The ODE beamline at SOLEIL: first results on XMCD and EXAFS under extreme conditions and kinetics experiments

Alberta Congeduti, Qingyu Kong, Sébastien Chagnot, Alexandre Monza, Gwenaëlle Abeille, Aurélien Delmotte, Olga Roudenko, and François Baudelet
Source: Bending Magnet

⇒ intrinsic angular aperture → few optical elements, short optical paths → huge stability
⇒ absence of spatial coherency effects
⇒ spatial distribution of X-ray polarization

SOLEIL bending magnet

Bent polychromator
Main bent mirror
Secondary mirror
Sample
CCD Detector

 нескольких оптических элементов,
короткие оптические пути → огромная стабильность
⇒ отсутствие эффектов пространственной коherence
⇒ пространственное распределение поляризации X-лучей

Intensity (photons/mrad²/0.1% Δλ/λ)
Circular polarization rate

Observation angle ψ mrad
ODE Bending Magnet Circular Polarization

Fe K edge 7112 eV

τ circular polarization rate
Iτ² merit factor

Intensity I

Best positions

XMCD ∝ τ
ODE layout: hutches and control rooms
ODE layout: optics and experiment
Optics

- Primary slits
- Focusing Mirror (1.2 meters)
- Secondary slits
- First imager
- Second imager
- Polychromator
- Front End
Optics: Focusing mirror

Winlight System

Useful area: 88 x 1200 mm
Coating Pd / Si
Slope error: 1.0 µrad RMS on 1m
Roughness: 1 à 2 Å RMS
Double bender → Curvature radius 0.8 km to ∞
Water cooled (InGaSn bath)
Focusing 8 mm → 35 µm
Optics: Vertical focusing

Optical simulations by
Mourad Idir Thierry Moreno

\[ I = \sqrt{(S \times G)^2 + (2 \times 2.35 \times 2\mu rad \times 4.465m)^2} \]
\[ I \approx 45 \mu m \]

1 pixel = 7 µm → measured FWHM = 35 µm
Optics

Primary slits
Focusing Mirror (1.2 meters)
Secondary slits
First imager
Second imager
Front End
Polychromator
Focusing Mirror (1.2 meters)
Optics: polychromator focusing

Si 111 and 311

Thierry Moreno and Mourad Idir
**Optics: polychromator focusing**

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_x$ (µm)</th>
<th>$\sigma_z$ (µm)</th>
<th>$\sigma'_x$ (µrad)</th>
<th>$\sigma'_z$ (µrad)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Soleil</strong></td>
<td>60.1</td>
<td>24.9</td>
<td>134.8</td>
<td>2.1</td>
</tr>
<tr>
<td><strong>Lure</strong></td>
<td>2500</td>
<td>1580</td>
<td>1070</td>
<td>170</td>
</tr>
</tbody>
</table>

**Twisting**

**spherical aberration**

**LURE**

**SOLEIL**
Optics: polychromator focusing

Si 111 and 311

Thierry Moreno and Mourad Idir
Optics: bender mechanical improvements

Old

developed from an ESRF original design

- Better contact between blade and bender
- Decoupling twisting and bending movements
  ⇒ Very small spot size

New

Sébastien Chagnon
Optics: 311 focus @ Fe K-edge

Focus Image

Horizontal Profile

1 pixel = 7 µm → FWHM 20 µm
Optics: high sensitivity to slope errors

Remarkable slope errors in our 111 blades!

More details in Thierry Moreno’s talk
Optics: more homogeneous focus with the new Si 311 blade

17 keV
ODE layout: optics and experiment
Sample environment

Multipurpose sample environment adapted to various kinds of studies: pressure, temperature, magnetic field, gas or liquid environment
Sample Environment:

*in situ* Pressure Measurement
Results: EXAFS STUDY OF a-Ge AT HIGH PRESSURE

ODE’s first measurement in Diamond Anvil Cell (0 – 10 GPa) at the Ge K-edge (11100 eV)

First high-pressure measurements in a diamond anvil cell (DAC) in dispersive mode using ODE beam-line at Soleil. Ge K-edge XAS a-Ge films of about 3 x 3 μm thickness (obtained by evaporation).

The films were amorphous as confirmed by XRD.

Spectra taken with less than 1 s of integration.

STRUCTURAL MODIFICATIONS:

• A clear transition is evidenced above 7.9 GPa.
• The spectra at 8.3 GPa and 9.8 GPa are different.
• The weak XAS structural signal obtained at 8.3 GPa is compatible with the presence of strong structural disorder (different amorphous phase).
• The strong signal at 9.8 GPa is compatible with a crystalline structure with elongated first-neighbour distances (like Ge II)

• At ~ 8 GPa: the surface shows a metal-like reflectivity, loss of the Raman signal and strong diffuse scattering.
Sample Environment: Drilled Diamond Anvil Cell for Low Energy HP measurement

Drilled diamond cell ⇒ thickness reduced of a factor 2.5
⇒ e.g. a factor ~150 on the transmitted intensity at the Mn k-edge

P = 0 - 30 GPa
T = 2 - 500 K

• Example: V K-edge (5480 eV) at 300 K, (20 s / scan)

F. Rodolakis (LPS / SOLEIL), J.-P. Rueff (SOLEIL / LCPMR), M. Marsi (LPS)

Collaboration with Bernard Couzinet IMPMC
Sample Environment:

*in situ* Pressure Measurement  2T Magnetic Coil for XMCD

+ Fast Feedback

Jean-Marc Filhol
Fabrice Marteau
Sébastien Chagnot
François Baudelet
Results: Magnetic transitions under pressure in magnetite

0 – 30 GPa, 2T

Verwey transition disappears at 8 GPa

Transition from indirect to direct spinel at 8 GPa

Only an abrupt magnetic transition between 12 and 16 GPa
Yang Ding et al. PRL 100 045508 (2000)

No transition from indirect to direct spinel but a continuous decrease of the magnetic moment between 8 and 30 GPa

F. Baudelet, O. Mathon, J.P.Itié, S.Pascarelli, A.Polian, M. d’Astuto and J.C. Chervin
Results: XMCD on Co at HIGH PRESSURE

0 – 94 GPa, 2T

Anomalous c/a ratio behaviour at HP

Magnetic moment vanishes at HP?

XAS

XMCD

Beamline limit → ID24 to get over

In good agreement with Iota et al.
Temperature variation induces a change in the redox state. It can be followed by:

- Changes in the White Line
- Changes in the Pre-Peak
Results: Time–resolved reduction of $\text{ReO}_x/\text{Al}_2\text{O}_3$ catalysts

Supported rhenium oxide is very selective towards dimethoxymethane during methanol partial oxidation. It has been proposed that an original redox couple ($\text{Re}^{\text{VI}}$-$\text{Re}^{\text{IV}}$) could be at the origin of this behavior.

Experimental setup: Powdered catalyst in a Lytle-type cell, with a mica window for Raman. EXAFS (Re L3-edge) spectra recorded on ODE beamline (ca. 2 spectra/minute).

XANES clearly evidence a fast and direct reduction from Re$^{\text{VII}}$ to Re$^0$ between 293°C and 303°C, well confirmed by the EXAFS analysis.

Elise Berrier, Sylvain Cristol, Camille La Fontaine, Valérie Briois, Françoise Villain
Developments in progress

- XMCD @ 7T, 2K, HP
- XRD/XAS combination
- Raman/XAS combination
- Stopped Flow
- New benders and blades for the polychromator (220 and 111, 311 with lower slope error)
- Fluorescence measurements
- Turbo EXAFS for diffusing samples’ kinetics
- Acquisition Graphic Interface and Live Energy Calibration
THANKS FOR YOUR ATTENTION!
Developments in progress: XMCD @ 7T, 2K, HP

Bernard Couzinet, Jean-Claude Chervin, IMPMC
Developments in progress: Combination of XAS/XRD

• First attempt: crystallization of a-Ge upon decreasing pressure at 6 GPa

Set-up

2.9 GPa diffraction pattern upon depressurization

MAR345 image

Federica Coppa, Emiliano Principi, Alberta Congeduti, Sebastien Chagnot and Andrea Di Cicco
Effect of diffusing materials on resolution

![Graph showing the effect of diffusing materials on resolution. The x-axis represents energy (E, eV) ranging from 8950 to 9150, and the y-axis represents absorption. The graph compares Cu foil and Cu foil + diffusing material.](image)
Informatics interfaces

• XMCD

• Kinetics

Qingyu Kong, Gwenaelle Abeillé, …
Informatics interfaces

• XMCD
Informatics interfaces

• XMCD

• Kinetics

Qingyu Kong, Gwenaelle Abeillé, …
Energy calibration

Calibration of spectra from DXAS beamlines
M.P. Ruffoni and R.F. Pettifer

\[ E_i = \sum_{k=0}^{K} c_k x^k \]
\[ A_i = a_0 + a_1 y_i + \sum_{m=1}^{M} b_m T_m(E_i) \]

Background correction using Chebyshev polynomials \( T_m \)

Highly multi-modal optimization problem

Find \( \{ c_k, a_l, b_m \} \), \( k = 1, \ldots, K \), \( l = 1,2 \), \( m = 1, \ldots, M \)

so as to \( \min_{c,a,b} \sum_i \left( \Phi(\bar{c}, \bar{a}, \bar{b}) (x_i, y_i) - \left( E_i^{ref}, A_i^{ref} \right) \right)^2 \)

The solution found by a local algorithm (such as Levenberg-Marquardt) is very sensitive to the starting point
Improved calibration tool

1. Finding a good starting point
given measured and reference spectra.

2. A slower **global** optimization algorithm replaces
quick local optimization (L.-M.) when the latter one fails.

The optimization method, based on *Covariance Matrix Adaptation*,
avoids local optima traps and achieves satisfactory calibration in more cases.
(Many thanks to **Nikolaus Hansen**, INRIA Saclay!)

Contact: olga.roudenko@synchrotron-soleil.fr
Live Energy Calibration

Olga Roudenko, Julien Malik …
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**Beamline specification**

<table>
<thead>
<tr>
<th>EXAFS</th>
<th>Measurements from 5 keV to 25 keV</th>
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<tbody>
<tr>
<td>XANES and XMCD</td>
<td>From 3.5 keV to 25 keV</td>
</tr>
<tr>
<td>Resolving power</td>
<td>E/ΔE: 3 (10^4) for Si(<em>{311}), 0.7 (10^4) for Si(</em>{111})</td>
</tr>
<tr>
<td>Focus size</td>
<td>40 µm x 40 µm FWHM</td>
</tr>
<tr>
<td>Detection mode</td>
<td>Transmission mode with a photodiode array or a CCD camera Fluorescence mode</td>
</tr>
</tbody>
</table>

**Source:** Bending magnet

**First mirror:** 1.2 meter long Ir and Rh bent mirror

**Polychromator:** Bragg geometry, Si\(_{111}\), Si\(_{311}\)

**High temperature limit:**
- 1100 K under controlled atmosphere for heterogeneous catalysis
- 800 K for high-pressure measurements

**Cryogenic temp. limit:** Down to 2 K for ambient and high pressure conditions

**Pressure:** Up to 100 GPa in quasi hydrostatic conditions

**Magnetic field:** Up to 6T
Future development: double beam XMCD?

Log (I0up/Iup)-log (I0down/Idown)

Quarter wave plate?
Optics: bender mechanical improvements

- Better contact between blade and bender
- Decoupling twisting and bending movements
  \[ \Rightarrow \text{Very small spot size} \]
Zn