SESAME-JSPS School

Soft X-ray Spectroscopy for Physics (and Chemistry)

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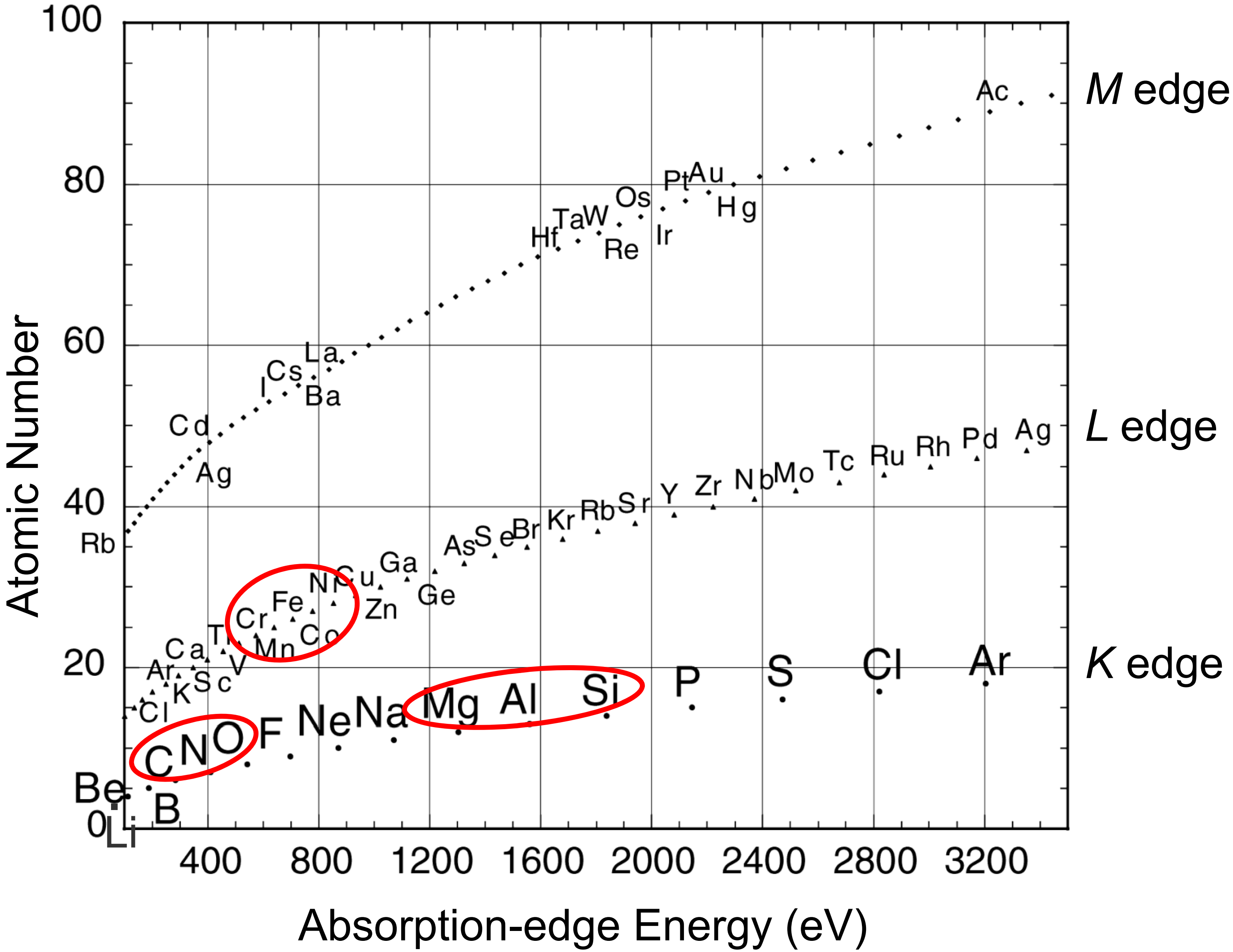
Studies using Soft X-ray

- Soft X-ray (& VUV) Beamlines
  - ~14/50 at Photon Factory (2.5 & 6.5 GeV)
  - ~5/50 at Spring-8 (8 GeV)
- Experimental Techniques
  - X-ray Absorption Spectroscopy (XAS)
  - Photoemission Spectroscopy
  - X-ray Scattering
- Applications:
  - Organic Molecules & Polymers
  - Magnetic Materials (Fe, Co, Ni, …)
  - Surface & Thin Film

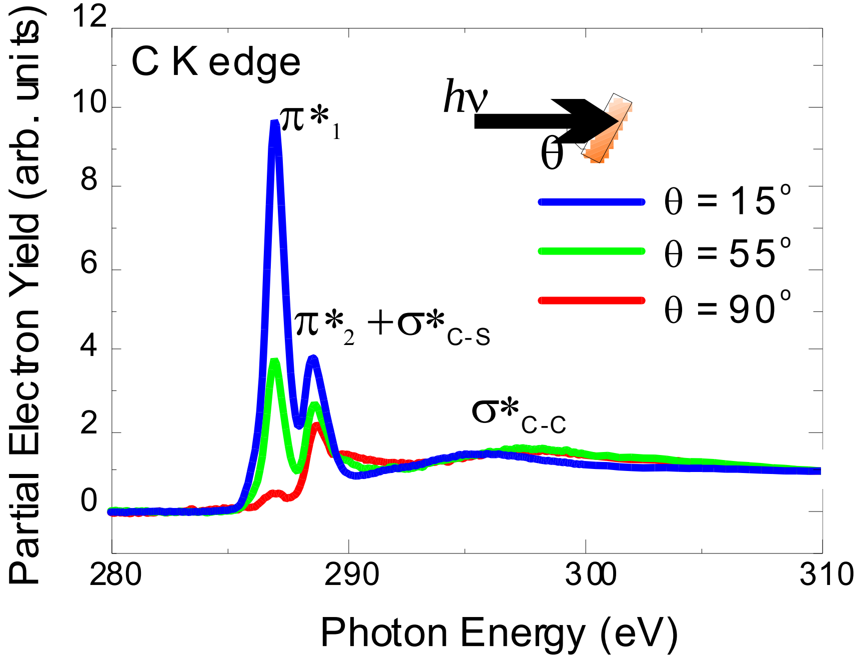
Absorption Edges in the Soft X-ray Region



Soft X-ray Absorption Spectroscopy

1. Advantages and Disadvantages of Soft X-ray Absorption Spectroscopy (SXAS)
2. SXAS studies on Surface and Thin films
3. Soft X-ray Beamlines
4. Novel SXAS Technique: Depth-resolved XAS

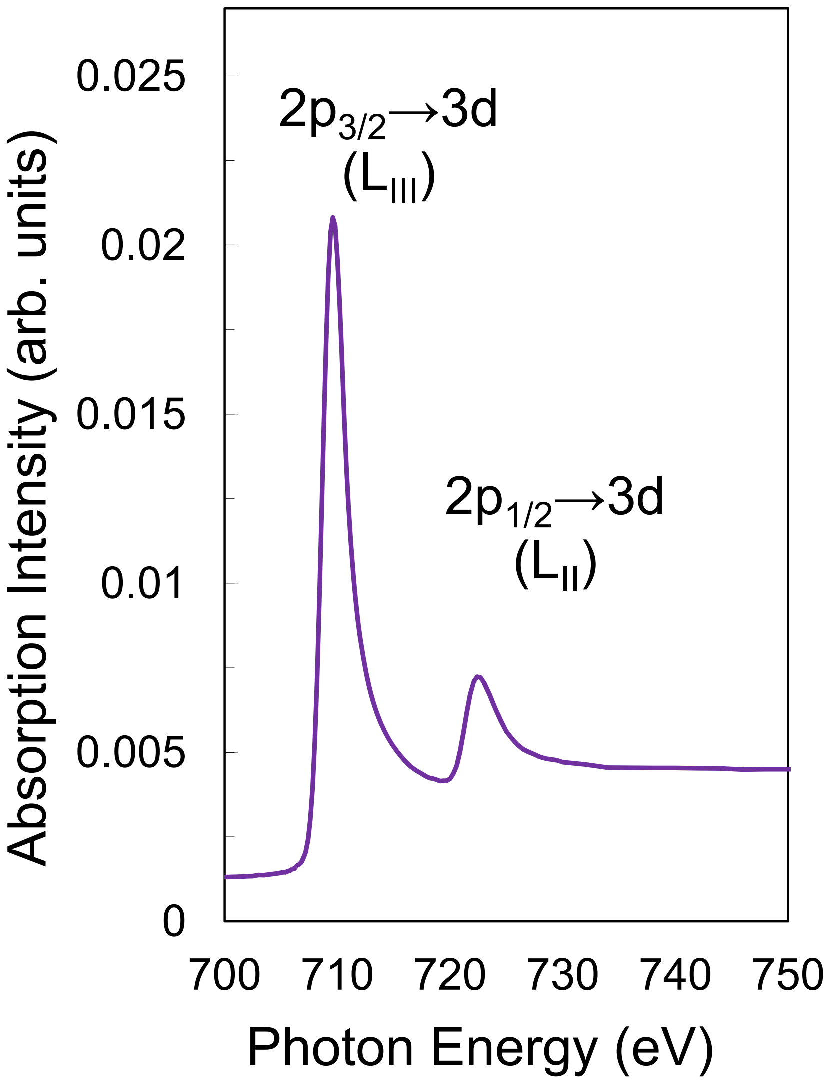
Soft X-ray Absorption Spectroscopy (~100-4000 eV)



1. Element selectivity
   <– Core-hole excitation (1s, 2p…)
   (C: 290 eV, O: 530 eV, Fe: 710 eV, Ni: 850 eV…)
2. Information on chemical species
   <– Characteristic spectral features (π*, σ*…)
3. Structural information (bond length, etc.)
   EXAFS (Extended X-ray Absorption Fine Structure)
4. Information on anisotropy
   <– Linear polarization
   (molecular orientation, lattice anisotropy)
5. Magnetic information
   <– Circular polarization
   XMCD (X-ray Magnetic Circular Dichroism)
6. High sensitivity

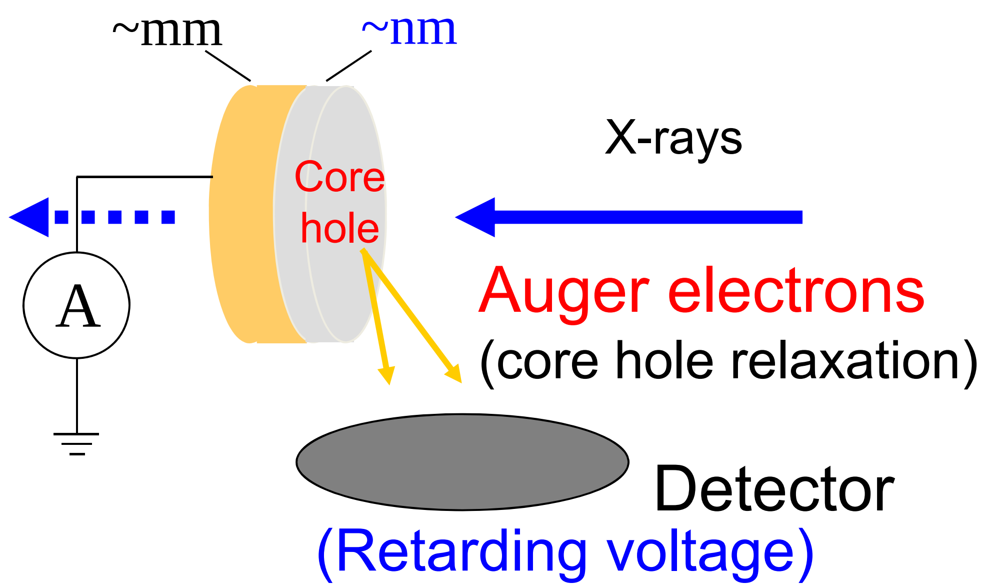
XAS Measurement in the Soft X-ray Region

3 ML Fe / Cu(100) Fe L-edge XAS



How can we measure

X-ray absorption spectrum ?



Electron yield XAS

Total electron yield (TEY)

Partial electron yield (PEY)

cf. Fluorescence yield (FY)

Advantages and Disadvantages of SXAS

Short Penetration Length

Transmission mode can be available only for a very thin sample on a very thin or without substrate.

- Electron yield mode is usually adopted because of high efficiency.
- Special care is necessary for insulators (powders might be OK).

Fluorescence yield efficiency is very small for light elements.

- <1 % for C, N, O

  Be careful for the self absorption (saturation) effect.

- Samples should be usually kept in vacuum (NOT ultra-high vacuum).
  - Some attempts have been made to realize ambient-pressure or liquid-state measurements.

Surface Sensitive

- Sub-monolayer samples can be investigated.

  (λ = several nm for electron yield.)

- Bulk information is hardly obtained, especially in the electron yield mode.

  (λ ~ 0.1 μm for fluorescence yield.)

Sensitive to Electronic and Magnetic States of light elements

- Valence electrons can be directly investigated by 1s–>2p excitation of C, N, O,… and 2p–>3d excitation of 3d transition metals (Fe, Co, NI,…).

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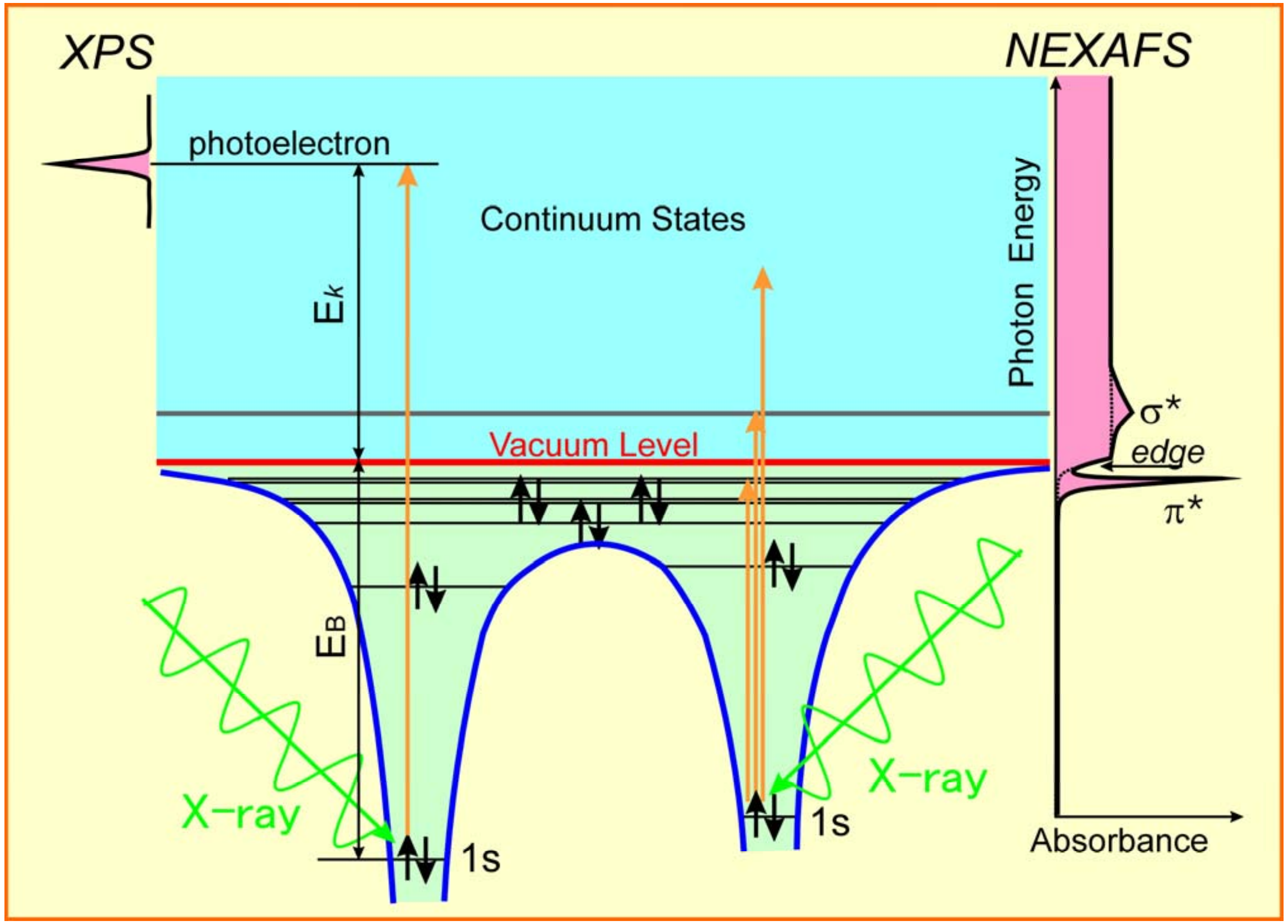
Near-edge Spectroscopy

Near-edge X-ray Absorption Fine Structure (NEXAFS)
X-ray Absorption Near-edge Structure (XANES)



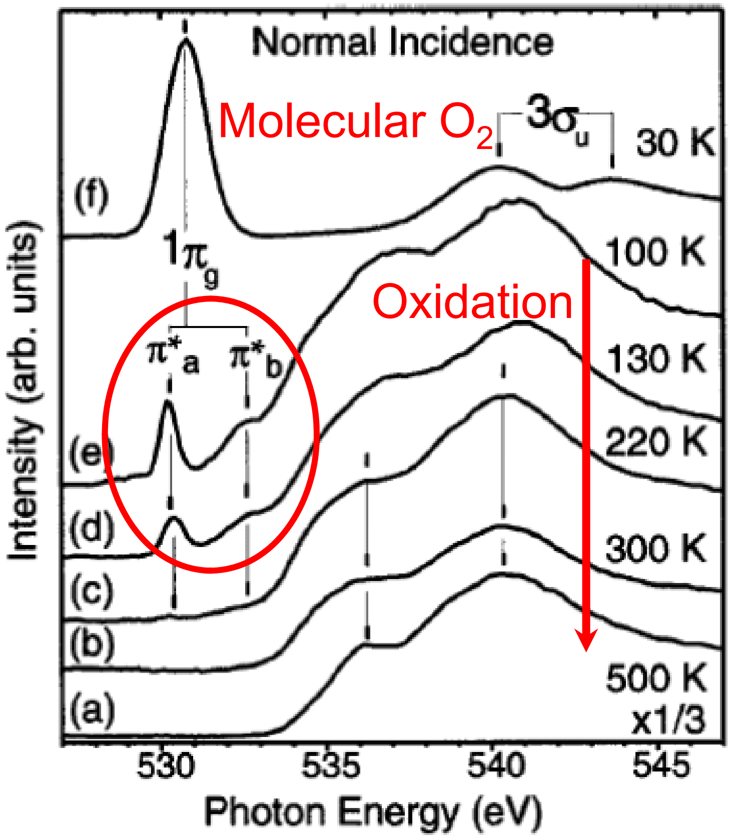
Chemical species

Structural information (orientation)

Near-edge Spectroscopy

Determination of Chemical Species

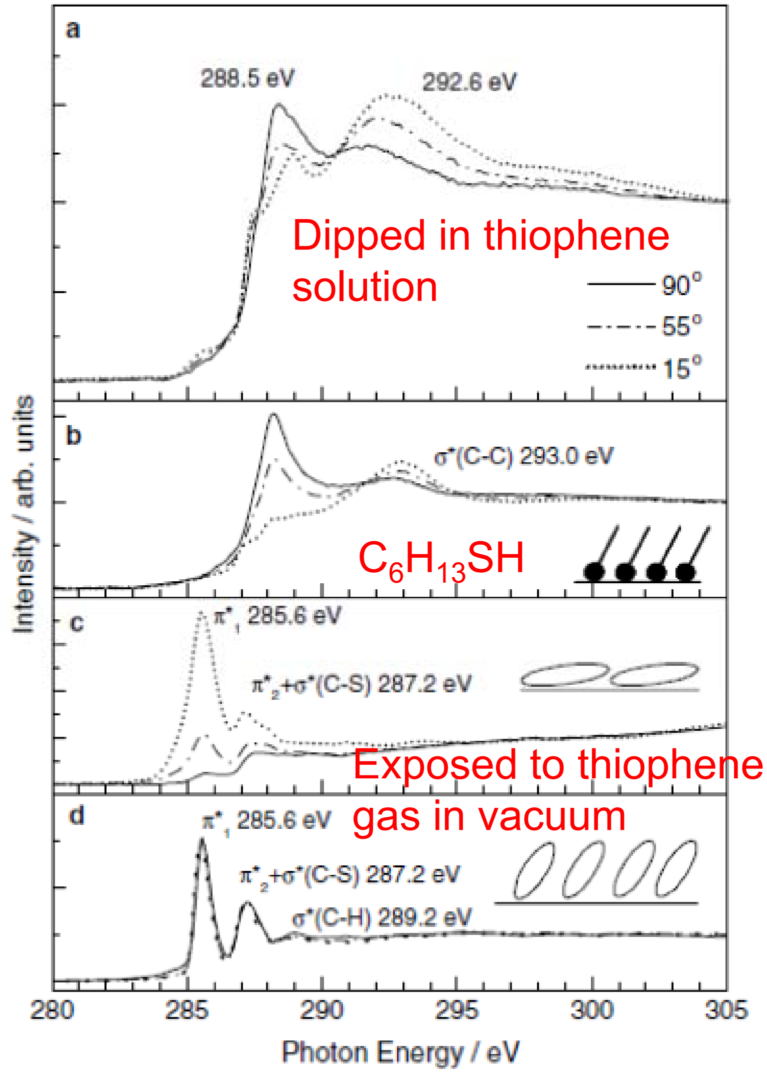
Initial oxidation process of Si



Existence of molecular oxygen in the initial stage of Si oxidation

Matsui et al., Phys. Rev. Lett. **85,** (2000) 630.

Thiophene (C_4H_4S) molecule on Au(111)

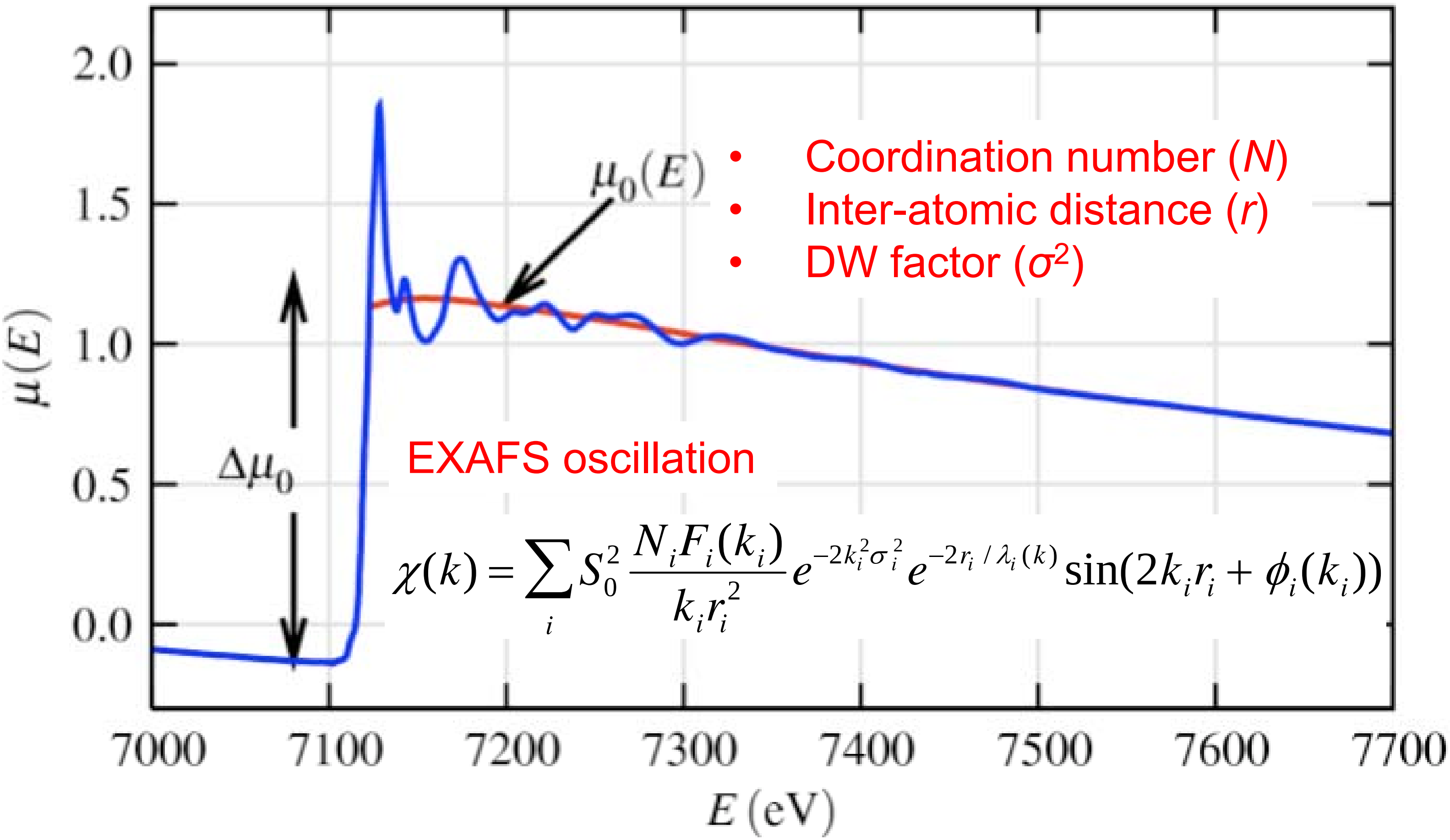


Different chemical species depending on preparation processes

Sako et al., Chem. Phys. Lett. **413,** (2005) 267.

Determination of Atomic Structure

Extended X-ray Absorption Fine Structure (EXAFS)



- Coordination number (*N*)
- Inter-atomic distance (*r*)
- DW factor (σ^2)

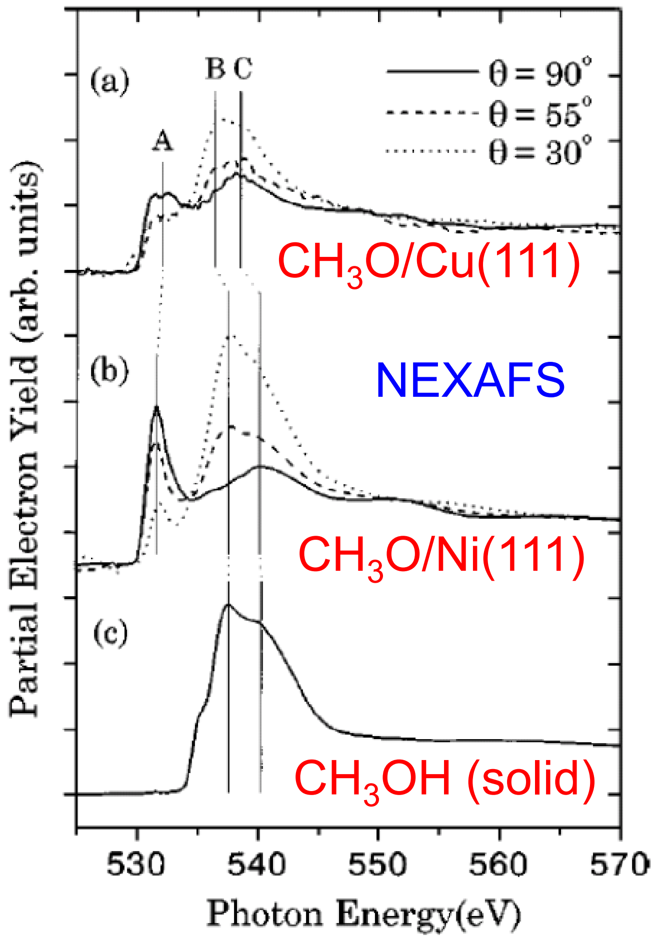
EXAFS oscillation

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

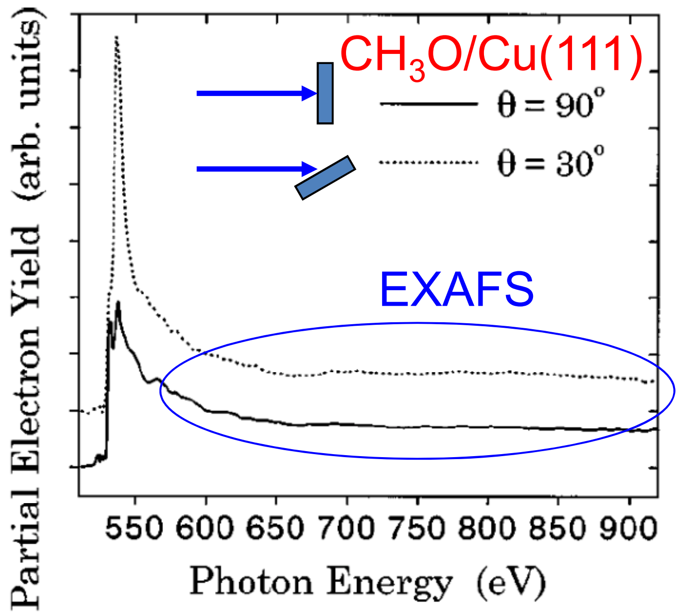
Fe *K*-edge XAFS spectrum $\mu(E)$ of FeO

Determination of Atomic Structure

Amemiya et al., Phys. Rev. B **59,** (1999) 2307.

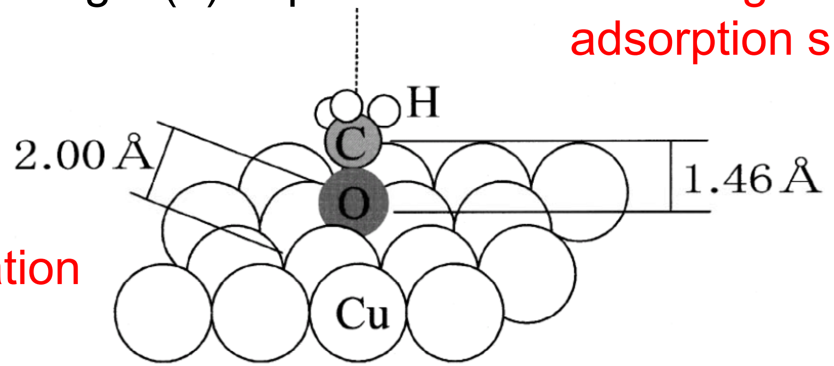


Application to surface molecule (CH_3O)



Oscillation period -> O-Cu bond length

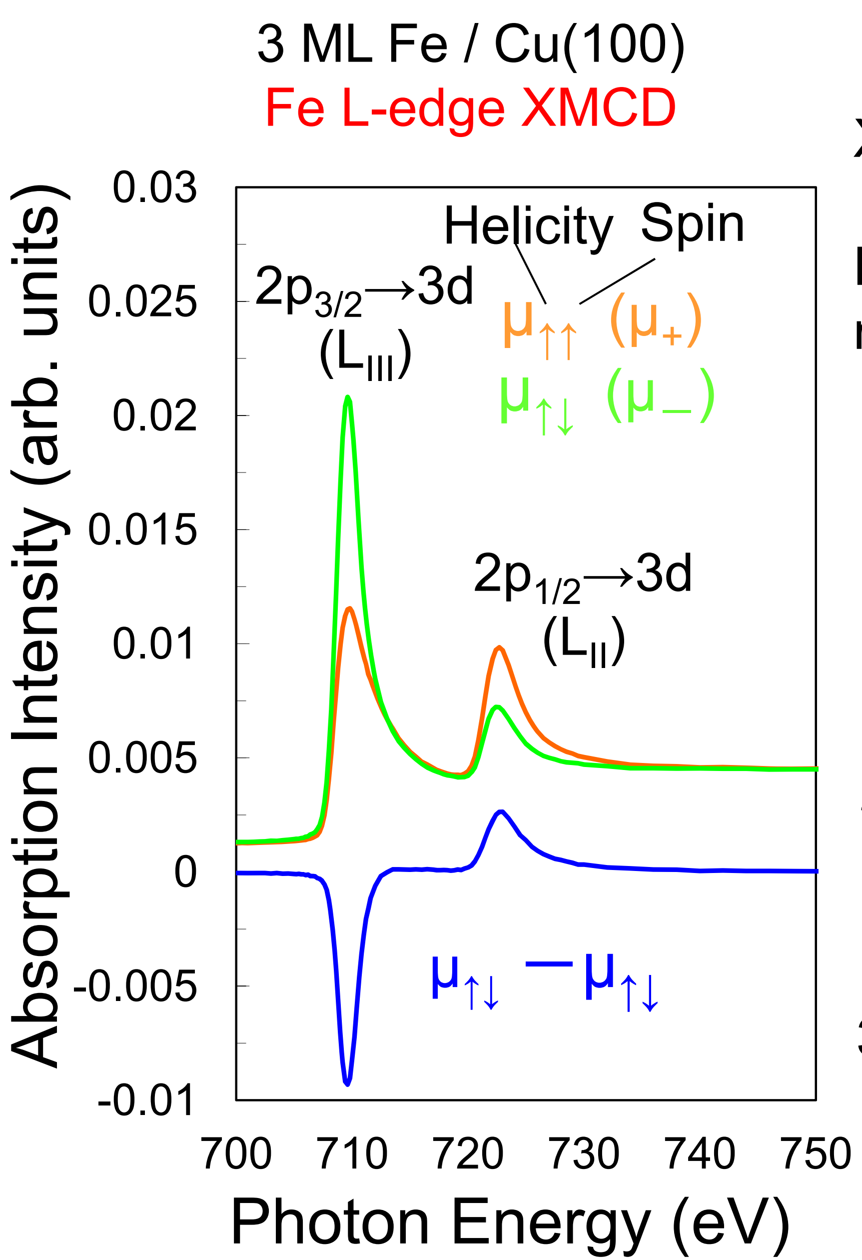
Angle (θ) dependence -> bond angle
adsorption site



Peak B (1s→σ^*_{CO}) -> C-O bond length

Angle (θ) dependence -> molecular orientation

Magnetic structures studied by XMCD



X-ray Magnetic Circular Dichroism (XMCD)

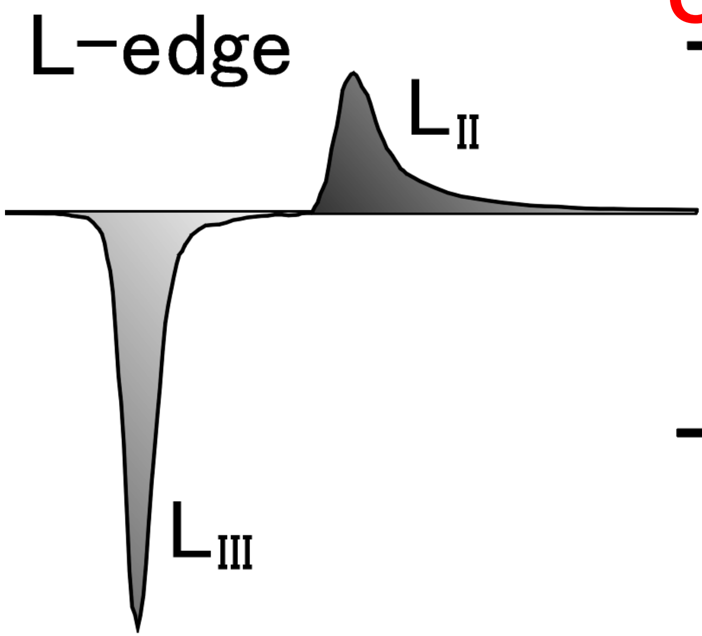
Difference in absorption intensities between right- and left-hand circular polarizations

1. Element selectivity
   <– resonant absorption
   2p -> 3d excitation for 3d transition metal
   3d -> 4f excitation for rare-earth elements

2. Determination of spin and orbital magnetic moments
   <– Sum rules

3. High sensitivity

XMCD Sum Rules



Orbital moment

$$\frac{m_l}{\int_{L_{III}}(\mu_+ - \mu_-) + \int_{L_{II}}(\mu_+ - \mu_-)}$$

$< 0 \rightarrow m_l > 0$

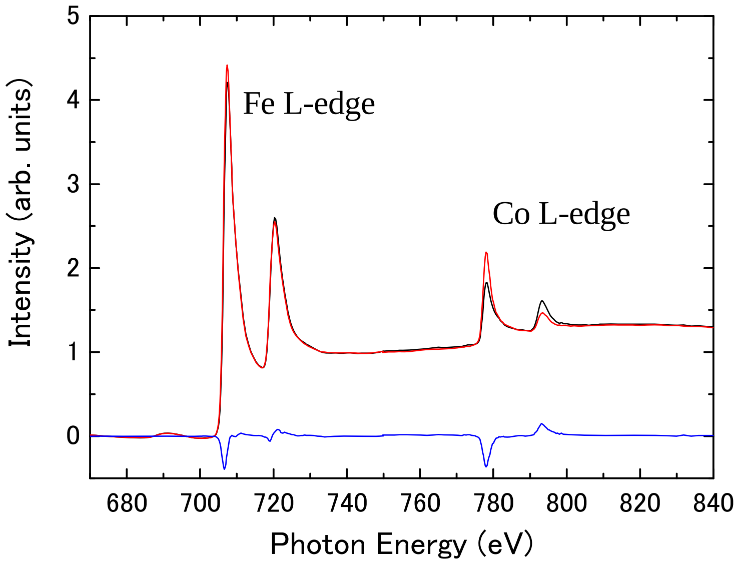
Spin moment

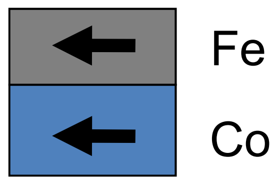
$$\frac{m_s}{\int_{L_{III}}(\mu_+ - \mu_-) - 2\int_{L_{II}}(\mu_+ - \mu_-)}$$

$< 0 \rightarrow m_s > 0$

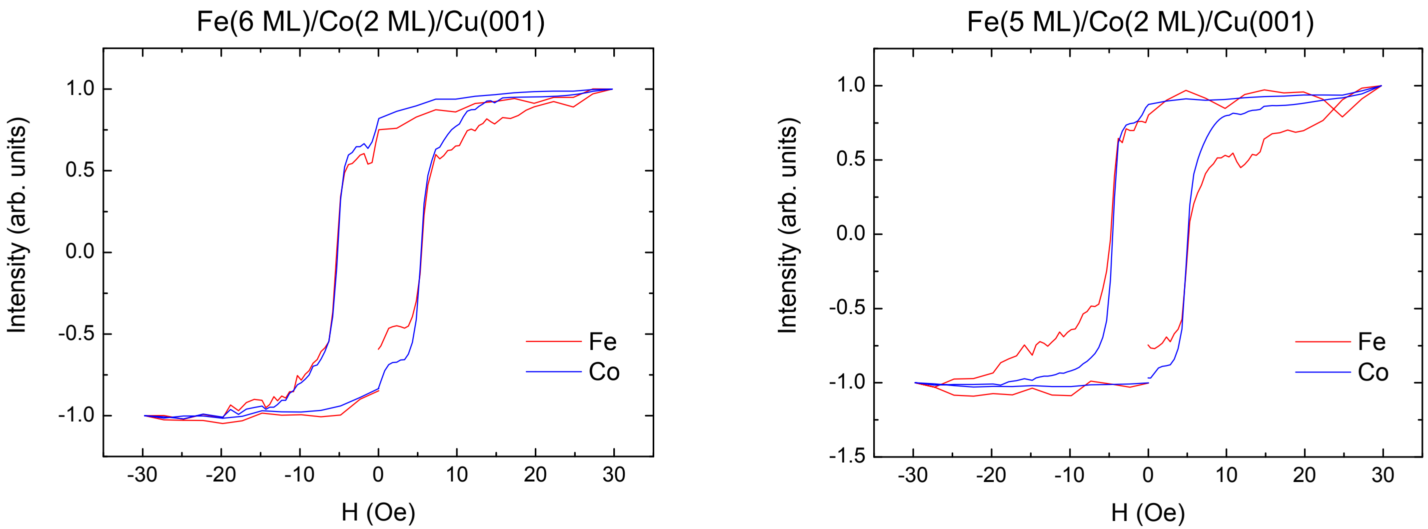
B.T. Thole et al., PRL **68**, 1943 (1992).
P. Carra et al., PRL **70**, 694 (1993).

Utilization of Element Selectivity of XMCD

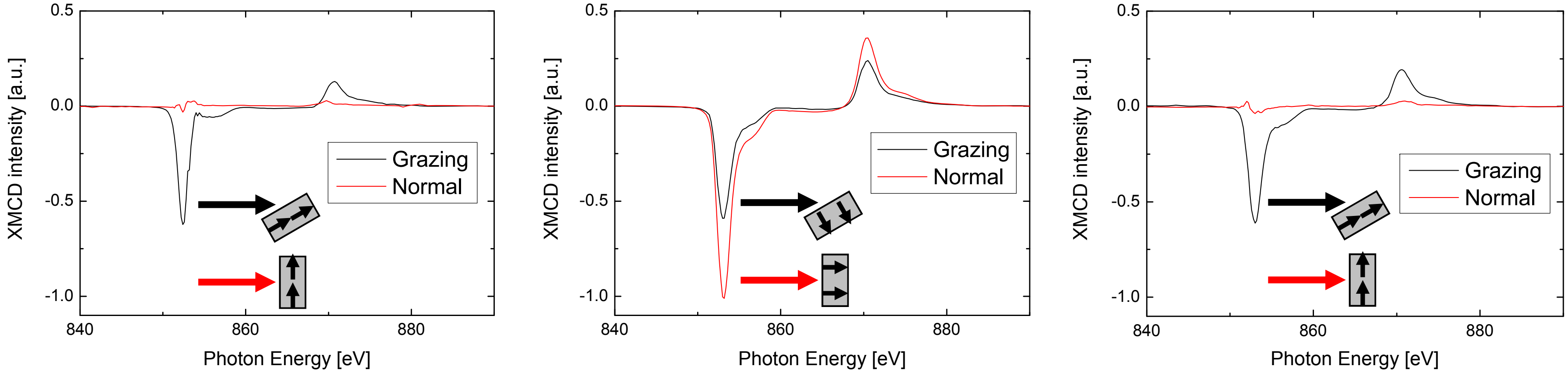


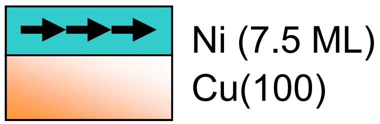


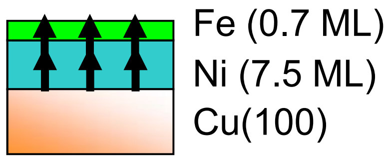
Magnetic-field dependence of XMCD at Fe and Co L edges

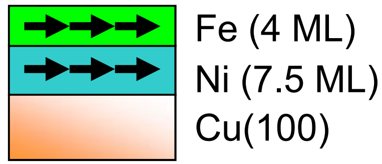


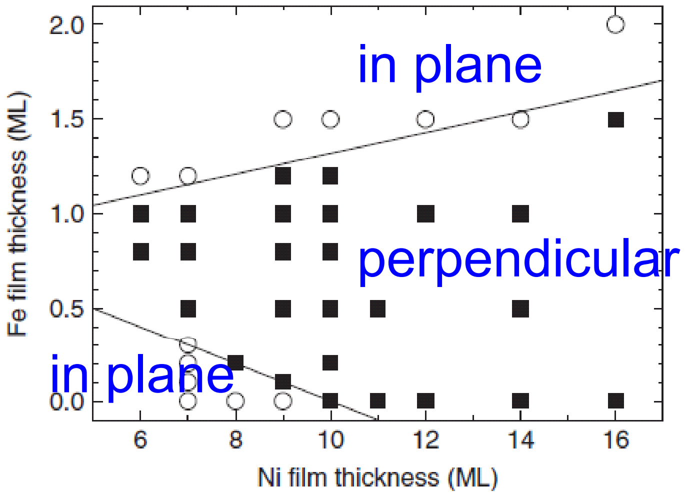
Angle Dependence of XMCD











XMCD reflects magnetic component which is parallel to X-ray beam.

–> determination of easy axis of magnetization

Information on orbital moment

–> estimation of magnetic anisotropy

Abe et al., J. Magn. Magn. Mater. 206 (2006) 86.

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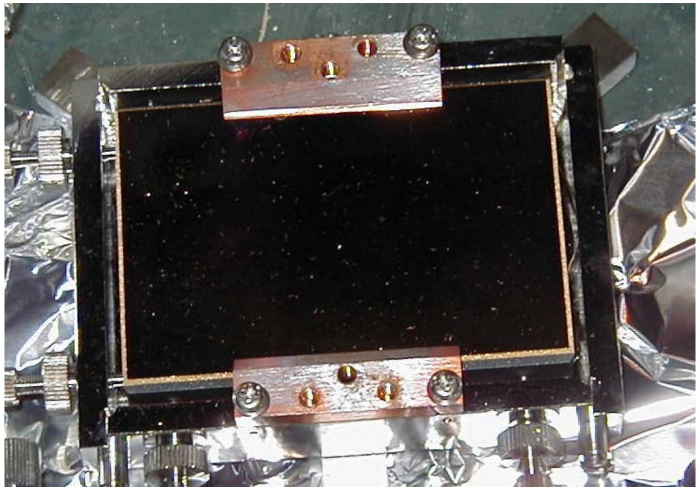
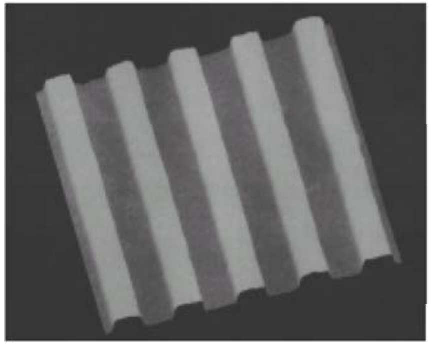
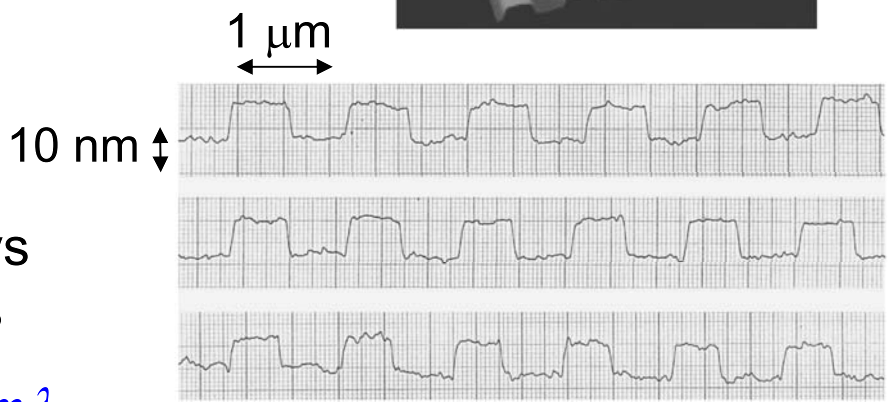
3.1. principle - wavelength dispersion -

Diffraction grating : Periodic grooves on a substrate

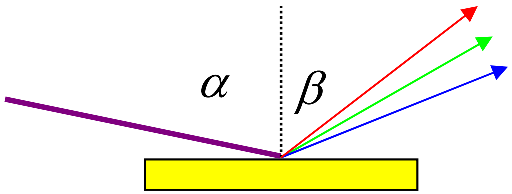






Principle : Interference between the rays reflected at different grooves

Enhanced when light path difference = $m\lambda$



* $\alpha > 0$

$\sin\alpha + \sin\beta = nm\lambda$

n: groove density

m: diffraction order

β depends on λ ⇒ Wavelength dispersion (conversion of wavelength to angle)

* $\alpha \neq -\beta$

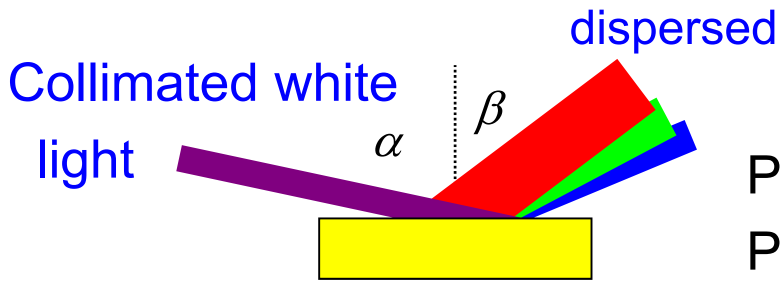
(if $\alpha = -\beta$, any λ satisfies the above condition at m = 0)

⇒ zero-th order light

3.2. energy resolution - dispersion and focus -

How can we monochromatize by using a diffraction grating?

Most basic mode: collimated-light illumination



$$\sin \alpha + \sin \beta = nm\lambda$$

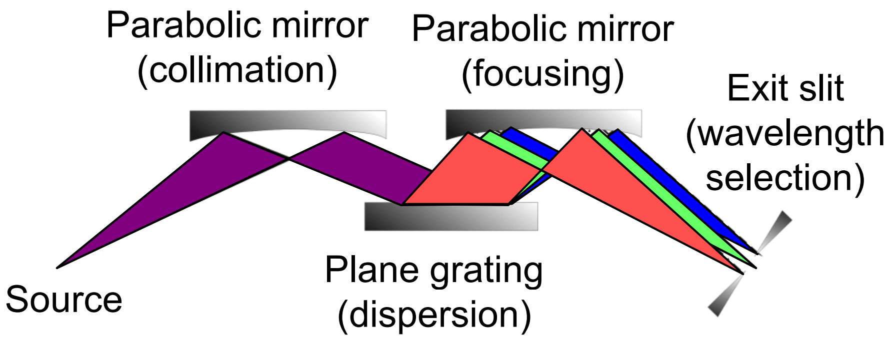
Problem 1 : SR is not a collimated light !

Problem 2: Superposition of diffracted lights

⇒ difficult to be resolved

Solution 1: Collimation of diverging light with a parabolic mirror

Solution 2: Focusing of diffracted lights with another parabolic mirror

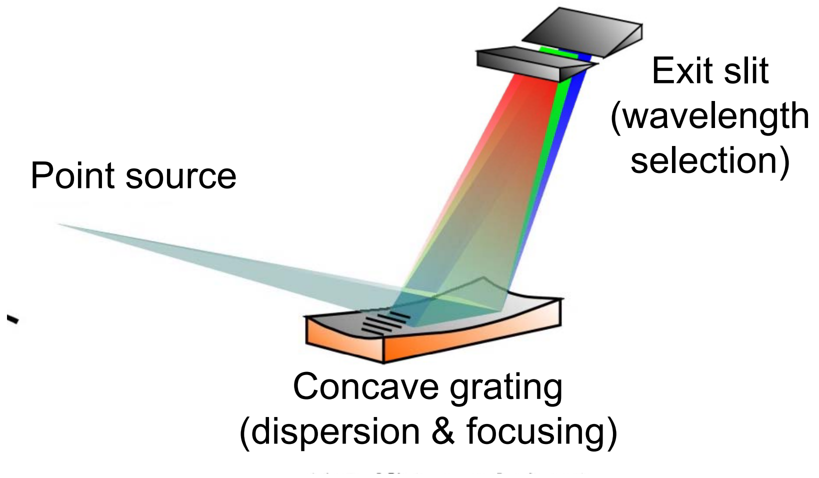


Focused diffracted lights are well resolved in wavelength at the exit slit !

Dispersion and Focus

3.2. energy resolution - dispersion and focus -

The simplest monochromator



Both the “dispersion” and “focus” are achieved by a diffraction grating only.

Is that really possible?

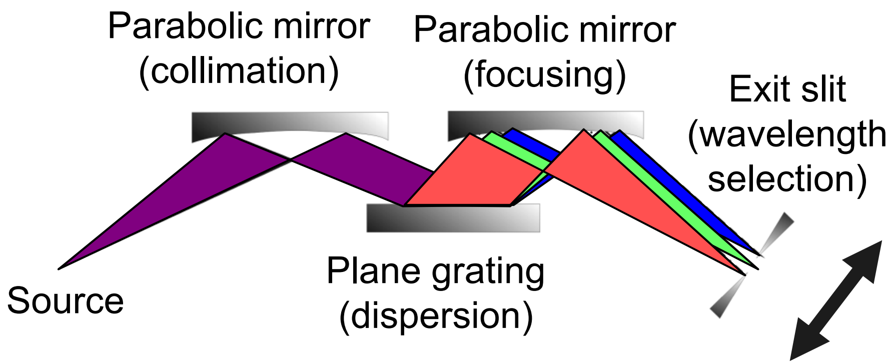
It is impossible to obtain a perfect focus at all wavelength

But, ”perfect focus” is not necessary !

Small number of optical elements

3.3. Monochromator operation

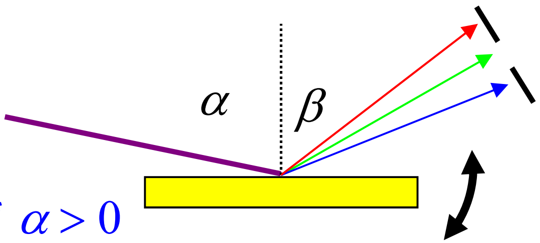
How can we select wavelength?



By moving exit slit?

-> Sample should be moved!

Simple rotation of grating!



* $\alpha > 0$

$\sin\alpha + \sin\beta = nm\lambda$

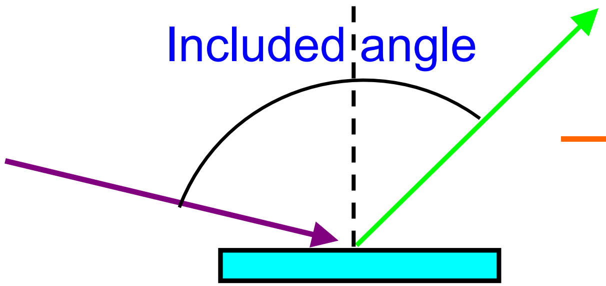
n: groove density

m: diffraction order

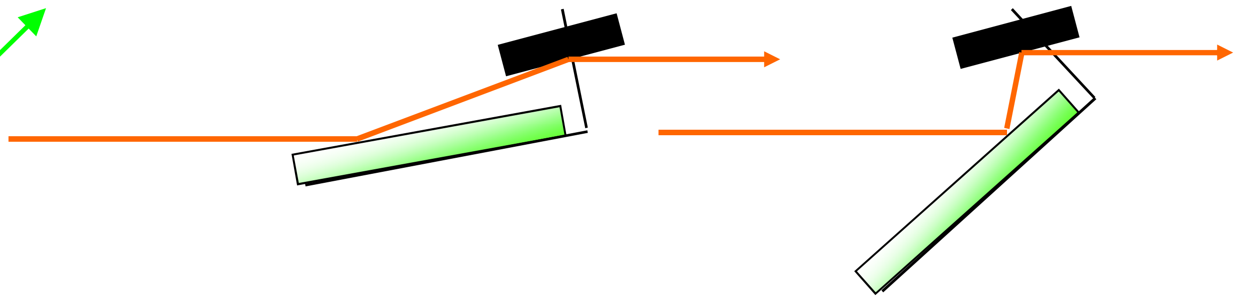
$\alpha - \beta =$ const. (included angle)

"Constant included angle monochromator"

Variable included angle system

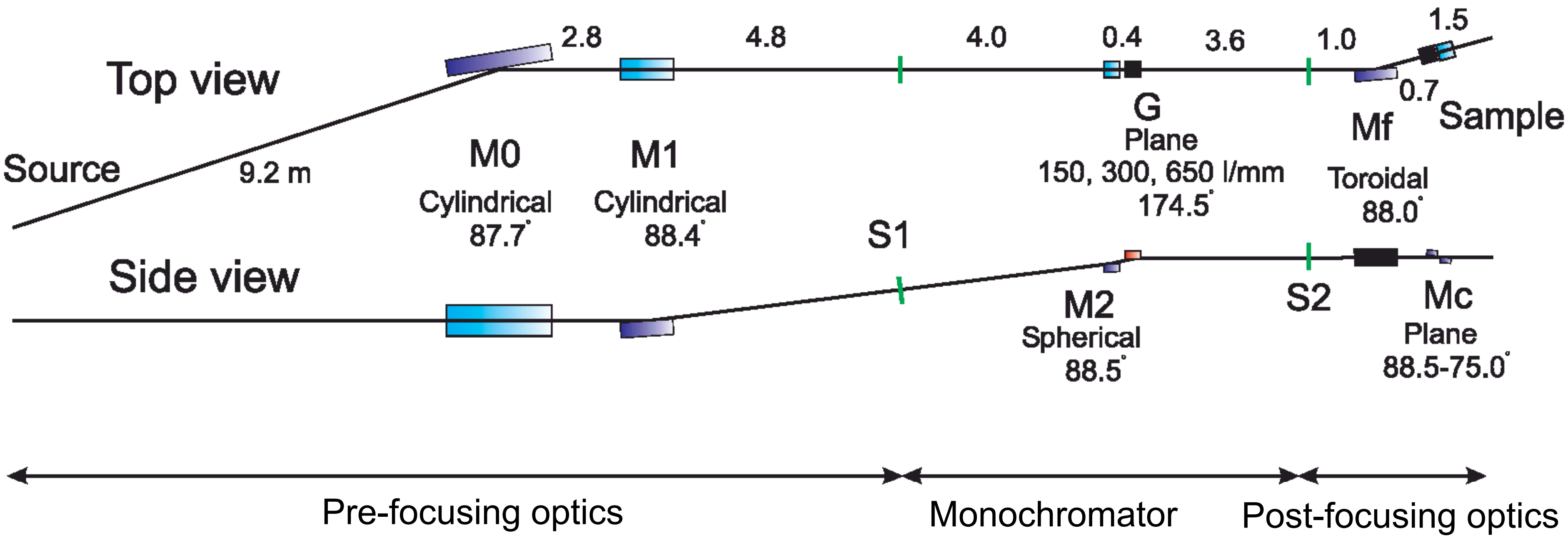


Wide energy range



3.4. Beamline components

Overview of a typical soft X-ray beamline



Pre-focusing optics : focuses X rays onto the entrance slit
Monochromator : from the entrance slit to the exit slit
Post-focusing optics : focuses monochromatized X rays onto sample position

Higher-order suppression :
utilizes energy dependence of reflectivity (or transmittance)

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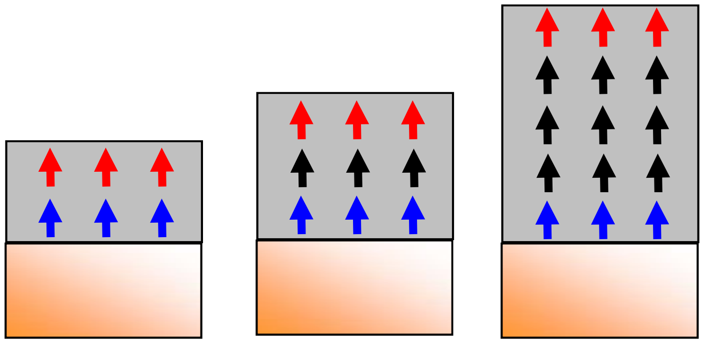
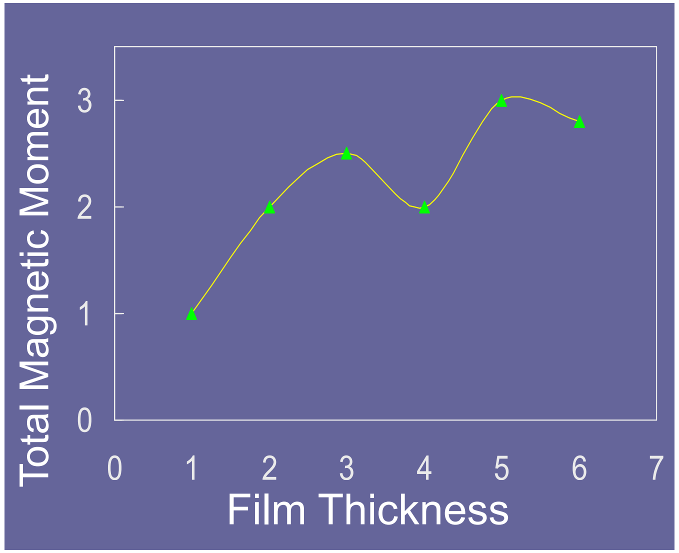
Conventional Technique for Magnetic Depth Profiling

SQUID, VSM, MOKE, XMCD…

Gives averaged information over the whole sample.

⇒ also averaged in depth



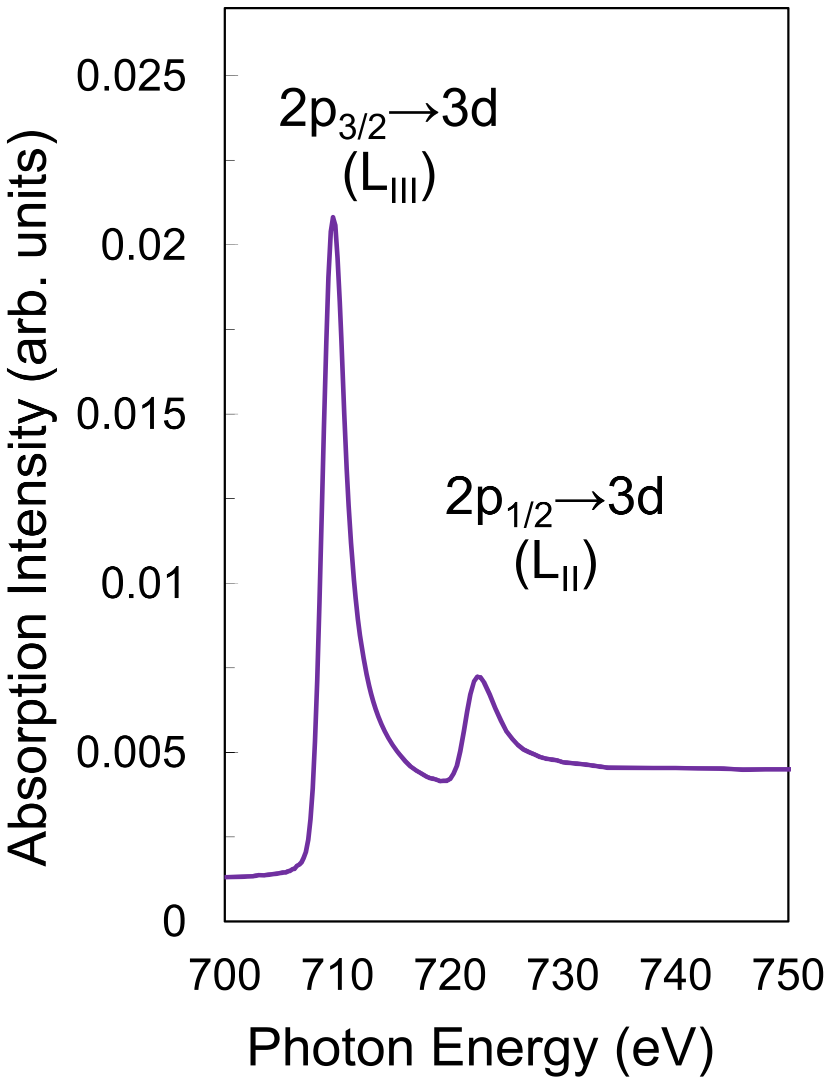


Based on an assumption
that magnetic structure of surface and interface
dose not change upon layer growth

→ Direct technique for depth profiling

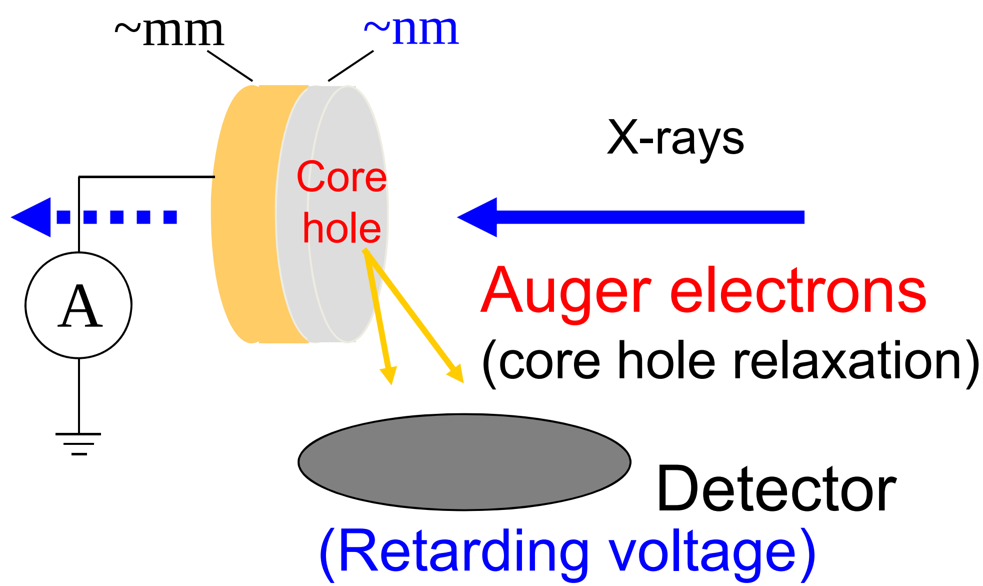
XAS Measurement in the Soft X-ray Region

3 ML Fe / Cu(100) Fe L-edge XAS



How can we measure

X-ray absorption spectrum ?



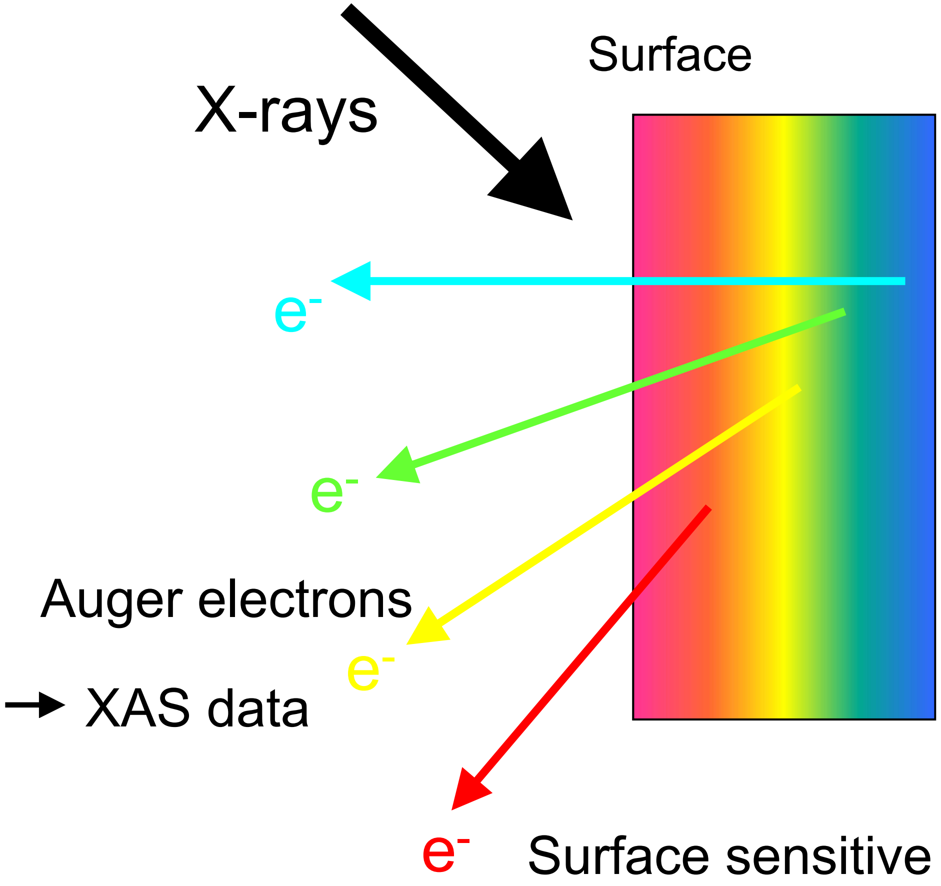
Electron yield XAS

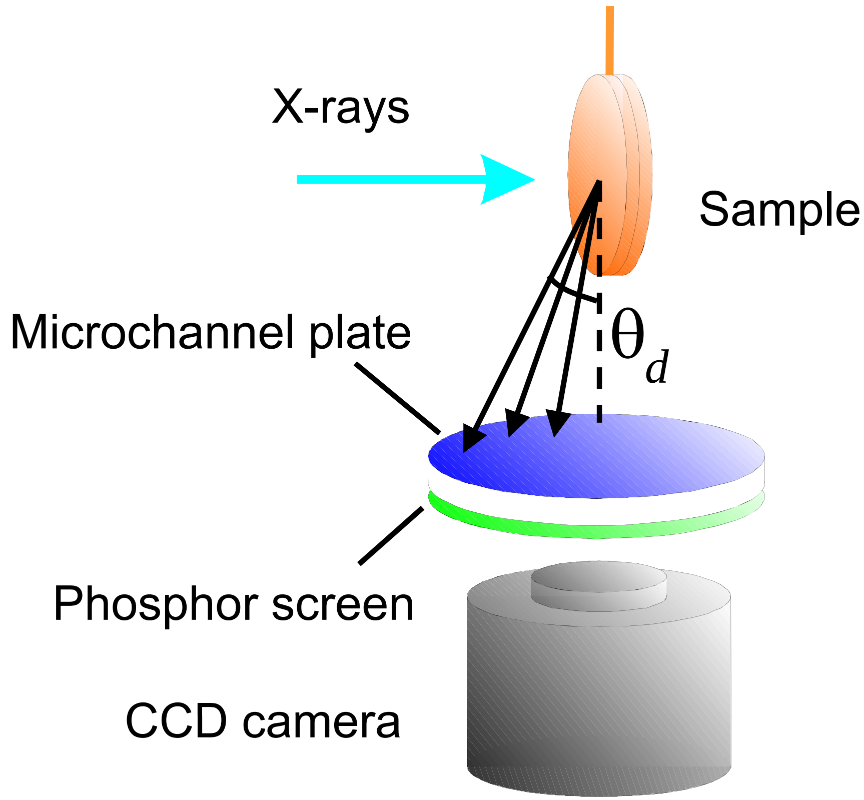
Total electron yield (TEY)

Partial electron yield (PEY)

cf. Fluorescence yield (FY)

Principle of Depth-resolved XAS

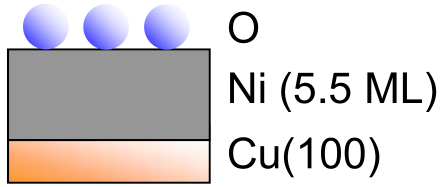


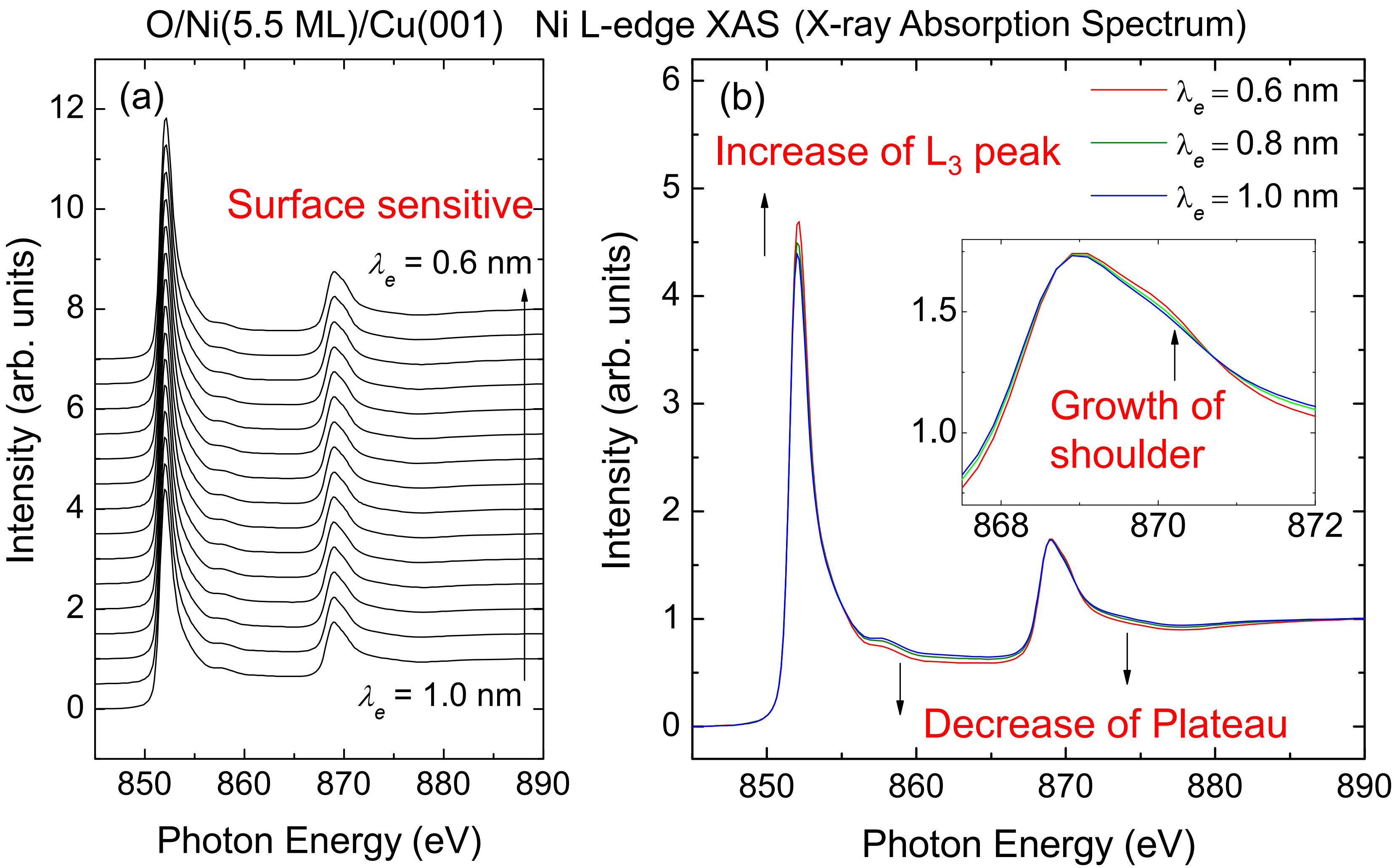


Electron yield XAS measurements at different detection angles

→ A set of XAS data with different probing depths

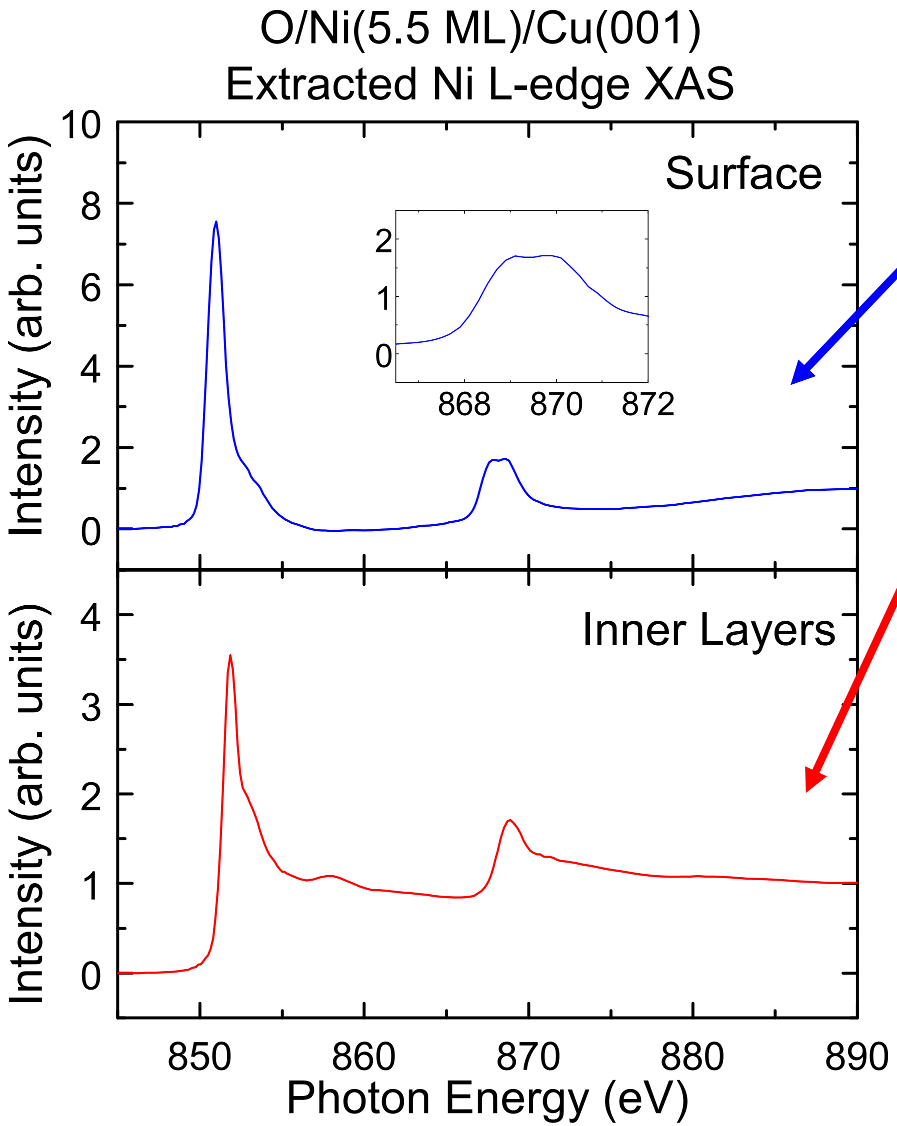
Surface of O/Ni/Cu(100) –raw data-

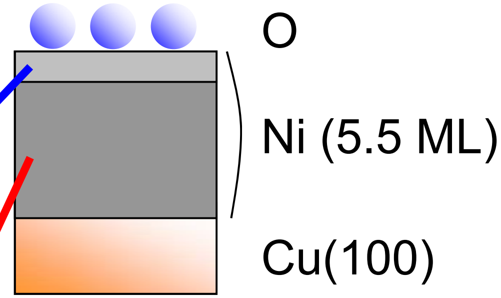




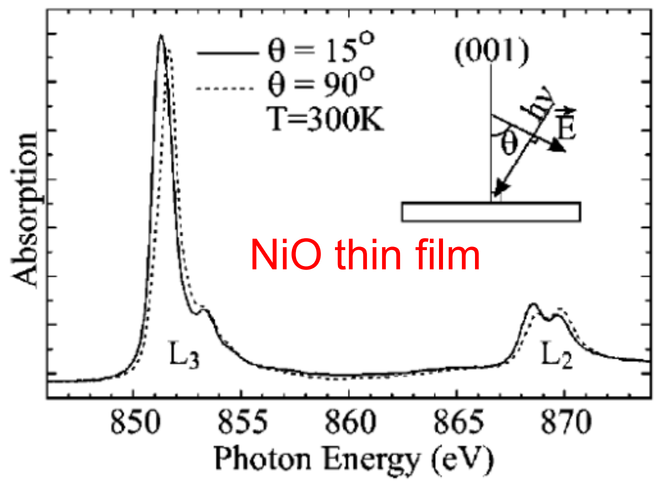
Extracted XAS

K. Amemiya and M. Sakamaki, Appl. Phys. Lett. 98 (2011) 012501.





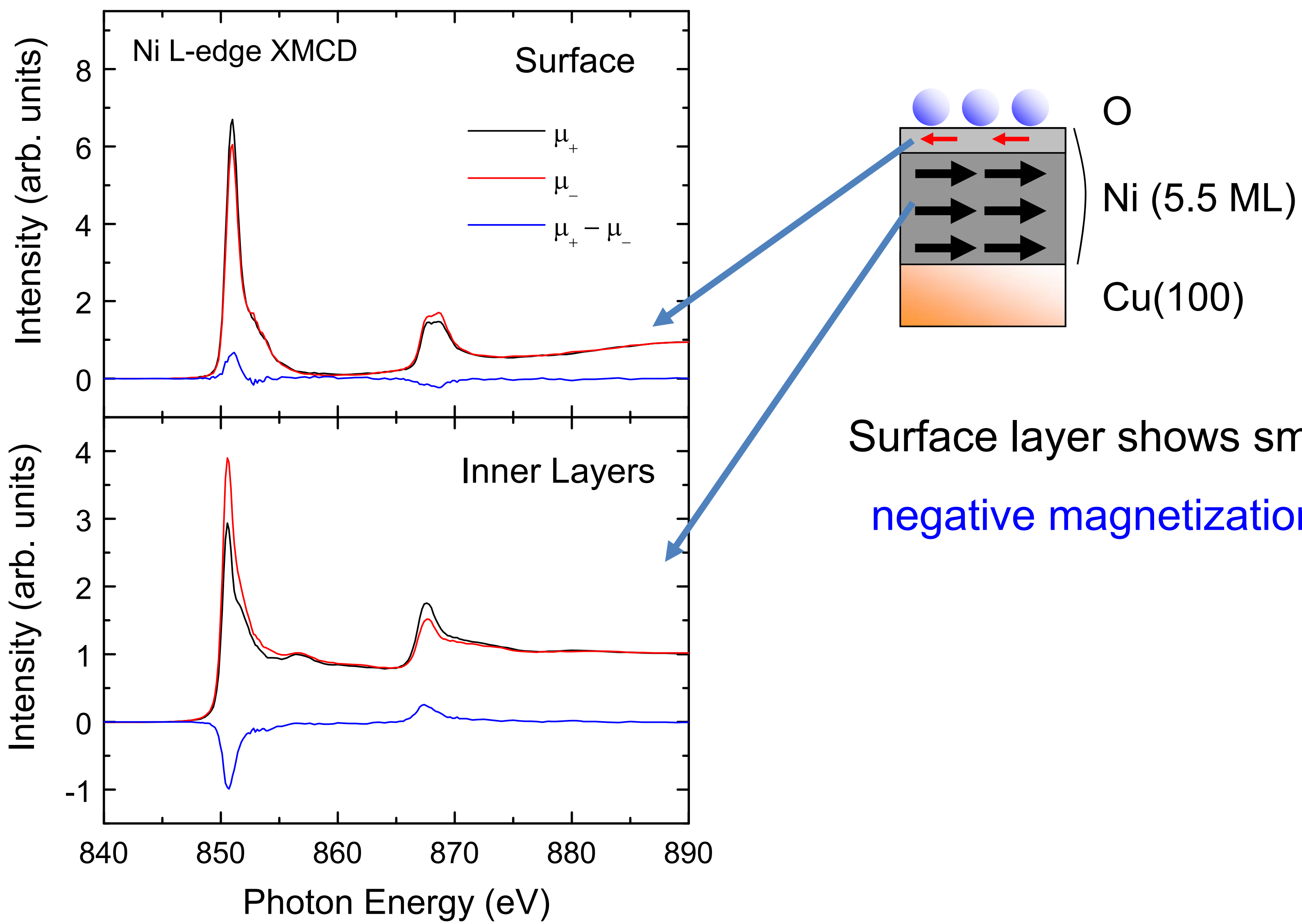
XAS spectra at surface shows NiO-like features



Haverkort et al., Phys. Rev. B 69, 020408(R).

Extracted XMCD spectra

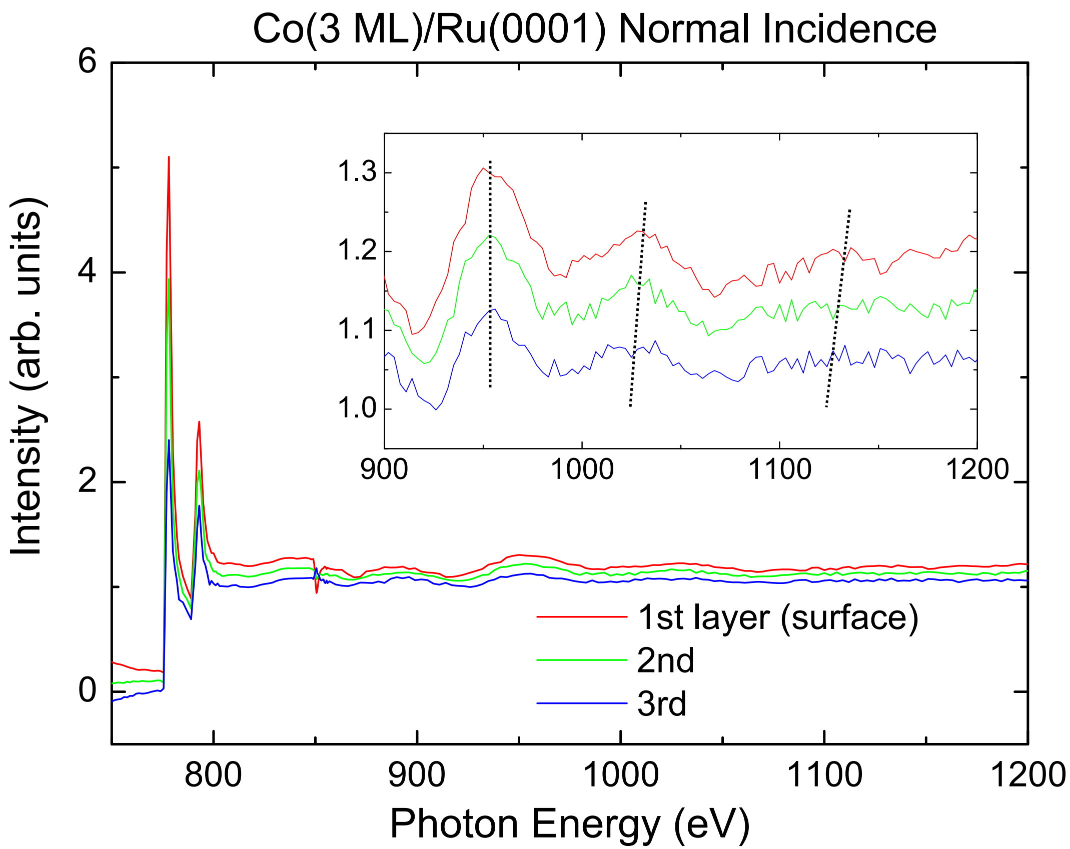
K. Amemiya and M. Sakamaki,
Appl. Phys. Lett. 98 (2011) 012501.

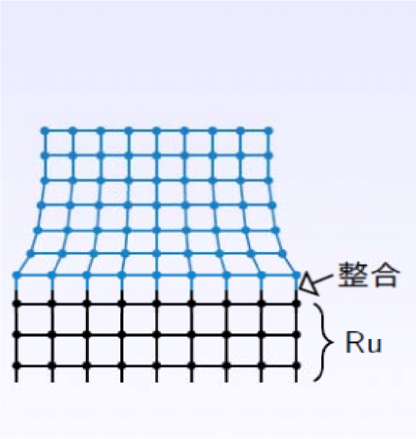


Surface layer shows small negative magnetization.

Depth profile of atomic structure

Layer-resolved EXAFS data





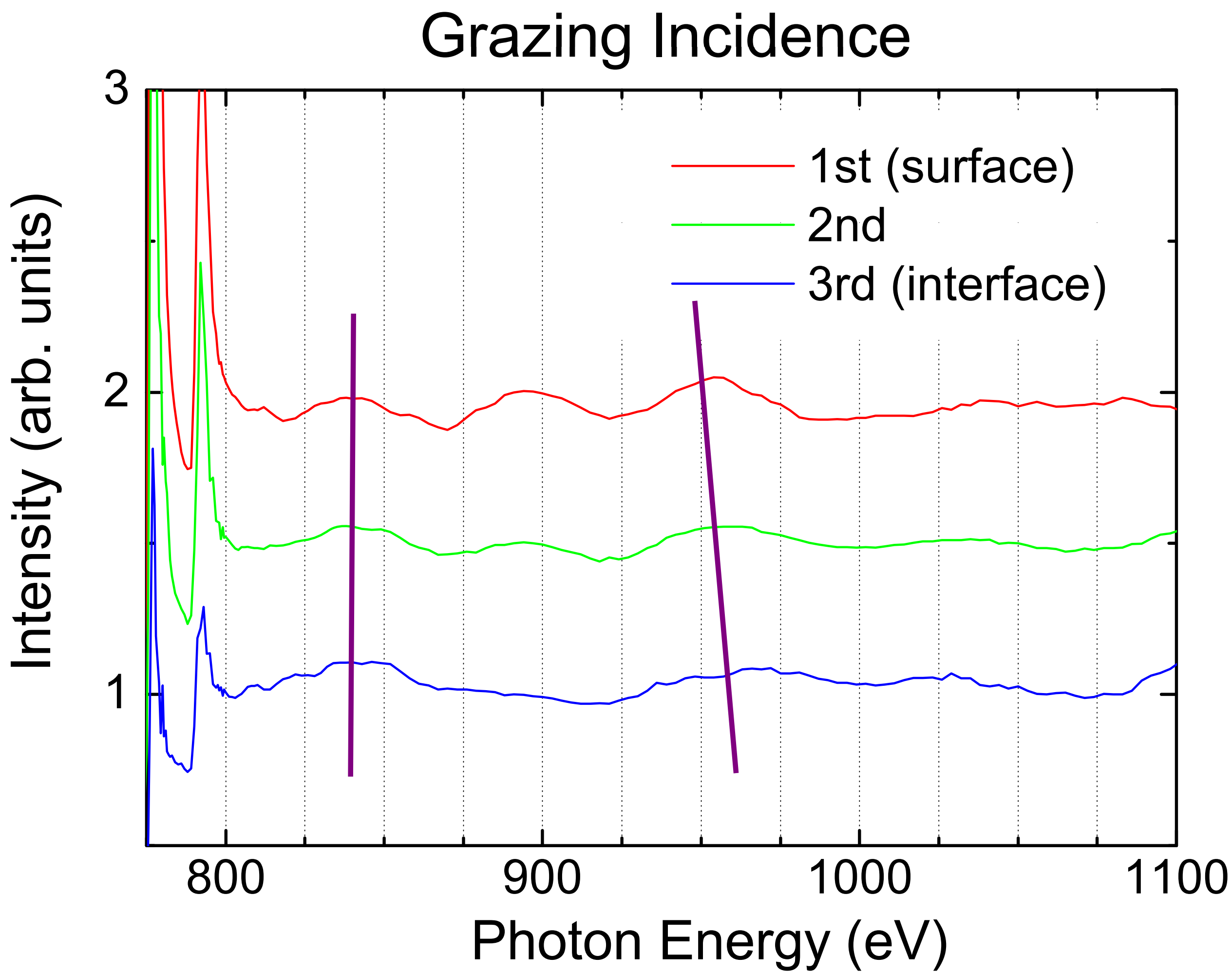
Relaxation of strain

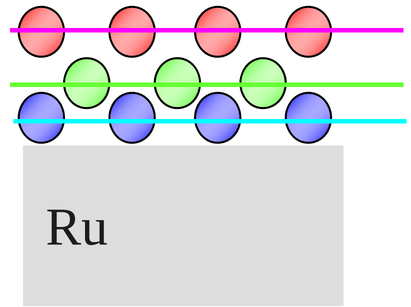
Normal incidence: dominated by in-plane distance

Surface shows longer oscillation period: shorter bond length

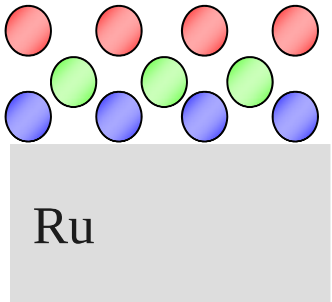
Depth-resolved EXAFS at grazing incidence

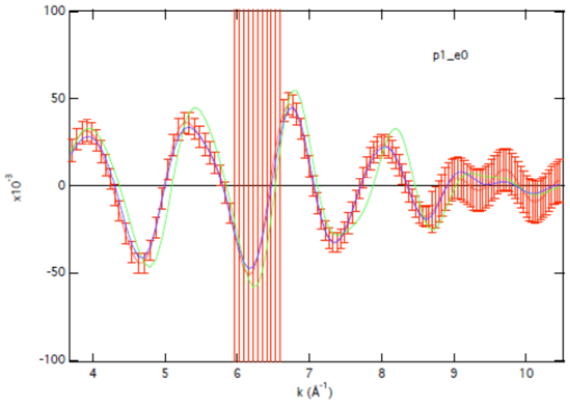
Longer out-of-plane bond length at surface?

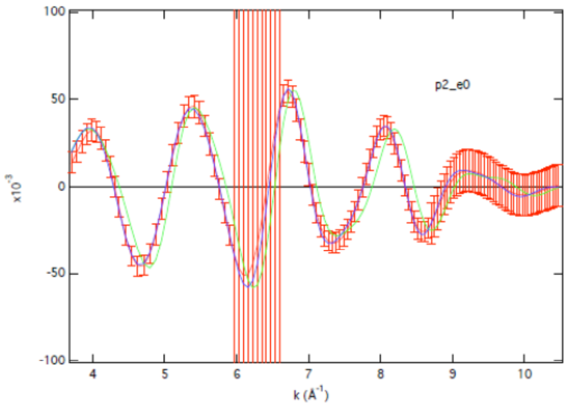


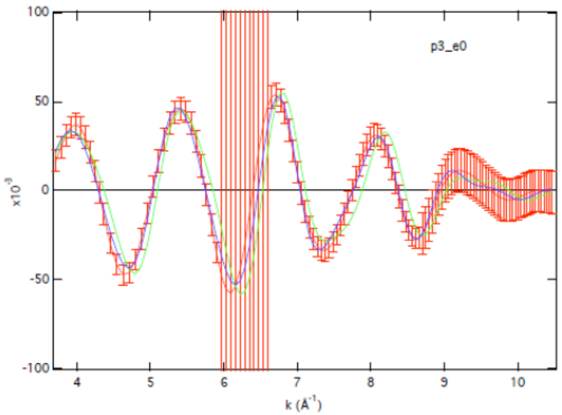


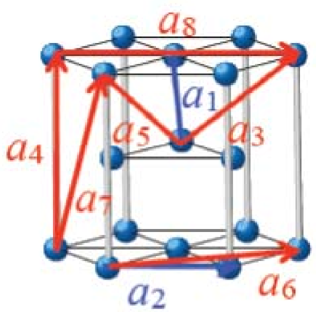
Preliminary analyses

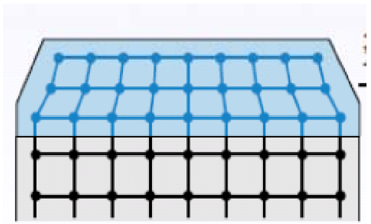












In plane	Out of plane
0.251 nm	0.260 nm
0.255 nm	0.252 nm
0.255 nm	0.252 nm

Let’s try soft X-ray absorption!!

You don’t have to be afraid of soft X ray.