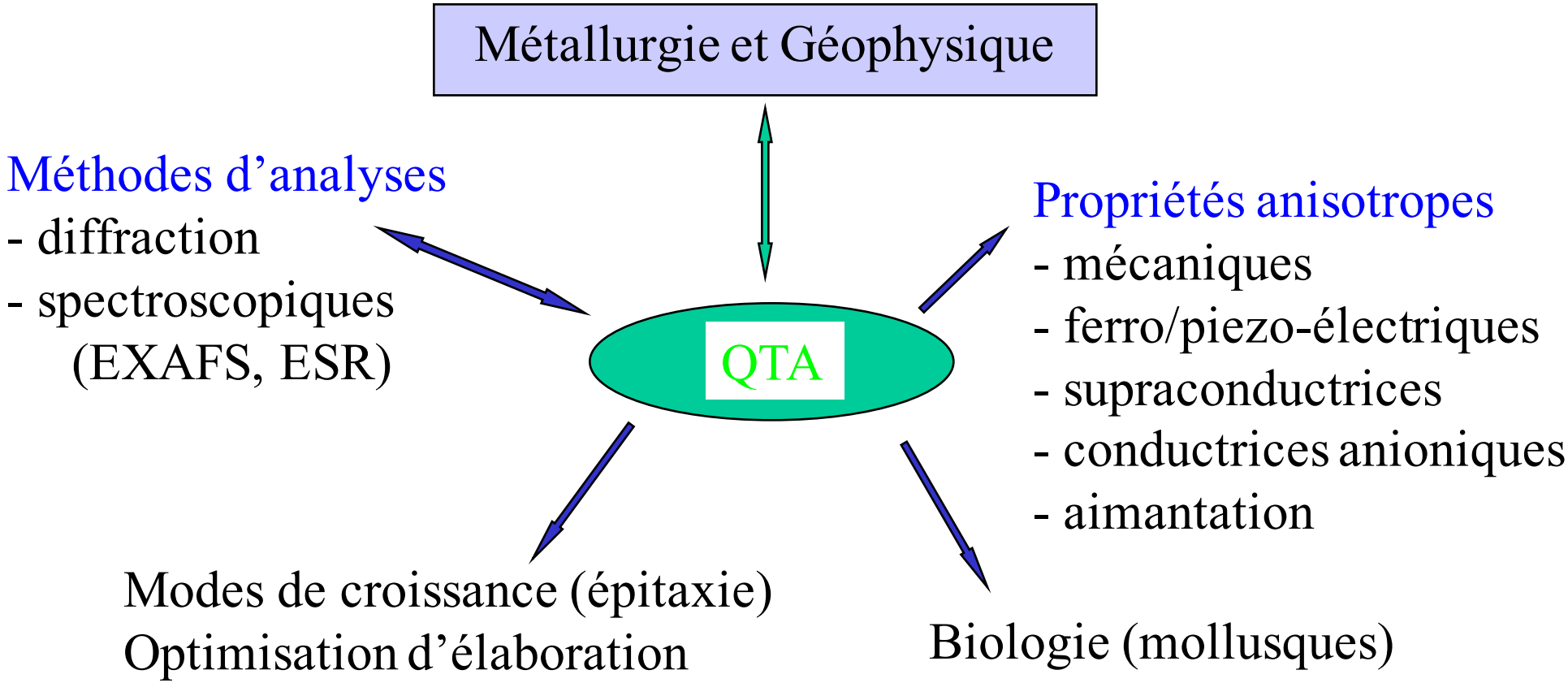
Combined Texture-Structure-Microstructure analysis using diffraction

matériaux ***cristallins*** ou micro-cristallisés à propriétés ***anisotropes***

- Elaboration de matériaux de complexité croissante, ***applications*** de + en + ***spécifiques***
- Désir d'***optimisation*** et de ***compréhension*** des anisotropies physico-chimiques de matériaux


Métallurgie et Géophysique
Méthodes d'analyses
- diffraction
- spectroscopiques
(EXAFS, ESR)
QTA
Propriétés anisotropes
- mécaniques
- ferro/piezo-électriques
- supraconductrices
- conductrices anioniques
- aimantation
Modes de croissance (épitaxie)
Optimisation d'élaboration
Biologie (mollusques)

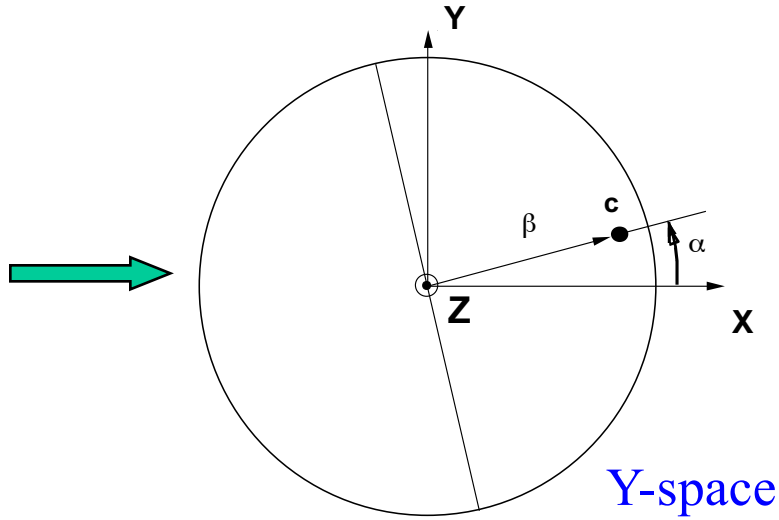
Summary

- Usual up-to-date approaches for polycrystals
  - Texture
  - Structure-Microstructure
  - Problems on ultrastructures
- Combined approach
  - Experimental needs
  - Methodology-Algorithm
  - Ultrastructure implementation
  - Case studies
- Future trends

Texture Analysis

{hkl} pole figure measurement + corrections:

$$\frac{dV(\chi\phi)}{V} = \frac{1}{4\pi} P(\chi\phi)\ \sin\chi\, d\chi\, d\phi$$

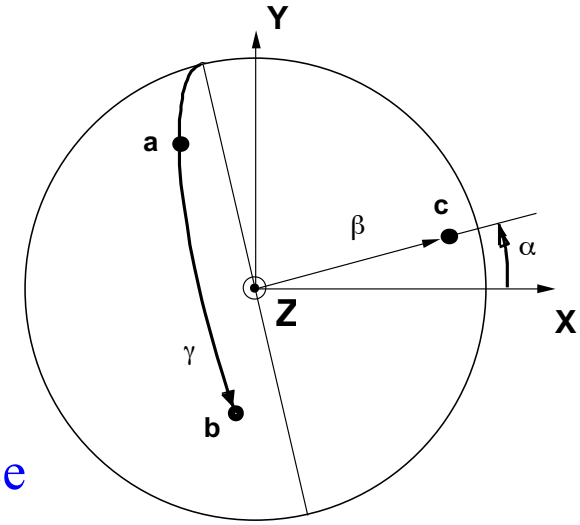


S-space

Y-space

We want f(g) (ODF): with g = (α,β,γ)

$$\frac{dV(g)}{V} = \frac{1}{8\pi^2} f(g)\ dg$$



G-space

We have to invert (Fundamental equation of Texture Analysis):

$$P_{hkl}(\vec{y}) = \frac{1}{2\pi} \int_{<hkl>//\vec{y}} f(g)\, d\tilde{\varphi}$$

WIMV refinement method:
Williams-Imhof-Matthies-Vinel

$$f^{n+1}(g) = N \left[\frac{f^{n}(g)\, f^{0}(g)}{\prod_{hkl} \left(P^{n}_{hkl}(\vec{y}) \right)^{\frac{1}{I}}} \right]$$

Recalculation of pole figures or inverse pole figures from the ODF

Bunge - Esling

$$f(g) = \sum_{\ell} \sum_{m} \sum_{n} C_{\ell}^{m,n} T_{\ell}^{m,n}(g)$$

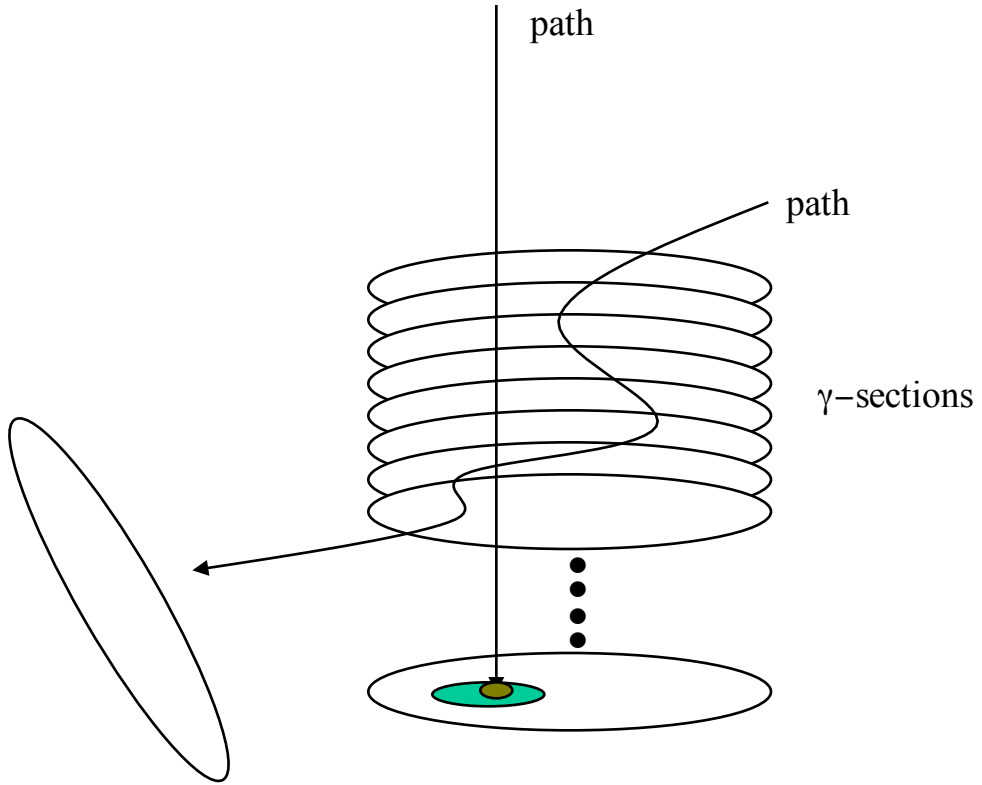
Ruer - Baro (vector method)

$$f(g) = |\sigma| P_{\vec{h}}(\vec{y})$$

Helming (Components)

$$f(g) = \sum_{\text{phases}} \sum_{i} S(g_i, s, FWHM)$$

Pawlik (ADC)

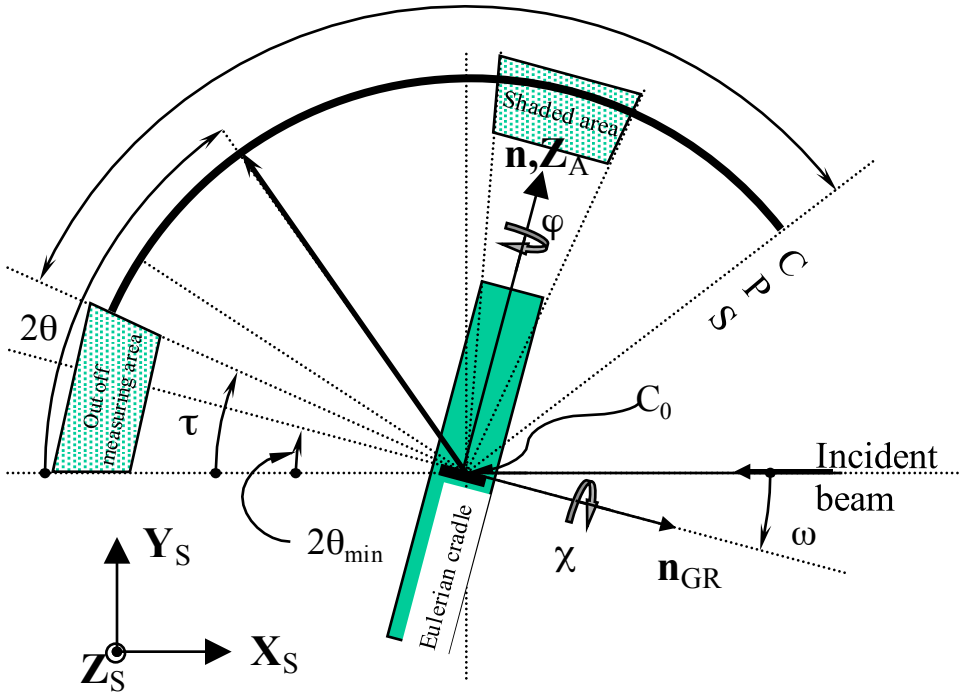


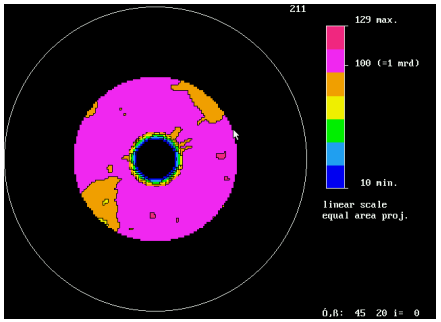
{hkl} pole figure

{001} pole figure for a cubic crystal system

ODF Completion

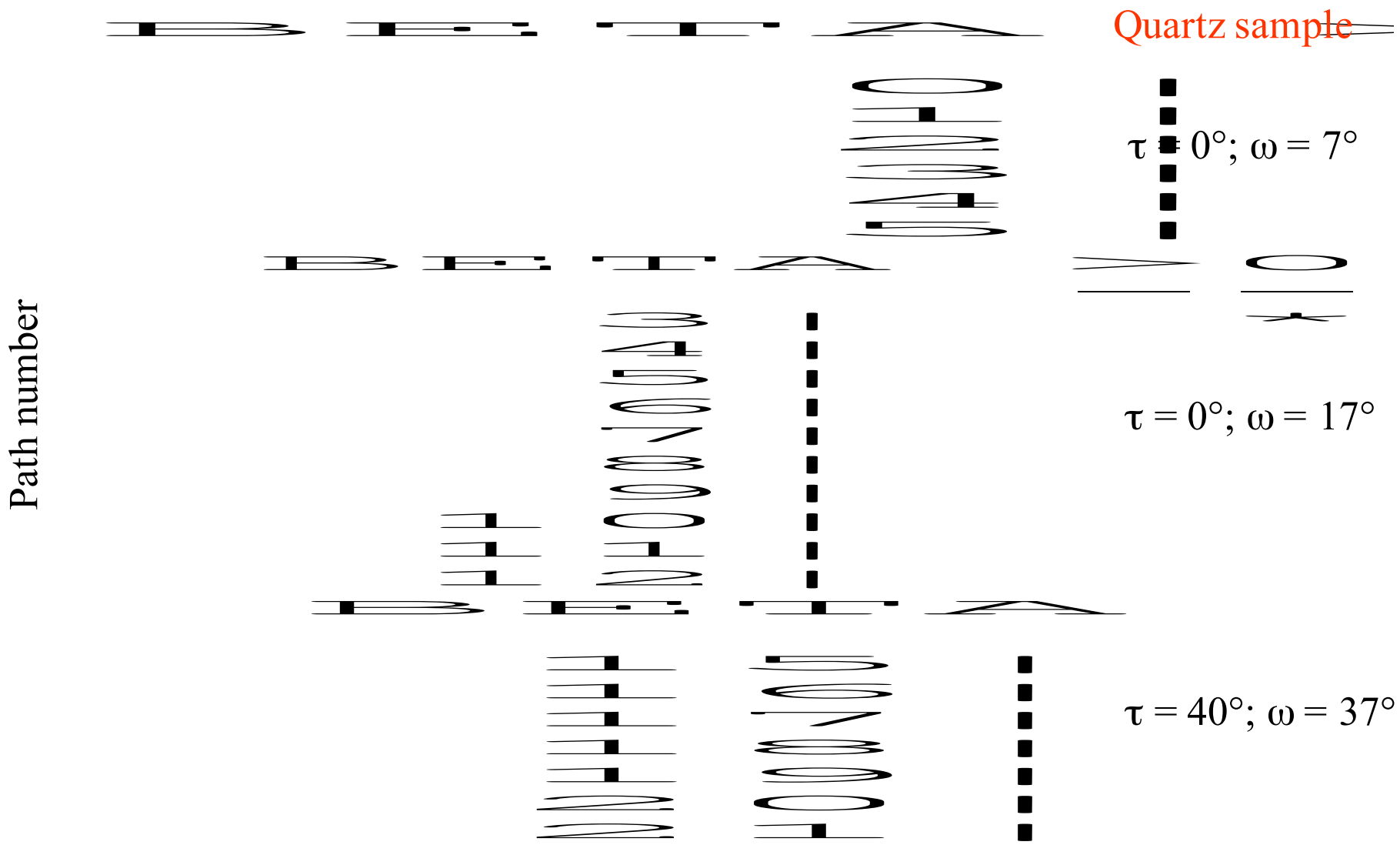
- Several {hkl} pole figures needed to calculate f(g)
- Each f(g) cell (98000 at total) needs 3 paths from experiments
- More than 3 is better !
- Spectrometer space is complicated (5 angles, 2 shaded area)
  - defocusing (high χ)
  - blind area (low χ)
  - increase at low ω, where high intensity peaks are (LP factor)

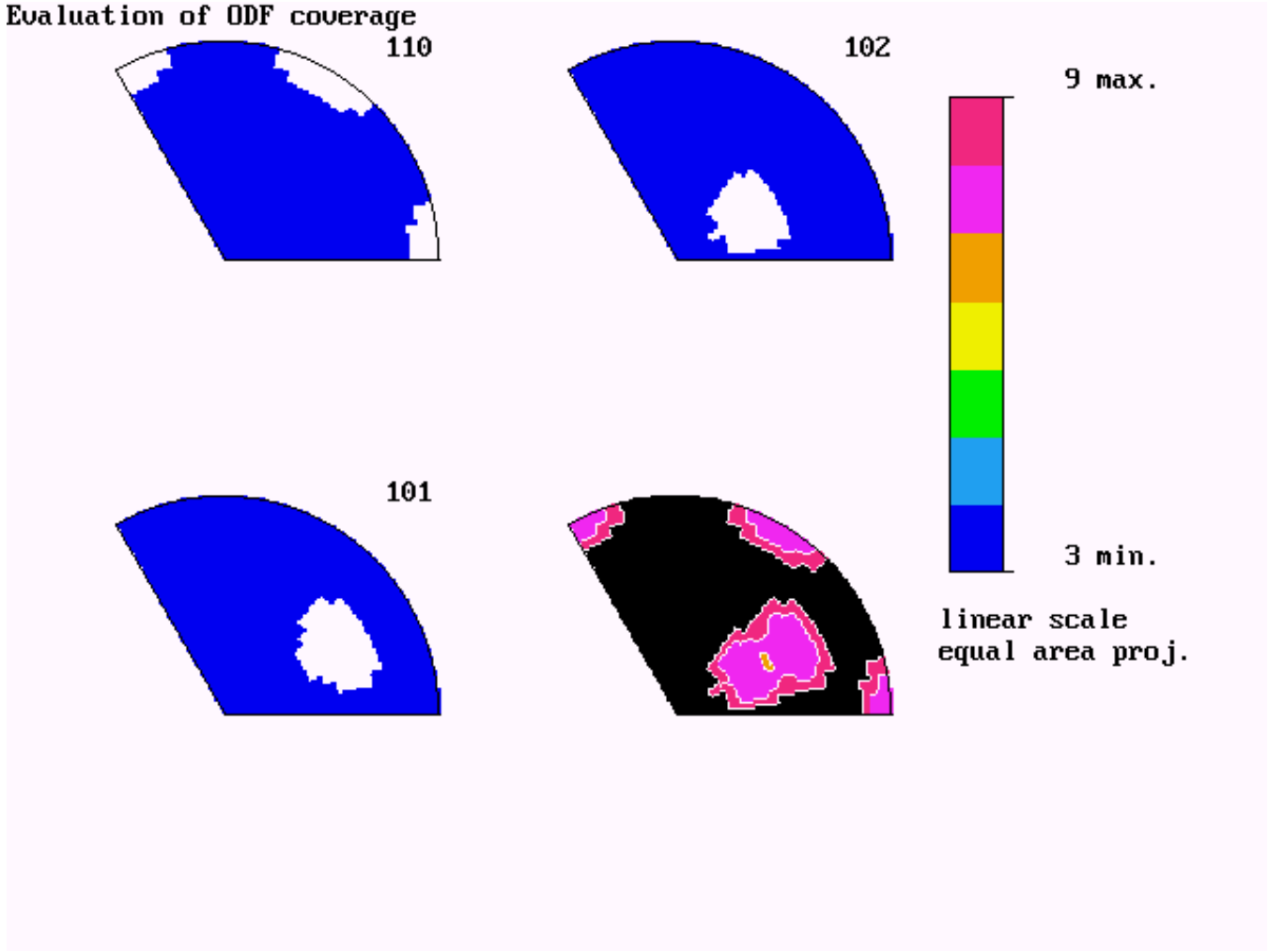




Needs for a tool for an automatic search of the best experimental conditions:

Fortran code to estimate the orientation space completion: τ, ω, χ, ϕ and CPS ranges, 2θ hkl's, cradle shades (in BEARTEX)

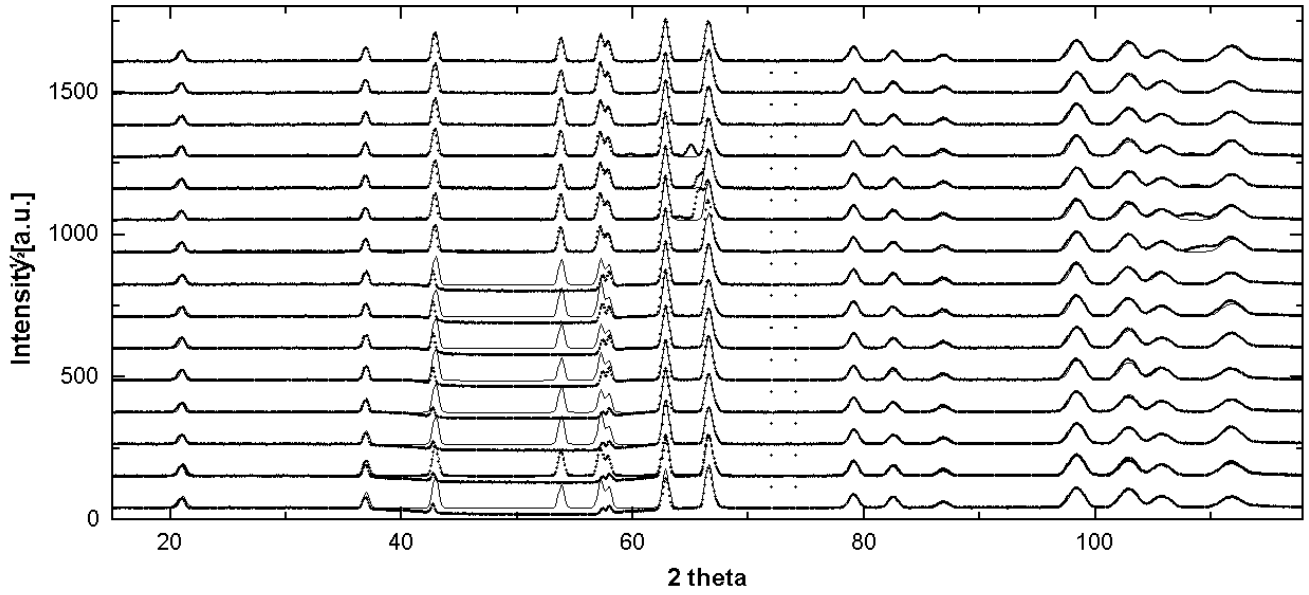



Evaluation of ODF coverage
110
102
101
9 max.
3 min.
linear scale
equal area proj.

Usual Structure-Microstructure Analysis

(Full pattern fitting, Rietveld Analysis)

Si_3N_4 matrix with SiC whiskers:



Random powder: $I(2\theta) = \sum_{hkl,\ phases} I_{hkl,\ phases}(2\theta) S_{hkl,\ phases}(2\theta) + bkg(2\theta)$

$$I_{hkl}(2\theta) = S\left|F_{hkl}\right|^2 m_{hkl} \frac{L_P}{V_c^2} P_{hkl}$$

S: scale factor (phase abundance)

F_{hkl}: structure factor (includes Debye-Waller term)

V_c: unit-cell volume

F_{hkl}: texture parameter (March-Dollase …)

$$S_{hkl}(2\theta) = S^I_{hkl}(2\theta) * S^S_{hkl}(2\theta)$$

S^I: instrumental broadening

S^S: Sample aberrations

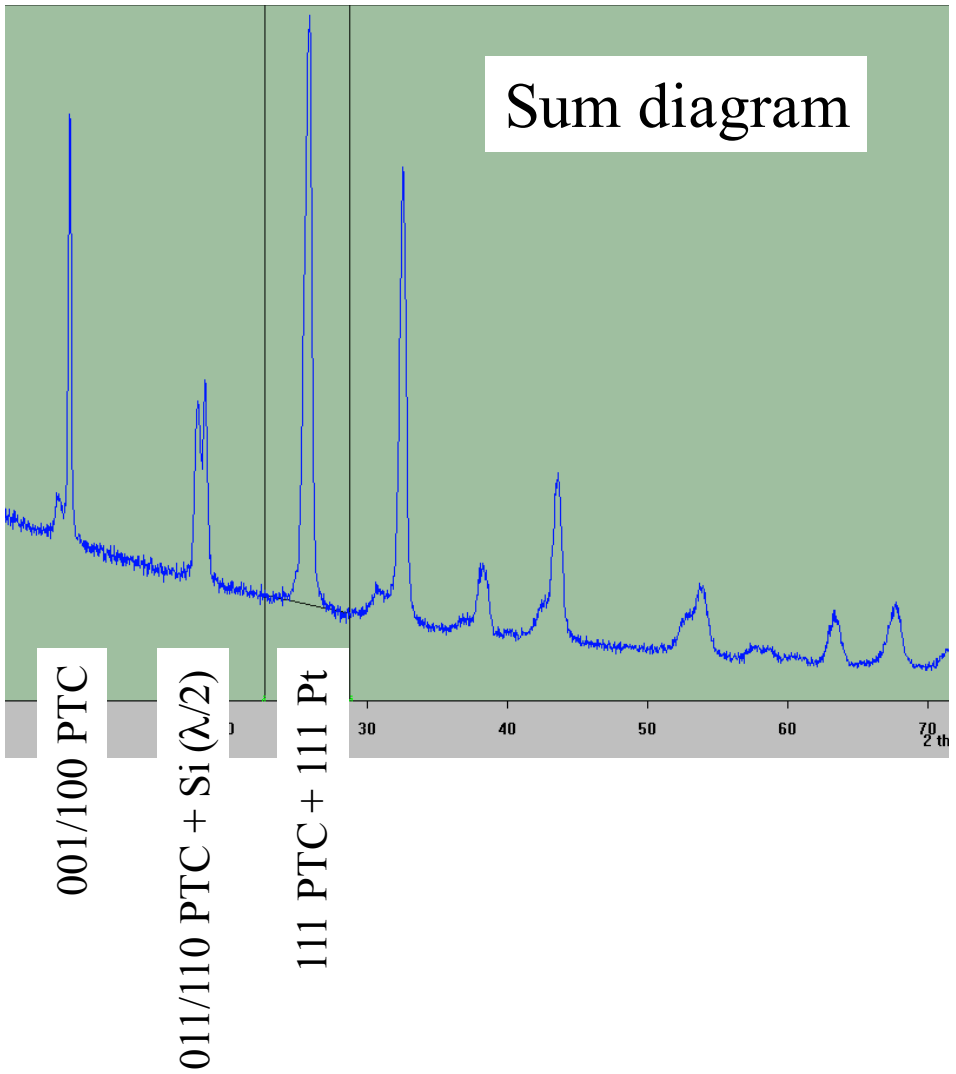
crystallite sizes (iso. or anisotropic)

rms microstrains ε

Problems on ultrastructures

Ferroelectric film (PTC)
Electrode (Pt)
Antidiffusion barrier (TiO_2)
Oxide (native, thermally grown)
SC Substrate (Si)

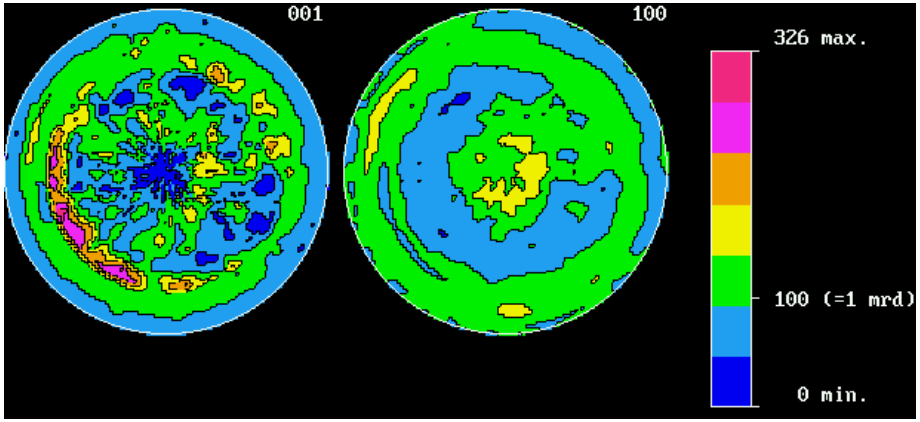
- Strong intra- and inter-phase overlaps
- Mixture of very strong and lower textures
- texture effect not fully removable: ~~structure~~
- structure unknown: ~~texture~~



Direct Integration of Peaks

up to recently: best existing technique for texture

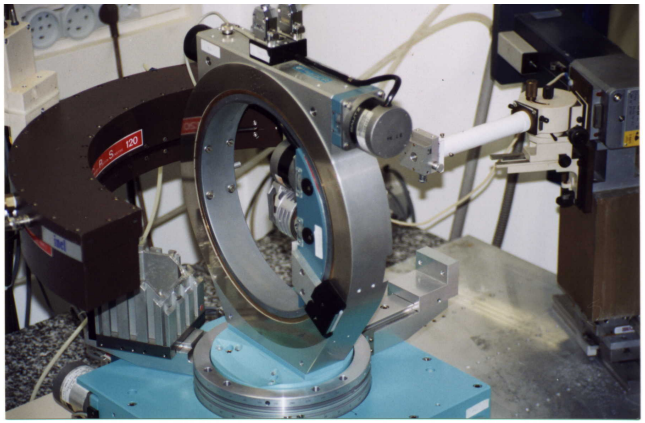
Integration + corrections
+ ODF refinement



Limited nb of PFs (polyphase)
Only access to PTC, badly !
No control of ultrastructure parameters

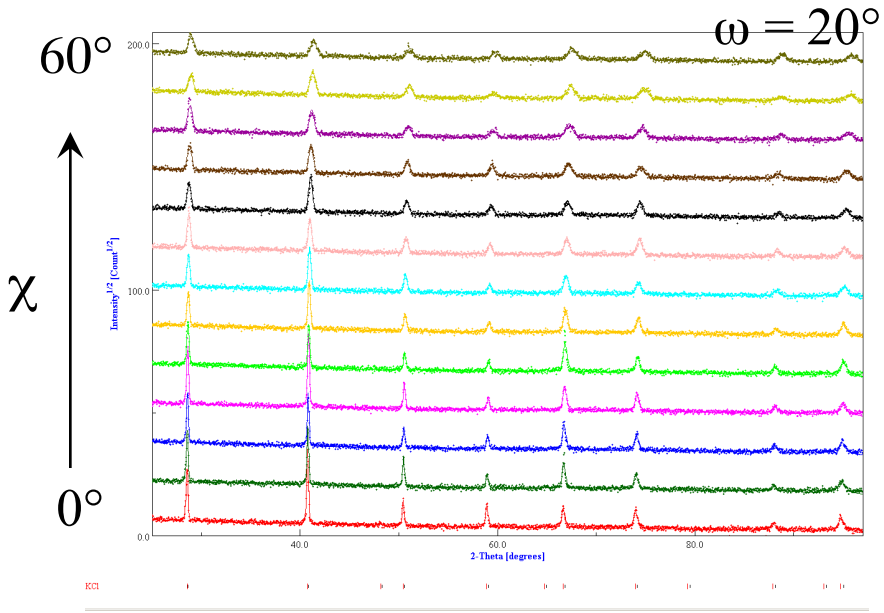
Combined approach

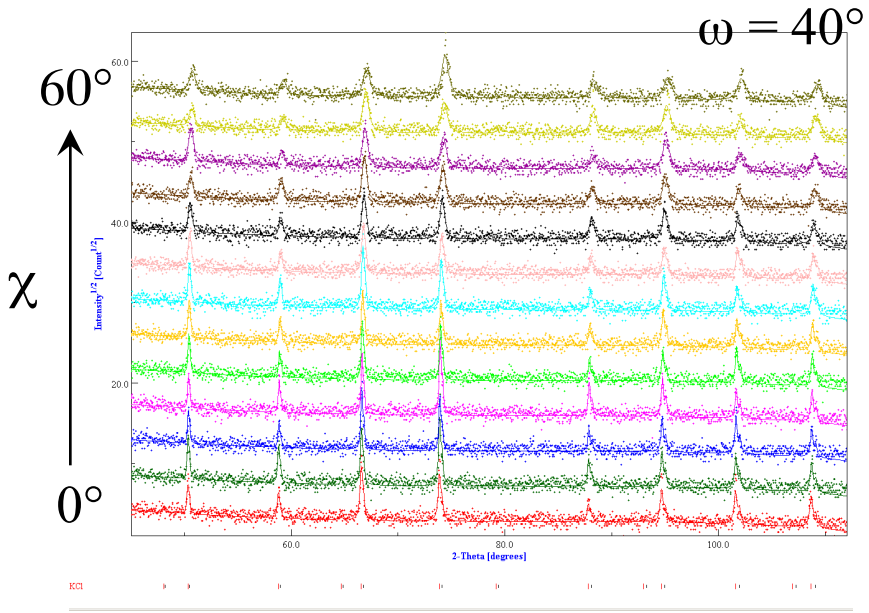
Experimental needs



Mapping Spectrometer space for correction of:

- instrumental resolution
- instrumental misalignments

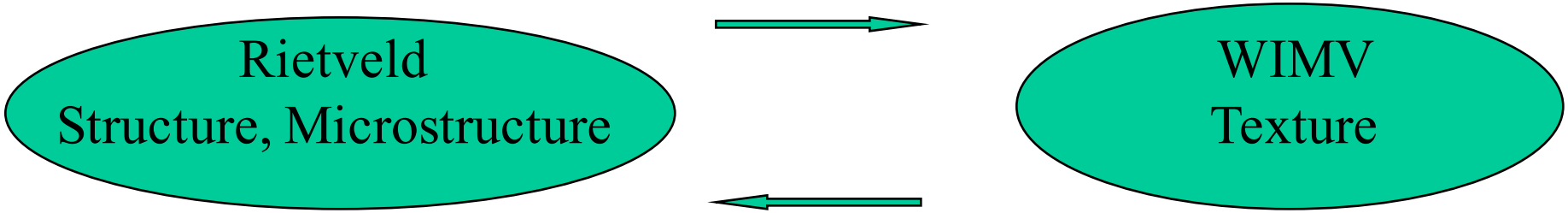




Methodology-Algorithm

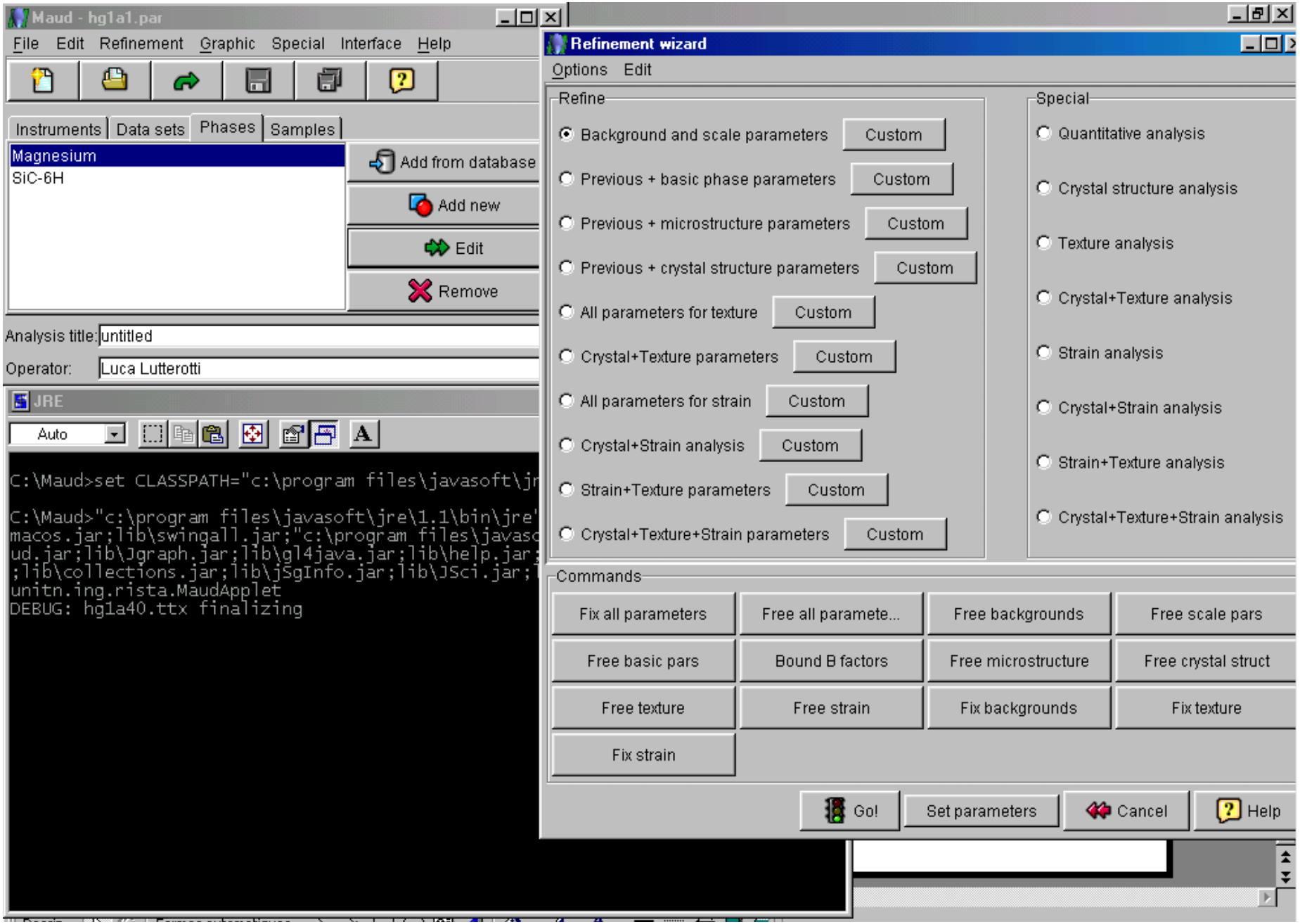
Correction of intensities for texture:

$$I_{hkl}(2\theta,\chi,\varphi) = I_{hkl}(2\theta)\, P_{hkl}(\chi,\varphi)$$



Pole figure extraction (Le Bail method): $P_{hkl}(\chi,\varphi)$

Rietveld and WIMV algorithm are alternatively used to correct for each others contributions: Marquardt non-linear least squares fit is used for the Rietveld.


Maud - hg1a1.par
File Edit Refinement Graphic Special Interface Help
Instruments Data sets Phases Samples
Magnesium
SiC-6H
Add from database
Add new
Edit
Remove
Analysis title: untitled
Operator: Luca Lutterotti
JRE
Auto
C:\Maud>set CLASSPATH="c:\program files\javasoft\jr
C:\Maud>"c:\program files\javasoft\jre\1.1\bin\jre"
macos.jar;lib\swingall.jar;"c:\program files\javasc
ud.jar;lib\Jgraph.jar;lib\gl4java.jar;lib\help.jar;
;lib\collections.jar;lib\jSgInfo.jar;lib\JSci.jar;l
unitn.ing.rista.MaudApplet
DEBUG: hg1a40.ttx finalizing
Refinement wizard
Options Edit
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Background and scale parameters Custom
Previous + basic phase parameters Custom
Previous + microstructure parameters Custom
Previous + crystal structure parameters Custom
All parameters for texture Custom
Crystal+Texture parameters Custom
All parameters for strain Custom
Crystal+Strain analysis Custom
Strain+Texture parameters Custom
Crystal+Texture+Strain parameters Custom
Special
Quantitative analysis
Crystal structure analysis
Texture analysis
Crystal+Texture analysis
Strain analysis
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Commands
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Free microstructure
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Free texture
Free strain
Fix backgrounds
Fix texture
Fix strain
Go!
Set parameters
Cancel
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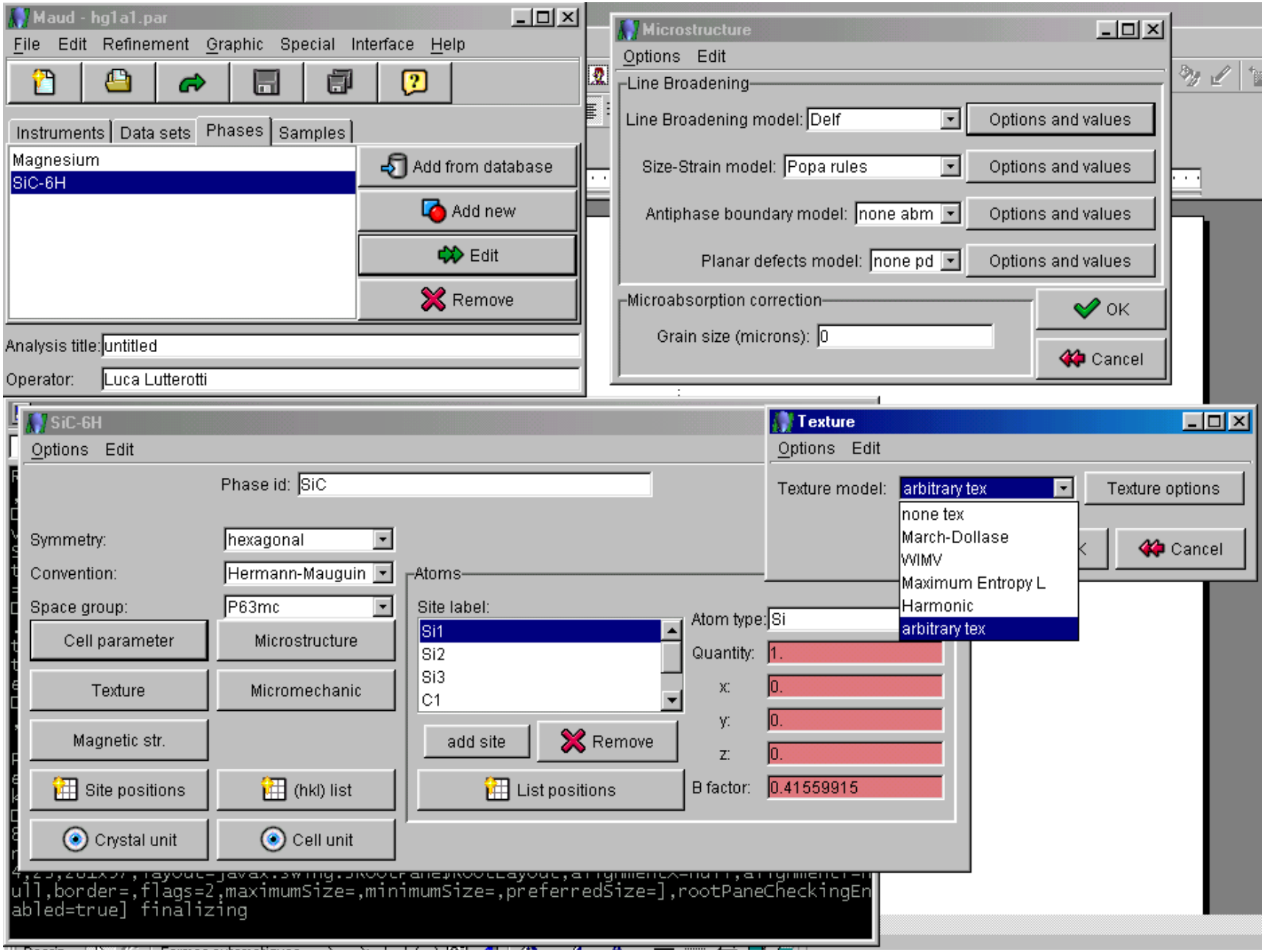
Maud - hg1a1.par
File Edit Refinement Graphic Special Interface Help
Instruments Data sets Phases Samples
Magnesium
SiC-6H
Add from database
Add new
Edit
Remove
Analysis title: untitled
Operator: Luca Lutterotti
Microstructure
Options Edit
Line Broadening
Line Broadening model: Delf
Options and values
Size-Strain model: Popa rules
Options and values
Antiphase boundary model: none abm
Options and values
Planar defects model: none pd
Options and values
Microabsorption correction
Grain size (microns): 0
OK
Cancel
SiC-6H
Options Edit
Phase id: SiC
Symmetry: hexagonal
Convention: Hermann-Mauguin
Space group: P63mc
Cell parameter
Microstructure
Texture
Micromechanic
Magnetic str.
Site positions
(hkl) list
Crystal unit
Cell unit
Atoms
Site label:
Si1
Si2
Si3
C1
add site
Remove
List positions
Atom type: Si
Quantity: 1.
x: 0.
y: 0.
z: 0.
B factor: 0.41559915
Texture
Options Edit
Texture model: arbitrary tex
Texture options
none tex
March-Dollase
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Maximum Entropy L
Harmonic
arbitrary tex
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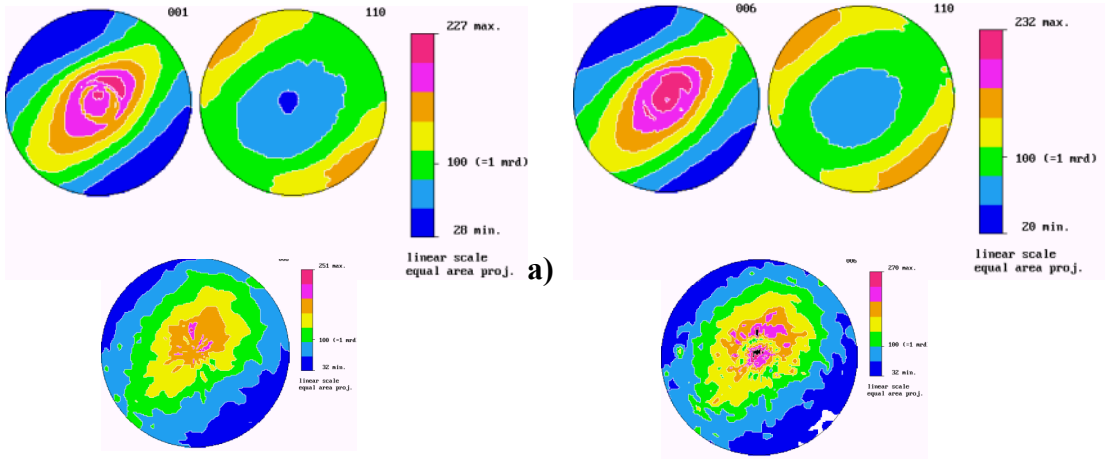
abled=true] finalizing

Polyphase texture analysis:
Direct Integration vs Combined

Dolomite/Calcite mixture: well separated peaks



Dolomite

Calcite

Direct

Combined

Textures show 0.2 mrd difference at max. only
texture reliability factors lowered by 3 %

+ microstructural parameters

Phase analyses:

Structures are found the ones in litterature

refined cell parameters:

dolomite a=4.8063(4)Å c=16.0098(4)Å

calcite a=4.9755(4)Å c=16.998(3)Å

Phase quantity:

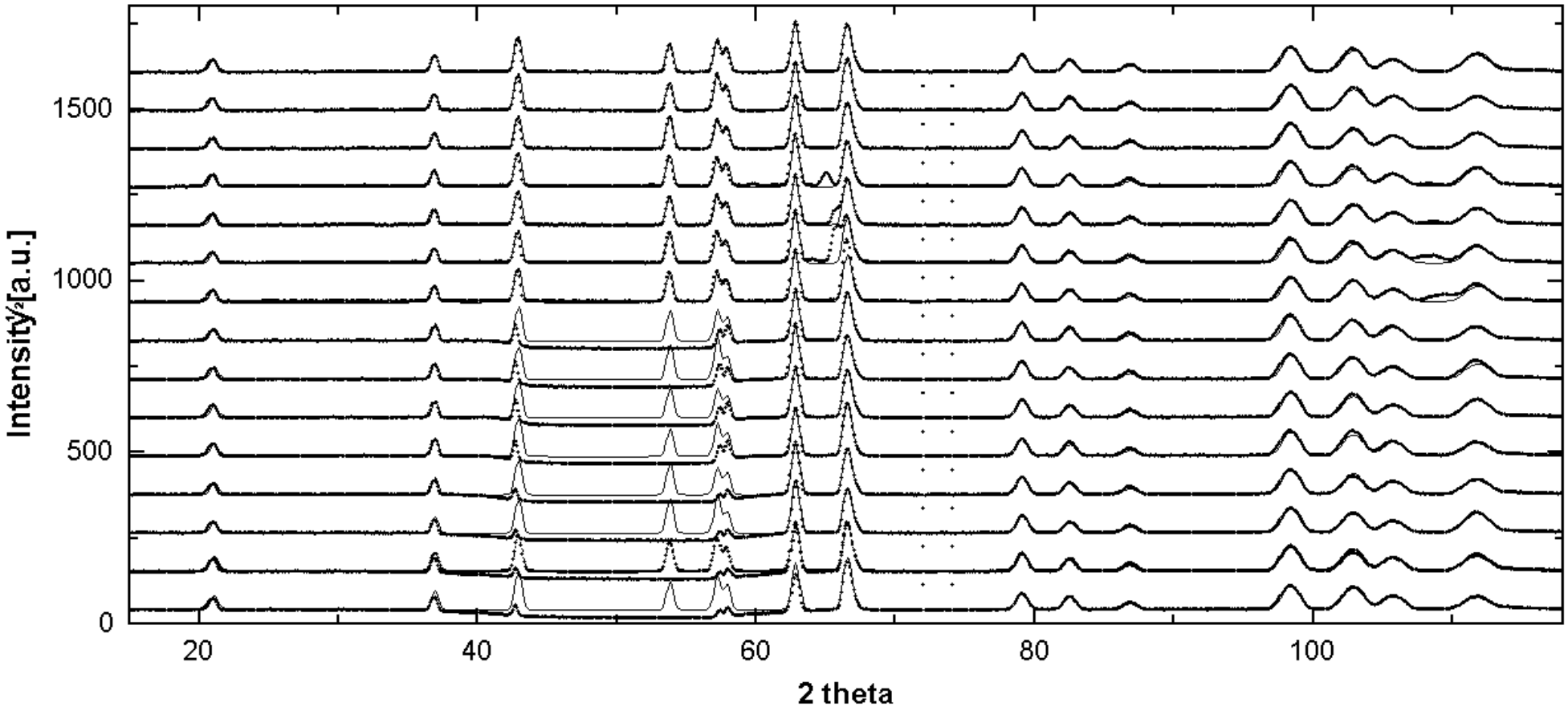
Combined approach:	dolomite	93.7 %
	calcite	6.3 %
Optically/Chemically:	dolomite	90 %
	calcite	10 %

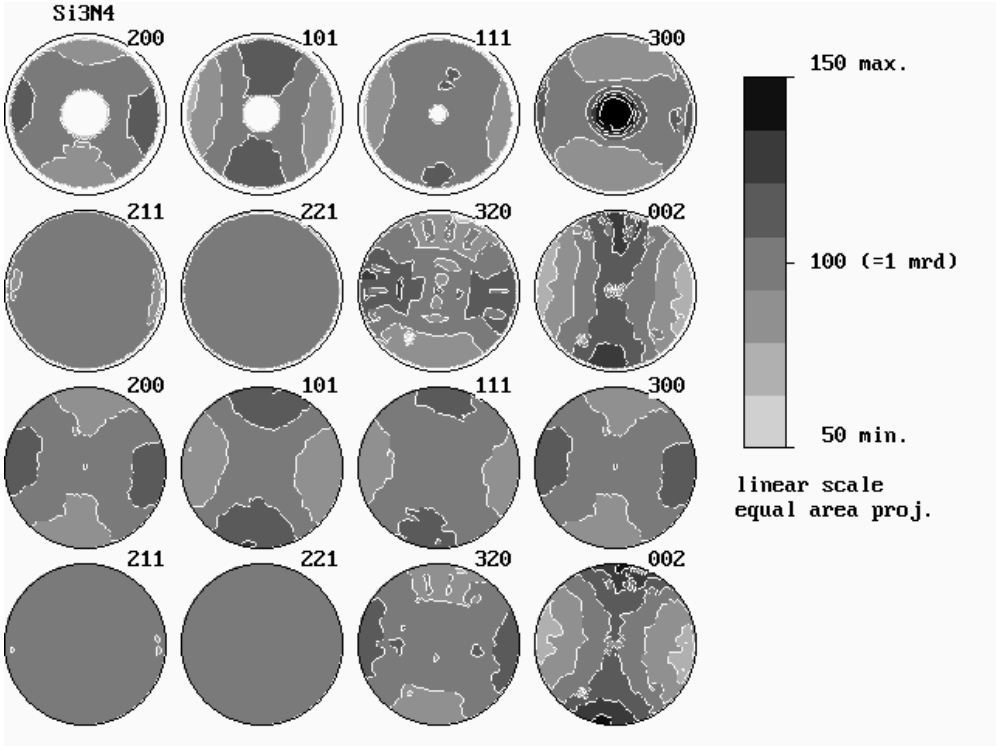
+ dolomite mean crystallite size: 2000(80) Å

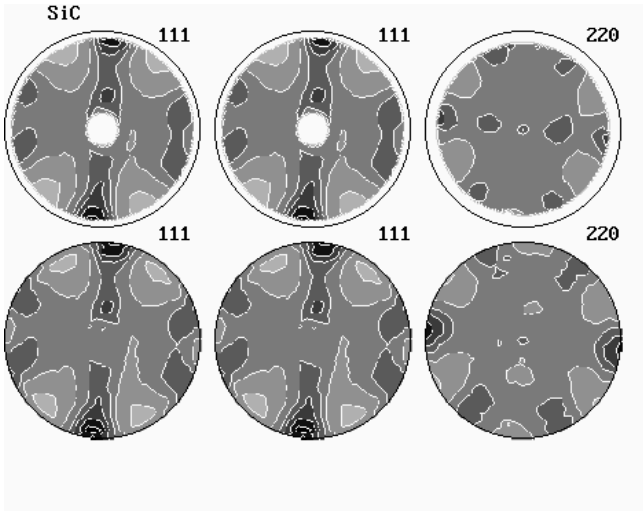
Quantitative phase and texture-analysis ceramic-matrix composites

Si_3N_4 matrix with SiC whiskers

Goodness of fit: 1.806665
Rwp (%): 17.10033
Rb (%): 12.54065
Rexp (%): 9.465139







	Si_3N_4	SiC
Vol. fraction (%):	75.8	24.2
Part. Size (Å):	3800	2200
rms micro-strains (%):	$4.2\ 10^{-4}$	$2.8\ 10^{-4}$

Ultrastructure implementation

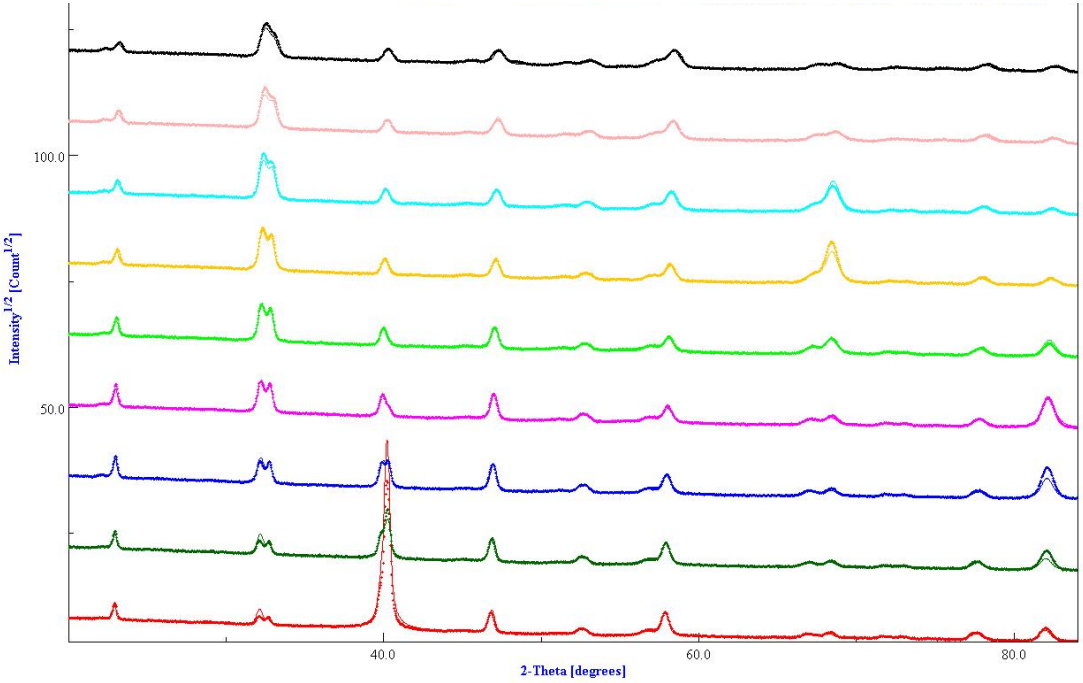
Corrections are needed for volumic/absorption changes when the samples are rotated. With a CPS detector, these correction factors are:

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

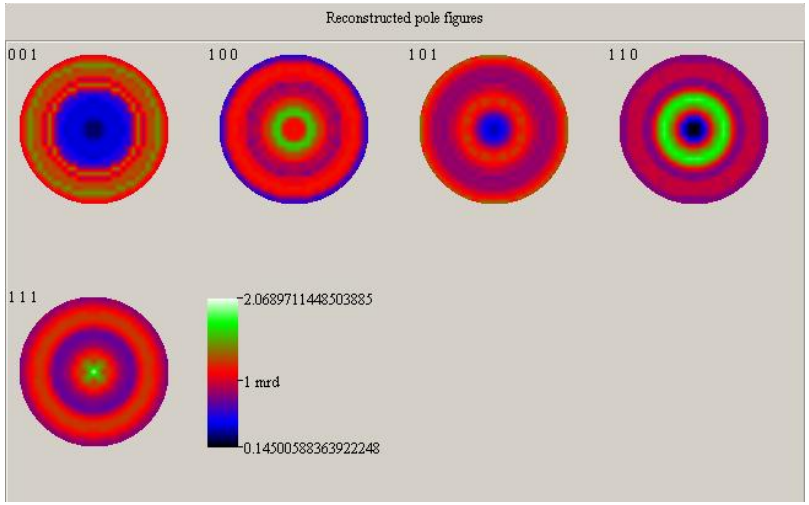
$$C_{\chi}^{\text{cov. layer}} = C_{\chi}^{\text{top film}}\left(\exp\left(-g_2\sum\mu_i' T_i'/\cos\chi\right)\right)/\left(\exp\left(-2\sum\mu_i' T_i'/\sin\omega\cos\chi\right)\right)$$

Gives access to individual Thicknesses
in the refinement

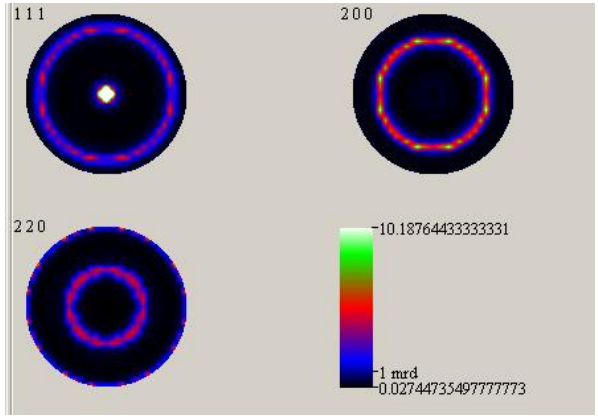
PTC/Pt/TiO_2/SiO_2/Si-(100)



PTC



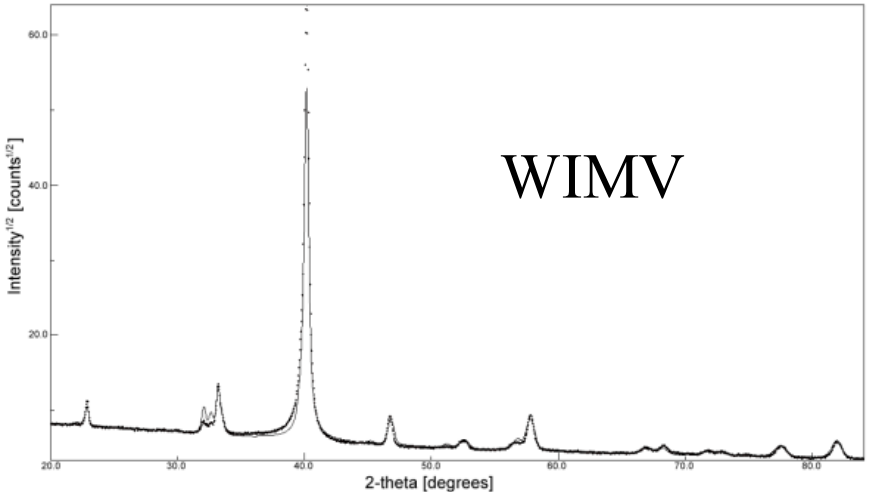
Pt

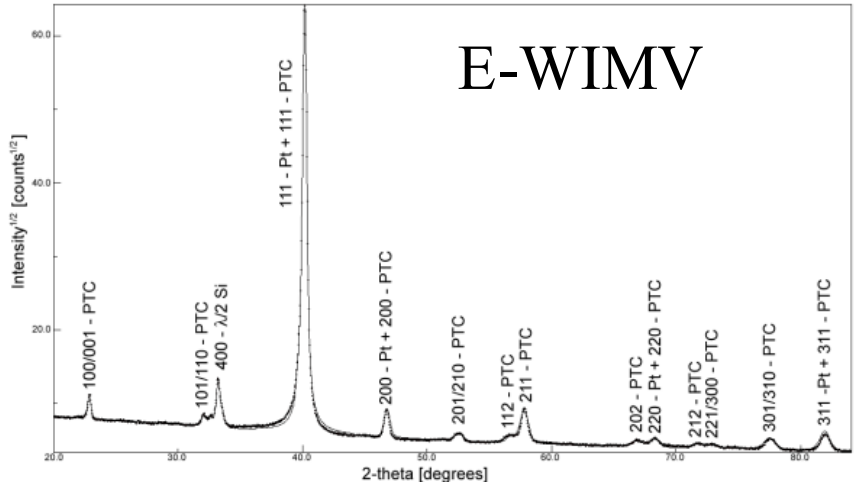


a = 3.955(1) Å
T' = 462(4) Å
t'_{iso} = 458(3) Å
ε' = 0.0032(1)

a = 3.945(1) Å
c = 4.080(1) Å
T = 4080(10) Å
t_{iso} = 390(7) Å
ε = 0.0067(1)

WIMV vs Entropy modified WIMV approach





Better refinement with E-WIMV:

- lower reliability factors (structure and texture)

- better high density level reproduction

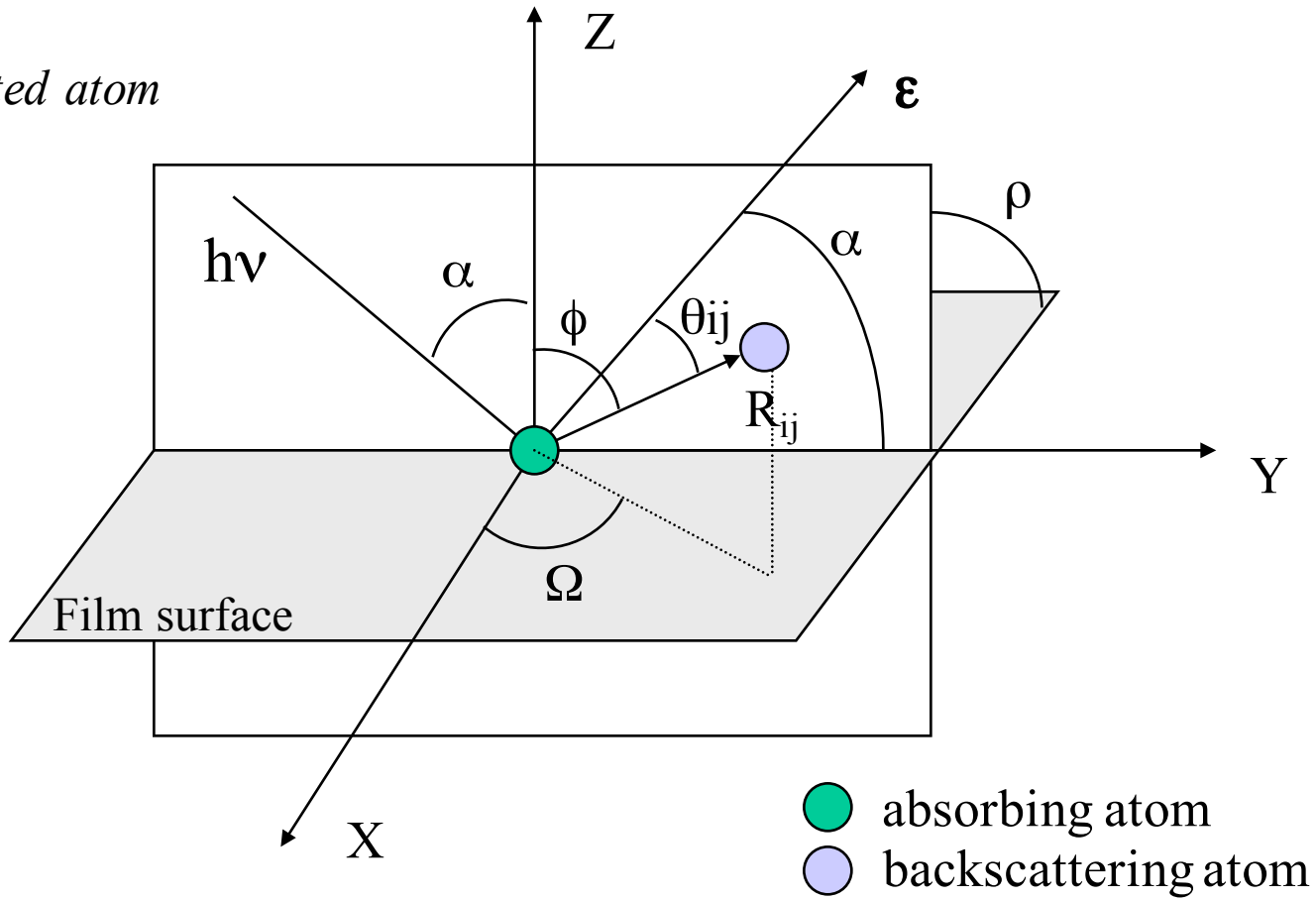
Texture	Pt Texture Index (m.r.d.^{2})	PTC Texture Index (m.r.d.^{2})	Pt RP_0 (%)	PTC RP_0 (%)	Rw (%)	R_{Bragg} (%)
WIMV	48.1	1.3	18.4	11.4	12.4	7.7
EWIMV	40.8	2	13.7	11.2	7	4.7

Polarised-EXAFS and QTA correlations: textured self-supporting films of clays

Main Collaborators:
A. Manceau, B. Lanson: LGIT, Grenoble, France

$$\chi = \frac{\mu - \mu_0}{\mu_0}$$

$\mu_0 = isolated\ atom$



Amplitude of EXAFS spectra (then RSF): *Stern & Heald, 1983*

plane-wave approx., single-scattering processes

$$\chi(\vec{k},\theta_{ij}) = \sum_j 3\left\langle \cos^2\theta_j \right\rangle \chi^j_{iso}(\vec{k})$$

$$= \sum_j \sum_{i=1}^{N_j} 3\left\langle \cos^2\theta_{ij} \right\rangle \chi^j_{iso}(\vec{k})$$

j: nb of neighbouring atomic shell

N_j: nb of backscatterers in the j^{th} shell

χ^j_{iso} taken at magic angle (α=35.3°) for fibre textures

⇨ P-EXAFS: provides directional structural information

Isotropic powder: $\chi(\vec{k}) = \chi(\vec{k}, \theta_{ij}) = \sum_j \chi^j_{iso}(\vec{k})$

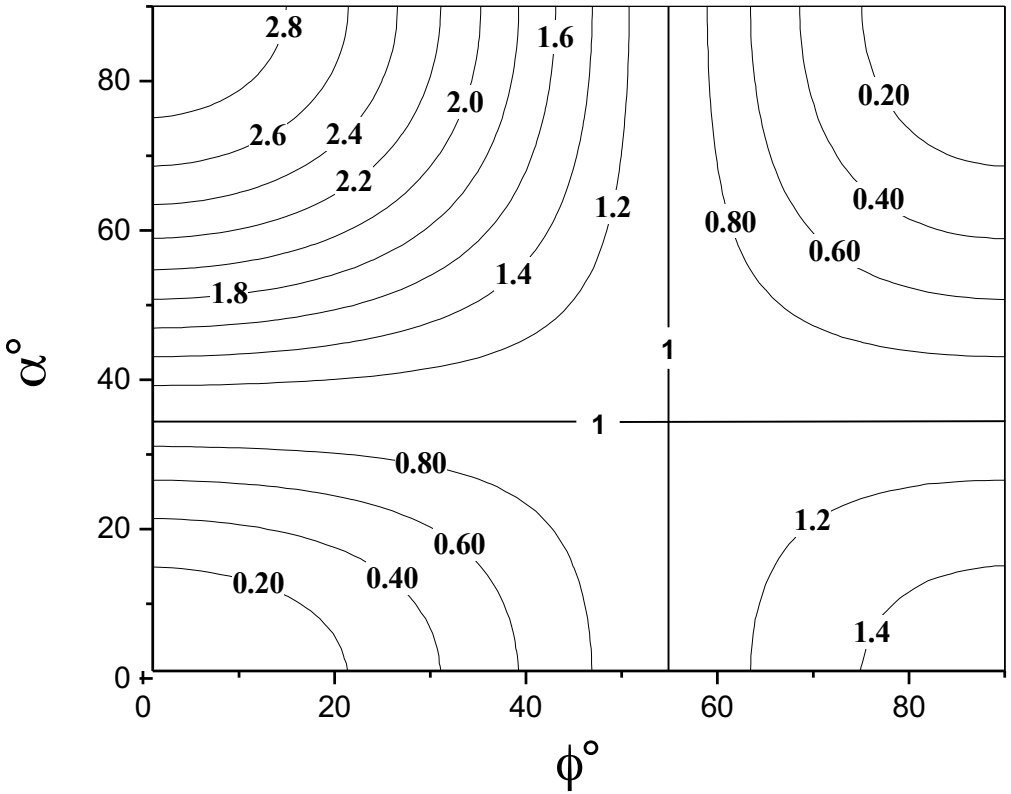
For fibre texture (around Z): signal averaged on Ω

$$\left\langle \cos^2 \theta_{ij} \right\rangle = \frac{1}{2\pi} \int_0^{2\pi} \cos^2 \theta_{ij} \, d\Omega = \cos^2 \phi \sin^2 \alpha + \frac{\cos^2 \alpha \sin^2 \phi}{2}$$

which allows to calculate the real number of j^{th} atoms:

$$N_{obs} = 3 N_{real} \left[\cos^2 \phi \sin^2 \alpha + \frac{\cos^2 \alpha \sin^2 \phi}{2} \right]$$

N_{obs} / 3 N_{real} correction factor

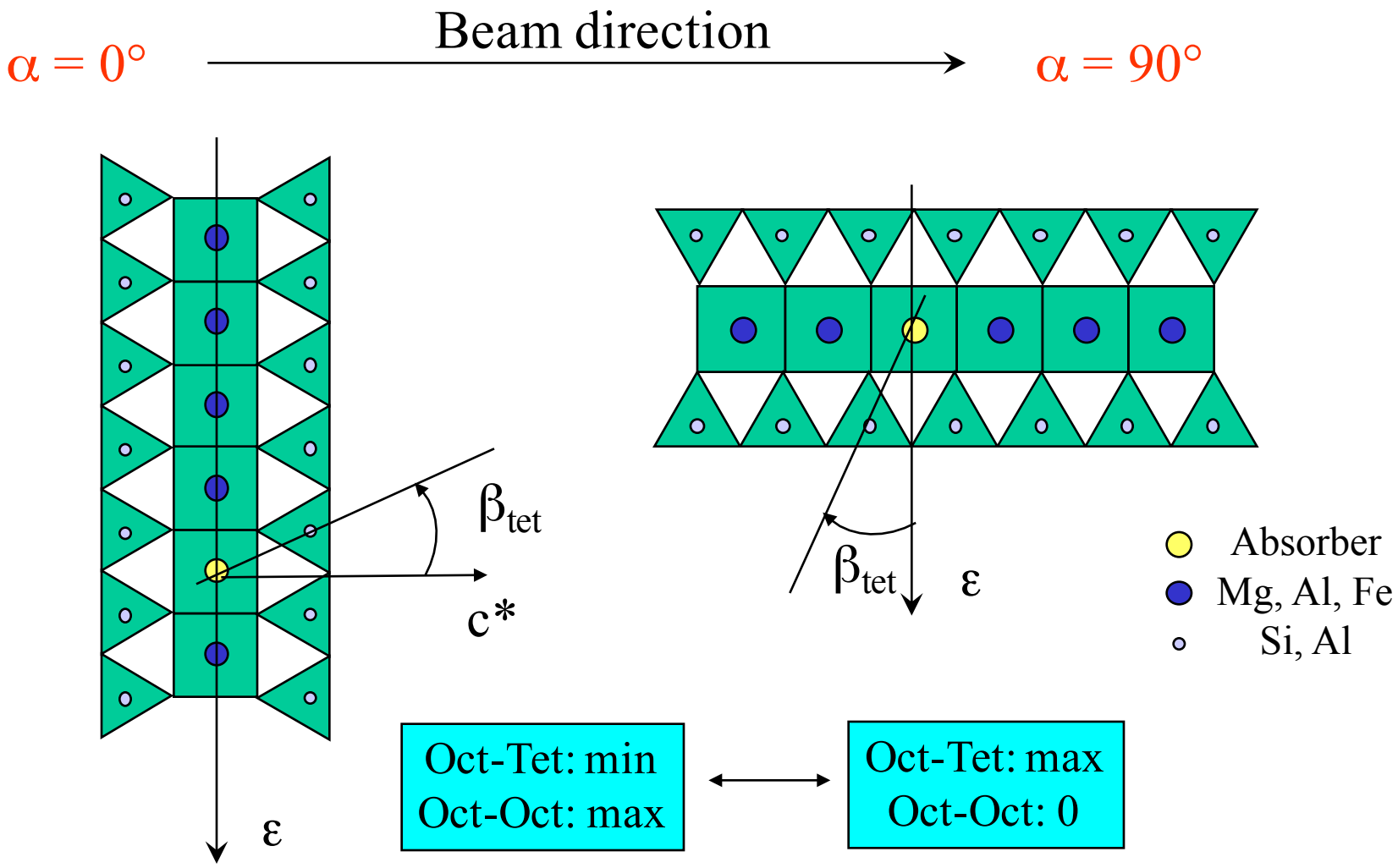


2 magic angles:

$\alpha = 35.3°$

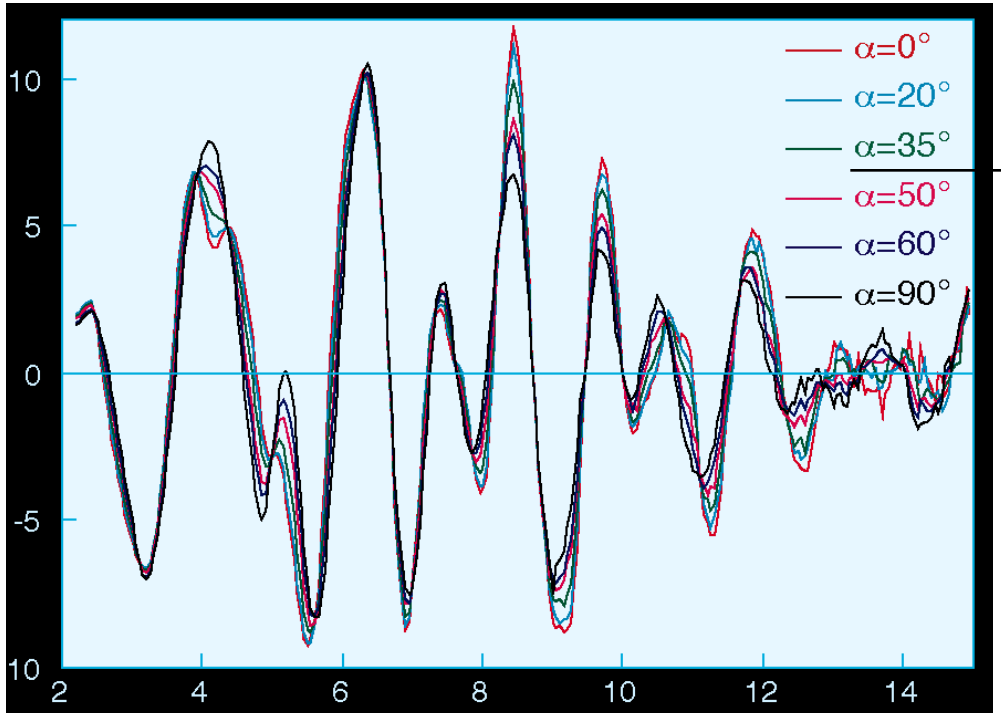
$\phi = 54.7°$

P-EXAFS of clays



P-EXAFS oscillations of Garfield nontronite

Fe K-edge

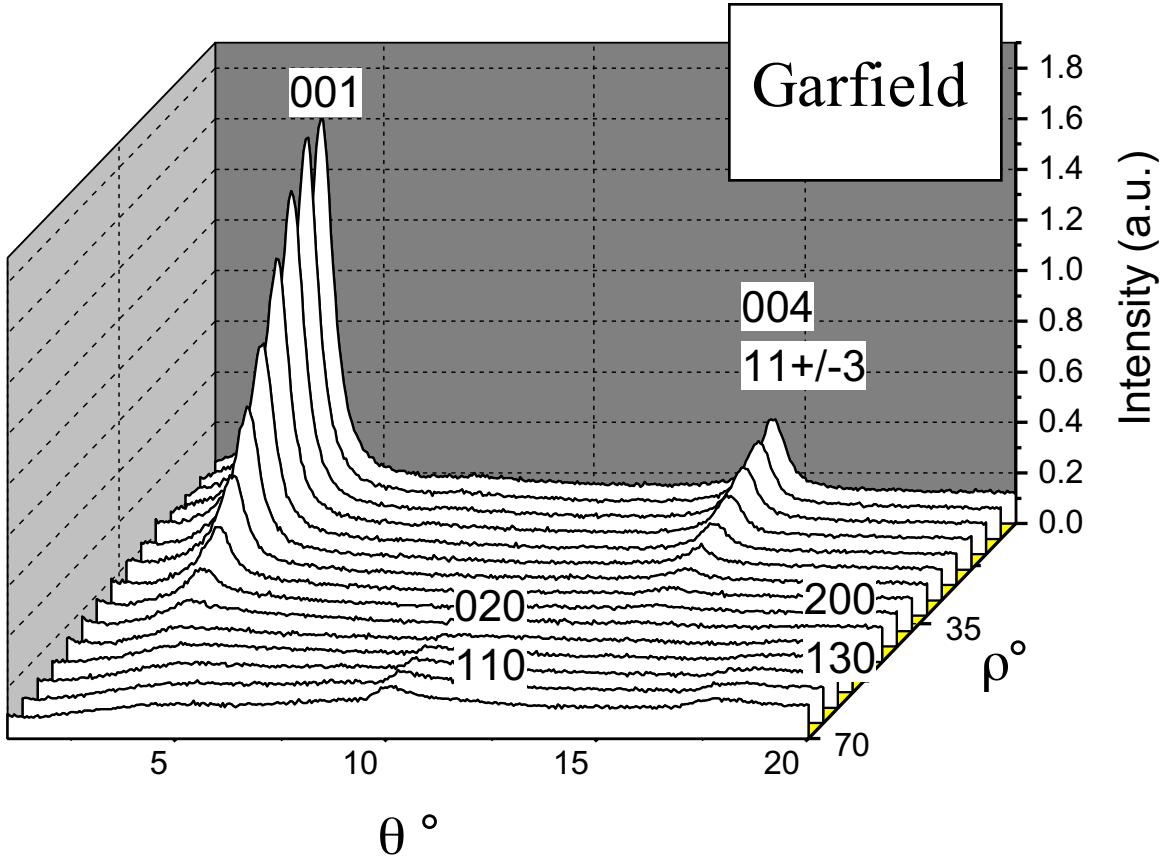


High quality range up to 14-15Å^{-1}

Powder spectra

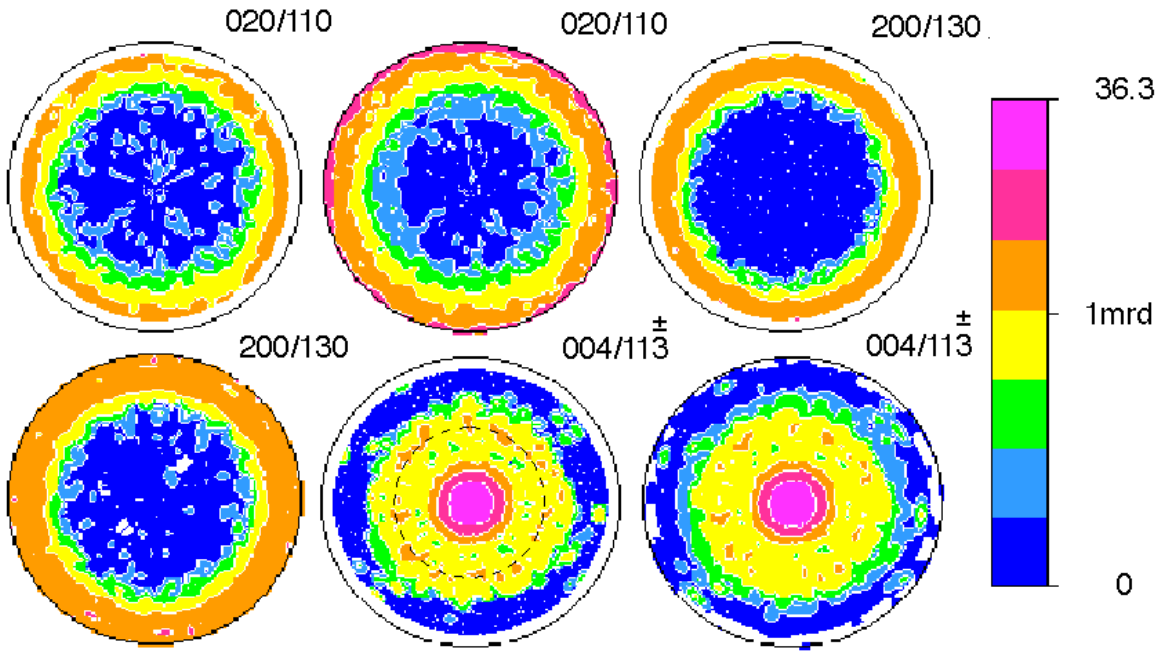
Strong α dependence
= strong texture

Texture experiments



OD-WIMV refinement

Crystal system: a=2.5749Å b=6.1484Å c=15.2693Å β=99.52°



Experimental and recalculated pole figures

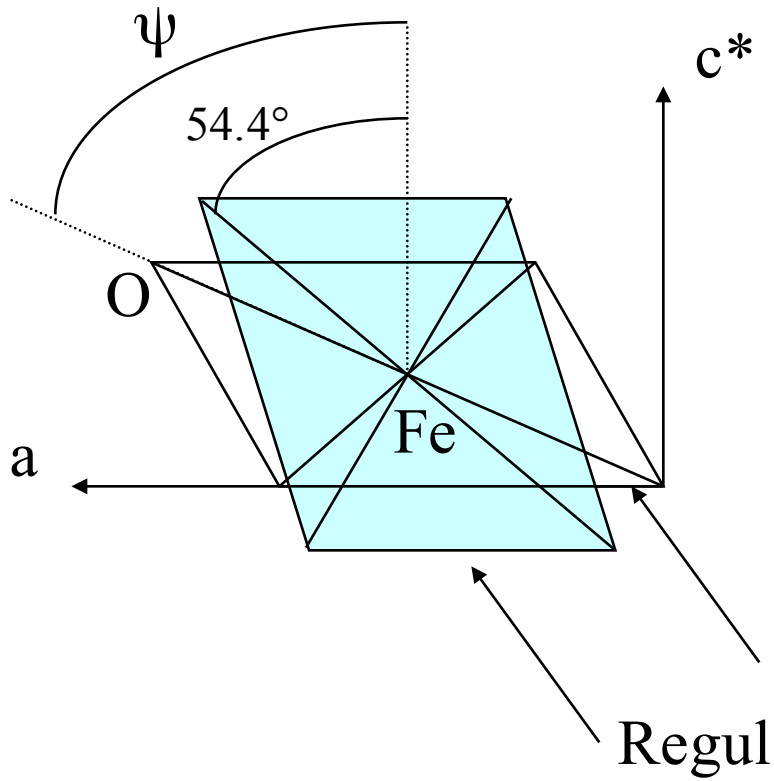
RP0 = 16.9%
RP1 = 10.1%
Rw0 = 6.8%
Rw1 = 5.6%

004/113/11-3 = 0.85/0.1/0.05
020/110 = 0.7/0.3
200/130 = 0.4/0.6

<001>* fibre, fibre axis ⊥ film plane

Octahedra flattening angle ψ

(Edge-sharing octahedral structures)



For ideally textured films:

(Stöhr, NEXAFS spect., 1992)

$$\frac{I_\alpha}{I_0} = \frac{1+\frac{1}{2}\left(3\sin^2\alpha-1\right)\left(3\cos^2\psi-1\right)}{1-\frac{1}{2}\left(3\cos^2\psi-1\right)}$$

Some conclusions

- The use of textured self-supporting films allow an extension of the **k** exploitable range of EXAFS spectra, when polarised radiation is used, and their quality

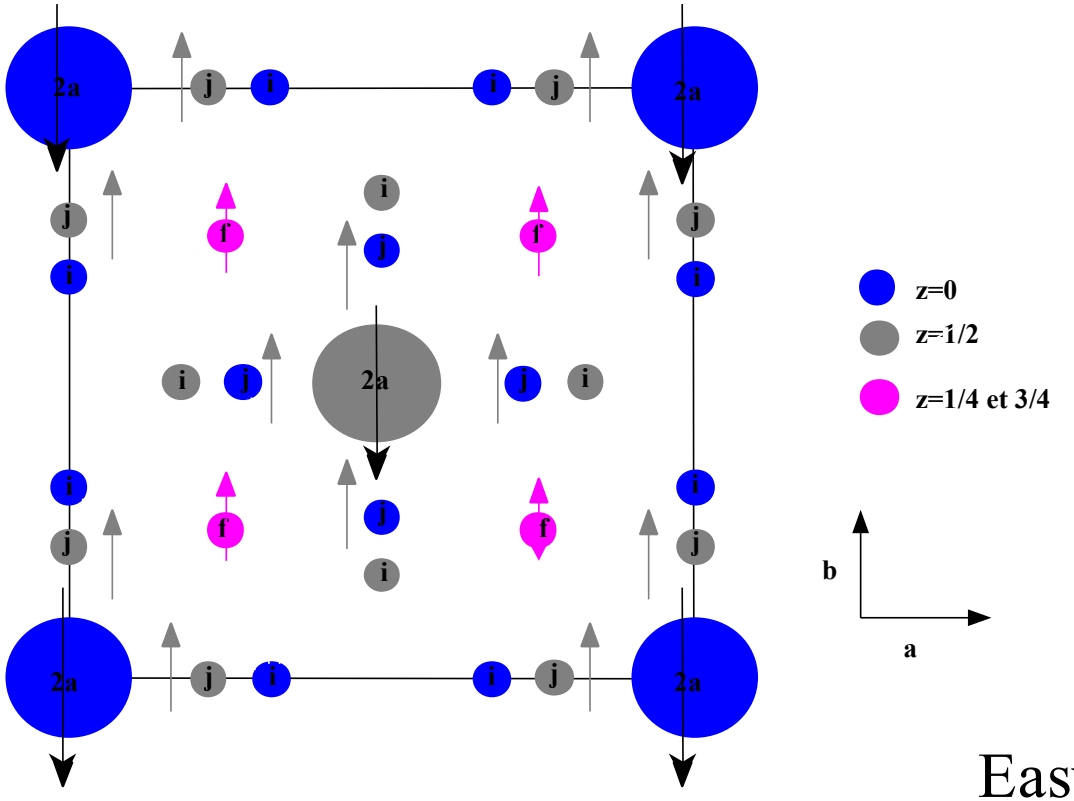
- Texture-corrected spectra permits the determination of the real number of neighbours

- The angular variation of the P-EXAFS spectra can provide the determination of structural distorsions

QTA and anisotropic magnetisation curves

Main Collaborator:
M. Morales: Lab. Cristallographie, Grenoble, France

$ErMn_4Fe_8C$



Structural determination:

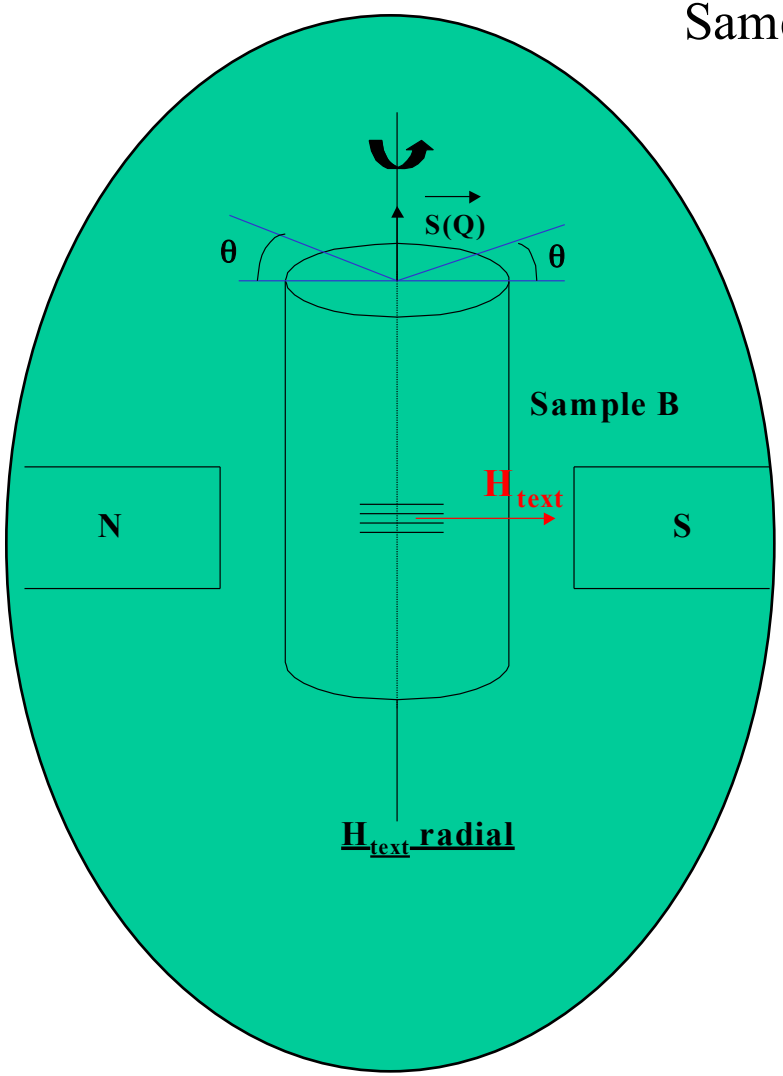
M. Morales et al.: J. Magn. And Magn. Mat. ***196*** *(1999) 703*

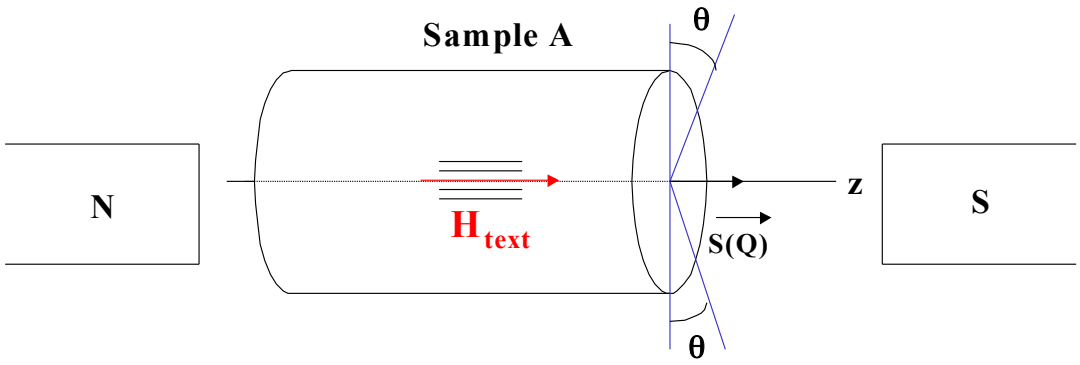
Easy-plane tetragonal phase

magnetic moments in the (a,b) planes

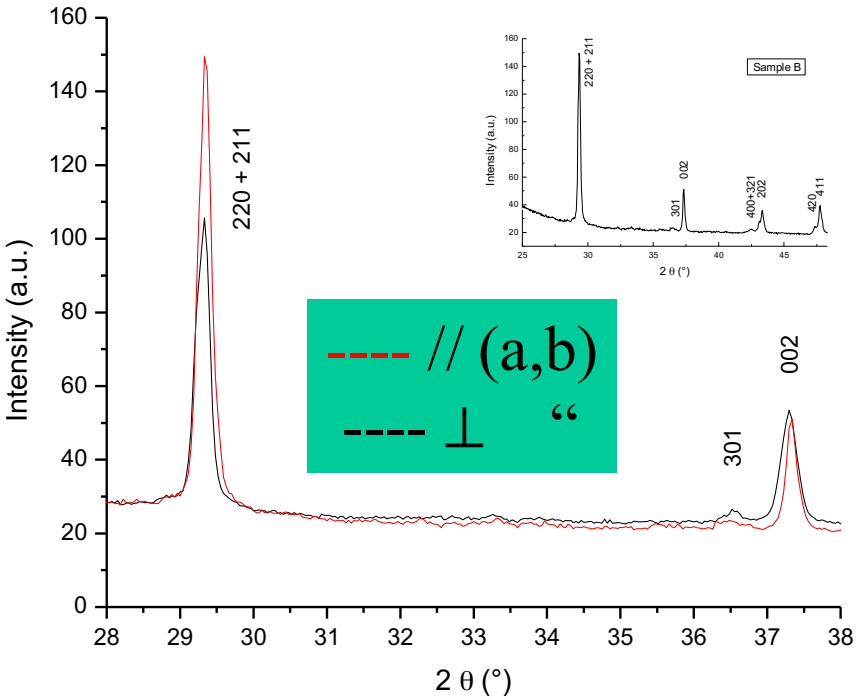
$\perp$ (a,b) ⟵ $\mathbf{H}_{meas}$ // **z** ⟶ // (a,b)

Same demagnetising factor





H text axial

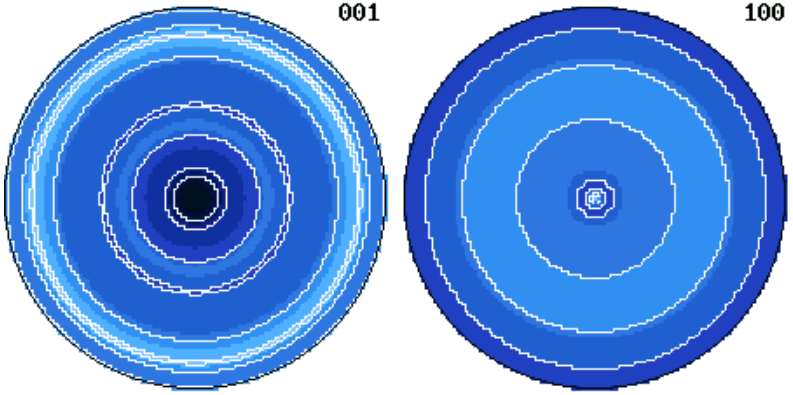


Quantitative Texture Analysis

$RP_0 = 1.2\ \%$

$F_2 = 1.3\ mrd^2$

$S = -0.13$

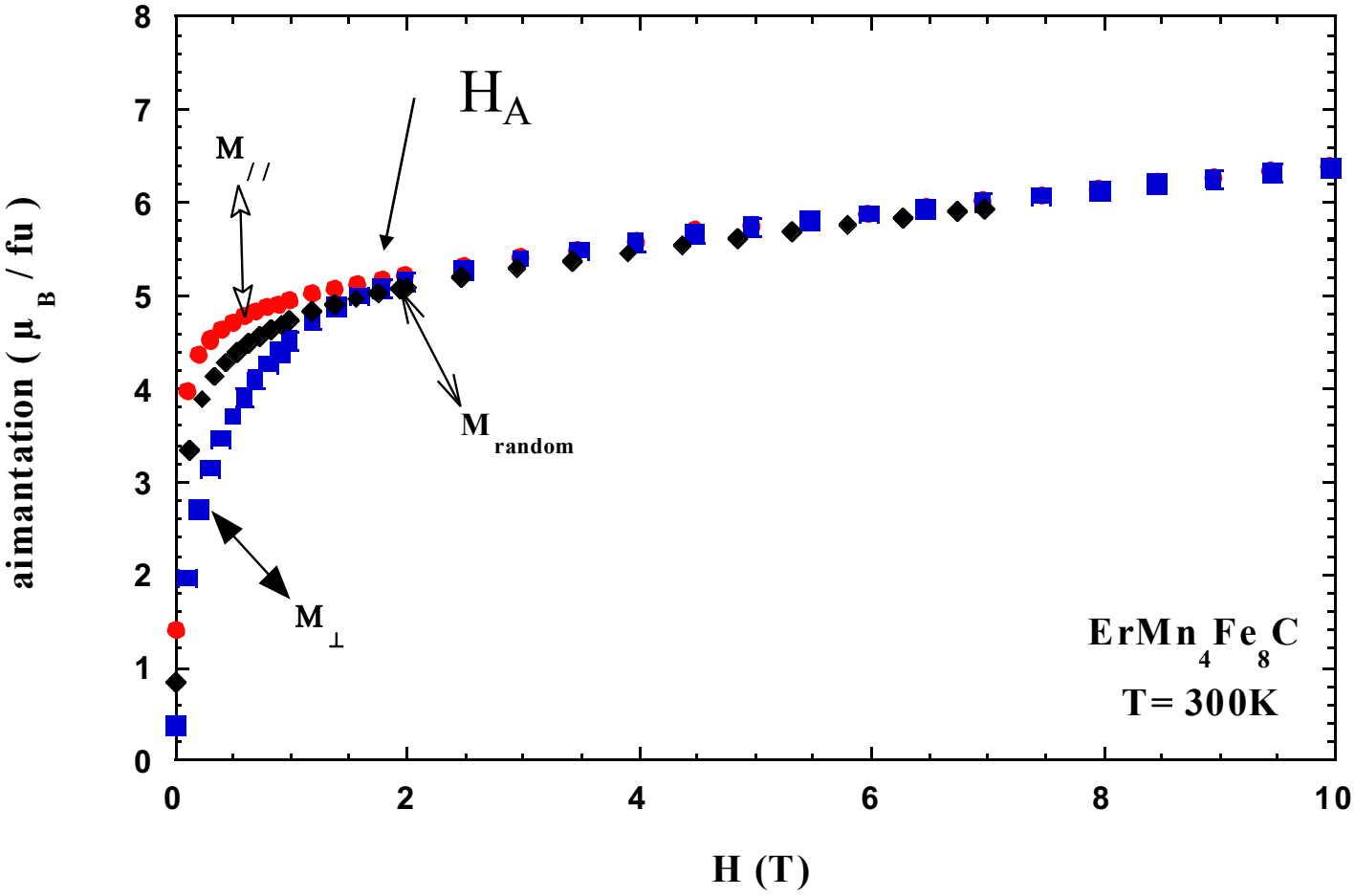


max {001}: 3.9 mrd

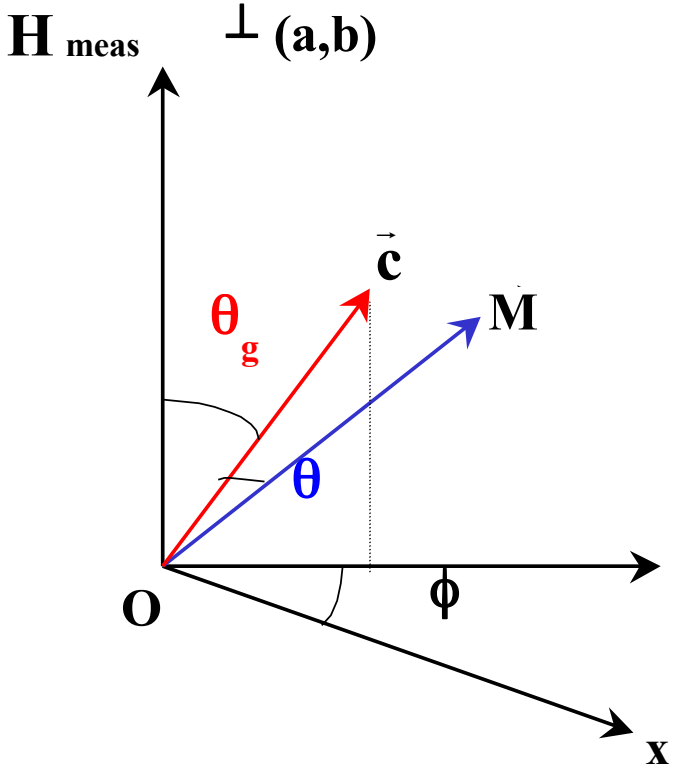
min: 0.5 mrd

{001} radial distribution: ρ_0 (0.5 mrd) + PV (HWHM = 12°)

Anisotropic magnetisation curves



Model for $M_{\perp}$:



$$M(H_{meas}) = M_S \cos(\theta_g - \theta)$$

$$E(H_{meas}) = K_1 \sin^2\theta - H M_S \cos(\theta_g - \theta)$$

anisotropy energy — Zeeman energy

$$\frac{dE}{d\theta} = 0 \quad \Rightarrow \quad H_{meas} = \frac{2 K_1 \sin\theta \cos\theta}{M_S \sin(\theta_g - \theta)}$$

$$H_A = 2K_1/M_S \qquad M_S = 5.24\ \mu_B/fu$$

$$\frac{H_{meas}}{H_A} = \frac{\sin\theta \cos\theta}{\sin(\theta_g - \theta)}$$

Normalised Probability function F, to find c-axes in d**y**:

$$\int_{\theta_g=0}^{\frac{\pi}{2}} \int_{\varphi=0}^{2\pi} F(\theta_g, \varphi) \sin\theta_g \, d\theta_g \, d\varphi = 1$$

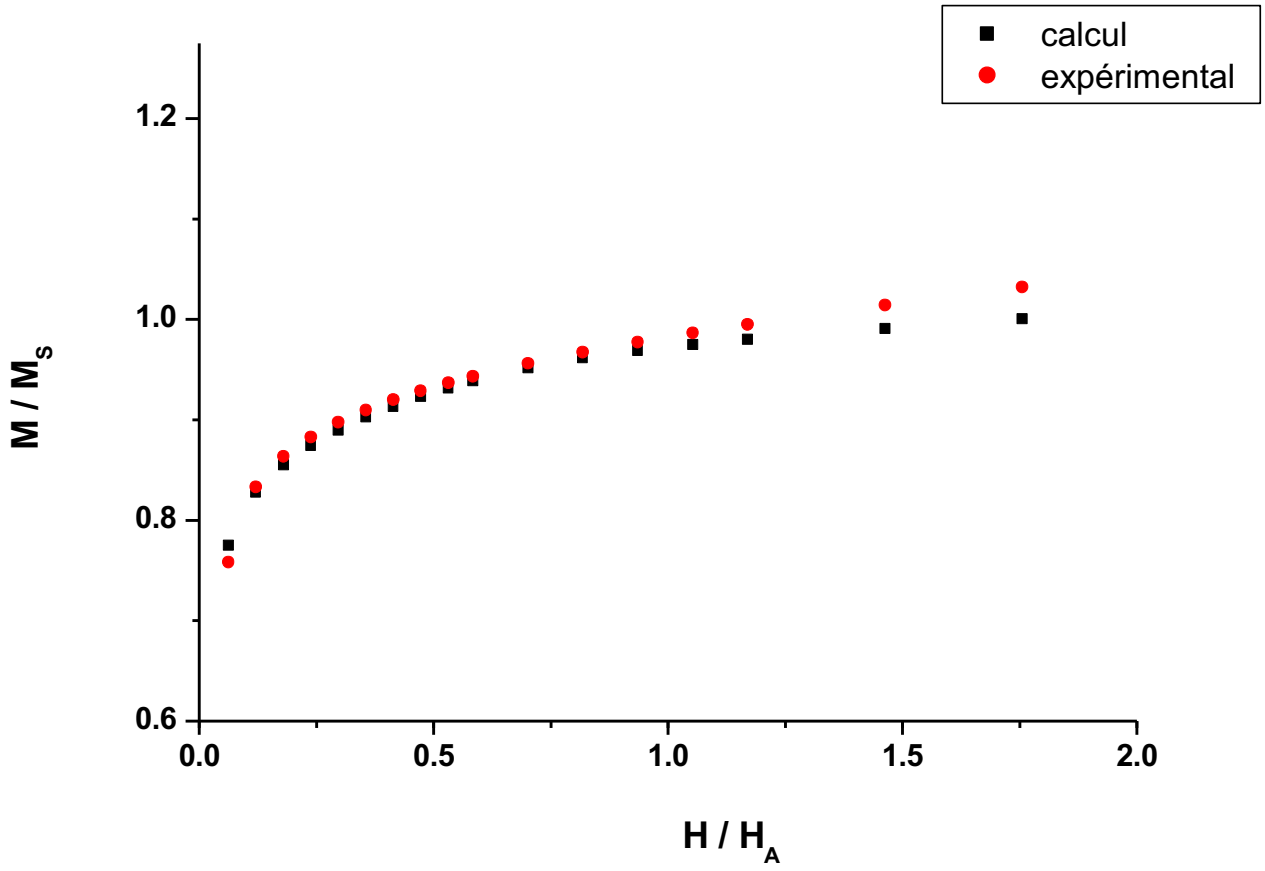
Fibre texture:

$$2\pi \int_{\theta_g=0}^{\frac{\pi}{2}} G(\theta_g) \sin\theta_g \, d\theta_g = 1$$

$$G(\theta_{\mathbf{g}}) = (1-\rho_0) PV(\theta_{\mathbf{g}})$$

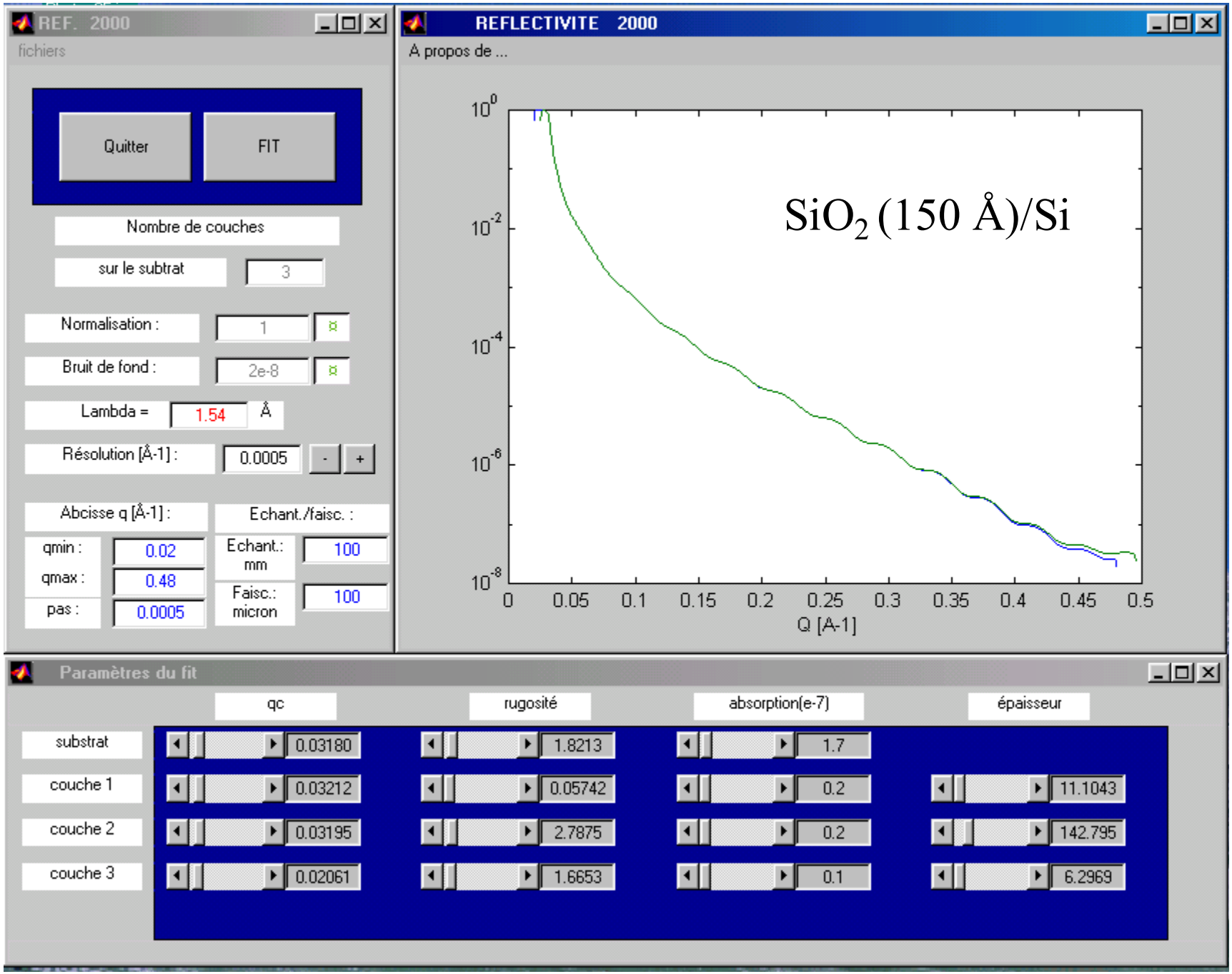
Finally:

$$\frac{M_\perp}{M_S} = 2\pi \int_0^{\frac{\pi}{2}} (1-\rho_0) PV(\theta_g) \sin\theta_g \cos(\theta_g - \theta) \, d\theta_g + \rho_0 M_{random}$$


calcul
expérimental
1.2
1.0
0.8
0.6
0.0
0.5
1.0
1.5
2.0
M / M_S
H / H_A

Some conclusions

- This model strongly deviates from reality at fields higher than 1.5 T
- But it takes account of the real (exp. measured) orientation distribution of crystallites, rather than trying to fit it
- Its merit is to separate purely magnetic and crystallographic effects


REF. 2000
fichiers
Quitter
FIT
Nombre de couches
sur le subtrat
3
Normalisation :
1
Bruit de fond :
2e-8
Lambda =
1.54
Å
Résolution [Å-1] :
0.0005
-
+
Abcisse q [Å-1] :
qmin :
0.02
qmax :
0.48
pas :
0.0005
Echant./faisc. :
Echant.: mm
100
Faisc.: micron
100
REFLECTIVITE 2000
A propos de ...
SiO_2 (150 Å)/Si
10^0
10^{-2}
10^{-4}
10^{-6}
10^{-8}
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
Q [A-1]
Paramètres du fit
qc
rugosité
absorption(e-7)
épaisseur
substrat
0.03180
1.8213
1.7
couche 1
0.03212
0.05742
0.2
11.1043
couche 2
0.03195
2.7875
0.2
142.795
couche 3
0.02061
1.6653
0.1
6.2969

Reflectivity and Electron Density Profile

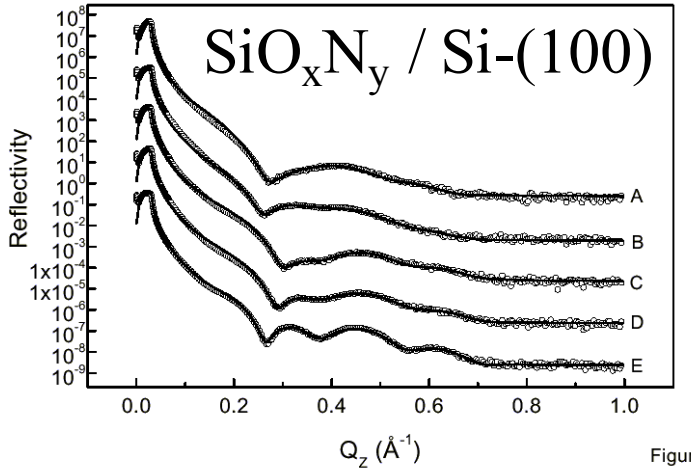


Figure 1

$$R(q_z) = \left| \frac{1}{\rho_\infty} \int_{-\infty}^{\infty} \frac{d\rho}{dz} e^{-iq_z z} dz \right|^2$$

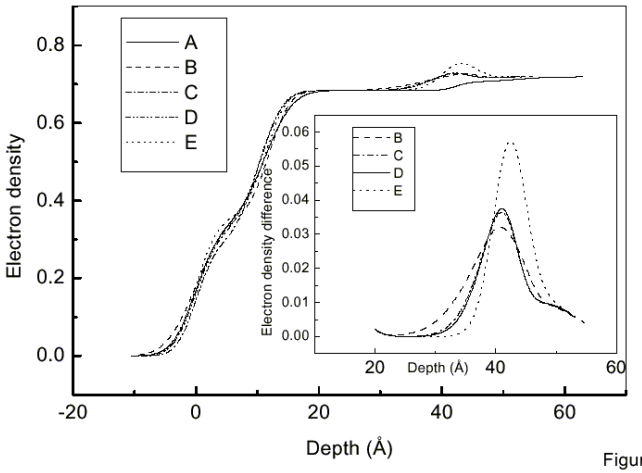
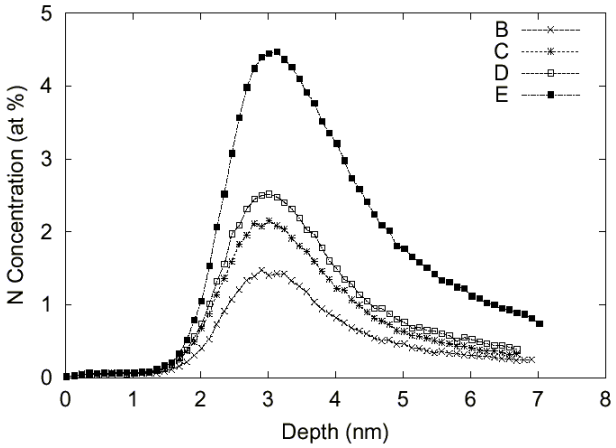


Figure 2



EDP

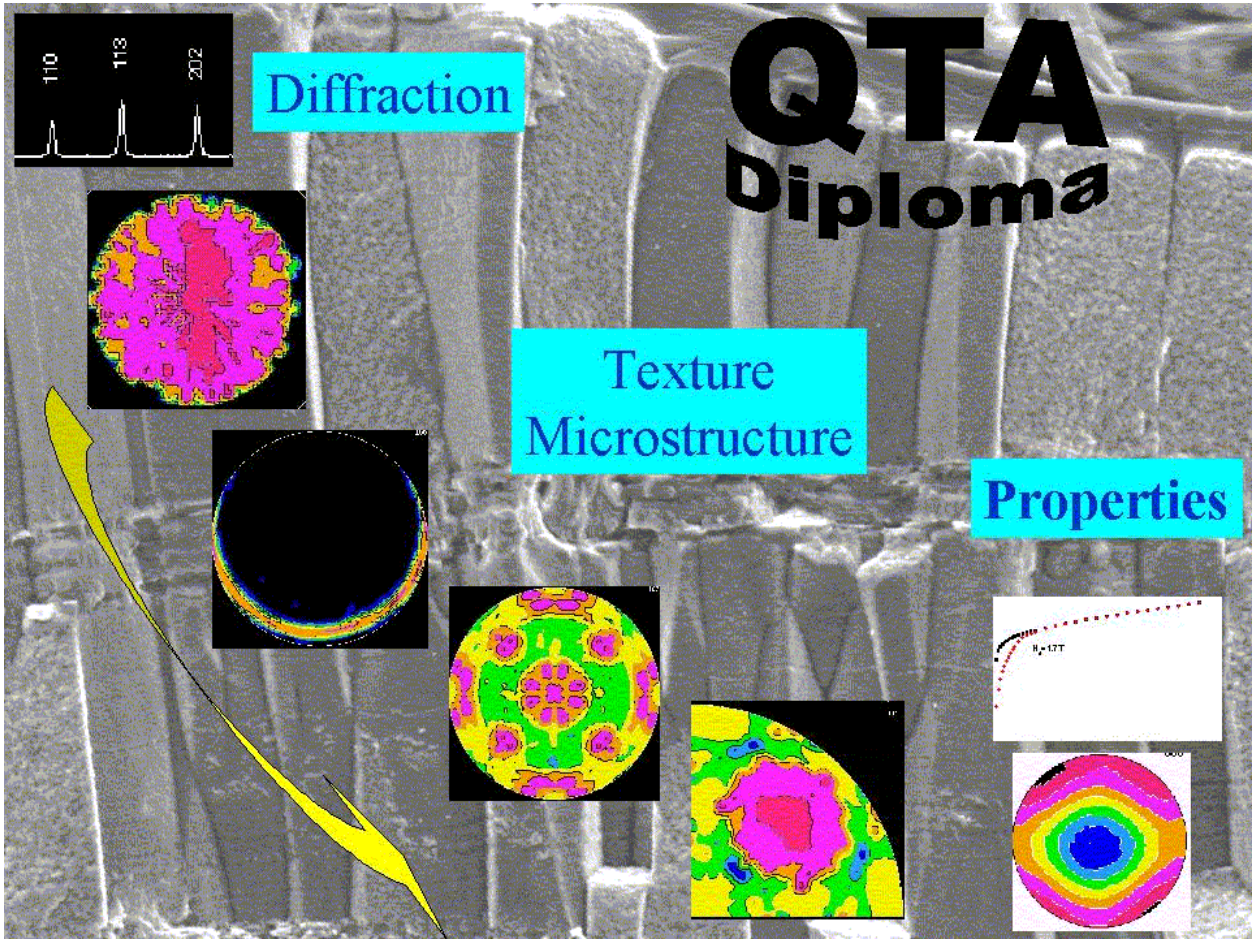
SIMS

Future trends

- Combining with reflectivity measurements: independently measured and refined thicknesses, electron densities and roughnesses
- Adding residual stress determinations

- Multiple Analysis Using Diffraction, a web-based tutorial for the combined approach: search MAUD (Luca Lutterotti)
- Quantitative Texture Analysis Internet Course: http://lpec.univ-lemans.fr/qta (Daniel Chateigner)

Quantitative Texture Analysis Internet Course



http://lpec.univ-lemans.fr/qta