Combined Analysis: Probing the crystallite sizes by XRD down to nm, together with structure, texture, phases, residual stresses, complemented by XRF, GiXRF and electron diffraction

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X-ray scattering "sees"

Texture
$f(g)_{\Phi,L}$

Structure
$|F_{\mathbf{h}}|^2_{\Phi,L}$

Raman, XRF

Phase ID

Real samples
Layered samples
thicknesses
roughnesses
$\rho(z)$…

Residual Stress
$<C_{ijkl}(g)>_{\Phi,L}$

Phase
$S_{\Phi,L}$

defects (0D .. nD)
broadening
asymmetry

Nanosizes: Line Broadening

- Instrumental broadening

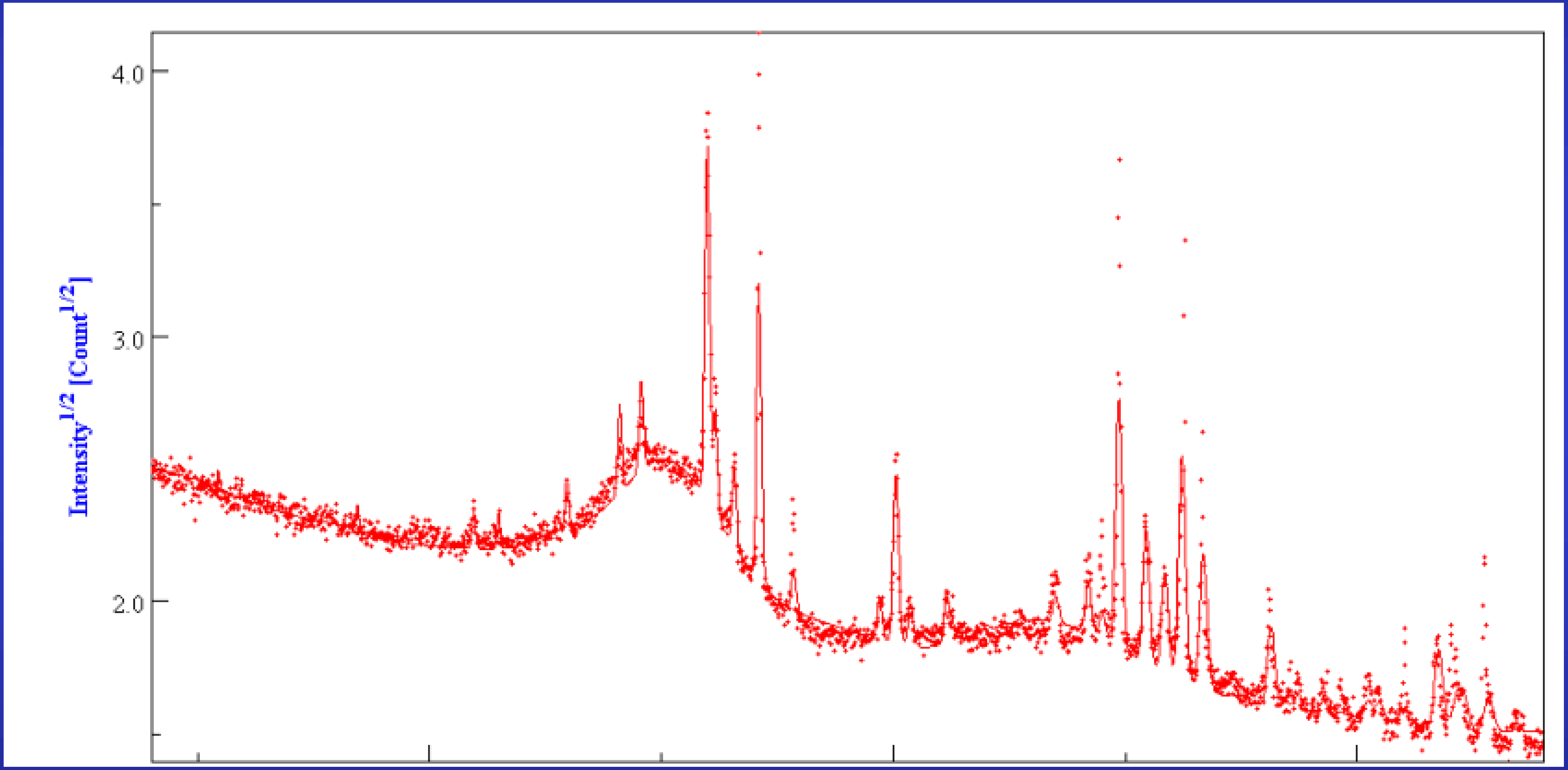
- Finite size of the crystals
  acts like a Fourier truncation: size broadening

- Imperfection of the periodicity
  due to d_h variations inside crystals: microstrain effect

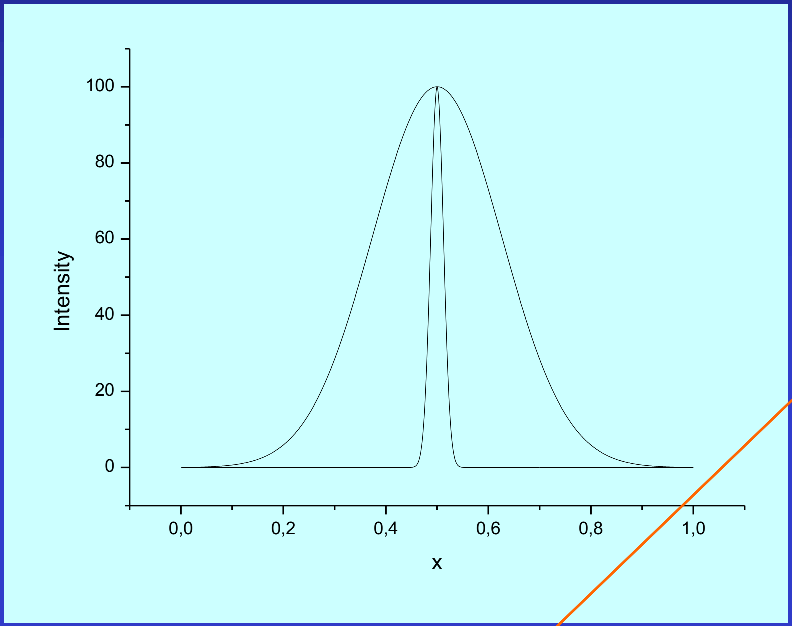
- Generally: 0D, 1D, 2D, 3D defects

- All quantities are average values over the probed volume
  electrons, x-rays, neutrons: complementary
  distributions: mean values depend on distributions' shapes

Irradiated Fluorapatites



Instrumental broadening



$$g(x) = g_{\lambda}(x) \otimes g_{g}(x)$$

Energy dispersion

Geometrical aberrations

$$h(x) = f(x) \otimes g(x) + b(x) = b(x) + \int_{-\infty}^{+\infty} f(y) g(x-y) dy$$

Measured profile

Sample contribution

Background

Rietveld: extended to lots of spectra

$$y_c(\mathbf{y}_S,\theta,\eta) = y_b(\mathbf{y}_S,\theta,\eta) + I_0 \sum_{i=1}^{N_L} \sum_{\Phi=1}^{N_\Phi} \frac{\nu_{i\Phi}}{V_{c\Phi}^2} \sum_h Lp(\theta) j_{\Phi h} |F_{\Phi h}|^2 \Omega_{\Phi h}(\mathbf{y}_S,\theta,\eta) P_{\Phi h}(\mathbf{y}_S,\theta,\eta) A_{i\Phi}(\mathbf{y}_S,\theta,\eta)$$

Texture:

$$P_h(\mathbf{y}_S) = \int_{\tilde{\varphi}} f(g,\tilde{\varphi})\,d\tilde{\varphi}$$

E-WIMV, components …

Strain-Stress:

$$\langle S \rangle_{geo}^{-1} = \left[\prod_{m=1}^{N} S_m^{\nu_m}\right]^{-1} = \prod_{m=1}^{N} S_m^{-\nu_m} = \prod_{m=1}^{N} \left(S_m^{-1}\right)^{\nu_m} = \left\langle S^{-1} \right\rangle_{geo} = \langle C \rangle_{geo}$$

Geometric mean, Voigt, Reuss, Hill …

Layering:

$$C_\chi^{top\,film} = g_1\left(1-\exp\left(-\mu T g_2 / \cos\chi\right)\right) / \left(1-\exp\left(-2\mu T / \sin\omega\cos\chi\right)\right)$$

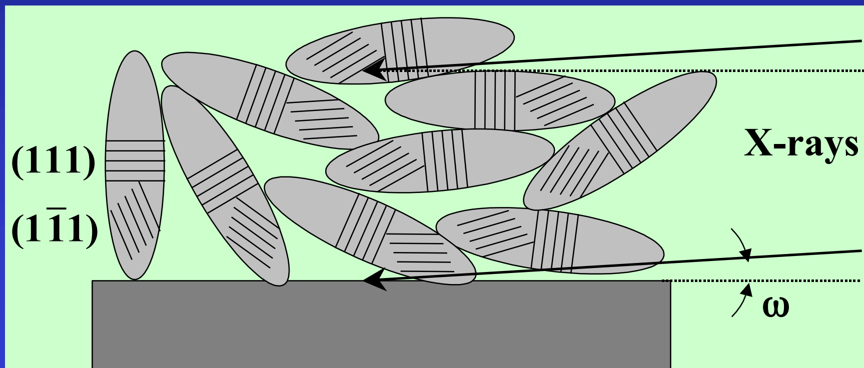
XRR:

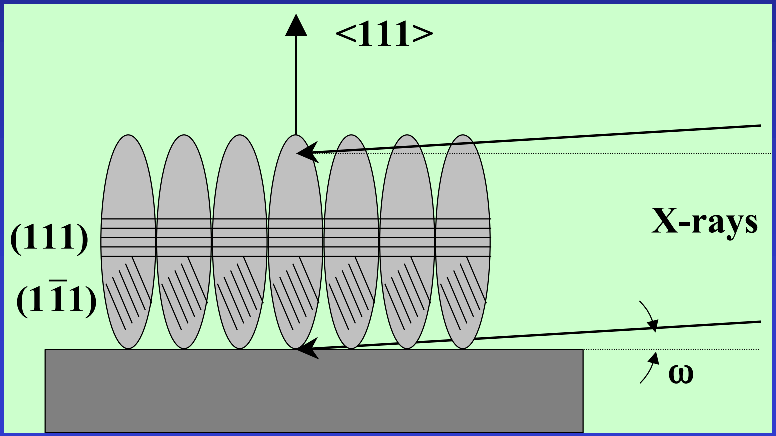
Parrat, DWBA, EDP …

XRF, PDF, Raman …

Popa Line Broadening model

Crystallite sizes, shapes, μstrains, distributions





- Texture helps the "real" mean shape determination

$$\left\langle R_{\vec{h}} \right\rangle = \sum_{\ell=0}^{L} \sum_{m=0}^{\ell} R_\ell^m K_\ell^m(\chi,\varphi)$$

Symetrised spherical harmonics

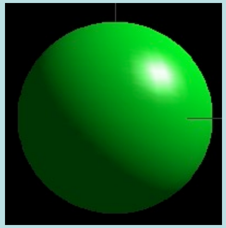
$$K_\ell^m(\chi,\varphi) = P_\ell^m(\cos\chi)\cos(m\varphi) + P_\ell^m(\cos\chi)\sin(m\varphi)$$

$$<R_{\mathbf{h}}> = R_0 + R_1P_2^0(x) + R_2P_2^1(x)\cos\varphi + R_3P_2^1(x)\sin\varphi + R_4P_2^2(x)\cos2\varphi + R_5P_2^2(x)\sin2\varphi + $$

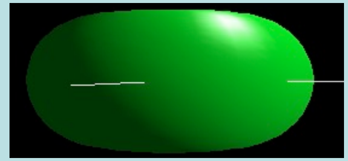
...

$$<\varepsilon_{\mathbf{h}}^2>E_{\mathbf{h}}^4 = E_1h^4 + E_2k^4 + E_3\ell^4 + 2E_4h^2k^2 + 2E_5\ell^2k^2 + 2E_6h^2\ell^2 + 4E_7h^3k + 4E_8h^3\ell + 4E_9k^3h + 4E_{10}k^3\ell + 4E_{11}\ell^3h + 4E_{12}\ell^3k + 4E_{13}h^2k\ell + 4E_{14}k^2h\ell + 4E_{15}\ell^2kh$$

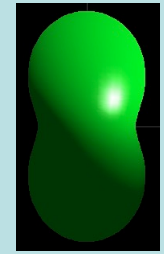
$\bar{1}$



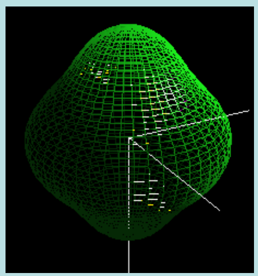
R_0



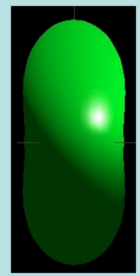
R_0, $R_1 < 0$



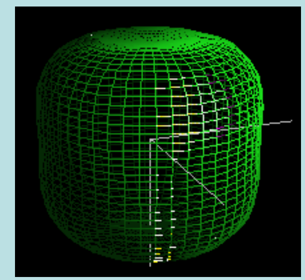
R_0, $R_1 > 0$



R_0, $R_6 > 0$

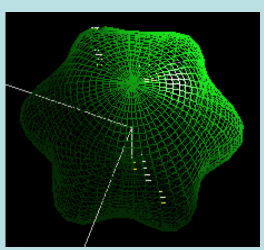


R_0,
R_2 and $R_6 > 0$

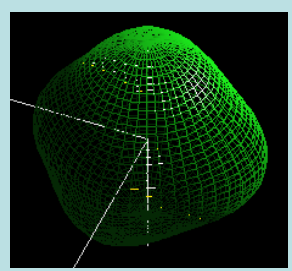


R_0, $R_6 < 0$

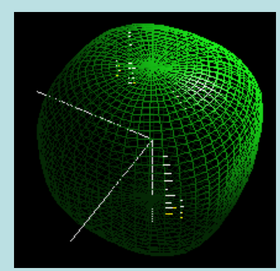
6/m



R_0, $R_4 > 0$



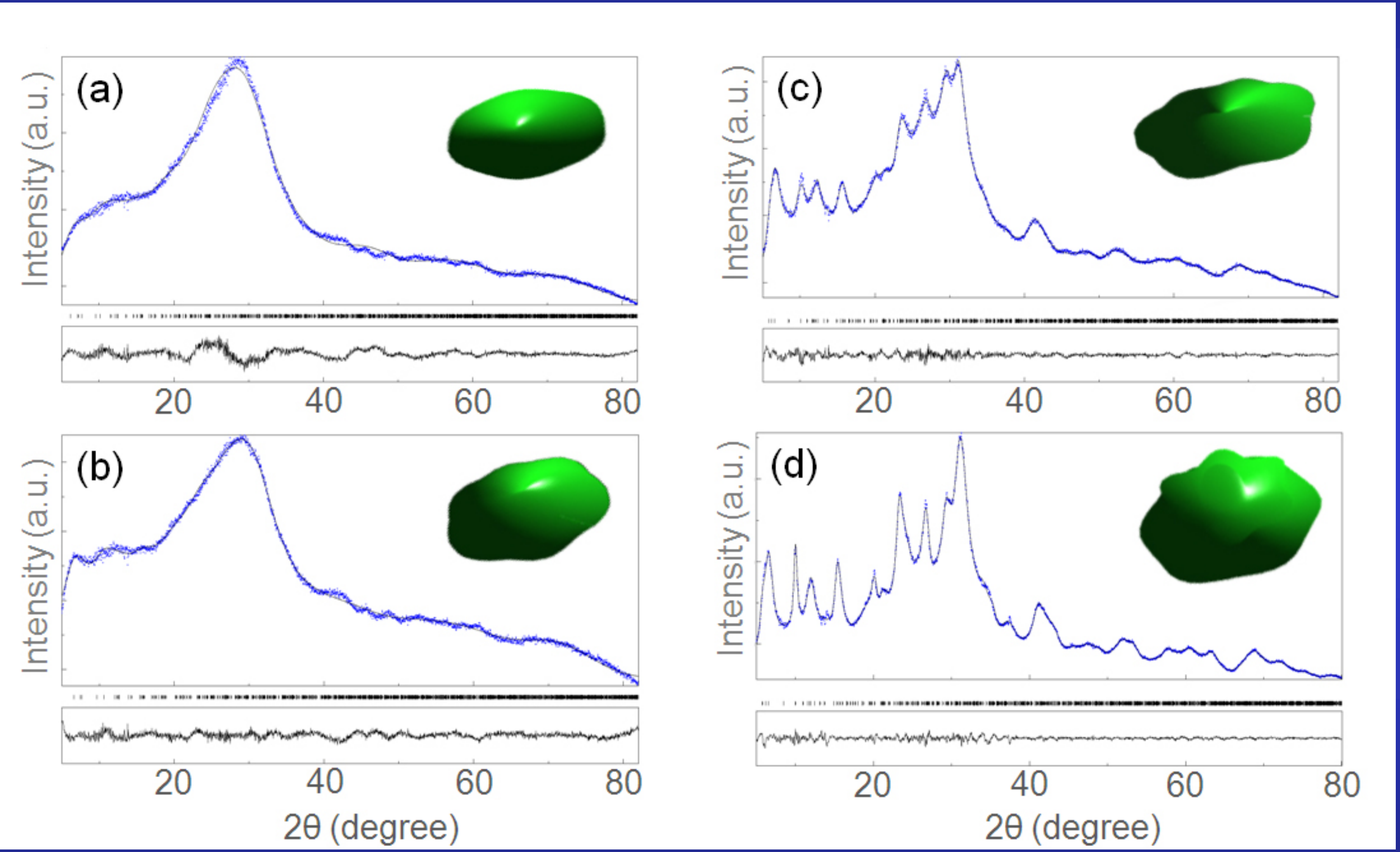
R_0, $R_1 > 0$



R_0, $R_1 < 0$

m3m

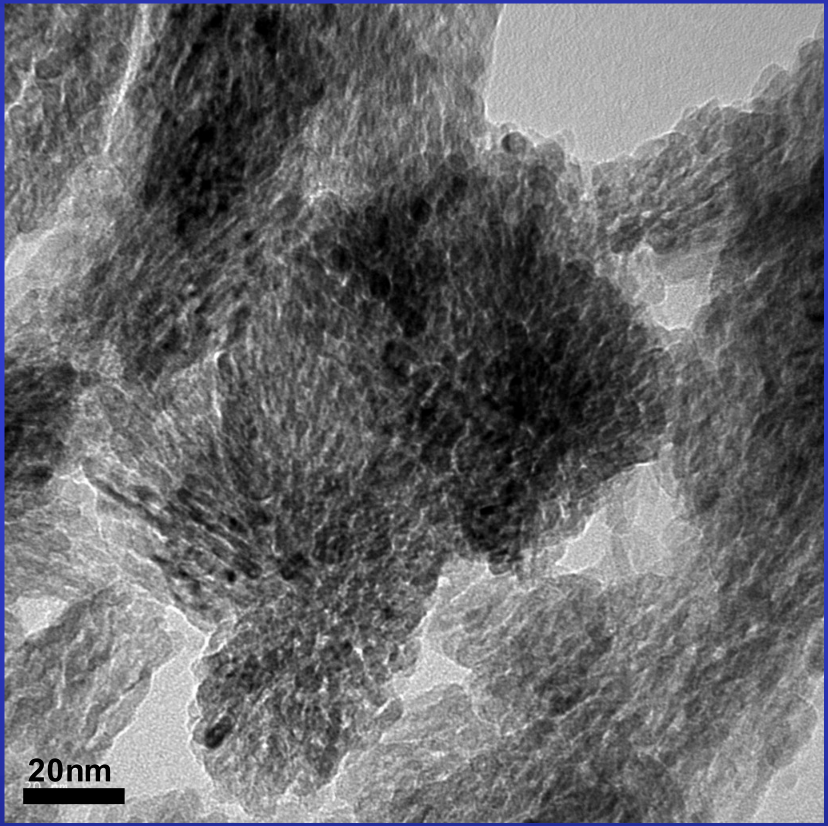
EMT nanocrystalline zeolite

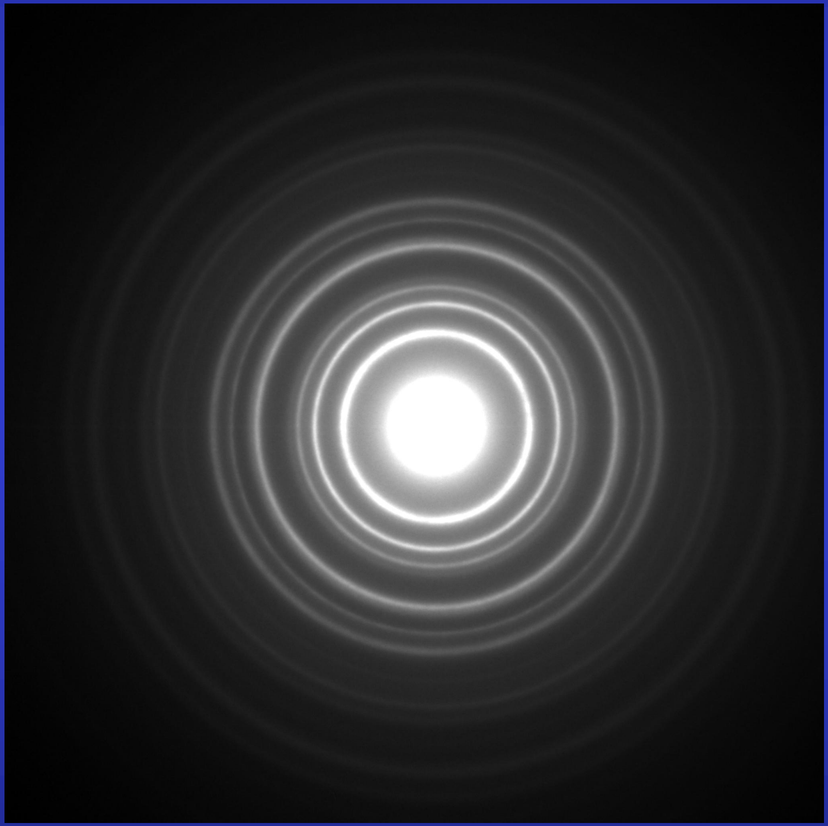


Ng, Chateigner, Valtchev, Mintova: *Science* **335** (2012) 70

Microstructure of nanocrystalline materials: TiO2 rutile

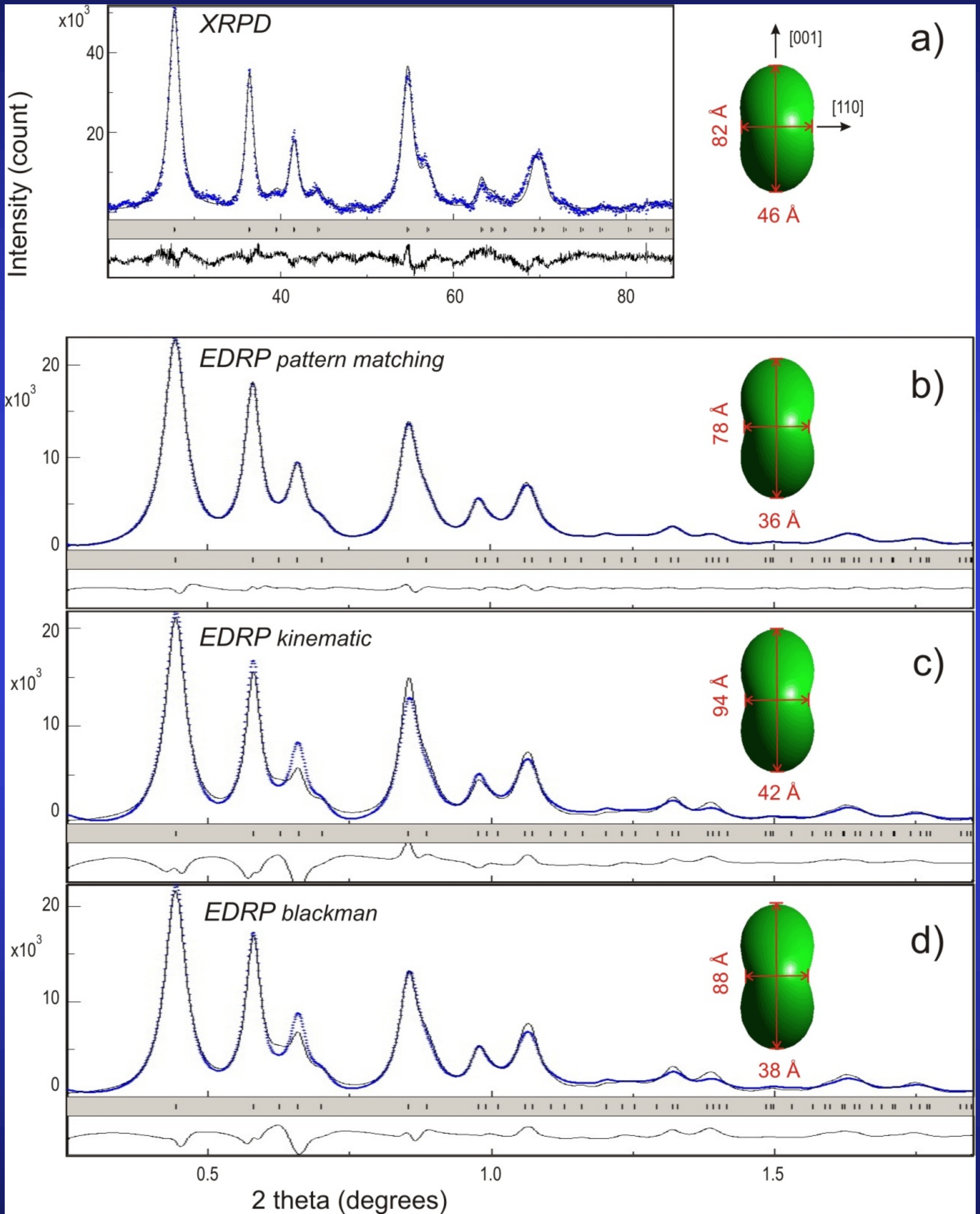
- *quantitative analysis of electron diffraction ring pattern ?*





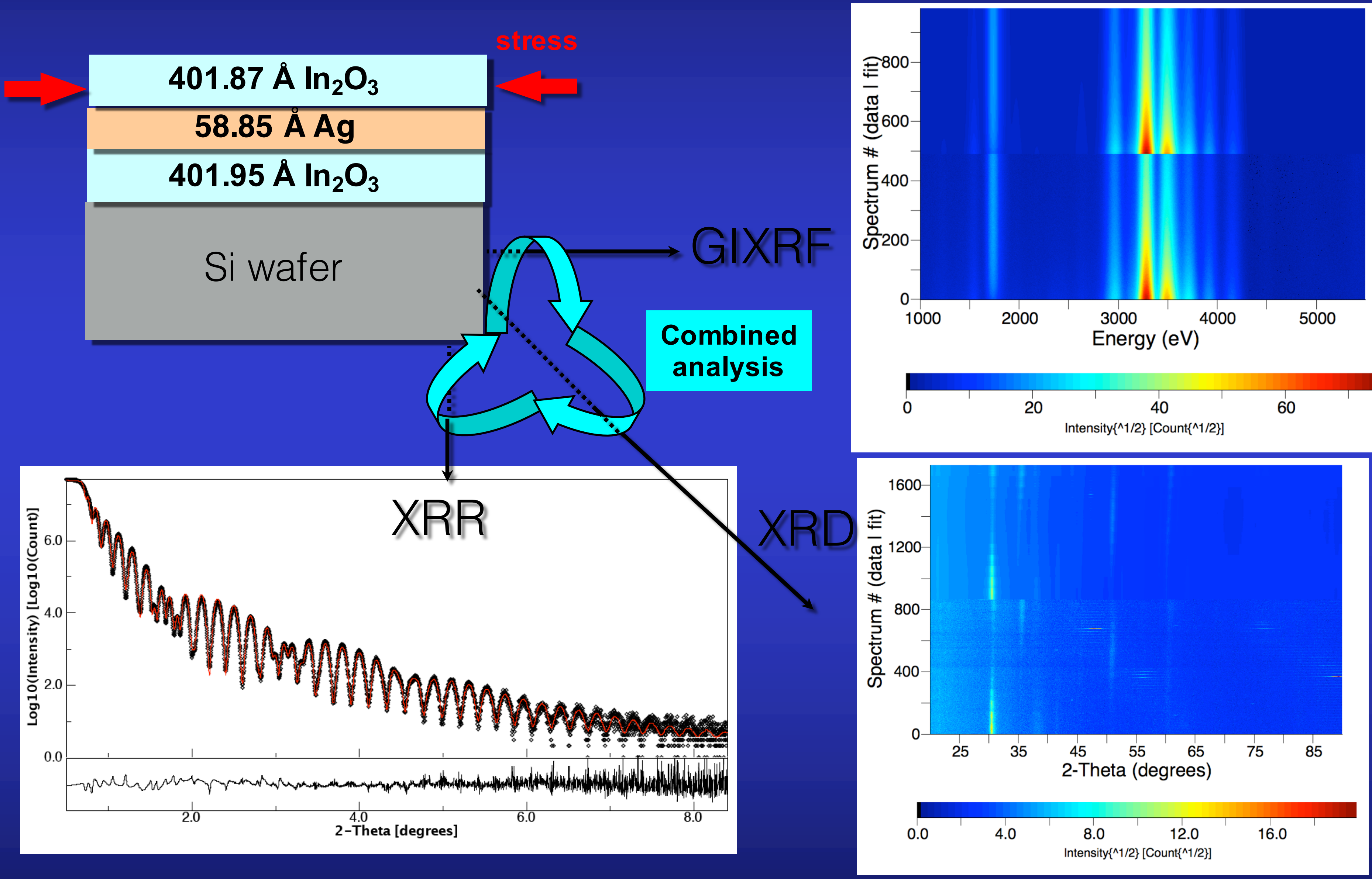
FEI Tecnai G2 (300kV) with an Ultrascan 1000 (2048x2048 14µm pixels)

Popa $R_0 + R_1$

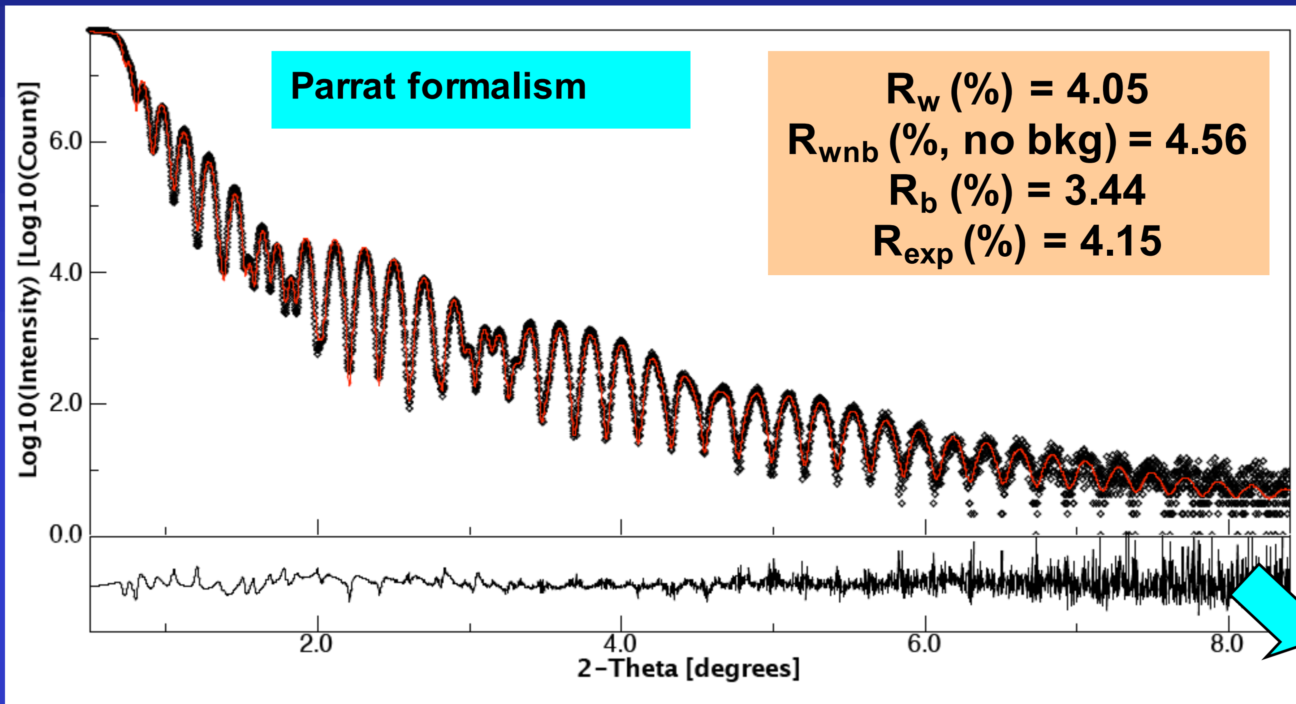


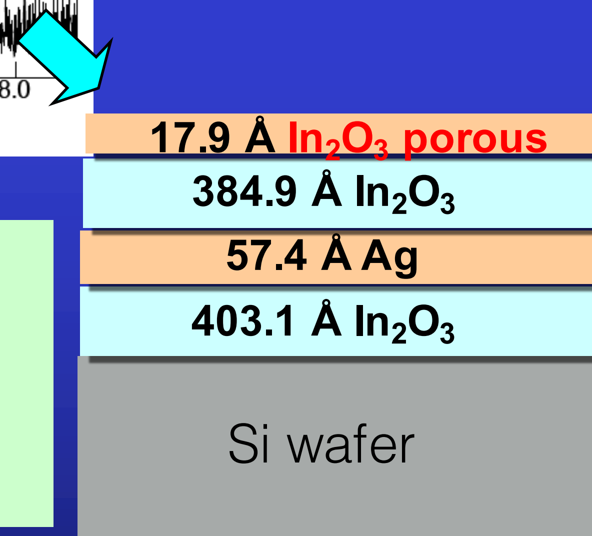
XRPD
a)
[001]
[110]
82 Å
46 Å
Intensity (count)
x10³
40
20
60
80
EDRP pattern matching
b)
78 Å
36 Å
EDRP kinematic
c)
94 Å
42 Å
EDRP blackman
d)
88 Å
38 Å
0.5
1.0
1.5
2 theta (degrees)

Combined XRR, XRD & GiXRF Analysis



XRR





Highly porous In_2O_3 layer

Top layer: q_c = 0.0294 $Å^{-1}$; roughness r =0.38nm

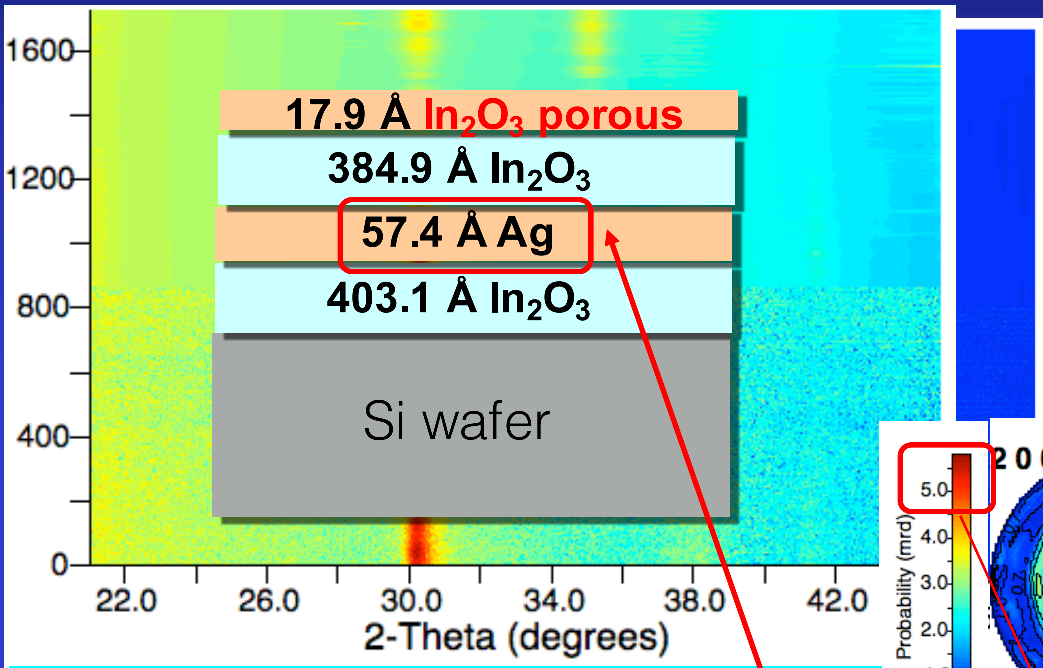
Top In_2O_3: q_c = 0.0504 $Å^{-1}$; r =2.06 nm

Ag : q_c = 0.0576 $Å^{-1}$; r =0.26 nm

Bottom In_2O_3: q_c = 0.04889 $Å^{-1}$; r =6.74 nm

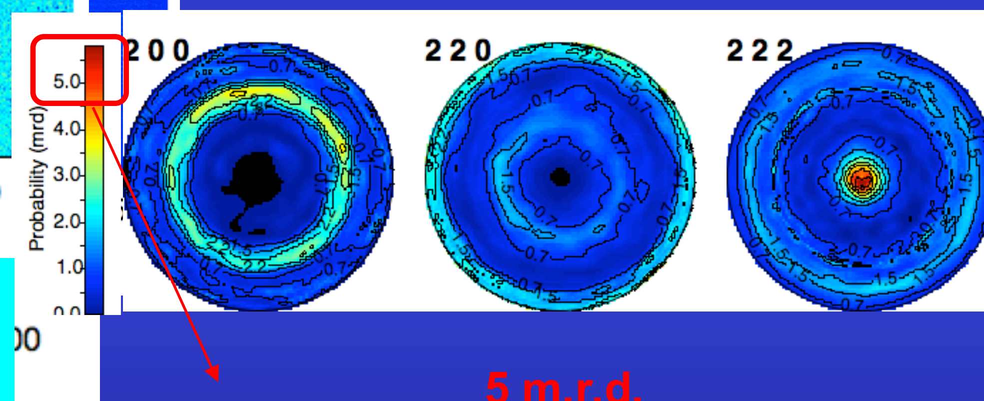
Si wafer: q_c = 0.0313 $Å^{-1}$; r = 0.73 nm

XRD



R_w (%) = 23.97
R_{wnb} (%, no bkg) = 58.31
R_b (%) = 18.71
R_{exp} (%) = 22.04

In_2O_3

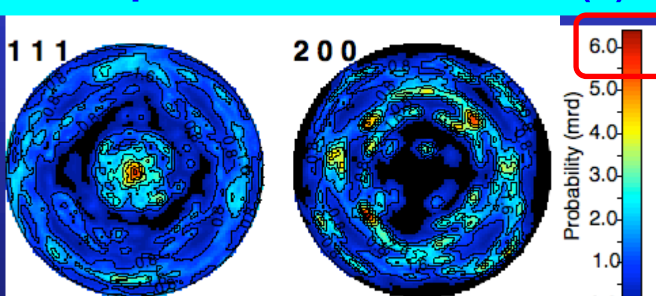


5 m.r.d.

Refined Ag phase parameters

- Isotropic crystallite size = 56.4 (1.3) Å
- Cell parameter: a = 4.0943(7) Å

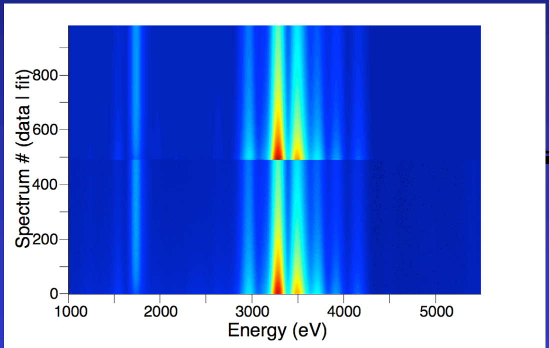
Ag:

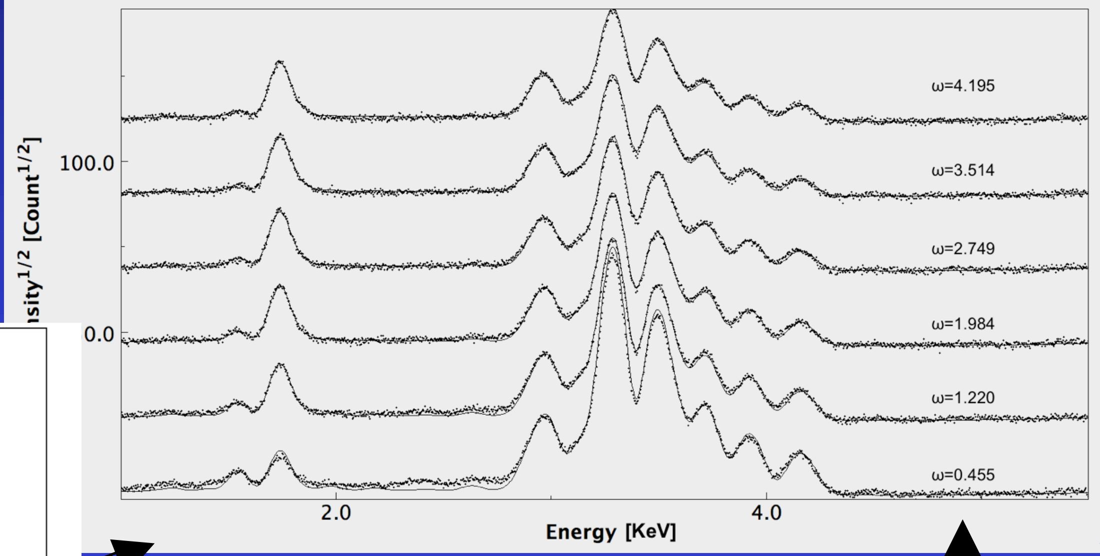


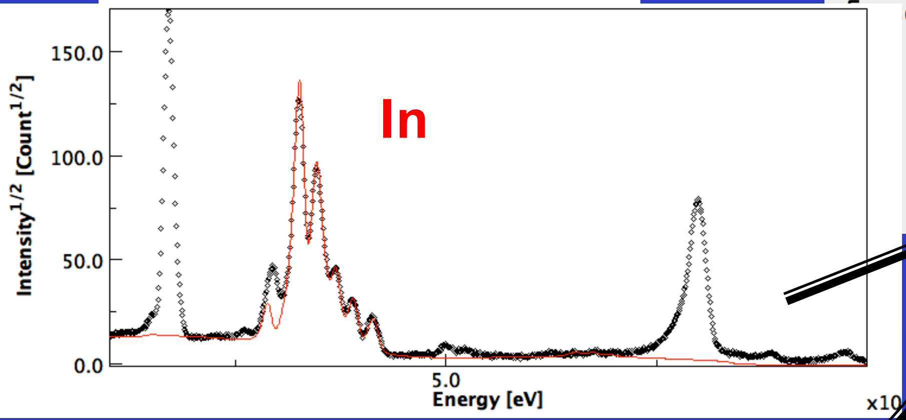
Refined In_2O_3 phase parameters

- σ_{XX} = - 1 GPa (in-plane compressive stress)
- Isotropic crystallite size = 153.2(5) Å
- Cell parameter: a = 10.2104(5) Å

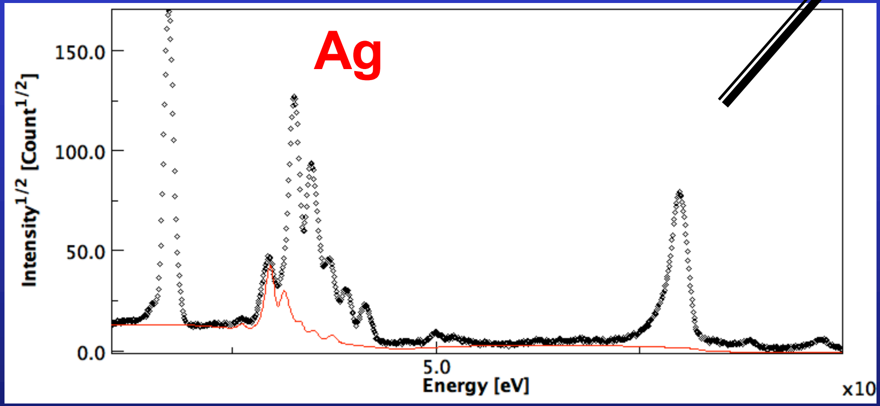
GiXRF

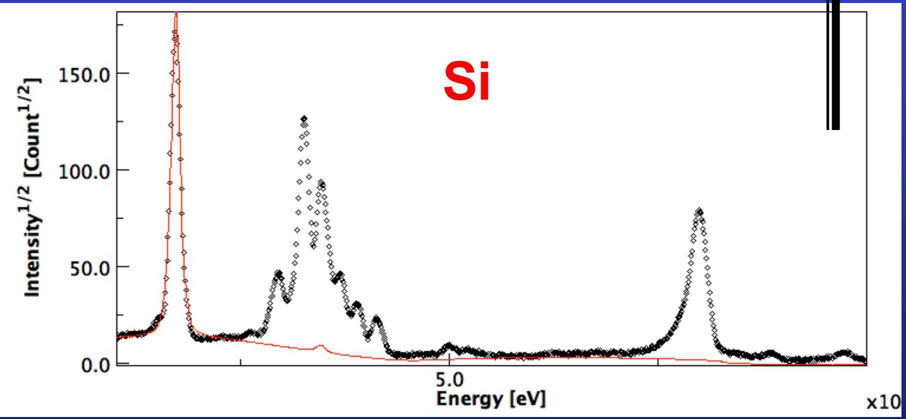




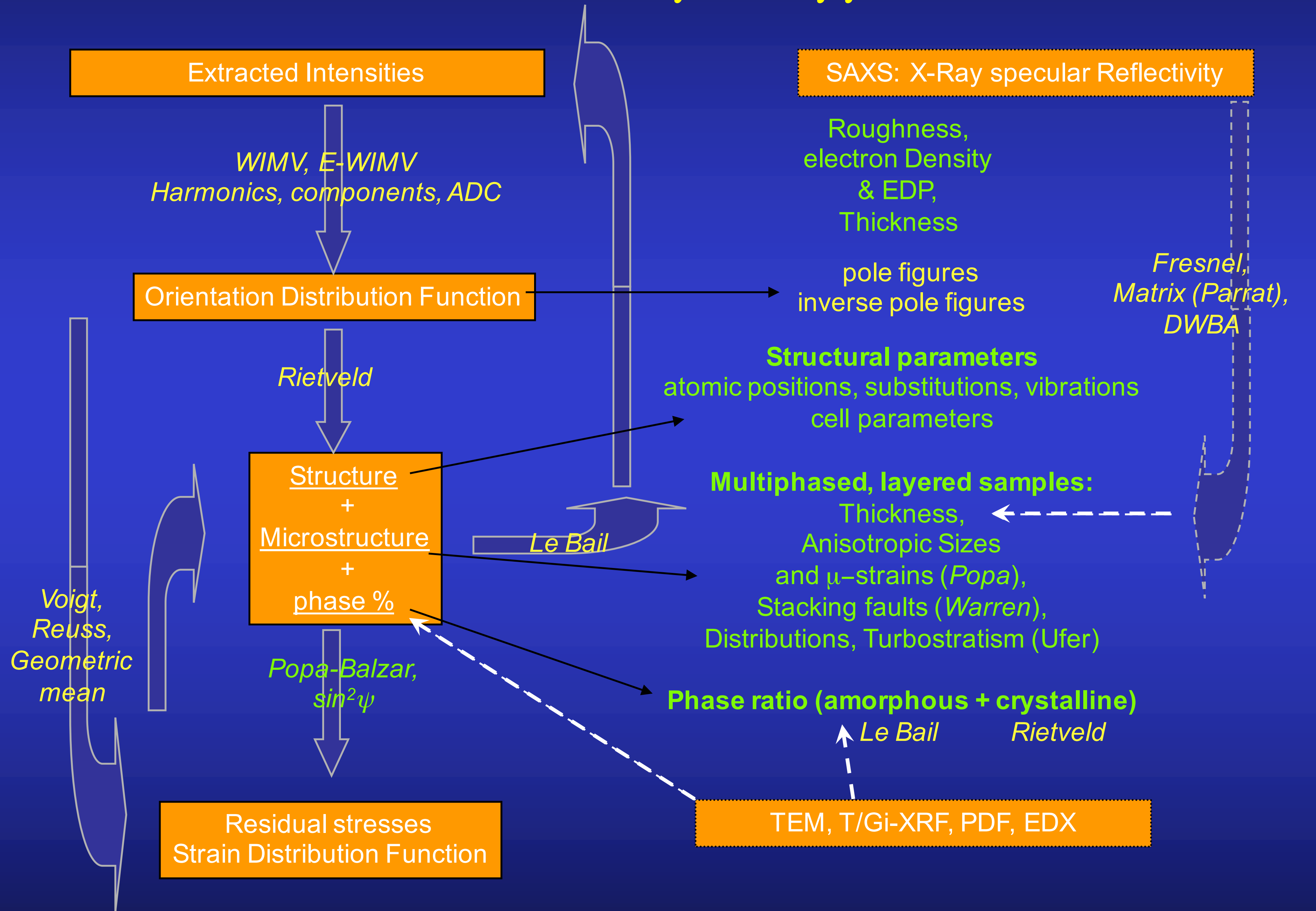


No presence of contaminant observed

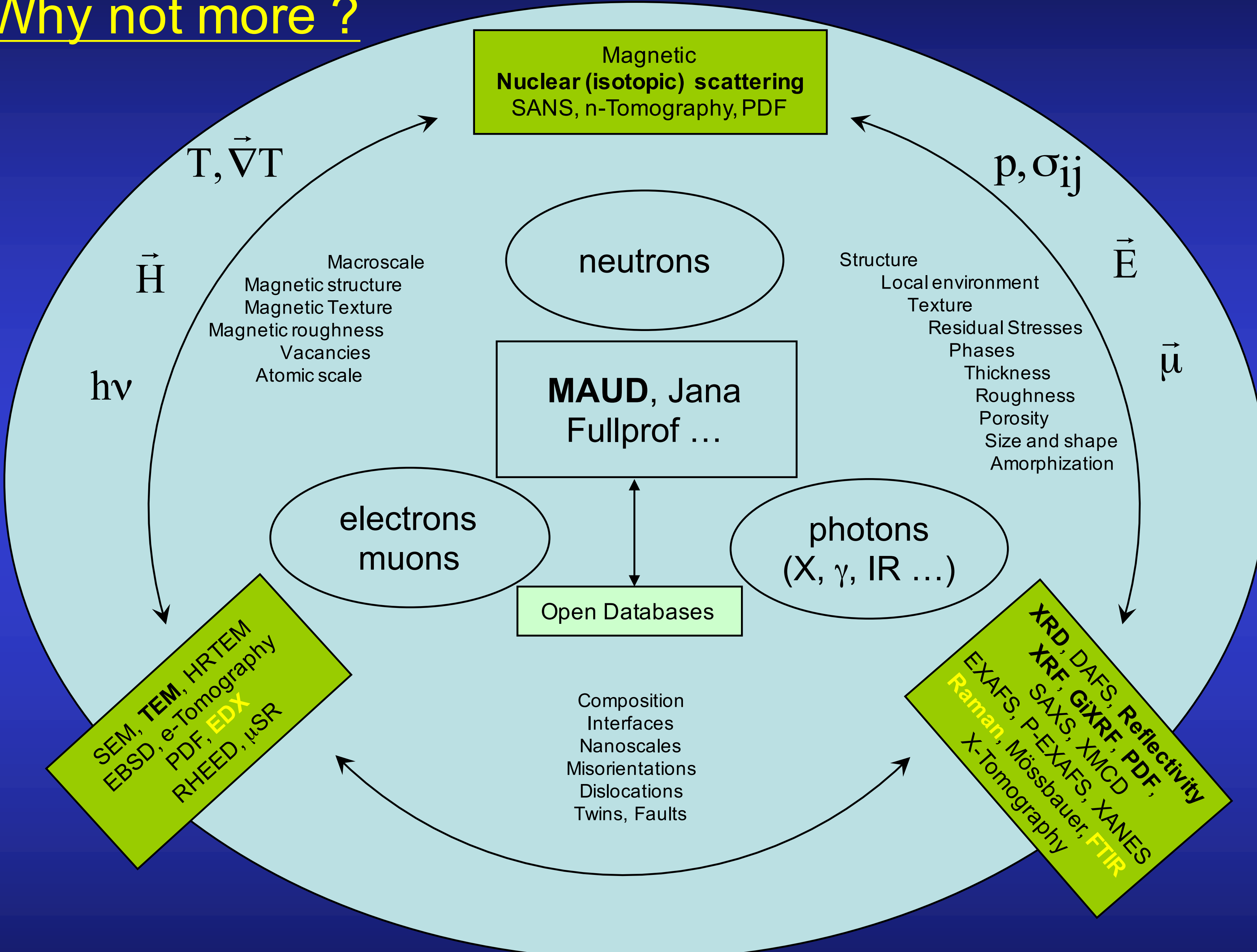




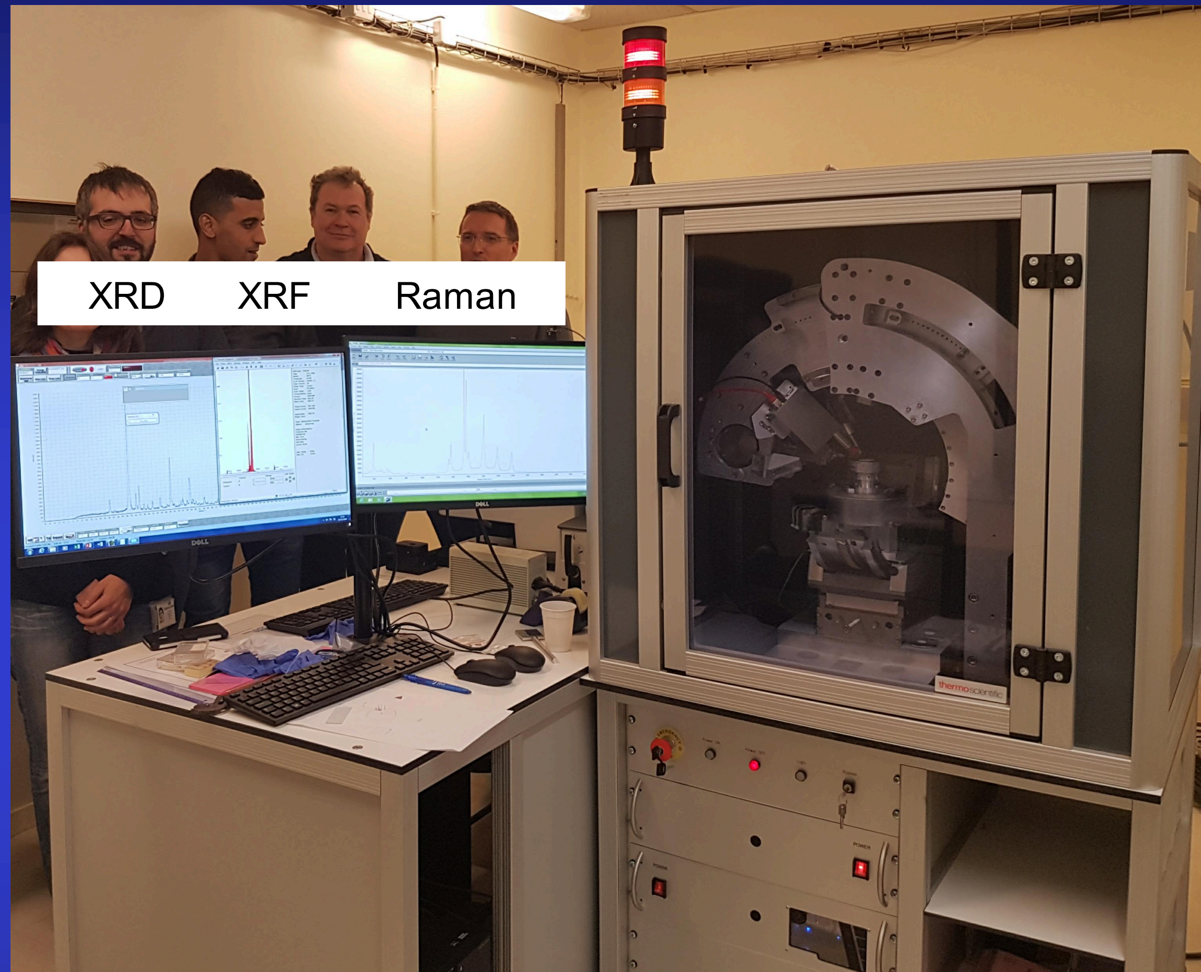
Combined Analysis approach



Why not more ?


Magnetic
Nuclear (isotopic) scattering
SANS, n-Tomography, PDF
$T, \vec{\nabla}T$
p, σ_{ij}
$\vec{H}$
$h\nu$
$\vec{E}$
$\vec{\mu}$
neutrons
Macroscale
Magnetic structure
Magnetic Texture
Magnetic roughness
Vacancies
Atomic scale
Structure
Local environment
Texture
Residual Stresses
Phases
Thickness
Roughness
Porosity
Size and shape
Amorphization
MAUD, Jana
Fullprof …
electrons
muons
photons
(X, γ, IR …)
Open Databases
SEM, TEM, HRTEM
EBSD, e-Tomography
PDF, EDX
RHEED, μSR
XRD, DAFS, Reflectivity
XRF, GiXRF, PDF,
SAXS, XMCD
EXAFS, P-EXAFS, XANES
Raman, Mössbauer, FTIR
X-Tomography
Composition
Interfaces
Nanoscales
Misorientations
Dislocations
Twins, Faults

SOLSA



Thanks !

Combined Analysis Workshop in Caen:

4th - 8th July 2018 !

www.ecole.ensicaen.fr/~chateign/formation/