Line Profile Analysis by the Whole Powder Pattern Fitting

Workshop W12

Denver X-Ray Diffraction Conference

Colorado Springs

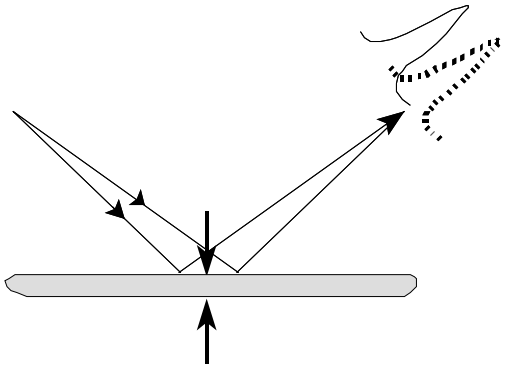
August 2, 2005

Outline of the Workshop

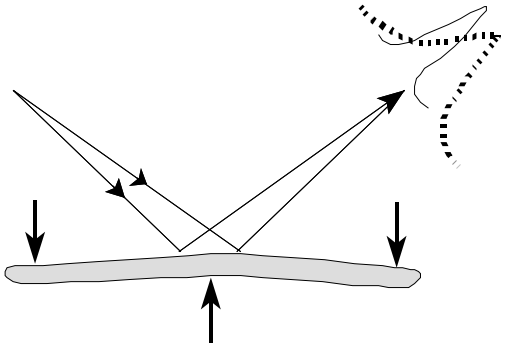
- Davor Balzar
  - Basics about diffraction-line broadening
  - Modeling of line broadening in Rietveld refinement programs
    - How to do it? - Recipes
  - Size-Strain Round Robin
- Jens Müller
  - Programs SHADOW, SLH, and BREADTH
- Matteo Leoni
  - Whole Powder Pattern Modeling (WPPM)
    - Theoretical 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



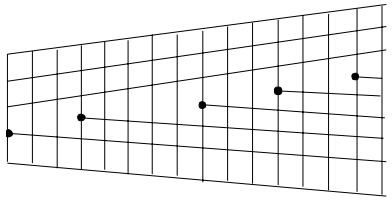
NONUNIFORM

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,...

$$\beta_S(2\theta) = \frac{K\lambda}{\langle D \rangle_v \cos\theta}$$

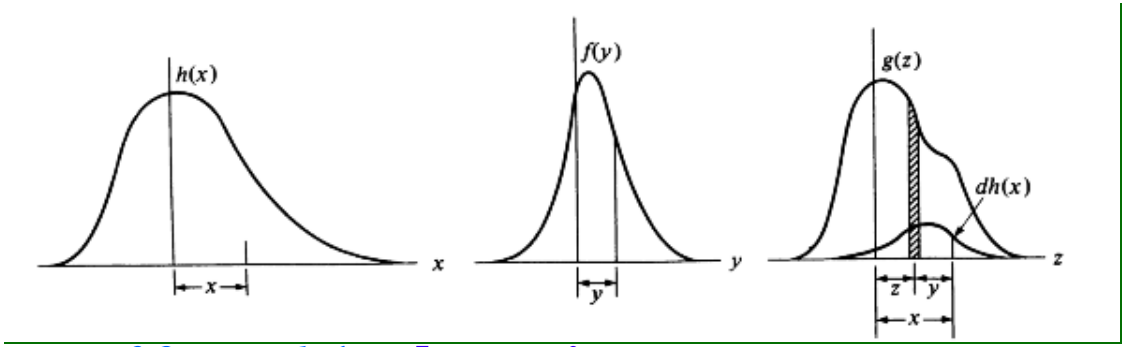
How to Extract This Information?

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

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

$$g(x) = (\omega \star \gamma)(x).$$

$$f(x) = (S \star D)(x).$$



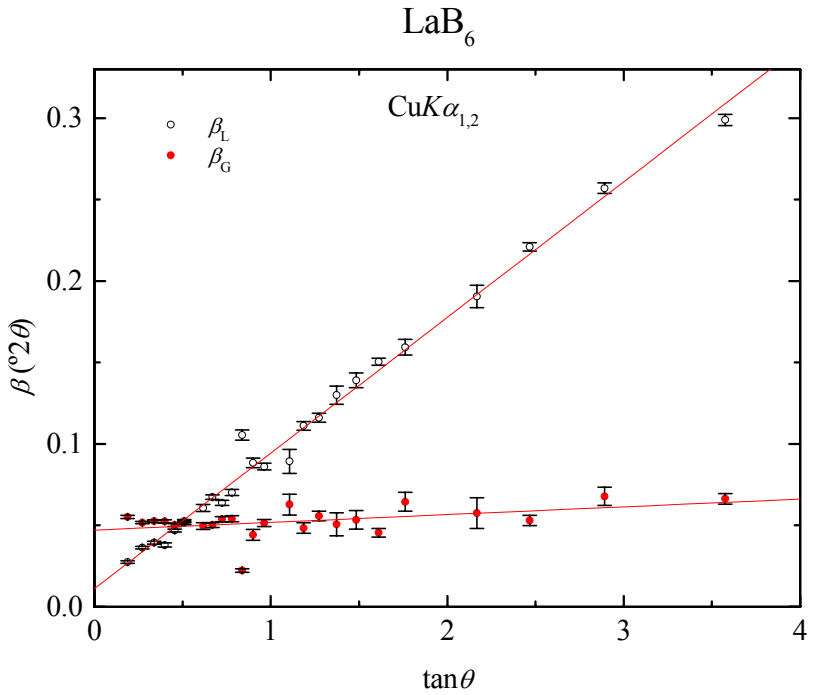
- Task: Extract *f* from *h* by **knowing** *g*:
  - Deconvolution (Stokes): $F(n)=H(n)/G(n)$
  - Convolution (profile fitting): preset **line-profile** function

Instrumental Broadening

- Determining instrumental intrinsic broadening:
  - "Fundamental parameters" approach
  - Measure a suitable material ("Standard")
    - NIST SRM 660a LaB_6

Generally complicated, but...!

Voigt-Function Fits to the LaB_6 Line Profiles



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

$$a = 2\Delta\lambda/\lambda$$

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

Physical Broadening

g known => instrumental-broadening unfolding
f contains physical information => correct!

- Model-independent:
  - Stokes Fourier deconvolution

$$F(n) = H(n)/G(n)$$

+

- unbiased

-

- peak overlap
- unstable
- truncation
- background
- standard

- Model-dependent:
  - Convolution-fitting

$$h(x) = f(x) \bigstar g(x)$$

-

- 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):

$$I(x) = I(0)\left(\frac{\beta}{\beta_C}\right)\ \mathrm{Re}\left[\mathrm{erfi}\left(\frac{\pi^{1/2}x}{\beta_G} + ik\right)\right]\ ;\quad k = \frac{\beta_C}{\pi^{1/2}\beta_G}$$

Experiment

- Ball-milled W (dislocations) → Isotropic strain broadening
- MgO (thermal decomposition of $MgCO_3$) → Isotropic size broadening

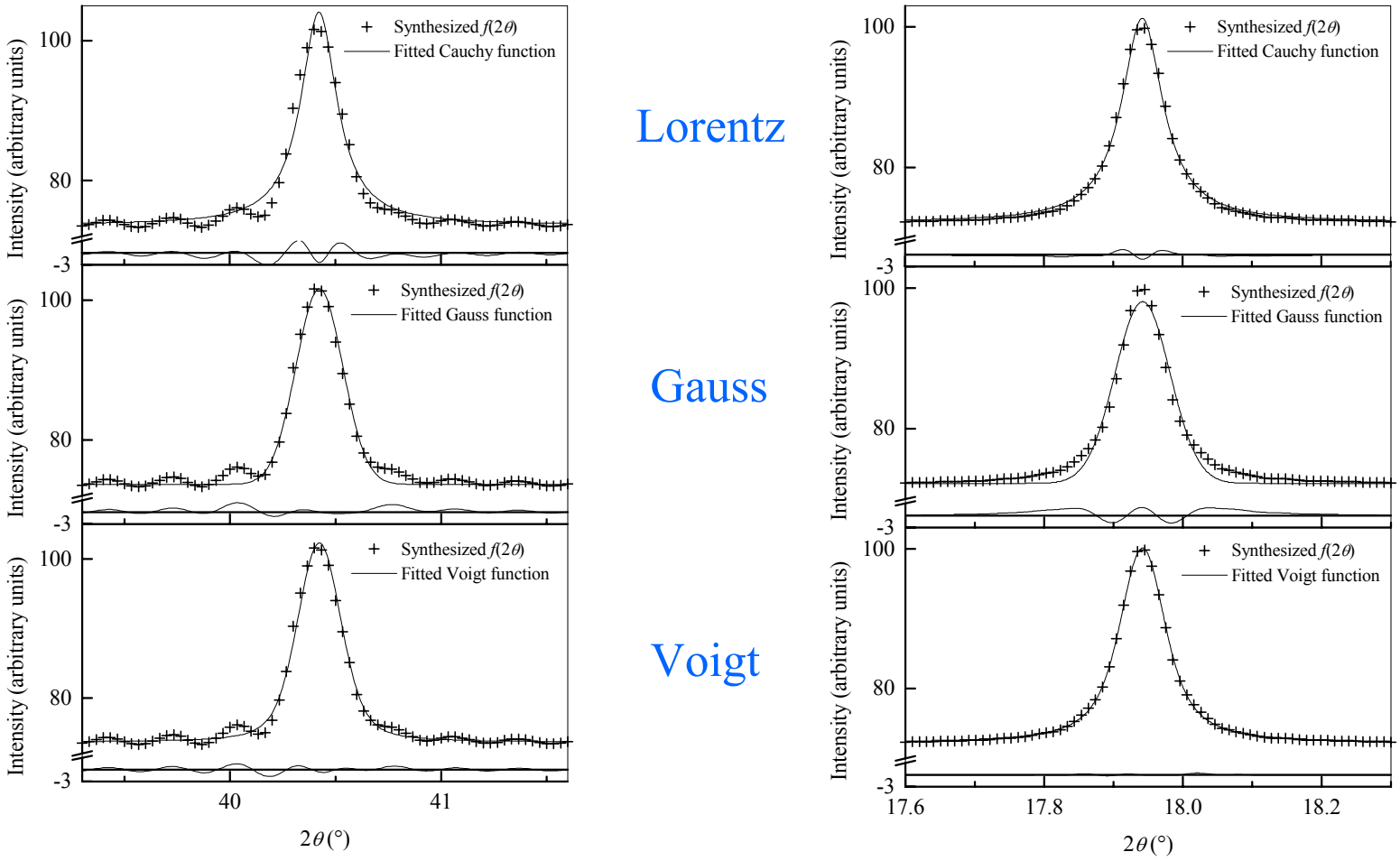
Data analysis

- Stokes method (optimal conditions):
  - non-overlapped lines (220, 400, 422) → Fitting with simple functions
  - MgO annealed as a standard
  - $FWHM_{sp} / FWHM_{st} = 4$

W Line Profiles (110)

Cu $K\alpha_{1,2}$

NSLS



Lorentz

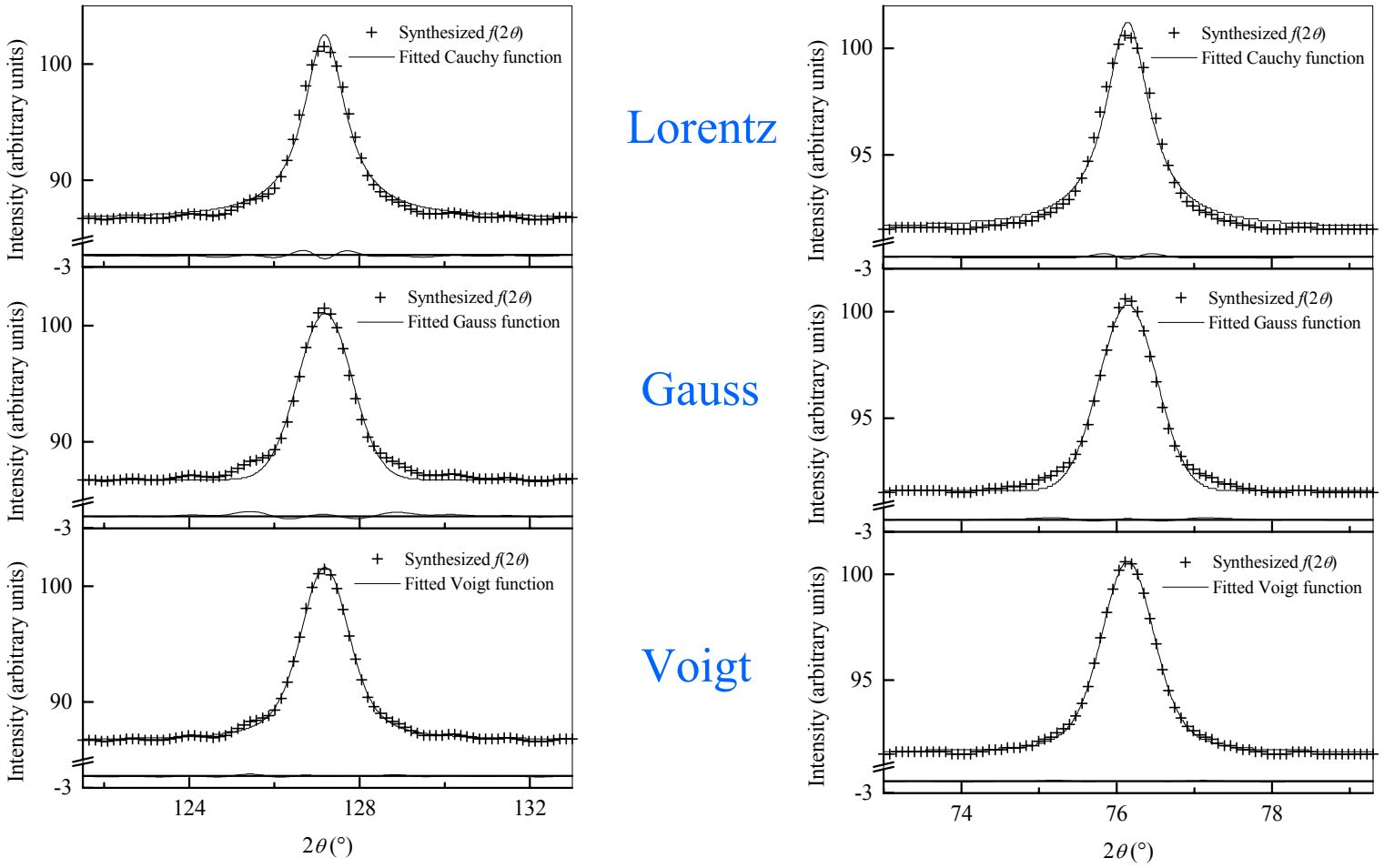
Gauss

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:
  - Krivoglaz-Wilkens theory (Levine & Thomson, 1997, Wu *et a*l., 1999)
  - Warren-Averbach analysis (Balzar & Ledbetter, 1993)
- G✯L = V; V✯V ... V = V (!):
  - Both *S* & *D* profiles ("double-Voigt" model)
    (Langford, 1980; Balzar, 1992)

$$\beta_{\mathrm{L}} = \sum_i (\beta_{\mathrm{L}})_i$$

$$\beta_{\mathrm{G}}^2 = \sum_i (\beta_{\mathrm{G}}{}^2)_i$$

Size-Strain Modeling in Rietveld Refinement

- Size broadening (Scherrer, 1918):

$$\beta_S(2\theta) = \frac{K\lambda}{\langle D \rangle_v \cos\theta}$$

- Strain broadening (Stokes & Wilson, 1944):

$$\beta_D(2\theta) = 4\, e \tan\theta$$

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

$$\Gamma_L = X/\cos\theta + Y\tan\theta + Z$$

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

Physical Significance of the 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* => size parameters
- *Y,U* => strain parameters
- *V,W,Z* => 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:

$$\Gamma_L = X/\cos\theta + Y\tan\theta + Z \qquad \Gamma_L = \gamma_1 d + \gamma_2 d^2 + \gamma_0$$

$$\Gamma_G^2 = P/\cos^2\theta + U\tan^2\theta + V\tan\theta + W \qquad \Gamma_G{}^2 = \sigma_1{}^2 d^2 + \sigma_2{}^2 d^4 + \sigma_0{}^2$$

CW TOF

- Correct for the instrumental broadening:

$$(X,P,U,Y)_{\text{PHYSICAL}} = (X,P,U,Y)_{\text{SAMLE}} - (X,P,U,Y)_{\text{STANDARD}}$$

- Size and strain:

Recombine into Voigt !

$X, P\ (\gamma_2,\ \sigma_2{}^2) \Rightarrow \beta_S \longrightarrow \beta_S(2\theta) = \dfrac{K\lambda}{\langle D\rangle_v \cos\theta}$

$Y, U\ (\gamma_1,\ \sigma_1{}^2) \Rightarrow \beta_D \longrightarrow \beta_D(2\theta) = 4\, e \tan\theta$

Voigt Function in Rietveld Refinement

- FWHM => Integral breadth
  - Voigt function

$$\frac{\beta_L}{\Gamma_L} = \frac{\pi}{2} \qquad \frac{\beta_G}{\Gamma_G} = \frac{1}{2}\sqrt{\frac{\pi}{\ln 2}} \qquad \frac{\beta_G}{\Gamma_G} = \sqrt{2\pi} \quad \text{(GSAS)}$$

$$\beta = \beta_G \frac{\exp(-k^2)}{1-\mathrm{erf}(k)} \qquad k = \frac{\beta_L}{\sqrt{\pi}\,\beta_G}$$

  - Pseudo-Voigt function (TCH)

$$\beta = \frac{\Gamma}{2}\left[\frac{\eta}{\pi} + (1-\eta)\left(\frac{\ln 2}{\pi}\right)^{\frac{1}{2}}\right]^{-1}$$

$$\eta = 1.36603\left(\frac{\Gamma_L}{\Gamma}\right) - 0.47719\left(\frac{\Gamma_L}{\Gamma}\right)^2 + 0.11116\left(\frac{\Gamma_L}{\Gamma}\right)^3$$

$$\Gamma = \left(\Gamma_G{}^5 + 2.69269\Gamma_G{}^4\Gamma_L + 2.42843\Gamma_G{}^3\Gamma_L{}^2 + 4.47163\Gamma_G{}^2\Gamma_L{}^3 + 0.07842\Gamma_G\Gamma_L{}^4 + \Gamma_L{}^5\right)^{\frac{1}{5}}$$

CW

$$D_V = \lambda / \beta^S$$

$$e = \beta^D / 4$$

TOF

$$D_V = DIFC / \beta^S$$

$$e = \beta^D / (2DIFC)$$

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 => comparison difficult !!!

Empirical approach => Round Robin

Published Results

- **The results of the round robin and comparative analysis using three different line-broadening methods were published:**
  - D. Balzar, N. Audebrand, M. Daymond, A. Fitch, A. Hewat, J.I. Langford, A. Le Bail, D. Louër, O. Masson, C.N. McCowan, N.C. Popa, P.W. Stephens, B. Toby, **Size-Strain Line-Broadening Analysis of the Ceria Round-Robin Sample,** *Journal of Applied Crystallography* **37** (2004) 911-924
  - 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

NIST

UNIVERSITY OF DENVER

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

CeO_2

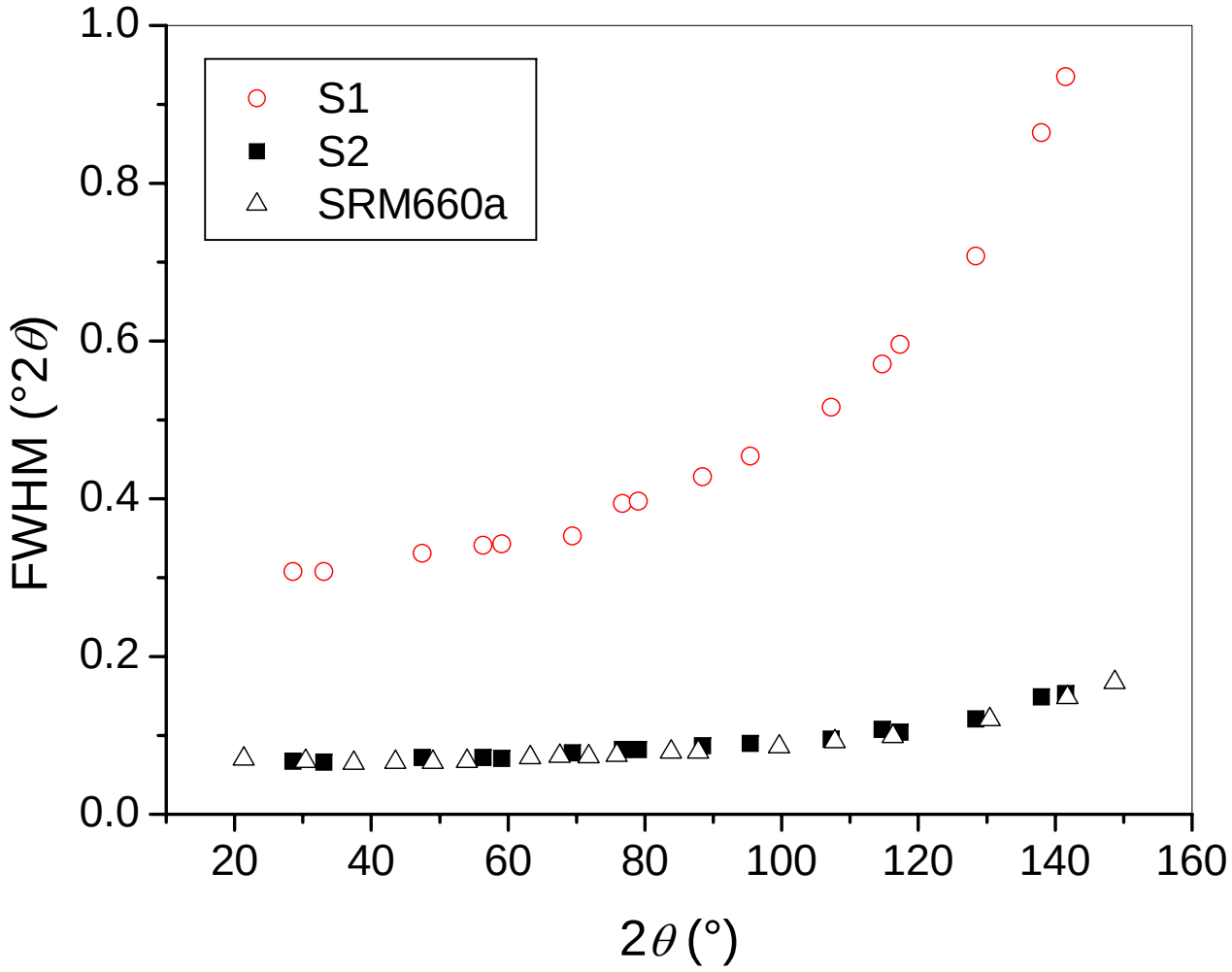
- Sample with broadened lines (University of Rennes)
  - Thermal treatment of hydrated ceria
  - Annealing at 650 °C for 45 h

S1

- Instrumental standard (NIST Boulder)
  - Annealing at 1300 °C for 3 h

S2

Comparison with the New LaB_6 NIST SRM660a

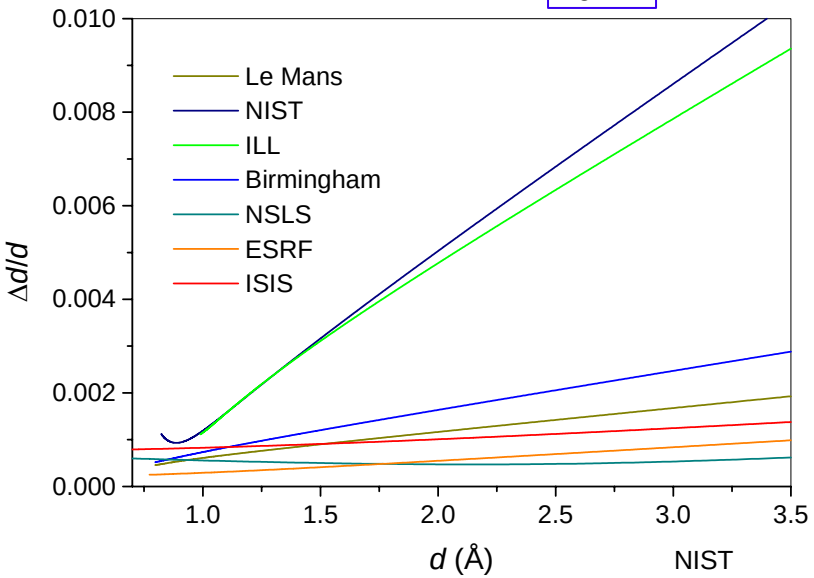


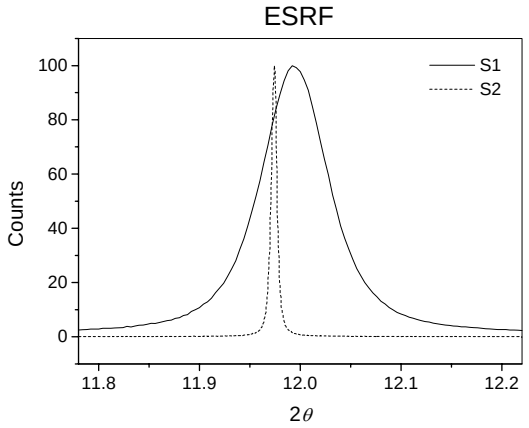
"Representative" Measurements

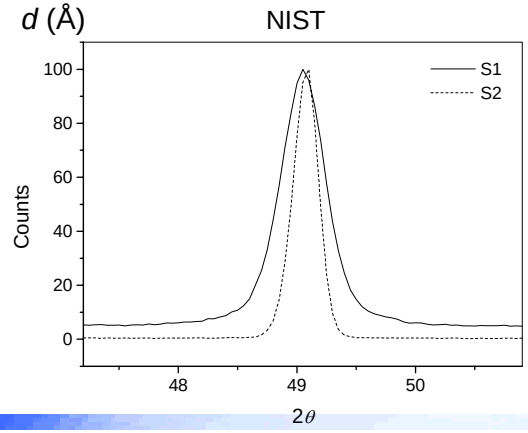
- Laboratory x-ray sources:
  - "Common" instrumental setup: University of Le Mans (Armel Le Bail)
  - Incident-beam monochromator: University of Birmingham (J. Ian Langford)
- Synchrotron sources:
  - 2nd generation, B-B geometry (flat plate): NSLS, Brookhaven National Laboratory (Peter W. Stephens)
  - 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)

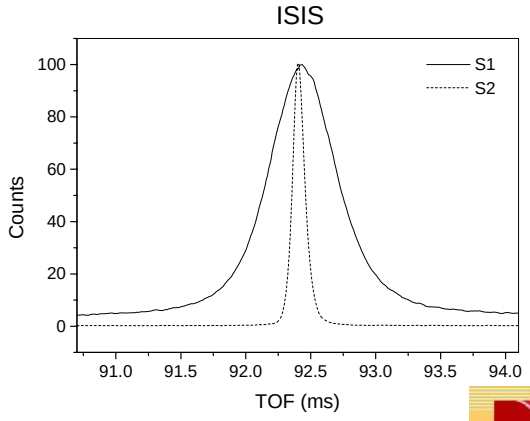
Instrument Resolution

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



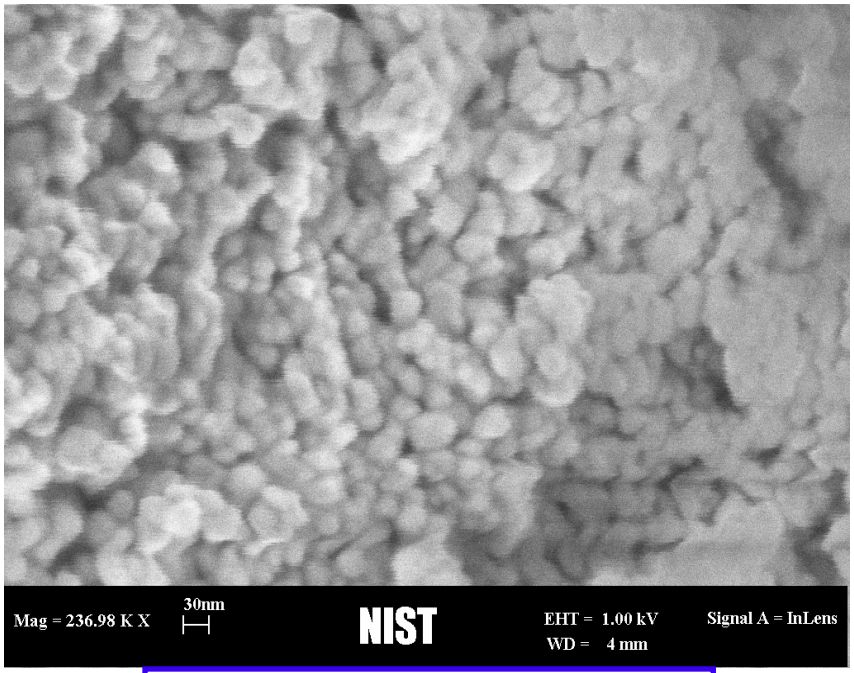




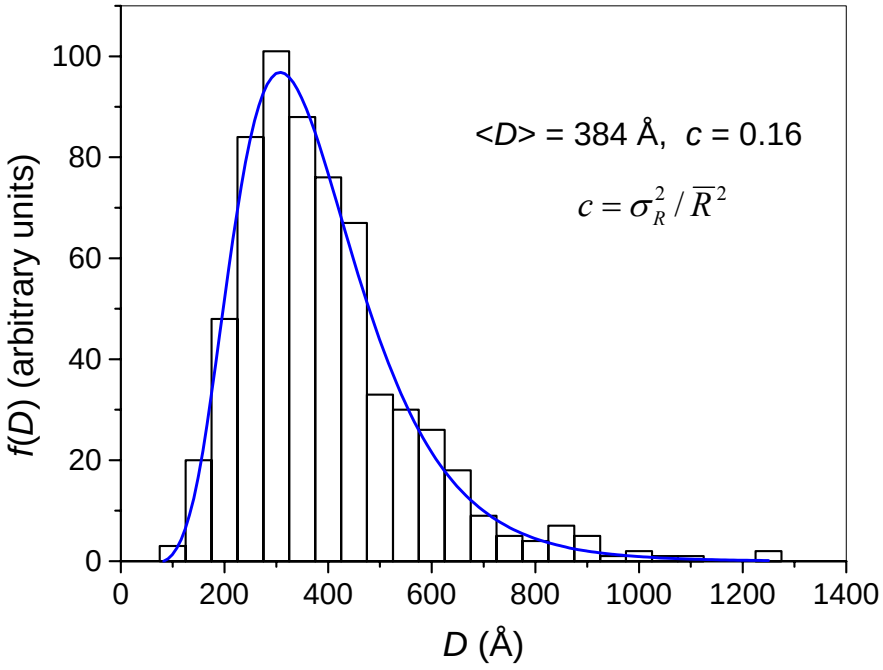


Sample Characterization

- Morphology



FESEM Micrograph



Lognormal size distribution

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

	$\overline{R}$ (Å)	c	D_A (Å)	D_V (Å)
Birmingham	89.0(10)	0.187(5)	167(3)	223(5)
Le Mans	90.9(3)	0.188(2)	171(1)	229(2)
ESRF	90.0(10)	0.192(6)	171(4)	229(6)
NSLS	93.3(7)	0.177(3)	172(2)	228(4)
ILL	93.0(20)	0.173(7)	171(6)	225(9)
NIST	93.0(40)	0.184(15)	174(12)	232(19)
ISIS	91.0(10)	0.191(4)	172(3)	231(5)

Warren-Averbach analysis

	D_A (Å)	D_V (Å)	RMSS (10^{-4})	RMSS = 0	
				D_A (Å)	D_V (Å)
Birmingham	177	238	4.4	159	228
Le Mans	198	241	6.6	181	226
ESRF	195	213	0[1]	187	224
NSLS	196	234	4.1	189	229
ILL	188	228	4.5	176	224
NIST	194	251	7.1	167	230
ISIS	165	248	5.0	177	240

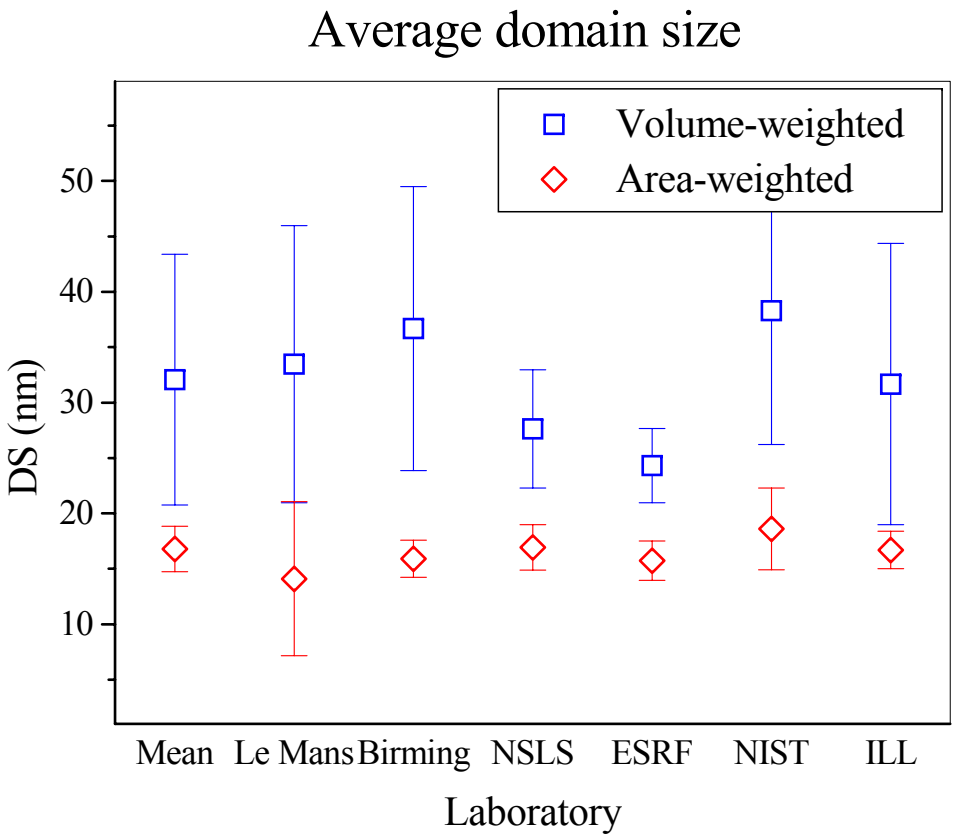
Rietveld refinement

	D_R (Å)	β_G/β_L	e (10^{-4})	$e = 0$[1]
				D_R (Å)
Birmingham	227(3)	0.85(2)	0	227(3)
Le Mans	235(2)	1.01(1)	2.2(1)	224(1)
ESRF	223(1)	0.704(7)	1.5(1)	219(1)
NSLS	236(2)	0.84(1)	2.3(1)	224(1)
ILL	221(3)	0.83(2)	0.1(3)	220(2)
NIST	231(6)	0.74(4)	4.5(8)	216(4)
ISIS	232(1)	0.831(8)	5.5(2)	224(1)

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



RR Average

$D_V = 320(110)$ Å $\quad D_A = 168(21)$ Å

3-way Analysis Average (with strain)

$D_V = 231$ Å $\quad D_A = 179$ Å

RR without significant strain

$D_V = 226(90)$ Å $\quad D_A = 168(21)$ 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 (LaB_6) 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)

$$\Gamma_L = (X + X_e \cos\phi) / \cos\theta + (Y + Y_e \cos\phi) \tan\theta; \qquad \phi = \sphericalangle(\mathrm{H_{hkl}}, \mathrm{A_p})$$

- 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