The LNLS dispersive XAS (DXAS) beam line

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X-ray Absorption Spectroscopy
Laboratório Nacional de Luz Síncrotron
Outline

• LNLS overview

• DXAS beam line

• Examples
LNLS- National Synchrotron Light Laboratory

Operated by **ABTLuS:**
**Associação Brasileira de Tecnologia de Luz Síncrotron,**
under contract with the Brazilian Ministry of Science and Technology

Population: 3 Million
Economy: Agriculture, Industry, Services (3% of national GNP)
Several Universities, Colleges and Research Institutes (10% of national scientific production)
LNLS Campus

- NMR
- Storage ring
- Electron microscopy
- Microfabrication
Open, multi-disciplinary and multi-user infrastructure for research at the LNLS

- synchrotron light source
- molecular biology
- protein crystallization
- NMR spectroscopy
- mass spectrometry
- electron microscopy
- scanning probe microscopy
- mechanical microfabrication
- chemical syntesis laboratory
- engineering (scientific instrumentation)
Light source layout and parameters

<table>
<thead>
<tr>
<th>LNLS UVX2 Parameters</th>
<th></th>
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<tbody>
<tr>
<td>Operating energy</td>
<td>1.37</td>
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<tr>
<td>Injection energy</td>
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<td>Critical photon energy</td>
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<tr>
<td>Natural emittance</td>
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<td>Circumference</td>
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<td>Straight section free length</td>
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<td>Revolution frequency</td>
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<td>Revolution period</td>
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<td>Harmonic number</td>
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<td>RF frequency</td>
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<tr>
<td>Vertical tune</td>
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<td>Momentum compaction factor</td>
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<td>Horizontal natural chromaticity</td>
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<tr>
<td>Vertical natural chromaticity</td>
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<td>Energy loss per turn</td>
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<td>Number of dipoles</td>
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<tr>
<td>Number of quadrupoles</td>
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<tr>
<td>Number of sextupoles</td>
<td>18</td>
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<tr>
<td>Number of horizontal correctors</td>
<td>18</td>
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<tr>
<td>Number of vertical correctors</td>
<td>12</td>
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<tr>
<td>Number of BPMs</td>
<td>24</td>
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</table>
Beam lines
VUV/Soft X-rays
• 3 in operation
• 1 commissioning
• 1 in construction

Hard X-rays
• 11 em operação
• 1 comissioning.
The LNLS dispersive XAS (DXAS) beam line – G. Azevedo – ESRF EDXAS Workshop, 04-Feb-2009

Tolentino, Cezar (2003)
The LNLS dispersive XAS (DXAS) beam line – G. Azevedo – ESRF EDXAS Workshop, 04-Feb-2009

DXAS Layout

X- Ray Source
Bending Magnet (BM)
Beam Size (Source): 0.25mm (V) × 0.89mm (H)
BM/Monochromator distance = 9.75m

Mirror
800mm-long Rh coated mirror
Bending mechanism ⇒ vertical focused beam ≈ 500μm

Slits
Two sets of water-cooled slits
Si $<111>$ Crystal

Bending mechanism:

LNLS Design – curvature is imposed by independent momenta on crystal extremities

All other rotations – High precision Huber goniometers

Typical vertical size of the focused beam ≈ 150 µm

Energy Range – 4 keV to 14 keV

Main Absorption edges

\[ \textbf{K} \rightarrow \text{Ti, Cr, Mn, Co, Ni, Ge, Fe, Cu, Ga} \]

\[ \textbf{L} \rightarrow \text{Pt, Au, Re, La, TR} \]
Detector

Cryogenically cooled CCD (1300 × 1340 pixels), each pixel ⇒ 20×20µm

GdOS Phosphor screen, optimized for 8KeV ⇒ conversion of the x-ray photons in visible photons

Lens set ⇒ project the phosphor screen image on the CCD with a demagnification factor of 1.75

Data acquisition: image or spectroscopy mode

Minimal acquisition time: 1ms

Typical readout time: 20ms
Experimental station
Beam line Parameters

Dispersive optics

Energy bandwidth

\[ \Delta E = E \cot \theta_B \left[ \frac{L}{R} - \frac{L \sin \theta_B}{p} \right] \]

- Synchrotron radiation source
- Rowland circle
- Focal point (sample position)
- Crystal surface circumference
- Detector

J. C. Cezar, PhD. Thesis – UNICAMP 2003
Energy resolution

Main contributing terms:

- CCD pixel width: $\delta \theta_1$
- Source size: $\delta \theta_2$
- Darwin width: $\Omega_D$

$$\delta \theta = \sqrt{\delta \theta_1^2 + \delta \theta_2^2 + \Omega_D^2}$$

$$\delta E = E \cot \theta \delta \theta$$

values for detector at 2$q$
Flux

Copper K edge - DXAS beam line - July 24, 2002

1 s acquisition (20 x 50 ms)

50 ms acquisition

pixel CCD
Scientific areas

Oversubscribed
25 experiments per year
~10 publications per year
Instrumentation

• Extreme conditions
  - Pressure (DAC´s)
  - Magnetic field (up to 6.5 Tesla)
  - Temperature (10 – 1400K)

• Kinetic studies
  - Furnaces and reactors (gases/liquids)
  - Mass spectrometer
  - Potentiostats & electrochemical cells
6.5T
UHV compatible
Cryo-free

vertical (CF60)
horizontal (CF100)
criostat, furnace, DAC etc...

Cryomagnetics INC.
Examples
Formation of NiO nanoparticles monitored in situ by Dispersive XAS
by Meneses et al.

Sol-Gel route to NiO nanoparticle synthesis:

\[ \text{Gelatin} \xrightarrow{} \text{Destilled Water} (60 \degree\text{C}) \xrightarrow{} \text{Solution} \xrightarrow{} \text{Gel} \xrightarrow{} \text{NiO nanoparticle} \]

250 < T < 300\degree C: Ni linked to aminoacids

T > 300\degree C: amorphous NiO in carbon matrix

Nanoparticle preparation

- Nucleation process
- Intermediate phases/structures
- Disorder x size
- Size control

Tailored properties

Halogen lamp furnace

Figure 1
Schematic of the furnace experimental set-up and components.


12 x 500 W lamps
Temperature range: 200-1000°C
50 x 30 ms frames per spectrum
Heating rate: 5°C/min


Formation of NiO nanoparticles
Ni dispersed in carbon
Ni(OH)$_2$
FEFF 8.0 calculations

C. T. Meneses et al
Depth-dependent chemical and magnetic properties in nanometric CoPt thin films
by Souza-Netto et al

Analysis of CoPt thin films presenting Perpendicular Magnetic Anisotropy (PMA)
Magnetization results

What is the correlation between magnetic and structural properties as a function of sample Thickness?

Grazing Incidence XAS (GIXAS)
Depth-dependent chemical information
Grazing incidence set-up at LNLS beam lines: XAFS and DXAS
The LNLS dispersive XAS (DXAS) beam line – G. Azevedo – ESRF EDXAS Workshop, 04-Feb-2009

GIXAS in dispersive mode

\[ \text{[Gd0.2 nmCo1 nm]} \times 40 / \text{Si.} \]


Figure 8
Intensity asymmetry ratio (a) and X-ray resonant scattering (b) at the Co K edge for the multilayer structure (Co_{001}/Gd_{0.7}Zn_{0.3})_{40} over SiO_{2}. The beam of about 70% circularly polarized photons reaches the sample with a grazing angle of 0.49°. The absorption cross section for Co metallic foil in transmission mode is also shown in (b).
\[ R_{XRMS} = \frac{I^+ - I^-}{I^+ + I^-} \]

- \(0.425^\circ\)
- \(0.475^\circ\)
- \(0.500^\circ\)
- \(0.550^\circ\)

CoPt 230 nm film

(a) Co film with planar anisotropy

(b) Co Pt 230 nm film

FCT / FCC
Order / Disorder
CoPt 50 nm:

FCT (ordem)

CoPt 10 nm:

Epitaxy

MgO Substrate + Pt Buffer

Grãos + termod

MgO Substrate + Pt Buffer
Jahn-Teller distortion in LaMnO$_3$ under pressure

by Ramos et al

LaMnO$_3$

(insulator) → (metal)
Orthorhombic → cubic
Jahn-Teller

\[ \sim 730 \text{ K (room pressure)} \]
\[ \text{RT (32 GPa)} \]

Theory: JT distortion stabilizes insulating phase

Diffraction: JT distortion quenched above 18 GPa
XAFS as a function of pressure

Difficulty: absorption by diamond anvils

FEFF calculations

XAFS as a function of pressure

Difficulty: absorption by diamond anvils

FEFF calculations

Local JT distortion vanishes above 30 GPa
It is closely related to insulator-to-metal transition

\[ \sigma_{JT} = \sqrt{\frac{1}{6} \sum |R_i - R|} \]
Orbital order in $\text{Ba}_2\text{FeReO}_6$

Azimonte et al

Structure x Magnetism: combination of many techniques
- NPD (Neutron diffraction)
- s-XPD (synchrotron powder diffraction)
- XMCD – X-ray absorption

Half-metallic compound (spintronics)
Deviation from Double perovskite Structure:

Tetragonal distortion of the oxygen tetrahedra at low temperatures

Cubic symmetry at high T.
Concomitant magnetic and structural transitions

Tetragonal to cubic perovskite transition
At 309K + Magnetic transition at 304 K

Relative tetragonal distortion

\[(\mu(Fe) - \mu(Re))^2\]

Magneto elastic transition – Crystalline structure compressed along the magnetic moment direction

H=0.9 Tesla
m_{\text{spin}}(\text{Fe}) = 2.8(2) \mu_B
m_{\text{orb}}(\text{Fe}) = 0.04(2) \mu_B
quenched 3d orbital moments

m_{\text{spin}}(\text{Re}) = -0.64(4) \mu_B
m_{\text{orb}}(\text{Re}) = 0.19(1) \mu_B
unquenched 5d orbital moments

Strong L.S coupling in 5d Magnetism of Re

XMCD helps understand diffraction data

Re unquenched orbital moments: Symmetry lowering around Re. Cooperative process bellow ordering temperature due to coupling of orbital and spin degrees of freedom, leading to magnetostructural phase transition