Two-dimensional Powder Diffraction

Bob He, Bruker AXS

Advanced School on High Resolution X-Ray Techniques
Atomic Force Microscopy and their Applications

Venue: S.N. Bose National Centre for Basic Sciences
Dates: 14 - 15 Dec, 2011
XRD²: Comparison with Conventional XRD (1)

The powder diffraction pattern in 3D space (blue) and the conventional diffractometer plane.
Conventional X-ray Diffractometer

- Bragg-Brentano Geometry.
- Scanning over 2θ range to collect XRD pattern.

![Diagram of X-ray diffractometer](image)

**Corundum Powder Diffraction**

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<th>Two Theta</th>
<th>Intensity</th>
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<tr>
<td>20</td>
<td></td>
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<tr>
<td>25</td>
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<td>30</td>
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<td>40</td>
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<tr>
<td>45</td>
<td></td>
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<tr>
<td>50</td>
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Parallel beam Geometry

- Parallel beam Geometry.
- Scanning over 2θ range to collect XRD pattern.
- Not sensitive to the sample height error and rough surface.
Bragg-Brentano Geometry

Equatorial

Axial

Target

Primary Soller Slit

Divergence Slit

Sample

Anti-Scatter Slit

Secondary Soller Slit

Receiving Slit
Soller slits are used to control axial divergence

- In Bragg-Brentano geometry, the line focus beam can be considered as a superposition of point beams.
- All in parallel with the diffractometer plane and the same geometry condition separated by soller slit foils.
XRD²: Two-dimensional X-ray Diffraction
Detective Quantum Efficiency (DQE):

- The DQE is a parameter defined as the square of the ratio of the output and input signal-to-noise ratios (SNR).

\[
DQE = \left( \frac{(S/N)_{\text{out}}}{(S/N)_{\text{in}}} \right)^2
\]

- The DQE of a real detector is less than 100% because not every incident x-ray photon is detected, and because there is always some detector noise.

- MiKroGap™ has the best overall performance.
XRD$^2$: Point Spread Function and Resolution

Consider a very small diffraction spot (blue line - delta function)

An adjacent spot – red line

RMS (root-mean-square) is another parameter for PSF:

A perfect detector - dashed blue line. A real detector - intensity in a spread distribution.

Can be measured if the separation is larger than FWHM.

FWHM = 2.3548 · RMS
VÅNTEC-500 – Outperform all previous gaseous detectors.

- High sensitivity: 80% DQE for Cu (detection quantum efficiency)
- High spatial resolution: The FWHM of the PSF is 200µm
- High maximum count rate: Global count rate: 1.5Mcps
  Local count rate: 250kcps/reflection
- Low background noise: <5 cps/global
- Maintenance-free: no re-gassing
$2\theta_{\text{range}} = 2 \arctan \frac{l}{D}$

$2\theta_{\text{max}} = \pi - \frac{m + h}{D}$

$2\theta_{\text{max}}$
XRD²: Diffraction vector approach

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**XRD²**: Diffraction pattern with both $\gamma$ and $2\theta$ information

Diffraction vector with $\gamma$:

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

Expressed in sample space:

$$\begin{bmatrix} h_1 \\ h_2 \\ h_3 \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} h_x \\ h_y \\ h_z \end{bmatrix}$$
**XRD²: Geometry Convention - Diffraction Space**

Diffraction rings (blue) in the laboratory axes (red).
The diffraction vector is given in laboratory coordinates by

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

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

\[
h = \frac{H}{|H|} = \begin{bmatrix} h_x \\ h_y \\ h_z \end{bmatrix} = \begin{bmatrix} -\sin \theta \\ -\cos \theta \sin \gamma \\ -\cos \theta \cos \gamma \end{bmatrix}
\]
Detector position in the laboratory coordinates is determined by the detector distance $D$ and swing angle $\alpha$. 

$\alpha_1 = 0$
XRD$^2$: From Pixel to $2\theta$ and $\gamma$ in Diffraction Space

Conversion of pixel intensity into $2\theta$ and $\gamma$ intensity based on the detector position in the laboratory coordinates $D$ and $\alpha$:

$$2\theta = \cos^{-1} \frac{x \sin \alpha + D \cos \alpha}{\sqrt{D^2 + x^2 + y^2}}, \quad (0 < 2\theta < \pi)$$

$$\gamma = \frac{x \cos \alpha - D \sin \alpha}{|x \cos \alpha - D \sin \alpha|} \cos^{-1} \frac{-y}{\sqrt{y^2 + (x \cos \alpha - D \sin \alpha)^2}}, \quad (-\pi < \gamma \leq \pi)$$
XRD^2: Phase ID Measurement Geometry
XRD$^2$: Single Frame Covering All

- 2θ coverage: 70° at 8 cm detector distance
- Sample with strong texture and large grain
Fast Phase Identification for time resolved Studies
Corundum data 0.03 to 1 sec

High Speed Analysis

Y + 75.0 mm - 1 Second Data Collection
Y + 50.0 mm - 0.5 Second Data Collection
Y + 25.0 mm - 0.1 Second Data Collection
0.03 Second Data Collection

Rel (cps)
1
2
3
4
5
6
7
8
9
10
11

2-Theta - Scale
32 40 50 60

0.03 Second Data Collection
Y + 25.0 mm - 0.1 Second Data Collection
Y + 50.0 mm - 0.5 Second Data Collection
Y + 75.0 mm - 1 Second Data Collection
**XRD²: Frame Merge and Integration**

- 4 frames at 20 cm
- Merged frames 2θ coverage: 100°
- Integrated profile for phase ID search/mat ch
XRD$^2$: reflection vs. transmission

Reflection mode frame from corundum at 5° incident angle.

Frame with perpendicular incident beam.
XRD$^2$:
Defocusing at low incident angle in reflection

Lower resolution when \( \theta_2 \) or \((2\theta - \omega) \rightarrow 90^\circ\)

\[
\frac{B}{b} = \frac{\sin \theta_2}{\sin \theta_1} = \frac{\sin(2\theta - \omega)}{\sin \omega}
\]
XRD²: Defocusing effect in reflection mode depends on detector and data collection strategy

- Cylinder detector with 5° incident angle for 5~80° 2θ
- Flat detector with several (5°, 15°, 25°, 35°) incident angles for 5~80° 2θ
XRD²: Defocusing effect with reflection sample depends on detector and data collection strategy.

Cylinder detector may collect large 2θ range, but with large defocusing effect at high 2θ angle.

Defocus effect can be minimized with data collection strategy.
The integrated intensity diffracted from random polycrystalline materials is given by:

\[ I_{hkl} = k_I \frac{p_{hkl}}{v^2} (LPA) \lambda^3 F_{hkl}^2 \exp\left(-2M_t - 2M_s\right) \]

where:

- \( k_I \) - instrument constant;
- \( p_{hkl} \) - the multiplicity of the planes;
- \( v \) - the volume of the unit cell;
- \( (LPA) \) - the Lorentz-polarization and absorption factors;
- \( F_{hkl}^2 \) - the structure factor of the crystal plane \((hkl)\) and \( \exp(-2M_t-2M_s) \) - the attenuation factor due to lattice thermal vibrations and weak static displacements.

\( \oplus \) Denotes the factors which are different between Bragg-Brentano geometry and XRD\(^2\) geometry. \( k_I \) is determined by the source, optics and detector \( (LPA) \) will be given in this presentation.
The polarization factor for Bragg-Brentano geometry with incident beam monochromator is:

\[ P_I = \frac{1 + \cos^2 2\theta_M \cos^2 2\theta}{1 + \cos^2 2\theta_M} \]

where \(2\theta_M\) is the Bragg angle of the monochromator.

The general polarization factor for the diffracted beam to point \(P\) is:

\[ P_G = \frac{(\cos^2 2\theta \cos^2 \rho + \sin^2 \rho) \cos^2 2\theta_M + \cos^2 2\theta \sin^2 \rho + \cos^2 \rho}{1 + \cos^2 2\theta_M} \]
The unit vector of the diffraction vector $\mathbf{H}_p$ and its projection on $Y_L$-$Z_L$ plane, $\mathbf{H'}_p$, in the laboratory system are given respectively as:

$$\mathbf{h}_L = \begin{bmatrix} h_x \\ h_y \\ h_z \end{bmatrix} = \begin{bmatrix} -\sin \theta \\ -\cos \theta \sin \gamma \\ -\cos \theta \cos \gamma \end{bmatrix} \quad \mathbf{h'}_L = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

The unit vector of $Y_L$ is $\mathbf{y}_L = [0, 1, 0]$, then:

$$\cos \rho = \cos (\mathbf{h'}_L, \mathbf{y}_L) = \mathbf{h}_L \cdot \mathbf{y}_L = -\sin \gamma$$

Therefore, $\cos^2 \rho = \sin^2 \gamma$ and $\sin^2 \rho = \cos^2 \gamma$

The polarization factor for XRD$^2$ can then be given as a function of both $\theta$ and $\gamma$:

$$P(\theta, \gamma) = \frac{(1 + \cos^2 2\theta_M \cos^2 2\theta) \sin^2 \gamma + (\cos^2 2\theta_M + \cos^2 2\theta) \cos^2 \gamma}{1 + \cos^2 2\theta_M}$$
The absorption can be measured by the transmission coefficient:

\[ A = \frac{1}{V} \int_V e^{-\mu \tau} \, dV \]

where \( \tau \) is the total beam path and \( A \) is the average over all the element \( dV \). For Bragg-Brentano geometry, we have:

\[ A_{BB} = \frac{1}{2\mu} \]

Absorption correction of flat slab:

(a) reflection

(b) transmission.

To make the relative intensity comparable to Bragg-Brentano geometry, we introduce a normalized transmission coefficient \( T \):

\[ T = \frac{A}{A_{BB}} = 2\mu A \]
XRD²: Sample Absorption Correction

For reflection mode diffraction with a thick plate:

\[
\begin{bmatrix}
1 \\
0 \\
0
\end{bmatrix}
\quad \quad \quad \quad
\begin{bmatrix}
\cos 2\theta \\
-\sin 2\theta \sin \gamma \\
-\sin 2\theta \cos \gamma
\end{bmatrix}
\]

and

\[
\begin{bmatrix}
-\sin \omega \cos \psi \\
\cos \omega \cos \psi \\
\sin \psi
\end{bmatrix}
\]

The normalized transmission coefficient:

\[
T = \frac{2\cos \eta}{(\cos \eta + \cos \zeta)}
\quad \quad \quad \quad \text{with} \quad \cos \eta = -s_o \cdot n = \sin \omega \cos \psi
\quad \quad \quad \quad \cos \zeta = s \cdot n = -\cos 2\theta \sin \omega \cos \psi
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad -\sin 2\theta \sin \gamma \cos \omega \cos \psi - \sin 2\theta \cos \gamma \sin \psi
\]
XRD²: Sample Absorption Correction

For transmission mode:

\[
\begin{bmatrix}
1 \\
0 \\
0 \\
\end{bmatrix}
\]

\[s_o = \begin{bmatrix}
\cos 2\theta \\
-\sin 2\theta \sin \gamma \\
-\sin 2\theta \cos \gamma \\
\end{bmatrix}
\]

\[
\begin{bmatrix}
\sin \omega \sin \psi \sin \phi + \cos \omega \cos \phi \\
-\cos \omega \sin \psi \sin \phi + \sin \omega \cos \phi \\
\cos \psi \sin \phi \\
\end{bmatrix}
\]

\[n = \begin{bmatrix}
\sin \omega \sin \psi \sin \phi + \cos \omega \cos \phi \\
-\cos \omega \sin \psi \sin \phi + \sin \omega \cos \phi \\
\cos \psi \sin \phi \\
\end{bmatrix}
\]

The normalized transmission coefficient:

\[
T = \frac{2 \sec \eta [\exp(-\mu t \sec \eta) - \exp(-\mu t \sec \zeta)]}{\sec \zeta - \sec \eta}
\]

\[
\cos \eta = s_o \cdot n = \sin \omega \sin \psi \sin \phi + \cos \omega \cos \phi
\]

\[
\cos \zeta = s \cdot n = (\sin \omega \sin \psi \sin \phi + \cos \omega \cos \phi) \cos 2\theta
\]

\[
+ (\cos \omega \sin \psi \sin \phi - \sin \omega \cos \phi) \sin 2\theta \sin \gamma
\]

\[- \cos \psi \sin \phi \sin 2\theta \cos \gamma
\]
The integrated intensity with texture is:

$$I_{hk} = k \frac{P_{hk}}{v^2} (LPA) \lambda^2 F_{hk}^2 g_{hk}(\alpha, \beta) \exp(-2M_t - 2M_s)$$

where $g()$ is the normalized pole density function.

For the BB geometry, $g_{hk}(\frac{\pi}{2},0)$

The texture effect for XRD$^2$:

$$I^c_{hk} = \frac{I^m_{hk}}{\langle g_{hk}(\Delta \gamma) \rangle}$$

Correct to the B-B equivalent with a texture effect:

$$I_{hk}^{BB} = g_{hk}(\frac{\pi}{2},0) I^m_{hk} \langle g_{hk}(\Delta \gamma) \rangle$$

For fiber texture:

$$\langle g_{hk}(\Delta \gamma) \rangle = \frac{\int_{\gamma_1}^{\gamma_2} g_{hk} [\chi(\gamma)] \gamma d\gamma}{\gamma_2 - \gamma_1}$$

and

$$\chi = \cos^{-1} |h_3|$$
XRD²: GADDS Microdiffraction

Horizontal th-2th, XYZ stage
Fatal Bicycle Accident
Collection of Evidence

traces of car paint found on the bicycle

Dr. W. Kugler
Landeskriminalamt
Baden-Württemberg
Stuttgart, Germany
Fatal Bicycle Accident
Mapping of Car Paint with GADDS

video image (for documentation)

2-dimensional diffraction pattern

integration of data: diffractogram for phase identification
Fatal Bicycle Accident
Phase Identification of Car Paint

- 36-0426 (*) - Dolomite - CaMg(CO3)2
- 05-0586 (*) - Calcite, syn - CaCO3
- 21-1276 (*) - Rutile, syn - TiO2

New Frame - File: 2708_07.raw - Start: 11.905 ° - End: 78.926 ° - Step: 0.040 °

Lin (Counts)

0 500 1000 1500 2000

2-Theta - Scale

12 20 30 40 50 60 70

- New Frame - File: 2708_07.raw - Start: 11.905 ° - End: 78.926 ° - Step: 0.040 °
- 21-1276 (*) - Rutile, syn - TiO2
- 05-0586 (*) - Calcite, syn - CaCO3
- 36-0426 (*) - Dolomite - CaMg(CO3)2
Fatal Bicycle Accident
The Car’s Identification

sequence of coatings is characteristic of car type
Car Paint Analysis
Five Layers of Car Paint
Police Officer’s Pistol – Excessive Force?
Death of a Bank Rober

Crime Scene Showing the Path of the Bank Robber
Police Officer’s Pistol – Excessive Force?
Contact Trace on the Barrel

XRD Pattern from the Contact Trace and the Material from the Sidewalk
Police Officer’s Pistol – Excessive Force?
Contact Trace on the Projectile

Projectile Mounted on the Stage

Measurement Point, Adjusted with the Laser Beam
Police Officer’s Pistol – Excessive Force? Negative.
Contact Trace and Control Specimen
Phase ID Mapping
High-throughput Screening (HTS)
Vertical theta-theta, Reflection/Transmission
**XRD²: High throughput screening**
Laser/video sample alignment

Easy and accurate sample positioning without touching the sample surface

Video image of each material library spot can be automatically stored during data scan.
PolySNAP for Combined Analysis:
Correlation among XRD, Raman and other probes

Cell display

Dendrogram

3D plots
XRD$^2$: Particle Size Analysis

- **2θ profile analysis**, including measurement from peak FWHM by Scherrer equation, or profile analysis by Stokes and Wilson, is suitable for particle size below 100 nm.

- **γ profile analysis** is suitable for particle size from sub-micrometer to a few millimeters.

- The size range of **γ profile analysis** can be further extended by instrumentation and data collection strategy.
XRD²: Particle size measurement by γ profile analysis.
Peak broadening - gold Nanoparticles
Particle size calculation:

Scherrer equation:

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

where \( \lambda \) is wavelength (Å), \( B \) is FWHM (radians) corrected for instrument broadening, \( \theta \) is Bragg angle, \( C \) is a crystal shape factor from 0.9~1.
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$^2$, the instrumental window $\Omega$ is given by

$$\Omega = \beta_1 \beta_2 = 2\beta \arcsin[\cos \theta \sin(\Delta \gamma / 2)]$$
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.
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. Quantitative Analysis.
13. Innovation and Future Development.
Visualization of 3D Reciprocal Space with MAX3D

Jim Britten, Weiguang Guan, Victoria Jarvis
McMaster University
Hamilton, Ontario, Canada
Nanowire Film Orientation Analysis

Jim Britten, Weiguang Guan, Victoria Jarvis
McMaster University
Hamilton, Ontario, Canada
XRD$^3$ and Ewald’s Sphere

Cones of diffraction in real space

Concentric spheres of intensity at radii $1/d$ in Reciprocal Space
The Extremes of 3D Diffraction

What can we see in between?
Residual Stress

Looking for subtle changes in 2θ position of line/arc.shell to indicate orientation dependent residual stresses. Hard to see visually – need mathematica analysis.

High angle snapshots of diffraction shell segments in two series of φ steps at two different ω (incident) angles. Looking for elliptical deviation from spheres where r = 1/d₀.
1D Ordering – Fibre Diffraction

Extruded, distorted polypropylene. Elnagmi / Jain

$C_\infty$ -axis in diffraction pattern
Example 1 – Random Orientation
GaAs NW on Carbon nanotube ‘fabric’

Why bother with XRD$^3$?
Sometimes there are surprises!
Example 2 – Multiple (8) Orientation GaAs NW’s on Si Substrate

2D scan

Full scan in MAX3D