Une approche globale pour caractériser les architectures minces: l'Analyse Combinée par diffraction-diffusion

D. Chateigner, L. Lutterotti, M. Morales, P. Boullay

IUT-UCBN, CRISMAT-ENSICAEN, Univ. Trento, CIMAP-ENSICAEN

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Problematic

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

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

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

Residual Stress
$\langle C_{ijkl}(g) \rangle_{\Phi,L}$

Phase
$S_{\Phi,L}$

defects (0D .. nD)
broadening
asymmetry

Structure determination on real (textured) samples
Problem 1

Structure and QTA: correlations ?

f(g) and $|F_{\mathbf{h}}|^2$ are different !

f(g):

-Angularly constrained: $[h_1k_1l_1]^*$ and $[h_2k_2l_2]^*$ make a given angle: more determined if F^2 high

- lot of data (spectra) needed

$|F_{\mathbf{h}}|^2$:

-Position, f_i, and Debye-Waller constrained

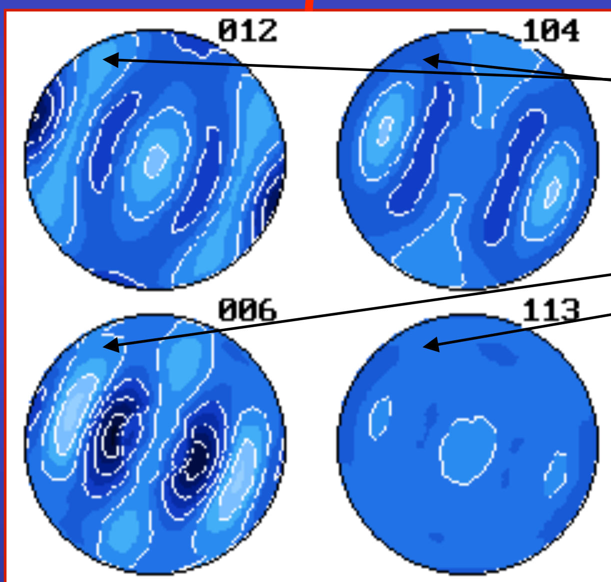
- work on the sum of all diagrams on average

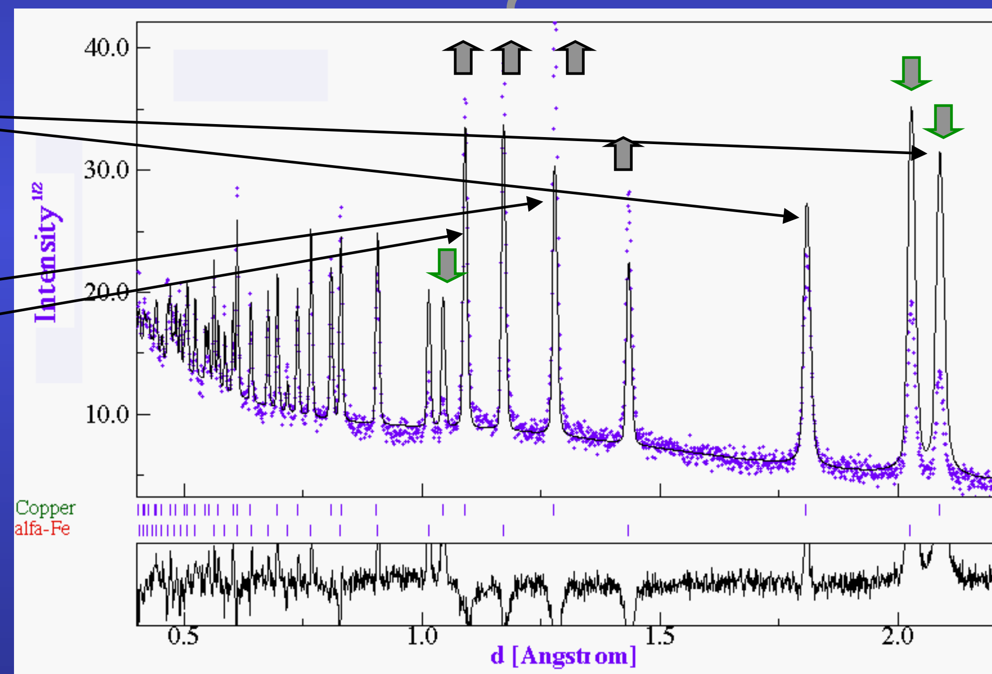
Texture from Spectra

Orientation Distribution Function (ODF)

From pole figures

From spectra





Le Bail extraction + ODF: WMV, E-WIMV, Generalized spherical harmonics, components, ADC, entropy maximisation …

Rietveld: extended to lots of spectra

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

Texture

$$P_k(\chi,\phi) = \int_\varphi f(g,\varphi)\, d\varphi$$

- Generalized Spherical Harmonics (Bunge):

$$P_k(\chi,\phi) = \sum_{l=0}^{\infty} \frac{1}{2l+1} \sum_{n=-l}^{l} k_l^n(\chi,\phi) \sum_{m=-l}^{l} C_l^{mn} k_n^{*m}(\Theta_k \phi_k)$$

$$f(g) = \sum_{l=0}^{\infty} \sum_{m,n=-l}^{l} C_l^{mn} T_l^{mn}(g)$$

- Components (Helming):

$$f(g) = F + \sum_c I^c f^c(g)$$

- WIMV (William, Imhof, Matthies, Vinel) iterative process:

$$f^{n+1}(g) = N_n \frac{f^n(g) f^0(g)}{\left(\prod_{\mathbf{h}=1}^{I} \prod_{m=1}^{M_h} P_{\mathbf{h}}^n(\mathbf{y}) \right)^{\frac{1}{IM_h}}}$$

$$f^0(g) = N_0 \left(\prod_{\mathbf{h}=1}^{I} \prod_{m=1}^{M_h} P_{\mathbf{h}}^{exp}(\mathbf{y}) \right)^{\frac{1}{IM_h}}$$

E-WIMV (Rietveld only):

$$f^{n+1}(g) = f^n(g) \prod_{m=1}^{M_h} \left(\frac{P_{\mathbf{h}}(\mathbf{y})}{P_{\mathbf{h}}^n(\mathbf{y})} \right)^{r_n \frac{w_h}{M_h}}$$

with $0 < r_n < 1$, relaxation parameter,
$M_{\mathbf{h}}$ number of division points of the integral around k,
$w_{\mathbf{h}}$ reflection weight

- Entropy maximisation (Schaeben):

$$f^{n+1}(g) = f^n(g) \prod_{m=1}^{M_h} \left(\frac{P_{\mathbf{h}}(\mathbf{y})}{P_{\mathbf{h}}^n(\mathbf{y})} \right)^{\frac{r_n}{M_h}}$$

- arbitrarily defined cells (ADC, Pawlik): Very similar to E-WIMV, with integrals along path tubes

Residual Stresses shift peaks with y

Problem 2

Stress and QTA: correlations ? f(g) and <C_{ijkl}>

f(g):

- Moves the $\sin^2\Psi$ law away from linear relationship
- Needs the integrated peak (full spectra)

strains:

- Measured with pole figures
- needs the mean peak position

Isotropic samples: triaxial, biaxial, uniaxial stress states

Textured samples: Reuss, Voigt, Hill, Bulk geometric mean approaches

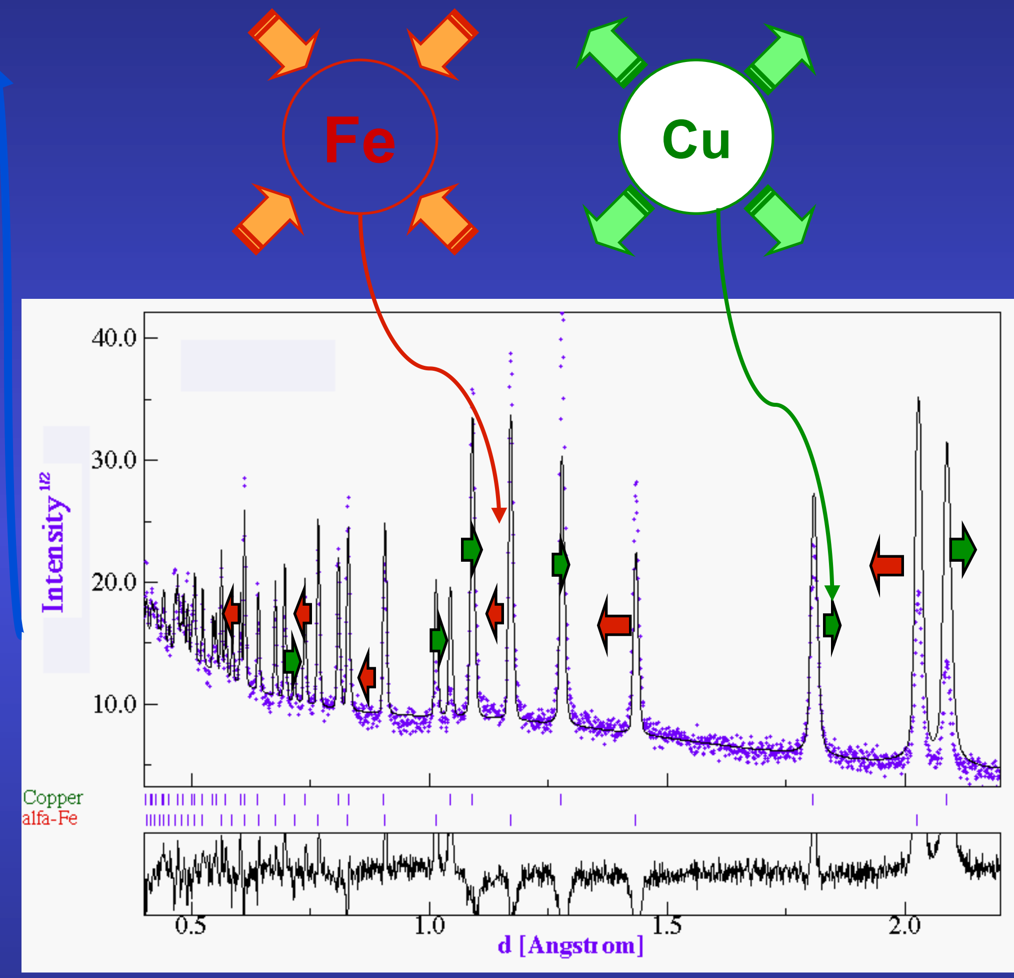
Residual Stresses and Rietveld

- Macro elastic strain tensor (I kind)
- Crystal anisotropic strains (II kind)

C

Macro and micro stresses

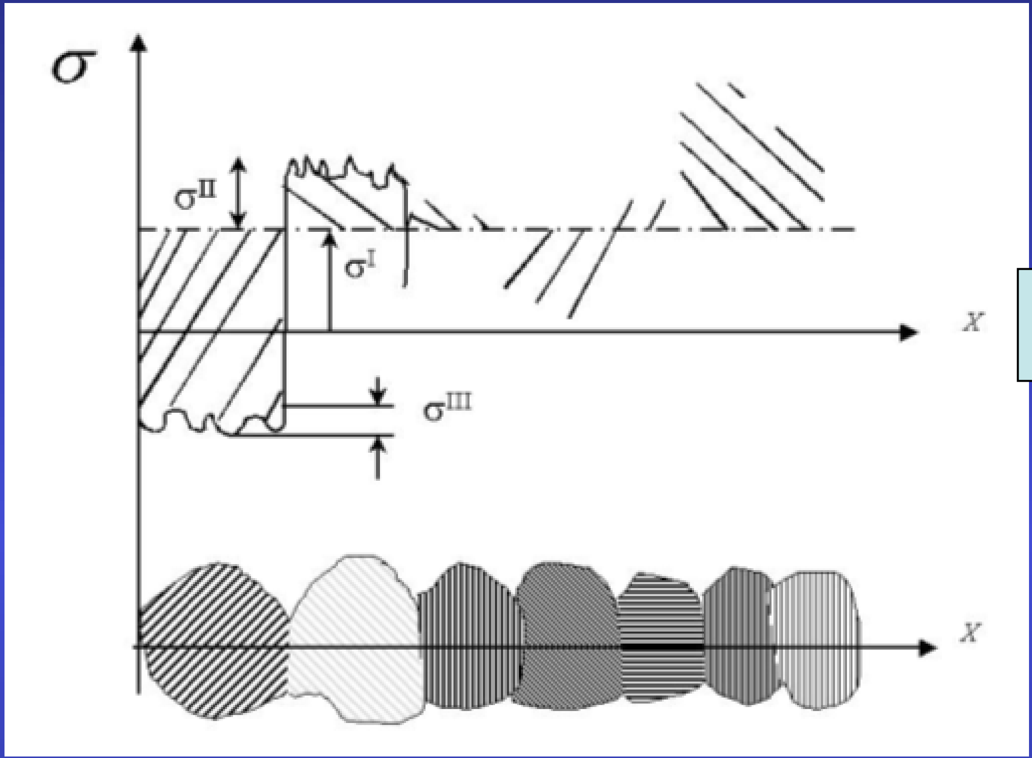
Applied macro stresses



Isotropic samples: triaxial, biaxial, uniaxial stress states

Textured samples: Reuss, Voigt, Hill, Bulk geometric mean approaches

Strain-Stress



$$\varepsilon(\mathbf{X}) = \varepsilon^{I} + \varepsilon^{II}(\mathbf{X}) + \varepsilon^{III}(\mathbf{X})$$

$$\langle S \rangle_{geo}^{-1} = \exp\left[-\sum_{m=1}^{N} \nu_m \ln S_m\right] = \exp\left[\sum_{m=1}^{N} \nu_m \ln S_m^{-1}\right] = \left\langle S^{-1} \right\rangle_{geo} = \langle C \rangle_{geo}$$

or

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

Layered systems

Problem 3

Layer, Rietveld and QTA: correlations: f(g), thicknesses and structure

f(g):

- Pole figures need corrections for abs-vol
- Rietveld also to correct intensities

layers:

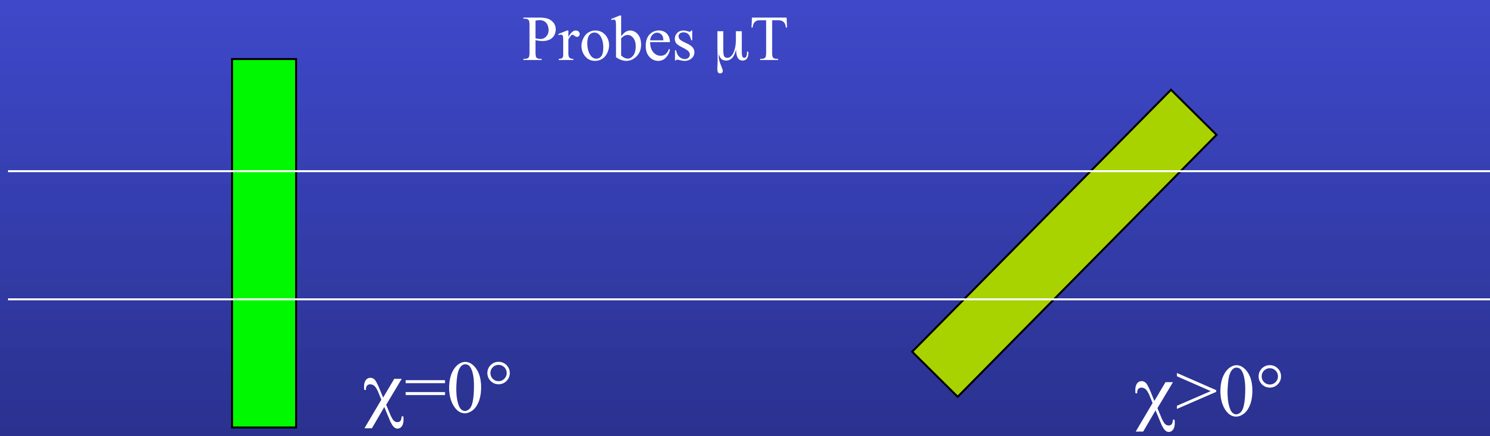
- unknown sample true absorption coefficient μ
- unknown effective thickness (porosity)

Layering

Asymmetric Bragg-Brentano

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

$$C_\chi^{\text{cov. layer}} = C_\chi^{\text{top film}}\left(\exp\left(-g_2\sum\mu_i' T_i'/\cos\chi\right)\right)/\left(\exp\left(-2\sum\mu_i' T_i'/\sin\omega\cos\chi\right)\right)$$



Phase and Texture

Problem 4

Phase and QTA: correlations: f(g), S_Φ

f(g):

- angular relationships
- plays on individual spectra
- essential to operate on textured sample

S_Φ:

- plays on overall scale factor (sum diagram)

Phase analysis

- Volume fraction

$$V_{\Phi} = \frac{S_{\Phi} V_{uc\Phi}^2}{\sum_{\Phi} \left(S_{\Phi} V_{uc\Phi}^2 \right)_{\Phi}}$$

- Weight fraction

$$m_{\Phi} = \frac{S_{\Phi} Z_{\Phi} M_{\Phi} V_{uc\Phi}^2}{\sum_{\Phi} \left(S_{\Phi} Z_{\Phi} M_{\Phi} V_{uc\Phi}^2 \right)_{\Phi}}$$

Z = number of formula units

M = mass of the formula unit

V = cell volume

Structure and Residual Stresses (shift peaks with **y**)
Problem 5

Stress and cell parameters: correlations: peak positions and C_{ijkl}

Cell parameters:
- Measured at high angles
- Bragg law evolution

strains:
- Measured precisely at high angles
- stiffness-based variation, also with Ψ

Shapes, microstrains, defaults, distributions
Problem 6

Shapes …. and stress-texture-structure: correlations ?

Shapes ….:
- line broadening problem
- average positions modified
- if anisotropic: modification changes with **y**

Stress-texture-structure:
- need "true" peak positions and intensities
- need deconvoluted signals

Why not benefit of texture in Structure determination ?

Perfect powders:
- overlaps (intra- and inter-
- no angular constrain
- anisotropy difficult to res

Single pattern

Single crystals:
- reduced overlaps
- max angular constrains
- Perfect texture: max anisotropy

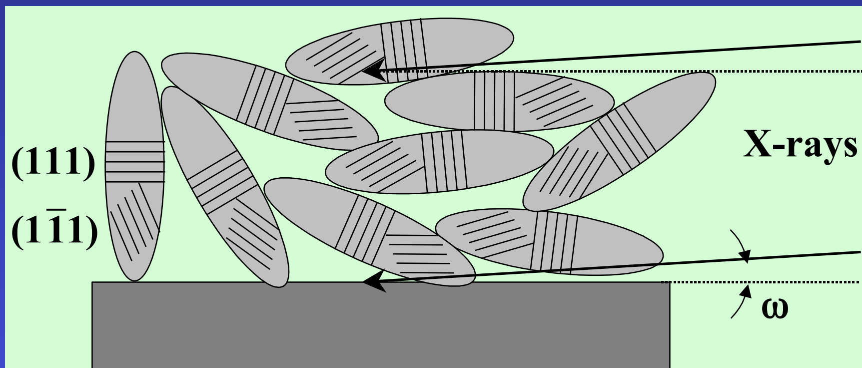
Many individual diffracted peaks

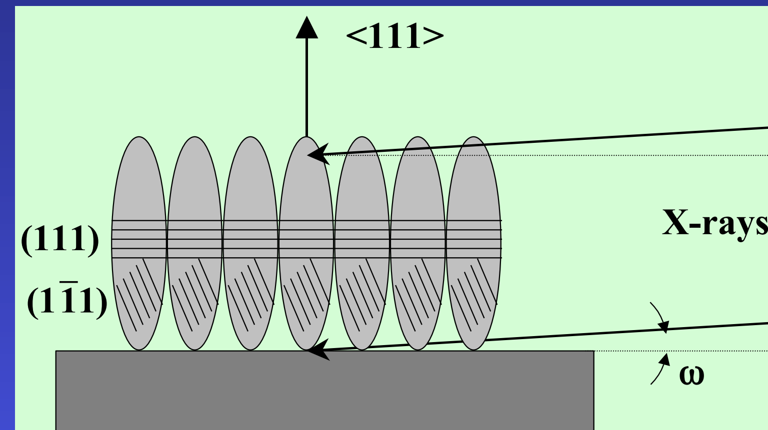
Textured powders:
- reduced overlaps
- angular constrain = f(texture strength)
- Intermediate anisotropy

Many patterns to measure and analyse

Line Broadening:

Crystallite sizes, shapes, μstrains, distributions



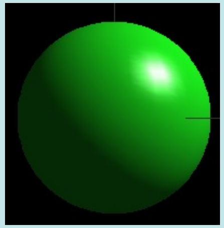


- Texture helps the "real" mean shape determination
- Modelled by peak convolution + Popa formalism

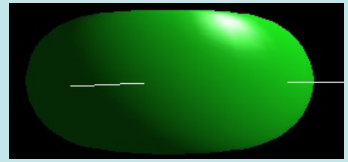
$$\langle R_{\mathbf{h}} \rangle = R_0 + R_1 P_2^{0}(x) + R_2 P_2^{1}(x)\cos\varphi + R_3 P_2^{1}(x)\sin\varphi + R_4 P_2^{2}(x)\cos 2\varphi + R_5 P_2^{2}(x)\sin 2\varphi + \ldots$$

$$\langle \varepsilon_{\mathbf{h}}^2 \rangle E_{\mathbf{h}}^4 = E_1 h^4 + E_2 k^4 + E_3 \ell^4 + 2E_4 h^2 k^2 + 2E_5 \ell^2 k^2 + 2E_6 h^2 \ell^2 + 4E_7 h^3 k + 4E_8 h^3 \ell + 4E_9 k^3 h + 4E_{10} k^3 \ell + 4E_{11} \ell^3 h + 4E_{12} \ell^3 k + 4E_{13} h^2 k \ell + 4E_{14} k^2 h \ell + 4E_{15} \ell^2 k h$$

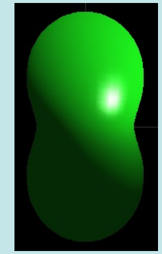
$\bar{1}$



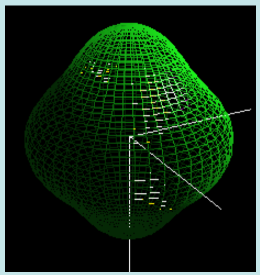
R_0



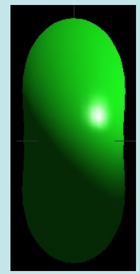
R_0, $R_1 < 0$



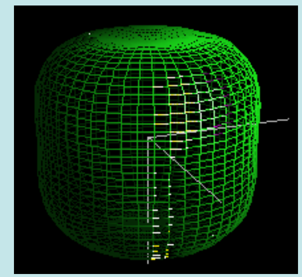
R_0, $R_1 > 0$



R_0, $R_6 > 0$

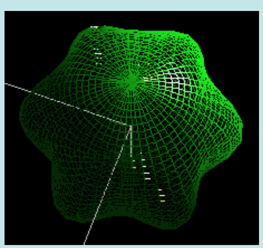


R_0,
R_2 and $R_6 > 0$



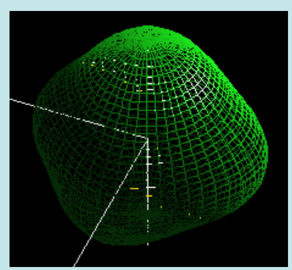
R_0, $R_6 < 0$

6/m

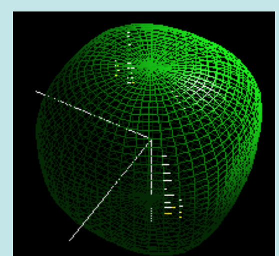


R_0, $R_4 > 0$

m3m



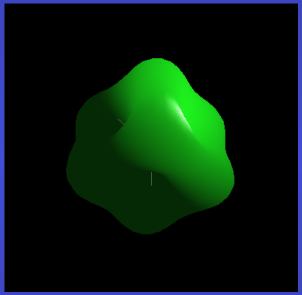
R_0, $R_1 > 0$



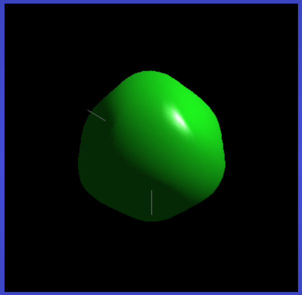
R_0, $R_1 < 0$

Gold thin films

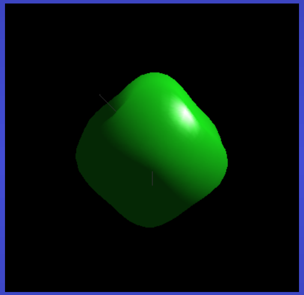
Crystallite size (Å) along	Film thickness					
	10nm	15nm	20nm	25nm	35nm	40nm
[111]	176	153	725	254	343	379
[200]	64	103	457	173	321	386
[202]	148	140	658	234	337	381



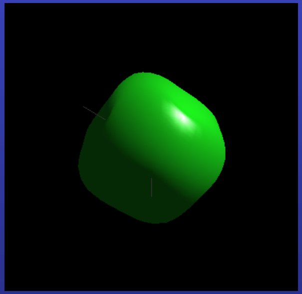
10 nm



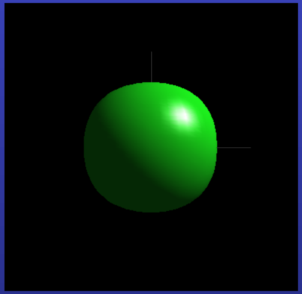
15 nm



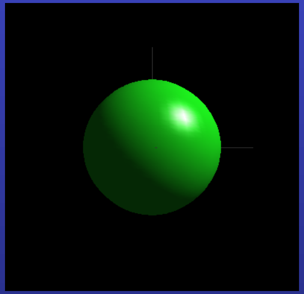
20 nm



25 nm



35 nm



40 nm

Why not grinding samples another problem !

Grinding: removes angular relationship, adds correlations

Texture:

- not measured
- removed ? hope to get a perfect powder

Strains, defaults, anisotropy … :

- some removed, some added

Same sample ?

Rare samples ?

Combined Analysis approach

Extracted Intensities

WIMV, E-WIMV
Harmonics, components, ADC

Orientation Distribution Function

Rietveld

Structure
+
Microstructure
+
phase %

Popa-Balzar,
$sin^2\psi$

Residual stresses
Strain Distribution Function

Voigt,
Reuss,
Geometric
mean

Le Bail

X-Ray specular Reflectivity

Roughness,
electron Density
& EDP,
Thickness

Fresnel,
Matrix (Parrat),
DWBA

pole figures
inverse pole figures

Structural parameters
atomic positions, substitutions, vibrations
cell parameters

Multiphased, layered samples:
Thickness,
Anisotropic Sizes
and μ-strains (*Popa*),
Stacking faults (*Warren*),
Distributions, Turbostratism (Ufer)

Phase ratio (amorphous + crystalline)
Le Bail *Rietveld*

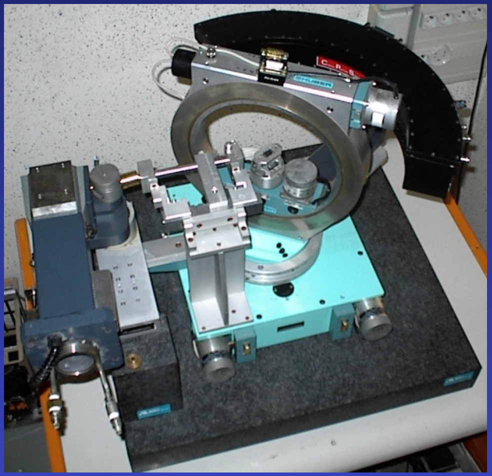
TEM, XRF, PDF

Minimization algorithms

- Can be fully used in the method (everywhere)

- Marquardt Least Squares (based on steepest decrease and Gauss-Newton)
  - Efficient, best with few parameters, near the solution
- Evolutionary computation (or genetic algorithm)
  - Slow, not efficient, requires a lot of resources
  - Unlimited number of parameters
  - Can start far from the solution
- Simulated annealing (the solution proceed like a random walk, but the walking step decreases as temperature decreases)
  - In between the Marquardt and evolutionary algorithms
- Simplex (generates n+1 starting solutions as vertices of a polygon, n number of parameters, and contract/expand the polygon around the minima)
  - Slow on convergence
  - Remains close to the solution, but explore more minima with respect to the Marquardt

Minimum experimental requirements



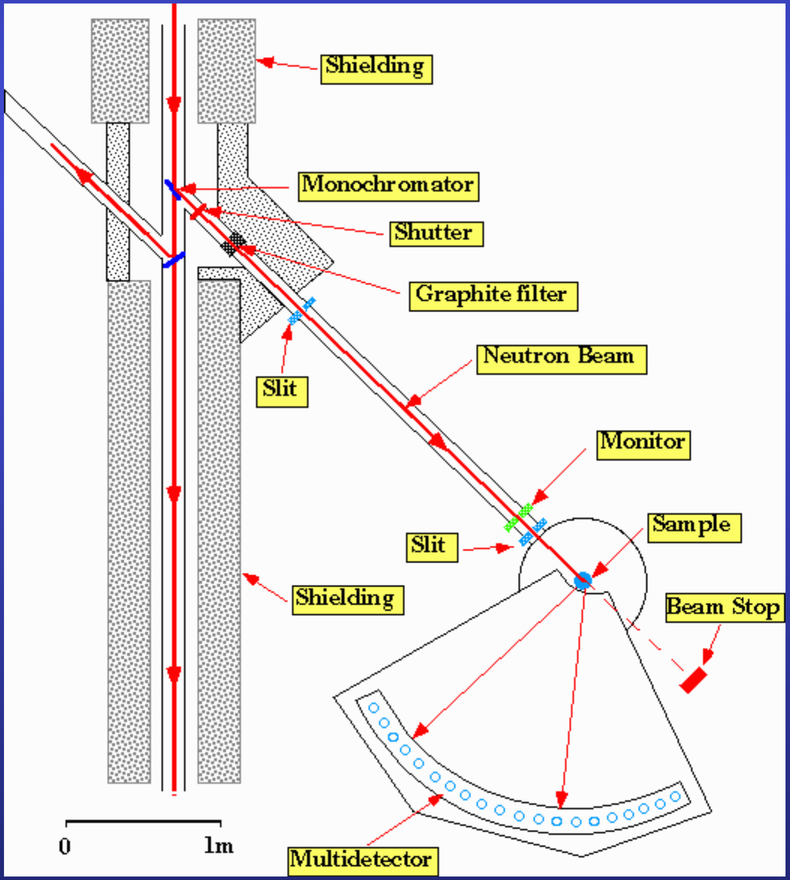
1D or 2D Detector + 4-circle diffractometer
(X-rays and neutrons)
CRISMAT, ILL

+

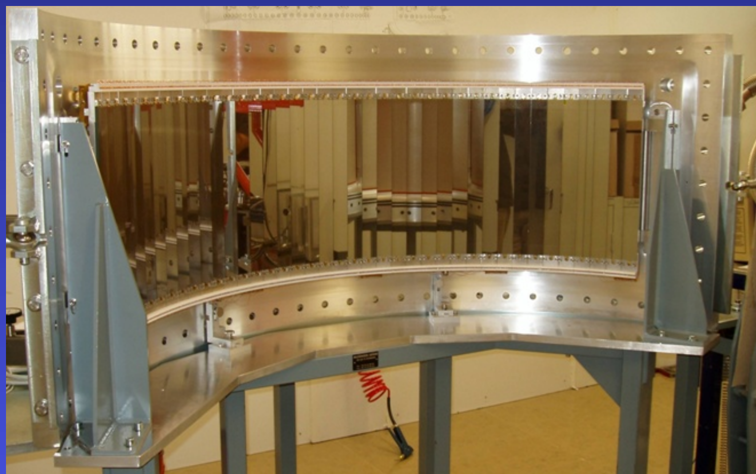
~1000 experiments (2θ diagrams)
in as many sample orientations

+

Instrument calibration
(peaks widths and shapes,
misalignments, defocusing …)



2D Curved Area Position Sensitive Detector

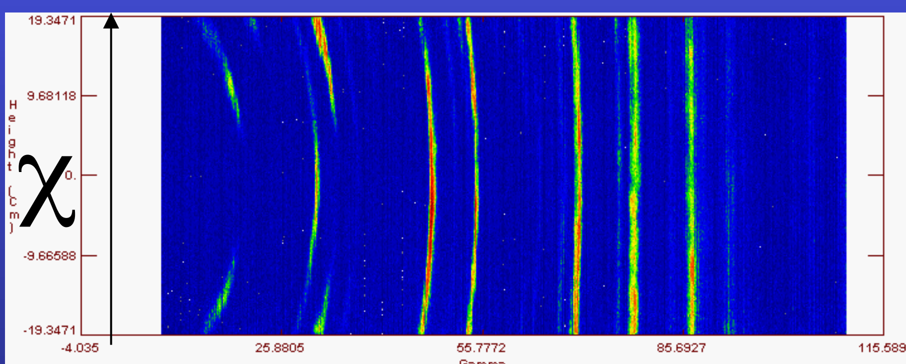


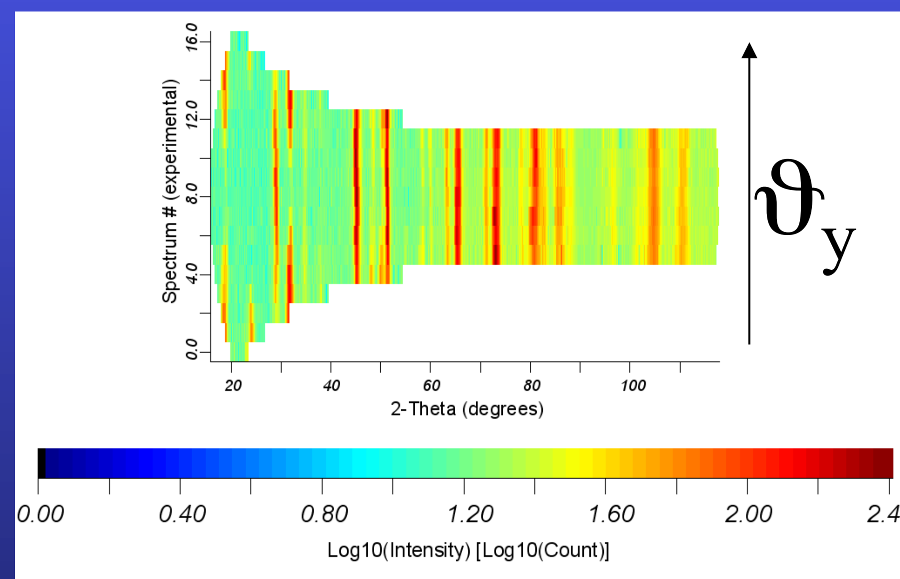
D19 - ILL

+

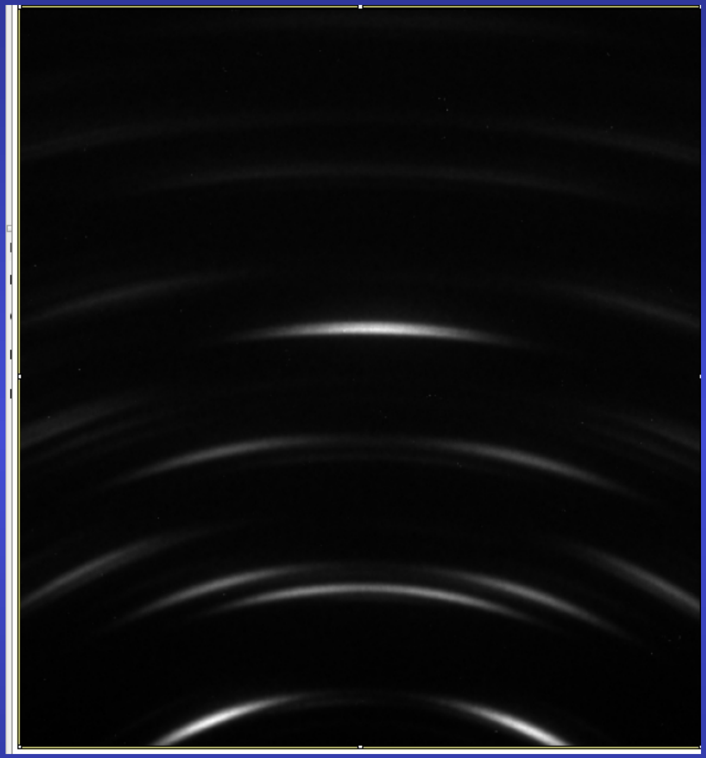
~100 experiments (2D Debye-Scherrer diagrams)

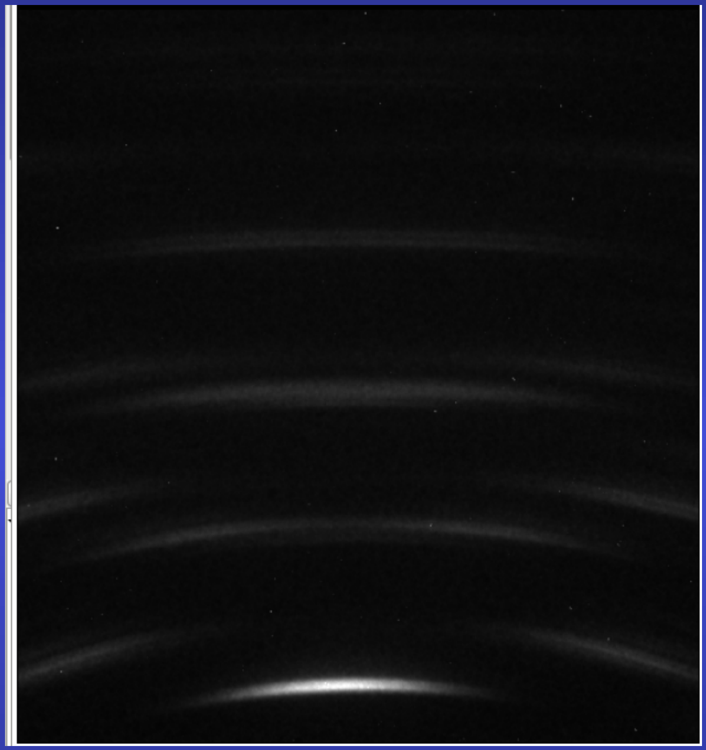
in as many sample orientations





Bruker CCD + «small» InCoatec μsource

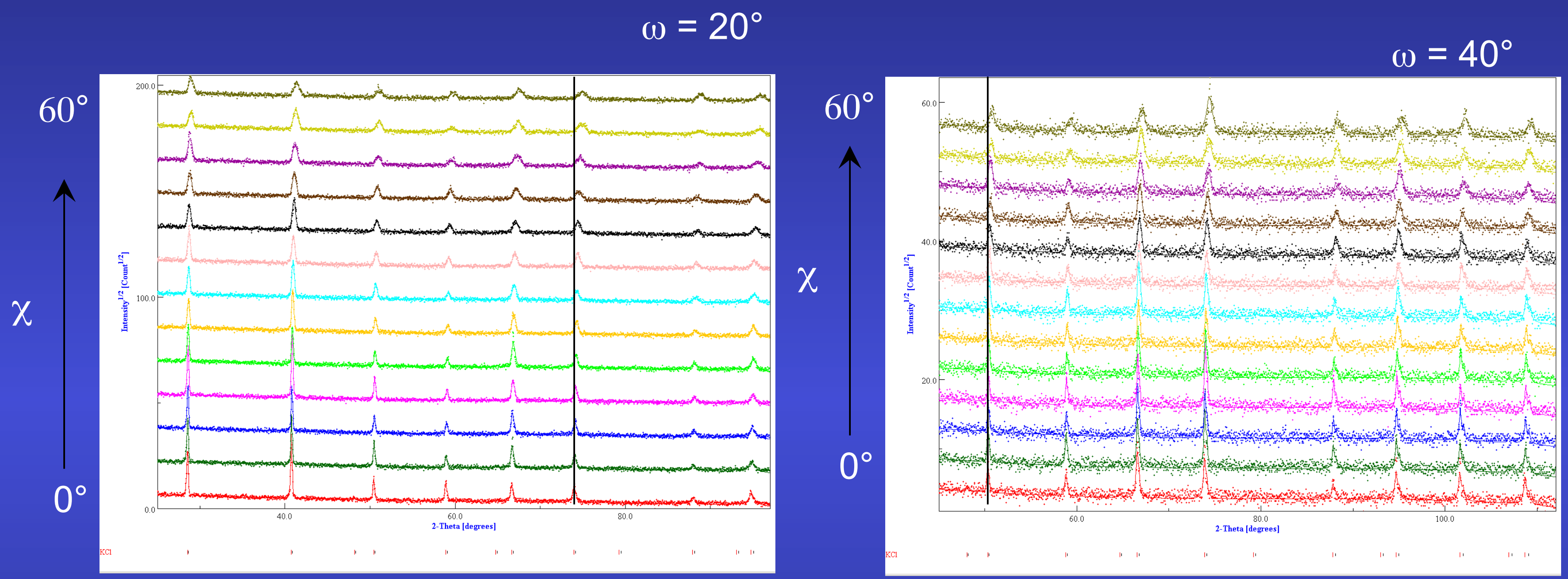




Reflection geometry
72 images
2-hours acquisition
60 mm sample-CCD distance

Compromises:
- resolution/pole figure coverage
- pixel size/distance
- wavelength/nb of lines

Calibration



KCl, LaB_6 …

FWHM (ω, χ, 2θ, η …)
2θ shift
gaussianity
asymmetry
misalignments ...

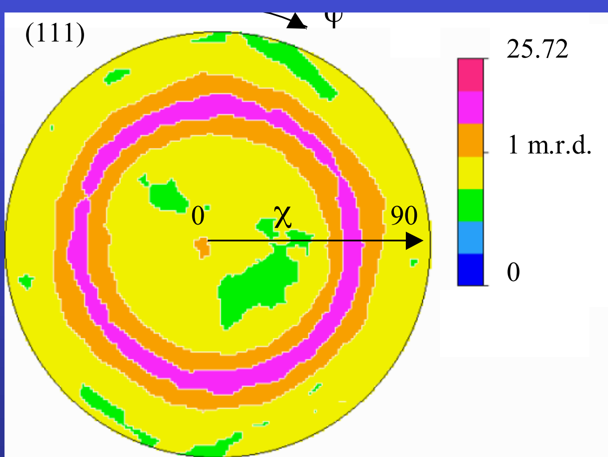
Ferroelectric PCT films

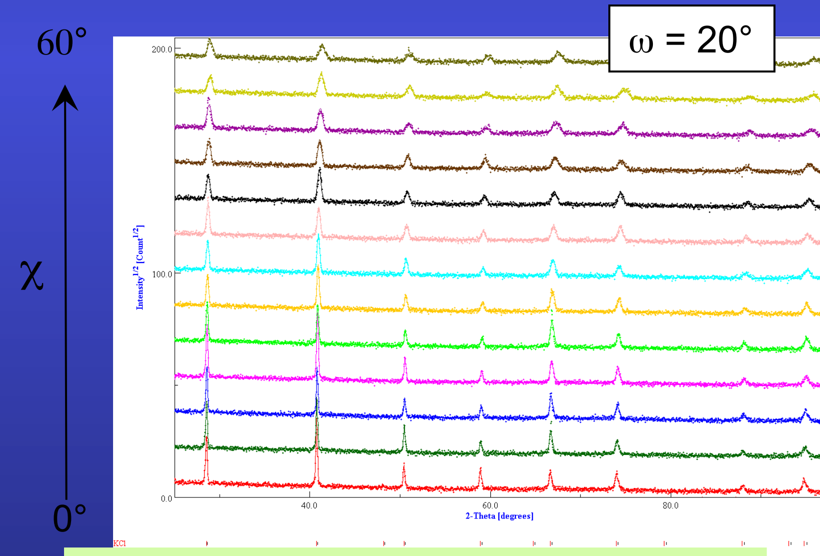
J. Ricote, Madrid

thin films:

$(Ca_{0.24}Pb_{0.76})TiO_3$ sol-gel synthesised solutions deposited by spin coating on a substrate of $Pt/TiO_2/Si$, with and without a treatment at 650ºC for 30 min.

All films are crystallised at 700ºC for 50 s by Rapid Thermal Processing (RTP; 30ºC/s). A series is also recrystallised at 650ºC for 1 to 3 h.





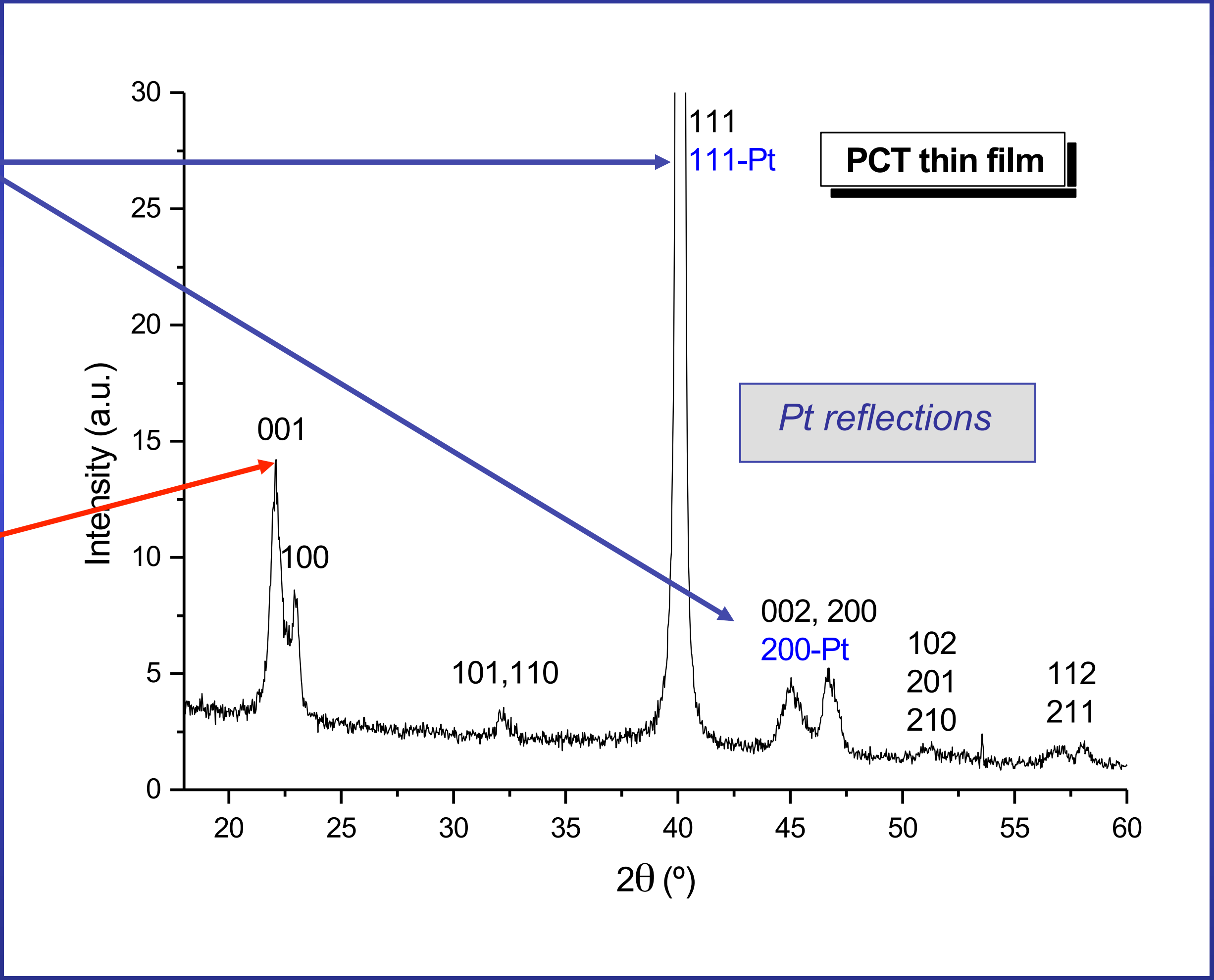
Refinement of individual spectra

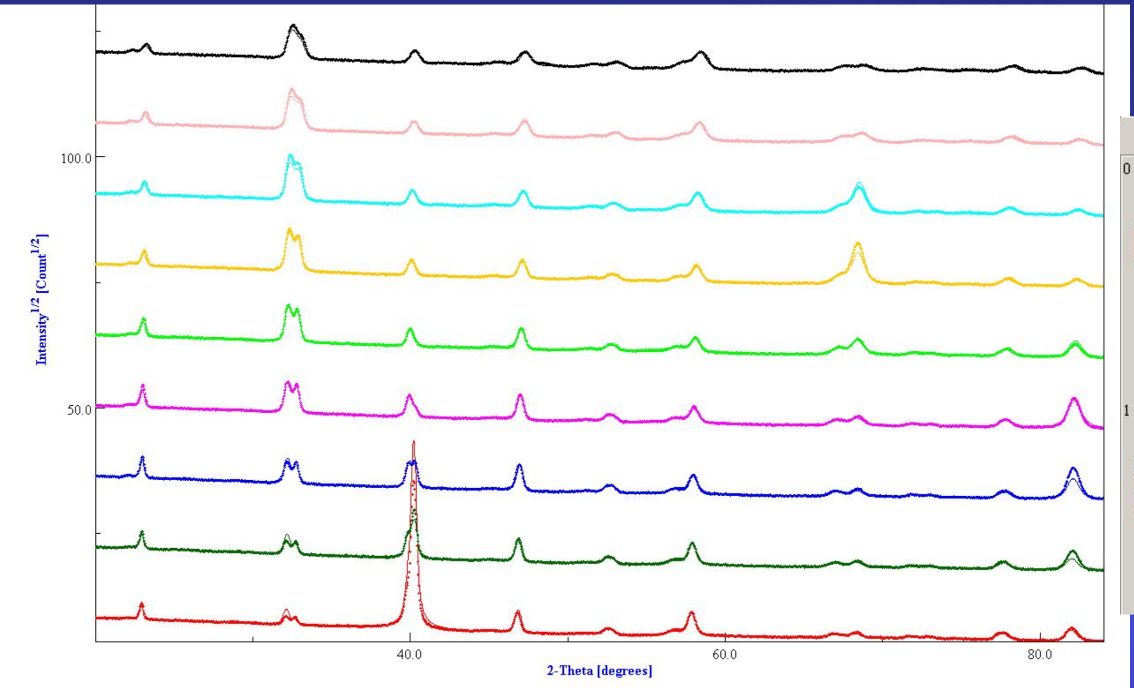
Limitations of the simple Quantitative Texture Analysis

Structural parameters are difficult to obtain due to:

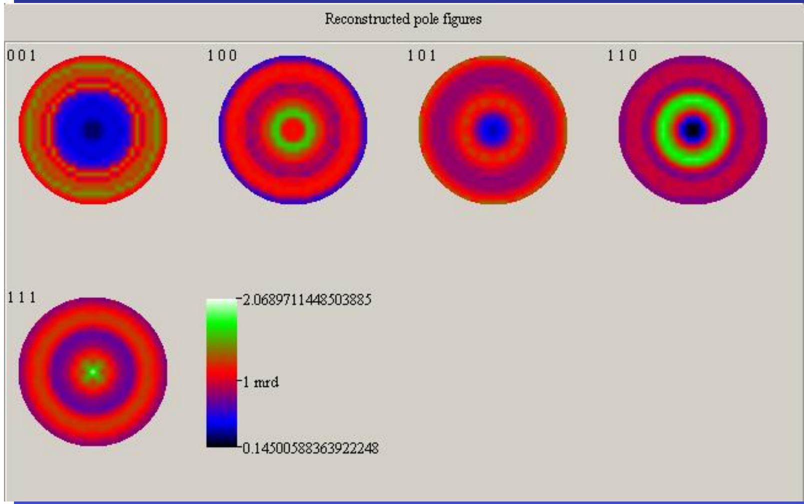
Substrate influence:
overlapping of reflections from the film and the substrate

TEXTURE effects:
peaks that do not appear at low χ angles



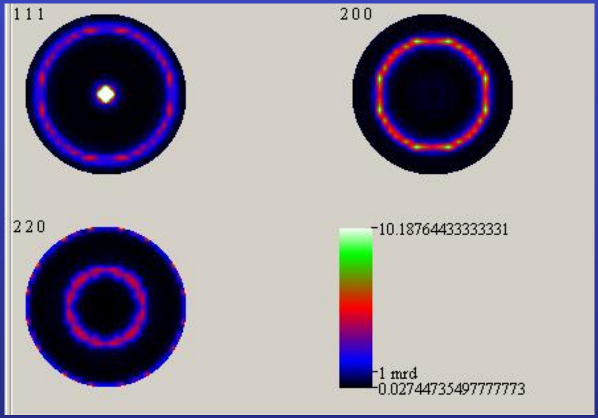


PCT



a = 3.9156(1) Å
c = 4.0497(3) Å
T = 2525(13) Å
t_{iso} = 390(7) Å
ε = 0.0067(1) rms

Pt



a = 3.9108(1) Å
T = 457(3) Å
t_{iso} = 458(3) Å
ε' = 0.0032(1) rms

R_W = 13%; R_B = 12%; R_{exp} = 22%.(Rietveld)
R_W = 5%; R_B = 6% (E-WIMV)

Structural parameters

Pt layer

	a (Å)	thickness (nm)	R factors (%)
non-treated substrate			
Pt	3.9108(1)	45.7(3)	R_W=13, R_B=12, R_{exp}=22
annealed substrate			
Pt	3.9100(4)	46.4(3)	R_W=8, R_B=14, R_{exp}=21
Pt (Recryst. 1h)	3.9114(2)	47.8(3)	R_W=9, R_B=20, R_{exp}=21
Pt (Recryst. 2h)	3.9068(1)	46.9(3)	R_W=9, R_B=14, R_{exp}=22
Pt (Recryst. 3h)	3.9141(4)	47.5(9)	R_W=27, R_B=12, R_{exp}=21

Annealing of the substrate does not introduce significant variations on the structure of the Pt layer

PTC film

	a (Å)	c (Å)	thickness (nm)
on non-treated substrate			
PCT	3.9156(1)	4.0497(6)	272.5(13)
on annealed substrate			
PCT	3.8920(6)	4.0187(8)	279.0(9)
PCT (Recryst. 1h)	3.8929(2)	4.0230(4)	266.1(11)
PCT (Recryst. 2h)	3.8982(2)	4.0227(4)	258.4(9)
PCT (Recryst. 3h)	3.9001(4)	4.0228(11)	253.6(29)

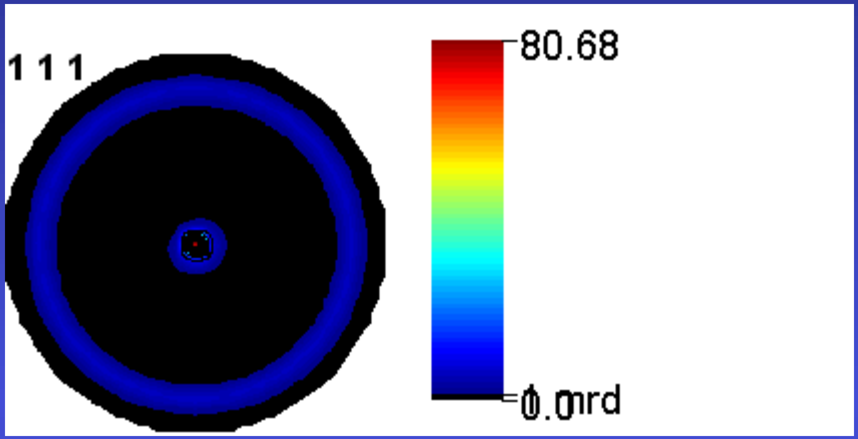
Recrystallisation reduces the stress on the film, and, increases the lattice parameters

Compliance coefficients $[10^{-3}\ GPa^{-1}]$	$PbTiO_3$ single crystal (data set A)	Film random orientation	PCT-Si <001> contrib≈17%	PLT <001> contrib.≈49%	PCT-Mg <001> contrib.≈68%
s_{11}	6.5	10.1	10.5	10.0	9.7
s_{22}	6.5	10.0	10.5	10.0	9.7
s_{33}	33.3	9.8	9.0	10.3	11.3
s_{44}	14.5	13.2	12.8	12.9	13.1
s_{55}	14.5	13.2	12.8	13.0	13.1
s_{66}	9.6	13.4	14.0	13.5	12.7
s_{12}	-0.35	-3.3	-3.5	-3.2	-3.0
s_{21}	-0.35	-3.3	-3.5	-3.2	-3.0
s_{13}	-7.1	-3.2	-3.1	-3.4	-3.6
s_{31}	-7.1	-3.2	-3.1	-3.4	-3.6
s_{23}	-7.1	-3.2	-3.1	-3.4	-3.6
s_{32}	-7.1	-3.2	-3.1	-3.4	-3.6
s_{33}/s_{11}	5.1	0.97	0.86	1.03	1.16
s_{13}/s_{12}	20.3	0.97	0.89	1.06	1.20

Geometric mean average + biaxial stress state

Ferroelectric PMN-PT films

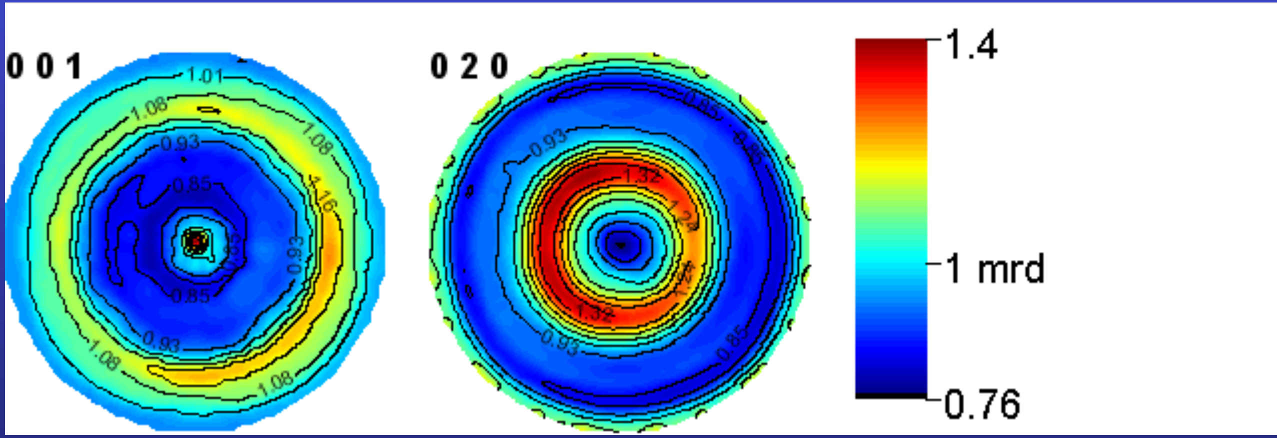
J. Ricote, DMF-Madrid



Pt

a = 3.91172(1) Å
T = 583(5) Å
t_{iso} = 960(1) Å
ε = 0.0032(1) rms
σ_{11}= 0.639(1) GPa
σ_{22}= 0.651(1) GPa
σ_{12}= -0.009(1) GPa

$Pb_{0.7} (Mg_{1/3}Nb_{2/3})O_3$-$Pb_{0.3}TiO_3$ /$Ti0_2$/Pt/Si-(100)



a = 5.67858(9) Å
b = 5.69038(9) Å
c = 3.99558(4) Å
β = 90.392(1) Å
T = 1322(9) Å
t_{iso} = 1338(2) Å
ε = 0.0067(1) rms

Si nanocrystalline thin films

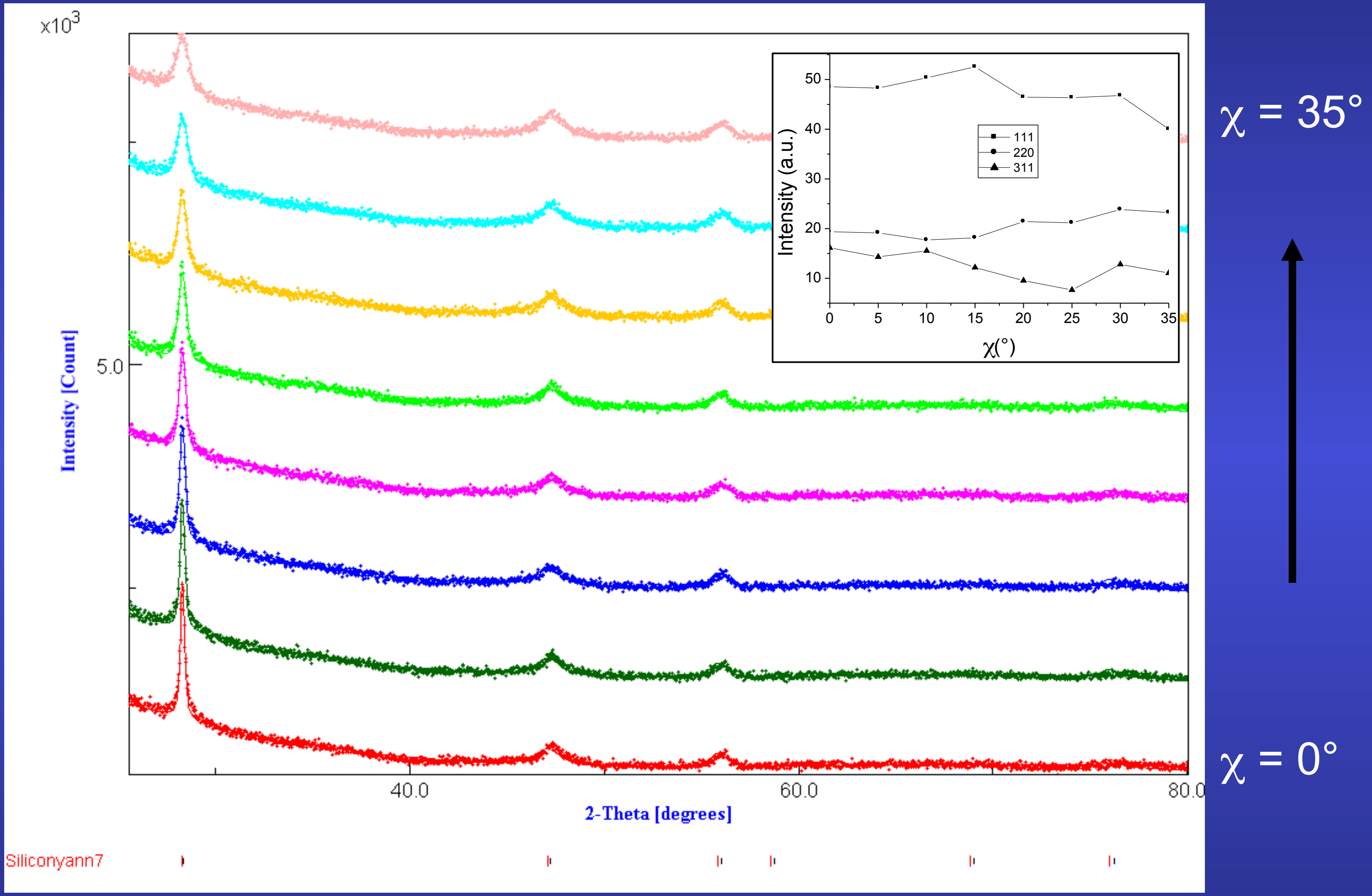
M. Morales, Caen

Silicon thin films deposition by reactive magnetron sputtering:

- power density $2 W/cm^2$
- total pressure: $p_{total} = 10^{-1}$ Torr
- plasma mixture: H_2 / Ar, pH_2 / p_{total} = 80 %
- temperature: 200°C
- substrates: amorphous SiO_2 (a-SiO_2)
  (100)-Si single-crystals
- target-substrate distance (d)
  - a-SiO_2 substrates: d = 4, 6, 7, 8, 10, 12 cm
    films A, B, C, D, E, F
  - (100)-Si: d = 6, 12 cm
    films G, H

Aim: quantum confinement, photoluminescence properties

Typical refinement

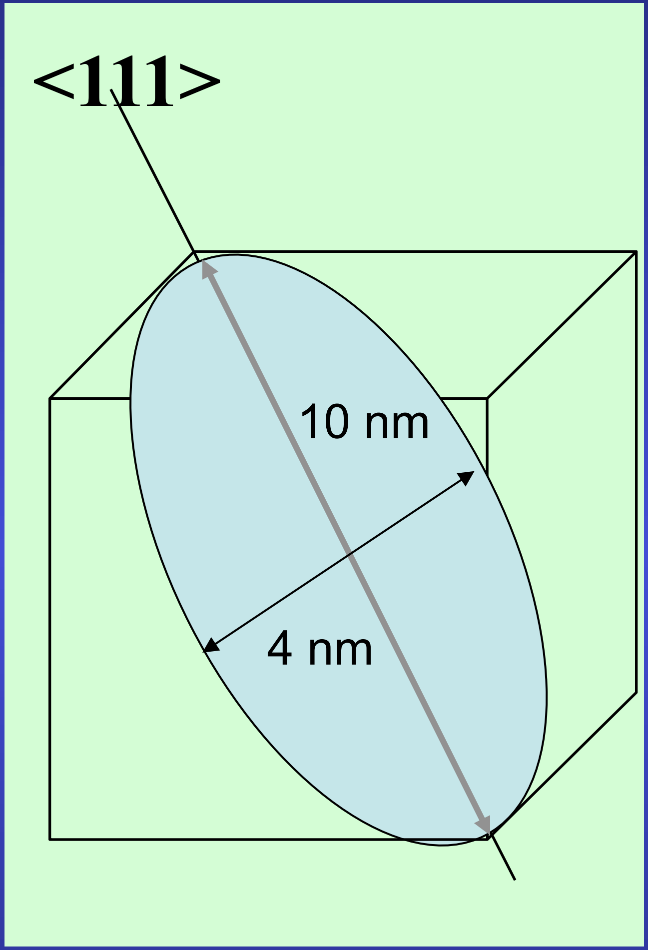


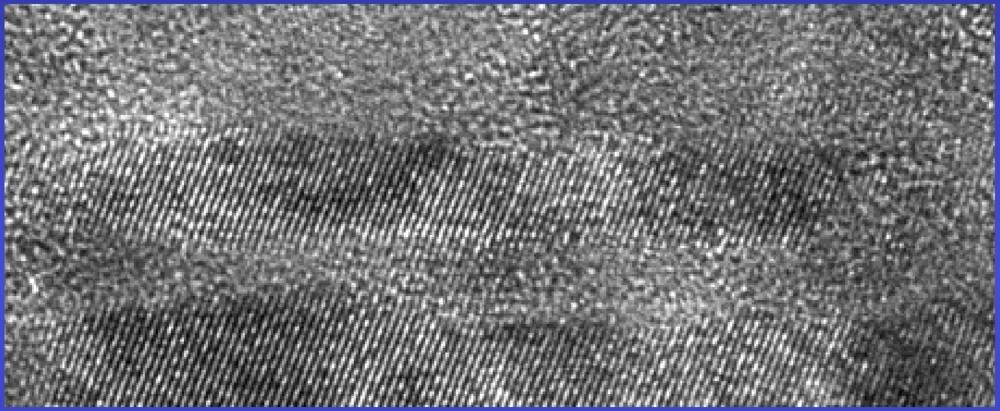
broad, anisotropic diffracted lines, textured samples

Refinement Results

Sample	d (cm)	a (Å)	RX thickness (nm)	Anisotropic sizes (Å)			Texture parameters			Reliability factors (%)			
				<111>	<220>	<311>	Maximum (m.r.d.)	minimum (m.r.d.)	Texture index F^2 (m.r.d^2)	RP_0	R_w	R_B	R_{exp}
A	4	5.4466 (3)	---	94	20	27	1.95	0.4	1.12	1.72	4.0	3.7	3.5
B	6	5.4439 (2)	711 (50)	101	20	22	1.39	0.79	1.01	0.71	4.9	4.3	4.2
C	7	5.4346 (4)	519 (60)	99	40	52	1.72	0.66	1.05	0.78	4.3	4.0	3.9
D	8	5.4461 (2)	1447 (66)	100	22	33	1.57	0.63	1.04	0.90	5.5	4.6	4.5
E	10	5.4462 (2)	1360 (80)	98	20	25	1.22	0.82	1.01	0.56	5.0	3.9	4.0
F	12	5.4452 (3)	1110 (57)	85	22	26	1.59	0.45	1.05	1.08	4.2	3.5	3.7
G	6	5.4387 (3)	1307 (50)	89	22	28	1.84	0.71	1.01	1.57	5.2	4.7	4.2
H	12	5.4434 (2)	1214 (18)	88	22	24	2.77	0.50	1.12	2.97	5.0	4.5	4.3

Mean anisotropic shape



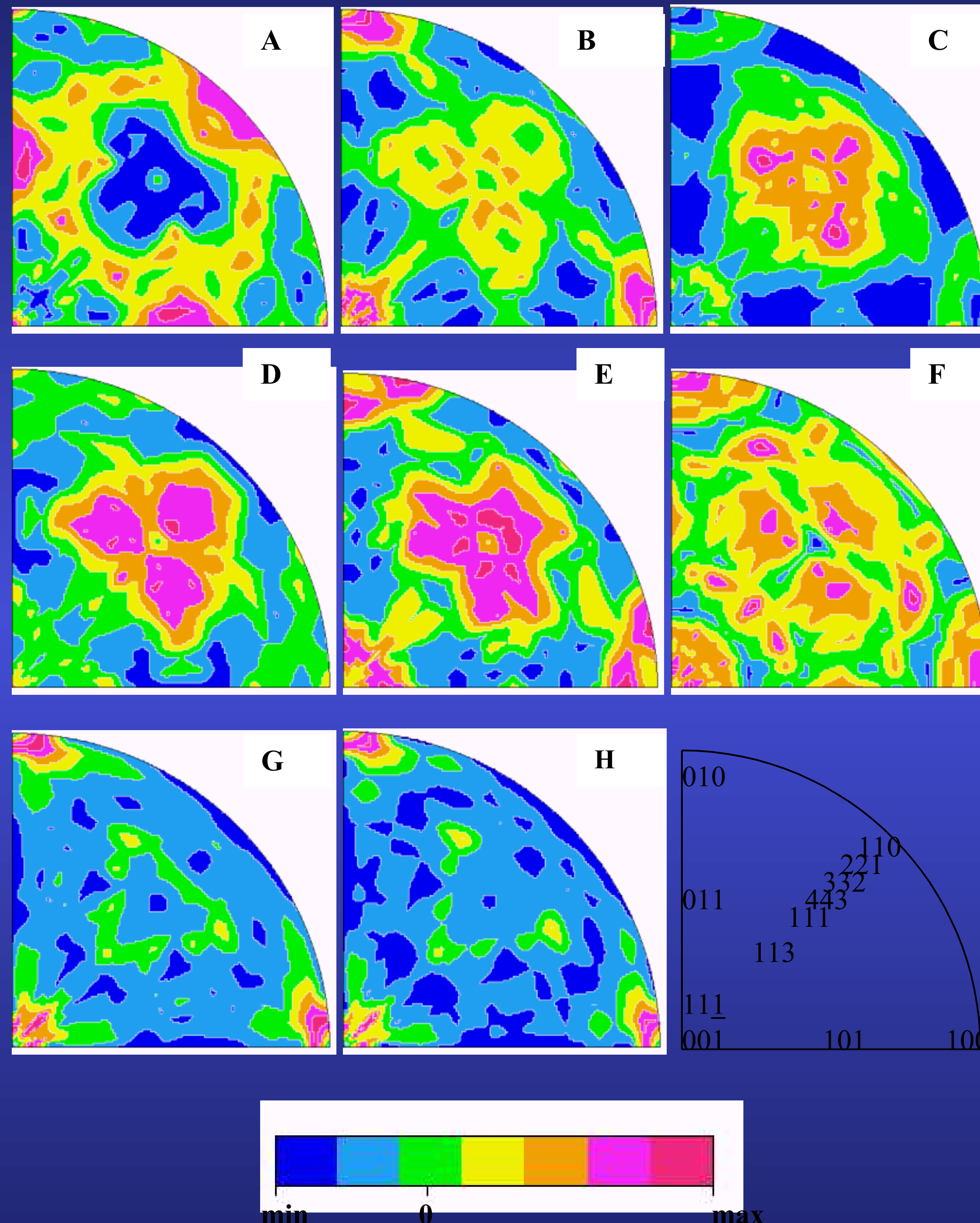


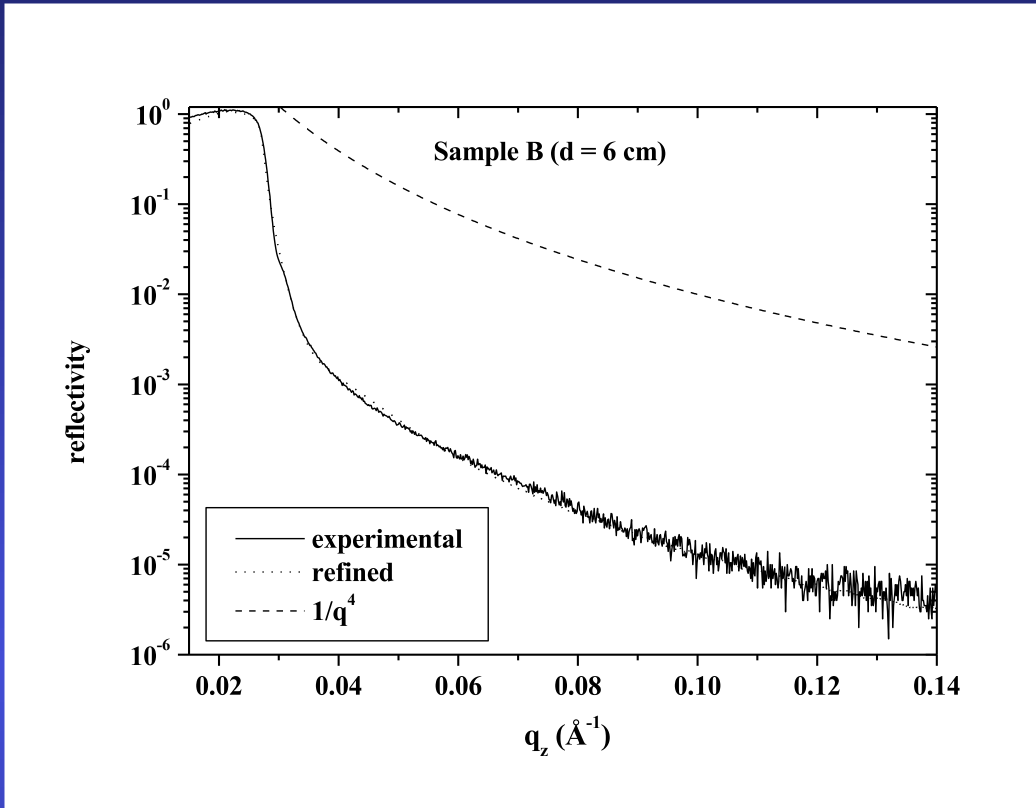
Schematic of the mean crystallite shape for Sample D represented in a cubic cell, as refined using the Popa approach and exhibiting a strong elongation along <111>, and TEM image

001 Inverse Pole Figures

a-SiO_2

(100)-Si



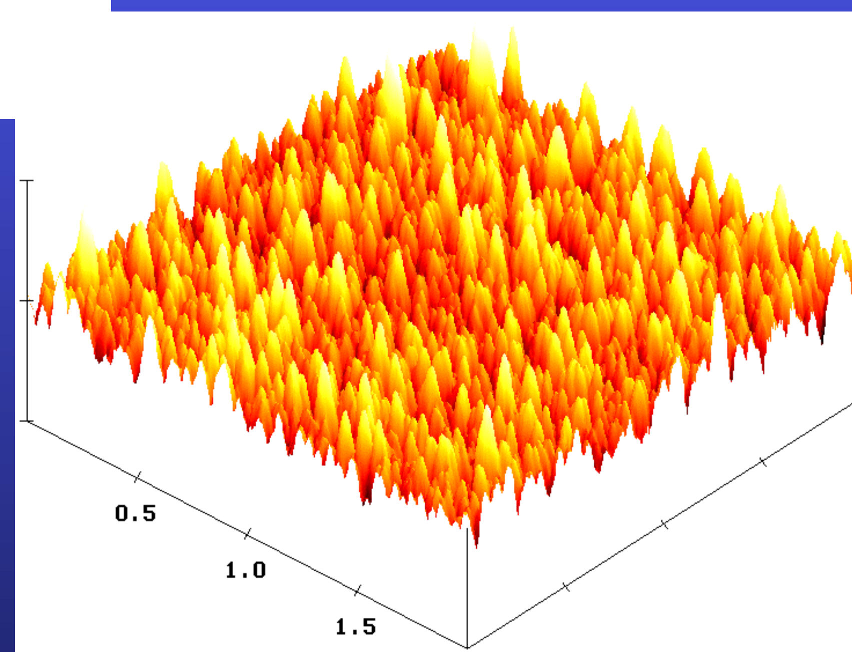


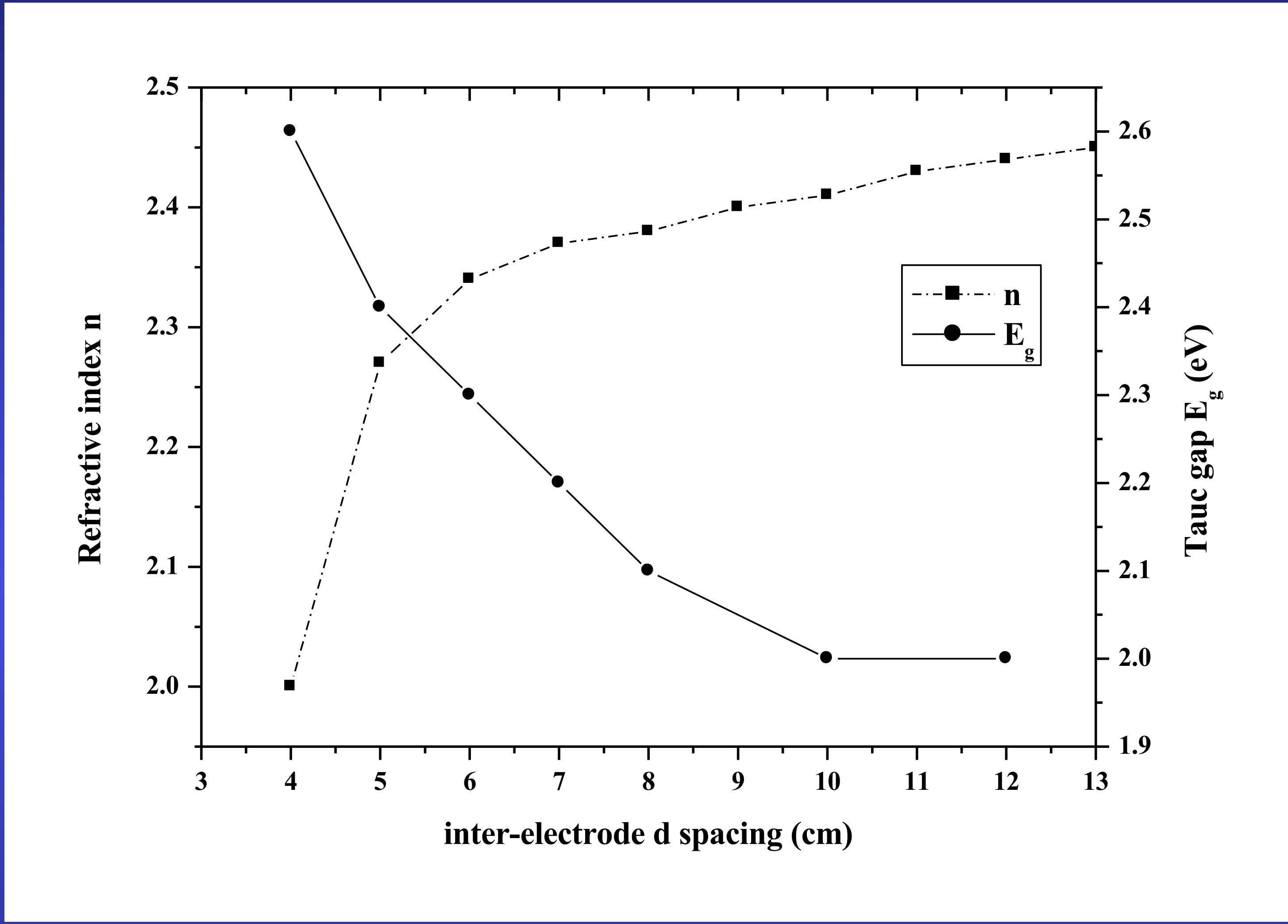
XRR:

Roughness governed

AFM:

homogeneous roughness

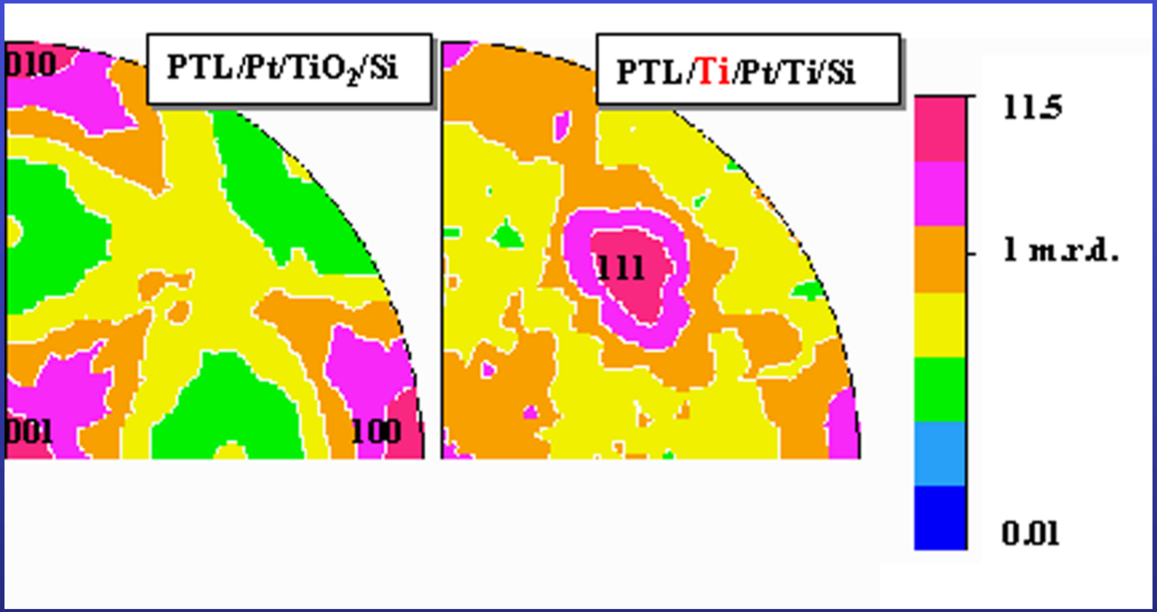




↬ Refractive index linked to film porosities:

Larger target-sample distances: increased compacity due to lower nanopowder filling

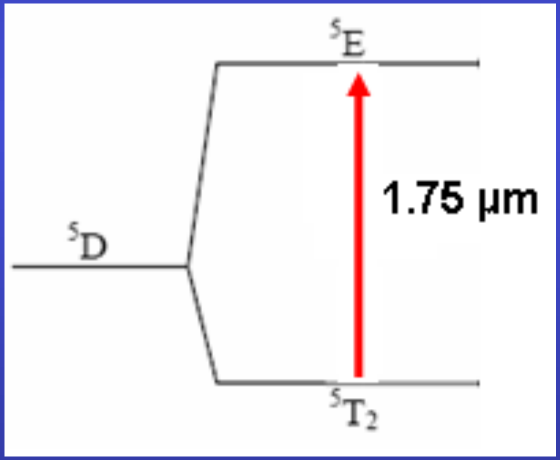
Atom	Occupancy	x	y	z
Pb	0.76	0.0	0.0	0.0
Ca	0.24	0.0	0.0	0.0
Ti	1.0	0.5	0.5	0.477(2)
O1	1.0	0.5	0.5	0.060(2)
O2	1.0	0.0	0.5	0.631(1)

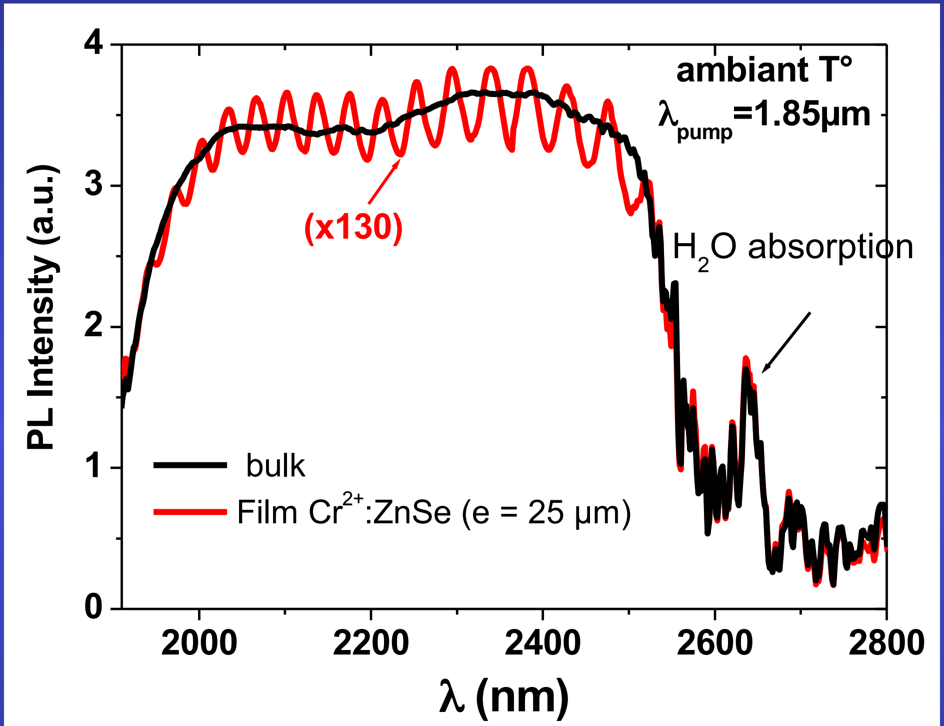


ZnSe:Cr^{2+} films
M. Morales

conditions:

- ♦ $20 \leq T_d \leq 385°C$
- ♦ P_{RF} = 50-200W
- ♦ P_{Ar} = 0.5 Pa and 2 Pa
- ♦ d = 7 and 10 cm

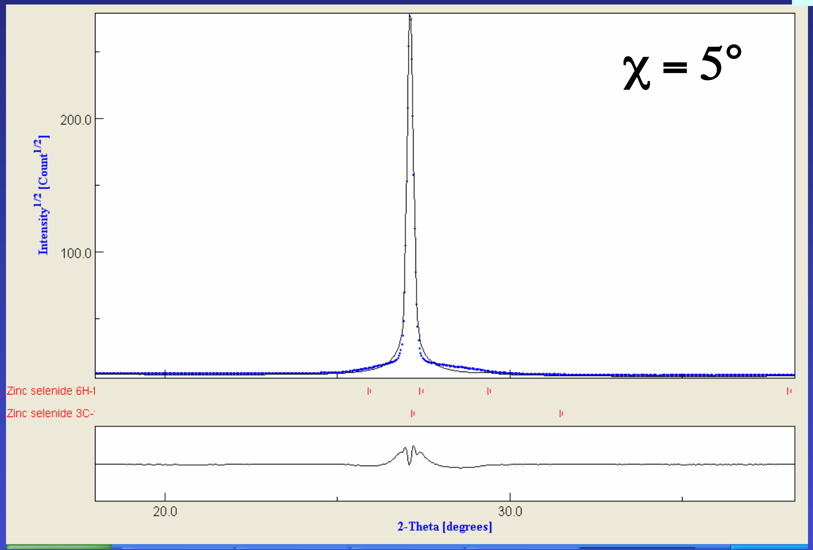


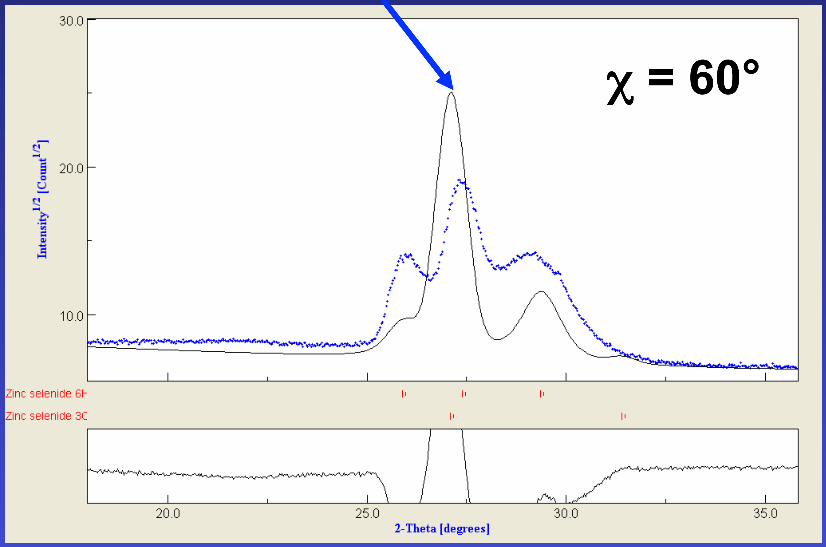


♦ **Large emission band centred at 2200nm: $^5E \rightarrow {}^5T_2$ transition (Cr^{2+})**

♦ **Single crystals and thin films: similar spectra**

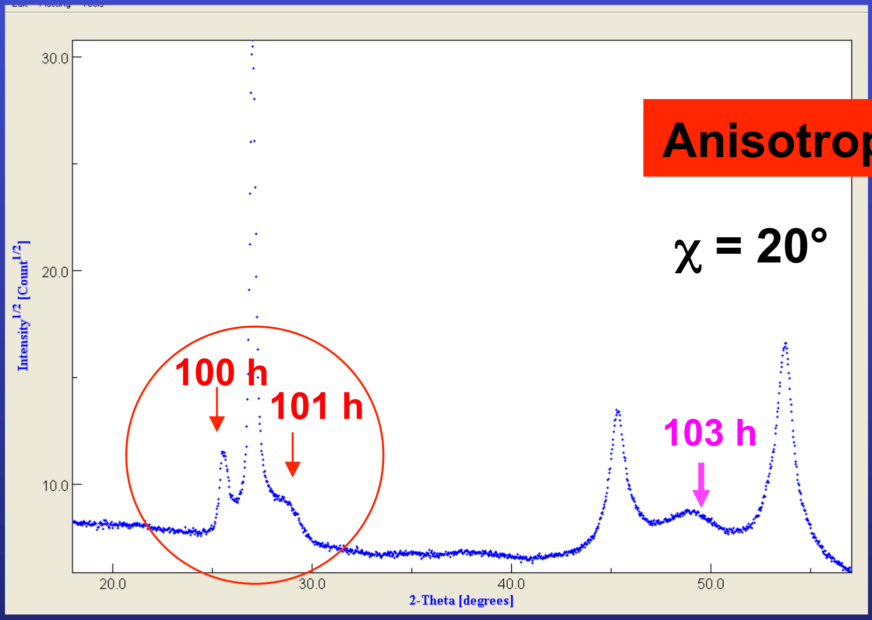
111 Peak shifts

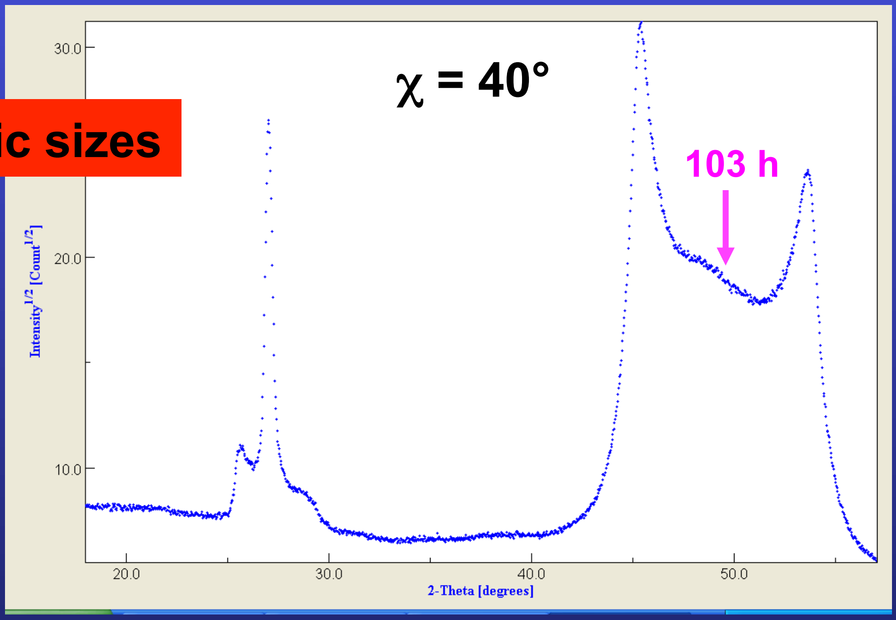




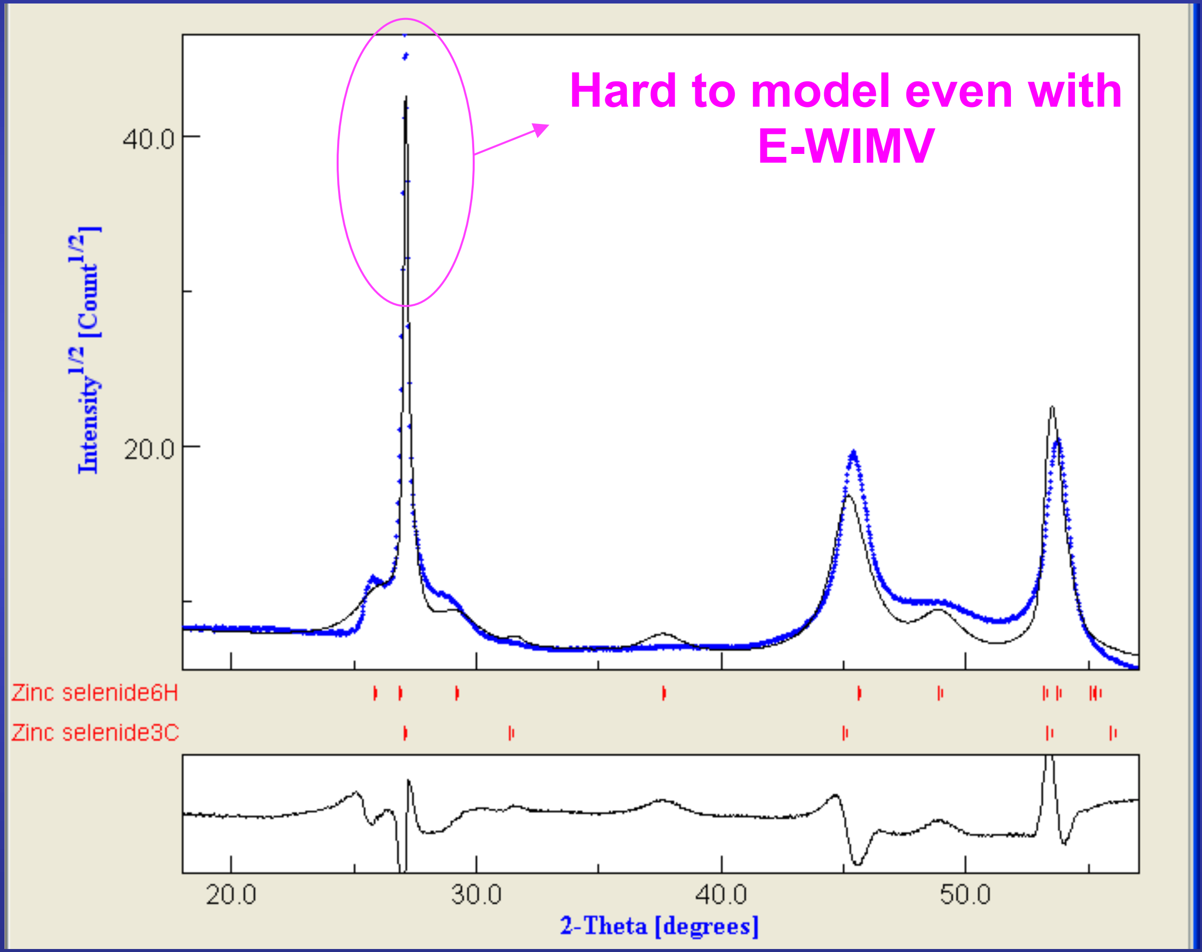
Residual stresses and/or stacking faults

Anisotropic sizes



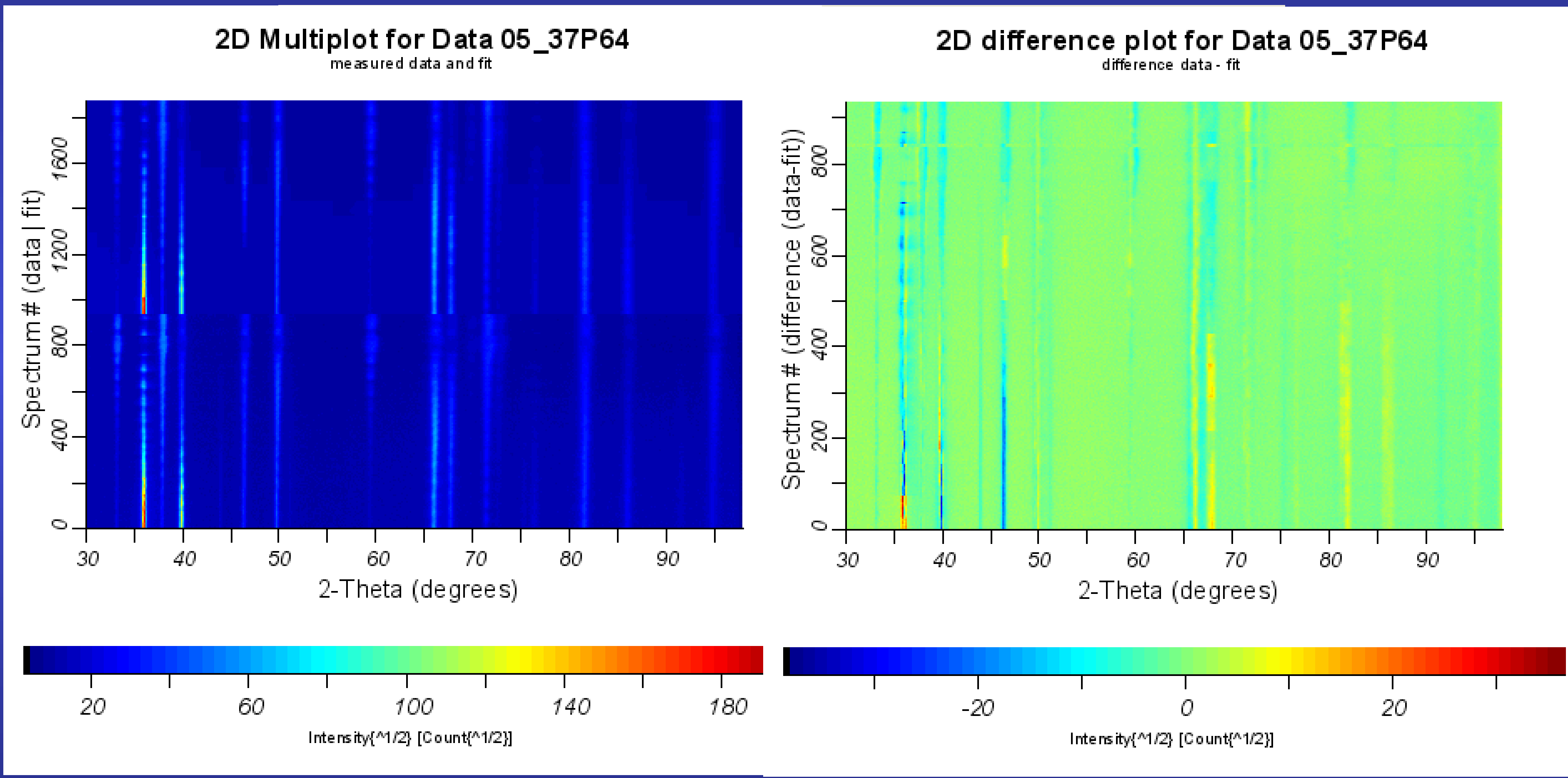


Fibre Texture + 2 polytypes (6H and 3C) + anisotropic sizes + residual stresses and/or stacking faults + layering



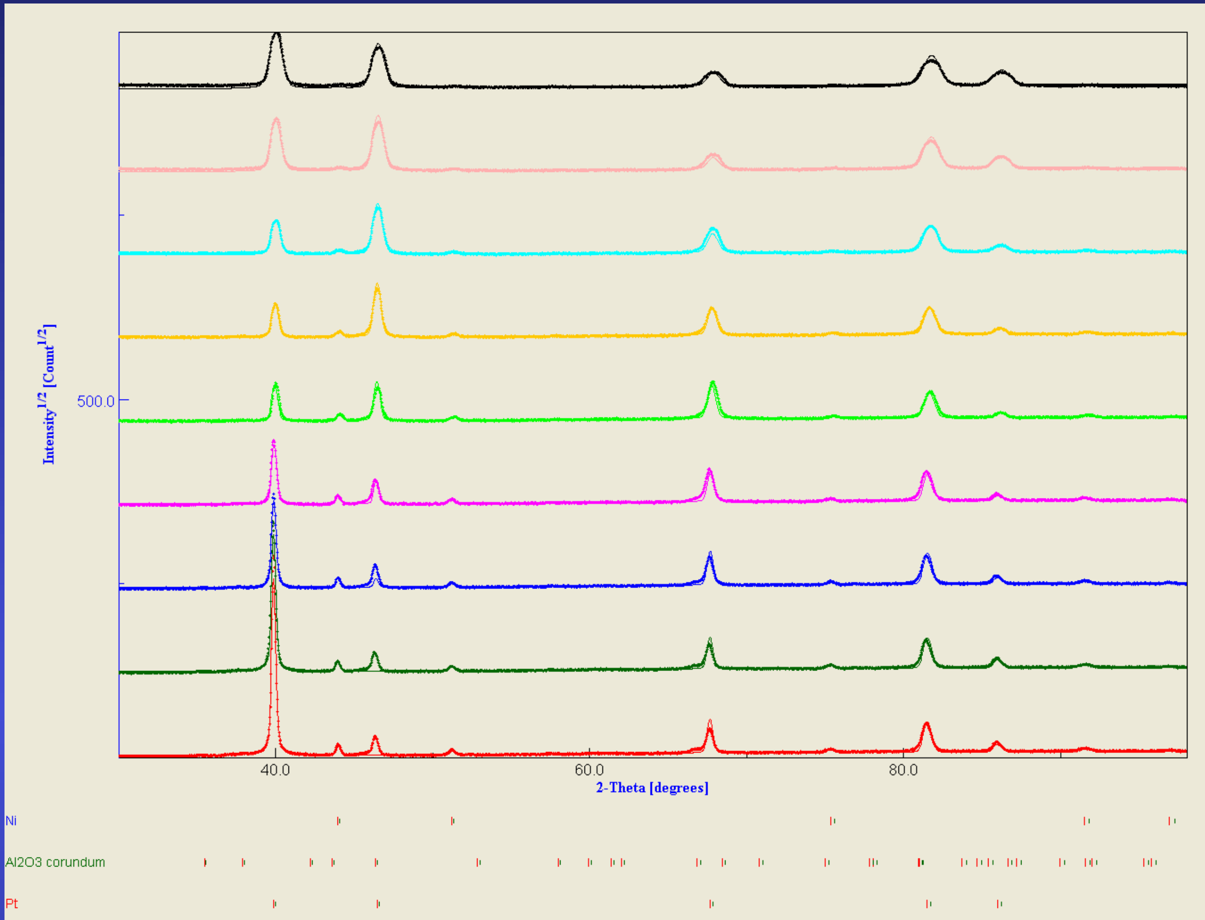
Sum diagram: ω =13.65°, P_{RF} = 200W

$AlN/Pt/TiO_x/Al_2O_3/Ni\text{-}Co\text{-}Cr\text{-}Al$



Rw (%) = 24.120445
Rexp (%) = 5.8517213

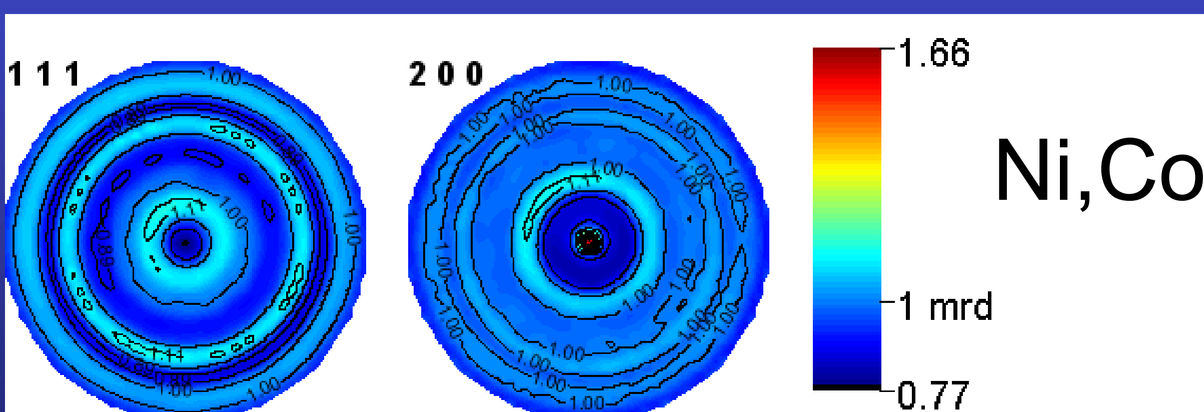
T(AlN) = 14270(3) nm
T(Pt) = 430(3) nm



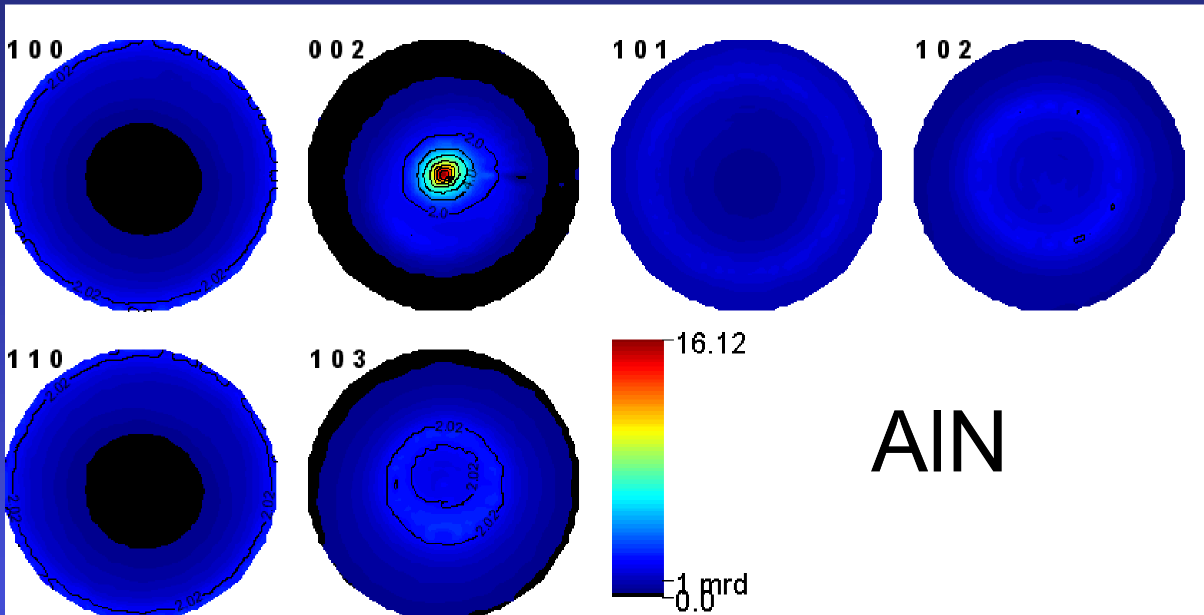
(χ,φ) randomly selected diagrams

Al_2O_3

a = 4.7562(6) Å
c = 12.875(3) Å
T= 7790(31) nm
<t> = 150(2) Å
<ε> = 0.008(3)

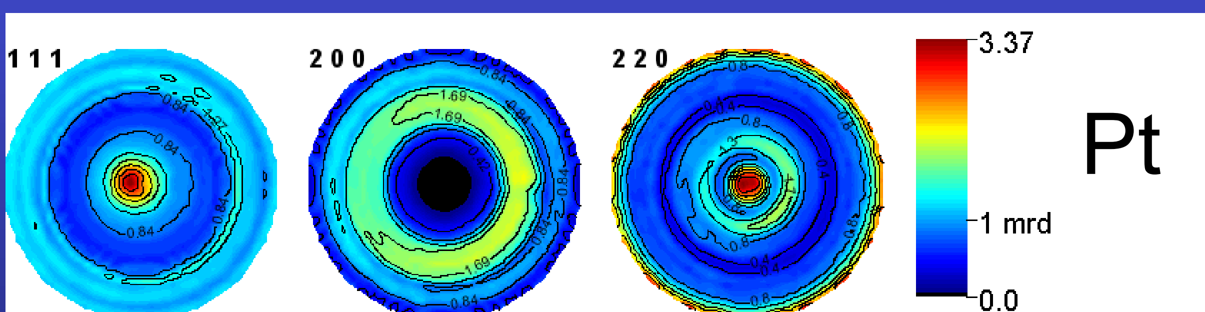


a = 3.569377(5) Å
<t> = 7600(1900) Å
<ε> = 0.00236(3)
σ_{11} = -328(8) MPa
σ_{22} = -411(9) MPa



Rw (%) = 4.1

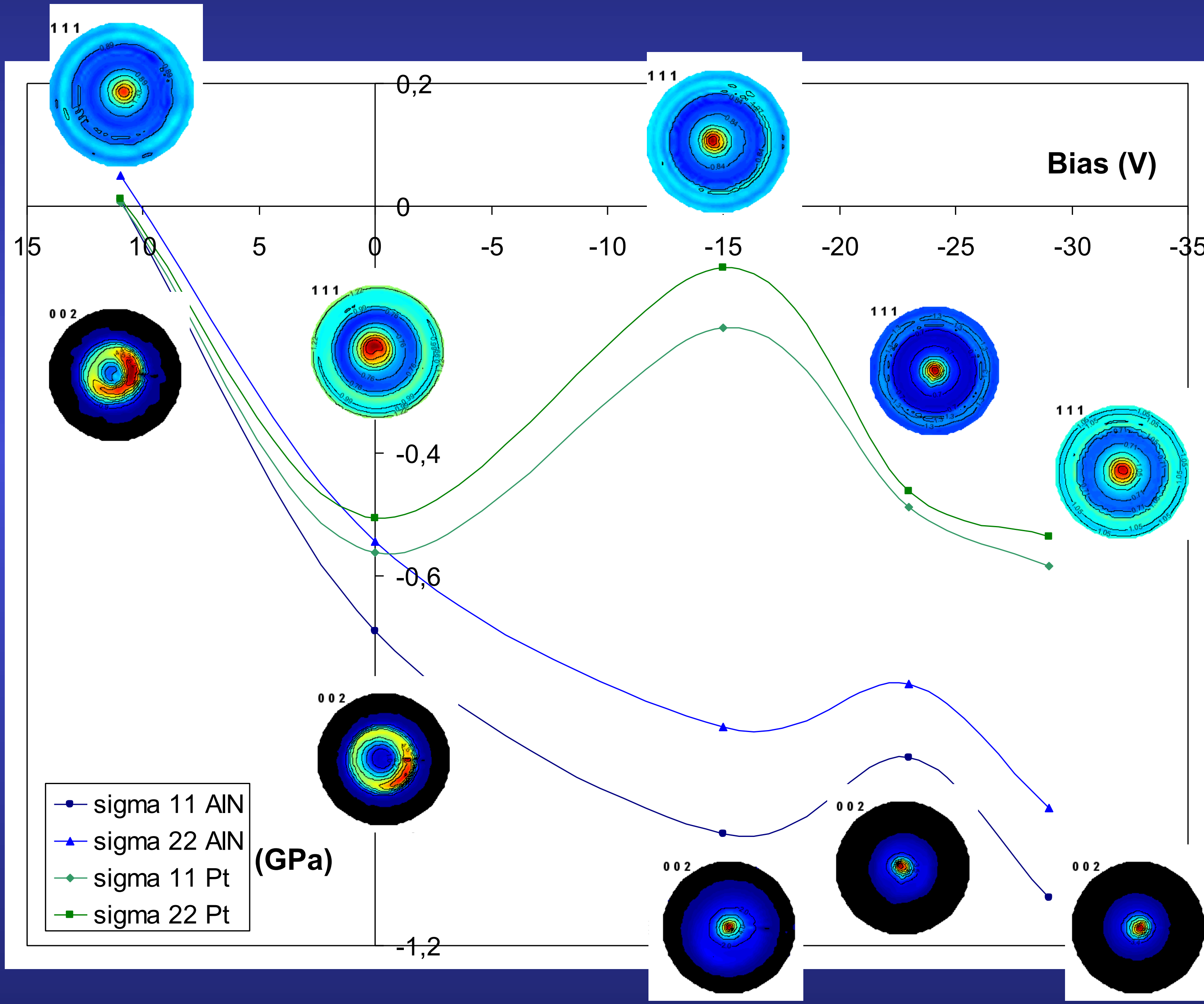
a = 3.11203(1) Å
c = 4.98252(1) Å
T = 14270(3) nm
<t> = 2404(8) Å
<ε> = 0.001853(2)
σ_{11} = -1019(2) MPa
σ_{22} = -845(2) MPa



Rw (%) = 33.3

a = 3.91198(1) Å
T = 1204(3) nm
<t> = 2173(10) Å
<ε> = 0.002410(3)
σ_{11} = -196.5(8)
σ_{22} = -99.6(6)

Substrate bias vs stress-texture evolution



Independent measurements: why not more

Different wavelengths and rays: TEM, RHEED

Reflectivity: thickness, roughness, electron density profiles

X-ray Fluorescence: composition

Spectroscopies: local structures (PDF, FTIR, Mossbauer …), eventually anisotropic (P-EXAFS, ESR, Raman …), Element profiles (SIMS, RBS …) …

Physical models: magnetisation, conductivity …

Environments: applied fields

Specular reflectivity: **q**=(0,0,z)

- Fresnel:

$$R(\mathbf{q}) = \left| \frac{q_z - \sqrt{q_z^2 - q_c^2 + \frac{32 i \pi^2 \beta}{\lambda^2}}}{q_z + \sqrt{q_z^2 - q_c^2 + \frac{32 i \pi^2 \beta}{\lambda^2}}} \right|^2 \delta q_x \delta q$$

- matrix:

$$R^{flat} = \frac{r_{0,1}^2 + r_{1,2}^2 + 2 r_{0,1} r_{1,2} \cos 2k_{Z,1} h}{1 + r_{0,1}^2 r_{1,2}^2 + 2 r_{0,1} r_{1,2} \cos 2k_{Z,1} h}$$

- Born approximation:
  Electron Density Profile

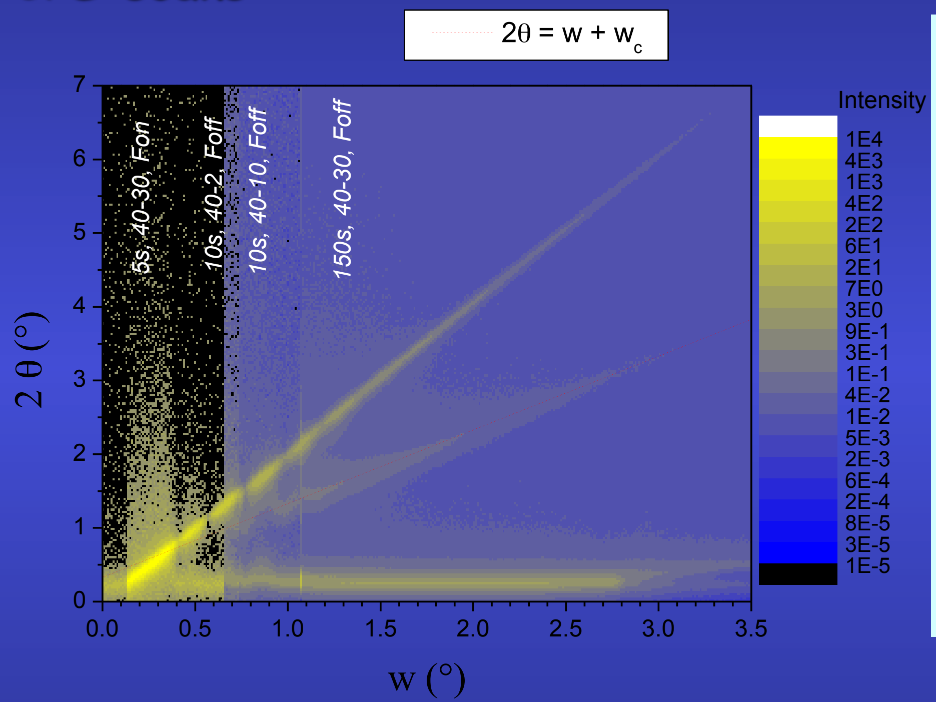
$$R(q_z) = r.r^* = R_F(q_z) \left| \frac{1}{\rho_s} \int_{-\infty}^{+\infty} \frac{d\rho(z)}{dz} e^{i q_z z} dz \right|^2$$

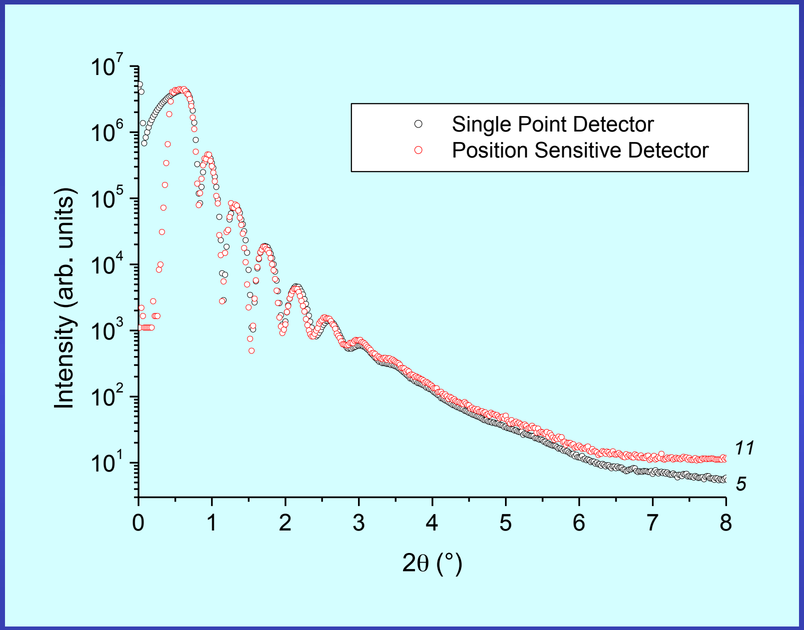
- Roughness:

$$R^{rough}(q_z) = R(q_z) \exp(-q_{z,0} q_{z,1} \sigma^2) \quad \text{Low-angles (reflectivity)}$$

$$S_R = 1 - p \exp(-q) + \mathrm{p} \exp\left(\frac{\text{-q}}{\sin\theta} \right) \quad \text{high-angle (Suortti)}$$

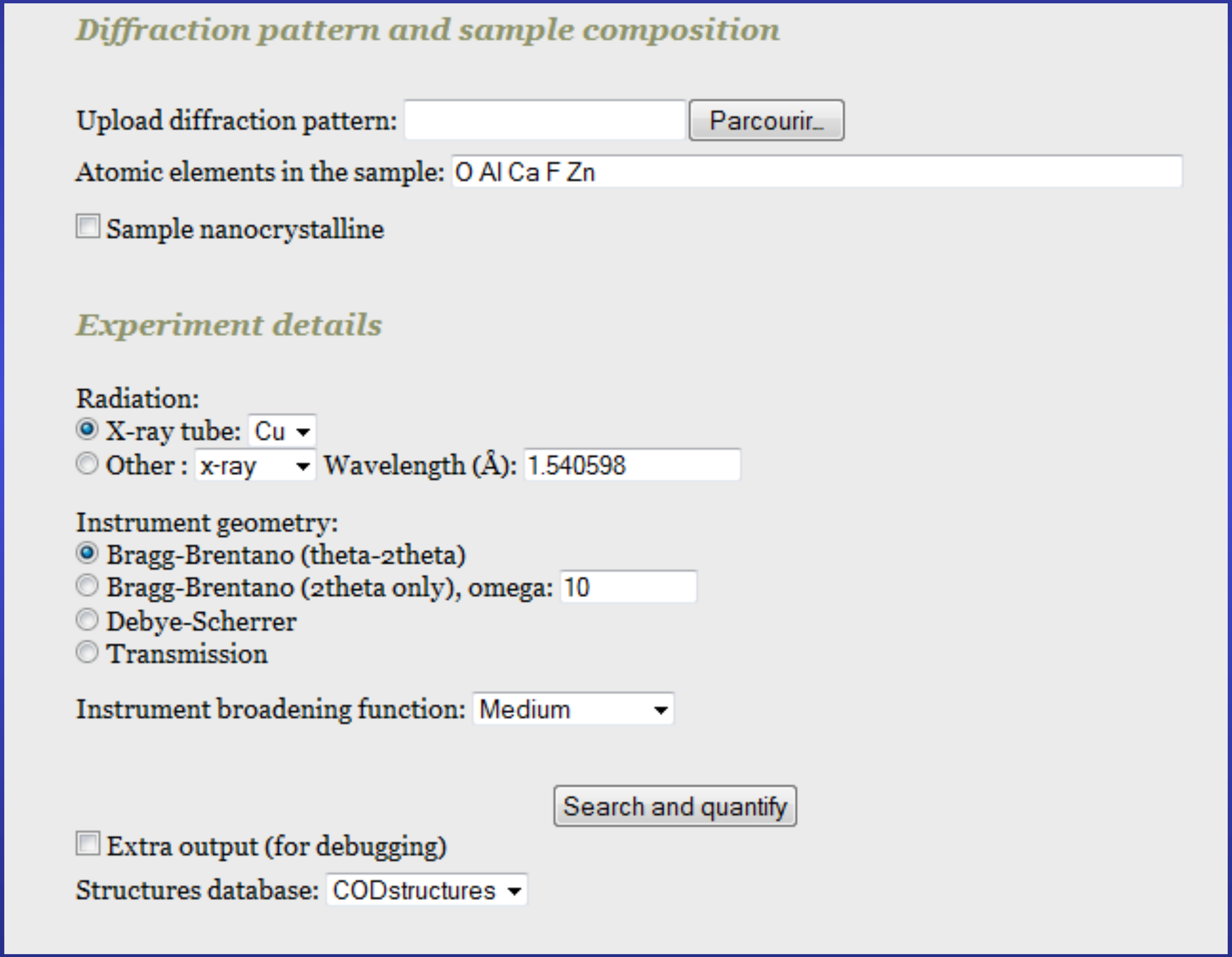
CPS scans





Useful for having bot specular and off-specular signals in one scan

Full-Profile Search-Match (FPSM)
a free internet tool for phase ID and Quant


Diffraction pattern and sample composition

Upload diffraction pattern: [ ] Parcourir...

Atomic elements in the sample: O Al Ca F Zn

☐ Sample nanocrystalline

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: Medium

Search and quantify

☐ Extra output (for debugging)

Structures database: CODstructures

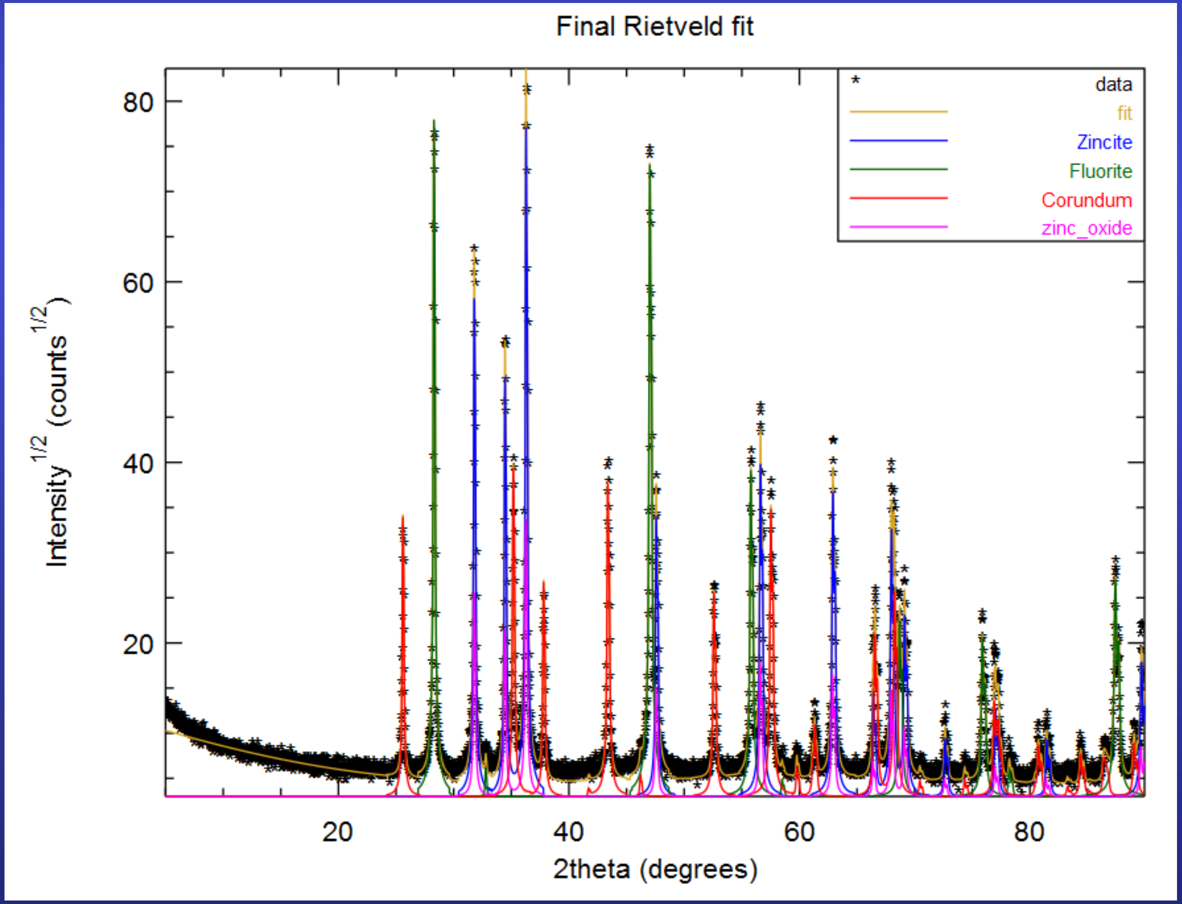
Lutterotti, Fontugne, Pillière, Boullay, Chateigner: *J. Appl. Cryst., to appear*

1 min later
>280000 COD structures

Found phases and quantification:

Phase ID	name	vol. (%)	wt. (%)	crystallites (Å)	microstrain
9004178	Zincite	16.8284	23.9708	2148.26	0.00028435
9009005	Fluorite	42.5522	33.9388	2117.08	0.000363147
9007498	Corundum	37.2197	37.2493	1889.82	0.000267779
2300112	zinc_oxide	3.39971	4.84114	1754.74	6.98311e-05

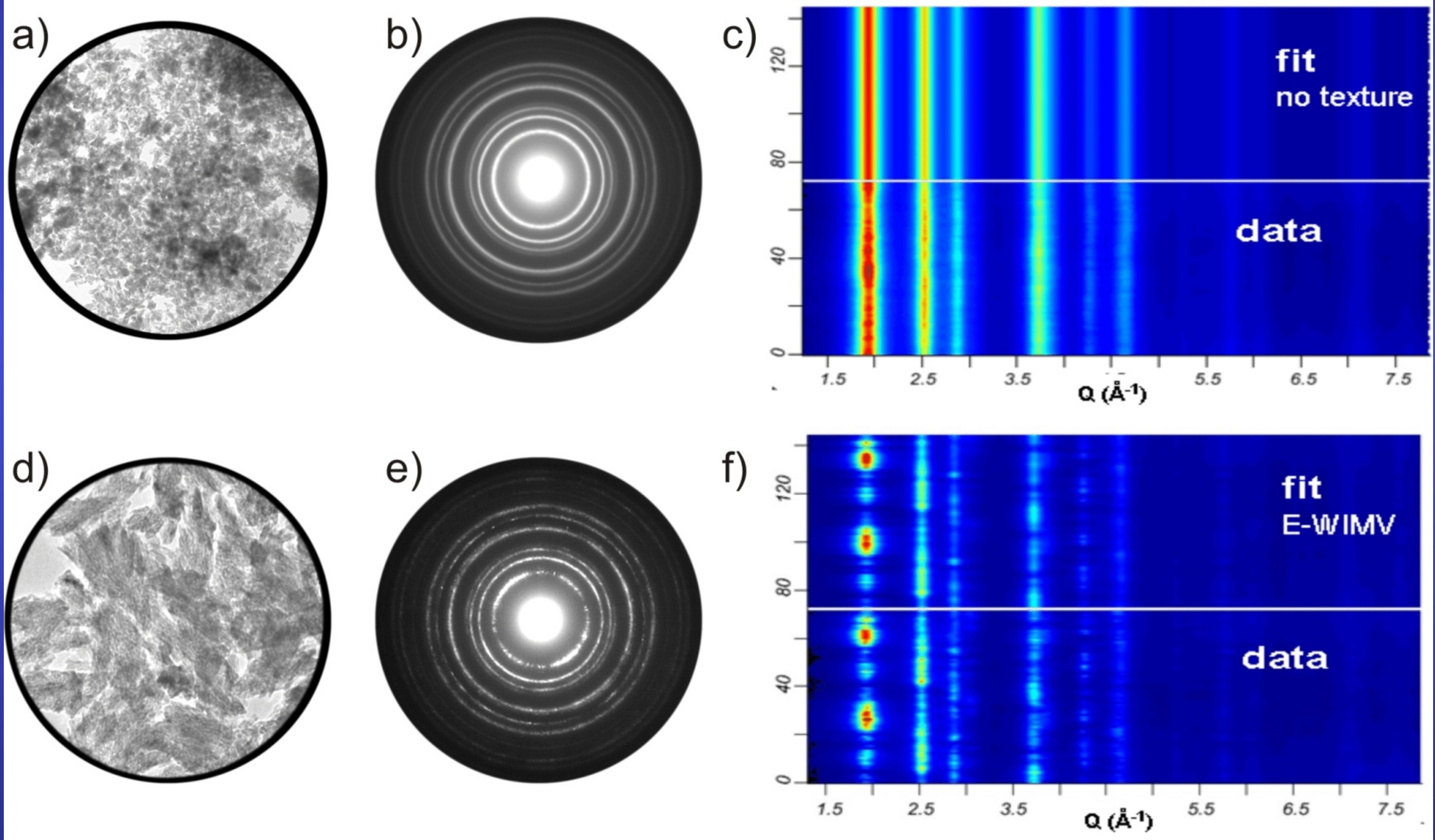
Final Rietveld analysis, Rw: 0.159468, GofF: 1.95869



TEM + QTA: local vs global

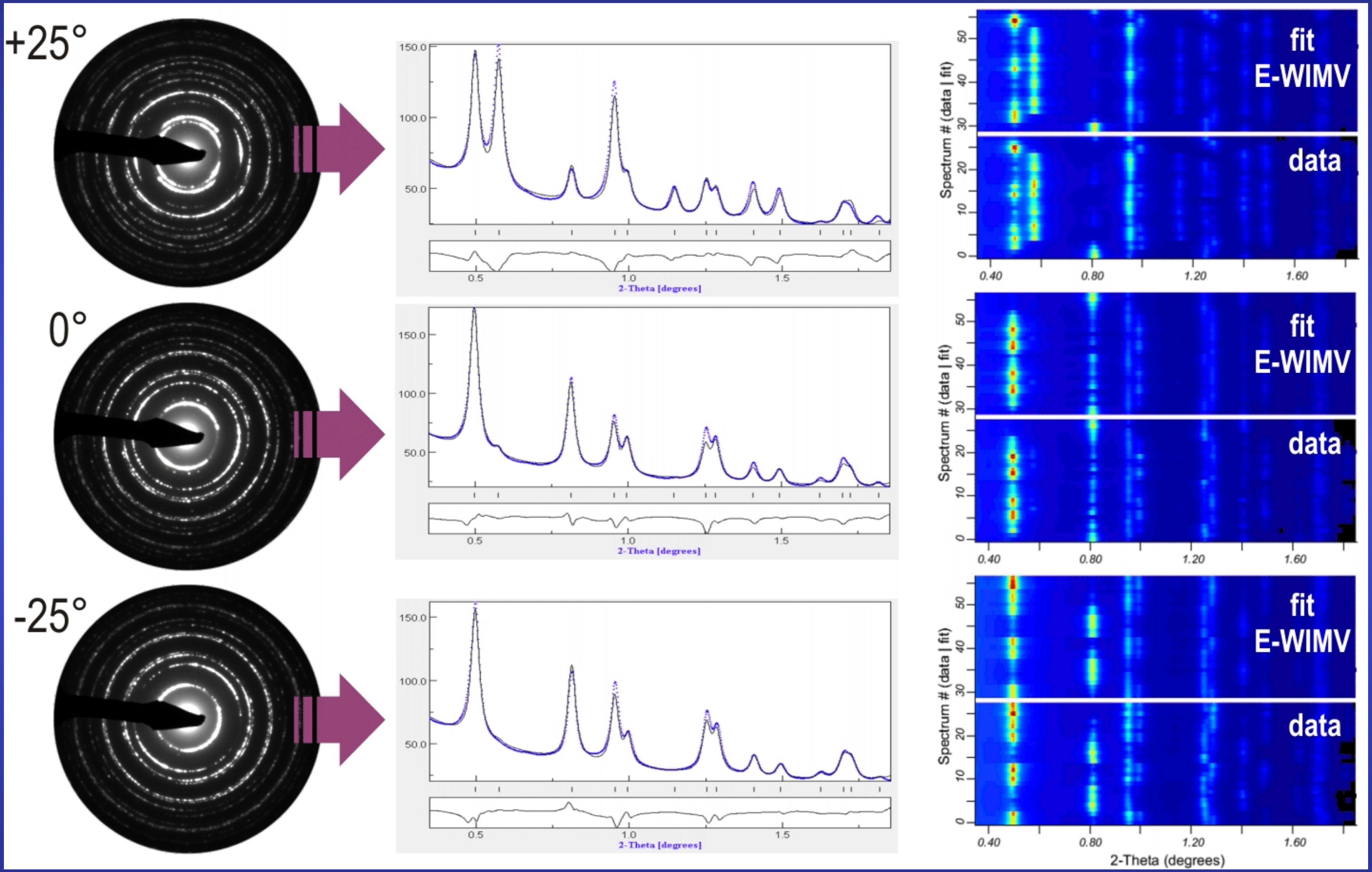
Pt thin film on Si

a) 6 µm diameter selected area, b) EPD and c) 2D plot.



d) 0.5 µm diameter selected area, e) EPD and f) 2D plot

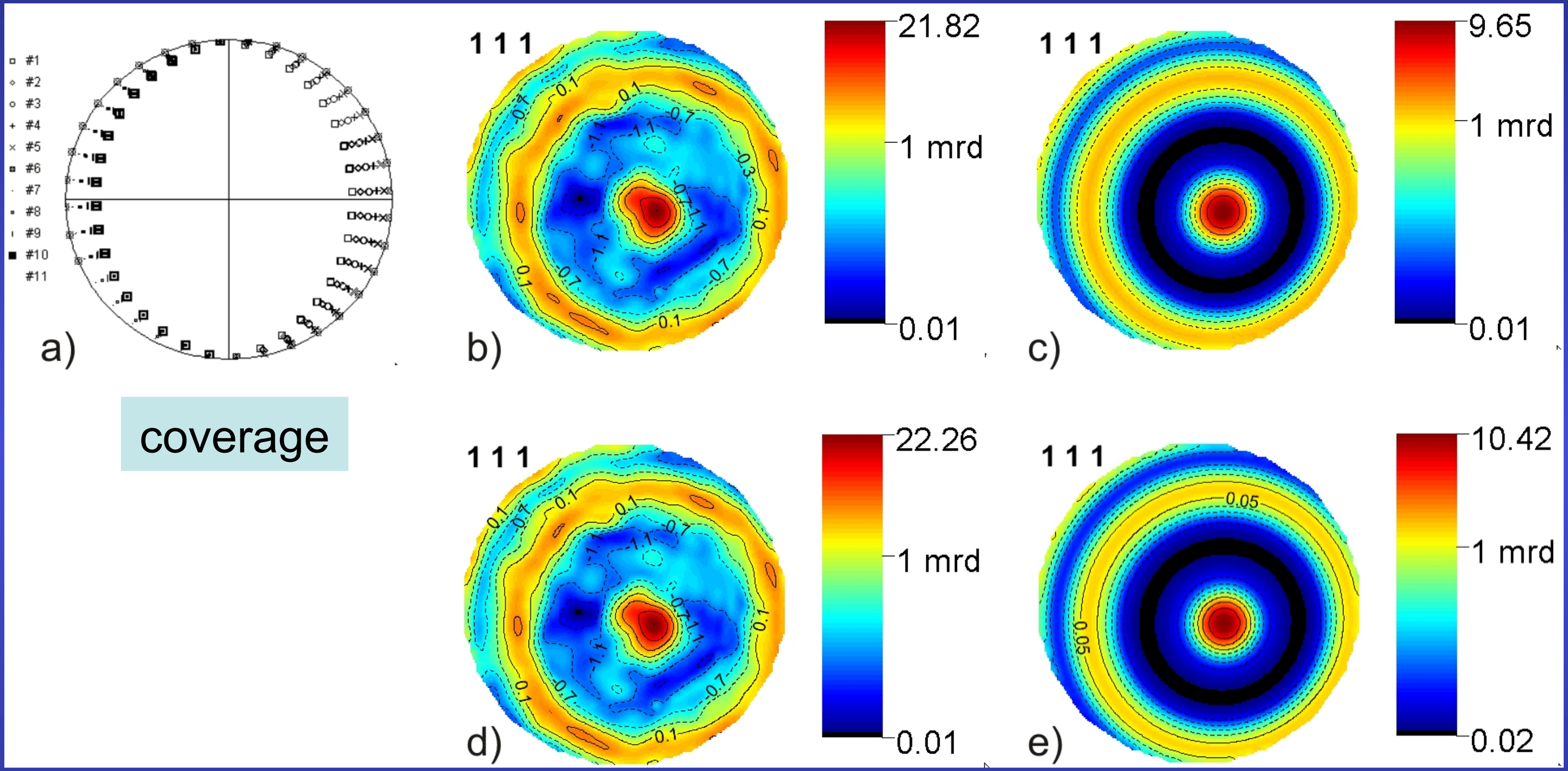
Paterns taken from +25° to -25° (step 5°) tilts: thin film prepared for TEM plan view



3 out of 11 EPD, 1D and 2D plots. Pattern matching (Pawley)

Pawley pattern matching

EWIMV Fiber component

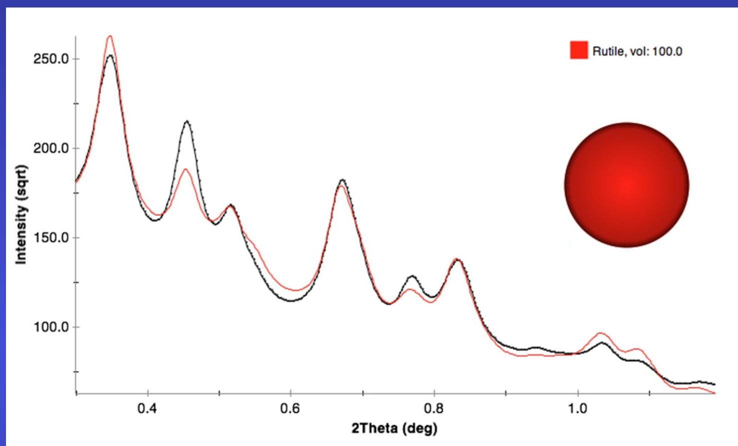


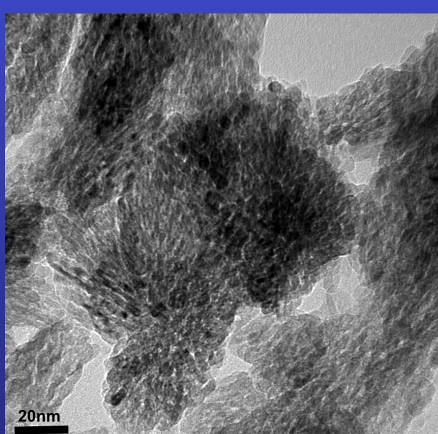
EWIMV Fiber component

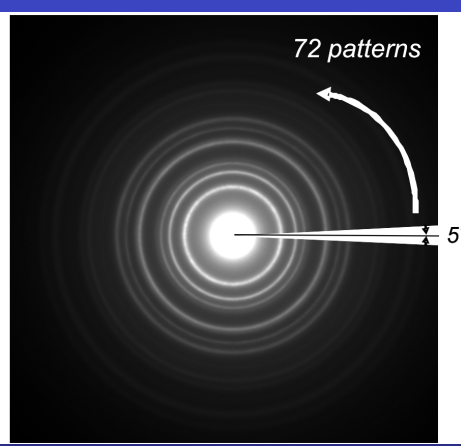
2-beams dynamical (Blackman)

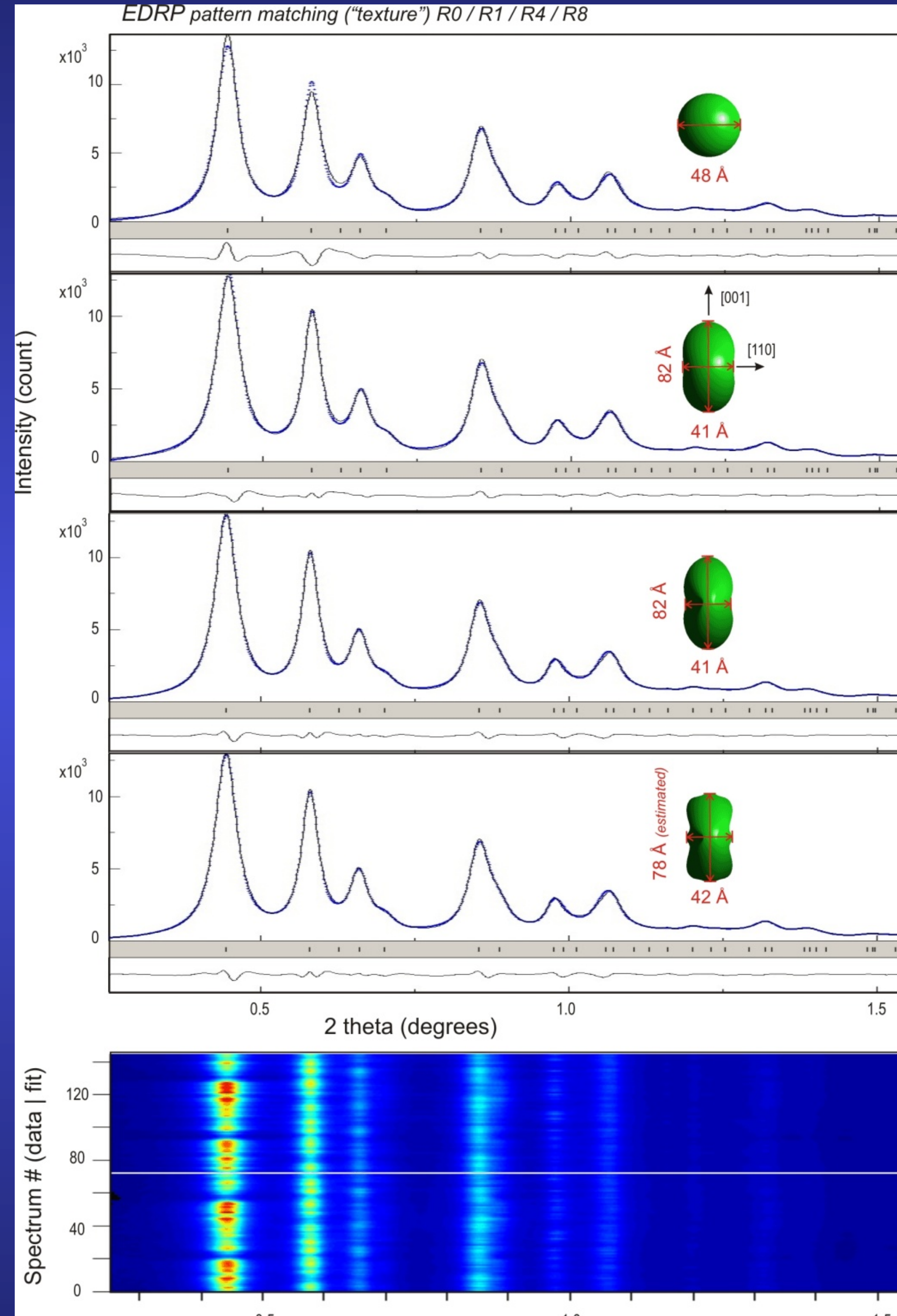
Boullay, Lutterotti, Chateigner, Sicard: *Acta Cryst. A, to appear*

TEM + QMA: TiO_2 nanopowder

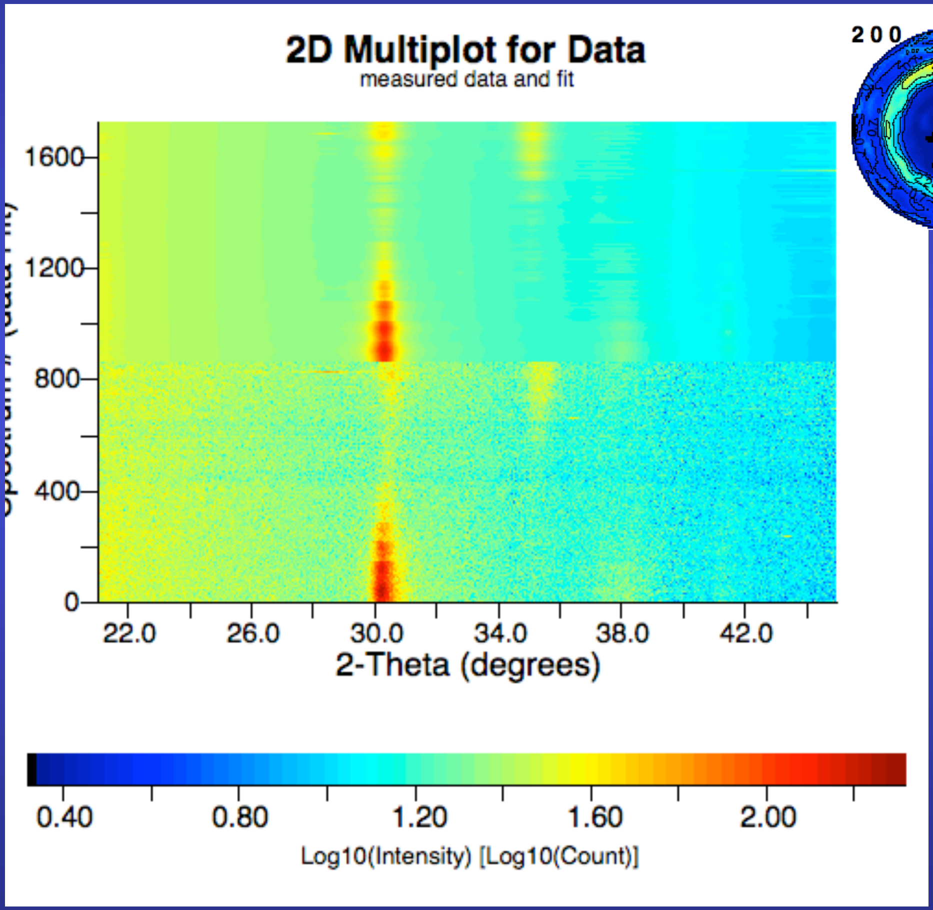


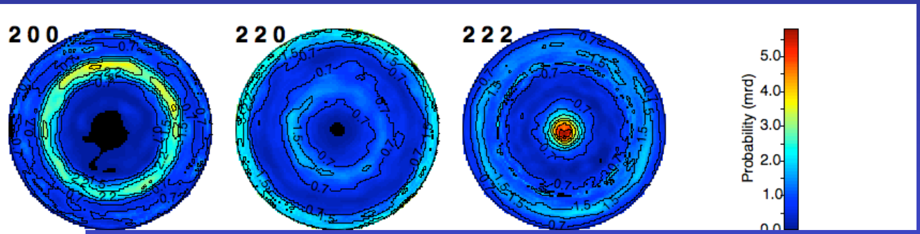




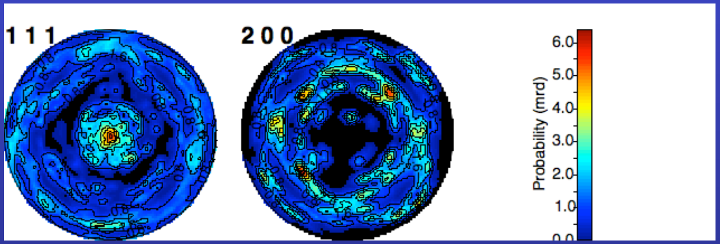


XRF + XRR + Combined Analysis: $In_2O_3/Ag/In_2O_3/Si$ stack



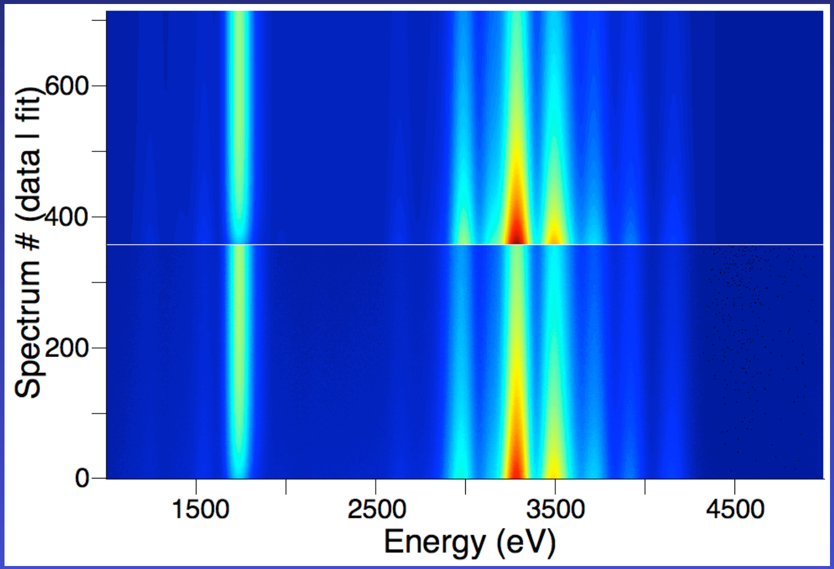


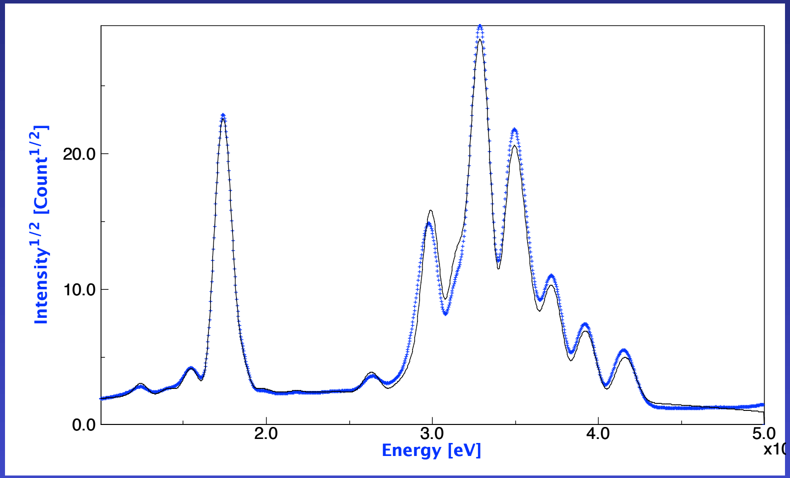
a = 1.02104(5) nm
<R> (spherical) : 153.2(5) nm
σ_{11} = 185(25) MPa

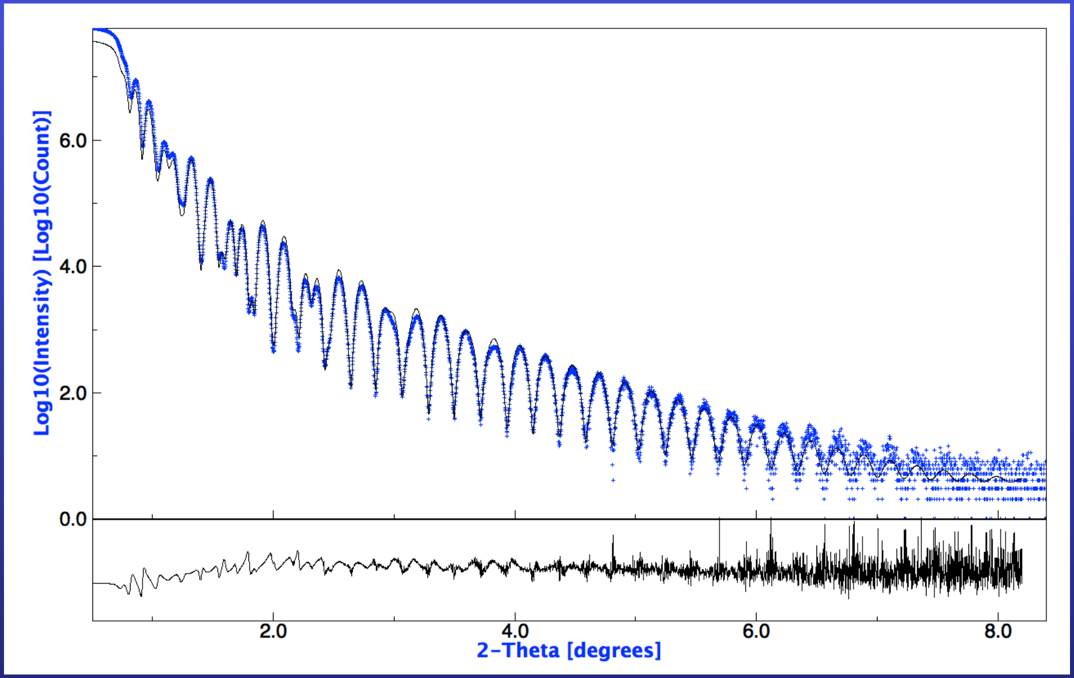


a = 0.40943(7) nm
<R> (spherical) : 97.4(1.3) nm

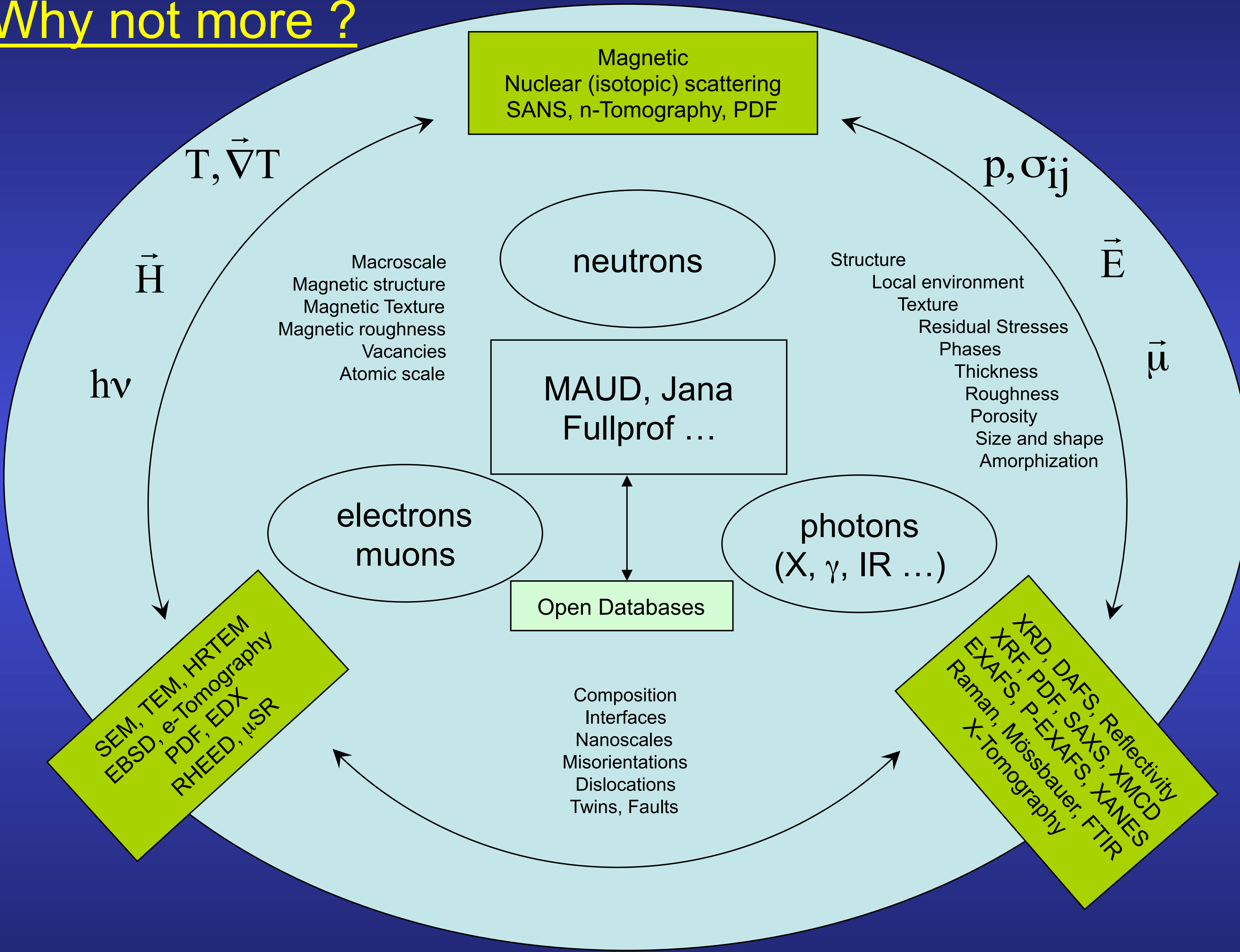
GoF = 1.09


Spectrum # (data I fit)
600
400
200
0
1500
2500
3500
4500
Energy (eV)


Intensity^1/2 [Count^1/2]
20.0
10.0
0.0
2.0
3.0
4.0
5.0
Energy [eV]


Log10(Intensity) [Log10(Count)]
6.0
4.0
2.0
0.0
2.0
4.0
6.0
8.0
2-Theta [degrees]

Why not more ?


Magnetic
Nuclear (isotopic) scattering
SANS, n-Tomography, PDF
$T, \vec{\nabla}T$
p, σ_{ij}
$\vec{H}$
$\vec{E}$
$h\nu$
$\vec{\mu}$
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, PDF, SAXS, XMCD
EXAFS, P-EXAFS, XANES
Raman, Mössbauer, FTIR
X-Tomography
Composition
Interfaces
Nanoscales
Misorientations
Dislocations
Twins, Faults

Conclusions

A lot of problems can be solved !

Texture helps to resolve them: good for real samples, good for nanomaterials description !

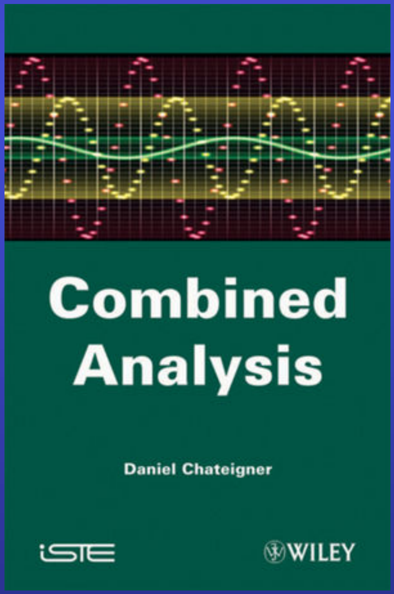
Anisotropy favours higher resolutions

Combined analysis may be a solution, unless you can destroy your sample or are not interested in macroscopic anisotropy ...

If you think you can destroy it, perhaps think twice

Combined Analysis Workshop in Caen:
30th June – 4th July 2014 !

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



Thanks !