Crystallite size broadening

Structure Analysis
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Degree of being "out-of-phase" that can be tolerated vs. crystallite size

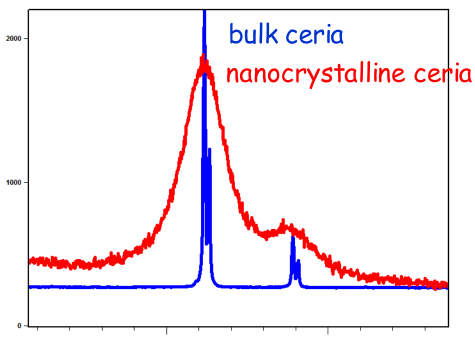
Cullity Chapter 5, 14-3, 14-4 & 14-6

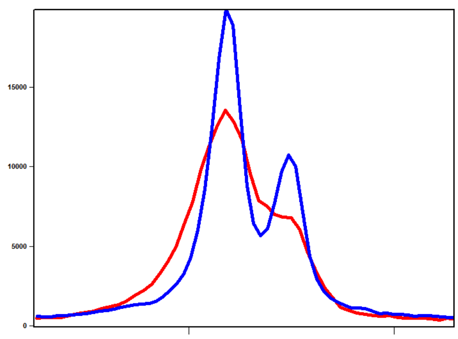
Hammond p180

Krawitz p343

Jenkins & Snyder p89

Peak broadening





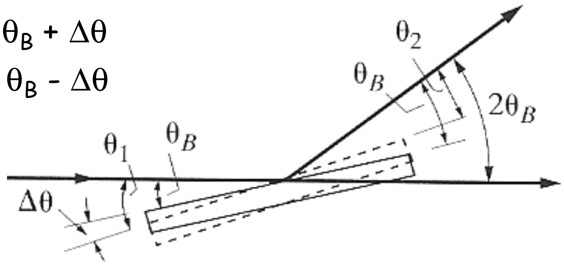
same sample run on two different instruments

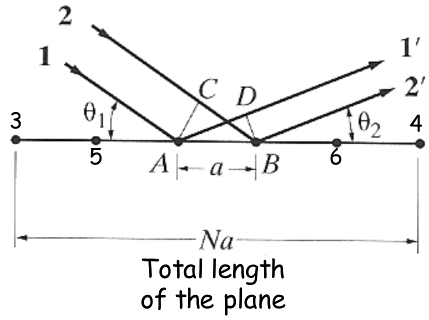
- Peak broadening may indicate:
  - ✓ Smaller crystallite size
  - ✓ More stacking faults, microstrain, and other defects in the crystal structure
  - ✓ An inhomogeneous composition in a solid solution or alloy
- Different instrument configurations can change the peak width, too

Geometrical factor – 1 of Lorenz Factor

$\theta_1 = \theta_B + \Delta\theta$

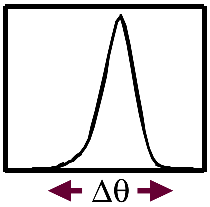
$\theta_2 = \theta_B - \Delta\theta$





$\delta_{1'2'} = 2a\Delta\theta \sin\theta_B$, → $2Na\ \Delta\theta \sin\theta_B$ Path difference b/w rays scattered by atoms at either end of the plane (3 & 4)

Diffracted intensity = zero when $2Na\ \Delta\theta \sin\theta_B = \lambda$,



$$\Delta\theta = \frac{\lambda}{2\ Na \sin\theta_B}$$

Max angular range of crystal rotation over which appreciable energy can be diffracted in the direction $2\theta_B$

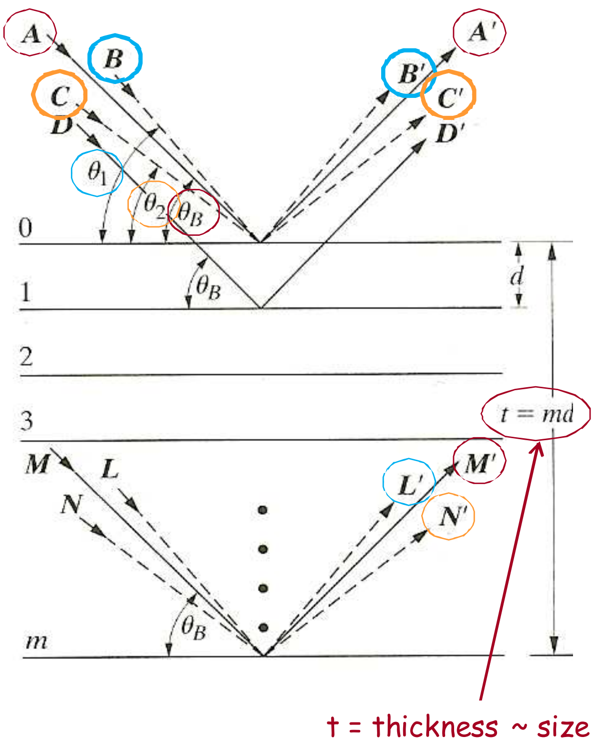
$I_{max} \propto 1/\sin\theta_B$

Size & strain broadening
$B \propto 1/\cos\theta_B$

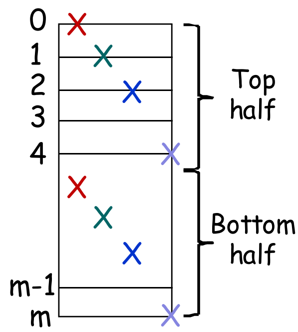
$$I_{max}\,B \propto (1/\sin\theta_B)(1/\cos\theta_B) \propto \frac{1}{\sin 2\theta}$$

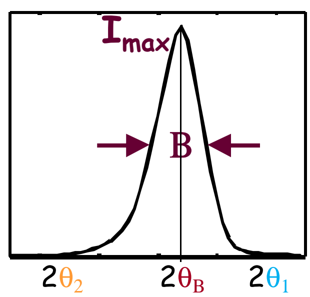
Crystallite size broadening

$\theta_1 = \theta_B + \Delta\theta$ (B, B') $\theta_2 = \theta_B - \Delta\theta$ (C, C')



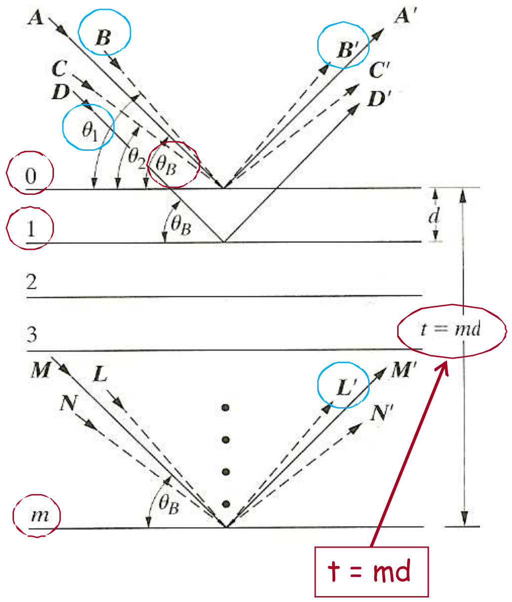
- m + 1 planes
- $\delta(A'D') = 1\lambda$, $\delta(A'M') = m\lambda$
- @ θ_1 or $\theta_2 \neq \theta_B$, incomplete destructive interference
- If $\delta(B'L') = (m+1)\lambda$, intensity zero
- If $\delta(C'N') = (m-1)\lambda$, intensity zero
- @ $2\theta_2 < 2\theta < 2\theta_1$, intensity is not zero





Crystallite size broadening

$\theta_1 = \theta_B + \Delta\theta$ (B, B′) $\theta_2 = \theta_B - \Delta\theta$ (C, C′)

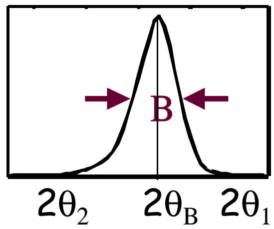


$$2t \sin \theta_1 = (m+1)\lambda$$

$$2t \sin \theta_2 = (m-1)\lambda$$

→ $t(\sin\theta_1 - \sin\theta_2) = \lambda$

- Ray B; $\theta_1 = \theta_B + \Delta\theta$, $\delta(B'L') = (m+1)\lambda$
- Compare when m = 10 and m = 10,000
- m = 10 → @ θ_1, $\delta(B'L') = \delta(0m) = 11\lambda$, $\delta(01) = 1.1\lambda$
- m = 10,000 → @ θ_1, $\delta(B'L') = \delta(0m) = 10{,}001\lambda$, $\delta(01) = 1.0001\lambda$
- $\theta_1(m = 10) >>> \theta_1(m = 10{,}000)$
- θ_1 ↑ as m ↓ θ_2 ↓ as m ↓
- $(2\theta_1 - 2\theta_2)$ ↑ as m ↓
- B ↑ as thickness ↓
- Peak width ↑ as size ↓



Cullity page 168

Crystallite size broadening

Assume diffraction line is triangular in shape

$$B = \frac{1}{2}(2\theta_1 - 2\theta_2) = \theta_1 - \theta_2.$$

$$2t \sin \theta_1 = (m+1)\lambda$$

$$2t \sin \theta_2 = (m-1)\lambda$$

$$t(\sin \theta_1 - \sin \theta_2) = \lambda,$$

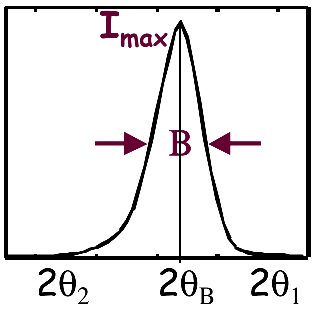
$$2t \cos\left(\frac{\theta_1 + \theta_2}{2}\right) \sin\left(\frac{\theta_1 - \theta_2}{2}\right) = \lambda$$

$$\theta_1 + \theta_2 = 2\theta_B \text{ (approx.)}$$

$$\sin\left(\frac{\theta_1 - \theta_2}{2}\right) = \left(\frac{\theta_1 - \theta_2}{2}\right) \text{(approx.)}$$

$$2t\left(\frac{\theta_1 - \theta_2}{2}\right) \cos \theta_B = \lambda$$

$$t = \frac{\lambda}{B \cos \theta_B}$$



B; an angular width, in terms of 2θ (not a linear width)

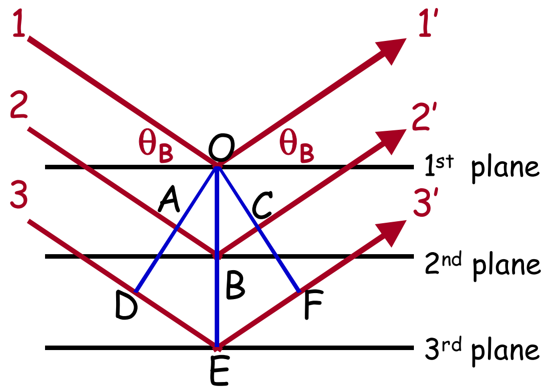
Shape factor; depends on the shape of the crystallites

$$t = \frac{0.9\lambda}{B \cos \theta_B}$$

Scherrer equation

Cullity p169

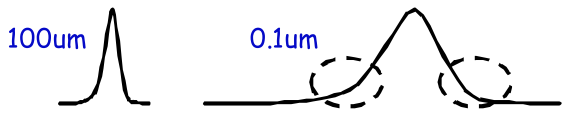
Crystallite size broadening



- @ θ_B; ABC = λ, DEF = 2λ → diffraction peak
- ABC = 0.5λ, DEF = 1λ → no diffraction peak
- ABC = 1.1λ, DEF = 2.2λ

  → PD (path diff.) in 6th plane = 5.5λ

  → 1' & 6' out of phase → no net diffraction
- ABC = 1.001λ → 1' & 501' out of phase; ABC = 1.00001λ → 1' & 50001' out of phase →→ Sharp diffraction peak @ θ_B
- When crystal is only 100nm in size, 5000' or 50000' are not present
- Peak begins to show intensity at a lower θ and ends at a higher θ than θ_B → particle size broadening
- Crystallites smaller than 1um can cause broadening → size can be determined using the peak width ← incomplete destructive interference



Jenkins & Snyder page 89

Crystallite size broadening

- In case λ = 1.5 Å, d= 1.0 Å, θ = 49 °,

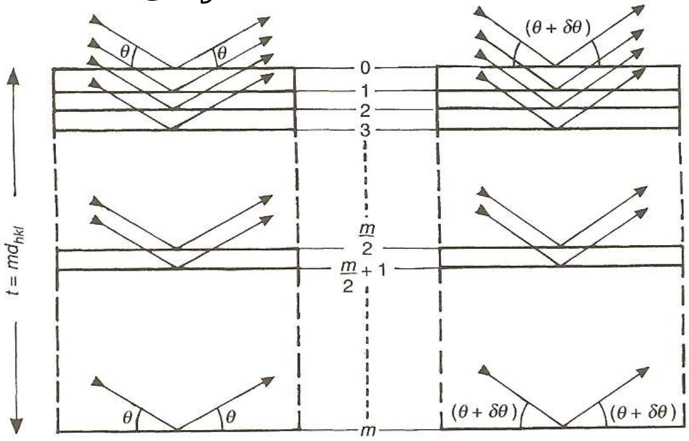
$$t = \frac{0.9\lambda}{B \cos \theta_B}$$

- 1mm(millimeter) diameter crystal → 10^7 parallel lattice planes, ~10^{-7} radian*, ~10^{-5} degree → too small to observe
- 500 Å diameter crystal → 500 parallel lattice planes, ~10^{-3} radian, ~0.2 degree → measurable

- Non-parallel incident beam, non-monochromatic incident beam → diffraction @ angles not exactly satisfying Bragg's law → line broadening

* B = $(0.9 \times 1.5 \times 10^{-10})/(10^{-3} \times \cos 49°) \sim 2 \times 10^{-7}$ rad

Cullity, p170



Crystallite size broadening

between planes 0 & (m/2)

Constructive interference at angle θ

$$(m/2)\lambda = (m/2)2d_{hkl}\sin\theta$$

Destructive interference at angle θ + δθ

$$(m/2)\lambda + \lambda/2 = (m/2)2d_{hkl}\sin(\theta + \delta\theta)$$

δ(1, (m/2)+1) = 0.5λ

$$\cos\delta\theta = 1 \text{ and } \sin\delta\theta \approx \delta\theta$$

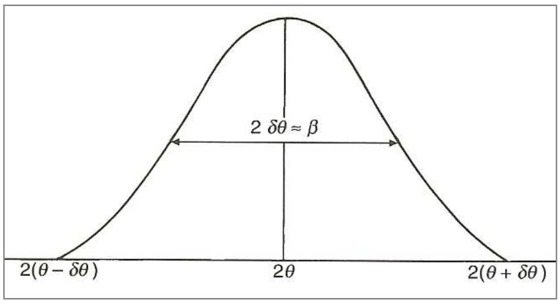
$$(m/2)\lambda + \lambda/2 = (m/2)2d_{hkl}\sin\theta + (m/2)2d_{hkl}\cos\theta\,\delta\theta$$

$$md_{hkl} = t$$

$$2\,\delta\theta = \frac{\lambda}{t\cos\theta}$$

$$B = \beta = \frac{\lambda}{t\cos\theta} = \frac{\lambda\sec\theta}{t}$$

Scherrer equation

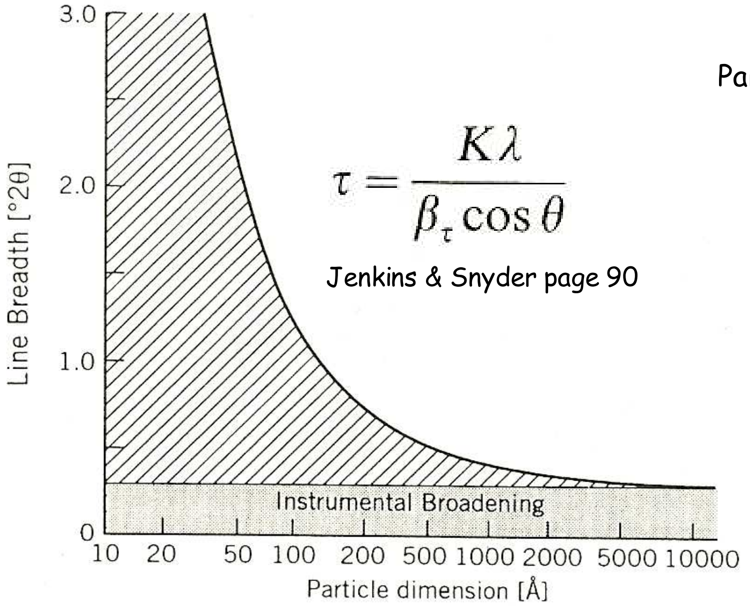


Hammond, Chapter 9.3, p180 ~ 181

Crystallite size broadening

Scherrer equation

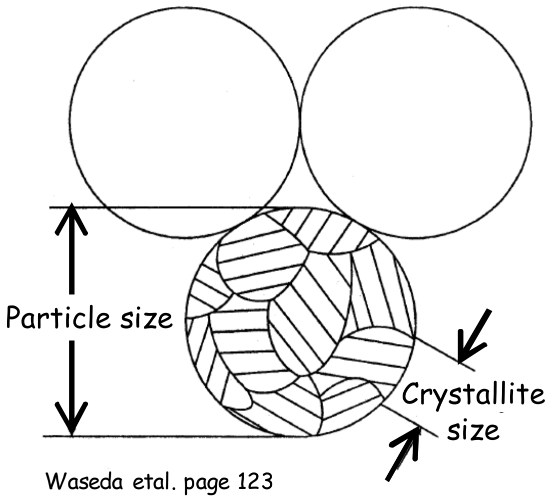
$$t = \frac{0.9\lambda}{B\cos\theta_B}$$



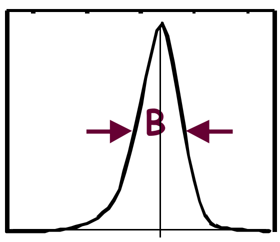
$$\tau = \frac{K\lambda}{\beta_\tau\cos\theta}$$

Jenkins & Snyder page 90

Figure 3.21. Line width as a function of particle dimension.



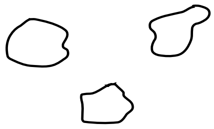
Waseda etal. page 123



Waseda & Matsubara, X-ray diffraction Crystallography, Springer, 2011

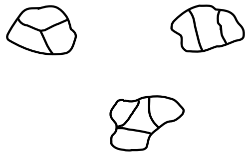
Particle size vs. Crystallite size

Particles can be
individual crystallites



Particle size = crystallite size

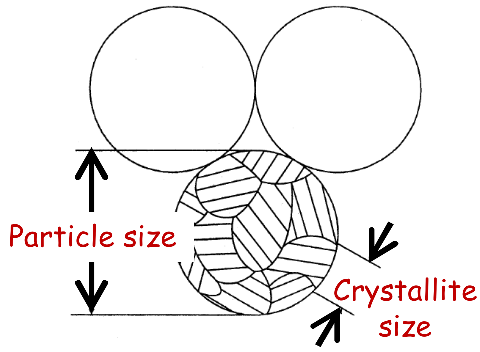
Particles may be
imperfect single crystals



Particle size > crystallite size

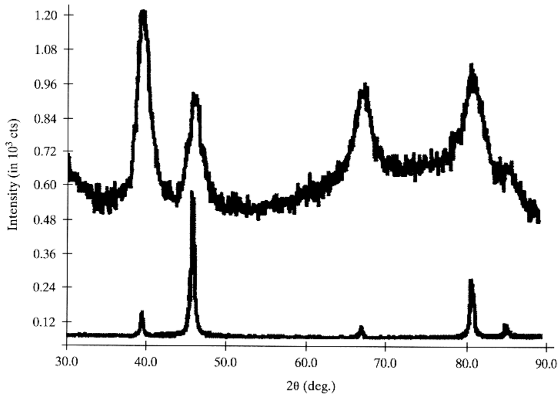
- Individual crystallites are perfect
- Boundaries
  - Dislocations
  - Twin walls
  - Anti-phase walls
  - Stacking faults

From presentation of Dr. Mark Rodriguez
@ DXC 2017 "What usually causes trouble?"



Waseda et al. page 123

Crystallite size broadening



platinum nano-particle in a matrix of amorphous carbon

rolled platinum sheet

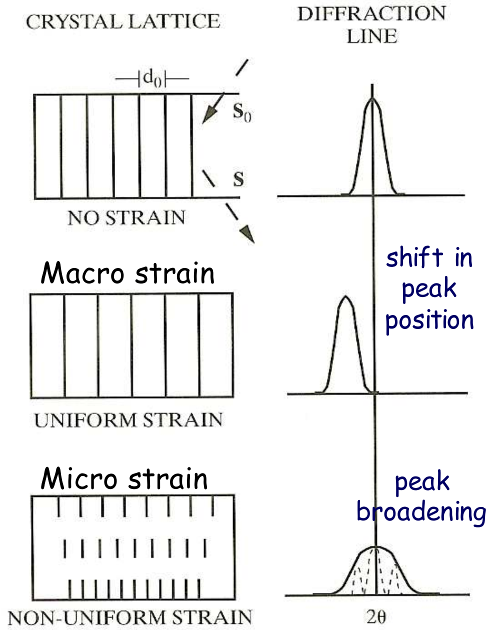
hkl	FWHM (°2θ)	t (Å)
111	1.9	50
200	1.7	55
220	2.1	50
311	2.5	45-50

Strain broadening

Strain/Stress

- Macrostrain/Macrostress → shift in peak position
  - ✓ stress is uniformly compressive or tensile over large distances ← lattice parameter measurement
- Microstrain/Microstress → peak broadening
  - ✓ Distribution of both tensile & compressive stress → distribution of d-values
  - ✓ Can come from dislocations, vacancies, defects, shear planes, thermal expansion/contraction, etc.

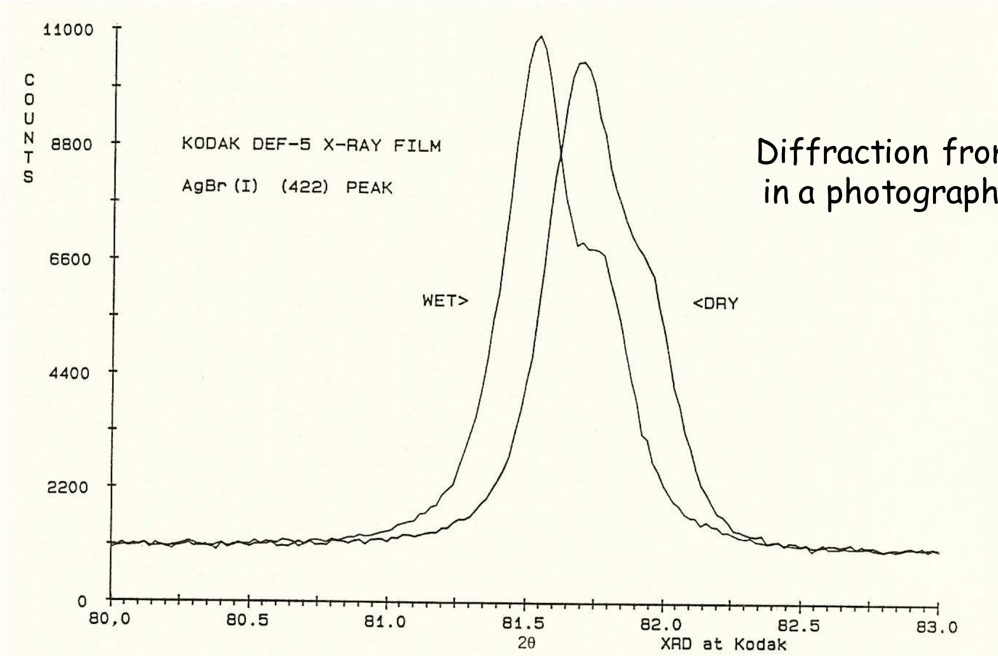
  ← peak profile analysis



Cullity page 176

Jenkins & Snyder, page 91~93

Peak shift ← macrostrain



Diffraction from AgBr in a photographic film

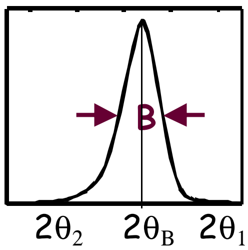
Differential expansion between the film substrate & AgBr causes macrostrain → changes lattice parameter → peak shift

Jenkins & Snyder, page 92

Strain broadening, Size & Strain broadening

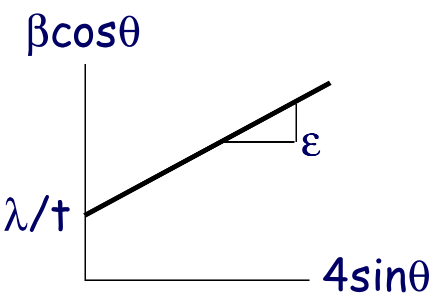
Strain broadening

- $\lambda = 2d \sin\theta$
- $0 = 2d \cos\theta\, \delta\theta + 2 \sin\theta\, \delta d$
- $\Delta(2\theta) = -2(\delta d/d)\tan\theta = B$; extra broadening produced by microstrain
- $\beta_\varepsilon = 4\varepsilon \tan\theta$ (Jenkins & Snyder p93)
- $\beta = -2\varepsilon \tan\theta$ (Hammond p214)



Size & Strain broadening

- $\beta_{size} = \lambda/(t\cos\theta)$, $\beta_{strain} = 4\varepsilon \tan\theta$, $\beta_{instrument}$
- $\beta(total) = \lambda/(t\cos\theta) + 4\varepsilon \tan\theta + \beta_{instrument}$
- $\beta = \lambda/(t\cos\theta) + 4\varepsilon (\sin\theta/\cos\theta)$
- $\beta\cos\theta = \lambda/t + 4\varepsilon \sin\theta$
- $\beta\cos\theta/\lambda = 1/t + (4\varepsilon \sin\theta)/\lambda$
- plot $\beta\cos\theta/\lambda$ vs $\sin\theta/\lambda$ (Williamson-Hall plot) → can separate size & strain contributions to line broadening --- semi-quantitative



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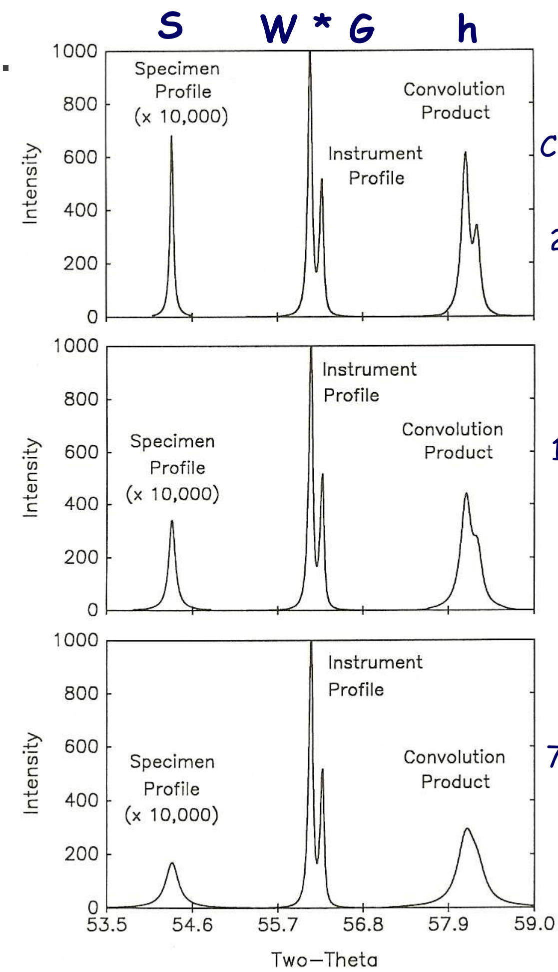
Broadening

- Darwin width
  - ✓ Incident photon is confined to certain volume
  - ✓ Result of uncertainty principle ($\Delta p \Delta x = h$) --- Location of the photon in a xtal is restricted to a certain volume
  - ✓ Δp must be finite → $\Delta\lambda$ must be finite → finite width of diffraction peak
- Specimen contribution (S)
- Spectral distribution (radiation source contribution) (W)
- Instrumental contribution (G)

- (W * G) ← X-ray source image, flat specimen, axial divergence of incident beam, specimen transparency, receiving slit, etc.
- (W * G) ; fixed for a particular instrument/target system → instrumental profile g(x)
- Overall line profile h(x) = (W * G) * S + background = g(x) * S + BKG

↑ LaB_6 SRM

h(x) = (W * G) * S



Crystallite size

286 nm

143 nm

70 nm

Line shape ← **<u>convolution</u>** of a profile representing instrument (W*G) and specimen (S) contributions

Intergrated line intensity of the convolution product remains the same while the peak broadens and the peak intensity decreases

$$B_{obs} = B_{size/strain} + B_{inst}$$ Lorentzian profile

$$B_{obs}^2 = B_{size/strain}^2 + B_{inst}^2$$ Gaussian profile

Bish & Post

Standard Reference Materials (SRMs)

- Powder Line Position + Line Shape Std for Powder Dif
  - ✓ **Silicon (SRM 640e)**; $741/7.5g
- Line position - Fluorophlogopite mica (SRM 675); $721/7.5g
- Line profile - **LaB_6 (SRM 660c)**; $1,002/6g
- Intensity
  - ✓ ZnO, TiO_2 (rutile), Cr_2O_3, CeO_2 (SRM 674b); $916/10g
- Quantitative phase analysis
  - ✓ Al_2O_3 (SRM 676a); "notify me"/20g, Silicon Nitride (SRM 656); $492/20g
- Instrument Response Std
  - ✓ Alumina plate (SRM 1976b); $700/1 disc

Gold
$41.46 / gram
(2017-12-28)
goldprice.org

Prices; 2017-12-28
www.nist.gov/srm/index.cfm

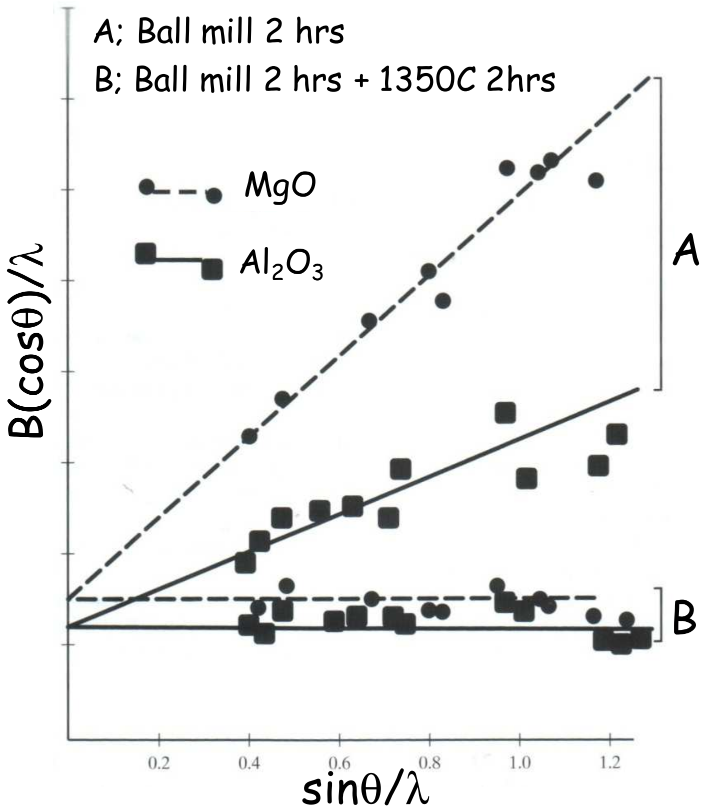
Conventional Williamson-Hall Plot

- Size + Strain

$$\frac{B\cos\theta}{\lambda} = \frac{0.9}{d} - 2\frac{\Delta d}{d}\frac{\sin\theta}{\lambda}$$

$$y = a + bx$$

- Size >> strain
  - ✓ Horizontal line
- Size << strain
  - ✓ Linear function



Cullity

Modified Williamson-Hall Plot

The effect of dislocation contrast on x-ray line broadening: A new approach to line profile analysis

T. Ungár[a)] and A. Borbély
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(Received 29 May 1996; accepted for publication 6 September 1996)

- explained strain broadening by dislocations

$$\frac{B\cos\theta}{\lambda} = \frac{0.9}{d} + \Delta K^D \qquad y = a + X$$

Classical $\quad X = -2\frac{\Delta d}{d}\frac{\sin\theta}{\lambda}$

Modified $\quad X = A(\rho^*)^{1/2} + A'(Q^*)^{1/2}$

Modified Williamson-Hall Plot

$$\frac{B\cos\theta}{\lambda} = \frac{0.9}{d} + A(\rho^*)^{1/2} + A'(Q^*)^{1/2}$$

- ρ^*: (formal) dislocation density
- Q^*: (formal) two-particle correlations in the dislocation ensemble
- A, A' : parameter determined by dislocations

- True values of dislocation density, correlation factor

$$\rho^* = \rho(\pi g^2 b^2 \overline{C})/2 \qquad Q^* = Q(\pi g^2 b^2 \overline{C})^2/4$$

- ✓ $\overline{C}$:average contrast factor of dislocation
- ✓ b:Burgers vector of dislocation
- ✓ Particular reflection $\quad g = \frac{2\sin\theta}{\lambda}$

Appl. Phys. Lett. 69 (21),3173 (1996)

Conventional vs. Modified W-H Plot

$$y = a + X$$

Modified

$$X = \underbrace{\left(\pi A b^2/2\right)^{1/2}\rho^{1/2}}_{b'}\underbrace{\frac{2\sin\theta}{\lambda}C^{1/2}}_{x'} + \underbrace{\left(\pi A' b^2/2\right)Q^{1/2}}_{b''}\underbrace{\left(\frac{2\sin\theta}{\lambda}C^{1/2}\right)^2}_{x'^2} = b'x' + b''x'^2$$

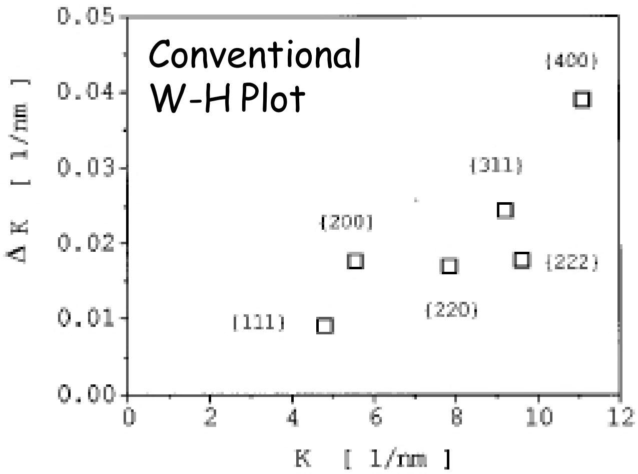
Conventional

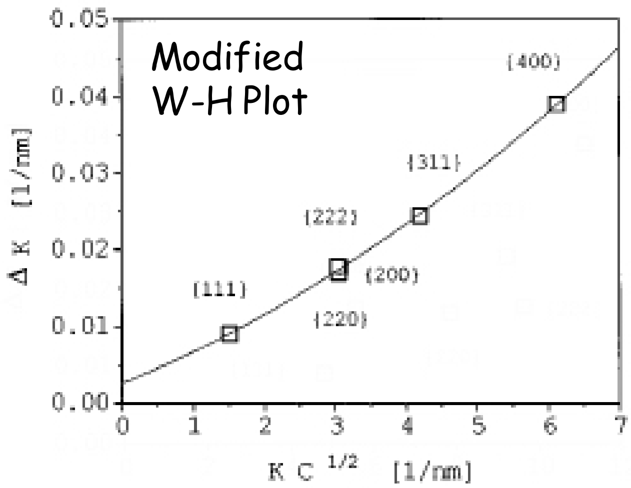
$$X = -2\underbrace{\frac{\Delta d}{d}}_{b}\underbrace{\frac{\sin\theta}{\lambda}}_{x} = bx$$

$$K = 2\frac{\sin\theta}{\lambda}$$

Appl. Phys. Lett. 69 (21),3173 (1996)

Conventional vs. Modified W-H Plot

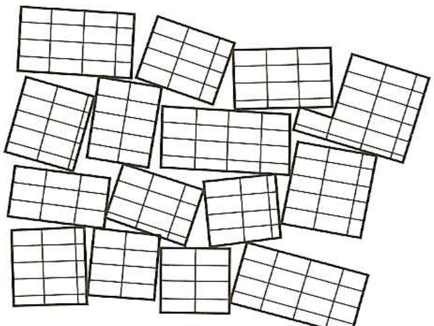




Appl. Phys. Lett. 69 (21),3173 (1996)

Mosaic structure

- Angle of disorientation between the tiny blocks is ε → diffraction occur at all angles between θ_B and $\theta_B + \varepsilon$
- Increases the integrated intensity relative to that obtained (or calculated) for an ideally perfect crystal ← strains & strain gradients associated with the groups of dislocations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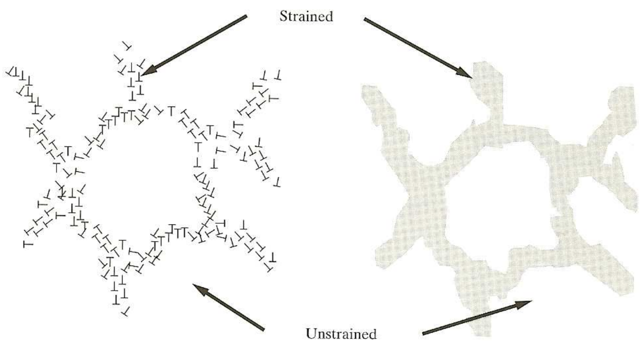
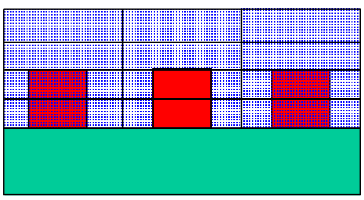
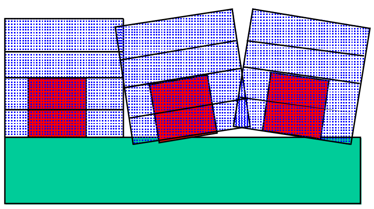


 Cullity page 174

Mosaic Spread

- Mosaicity is created by slight misorientations of different crystals as they nucleate and grow on the substrate. When the crystals join, they form low energy grain boundaries.





In an ideal case, each nuclei (red) is per fectly oriented.
When the crystals grow and meet, there is perfect bounding between the crystallites → no grain boundary.

If the nuclei (red) are slightly misa ligned, then low angle grain boundaries will be formed.

 Scott A Speakman

Mosaic Spread - reciprocal space

- Mosaic Spread can be quantified by measuring the broadening of the lattice point in reciprocal space
- The amount of broadening of the reciprocal lattice point that is perpendicular to the reflecting plane normal can be attributed to mosaic spread
- The peak broadening parallel to the interface can be attributed to lateral correlation length