



Line Broadening Analysis

- ◆ Deviations from ideal crystallinity, such as finite crystallite size and strain (at the atomic level) lead to broadening of the diffraction lines. By analyzing this broadening it is possible to extract information about the microstructure of a material. This presentation covers:
 - ◆ Sources of Line Broadening
 - Instrumental Broadening
 - Crystallite Size Broadening
 - Strain Broadening
 - ◆ Methods of Analysis
 - Simplified Integral Breadth Methods
 - Fourier Methods
 - Double Voigt Methods

References

Much of my material was drawn from the following literature and web references

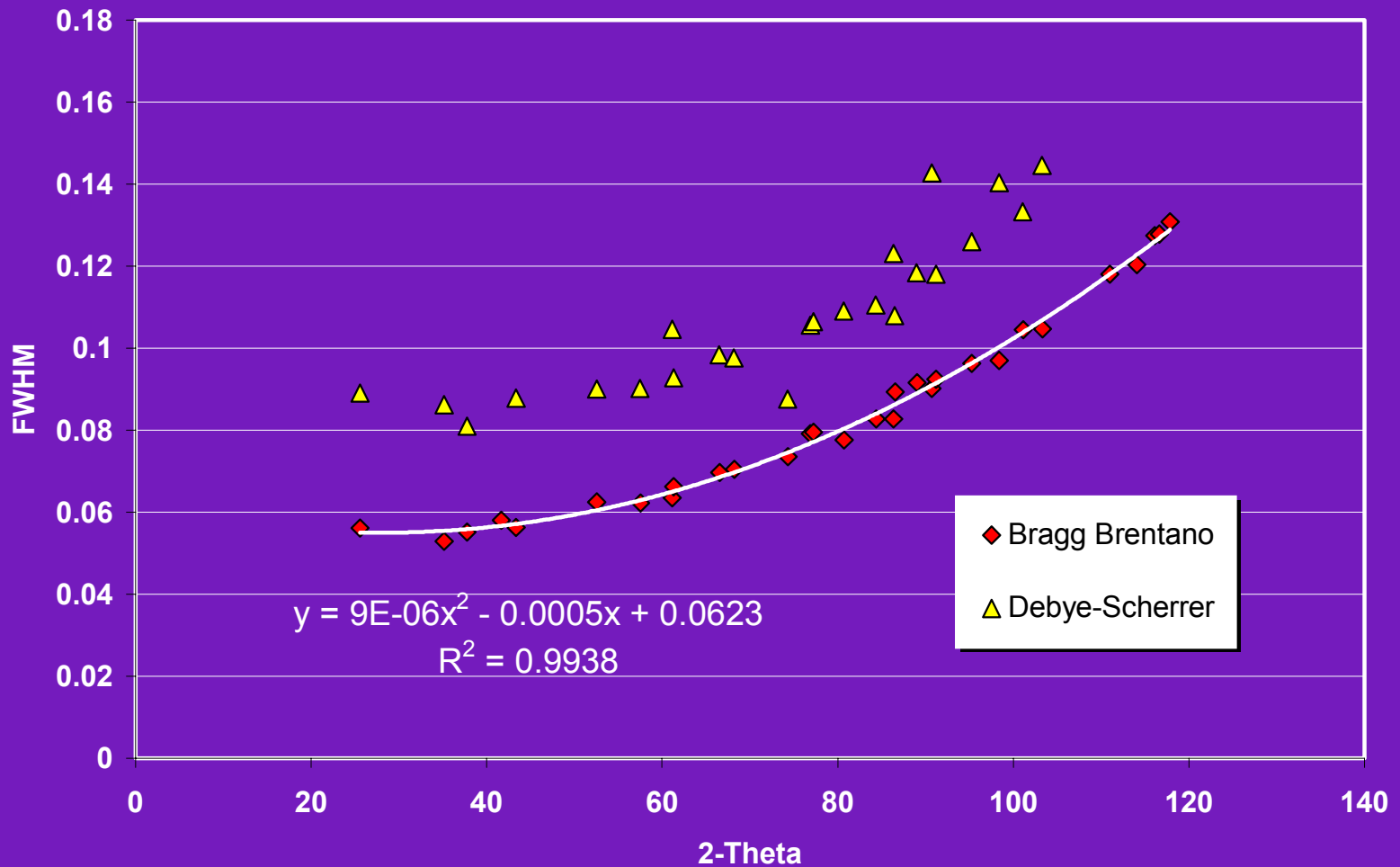
- ◆ **Davor Balzar's Web Site**
<http://www.boulder.nist.gov/div853/balzar/>
- ◆ ***"Crystal Imperfection broadening and peak shape in the Rietveld Method"*** R. Delhez, T.H. Keijser, J.I. Langford, D. Louer, E.J. Mittemeijer, & E.J. Sonneveld, in *"The Rietveld Method"* edited by R.A. Young, IUCr Monograph #5, Oxford University Press, Ch. 8 (1993)
- ◆ ***"Modern Powder Diffraction"*** S.A. Howard & K.D. Preston, (edited by D.L. Bish and J.E. Post), Reviews in Mineralogy, Vol. 20, Mineralogical Society of America, Ch. 8 (1989).
- ◆ ***"Liquid-Mix Disorder in Crystalline Solids: ScMnO₃"***
P. Karen & P.M. Woodward, *J. Solid State Chem.* **141**, 78-88 (1998).



Sources of Line Broadening

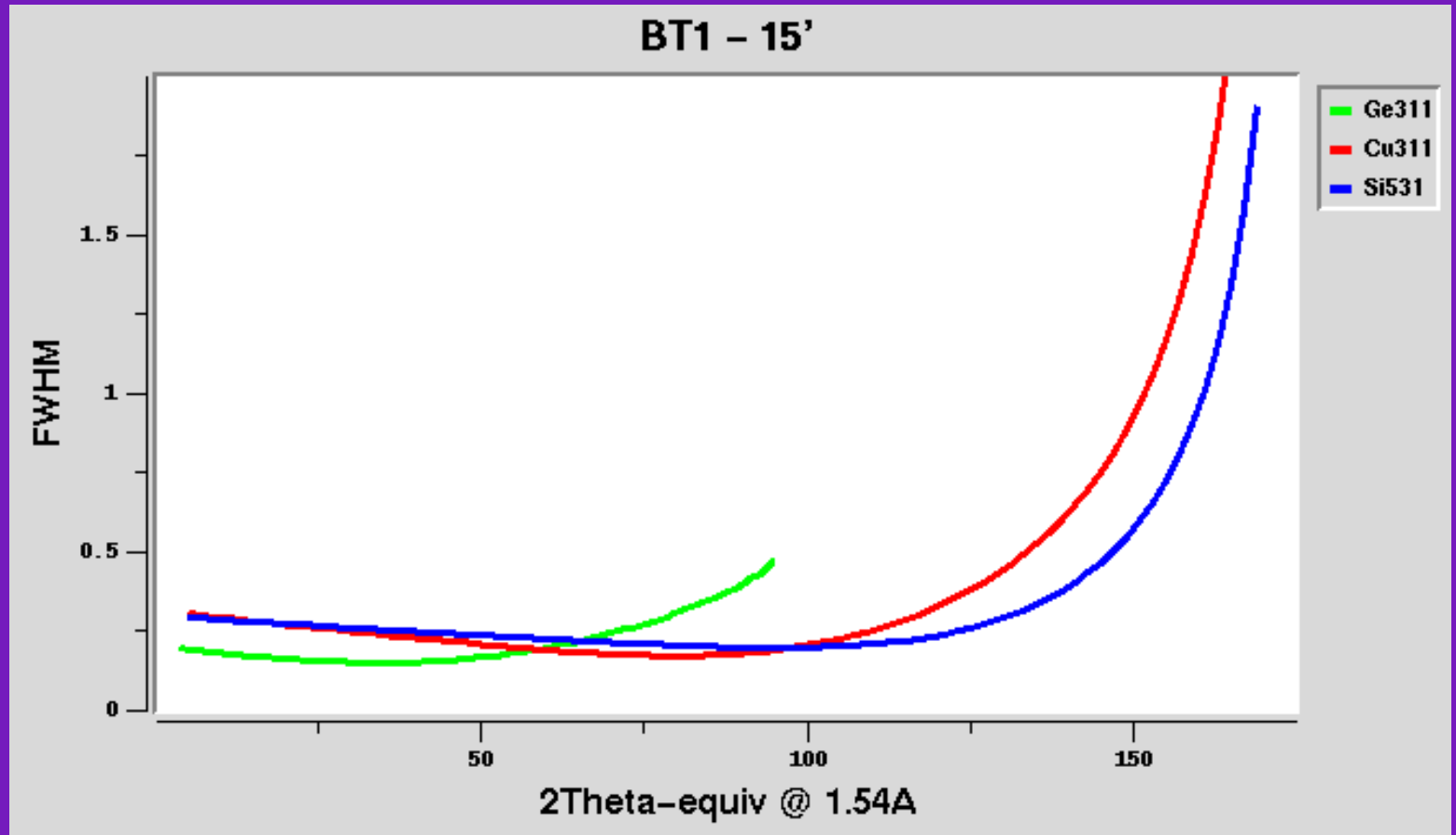
- ◆ **Instrumental Broadening**
 - **Non ideal optics**
 - **Wavelength Dispersion**
 - **Sample Transparency**
 - **Axial Divergence**
 - **Flat Sample Effect**
 - **Detector resolution (area det. & PSD's)**
- ◆ **Finite Crystallite Size**
- ◆ **Extended Defects**
 - **Stacking Faults**
 - **Antiphase Boundaries**
- ◆ **Lattice Strain (microstrain)**

Typical Instrumental Broadening



This data corresponds to a Bruker D8 Diffractometer, equipped with an incident beam Ge monochromator and Braun Position Sensitive Detector (masked to use $\sim 4^\circ 2\theta$)

Typical Instrumental Broadening



This data corresponds to a High Resolution Powder Neutron Diffractometer located on Beamline BT1 at NIST. See http://www.ncnr.nist.gov/instruments/bt1/bt1_for_xtal.html for more information.

Finite Crystallite Size

- ◆ A perfect crystal would extend in all directions to infinity, so we can say that no crystal is perfect due to its finite size. This deviation from perfect crystallinity leads to a broadening of the diffraction peaks. However, above a certain size ($\sim 0.1 - 1$ micron) this type of broadening is negligible.
- ◆ Crystallite size is a measure of the size of a coherently diffracting domain. Due to the presence of polycrystalline aggregates **crystallite size is not generally the same thing as particle size.**
- ◆ Other techniques for measuring size, measure the particle size rather than the crystallite size
 - BET
 - Light (Laser) Scattering
 - Electron Microscopy (SEM)

Extended Defects

- ◆ Extended defects disrupt the atomic arrangement of a crystal, typically along a 2D plane. These defects effectively terminate a crystallographically ordered domain of the crystal. Thus as far as x-rays are concerned one crystal ends and a new crystal begins at the extended defect.
- ◆ Crystallite size analysis on a sample containing extended defects can be used to estimate the ordered domain size (the size of the region between defects) in the same manner that XRD is used to determine crystallite size.
- ◆ Types of extended defects
 - Stacking faults (ABCABCBCBACBACBA...)
 - Dislocations in "layered" materials (graphite, MoS_2 , clays, ZrNCl , etc.)
 - Antiphase boundaries, which arise in partially ordered materials (Cu_3Au , $\text{Sr}_2\text{AlTaO}_6$)



Lattice Strain (Microstrain)

- ◆ Strain is a term used more often in engineering than in chemistry. Strain is defined as the deformation of an object divided by its ideal length, $\Delta d/d$. In crystals there we can observe two types of strain
 - Uniform strain
 - Non-uniform strain
- ◆ Uniform strain causes the unit cell to expand/contract in an isotropic way. This simply leads to a change in the unit cell parameters and shift of the peaks. There is no broadening associated with this type of strain.
- ◆ Non-uniform strain leads to systematic shifts of atoms from their ideal positions and to peak broadening. This type of strain arises from the following sources:
 - Point defects (vacancies, site-disorder)
 - Plastic deformation (cold worked metals, thin films)
 - Poor crystallinity

Accurate Size Range

- ◆ Line broadening analysis is most accurate when the broadening due to crystallite size effects is at least twice the contribution due to instrumental broadening. If we use this criterion we can calculate the size range over which this technique will be the most accurate. We could also estimate a rough upper limit for reasonable accuracy by looking at the crystallite size that would lead to broadening equal to the instrumental broadening.
 - **Conv. Diffractometer (FWHM $\sim 0.10^\circ$ at $20^\circ 2\theta$)**
 - Accurate Size Range < 45 nm (450 Å)
 - Rough Upper Limit = 90 nm (900 Å)
 - **Monochromatic Lab X-ray (Cu K_α FWHM $\sim 0.05^\circ$ at $20^\circ 2\theta$)**
 - Accurate Size Range < 90 nm (900 Å)
 - Rough Upper Limit = < 180 nm (1800 Å)
 - **Synchrotron ($\lambda = 0.8$ Å, FWHM $\sim 0.01^\circ$ at $20^\circ 2\theta$)**
 - Accurate Size Range < 233 nm (2330 Å)
 - Rough Upper Limit = 470 nm (4700 Å)
 - **High Res. Neutron ($\lambda = 1.54$ Å, FWHM $\sim 0.25^\circ$ at $20^\circ 2\theta$)**
 - Accurate Size Range < 18 nm (180 Å)
 - Rough Upper Limit = 36 nm (360 Å)

Measures of Line Broadening

- ◆ The width of a diffraction line can be estimated by more than one criterion. The two most common width parameters are:
 - Full Width at Half Maximum (FWHM or Γ) - The width of the peak at 1/2 its maximum intensity.
 - Integral Breadth (β)- The width of a rectangle with the same height and area as the diffraction peak.
- ◆ Most profile fitting programs give FWHM, but for accurate size-strain broadening one should use integral breadth as a measure of the peak width.
- ◆ The integral breadth (β) and FWHM (Γ) can be related for various peak shapes
 - Lorentzian $\rightarrow \beta = (\pi/2) \Gamma$
 - Gaussian $\rightarrow \beta = \{\pi/(4 \ln 2)\}^{1/2} \Gamma$
 - Voigt, Pseudo-Voigt \rightarrow See Delhez et al., in "The Rietveld Method" ed. by R.A. Young, Oxford Science (1993).

Size Broadening

- ◆ Scherrer (1918) first observed that small crystallite size could give rise to line broadening. He derived a well known equation for relating the crystallite size to the broadening, which is called the “Scherrer Formula”

$$D_v = K\lambda / \{\beta \cos \theta\}$$

- ◆ D_v = Volume Weighted crystallite size
- ◆ K = Scherrer constant, somewhat arbitrary value that falls in the range 0.87-1.0. I usually assume $K = 1$.
- ◆ λ = The wavelength of the radiation
- ◆ β = The integral breadth of a reflection (in radians 2θ) located at 2θ .

Strain Broadening

- ◆ Stokes and Wilson (1944) first observed that strained or imperfect crystals containing line broadening of a different sort, than the broadening that arises from small crystallite size.

$$\varepsilon_{\text{str}} = \beta / \{4 \tan \theta\}$$

- ◆ ε_{str} = weighted average strain
- ◆ β = The integral breadth of a reflection (in radians 2θ) located at 2θ .
- ◆ Note that “size” and “strain” broadening show a different θ dependence. This provides a way to separate the two effects.

Correcting for Instrumental Effects

- ◆ To do an accurate analysis for size and/or strain effects one must accurately account for instrumental broadening. The manner of doing this differs depending upon the peak shape.

- **Lorentzian**

$$\beta_{\text{obs}} = \beta_{\text{size}} + \beta_{\text{strain}} + \beta_{\text{inst}}$$

$$\{\beta_{\text{obs}} - \beta_{\text{inst}}\} = \beta_{\text{size}} + \beta_{\text{strain}}$$

- **Gaussian**

$$\beta^2_{\text{obs}} = \beta^2_{\text{size}} + \beta^2_{\text{strain}} + \beta^2_{\text{inst}}$$

$$\{\beta^2_{\text{obs}} - \beta^2_{\text{inst}}\} = \beta^2_{\text{size}} + \beta^2_{\text{strain}}$$

- **Voigt, Pseudo-Voigt**

- Generally it is necessary to first deconvolute into gaussian and lorentzian fractions before subtracting out the instrumental effects.



Williamson-Hall Analysis

Simplified Integral Breadth Methods

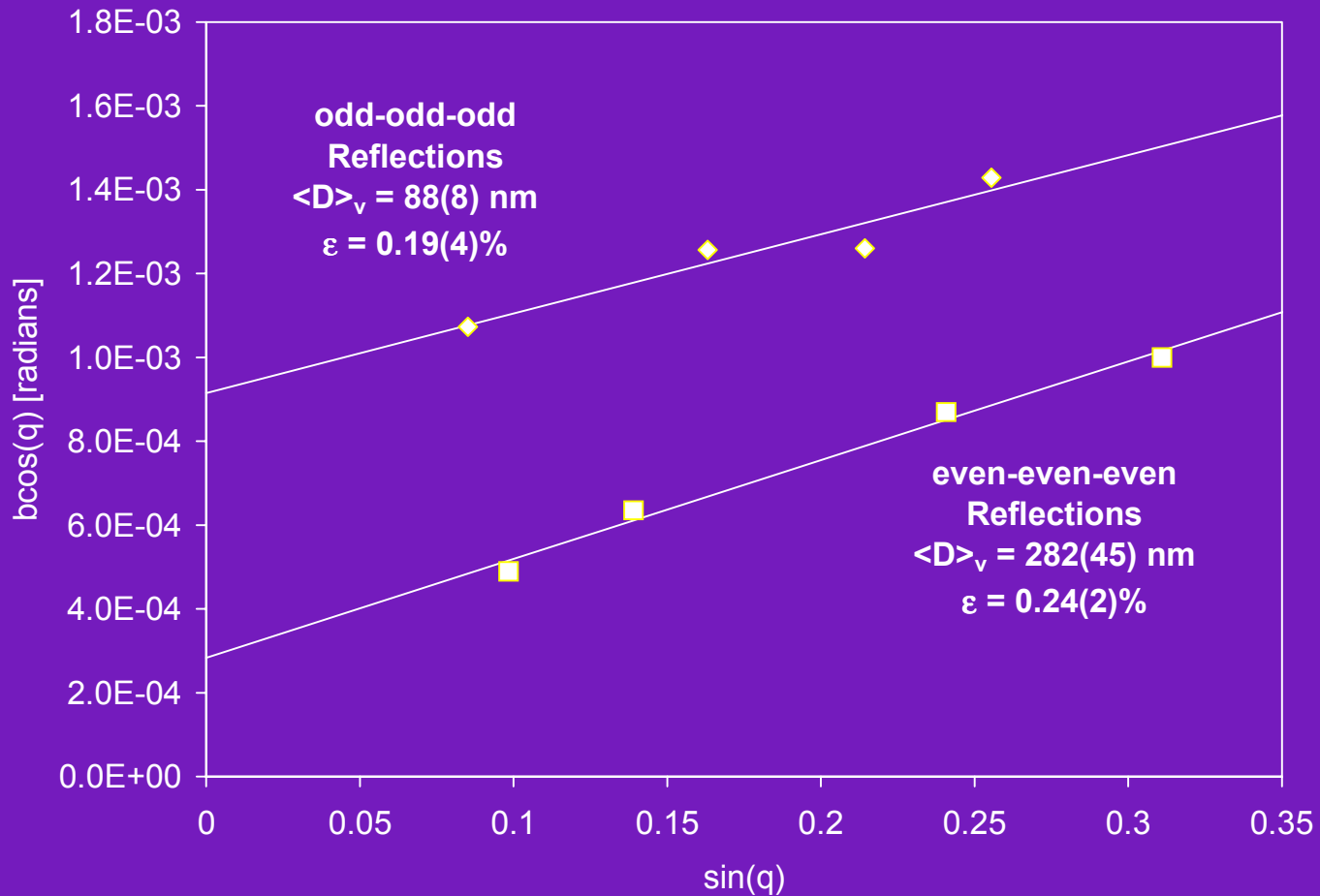
- ◆ Williamson and Hall (1953) proposed a method for deconvoluting size and strain broadening by looking at the peak width as a function of 2θ . Here I derive the Williamson-Hall relationship for the Lorentzian peak shape, but it can be derived in a similar manner for the Gaussian peak shape

$$\{\beta_{\text{obs}} - \beta_{\text{inst}}\} = \lambda / \{D_v \cos \theta\} + 4 \varepsilon_{\text{str}} \{\tan \theta\}$$

$$\{\beta_{\text{obs}} - \beta_{\text{inst}}\} \cos \theta = \lambda / D_v + 4 \varepsilon_{\text{str}} \{\sin \theta\}$$

- ◆ To make a Williamson-Hall plot
 - Plot $\{\beta_{\text{obs}} - \beta_{\text{inst}}\} \cos \theta$ on the y-axis (in radians 2θ)
 - Plot $4 \sin \theta$ on the x-axis
- ◆ If you get a linear fit to the data you can extract
 - the crystallite size from the y-intercept of the fit
 - the strain from the slope of the fit

Williamson-Hall Plot



A Williamson-Hall plot for $\text{Pb}_2\text{ScTaO}_6$. The size extracted from the even-even-even reflections gives the volume weighted crystallite size, while the size extracted from the odd-odd-odd reflections gives the volume weighted size of the regions over which the Sc and Ta atoms are well ordered. For more details see P.M. Woodward & K.Z. Baba Kishi, *J. Appl. Cryst.* In press (2002).

Size-Strain Analysis from Rietveld Profile Parameters

If we look at the Lorentzian and Gaussian terms in the Thompson-Cox-Hastings pseudo-voigt function (GSAS reverses the definition of X and Y from the original work I think) we can see how size and strain parameters can be extracted from the refined profile parameters [see also P. Karen & P.M. Woodward, *J. Solid State Chem.* **141**, 78-88 (1998)].

- **Lorentzian**

- TCH Function

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

- W-H Analysis

$$\{\beta_{\text{obs}} - \beta_{\text{inst}}\} = \lambda / \{D_v \cos \theta\} + 4 \varepsilon_{\text{str}} \{\tan \theta\}$$

- Correcting for FWHM vs. Integral breadth, and realizing that GSAS counts steps in centidegrees we can come up Size and Strain from X and Y

$$D_v = 36000 \lambda / \{\pi^2 X\}$$

$$\varepsilon_{\text{str}} = \pi^2 \{Y - Y_{\text{inst}}\} / 144000$$

Size-Strain Analysis from Rietveld Profile Parameters

If we look at the Lorentzian and Gaussian terms in the Thompson-Cox-Hastings pseudo-voigt function we can see how size and strain parameters can be extracted from the refined profile parameters [see also P. Karen & P.M. Woodward, *J. Solid State Chem.* **141**, 78-88 (1998)].

- **Gaussian**

- TCH Function

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

- W-H Analysis

$$\{\beta_{\text{obs}}^2 - \beta_{\text{inst}}^2\} = \lambda^2 / \{(D_v)^2 \cos^2\theta\} + 16(\epsilon_{\text{str}})^2 \tan^2\theta$$

- Correcting for FWHM vs. Integral breadth, and realizing that GSAS counts steps in centidegrees we can come up Size and Strain from P and U

$$D_v = 18000 \lambda / \sqrt{2\pi^3 P}$$

$$\epsilon_{\text{str}} = \sqrt{2\pi^3 (U - U_{\text{inst}})} / 72000$$



Fourier Methods

The most accurate way of extracting size and strain information is to analyze the entire shape of several reflections in the pattern (ideally higher order reflections of the same type I.e. 100, 200, 300, etc. or 111, 222, 333, etc.), by the method developed by Warren and Averbach [*J. Appl. Phys.* **21**, 596 (1950).] This is done using the following steps:

- Fit each reflection of interest with a Fourier series.
- Repeat this procedure for a pattern of a sample which gives no broadening, in order to determine the instrumental contribution to broadening.
- Use these results to deconvolute the sample broadening from the instrumental broadening, via a Stokes Fourier deconvolution.
- Extract information regarding the size distribution and strain profile by analyzing the theta dependence of the cosine Fourier coefficients (which describe the symmetric broadening)

Fourier Methods: Practical Considerations

◆ Advantages vs. the Integral Breadth Methods

- The Fourier methods give a distribution of crystallite sizes instead of an average value
- The correction for instrumental broadening is more rigorous when the peak shape is not purely Gaussian or Lorentzian

◆ Disadvantages vs. the Integral Breadth Methods

- Prone to error if peak tails are not accurately modeled. This makes the Fourier methods difficult to use when peak overlap is significant.
- Fourier decomposition is not always very stable.

◆ Distinctions between Fourier & Integral Breadth Methods


- The crystallite size determined from Integral Breadth methods is a volume weighted average (D_V), whereas the Fourier methods return an area weighted average (D_A). If we assume spherical particles all of the same size the sphere diameter, d , is related to the size by:

$$d = (4/3)D_V = (3/2)D_A. \text{ Therefore } D_V = (9/8)D_A.$$

Double Voigt Methods

- ◆ Double Voigt methods of analyzing peak broadening were first introduced by J.I. Langford (1980) and developed by D. Balzar. They give much the same information that one could obtain from the Fourier methods (i.e. Warren-Averbach). The double Voigt method proceeds along the following lines:
 - The peaks are fit analytically using a Voigt function (can be extended to Pseudo-voigt and Split Pearson functions), so that the Lorentzian breadth (β_L) and Gaussian breadth (β_G) of each peak can be determined.
 - The integral breadths are corrected for instrumental broadening ($\beta_{L(\text{sample})} = \beta_{L(\text{fit})} - \beta_{L(\text{instr})}$) and ($\beta_{G(\text{sample})}^2 = \beta_{G(\text{fit})}^2 - \beta_{G(\text{instr})}^2$).
 - Williamson-Hall plots are constructed from for both the Lorentzian and Gaussian peak widths.
 - The crystallite size is extracted from the Lorentzian W-H plot and the strain is taken to be a combination of the Lorentzian and Gaussian strain terms.

Double Voigt Methods

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- ◆ Balzar has shown the Double-Voigt method to have several advantages vs. the simplified Integral Breadth and Fourier methods
 - While the Lorentzian/Gaussian mixing parameter is somewhat sensitive to accurate fitting of the peak tails, this method is more robust than the Fourier methods to the errors associated with peak overlap.
 - Unlike the Williamson-Hall approach Double Voigt methods can be used when the peak shape is neither pure Lorentzian nor pure Gaussian.
 - Crystallite size distributions can be obtained.
 - ◆ For a much more complete description see the Davor Balzar's web site at NIST-Boulder
<http://www.boulder.nist.gov/div853/balzar/>
 - ◆ I recommend using Balzar's program BREADTH to carry out this type of analysis.

Conclusions

- ◆ Crystallite sizes below roughly 100 nm can accurately be evaluated using powder diffraction techniques.
- ◆ Microstrain, which arises due to point defects (vacancies, site disorder), dislocations and even extended defects can be evaluated using powder diffraction techniques.
- ◆ It is generally necessary to correct for instrumental broadening and to use integral breadths (rather than FWHM) to obtain the most accurate analysis.
- ◆ Simplified integral breadth methods work well if the peak shapes are either pure Gaussian or pure Lorentzian.
- ◆ Size-strain analysis can be extracted directly from Rietveld peak profile parameters, with some thought.
- ◆ Fourier Methods are the most general method of extracting size-strain information but they are susceptible to error due to peak overlap. This limits their use for crystal structures of moderate and higher complexity.
- ◆ The Double-Voigt methods are perhaps the most rigorous way to analyze peak broadening. I recommend the program BREADTH, written by Davor Balzar (NIST and U of Colorado-Boulder).