XRD Line Broadening

With effects on Selected Area Diffraction (SAD) Patterns in a TEM

Part of

MATERIALS SCIENCE & ENGINEERING

A Learner's Guide

AN INTRODUCTORY E-BOOK

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Crystallite size and Strain

- Bragg's equation assumes:
  - Crystal is perfect and infinite
  - Incident beam is perfectly parallel and monochromatic
- Actual experimental conditions are different from these leading various kinds of deviations from Bragg's condition
  - Peaks are not 'δ' curves → Peaks are broadened *(in addition to other possible deviations)*
- There are also deviations from the assumptions involved in the generating powder patterns
  - Crystals may not be randomly oriented *(textured sample)* → Peak intensities are altered w.r.t. to that expected

- In a powder sample if the crystallite size < 0.5 μm
  - there are insufficient number of planes to build up a sharp diffraction pattern

  ⇒ *peaks are broadened*

When considering constructive and destructive interference we considered the following points:

- In the example considered θ' was 'far away' (at a larger angular separation) from θ (θ_{Bragg}) and it was easy to see the destructive interference
- In other words for incidence angle of θ' the phase difference of π is accrued just by traversing one 'd'.
- If the angle is just away from the Bragg angle (θ_{Bragg}), then one will have to go deep into the crystal (many 'd') to find a plane (belonging to the same parallel set) which will scatter out of phase with this ray (phase difference of π) and hence cause destructive interference
- If such a plane which scatters out of phase with a off Bragg angle ray is absent (due to finiteness of the crystal) then the ray will not be cancelled and diffraction would be observed just off Bragg angles too → line broadening!
  (i.e. the diffraction peak is not sharp like a δ-peak in the intensity versus angle plot)
- This is one source of line broadening of line broadening. Other sources include: residual strain, instrumental effects, stacking faults etc.

XRD Line Broadening

Instrumental B_i

- Unresolved α_1 , α_2 peaks
- Non-monochromaticity of the source (finite width of α peak)
- Imperfect focusing

Crystallite size B_C

- In the vicinity of θ_B the −ve of Bragg's equation not being satisfied

Strain B_S

- 'Residual Strain' arising from dislocations, coherent precipitates etc. leading to broadening

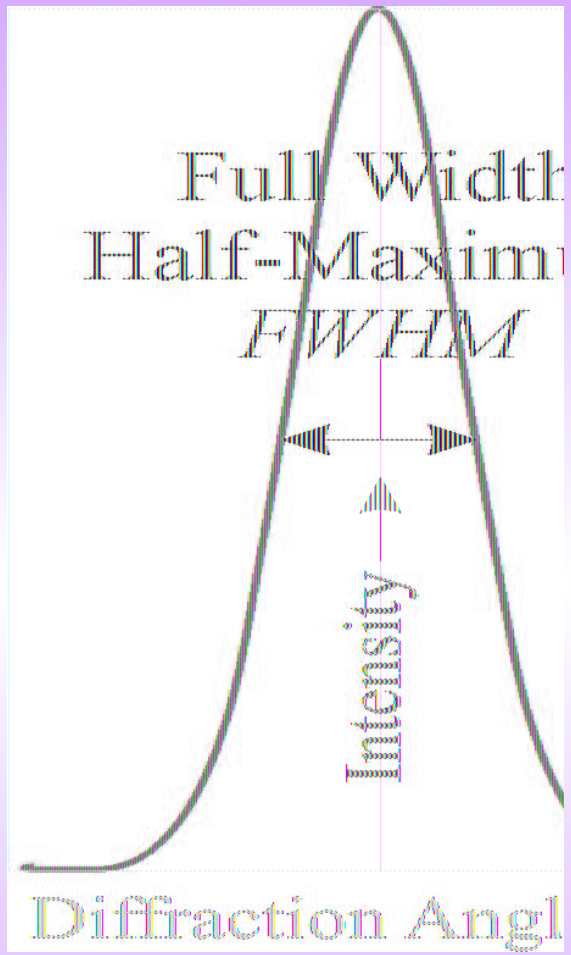
Stacking fault B_{SF}

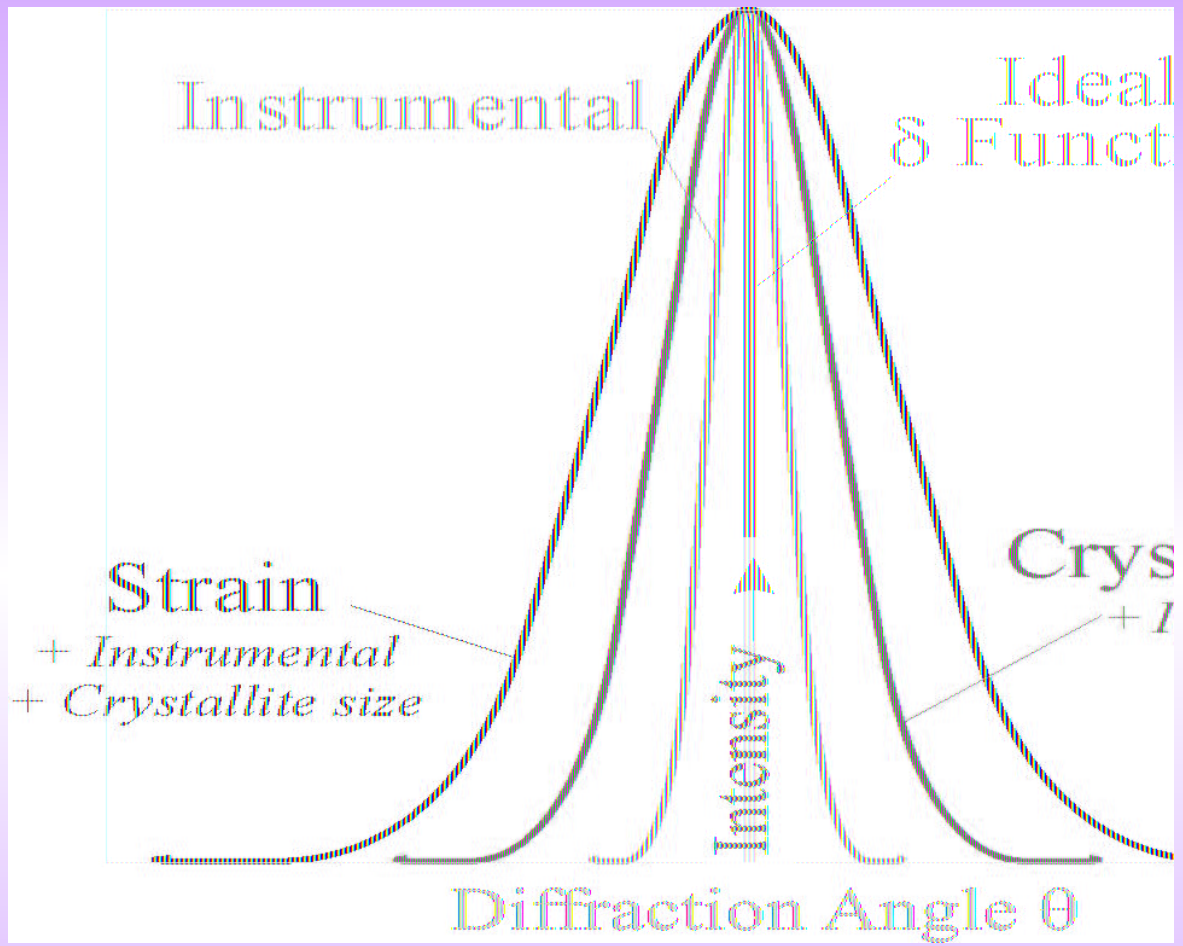
Other defects

In principle every defect contributes to some broadening

$$B(FWHM) = B_i + B_c + B_s + B_{SF} + \ldots$$

The diffraction peak we see is a result of various broadening ‘mechanisms’ at work





Full Width at Half-Maximum (FWHM) is typically used as a measure of the peak ‘width’

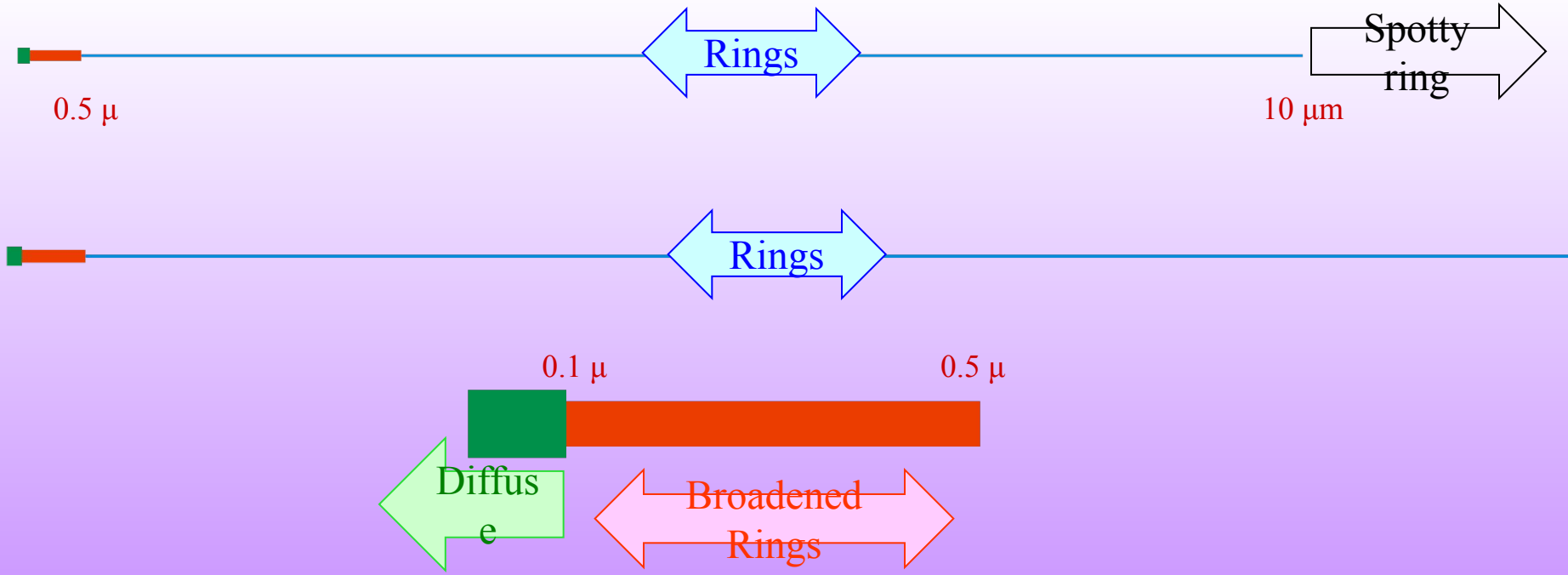
$$B(FWHM) = B_i + B_c + B_s + B_{SF} + \ldots$$

Line Broadening in SAD patterns in the TEM

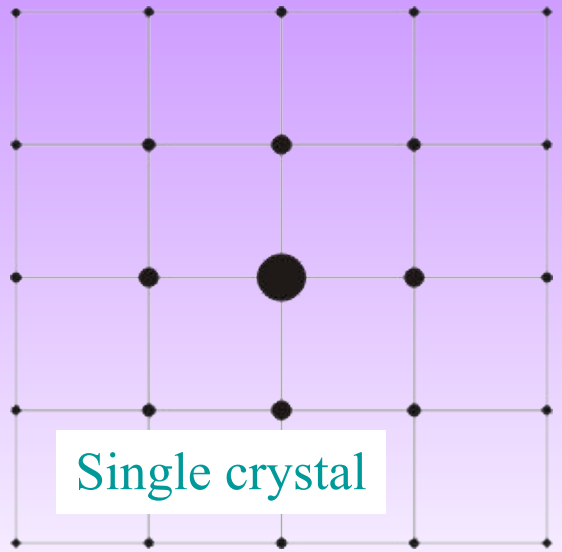
Crystallite size

In a TEM Selected Area Diffraction (SAD) pattern, with decreasing crystallite size the following effects are observed on the pattern obtained

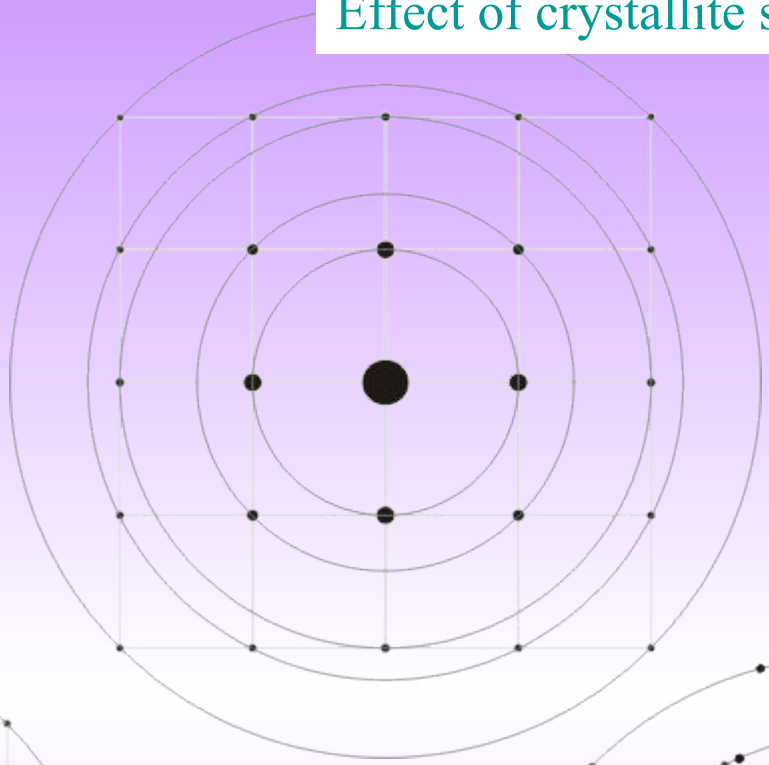
- Size $> 10\ \mu m$ □ Spotty ring
  (no. of grains in the irradiated portion insufficient to produce a ring)
- Size $\in (10, 0.5)\ \mu$ □ Smooth continuous ring pattern
- Size $\in (0.5, 0.1)\ \mu$ □ Rings are broadened
- Size $< 0.1\ \mu$ □ No ring pattern
  (irradiated volume too small to produce a diffraction ring pattern & diffraction occurs only at low angles)



Effect of crystallite size on SAD patterns



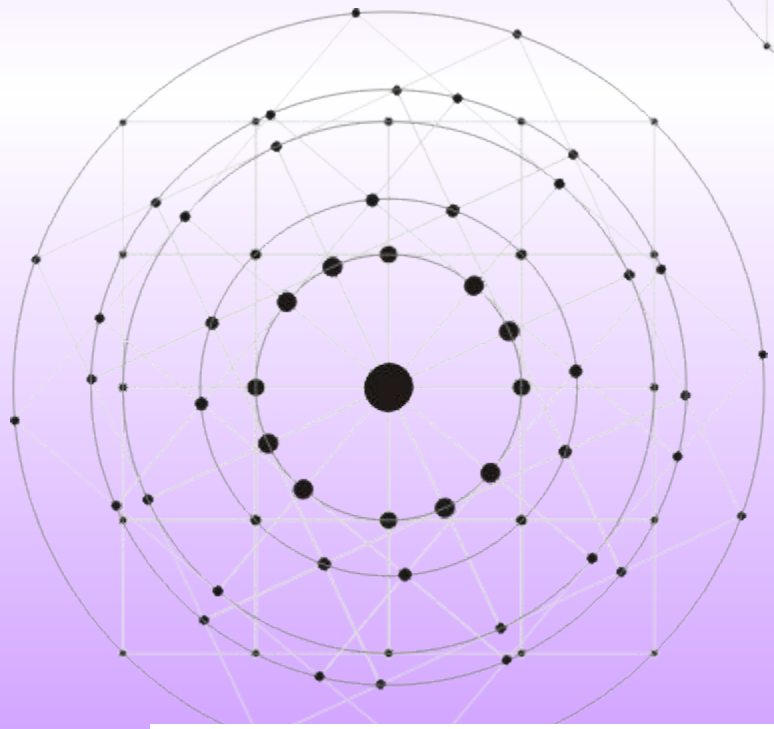
Single crystal



Schematics

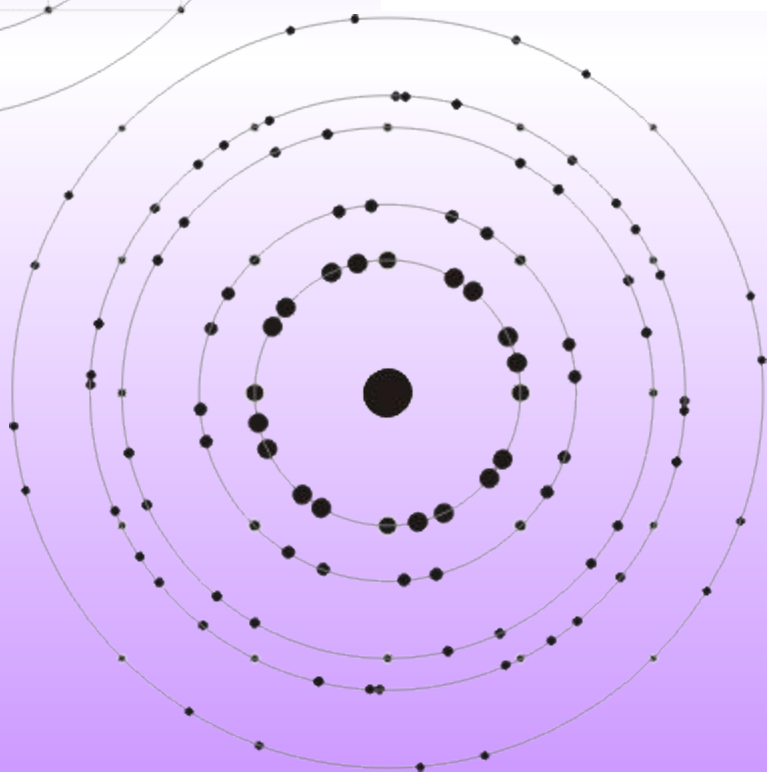
Rotation has been shown only along one axis for easy visualization

Rotation in along all axes should be considered to 'simulate' random orientation



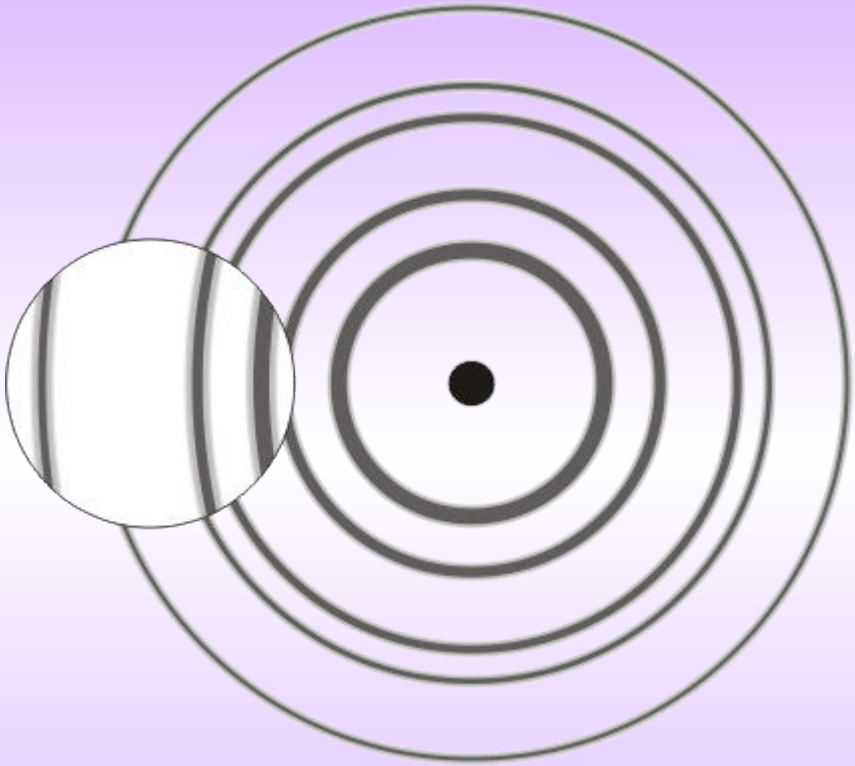
Few crystals in the selected region

"Spotty" pattern



Effect of crystallite size on SAD patterns

Ring pattern



Broadened Rings

Schematics

Subtracting Instrumental Broadening

- Instrumental broadening has to be subtracted to get the broadening effects due to the sample

1

- Mix specimen with known coarse-grained (~ 10μm), well annealed *(strain free)*
  → does not give any broadening due to strain or crystallite size *(the broadening is due to instrument only ('Instrumental Broadening')).*
  A brittle material which can be ground into powder form without leading to much stored strain is good for this purpose.
- If the pattern of the test sample (standard) is recorded separately then the experimental conditions should be identical *(it is preferable that one or more peaks of the standard lies close to the specimen's peaks)*

2

- Use the same material as the standard as the specimen to be X-rayed but with large grain size and well annealed

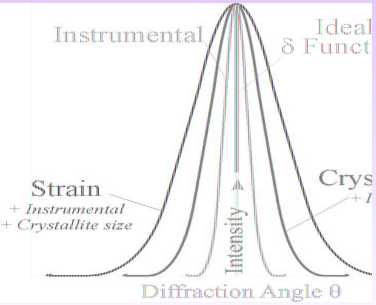
The peaks are fitted to various profiles…

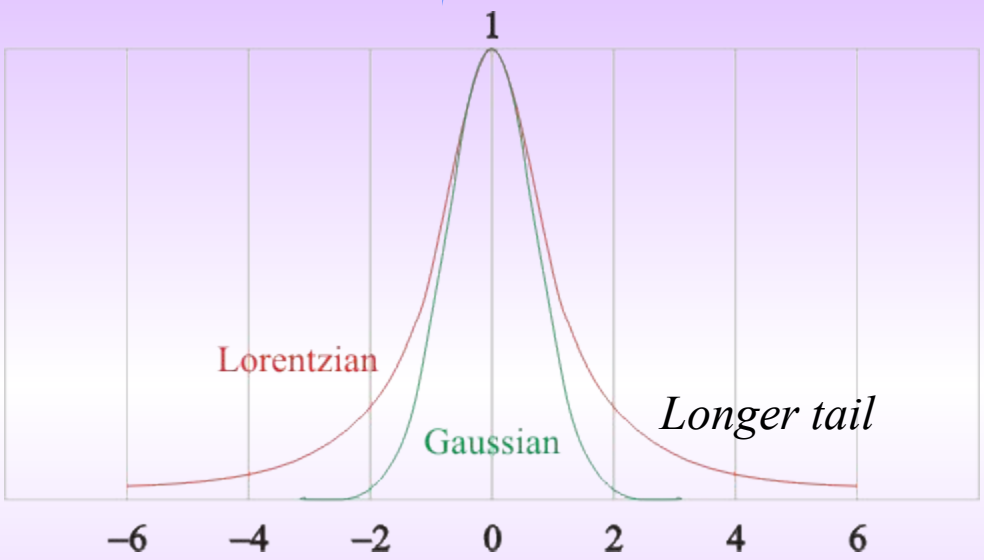
$$B(FWHM) = B_i + B_c + B_s + B_{SF} + \ldots$$

For a peak with a Lorentzian profile

$$B - B_i \approx B_c + B_s = B_r$$

$$L(x) = \frac{1}{\pi} \frac{\frac{1}{2}\Gamma}{(x - x_0)^2 + (\frac{1}{2}\Gamma)^2}$$





- B_i → Instrumental broadening
- B_c → Crystallite size broadening
- B_s → Strain broadening

For a peak with a Gaussian profile

$$B_r^2 = B^2 - B_i^2$$

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

A geometric mean can also used

$$B_r^2 = (B - B_i)\sqrt{B^2 - B_i^2}$$

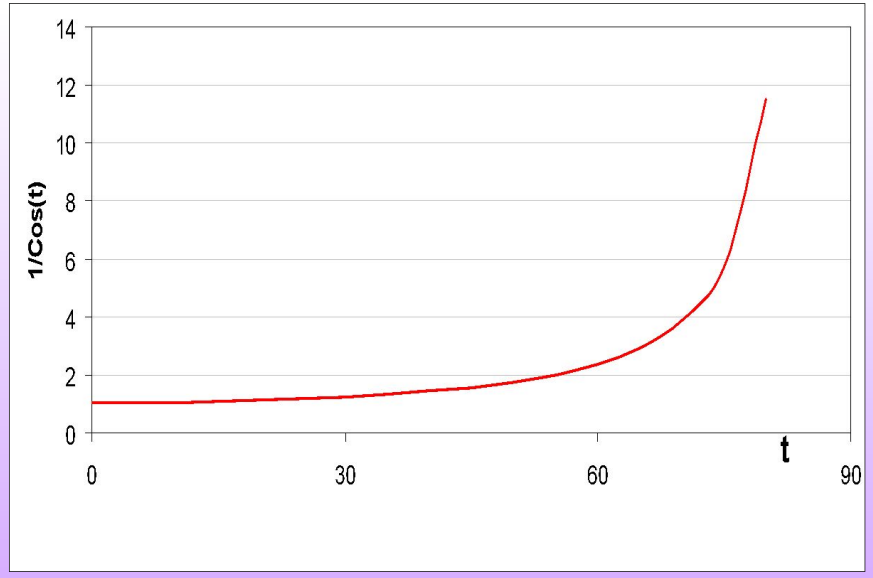
Scherrer's formula

For Gaussian line profiles and cubic crystals

The Scherrer's formula is used for the determination of grain size from broadened peaks. The formula is not expected to be valid for very small grain sizes (<10 nm)

$$B_c = \frac{k\lambda}{L\,Cos(\theta_B)}$$

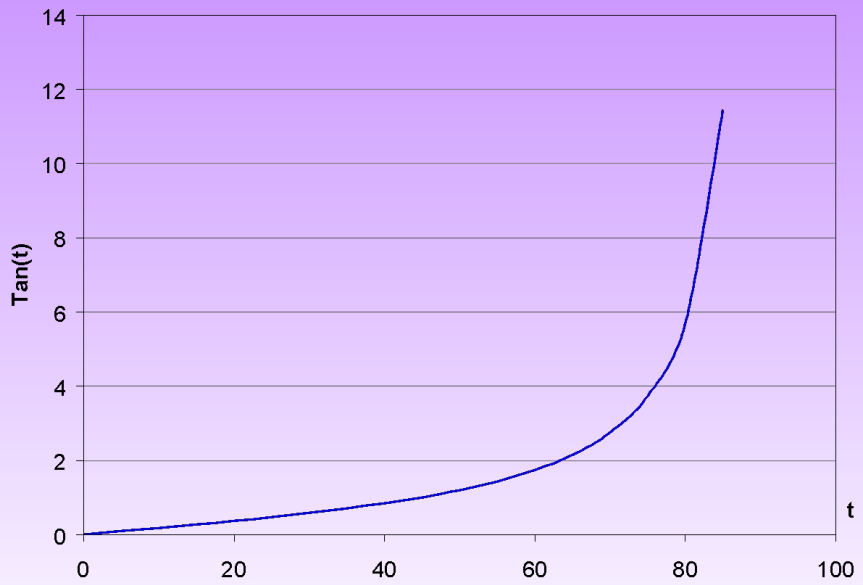
- λ → Wavelength
- L → Average crystallite size *(⊥ to surface of specimen)*
- k → 0.94 [k ∈ (0.89, 1.39)]
  ~ 1 *(the accuracy of the method is only 10%?)*

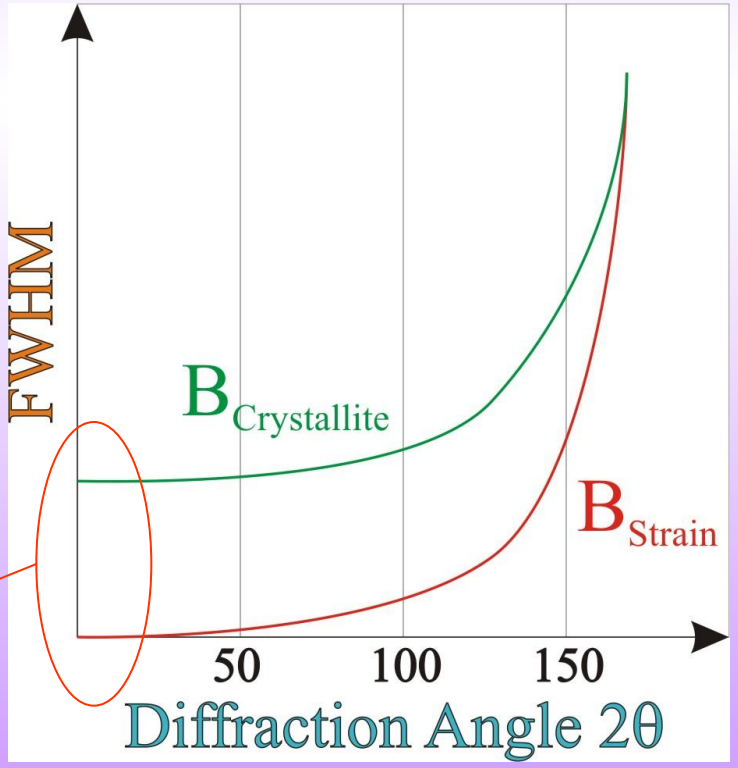


Strain broadening

$$B_s = \eta \quad Tan(\theta_B)$$

- η → Strain in the material





Smaller angle peaks should be used to separate B_s and B_c

Separating crystallite size broadening and strain broadening

$$B_r = B_c + B_s$$

$$B_c = \frac{k\lambda}{L\,Cos(\theta)}$$

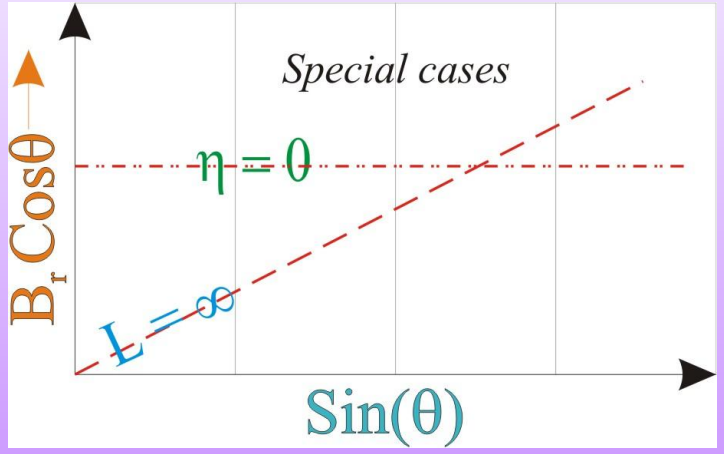
Crystallite size broadening

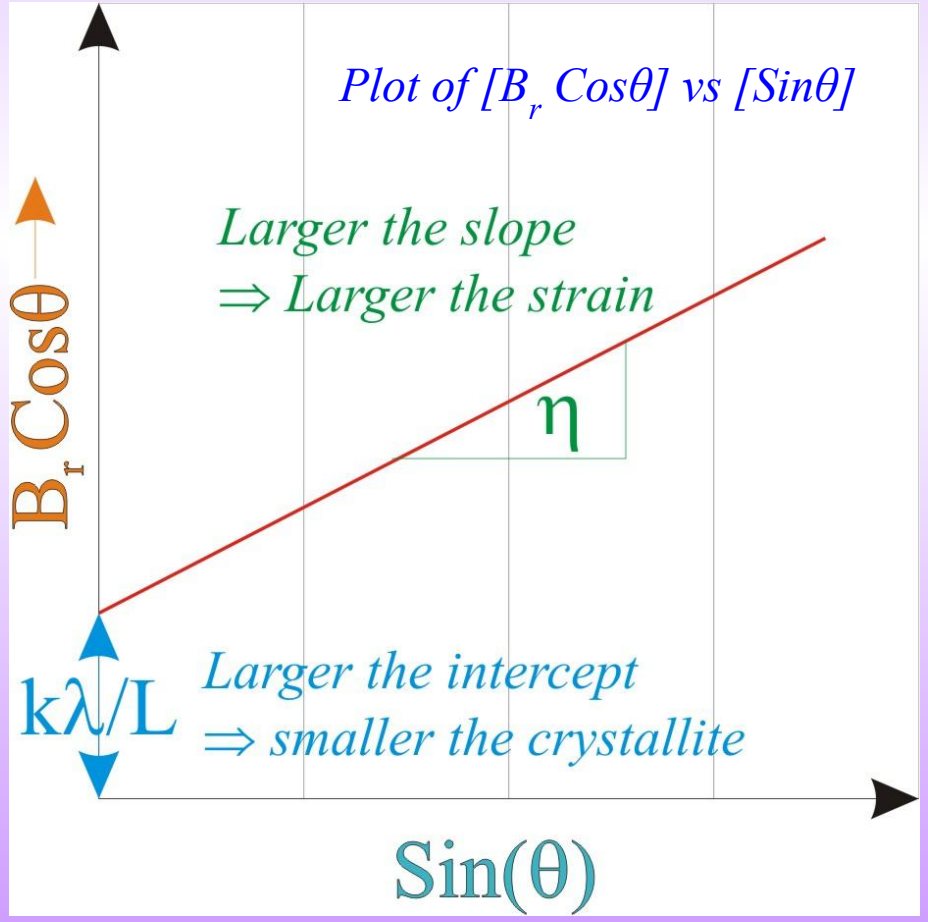
$$B_s = \eta\,Tan(\theta)$$

Strain broadening

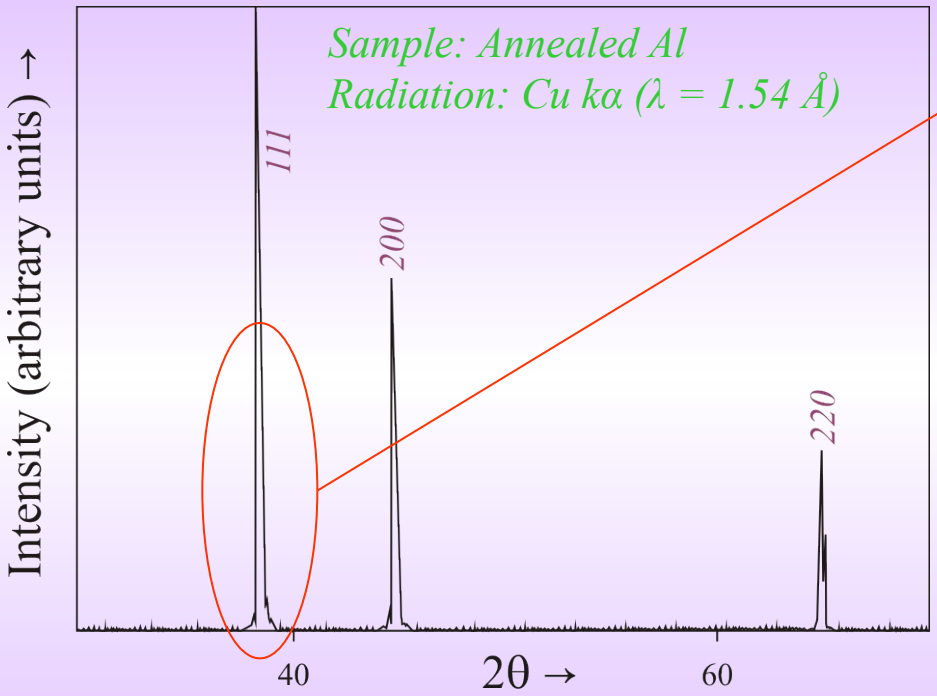
$$B_r = \frac{k\lambda}{L\,Cos(\theta)} + \eta\,Tan(\theta)$$

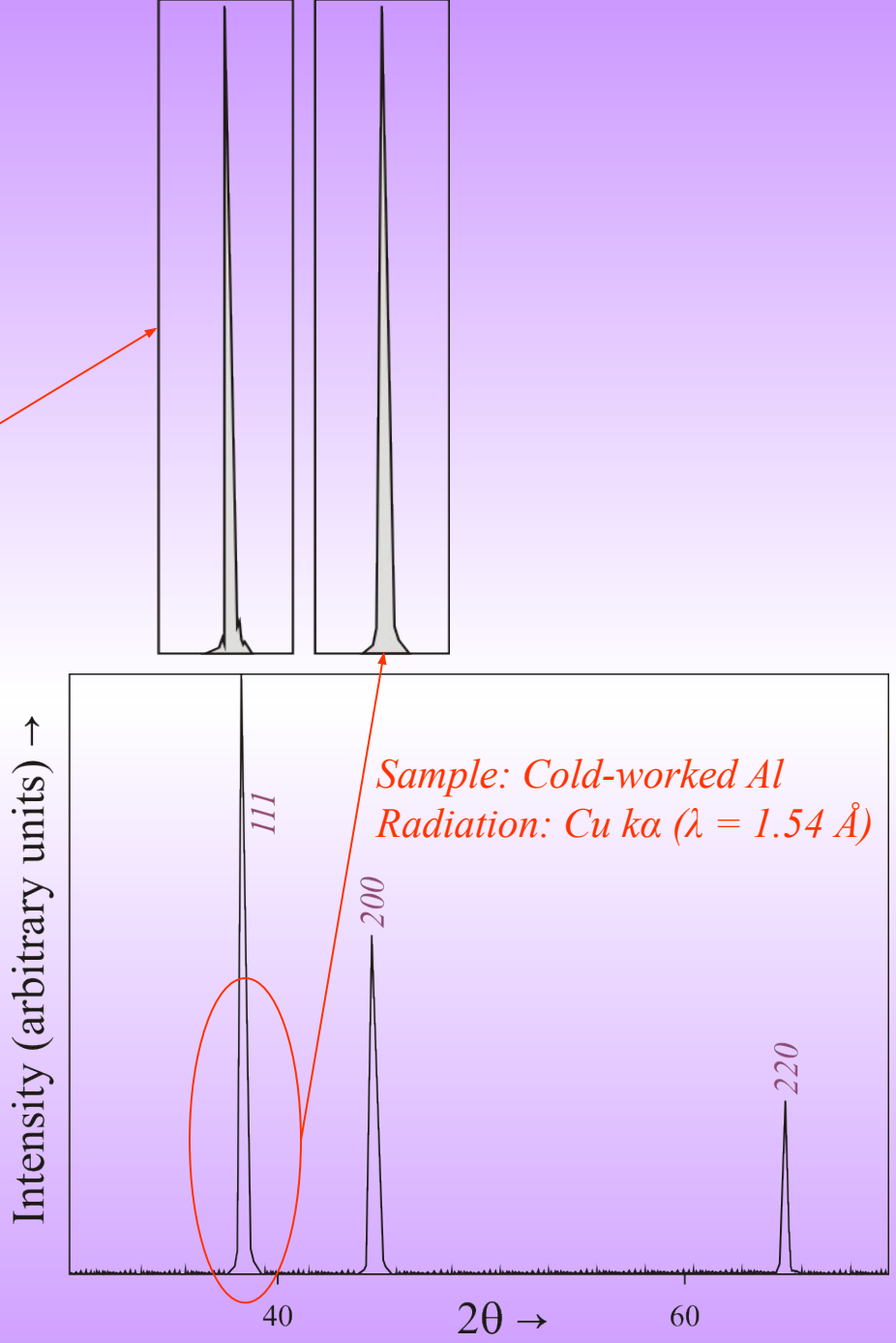
$$B_r\,Cos(\theta) = \frac{k\lambda}{L} + \eta\,Sin(\theta)$$





Example of a calculation



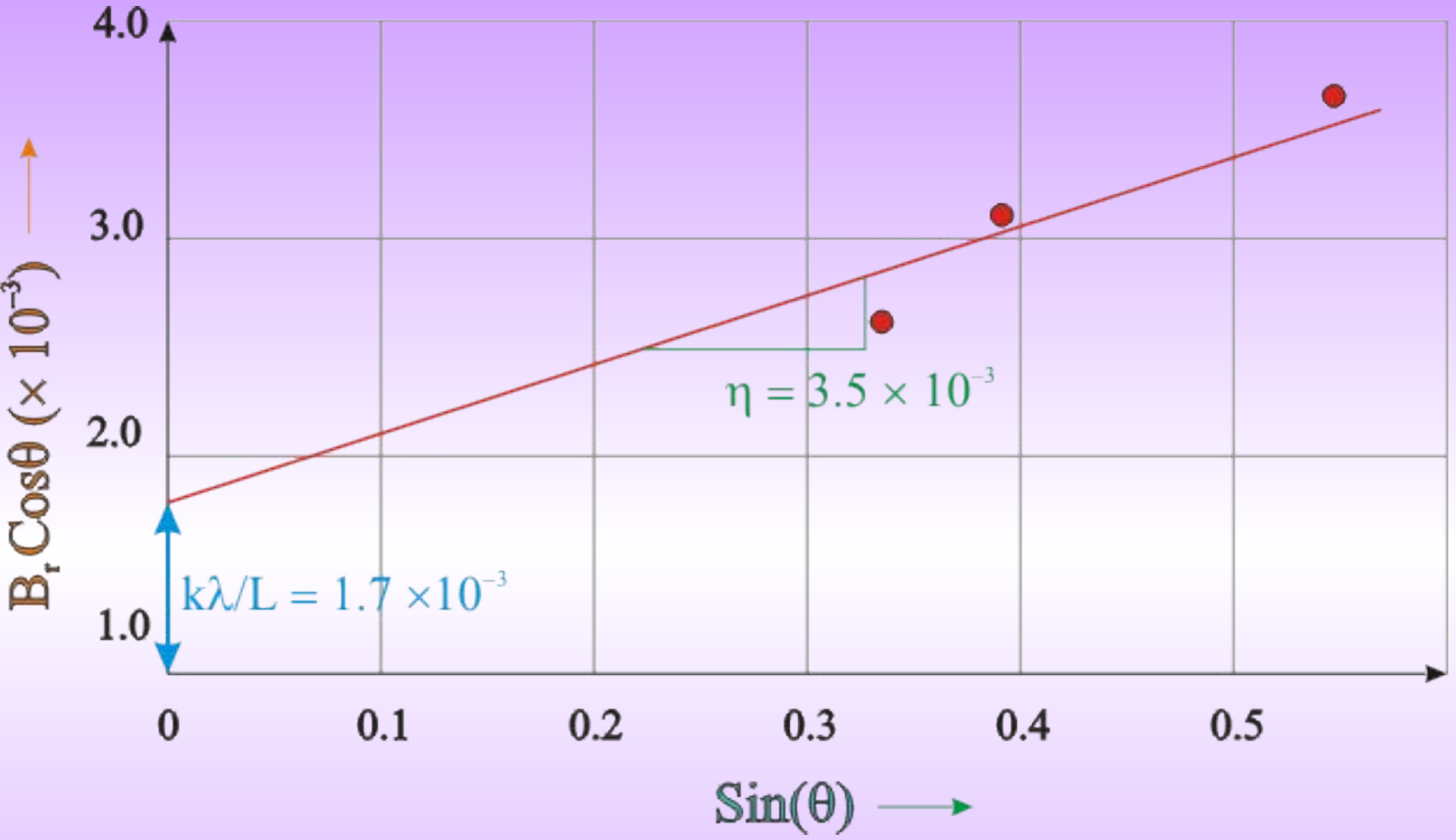


Annealed Al

Peak No.	2θ (°)	hkl	B_i = FWHM (°)	B_i = FWHM (rad)
1	38.52	111	0.103	1.8×10^{-3}
2	44.76	200	0.066	1.2×10^{-3}
3	65.13	220	0.089	1.6×10^{-3}

Cold-worked Al

	2θ (°)	Sin(θ)	hkl	B (°)	B (rad)	$B_r^2 = B^2 - B_i^2$	B_r Cosθ (rad)
1	38.51	0.3298	111	0.187	3.3×10^{-3}	2.8×10^{-3}	2.6×10^{-3}
2	44.77	0.3808	200	0.206	3.6×10^{-3}	3.4×10^{-3}	3.1×10^{-3}
3	65.15	0.5384	220	0.271	4.7×10^{-3}	4.4×10^{-3}	3.7×10^{-3}



$$\frac{k\lambda}{L} = 1.7 \times 10^{-3}$$

$$Grain\ Size\ (L) = 90\ nm$$