Synchrotron Radiation Spectroscopies on Solids, Surfaces, and Interfaces

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Main argument of the course:
Characterization and analysis of solids and surfaces with Synchrotron Radiation

1. Basics of Synchrotron Radiation (why, what, where, who)

   Beamlines, Devices
   Material Science and SR

2. Electron Spectroscopies with X-rays INTENSITY OF SR

   Interaction of radiation with matter
   Absorption and Photoemission (bulk and surface)
   Applications to Model Systems
3. Polarization dependent Spectroscopies SYMMETRY OF SR

Chirality and Dichroism
Measure and analysis of Spin
Nanoscience and magnetism with SR
Hot topics in Low dimensional Magnetism

4. Beyond the surface (UPS, XPS, HX-PES) TUNABILITY OF SR

Analysis of Correlated systems with SR
Surface sensitivity: advantages and problems
Volume sensitive photoemission
Objective:

Design, prepare, ‘virtually perform’ a specific experiment at SR source

1) Subject of the experiment
   Electronic, Structural, Chemical, Magnetic properties of a solid

2) Choice:
   Synchrotron source, beamline, spectroscopy, experimental setup

3) Preparation:
   Samples, Parameters, Environmental Conditions

4) Measurements and Analysis

  Tutorials, Seminars, Practicals on data analysis
Les installations de RS en 1997

Asie + Amérique du Sud : ~ 10
Amerique du Nord : ~ 20
Europe : ~ 20  Japon : ~ 20
European Synchrotron Radiation Facility (ESRF)
Grenoble, France
Canadian Light Source Inc.
University of Saskatchewan
101 Perimeter Road
Saskatoon,
Saskatchewan S7N 0X4

www.lightsource.ca
Homework n. 1

Find and list main differences
www.lightsources.org

SOLEIL, Paris, France

Spring8,
Hyogo, Japan
As the speed of the particle approaches the speed of light, the radiation pattern is distorted by relativistic effects and changes to a narrow cone of radiation, called Synchrotron Radiation.

A charged particle constrained to move in curved path experiences a centripetal acceleration. Due to this acceleration, the particle radiates energy according to Maxwell equations.

As the speed of the particle approaches the speed of light, the radiation pattern is distorted by relativistic effects and changes to a narrow cone of radiation, called Synchrotron Radiation.

Lesson II, next Tuesday. Production of Synchrotron Radiation
Production of Synchrotron Radiation: relativistic electrons

Frame moving with electrons

Lorentz Transformation

Laboratory frame of reference

Synchrotron radiation

$$\gamma = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} = \frac{1}{\sqrt{1 - \beta^2}} ; \quad \beta = \frac{v}{c}$$

$$E_e = \gamma mc^2, \quad p = \gamma mv$$

$$\gamma = \frac{E_e}{mc^2} = 1957 \, E_e \text{(GeV)}$$

$$\hbar \omega \cdot \lambda = 1239.842 \text{ eV} \cdot \text{nm}$$

$$1 \text{ watt} \Rightarrow 5.034 \times 10^{15} \lambda \text{[nm]} \frac{\text{photons}}{\text{s}}$$

Homework n. 2

Only electrons radiate?
What about ions? Positrons?
Basics of Synchrotron Radiation 1 (a bit of history)

X-Ray dates [http://xdb.lbl.gov/Section2/Sec_2-2.html](http://xdb.lbl.gov/Section2/Sec_2-2.html)

1909: Barkla and Sadler discover characteristic x-ray radiation (1917 Nobel Prize, Barkla)
1912: von Laue, Friedrich, and Knipping observe x-ray diffraction (1914 Nobel Prize, von Laue)
1913: Bragg, father and son, build an x-ray spectrometer (1915 Nobel Prize)
1913: Moseley develops quantitative x-ray spectroscopy and Moseley’s Law
1916: Siegbahn and Stenstrom observe emission satellites (1924 Nobel Prize, Siegbahn)
1921: Wentzel observes two-electron excitations
1922: Meitner discovers Auger electrons
1924: Lindh and Lundquist resolve chemical shifts
1927: Coster and Druyvesteyn observe valence-core multiplets
1931: Johann develops bent-crystal spectroscopy
Basics of Synchrotron Radiation 2

http://www.lightsources.org/cms/ In section history

>1920 Interest in the radiation as an energy-loss mechanism

1930-40 Betatron, i.e. X-rays production via electron accelerators

1940-41 Kerst (Univ. Illinois) first 2.3 MeV betatron
   General Electrics

1944 Ivanenko and Pomeranchuk (USSR), calculations of energy losses due to radiating electrons

1945 Schwinger (US), theory (non-relativistic) on dipole Radiation of circular trajectories (not published)
   1965 Nobel Prize for relativistic electrodynamics

1949 Sokolov and Tersov (USSR) quantum calculation

However these early betatrons (General Electrics) did not have transparent vacuum tubes.
24 April 1947, H. Pollock, R. Langmuir, F. Elder and A. Gurewitsch saw a gleam of bluish-white light emerging from the transparent vacuum tube of their new 70 MeV electron synchrotron at General Electric's Research Laboratory, Schenectady, New York. Synchrotron radiation had been seen.

First visible light for machine testing NSLS (US), 1982.

Homework 3
Three Generations of Synchrotrons

1) Parasitic
2) Storage Rings
3) Dedicated Sources
What about fourth generation?
Why Synchrotron Radiation? 1

How Bright Is the Advanced Light Source?

- ALS Undulator
- ALS Bend Magnet

Brightness (photons/sec/mm²/mrad²/0.1% BW):

- $10^{20}$
- $10^{19}$
- $10^{18}$
- $10^{16}$
- $10^{15}$
- $10^{14}$
- $10^{13}$
- $10^{12}$
- $10^{11}$
- $10^{10}$
- $10^{9}$
- $10^{8}$
- $10^{7}$
- $10^{6}$
- $10^{5}$
- $10^{4}$
- $10^{3}$
- $10^{2}$

(www.coe.berkeley.edu/AST/sxreuv)
**Why Synchrotron Radiation? 2**

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Accelerator-based Light Sources</th>
<th>Common Sources</th>
<th>Frequency (waves per second)</th>
<th>Energy of One Photon (electron volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radio Waves</td>
<td>AM Radio</td>
<td>People</td>
<td>$10^6$</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>Infrared</td>
<td>FM Radio</td>
<td>Light Bulb</td>
<td>$10^7$</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>Ultraviolet</td>
<td>Microwave Oven</td>
<td>UV Lamp</td>
<td>$10^8$</td>
<td>$10^{-7}$</td>
</tr>
<tr>
<td>Visible</td>
<td>Radar</td>
<td>X-ray Machine</td>
<td>$10^9$</td>
<td>$10^{-6}$</td>
</tr>
<tr>
<td>“Hard” X Rays</td>
<td>“Soft” X Rays</td>
<td>Radioactive Elements</td>
<td>$10^{10}$</td>
<td>$10^{-5}$</td>
</tr>
<tr>
<td>Gamma Rays</td>
<td>Terahertz</td>
<td><strong>Duality Particle-waves</strong></td>
<td>$10^{11}$</td>
<td><strong>$10^{-4}$</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>Extremely broad spectral range</strong></td>
<td>$10^{12}$</td>
<td><strong>$10^{-3}$</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>Vision of the ‘invisible’</strong></td>
<td>$10^{13}$</td>
<td><strong>$10^{-2}$</strong></td>
</tr>
</tbody>
</table>
Characteristics of Synchrotron Radiation

- Tunable Energy (Element Selective)
- High Intensity
- Time Structure
- Polarization
- Coherence
- Focalisation
Why Synchrotron Radiation? Facilities for users

Costs, average 1000/4000 euro/hour
Experiments have time limit, fixed time window

- 70% beamtime open to external users
- Program committee, external members
- Annual Budget: 30/200 M€
- 700/2000 users/yrs
- 50% users from abroad
- Staff: 400 persons
- 24/24 h, >5000 hrs/yr

1. electron gun
2. linac
3. booster ring
4. storage ring
5. beamline
6. end station
Science with Light Sources

Spectroscopy  Structure

Valence Electrons  Core Electrons

Photon Energy

10eV  100eV  1keV  10keV

Wavelength

100nm  10nm  1nm  1Å

Lithography  Nanostructures  Proteomics

Protein Crystallography

Z. Hussain, UCB lecture, 2007

Adopted from: Franz Himpsel, CMMP ‘07
What experiment at Synchrotron Radiation?

**Electron Spectroscopies** (photon in – electron out)

- **Photon (probe mode):**
  - Energy
  - Polarisation

- **Electron (detection mode):**
  - Energy
  - Spin
  - Angle
Photons Interaction

Incident photon interacts with electrons
Core and Valence

- Photon is
  - Adsorbed
  - Elastic Scattered
  - Inelastic Scattered

- Electron is
  - Emitted
  - Excited
  - Dexcitated

Cross Sections

- Photoelectric
- Elastic Scattering (Rayleigh)
- Inelastic Scattering (Compton)

Stöhr, NEXAPS spectroscopy

Below 100 keV
Photoelectric cross section dominates
Spectroscopy

A. Nilsson, SSRL and Stockholm Univ.
Photon sources and insertion devices

(http://www.coe.berkeley.edu/AST/srms)

Lesson II and III, next Thursday. Bending Magnets, Undulators, Wigglers
Beamline: from the source to the sample

(http://www.coe.berkeley.edu/AST/srms)

X-ray optics

Energy selection
Energy resolution vs. flux
Focusing
Beamlines and scientific activity

**Materials science**

- **ALOISA**: structure of surfaces
- **McX**: atomic structure of materials, characterization of new compounds
- **Gas Phase Photoemission**: atoms, molecules, ions
- **SYRMEP**: medical physics; absorption and phase contrast radiography imaging
- **XRD1 Protein Crystallography**: microfabrication: manufacturing of micromechanical components by means of deep-etch lithography (LIGA process)
- **XAFS**: local atomic structure
- **XMOSS**: electronic valence states of solids and surfaces
- **LILIT**: lithography, microfabrication of electronic components
- **BACH**: studies of electronic structure and magnetic properties of solids by circularly polarized light absorption and scattering
- **APE**: photoemission studies of electronic structure and magnetic properties of solids and surfaces
- **Microfabrication**: manufacturing of micromechanical components by means of deep-etch lithography (LIGA process)
- **VUV Photoemission**: surfaces and interfaces of metals and semiconductors
- **Circularly polarized light**: magnetic materials, thin films for memories, multilayers; dichroism of organic molecules
- **SAXS Small-Angle Scattering**: polymers, gels, natural and artificial fibers, cell membranes, biological tissues
- **Nanospectroscopy**: multitechnical surface analysis, chemical mapping with lateral resolution of ≈10 nm
- **FEL**: VUV free electron laser
- **VUV Photoemission**: surfaces and interfaces of metals and semiconductors
- **Elastic VUV scattering**: collective excitations of liquids, amorphous and disordered systems, relaxation and diffusion in biological systems
- **Spectromicroscopy**: electronic structure of surfaces on a submicron scale
- **SuperESCA**: time-resolved studies of surface processes, growth, reconstruction, catalysis
- **ESCA Microscopy**: mapping of surface chemical species with spatial resolution of ≈100 nm
- **Electron beam profile monitor**
- **Beamlines and scientific activity**

<table>
<thead>
<tr>
<th>Beamlines</th>
<th>Construction</th>
<th>Commissioning</th>
<th>Operational</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bend magnet beamlines</td>
<td></td>
<td></td>
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<tr>
<td>Insertion device beamlines</td>
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</tbody>
</table>

AS: 6.1.00
Beamlines and scientific activity

Plane Grating Monochromator (PGM)

Pre-focusing Mirror

Grating

Exit Slit

Re-focusing mirror

Sample

Photon Source (Undulator)

Mirror
Science with Light Sources

- Spectroscopy
- Structure

- Valence Electrons
- Core Electrons

Photon Energy
- 10eV
- 100eV
- 1keV
- 10keV

Wavelength
- 100nm
- 10nm
- 1nm
- 1Å

Lithography
- Nanostructures
- Proteomics
- Protein Crystallography

Adopted from: Franz Himpsel, CMMP '07

Z. Hussain, UCB lecture, 2007
Example 1: Protein Crystallography  
Baton Rouge CAMD beamline (http://www.camd.lsu.edu/)

STEP 1. Background
Revealing the structure of a protein that the Venezuelan Equine Encephalitis (VEE) virus requires for replication. VEE is a mosquito-borne virus found in Central and South America, and southern Texas. The virus was developed into a biological weapon during the Cold War.

STEP 2. Scope of the experiment
Developing an inhibitor of nsP2 protease to prevent the virus from replicating and causing encephalitis.

STEP 3. Preparation and Results
Dr. A. Russo, (Univ. of Texas at Galveston (UTMB), solved the structure of a protein called nsP2 protease. It is an enzyme that divides a large viral protein into smaller segments at specific locations. Only the smaller segments are active for the replication of the virus.
Example 2: Medical Diagnostic
(Syrmep medical beamline (ELETTRA-Italy), www.elettra.trieste.it)

Metastases formation
Increased details with image processing with SR
Earlier diagnose possible

Figure 1. DEI images of a preserved mouse liver. The first (a) shows a radiogram taken with no analyser crystal. This would be similar to, but somewhat better than an image taken with a conventional x-ray generator / film system. The next (b) shows the image taken with the analyser crystal at the peak of its reflectivity curve. Finally image (c) shows an image processed to show only the refraction changes.

Images of mouse leg

Conventional source  Synchrotron source
Example 3: Biology and Paleontology
(ID19 High-resolution Diffraction Topography Beamline, ESRF, France, www.esrf.fr)

STEP 1. Background
Origin of complex animals with symmetry in a central plane (bilaterian). Embryonic development?

STEP 2. Scope of the experiment
To investigate the internal structures of fossilised embryos from China in a non-destructive manner

STEP 3. Results
Striking resemblance between the cellular cleavage pattern in the fossil embryos and that of modern polar lobe-forming embryos (580 millions years ago). This is 40 million years earlier than previously thought.


Chinese embryo. Different colours correspond to each of the 3 embryonic cells (blastomeres). Calculation of volume of each blastomere shows that the blue one is twice the volume of the others, strengthening the polar-lobe formation interpretation.
Science with Light Sources

Spectroscopy  Structure

Valence Electrons  Core Electrons

Photon Energy
10eV  100eV  1keV  10keV

Wave-length
100nm  10nm  1nm  1Å

Lithography  Nanostructures  Proteomics

Protein Crystallography

Adopted from: Franz Himpsel. CMMP ‘07

Z. Hussain, UCB lecture, 2007
Example 4: Production of micro-nano objects
(Deep X-ray Litography beamline (ELETTRA-Italy), www.elettra.trieste.it)

LIGA process

SEM images after LIGA process
PMMA structures
Example 4: Production of micro-nano objects
(Deep X-ray Litography beamline (ELETTRA-Italy), www.elettra.trieste.it)
Science with Light Sources

Spectroscopy

Structure

Valence Electrons

Core Electrons

Photon Energy

10eV

100eV

1keV

10keV

Wave-length

100nm

10nm

1nm

1Å

Lithography

Nanostructures

Proteomics

Protein Crystallography

Adopted from: Franz Himpsel, CMMP ‘07

Z. Hussain, UCB lecture, 2007
Part 3 and Part 4. Spectroscopy: NANO = Lithography + Spectroscopy + Focalisation of SR

Aim = Study of the collective vs. local properties in laterally confined systems

Diameter $\sim 420\text{nm}$  Period $\sim 1\text{ micron}$

Nickel

Silicon Nitride

Co dots on GaAs(100)

Diameter 530 nm
Part 3 and Part 4. Spectroscopy:
Photoemission (Regimes of Photoemission, UPS, XPS…)

1) High Energy Resolution

1 – 10 meV @ Kinetic Energy < 50 eV

~ 100 meV @ Kinetic Energy > 500 eV

2) \( E = E(k) \)

Homework n. 4
Regimes of Photoemission
UPS, XPS ??
Band structure via Photoemission

\[ E_{\text{Band}} = \frac{1}{2} m v^2 \]
\[ = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \]

E. Rotenberg (ALS)
The Fermi Surface

Brillouin Zone Boundary

E_F - Fermi Level

1-dimension

2-dimension

3-dimension

Eli Rotenberg

Angular Resolved PES

Cu(111) surface state

Matrix Element + Polarization dep.

in the crystal reflection plane

not in the crystal reflection plane
FERMI SURFACE MAPPING
Fe(001) single crystal

40 eV step
25 meV
2D (and < 2D…) Surface science and Magnetism

What kind of control is mandatory?

Growth
Defects/Roughness
Interfacial effects
Magnetic coupling
Relaxation/Expansion/Contraction

Sample Prep. +

Chemical Sensitivity

Probe \( \text{Measure} \)

M = M (H, T)
Spin + Time + Lateral Res.

IDEAL
REAL
Part 3 and Part 4. **Interface and growth control.**
Model systems: Epitaxial AFM/FM interface

**Frustration, Interface and Proximity Effects**

- Phenomenon poorly understood
- Interface effects dominate
- Need element-specific probes
- Growth of ideal structures - epitaxy
- Technology

![Diagram showing AFM/FM interface and related phenomena](image-url)
Electron Spectroscopy with SR = CONTROL

Variable polarization photons 150-1200 eV

Users’ docking ports

Load-lock

Sample preparation

Variable polarization photons 8-120 eV

APE-HE

Distribution center

Sample growth and prep.

STM

XPS vs. thickness in wedge sample

S segregation on Fe(100)

Fe(100) Fermi surface
Useful References

http://www.lightsources.org/cms/

http://www.iucr.org/cww-top/his.sync50.html

http://xdb.lbl.gov/Section2/Sec_2-2.html (x-ray data booklet)

Book and review articles

1) Soft X-Rays and Extreme Ultraviolet Radiation
(www.coe.berkeley.edu/AST/sxreuv)

