Line-Profile Analysis and Standards

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EPDIC-6
Budapest
August 25, 1998
Outline

- Diffraction-line profile

- Broadening:
  - Instrumental Contribution
    - Model or measure?
    - Synchrotron
    - Standards
  - Physical contribution
    - Convolute or deconvolute?
    - Experiment
    - Voigt function

- RR
  - Triple-Voigt model
  - Anisotropy modeling

- Conclusions and call for your contribution
Anything in common?

CuKα_{1,2}

NSLS 1.3 Å

LANSCE
How to obtain the information?

- Both instrument and specimen contributions (Bragg 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):
    \[ F(n) = \frac{H(n)}{G(n)}. \]
  - Convolution (profile fitting):
    preset **line-profile** function

LINE SHAPE & INSTRUMENTAL SIGNATURE
Instrumental line profile

SCHEMATIC DIAGRAM OF THE X3B1 NSLS BEAMLINE

Final line shape by convolution (numerical!)

- Measure (“empirical” or “standard” approach):
  - Analytical-function fit (Lorentz, Gauss, Voigt, …)
  - Model the angular dependence

- Calculate (“fundamental parameter” approach):
  - Wilson, Klug & Alexander
  - KOALARIET (Coelho & Cheary)
  - BGMN (Bergmann)

Adapted from Klug and Alexander (1974).
“Fundamental-parameter” approach

- Advantages:
  - Understanding of a physical background
  - Relative importance of different factors
  - More accurate modeling of profiles?

- Deficiencies:
  - Some contributions cannot be modeled
  - Optical elements imperfect

STANDARDS

Fewer parameters?

<table>
<thead>
<tr>
<th></th>
<th>BGMN</th>
<th>KOALARIET</th>
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<tbody>
<tr>
<td>γ</td>
<td>7 L</td>
<td>AF</td>
</tr>
<tr>
<td>ω</td>
<td>4 L²</td>
<td>PV, PVII</td>
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<td>S</td>
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<tr>
<td>D</td>
<td>L²</td>
<td>G</td>
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Voigt-function fits to the LaB₆ line profiles

1st approximation:

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

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

A measurement at only one angle suffices to estimate the instrumental contribution!
Asymmetry

- Exponential, split-Pearson VII:

- Axial divergence (Finger et al, 1994):

\[
D(2\phi, 2\theta) = \frac{L}{2H} h(2\phi) \cos 2\phi W(2\phi, 2\theta)
\]

\[
h(2\phi) = L \left(\frac{\cos^2 2\phi}{\cos^2 2\theta} - 1\right)^{1/2}
\]

\[
W(2\phi, 2\theta) = \begin{cases} 
0 & 2\phi < 2\phi_{\text{min}} \text{ or } 2\phi > 2\theta \\
H + S - h(2\phi) & 2\phi_{\text{min}} \leq 2\phi < 2\phi_{\text{infl}} \\
2 \min(H, S) & 2\phi_{\text{infl}} \leq 2\phi < 2\theta
\end{cases}
\]
Synchrotron line profiles

LaB$_6$

- $\beta_L$
- $\beta_G$

1.3 Å 0.25 mm ES

1.3 Å 0.75 mm ES
“Super-Gaussian” synchrotron line profile

\[ g(z) = \begin{cases} 
1 & |z| \leq a/2 \\
0 & |z| > a/2
\end{cases} \]

\[ f(z) = C \exp \left( -b^2 z^2 \right) \]

\[ b = \frac{2 \sqrt{\ln 2}}{\text{FWHM}} \]

\[ f \ast g = \int_{-a/2}^{a/2} \exp \left[ -b^2 (x-z)^2 \right] dz \]

\[ = \frac{\sqrt{\pi}}{2b} \left[ \text{erf} \left( b \frac{a}{2} - bx \right) + \text{erf} \left( b \frac{a}{2} + bx \right) \right] \]
Variance of the profile (mean-square broadening)

\[ \Delta \lambda / \lambda = \left[ \omega_M^2 + \omega_A^2 + (\text{FWHM}_\phi \cot \theta)^2 \right]^{1/2} \]

\[ \Gamma^2 \approx \phi^2 \left( 2\tan \theta / \tan \theta_M - \tan \theta_A / \tan \theta_M - 1 \right)^2 \]

\[ + \left( \frac{w_{ES}}{D_{SS}} \right)^2 / 12 \]

FWHM_\phi (2.5 GeV, 8 keV) = 0.0190°; \quad w_{ES} / D_{SS} = 0.0286°

\omega_M(111 \text{ Si, 8 keV}) = 0.0021°; \quad \omega_A(111 \text{ Ge, 8 keV}) = 0.0045°

\[ g_M(z) = s^2 / \left[ z \pm (z^2 - s^2)^{1/2} \right]^2 \]
“Standards” against Standards

- Common ("uncertified" or "nonstandarized") materials:
  - W, Ag, Si,…
  - BaF₂, KCl,…

- NIST SRMs:
  - Si (640a,b,c)
  - LaB₆ (660 a)
  - Al₂O₃ plate (1976)
  - Low-angle standard (mica)
  - ………
  - ………

NARROW LINES!
Physical origins of broadening
(Microscopic approaches)

- Krivoglaz & Ryaboshapka, 1963
- Wilkens
- Ungár, Groma & Mughrabi

Density and arrangement of dislocations

Crystal symmetries:
- Cubic (monoatomic lattice!)
- Hexagonal (Klimanek & Kužel)

Weak line broadening, size broadening, instrumental contribution?
Physical broadening

\( g \) known => instrumental-broadening unfolding

\( f \) contains physical information => correct!

- Model-independent:
  - Stokes Fourier deconvolution

\[
F(n) = \frac{H(n)}{G(n)}
\]

- unbiased

- peak overlap
- unstable
- truncation
- background
- standard

- Model-dependent:
  - Convolution-fitting

\[
h(x) = g(x) \ast f(x)
\]

- biased

- fast and easy
- stable
- suitable for RR

“Good” analytical function (if exists)
Simple analytical functions

- Gauss

\[ G(x) = I(0) \exp\left(-\pi x^2 / \beta_G^2\right) \]

- Lorentz (Cauchy)

\[ L(x) = I(0) \frac{1}{\beta_L^2 / \pi^2 + x^2} \]

- Voigt (G★L)

\[ V(x) = I(0) \left( \frac{\beta}{\beta_L} \right) \Re \left[ \text{erfi} \left( \frac{\pi^{1/2} x}{\beta_G} + i k \right) \right]; \quad k = \frac{\beta_L}{\pi^{1/2} \beta_G} \]
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
  - $\text{FWHM}_{sp}/\text{FWHM}_{st}=4$
- Convolution-fitting (optimal conditions):
  - $g$ (SPVII fit to standard’s profiles)
  - $f$ (preset exact Voigt)
110 W (Cu Kα_{1,2})

[Graph showing intensity vs. 2θ with fits for Cauchy, Gauss, and Voigt functions]
422 MgO (Cu K$\alpha_{1,2}$)

Intensity (arbitrary units)

$2\theta$ (°)

-3
-3
-3

Synthesized $f(2\theta)$

Fitted Cauchy function

Fitted Gauss function

Fitted Voigt function

Intensity (arbitrary units)
110 W (synchrotron)
400 MgO (synchrotron)
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)

- $G\star L = V; \quad V\star V ... \quad V = V (!)$:
  - Both $S$ & $D$ profiles (“double-Voigt” model) (Langford, 1980; Balzar, 1992)

  \[
  \beta_L = \sum_i (\beta_L)_i \\
  \beta^2_G = \sum_i (\beta^2_G)_i
  \]
Integral-breadth methods

\[ x = \frac{\beta_2}{\beta_1} \]
\[ s_2 = 2s_1 \]
\[ c_1 = \frac{1}{\beta_1} \]
\[ c_2 = \frac{\beta_1}{(2s_1)} \]

\[ \beta = \frac{1}{\langle D \rangle_v} + 2es \quad \text{(Cauchy–Cauchy)} \]
\[ \beta = \frac{1}{\langle D \rangle_v} + \frac{4e^2s^2}{\beta} \quad \text{(Cauchy–Gauss)} \]
\[ \beta^2 = \frac{1}{\langle D^2 \rangle_v} + 4e^2s^2 \quad \text{(Gauss–Gauss)} \]
\[ \beta^2 = \frac{1}{\langle D^2 \rangle_v} + 2es\beta \quad \text{(Gauss–Cauchy)} \]
Line broadening in Rietveld refinement

- Size broadening (Scherrer, 1918)

\[
\langle D \rangle_v = \frac{K\lambda}{\beta_s(2\theta) \cos \theta} = \frac{1}{\beta_s}
\]

- Strain broadening (Stokes & Wilson, 1944)

\[
\Delta d/d \approx e = \frac{\beta_D(2\theta)}{4 \tan \theta} = \frac{\beta_D}{2s}
\]

- Observed profile is a Voigt function

\[
\Gamma_L = X/\cos \theta + Y \tan \theta + Z
\]

\[
\Gamma_G^2 = P/\cos^2 \theta + U \tan^2 \theta + V \tan \theta + W
\]

Modified TCH pVoigt

(Thompson, Cox & Hastings, 1987)
Physical significance of the TCH parameters?

\[ \Gamma_L = X / \cos \theta + Y \tan \theta + Z \]

\[ \Gamma_G^2 = P / \cos^2 \theta + U \tan^2 \theta + V \tan \theta + W \]

- \( X, P \Rightarrow \) 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 !

\[ \text{Triple-Voigt model!} \]
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)

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

- Elastic-dependent anisotropic strain
  - Thompson, Reilly, and Hastings, 1987 (hexagonal)
    \[
    \Gamma_G = \left[ A + \frac{Bl^4 + C(h^2k^2 + k^2l^2) + Dh^2k^2}{(h^2 + k^2 + l^2)^2} \right]^{1/2} \tan \theta
    \]
  - Stephens, in press (all Laue classes)
    \[
    \Gamma_A = \left[ \sum_{HKL} A_{HKL} h^H k^K l^L \right]^{1/2} d^2 \tan \theta
    \]
    \[
    15 A_{HKL} \text{ (triclinic); } 2 A_{HKL} \text{ (cubic)}
    \]

- Voigt strain-broadened profile
  \[
  \Gamma_L = X / \cos \theta + Y \tan \theta + \zeta \Gamma_A(hkl)
  \]
  \[
  \Gamma_G^2 = P / \cos^2 \theta + U \tan^2 \theta + V \tan \theta + W + (1 - \zeta)^2 \Gamma_A^2(hkl)
  \]
Anisotropic line broadening in Rietveld refinement

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

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

Gauss strain + Lorentz size broadened profile
Physical background

- Stephens & Popa’s strain model
  \[ \Gamma = \left[ A + B \frac{h^2k^2 + k^2l^2 + h^2l^2}{(h^2 + k^2 + l^2)^2} \right]^{1/2} \tan \theta \]

  and

  Groma, Ungár & Wilkens (1988)

  microscopic line-broadening theory

  \[ \overline{C} = A + B \frac{h^2k^2 + k^2l^2 + h^2l^2}{(h^2 + k^2 + l^2)^2} \]

  Reuss approximation

- Other (Voigt, Hill, Eshelby-Kröner)?
Strains of I and II kind and texture in Rietveld refinement

- Elastic-strain tensor
  (Balzar, Von Dreele, Bennett & Ledbetter, in press)

- Stress and texture
  (Ferrari & Lutterotti, 1994)

- Texture
  - 2-step iterative approach
    (Matthies, Lutterotti & Wenk, 1997)
  - Direct refinement of texture coefficients
    (Von Dreele, 1997)

After J. B. Cohen
Future?

Any specimen property!
Just name it!

RESULTS
Future directions (instead of Conclusions)

- **Instrumental broadening**
  - Refine the “fundamental-parameter” approach
  - New SRMs

- **Physical broadening**
  - Microscopic approach (Krivoglaz-Wilkens-Mughrabi-Ungár) incorporate into widely-used methods
    - W-A & W-H (Ungár & Borbély, 1996)
    - RR (Wu, Gray & Kisi, in press)
  - Stacking faults, twins, antiphase domains,..
    - RR (GSAS)

- **Analytical approximation to physical model**
  - Voigt or something else?
Line-broadening “study”  
(Round Robin)

● Standards
  ▶ Instrumental standards
    • New material?
    • Comparison to “fundamental-parameter” approaches?
  ▶ Broadening standards?

● Methods
  ▶ Integral breadth
  ▶ Fourier
  ▶ Microscopic
  ▶ ?

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