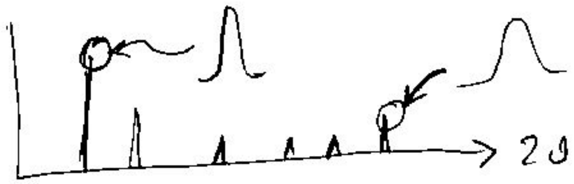
13. Lineshape Analysis for Powder Diffraction



Two standard lineshapes:

- Gaussian (narrowest) } most fall
- Lorentzian (Cauchy) (widest) } in between

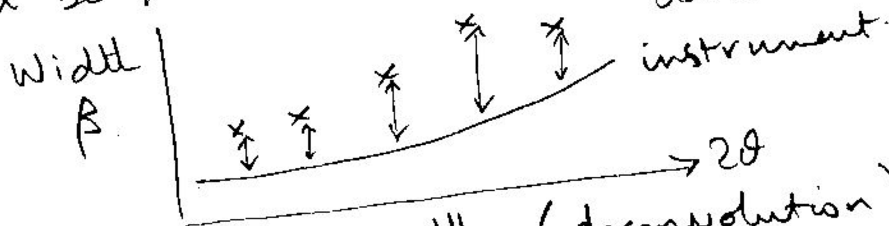
G tends to come from random variables combined together

L comes from specific features causing broadening of lineshape: slits, sample shape.

General list of contributions:

Instrumental	Sample
Slits of instrument	Size
Monochromaticity	Strain
Instrument errors.	Homogeneity
Speed of scan	Composition } variation
Detector speed.	Temperature } variation

Procedure is to measure a standard sample with no sample width, eg Si powder. This measures all instrument widths, which can be fit to a smooth function



Subtract inst width (deconvolution)

$$\beta = \beta_0 + \beta_S \quad (L)$$

$$\beta^2 = \beta_0^2 + \beta_S^2 \quad (G)$$

} other rules in between.

3.11

i) Sample Size.

Assumed this is the main contribution.

Scherrer formula

$$\beta_L = \frac{K\lambda}{L\cos\theta} \qquad L = \text{size (same units as } \lambda)$$

K = dimensionless const to account for choice of definition of "width", usually FWHM.

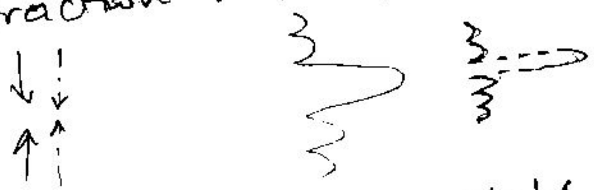
But FWHM is not the natural choice for G.

K = 0.9 typically

Scherrer accounts for slight increase of width with angle – important near $\theta = 90°$.

$\beta \propto \frac{1}{L}$ is standard behaviour expected for all diffraction : reciprocal space.

eg slit



$\frac{\sin x}{x}$

Slit function

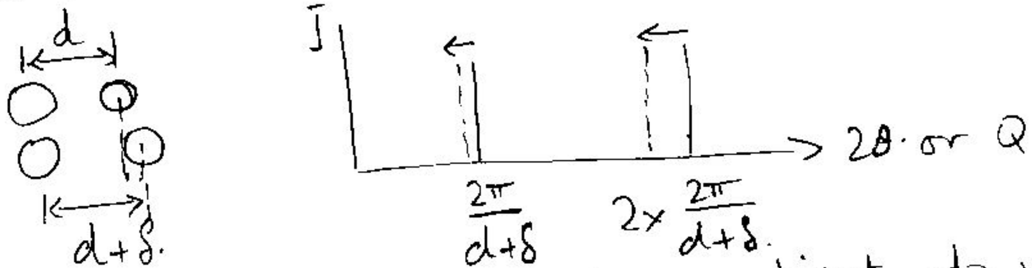
Narrow peaks $\Rightarrow$ large crystals

Normal instrument sees up to 0.3 μm

Hi-Res instrument (synchrotron) maybe 5 μm

ii) Sample Strain

If the whole sample is strained, we just see a change of lattice parameter: peaks shift, but do not broaden.



Only if there is a strain gradient do we see a broadening. Eg mixture of two cases above.

Range of δ's. defines a strain ε

if $0 < \delta < \delta_{max}$: $\varepsilon = \frac{\delta_{max}}{d}$ as percentage.

Width in θ is given by Braggs Law:

$$\left.\begin{aligned} 2d \sin\theta &= \lambda. \\ \sin\theta &= \frac{\lambda}{2d} \end{aligned}\right\} \quad \theta \to \theta + \delta\theta \quad d \to d+\delta.$$

Differentiate both sides:

$$\cos\theta\,\delta\theta = \frac{-\lambda}{2d^2}\delta = -\sin\theta\,\frac{\delta}{d}.$$

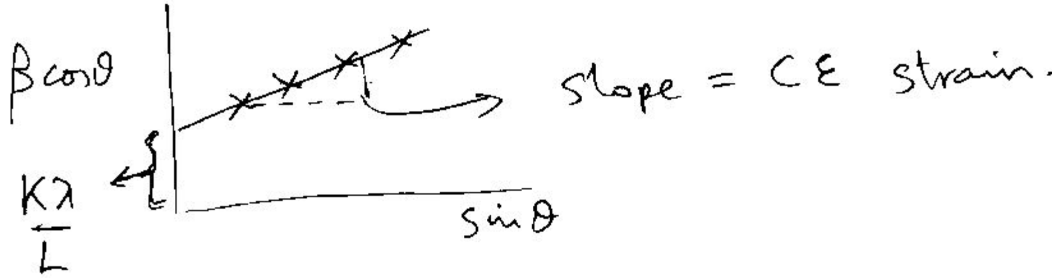
$$\Rightarrow \delta\theta = -\frac{\sin\theta}{\cos\theta}\,\varepsilon = -\varepsilon\tan\theta$$

This shows how the width increases with θ due to strain.

Definition of δ_{max} and FWHM needs an adjustment constant C, like Scherrer

$$\beta_\varepsilon = C\,\varepsilon\tan\theta \qquad C \sim 4.5 \text{ typical.}$$

Plot $\beta \cos\theta$ vs $\sin\theta$



Scherrer size

Williamson–Hall (WH) method.

14. Indexing of powder patterns
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