A Brief Introduction to XAFS

focusing on the fundamental concepts and methods for those who will start XAFS experiments

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Outline

- What is XAFS?
- How do we measure “lengths”?
- Things XAFS spectra give us
- Fundamental concepts & Basic equation of XAFS
- How to carry out XAFS measurements
  - Transmission mode
  - Fluorescence mode
- Some topics

What is XAFS?

XAFS: **X**-ray **A**bsorption **F**ine **S**tructure

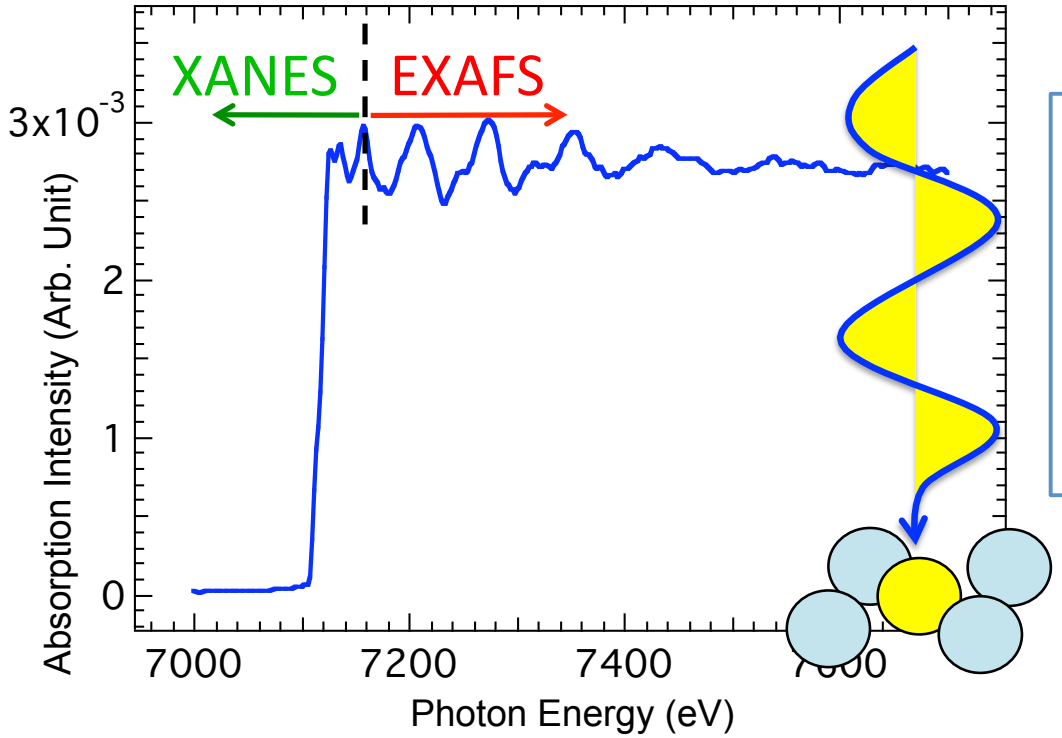
electronic state (valence)

Symmetry

Bond length

Number of surrounding atoms (Coordination number)

Distribution, Thermal vibration



Element specific

to observe **Local structure**

(long range periodicity is not required)

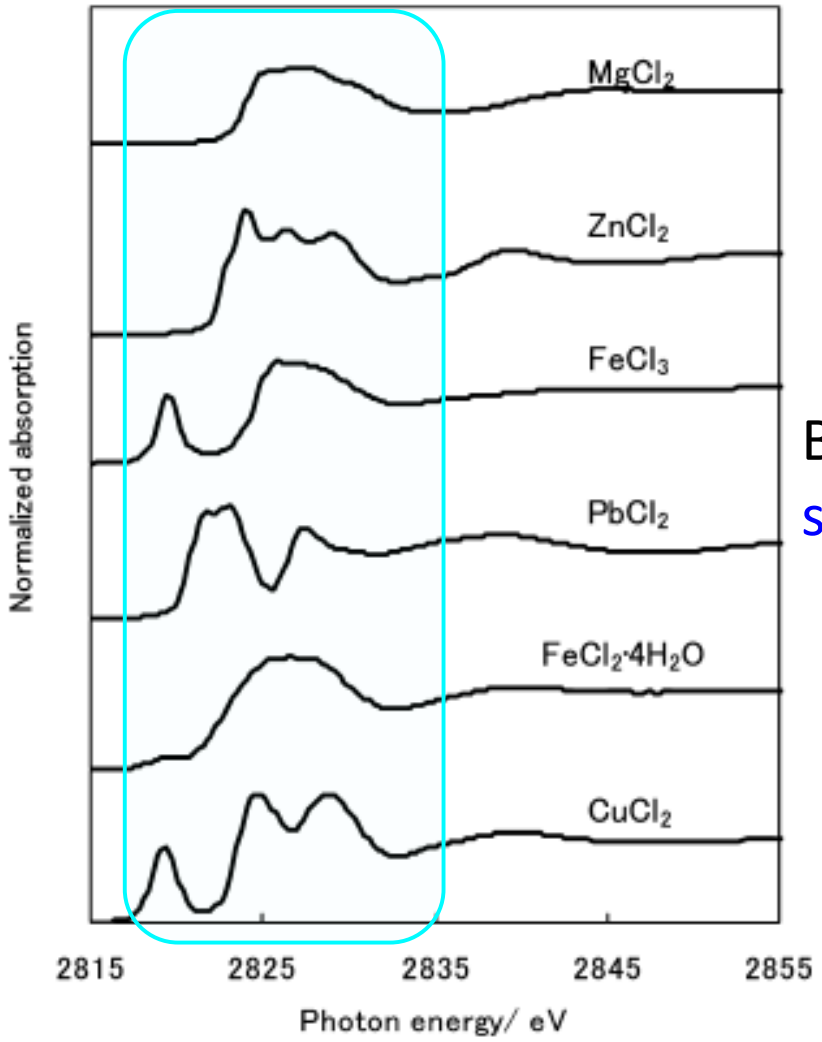
Solid, Liquid, Gas, whatever

XANES: X-ray Absorption Near Edge Structure

EXAFS: Extended X-ray Absorption Fine Structure

XANES tells us what your sample is.

Cl *K*-edge XANES



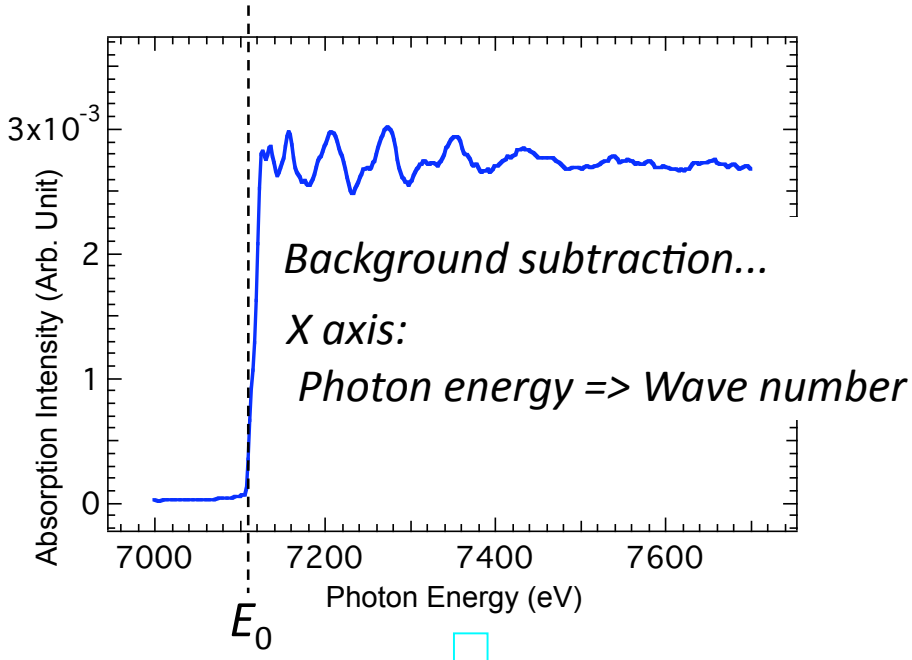
All these are metal chlorides.

But you can see some specific features in each spectrum.

So you would recognize what your sample is.

F. Zhu, *et al.,* Environ. Sci. Technol. **42**, 3932 (2008)

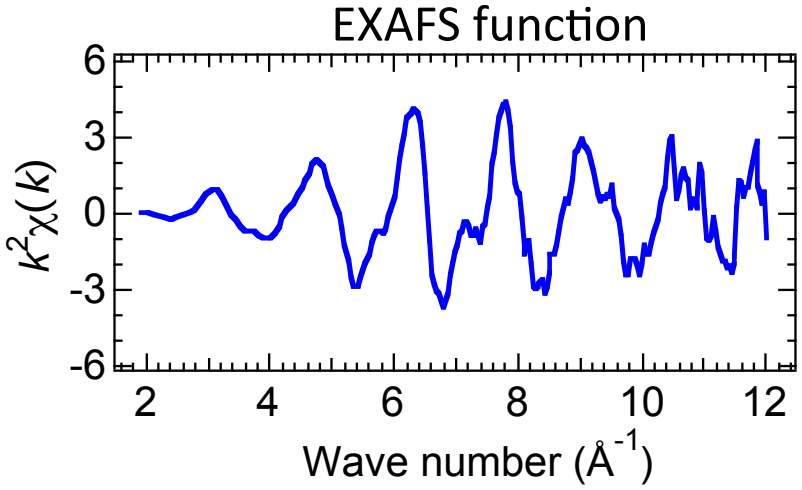
How to Obtain Bond Length by EXAFS



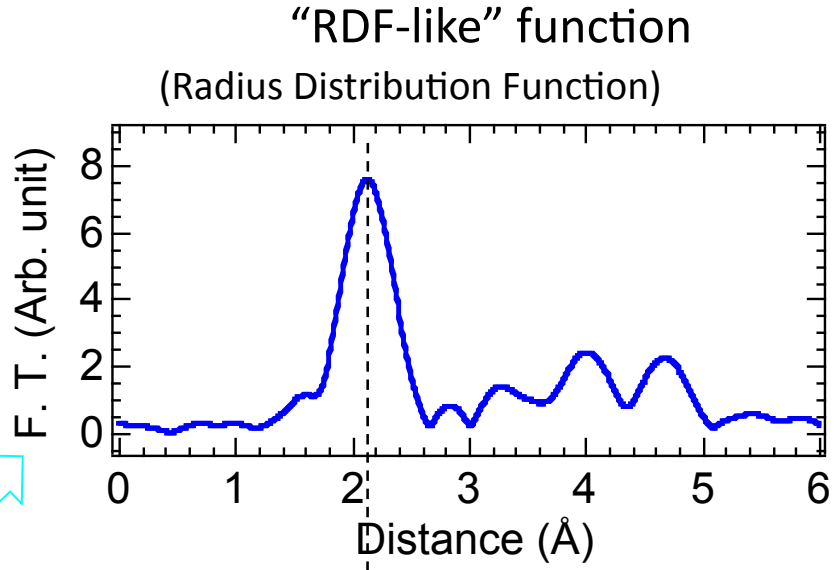
Background subtraction...

X axis:

Photon energy => Wave number



Fourier Transform



Nearest neighbor atomic distance

+ phase shift

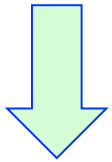
Bond length

Peak area

Coordination number

How do we measure lengths?

What *would you use when you measure a length of something?*



Ruler: with graduations, easy to measure the length

OK, if you don't have a ruler, what would you do?

You can use your **hand, arm or height** as a standard of length.

Proper standard "ruler" for a certain thing to be measured

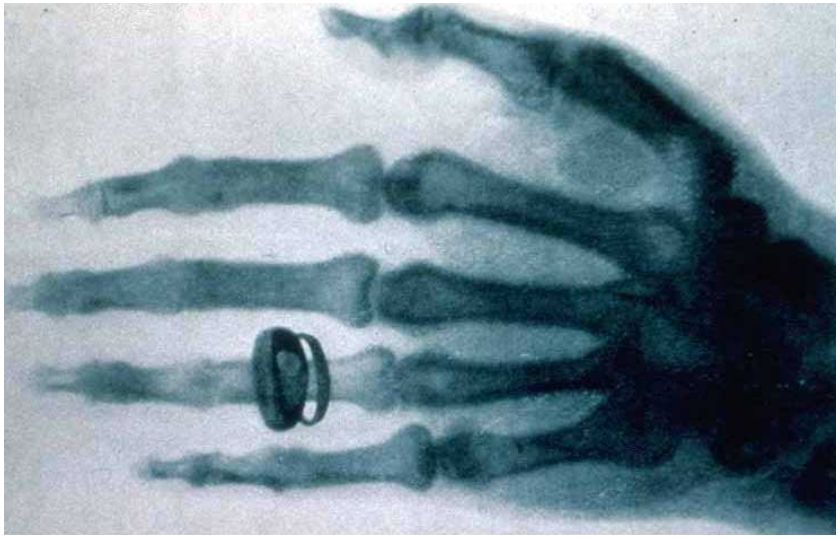
(We never measure the length of pens with our heights.)

Things to be measured: Periodicity of crystal, bond length, ...

Proper standard "ruler": **Wave length of x-ray**, **Wave property of electron**,...

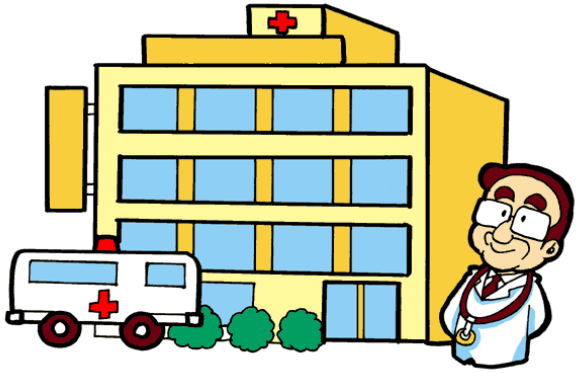
Discovery of x-ray

W. C. Röntgen (1845-1923)

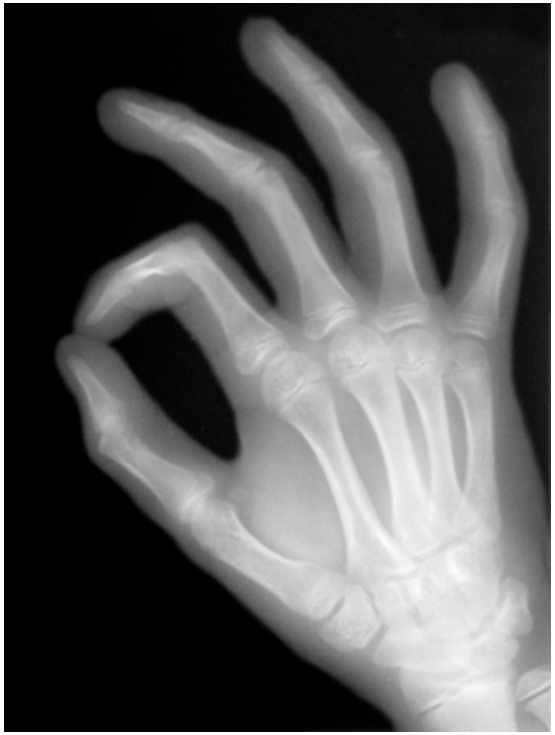


1901, the 1st Nobel prize in Physics for discovery of x-ray

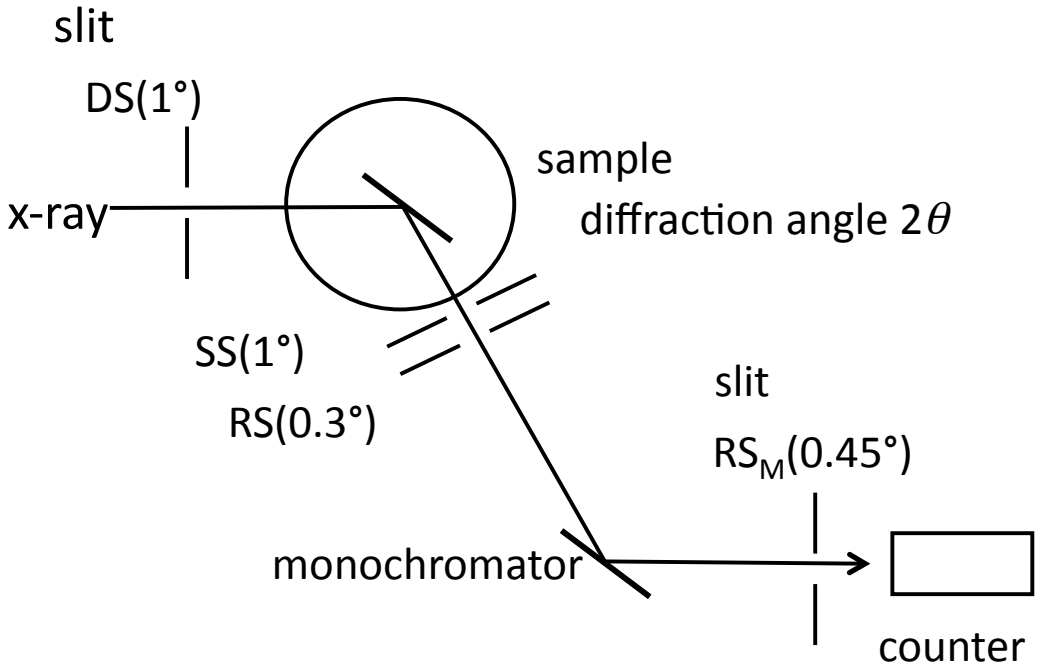
He discovered “x-ray” by earnestly “endlessly” increasing the voltage of electrodes in his discharge tube.



hospital



X-ray diffraction (XRD)



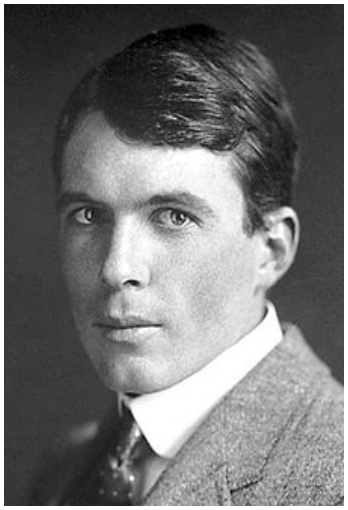
a machine for XRD measurements

RINT-TTR III, Rigaku

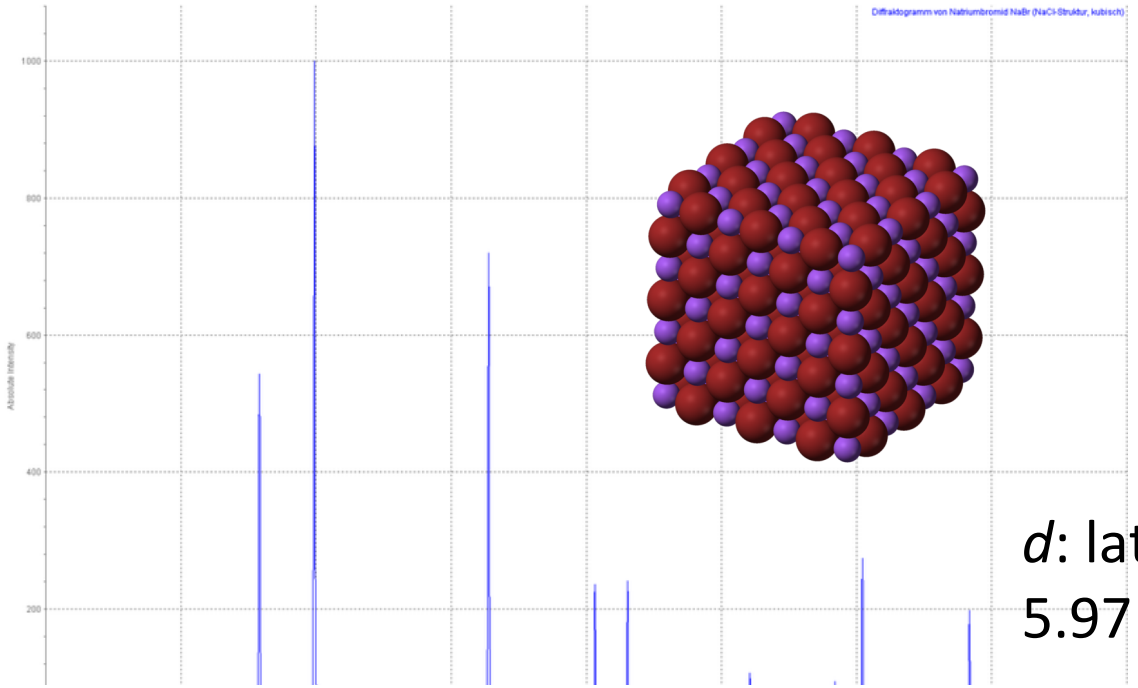
an XRD spectrum of NaBr

What is the ruler here?

The wave length of the x-ray is used as **a ruler** to measure the lattice constant.



W. L. Bragg
(1890-1971)



Bragg's law

$$2d\sin\theta = n\lambda$$

d: lattice constant
5.97 Å

Long range order is required *for XRD measurements.*

No *(practical)* ***element specificity***

Simple things XAFS spectra give us

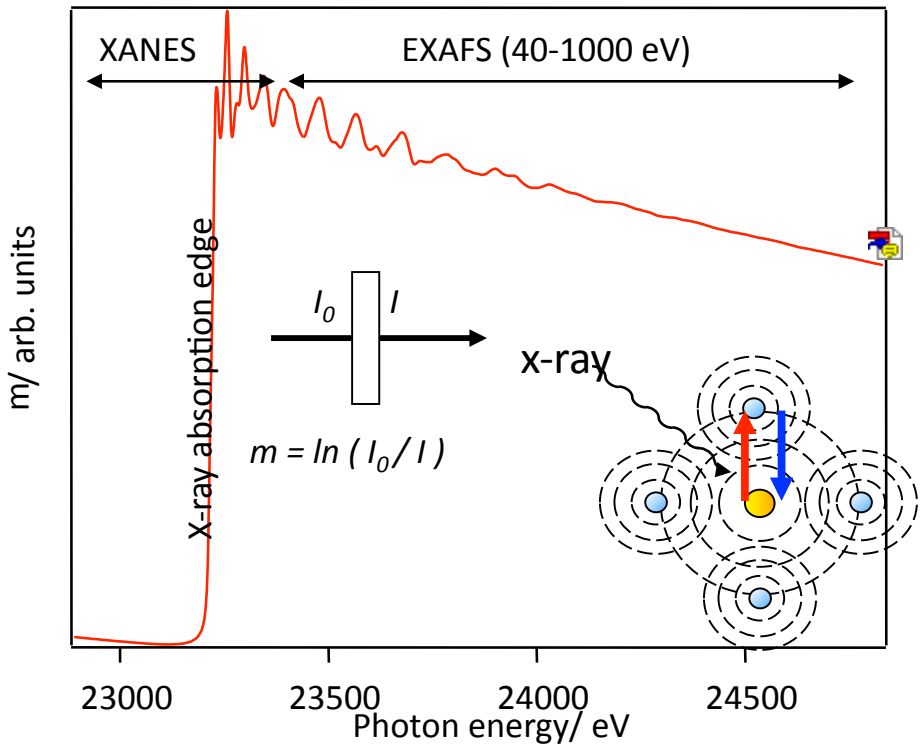
- XANES gives us...
  - Valence state
    - We can determine our sample as a certain molecule or material.
  - Symmetry

with element specificity

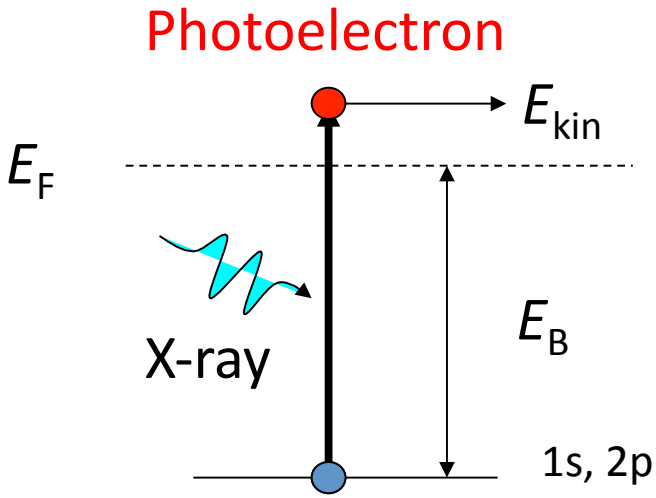
- EXAFS gives us...
  - Bond length
    - **A local structure** is given.
    - **Crystallinity, or long range order is not required**.
  - Coordination number (CN)
    - Simply, the number of atoms around the atom.
    - CN enables us to estimate sizes of nano clusters.

XAFS

- ✓ X-ray Absorption Fine Structure(XAFS)
  - ✓XANES(X-ray Absorption Near Edge Structure）
  - ✓EXAFS(Extended X-ray Absorption Fine Structure）



X-ray absorption spectrum

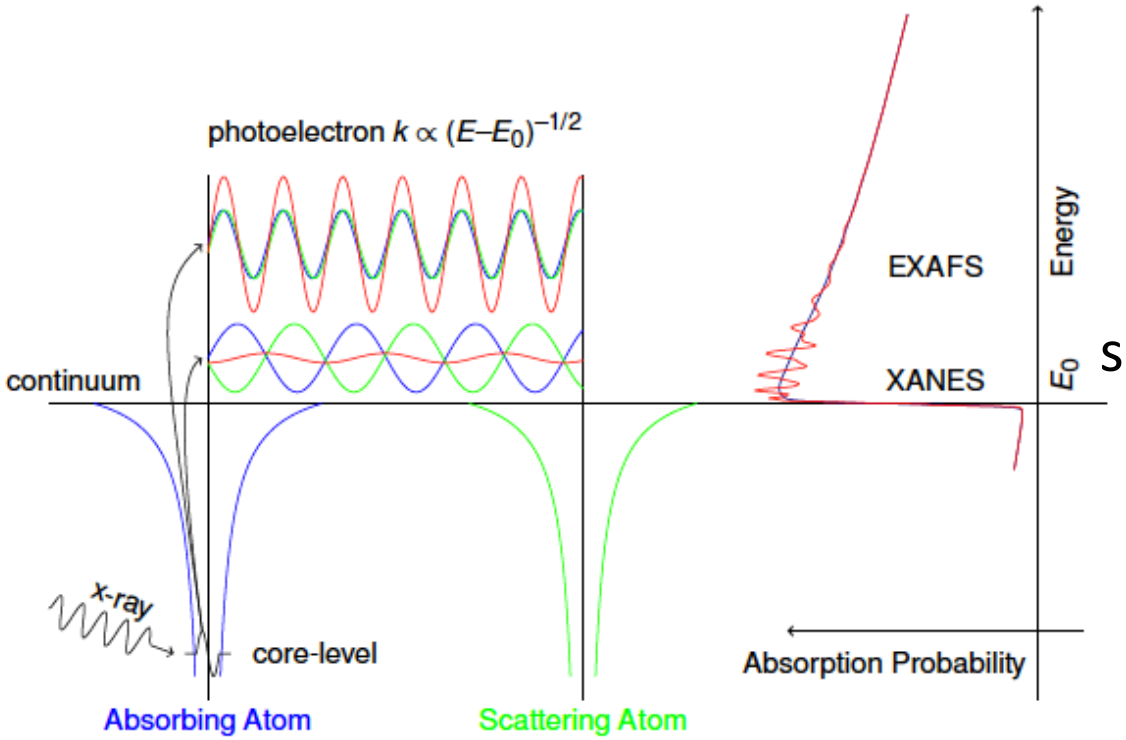


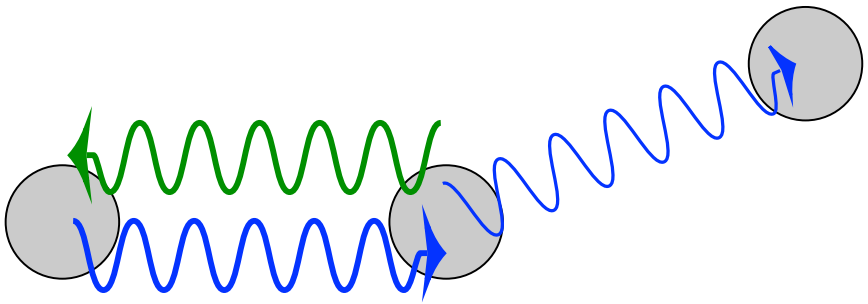
$E_{kin} = h\nu - E_B$

1s electron *K* shell

2p electron *L* shell

Picture of the wave function of final state in EXAFS





"Photoelectron (wave)" emitted

↓

scattered by the surrounding atoms

↓

Wave function of the final state pictured by "quantum theory of scattering"

Scattering of electron and interference

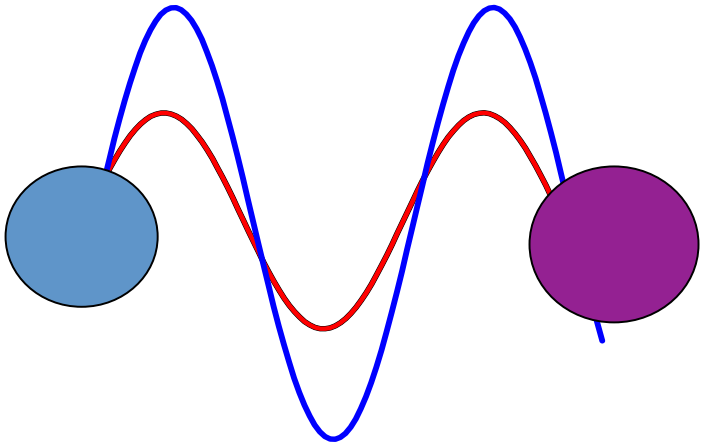
$$\frac{\hbar^2 k^2}{2m} = E - E_0$$

K : wave vector

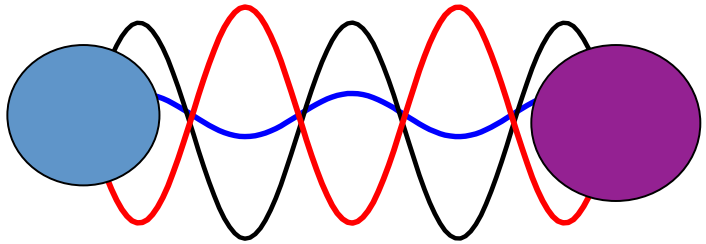
$\hbar$: Plank Const.

E : Photon energy

E_0 : threshold (edge)

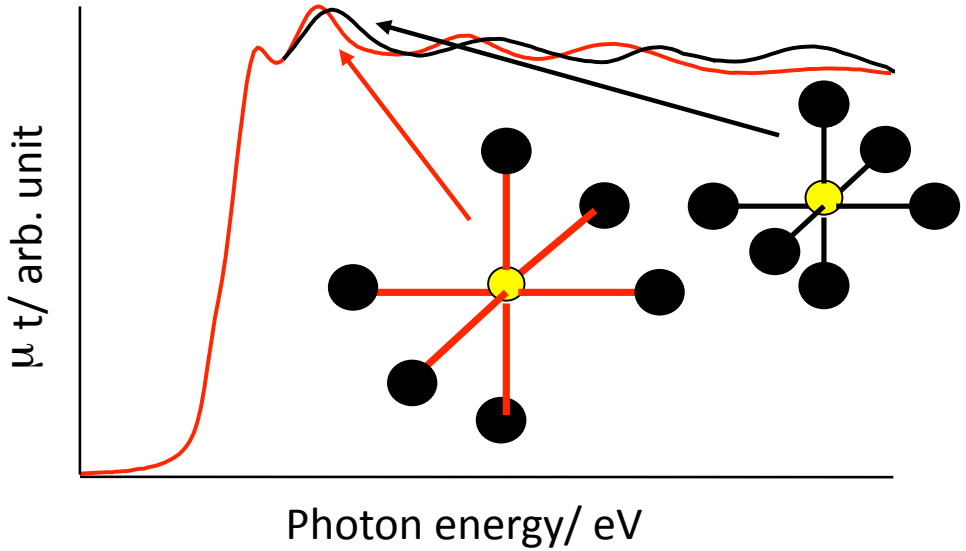


Enhancement



suppression

Bond length and Coordination number

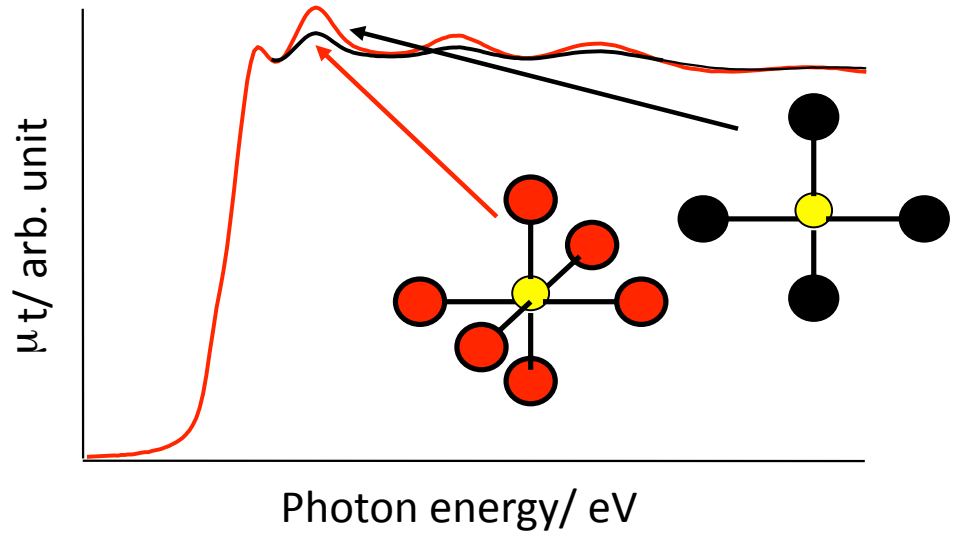


Higher frequency

(Shorter Period of Oscillation)

⇩

Longer Bond Length

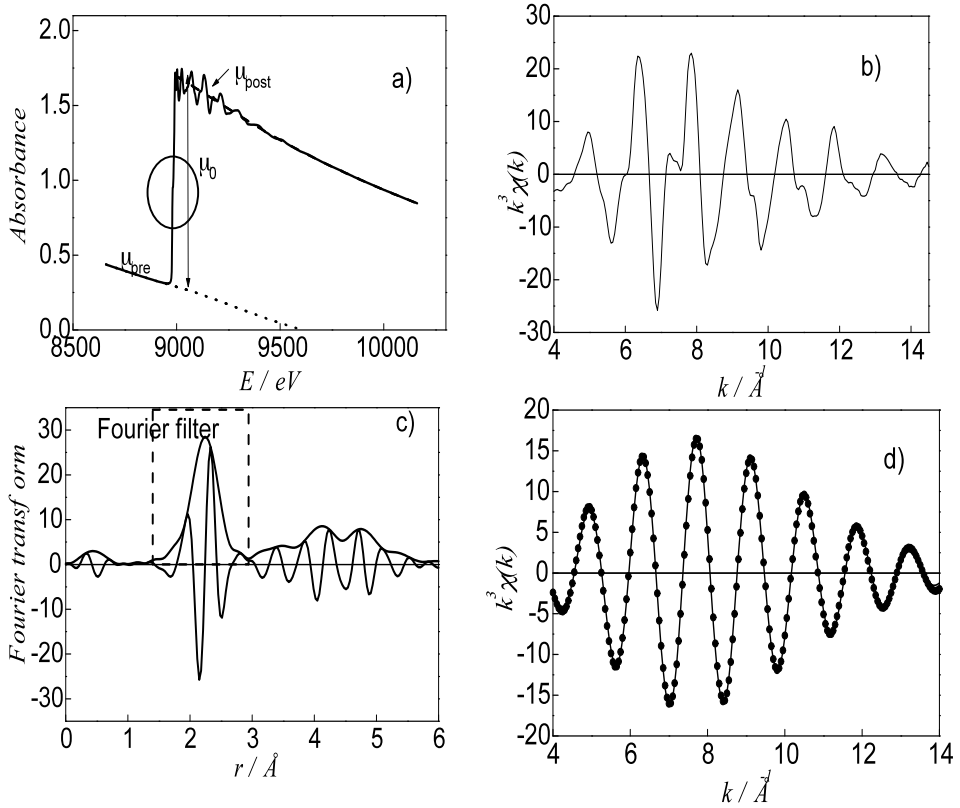


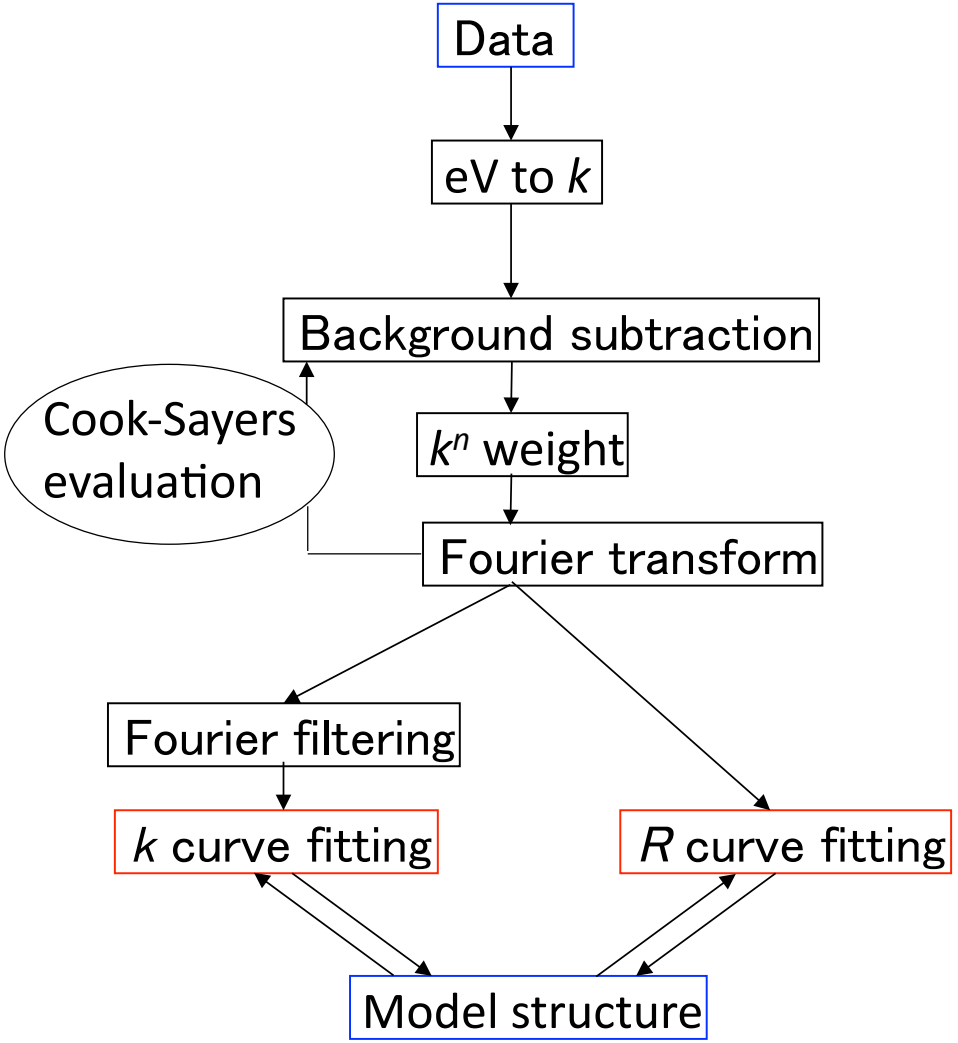
Larger Amplitude

⇩

Larger Coordination Number

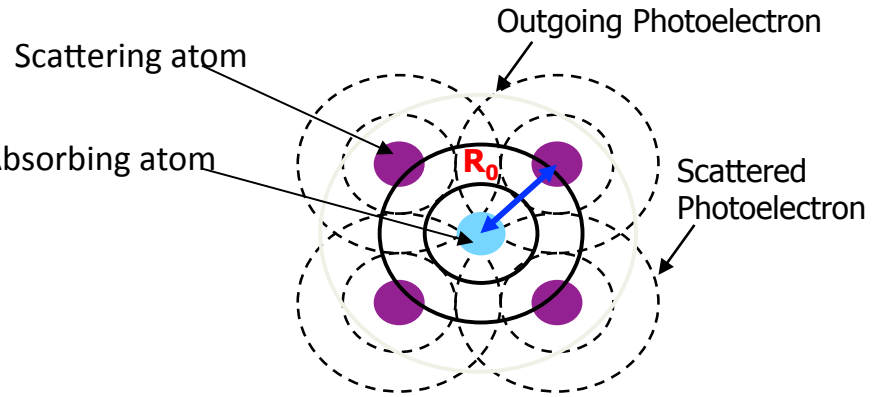
Sketch of XAFS analysis





The EXAFS equation

1. **leaving the absorbing atom**
2. **scattering from the neighbor atom**
3. **returning to the absorbing atom**



XAFS oscillation — Absorbance — Smooth backgroun

$$\chi(k) = \frac{\mu(E) - \mu_s(E)}{\mu_0(E)} = S_0^2 \sum_i \frac{N_i F_i(k_i)}{k_i r_i^2} e^{-2k_i^2\sigma_i^2} \sin(2k_i r_i + \phi_i(k_i))$$

Edge-jump

$$k = \sqrt{2m_e(E - E_0)/\hbar}$$

Theorptically or empirically derived Parameters

F_i : Backscattering amblitude

$* e^{-2r_i/\lambda(k_i)}$

ϕ_i : Phase shift

Curve-Fitting Parameters

N_i Coordination number

σ_i^2 DWfactor

E_0 energy shift

r distance

Fermi's Golden Rule to express μ of XAFS

Born-Oppenheimer approximation

velocity of nuclear motion << that of electronic motion

(due to the high ratio between nuclear and electronic masses)

Time-dependent Perturbation theory

Fermi's Golden Rule

$$\mu \propto \sum_f \left| \left\langle \Psi_f \left| H' \right| \Psi_i \right\rangle \right|^2 \delta\left(E_f - E_i - \hbar\omega\right) \quad \text{...(1)}$$

$$H' = -\frac{e}{mc} A(r) \cdot P$$

$A(r)$: vector potential of X-ray

P: momentum of electron

$$A(r) = \hat{e} A_0 e^{ik \cdot r}$$

$\hat{e}$: unit vector of electric field

r: position of electron

k: wave number vector of X-ray

One-electron approx. & Dipole approx.

$$\mu \propto \sum_f \left| \left\langle \Psi_f \left| H' \right| \Psi_i \right\rangle \right|^2 \delta\left(E_f - E_i - \hbar\omega\right) \quad \text{...(1)}$$

EXAFS is "just" an absorption spectroscopy!!

(described by a simple dipole term)

Don't be afraid to get in it!!

$$\mu \propto \sum_f \left| \left\langle \psi_f \left| \hat{e} \cdot r \right| \psi_i \right\rangle \right|^2 \delta\left(E_f - E_i - \hbar\omega\right) \quad \text{...(2)}$$

fundamental equation to express XAFS

Eq. of single scattering EXAFS

Amplitude

Oscillation (phase)

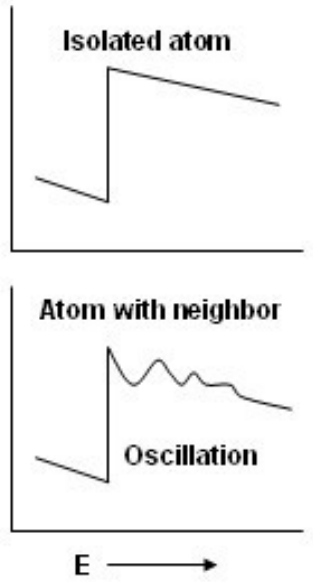
$$\chi(k) = -S_0^2 \sum_j \frac{N_j}{kR_j^2} F_j(k) \exp\left(-2\sigma_j^2 k^2\right) \sin\left(2kR_j + 2\delta_{A,1}(k) + \varphi_j(k)\right)$$

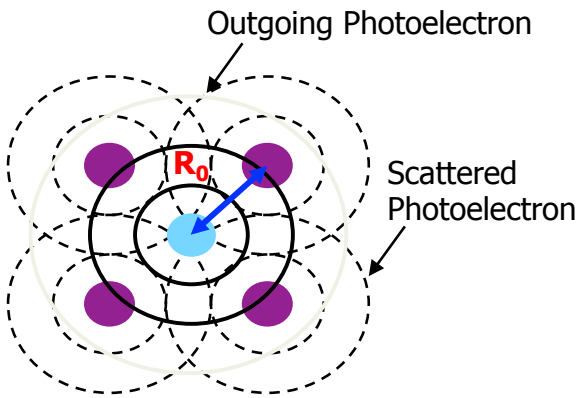
"Round trip" of the wave

Phase shift

of absorbing atom

of scattering atom





Fourier Transform…

Bond length R_j , etc.,

(Parameters high-lightened by yellow are fitting parameters.)

de Broglie wave as a Ruler

A particle with the momentum of *p*
having the wave character described by the below Eq.

as for Electron

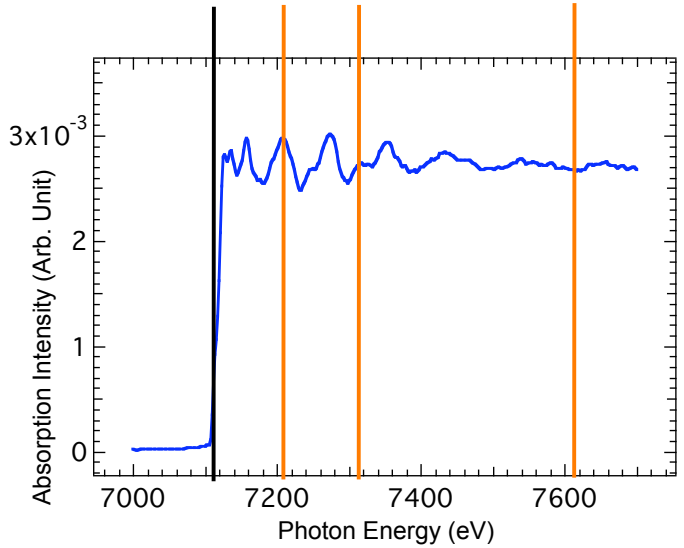
$$\lambda = \frac{h}{p} = \frac{h}{\left(2m_e eV\right)^{1/2}}$$

considering a bond length of ~2.5 Å

100 eV: 1.226 Å	2 waves
200 eV: 0.867 Å	3 waves
500 eV: 0.548 Å	4-5 waves

EXAFS

We use **de Broglie wave of electron** as a **Ruler**, in order to measure bond length

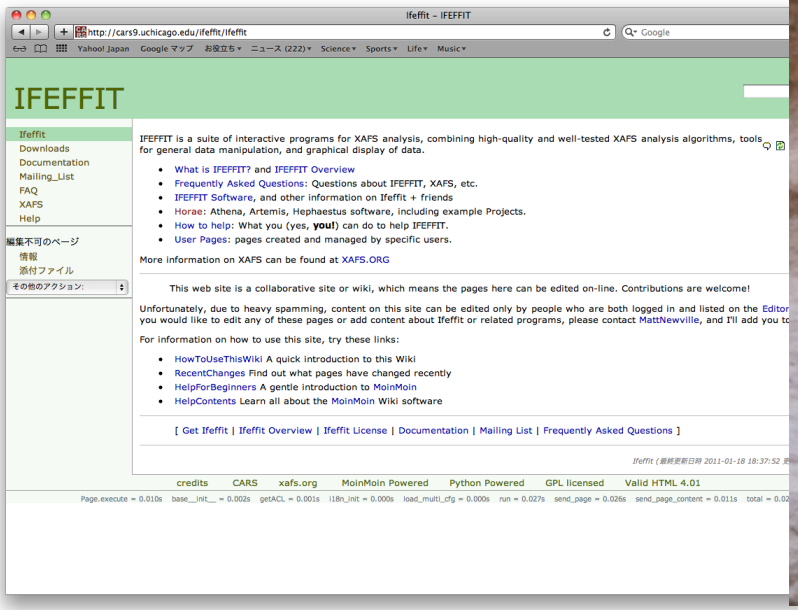


Software for XAFS analyses

Athena, Artemis (Ifeffit)

by a group at U. Chica

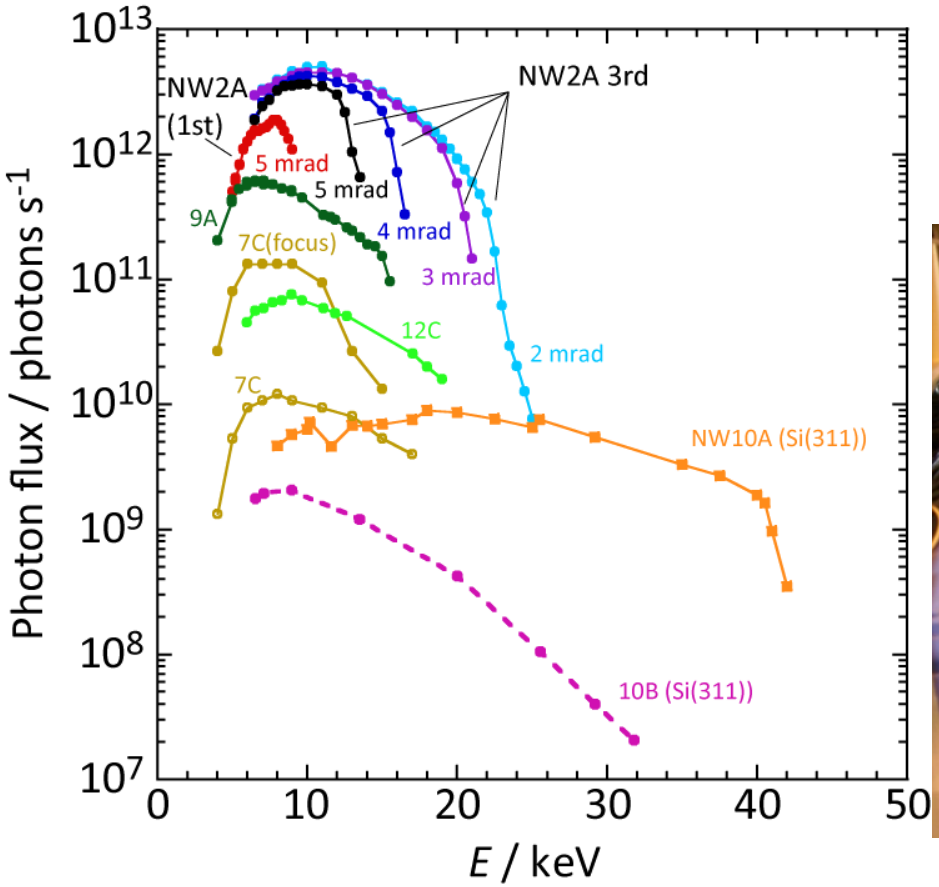
http://cars9.uchicago.edu/ifeffit/Ifef



Of course, there are many other softwares, and you can use what you'd like to.

Experiments of XAFS

Stations of XAFS experiments at PF

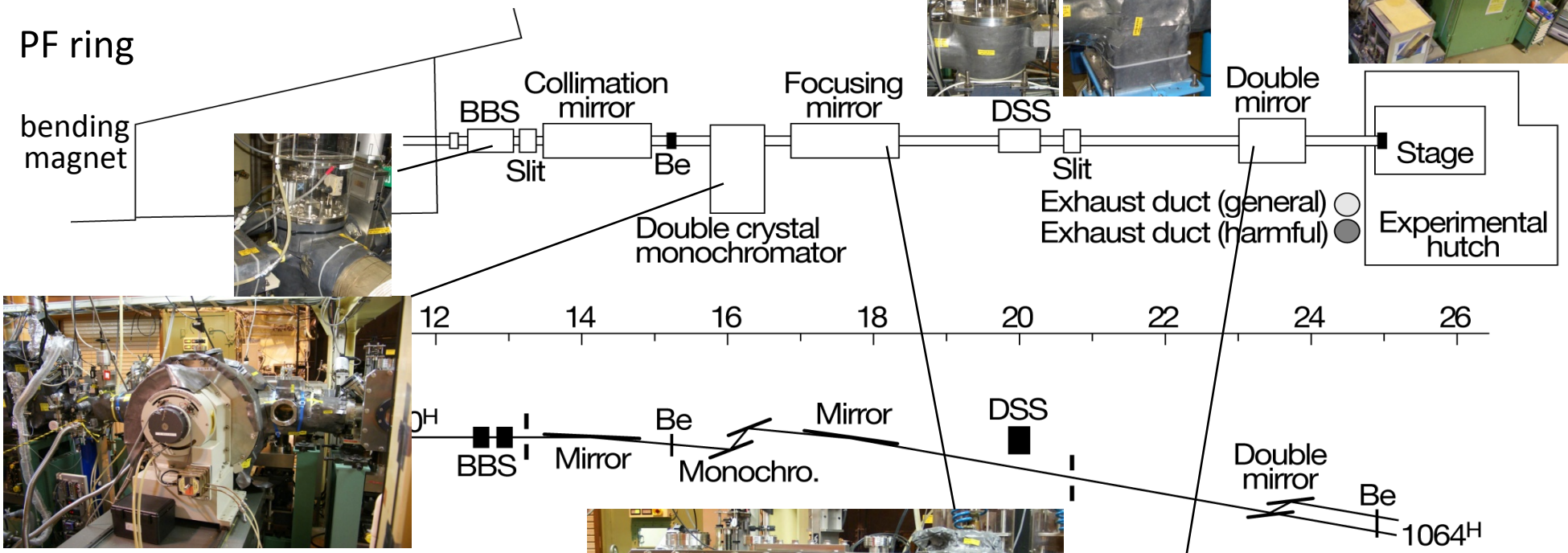


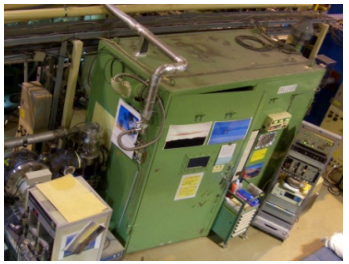
PF BL-9A

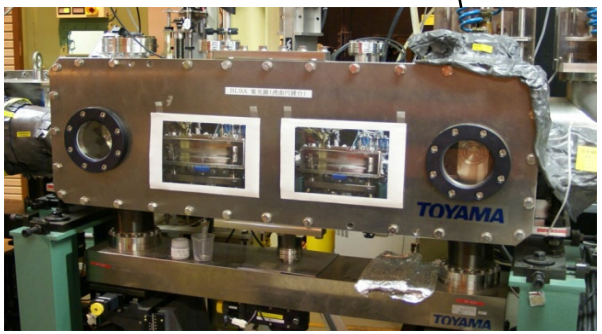
K edges: from P (~2.1 keV) to Ce (~40 keV)

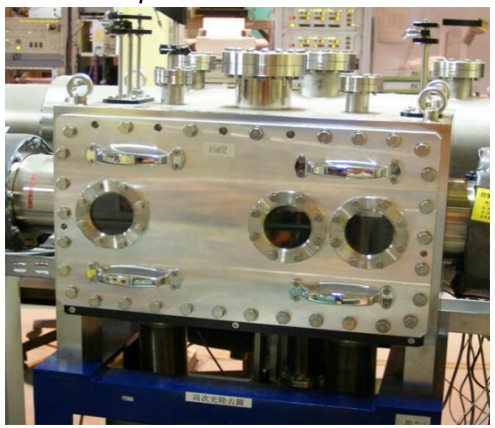
L edges: from Mo (~2.5 keV) to U (~21 keV)

Schematic of BL-9A



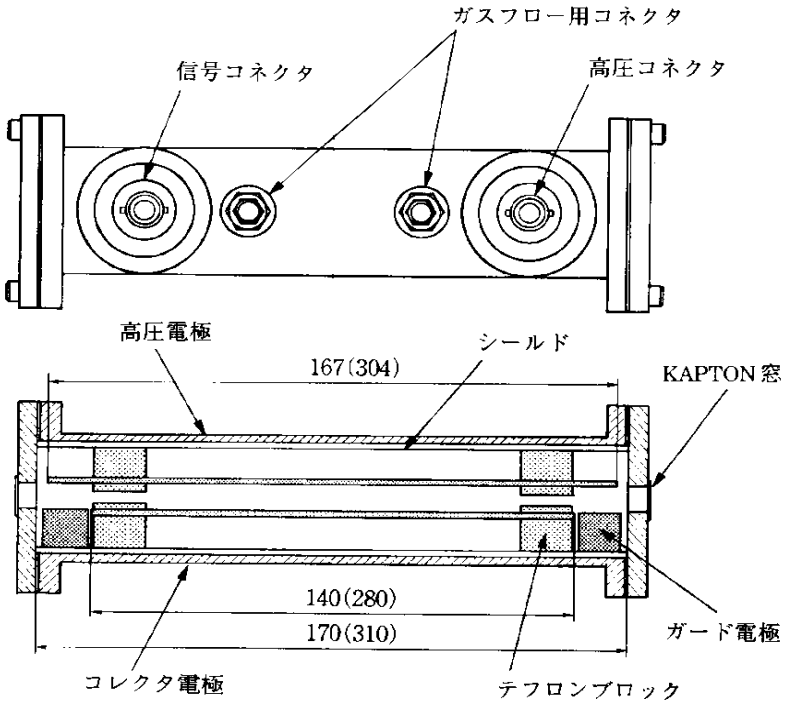






Ionization chamber for x-ray detection

We measure the current produced by ionization of gas by incoming x-ray.



Current i ; measuring wih N_2 flowing Ion chamber to detect x-ray of 8 keV;

$$i \approx 8.5 \times 10^{-8}\ \mathrm{A}$$

$$i = \alpha E e N / W$$

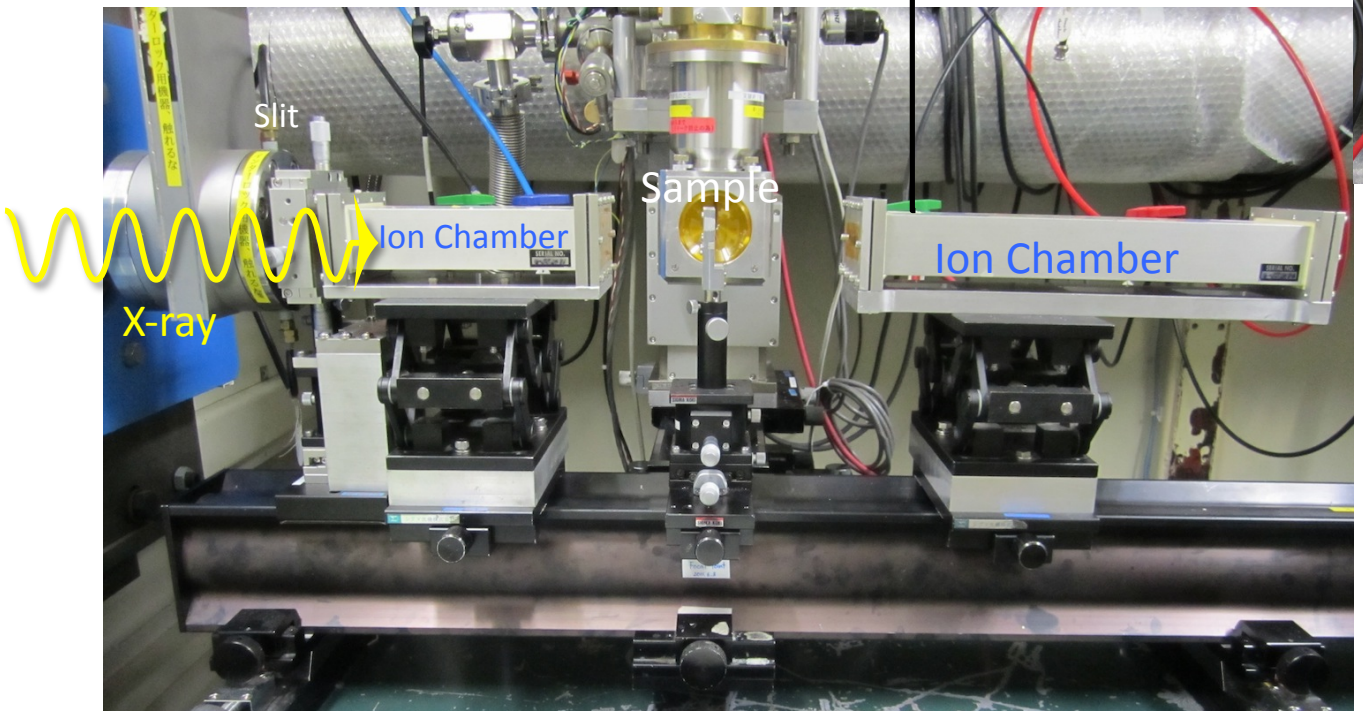
α ：検出効率（0.2）
E ：光子エネルギー（8000 eV）
e ：電荷素量（1.6×10^{-19} C）
N ：入射光子数（10^{10} photons/s）
W ：窒素ガスのイオン化エネルギー（30 eV）

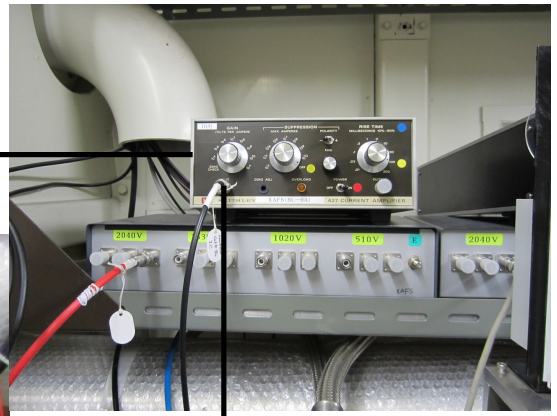
Setup of transmission mode XAFS

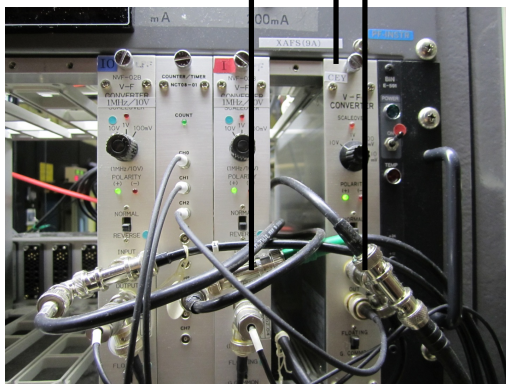
Ion Chamber → Amp → V-F Converter → Counter

Current prop. to x-ray intensity　　Cur. => Volt.　　Volt. => Frequency

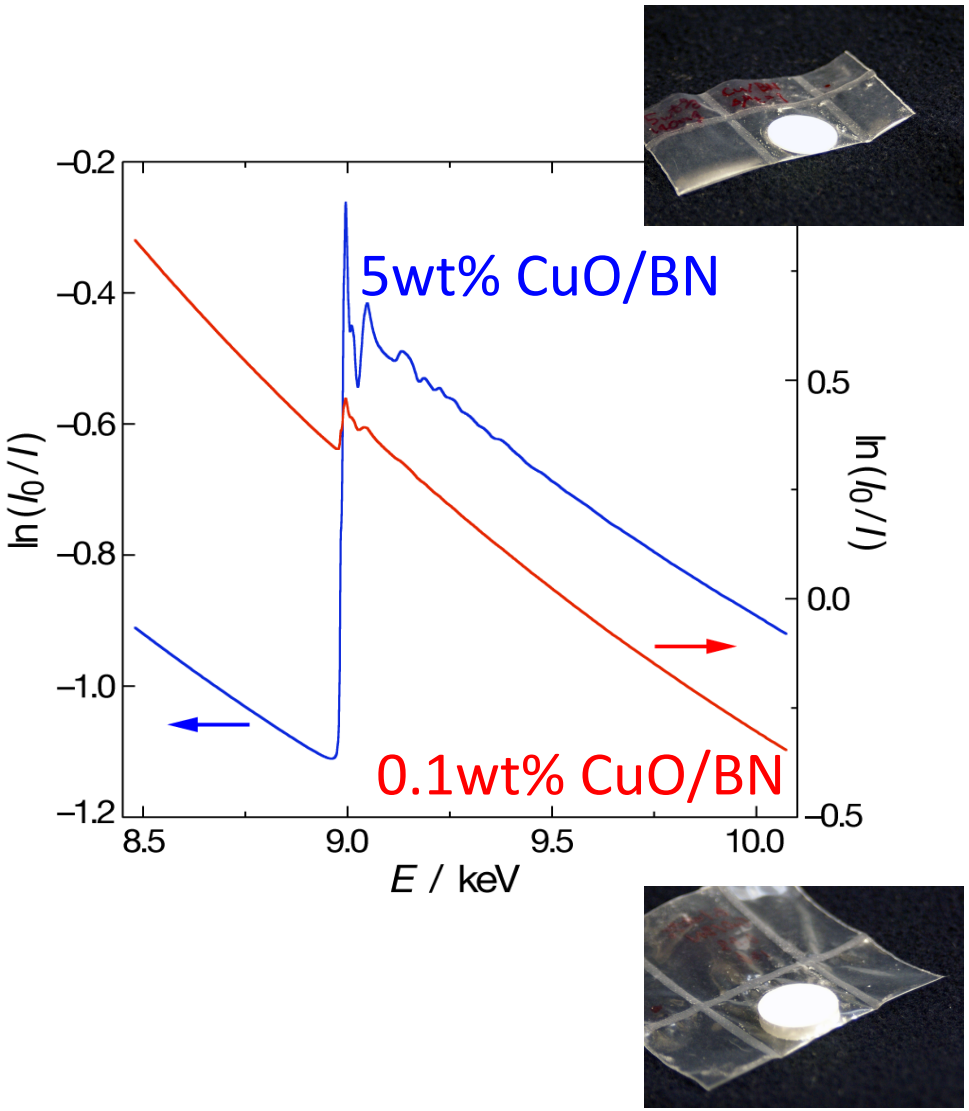
Absorption $\mu t(\lambda) = \ln\left(\frac{I_0(\lambda)}{I(\lambda)}\right)$

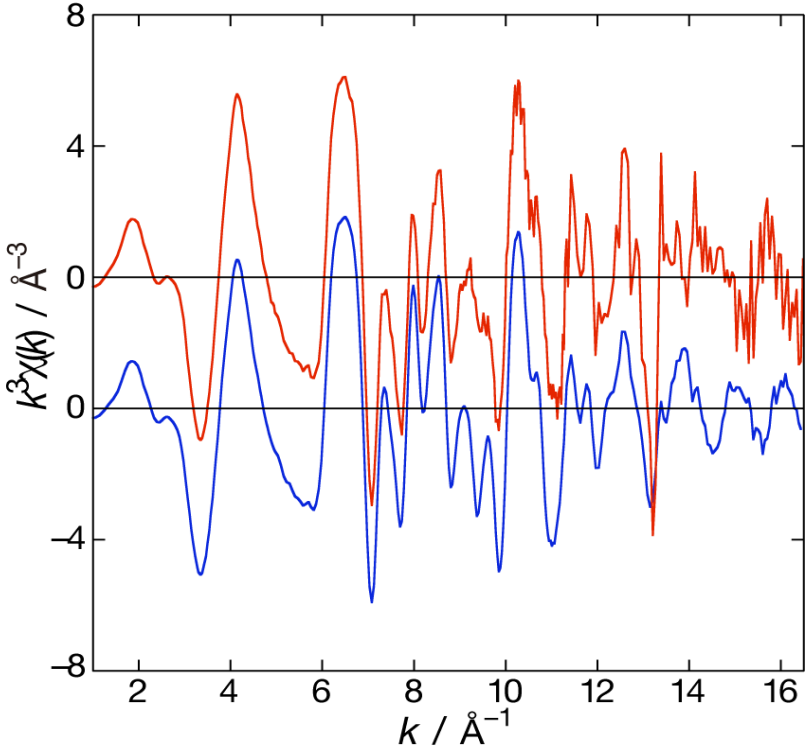




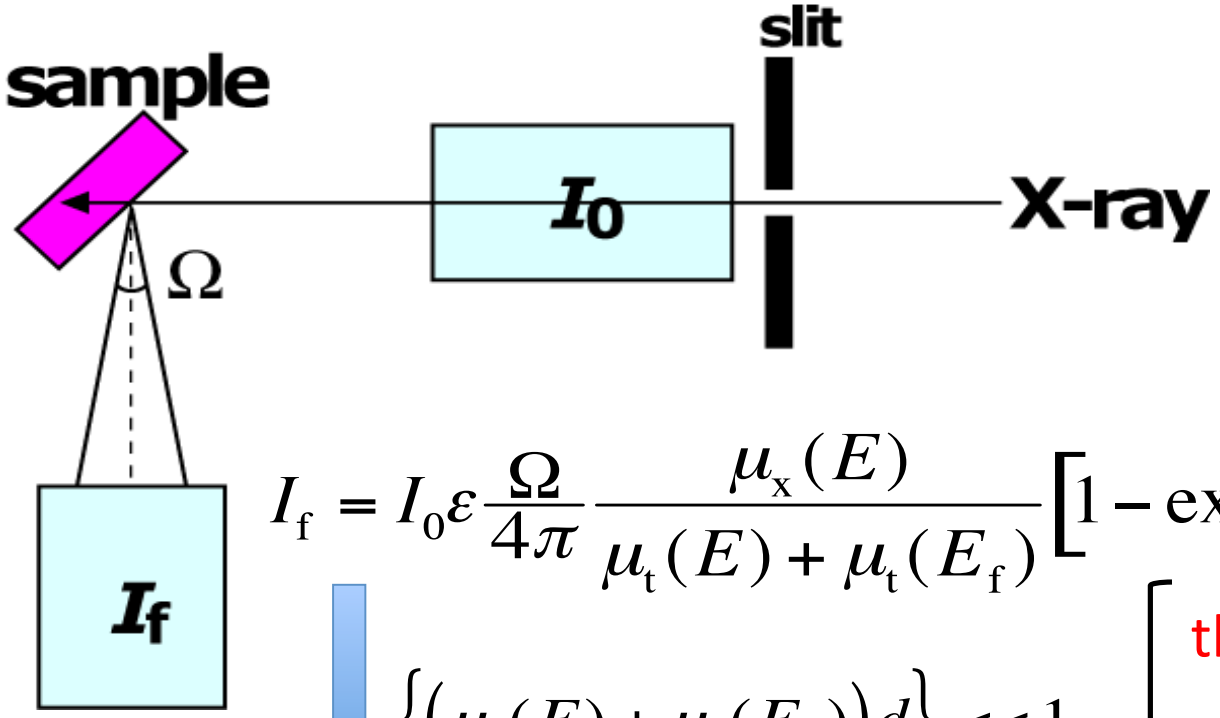


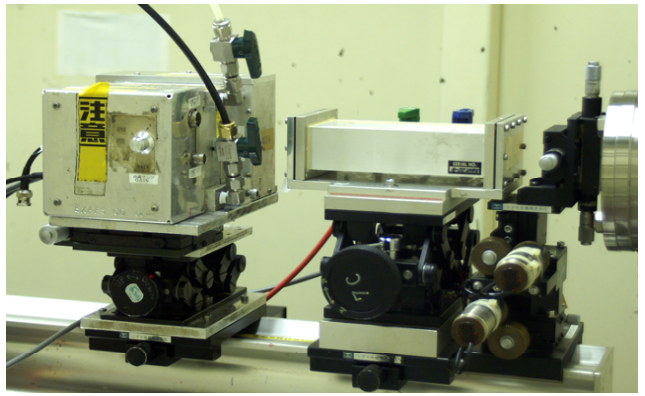
Transmission mode XAFS spectra





Fluorescence mode XAFS





$$I_f = I_0 \varepsilon \frac{\Omega}{4\pi} \frac{\mu_x(E)}{\mu_t(E) + \mu_t(E_f)} \left[1 - \exp\left\{-\left(\mu_t(E) + \mu_t(E_f)\right)d\right\}\right]$$

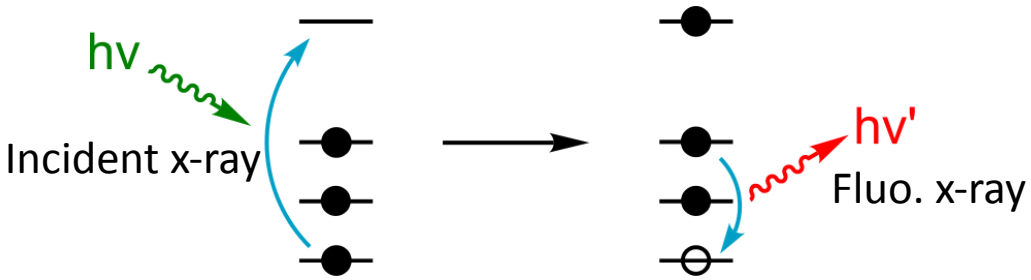
$$\left\{\left(\mu_t(E) + \mu_t(E_f)\right)d\right\} << 1$$

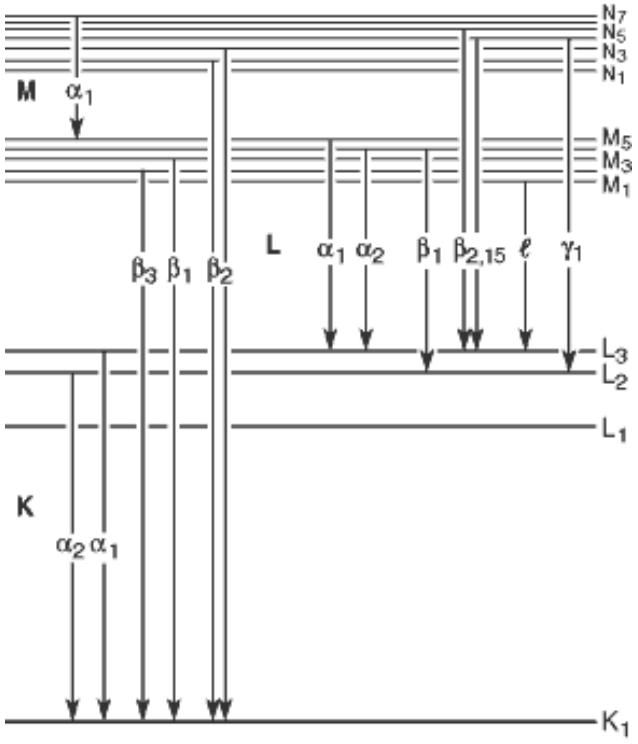
- thick but dilute
  - (ex. 0.01 M aq.)
- concentrated but thin
  - (ex. 1000 Å film)

$$I_f = I_0 \varepsilon \frac{\Omega}{4\pi} \mu_x(E) d$$

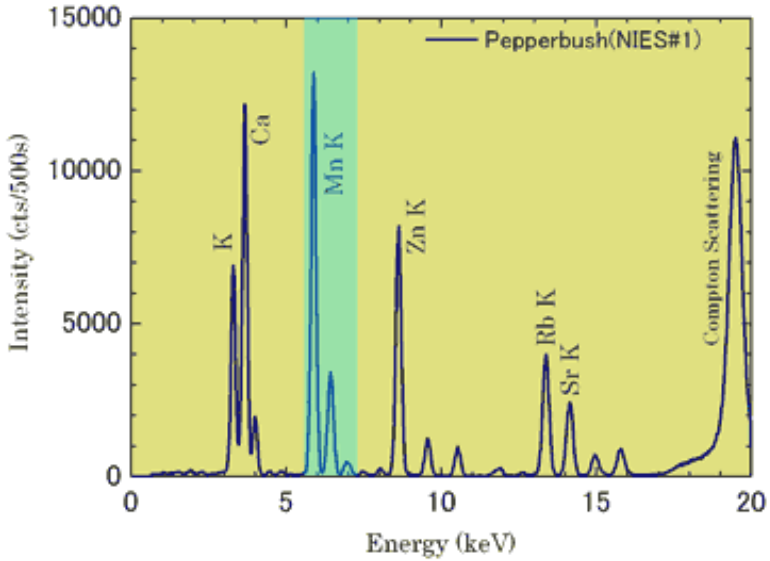
$$\therefore \frac{I_f}{I_0} \propto \mu_x(E)$$

Element specific emission: Fluorescent x-ray



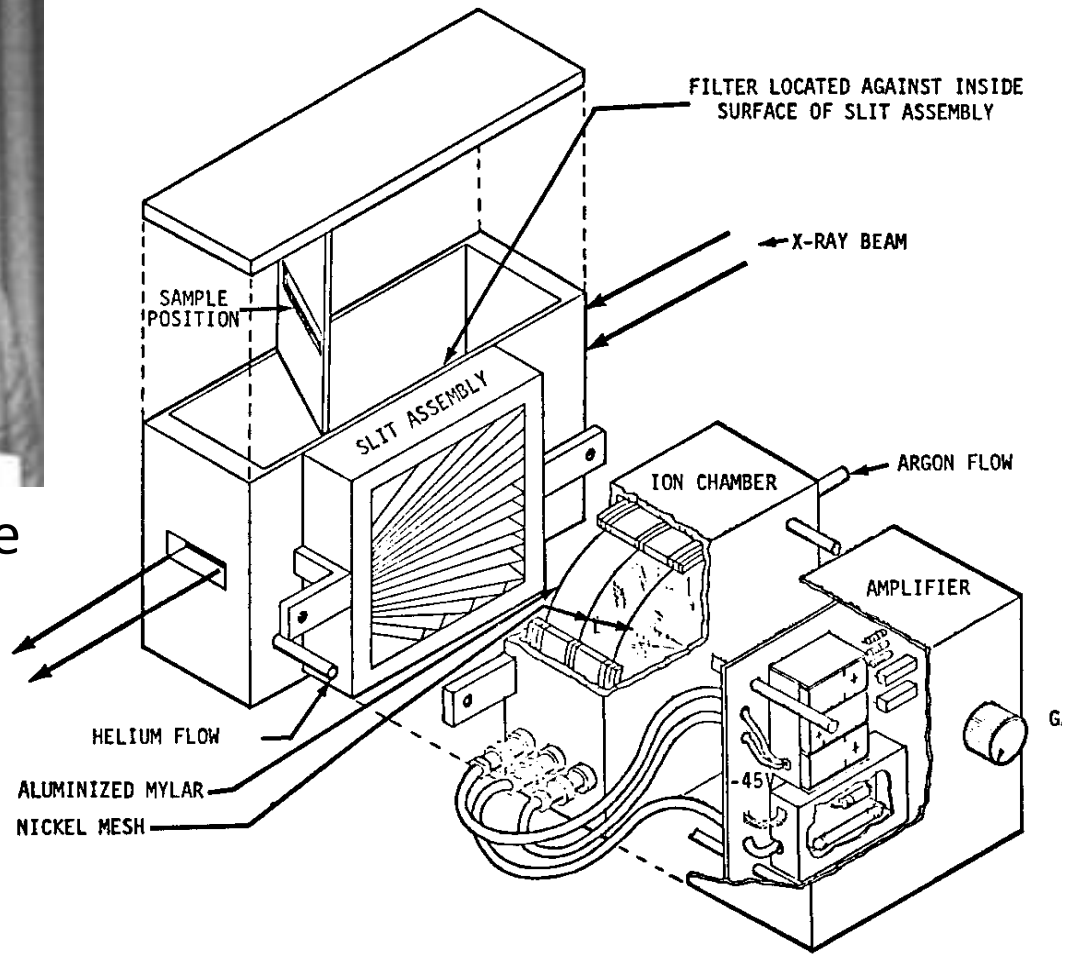


Element	Kα1	Kα2
22 Ti	4,510.84	4,504.86
23 V	4,952.20	4,944.64
24 Cr	5,414.72	5,405.509
25 Mn	5,898.75	5,887.65
26 Fe	6,403.84	6,390.84
27 Co	6,930.32	6,915.30
28 Ni	7,478.15	7,460.89
29 Cu	8,047.78	8,027.83
30 Zn	8,638.86	8,615.78



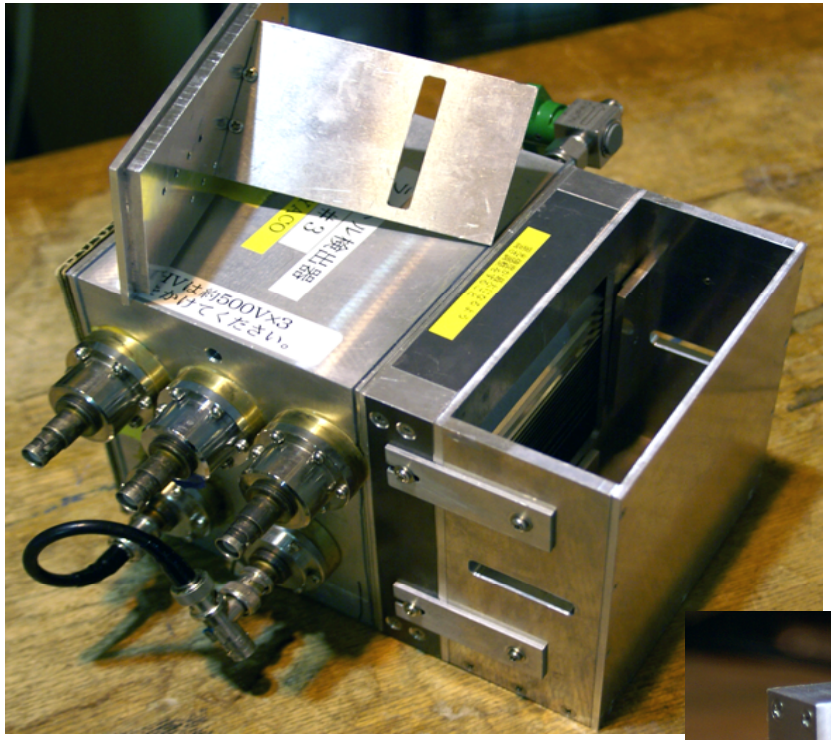
Ion chamber for Fluo. XAFS: Lytle Detector

Dr. Farrel W. Lytle

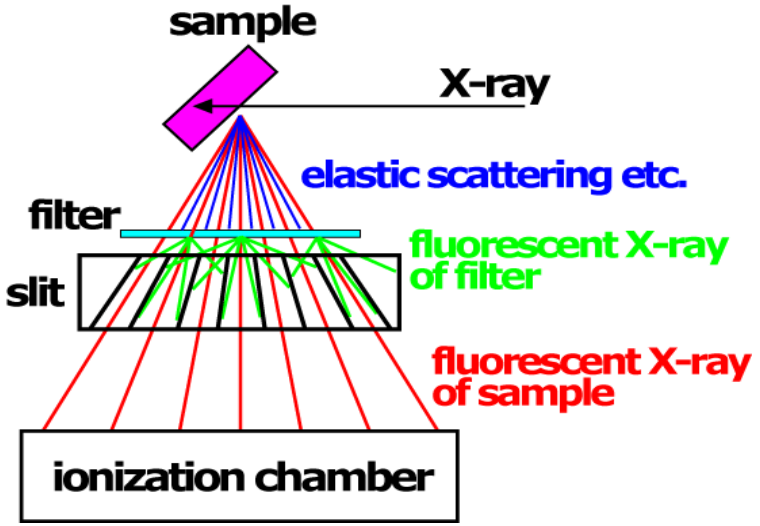


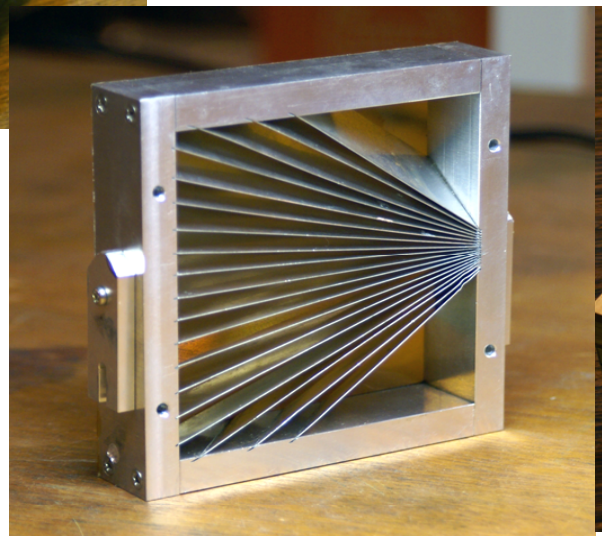
Not expensive, large solid angle, home made possible

Ion chamber for Fluo. XAFS: Lytle Detector



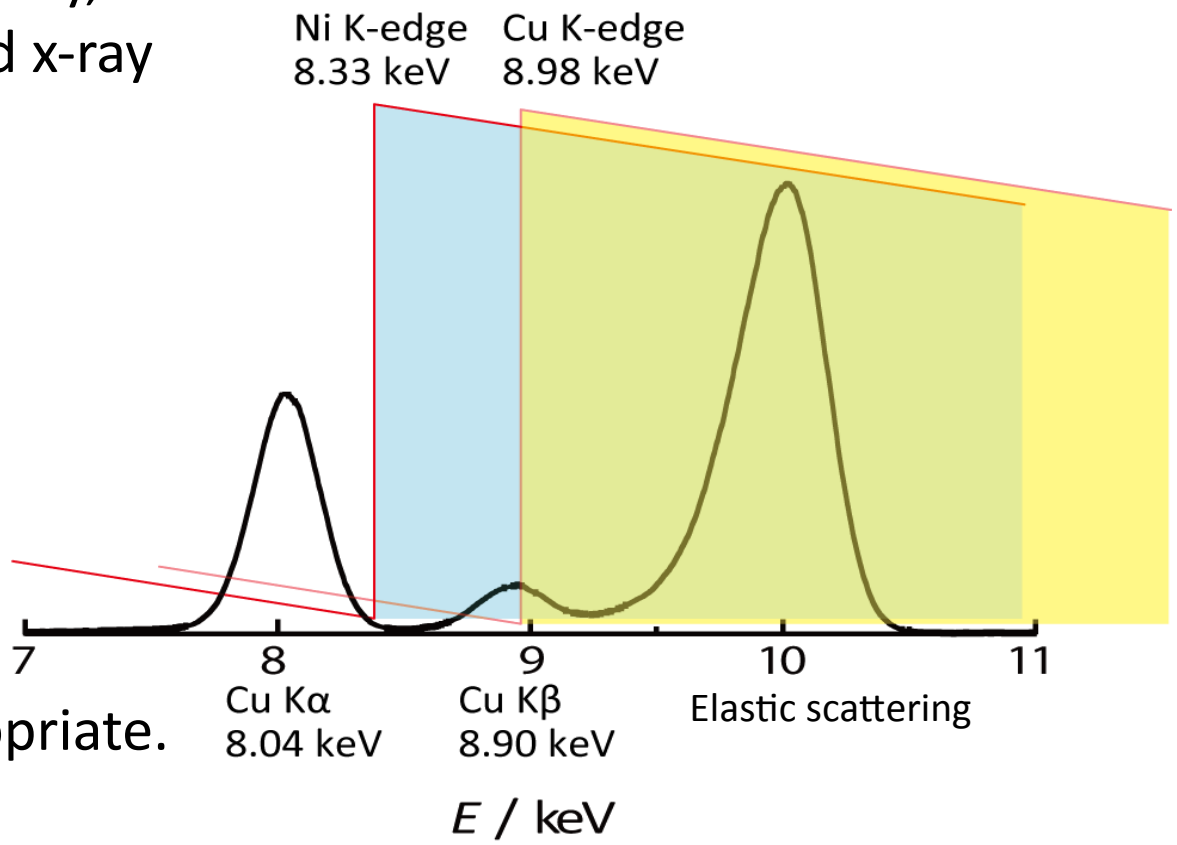
Lytle Detector made at PF





Function of the filter

Transparent for Fluorescent x-ray,
absorbing elastically scattered x-ray

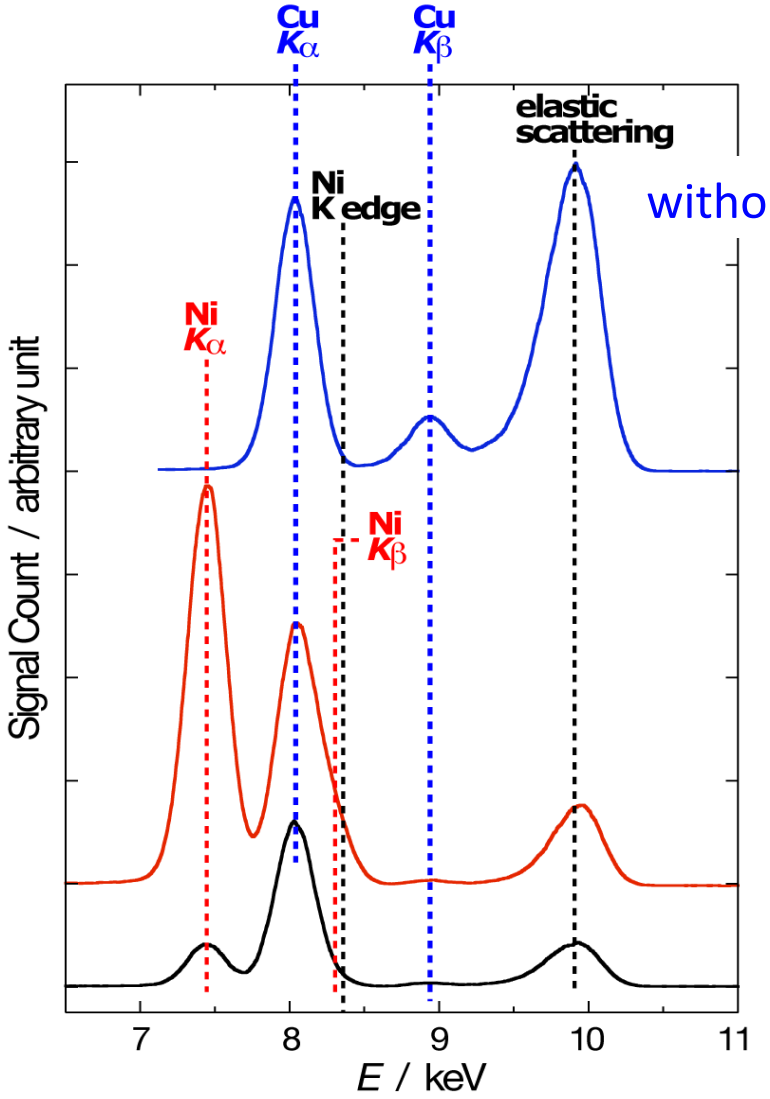


A "Z-1" filter is mostly appropriate.

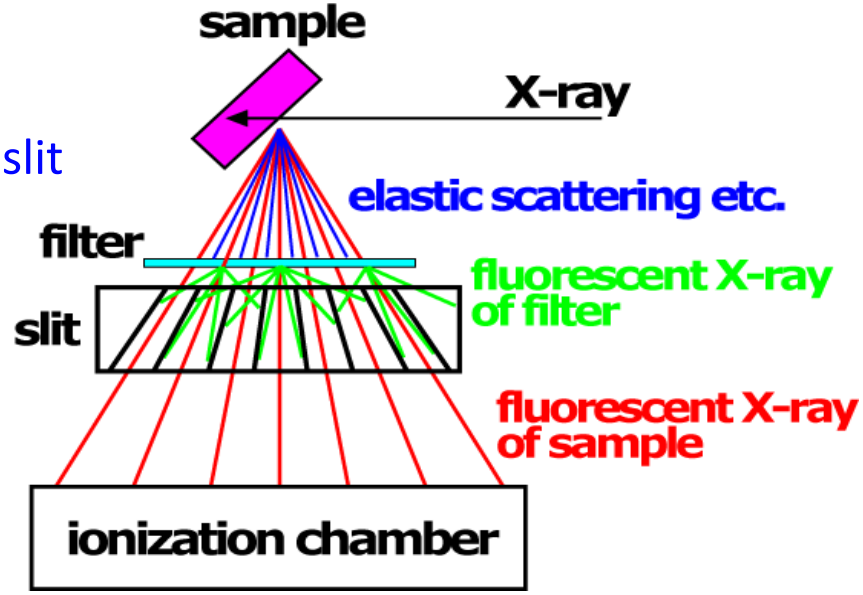
when we would like to detect Cu K_α x-ray,

A Ni filter is appropriate.

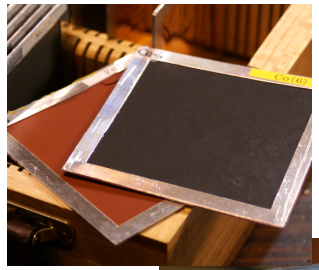
Function of Filter & Soller slit of Lytle detector



without filter or soller slit

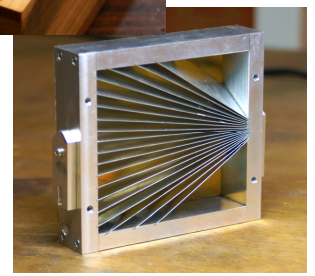


with Ni filter (μt=6)
but without soller slit



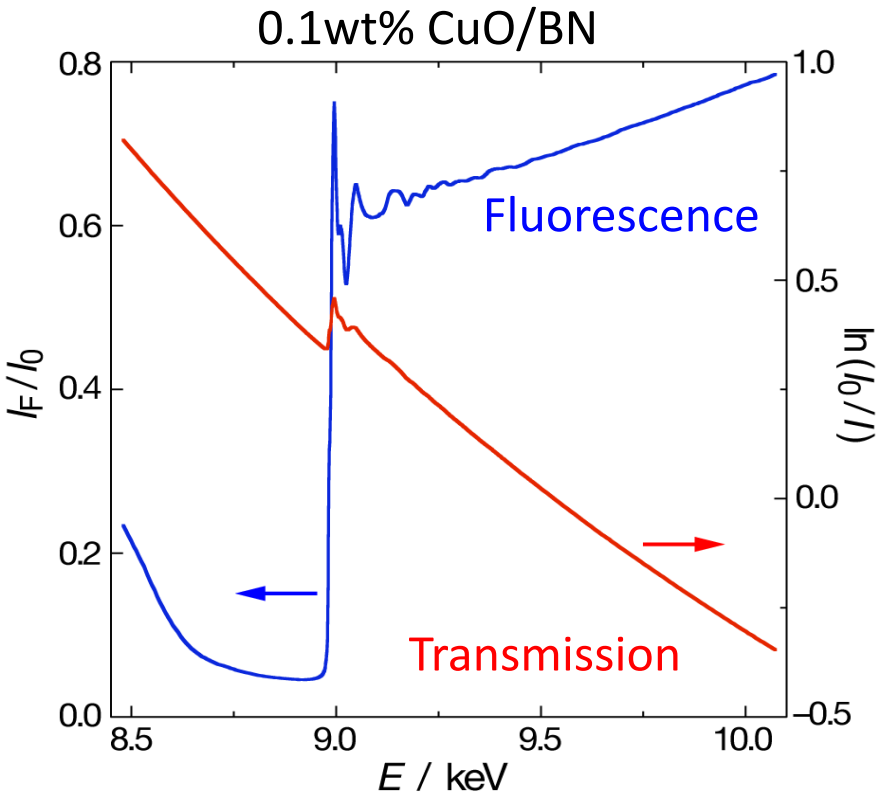
with Ni filter (μt=6) & soller slit

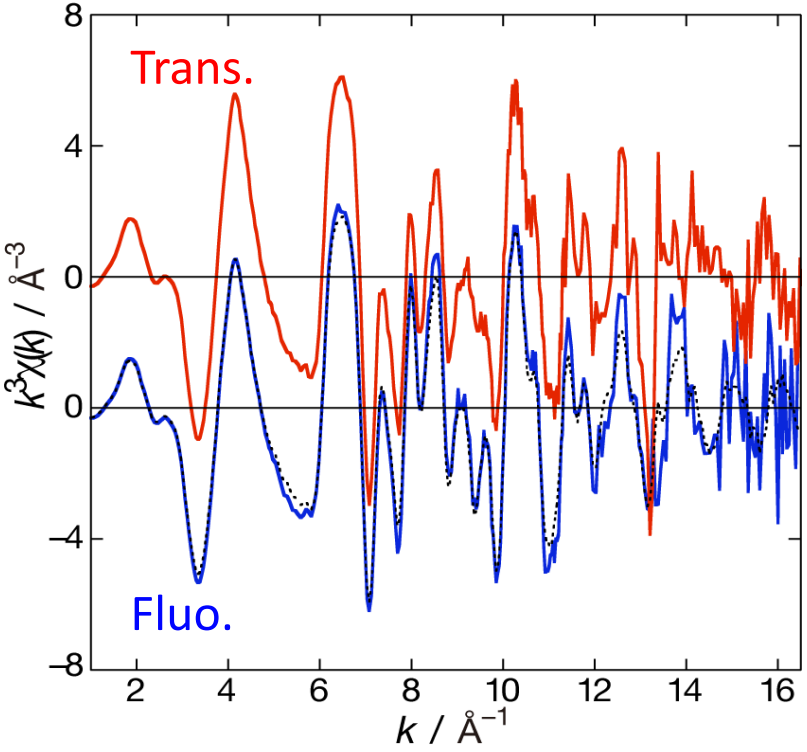
+



Sample: 2 mM CuSO4 aq.

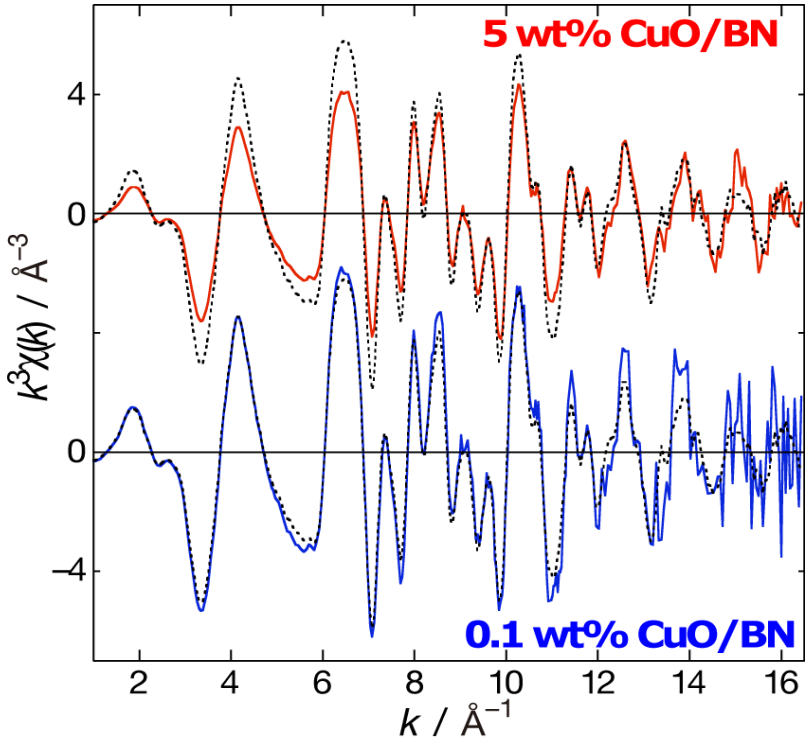
Trans. mode & Fluo. mode

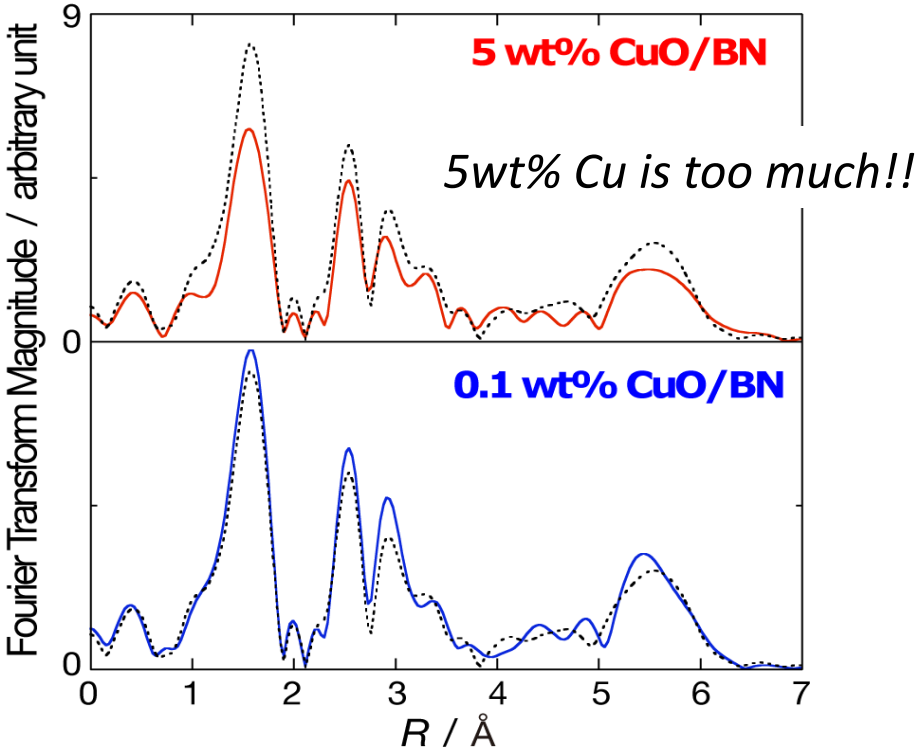




Suitable sample for Fluo. mode XAFS

dotted line: trans mode XAFS for 5wt% sample



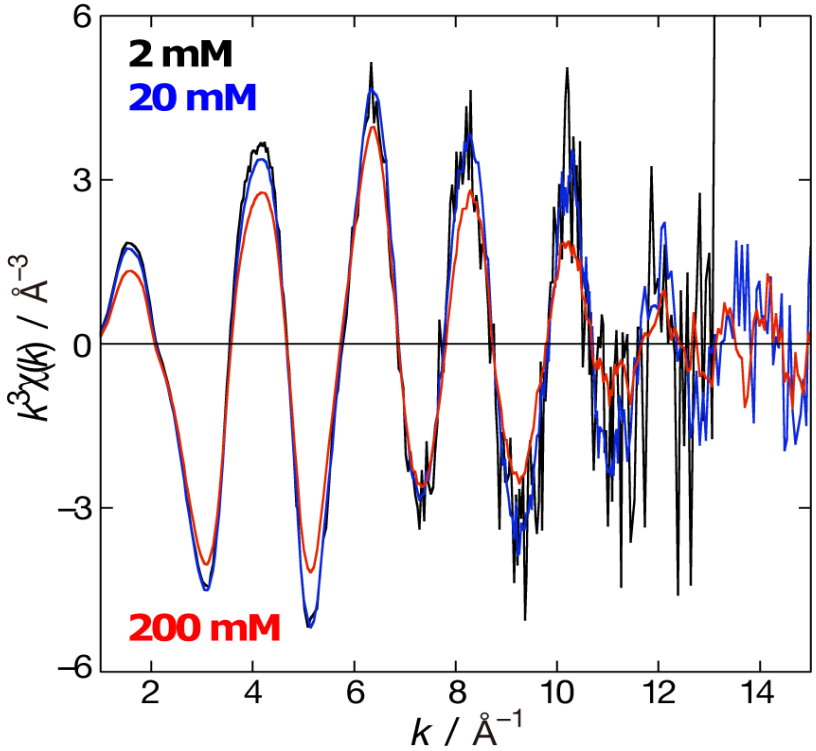


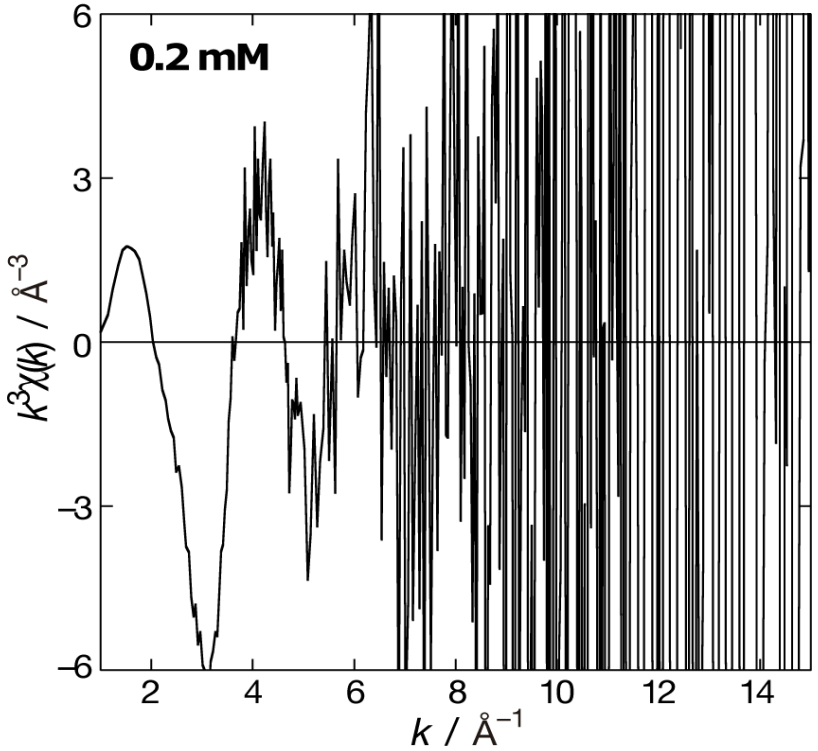
5wt% Cu is too much!!

Samples for Fluo. mode XAFS must be...

- thick but **dilute**: ex. 0.01 M (10 mM) aq.
- concentrated but **thin**: ex. 1000 Å thin film

Suitable sample condition for Fluo. mode XAFS





for $CuSO_4$ solution

dencity	0.2 mM	2 mM	20 mM	200 mM
weight percent	0.0013 wt%	0.013 wt%	0.13 wt%	1.3 wt%
atomic percent	0.00036 at%	0.0036 at%	0.036 at%	0.36 at%

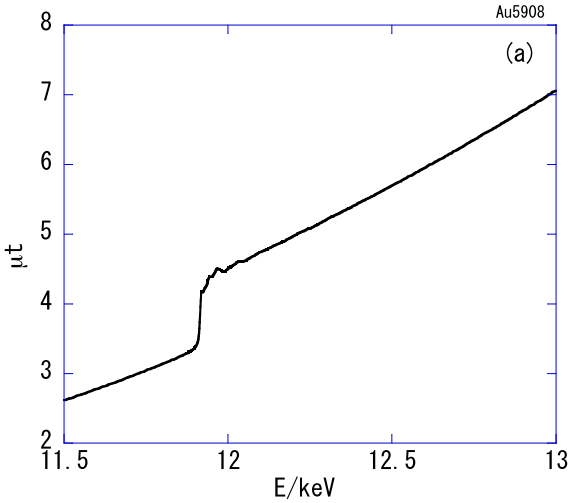
Si detector (Solid State Detector , SSD)

electrically energy analized,
not filter or slit

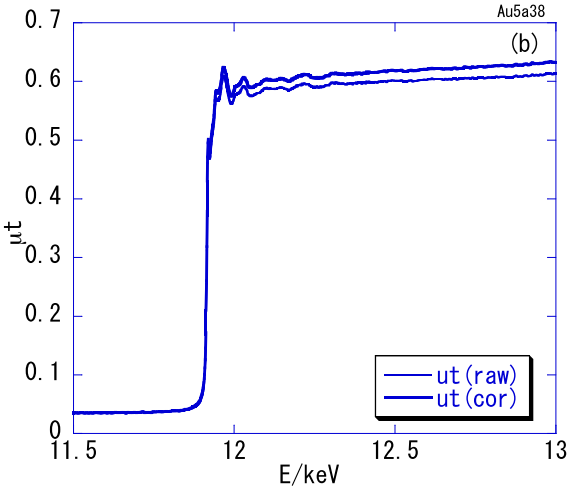
4×10^{-4} Au in AgX

19-element SSD

Lytle detector

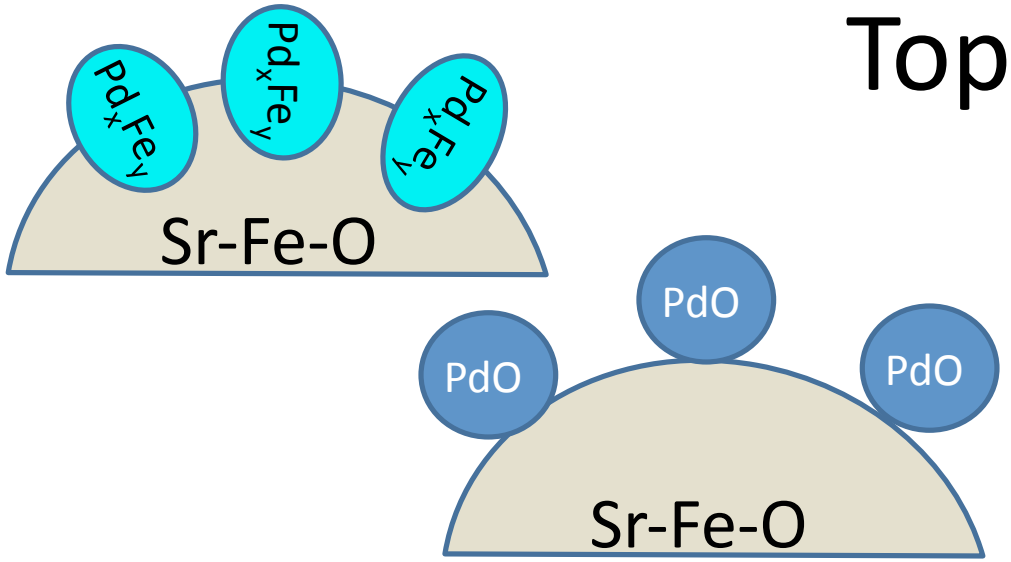


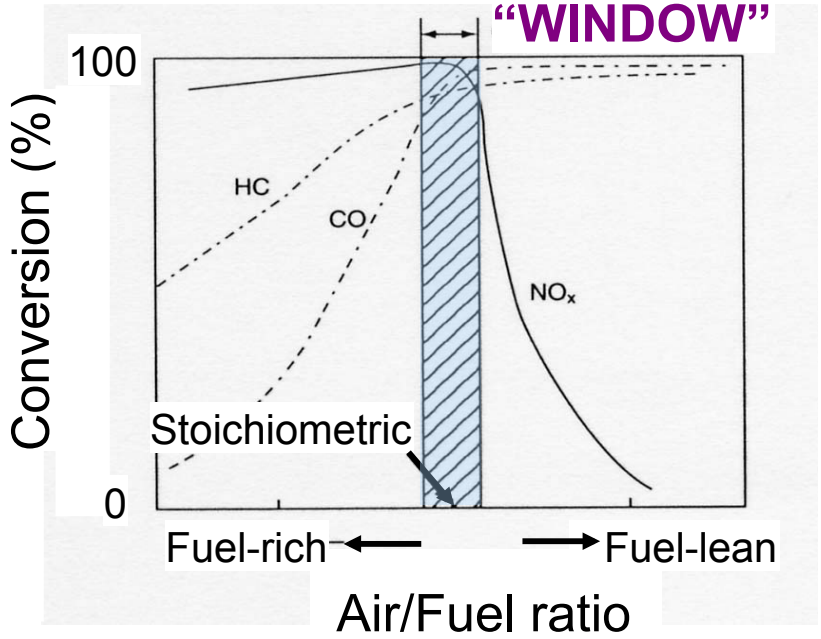
Si detector

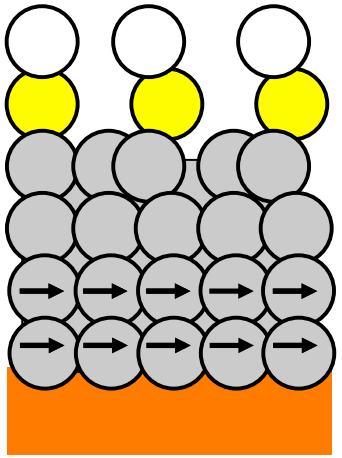


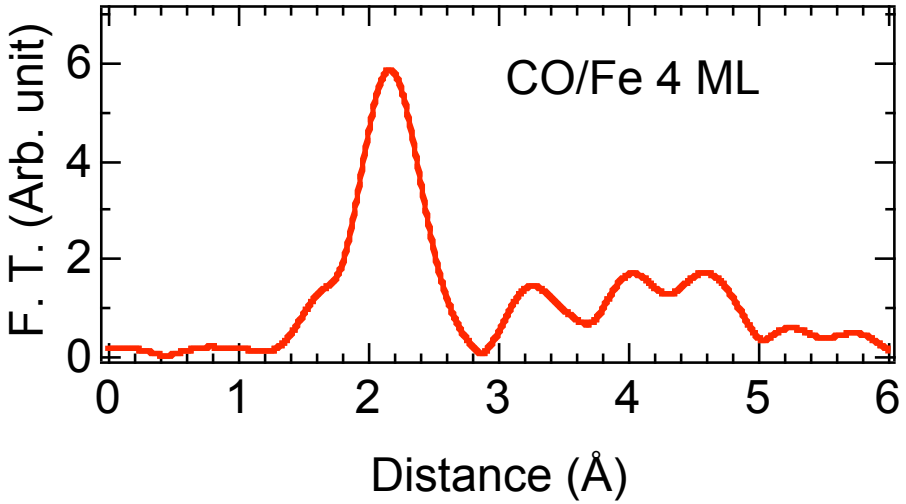
expensive, skills required for usage and maintenance

Topics


Pd_xFe_y
Pd_xFe_y
Pd_xFe_y
Sr-Fe-O
PdO
PdO
PdO
Sr-Fe-O


"WINDOW"
100
0
Conversion (%)
HC
CO
NO_x
Stoichiometric
Fuel-rich
Fuel-lean
Air/Fuel ratio




CO/Fe 4 ML
F. T. (Arb. unit)
0
2
4
6
0
1
2
3
4
5
6
Distance (Å)

RedOx mechanisms of Pd catalysts for automotive emission studied by XAFS

Y. Niwa[1], M. Kimura[2], K.Uemura[2]▪, Y. Uemura[1], Y. Inada[3], M. Nomura[1]

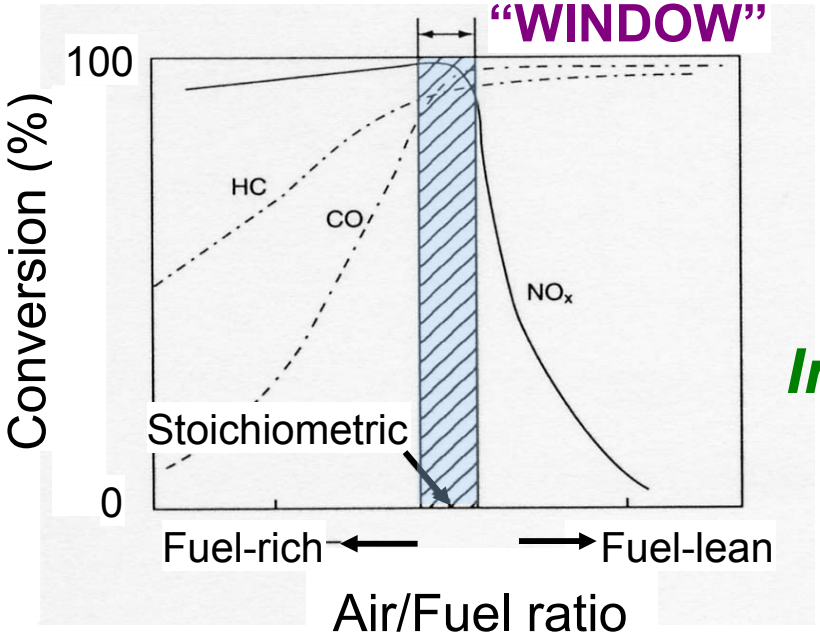
KEK-PF[1], Nippon Steel[2], Ritsumeikan Univ.[3]

Catalysts for automotive emission

Rh $NO_x \rightarrow N_2 + O_2$

Pt、Pd $2CO + O_2 \rightarrow 2CO_2$

Pt、Pd $4HC + 3O_2 \rightarrow 2CO_2 + 2H_2O$

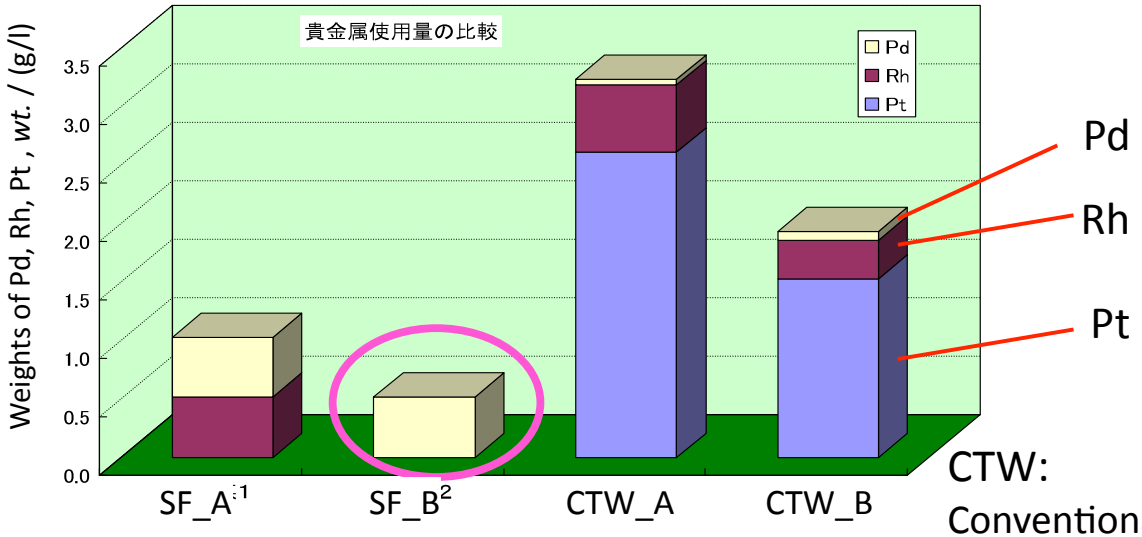


Performance of the catalyst depends on A/F

***In situ* observation of the catalyst during RedOx cycles**

Performance of the new catalyst

> Amounts of precious metals



Pd

Rh

Pt

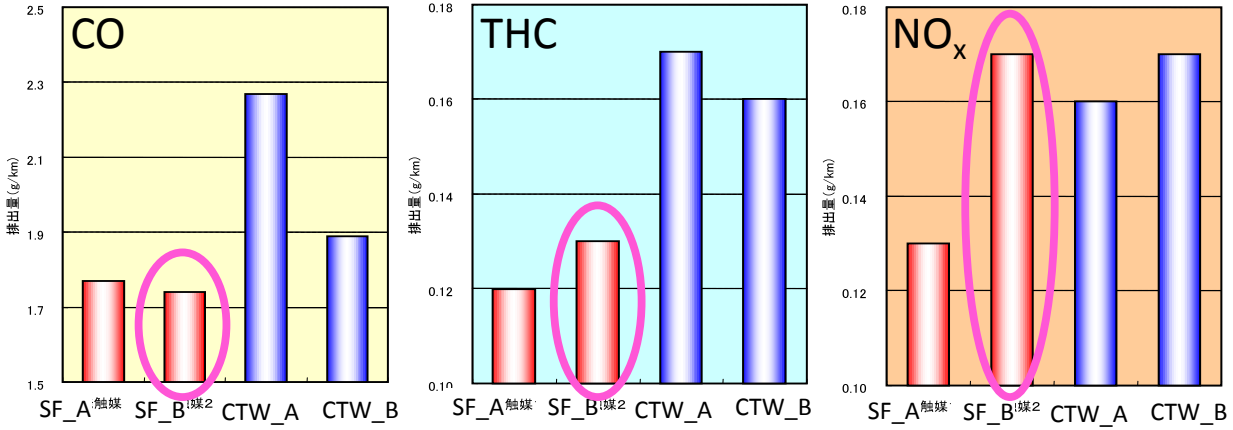
SF:

New catalysts
(Pd,Rh)/Sr-Fe-O

CTW:

Conventional three-way catalysts
(Pd,Rh,Pt)/(CeO_2+ZrO_2)

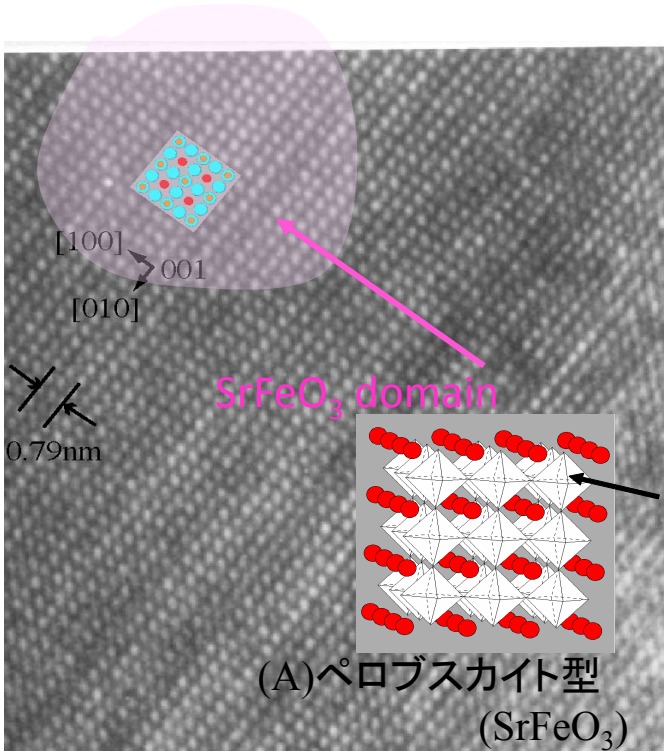
> Results of the performance test



Adv. Tech. Res. Lab., NIPPON STEEL, Dr. M. Kimura

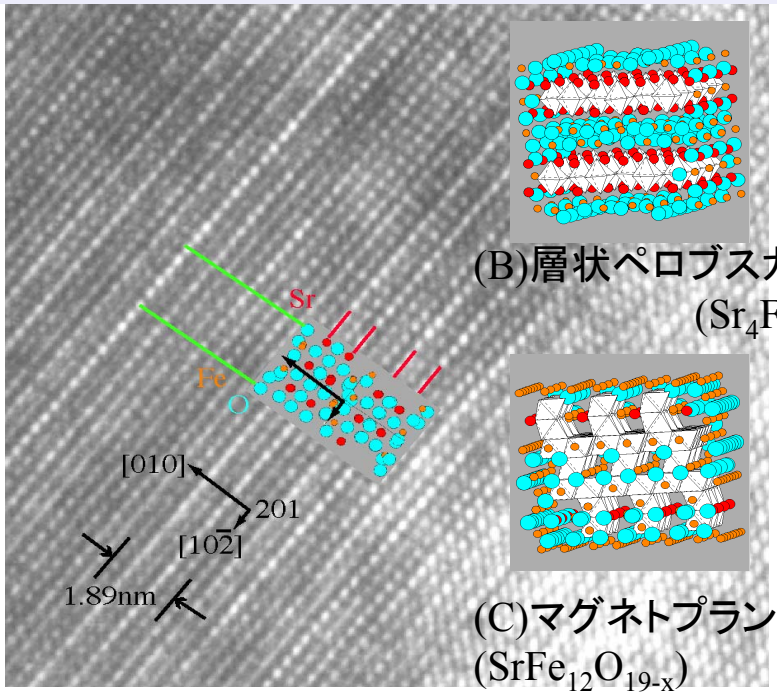
Microstructures of the Pd / Sr-Fe-O catalyst

Unique structure of the oxide:
"Multi-Phase Domain structures"



Other phases:

$SrFeO_3$ + $Sr_4Fe_6O_3$ + $SrFe_{12}O_{19}$



>Perovskite-type oxides

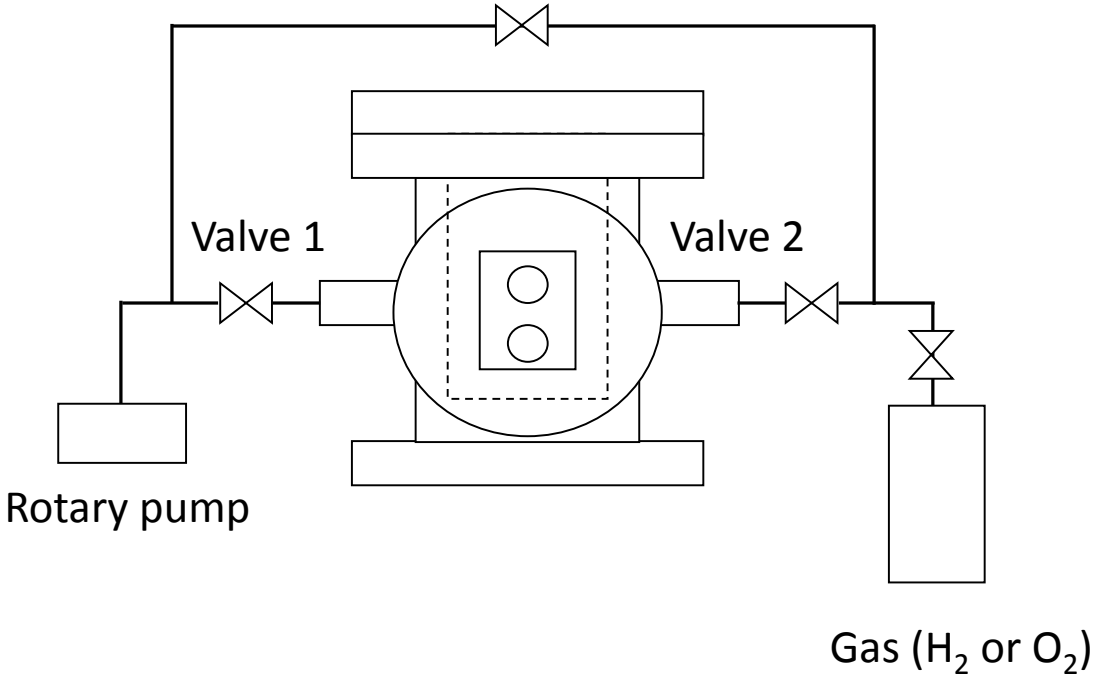
>The new catalyst showed an excellent performance of oxygen storage capacity (OSC) in 800 K< *T* < 1200 K

Experiment

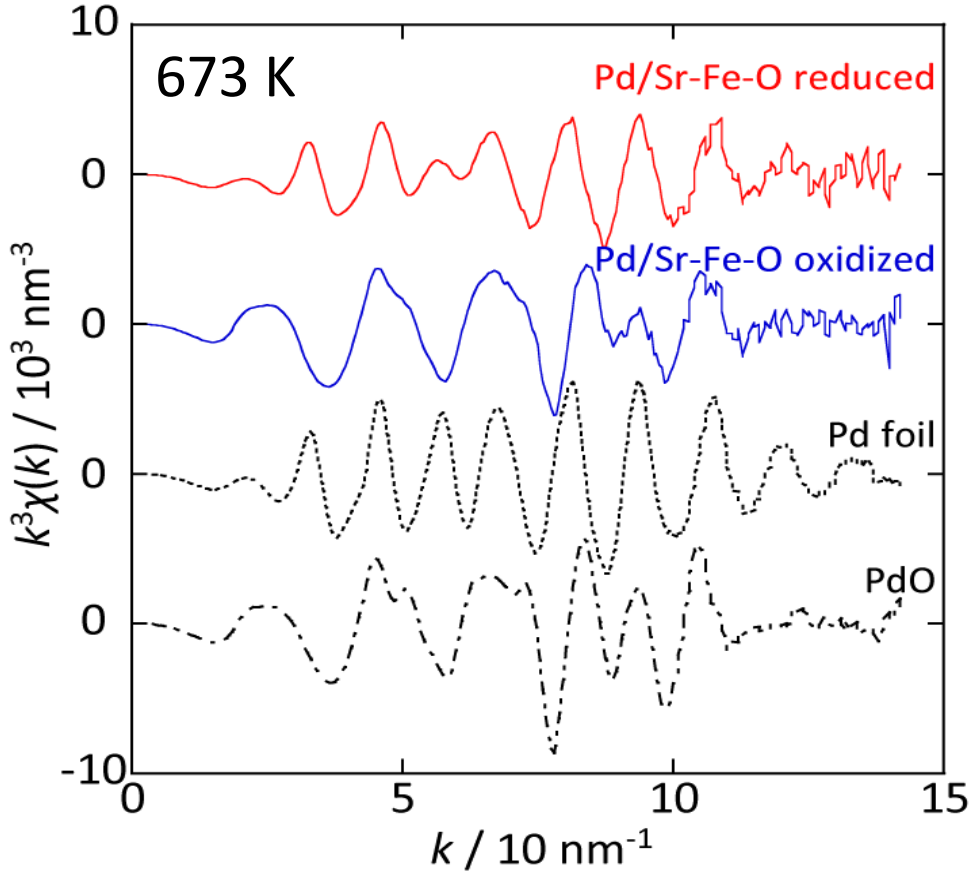
Sample: Pd/Sr-Fe-O (Pd 3wt%)

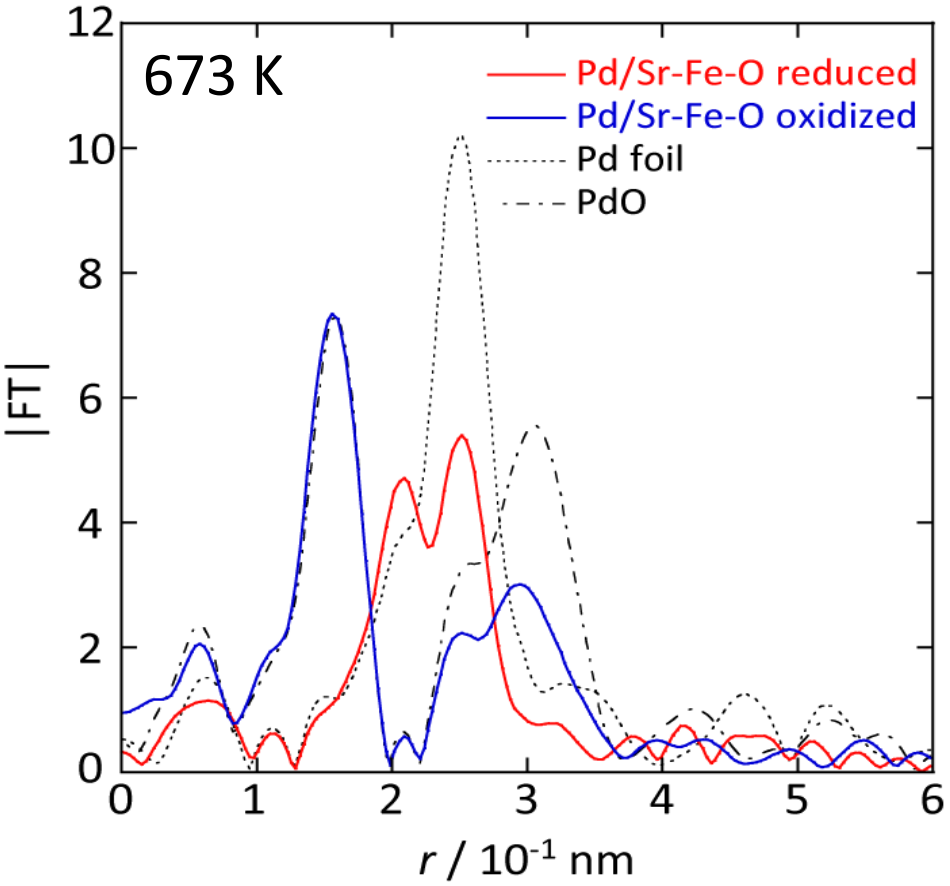
Reduction: H_2 (4.0 - 49.5 kPa)
Oxidation: O_2 (4.1 - 61.8 kPa)
Temp.: 673 K

Cell for *in situ* experiment



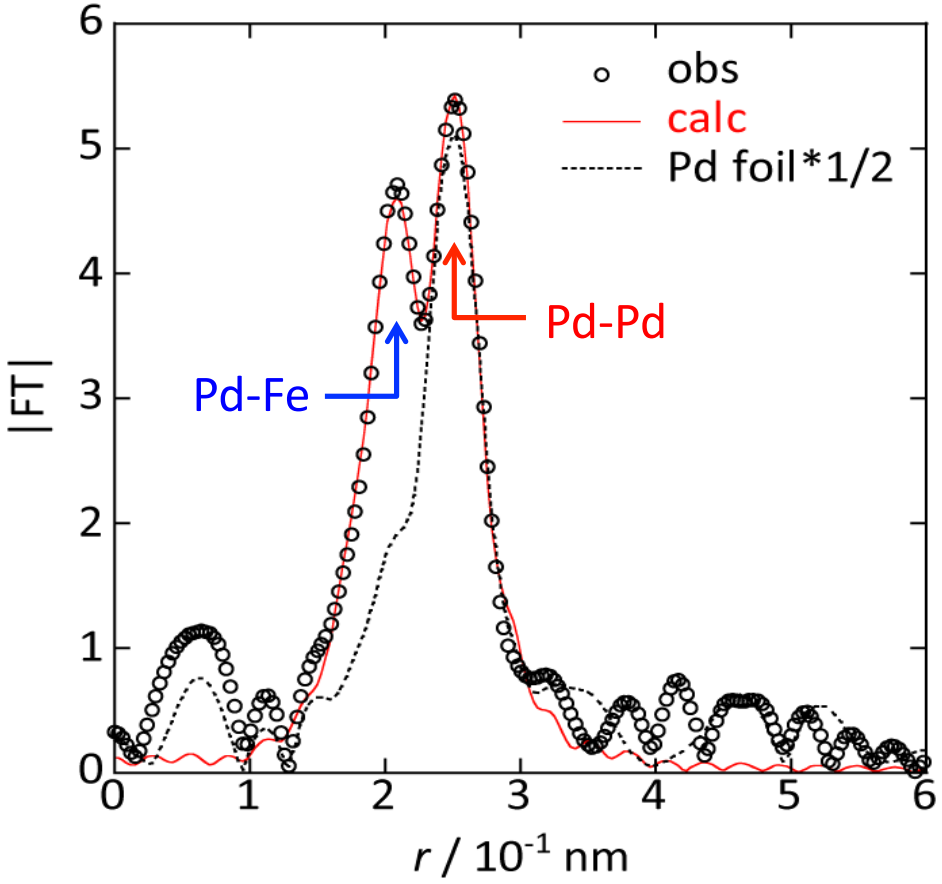
Pd structures of reduced and oxidized states



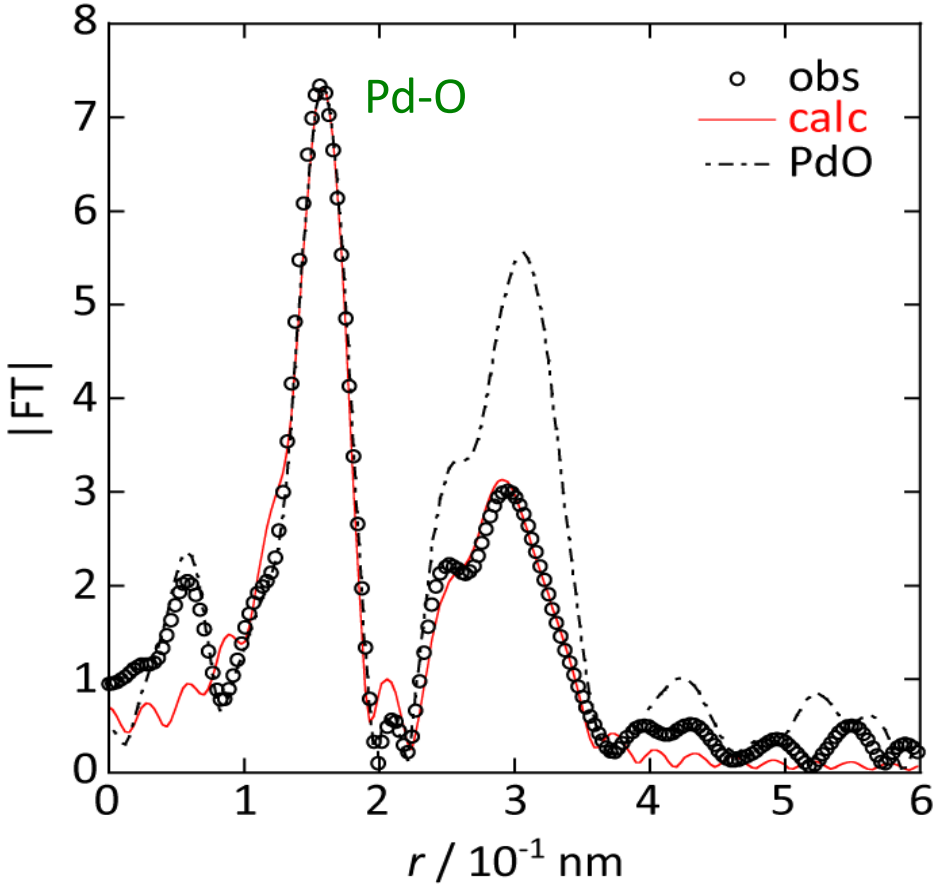


EXAFS fitting analyses with standards

Reduced



Oxidized



An interaction of Pd-Fe was considered.

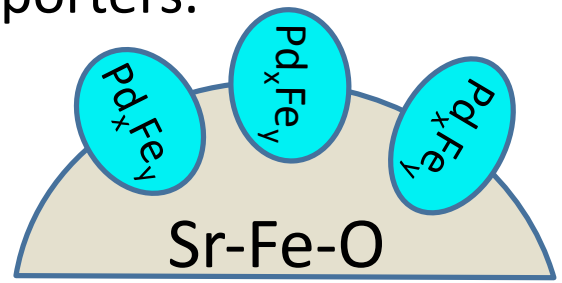
Structural parameters obtained by EXAFS analyses

		Pd/Sr-Fe-O @673 K		Reference@673 K	
		Reduced	Oxidized	PdO	Pd foil
	S_0^2	0.968918*2	1.018803*1	1.018803*1	0.968918*2
Pd(II)-O	N		3.6	3.3	
	r / 10^{-1} nm		2.02	2.03	
	σ^2 / 10^{-2} nm^2		0.0055	0.0050	
	ΔE_0 / eV		12.87	13.92	
Pd(0)-Fe	N	1.5			
	r / 10^{-1} nm	2.58			
	σ^2 / 10^{-2} nm^2	0.0098			
	ΔE_0 / eV	-3.372			
Pd(0)-Pd(0)	N	5.6			10.2
	r / 10^{-1} nm	2.72			2.73
	σ^2 / 10^{-2} nm^2	0.013			0.012
	ΔE_0 / eV	2.10			3.26
Pd(II)-Pd(II)	N		1.7	3.3	
	r / 10^{-1} nm		3.02	3.05	
	σ^2 / 10^{-2} nm^2		0.0074	0.0084	
	ΔE_0 / eV		6.689	11.10	
Pd(II)-Pd(II)	N		3.6	5.6	
	r / 10^{-1} nm		3.41	3.43	
	σ^2 / 10^{-2} nm^2		0.010	0.0092	
	ΔE_0 / eV		8.640	10.54	
*fixed value					
[1] The value was determined by the fitting procedure for PdO at 298 K.					
[2] The value was determined by the fitting procedure for Pd foil at 298 K.					

Pictures of the Pd catalysts

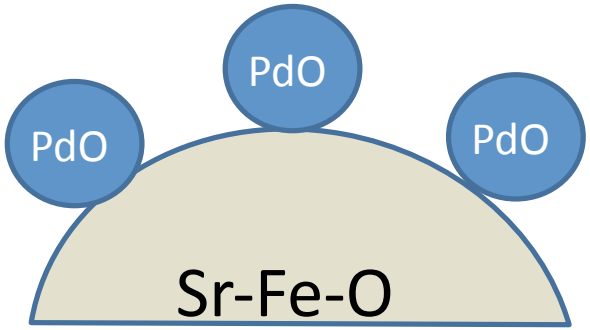
Reduced state

Pd strongly interacts with Fe in the supporter. Alloys should be formed. They are in the form of clusters on the supporters.



Oxidized state

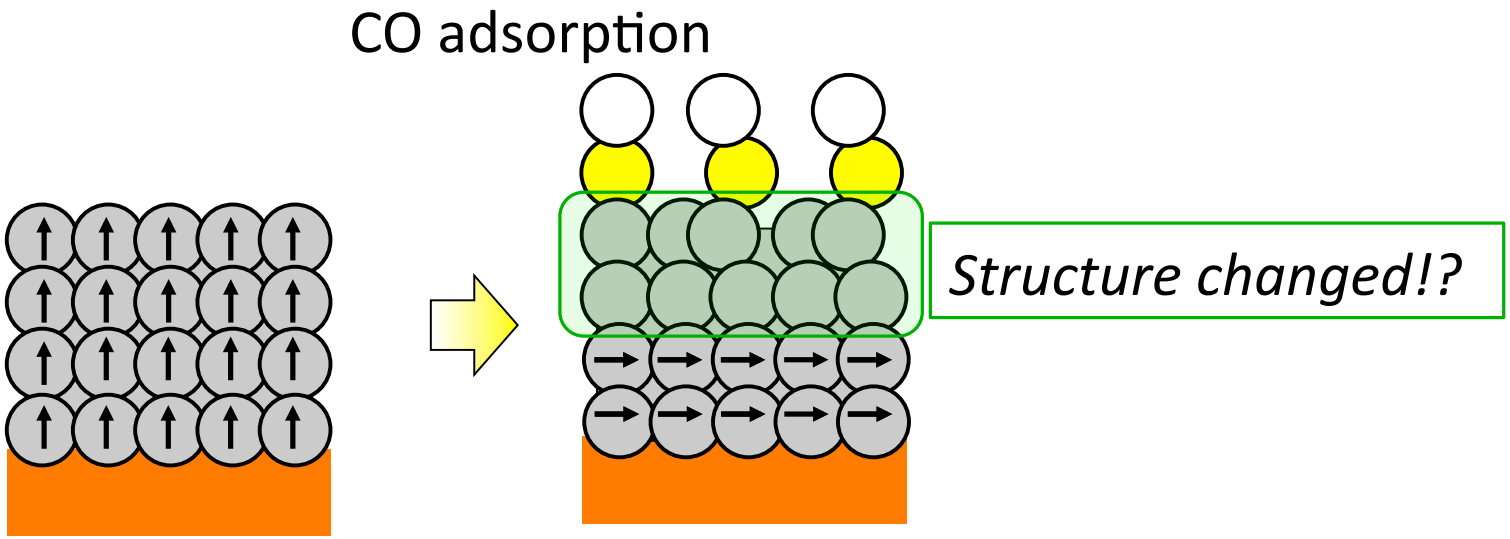
Pd are oxidized to PdO, and formed as clusters.



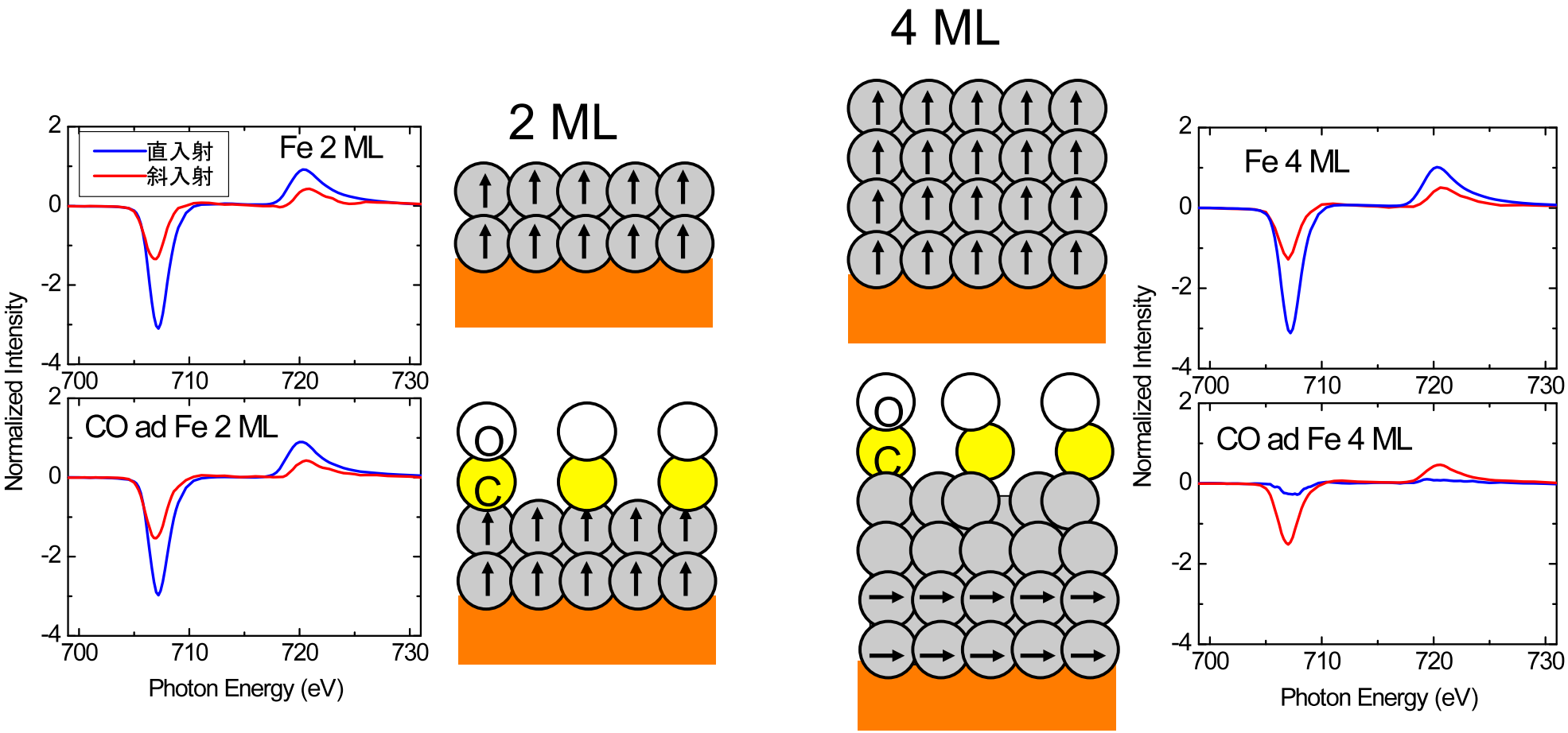
EXAFS study of Magnetic thin films

CO adsorption on Fe(4 ML)/Cu(001)changes the magnetic structure of the film.

What's going on its structure?



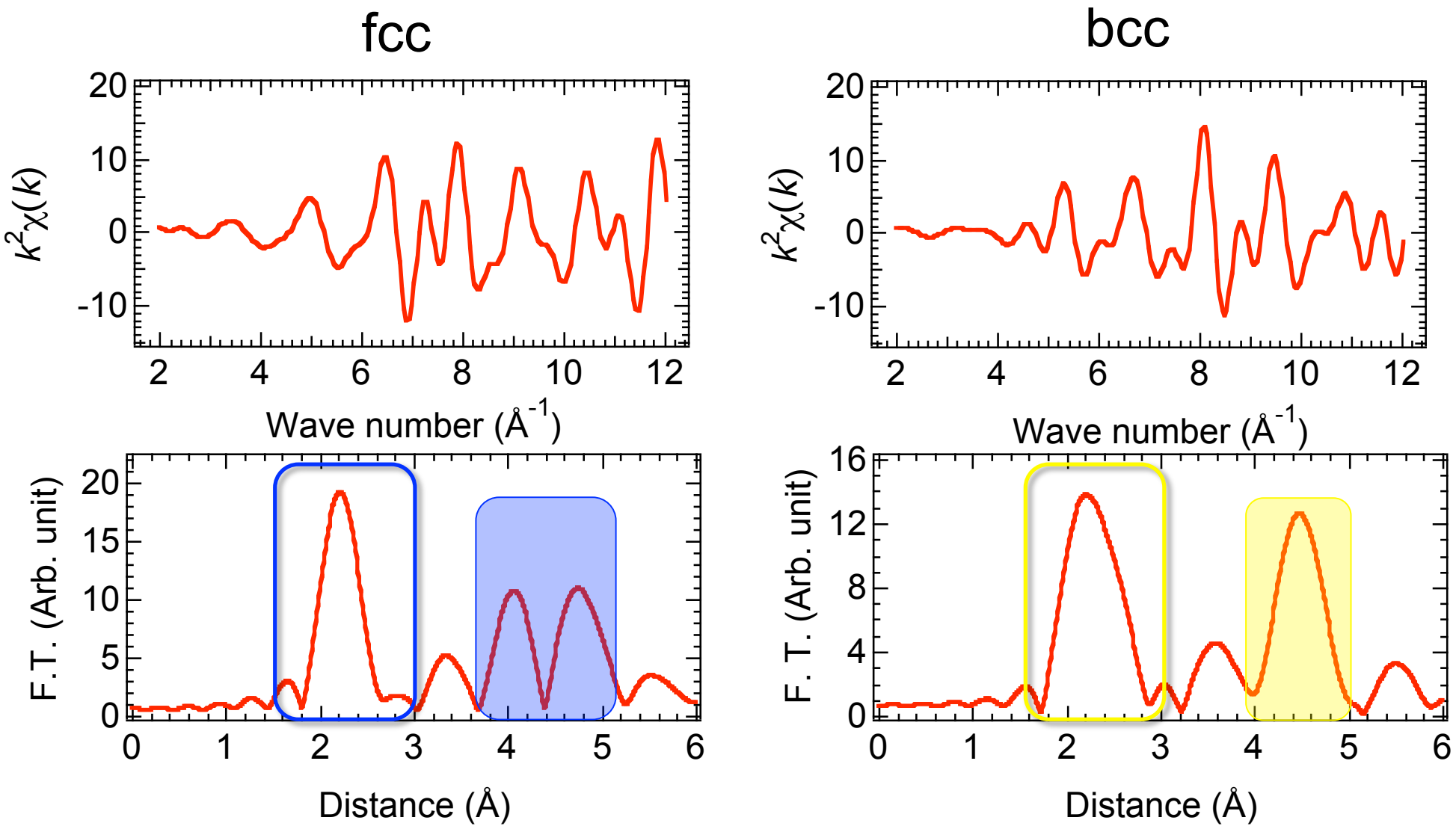
EXAFS experiment of magnetic thin films



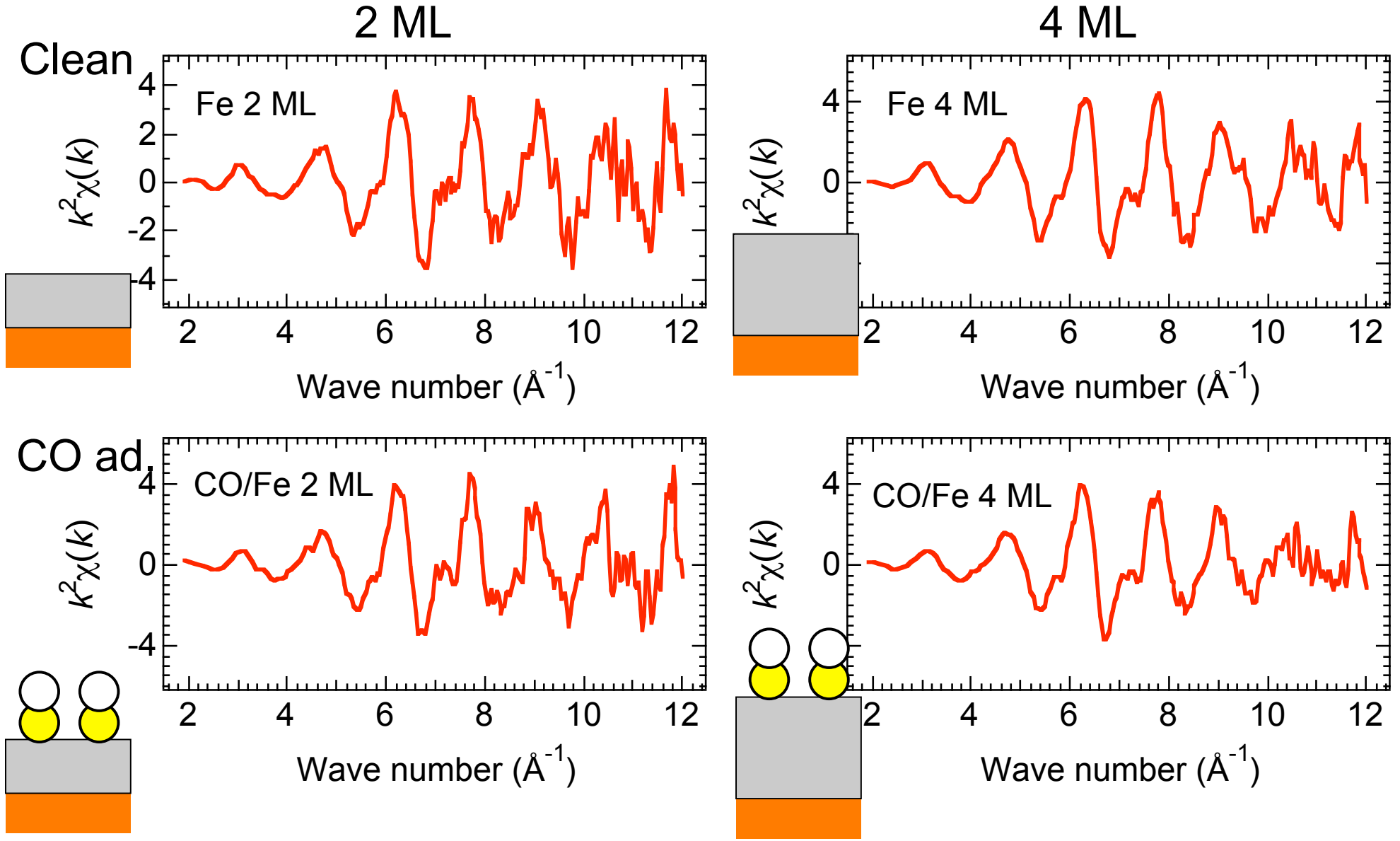
A structural change of the surface!?

→ EXAFS experiment

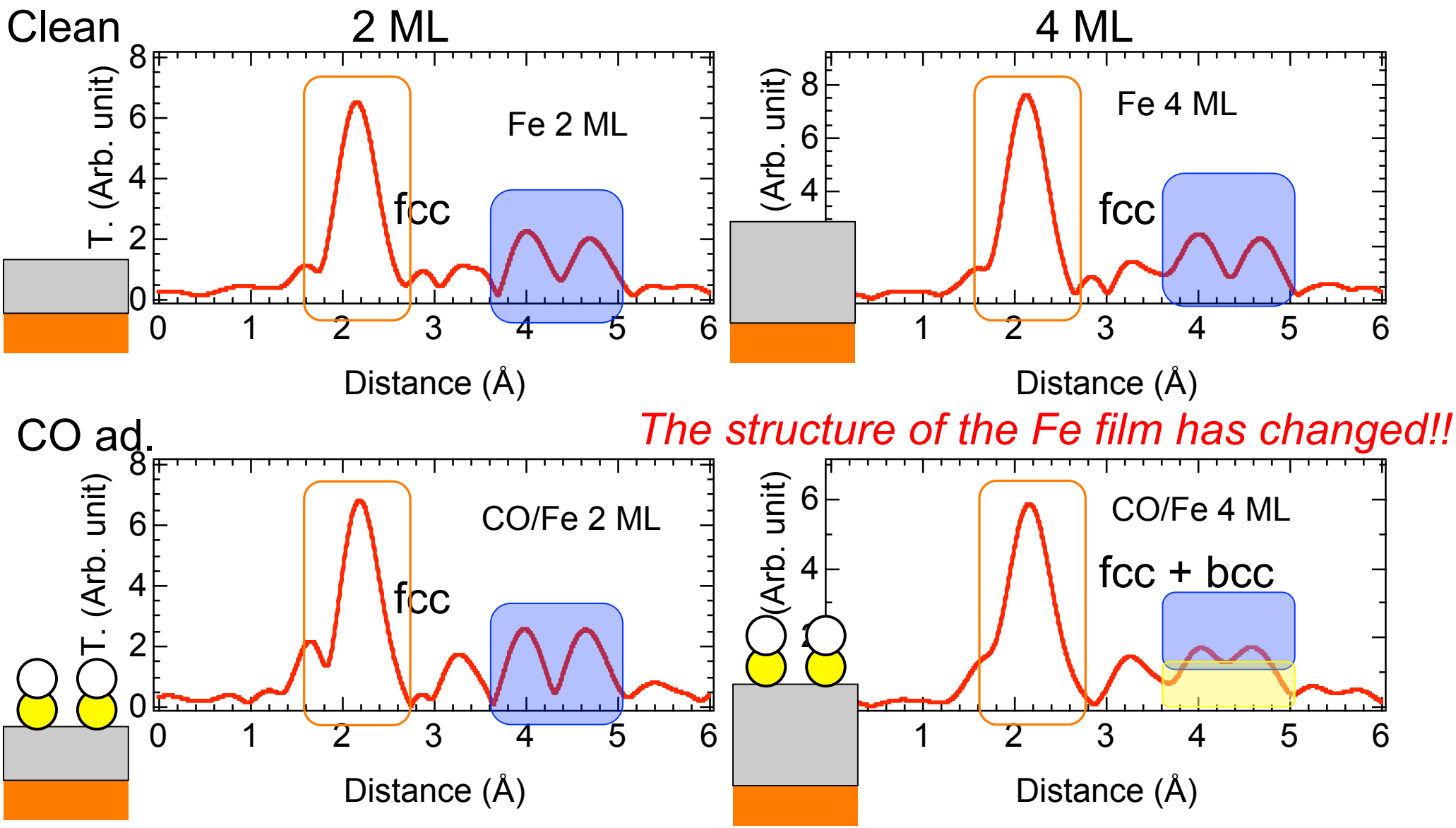
Fe-*K* EXAFS, FEFF simulation



Obtained EXAFS functions



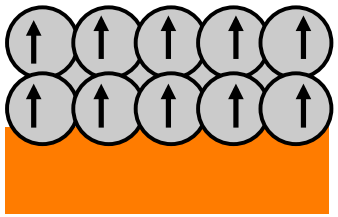
Fourier Transforms of $\chi(k)$



Possible model of structures of the films

Before CO ad. : fcc

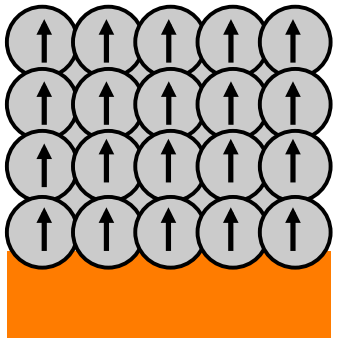
2 ML



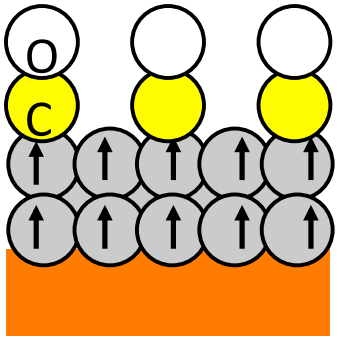
fcc

4 ML

fcc



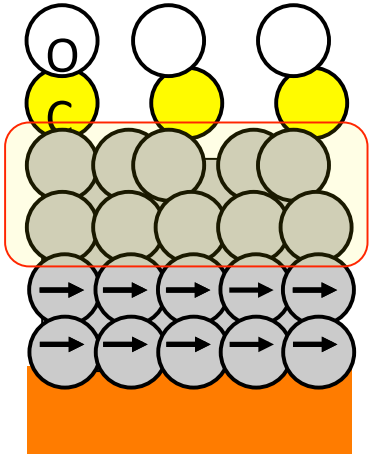
Changed to be fcc + strained-bcc



fcc

strained-bcc

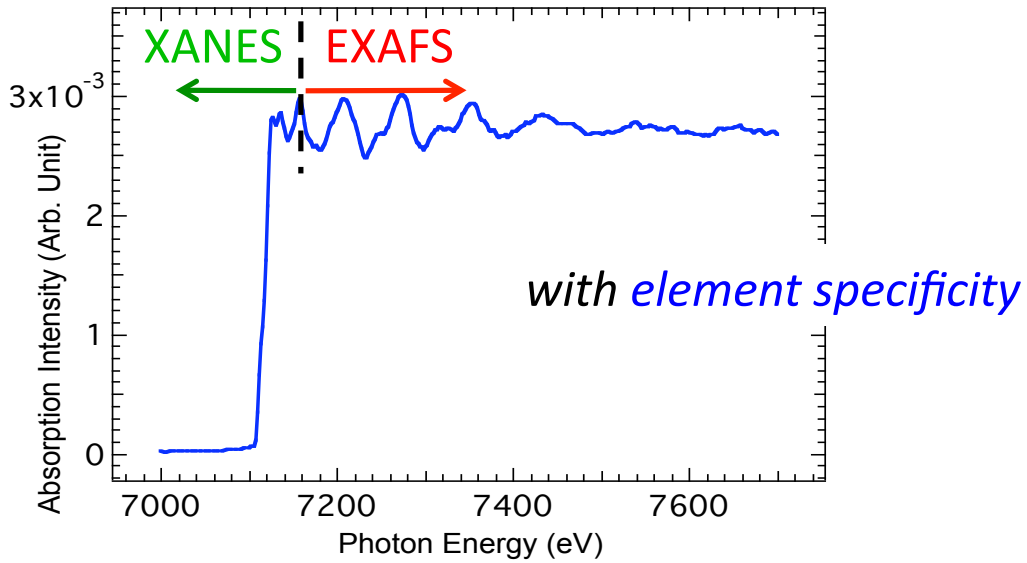
fcc



Take-home massage

XAFS : XANES + EXAFS

- XANES gives us...
  - Valence state
  - Symmetry



The ruler is de Broglie wave of electron!!

- EXAFS gives us...
  - Bond length
    - **A local structure** is given.
    - **Crystallinity, or long range order is not required**.
  - Coordination number (CN)
    - Simply, the number of atoms around the atom.
    - CN enables us to estimate sizes of nano clusters.

Thank you for your attention