Soft X-ray Absorption Spectroscopy

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Absorption Edges in the Soft X-ray Region

Absorption-Edge Energy (eV)

Atomic Number

M edge

L edge

K edge
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
How can we measure X-ray absorption spectrum?

Electron yield XAS

Total electron yield (TEY) $\lambda \sim 3$ nm

Partial electron yield (PEY) $\lambda \sim 1$-$2$ nm

cf. Fluorescence yield (FY) $\lambda \sim 100$ 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.
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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
Molecular O$_2$

Different chemical species depending on preparation processes

Determination of Geometric Structure

Extended X-ray Absorption Fine Structure (EXAFS)

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

$\chi(k) = (\mu - \mu_S) / \mu_0$

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

- Coordination number ($N$)
- Inter-atomic distance ($r$)
- DW factor ($\sigma^2$)
Determination of Geometric Structure

Application to surface molecule (CH$_3$O)


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

<table>
<thead>
<tr>
<th>$m_l$</th>
<th>+2</th>
<th>+1</th>
<th>0</th>
<th>-1</th>
<th>-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d</td>
<td>18</td>
<td>6</td>
<td>3</td>
<td>12</td>
<td>2</td>
</tr>
</tbody>
</table>

$\mu_{\uparrow\uparrow} = 3 + 6 + 6 = 15$
$\mu_{\uparrow\downarrow} = 18 + 6 + 1 = 25$

Finite 3d orbital moment

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<th>$m_l$</th>
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$\mu_{\uparrow\uparrow} < 15$
$\mu_{\uparrow\downarrow} > 25$

Dipole transition probability

$2p_{3/2}$

$2p_{1/2}$

Helicity

Majority

$+1$

$H$

$H$

$\pm 1$

$\mu_{\uparrow\uparrow} = 3 + 12 = 15$
$\mu_{\uparrow\downarrow} = 3 + 2 = 5$

$\mu_{\uparrow\uparrow} > 15$
$\mu_{\uparrow\downarrow} < 5$
**XMCD Sum Rules**

**Orbital moment**

\[
\frac{m_l}{\int L_{\text{III}} (\mu_+ - \mu_-) + \int L_{\text{II}} (\mu_+ - \mu_-)} < 0 \rightarrow m_l > 0
\]

**Spin moment**

\[
\frac{m_s}{\int L_{\text{III}} (\mu_+ - \mu_-) - 2 \int L_{\text{II}} (\mu_+ - \mu_-)} < 0 \rightarrow m_s > 0
\]

P. Carra et al., PRL 70, 694 (1993).
Magnetism of Thin Films Studied by XMCD

Co $L$-edge XMCD spectra


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

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

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

$$T = \sum_i s_i - 3r_i (r_i \cdot s_i) / r_i^2.$$
Angle-dependent XMCD Sum Rules

Orbital sum rule

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

Spin sum rule

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

P. Carra et al., PRL 70, 694 (1993).

\[m_l^\theta = m_l^\perp \cos^2 \theta + m_l^\parallel \sin^2 \theta\]

\[m_T^\theta = m_T^\perp \cos^2 \theta + m_T^\parallel \sin^2 \theta\]

\[m_s \text{ does not depend on } \theta\]

\[\Rightarrow \text{ Direct determination of } m_s, m_l^\parallel, m_l^\perp, m_T^\parallel, m_T^\perp\]
Investigation of Interface Magnetism

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 $m_s$, $m_{//}$, $m_{\perp}$, $m_{T//}$, $m_{T\perp}$
Angle-dependent XMCD Measurements


Angle dependence in XMCD

\[ m_j^\theta = m_j^\perp \cos^2 \theta + m_j^\parallel \sin^2 \theta \]

\( (j = l \text{ or } T) \)

\[ m_T^\perp + 2 m_T^\parallel = 0 \]

⇒ Determination of all moments including their anisotropy
Determined Magnetic Moments


Cluster-size dependent phase transition

FM: ferromagnetic
SPM: super-paramagnetic
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Conventional Technique for Depth Profiling

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

⇒ also averaged in depth

Gives averaged information over the whole sample.

SQUID, VSM, MOKE, XMCD…

Direct technique for depth profiling
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

How can we measure X-ray absorption spectrum?

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

Absorption Intensity (arb. units)

Photon Energy (eV)

2p_{3/2} \rightarrow 3d (L_{III})

2p_{1/2} \rightarrow 3d (L_{II})

~mm ~nm

X-rays

Auger electrons (core hole relaxation)

Core hole

Detector (Retarding voltage)

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, $\theta_d$

A set of XAS data with different probing depths
Probing Depth (effective escape depth): $\lambda_e$

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

$I_0$: Original number of emitted electrons

**Smaller $\lambda_e$**

$\Rightarrow$ 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)


3 ML Fe

7 ML Fe

Uniform Magnetization

Surface Sensitive

Surface Sensitive

Fe

Cu(100)
Interpretation of depth-resolved XMCD data

![Graph showing effective spin moment vs probing depth for different thicknesses of Fe on Cu(100) at 130 K and 200 K.](image)

**Effective Spin Moment**

$$m_s + 7m_T \, (\mu_B)$$

**Probing Depth**

(Å)

6 8 10 12 14 16 18 20

**3 ML (130 K)**

**7 ML (130 K)**

**7 ML (200 K)**

**SDW**: Spin density wave

**Fe**

**Cu(100)**

FM

SDW

$$q = 2\pi/2.6d$$
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

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)

(a) Surface sensitive

(b) Increase of L₃ peak

Decrease of Plateau

Growth of shoulder

Photon Energy (eV)
Layer-resolved X-ray absorption spectra

O/Ni(5.5 ML)/Cu(001) Ni L-edge XAS ($E//x$) Extracted 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

O/Ni(5.5 ML)/Cu(001)  
Extracted Ni L-edge XAS

Intensities (arb. units) vs Photon Energy (eV) for Surface and Inner Layers

XAS spectra at surface shows NiO-like features


K. Amemiya and M. Sakamaki,  

NiO thin film
Surface layer shows small negative magnetization.

Uncompensated spin at the interface?

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

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

- Interface Co layer is commensurate to Ru
- Rapid relaxation upon further Co deposition

Effects of Ru capping

- Relaxation of Co distortion upon Ru capping


Is that true?
**Depth profile of atomic structure**

Normal incidence: dominated by in-plane distance

Layer-resolved EXAFS

Co(3 ML)/Ru(0001) Normal Incidence

Intensity (arb. units)

Photon Energy (eV)

1st layer (surface)
2nd
3rd

Surface shows longer oscillation period: **shorter bond length**

It might be true…

Depth-resolved EXAFS at grazing incidence

Longer out-of-plane bond length at surface?

Grazing Incidence

![Graph showing intensity vs. photon energy for different layers: 1st (surface), 2nd, and 3rd (interface).]

Intensity (arb. units) vs. Photon Energy (eV)

Preliminary analyses
Effects of Ru capping

Normal incidence: in-plane bond length

Layer-resolved EXAFS

Ru(4 ML)/Co(3 ML)/Ru(0001)  Normal Incidence

![Graph showing EXAFS intensity vs photon energy for different layers.]

Little difference in the bond length

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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


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): $\text{CO} + \text{O} \rightarrow \text{CO}_2$

Adsorption of C$_4$H$_4$S on Au(111)

Orientation change with increasing coverage

Development of Real-time Observation of Orientation

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

Dispersive XAFS

Polarization dependence

θ = 90°


Polarization switching

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


1 Hz switching

(a) NO/Ir(111) N K edge

(b) N₂O/Ir(111)
Polarization Dependence at Saturation Coverage


(a) NO/Ir(111)

N 1s $\rightarrow$ NO $\pi^*$

Vertical Polarization
Horizontal Polarization

Intensity (arb. units)

Photon Energy (eV)

20(+15/-20)$^\circ$

(b) N$_2$O/Ir(111)

N 1s $\rightarrow$ N$_2$O $\pi^*$

Intensity (arb. units)

Photon Energy (eV)

45 (+/-10)$^\circ$

N K edge
Molecular orientation change during NO adsorption


Molecular adsorption of NO at 140 K

Simultaneous increase between vertical and horizontal polarizations

=> Constant orientation during adsorption
Molecular Orientation Change during N$_2$O Adsorption

N$_2$O adsorption at 140 K


Three stages with different adsorption rates

Averaged orientation gradually increases

1$^{\text{st}}$ stage: Fast adsorption up to ~2/3 of saturation. **Constant orientation at ~35°.**

2$^{\text{nd}}$ stage: Up to ~90% of saturation. Gradual increase in orientation angle.

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

3$^{\text{rd}}$ 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

Soft X rays

$e$, $e$, $h\nu$, $h\nu$, $\sim$ nm, $\sim$ 0.1 $\mu$m