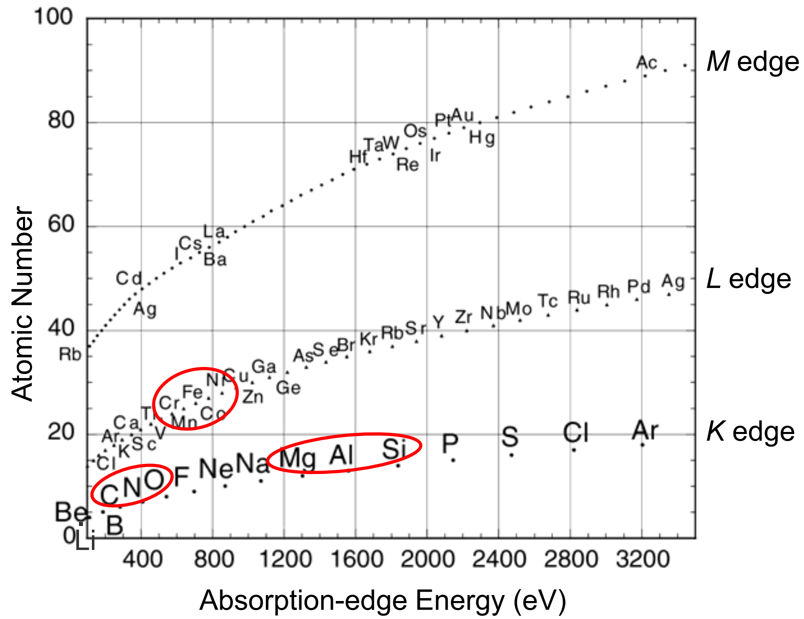
Cheiron School 2012

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
- ~14/53 at Photon Factory (2.5 & 6.5 GeV)
- ~5/50 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

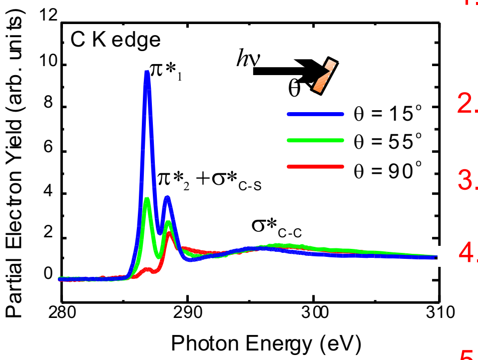
Soft X-ray Absorption Spectroscopy

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)



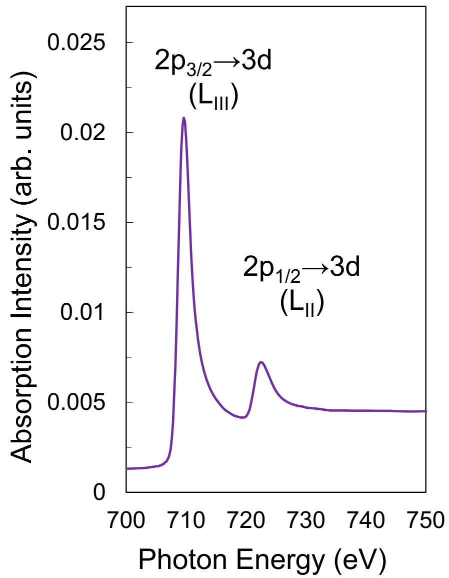
1. Element selectivity
   <– Core-hole excitation (1s, 2p…)
   (C: 290 eV, O: 530 eV, Fe: 710 eV, Ni: 850 eV…)
2. Information on chemical species
   <– Characteristic spectral features (π*, σ*…)
3. Structural information (bond length, etc.)
   EXAFS (Extended X-ray Absorption Fine Structure)
4. Information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

In the Soft X-ray region,

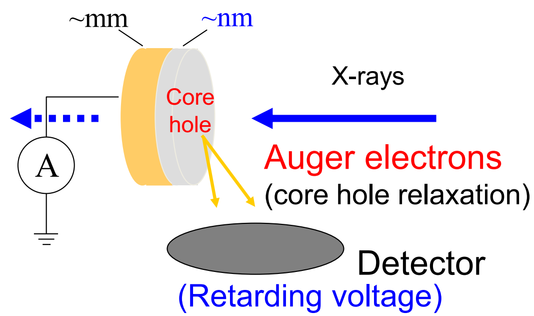
1. Vacuum environment is normally required. (NOT ultra-high vacuum)
   Special sample cell or He atmosphere is available for ambient pressure.
2. Surface sensitive
   λ = several nm for electron yield, ~0.1 μm for fluorescence yield

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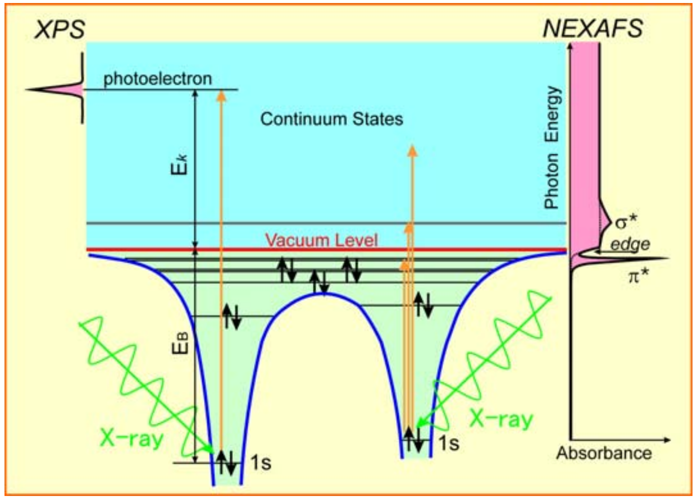
3. Novel SXAS Techniques
   3-1. Depth-resolved XAS
   3-2. Wavelength-dispersive XAS

Near-edge Spectroscopy

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

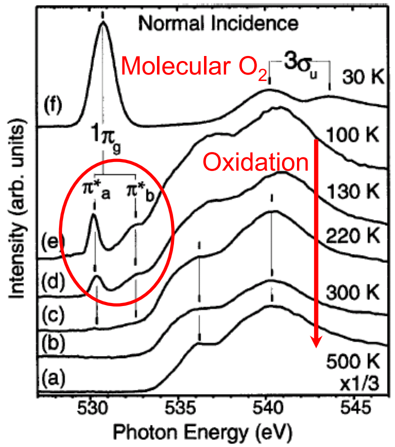


Chemical species
Structural information (orientation)

Near-edge Spectroscopy

Determination of Chemical Species

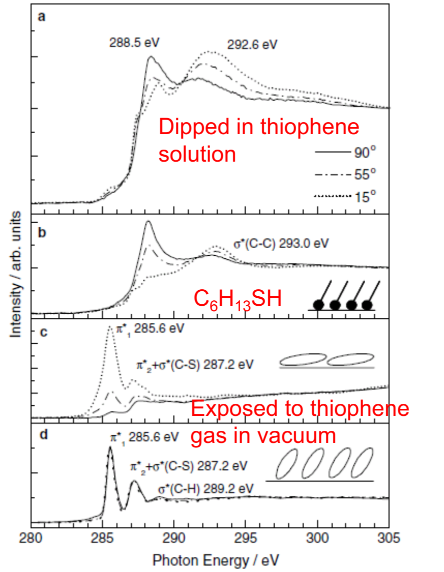
Initial oxidation process of Si



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)

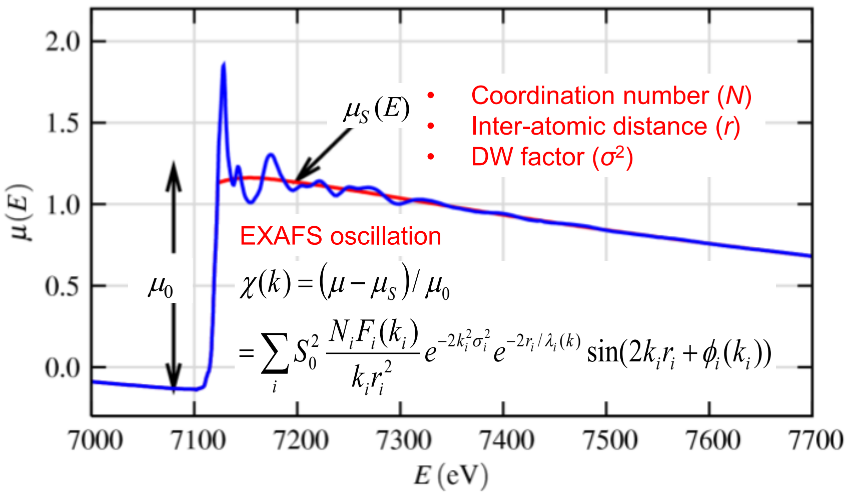


Different chemical species depending on preparation processes

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

Determination of Atomic Structure

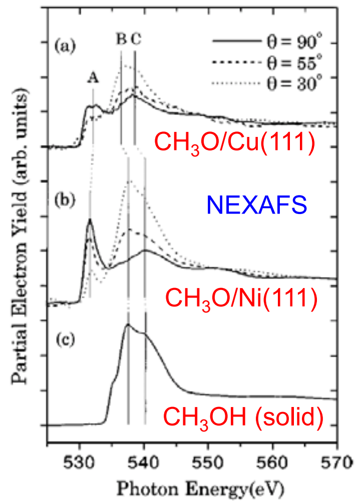
Extended X-ray Absorption Fine Structure (EXAFS)



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

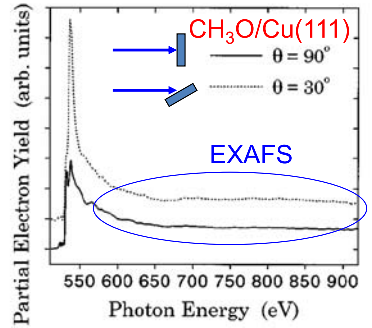
Determination of Atomic Structure

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

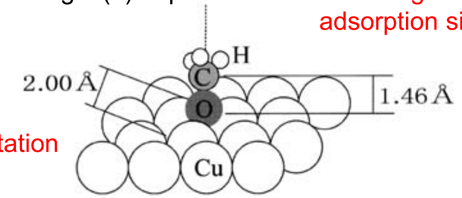


Peak B (1s→σ^*_{CO}) -> C-O bond length
Angle (θ) dependence -> molecular orientation

Application to surface molecule (CH_3O)

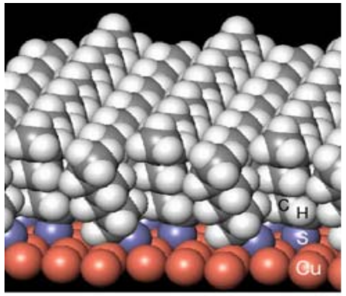


Oscillation period -> O-Cu bond length
Angle (θ) dependence -> bond angle
adsorption site

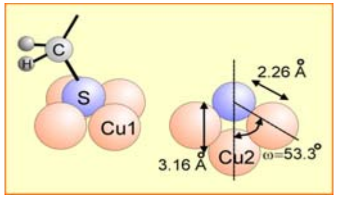


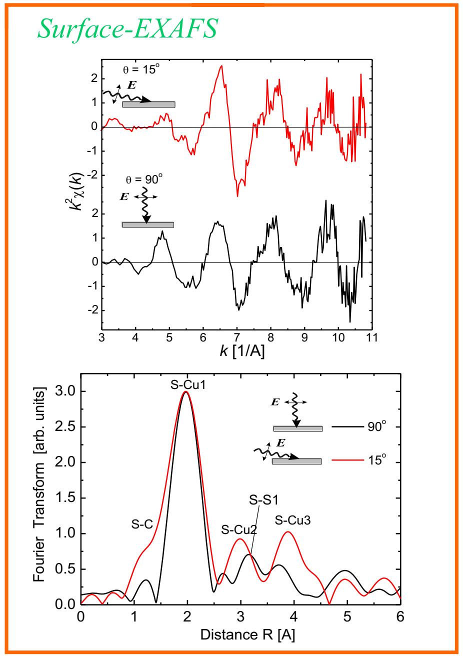
Determination of Atomic Structure

S K-edge EXAFS



$C_6H_{13}S$/Cu(100)

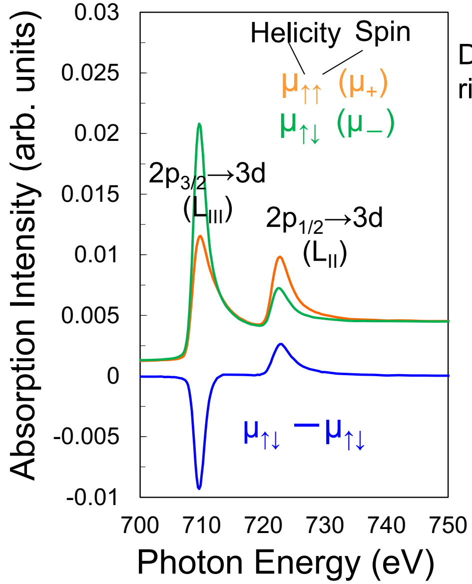




Magnetic structures studied by XMCD

3 ML Fe / Cu(100)

Fe L-edge XMCD

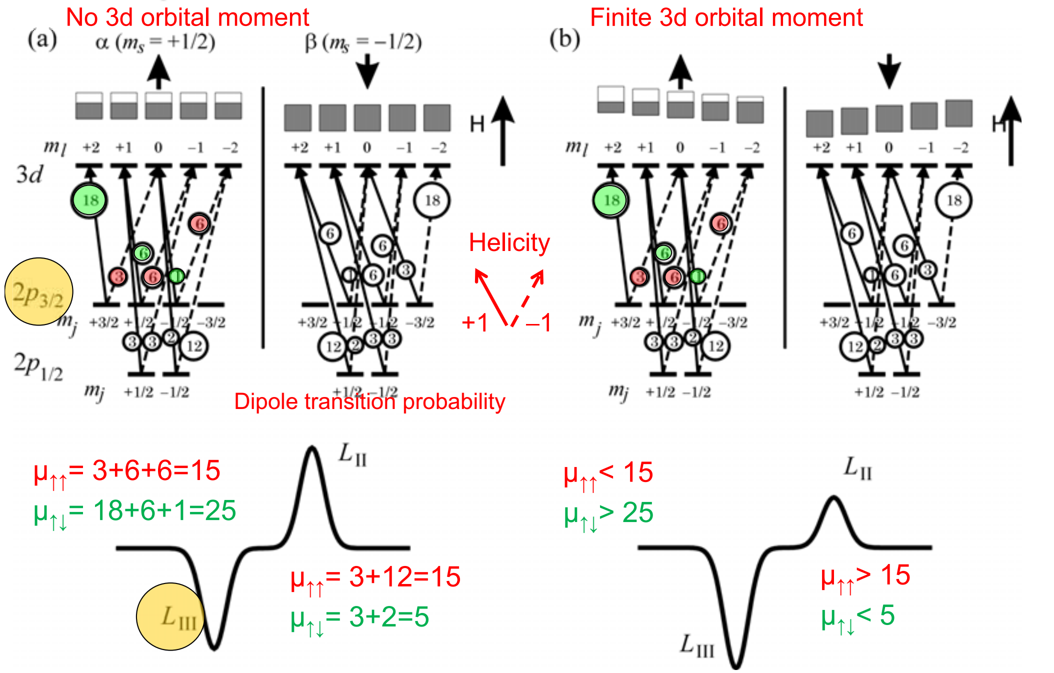


X-ray Magnetic Circular Dichroism (XMCD)

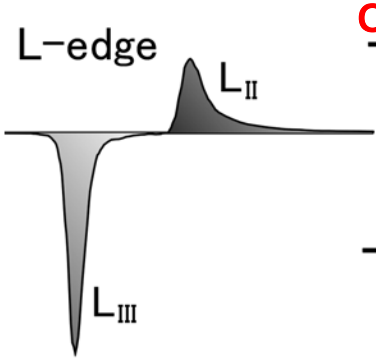
Difference in absorption intensities between right- and left-hand circular polarizations

1. Element selectivity
   <– resonant absorption (2p->3d…)
2. Determination of spin and orbital magnetic moments
   <– Sum rules
3. High sensitivity

Principle of XMCD



XMCD Sum Rules



Orbital moment m_l

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

$< 0 \rightarrow m_l > 0$

Spin moment m_s

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

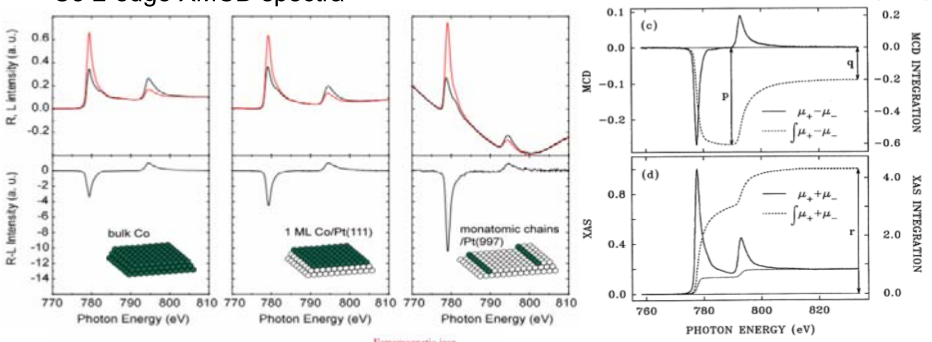
$< 0 \rightarrow m_s > 0$

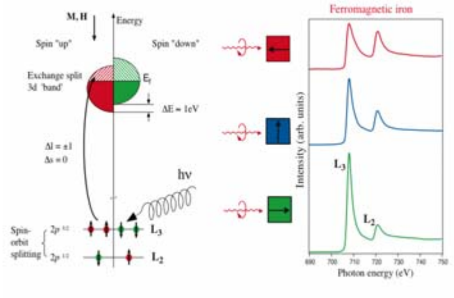
B.T. Thole et al., PRL **68**, 1943 (1992).
P. Carra et al., PRL **70**, 694 (1993).

Magnetism of Thin Films Studied by XMCD

Co *L*-edge XMCD spectra

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





XMCD sum rules

$$m_{orb} = \frac{4q}{3r}(10 - n_{3d})$$

$$m_s = \frac{6p - 4q}{r}(10 - n_{3d})$$

$$\frac{m_{orb}}{m_s} = \frac{2q}{9p - 6q}$$

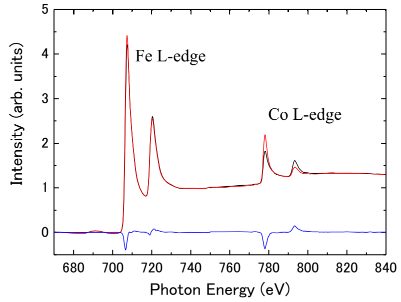
$$r = \int_{L_{2,3}} (\mu_+ + \mu_-) d\omega$$

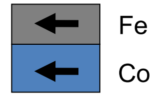
$$p = \int_{L_3} (\mu_+ - \mu_-) d\omega$$

$$q = \int_{L_{2,3}} (\mu_+ - \mu_-) d\omega$$

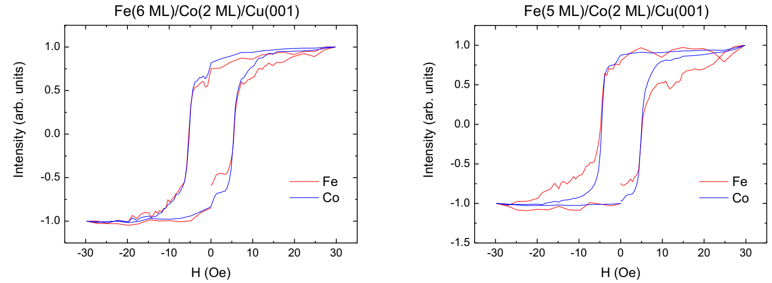
C.T. Chen et al., PRL **75**, 152 (1995).

Utilization of Element Selectivity of XMCD

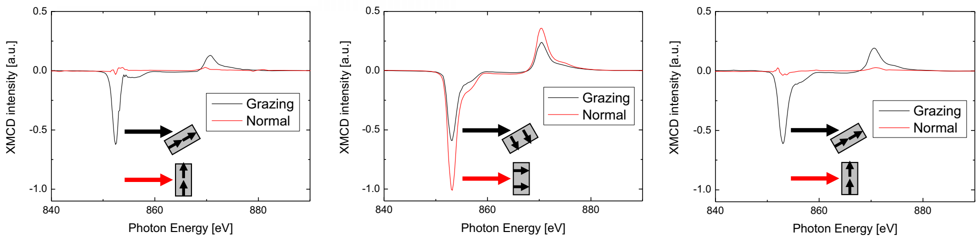


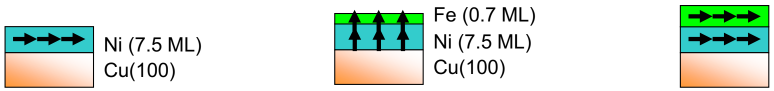


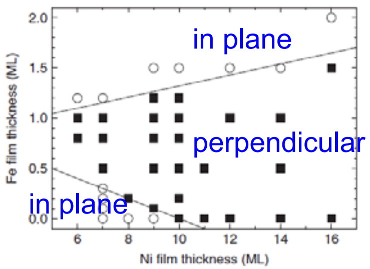
Magnetic-field dependence of XMCD at Fe and Co L edges



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







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.

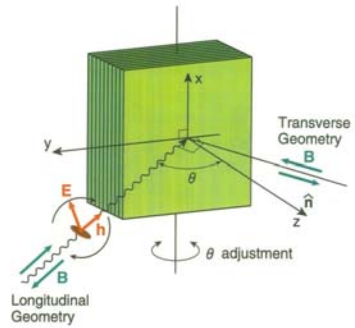
Sakamaki and Amemiya, Appl. Phys. Express 4 (2011) 073002.

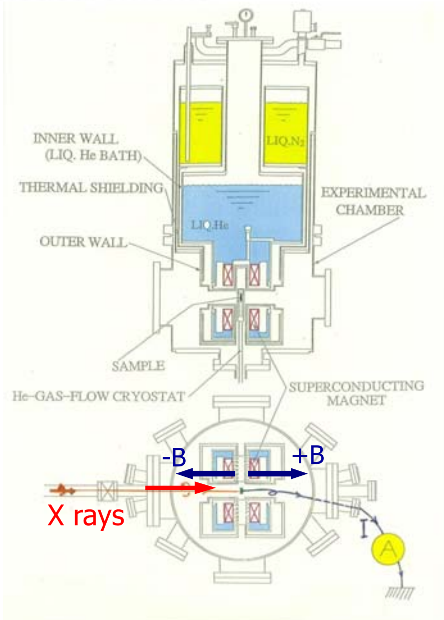
Angle Dependence of XMCD
(2) High magnetic field measurements

Angle-dependent XMCD

=> **Magnetic anisotropy**

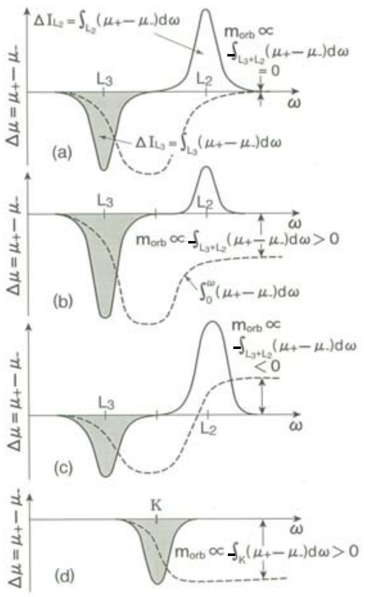
Separation of m_s from m_T





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

Angle-dependent XMCD Sum Rules



Orbital sum rule

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

Spin sum rule

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

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).

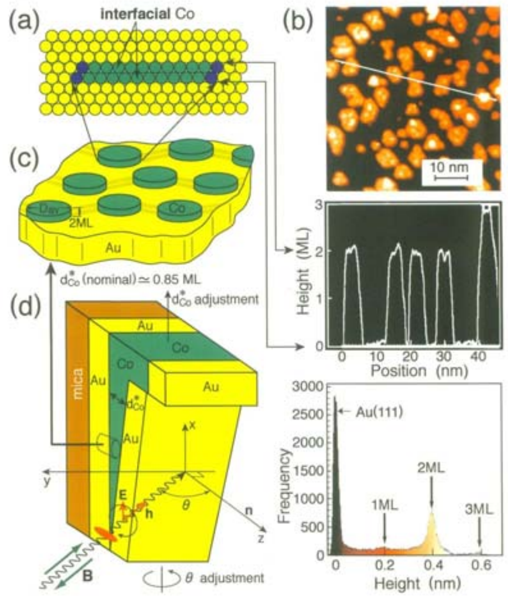
Au/Co(2 ML)/Au(111)

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

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

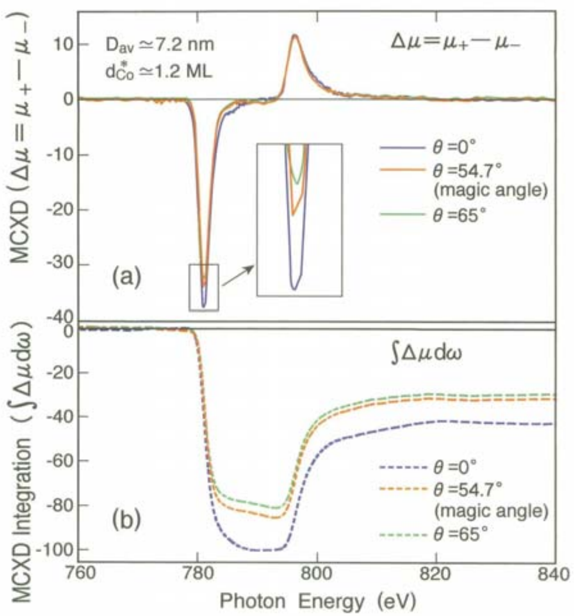
⇒ Direct observation of interface magnetism

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).



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Angle dependence in XMCD
<– Anisotropy in m_l, m_T

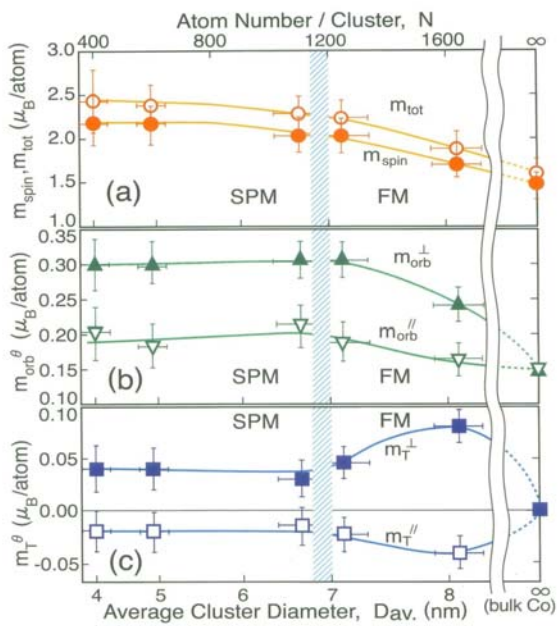
$m_j^{\theta} = m_j^{\perp}\cos^2\theta + m_j^{//}\sin^2\theta$
($j = l$ or T)

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

⇒ 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

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3. Novel SXAS Techniques

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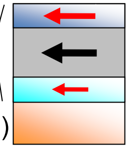
   3-2. Wavelength-dispersive XAS

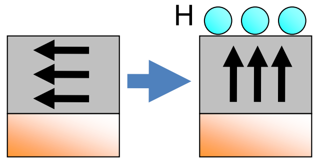
Introduction: Exploring Magnetic Depth Profile



Surface and interface show different magnetism from inner layers

Surface and Interface sometimes affect magnetism of whole film

Surface effect: Gas adsorption



Vollmer, et al., Phys. Rev. B 60 (1999) 6277.

Adsorption-induced change in magnetic easy axis

⇒ What happens at surface?

Interface effect: TMR

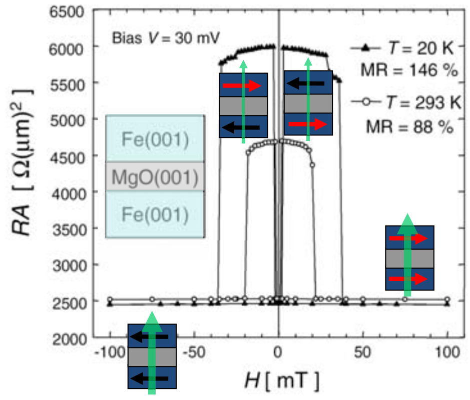


Fig. 3. Magnetoresistance curves for Fe(001)/MgO(001)(20 Å)/Fe(001) MTJ at $T = 293$ and 20 K. The MR ratios were 88% and 146%, respectively.

Yuasa, et al., Jpn. J. Appl. Phys. 43 (2004) L588.

Chemical and magnetic states at interface affect MR ratio

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

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

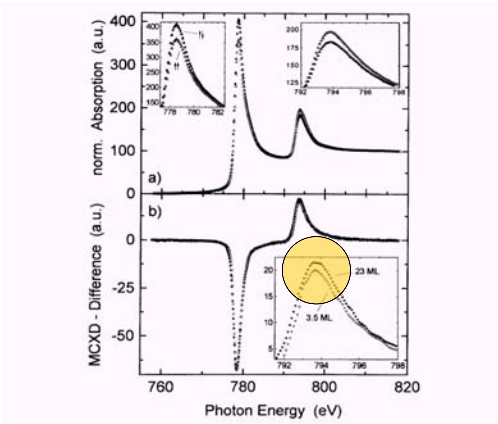


FIG. 2. (a) The normalized absorption spectrum for 3.5 ML Co/Cu(100). Open triangles indicate the photon spin parallel to the remanent magnetization, full triangles antiparallel. (b) MCXD difference for the 3.5 ML film (triangles) and a thick 23 ML film (circles). Both are normalized to the same L_3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

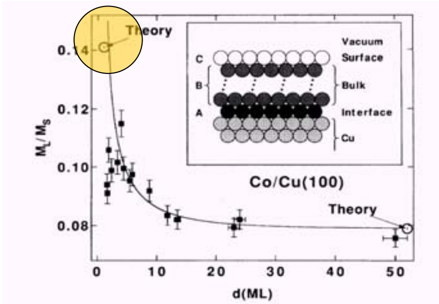


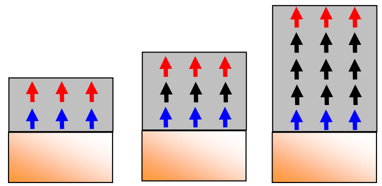
FIG. 3. The ratio of orbital versus spin moment M_L/M_S as a function of film thickness d. The open circles give the theory taken from Table I. The full squares show the experiment. The solid line is a fit using Eq. (1) with the parameters given in the last row of Table I. Note that the fit was performed 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.

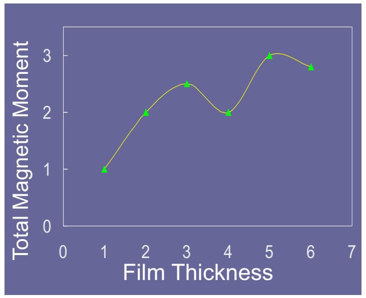
Conventional Technique for Depth Profiling

SQUID, VSM, MOKE, XMCD…

Gives averaged information over the whole sample.

⇒ also averaged in depth



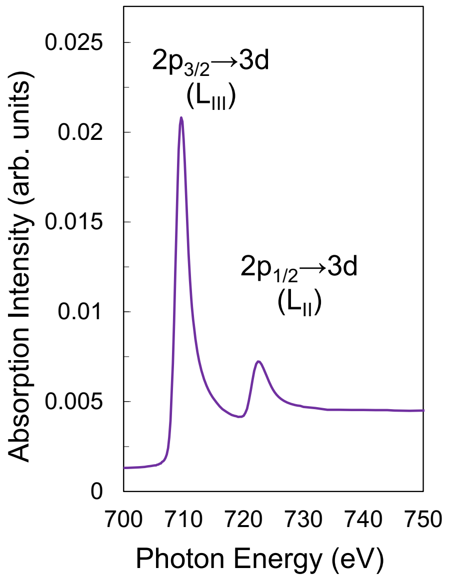


Based on an assumption that magnetic structure of surface and interface dose not change upon layer growth

→ Direct technique for depth profiling

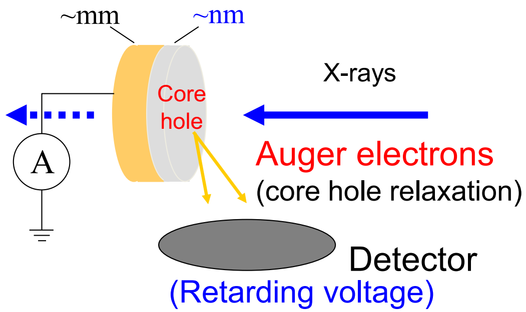
XAS Measurement in the Soft X-ray Region

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



How can we measure

X-ray absorption spectrum ?



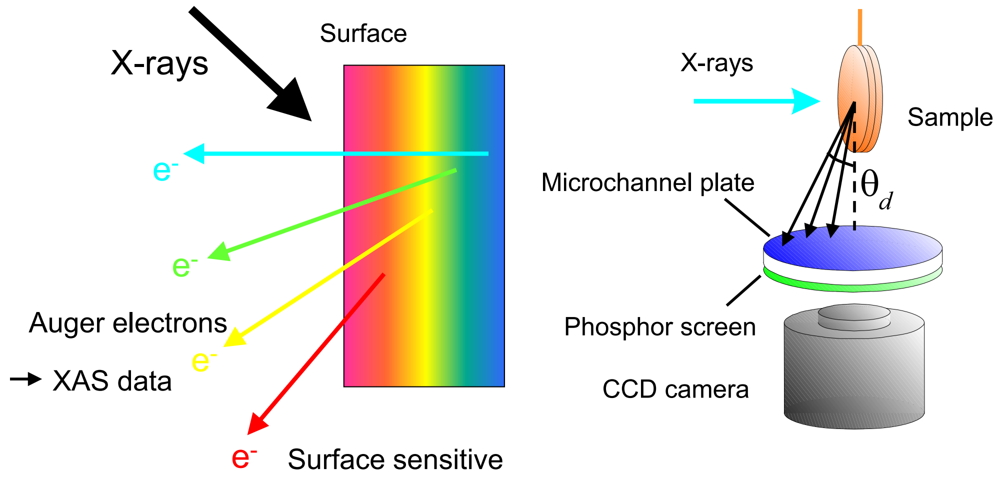
Electron yield XAS

Total electron yield (TEY)

Partial electron yield (PEY)

cf. Fluorescence yield (FY)

Principle of Depth-resolved XAS



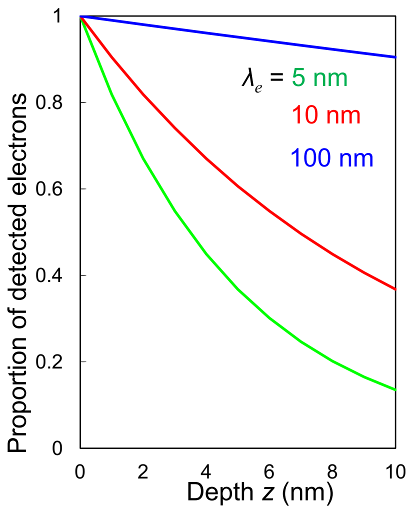
Electron yield XAS measurements at different detection angles

→ A set of XAS data with different probing depths

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

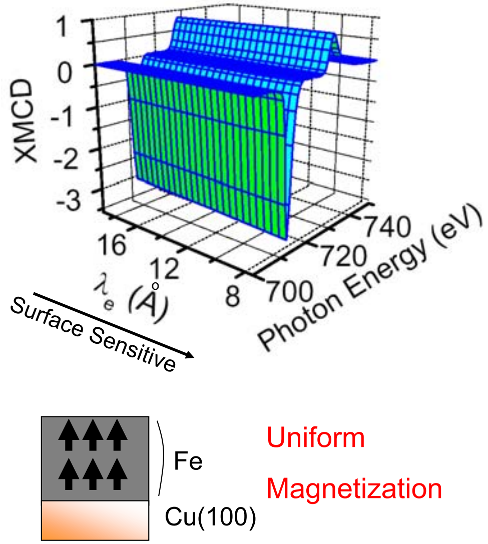
Depth-resolved XAS :

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

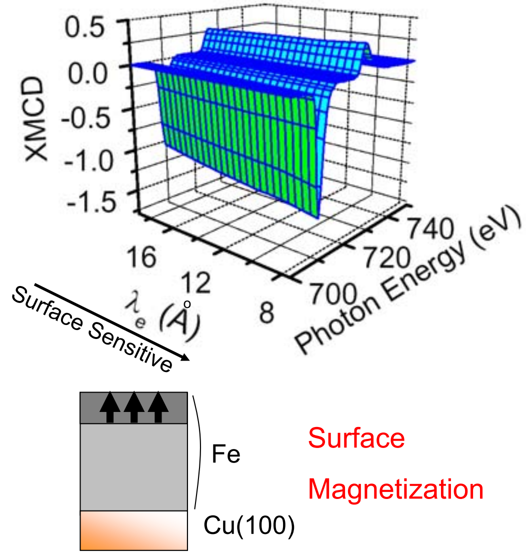
Feasibility Study: Depth-resolved XMCD of Fe/Cu(100)

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

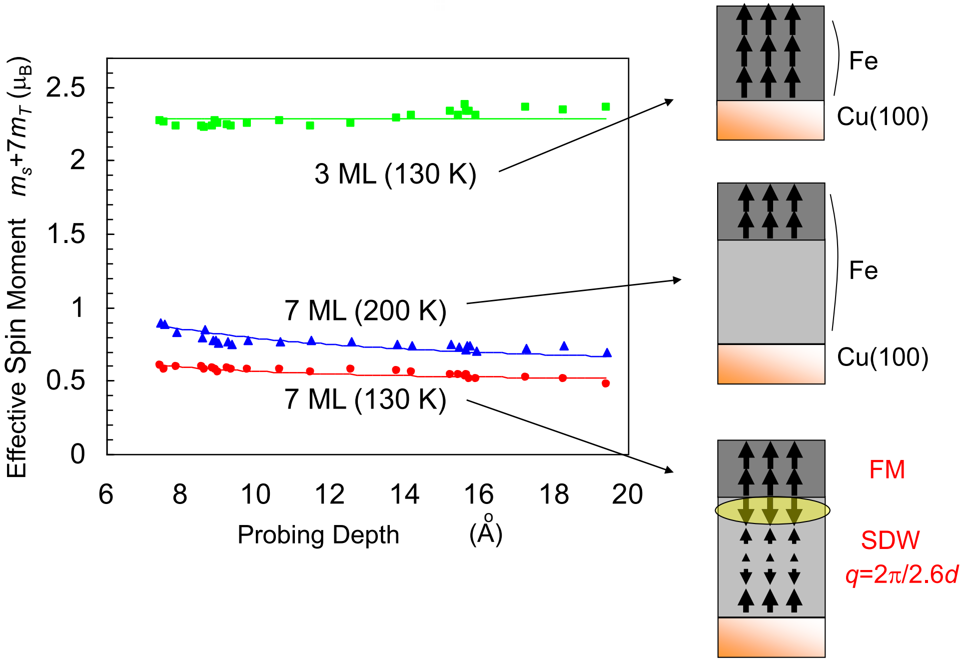
3 ML Fe



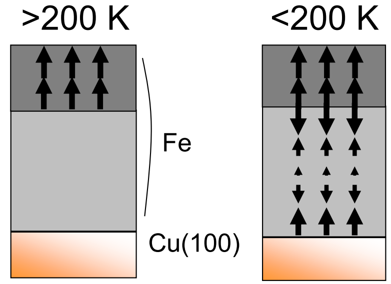
7 ML Fe



Interpretation of depth-resolved XMCD data



Fe/Cu(100)

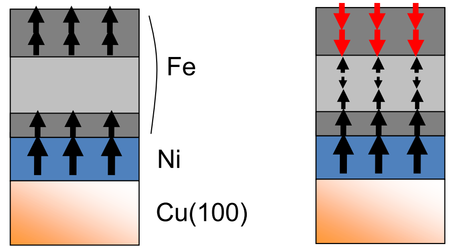


Surface (FM)

Inner layers (AFM or SDW)

No (little) magnetic interaction between Cu and interface (bottom) Fe

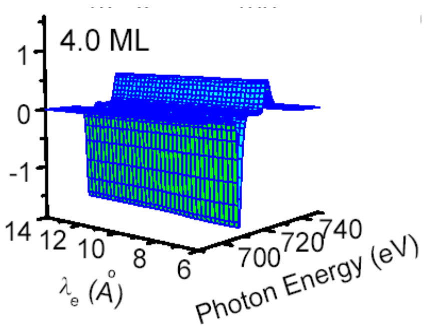
Fe/Ni/Cu(100)

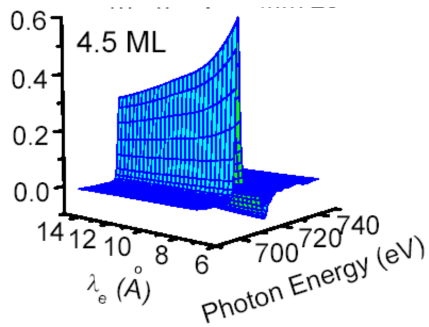


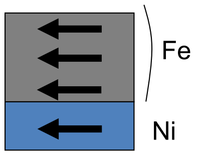
Any magnetic interaction among surface, inner layers and interface ?

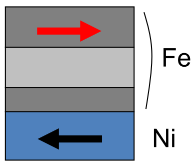
Fe(x ML)/Ni(6 ML)/Cu(100)

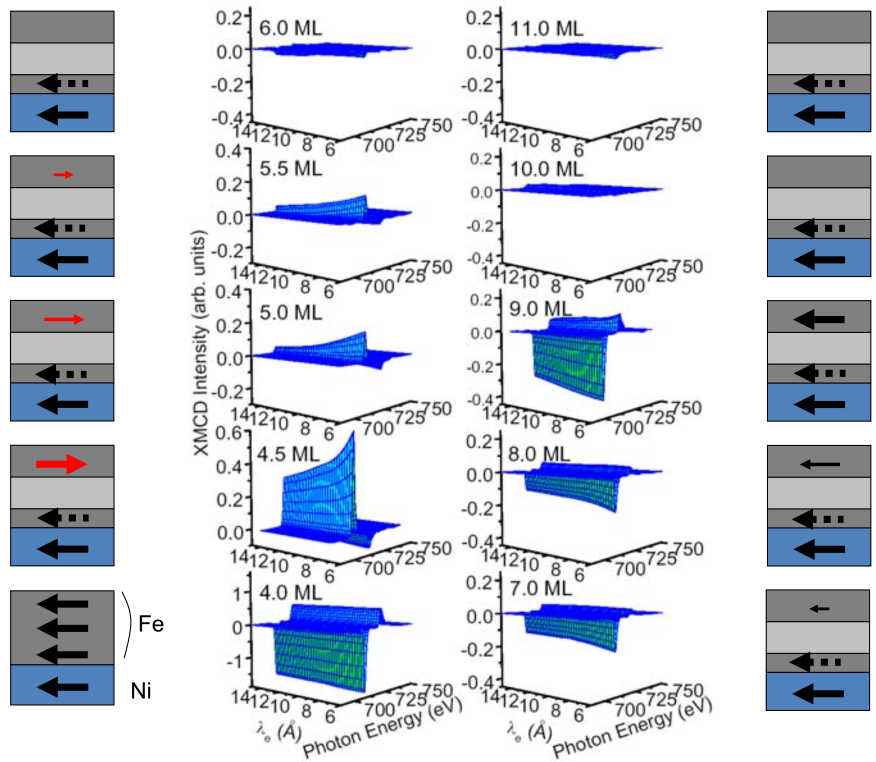
Fe L-edge Depth-resolved XMCD
Grazing Incidence (200 K)



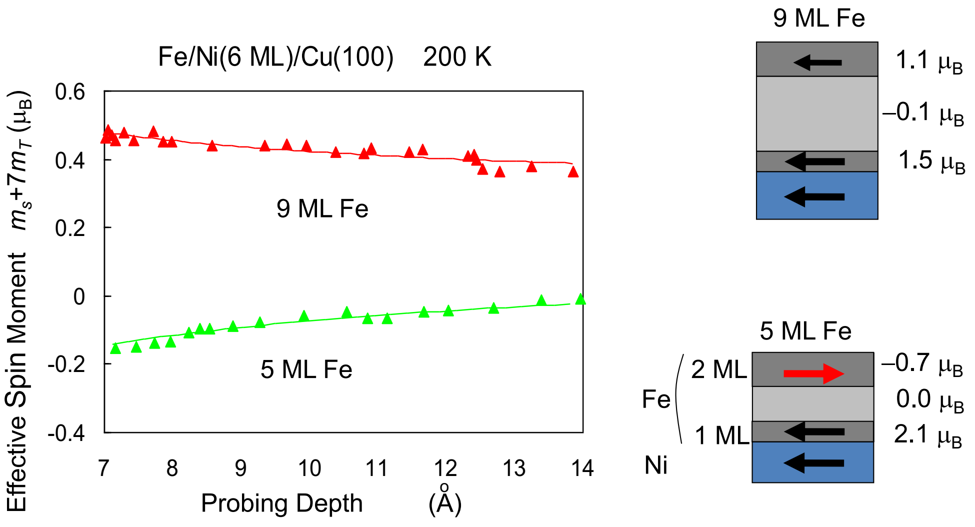




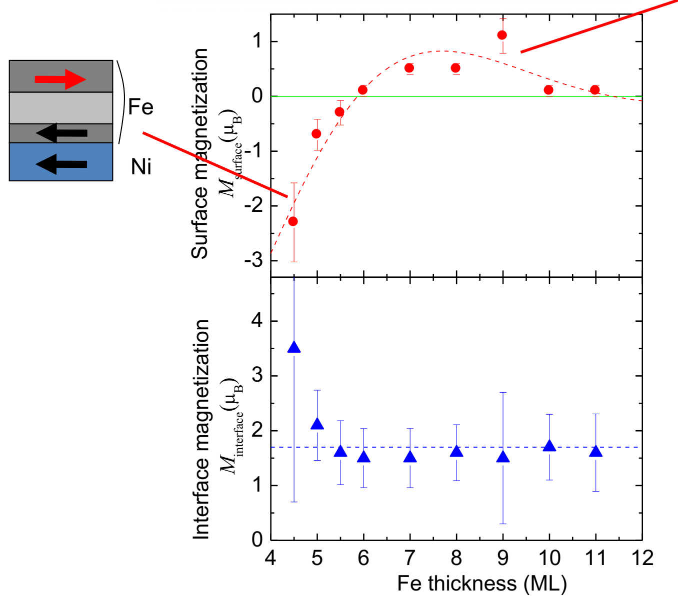


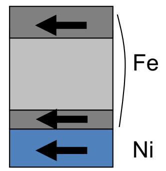


Curve fitting with a three-region model



Fe thickness dependence at 200 K





Oscillatory
surface magnetization

Positive
interface magnetization

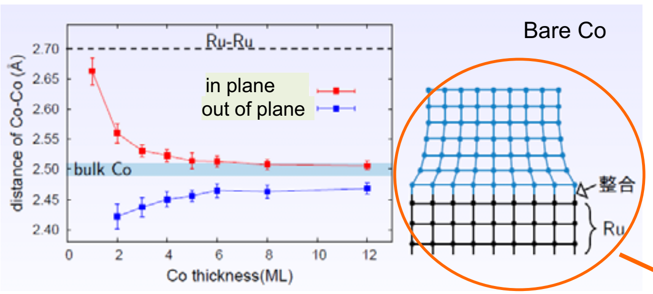
↓

Oscillatory
magnetic coupling
between
surface and interface

Amemiya et al., Phys. Rev. B 70 (2004) 195405.

Atomic structure of Ru/Co/Ru(0001) thin films

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

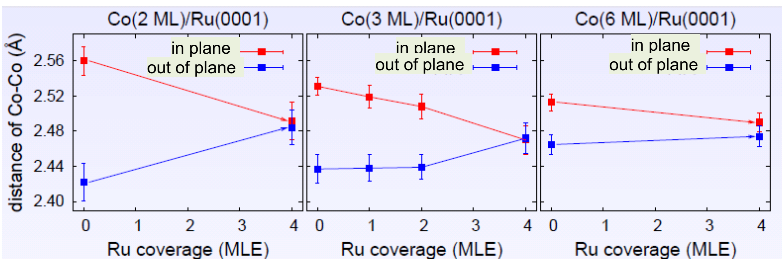


Miyawaki et al., Phys. Rev. B 80 (2009) 020408(R).

Interface Co layer is commensurate to Ru

Rapid relaxation upon further Co deposition

Effects of Ru capping



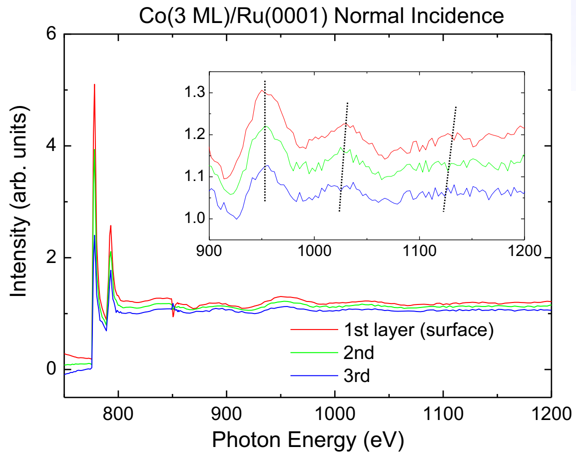
Is that true?

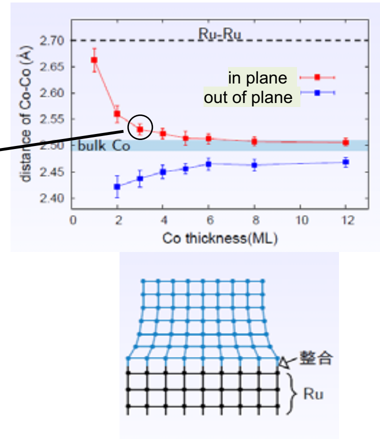
Relaxation of Co distortion upon Ru capping

Depth profile of atomic structure

Normal incidence: dominated by in-plane distance

Layer-resolved EXAFS



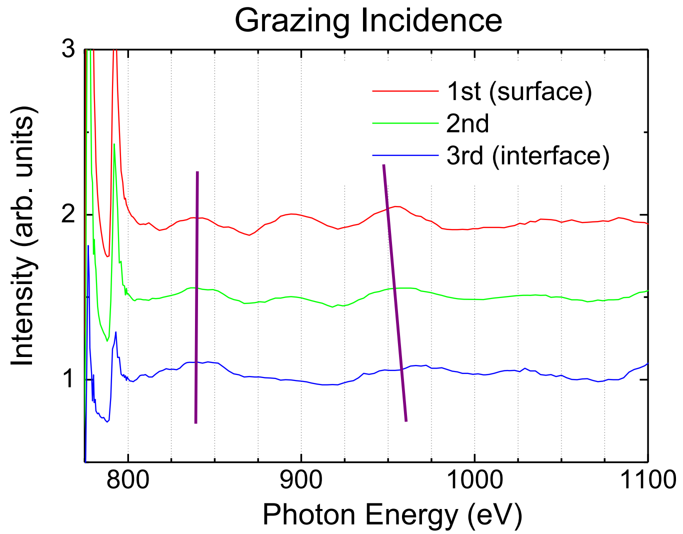


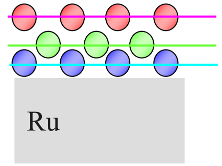
It might be true…

Surface shows longer oscillation period: shorter bond length

Depth-resolved EXAFS at grazing incidence

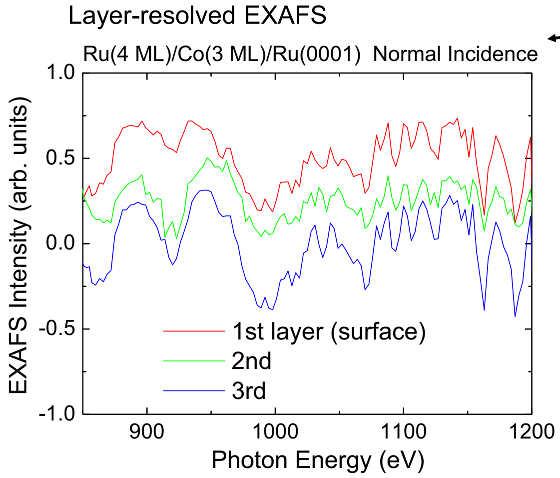
Longer out-of-plane bond length at surface?

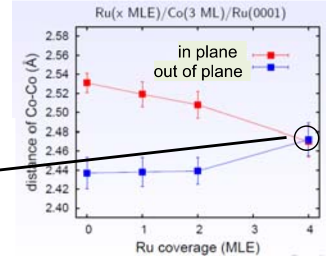


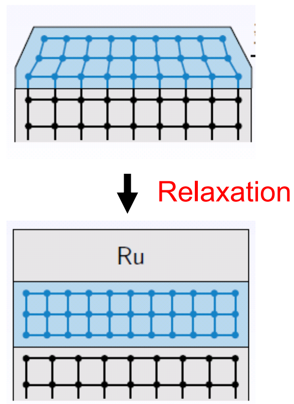


Effects of Ru capping

Normal incidence: in-plane bond length







Little difference in the bond length

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

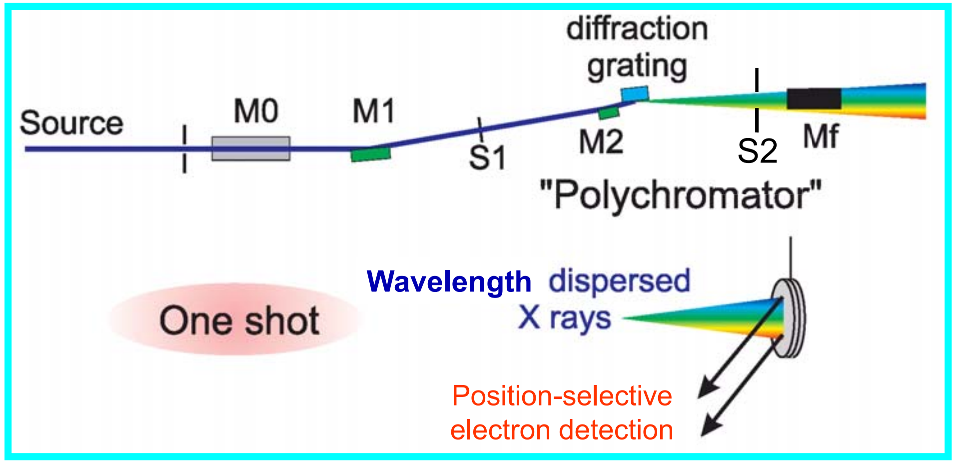
   3-2. Wavelength-dispersive XAS

Development of Wavelength-dispersive XAS

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

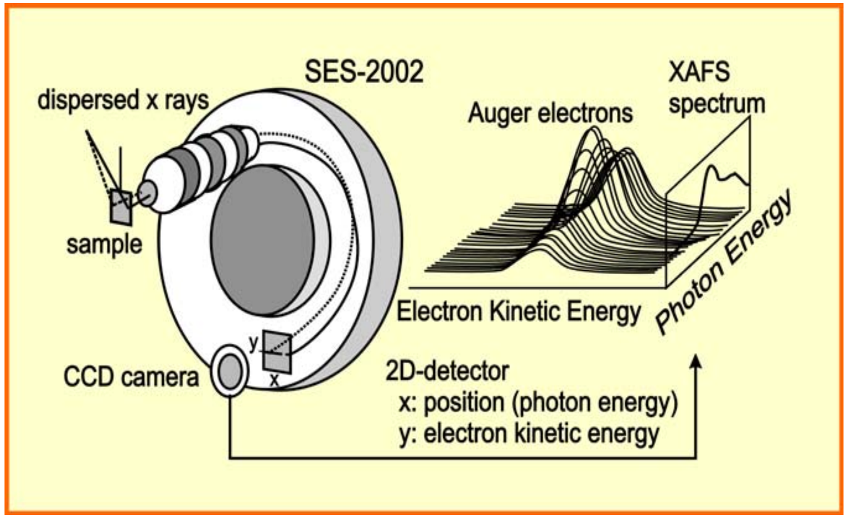
Takes long time (~5 min/spectrum) for a measurement.

Possibility of "One shot" measurement.



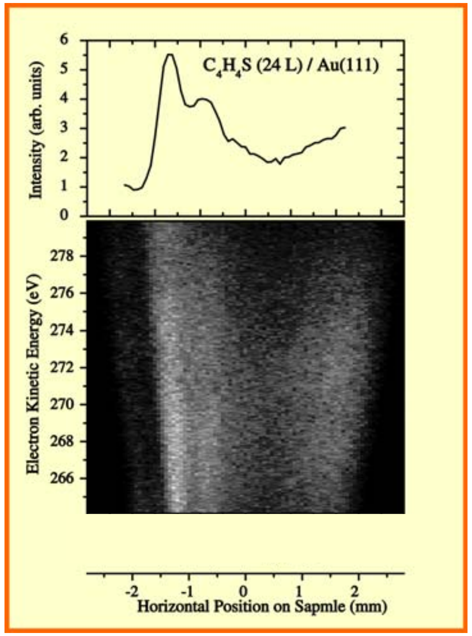
Experimental setup for wavelength-dispersive XAS

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

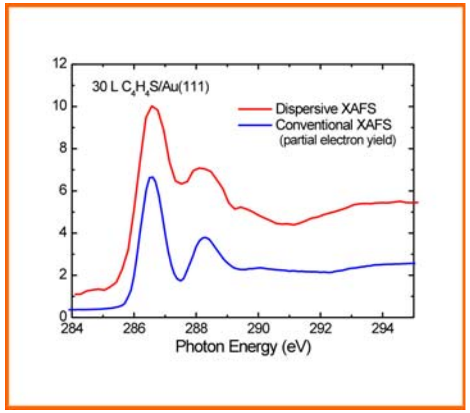


Test Measurement

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



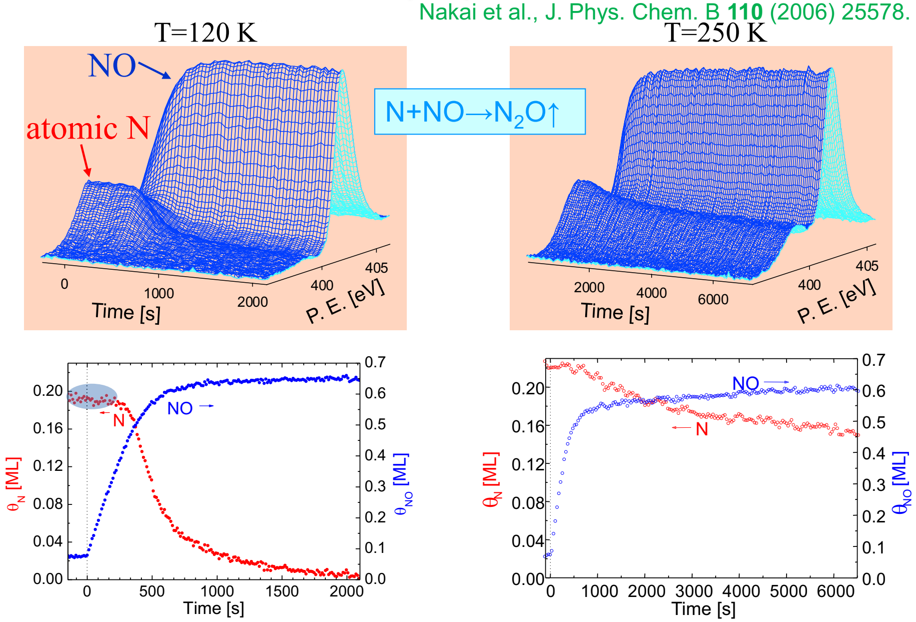
Comparison with conventional XAS



~100 times faster!

Chemical Reaction : NO/N/Rh(111)

Nakai et al., J. Phys. Chem. B **110** (2006) 25578.

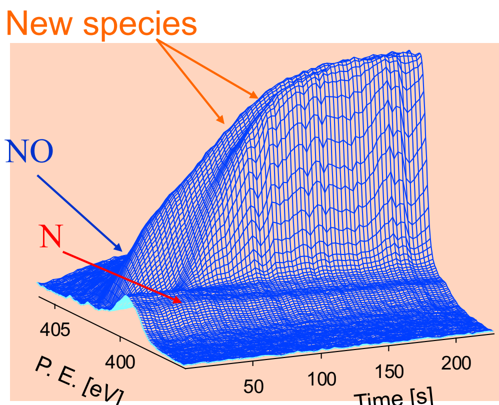


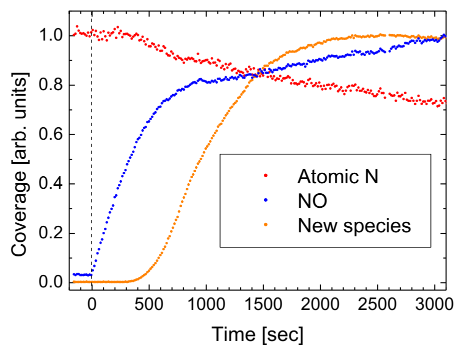
- Induction period: reaction does not start immediately
- Faster reaction at lower temperature

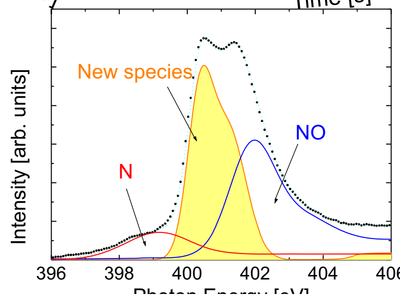
Lower Temperature

T=70 K, P_{NO}=5x10^{-9} Torr

Nakai et al., J. Phys. Chem. B **126** (2007) 044704.







Appearance of new species

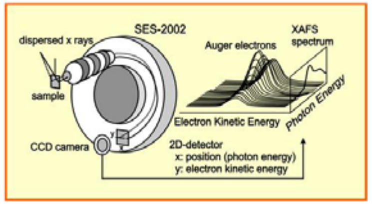
⇒ NO dimer

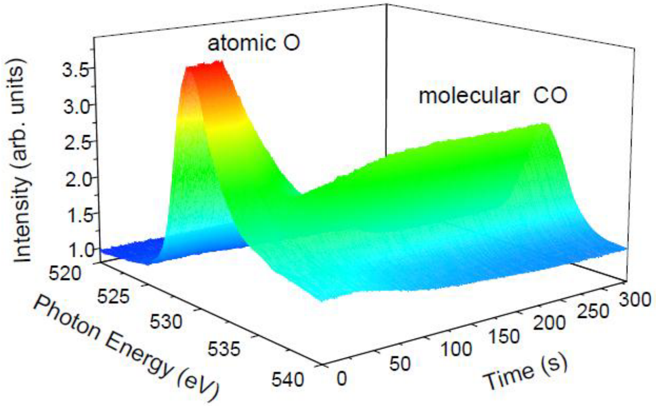
"New species" might be precursor.

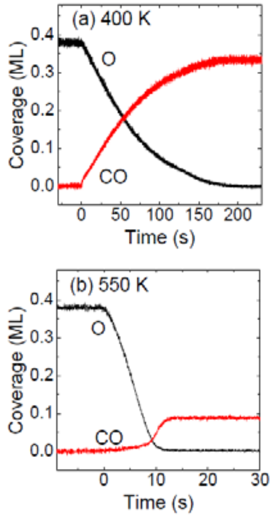
Recent Development

Undulator beamline (BL-16A)
Video rate (~30 Hz)

CO + O reaction on Ir(111)



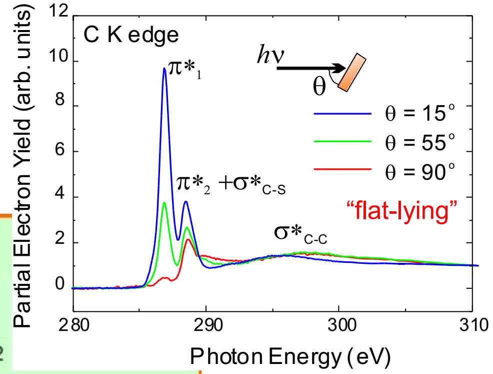


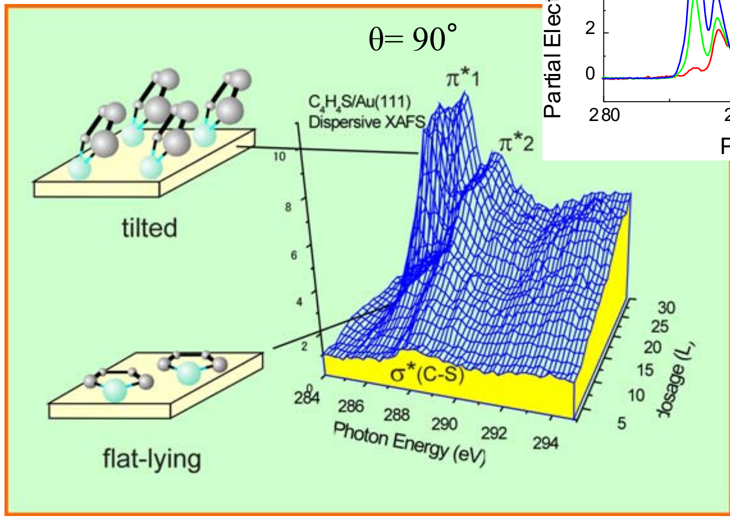


Amemiya et al., Appl. Phys. Lett. **99** (2011) 074104.

Utilization of Linear Polarization:

Adsorption of C_4H_4S on Au(111)





Orientation change
with increasing coverage