X-Ray Nano-Analysis Activities at the Beamline ID16B

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Acknowledgments

Teams: ID16 A & ID16B
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Marie-Curie ITN NANOWIRING

ESRF
Talk outline

1. A brief historical introduction
2. Beamline Layout
3. End Station
4. Methods
5. Recent Applications
2004: Beamline ID22 & pilot project

Optics hutch

Experimental hutch 1

Experimental hutch 2

"ID22NI"

Microprobe @ 41m
Beam size: 1 x 3.5 μm² (VxH)

Nanoprobe @ 64m - SS
Beam size: 60 x 60 nm² (VxH)

ESRF Upgrade Project

- Nanoscience and Nanotechnology
- Structural and Functional **Biology and Soft Matter**
- Pump-and-Probe Experiments and Time-Resolved Science
- Science at **Extreme Conditions**
- X-ray Imaging

Two complementary nano-focusing projects:

- **Beamline XMAN:**
  - *X*-ray Spectroscopy **Multi-Imaging Analysis*
  - *Evolution of Microprobe EH1* $40 \text{ m} \rightarrow 100 \text{ m}$

- **Beamline SFINX:**
  - *Scanning Fluorescence and Imaging at the Nanoscale using X-rays*
  - *Evolution of Nanoprobe EH2-ID22NI* $64 \text{ m} \rightarrow 200 \text{ m}$
NINA consists of two independently operating beamlines:

- **ID16A-NI**: ultimate nanofocus pink beam for imaging and XRF
- **ID16B-NA**: nanofocus monochromatic beam for spectroscopy

### Nano-Imaging & Nano-Analysis

<table>
<thead>
<tr>
<th></th>
<th>NI</th>
<th>NA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Length</strong></td>
<td>185 meters</td>
<td>165 meters</td>
</tr>
<tr>
<td><strong>Spatial Res.</strong></td>
<td>10 – 100 nm</td>
<td>50 nm - 1 m</td>
</tr>
<tr>
<td><strong>E/E (%)</strong></td>
<td>1</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>Energy range</strong></td>
<td>Discrete 11 – 17 – 33 keV</td>
<td>Scanning 5 → 70 keV</td>
</tr>
<tr>
<td><strong>Main goals</strong></td>
<td>XRF, coherent XRI-2D/3D Cryo environment</td>
<td>XAS, XRD, XRF, XRI-2D/3D in-situ experiments</td>
</tr>
<tr>
<td><strong>Main fields</strong></td>
<td>Biology &amp; Life Sciences Nanotechnology &amp; Nanomedicine</td>
<td>Biology, environmental sciences, geoscience, materials sciences, ...</td>
</tr>
</tbody>
</table>

Common satellite building
Based on a canted undulator solution
Two parallel and independent branches
- Long, canted, high beta beamline – horizontal sec. source
- Additional 16 mrad deflection by multilayer optics

ID16A-NI

NI-branch
Nano-Imaging
- 18.7 mrad

Multilayer Optics
- 2.7 mrad
0 mrad

Revolvers U18.3/U22.8

In-vacuum U26

ID16B-NA
NA-branch
Nano-Analysis
+ 2.7 mrad
# ID16B X-Ray Source

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period [mm]</td>
<td>26</td>
</tr>
<tr>
<td>Length [m]</td>
<td>2.5</td>
</tr>
<tr>
<td>Magnet material</td>
<td>Sm$<em>2$Co$</em>{17}$</td>
</tr>
<tr>
<td>Minimum gap [mm]</td>
<td>6.5</td>
</tr>
<tr>
<td>Peak field at min. gap [T]</td>
<td>0.935</td>
</tr>
<tr>
<td>Deflection parameter at min. gap</td>
<td>2.27</td>
</tr>
<tr>
<td>Fundamental energy [keV]</td>
<td>3.73</td>
</tr>
<tr>
<td>Total power emitted at min. gap (I=0.2 A) [kW]</td>
<td>10.1</td>
</tr>
<tr>
<td>Power density at min. gap (I=0.2 A) [kW/mrad$^2$]</td>
<td>258</td>
</tr>
</tbody>
</table>
- **Vibrations** - wind induced: single storey, aerodynamic building
- **Vibrations** - internal sources: HVAC etc away from golden slab
- **Golden slab**: special attention to thermal uplift (exp. close to edges)
- **Thermal stability**:
  - Satellite building: +/- 0.5 °C
  - Experimental hutch: +/- 0.05 °C
removable wall

BPM Box Including Shutter Special shielding
Stability: combination of material/design choices & control of thermal environment
- Single granite table
ID16B Focusing Optics

- Dynamically bent KB optics
- Multilayer coated for high energies & mostly pink beam operation
- Good efficiency
- Large acceptance (x 2.3) and NA (x 2)
- Working distance 35 mm
- Large bandwidth (ML) 'achromatic' (coated)

<table>
<thead>
<tr>
<th>Coating</th>
<th>Multilayer $[\text{W/B}<em>4\text{C}]</em>{25}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length vert. reflect. mirror $M_v$ (mm)</td>
<td>112</td>
</tr>
<tr>
<td>Length horiz. reflect. mirror $M_h$ (mm)</td>
<td>76</td>
</tr>
<tr>
<td>Useful length $M_v$ (mm)</td>
<td>70</td>
</tr>
<tr>
<td>Useful length $M_h$ (mm)</td>
<td>40</td>
</tr>
<tr>
<td>$p_v$ (m), $q_v$ (m)</td>
<td>165, 0.18</td>
</tr>
<tr>
<td>$p_h$ (m) (with 2$^{\text{nd}}$ source), $q_h$ (m)</td>
<td>125, 0.083</td>
</tr>
<tr>
<td>Working distance from enclosure (mm)</td>
<td>35</td>
</tr>
<tr>
<td>Incident angles (mrad)</td>
<td>2 - 8</td>
</tr>
<tr>
<td>Metrology</td>
<td>Bending</td>
</tr>
</tbody>
</table>
# ID16B Beam Operation Modes

<table>
<thead>
<tr>
<th>Beam Operation Mode</th>
<th>Energy range (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mirror reflected + DCM diffracted beam (\Delta E/E \approx 10^{-4})  (monochromatic - low)</td>
<td>5-33</td>
</tr>
<tr>
<td>DCM diffracted beam (\Delta E/E \approx 10^{-4})  (monochromatic - high)</td>
<td>33-65</td>
</tr>
<tr>
<td>Mirror reflected beam (\Delta E/E \approx 10^{-2})  (pink)</td>
<td>15-33</td>
</tr>
</tbody>
</table>

3 different beams available:
- Pink beam
- White beam
- Mirrors + Mono
- Only Mono

Sample piezo-stage

Source: White beam

Double Deflecting Mirror

Double Crystal Monochromator

Kirkpatrick-Baez mirrors

ID16B Beam Operation Modes
**Estimated ID16B Beam Properties**

**ID16B Source @ High β (FWHM\(_{H \times V}\)):** 940 × 22 μm\(^2\) → Horizontal Secondary Source

\[ s_G = \sum \frac{q}{p} \]

\[ s_{DL} = 0.44 \frac{\lambda}{NA} \]

\[ s = \sqrt{s_G^2 + s_{DL}^2} \]

\[ NA = n \sin \alpha = \frac{w}{2q} \]

<table>
<thead>
<tr>
<th>Beam Operation Mode</th>
<th>(\Delta E/E)</th>
<th>Energy (keV)</th>
<th>Spot Size (nm×nm) (H \times V)</th>
<th>Photon flux (ph/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>monochromatic - low</td>
<td>1.5×10(^{-4})</td>
<td>10</td>
<td>60-460 × 40</td>
<td>1.5×10(^{10}) – 1.4×10(^{11})</td>
</tr>
<tr>
<td>monochromatic - high</td>
<td>2×10(^{-4})</td>
<td>65</td>
<td>35-460 × 40</td>
<td>2.5×10(^{7}) – 3.2×10(^{8})</td>
</tr>
<tr>
<td>pink</td>
<td>1.5×10(^{-2})</td>
<td>17</td>
<td>40 × 40</td>
<td>2×10(^{12})</td>
</tr>
</tbody>
</table>
Multimodal Approach

- X-Ray Fluorescence
- X-Ray Absorption
- X-Ray Diffraction
- XRF-tomo, XRD-tomo
- Magnified Holotomo
- X-Ray Excited Optical L.

Source: White beam

double deflecting mirror

Double Crystal Monochromator

Kirkpatrick-Baez mirrors

Sample piezo-stage
### First tests: 29.6 keV in uniform filling

**Emittance**
- \( H = 4.37 \text{ nm} \)
- \( V = 0.007 \text{ nm} \)

**Energy**
- \( E = 29.6 \text{ keV} \)
- \( \Delta E/E \approx 10^{-2} \)

**Flat Mirror Aperture**
- \( \text{Aperture (HxV) 200x270 } \mu\text{m}^2 \)

### Table 1: Horizontal Primary Slit = 1

<table>
<thead>
<tr>
<th>Horizontal Secondary Slit (mm)</th>
<th>Horiz. Spot Size (nm)</th>
<th>Photon flux @200mA (ph/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>40</td>
<td>( 1.6 \times 10^{11} )</td>
</tr>
<tr>
<td>0.15</td>
<td>89</td>
<td>( 4.3 \times 10^{11} )</td>
</tr>
<tr>
<td>0.25</td>
<td>136</td>
<td>( 7.2 \times 10^{11} )</td>
</tr>
</tbody>
</table>

### Table 2: Horizontal Secondary Slit = 2

<table>
<thead>
<tr>
<th>Horizontal Primary Slit (mm)</th>
<th>Horiz. Spot Size (nm)</th>
<th>Photon flux @200mA (ph/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>45</td>
<td>( 1.1 \times 10^{11} )</td>
</tr>
<tr>
<td>0.10</td>
<td>59</td>
<td>( 2.8 \times 10^{11} )</td>
</tr>
<tr>
<td>0.20</td>
<td>110</td>
<td>( 5.3 \times 10^{11} )</td>
</tr>
</tbody>
</table>
First tests: 29.6 keV in 16 bunch

Emittance
H = 4.37 nm
V = 0.042 nm
E = 29.6 keV
ΔE/E ~ 10^{-2}
Aperture (H×V)
200×270 μm²
S2HG=0.05

Flat Mirror

Bend Mirror
2 × more flux!
First tests: 17.5 keV in 16 bunch

Emittance
H = 4.37 nm
V = 0.042 nm
E = 17.5 keV
\(\Delta E/E \sim 10^{-2}\)
Aperture (H x V) 270x420 \(\mu m^2\)
S2HG=0.05

Flat Mirror

Bend Mirror
2 \(\times\) more flux?
### Preliminary results: 3 elt Si Drift Array

**E=17.5 keV; 40 mm from reference sample: thin film (RF8-200-S2453); Kapton protection cap; Tchiller=18°C; XIA Xmap; Fe K\(_\alpha\); ICR< 100kcps**

<table>
<thead>
<tr>
<th>Peaking time FWHM (eV)</th>
<th>4 μs</th>
<th>1 μs</th>
<th>0.5 μs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Channel 1</strong></td>
<td>148 (135)</td>
<td>183 (152)</td>
<td>270 (240)</td>
</tr>
<tr>
<td><strong>Channel 2</strong></td>
<td>148 (136)</td>
<td>191 (173)</td>
<td>286 (242)</td>
</tr>
<tr>
<td><strong>Channel 3</strong></td>
<td>149 (136)</td>
<td>186 (163)</td>
<td>282 (236)</td>
</tr>
</tbody>
</table>

(SGX)
### ID16B Setup in Progress

<table>
<thead>
<tr>
<th>Round 2014/I</th>
<th>Round 2015/I</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. Nanofocusing optics</strong></td>
<td><strong>1. Nanofocusing optics</strong></td>
</tr>
<tr>
<td>Graded ML coated KB (76x112)</td>
<td>Graded ML coated KB Pd coated KB (112x170)-XAS</td>
</tr>
<tr>
<td>2-8 mrad</td>
<td>2-6 mrad</td>
</tr>
<tr>
<td><strong>2. X-ray fluorescence detectors</strong></td>
<td><strong>2. X-ray fluorescence detectors</strong></td>
</tr>
<tr>
<td>2 x Single Element Si Drift Detectors (2x50mm²) 5-30 keV</td>
<td>2 x 3 Element SDDs (2x3x100mm²) 5-30 keV 8 Element HPGe w/o LN2 (8x50 mm²) 5-65 keV</td>
</tr>
<tr>
<td><strong>3. Sample environments</strong></td>
<td><strong>3. Sample environments</strong></td>
</tr>
<tr>
<td>T=80K; LN2 Biological samples</td>
<td>T=800K</td>
</tr>
<tr>
<td>T=10K; He Materials science samples</td>
<td></td>
</tr>
</tbody>
</table>
**Superconducting YBCO whiskers**

Nano Letters 14, 1583 (2014)

**Daphnia Magna: ecotoxicology**

ABC 405, 6061 (2013)

**Low-enriched U-Mo nuclear fuel**

APL (2014) in press

**Core-shell nanowires**

Nano Letters 14, 1300 (2014)

**Quantum confinement**

Advanced Materials 14, 1300 (2014)

**Solid-oxide fuel cells**

JPS 243, 841 (2013)
Most lithographic techniques: based on photoinduced chemical modifications of photoresist layers → introduction of both a development and an etching stage

Alternative: nanolithography with a hard X-ray nanobeam
Doping change in Bi-2212 superconducting whiskers directly induced by the hard X-ray nanobeam

Pagliero, ... Martinez-Criado, Nano Letters 14, 1583 (2014)
Solid Oxide Fuel Cells (SOFCs)

- High-performance electrochemical devices for energy conversion
- Reduced greenhouse gas
- Made of ceramic materials
- Operated at high T (~800°C)

😊 Very high efficiency
😃 Rapid degradation

Gaps in understanding
- High T related effects: i) Residual stresses, ii) elemental diffusion and iii) microstructure evolution
For the first time, the 3D reconstruction of the 3 phases (pores, Ni and YSZ) on a representative volume was obtained.
Spintronics: Dilute Magnetic Semiconductors

ID22NI: TM doped ZnO Nanowires

Gaps in understanding
Is the ion implantation uniform along the NWs? Does the TM induce structural distortions?
Tetrahedral order recovered after Co implantation on ZnO nanowires along radial and axial directions
Post-growth thermal annealing in Co doped ZnO: effective way to reduce structural defects induced along the NW by the ion implantation process
Carrier Confinement phenomena at hexagon corners probed by hard X-ray nanobeam
MQWs: No improvement in decay time at hexagon corners
GaN: typical long times associated to defects
1D confinement at hexagonal corners: increases electron-hole wavefunction overlapping
Ultrafast recombination processes related to the intriguing quantum size effects

Spatio-temporal regime: several nanometer scale + tens of picosecond
Unintentional impurities & No junction dependent distortion of the local chemical environment around Ga sites
**ID22NI: Phase separation in Nanowires**

Great potential for solar cells, but suffer from defects!

*Single InGaN nanowires grown by MBE: compositional modulation in the axial and radial directions*

Nonuniform chemical distribution accompanied by an structural phase separation.
Thank you for your attention