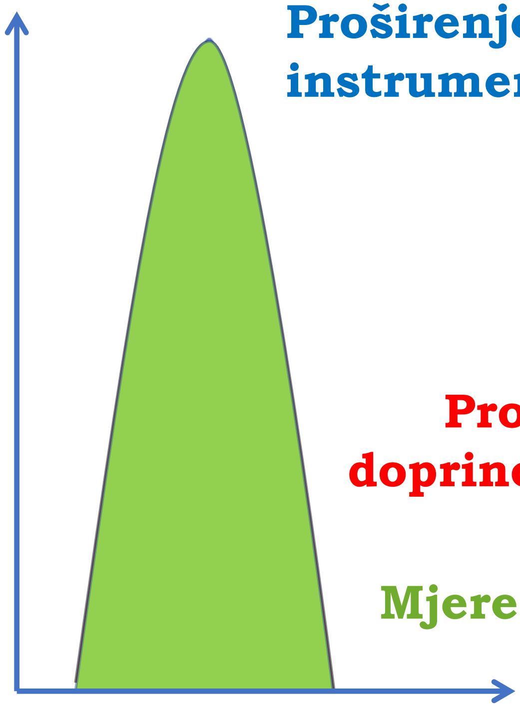
Proširenje difrakcijske linije zbog male veličine kristalita i deformacije

Difrakcijska linija - delta funkcija



Proširenje difrakcijske linije zbog doprinosa instrumenta

Proširenje difrakcijske linije zbog doprinosa deformacija kristalne rešetke i veličine kristalita uzora

Mjerena difrakcijska linija

Konvolucija INSTRUMENTALNOG PROFILA i ČISTOG FIZIKALNOG DIFRAKCIJSKOG PROFILA

$$h(\varepsilon) = \int_{-\infty}^{+\infty} g(t)\, f(\varepsilon - t)\, \mathrm{d}t$$

Dekonvolucija Stokesovom metodom

Bez pretpostavki o obliku mjerenih $h(\varepsilon)$ and $g(\varepsilon)$!

U recipročnom prostoru dekonvolucija se svodi na dijeljenje!

Recept:

- Napravi se Foureriova transformacija profila *h* i *g*

$$\boxed{F(t)=\frac{H(t)}{G(t)}=F_r(t)+\mathrm{i}F_i(t)}$$

Nužno: - izmjeriti $h(\varepsilon)$ i $g(\varepsilon)$ što je točnije moguće
- ne precijeniti pozadinu
- mjereni interval $[-\varepsilon_M, \varepsilon_M]$ uključuje „repove” profila

ČISTI FIZIKALNI DIFRAKCIJSKI PROFIL

OPAŽENI DIFRAKCIJSKI PROFIL

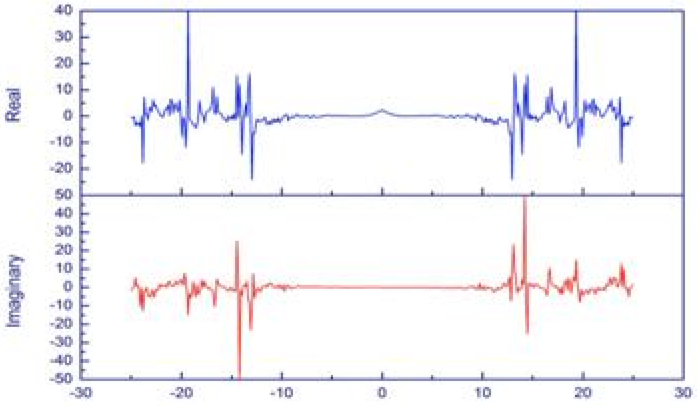
$$h(\varepsilon) = \int_{-\infty}^{+\infty} g(t)\, f(\varepsilon - t)\, \mathrm{d}t$$

INSTRUMENTALNI PROFIL

FOURIEROVI KOEFICIJENTI ČISTOG DIFRAKCIJSKOG PROFILA

$$F_r(t) = \frac{H_r(t)G_r(t) + H_i(t)G_i(t)}{G_r^2(t) + G_i^2(t)}$$

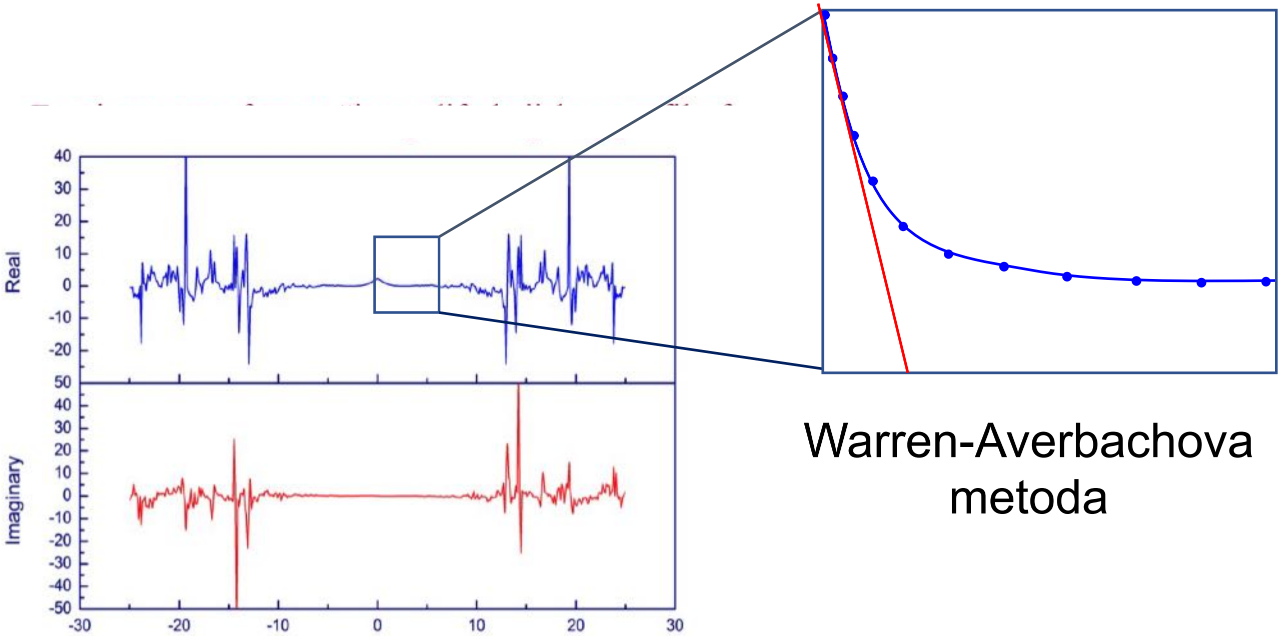
$$F_i(t) = \frac{H_i(t)G_r(t) - H_r(t)G_i(t)}{G_r^2(t) + G_i^2(t)}$$



FOURIEROVI KOEFICIJENTI ČISTOG DIFRAKCIJSKOG PROFILA

$$F_r(t) = \frac{H_r(t)G_r(t) + H_i(t)G_i(t)}{G_r^2(t) + G_i^2(t)}$$

$$F_i(t) = \frac{H_i(t)G_r(t) - H_r(t)G_i(t)}{G_r^2(t) + G_i^2(t)}$$



Warren-Averbachova metoda

prva derivacija krivulje u točki $L = 0$ daje recipročnu vrijednost površinski usrednjene veličine kristalita L_{WA}

Integralne širine

$$f(\varepsilon) = \int p(t)s(\varepsilon - t)\,\mathrm{d}t$$

$p(\varepsilon)$ – profil od veličine kristalita, β_{pi}, $\beta_{\mathrm{p}½}$
$s(\varepsilon)$ – profili od deformacija, β_{pi}, $\beta_{\mathrm{p}½}$

β_i je određena, *npr. Iz Stokesove metode*:

$$\beta_i = \frac{F_r(0)}{f(0)}\left(2\theta_{+\mathrm{M}} - 2\theta_{-\mathrm{M}}\right) = \frac{F_r(0)}{f(0)} \cdot 2\varepsilon_{\mathrm{M}}$$

Izvod β_{pi} i β_{si} ovisi o pretpostavljenom obliku $p(\varepsilon)$ i $s(\varepsilon)$!!!

Na primjer

$$p(\varepsilon) = \left(1 + \mathrm{K}_{\mathrm{C}}^2\varepsilon^2\right)^{-1}$$ Cauchyeva funkcija ($\beta_{pi} = \beta_{Ci}$)

$$s(\varepsilon) = \exp\left(-\mathrm{K}_{\mathrm{G}}^2\varepsilon^2\right)$$ Gaussova funkcija ($\beta_{si} = \beta_{Gi}$)

⇒ Aproksimativna jednadžba [N. C. Halder, C. N. J. Wagner, Acta Cryst. **20** (1966) 312-313]:

$$\beta_i^2 = \beta_i \beta_{Ci} + \beta_{Gi}^2 \qquad (*)$$

Tada vrijedi:

Scherrerova jednadžba
L_{hkl} – volumno usrednjena veličina

$$L_{hkl} = \frac{\lambda}{\beta_{Ci} \cos\theta_0}$$

Wilsonova jednadžba
e_{hkl} – gornja granica deformacija

$$4e_{hkl} = \frac{\beta_{Gi}}{\tan\theta_0}$$

Ili, iz ($*$):

$$\boxed{\frac{\gamma^2}{\sin^2\theta_0} = \frac{\lambda}{L_{hkl}} \cdot \frac{\gamma}{\sin^2\theta_0} + \left(4e_{hkl}\right)^2} \qquad (**) \qquad \left(\gamma = \beta_i \cdot \cos\theta_0\right)$$

L_{hkl} ⇔ nagib

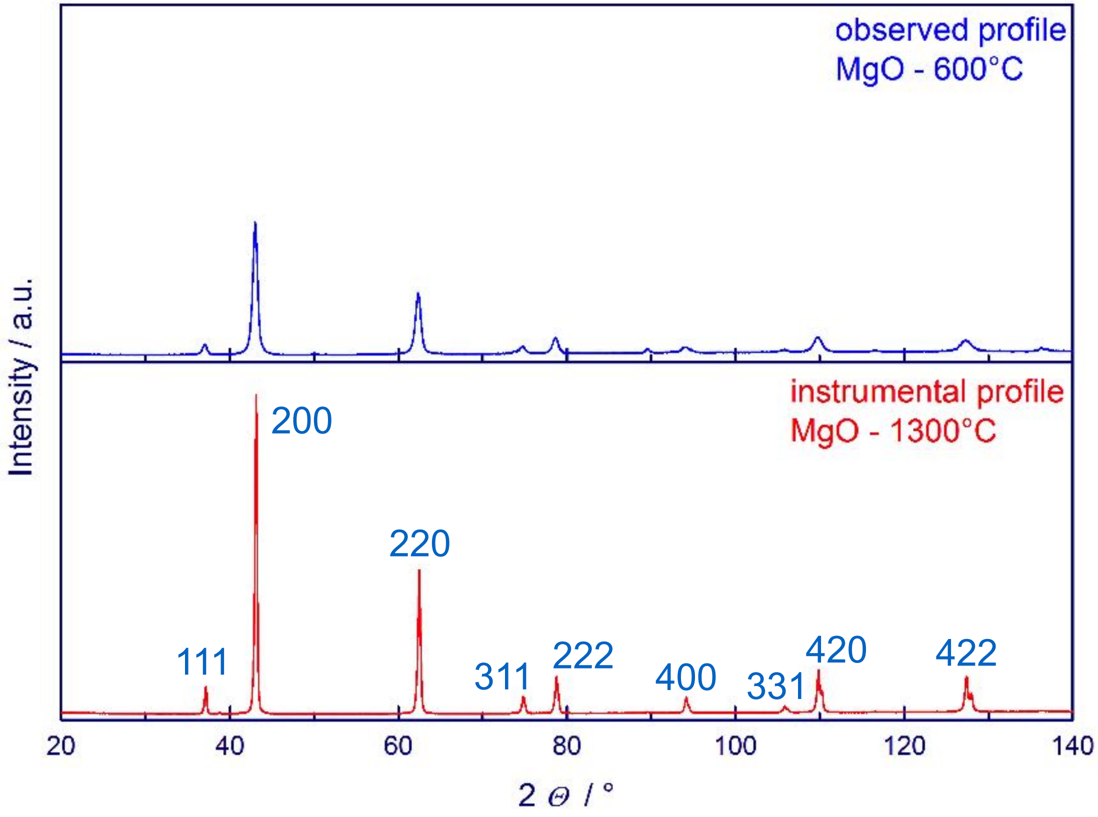
e_{hkl} ⇔ odsječak na osi y

Example:

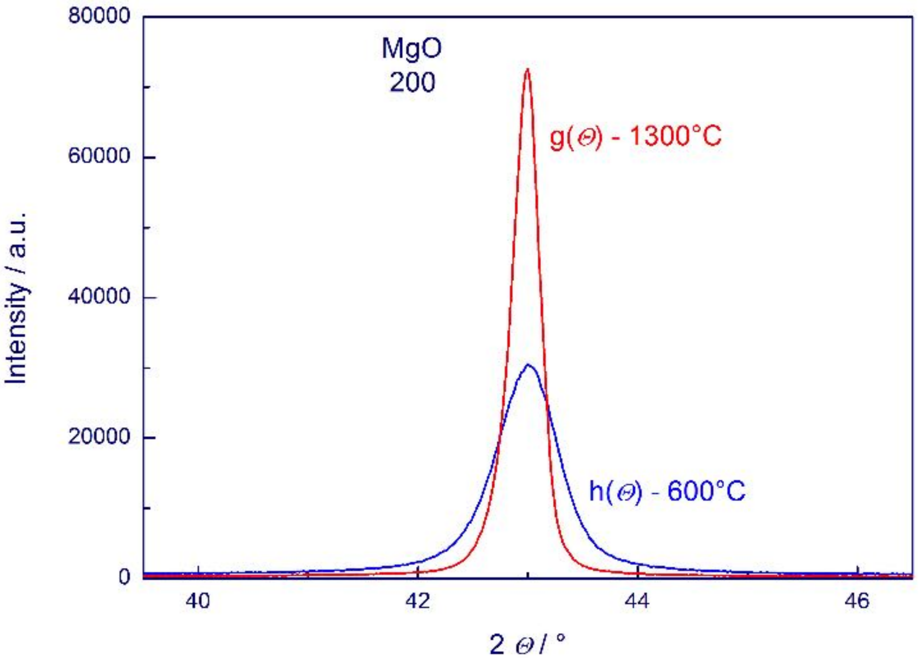
MgO $\left(Fm\overline{3}m\right)$, prepared by calcination of basic magnesium carbonate at 600°C to 1300°C.

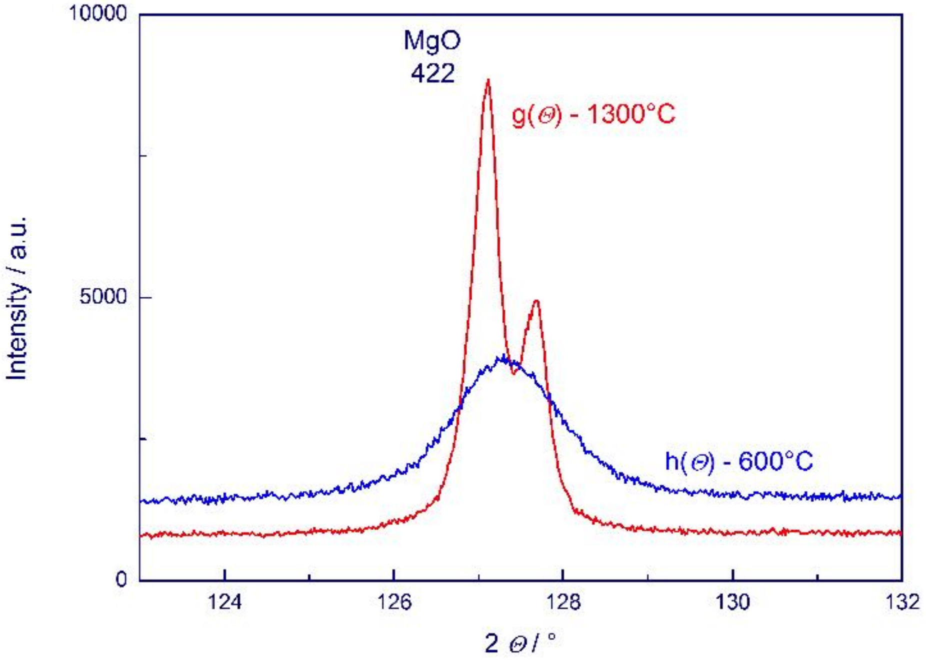
Diffraction broadening decreased as the temperature increased.

$\mathrm{MgO}_{1300} \rightarrow g(\varepsilon)$ – instrumental profile, used to obtain $f(\varepsilon)$ for MgO_{600}.



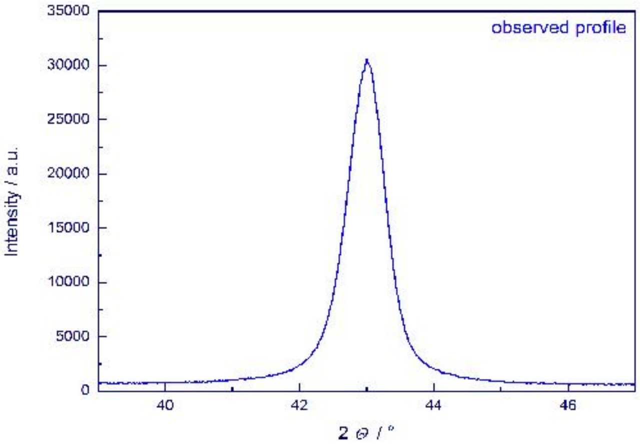
Comparison of some diffraction lines of the measured and instrumental profile

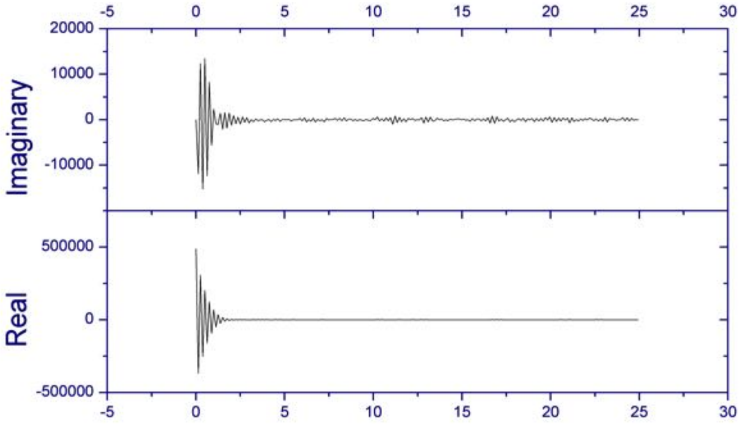




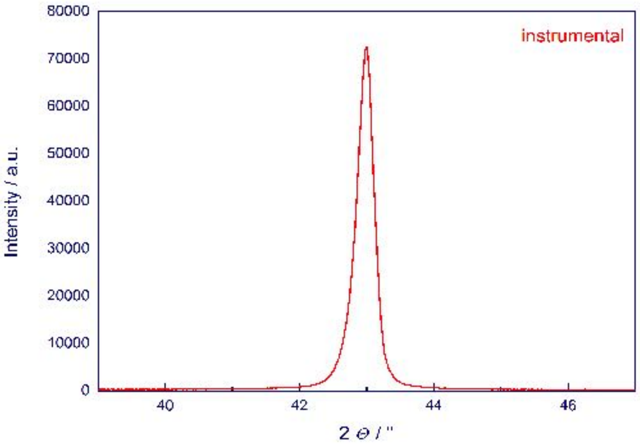
- It is expected that thermal decomposition of $MgCO_3$ gives rise to size broadening only!
- MgO standard was prepared by decomposing $MgCO_3$ powder at 1300°C for 6 hours and allowed to cool slowly in the furnace to minimize possible lattice defects.

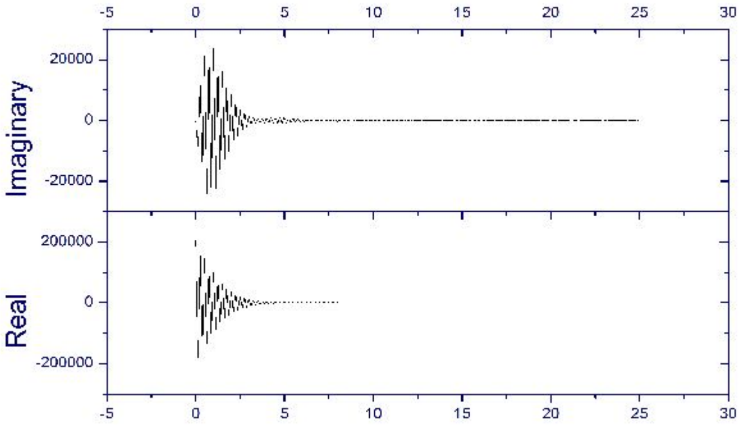
Fourier analysis:





Fourier transform of profile *h* (600°C)





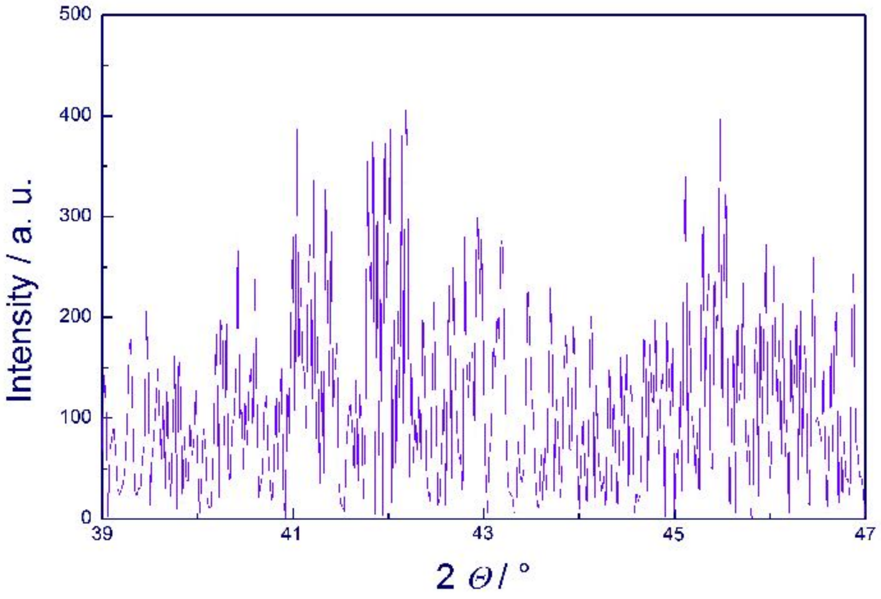
Fourier transform of profile *g* (1300°C)

$$F_{re}(t)=\frac{H_{re}(t)\cdot G_{re}(t)+H_{im}(t)\cdot G_{im}(t)}{G_{re}^2(t)+G_{im}^2(t)}$$

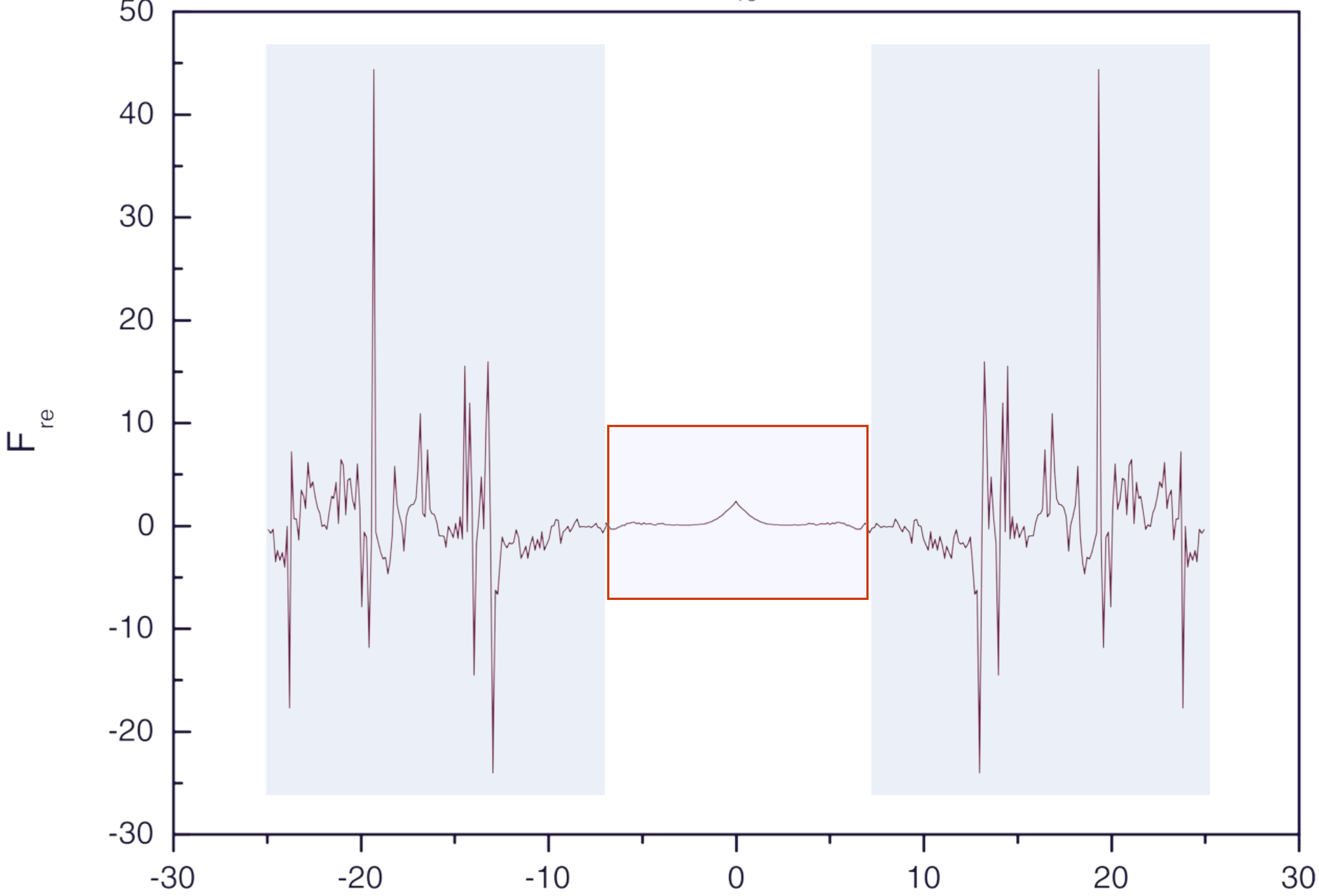
$$F_{im}(t)=\frac{H_{im}(t)\cdot G_{re}(t)-H_{re}(t)\cdot G_{im}(t)}{G_{re}^2(t)+G_{im}^2(t)}$$


Fourier transform of pure diffraction profile *f*

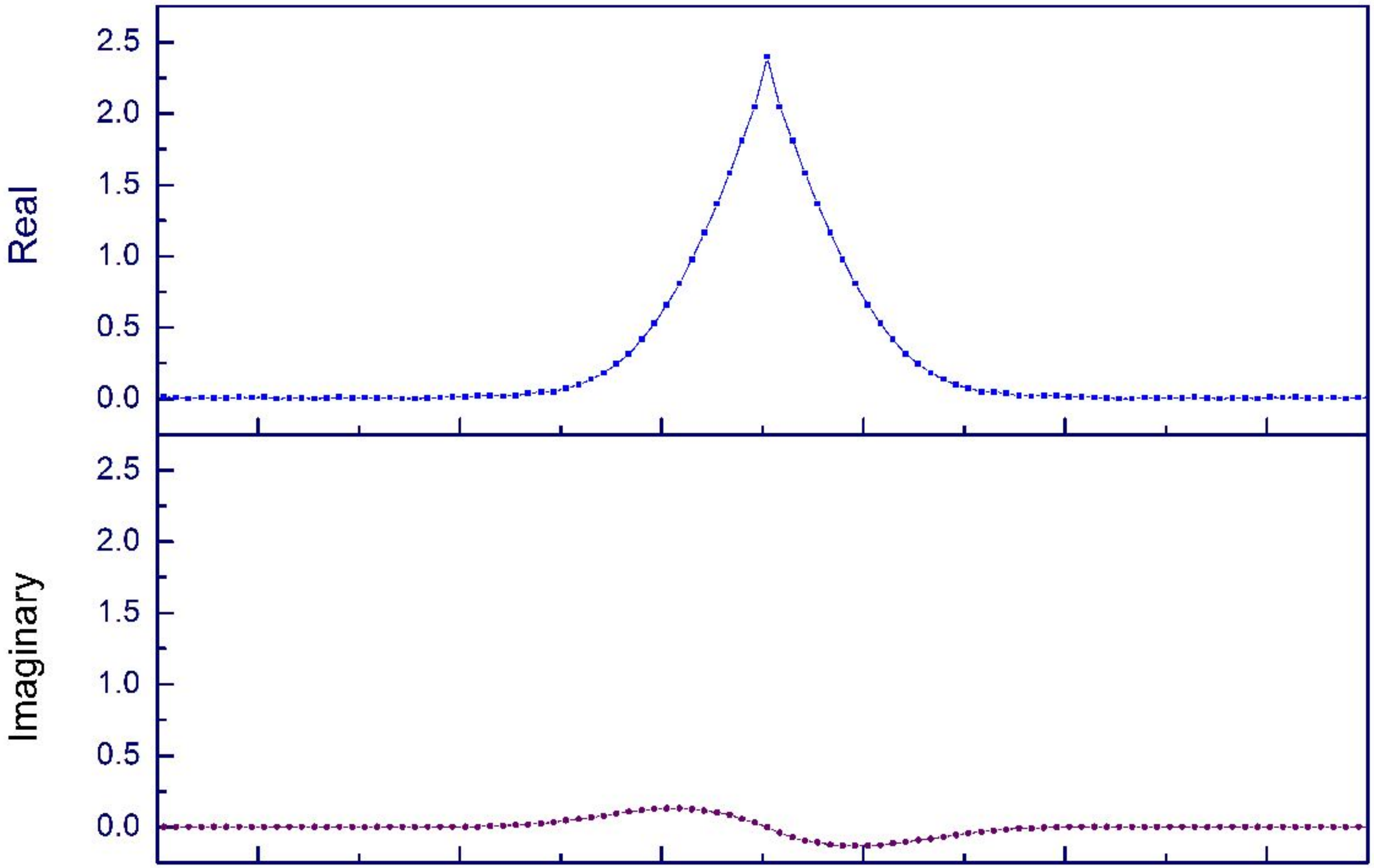
Pure diffraction profile:



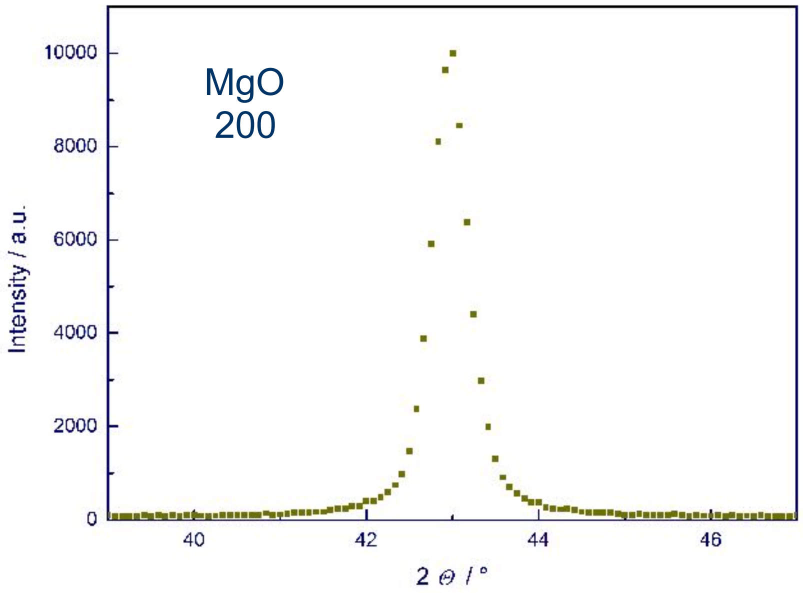
Real parts of the Fourier coefficients of pure diffraction profile (*f*), F_{re}.



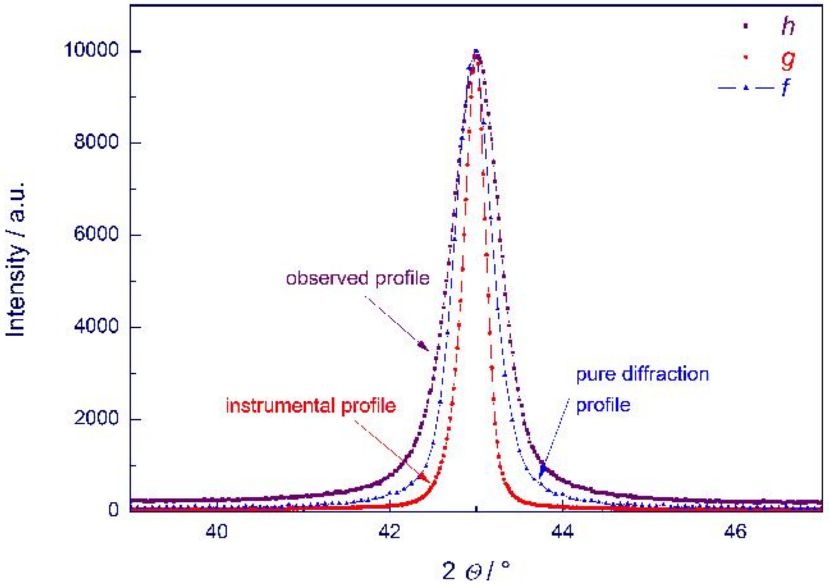
Fourier coefficients of pure diffraction profile *f* used in synthesis



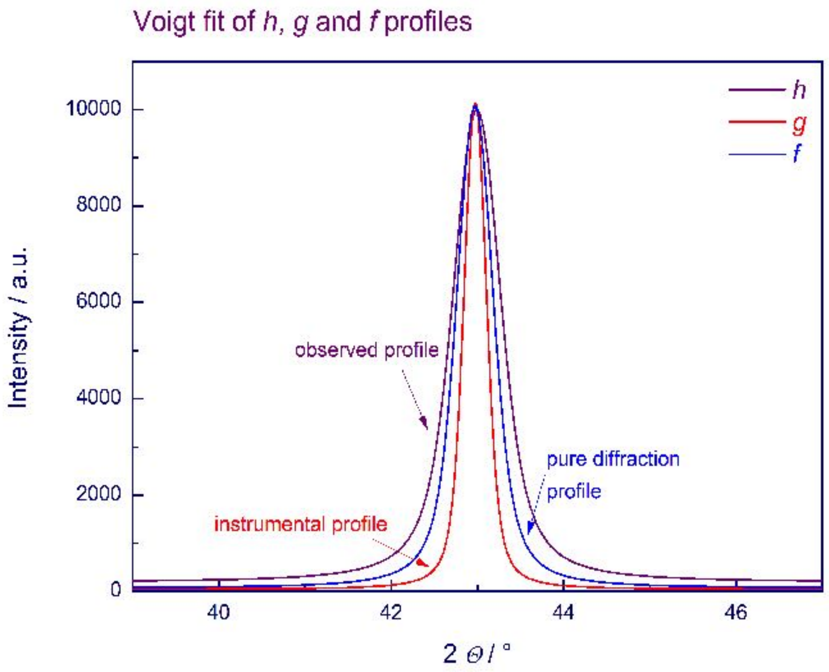
Pure diffraction profile:



- *observed profile*
- *pure diffraction profile*
- *instrumental profile*

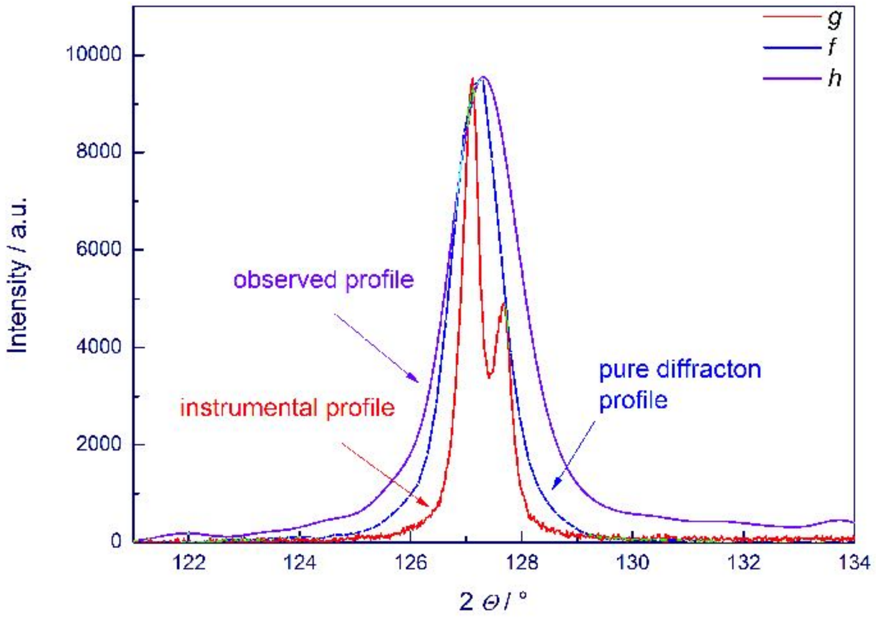


Voigt

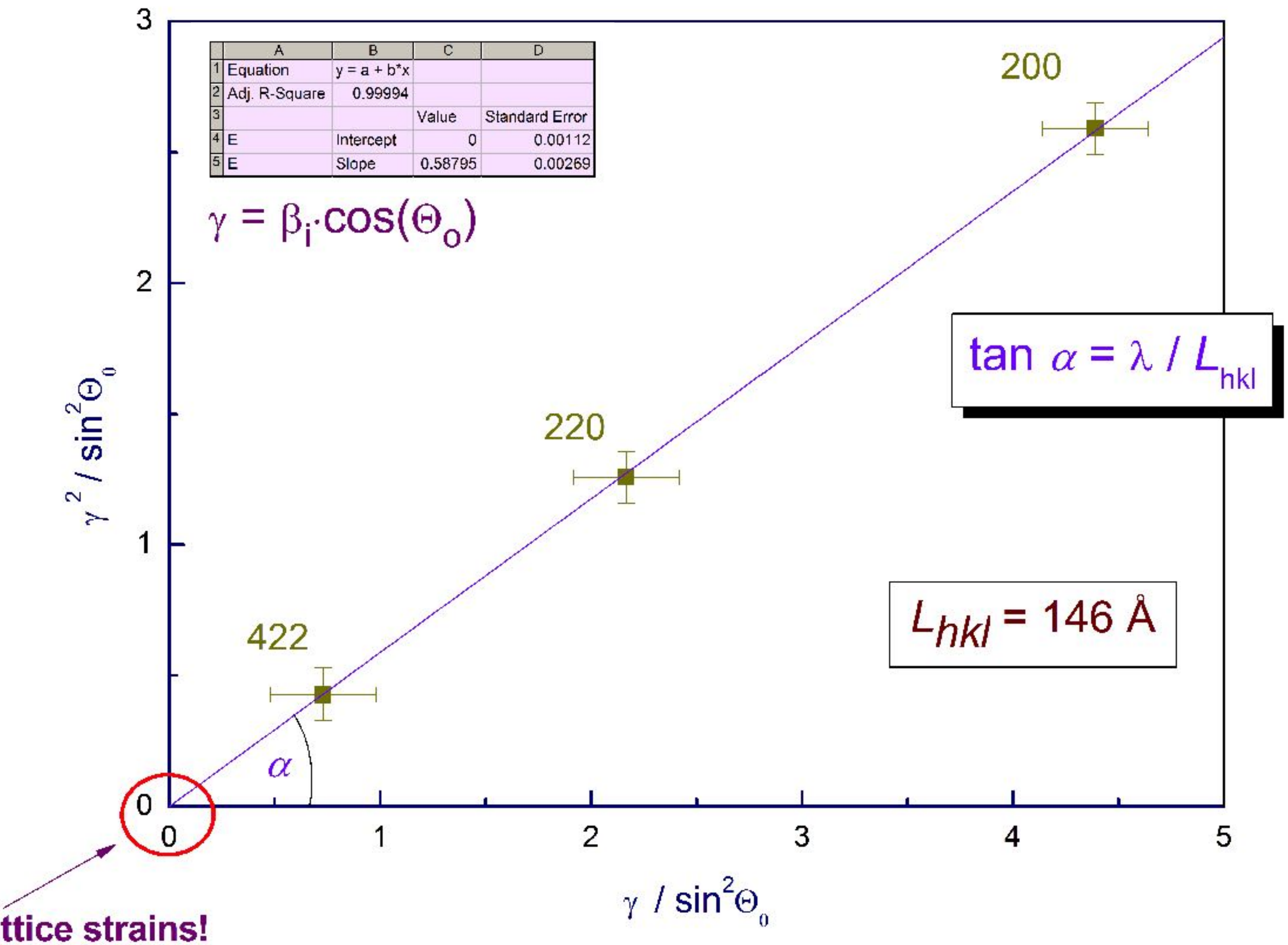


200 reflection

No fitting



422 reflection



	A	B	C	D
1	Equation	y = a + b*x		
2	Adj. R-Square	0.99994		
3			Value	Standard Error
4	E	Intercept	0	0.00112
5	E	Slope	0.58795	0.00269

$\gamma = \beta_i \cdot \cos(\Theta_o)$

$\tan \alpha = \lambda / L_{hkl}$

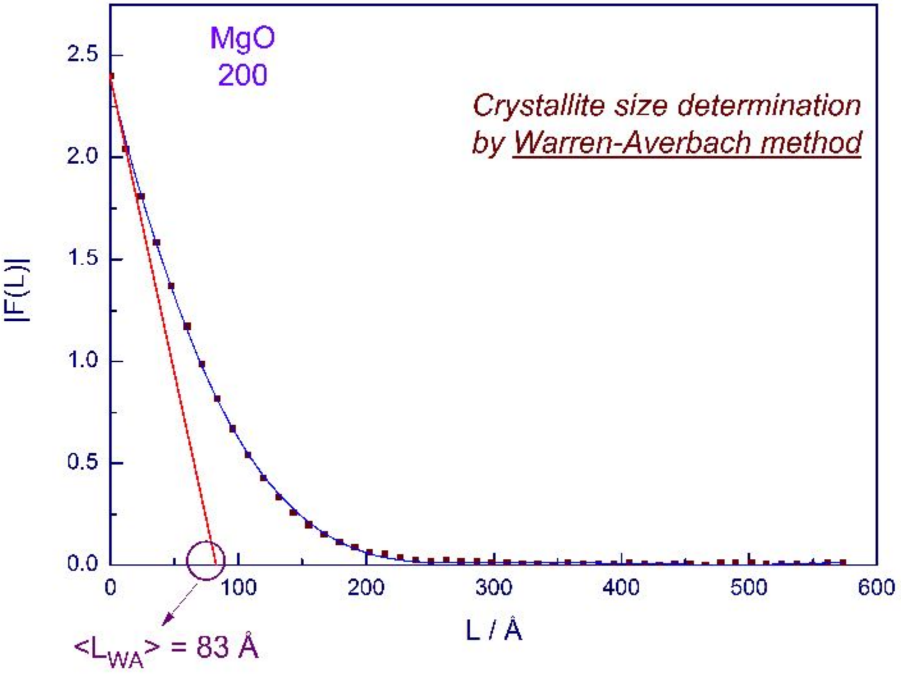
$L_{hkl} = 146$ Å

No lattice strains!

$$-\left.\frac{\mathrm{d}F_{\mathrm{pf}}(L)}{dL}\right|_{L=0}=\frac{1}{\langle L\rangle_{\mathrm{WA}}}+\frac{1}{\langle L_f\rangle_{\mathrm{WA}}},$$

$\langle L\rangle_{\mathrm{WA}}$ - crystallite size perp. (*hkl*) (surface-averaged)

$$\boxed{\langle L\rangle_{\mathrm{WA}}=83\,\mathrm{A}}$$

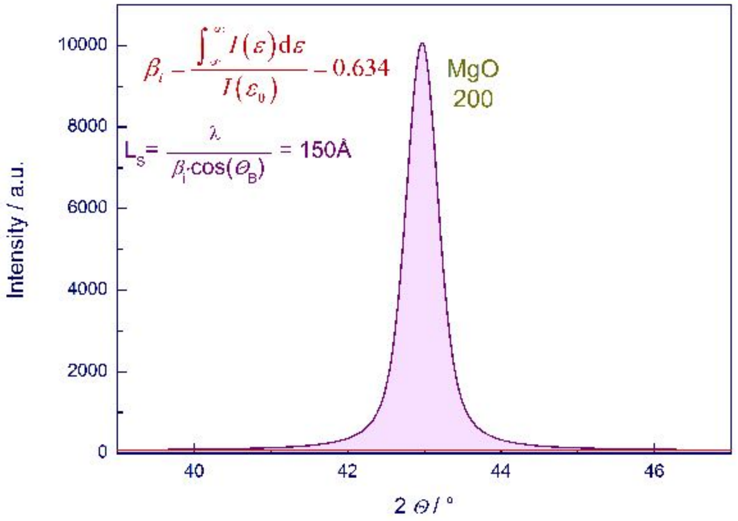


$\langle L\rangle_{\mathrm{Sch}}$ - crystallite size perp. (*hkl*) (volume-averaged)

$$\boxed{\langle L\rangle_{\mathrm{Sch}}=145\,\mathrm{A}}$$

$$\boxed{1.31\leq\frac{\langle L\rangle_{\mathrm{Sch}}}{\langle L\rangle_{\mathrm{WA}}}<2}$$

D. Balzar, International Union of Crystallography Monographs on Crystallography No. 10, 1999., 94-126

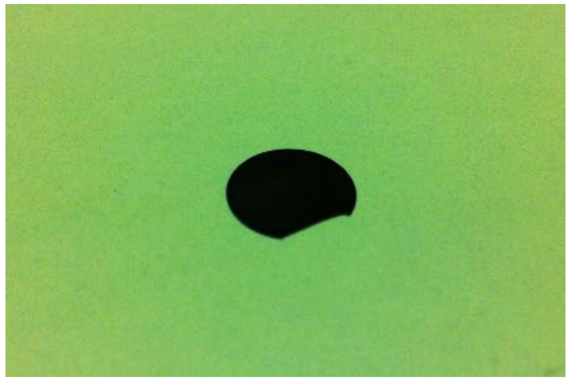


Xbroad – examples

1. Sputter-deposited tungsten

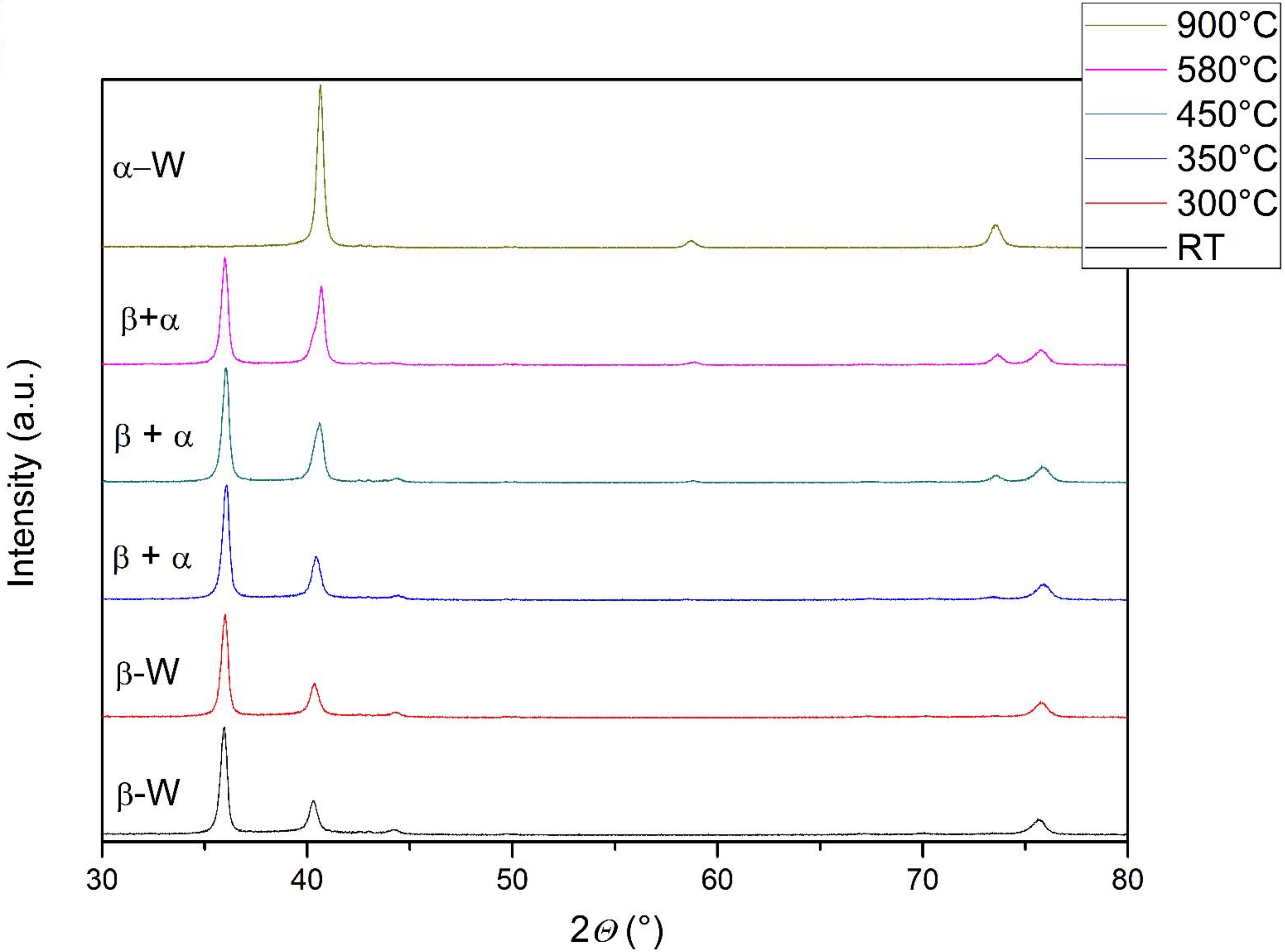
- thin tungsten films were prepared in a sputtering system with two cylindrical magnetrons
- the base pressure in the system was cca. 10^{-4} Pa
- working gas pressure was 1.4 Pa
- pure tungsten was used as a cylindrical target, substrates were discs made of sapphire and silicon

- W comes in two modifications:
  1. thermodynamically stable bcc α-W
  2. metastable β-W with A15-like crystal lattice, which converts to α-W during heating



Results:

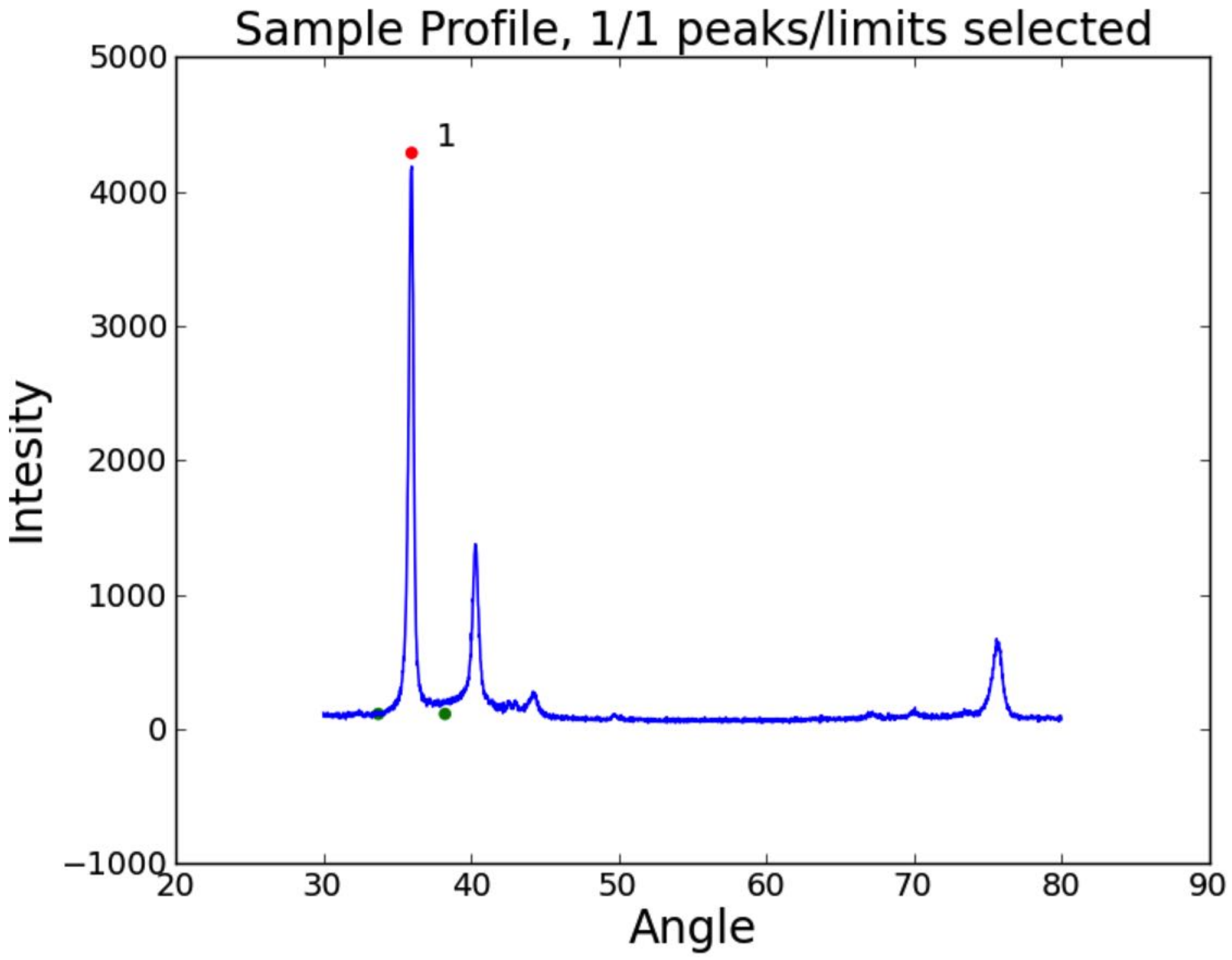
α-W
β-W



Results:

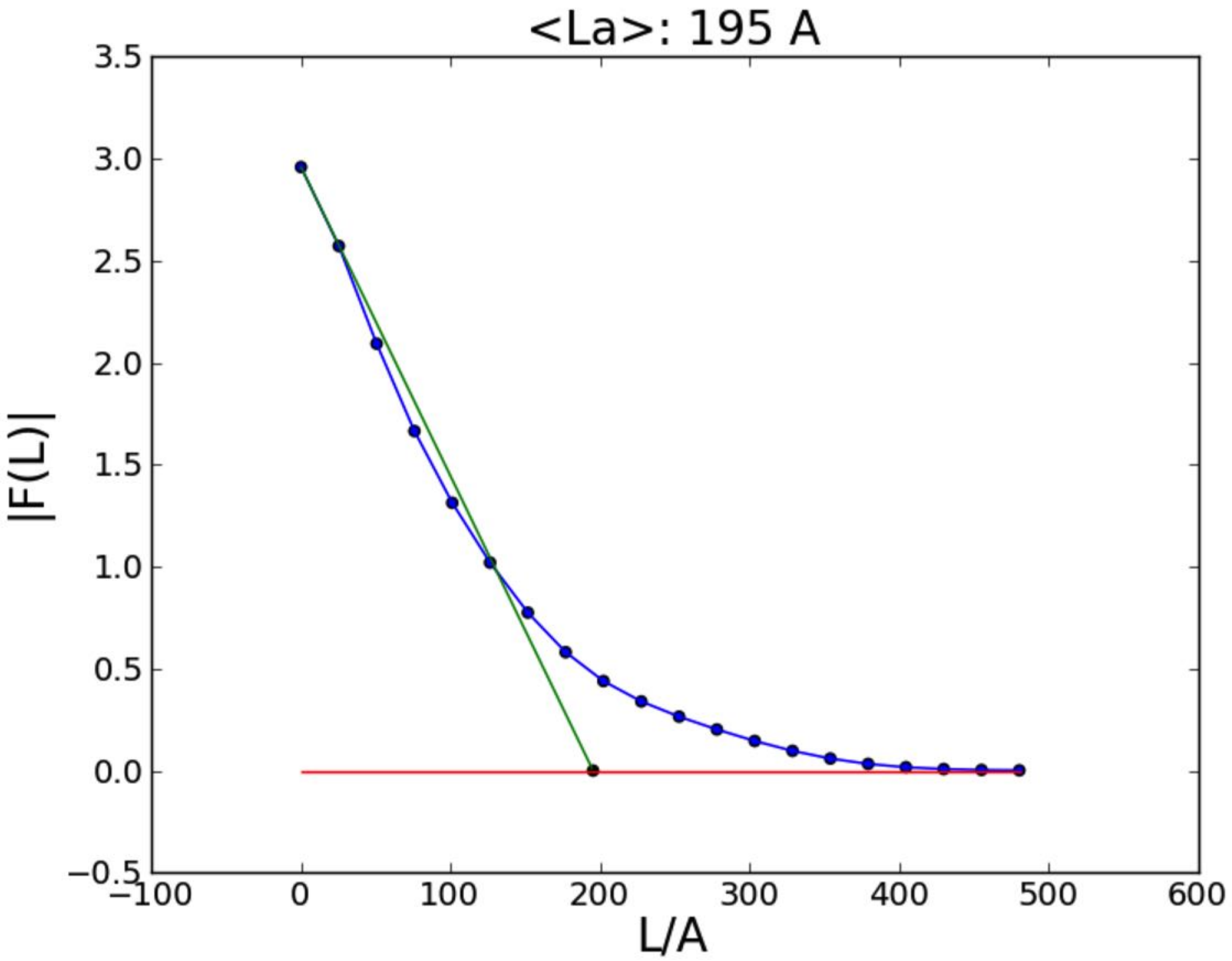
T (ºC)	Warren-Averbach		Willamson-Hall			
	β-W	α-W	β-W		α-W	
	size (Å)	size (Å)	size (Å)	strain (%)	Size (Å)	strain (%)
RT	114	-	195	0.106	-	-
300	115	-	210	0.106	-	-
350	140	-	235	0.100	-	-
450	150	115	250	0.098	198	0.104
580	156	120	260	0.098	205	0.098
900	-	150	-	-	245	0.097

Common mistakes: “hook effect”



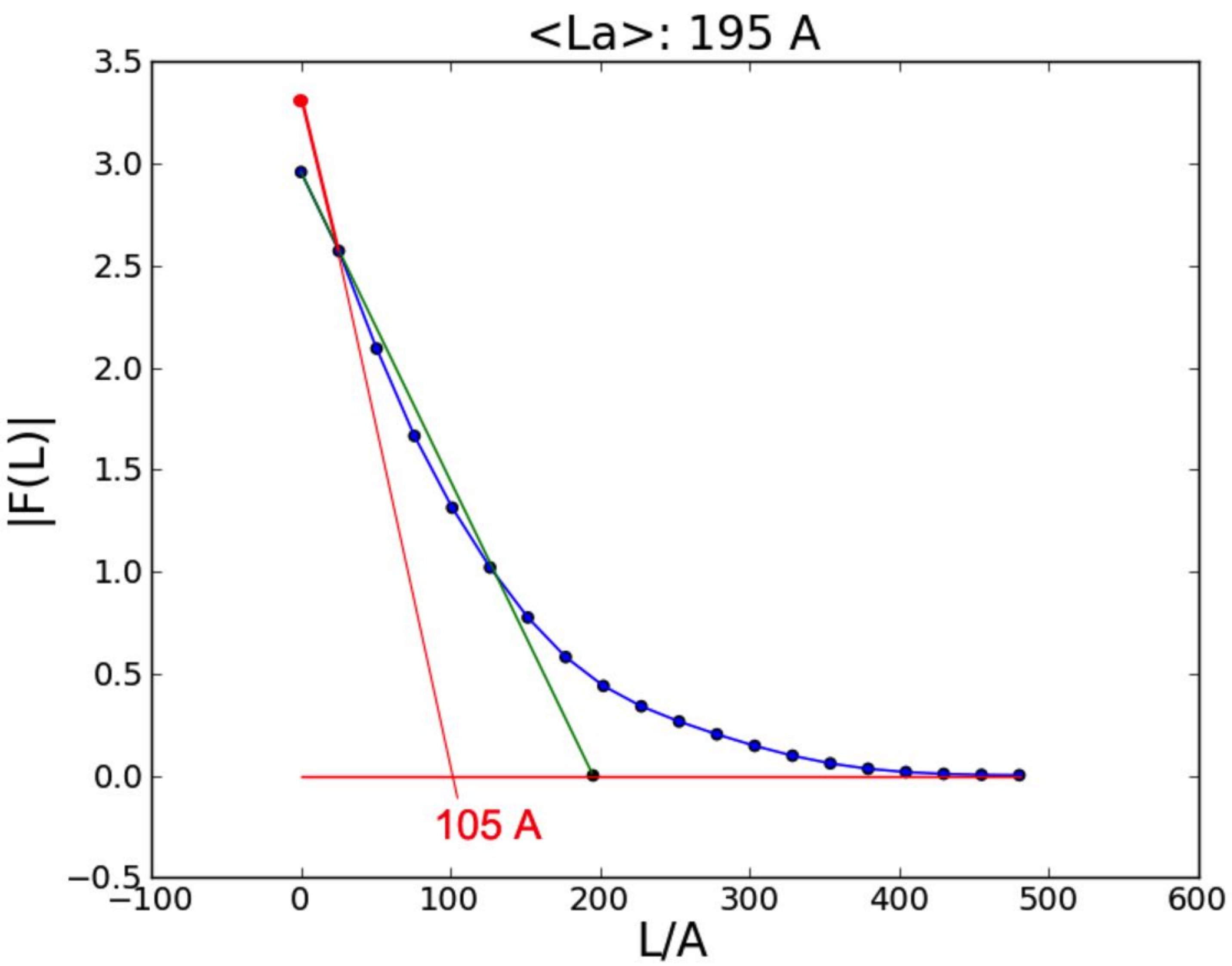
- two maxima are too close to each other
- overlap of the tails: background in between is too high
- calculated integral breadth is too small

Common mistakes: “hook effect”



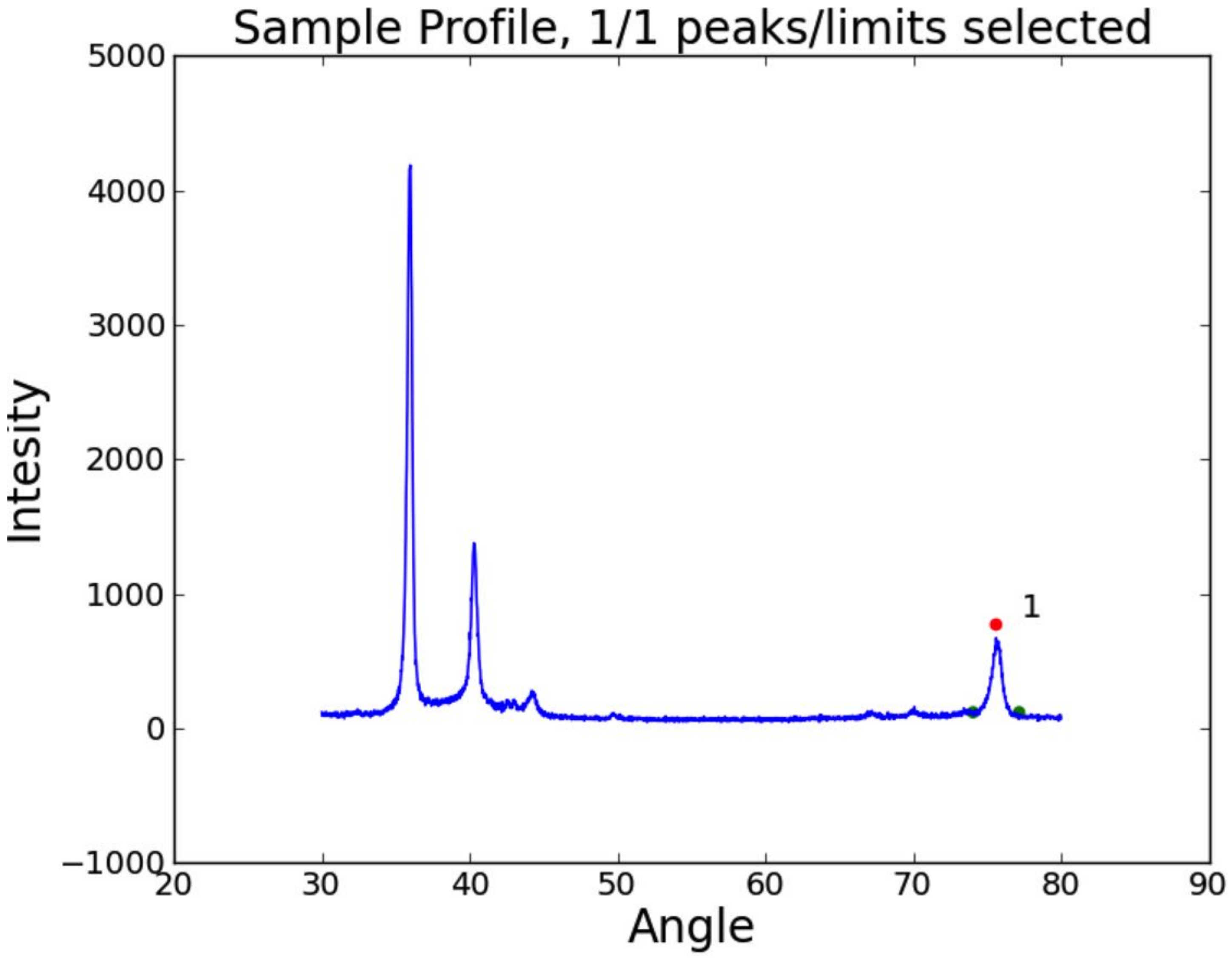
- the first (zeroth) coefficient is smaller than it should be
- obtained size value is larger than it really is
- correction is necessary

Common mistakes: “hook effect”



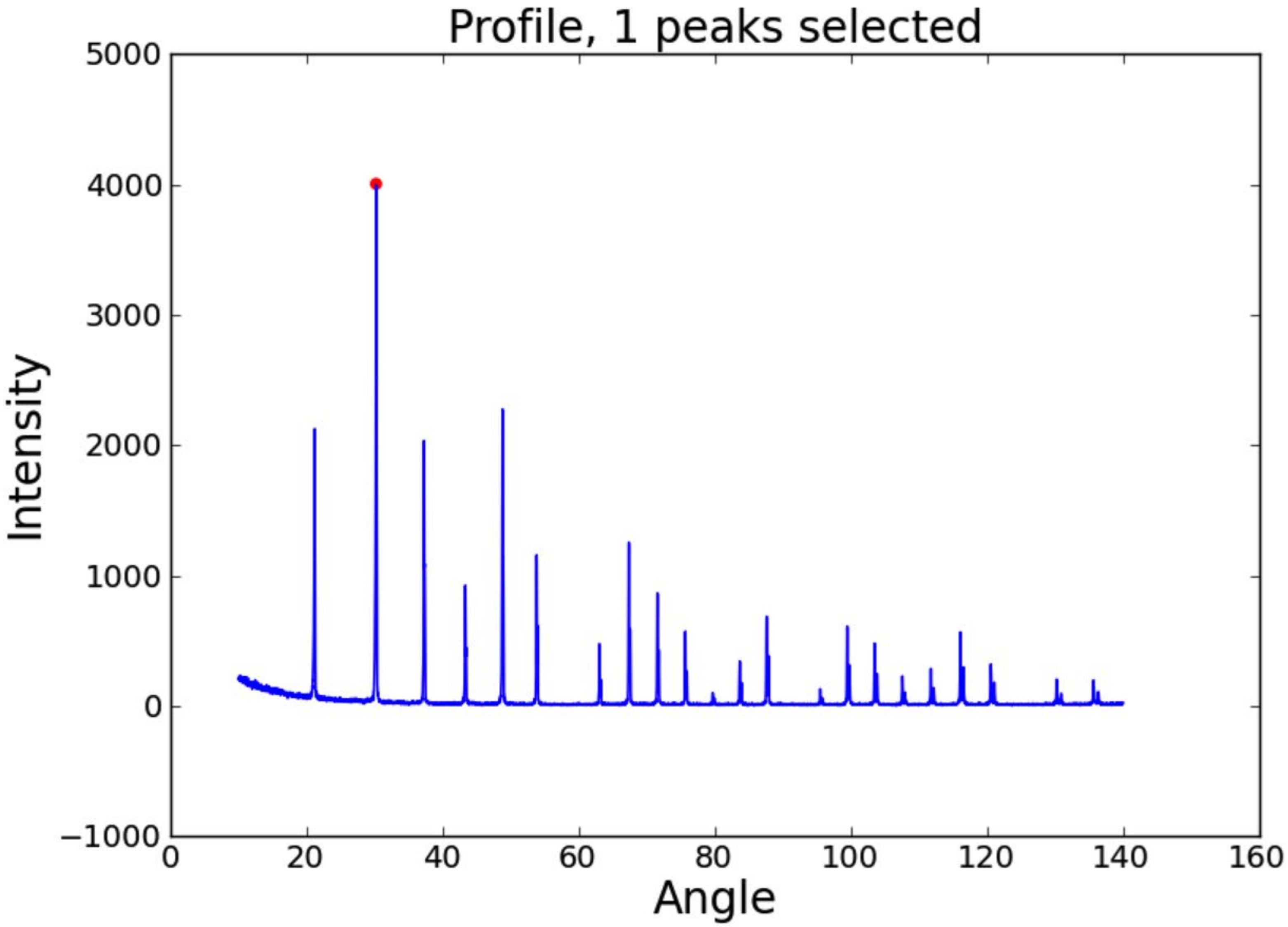
This is more realistic value!

Common mistakes: “wrong” instrumental peak chosen



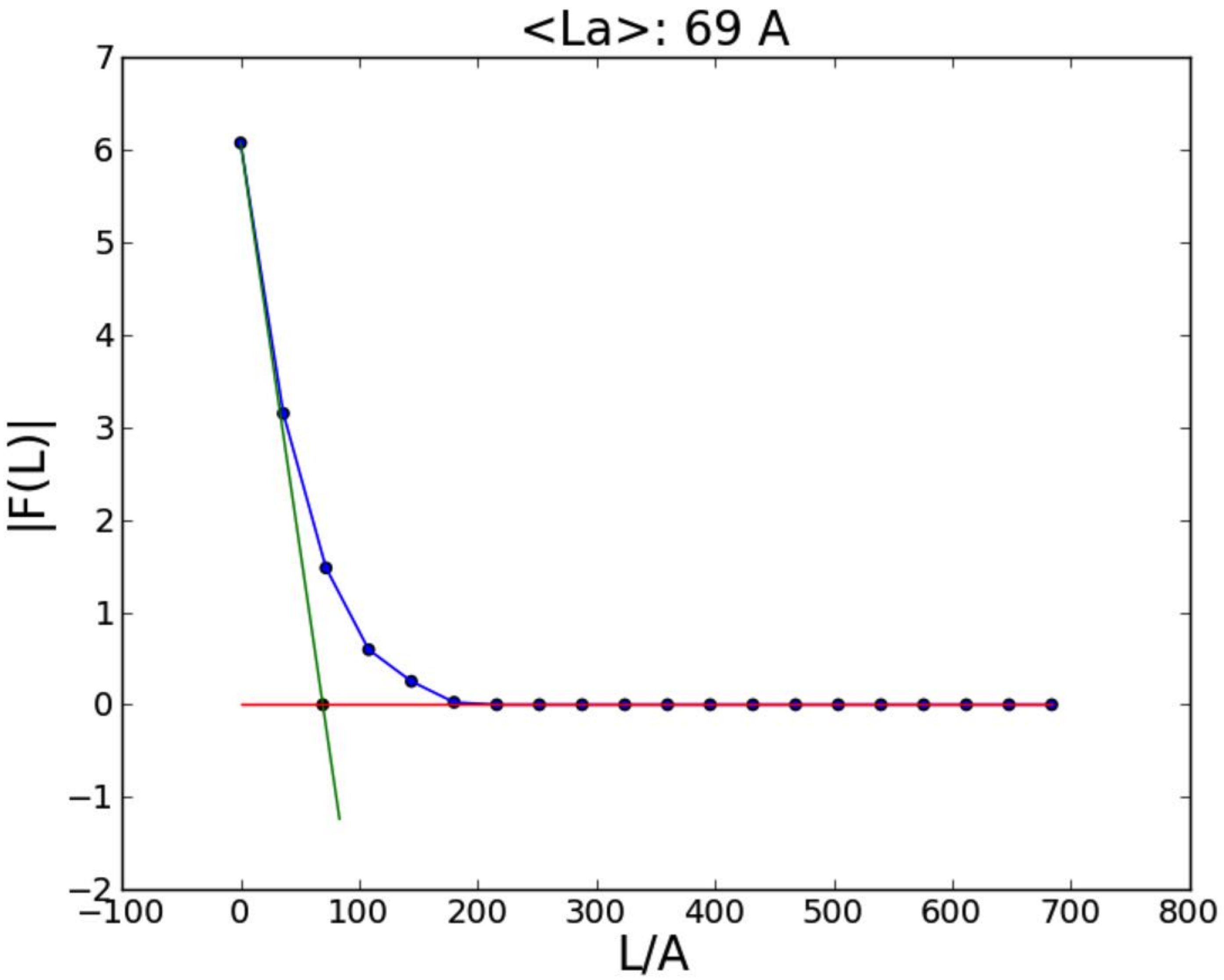
- peak at around 77º 2*Θ* taken for analysis

Common mistakes: “wrong” instrumental peak chosen

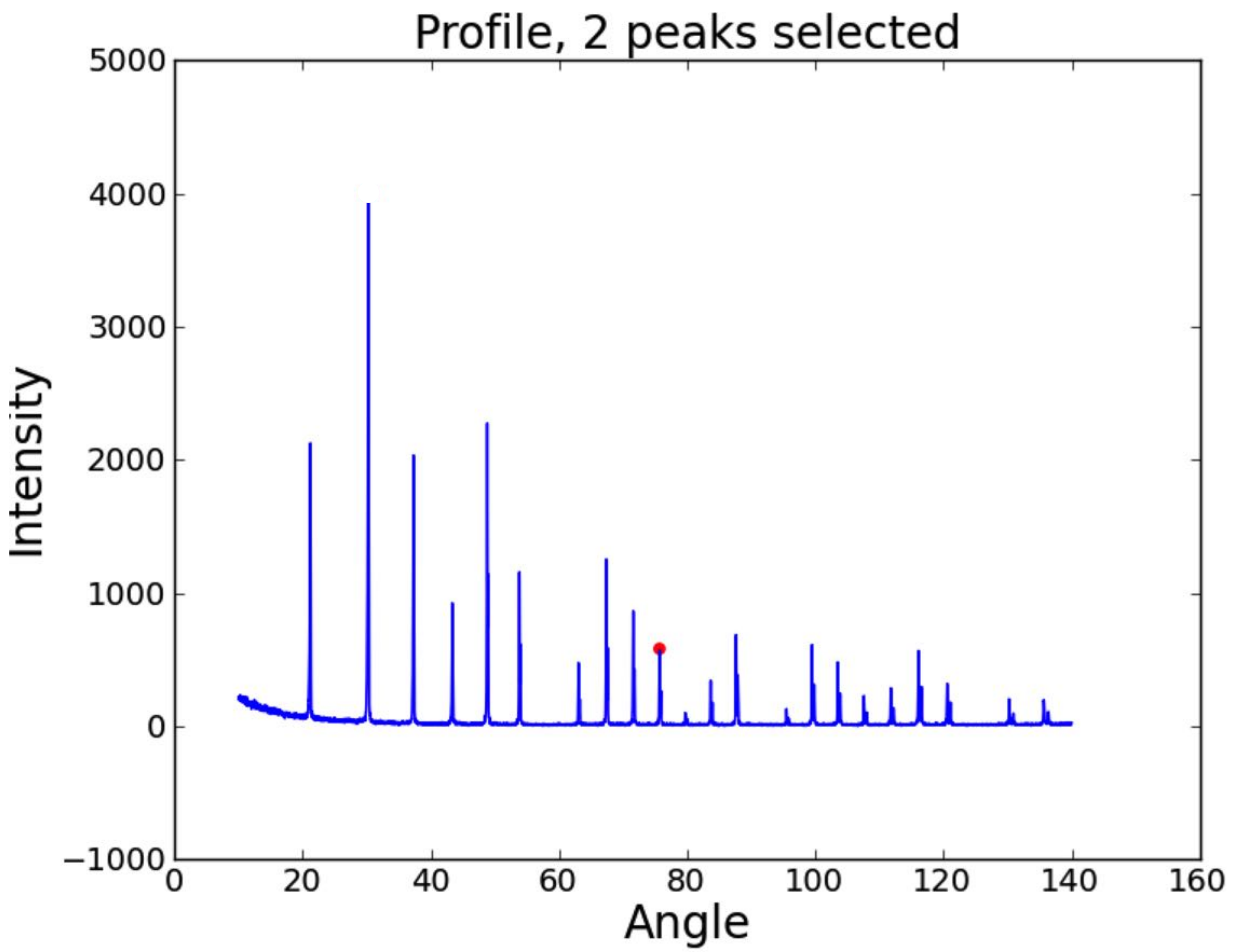


- intstrumental peak at around 32º 2*Θ* taken for deconvolution

Common mistakes: “wrong” instrumental peak chosen

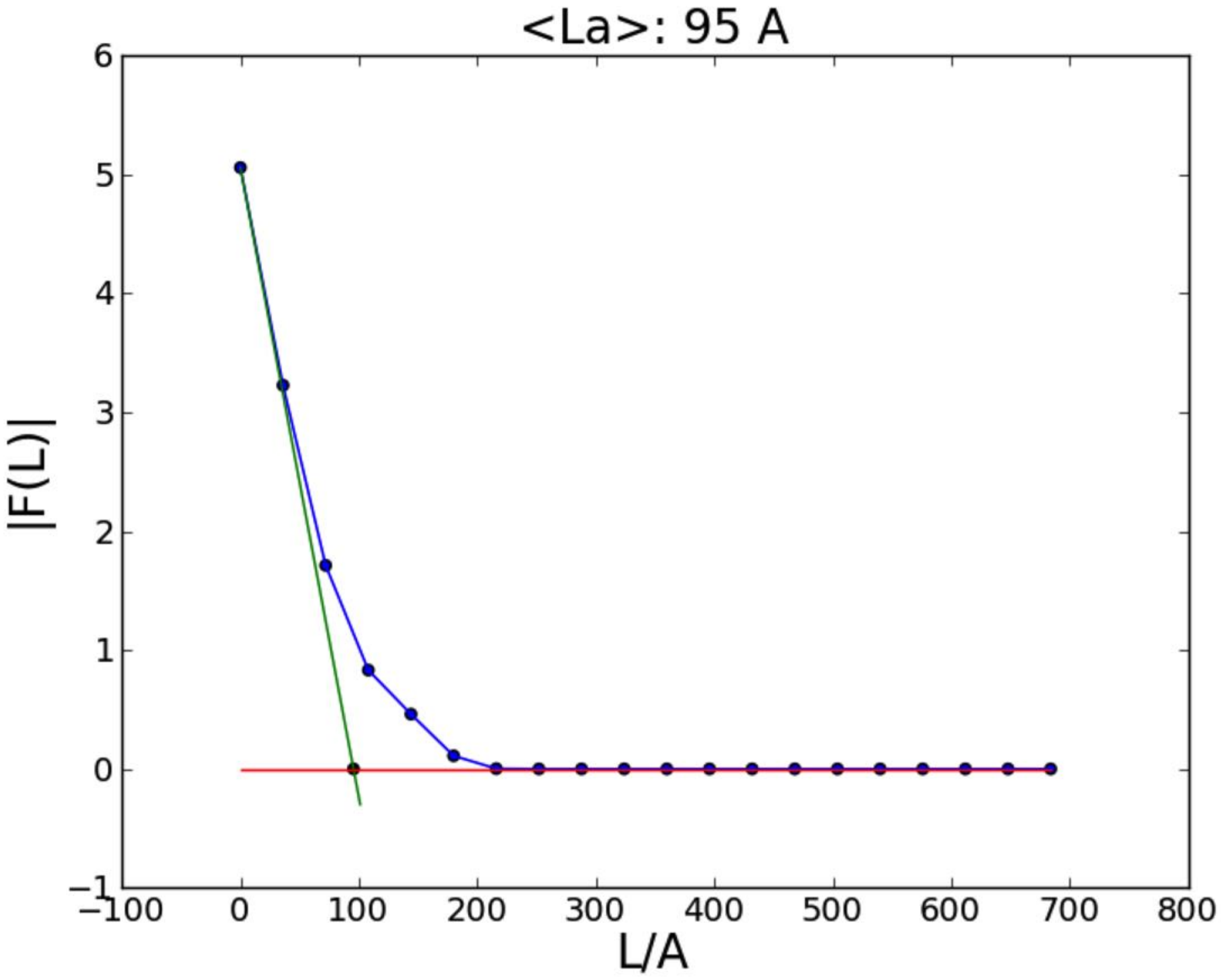


Common mistakes: “wrong” instrumental peak chosen



- repeated analysis with the instrumental peak whose position is close to the analysed peak

Common mistakes: “wrong” instrumental peak chosen



- obtained size is greater now (compared to 69 Å)
- instrumental broadening increses with 2*Θ* and in the first case instrumental peak was too narrow
- convoluted peak was too broad, the crystallite size obtained was smaller

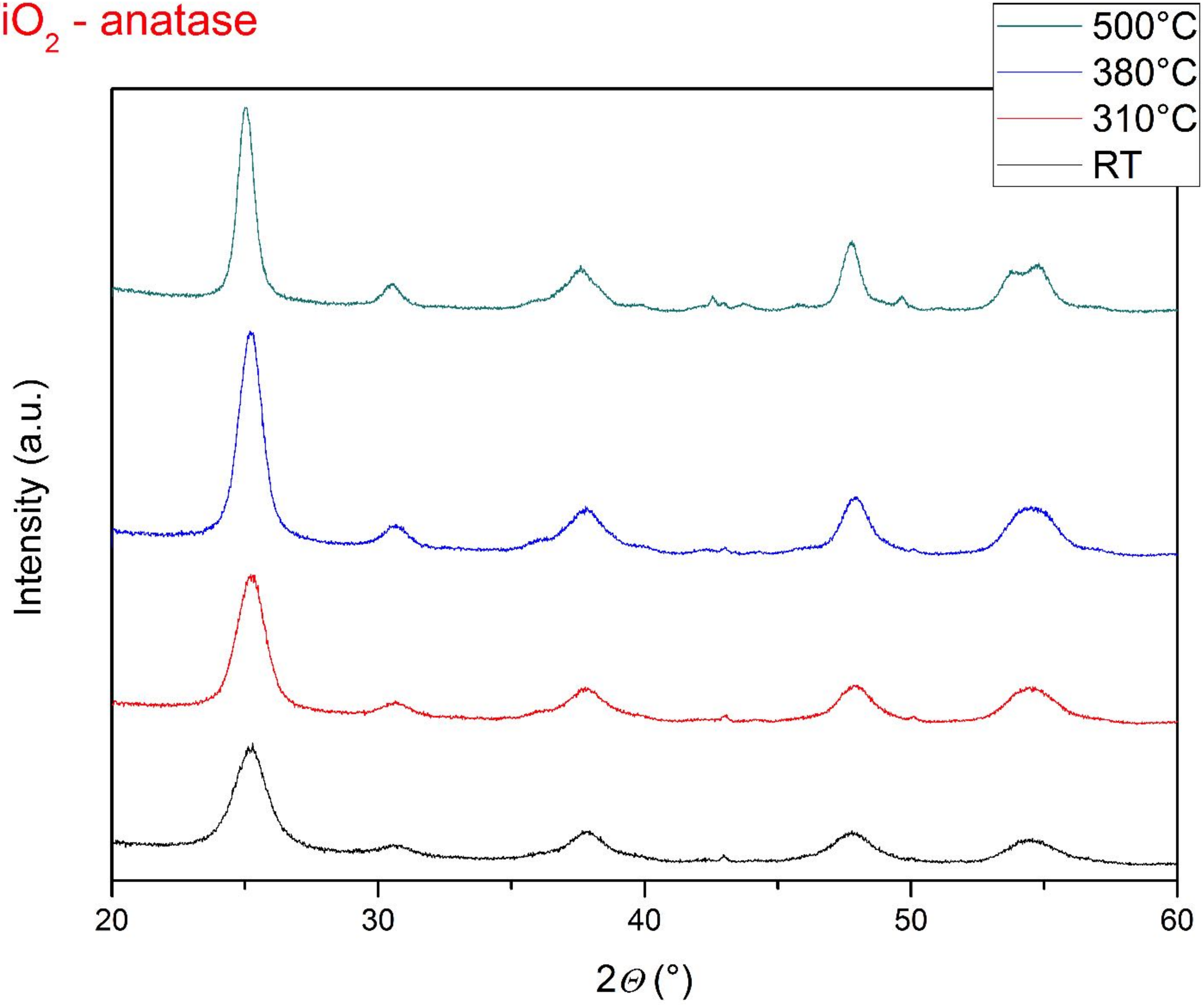
Xbroad – examples

2. Evolution of the crystallite size-strain in nanocrystalline TiO_2 anatase

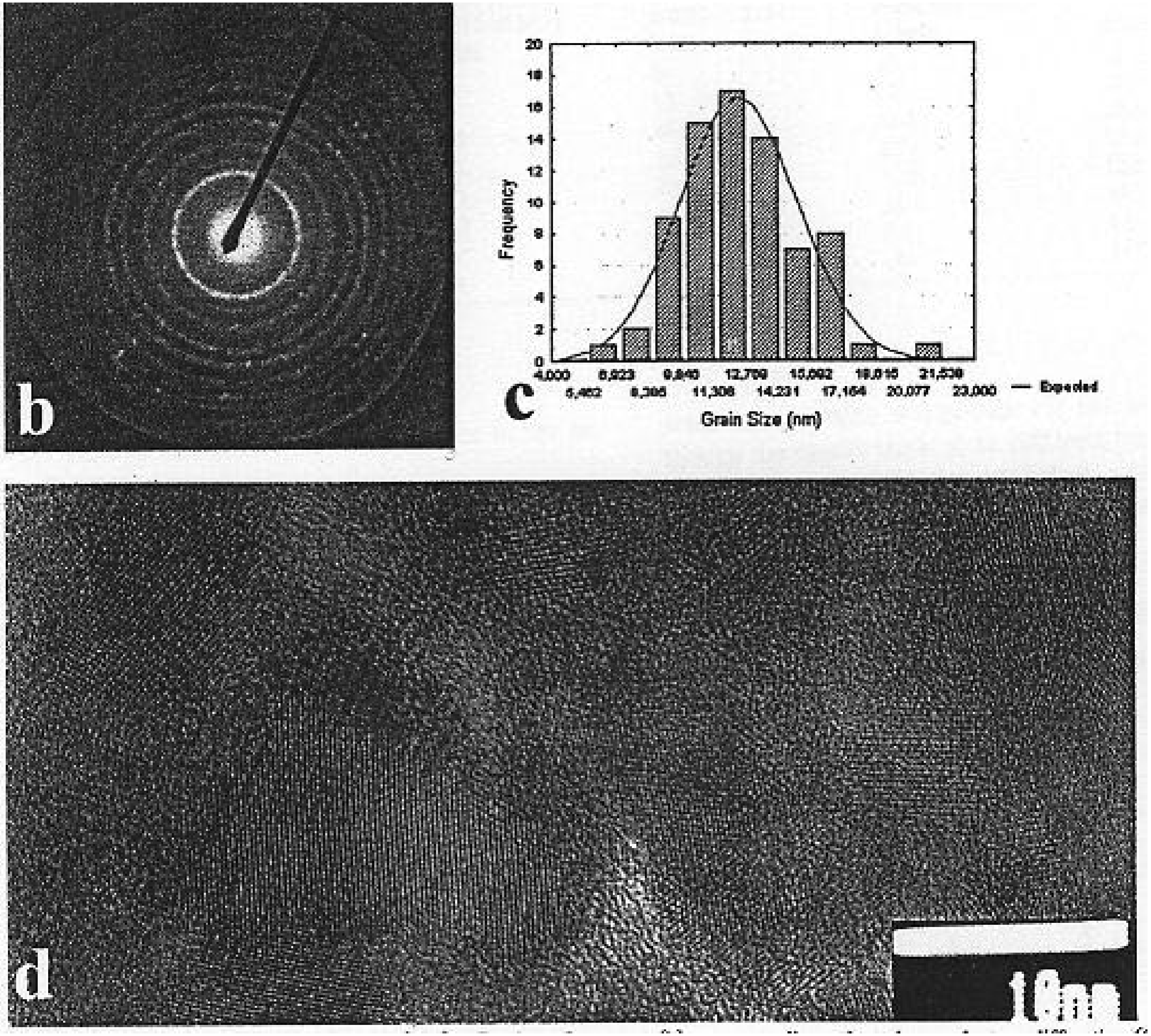
- the samples of nanosized TiO_2 were synthesized by sol-gel method based on the hydrolysis of Ti(IV)-isopropoxide in the nitrogen atmosphere
- after drying in air composite gels, containing small TiO_2 nanocrystallites of different mean sizes and widths of size distributions are synthesized
- to obtain large crystallites, the as-prepared TiO_2 sample was thermally treated for 1 h at temperatures: 310, 380 and 500º C
- the TiO_2 samples were examined by complementary TEM techniques including conventional microscopy in brigth-field and dark-field, selected area electron diffraction and HRTEM, as well as PXRD.

Results:

TiO_2 - anatase



Results:

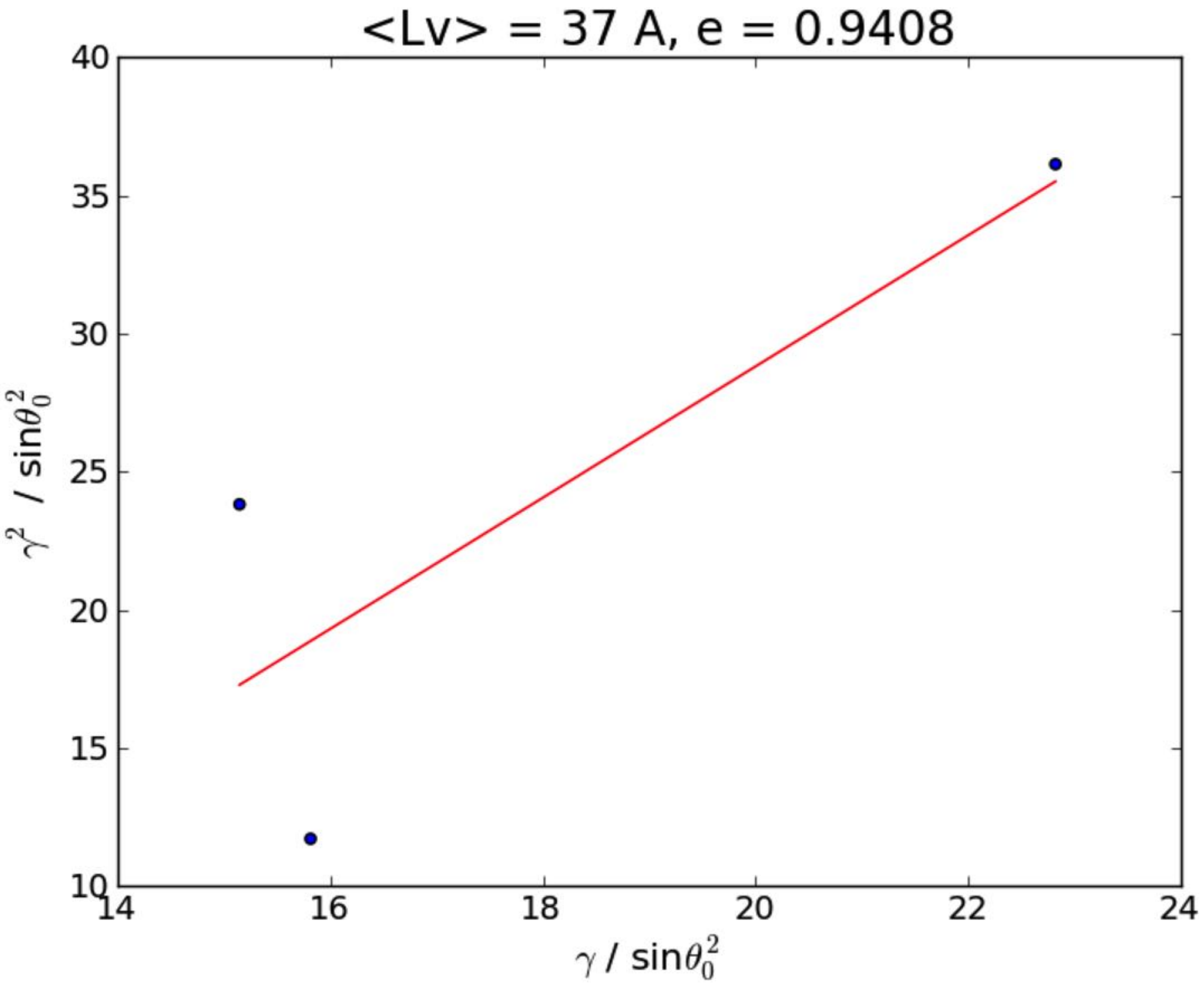


SAED, distribution of grain sizes and HRTEM of TiO_2 at 500ºC

Results:

T (ºC)	TiO_2 anatase			
	W-A (Å)	W-H (Å)	HRTEM (Å)	Scherrer (Å)
RT	50	61	58	59
310	66	77	73	75
380	78	99	80	96
500	121	138	130	135

Common mistakes: bad quality data



Not a very reliable linear regression!

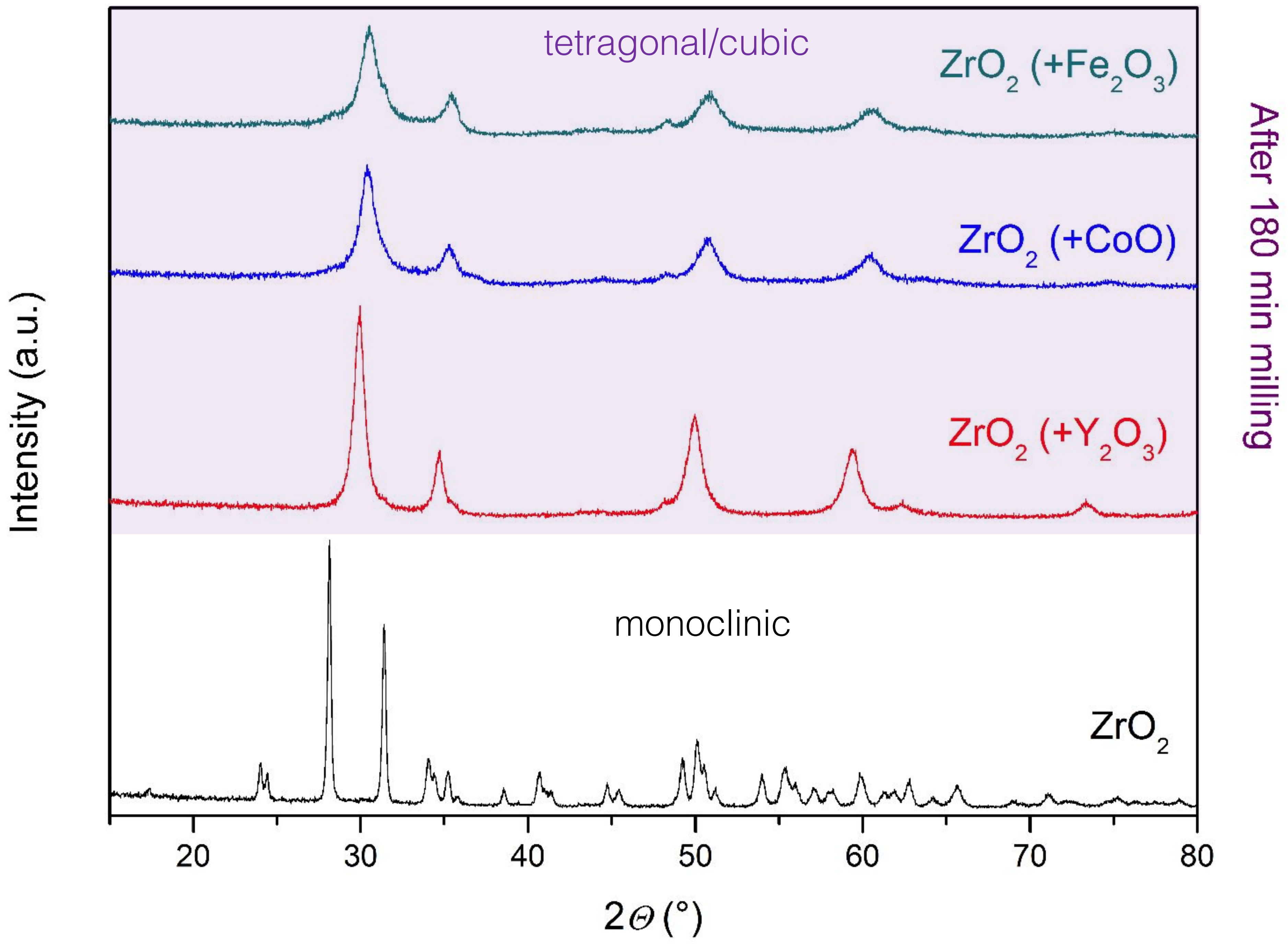
Xbroad – examples

3. Zirconia solid solutions ZrO_2-Y_2O_3 (CoO or Fe_2O_3)

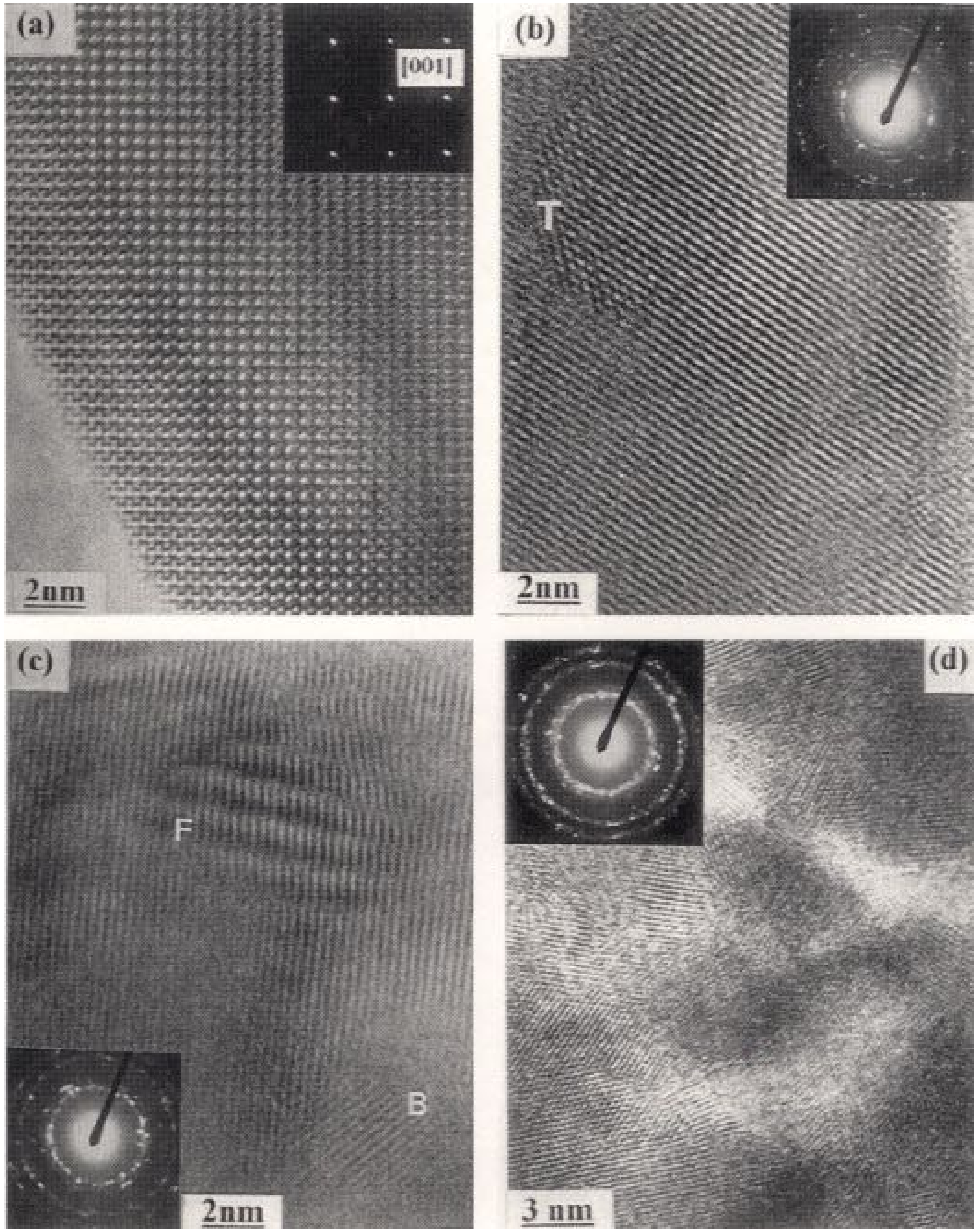
- ZrO_2 monoclinic powder and 16.7wt.% Y_2O_3 (CoO or Fe_2O_3) were mechanically milled using a Fritsch planetary micro-ball mill Pulverisette 7, with a vial and balls made of tungsten carbid (WC)
- the milling processes were characterized by PXRD and TEM

- at the beginning: ZrO_2+Y_2O_3 (CoO, Fe_2O_3)
- after 10 min: broad ZrO_2 peaks + Y_2O_3 (CoO, Fe_2O_3)
- after 50 min: monoclinic ZrO_2 + tetragonal/cubic ZrO_2
- after 180 min: tetragonal/cubic ZrO_2

Results:


tetragonal/cubic
ZrO_2 (+Fe_2O_3)
ZrO_2 (+CoO)
ZrO_2 (+Y_2O_3)
After 180 min milling
monoclinic
ZrO_2
Intensity (a.u.)
20
30
40
50
60
70
80
2Θ (°)

Results:



monoclinic ZrO_2 viewed along [001] directon

d_{111} lattice image of ZrO_2+Y_2O_3 milled for 10 min

T – tetragonal crystallite stuck on large monoclinic ZrO_2 oxide

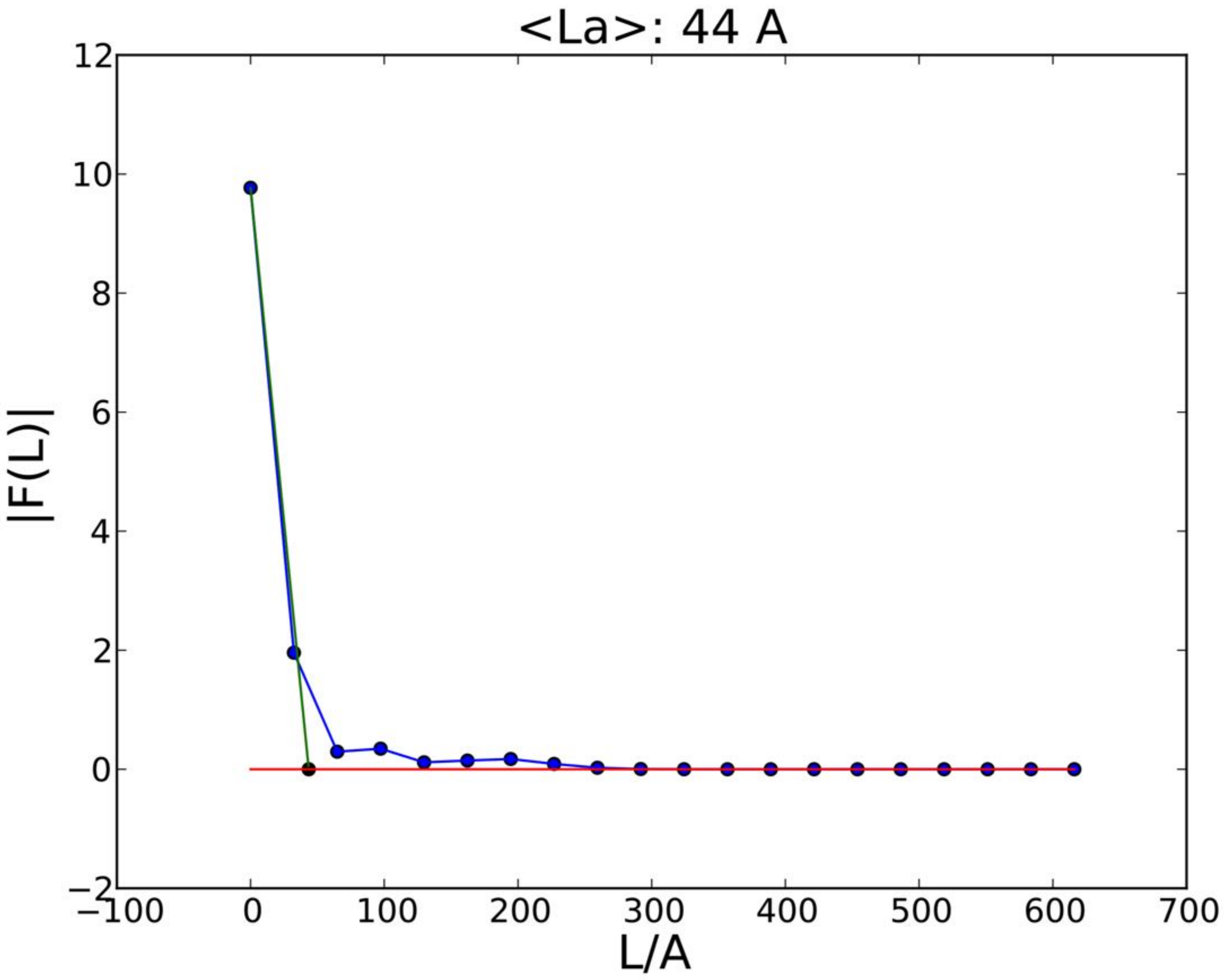
ZrO_2+Y_2O_3 milled for 1 h

ZrO_2+Y_2O_3 milled for 3 h crystallites from 2 to 20 nm

Results:

sample	time (min)	Waren-Averbach	Williamson-Hall		HRTEM
		size (Å)	size (Å)	strain (%)	size (Å)
ZrO_2	0	381	439	0.07	
ZrO_2+Y_2O_3	180	48	74	0.177	50
ZrO_2+CoO	180	44	72	0.175	45
ZrO_2+Fe_2O_3	180	44	73	0.163	46

Common mistakes: background noise



oscillations of the Fourier coefficients due to background noise – should be smoothed before further analysis

Xbroad – examples

4. CeO_2 – “ideal” sample used in Size/Strain round robin by Davor Balzar

D. Balzar, N. Audebrand, M. Daymond, A. Fitch, A. Hewat, J.I. Langford, A. Le Bail, D. Louër, O. Masson, C.N. McCowan, N.C. Popa, P.W. Stephens, B. Toby,
Size-Strain Line-Broadening Analysis of the Ceria Round-Robin Sample,
*Journal of Applied Crystallography **37** (2004) 911-924*

- A line-broadening study on a ceria sample and a size–strain round robin on diffraction line-broadening methods, which was sponsored by the Commission on Powder Diffraction of the International Union of Crystallography.
- The sample was prepared by heating hydrated ceria at 923 K for 45 h.
- Another ceria sample was prepared to correct for the effects of instrumental broadening by annealing commercially obtained ceria at 1573K for 3h and slowly cooling it in the furnace.
- The diffraction measurements were carried out with two laboratory and two synchrotron X-ray sources, two constant-wavelength neutron and a time-of-flight (TOF) neutron source.
- Diffraction measurements were analyzed by three methods: the model assuming a lognormal size distribution of spherical crystallites, Warren–Averbach analysis and Rietveld refinement.
- The last two methods detected a relatively small strain in the sample, as opposed to the first method. Assuming a strain-free sample, the results from all three methods agree well.

Results:

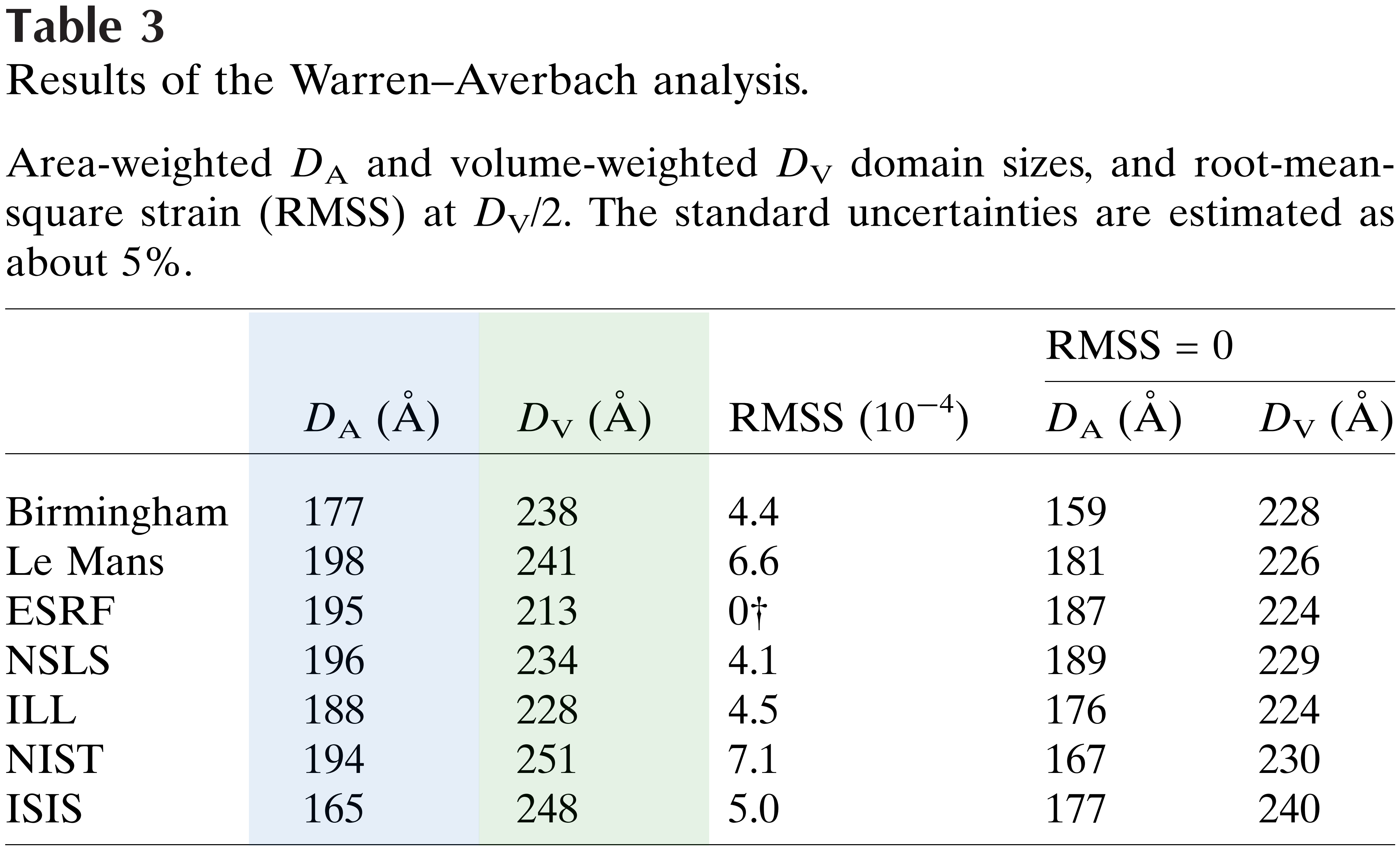


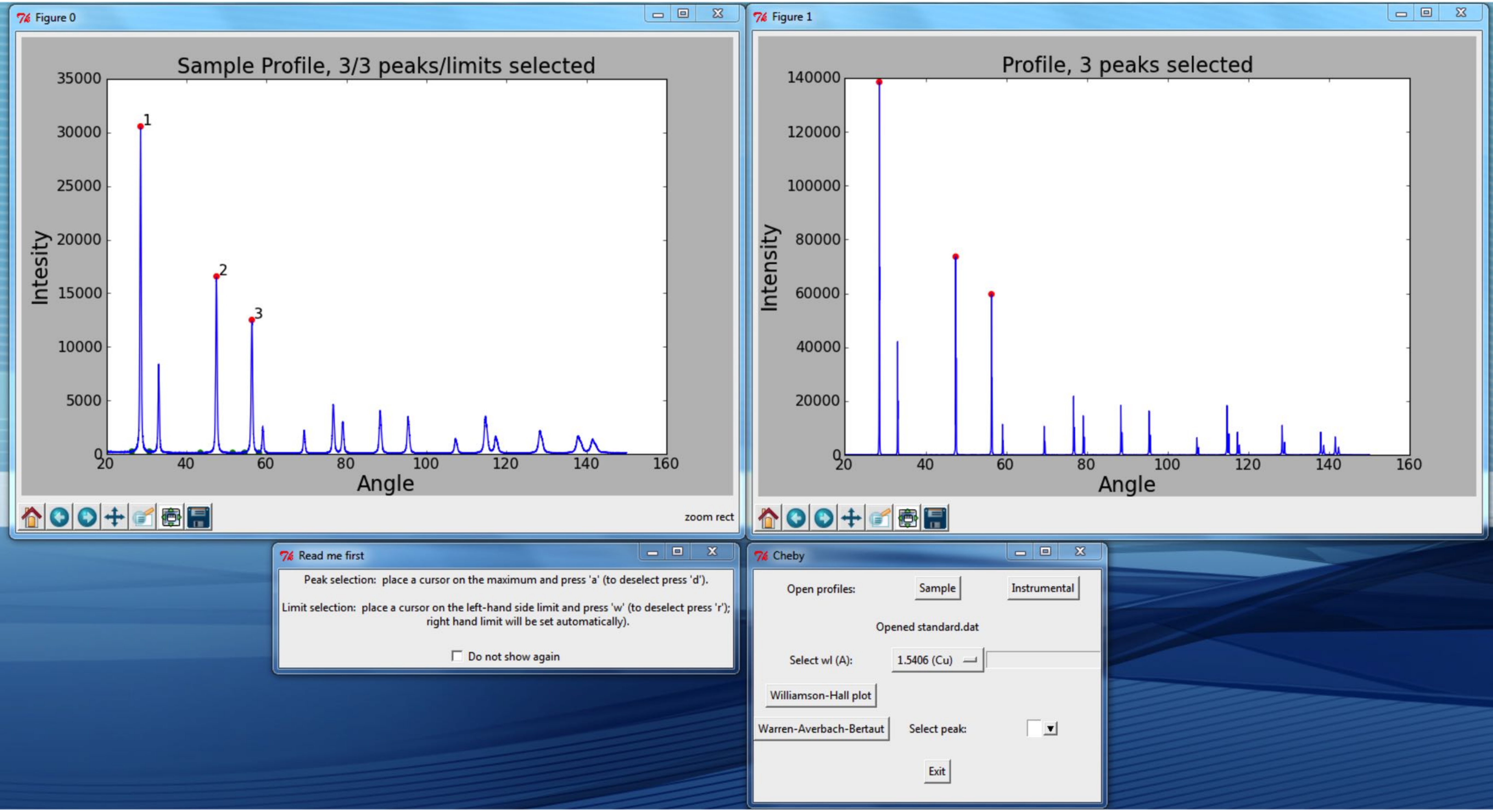
Table 3
Results of the Warren–Averbach analysis.

Area-weighted D_A and volume-weighted D_V domain sizes, and root-mean-square strain (RMSS) at $D_V/2$. The standard uncertainties are estimated as about 5%.

				RMSS = 0	
	D_A (Å)	D_V (Å)	RMSS (10^{-4})	D_A (Å)	D_V (Å)
Birmingham	177	238	4.4	159	228
Le Mans	198	241	6.6	181	226
ESRF	195	213	0†	187	224
NSLS	196	234	4.1	189	229
ILL	188	228	4.5	176	224
NIST	194	251	7.1	167	230
ISIS	165	248	5.0	177	240

Xbroad: $\langle L_A \rangle = 170\,\text{Å}, \quad \langle L_V \rangle = 234\,\text{Å}$

No problems – excellent measurement, no overlapping, good background!



Read me first

Peak selection: place a cursor on the maximum and press 'a' (to deselect press 'd').

Limit selection: place a cursor on the left-hand side limit and press 'w' (to deselect press 'r'); right hand limit will be set automatically).

☐ Do not show again

Cheby

Open profiles: Sample Instrumental

Opened standard.dat

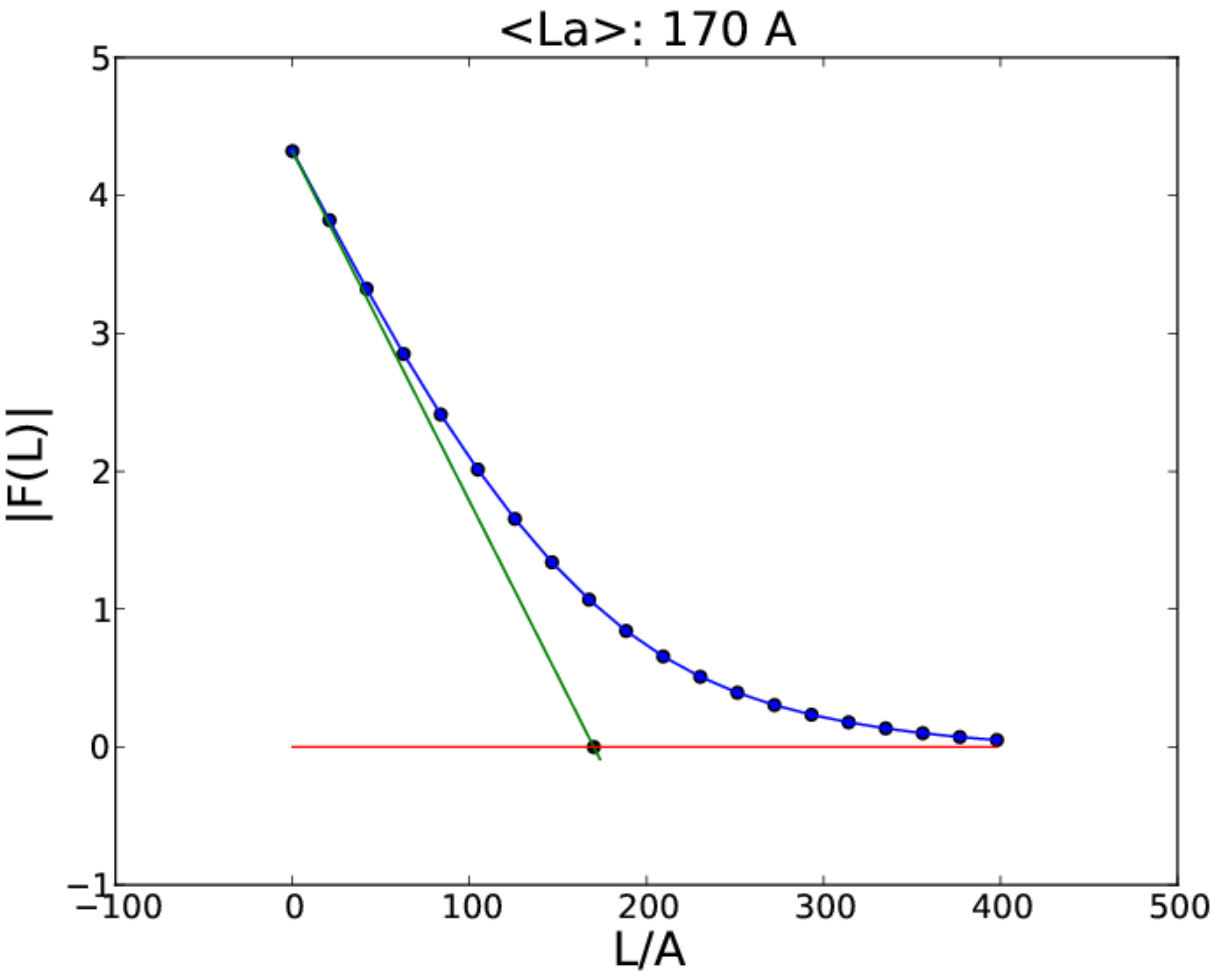
Select wl (A): 1.5406 (Cu)

Williamson-Hall plot

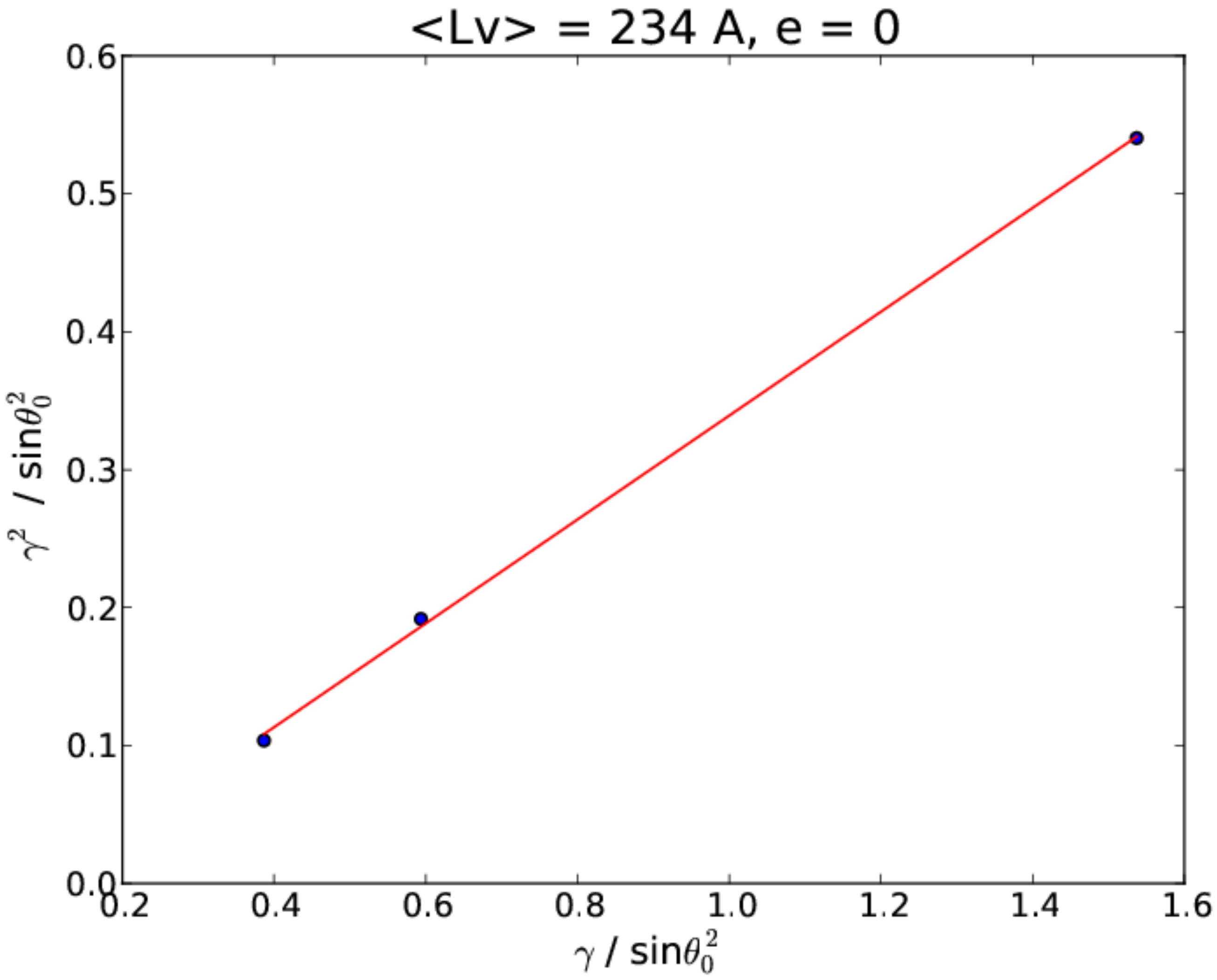
Warren-Averbach-Bertaut Select peak:

Exit

No problems – excellent measurement, no overlapping, good background!



Warren-Averbach



Williamson-Hall