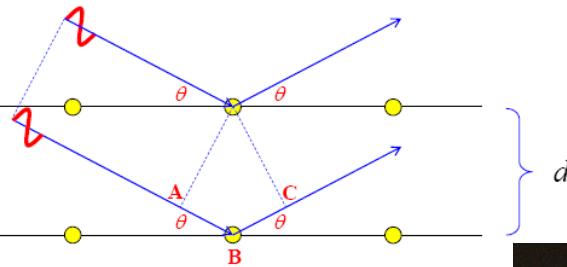


## Lecture on X-ray diffraction peak broadening

- Provide a quick overview of the theory behind peak broadening and profile analysis
- Discuss practical considerations for analysis

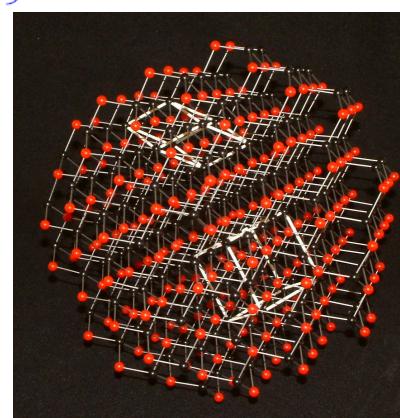
1

### Bragg's Law



$$\delta = \text{path difference} = AB + BC = 2d \sin \theta$$

∴



2

**Bragg's Law**

$$\delta = \text{path difference} = AB + BC = 2d \sin \theta$$

For constructive interference  $\delta = n\lambda$

$$\therefore$$

$$\delta = 2d \sin \theta = n\lambda$$

$$d_{hkl} = \frac{d}{n}$$

$$\lambda = 2d_{hkl} \sin \theta \text{ (or } n\lambda = 2d \sin \theta)$$



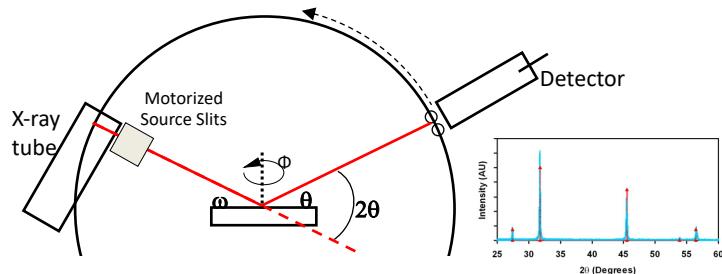
3

**Bragg- Brentano geometry**

- The incident angle,  $\omega$ , is defined between the X-ray source and the sample.
- The diffraction angle,  $2\theta$ , is defined between the incident beam and the detector.
- The incident angle  $\omega$  is always  $\frac{1}{2}$  of the detector angle  $2\theta$ .
  - In a  $\theta:2\theta$  instrument (e.g. Rigaku H3R), the tube is fixed, the sample rotates at  $\theta$  °/min and the detector rotates at  $2\theta$  °/min.
  - In a  $\theta:\theta$  instrument (e.g. PANalytical X'Pert Pro), the sample is fixed and the tube rotates at a rate  $-\theta$  °/min and the detector rotates at a rate of  $\theta$  °/min.
- In the Bragg-Brentano geometry, the diffraction vector ( $s$ ) is always normal to the surface of the sample.**
  - The diffraction vector is the vector that bisects the angle between the incident and scattered beam

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## Coupled 2θ Measurements

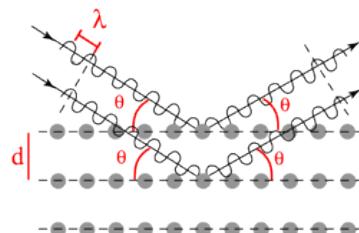
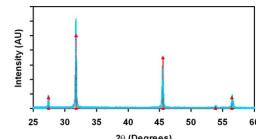


- In "Coupled 2θ" Measurements:
  - The incident angle  $\omega$  is always  $\frac{1}{2}$  of the detector angle  $2\theta$ .
  - The x-ray source is fixed, the sample rotates at  $\theta$  °/min and the detector rotates at  $2\theta$  °/min.
- Angles
  - The incident angle ( $\omega$ ) is between the X-ray source and the sample.
  - The diffracted angle ( $2\theta$ ) is between the incident beam and the detector.
  - In plane rotation angle ( $\Phi$ )

5

## Bragg's law and Peak Positions.

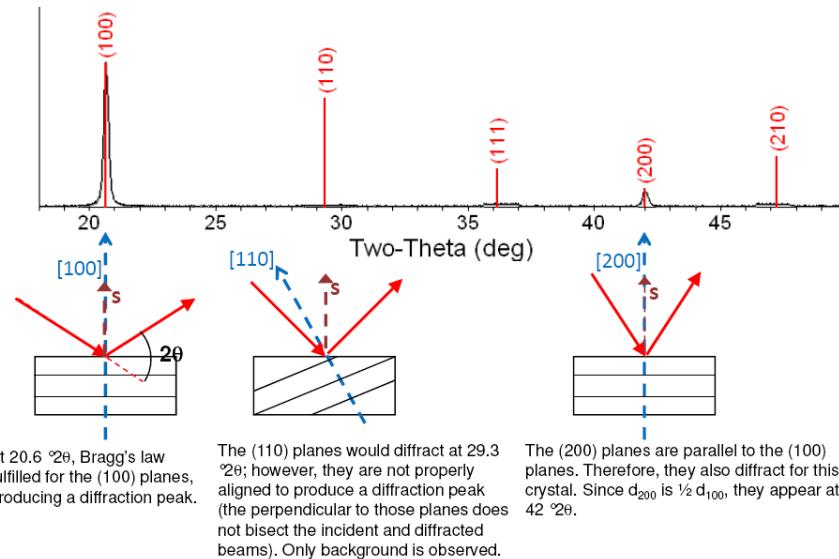
$$\lambda = 2d_{hkl} \sin \theta$$



- For parallel planes of atoms, with a space  $d_{hkl}$  between the planes, constructive interference only occurs when Bragg's law is satisfied.
  - First, the plane normal must be parallel to the diffraction vector
    - Plane normal: the direction perpendicular to a plane of atoms
    - Diffraction vector: the vector that bisects the angle between the incident and diffracted beam
  - X-ray wavelengths  $\lambda$  are:
    - Cu K<sub>α1</sub>=1.540598 Å and Cu K<sub>α2</sub>=1.544426 Å
    - Or Cu K<sub>α(avg)</sub>=1.54278 Å
  - $d_{hkl}$  is dependent on the lattice parameter (atomic/ionic radii) and the crystal structure
  - $I_{hkl}=I_0 p C L_p [F_{hkl}]^2$  determines the intensity of the peak

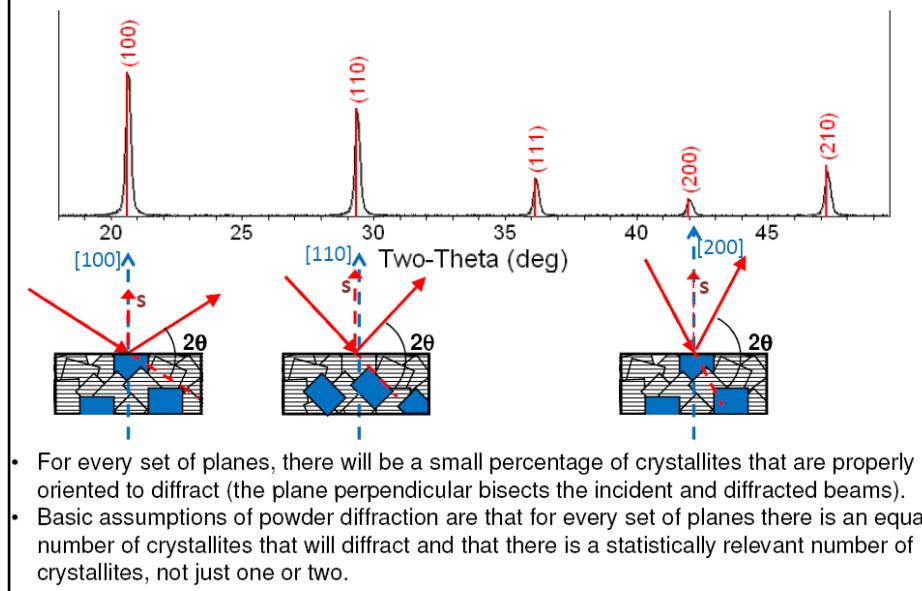
6

A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern.

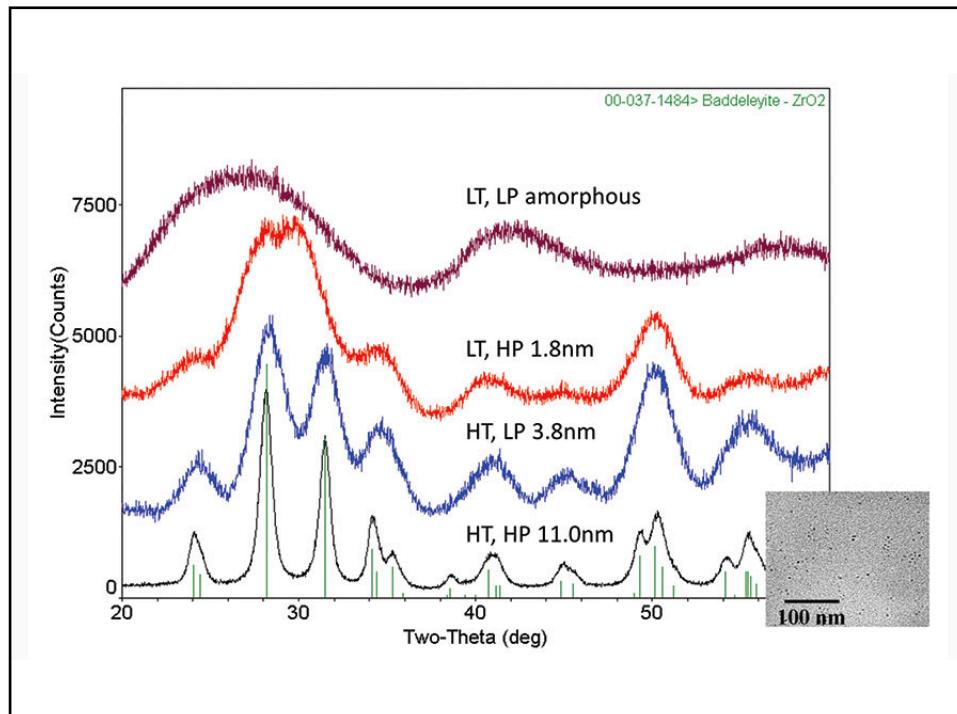


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A polycrystalline sample should contain thousands of crystallites. Therefore, all possible diffraction peaks should be observed.

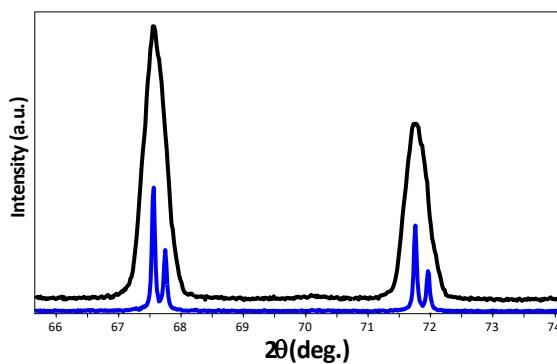


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Which of these diffraction patterns comes from a nanocrystalline material?



- 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***

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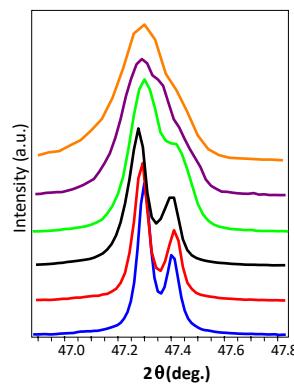
## Many factors may contribute to the observed peak profile

- 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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## 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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## 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

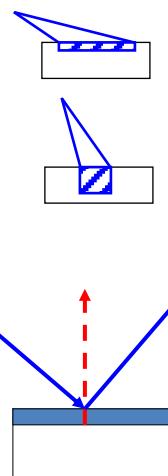
- Rigaku XRPD is better for very small nanocrystallites, <80 nm (upper limit 100 nm)
- PANalytical X' Pert Pro is better for larger nanocrystallites, <150 nm

<http://prism.mit.edu/xray>

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## Other Instrumental Considerations for Thin Films

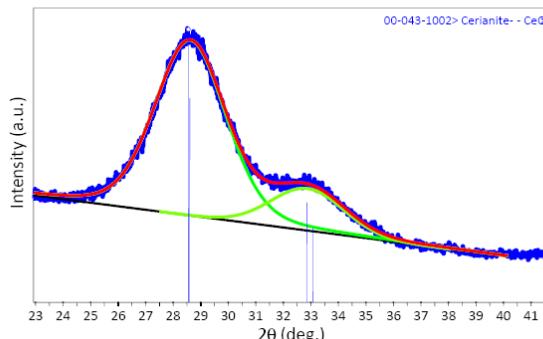
- The irradiated area greatly affects the intensity of high angle diffraction peaks
  - GIXD or variable divergence slits on the PANalytical X' Pert Pro will maintain a constant irradiated area, increasing the signal for high angle diffraction peaks
  - both methods increase the instrumental FWHM
- Bragg-Brentano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

- Crystallites smaller than ~120nm create broadening of diffraction peaks
  - this peak broadening can be used to quantify the average crystallite size of nanoparticles using the Scherrer equation
  - must know the contribution of peak width from the instrument by using a calibration curve
- microstrain may also create peak broadening
  - analyzing the peak widths over a long range of 2theta using a Williamson-Hull plot can let you separate microstrain and crystallite size



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

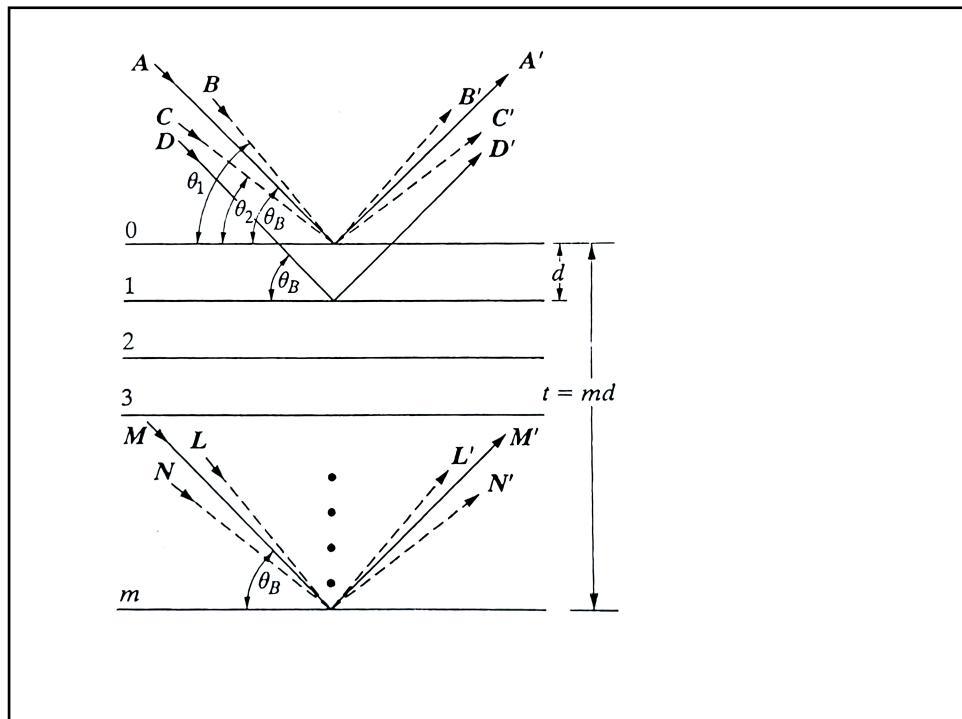
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## The Scherrer Equation was published in 1918

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

- 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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## 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  $2\theta$  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

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

- 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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## How is Crystallite Size Defined

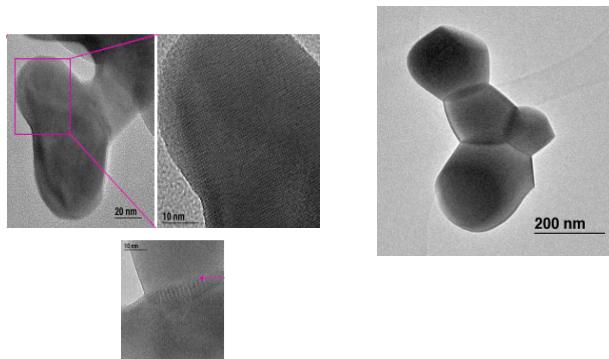
- Usually taken as the cube root of the volume of a crystallite
  - assumes that all crystallites have the same size and shape
- For a distribution of sizes, the mean size can be defined as
  - the mean value of the cube roots of the individual crystallite volumes
  - the cube root of the mean value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

<http://prism.mit.edu/xray>

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## 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

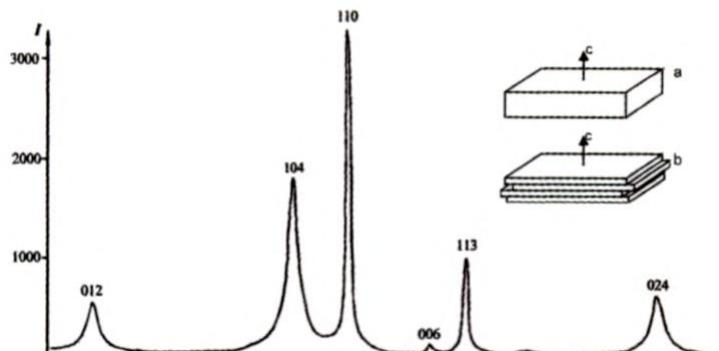


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## Crystallite Shape

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

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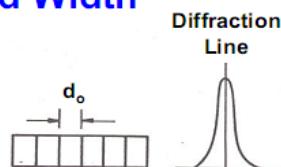


X-ray powder diffraction pattern of  $\alpha\text{-Fe}_2\text{O}_3$

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## Effect of Lattice Strain on Diffraction Peak Position and Width

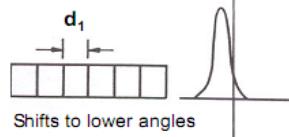
No Strain



Uniform Strain

$$(d_1 - d_0)/d_0$$

Peak moves, no shape changes



Non-uniform Strain

$$d_1 \neq \text{constant}$$

Peak broadens

Shifts to lower angles



RMS Strain

Exceeds  $d_0$  on top, smaller than  $d_0$  on the bottom

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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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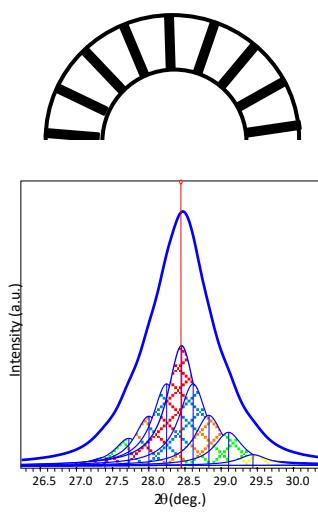
## Contributions to Microstrain Broadening

- 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

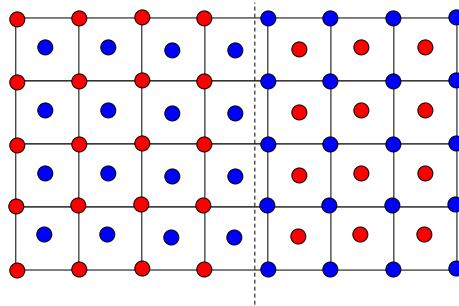
- Rather than a single d-spacing, the crystallographic plane has a distribution of d-spaces
- This produces a broader observed diffraction peak
- Such distortions can be introduced by:
  - surface tension of nanocrystals
  - morphology of crystal shape, such as nanotubes
  - interstitial impurities



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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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## 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

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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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## Determination of Size and Strain- Williamson-Hall Plot

$$\beta_D = K\lambda/D \cos\theta$$

$$\beta_\epsilon = C\varepsilon \tan\theta$$

$$\beta_{\text{tot}} = \beta_\epsilon + \beta_D = C\varepsilon \tan\theta + K\lambda/D \cos\theta$$

$$\beta_{\text{tot}} \cos\theta = C\varepsilon \sin\theta + K\lambda/D$$

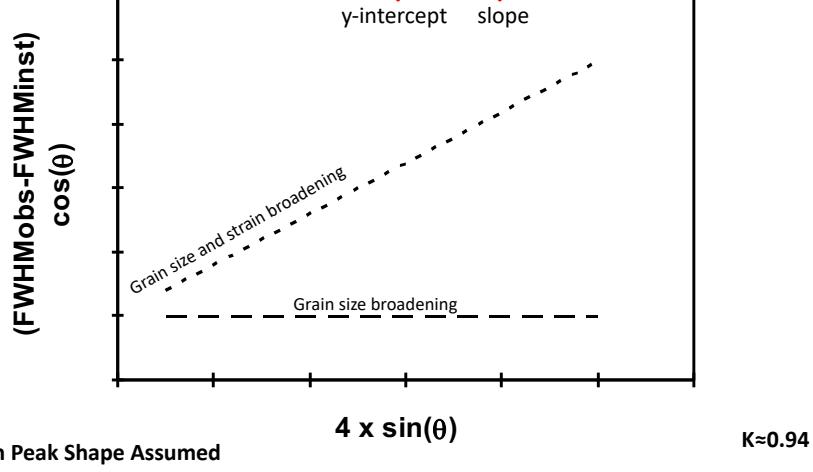
$$FWHM \times \cos(\theta) = \frac{K \times \lambda}{Size} + Strain \times 4 \times \sin(\theta)$$

y-intercept    slope

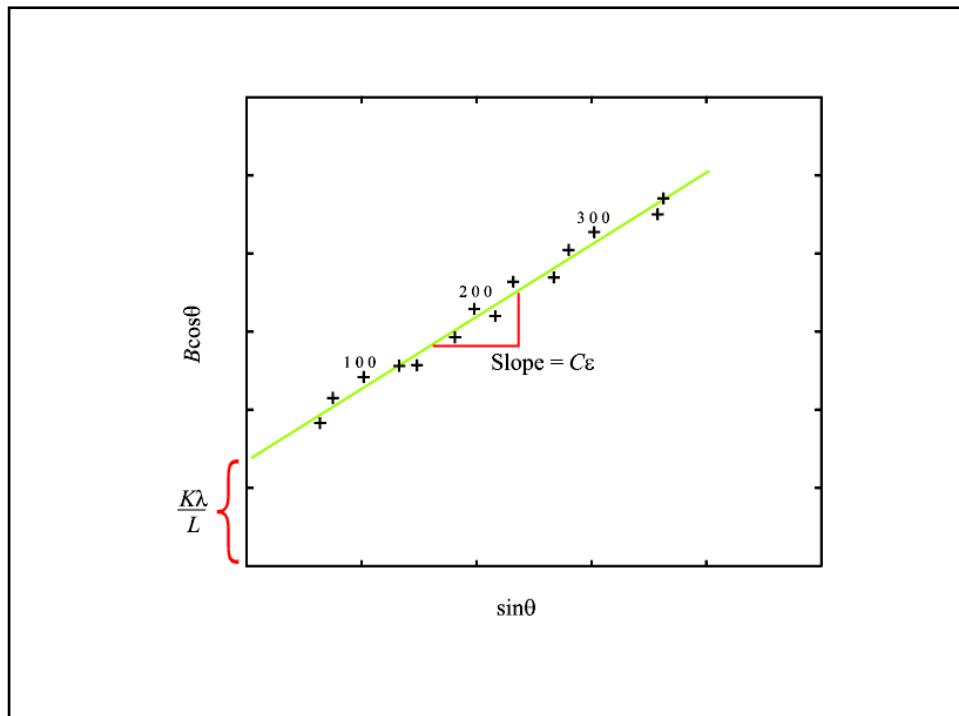
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## Williamson-Hall Plot

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



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## Warren-Averbach method

J.Appl.Phys. 21, 595(1950) and ibid 23, 497 (1952)

more rigorous and widely used methods for separating the effects of size and strain

expressing the peak intensity in terms of a Fourier sum

most commercial powder diffractometer systems provide a Warren-Averbach analysis routine on their software

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