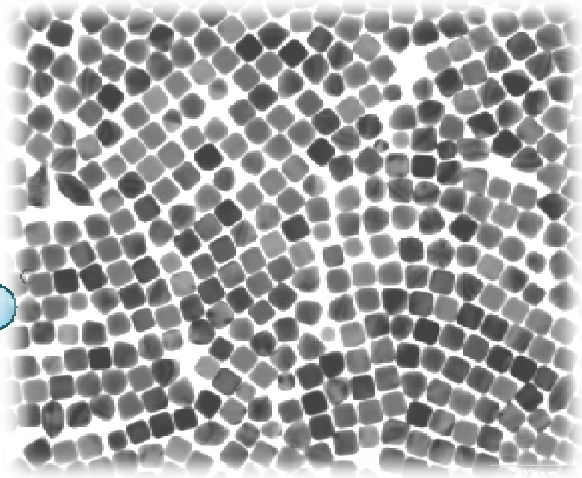

Microstructure from diffraction: progress in line profile analysis

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DICAM- University of Trento - Italy
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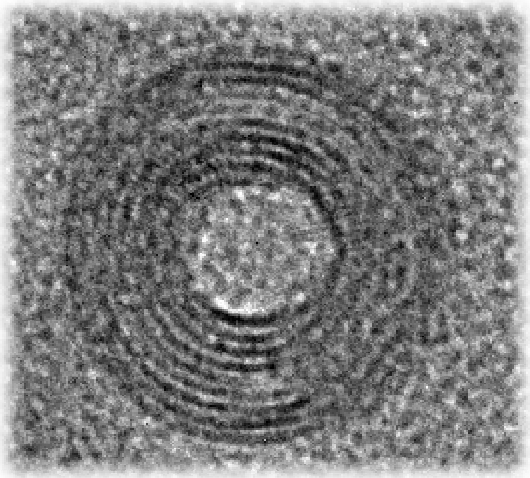
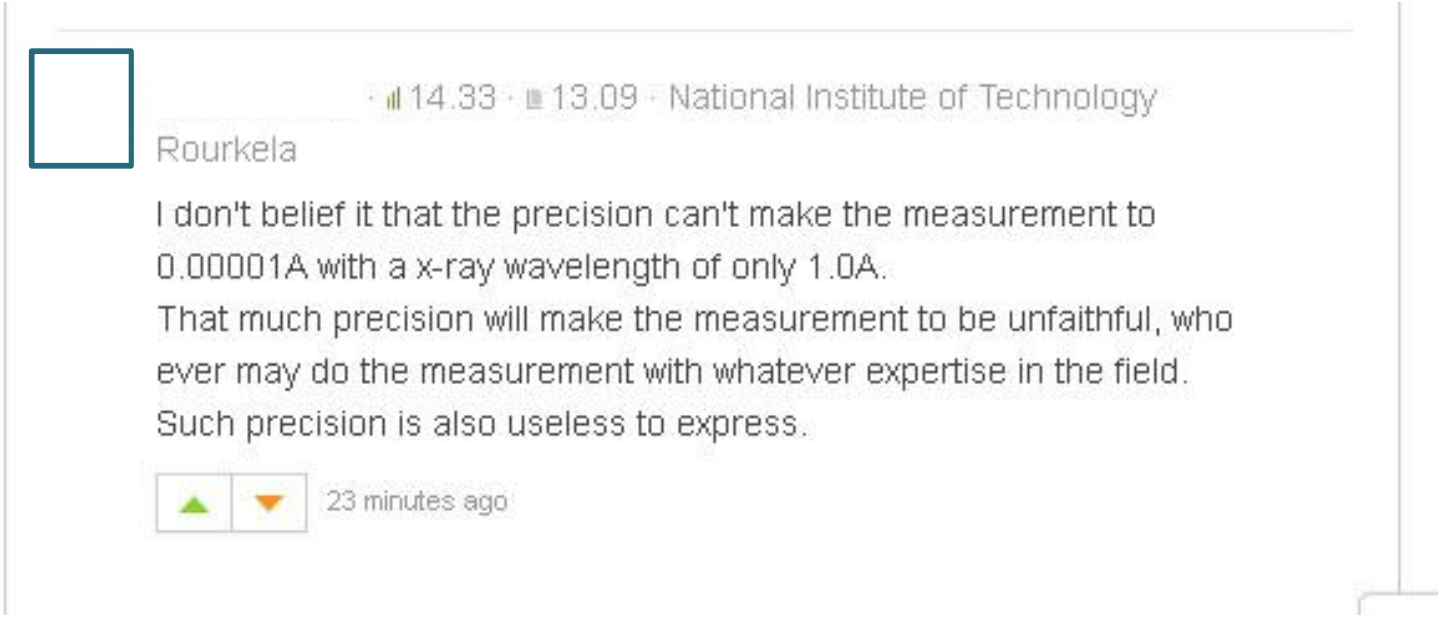


Foreword



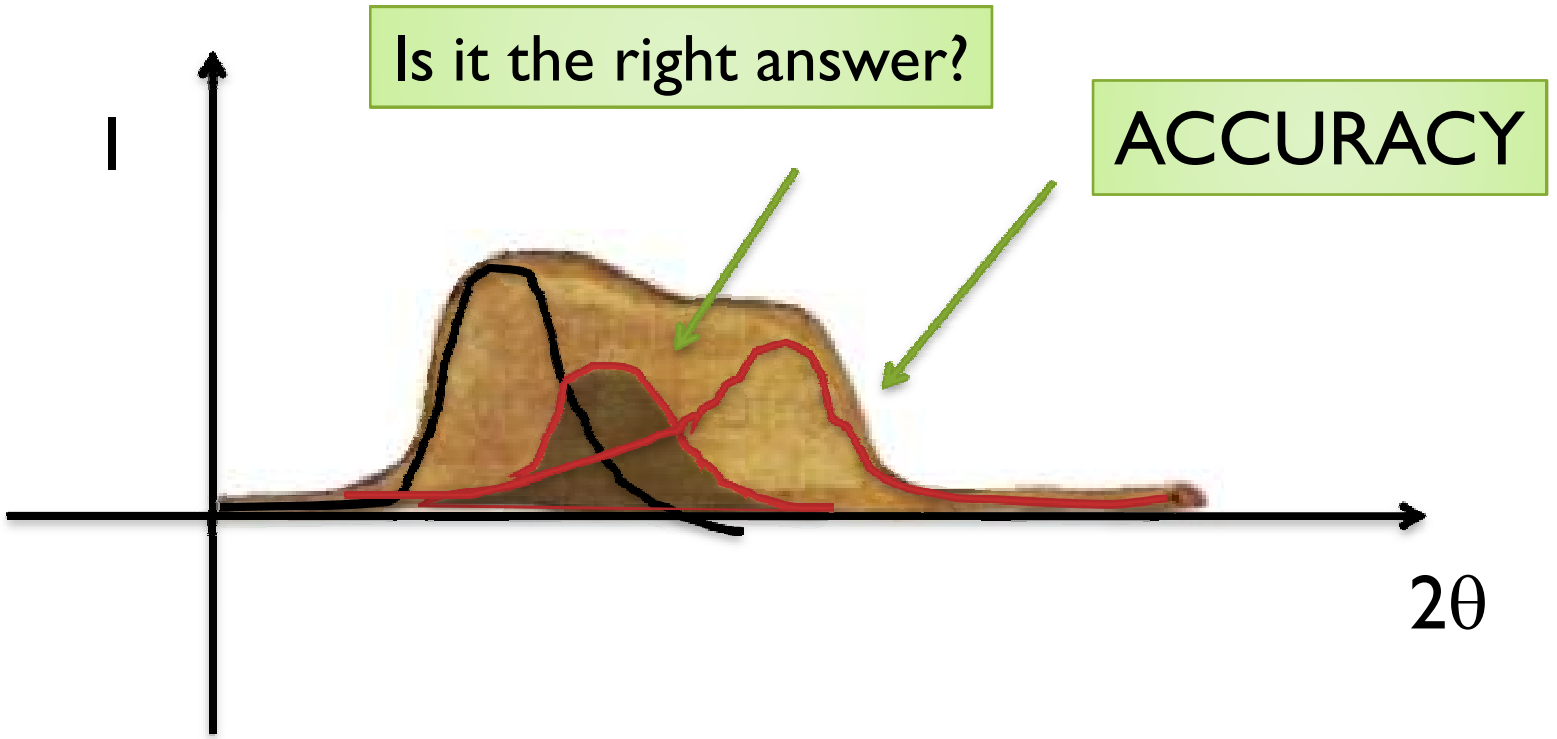
So people don't care/know about accuracy and precision….

How far from the truth?

How many decimal places?

Accuracy and microstructure

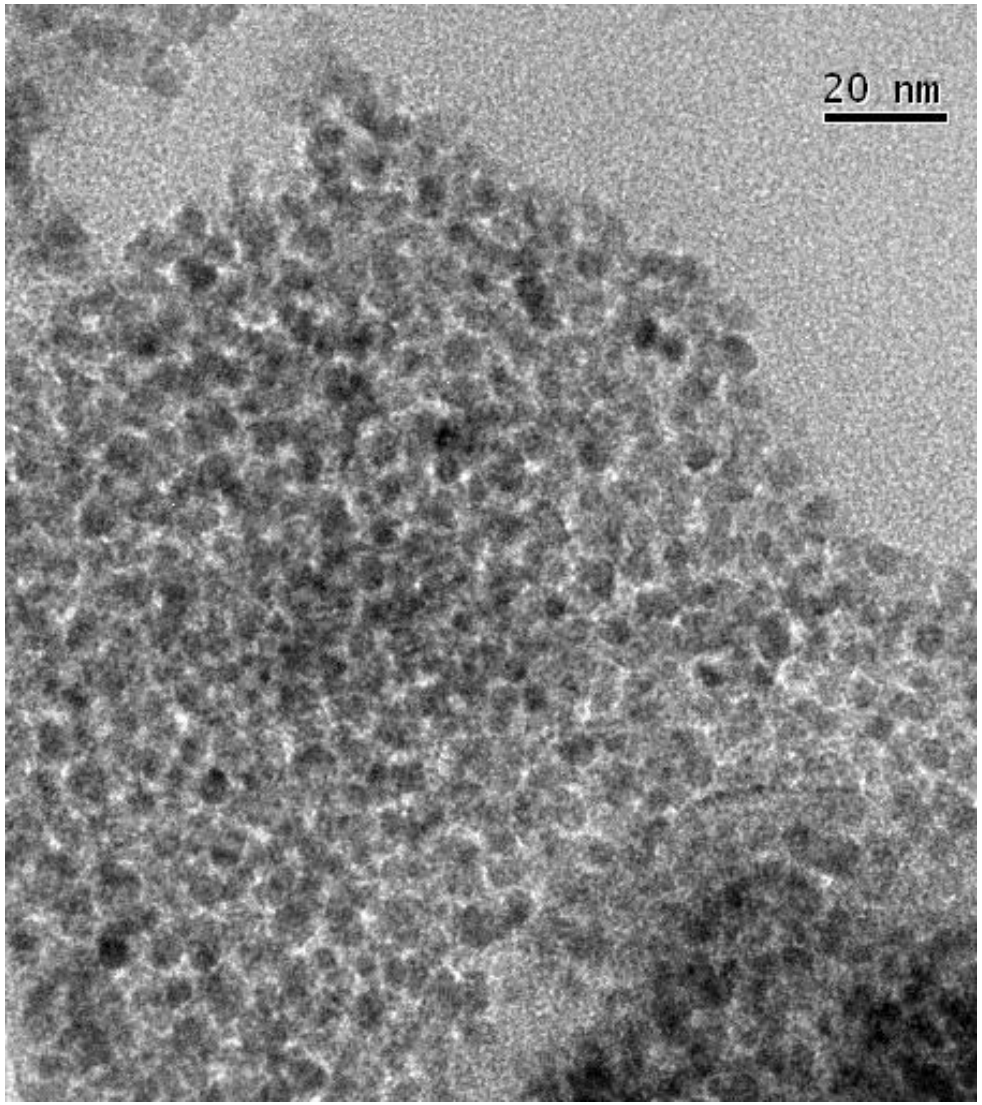
Are you frightened by this?



"Frighten? Why should any one be frightened by a hat?"

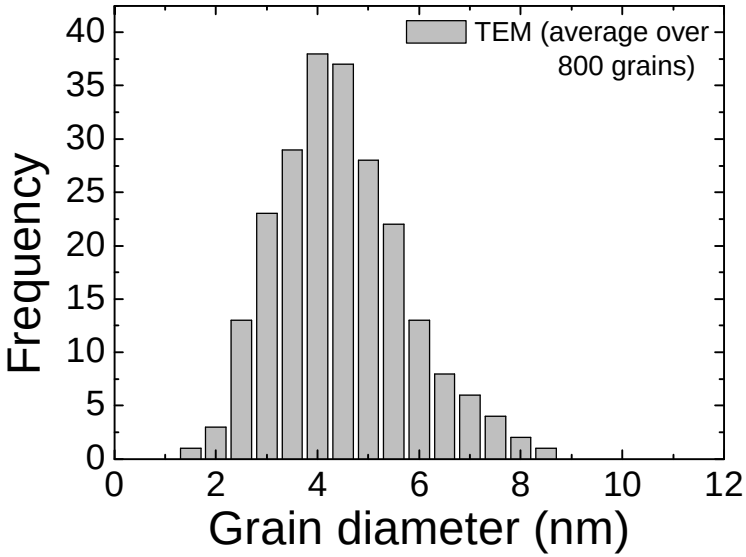
Antoine de Saint-Exupéry (1943) *The little prince. Chapter 1*

Nanocrystalline ceria - TEM



CeO_2 calcinated at 400°C for 1h

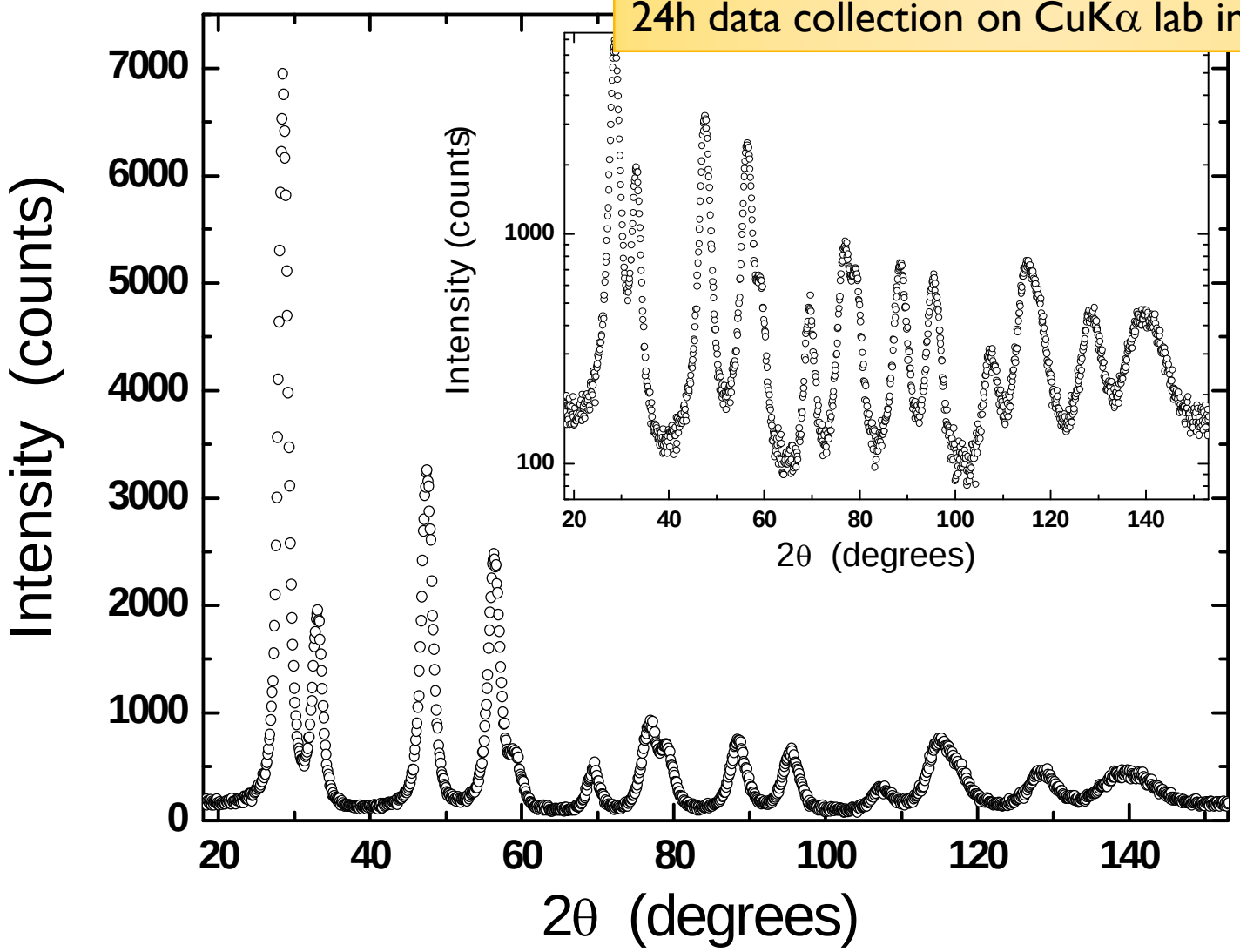
Grains are almost spherical and well separated



How does an XRD analysis result compare to this?

Nanocrystalline ceria - XRD

24h data collection on CuKα lab instrument



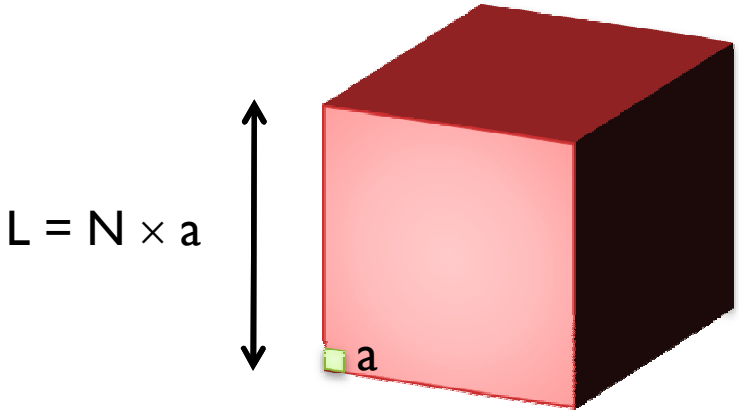
A high quality pattern is NEEDED to obtain accurate results

HOW DO WE ANALYZE THE DATA?

OLD VS. NEW

1918: Scherrer formula

Let's take a crystal of cube shape (edge L = N × a where a is the unit cell size)



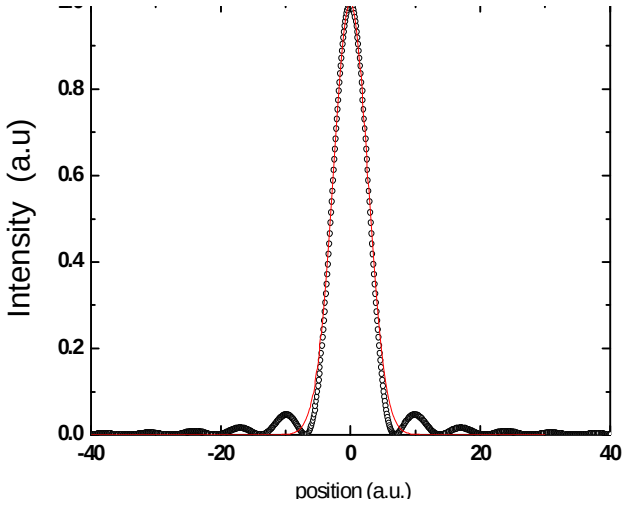
We have N^3 cells in the cube

The diffracted intensity can be calculated in terms of trigonometric functions:

$$I_P \propto \frac{\sin\left(\pi N\Delta\mathbf{s}\cdot\mathbf{a}/\lambda\right)^2}{\sin\left(\pi\Delta\mathbf{s}\cdot\mathbf{a}/\lambda\right)^2}\frac{\sin\left(\pi N\Delta\mathbf{s}\cdot\mathbf{b}/\lambda\right)^2}{\sin\left(\pi\Delta\mathbf{s}\cdot\mathbf{b}/\lambda\right)^2}\frac{\sin\left(\pi N\Delta\mathbf{s}\cdot\mathbf{c}/\lambda\right)^2}{\sin\left(\pi\Delta\mathbf{s}\cdot\mathbf{a}/\lambda\right)^2}$$

conveniently approximated by **Gaussians**:

$$I_P \propto e^{-\pi\left(\frac{Na\Delta s}{\lambda}\right)^2} = e^{-\pi\left(\frac{Na\Delta(2\theta)\cos(\theta)}{\lambda}\right)^2}$$



Scherrer formula

The **Full Width at Half Maximum (FWHM)** of the Gaussian is:

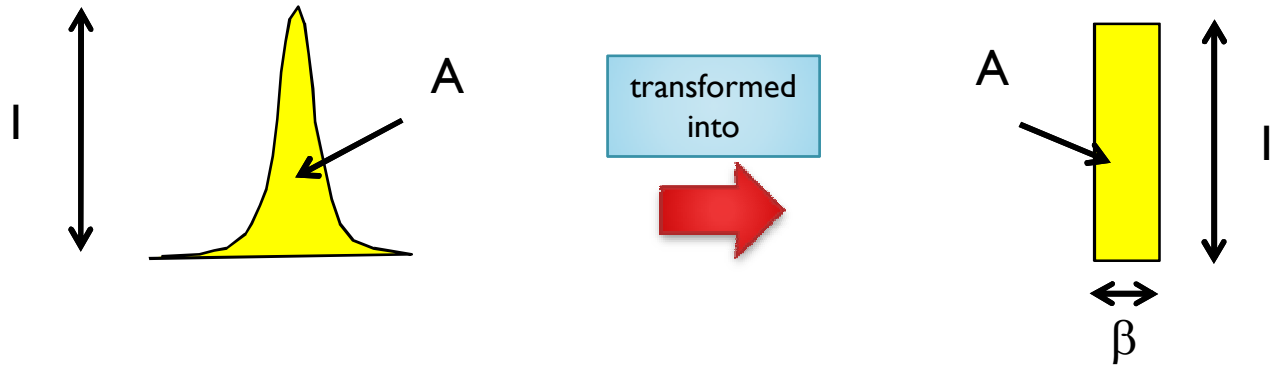
$$\frac{1}{2} = e^{-\pi\left(\frac{L\cos(\theta)\cdot FWHM}{2\lambda}\right)^2} \quad \Rightarrow \quad FWHM\,(2\theta) = \frac{2\lambda\sqrt{Ln(2)/\pi}}{L\cos(\theta)}$$

$$FWHM\,(2\theta) = \frac{0.94\lambda}{L\cos(\theta)}$$ **Scherrer formula (1918)**

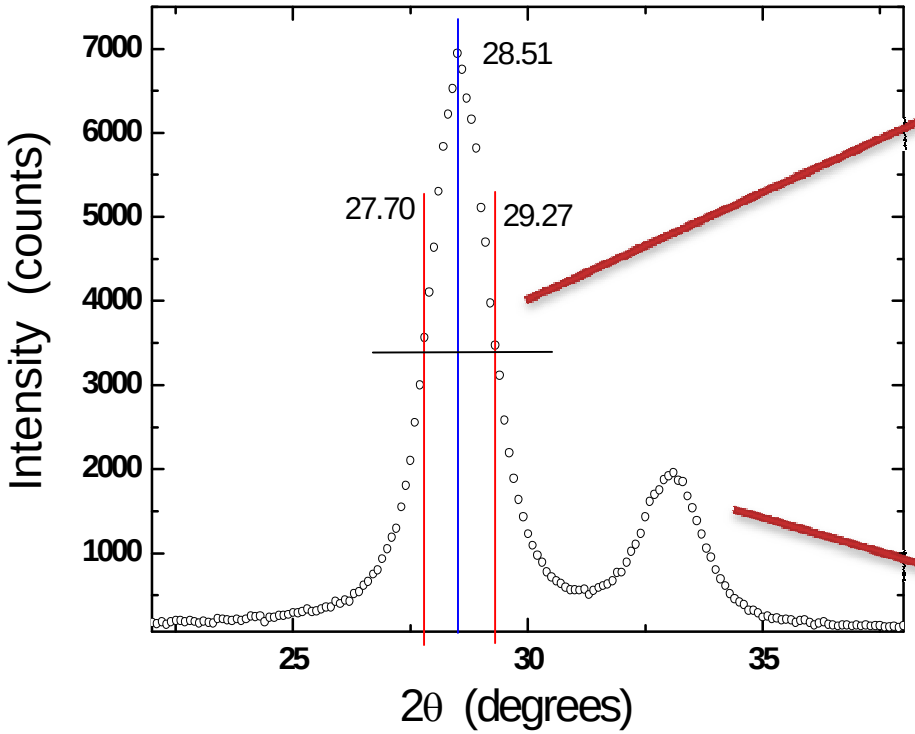
usually written as:

$$\beta_{hkl}\,(2\theta) = \frac{\lambda K_\beta}{< D >_V \cos\theta_{hkl}}$$ Any profile shape

in terms of Integral breadth β = A/I where A is the area and I the max intensity



Scherrer formula (111) and (200) peaks



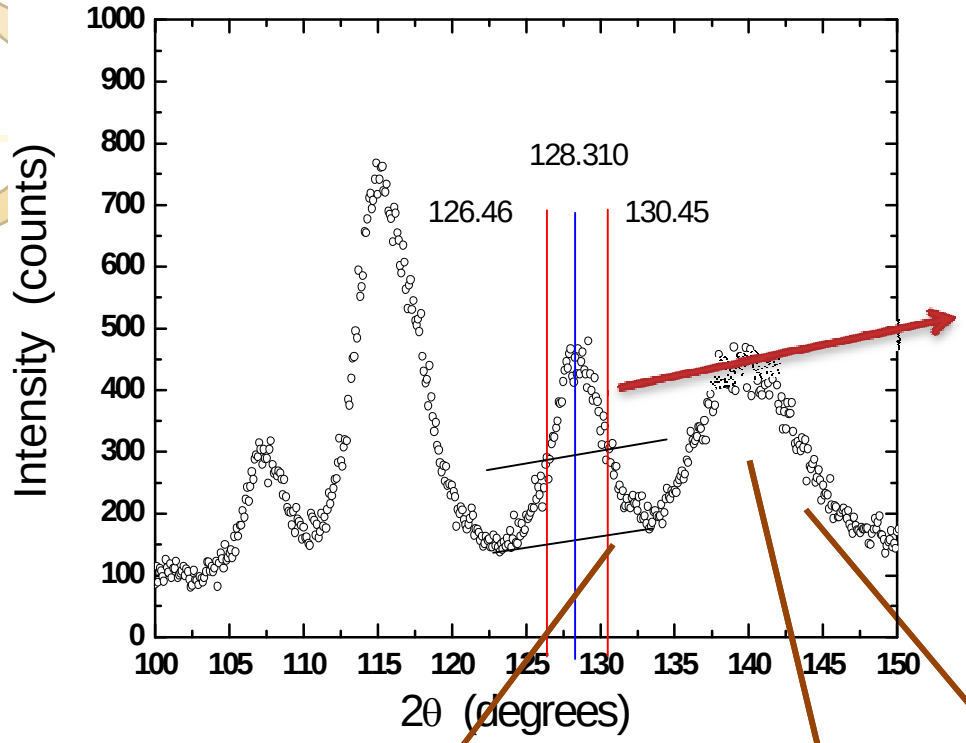
$$\left.\frac{\langle D\rangle_V}{K_\beta}\right|_{111} = 5.8\,nm$$

$$\left.\frac{\langle D\rangle_V}{K_\beta}\right|_{200} = 5.7\,nm$$

This is still applied by most "nanomaterials experts" in the literature

Formula obtained for GAUSSIAN/ANY peak and for a given shape of the domains (not yet decided)

Scherrer formula (620) peak



$$\left.\frac{\langle D\rangle_V}{K_\beta}\right|_{620} = 5.1nm$$

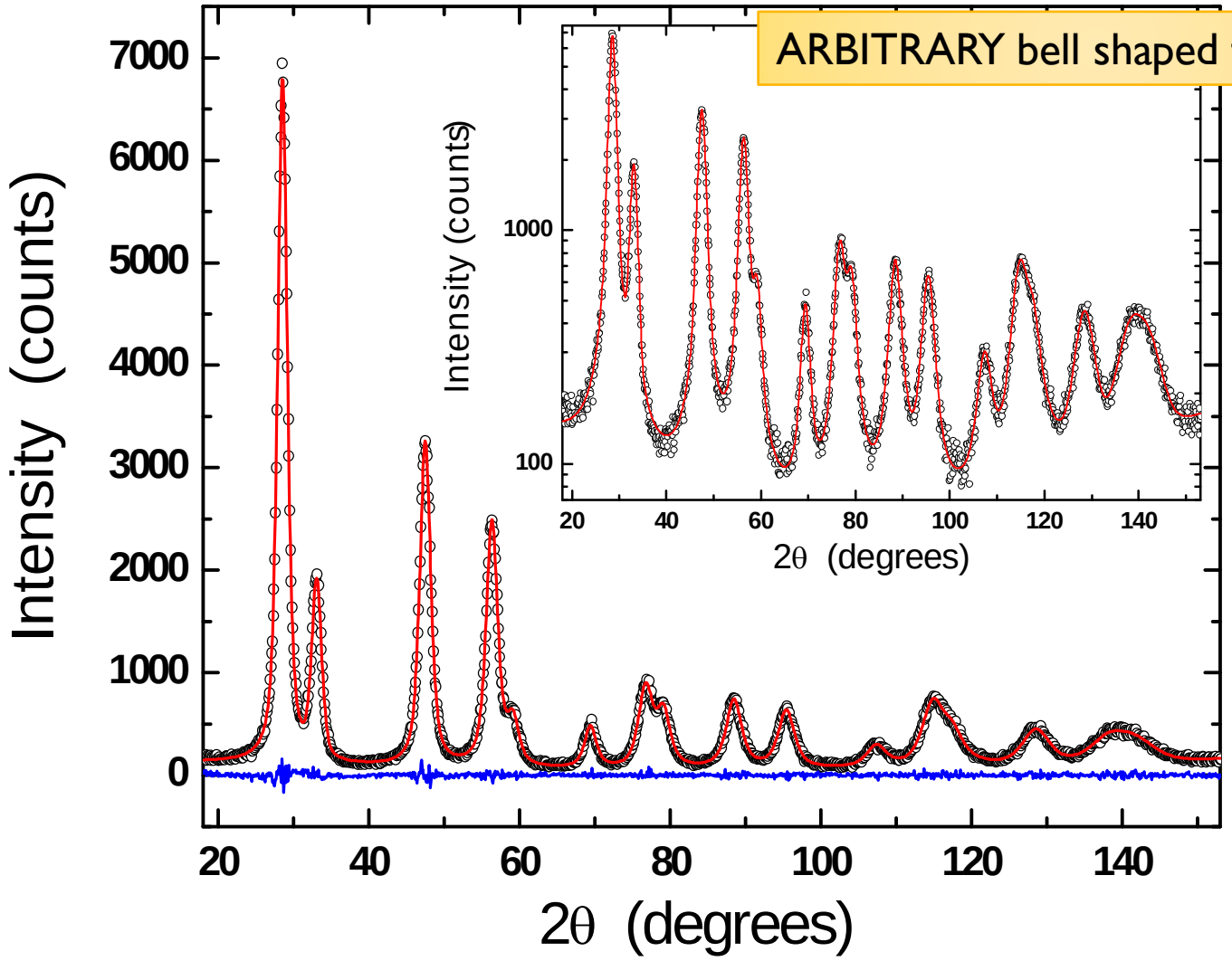
How can we analyze those two peaks? Where is $K\alpha_2$?

Why did we select this background shape/level?

Does the instrument give no breadth contribution?

We have several different size values!

Pattern decomposition



Use of bell-shaped functions to account for superposition

1953: Williamson-Hall plot

Williamson-Hall plot includes Scherrer formula (1918) for "average size determination" with differential of Bragg law to get information on defects present in the material

$$\beta\left(d^*\right) = \frac{K_\beta}{\langle D \rangle_V} + 2 \cdot \langle \varepsilon^2 \rangle^{1/2} \cdot d^*$$

The β is the sum of the component only for Gaussian peaks

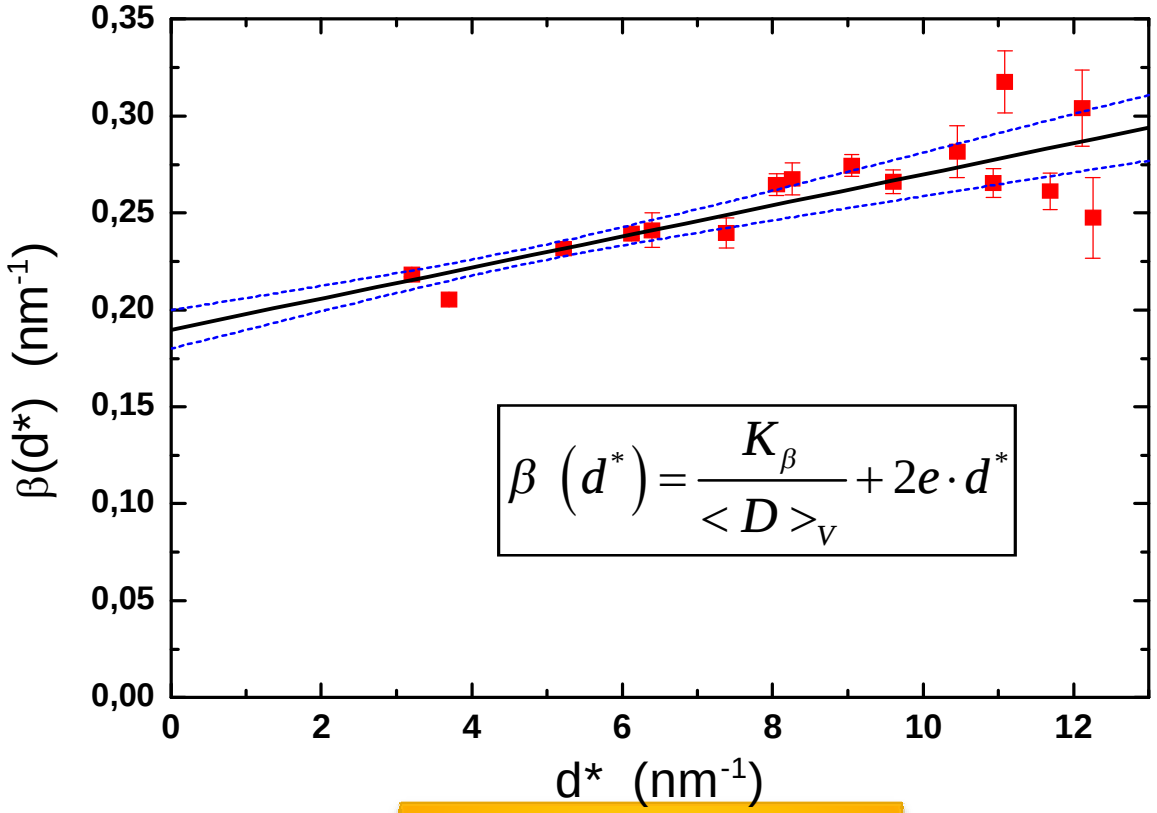
intercept related to "average domain size"

slope related to "microstrain"

$$0 = 2\Delta d \sin(\theta) + 2d \cos(\theta) \Delta\theta \quad \Rightarrow \quad \Delta(2\theta) = -2\frac{\Delta d}{d}\tan(\theta) = -2e\tan(\theta)$$

In a $\beta(d^*)$ vs. d^* plot, intercept and slope of linear regression are related, respectively, to $\langle D \rangle_V$ and e

Williamson-Hall plot



$$\beta\left(d^*\right) = 0.019 + 0.008 d^*$$

$$\frac{< D >_V}{K_\beta} = 5.3nm$$

$$e = \frac{0.008}{2} = 0.004$$

"average domain size" is NOT the average size of the (nano) particles
"microstrain" is a quite general term and does not identify the defect types

1950: Warren-Averbach method

Actually, in RECIPROCAL SPACE the profile is a convolution of effects!

$$h(s) = \left[f^{size}(s) \otimes f^{strain}(s) \right] \otimes g(s)$$

instrument

Fourier transform

$$F(h(s)) = F\left(f^{size}(s)\right) F\left(f^{strain}(s)\right) F(g(s))$$

We can remove the known instrument effects

$$C(L) = A^{size}(L)\, A^{strain}(L)$$

We have a description of the profile(s) in Fourier space, from which:

$$\ln(C(L)) = \ln\left(A^{size}(L)\right) + \ln\left(A^{strain}(L)\right)$$

Warren-Averbach method

The strain term (related to displacement between couples) can be written as:

$$A^{strain}(L) = \left\langle \cos\left(2\pi L \varepsilon_{hkl}(L) d_{hkl}^{*2}\right)\right\rangle$$
$$= \left(1 - 2\pi^2 L^2 \left\langle \varepsilon_{hkl}^2(L)\right\rangle d_{hkl}^{*} + O\left(L^4\right)\right)$$

The first order approximation for the Fourier coefficients read

$$C(L) = A^{size}(L) \cdot \left(1 - 2\pi^2 L^2 \left\langle \varepsilon_{hkl}^2(L)\right\rangle h_0^2 / a^2\right)$$

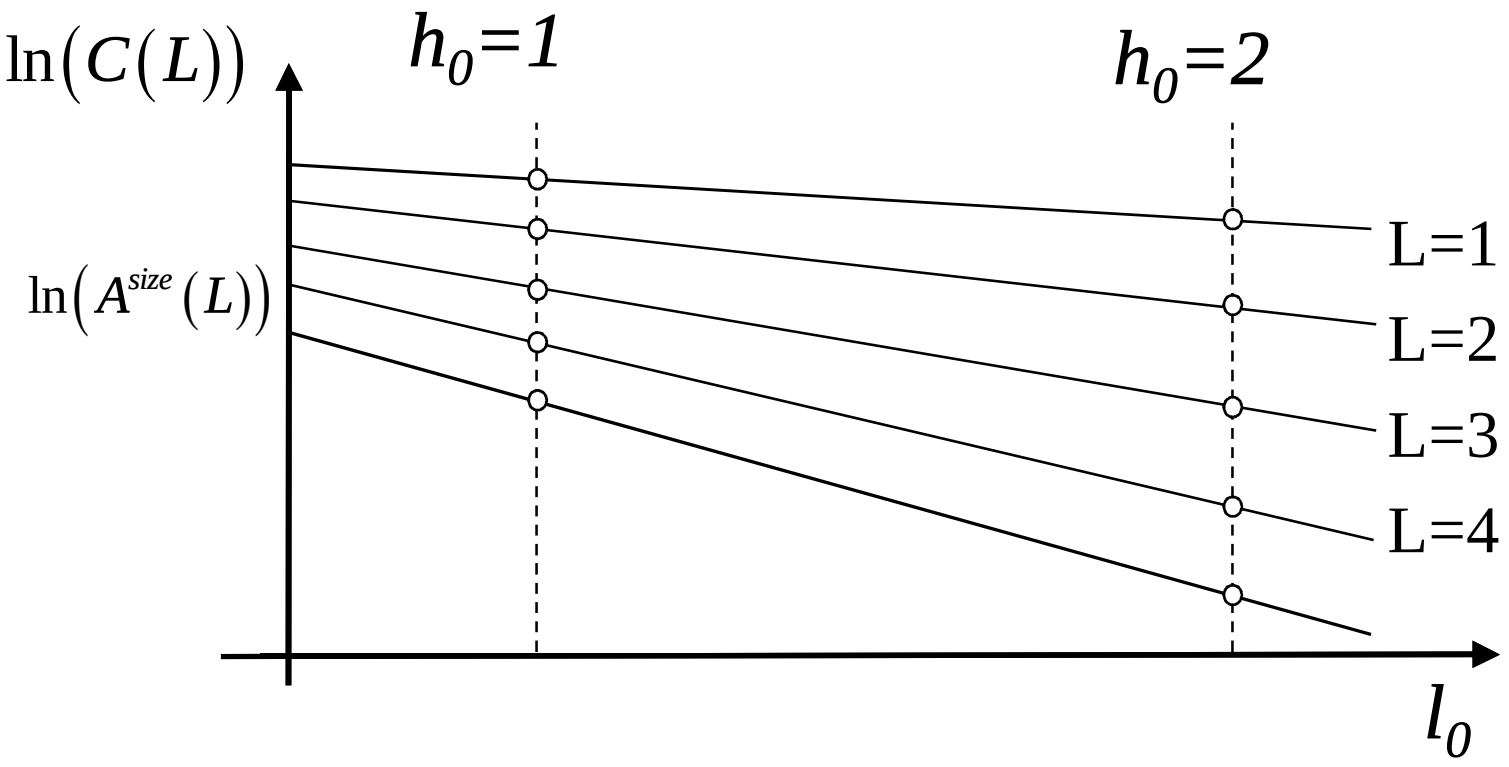
Cubic case, but can be generalised

and then, taking the logarithm of both sides we obtain:

$$\ln\left(C(L)\right) = \ln\left(A^{size}(L)\right) - 2\pi^2 L^2 \left\langle \varepsilon_{hkl}^2(L)\right\rangle h_0^2 / a^2$$

Again linear plot gives size and strain contributions

Warren-Averbach method

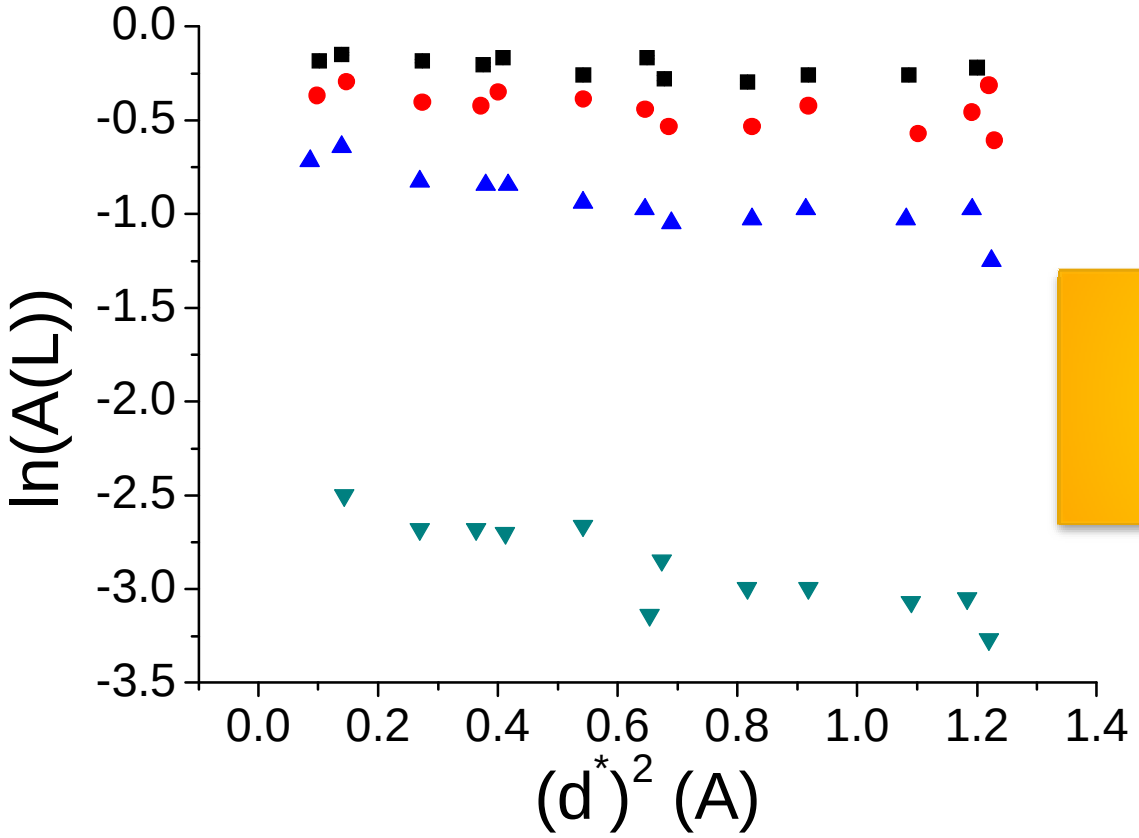


$$\ln(C(L)) = \ln(A^{size}(L)) - 2\pi^2 L^2 \langle \varepsilon_{hkl}^2(L) \rangle h_0^2 / a^2$$

intercept gives (INDIRECTLY) the size effect

slope gives DIRECTLY the strain effect

Warren-Averbach plot



$$\langle D \rangle_s = 3.6\,nm$$

Taking the instrument into account, the value we obtain in much lower than the Round Robin one

Warren-Averbach method

Provided that the procedure has been carried out properly (calculate Fourier Coefficients, account for background, instrumental component and peak overlapping, presence of faulting, other defects …):

Size coefficients

to be related to the column length distribution $p(L) \propto d^2 A^{size}(L) / dL^2$

So-called "Microstrain"

$$\left\langle \varepsilon_{hkl}^2(L) \right\rangle^{1/2}$$

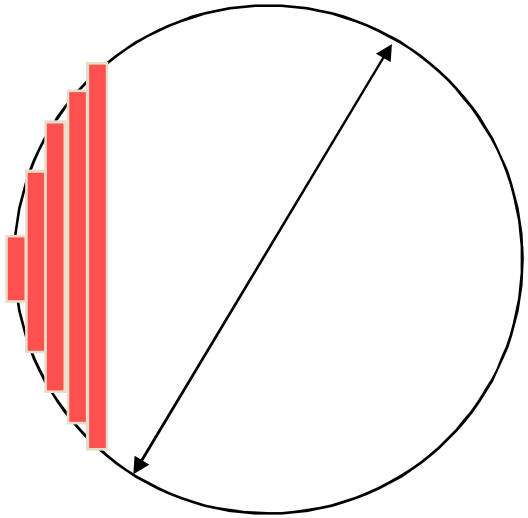
to be related to the strain distribution $p(\varepsilon_{hkl}(L))$ generated by the specific source of lattice strain)

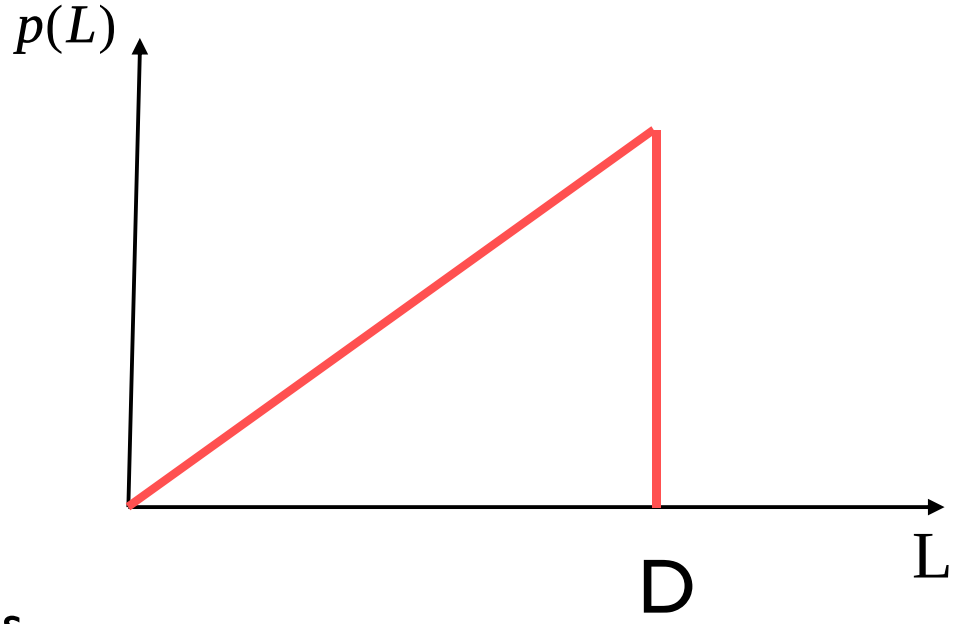
WHICH column length distribution?

Microstrain is NOT a strain!!!! WHICH source of lattice strain?

Meaning of the size term

Column length distribution…. e.g. for a single sphere:





.. and for a distribution of domains

$$< L >_V = \frac{< D >_V}{K_\beta} = \frac{M_4}{M_3 \cdot K_\beta} = \int D^4 p(D) dD \Big/ \int D^3 p(D) dD$$

Williamson-Hall

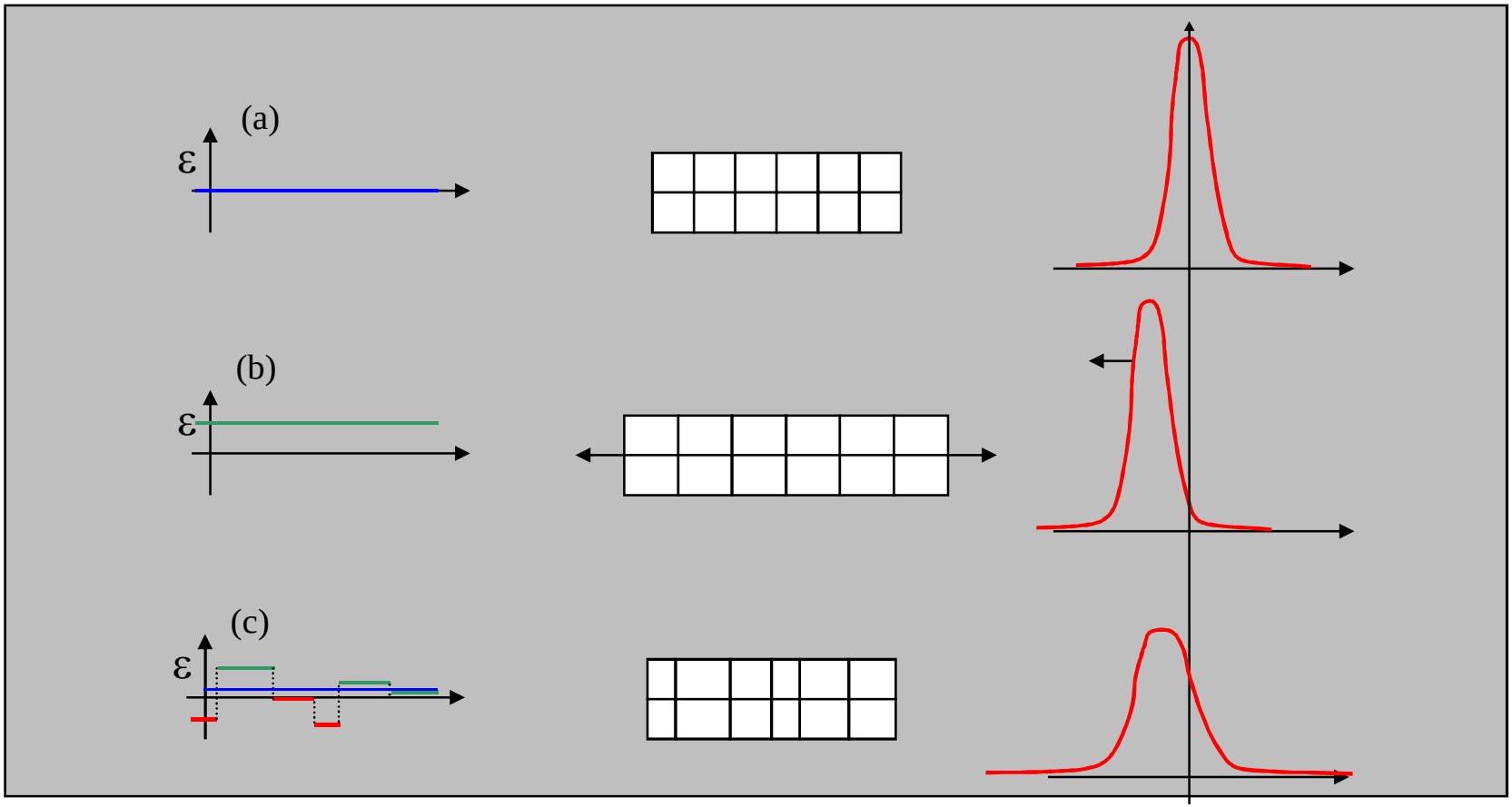
$$< L >_S = \frac{< D >_S}{K_\kappa} = \frac{M_3}{M_2 \cdot K_\kappa} = \int D^3 p(D) dD \Big/ \int D^2 p(D) dD$$

Warren-Averbach

Meaning of strain (distortion) term

When the deformation is non uniform, we can introduce the microstrain

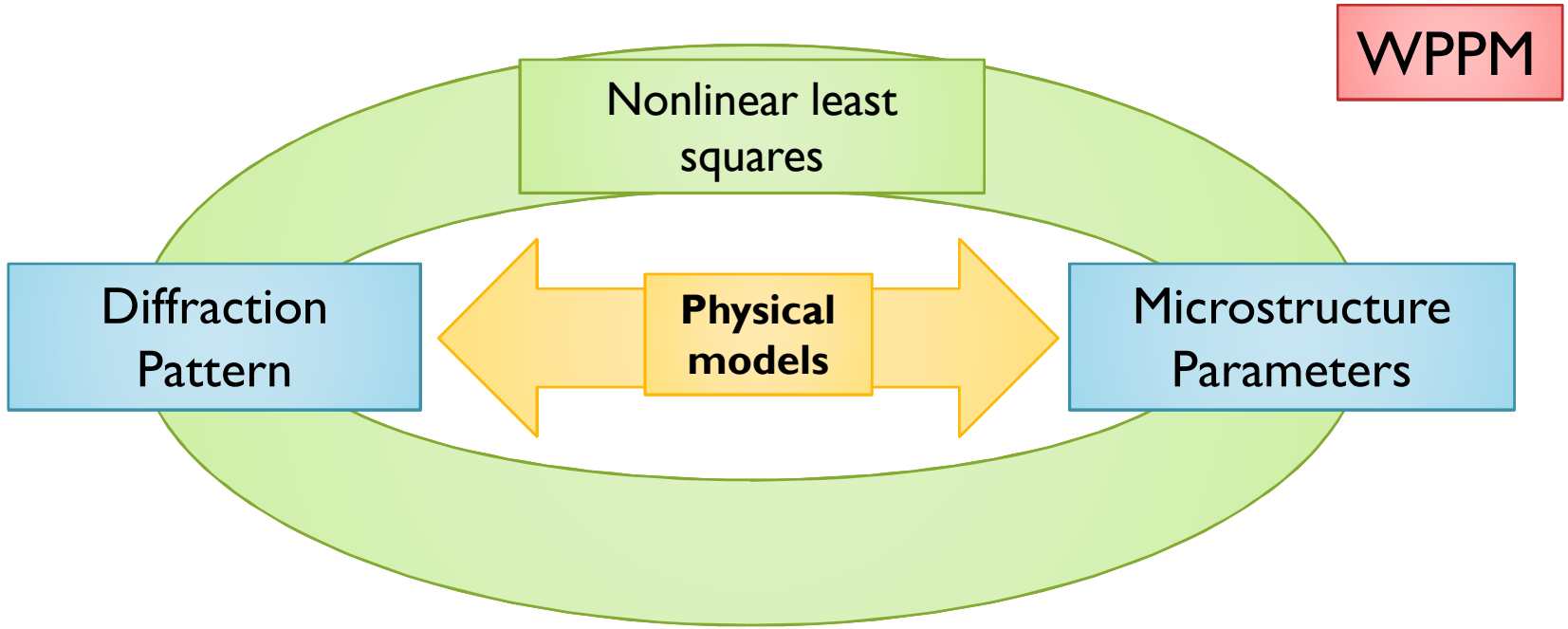
$$\left\langle \varepsilon^2 \right\rangle^{1/2} = \left\langle \left(\Delta d/d \right)^2 \right\rangle^{1/2}$$



MICROSTRAIN is NOT a strain!!!!

2000: Whole Powder Pattern Modelling

Instead of doing a deconvolution, we directly model the whole pattern in terms of physical models of the microstructure:

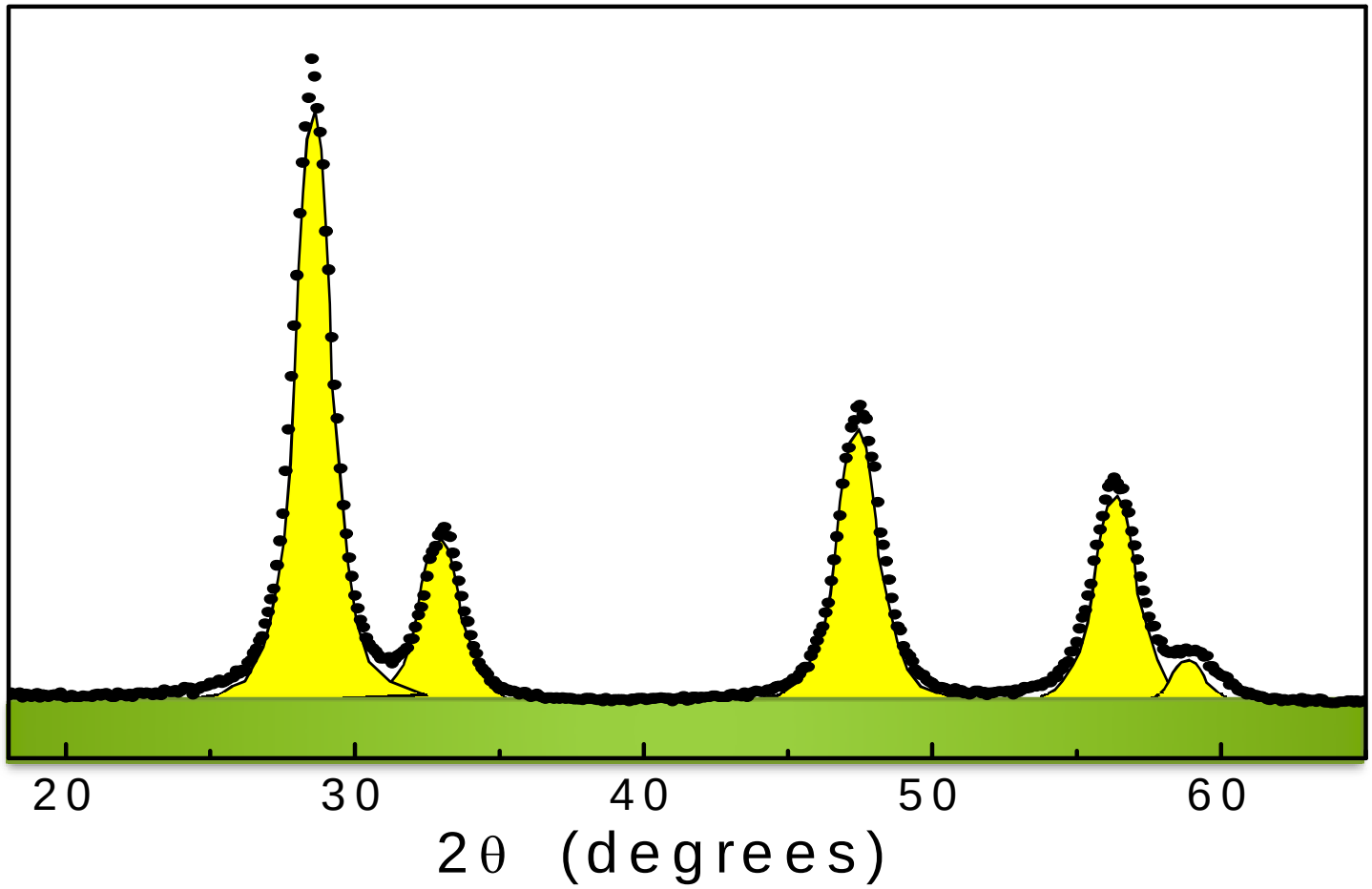


Self-consistent one-step procedure: we work on the measured data!

Structure is decoupled from microstructure, i.e. **there are no structural constraints (peak intensity is a fitting parameter).**

WPPM basics

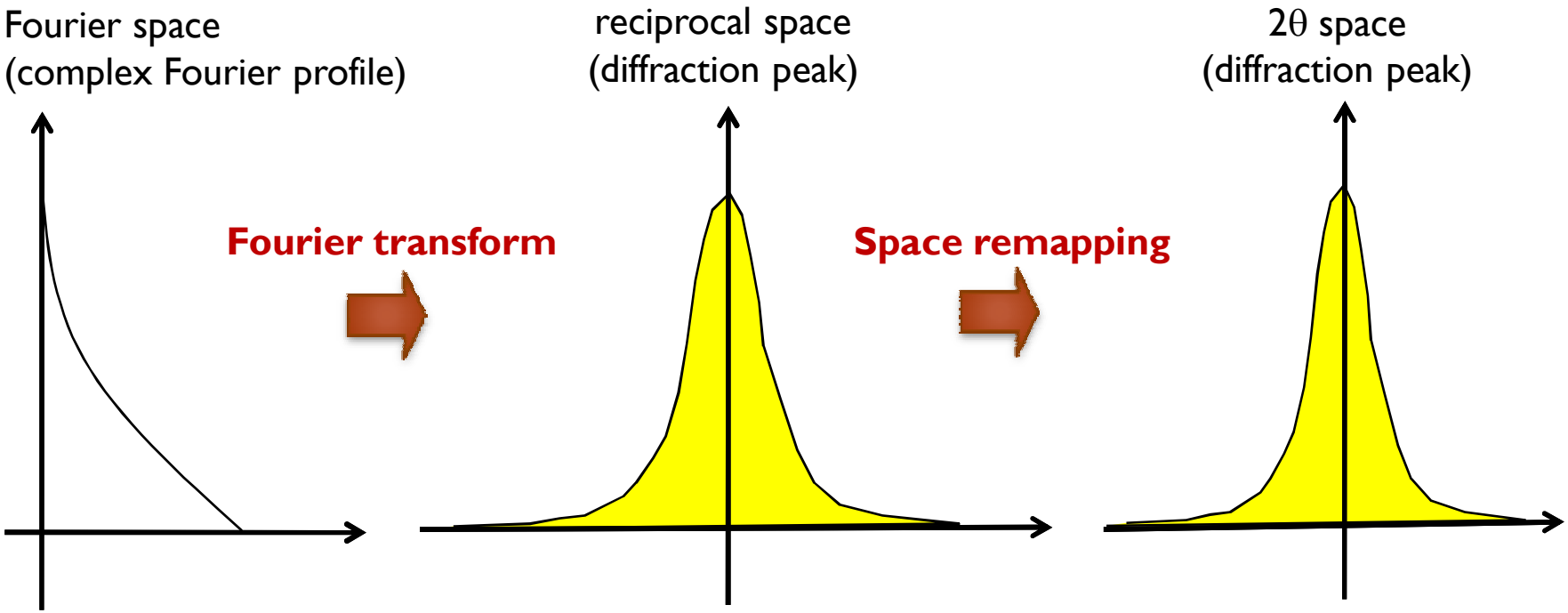
Pattern as sum of broadened peaks + background + …



…a kind of "Pawley" or "Rietveld-like" approach… **BUT**….

WPPM basics

Each profile synthesised (in reciprocal space) from its Fourier transform calculated by physical modelling of all broadening sources



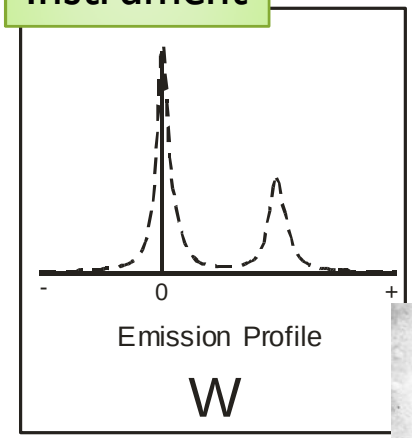
$C(L)$

... we use the Warren-Averbach trick...

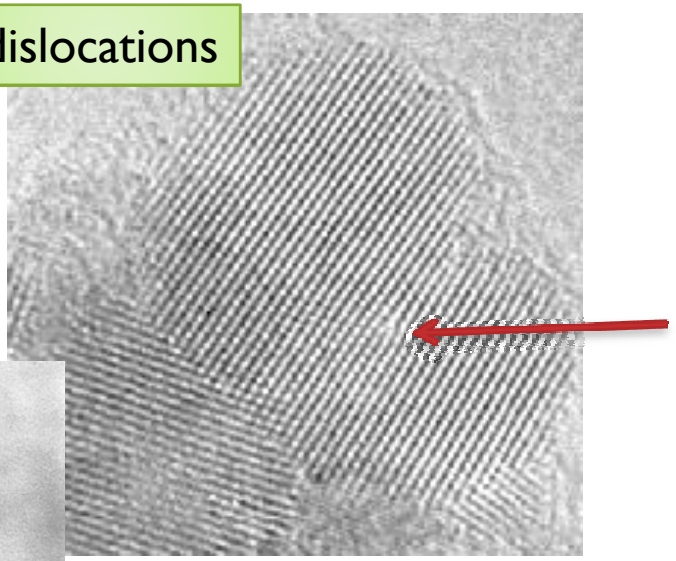
WPPM basics

Broadening sources

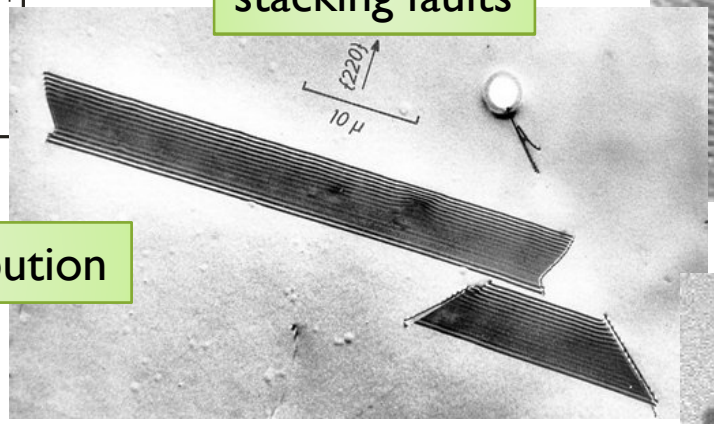
Instrument



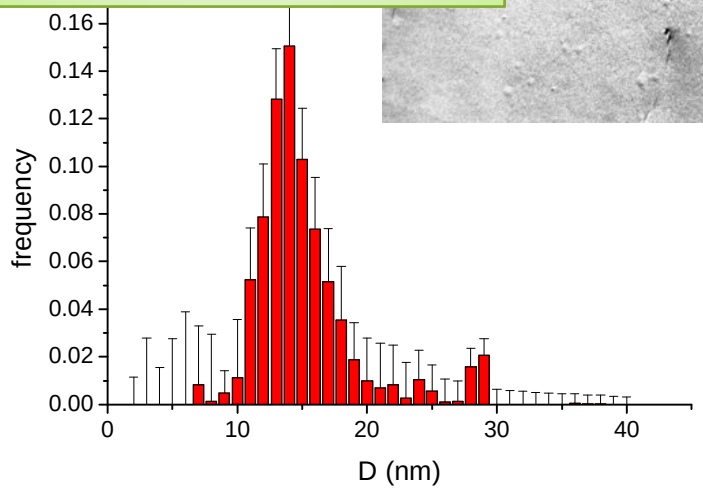
dislocations



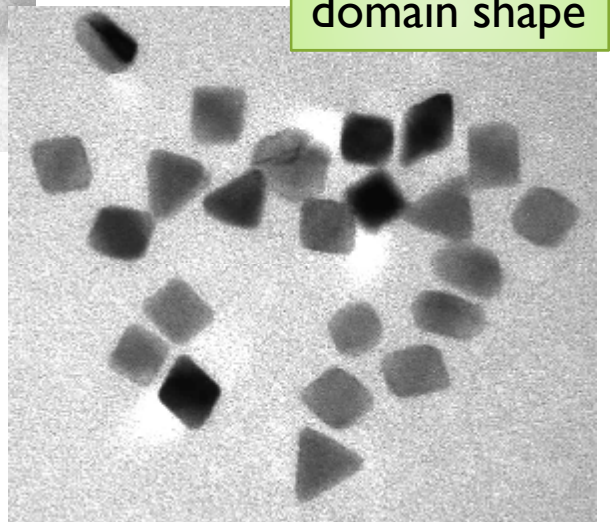
stacking faults



domain-size distribution



domain shape



WPPM: plug and play

The intensity is obtained as Fourier transform of the global broadening function:

$$I_{\{hkl\}}\left(d^*, d^*_{\{hkl\}}\right) = k\left(d^*\right) \cdot \sum_{hkl} w_{hkl} \int_{-\infty}^{\infty} \mathbb{C}_{hkl}(L) \exp\left(2\pi i L \cdot s_{hkl}\right) dL$$

Profile in recprocal space

Profile in Fourier space

$$T_{pV}^{IP} \cdot A_{\{hkl\}}^{S} \cdot A_{\{hkl\}}^{D} \cdot \left(A_{hkl}^{F} + iB_{hkl}^{F}\right) \cdot A_{\{hkl\}}^{APB} \cdot \left(A_{hkl}^{GSR} + iB_{hkl}^{GSR}\right) \cdot \left(A_{hkl}^{CF} + iB_{hkl}^{CF}\right) \cdot \ldots$$

- Instrumental Profile
- Domain size
- Dislocations
- Faulting
- APB
- Grain surface relaxation
- Stoichiometry fluctuations

Additional line broadening sources can be included through the corresponding FTs

We have a fingerprint of the microstructure

General dislocation model

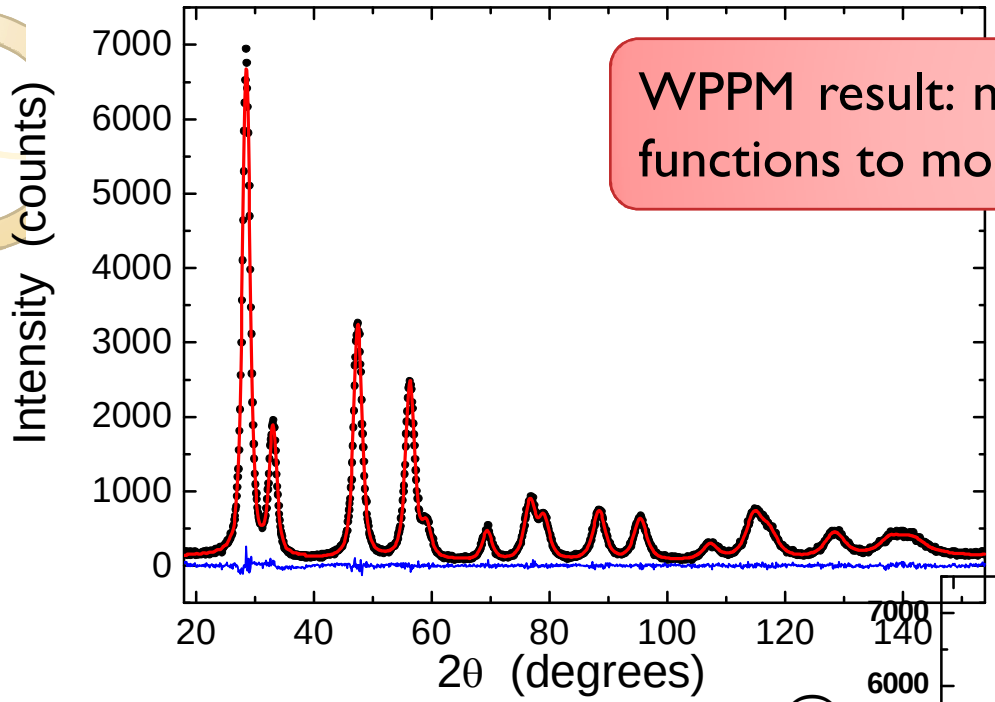
Wilkens model for dislocation-related broadening extended to any symmetry

$$A^{D}_{\{hkl\}}(L) = \exp\left[-\frac{\pi |b|^2}{2} Inv(E_1 \ldots E_{15}, h, k, l)\, \rho d^{*2}_{\{hkl\}} L^2 f^*(L/R'_e)\right]$$

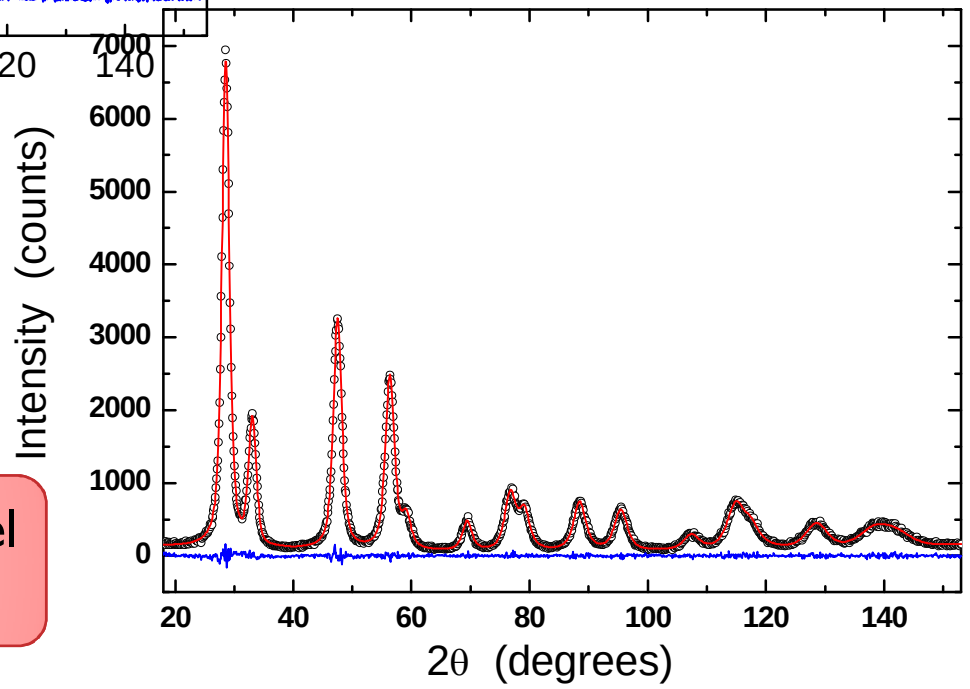
$$\Big[E_1 h^4 + E_2 k^4 + E_3 l^4 + 2\left(E_4 h^2 k^2 + E_5 k^2 l^2 + E_6 h^2 l^2\right) +$$
$$+4\left(E_7 h^3 k + E_8 h^3 l + E_9 k^3 h + E_{10} k^3 l + E_{11} l^3 h + E_{12} l^3 k\right) +$$
$$+4\left(E_{13} h^2 k l + E_{14} k^2 h l + E_{15} l^2 h k\right)\Big] / d^4_{\{hkl\}}$$

Coefficients **calculated** from slip system and single-crystal elastic constants or refined on the data (in this last case the meaning of ρ is watered down)

Nano CeO_2 - WPPM

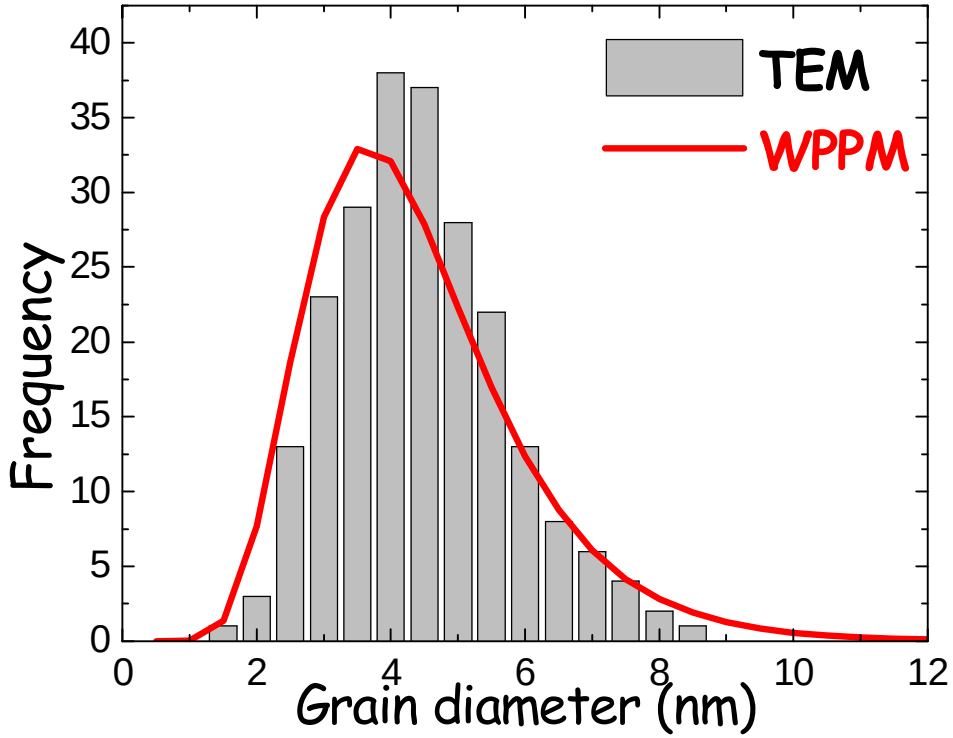


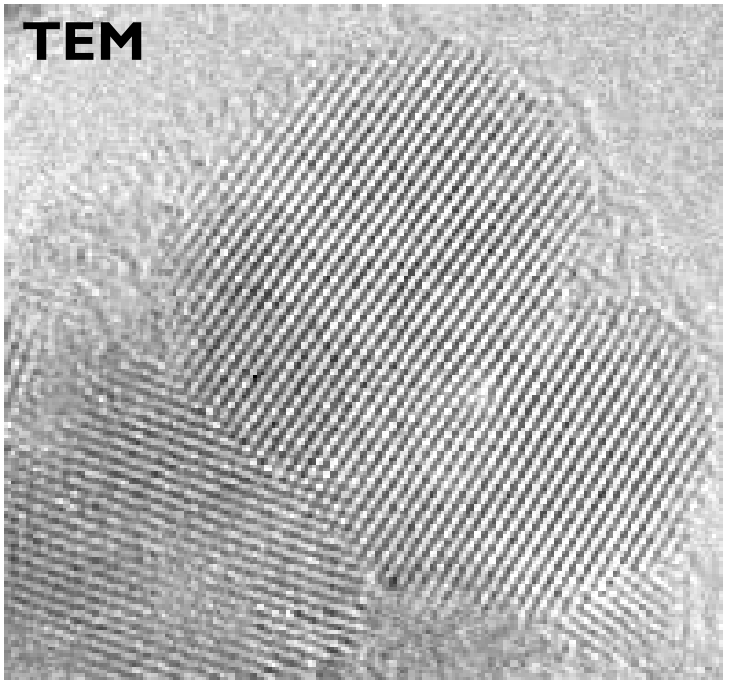
WPPM result: no Voigt or bell shaped arbitrary functions to model the data, 29 par, GoF 1.03



Pseudo-Voigt profiles to model the data, 70 par, GoF 1.01

Nano CeO_2 – WPPM vs TEM





$\rho \approx 1.4(9) \cdot 10^{16}$ m^{-2}

ca. 1 dislocation every 3-4 grains

$$\langle D \rangle = 4.4\,nm$$

We just assumed a lognormal distribtion of spheres with dislocations on the primary slip system

Ceria summary

$$\frac{< D >_V}{K_\beta} = 5.3nm$$

Williamson-Hall

$$\langle D \rangle_s = 3.6\,nm$$

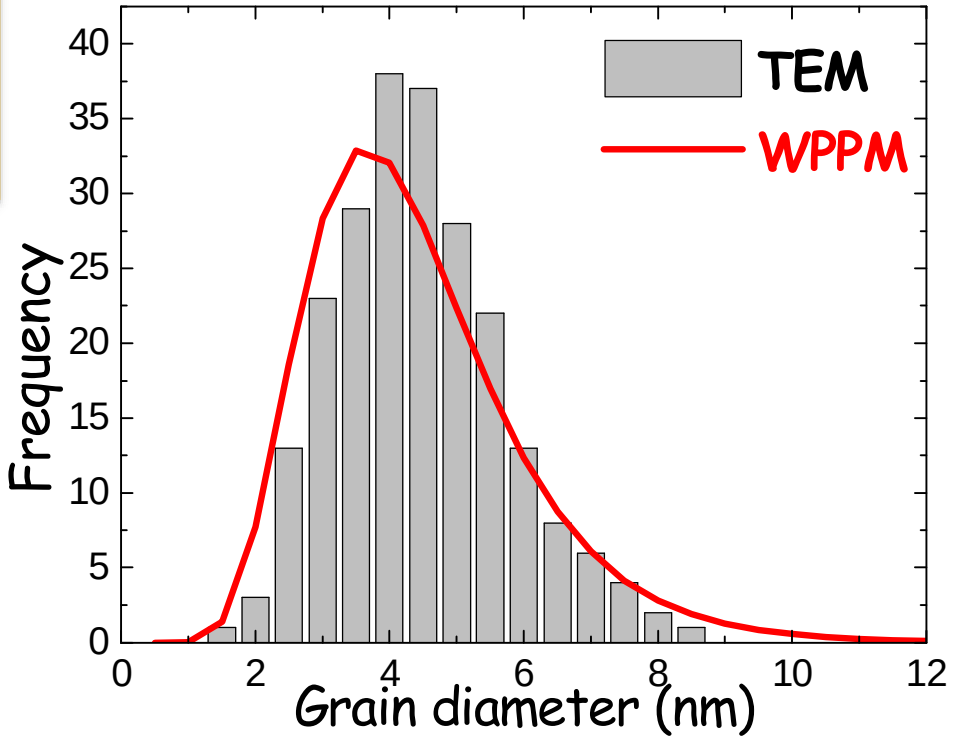
Warren-Averbach

WPPM

$$\langle D \rangle = 4.4(2)\,nm$$

$$\frac{\langle D \rangle_V}{K_\beta} = 5.1 - 5.8\,nm$$

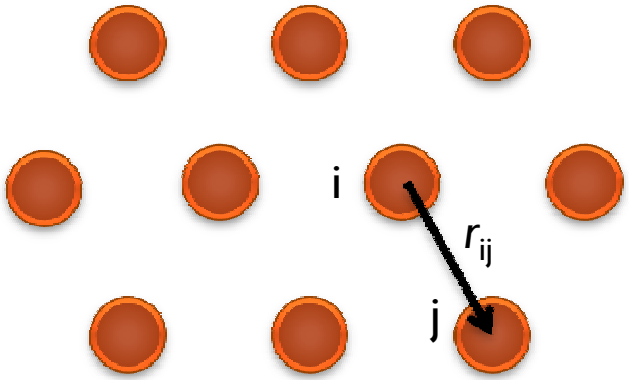
Scherrer



FURTHER ACCURACY PROBLEMS

WPPM versus Debye equation

The Debye equation links atomic coordinates and diffraction pattern:



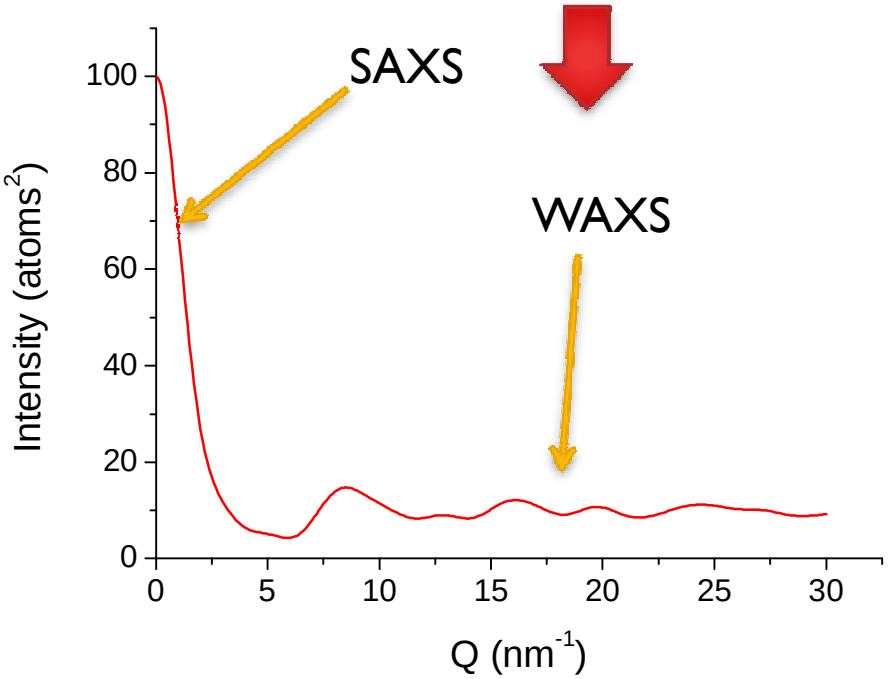
N atoms

$$I(Q) \propto \sum_{i}^{N} \sum_{j}^{N} \mathrm{sinc}\left(\mathbf{r}_{ij} \cdot \mathbf{Q}\right)$$

The formula gives directly the powder diffraction pattern in reciprocal space

$$Q = \frac{4\pi \sin\theta}{\lambda}$$

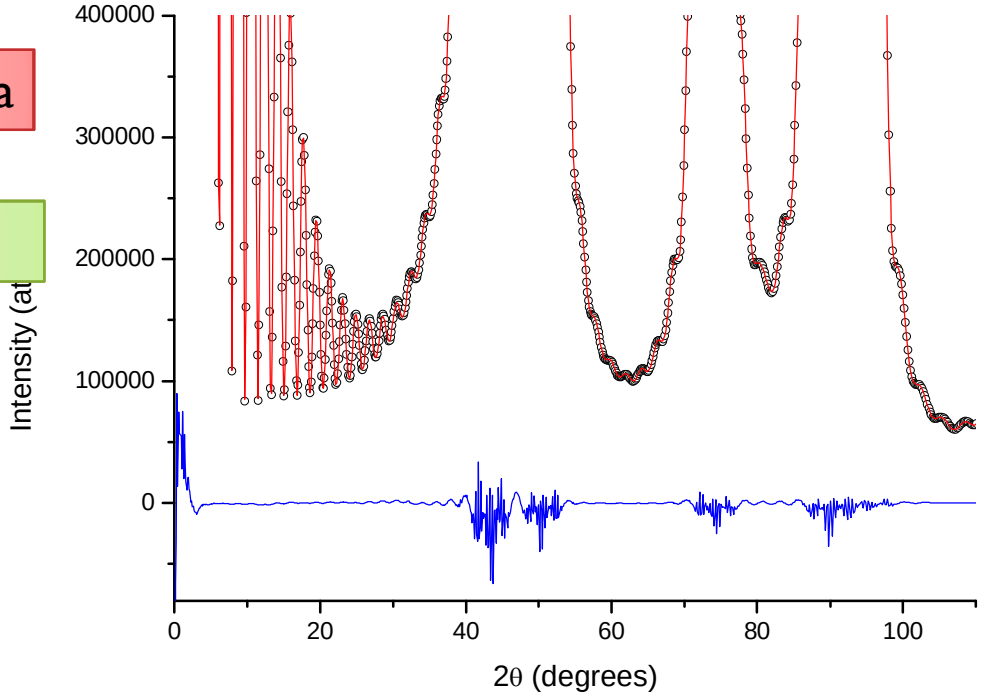
SAXS is in the ideally diluted limit



WPPM versus Debye equation

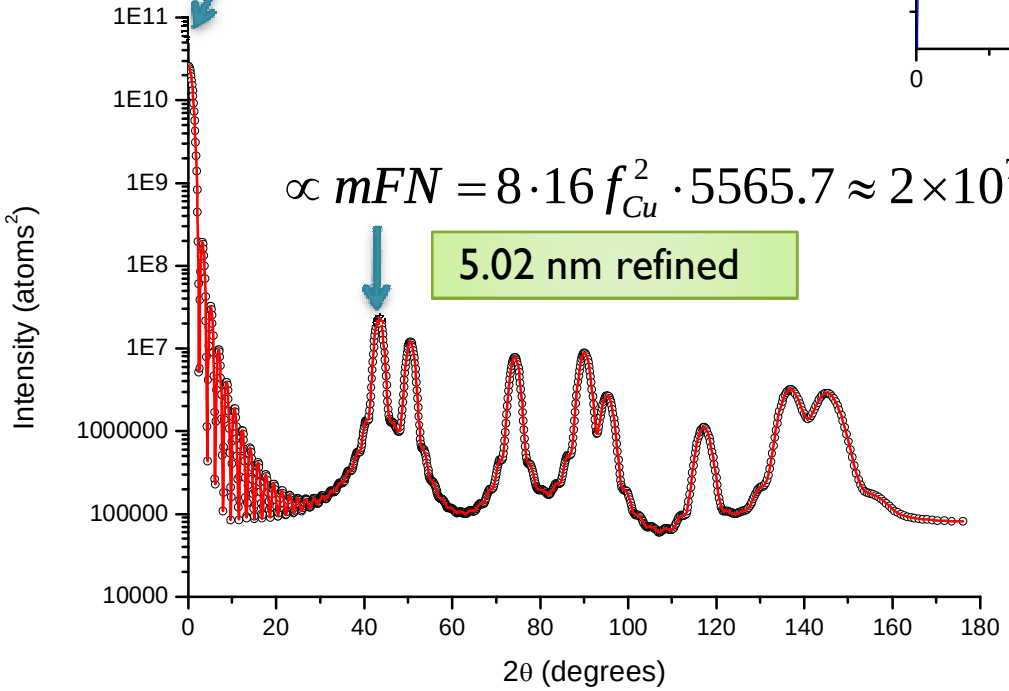
single 5 nm Cu domain, CuK_α data

atoms: 5565.7 vs 5566 simulated



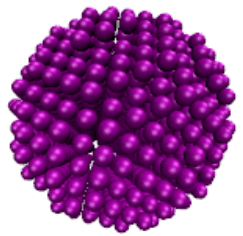
$$I(0) = f_{Cu}^2 N^2 \approx 2.6\times10^{10}$$

5.00 nm refined



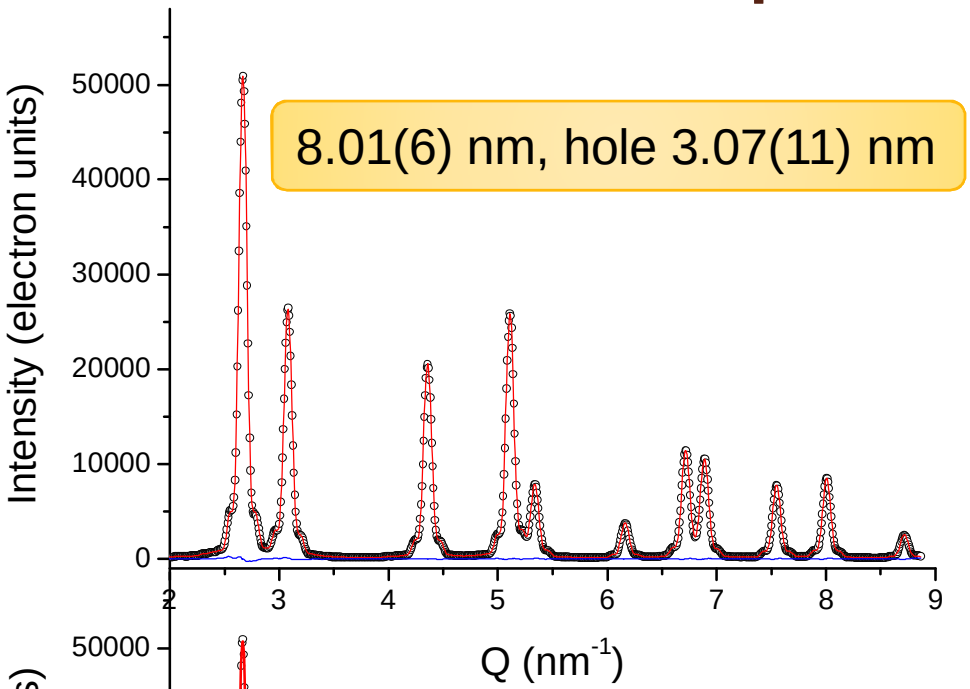
$$\propto mFN = 8\cdot16\, f_{Cu}^2 \cdot 5565.7 \approx 2\times10^7$$

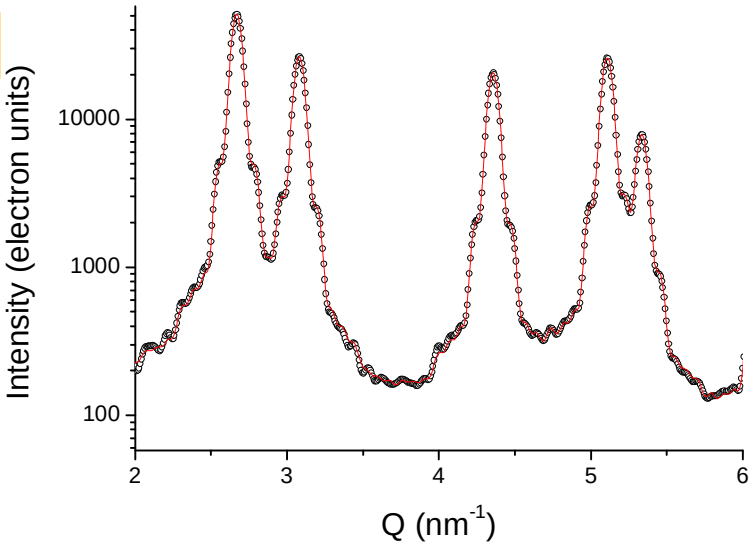
5.02 nm refined

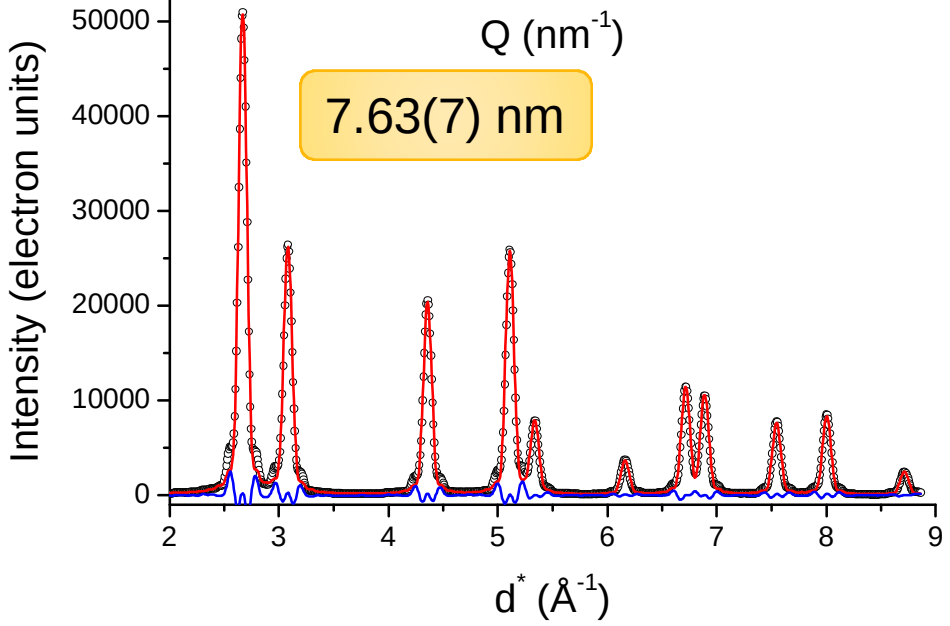


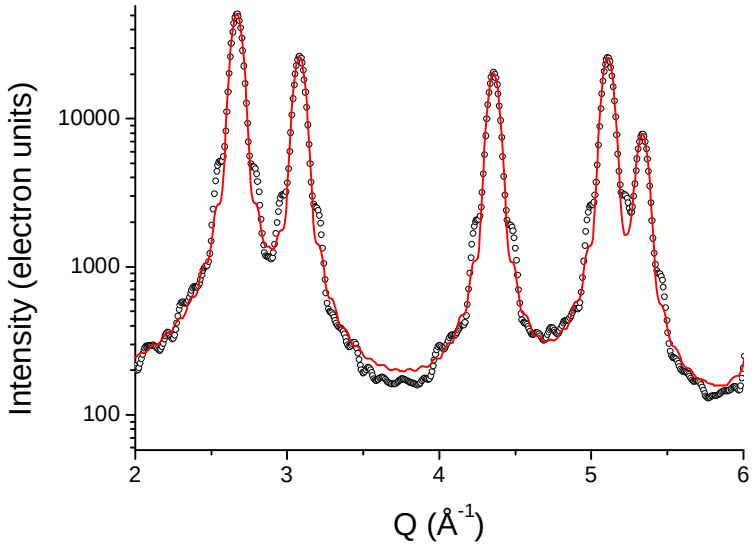
SAXS (sphere)
WPPM (sphere)
Warren intensity formula
Patterson sphere correction

Hollow 8nm Au sphere (3nm hole)



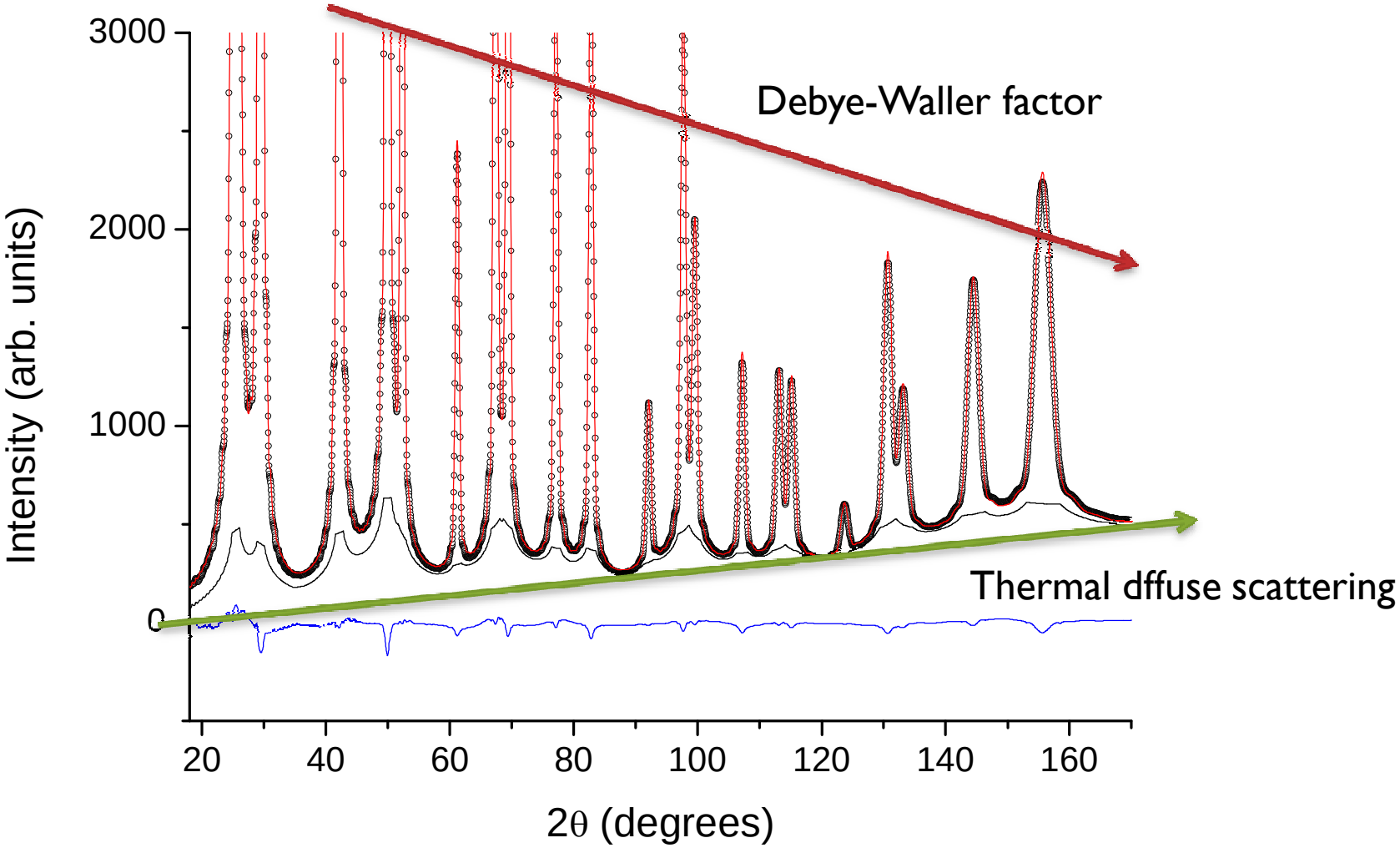






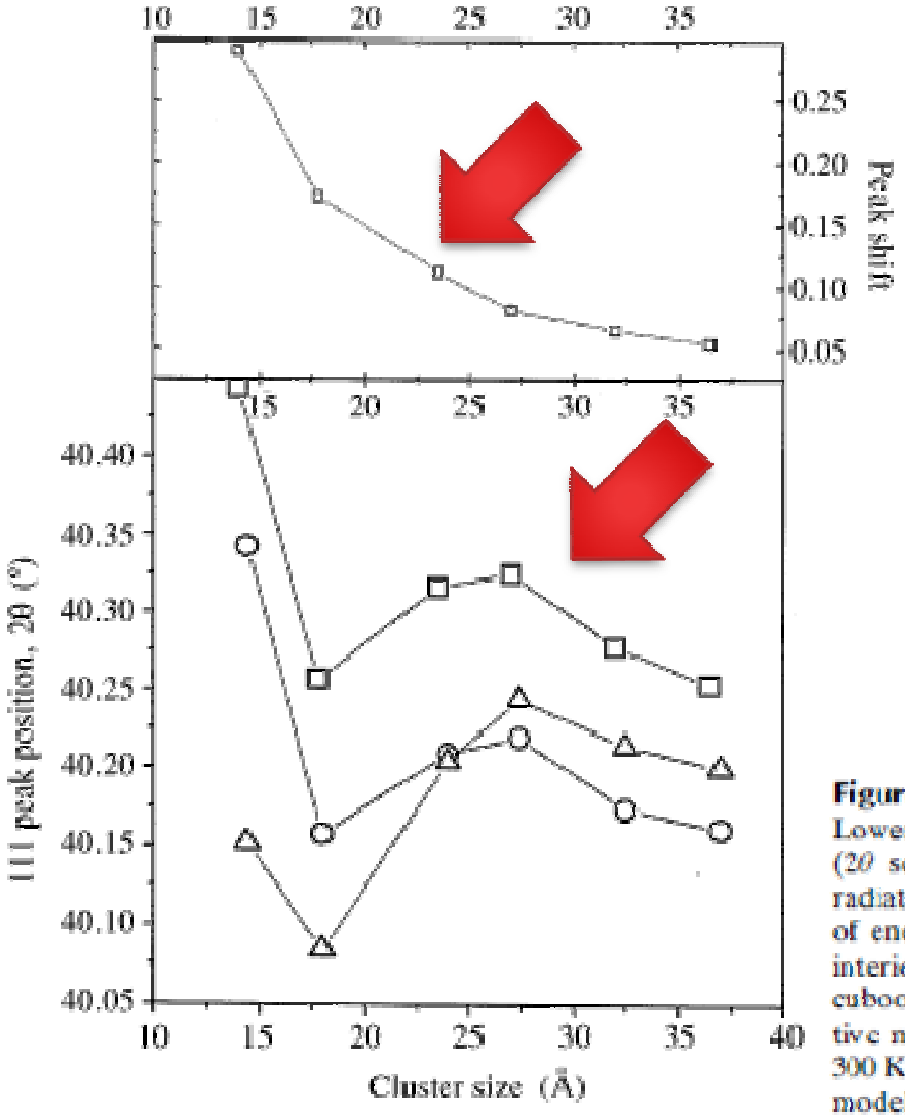
What if the crystal is thermalised?

single 10 nm Cu domain, 300K, 1Å data



Refines to 9.96(5) with TDS and 9.71(3) without TDS

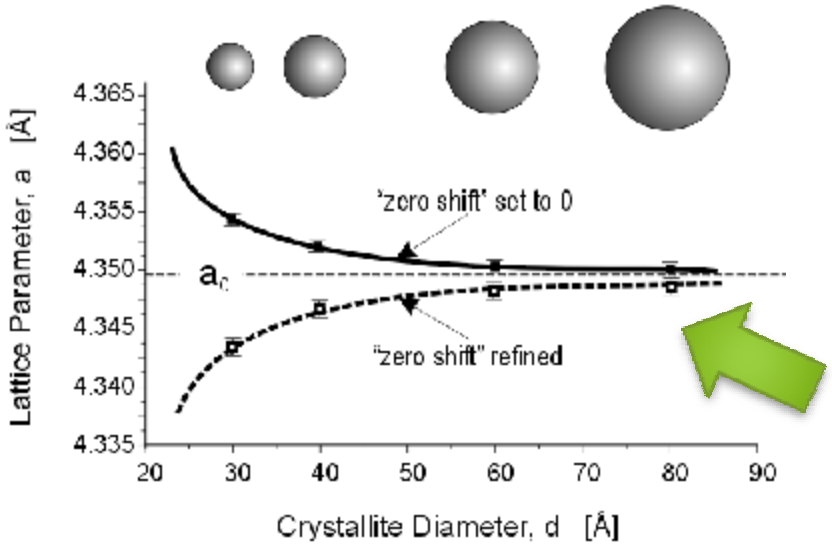
Problems wih cell parameter…



Z. Kaszkur, "Nanopowder diffraction analysis beyond the Bragg law applied to palladium", J.Appl. Cryst. (2000). 33, 87–94

Figure 2
Lower plot: the first diffraction maximum (apparent 111 peak) position (2θ scale) of the calculated pattern (measured using Cu $K\alpha$ X-ray radiation). The points correspond to: patterns calculated from the models of energy-relaxed cuboctahedra (squares), patterns calculated for the interior (all except outer shell) of the energy-relaxed next magic number cuboctahedra (see §3) (triangles), patterns calculated for the consecutive magic number cuboctahedra as an average over the MD run at 300 K (circles). All the peak positions are plotted *versus* approximate model cuboctahedron size (Å). Upper plot: the difference between the square and triangle points of the lower plot.

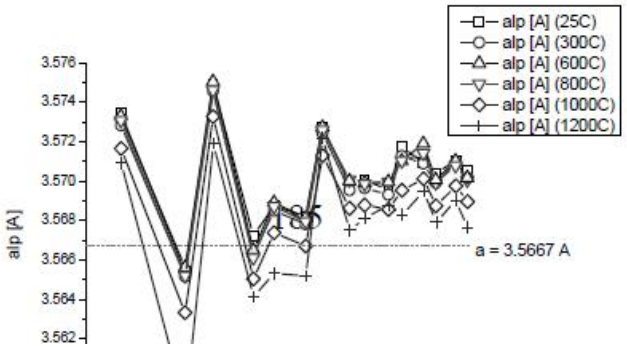
.. found several times



B. Palosz, E. Grzanka, S. Gierlotka, S. Stelmakh, et al. "Diffraction studies of nanocrystals: theory and experiment." Acta Physica Polonica Series A, 102 (2002) 57–82.

Apparent Lattice Parameter, *alp*

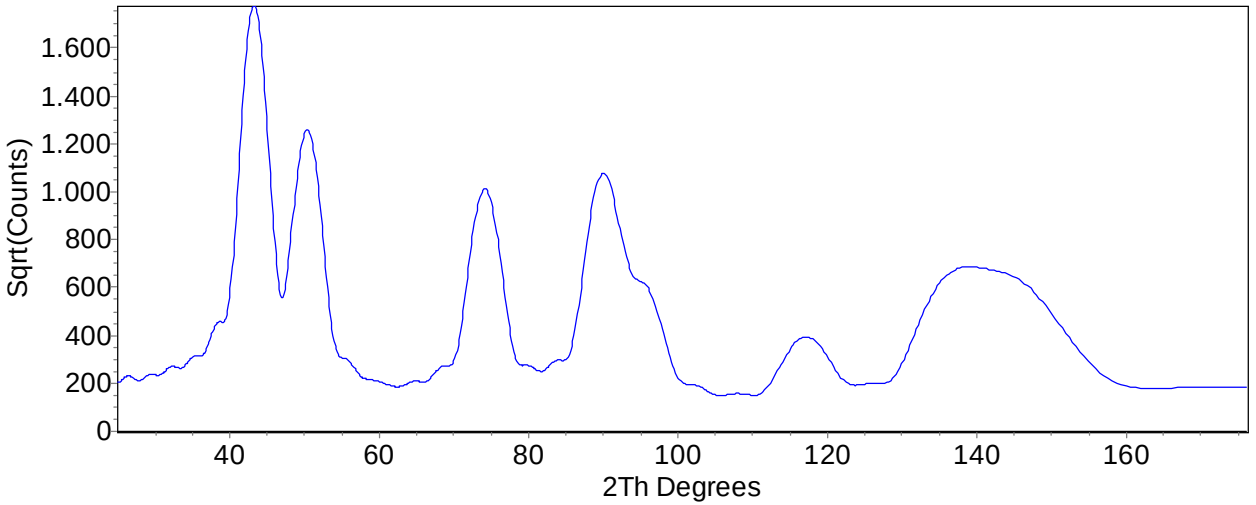
In reciprocal space, the Bragg Law is not valid anymore due to the fact that the coherent scattering length is of the same order of magnitude with the size of the crystals. To characterise such materials, the methodology of the apparent lattice parameter (*alp*) was intruduced[3]. The alp analysis, see Fig.3, is showing that major changes take place at temperatures higher than 1000°C, similarly to the PDF analysis.

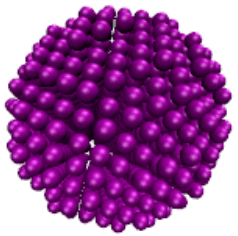


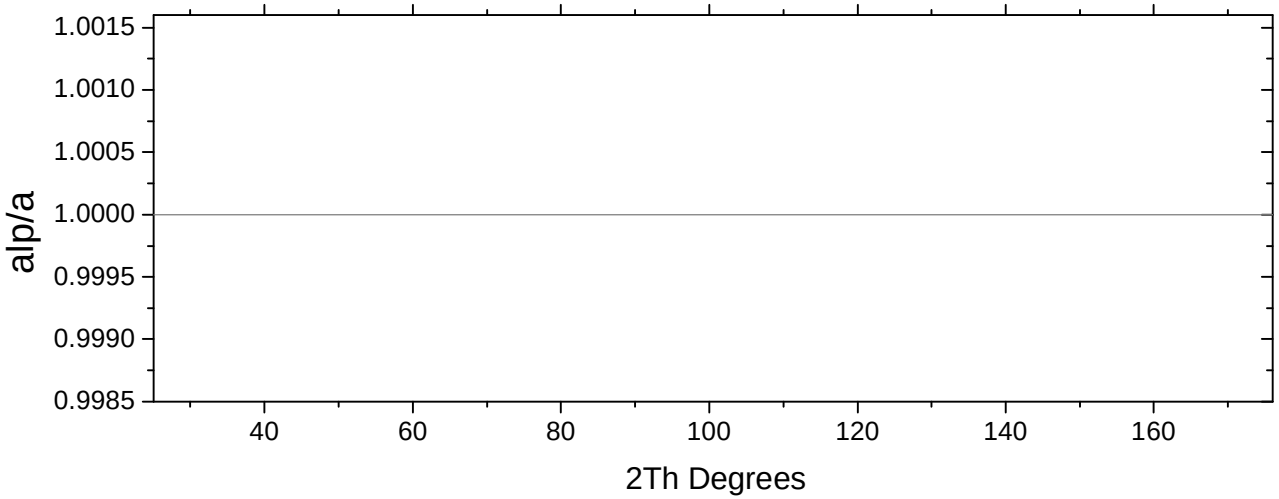
E. Grzanka, S.Stelmakh, C.Pantea, W. Zerda, B. Palosz, "Investigation of the relaxation of the nano- diamond surface in real and reciprocal spaces", 4-th Nanodiamond and Related Materials jointly with 6-th Diamond and Related Films, June 28th - July 1st, 2005, Zakopane, POLAND

Testing for accuracy

Calculation via Debye scattering formula, Cu domain 3 nm, 1202 atoms

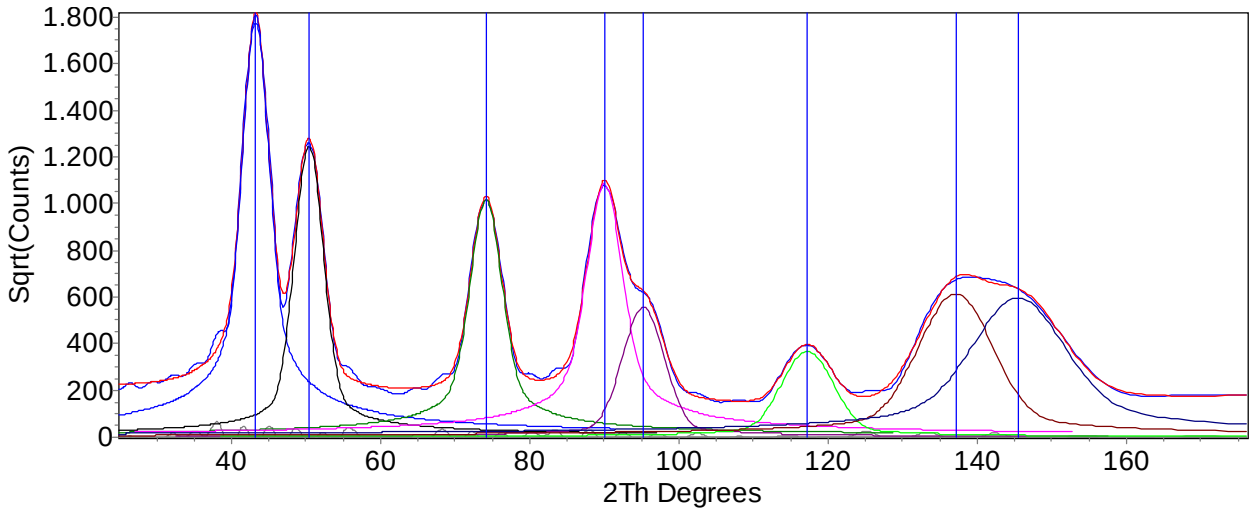


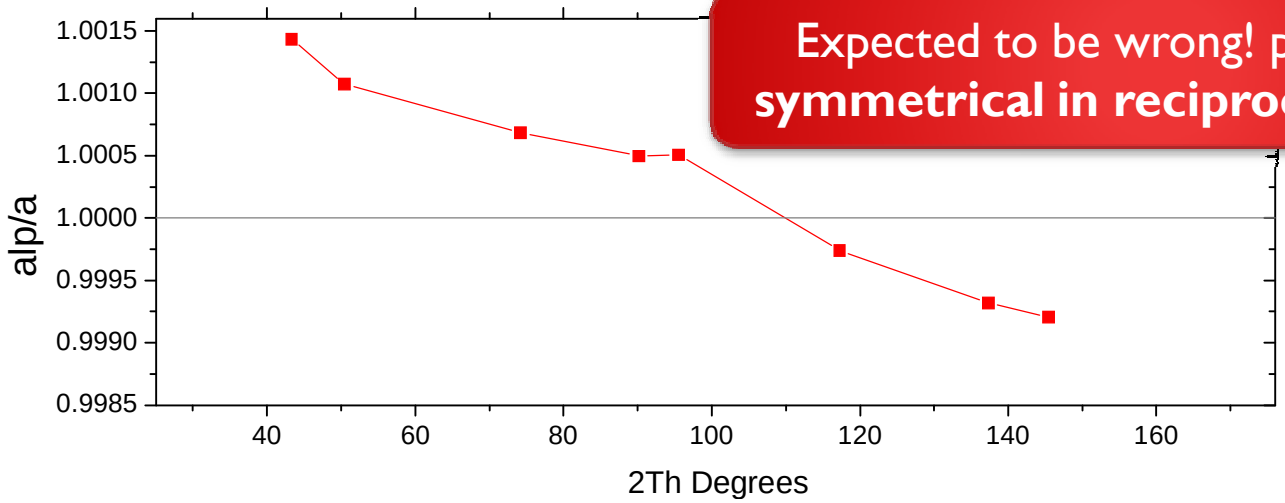




The risk of fitting in 2θ

Single peak fitting in 2θ using pV functions

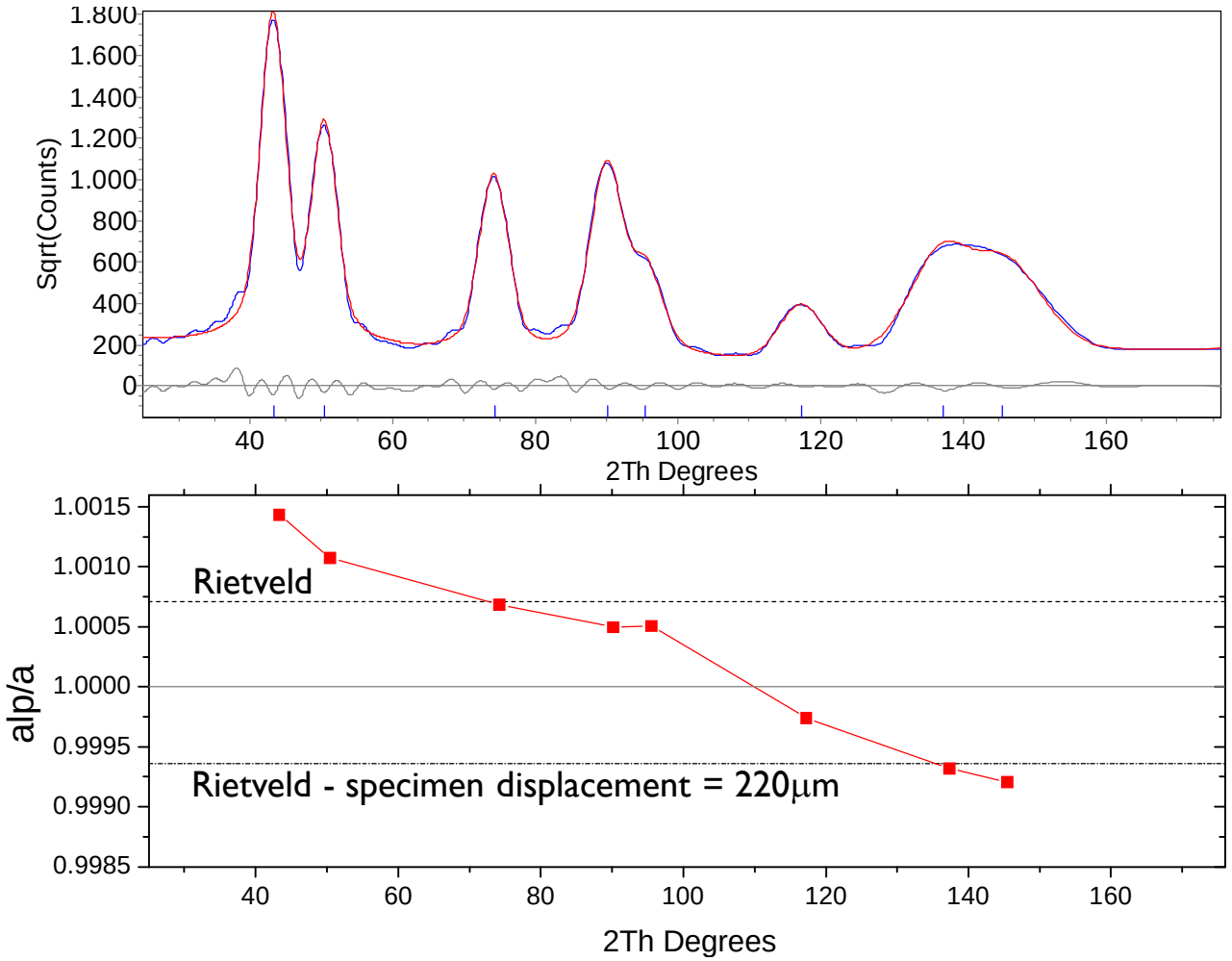




Expected to be wrong! pV MUST be **symmetrical in reciprocal space!!!!!!**

Rieveld modelling: same story!

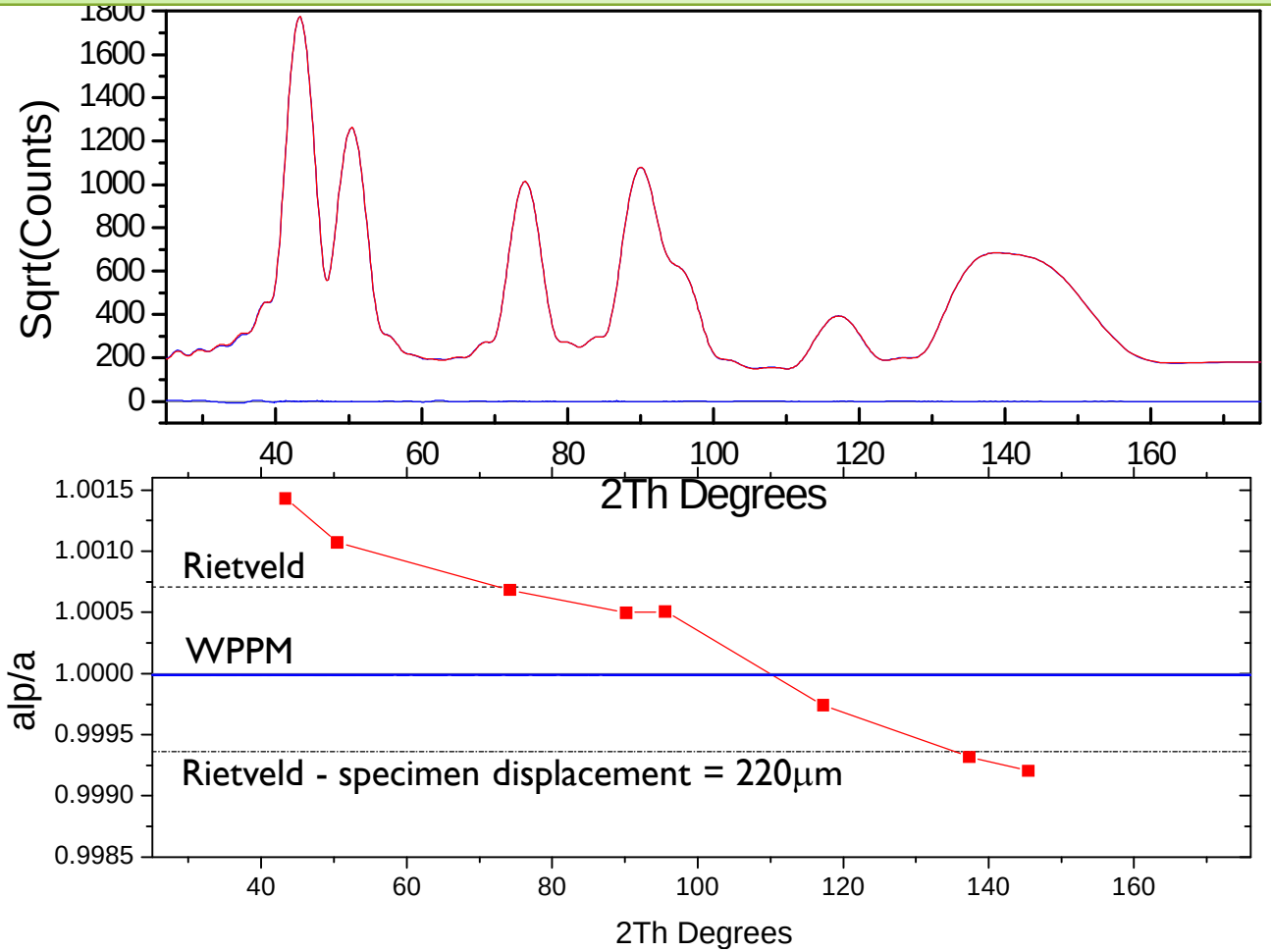
Rietveld refinement using FPA considering a specimen displacement



Why is it wrong? First hint: pV is symmetrical in the wrong space. But not just that...

Whole Powder Pattern Modelling

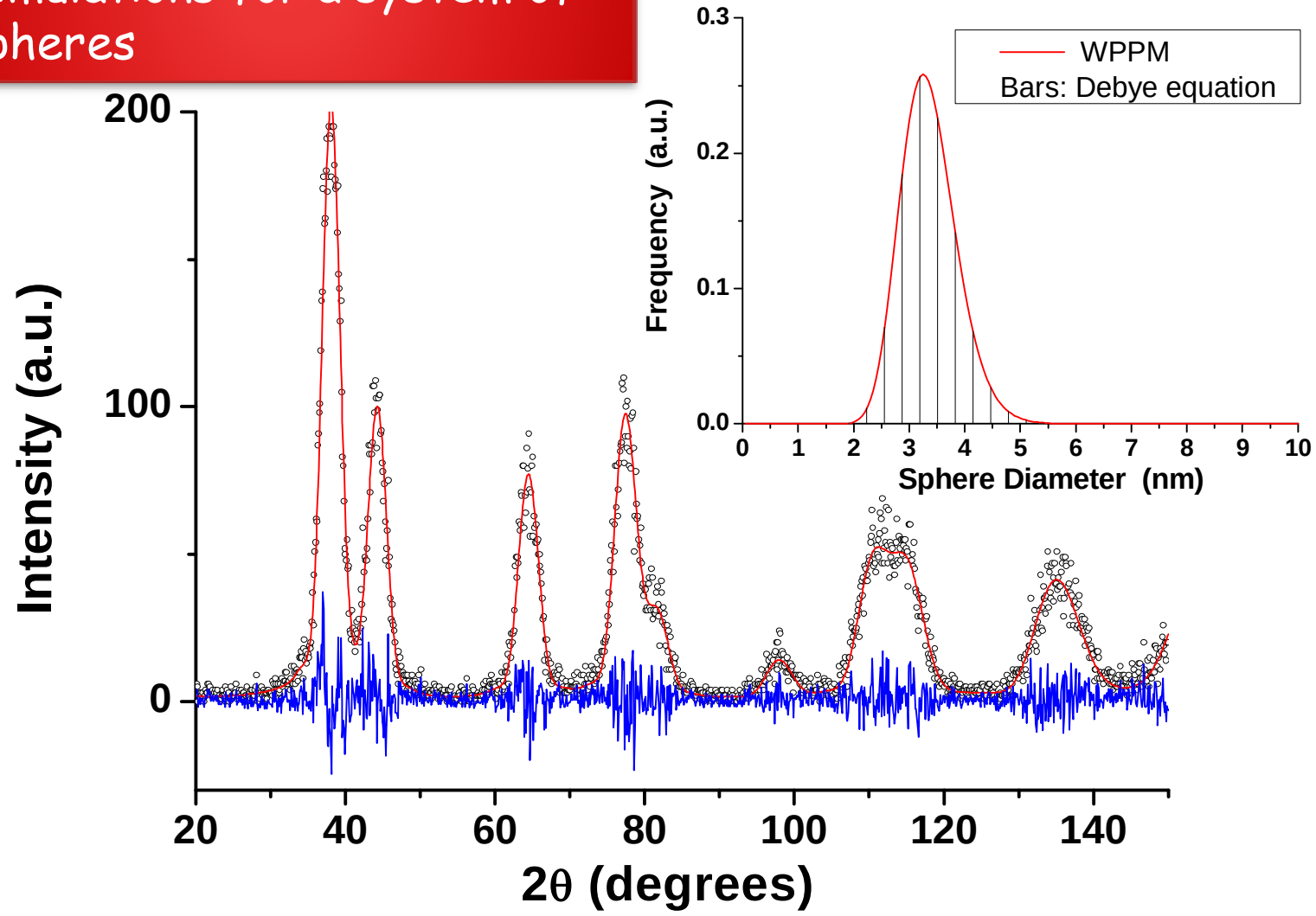
"Ab initio" using fixed cell parameter, Patterson (1939) formula, symmetric profiles in Q, correct Lorentz factor and addition of SAXS tail



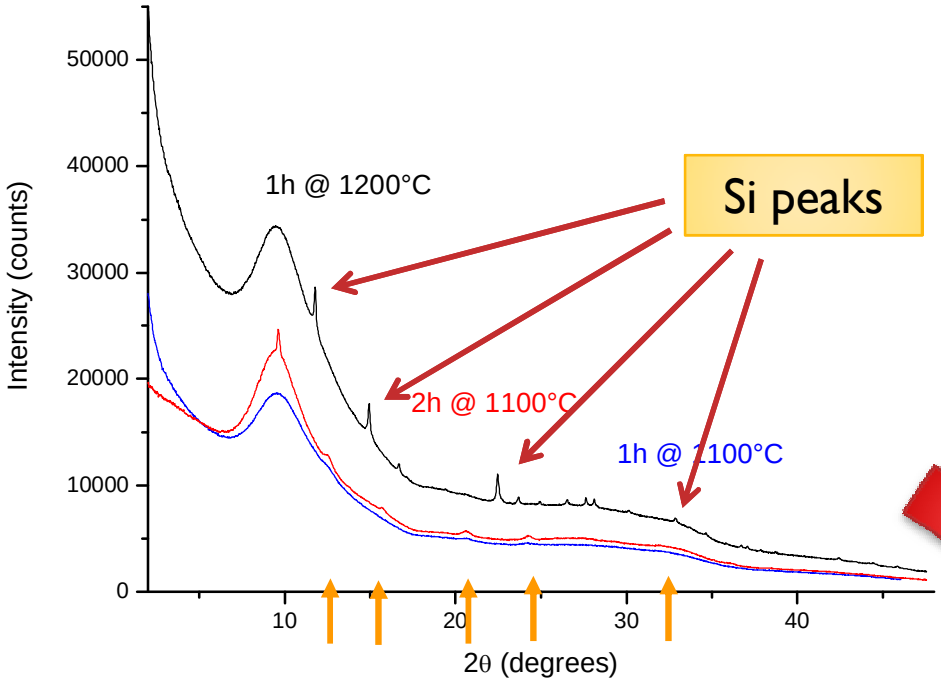
Apparent lattice parameter can therefore be an artefact!

WPPM versus Debye equation

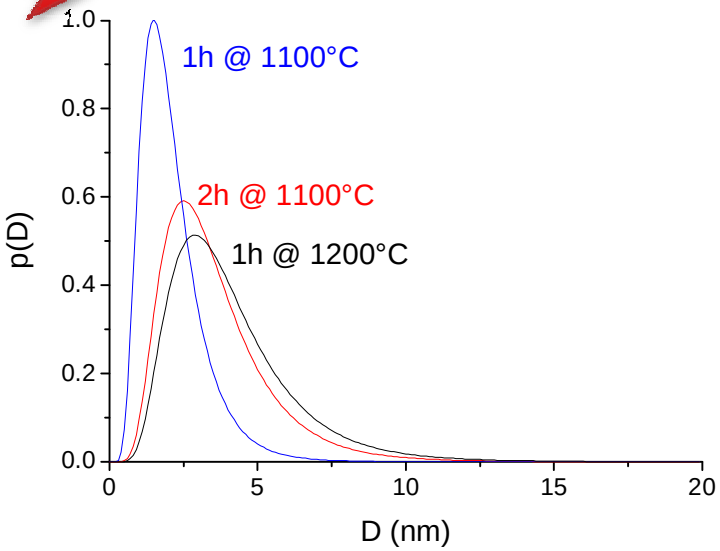
What is the limit of WPPM ? Simulations for a system of spheres

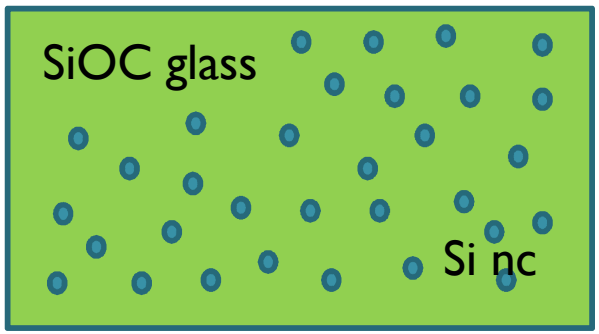


Si-nc in oxycarbide glass



Microstructure extraction via WPPM

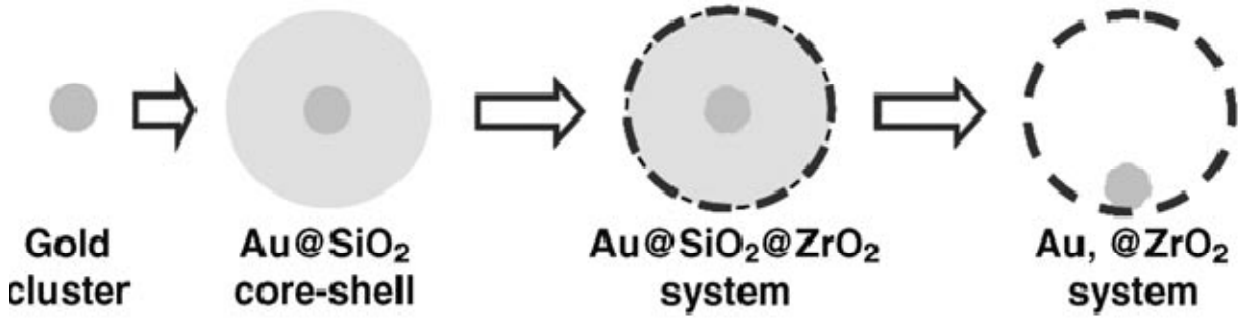




synchrotron radiation data: GILDA beamline @ ESRF

EXAMPLE: CATALYSTS

$Au@ZrO_2$ yolk-shell catalysts



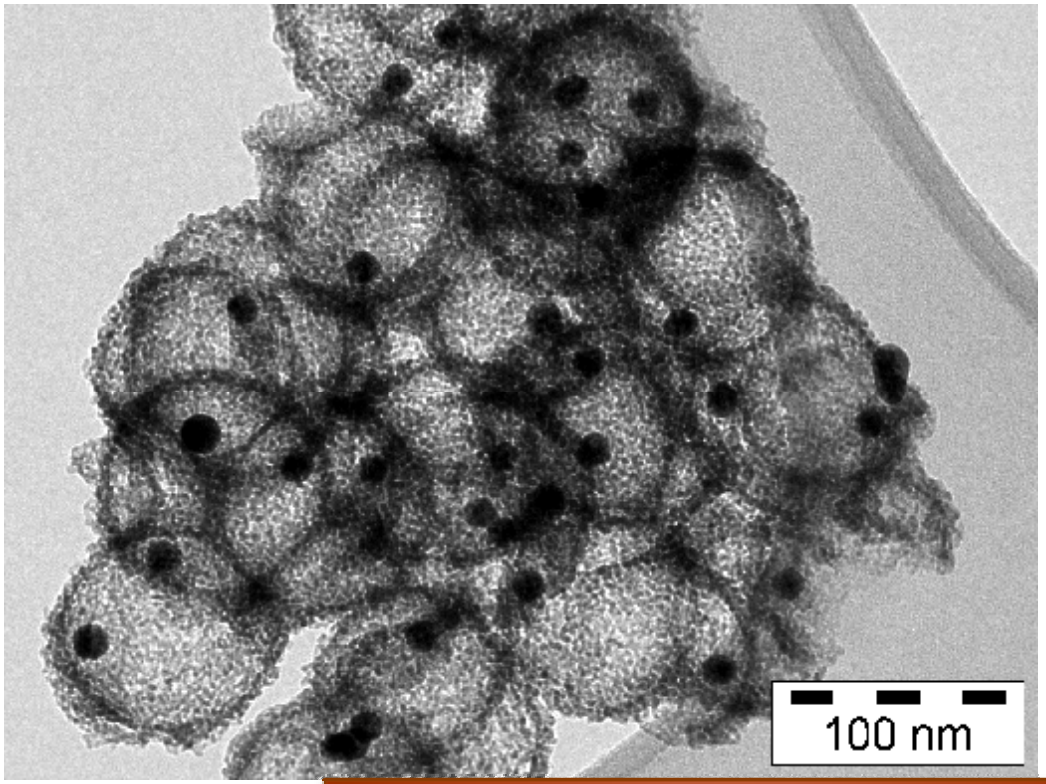
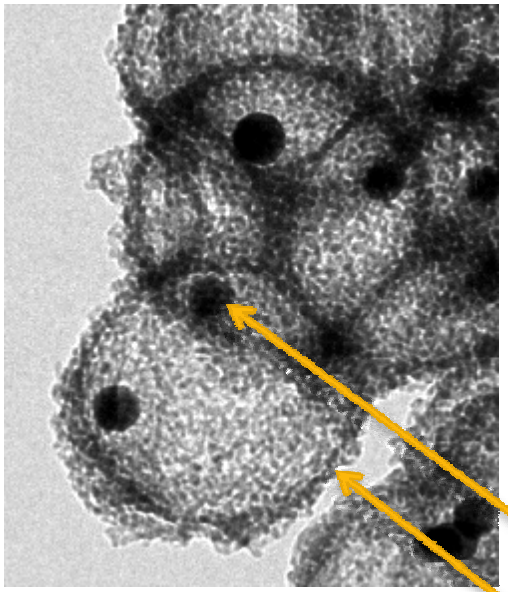


Image courtesy of C. Weidenthaler, MPI fuer Kohlenforschung, Muelheim

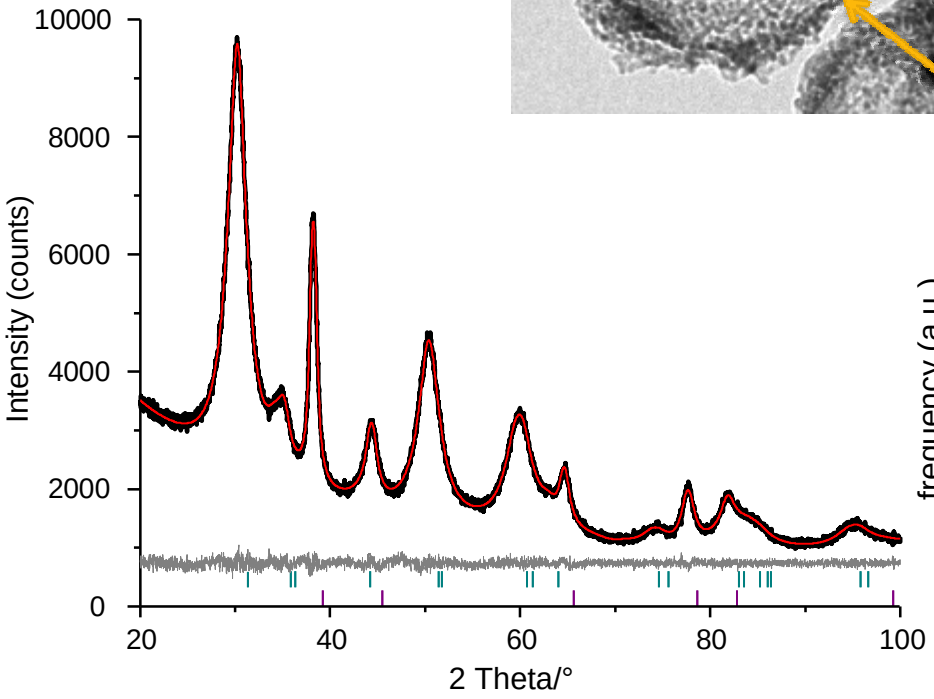
Complex system, hard to characterize with the TEM

$Au@ZrO_2$ yolk-shell catalysts

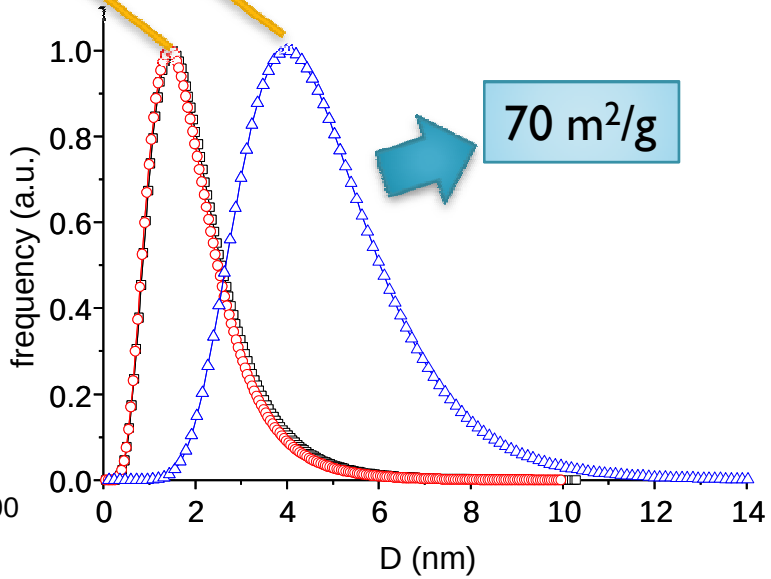


Nanocrystalline Au inside a cage of porous nanocrystalline ZrO_2

WPPM for phases and size distribution

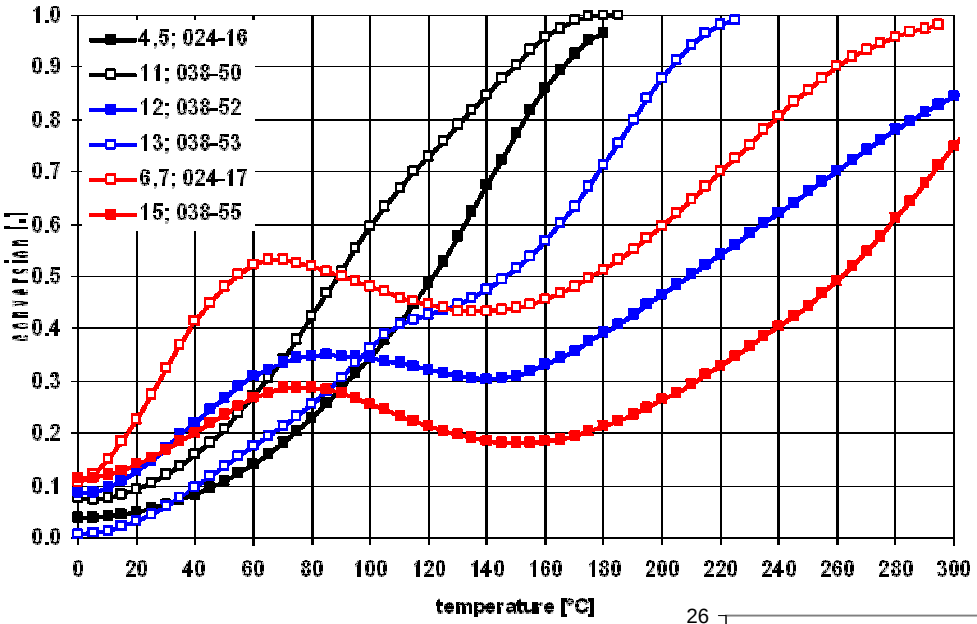


Phase-selective specific area calculation!



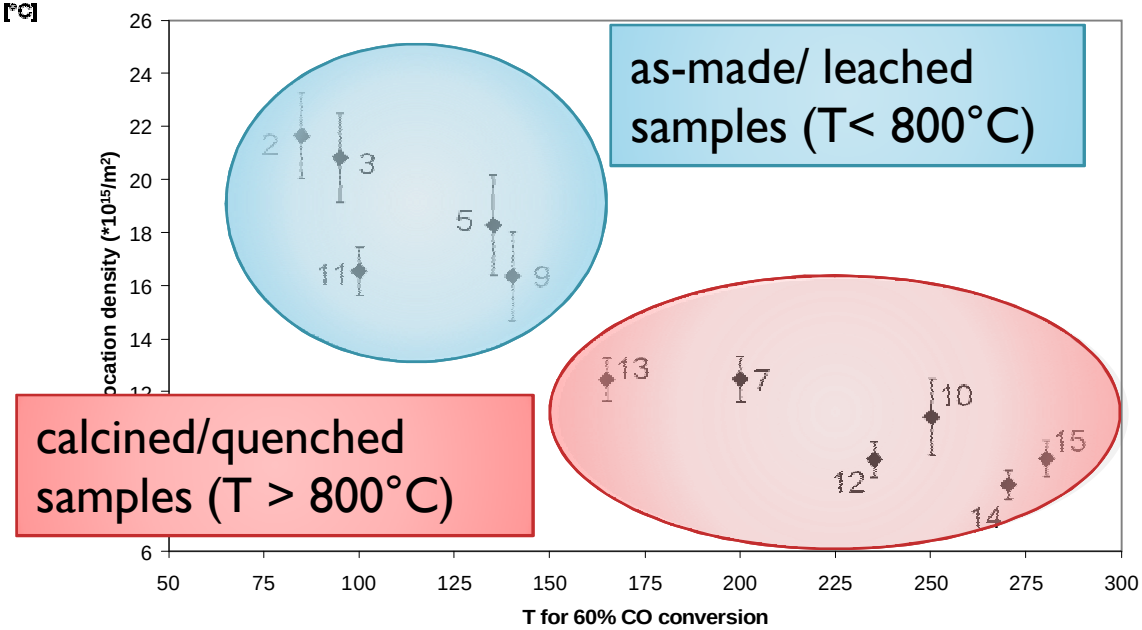
70 m^2/g

$Au@ZrO_2$ yolk-shell catalysts



CO conversion as a function of T for:
11: as made;
5: leached
13: heated to 800 °C and slow cooling
7: heated to 900 °C and quenched
12: heated to 900 °C and slow cooling
15: heated to 900 °C and quenched

Defects outcrop increase the activity of the catalyst!!

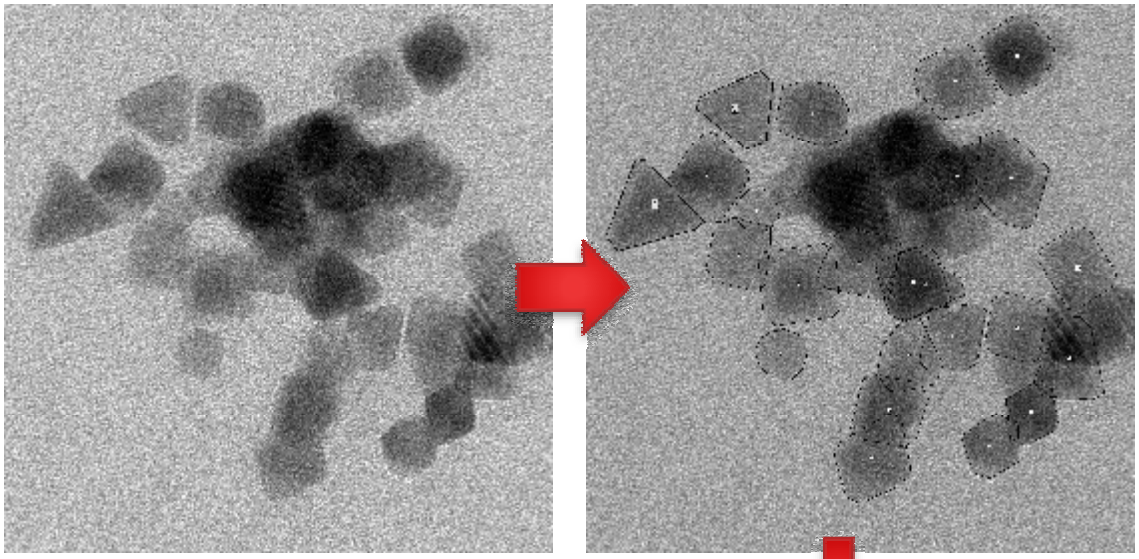


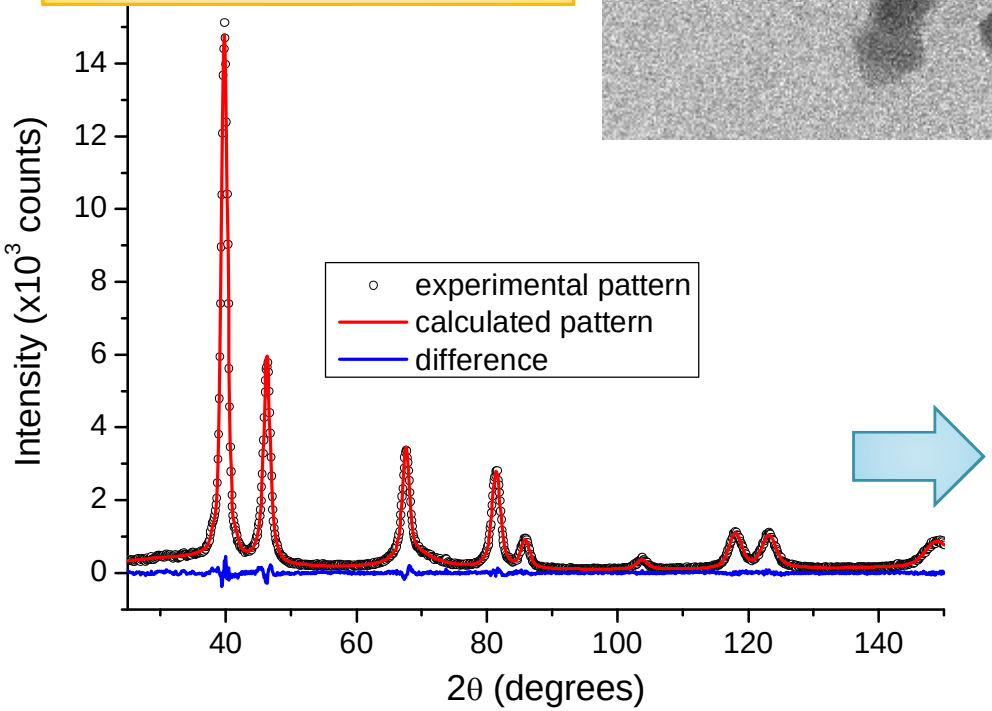
Pt nanocatalysts

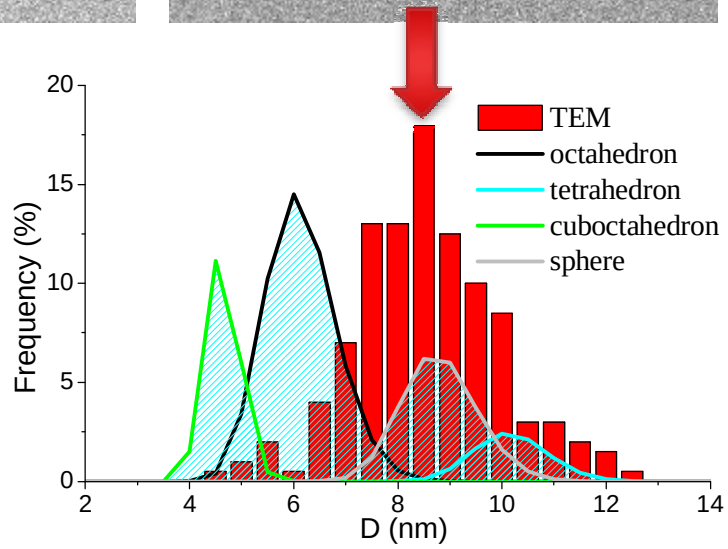
Nano-Pt by reducing H_2PtCl_6 using H_2 in presence of sodium polyacrylate

Soft chemistry employed to control the shape of the particles

WPPM to check the distribution of size and shapes

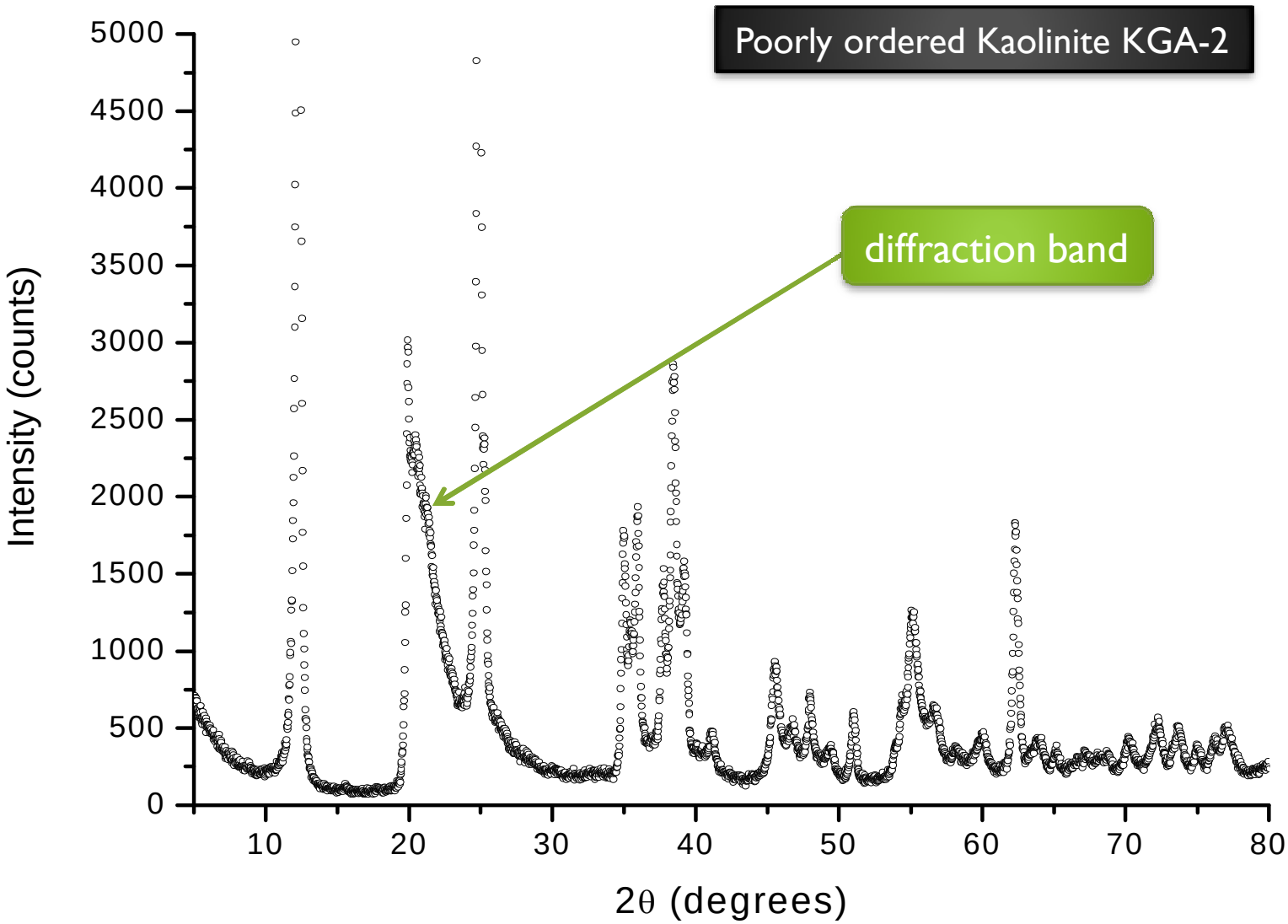






CONCLUDING REMARKS

(yet) Hard-to-treat case



WPPM cannot alove all cases: it deals with "well behaving" defects only

Concluding remarks/caveats

Accuracy in line profile analysis has definitely improved in the last years

Good fit does not always mean good/accurate result

Fit the models on the measured data (not viceversa)

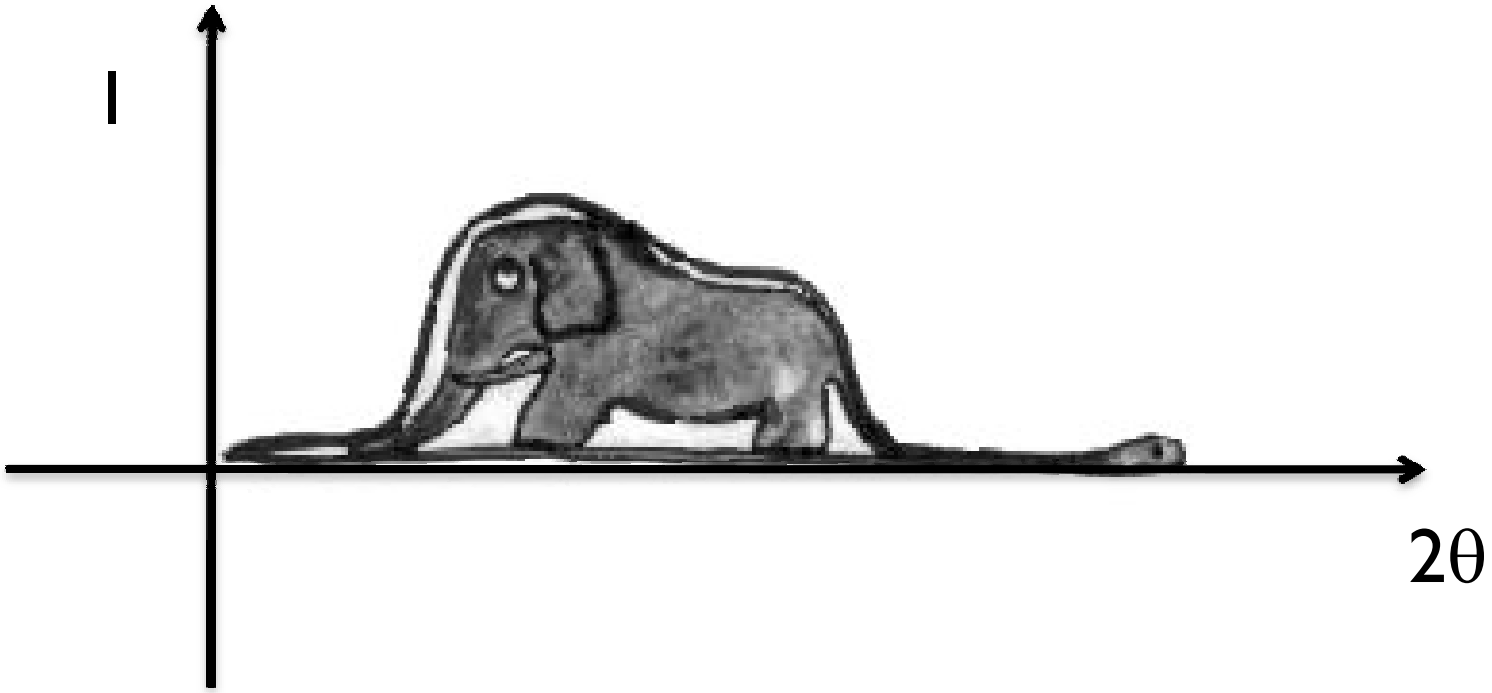
Use the quick and dirty tools for comparison and a WPPM-type approach for more quantitative studies

NEVER EVER use any result from microstructure analysis without knowing what you are doing / how you obtained it!

Conclusions

My drawing was not a picture of a hat. It was a picture of a boa constrictor digesting an elephant. But since the grown-ups were not able to understand it, I made another drawing: I drew the inside of the boa constrictor, so that the grown-ups could see it clearly.

They always need to have things explained.



ResearchGate: Matteo Leoni Matteo.Leoni@unitn.it