Estimating Crystallite Size Using XRD

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http://prism.mit.edu/xray

Warning

- These slides have not been extensively proof-read, and therefore may contain errors.

- While I have tried to cite all references, I may have missed some– these slides were prepared for an informal lecture and not for publication.

- If you note a mistake or a missing citation, please let me know and I will correct it.

- I hope to add commentary in the notes section of these slides, offering additional details. However, these notes are incomplete so far.

Goals of Today's Lecture

- Provide a quick overview of the theory behind peak profile analysis
- Discuss practical considerations for analysis
- Demonstrate the use of lab software for analysis
  - **empirical peak fitting using MDI Jade**
  - Rietveld refinement using HighScore Plus
- Discuss other software for peak profile analysis
- Briefly mention other peak profile analysis methods
  - Warren Averbach Variance method
  - Mixed peak profiling
  - whole pattern
- Discuss other ways to evaluate crystallite size

- *Assumptions: you understand the basics of crystallography, X-ray diffraction, and the operation of a Bragg-Brentano diffractometer*

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A Brief History of XRD

- 1895- Röntgen publishes the discovery of X-rays

- 1912- Laue observes diffraction of X-rays from a crystal

- *when did Scherrer use X-rays to estimate the crystallite size of nanophase materials?*

The Scherrer Equation was published in 1918

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

- **Peak width (B) is inversely proportional to crystallite size (L)**

- P. Scherrer, "Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen," *Nachr. Ges. Wiss. Göttingen* **26** (1918) pp 98-100.

- J.I. Langford and A.J.C. Wilson, "Scherrer after Sixty Years: A Survey and Some New Results in the Determination of Crystallite Size," *J. Appl. Cryst.* **11** (1978) pp 102-113.

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The Laue Equations describe the intensity of a diffracted peak from a single parallelopipeden crystal

$$I = I_e F^2 \frac{\sin^2(\pi/\lambda)(s-s_O)\bullet N_1 a_1}{\sin^2(\pi/\lambda)(s-s_O)\bullet a_1} \frac{\sin^2(\pi/\lambda)(s-s_O)\bullet N_2 a_2}{\sin^2(\pi/\lambda)(s-s_O)\bullet a_2} \frac{\sin^2(\pi/\lambda)(s-s_O)\bullet N_3 a_3}{\sin^2(\pi/\lambda)(s-s_O)\bullet a_3}$$

- N_1, N_2, and N_3 are the number of unit cells along the a_1, a_2, and a_3 directions
- When N is small, the diffraction peaks become broader
- The peak area remains constant independent of N
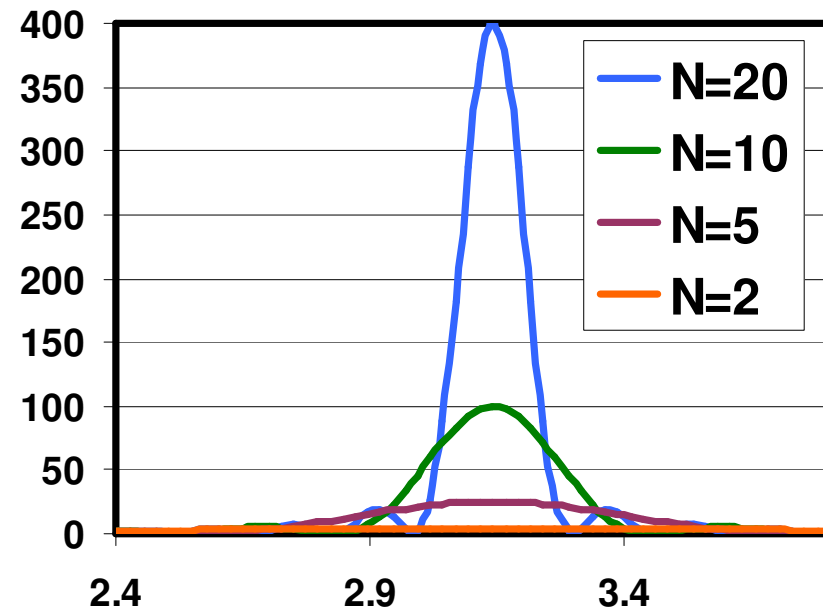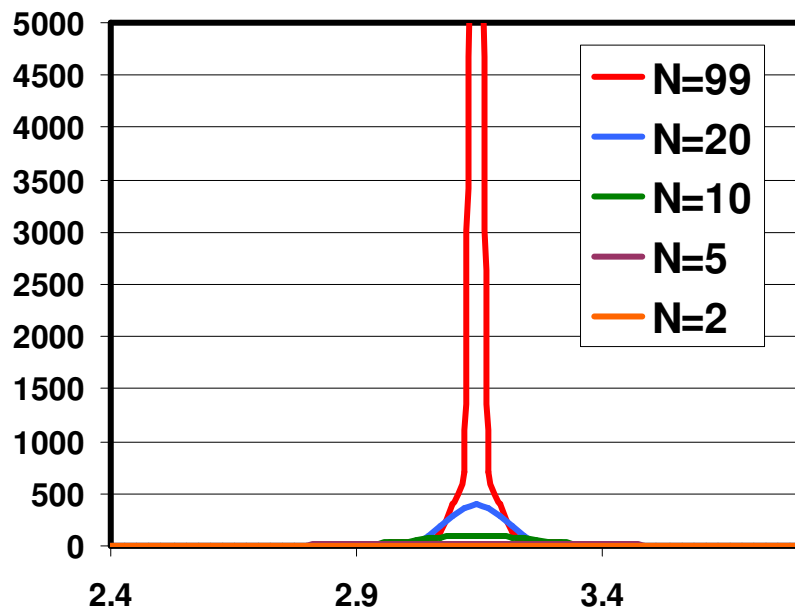
Which of these diffraction patterns comes from a nanocrystalline material?
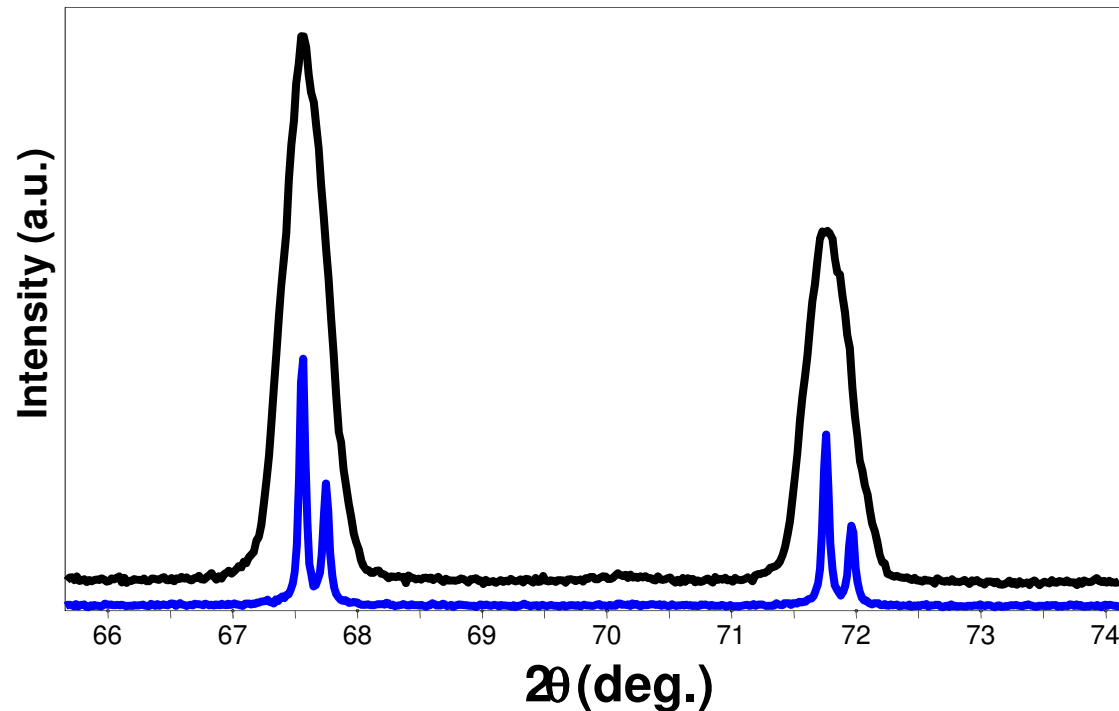
- These diffraction patterns were produced from the **exact same sample**
- Two different diffractometers, with different optical configurations, were used
- *The apparent peak broadening is due solely to the instrumentation*

Many factors may contribute to the observed peak profile

- Instrumental Peak Profile

- Crystallite Size

- Microstrain

  - Non-uniform Lattice Distortions

  - Faulting

  - Dislocations

  - Antiphase Domain Boundaries

  - Grain Surface Relaxation

- Solid Solution Inhomogeneity

- Temperature Factors

- ***The peak profile is a convolution of the profiles from all of these contributions***

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Instrument and Sample Contributions to the Peak Profile must be Deconvoluted

- In order to analyze crystallite size, we must deconvolute:
  - Instrumental Broadening FW(I)
    - also referred to as the Instrumental Profile, Instrumental FWHM Curve, Instrumental Peak Profile
  - Specimen Broadening FW(S)
    - also referred to as the Sample Profile, Specimen Profile

- We must then separate the different contributions to specimen broadening
  - Crystallite size and microstrain broadening of diffraction peaks

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Contributions to Peak Profile

1. Peak broadening due to crystallite size
2. Peak broadening due to the instrumental profile
3. Which instrument to use for nanophase analysis
4. Peak broadening due to microstrain
   - the different types of microstrain
- Peak broadening due to solid solution inhomogeneity and due to temperature factors

Crystallite Size Broadening

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

- Peak Width due to crystallite size varies inversely with crystallite size
  - as the crystallite size gets smaller, the peak gets broader
- The peak width varies with 2θ as $\cos\theta$
  - The crystallite size broadening is most pronounced at large angles 2Theta
    - However, the instrumental profile width and microstrain broadening are also largest at large angles 2theta
    - peak intensity is usually weakest at larger angles 2theta
  - If using a single peak, often get better results from using diffraction peaks between 30 and 50 deg 2theta
    - below 30deg 2theta, peak asymmetry compromises profile analysis

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The Scherrer Constant, K

$$B(2\theta) = \frac{K\lambda}{L\cos\theta} \qquad\qquad B(2\theta) = \frac{0.94\lambda}{L\cos\theta}$$

- The constant of proportionality, K (the Scherrer constant) depends on the how the width is determined, the shape of the crystal, and the size distribution
  - the most common values for K are:
    - 0.94 for FWHM of spherical crystals with cubic symmetry
    - 0.89 for integral breadth of spherical crystals w/ cubic symmetry
    - 1, because 0.94 and 0.89 both round up to 1
  - K actually varies from 0.62 to 2.08
- For an excellent discussion of K, refer to JI Langford and AJC Wilson, "Scherrer after sixty years: A survey and some new results in the determination of crystallite size," *J. Appl. Cryst.* **11** (1978) p102-113.

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Factors that affect K and crystallite size analysis

- how the peak width is defined
- how crystallite size is defined
- the shape of the crystal
- the size distribution

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Methods used in Jade to Define Peak Width

- Full Width at Half Maximum (FWHM)
  - the width of the diffraction peak, in radians, at a height half-way between background and the peak maximum

- Integral Breadth
  - the total area under the peak divided by the peak height
  - the width of a rectangle having the same area and the same height as the peak
  - requires very careful evaluation of the tails of the peak and the background

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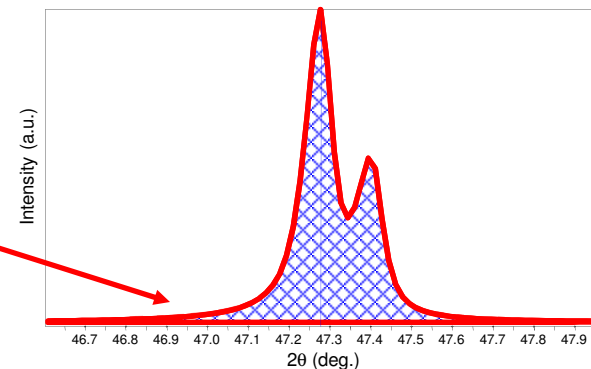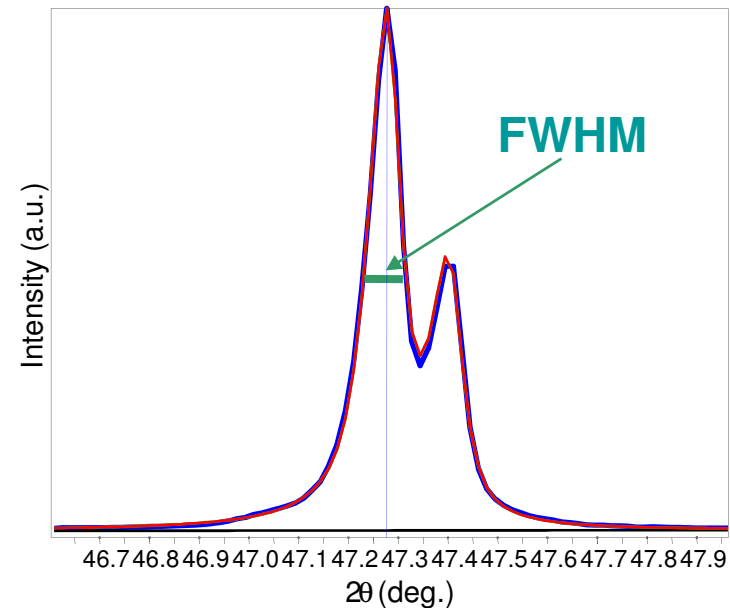
Integral Breadth

$$\beta(2\theta) = \frac{\lambda}{L\cos\theta}$$

- Warren suggests that the Stokes and Wilson method of using integral breadths gives an evaluation that is independent of the distribution in size and shape
  - L is a volume average of the crystal thickness in the direction normal to the reflecting planes
  - The Scherrer constant K can be assumed to be 1

- *Langford and Wilson suggest that even when using the integral breadth, there is a Scherrer constant K that varies with the shape of the crystallites*

Other methods used to determine peak width

- These methods are used in more the variance methods, such as Warren-Averbach analysis
  - Most often used for dislocation and defect density analysis of metals
  - Can also be used to determine the crystallite size distribution
  - ***Requires no overlap between neighboring diffraction peaks***

- Variance-slope
  - the slope of the variance of the line profile as a function of the range of integration

- Variance-intercept
  - negative initial slope of the Fourier transform of the normalized line profile

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How is Crystallite Size Defined

- Usually taken as the cube root of the volume of a crystallite
  - assumes that all crystallites have the same size and shape
- For a distribution of sizes, the mean size can be defined as
  - the mean value of the cube roots of the individual crystallite volumes
  - the cube root of the mean value of the volumes of the individual crystallites

- **Scherrer** method (using FWHM) gives the ratio of the root-mean-fourth-power to the root-mean-square value of the thickness
- **Stokes and Wilson** method (using integral breadth) determines the volume average of the thickness of the crystallites measured perpendicular to the reflecting plane
- **The variance methods** give the ratio of the total volume of the crystallites to the total area of their projection on a plane parallel to the reflecting planes

Remember, Crystallite Size is Different than Particle Size

- A particle may be made up of several different crystallites

- Crystallite size often matches grain size, but there are exceptions

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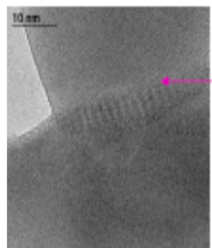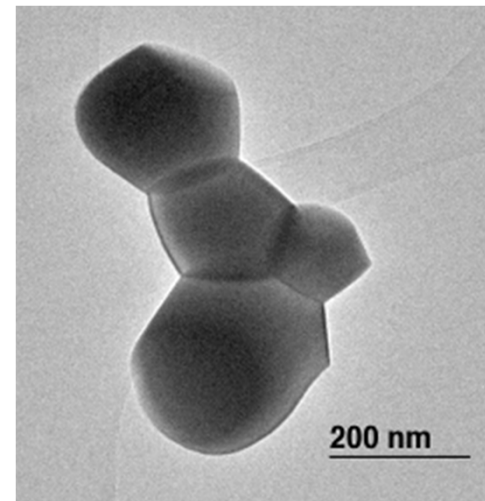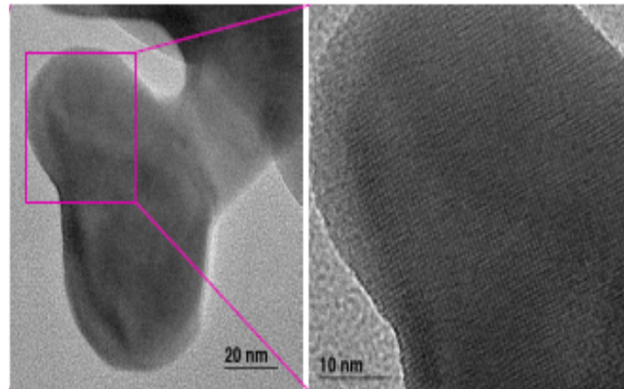
Crystallite Shape

- Though the shape of crystallites is usually irregular, we can often approximate them as:
  - sphere, cube, tetrahedra, or octahedra
  - parallelepipeds such as needles or plates
  - prisms or cylinders
- Most applications of Scherrer analysis assume spherical crystallite shapes
- If we know the average crystallite shape from another analysis, we can select the proper value for the Scherrer constant K

- Anistropic peak shapes can be identified by anistropic peak broadening
  - if the dimensions of a crystallite are 2x * 2y * 200z, then (h00) and (0k0) peaks will be more broadened then (00l) peaks.

Anistropic Size Broadening

- The broadening of a single diffraction peak is the product of the crystallite dimensions in the direction perpendicular to the planes that produced the diffraction peak.

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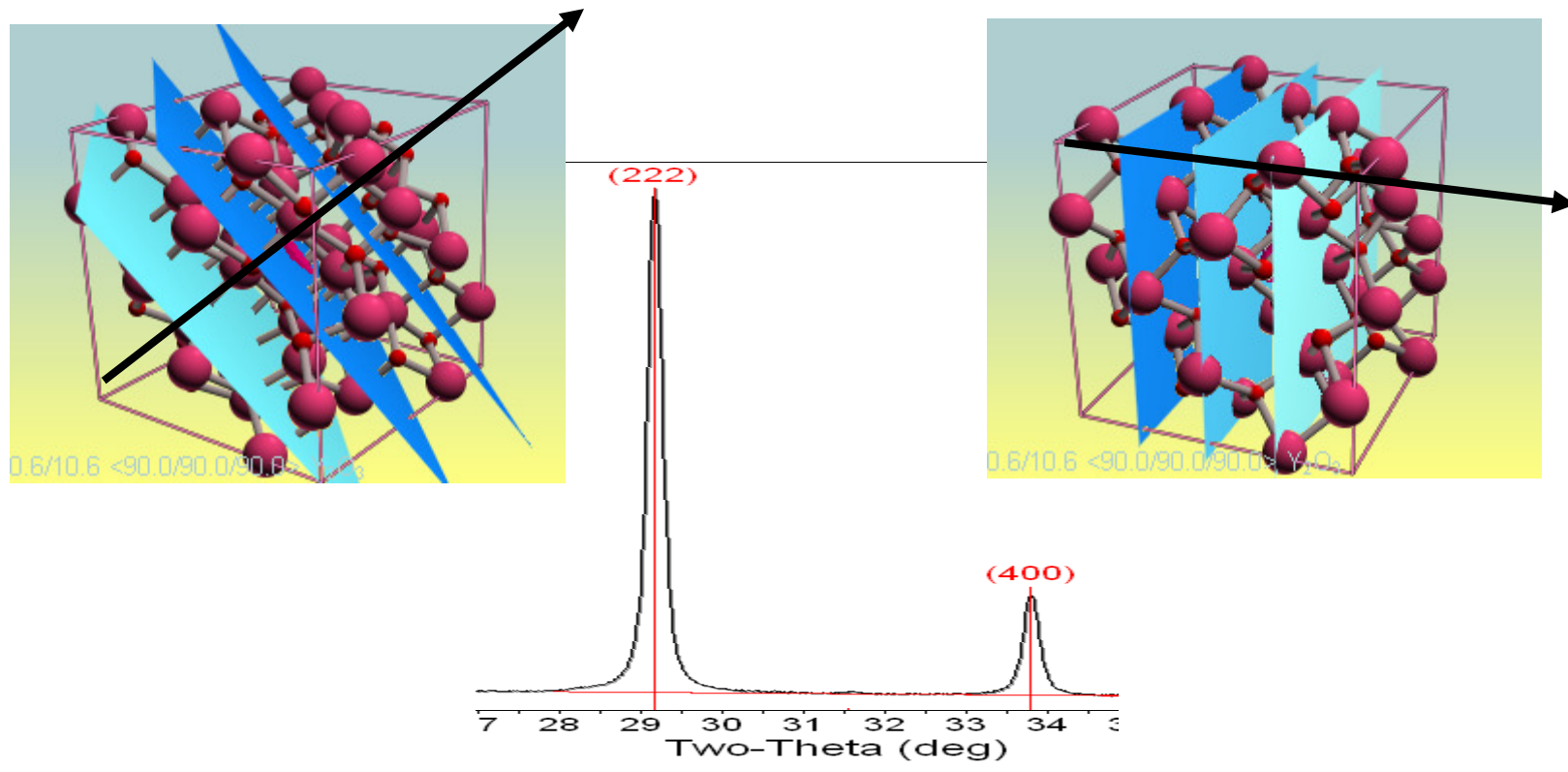
Crystallite Size Distribution

- is the crystallite size narrowly or broadly distributed?

- is the crystallite size unimodal?

- XRD is poorly designed to facilitate the analysis of crystallites with a broad or multimodal size distribution

- Variance methods, such as Warren-Averbach, can be used to quantify a unimodal size distribution
  - Otherwise, we try to accommodate the size distribution in the Scherrer constant
  - Using integral breadth instead of FWHM may reduce the effect of crystallite size distribution on the Scherrer constant K and therefore the crystallite size analysis

Instrumental Peak Profile

- A large crystallite size, defect-free powder specimen will still produce diffraction peaks with a finite width

- The peak widths from the instrument peak profile are a convolution of:
  - X-ray Source Profile
    - Wavelength widths of $K\alpha_1$ and $K\alpha_2$ lines
    - Size of the X-ray source
    - Superposition of $K\alpha_1$ and $K\alpha_2$ peaks
  - Goniometer Optics
    - Divergence and Receiving Slit widths
    - Imperfect focusing
    - Beam size
    - Penetration into the sample
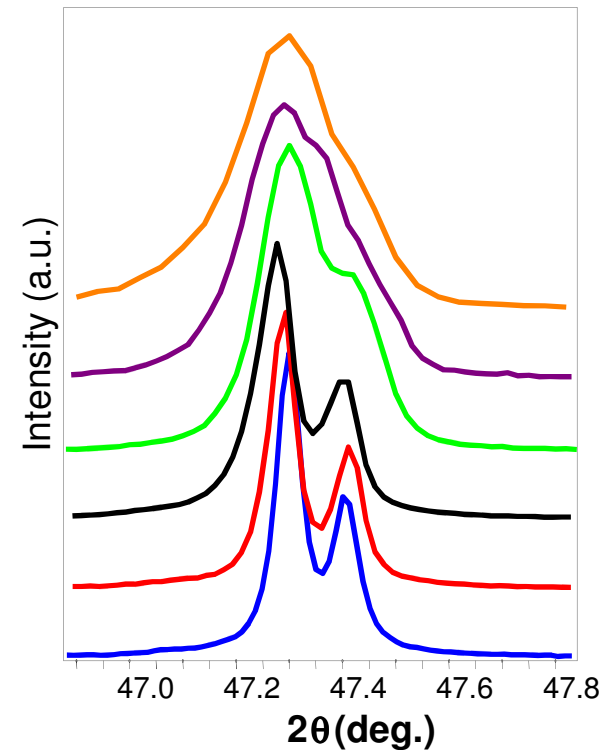
Patterns collected from the same sample with different instruments and configurations at MIT

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What Instrument to Use?

- The instrumental profile determines the upper limit of crystallite size that can be evaluated
  - if the Instrumental peak width is much larger than the broadening due to crystallite size, then we cannot accurately determine crystallite size
  - For analyzing larger nanocrystallites, it is important to use the instrument with the smallest instrumental peak width

- Very small nanocrystallites produce weak signals
  - the specimen broadening will be significantly larger than the instrumental broadening
  - the signal:noise ratio is more important than the instrumental profile

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Comparison of Peak Widths at 47° 2θ for Instruments and Crystallite Sizes

Configuration	FWHM (deg)	Pk Ht to Bkg Ratio
Rigaku, LHS, 0.5° DS, 0.3mm RS	0.076	528
Rigaku, LHS, 1° DS, 0.3mm RS	0.097	293
Rigaku, RHS, 0.5° DS, 0.3mm RS	0.124	339
Rigaku, RHS, 1° DS, 0.3mm RS	0.139	266
X'Pert Pro, High-speed, 0.25° DS	0.060	81
X'Pert Pro, High-speed, 0.5° DS	0.077	72
X'Pert, 0.09° Parallel Beam Collimator	0.175	50
X'Pert, 0.27° Parallel Beam Collimator	0.194	55

Crystallite Size	FWHM (deg)
100 nm	0.099
50 nm	0.182
10 nm	0.871
5 nm	1.745

- Rigaku XRPD is better for very small nanocrystallites, <80 nm (upper limit 100 nm)
- PANalytical X'Pert Pro is better for larger nanocrystallites, <150 nm

Other Instrumental Considerations for Thin Films

- The irradiated area greatly affects the intensity of high angle diffraction peaks
  - GIXD or variable divergence slits on the PANalytical X'Pert Pro will maintain a constant irradiated area, increasing the signal for high angle diffraction peaks
  - both methods increase the instrumental FWHM

- Bragg-Brentano geometry only probes crystallite dimensions through the thickness of the film
  - in order to probe lateral (in-plane) crystallite sizes, need to collect diffraction patterns at different tilts
  - this requires the use of parallel-beam optics on the PANalytical X'Pert Pro, which have very large FWHM and poor signal:noise ratios

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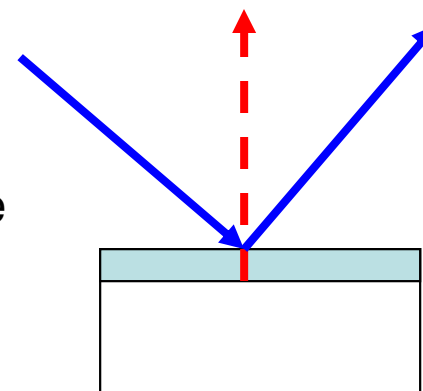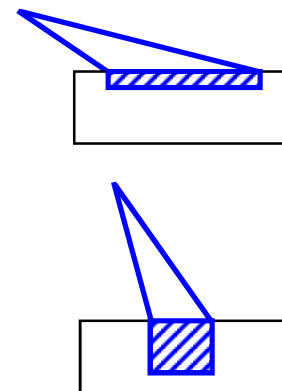
Microstrain Broadening

- lattice strains from displacements of the unit cells about their normal positions
- often produced by dislocations, domain boundaries, surfaces etc.
- microstrains are very common in nanocrystalline materials
- the peak broadening due to microstrain will vary as:

$$B(2\theta) = 4\varepsilon \frac{\sin\theta}{\cos\theta}$$

compare to peak broadening due to crystallite size:
$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

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Contributions to Microstrain Broadening

- Non-uniform Lattice Distortions

- Dislocations

- Antiphase Domain Boundaries

- Grain Surface Relaxation

- Other contributions to broadening
    - faulting
    - solid solution inhomogeneity
    - temperature factors

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Non-Uniform Lattice Distortions

- Rather than a single d-spacing, the crystallographic plane has a distribution of d-spaces

- This produces a broader observed diffraction peak

- Such distortions can be introduced by:
  - surface tension of nanocrystals
  - morphology of crystal shape, such as nanotubes
  - interstitial impurities

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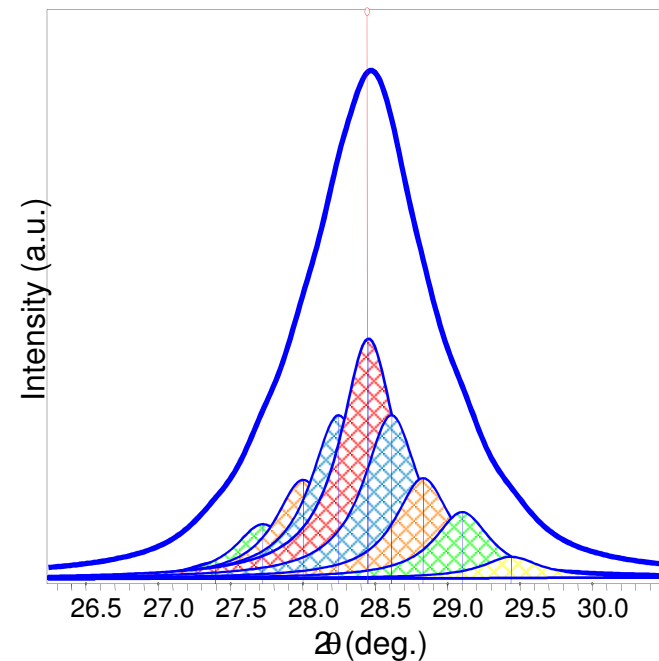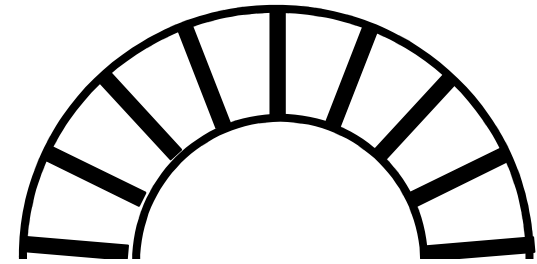
Antiphase Domain Boundaries

- Formed during the ordering of a material that goes through an order-disorder transformation
- The fundamental peaks are not affected
- the superstructure peaks are broadened
  - the broadening of superstructure peaks varies with *hkl*

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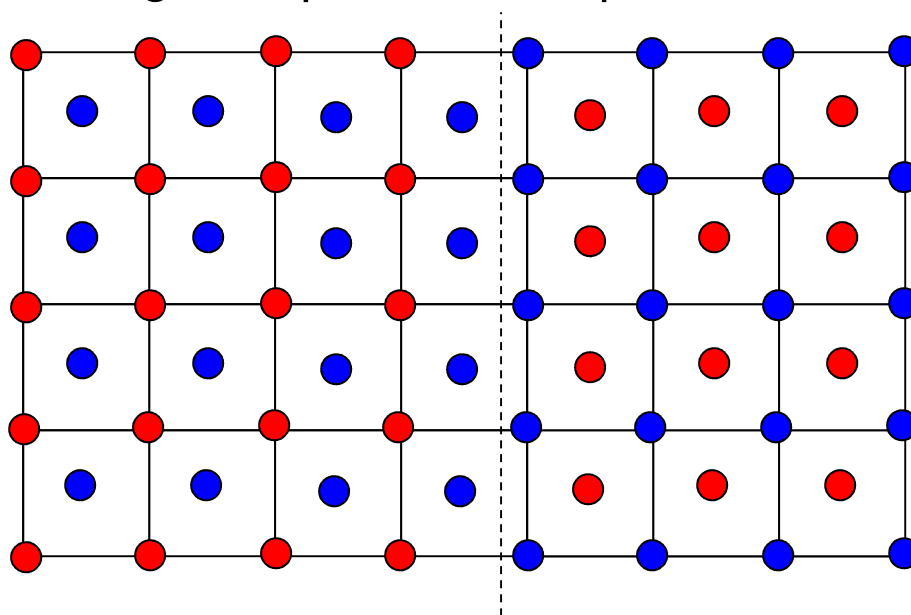
Dislocations

- Line broadening due to dislocations has a strong *hkl* dependence

- The profile is Lorentzian

- Can try to analyze by separating the Lorentzian and Gaussian components of the peak profile

- Can also determine using the Warren-Averbach method
  - measure several orders of a peak
    - 001, 002, 003, 004, …
    - 110, 220, 330, 440, …
  - The Fourier coefficient of the sample broadening will contain
    - an order independent term due to size broadening
   - an order dependent term due to strain

Faulting

- Broadening due to deformation faulting and twin faulting will convolute with the particle size Fourier coefficient
  - The particle size coefficient determined by Warren-Averbach analysis actually contains contributions from the crystallite size and faulting
  - the fault contribution is hkl dependent, while the size contribution should be hkl independent (assuming isotropic crystallite shape)
  - the faulting contribution varies as a function of hkl dependent on the crystal structure of the material (fcc vs bcc vs hcp)
  - See Warren, 1969, for methods to separate the contributions from deformation and twin faulting

Solid Solution Inhomogeneity

- Variation in the composition of a solid solution can create a distribution of d-spacing for a crystallographic plane
    - Similar to the d-spacing distribution created from microstrain due to non-uniform lattice distortions

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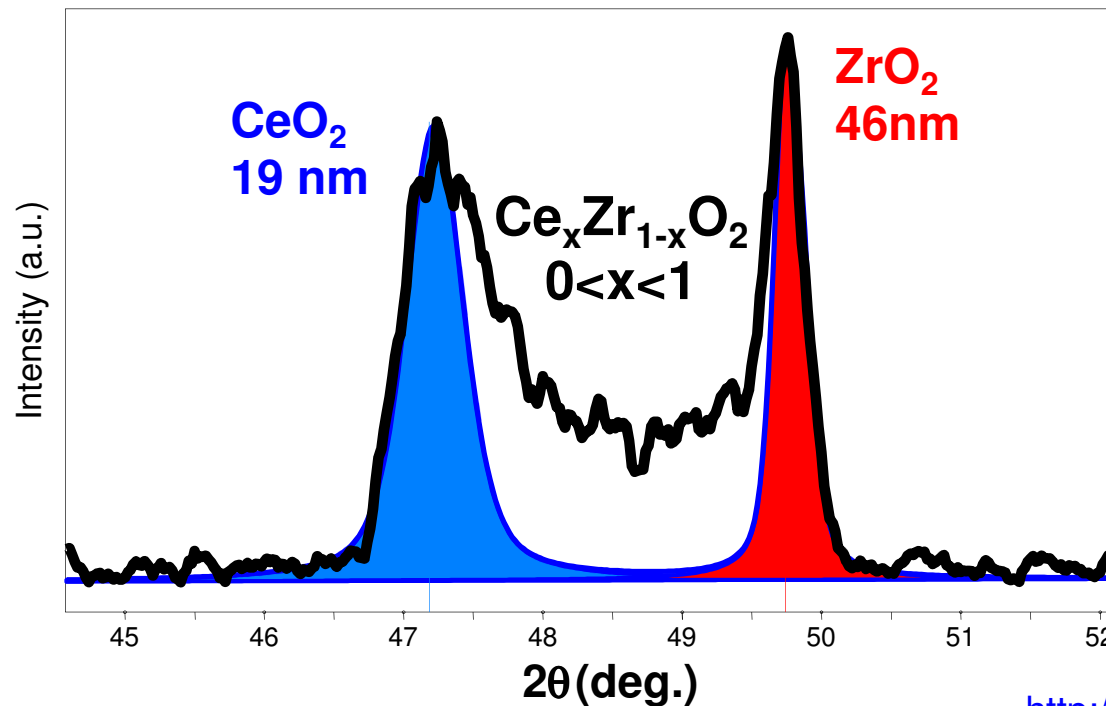
Temperature Factor

- The Debye-Waller temperature factor describes the oscillation of an atom around its average position in the crystal structure
- The thermal agitation results in intensity from the peak maxima being redistributed into the peak tails
  - it does not broaden the FWHM of the diffraction peak, but it does broaden the integral breadth of the diffraction peak
- The temperature factor increases with 2Theta
- The temperature factor must be convoluted with the structure factor for each peak
  - different atoms in the crystal may have different temperature factors
  - each peak contains a different contribution from the atoms in the crystal

$$F = f \exp(-M) \qquad M = 2\pi^2 \left(\frac{\Delta X / \sqrt{3}}{d} \right)^2$$

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Determining the Sample Broadening due to crystallite size

- The sample profile FW(S) can be deconvoluted from the instrumental profile FW(I) either numerically or by Fourier transform
- In Jade size and strain analysis
  - you individually profile fit every diffraction peak
  - deconvolute FW(I) from the peak profile functions to isolate FW(S)
  - execute analyses on the peak profile functions rather than on the raw data
- Jade can also use iterative folding to deconvolute FW(I) from the entire observed diffraction pattern
  - this produces an entire diffraction pattern without an instrumental contribution to peak widths
  - this does not require fitting of individual diffraction peaks
  - folding increases the noise in the observed diffraction pattern
- Warren Averbach analyses operate on the Fourier transform of the diffraction peak
  - take Fourier transform of peak profile functions or of raw data

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Analysis using MDI Jade

- The data analysis package Jade is designed to use empirical peak profile fitting to estimate crystallite size and/or microstrain

- Three Primary Components
  - Profile Fitting Techniques
  - Instrumental FWHM Curve
  - Size & Strain Analysis
   - Scherrer method
    - Williamson-Hall method

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Important Chapters in Jade Help
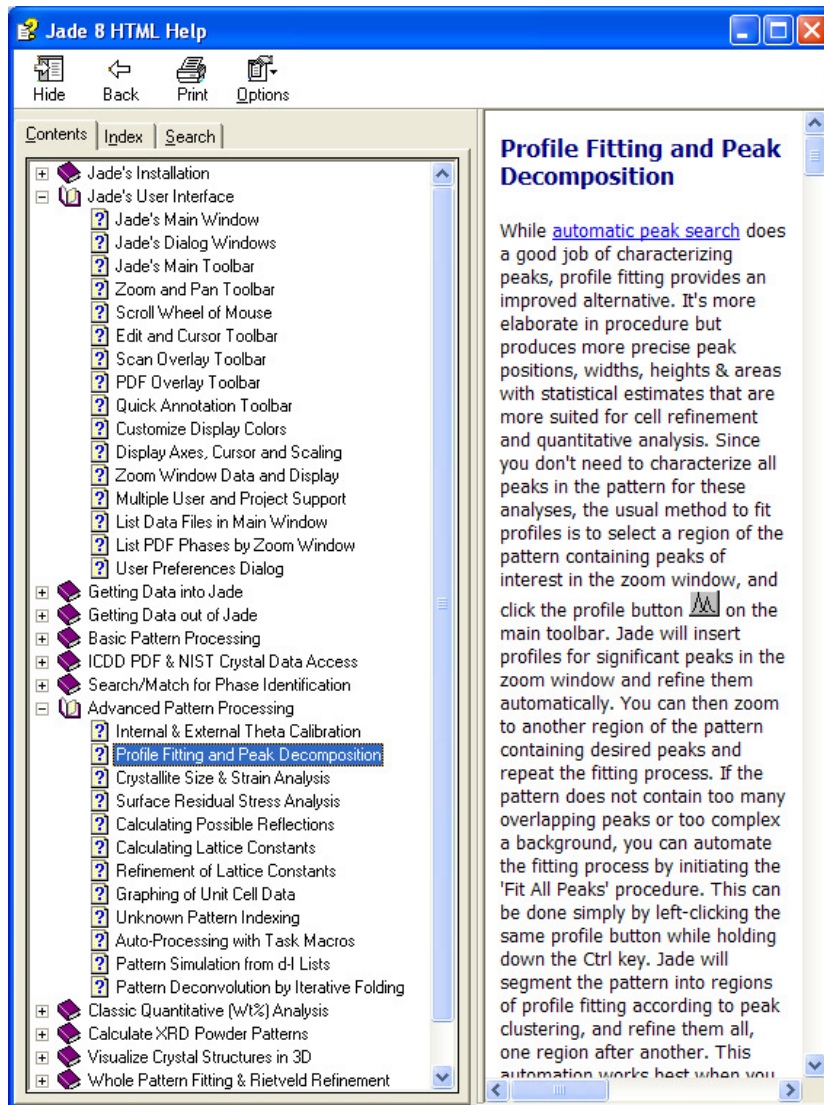
- Jade's User Interface
  - User Preferences Dialog

- Advanced Pattern Processing
  - Profile Fitting and Peak Decomposition
  - Crystallite Size & Strain Analysis

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Profile Fitting

- Empirically fit experimental data with a series of equations
  - fit the diffraction peak using the profile function
  - fit background, usually as a linear segment
    - this helps to separate intensity in peak tails from background
- To extract information, operate explicitly on the equation rather than numerically on the raw data
- **Profile fitting produces precise peak positions, widths, heights, and areas with statistically valid estimates**

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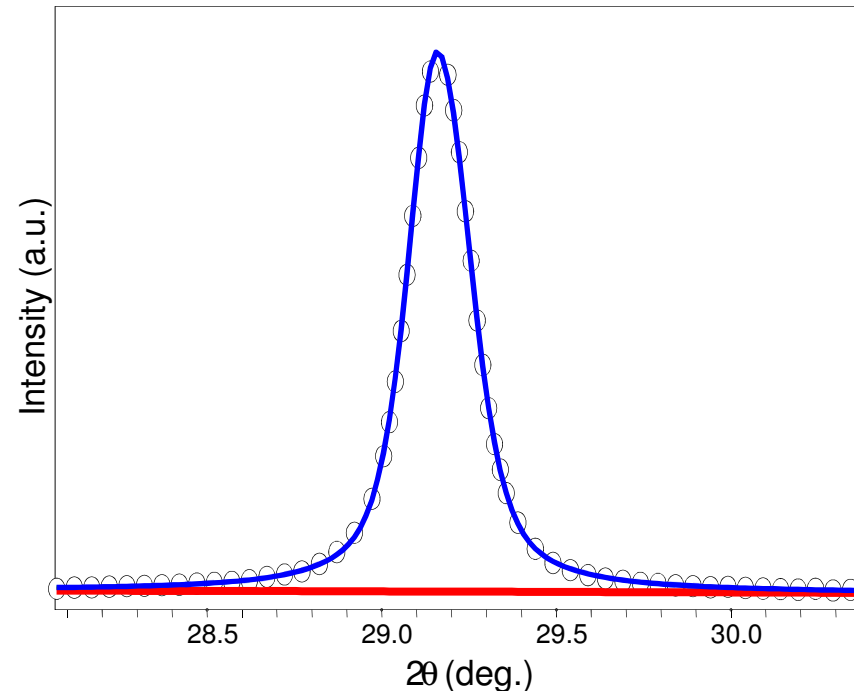
Profile Functions

- Diffraction peaks are usually the convolution of Gaussian and Lorentzian components

- Some techniques try to deconvolute the Gaussian and Lorentzian contributions to each diffraction peak; this is very difficult

- More typically, data are fit with a profile function that is a pseudo-Voigt or Pearson VII curve

  – pseudo-Voigt is a linear combination of Gaussian and Lorentzian components
    - a true Voigt curve is a convolution of the Gaussian and Lorentzian components; this is more difficult to implement computationally
  – Pearson VII is an exponential mixing of Gaussian and Lorentzian components

- SA Howard and KD Preston, "Profile Fitting of Powder Diffraction Patterns,", <u>Reviews in Mineralogy vol 20: Modern Powder Diffraction</u>, Mineralogical Society of America, Washington DC, 1989.
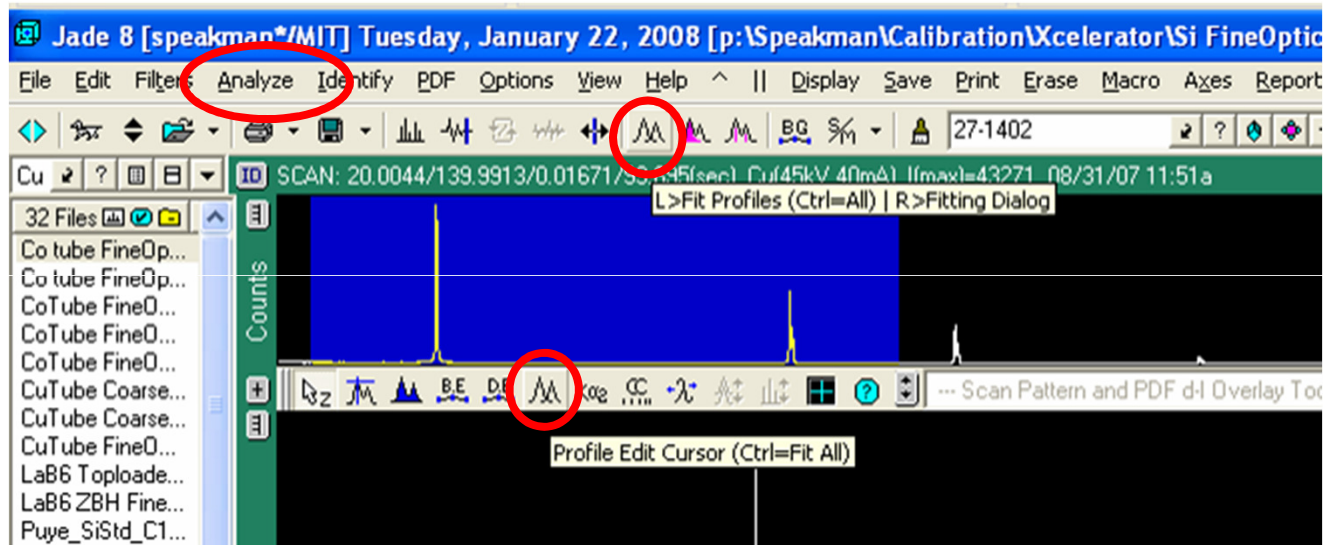
Important Tips for Profile Fitting

- Do not process the data before profile fitting
  - do not smooth the data
  - do not fit and remove the background
  - do not strip Ka_2 peaks
- Load the appropriate PDF reference patterns for your phases of interest
- Zoom in so that as few peaks as possible, plus some background, is visible
  - Fit as few peaks simultaneously as possible
  - preferably fit only 1 peak at a time
- Constrain variables when necessary to enhance the stability of the refinement

To Access the Profile Fitting Dialogue Window

- Menu: *Analyze > Fit Peak Profile*
- Right-click **Fit Profiles** button
- Right-click **Profile Edit Cursor** button

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- open Ge103.xrdml

- overlay PDF reference pattern 04-0545

- Demonstrate profile fitting of the 5 diffraction peaks
  - fit one at a time
  - fit using 'All' option

Important Options in Profile Fitting Window

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1. Profile Shape Function

- select the equation that will be used to fit diffraction peaks
- Gaussian:
  - more appropriate for fitting peaks with a rounder top
  - strain distribution tends to broaden the peak as a Gaussian
- Lorentzian:
  - more appropriate for fitting peaks with a sharper top
  - size distribution tends to broaden the peak as a Lorentzian
  - dislocations also create a Lorentzian component to the peak broadening
- The instrumental profile and peak shape are often a combination of Gaussian and Lorentzian contributions
- pseudo-Voigt:
  - emphasizes Guassian contribution
  - preferred when strain broadening dominates
- Pearson VII:
  - emphasize Lorentzian contribution
  - preferred when size broadening dominates

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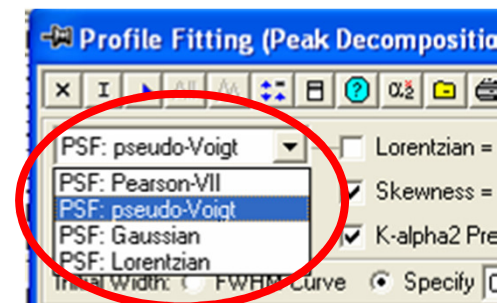
2. Shape Parameter

- This option allows you to constrain or refine the shape parameter
  - the shape parameter determines the relative contributions of Gaussian and Lorentzian type behavior to the profile function
- shape parameter is different for pseudo-Voigt and Pearson VII functions
  - pseudo-Voigt: sets the Lorentzian coefficient
  - Pearson VII: set the exponent

- Check the box if you want to constrain the shape parameter to a value
  - input the value that you want for the shape parameter in the numerical field
- **Do not check the box if you want the mixing parameter to be refined during profile fitting**
  - **this is the much more common setting for this option**

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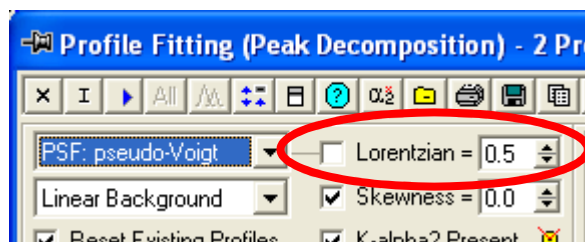
3. Skewness

- Skewness is used to model asymmetry in the diffraction peak
  - Most significant at low values of 2θ
- Unchecked: skewness will be refined during profile fitting
- Checked: skewness will be constrained to the value indicated
  - **usually check this option to constrain skewness to 0**
  - skewness=0 indicates a symmetrical peak
- Hint: constrain skewness to zero when
  - refining very broad peaks
  - refining very weak peaks
  - refining several heavily overlapping peaks
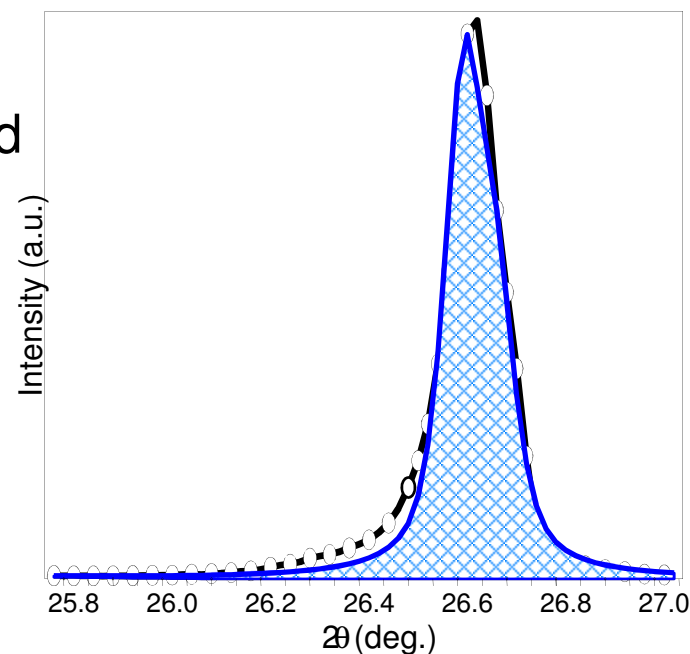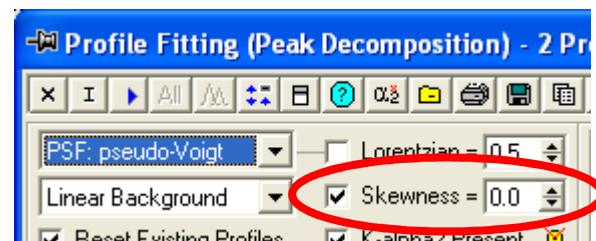
an example of the error created when fitting low angle asymmetric data with a skewness=0 profile

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4. K-alpha2 contribution

- Checking this box indicates that $K\alpha_2$ radiation is present and should be included in the peak profile model
  - this should almost always be checked when analyzing your data
- It is much more accurate to model $K\alpha_2$ than it is to numerically strip the $K\alpha_2$ contribution from the experimental data
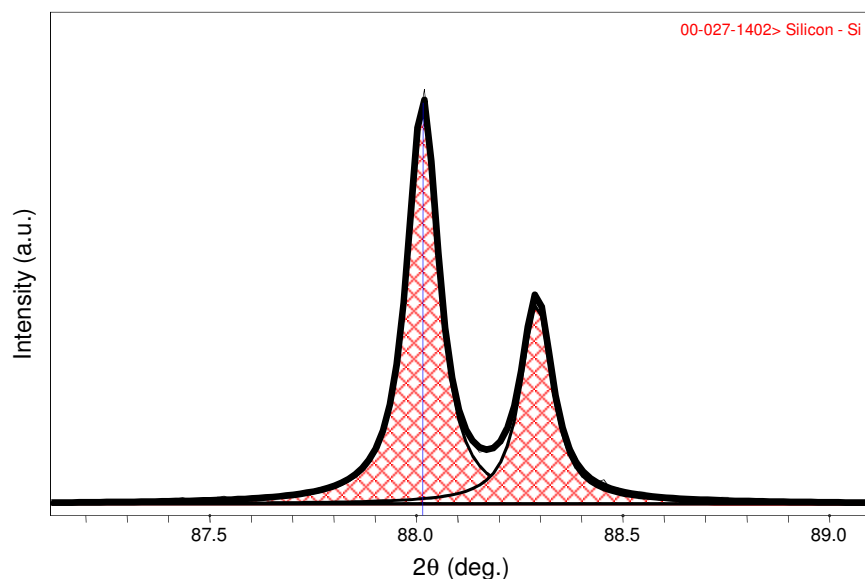
This is a single diffraction peak, featuring the $K\alpha_1$ and $K\alpha_2$ doublet

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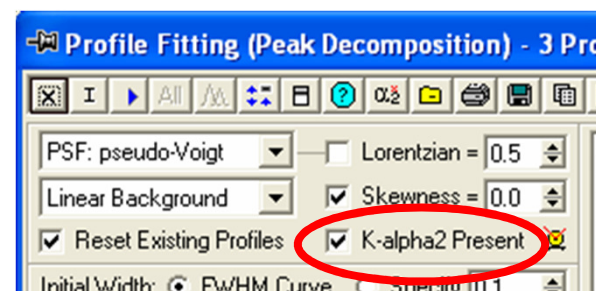
5. Background function

- Specifies how the background underneath the peak will be modeled
  - usually use "Linear Background"
  - "Level Background" is appropriate if the background is indeed fairly level and the broadness of the peak causes the linear background function to fit improperly
  - manually fit the background (*Analyze > Fit Background*) and use "Fixed Background" for very complicated patterns
  - more complex background functions will usually fail when fitting nanocrystalline materials
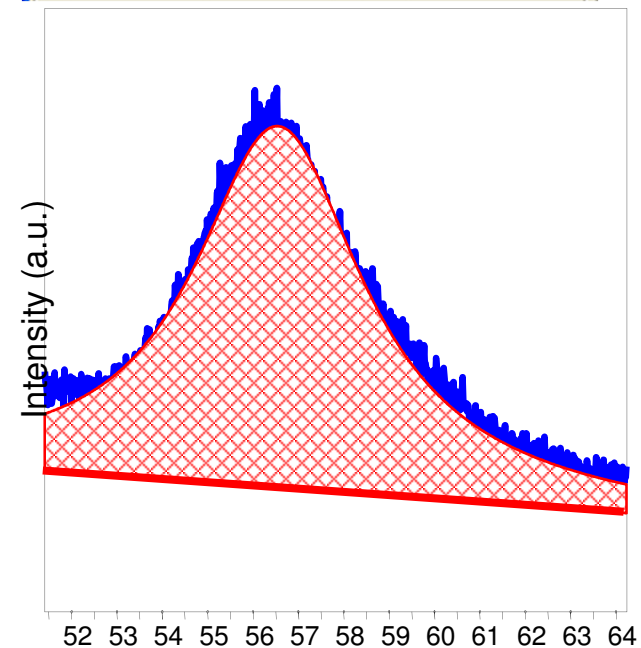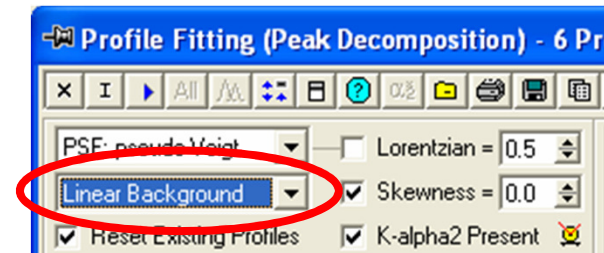
This linear background fit modeled the background too low. A level fit would not work, so the fixed background must be used.

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6. Initial Peak Width
7. Initial Peak Location

- These setting determine the way that Jade calculates the initial peak profile, before refinement

- Initial Width
  - if the peak is not significantly broadened by size or strain, then use the FWHM curve
  - if the peak is significantly broadened, you might have more success if you *Specify* a starting FWHM

- Initial Location
  - using PDF overlays is always the preferred option
  - if no PDF reference card is available, and the peak is significantly broadened, then you will want to manually insert peaks- the Peak Search will not work
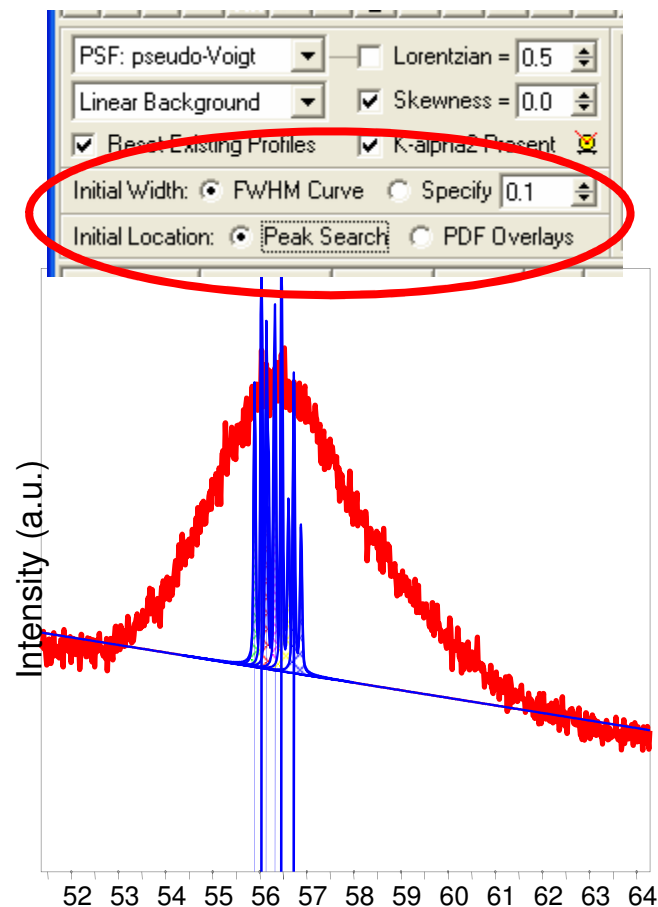
Result of auto insertion using peak search and FWHM curve on a nanocrystalline broadened peak. Manual peak insertion should be used instead.

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8. Display Options

- Check the options for what visual components you want displayed during the profile fitting
  - Typically use:
    - Overall Profile
    - Individual Profiles
    - Background Curve
    - Line Marker
  - Sometimes use:
    - Difference Pattern
    - Paint Individuals

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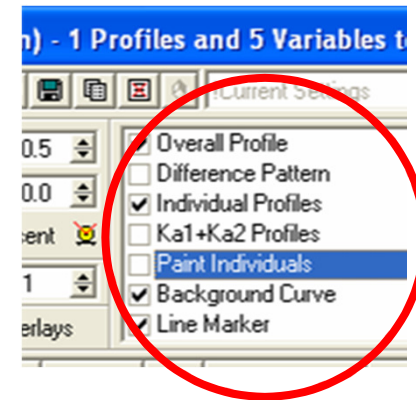
9. Fitting Results

@ 2-Theta	d(nm)	Centroid	Height	BG	Area(a1)	Area%	Shape	Skew	FWHM	Breadth	XS(Å)	
☐ 28.426 (0.000)	0.31373 (0.00001)	28.426	40998 (535)	476	174410 (2584)	100.0	0.721v	0.000	0.050 (0.001)	0.071 (0.001)	>1000 (?)	
☐ 47.294 (?)	0.19205 (?)	47.294	17769 (?)	233	65299 (?)	37.4	0.500v	0.000	0.047 (?)	0.061 (?)	>1000 (?)	
☐ 56.106 (0.000)	0.16379 (0.00000)	56.106	10532 (119)	174	60452 (815)	34.7	0.901v	0.000	0.064 (0.001)	0.096 (0.002)	>1000 (?)	
☐ 69.114 (0.001)	0.13580 (0.00000)	69.114	1885 (40)	124	13802 (357)	7.9	0.951v	0.000	0.080 (0.003)	0.122 (0.004)	>1000 (?)	
☐ 76.360 (0.000)	0.12462 (0.00000)	76.360	3324 (47)	122	24256 (407)	13.9	0.854v	0.000	0.083 (0.002)	0.122 (0.003)	>1000 (?)	

Total Area = 463607 (2916) | Area = 13.04(0.19)% | Crystallinity = ? | R = (Un-refined)

- This area displays the results for profile fit peaks
- Numbers in () are estimated standard deviations (ESD)
  - if the ESD is marked with (?), then that peak profile function has not yet been refined
- Click once on a row, and the Main Display Area of Jade will move to show you that peak, and a blinking cursor will highlight that peak
- You can sort the peak fits by any column by clicking on the column header

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Other buttons of interest

Execute
Refinement

Autofit
All Peaks

See Other
Options

Help

Save Text File
of Results

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Clicking Other Options

Unify Variables: force all peaks to be fit using the same profile parameter

Select What Columns
to Show in the
Results Area

**Use FWHM or Integral Breadth
for Crystallite Size Analysis**

Procedure for Profile Fitting a Diffraction Pattern

1. Open the diffraction pattern
2. Overlay the PDF reference
3. Zoom in on first peak(s) to analyze
4. Open the profile fitting dialogue to configure options
5. Refine the profile fit for the first peak(s)
6. Review the quality of profile fit
7. Move to next peak(s) and profile fit
8. Continue until entire pattern is fit

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Procedure for Profile Fitting

1. Open the XRD pattern

2. Overlay PDF reference for the sample

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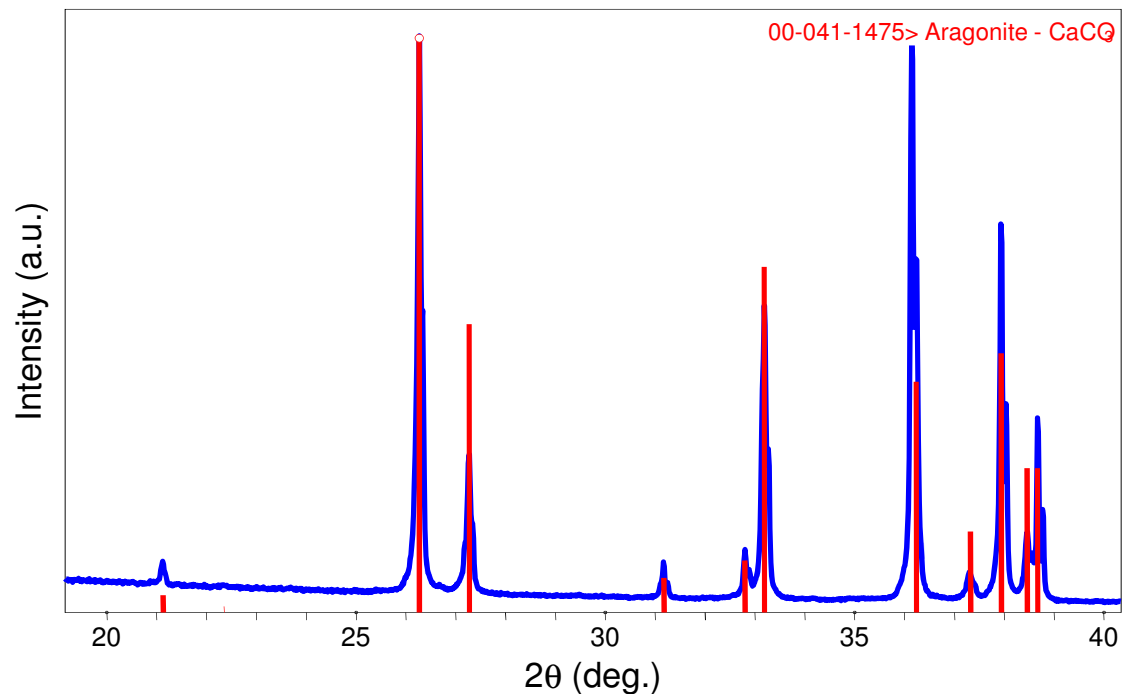
Procedure for Profile Fitting

3. Zoom in on First Peak to Analyze
   – try to zoom in on only one peak
   – be sure to include some background on either side of the peak
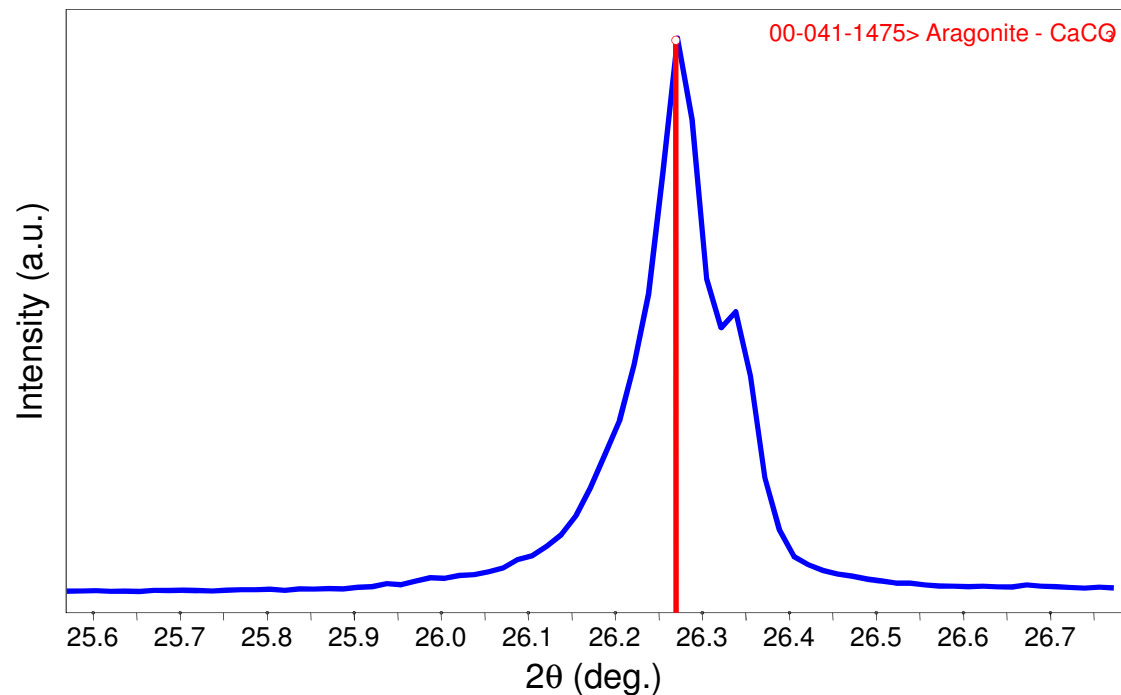
Procedure for Profile Fitting

4. Open profile fitting dialogue to configure parameter

- when you open the profile fitting dialogue, an initial peak profile curve will be generated

- if the initial profile is not good, because initial width and location parameters were not yet set, then delete it
  - highlight the peak in the fitting results
  - press the delete key on your keyboard
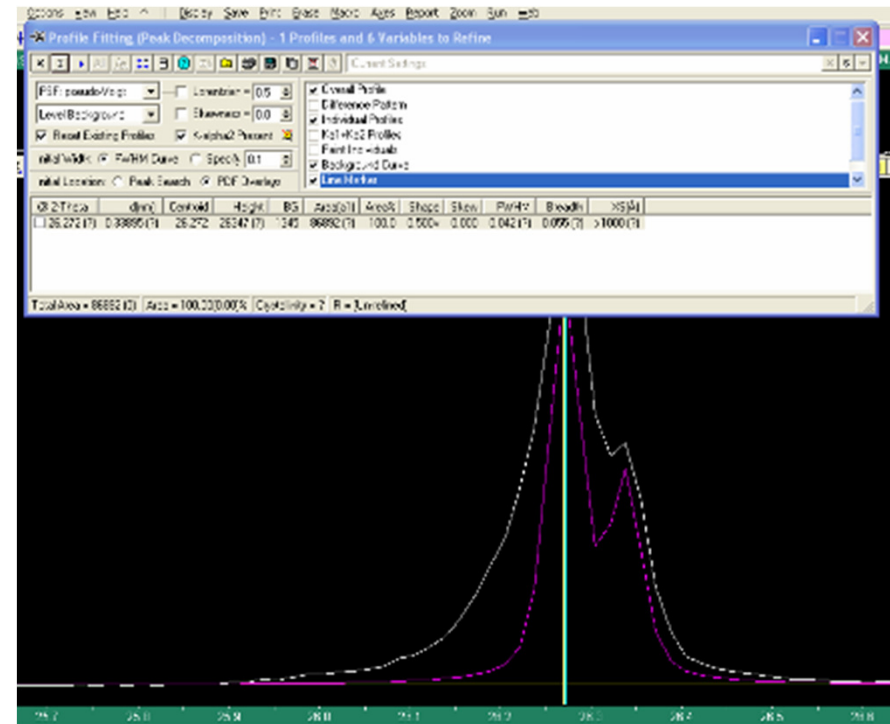
5. Once parameters are configured properly, click on the blue triangle to execute "Profile Fitting"

• you may have to execute the refinement multiple times if the initial refinement stops before the peak is sufficiently fit

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Procedure for Profile Fitting

6. Review Quality of Profile Fit

- The least-squares fitting residual, R, will be listed in upper right corner of screen
  - the residual R should be less than 10%
- The ESD for parameters such as 2-Theta and FWHM should be small, in the last significant figure

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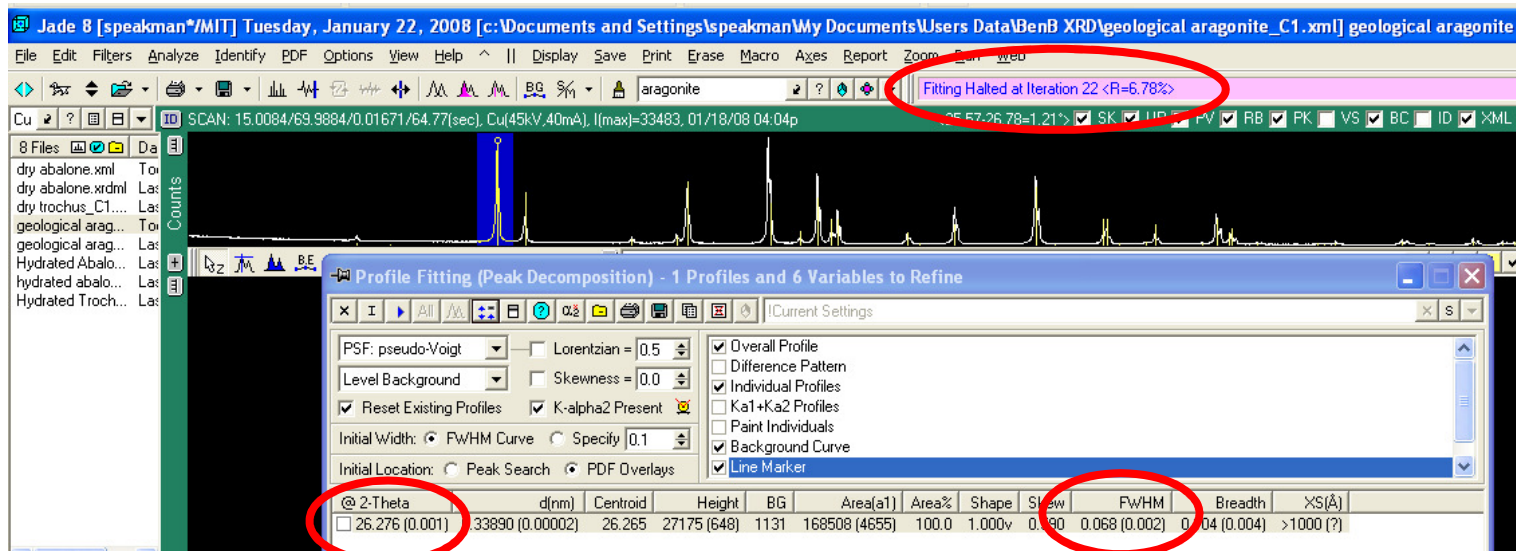
Procedure for Profile Fitting

7. Move to Next Peak(s)

- In this example, peaks are too close together to refine individually
- Therefore, profile fit the group of peaks together
- Profile fitting, if done well, can help to separate overlapping peaks

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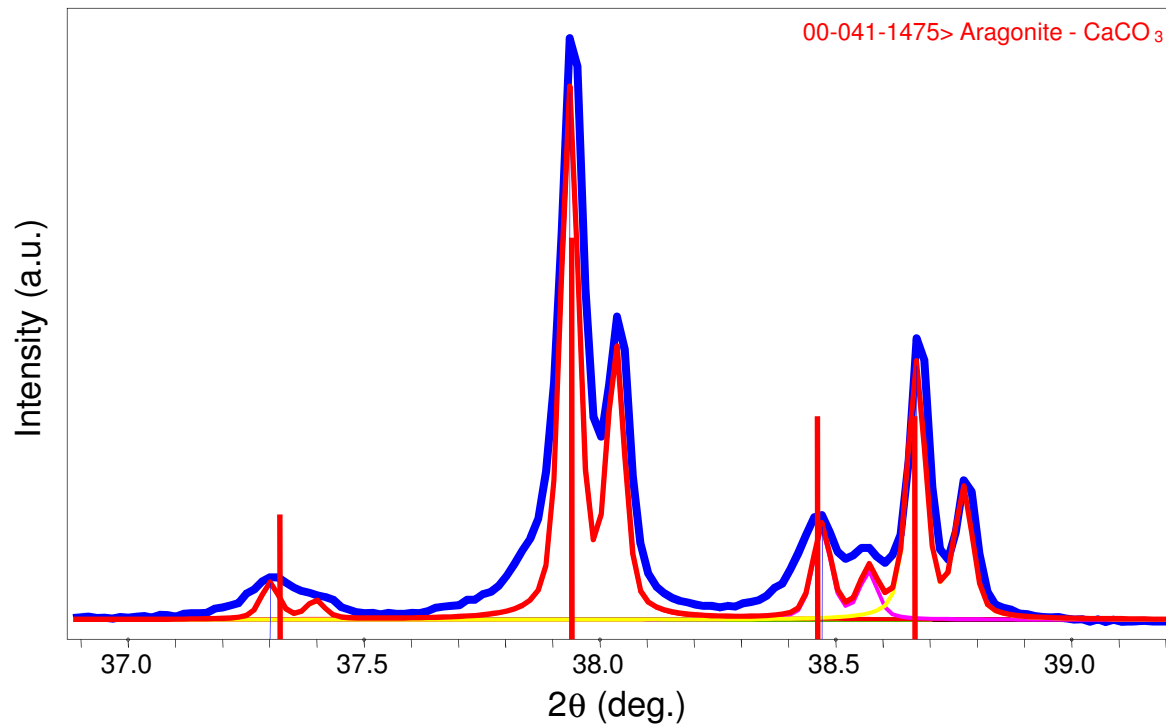
Procedure for Profile Fitting

8. Continue until the entire pattern is fit

- The results window will list a residual R for the fitting of the entire diffraction pattern

- The difference plot will highlight any major discrepancies

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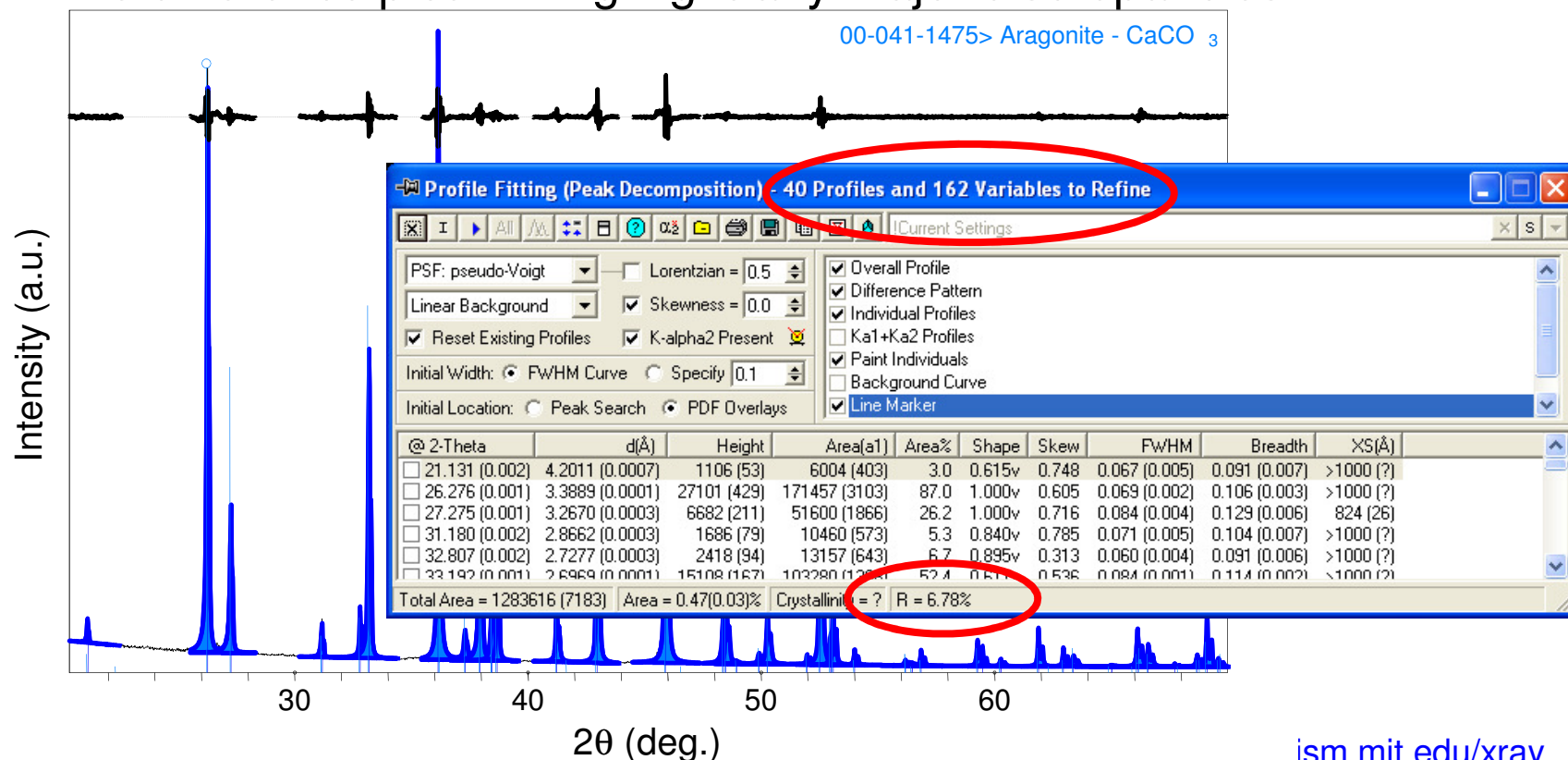
Instrumental FWHM Calibration Curve

- The instrument itself contributes to the peak profile
- Before profile fitting the nanocrystalline phase(s) of interest
    - *profile fit a calibration standard to determine the instrumental profile*

- Important factors for producing a calibration curve
    - Use the exact same instrumental conditions
        - same optical configuration of diffractometer
        - same sample preparation geometry
        - calibration curve should cover the 2theta range of interest for the specimen diffraction pattern
            - do not extrapolate the calibration curve

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Instrumental FWHM Calibration Curve

- Standard should share characteristics with the nanocrystalline specimen

  - similar mass absorption coefficient

  - similar atomic weight

  - similar packing density

- The standard should not contribute to the diffraction peak profile

  - macrocrystalline: crystallite size larger than 500 nm

  - particle size less than 10 microns

  - defect and strain free

- There are several calibration techniques

  - Internal Standard

  - External Standard of same composition

  - External Standard of different composition

Internal Standard Method for Calibration

- Mix a standard in with your nanocrystalline specimen

- a NIST certified standard is preferred
  - use a standard with similar mass absorption coefficient
  - NIST 640c Si
  - NIST 660a LaB$_6$
  - NIST 674b CeO$_2$
  - NIST 675 Mica

- standard should have few, and preferably no, overlapping peaks with the specimen
  - overlapping peaks will greatly compromise accuracy of analysis

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Internal Standard Method for Calibration

- ## Advantages:
  - know that standard and specimen patterns were collected under identical circumstances for both instrumental conditions and sample preparation conditions
  - the linear absorption coefficient of the mixture is the same for standard and specimen

- ## Disadvantages:
  - difficult to avoid overlapping peaks between standard and broadened peaks from very nanocrystalline materials
  - the specimen is contaminated
  - only works with a powder specimen

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External Standard Method for Calibration

- If internal calibration is not an option, then use external calibration

- Run calibration standard separately from specimen, keeping as many parameters identical as is possible

- **The best external standard is a macrocrystalline specimen of the same phase as your nanocrystalline specimen**
  - How can you be sure that macrocrystalline specimen does not contribute to peak broadening?

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Qualifying your Macrocrystalline Standard

- select powder for your potential macrocrystalline standard
  - if not already done, possibly anneal it to allow crystallites to grow and to allow defects to heal
- use internal calibration to validate that macrocrystalline specimen is an appropriate standard
  - mix macrocrystalline standard with appropriate NIST SRM
  - compare FWHM curves for macrocrystalline specimen and NIST standard
  - if the macrocrystalline FWHM curve is similar to that from the NIST standard, than the macrocrystalline specimen is suitable
  - collect the XRD pattern from pure sample of you macrocrystalline specimen
    - do not use the FHWM curve from the mixture with the NIST SRM

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Disadvantages/Advantages of External Calibration with a Standard of the Same Composition

- Advantages:
    - will produce better calibration curve because mass absorption coefficient, density, molecular weight are the same as your specimen of interest
    - can duplicate a mixture in your nanocrystalline specimen
    - might be able to make a macrocrystalline standard for thin film samples

- Disadvantages:
    - time consuming
    - desire a different calibration standard for every different nanocrystalline phase and mixture
    - macrocrystalline standard may be hard/impossible to produce
    - calibration curve will not compensate for discrepancies in instrumental conditions or sample preparation conditions between the standard and the specimen

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External Standard Method of Calibration using a NIST standard

- As a last resort, use an external standard of a composition that is different than your nanocrystalline specimen
  - This is actually the most common method used
  - Also the least accurate method
- Use a certified NIST standard to produce instrumental FWHM calibration curve

Advantages and Disadvantages of using NIST standard for External Calibration

- Advantages
  - only need to build one calibration curve for each instrumental configuration
  - I have NIST standard diffraction patterns for each instrument and configuration available for download from http://prism.mit.edu/xray/standards.htm
  - know that the standard is high quality if from NIST
  - neither standard nor specimen are contaminated

- Disadvantages
  - The standard may behave significantly different in diffractometer than your specimen
    - different mass absorption coefficient
    - different depth of penetration of X-rays
  - NIST standards are expensive
  - cannot duplicate exact conditions for thin films

Consider- when is good calibration most essential?

FWHM of Instrumental Profile at 48° 2θ

0.061 deg

Broadening Due to Nanocrystalline Size

Crystallite Size	B(2θ) (rad)	FWHM (deg)
100 nm	0.0015	0.099
50 nm	0.0029	0.182
10 nm	0.0145	0.871
5 nm	0.0291	1.745

- For a very small crystallite size, the specimen broadening dominates over instrumental broadening
- Only need the most exacting calibration when the specimen broadening is small because the specimen is not highly nanocrystalline

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Steps for Producing an Instrumental Profile

1. Collect data from calibration standard
2. Profile fit peaks from the calibration standard
3. Produce FWHM curve
4. Save FWHM curve
5. Set software preferences to use FHWH curve as Instrumental Profile

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Steps for Producing an Instrumental Profile

1. Collect XRD pattern from standard over a long range

2. Profile fit all peaks of the standard's XRD pattern

   - use the profile function (Pearson VII or pseudo-Voigt) that you will use to fit your specimen pattern

   - indicate if you want to use FWHM or Integral Breadth when analyzing specimen pattern

3. Produce a FWHM curve

   - go to *Analyze > FWHM Curve Plot*
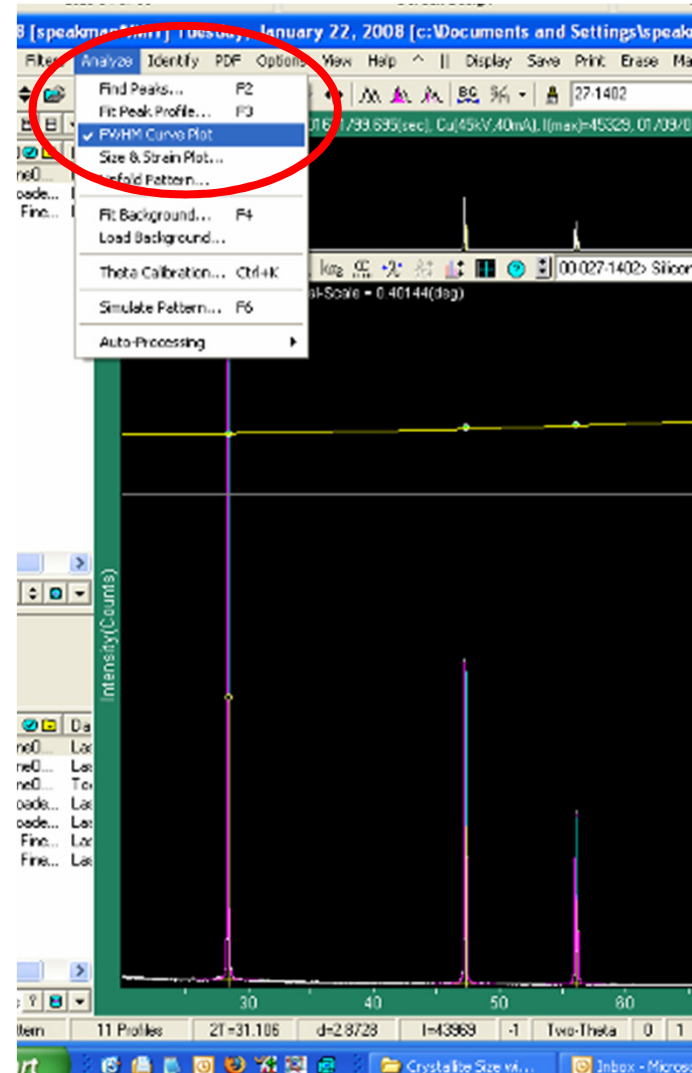
Steps for Producing an Instrumental Profile

4. Save the FWHM curve

- go to *File > Save > FWHM Curve of Peaks*
- give the FWHM curve a name that you will be able to find again
  - the FWHM curve is saved in a database on the local computer
  - you need to produce the FWHM curve on each computer that you use
  - everybody else's FHWM curves will also be visible
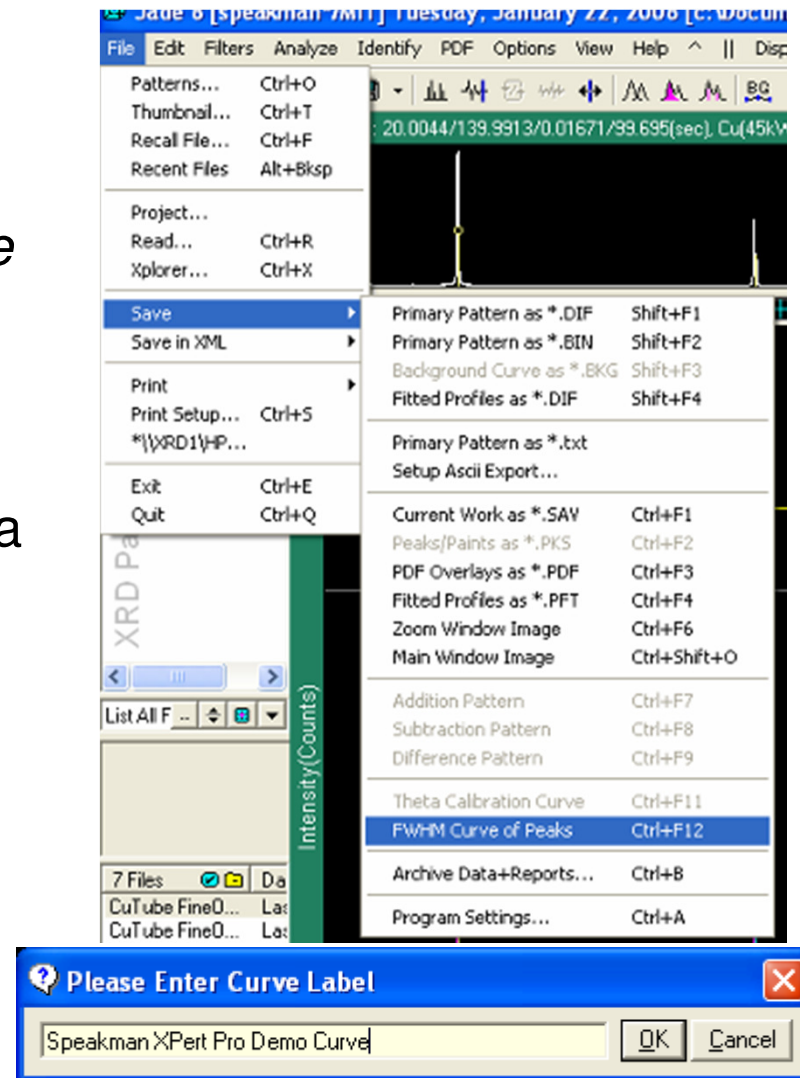
Steps for Producing an Instrumental Profile

5. Set preferences to use the FWHM curve as the instrumental profile

- Go to *Edit > Preferences*
- Select the <u>Instrument</u> tab
- Select your FWHM curve from the drop-down menu on the bottom of the dialogue
- Also enter Goniometer Radius
  – Rigaku Right-Hand Side: 185mm
  – Rigaku Left-Hand Side: 250mm
  – PANalytical X'Pert Pro: 240mm

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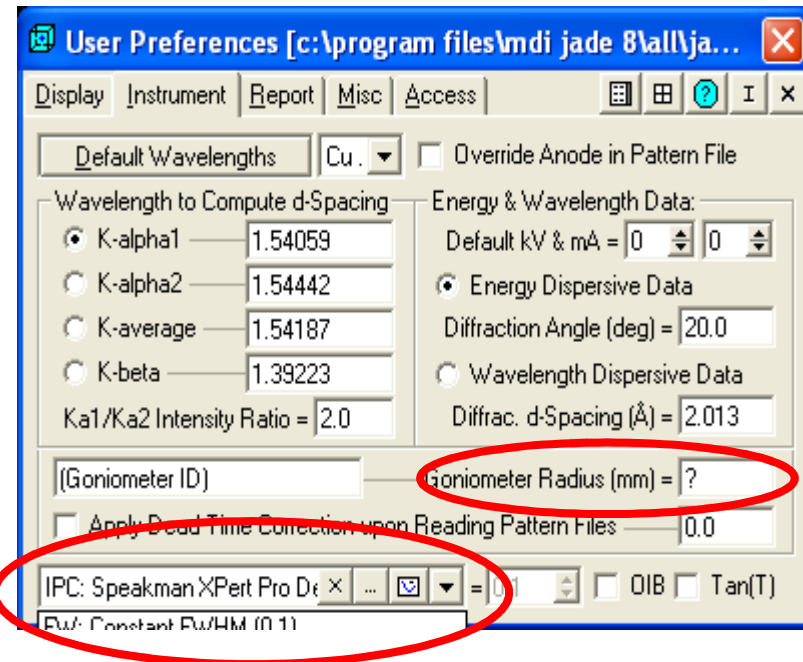
Other Software Preferences
That You Should Be Aware Of

- ## Report Tab
  - Check to calculate Crystallite Size from FWHM
  - set Scherrer constant

- ## Display tab
  - Check the last option to have crystallite sizes reported in nanometers
  - Do not check last option to have crystallite sizes reported in Angstroms

http://prism.mit.edu/xray
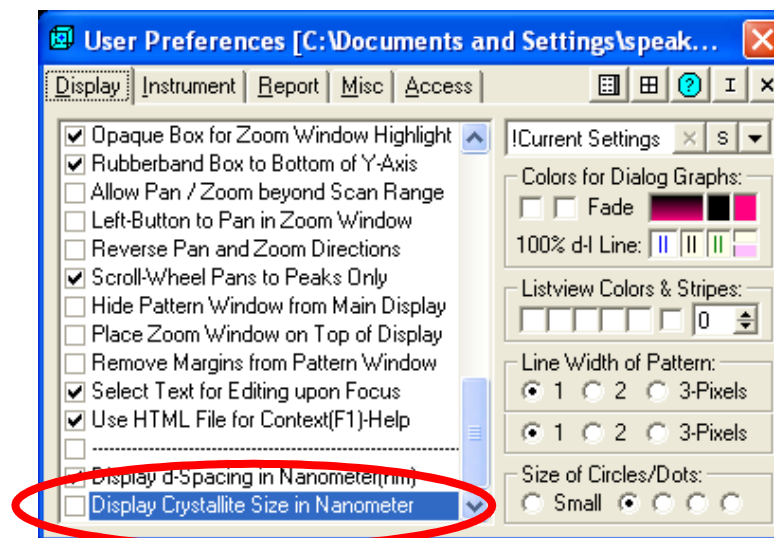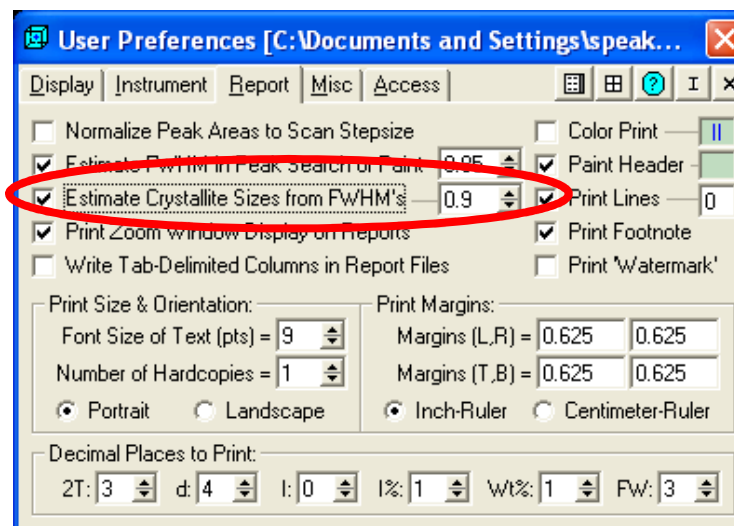
Using the Scherrer Method in Jade to Estimate Crystallite Size

- load specimen data

- load PDF reference pattern

- Profile fit as many peaks of your data that you can

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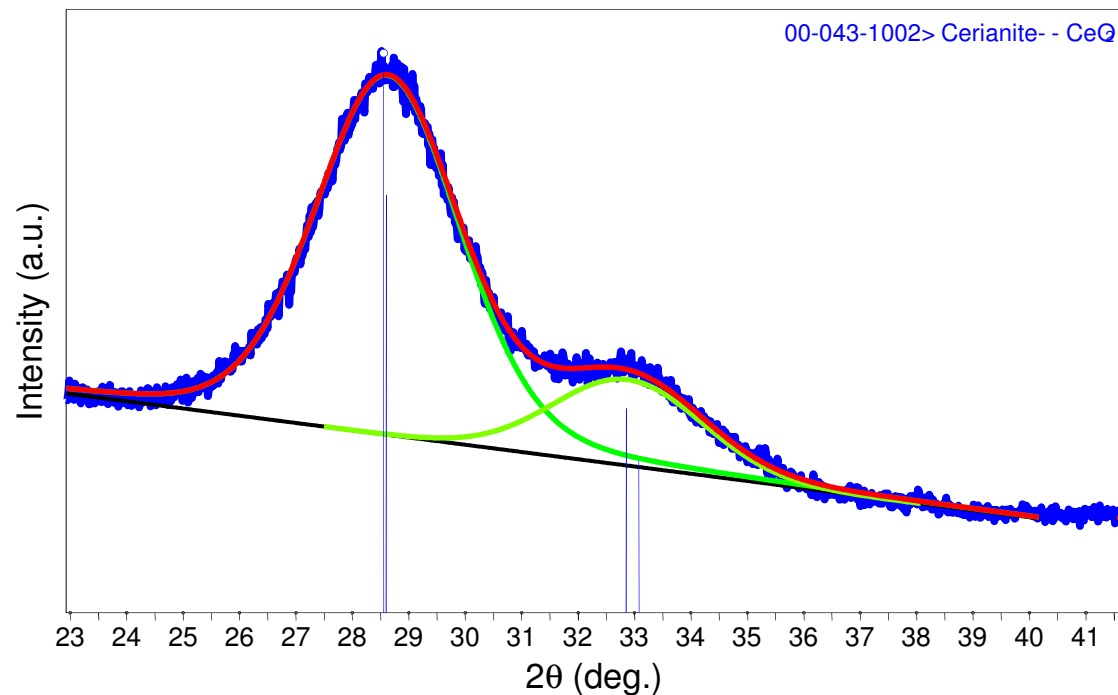
Scherrer Analysis Calculates Crystallite Size based on each Individual Peak Profile

- Crystallite Size varies from 22 to 30 Å over the range of 28.5 to 95.4° 2θ
  - Average size: 25 Å
  - Standard Deviation: 3.4 Å

- Pretty good analysis

- Not much indicator of crystallite strain

- We might use a single peak in future analyses, rather than all 8

Profile Fitting (Peak Decomposition) - 8 Profil...

PSF: pseudo-Voigt   ☐ Lorentzian = 0.5
Linear Background   ☑ Skewness = 0.0
☑ Reset Existing Profiles   ☑ K-alpha2 Present
Initial Width: ⦿ FWHM Curve ○ Specify 0.1
Initial Location: ○ Peak Search ⦿ PDF Overlays

☑ Overall Profile
☑ Difference Pat
☑ Individual Prof
☐ Ka1+Ka2 Profi
☑ Paint Individua
☐ Background C
☑ Line Marker

@ 2-Theta	d(Å)	FWHM	Breadth	XS(Å)
28.598 (0.008)	3.1188 (0.0018)	3.041 (0.015)	3.459 (0.016	27 (1)
32.853 (0.028)	2.7240 (0.0046)	3.094 (0.044)	3.293 (0.05)	27 (1)
47.429 (0.011)	1.9153 (0.0008)	3.466 (0.019)	3.744 (0.03)	25 (1)
56.573 (0.014)	1.6255 (0.0008)	4.195 (0.034)	5.383 (0.03)	22 (1)
69.267 (0.059)	1.3554 (0.0020)	3.203 (0.111)	3.408 (0.18)	30 (2)
77.850 (0.027)	1.2260 (0.0007)	5.166 (0.057)	5.499 (0.08)	20 (1)
88.568 (0.063)	1.1032 (0.0012)	4.311 (0.093)	4.969 (0.14)	26 (2)
95.390 (0.083)	1.0415 (0.0014)	4.935 (0.209)	5.186 (0.327	24 (2)

Total Area = 0 (0)   Area = ?   Crystallinity = ?   R = 5.17%

FWHM vs Integral Breadth

- Using FWHM: 25.1 Å (3.4)
- Using Breadth: 22.5 Å (3.7)
- Breadth not as accurate because there is a lot of overlap between peaks- cannot determine where tail intensity ends and background begins

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Analysis Using Different Values of K

- For the typical values of 0.81 < K < 1.03
  - the crystallite size varies between 22 and 29 Å
  - The precision of XRD analysis is never better than ±1 nm
  - The size is reproducibly calculated as 2-3 nm

K	0.62	0.81	0.89	0.94	1	1.03	2.08
28.6	19	24	27	28	30	31	60
32.9	19	24	27	28	30	31	60
47.4	17	23	25	26	28	29	56
56.6	15	19	22	23	24	25	48
69.3	21	27	30	32	34	35	67
77.8	14	18	20	21	22	23	44
88.6	18	23	26	27	29	30	58
95.4	17	22	24	25	27	28	53
Avg	**17**	**22**	**25**	**26**	**28**	**29**	**56**

For Size & Strain Analysis using Williamson-Hull type Plot in Jade

- after profile fitting all peaks, click size-strain button
  – or in main menus, go to *Analyze > Size&Strain Plot*

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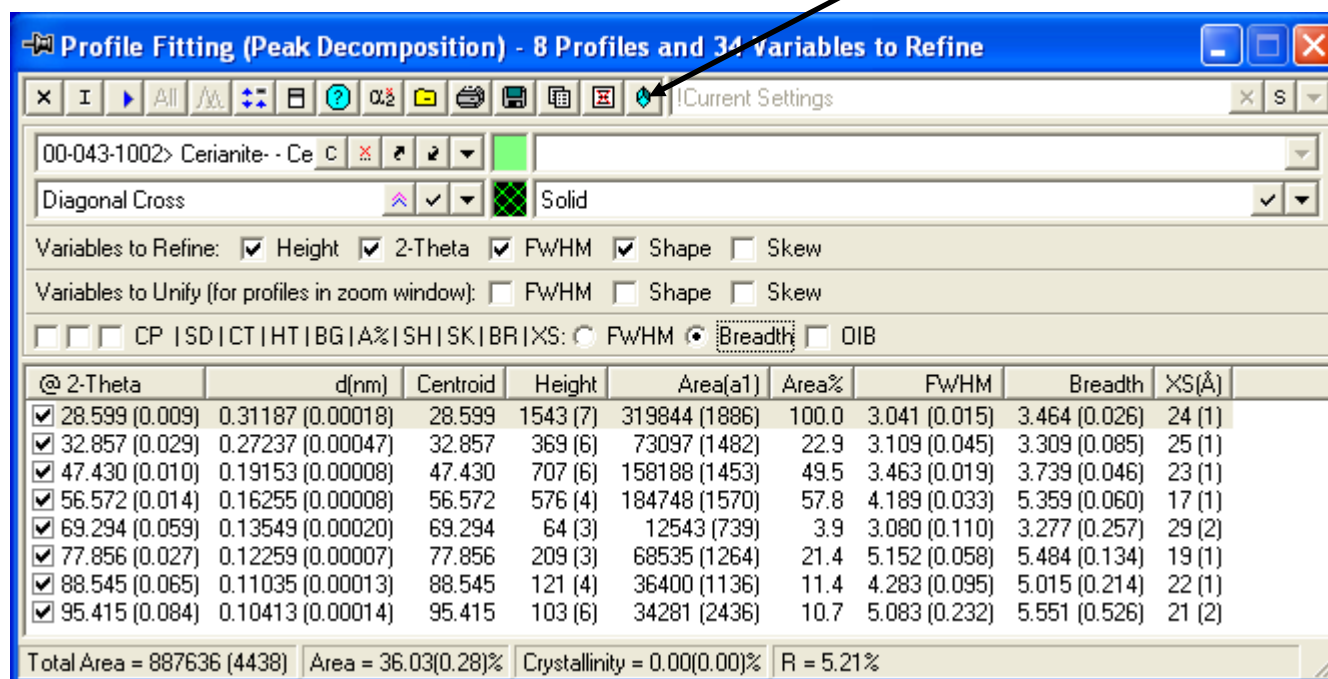
Williamson Hull Plot

$$FW(S) \times \cos(\theta) = \frac{K \times \lambda}{Size} + 4 \times Strain \times \sin(\theta)$$

y-intercept   slope

*Fit Size/Strain: XS(Å) = 33 (1), Strain(%) = 0.805 (0.0343), ESD of Fit = 0.00902, LC = 0.751

y-axis: **FW(S)*Cos(Theta)**, range 0.000 to 4.244

x-axis: **Sin(Theta)**, range 0.000 to 0.784

http://prism.mit.edu/xray
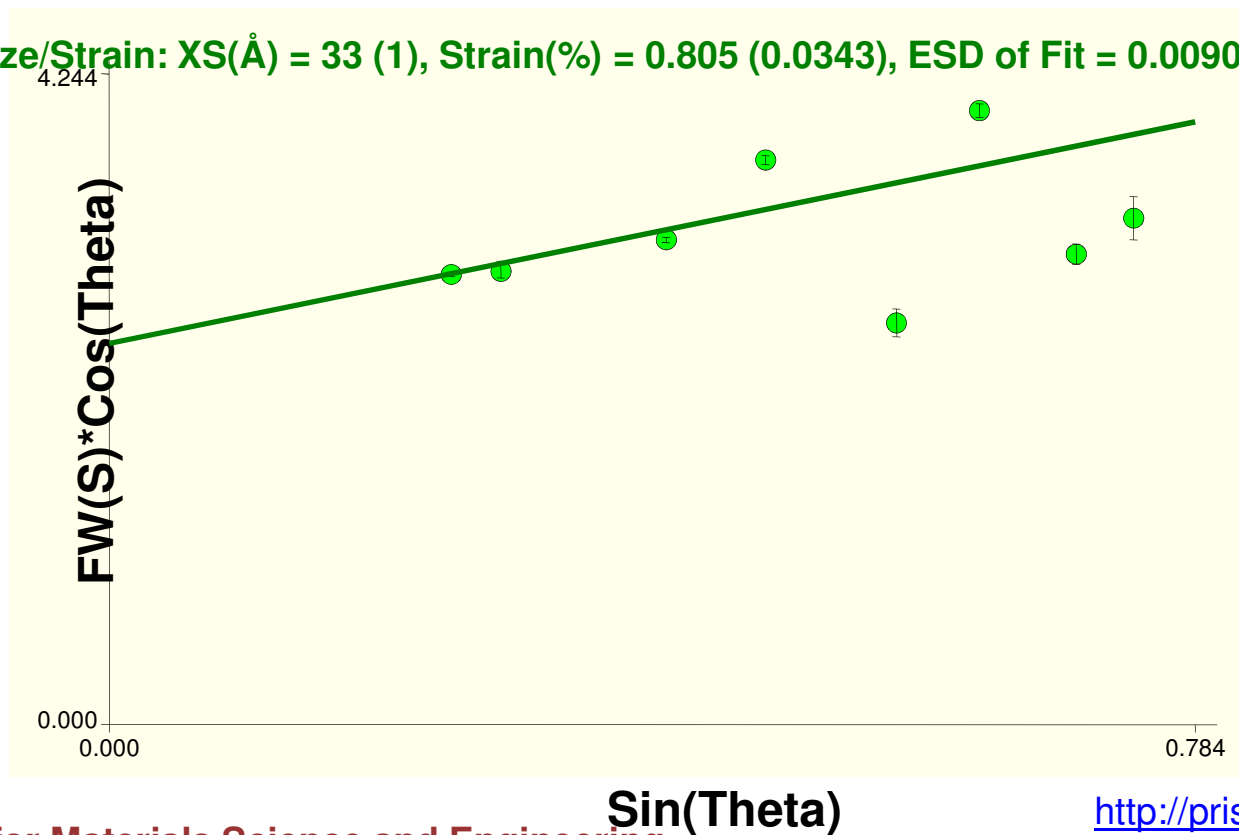
Manipulating Options in the Size-Strain Plot of Jade

1. Select Mode of Analysis
   - Fit Size/Strain
   - Fit Size
   - Fit Strain
2. Select Instrument Profile Curve
3. Show Origin
4. Deconvolution Parameter
5. Results
6. Residuals for Evaluation of Fit
7. Export or Save

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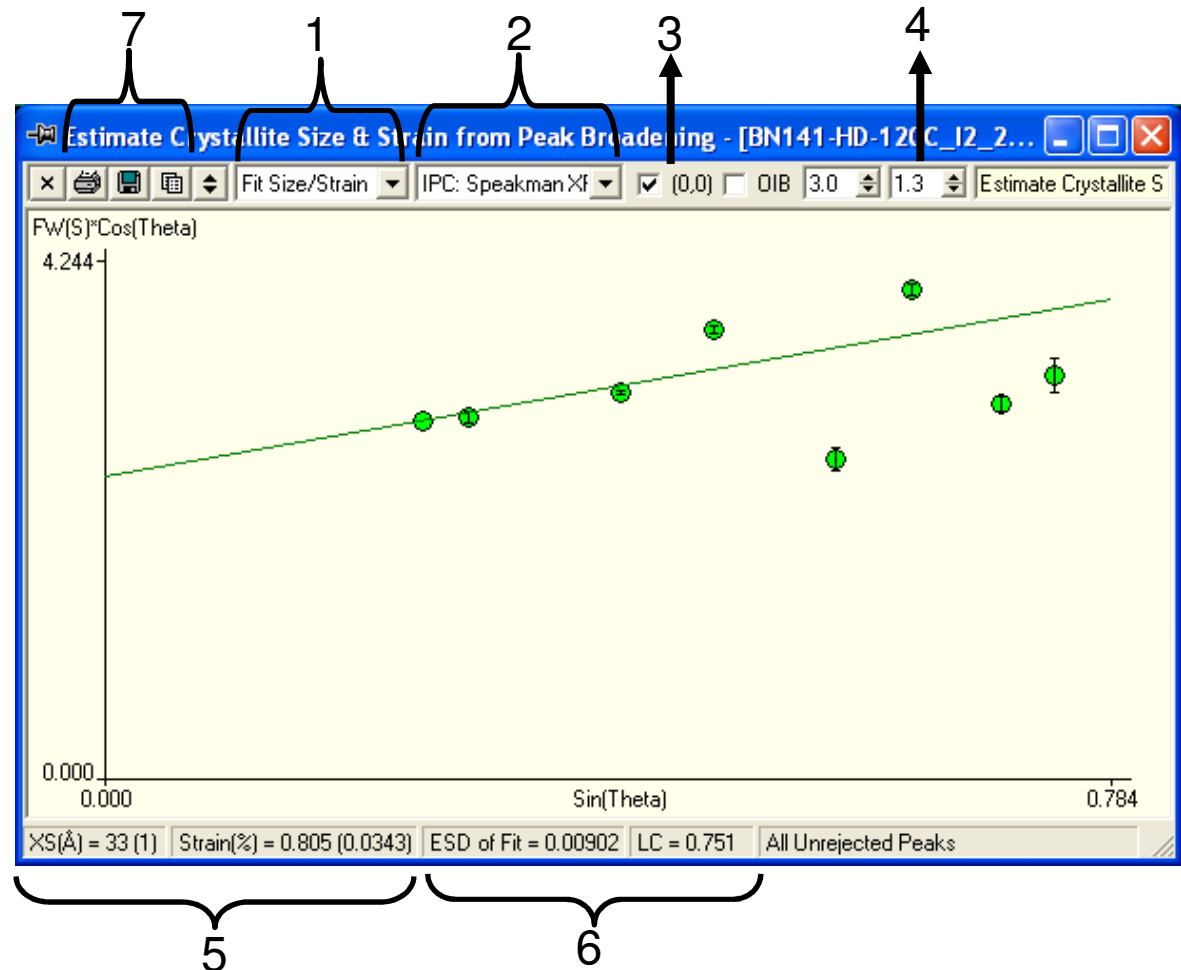
Analysis Mode: Fit Size Only

$$FW(S) \times \cos(\theta) = \frac{K \times \lambda}{Size} + \underbrace{4 \times Strain \times \sin(\theta)}_{slope= 0= strain}$$

*Fit Size Only: XS(Å) = 26 (1), Strain(%) = 0.0, ESD of Fit = 0.00788, LC = 0.751

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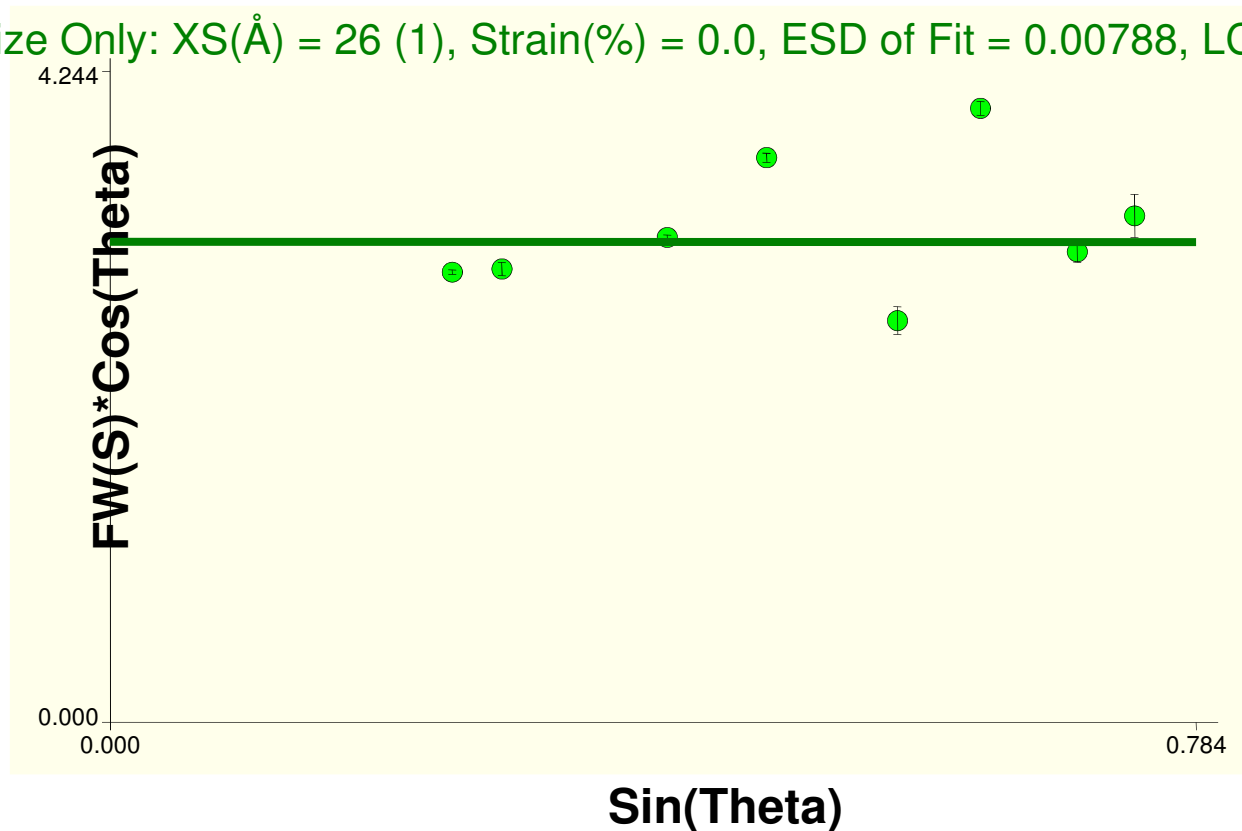
Analysis Mode: Fit Strain Only

$$FW(S) \times \cos(\theta) = \frac{K \times \lambda}{\underbrace{Size}} + 4 \times Strain \times \sin(\theta)$$

y-intercept= 0

size= ∞

*Fit Strain Only: XS(Å) = 0, Strain(%) = 3.556 (0.0112), ESD of Fit = 0.03018, LC = 0.751
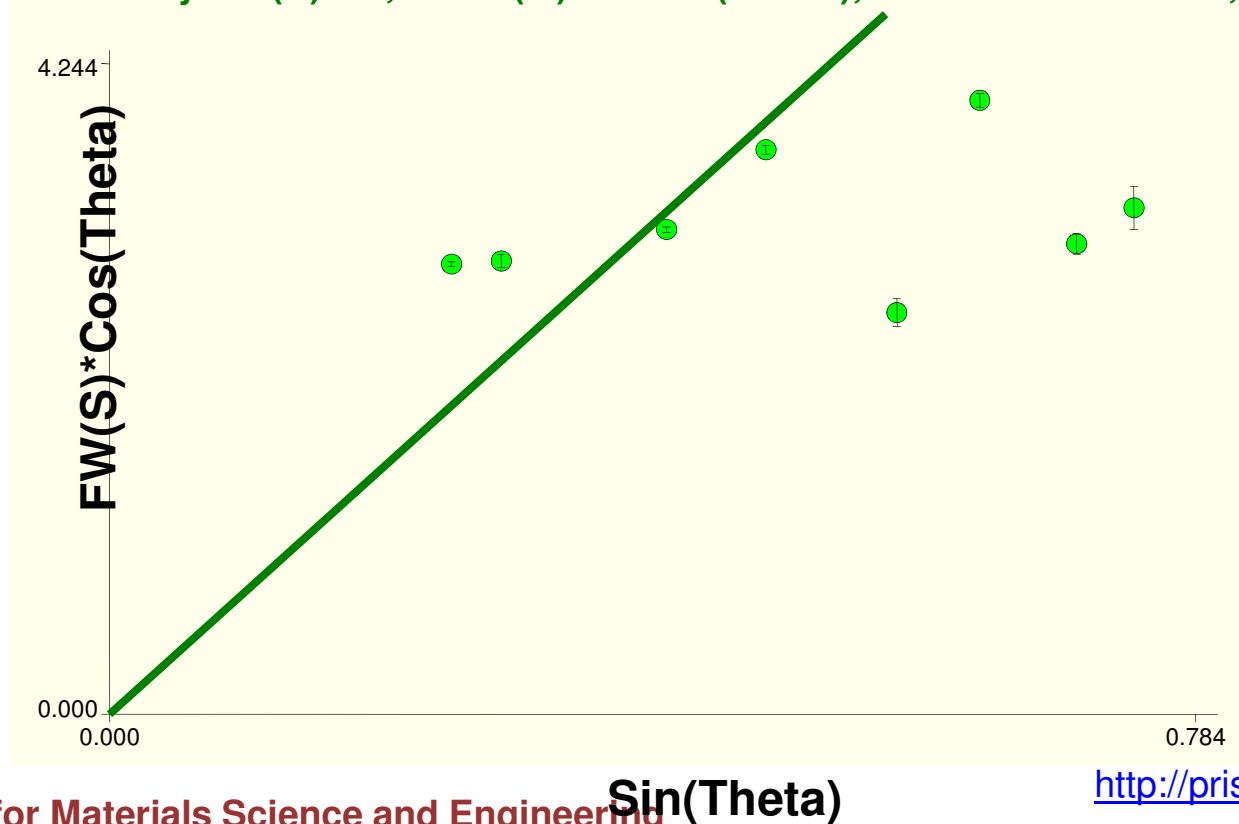
Analysis Mode: Fit Size/Strain

$$FW(S) \times \cos(\theta) = \frac{K \times \lambda}{Size} + 4 \times Strain \times \sin(\theta)$$

*Fit Size/Strain: XS(Å) = 33 (1), Strain(%) = 0.805 (0.0343), ESD of Fit = 0.00902, LC = 0.751

http://prism.mit.edu/xray
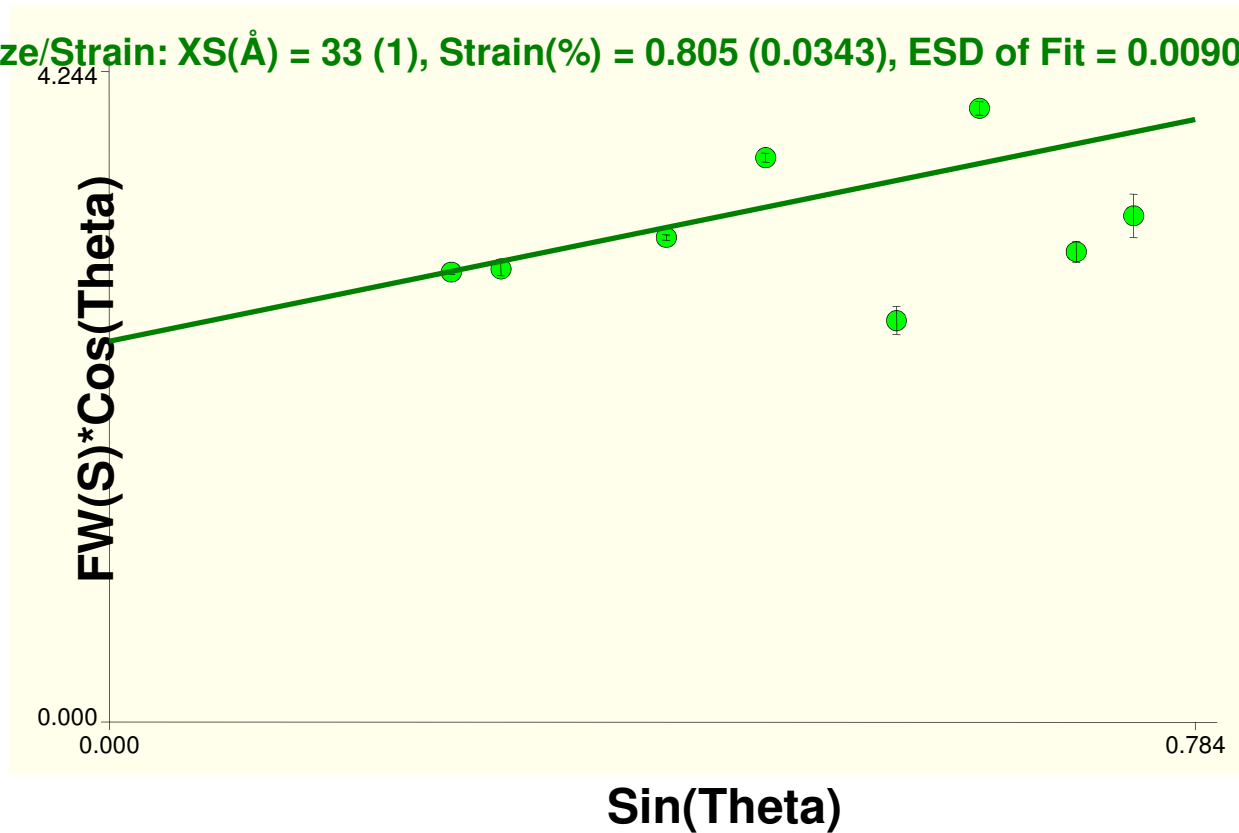
Comparing Results

	Integral Breadth			**FWHM**		
	Size (A)	Strain (%)	ESD of Fit	Size(A)	Strain(%)	ESD of Fit
Size Only	22(1)	-	0.0111	25(1)		0.0082
Strain Only	-	4.03(1)	0.0351		3.56(1)	0.0301
Size & Strain	28(1)	0.935(35)	0.0125	32(1)	0.799(35)	0.0092
Avg from Scherrer Analysis	22.5			25.1		

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Manually Inserting Peak Profiles

- Click on the 'Profile Edit Cursor' button

- Left click to insert a peak profile

- Right click to delete a peak profile

- Double-click on the 'Profile Edit Cursor' button to refine the peak

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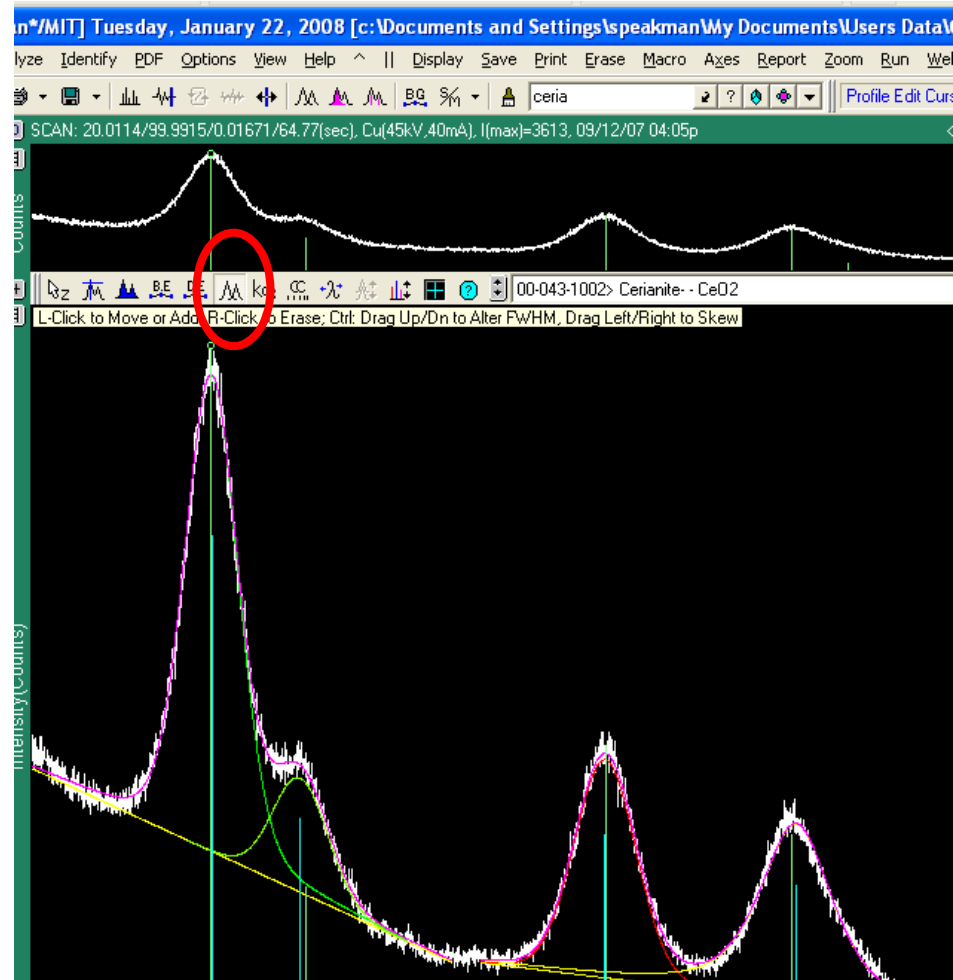
Examples

- Read Y2O3 on ZBH Fast Scan.sav
  - make sure instrument profile is "IAP XPert FineOptics ZBH"
  - Note scatter of data
  - Note larger average crystallite size requiring good calibration
  - data took 1.5 hrs to collect over range 15 to 146° 2θ
  - could only profile fit data up to 90° 2θ; intensities were too low after that
- Read Y2O3 on ZBH long scan.sav
  - make sure instrument profile is "IAP XPert FineOptics ZBH"
  - compare Scherrer and Size-Strain Plot
  - Note scatter of data in Size-Strain Plot
  - data took 14 hrs to collect over range of 15 to 130° 2θ
  - size is 56 nm, strain is 0.39%

- by comparison, CeO_2 with crystallite size of 3 nm took 41min to collect data from 20 to 100° 2θ for high quality analysis

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Examples

- Load CeO2/BN*.xrdml
- Overlay PDF card 34-0394
  - shift in peak position because of thermal expansion
- make sure instrument profile is "IAP XPert FineOptics ZBH"
- look at patterns in 3D view
- Scans collected every 1min as sample annealed *in situ* at 500°C
- manually insert peak profile
- use batch mode to fit peak
- in minutes have record of crystallite size vs time

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Examples

- Size analysis of Si core in SiO2 shell
  - read Si_nodule.sav
  - make sure instrument profile is "IAP Rigaku RHS"
  - show how we can link peaks to specific phases
  - show how Si broadening is due completely to microstrain
  - ZnO is a NIST SRM, for which we know the crystallite size is between 201 nm
    - we estimate 179 nm- shows error at large crystallite sizes

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We can empirically calculate nanocrystalline diffraction pattern using Jade

1. Load PDF reference card

2. go to *Analyze > Simulate Pattern*

3. In Pattern Simulation dialogue box
    1. set instrumental profile curve
    2. set crystallite size & lattice strain
    3. check fold (convolute) with instrument profile

4. Click on 'Clear Existing Display and Create New Pattern'

5. or Click on 'Overlay Simulated Pattern'
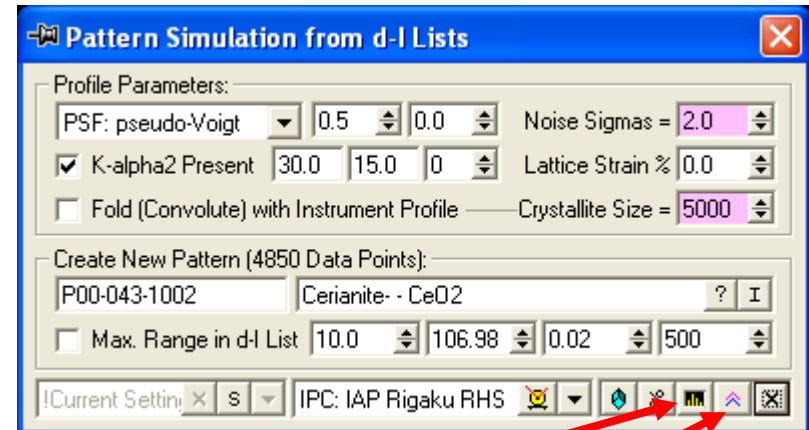
demonstrate with card 46-1212
observe peak overlap at 36° 2θ as peak broaden

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Whole Pattern Fitting

Emperical Profile Fitting is sometimes difficult

- overlapping peaks

- a mixture of nanocrystalline phases

- a mixture of nanocrystalline and macrocrystalline phase

00-008-0459> Cadmoselite - CdSe

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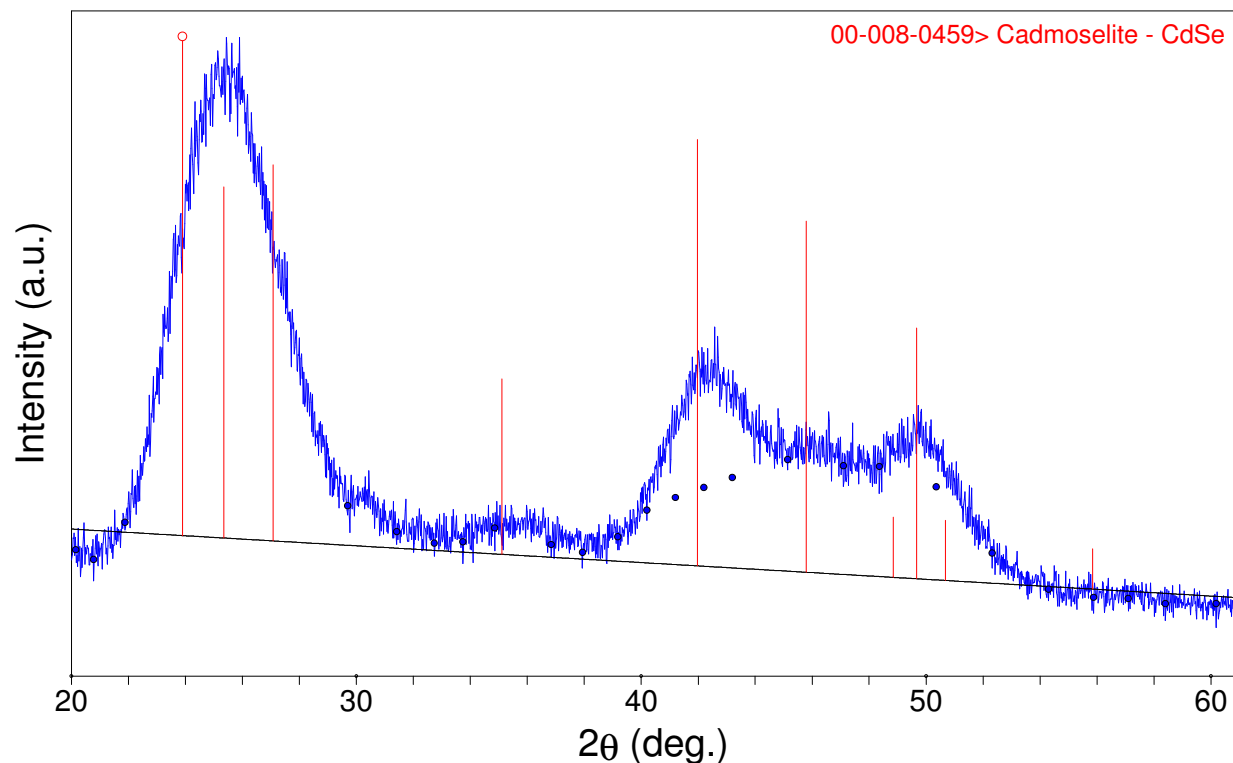
Or we want to learn more information about sample

- quantitative phase analysis
  - how much of each phase is present in a mixture
- lattice parameter refinement
  - nanophase materials often have different lattice parameters from their bulk counterparts
- atomic occupancy refinement

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For Whole Pattern Fitting, Usually use Rietveld Refinement

- model diffraction pattern from calculations
  - With an appropriate crystal structure we can precisely calculate peak positions and intensities
    - this is much better than empirically fitting peaks, especially when they are highly overlapping
  - We also model and compensate for experimental errors such as specimen displacement and zero offset
  - model peak shape and width using empirical functions
    - we can correlate these functions to crystallite size and strain

- we then refine the model until the calculated pattern matches the experimentally observed pattern

- for crystallite size and microstrain analysis, we still need an internal or external standard

Peak Width Analysis in Rietveld Refinement

- HighScore Plus can use pseudo-Voigt, Pearson VII, or Voigt profile functions

- For pseudo-Voigt and Pearson VII functions
  - Peak shape is modeled using the pseudo-Voigt or Pearson VII functions
  - The FWHM term, H_K, is a component of both functions
    - The FWHM is correlated to crystallite size and microstrain
  - The FWHM is modeled using the Cagliotti Equation
    - U is the parameter most strongly associated with strain broadening
    - crystallite size can be calculated from U and W
    - U can be separated into (hkl) dependent components for anisotropic broadening

$$H_K = \left(U \tan^2 \theta + V \tan \theta + W \right)^{1/2}$$

Using pseudo-Voigt and Pears VIII functions in HighScore Plus

- Refine the size-strain standard to determine U, V, and W for the instrumental profile
  - also refine profile function shape parameters, asymmetry parameters, etc
- Refine the nanocrystalline specimen data
  - Import or enter the U, V, and W standard parameters
  - In the settings for the nanocrystalline phase, you can specify the type of size and strain analysis you would like to execute
  - During refinement, U, V, and W will be constrained as necessary for the analysis
    - Size and Strain: Refine U and W
    - Strain Only: Refine U
    - Size Only: Refine U and W, U=W

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Example

- Open ZnO Start.hpf
- Show crystal structure parameters
  - note that this is hexagonal polymorph
- Calculate Starting Structure
- Enter U, V, and W standard
  - U standard= 0.012364
  - V standard= -0.002971
  - W standard= 0.015460
- Set Size-Strain Analysis Option
  - start with Size Only
  - Then change to Size and Strain
- Refine using "Size-Strain Analysis" Automatic Refinement

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The Voigt profile function is applicable mostly to neutron diffraction data

- Using the Voigt profile function may tries to fit the Gaussian and Lorentzian components separately, and then convolutes them
  - correlate the Gaussian component to microstrain
    - use a Cagliotti function to model the FWHM profile of the Gaussian component of the profile function
  - correlate the Lorentzian component to crystallite size
    - use a separate function to model the FWHM profile of the Lorentzian component of the profile function
- This refinement mode is slower, less stable, and typically applies to neutron diffraction data only
  - the instrumental profile in neutron diffraction is almost purely Gaussian

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HighScore Plus Workshop

- Jan 29 and 30 (next Tues and Wed)
  - from 1 to 5 pm both days

- Space is limited: register by tomorrow (Jan 25)
  - preferable if you have your own laptop

- Must be a trained independent user of the X-Ray SEF, familiar with XRD theory, basic crystallography, and basic XRD data analysis

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Free Software

- Empirical Peak Fitting
  - XFit
  - WinFit
    - couples with Fourya for Line Profile Fourier Analysis
  - Shadow
    - couples with Breadth for Integral Breadth Analysis
  - PowderX
  - FIT
    - succeeded by PROFILE
- Whole Pattern Fitting
  - GSAS
  - Fullprof
  - Reitan
- All of these are available to download from http://www.ccp14.ac.uk

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Other Ways of XRD Analysis

- Most alternative XRD crystallite size analyses use the Fourier transform of the diffraction pattern
- Variance Method
  - Warren Averbach analysis- Fourier transform of raw data
  - Convolution Profile Fitting Method- Fourier transform of Voigt profile function
- Whole Pattern Fitting in Fourier Space
  - Whole Powder Pattern Modeling- Matteo Leoni and Paolo Scardi
  - Directly model all of the contributions to the diffraction pattern
  - each peak is synthesized in reciprocal space from it Fourier transform
    - for any broadening source, the corresponding Fourier transform can be calculated
- Fundamental Parameters Profile Fitting
  - combine with profile fitting, variance, or whole pattern fitting techniques
  - instead of deconvoluting empirically determined instrumental profile, use fundamental parameters to calculate instrumental and specimen profiles

Complementary Analyses

- TEM
  - precise information about a small volume of sample
  - can discern crystallite shape as well as size

- PDF (Pair Distribution Function) Analysis of X-Ray Scattering

- Small Angle X-ray Scattering (SAXS)

- Raman

- AFM

- Particle Size Analysis
  - while particles may easily be larger than your crystallites, we know that the crystallites will never be larger than your particles

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Textbook References

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Instrumental Profile Derived from different mounting of LaB$_6$
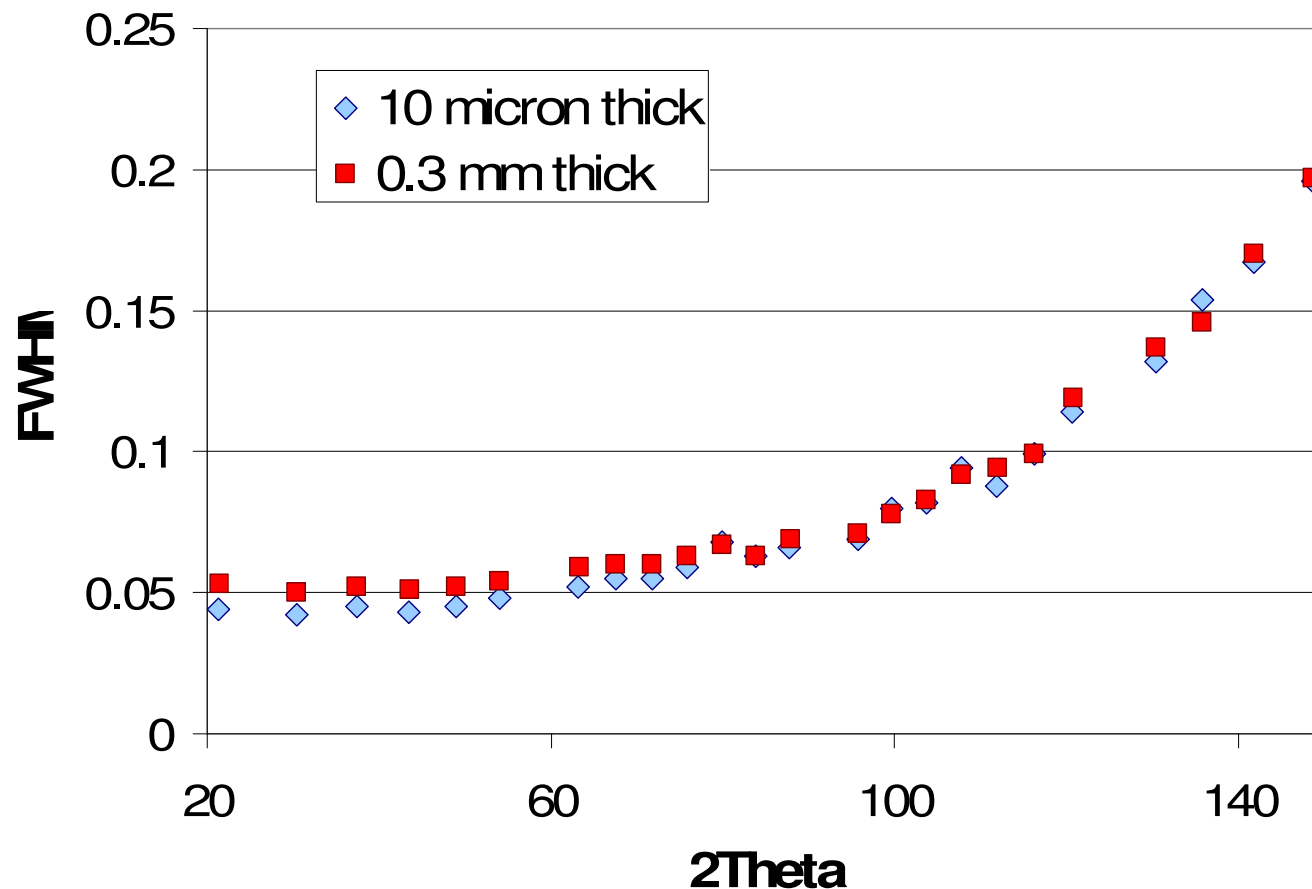
In analysis of Y$_2$O$_3$ on a ZBH, using the instrumental profile from thin SRM gives a size of 60 nm; using the thick SRM gives a size of 64 nm

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