Combined Analysis: structure, microstructure, texture, stresses, phase, reflectivity

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Structure determination on real (textured) samples
Dilemma 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

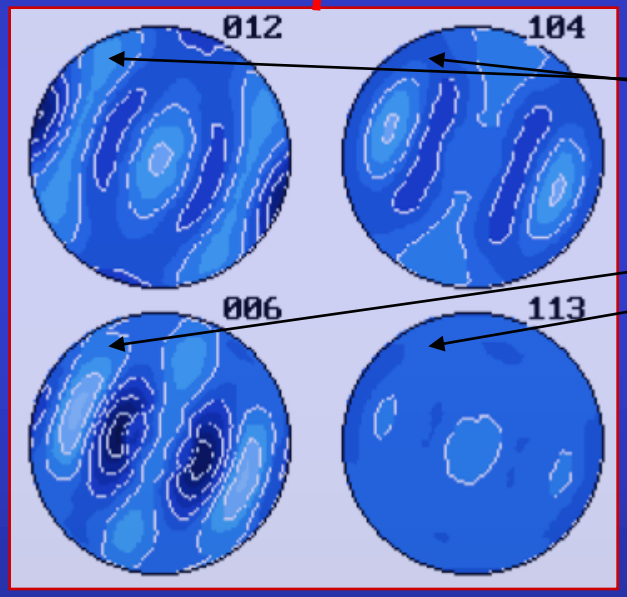
- work on the sum of all diagrams on average

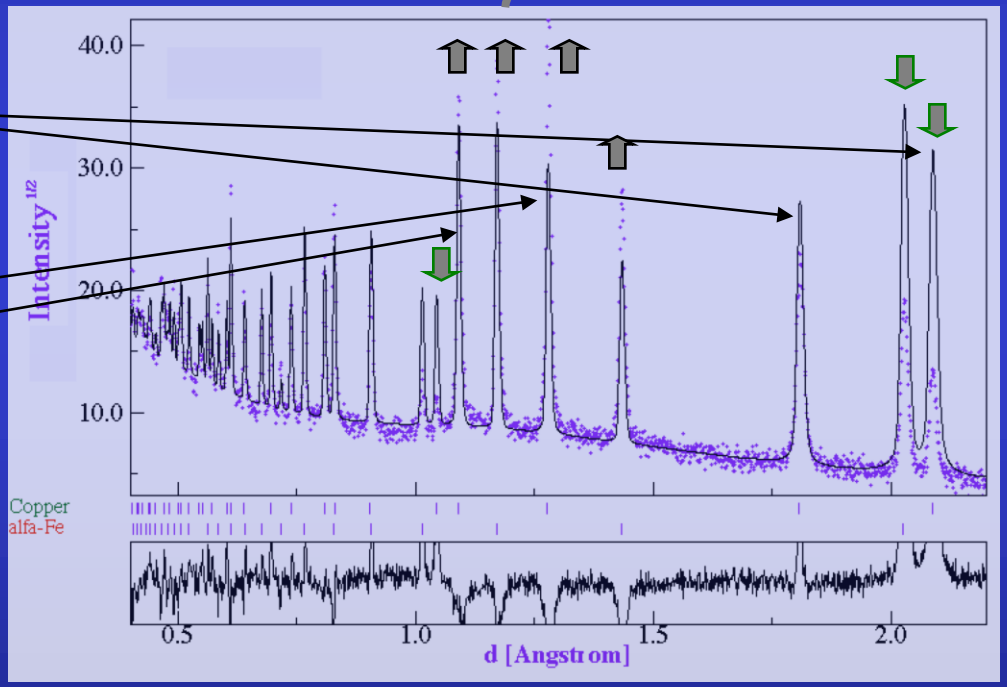
Texture from Spectra

Orientation Distribution Function (ODF)

From pole figures

From spectra





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

Residual Stresses shift peaks with **y**

Dilemma 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

Layered systems
Dilemma 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)

Phase and Texture
Dilemma 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)

Residual Stresses shift peaks with **y**
Dilemma 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

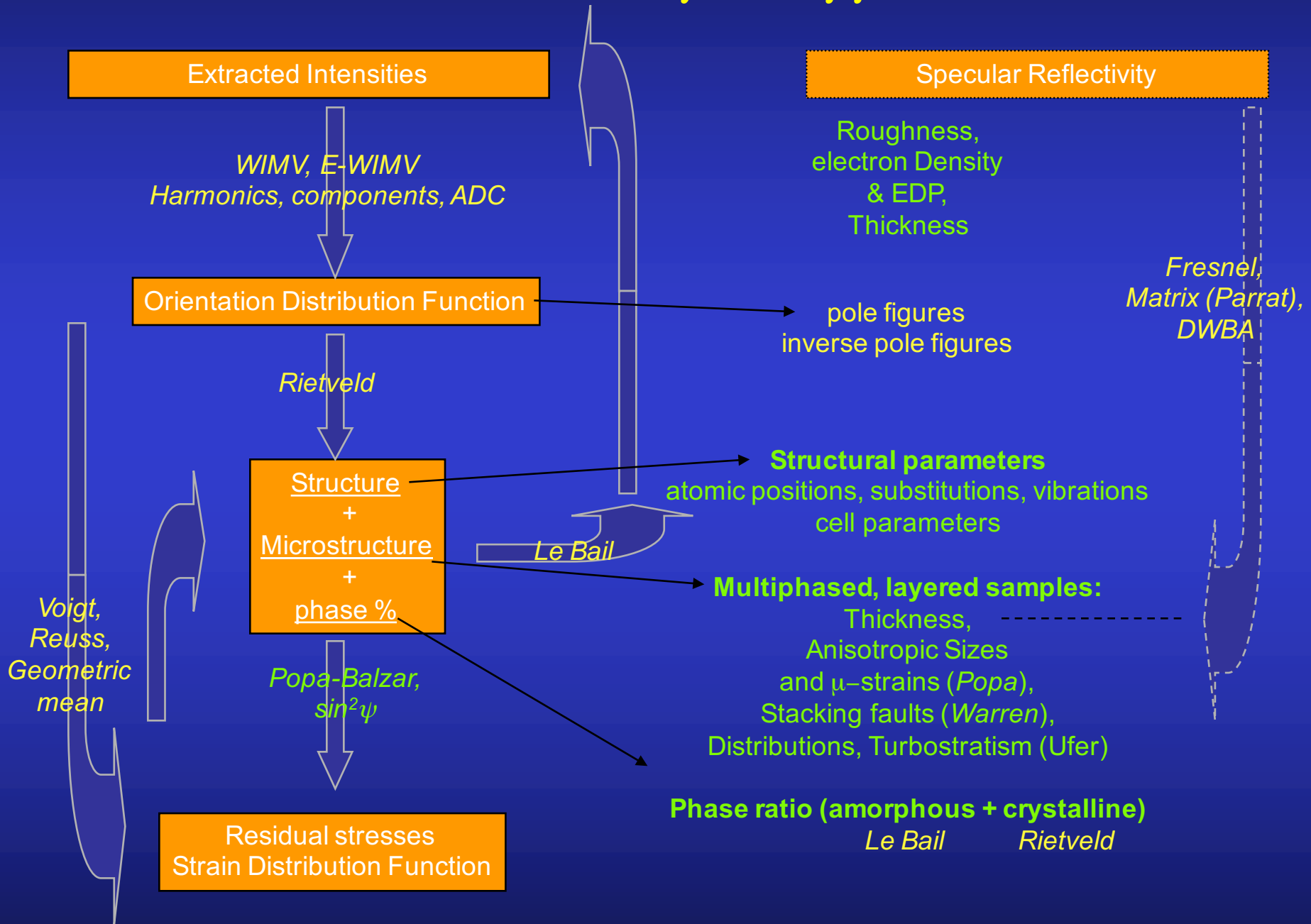
Shapes, microstrains, defaults, distributions
Dilemma 6

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

Combined Analysis approach



Grinding to powderise another dilemma !

Grinding: removes angular relationship, adds correlations

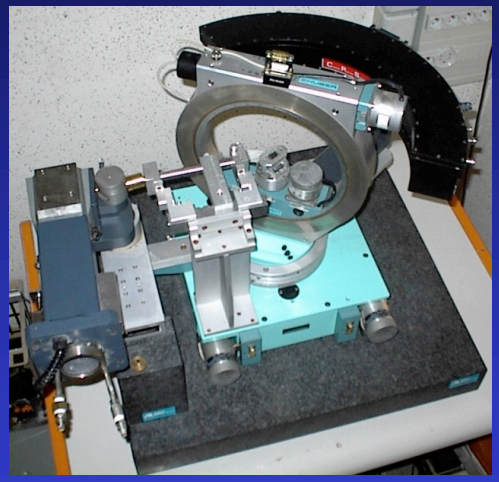
Texture:
- not measured
- removed ? hope to get a perfect powder

Strains, defaults, anisotropy … :
- some removed, some added

Same sample ?

Rare samples ?

Minimum experimental requirements



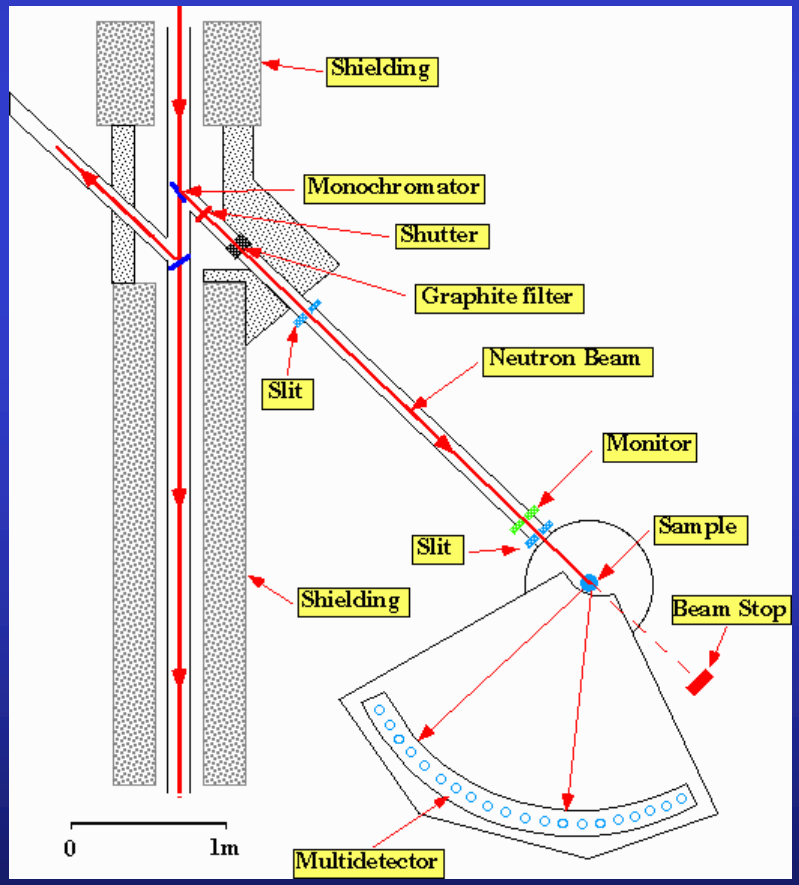
1D or 2D Detector + 4-circle diffractometer
(X-rays and neutrons)
CRISMAT, ILL

+

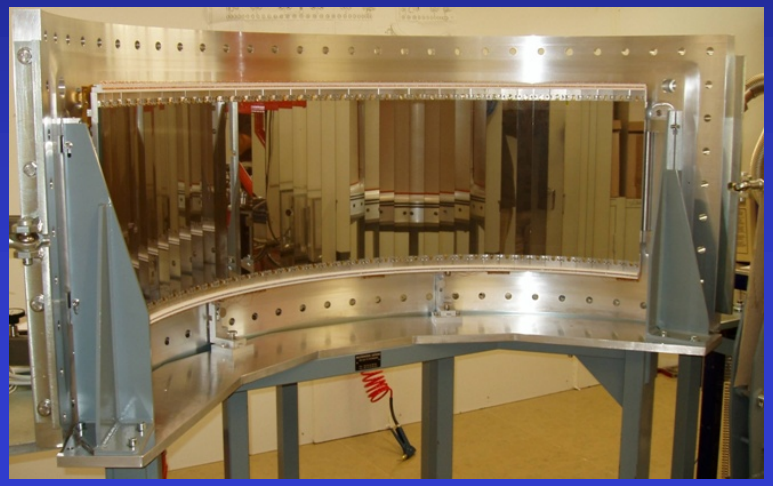
~1000 experiments (2θ diagrams)
in as many sample orientations

+

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



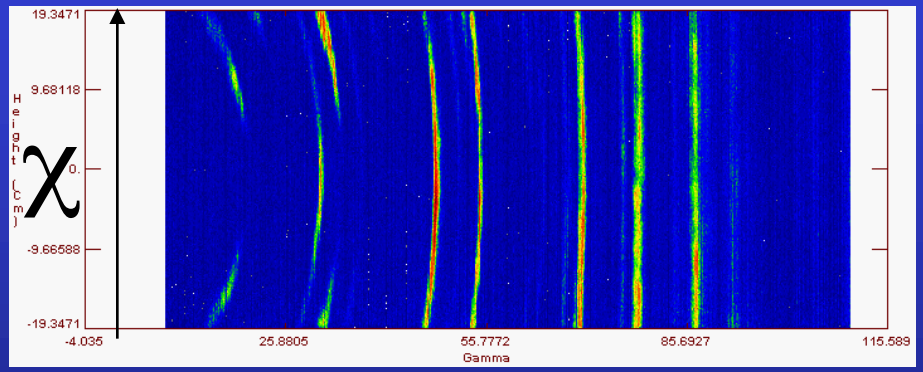
2D Curved Area Position Sensitive Detector

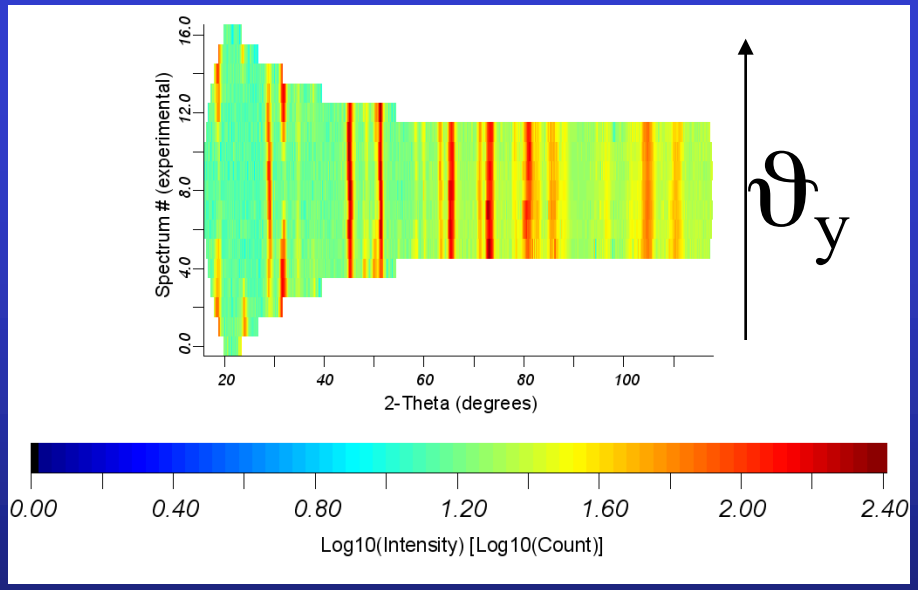


D19 - ILL

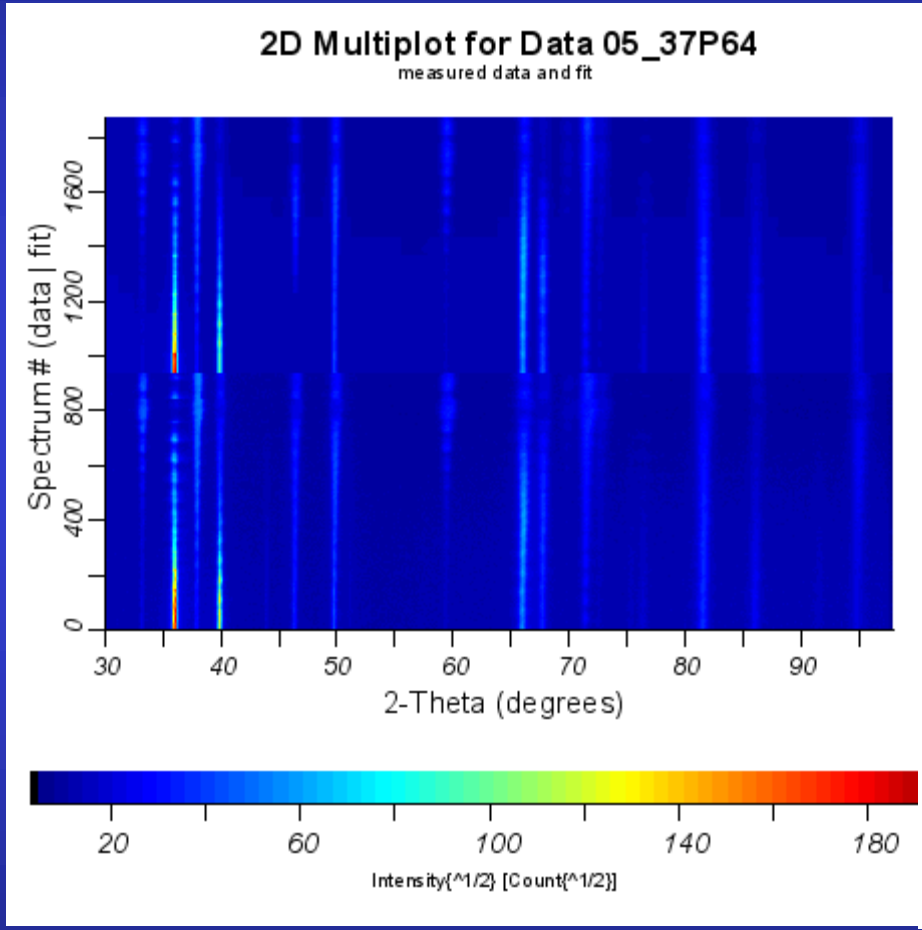
+

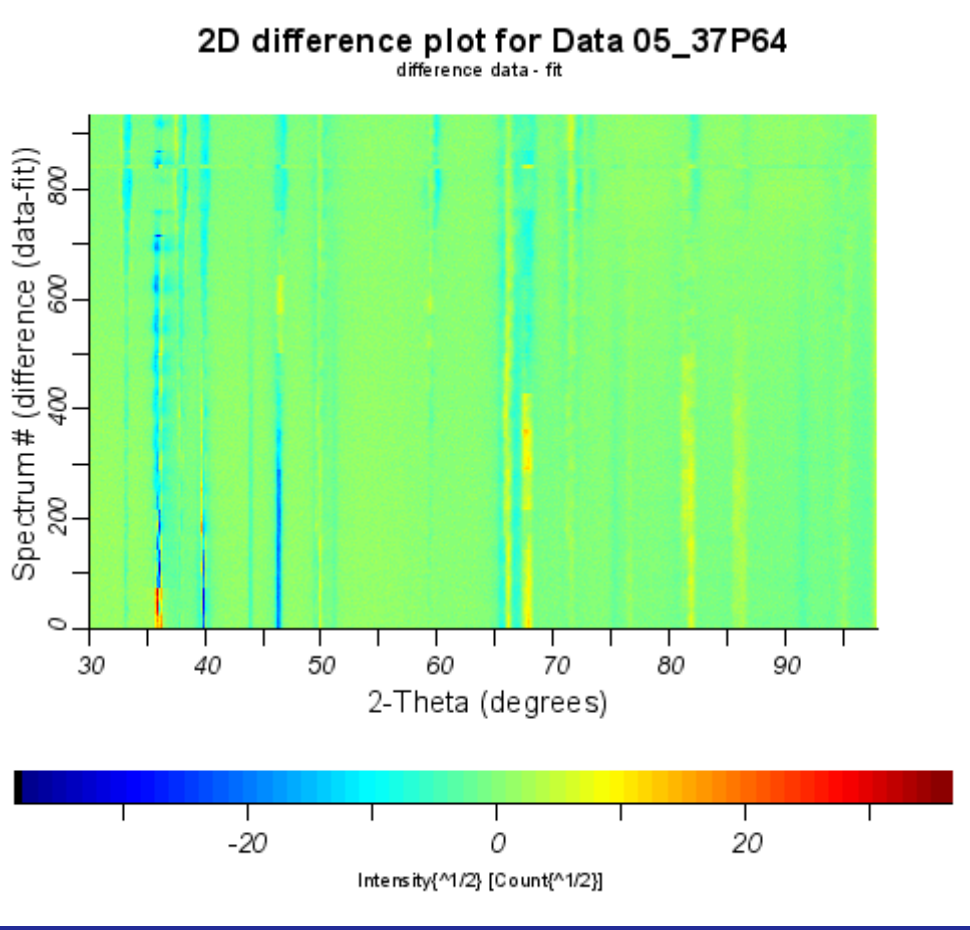
~100 experiments (2D Debye-Scherrer diagrams)
in as many sample orientations





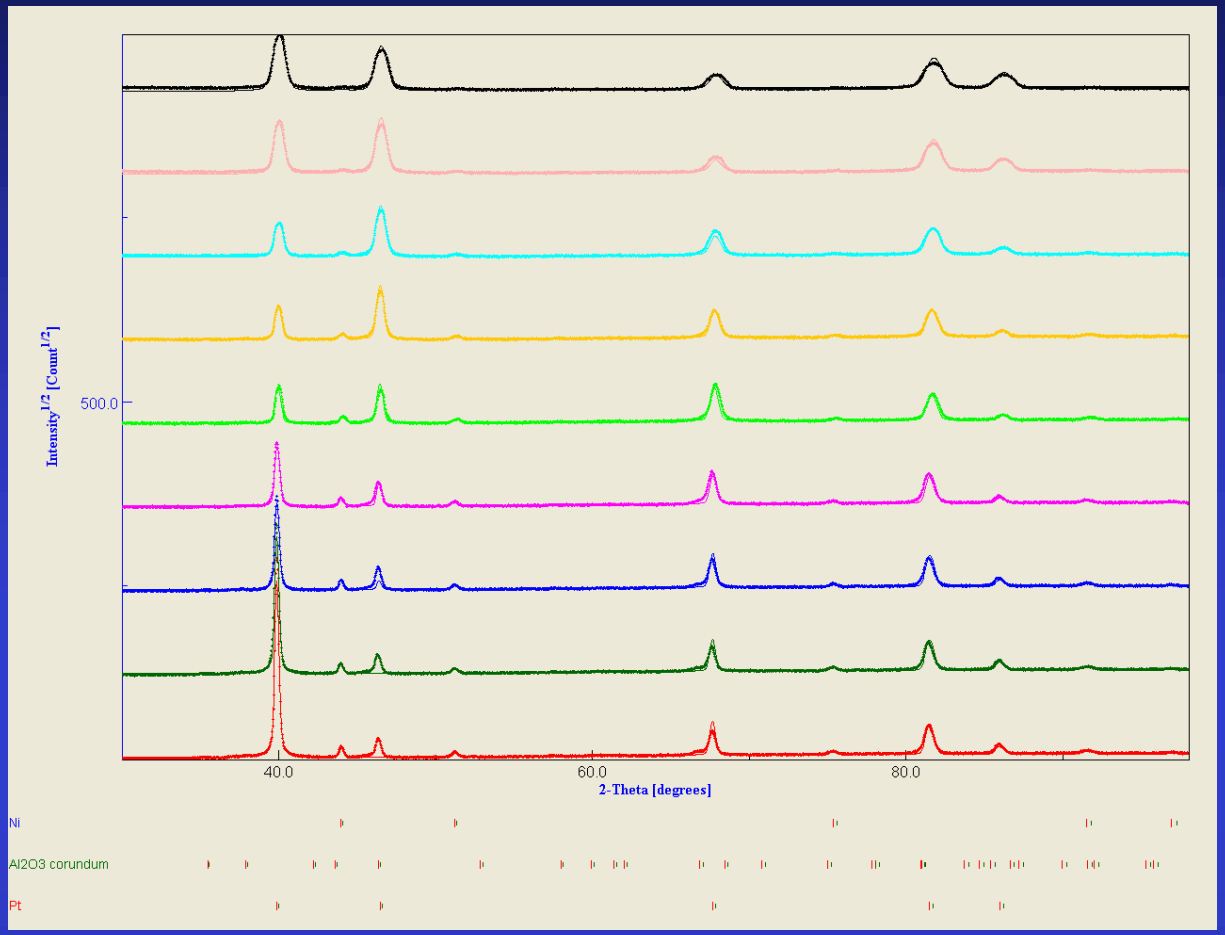
$AlN/Pt/TiO_x/Al_2O_3/Ni\text{-}Co\text{-}Cr\text{-}Al$





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

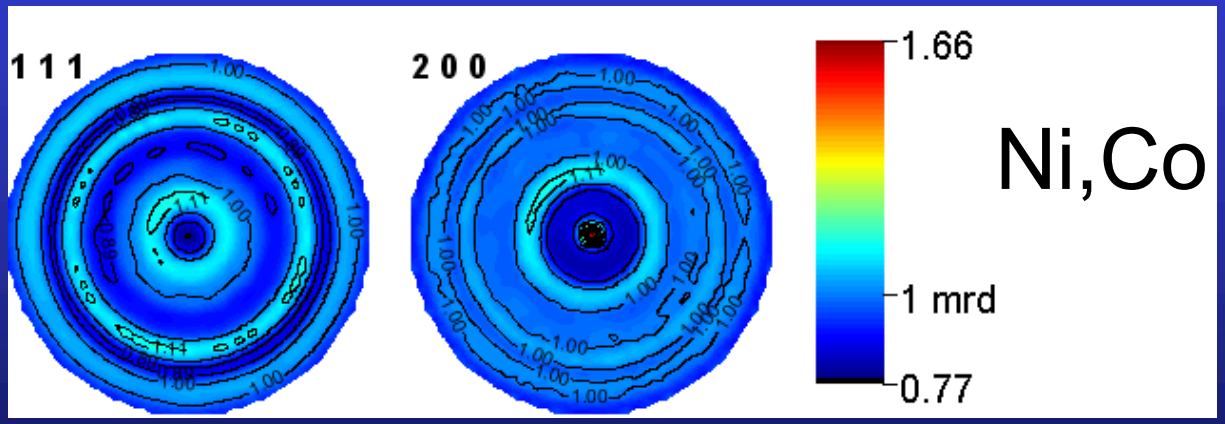
T(AlN) = 14270(3) nm
T(Pt) = 430(3) nm



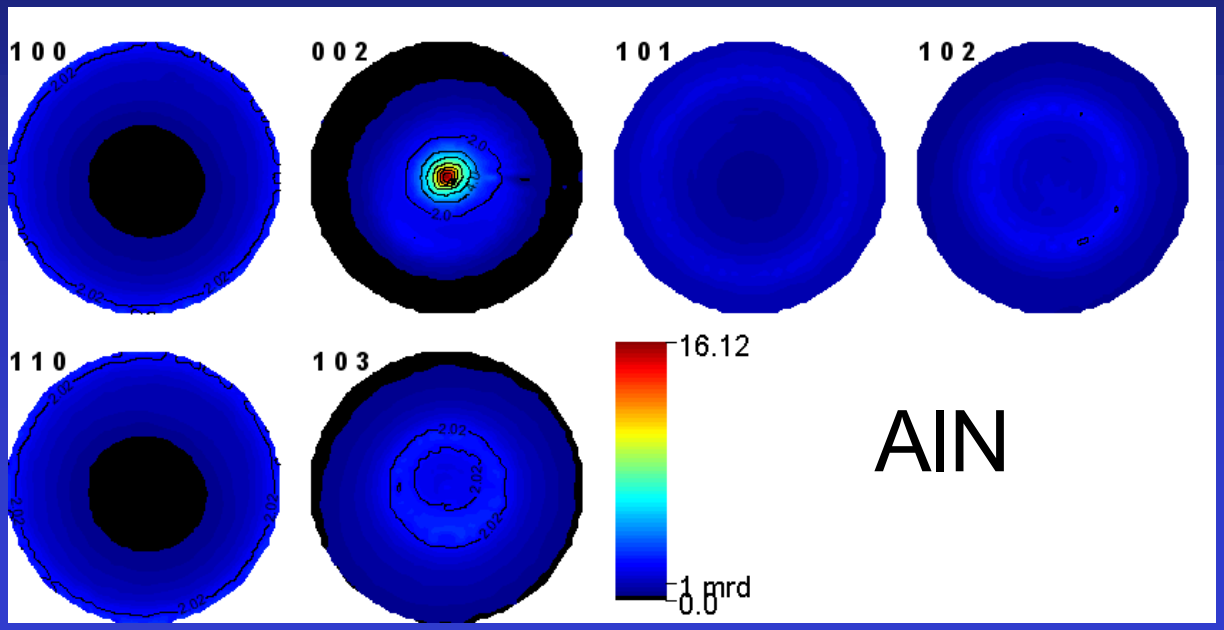
(χ,φ) randomly selected diagrams

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)

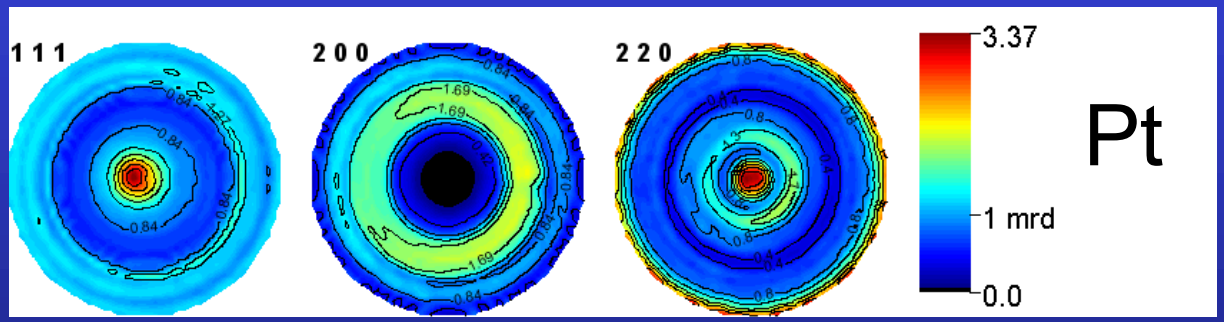


a = 3.569377(5) Å
<t> = 7600(1900) Å
<ε> = 0.00236(3)
σ_{11} = -328(8) MPa
σ_{22} = -411(9) MPa



Rw (%) = 4.1

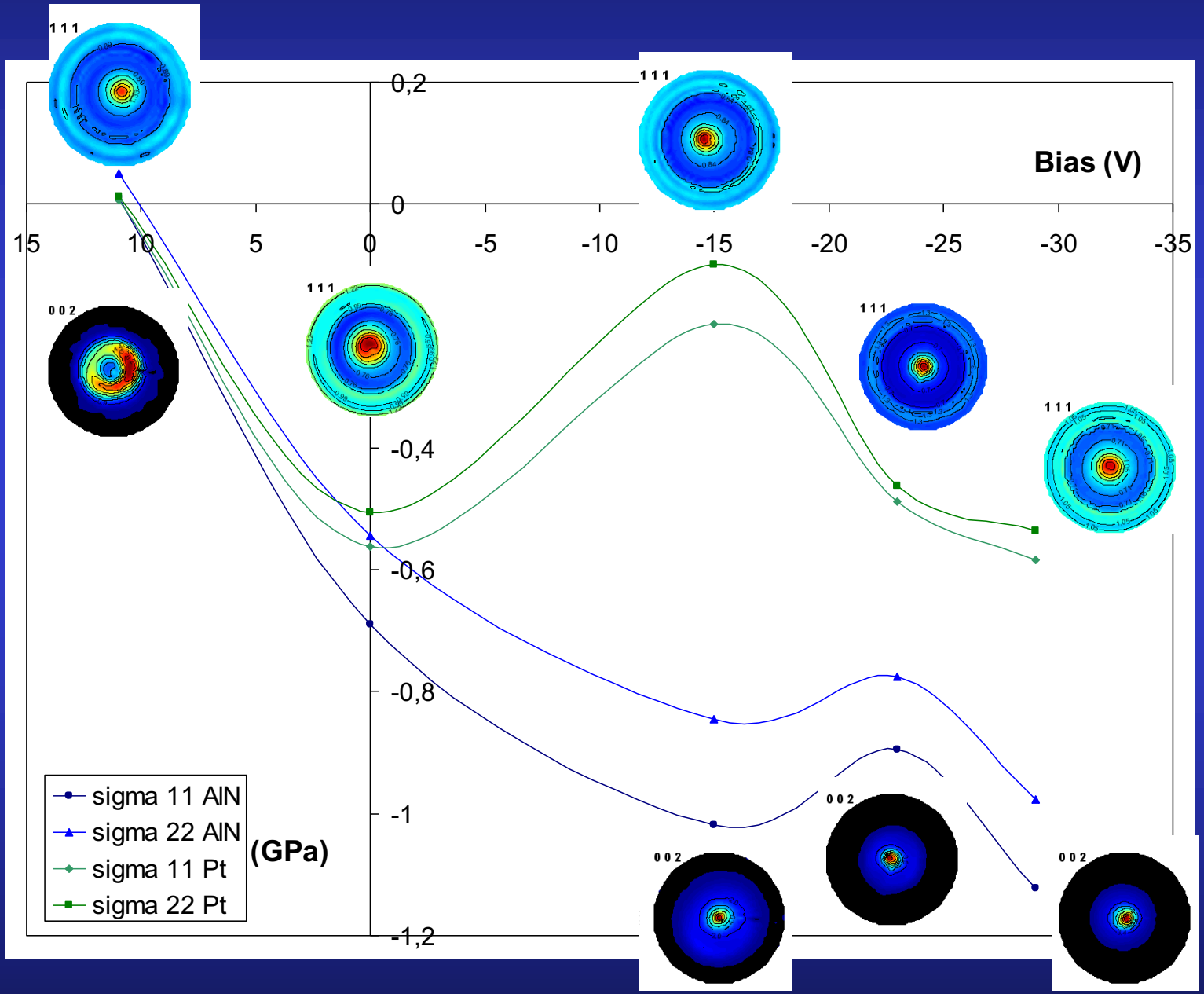
a = 3.11203(1) Å
c = 4.98252(1) Å
T = 14270(3) nm
<t> = 2404(8) Å
<ε> = 0.001853(2)
σ_{11} = -1019(2) MPa
σ_{22} = -845(2) MPa



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



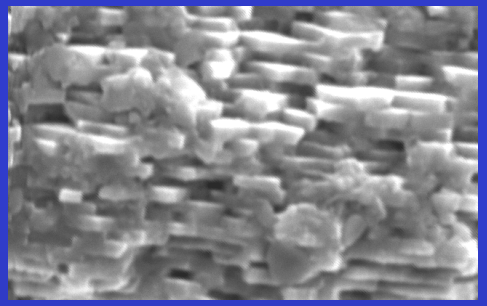
Aragonitic layers in mollusc shells

Gastropods

Crossed lamellar layers

Charonia lampas lampas (triton or trumpet cousin)

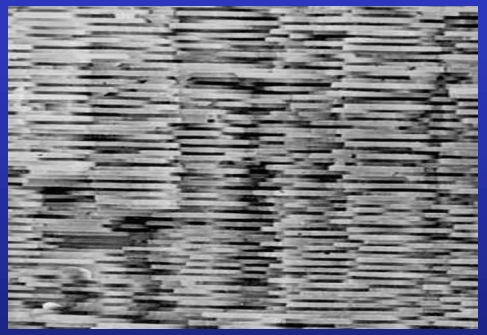
Columnar Nacre



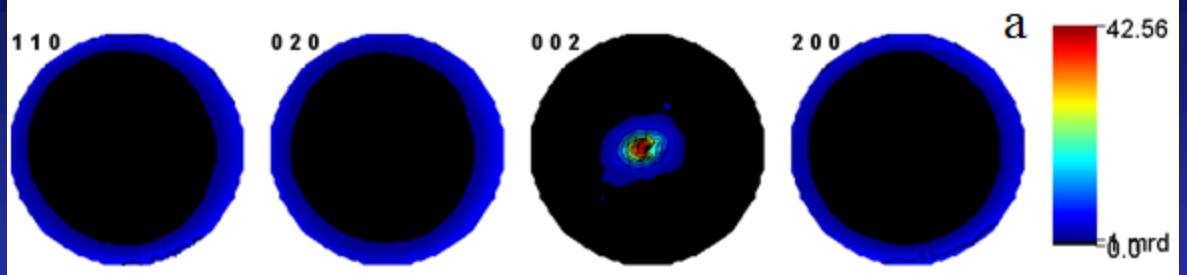
Haliotis tuberculata (common abalone)

Bivalves

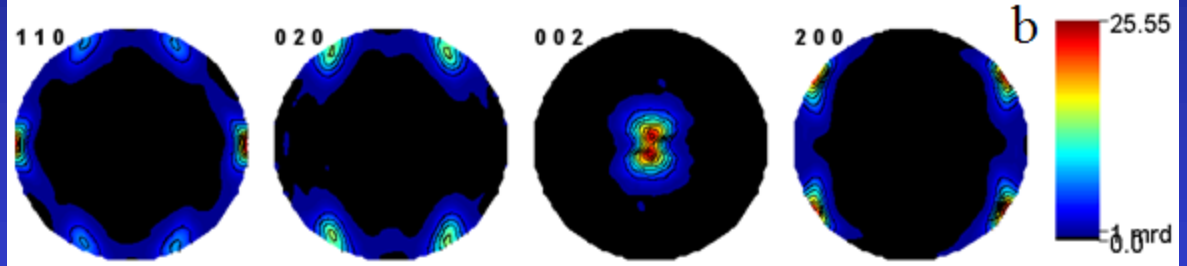
Sheet Nacre



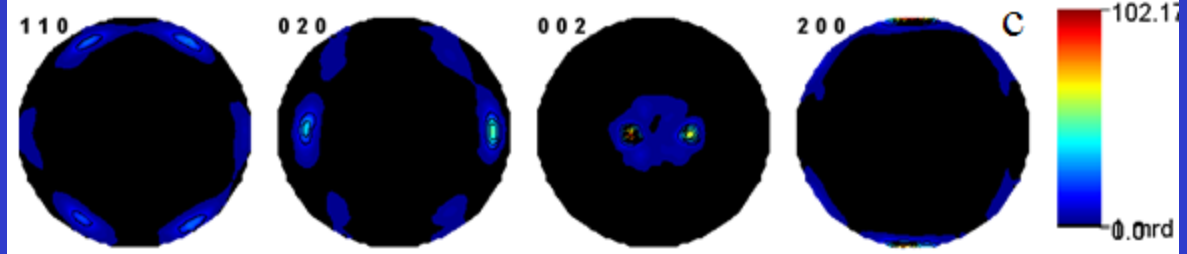
Pinctada maxima (Mother of pearl oyster)



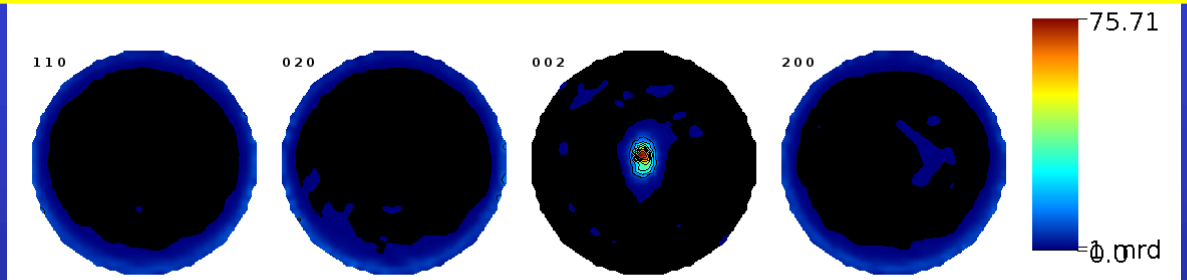
Outer CL
43 mrd^2



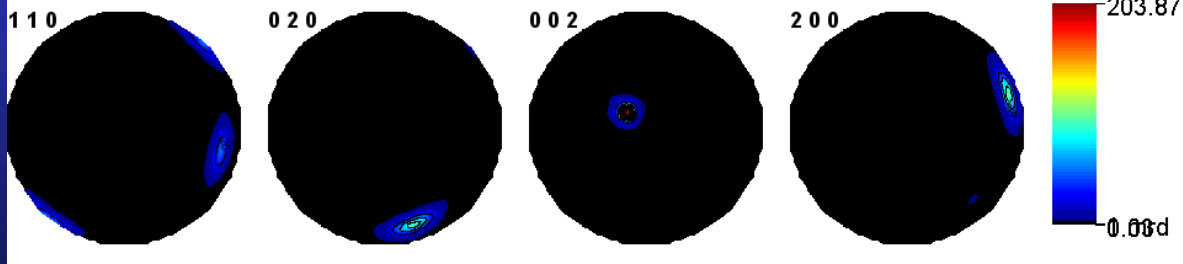
Interm Radial CL
47 mrd^2



Inner Com CL
721 mrd^2



Inner Columnar Nacre
211 mrd^2



Inner Sheet Nacre
1100 mrd^2

Unit-cell distortions

	OCL	*Charonia* IRCL	ICCL	*Pinctada* ISN	*Haliotis* ICN
a (Å)	4,98563(7)	4,97538(4)	4,9813(1)	4,97071(4)	4.9480(2)
b (Å)	8,0103(1)	7,98848(8)	7,9679(1)	7,96629(6)	7.9427(6)
c (Å)	5,74626(3)	5,74961(2)	5,76261(5)	5,74804(2)	5.7443(6)
Δa/a	0,0047	0,0026	0,0038	0.0017	-0.0029
Δb/b	0,0053	0,0026	0,0000	-0.0002	-0.0032
Δc/c	0,0004	0,0010	0,0033	0.0007	0.0007
ΔV/V (%)	1,05	0,62	0,71	0.22	-0.60

Anisotropic cell distortion - depends on the layer

Only nacres exhibit (**a**,**b**) contraction

Due to inter- and intra-crystalline molecules

Distortions and anisotropies larger than pure intra- effect (Pokroy et al. 2007)

Elastic stiffnesses

Single crystal	160	37.3 87.2	1.7 15.7 84.8	41.2	25.6	42.7
ICCL	96.5	31.6 139	13.7 9.5 87.8	29.8	36.6	40.2
RCL	130.1	32.6 103.3	10.3 14.1 84.5	36.3	31.1	40.5
OCL	111.1	32.9 119	13.2 11.8 84.8	32.8	34.6	40.9

Atomic Structures

		Geological reference	*Charonia lampas* OCL	*Charonia lampas* IRCL	*Charonia lampas* ICCL	*Strombus decorus* mixture	*Pinctada maxima* ISN
Ca	y z	0.41500 0.75970	0.41418(5) 0.75939(3)	0.414071(4) 0.76057(2)	0.41276(9) 0.75818(8)	0.4135(7) 0.7601(8)	0.41479 (3) 0.75939 (2)
C	y z	0.76220 -0.08620	0.7628(2) -0.0920(1)	0.76341(2) -0.08702(9)	0.7356(4) -0.0833(2)	0.7607(4) -0.0851(7)	0.7676 (1) -0.0831 (1)
O1	y z	0.92250 -0.09620	0.9115(2) -0.09205(8)	0.9238(1) -0.09456(6)	0.8957(3) -0.1018(2)	0.9228(4) -0.0905(9)	0.9134 (1) -0.09255 (7)
O2	x y z	0.47360 0.68100 -0.08620	0.4768(1) 0.6826(1) -0.08368(6)	0.4754(1) 0.68332(9) -0.08473(5)	0.4864(3) 0.6834(2) -0.0926(1)	0.4763(6) 0.6833(3) -0.0863(7)	0.4678 (1) 0.68176 (7) -0.09060 (4)
ΔZ_{C-O1} (Å)		**0.05744**	**0.00029**	**0.04335**	**0.1066**	**0.031**	**0,054**

Carbonate group aplanarity specific to a given layer

Aplanarity decreases from inner to outer shell layers (CL layers)

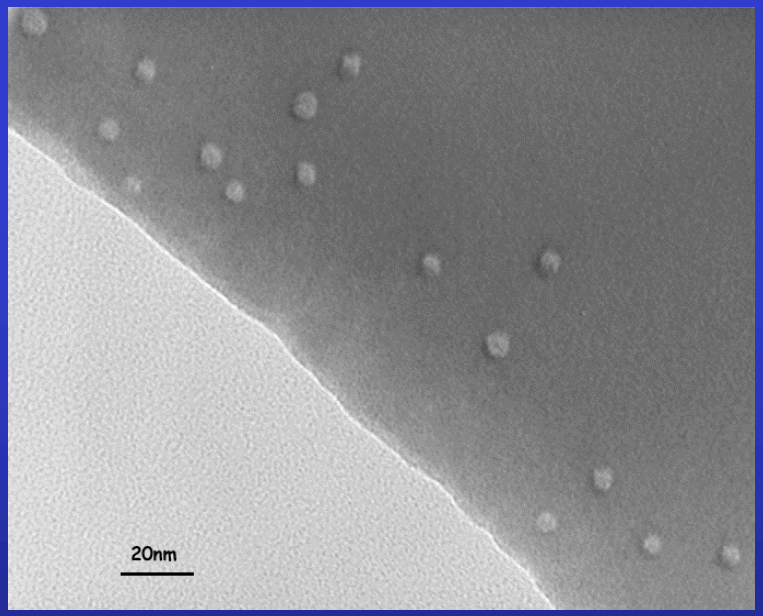
-> up to quite $\Delta Z=0$ outside (nearly the calcite value)

Average aplanarity on the whole shell = geological reference (Strombus)

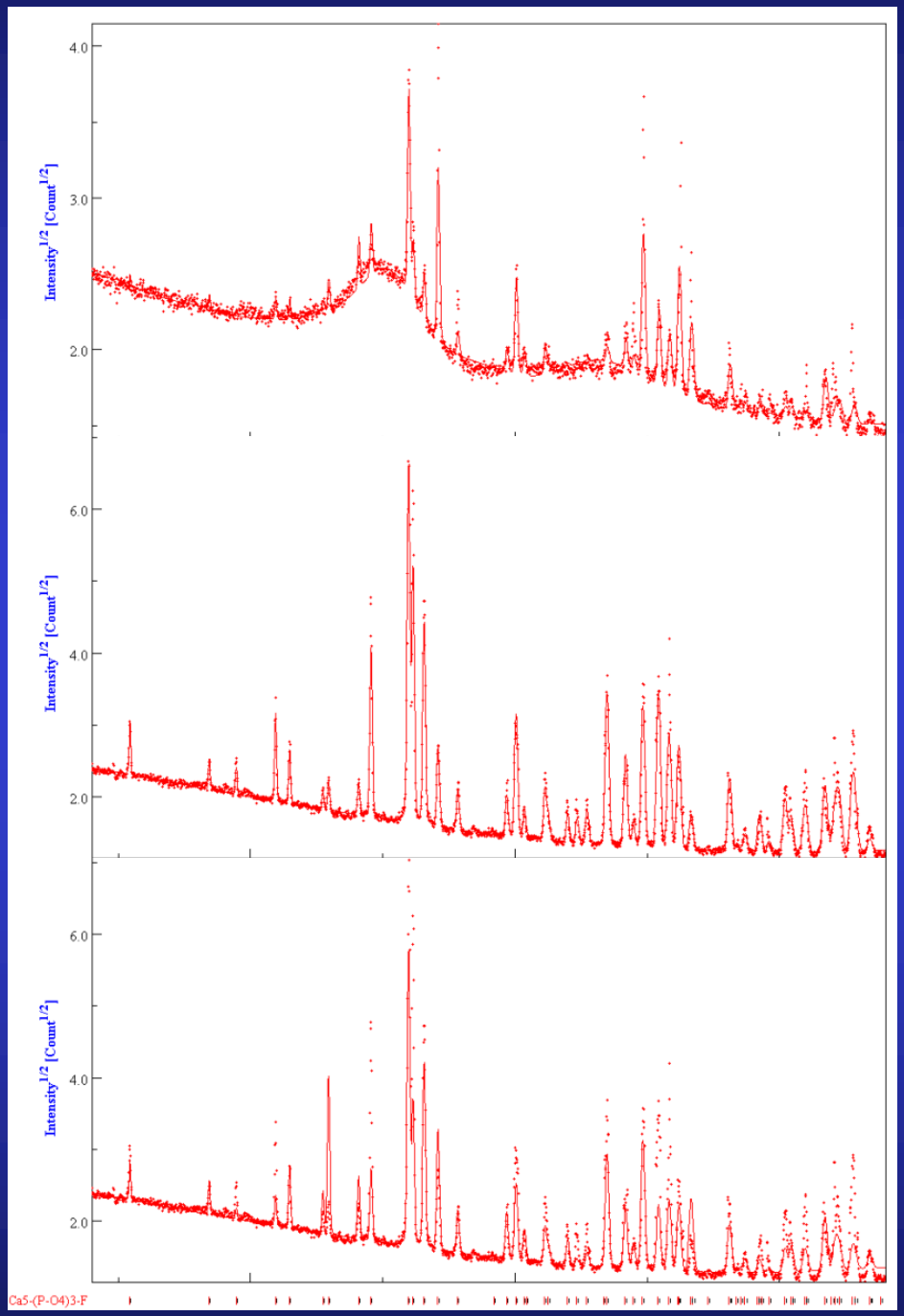
In Haliotis nacre: large $\Delta Z=0.08$, + strong anisotropy: less stable nacre

Irradiated FluorApatite (FAp) ceramics

Self-recrystallisation under irradiation, depending on SiO_4 / PO_4 ratio (FAp / Nd-Britholite) and on irradiating species



TEM of FAp irradiated with 70 MeV, 10^{12} Kr cm^{-2} ions



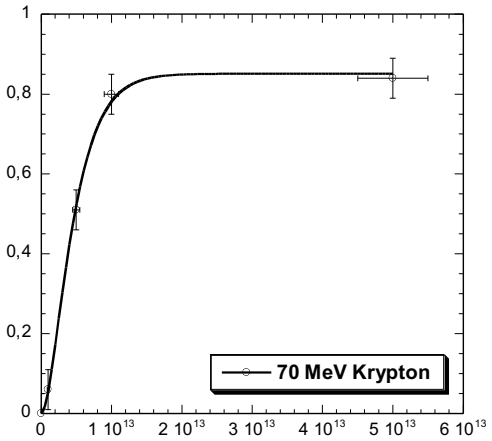
texture corrected,

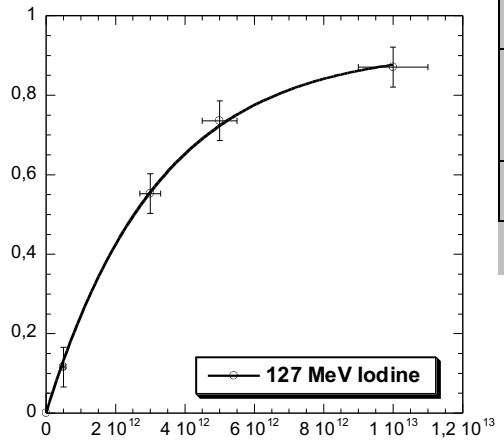
10^{13} Kr cm^{-2}

Virgin, with texture correction

Virgin, no texture correction

Amorphous/crystalline volume fraction (damaged fraction Fd = Va / V) as determined by x-ray diffraction

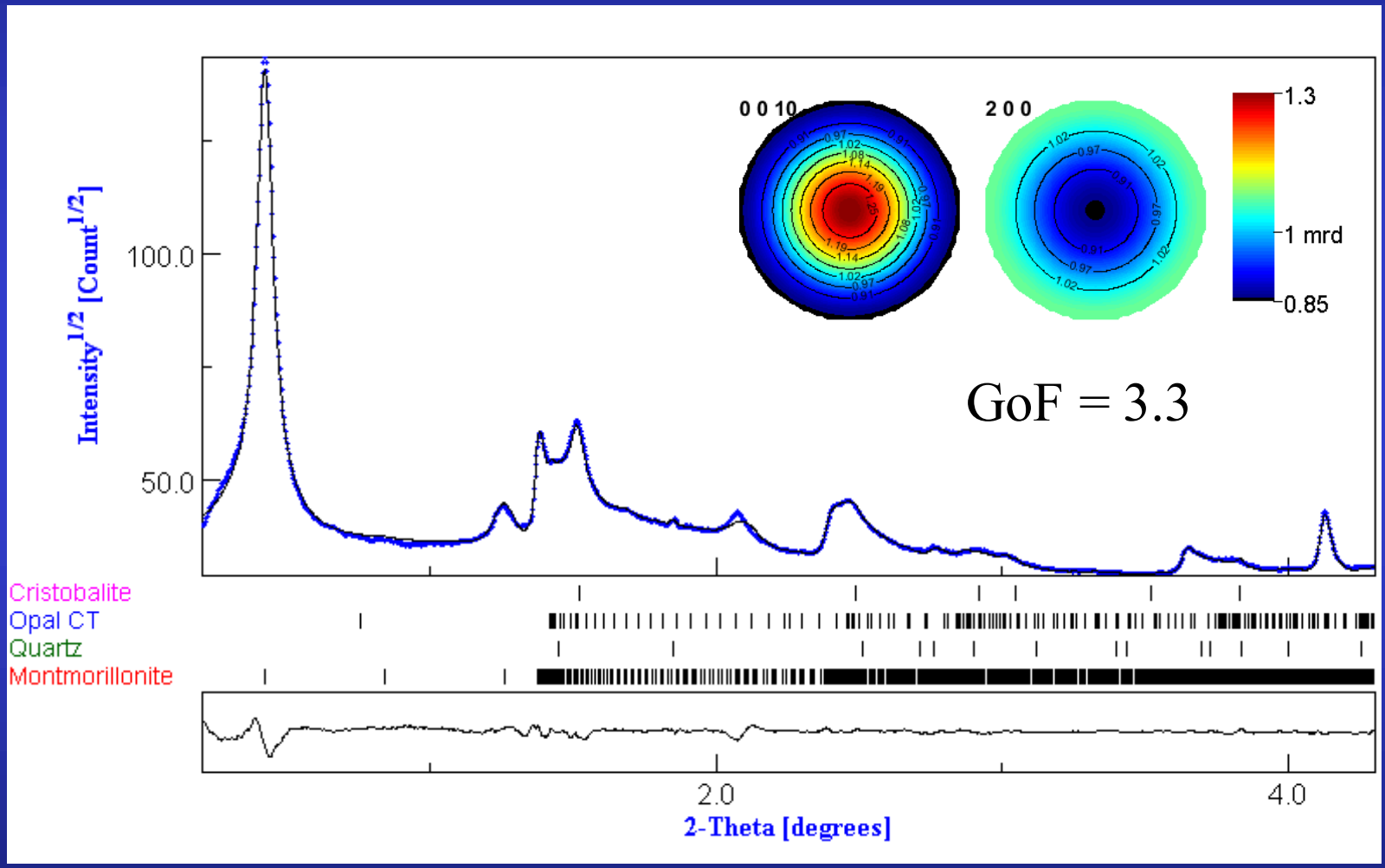




B

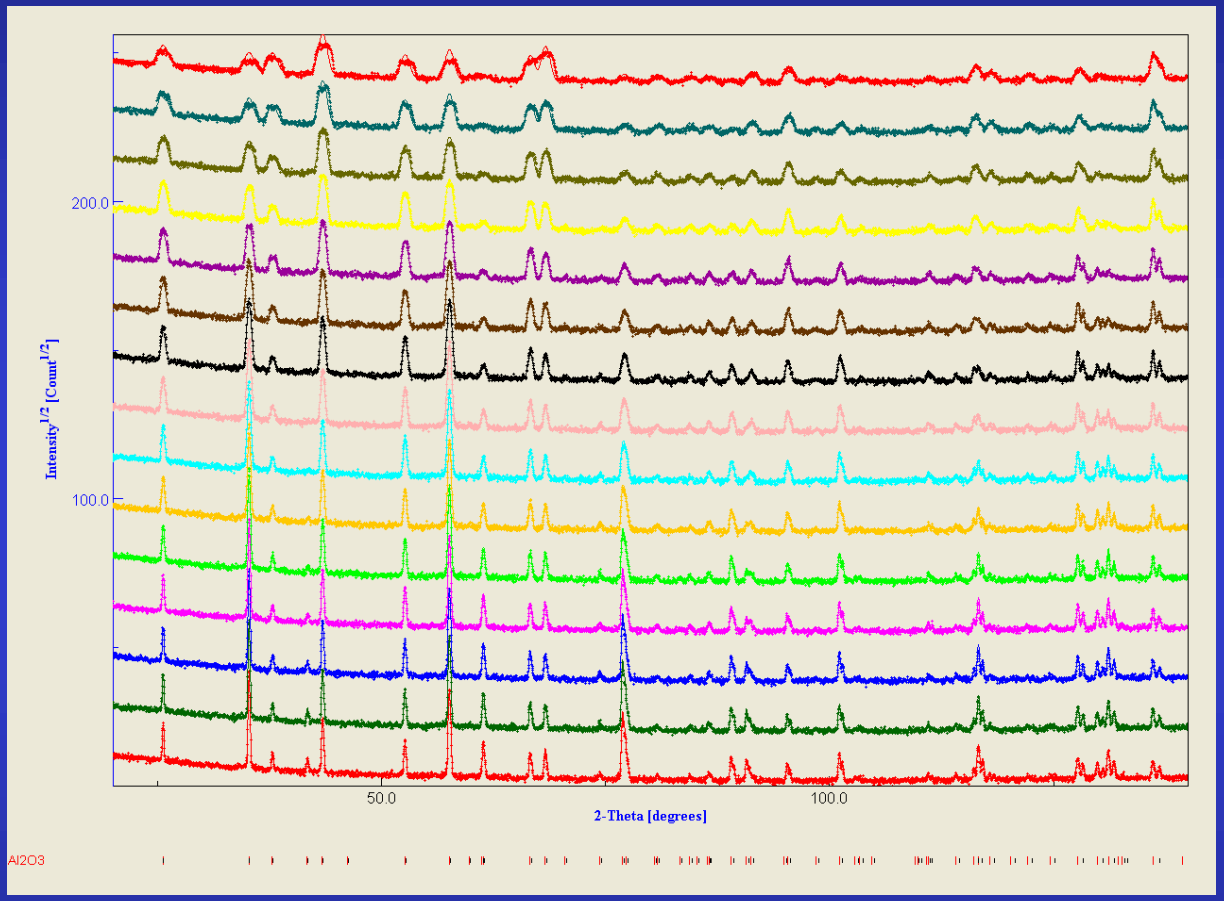
Fitting parameters	Krypton		Iodine
	Single impact $Fd = B(1- \exp(-A\phi t))$	**Double impact** $Fd = B(1 - (1+ A\phi t) \exp(-A\phi t))$	**Single impact** $Fd = B(1- \exp(-A\phi t))$
$A = \pi R^2$ (cm^2)	$1.85 \pm 0.15\ 10^{-13}$	$4.1 \pm 0.15\ 10^{-13}$	$3.3 \pm 0.15\ 10^{-13}$
Radius R (nm)	2.4 ± 0.2	3.6	3.2
B (Max.damage rate)	0.87	0.85 ± 0.2	0.92 ± 0.2
$\chi 2$	0.013	0.0006	0.0004

Turbostratic phyllosilicate aggregates



V%
1.45(2)
6.6(1)
0.19(1)
91.8(3)

Al_2O_3 « standard » powder from Almelo



2θ-scans:

GoF = 1.92

R_W = 15.60 %

R_B = 11.94 %

θ–2θ-scans:

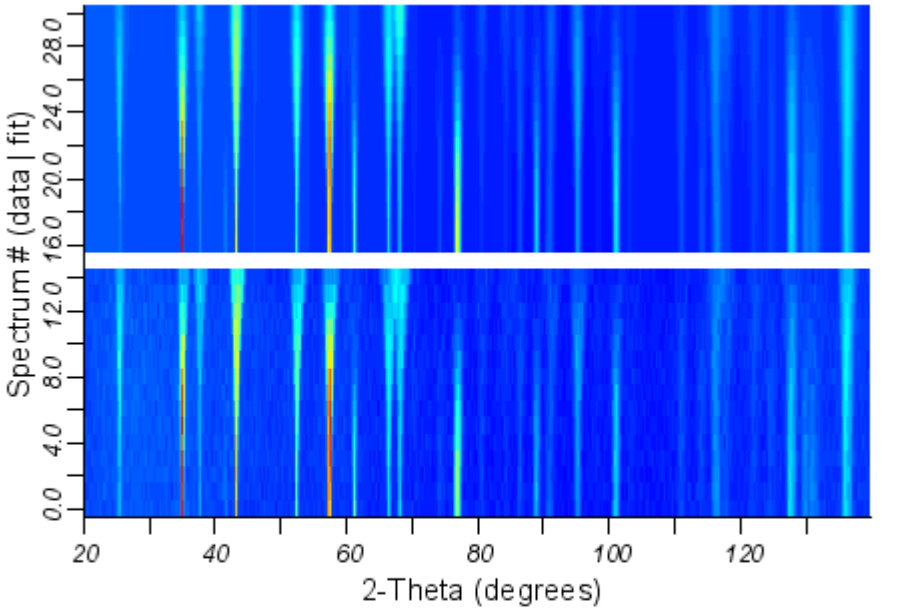
GoF = 1.86

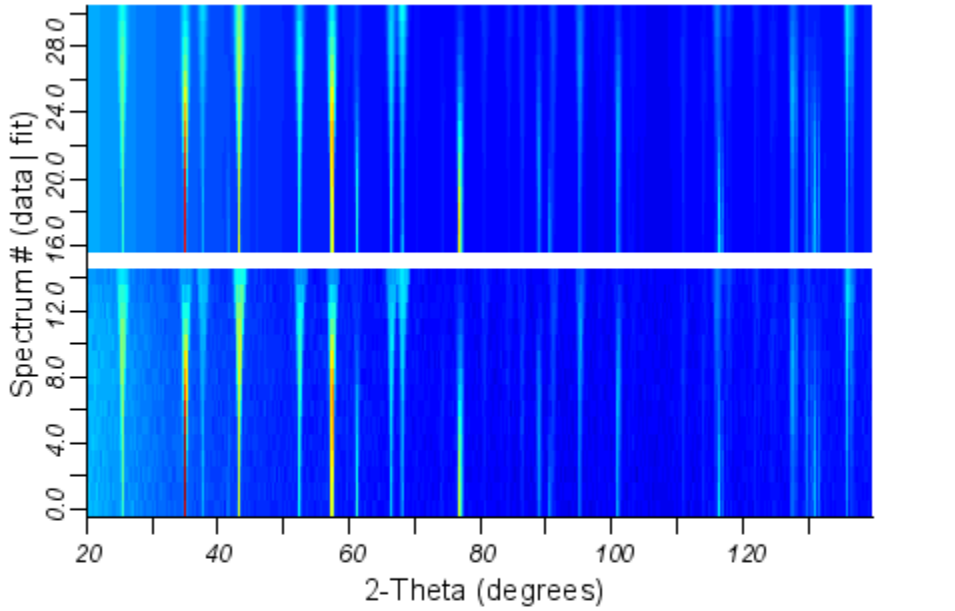
R_W = 16.11 %

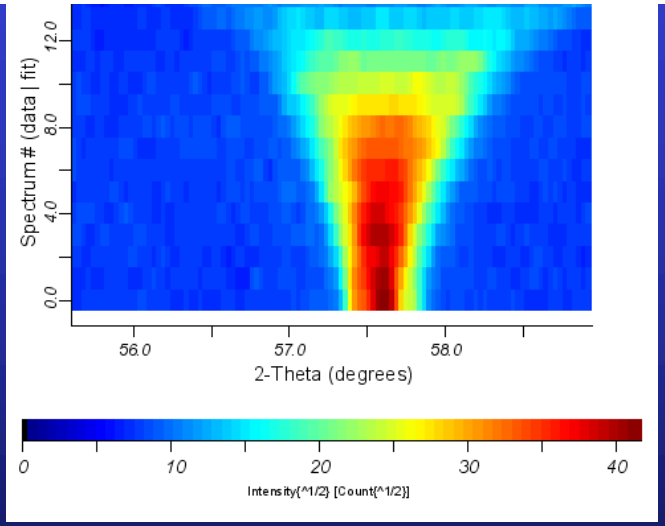
R_B = 12.40 %

15 diagrams x 5 mn (fibre texture): 1.25 h

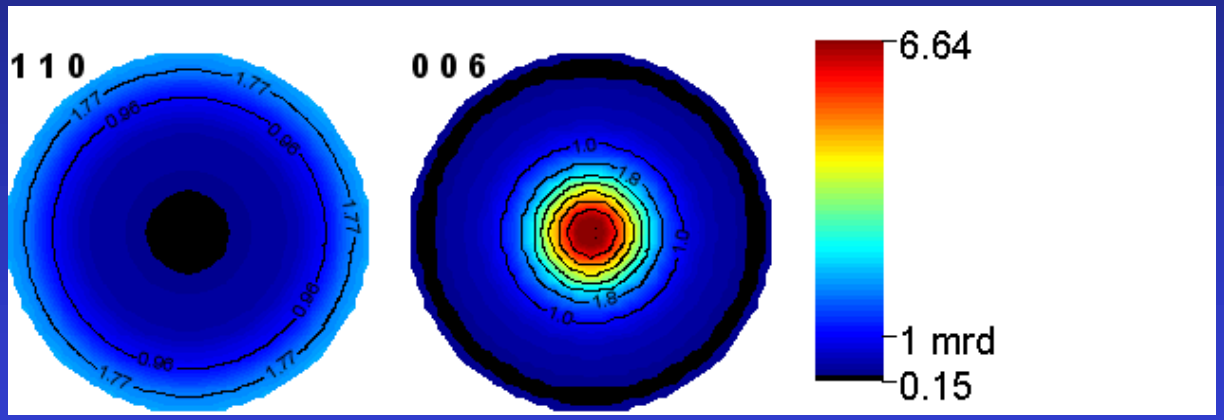
936 diagrams x 5 mn (non symmetric texture): 3.25 days







-70 microns x shift in χ
And texture !!

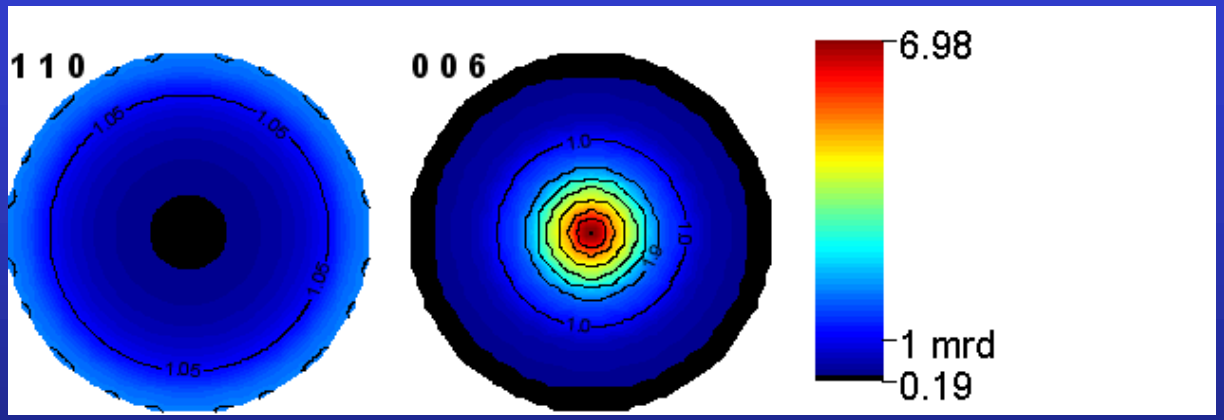


R_W (%) = 9.23
R_B (%) = 7.40

a = 4.75611(6) Å
c = 12.9806(1) Å

z_{Al} = 0.35266(3) Å
x_O = 0.6923(2) Å

Cyclic-fibre texture assumed



R_W (%) = 7.14
R_B (%) = 5.64

a = 4.75874(3) Å
c = 12.99373(7) Å

z_{Al} = 0.35225(2) Å
x_O = 0.6943(2) Å

Conclusions

a) Texture affects phase ratio and structure determination

b) Microstructure (crystallite size) affects texture (go to a)

c) Stresses shift peaks then affects structure and texture determination

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

e) If you think you can destroy it, perhaps think twice

f) more information is always needed: local probes …

g) Combined Analysis (D. Chateigner Ed), Wiley-ISTE 2010

Merci de votre attention !

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