Introduction to Synchrotron X-Ray Micro/Nanodiffraction

Nobumichi Tamura

Microstructural characterization of Ni-based superalloy (K. Chen et al., 2013-2017)

Calcite co-orientation in sea urchin tooth (Y. Ma et al., 2009)

Measuring volcanic stress in zircon (T.C. Leonhardi et al., 2017)
Outline

1. Introduction to X-Ray Diffraction
2. X-Ray Micro/Nanodiffraction – Why small beams?
3. The X-Ray Microdiffraction Beamline 12.3.2 at the Advanced Light Source
4. X-Ray Micro/Nanodiffraction Data Processing
   - Powder micro/nanodiffraction
   - Laue micro/nanodiffraction
5. A “Big Data” problem
6. Future Perspectives
1. Introduction to X-Ray Diffraction

A century old technique
Max von Laue (1879-1960)
Nobel prize in 1914
**Principle of X-Ray diffraction measurements:**

Bragg’s law:

\[ 2d_{hk\ell} \sin(\theta) = n \lambda \]

Note: X-ray Detectors of choice today are digital area detectors!
“Bragg condition” is rarely satisfied!

To reconstruct the crystal lattice, several interatomic distances need to be measured:

$$d_1, d_2, d_3, d_4, \ldots$$

X-Ray Crystallography needs a usable set of reflections... how to achieve this?
Three basic methods:

“Conventional” Single Crystal X-Ray Diffraction

Powder X-Ray Diffraction

Laue (Polychromatic) X-Ray Diffraction
“Conventional” Single Crystal X-Ray Diffraction

Sample is rotated to bring many set of atomic planes into Bragg’s condition and obtain many reflections

Single Crystal X-Ray Diffraction is the crystallographic method of choice for solving crystal structures
“Powder” X-Ray Diffraction/Polycrystalline X-Ray Diffraction

Sample is a powder of a polycrystals with randomly oriented crystals with sizes smaller than beam size.
Laue (polychromatic) X-Ray Diffraction

Polychromatic X-ray ($\Delta \lambda$)

Laue pattern

Bragg’s condition is satisfied simultaneously for many reflections
2. X-Ray Micro/Nanodiffraction: Why would you want a small x-ray beam (1 micron or less)?

Inter- and intragranular characterization of materials properties (ex: crack propagation)

Characterization of very small devices (ex: 3D interconnect test structure)

Characterization of heterogeneous samples (ex: ferromanganese nodules in soil) and hierarchical materials
Some caveats of performing X-ray Diffraction with a very small X-ray beam...

- The effect of rotating a small sample under a small beam
- Limits pertaining to average crystal size for polycrystalline samples
- X-ray penetration: benediction or curse?
The effect of rotating a small sample under a small beam

• "Sphere of confusion" problem

With a small beam, best to avoid sample rotation

Two techniques do not require sample rotation:

Powder X-Ray Micro/Nanodiffraction

Laue (Polychromatic) X-Ray Micro/Nanodiffraction

• Different angle results in different probed region

The good news of avoiding sample rotation:
- Measurements on a single point can be very fast
  - Sample mapping
  - Time resolved experiments
## Choose your technique...

<table>
<thead>
<tr>
<th>Crystal size</th>
<th>Powder X-ray Micro/Nanodiffraction</th>
<th>Laue X-ray Micro/Nanodiffraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; X-ray beam size (macro) or single crystal</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>~ X-Ray beam size (micro), polycrystals</td>
<td>Possible</td>
<td>Possible</td>
</tr>
<tr>
<td>&lt; X-ray beam size (nano), polycrystals</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

**Max Planck Institute for Chemical Physics of Solids**

**Crystallography and Structural Analysis Branch**

**Advanced Light Source**
X-Ray penetration: good or bad?

Good to access buried samples

Bad if too many grains diffract at the same time (typical case for Laue)
Combined Laue/powder micro/nanodiffraction synchrotron beamlines around the world

- CLS 07B2-1 VESPERS
- APS ID 34-E
- ALS 12.3.2
- ESRF BM32
- PLS 1B2
- SSRF
- TPS 21A
- AS MMC
3.- The X-Ray Microdiffraction beamline at the Advanced Light Source
Synchrotron Radiation Facility: The Advanced Light Source at LBNL

- 3rd generation synchrotron source
- Construction started in 1987, in operation since 1993
- 40 beamlines
- 1.9 GeV, 500 mA
- 200 staff
- >5000 hours of user operation/year
Advanced Light Source (ALS) 12.3.2 Beamline Layout

- Superconducting magnet source
- 1 micron x-ray beam focus provided by elliptically bent Kirkpatrick-Baez (KB) mirrors
- Polychromatic or monochromatic radiation (6-22 keV)
- \~ 4 \times 10^9 (10 \text{ keV}); > 1 \times 10^{12} (white) ph/s in a 1 \text{ um} spot
How to make X-Ray beam small: X-Ray focusing optics

a) Fresnel zone plate, b) Multilayer Laue Lenses c) Bragg-Fresnel lens, d) Compound Refractive Lenses, e) Waveguide, f) Kinoform lenses, g) multi-bounce capillary, h) single bounce capillary, i) Kirkpatrick-Baez total external reflection mirrors, j) Multilayer mirrors in KB configuration
How to make X-Ray beam small: X-Ray focusing optics

Choosing the right focusing optics...

<table>
<thead>
<tr>
<th></th>
<th>Flux Density Gain</th>
<th>Resolution (nm)</th>
<th>Chromatic aberration</th>
<th>Radiation at exit</th>
<th>Scan in Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresnel Zone Plate (FZP)</td>
<td>~ 300 000</td>
<td>60-5000 (4-15 keV)</td>
<td>~ 1/λ</td>
<td>Monochromatic</td>
<td>Possible</td>
</tr>
<tr>
<td>Bragg-Fresnel Lens (BFL)</td>
<td>~ 1000</td>
<td>100-5000</td>
<td>No</td>
<td>Monochromatic</td>
<td>Difficult</td>
</tr>
<tr>
<td>Compound Refractive Lenses (CRL)</td>
<td>~ 500 (λ dependant)</td>
<td>40-5000</td>
<td>~ 1/λ²</td>
<td>Monochromatic</td>
<td>Difficult</td>
</tr>
<tr>
<td>Tapered Capillary</td>
<td>~ 100</td>
<td>100-5000</td>
<td>No</td>
<td>Polychromatic or Monochromatic</td>
<td>Yes</td>
</tr>
<tr>
<td>Kirkpatrick-Baez Mirrors</td>
<td>~ 300 000</td>
<td>60-5000</td>
<td>No</td>
<td>Polychromatic or Monochromatic</td>
<td>Yes</td>
</tr>
<tr>
<td>X-Ray Waveguide</td>
<td>~ 500 (λ dependant)</td>
<td>35-200</td>
<td>~ 1/λ²</td>
<td>Monochromatic</td>
<td>Difficult</td>
</tr>
</tbody>
</table>

Flux Density Gain = Beam Compression Ratio x Efficiency
Kirkpatrick-Baez (KB) Elliptical Mirrors

- Use total external reflection on two orthogonal ultrasmooth elliptically shaped mirrors
- Thin metal layers on top of a thick silicon or silica substrate
- Elliptical shape is obtained by
  - Bending of a flat mirror
  - Differential coating of a spherical mirror
  - Further figure errors correction by ion-beam sputtering, …
- Characteristics:
  - Achromatic (no wavelength dependence)
  - High efficiency

KB mirror system developed at the ALS (bending of flat mirrors)
Beamline end-station instrumentation: Sample stage, x-ray detectors, sample positioning

- DECTRIS Pilatus 1M area detector
- Vortex-EM (SII Nanotech.) single element Si-drift fluorescence detector, 50 mm² active area
- Sample mounted on a XYZ-ϕ stage
- χ cradle for changing X-ray incidence angle
- Heating/Cooling stage
- Flexible positioning of sample and detector allow for both reflection and transmission geometries

- Laser triangulation sample positioning system (Keyence)
Comparing ALS BL12.3.2 with TPS 21A: old and new

<table>
<thead>
<tr>
<th></th>
<th>ALS Beamline 12.3.2</th>
<th>TPS Nanodiffraction 21A</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Year commissioned</strong></td>
<td>2008 (1999)</td>
<td>2016</td>
</tr>
<tr>
<td><strong>Source</strong></td>
<td>Superbend</td>
<td>Tapered undulator</td>
</tr>
<tr>
<td><strong>Flux at sample (1 micron spot)</strong></td>
<td>4. $10^9$ ph/s at 10keV</td>
<td>3 $10^{11}$ ph/s at 10 keV</td>
</tr>
<tr>
<td><strong>Monochromator</strong></td>
<td>4 bounce Si(111)</td>
<td>4 bounce Si(111)</td>
</tr>
<tr>
<td><strong>Focusing optics</strong></td>
<td>KB with in-house benders</td>
<td>KB from J-TEC</td>
</tr>
<tr>
<td><strong>Routine X-ray beam size</strong></td>
<td>1000 nm</td>
<td>70 nm</td>
</tr>
<tr>
<td><strong>Area detector</strong></td>
<td>DECTRIS Pilatus 1 M</td>
<td>DECTRIS Pilatus 6 M</td>
</tr>
<tr>
<td><strong>Angular resolution</strong></td>
<td>0.01°</td>
<td>0.003°</td>
</tr>
<tr>
<td><strong>Angular range</strong></td>
<td>68°</td>
<td>48°</td>
</tr>
<tr>
<td><strong>Strain resolution</strong></td>
<td>~ 2.10^{-4}</td>
<td>~ 5. 10^{-5}</td>
</tr>
<tr>
<td><strong>FTE for Beamline Op</strong></td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td><strong>Data Analysis</strong></td>
<td>Cluster</td>
<td>Cluster</td>
</tr>
</tbody>
</table>
4. X-Ray Micro/Nanodiffraction data collection and processing

- Contrast, topography (average pattern intensity, average background intensity)
- Sea urchin tooth
- Microtexture (orientation, misorientation)
- Deformation (defect density, strain or lattice parameter deviations)
4.1. X-Ray Powder Diffraction Data
What can we learn from a powder pattern?

2D powder pattern

azimuthal integration (1D pattern)

Unwarping into 20–χ angular space
What can we learn from a powder pattern?

Phase identification: match ring/peak position with structural database

Aragonite
What can we learn from a powder pattern?

Phase identification: match ring/peak position with structural database

Dolomite
What can we learn from a powder pattern?

Texture, Preferred Orientation

Copper thin film
What can we learn from a powder pattern?

Texture, Preferred Orientation

Pole figure
What can we learn from a powder pattern?

Macro Strain/Stress
What can we learn from a powder pattern?

Converting the pattern into $2\theta-\chi$ angular space

Macro Strain/Stress

No strain

Macro strain

What can we learn from a powder pattern?
What can we learn from a powder pattern?

\[
\frac{d_{\Phi\Psi} - d_0}{d_0} = \varepsilon_{xx} \cos^2 \Phi \sin^2 \Psi + \varepsilon_{xy} \sin 2\Phi \sin^2 \Psi + \\
\varepsilon_{yy} \sin^2 \Phi \sin^2 \Psi + \varepsilon_{zz} \cos^2 \Psi + \\
\varepsilon_{xz} \cos \Phi \sin 2\Psi + \varepsilon_{yz} \sin \Phi \sin 2\Psi
\]

Macro Strain/Stress

Stress tensor: \( \sigma_{ij} = C_{ijkl} \varepsilon_{kl} \)
What can we learn from a powder pattern?

- **Lithiophorite**: continuous rings (nanocrystallized, ~ 10 nm)
- **Quartz**: discontinuous rings (microcrystallized, ~ 100 nm)
- **Feldspar**: isolated peaks (large or isolated crystals >= 1 um)

Ferromanganese nodule
What can we learn from a powder pattern?

Powder pattern

Conversion to $2\theta-\chi$ space

Al foil

Grain Size/Microstrain

Azimuthal integration over one ring

Peak profile analysis ($W = \text{integral peak breath} - \text{instrumental broadening}$):

$$W_f = K \frac{\lambda}{(D \cos \theta_0)} \ [\text{Scherrer}]$$

$$W_f = 2 \xi \tan \theta_0 \ [\text{Stokes-Wilson}]$$
What can we learn from a powder pattern?

Williamson-Hall (W-H) plot
\[ W \cos \theta = K \frac{\lambda}{D} + 4 \xi \sin \theta \]

W \cos \theta = f(\sin \theta)
Intercept -> coherent size
Slope -> strain

4.1. X-Ray Laue Micro/Nano Diffraction Data
4.2. Laue X-Ray Diffraction Data

The sample is scanned under a white X-ray microbeam. At each step a diffraction (Laue) pattern is collected with the area detector. A preliminary X-ray fluorescence scan can be used to precisely locate the region of interest.

White beam (Laue) diffraction pattern of an Al(Cu) interconnect. The brighter spots are from Si wafer.
The indexation of the Laue patterns provide the crystal orientation matrix of the area illuminated by the X-ray microbeam. The analysis of the entire scan gives the grain orientation map of the sample.

Si spots from the wafer have been digitally removed. The remaining Al spots are indexed.
Measuring strain/stress with Laue X-Ray micro/nanodiffraction

Measuring “shifts” of the Laue reflection positions from their “unstrained” ones provide the deviatoric strain tensor.

Homogeneity property:

\[ R_0 X_0 = RX \]

Transformation matrix:

\[ T_{ij} = R^{-1} R_0 \]

Deviatoric strain tensor:

\[ \varepsilon'_{ij} = \frac{T_{ij} + T_{ji}}{2} - \delta_{ij} \]
Measuring strain/stress with Laue X-Ray micro/nanodiffraction

Deviations of the Laue peaks positions from their “unstrained” positions provide the distortional strain tensor.

\[ \varepsilon_{ij} = \begin{pmatrix} \varepsilon'_{11} & \varepsilon'_{12} & \varepsilon'_{13} \\ \varepsilon'_{21} & \varepsilon'_{22} & \varepsilon'_{23} \\ \varepsilon'_{31} & \varepsilon'_{32} & \varepsilon'_{33} \end{pmatrix} + \begin{pmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & \delta \end{pmatrix} = \varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33} \]

Measured from deviations in crystal Laue pattern (Using White Beam)

Measured from energy of Laue spot (Using Monochromatic beam)

\( \delta = \frac{\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}}{3} \)

Shear strain
\[ \varepsilon_{12} = \varepsilon_{21} \]

Tensile/compressive distortional strain
\[ \varepsilon'_{11}, \varepsilon'_{22} \]

Dilatational strain
\[ \delta \]

-Stress tensor:
\[ \sigma_{ij} = C_{ijkl} \varepsilon_{kl} \]
Plasticity effect on Laue peaks: GND and GNBs

Excess dislocations of the same sign (Geometrically Necessary Dislocations or GNDs) cause lattice curvatures that can be measured by Laue...

1) If GND are randomly distributed, the resulting deformation is equivalent to a pure bending

\[ \rho = \frac{1}{Rb} \]

Cahn-Nye Relation

2) Subgrains boundaries (GNBs) are the result of redistribution of dislocations in dislocation walls

\[ \tan \theta = \frac{b}{L} \]
Peak shapes provide information on plastic deformation and dislocation distribution in the diffracted volume.

\[ \rho = \frac{1}{Rb} \]

Cahn-Nye Relation

\[ \tan \theta = \frac{b}{L} \]

Burgers vector and dislocation line directions can be derived from the shape of the Laue reflections (Barabash et al., 2002 and 2003)
5.- Synchrotron Micro/Nano Diffraction is now a “Big Data” problem looking for a solution
Development of X-ray brightness vs computer speed: an interesting comparison

NERSC Cori supercomputer:
- 2388 Haswell nodes (16-core Intel® Xeon™ Processor E5-2698 v3 ("Haswell") at 2.3 GHz)
- 9688 KNL nodes (Intel® Xeon Phi™ Processor 7250 ("Knights Landing") processor with 68 cores per node @ 1.4 GHz)

Synchrotron increasingly becoming a big data problem (data storage, data processing)…
From Scanning Laue X-Ray Microdiffraction to Laue X-Ray Nanodiffraction Imaging

Average Laue intensity

Data collection: ~ 12 hours

Data Processing time on:
- A regular PC: ~ 1 month
- LRC cluster using 500 nodes: ~ 1 h 30 min

Coral
40,000 Laue patterns of Aragonite crystals
Worst case scenario:
- 1 s exposure/LP
- Low symmetry (orthorhombic)
- Multigrain analysis (several grains/LP)
Working with NERSC (National Energy Research Scientific Computing Center) and LRC (Laboratory Research Computing) at LBNL

1) Automated data transfer directly from beamline to NERSC/LRC storage

2) XMAS interface to submit jobs at NERSC/LRC cluster

3) XMAS parallel code on CORI at NERSC and XMAS cluster at LRC

4) Processed data visualization in XMAS

A collaborative work between ALS, CRD, ESNET and NERSC
6. Summary and Future Perspectives for nanodiffraction

**Powder x-ray micro/nanodiffraction**

- **Phase identification:** match peak/ring positions with structure database
- **Macro-Strain/Stress:** Deviation of the position and shape of the rings
- **Texture:** Intensity distribution along rings
- **Structure refinement:** Rietveld method

**μXRD pattern of a ferromanganese nodule (6keV)**

- Goethite (0.54 Å)
- Khombiite (2.1 Å)
- Chondrite (2.3 Å)
- Goethite (2.7 Å)

**Grain Size:** ring “rugosity” (rms)

- Big grain (Primary mineral)
- Microcrystallized (Quartz)
- Nanocrystallized (Goethite)

**Laue x-ray micro/nanodiffraction**

- **Phase identification/ Crystal orientation:** pattern indexation (~0.01° resolution)
- **Devicotoric strain tensor:** Small shifts in spot positions -> Crystal
- **Total strain:** Kossel lines
- **Plastic deformation/dislocation distribution:** Spot shapes
- **Total strain and d-spacings:** Energy scan on a peak

**A quantitative microstructural imaging tool**

- Ex: effects of heat treatment on a 3D printed Ni-based superalloy
6.- Summary and Future Perspectives for nanodiffraction

What users want?
• Higher spatial resolution
• Higher flux in monochromatic mode
• 3D resolution (DAXM, Diffraction tomography)
• Automated Texture Analysis capability (monochromatic mode)
• Routine multiphase analysis in Laue mode
• Structure refinement
• High involvement of beamline personnel in data interpretation
• Remote users
• Harder x-rays
• Light element sensitivity
• More beamtime …
6.- Summary and Future Perspectives for nanodiffraction

New capabilities in the making

Structure determination of unknown mineral by Laue (submitted 2018)

Energy resolved Laue Diffraction

3D resolution by pencil beam Laue diffraction tomography

Ultrafast analysis on a PC

More info:
ntamura@lbl.gov
https://sites.google.com/a/lbl.gov/bl12-3-2/