Line broadening analysis with MAUD

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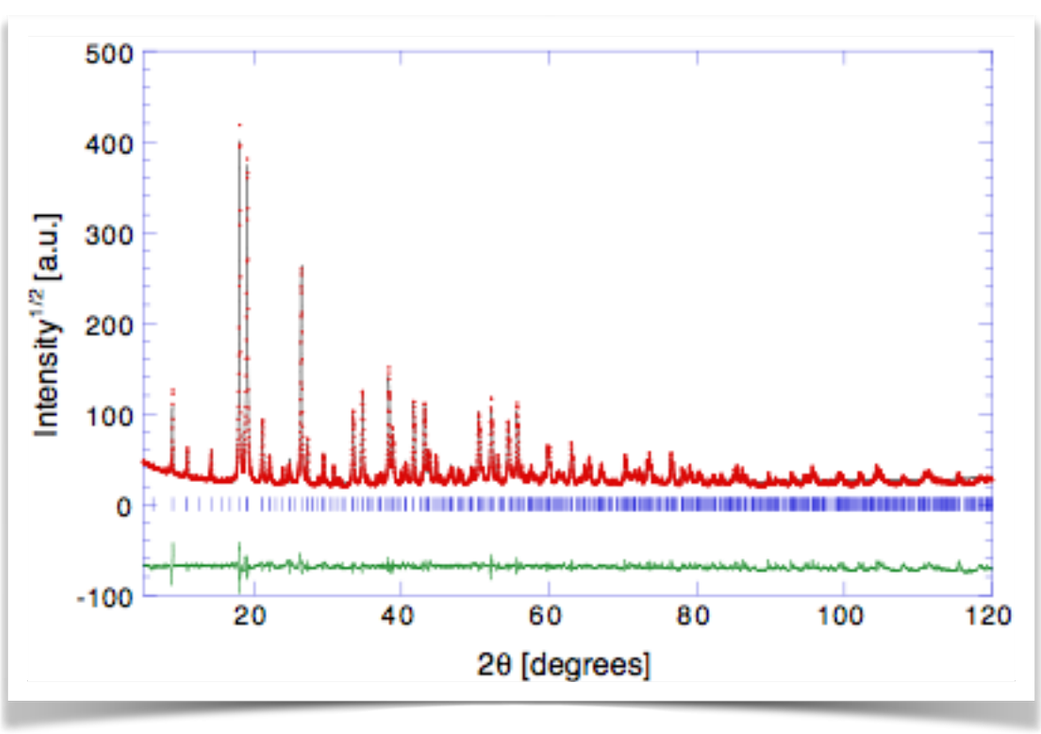
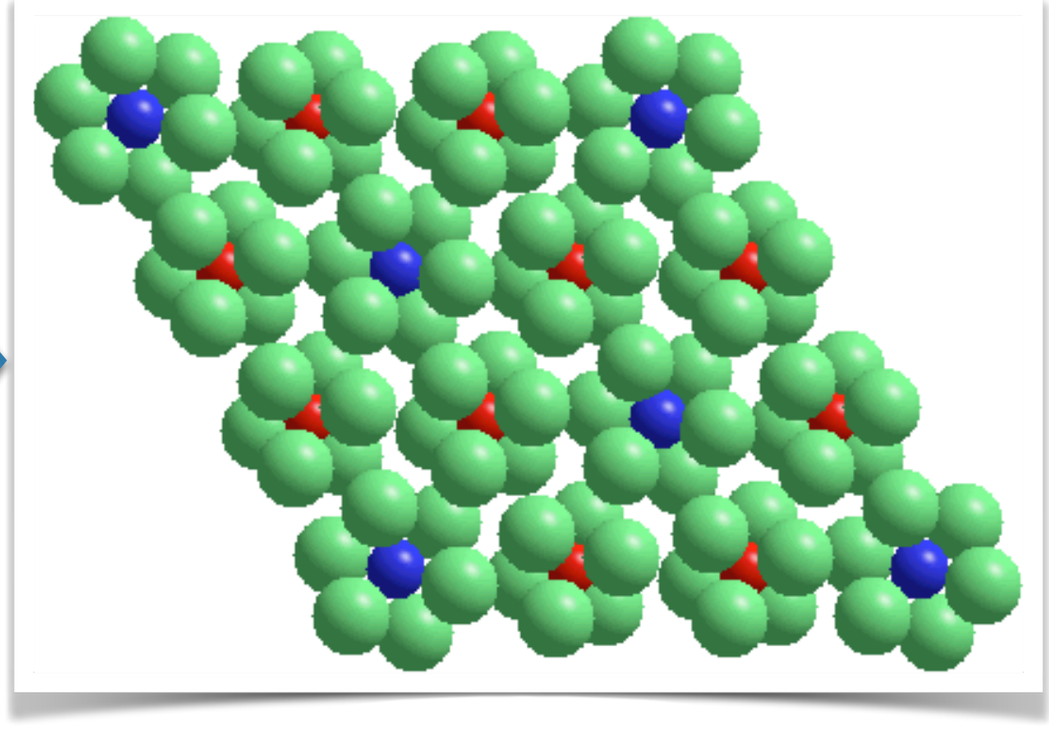
Pattern fitting: the Rietveld method

- Least squares minimization of:

$$WSS = \sum_i w_i \left(I_i^{\exp} - I_i^{calc} \right)^2 , w_i = \frac{1}{I_i^{\exp}}$$





XRD Pattern calculation: general formula

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left|F_{k,j}\right|^2 S_j\left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i$$

Crystal structure

Phase quantities

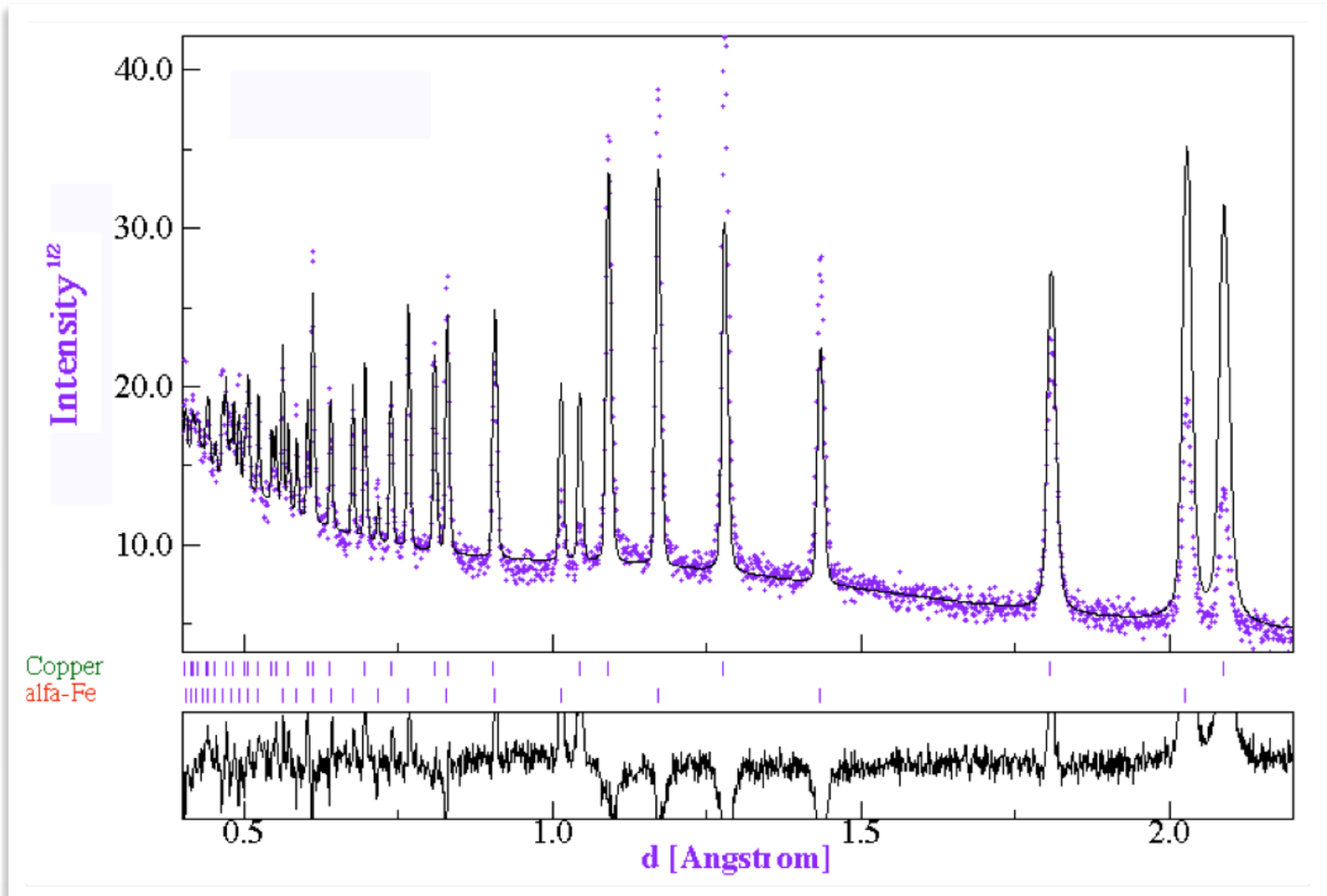
Crystallite sizes and microstrains

Residual stresses (and cell parameters)

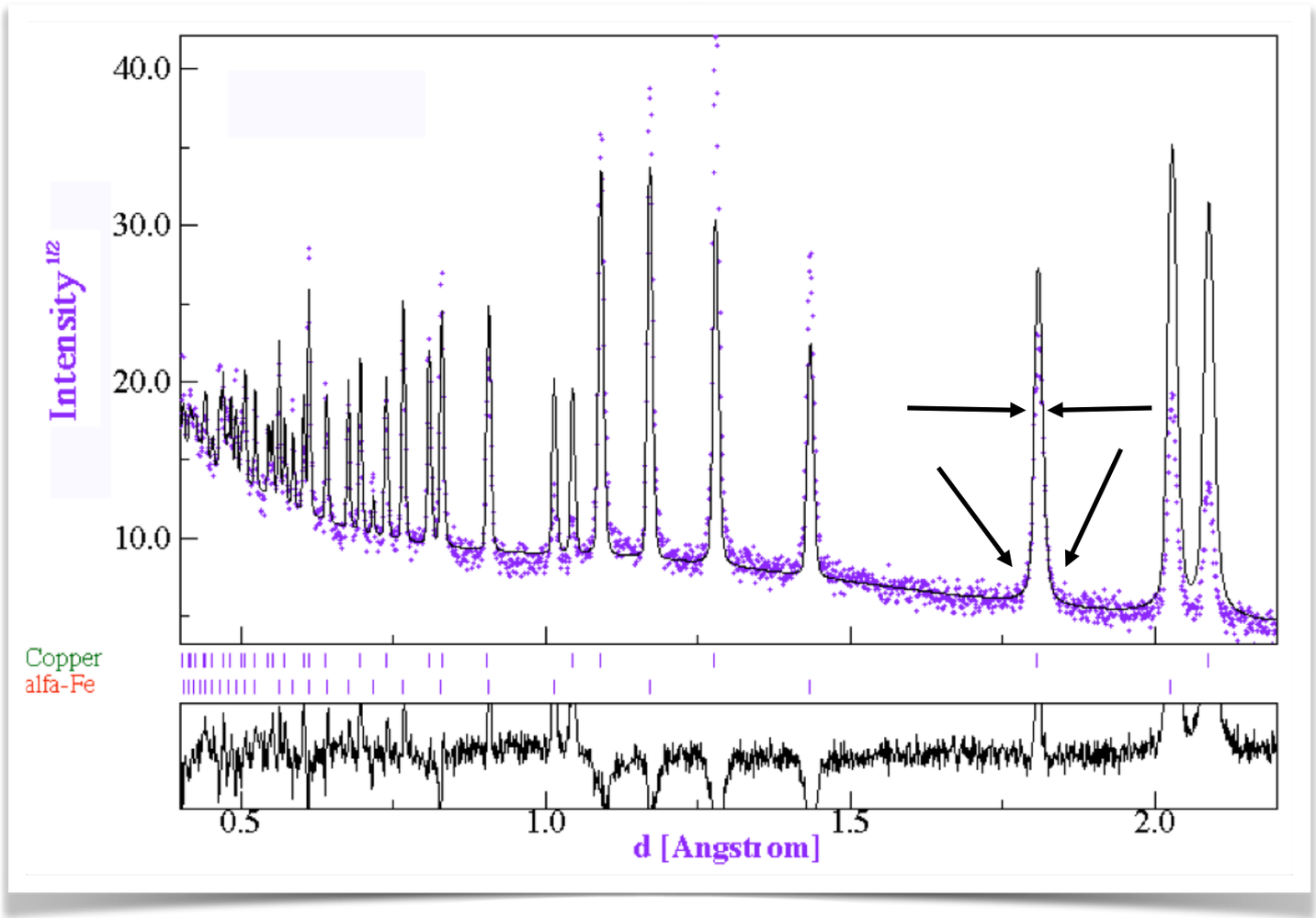
Texture (ODF)

Film thickness

Informations: microstructure

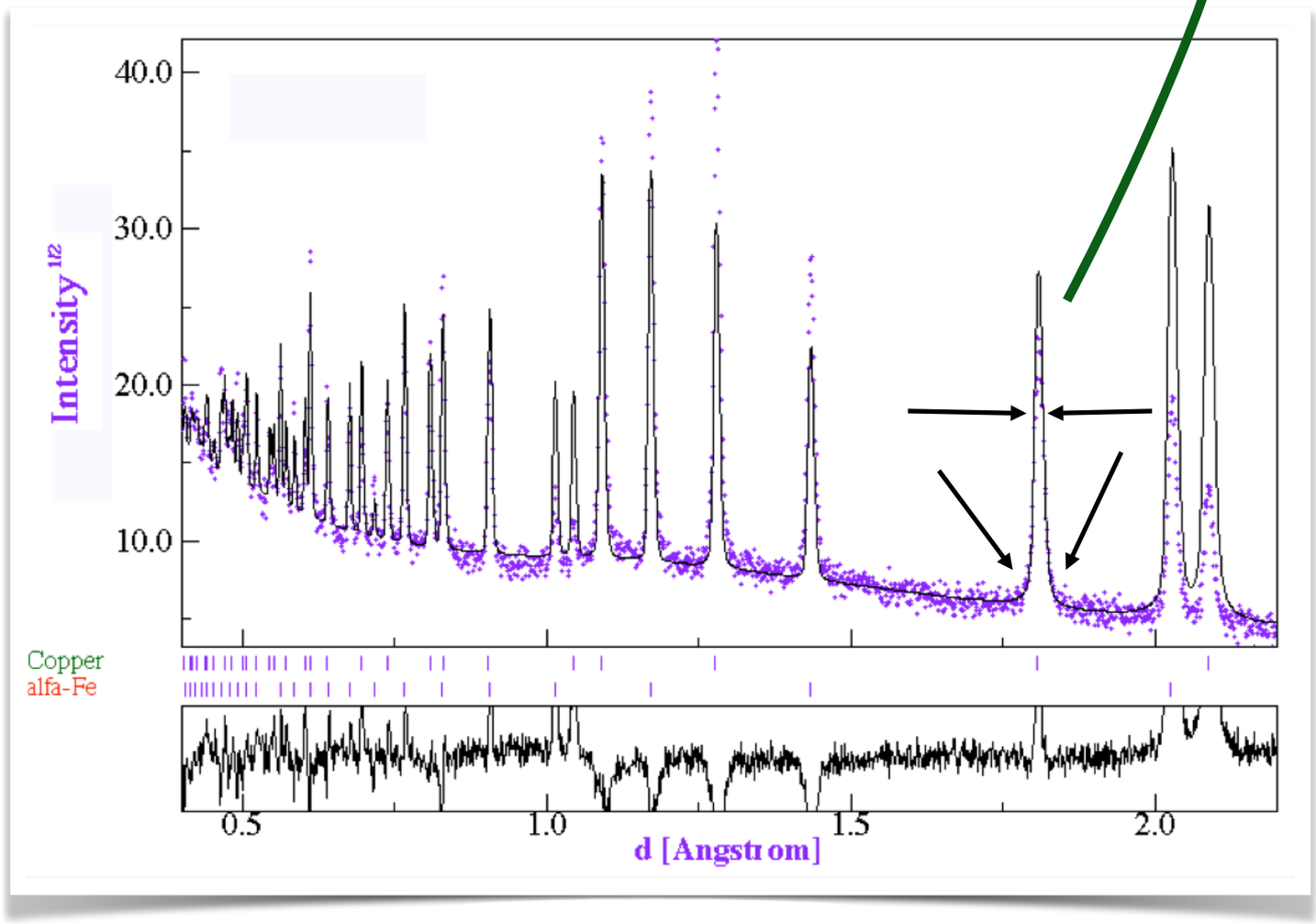


Informations: microstructure



Informations: microstructure

- Crystallite sizes, anisotropic, distribution
- Microstrain (III kind), distribution, dislocation or point defects density



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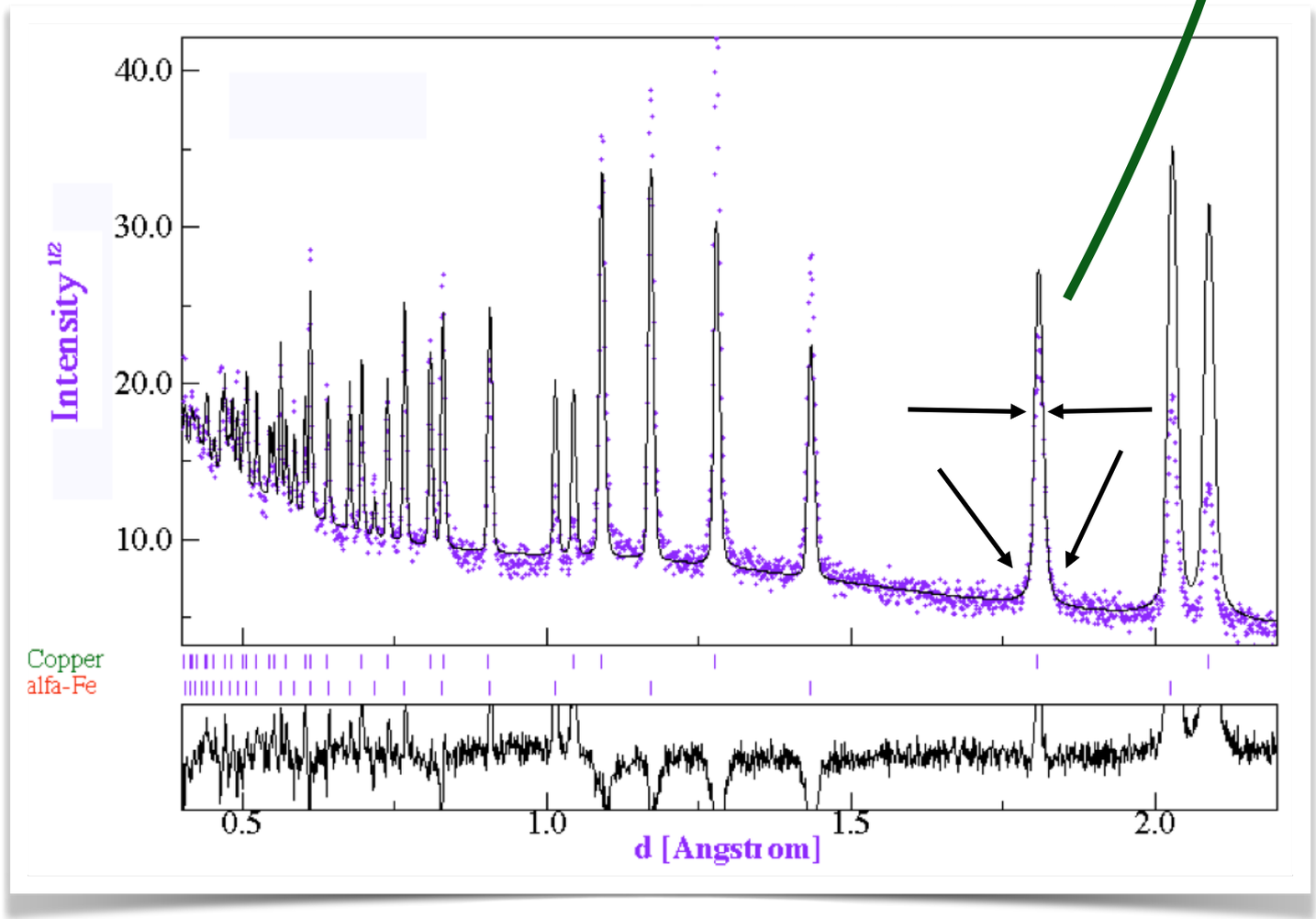
- Antiphase domains (intermetallics…)
- Stacking and deformation faults probability, intrinsic, extrinsic



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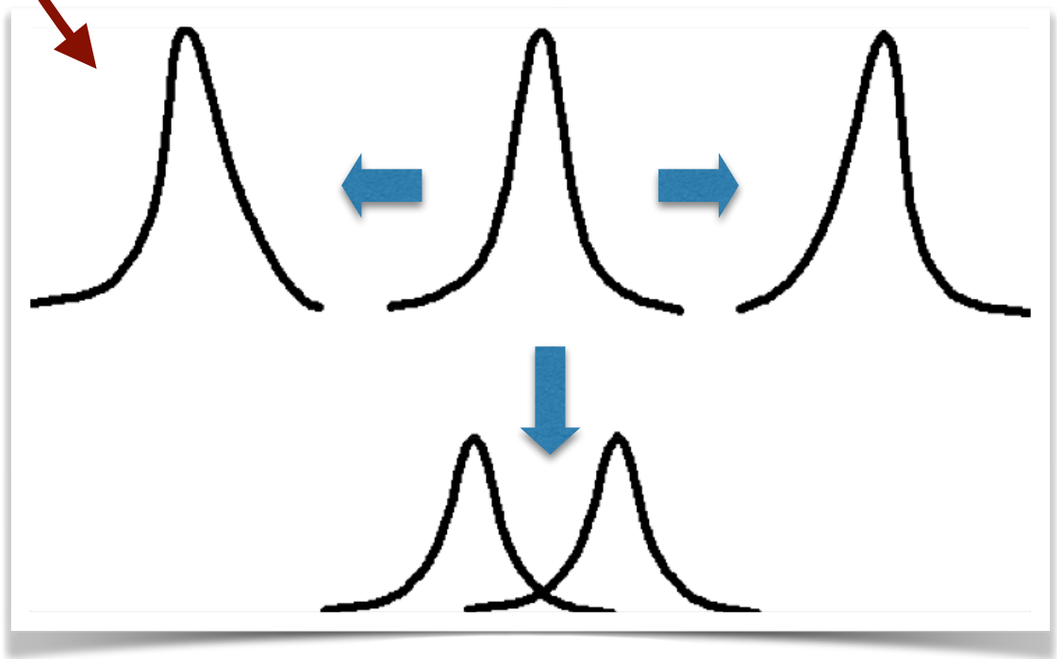
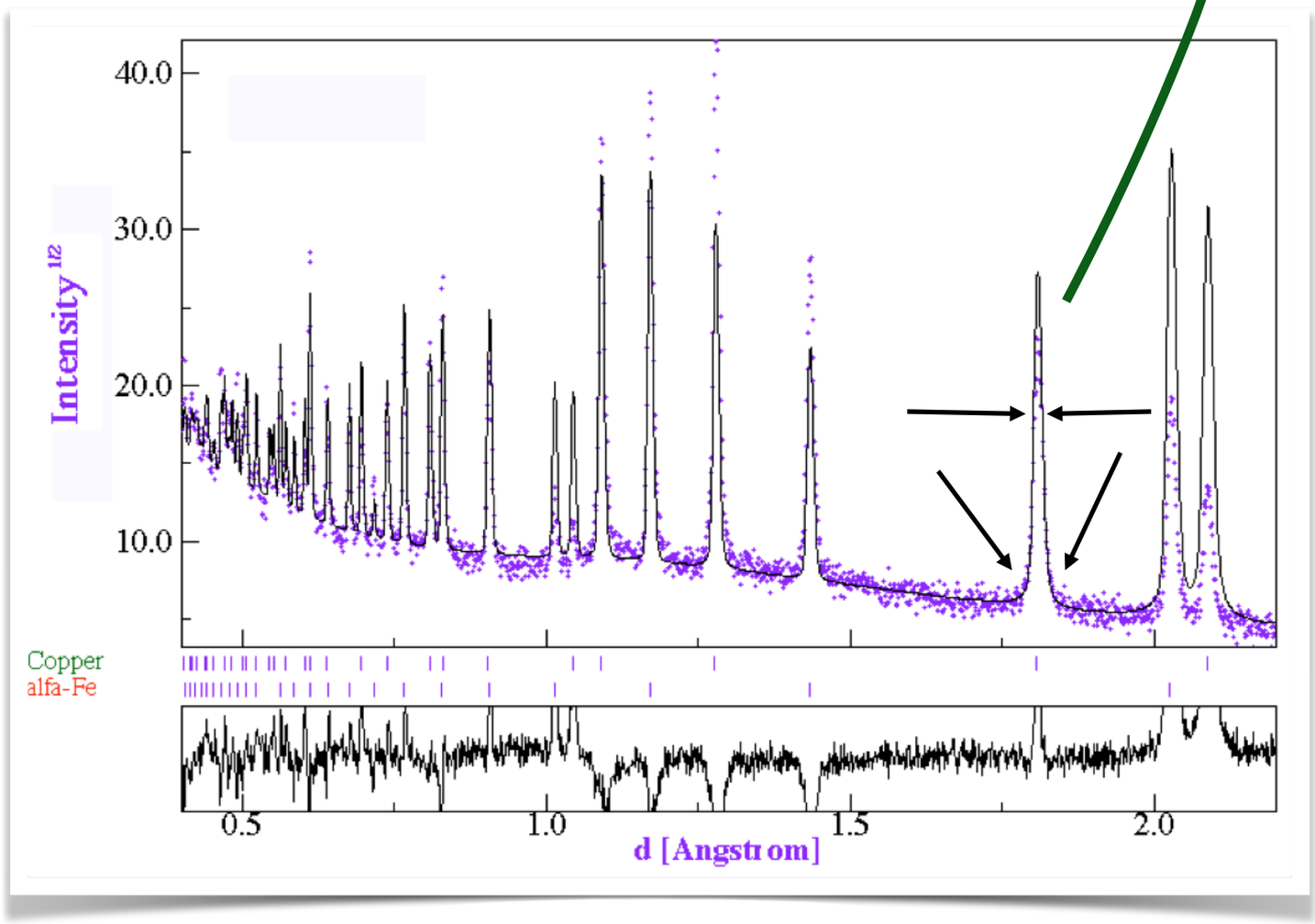
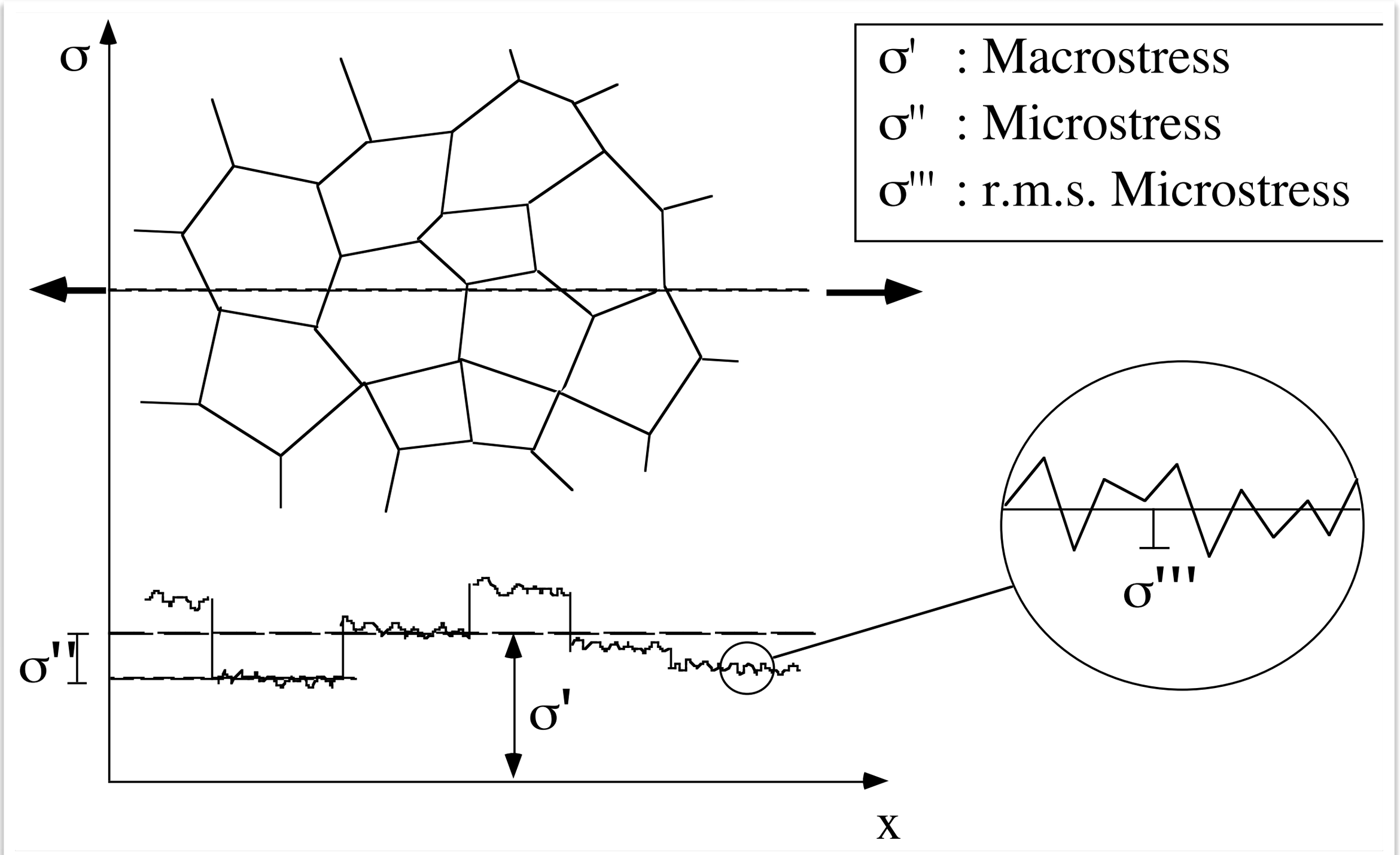
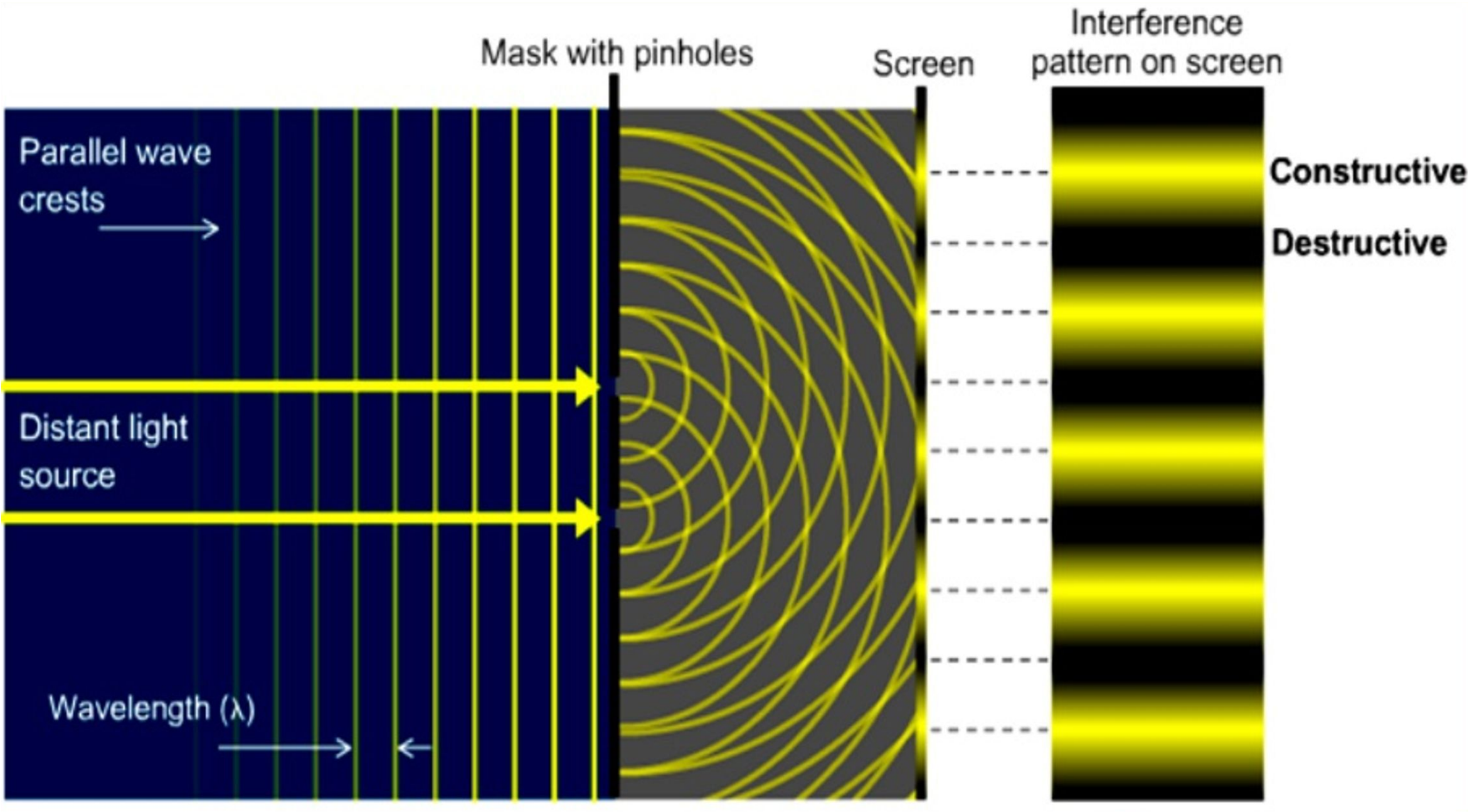




Microstrain definition



Diffraction and interference



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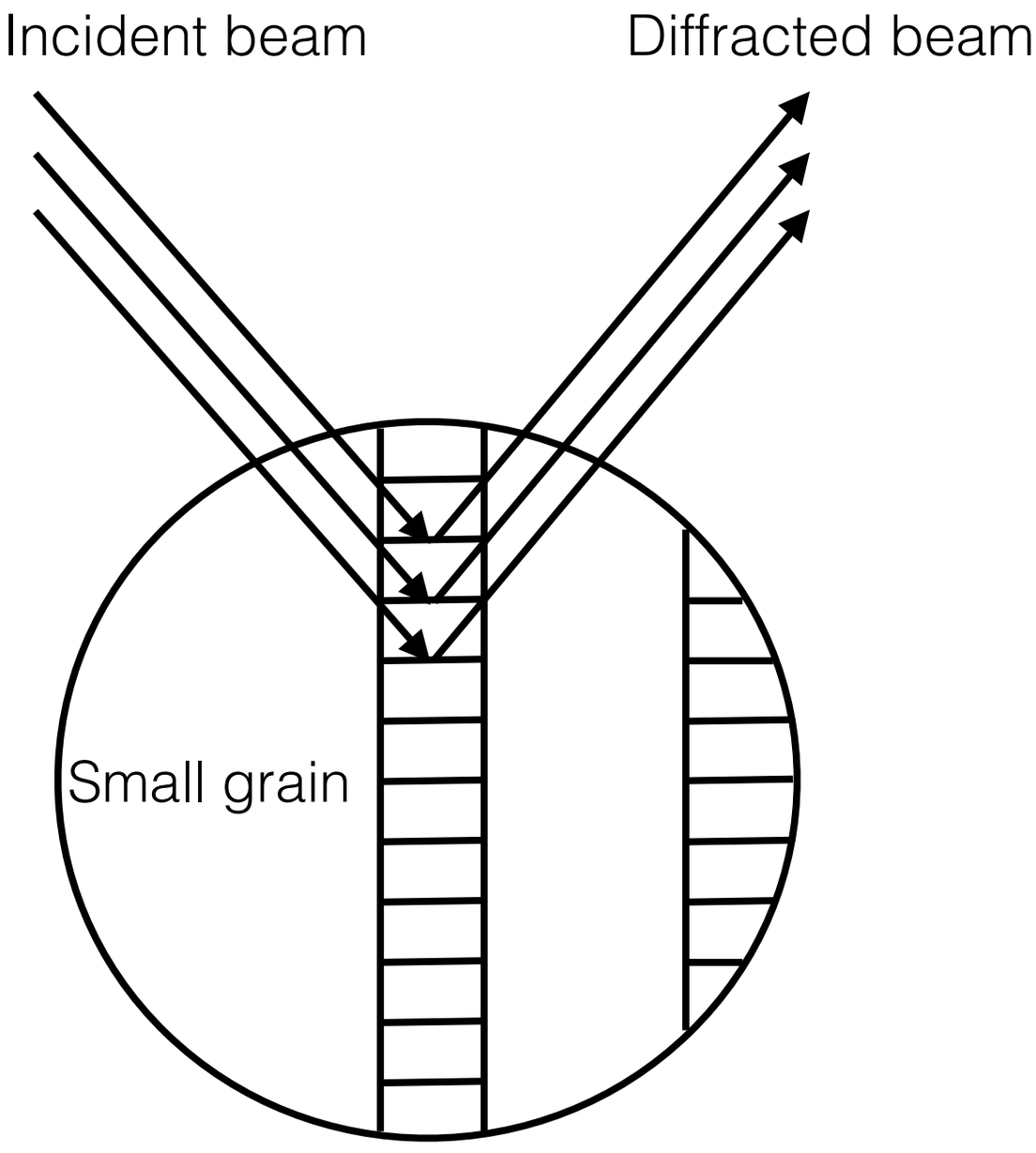

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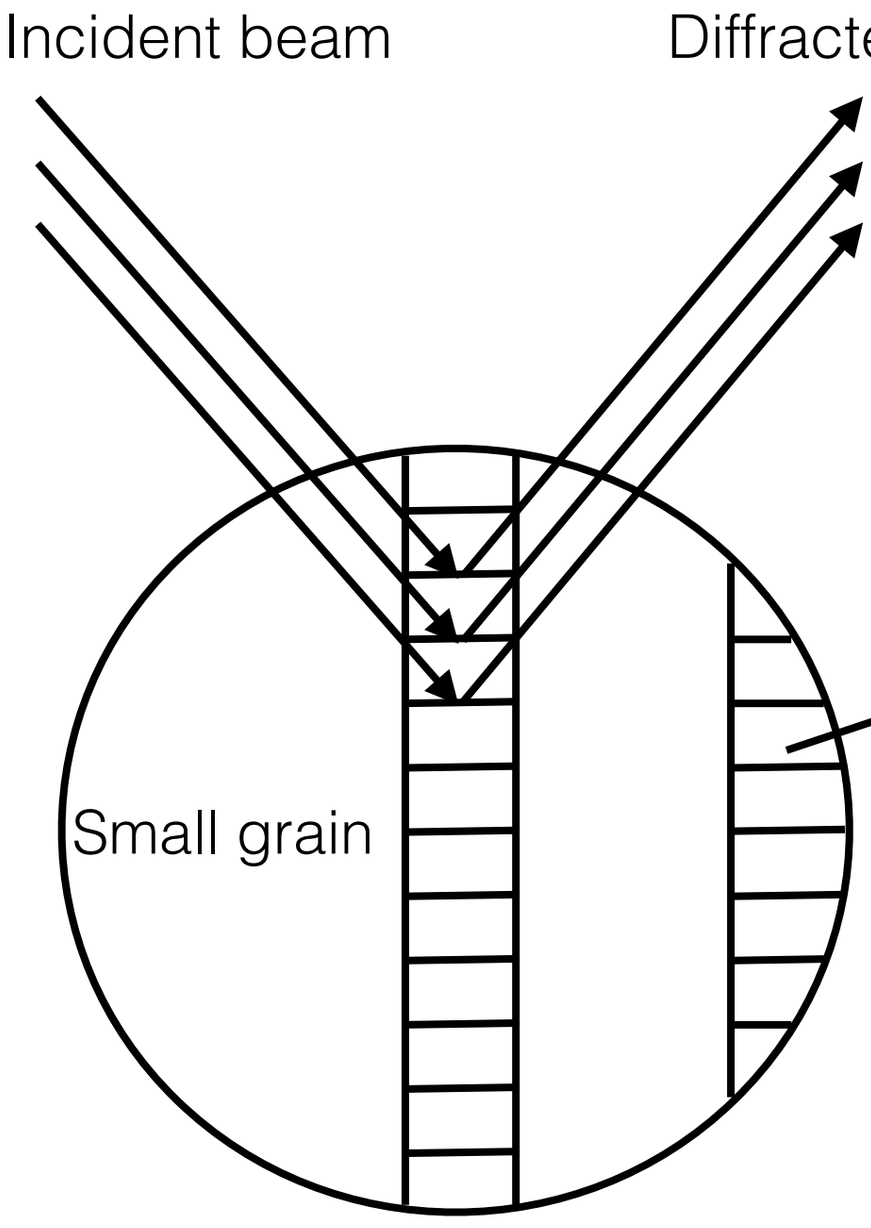

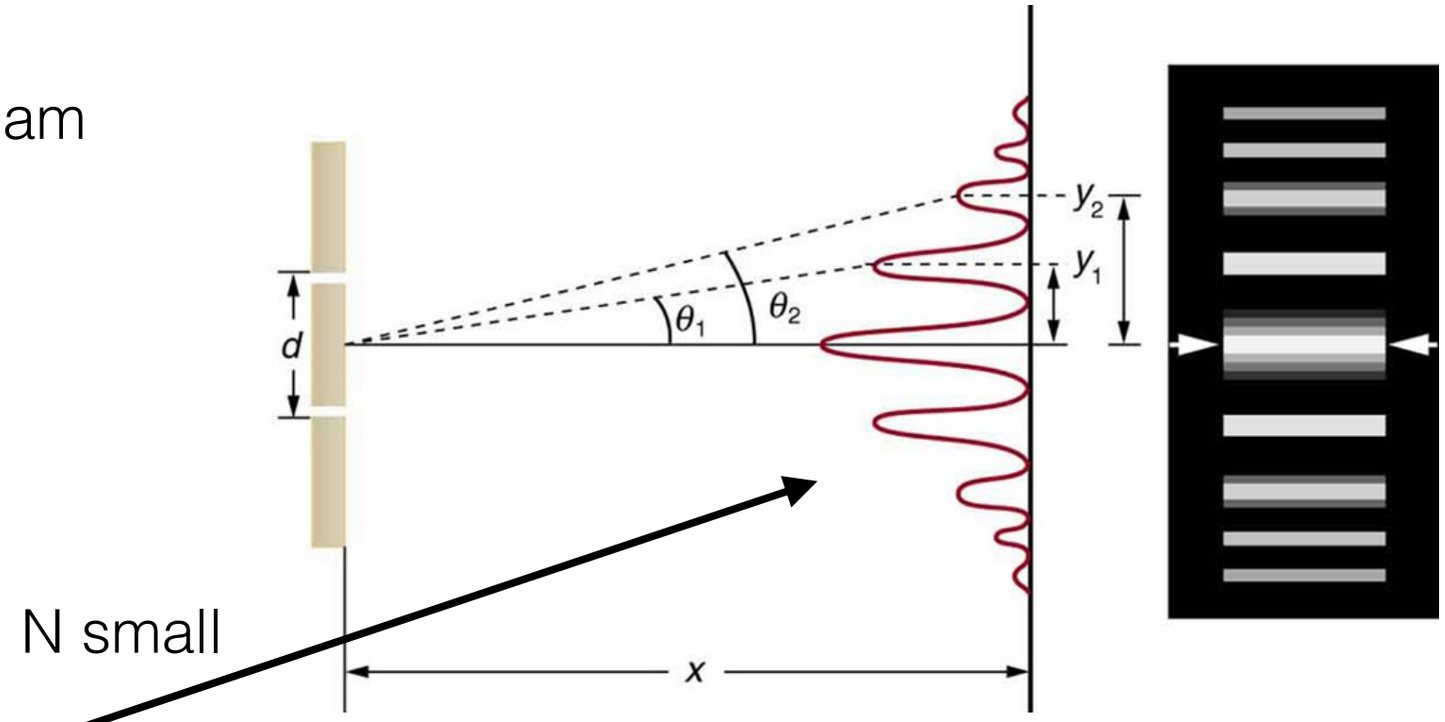

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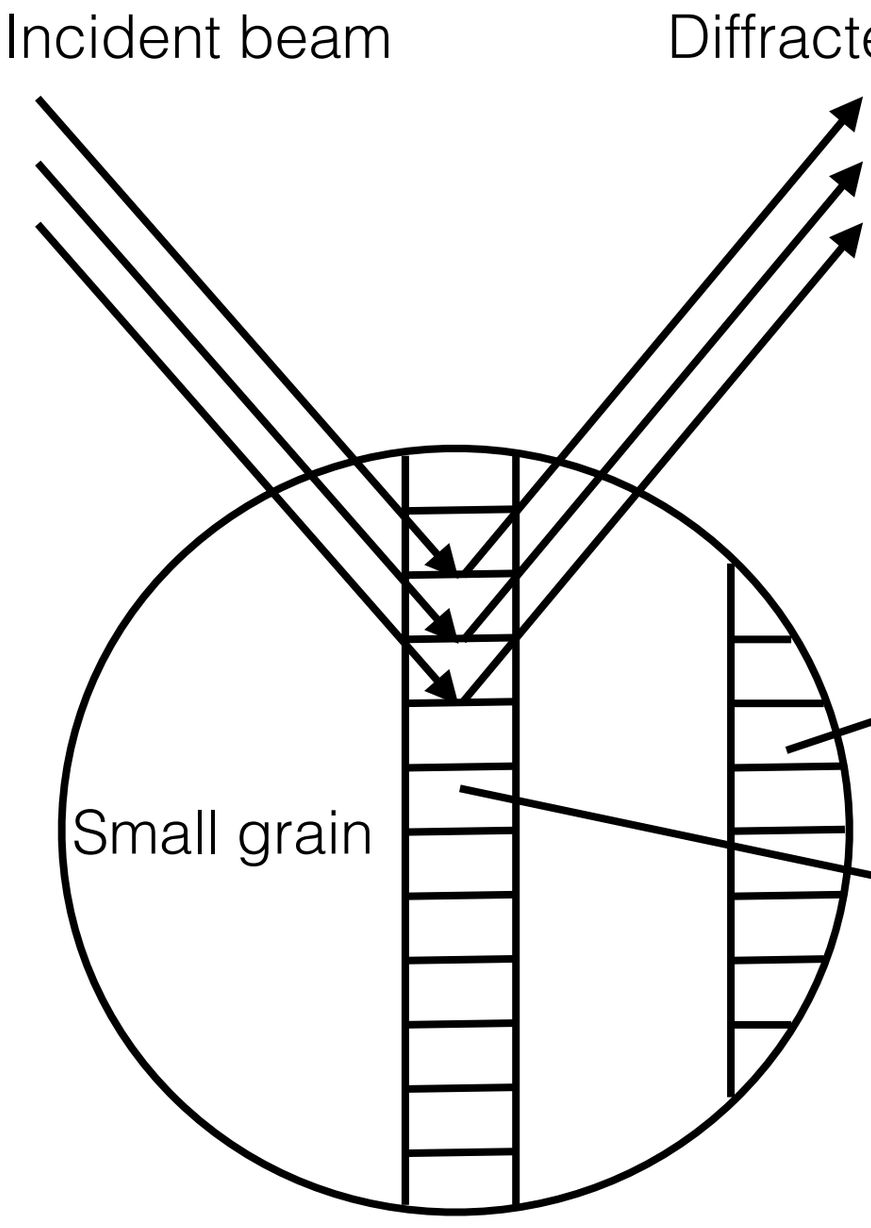
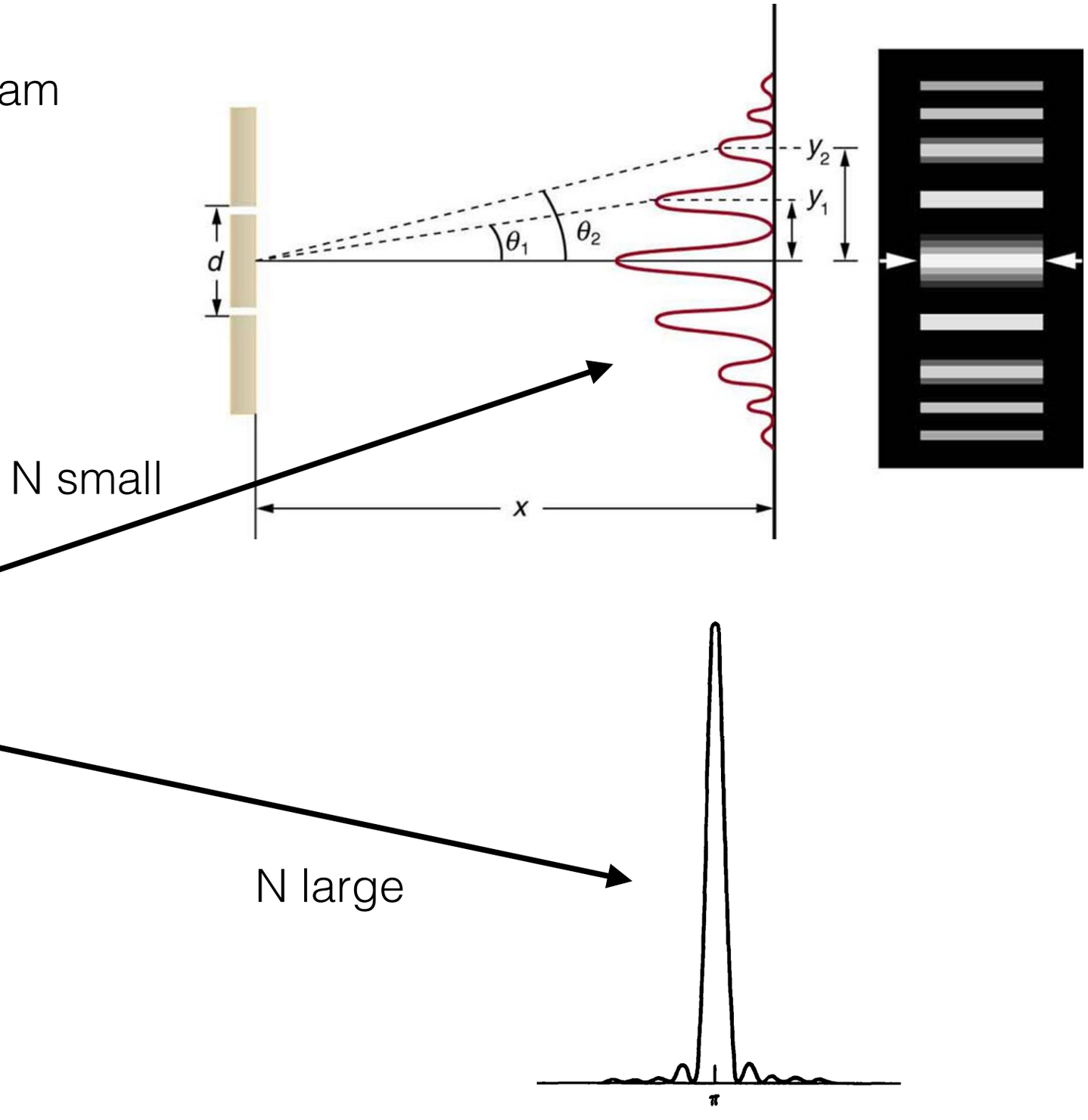
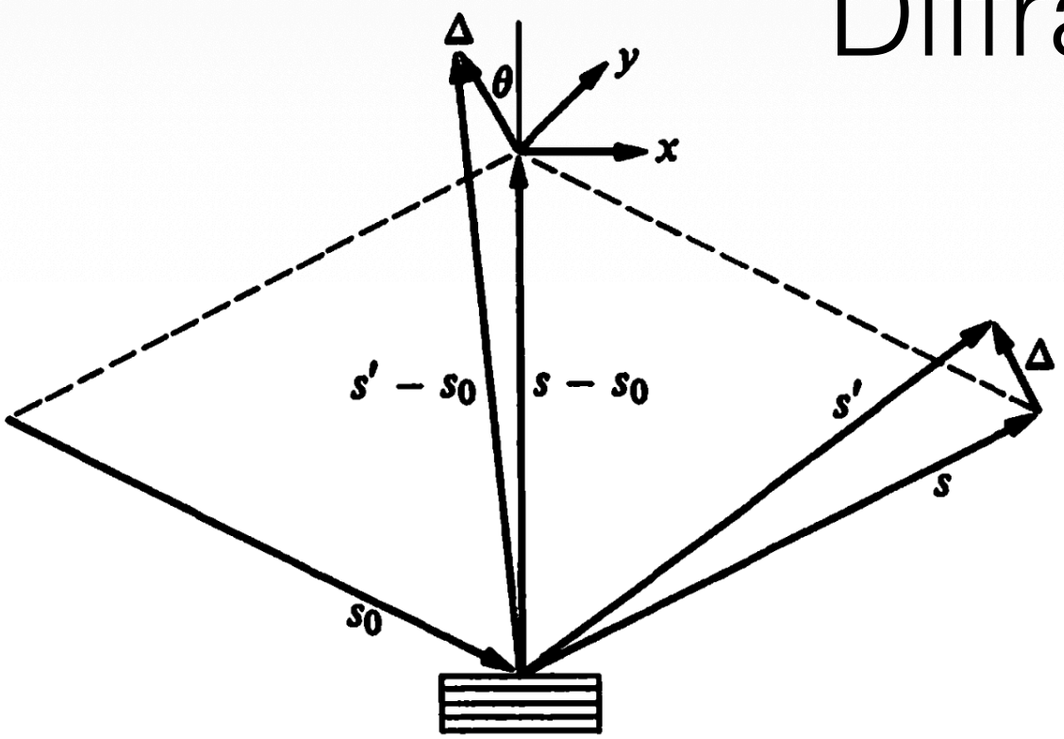
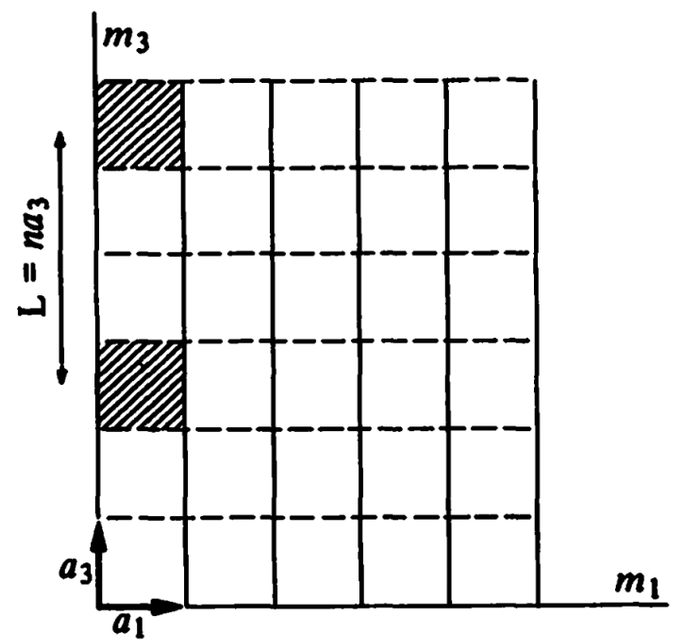




Diffraction from small crystals





$$(\mathbf{s} - \mathbf{s}_0)/\lambda = h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3$$

$$\mathbf{s}' - \mathbf{s}_0' = \mathbf{s} - \mathbf{s}_0 + \Delta\mathbf{s}$$

B. E. Warren: X-ray Diffraction, 1990 ed.

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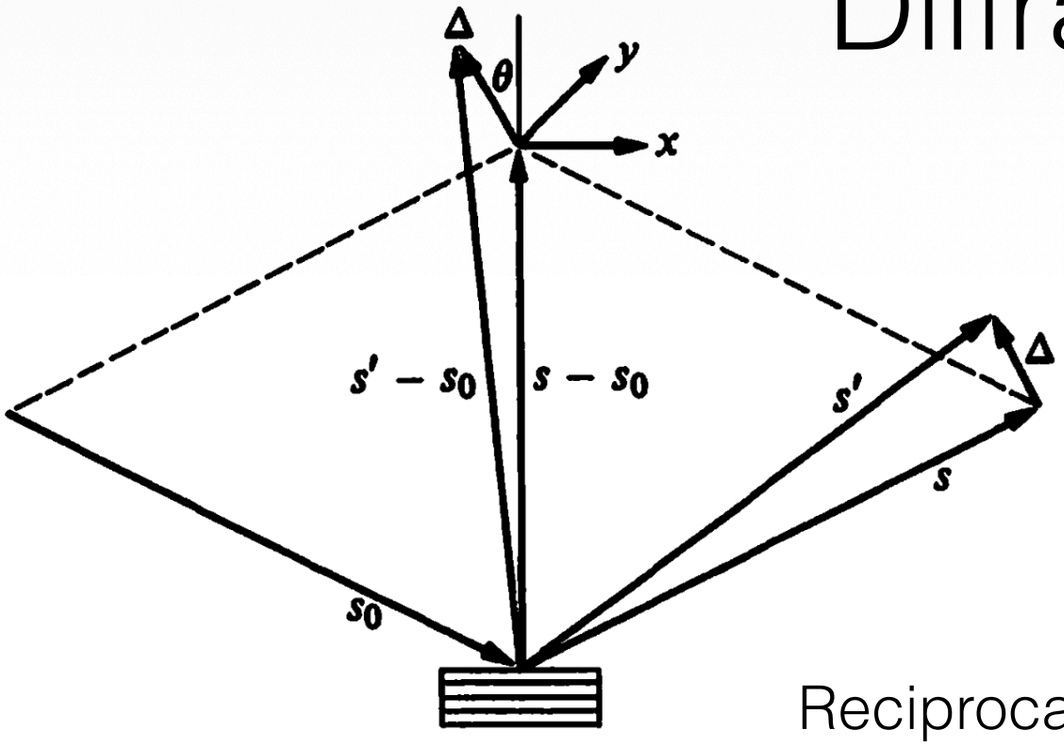

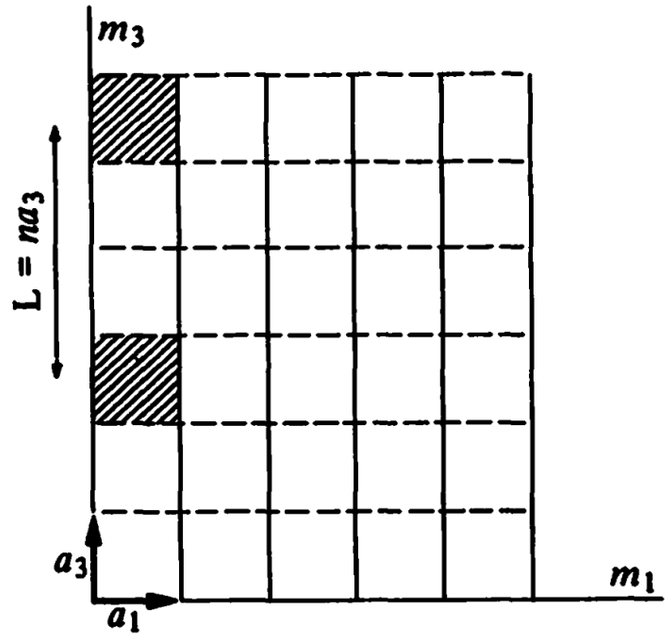

Reciprocal lattice

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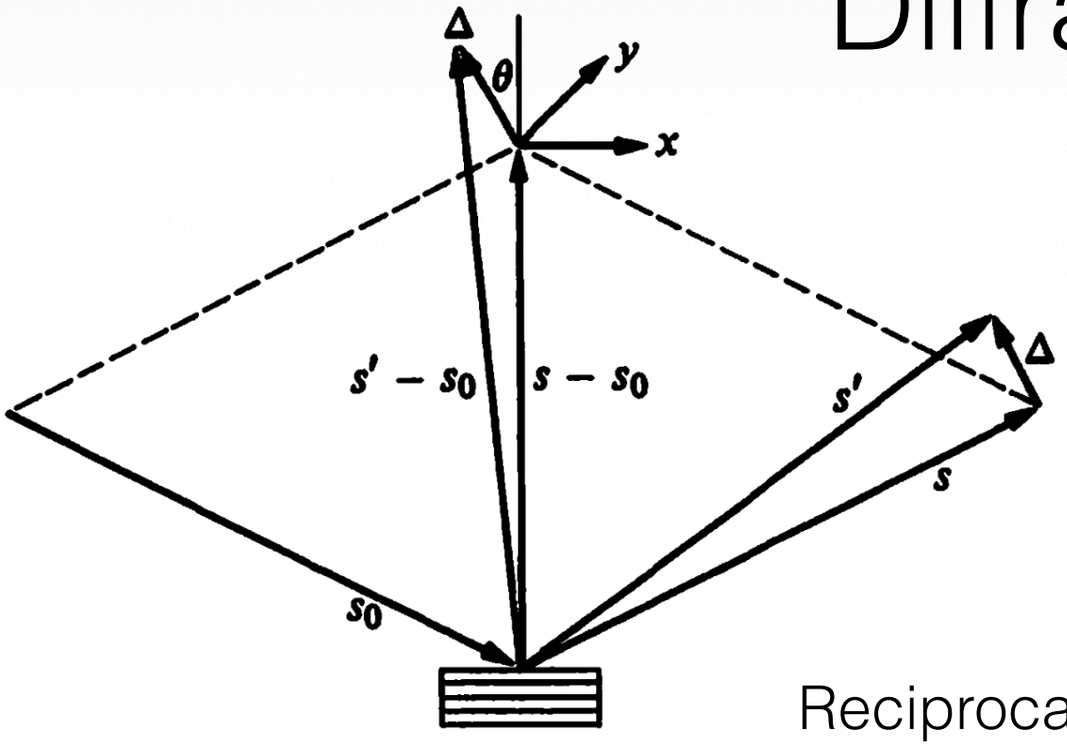

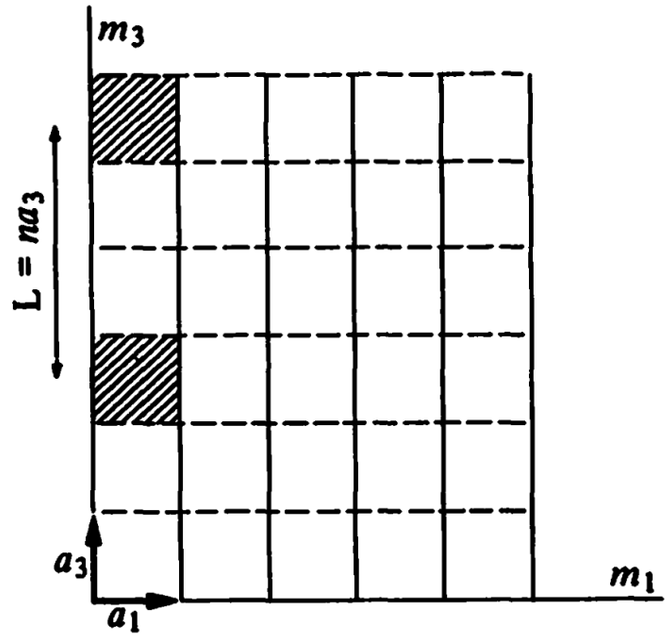

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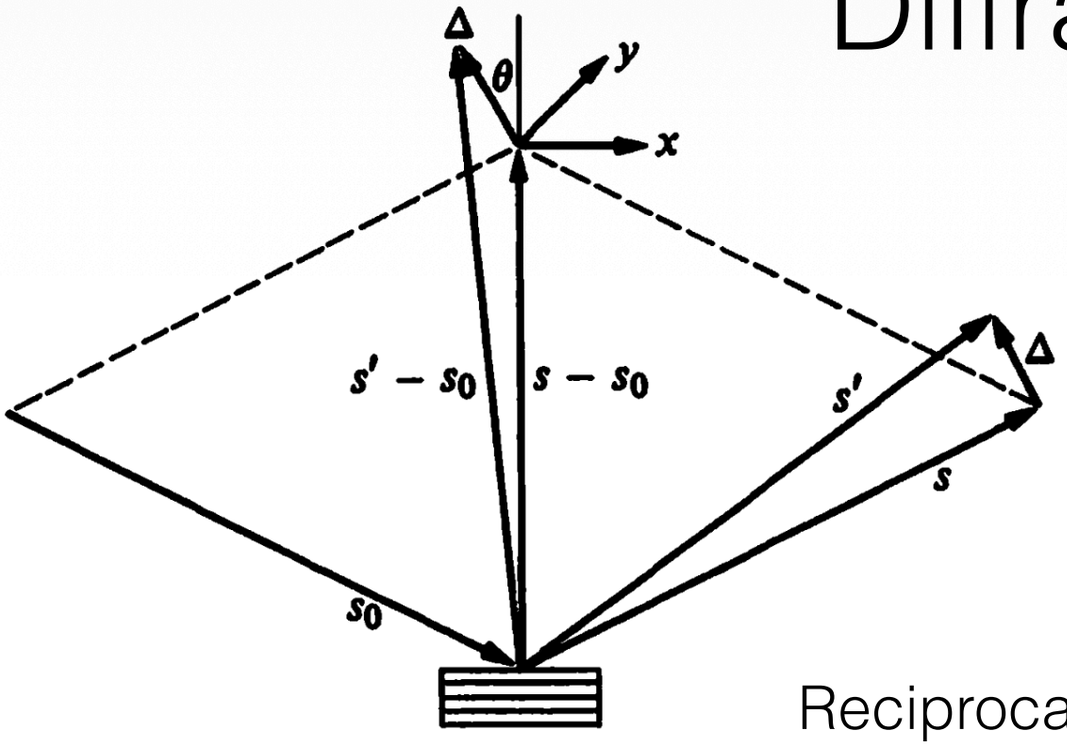

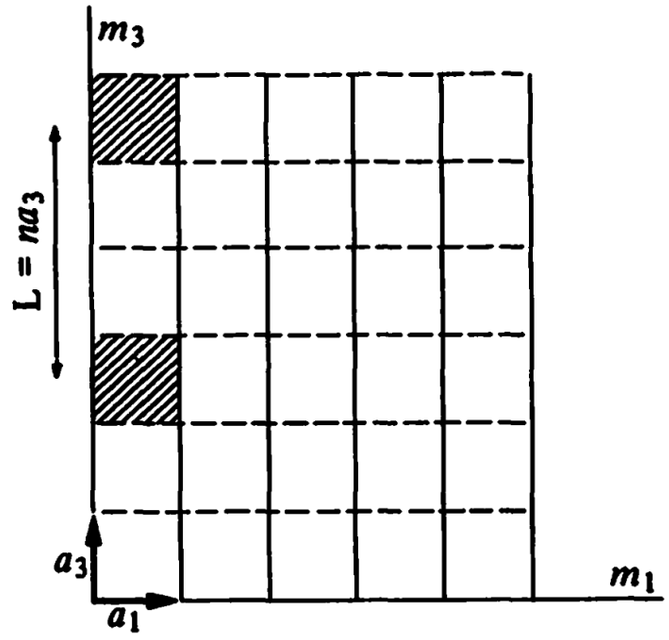

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$$\frac{\sin^2 Nx}{\sin^2 x} \to N^2 e^{-(Nx)^2/\pi} \Rightarrow I = I_e F^2 N^6 e^{-(\pi/\lambda^2)N^2\{(\Delta\mathbf{s}\cdot\mathbf{a}_1)^2+(\Delta\mathbf{s}\cdot\mathbf{a}_2)^2+(\Delta\mathbf{s}\cdot\mathbf{a}_3)^2\}}$$

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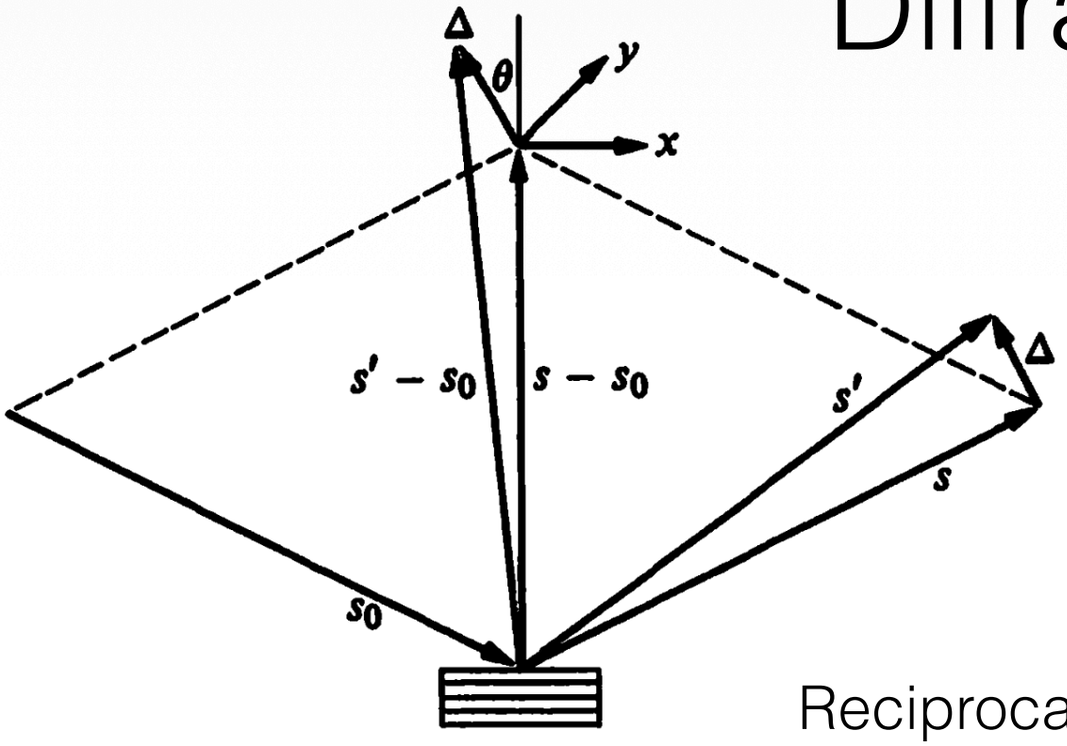

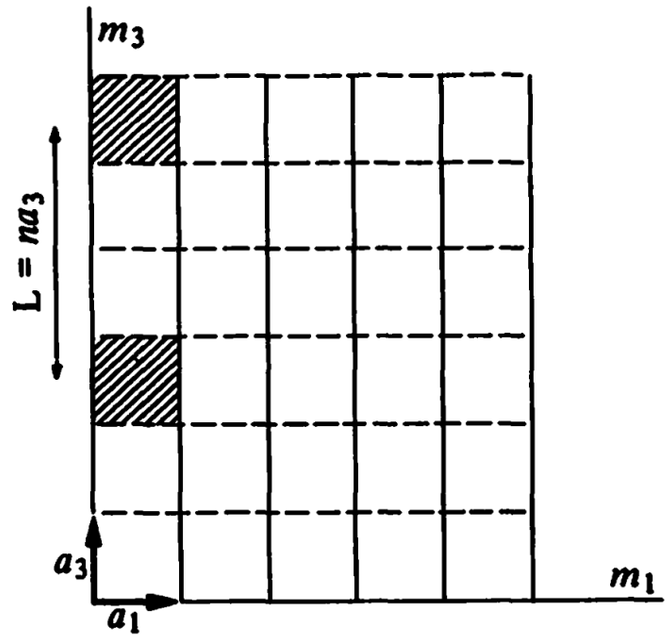

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(00l) reflection $\Rightarrow$ $I = I_e F^2 N^6 e^{-(\pi/\lambda^2)(Na)^2(\Delta s)^2}$

B. E. Warren: X-ray Diffraction, 1990 ed.

Diffraction from small crystals

$$I = I_e F^2 \frac{\sin^2(\pi/\lambda)\,\Delta\mathbf{s}\cdot N_1\mathbf{a}_1}{\sin^2(\pi/\lambda)\,\Delta\mathbf{s}\cdot\mathbf{a}_1} \frac{\sin^2(\pi/\lambda)\,\Delta\mathbf{s}\cdot N_2\mathbf{a}_2}{\sin^2(\pi/\lambda)\,\Delta\mathbf{s}\cdot\mathbf{a}_2} \frac{\sin^2(\pi/\lambda)\,\Delta\mathbf{s}\cdot N_3\mathbf{a}_3}{\sin^2(\pi/\lambda)\,\Delta\mathbf{s}\cdot\mathbf{a}_3}$$

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$$B(2\theta) = \frac{2[(\ln 2)/\pi]^{1/2}\lambda}{Na\cos\theta} \qquad B(2\theta) = \frac{0.94\lambda}{L\cos\theta}$$

Scherrer formula

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Scherrer formula

$$\beta(2\theta) = \frac{\lambda V}{\cos\theta\int T\,dV} = \frac{\lambda}{L\cos\theta}$$

$$L = \frac{1}{V}\int T\,dV$$

L is the volume average value

B. E. Warren: X-ray Diffraction, 1990 ed.

Line broadening: the simple Delft model

- The peak broadening is the result of the convolution of the instrumental and sample broadening

$$S(2\theta) = \int S_S(2\theta - z) S_I(z)\, dz$$

- The broadening due to the sample is the convolution of the broadening due to the finite size of crystallites and the r.m.s. microstrain (a generalization for the effect of several defects)

- The instrumental broadening can be described through the Caglioti formula

- The Delft model for sample broadening (gives the integral breadths for the Gaussian and Lorentzian components):

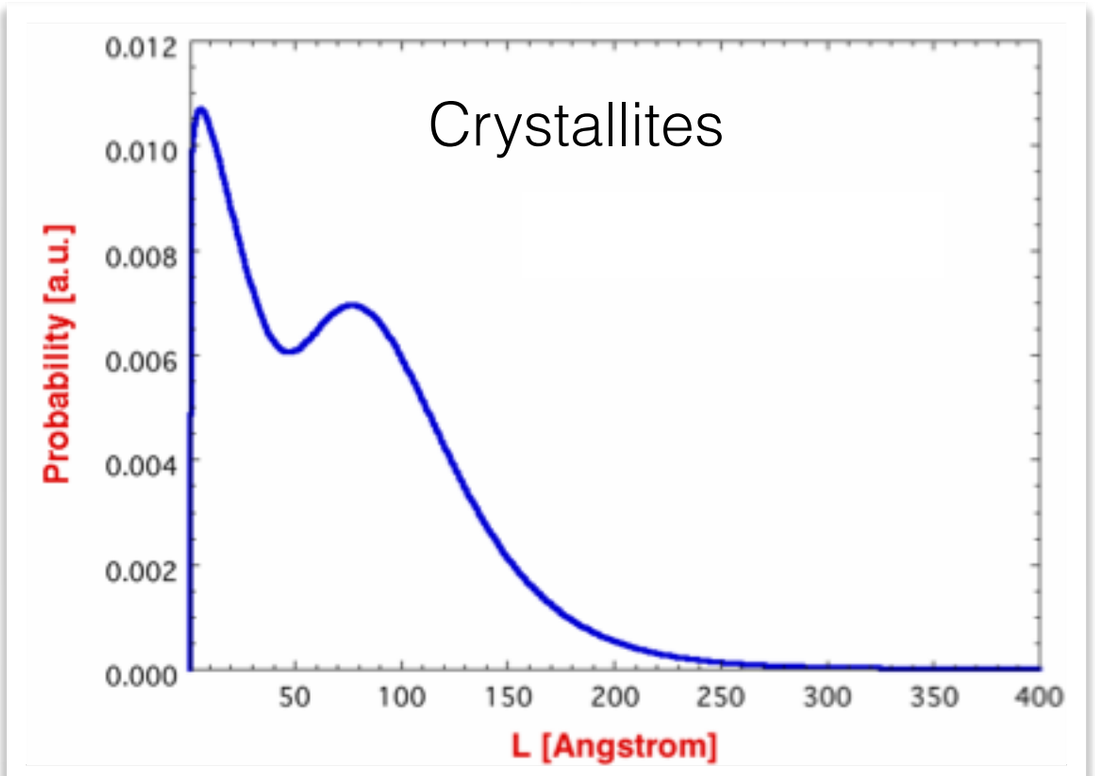
$$\beta_{fG} = 4\varepsilon \tan\theta_i \qquad \beta_{fL} = \lambda / D \cos\theta_i$$

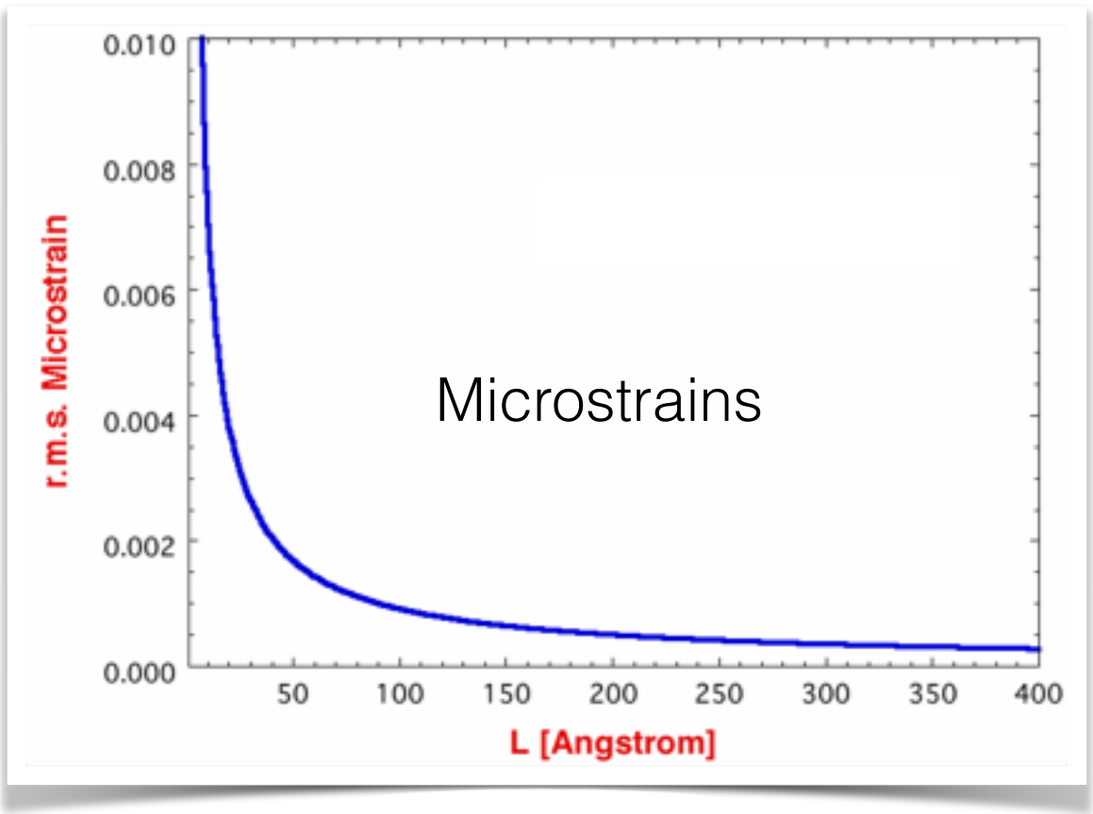
r.m.s. microstrain

radiation wavelength

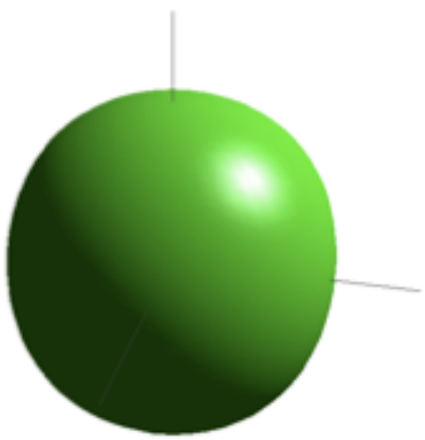
mean crystallite

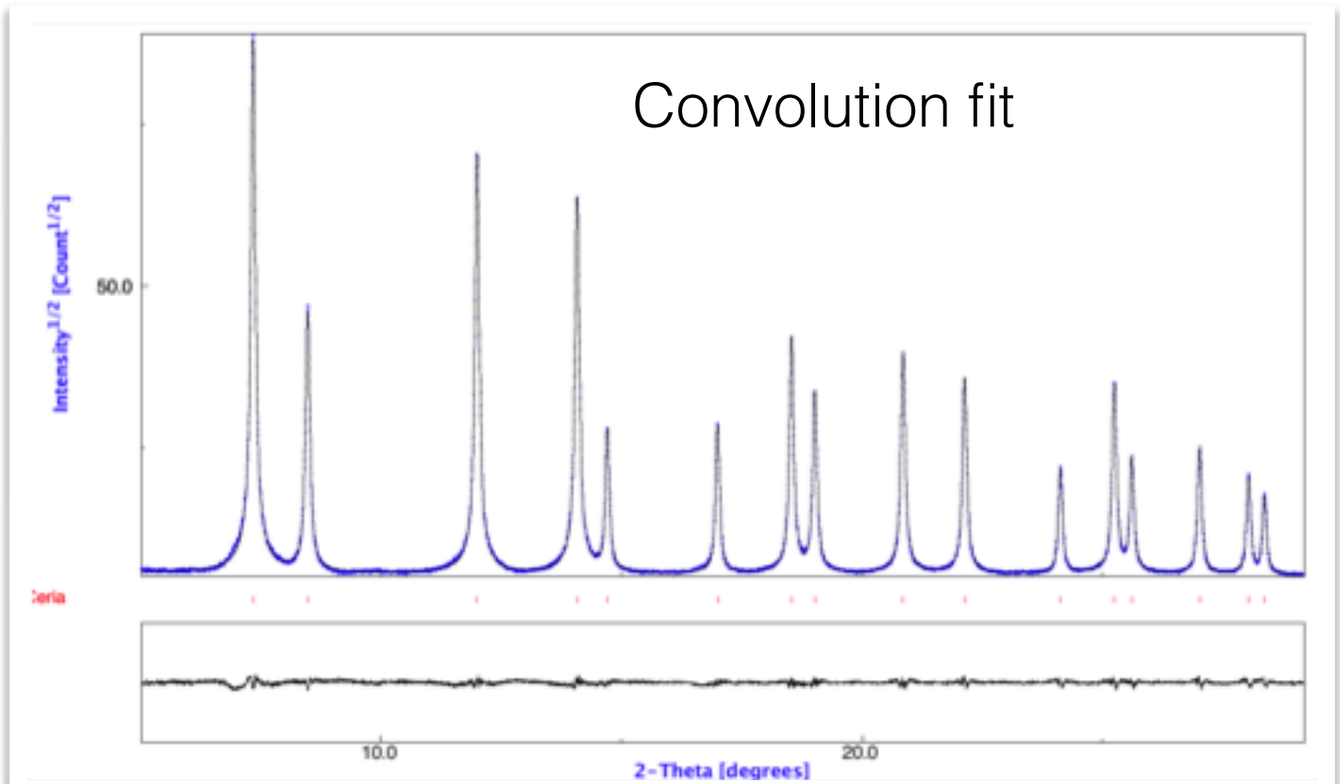
Profile fitting by distributions



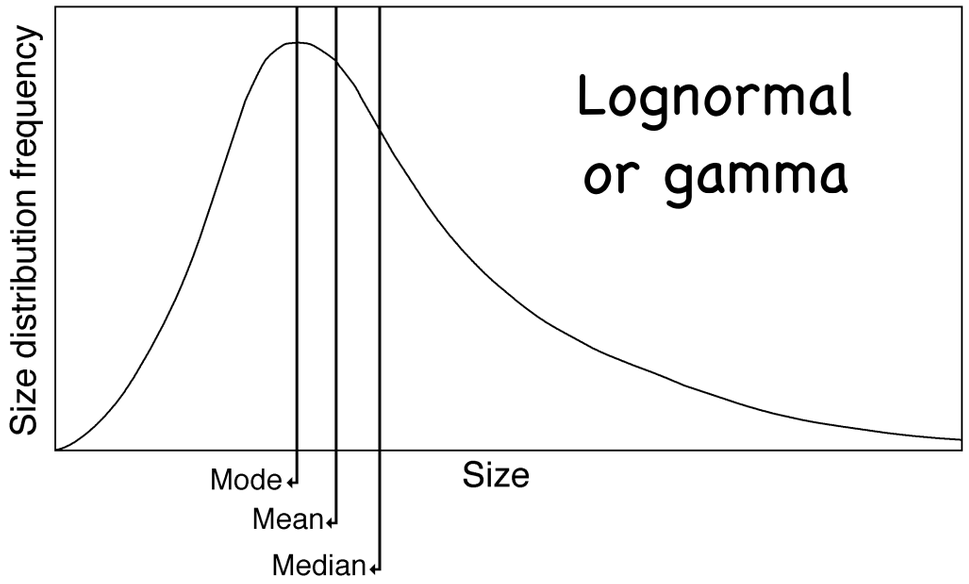


Anisotropic shape and size-strain in the Rietveld





Crystallite-microstrain distributions



Given a size distribution p(i):

$$A_n^S = \frac{N_n}{N_3} = \frac{1}{N_3}\sum_{i=|n|}^{\inf}(i-|n|)p(i)$$

Fourier coefficients

and a microstrain distribution

$$A_n = A_n^S A_n^D = \frac{N_n}{N_3}\langle \cos 2\pi l Z_n \rangle$$

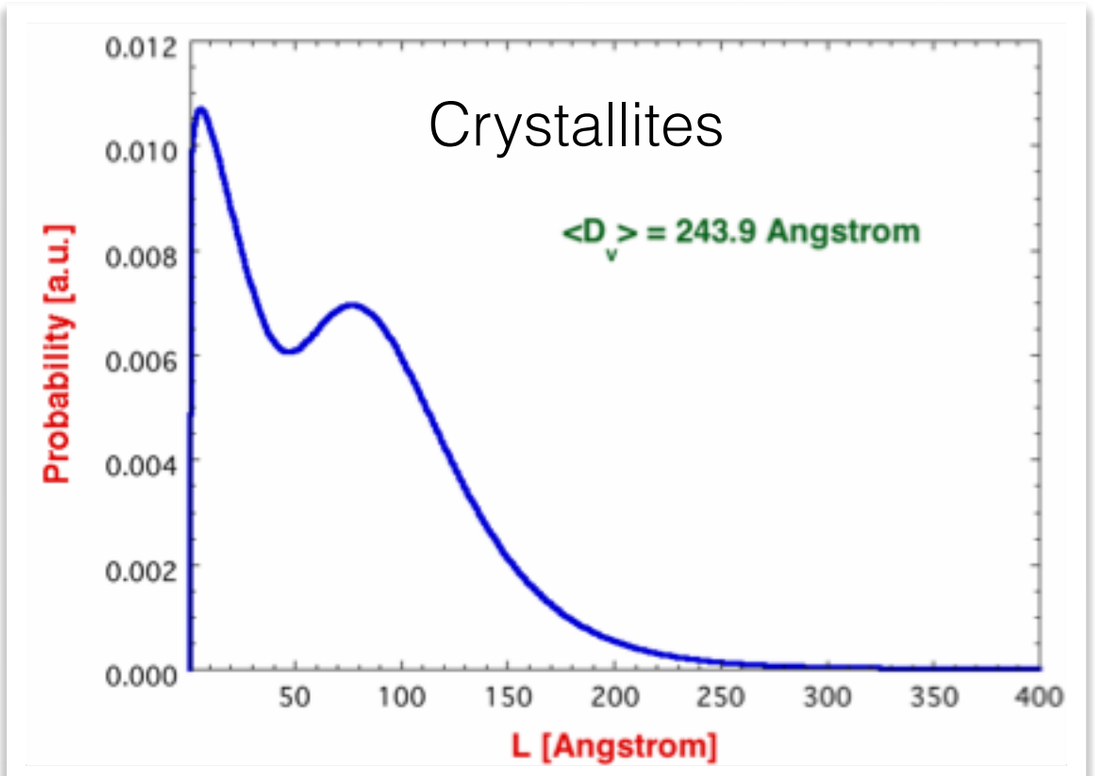
$$\left\langle \varepsilon_n^2 \right\rangle^{\frac{1}{2}} = \frac{\left\langle \varepsilon_{N_3}^2 \right\rangle^{\frac{1}{2}}}{(na_3)^k}$$

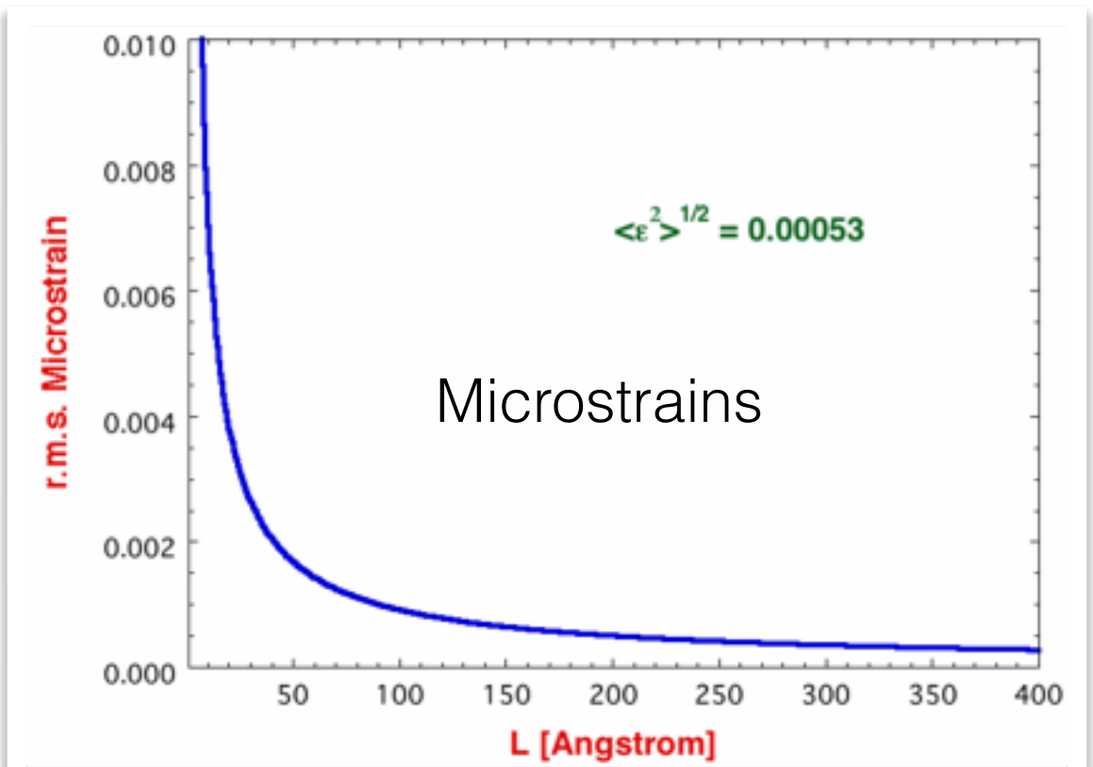
$$S(2\theta) = \int S_S(2\theta - z)S_I(z)\,dz$$

Instrumental aberration

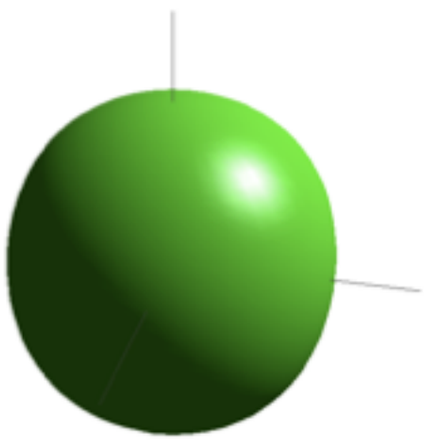
$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Npeaks} L_k \left|F_{k,j}\right|^2 S_j\left(2\theta_i - 2\theta_{k,j}\right) P_{k,j} A_j + bkg_i$$

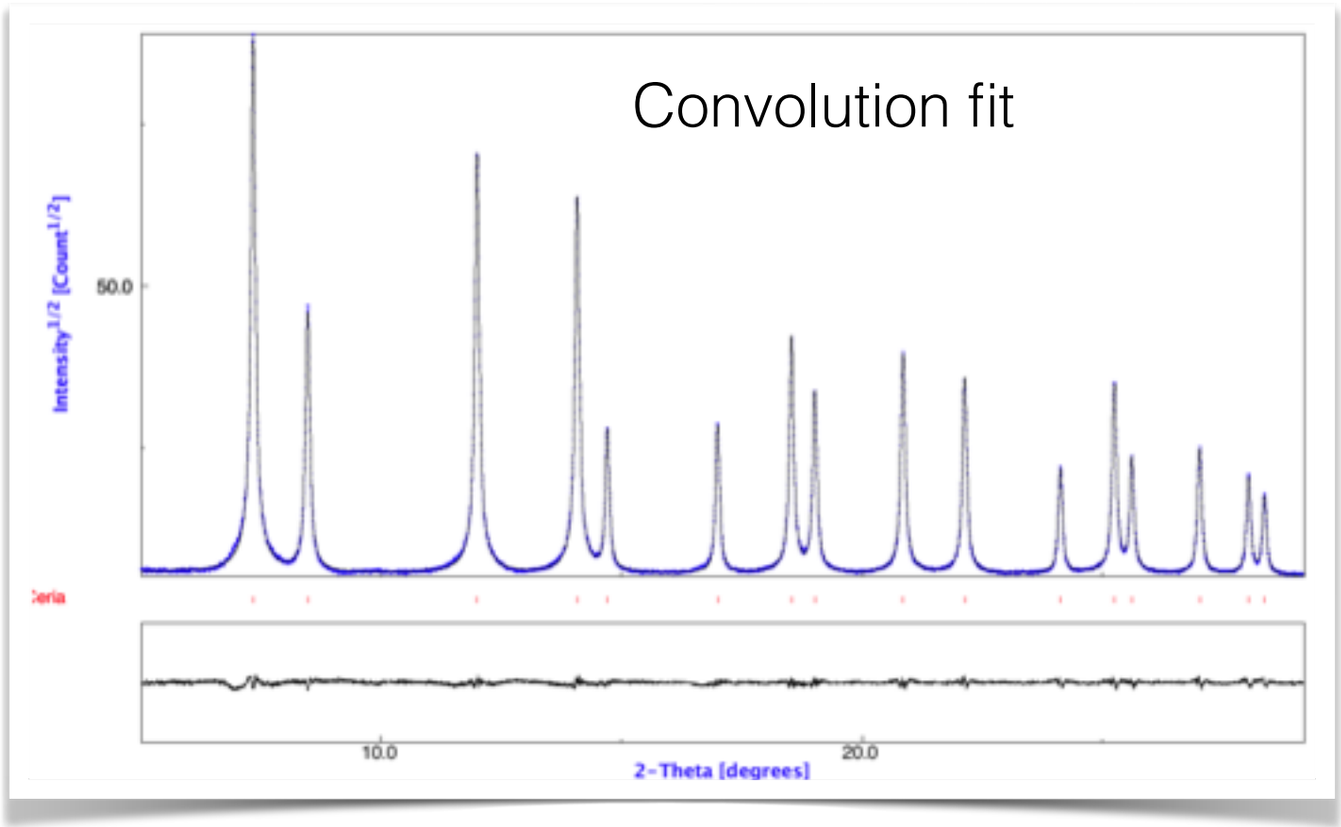
Cerium oxide bimodal size distribution



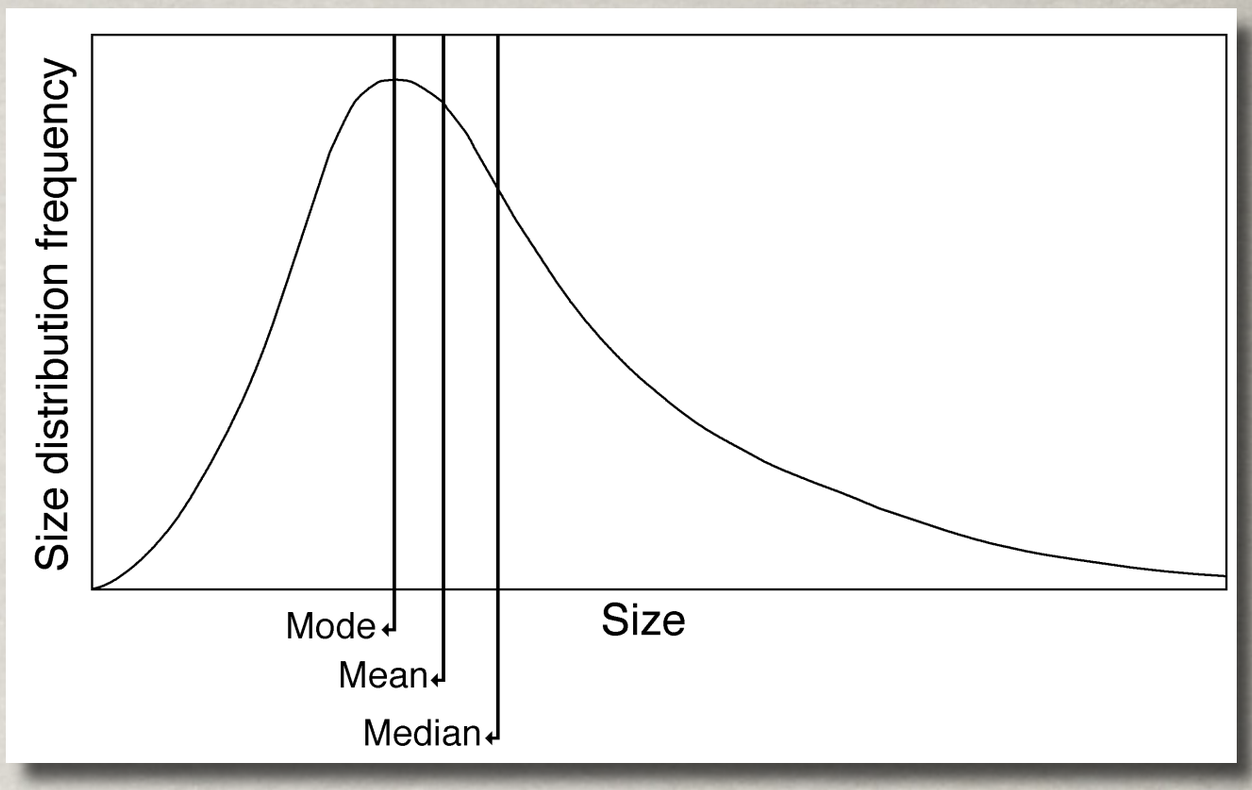


Anisotropic shape and size-strain in the Rietveld





Crystallites distribution



Name	Definition
Mean length	$\langle M \rangle = \frac{\sum_{i=1}^{N} n_i d_i}{\sum_{i=1}^{N} n_i}$
Length weighted or area-length	$\langle D \rangle = \frac{\sum_{i=1}^{N} n_i d_i^2}{\sum_{i=1}^{N} n_i d_i}$
Area weighted or volume-area	$\langle D_a \rangle = \frac{\sum_{i=1}^{N} n_i d_i^3}{\sum_{i=1}^{N} n_i d_i^2}$
Volume-weighted	$\langle D_V \rangle = \frac{\sum_{i=1}^{N} n_i d_i^4}{\sum_{i=1}^{N} n_i d_i^3}$

Distributions profiles in Maud

- Lognormal and gamma crystallite distributions

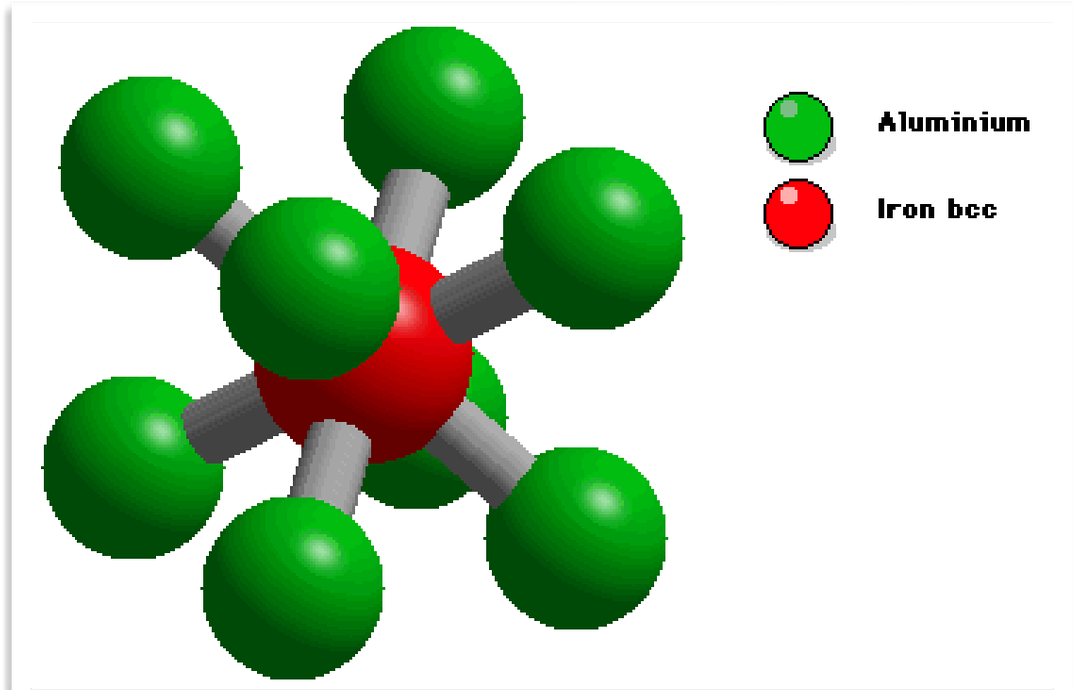
D. Balzar et al. (2004). J. Appl. Cryst., 37, 911-924.

- Microstrain distribution: $\left\langle \varepsilon^2 \right\rangle_L^{1/2} = \dfrac{\left\langle \varepsilon^2 \right\rangle^{1/2}}{\left(\dfrac{2L}{\langle M \rangle} \right)^a}, \qquad 0 \le a \le 1$

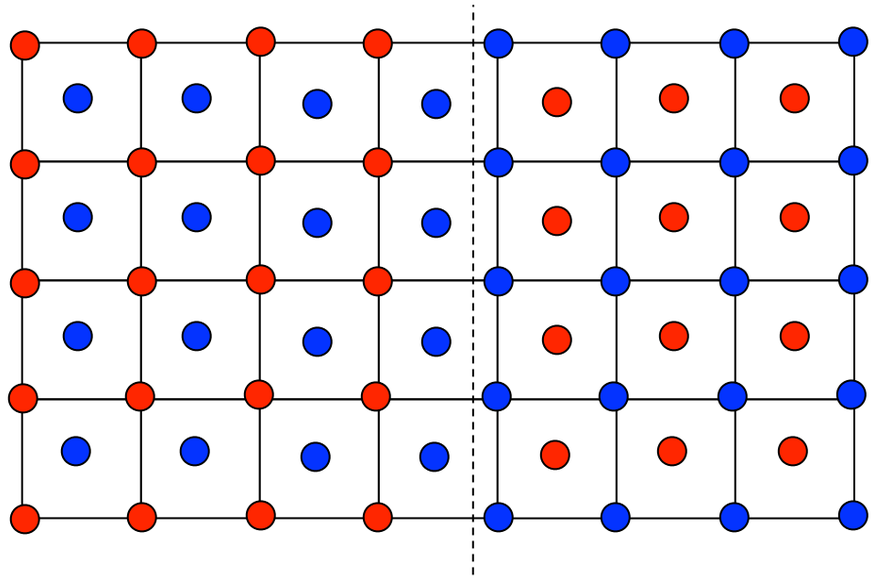
L. Lutterotti, P. Scardi,
Adv. X-ray Anal. 35A (1992) 577.

Order-disorder transition in intermetallic

- Applications:
  - High temperature structural material
  - Oxidation resistance
  - Blade material for Gas turbine
- Main problem:
  - Ductility (forming and shaping)
  - Brittle at low temperature
  - Disordered phase is more ductile
- Materials:
  - FeAl, Ni3Al, NiAl, TiAl...



Antiphase domains

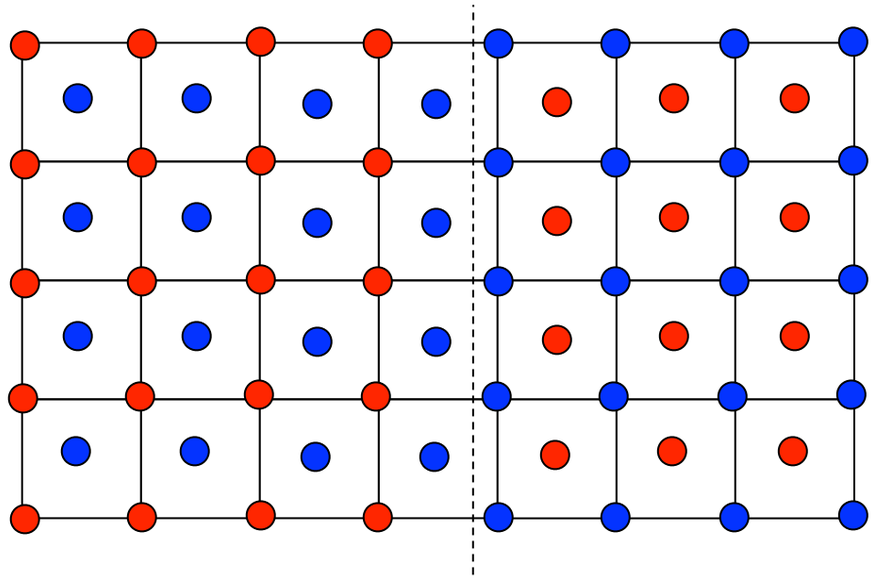


- In “FCC” antiphase domains broadened the superstructure reflections (fundamental peaks not affected)

- If h+k=even & k+l=odd & l+h=odd (same parity):

$$\beta(2\theta) = \frac{\lambda\gamma\left(|h| + |k|\right)}{a\cos\theta\sqrt{h^2 + k^2 + l^2}}$$

Antiphase domains



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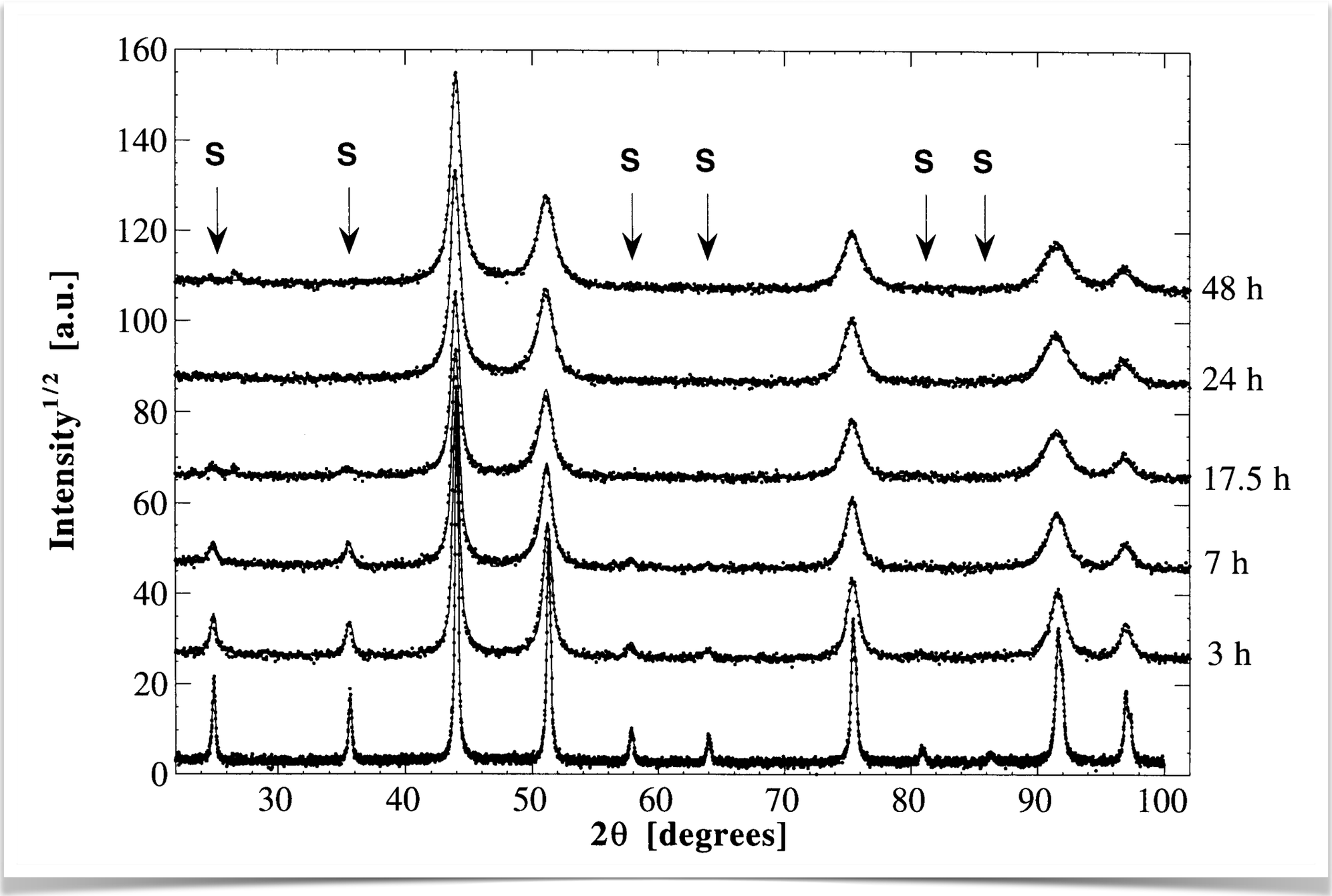
Antiphase domain probability of crossing a domain in the distance a

Antiphase domains in Ni_3Al

Ball milling at high energy for different time (up to 24 hours)



Stacking/deformation faults

- Warren treatment (FCC)
  - Peak shift:

$$\Delta(2\theta)^{\circ} = \frac{90\sqrt{3}(\alpha' - \alpha'')\tan\theta}{\pi^2 h_0^2 (u+b)} \sum_b (\pm L_0)$$

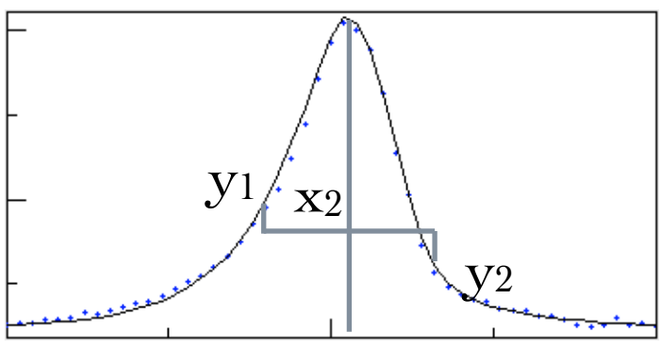
  - Peak broadening:

$$\frac{1}{D_{eff}} = \frac{1}{D} + \frac{\left[1.5(\alpha' + \alpha'') + \beta'\right]}{a h_0 (u+b)} \sum_b |L_0|$$

  - Peak asymmetry:

$$y_2 - y_1 = \frac{2A(4.5\alpha'' + \beta')}{c_2 x_2 \sqrt{3}\pi(u+b)} \sum_b (\pm) \frac{L_0}{|L_0|}$$

$$c_2 = 1 + \left\{ \frac{\lambda}{4\pi D_{eff}\left[\sin(\theta_0 + x_2) - \sin\theta_0\right]} \right\}^2$$



$$h_0^2 = h^2 + k^2 + l^2$$

α′=intrinsic faults probability
α″=extrinsic faults probability
β=twin faults probability

$L_0 = h+k+l$

b=number broadened reflections
u=number unbroadened reflections

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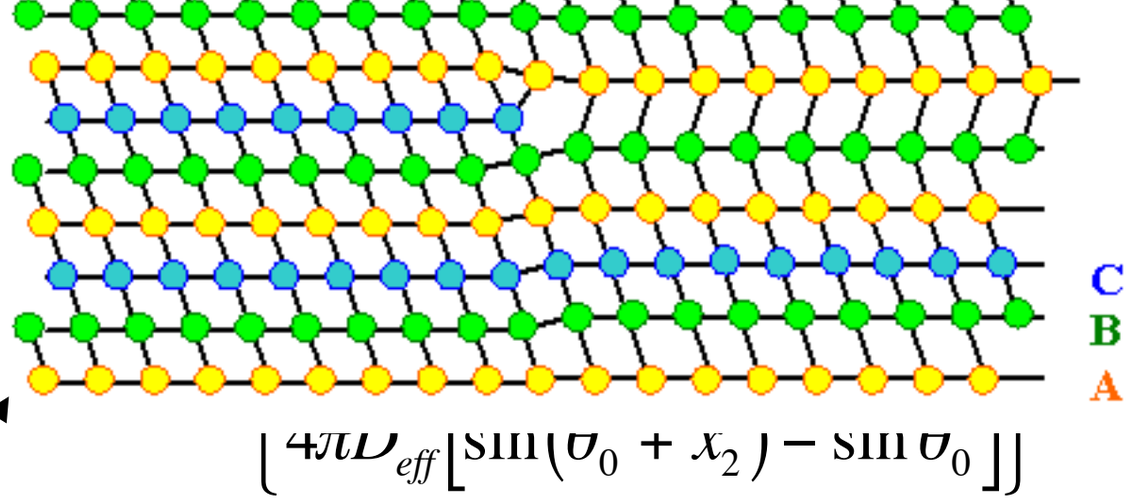
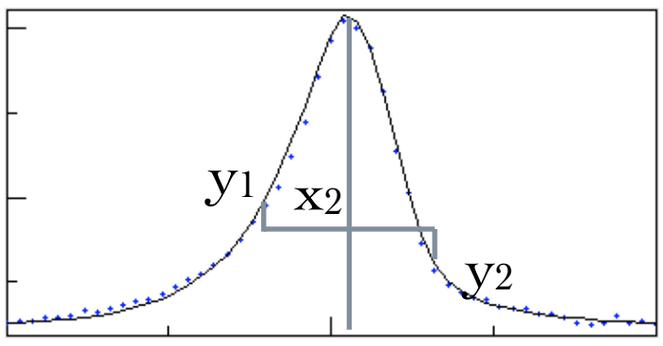
$$\frac{1}{\lfloor 4\pi D_{eff} \lfloor \sin(\sigma_0 + x_2) - \sin\sigma_0 \rfloor \rfloor} \quad \frac{1}{\lceil 1.5(\alpha' + \alpha'') + \beta' \rceil}$$



  - Peak asymmetry:



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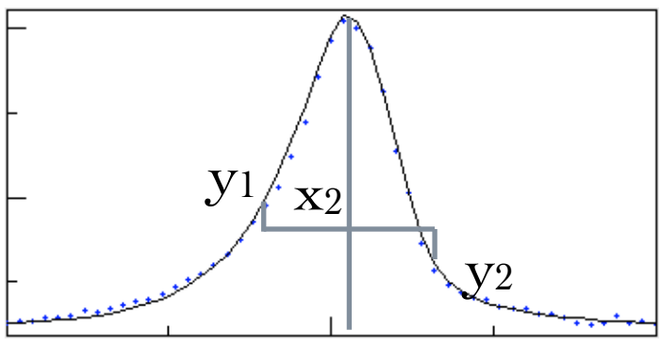
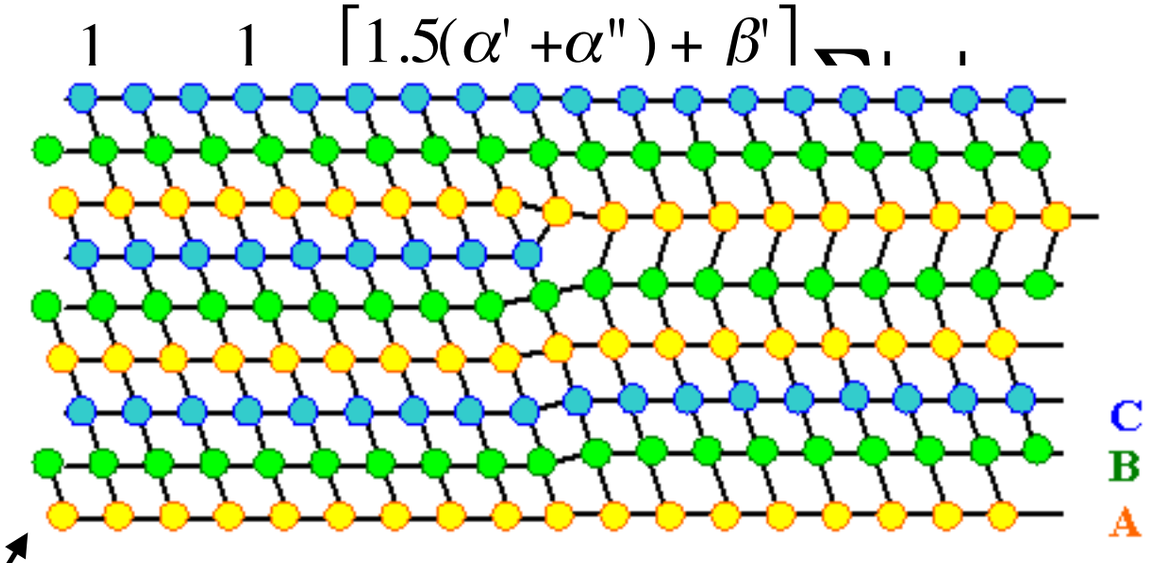
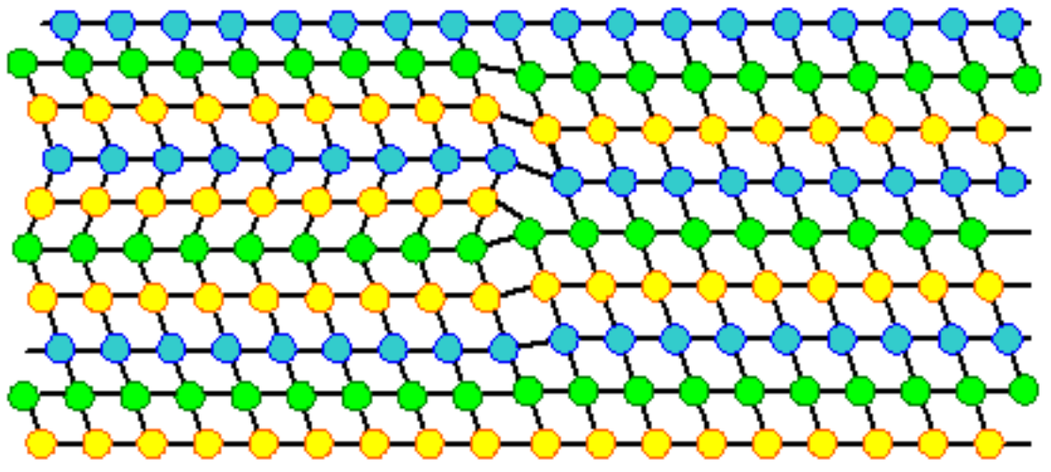
  - Peak asymmetry:







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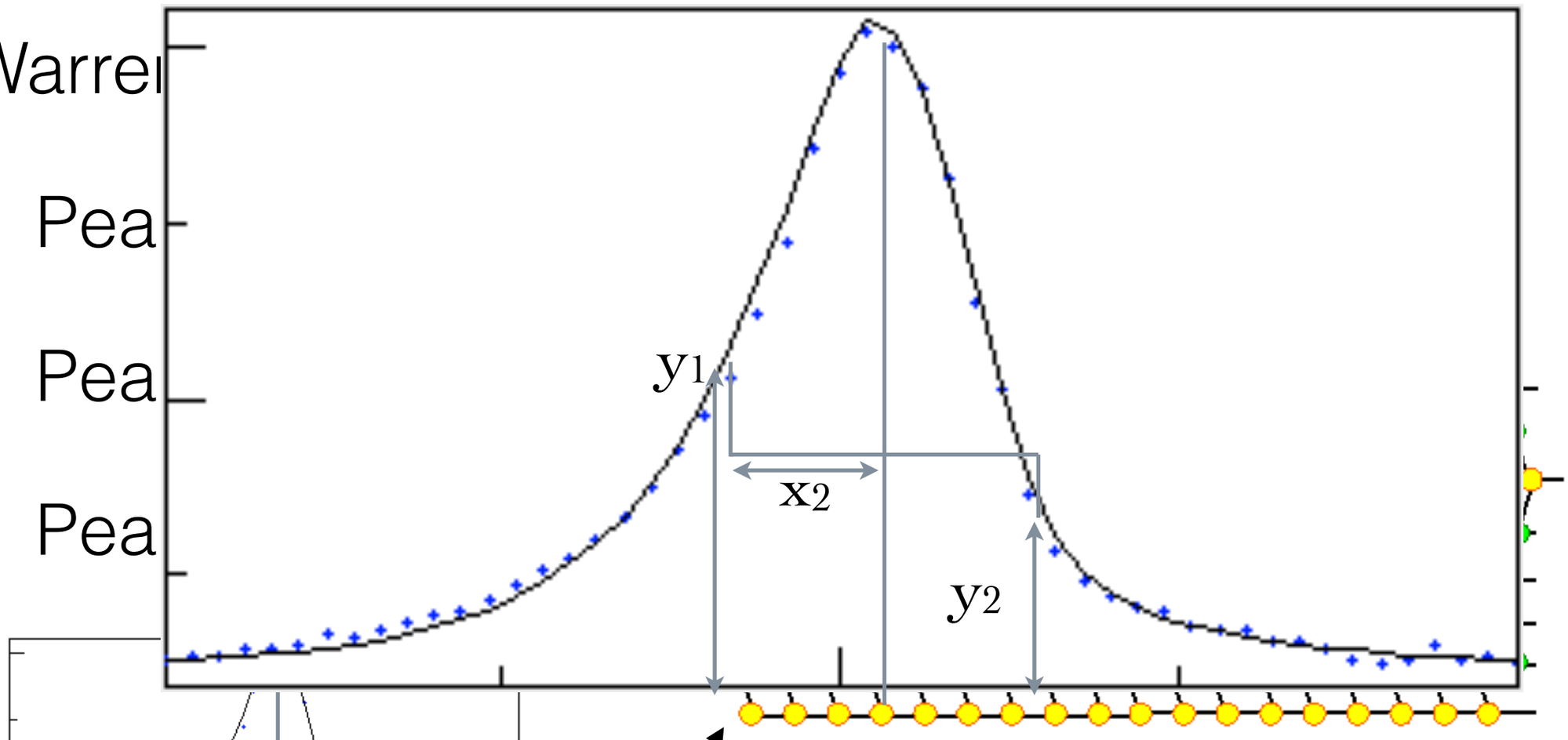
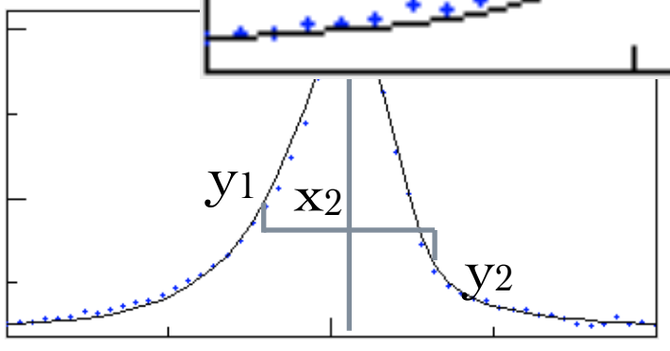
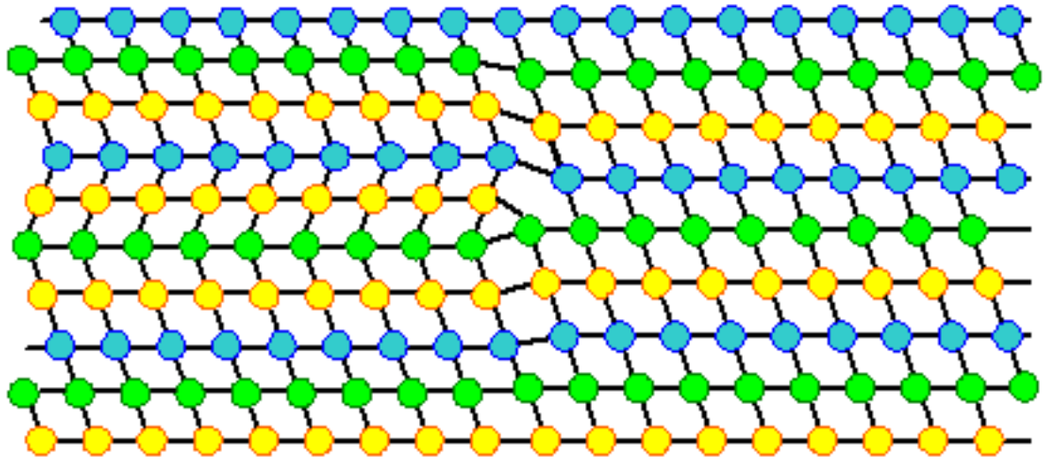
Stacking/deformation faults

- Warren
  - Pea
  - Pea
  - Pea





$|4\pi D_{eff}|\sin(\sigma_0 + x_2) - \sin\sigma_0|$



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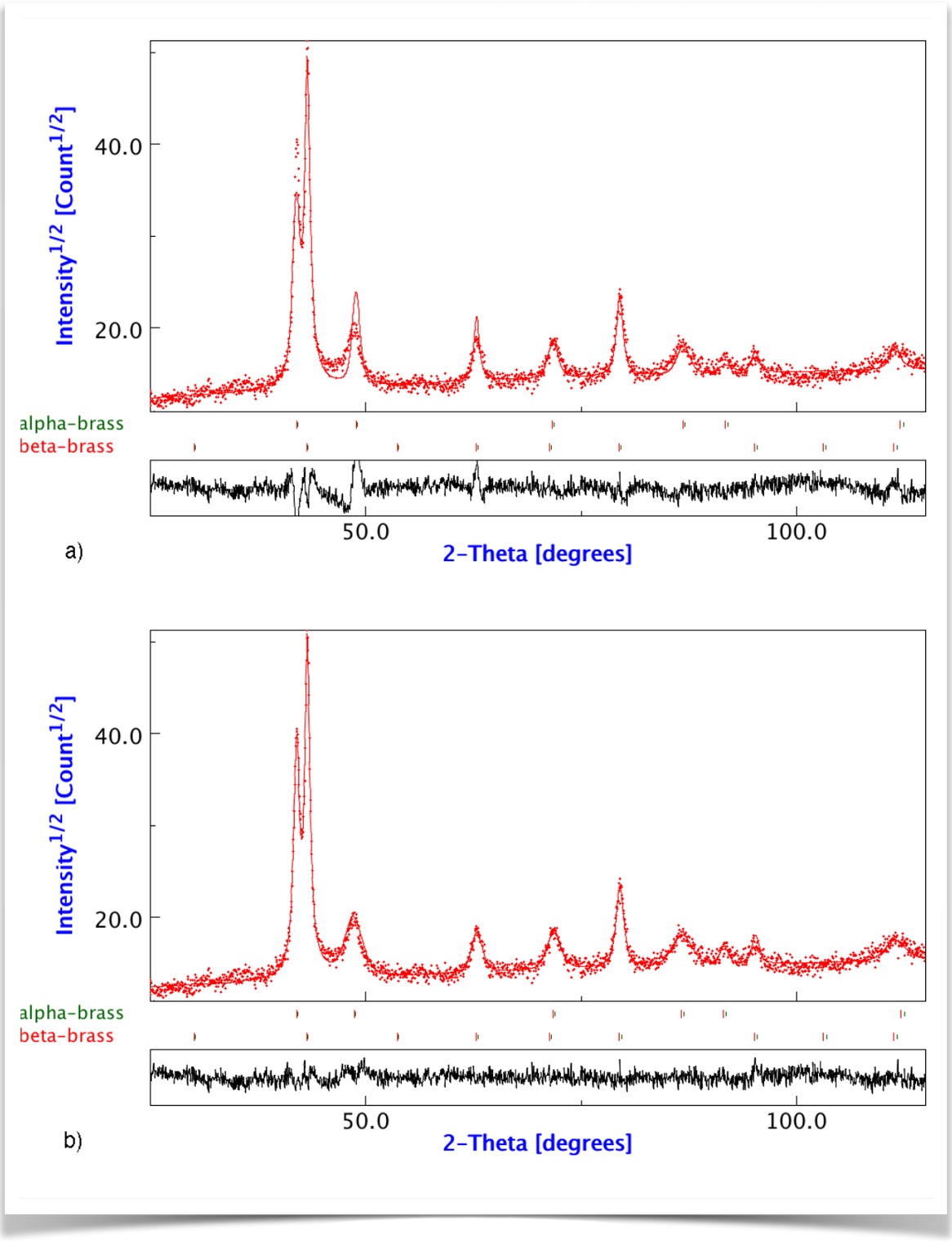
Planar defects in α/β-brass

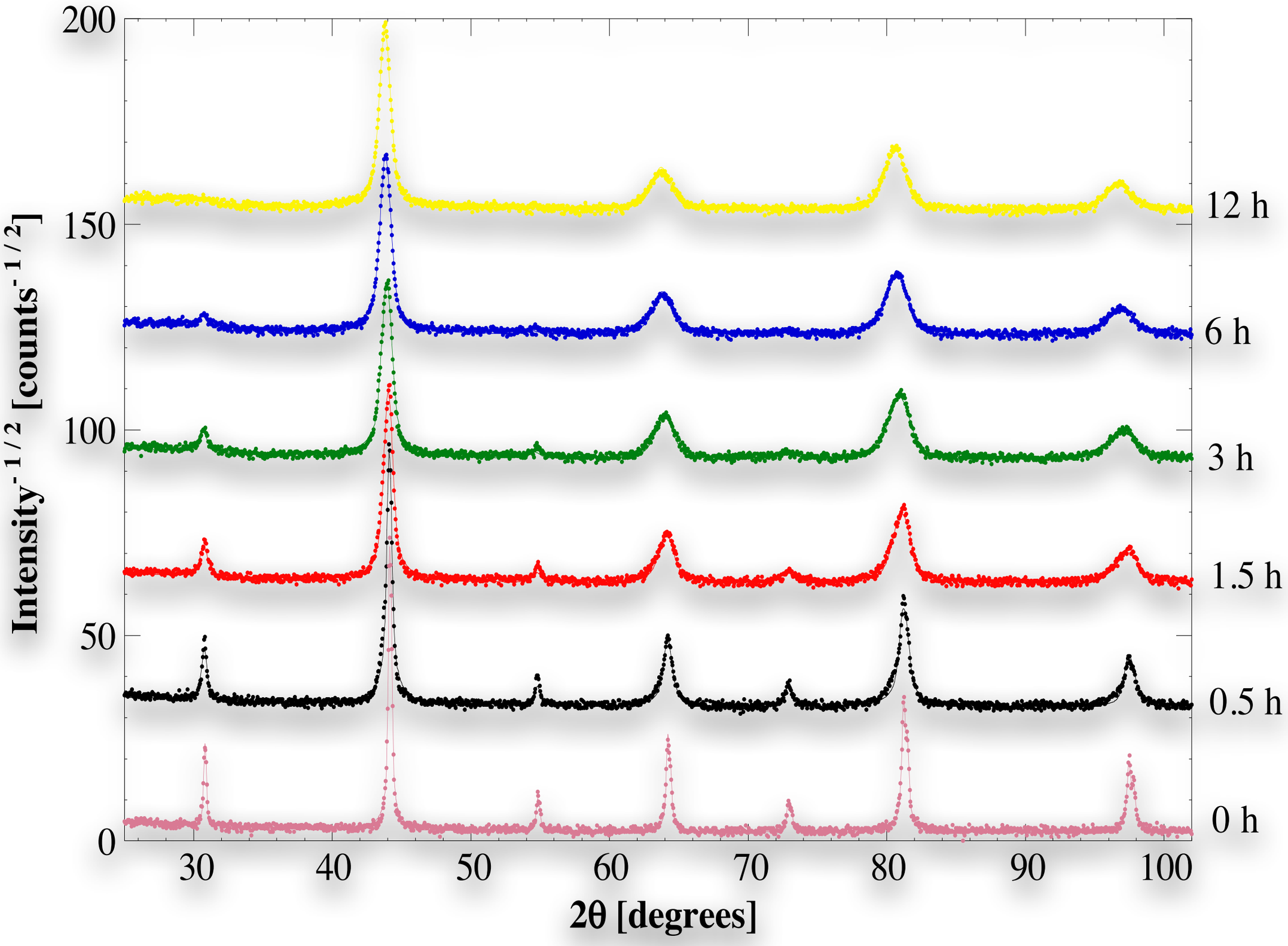
Ball milling for 48 hours



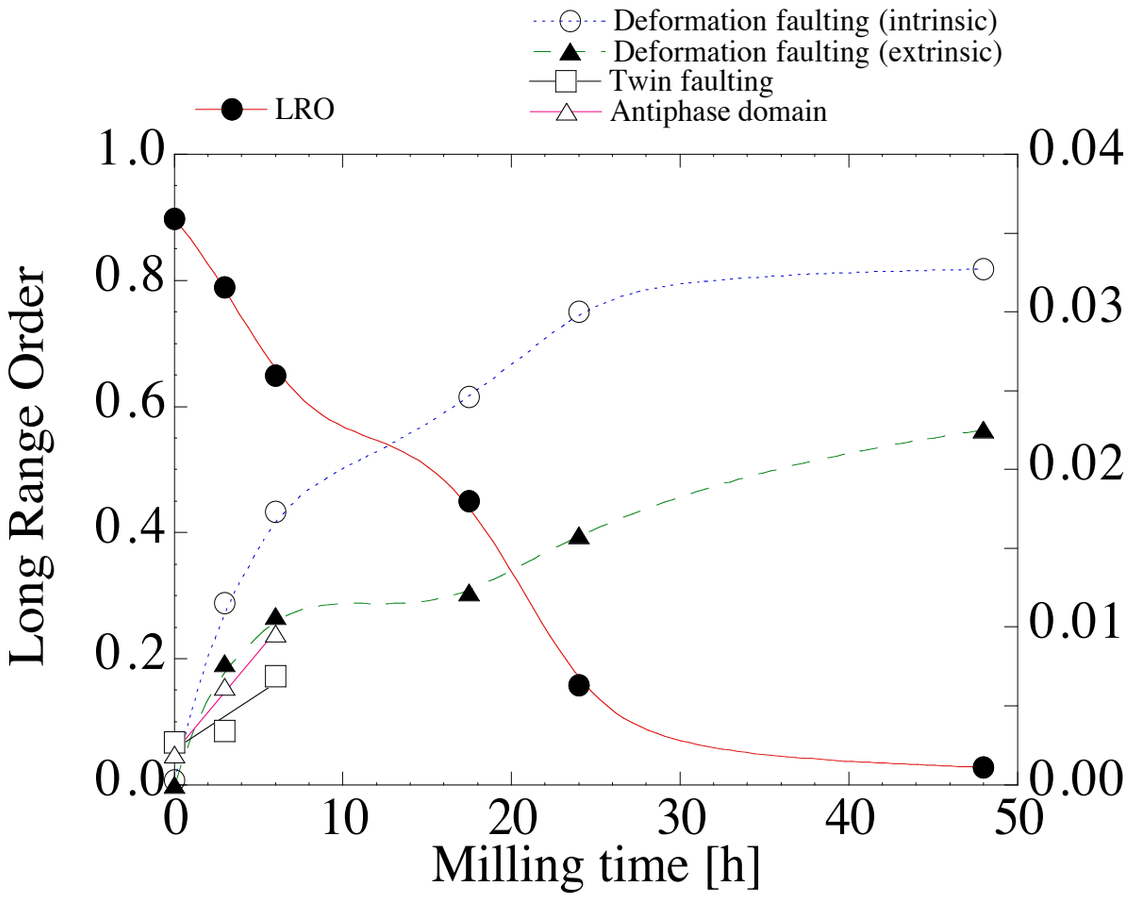
No faults assumed
(deformation, twin etc.)

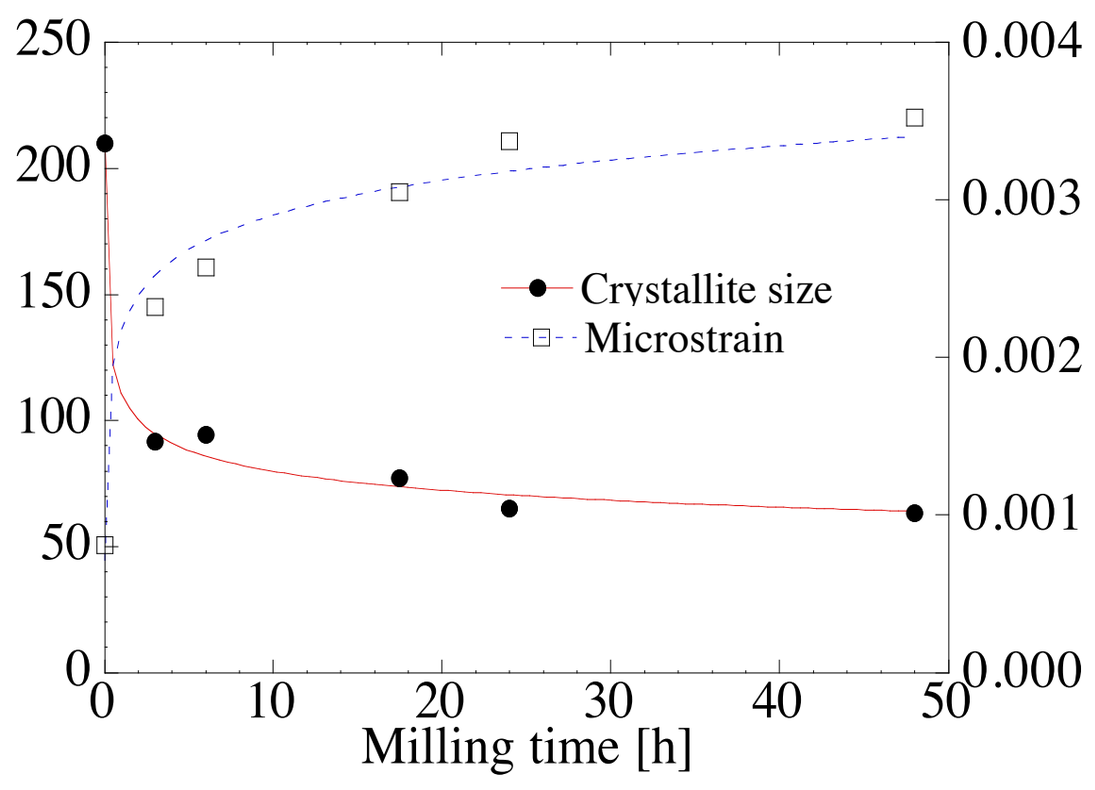
Stacking and deformation faults modeled using the Warren model

Disordering FeAl by ball-milling



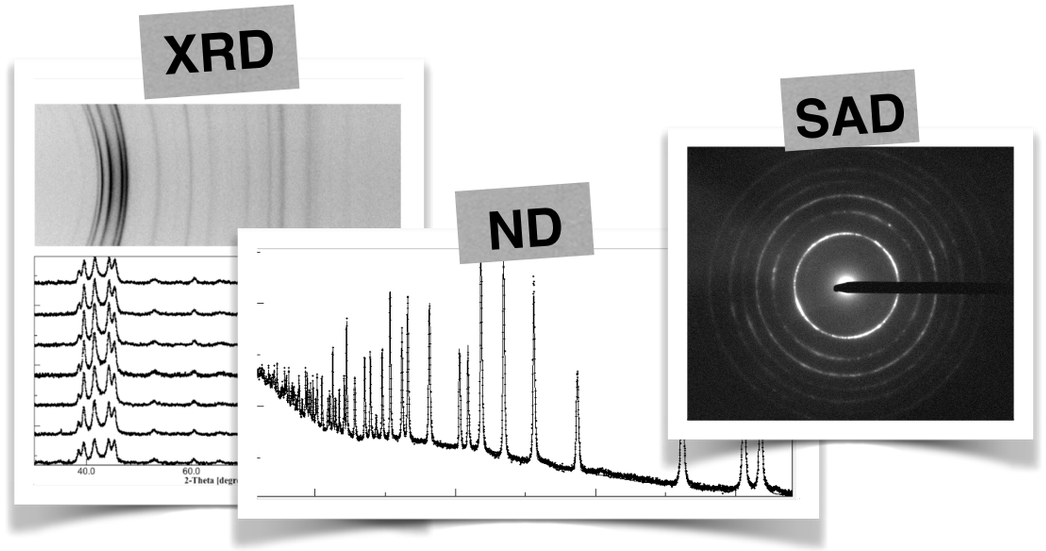
Defect analysis on ball-milled FeAl





Analysis of nano-materials

- Crystal structure solution
- Crystal structure refinement
- Quantitative Phase Analysis
- Size-Strain and Defects
- Texture/Stress/Strain Analysis



- Amorphous/Disordered/Nano:
  - Pseudo-amorphous approximation
  - Debye computation (like the PDF but in the real space)
  - PDF

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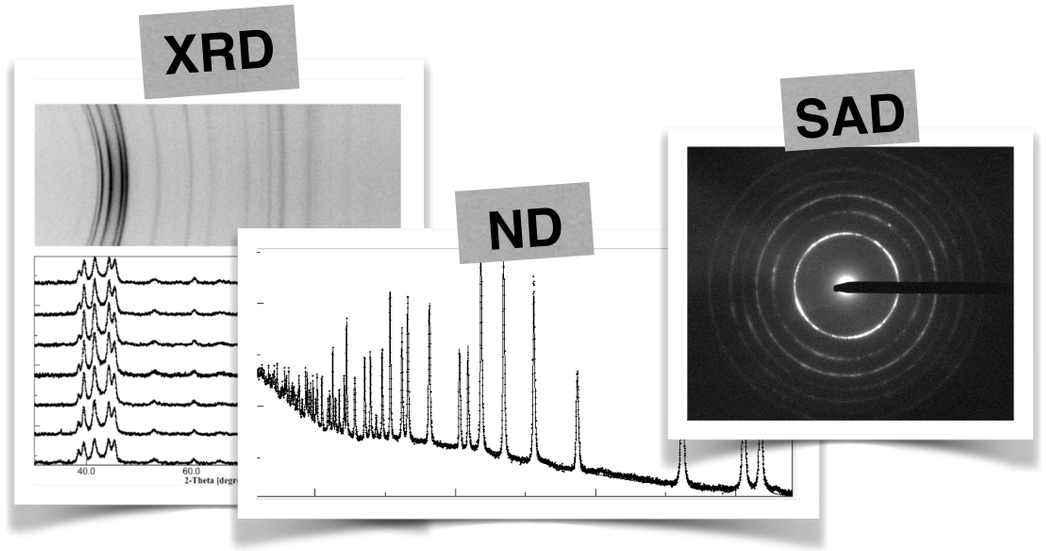

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Problems with the PDF:
- requires single phase
- normalization and background removal
- difficult to get domains info
- how to get structural informations out of it

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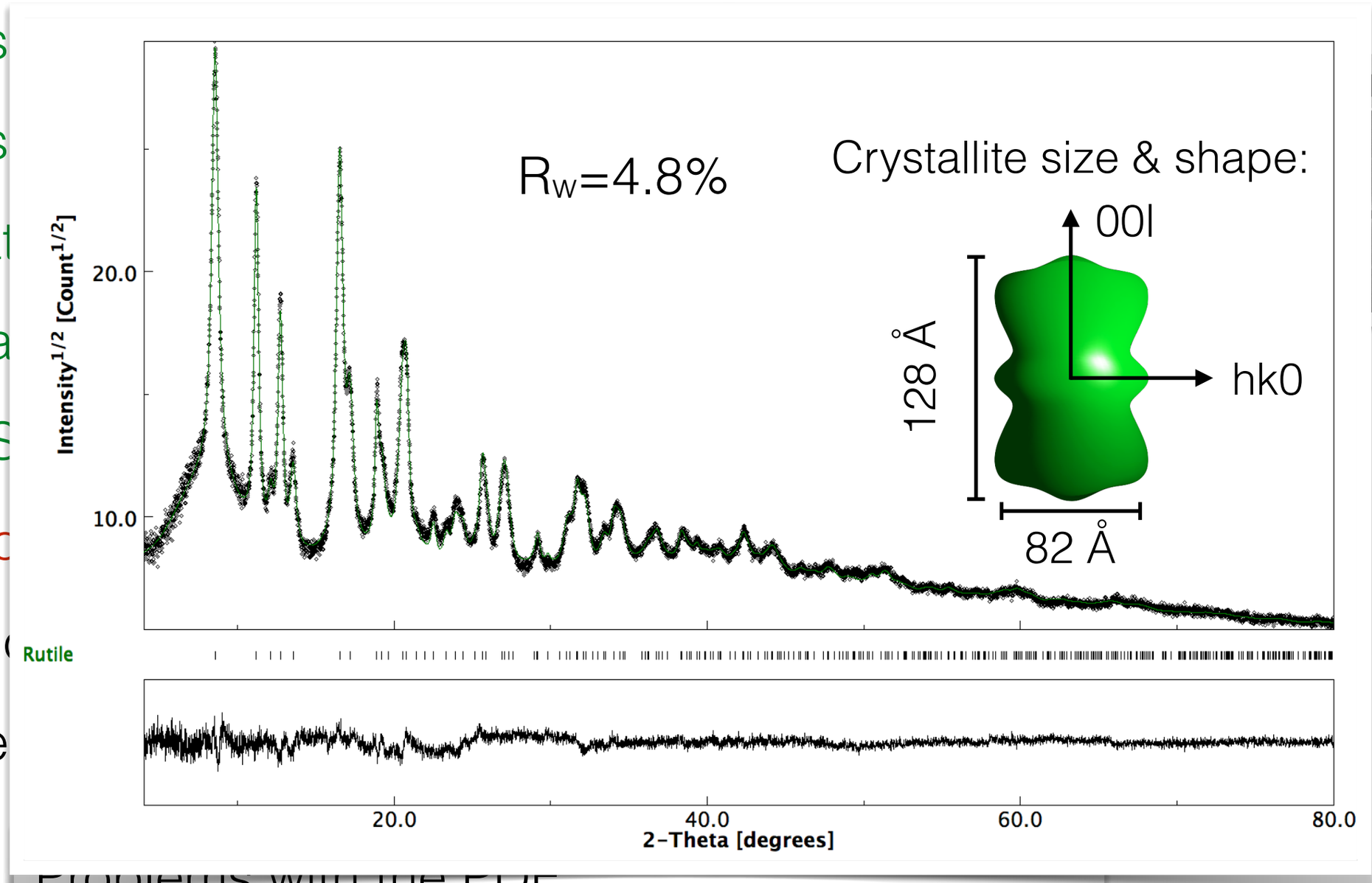

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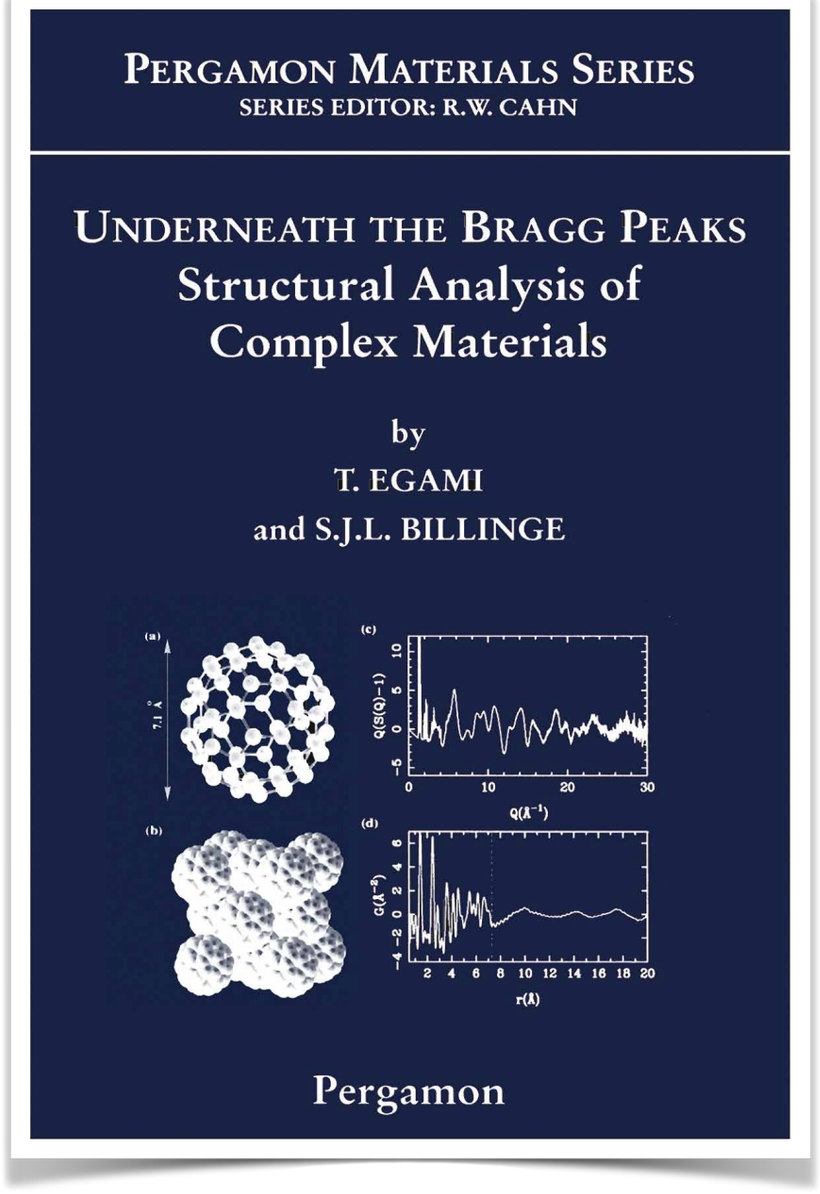
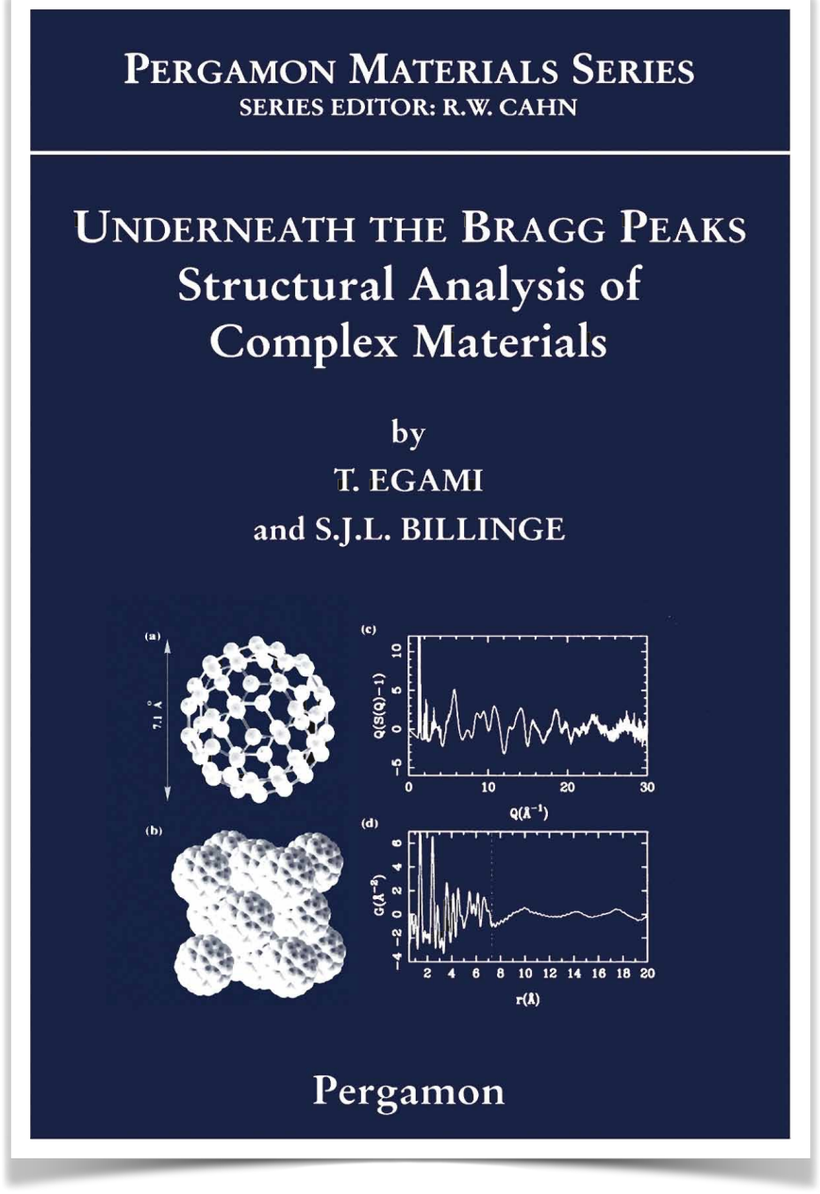


PDF with the Rietveld?

6.3. Modeling the PDF
- 6.3.1 Real-Space Rietveld Analysis
  - 6.3.1.1. Example of Real-Space Rietveld: PDFfit
  - 6.3.1.2. Real-Space Rietveld Example: $Yba_2Cu_3O_{6+\delta}$
- 6.3.2 Monte-Carlo Simulated Annealing Based Regression Schemes
- 6.3.3 Empirical Potential Based Modeling Schemes



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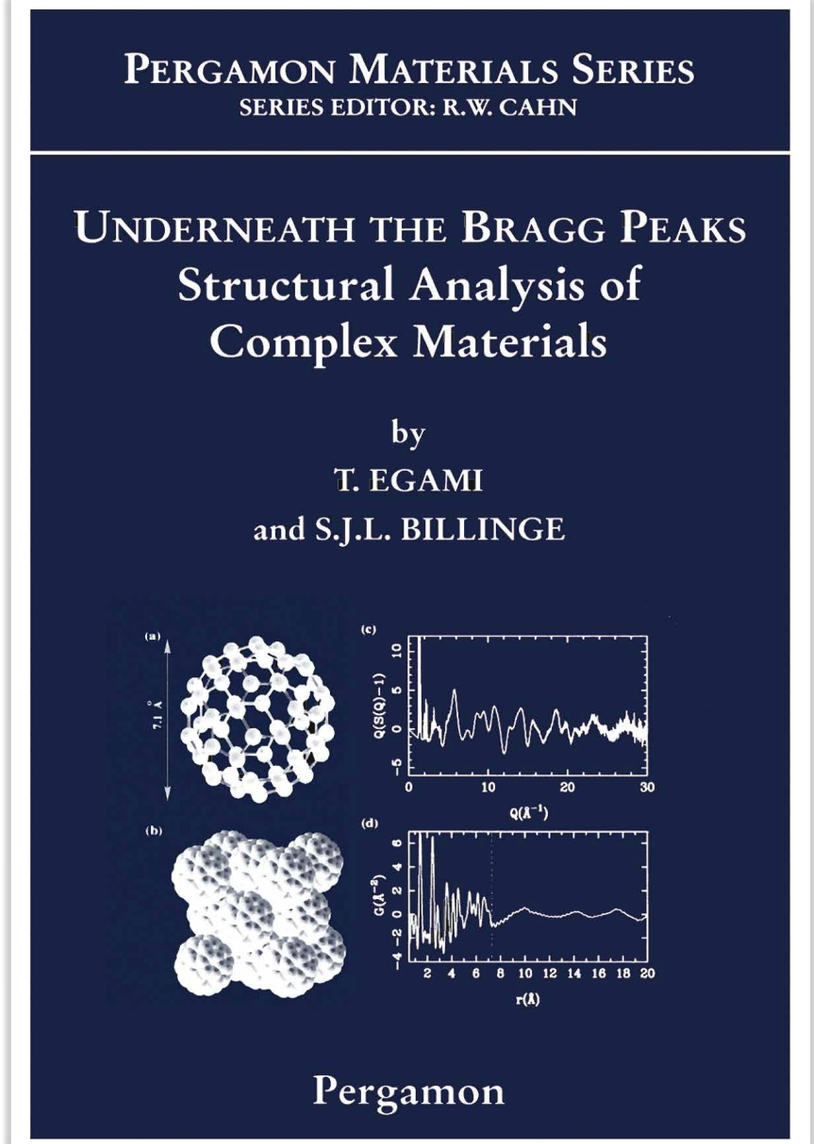
- Use large range in Q (10 $Å^{-1}$ or larger)
- Use proper statistic modifiers during refinement
- Add diffuse computation (?)
- More sensitivity to light atoms and small distorsions (like PDF)



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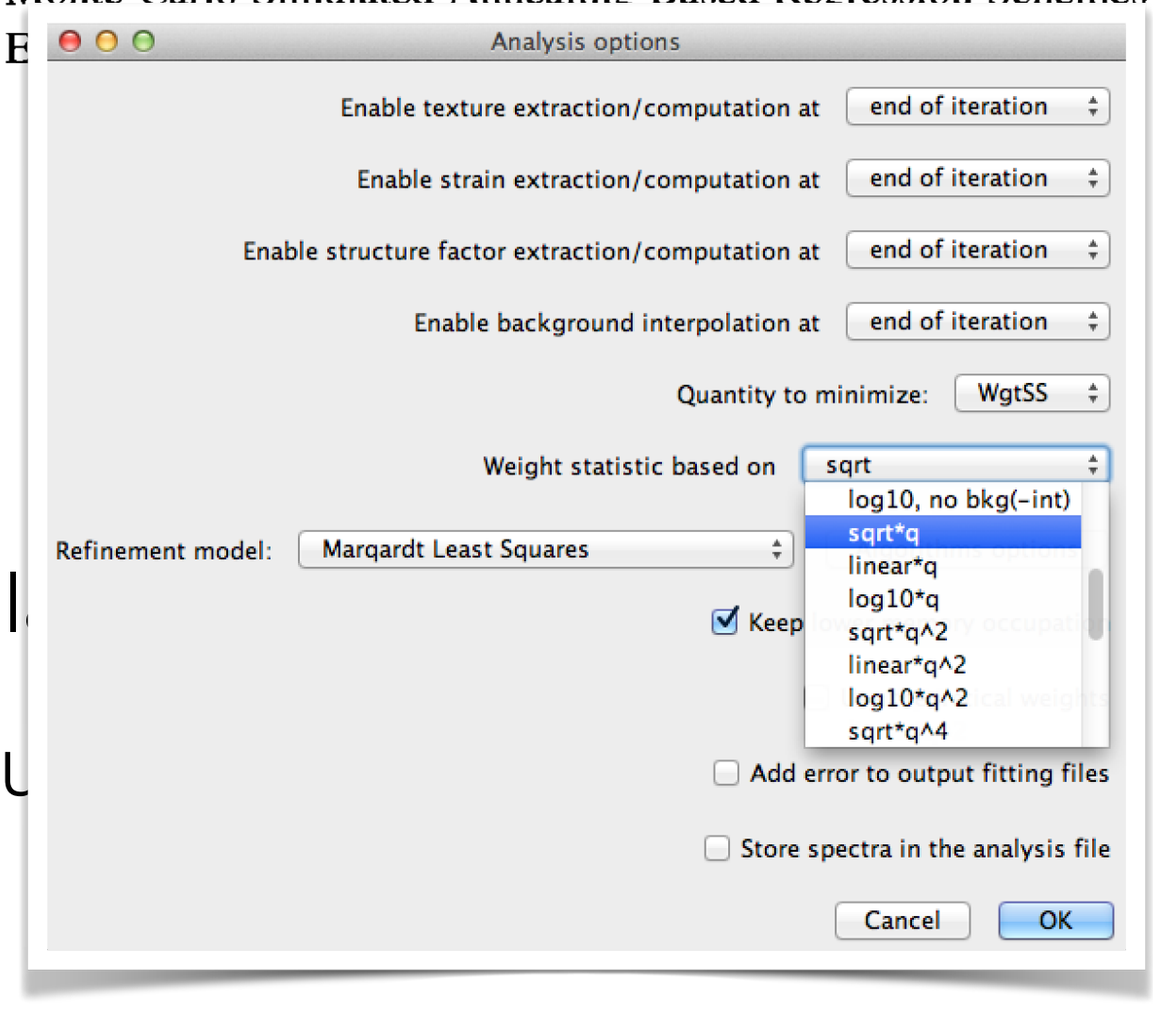

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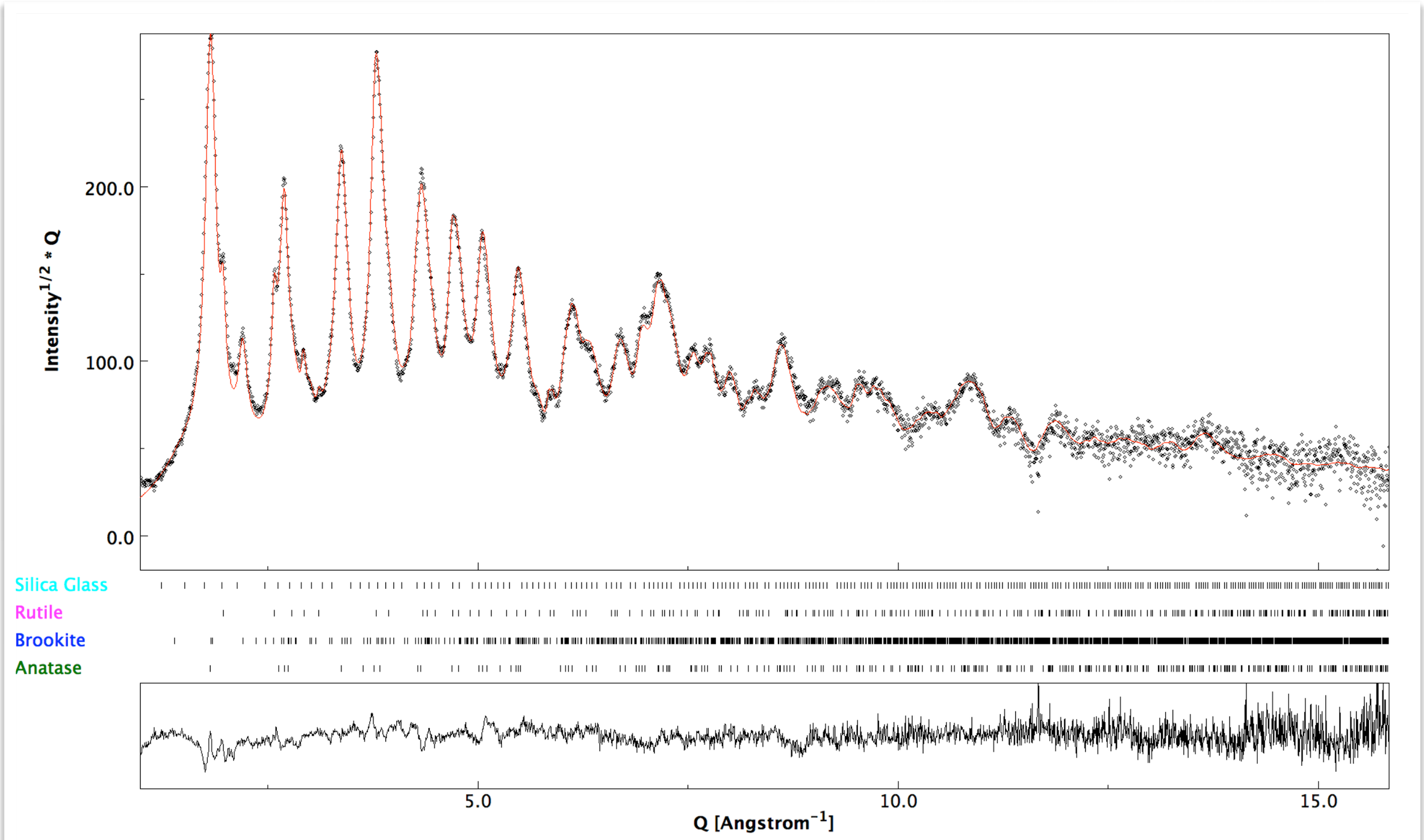
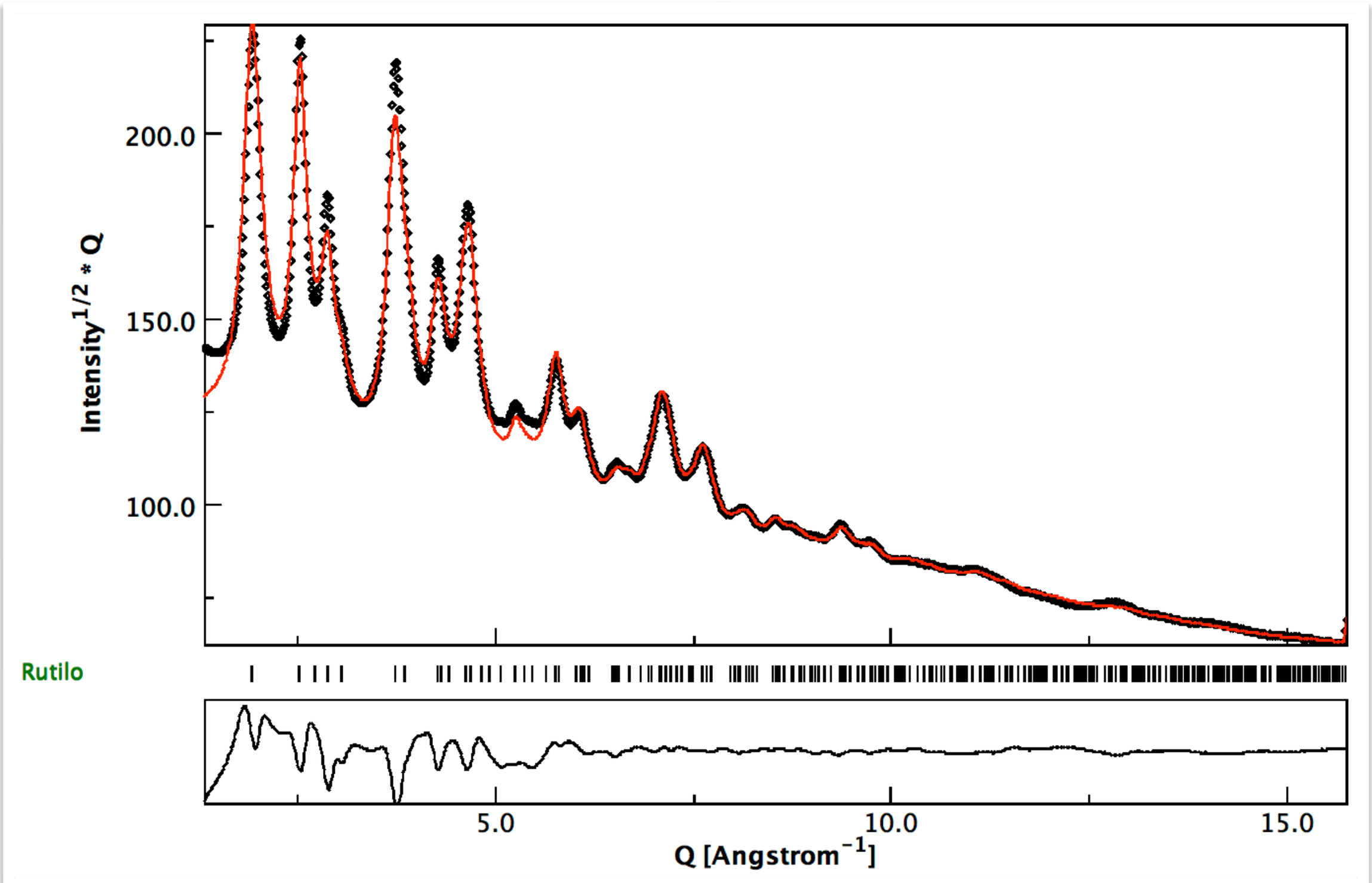
We are not limited to one phase



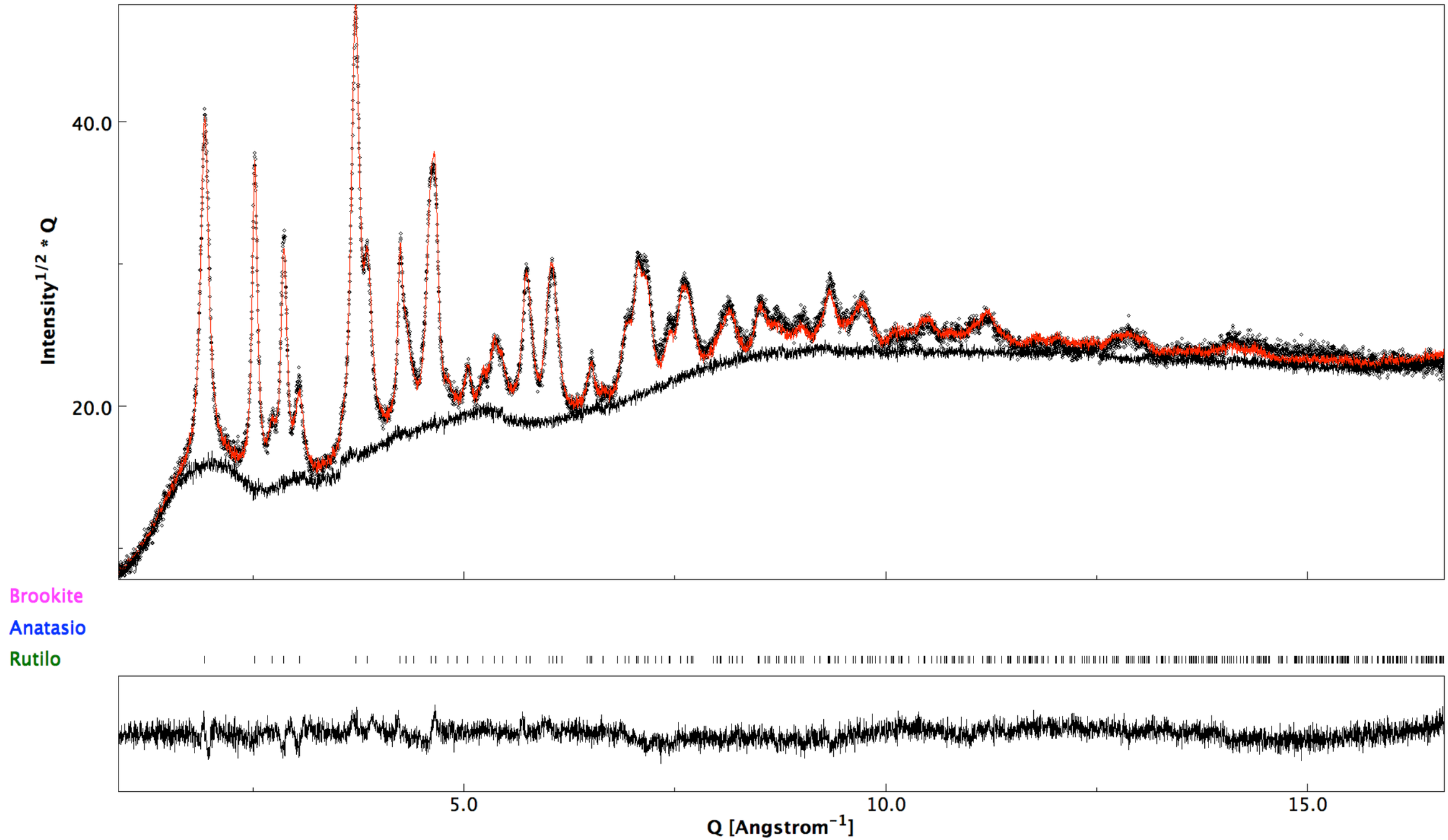
INEL CPS 120˚ Ag Kα, capillary sample holder

Works with electron diffraction



We can apply the Blackman dynamical correction

TiO_2 @ MARS-Soleil



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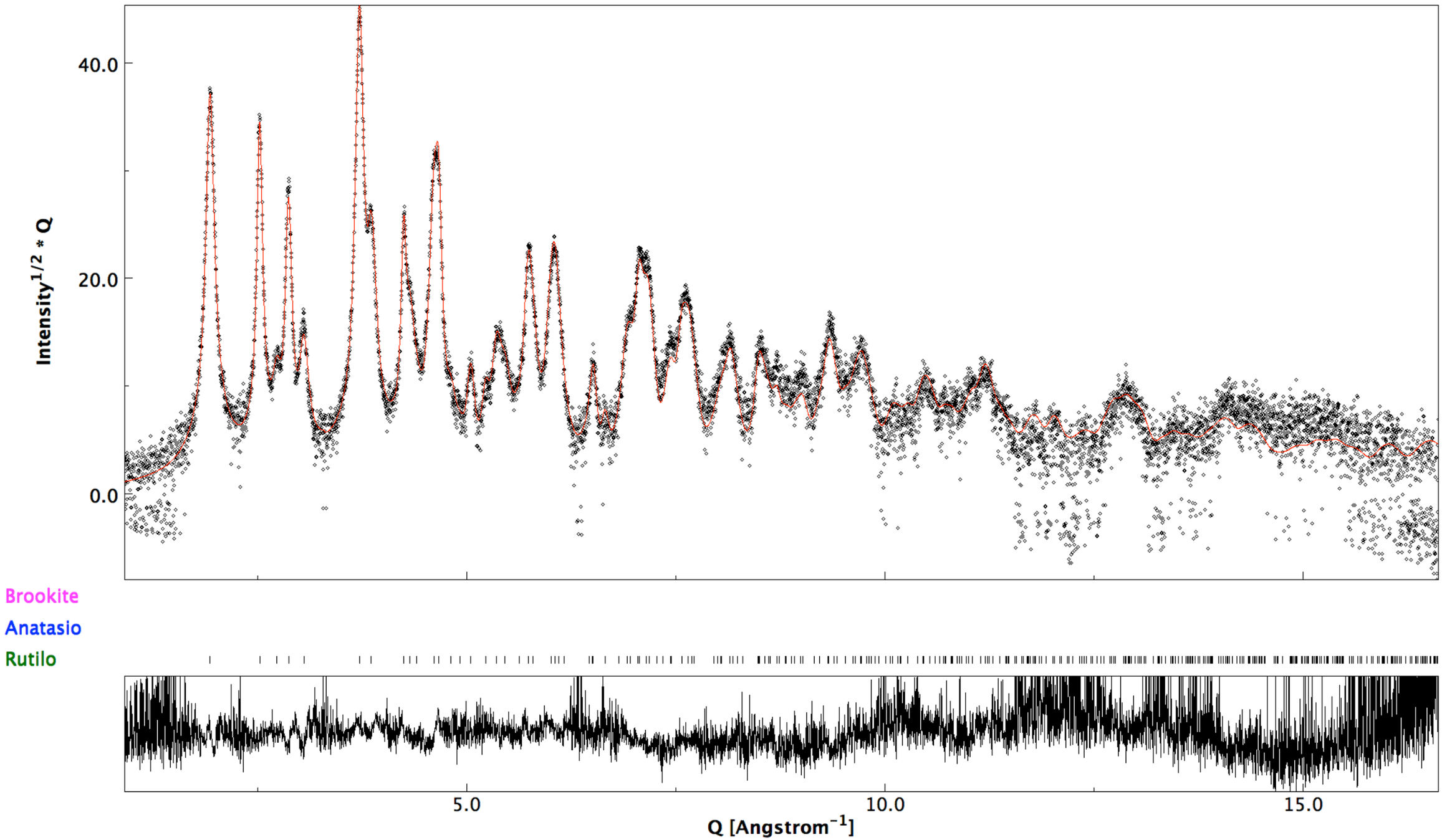
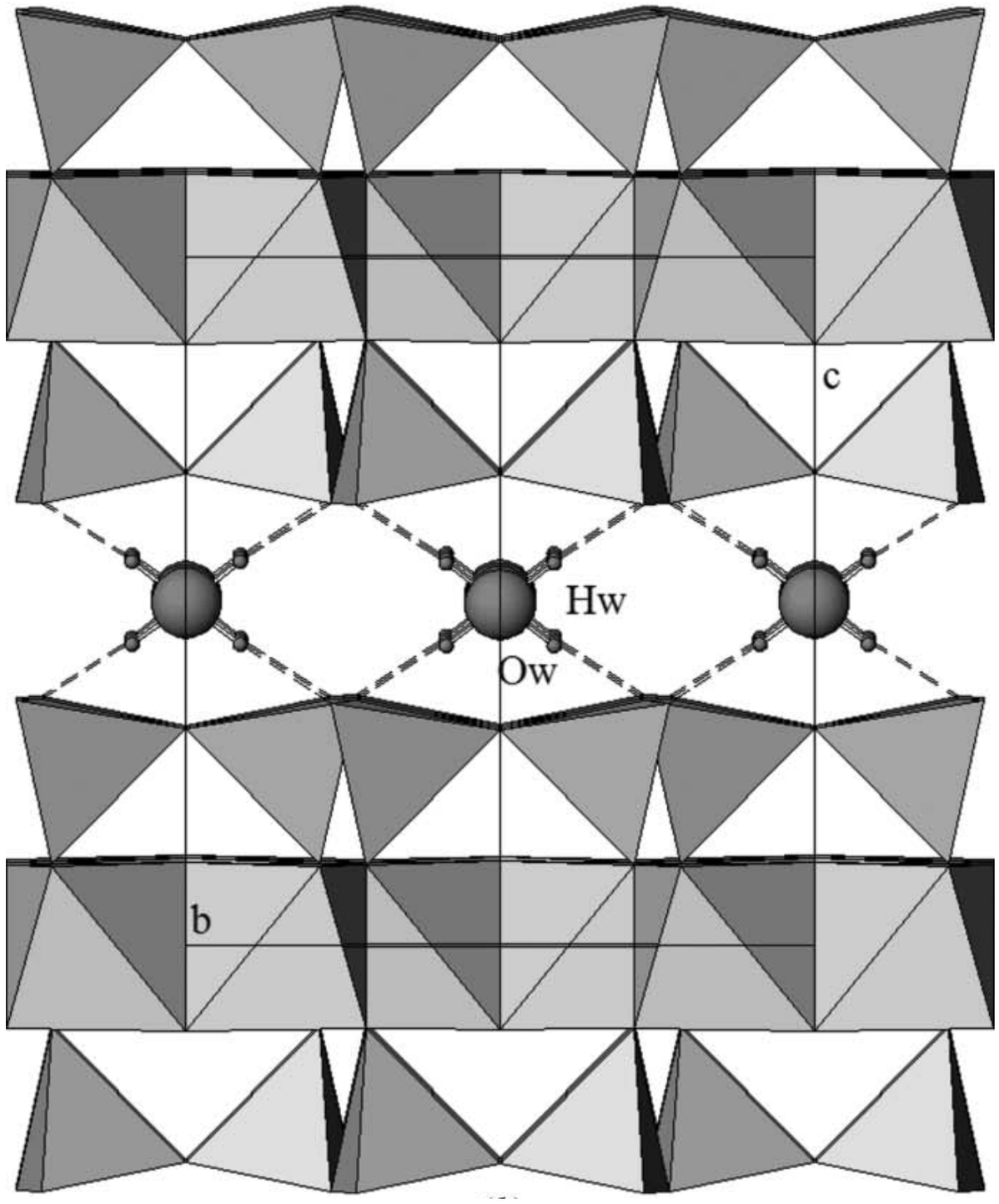




Smectite layers and interlayers water

The material

- STx-1 Ca-montmorillonite from Texas (american Clay Society)
- Samples prepared by cold pressing (uniaxial)
  - Sample 1: 10 MPa / 7 days (porosity: 36.5 %)
  - Sample 2: 15 MPa / 10 days (porosity: 17.4 %)
- Thomsen parameters:

sample	ε	Υ
1	0.06	0.02
2	0.24	0.1

XRD measurement at APS (Argonne)

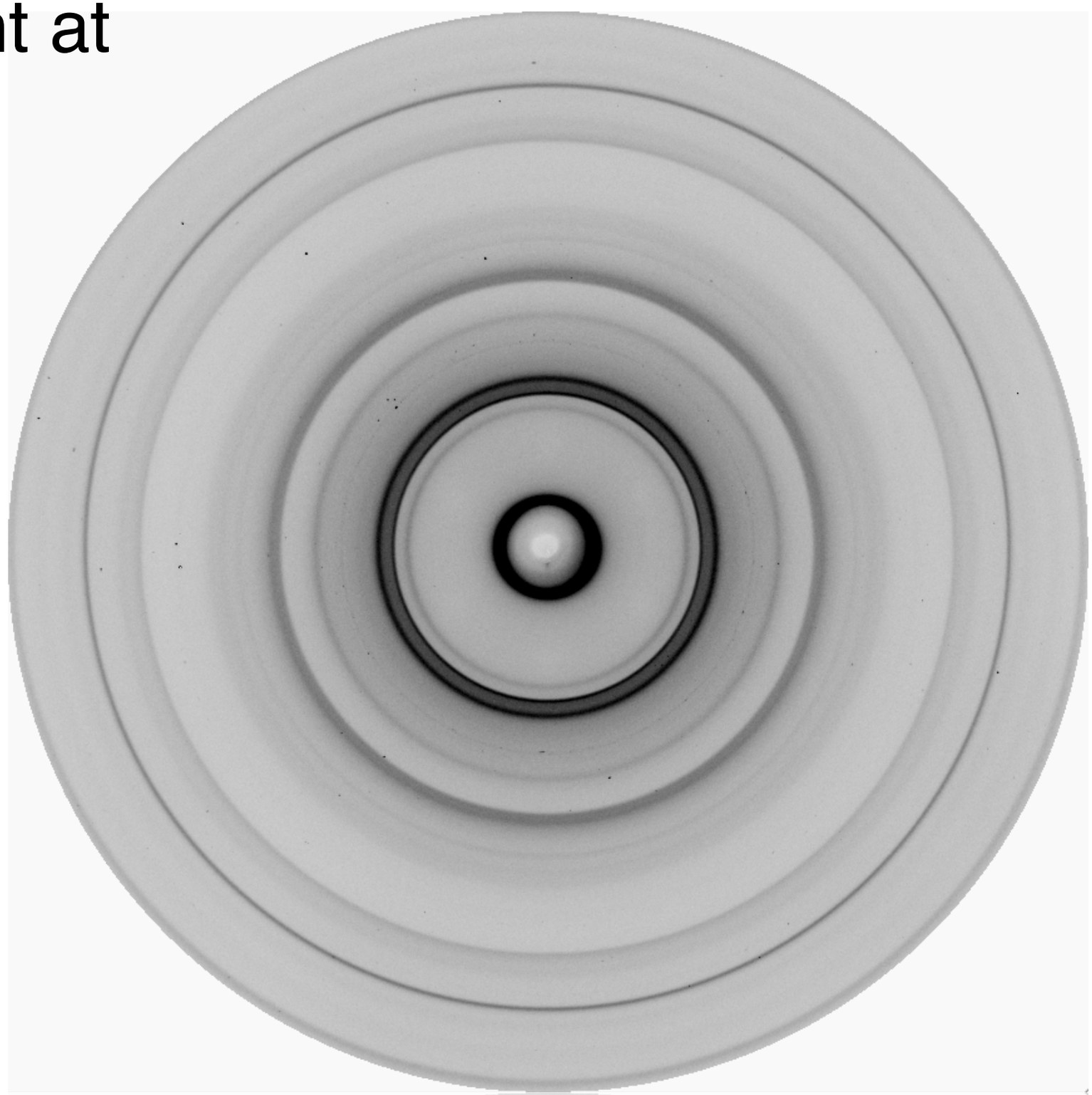
Slab of 3 mm cut from the compressed cylinder

BESSRC 11-ID-C (with Mar345 image plate detector)

Transmission geometry

$\lambda = 0.107877$ Å

Compression axis perpendicular to beam



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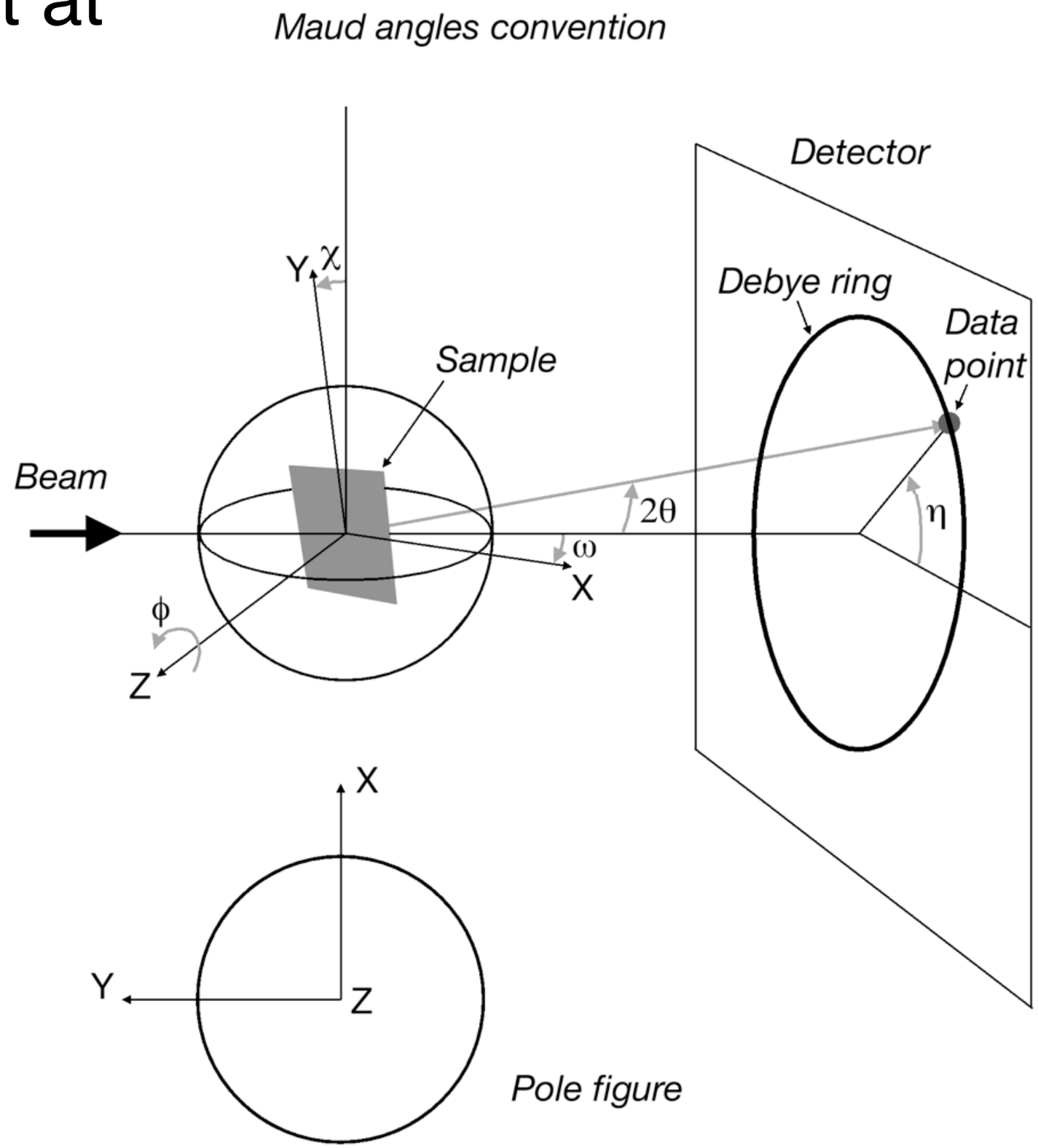
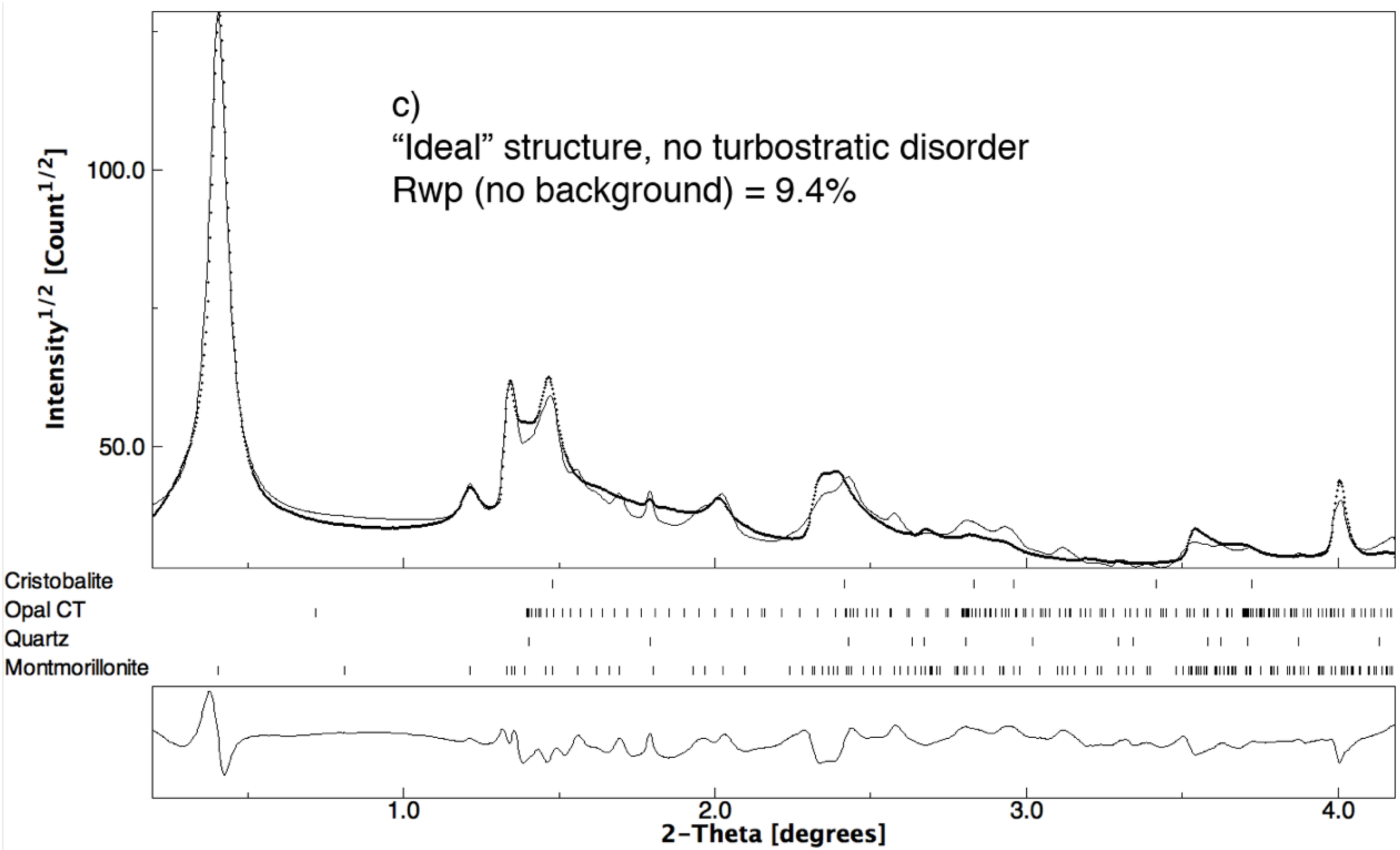


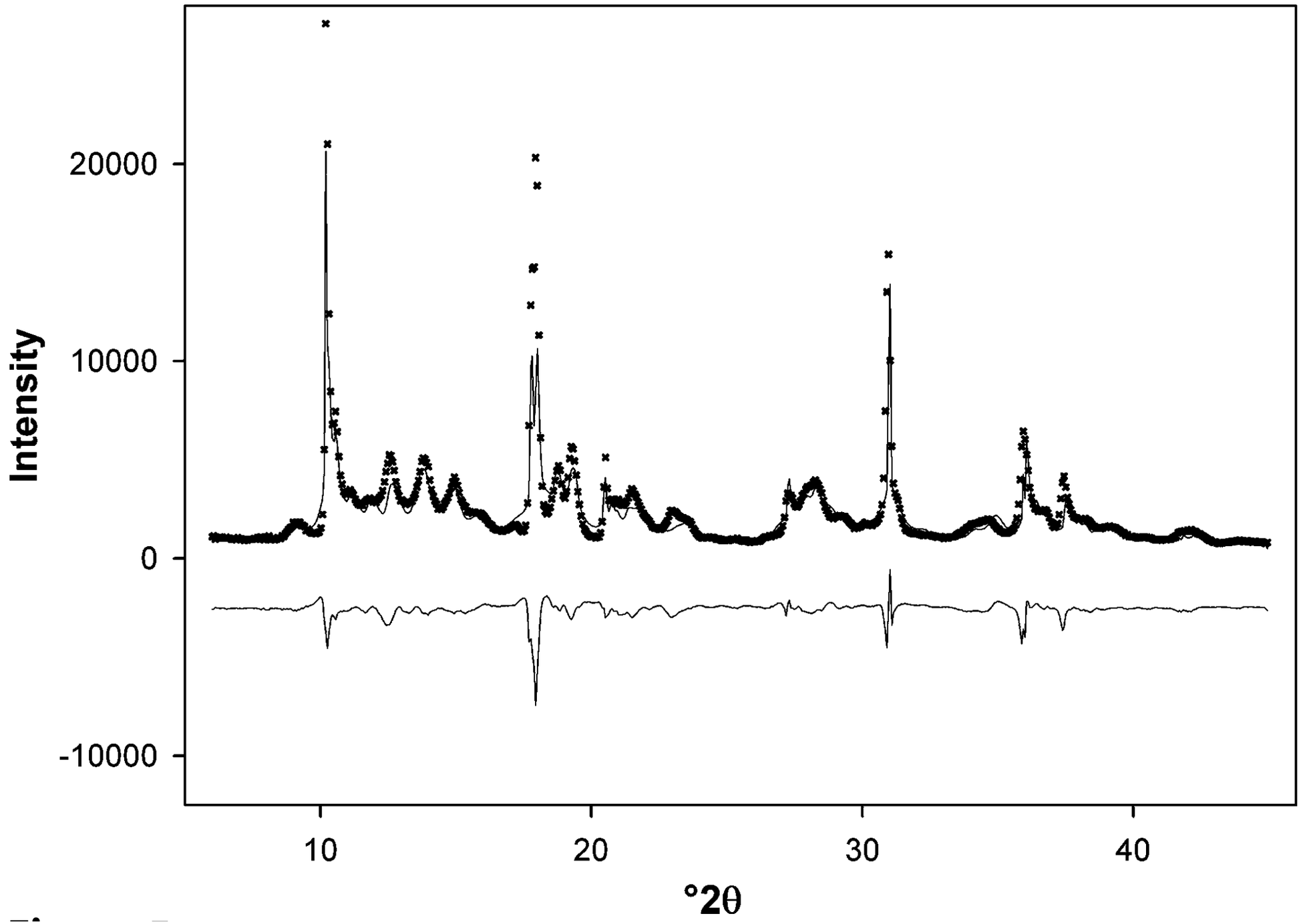
Rietveld texture analysis

- Maud program: images sampled in 72 patterns
- Crystal structure refinement: Rietveld with fragments
- Microstructure:
    - Popa anisotropic model for crystallite sizes and microstrains
    - Single Layer model for turbostratic disorder
- Texture: standard functions (EWIMV in the first step)
- Phases: Montmorillonite, Opal-CT, Quartz

Crystal structure refinement (texture)

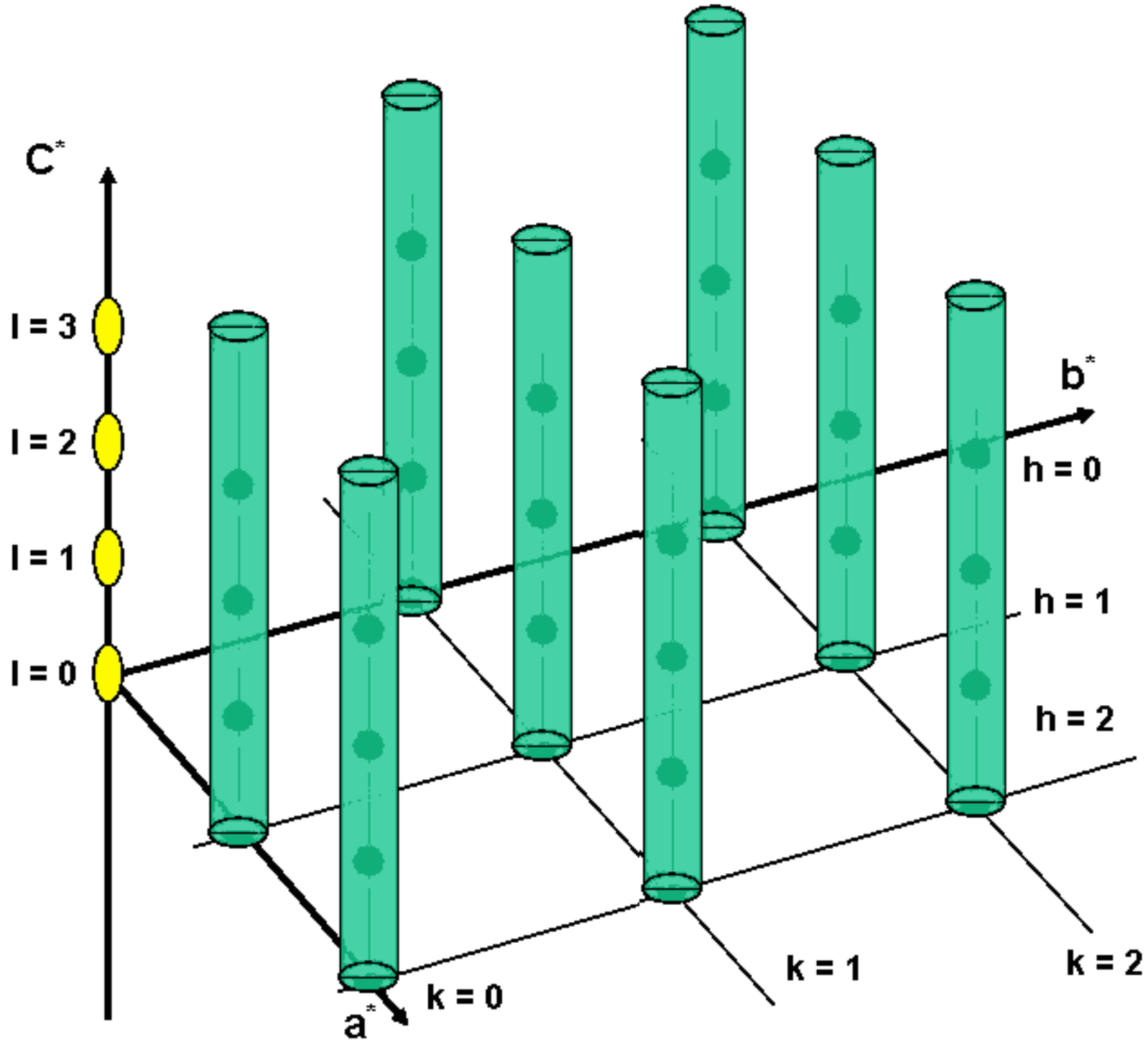


DiffaX+ simulation



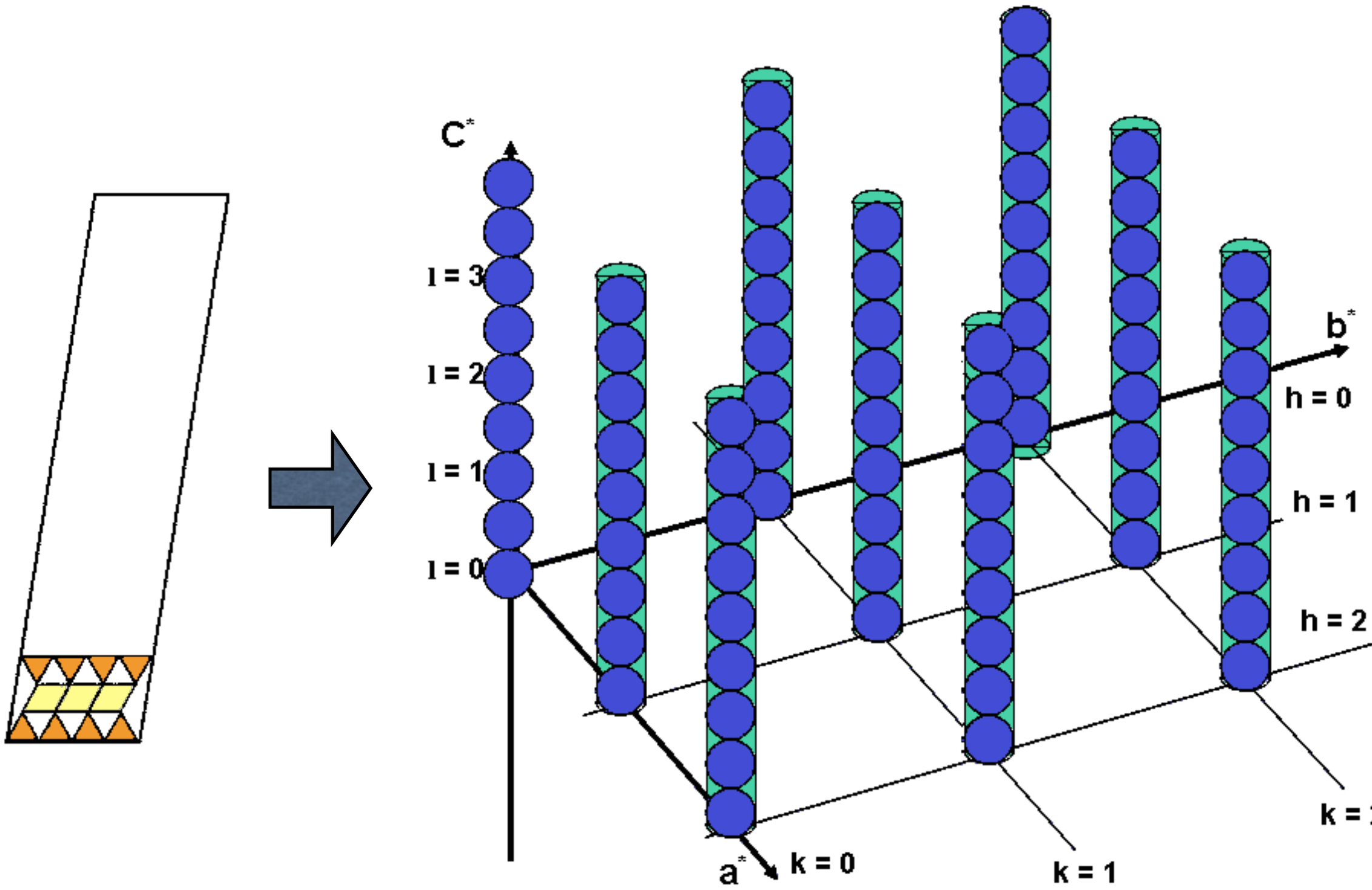
Gualtieri et al., J. Appl. Cryst., (2008) 41, 402-415

Turbostratic disorder: reciprocal lattice



Ufer et al., (2004), Z. Kristallogr. 219: 519-527

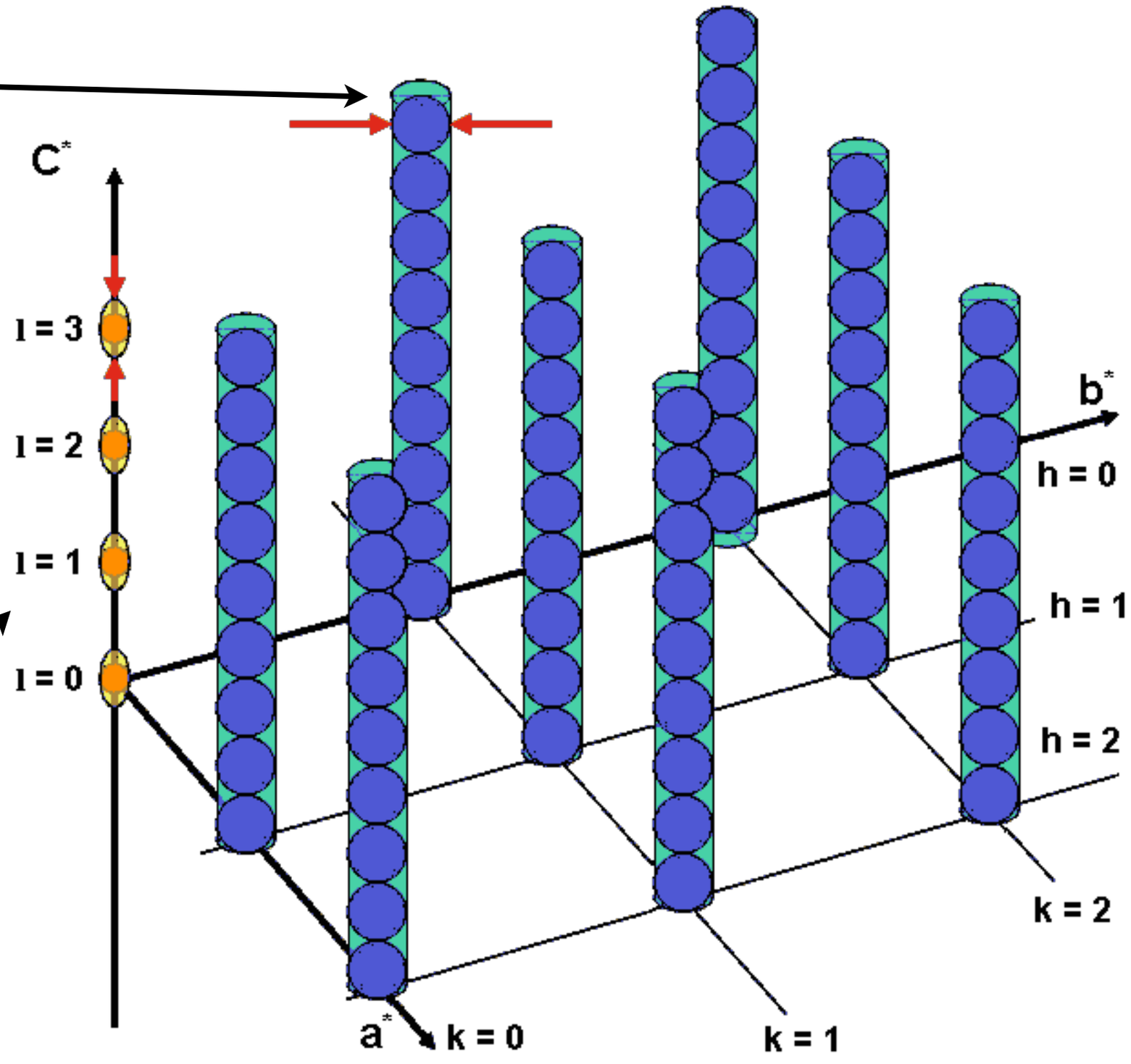
Single layer model



Ufer et al., (2004), Z. Kristallogr. 219: 519-527

Final model: 00l and line broadening

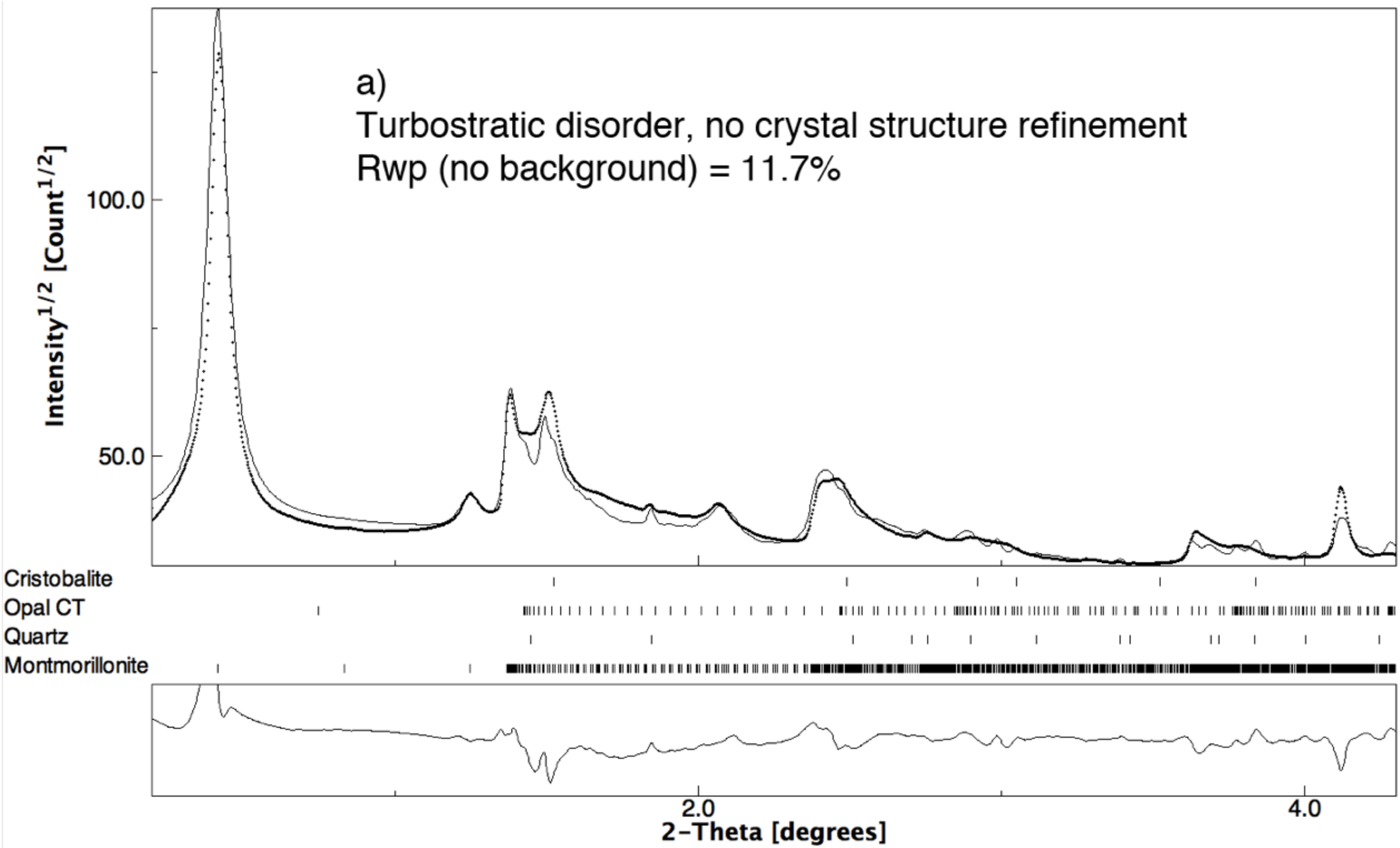
Additional or reduced broadening



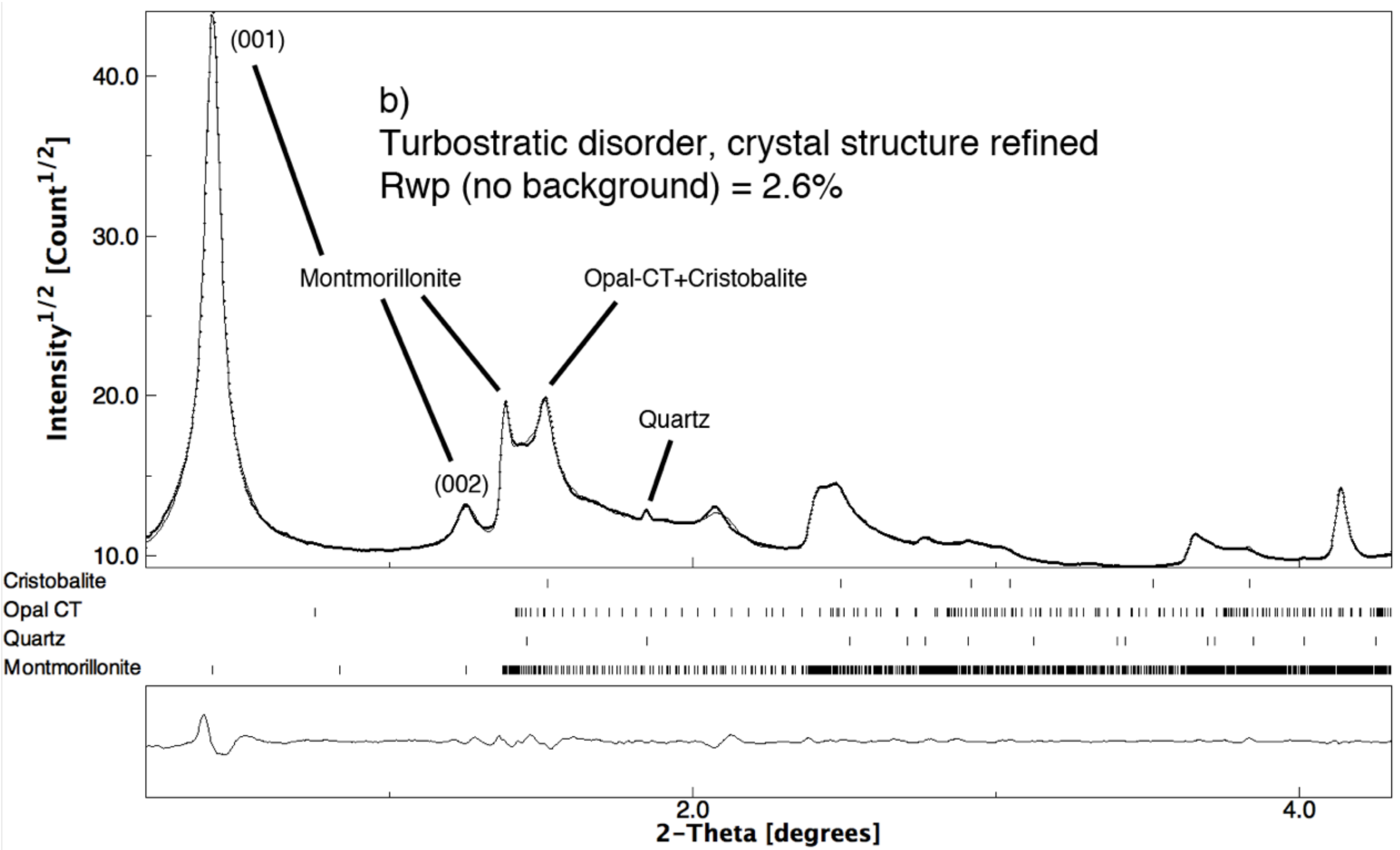
00l intensities are computed from the original structure (no supercell)

Ufer et al., (2004), Z. Kristallogr. 219: 519-527

Single layer model - ideal structure



Final crystal structure refinement



Crystallite sizes & microstrains

Sample 1

hkl direction	*Crystallite size (Å)*	*Microstrain ($x10^{-3}$)*
001	196	17.5
010	427	0.053
100	622	0.11
110	679	0.32

Sample 2

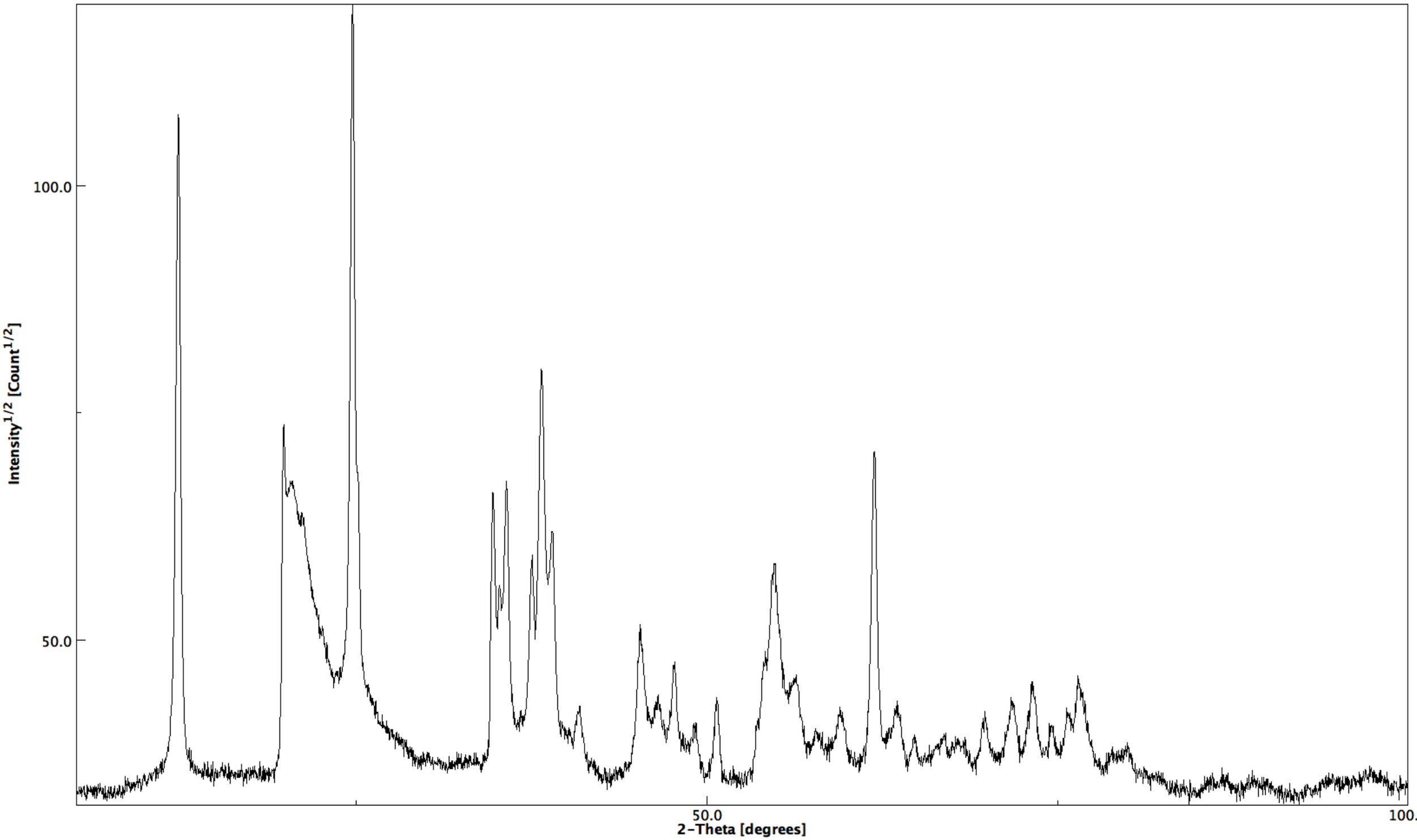
hkl direction	*Crystallite size (Å)*	*Microstrain ($x10^{-3}$)*
001	293	22.3
010	434	0.023
100	686	0.01
110	655	1.75

Other results

Sample	Opal-CT	Quartz
1	8%	0.2%
2	7%	0.3%

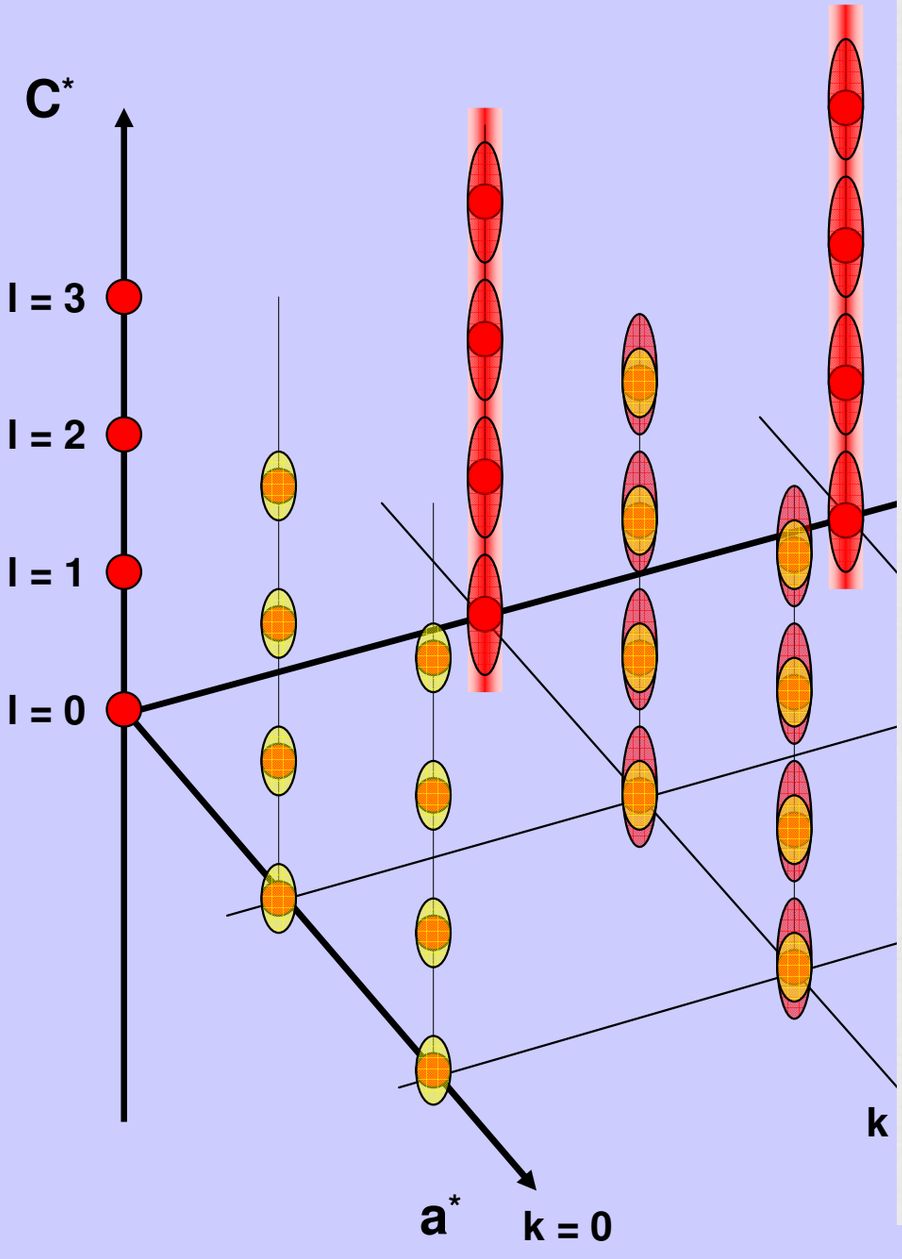
- No Al in cis-sites
- Water/Ca occupation around 40%

Kaolinite: modulated disorder



Kaolinite: modulated disorder

Kleeberg, Ufer, Bergmann, CMS 05



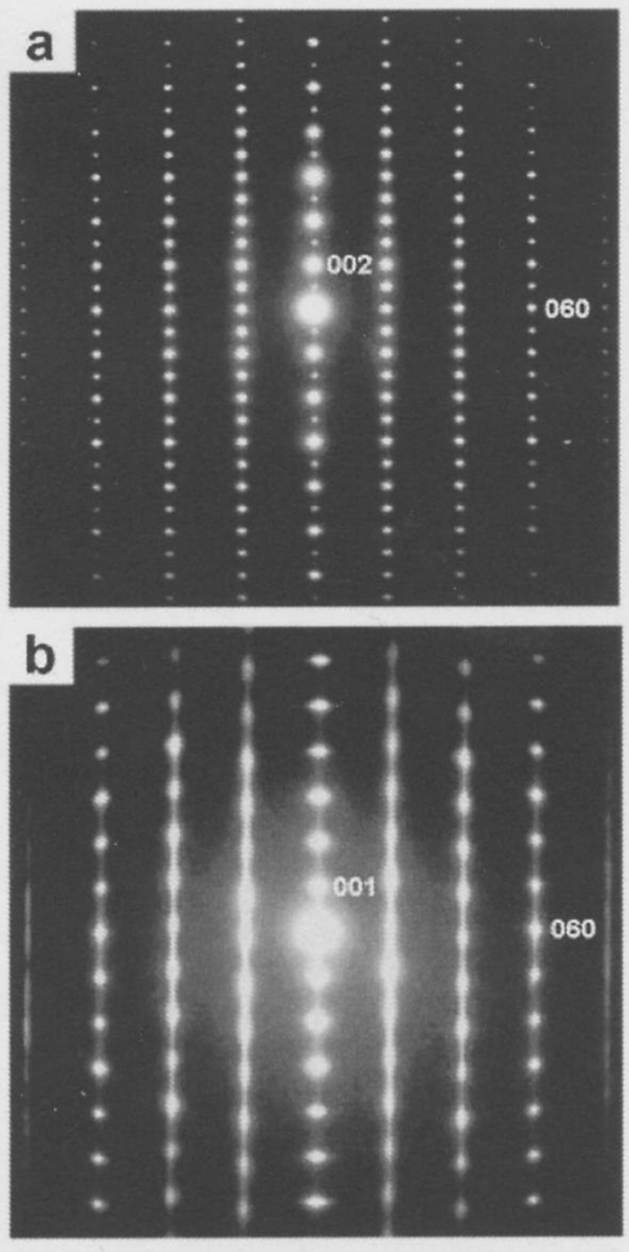
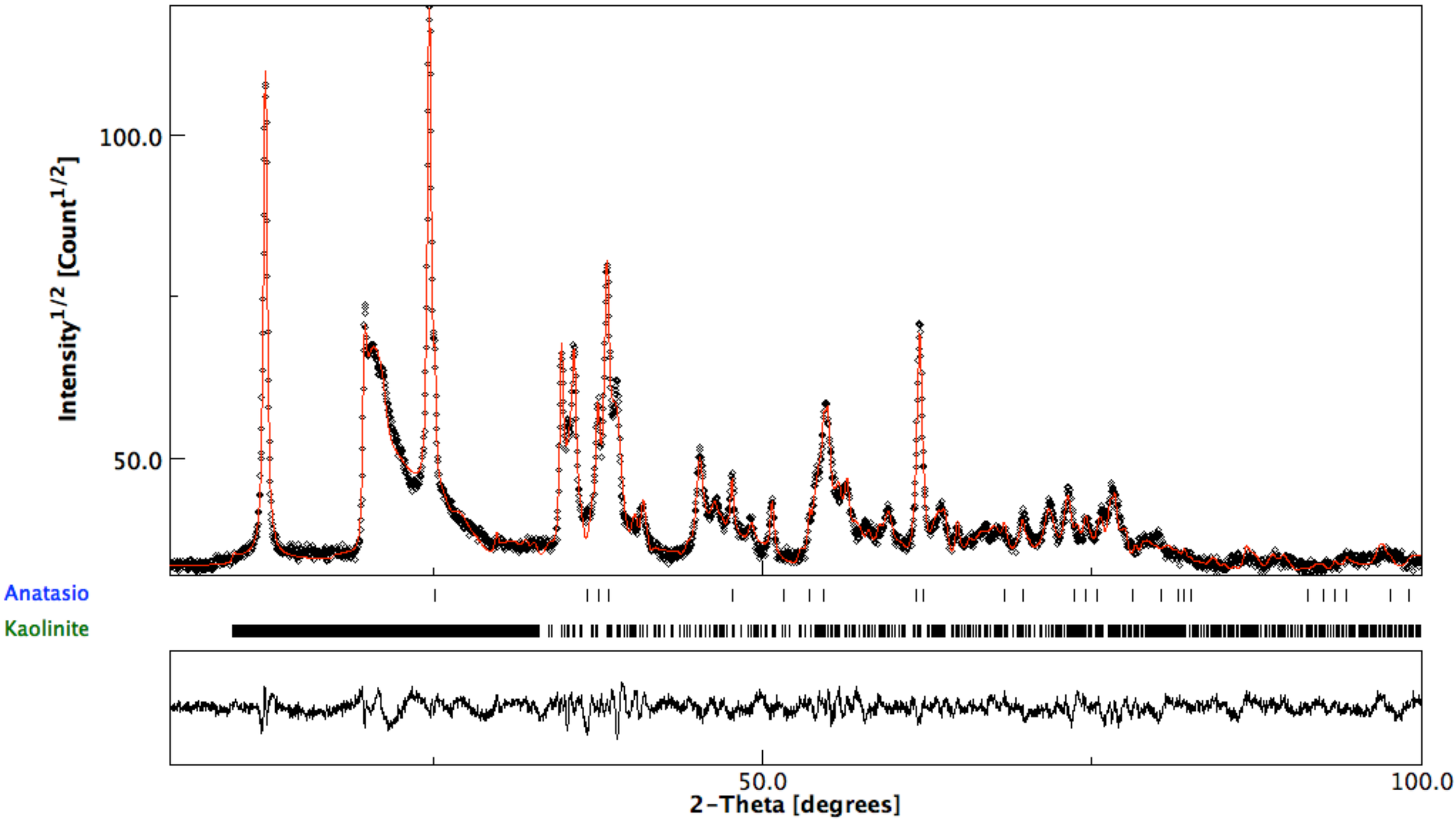


FIGURE 5. Selected-area diffraction patterns from (**a**) dickite and (**b**) kaolinite, with the beam direction parallel to [100]. Note that no streak exists in (**a**) but 0*kl* reciprocal rows are heavily streaked in (**b**).

Kogure & Inoue, 2005

Kaolinite: modulated disorder



Kaolinite: modulated disorder