Line Profile Analysis by the Whole Powder Pattern Fitting

Workshop W12
Denver X-Ray Diffraction Conference

Colorado Springs
August 2, 2005
Outline of the Workshop

- **Davor Balzar**
  - Basics about diffraction-line broadening
  - Modeling of line broadening in Rietveld refinement programs
    - How to do it? - Recipes
  - Size-Strain Round Robin

- **Jens Müller**
  - Programs SHADOW, SLH, and BREADTH

- **Matteo Leoni**
  - Whole Powder Pattern Modeling (WPPM)
    - Theoretical Overview
    - Program PM2K
    - Examples

- **Iuliana Dragomir-Cernatescu**
  - Multiple Whole Profile (MWP) or Convolution Multiple Whole Profile (CMWP) programs
    - Theoretical Overview
    - Examples
Origins of Line Broadening

Deformation:

**UNIFORM**

**NONUNIFORM**

Lattice parameters

Line broadening

**STRAIN:** Dislocations, vacancies, interstitials, substitutions,...

\[ \beta_D(2\theta) = 4 e \tan\theta \]

**SIZE:** Stacking faults, twins, dislocation arrays, domains, grains,...

\[ \beta_S(2\theta) = \frac{K\lambda}{<D>_v \cos\theta} \]
How to Extract This Information?

- Both instrument and specimen broaden the diffraction lines, and the observed line profile is a convolution (Bragg peaks only):

\[ h(x) = [g \ast f](x) + \text{background}. \]

\[ g(x) = (\omega \ast \gamma)(x). \]

\[ f(x) = (S \ast D)(x). \]

- **Task:** Extract \( f \) from \( h \) by **knowing** \( g \):
  - Deconvolution (Stokes): \( F(n)=H(n)/G(n) \)
  - Convolution (profile fitting): preset **line-profile** function
Instrumental Broadening

- Determining instrumental intrinsic broadening:
  - “Fundamental parameters” approach
  - Measure a suitable material ("Standard")
    NIST SRM 660a LaB₆

Generally complicated, but...!

\[ \beta_L^g(2\theta) = a \tan \theta \quad ; \quad \beta_G^g(2\theta) = b \.
\]

\[ a = 2 \Delta \lambda / \lambda \]

A measurement at only one angle suffices to estimate the instrumental contribution! – lab x-rays only!
Physical Broadening

\[ g \text{ known } \Rightarrow \text{instrumental-broadening unfolding} \]
\[ f \text{ contains physical information } \Rightarrow \text{correct!} \]

- **Model-independent:**
  - Stokes Fourier deconvolution
  \[ F(n) = \frac{H(n)}{G(n)} \]
  - unbiased
  - peak overlap
  - unstable
  - truncation
  - background
  - standard

- **Model-dependent:**
  - Convolution-fitting
  \[ h(x) = f(x) \ast g(x) \]
  - biased
  - fast and easy
  - stable
  - suitable for RR

“Good” analytical function (if it exists)
Simple Analytical Functions

- Gauss:
  \[ I(x) = I(0) \exp\left(-\pi \frac{x^2}{\beta_G^2}\right) \]

- Lorentz (Cauchy):
  \[ I(x) = I(0) \frac{1}{\beta_C^2 / \pi^2 + x^2} \]

- Voigt (G\#L):
  \[ I(x) = I(0) \left( \frac{\beta}{\beta_C} \right) \text{Re} \left[ \text{erfi} \left( \frac{\pi^{1/2}x}{\beta_G} + ik \right) \right] ; \quad k = \frac{\beta_C}{\pi^{1/2} \beta_G} \]
Experiment

- Ball-milled W (dislocations) → Isotropic strain broadening
- MgO (thermal decomposition of MgCO₃) → Isotropic size broadening

Data analysis

- Stokes method (optimal conditions):
  - non-overlapped lines (220, 400, 422)
  - MgO annealed as a standard
  - $\text{FWHM}_{sp} / \text{FWHM}_{st} = 4$
- Fitting with simple functions
W Line Profiles (110)

Cu Kα_{1,2}

NSLS

Lorentz

Gauss

Voigt
MgO Line Profiles (422)

Cu K$\alpha_{1,2}$

NSLS

Lorentz

Gauss

Voigt
Physical Broadening Modeled by a Voigt Function

**Other experimental evidence**

- Pressed Ni-powder (least-squares deconvolved)
  (Suortti *et al.*, 1979)
- Chlorite (Ergun’s iterative unfolding)
  (Reynolds, 1989)

**Theoretical evidence:**

- Warren-Averbach analysis (Balzar & Ledbetter, 1993)

**$G \star L = V; \ V \star V \ldots \ V = V (!):**

- Both $S$ & $D$ profiles (“double-Voigt” model)
  (Langford, 1980; Balzar, 1992)

\[
\beta_L = \sum_i (\beta_L)_i
\]
\[
\beta_G^2 = \sum_i (\beta_G^2)_i
\]
Size-Strain Modeling in Rietveld Refinement

• **Size broadening (Scherrer, 1918):**

\[
\beta_S(2\theta) = \frac{K\lambda}{<D>_v \cos\theta}
\]

• **Strain broadening (Stokes & Wilson, 1944):**

\[
\beta_D(2\theta) = 4\ e\ \tan\theta
\]

• **Modified TCH pVoigt (Thompson, Cox & Hastings, 1987):**

\[
\Gamma_L = \frac{X}{\cos\theta} + Y\tan\theta + Z
\]

\[
\Gamma_G^2 = \frac{P}{\cos^2\theta} + U\tan^2\theta + V\tan\theta + W
\]
Physical Significance of the Parameters

\[ \Gamma_L = \frac{X}{\cos \theta} + Y \tan \theta + Z \]

\[ \Gamma_G^2 = \frac{P}{\cos^2 \theta} + U \tan^2 \theta + V \tan \theta + W \]

- \( X, P \Rightarrow \) size parameters
- \( Y, U \Rightarrow \) strain parameters
- \( V, W, Z \Rightarrow \) instrumental contribution !?
  - \( Y, W \) sufficient for approximate results with laboratory data
  - More parameters with synchrotron and neutron data \((Y, W, V, U)\)

Recombine into Voigt!

Triple-Voigt model

\[ \beta_L = \sum_i (\beta_L)_i \]

\[ \beta_G^2 = \sum_i (\beta_G^2)_i \]
Voigt Function in Rietveld Refinement

- Modified TCH model:
  \[ \Gamma_L = X / \cos \theta + Y \tan \theta + Z \]
  \[ \Gamma_G = P / \cos^2 \theta + U \tan^2 \theta + V \tan \theta + W \]

- Correct for the instrumental broadening:
  \[ \left( X, P, U, Y \right)_{\text{PHYSICAL}} = \left( X, P, U, Y \right)_{\text{SAMLE}} - \left( X, P, U, Y \right)_{\text{STANDARD}} \]

- Size and strain:
  \[ X, P \left( \gamma_2, \sigma_2^2 \right) \Rightarrow \beta_S \]
  \[ Y, U \left( \gamma_1, \sigma_1^2 \right) \Rightarrow \beta_D \]
  \[ \beta_S(2\theta) = \frac{K\lambda}{<D>_v \cos \theta} \]
  \[ \beta_D(2\theta) = 4 \, e \tan \theta \]
Voigt Function in Rietveld Refinement

- FWHM => Integral breadth
  - Voigt function
    \[
    \frac{\beta_L}{\Gamma_L} = \frac{\pi}{2}, \quad \frac{\beta_G}{\Gamma_G} = \frac{1}{2} \sqrt{\frac{\pi}{\ln 2}}, \quad \frac{\beta_G}{\Gamma_G} = \sqrt{2\pi} \quad \text{(GSAS)}
    \]
    \[
    \beta = \beta_G \frac{\exp(-k^2)}{1 - \text{erf}(k)} \quad k = \frac{\beta_L}{\sqrt{\pi} \beta_G}
    \]
  - Pseudo-Voigt function (TCH)
    \[
    \beta = \frac{\Gamma}{2} \left[ \frac{\eta}{\pi} + (1 - \eta) \left( \frac{\ln 2}{\pi} \right)^2 \right]
    \]
    \[
    \eta = 1.36603 \left( \frac{\Gamma_L}{\Gamma} \right) - 0.47719 \left( \frac{\Gamma_L}{\Gamma} \right)^2 + 0.11116 \left( \frac{\Gamma_L}{\Gamma} \right)^3
    \]
    \[
    \Gamma = \left( \Gamma_G^5 + 2.69269 \Gamma_G^4 \Gamma_L + 2.42843 \Gamma_G^3 \Gamma_L^2 + 4.47163 \Gamma_G^2 \Gamma_L^3 + 0.07842 \Gamma_G \Gamma_L^4 + \Gamma_L^5 \right)^{\frac{1}{5}}
    \]

CW

\[
D_V = \lambda / \beta^S
\]
\[
e = \beta^D / 4
\]

TOF

\[
D_V = \frac{\text{DIFC}}{\beta^S}
\]
\[
e = \beta^D / (2 \text{DIFC})
\]
Crystallite-size Distribution Determination

• Important for many materials:
  ‣ Biomedical applications
    Polymer-based nanocomposites
    Drug encapsulation
  ‣ Gas sensors

• Characterization of the size-related line broadening
  ‣ Sample with characterized defects
  ‣ Methods
    Physically based ("bottom-top")
    - Dislocations
    - Size distributions
    Phenomenological ("top-bottom")
    Different definition of the parameters =&gt; comparison difficult !!!

Empirical approach =&gt; Round Robin
Published Results

The results of the round robin and comparative analysis using three different line-broadening methods were published:

- The reprint and original measurements are available at the Web site www.du.edu/~balzar
Size-Strain Round Robin Co-Authors

- N. Audebrand and D. Louër, University of Rennes
- M. R. Daymond, ISIS, Rutherford-Appleton Laboratory, Didcot
- A. Fitch and O. Masson, ESRF, Grenoble
- A. Hewat, ILL, Grenoble, France
- J. I. Langford, University of Birmingham
- A. Le Bail, University of Maine, Le Mans
- C. N. McCowan, NIST, Boulder, Colorado
- N. C. Popa, National Institute for Materials Physics, Bucharest
- P. W. Stephens, NSLS, Brookhaven National Laboratory, Upton
- B. Toby, NCNR, NIST, Gaithersburg, Maryland

Round-robin participants and CPD gratefully acknowledged
Round-Robin Sample

• **Choice**
  ‣ Chemically stable, easy control of stoichiometry, size, and strain
  ‣ Line overlap => simple crystal structure
  ‣ Anisotropic line broadening modeling => spherical crystallites
  ‣ Size-strain separation => predominantly size broadened
  ‣ Broad size distribution => controlled synthesis

\[ \text{CeO}_2 \]

• **Sample with broadened lines (University of Rennes)**
  ‣ Thermal treatment of hydrated ceria
  ‣ Annealing at 650 °C for 45 h

• **Instrumental standard (NIST Boulder)**
  ‣ Annealing at 1300 °C for 3 h
Comparison with the New LaB₆ NIST SRM660a
“Representative” Measurements

- **Laboratory x-ray sources:**
  - “Common” instrumental setup: University of Le Mans (Armel Le Bail)
  - Incident-beam monochromator: University of Birmingham (J. Ian Langford)

- **Synchrotron sources:**
  - 2nd generation, B-B geometry (flat plate): NSLS, Brookhaven National Laboratory (Peter W. Stephens)
  - 3rd generation, D-S geometry (capillary): ESRF, Grenoble (Olivier Masson and Andy Fitch)

- **Neutron sources:**
  - CW:
    - High resolution: BT-1, NCNR, NIST, Gaithersburg (Brian Toby)
    - Low resolution: D1A, ILL, Grenoble (Alan Hewat)
  - TOF:
    - High-resolution: HRPD, ISIS, Oxford (Mark Daymond)
Instrument Resolution

- Instrument resolution and precision of the size-strain determination
  - “Signal-to-noise” $\frac{\beta_p}{\beta_g} \gg$

![Graph showing Δd/d vs d (Å) for different facilities including Le Mans, NIST, ILL, Birmingham, NSLS, ESRF, and ISIS.]

![Graphs showing Counts vs 2θ for NIST and ISIS facilities.]

![Graph showing Counts vs TOF (ms) for ESRF facility.]

![Graph showing Counts vs 2θ for some other facility.]

[Logos of NIST and University of Denver.]
Sample Characterization

- Morphology

FESEM Micrograph

Lognormal size distribution

$<D> = 384\,\text{Å}, \quad c = 0.16$

$c = \sigma_R^2 / R^2$
Analysis of Results

- **Line-broadening methods:**
  - Physical model:
    - Lognormal size distribution of spherical crystallites
  - Phenomenological approach:
    - Bayesian deconvolution + Warren-Averbach analysis
  - Rietveld refinement:
    - Important, used
    - No clear understanding of microstructural parameters that can be extracted
### Comparison of Results

#### Lognormal size distribution

<table>
<thead>
<tr>
<th>Location</th>
<th>$\bar{R}$ (Å)</th>
<th>$C$</th>
<th>$D_D$ (Å)</th>
<th>$D_V$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birmingham</td>
<td>89.0(10)</td>
<td>0.187(5)</td>
<td>167(3)</td>
<td>223(5)</td>
</tr>
<tr>
<td>Le Mans</td>
<td>90.9(3)</td>
<td>0.188(2)</td>
<td>171(1)</td>
<td>229(2)</td>
</tr>
<tr>
<td>ESRF</td>
<td>90.0(10)</td>
<td>0.192(6)</td>
<td>171(4)</td>
<td>229(6)</td>
</tr>
<tr>
<td>NSLS</td>
<td>93.3(7)</td>
<td>0.177(3)</td>
<td>172(2)</td>
<td>228(4)</td>
</tr>
<tr>
<td>ILL</td>
<td>93.0(20)</td>
<td>0.173(7)</td>
<td>171(6)</td>
<td>225(9)</td>
</tr>
<tr>
<td>NIST</td>
<td>93.0(40)</td>
<td>0.184(15)</td>
<td>174(12)</td>
<td>232(19)</td>
</tr>
<tr>
<td>ISIS</td>
<td>91.0(10)</td>
<td>0.191(4)</td>
<td>172(3)</td>
<td>231(5)</td>
</tr>
</tbody>
</table>

#### Warren-Averbach analysis

<table>
<thead>
<tr>
<th>Location</th>
<th>$D_D$ (Å)</th>
<th>$D_V$ (Å)</th>
<th>RMSS (10$^{-4}$)</th>
<th>$D_D$ (Å)</th>
<th>$D_V$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birmingham</td>
<td>177</td>
<td>238</td>
<td>4.4</td>
<td>159</td>
<td>228</td>
</tr>
<tr>
<td>Le Mans</td>
<td>198</td>
<td>241</td>
<td>6.6</td>
<td>181</td>
<td>226</td>
</tr>
<tr>
<td>ESRF</td>
<td>195</td>
<td>213</td>
<td>0$^i$</td>
<td>187</td>
<td>224</td>
</tr>
<tr>
<td>NSLS</td>
<td>196</td>
<td>234</td>
<td>4.1</td>
<td>189</td>
<td>229</td>
</tr>
<tr>
<td>ILL</td>
<td>188</td>
<td>228</td>
<td>4.5</td>
<td>176</td>
<td>224</td>
</tr>
<tr>
<td>NIST</td>
<td>194</td>
<td>251</td>
<td>7.1</td>
<td>167</td>
<td>230</td>
</tr>
<tr>
<td>ISIS</td>
<td>165</td>
<td>248</td>
<td>5.0</td>
<td>177</td>
<td>240</td>
</tr>
</tbody>
</table>

#### Rietveld refinement

<table>
<thead>
<tr>
<th>Location</th>
<th>$D_R$ (Å)</th>
<th>$\beta_C/\beta_L$</th>
<th>$e$ (10$^{-4}$)</th>
<th>$e = 0^i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birmingham</td>
<td>227(3)</td>
<td>0.85(2)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Le Mans</td>
<td>235(2)</td>
<td>1.01(1)</td>
<td>2.2(1)</td>
<td></td>
</tr>
<tr>
<td>ESRF</td>
<td>223(1)</td>
<td>0.704(7)</td>
<td>1.5(1)</td>
<td></td>
</tr>
<tr>
<td>NSLS</td>
<td>236(2)</td>
<td>0.84(1)</td>
<td>2.3(1)</td>
<td></td>
</tr>
<tr>
<td>ILL</td>
<td>221(3)</td>
<td>0.83(2)</td>
<td>0.1(3)</td>
<td></td>
</tr>
<tr>
<td>NIST</td>
<td>231(6)</td>
<td>0.74(4)</td>
<td>4.5(8)</td>
<td></td>
</tr>
<tr>
<td>ISIS</td>
<td>232(1)</td>
<td>0.831(8)</td>
<td>5.5(2)</td>
<td></td>
</tr>
</tbody>
</table>
Round Robin

- 49 participants
- 16 result sets returned
- Methods employed:
  - Simplified integral breadth
  - Double-Voigt integral breadth
  - Rietveld refinement
  - Warren-Averbach analysis
  - Lognormal size distribution + Gaussian strain broadening
  - “Fundamental-parameters” approach
  - …
Round Robin Results

Average domain size

RR Average

\[ D_V = 320(110) \text{ Å} \quad D_A = 168(21) \text{ Å} \]

3-way Analysis Average (with strain)

\[ D_V = 231 \text{ Å} \quad D_A = 179 \text{ Å} \]

RR without significant strain

\[ D_V = 226(90) \text{ Å} \quad D_A = 168(21) \text{ Å} \]
RR Conclusions

• Instrument resolution not so important (at this level of broadening)

• Analysis methods introduce more uncertainty than the instrument

• Size-strain separation a problem

• Size-broadened profile has a significant Gauss contribution

• Rietveld refinement
  ‣ Potential correlation of size-strain parameters with others
  ‣ Non-Voigtian profiles problematic
Programs SHADOW and BREADTH

- Old-fashioned line–broadening analysis
- "Double-Voigt" approach
  - Both size-broadened and strain-broadened profiles are assumed to be Voigt functions
- SHADOW (Scott Howard & Bob Snyder) used to fit both instrumental broadening (LaB₆) and broadened patterns
- BREADTH used to analyze results obtained by SHADOW and yields:
  - Both area-weighted and volume-weighted domain sizes => determines a crystallite-size distribution
  - Strain as a function of averaging distance in crystallites
- Procedure simplified and new auxiliary programs added by Jens Müller
  - SLH (SHADOW’s Little Helper)
- Details at:
  - www.du.edu/~balzar
Anisotropic Line Broadening in Rietveld Refinement

- Thermal-parameters-like ellipsoids (size + strain) (Le Bail, 1985)
  - Cubic symmetry => SPHERES

- Platelets (Greaves, 1985; Larson & Von Dreele, 1987)

\[ \Gamma_L = \frac{X + X_e \cos\phi}{\cos\theta} + (Y + Y_e \cos\phi) \tan\theta; \quad \phi = \angle(H_{hkl}, A_p) \]

- Elastic-dependent anisotropic strain, Thompson, Reilly, and Hastings, 1987 (hexagonal)

\[ \Gamma_G = \left[A + \frac{Bl^4 + C(h^2k^2 + k^2l^2) + Dh^2k^2}{(h^2 + k^2 + l^2)^2}\right]^{1/2} \tan\theta \]
Anisotropic Line Broadening in Rietveld Refinement

- Stephens, 1999 (all Laue classes)

\[
\Gamma_A = \left[ \sum_{HKL} A_{HKL} h^H k^K l^L \right]^{1/2} d \tan \theta
\]

15 \( A_{HKL} \) (triclinic); 2 \( A_{HKL} \) (cubic)

Voigt strain-broadened profile

\[
\Gamma_L = X / \cos \theta + Y \tan \theta + \zeta \Gamma_A (hkl)
\]
\[
\Gamma_G^2 = P / \cos^2 \theta + U \tan^2 \theta + (1 - \zeta)^2 \Gamma_A^2 (hkl)
\]
Anisotropic Line Broadening in Rietveld Refinement

- Popa, 1998: Elastic-dependent anisotropic strain and size
  - Strain model **effectively** identical to Stephen’s approach for all Laue classes
  - Size model: expansion in a series of spherical harmonics

\[
< D > = D_0 + \sum_{l, m} D_l P_l^m (\cos \phi) e^{im\phi}
\]

ITERATION!

Gauss strain + Lorentz size broadened profile