Estimating Crystallite Size Using XRD

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I have tried to cite all references, I may have missed some– these slides were prepared for an informal lecture and not for publication.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

A Brief History of XRD

- 1895- Röntgen publishes the discovery of X-rays
- 1912- Laue observes diffraction of X-rays from a crystal
- 1913- Bragg solves the first crystal structure from X-ray diffraction data

- *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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X-Ray Peak Broadening is caused by deviation from the ideal crystalline lattice

- The Laue Equations describe the intensity of a diffracted peak from an ideal parallelopipeden crystal
- The ideal crystal is an **infinitely large** and **perfectly ordered** crystalline array
  - From the perspective of X-rays, "infinitely" large is a few microns
- Deviations from the ideal create peak broadening
  - A nanocrystallite is not "infinitely" large
  - Non-perfect ordering of the crystalline array can include
    - Defects
   - Non-uniform interplanar spacing
    - disorder

As predicted by the Laue equations, the diffraction peaks becomes broader when N is not infinite

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

- N_1, N_2, and N_3 are the number of unit cells along the a_1, a_2, and a_3 directions
- The calculated peak is narrow when N is a large number (ie infinitely large)
- When N is small, the diffraction peaks become broader
  - A nanocrystalline phase has a small number of N
- The peak area remains constant independent of N

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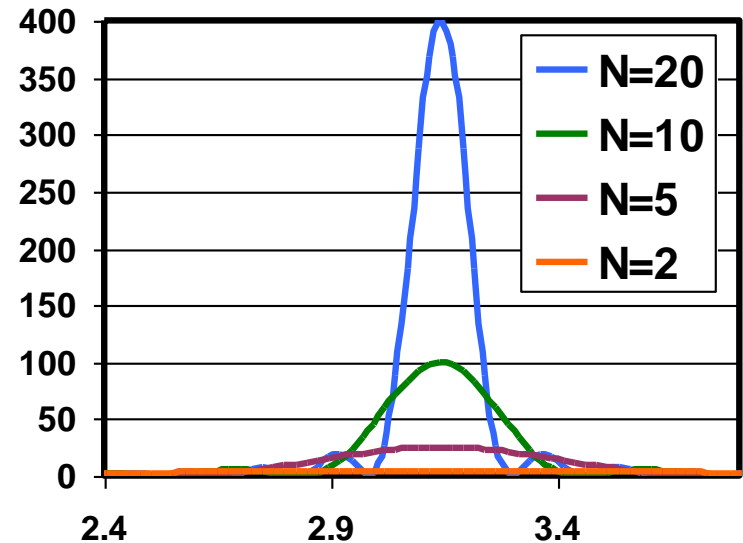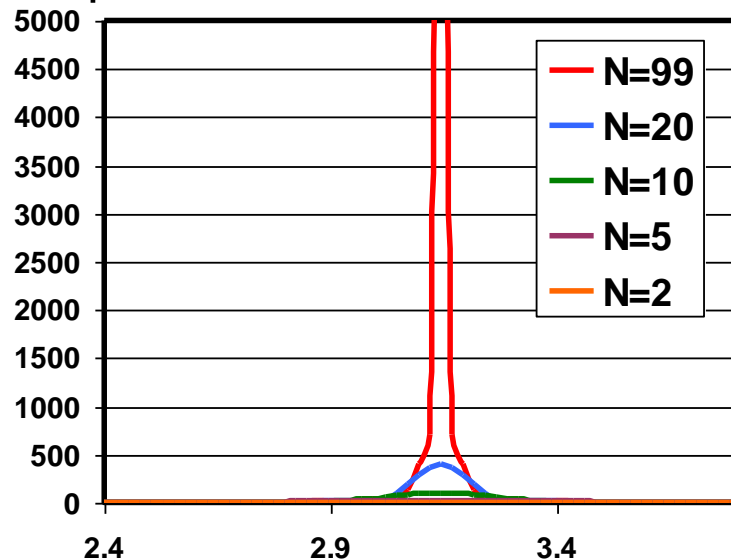
# We cannot assume that all broad peaks are produced by nanocrystalline materials
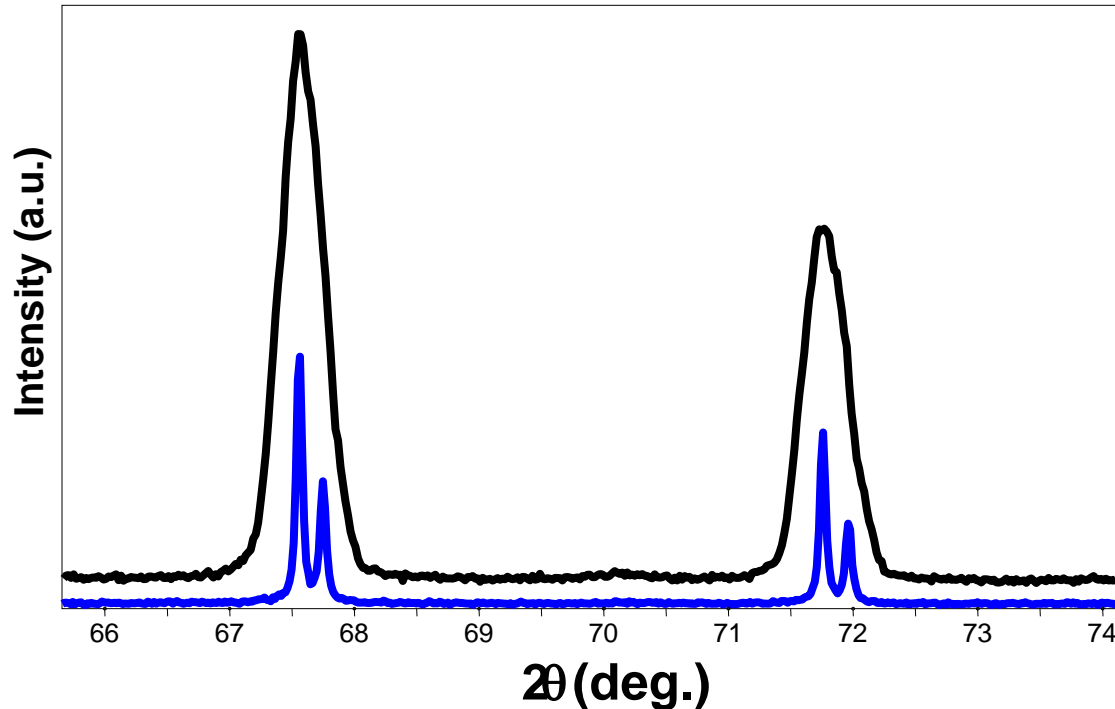
- These diffraction patterns were produced from the **exact same sample**
- Two different diffractometers, with different optical configurations, were used
- *The apparent peak broadening is due solely to the instrumentation*

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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Before analysis, you must decide how you will 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
  - This was most often used in older research because it is easier to calculate

- **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
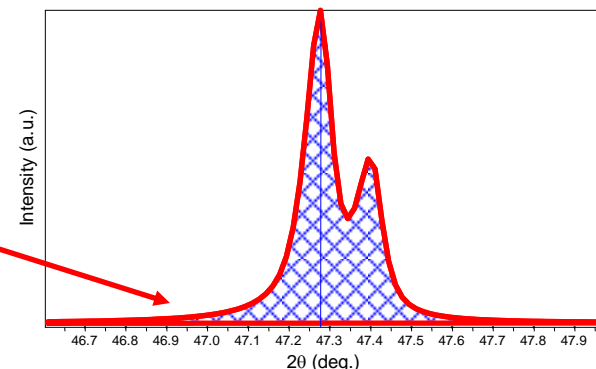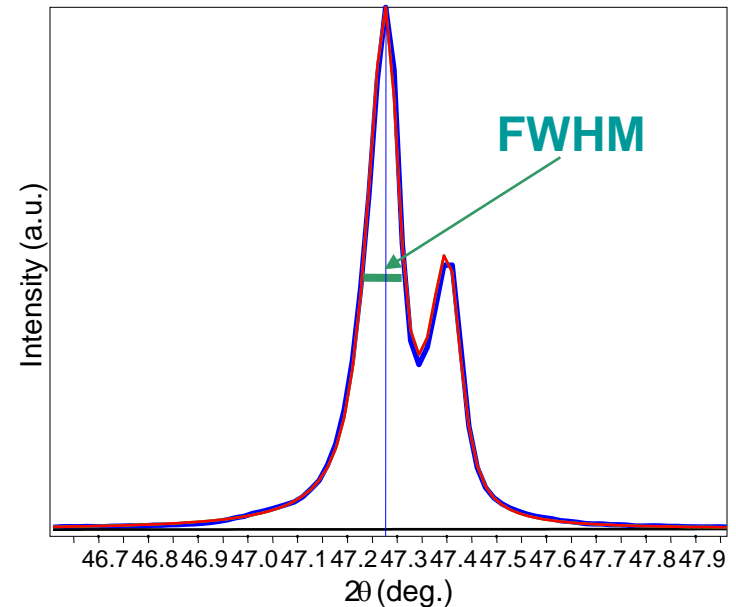
Integral Breadth may be the way to define peak width with modern analysis software

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

- 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

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

- This requires an Instrument Profile Calibration Curve

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The Instrument Peak Profile Calibration Curve quantifies the contribution of the instrument to the observed peak widths

- 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
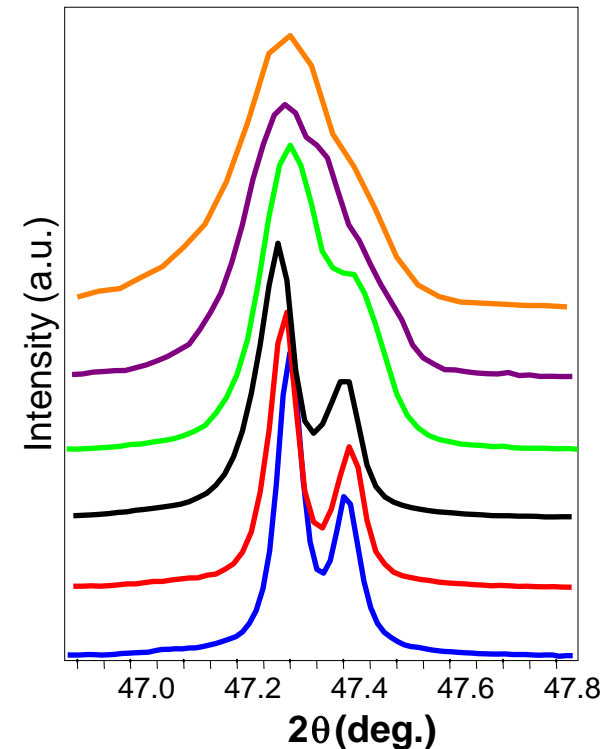
Patterns collected from the same sample with different instruments and configurations at MIT

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Other Instrumental and Sample 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
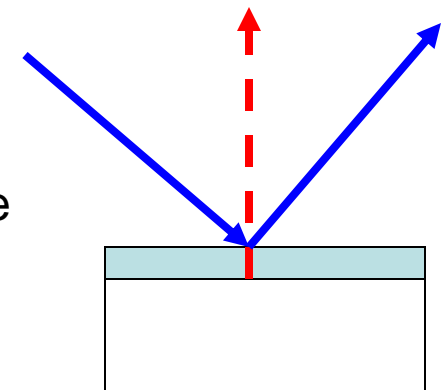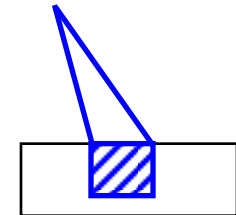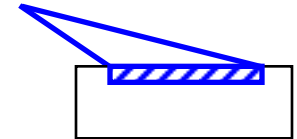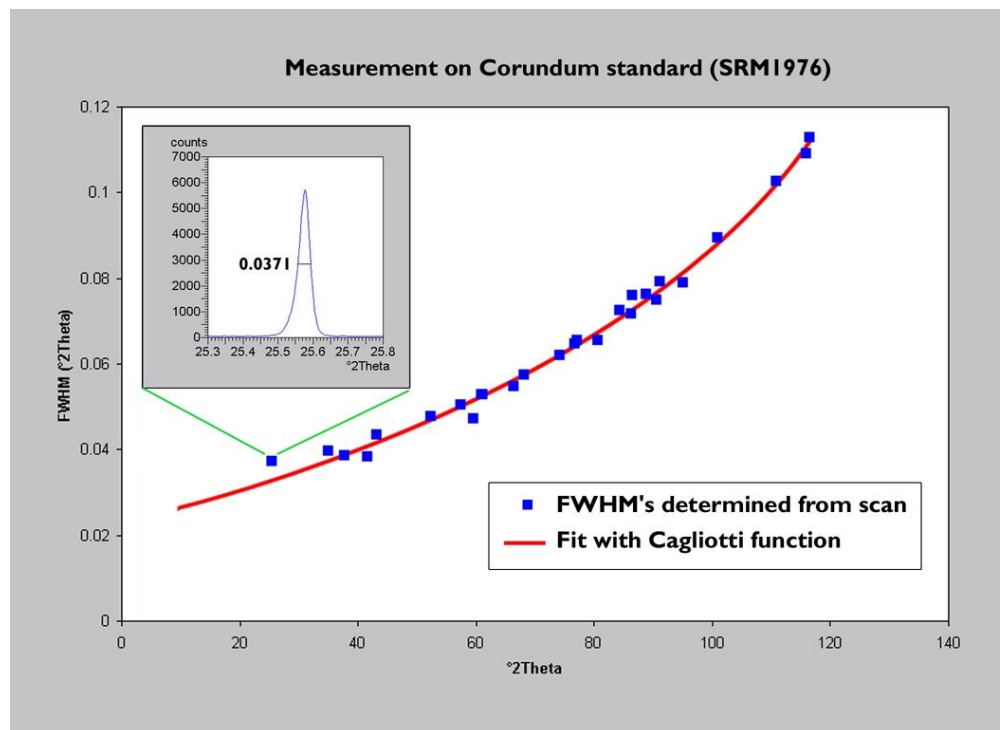
In order to build a Instrument Peak Profile Calibration Curve

- Collect data from a standard using the exact instrument and configuration as will be used for analyzing the sample
  - same optical configuration of diffractometer
  - same sample preparation geometry
  - You need a separate calibration curve for every different instrument and instrument configuration
    - Even a small change, such as changing the divergence slit from ½ to ¼° aperture, will change the instrument profile
  - calibration curve should cover the 2theta range of interest for the specimen diffraction pattern
    - do not extrapolate the calibration curve
- Profile fit the diffraction peaks from the standard
- Fit the peak widths to a function such as the Cagliotti equation. Use this function as the calibration curve.

The Cagliotti equation describes how peak width varies with 2theta

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

- H_k is the Cagliotti function where U, V and W are refinable parameters

Measurement on Corundum standard (SRM1976)

FWHM's determined from scan
Fit with Cagliotti function

Selecting a standard for building the Instrument Peak Profile Calibration Curve

- Standard should share characteristics with the nanocrystalline specimen
  - Similar linear absorption coefficient
    - 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

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 becomes contaminated
  - only works with a powder specimen

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

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

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
  - Use the standard that has the most similar linear absorption coefficient

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

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

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

Configuration	FWHM (deg)	Pk Ht to Bkg Ratio
185mm radius, 0.5° DS, diffracted-beam monochromator, point detector	0.124	339
240mm radius, 0.25° DS, beta-filter, linear PSD	0.060	81
240mm radius, 0.5° DS, beta-filter, linear PSD	0.077	72
240mm radius, 0.5° DS, diffracted-beam monochromator, linear PSD	0.073	111
Gobel mirror, 0.09° Parallel Beam Collimator	0.175	50
Gobel mirror, 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

- Instruments with better peak height to background ratios are better for small nanocrystallites, <20nm
- Instruments with smaller instrumental peak widths are better for larger nanocrystallites, >80 nm

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For line profile analysis, must remove the instrument contribution to each peak list

- When analyzing the diffraction pattern from the sample, the instrument contribution to the peak width must be removed
- The instrument contribution is convoluted with the specimen contribution to peak broadening
  - Peak deconvolution is a difficult process, so simpler calculations are often used
- Most commonly, the observed peak width is treated as the sum of the instrument and specimen contributions
  - $B_{obs} = B_{specimen} + B_{instrument}$
  - This works well when:
    - crystallite size is the dominant contribution to peak broadening
    - The peak broadening is largely Lorentzian in shape
- Other analysis will treat the observed peak as the sum of the squares of the instrument and specimen contributions
  - $B_{obs} = \sqrt{B_{specimen}^2 + B_{instrument}^2}$
  - This works well when:
    - microstrain is the dominant contribution to peak broadening
    - The peak broadening is largely Gaussian in shape

Once the instrument broadening contribution has been remove, the specimen broadening can be analyzed

- Contributions to specimen broadening
  - 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***

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 θ
  - 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

The Scherrer Constant, K

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

- 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
  - K actually varies from 0.62 to 2.08
  - 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

- 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.

Factors that affect K and crystallite size analysis

- how the peak width is defined
  - Whether using FWHM or Integral Breadth
    - Integral breadth is preferred
- how crystallite size is defined
- the shape of the crystal
- the size distribution

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
  - None of the X-ray diffraction techniques give a crystallite size that exactly matches this definition
- 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

The Stokes and Wilson method considers that each different diffraction peak is produced from planes along a different crystallographic direction

- **Stokes and Wilson** method (using integral breadth) determines the volume average of the thickness of the crystallites measured perpendicular to the reflecting plane

- This method is useful for identifying anisotropic crystallite shapes

a-axis
// [200]

c-axis,
// [002]

Counts

(002)

(200)

4000

2000

0
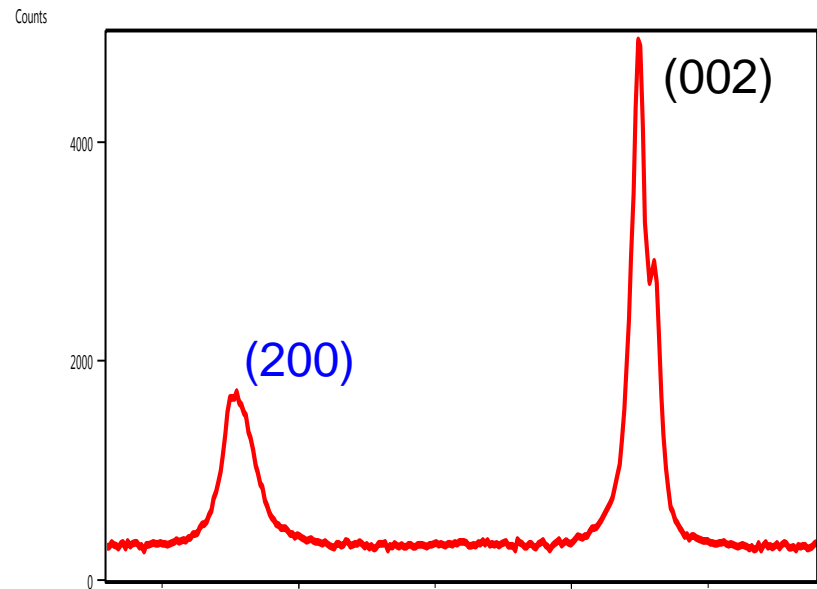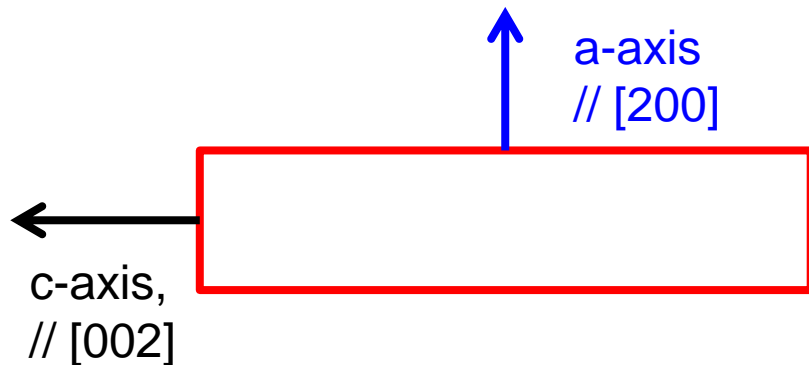
Remember, Crystallite Size is Different than Particle Size

- A particle may be made up of several different crystallites

- Crystallite size often matches grain size, but there are exceptions
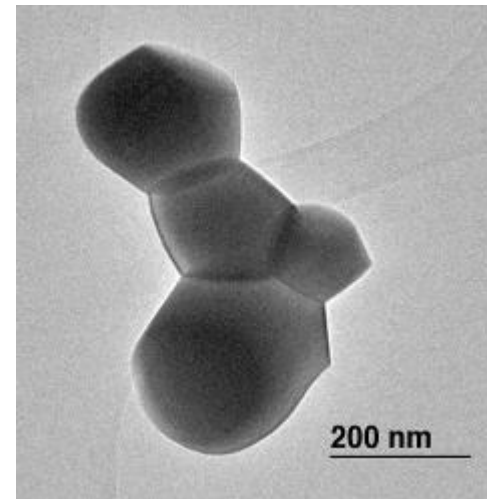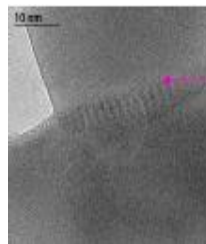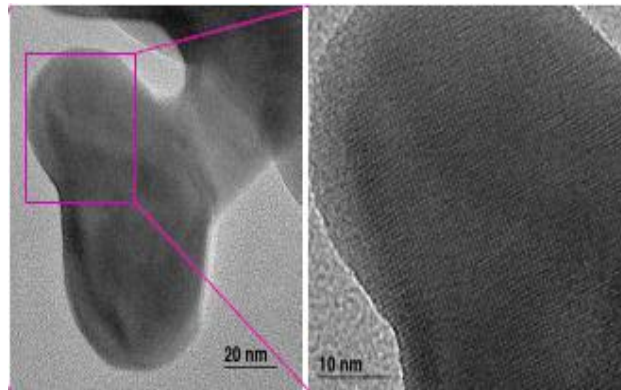
The crystallite size observed by XRD is the smallest undistorted region in a crystal

- Dislocations may create small-angle domain boundaries

- Dipolar dislocation walls will also create domain boundaries

TEM size

X-Ray size

http://prism.mit.edu/xray
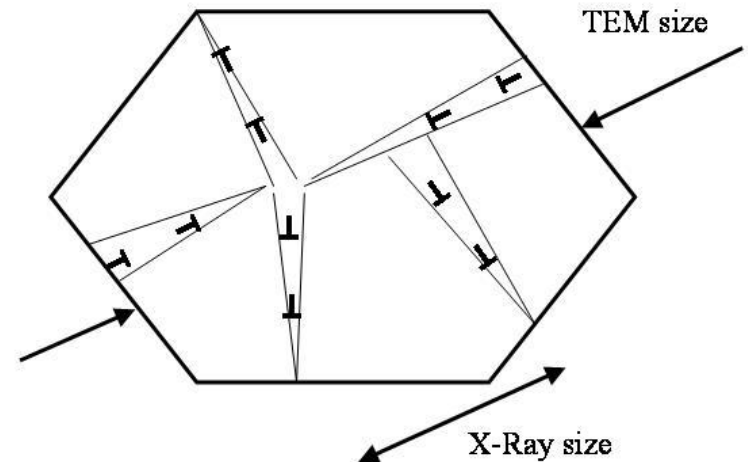
Crystallite Shape

- 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.
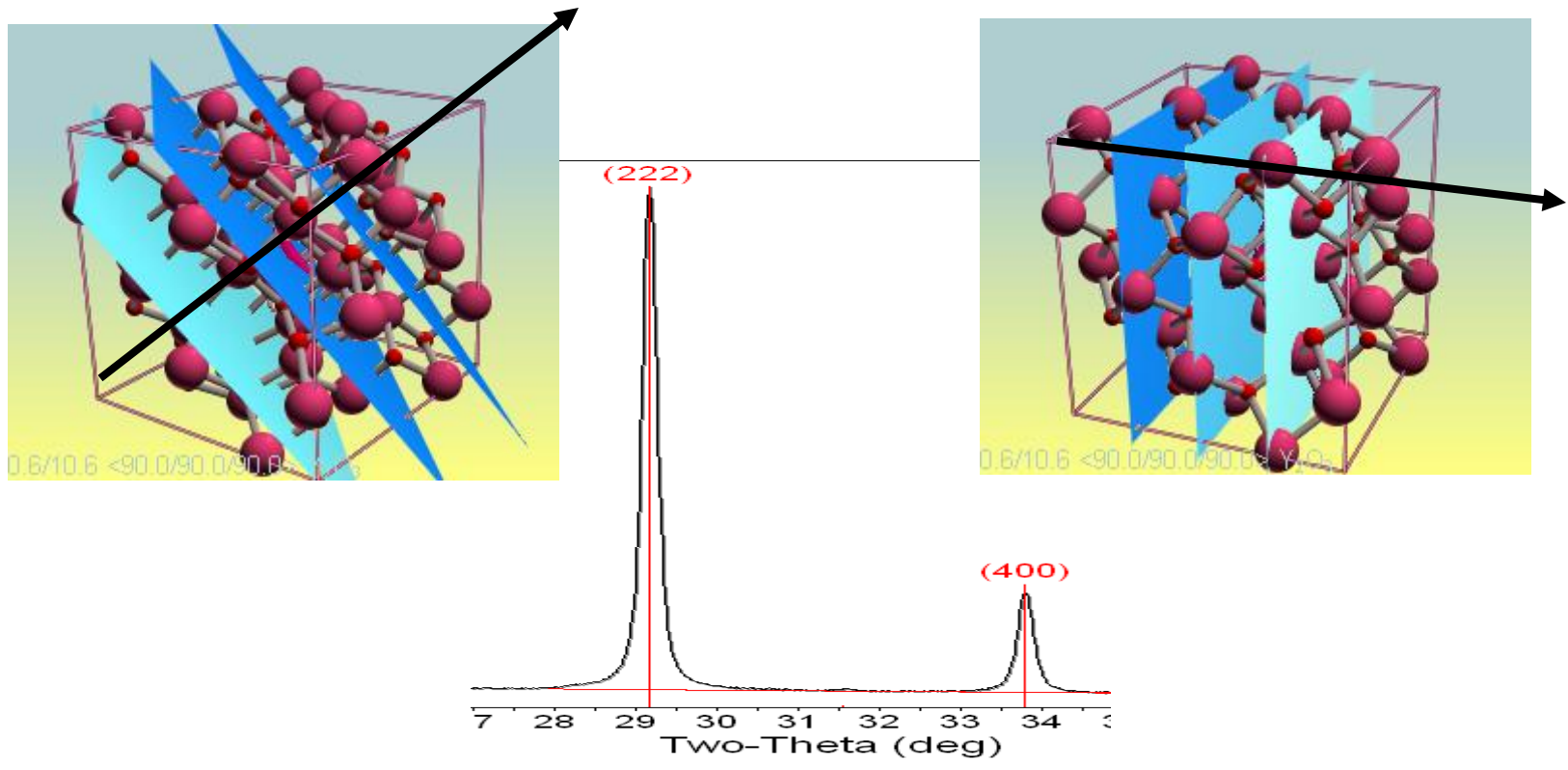
Crystallite Size Distribution

- 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

Values for K referenced in HighScore Plus

- Values of K from Langford and Wilson, *J. Appl. Cryst* (1978) 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

- Assuming the Scherrer definition of crystallite size, values of K listed in the Help for HighScore Plus are:

Crystallite Shape	FWHM	Integral Breadth
Spheres	0.89	1.07
Cubes	0.83 - 0.91	1.00 – 1.16
Tetrahedra	0.73 - 1.03	0.94 – 1.39
Octahedra	0.82 - 0.94	1.04 – 1.14

Limits for crystallite size analysis

- There is only broadening due to crystallite size when the crystallite is too small to be considered infinitely large
  - Above a certain size, there is no peak broadening
  - The instrument usually constrains the maximum size rather than this limit; this limit only matters for synchrotron and other high resolution instruments
- The instrument contribution to the peak width may overwhelm the signal from the crystallite size broadening
  - If the instrument profile is 0.120° with an esd of 0.001°, the maximum resolvable crystallite size will be limited by
    - The precision of the profile fitting, which depends on the peak intensity (weaker peaks give less precise widths) and noise
    - The amount of specimen broadening should be at least 10% of the instrument profile width
  - In practice, the maximum observed size for a standard laboratory diffractometer is 80 to 120 nm
- The minimum size requires enough repeating atomic planes to produce the diffraction phenomenon
  - This depends on the size of the unit cell
  - The minimum size is typically between 3 to 10 nm, depending on the material
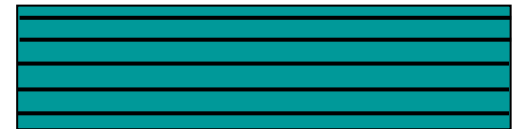
Microstrain Broadening

- 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 nanoparticle materials

- the peak broadening due to microstrain will vary as:

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

Ideal crystal

$$\varepsilon = \frac{\Delta d}{d} \ (\%)$$

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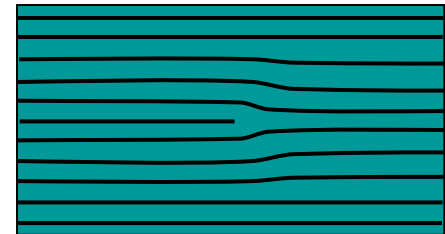
compare to peak broadening due to crystallite size: $B(2\theta) = \dfrac{K\lambda}{L\cos\theta}$

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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

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 nanoparticles
  - morphology of crystal shape, such as nanotubes
  - interstitial impurities

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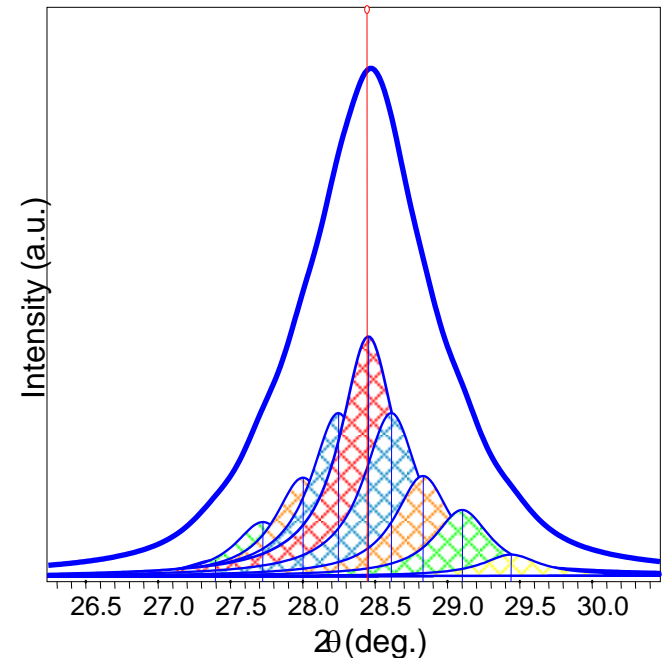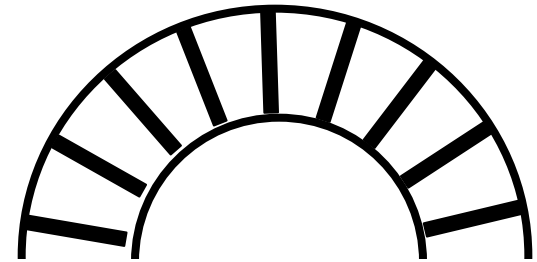
Antiphase Domain Boundaries

- 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*
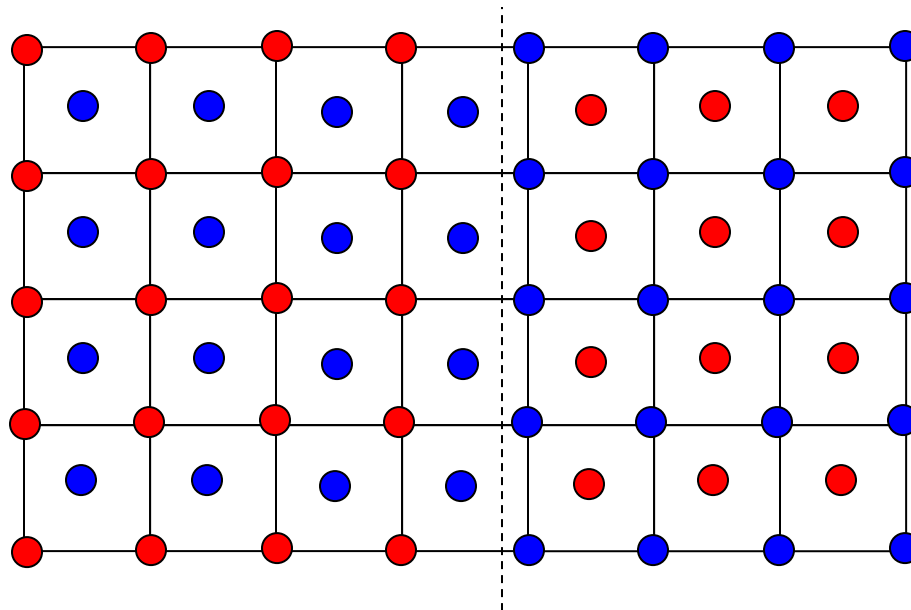
Dislocations

- 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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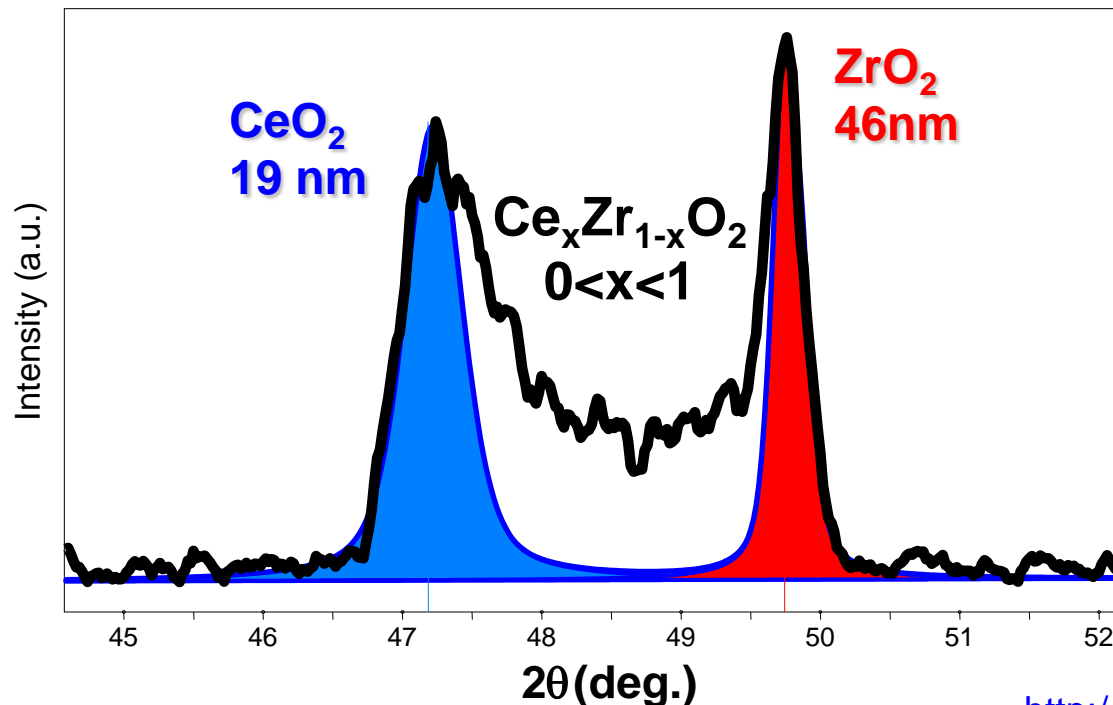
Temperature Factor

- 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

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

Scherrer Analysis Calculates Crystallite Size based on each Individual Peak Profile

- Both crystallite size and microstrain can be calculated based on individual peak profiles **IF** you assume the other factor is insignificant
- To test this assumption, look at how the calculated values vary over a long range of 2theta
  - If the calculated crystallite size or microstrain is consistent over a large range of 2theta, this could indicate that the other factor can be ignored
  - You cannot make this determination if you use a single diffraction peak
  - If crystallite size and/or microstrain varies as a function of 2theta, then additional analysis is required.
- If you have confirmed that crystallite size or microstrain is the only source of specimen broadening for a few samples from a family of specimens, then you MIGHT consider using only single diffraction peak for future analysis.

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In this example, crystallite size is consistent over a long range of 2theta

- Crystallite size varies from 45 to 38 A from 28 to 95 degrees 2theta
  - The average crystallite size is 4 nm
  - XRD analysis is only precise to a nm level, not 0.000001 A as the software suggests
  - In the future, we might use only 1 peak to analyze similar samples

Pos. [°2Th.]	FWHM Left [°2Th.]	Integral Breadth [°2Th.]	Crystallite Size only [Å]	Micro Strain only [%]	Shape Left
28.376(2)	1.328(5)	2.086657	45.593120	3.446514	1.00(2)
32.929(9)	1.52(3)	2.381582	40.170720	3.382894	1.00(5)
47.261(5)	1.48(1)	2.305790	43.686260	2.199457	0.98(2)
56.119(5)	1.62(2)	2.492787	41.892780	1.954495	0.95(5)
58.85(2)	1.6(1)	2.393380	43.497700	1.802185	0.9(2)
69.14(1)	1.75(5)	2.284294	48.002510	1.413983	0.6(3)
76.42(1)	1.88(4)	2.934949	39.835410	1.563126	1.0(1)
78.80(2)	1.96(8)	3.074942	38.521520	1.575137	1.0(2)
88.12(1)	2.05(7)	3.223483	39.598130	1.398606	1.0(3)
95.10(1)	2.3(1)	3.550867	38.271300	1.363908	1.0(4)

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When both Crystallite Size and Microstrain vary as 2theta, then both are probably present

- When microstrain is present, the calculated "Crystallite Size only" will tend to decrease as a function of 2theta
- When crystallite size broadening is present, the calculated "Microstrain only" will tend to decrease as a function of 2theta

Pos. [°2Th.]	FWHM Left [°2Th.]	Integral Breadth [°2Th.]	Crystallite Size only [Å]	Micro Strain only [%]	Shape Left
40.2733(5)	0.829(1)	1.302793	77.175430	1.449652	1.000(3)
58.282(2)	1.188(5)	1.506254	69.711210	1.134575	0.50(1)
73.221(2)	1.371(4)	2.154261	53.542790	1.206182	1.000(7)
87.053(5)	1.67(1)	2.514615	50.565380	1.105996	0.91(2)
100.729(5)	2.18(2)	3.406238	42.566990	1.174899	0.99(2)

A lack of a systematic angular trend for crystallite size or microstrain indicates a more complex complication

Pos. [°2Th.]	FWHM Left [°2Th.]	Integral Breadth [°2Th.]	Crystallite Size only [Å]	Micro Strain only [%]	Shape Left
21.3278(6)	0.143(3)	0.224194	635.645200	0.327440	1.00(3)
22.7156(4)	0.118(1)	0.164880	1096.456000	0.178367	0.74(2)
31.3943(2)	0.117(1)	0.168718	1098.269000	0.129619	0.81(1)
32.3770(3)	0.119(1)	0.170563	1043.411000	0.132399	0.79(2)
39.1359(3)	0.0990(9)	0.142933	1739.008000	0.066127	0.82(1)
43.523(1)	0.200(5)	0.294495	434.860500	0.238896	0.86(4)
46.4813(4)	0.114(1)	0.167796	1171.474000	0.083319	0.85(2)
49.674(1)	0.179(4)	0.272466	523.242800	0.175241	0.93(4)
51.7064(8)	0.112(3)	0.176432	1020.258000	0.086570	1.00(4)
52.368(1)	0.119(3)	0.174215	1089.147000	0.080140	0.86(4)
55.3112(8)	0.173(3)	0.260163	563.506700	0.147254	0.90(2)
57.1989(3)	0.108(1)	0.163817	1429.535000	0.056284	0.92(1)

When both crystallite size and microstrain are present, a Williamson-Hall Plot is used

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

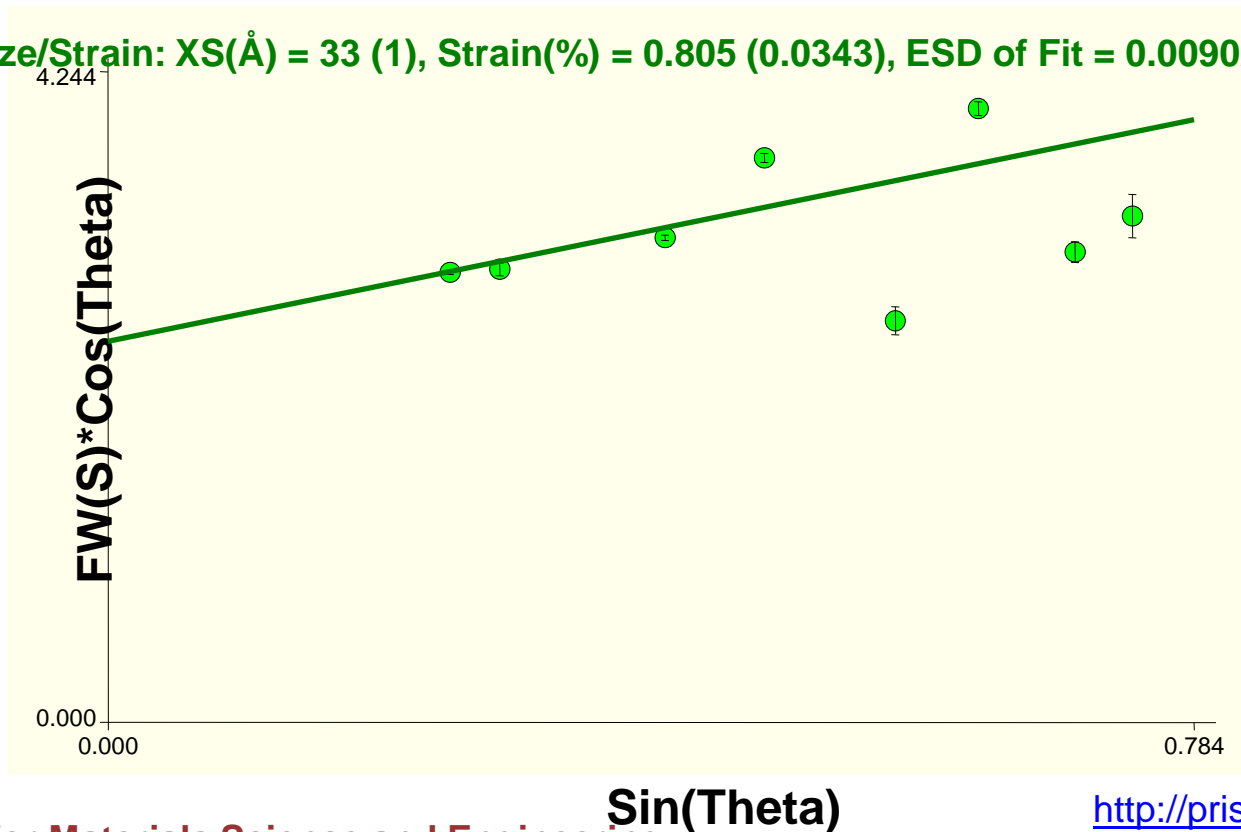$$B(2\theta) = 4\varepsilon\frac{\sin\theta}{\cos\theta}$$ Microstrain broadening

$$B_{specimen} = \frac{K\lambda}{L\cos\theta} + 4\varepsilon\frac{\sin\theta}{\cos\theta}$$

$$B_{specimen} \times \cos(\theta) = \underbrace{\frac{K\times\lambda}{Size}}_{\text{y-intercept}} + \underbrace{4\times Strain\times\sin(\theta)}_{\text{slope}}$$

When both crystallite size and microstrain are present, a Williamson-Hall Plot is used

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

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

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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

FW(S)*Cos(Theta) vs **Sin(Theta)**
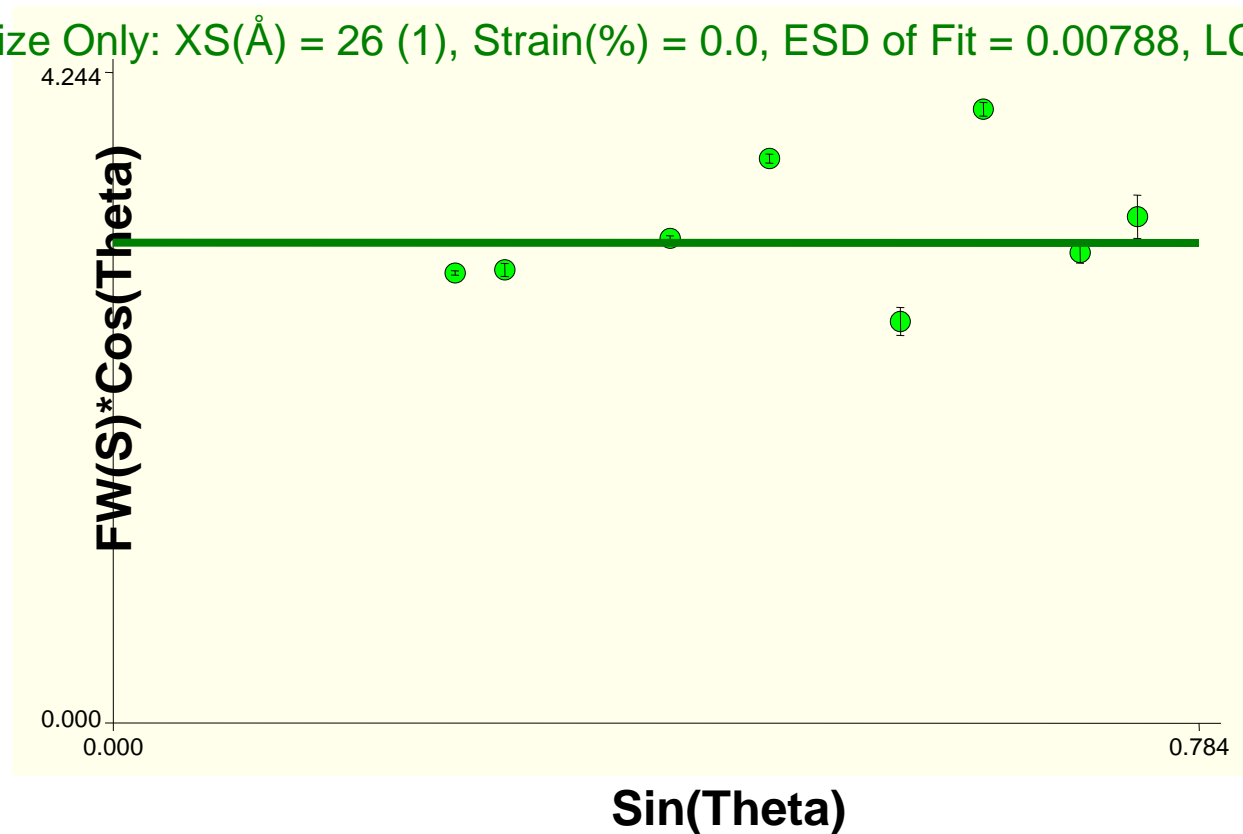
Analysis Mode: Fit Strain Only

$$FW(S) \times \cos(\theta) = \underbrace{\frac{K \times \lambda}{Size}} + 4 \times Strain \times \sin(\theta)$$
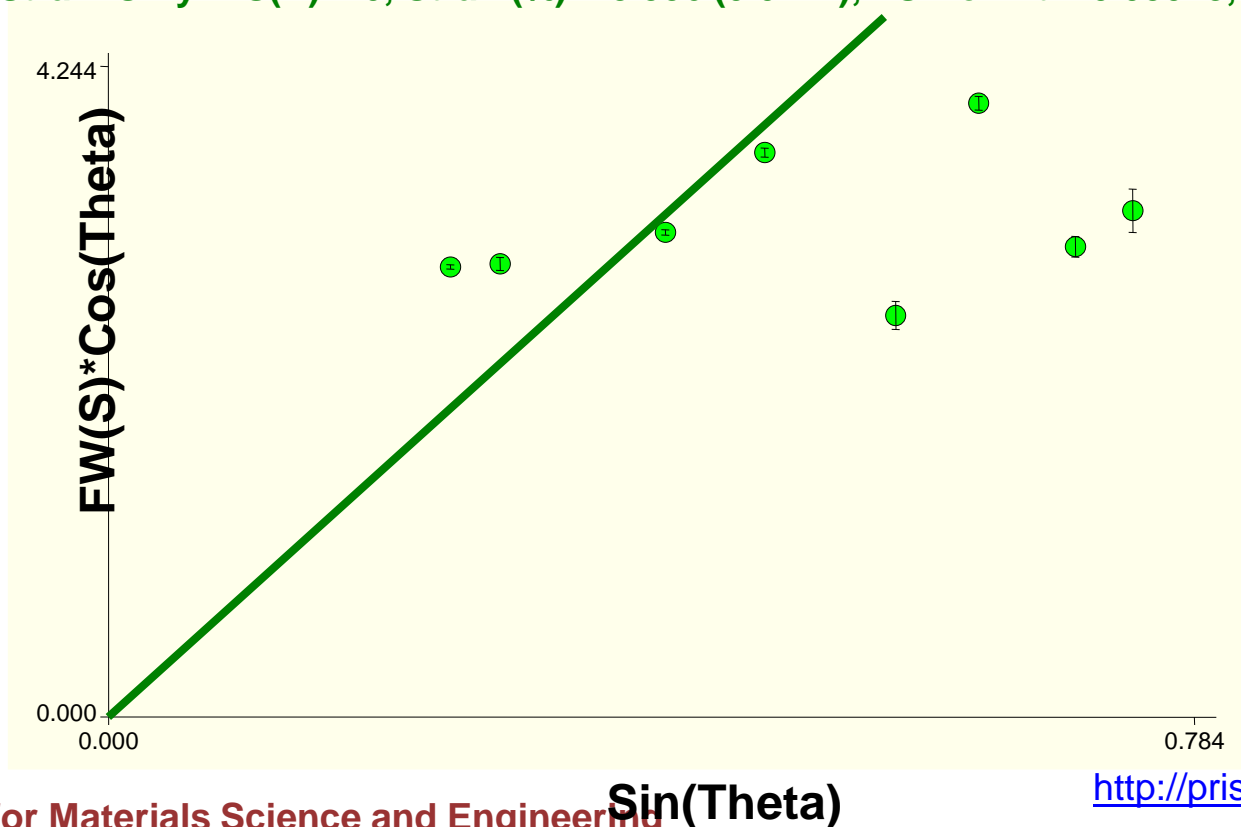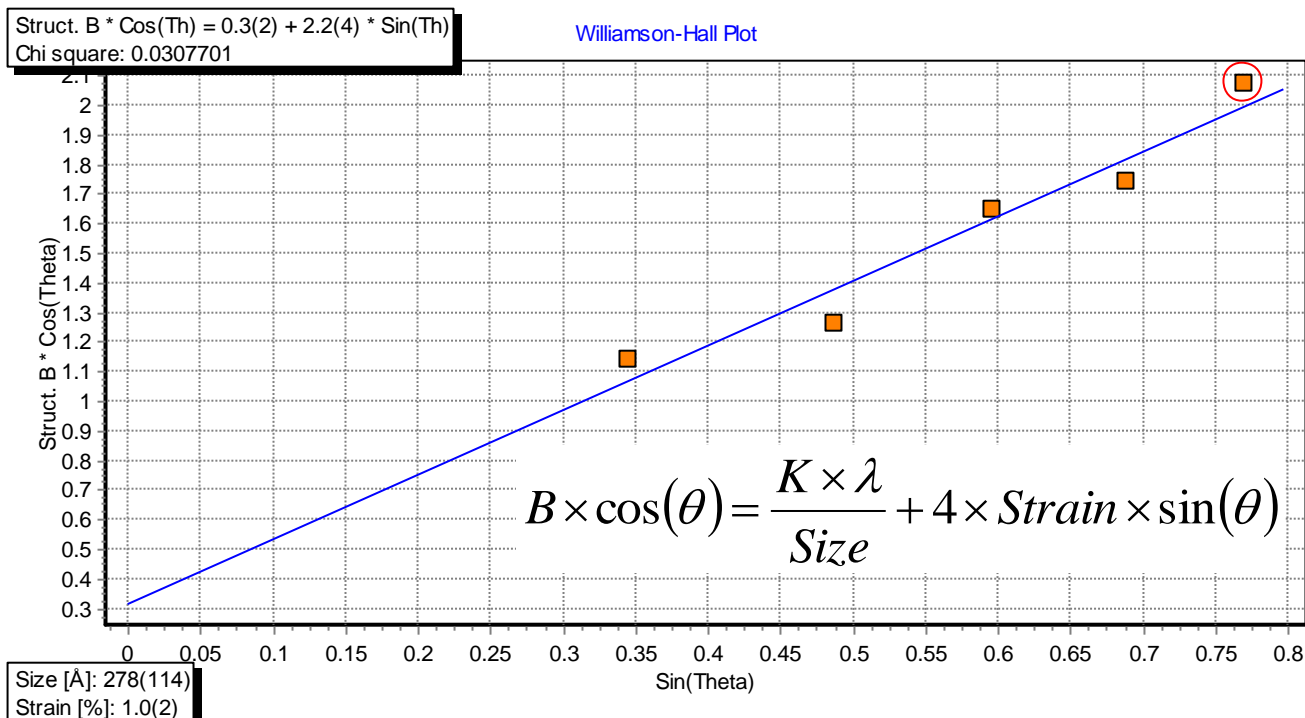
y-intercept= 0
size= ∞

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

Analysis Mode: Fit Size/Strain

Struct. B * Cos(Th) = 0.3(2) + 2.2(4) * Sin(Th)
Chi square: 0.0307701

Williamson-Hall Plot

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

Size [Å]: 278(114)
Strain [%]: 1.0(2)

Pos. [°2Th.]	FWHM Left [°2Th.]	Integral Breadth [°2Th.]	Crystallite Size only [Å]	Micro Strain only [%]	Shape Left
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100.729(5)	2.18(2)	3.406238	42.566990	1.174899	0.99(2)

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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		

A large amount of crystallite size or microstrain will hinder analysis of the other term

- Both microstrain and crystallite size can be analyzed only when the broadening due to both is equivalent
- When the amount of microstrain is large, the maximum observable crystallite size will be limited
  - A 1% microstrain might limit the maximum crystallite size to as little as 40 nm. The small amount of broadening due to a larger crystallite size will not be accuratey quantified
- When the crystallite size is small, the maximum quantifiable microstrain will be limited

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

Textbook References

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Articles

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  - "A Profile-Fitting Procedure for Analysis of Broadened X-ray Diffraction Peaks. II. Application and Discussion of the Methodology" *J. Appl. Cryst.* (1988) **21**, 543-549
- B Marinkovic, R de Avillez, A Saavedra, FCR Assunção, "A Comparison between the Warren-Averbach Method and Alternate Methods for X-Ray Diffraction Microstructure Analysis of Polycrystalline Specimens", *Materials Research* **4** (2) 71-76, 2001.
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- A Leineweber, EJ Mittemeijer, "Anisotropic microstrain broadening due to compositional inhomogeneities and its parametrisation", Z. Kristallogr. Suppl. **23** (2006) 117-122
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Instrumental Profile Derived from different mounting of LaB$_6$
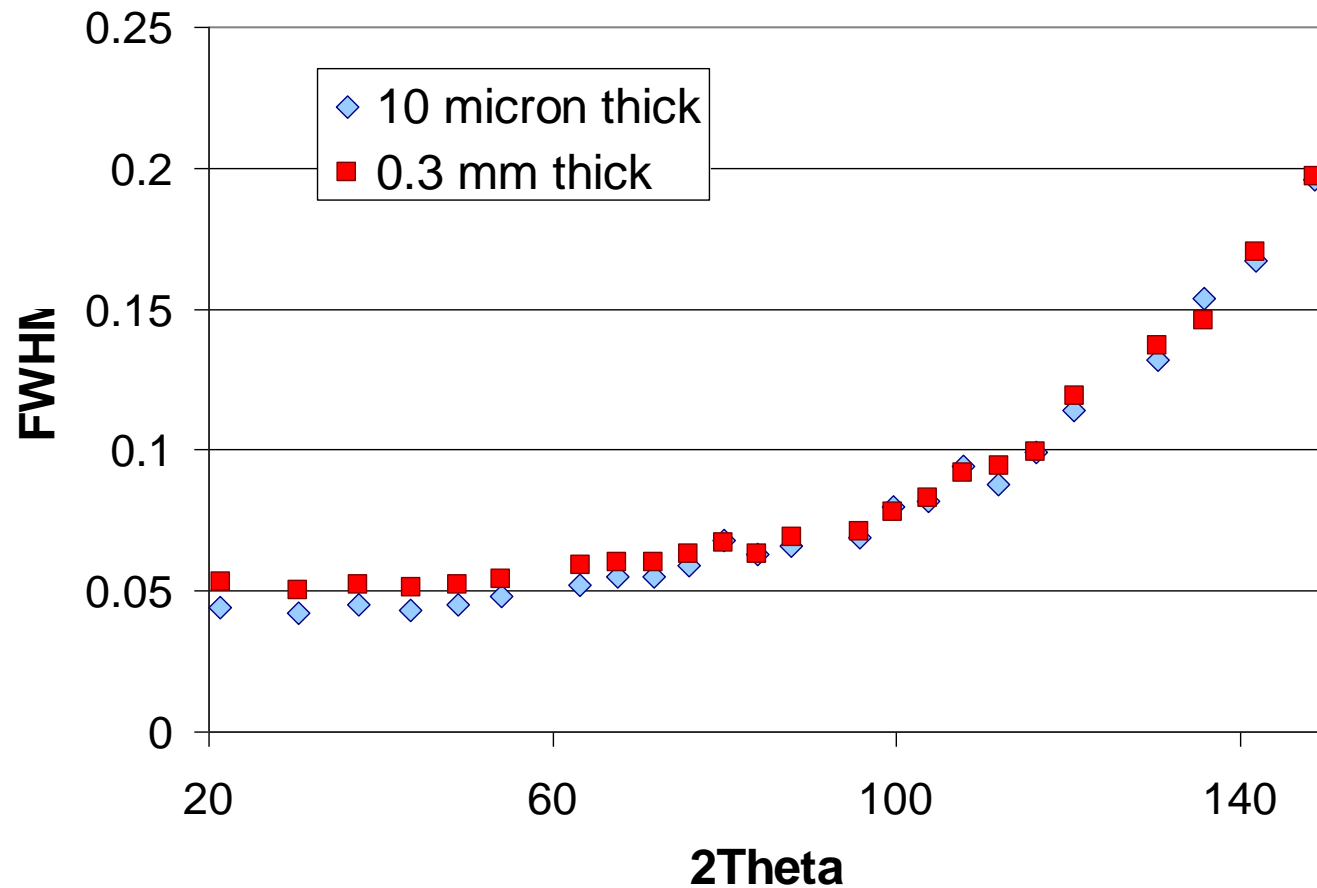
In analysis of Y$_2$O$_3$ on a ZBH, using the instrumental profile from thin SRM gives a size of 60 nm; using the thick SRM gives a size of 64 nm

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