

EXAFS spectroscopy: fundamentals, experiment, data analysis, application examples and recent extensions

K. Klementiev,
MAX IV Laboratory
Lund, Sweden

MAX IV: Next-generation low emittance synchrotron radiation facility Inauguration on 21st of June 2016



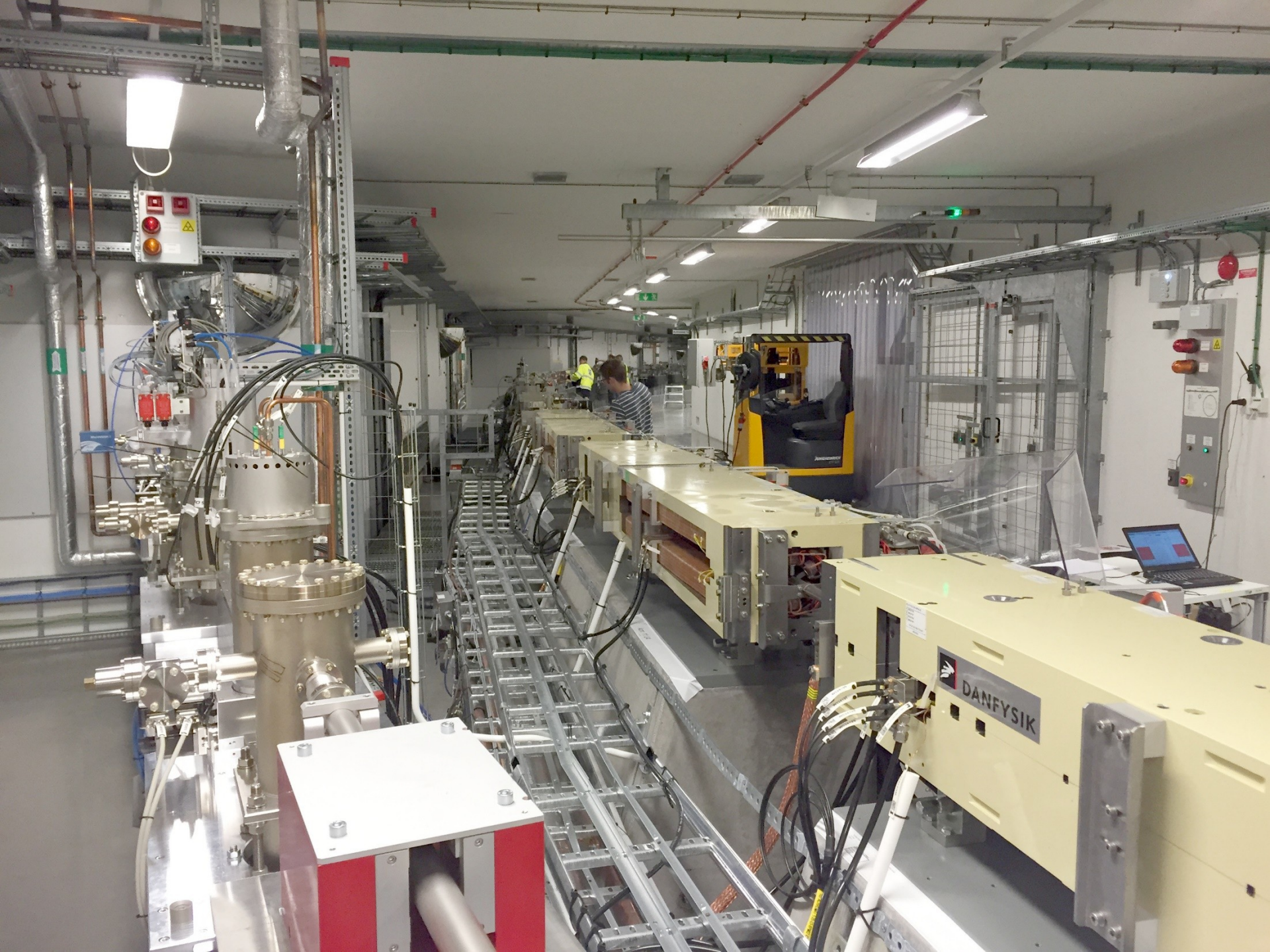
Foto: Magnus Högfeldt



C4 C3 C2 C1

11

NO ENTRY

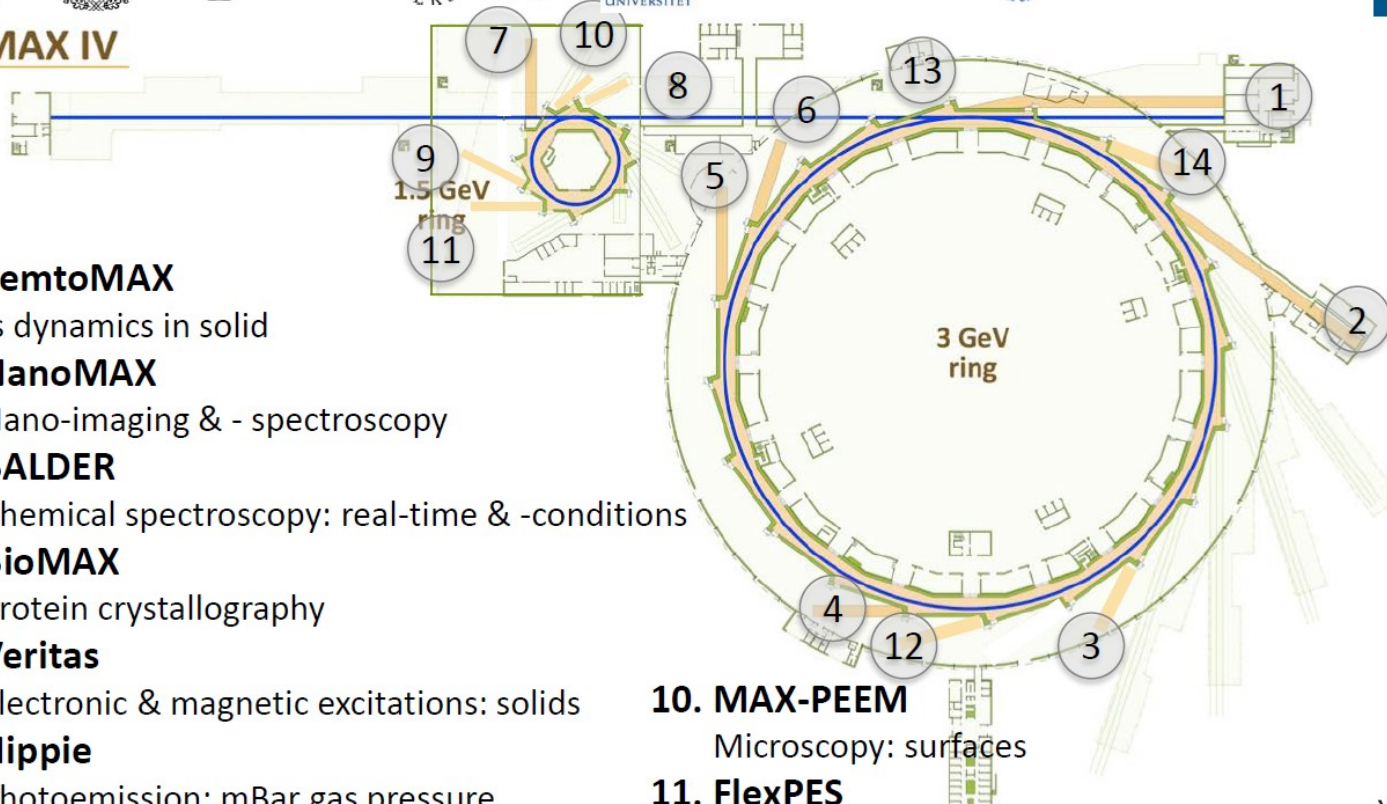


DANFYSIK

Beamlines at MAX IV



MAX IV



1. FemtoMAX

fs dynamics in solid

2. NanoMAX

Nano-imaging & - spectroscopy

3. BALDER

Chemical spectroscopy: real-time & -conditions

4. BioMAX

Protein crystallography

5. Veritas

Electronic & magnetic excitations: solids

6. Hippie

Photoemission: mBar gas pressure

7. ARPES

Electronic structure: solids

8. FinEstBeaMS



Electronic structure: gases, aerosols

9. SPECIES

Electronic & magnetic excitations: surfaces

10. MAX-PEEM

Microscopy: surfaces

11. FlexPES

Electronic structure: surfaces & gases

12. CoSAXS

Geometric structure & correlation: (bio) liquids

13. SoftiMAX

Microscopy & method development

14. DanMAX

Powder diffraction & imaging: materials science



Outlook

- Basic definitions and qualitative picture of XAFS
- The EXAFS formula and the need for amplitudes and phases
- XANES fingerprints
- An example of EXAFS study
- Deeper insights:
 - X-ray optics
 - Detection
 - Samples. Radiation damage
- Extensions:
 - Quick scanning
 - X-ray emission spectrometer

Reading

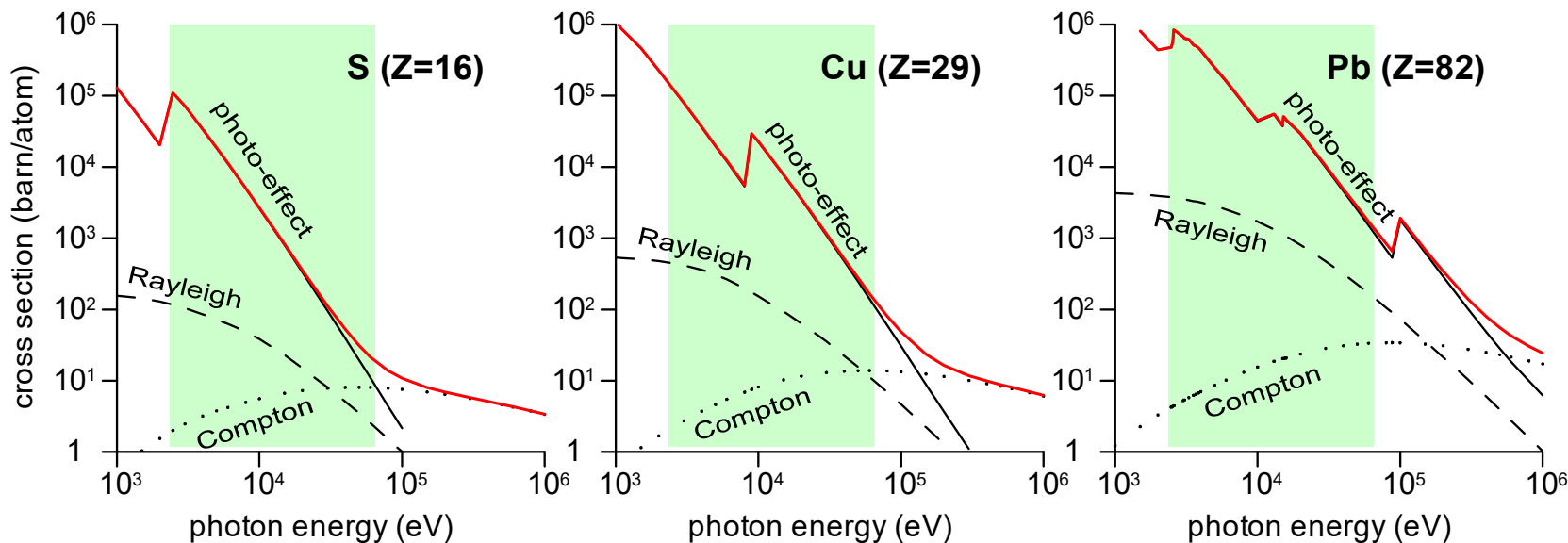
Proceedings of the HERCULES (Higher European Research Course for Users of Large Experimental Systems),
Neutron and synchrotron radiation for condensed matter studies. Vol. 1. Theory, instruments and methods. J.Baruchel, J.-L.Hodeau, M.S.Lehmann, J.-R.Regnard, C.Schlenker (eds.), Springer-Verlag, Berlin, 1994

Extended x-ray absorption fine structure—its strengths and limitations as a structural tool
P. A. Lee, P. H. Citrin, P. Eisenberger, and B. M. Kincaid
Rev. Mod. Phys. 53, 769 – Published 1 October 1981

Кочубей Д.И., Бабанов Ю.А., Замараев К.И. и др. EXAFS-спектроскопия. Новосибирск: Наука, 1988. 306 с.

Interaction cross sections

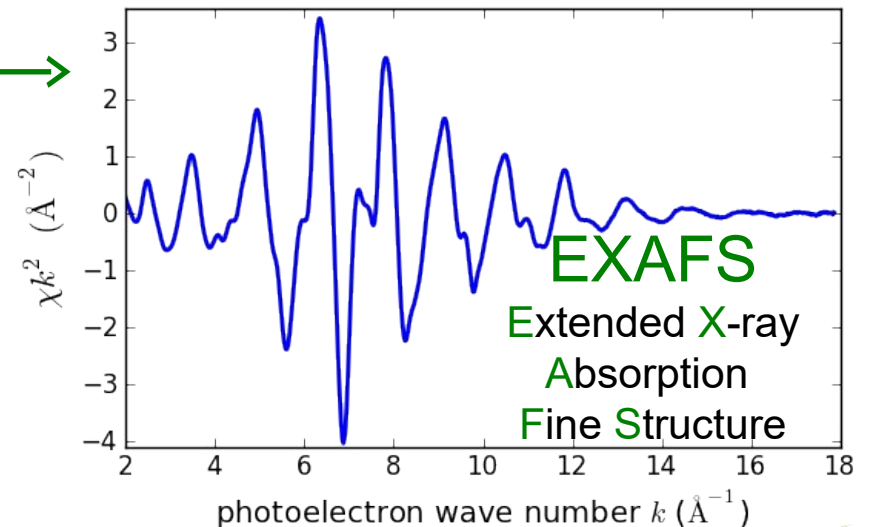
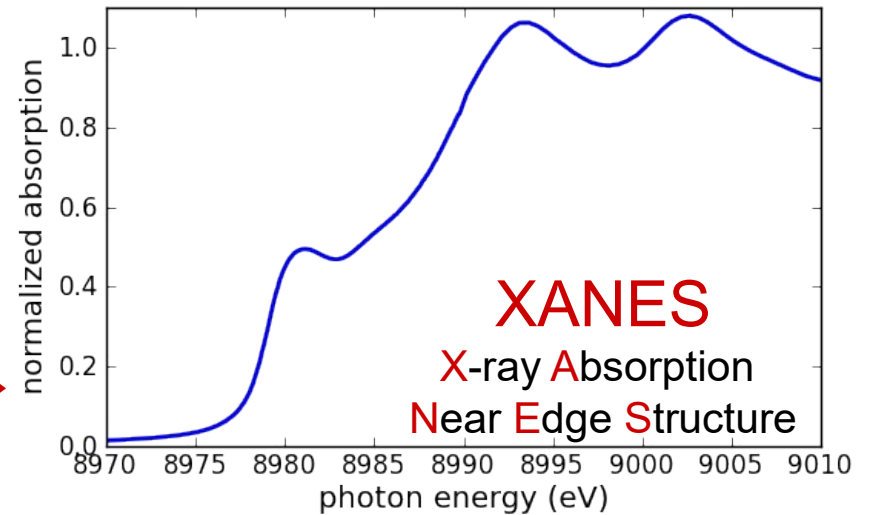
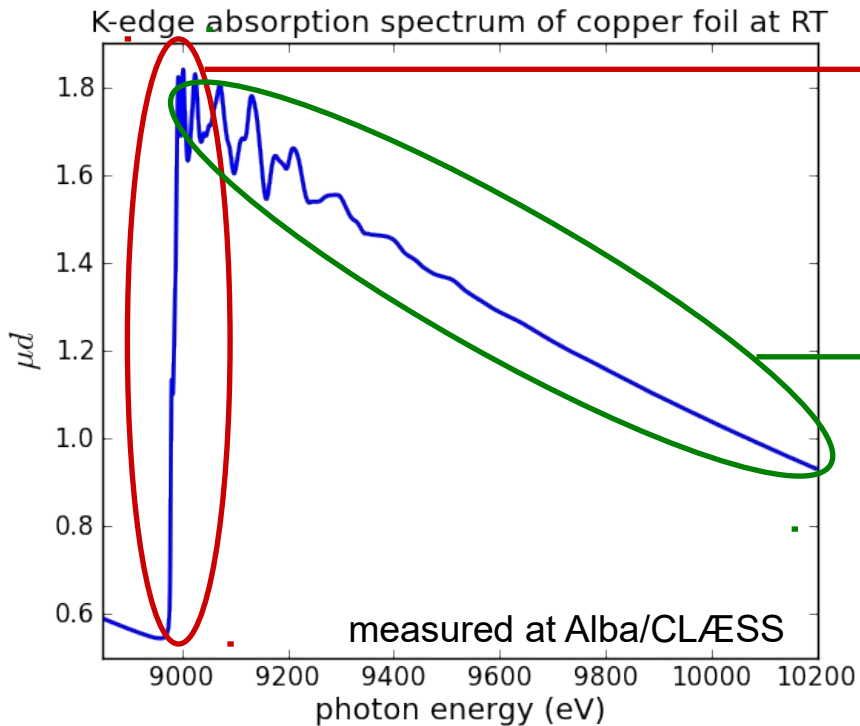
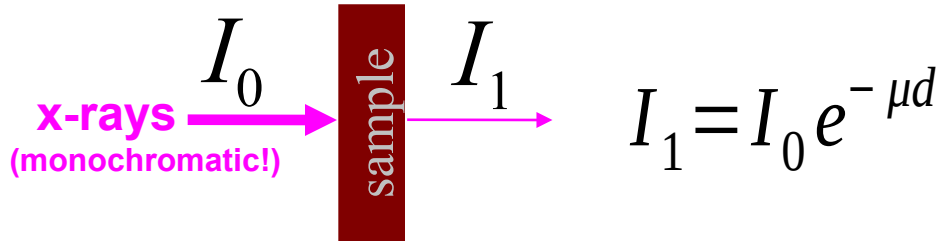
data from physics.nist.gov/PhysRefData/Xcom/Text/XCOM.html



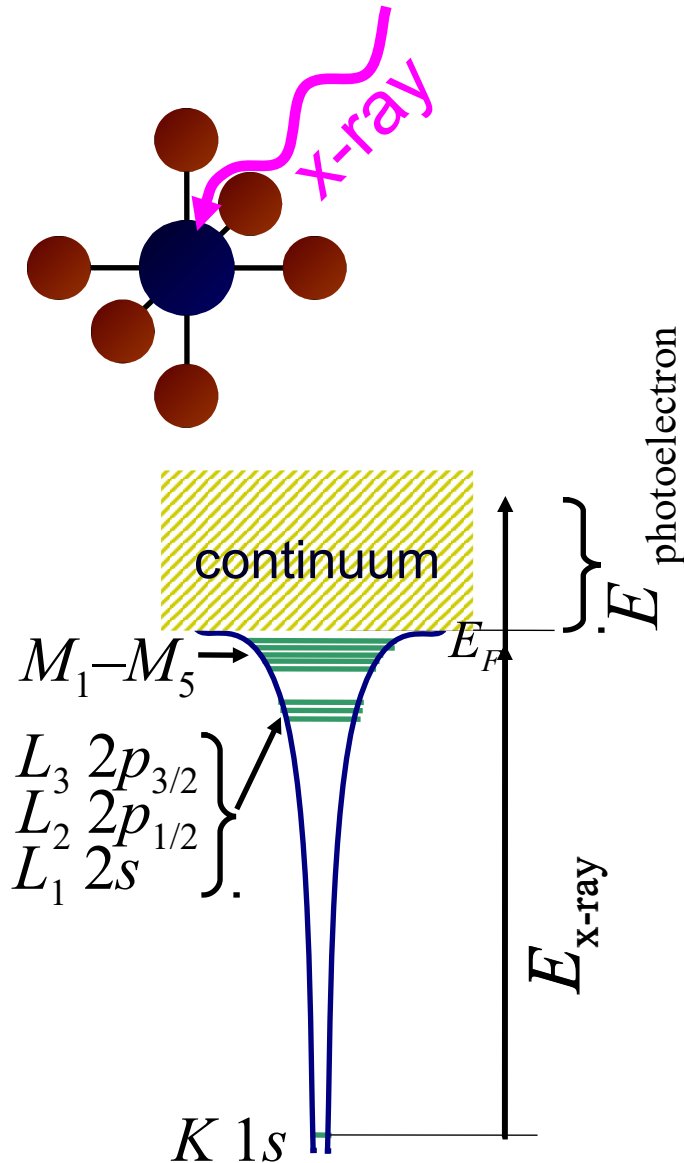
- Two principal channels: absorption and scattering. The cross sections are Z- and energy-dependent.
- **Photoelectric process** is the most probable in the synchrotron energy range (the range of the Balder@MAX-IV beamline is marked by green).
- The shown cross-sections are for a single atom. The *collective* effects, like Bragg peaks, can be more intense.

X-ray Absorption Spectra

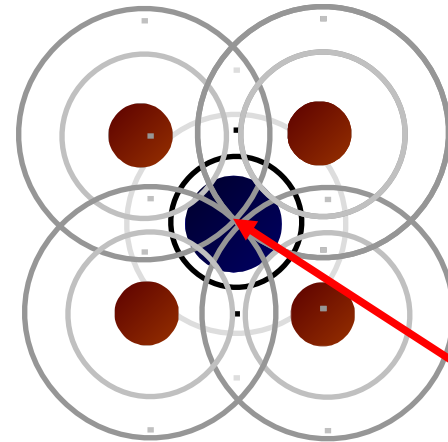
transmission experiment



Qualitative Picture of XAFS

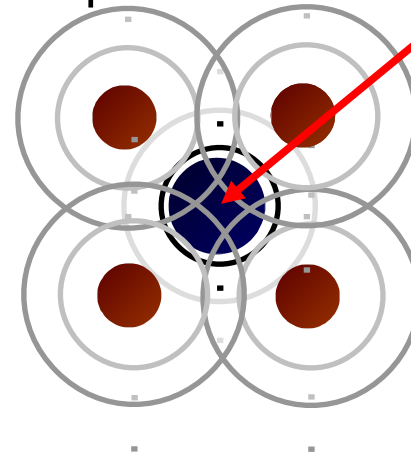


constructive interference –
absorption maximum



Here is where
the interference
is important!

destructive interference –
absorption minimum



Theoretical Description

Fermi's Golden Rule
in one-electron approximation:

$$\sigma(E) \propto \sum_f^{E_f > E_F} |\langle f | H_{\text{int}} | i \rangle|^2 \delta(E - E_f + E_i)$$

- $|i\rangle$ is an initial deep core state (e.g. $|1s\rangle = 2Z^{3/2}e^{-Zr}/\sqrt{4\pi}$): strongly localized.
 - $\langle f|$ is an *unoccupied* state in the presence of a core hole [a collective response of the other electrons which is effectively described as a single particle of a positive charge called 'hole'],
 - H_{int} is the electron transition operator:
 - $H_{\text{int}} = \mathbf{p} \cdot \mathbf{A}(\mathbf{r})$;
 - The photon is taken to be a classical wave: $\mathbf{A}(\mathbf{r}) = eA_0 e^{i\mathbf{k} \cdot \mathbf{r}}$:
 - For deep-core excitations $e^{i\mathbf{k} \cdot \mathbf{r}} \approx 1$ (dipole approximation) because r is small due to the strong localization of the initial state
 - The next term $+i\mathbf{k} \cdot \mathbf{r}$ (quadrupole approximation) is $\sim Z/(2 \cdot 137)$ times weaker, and for heavy elements like Pb, Au, Pt is not negligible (but anyway is normally neglected)
 - equivalent representations: momentum form $\mathbf{p} \cdot \mathbf{e}$ and position form $(\hbar\omega/m)\mathbf{r} \cdot \mathbf{e}$.
- For example, consider a photon propagating along z with $\mathbf{e}||x$ and its K-absorption: Then $\mathbf{r} \cdot \mathbf{e} = x = r \sin\theta \cos\phi \propto Y_1^{\pm 1}(\theta, \phi)$ and $\sigma(E) \propto |\langle f | Y_1^{\pm 1} Y_0^0 \rangle d\Omega|^2$.
- Hence for K absorption the final states $\langle f|$ can only be of $Y_1^{\pm 1}$ (i.e. p) symmetry (in general, $\Delta l = \pm 1$).

Theoretical Description

In the MS theory, the expression for μ can be factored in terms of an atomic background μ_0 and the oscillatory part χ

$$\mu = \mu_0(1 + \chi)$$

In the photoelectron momentum space,
 $k = [2m/\hbar^2(E - E_F)]^{1/2}$,
the χ function is parameterized as:

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

For each coordination shell j :

R_j , N_j , σ_j^2 are the sought distance, coord. number and variance of distance

$f_j(k) = |f_j(k)| e^{i\phi_j(k)}$ is the scattering amplitude (calculated),

λ is the electron free path (calculated),

S_0^2 accounts for many-electron excitations.

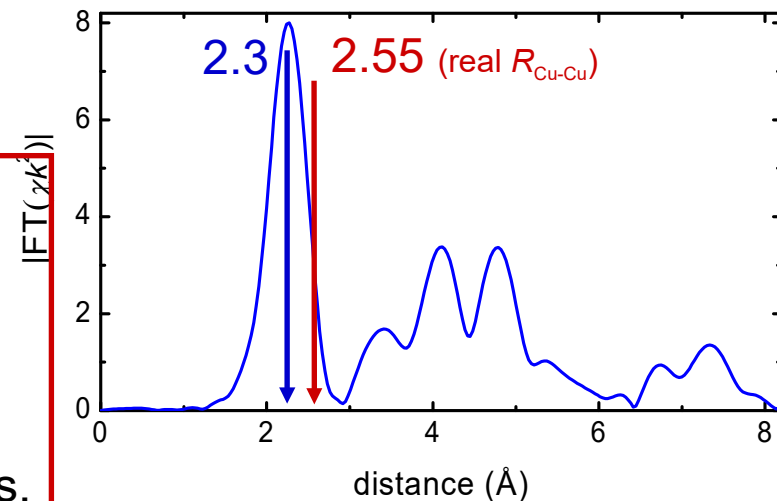
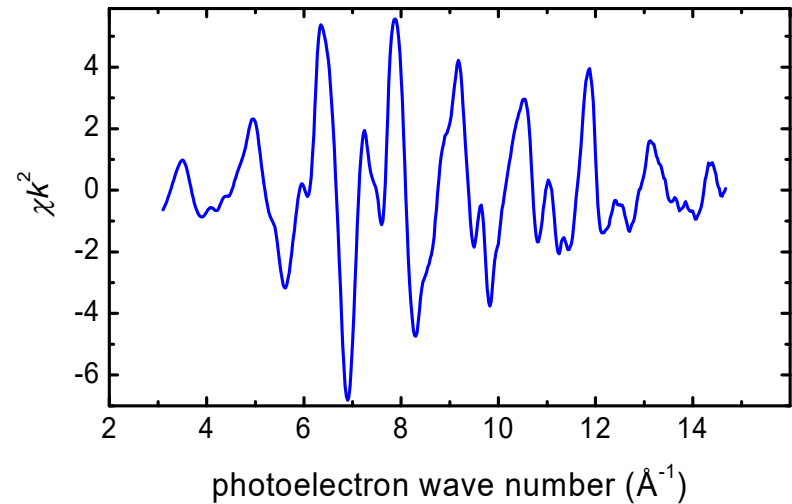
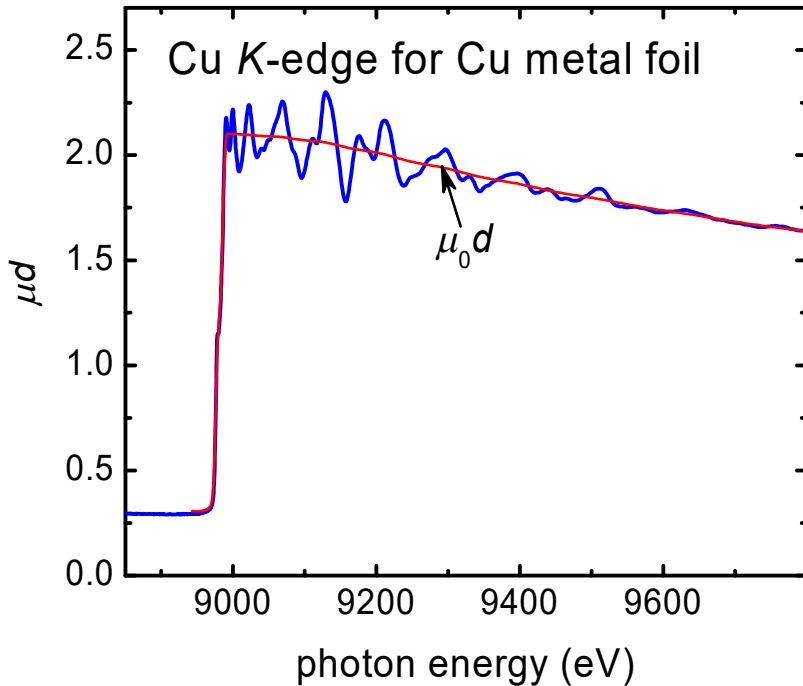
The present theory cannot give reliable μ_0 .

- For XANES region this is a problem, because μ_0 there is a rapidly changing function with features comparable with χ .
- In EXAFS region μ_0 is a smooth function and can be constructed empirically.

Thus, XANES spectra are mostly *interpreted*, not analyzed.
EXAFS spectra can be analyzed quantitatively.

Importance of EXAFS phases

$$\mu = \mu_0(1 + \chi), \quad \chi(k) = S_0^2 \sum_j N_j \frac{|f_j(k)|}{kR_j^2} \sin(2kR_j + \phi_j(k)) e^{-2R_j/\lambda(k)} e^{-2\sigma^2 k^2}$$



Unpleasant thing about EXAFS:
 FT positions are shifted towards small distances.
 More unpleasant: Each FT peak has its own shift.
 Because of the phase shifts, extracting the
 structural information from EXAFS requires
 curve fitting with assumed (calculated) phase shifts.

EXAFS amplitudes and phases

<http://feffproject.org/>

The FEFF9 code

Home » Codes » The FEFF9 code

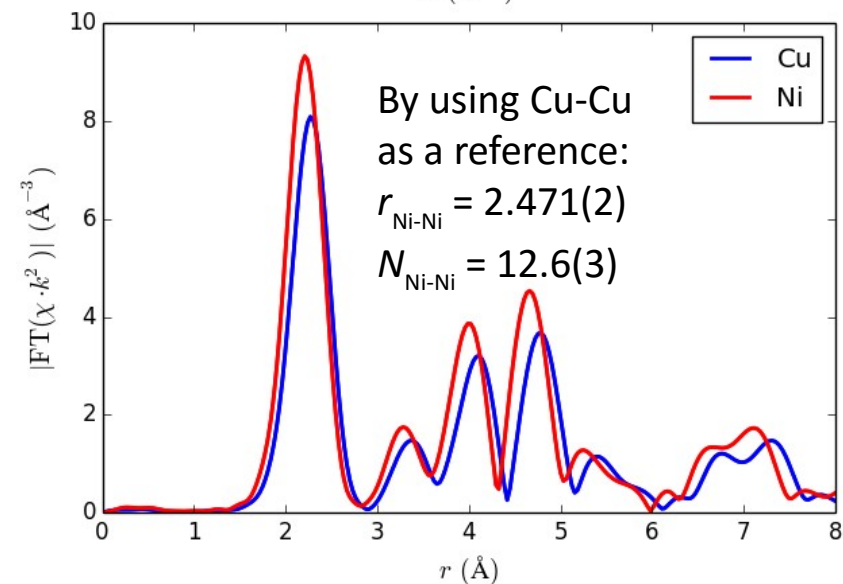
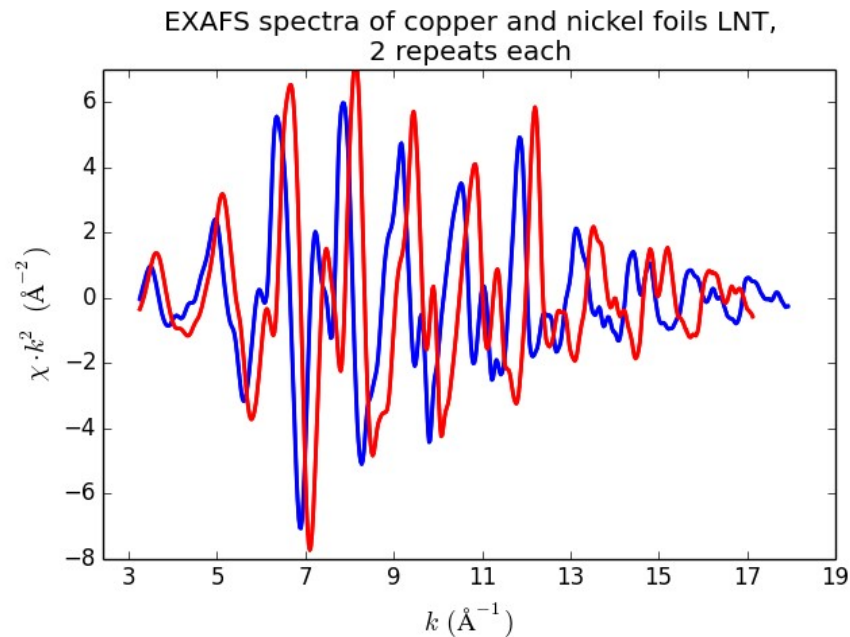
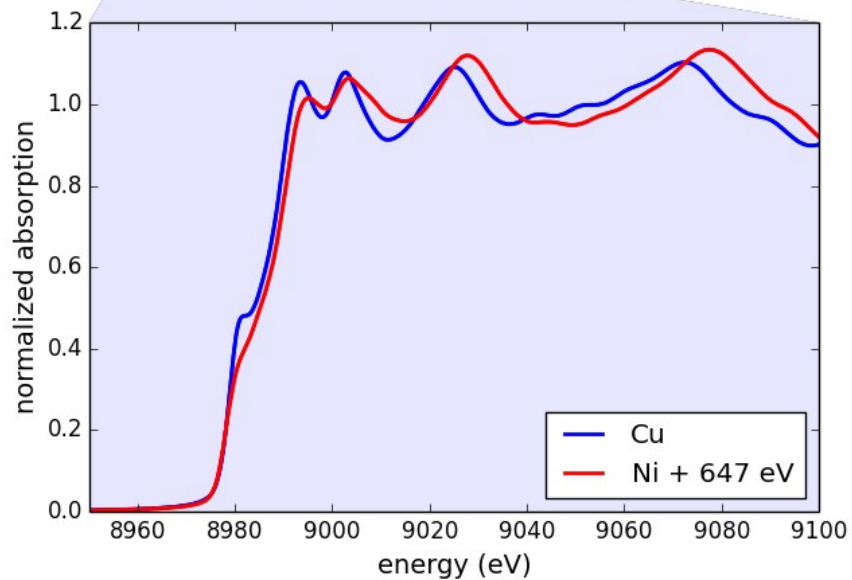
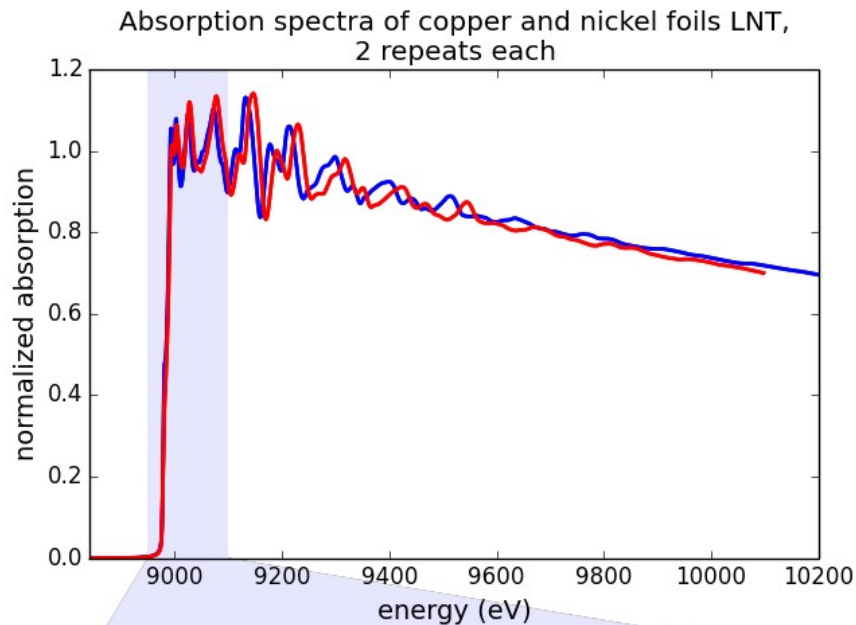
Search

Overview Documentation Download Order Troubleshooting XAFS Data Analysis

The screenshot displays the FEFF9 software interface. It includes a terminal window showing the execution of the FEFF 9.5.1 code for the compound ThomsonV(Bismutator)Bismut(Dihydrate). A plot window shows the EXAFS amplitude $k^3 \chi(k)$ versus k (Å⁻¹), with a peak at approximately 1.704 Å⁻¹. A 3D ball-and-stick model of the bismuth atom's coordination environment is shown. A parameter adjustment window for the EXCHANGE interaction is visible, with parameters like μ_{exch} and μ_{corehole} set to 0.0. An 'Atom Data Editor' window displays a table of atomic parameters:

Atom	Z	Site	Occupancy	Atom 1	Atom 2	Atom 3	Atom 4	Atom 5	Atom 6
1	80	Tb	1	1	1	1	1	1	1
2	8	O	1	1	1	1	1	1	1
3	6	C	1	1	1	1	1	1	1

Spectra of similar structures



What can we learn from XANES: a) Pre-edge Peak

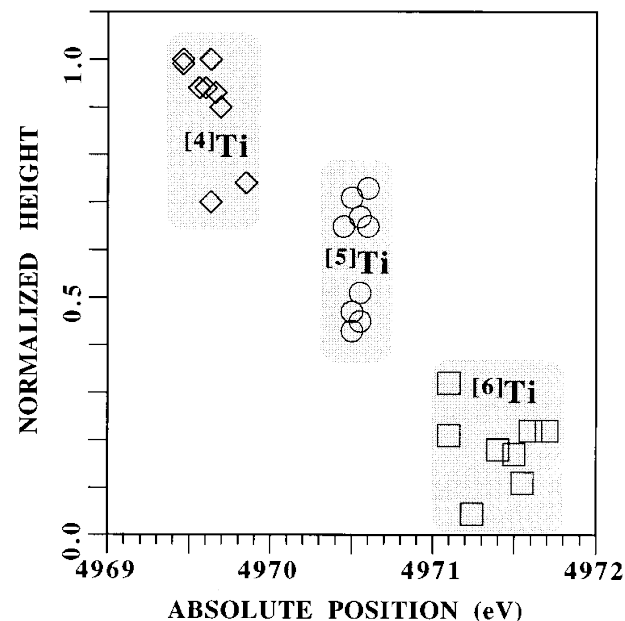
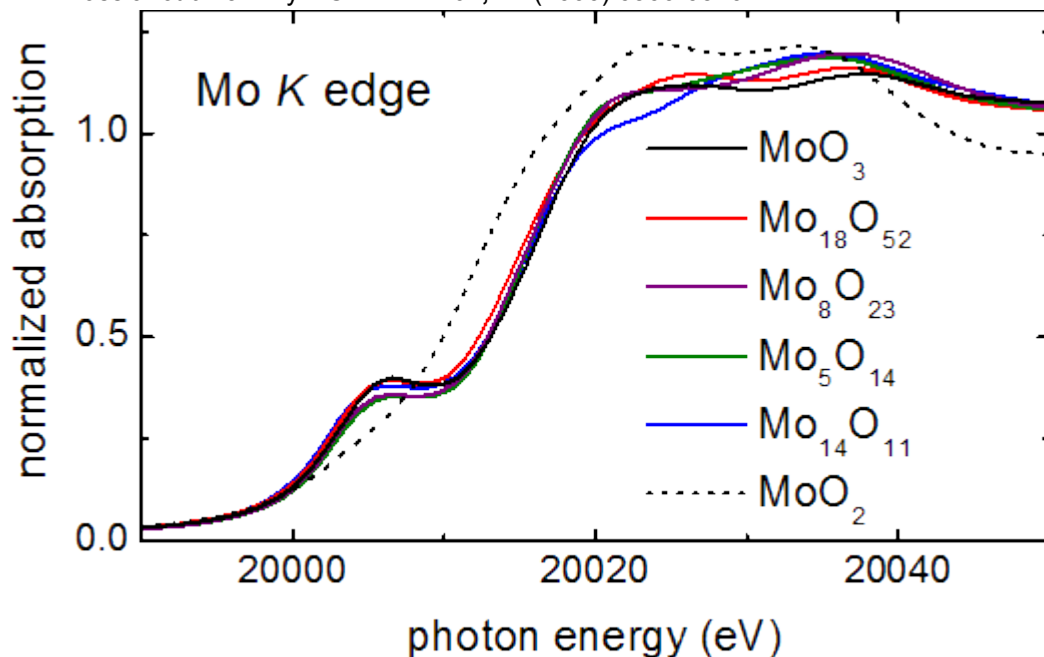
Dipole selection rule (only in central-symmetric case!): $\Delta l = \pm 1$

Consider K -absorption for transition metals:

- initial state = $1s$ ($l=0$)
- states near E_F are formed by nd electrons ($l=2$)

central-symmetry	non-central symmetry
no resonance	resonance (pre-edge peak)

T. Ressler et al. J. Phys. Chem. B **104**, 27 (2000) 6360-6370

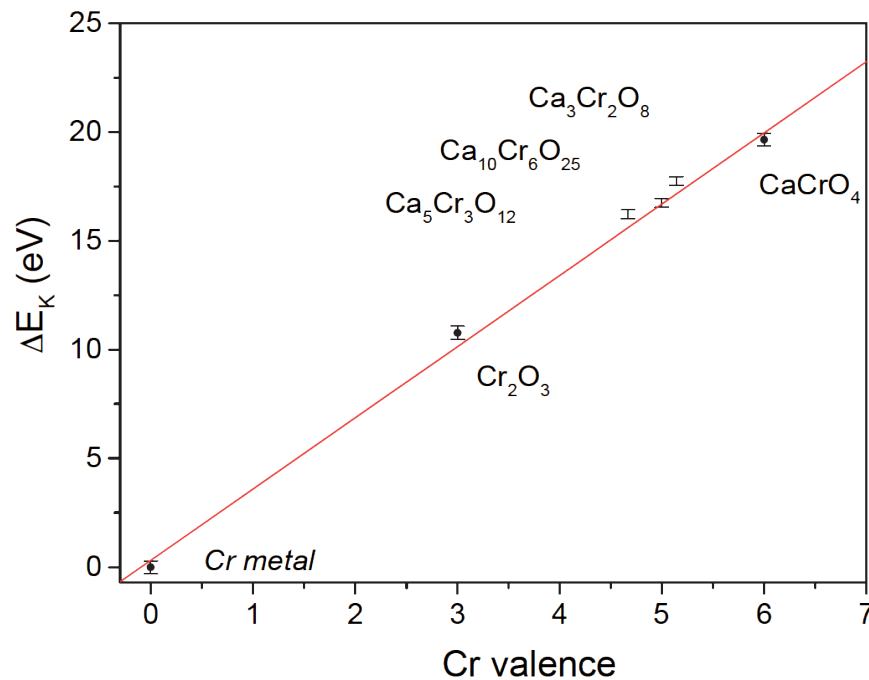
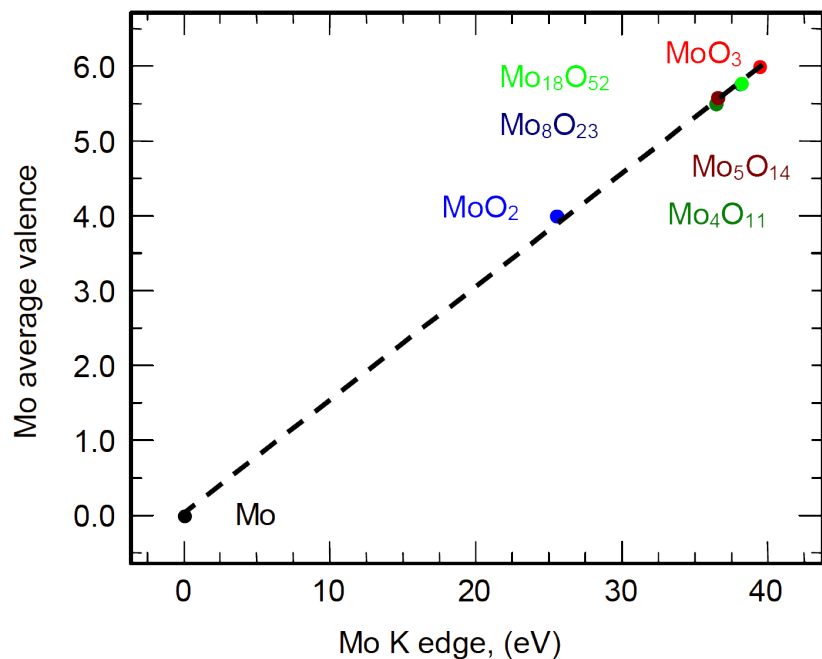


from [F. Farges, G. E. Brown, J. J. Rehr, Phys. Rev. B **56** (1997) 1809]

What can we learn from XANES: b) Edge Shift

T. Ressler, R. E. Jentoft, J. Wienold, M. M. Günter and O. Timpe:
J. Phys. Chem. B **104**, **27** (2000) 6360-6370

I. Arčon, B. Mirtič, A. Kodre,
J. Am. Ceram. Soc. **81** (1998) 222–224



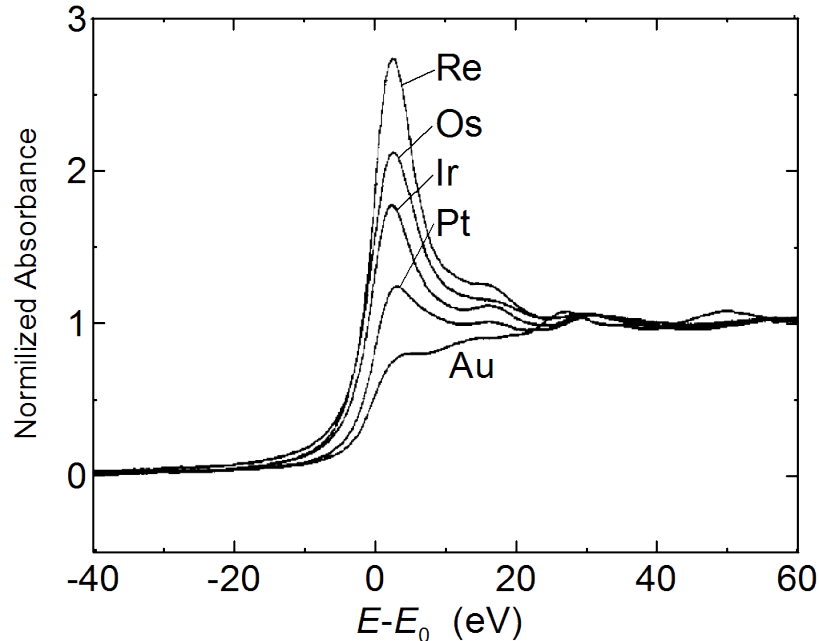
Why does it shift?

- 1) Electrostatic: it is harder for the photoelectron to leave a positive (oxidized) atom
- 2) Shorter bonds at higher oxidation states \Rightarrow Fermi energy is higher

What we can learn from XANES: c) White Line

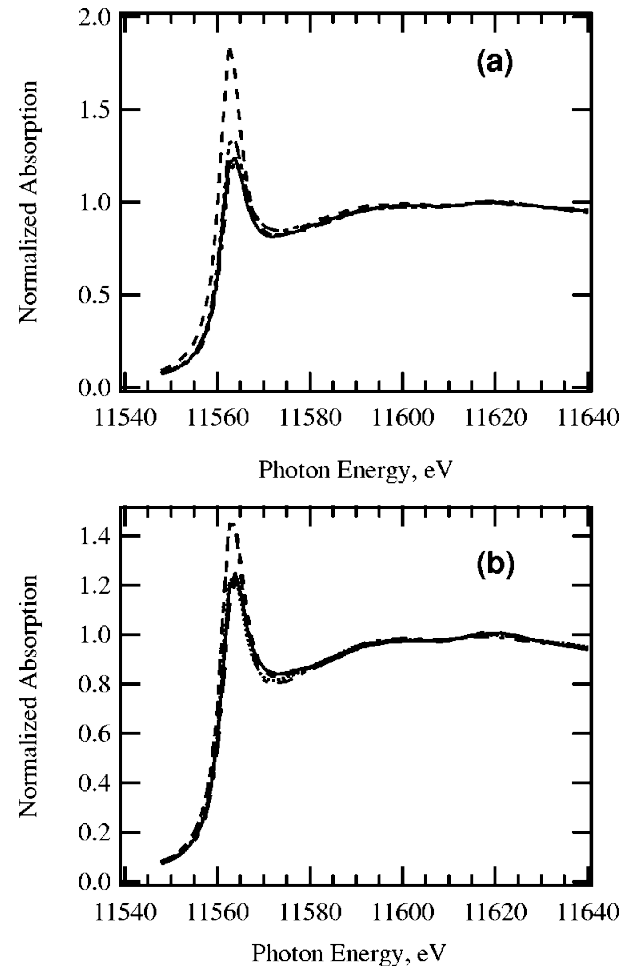
L_3 absorption edges for $5d$ metals:
(transition $2p_{3/2} \rightarrow 5d$)

G. Meitzner, G. H. Via, F. W. Lytle, and J. H. Sinfelt,
J. Phys. Chem. **96** (1992) 4960



Intensity is proportional to the number of free $5d$ states and also depends on valence state. But...

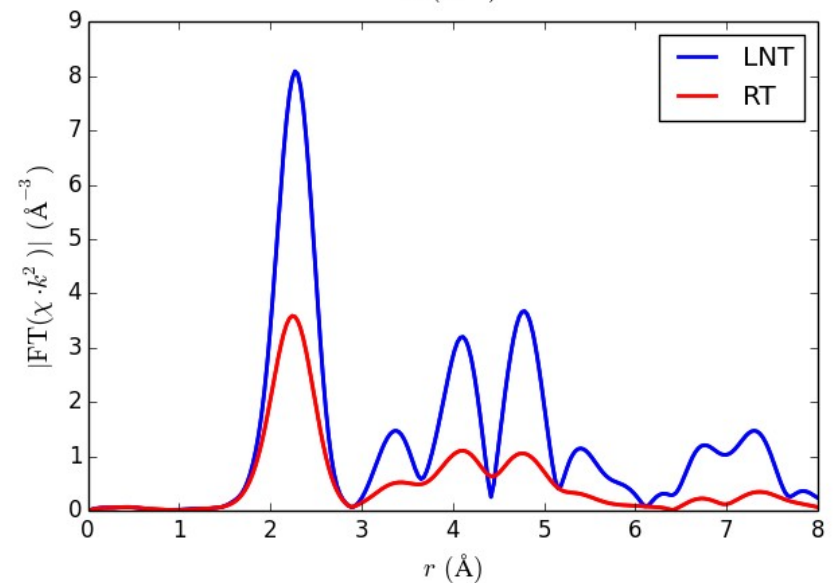
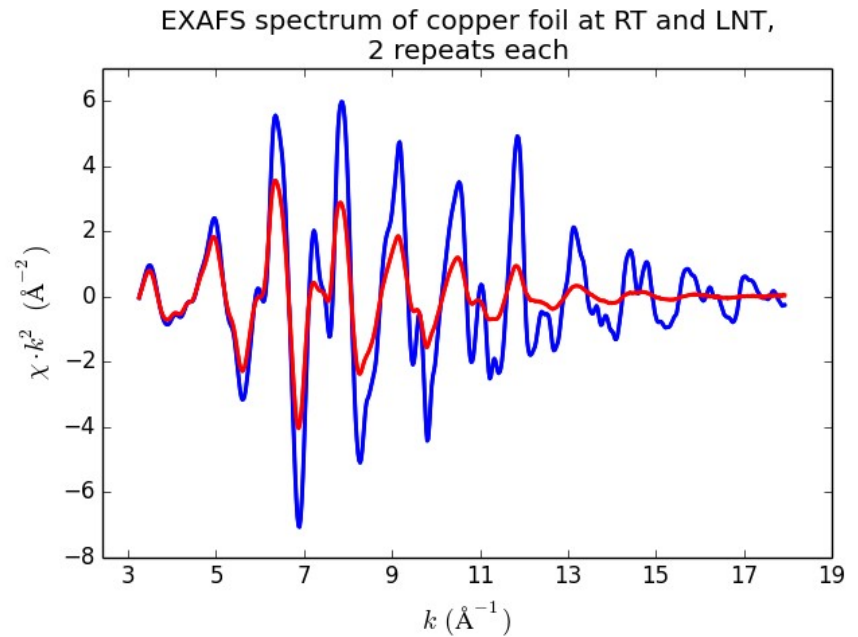
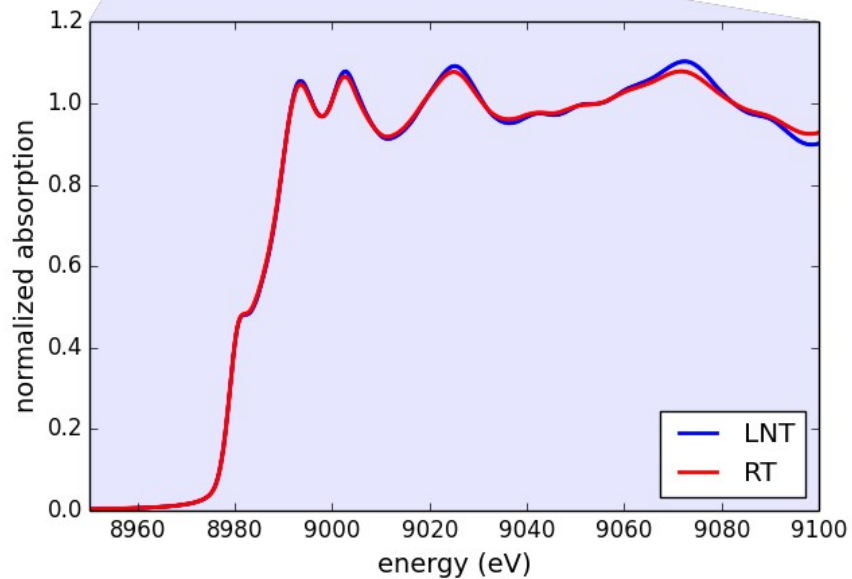
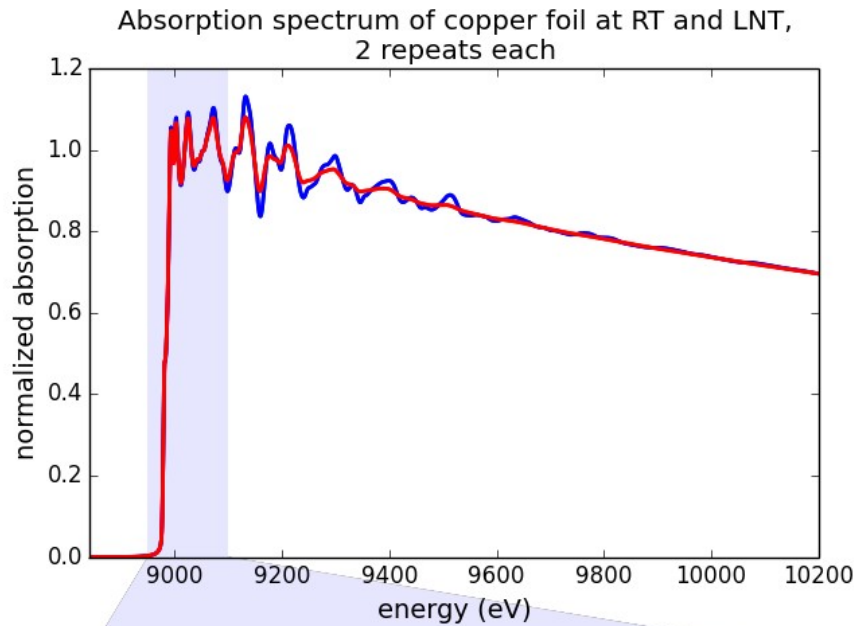
...white line also depends on particle size and morphology:



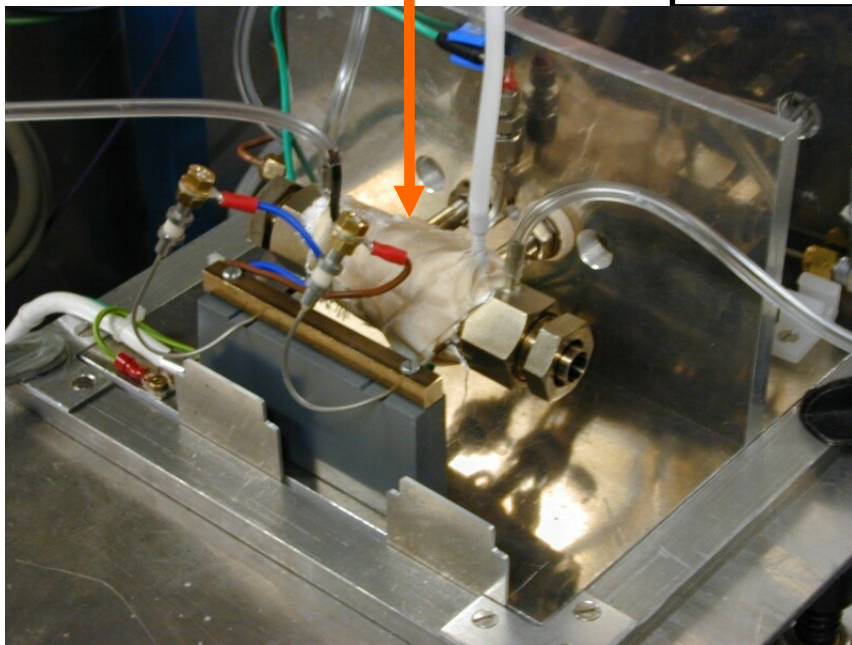
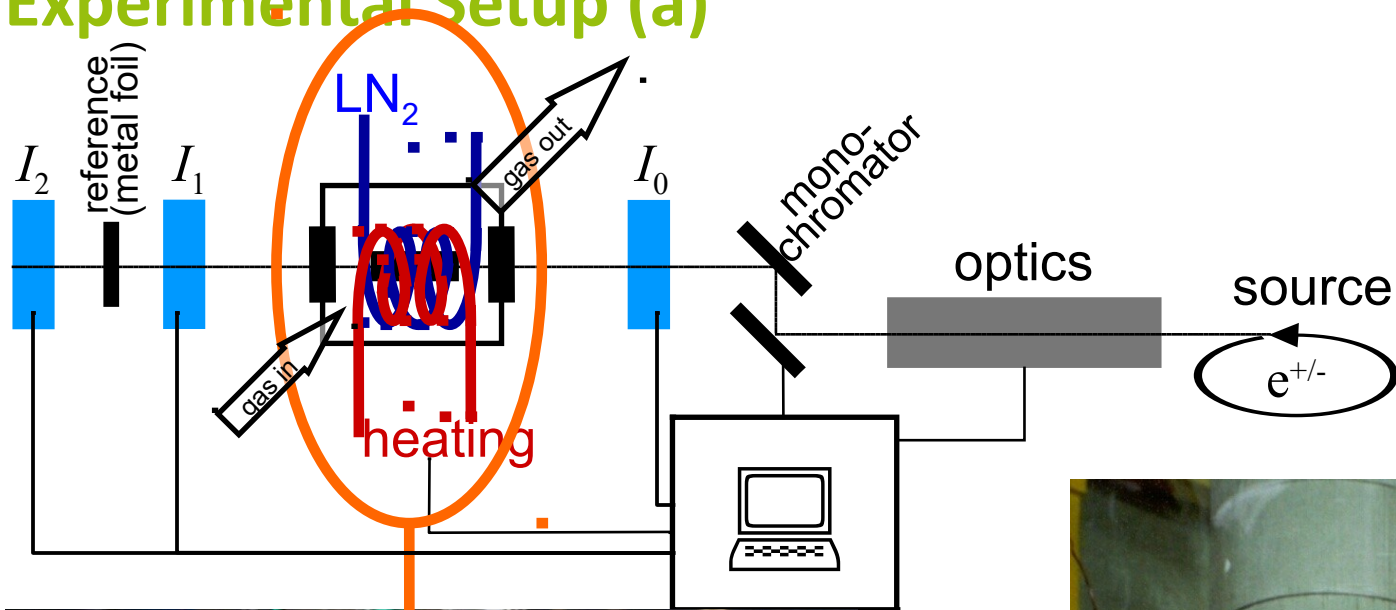
a) Pt₃ triangle (dashes), Pt₄ tetrahedron (solid), Pt₅ triangular bipyramid (dash-dot), and Pt₆ octahedron (dash-dot-dot);
(b) Pt₇ and Pt₄ clusters of different shape: planar "honeycomb" (dashes), D5h bipyramid (solid), single-capped octahedron (long dash-dot), Pt₄ tetrahedron (dots), and Pt₄ planar rhombus (dash-dot).

from A. L. Ankudinov, J. J. Rehr, J. J. Low, and S. R. Bare, J. Chem. Phys. **116** (2002) 1911

XAS spectra at various T



Experimental Setup (a)



Experimental Setup (b)



Example: Application of EXAFS to Pd,Pt/C Catalysts (a)

Supported noble metal catalysts are used in a number of commercial chemical processes (Pd,Pt/C → toluene and benzene hydrogenation).

Pd,Pt/C catalyst

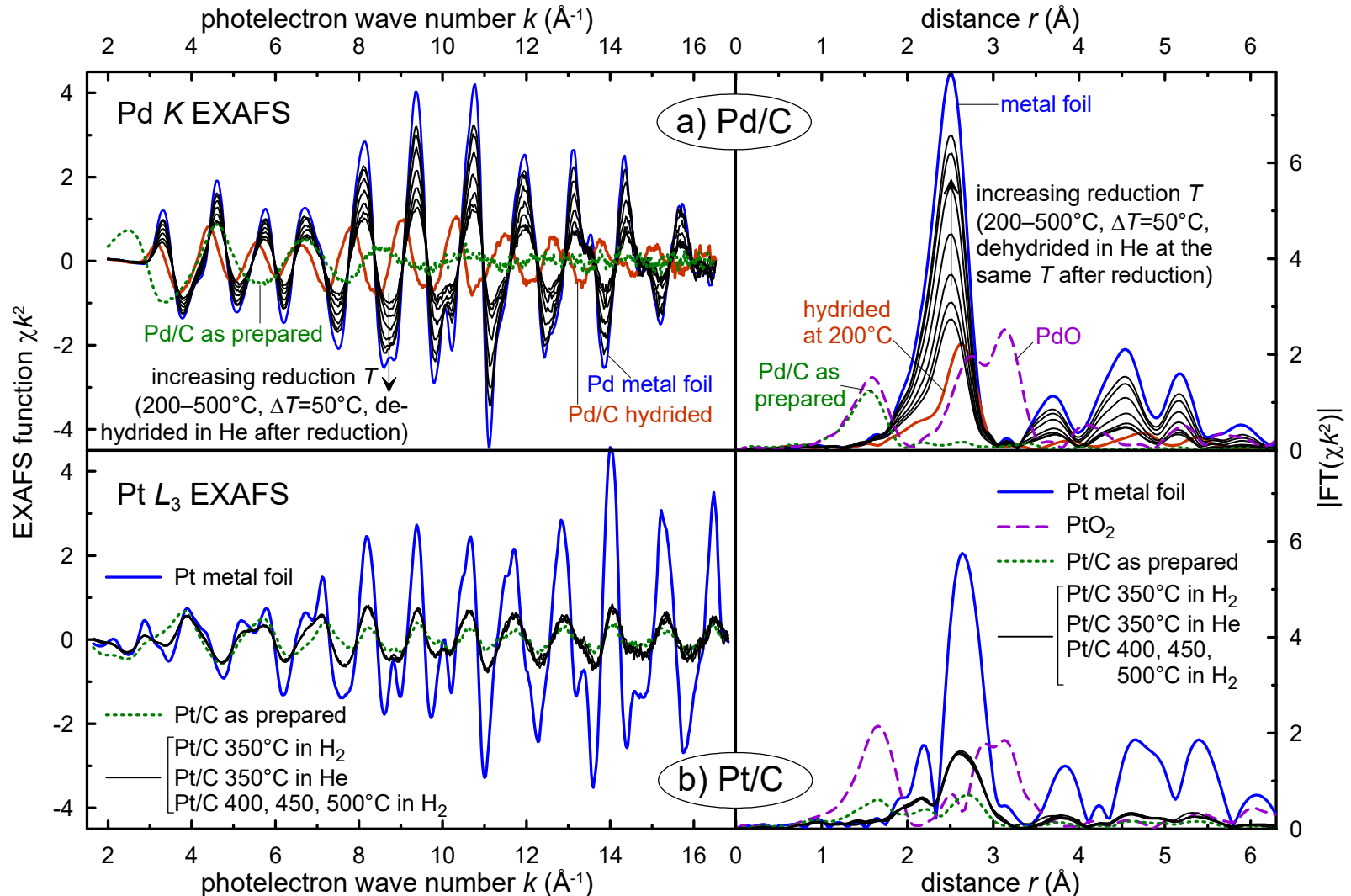
- **Support:** graphite-like carbon (sibunit)
- **Preparation:** mild oxidative treatment of the support followed by ion exchange with Pd or Pt amine complexes
- **Characterization:** XPS, TPR, catalytic studies
- **Outcome:** highly dispersed metal clusters with ~1.1 wt% of Pd and ~0.9 wt% of Pt

XAFS measurements

- X1 beamline at Hasylab/DESY with a Si 311 double crystal monochromator, transmission mode
- Samples: non-pressed powders

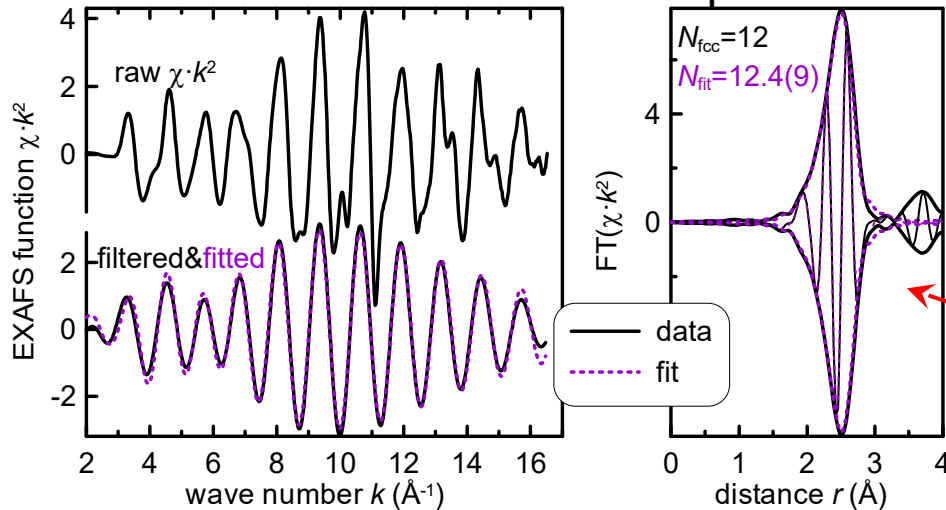
Example: Application of EXAFS to Pd,Pt/C Catalysts (b)

Reduction treatment: in 5% H_2 /He atmosphere, stepwise with $\Delta T=50^\circ C$. Measurements at LN₂ temperature in order not to have interference of two effects: (i) due to different temperature vibrations and (ii) due to different particle sizes.



Example: Application of EXAFS to Pd,Pt/C Catalysts (c)

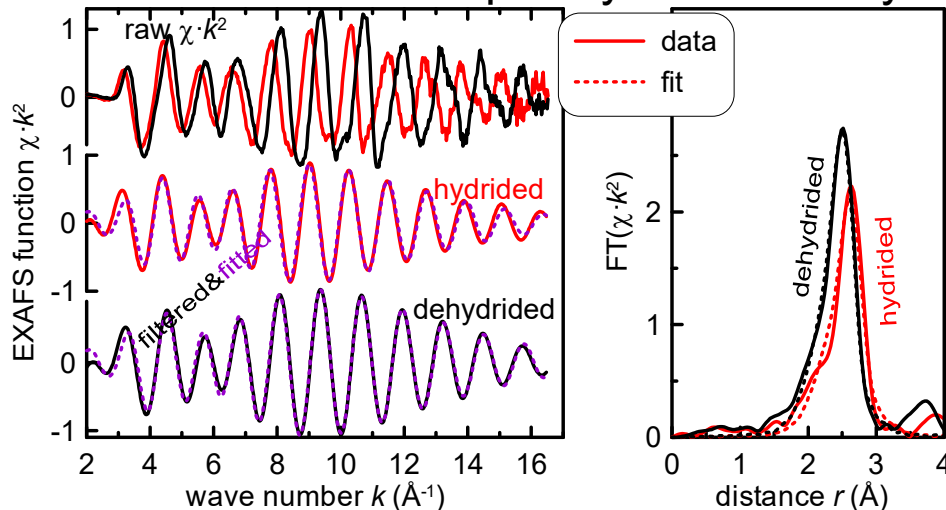
Reference compound: metallic Pd foil



EXAFS results for Pd metal (measured at LN₂ temperature)
 Path r (Å) r_{cryst} ^a (Å) CN CN_{cryst} σ^2 (10⁻³ Å²) ΔE (eV)
 Pd-Pd 2.742(4) 2.751 12.4(9) 12 3.4(5) 6.2(7)
^a at room temperature [Kittel]

Checking your amplitudes and phases with reference spectra must be always the first step in every EXAFS study!

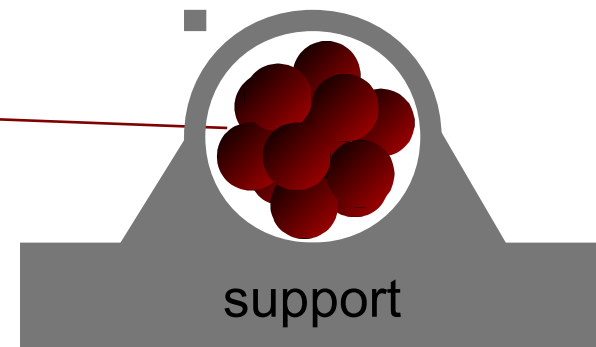
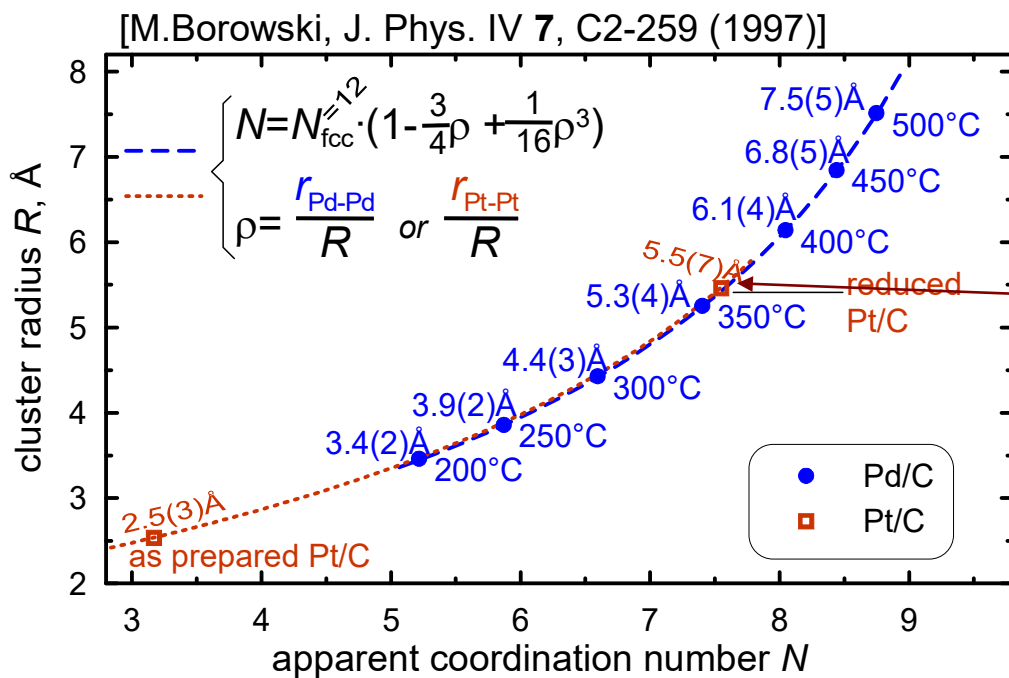
The difference between a simply reduced Pd/C sample (hydrated) and one subsequently blown out by He flow (dehydrated)



EXAFS results for Pd/C sample during the reduction process

reduction temperature, °C	Path	r (Å)	CN	σ^2 (10 ⁻³ Å ²)	ΔE (eV)
200, hydrated	Pd-Pd	2.83(1)	5.5(8)	6(1)	6(1)
200, dehydrated	Pd-Pd	2.733(6)	5.2(5)	4.4(7)	5.3(7)
250, dehydrated	Pd-Pd	2.732(6)	5.9(5)	4.5(6)	5.4(7)
300, dehydrated	Pd-Pd	2.733(5)	6.6(6)	4.2(6)	5.5(7)
350, dehydrated	Pd-Pd	2.735(5)	7.4(6)	3.8(9)	5.5(7)
400, dehydrated	Pd-Pd	2.738(4)	8.0(6)	3.2(5)	5.7(7)
450, dehydrated	Pd-Pd	2.740(4)	8.4(6)	2.9(4)	6.0(7)
500, dehydrated	Pd-Pd	2.742(8)	8.7(6)	2.8(7)	6.2(7)

Example: Application of EXAFS to Pd,Pt/C Catalysts (d)



Catalytic properties:

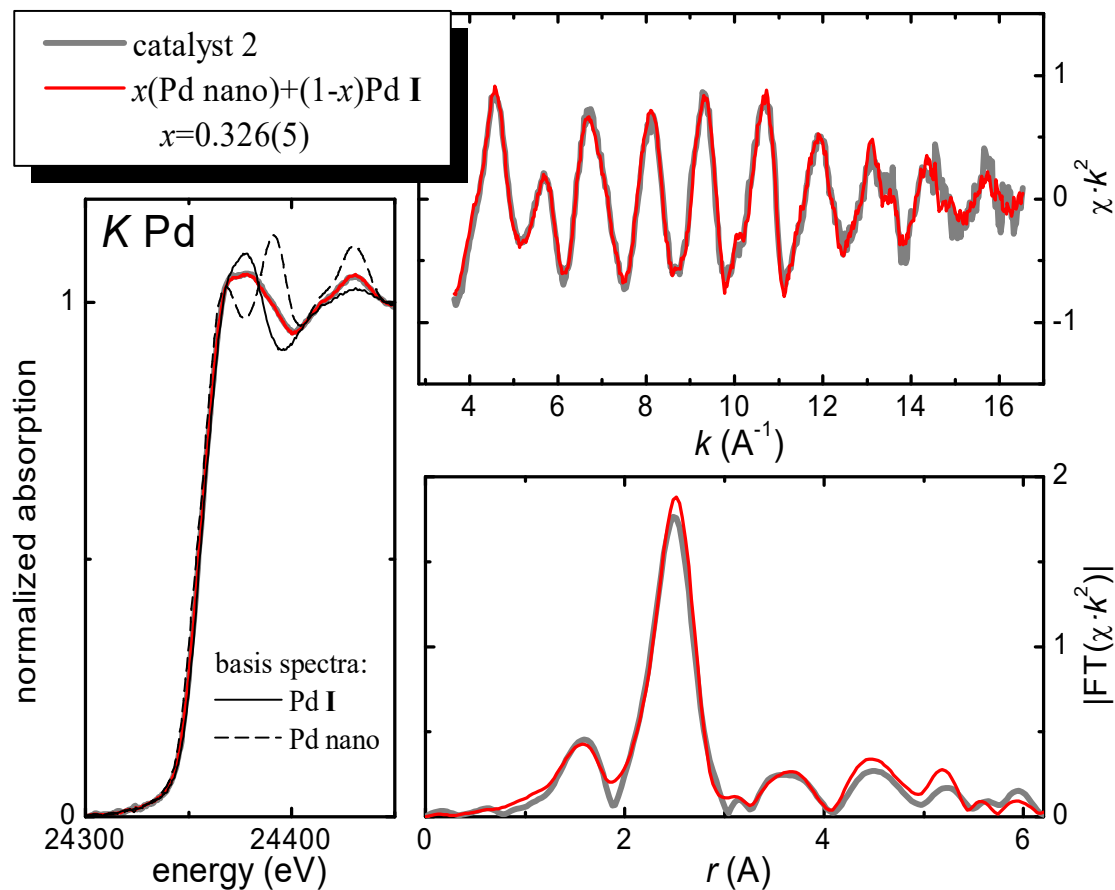
- The catalytic activity in toluene and benzene hydrogenation was found to exceed the activity of conventional Pd/Al₂O₃ and Pt/Al₂O₃ fourfold for Pd/C and almost ten-fold for Pt/C.
- If the reduction temperature exceeds 350°C the activity of both catalysts sharply decreases.

The EXAFS study made it possible to exclude intense metal sintering, or Pd carbide formation as possible reasons of the activity drop.

Stakheev et al., *Russ.Chem.Bull.Int.Ed.* **53** (2004) 528

Linear combination of spectra

1. *Basis spectra*: precursor (Pd I) and metallic Pd particles.
2. The spectrum “catalyst 2” shows coincidence with its *target transformation*.
3. Linear combination fitting of **XANES** of “catalyst 2” by the two basis spectra.
4. The found linear combination is then successfully applied to **EXAFS**.

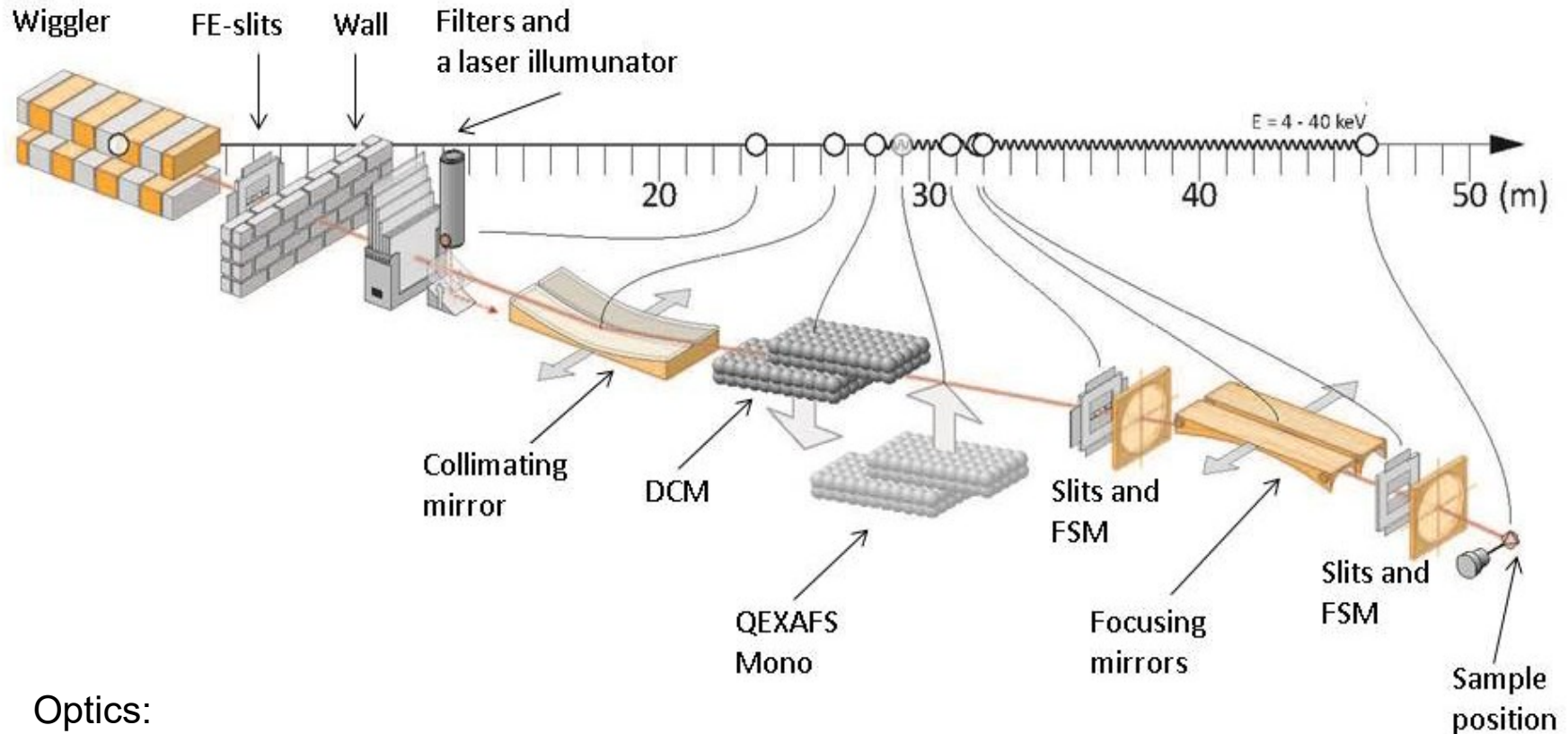


Palladium Nanoparticles immobilized on Mesoporous Silica Support – New Efficient Catalysts for Aerobic Alcohol Oxidation in Supercritical Carbon Dioxide
Z. Hou et al., *J. of Catalysis* **258** (2008) 315

In detail 1. Optics

What you need to know about x-ray optics

Balder beamline at MAX IV: optics



Optics:

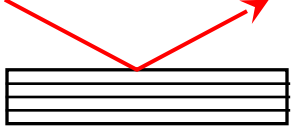
- In vacuum wiggler, 10^{13} photons/s, energy range 2.4 –... keV
- Focusing down to $100 \times 100 \mu\text{m}^2$
- Fast scans: full EXAFS up to sub-second repetition
- Fixed-exit *double mirror* setup. Two equal toroidal focusing mirrors (different coating). Fast change of energy range, focusing/defocusing

Quick acquisition and quick alignment/adjustment → high throughput

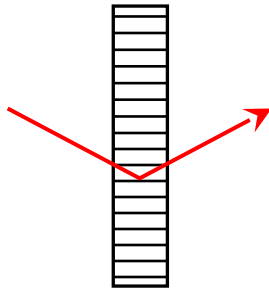
Harmonics in monochromator

Usual geometries

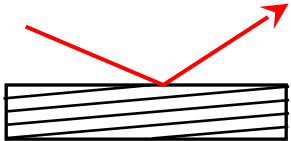
symmetric Bragg



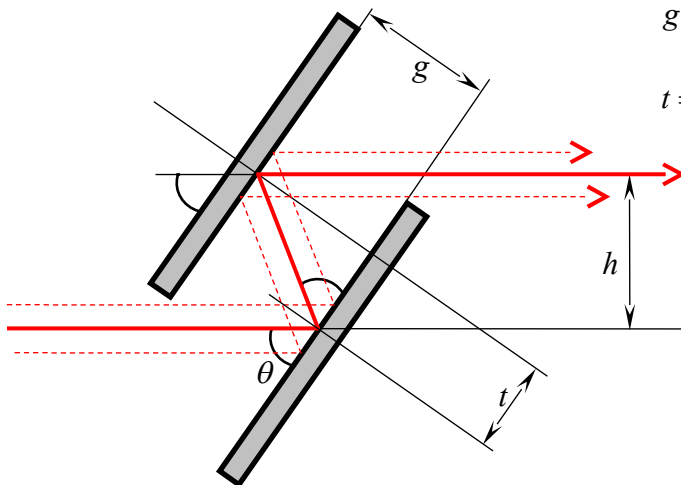
symmetric Laue



asymmetric Bragg



Fixed exit DCM

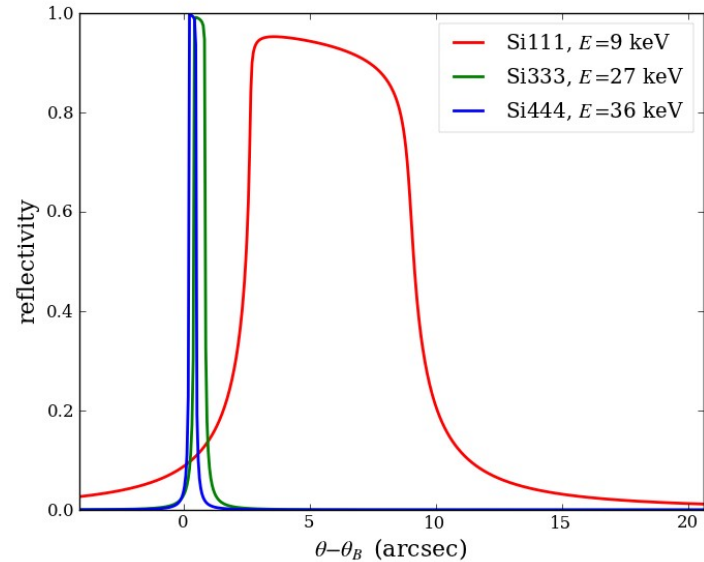


$$g = \frac{h}{2 \cos \theta}$$

$$t = \frac{h}{2 \sin \theta}$$

Rocking curves

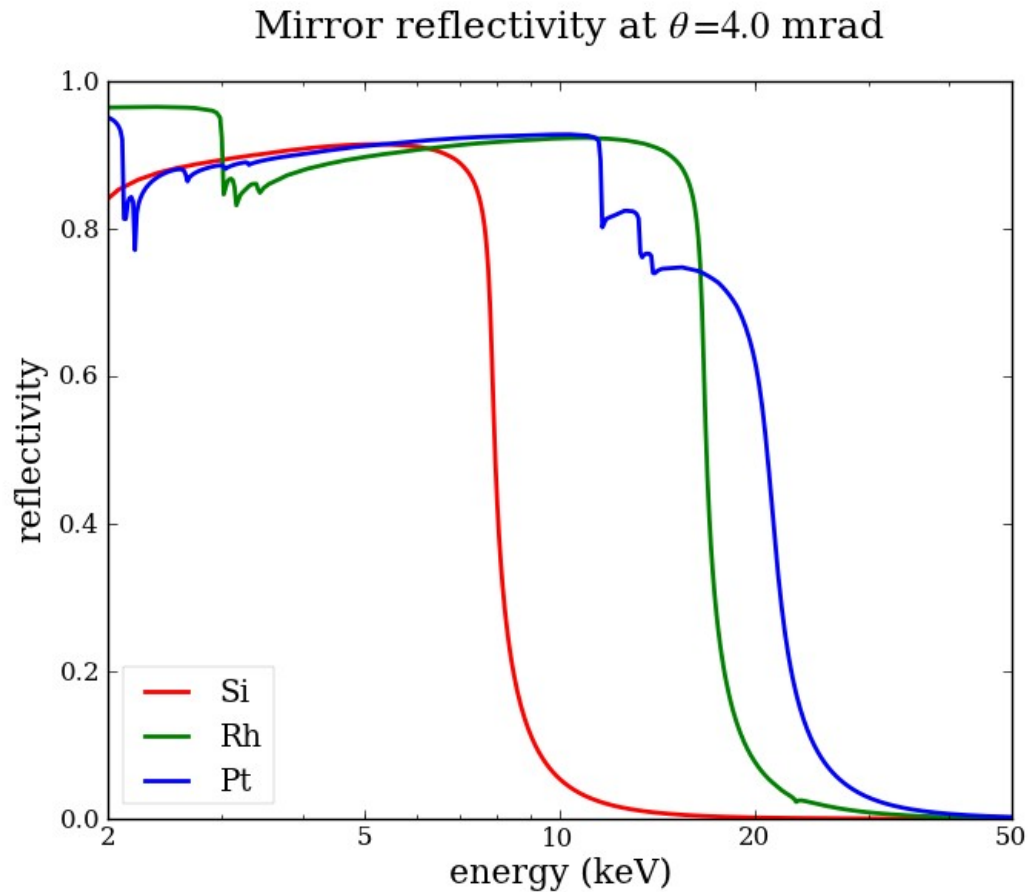
Rocking curves at $\theta_B = 12.690^\circ$



Not only the fundamental energy is passed through a monochromator but also high harmonics.

Harmonics can be suppressed by detuning

Mirror reflectivity



With appropriate mirrors (coatings) at appropriate incidence angles the harmonics can be suppressed due to reflectivity properties.

Importance of harmonics

Consider a transmission experiment with two ionization chambers. Their signals i_0 and i_1 give the absorption coefficient: $\mu d = \ln[i_0/i_1]$.

i_0 and i_1 are strongly correlated. You can check this if you take i_0 and i_1 from *different* repetitions of the same scan; the resulted μd would be much noisier. Therefore it is important to always keep the two signals in the ratio.

Let the beam be contaminated by some harmonics. The experimental absorption is then $\mu d = \ln[(i_0+h_0)/(i_1+h_1)]$ and the fluctuations in i_0 and i_1 do not cancel and thus the spectrum is noisier.

In summary, in the presence of harmonics the absorption coefficient μd :

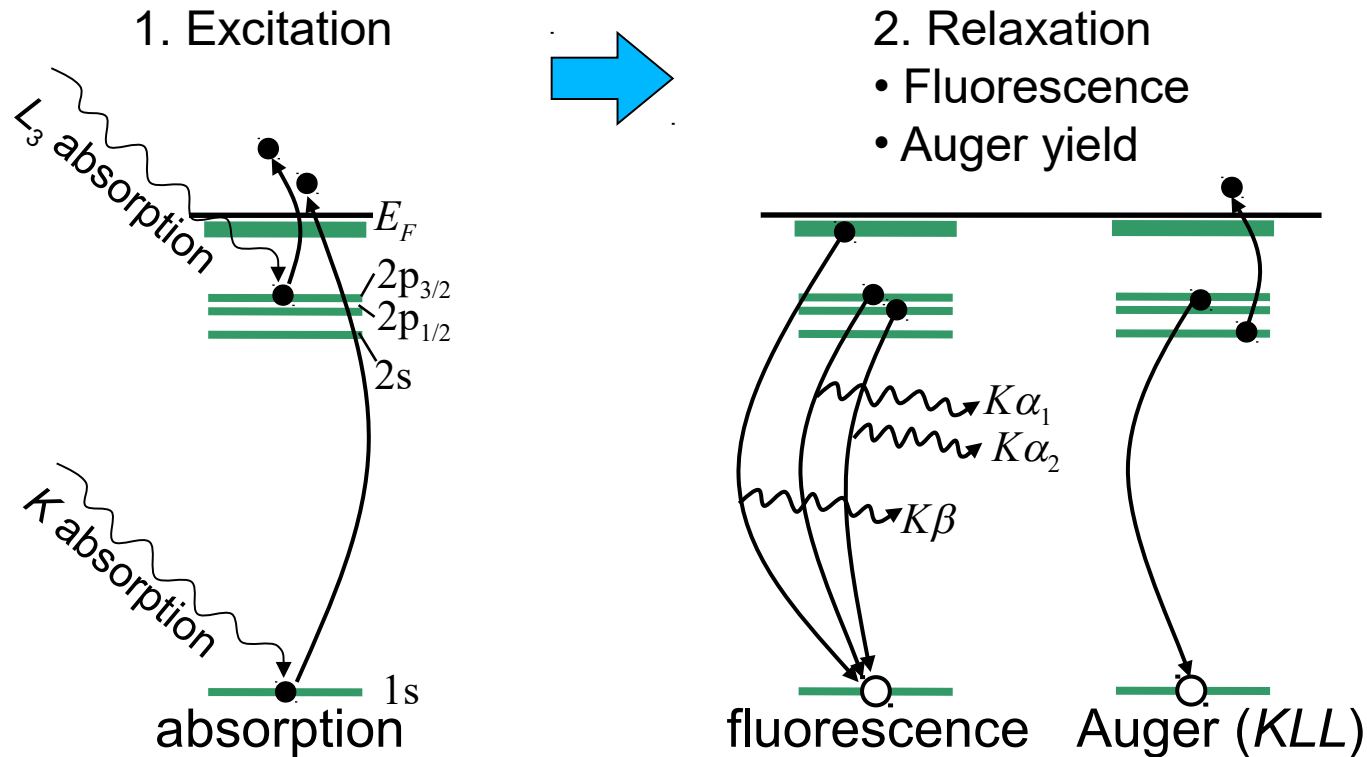
- 1) is distorted (typically suppressed) and
- 2) is noisier.

Therefore you should select the right mirrors and/or detune the monochromator.

In detail 2. Detection

Your samples determine which detection to choose

Relaxation channels



- $2p_{3/2}$ is 4-fold, $2p_{1/2}$ is 2-fold. $\Rightarrow K\alpha_1$ is as twice more intense as $K\alpha_2$.
- $K\alpha$ is more intense than $K\beta$ ($\sim 7-8$ times for $3d$ metals).
- The core hole filling is a cascade process.
- The fluorescence energies are tabulated \Rightarrow used in x-ray fluorescence analysis.
- The core hole width $\Delta E = \hbar/\tau$. ($\Delta E \sim 1\text{eV}$ for $1s$ hole in $3d$ elements $\Rightarrow \tau \sim 10^{-16}$ s)

Ways of detection

1. Direct intensity measurements in **transmission** geometry

- ionization chambers
- photodiodes with scattering foils

2. **Fluorescence** yield

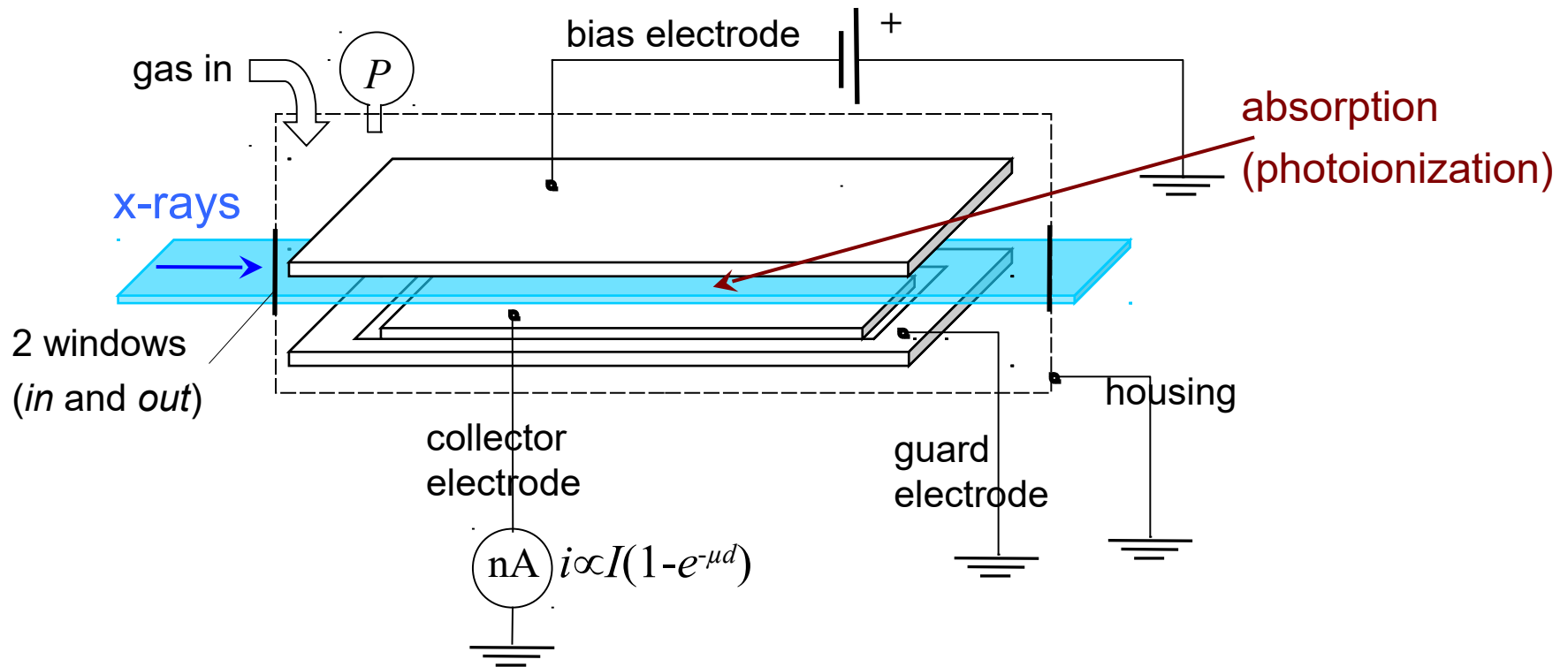
- semiconductor detectors, e.g. Ge and Si(Li)
- crystal analyzers
- Lytle detector

3. **Total electron** yield

- current from biased collector electrode
- channeltron

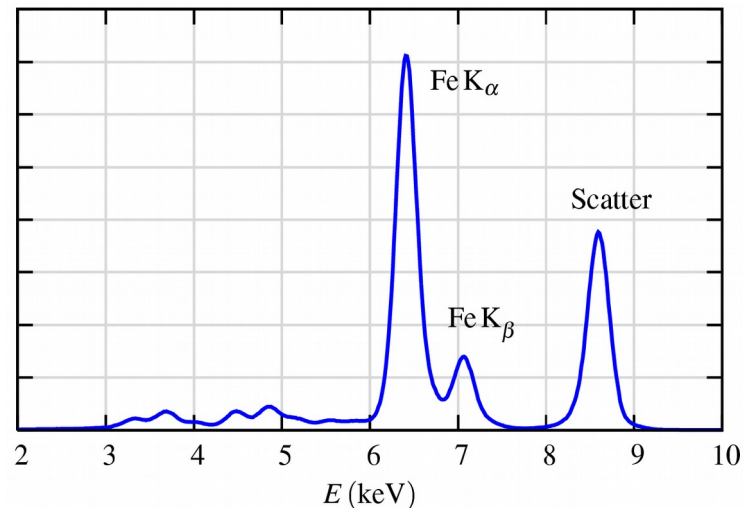
Ionization chamber

The principle of ionization chambers and semiconductor detectors (as reverse biased diodes) is the same: creation of electron-ion (hole) pairs in the inter-electrode medium and registering the current:



Fluorescence detectors

A typical energy resolved fluorescence spectrum:

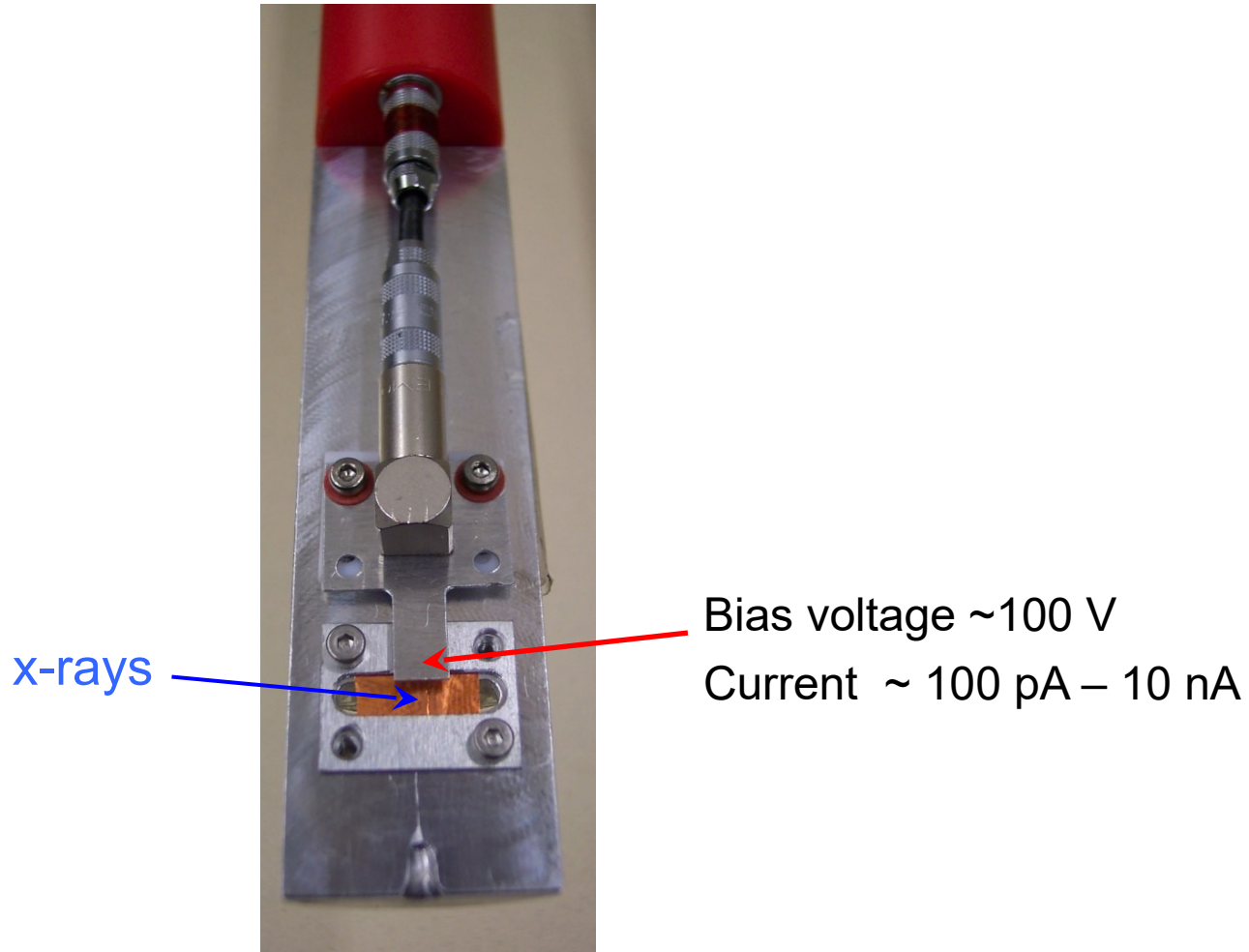


Fluorescence detectors
SDD and CdTe:



Total electron yield

A sample holder for electron (Auger) yield measurements with He gas as amplifying media



Summary on detection. Applicability

Probing depth:

- **transmission**: the full sample thickness (bulk sensitivity)
- **fluorescence**: $\sim(\text{absorption length}) * \sin(\varphi)$, 0.1 – 10 μm
- **total electron yield**: \sim electron mean free path, 10 – 100 \AA

Which detection mode to use:

- concentrated samples, transparent to x-rays – **transmission**
- dilute samples – **fluorescence**
- not transparent samples (low- E or thick) – **total electron yield** or **fluorescence** (with self-absorption correction)

In detail 3. Samples

How to prepare your samples

Suitable samples

There are good reviews on sample preparation, for example:

- Matt Newville, Anatomy of an XAFS Measurement

- Rob Scarrow, Sample Preparation for EXAFS Spectroscopy

google for them

- **General requirements**

- uniform on a scale of the absorption length of the material (typ. $\sim 10 \mu\text{m}$)
- prepared without pinholes

- **Shape, aggregative state**

- Solids: powders, foils etc.; single crystals and thin foils can utilize polarization properties of SR.
- Liquids
- Gases

- **Concentrations**

- for transmission: typ. $>1 \text{ wt}\%$
- for fluorescence: typ. $>100 \text{ ppm}$ and 1 mM

Suitable amount

Program XAFSmass (see its web-page for detailed description):

powder:

The screenshot shows the 'powder' mode of the XAFSmass software. The window title is 'XAFS mass'. A dropdown menu is set to 'Powder'. The formula $v = (\mu_{\tau}d)S \left(\sum N_i Z_i^2 r_0^2 \lambda_i^4 \right)^{-1}$; $m = Mv$ is displayed. The compound is 'Cu%4SiO_2' with a molar mass $M = 62.5883$ g/mol. Input fields show $\mu_{\tau}d = 2.6$ and $S(\text{cm}^2) = 0.72$. The energy $E(\text{eV})$ is set to 8979. The data table is 'Henke'. The calculated mass $m(\text{mg})$ is 53.389. The absorption step is 'Cu(m=2.136): 0.734'. There are empty fields for $\rho(\text{g/cm}^3)$ and $d(\mu\text{m})$. Buttons for 'Calculate', 'About...', and 'Help' are at the bottom.

foil:

The screenshot shows the 'foil' mode of the XAFSmass software. The window title is 'XAFS mass'. A dropdown menu is set to 'Foil, Film, Glas etc.'. The formula $d = (\mu_{\tau}d)M \left(\rho \sum N_i Z_i^2 r_0^2 \lambda_i^4 \right)^{-1}$ is displayed. The compound is 'Cu' with a molar mass $M = 63.5460$ g/mol. Input fields show $\mu_{\tau}d = 2.6$ and $\rho(\text{g/cm}^3) = 8.96$. The energy $E(\text{eV})$ is set to 8979. The data table is 'Henke'. The calculated thickness $d(\mu\text{m})$ is 10.212. The absorption step is 'Cu: 2.266'. Buttons for 'Calculate', 'About...', and 'Help' are at the bottom.

gas:

The screenshot shows the 'gas' mode of the XAFSmass software. The window title is 'XAFS mass'. A dropdown menu is set to 'Gas'. The formula $p = -\ln(1 - \text{abs.level})kT \left(d \sum N_i Z_i^2 r_0^2 \lambda_i^4 \right)^{-1}$ is displayed. The compound is 'Ar' with a molar mass $M = 39.9480$ g/mol. Input fields show 'absorption level = 1 - exp(- $\mu_{\tau}d$) = 0.22' and $d(\text{cm}) = 10$. The energy $E(\text{eV})$ is set to 9500. The data table is 'Henke'. The calculated pressure $p(\text{mbar})$ is 203.391. Buttons for 'Calculate', 'About...', and 'Help' are at the bottom.

A typical value for total absorption is about 2. It can be as twice as smaller or bigger without significant change in spectrum quality. More important is the sample uniformity (particle size).

Pellets



Ø5 mm pellets	Ø13 mm pellets
weights 2–20 mg, less consumption but more difficult to handle	weight 10–100 mg
easier to remove from dies	
more samples in the holder	

Mixing and pressing

Dilute your powder with a supporting agent: BN (boron nitride), polyethylene, cellulose, sugar etc.

Probably, the mostly used one is BN. To my experience, it gives fragile pellets strongly adhesive to dies.

With PE and cellulose the pellets are more durable and easier to press. We will provide cellulose.

Do not put more than 1 ton! By pressing stronger you destroy the pellets rather than make them firmer. For \varnothing 5 mm dies 0.5 ton is enough.



XAS of Metallobiomolecules

XAS can provide unique information about the kinds of ligands holding a particular metal in a metallobiomolecule.

Symmetry information provided by XANES can help determine qualitatively the molecular geometry. For example, there is often a significant distinction between tetrahedral 4-coordinate and square planar 4-coordinate.

XAS is particularly good at elucidating differences between one sample and another: e.g. active site before and after addition of substrate, or competitive inhibitor, or reductant/oxidant etc.

Sample Limitations

Amorphous frozen solutions with glassing agent (e.g., 20% glycerol); cryogenic T to avoid radiation damage.

Concentration ~ 1 mM or even ~ 0.2 mM (for 3d metals)

Volume ~ 0.05 - 0.2 ml.

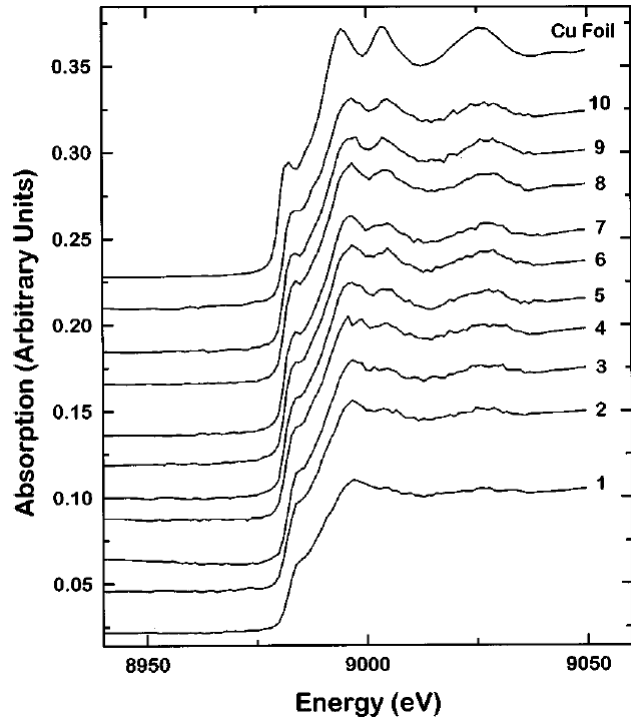
Homogenous metal site structure! XAS is not able to distinguish multiple site structures within a given sample: the resulting XAS-derived structure is an "average" one.

Radiation damage

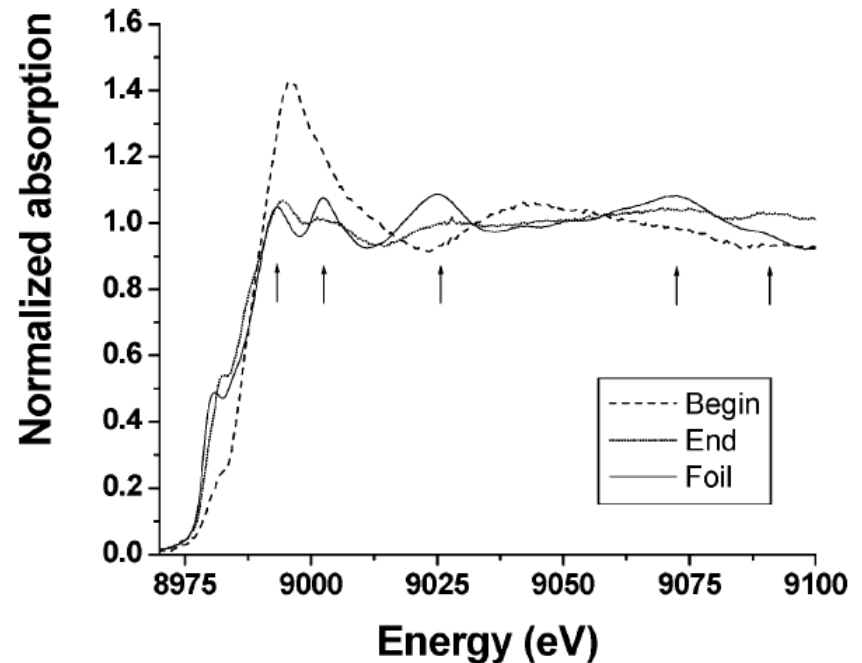
We have $\sim 10^{13}$ photons/s at the sample, focused into $\sim 300\text{h} \times 200\text{v} \mu\text{m}^2$.

In hard x-ray XAFS the radiation damage is mostly seen (if seen) in the form of photo-reduction.

In solutions the x-ray induced reduction is more common due to radiolysis:

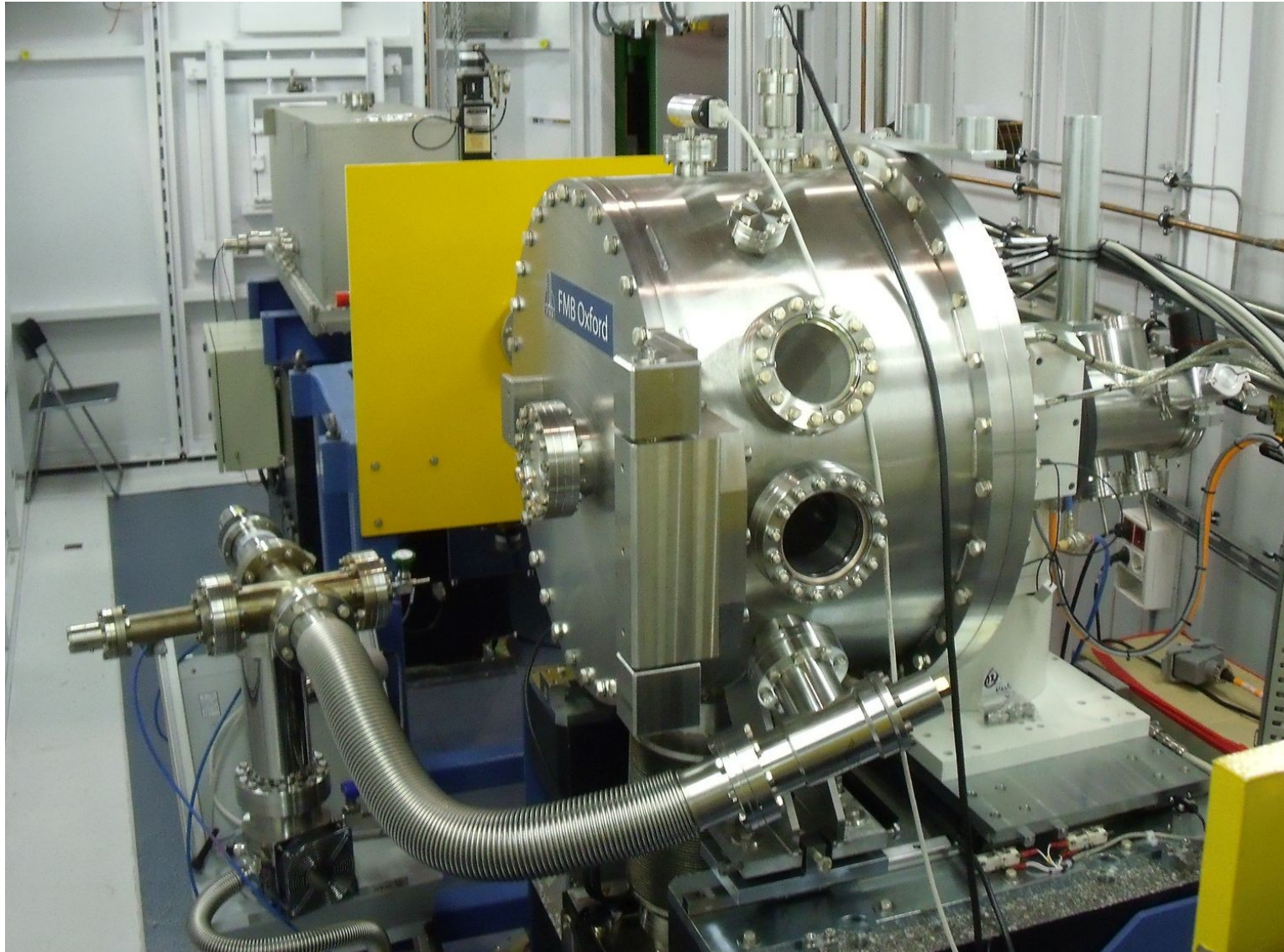


from S. Jayanetti et al, J. Chem. Phys **115** (2001) 954

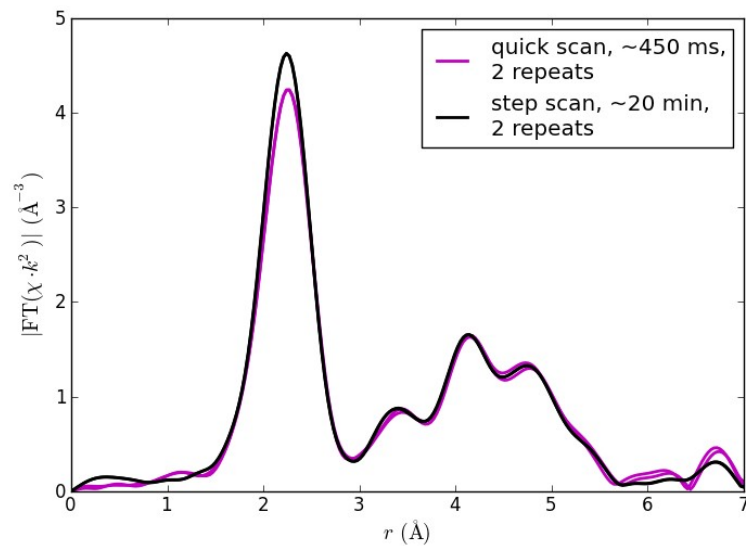
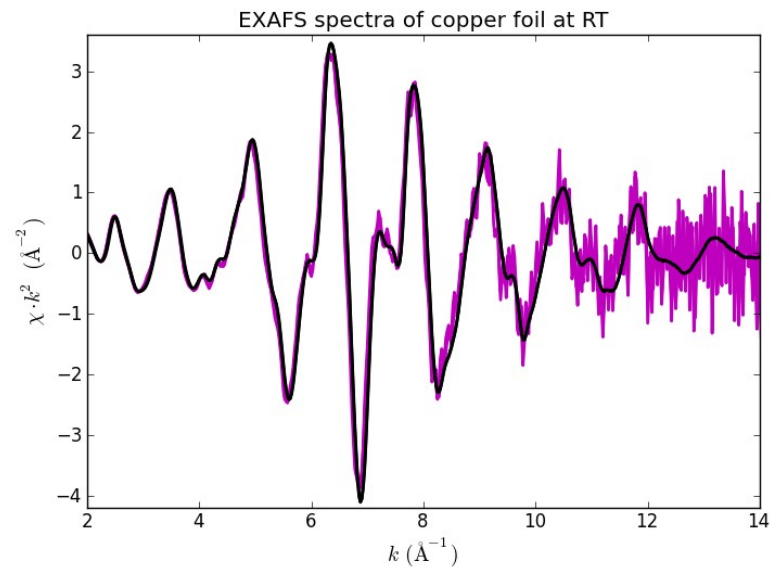
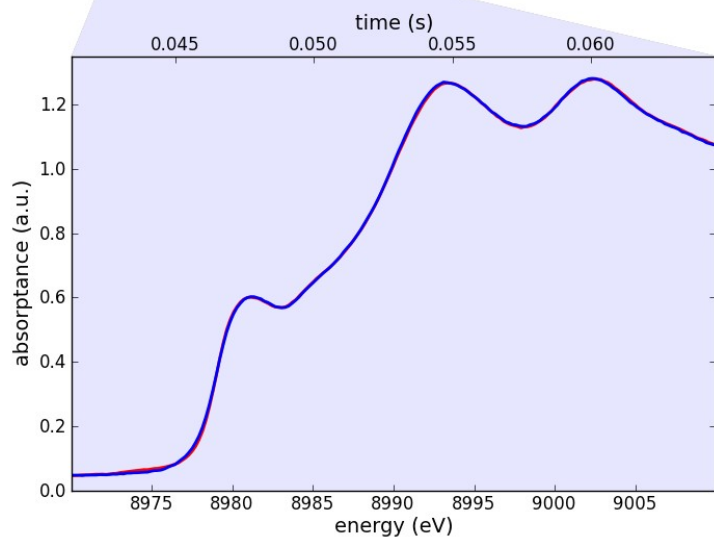
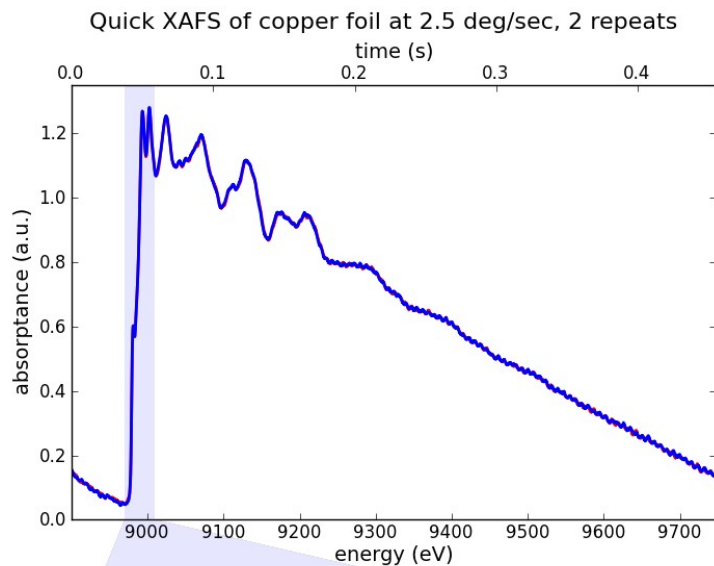


from J. G. Mesu et al, J. Phys. Chem. B **109** (2005) 4042

Extensions 1. Quick scanning



Quick scanning



Radiation damage

We have $\sim 10^{13}$ photons/s at the sample, focused into $\sim 300\text{h} \times 200\text{v} \mu\text{m}^2$.

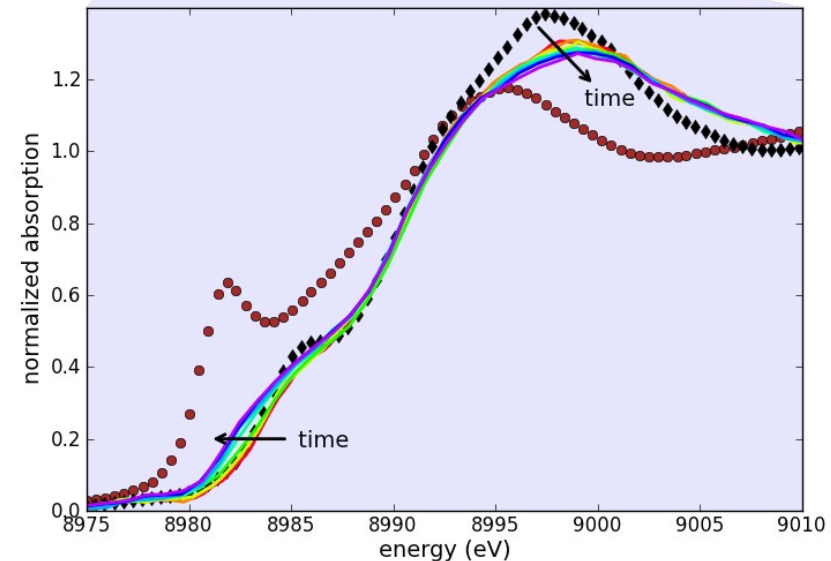
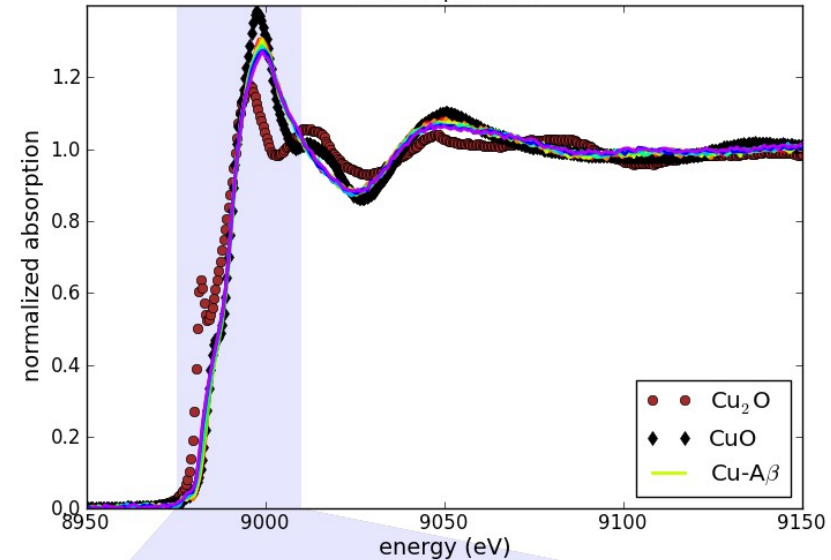
In hard x-ray XAFS the radiation damage is mostly seen (if seen) in the form of photo-reduction. I had it for oxidized Au samples.

In solutions the x-ray induced reduction is more common due to radiolysis:



The figure on the right shows XANES spectra of a copper containing peptide which demonstrate x-ray induced reduction from Cu(II) towards Cu(I). The quick scanning allows one to select a few first spectra referring to the pristine structure.

Absorption spectra of Cu-A β peptide and copper oxides, 2 min/spectrum

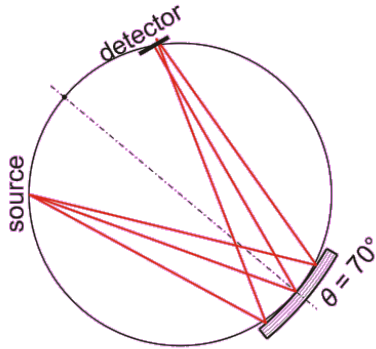


Extensions 2. Crystal analyzers

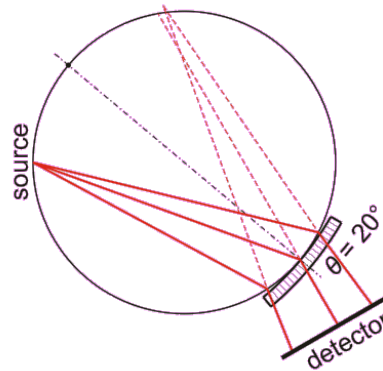
Why:

- to work with high flux fluorescence (>10 Mcps)
- to measure RIXS, x-ray Raman etc.

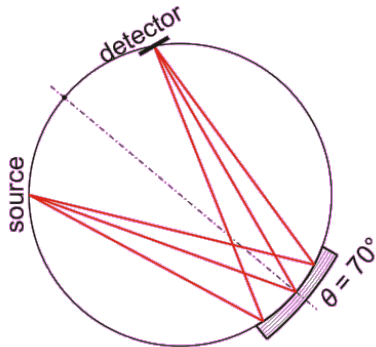
Bragg bent (Johann)



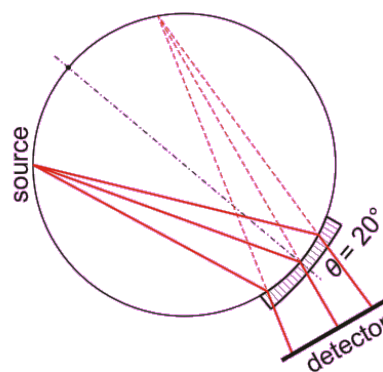
Laue bent (duMond)



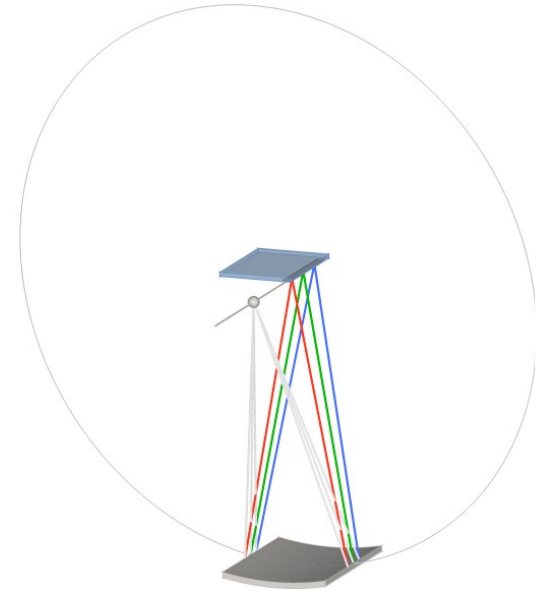
Bragg ground-bent (Johansson)



Laue ground-bent

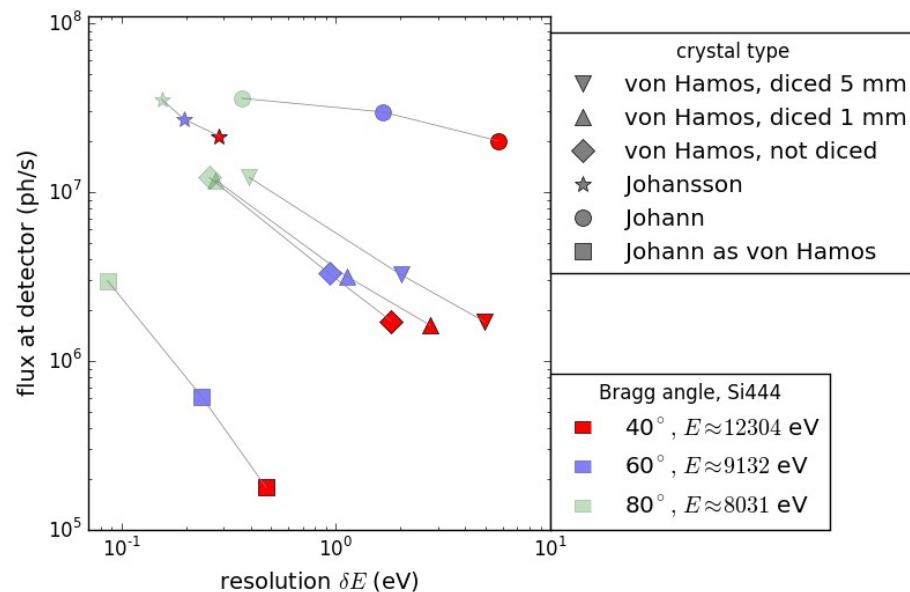
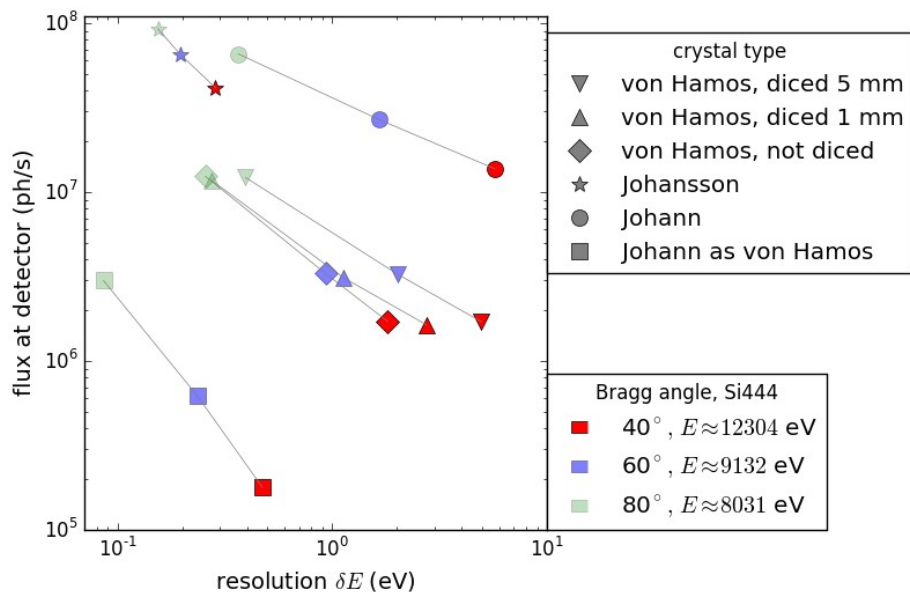


von Hamos

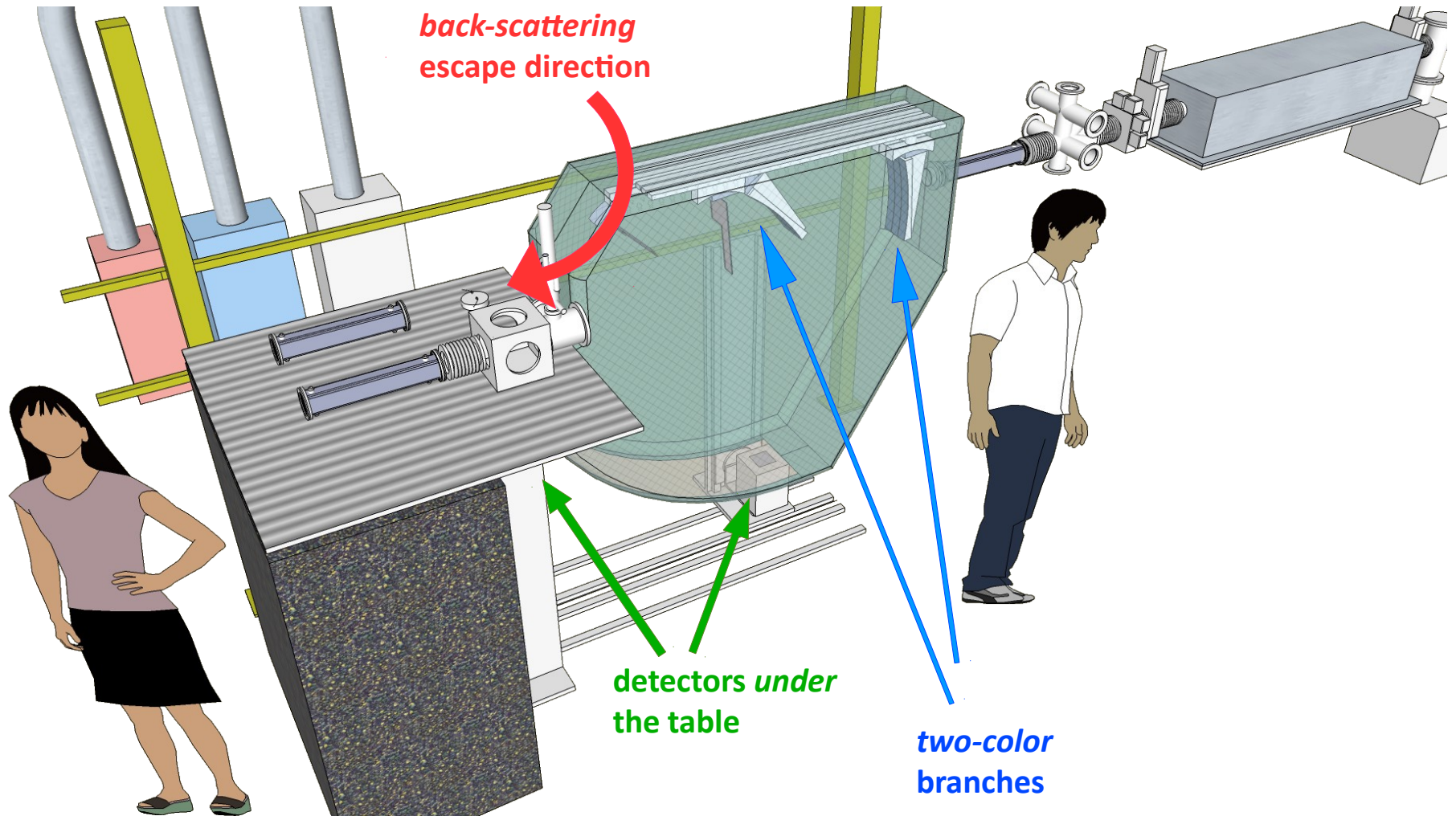


Comparison of 1D-bent crystal analyzers

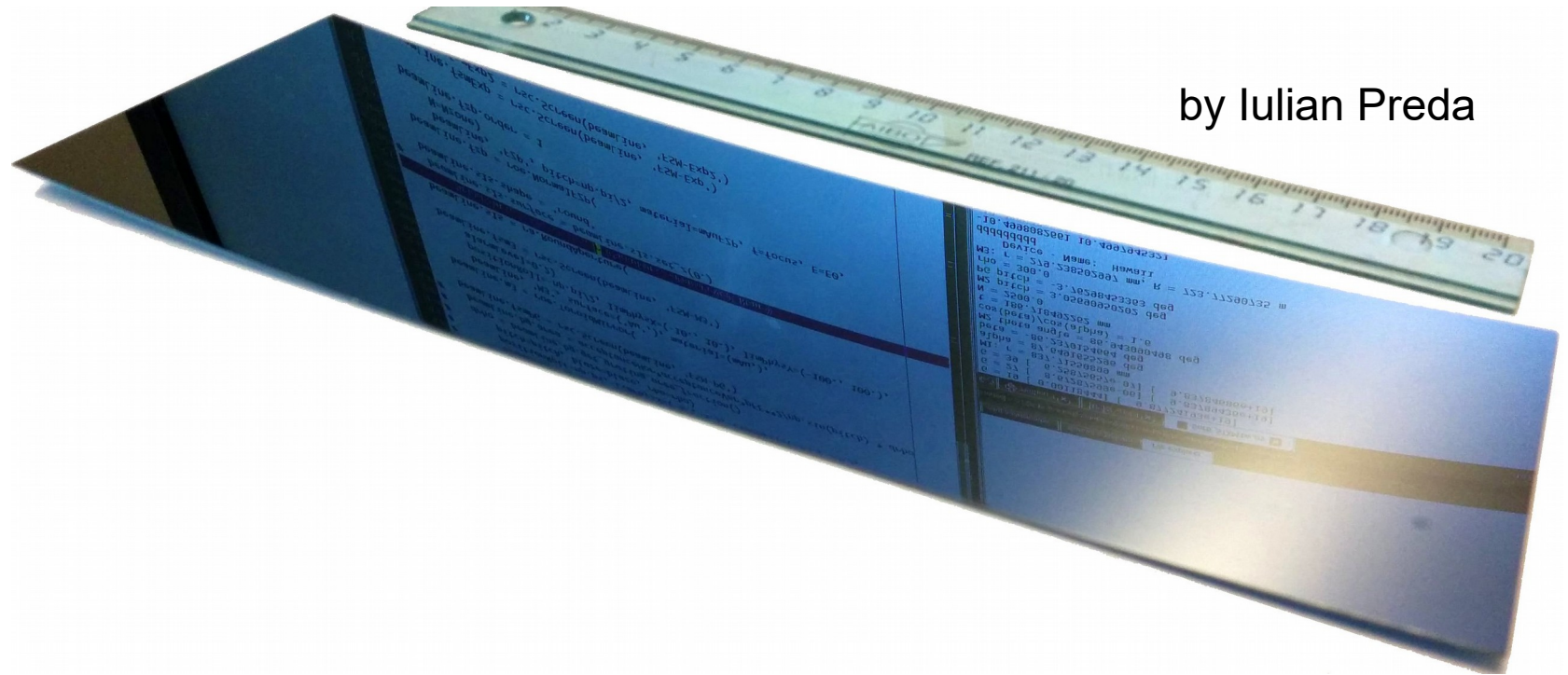
Resolution-efficiency charts of 1D-bent Si444 crystal analyzers at 10^{13} ph/s incoming flux. The left chart is with a narrow source energy band equal to the 6-fold energy resolution; the right one is with a wide energy band equal to $8 \cdot 10^{-4} \cdot E$ (approx. width of $K \beta$ lines).



Spectrometer design



Crystals



by Iulian Preda

The next processing stage is the surface treatment.
Recrystallization in an ultra-high vacuum oven.

A small test piece has exhibited re-appearance of a LEED pattern measured in situ in the oven. We are building a larger volume oven, also with an in situ LEED instrument, to work on the production crystals.

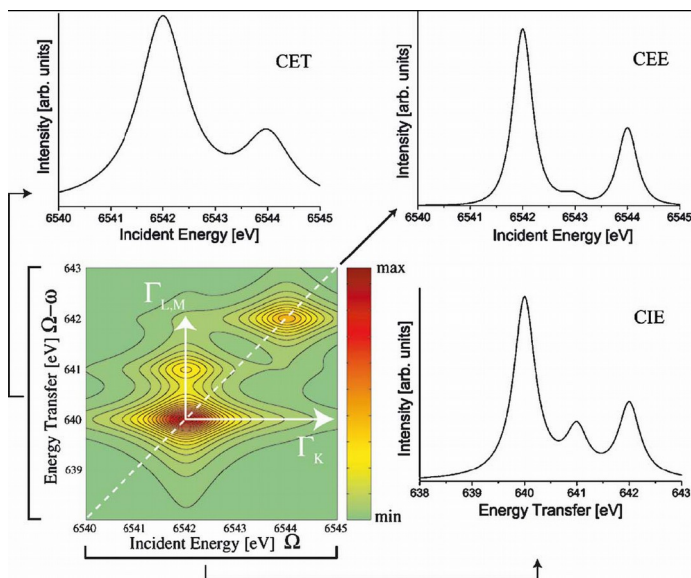
Crystals

6 production crystals $310 \times 50 \text{ mm}^2$ ground to 1.5 m radius:

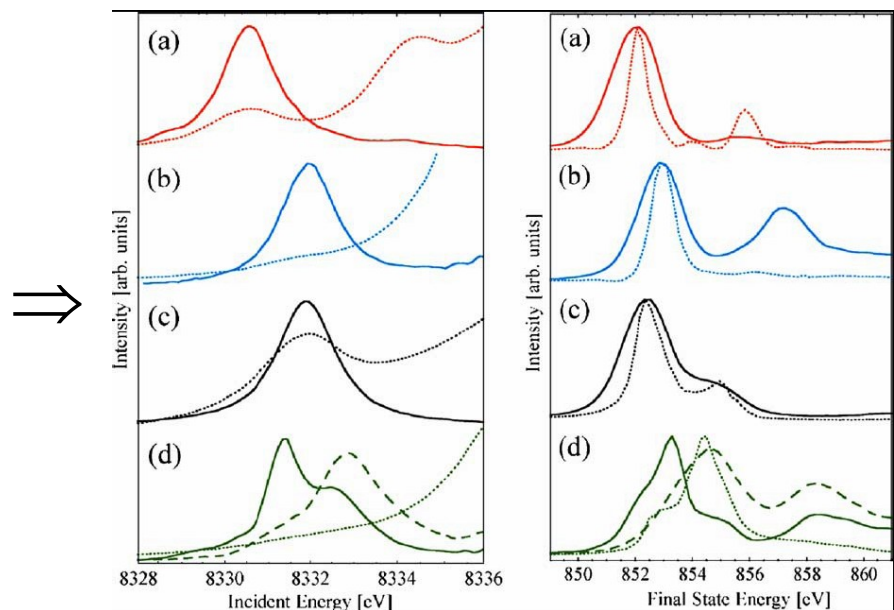


X-ray emission analyzer. Application examples

- $K\alpha$ and $K\beta_{1,3}$ lines: FWHM $K\alpha$ and peak position of $K\beta_{1,3}$ give effective electron spin in the atomic d orbitals.
- $K\beta_{1,3}$ lines: **site selective** EXAFS scans
- $K\beta$ satellite lines: **sensitivity to ligands** (also with angular dependence for oriented samples)
- RIXS: 1) better resolved K pre-edge peaks; 2) soft edges with hard x-rays



Glatzel & Bergmann,
Coordination Chemistry Reviews **249** (2005) 65–95



P. Glatzel et al. J. Am. Chem. Soc. **124** (2002) 9668.

Conclusions

- XAFS (XANES and EXAFS) spectroscopies:
 - suitable under reaction conditions (no high vacuum)
 - do not require long-range order
 - element specific
- XANES spectroscopy for:
 - symmetry information from the pre-edge peaks
 - valence state from the edge shift
 - analysis of mixtures using basis spectra
- XANES is experimentally simpler than EXAFS
 - signal is stronger (one can measure faster and at lower concentrations)
 - does not depend on T (if without phase transitions, of course)
- EXAFS gives:
 - inter-atomic distances and coordination numbers
 - identification of neighbor atoms
- Extensions (excluding sample environment):
 - quick scanning for higher throughput and lower radiation damage
 - x-ray emission spectrometer for high flux fluorescence and RIXS