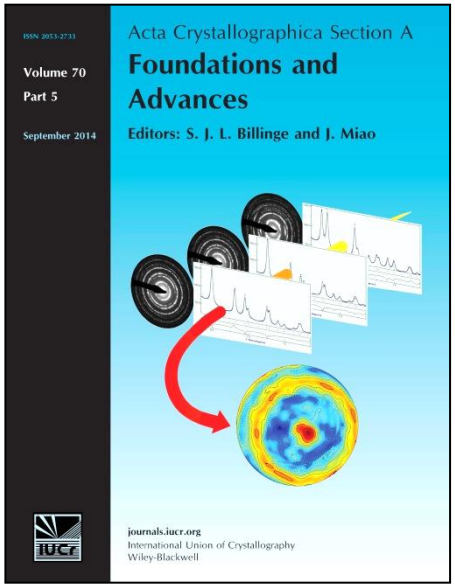
Structure and Phase Analyses of Nanoparticles using Combined Analysis of TEM scattering patterns

P. Boullay[1], L. Lutterotti[2] and D. Chateigner[1]

[1] CRISMAT, UMR 6508 CNRS / ENSICAEN, 6 Bd du Maréchal JUIN 14050 CAEN Cedex, France

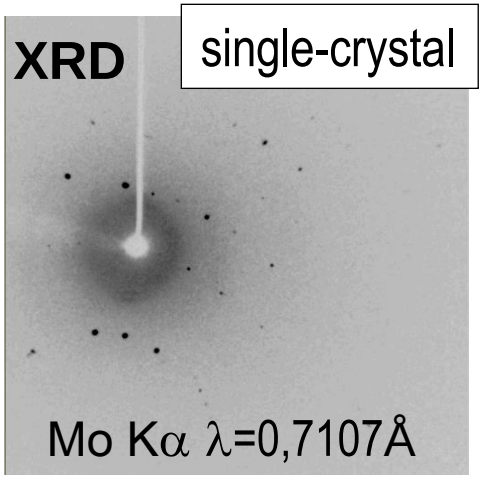
[2] Department of Industrial Engineering, University of Trento, 38123 TRENTO, Italy



1. Phase search and indexing
2. Sizes, shapes and textures
3. Structure refinements

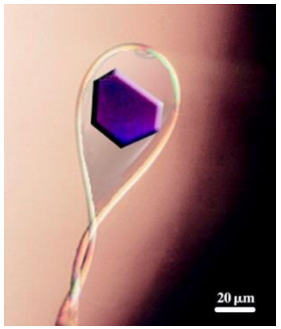
Quantitative Analysis of Electron Powder Diffraction

XRD single-crystal

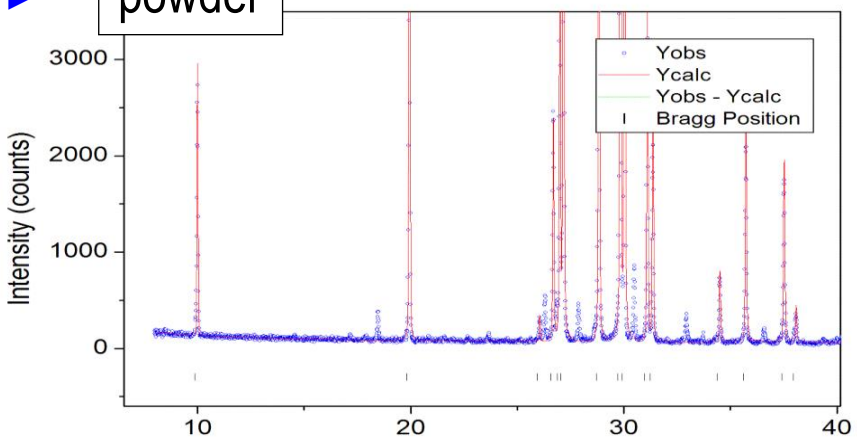


◄ tens of micrometer ►

cell, symmetry and structure



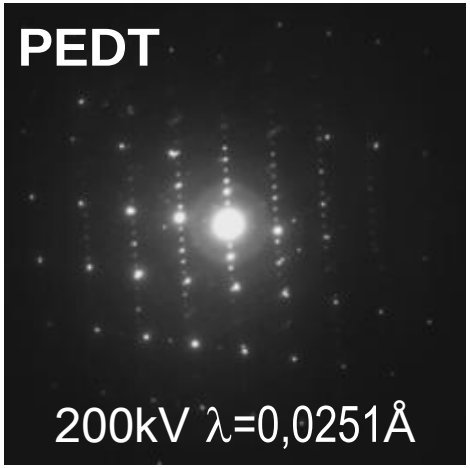
powder



phase S/M, structure and microstructure

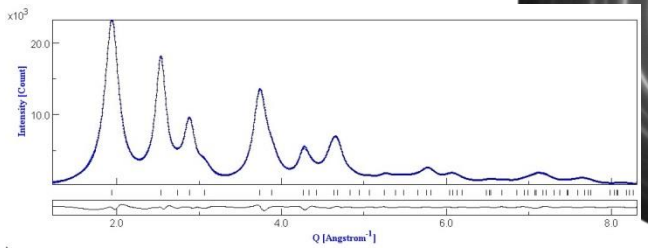
(size, shape, texture)

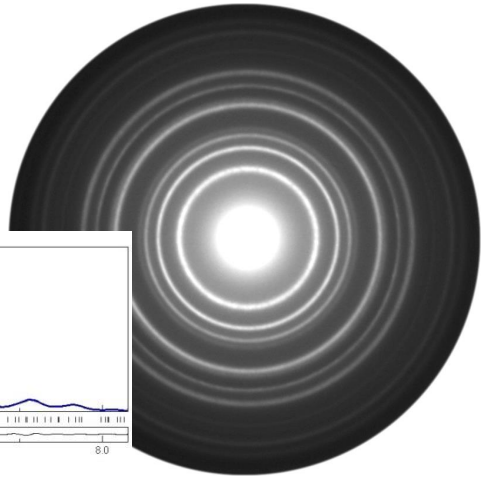
PEDT



◄ tens of nanometer ►

Nanoparticles (NP)





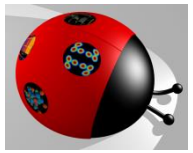
Precession Electron Diffraction Tomography

Electron Powder Diffraction (EDP) patterns

Quantitative and statistically representative analysis of crystallite sizes and shapes, structure and crystallographic texture of nanoparticles in the form of powders and thin films?

Extraction of intensities from electron diffraction “ring patterns” for quantitative or semi-quantitative analysis …

- Vainshtein (1964), …
- PCED 2.0 : *X.Z. Li, Ultramicroscopy 110 (2010) 297-304*
- ProcessDiffraction : *J.L. Labar, Microsc. Microanal. 15 (2009) 20-29*
- TextPat : *P. Oleynikov, S. Hovmoller and X.D. Zou in Electron Crystallography*
- **The MAUD program** : **L. Lutterotti** *Nuclear Inst. and Methods in Physics Res. B268 (2010) 334-340.*



http://www.ing.unitn.it/~maud/

MAUD
Rietveld pattern fitting

Evolutionary
Simulated Annealing
Marquardt (Least squares)
Metadynamics optimization
Simplex (Nelder-Mead)
Genetic

Delft size-strain (PV)
Popa anisotropic
Size/Strain distributions
Planar faulting (Warren)
Turbostratic (Ufer)

Size-Strain

Indexing
(COD phase search procedure)

Peak location

X-ray
Neutron
Electron

March-Dollase
Harmonic
(E)WIMV
Standard Functions

Texture

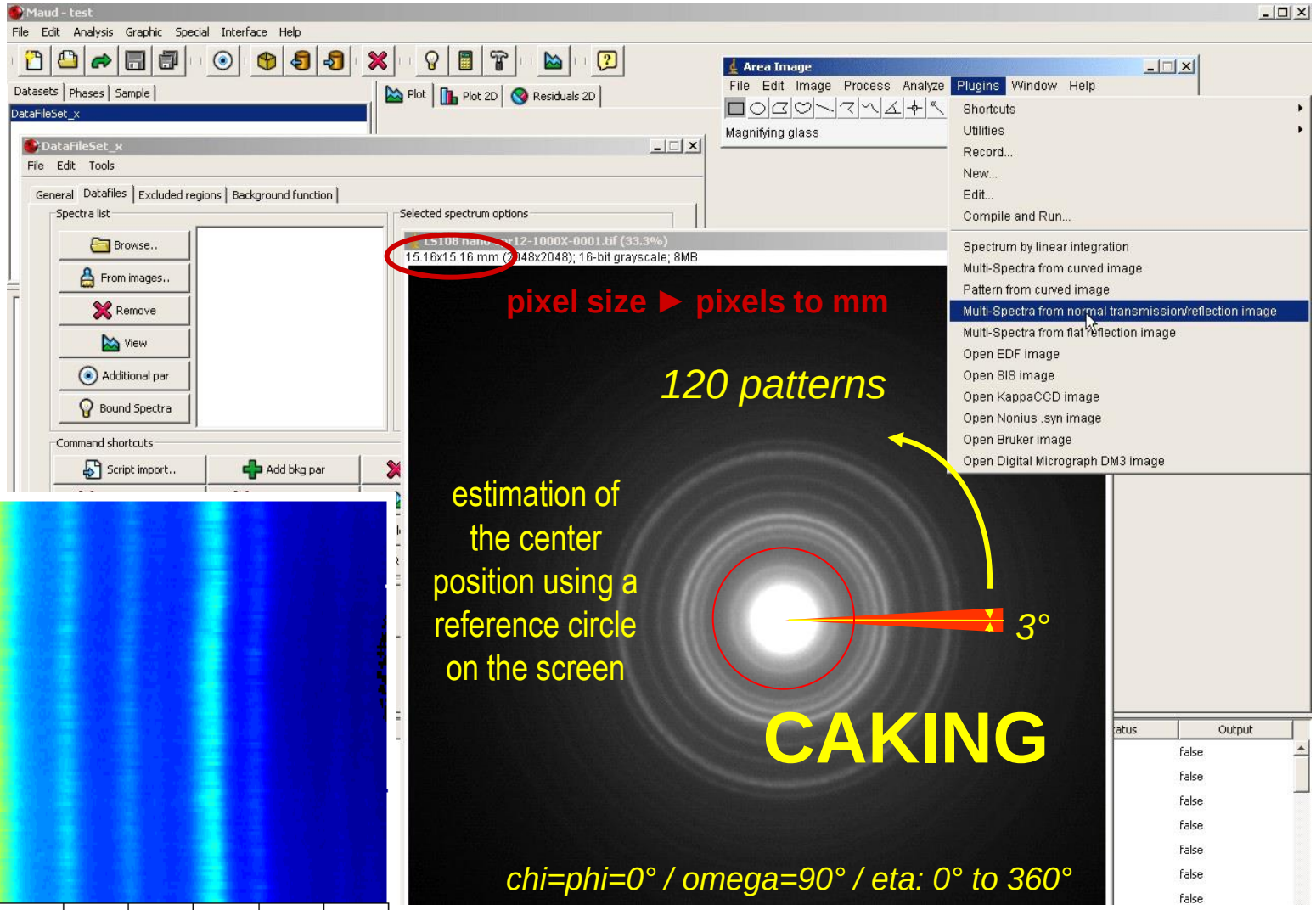
Peak fitting

Residual stresses

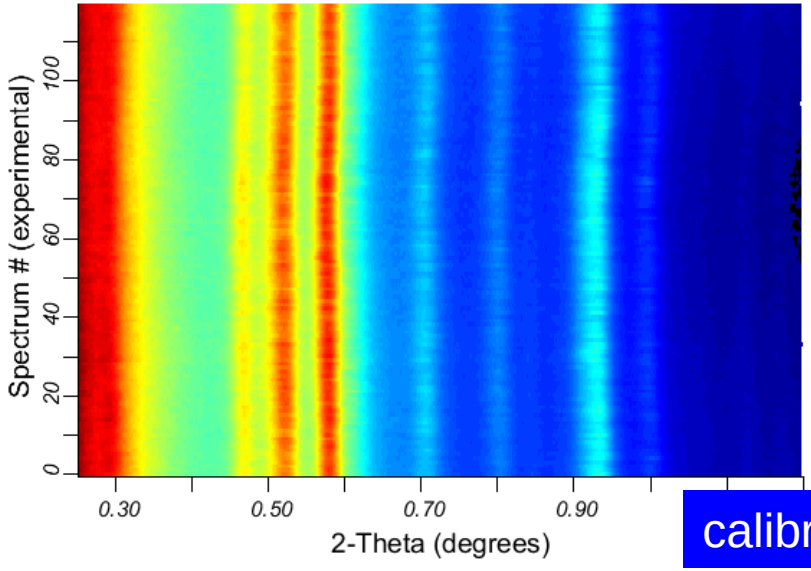
Geometric
Voigt, Reuss, Hill
Triaxial Stress

Structure refinement

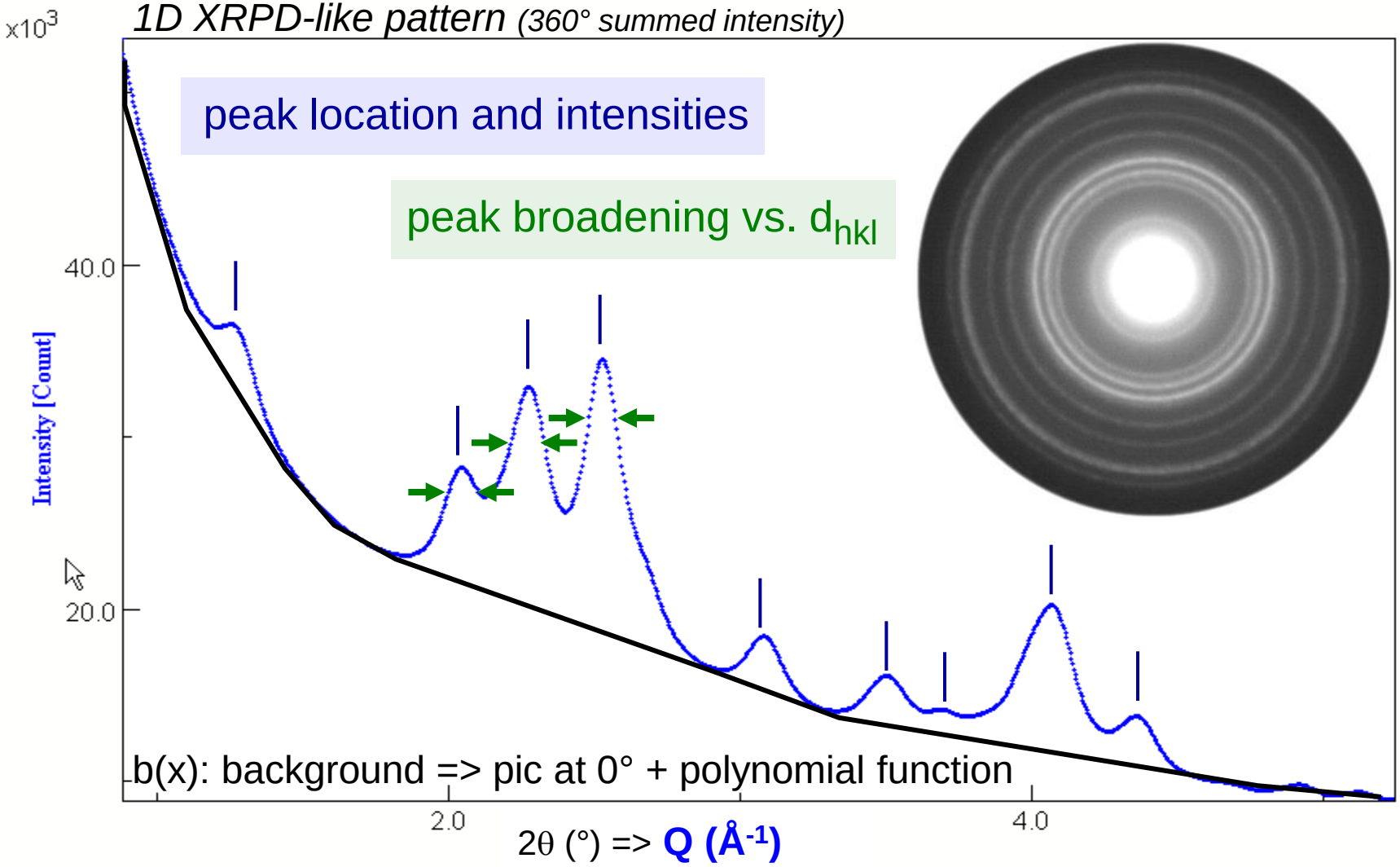
Intensity extraction along the rings by segments using an ImageJ plugin



2D plot



calibrate the distance specimen/detector ► mm to 2θ



measured profile h(x) = f(x) ⊗ g(x) + b(x)

Line broadening causes

$$h(x) = f(x) \otimes g(x) + b(x)$$

sample contribution | instrumental broadening

- instrumental broadening
- finite size of the crystals (acts like a Fourier truncation: size broadening)
- imperfection of the periodicity (due to d_h variations inside crystals: microstrain effect)
- generally: 0D, 1D, 2D, 3D defects

All quantities are average values over the probed volume

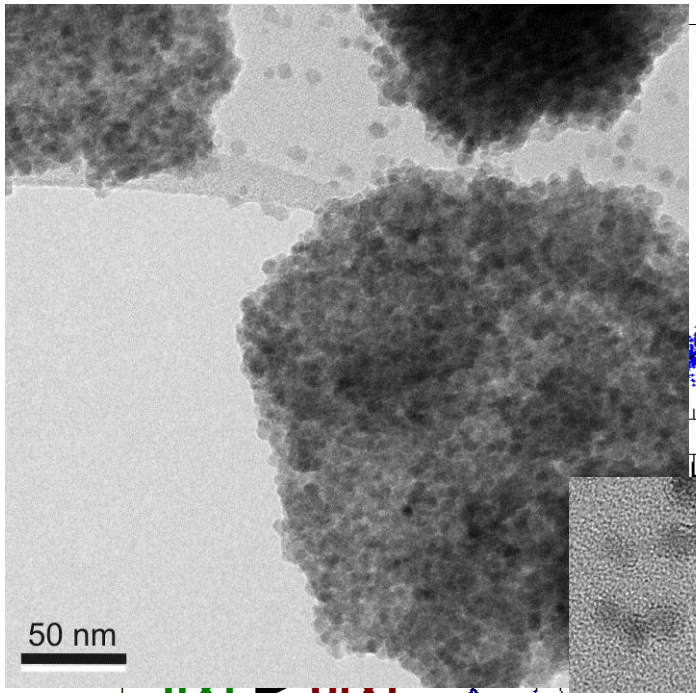
- ► electrons, x-rays, neutrons: complementary
- ► distributions: mean values depend on distributions' shapes

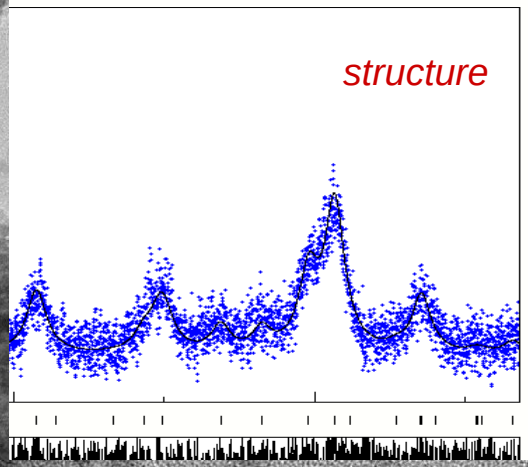
Extraction of f(x) can be obtained by a whole-pattern (Rietveld) analysis

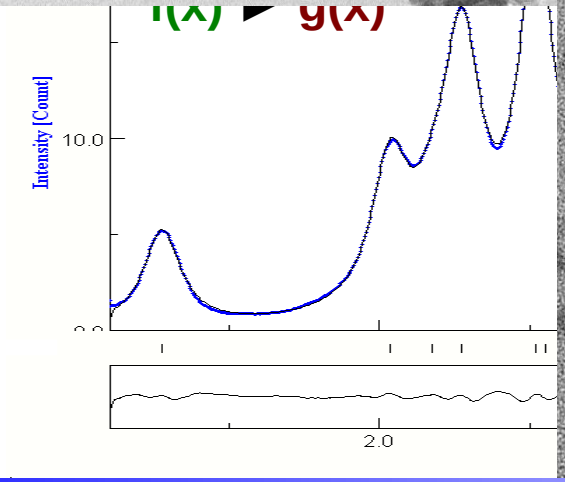
Need to know g(x) the instrumental broadening !

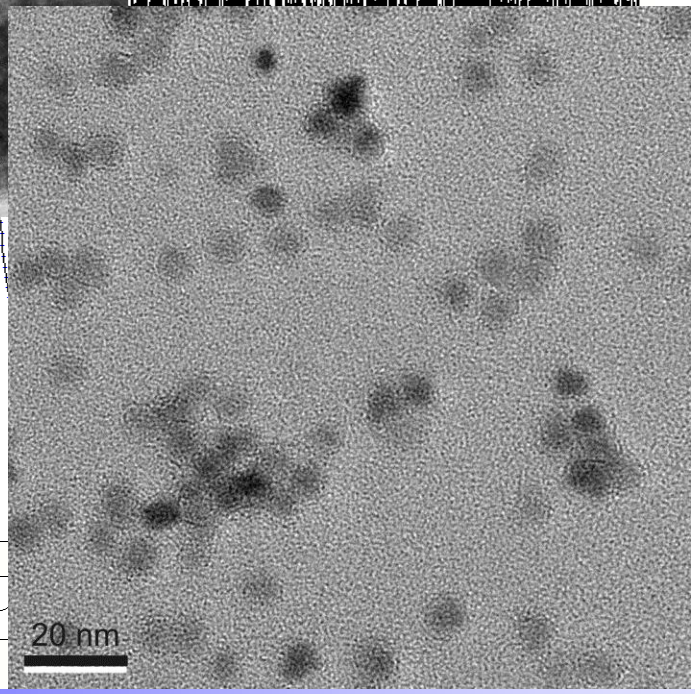
The instrumental Peak Shape Function is obtained by analysing nanoparticules of known sizes and shapes as obtained from X-ray analyses

Mn_3O_4 hausmannite *(L. Sicard et al, J. Magn. Magn. Mater. 322 (2010) 2634-2640)*







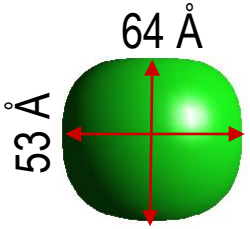


Bruker D8 / Lynx Eye 1D

λ=1.54056 Å (Cu Kα_1)

SG: I 4_1/a m d

a=5.764(2)Å and c=9.448(4)Å

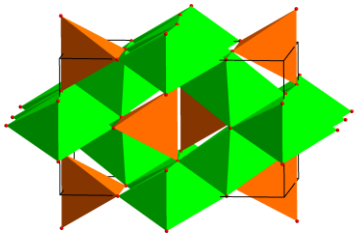


POPA anisotropic shape

TOPCON 2B / CCD ORIUS

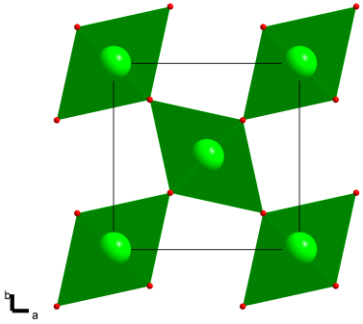
λ=0.0251Å

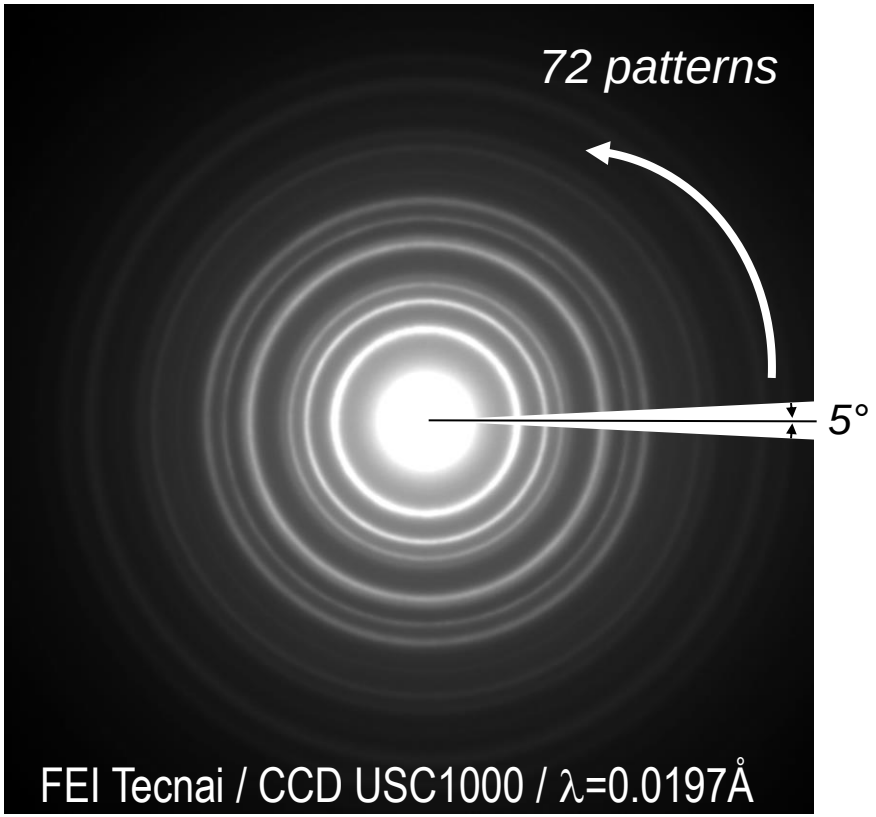
a=5.7757(2)Å and c=9.4425(4)Å



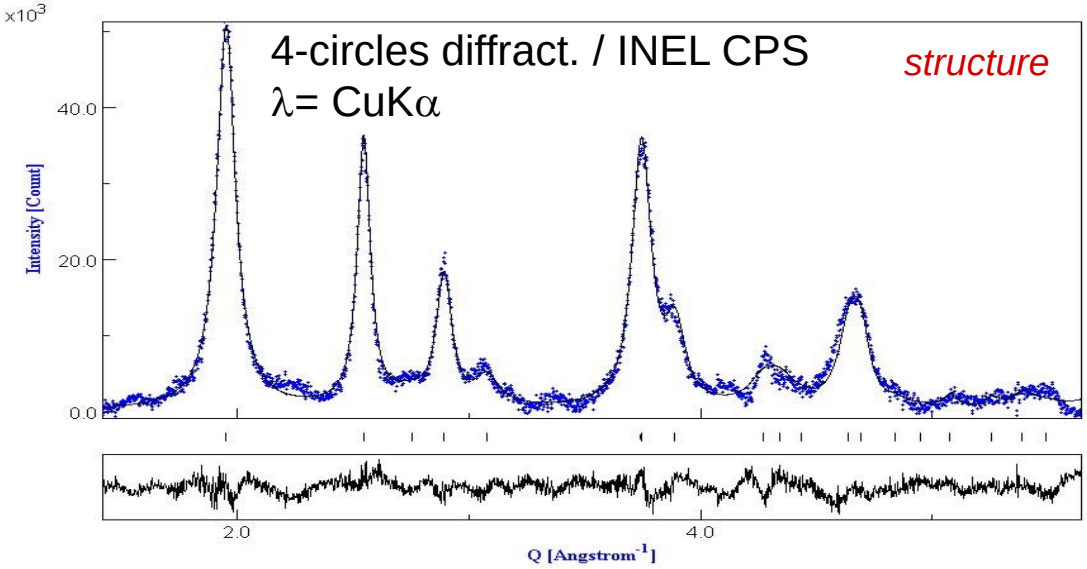
Microstructure of nanocrystalline materials: TiO_2 rutile (1)

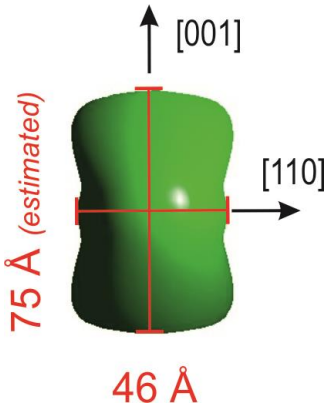
from phase search: TiO2 rutile $P4_2/mnm$ a= 4.592Å a=2.957Å (COD database ID n°9001681)



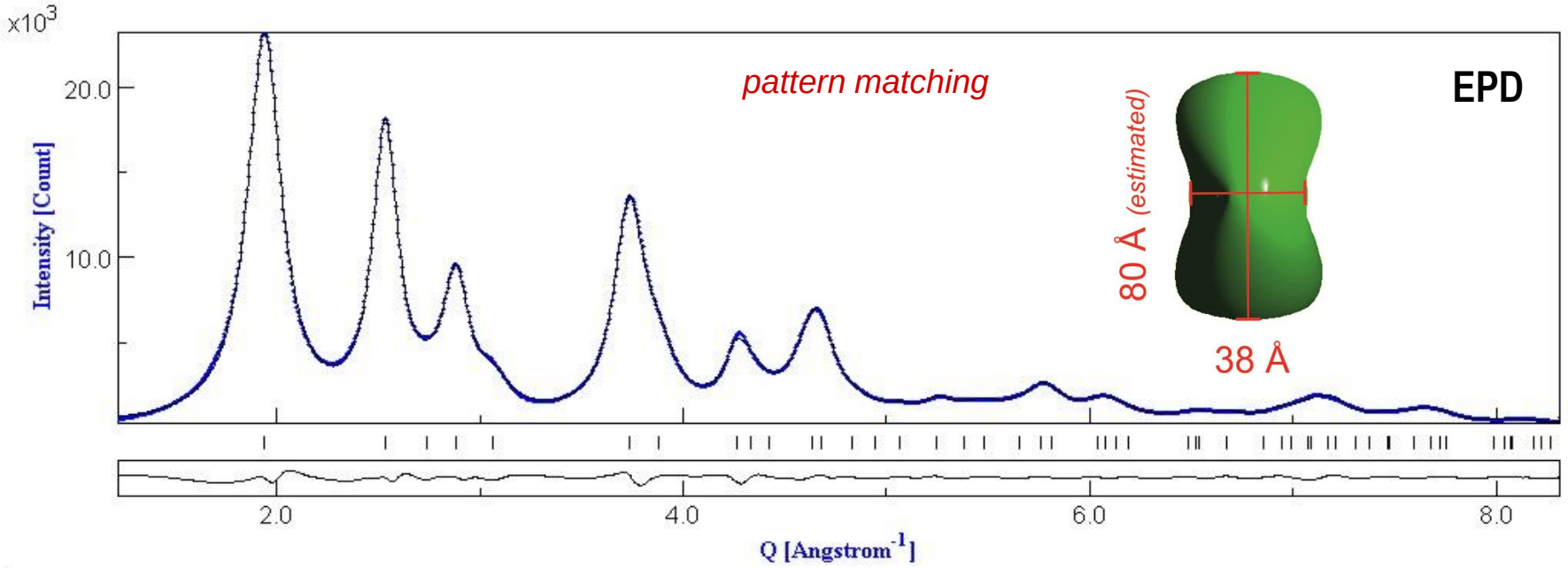


(1) *M. Reddy et al., ElectroChem. Com. 8 (2006) 1299-1303*



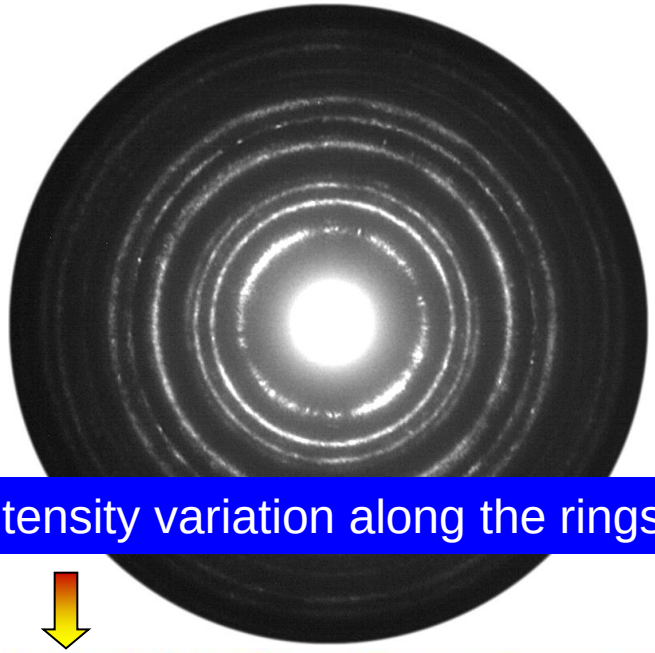


average anisotropic crystallite size

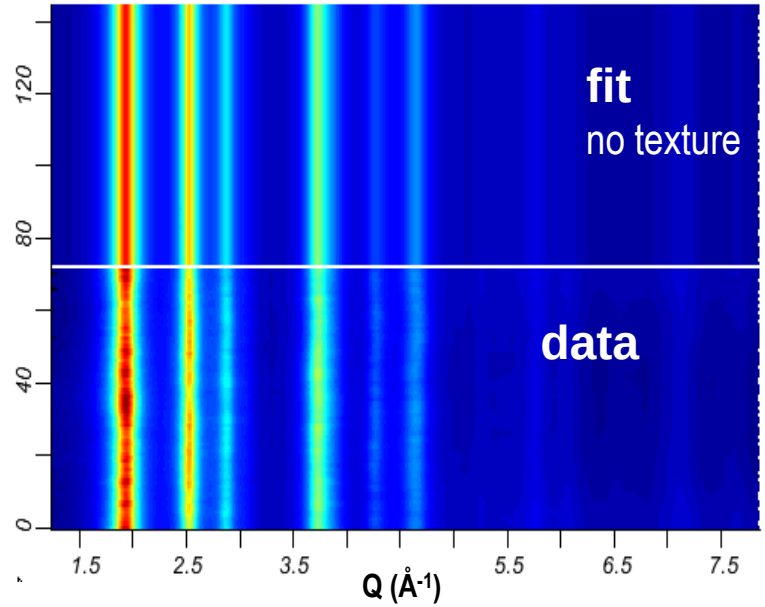


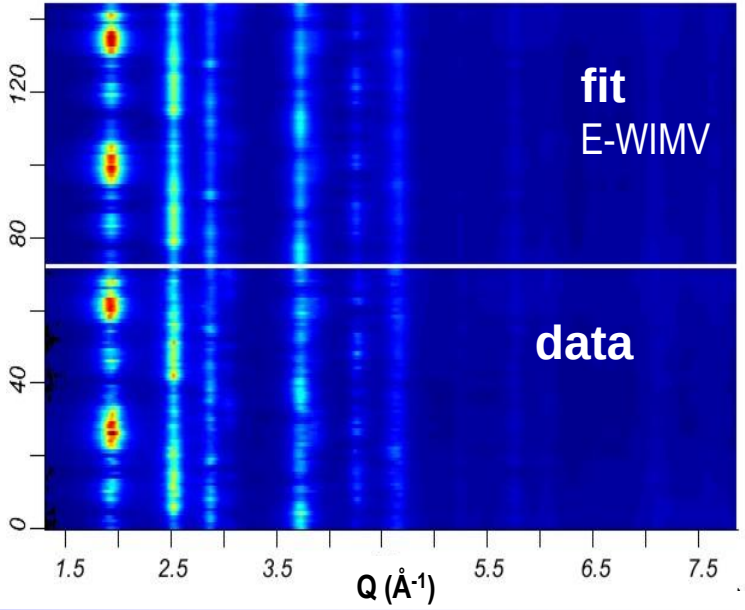
6µm ⇨ **0.5µm**

decreasing the selected area

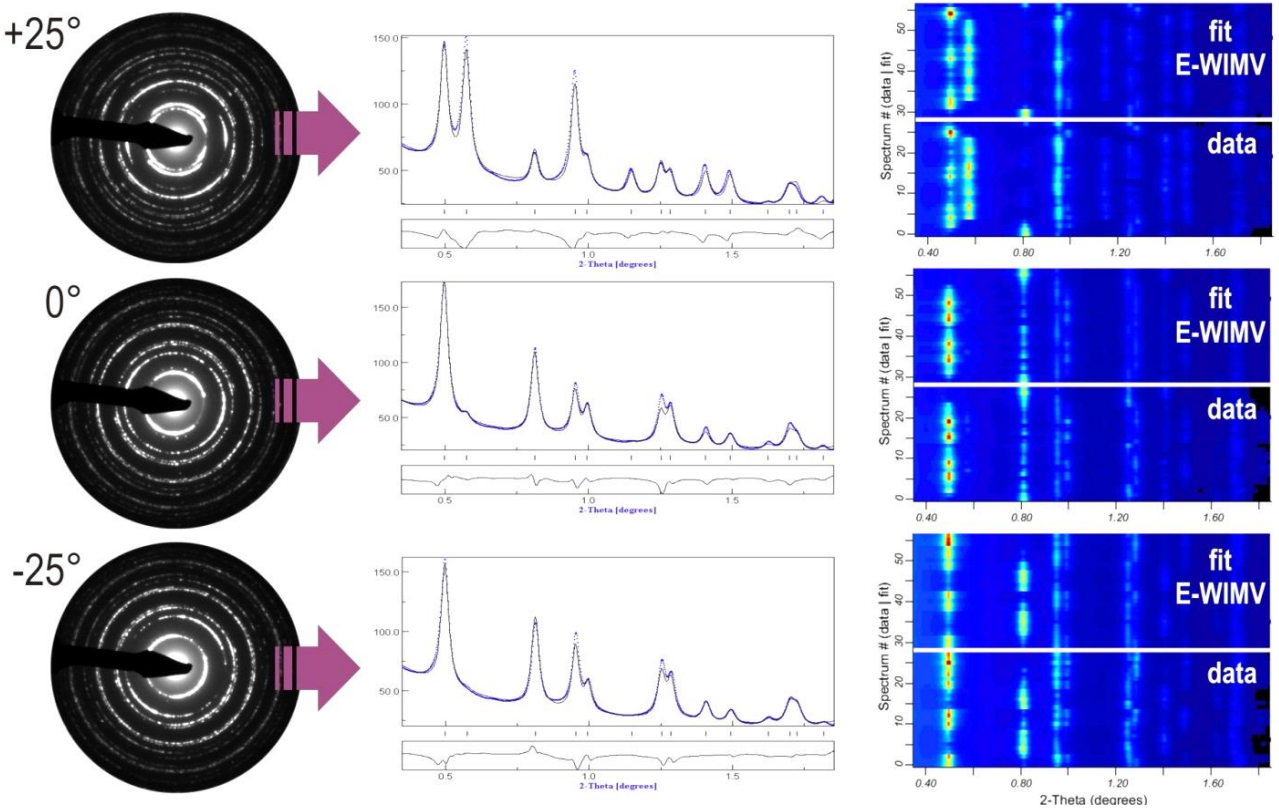


Texture :: intensity variation along the rings



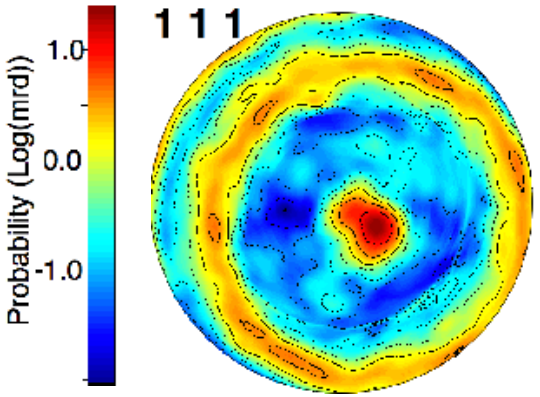


The features available in MAUD allow a full quantitative texture analysis for general cases (not only fiber textures) from EPD patterns with the obtention of accurate pole figures



+25° to -25° step 5°

QTA analysis of Pt thin film deposited on Si



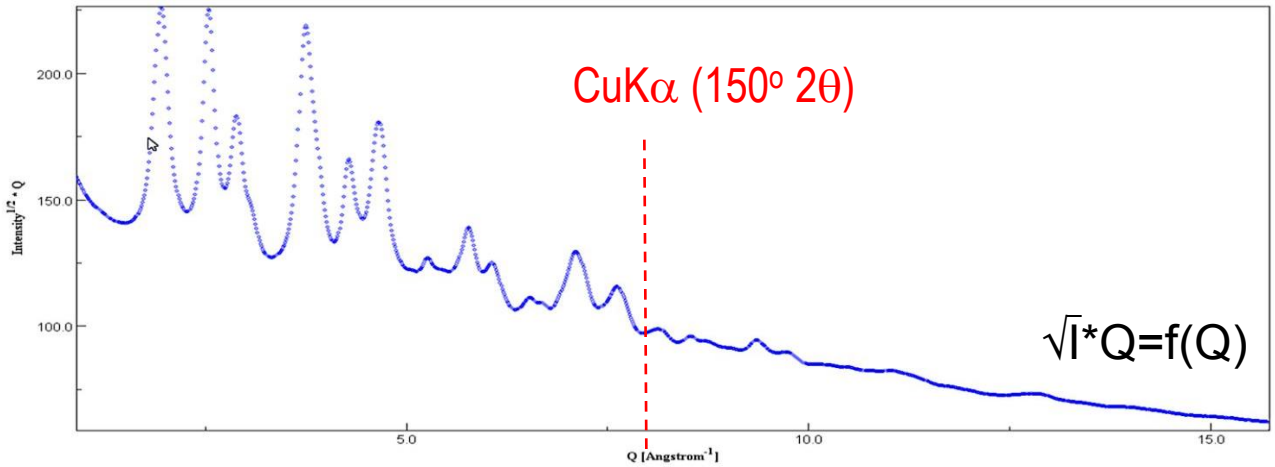
{111} pole figure from ODF refinement

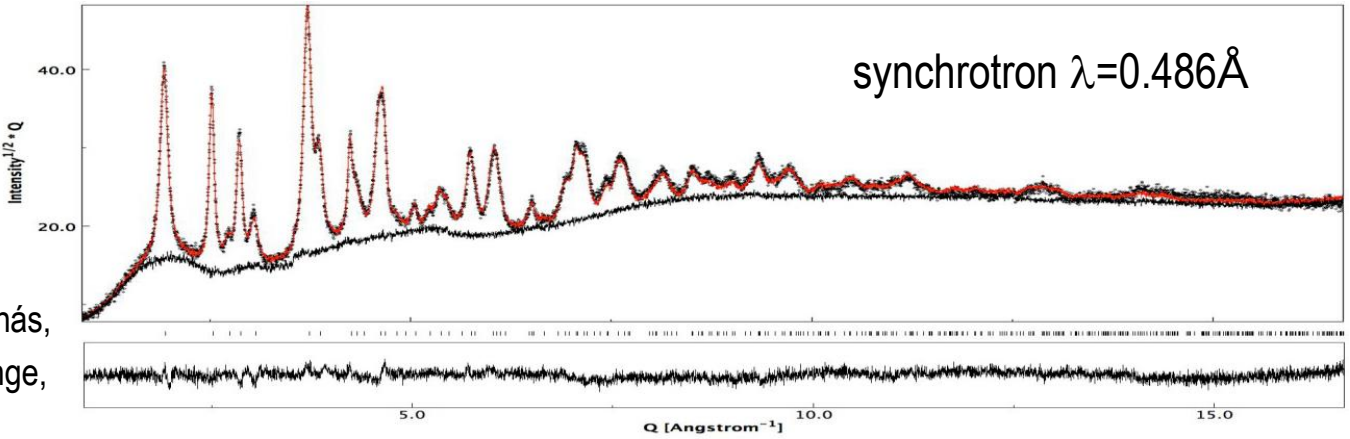
For application on textured thin film see also M. Gemmi et al., J. Appl. Cryst. 44 (2011)

- microstructural features can be obtained in the pattern-matching mode
- not convincing using structure factors from kinematical approximation …

… much better when using the 2-beam or Blackman correction

NP TiO_2 rutile





Pair Distribution Function analyses on EPD

▼

A.M.M. Abeykoon, C.D. Malliakas, P. Juhás, E.S. Božin, M.G. Kanatzidis, S.J.L. Billinge, **Z. Kristallogr. 227 (2012) 248**

- ► microstructural features can be obtained in the pattern-matching mode
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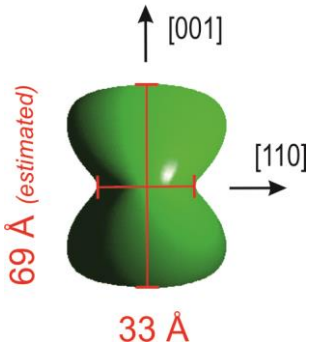
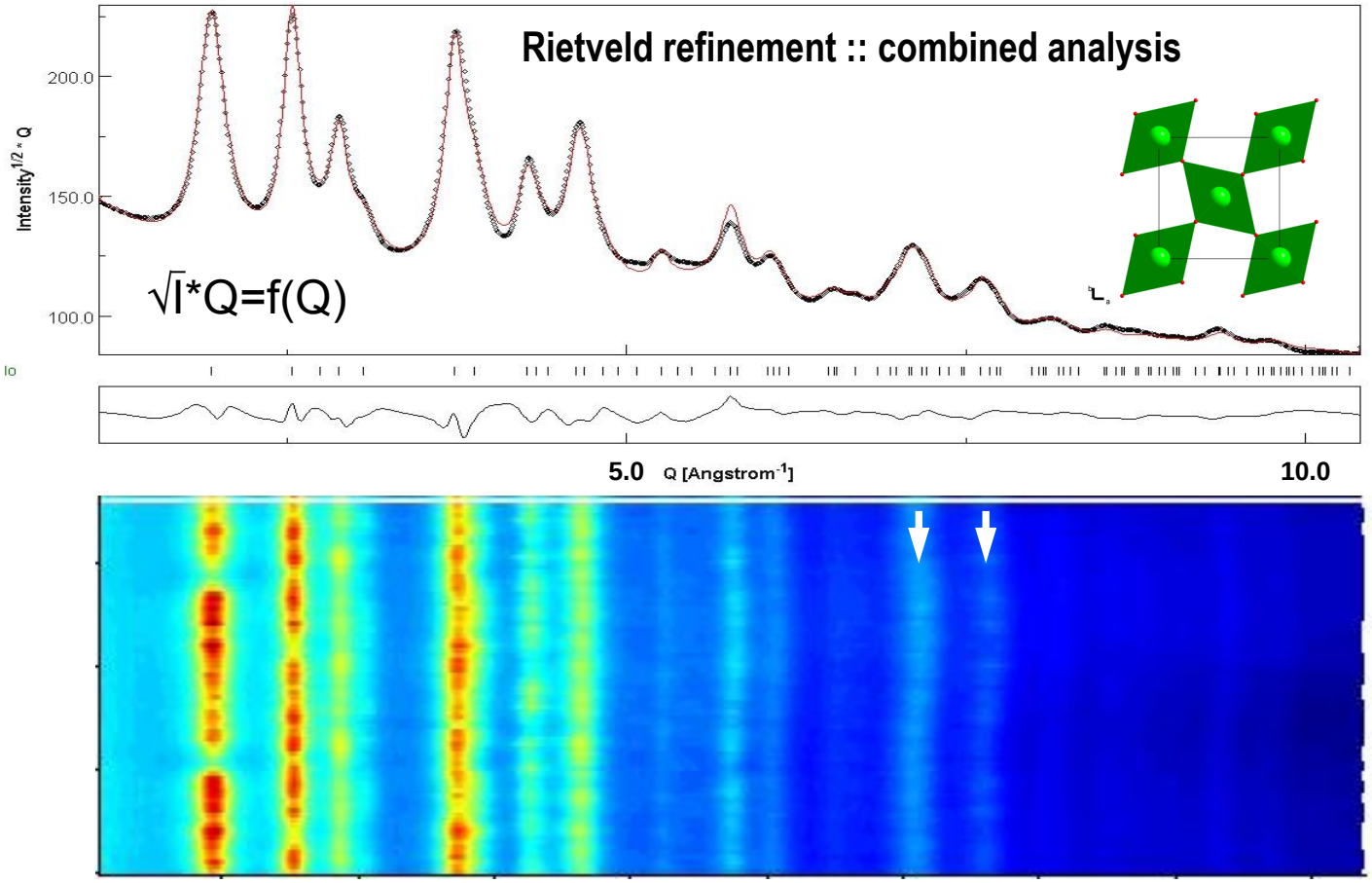
NP TiO_2 rutile





Structure and Phase Analyses of Nanoparticles using Combined Analysis of TEM scattering patterns

- automatic phase search procedure (COD database, multi-phases)

Diffraction pattern and sample composition

Upload diffraction pattern: Choose File no file selected
Structures database: COD_all.sqlite
Atomic elements in the sample: O Al Ca F Zn
Threshold phase density: 0.95 Maximum number of phases: 7
Crystallisation: normal

Experiment details

Radiation:
X-ray tube: Cu
Other : x-ray Wavelength (Å): 1.540598

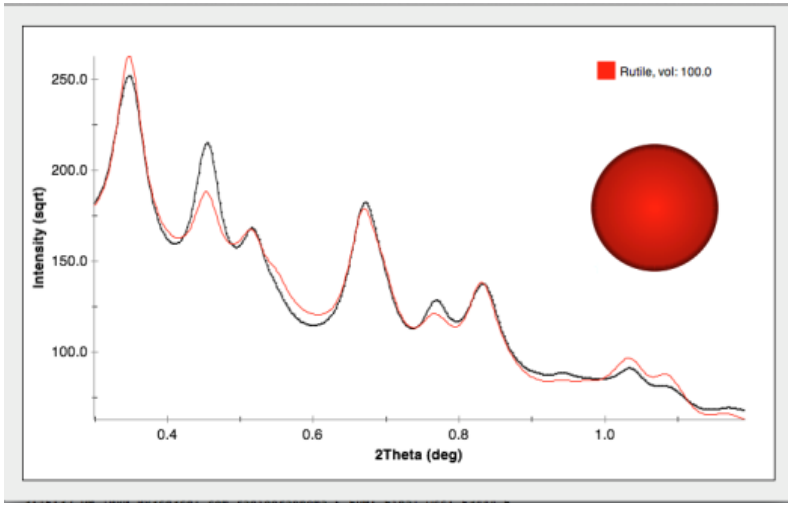
Instrument geometry:
Bragg-Brentano (theta-2theta)
Bragg-Brentano (2theta only), omega: 10
Debye-Scherrer
Transmission

Instrument broadening function: High

Search and quantify

whole-pattern S/M procedure

(kinematical approximation)



http://nanoair.dii.unitn.it:8080/sfpm and **http://cod.iutcaen.unicaen.fr**

Structure and Phase Analyses of Nanoparticles using Combined Analysis of TEM scattering patterns

- automatic phase search procedure (COD database, multi-phases)
- average lattice cell parameters and crystallite size (anisotropic shapes)
- accurate texture analysis (general cases, ODF, …)

  … can be obtained in the Pattern matching mode
- structure refinements are possible within MAUD (kinematic or Blackman)

  … implementation of PDF approach soon

Thank you for your attention

V. Pralong and V. Caignaert (TiO_2 nanoparticules) @ CRISMAT – Caen

L. Sicard and S. Ammar (Mn_3O_4 nanoparticules) @ ITODYS – Paris 7

S. Gascoin (XRD measurements) @ CRISMAT – Caen

ANR FURNACE, BAMBI