Introduction to Synchrotron X-ray Scattering Techniques

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1. Why do x-ray scattering?
2. Basics of an x-ray scattering experiment
3. SSRL scattering beamlines
4. Some examples
   - SAXS: porous films
   - Powder: Pd nanoparticles
   - Textured films: ZnO nanostructures
5. Summary
Why do SR X-ray scattering?

- Materials properties are caused or affected by their physical structure and morphology
- Improve your materials by understanding the structure.

- Phase identification & quantify
- Where are the atoms: Atomic or molecular arrangement, crystal & surface structure
- Strain, lattice parameters (unit cell size)
- Grain/crystallite size (diffraction)
- Pore/particle size (SAXS)
- Other defects & disorder (faults, positional disorder)
- Crystallite orientation or texture
SR Scattering Experiment

sample

monochromator
- double crystal
- Si(111) or Si(220)
- LN or water cooled
- selects wavelength

slits (horz or vert)
- variable aperture
- define beam shape and acceptance

M0 mirror
- cylindrical or toroidal
- Rhodium-coated silicon
- harmonic rejection, power filter, collimating or focusing

variable aperture
define beam shape and acceptance

beam

source

Area detector

Point detector

Q = k' - k

collect I(Q)

All you care about is Q
SR Scattering Experiment

Area detector

Point detector

Diffraction: peaks

Scattering: the rest

$Q = k' - k$

All you care about is $Q$

At SSRL:

- Area detector: 11-3
- Point detectors: 2-1, 7-2, 10-2
- SAXS: 1-4
# SR Scattering Experiment

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SR Scattering Experiment

Area detector (11-3)

Advantages
- Fast measurement
- Collect whole pattern

Disadvantages
- Fixed wavelength
- Low resolution
- Peak shape & position inaccurate
- Weak peaks difficult

Used for
- Texture (crystallite orientation)
- Real time experiments (electrochemistry, stress-strain)
- Polycrystalline, small grains
- Thin films

$2\theta = \text{scattering angle}$

$Q = \left(\frac{4\pi}{\lambda}\right) \sin \theta$
SR Scattering Experiment

Area detector (1-5) - clone of 11-3

Pil Sung Jo, graduate student in the Materials Sciences department of Stanford, setting up diffraction experiment on organic semiconductors

Used for
- Texture (crystallite orientation)
- Thin films

Advantages
- Fast measurement
- Collect whole pattern

Disadvantages
- Low resolution
- Inaccurate peak shape/position
- Weak peaks difficult

Goal: Easy, seamless access for students from universities when research requires higher intensity & resolution than laboratory sources.

Phase I: Reconfigured bending magnet for thin film x-ray diffraction. Stanford Nanocharacterization Laboratory will pilot access.
SR Scattering Experiment

Point detector (2-1)

Advantages
- High resolution
- Accurate peak position & shape
- Weak peaks
- Variable energy
- Reflectivity

Disadvantages
- Slow
- Only 2 degrees of motion ($\theta, 2\theta$)

Used for
- Powders
- Phase determination
- Reflectivity
- Anomalous diffraction
- $\theta$-2$\theta$ measurements

$2\theta = \text{scattering angle}$
$Q = (4\pi/\lambda) \sin \theta$
SR Scattering Experiment

Point detector (7-2/ 10-2)

Advantages
- High resolution
- Accurate peak position & shape
- Weak peaks
- Variable energy
- 4 degrees of motion (θ, 2θ, χ, φ)

Disadvantages
- Slow
- Complicated
- Can be difficult to find peaks

Used for
- Single crystals
- Grazing-incidence
- Anomalous diffraction
- Thin films
- Surface studies

\[2\theta = \text{scattering angle}\]
\[Q = (4\pi/\lambda) \sin \theta\]
SR Scattering Experiment

Point detector (7-2/10-2)

diffracted x-rays

incident x-rays

sample

2θ
Types of scattering experiments

- **Small Angle X-ray Scattering (SAXS)**
  - probes structures 1-100 nm
- **Powder Diffraction, including in-situ**
  - random or isotropic; nanoparticles
  - poor crystalline order
- **Thin Films: random, textured, epitaxial**
  - wide variety
- **Surface Scattering/monolayers**
  - atomic structure at surface or interface

Fe oxide
iron metal
Lengths Accessed by Probes

USAXS  SAXS  XRD

Graph showing the lengths accessed by different probes: USAXS, SAXS, and XRD, with scales ranging from 10^5 to 10^1 Å and corresponding visual representations.
Summary: SR Scattering

**SR Scattering:**
- **Q** is important variable: measure $I(Q)$
- choose $Q$ to match length scale
- variety of materials

**What can we learn:**
- Phase identification & quantify
- Where are the atoms: crystal & surface structure
- Strain, lattice parameters
- Grain/crystallite size
- Pore/particle size
- Other defects & disorder
- Crystallite orientation or texture
Small Angle Scattering

\[ Q = k' - k \]

\[ |Q| = (4\pi/\lambda)\sin \theta \]

- Measure \( I(Q) \) with \( Q \sim 0.0001 \text{–} 1 \text{ Å}^{-1} \)
- Scattering from 1-100 nm density inhomogeneities

**APS 15-ID-D USAXS**
Small Angle Scattering

Scattering from density inhomogeneities with sizes 1-100 nm

- nanoparticles (catalysts, bio-oxides, geo-oxides)
- nanoporous materials
- co-polymers
- dendimers
- supramolecular assemblies
- micelles
- colloids
- metallic glasses
Small Angle Scattering

Hexagonal packed cylinders

Isolated particles or pores with diameter D

- Need large Q range:
  \[ \frac{1}{D} \leq Q \leq \frac{10}{D} \]
Example 1: Nanoporous Films

Matrix: Methyl Silsesquioxane (MSSQ), \( \text{CH}_3\text{SiO}_{1.5} \)

Porogen (thermally labile polymer): copolymer poly(methyl methacrylate-co-dimethylaminoethyl methacrylate) or P(MMA-co-DMAEMA)

1. Spin coat MSSQ/Porogen solution

2. Heat to 450°C, at 5°C/min under argon

\[ \Delta \text{ Argon} \]

MSSQ crosslinks at 200°C
Poragen fully degrades at 400°C

3. Cool to room temperature

References:
Nanoporous Films: SAXS Results

Find:
- reasonably small pores (good)
- broad distribution of pore sizes (bad)
- size increases with loading => agglomeration (bad)

Goal: obtain representative real space picture (correct size scale and extent of interconnection)

Approximations:
- morphology is “disordered” or random with no preferred direction
- morphology described by cosine waves:
  - with random phase and direction
  - non-random distribution of wavelengths (from SAXS)

Summary: SAXS

- Isolated Particles/Pores (not ordered)
  - Obtain average size & particle/pore size distribution (need large Q range)

- (More) Ordered Structures
  - particle/pore spacing and morphology

- Dense Network of Pores/Particles
  - Obtain representative morphology
  - Good for interconnected & bicontinuous morphologies

*John Pople, up next!*
Example 2: Nanoparticles

Motivation:

- Pd absorbs hydrogen at an atomic level
- Clusters behave differently to bulk
- Pd clusters:
  - size dependence
  - surface/volume ratio
Nanoparticles: X-ray diffraction

Reflection

Transmission

Point detector (2-1, 7-2)
Nanoparticles: X-ray diffraction

In-situ Experiments – more later
APS sector 12

Summary: Nanoparticles

This work:
- Observe peaks corresponding to fcc Pd
- Lattice expansion upon addition of hydrogen
- Dependence on cluster size

Powder diffraction:
- Phase identification
- Structure determination
- Strain
- Crystallite size
- Defects
- In situ measurements
- Transmission and reflection geometries

Apurva, Linda, Marc, Misra, Yezhou: this afternoon
Example 3: ZnO

**Motivation:**
- ZnO exhibits a wide variety of nanostructures
- Electrochemical processing has many advantages
- Experimental parameters determine morphology

How does crystallography affect the growth of the nanostructures?
Thin Film Diffraction

Area Detector

Beam line 11-3

\[ Q - 2\theta \]

incident

\[ \alpha \sim 0.1-0.2 \text{ deg} \]
ZnO: experiments

Ex situ:
Summary:

- Texture increases with deposition time
- Nanostructures are oriented along 002 direction
- Films deposited at less negative electrochemical potentials have poorer epitaxy

Thin films and texture:

- Surfaces, interfaces
- Structure, strain
- Orientation
- Crystallite size in-plane and out-of-plane

Arturas, Chad, Stefan, Chris, this afternoon
Typical SR x-ray scattering experiment & some examples: porous films, nanoparticles, textured films

To be covered in this workshop:
- Films: random, textured, epitaxial
- SAXS
- Powder
- Poorly ordered
- Surfaces
Bibliography


Structural data for thousands of minerals: database.iem.ac.ru/mincryst/

Lawrence Berkeley: X-ray interactions with matter, data & calculations www-cxro.lbl.gov/optical_constants/

International Centre for Diffraction Data - purveyors of the Powder Diffraction File (PDF) www.icdd.com