Line-Profile Analysis and Standards

Davor Balzar

Materials Science and Engineering Laboratory
National Institute of Standards and Technology
and
Physics Department
University of Colorado
Boulder, Colorado

EPDIC-6

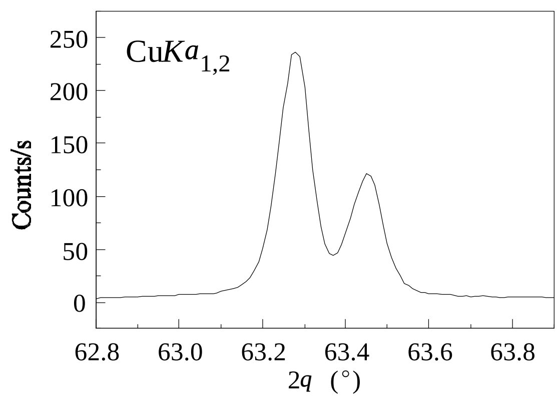
Budapest

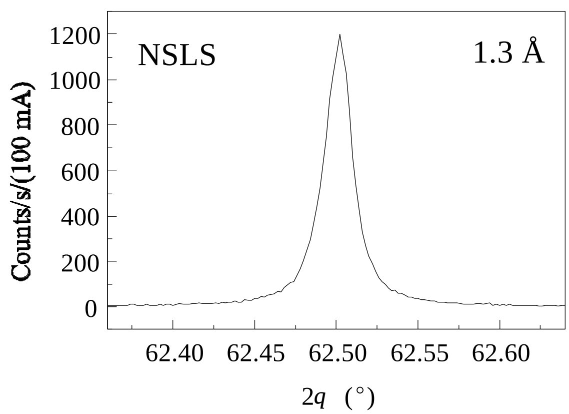
August 25, 1998

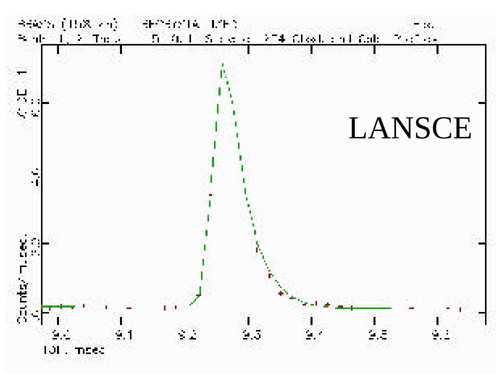
Outline

- 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?







How to obtain the information?

- Both instrument and specimen contributions (Bragg only):

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

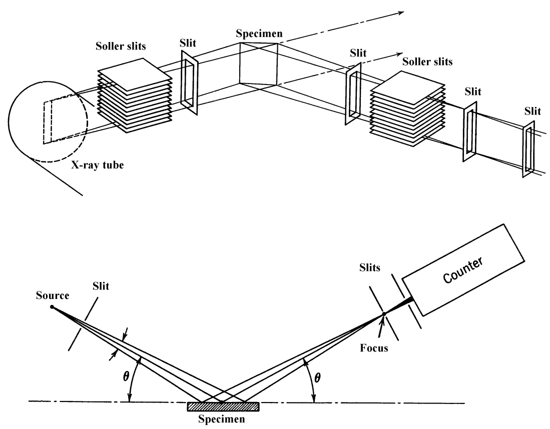
$$g(x) = (\omega \star \gamma)(x).$$

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

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

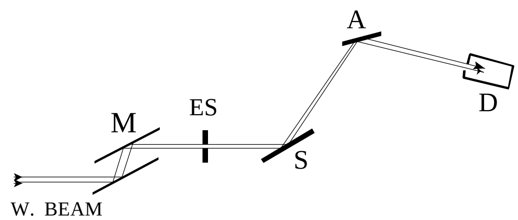
LINE SHAPE & INSTRUMENTAL SIGNATURE

Instrumental line profile



Adapted from Klug and Alexander (1974).

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)

"Fundamental-parameter" approach

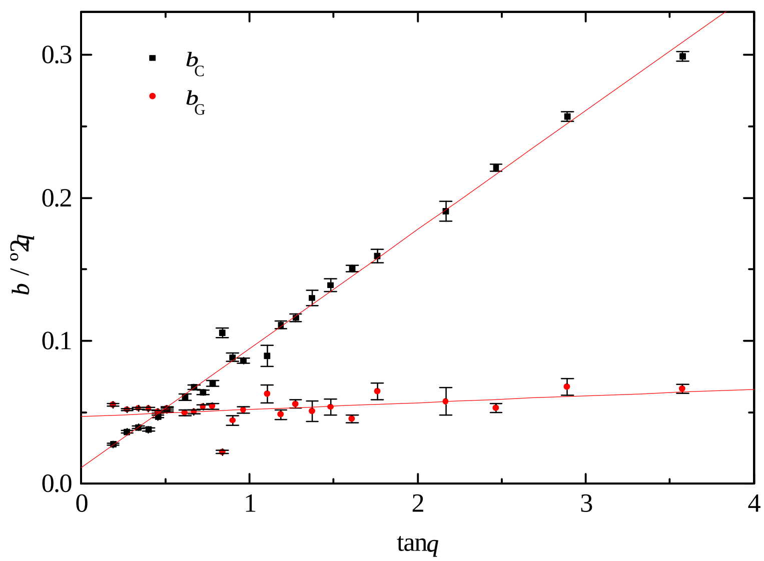
- Advantages:
  - Understanding of a physical background
  - Relative importance of different factors
  - More accurate modeling of profiles?
- Deficiencies:
  - Some contributions cannot be modeled
  - Optical elements imperfect

STANDARDS

Fewer parameters?

	BGMN	KOALARIET
γ	7 L	AF
ω	4 L^2	PV, PVII
S	L	L
D	L^2	G

Voigt-function fits to the LaB_6 line profiles



1st approximation:

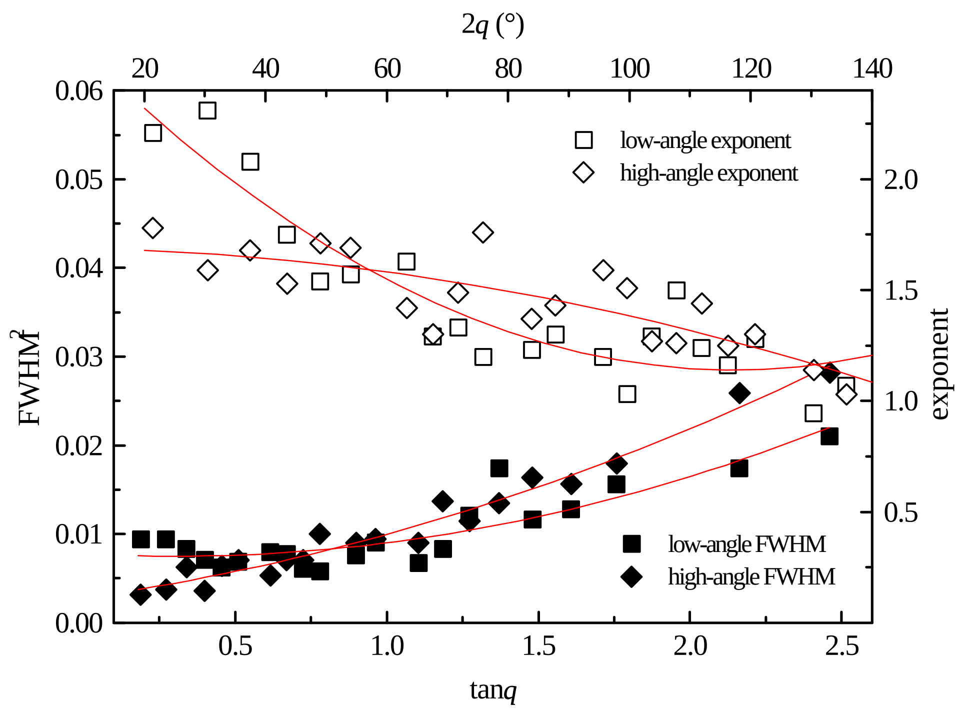
$$\beta_C^g(2\theta) = a \tan\theta \quad ; \quad \beta_G^g(2\theta) = b \ .$$

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

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

Asymmetry

- Exponential, split-Pearson VII:



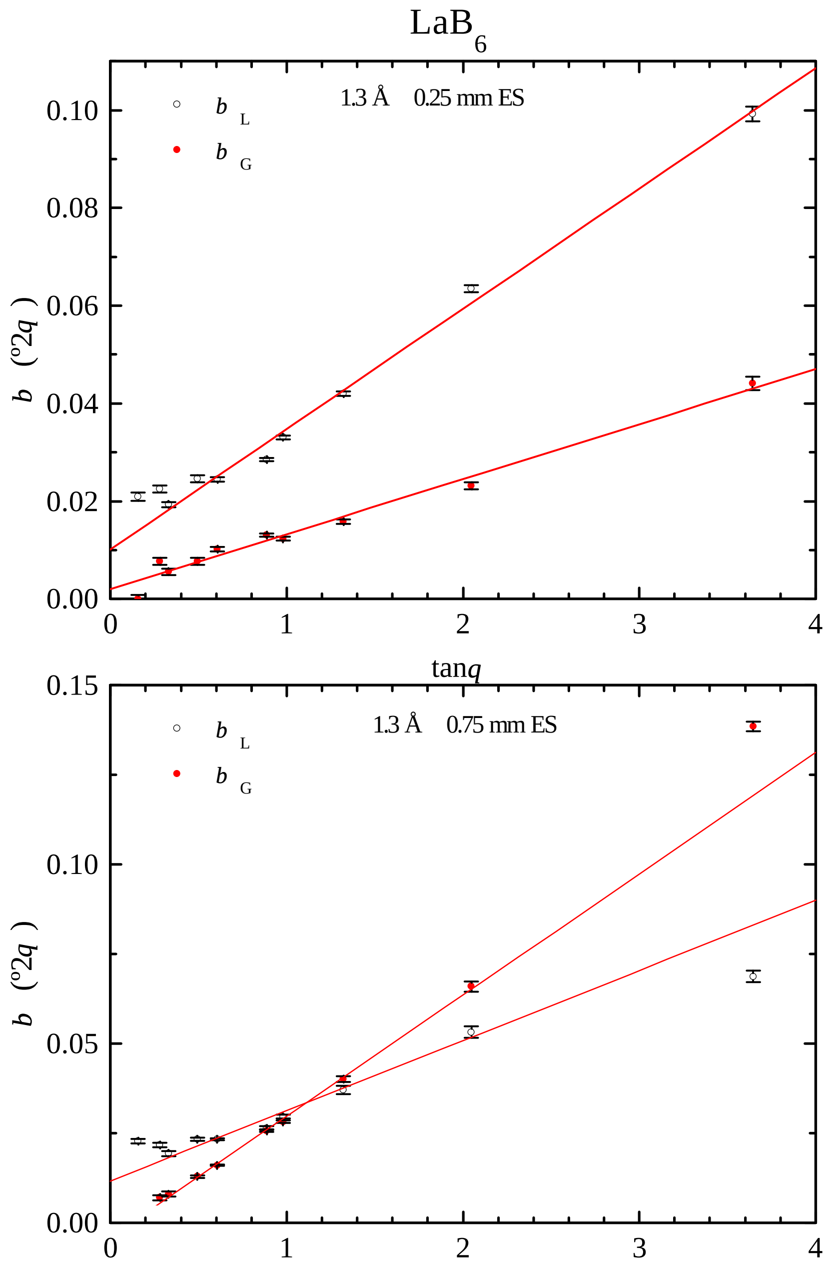
- Axial divergence (Finger *et al*, 1994):

$$D(2\phi,2\theta) = L/2H\ h(2\phi)\cos 2\phi\ W(2\phi,2\theta)$$

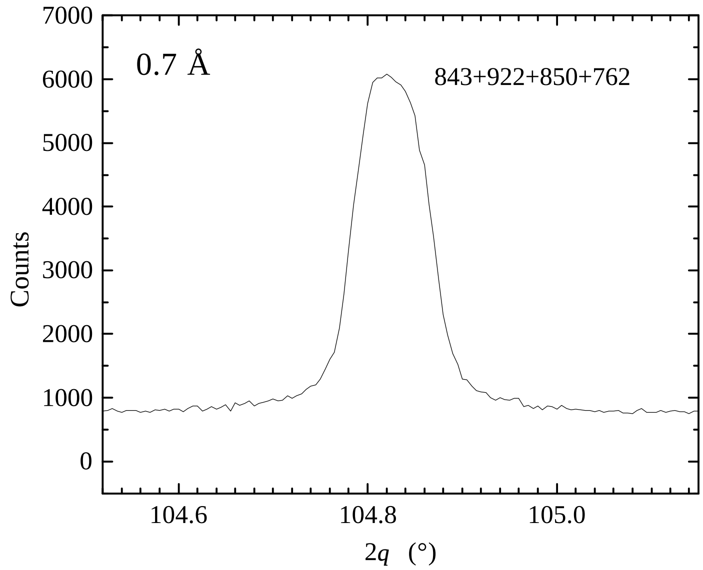
$$h(2\phi) = L\,(\cos^2 2\phi/\cos^2 2\theta - 1)^{1/2}$$

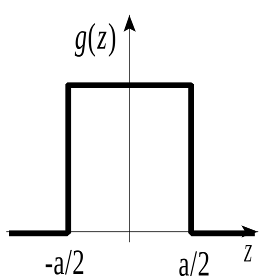
$$W(2\phi,2\theta) = \begin{cases} 0 & 2\phi < 2\phi_{min}\ \ V\ \ 2\phi > 2\theta \\ H + S - h(2\phi) & 2\phi_{min} \le 2\phi < 2\phi_{infl} \\ 2\min(H,S) & 2\phi_{infl} \le 2\phi < 2\theta \end{cases}$$

Synchrotron line profiles



“Super-Gaussian” synchrotron line profile





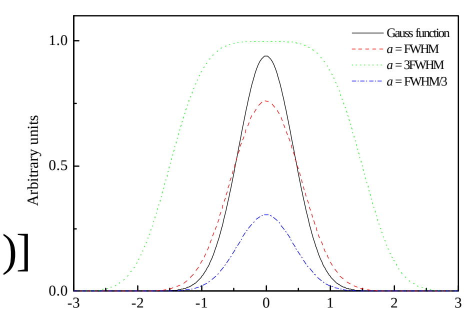
$$g(z) = \begin{cases} 1 & |z| \leq a/2 \\ 0 & |z| > a/2 \end{cases}$$

$$f(z) = C \exp(-b^2 z^2)$$

$$b = \frac{2\sqrt{\ln 2}}{\text{FWHM}}$$

$$f * g \equiv \int_{-a/2}^{a/2} \exp[-b^2 (x-z)^2]\, \mathrm{d}z$$

$$= \frac{\sqrt{\pi}}{2b}\left[\operatorname{erf}\left(b\frac{a}{2} - bx\right) + \operatorname{erf}\left(b\frac{a}{2} + bx\right)\right]$$

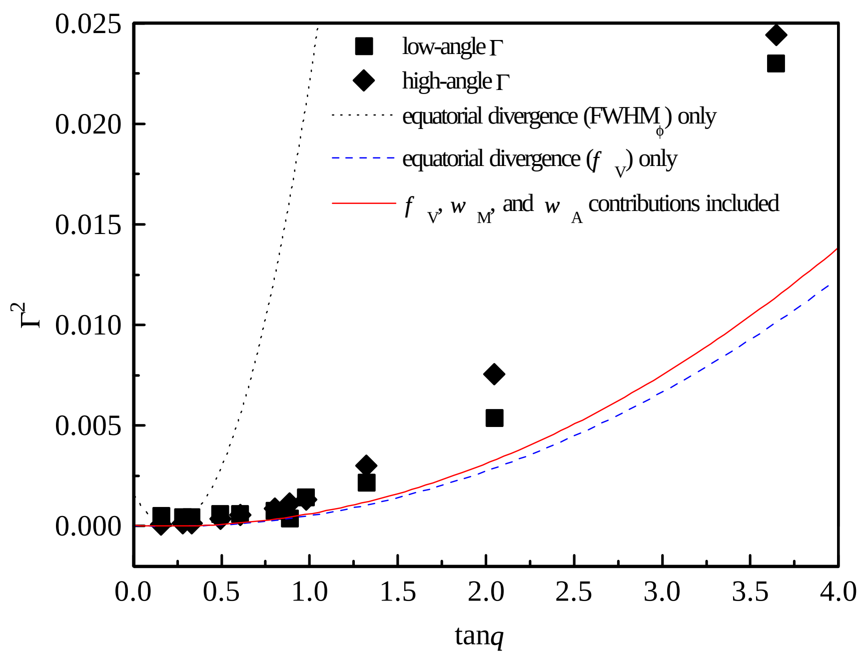


Variance of the profile (mean-square broadening)

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

$$\Gamma^2 \approx \phi^2(2\tan\theta/\tan\theta_M - \tan\theta_A/\tan\theta_M - 1)^2 + (w_{ES}/D_{SS})^2/12$$

$$\mathrm{FWHM}_\phi\,(2.5\ \mathrm{GeV}, 8\ \mathrm{keV}) = 0.0190^\circ;\quad w_{ES}/D_{SS} = 0.0286^\circ$$
$$\omega_M(111\ \mathrm{Si}, 8\ \mathrm{keV}) = 0.0021^\circ;\quad \omega_A(111\ \mathrm{Ge}, 8\ \mathrm{keV}) = 0.0045^\circ$$



$$g_M(z) = s^2/[z \pm (z^2 - s^2)^{1/2}]^2$$

“Standards” against Standards

- Common (“uncertified” or “nonstandarized”) materials:
  - W, Ag, Si,…
  - BaF_2, KCl,...
- NIST SRMs:
  - Si (640a,b,c)
  - LaB_6 (660 a)
  - Al_2O_3 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

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

+

- unbiased

-

- peak overlap
- unstable
- truncation
- background
- standard

- Model-dependent:
  - Convolution-fitting

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

-

- biased

+

- fast and easy
- stable
- suitable for RR

"Good" analytical function (if exists)

Simple analytical functions

- Gauss

$$G(x) = I(0)\ \exp\ (-\pi x^2/\beta_G^2)$$

- Lorentz (Cauchy)

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

- Voigt (G★L)

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

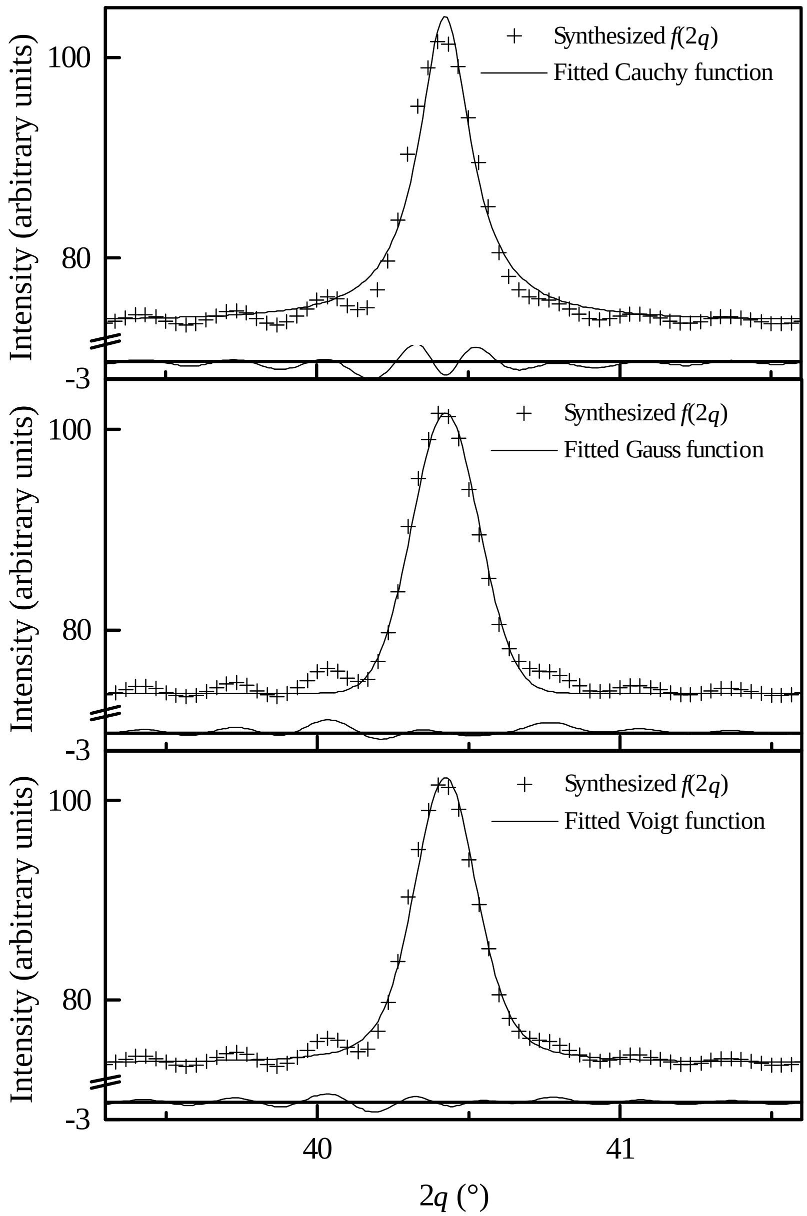
Experiment

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

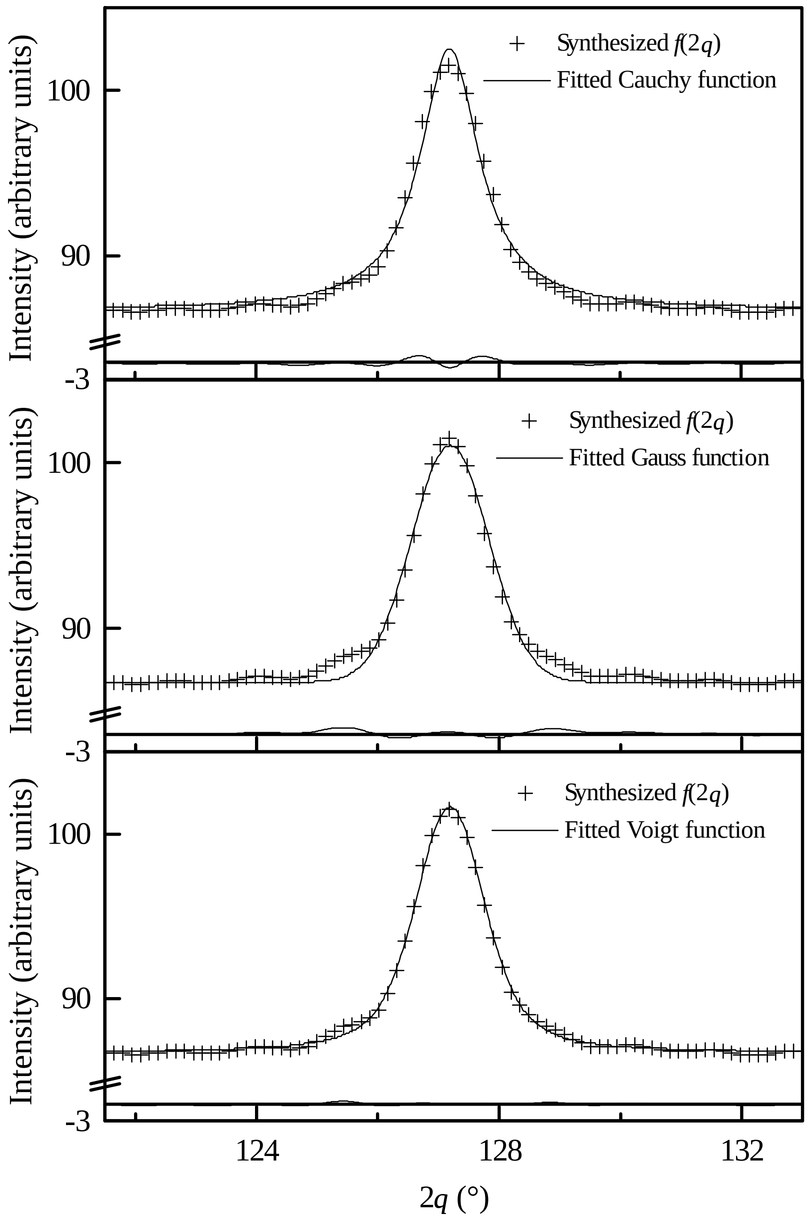
Data analysis

- Stokes method (optimal conditions):
  - non-overlapped lines (220, 400, 422)
  - MgO annealed as a standard
  - $FWHM_{sp}/FWHM_{st}=4$
- Convolution-fitting (optimal conditions):
  - ***g*** (SPVII fit to standard's profiles)
  - ***f*** (preset exact Voigt)

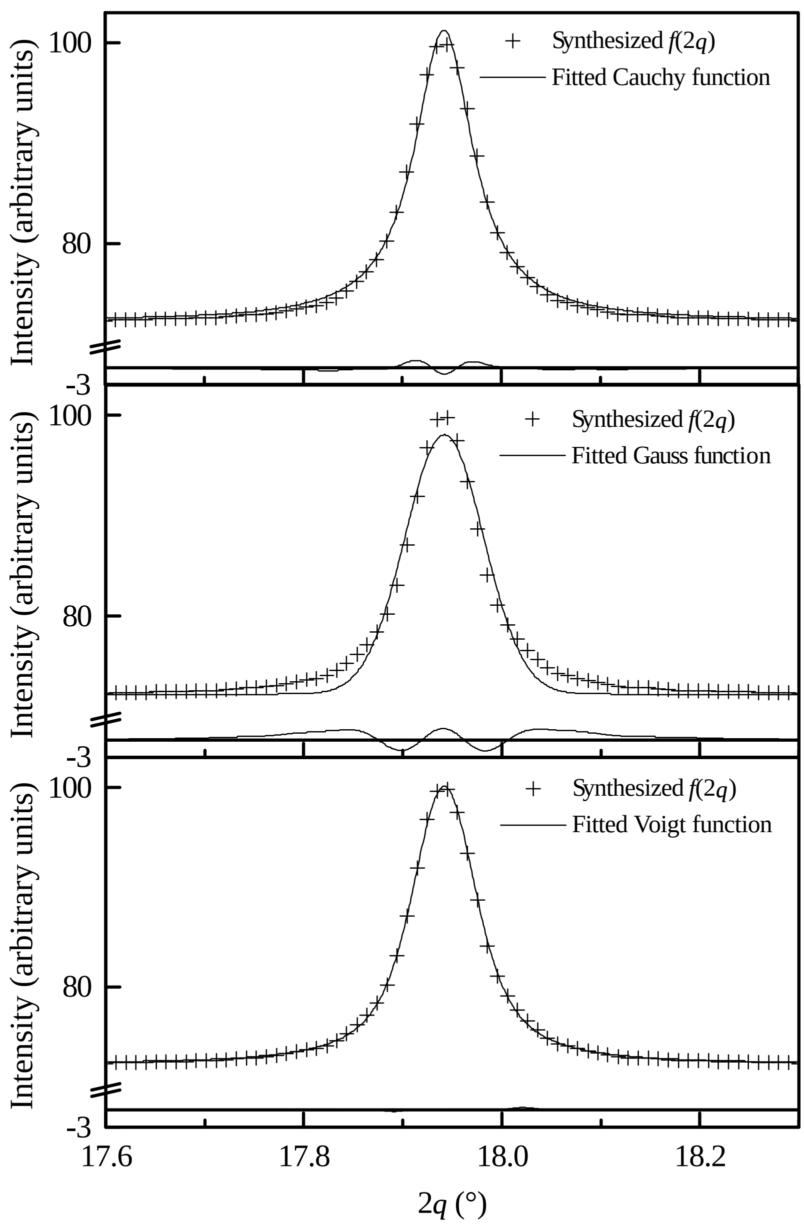
110 W (Cu K$\alpha_{1,2}$)



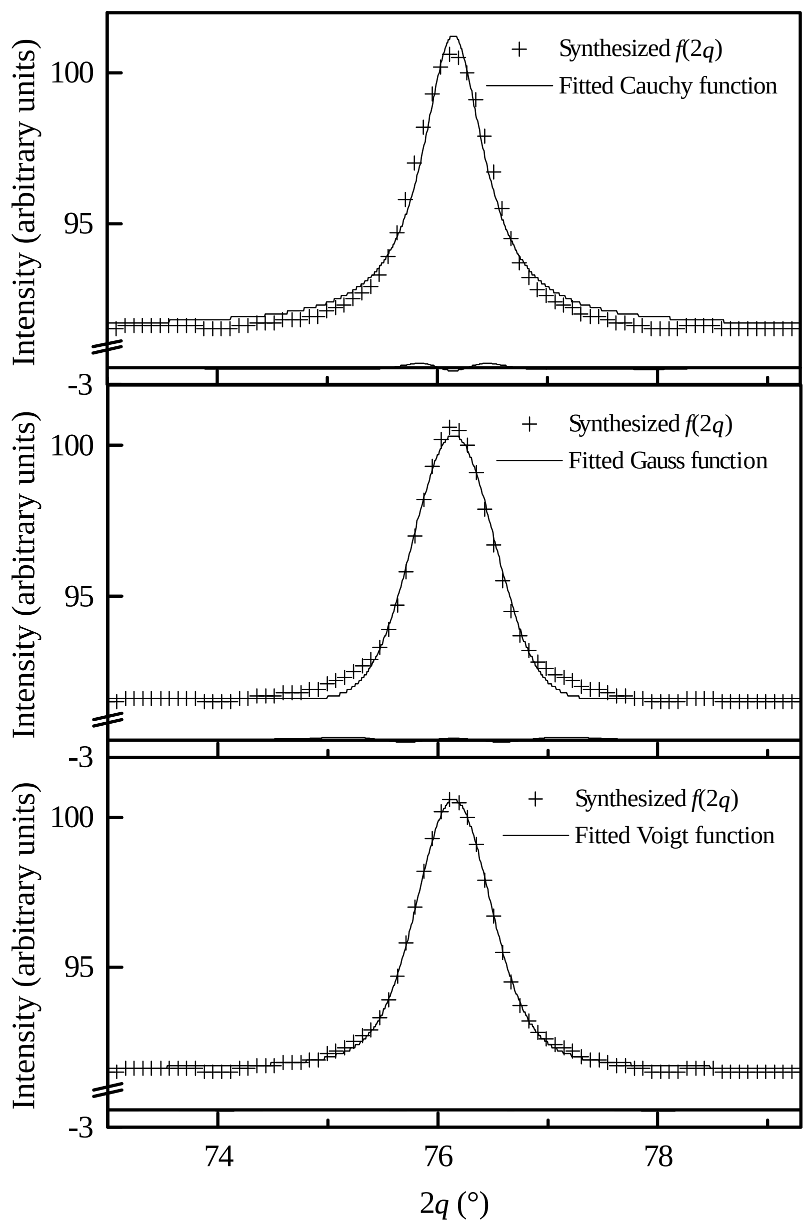
422 MgO (Cu K$\alpha_{1,2}$)



110 W (synchrotron)



400 MgO (synchrotron)



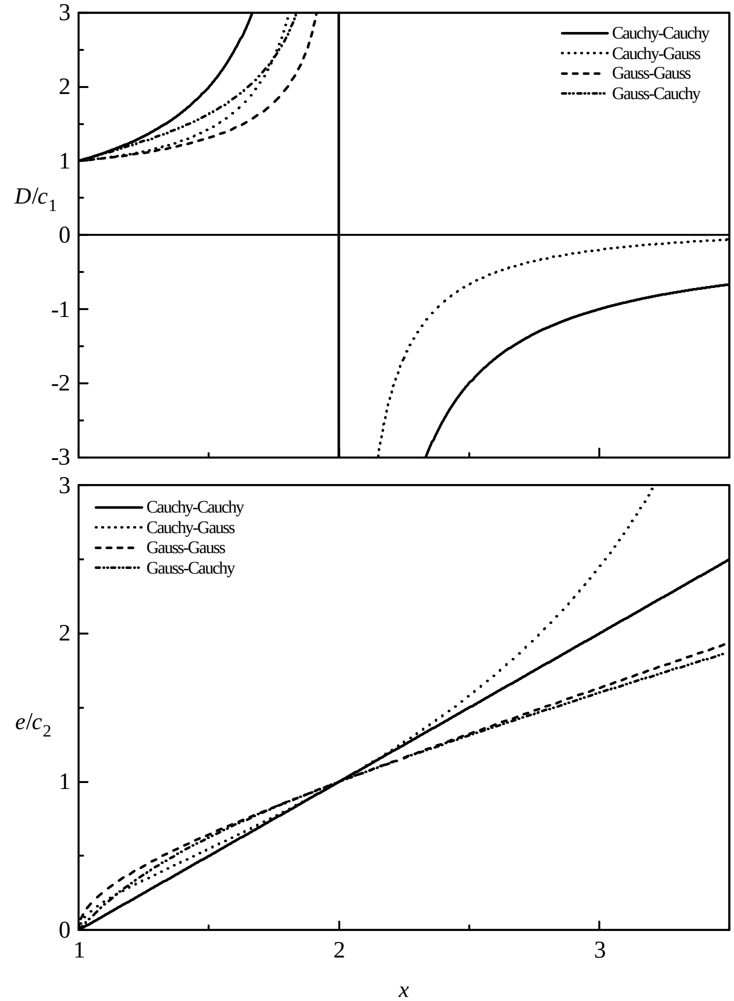
Physical broadening modeled by a Voigt function

- Other experimental evidence
  - Pressed Ni-powder (least-squares deconvolved) (Suortti *et al.*, 1979)
  - Chlorite (Ergun's iterative unfolding) (Reynolds, 1989)
- Theoretical evidence:
  - Krivoglaz-Wilkens theory (Levine & Thomson, 1997, Wu *et al.*, in press)
  - Warren-Averbach analysis (Balzar & Ledbetter, 1993)
- G★L = V; V★V ... V = V (!):
  - Both *S* & *D* profiles ("double-Voigt" model) (Langford, 1980; Balzar, 1992)

$$\beta_L = \sum_i (\beta_L)_i$$

$$\beta_G^2 = \sum_i (\beta_G{}^2)_i$$

Integral-breadth methods



$x = \beta_2/\beta_1$

$s_2 = 2s_1$

$c_1 = 1/\beta_1$

$c_2 = \beta_1/(2s_1)$

$$\beta = \frac{1}{\langle D\rangle_v} + 2es \qquad \text{(Cauchy-Cauchy)}$$

$$\beta = \frac{1}{\langle D\rangle_v} + \frac{4e^2s^2}{\beta} \qquad \text{(Cauchy-Gauss)}$$

$$\beta^2 = \frac{1}{\langle D\rangle_v^2} + 4e^2s^2 \qquad \text{(Gauss-Gauss)}$$

$$\beta^2 = \frac{1}{\langle D\rangle_v^2} + 2es\beta \qquad \text{(Gauss-Cauchy)}$$

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?

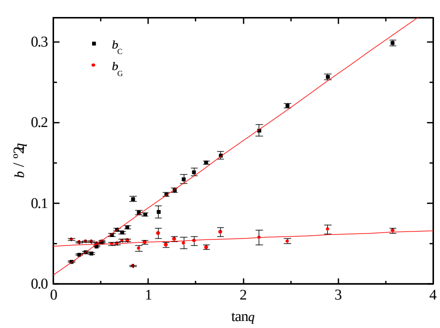
$$\Gamma_L = X/\cos\theta + Y\tan\theta + Z$$

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

- *X*,*P* => size parameters
- *Y*,*U* => strain parameters
- *V*,*W*,*Z* => instrumental contribution !?

Recombine into Voigt !

- *Y*,*W* sufficient for approximate results with laboratory data



- More parameters with synchrotron and neutron data (*Y*,*W*,*V*,*U*)

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)

$$\Gamma_L = (X + X_e \cos\phi)/\cos\theta + (Y + Y_e \cos\phi)\tan\theta; \quad \phi = \sphericalangle(\mathbf{H}_{hkl}, \mathbf{A}_p)$$

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

Voigt strain-broadened profile

$$\Gamma_L = X/\cos\theta + Y\tan\theta + \zeta\Gamma_A(hkl)$$

$$\Gamma_G^2 = P/\cos^2\theta + U\tan^2\theta + V\tan\theta + W + (1-\zeta)^2\Gamma_A^2(hkl)$$

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

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

ITERATION!

Gauss strain + Lorentz size broadened profile

Physical background

- Stephens & Popa's strain model

  <=>

  Stokes & Wilson (1944) approach !

$$\Gamma = \left[A + B \frac{h^2k^2 + k^2l^2 + h^2l^2}{(h^2+k^2+l^2)^2} \right]^{1/2} \tan\theta$$

  and

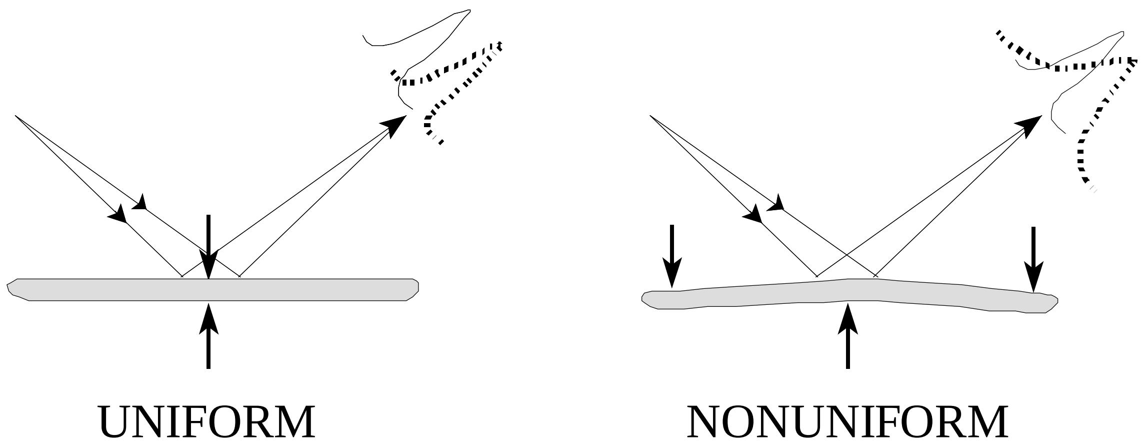
  Groma, Ungár & Wilkens (1988) microscopic line-broadening theory

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

Reuss approximation

- Other (Voigt, Hill, Eshelby-Kröner)?

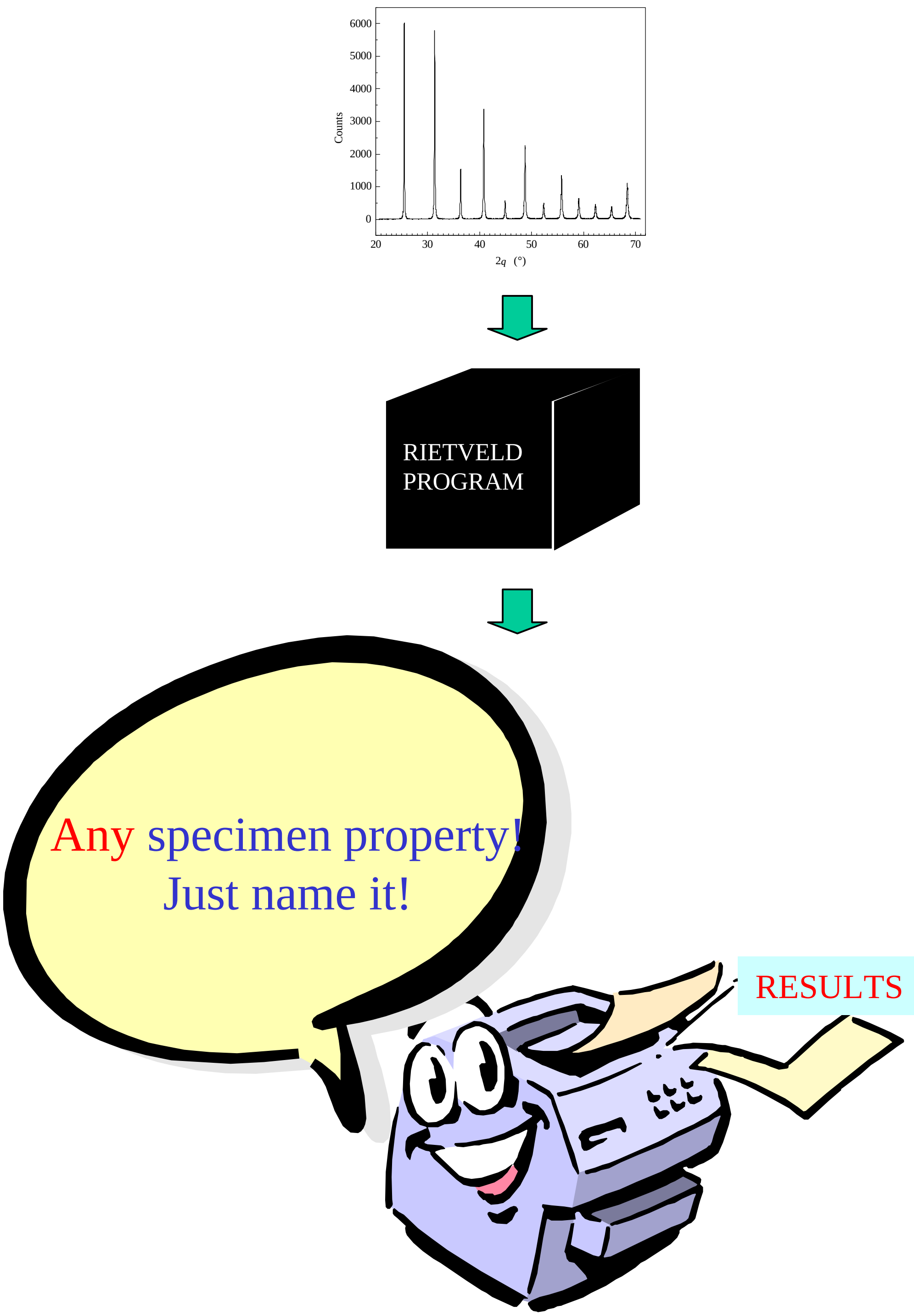
Strains of I and II kind and texture in Rietveld refinement



After J. B. Cohen

- 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)

Future ?



6000
5000
4000
3000
2000
1000
0
Counts
20
30
40
50
60
70
2q (°)
RIETVELD
PROGRAM
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
  - ?

- balzar@nist.gov

Web page