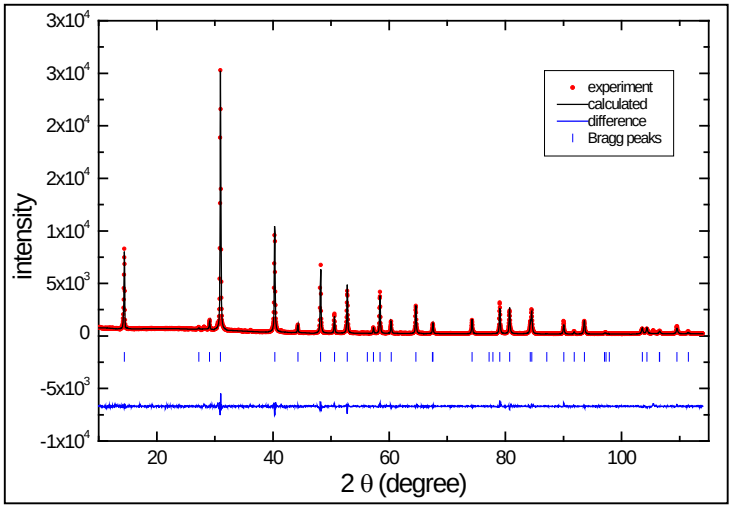
Powder structural refinement and microstructure

Rietveld method
expression of diffracted intensity



Function To minimize: $M = \sum P_i (Y_i - Y_{ci})^2$

with : $P_i = 1 / Y_i$ **(least square refinement)**

$$Y_{ci} = Y_{bi} + \sum_{\Phi=1}^{N} S_\Phi \sum_k J_{\Phi k} \cdot Lp_{\Phi k} \cdot O_{\Phi k} \cdot |F_{\Phi k}|^2 \cdot \Omega_{i\Phi k}$$

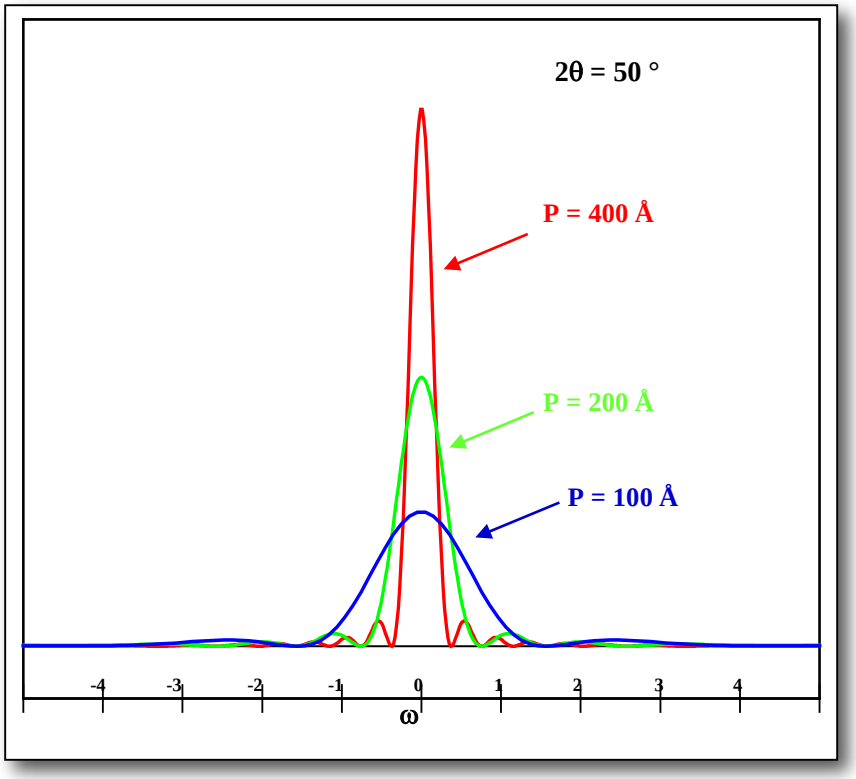
$$F(hkl) = \sum_{atoms} f_j \exp\left\{2\pi i\left(hx_j + ky_j + lz_j\right)\right\}$$

Y_{bi}	:background at point *i*
S_Φ	:scale factor for phase Φ
$J_{\Phi k}$	:multiplicity of reflection *k*
$Lp_{\Phi k}$	:Lorentz / polarization factor
$O_{\Phi k}$	:preferred orientation for reflection *k*
$F_{\Phi k}$	:scale factor for phase Φ
$\Omega_{i\Phi k}$	:profile function (instrument + sample)

intensity and peak profile

Diffracted intensity $\propto |F^2|$

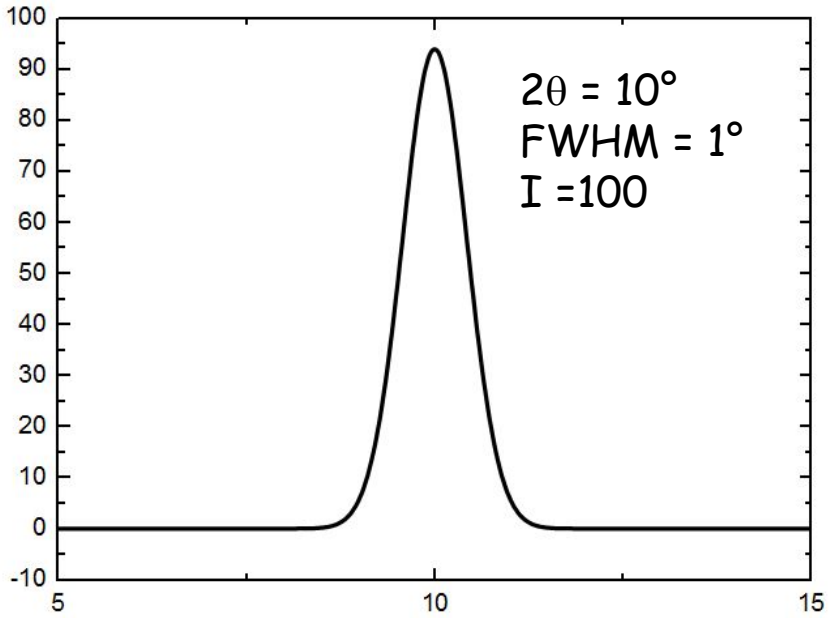
Reminder: reflexion intensity = reflexion area



Necessity to model reflection profiles to extract their intensity

Gaussian peak profile

$$G(\varepsilon) = a_G \exp\left(-b_G \varepsilon^2\right) \qquad \left(\varepsilon = 2\theta_i - 2\theta_k\right)$$



$$a_G = \frac{2}{H}\sqrt{\frac{\ln(2)}{\pi}}$$

$$b_G = \frac{4\ln(2)}{H^2}$$

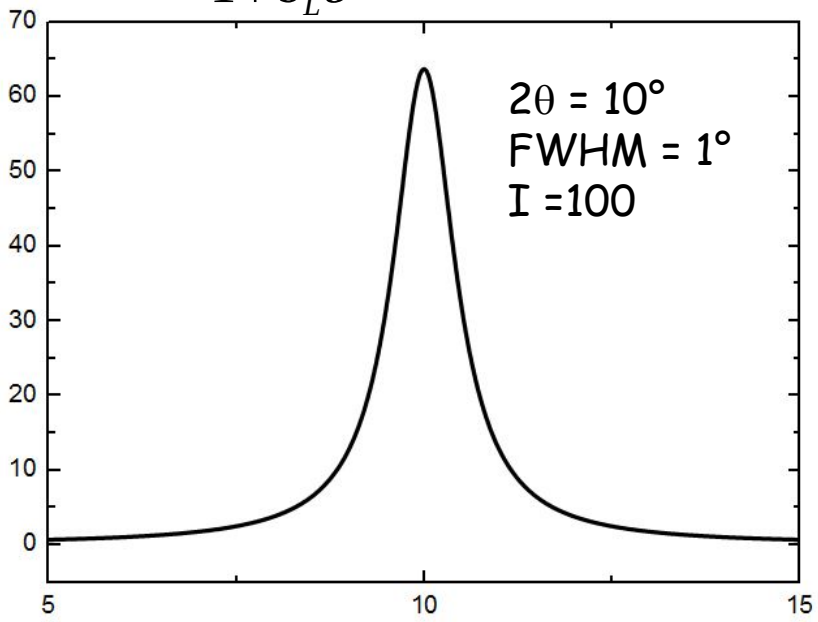
2 Gaussian convolution:

$$G\left(\varepsilon, H_{G_1}\right) \otimes G\left(\varepsilon, H_{G_2}\right) = G\left(\varepsilon, H_G\right)$$

$$H_G = \sqrt{H_{G_1}^2 + H_{G_2}^2}$$

Lorentzian peak profile

$$L(\varepsilon) = \frac{a_L}{1 + b_L \varepsilon^2} \qquad (\varepsilon = 2\theta_i - 2\theta_k)$$



$$a_L = \frac{2}{\pi H}$$

$$b_L = \frac{4}{H^2}$$

2 Lorentzian convolution:

$$L(\varepsilon, H_{L_1}) \otimes L(\varepsilon, H_{L_2}) = L(\varepsilon, H_L)$$

$$H_L = H_{L_1} + H_{L_2}$$

Actual peak profile or its best approximation…

Gaussian an Lorentzian convolution: Voigt's function

$$G(\varepsilon, H_G) \otimes L(\varepsilon, H_L) = V(\varepsilon, H_G, H_L)$$

Mathematically complex. Very often approximated by the **pseudo-Voigt** function:

$$pV(\varepsilon) = \eta L(\varepsilon) + (1-\eta) G(\varepsilon)$$

$$pV(\varepsilon) = pV(\varepsilon, \eta, H) \qquad H^2 = FWHM^2 = U \tan^2\theta + V \tan\theta + W$$

Caglioti G. , Paoletti A., Ricci F.P., Nuclear Instruments 3 223–228, (1958) .

Drawback: The two width components are considered to present the same variation versus 2θ.

The **Thompson, Cox and Hastings (TCH)** function makes it possible to approach the Voigt's function as well as possible.

a posteriori modeling of peak profiles

- *TCH* (modified Thompson-Cox-Hastings):

with :

$$\eta = 1.36603q - 0.47719q^2 + 0.1116q^3$$

$$q = H_L / H$$

$$H = \left(H_G^5 + AH_G^4 H_L + BH_G^3 H_L^2 + CH_G^2 H_L^3 + DH_G H_L^4 + H_L^5\right)^{0.2} = FWHM$$

A = 2.69269, *B* = 2.42843, *C* = 4.47163 et *D* = 0.07842

$$H_G = (U\tan^2\theta + V\tan\theta + W + P/\cos^2\theta)^{1/2}$$

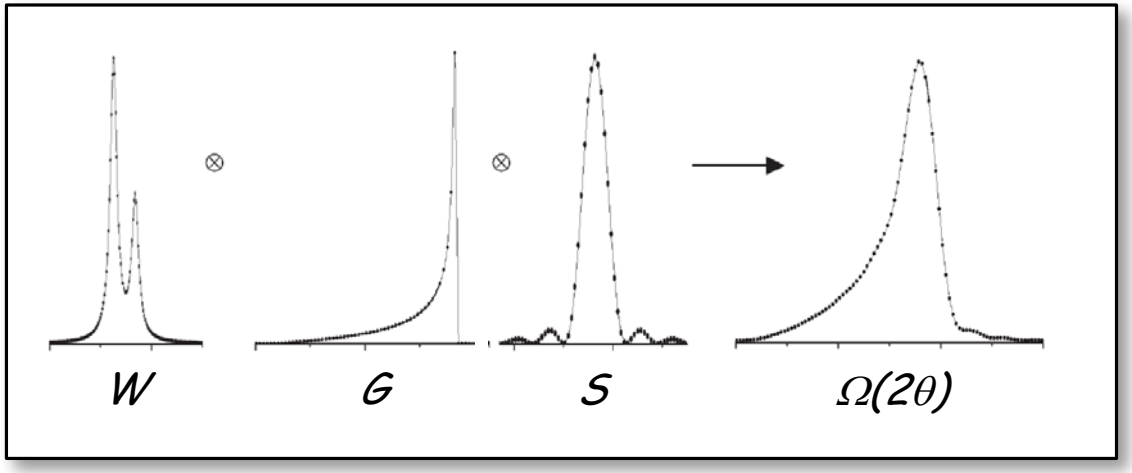
$$H_L = X\tan\theta + Y/\cos\theta$$

Caution: X and Y can be reversed in some refinement software!

Parameters for instrument resolution

classical determination

$$\Omega(2\theta) = \underbrace{(W \otimes G)}_{\text{instrument}} \otimes S$$



A standard compound is used to determine the instrument resolution.

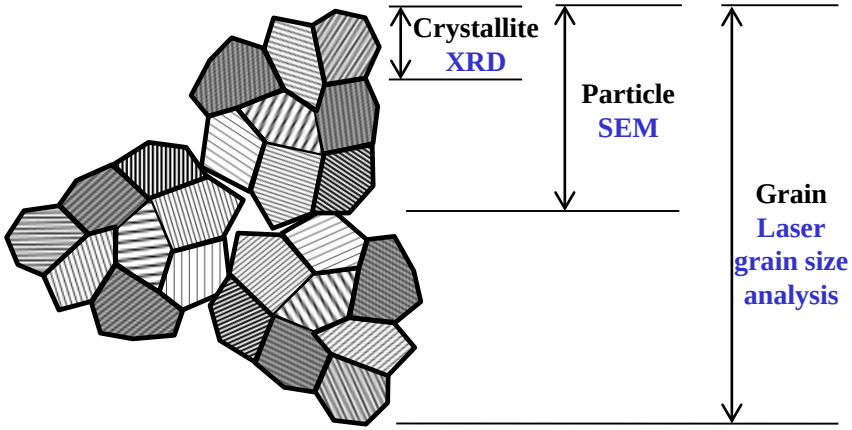
$Cu_{K\alpha}$	$U \approx 0$	$V \approx 0$	$W \approx 0.002$	$X \approx 0.035$	$Y \approx 0$
Synchrotron	$U \approx 0.001$	$V \approx 0$	$W \approx 0.001$	$X \approx 0$	$Y \approx 0$

X-ray lab: $H_G = W^{1/2}$ and $H_L = X.\tan\theta$

With principally: X, spectral distribution and W, source focus profile and reception slit width.

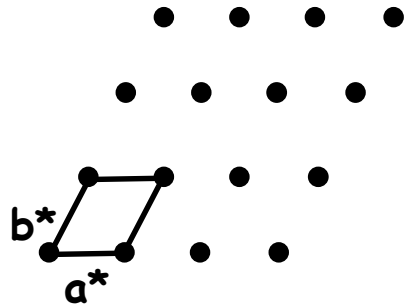
Crystallite size and micro-strain

Crystallite size:



Widening of reciprocal space nodes leading to a relaxation of the diffraction conditions (see Ewald sphere construction).

Homogeneous effect on all the nodes of the reciprocal space whatever their distance to the origin.

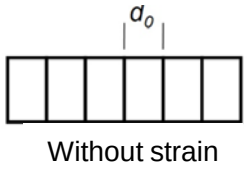


Widening of the Bragg reflections: $\beta = K\lambda / T\cos\theta$

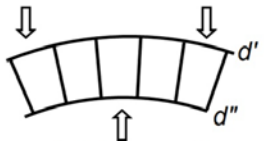
Micro-strain:

Local relaxation of the structure around a defect causing a distribution of inter-reticular distances around a mean distance d_0

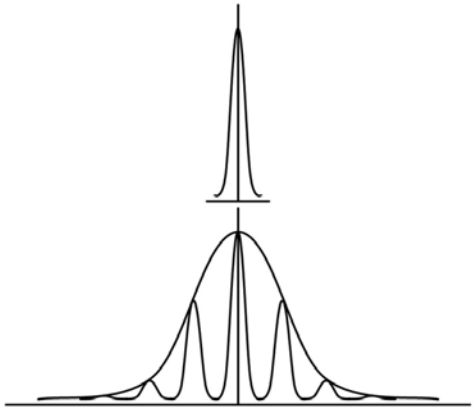
Quantification of the distortion by the upper limit of deformation: $\varsigma = \Delta d / d$

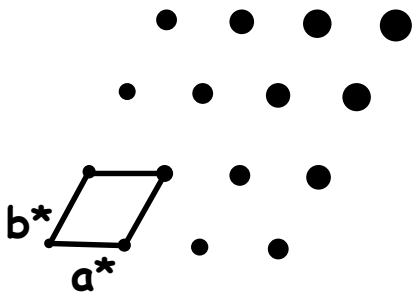


Without strain



With a non uniform strain





Widening of the Bragg reflections: $\beta = 4\varsigma\tan\theta$

Crystallite size and micro-strain
values from profiles

Matching with the *TCH* function terms

$$H_G = (U\tan^2\theta + V\tan\theta + W + P/\cos^2\theta)^{1/2}$$

$$H_L = X\tan\theta + Y/\cos\theta$$

Crystallite size: $\beta = K\lambda/T\cos\theta$

Micro-strain: $\beta = 4\varepsilon\tan\theta$

Crystallite size:

Isotropic : $T_L = \dfrac{180\cdot K\cdot\lambda}{\pi\cdot Y}$

Anisotropic : $T_{L\perp} = \dfrac{180\cdot K\cdot\lambda}{\pi\cdot Y}$ $\quad T_{L-} = \dfrac{180\cdot K\cdot\lambda}{\pi\cdot(Y+Y_e)}$

Micro-strain:

Isotropic :

$$\varepsilon_G(\%) = \frac{\pi}{1.8}\left[U - U_i\right]^{1/2}$$

$$\varepsilon_L(\%) = \frac{\pi}{1.8}\left[X - X_i\right]$$

Anisotropic :

$$\varepsilon_{G\perp}(\%) = \frac{\pi}{1.8}\left[U - U_i\right]^{1/2}$$

$$\varepsilon_{G-} = \frac{\pi}{1.8}\left[U + U_e - U_i\right]^{1/2}$$

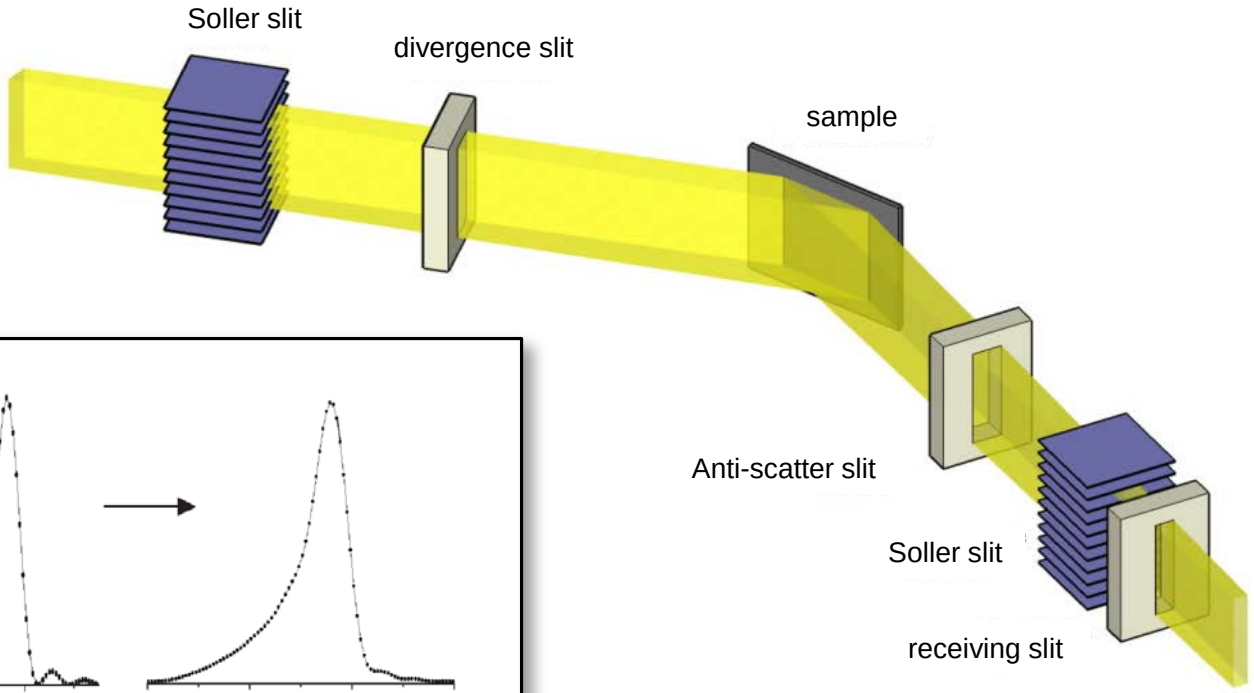
U_i, X_i: instrument contribution

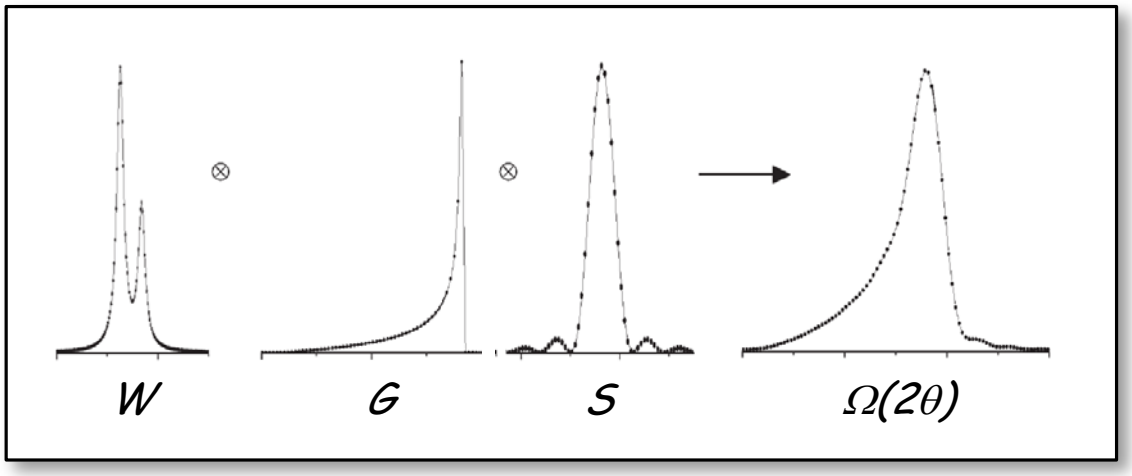
U_e, Y_e: anisotropy factor

Predefined instrument function
the so-called fundamental parameters approach

Profile function: from observation to anticipation

$$\Omega(2\theta) = (\underbrace{W \otimes G}_{\text{instrument}}) \otimes S$$

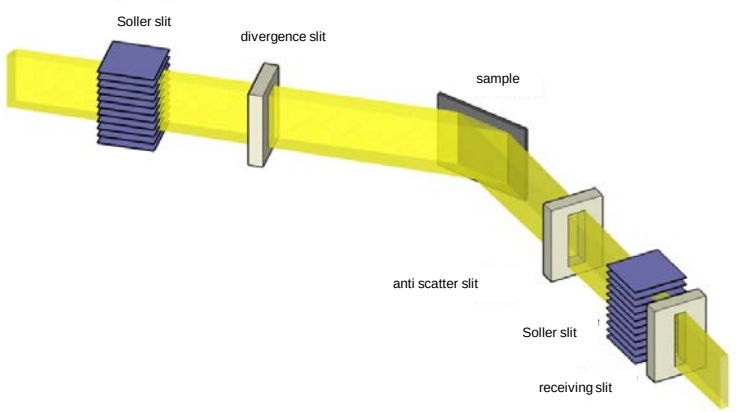




Predefined instrument function
the so-called fundamental parameters approach

A complete description of the diffractometer and its optics must be provided to the refinement program.

$$\Omega(2\theta) = \underbrace{(W \otimes G)}_{\text{instrument}} \otimes S$$



W : source emission profile
5 Lorentzian

G : diffractometer optics
- divergence slit
- receiving slit

} Radial divergence

- source length
- sample length
- Receiving slit length
- Soller slit

} Axial divergence

Crystallite size and **micro-strain** are the only variables of the refinement (S term of the profile function).

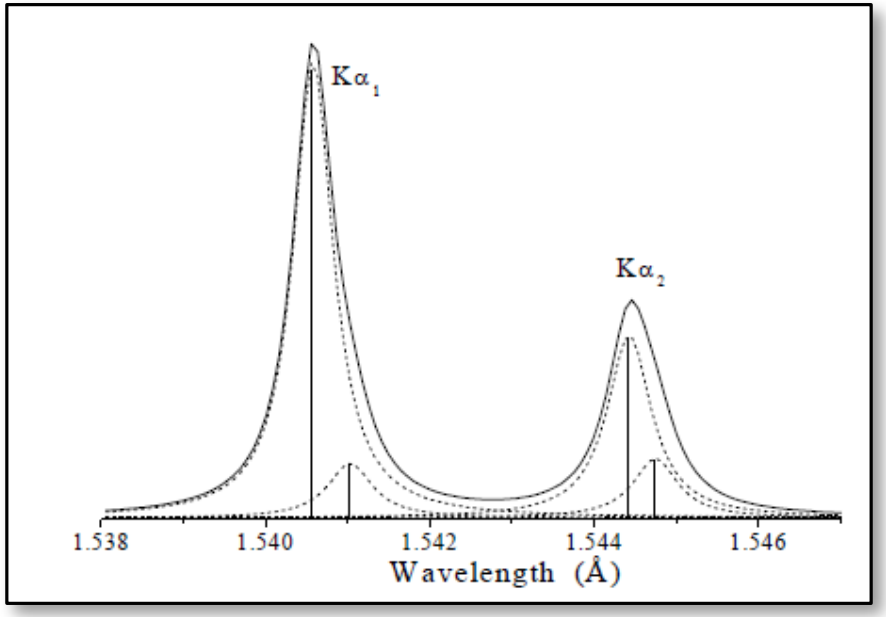
Fundamental parameters approach: **fewer parameters** to refine, parameters having a **physical meaning**, **no need to re determine the instrument contribution** in case of geometry change.

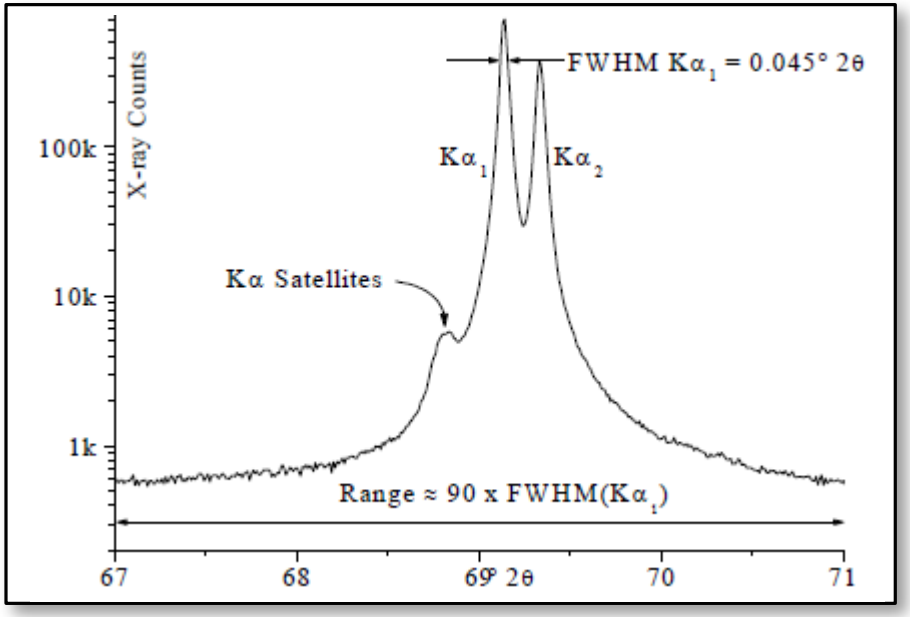
Fundamental parameters approach
source spectral distribution

$K_{\alpha 1,2}$ emission profile from a lab X-ray tube.

None of the two components is purely Lorentzian. Both are asymmetrical and have a "tail" towards the high values in wavelength.

In addition, the width and asymmetry of the two components differ!





Double ionization : principal transition 1s→2p + 3d contribution written 1s3d →2p3d. Hence, a modeling with 4 Lorentzian is better.

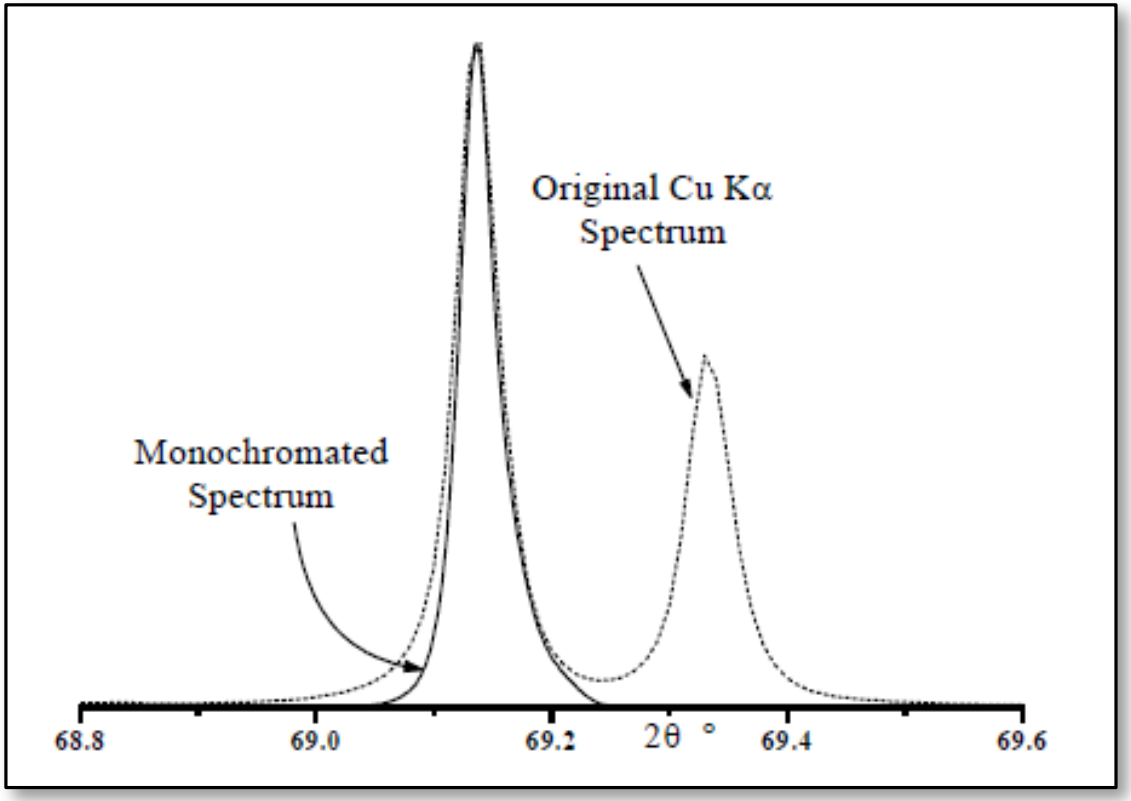
+ modeling of the "tail" towards high energies (satellites modeled by a wide Lorentzian)

Hölzer, G., Fritsch, M., Deutsch, M., Härtwig, J. & Förster, E. (1997)

Fundamental parameters approach

source spectral distribution

Example of $K_{\alpha 1}$ emission profile of a laboratory tube with a Ge(111) front monochromator.



Disappearance of K_{α} satellites and almost all of $K_{\alpha 2}$ (99.98%)
Modeling with only one Lorentzian.

Fundamental parameters approach

source spectral distribution

Used profile parameters:

Emission profile	Component	λ(Å)	Relative intensity	Lorent. FWHM (Å x 10^{-3})
CuKa5	satellites	1.534753	1.59	3.6854
	$K_{\alpha 1a}$	1.540596	57.91	0.437
	$K_{\alpha 1b}$	1.541058	7.62	0.6
	$K_{\alpha 2a}$	1.544410	24.17	0.52
	$K_{\alpha 2b}$	1.544721	8.71	0.62
CuKa1	$K_{\alpha 1}$	1.540596	100	0.5

Fundamental parameters approach

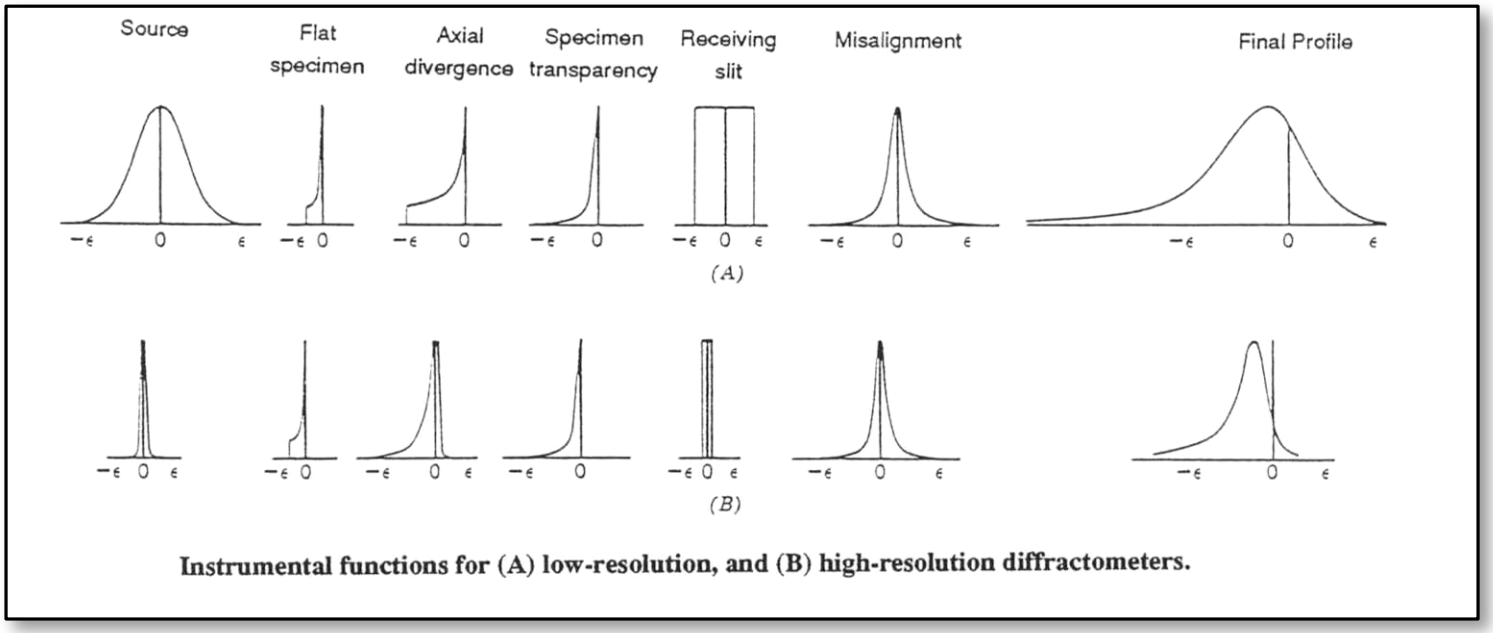
General principle: $\Omega(2\theta) = \underbrace{(W \otimes G)}_{\text{instrument}} \otimes \underbrace{(T_R \otimes S)}_{\text{sample}}$

The T_R term must, strictly speaking, be added to take into account the transparency of the sample that can influence the final profile (sample not infinitely thick).

Instrument contribution $\Omega_I(2\theta)$:

$$\Omega_I(2\theta) = W \otimes G_1(2\theta) \otimes G_2(2\theta) \otimes G_i(2\theta) \ldots \otimes G_n(2\theta)$$

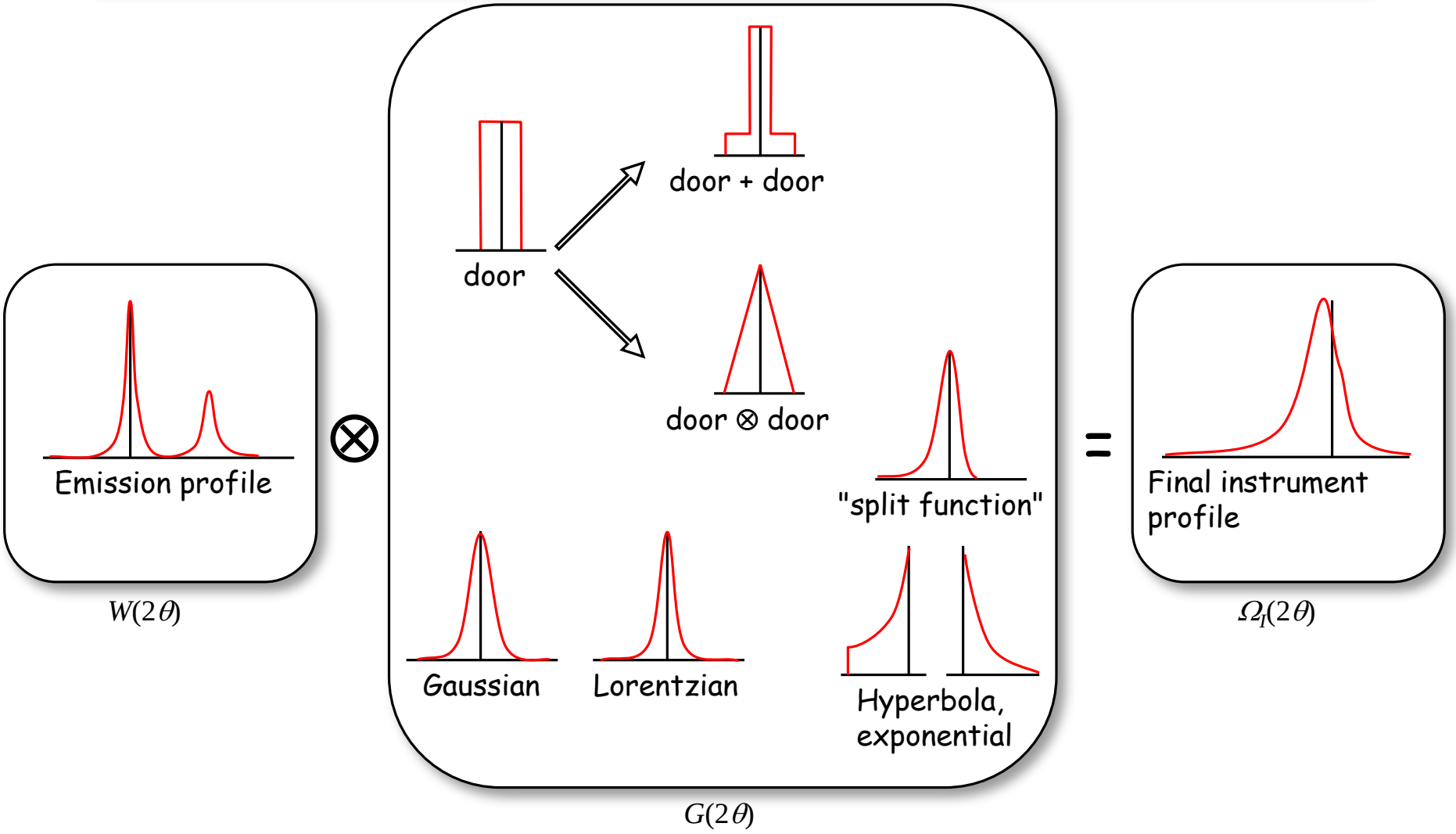
The $G_i(2\theta)$ terms correspond to the various aberration functions related to the instrument.



Instrumental functions for (A) low-resolution, and (B) high-resolution diffractometers.

Fundamental parameters approach

instrument profile: function types



Principle of the fundamental parameters approach: the final profile is obtained by convolution of functions describing the instrument aberrations applied to the emission profile

Fundamental parameters approach
instrument (+sample transparency)

$\varepsilon = 2\theta - 2\theta_k$ R_P et R_S, primary and secondary diffractometer radius

Aberration	name	unit	Function	
Instrument:				
Equatorial divergence (fixed slit)	*FDS*	°	$Fn(\varepsilon) = (4\varepsilon_m \varepsilon)^{-1/2}$ from ε = 0 to $\varepsilon_m = -(\pi/360)\cot(\theta_k) FDS^2$	$°2\theta$
Equatorial divergence (variable slit)	*VDS*	mm	$Fn(\varepsilon) = (4\varepsilon_m \varepsilon)^{-1/2}$ from $\varepsilon = 0$ to $\varepsilon_m = -VDS^2 \sin(2\theta_k)(180/\pi)/4R_S^2$	$°2\theta$
Source length in the equatorial plane	*TA*	mm	$Fn(\varepsilon)$ = door function for $-\varepsilon_m/2 < \varepsilon < \varepsilon_m/2$ with $\varepsilon_m = (180/\pi) TA/R_S$	$°2\theta$
Sample tilt: thickness of the sample surface projected on the equatorial plane	*ST*	mm	$Fn(\varepsilon)$ = door function for $-\varepsilon_m/2 < \varepsilon < \varepsilon_m/2$ with $\varepsilon_m = (180/\pi)\cos(\theta_k) ST/R_S$	$°2\theta$

.../...

Fundamental parameters approach

instrument (+sample transparency)

Aberration	name	unity	function	
Instrument:				
Receiving slit length in the axial plane	*RSL*	mm	$Fn(\varepsilon) = (1/\varepsilon_m)\left(1-(\varepsilon_m/\varepsilon)^{1/2}\right)$ from $\varepsilon = 0$ to $\varepsilon_m = -(90/\pi)(SL/R_S)^2\cot(2\theta_k)$	$°2\theta$
Receiving slit width in the equatorial plane	*RSW*	mm	$Fn(\varepsilon)$ = door function for $-\varepsilon_m/2 < \varepsilon < \varepsilon_m/2$ with $\varepsilon_m = (180/\pi)RSW/R_S$	$°2\theta$
Sample:				
Linear absorption coefficient	*AB*	cm^{-1}	$Fn(\varepsilon) = (1/\delta)\exp(-\varepsilon/\delta)$ for $\varepsilon \le 0$ avec $\delta = 900\sin(2\theta_k)/(\pi.AB.R_S)$	$°2\theta$

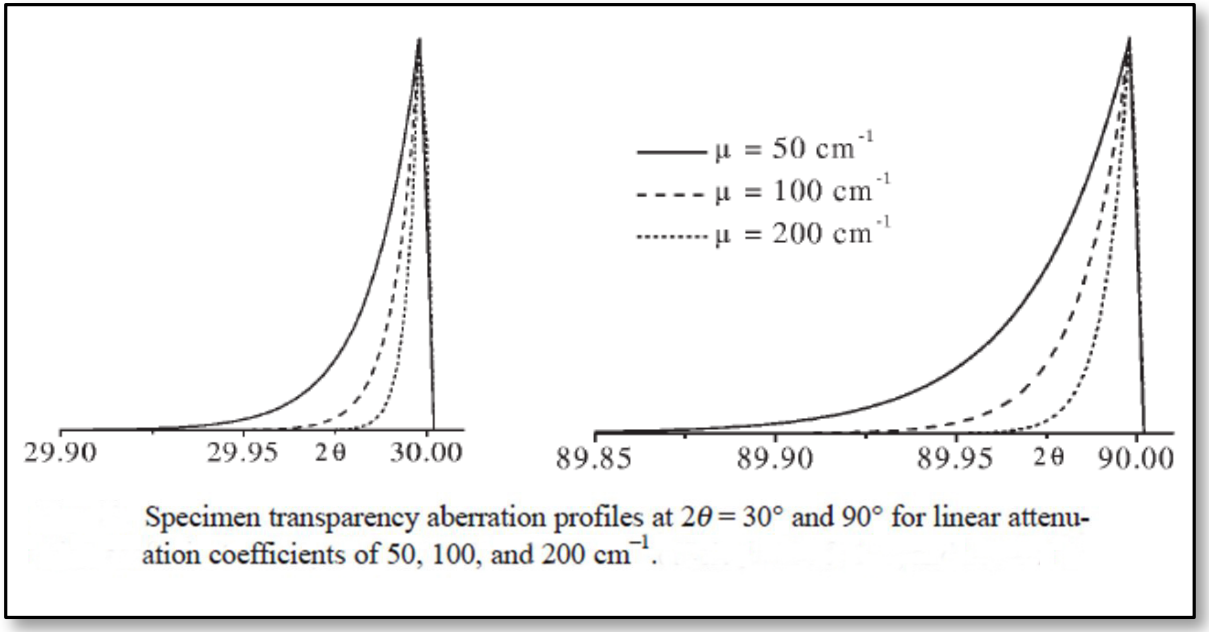
Fundamental parameters approach
sample

Sample contribution $\Omega_S(2\theta)$:

$$\Omega_S(2\theta) = S_{T_{cryst}}(2\theta) \otimes S_{\mu def}(2\theta) \otimes \ldots$$

Using of different standard functions based on Gaussian or Lorentzian components whose width at half height is constrained to account for a particular 2θ or *hkl* dependency.

Back to the transparency effect T_R on profile:



Specimen transparency aberration profiles at $2\theta = 30°$ and 90° for linear attenuation coefficients of 50, 100, and 200 cm^{-1}.

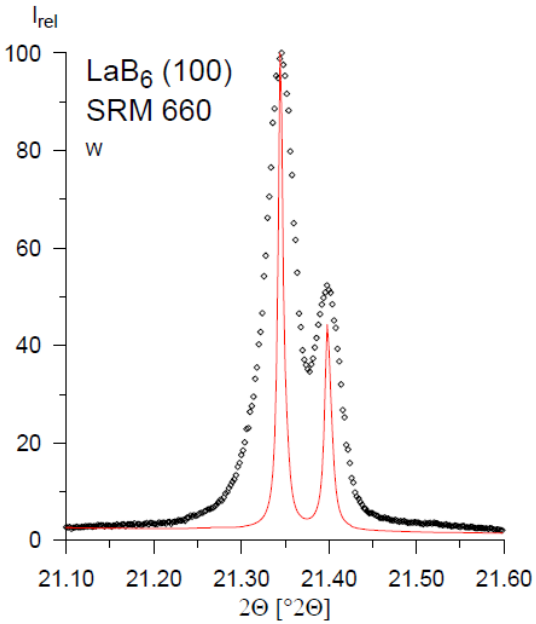
Cheary, R. W., Coelho, A. A. & Cline, (2004)

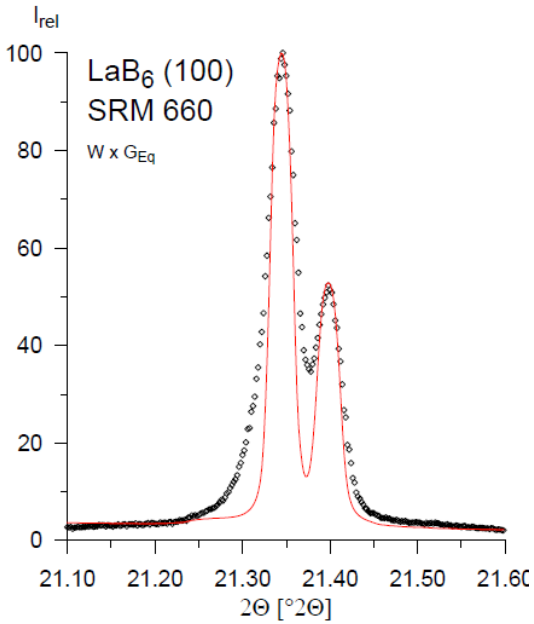
Significant effect for highly porous organic or inorganic materials (eg Si or MgO).

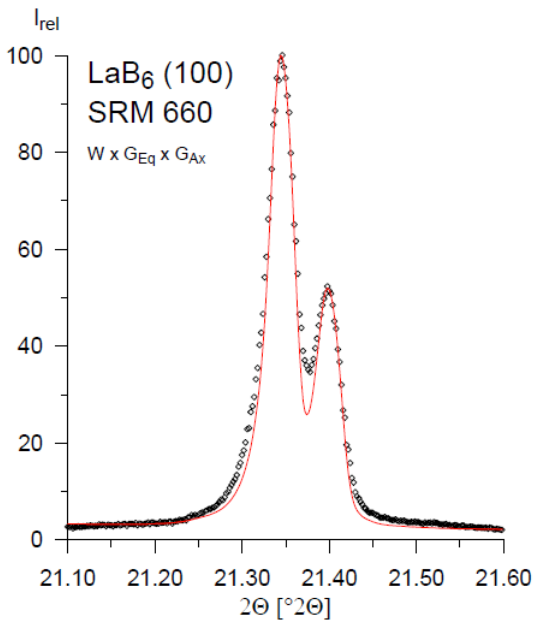
For example:
μ_{TiO2} = 530 cm^{-1} for $K_{Cu\alpha}$

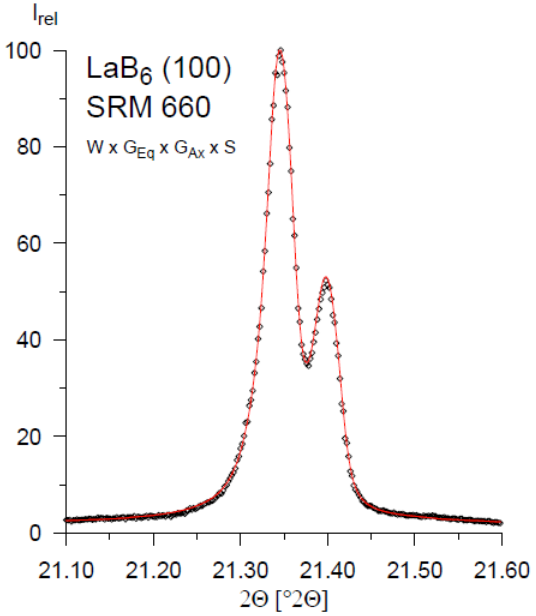
Fundamental parameters approach

instrument + sample



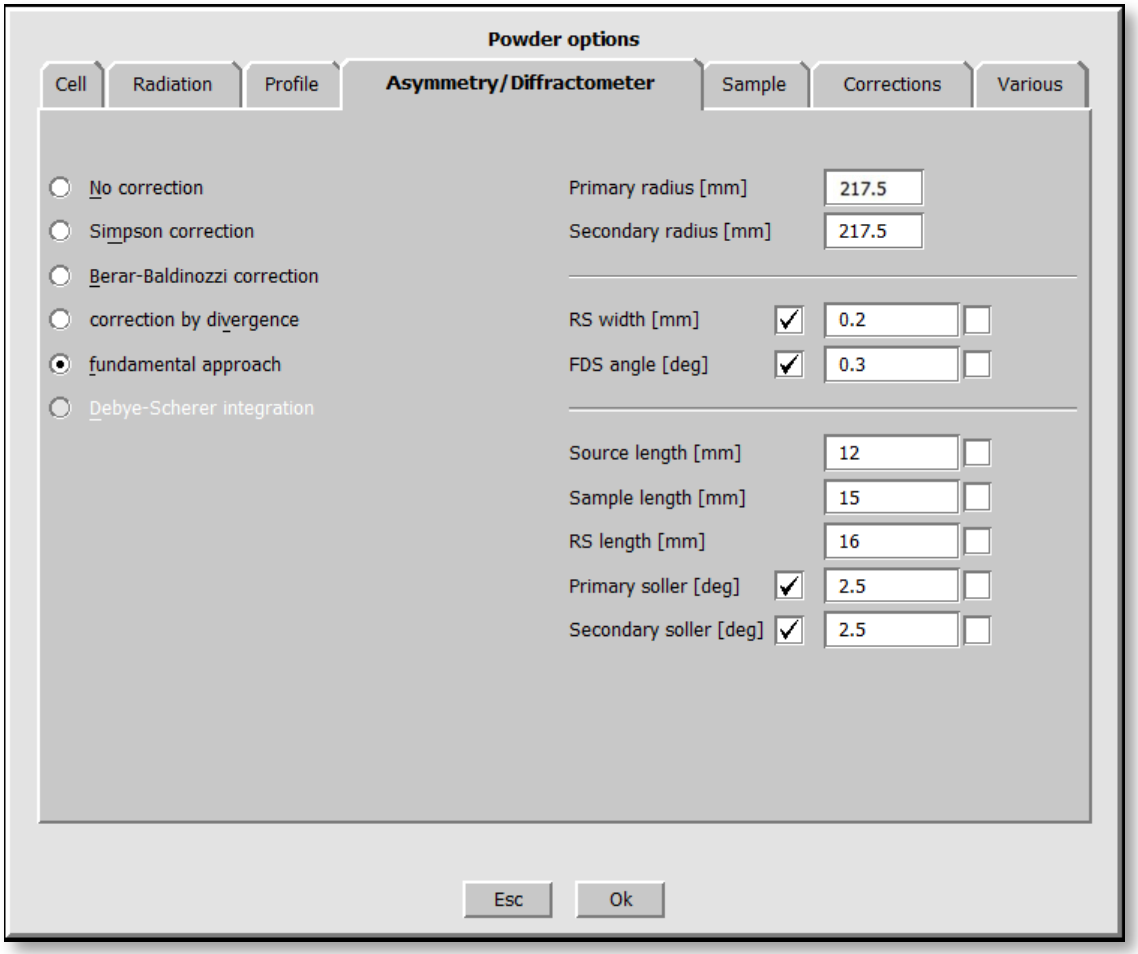




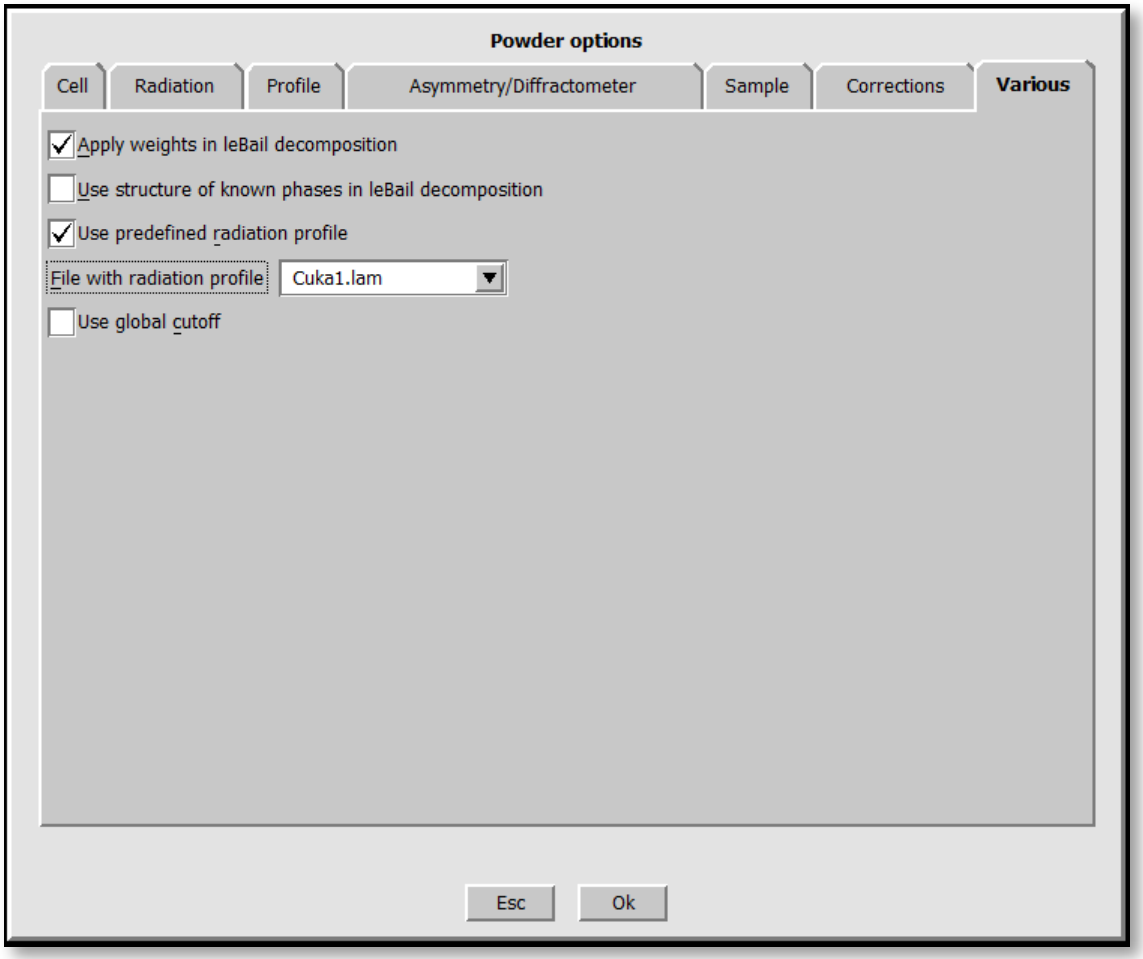


Example of LaB6 on single peak with maximum intensity adjustment.(Kern & Coelho, 1998)

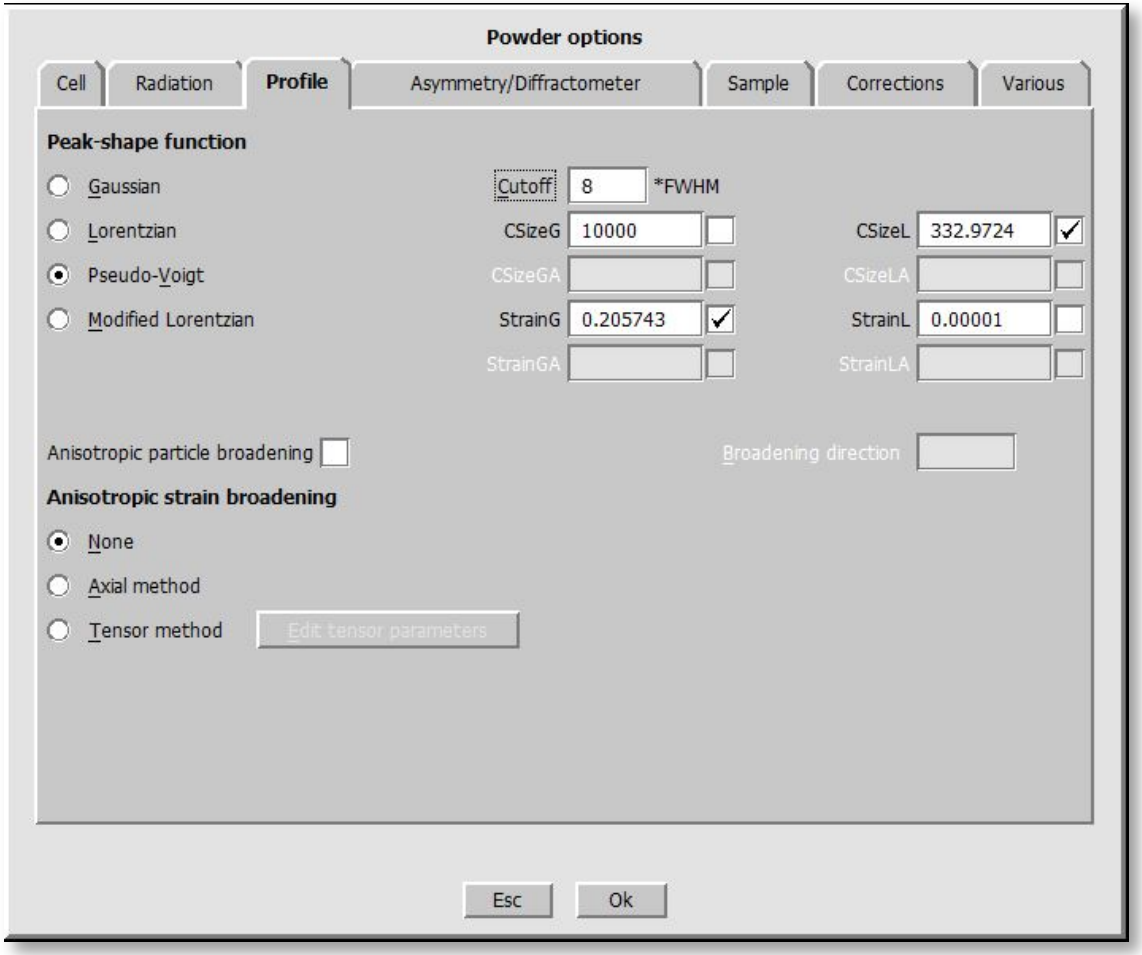
Jana 2006 and fundamental parameters



Jana 2006 and fundamental parameters



Jana 2006 and fundamental parameters

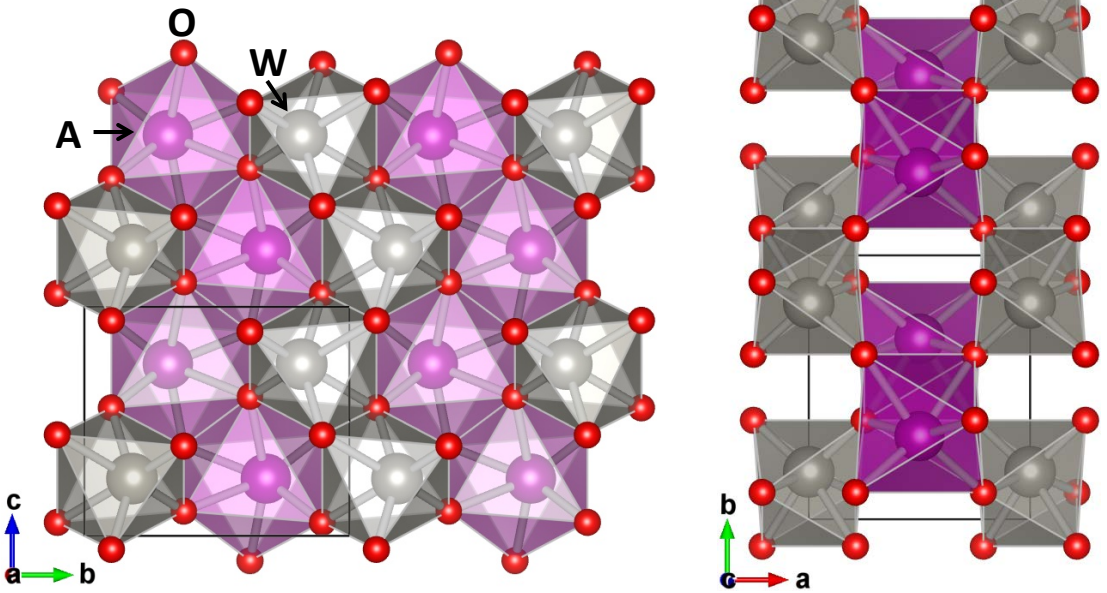


Fundamental parameters example (JANA 2006)

$MnWO_4$

Wolframite structure
Space group *P2/c*
a=4.82260 Å
b=5.75330 Å
c=4.99230 Å
γ=91.0750°

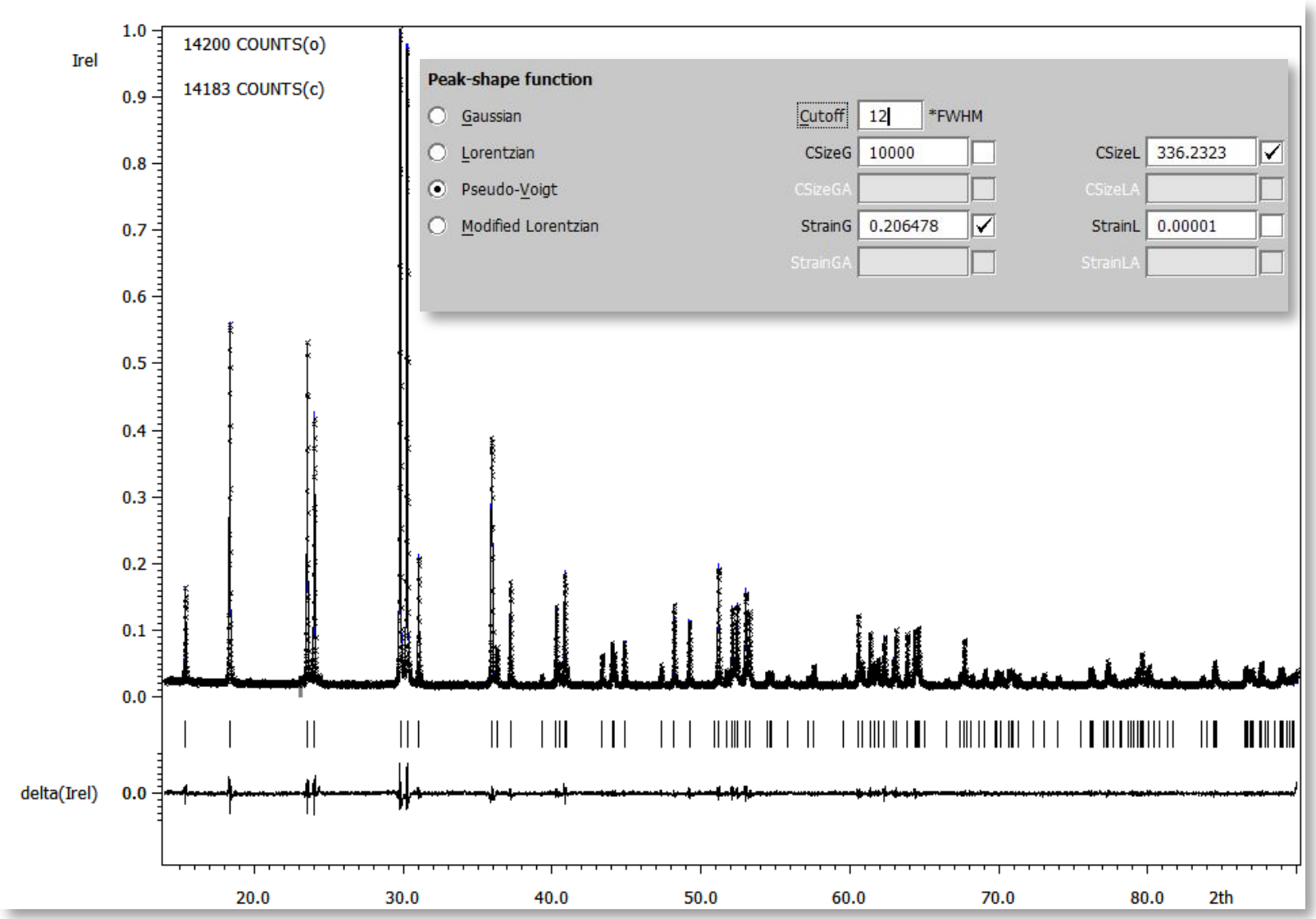
A : Mn with a possible substitution by Cu.



Double zig-zag chain of octahedra

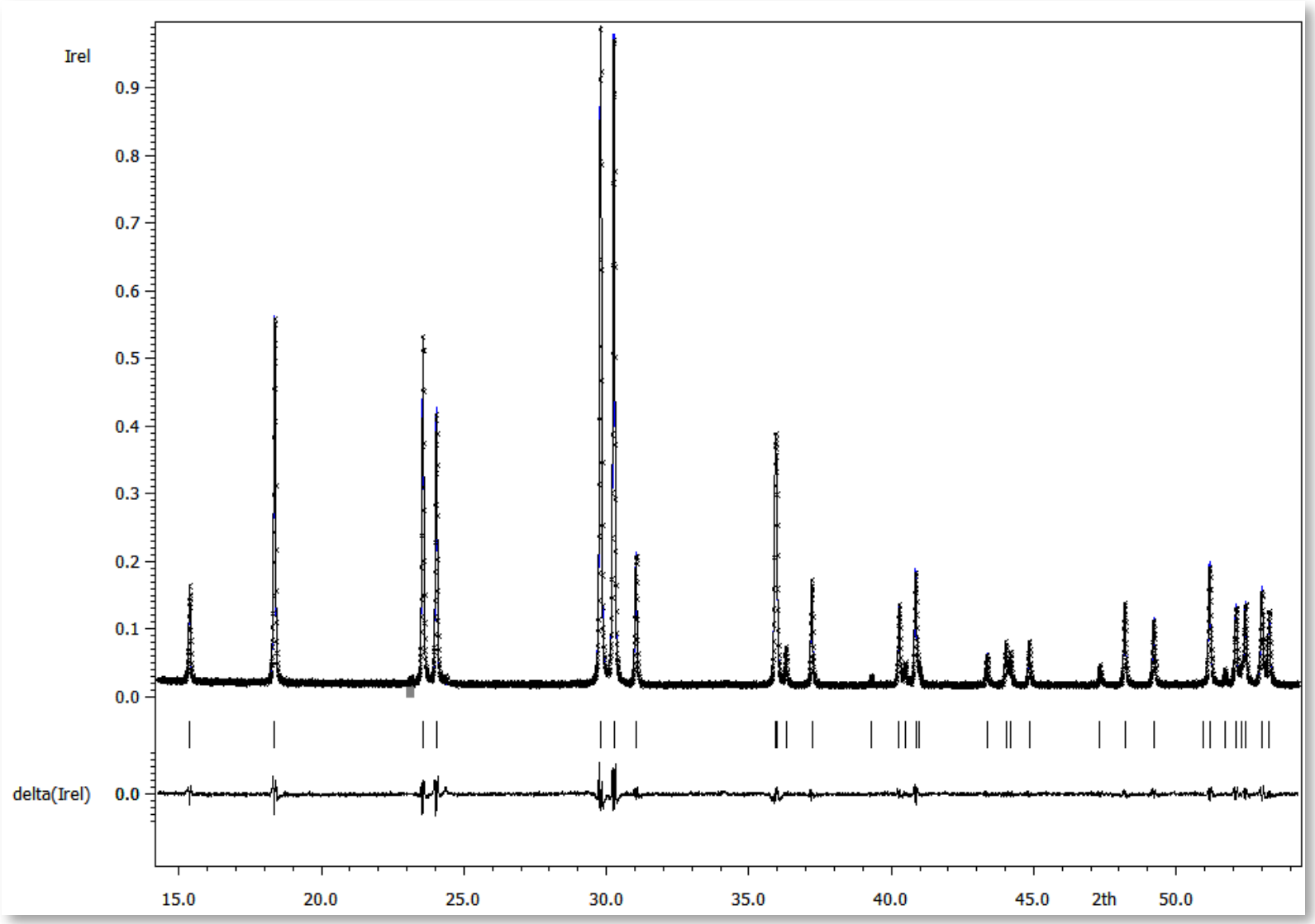
Fundamental parameters example (JANA 2006)

$MnWO_4$



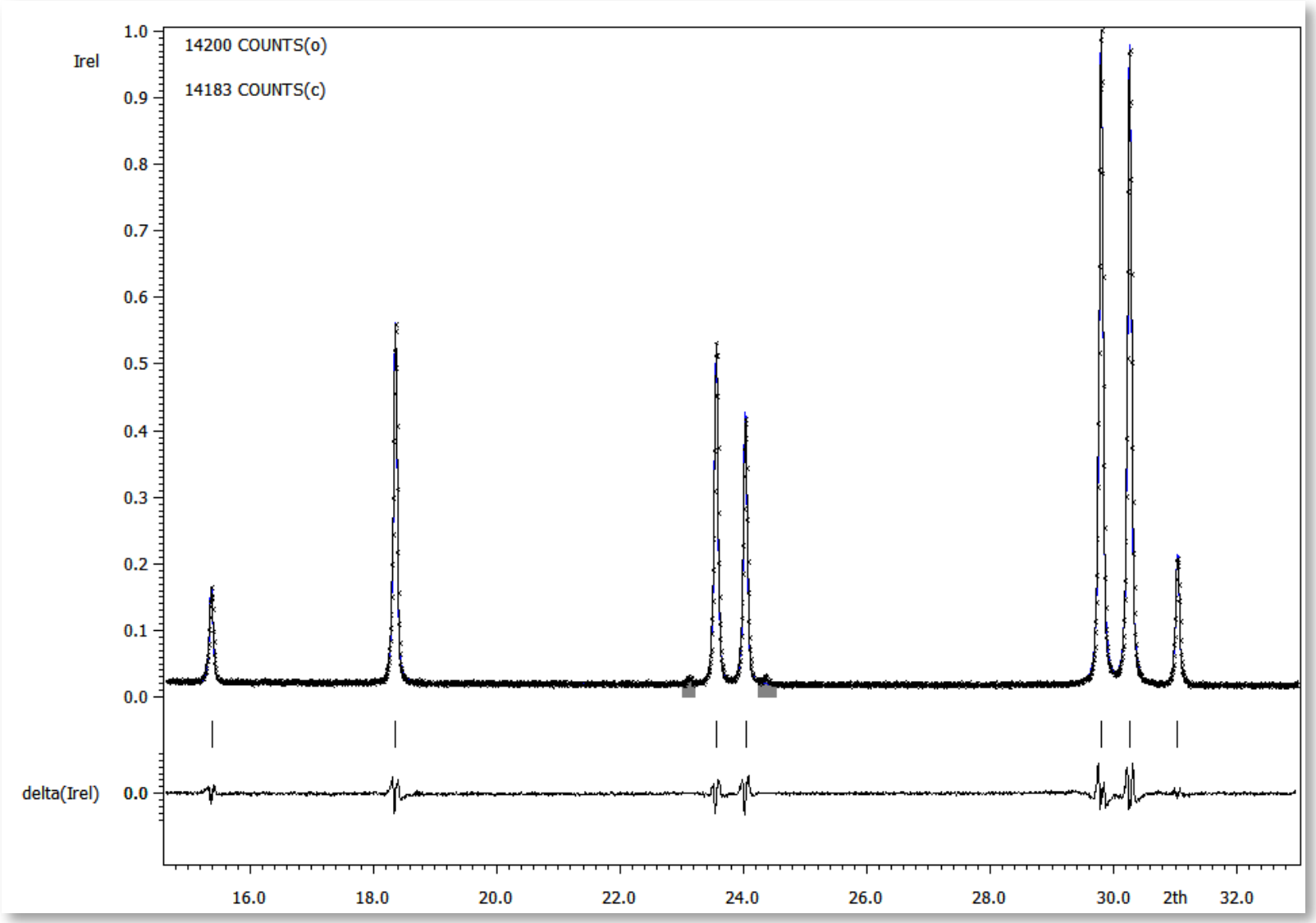
Fundamental parameters example (JANA 2006)

$MnWO_4$



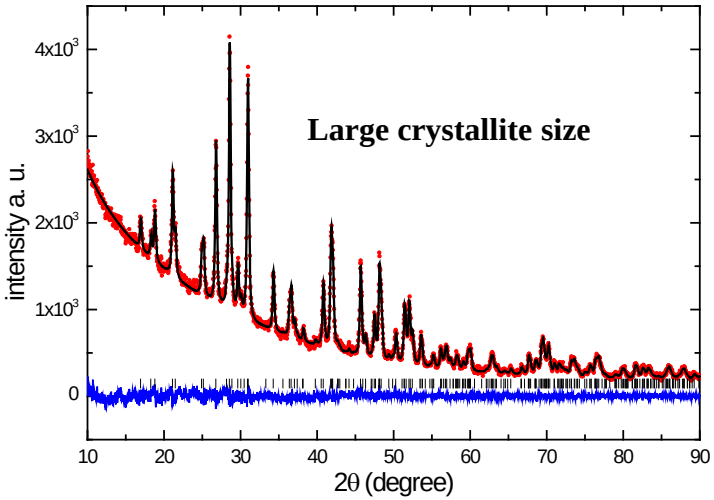
Fundamental parameters example (JANA 2006)

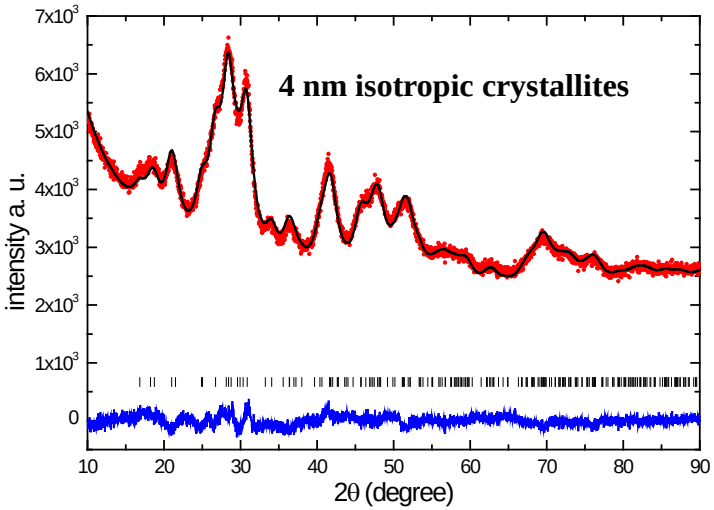
$MnWO_4$

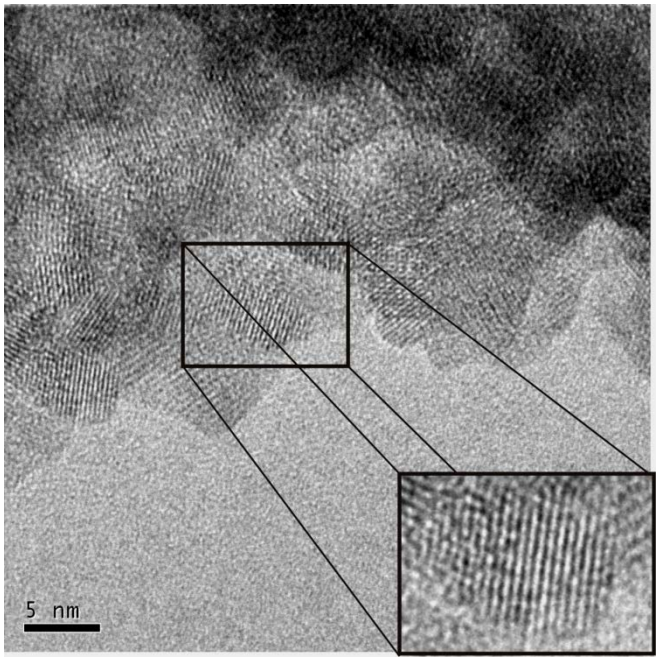


Fundamental parameters example (JANA 2006)

Monazite ($LaPO_4$)







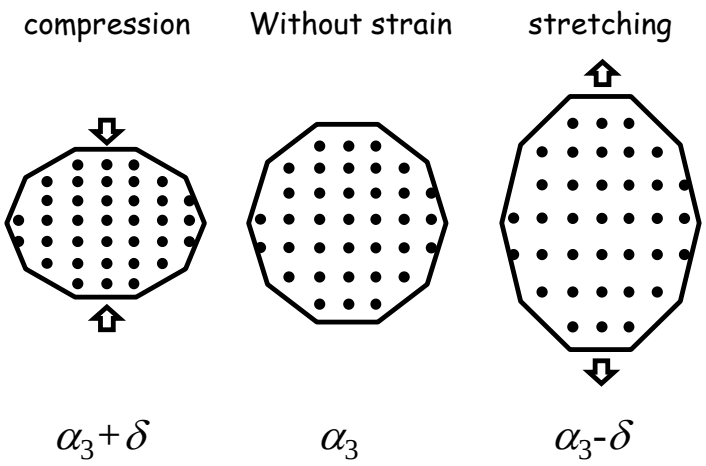
Good agreement between TEM and XRD.

Micro-strain anisotropy
Stephens formalism

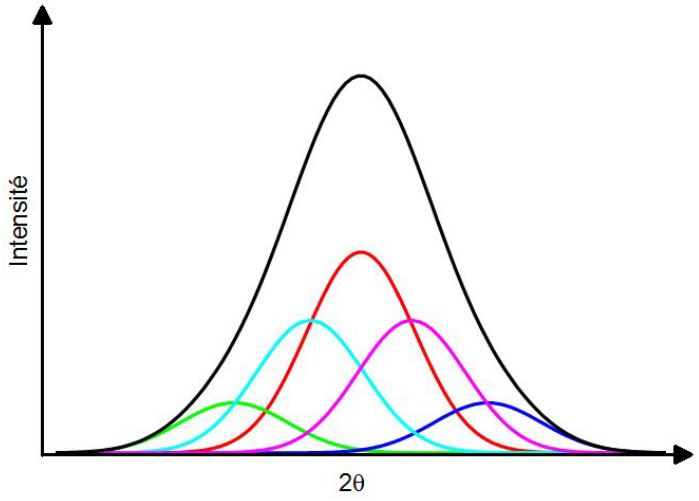
$$1/d^2 = M_{hkl} = \alpha_1 h^2 + \alpha_2 k^2 + \alpha_3 l^2 + \alpha_4 kl + \alpha_5 hl + \alpha_6 hk$$

$\{\alpha_i\}$: reciprocal metric parameters

Unidirectional anisotropic micro-strain case:



Example of unidirectional strain along c axis



Wide peak: envelope due to the distribution of individual inter-reticular distances = Gaussian

⇨ As many values of α_3 as of stress situations along the axis c

Microstrain anisotropy
Stephens formalism

In the most general case, microstrains are distributed in directions.

Each crystallite has its own set of reciprocal parameters affecting all the $\{\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5, \alpha_6\}$ parameters which therefore deviate from $\{<\alpha_1>, <\alpha_2>, <\alpha_3>, <\alpha_4>, <\alpha_5>, <\alpha_6>\}$

The width of each reflection can be expressed in terms of moments of the distribution of these parameters.

Local values of $\{\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5, \alpha_6\}$ may not respect the symmetry of the overall sample.

α_i parameters are considered to have a **Gaussian distribution** with a covariance matrix C_{ij}.

$$C_{ij} = \left\langle \left(\alpha_i - \langle \alpha_i \rangle\right)\left(\alpha_j - \langle \alpha_j \rangle\right) \right\rangle$$

with $C_{ii} = \sigma^2(\alpha_i)$

M_{hkl} is linear in α_i thus the variance of M_{hkl} is given by:

$$\sigma^2(M_{hkl}) = \sum_{i,j} C_{i,j} \frac{\partial M}{\partial \alpha_i} \frac{\partial M}{\partial \alpha_j}$$

As $\partial M/\partial \alpha_1 = h^2$, …, $\partial M/\partial \alpha_6 = hk$, the above relation can be written as:

$$\sigma^2(M_{hkl}) = \sum_{HKL} S_{HKL} h^H k^K l^L$$ with terms S_{HKL} defined for $H + K + L = 4$

Stephens formalism

Restrictions on anisotropic strain parameters

$$\sigma^2(M_{hkl}) = \sum_{HKL} S_{HKL} h^H k^K l^L \quad \text{with } S_{HKL} \text{ defined for } H + K + L = 4$$

Restrictions on anisotropic strain parameters for the seven crystal systems

Those S_{hkl} not listed in the last column must be zero

Crystal system	Restrictions on α_i parameters	Anisotropic strain parameters
Cubic	$\alpha_1=\alpha_2=\alpha_3$, $\alpha_4=\alpha_5=\alpha_6=0$	$S_{400} = S_{040} = S_{004}$, $S_{220} = S_{202} = S_{022}$
Tetragonal	$\alpha_1=\alpha_2$, $\alpha_4=\alpha_5=\alpha_6=0$	$S_{400} = S_{040}$, $S_{202} = S_{022}$, S_{004}, S_{220}
Orthorhombic	$\alpha_4=\alpha_5=\alpha_6=0$	S_{400}, S_{040}, S_{004}, S_{220}, S_{202}, S_{022}
Monoclinic	$\alpha_4=\alpha_6=0$	S_{400}, S_{301}, S_{220}, S_{202}, S_{121}, S_{103}, S_{040}, S_{022}, S_{004}
Trigonal (*R*3 etc.)	$\alpha_1=\alpha_2=\alpha_3$, $\alpha_4=\alpha_5=\alpha_6$	Rhombohedral indices: $S_{400} = S_{040} = S_{004}$, $S_{220} = S_{202} = S_{022}$, $S_{211} = S_{121} = S_{112}$, $S_{310} = S_{130} = S_{301} = S_{103} = S_{031} = S_{013}$
		Hexagonal indices: $S_{400} = S_{040} = S_{310}/2 = S_{130}/2 = S_{220}/3$, $S_{202} = S_{022} = S_{112}$, S_{004}, $S_{301}/2 = -S_{031}/2 = S_{211}/3 = -S_{121}/3$
Hexagonal, trigonal (*P*3 etc.)	$\alpha_1=\alpha_2=\alpha_6$, $\alpha_4=\alpha_5=0$	$S_{400} = S_{040} = S_{310}/2 = S_{130}/2 = S_{220}/3$, $S_{202} = S_{022} = S_{112}$, S_{004}
Triclinic		All 15 S_{HKL} allowed

Stephens formalism
Effect on line width

From the Bragg equation, $\sin\theta = \lambda/(2d) = \lambda M^{1/2}/2$, the anisotropic broadening contribution to the FWHM of a diffraction line is given by:

$$H_{\mu defAniso} = \left[\sigma^2(M_{hkl})\right]^{1/2} \tan\theta / [M_{hkl}] = \left[\sum_{HKL} h^H k^K l^L\right]^{1/2} \tan\theta / [M_{hkl}]$$

Hypothesis : the same treatment is applicable to the Lorentzian component with ζ the Gaussian/Lorentzian mixing parameter (The Lorentzian function does not have a second moment). Hence:

$$H_G = \left[U\tan^2\theta + V\tan\theta + W + (1-\zeta)^2 H^2_{\mu defAniso}\right]^{1/2}$$

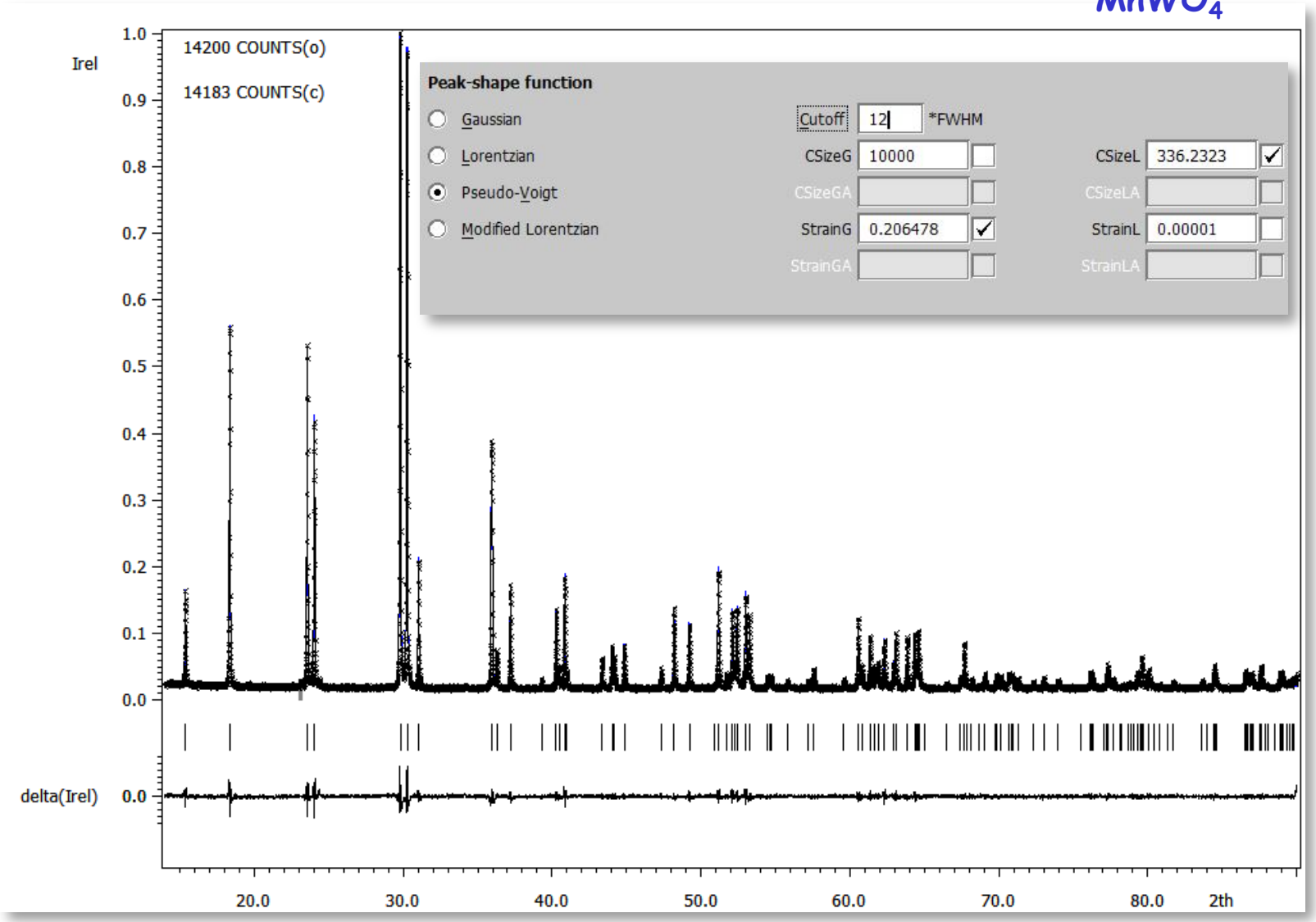
$$H_L = X\tan\theta + Y/\cos\theta + \zeta H_{\mu defAniso}$$

The Stephens formalism can be combined with the fundamental parameters approach.

Stephens formalism

example of coupling with the fundamental parameters approach

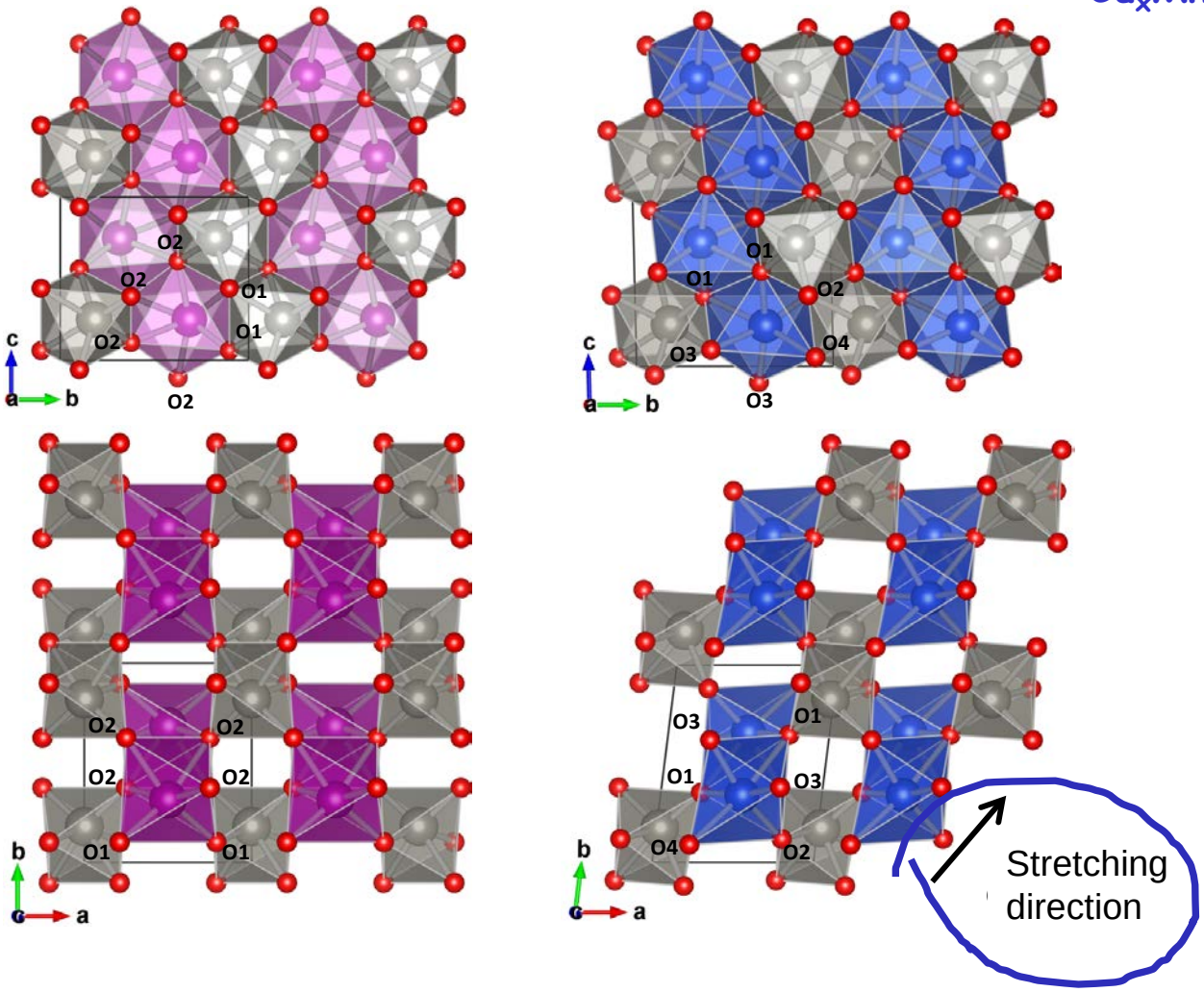
$MnWO_4$



Stephens formalism

example of coupling with the fundamental parameters approach

$Cu_xMn_{1-x}WO_4$ Solid solution



$MnWO_4$ (monoclinic)

$CuWO_4$ (triclinic)

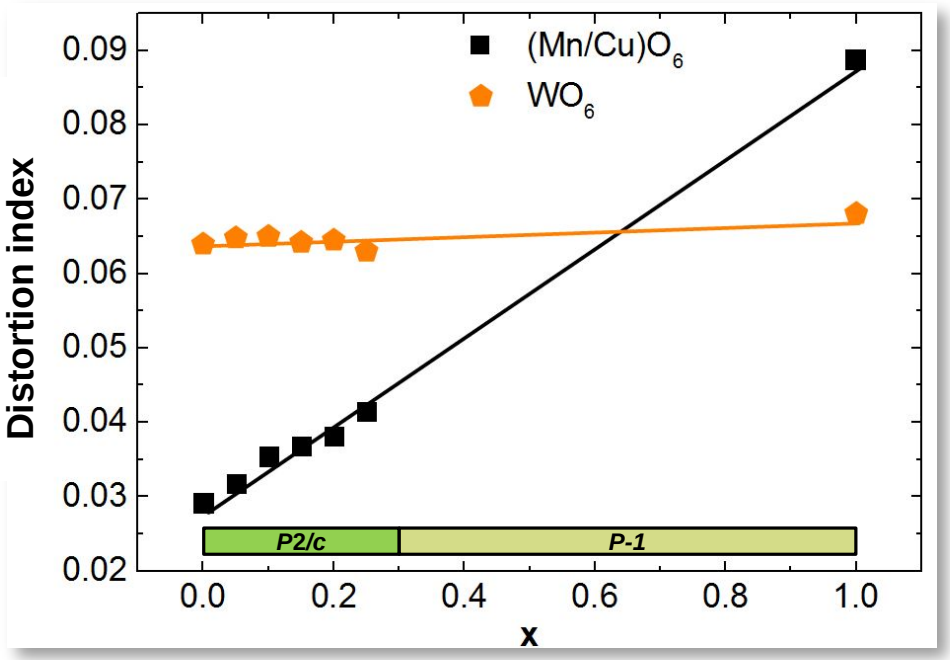
Stephens formalism

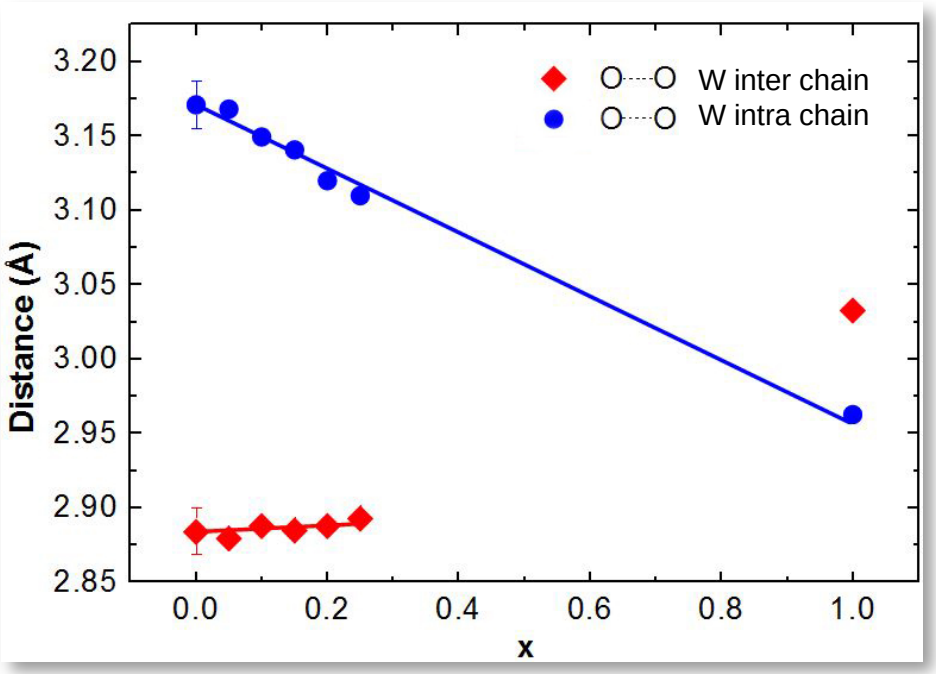
example of coupling with the fundamental parameters approach

$Cu_xMn_{1-x}WO_4$ Solid solution

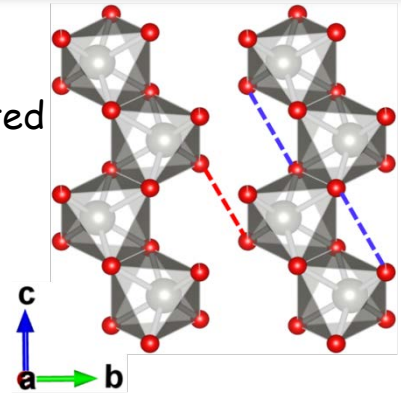
Combined X-ray/neutron refinement:
Solid solution for x ≤ 0.30

Distortion index $\Delta = \frac{1}{6}\sum_{i=1}^{6}\frac{|d_i - \bar{d}|}{\bar{d}}$





Rigid WO_6 articulated along one edge

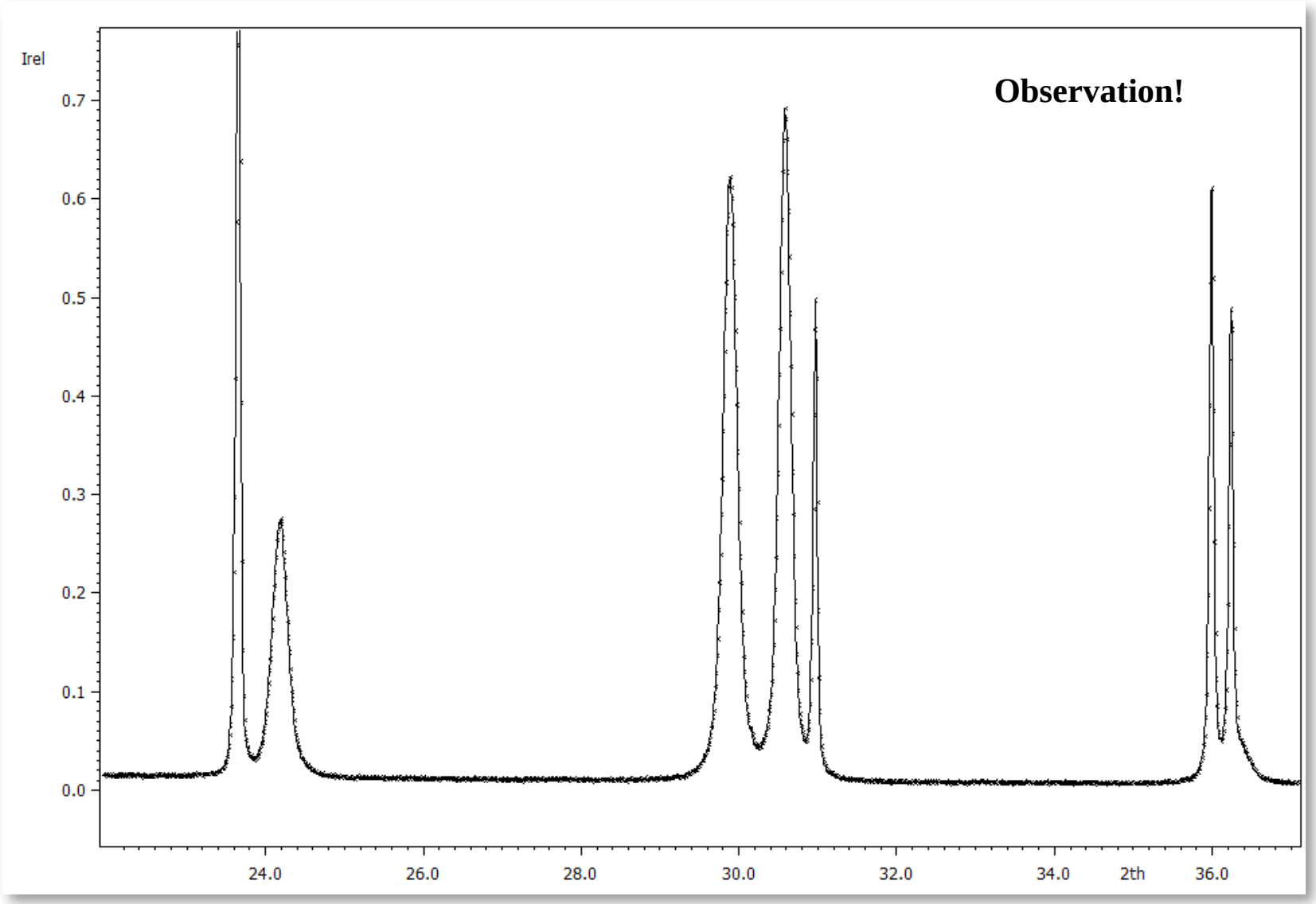


What about Bragg linewidth?

Stephens formalism

example of coupling with the fundamental parameters approach

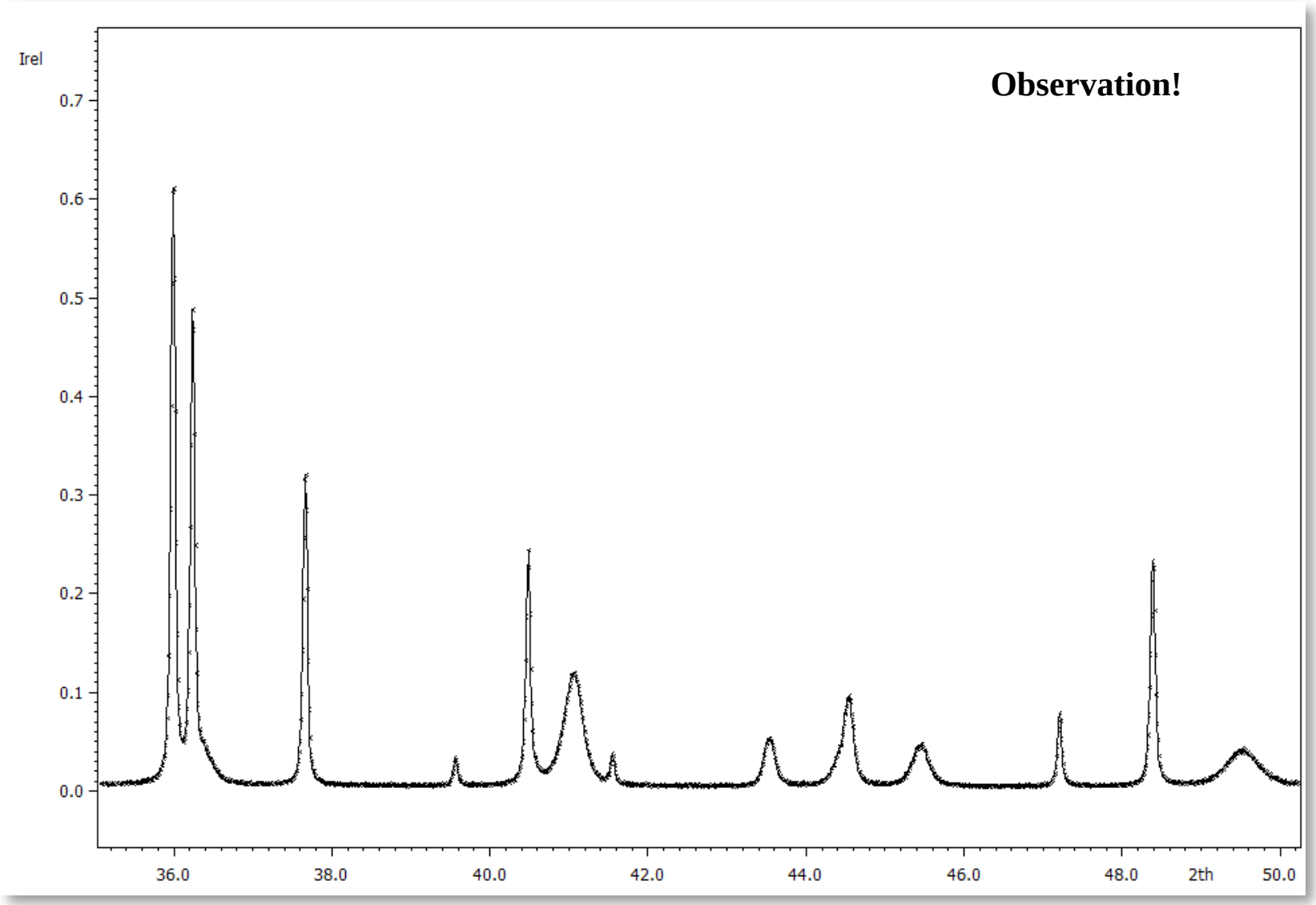
$Cu_xMn_{1-x}WO_4$ Solid solution, x = 0.3



Stephens formalism

example of coupling with the fundamental parameters approach

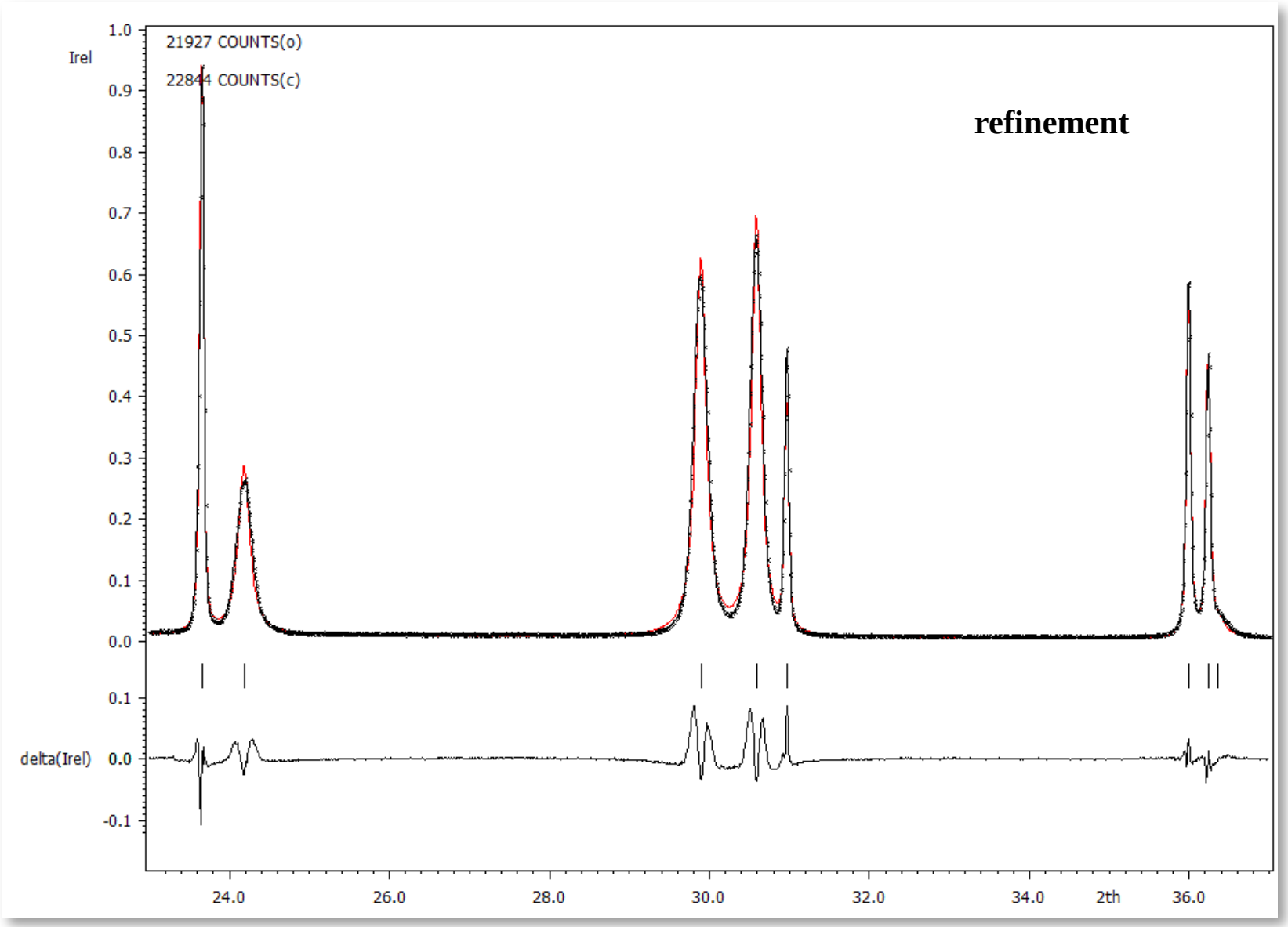
$Cu_xMn_{1-x}WO_4$ Solid solution, x = 0.3



Stephens formalism

example of coupling with the fundamental parameters approach

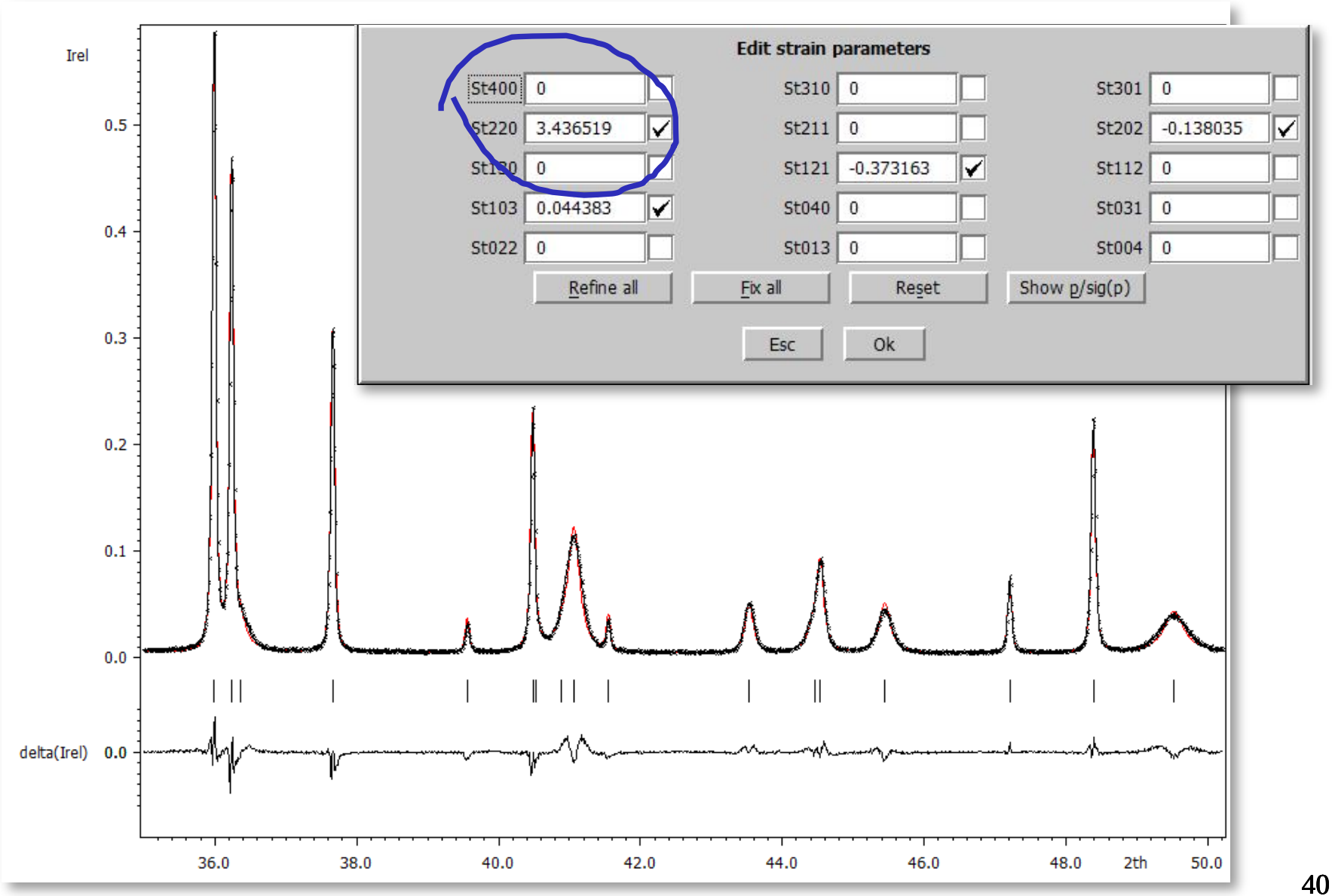
$Cu_xMn_{1-x}WO_4$ Solid solution, x = 0.3



Stephens formalism

example of coupling with the fundamental parameters approach

$Cu_xMn_{1-x}WO_4$ Solid solution, x = 0.3



Summary

- *a posteriori* profile analysis:
  - TCH function
  - The instrument resolution has to be determined
    - ⇒ Crystallite size
    - ⇒ Micro strain

    } With a possible unidirectional anisotropy

- fundamental parameters:
  - Instrument resolution calculated from physical parameters
    - ⇒ Crystallite size
    - ⇒ Micro strain

    } With a possible unidirectional anisotropy

    Refined parameters

- Stephens formalism:
  - Complex micro strain anisotropy
    - $\Rightarrow (S_{HKL})$
  - Possible combination with the fundamental parameters approach

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