Two-Dimensional X-ray Diffraction

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XRD$^2$: Outlines

- Geometry and fundamentals
- Instrumentation: configuration, X-ray source and 2D detector
- Application examples:
  - Phase identification
  - Stress measurement
  - Texture, orientation and fiber analysis
  - Crystallite size measurement
  - Thin films
  - Reciprocal space mapping
Geometry and Fundamentals
Conventional X-ray Diffractometer

- Bragg-Brentano Geometry.
- Point (0D) detector.
- Scanning over $2\theta$ range to collect XRD pattern.

Bragg law: $2d_{hkl} \sin \theta = \lambda$

Corundum Powder Diffraction

$\theta$ $\sin \theta = \frac{\lambda}{2d_{hkl}}$
XRD$^2$: Two-dimensional X-ray Diffraction
XRD²: Single Frame from Battery Anode Collected with Vantec-500 Detector

- 2θ coverage: 70° at 8 cm detector distance
- Contains information on phase, stress, texture and grain size
**XRD²: 2D pattern in I distribution on γ-2θ coordinates**

Characteristics of diffraction rings:

- (a): Random powder Constant 2θ and I along γ;
- (b): Texture Intensity (I) variation along γ;
- (c): Stress 2θ variation along γ;
- (d): Large crystal size: Spotty diffraction rings (many peaks on I vs. γ profile).
**XRD²**: Geometry Convention - Diffraction Space

Diffraction rings in the laboratory coordinates (green).
Detector position in the laboratory coordinates is determined by detector distance $D$ and swing angle $\alpha$. 
The angular relationships between $X_L Y_L Z_L$ and $S_1 S_2 S_3$ are:

<table>
<thead>
<tr>
<th></th>
<th>$X_L$</th>
<th>$Y_L$</th>
<th>$Z_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>$a_{11}$</td>
<td>$a_{12}$</td>
<td>$a_{13}$</td>
</tr>
<tr>
<td>$S_2$</td>
<td>$a_{21}$</td>
<td>$a_{22}$</td>
<td>$a_{23}$</td>
</tr>
<tr>
<td>$S_3$</td>
<td>$a_{31}$</td>
<td>$a_{32}$</td>
<td>$a_{33}$</td>
</tr>
</tbody>
</table>

The transformation matrix from the diffraction space to the sample space is:

$$
\begin{bmatrix}
  a_{11} & a_{12} & a_{13} \\
  a_{21} & a_{22} & a_{23} \\
  a_{31} & a_{32} & a_{33}
\end{bmatrix}
\begin{bmatrix}
  -\sin \omega \sin \psi \sin \phi & \cos \omega \sin \psi \sin \phi & -\cos \psi \sin \phi \\
  -\cos \omega \cos \phi & -\sin \omega \cos \phi & 0 \\
  \sin \omega \sin \psi \cos \phi & -\cos \omega \sin \psi \cos \phi & \cos \psi \cos \phi \\
  -\cos \omega \sin \phi & -\sin \omega \sin \phi & 0 \\
  -\sin \omega \cos \psi & \cos \omega \cos \psi & 0
\end{bmatrix}
$$
The diffraction vector is given in laboratory coordinates by

\[
H = \frac{s - s_0}{\lambda} = \frac{1}{\lambda} \begin{bmatrix} s_x - s_{0x} \\ s_y - s_{0y} \\ s_z - s_{0z} \end{bmatrix} = \frac{1}{\lambda} \begin{bmatrix} \cos 2\theta - 1 \\ -\sin 2\theta \sin \gamma \\ -\sin 2\theta \cos \gamma \end{bmatrix}
\]

The direction of each diffraction vector can be represented by its unit vector given by:

\[
h_L = \frac{H}{|H|} = \begin{bmatrix} h_x \\ h_y \\ h_z \end{bmatrix} = \begin{bmatrix} -\sin \theta \\ -\cos \theta \sin \gamma \\ -\cos \theta \cos \gamma \end{bmatrix}
\]
The components of the unit vector $h_S$ in the sample coordinates $S_1S_2S_3$ is then given by

$$
\begin{bmatrix}
 h_1 \\
 h_2 \\
 h_3 
\end{bmatrix} =
\begin{bmatrix}
 a_{11} & a_{12} & a_{13} \\
 a_{21} & a_{22} & a_{23} \\
 a_{31} & a_{32} & a_{33} 
\end{bmatrix}
\begin{bmatrix}
 h_x \\
 h_y \\
 h_z 
\end{bmatrix}
$$

Or in expanded form for Eulerian geometry:

$$
\begin{align*}
 h_1 &= \sin \theta (\sin \phi \sin \psi \sin \omega + \cos \phi \cos \omega) + \cos \theta \cos \gamma \sin \phi \cos \psi \\
 &\quad - \cos \theta \sin \gamma (\sin \phi \sin \psi \cos \omega - \cos \phi \sin \omega) \\
 h_2 &= -\sin \theta (\cos \phi \sin \psi \sin \omega - \sin \phi \cos \omega) - \cos \theta \cos \gamma \cos \phi \cos \psi \\
 &\quad + \cos \theta \sin \gamma (\cos \phi \sin \psi \cos \omega + \sin \phi \sin \omega) \\
 h_3 &= \sin \theta \cos \psi \sin \omega - \cos \theta \sin \gamma \cos \psi \cos \omega - \cos \theta \cos \gamma \sin \psi
\end{align*}
$$
Laue equations with 3 lattice axes:
\[ a \cdot (s - s_0) = h\lambda \]
\[ b \cdot (s - s_0) = k\lambda \]
\[ c \cdot (s - s_0) = l\lambda \]

Diffraction condition in vector form:
\[ \frac{s - s_0}{\lambda} = H_{hkl} \]

The magnitude of the vector leads to Bragg law:
\[ \frac{2\sin\theta}{\lambda} = \left| H_{hkl}\right| = \frac{1}{d_{hkl}} \]

\[ 2d_{hkl}\sin\theta = \lambda \]

Introduce \( \gamma \) for XRD\(^2\):
\[ H = \frac{s - s_0}{\lambda} = \frac{1}{\lambda} \begin{bmatrix} \cos 2\theta - 1 \\ -\sin 2\theta \sin\gamma \\ -\sin 2\theta \cos\gamma \end{bmatrix} \]

Unit vector in laboratory coordinates (diffraction space)
\[ h_L = \begin{bmatrix} h_x, & h_y, & h_z \end{bmatrix} \]
XRD\(^2\) analysis in diffraction space

Example 1: Polarization
\[ P(\theta, \gamma) = P_0 \sin^2\gamma + P_0\cos^2\gamma \]

Example 2: Virtual Oscillation
\[ \Delta\psi = 2\arcsin[\cos\theta \sin(\Delta\gamma/2)] \]
\[ \cos\Delta\psi = h_{L,1} \cdot h_{L,2} \]

Unit vector in sample coordinates (sample space)
\[ h_s = \begin{bmatrix} h_1, & h_2, & h_3 \end{bmatrix} \]
XRD\(^2\) analysis in sample space

Example 1: Stress
\[ \varepsilon_{(\gamma, \phi, \psi)} = \varepsilon_{ij} \cdot h_i \cdot h_j \]

Example 2: Texture
\[ \beta = \pm \arccos(h_1 / \sqrt{h_1^2 + h_2^2}) \]
\[ \alpha = \arcsin|h_3| \]
Instrumentation:
configuration,
X-ray source,
2D detector.
XRD²: Typical Configurations

- Horizontal θ-2θ (a&c).
- IµS X-ray source.
- Laser/video.
- Eulerian cradle.
- VÅNTEC-500 detector.

- Vertical θ-2θ (b&d).
- Sealed X-ray tube.
- Laser/video.
- Eulerian cradle.
- VÅNTEC-500 detector.
How to make brighter source I: Microfocus sources

- Brightness \( B \) is proportional to power loading \( p \)
- Power loading is higher for *smaller spot focus*

\[
p_{\text{max}} = \frac{2\kappa(T_m - T_0)}{r\sqrt{\pi \ln(2)}}
\]

- Large spot
- Quasi-one dimensional heat flow limits power loading
- Small spot
- Two dimensional heat flow (more efficient cooling)
- Relative performance improved by 10 times
I_μS microfocus source

- Intensity $3 \times 10^{10}$ X-rays/mm$^2$-sec (Cu Kα)
  - 8 times higher than conventional 5.4 kW rotating anode
- Typical lifetime >5 years
  - High reliability
  - 3 year warranty
  - >300 installed
- Air-cooled
- Available in Cr, Cu, Mo, Ag
Conventional Sealed Tube and IμS with VÅNTEC-2000 Corundum Comparison

Sealed Tube with Göbel Mirror
45kV, 40mA, (1800 W)
0.3mm collimator

**total counts:** 78K

Intensity: 15.8x; Efficiency: 948x!
VÅNTEC-500 – Outperforms all previous gaseous detectors.

- Large active area: 140 mm in dia.
- Frame size:
  - 2048 x 2048 pixels
  - 1024 x 1024 pixels
  - 512 x 512 pixels
- Pixel size:
  - 68 µm x 68 µm
  - 136 µm x 136 µm
  - 272 µm x 272 µm
- High sensitivity: 80% DQE for Cu
- High max linear count rate:
  - 0.9 Mcps – global;
  - 160 kcps/reflection -local
- Low background noise:
  - <10⁻⁵ cps/pix
- Maintenance-free:
  - no re-gassing
EIGER2 R 500K
New! HPC Detector for the Best XRD Platform

Large Active Area: $77.2 \times 38.6 = 2,978 \text{ mm}^2$
Most Pixels: $1,030 \times 514 = 529,420$
Perfect Pixel Size: $75 \times 75 \text{ \mu m}^2$
Maximum Count Rate: $3.6 \times 10^8 \text{ ph/s/mm}^2$
High Dynamic Range: $> 10^9 \text{ ph/s/mm}^2$
Media-Free Operation: No gas or water cooling
EIGER2 R 500K
Relation between DQE and reflection size for a HPC detector with 75 \( \mu \text{m} \) pixel

- For most laboratory XRD\(^2\) applications, the beam size is from 50 \( \mu \text{m} \) to 1000 \( \mu \text{m} \);
- Plus broadening effect from the sample, the reflection size is typically 100 \( \mu \text{m} \) or above;
- 75 \( \mu \text{m} \) pixel is an optimal choice with both high DQE and high resolution.
XRD^2: Choice of Detectors: Active Area and Orientation

NIST 1976 (corundum) data collected at sample-to-detector distance of 20 cm.

Left: PILATUS3 R 100K-A (2Theta-optimized Mode)
Middle: PILATUS3 R 100K-A (Gamma-optimized Mode)
Right: VÄNTEC-500
XRD$^2$: Detector Orientation and Distance: frames collected with Aspirin

$\gamma$ optimized – 0° Mode

2$\theta$ optimized – 90° Mode

30 mm

50 mm & offset 19deg

50 mm

10 mm & 20 deg off
XRD\(^2\): Increase angular coverage by scanning in \(\gamma\)-optimized mode

- 2D scanning in \(\gamma\)-optimized mode creates a large cylindrical detector with march large active area.
- Height by detector size and
- Length by scanning range.
Smearing of the diffraction (rings) pattern by simple pixel-to-pixel integration
XRD$^2$: Scanning of 2D Detector Project to a Cylinder Surface

Geometry and algorithms to project flat 2D image onto cylindrical surface

\[ u = D(\arctan \frac{x}{D} - \alpha) \]

\[ v = \frac{Dy}{\sqrt{x^2 + D^2}} \]

\[ 2\theta = \cos^{-1} \left( \frac{R \cos \left( \frac{u}{R} \right)}{\sqrt{R^2 + v^2}} \right) \]

\[ \gamma = \frac{u}{|u|} \cos^{-1} \left( \frac{-v}{\sqrt{v^2 + R^2 \sin^2 \left( \frac{u}{R} \right)} \right) \]

US Patent # 9,897,559
Integration by cylindrical projection produce a final image without smearing effect.
XRD²: Scanning of 2D Detector
Scanned image, no smearing

Coverage of selected region from EIGER2 R 500K™ detector in γ-optimized mode. The area with reduced exposure are removed. Equivalent to a cylindrical detector of 70mm x 157mm (or more).
Application examples:

- Phase identification
- Stress measurement
- Texture, orientation and fiber analysis
- Crystallite size measurement
- Thin films
- Reciprocal space mapping
$\text{XRD}^2$: Phase ID Measurement Geometry
XRD²: Single Frame Covering All

- Multilayer battery anode.
- 2θ coverage: 70° at 8 cm detector distance
- A single frame showing information on phase, stress, texture and grain size
- 2D detector is essential for In-situ measurement
XRD$^2$: Frame Merge and Integration

- 4 frames at 20 cm
- Merged frames 2θ coverage: 100°
- Integrated profile for phase ID search/match
Application examples:

- Phase identification
- Stress measurement
- Texture, orientation and fiber analysis
- Crystallite size measurement
- Thin films
- Reciprocal space mapping
XRD²: Stress (Strain) and X-ray Diffraction

Non-stress: \[2d_o \sin \theta_o = \lambda\]

With stress: \[2d \sin \theta = \lambda\]

True strain:
\[
\varepsilon_n = \ln \frac{d}{d_o} = \ln \frac{\sin \theta_o}{\sin \theta}
\]
XRD²: Fundamental Equation for Stress Measurement

As a second order tensor, the relationship between the measured strains and the strain tensor is given by:

$$ \varepsilon_{(\gamma, \omega, \psi, \phi)}^{\{hkl\}} = \varepsilon_{ij} \cdot h_i \cdot h_j $$

Introduce the macroscopic elastic constants: $S_1$ and $\frac{1}{2}S_2$

$$ S_1 (\sigma_{11} + \sigma_{22} + \sigma_{33}) + \frac{1}{2} S_2 (\sigma_{11} h_1^2 + \sigma_{22} h_2^2 + \sigma_{33} h_3^2) $$

$$ + 2\sigma_{12} h_1 h_2 + 2\sigma_{13} h_1 h_3 + 2\sigma_{23} h_2 h_3 = \ln \left( \frac{\sin \theta_0}{\sin \theta} \right) $$
The D8 DISCOVER with DAVINCI VÅNTEC-500 for stress measurement

- Almen strip (spring steel)
- (211) & (200) rings
- Ring distortion when sample rotates with $\psi$ and $\phi$
XRD²: Stress Measurement Example – Single Tilt Method on Coating

- A proprietary cutting insert with multiple layered structure on WC substrate.
- Al₂O₃ coating: <1μm thick, (116) ring, 2θ=57.5°.
- Single tilt method can effectively minimize the sample height error due to low incident angle:
  - no ψ change during data collection;
  - φ rotation only has least spherical error (height error)
XRD$^2$: Diffraction Vector Distribution– Low 2θ
Single Tilt Method

Diffraction vector distribution with tilt: e.g. $\psi=22.5^\circ$
Diffraction vector distribution without tilt: $\psi=0$
Side-inclination with point detector: multiple tilts

Measured diffraction ring

2D detector

Sample

Incident x-ray
XRD$^2$: Stress Measurement Scheme – Low 2θ Single Tilt Method

- Side-inclination
- Cu-K$\alpha$
- Sample to detector distance: 15 cm.
- $2\theta_0=57.5^\circ$ Al$_2$O$_3$(116) peak, $E=375940$ MPa, $\nu = 0.25$
- 8 frames at single tilt $\psi = 22.5^\circ$ with complete $\phi$ rotation with 45° steps.
- At 57° 2θ, the $\gamma$ range can provide the orientation coverage near 45°
A set of data collected on Al2O3 layer in 20 minutes (150s per frame).

The data integration region
\[ \theta: \ 56^\circ \sim 59^\circ \]
\[ \gamma: \ -65^\circ \sim -115^\circ. \]

Subregions: 10
10 x 5° for 50° γ.

The counts within each subregion are integrated into a diffraction profile.

2θ peak position is determined with Pearson VII fitting.
XRD$^2$: Stress Measurement – Single Tilt Stress Evaluation Results

- **A** – Data points on 2D frames.
- **B** – Data points in $\gamma$-2$\theta$ plot with:
  - $2\theta_0$ ;
  - X data points from the profile fitting;
  - calculated diffraction rings from stress results.
- **C** – Integrated diffraction profile of any subregion.
- **D** – Stress results
  - $\sigma_{11} = 954 \pm 27$ MPa
  - $\sigma_{22} = 958 \pm 27$ MPa
Application examples:

• Phase identification
• Stress measurement
• Texture, orientation and fiber analysis
• Crystallite size measurement
• Thin films
• Reciprocal space mapping
XRD²: Crystal Orientation and Pole Figure

- The direction of poles is defined by $a$ and $b$ angles in spherical coordinates.
- The pole densities at all directions are mapped on the equatorial plane by Stereographic Projection.
- The 2D map is called pole figure
The pole figure angles \((\alpha, \beta)\) can be calculated from the unit vector components by the pole mapping equations:

\[
\alpha = \sin^{-1} |h_3| = \cos^{-1} \sqrt{h_1^2 + h_2^2}
\]

\[
\beta = \pm \cos^{-1} \frac{h_1}{\sqrt{h_1^2 + h_2^2}} \quad \begin{cases} 
\beta \geq 0^\circ & \text{if } h_2 \geq 0 \\
\beta < 0^\circ & \text{if } h_2 < 0
\end{cases}
\]
The D8 DISCOVER with DAVINCI VÅNTEC-500 for texture measurement

- Steel can
- (200) & (110) rings
- Intensity variation during $\phi$ scan
Texture Measurement Using VANTEC-500: Magnetron sputter-deposited Cu films

- Four diffraction rings are observed at 10 cm detector distance.
- Four pole figures can be measured simultaneously.
- Diffraction spots from Si wafer appear on some frames.
Combined pole-figure of film Cu (111) and substrate Si (400)

- Pole-figure in 2D projection
- Pole-figure in 3D surface plot
**XRD²**: Miscut angle (α) of a Si wafer

- Two spots are produced by sample rotates during data collection
- 2theta integration shows the gamma angle between two spots

\[ \alpha = 2 \arcsin[\cos \theta \sin(\Delta \gamma / 4)] \]
D8 Discover with VÅNTEC-500
PE Fiber: Orientation and Crystallinity
XRD²: Fiber with VÅNTEC-500
Application examples:

• Phase identification
• Stress measurement
• Texture, orientation and fiber analysis
• Crystallite size measurement
• Thin films
• Reciprocal space mapping
XRD²: Data Collection:

Acetaminophen powder

- The spotty diffraction ring is due to the large crystallites compared to the sampling volume (beam size).
- The number of spots on the ring is determined by crystallite size, instrumental window (\(\gamma\)-range), multiplicity of the crystal plane, and effective diffraction volume.
- The size of jelly beans and candy bin determines how many you can fill.
For XRD\textsuperscript{2}, the instrumental window $\Omega$ is given by

$$\Omega = \beta_1 \beta_2 = 2\beta \arcsin[\cos \theta \sin(\Delta \gamma / 2)]$$
XRD$^2$: Particle size measurement by $\gamma$ profile analysis:

For XRD$^2$ in reflection mode, the crystallite size is given by

$$d = k \left\{ \frac{p_{hkl} b^2 \arcsin[\cos \theta \sin(\Delta \gamma / 2)]}{2 \mu N_s} \right\}^{1/3}$$

where $\mu$ is the linear absorption coefficient.

For transmission mode with the incident beam perpendicular to the sample surface, the crystallite size is given by

$$d = k \left\{ \frac{p_{hkl} b^2 t \arcsin[\cos \theta \sin(\Delta \gamma / 2)]}{N_s} \right\}^{1/3}$$

where $t$ is the sample thickness.

$k$ is the instrument calibration factor or can be calculated from:

$$k = \left( \frac{3 \beta}{4 \pi} \right)^{1/3}$$

if the instrument broadening in $2\theta$ direction is known.
**XRD²: Crystal Size Analysis**

2θ profile analysis  \quad \gamma profile analysis

1 nm \quad 10 nm \quad 100 nm \quad 1 \mu m \quad 10 \mu m \quad 100 \mu m \quad 1 \text{mm}

### Scherrer equation:

(P. Scherrer, Göttinger Nachrichten Gesell., Vol. 2, 1918, p 98.)

\[ t = \frac{C \lambda}{B \cos \theta} \]

Gold nano-particle
Grain size measurement from two-dimensional micro-X-ray diffraction: Laboratory application of a radial integration technique

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American Mineralogist, Volume 100, pages 1899–1911, 2015

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TABLE 1. Grain sizes of sieved pyroxene samples as calculated by $\chi$-profile grain size analysis

<table>
<thead>
<tr>
<th>Sieve size (µm)</th>
<th>Avg calc poly (µm)</th>
<th>S.D. (µm)</th>
<th>Avg calc lin (µm)</th>
<th>S.D. (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;5 wet, ground</td>
<td>15.76</td>
<td>1.34</td>
<td>15.79</td>
<td>1.24</td>
</tr>
<tr>
<td>&lt;10 wet</td>
<td>17.97</td>
<td>1.32</td>
<td>18.44</td>
<td>2.60</td>
</tr>
<tr>
<td>&lt;20 dry</td>
<td>17.77</td>
<td>0.38</td>
<td>17.34</td>
<td>0.99</td>
</tr>
<tr>
<td>&lt;25 dry</td>
<td>22.73</td>
<td>2.52</td>
<td>24.35</td>
<td>3.91</td>
</tr>
<tr>
<td>10–15 wet</td>
<td>20.22</td>
<td>2.14</td>
<td>20.85</td>
<td>2.57</td>
</tr>
<tr>
<td>15–20 wet</td>
<td>18.56</td>
<td>3.70</td>
<td>19.26</td>
<td>4.99</td>
</tr>
<tr>
<td>20–25 wet</td>
<td>22.32</td>
<td>0.48</td>
<td>23.15</td>
<td>1.40</td>
</tr>
<tr>
<td>25–38 wet</td>
<td>21.63</td>
<td>7.05</td>
<td>22.35</td>
<td>6.27</td>
</tr>
<tr>
<td>25–38 dry</td>
<td>25.88</td>
<td>4.24</td>
<td>28.27</td>
<td>5.77</td>
</tr>
<tr>
<td>38–45 dry</td>
<td>22.70</td>
<td>6.07</td>
<td>28.01</td>
<td>10.68</td>
</tr>
<tr>
<td>75–90 dry</td>
<td>36.16</td>
<td>20.67</td>
<td>42.12</td>
<td>22.63</td>
</tr>
</tbody>
</table>

Notes: Samples are identified by the sieve size used and whether they were wet or dry sieved. A value averaging the grain size from multiple Debye rings for the sample is given as well as the standard deviation (S.D.). This process was executed for both the polynomial data set (poly) and the linear average intensity line data set (lin).

**FIGURE 1.** A two-dimensional X-ray diffraction frame (a) with a selected window to be integrated in $\chi$. The frame is of a 10–15 µm wet sieve size pyroxene. The corresponding $\chi$-profile is shown (b) in a plot of intensity vs. $\chi$. An average intensity line is plotted (red) and every two times the $\chi$-profile intersects this average intensity line is counted as a single grain. (Color online.)
Estimation of Drug Particle Size in Intact Tablets by 2-Dimensional X-Ray Diffractometry

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2 Characterization Facility, University of Minnesota, Minneapolis, Minnesota 55455

Table 2: Tablet Weight and Estimated Grain Size of Acetaminophen in the Marketed Products

<table>
<thead>
<tr>
<th>Brand Number</th>
<th>Tablet Weight (mg)</th>
<th>Estimated Grain Size by γ-Profile Integration (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>592 ± 7</td>
<td>89 ± 14</td>
</tr>
<tr>
<td>2</td>
<td>590 ± 2</td>
<td>32 ± 7</td>
</tr>
<tr>
<td>3</td>
<td>588 ± 2</td>
<td>38 ± 4</td>
</tr>
<tr>
<td>4</td>
<td>597 ± 4</td>
<td>83 ± 16</td>
</tr>
<tr>
<td>5</td>
<td>641 ± 2</td>
<td>35 ± 6</td>
</tr>
<tr>
<td>6</td>
<td>577 ± 3</td>
<td>29 ± 6</td>
</tr>
<tr>
<td>7</td>
<td>581 ± 3</td>
<td>38 ± 7</td>
</tr>
<tr>
<td>8</td>
<td>556 ± 5</td>
<td>28 ± 8</td>
</tr>
<tr>
<td>9</td>
<td>559 ± 3</td>
<td>30 ± 7</td>
</tr>
<tr>
<td>10</td>
<td>576 ± 4</td>
<td>35 ± 3</td>
</tr>
<tr>
<td>11</td>
<td>559 ± 4</td>
<td>78 ± 18</td>
</tr>
</tbody>
</table>

All data are mean ± SD (n = 3).

Figure 2. Representative 2D XRD frames for (a) LMH (b) sucrose. The Debye rings used for grain size determination are marked with arrows.
Application examples:

• Phase identification
• Stress measurement
• Texture, orientation and fiber analysis
• Crystallite size measurement
• Thin films
• Reciprocal space mapping
Innovative XRD² Techniques

Lattice Parameter Refinement with DIFFRAC.TOPAS

<table>
<thead>
<tr>
<th>Layer</th>
<th>Space Group</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>NGO</td>
<td>62</td>
<td>5.431*</td>
<td>5.499*</td>
<td>7.701</td>
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<td>LZO</td>
<td>62</td>
<td>9.256</td>
<td>9.256</td>
<td>10.886</td>
<td>932.64</td>
</tr>
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<td>10.919</td>
<td>991.67</td>
</tr>
<tr>
<td>PIO</td>
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<td>9.590</td>
<td>9.590</td>
<td>11.315</td>
<td>1040.55</td>
</tr>
</tbody>
</table>

Layer

- NGO (002)
- LZO (113)
- PIO (113)
- PIO (004)
- NGO (004)
- LZO (004)
- LZO (008)
- NGO (006)
- PIO (008)

April 17, 2019
Innovative XRD\textsuperscript{2} Techniques
Rapid X-ray Reflectometry with XRD\textsuperscript{2}

Instrument Setup
- \(I_\mu S\) microfocus Cu Tube
- Montel Optic
- 0.5 mm Collimator
- Knife Edge
- VÅNTEC 500

2D XRR pattern from thin films of various thickness
Film thickness evaluated from the integrated profile
Application examples:

• Phase identification
• Stress measurement
• Texture, orientation and fiber analysis
• Crystallite size measurement
• Thin films
• Reciprocal space mapping
XRD$^2$: Reciprocal space coverage of 0D, 1D, 2D and 3D detectors on Ewald sphere

- Zero-dimensional (P), one-dimensional (L) and two-dimensional (A) detectors.
- Three-dimensional detector with X-ray photon energy as the 3$^{rd}$ dimension.
XRD\(^2\): Reciprocal space mapping

- The 3\(^{rd}\) dimension in reciprocal space can also be achieved by scanning over one or a combination of three Eulerian angles (\(\omega, \psi, \phi\)).
- \(Q\) vector can be given by:
  \[
  Q = 2\pi H = \frac{4\pi \sin \theta}{\lambda} h_s
  \]
  \[
  \begin{align*}
  \{q_x\} &= \frac{4\pi \sin \theta}{\lambda} \begin{pmatrix} h_1 \\ h_2 \\ h_3 \end{pmatrix} \\
  \{q_y\} &= \frac{4\pi \sin \theta}{\lambda} \begin{pmatrix} h_1 \\ h_2 \\ h_3 \end{pmatrix}
  \end{align*}
  \]
Partial Ordering – Texture
High Orientation Preference

CdTe (111) on stepped substrate
Preston, Mascher, et al.

Received from Jim Britten (McMaster University, Hamilton, Ontario, Canada) with permission.
3D Display – Fibre Diffraction

Extruded, distorted polypropylene.
Elnagmi / Jain

C$_\infty$-axis in diffraction pattern

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Example 1 – Random Orientation
GaAs NW on Carbon nanotube ‘fabric’

Why bother with XRD$^3$?
Sometimes there are surprises!

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Example 2 – Multiple (8) Orientation GaAs NW’s on Si Substrate

2D scan sequence

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Laue equations with 3 lattice axes:
\[ a \cdot (s - s_0) = h \lambda \]
\[ b \cdot (s - s_0) = k \lambda \]
\[ c \cdot (s - s_0) = l \lambda \]

The magnitude of the vector leads to Bragg law:
\[ \frac{|s - s_0|}{\lambda} = \frac{2 \sin \theta}{\lambda} = \frac{|H_{hkl}|}{d_{hkl}} \]

\[ 2d_{hkl} \sin \theta = \lambda \]

Diffraction condition in vector form:
\[ \frac{s - s_0}{\lambda} = H_{hkl} \]

\[ H = \frac{s - s_0}{\lambda} = \frac{1}{\lambda} \begin{bmatrix} \cos 2\theta - 1 \\ -\sin 2\theta \sin \gamma \\ -\sin 2\theta \cos \gamma \end{bmatrix} \]

Unit vector in laboratory coordinates (diffraction space):
\[ h_L = \begin{bmatrix} h_x \\ h_y \\ h_z \end{bmatrix} \]

XRD² analysis in diffraction space:
Example 1: Polarization
\[ P(\theta, \gamma) = P_i \sin^2 \gamma + P_{II} \cos^2 \gamma \]
Example 2: Virtual Oscillation
\[ \Delta \psi = 2 \arcsin[\cos \theta \sin(\Delta \gamma / 2)] \]
\[ \cos \Delta \psi = h_{L1} \cdot h_{L2} \]

Unit vector in sample coordinates (sample space):
\[ h_s = Ah_L \]

Example 1: Stress
\[ \varepsilon_{ij} = \varepsilon_{ij} \cdot h_i \cdot h_j \]
Example 2: Texture
\[ \beta = \pm \arccos(h_i / \sqrt{h_i^2 + h_j^2}) \]
\[ \alpha = \arcsin|h_s| \]
More About XRD\textsuperscript{2} : The 2\textsuperscript{nd} Edition of «Two-Dimensional X-ray Diffraction»

1. Introduction.
2. Geometry Conventions.
3. X-Ray Source and Optics.
4. X-Ray Detectors.
5. Goniometer and Sample Stages.
6. Data Treatment.
7. Phase Identification.
8. Texture Analysis.
10. Small-Angle X-Ray Scattering.
11. Combinatorial Screening.
12. Miscellaneous Applications.
13. Innovation and Future Development.

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