# XRD Line Broadening

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



- Bragg's equation assumes:
  - $\hfill\square$  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
  - $\Box Peaks are not `\delta' curves \rightarrow Peaks are broadened (in addition to other possible deviations)$
- There are also deviations from the assumptions involved in the generating powder patterns
  - $\Box$  Crystals may not be randomly oriented *(textured sample)*  $\rightarrow$  Peak intensities are altered w.r.t. to that expected
- In a powder sample if the crystallite size < 0.5 µm</li>
   □ there are insufficient number of planes to build up a sharp diffraction pattern
   ⇒ *peaks are broadened*

When considering <u>constructive and destructive interference</u> we considered the following points:

- In the example considered  $\theta'$  was 'far away' (at a larger angular separation) from  $\theta(\theta_{\text{Bragg}})$  and it was easy to see the destructive interference
- In other words for incidence angle of  $\theta$ ' the phase difference of  $\pi$  is accrued just by traversing one 'd'.
- If the angle is just away from the Bragg angle  $(\theta_{Bragg})$ , 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  $\pi$ ) 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 <sub>i</sub>	<ul> <li>Unresolved α<sub>1</sub>, α<sub>2</sub> peaks</li> <li>Non-monochromaticity of the source (finite width of α peak)</li> <li>Imperfect focusing</li> </ul>
Crystallite size B <sub>C</sub>	• In the vicinity of $\theta_B$ the –ve of Bragg's equation not being satisfied
Strain B <sub>S</sub>	<ul> <li>'Residual Strain' arising from dislocations, coherent precipitates etc. leading to broadening</li> </ul>
Stacking fault B <sub>SF</sub>	In principle every defect contributes to some broadening
Other defects	

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

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'

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







Few crystals in the selected region

## Effect of crystallite size on SAD patterns



**Schematics** 

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

$$B(FWHM) = B_i + B_c + B_s + B_{SF} + \dots$$
For a peak with a Lorentzian profile
$$B - B_i \approx B_c + B_s = B_r$$

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

$$B_i \rightarrow \text{Instrumental broadening}$$

$$B_i \rightarrow \text{Crystallite size broadening}$$

$$B_i \rightarrow \text{Crystallite size broadening}$$

$$B_i \rightarrow \text{Crystallite size broadening}$$

$$B_i \rightarrow \text{Strain broadening}$$

#### 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)



- $\lambda \rightarrow$  Wavelength
- L  $\rightarrow$  Average crystallite size ( $\perp$  to surface of specimen)

$$k \to 0.94 \ [k \in (0.89, 1.39)]$$

~ 1 (the accuracy of the method is only 10%?)



### Strain broadening



•  $\eta \rightarrow$  Strain in the material

FWHIN



Smaller angle peaks should be used to separate B<sub>s</sub> and B<sub>c</sub> Separating crystallite size broadening and strain broadening

$$B_r = B_c + B_s$$

$$B_c = \frac{k\,\lambda}{L\,Cos(\theta)} \,\left[ \right]$$

*Crystallite size broadening* 

$$B_{s} = \eta Tan(\theta)$$

Strain broadening

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

$$B_r \cos(\theta) = \frac{k \lambda}{L} + \eta \sin(\theta)$$







Annealed Al

Peak No.	20 (°)	hkl	$B_i = FWHM (^\circ)$	$B_i = FWHM (rad)$
1	38.52	111	0.103	$1.8 \times 10^{-3}$
2	44.76	200	0.066	$1.2 \times 10^{-3}$
3	65.13	220	0.089	$1.6 \times 10^{-3}$

### Cold-worked Al

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

