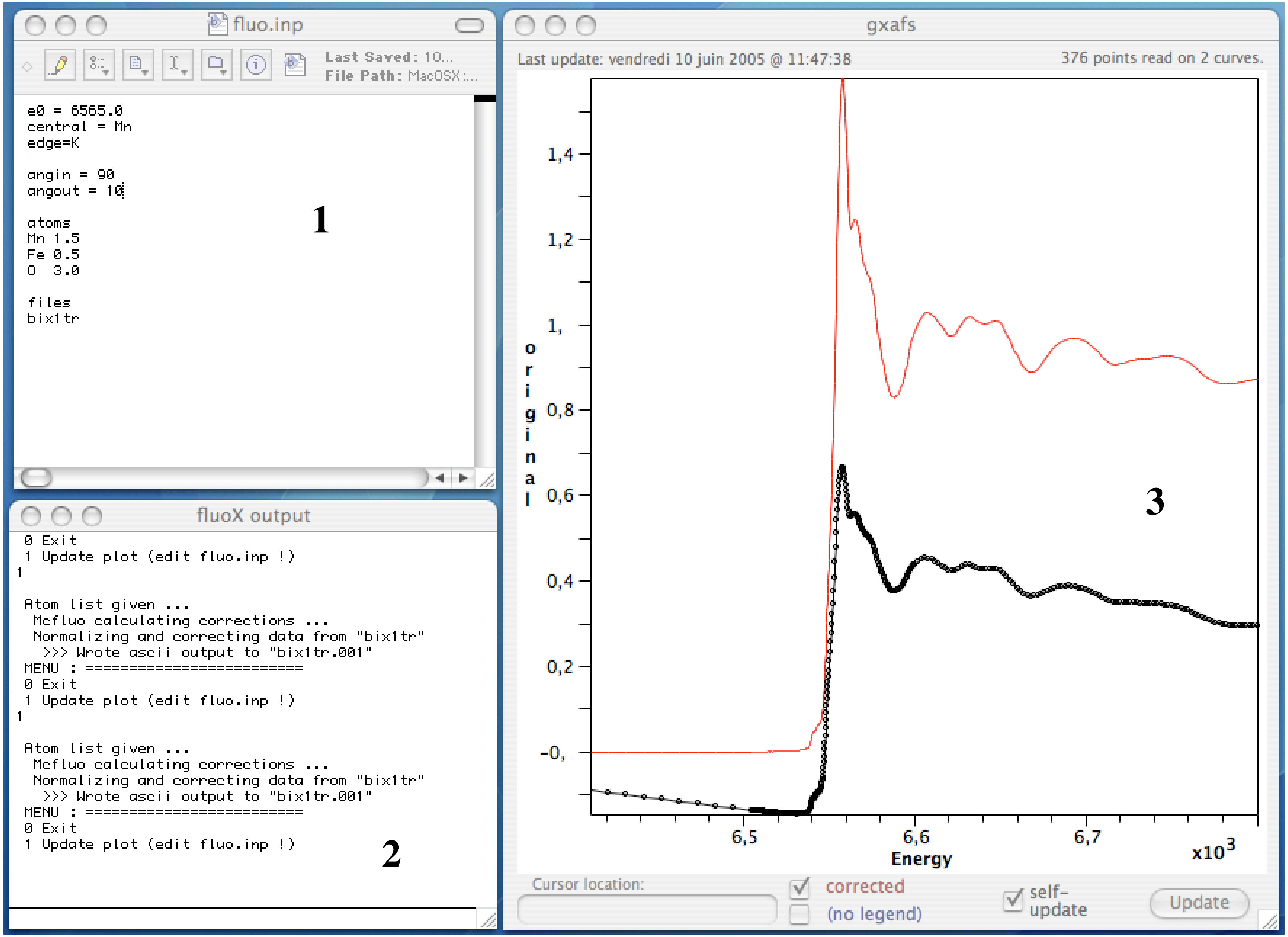


Tricks :

Use either 90° OR 45° geometries

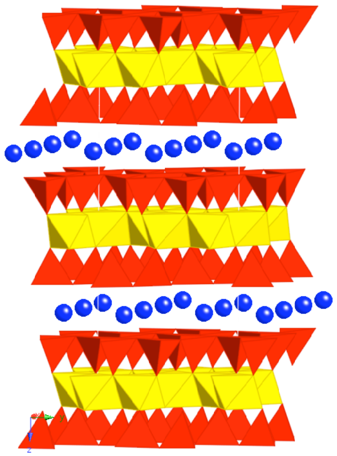
Diluting in a non-absorbing matrix won't help !!

FLUO-X *(home-made, with graphical interface)* 1-2-3



4) Polarization artefacts :

atoms along the polarization direction of the X-ray beam are preferentially probed (and ± attenuated)



important for layered structures :

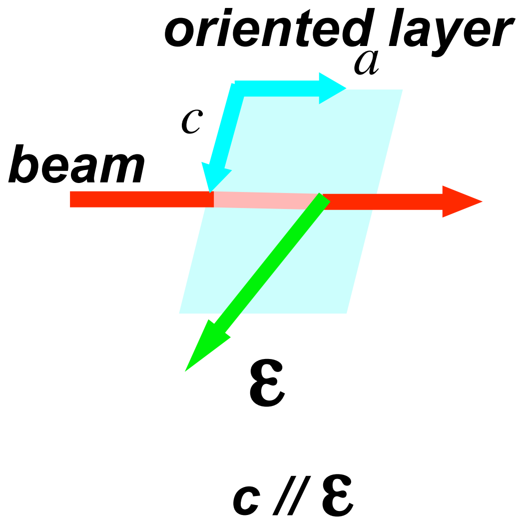
micas, *clays, phyllomanganates …*

angle-dependant approach : α

angle between the **ε** vector and the **layer plane**

yields P-corrected amplitudes

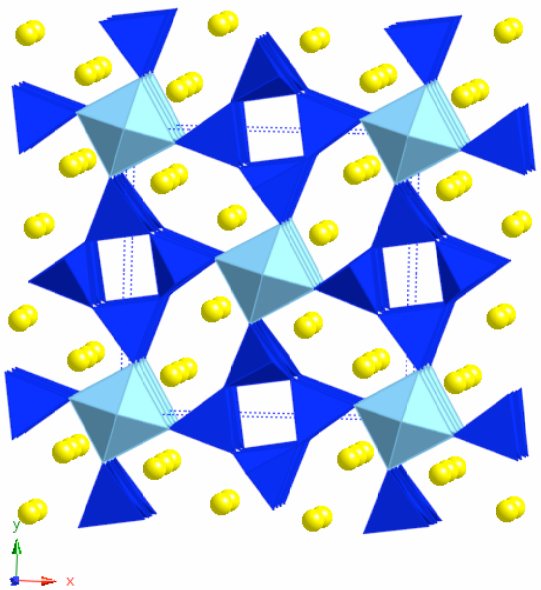
Manceau et al. 1988, 1990; Manceau and Schlegel, 2001

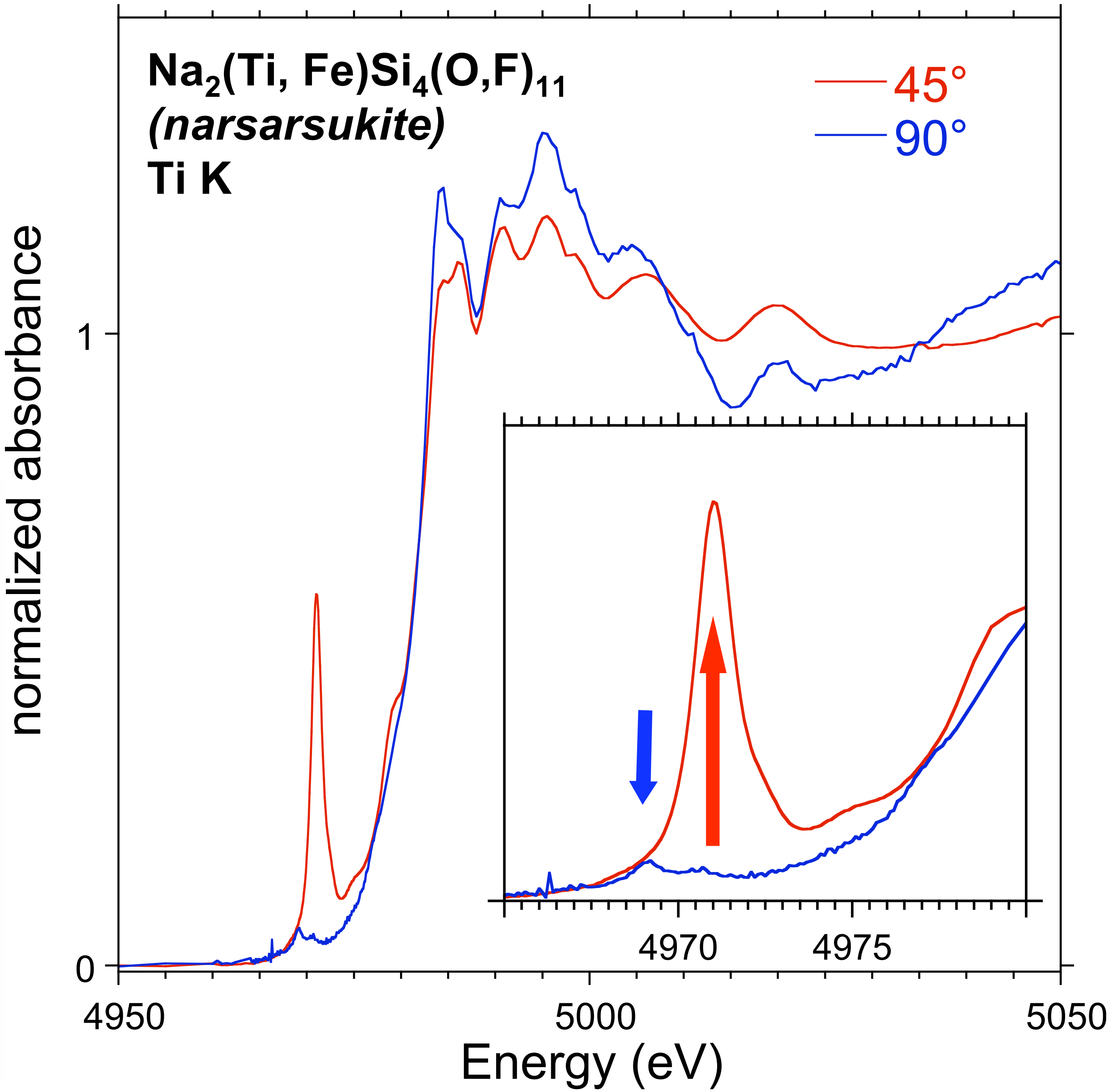


help discriminate between neighbors

can be applied to textural analyses

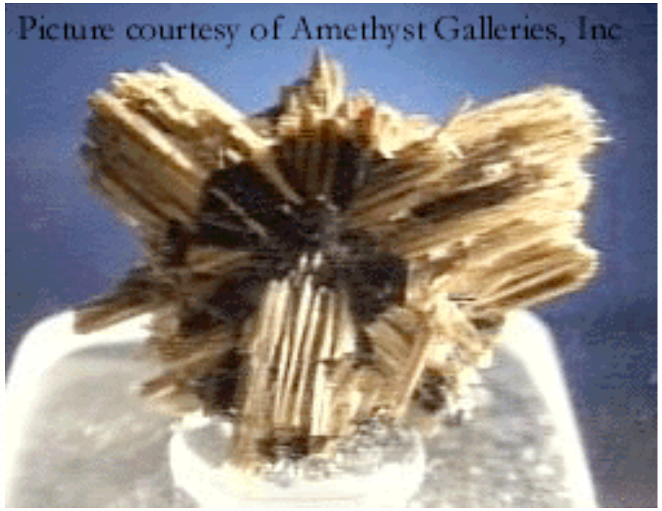
WARNING : self-absorption vs. polarization

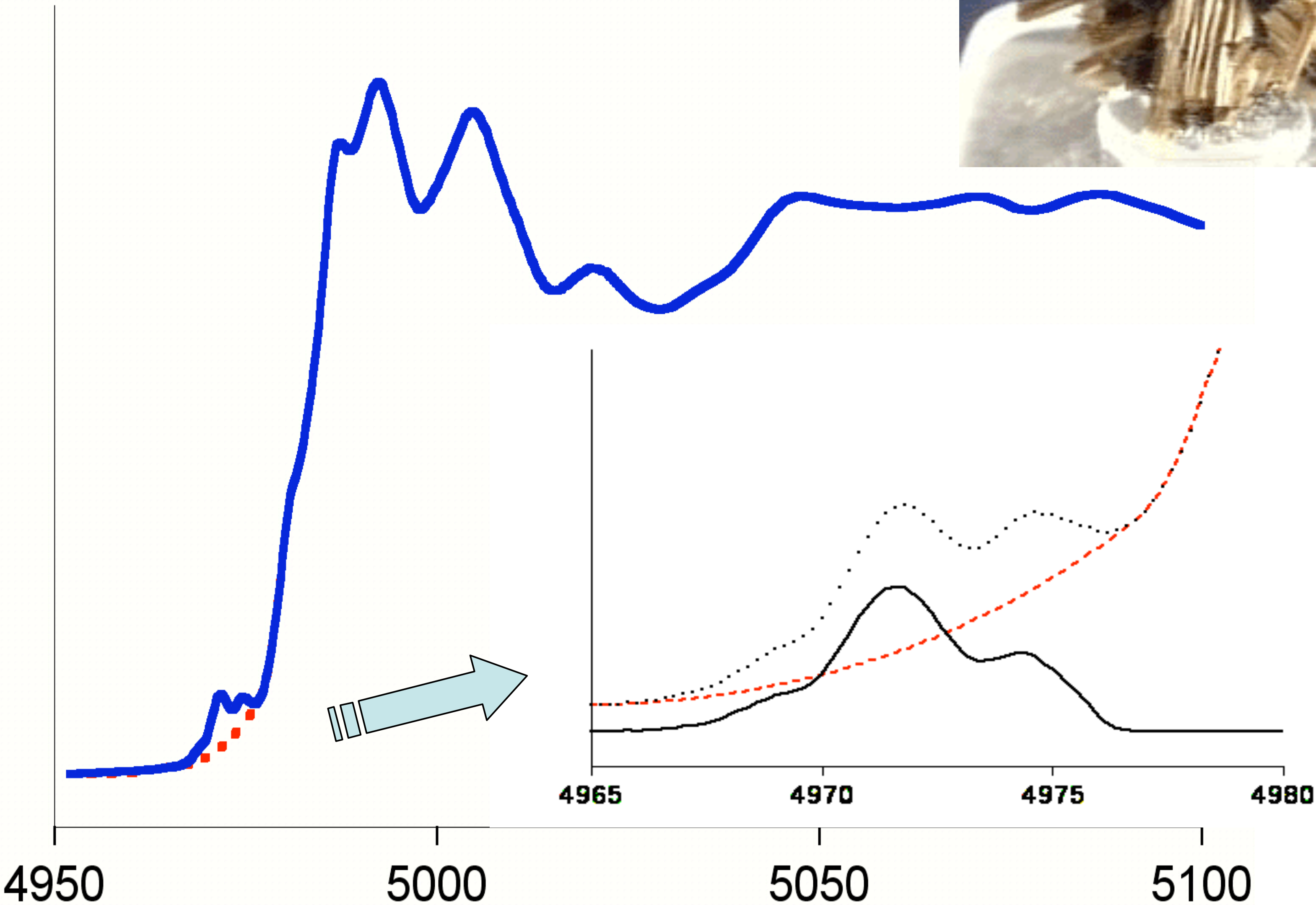




II) pre-edge region

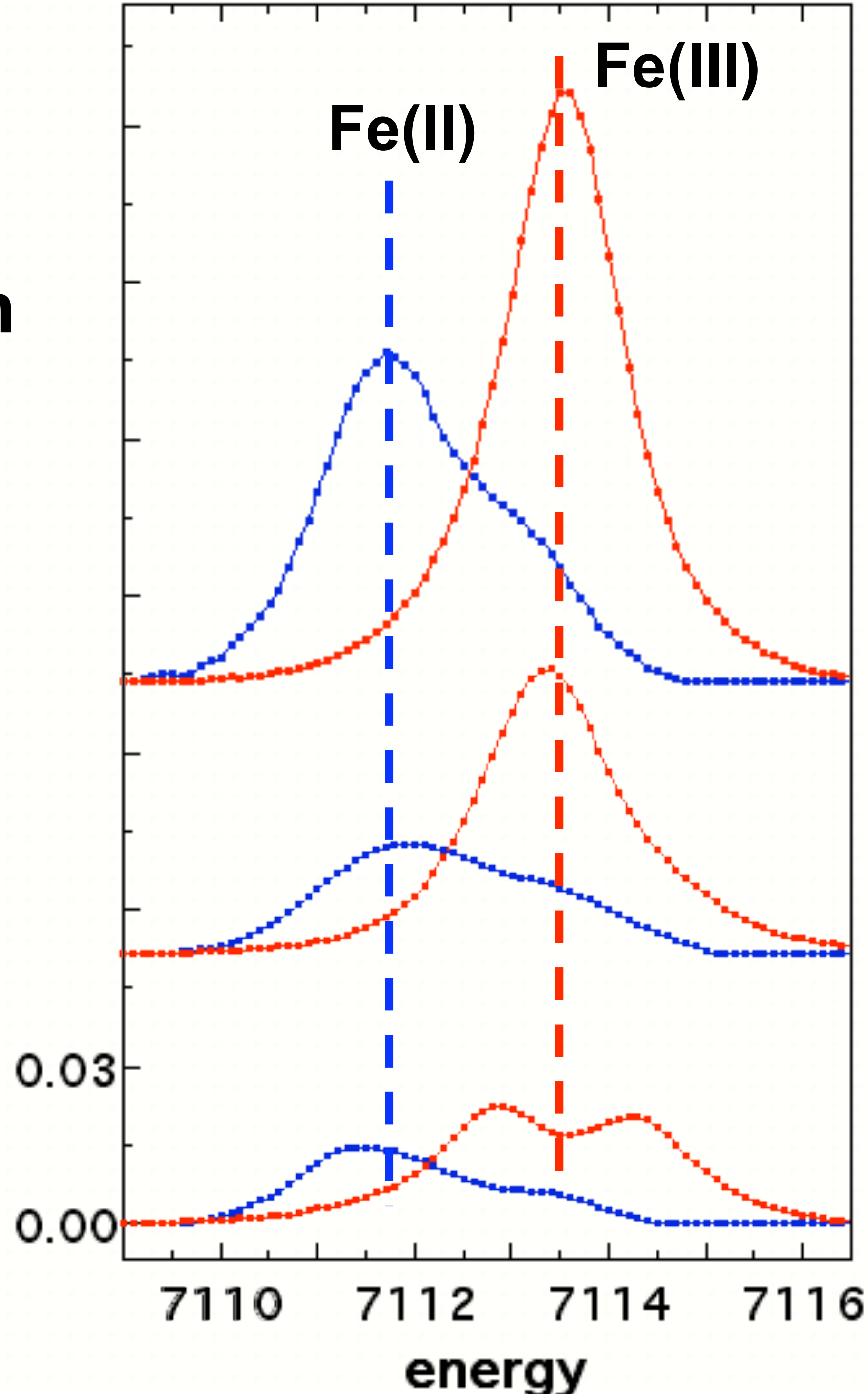
rutile (TiO_2) at the Ti K-edge :

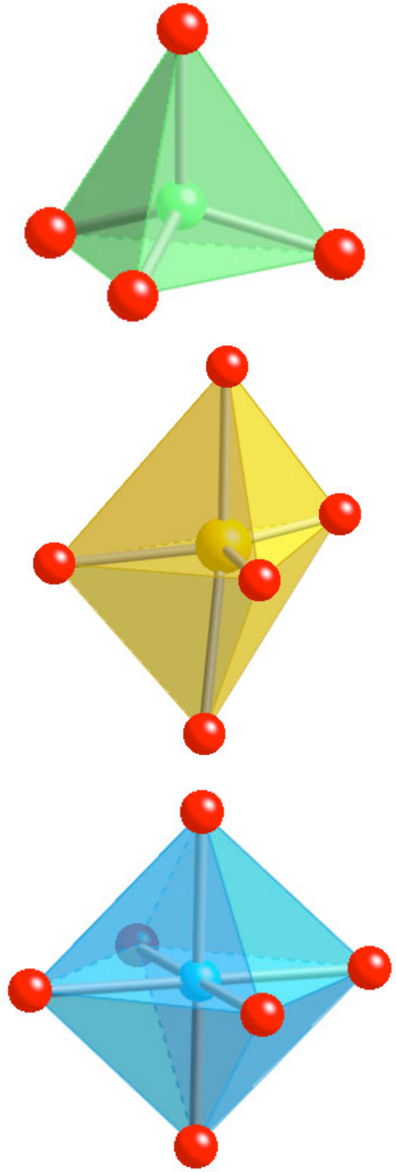




• **variation with**

  - **redox**
  - **symetry**





Modeling :

- « peak-fitting » or deconvolution

  - number of lines to fit ?

  - with which shape ?

    ♦ core hole : *lorentzian*

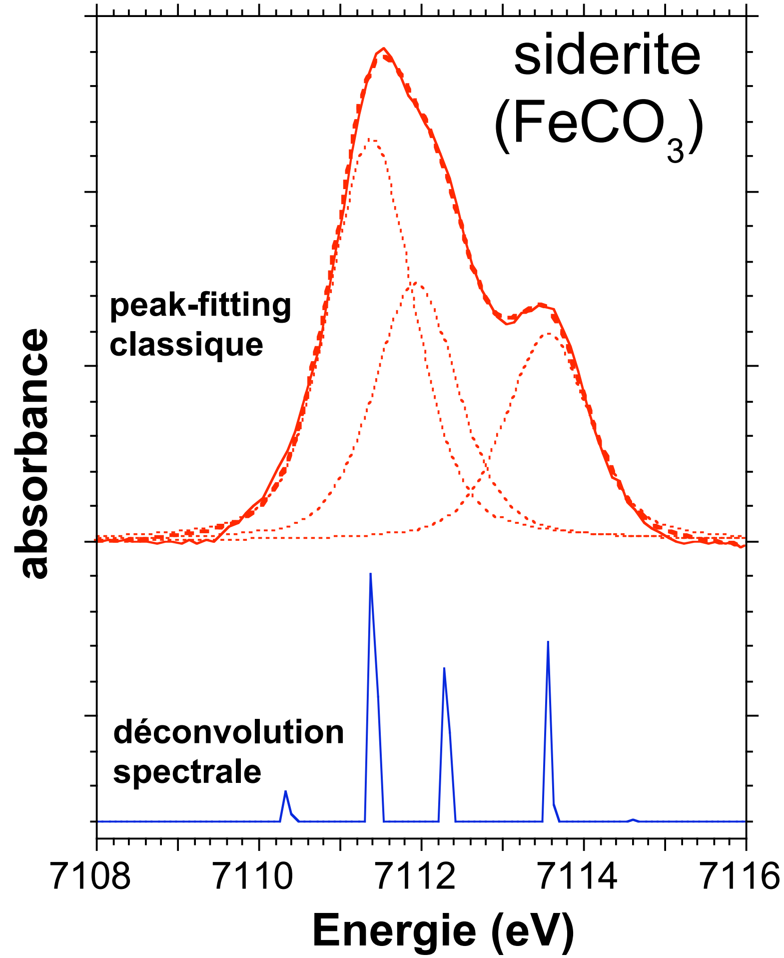
    tabulated by Krause & Oliver (1979)

    ♦ experimental resolution (mono, source size….) : *gaussienne*

    measured by the beamline scientist

true Voigt ~ pseudo-Voigt (sum or product L/G)

% Gaussian ? width ?? intensity ???

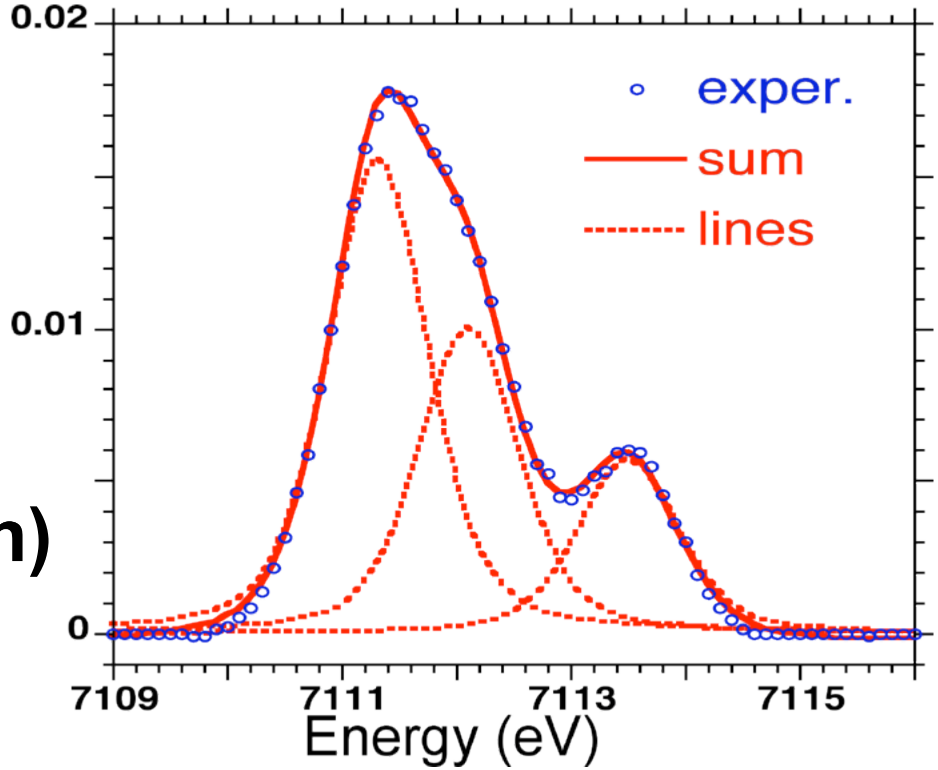


correlation with theoretical models (multiplets):

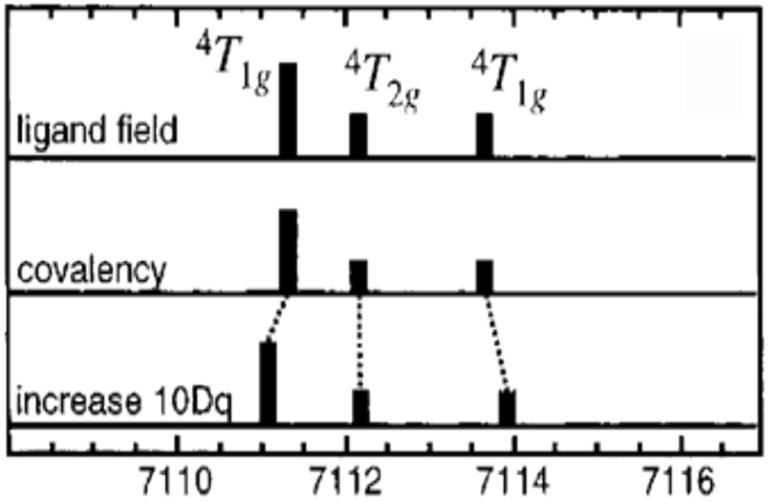
siderite

($FeCO_3$)

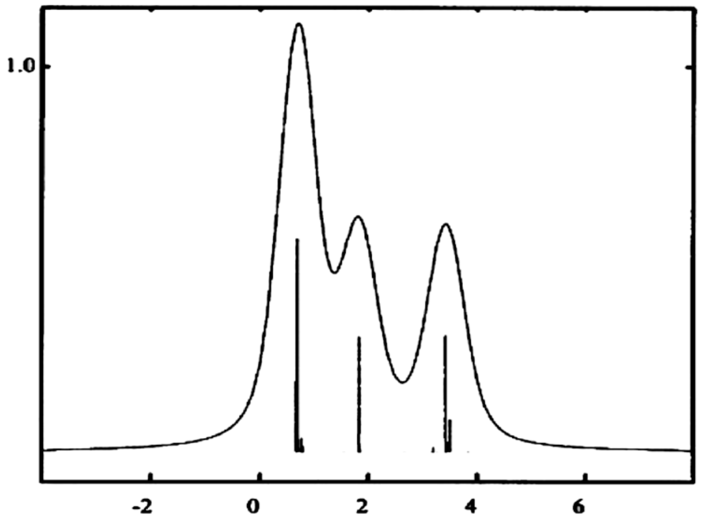
Fe(II)
(high-spin)
O_h



Siderite, mine "Pfannenberger Einigkeit", Salchendorf, Siegerland, Germany. Height 4 cm. Collection: Mineralogisches Institut Universität Mainz. Photo: © Rainer Bode, Haltern



Westre et al. 1997
JACS



de Groot, 1999
(pers. com.)

warning :

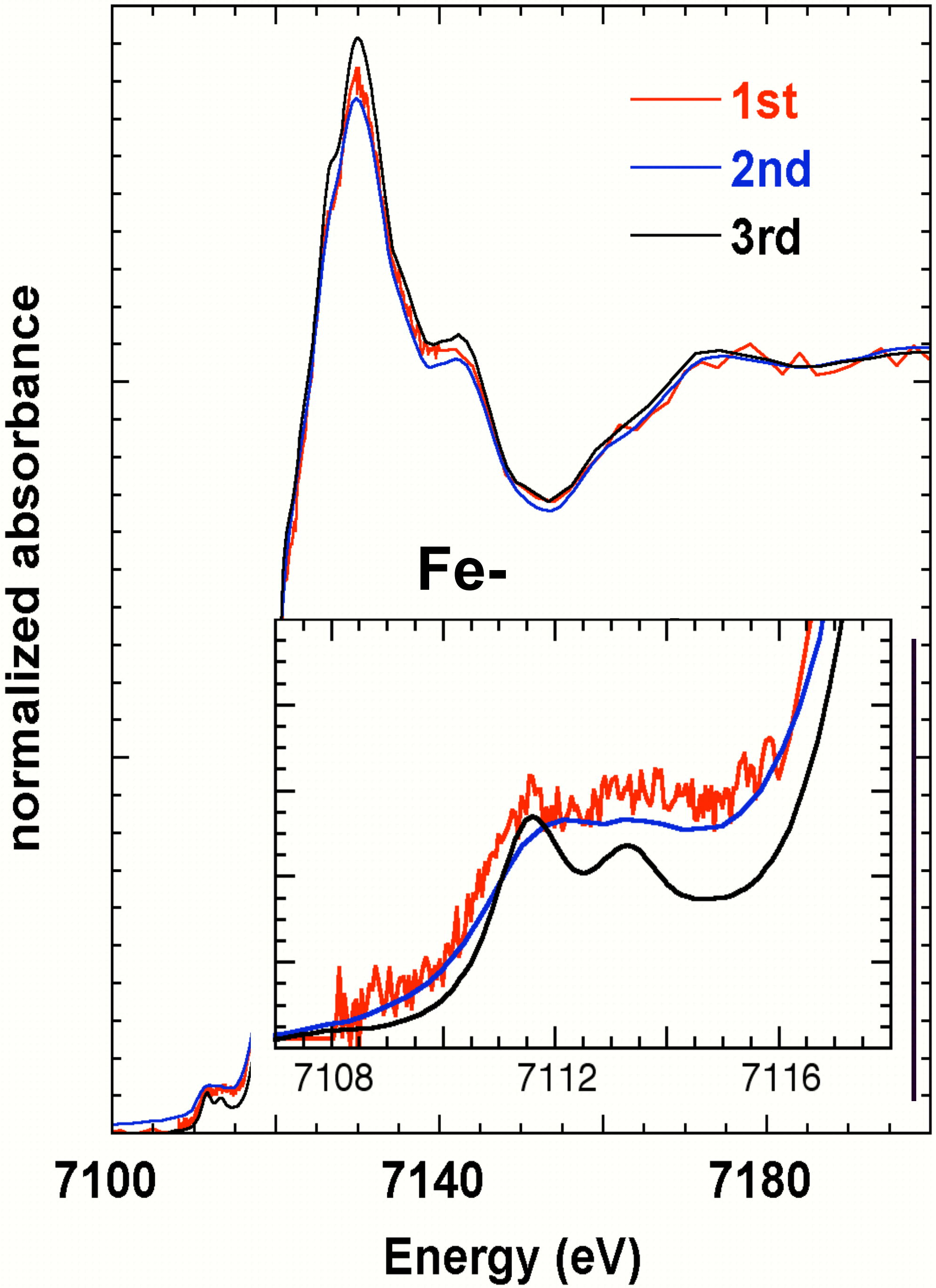
• need energetic resolution

• high signla/noise ratio

• baseline tough to model

• some features are still not well understood

• measure, as usual with XAFS, an average redox

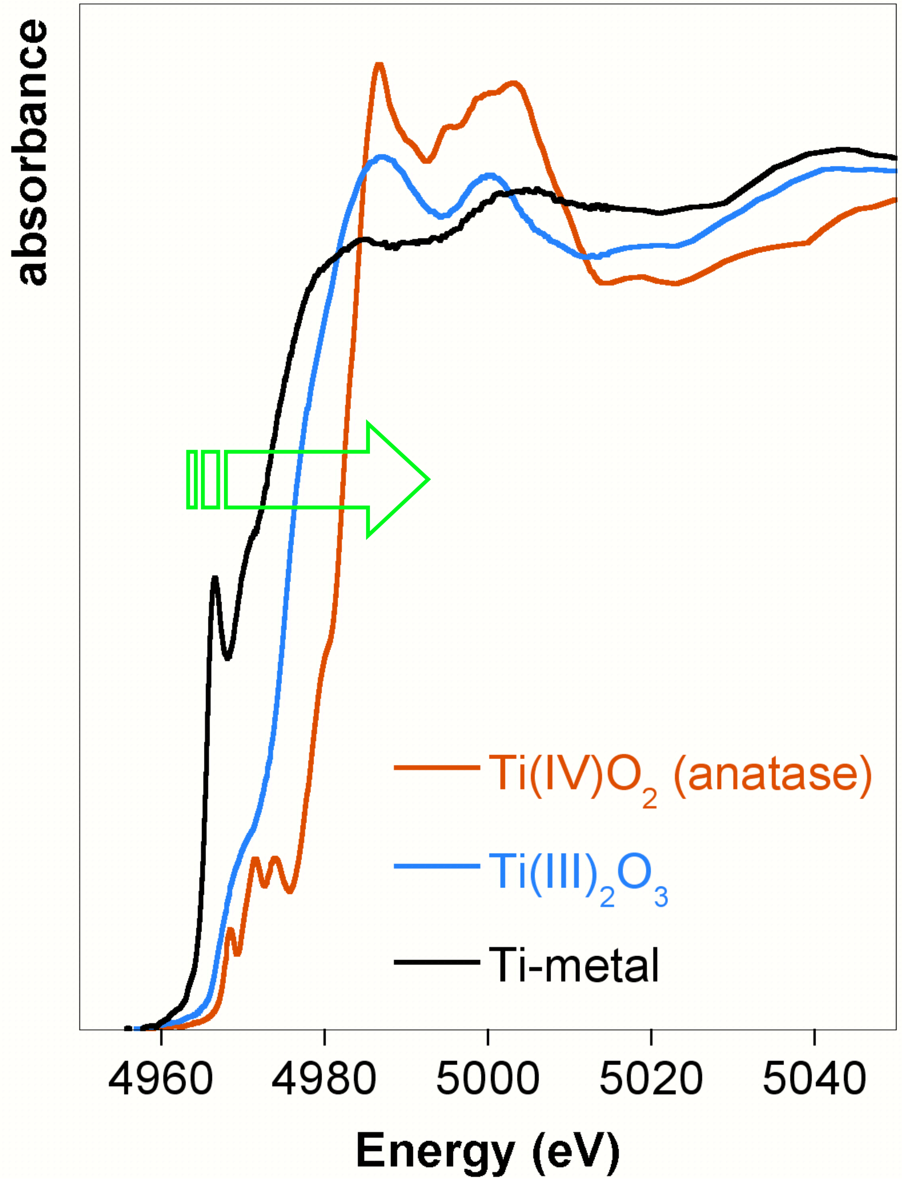


3) Absorption edge :

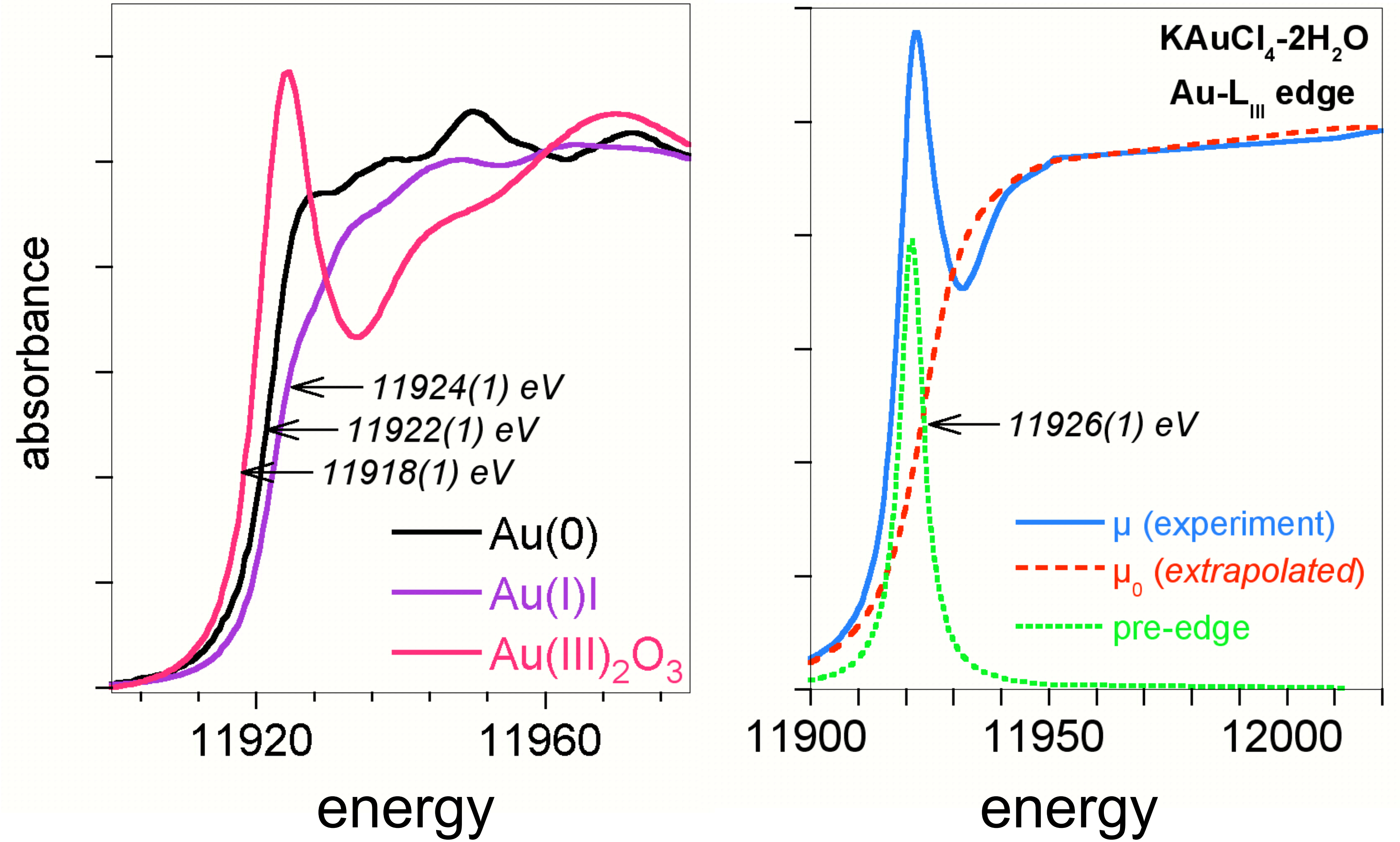
The edge position

is sensitive to redox

(roughly ~ 1 eV par e-)



Exemple:

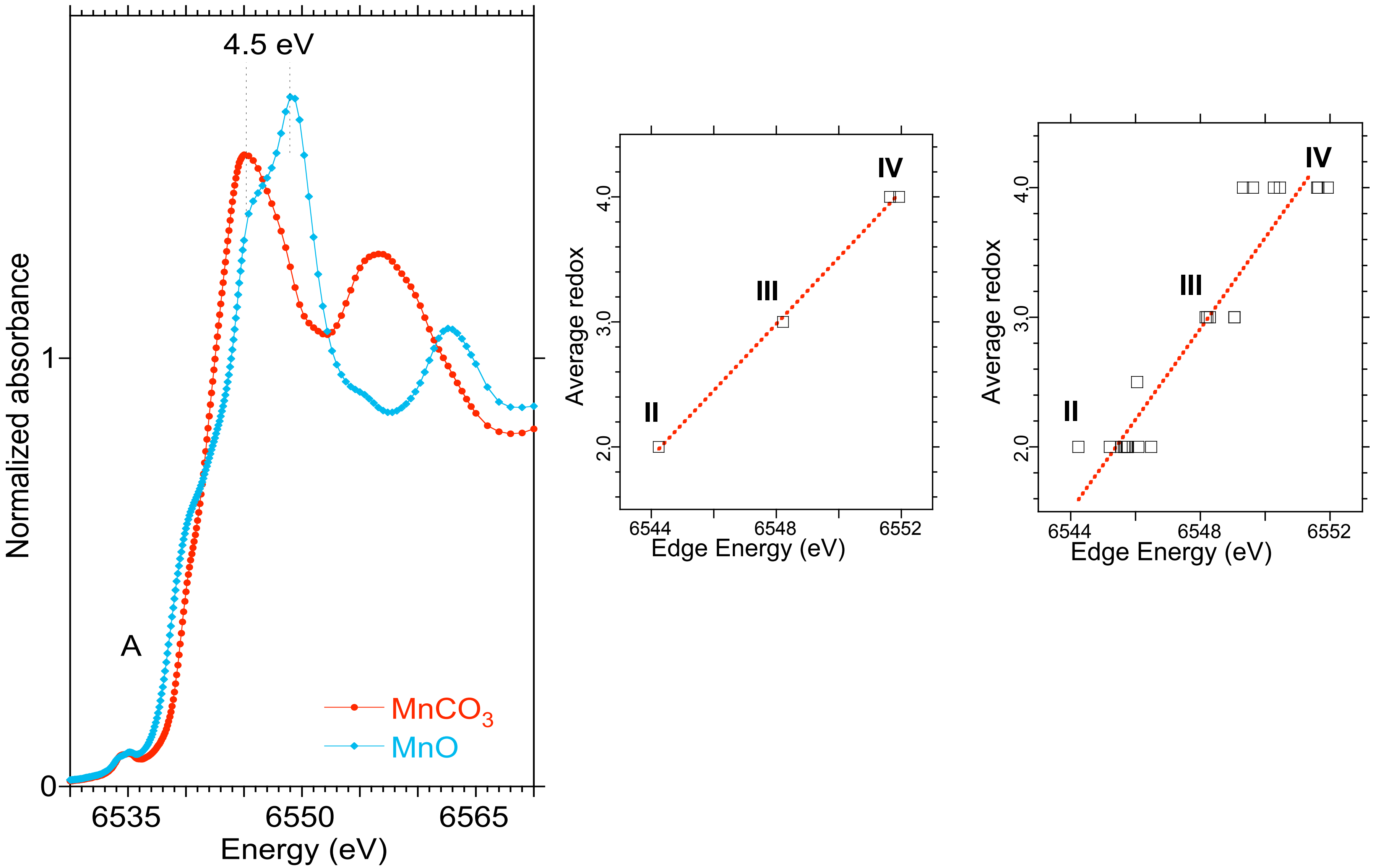


Edge of Au(III) BEFORE that of metal …

=> The edge is, in fact, a gigantic pre-edge !

Bad :

Inventing ourselves new junky edge theories or protocols

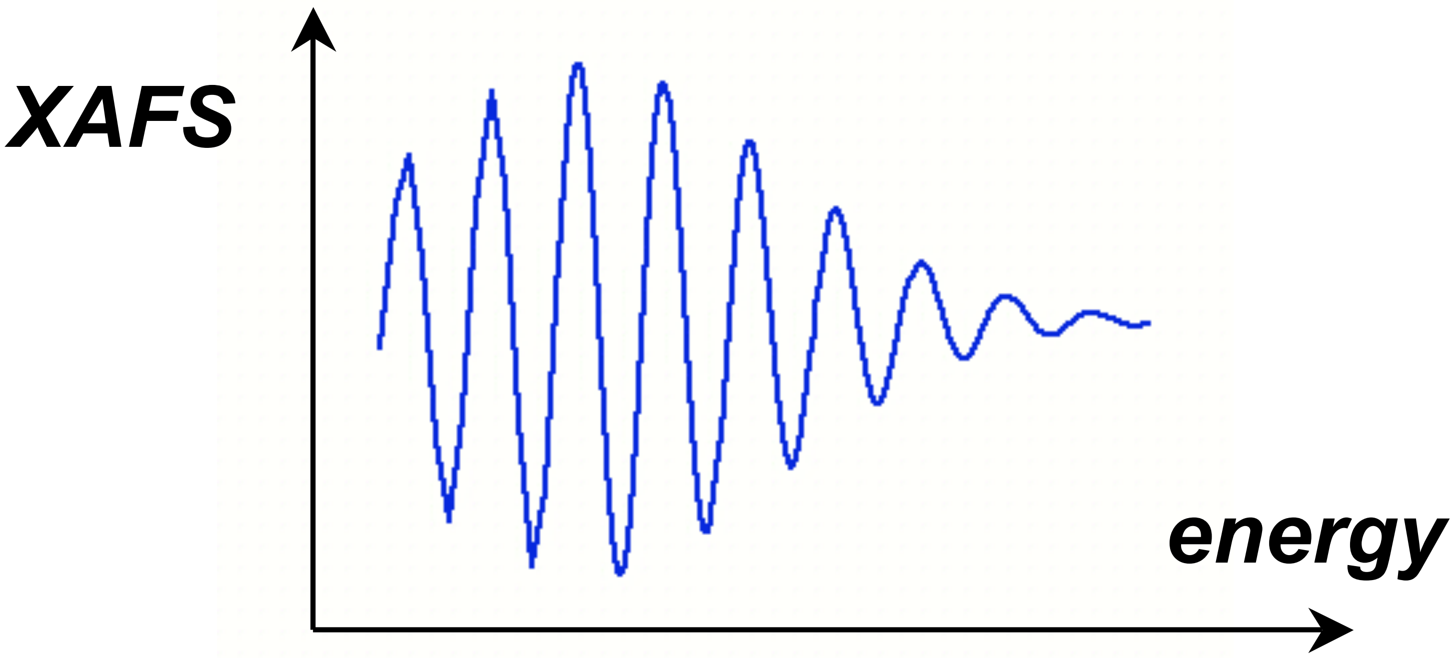


4) XAFS Interferences

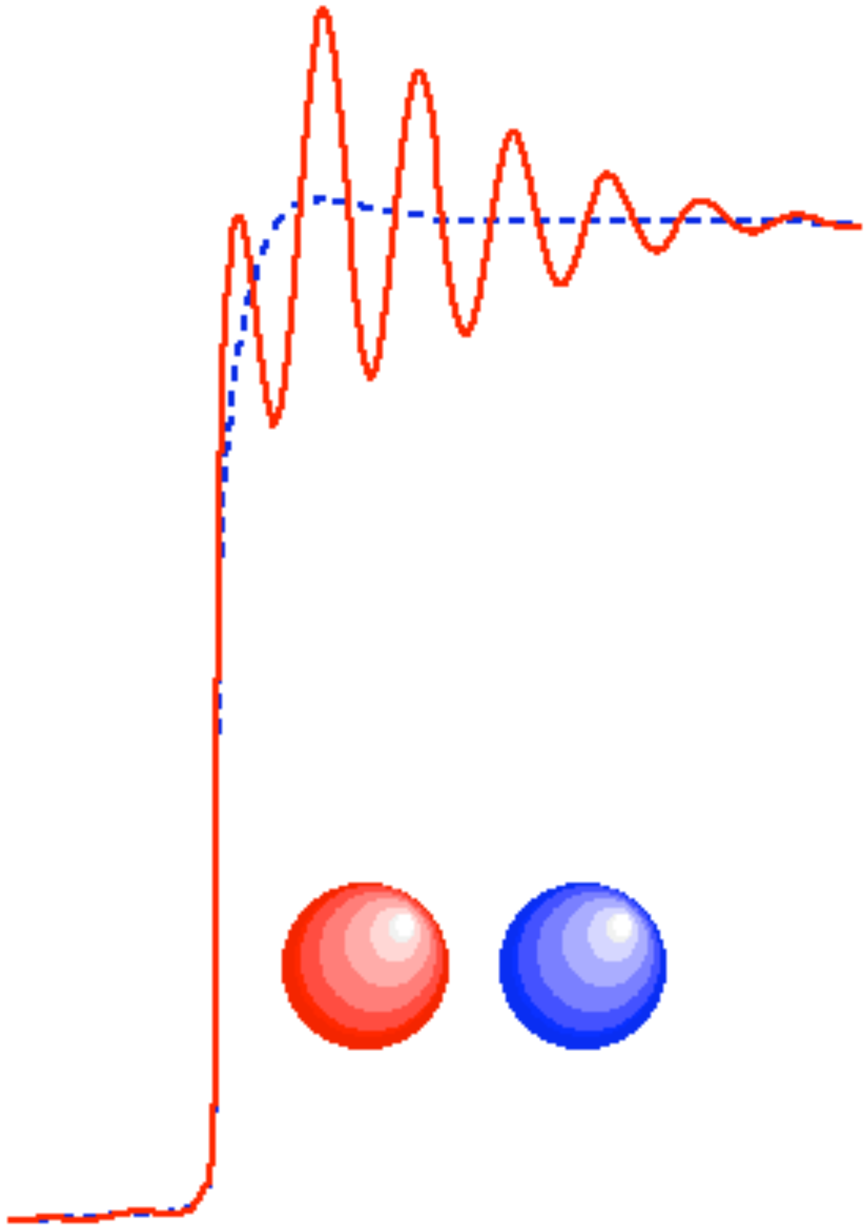
$$\chi = A \bullet \sin(\phi)$$

$A = f$ (Type , Number , disorder …)

$\phi = f$ (Type , distance , disorder …)

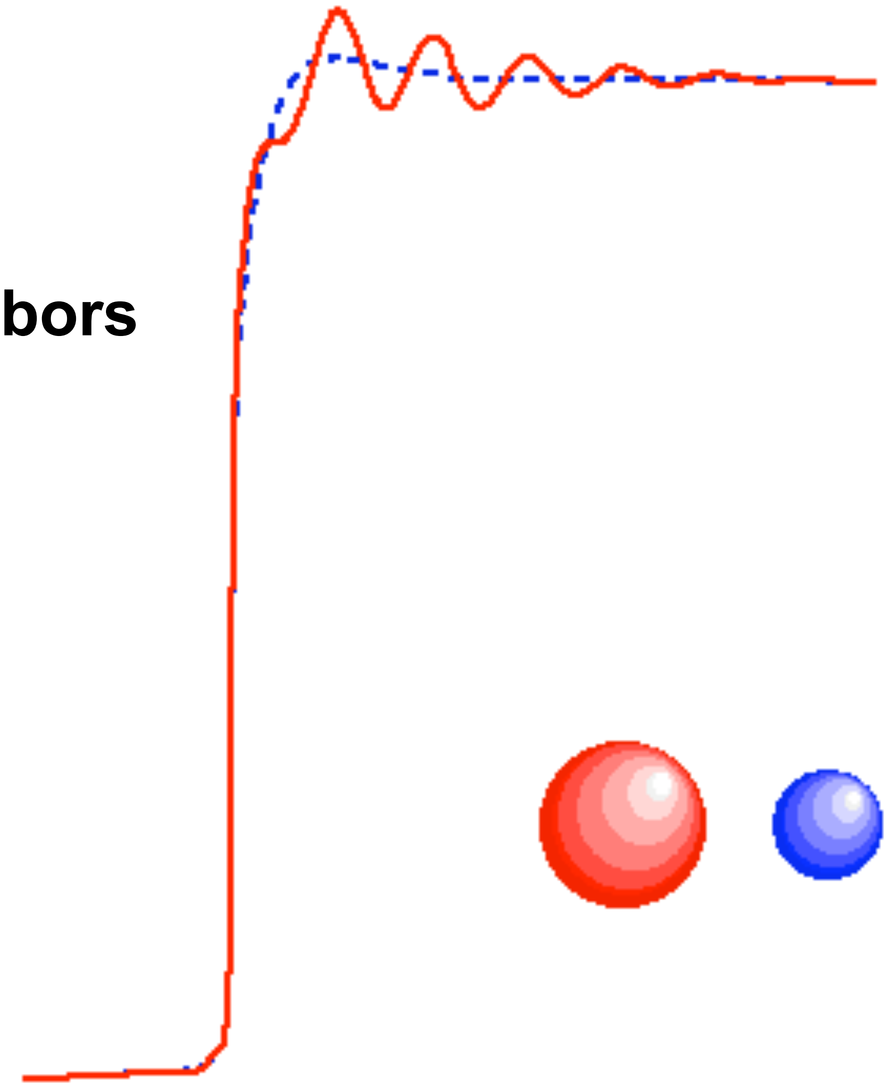


effect of
inter-atomic distance



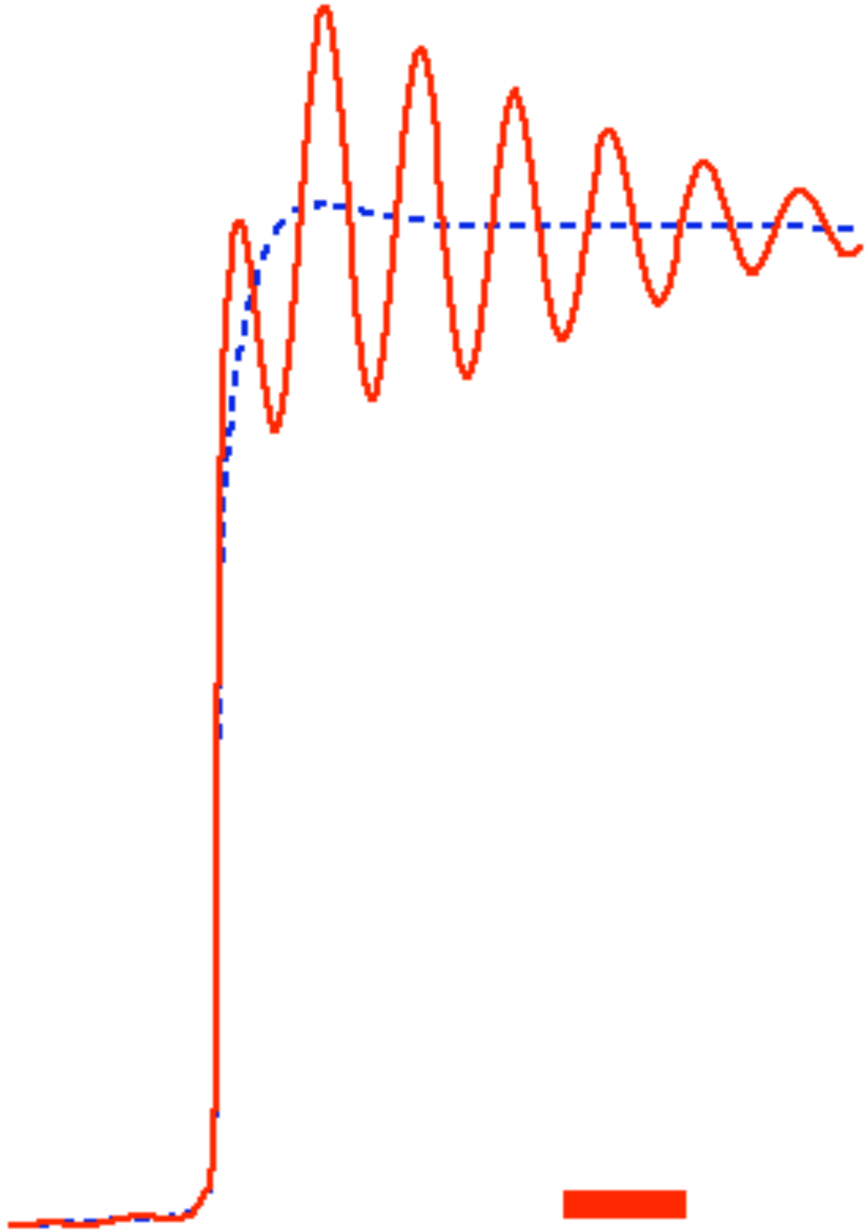
effect of the number of neighbors

(and NOT coordination !!)



effect of disorder

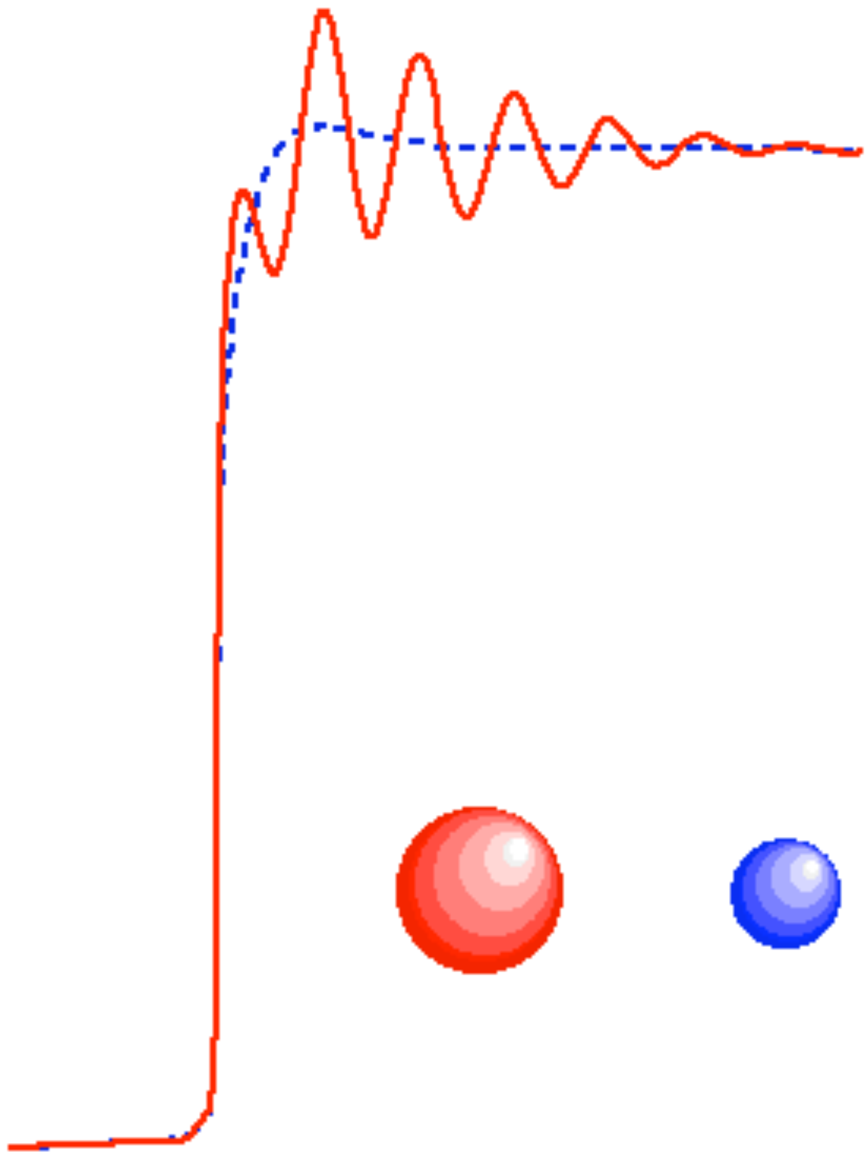
- thermal (kT)
- static (structural)



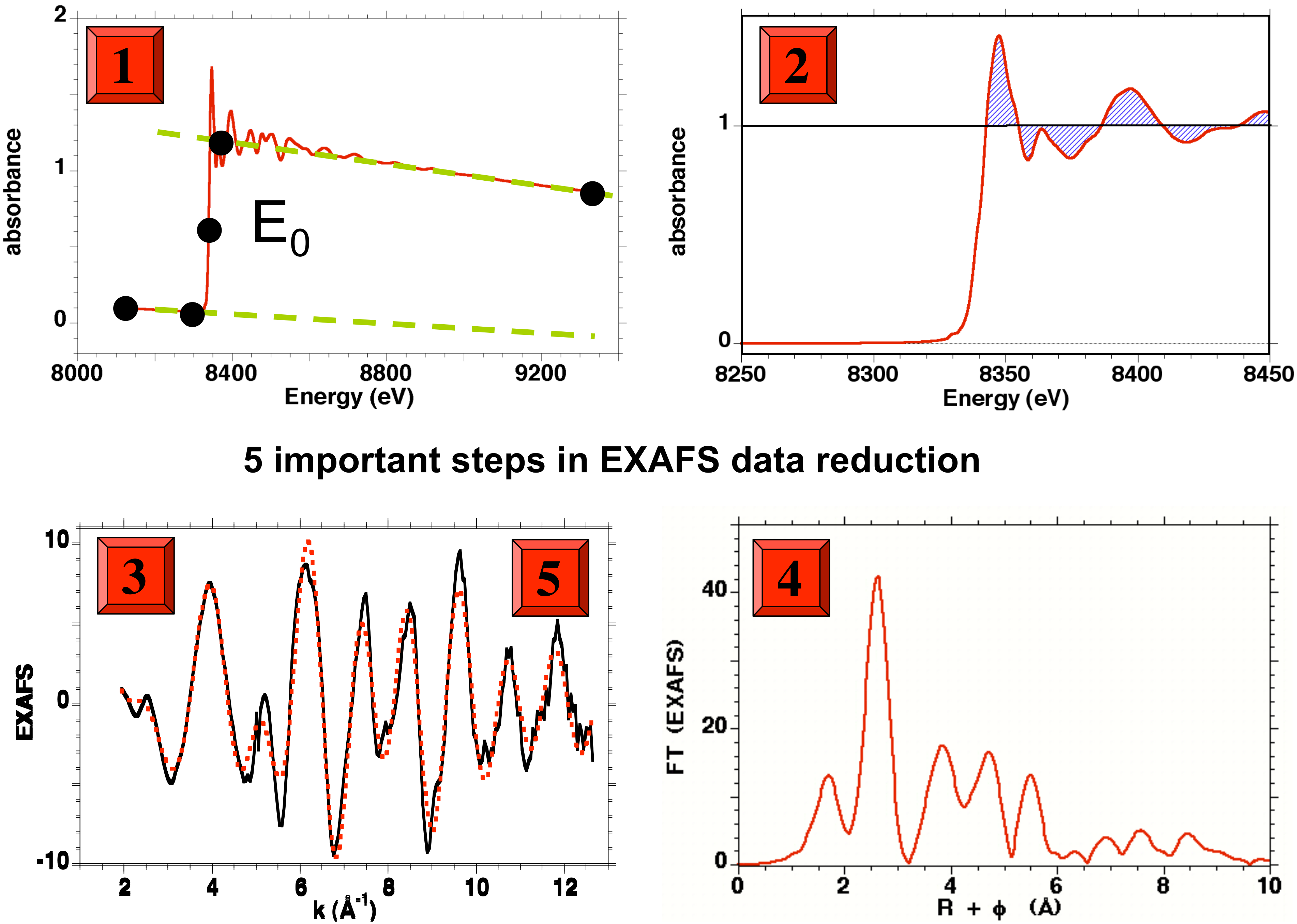
effect of the

next-nearest neighbors

Z-number

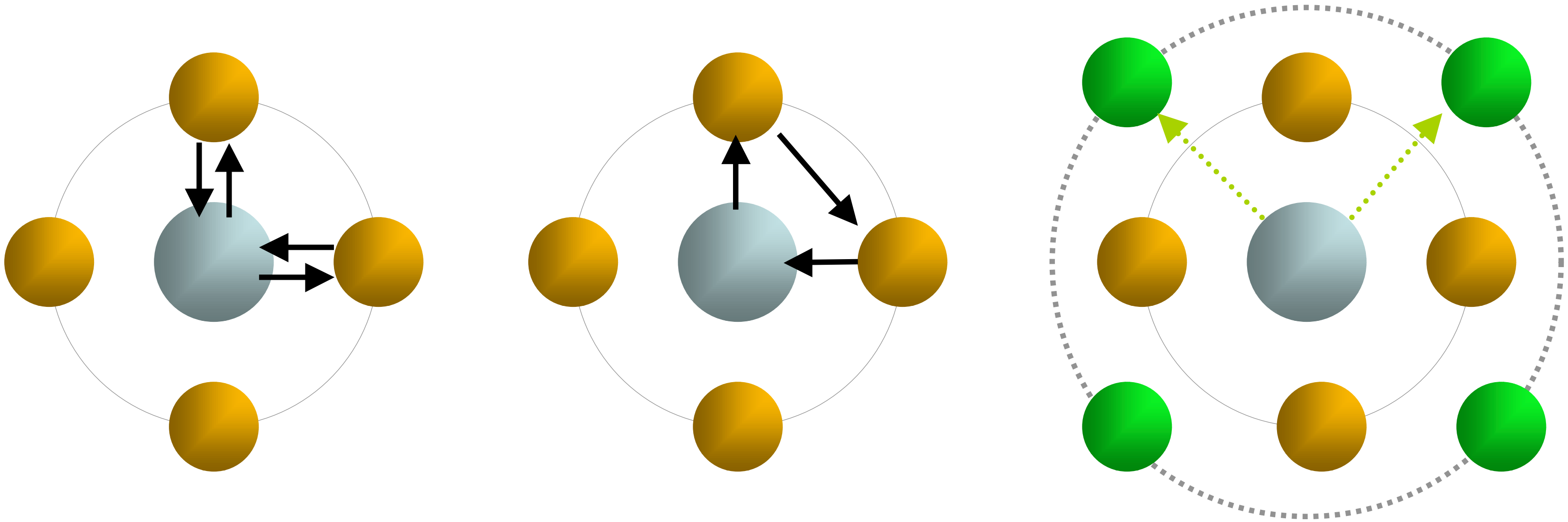


5 important steps in EXAFS data reduction



complex : multiple-scattering (MS) vs. second neighbors (SN)

$$\mu(E) = \mu_{atomic}(E)\,(1 + \chi_{SS}(E) + \chi_{MS}(E) + \chi_{SN}(E))$$



- MS is important when atomes are in a special 2D geometry
  2D (colinearity, triangles, square planar…)

- symetry should be estimated thanks to other methods
  (pre-edge, Raman, MCD, Vis-UV-IR)

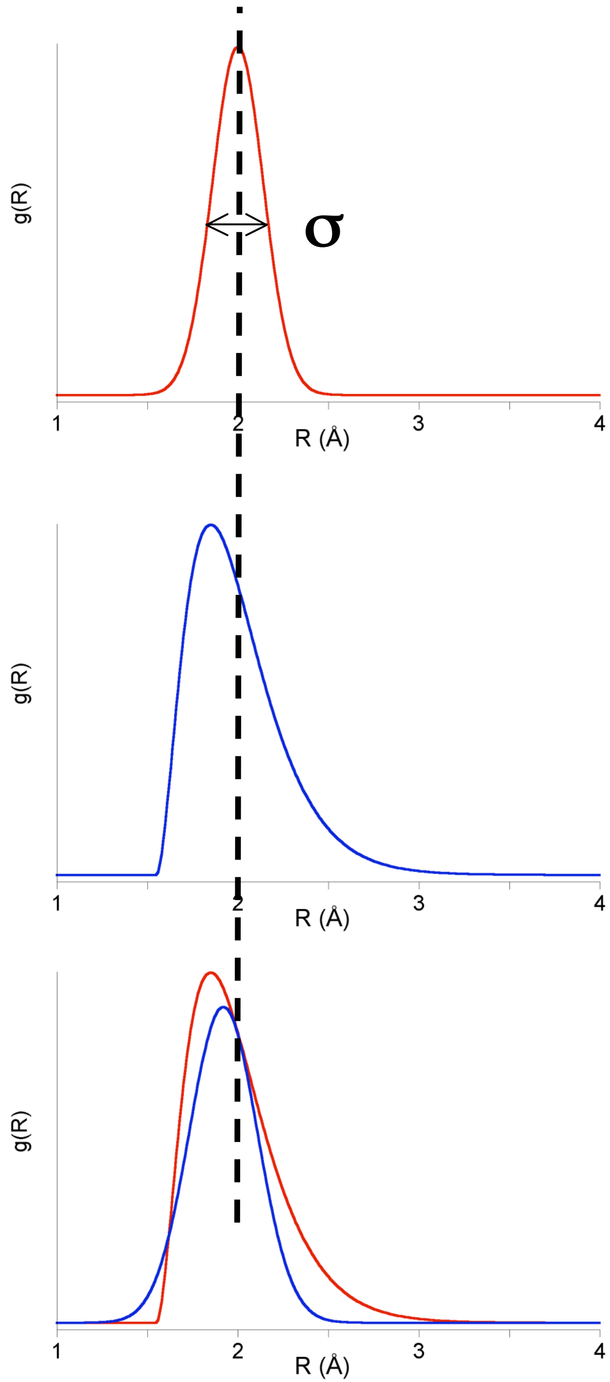
- and/or XAFS *ab-initio calculations (FEFF, gnxas etc)*

More complex : disorder effect ….

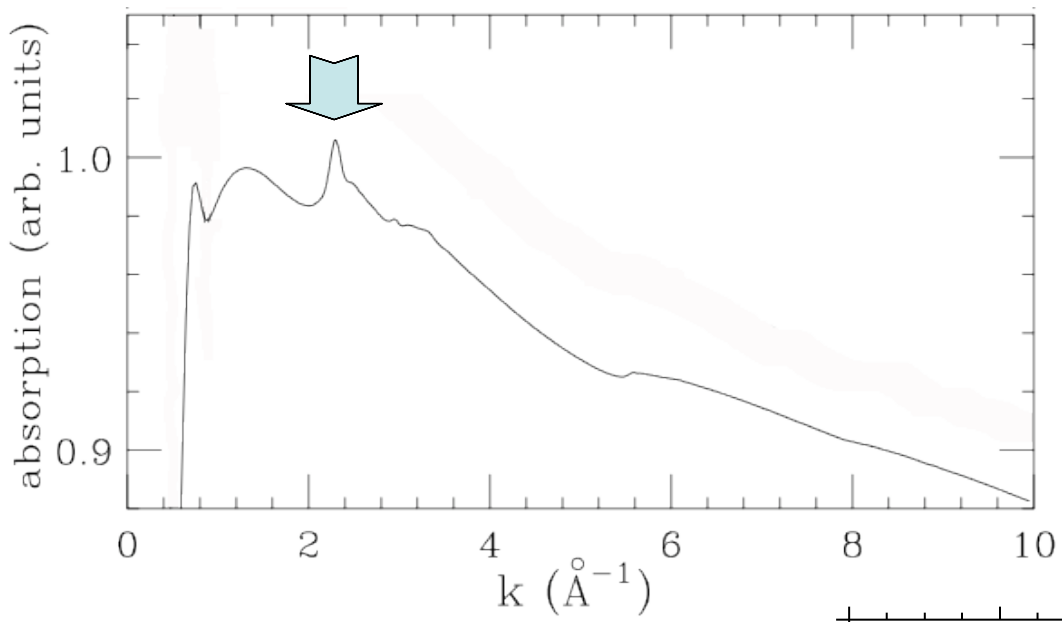
low temperature
and/or covalent bonding

high temperature
and/or ionic bonding

and when it shakes too much….



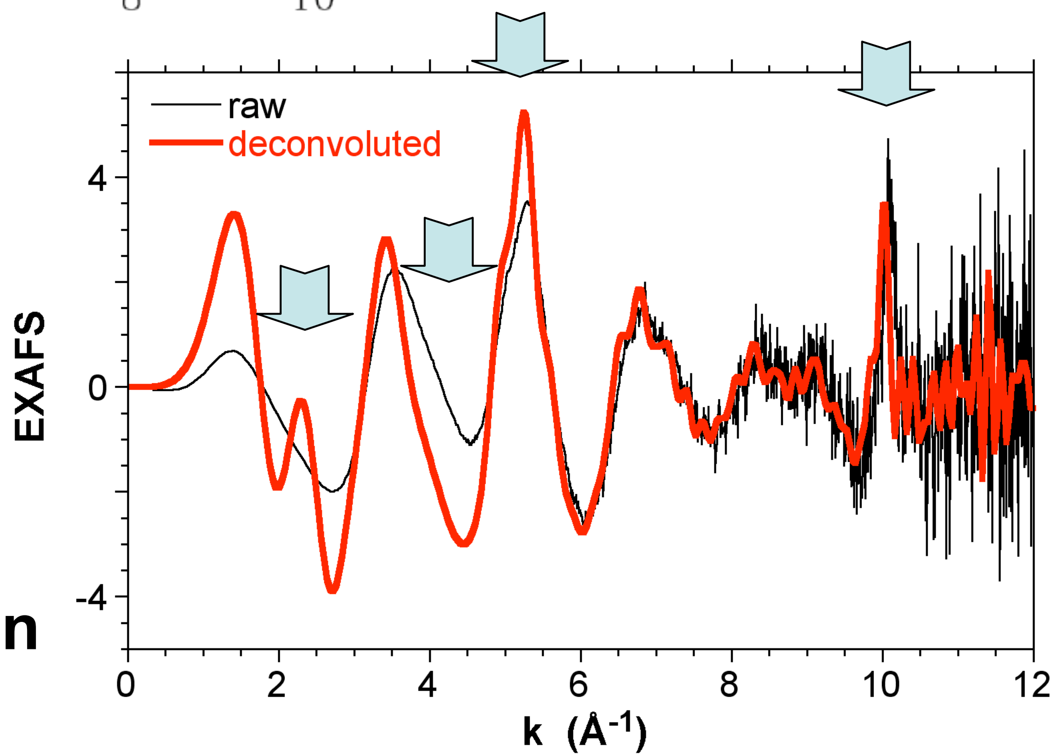
complex : multi-electronic edges (MEE) :



krypton (gaz)
au seuil K de Kr

(after Fillipponi, 2000; Ito et al., 1992)

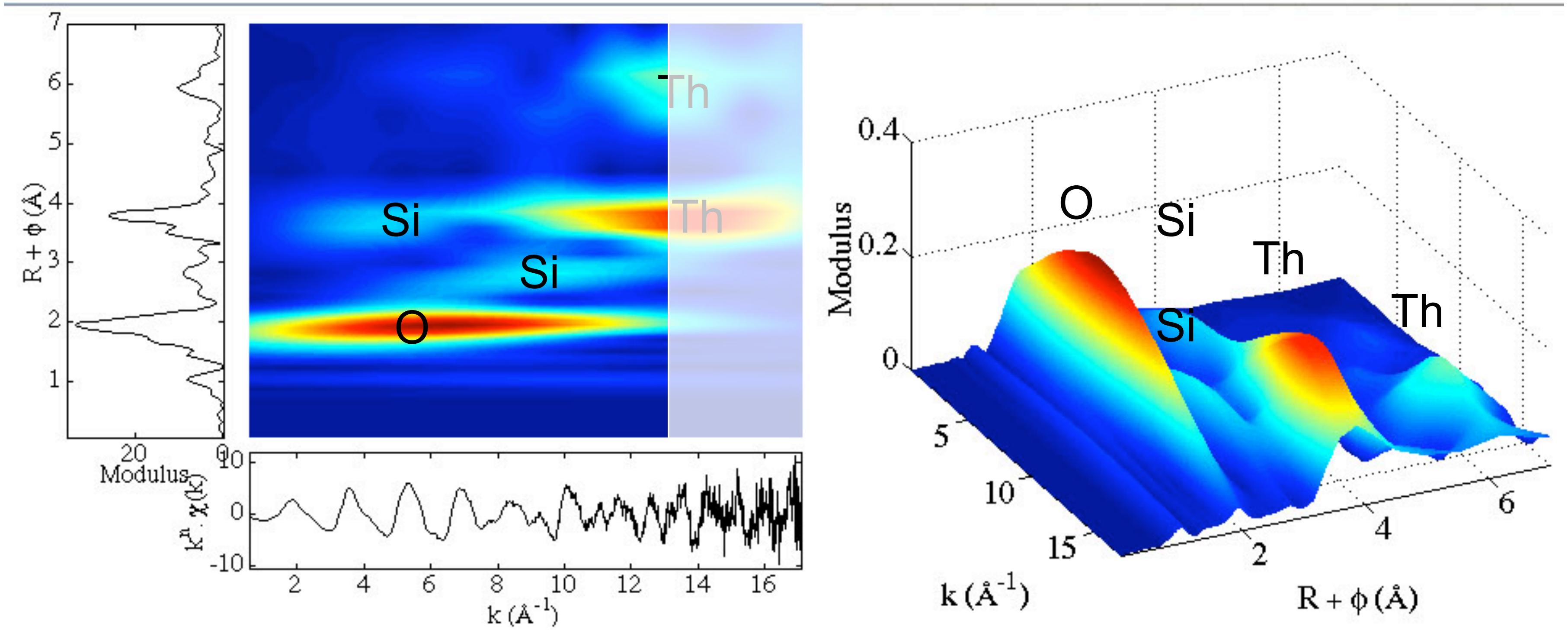
Th in $ZrSiO_4$
At the L_{III} of Th
(after Farges et al., 2002)



- **difficult to detect**
- **affects XAFS normalisation**

• **a new EZ tool to help : wavelets decompositions**

Th in $ThSiO_4$:



• **Si near 3 et 4 Å are detected until ~ 6 Å^{-1}**

• **destructive interf. between Si and Th near (k = 8, R = 3.9)**

• **if data is collected to k = 13Å^{-1} : not correct for Th !!**

Equation that we model (EXAFS) :

$$\langle \chi(k, R) \rangle = \int_0^{\infty} g(R)\, \chi(k, R)\, dR$$

with :

$$\Rightarrow \chi(k, R) = \left[S_0^2 \, Rf \, |F_{cw}| \right] \frac{N}{k R^2} e^{-2R/\lambda} \sin\left(2kR + \sum \phi \right)$$

$$\Rightarrow g(R) = \frac{\frac{U(R)}{k_B T}}{\int_0^{\infty} \frac{U(R)}{k_B T} dR} \; ; \; U(R) = U(R)_{harmonic} + U(R)_{anharmonic}$$

with S_0^2 is the amplitude reduction « many body » factor); Rf is the amplitude reduction for the central atom loss; N is the number of backscattering neighbors ré; $|F_{cw}|$ is the effective curve-wave amplitude of the neighbors; λ is the mean free path of the photoelectron AND $\Sigma\phi$ is the sum of the phase-shifts (central and rbackscattering).

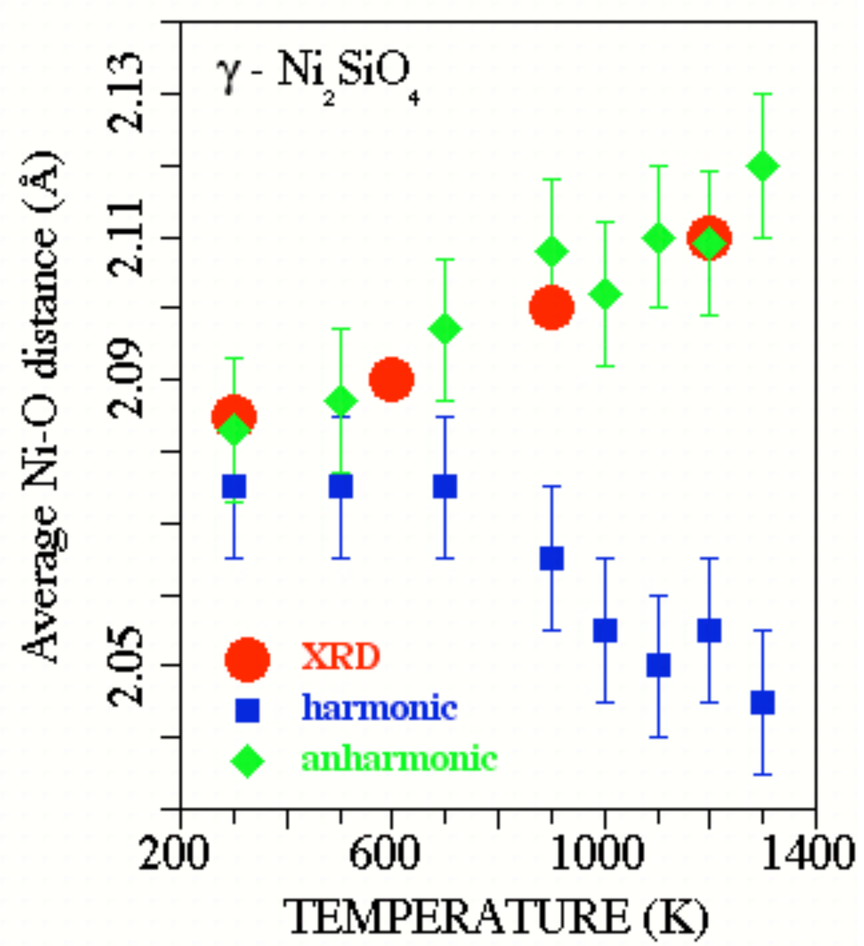
• **if the studied dipole is an harmonic oscillator :**

$$\Rightarrow \chi(k) = \left[S_0^2 \, Rf \, |F_{cw}| \right] \frac{N}{k R_0^2} \, e^{-\left[2R_0/\lambda + 2k^2\sigma^2 \right]} \sin\left(2kR_0 + \sum \phi \right)$$

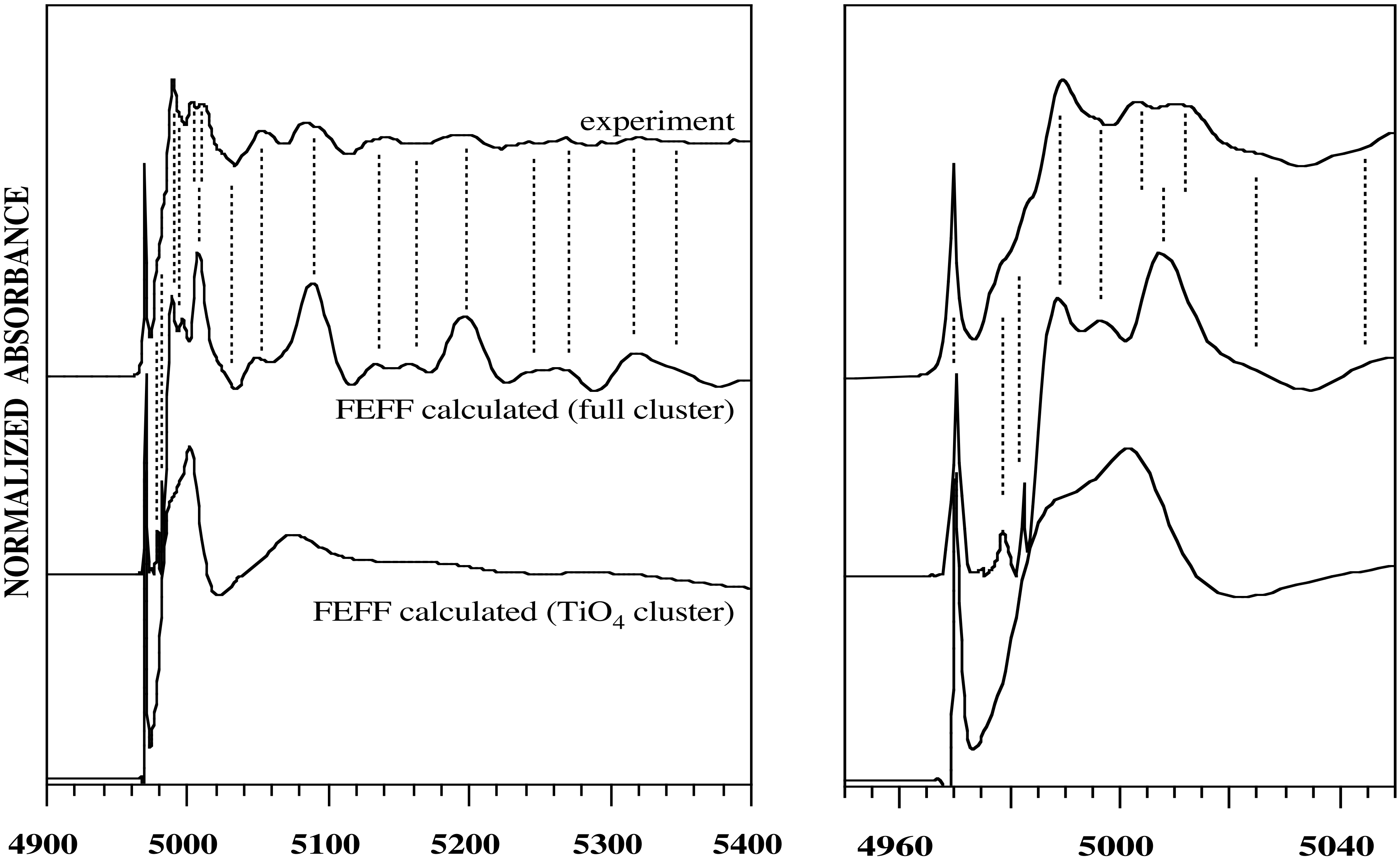
• **otherwise, anharmonicity of the potential must be considered :**

- **cumulants**
- **asymetric g(r)**
- **asymetric potential (incl. double-well etc.)**

• **otherwise, data reduction is not reliable :**



• **possibility to calculate rather easily all spectra :**



software	pros	cons
IFEFFIT (+FEFF)	powerful, modular, many updates, conisder MS, anharmonicity, support	Tougher for beginners or occasional users
WinXAS	interface, do dispersive EXAFS, many fonctions, support	costs $100+, Windows only, some missing functions
XAFS	intuitive, powerful, run on Win via emulation(*), does also RMC fits	can go just too fast easily think the software is bad
SamPack	Easy interface, many modern methods (PCA, self-abs.)	Need a huge screen, portable to other plateforms uneasy
GNXAS	powerful, modular, uses state of the art MS, anharmonicity and MEE	UNIX only, support and documentation needs better
Excurv98	powerful, modular, uses MS, good anharmonicity evaluations	commercial, UNIX, poor interface (to be better soon)
EXAFSPAK	modular, robust models, runs on Win via Hummingbird	fairly VMS dedicated, missing anharmonicity
XANDA - VIPER	powerful, numerous very unique possibilities, free	Stability recently improved, no documentation

Not or poorly tested : DARESBURY, LASE, CDXAS, XFIT, SEDEM, EDA and many others.
These opinions just reflect the author's use, sometimes in ratehr quick conditions.

“COMMANDEMENTS” OF AN OK-XAFS USER :

1) Physics always works, we sometimes don’t

2) Make up your mind first and double-check everything being told or “recommanded”. Track any bugs everywhere.

3) Make sure other methods are not as good (Mossbauer, optical spectroscopy, EPR and many others) AND always do complementary work

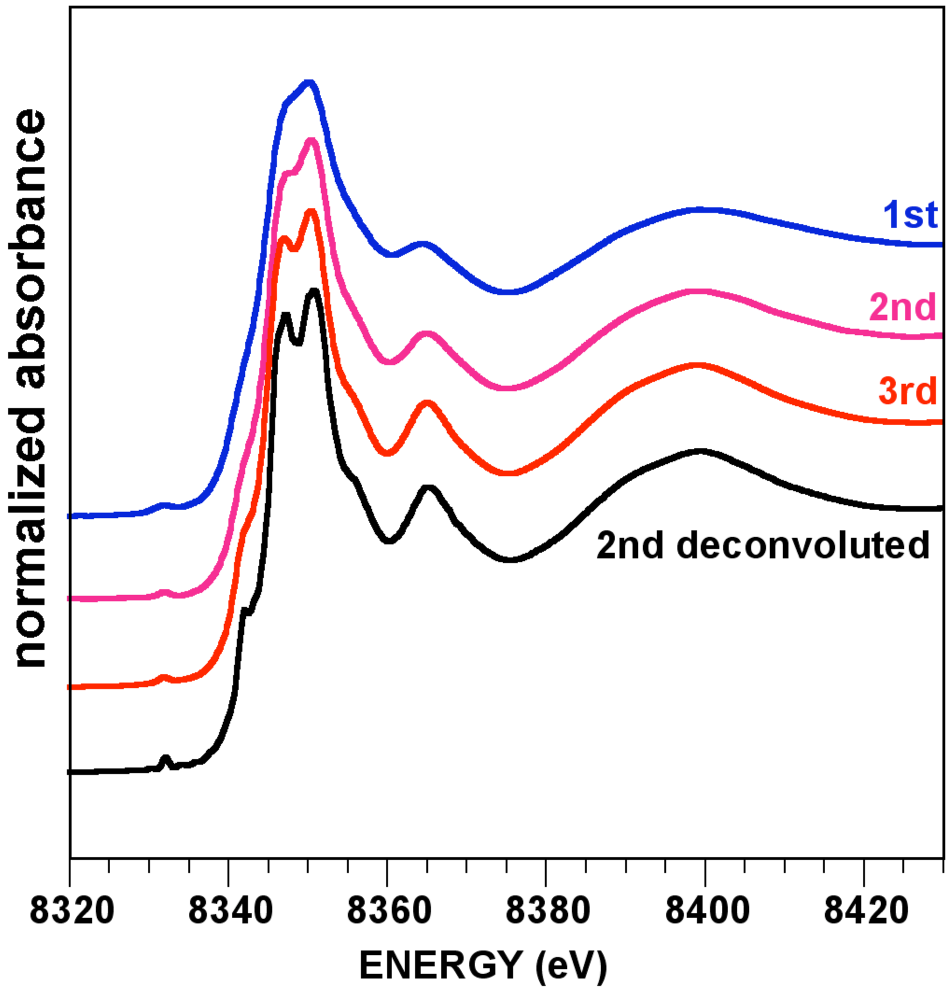
4) OK to spend as muhc time/efforts to (1) write proposal, (2) collect data, (3) reduce data or (4) discuss data

5) XAFS methods are usually among the very last of a project AND not the first to start with (as microscopic, elemental, istotopic methods)

6) Don’t choose Win software because you can only run *.exe’s : the choice of a software is first and then you find the right computer afterwards. Otherwise, UNIX is, then, THE safest choice.

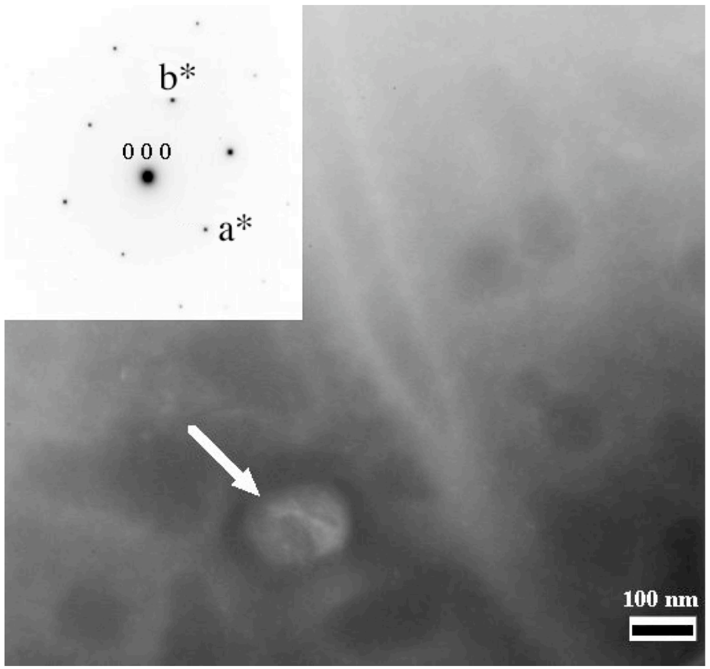
Failure(s) in any of these points might led to unreliable research

Example 1 : deconvolutions

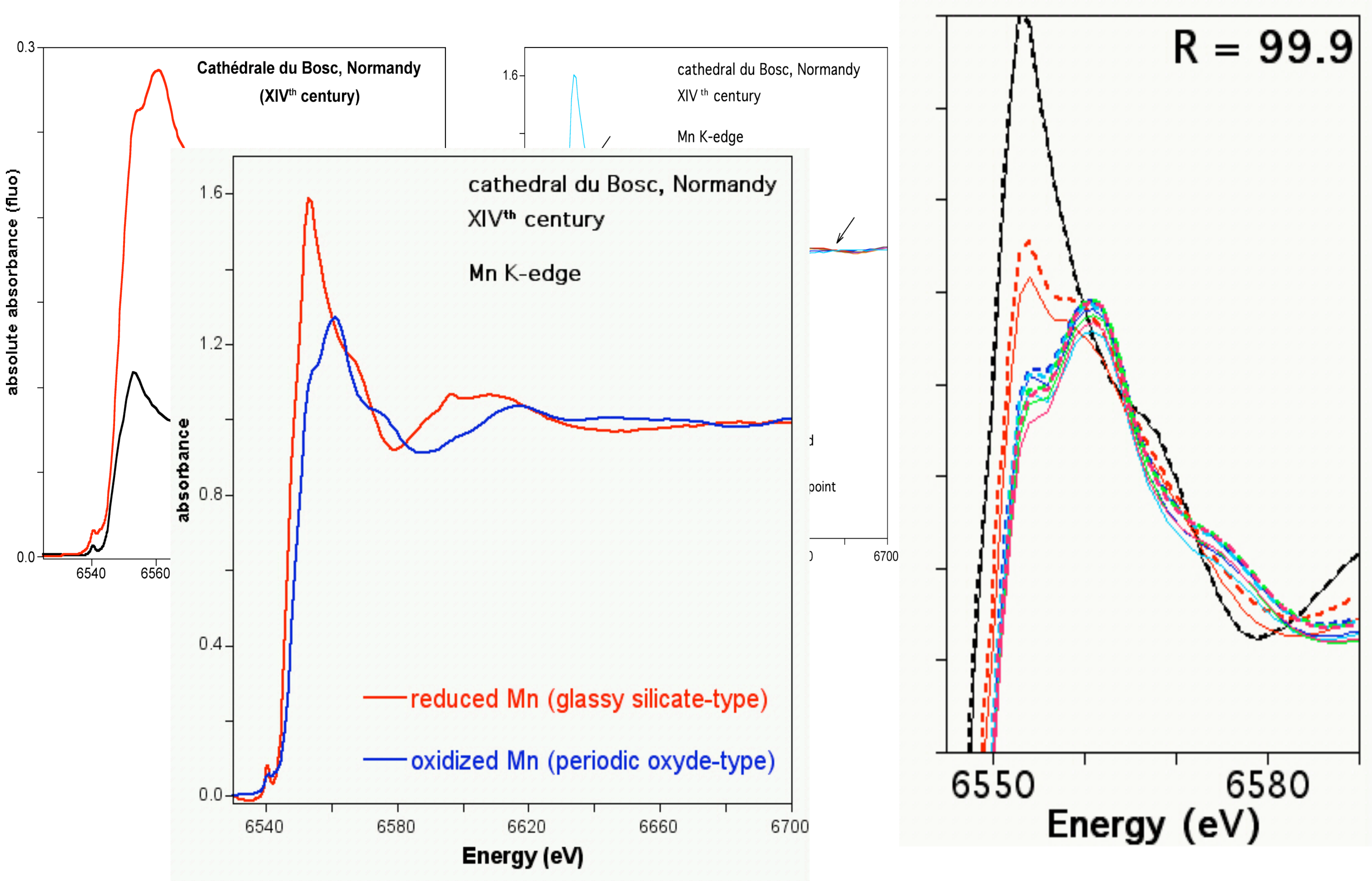


• imporant effect of experimentale résolution on the spectra

• deconvolution evidences nanocrystalline domains, that TEM can evidence too :

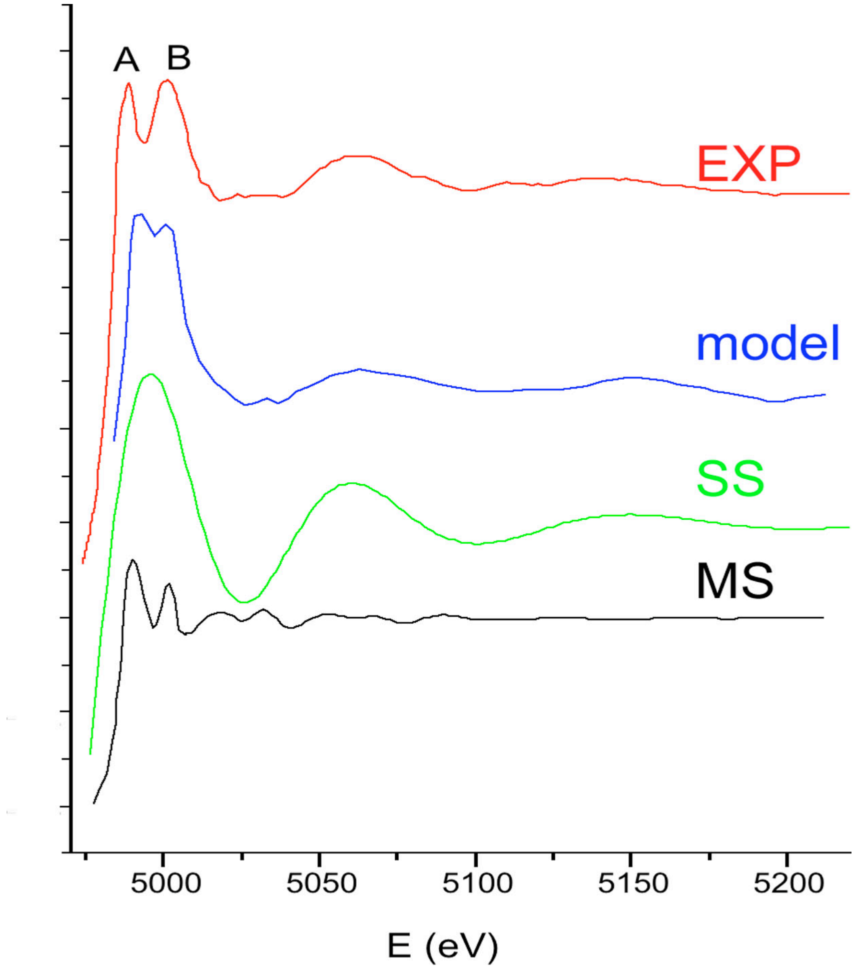


Manganese in a stained glass (XIVth century, France)
fresh versus weathered sides : a PCA analysis



Exemple 3 : radiation damage in titanite ($CaTiSiO_5$)

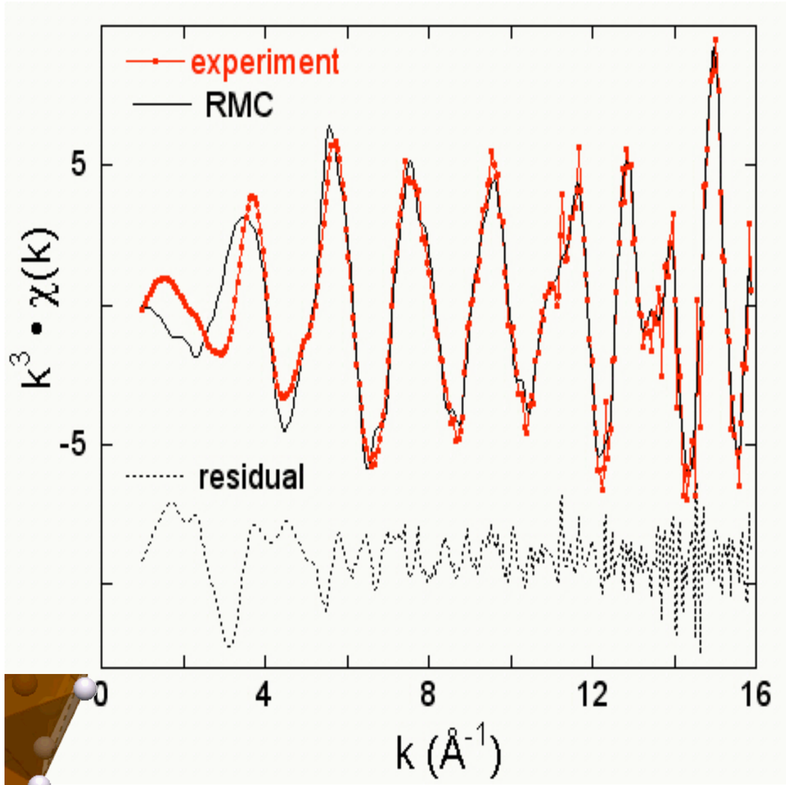
XANES of Ti in various titanites (cristalline and amorphous) can be modeled (CAUTIOUSLY) as EXAFS :

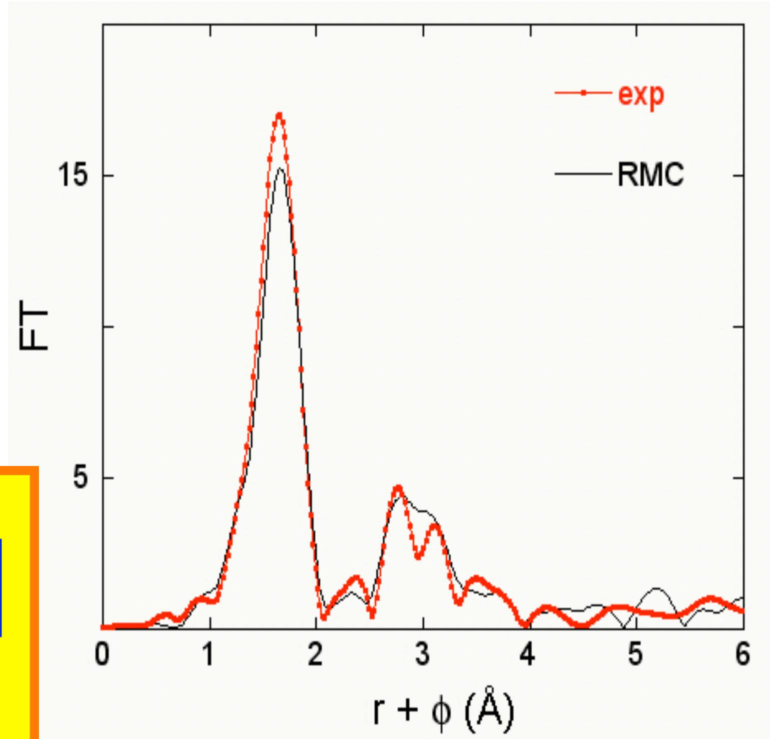


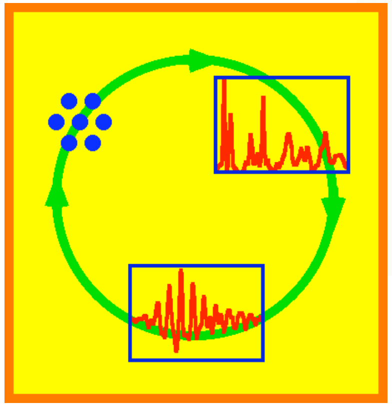
SELFCOMP models (Bugaev et al., 2002)

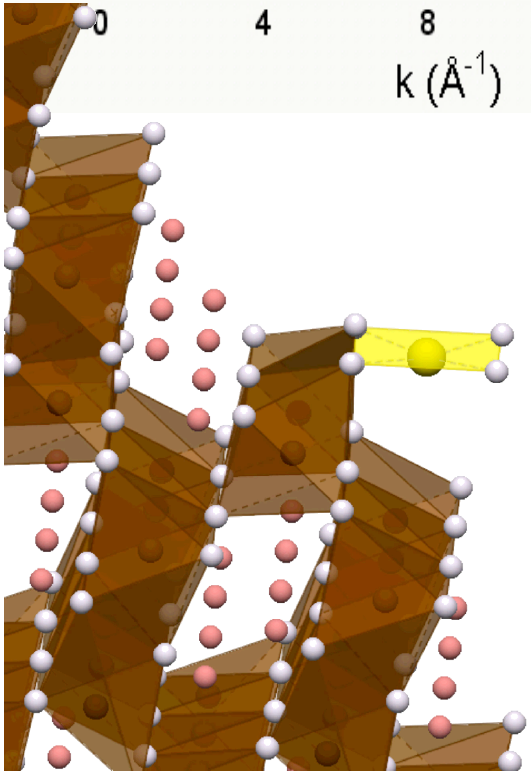
samples	N of oxygens	< Ti-O >	R-factor
crystalline	**6.1**	**1.99**	**0.005**
glassy	**4.9**	**1.95**	**0.001**
irradiated +	**5.7**	**1.98**	**0.005**
irradiated ++	**5.5**	**1.97**	**0.002**

“quantitative” XANES modeled nearly as EXAFS

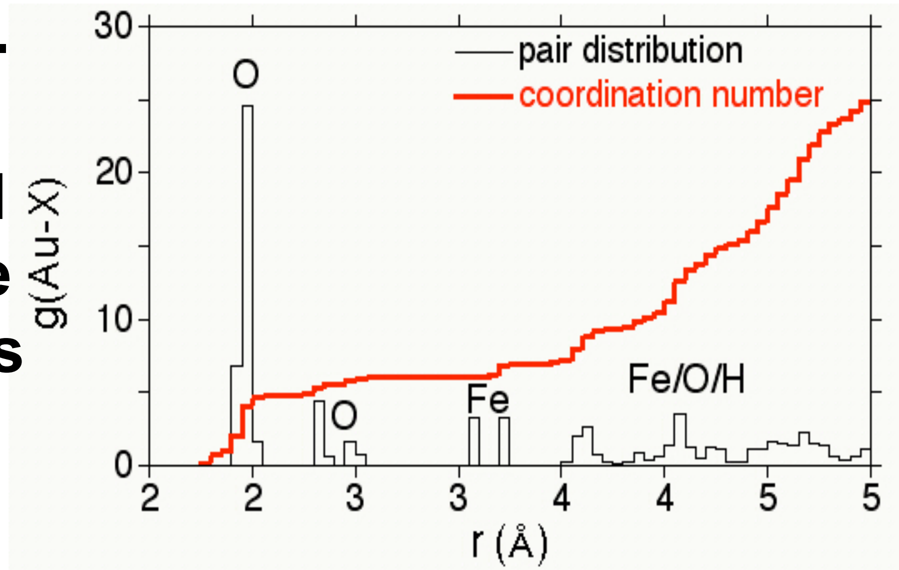








Reverse Monte-Carlo of the EXAFS coupled to bond valence => sorption sites and EXAFS limitations



References :

There are so much papers that it is impossible to list them. In addition, outside the rather outdated book of Teo (1986), a good « EXAFS for dummies » kind of book (updated and extended to XANES) is really missing.

Remains some « must read first » for the mineralogists/geochemists :

Crozier E.D., Rehr J.J., and Ingalls R. (1988) Amorphous and liquid systems. In *X-ray absorption. Principles, applications, techniques of EXAFS, SEXAFS and XANES* (ed. D.C. Koningsberger and R. Prins) pp. 373-442, Chemical Analysis, vol. **92**, John Wiley, New-York.

Teo B.K. (1986) *EXAFS: basic principles and data analysis (Inorganic Chemistry Concepts, Vol. 9).* Springer-Verlag, New York, 350 p.

Brown G.E., JR., Calas G., Waychunas G.A. and Petiau J. (1988) X-ray absorption spectroscopy: Applications in mineralogy and geochemistry. In *Spectroscopic Methods in Mineralogy and Geology* (ed. F.C. Hawthorne), pp. 431-512, *Reviews In Mineralogy*, Vol. 18, Mineralogical Society of America, Washington, DC.

Brown G.E., Jr., Farges F. and Calas G. (1995) X-ray scattering and x-ray spectroscopy studies of silicate melts. In *Structure, dynamics and properties of silicate melts* (ed. J.F. Stebbins, P.F. McMillan and D.B. Dingwell), pp. 317-410, *Reviews In Mineralogy*, Vol. 32, Mineralogical Society of America, Washington, DC.