X-ray magnetic circular dichroism study on spin reorientation transitions of magnetic thin films induced by surface chemisorption

Toshihiko Yokoyama\textsuperscript{1}, Daiju Matsumura\textsuperscript{2}, Kenta Amemiya\textsuperscript{2}, Soichiro Kitagawa\textsuperscript{2} and Toshiaki Ohta\textsuperscript{2}

\textsuperscript{1} Institute for Molecular Science, Okazaki, Japan
\textsuperscript{2} Department of Chemistry, Graduate School of Science, The University of Tokyo, Tokyo, Japan

All the works presented today were done in Ohta Lab, my previous affiliation.
Surface anisotropy contributes to the stabilization of the in-plane magnetization in both cases.

$$\Delta E = -2\pi M_s^2 + K_{2v} + \frac{(K_{2s} + K_{2i})}{d}$$

When $\Delta E < 0$

When $\Delta E > 0$

Co/Pd(111), Co/Pt(111), Co/Au(111) etc.

$$K_{2v} < 0, K_{2s} < 0, K_{2i} > 0$$ Interface anisotropy stabilizes PMA

Ni/Cu(001)

$$K_{2v} > 0, K_{2s} < 0, K_{2i} < 0$$ Bulk magnetoelastic anisotropy stabilizes PMA

Note: Surface anisotropy contributes to the stabilization of the in-plane magnetization in both cases.
Spin-orbit interaction anisotropic

*cf.* exchange (spin-spin) interaction not anisotropic

\[ S_i \cdot S_j \text{ scalar product} \]

\[ S_i \leftrightarrow S_j \quad S_i \uparrow \uparrow S_j \text{ same energies without spin-orbit interaction} \]

Orbital angular momentum \( L_i \)

*anisotropic* in ultrathin films or more generally, except for spherical symmetry

spin-orbit interaction \( \xi_j L_i \cdot S_i \)

\[ L_i S_i \leftrightarrow S_j L_j \text{ different energies with spin-orbit interaction} \]
\[
\begin{align*}
L_{III,II}-\text{edge sum rules} \\
\text{Orbital } & m_l = -\frac{4}{3} \frac{n_h \mu_B}{P_c \cos \theta} \left[ \int_{L_{III}+L_{II}} \Delta \mu dE - 2 \int_{L_{III}+L_{II}} \mu^- dE - 2 \mu_{BG} \right] dE \\
\text{Spin } & m_s = -\frac{2 n_h \mu_B}{P_c \cos \theta} \left[ \frac{\int_{L_{III}+L_{II}} \Delta \mu dE - 2 \int_{L_{III}+L_{II}} \Delta \mu dE}{\int_{L_{III}+L_{II}} \int_{L_{III}+L_{II}} \mu^+ + \mu^- - 2 \mu_{BG}} \right] + 7 < T_z > \mu_B \\
n_h & \text{ hole number} \quad < T_z > \quad < T_z > \quad \text{magnetic dipole moment} \\
P_c & \text{ circular polarization factor} \\
\theta & \text{ angle between } k \text{ and } M \\
\mu^+ & \text{ spectrum} \\
\mu^- & \text{ spectrum} \\
\mu_{BG} & \text{ continuum step} \\
\Delta \mu & = \frac{\mu^+ - \mu^-}{P_c \cos \theta} \\
\text{fe } m_l & = 0.071 \\
m_s & = 2.36 \\
\text{cf. } K \text{ edge} \\
\text{Orbital } & m_l = -\frac{2}{3} \frac{n_h \mu_B}{P_c \cos \theta} \left[ \int_K \Delta \mu dE - 2 \int_K \mu^- dE - 2 \mu_{BG} \right] dE \\
\text{Spin } & m_s = -\frac{2 n_h \mu_B}{P_c \cos \theta} \left[ \frac{\int_K \Delta \mu dE - 2 \int_K \Delta \mu dE}{\int_K \int_K \mu^+ + \mu^- - 2 \mu_{BG}} \right] + 7 < T_z > \mu_B \\
\text{element-specific magnetization}
\end{align*}
\]
Co/Pt sandwiched films (PMA)


Normal incidence Co $L_{3,2}$-edge XMCD in $H = 2$ T

Perpendicular Orbital moments as a function of Co thickness

Orbital moment is enhanced as thickness decreases

Interface anisotropy favors PMA
Spin reorientation transition (SRT) induced by adsorption

**Stabilization of PMA**

<table>
<thead>
<tr>
<th>System</th>
<th>Authors</th>
<th>Journal/Volume/Issue, Pages (Year)</th>
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**Phenomenological understanding**

Gas adsorption → Decrease in surface anisotropy \( |K_{2s}| \), which favors in-plane magnetization → Stabilization of PMA

**Other examples of SRT induced by adsorption**

**Structure change of the metal films**

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<tr>
<td></td>
<td></td>
<td>PMA stabilized by H adsorption</td>
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**SRT within the surface plane**

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**Effect of adsorption on magnetic anisotropy**

**H adsorption on Ni/Cu(001)**


**easy axis [001] (PMA)**

H ads.  
$d_c = 10$ ML

H des.

H ads.  
$d_c = 7$ ML

7-10 ML Ni
Effect of adsorption on magnetic anisotropy

CO adsorption on Co/Cu(110)


Easy axis [001]

Easy axis [1-10]

Time (CO ads.)

[001]

[1-10]
Origins of the spin reorientation transition (SRT) induced by adsorption

Relation of SRT to the changes of the orbital magnetic moments upon adsorption

1) CO adsorption on Co/Pd(111)
   Observation of SRT upon CO adsorption
   Discussion on the microscopic origin of the SRT

2) NO, H, O and CO adsorption on Co/Pd(111)
   Dependence of the adsorbates
   Which molecules induce SRT ?

3) CO and H adsorption on Ni/Cu(001)
   Discussion on the microscopic origin of the SRT
   Difference between CO and H

4) Absorbate K-edge XMCD of CO and NO on Co and Ni films
Retarding bias improves surface sensitivity.

KEK-PF BL7A bending magnet

±0.4 mrad \( h_v \)

\( P_c = 0.80 \)

GRD
-500V
2000V
3000V

Retarding bias improves surface sensitivity

Amplifier

Normal x-ray incidence for perpendicular magnetization

Grazing x-ray incidence for in-plane magnetization

MCP

Pulse supply

Remanent magnetization investigated

\( H \)

\( I \)

Experimental setup for XMCD measurements
SRT induced by CO adsorption on Co/Pd(111)

Co L-edge XMCD of 4.5 ML Co/Pd(111) at 200 K

Clean surface

CO adsorbed surface

Change of the magnetic easy axis
Co spin in clean and CO-adsorbed Co/Pd(111)

Above the critical thickness $d_C$, the easy axis is in plane.

CO adsorption extends the PMA stable region.
CO adsorption reduces only the in-plane orbital moments.

Co 3d orbital moment in clean and CO-adsorbed Co/Pd(111)

T=200 K

Clean surface

CO adsorbed

Orbital moment (μ_B)

Co thickness (ML)
Co L-edge XMCD of NO- and H-adsorbed 4.5 ML Co/Pd(111)

NO saturated adsorption \( T = 200 \text{ K} \)

<table>
<thead>
<tr>
<th></th>
<th>( m_l ) (( \mu_B ))</th>
<th>( m_S ) (( \mu_B ))</th>
<th>( m_l / m_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean</td>
<td>0.25</td>
<td>1.89</td>
<td>0.13</td>
</tr>
<tr>
<td>NO ads.</td>
<td>0.16</td>
<td>1.06</td>
<td>0.15</td>
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</table>

H saturated adsorption \( T = 200 \text{ K} \)

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<th></th>
<th>( m_l ) (( \mu_B ))</th>
<th>( m_S ) (( \mu_B ))</th>
<th>( m_l / m_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean</td>
<td>0.30</td>
<td>2.05</td>
<td>0.14</td>
</tr>
<tr>
<td>H ads.</td>
<td>0.25</td>
<td>1.78</td>
<td>0.14</td>
</tr>
</tbody>
</table>
Co L-edge XMCD of O-adsorbed Co/Pd(111)

O-Adsorbed Co/Pd(111)  
(O₂ 3 L)  
T = 200 K

Oxidized Co/Pd(111)  
(O₂ 24 L)  
T = 200 K

O adsorption does not induce SRT
Oxidation leads to SRT due to reduction of Co thickness.
Ni $L_{III,II}$-edge XMCD of CO, H/Ni/Cu(001) films

**Graphs and Data**

- **Clean Ni 8 ML**
  - XAS
  - XMCD
  - Normal and Grazing Intensity

- **0.5ML CO/Ni 8 ML**
  - XAS
  - XMCD
  - Normal and Grazing Intensity

- **Clean Ni 7 ML**
  - XAS
  - XMCD
  - Normal and Grazing Intensity

**Processes**

- 0.5ML CO
- 1ML H2
- Annealed

**Electronic Structure**

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

**Films**

- Ni 8ML
- Ni 7ML

**Comparisons**

- Clean vs. CO-covered films
- Normal vs. Grazing incidence

**Annotations**

- Normal vs. Grazing XAS and XMCD patterns
- Changes in intensity with CO and hydrogen treatment
H₂ adsorption results in the decrease in both the parallel and perpendicular orbital moments.
Atop site adsorption leads to the reduction of the in-plane orbital moment only.

Spin-orbit interaction

\[ E_{SO} \propto -l \cdot s \]

\( l \parallel s \) in Fe, Co and Ni

Instabilization of the in-plane magnetization
Stabilization of PMA

NO/Co/Pd(111) and CO/Ni/Cu(001) can be explained similarly.
The reason why SRT does not take place in H/Co/Pd(111) or O/Co/Pd(111) may be smaller coverages: 1 ML H/Ni/Cu(001) vs 1/3 ML O/Co/Pd(111).

**H adsorption reduces both // and ⊥ orbital moments.** Since the // moment is larger on the clean film, the effect should be larger.
O K-edge XMCD of CO on Co/Cu(001) and Ni/Cu(001)


Induced magnetization on CO $2\pi^*$ due to the hybridization of metal 3d levels.

Orbital magnetic moment

in-plane: negative antiparallel to the substrate magnetization

PMA: positive parallel to the substrate magnetization
N K- and O K-edge XMCD of NO/Co(001)

negative XMCD at $2\pi^*$ → positive orbital moment
Open question: Why not SRT induced by CO at 300 K?

No shift in the critical thickness between clean and CO-adsorbed Co/Pd(111) at 300 K, though the saturation coverage of CO at 300 K is greater than the critical CO coverage at 200 K!!
Concluding remarks

1) Experimental findings in NO, H, O and CO adsorption on Co/Pd(111)
   Discovered new SRT on Co/Pd(111) induced by CO and NO chemisorption at 200 K
   O or H adsorption does not affect $d_c$ of SRT
   CO does not affect $d_c$ of SRT at 300 K

2) Experimental findings in CO and H adsorption on Ni/Cu(001)
   Confirmed SRT on Ni/Cu(001) induced by CO and H

3) Origin of SRT on Co and Ni films upon CO and NO adsorption
   Reduction of the in-plane orbital magnetic moment
   Perpendicular orbital moment is not so influenced
   Stabilization of PMA through the spin-orbit interaction

4) Origin of SRT on Ni/Cu(001) upon H adsorption
   Reduction of both the in-plane and perpendicular orbital magnetic moments
   In-plane orbital moment is more influenced
   Different adsorption geometry leads to different SRT mechanism

5) Experimental findings of induced orbital magnetic moments on CO and NO on Co and Ni films
   by means of N and O K-edge XMCD measurements
   CO and NO $2\pi^*$ orbitals are magnetically polarized.
   PMA: parallel orbital moment to the substrate
   In-plane: antiparallel orbital moment