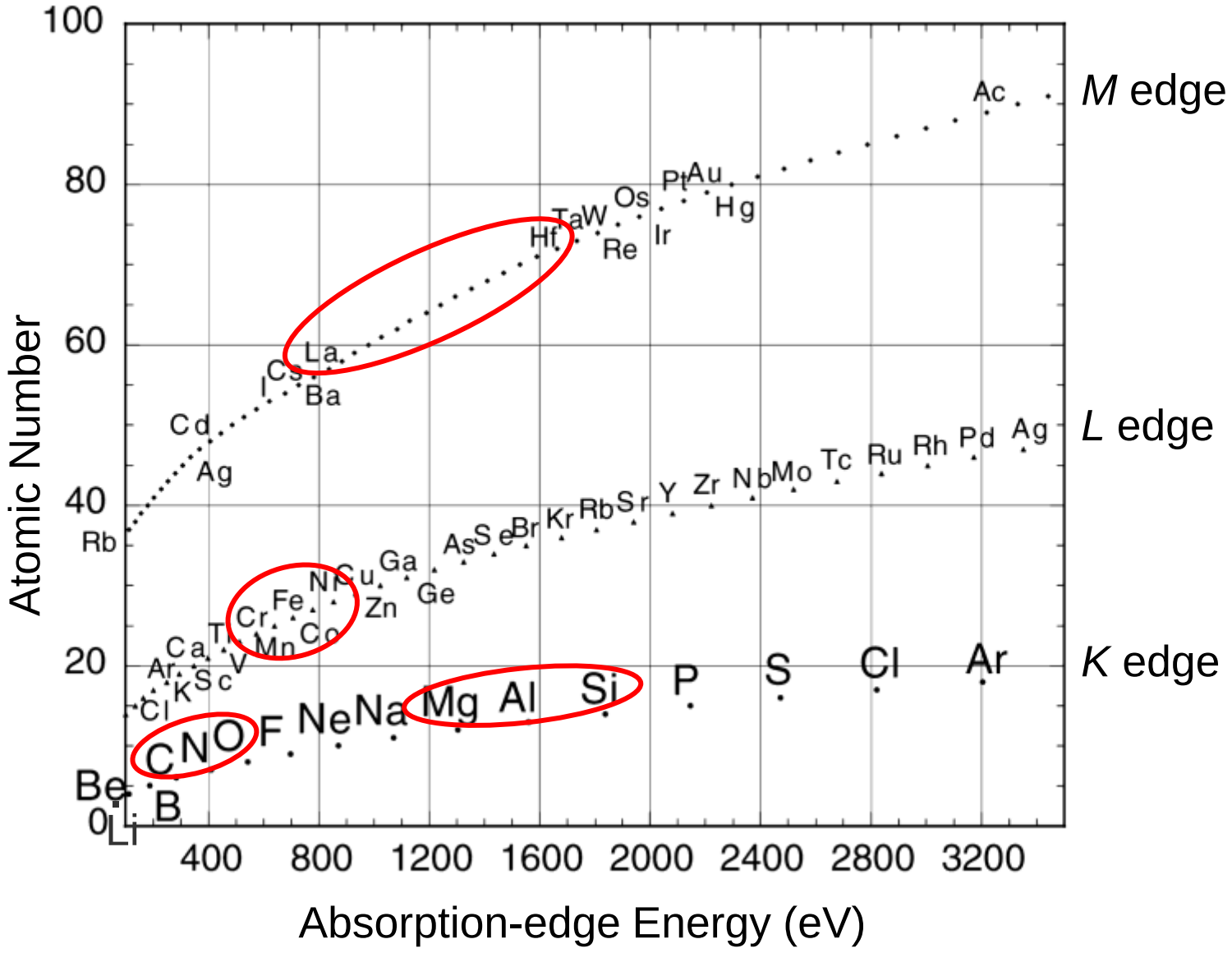
Soft X-ray Absorption Spectroscopy

Kenta Amemiya (KEK-PF)

Absorption Edges in the Soft X-ray Region



Studies using Soft X-ray

Soft X-ray Beamlines

~15/50 at Photon Factory (2.5 & 6.5 GeV)

~5/55 at Spring-8 (8 GeV)

Experimental Techniques

X-ray Absorption Spectroscopy (XAS)

Photoemission Spectroscopy (PES)

Resonant X-ray Scattering (RXS)

Applications:

Organic Molecules & Polymers (C, N, O…)

Magnetic Materials (Fe, Co, Ni, …)

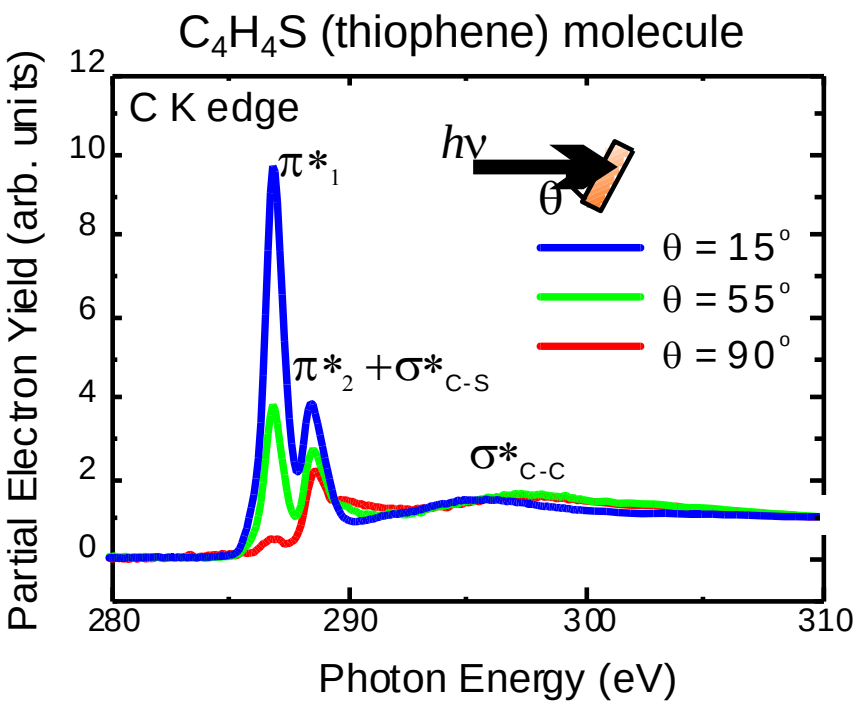
Surface & Thin Film

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. Novel SXAS Techniques
    - 3-1. Depth-resolved XAS
    - 3-2. Wavelength-dispersive XAS

X-ray Absorption Spectroscopy (XAS)

- Transition from core to unoccupied states -



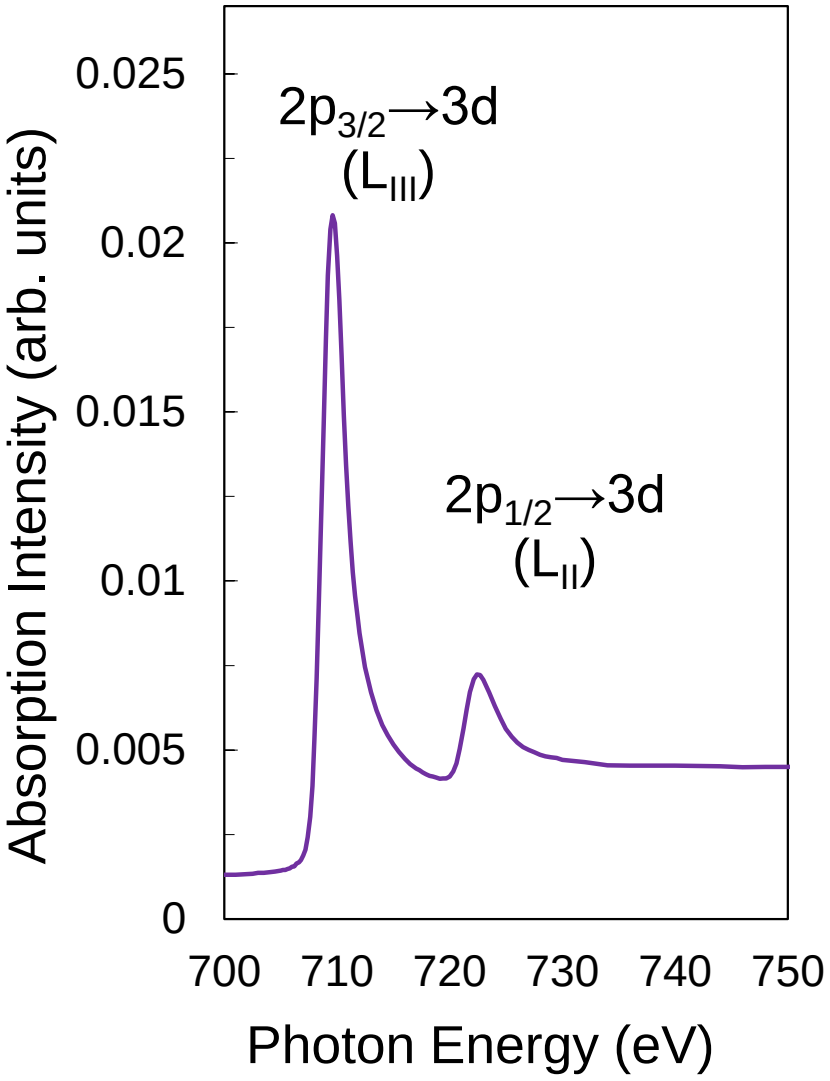
1. Element selectivity
   <– Core-hole excitation (1s, 2p…)
   (C: 290 eV, O: 530 eV, Fe: 710 eV, Ni: 850 eV…)
2. Information on chemical species
   <– Characteristic spectral features (π*, σ*…)
3. Structural information (bond length, etc.)
   EXAFS (Extended X-ray Absorption Fine Structure)
4. Information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

In the Soft X-ray region,

1. Vacuum environment is normally required. (NOT ultra-high vacuum)
   Special sample cell is available for ambient pressure.
2. Surface sensitive
   λ (probing depth):
   several nm for electron yield, ~0.1 μm for fluorescence yield

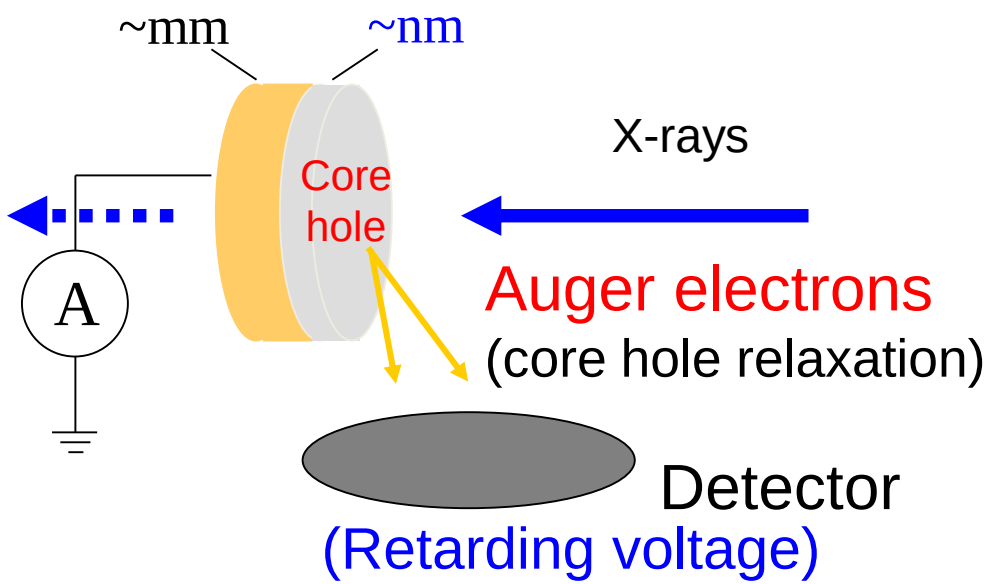
XAS Measurement in the Soft X-ray Region

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



How can we measure

X-ray absorption spectrum ?



Electron yield XAS

Total electron yield (TEY) λ~3 nm

Partial electron yield (PEY) λ~1-2 nm

cf. Fluorescence yield (FY) λ~100 nm

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

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.

1. Advantages and Disadvantages of

   Soft X-ray Absorption Spectroscopy (SXAS)

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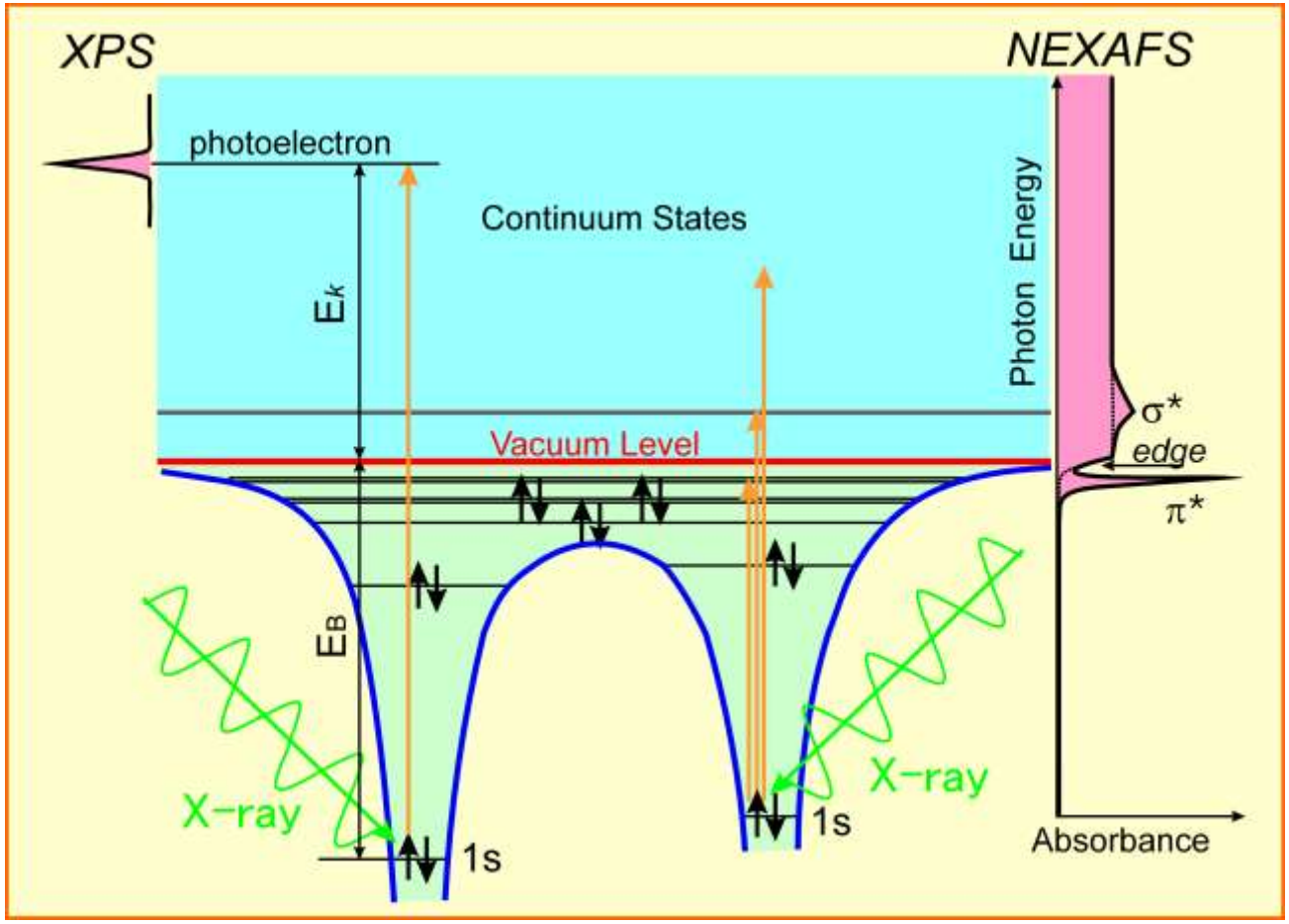
   3-1. Depth-resolved XAS

   3-2. Wavelength-dispersive XAS

Near-edge Spectroscopy

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



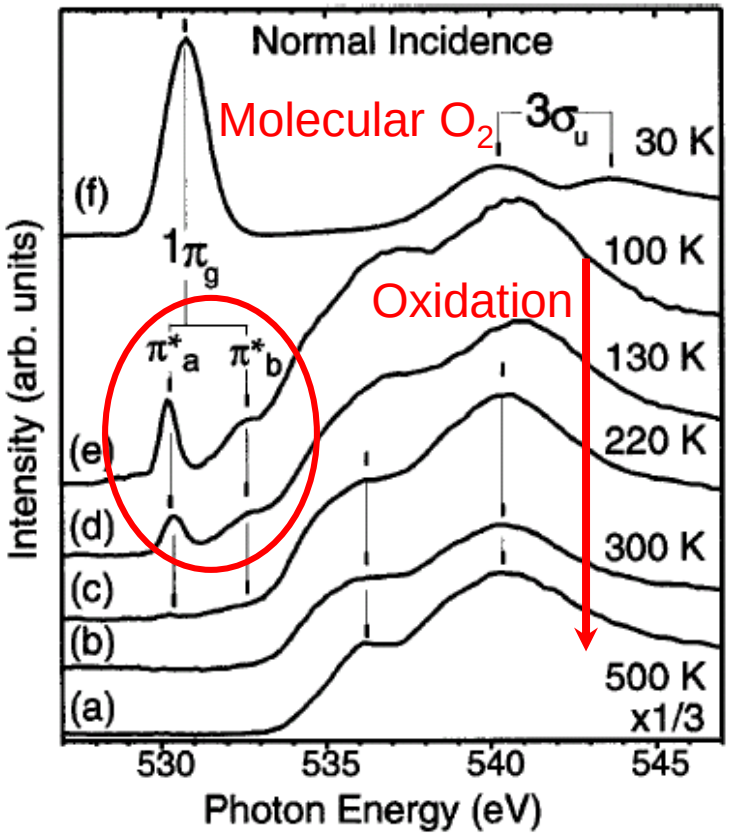
Chemical species

Structural information (orientation)

Near-edge Spectroscopy

Determination of Chemical Species

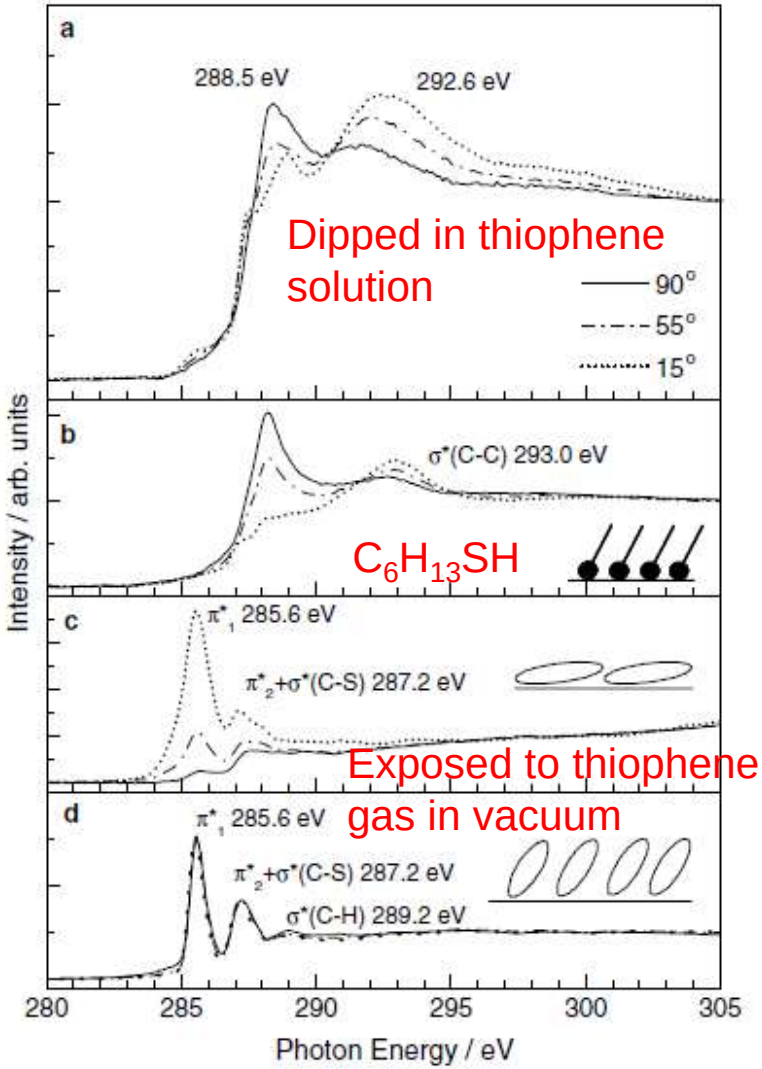
Initial oxidation process of Si



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)

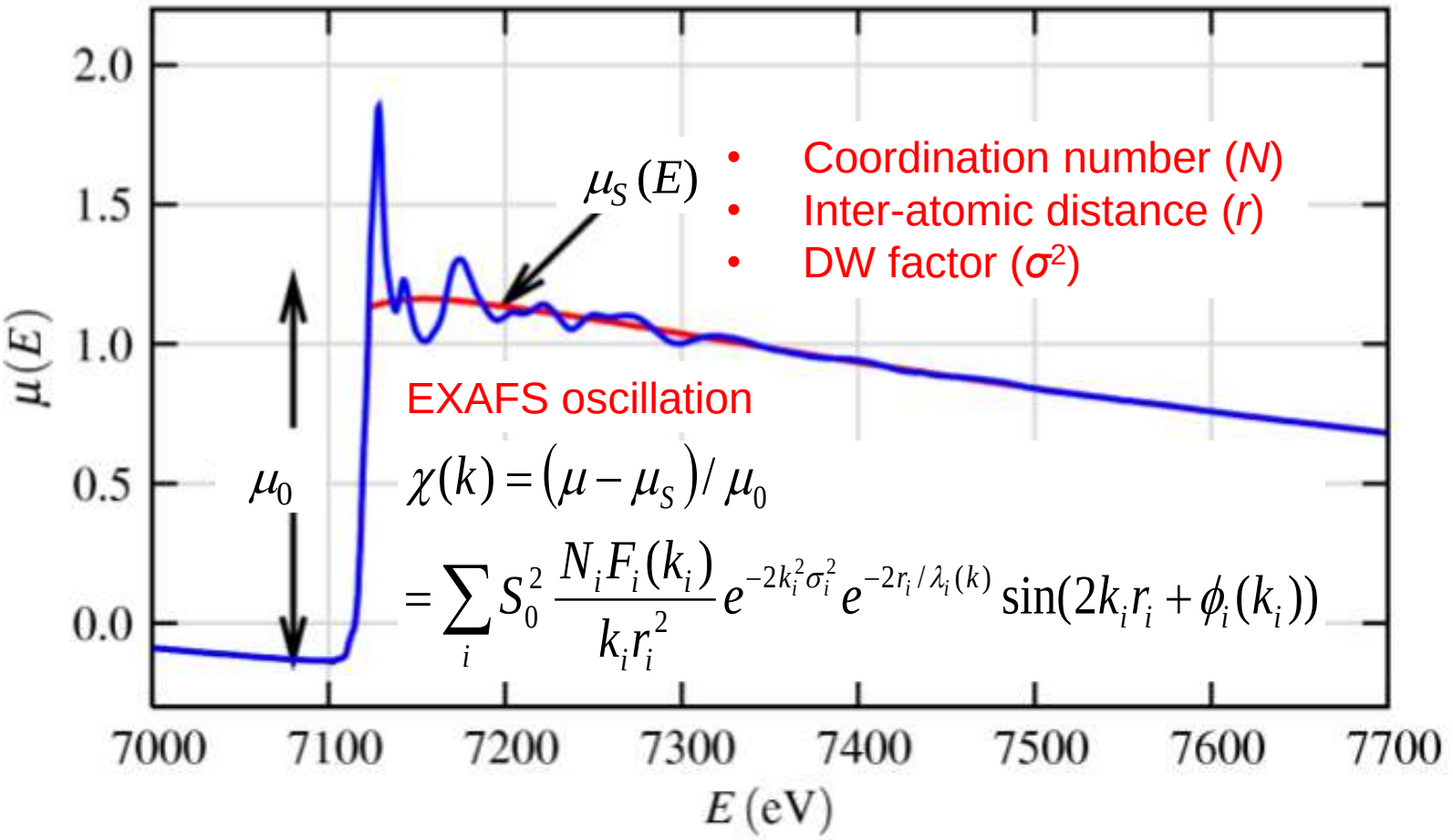


Different chemical species depending on preparation processes

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

Determination of Geometric Structure

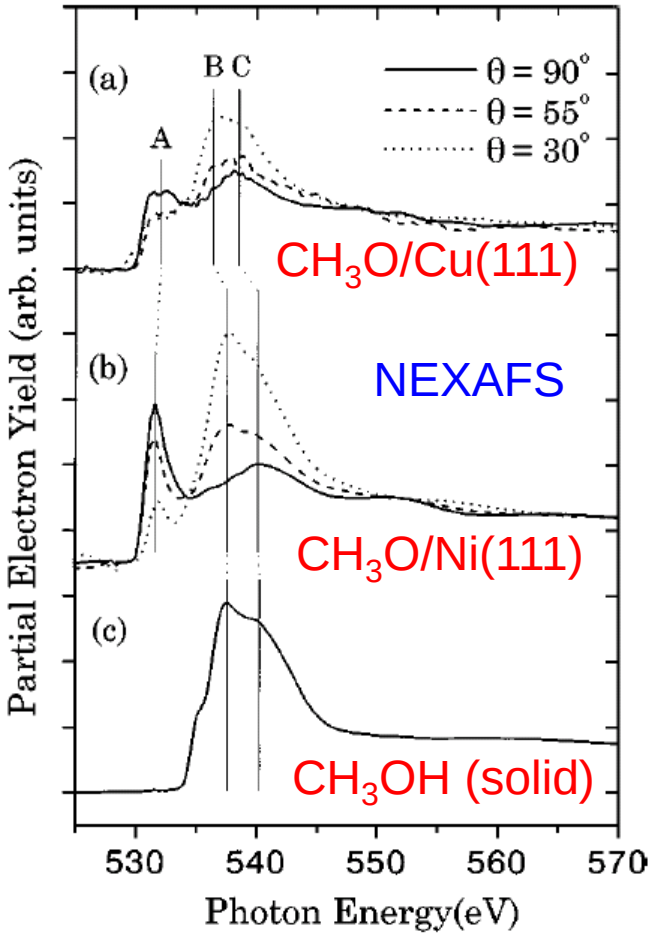
Extended X-ray Absorption Fine Structure (EXAFS)



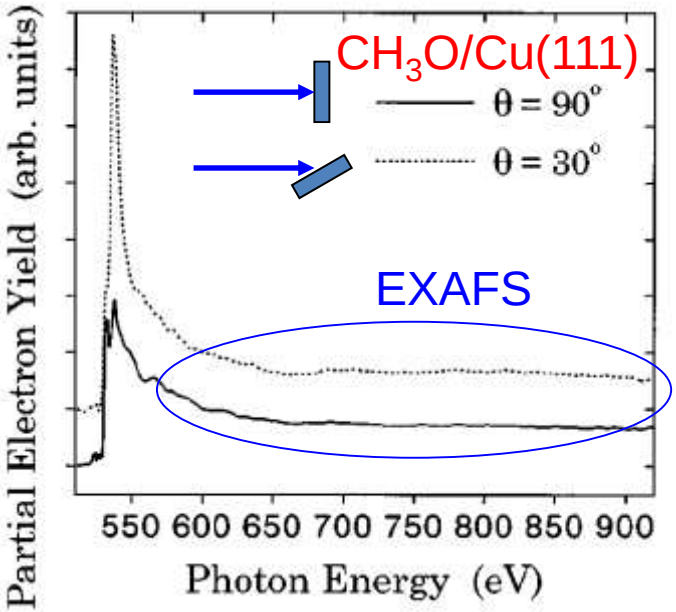
Fe *K*-edge XAFS spectrum $\mu(E)$ of FeO

Determination of Geometric Structure

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

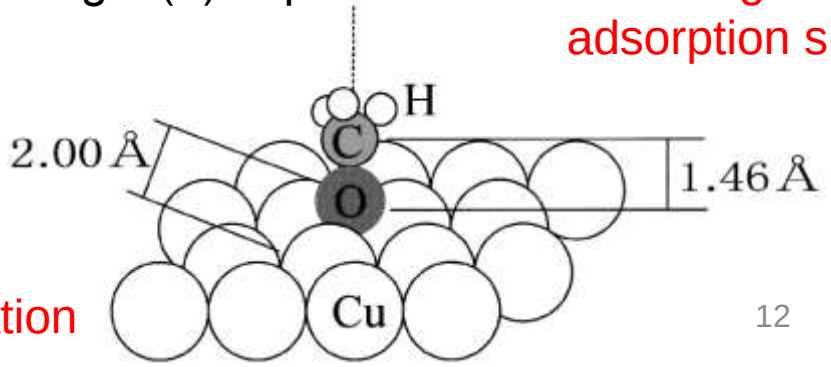


Application to surface molecule (CH_3O)



Oscillation period -> O-Cu bond length

Angle (θ) dependence -> bond angle adsorption site

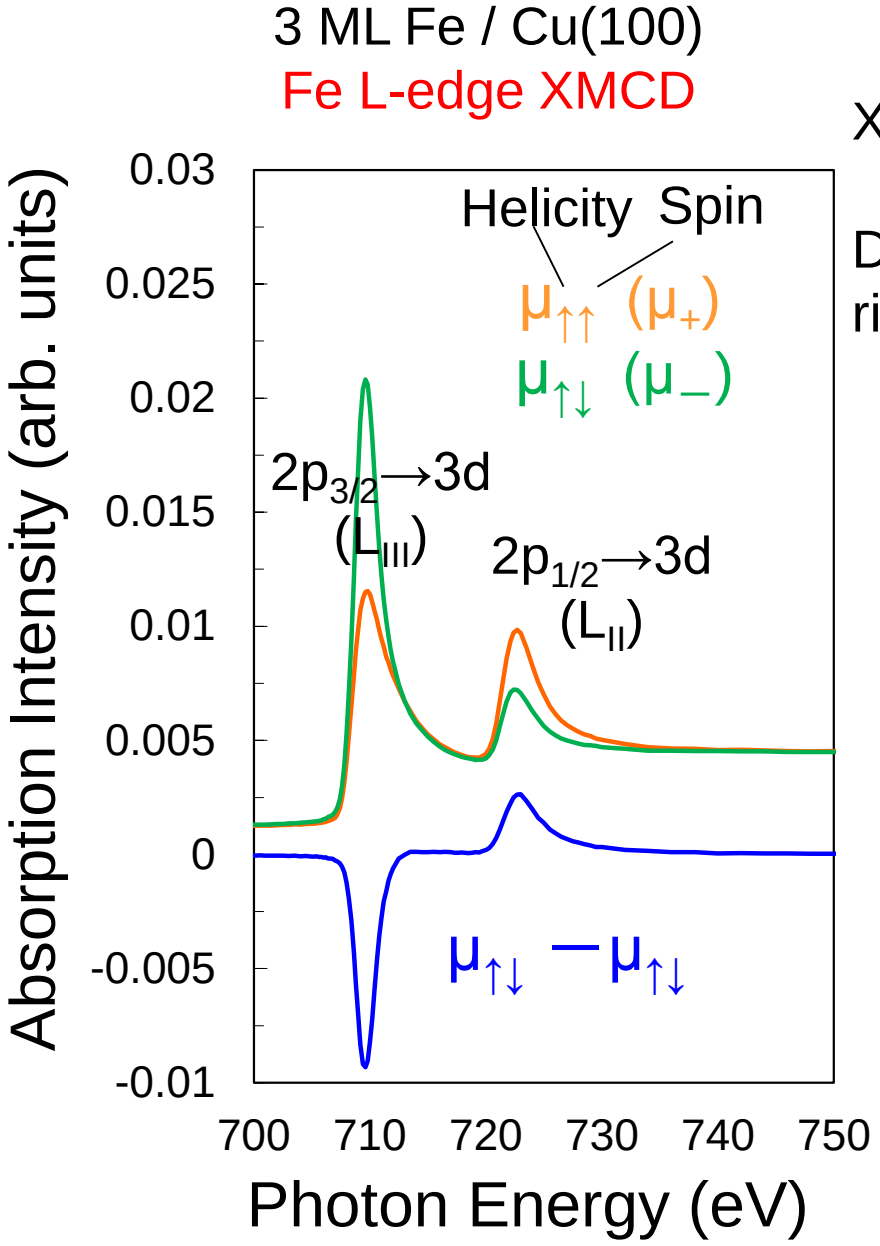


Peak B ($1s \rightarrow \sigma^*_{CO}$) -> C-O bond length

Higher energy -> Shorter bond

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…)
2. Determination of spin and orbital magnetic moments
   <– Sum rules
3. High sensitivity

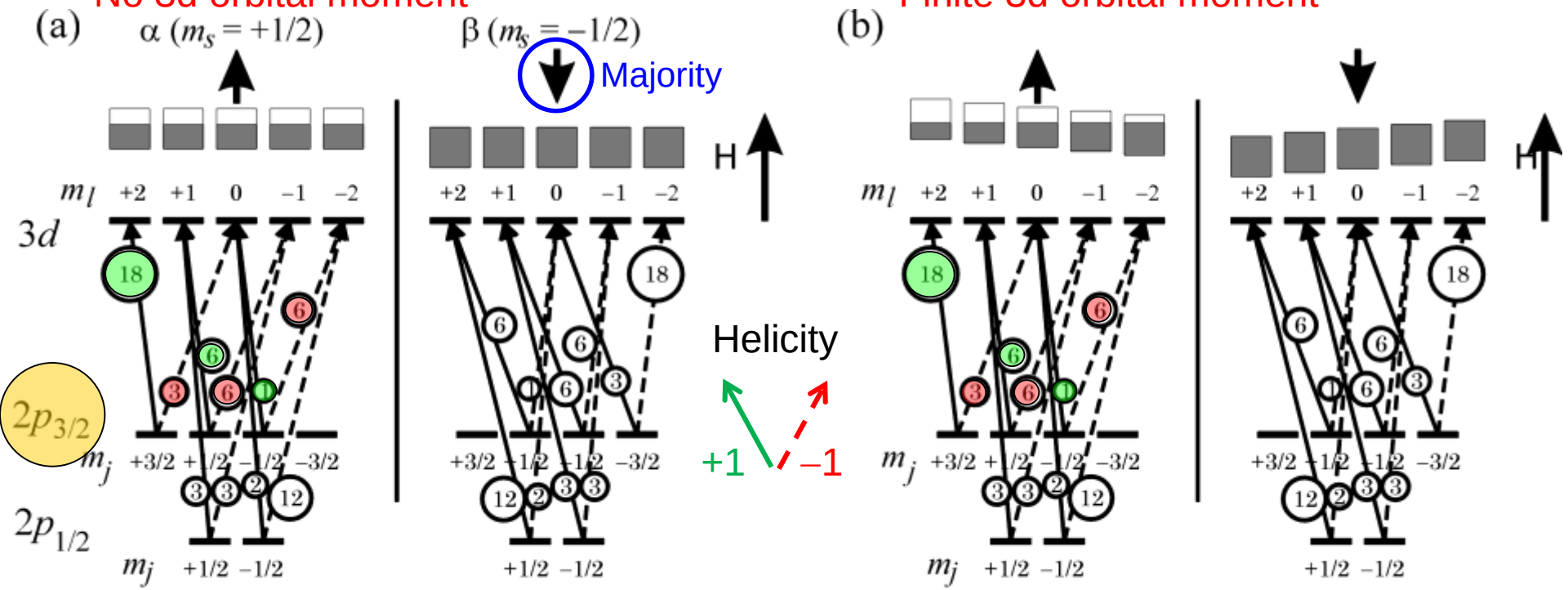
Element-specific vector average of magnetic moment over the whole investigation area

Fe↑ Gd↓ Fe↑ Gd↓ → Fe and Gd XMCD
Fe↑ Gd↑ Fe↑ Gd↓ → no Gd XMCD

Principle of XMCD

No 3d orbital moment

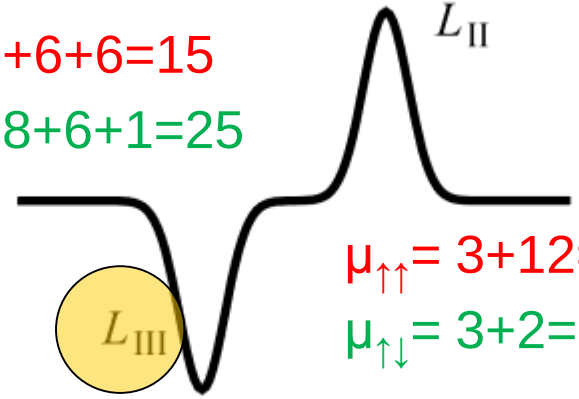
Finite 3d orbital moment



Dipole transition probability

$\mu_{\uparrow\uparrow}$= 3+6+6=15

$\mu_{\uparrow\downarrow}$= 18+6+1=25

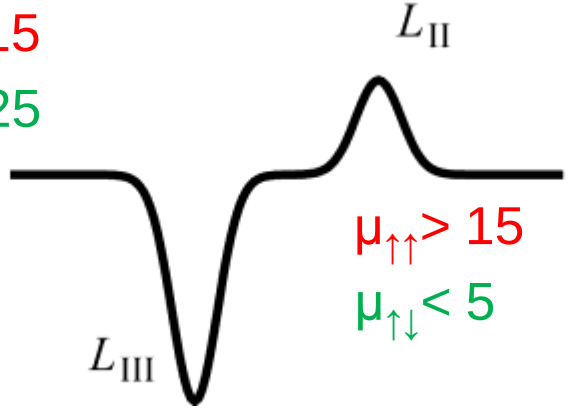


$\mu_{\uparrow\uparrow}$= 3+12=15

$\mu_{\uparrow\downarrow}$= 3+2=5

$\mu_{\uparrow\uparrow}$< 15

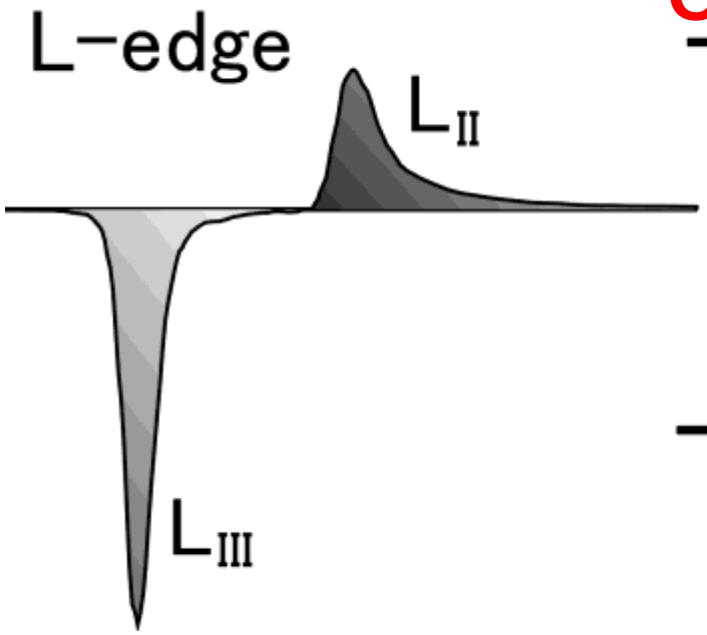
$\mu_{\uparrow\downarrow}$> 25



$\mu_{\uparrow\uparrow}$> 15

$\mu_{\uparrow\downarrow}$< 5

XMCD Sum Rules



Orbital moment m_l

$$\frac{\int L_{III}(\mu_+ - \mu_-) + \int L_{II}(\mu_+ - \mu_-)}{} \quad < 0 \rightarrow m_l > 0$$

Spin moment m_s

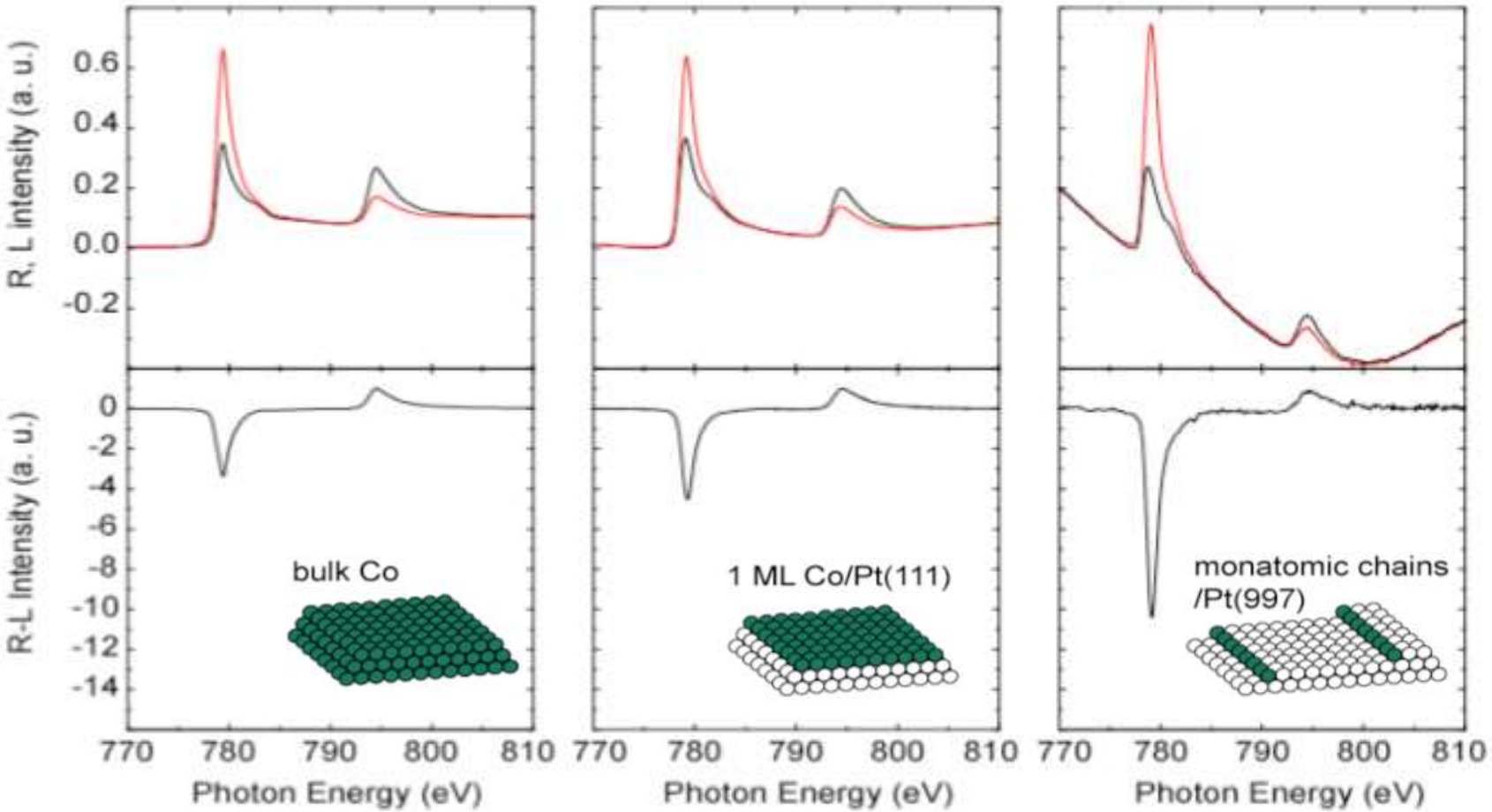
$$\frac{\int L_{III}(\mu_+ - \mu_-) - 2\int L_{II}(\mu_+ - \mu_-)}{} \quad < 0 \rightarrow m_s > 0$$

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

Magnetism of Thin Films Studied by XMCD

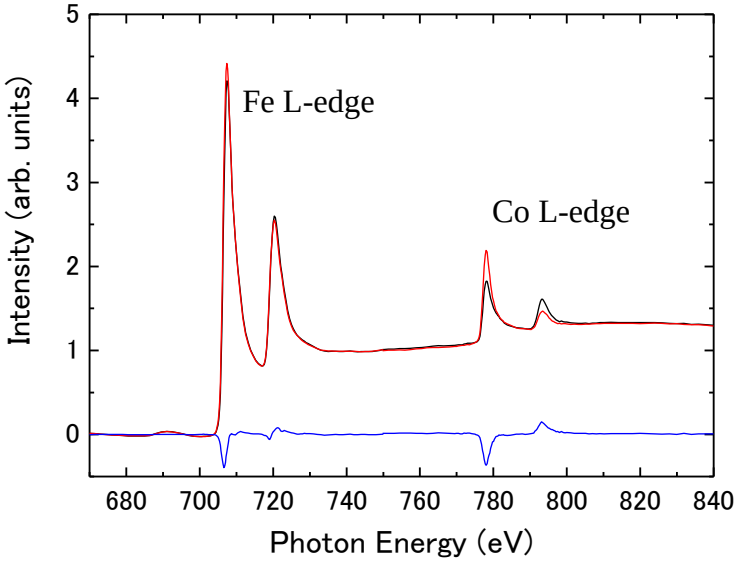
Co *L*-edge XMCD spectra

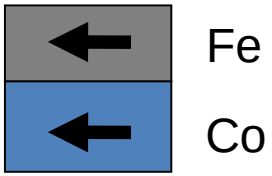
P. Gambardella, Nature **416**, 301 (2002)



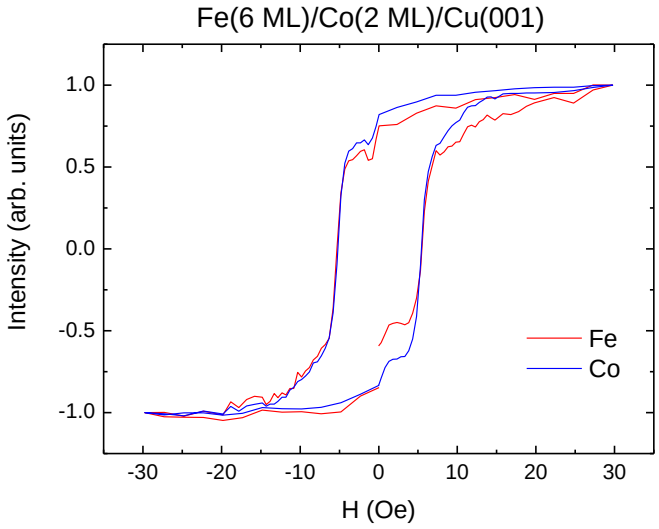
Larger orbital moment, m_l
due to lower dimension

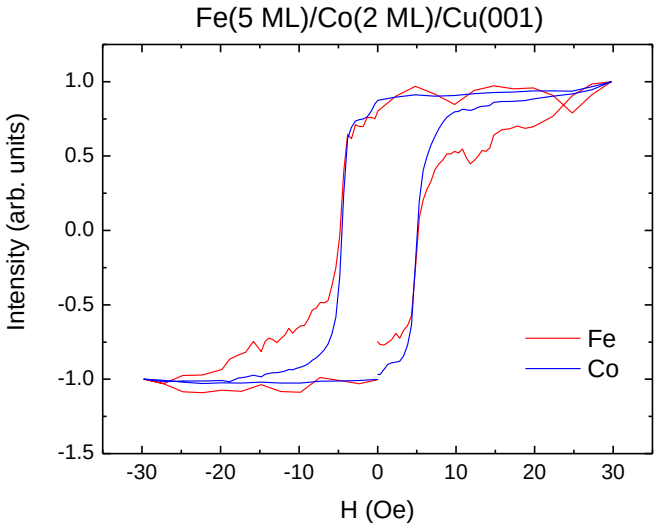
Utilization of Element Selectivity of XMCD



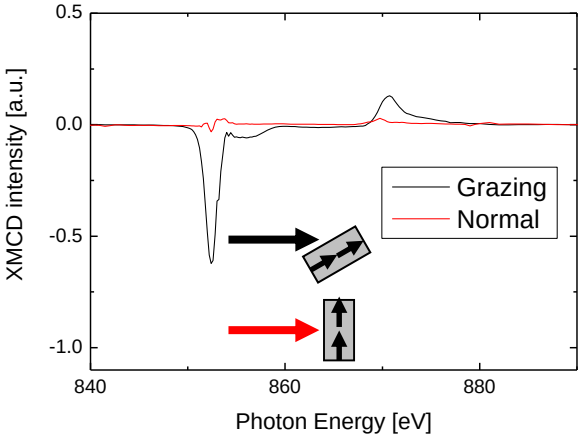


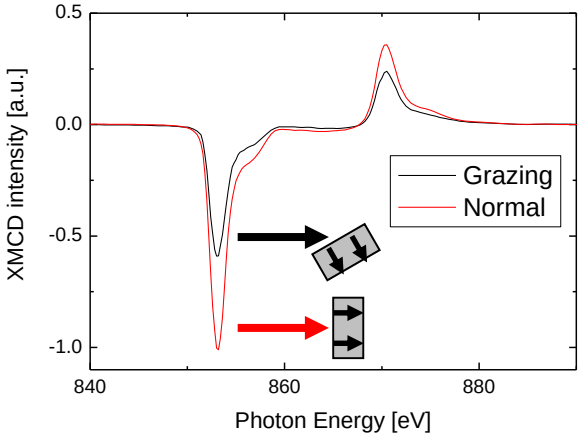
Magnetic-field dependence of XMCD at Fe and Co L edges

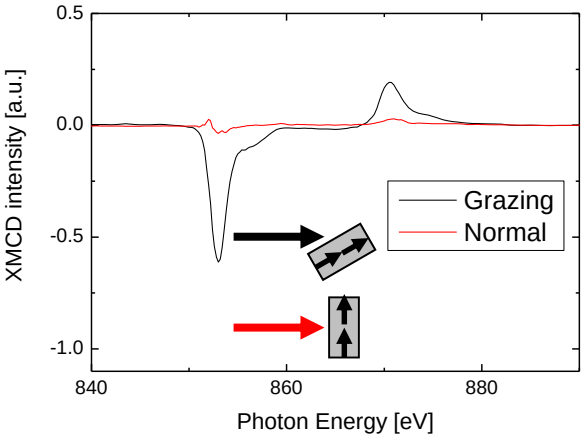


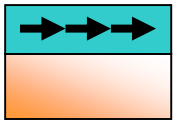


Angle Dependence of XMCD
(1) Weak magnetic field or remanent measurements

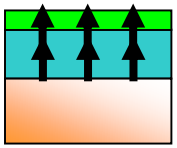




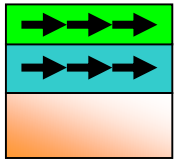




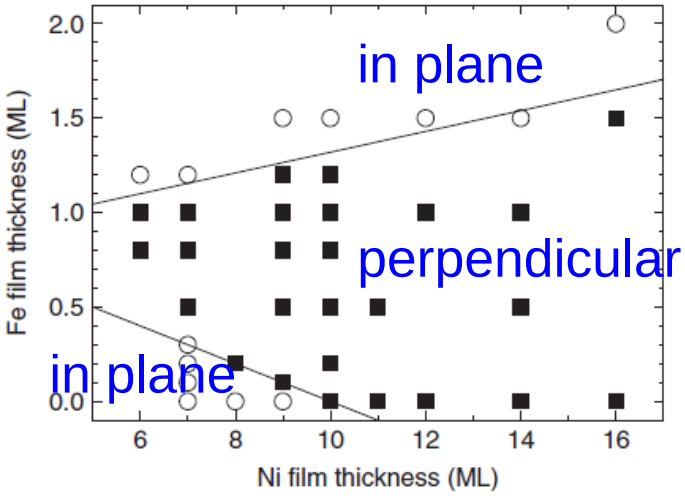
Ni (7.5 ML)
Cu(100)



Fe (0.7 ML)
Ni (7.5 ML)
Cu(100)



Fe (4 ML)
Ni (7.5 ML)
Cu(100)



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

–> determination of easy axis of magnetization

Information on anisotropy of orbital moment

–> estimation of magnetic anisotropy

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

Sakamaki and Amemiya, Appl. Phys. Express 4 (2011) 073002.

Sakamaki and Amemiya, Phys. Rev. B 87 (2013) 014428.

Angle Dependence of XMCD
(2) High magnetic field measurements

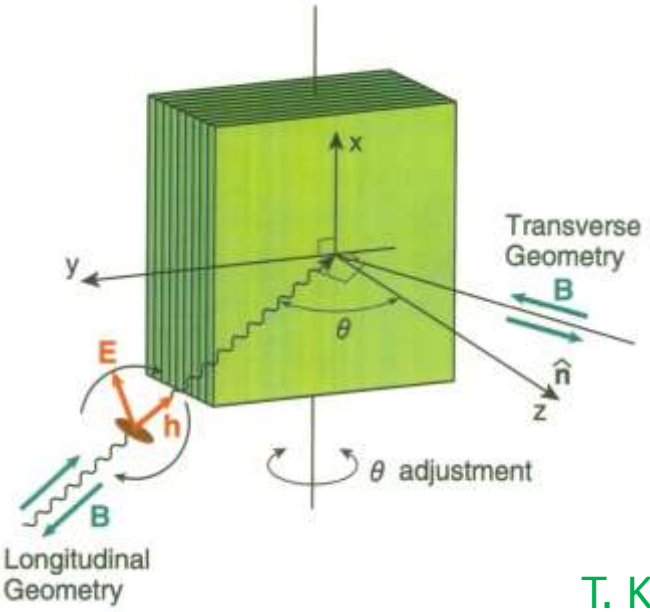
Angle-dependent XMCD

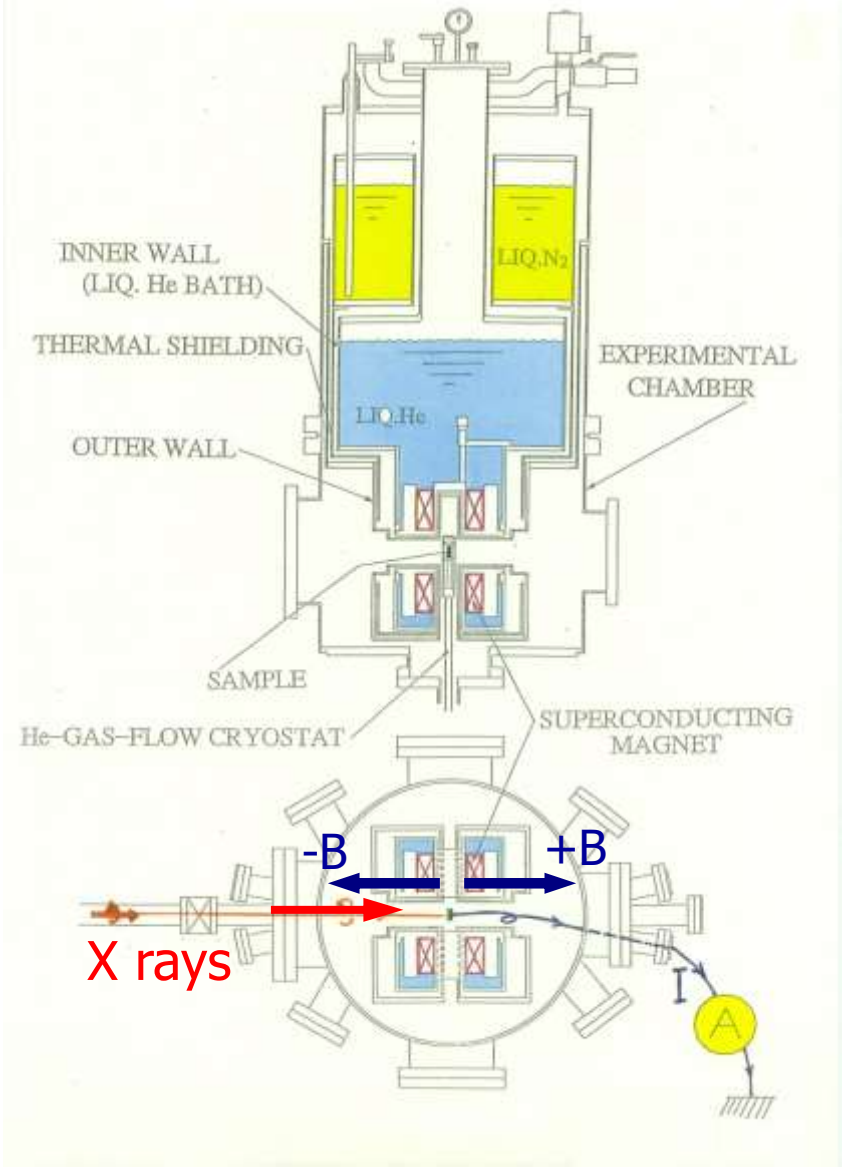
=> **Magnetic anisotropy**

Direct determination of m_s and m_T

m_T : dipole magnetic moment

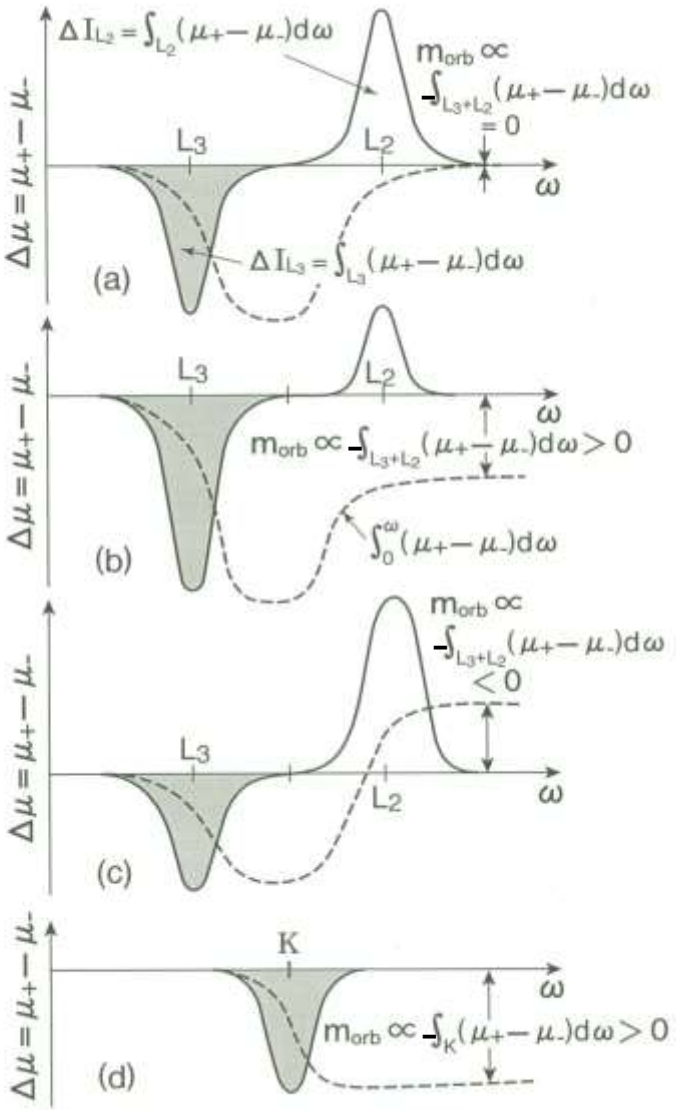
$$\mathbf{T} = \sum_i \mathbf{s}_i - 3\mathbf{r}_i(\mathbf{r}_i \cdot \mathbf{s}_i)/r_i^2 .$$





T. Koide et al., Rev. Sci. Instrum. **63**, 1462 (1992).

Angle-dependent XMCD Sum Rules



Orbital sum rule

$$\frac{[\Delta I_{L_3} + \Delta I_{L_2}]^{\theta}}{I_{L_3} + I_{L_2}} = -\frac{3 \cdot m_l^{\theta}}{4 n_h \cdot \mu_B}$$

Spin sum rule

$$\frac{[\Delta I_{L_3} - 2 \cdot \Delta I_{L_2}]^{\theta}}{I_{L_3} + I_{L_2}} = -\frac{(m_s + 7 \cdot m_T^{\theta})}{2 n_h \cdot \mu_B}$$

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

$m_l^{\theta} = m_l^{\perp} \cos^2\theta + m_l^{//} \sin^2\theta$

$m_T^{\theta} = m_T^{\perp} \cos^2\theta + m_T^{//} \sin^2\theta$

m_s does not depend on θ

⇒ **Direct determination of**

m_s, $m_l^{//}$, $m_l^{\perp}$, $m_T^{//}$, $m_T^{\perp}$

Investigation of Interface Magnetism

T. Koide et al., Phys. Rev. Lett. 87, 257201 (2001).

Au/Co(2 ML)/Au(111)

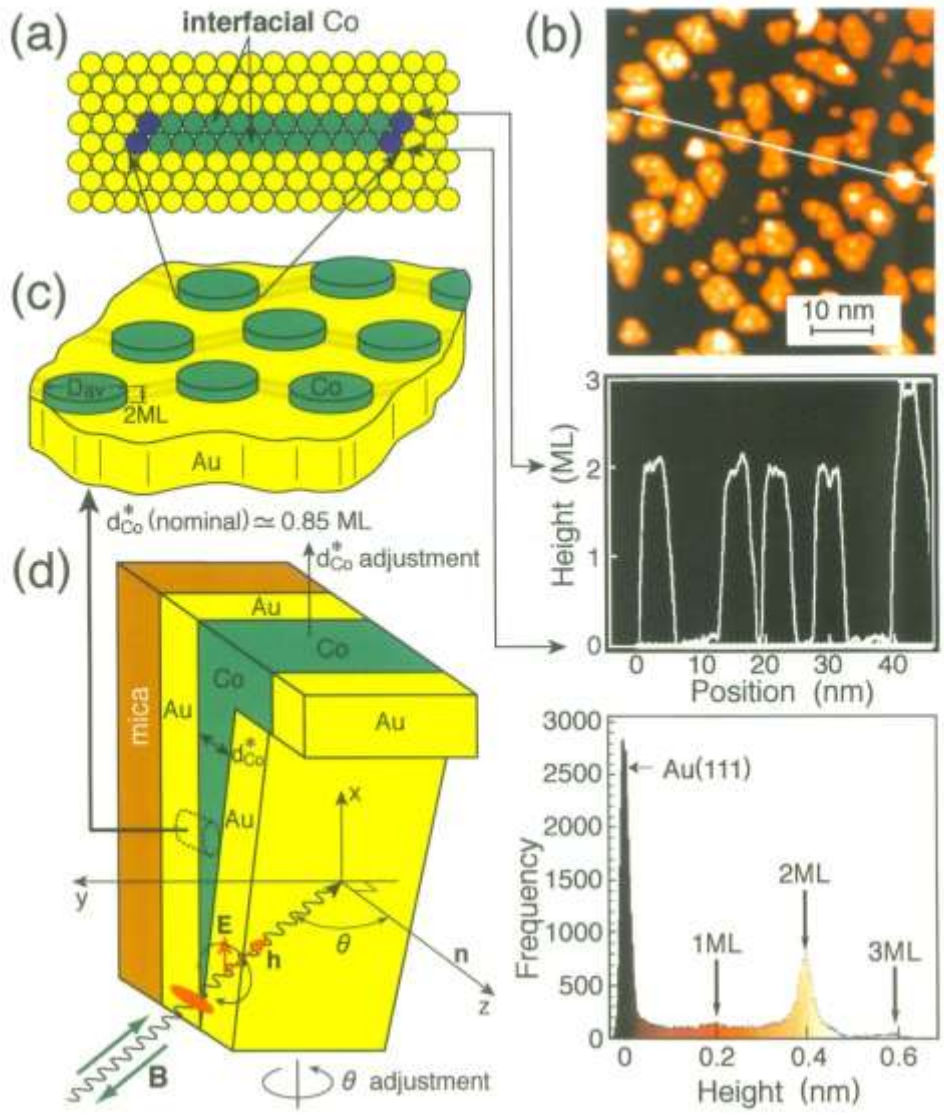
Self-assembled Co islands due to a reconstruction of Au surface

All Co atoms are regarded to "interface" because of 2 ML thickness

⇒ **Direct observation of interface magnetism**

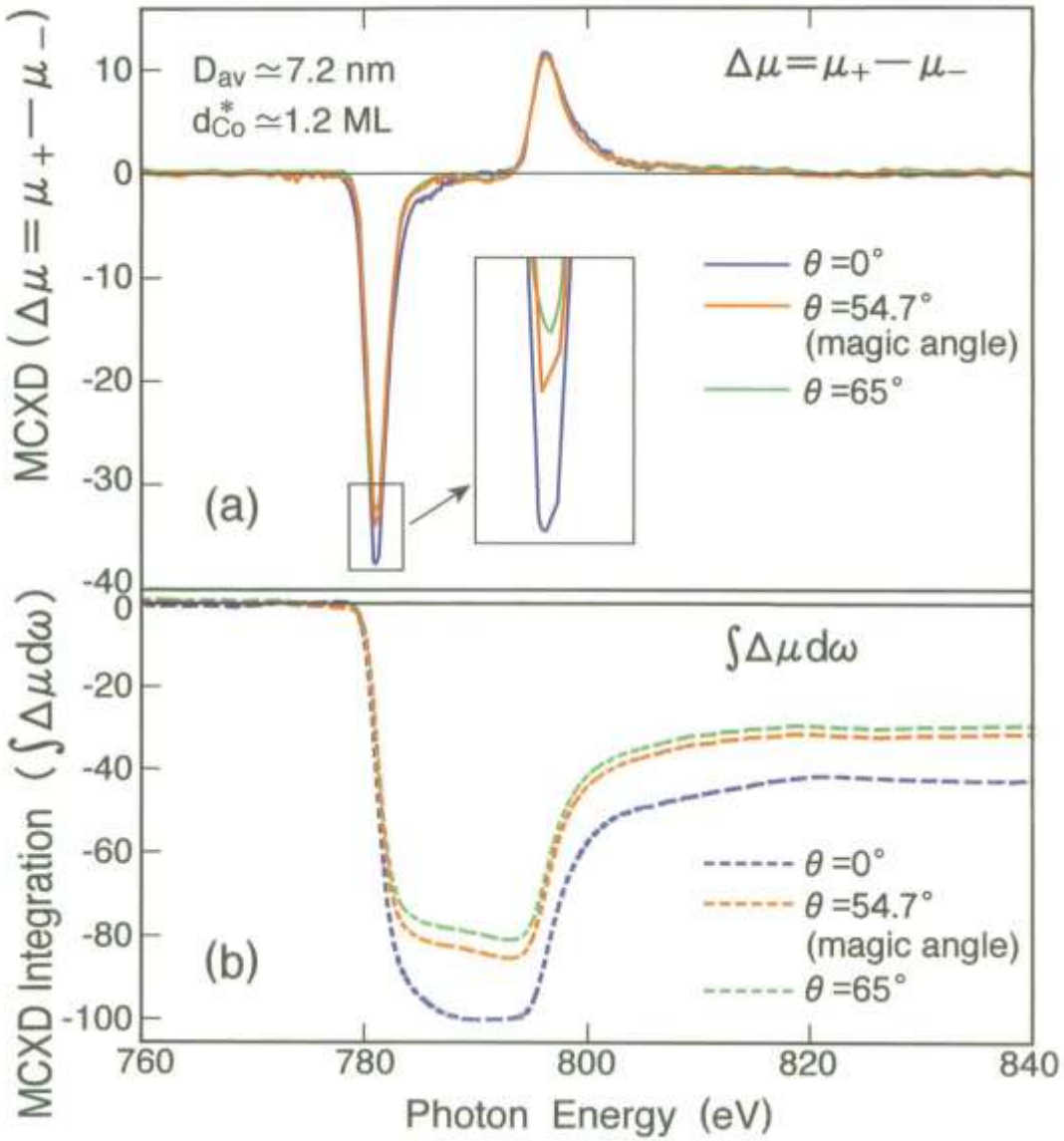
Determination of

m_s, $m_l^{//}$, $m_l^{\perp}$, $m_T^{//}$, $m_T^{\perp}$



Angle-dependent XMCD Measurements

T. Koide et al., Phys. Rev. Lett. 87, 257201 (2001).



PF BL-11A

Angle dependence in XMCD

<– Anisotropy in m_l, m_T

$$m_j^{\theta} = m_j^{\perp}\cos^2\theta + m_j^{//}\sin^2\theta$$

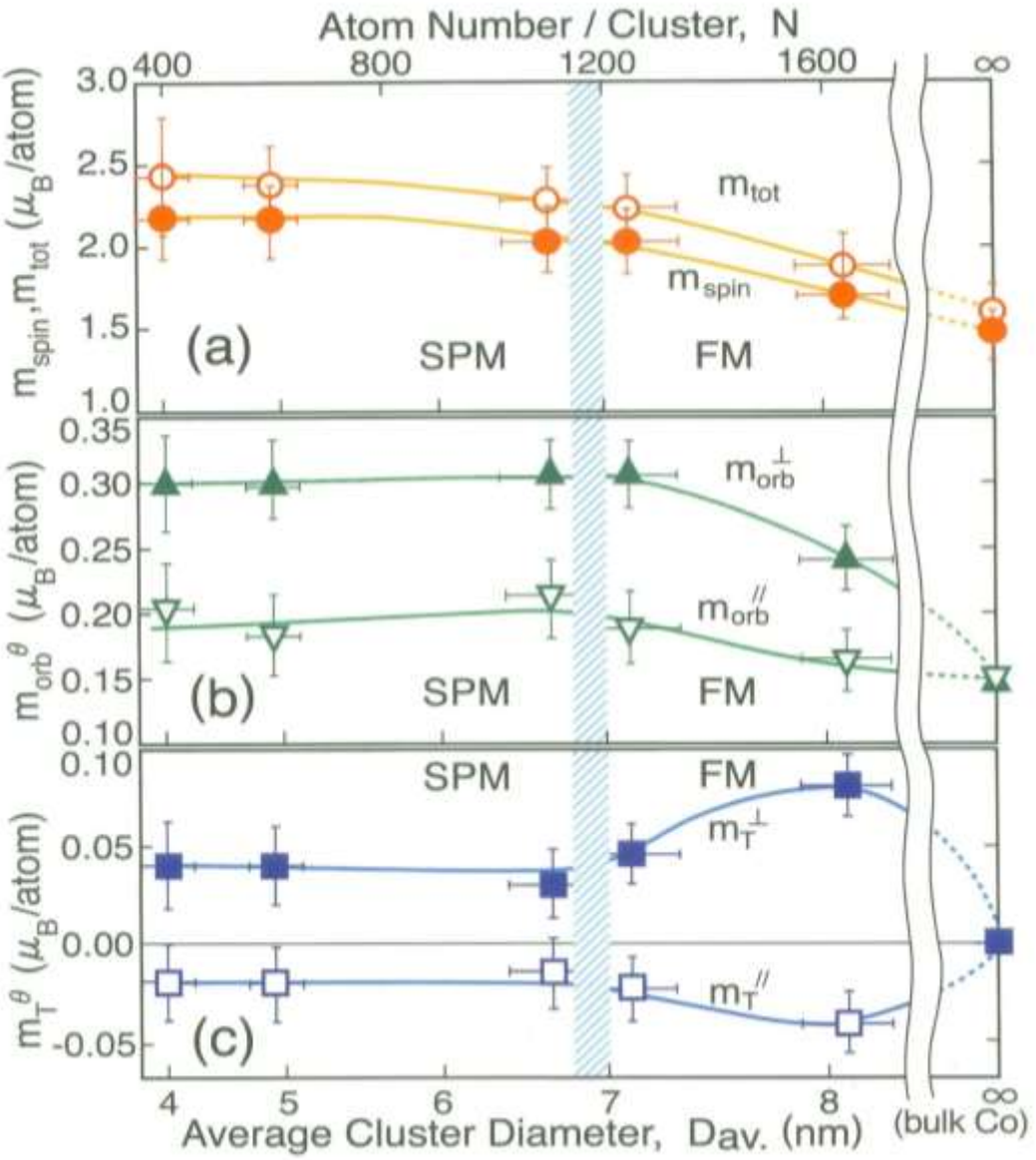
($j = l$ or T)

$$m_T^{\perp} + 2\, m_T^{//} = 0$$

⇒ Determination of all moments including their anisotropy

Determined Magnetic Moments

T. Koide et al., Phys. Rev. Lett. 87, 257201 (2001).



Cluster-size dependent phase transition

FM: ferromagnetic

SPM: super-paramagnetic

1. Advantages and Disadvantages of

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2. SXAS studies on Surface and Thin films

3. Novel SXAS Techniques

   3-1. Depth-resolved XAS

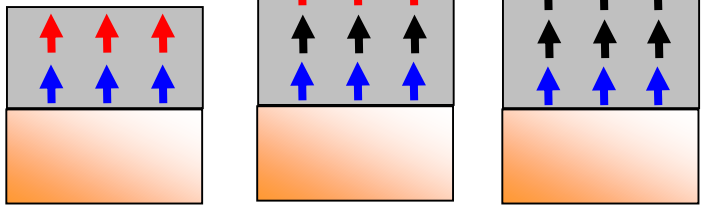
   3-2. Wavelength-dispersive XAS

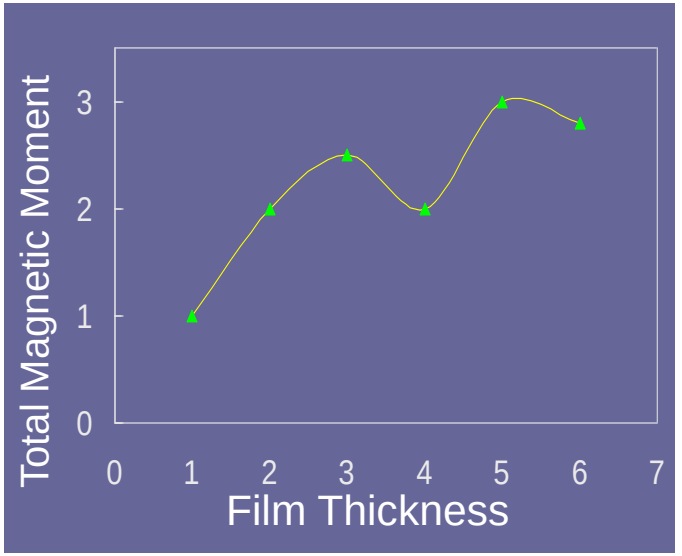
Conventional Technique for Depth Profiling

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

Co/Cu(100) - Surface & interface orbital moment -

Tischer et al., Phys. Rev. Lett. 75 (1995) 1602.

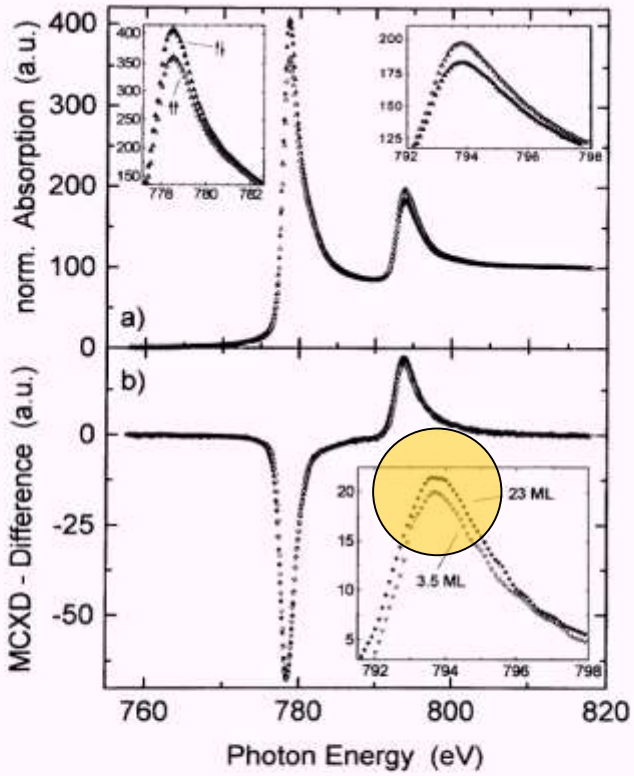


FIG. 2. (a) The normalized absorption spectrum for 3.5 ML Co/Cu(100). Open triangles indicate the photon spin parallel to the remanent magnetization, full triangles antiparallel. (b) MCXD difference for the 3.5 ML film (triangles) and a thick 23 ML film (circles). Both are normalized to the same L_3 intensity to demonstrate that the dichroic response around the L_2 edge is relatively smaller for the thin film.

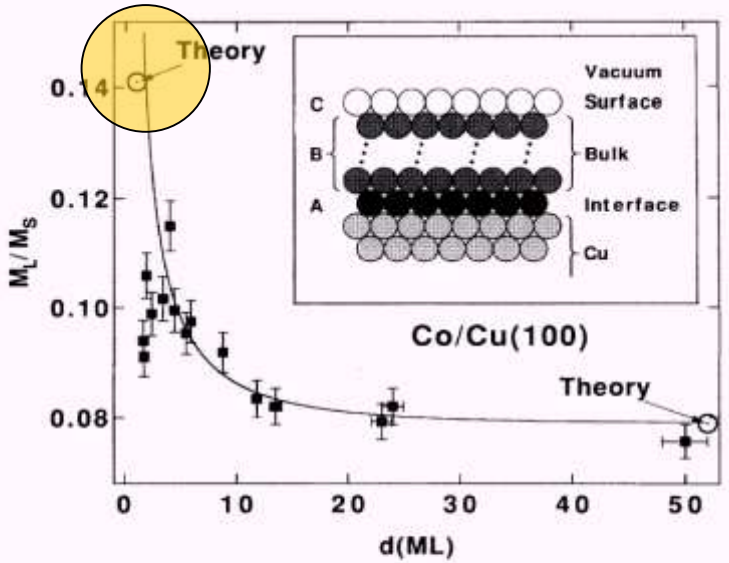
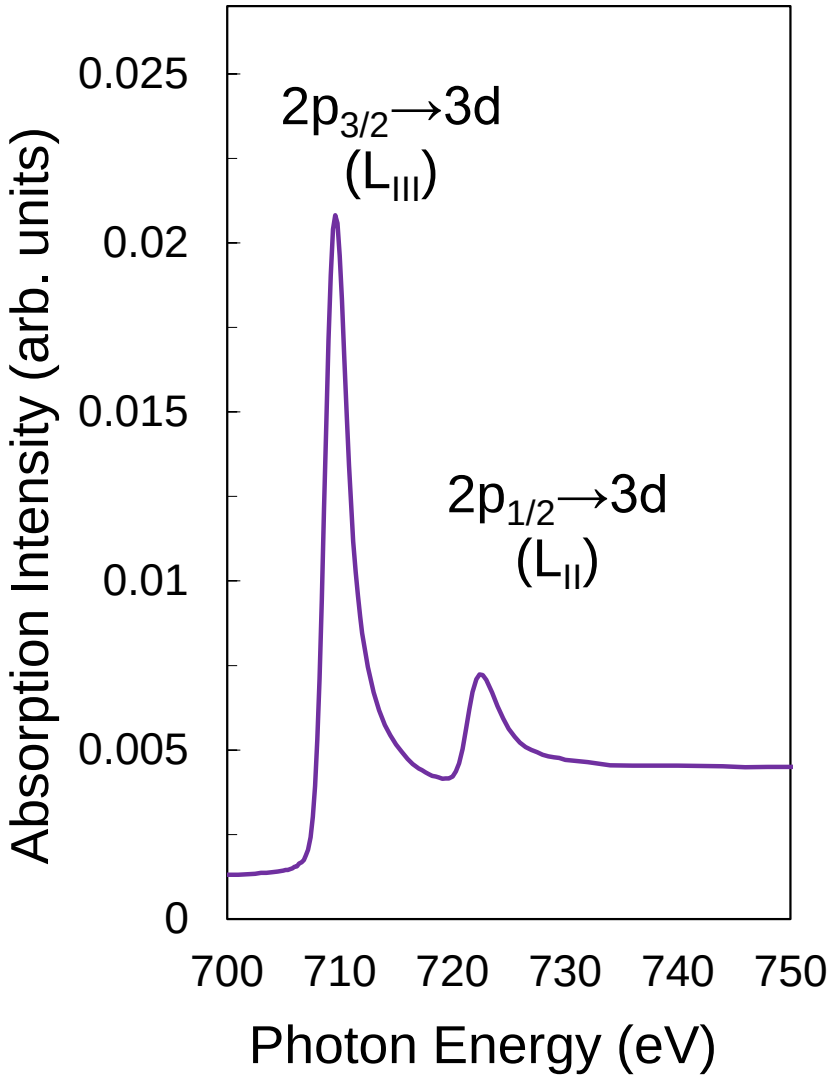


FIG. 3. The ratio of orbital versus spin moment M_L/M_S as a function of film thickness d. The open circles give the theory taken from Table I. The full squares show the experiment. The solid line is a fit using Eq. (1) with the parameters given in the last row of Table I. Note that the fit was performed only for $d \geq 3$ ML, corresponding to well-defined, epitaxial growth. The surface, interface, and bulk contributions used in Eq. (1) are schematically shown in the inset.

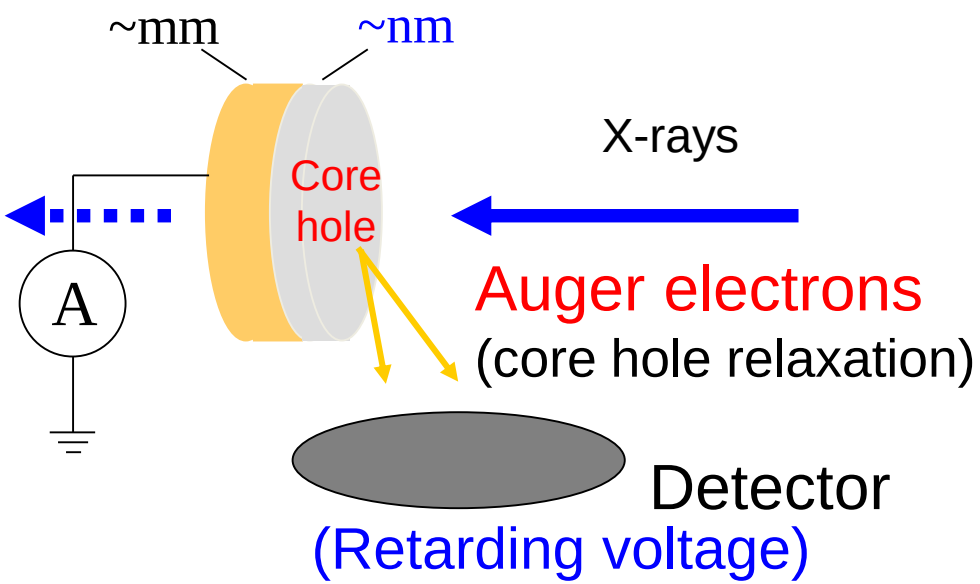
XAS Measurement in the Soft X-ray Region

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



How can we measure

X-ray absorption spectrum ?



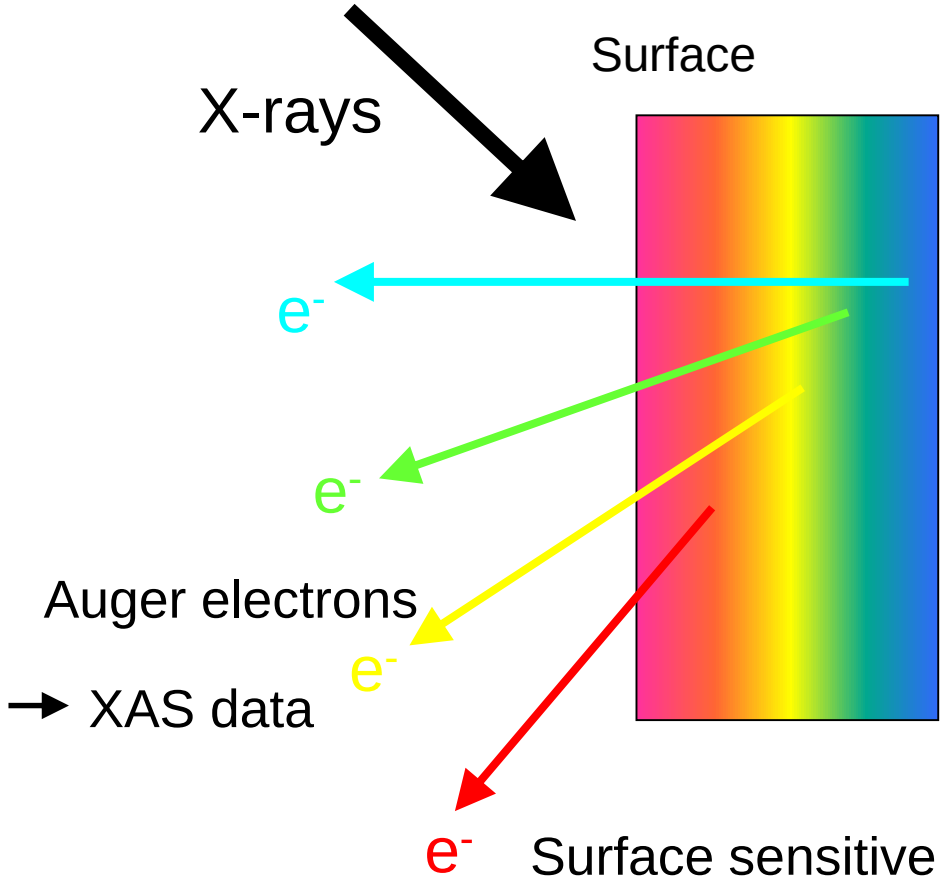
Electron yield XAS

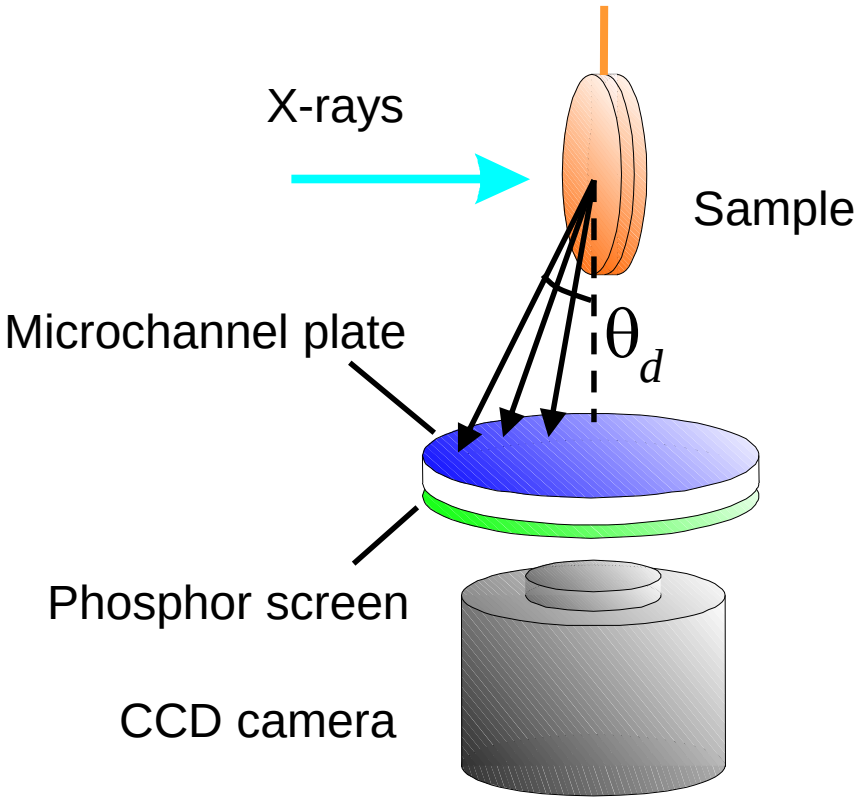
Total electron yield (TEY)

Partial electron yield (PEY)

cf. Fluorescence yield (FY)

Principle of Depth-resolved XAS





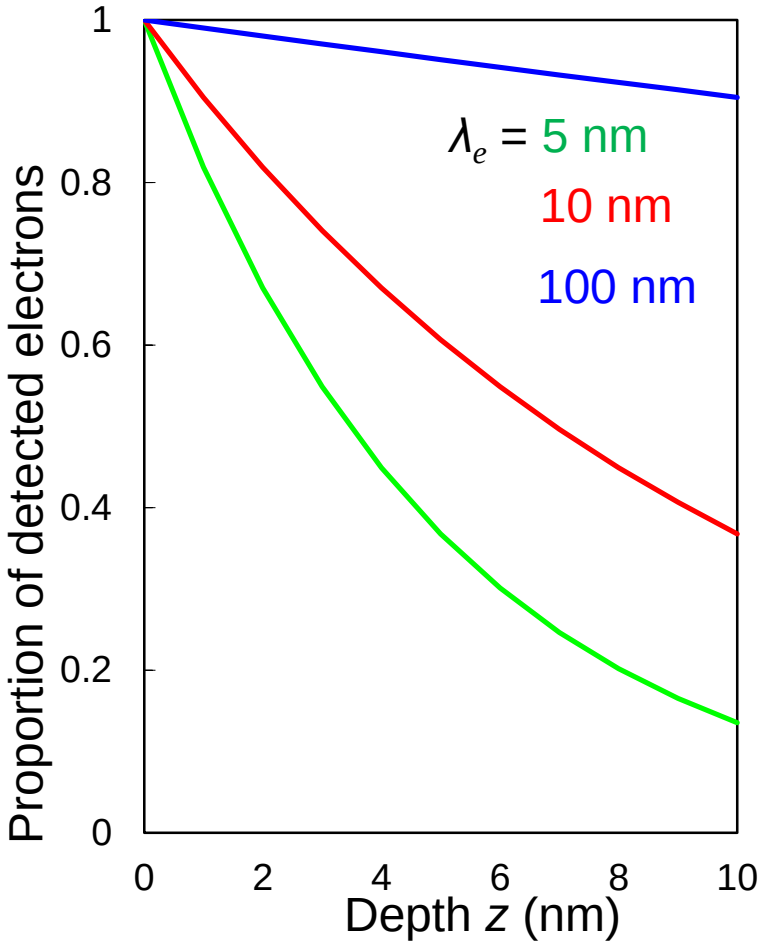
Electron yield XAS measurements at different detection angles, θ_d

→ A set of XAS data with different probing depths

Probing Depth (effective escape depth) : λ_e

Number of detected electrons emitted at depth z : $I = I_0 \exp(-z/\lambda_e)$

I_0 : Original number of emitted electrons



Smaller λ_e

⇒ Larger contribution from surface

XAS:

Averaged information per atom

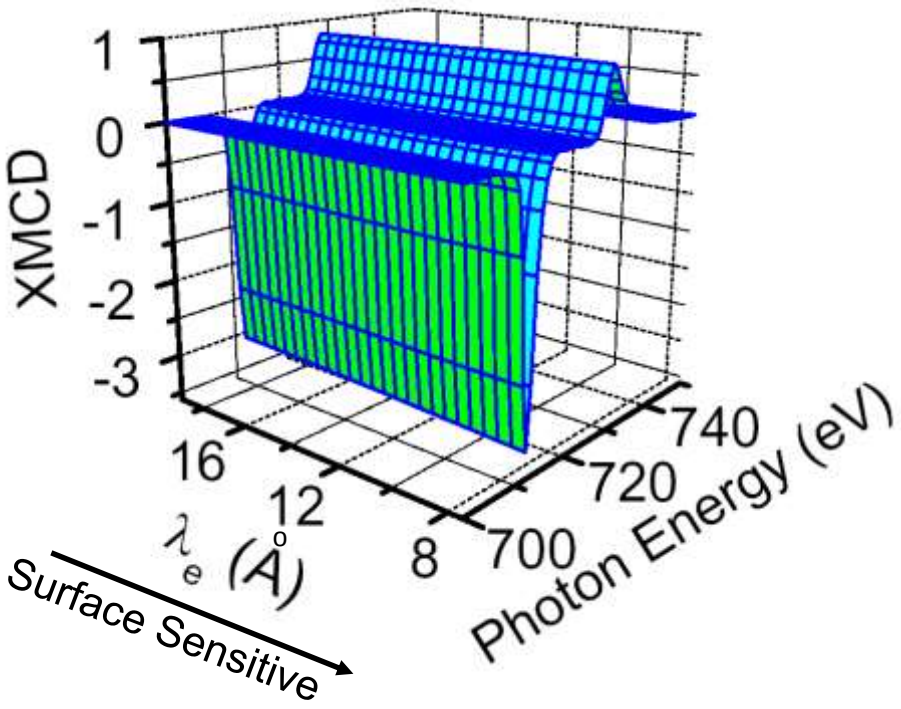
Depth-resolved XAS :

$\exp(-z/\lambda_e)$-weighted average

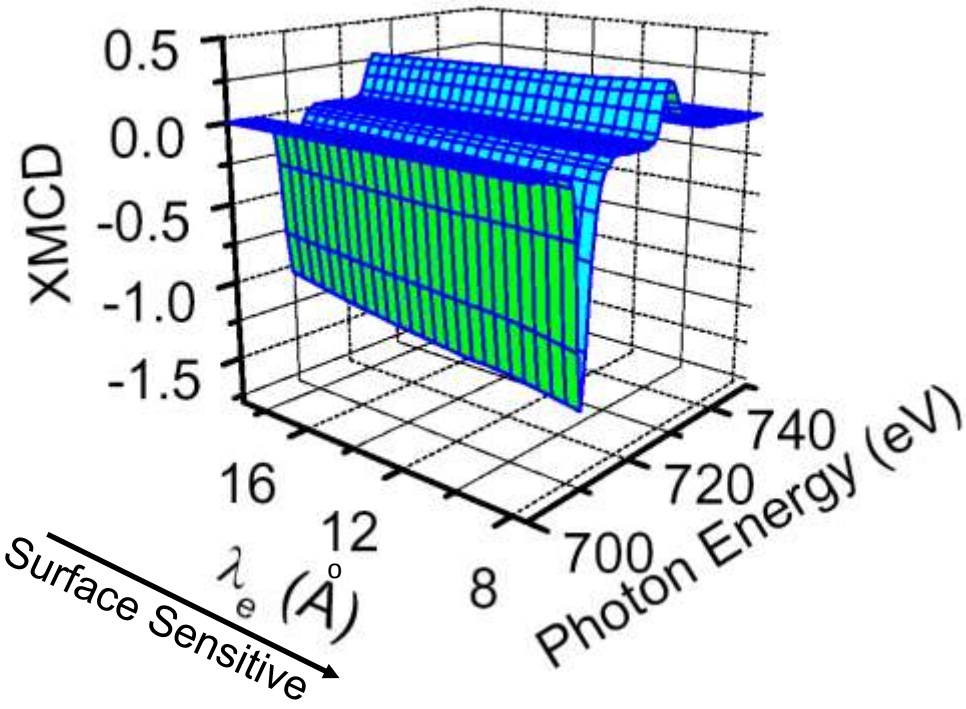
Feasibility Study: Depth-resolved XMCD of Fe/Cu(100)

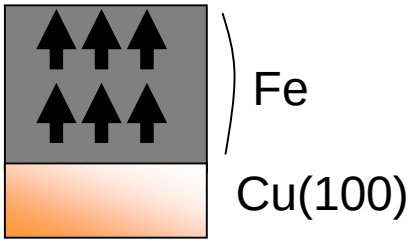
Amemiya et al., Appl. Phys. Lett. 84 (2004) 936. Normal Incidence, 130 K

3 ML Fe

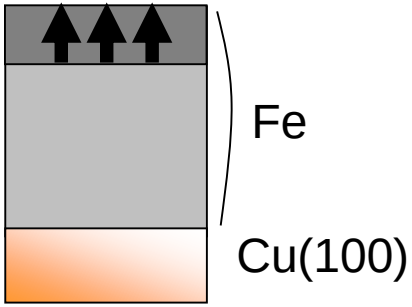


7 ML Fe



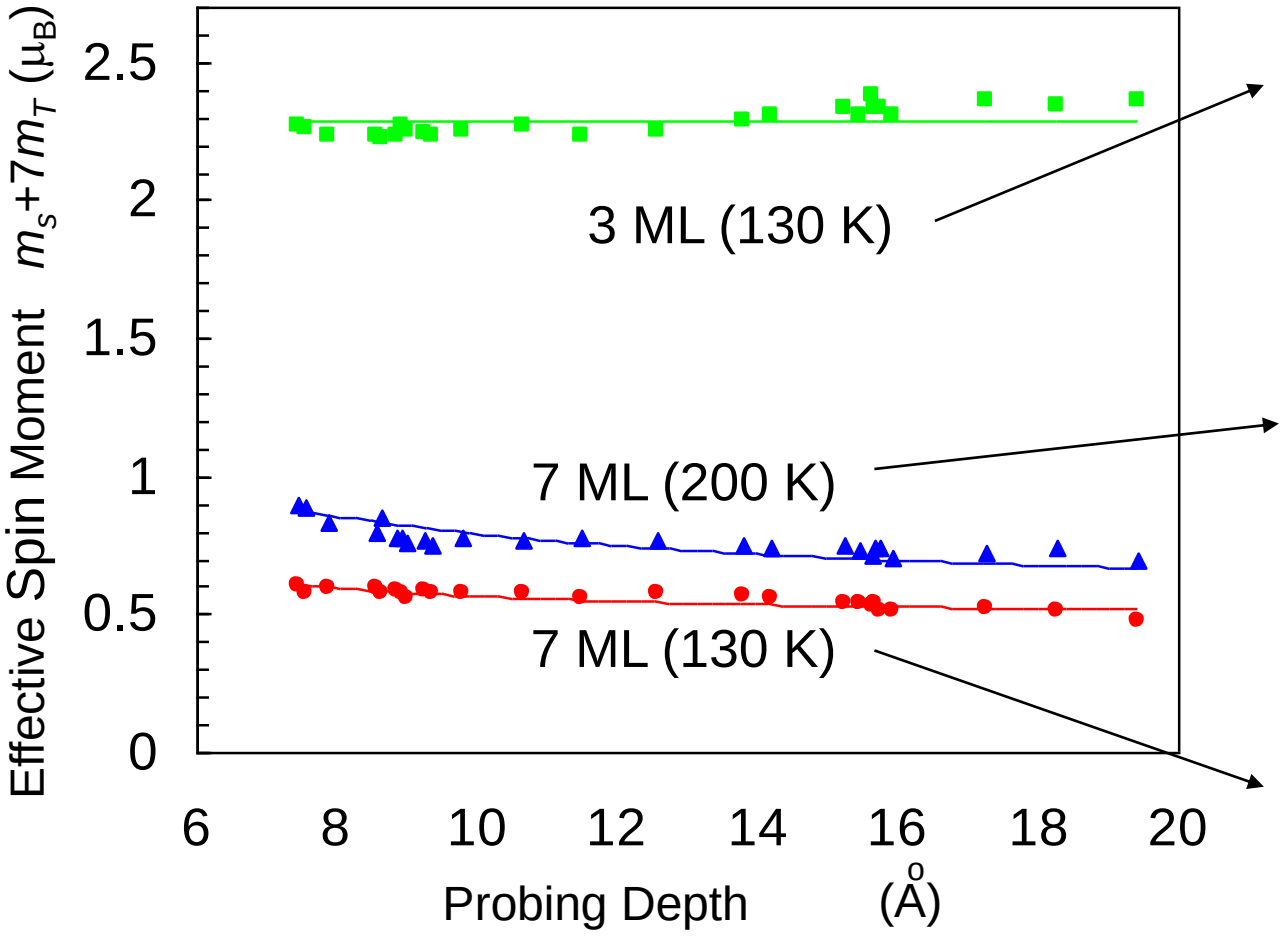


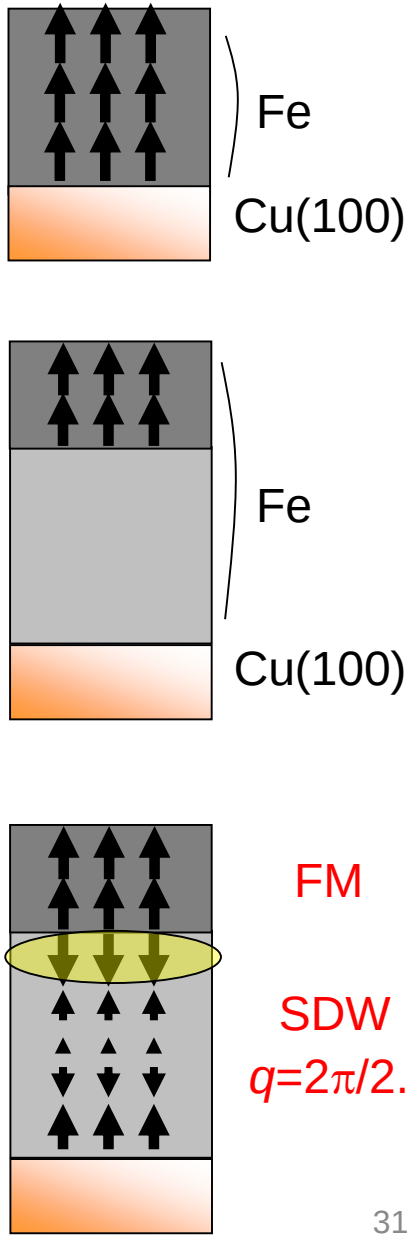
Uniform Magnetization



Surface Magnetization

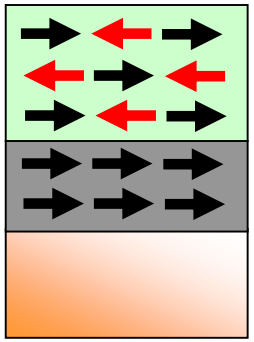
Interpretation of depth-resolved XMCD data





SDW: Spin density wave

Application 1: Ferromagnetic/Antiferromagnetic interface



Exchange bias

Uncompensated spin

Intermixing

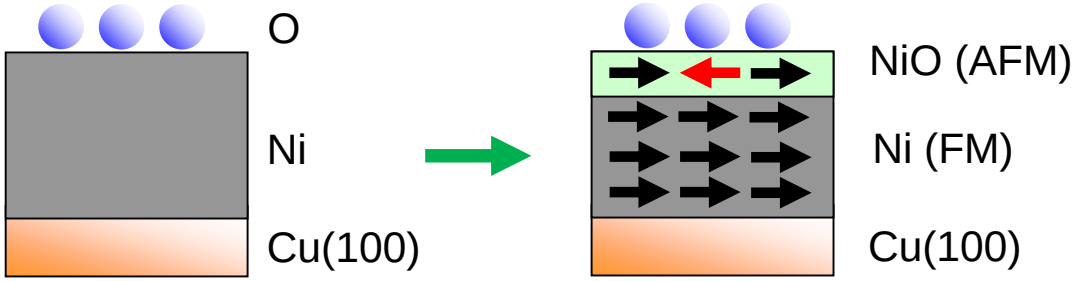
Roughness

…

Atomically sharp interface

is desirable

Idea of our study



Single-layer NiO ?

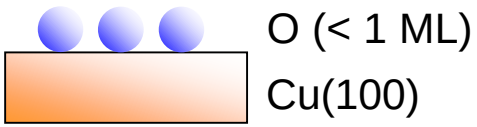
Ideal FM-AFM interface

Sample preparation

R. Nunthel et al., Surf. Sci. 531, 53 (2003).

(1) Oxygen adsorption

$5X10^{-4}$ Pa, 300 s @ 500 K

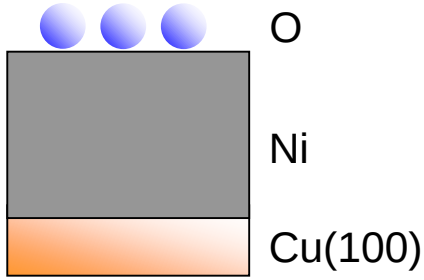


(2) Ni deposition (in UHV)

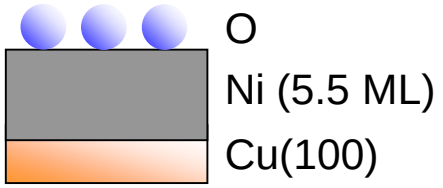
EB heating of a Ni rod

room temperature

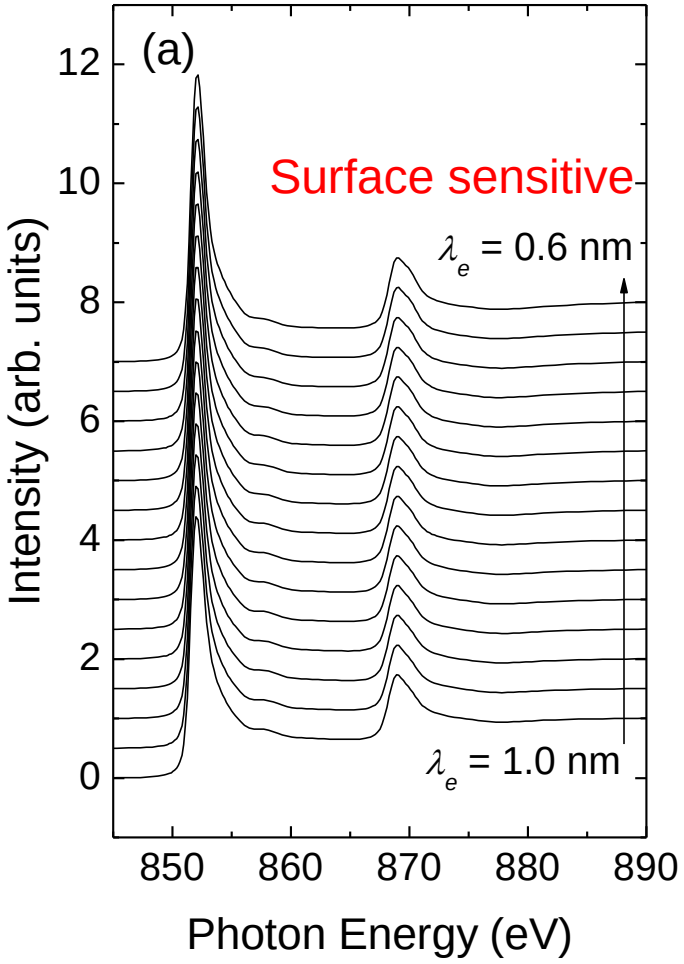
in situ RHEED

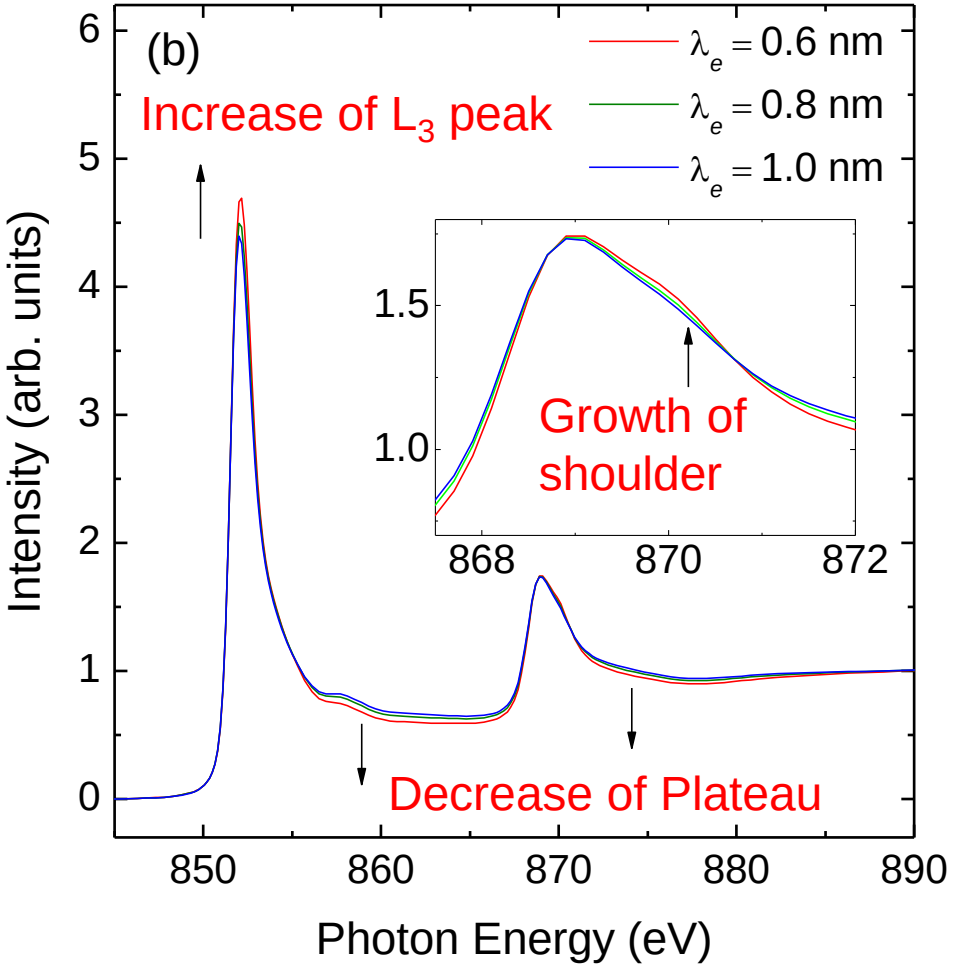


Depth-resolved XAFS for O/Ni/Cu(100)

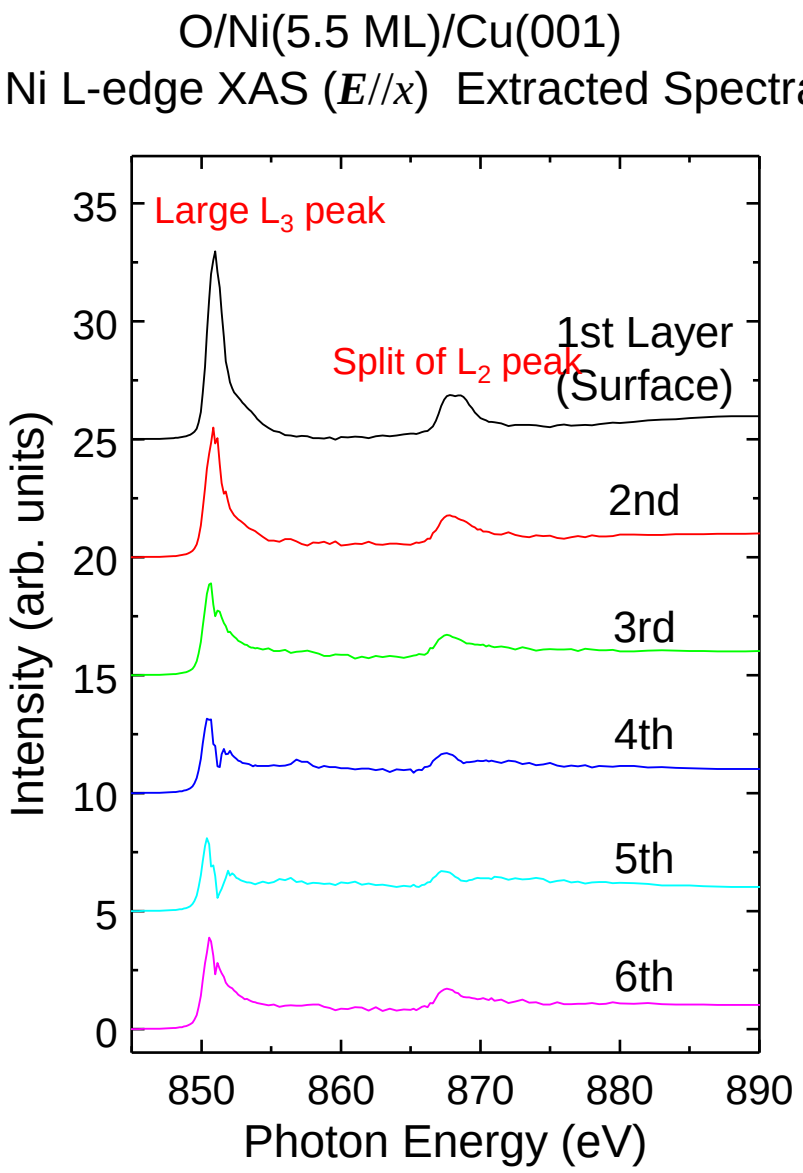


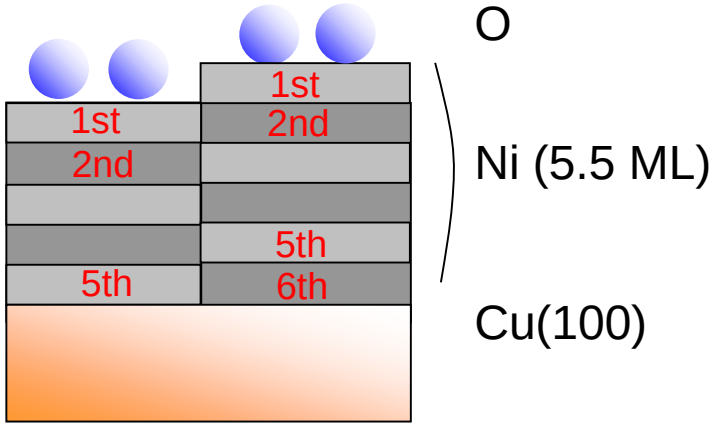
O/Ni(5.5 ML)/Cu(001) Ni L-edge XAS (X-ray Absorption Spectrum)





Layer-resolved X-ray absorption spectra





XAS for the 1st layer is different from those in the underlying layers

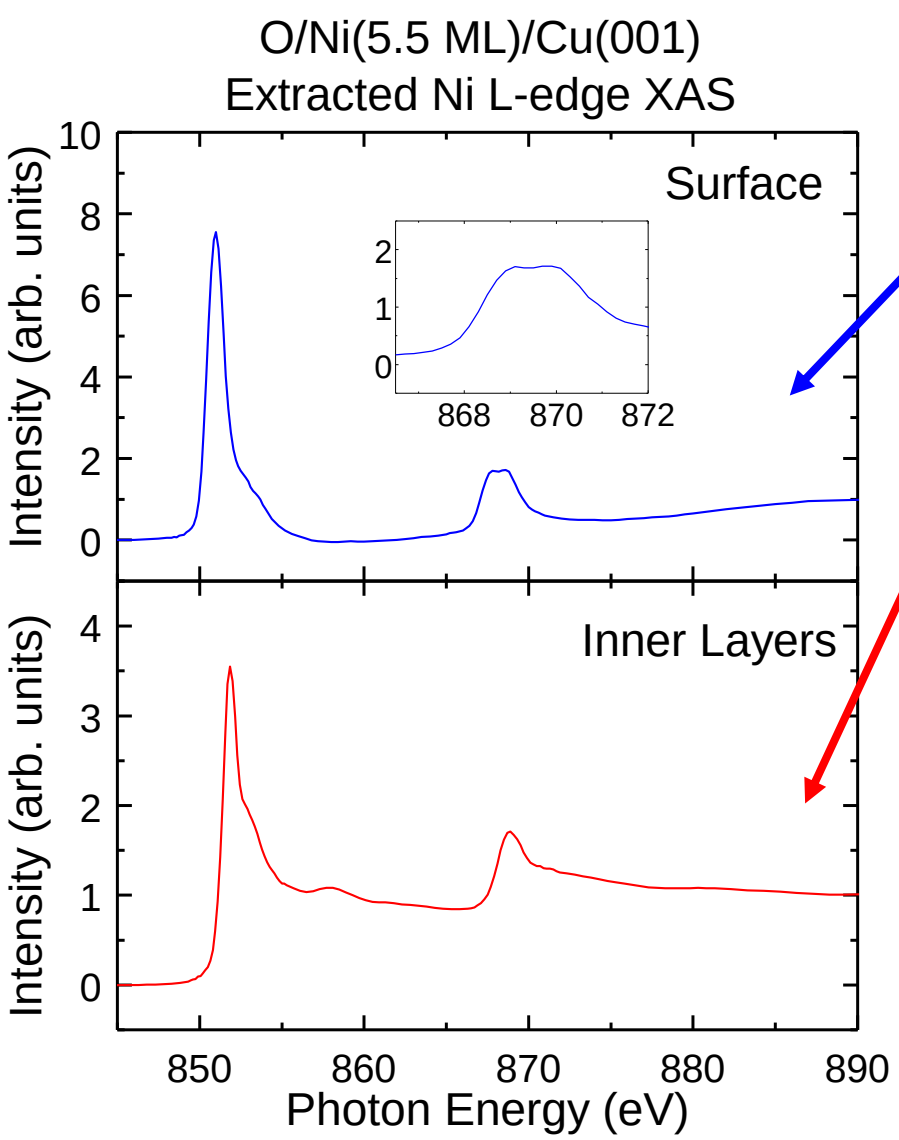
=> suggests single-layer oxidation

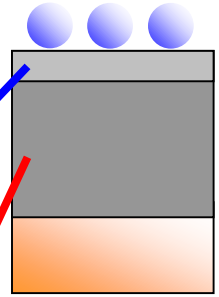
=> 2-region model is adopted.

Extracted X-ray absorption Spectra

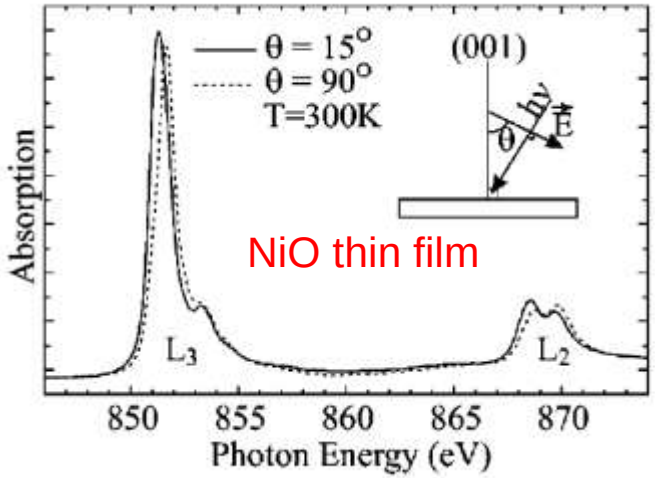
K. Amemiya and M. Sakamaki,

Appl. Phys. Lett. 98 (2011) 012501.



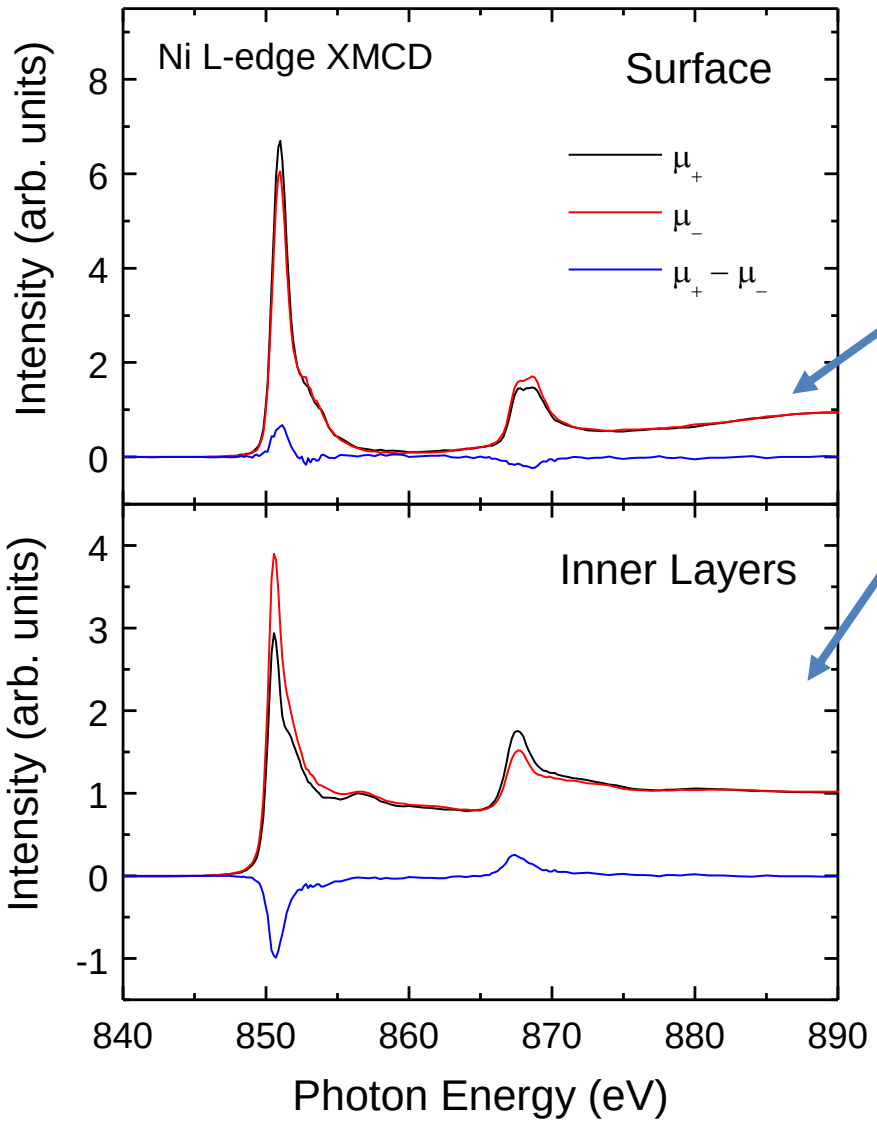


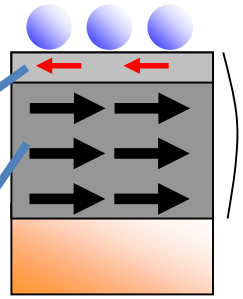
XAS spectra at surface shows NiO-like features



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

Extracted XMCD spectra





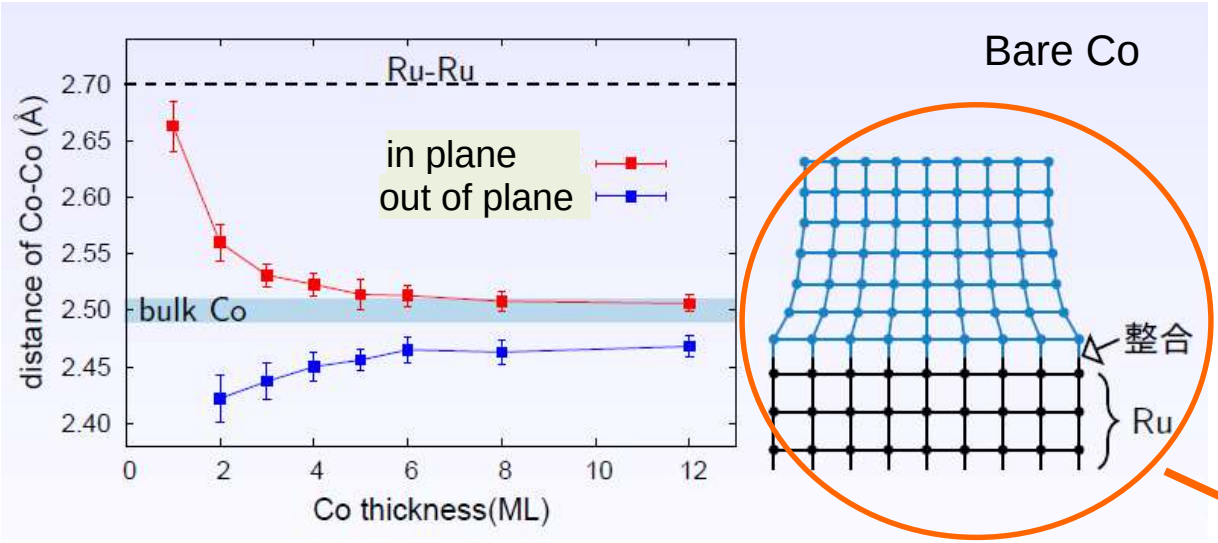
Surface layer shows small negative magnetization.

Uncompensated spin at the interface?

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

Application 2: Atomic structure of Ru/Co/Ru(0001) thin films

Fluorescence-yield EXAFS (Co K edge) : average over the whole film



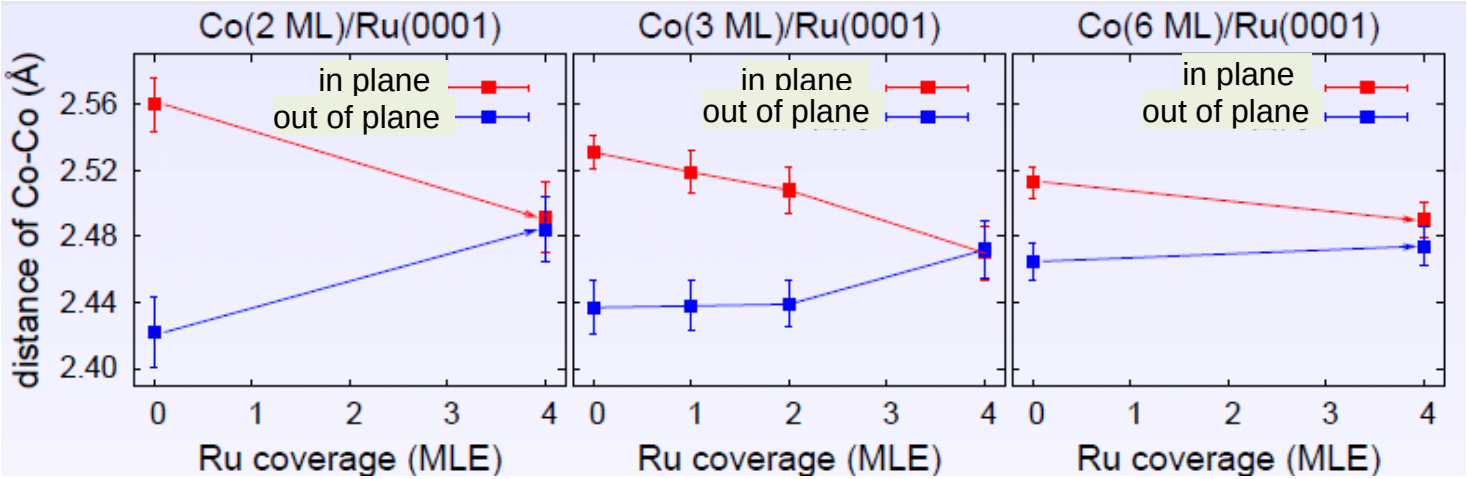
Miyawaki et al., Phys. Rev. B 80 (2009) 020408(R).

Interface Co layer is commensurate to Ru

Rapid relaxation upon further Co deposition

Is that true?

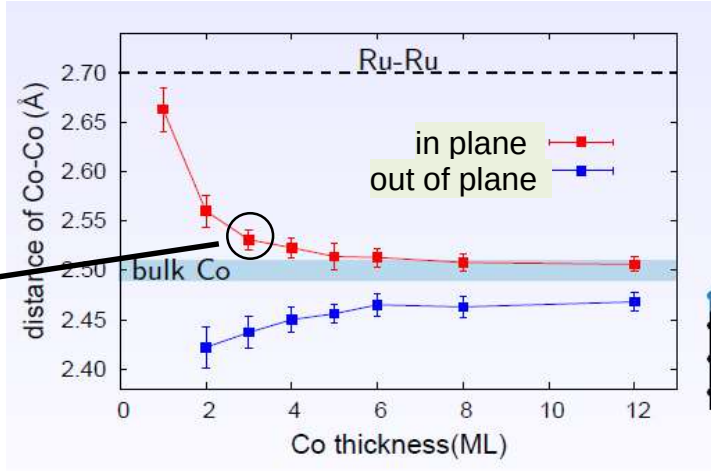
Effects of Ru capping



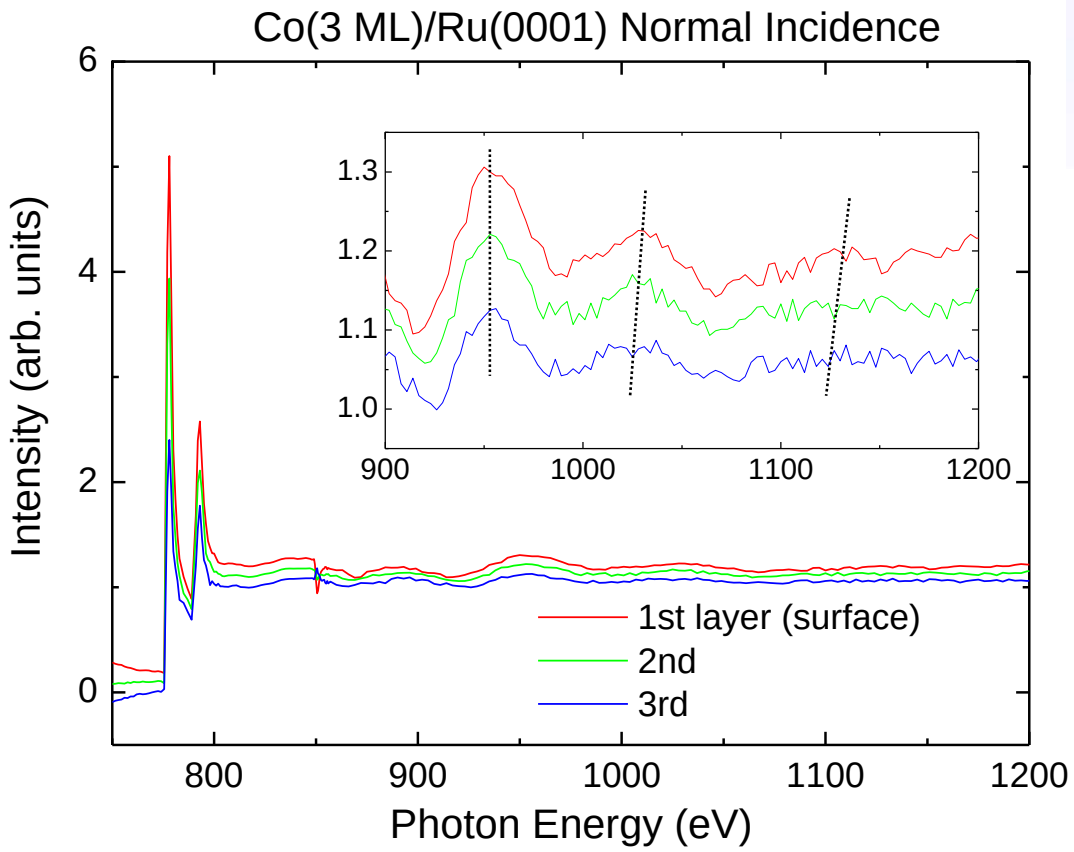
Relaxation of Co distortion upon Ru capping

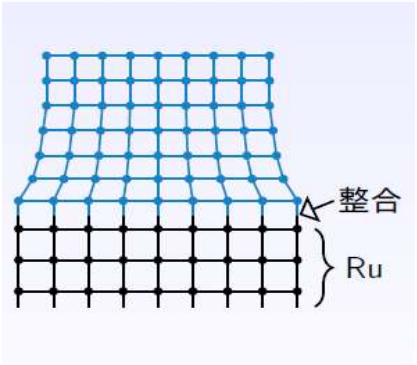
Depth profile of atomic structure

Normal incidence: dominated by in-plane distance



Layer-resolved EXAFS





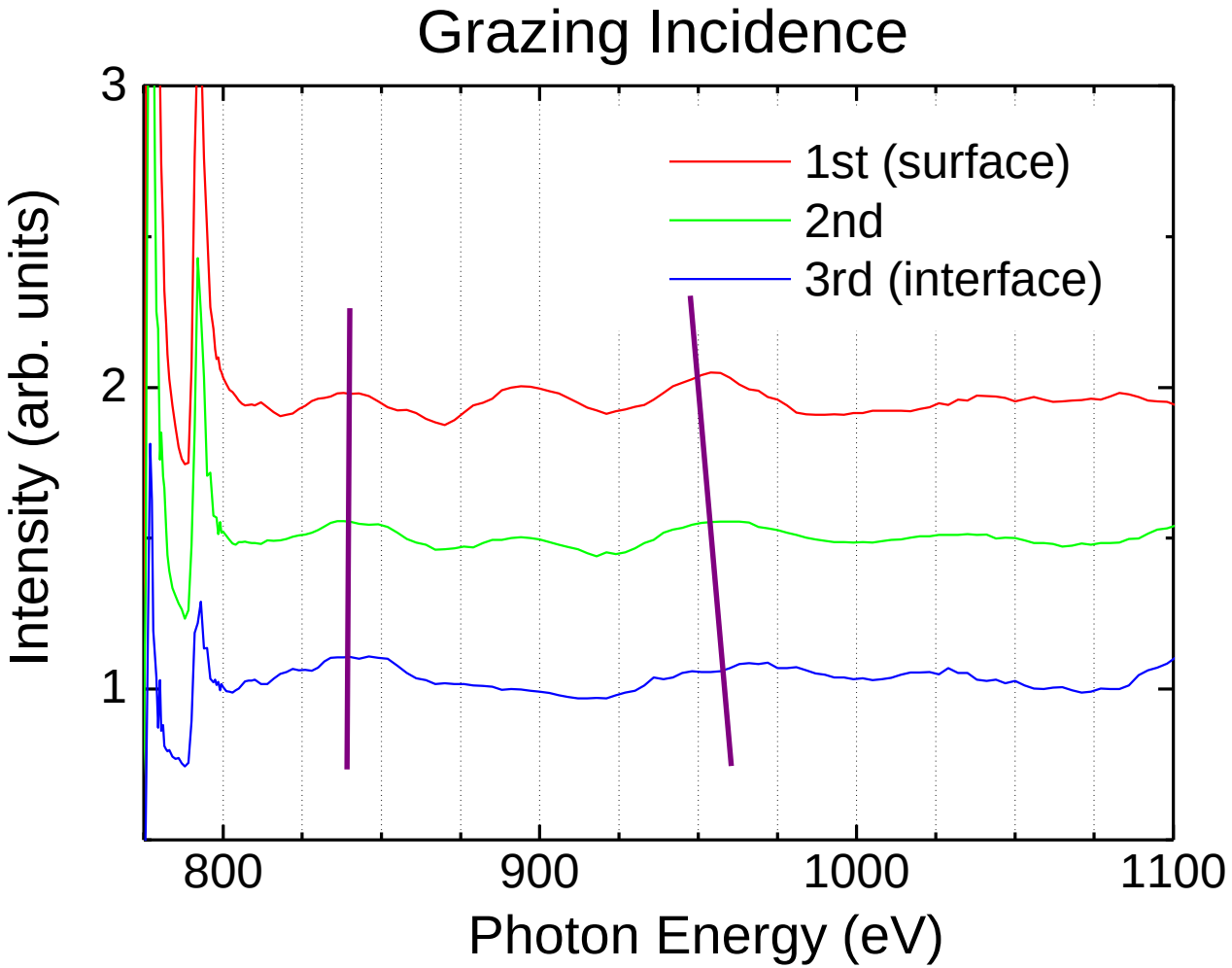
It might be true…

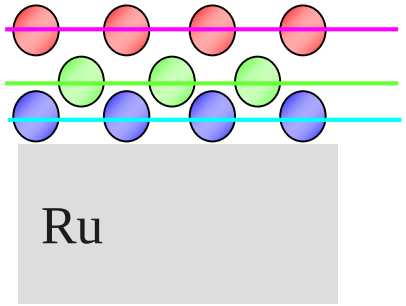
Surface shows longer oscillation period: shorter bond length

K.Amemiya et al., J. Phys.: Conf. Ser. 190 (2009) 012108.

Depth-resolved EXAFS at grazing incidence

Longer out-of-plane bond length at surface?





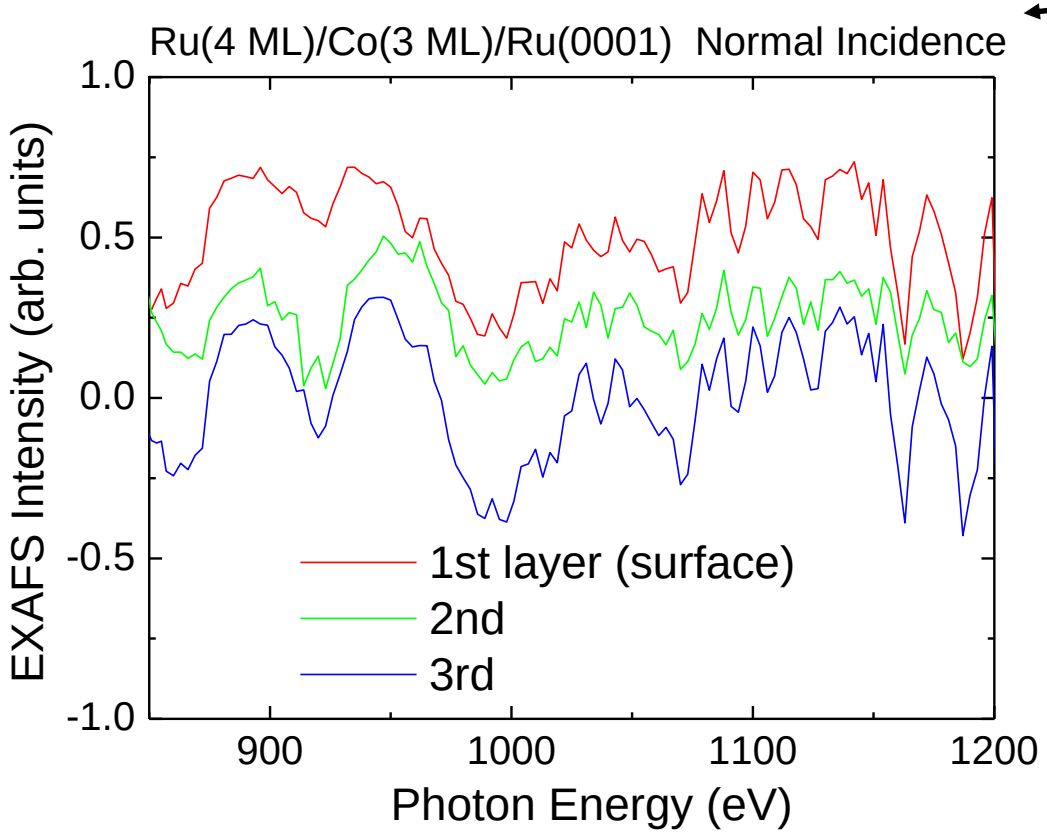
K.Amemiya et al., J. Phys.: Conf. Ser. 190 (2009) 012108.

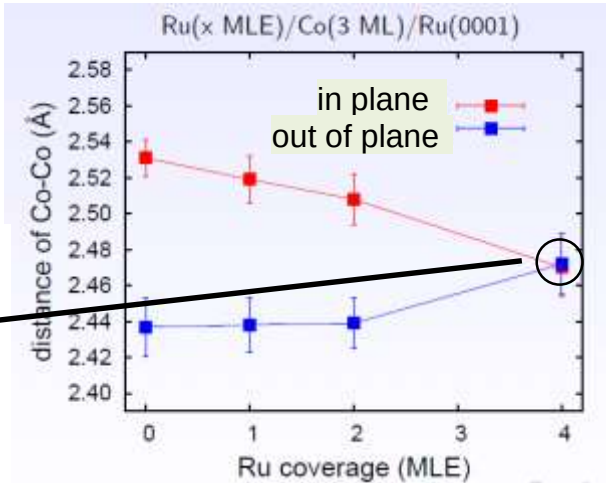
Preliminary analyses

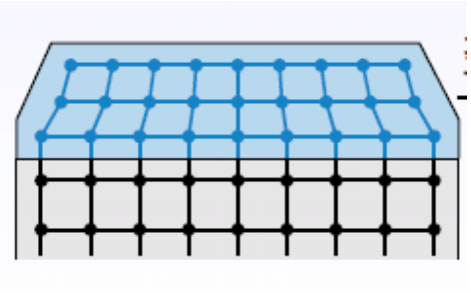
Effects of Ru capping

Normal incidence: in-plane bond length

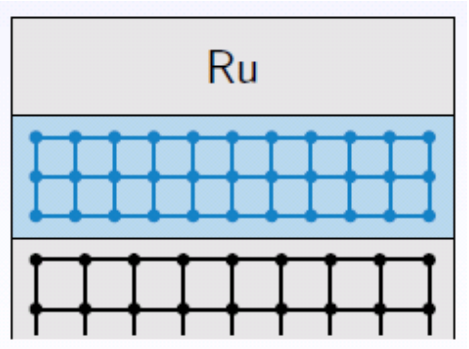
Layer-resolved EXAFS







Relaxation



Little difference in the bond length

K.Amemiya et al., J. Phys.: Conf. Ser. 190 (2009) 012108.

1. Advantages and Disadvantages of

   Soft X-ray Absorption Spectroscopy (SXAS)

2. SXAS studies on Surface and Thin films

3. Novel SXAS Techniques

   3-1. Depth-resolved XAS

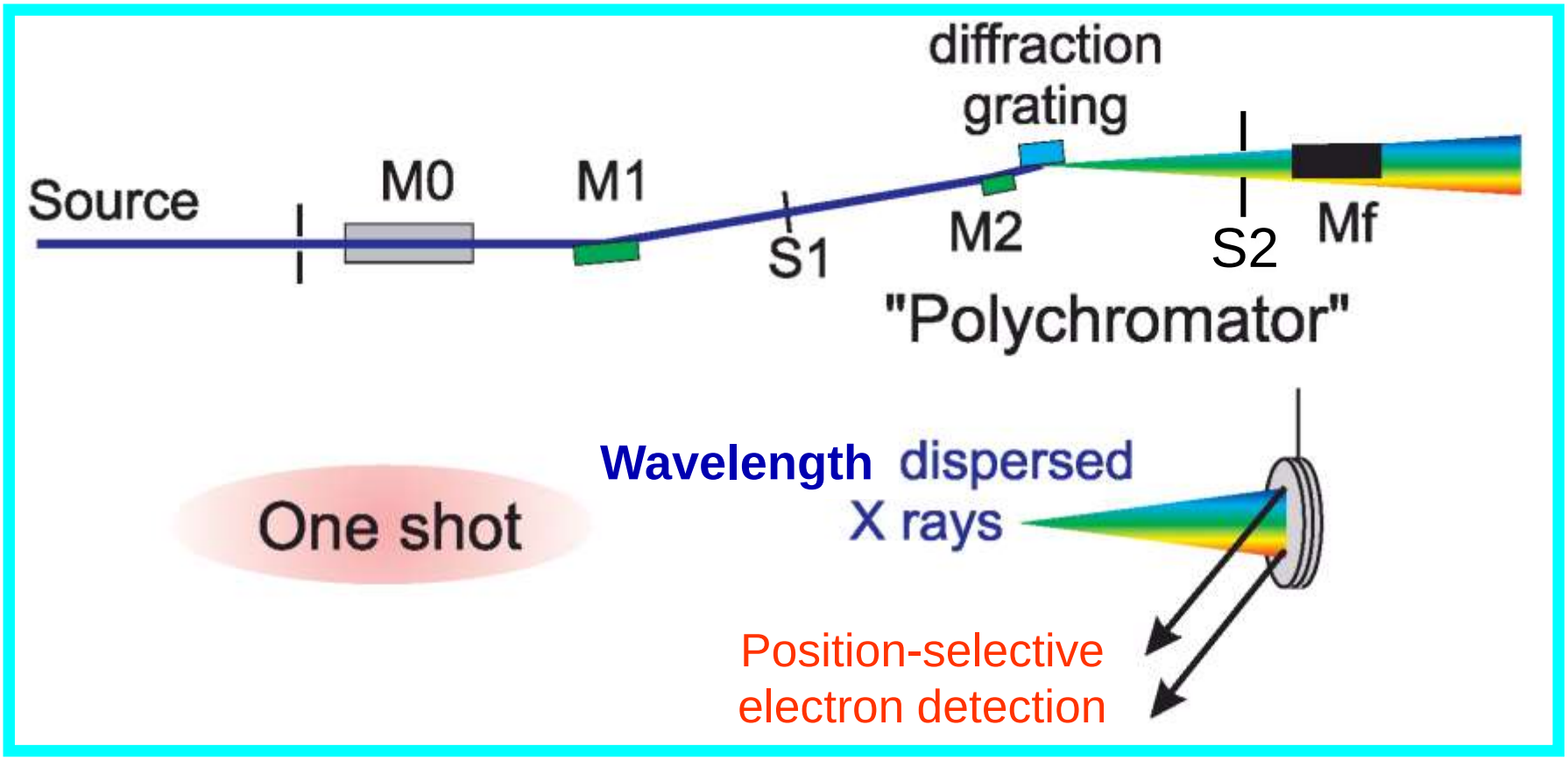
   3-2. Wavelength-dispersive XAS

Development of Wavelength-dispersive XAS

XAS: Element selectivity, Chemical species determination, Structural information,…

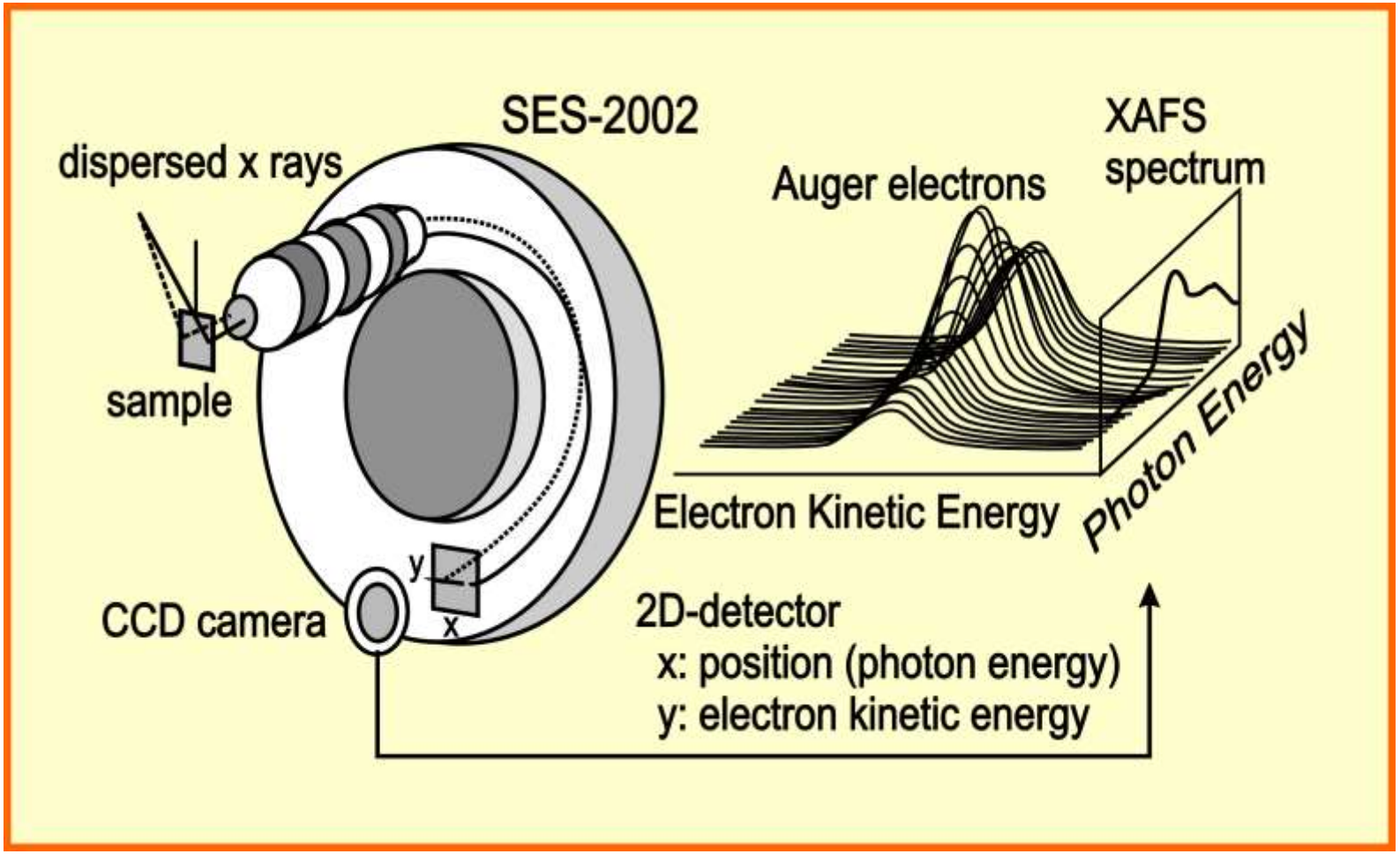
Takes long time (~5 min/spectrum) for a measurement.

Possibility of "One shot" measurement.



Experimental setup for wavelength-dispersive XAS

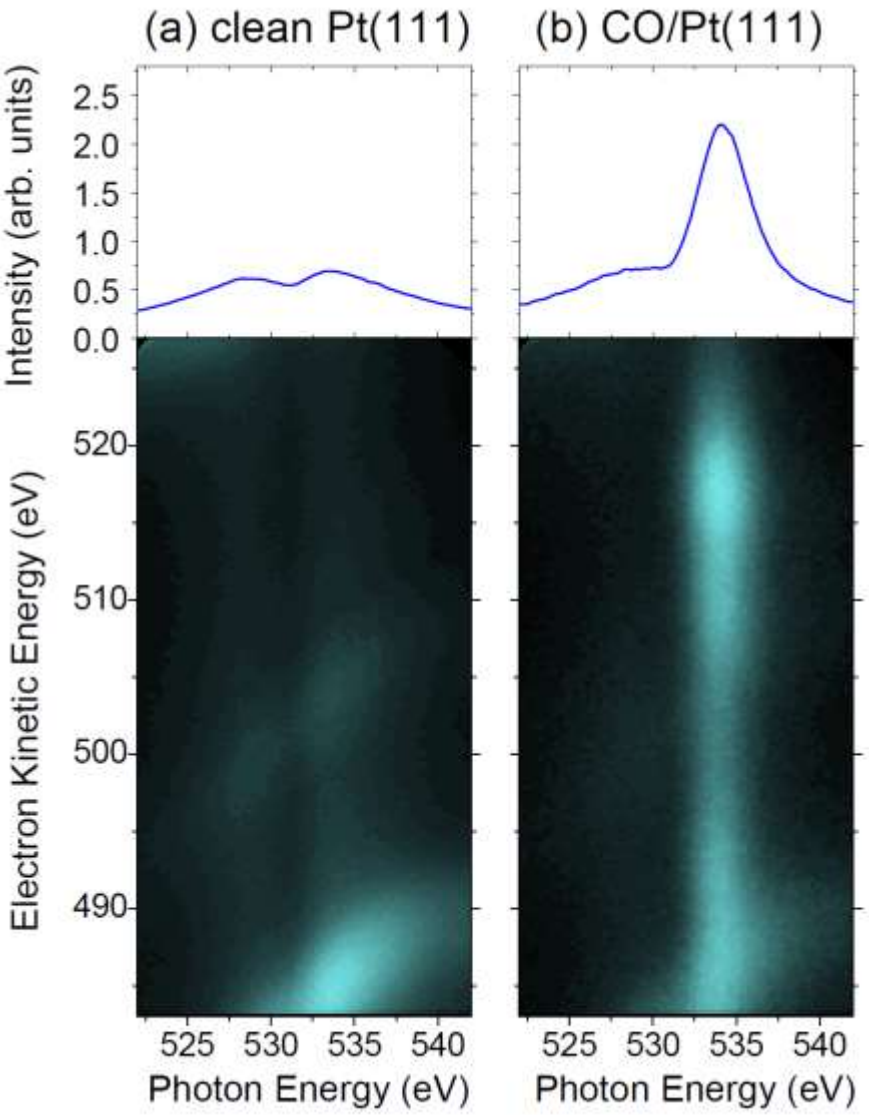
- Wavelength-dispersed X rays + Position-sensitive electron detector

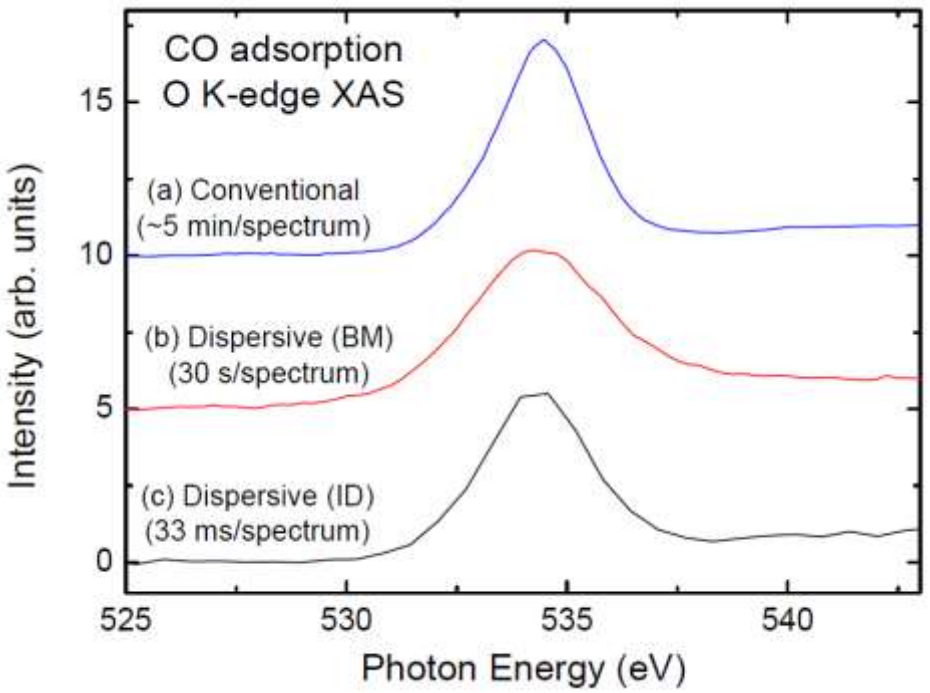


Comparison with conventional XAS

Amemiya et al., Jpn. J. Appl. Phys. **40** (2001) L718.

Amemiya, 放射光, **25** (2012) 269.



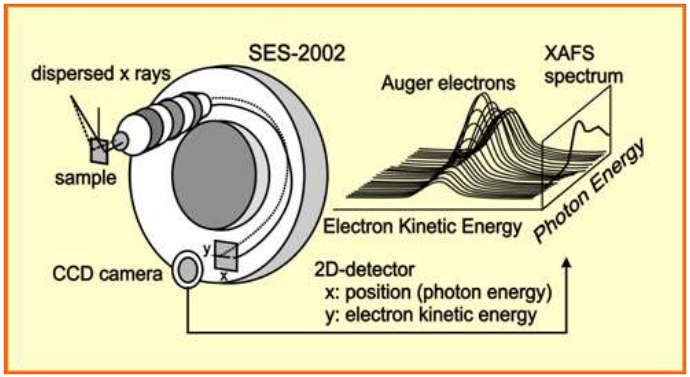


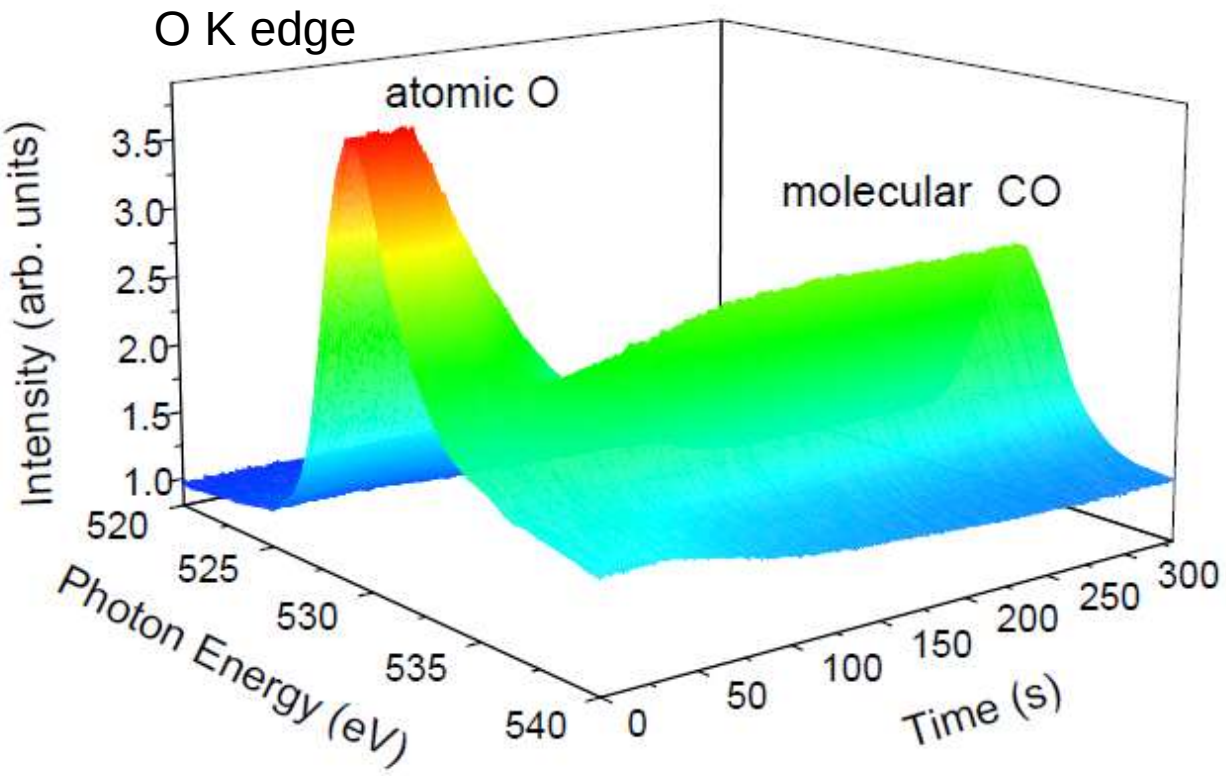
Data acquisition time: 1/10,000 !

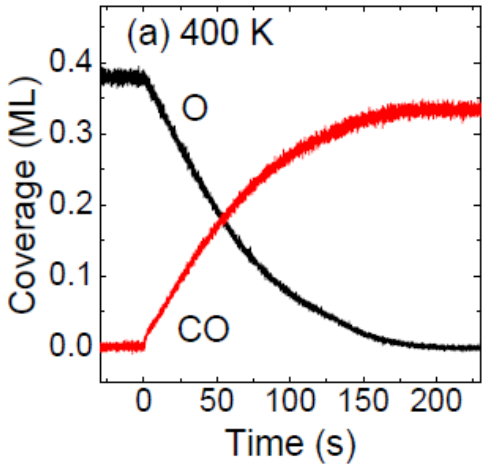
Observation of Chemical Reaction

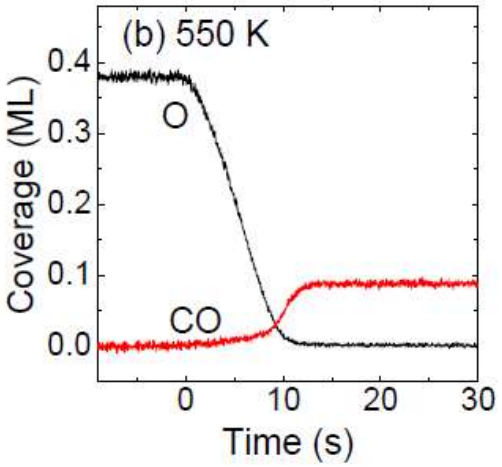
Undulator beamline (BL-16A)
Video rate (30 Hz: 33 ms resolution)

CO + O reaction on Ir(111): CO + O → CO_2↑





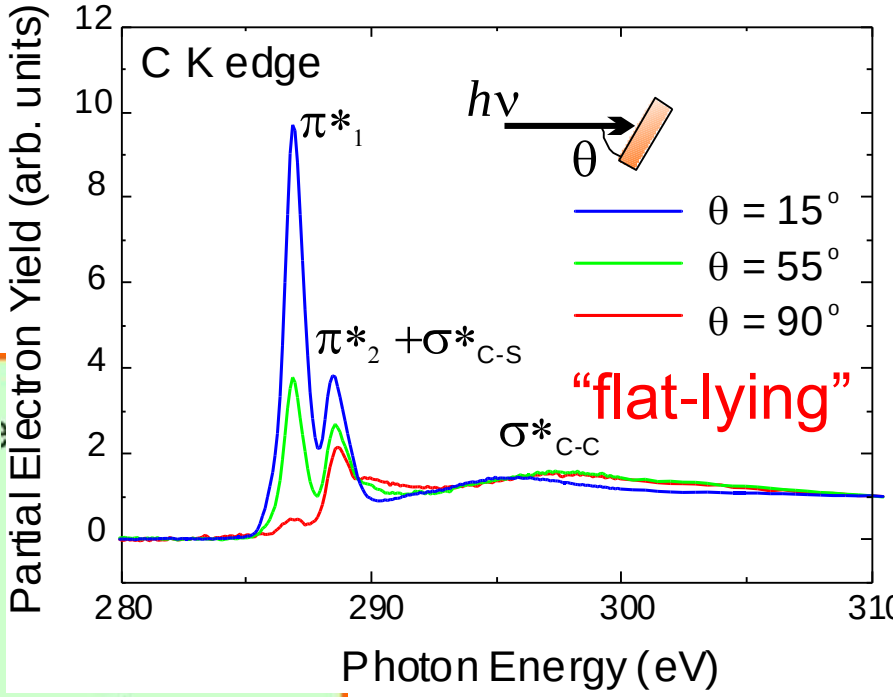


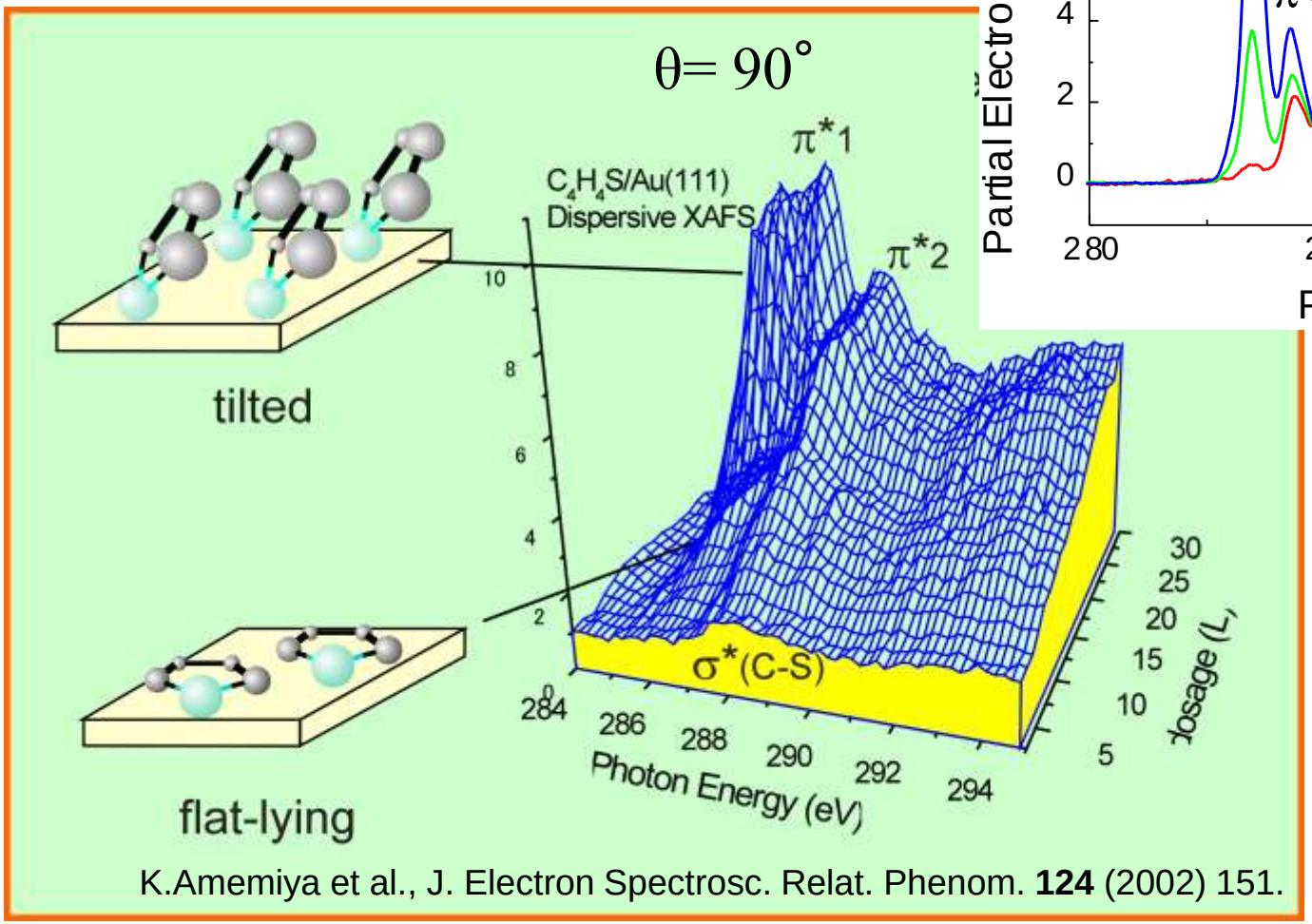


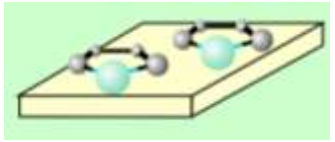
K.Amemiya et al., Appl. Phys. Lett. **99** (2011) 074104.

Determination of Molecular Orientation

Adsorption of C_4H_4S on Au(111)







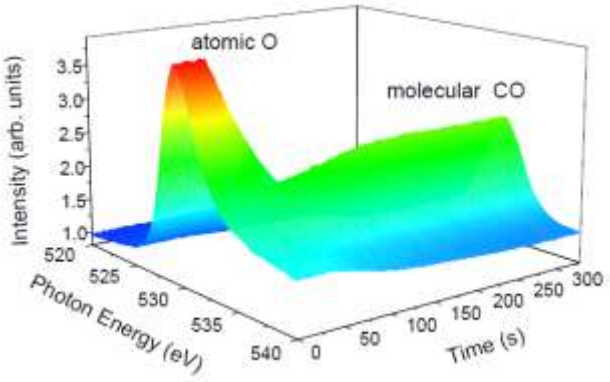
Orientation change with increasing coverage

K.Amemiya et al., J. Electron Spectrosc. Relat. Phenom. **124** (2002) 151.

Development of Real-time Observation of Orientation

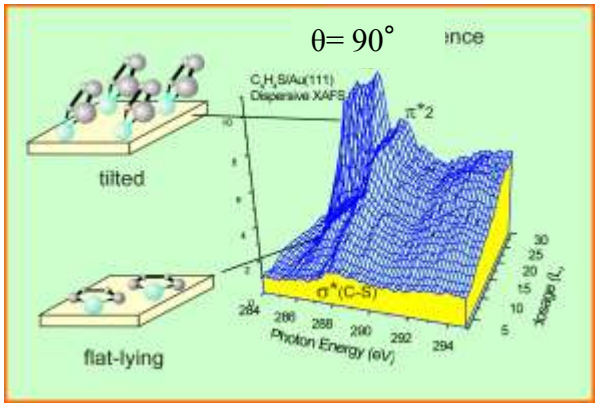
Combination of dispersive XAFS and linear polarization switching between horizontal and vertical polarizations

Dispersive XAFS



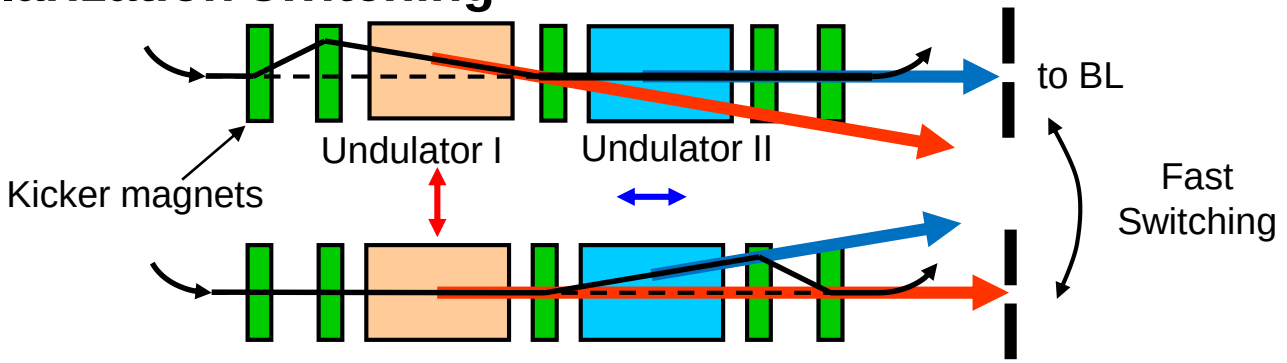
K.Amemiya et al., Appl. Phys. Lett. **99** (2011) 074104.

Polarization dependence



K.Amemiya et al., J. Electron Spectrosc. Relat. Phenom. **124** (2002) 151.

Polarization switching

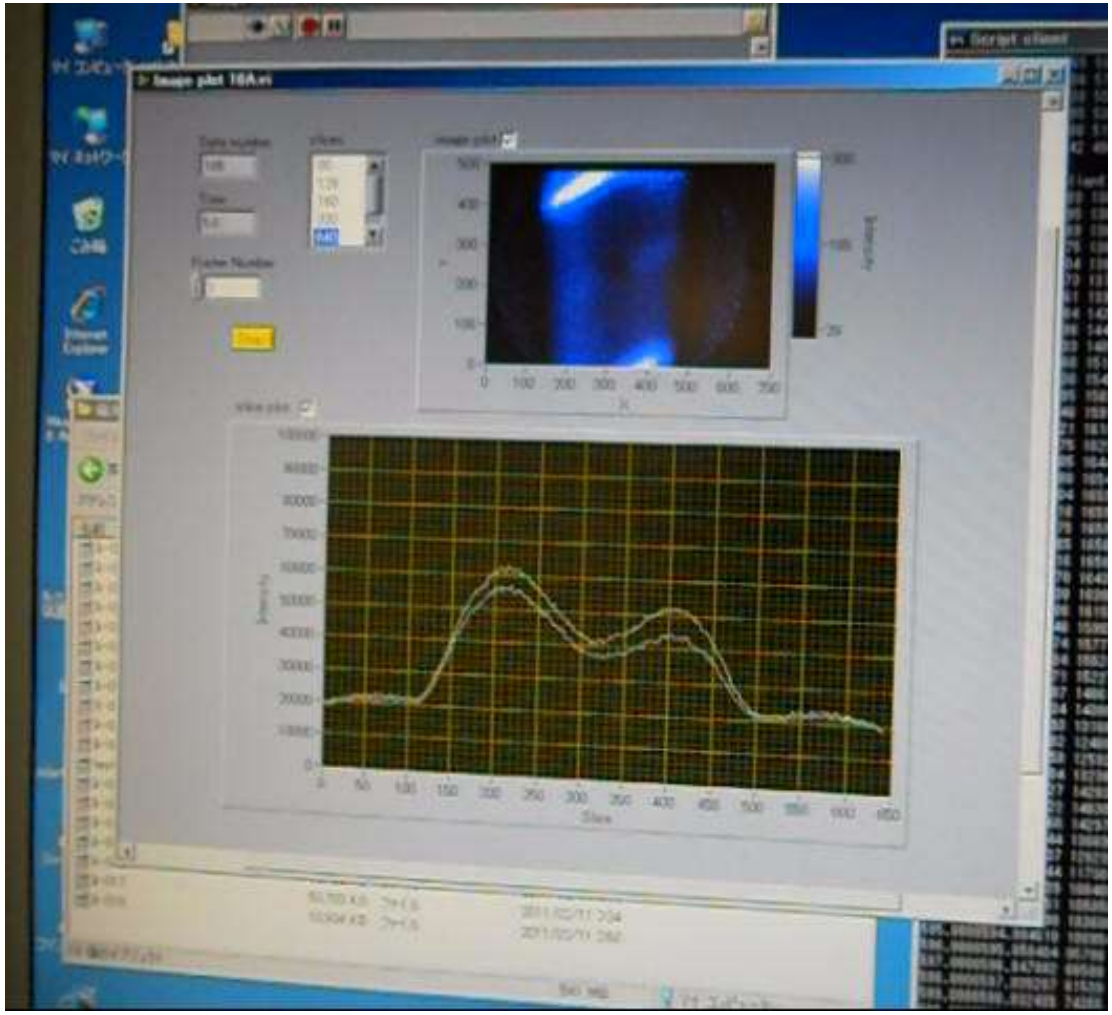


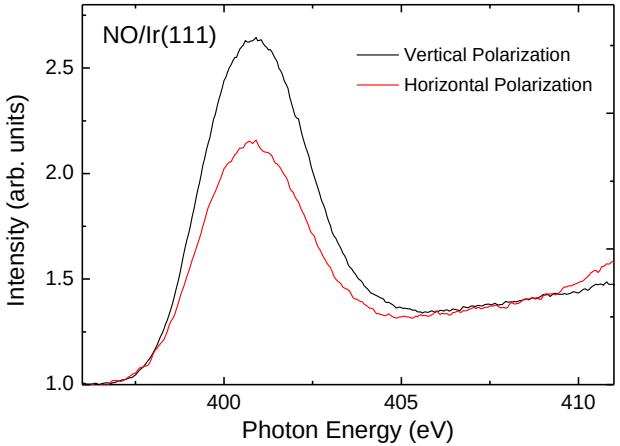
T. Muro et al., AIP Conf. Proc. 705, 1051 (2004); 879, 571 (2007).
T. Muro et al., J. Electron Spectrosc. Relat. Phenom. 144-147, 1101 (2005).
K. Amemiya et al., J. Phys.: Conf. Ser. 425, 152015 (2013).

Combination of Dispersive XAFS and Polarization Switching

Adsorption of NO molecule on Ir(111)

1 Hz switching between horizontal and vertical linear polarizations

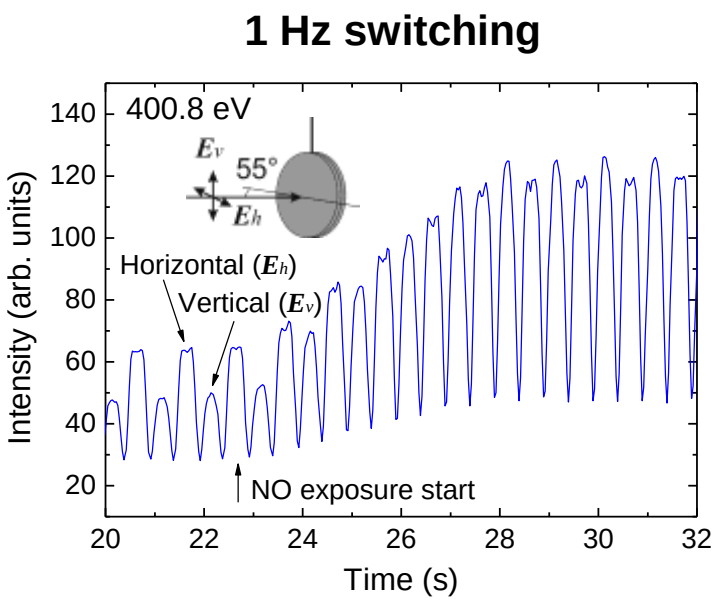


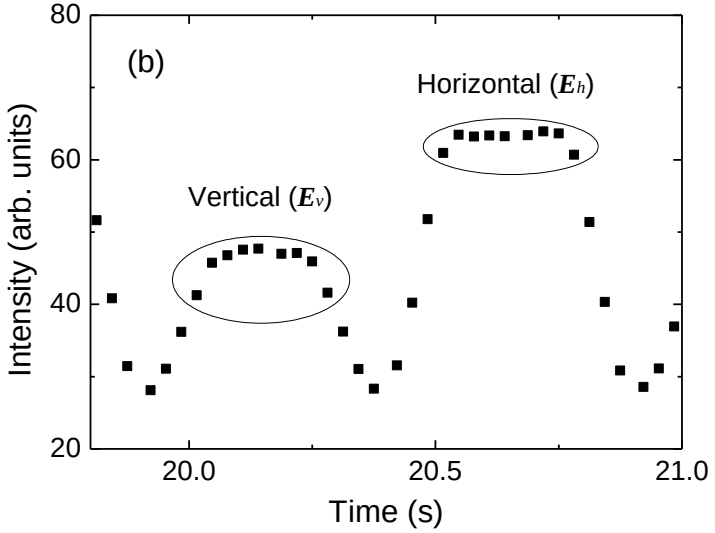


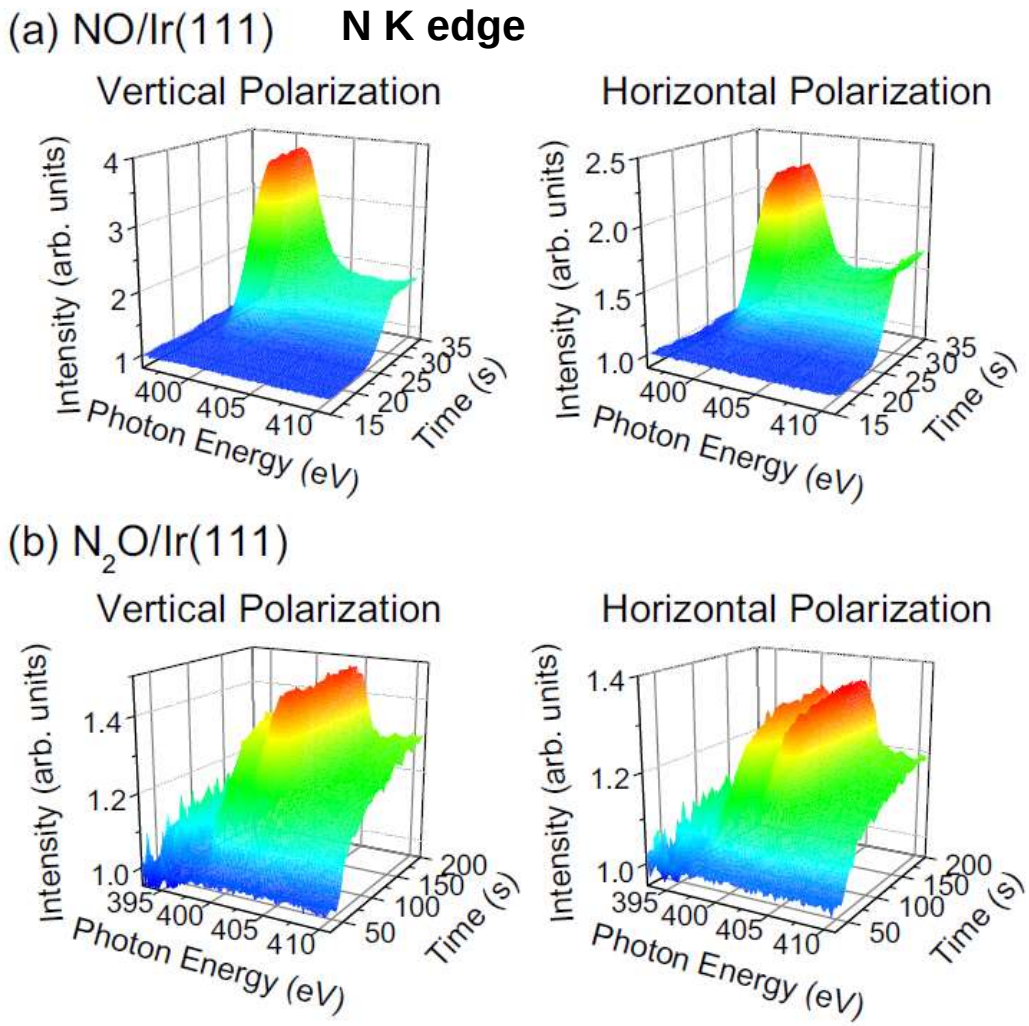
10 Hz switching is now available (measurement: 1000 Hz)

Real-time Observation of Molecular Orientation

Amemiya et al., Appl. Phys. Lett., 101 (2012) 161601.

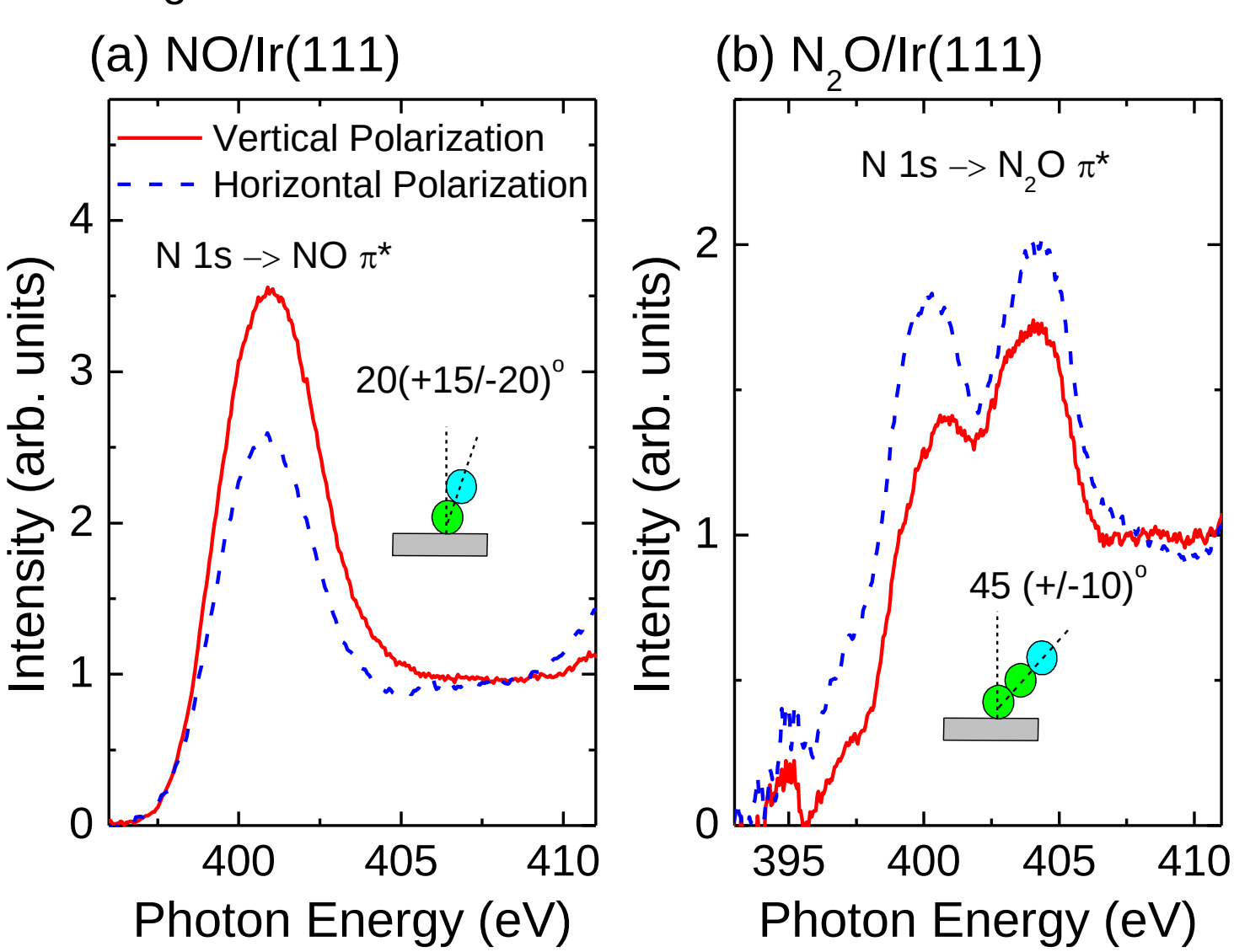






Polarization Dependence at Saturation Coverage

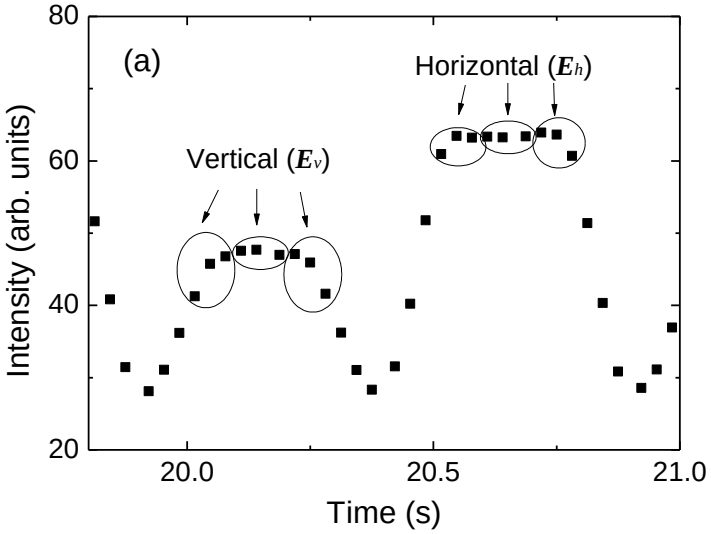
Amemiya et al., Appl. Phys. Lett., 101 (2012) 161601.

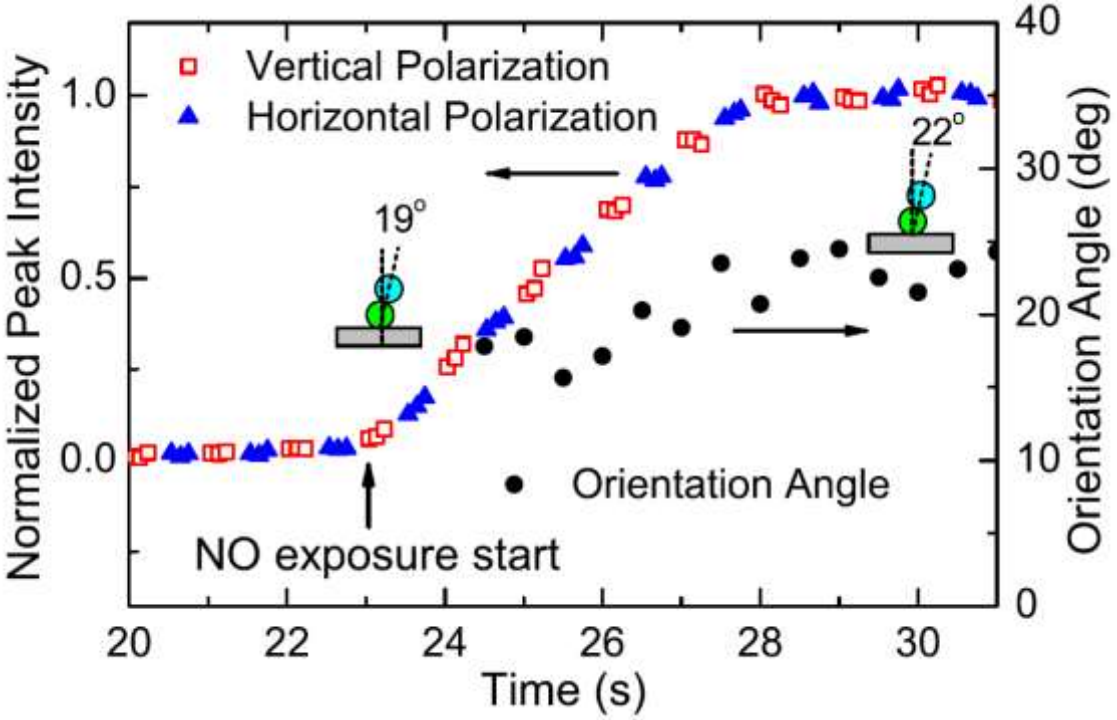


Molecular Orientation Change during NO Adsorption

Amemiya et al., Appl. Phys. Lett., 101 (2012) 161601.

Molecular adsorption of NO at 140 K



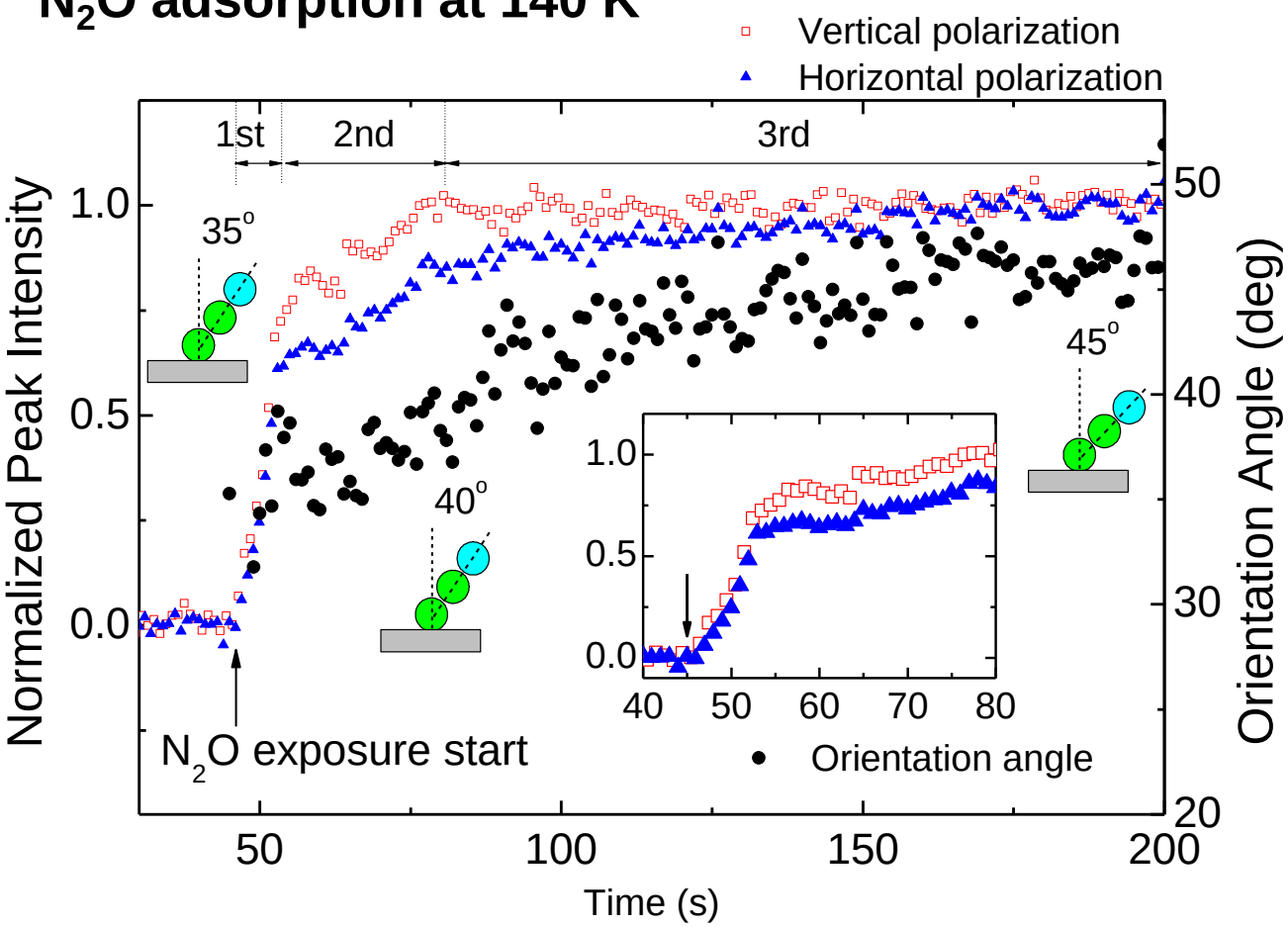


Simultaneous increase between vertical and horizontal polarizations

=> Constant orientation during adsorption

Molecular Orientation Change during N_2O Adsorption

Amemiya et al., Appl. Phys. Lett., 101 (2012) 161601.



Three stages with different adsorption rates

Averaged orientation gradually increases

1st stage: Fast adsorption up to ~2/3 of saturation. Constant orientation at ~35º.

2nd stage: Up to ~90% of saturation. Gradual increase in orientation angle.

⇒ Suggests another adsorption site with 45-50º orientation.

3rd stage: Very slow changes towards saturation adsorption state.

Soft X-ray absorption spectroscopy

- Suitable for familiar materials

  Organic molecules & polymers

  Magnetic nano-materials

- Surface sensitive

  a double-edged sword