EXAFS data analysis of supported metal catalysts and Fuel Cell electrocatalysts

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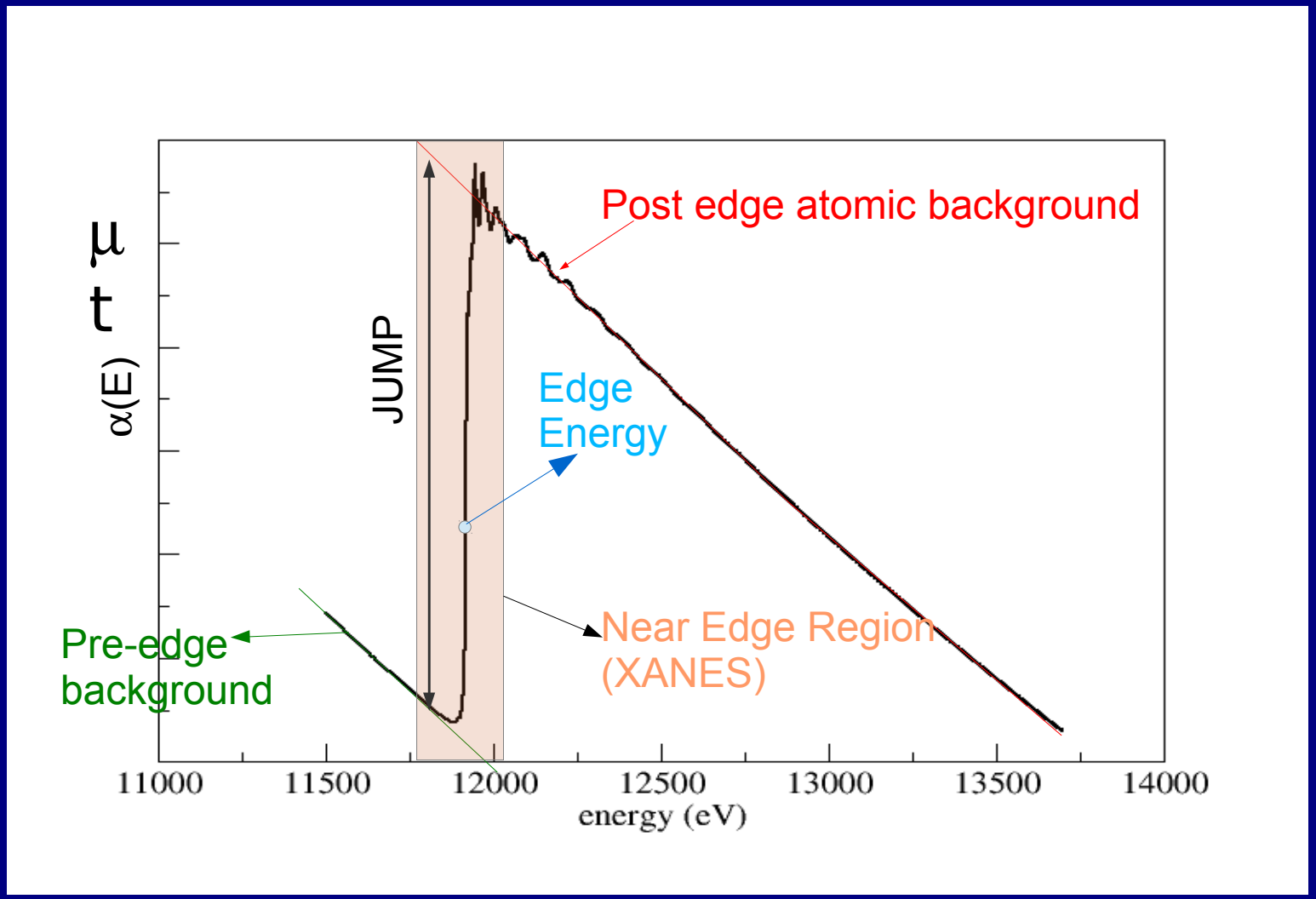
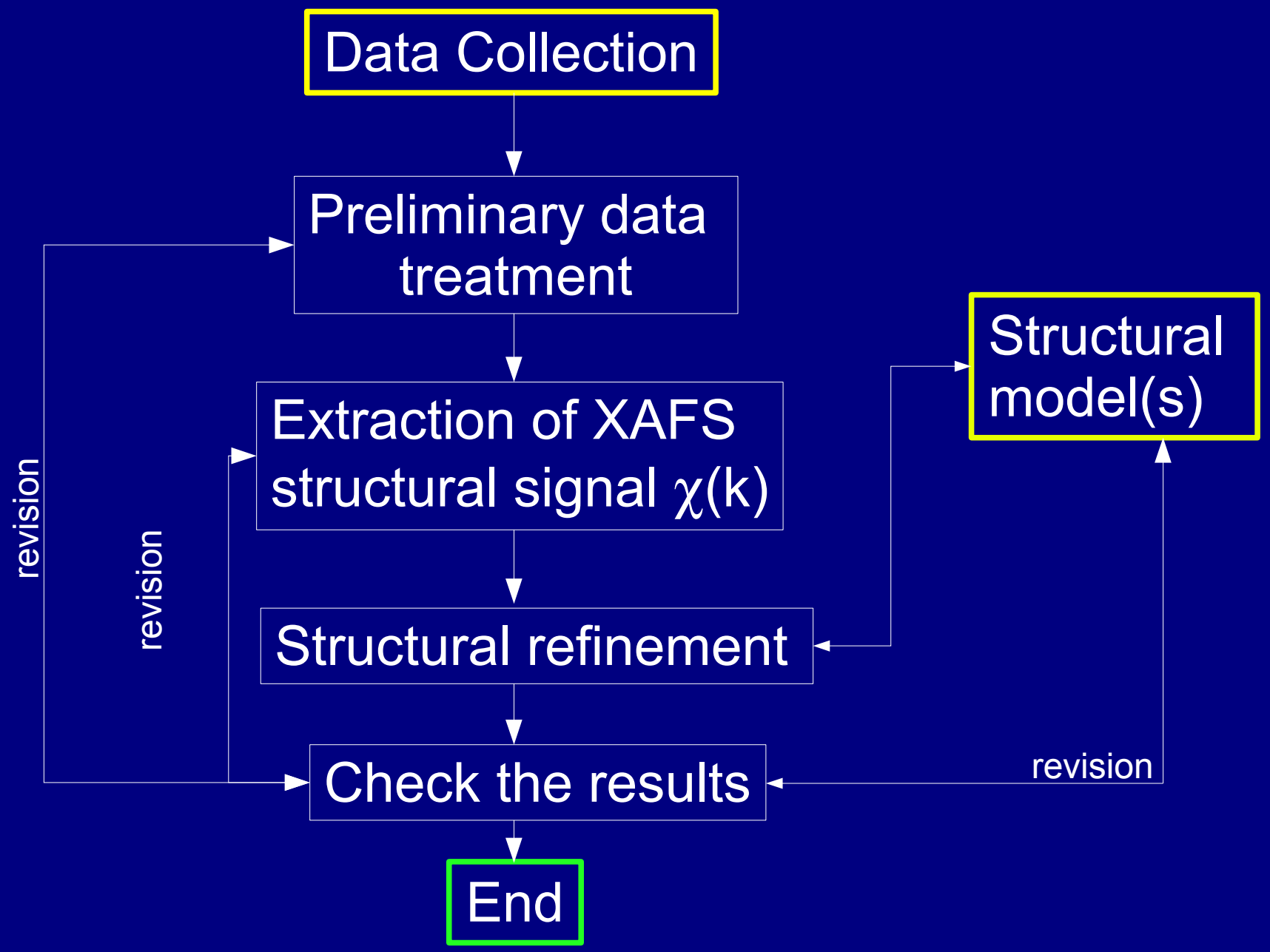
- EXAFS: introduction to data analysis
- Example. Dopants and defects: local structure in barium cerates and zirconates
- On line tutorial (VIPER package)

THE EXAFS SPECTRUM



Data analysis: get quantitative information

XAFS ANALYSIS: from the experimental data to results



DATA Collection

a Choose properly the experimental set-up (XANES/EXAFS Fluo/TEY/Transmission) and Sample preparation

b **Check the data quality During the experiment**

Quality is better than the quantity

c Choose properly the data collection strategy

d **Always measure Reference data**

XAFS rarely gives absolute quantitative details

OPTIMIZE YOUR BEAMTIME

Plan your EXPERIMENT!

Proposal submission +
proposal evaluation +
beam time scheduling
= **6 +12** months!

DUBBLE: 1-10 + 1-04
ESRF: 01-09 + 01-03

It is difficult to obtain
new beam time
for the same proposal
In case of failure

-Check the proposal deadline
-discuss your experiment with local contacts
-check your data during the experiment

DATA Collection

Mistake in XAFS data analysis are dominated by systematic errors:

Moreover:
- spurious structures
- background subtraction
- wrong models
- inaccurate theory

Experimental set-up & sample preparation

1. Transmission: massive concentrated samples
inhomogeneities, holes, not parallel surfaces, etc...
2. Fluorescence: thin concentrated thick diluted samples
Self absorption, detector linearity, Bragg reflections
3. TEY: thick concentrated
Surface sensitivity, sample charge, Bragg reflections

Data quality

Noise evaluation
glitches
discontinuities

Collection strategy

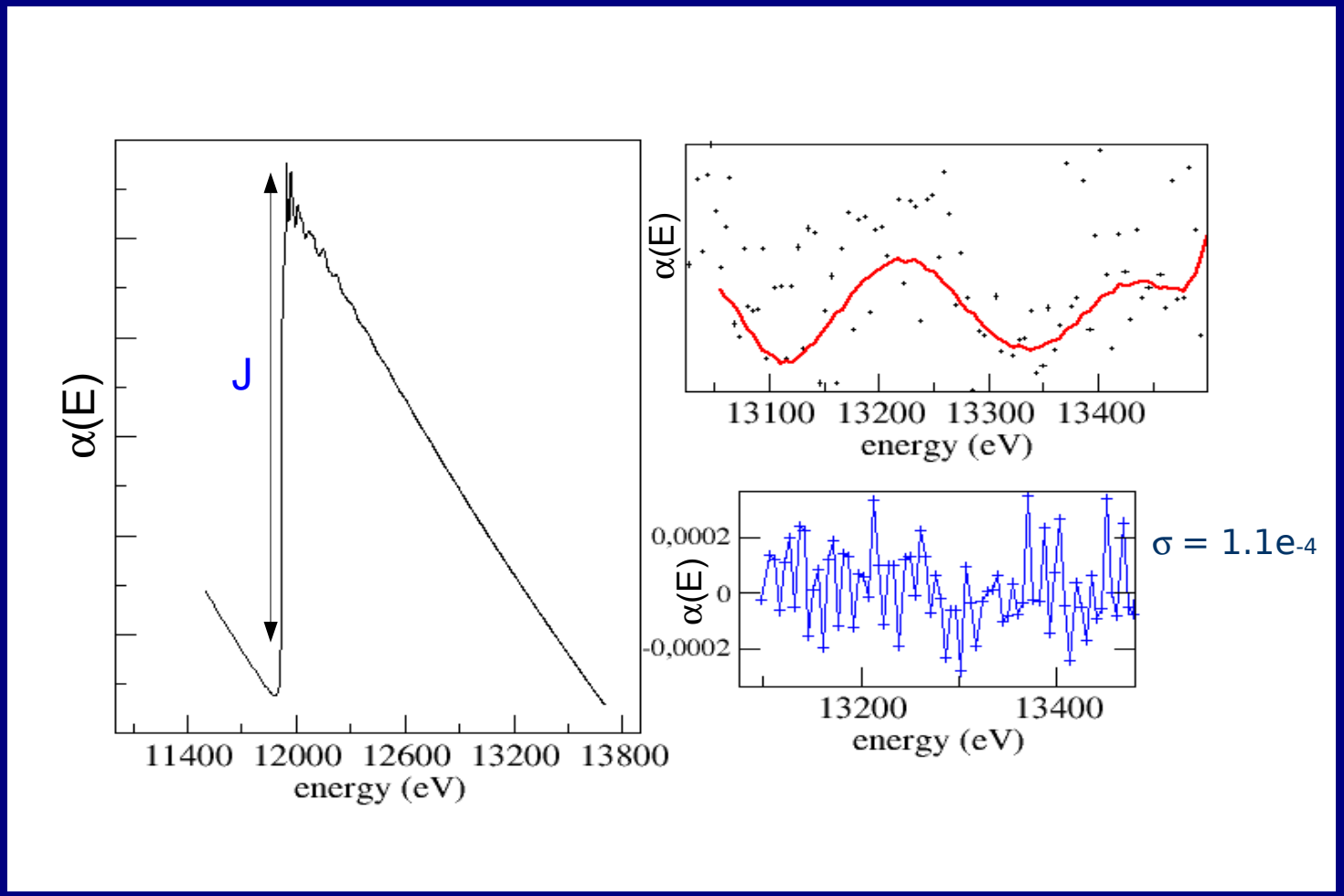
- step scan / quick EXAFS
- Fixed Energy or K steps
- single scan/repeated scans
- temperature points ...

Measure reference samples

1-energy calibration
2-data analysis procedures calibration

The power of XAFS technique consists in highlighting the smallest structural differences

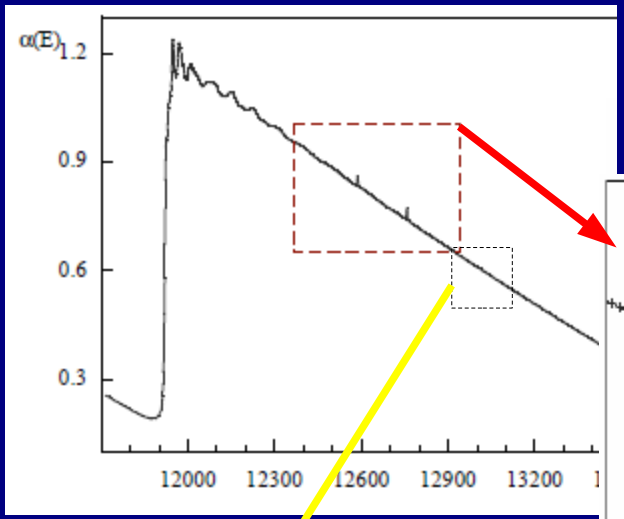
NOISE evaluation



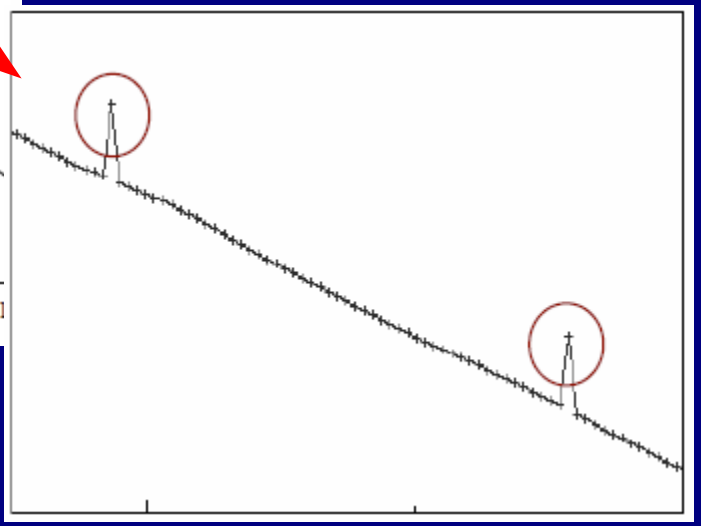
S/N ~ J/s

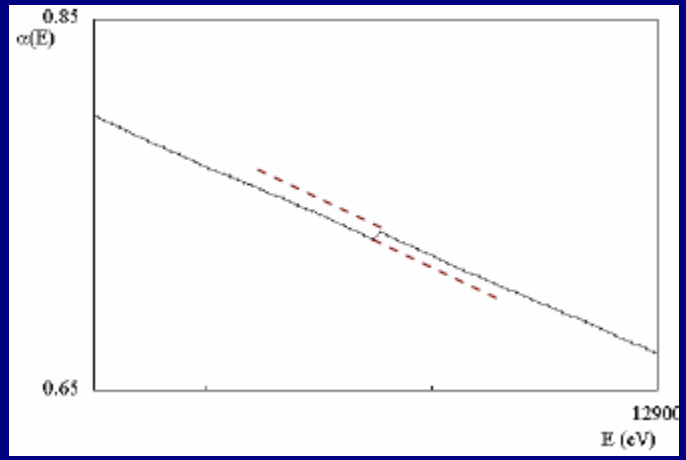
It must be Checked regularly during the experiment!

Check systematically during the experiment

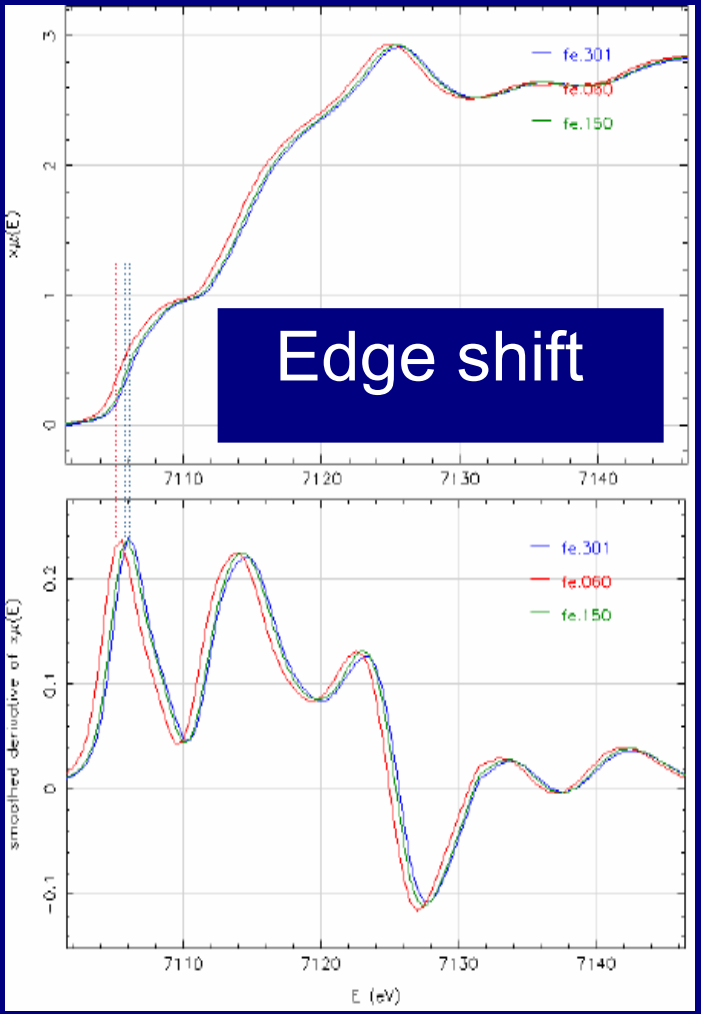


Glitches

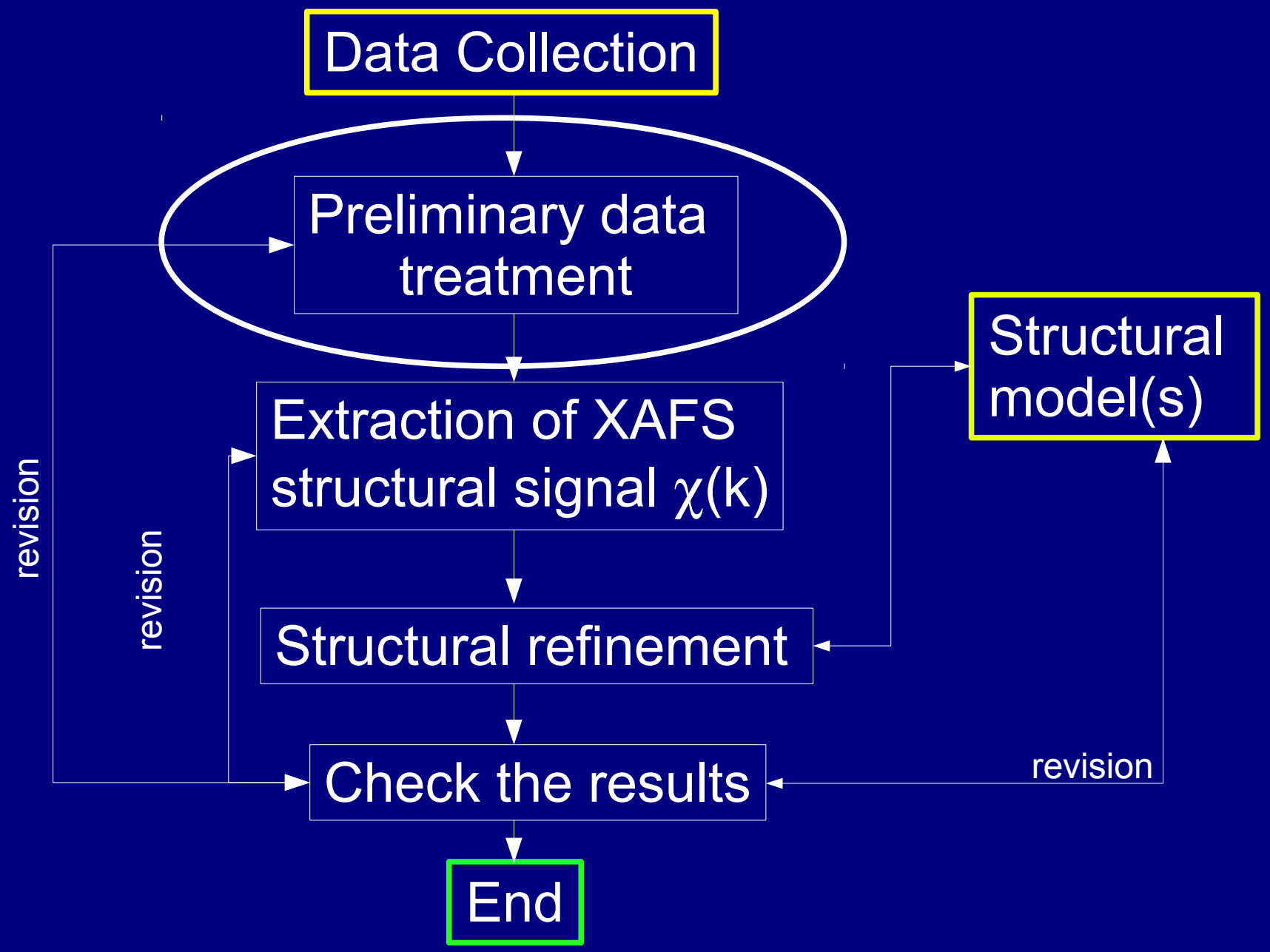




Discontinuities



XAFS ANALYSIS: from the experimental data to results



Preliminary data treatment

Select properly the best spectra and
useful data regions

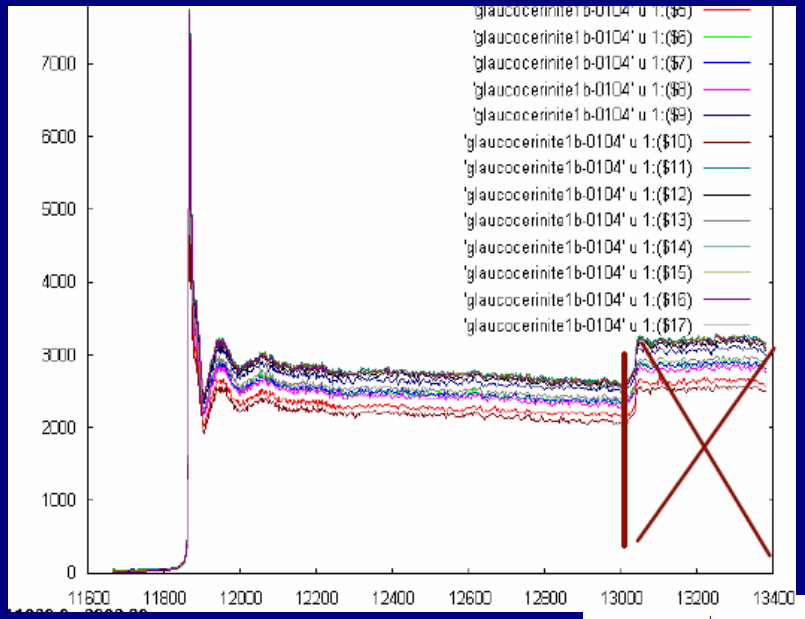
Preliminary data treatment

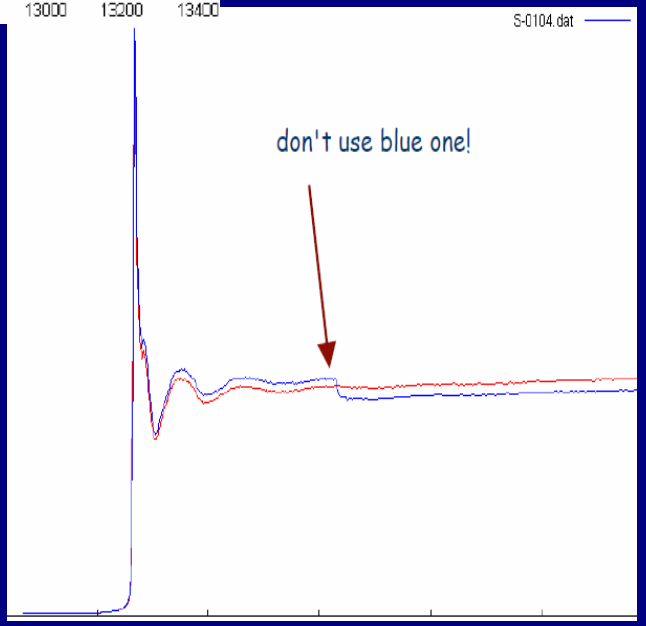
- Self absorption corrections
- de-glitching (if it possible!)
- data interpolation
- data alignment

Sum together the best spectra

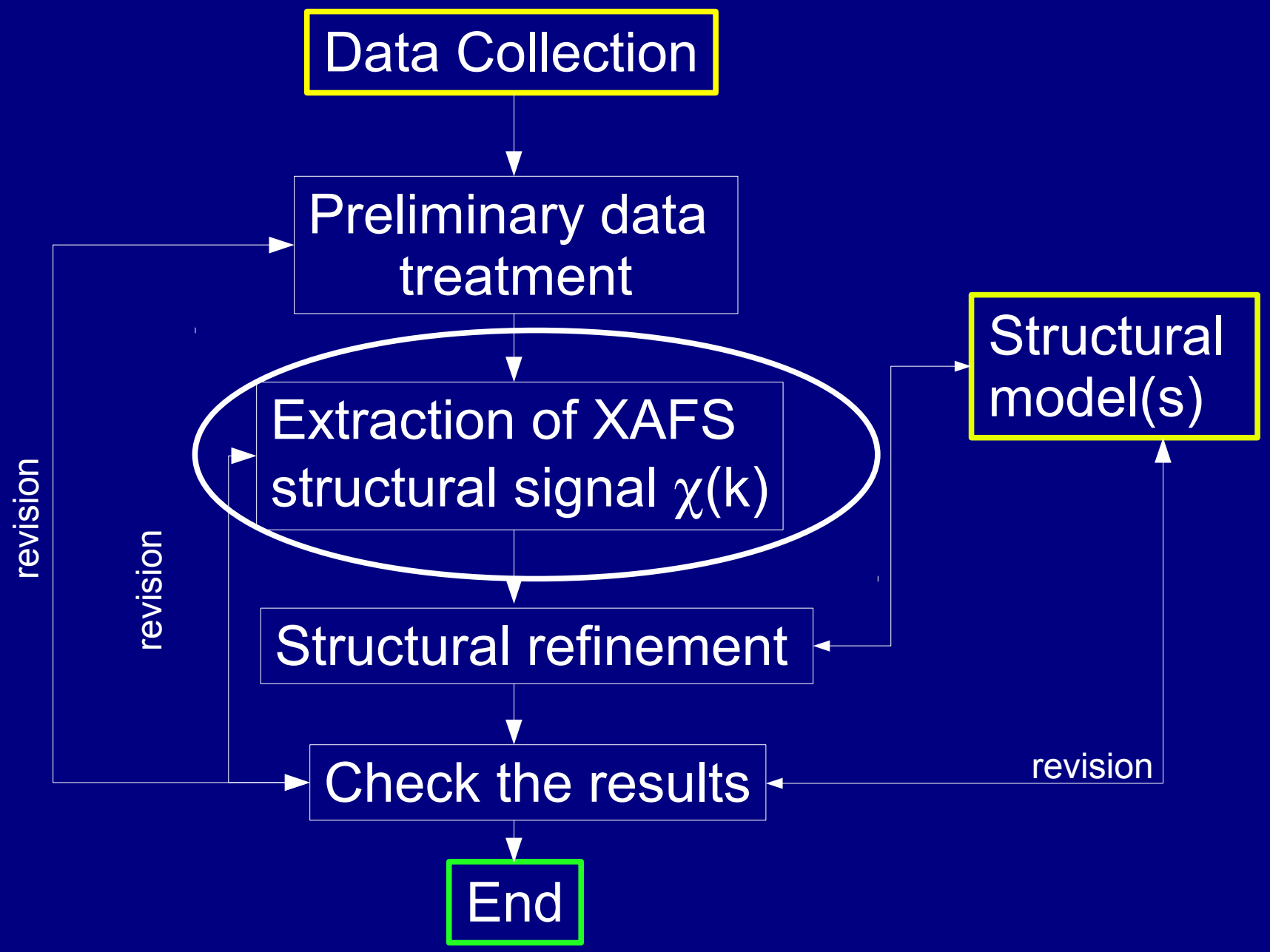
don't use blue one!

Weighting by S/N



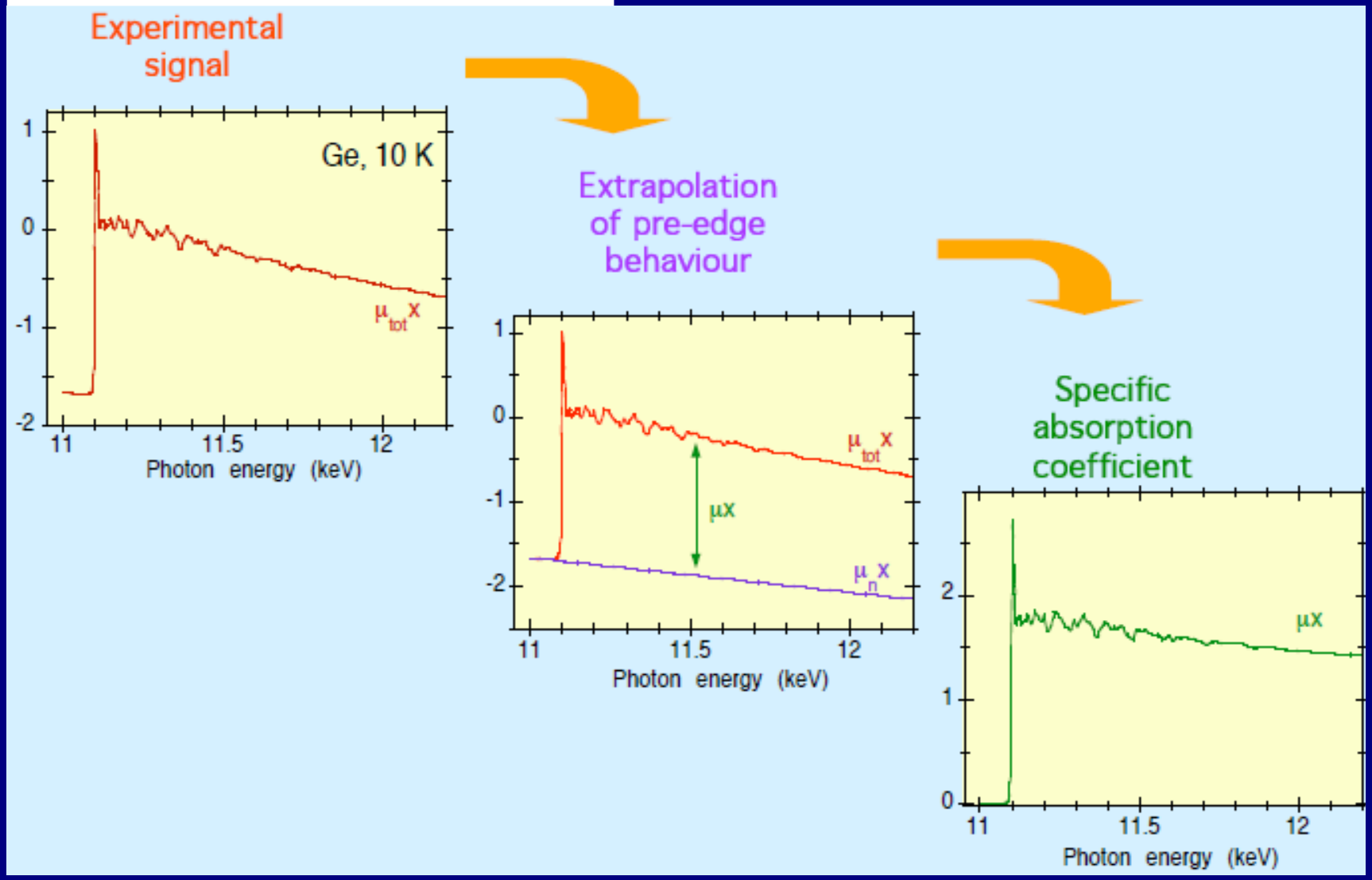


XAFS ANALYSIS: from the experimental data to results



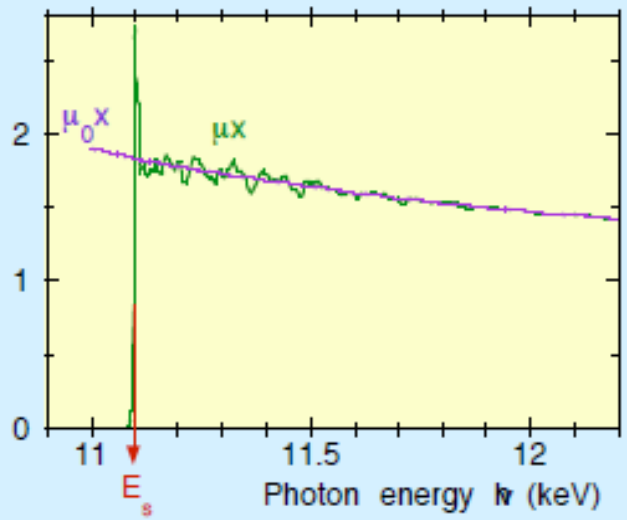
Extract $\chi(k)$ structural signal

EXAFS analysis: step 1

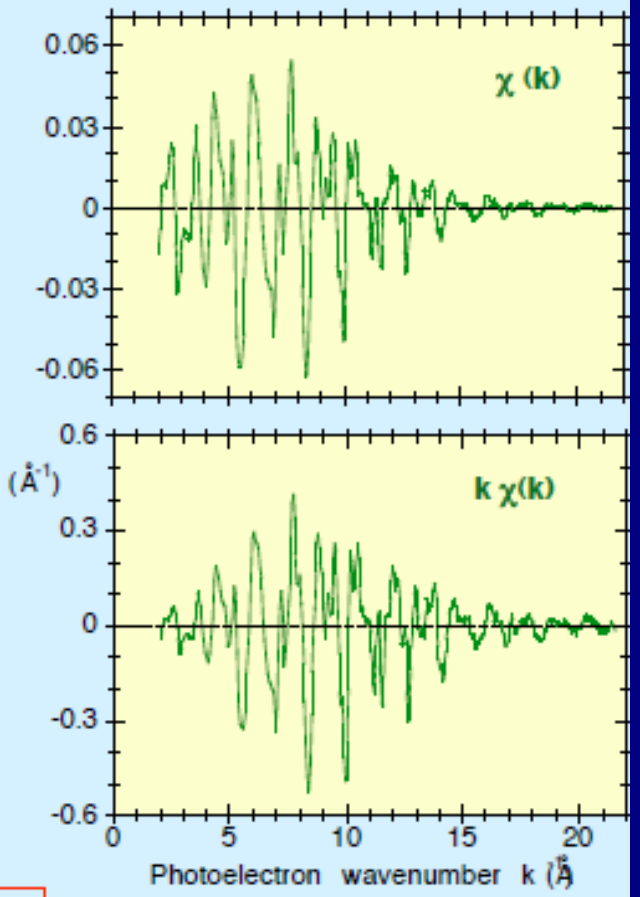


EXAFS analysis: step 2

Atomic absorption coefficient



EXAFS signal



Edge energy

$$k = \sqrt{\frac{2m}{\hbar^2}(h\nu - E_s)}$$

Photoelectron wavenumber

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

μ_0=represents the bare atom absorption.

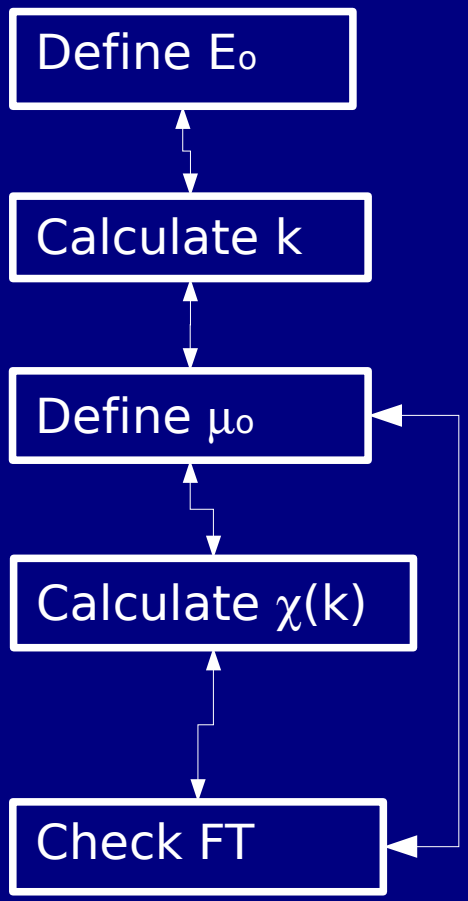
It is calculated empirically as a smooth curve across the data. **Different XAFS data analysis software apply different (generally equivalent) methods.**

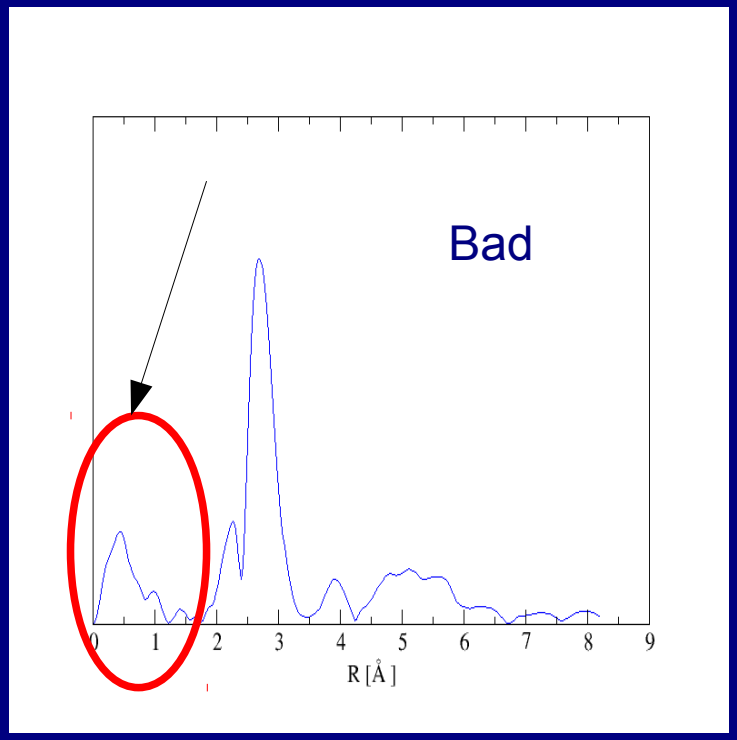
Requirements for μ_0:

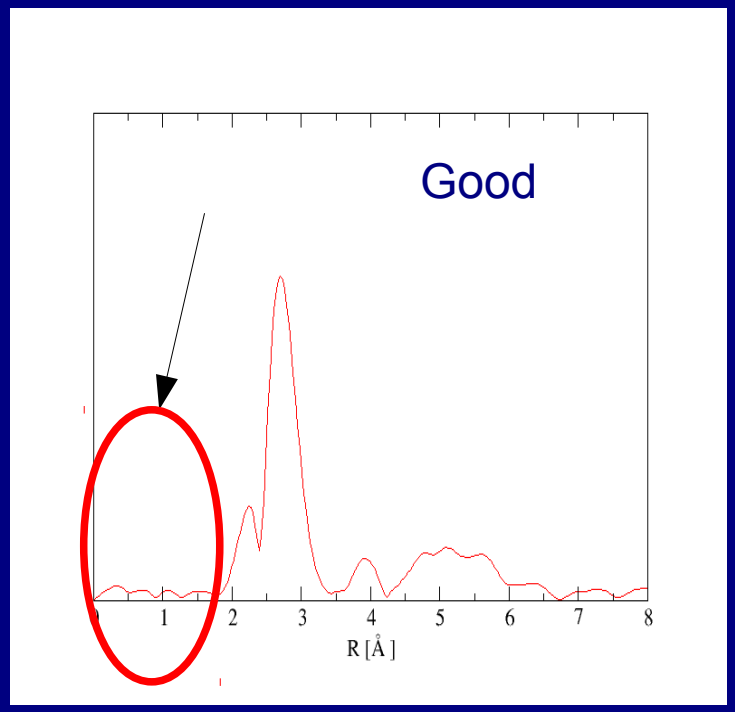
1) Smooth enough to not remove true structural features
2) Structured enough to remove background structures

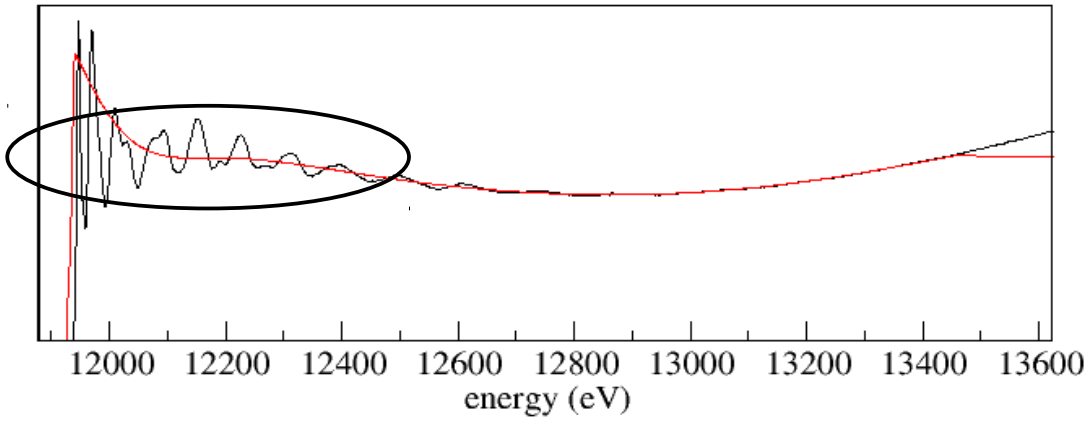
How to control he extraction?

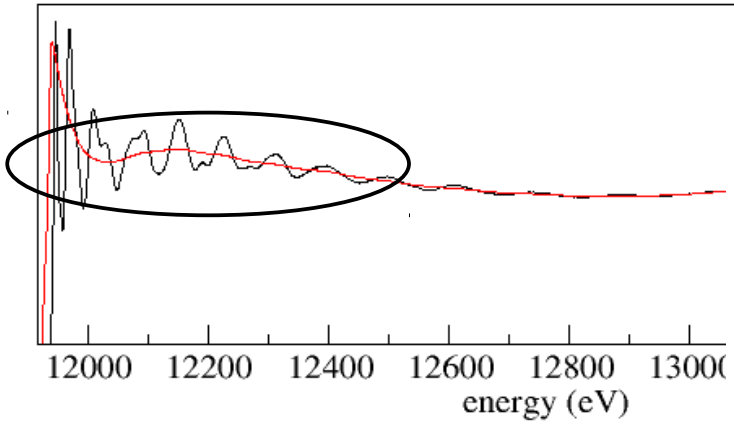
Large |FT| contributions at low (unphysical) distances may signify "wrong μ_0"

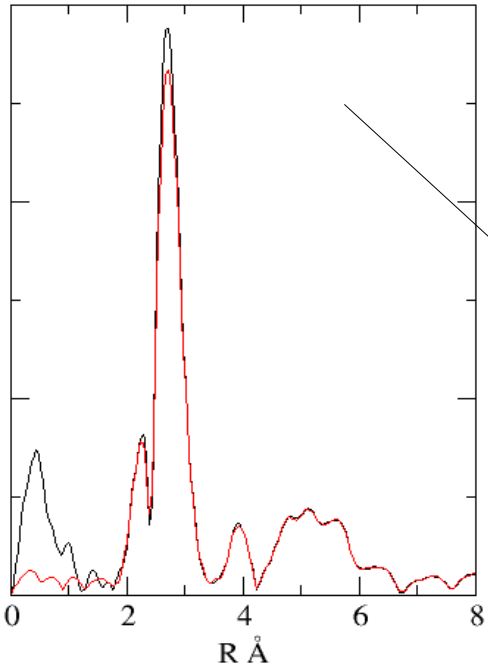


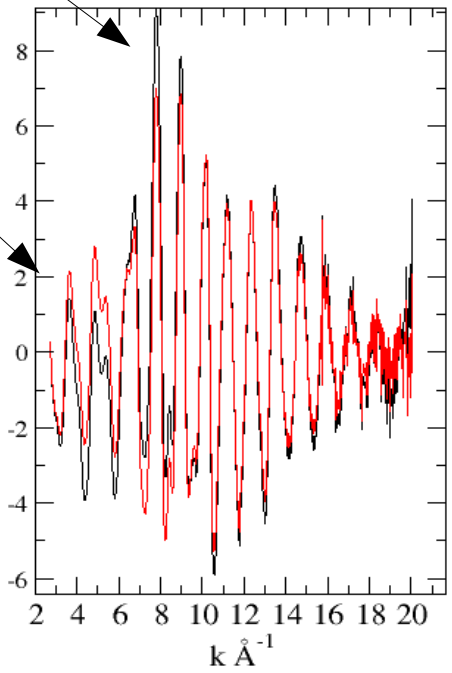












How to control the background extraction?

MAIN EXAFS approximations:

One electron

- 1 core electron excited
- N-1 passive electrons relaxed

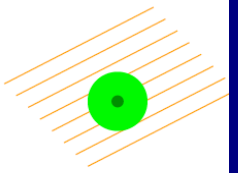
EXAFS coherent signal

- 1 core electron excited
- Other electrons excited

$$\mu_{el}(\omega) \propto \left|\left\langle \Psi_i^{N-1}\psi_i \right| e^{i\vec{k}\cdot\vec{r}}\hat{\eta}\cdot\vec{p} \left|\psi_f \Psi_f^{N-1}\right\rangle\right|^2 \rho(\varepsilon_f)$$

dipole

$$e^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k}\cdot\vec{r} - \ldots \approx 1$$



$$H_I \propto e^{i\vec{k}\cdot\vec{r}}\hat{\eta}\cdot\vec{p} \approx \hat{\eta}\cdot\vec{p} = \omega^2\hat{\eta}\cdot\vec{r}$$

$$\mu_{el}(\omega) \propto \left|\left\langle \Psi_i^{N-1}\psi_i \right| \hat{\eta}\cdot\vec{r} \left|\psi_f \Psi_f^{N-1}\right\rangle\right|^2$$

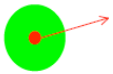
Dipole selection rules:

$\Delta\ell = \pm 1$ $\quad \Delta s = 0$

$\Delta j = \pm 1, 0$ $\quad \Delta m = 0$

Sudden

ssive electrons



$$|\Psi^{N-1}\psi\rangle = |\Psi^{N-1}\rangle|\psi\rangle$$

1 active electron — N-1 passive electrons

$$\mu_{el}(\omega) \propto \left|\langle \psi_i | \hat{\eta}\cdot\vec{r} | \psi_f \rangle\right|^2 \rho(\varepsilon_f) \left|\langle \Psi_i^{N-1} | \Psi_f^{N-1} \rangle\right|^2$$

$$S_0^2 \approx 0.6 \div 0.9$$

Structural information

Intrinsic inelastic effects

Photo-electron mean-free-path

$$\chi(k) = \frac{S_0^2}{k}\sum_{shell} N_s \,\mathrm{Im}\left[f_s(k,\pi)\, e^{2i\delta_1} \frac{e^{-2R_s/\lambda(k)}}{R_s^2} \exp(2ikR_s)\right]$$

Atoms frozen in equilibrium positions !

Multi-electron excitations

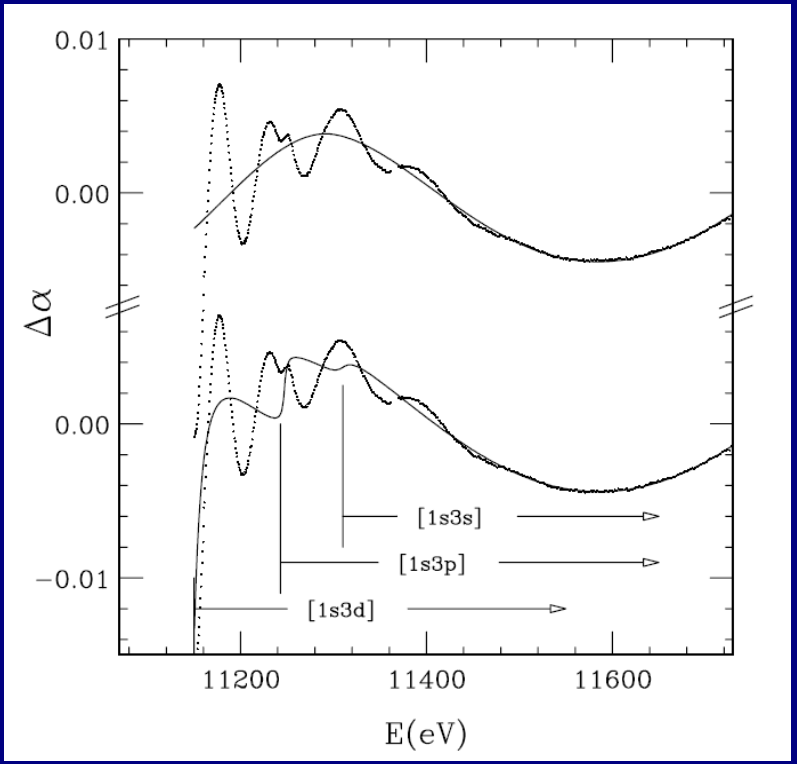
The approximations outlined neglect several important many-body effects.

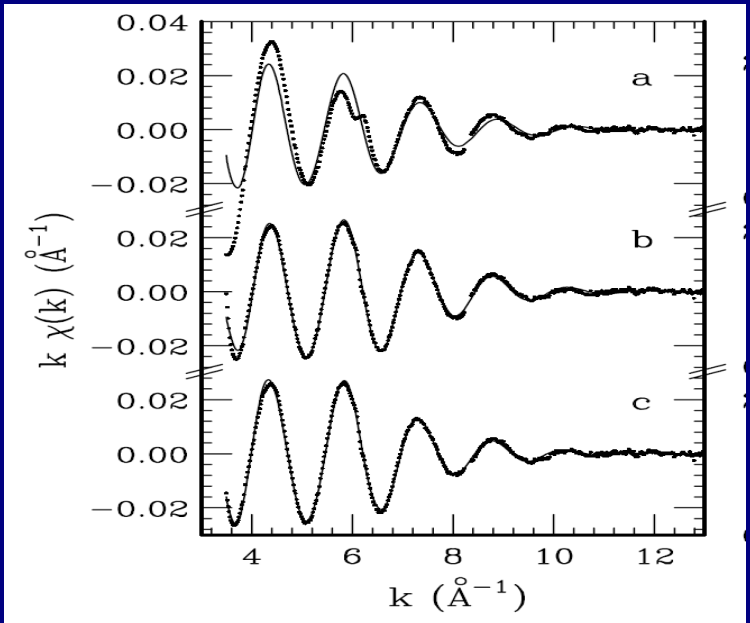
A first class of effects, usually referred to as '*intrinsic*', is that associated with the multi-electron response of the photoabsorber atom.

besides the core level involved in the main edge, **non-negligible transition** are excited

All these transitions contribute to a complex atomic background shape.

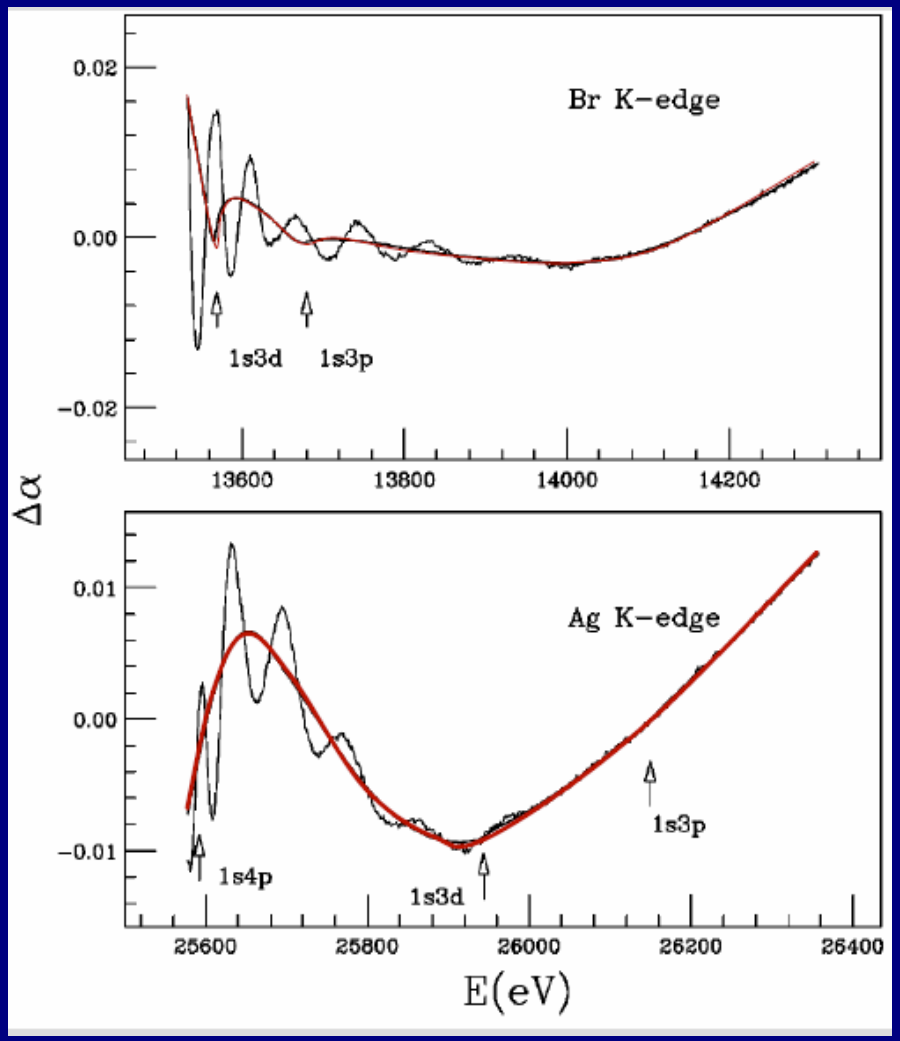
The intensity of these channels is predicted to be of the order of up to a few % of the main K-edge channel.





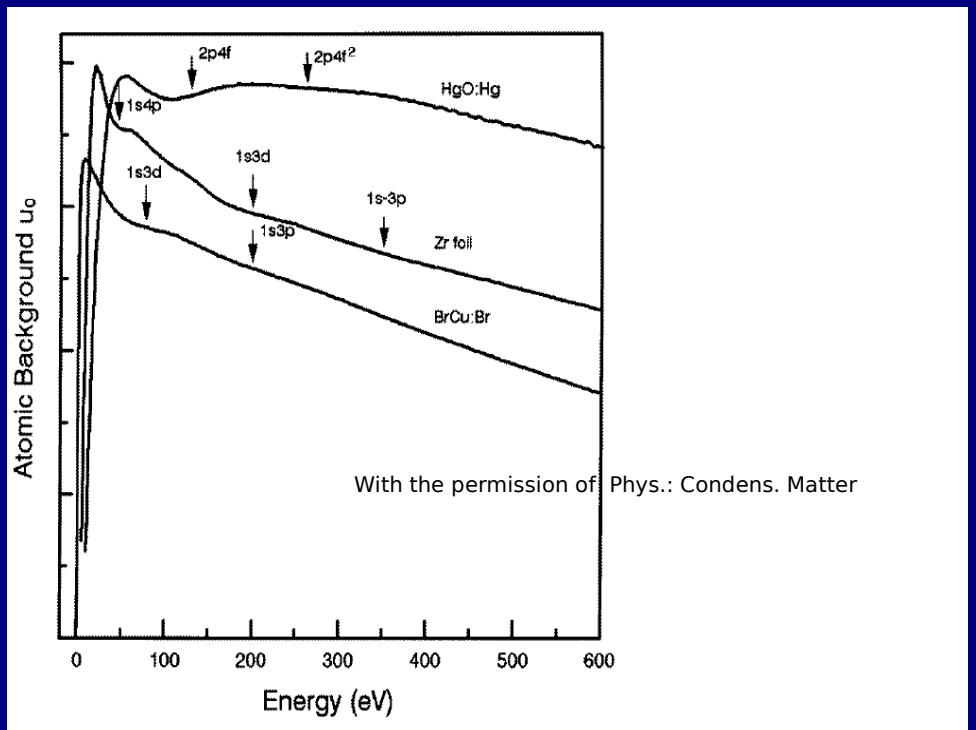
Thanks to Adriano Filipponi

J. Phys.: Condens. Matter 13 (2001) R23–R60



A. Di Cicco et Al. Phys. Rev. B 62, 12001 (2000)

Multiple excitations can affect the background with (small) discontinuities visible as peaks at distances smaller than 1

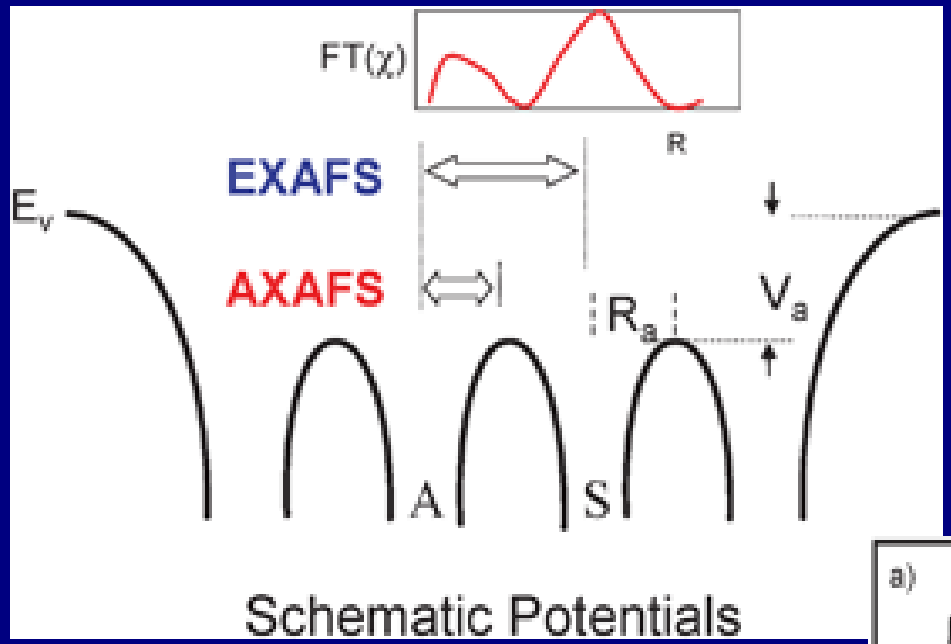


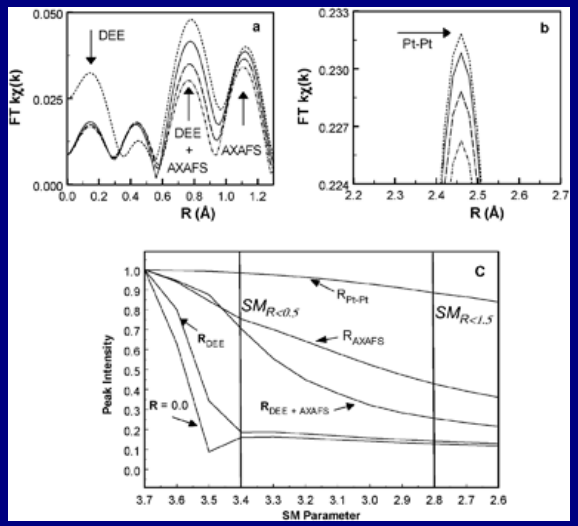
With the permission of Phys.: Condens. Matter

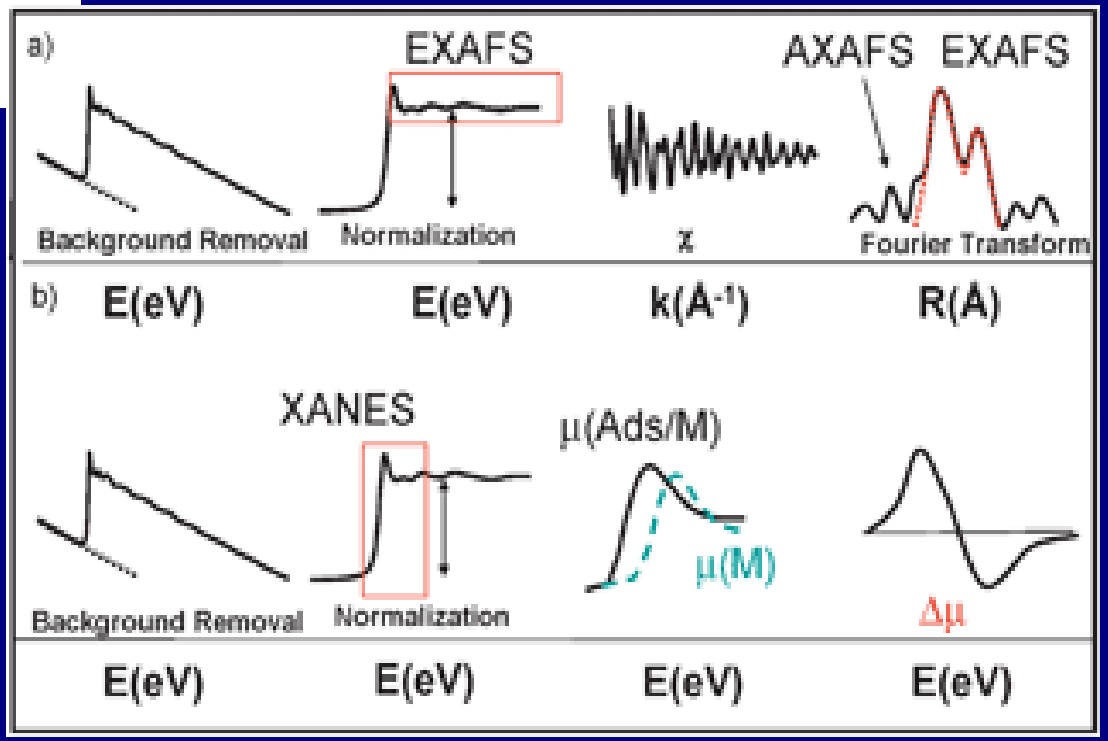
Figure 5. The atomic background of the K edge of Zr and Br, and the L_3 edge of Hg in Zr foil, CuBr, and HgO, respectively.

J. Phys.: Condens. Matter 9 (1997) 5507–5515.

AXAFS







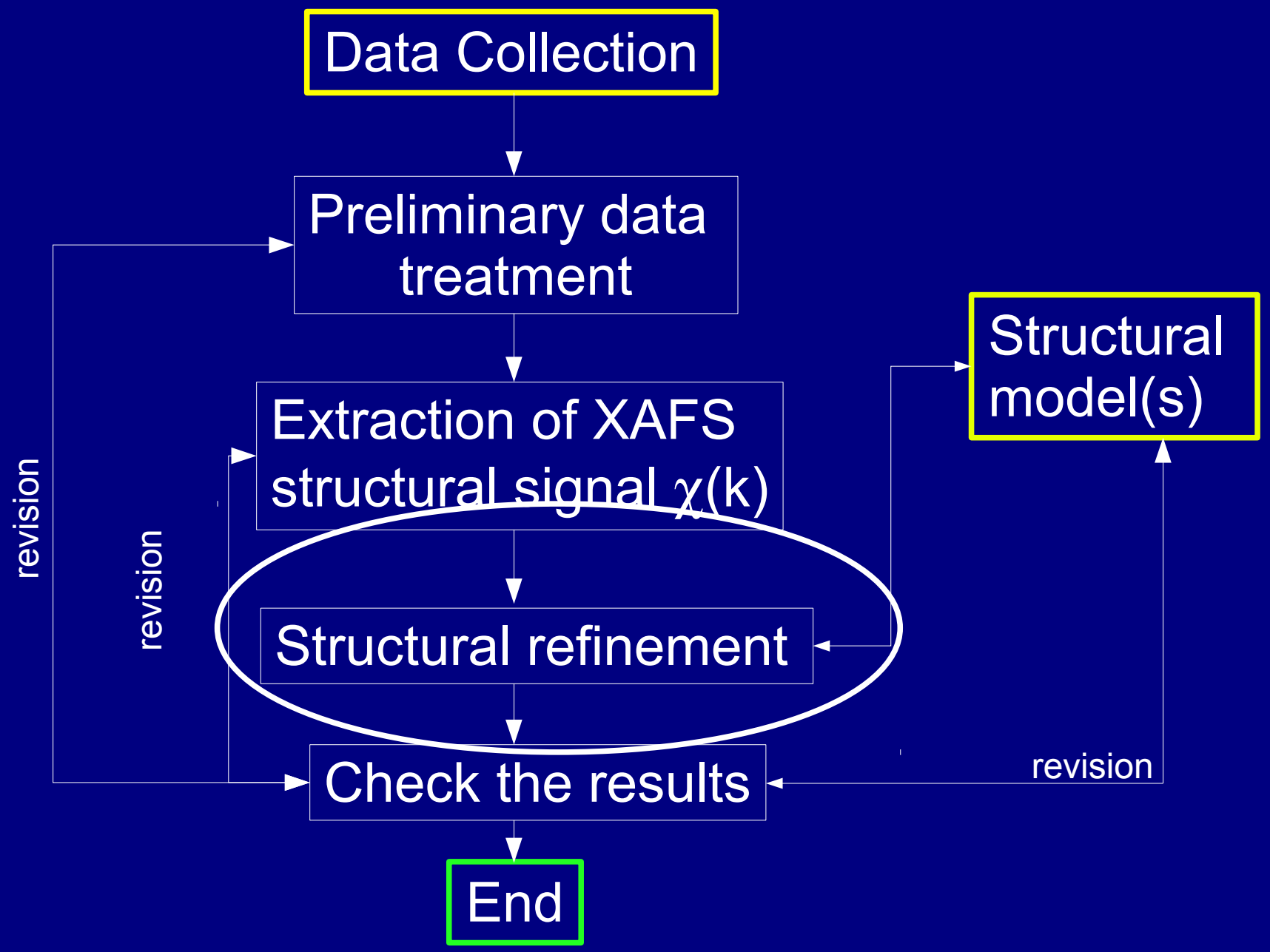
The atomic AXAFS and Δμ XANES techniques as applied to heterogeneous catalysis and electrocatalysis

D. E. Ramaker*a and
D. C. Koningsberger

Phys. Chem. Chem. Phys., 2010,12, 5514-5534

J. Phys.: Condens. Matter 14 (2002) 13529-13541

XAFS ANALYSIS: from the experimental data to results



Two methods of analysis

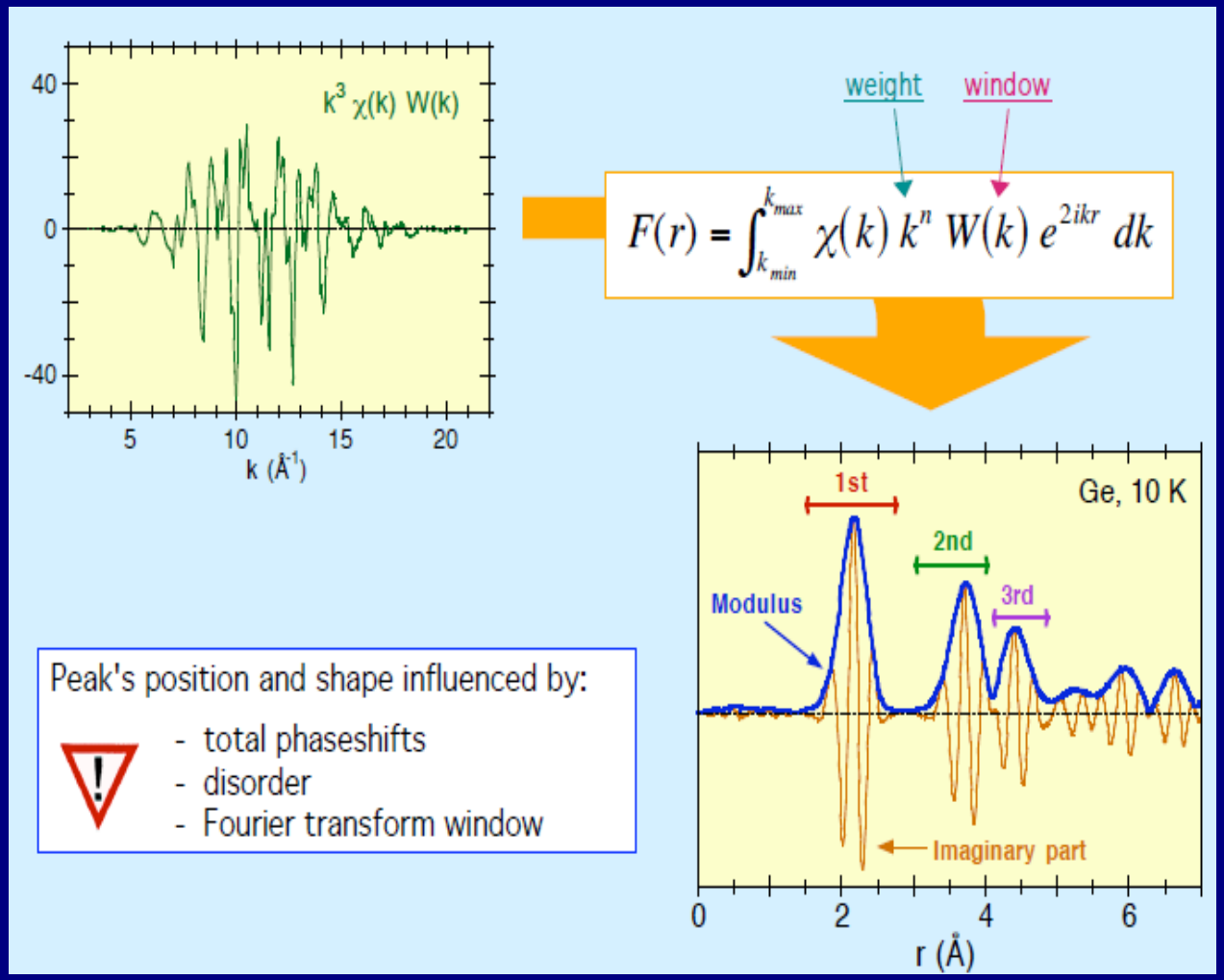
FOURIER FILTERING
(ARTEMIS, Viper, etc…)

The method allows isolating contributions of selected regions of the FT

WHOLE FITTING
GNXAS, EXCURVE....

All the coordinations shells are considering in the data analysis

EXAFS analysis: Fourier Filtering



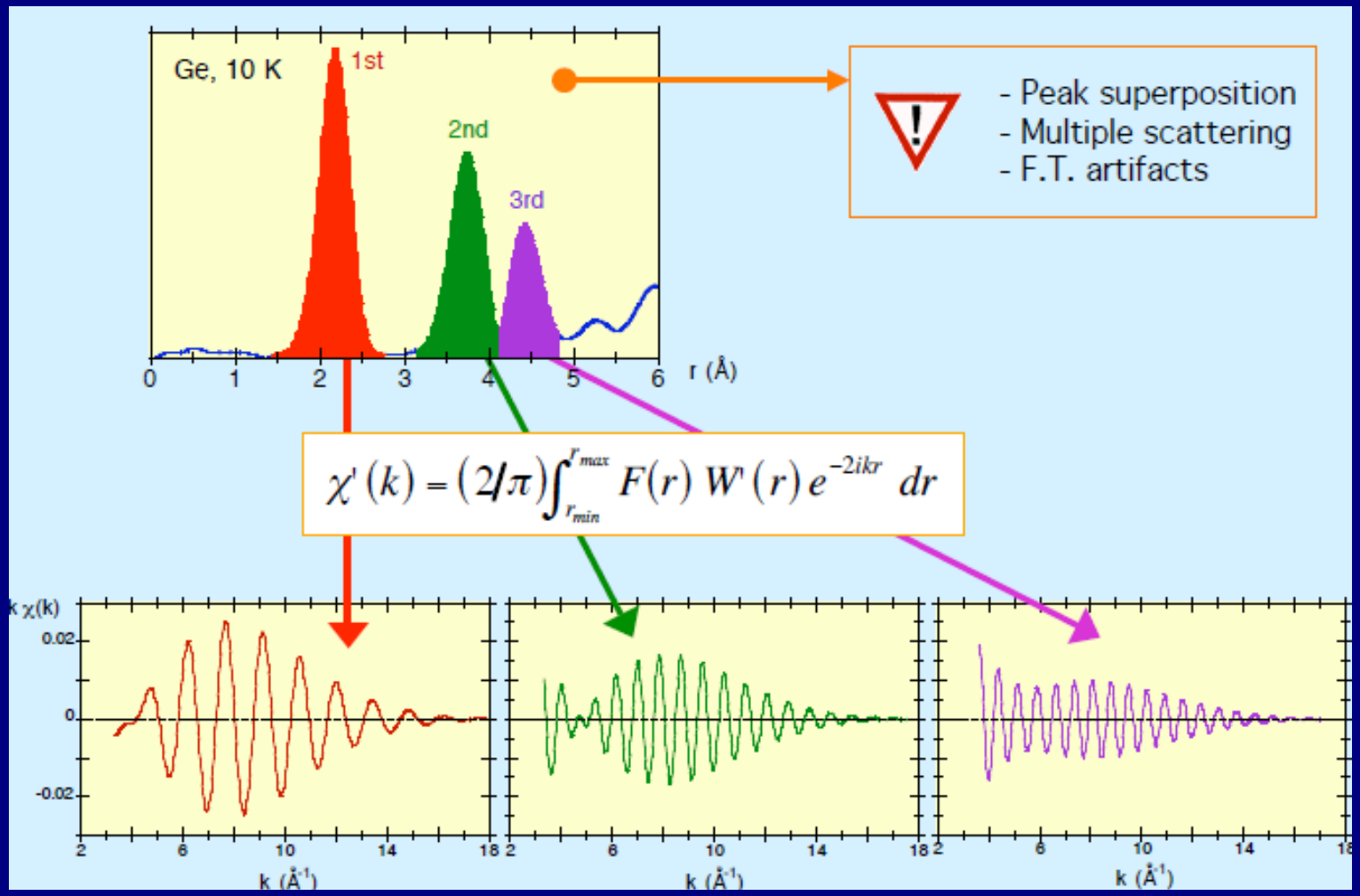
Shape of FT widely changes as a function of:

- FT window
- k_w weight
- data range

FT shows more intuitively the main structural features in the real space: the FT modulus represent a *pseudoradial distribution function* modified by the effect of amplitude, phase and mean free path parameters: |FT| peaks point out interatomic correlations

Peak positions are not the true distances due to the photoelectron phase shift!

EXAFS analysis: Fourier Filtering

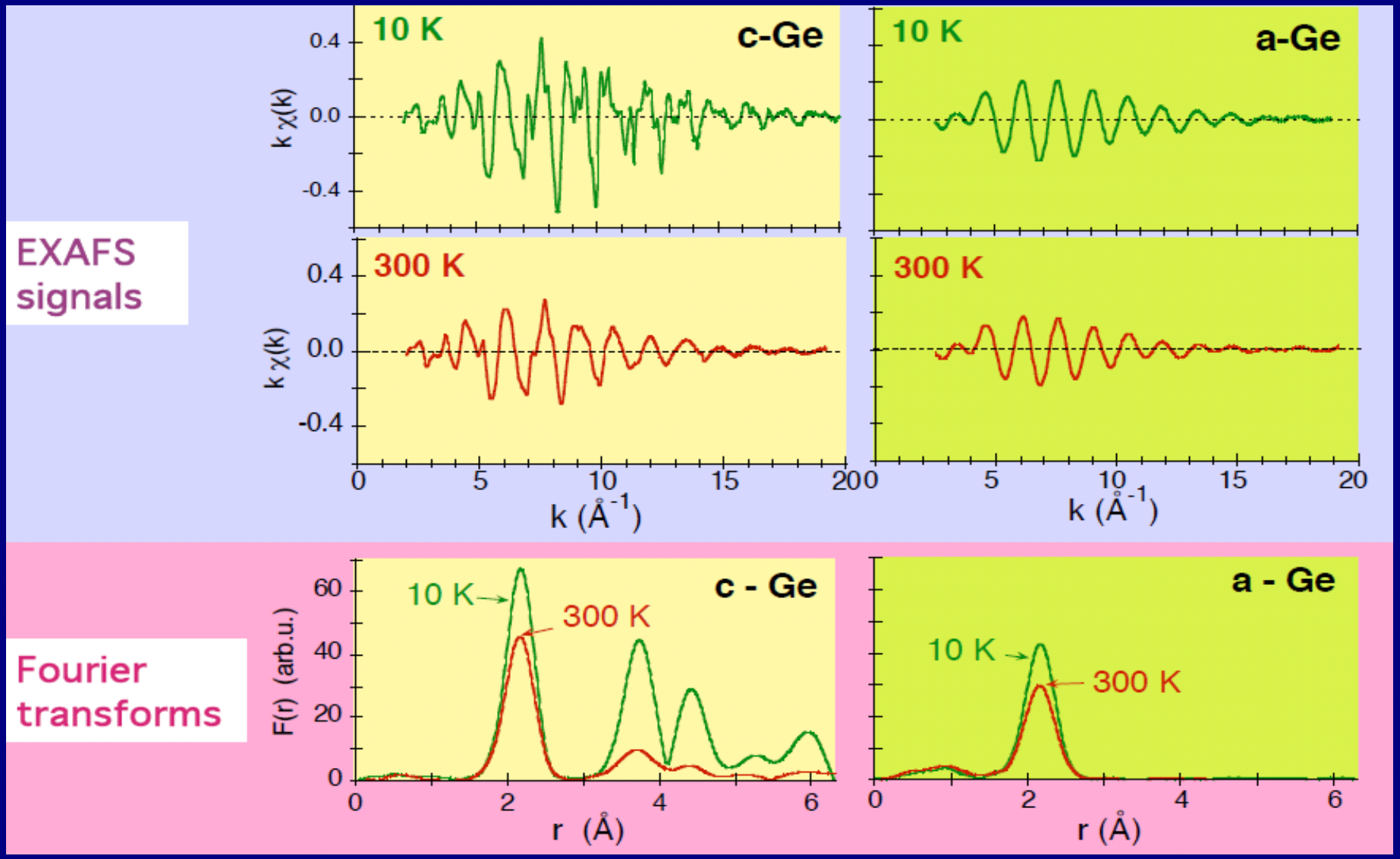


$N_1\ R_1\ \sigma_1$ $N_2\ R_2\ \sigma_2$ $N_3\ R_3\ \sigma_3$

N_i number of coordination i^{th} shell, R_i i^{th} distance between the absorber and i^{th} shell

σ_i is the Debye-Waller factor (disorder term) of the ith shell

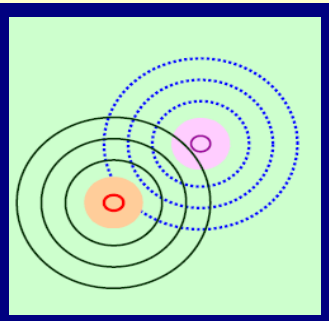
EXAFS analysis: Fourier Filtering thermal factor

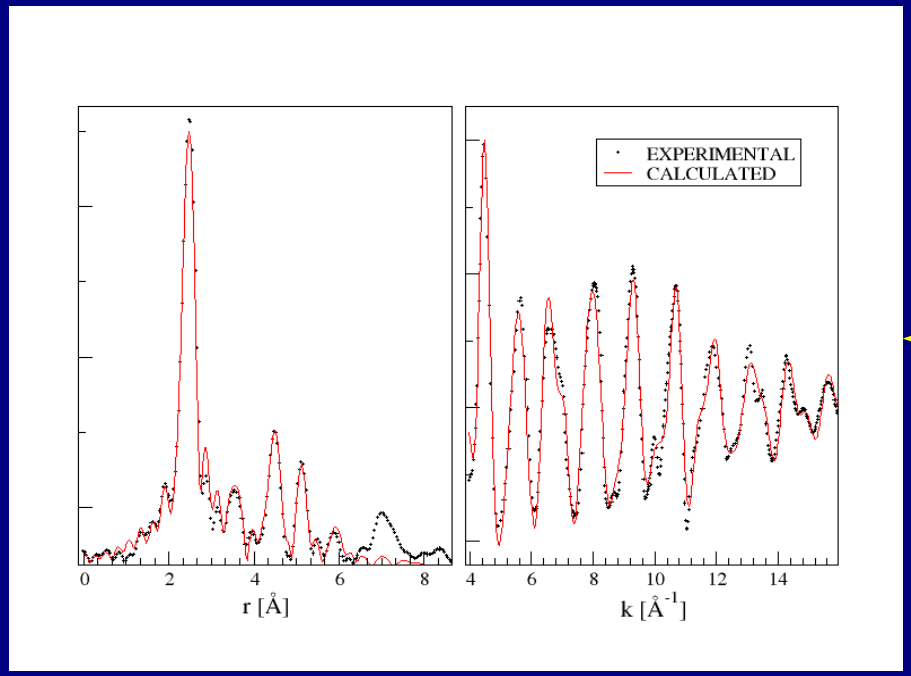


Data (structural) refinement

Theoretical $\chi(k)$

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





Choose a model

Exp. $\chi(k)$

Select the relevant structural contributions

Refine the structural parameters: N, R, σ^2

add new contributions?

Change the model?

Revise your data extraction?

END

HOW choose a structural model

How to find a model structure

How to visualize the structure

How to calculate distances and geometries

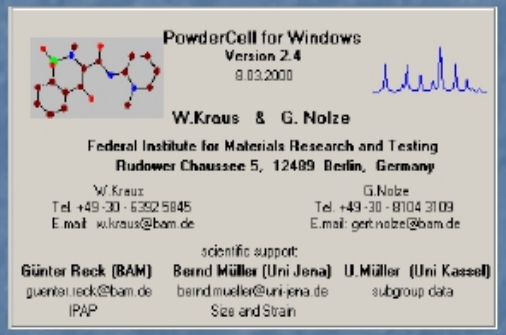
NEUTRONS FOR SCIENCE

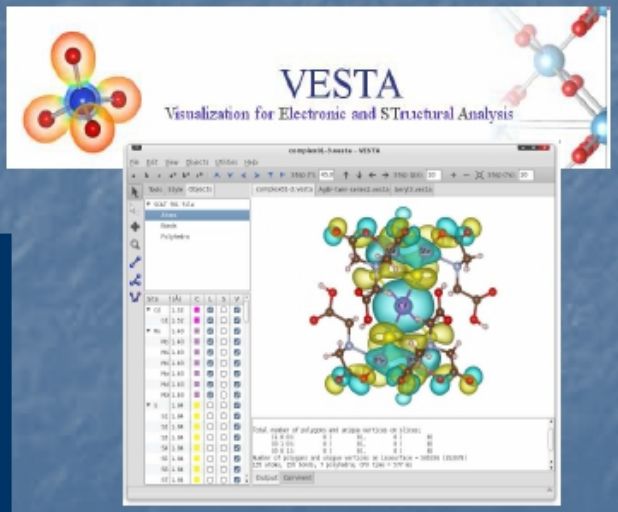
Barns.ill.fr

http://database.iem.ac.ru/mincryst/

Full inorganic structure database (ICSD) (registration fees)

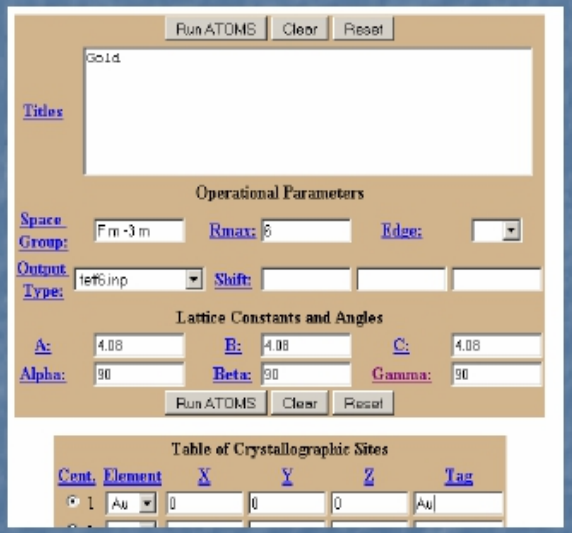
Protein Data Base (Free)





ATOMS on the Web

http://millenia.cars.aps.anl.gov/cgi-bin/atoms/atoms.cgi

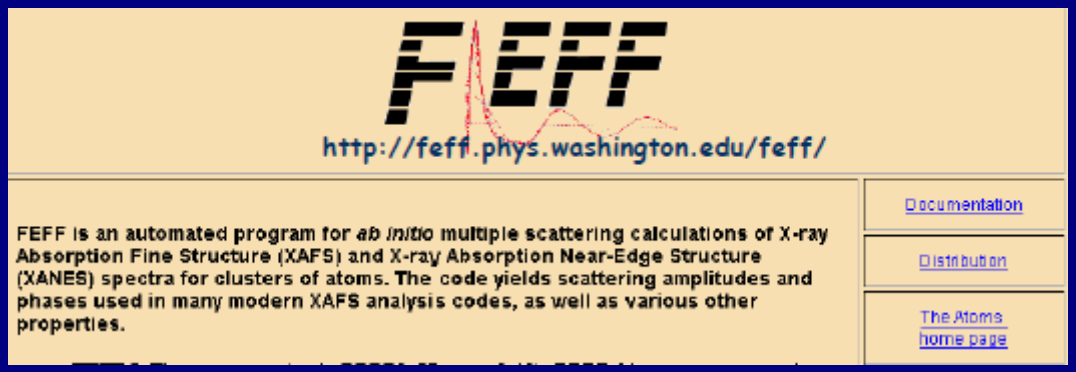


XAFS data analysis software

XAFS organizations

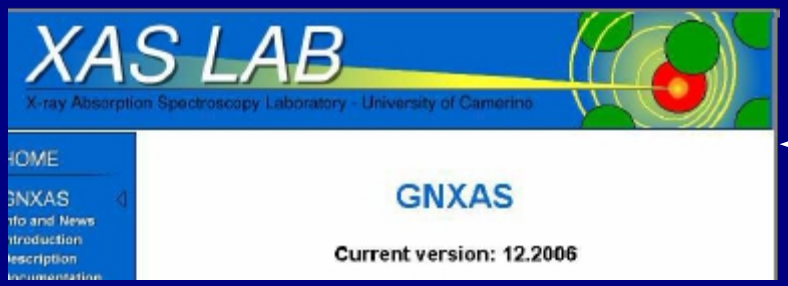
XAFS data analysis

www.esrf.fr



FEFF home-page

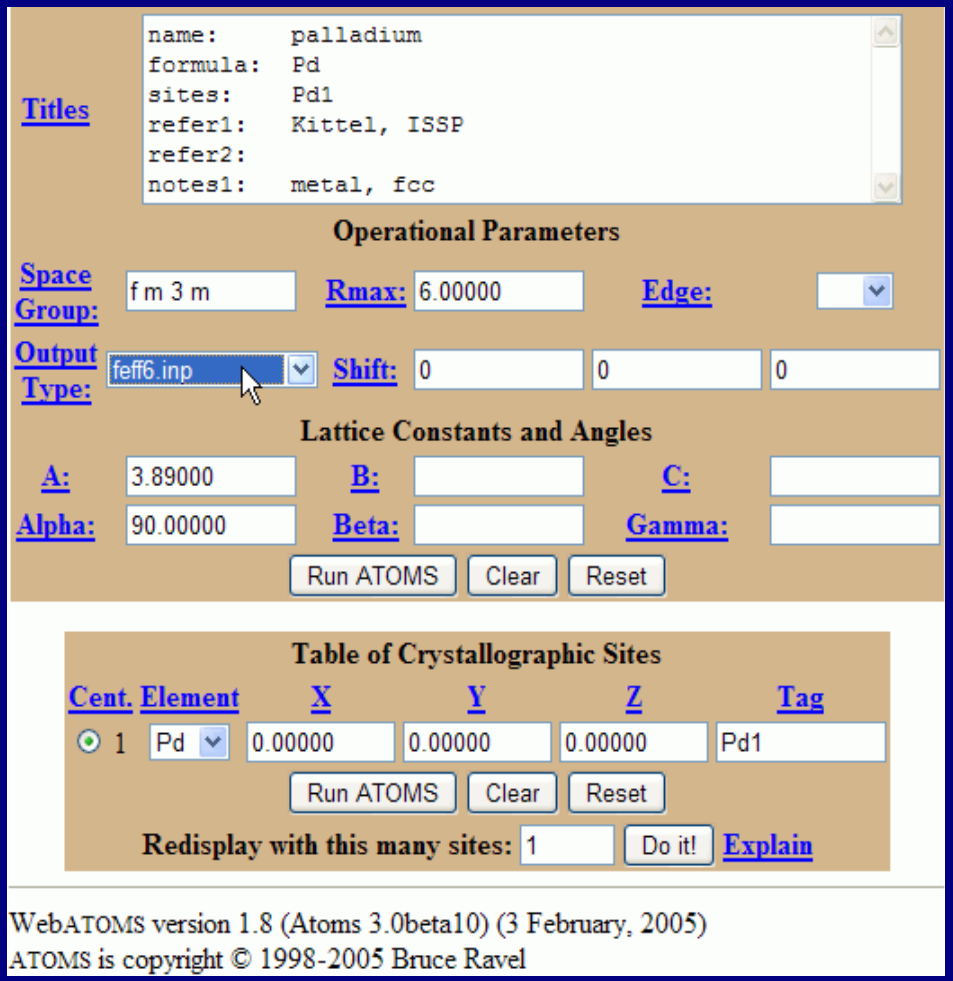
FEFF calculate the phase shift and amplitude. Fitting with Artemis (HORAE suite) or Viper ....

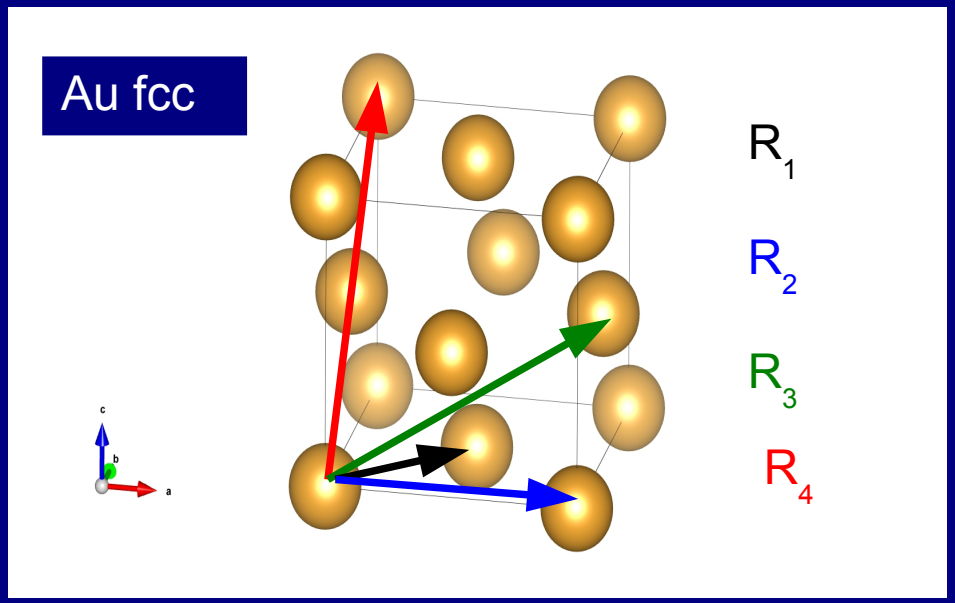


GNXAS
home-page

GNAXS calculate the phase shift and amplitude and does the fitting

EXAMPLE ANALYSIS





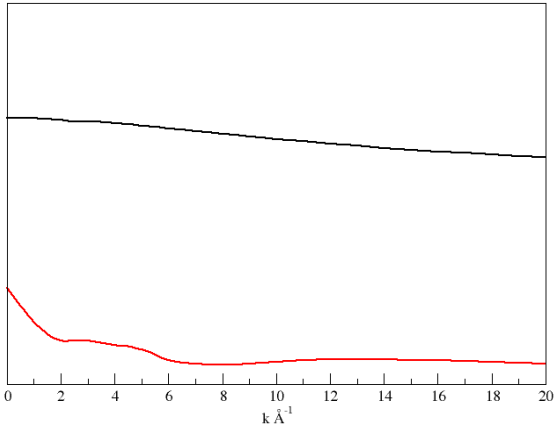
Sh R	N	R_{Au}(Å)
I: a/sqrt(2)	12	2.880
II: a	6	4.0789
III: axsqrt(1.5)	24	
IV: axsqrt(2)	12	
V: axsqrt(2.5)	24	

Visit ATOMS and FEFF web-pages for more information!

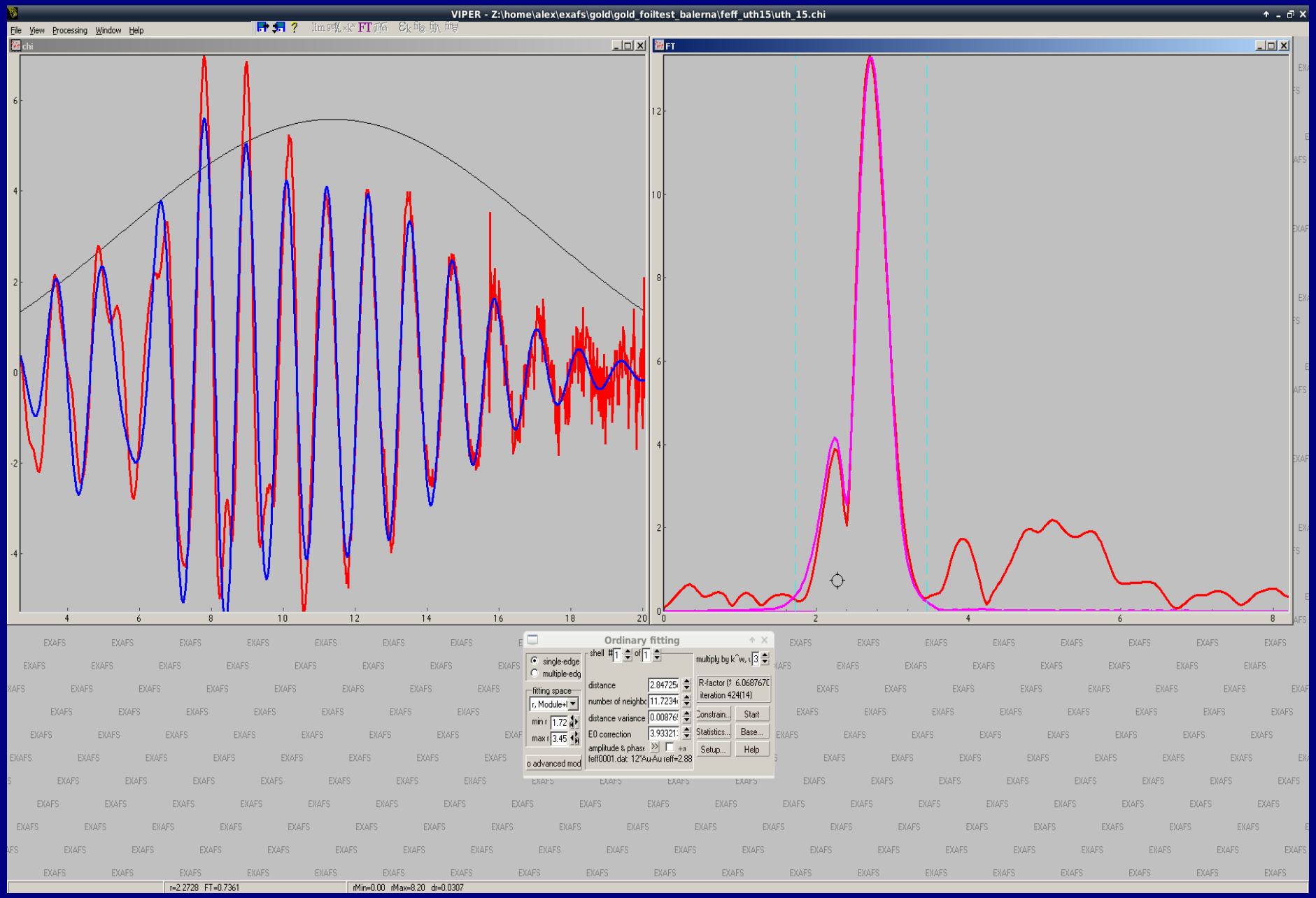
```
 Au L3 edge energy = 11919.0 eV
EDGE      L3
S02       1.0

*        pot    xsph  fms   paths genfmt ff2chi
CONTROL   1      1     1     1     1      1
PRINT     1      0     0     0     0      1

                    *** ixc=0 means to use Hedin-Lundqvist
*        ixc  [ Vr  Vi ]
EXCHANGE  0
                    *** l_scf = 0 for a solid, 1 for a molecule
*        r_scf  [ l_scf   n_scf   ca ]
SCF       4.0
*        kmax   [ delta_k  delta_e ]
*XANES     4.0
                    *** Radius of cluster for Full Multiple
                    *** Scattering calculation
                    *** l_fms = 0 for a solid, 1 for a molecule
*        r_fms     l_fms
*FMS       6.3470  0
                    *** for EXAFS:  RMAX   7.0 and uncomment
                    *** the EXAFS card
RPATH     7.1
EXAFS     20

POTENTIALS
*    ipot   Z  element          l_scmt  l_fms   stoichiometry
      0   79  Au                 3       3       0.001
      1   79  Au                 3       3       4
ATOMS                            * this list contains 79 atoms

 *   x          y          z      ipot  tag          distance
   0.00000    0.00000    0.00000  0    Au1          0.00000     0
   2.04000    2.04000    0.00000  1    Au1          2.88500     1
  -2.04000    2.04000    0.00000  1    Au1          2.88500     2
   2.04000   -2.04000    0.00000  1    Au1          2.88500     3
  -2.04000   -2.04000    0.00000  1    Au1          2.88500     4
   2.04000    0.00000    2.04000  1    Au1          2.88500     5
  -2.04000    0.00000    2.04000  1    Au1          2.88500     6
   0.00000    2.04000    2.04000  1    Au1          2.88500     7
   0.00000   -2.04000    2.04000  1    Au1          2.88500     8
   2.04000    0.00000   -2.04000  1    Au1          2.88500     9
  -2.04000    0.00000   -2.04000  1    Au1          2.88500    10
   0.00000    2.04000   -2.04000  1    Au1          2.88500    11
   0.00000   -2.04000   -2.04000  1    Au1          2.88500    12
     .........
```

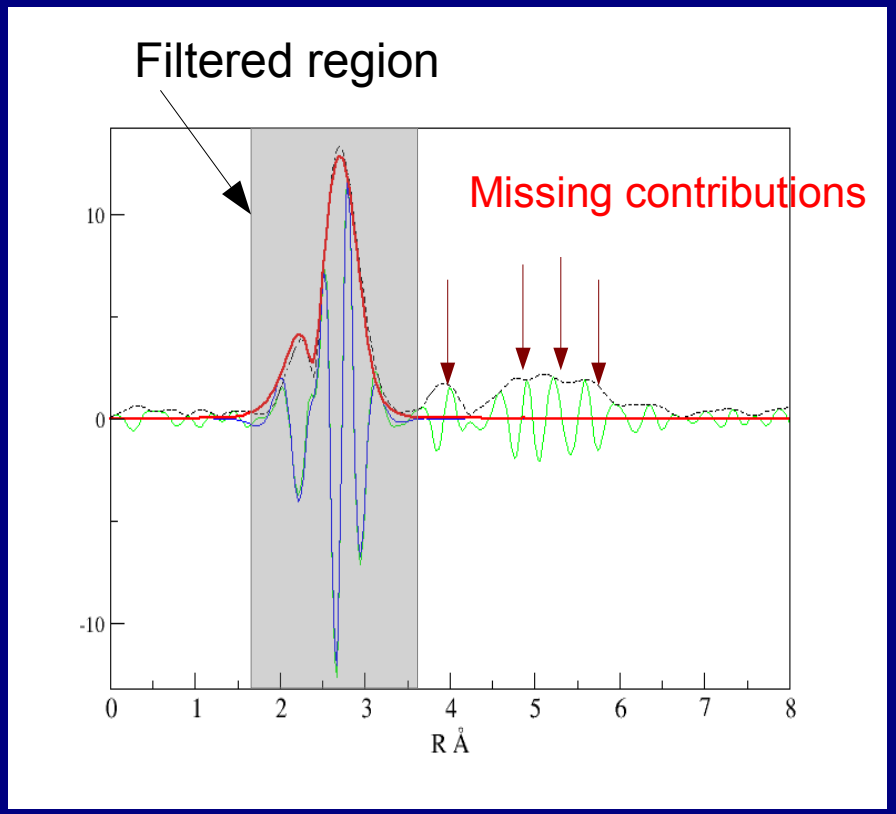
```
 # POT  Non-SCF, core-hole, AFOLP (folp(0)= 1.150)
 # Abs   Z=79 Rmt= 1.554 Rnm= 1.597 L3 shell
 # Pot 1 Z=79 Rmt= 1.532 Rnm= 1.571
 # Gam_ch=5.284E+00 H-L exch
Vi= 0.000E+00 Vr= 0.000E+00
 # Mu=-5.283E-01eV kf=1.855E+00
Vint=-1.364E+01eV Rs_int= 1.955
 # PATH  Rmax= 7.100,
Keep_limit= 0.00, Heap_limit 0.00  Pwcrit= 2.50%
 ----------------------------------------------------------------------
   file        sig2   amp ratio    deg    nlegs  r effective
 feff0001.dat 0.00000   100.000    12.000    2   2.8850
 feff0002.dat 0.00000    24.390     6.000    2   4.0800
 feff0003.dat 0.00000    11.460    48.000    3   4.3275
 feff0004.dat 0.00000     5.109    48.000    3   4.9250
 feff0005.dat 0.00000    56.390    24.000    2   4.9970
 feff0006.dat 0.00000     9.115    48.000    3   5.3835
 feff0007.dat 0.00000    23.250    96.000    3   5.3835
 feff0008.dat 0.00000    18.370    12.000    2   5.7700
 feff0009.dat 0.00000     7.733    12.000    3   5.7700
 feff0010.dat 0.00000    74.300    24.000    3   5.7700
```

Amplitude and phase shift
Feff0001.dat =first shell

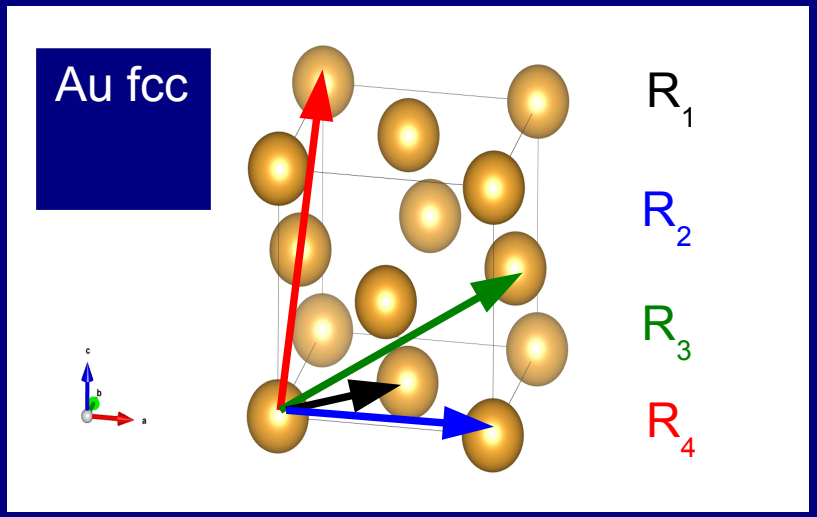


Fitting procedure

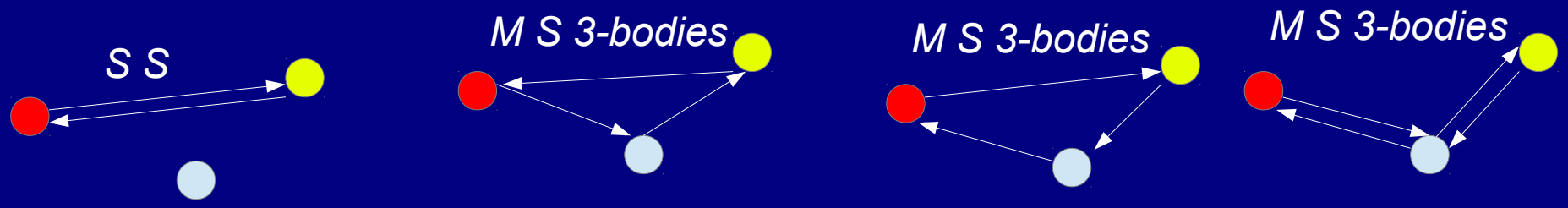




Visualize the structure and understand the neighbor shells!



… and take care about multiple scattering contributions

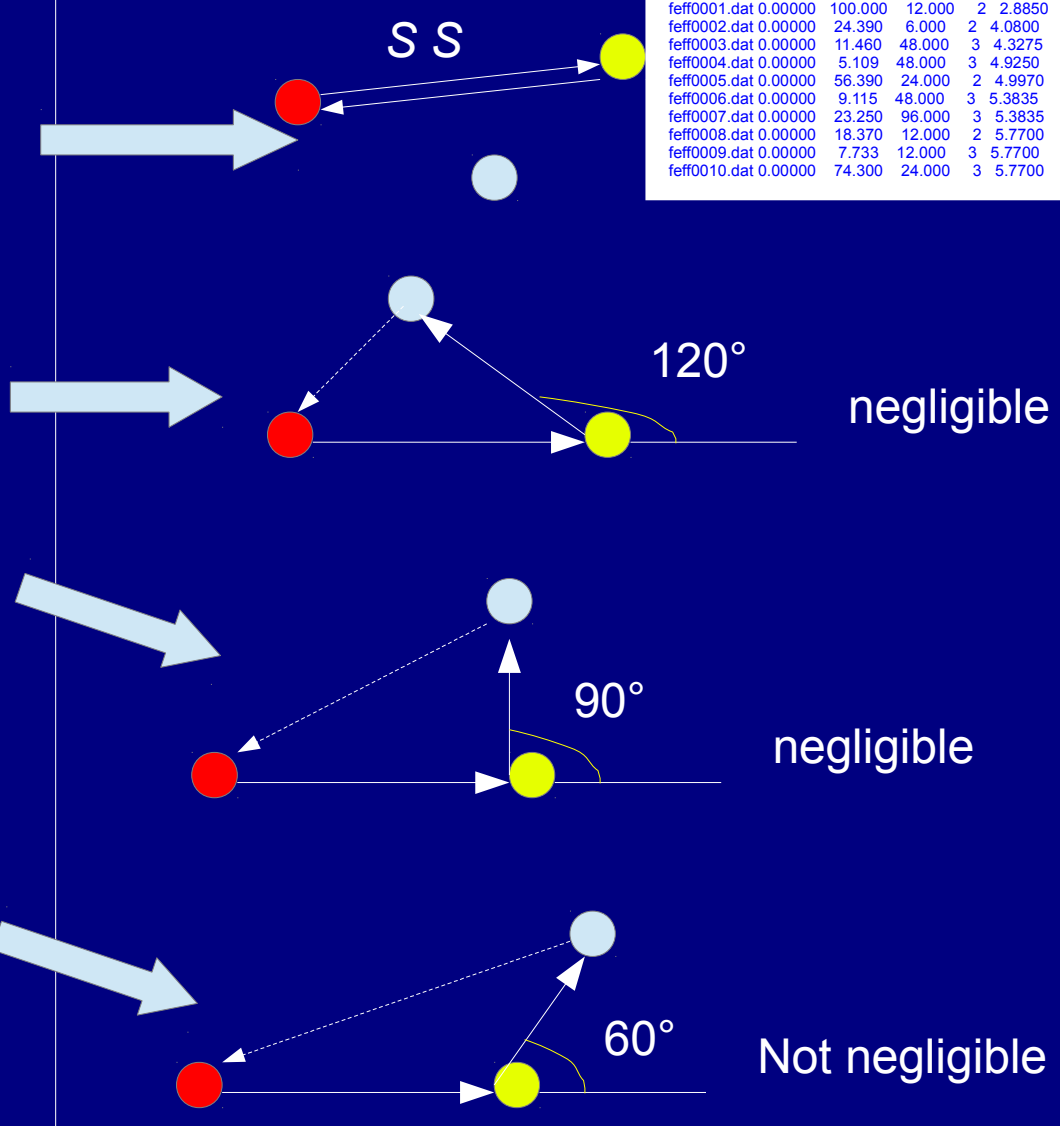


Important when the angle is > 120° .
The MS at 180° has highest contribution due to the “focusing effect”

How to choose the MS path

```
ATH  Rmax= 7.100,  Keep_limit= 0.00, Heap_limit 0.00  Pwcrit= 2.50%
 ----------------------------------------------------------------------
    1    2  12.000  index, nleg, degeneracy, r=  2.8850
     x          y          z     ipot  label      rleg      beta       eta
   0.000000   -2.040000    2.040000   1 'Au    '     2.8850  180.0000    0.0000
   0.000000    0.000000    0.000000   0 'Au    '     2.8850  180.0000    0.0000
    2    2   6.000  index, nleg, degeneracy, r=  4.0800
     x          y          z     ipot  label      rleg      beta       eta
  -4.080000    0.000000    0.000000   1 'Au    '     4.0800  180.0000    0.0000
   0.000000    0.000000    0.000000   0 'Au    '     4.0800  180.0000    0.0000
    3    3  48.000  index, nleg, degeneracy, r=  4.3275
     x          y          z     ipot  label      rleg      beta       eta
   2.040000    2.040000    0.000000   1 'Au    '     2.8850  120.0000    0.0000
   0.000000    2.040000   -2.040000   1 'Au    '     2.8850  120.0000    0.0000
   0.000000    0.000000    0.000000   0 'Au    '     2.8850  120.0000    0.0000
    4    3  48.000  index, nleg, degeneracy, r=  4.9250
     x          y          z     ipot  label      rleg      beta       eta
   4.080000    0.000000    0.000000   1 'Au    '     4.0800  135.0000    0.0000
   2.040000    2.040000    0.000000   1 'Au    '     2.8850   90.0000    0.0000
   0.000000    0.000000    0.000000   0 'Au    '     2.8850  135.0000    0.0000
    5    2  24.000  index, nleg, degeneracy, r=  4.9970
     x          y          z     ipot  label      rleg      beta       eta
  -2.040000   -2.040000    4.080000   1 'Au    '     4.9970  180.0000    0.0000
   0.000000    0.000000    0.000000   0 'Au    '     4.9970  180.0000    0.0000
    6    3  48.000  index, nleg, degeneracy, r=  5.3835
     x          y          z     ipot  label      rleg      beta       eta
  -2.040000   -2.040000    0.000000   1 'Au    '     2.8850  150.0000    0.0000
   2.040000    0.000000    2.040000   1 'Au    '     4.9970  150.0000    0.0000
   0.000000    0.000000    0.000000   0 'Au    '     2.8850   60.0000    0.0000
    7    3  96.000  index, nleg, degeneracy, r=  5.3835
     x          y          z     ipot  label      rleg      beta       eta
   4.080000   -2.040000   -2.040000   1 'Au    '     4.9970  150.0000    0.0000
   2.040000   -2.040000    0.000000   1 'Au    '     2.8850   60.0000    0.0000
   0.000000    0.000000    0.000000   0 'Au    '     2.8850  150.0000    0.0000
    8    2  12.000  index, nleg, degeneracy, r=  5.7700
     x          y          z     ipot  label      rleg      beta       eta
  -4.080000    0.000000    4.080000   1 'Au    '     5.7700  180.0000    0.0000
   0.000000    0.000000    0.000000   0 'Au    '     5.7700  180.0000    0.0000
    9    3  12.000  index, nleg, degeneracy, r=  5.7700
```

```
# POT  Non-SCF, core-hole, AFOLP (folp(0)= 1.150)
# Abs   Z=79 Rmt= 1.554 Rnm= 1.597 L3 shell
# Pot 1 Z=79 Rmt= 1.532 Rnm= 1.571
# Gam_ch=5.284E+00 H-L exch
Vi= 0.000E+00 Vr= 0.000E+00
# Mu=-5.283E-01eV kf=1.855E+00
Vint=-1.364E+01eV Rs_int= 1.955
# PATH  Rmax= 7.100,
Keep_limit= 0.00, Heap_limit 0.00  Pwcrit= 2.50%
 ----------------------------------------------------------------------
   file        sig2   amp ratio    deg    nlegs  r effective
 feff0001.dat 0.00000   100.000   12.000    2   2.8850
 feff0002.dat 0.00000    24.390    6.000    2   4.0800
 feff0003.dat 0.00000    11.460   48.000    3   4.3275
 feff0004.dat 0.00000     5.109   48.000    3   4.9250
 feff0005.dat 0.00000    56.390   24.000    2   4.9970
 feff0006.dat 0.00000     9.115   48.000    3   5.3835
 feff0007.dat 0.00000    23.250   96.000    3   5.3835
 feff0008.dat 0.00000    18.370   12.000    2   5.7700
 feff0009.dat 0.00000     7.733   12.000    3   5.7700
 feff0010.dat 0.00000    74.300   24.000    3   5.7700
```



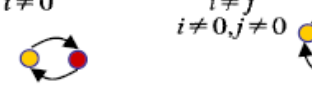
Expansion in terms of γ^n signals

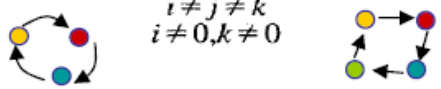
The GnXAS approach

A. Filipponi et al. Phys. Rev. B 52, 12122 (1995)

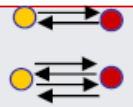
gnxas.unicam.it/

$$\sigma(\omega)=\sigma_0\left[1+\sum_{i\neq 0}\chi_2^{0i0}+\sum_{\substack{i\neq j\\ i\neq 0, j\neq 0}}\chi_3^{0ij0}+\sum_{\substack{i\neq j\neq k\\ i\neq 0, k\neq 0}}\chi_4^{0ijk0}+\cdots\right]$$





$$\chi=\sum_i\gamma^{(2)}(0,i)+\sum_{i,j}\gamma^{(3)}(0,i,j)+\sum_{i,j,k}\gamma^{(4)}(0,i,j,k)+\ldots.$$



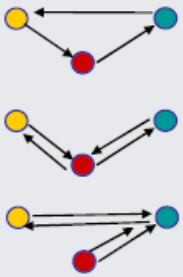
...

r

$$\left\{\begin{pmatrix} t_0 & 0\\ 0 & t_i\end{pmatrix}\sum_{n=1}^{\infty}\left[\begin{pmatrix} 0 & G_{0,i}\\ G_{i,0} & 0\end{pmatrix}\begin{pmatrix} t_0 & 0\\ 0 & t_i\end{pmatrix}\right]^n\right\}^{0,0}$$

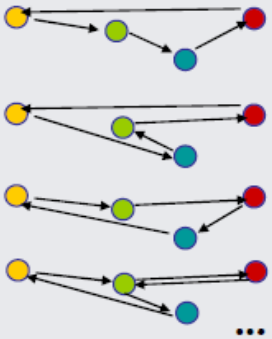
$$=t_0G_{0i}t_iG_{i0}t_0+t_0G_{0i}t_iG_{i0}t_0G_{0i}t_iG_{i0}t_0+$$

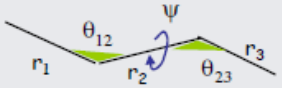
Continuous fraction expansion



...

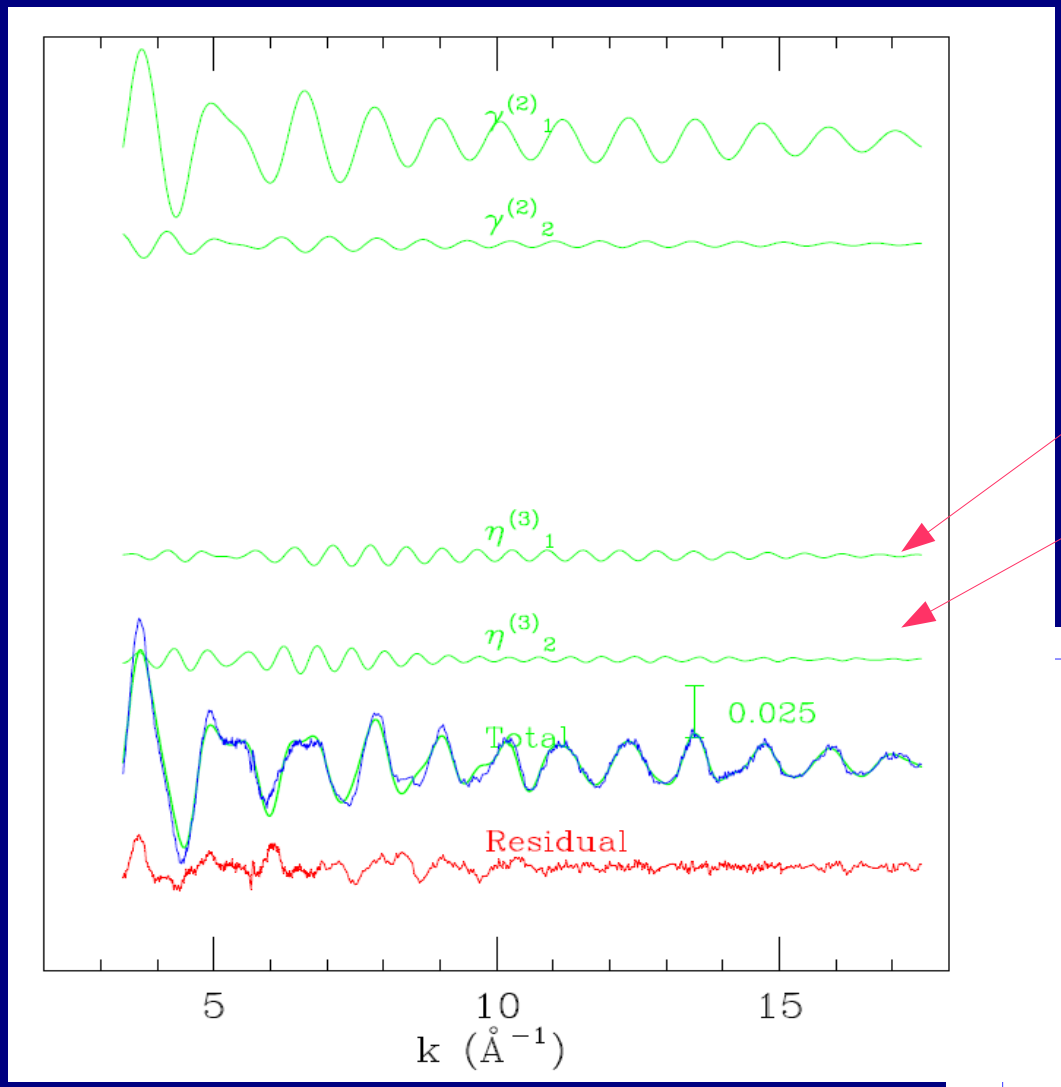
r_1, r_2, θ_{12}

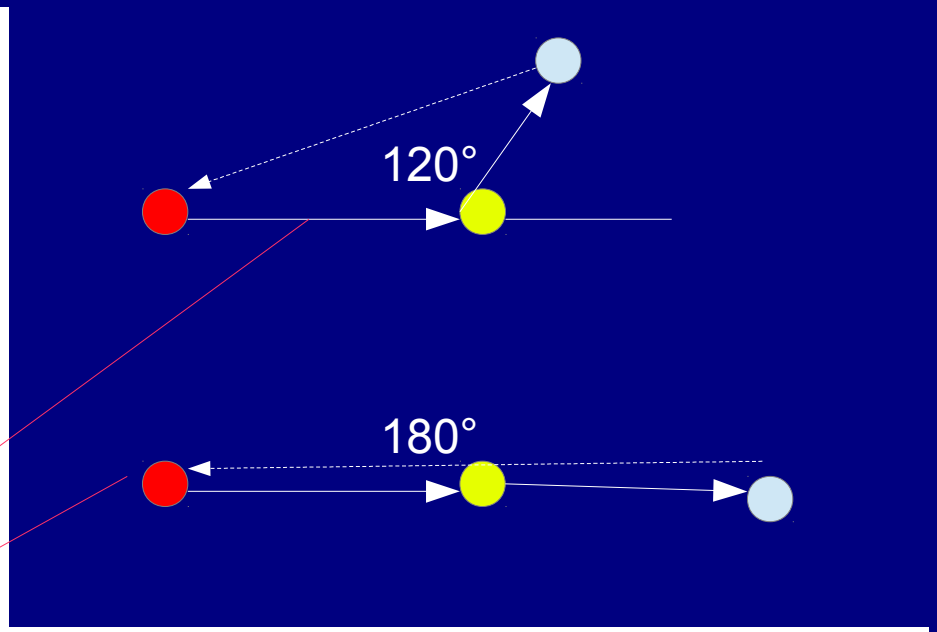


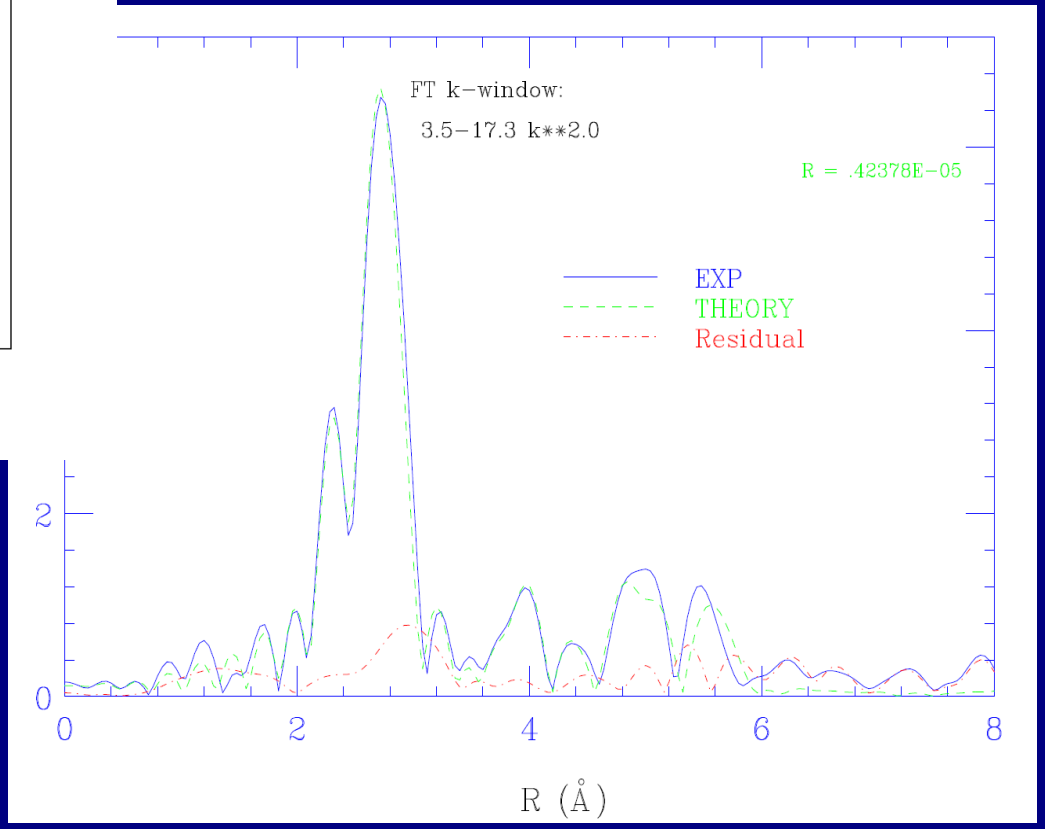


...

r_1, r_2, r_3 θ_{12}, θ_{23}, ψ


$\gamma^{(2)}_1$
$\gamma^{(2)}_2$
$\eta^{(3)}_1$
$\eta^{(3)}_2$
0.025
Total
Residual
5
10
15
k (Å^{-1})


120°
180°


FT k-window:
3.5-17.3 k**2.0
R = .42378E-05
EXP
THEORY
Residual
2
0
0
2
4
6
8
R (Å)

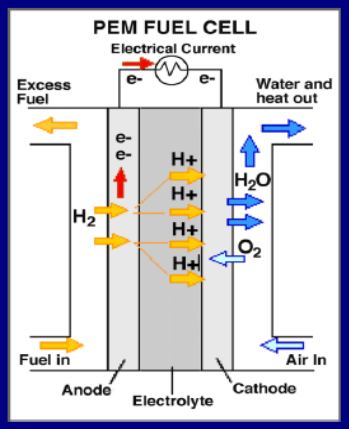
- EXAFS: introduction to data analysis

- Example. Dopants and defects: local structure in barium cerates and zirconates

- On line tutorial (VIPER package)

Dopants and defects: local structure in barium cerates and zirconates

Proton conductors

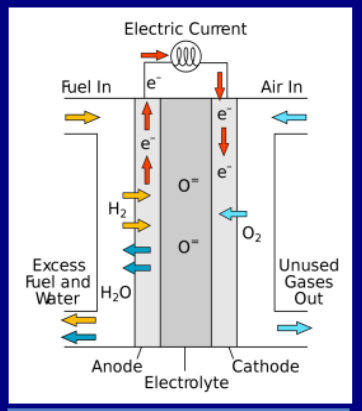


Cathode: Sr-doped LaMnO3 /Sr-doped/Yttria stabilized Zriconia (YSZ)

Electrolyte: $Y:BaZr(Ce)O_4$

Anode: Ni/(YSZ) CERMET

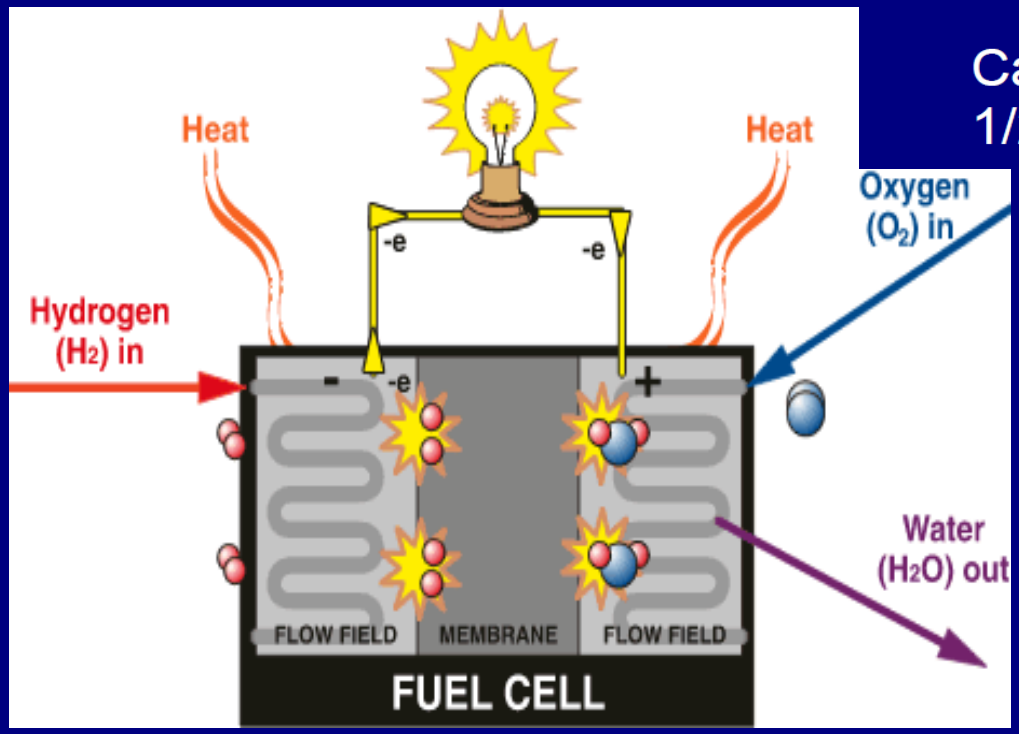
Anionic conductors



Cathode: Sr-doped $LaMnO_3$ /Sr-doped/Yttria stabilized Zriconia (YSZ)

Electrolyte: YSZ

Anode: Ni/(YSZ) CERMET



Cathode :

$1/2O_2+2e^- = O^{2-}$

Anode :

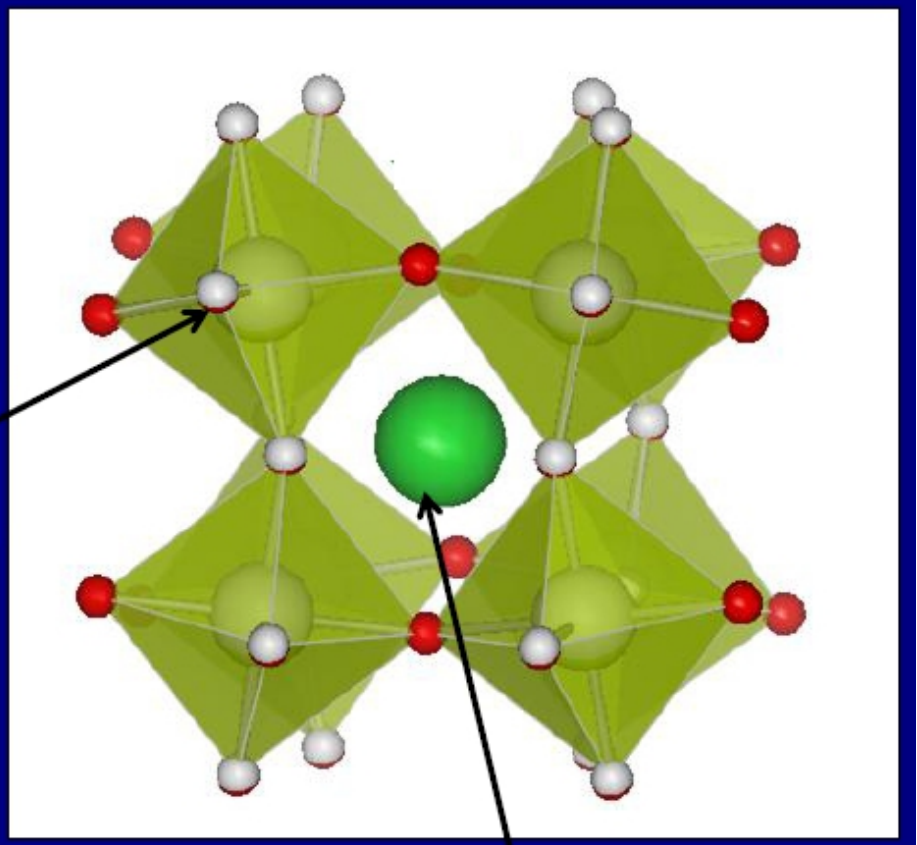
$H_2+ O^{2-} = H_2O+2e^-$

Problems:

- High temperature
- Chemical stability
- Low ion/electron conductivity
- High production cost

Open questions: conduction **mechanisms,** its correlation with the **structure** and perovskite chemistry

ABO_3 perovskite
(e.g. $BaCeO_3$ = BCY)



B-site
smaller Ce^{4+} cation

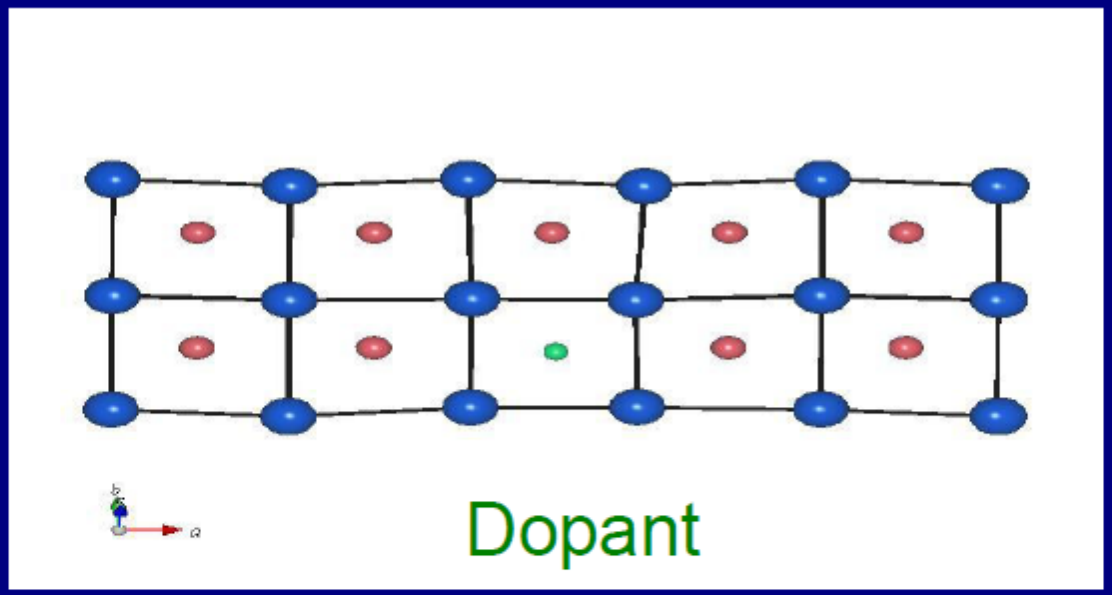
A-site
larger Ba^{2+} cation

Doping

$$2\ Ce_{Ce}^{x} + O_o^{x} + Y_2O_3 = 2\ YC_e' + V_o^{\bullet\bullet} + 2\ CeO_2$$

(De)-hydration

$$H_2O(g) + V_o^{\bullet\bullet} + O_o^{x} = 2\ OH_o^{\bullet}$$



Averaging: higher thermal factors, modified positions deceiving!

Local: two different local environments, each with its own features

Takeuchi et al, SSI 2000

...

Azad et al, J Mater Chem 2008

But only neutron scattering/XRD, i.e. no local information

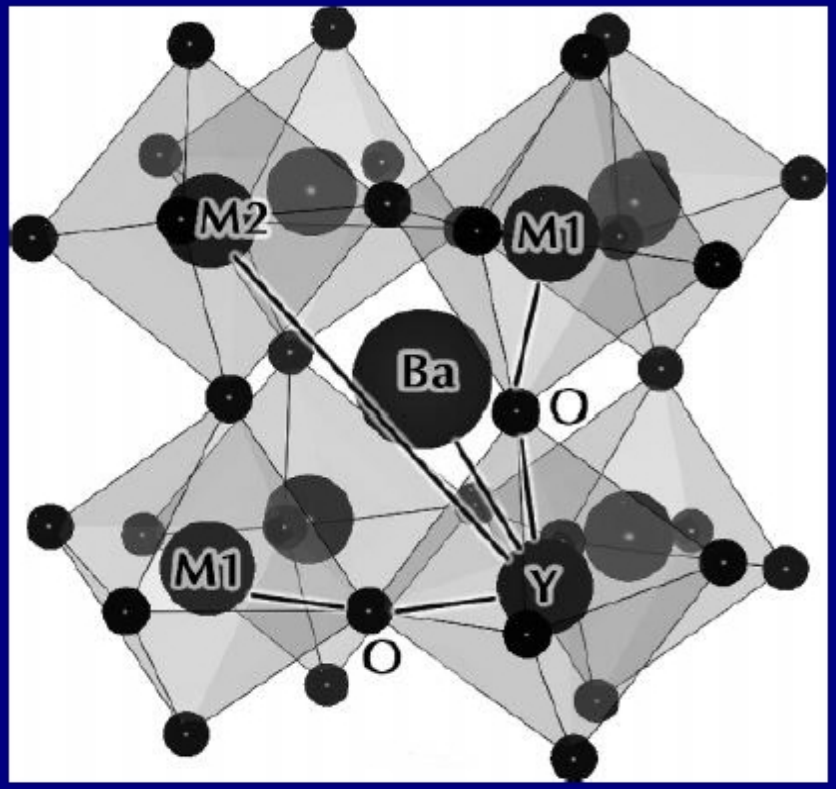
Lots of simulations
but almost no measurements until 2005

Local information required

Diffraction can be deceiving, because it averages out doped and undoped sites that are not equivalent from a local point of view!

EXAFS is a good complementary technique

In situ EXAFS of Y:$BaCeO_3$



EXAFS collected @ BM26 and BM08

Longo et al. *Chem. Mater. (2006).*

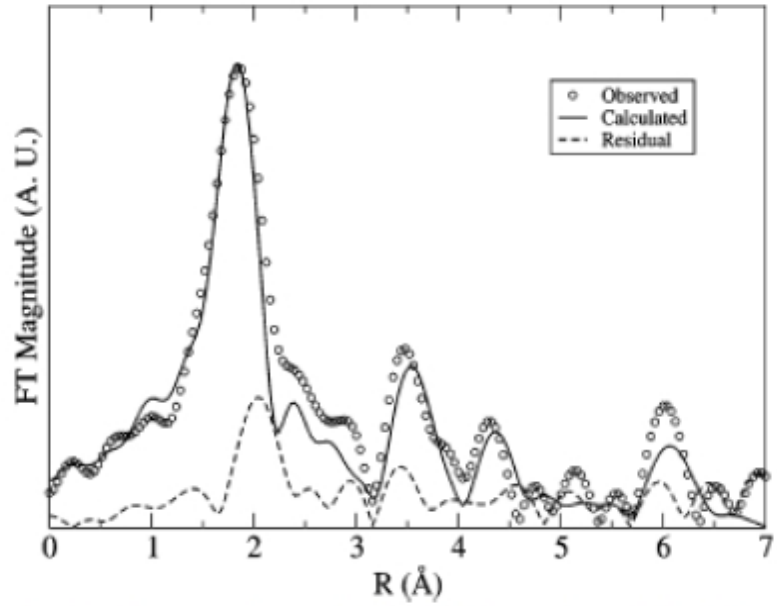


Figure 5. Fourier transform of XAFS data and model relative to dry $BaCe_{0.98}Y_{0.02}O_{3-\delta}$. The model FT corresponds to a regular octahedral oxygen shell around yttrium.

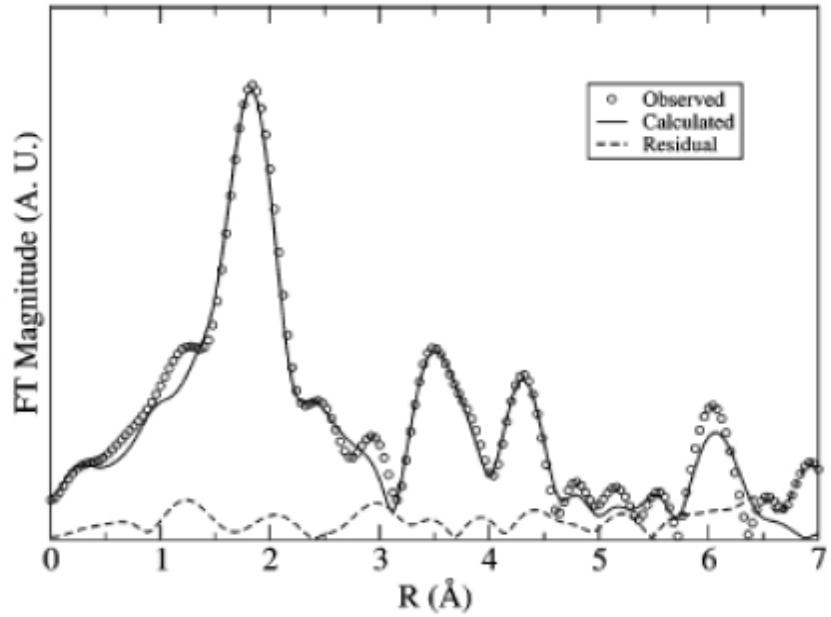
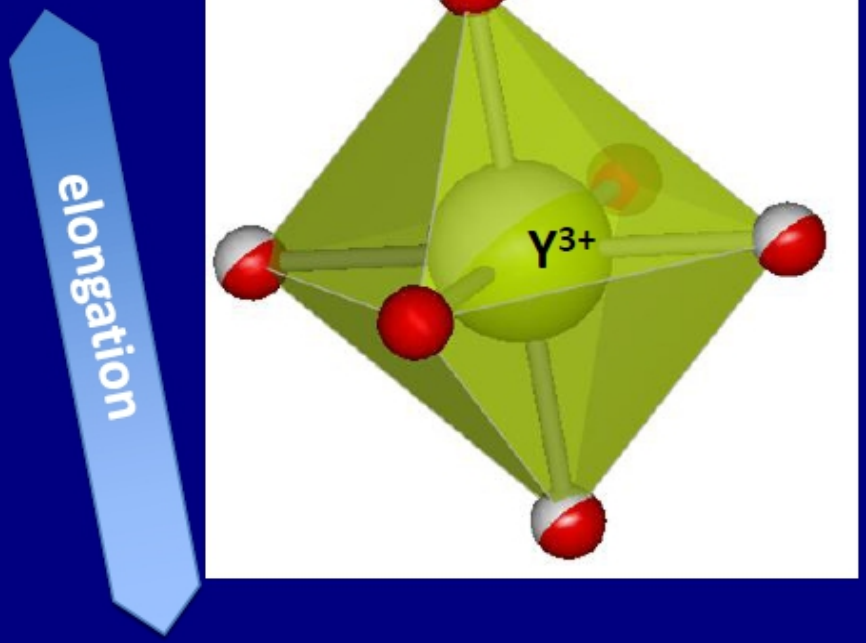


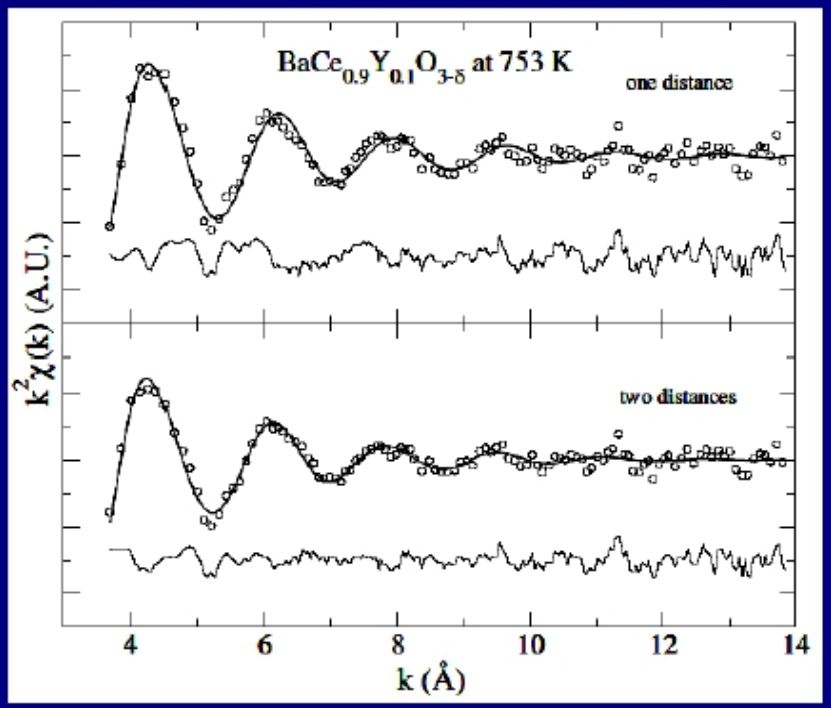
Figure 8. Fourier transform of XAFS data and model of the dry $BaCe_{0.98}Y_{0.02}O_{3-\delta}$ assuming a distorted octahedral yttrium environment.

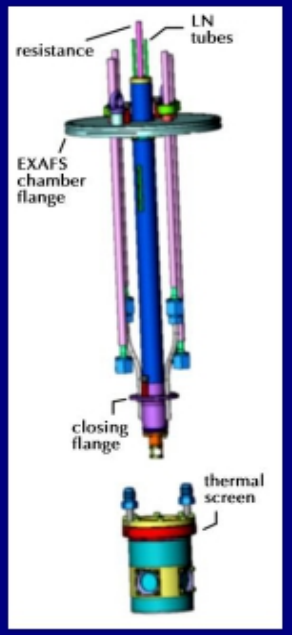
Y^{3+} in BCY

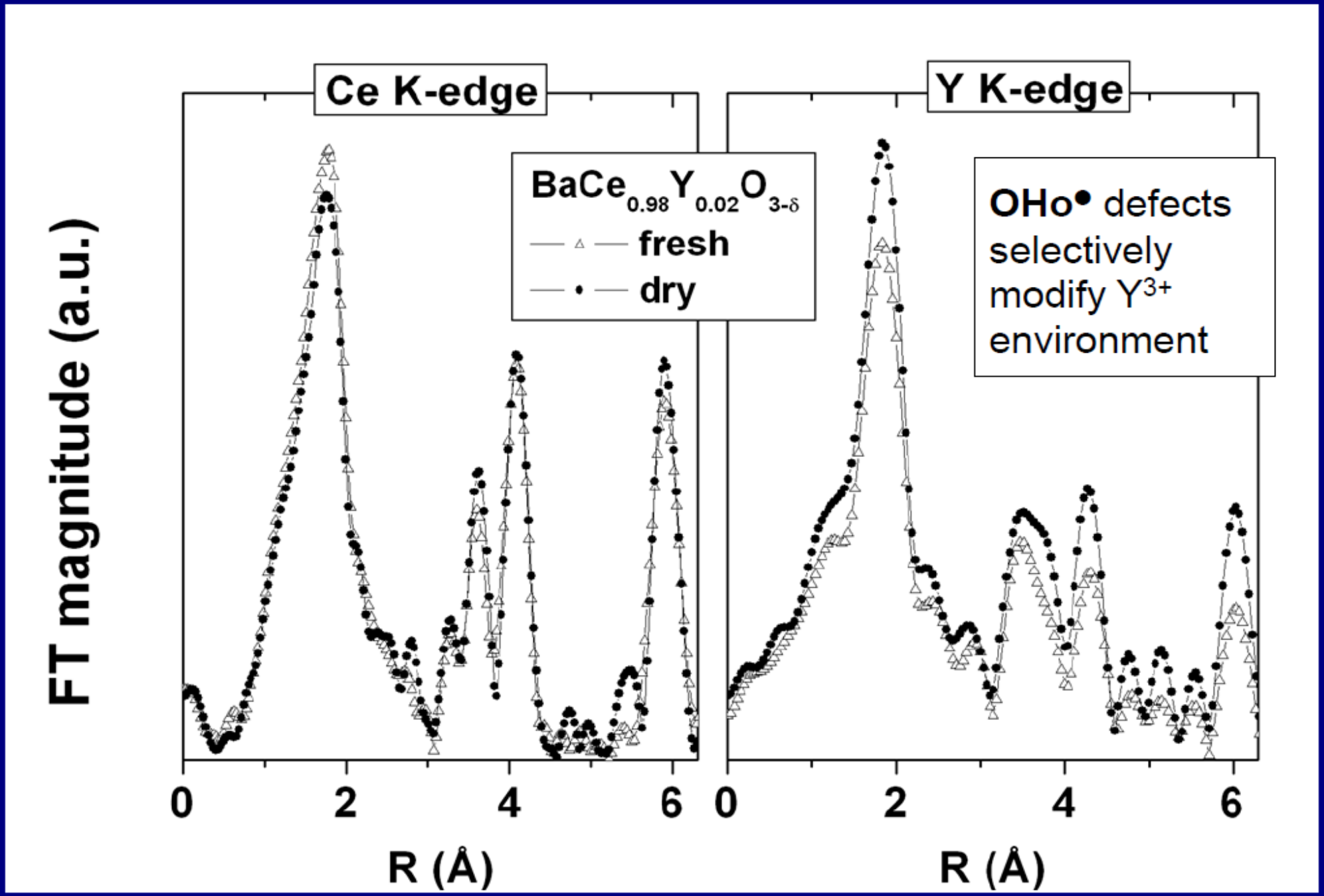


Longo et al. ***Chem. Mater.*** *(2006).*

550° C in wet flux



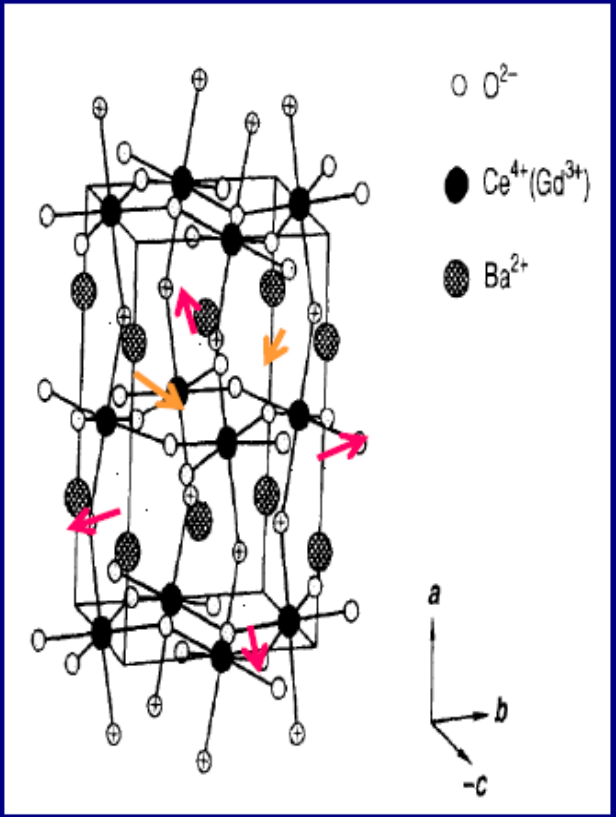




Giannici, Longo et al Solid State Ionics (2007).

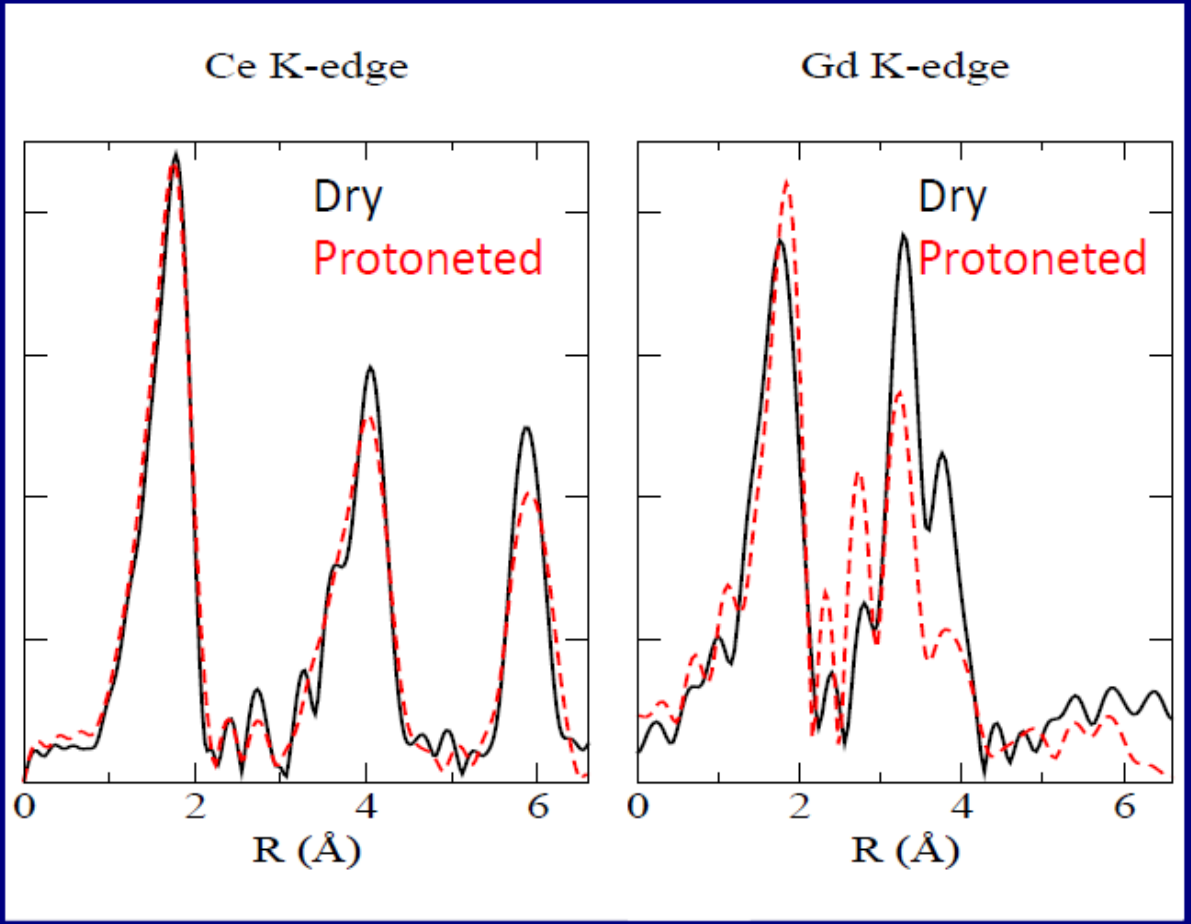
Gd^{3+} in BCG

O octahedron expands



Ba polyhedron contracts (!?)

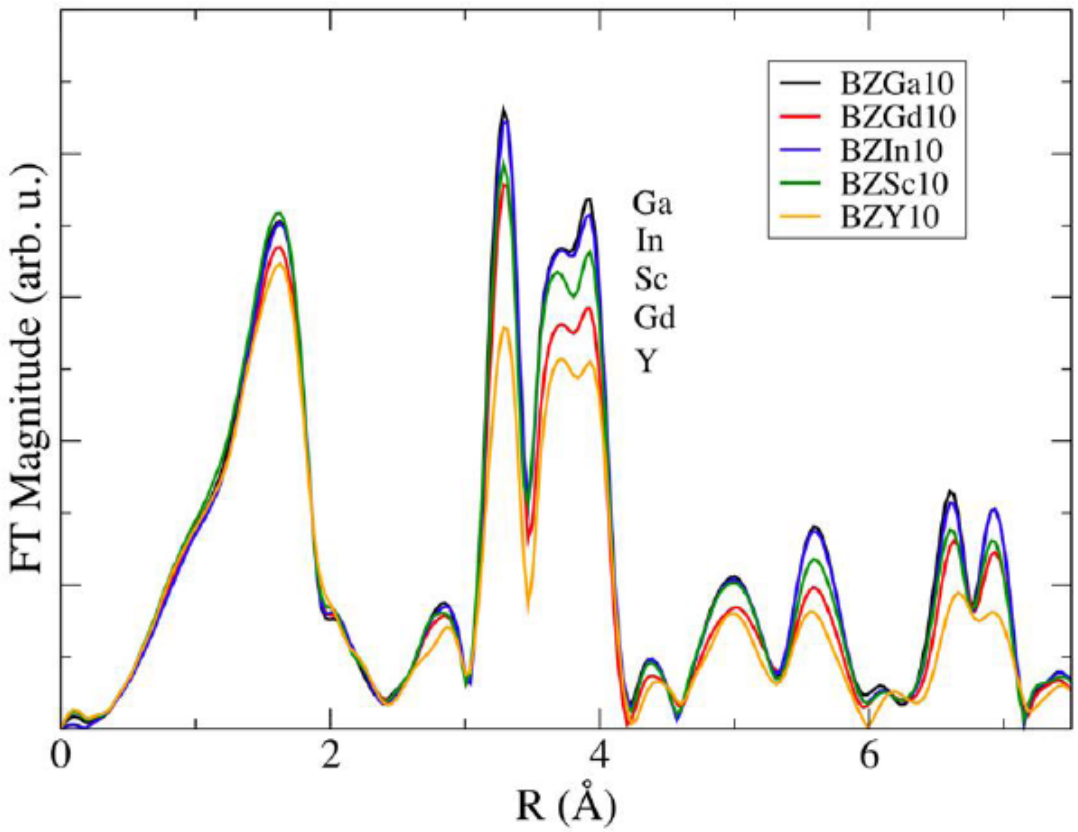
Proton (de)insertion has strong effects on dopant environment



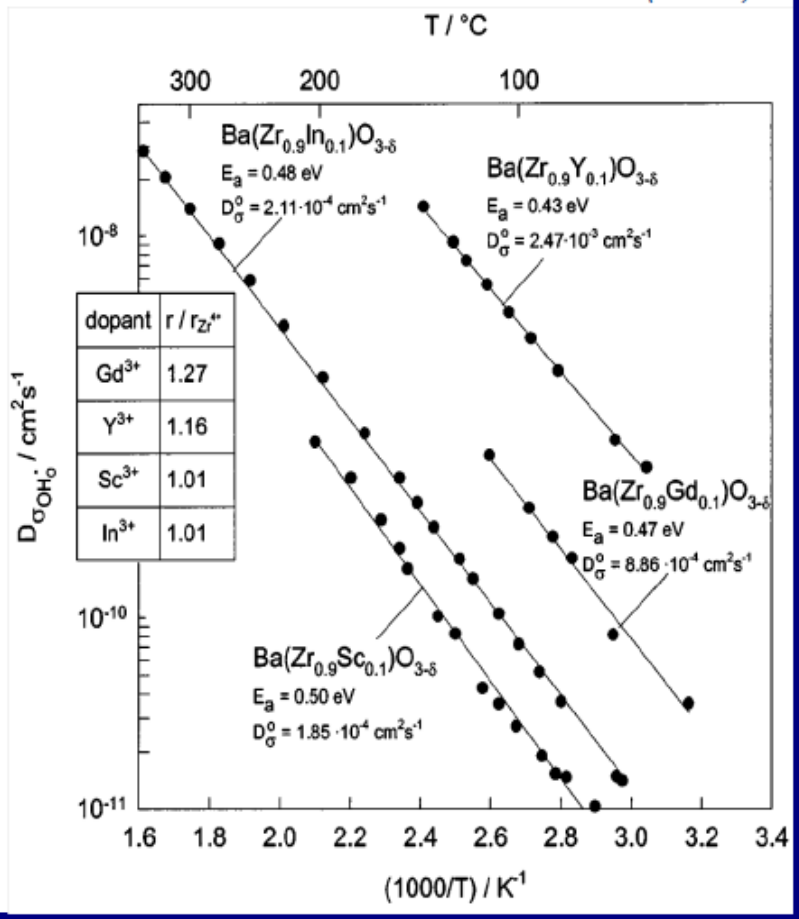
EXAFS @ BM29

Giannici et al. Chem. Mater. *(2009)*.

F. Giannici et al. *Solid State Ionics (2010).*



K.D. Kreuer et al. *Solid State Ionics (2001).*



mobility

Ga < Sc < In < Gd < Y

disorder

EXAFS @ BM29

Giannici , Longo et al. Chem. Mater. (2011).
ESRF Highlights (2011)

- EXAFS: introduction to data analysis

- example: Dopants and defects: local structure in barium cerates and zirconates

- On line tutorial (VIPER package)

THANK you for your attention