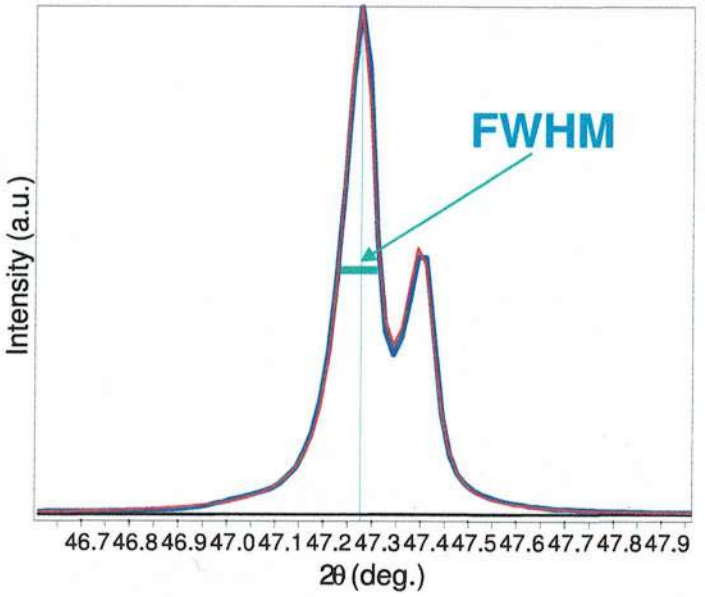
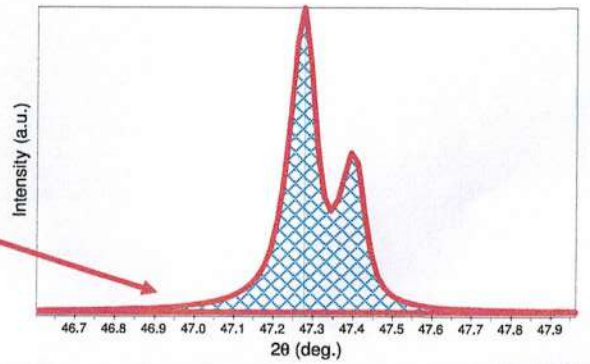
Methods used in Jade to Define Peak Width

- 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





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

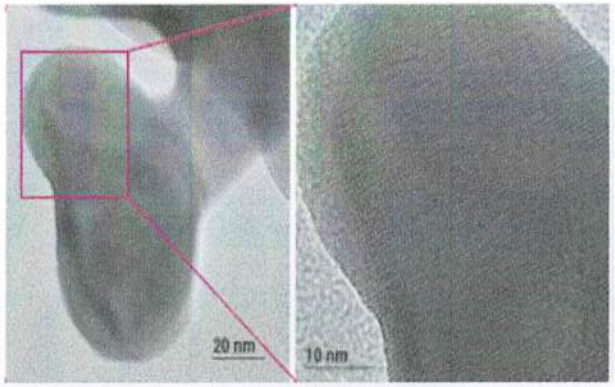
How is Crystallite Size Defined

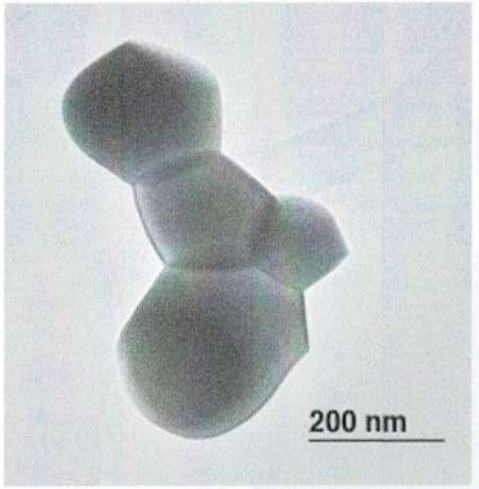
- Usually taken as the cube root of the volume of a crystallite
  - assumes that all crystallites have the same size and shape
- For a distribution of sizes, the mean size can be defined as
  - the mean value of the cube roots of the individual crystallite volumes
  - the cube root of the mean value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





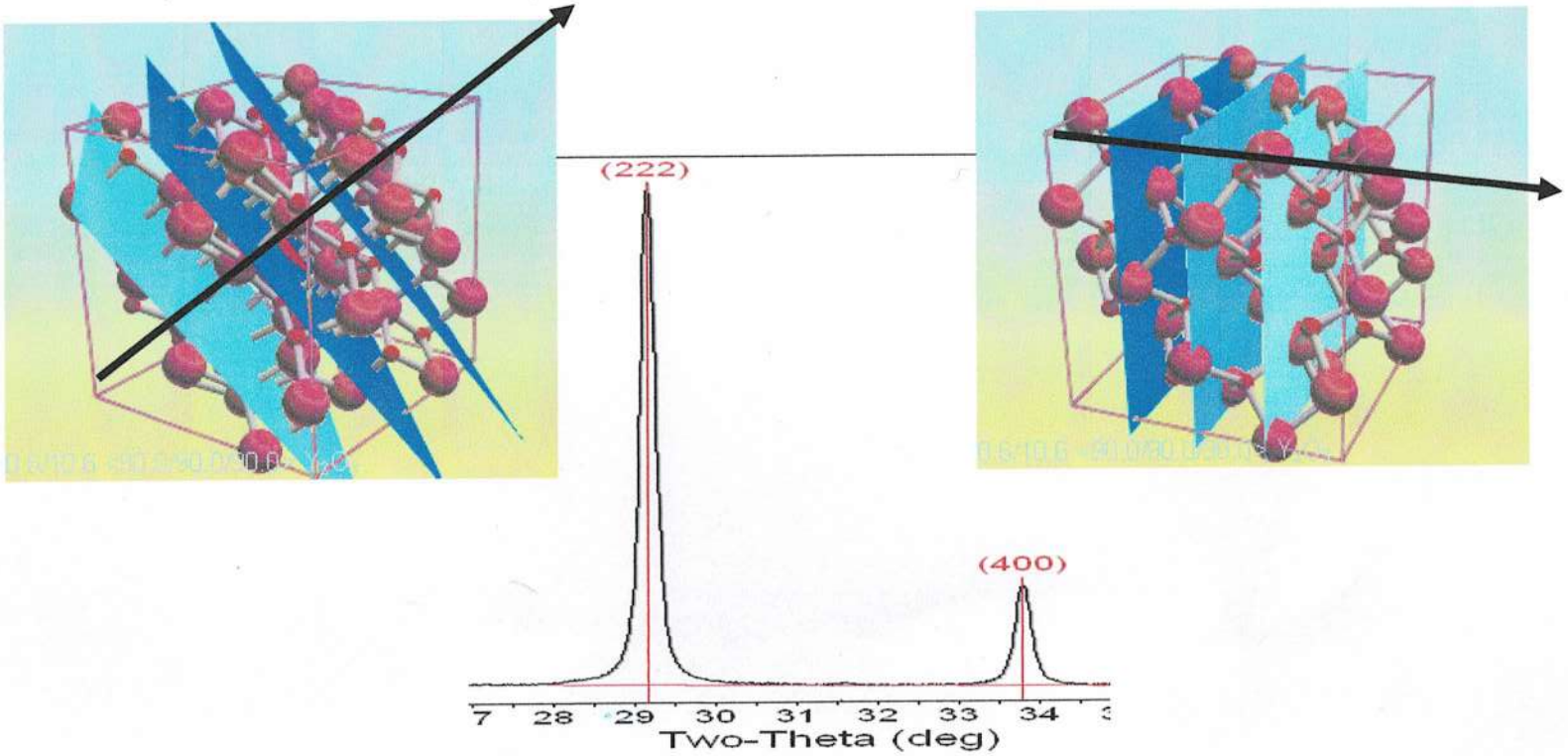
Crystallite Shape

- 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

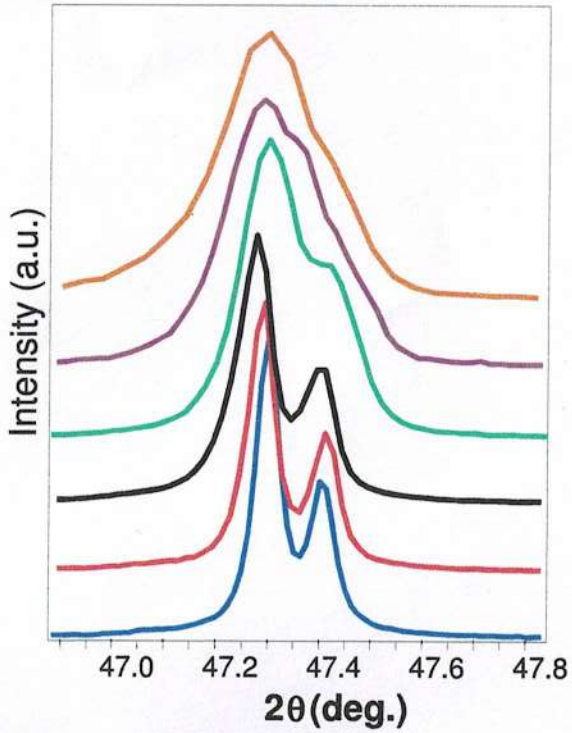
- is the crystallite size narrowly or broadly distributed?
- is the crystallite size unimodal?

- 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

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

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
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