Advanced Soft X-Ray Microscopy for Nanomaterials Sciences

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- Materials aspects in nanosciences
- Soft X-ray microscopies as valuable tools
- Current achievements and future directions
Key elements to nanoscience

SYNTHESIS

MODELING

ANALYSIS
Why soft X-rays?

access to elements relevant in materials sciences down to fundamental length and time scales
Imaging with soft X-rays
Various X-ray imaging techniques

in real space


in reciprocal space

Suite of X-ray microscopes at ALS

- **PEEM-3 (11.0.1)**
- **STXSM (11.0.2)**
- **STXSM (5.3.2)**
- Coherent/diffractive imaging (9.0.1)
- **XM-2 (2.1)**
- **XM-1 (6.1.2) (operated since 1994)**
Full-field TXMs

ALS


BESSY II

U41

P. Guttmann et al, JOP Conf Ser. 186 012064 (2009)
# From XM-1 to XM-3

<table>
<thead>
<tr>
<th></th>
<th>XM-1</th>
<th>XM-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral resolution</td>
<td>400-600 (elemental mapping)</td>
<td>2000-4000 (true microspectroscopy)</td>
</tr>
<tr>
<td>Photon E-range</td>
<td>500-1200eV</td>
<td>280-2000eV</td>
</tr>
<tr>
<td>Polarization</td>
<td>elliptical polarisation via movable aperture</td>
<td>EPU: circular and linear</td>
</tr>
<tr>
<td>Sample environment</td>
<td>magnetic field &lt;0.2T</td>
<td>magnetic fields 2T</td>
</tr>
<tr>
<td></td>
<td>ambient T</td>
<td>variable T (4-600K)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>variable pressure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>In-situ experiments</td>
</tr>
<tr>
<td>Spatial resolution</td>
<td>25nm (standard)</td>
<td>&lt;15nm (standard)</td>
</tr>
<tr>
<td></td>
<td>10nm (demo)</td>
<td>&lt;&lt;=10nm (demo)</td>
</tr>
<tr>
<td>Time resolution</td>
<td>&lt;100ps</td>
<td>&lt;100ps</td>
</tr>
<tr>
<td>tomography</td>
<td>(yes) limited capabilities</td>
<td>YES, optimized for materials science</td>
</tr>
<tr>
<td>reflection geometry</td>
<td>NO</td>
<td>YES, access to interfaces</td>
</tr>
</tbody>
</table>
Progress in spatial resolution

- **2005**

- **2009**

- **2010**

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Halbach Award 2010

W. Chao, CXRO
**Development of green cements**

**Problem to our environment:** The production of Portland cement is responsible for 5-8% of the CO₂ generation worldwide.

**Challenge:** New cements have to demonstrate long-term stability and durability for over 120 years.

This 2d TXM image seems to show that the “sheet of wheat” have a core which acts as a nucleation point (see arrows)

This assumption is wrong as verified by rotating the sample (done at BESSY II)

Work with Brisard, Levitz and Chae
Colloids in soil science

- Fe is abundant in soils and groundwater aquifers, but occurs in various oxidation states.
- Problem: Too much iron in water used in engineering purposes may cause corrosion.

**XM-1**

- Elemental mapping
  - 704eV
  - 711eV

- Stereomicroscopy
  - $\Theta = 15^\circ$


But where exactly are the elements and what oxidation state are they in?
Atomically controlled synthesis of Mono and Bimetallic clusters in catalysis

Core-shell nanoparticles and Nanostructured Mesoporous Materials (NMMs) offer a great opportunity to modulate the properties of materials. Delineating the size, size distribution, shape, core-shell dependent electronic and geometric properties of nanomaterials allows to tune specific properties such as magnetism, heat capacity, optical, photoconductivity and charge transfer, electronic, melting point, catalytic by varying the size/shape of the nanomaterials.

NMMs is a new class of catalysts and are one of the key class of materials investigated by the DOE funded EFRC at LSU.

Soft X-ray nanotomography is an essential tool to characterize these 3-dim structures.
Imaging buried interfaces

Standing-wave depth resolution

EPU Polarized soft X-rays

Applied magnetic field

lateral resolution

Micro zone plate

Soft x-ray sensitive CCD

Combing in a unique way high lateral resolution with depth resolution \(\Rightarrow\) access to magnetic interface

Goal: combining with time resolution to study the dynamics at interfaces
**Calorimetry**: powerful technique, hard to do on thin films!

- Membrane-based micro/nanocalorimetry, calorimeter-on-a-chip; 0.3-800K, 0-8T; ~2% accuracy for <1μg, 20 nm thick films
- Electron, phonon, magnon density of states; crystal field levels; phase transitions; entropy, enthalpy
- Basis for proposed integrated *in situ* ALS heater/sample imaging stage

Example: high anisotropy Fe$_{38}$Rh$_{62}$ nanoparticles produced from amorphous alloy by annealing

GOAL: image DURING heating to understand the evolution
Longer term goal: measure thermodynamics of process

courtesy T. Suzuki/H. Yu Yu Ko
Mapping spin and orbital moments

Magnetic-circular-dichroism microspectroscopy at the spin reorientation transition in Ni(001) films

W. Kach, J. Gilles, and S. S. Kang
Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

S. Imada and S. Suga
Osaka University, Graduate School of Engineering Science, 1-3 Machikaneyama, Toyonaka 560-8531, Japan

J. Kirschner
Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle
(Received 10 November 1999)

The spin reorientation transition in fcc Co-Ni-Cu(001) epitaxial ultrathin films as a film thickness is studied by the combination of photoelectron emission microspectroscopic circular-dichroism spectroscopy at the Ni L\textsubscript{3,2} edge. This microspectroscopic technique provides quantitative information about the Ni magnetic properties on a submicrometer scale. In the thickness range of 1.4–3.5 atomic monolayers (ML) Co and 11–14 ML Ni show the transition, which was reported as a function of both Co and Ni thicknesses. Increasing the Co thickness or decreasing the Ni thickness leads to a switching of the magnetic easy axis from [001] out-of-plane to [110] in-plane effective Ni spin moment similar to the bulk magnetic moment. The transition is observed by the Ni ratio at ~10 ML Ni thickness shows distinctly different values for out-of-plane magnetization (0.88±0.005) and (0.65±0.005). This is discussed in terms of the connection to the Ni magnetocrystalline anisotropy density of the perpendicular magnetization increases towards the spin reorientation.
Heusler alloys: Shape memory phase transitions in Ni$_2$MnGa

Heusler compounds are a plethora of many spintronics and multiferroic applications incl. MTJs and spin momentum transfer devices.

- Martensitic phase transition between cubic and tetragonal phase
- Magnetic easy axis coupled to tetragonal distortion $\Rightarrow$ ferromagnetically driven, ferroelastic actuation
- Anisotropy vs. orbital moments in Heusler alloys
Fast dynamics in nanostructures

Magnetic vortices
- Chirality in-plane circular domain structure
- Polarity out-of-plane component of magnetization

Z. Qiu, UCB


F. Marcia, NYU

A. Kent, Nature Mat, 6 399 (2007)

P. Fischer, S. Kasai, A. Thiaville et al., in preparation (2010)

S.-K. Kim, SNU

S.-K. Kim et al. APL 92, 022509 (2008)

Courtesy S.-K. Kim

Vortex-RAM
Stroboscopic pump-probe setup for time resolved soft X-ray microscopy

- j=1.3×10^{11} A/m^2
- 10^{8-9} pump-probe events/image

- perfect repeatability of the dynamics required
- no access to non-deterministic components e.g. spin fluctuations

Deriving spin polarisation of currents $P$

Permalloy ($\text{Fe}_{80}\text{Ni}_{20}$)
- $t=40$ nm
- $f=220$ MHz
- $\Delta t=0...9$ ns

- CW rotation $\Rightarrow$ polarity = -1
- gyration radius $R\sim80$ nm

Solving Thiele eqn with STT for $u$

$$\vec{G} \times \vec{v} + \alpha D\vec{v} + k\vec{X} - \vec{G} \times \vec{u} = 0$$


- Measuring $R(\omega) \Rightarrow P=0.67\pm0.15$
The road to spin currents

Moore’s law

Beyond CMOS

Magnetic Storage
HDD, MRAM controlled by Magnetic field

Magnetic Logic (ML)
STT MRAM, DW spin-polarized charge current

High Integration ML Circuits
control by Electric field
manipulate magnetization, transport, with gate voltage

pure Spin-currents
spin transfer and logic with pure spin currents

Courtesy C. Chappert
Future goal: imaging at the fsec scale

- soft X-ray source
  - fsec pulse length
  - variable polarization
  - high photons/pulse

- pump stimulus

snapshot images of fs dynamics with nanometer spatial resolution
Agenda

10:00  P. Fischer (CXRO/LBNL)  “Overview of recent advances and future opportunities in soft X-ray microscopy”
10:30  A. Hoffmann (ANL)  “New Insights into Spin Relaxation from Pure Spin Currents”
11:00  S.-K. Kim (Seoul Natl. U)  “Soft x-ray microscopy study of vortex dynamics in soft magnetic dots at XM-1”
11:30  F. Marcia (NYU)  “Spin-wave interference patterns created by spin-torque oscillators”
12:00  LUNCH
13:15  K. Jenkins (ALS/LBNL)  “Design and application of multifunctional manganese intermetallics”
13:45  C. Baldasseroni (UCB)  “Development of a membrane based nanocalorimeter as an X-ray transparent heater stage”
14:15  C.S. Fadley (LBNL/UCD)  “Adding depth resolution to soft x-ray photoelectron microscopy with standing-wave excitation: applications to spintronic nanostructures”
14:45  Q. Qiu (UCB)  “Microscopy study of magnetic nanostructures using X-rays”
15:15  BREAK
15:35  C. Kumar (LSU)  “Design and Engineering of Core-shell Magnetic Nanomaterials – Current Challenges”
16:05  J. Thieme (NSLSII/BNL)  “Anthropogenic and natural nanoparticles in the environment – dynamics and interactions”
16:35  R. Chae (UCB)  “Probing the nanostructure and morphology of cementitious and pozzalonic materials using x-rays”
17:05  W. Chao (CXRO/LBNL)  “Ultrahigh Resolution Soft X-ray Zone Plate Microscopy at ALS”
17:35  Adjourn