School on Synchrotron and FEL Based Methods and their Multi-Disciplinary Applications

19 - 30 March 2012

Time resolved and high pressure science

S. Pascarelli
ESRF (France)
Outline

XAS, XANES, EXAFS, and XMCD

• X-ray Absorption
• X-ray Absorption Fine Structure
• Simple Theoretical Description
• XANES
• Major historical EXAFS breakthroughs
• Examples of applications at ELETTRA
• EXAFS data analysis
• Introduction to XMCD

Energy Dispersive XAS

• X-ray Absorption Spectrometers
• EDXAS
  • Basic principles, historical evolution
  • Examples of applications at ESRF
  • Future opportunities for studies of matter at extremes
  • Probing laser induced extreme states of matter
XAS measures the energy dependence of the x-ray absorption coefficient $\mu(E)$ at and above the absorption edge of a selected element. $\mu(E)$ can be measured two ways:

**Transmission:**
The absorption is measured directly by measuring what is transmitted through the sample:

$$I = I_0 e^{-\mu(E) t}$$

$$\mu(E) t = -\ln (I/I_0)$$

**Fluorescence:**
The re-filling the deep core hole is detected. Typically the fluorescent x-ray is measured.

$$\mu(E) \sim \frac{I_F}{I_0}$$
XAFS beamlines at the ESRF

Energy scanning XAS

• ID12, ID26, ID32, ID22, etc..
• BM23
• CRGs (BM08, BM20, BM30 etc.)

Energy dispersive XAS

• ID24
XAFS beamlines at the ESRF

BM23
- excellent S/N ratio over a large k-range
- large energy range 4.5 - 75 KeV
- versatility
- high automation level

ID24
- small focal spot (~ 5 x 5 μm²)
- fast parallel acquisition (~ 1 msec)
- high flux (~ 10¹³ ph/s/0.1%BW)
Refl-EXAFS station

Reference sample

Experimental station

Vertical focusing double mirror

Monochromator

Bending Magnet

Sample environment:
- HP cell
- cryostat
- catalytic cell
- etc..

$I_2$  $I_1$  $I_0$

42  37 - 40  33  28.5  0
Sample environment:
- HP cell
- catalytic cell
- electromagnet
- etc.
Combining time resolved and extreme conditions XAS

1. Technical Challenges

   Source
   - high brilliance
   - energy tunability

   Optics
   - small focal spot (μm → nm) - stability
   - energy range (50-1000 eV) - stability

   Detection
   - fast acquisition (ms → ps)
   - synchronization

2. Acquisition schemes

   Pump-probe
   - reversible processes
   - sample translation/cycle, ....

   Single-shot
   - non-reversible processes
   - destruction of sample environment
   - limited pump repeatability

3. Energy scanning vs energy dispersive spectroscopy
<table>
<thead>
<tr>
<th></th>
<th><strong>Energy Scanning</strong></th>
<th><strong>Energy Dispersive</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>stability</strong></td>
<td>mechanical movement</td>
<td>no movement of optics during acquisition</td>
</tr>
<tr>
<td><strong>speed</strong></td>
<td>energy points acquired sequentially</td>
<td>all energy points acquired simultaneously</td>
</tr>
<tr>
<td><strong>optical scheme</strong></td>
<td>simple</td>
<td>less simple</td>
</tr>
<tr>
<td><strong>detection de-excitation channels (XRF, XES, RIXS)</strong></td>
<td>straightforward</td>
<td>flux-energy resolution tradeoff</td>
</tr>
<tr>
<td><strong>demands on sample microstruct</strong></td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td><strong>focal spot min</strong></td>
<td>50-100 nm</td>
<td>2-3 µm</td>
</tr>
<tr>
<td><strong>pump-probe</strong></td>
<td>ps/energy point</td>
<td>ps/full spectrum</td>
</tr>
<tr>
<td><strong>single shot</strong></td>
<td>50 - 100 ms/spectrum</td>
<td>1 µs/spectrum at 3(^{rd}) gen</td>
</tr>
</tbody>
</table>
Detection limits for single shot studies on ID24

Edge shifts and XANES features clearly detectable with 50 bunches (3 μs in Uniform mode)

J. Headspith et al., IEEE, 2421 (2007).
Exploiting time resolution: present and future

<table>
<thead>
<tr>
<th>Time scale (s)</th>
<th>$10^0$</th>
<th>$10^{-3}$</th>
<th>$10^{-6}$</th>
<th>$10^{-9}$</th>
<th>$10^{-12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time structure synchrotron</td>
<td>Continuous</td>
<td>Pulsed</td>
<td>Continuous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optimal filling modes</td>
<td>Multibunch</td>
<td>Single bunch</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acquisition mode</td>
<td>film (single shot)</td>
<td>pump-and-probe</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detection</td>
<td>FReLoN</td>
<td>ULTRA</td>
<td>XH</td>
<td>streak</td>
<td></td>
</tr>
<tr>
<td>Application</td>
<td>Heterogeneous catalysis</td>
<td>Kinetics of chemical reactions</td>
<td>Melting at extremes</td>
<td>Shocked matter at local thermal equilibrium</td>
<td>Photochemistry</td>
</tr>
</tbody>
</table>
Energy Dispersive XAS

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• EDXAS
  • Basic principles, historical evolution
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In 1978, a small workshop was held in Osaka on an EXAFS spectrometer to be constructed at the Photon Factory which started construction at that time.

A professor of Tohoku university commented about the necessity of a quick EXAFS spectrometer for time-resolved study of reacting objects.

**1978**

**In the conference room**

No mechanical movement during the measurement

**On the train back to Tokyo**

Focalization by a Laue-case single crystal

Taken from Prof. Matsushita’s talk at 2009 Workshop @ ESRF
A Fast X-Ray Absorption Spectrometer for Use with Synchrotron Radiation

Tadashi Matsushita* and R. Paul Phizackerley

Stanford Synchrotron Radiation Laboratory, Stanford University, SLAC, P.O. Box 4349, Bin 69, Stanford, California 94305, USA

(Received July 6, 1981; accepted for publication August 22, 1981)

A quasi-parallel and polychromatic beam of synchrotron radiation is focused and dispersed by a curved crystal, so that the energy of each ray of the focused beam varies as a function of convergence angle through the focus. The specimen is placed at the focus. By measuring the X-ray intensity distribution across the beam behind the focus, in the presence and absence of the specimen, the absorption spectra of Cu and Ni metal foils were obtained. Using an X-ray film as the detector, a spectrum from a Cu foil was obtained in 0.1 seconds when the SPEAR storage ring at Stanford was operated at 3.1 GeV and 80 mA. The energy resolution is approximately 2.0 eV and the energy range of the spectrum is approximately 1 keV.
EXAFS Spectroscopy of Some Iron(III) Compounds by Use of Dispersive-type In-laboratory X-Ray Spectrometer

Masaharu Nomura, Kiyotaka Asakura, Ukio Kaminaga,† Tadashi Matsushita,† Kazutake Kohra,† and Haruo Kuroda*

Department of Chemistry and Research Center for Spectrochemistry, Faculty of Science,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
†Photon Factory, National Laboratory for High Energy Physics, Oho-Machi, Tsukuba, Ibaraki 305
(Received June 28, 1982)

Fe foil (4 µm thick)
Mo, 20 keV, 25 mA
3h 45 min

FeCl₃·6H₂O
Fe(ClO₄)₃·6H₂O
anhydrous FeCl₃
EDXAS around the world

* pioneers
<table>
<thead>
<tr>
<th>BL</th>
<th>Source</th>
<th>Synch. facility</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>BL-4A</td>
<td>BM</td>
<td>PF</td>
<td>Tsukuba, Japan</td>
</tr>
<tr>
<td>D11</td>
<td>BM</td>
<td>Lure</td>
<td>Orsay, France</td>
</tr>
<tr>
<td>7.4</td>
<td>BM</td>
<td>SRS</td>
<td>Daresbury, UK</td>
</tr>
</tbody>
</table>


Twenty-Five Millisecond Resolution Time-Resolved X-Ray Absorption Spectroscopy in Dispersive Mode

Tadashi Matsushita, Hiroyuki Oyanagi, Satoshi Saigo, Ukyo Kaminaga, Hideki Hashimoto, Hitoshi Kihara, Noboru Yoshida and Masatoshi Fujiwara

Photon Factory, National Laboratory for High Energy Physics, Oho-machi, Tsukuba-gun, Ibaraki 305
Electrotechnical Laboratory, Umezono, Sakura-mura, Niihari-gun, Ibaraki 305
11Department of Physics, Jichi Medical School, Minamikawachi-machi, Kawachi-gun, Tochigi 329-04
111Rigaku Corporation, Matsubara-cho, Akishima, Tokyo 196
*Toray Research Center Inc., Sonoyama, Ohtsu, Shiga 520
**Department of Chemistry, Faculty of Science, Hokkaido University, Kita-ku, Sapporo, Hokkaido 060

(Received May 22, 1986, accepted for publication June 21, 1986)

1983
Pioneering work at BL-4A, D11 and 7.4

Stopped flow chemistry
Heterogeneous catalysis
Electrochemistry
High pressure
X-ray magnetic circular dichroism
EDXAS around the world

- pioneers
- operational
- upcoming
Advances in detection: \( \mu \)-sec resolved XANES

\[
\Delta E \sim -0.5 \text{ eV}
\]

\[
\frac{\partial}{\partial \text{spectrum}} \quad F(a, \text{ u.})
\]

\[
\begin{array}{c}
\text{Exp [8]} \\
\text{from EXAFS fit} \\
\text{Birch Murnagan Fit}
\end{array}
\]

Collaboration with:
F. Occelli and P. Loubeyre, CEA Bruyères-les-Chatel

European Synchrotron Radiation Facility
S. Pascarelli - FEL School, ICTP (Trieste) - March 22, 2012
Polychromator

Vertical focusing mirror

Position sensitive detector

Beamline ID24 @ ESRF

Hagelstein J. Phys. IV France 1997

Pascarelli J. Synchrotron Rad. 2006

5 x 5 μm²
Main areas of applications

Time resolved XAS
- Full energy spectrum acquired simultaneously

Differential XAS
- Monitor subtle changes in XAS exploiting X-ray polarization

Micro XAS
- Extreme conditions
- Structural studies on tiny samples in extreme environments
- 2D mapping
- Full XAS spectrum in each pixel (fluorescence or transmission)

Review paper: Pascarelli PCCP 2010
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- Structure and magnetism in compressed matter
- Geochemistry
- Element selective magnetism at pulsed 30T fields
Metallization and dissociation of diatomic molecules

- Heavier halogens (Br₂, I₂), constitute model systems for the study of simple molecular solids under high pressure
- Metallization and dissociation: Br₂ ~ 60 GPa and 115 GPa [84 GPa IP]
- XRD: Molecular phase stable up to 80 GPa - intramolecular distance rigid

New phase transition at 25 GPa with a loss of molecular character


A. San Miguel et al., PRL 99 015501 (2007)
In the 3d metals, application of pressure leads to the loss of ferromagnetism.

**K-edge XMCD**

- **Fe**
- **Co**
- **Ni**

**Pressure (GPa)**

- 0, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220

**Magnetization ($\mu_B$)**

- 0, 0.5, 1.0, 1.5, 2.0

**Fe**: bcc $\rightarrow$ hcp

**Co**: hcp $\rightarrow$ fcc

**Ni**

- fcc $\rightarrow$ ?

**Iota et al. 2007**

**Ishimatsu et al. 2007**

**our work**

- $I \times \text{DOS} (E_F) > 1$

Stoner (1939)
**Collapse of ferromagnetism in Co**

1. XMCD signal disappears at 120 GPa
2. 80 GPa: onset of local fcc-like atomic config.
3. major differences with Fe case

R. Torchio et al., *PRB 84, 060403R 2011*
1. no structural change observed
2. fcc Ni still ferromagnetic at 200 GPa
3. comparison with DFT calculations
4. expected collapse above 400 GPa

R. Torchio et al., PRL 107, 237202 2011
Structure and magnetism in compressed matter

Geochemistry

Element selective magnetism at pulsed 30T fields
\(\mu\)-XAS 2D mapping


European Synchrotron Radiation Facility

S. Pascarelli - FEL School, ICTP (Trieste) - March 22, 2012
Redox and speciation mapping in the DAC

lack of in situ experiments under relevant P and T conditions

- opens the way to quantitative «in situ» observations of absorber redox & speciation
- allows to quantify P and T gradients & absorber inhomogeneities across the laser heated spot

Effect of spin crossover on Fe partitioning?

How much Fe in PPv?

Valence of Fe in PPv?

Structural decomposition of \((\text{Mg}_{1-x}\text{Fe}_x)_2\text{SiO}_4\) ringwoodite

\[(\text{Mg}_{1-x}\text{Fe}_x)_2\text{SiO}_4 (Rw) \rightarrow (\text{Mg,Fe})\text{O} (Fp) + (\text{Mg,Fe})\text{SiO}_3 (Pv)\]

\[P \sim 24 \text{ GPa}\]
\[T \sim 1600 \text{ K}\]


---

Partitioning of Fe between Pv and Fp

1. T promotes Fe partitioning in Pv, P acts oppositely
2. no major effect of spin crossover on Fe partitioning
3. no appreciable chemical dishomogeneity in lower mantle

Valence of Fe in (Mg,Fe)SiO$_3$ postperovskite phase

\[
(Mg_{1-x}Fe_x)_2SiO_4 \rightarrow \text{Pv} \rightarrow \text{PPv}
\]

- **Al-free Pv** → **Al-bearing Pv**
  - some $Fe^{2+} \rightarrow Fe^{3+}$

- **Pv** → **PPv**
  - no valence change

\[
\begin{align*}
&\text{Pv} \rightarrow \text{PPv} \\
&P > 100 \text{ GPa} \\
&T > 3000 \text{ K}
\end{align*}
\]

\[
\begin{align*}
&(Mg,Fe)O \rightarrow \text{Fp} + (Mg,Fe)SiO_3 \rightarrow \text{Pv} \\
&P \sim 24 \text{ GPa} \\
&T \sim 1600 \text{ K}
\end{align*}
\]

\[
\begin{align*}
&(Mg_{1-x}Fex)_2SiO_4 \rightarrow \text{Rw} \\
&P \sim 24 \text{ GPa} \\
&T \sim 1600 \text{ K}
\end{align*}
\]

D. Andrault et al., EPSL 293, 90-96 (2010)
Partitioning of Fe between perovskite and postperovskite phase

\((\text{Fe,Al})_{19} \, (\text{Mg,Si})_{81} \, \text{O}_3\)

Fe K-edge XANES (ID24)

The PPv phase appears largely depleted in Fe compared to Pv

\[ K_{Fe}^{Pv/PPv} = 4.2 \pm 0.5 \]

D. Andrault et al., EPSL 293, 90 (2010)

X-ray Diffraction (ID27)
- Structure and magnetism in compressed matter
- Geochemistry
- Element selective magnetism at pulsed 30T fields
Ferrimagnetic materials: high fields

- spinel ferrites $PQ_2X_4$: $Fe_3O_4$, $MgFe_2O_4$, $MnO_3$ ...
- rare earth iron garnets $P_3Q_2R_3O_{12}$: $Y_3Fe_5O_{12}$, $Er_3Fe_5O_{12}$, $Yb_3Fe_5O_{12}$
- double perovskites $A_2BB'O_6$: $Ca_2FeReO_6$, $Sr_2FeMoO_6$ ...
- intermetallics $R-T$: $ErCo_2$, $GdNi_2$, $Ho_2Fe_{17}$...
- hexagonal magnetoplumbites $PO\cdot 6Fe_2O_3$: $BaFe_{12}O_{19}$ ...
- ...

High fields are required to break ferrimagnetic correlations

X-ray Magnetic Circular Dichroism allows to address sublattices independently

$$HR = H_0 + \lambda_{RR}M_R - \lambda M_Fe$$

$$H_{Fe} = H_0 - \lambda M_R + \lambda_{FeFe}M_{Fe}$$
Pulsed high magnetic fields at ID24

- compact size
- high repetition rate, 30 T every 12 seconds
- independent sample cryostat 5 K – 300 K


Field pulse and acquisition windows

- fast PSD “Ultra System”: Headspith et al. proc. of NSS-MIC2007
Fe K-edge XMCD in $\text{Er}_3\text{Fe}_5\text{O}_{12}$

Phase diagram (field along 100)

Fe K edge XMCD spectra

Energy (eV)
Fe sublattice magnetization in $\text{Er}_3\text{Fe}_5\text{O}_{12}$

- XMCD amplitude – direct probe of Fe-sublattice magnetization
- Direct observation of spin reorientation in canted phase

C. Strohm et al. *in preparation*
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UPBL11: Time Resolved and Extreme Conditions XAS

- Transfer of EXAFS bl BM29 to BM23
- Re-design of EDXAS bl ID24

Stability → re-design of optics and experimental stations
Focal spot → double branch (3 vs 100 μm) on time-shared basis
Detection → new generation of micro-strip detectors (μs)

Opening dates for public:
- BM23: March 2011
- ID24: May 2012
UPBL11: scientific case

time resolved extreme conditions

heterogeneous catalysis
radiative decay
solution chemistry
microfluidics
photochemistry
recombination
radiative decay
rotational motion

P > 100 GPa; T > 3000 K
melts
local order
electronic structure
earth and planetary science
speciation, oxidation states
partition coefficients
complexation in aqueous fluids

materials science
HP properties of catalysts
synthesis of new materials

P > 100 GPa; T < 10 K
structure and magnetism at HP
magnetism/structure correlation
breakdown of ferromagnetism
local structure

fm atomic displacements
magnetostriction, piezoelectricity
reversible H₂ storage processes
energy-driven magnetic materials

ms cleaner chemical processes
emission free vehicles
new energy resources

μs

ns

ps
Melting of Fe in the DAC

Fiber pumped near infrared laser ($P=110$ W, $\lambda=1070$ nm)

- spherical shape
- size commensurate with laser beam (< 30 µm)

UPBL11: commissioning of laser heating facility

Innokenty Kantor

HP/HT laser setup installed on EDXAS-S for commissioning (Nov 2011)
Electric discharge through a conducting sample: first attempts to probe warm dense Fe

Fe sample: 5μm thick

Confinement layer (CHON)

Diamond windows: 200μm thick

X-rays

Power ramp monitoring

Current: I from 0 to ~12 A in ~20ms.

Warm zone:
Pyrometry

& Fast imaging

sample loss
DAC explosion
First data on Fe

\[ \Delta E \approx -0.5 \text{ eV} \]

\[ \chi(\text{a. u.}) \]

\[ \text{FT}(\chi) \]

\[ a \approx 3.61 \text{ Å} \quad P \approx 7 \text{ GPa} \]

Collaboration with:
F. Occelli and P. Loubeyre, CEA Bruyeres-les-Chatel