Analytical Methods for Materials

Laboratory Module #5

Determination of Crystallite Size
and Lattice Strain

Suggested Reading

- C. Suryanarayana and M.G. Norton, *X-ray Diffraction A Practical Approach*, (Plenum Press, New York, 1998), pages 207-221.
- B.D. Cullity and S.R. Stock, *Elements of X-ray Diffraction, 3rd Edition*, (Prentice-Hall, Upper Saddle River, NJ, 2001), Ch. 5, pages 167-176; and Ch. 14, pages 385-402.
- Y. Waseda, E. Matsubara, and K. Shinoda, *X-ray Diffraction Crystallography*, (Springer, New York, NY, 2011), Ch. 4, pages 123-126, 164-167.

Objectives

- Upon completion of this module, the student will be able to determine the average crystal size and lattice strain in a specimen using X-ray peak broadening analyses.

Background

- Bragg's law assumes that ideal conditions are maintained during diffraction.
  - The crystal is perfect
  - The X-ray beam is collimated and monochromatic
  - Etc…
- In practice, this condition never exists.

Ideal Particle Size

- With powder XRD, the ideal particle size depends on the “relative” perfection of the polycrystalline sample.
  - Usually 0.5 μm to 10 μm
- What are the implications of smaller crystals?
  - *The number of parallel planes (for XRD) is too low for a sharp diffraction maximum to build up. Thus, XRD peaks become “broadened”.*

Crystal Size and Lattice Strain

- Measurements depend upon:
  - XRD peak locations
  - XRD peak widths

- Must take peak broadening into account
  - What causes peak broadening?

Crystal Size and Lattice Strain – cont'd

- *d*-spacings directly influence peak width.
- What can change *d*-spacing?
  - strains
  - compositional variations
  - instrumental variables
    - slits (filtering and focusing)
    - sample area
    - diffracting layer thickness
  - particle size

More on the causes of broadening

- Instrument effects:
  - Imperfect focusing of diffracted beam
  - Unresolved α_1 and α_2 peaks
  - Finite widths of α_1 and α_2 peaks when resolved
- Crystal size
- Lattice strain

Some Terminology

- Domain size:
  - Domains are the parts of an XRD specimen that diffract X-rays coherently. They form “substructure.” Domains are usually regions that are misoriented relative to one another (usually by <1°).
    - Subgrain boundaries, tilt boundaries, etc…
- Crystal (or crystallite) size:
  - Often used interchangeably with grain size. Refer to regions separated by large misorientation angles.
- Grain size:
  - Single crystal regions separated by large misorientation angles

Corrections for instrumental broadening

We must first determine the individual contributions to peak broadening

Peak Broadening

||

instrumental component

+

strain/particle size

Corrections for instrumental broadening

- Let β = peak width

- $\beta_{observed} = \beta_{instrumental} + \beta_{strain\ and\ particle\ size}$

or

- $\beta_o = \beta_i + \beta_r$

- β_o is usually determined using well-annealed powders

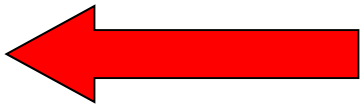
Corrections -- Cont'd

- Rewrite equation for lattice strain and particle size effects:

$$\beta_r = \beta_o - \beta_i$$

- This expression holds for a Lorentzian* peak profile, however, many peaks have a Gaussian¥ profile:

$$\beta_r^2 = \beta_o^2 - \beta_i^2$$



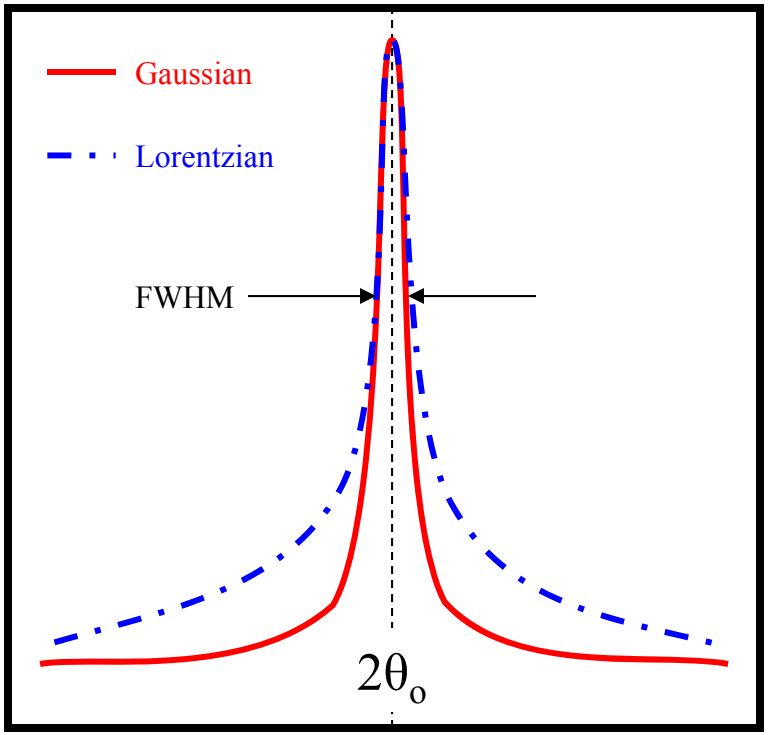
Most texts use this expression for simplicity

- When in doubt, however, use:

$$\beta_r = \sqrt{(\beta_o - \beta_i)\sqrt{(\beta_o^2 - \beta_i^2)}}$$

Corrections -- Cont'd

- Lorentzian* peak profile:
  - The peak falls away slowly as $(2\theta\text{-}2\theta_o)^{-2}$ from the center of the peak ($2\theta_o$)



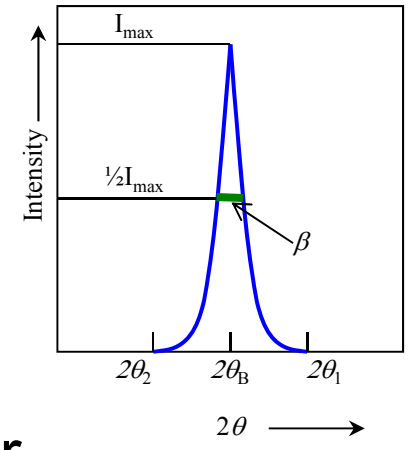
- Gaussian¥ peak profile:
  - The peak is "sharper."
  - Actually there is more to it than this.

- Modern XRD systems generally include software to assist you in fitting peaks.

Broadening due to crystallite Size

- Scherrer Formula:

$$D = \frac{k\lambda}{\beta \cos\theta} \Leftrightarrow \beta = \frac{k\lambda}{D \cos\theta}$$



D = grain diameter

β = peak width in radians at FWHM after correcting for instrumental broadening

k = 0.9 to 1.0 depending upon grain shape

- Equation applies for particle/grain sizes down into the nm range. Works best for particles in the range 2 to 300 nm.

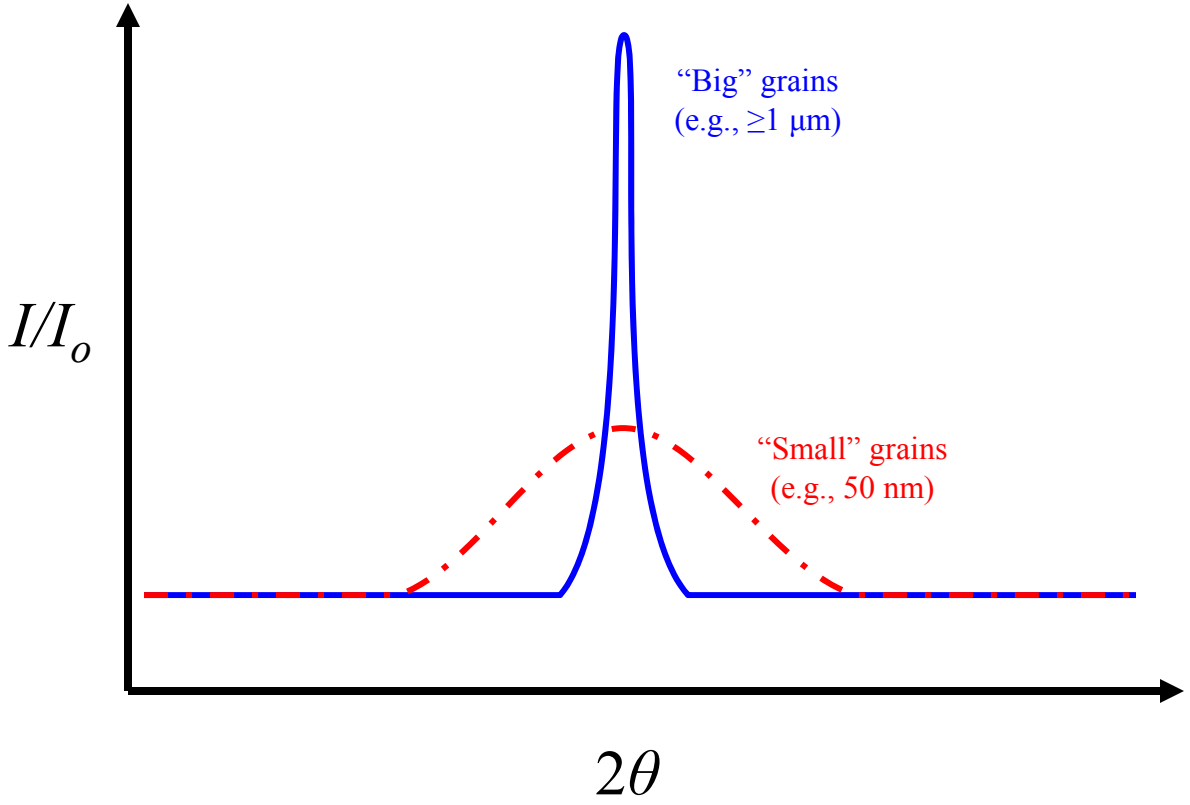
Scherrer Equation

- This formula was derived based on the assumption of Gaussian peak profiles and small cubic crystals of uniform size (where $k = 0.94$).

- The constant k actually varies between 0.89 and 1.39 depending upon crystallite size and shape. It is generally assumed to be around 1.0 which provides a precision of ±10%.

- Be careful because strain also influences peak width.

Schematic illustration of influence of grain size on peak width



- Keep in mind that peak width can be influenced by strain as well as particle size.

Broadening due to strain

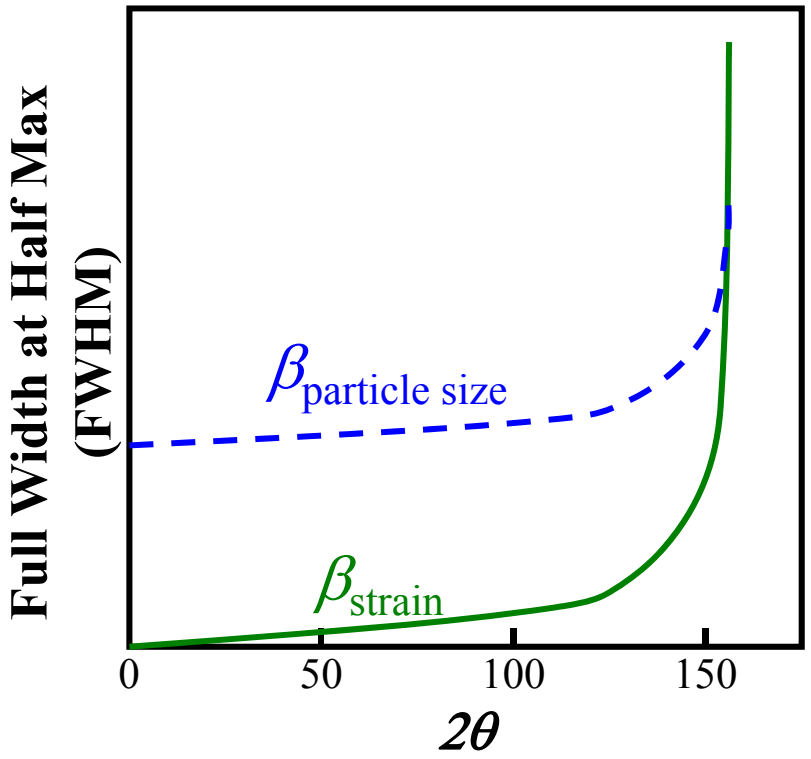
- Deformation causes local changes in atomic spacing.
- This causes local changes in the 2θ positions for diffracted x-rays.
- Lattice strain causes peak broadening.
- Broadening due to strain can be represented by the relationship:

$$\beta_{strain} = \eta \tan\theta$$

Strain in material

Variation with Bragg Angle

- Amount of peak broadening increases with Bragg angle (θ).
- Most materials exhibit broadening due to crystal size & strain.
- Must use low θ peaks to separate effects.



Now we can do something!

- Width of diffraction peak after subtracting instrumental effects equals the sum of the widths due to lattice strain and crystal size

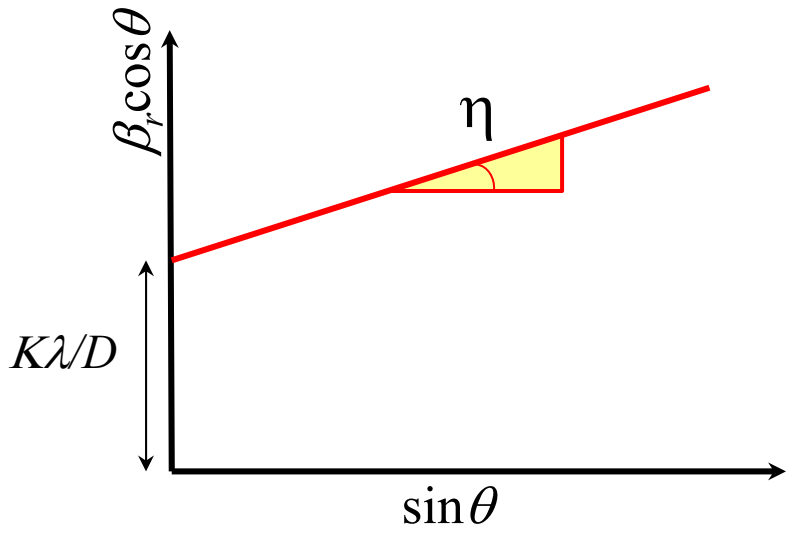
$$\beta_r = \beta_{particle} + \beta_{strain}$$

- Substituting appropriate equations yields:

$$\beta_r = \frac{K\lambda}{D\cos\theta} + \eta\tan\theta \quad \Rightarrow \quad \beta_r\cos\theta = \frac{K\lambda}{D} + \eta\sin\theta$$

This equation is in the general form of a straight line ($y = mx+b$).

- Now, **plot $\beta_r \cos\theta$ vs. $\sin\theta$**. Get straight line w/ slope ≈ the lattice strain, η, and an intercept equal to $K\lambda/D$.



- Basically, the larger the intercept, the smaller the particle size.
- The method works best for smaller crystals.
- Remember, there will be no peak broadening for extremely large crystals.

- Using these relationships you should be able to calculate crystallite size and qualitatively assess strain based upon peak broadening.

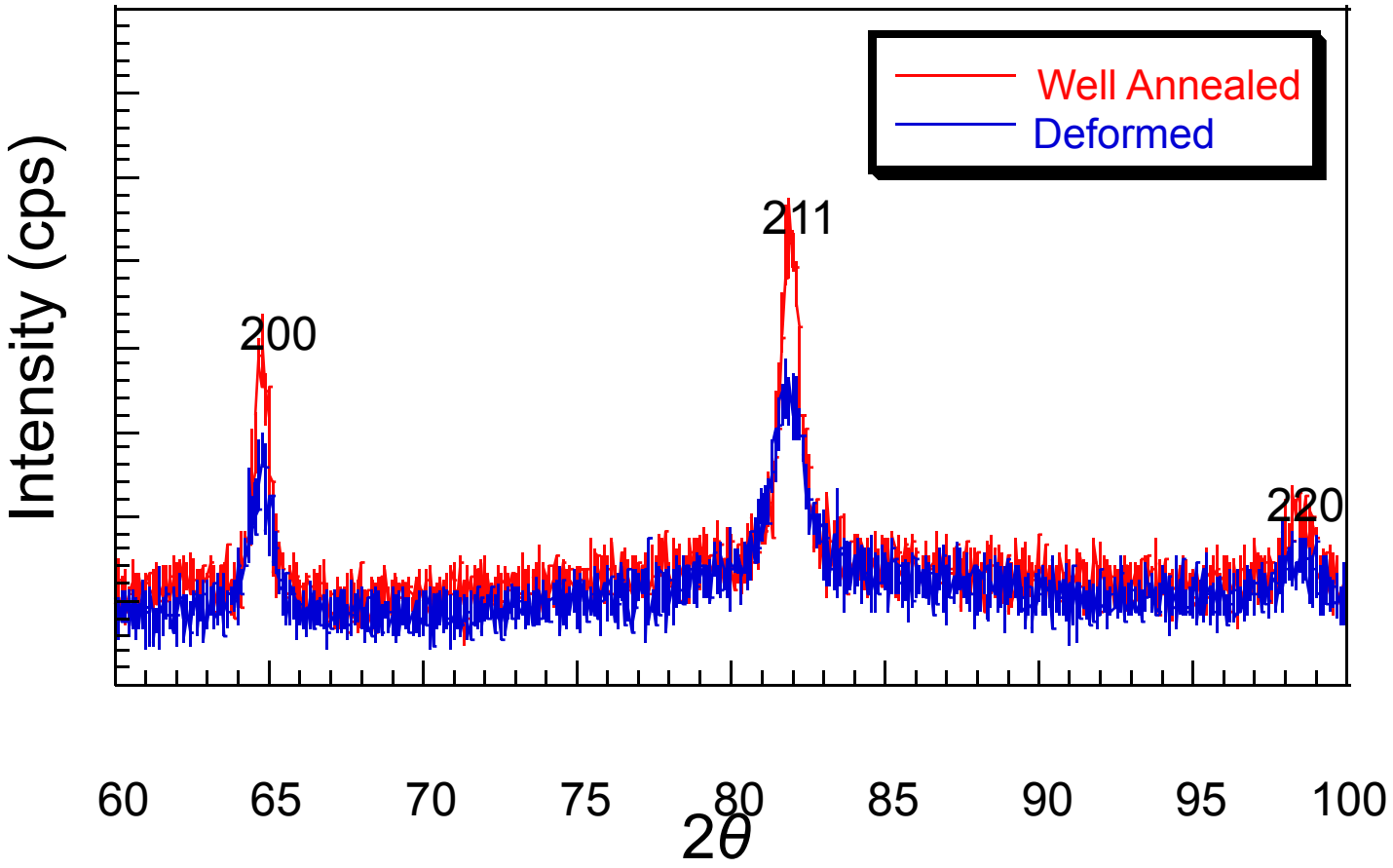
Steps

1. Collect and index diffraction patterns
   A. Well annealed specimen
   B. Deformed specimen
2. In well annealed specimen, calculate FWHM for each reflection and determine instrumental broadening to get β_i
3. Repeat calculations for experimental (*i.e.*, deformed) specimen to get β_o
4. Determine β_r (true width after subtracting instrumental broadening;

$$\beta_r = \sqrt{\beta_o^2 - \beta_i^2}$$

5. Calculate $\beta_r \cos\theta$ and plot versus $\sin\theta$

Collect and Index

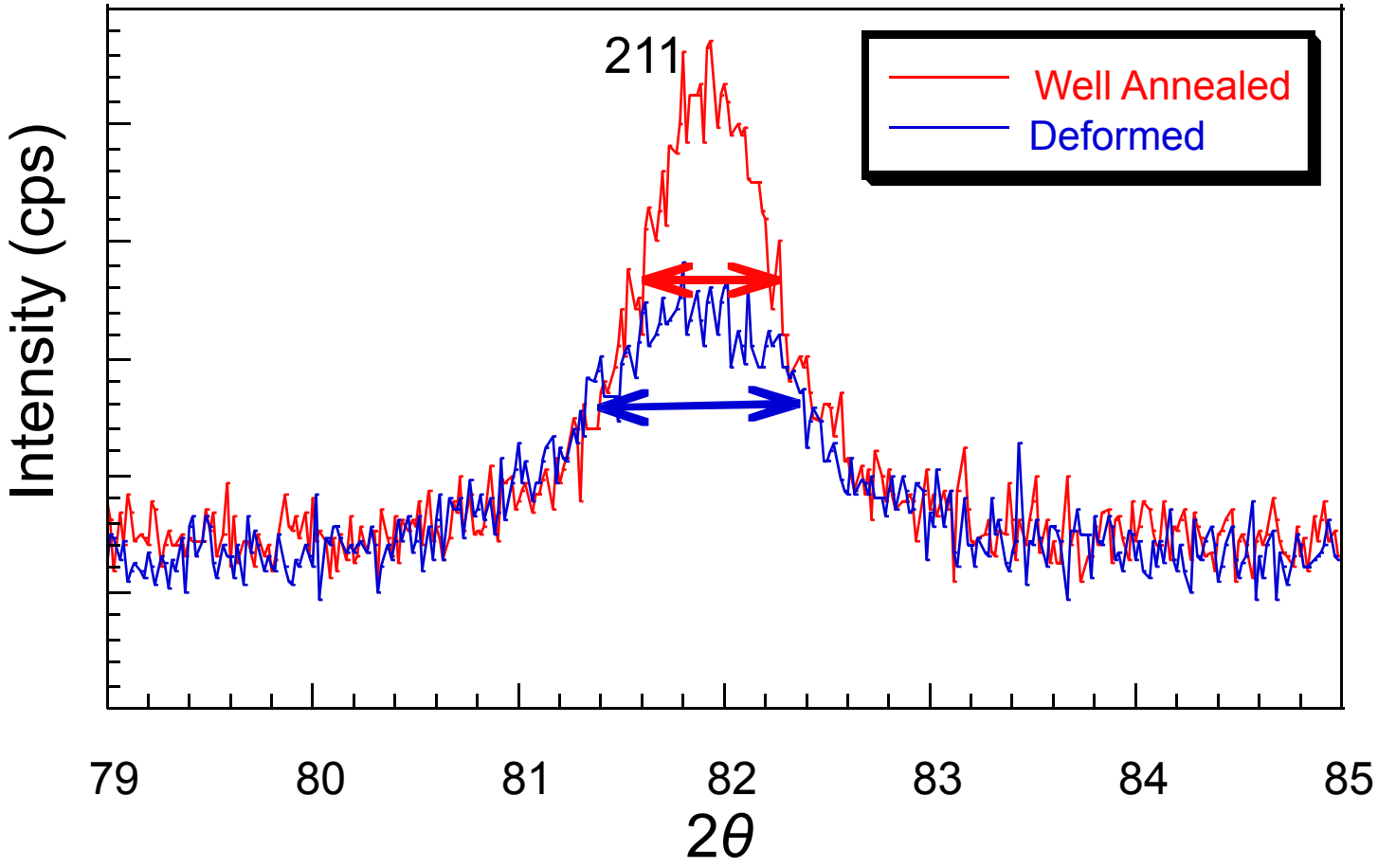


Steps

1. Collect and index diffraction patterns
   A. Well annealed specimen
   B. Deformed specimen
2. In well annealed specimen, determine FWHM for each reflection and the instrumental broadening to get β_i;
3. Repeat calculations for the deformed specimen to get β_o;
4. Determine β_r (true width after subtracting instrumental broadening);
5. Calculate $\beta_r \cos\theta$ and plot versus sin θ.

$$\beta_r = \sqrt{\beta_o^2 - \beta_i^2}$$

Determine FWHM for Each



Compile Data

Data

Annealed particles **CuKα radiation:** **1.54056 Å**

Peak#	2θ (°)	*hkl*	FWHM (°)	FWHM (radians) = β_i
1	64.9	200	0.5	8.73E-03
2	82.0	211	0.6	1.05E-02
3	98.5	220	1.1	1.92E-02

Deformed particles **CuKα radiation:** **1.54056 Å**

Peak#	2θ (°)	sin θ	*hkl*	FWHM (°) = β_o	FWHM (radians) = β_o	$\beta_r = \sqrt{\beta_o^2 - \beta_i^2}$	$\beta_r \cos\theta$
1	64.9	0.5366	200	0.75	1.31E-02		
2	82.0	0.6561	211	1	1.75E-02		
3	98.5	0.7576	220	1.5	2.62E-02		

Remember to convert all peak widths to radians!

Steps

- ☑ Collect and index diffraction patterns
  - A. Well annealed specimen
  - B. Deformed specimen
- ☑ In well annealed specimen, determine FWHM for each reflection and the instrumental broadening to get β_i
- ☑ Repeat calculations for the deformed specimen to get β_o
- → 4. Determine β_r (true width after subtracting instrumental broadening;
- → 5. Calculate $\beta_r \cos\theta$ and plot versus $\sin\theta$

Data

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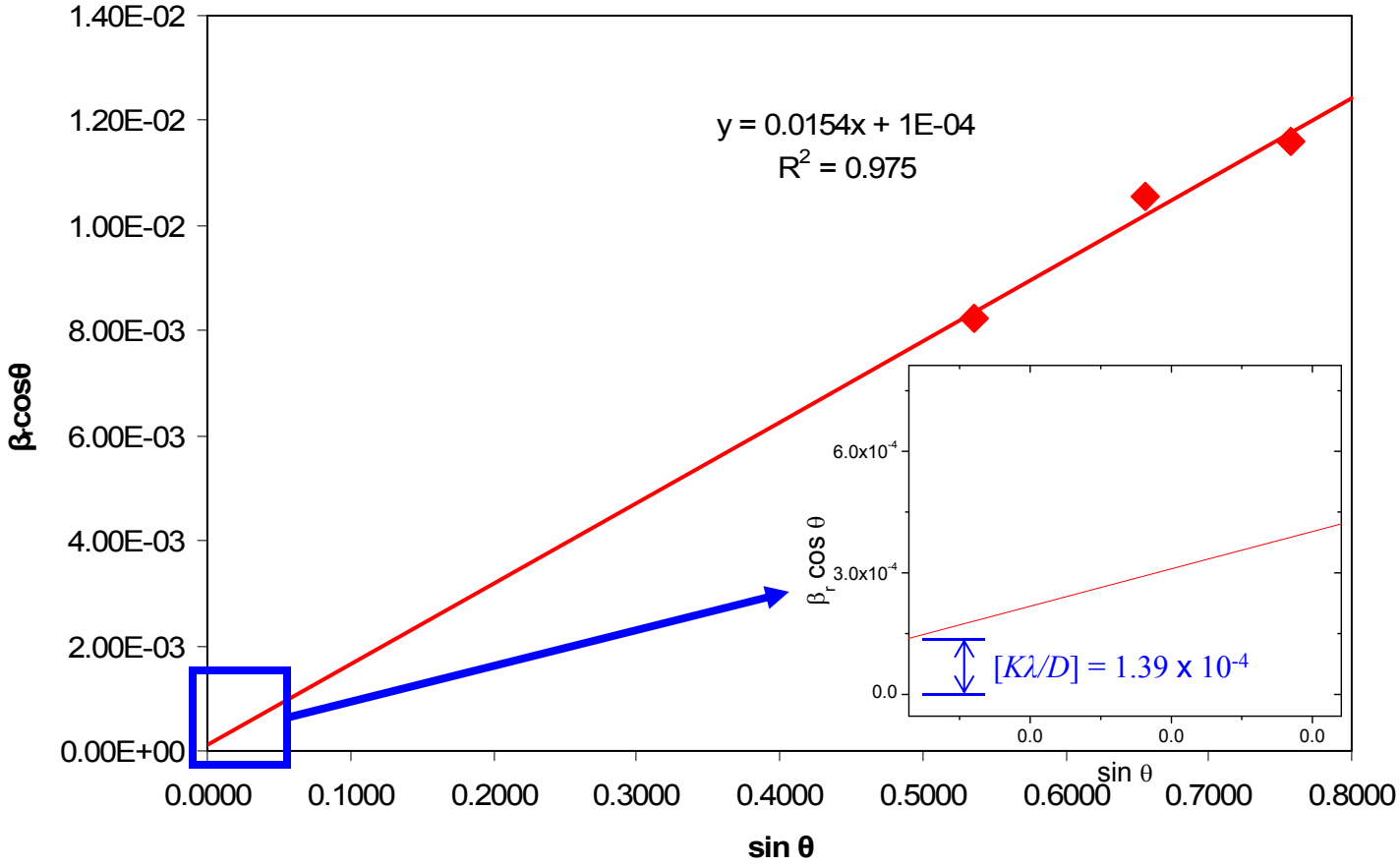
Peak#	2θ (°)	sin θ	*hkl*	FWHM (°) = β_o	FWHM (radians) = β_o	$\beta_r = \sqrt{\beta_o^2 - \beta_i^2}$	$\beta_r \cos\theta$
1	64.9	0.5366	200	0.75	1.31E-02	9.76E-03	8.23E-03
2	82.0	0.6561	211	1.0	1.75E-02	1.40E-02	1.05E-02
3	98.5	0.7576	220	1.5	2.62E-02	1.78E-02	1.16E-02

Plot these two quantities



- Slope of line is proportional to strain.

$$\beta_r \cos\theta = \frac{K\lambda}{D} + \eta \sin\theta$$

- Y-intercept is related to grain/particle size.

Particle Size

$$\frac{k\lambda}{D} = 1.39\times10^{-4} = \frac{(\sim 1)(1.54056)}{D}$$

$$\therefore$$

$$D = \frac{1.54056}{1.39\times10^{-4}} = 11,083 \ \text{Å} \ \text{ or } 1.1 \ \mu\text{m}$$

Strain

Slope of line = 0.0154 or 1.5%

This method only provides “ballpark” numbers

Let's stop for now.

The rest of this packet includes information on residual stress determination.

We'll go through later it if we have time.