Quantitative Texture Analysis

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Outline

Qualitative aspects of crystallographic textures
  Grains, Crystallites and Crystallographic planes
  Normal diffraction
Effects on diffraction diagrams, their limitations
  $\theta$-$2\theta$ scans
  Asymmetric scans
  $\omega$-scans (rocking curves)

Representations of texture: pole figures
  Pole Sphere
  Stereographic projection
  Equal-area projection: Lambert/Schmidt projection

Pole figures
  Localisation of crystallographic directions from pole figures
  Direct and normalised pole figures
  Normalisation
  Incompleteness and corrections of pole figures
  Single texture component
  Multiple texture components
  Pole figures and $(hk\ell)$ multiplicity
  A real example
Pole figure types
  - Random texture
  - Planar textures
  - Fibre textures
  - Three-dimensional texture

Pole Figures and Orientation spaces
  - Mathematical expression of diffraction pole figures and ODF
  - From pole figures to the ODF
  - Orientations $g$ and pole figures
  - Euler angle conventions
  - From $f(g)$ to pole figures
  - Deal with ODF in the $\mathcal{O}$ space
  - Plotting the ODF

Inverse pole figures

ODF refinement
  - Generalised spherical harmonics
  - WIMV
  - Entropy modified WIMV and Entropy maximisation
  - ADC, Vector and component methods
  - ODF coverage
  - Reliability and texture strength estimators

Magnetic QTA
Why needing QTA!!

- correcting texture effects
  powder XRD
  spectroscopic methods (P-EXAFS, ESR, Raman …)
- mollusc phylogeny, fossils
- predicting texture effect on macroscopic anisotropic properties
  average to get macroscopic tensors
  simulating elasticity, electric polarisation
  Bulk Acoustic Waves
  anisotropic magnetisation
- correlation texture - macroscopic anisotropic properties
  Thermoelectric Power Factor
  Pyroelectric coefficients
  Tauc gap
  Jc in superconductors
  Levitation forces and trapped flux

But why classical QTA vanishes

Why needing Combined analysis

Minimum experimental requirements ….
Qualitative aspects of texture

- **Polycrystal:** aggregate of grains, different phases, sizes, shapes, orientations, stress state, crystallinity, faults ... 

- **Diffraction:**
  - probes lattice planes: crystallites, not grains
  - x-rays, neutrons or electrons

- **SEM:**
  - grains, not crystallites (coherent, single crystal domains)
  - shape vs crystallographic texture (EBSD)
Grains, crystallites, crystallographic planes

\{hk\ell\} planes

crystallite

grain

sample

Friedel's law: \( I_{hk\ell} = I_{-h-k-\ell} \) using normal diffraction
+ or - directions not distinguished
Texture effects on diffraction diagrams

\( \theta-2\theta \text{ scan}: \) probes only parallel planes
$Li_{0.12}La_{0.88}TiO_3$ random bulk

$Li_{0.12}La_{0.88}TiO_3/(100)$-MgO

Oriented film

001

002

003
asymmetric scan: probes only inclined planes
mixed scan: probes specific planes for specific orientations

\[ \theta, \quad \omega = \theta \]
$\omega$ scan: probes orientation of only one plane type (fixed $\theta$), only for small $\omega$-$\theta$
limitations: available $\theta$ (or other) range diamond (Fd3m), 2.52 Å neutrons, up to $2\theta = 150^\circ$
limitations: 2 texture components
same c-axes direction, but not same a-axes orientation

\[ L_{hk\ell} = \frac{p - p_0}{1 - p_0}; p_0: \text{random} \]

\[ p = \frac{\sum I_{\{00\ell\}}}{\sum I_{\{hk\ell\}}} = 1 = L_{00\ell} \]
limitations: 2 texture components, one inclined
Representations of texture: pole figures

One crystallite oriented in the Pole sphere:
- location of all $[hkl] \in$ unit sphere
- $dS = \sin \chi \, d\chi \, d\varphi$
- $(\chi, \varphi)$: angles in the diffractometer space $S$

Hard to visualise: needs pole figures
Stereographic projections: equal angle

Poles: $p(r', \varphi)$:

$r' = R \tan(\chi/2)$
Lambert projections (equal area)

Poles: \( p(r', \varphi) \):

\[ r' = 2R \sin(\chi/2) \]
$5^\circ \times 5^\circ$ grid: 1368 points
Pole figures

{hkl}-Pole figure: location of distribution densities, for the \{hkl\} diffracting plane, defined in the crystallite frame \(K_B\), relative to the sample frame \(K_A\).

**Pole figures space:** \(Y\), with \(y = (\vartheta_y, \varphi_y) = [hkl]^*\)

**Direct Pole Figure:** built on diffracted intensities \(I_h(y)\), \(h = <hk\ell>^*\)

**Normalised Pole Figure:** built on distribution densities \(P_h(y)\)

Density unit: the "multiple of a random distribution", or "m.r.d."
Usual pole figure frames $K_A$

- **metallurgy**
- **malacology**
- **geophysics**

Thin films: substrate directions ... $X_A, Y_A, Z_A$
Normalisation

\[ I_{h \text{ total}}^\text{total} = \int \int_{\varphi_y = 0}^{\theta_y = 0} I_h(\vartheta_y, \varphi_y) \sin \vartheta_y \, d\vartheta_y \, d\varphi_y \]

\[ I_{h \text{ random}} = I_{h \text{ total}}^\text{total} / \int \int_{\varphi_y = 0}^{\theta_y = 0} \sin \vartheta_y \, d\vartheta_y \, d\varphi_y \]

\[ P_h(y) = I_h(y) \]

- Only valid for complete pole figures:
  neutrons in symmetric geometry

- Needs a refinement strategy to get \( I_{\text{random}} \) for all \( h \)'s
Incompleteness and corrections of pole figures

- Missing Bragg peaks
- Absorption + volume
- Defocusing (x-rays)
- Blind area
- Localisation
ω-defocusing

χ-defocusing

2θ-defocusing
Defocusing corrections:

- Calibration on a random powder

\[ I_{\text{cor}}^{\chi,\varphi,\omega,\theta} = I_{\text{meas}}^{\chi,\varphi,\omega,\theta} \frac{I_{\text{rand}}^{\chi,\omega,\theta}}{I_{\text{rand}}^{\chi,\varphi,\omega,\theta}} \]

Net intensities (point detector)

\[ = \left[ I_{\text{meas}}^{\chi,\varphi,\omega,\theta} - I_{\text{bkg}}^{\chi,\varphi,\omega,\theta} \right] \frac{I_{\text{rand}}^{b,\omega,\theta}}{I_{\text{bkg}}^{b,\omega,\theta}} - \frac{I_{\text{rand}}^{b,\chi,\omega,\theta}}{I_{\text{bkg}}^{b,\chi,\omega,\theta}} \]

- Total integration of the peak (direct integration or fit)

Peak maximum (point detector)
Integrated intensity (1D or 2D detector)
Overlaps enhance the problems!
Absorption/Volume corrections:

Specific to each instrumental geometry
Sample dependent (films, multilayers …)
Modifies the defocusing curves
Can be integrated in fitting procedures

Top film

\[ I(0) = I(\chi) \frac{(1 - \exp(-2\mu T / \sin \theta_i))}{(1 - \exp(-2\mu T / \sin \theta_i \cos \chi))} \]

Covered layer

\[ I(0) = I(\chi) \frac{(1 - \exp(-2\mu T / \sin \theta_i)) \exp\left(-2 \sum_j \mu_j T_j \frac{1}{\sin \theta_i}\right)}{(1 - \exp(-2\mu T / \sin \theta_i \cos \chi)) \exp\left(-2 \sum_j \mu_j T_j \frac{1}{\sin \theta_i \cos \chi}\right)} \]
Single or multiple texture components, multiplicity

- Single
- Double
- Cubic
- Tetragonal
Program convention!
orientations are ... oriented objects
A real example

Cypraea testudinaria

Outer aragonite layer
Pnma space group
Texture types

Random texture
3 degrees of freedom
All $P_h(y)$ homogeneous
1 m.r.d. density whatever $y$

Planar texture
2 degrees of freedom
1 $[hkl]$ at random in a plane
**Fibre texture**

1 degree of freedom

1 \([hkl]\) along 1 \(y\) direction

**Cyclic-Fibre texture**

\(\mathbf{c} \parallel Z_A\)

**Cyclic-Planar texture**

\(\mathbf{c} \parallel (X_A, Y_A)\)
Single crystal-like texture

0 degree of freedom
2 [hkl]'s along 2 y directions

Single-crystal and perfect 3D orientation not distinguished
Pole figure and Orientation spaces

Pole figure expression:

\[
\frac{\mathrm{d}V(y)}{V} = \frac{1}{4\pi} P_h(y) \, \mathrm{d}y
\]

\[
\mathrm{d}y = \sin \vartheta_y \, \mathrm{d}\vartheta_y \, \mathrm{d}\varphi_y
\]

Orientation Distribution Function \( f(g) \):

\[
\frac{\mathrm{d}V(g)}{V} = \frac{1}{8\pi^2} f(g) \, \mathrm{d}g
\]

\[
\mathrm{d}g = \sin(\beta) \, \mathrm{d}\beta \, \mathrm{d}\alpha \, \mathrm{d}\gamma
\]

\[
\int_{\alpha=0}^{2\pi} \int_{\beta=0}^{\pi/2} \int_{\gamma=0}^{2\pi} f(g) \, \mathrm{d}g = 8\pi^2
\]
From Pole figures to the ODF

Pole figure: one direction fixed in $K_A$

Orientation: two directions fixed in $K_A$

Fundamental Equation of QTA

$P_h(y) = \frac{1}{2\pi} \int f(g) \, d\tilde{\varphi}$

Needs several pole figures to construct $f(g)$
Pole figures from $g$

- Rotation of $K_A$ about the axis $Z_A$ through the angle $\alpha$:  
  \[ [K_A \mapsto K'_A]; \text{ associated rotation } g_1 = \{\alpha,0,0\} \]

- Rotation of $K'_A$ about the axis $Y'_A$ through the angle $\beta$:  
  \[ [K'_A \mapsto K''_A]; \text{ associated rotation } g_2 = \{0,\beta,0\} \]

- Rotation of $K''_A$ about the axis $Z''_A$ through the angle $\gamma$:  
  \[ [K''_A \mapsto K'''_A//K_B]; \text{ associated rotation } g_3 = \{0,0,\gamma\} \]

finally:  
\[ g = g_1 \, g_2 \, g_3 = \{\alpha,0,0\} \{0,\beta,0\} \{0,0,\gamma\} = \{\alpha,\beta,\gamma\} \]

\[
g_1 = \{45,0,0\} \quad g_2 = \{45,45,0\} \quad g_3 = \{45,55,45\} \]
## Euler angles conventions

<table>
<thead>
<tr>
<th>Matthies</th>
<th>Roe</th>
<th>Bunge</th>
<th>Canova</th>
<th>Kocks</th>
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</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>$\Psi$</td>
<td>$\varphi_1 = \alpha + \pi/2$</td>
<td>$\omega = \pi/2 - \alpha$</td>
<td>$\Psi$</td>
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<tr>
<td>$\beta$</td>
<td>$\Theta$</td>
<td>$\Phi$</td>
<td>$\Theta$</td>
<td>$\Theta$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>$\Phi$</td>
<td>$\varphi_2 = \gamma + 3\pi/2$</td>
<td>$\phi = 3\pi/2 - \gamma$</td>
<td>$\Phi = \pi - \gamma$</td>
</tr>
</tbody>
</table>

**Bunge's convention**

**Roe/Matthies's convention**
From $f(g)$ to the pole figures
Deal with components in the ODF space

Component: (Hexagonal system)
\( g = \{85,80,35\} \)
Plotting $f(g)$

A 3D plotting program: ODF plot

ODF sections ($\alpha$, $\beta$, or $\gamma$)

ODF 3D-isometric view
Cartesian or Polar f(g) view

\[ \beta = 0: \text{space deformation} \]
Inverse pole figures

\[ P_h(y) = \frac{1}{2\pi} \int f(g) \, d\tilde{\varphi} \]

Pole figures

\[ R_y(h) = \frac{1}{2\pi} \int f(g) \, d\tilde{\varphi} \]

Inverse Pole figures

24 equivalent cubic sectors for the Inverse pole figure of a cubic system
ODF refinement

One has to invert:

\[ P_h(y) = \frac{1}{2\pi} \int f(g) \, d\tilde{\varphi} \]

from Generalized Spherical Harmonics (Bunge):

\[ f(g) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} C_l^{mn} T_l^{mn}(g) \]

\[ P_h(y) = \sum_{l=0}^{\infty} \frac{1}{2l + 1} \sum_{n=-l}^{l} k_l^n(y) \sum_{m=-l}^{l} C_l^{mn} k_n^m(\Theta_h \phi_h) \]

Least-squares Refinement procedure

\[ \sum_h \sum_y \left[ I_h(y) - N_h P_h(y) \right]^2 dy \]

But even orders are the only available parts:

\[ f^{ev}(g) = \sum_{\lambda=0(2)}^{\infty} \sum_{m=-\lambda}^{\lambda} \hat{C}_\lambda^{mn} T_\lambda^{mn}(g) \]
from the WIMV iterative process (Williams-Imhof-Matthies-Vinel):

\[ f^{n+1}(g) = N_n \frac{f^n(g) f^0(g)}{\left( \prod_{h=1}^{M_h} \prod_{m=1}^{M_h} P^n_m(y) \right)^{1/M_h}} \]

and

\[ f^0(g) = N_0 \left( \prod_{h=1}^{M_h} \prod_{m=1}^{M_h} P^\exp_m(y) \right)^{1/M_h} \]

E-WIMV (Rietveld only):

with \( 0 < r_n < 1 \), relaxation parameter, \( M_h \) number of division points of the integral around \( k \), \( w_h \) reflection weight

Entropy maximisation (Schaeben) and exponential harmonics (van Houtte):

\[ f^{n+1}(g) = f^n(g) \prod_{m=1}^{M_h} \left( \frac{P_h(y)}{P^n_h(y)} \right)^{r_n/M_h} \]

\[ f_s(g) = e^{h(g)} \geq 0 \]

\[ C_{s\lambda}^{mn} = (2\lambda + 1) \int e^{h(g)} T_{\lambda}^{mn}(g) dg \]
arbitrarily defined cells (ADC, Pawlik):

Very similar to E-WIMV, with integrals along path tubes

Vector method (Ruer, Baro, Vadon):

I linear equations for J unknown quantities:

\[ P_i(h) = [\sigma_{ij}(h)] f_j \]

Component method (Helming):

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

Gaussian component:

\[ f(g, g^c) = f(\tilde{g}) = \frac{2\sqrt{\pi}}{\zeta \left(1 - \exp\left( -\left(\frac{\zeta}{2}\right)^2\right)\right)} \exp\left( -\left(\frac{g}{\zeta}\right)^2\right) \]

\[ S = \frac{\ln 2}{\sqrt{\frac{\zeta}{2}}} \]

\[ N(S) = \frac{1}{I_0(S) - I_1(S)} \]
Evaluation of the OD coverage

Say 20 measured (5° x 5°) complete pole figures:

\[= 20 \times 1368 = 27360 \text{ experimental points}\]

ODF (5° x 5° x 5°, triclinic): 98496 points to refine

\{100\} pole figure, measured up to \(\chi = 45°\):

\{100\} + \{110\}, measured up to \(\chi = 45°\):

\{100\} + \{110\} + \{111\}, up to \(\chi = 45°\):
Estimators of Refinement Quality

Visual assessment

*Helix pomatia* (Burgundy land snail: Outer com. crossed lamellar layer)

*Bathymodiolus thermophilus* (deep ocean mussel: Outer Prismatic layer)
RP Factors:

Individual pole figures:

\[
RP_x (h_i) = \frac{\sum_{j=1}^{J} |\tilde{P}_{h_i}^o (y_j) - \tilde{P}_{h_i}^c (y_j)|}{\sum_{j=1}^{J} \tilde{P}_{h_i}^o (y_j)} \theta(x, \tilde{P}_{h_i}^o (y_j))
\]

Averaged on all pole figures:

\[
\overline{RP}_x = \frac{1}{I} \sum_{i=1}^{I} RP_x (h_i)
\]

\[
\theta(x, t) = \begin{cases} 
1 & \text{for } t > x \\
0 & \text{for } t \leq x 
\end{cases}
\]

\[x = \varepsilon, 1, 10 \ldots\]
Bragg R-Factors:

\[
RB_x (h_i) = \frac{\sum_{j=1}^{J} \left[ \tilde{P}_h^o (y_j) - \tilde{P}_h^c (y_j) \right]}{\sum_{j=1}^{J} \tilde{P}_h^o (y_j)^2} \theta(x, \tilde{P}_h^o (y_j))
\]

Weighted Rw-Factors:

\[
Rw_x (h_i) = \frac{\sum_{j=1}^{J} \left[ w_{ij}^o I_{h_i}^o (y_j) - w_{ij}^c I_{h_i}^c (y_j) \right]}{\sum_{j=1}^{J} w_{ij}^o I_{h_i}^z (y_j)^2} \theta(x, \tilde{P}_h^o (y_j))
\]

\[
w_{ij} = \frac{1}{\sqrt{I_{h_i}^o (y_j)}}
\]
Texture strength estimators

**ODF Texture Index:**

\[ F^2(m.r.d.) = \frac{1}{8\pi^2} \sum_i f^2(g_i)\Delta g_i \]

- \( F^2 \in [1, \infty[ \)
- \( > 1 \) m.r.d.
- \( = 1 \): powder
- \( = \infty \): single crystal

**Discrete ODF**

\[ F^2 = 1 + \sum_{\lambda=2}^{L} \left[ \frac{1}{2\lambda + 1} \right] \sum_{m=-\lambda}^{\lambda} \sum_{n=-\lambda}^{\lambda} |C_{\lambda}^{mn}|^2 \]

**Continuous ODF**

**Pole figures Texture Index:**

\[ J_h^2 = \frac{1}{4\pi} \sum_i [P_h(y_i)]^2 \Delta y_i \]
Texture Entropy:

\[ S \in [0,-\infty[ \leq 0 \]

\[ = 0: \text{powder} \]

\[ = -\infty: \text{single crystal} \]

\[ S = \frac{-1}{8\pi^2} \sum_i f(g_i) \ln[f(g_i)] \Delta g_i \]

**S - F^2:**

Fon + smooth texture component(s)

Fon + Dirac-like texture component

Lower bound: Fon = 0
Crystallographic texture

Corrections (defocusing, localization, Volume-absorption)

Pole figures
Y space, $I_h(y)$

Normalization
$P_h(y)$

Diffraction Measurements
S space, $I(\chi, \varphi, \omega, \eta, 2\theta)$

Orientation Distribution Function
G space, $f(g)$

Macrosopic anisotropic properties ($M_i$, $C_{ijkl}$, $\sigma_{ij}$, $d_{ijk} \ldots)_M$

Elastic wave velocities (geophysics)

Anisotropic spectroscopies (P-EXAFS, ESR \ldots)

Character analyses (phylogeny, palaeontology)

Art and Cultural Heritage
Magnetic QTA

\[ I_n^m (\vec{y}, 0) = I_h (\vec{y}, 0) + I_m^m (\vec{y}, 0) \]

\[ I_h (\vec{y}, \vec{B}) = I_h^m (\vec{y}, 0) + I_m (\vec{y}, \vec{B}) \]

\[ \Delta I_h^m (\vec{y}, \vec{B}) = I_h (\vec{y}, \vec{B}) - I_h (\vec{y}, 0) \]
**** True iteration step #120 ****

ODF min max: 0.64 2.26
Texture Index $\langle F_2 \rangle$ 1.0294
Entropy -0.0144
Average RP 0.2427
Average RP1 0.3041
Why needing QTA

- Correct for QTA effects in XRD: structure analysis

QTA and structure correlations: yes, but $f(g)$ and $|F_h|^2$ are different!

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<tbody>
<tr>
<td>OD maximum (m.r.d.)</td>
<td>299</td>
<td>196</td>
<td>2816</td>
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<td>OD minimum (m.r.d.)</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Texture index (m.r.d.²)</td>
<td>42.6</td>
<td>47</td>
<td>721</td>
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<td>Texture reliability factors</td>
<td>$R_w$ (%)</td>
<td>14.3</td>
<td>11.2</td>
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<td>$R_B$ (%)</td>
<td>15.6</td>
<td>12.7</td>
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<td>Rietveld reliability factors</td>
<td>GoF (%)</td>
<td>1.72</td>
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<td>$R_w$ (%)</td>
<td>29.2</td>
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<td>$R_B$ (%)</td>
<td>22.9</td>
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<td>$R_{exp}$ (%)</td>
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Charonia lampas lampas
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<th>Geological reference</th>
<th>Charonia lampas OCL</th>
<th>Charonia lampas RCL</th>
<th>Charonia lampas ICCL</th>
<th>Strombus decorus</th>
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<tbody>
<tr>
<td>a (Å)</td>
<td>4.9623(3)</td>
<td>4.98563(7)</td>
<td>4.97538(4)</td>
<td>4.9813(1)</td>
<td>4.9694(3)</td>
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<tr>
<td>b (Å)</td>
<td>7.968(1)</td>
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<td>7.98848(8)</td>
<td>7.9679(1)</td>
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<tr>
<td>c (Å)</td>
<td>5.7439(3)</td>
<td>5.74626(3)</td>
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<td>5.76261(5)</td>
<td>5.7528(1)</td>
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<tr>
<td>Ca y</td>
<td>0.41500</td>
<td>0.41418(5)</td>
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<td>Ca z</td>
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<td>C z</td>
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<td>O1 y</td>
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<td>O1 z</td>
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<td>O2 x</td>
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<tr>
<td>O2 y</td>
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<td></td>
<td>0.4763(6)</td>
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<tr>
<td>O2 z</td>
<td></td>
<td></td>
<td></td>
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<td>0.6833(3)</td>
</tr>
<tr>
<td>( \Delta Z_{\text{C-O1}} ) (Å)</td>
<td>0.05744</td>
<td>0.00029</td>
<td>0.04335</td>
<td>0.1066</td>
<td>0.031</td>
</tr>
</tbody>
</table>

Calcite: \( \Delta Z = 0 \)  
Biogenic intercrystalline effect
Correct for QTA effects in XRD: QPA
QTA and QPA correlations: yes, but
\( f(g) \) and \( S_\Phi \) are different!

\( f(g) \) is on the individuals

\( S_\Phi \) is on the sum
- Correct for QTA effects in spectroscopies: P-EXAFS on clays

\[ \alpha = 0^\circ \rightarrow \alpha = 90^\circ \]

Beam direction

Oct-Tet: min
Oct-Oct: max

Oct-Tet: max
Oct-Oct: 0

Absorber
Mg, Al, Fe
Si, Al
\[
\left\langle \cos^2 \theta_{ij} \right\rangle = \frac{1}{2\pi} \int_{0}^{2\pi} \cos^2 \theta_{ij} d\Omega = \cos^2 \phi \sin^2 \alpha + \frac{\cos^2 \alpha \sin^2 \phi}{2}
\]
Fe K-edge

High quality range up to 14-15Å$^{-1}$

Powder spectra

Strong $\alpha$ dependence = strong texture

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

\[
\frac{I_\alpha}{I_0} = \frac{1 + \frac{1}{2} (3 \sin^2 \alpha - 1)(3 \cos^2 \psi - 1)}{1 - \frac{1}{2} (3 \cos^2 \psi - 1)}
\]
Mollusc shells and fossils: **phylogeny**

Closely related species, close textural characters, but significant variations: **textural parameters** can serve character analysis.

- **Bivalvia**
  - *Atrina maurea* \( \langle \perp | \text{ISN}^a_{44}, 20 \rangle \)
  - *Pinna nobilis* \( \langle \perp | \text{ISN}^a_{25}, 95 \rangle \)
  - *Lampsilis alatus* \( \langle \perp | \text{ISN}^a_{25}, 90 \rangle \)
  - *Fragum fragum* \( \langle \forall, 15 | \text{ICCL} | x^{110} < 50 \rangle \)
  - *Glycymeris gigantea* \( \langle \forall, 15 | \text{ICCL} | x^{110} < 50 \rangle \)
  - *Spondylus princeps* \( \langle \forall, 15 | \text{ICCL} | x^{110}, -15 \rangle \)
  - *Paphia solanderi* \( \langle \perp | \text{ICCL} | \text{O} \rangle \langle \angle, 20 | \text{OSiP} | \text{O} \rangle \)
  - *Neotrigonia sp.* \( \langle \perp | \text{ISN}^a_{12}, 90 \rangle \)
  - *Pinctada margaritifera* \( \langle \perp | \text{ISN}^a_{8}, 90 \rangle \)
  - *Pinctada maxima* \( \langle \perp | \text{ISN}^a_{14}, 90 \rangle \)
  - *Pteria penguin* \( \langle \perp | \text{ISN}^a_{15}, -30 \rangle \)
Monoplacophora: Neopilina galatheae \( \langle \bot | \text{IN} | \text{O} \rangle \), Rokopella zografi \( \langle \bot | \text{IN} | \text{O} \rangle \)

Cephalopoda: Nautilus pompilius \( \langle \bot | \text{ICN} | ^*_{a,75} \rangle \), Nautilus macromphalus \( \langle \bot | \text{ICN} | ^*_{a,80} \rangle \)

Scutellaster tabularis \( \langle v, 25 | \text{IRCL} | x_{50}^{<110>, -10} \rangle \)

Conus leopardus \( \langle \bot | \text{ICCL} | x_{47}^{a,60} \rangle \), \( \langle \bot | \text{ORCL} | \text{O} \rangle \)

Muricanthus nigritus \( \langle \bot | \text{ICCL} | x_{47}^{a,-50} \rangle \)

Cyclophorus woodianus \( \langle \bot | \text{IRCL} | l_{a,20} \rangle \)

Cypraea mus \( \langle \bot | \text{IP} | ^*_{a,45} \rangle \)

Cypraea testudinaria \( \langle v, 15 | \text{ICCL} | l_{a,10} \rangle \)

Oliva miniacea \( \langle \bot | \text{OCCL} | x_{50}^{a,30} \rangle \)

Euglandina sp. \( \langle \bot | \text{ICCL} | l_{a,-80} \rangle \)

Helix aspera \( \langle \bot | \text{OCCL} | l_{a,90} \rangle \)

Helix pomatia \( \langle \bot | \text{OCCL} | l_{a,90} \rangle \)

Gastropoda
Gastropoda

Entemnotrochus adansonianus (⊥ICN|O)
Perotrochus quoyanus (⊥ICN|O)

Haliotis cracherodi (∠, 15|ICN|O)
Haliotis rufescens (⊥ICN|O)

Tectus niloticus (⊥ICN|O)
Tectus pyramis (∠, 15|OSP|O)
Turbo petholatus (⊥OSP|O)

Phasianella australis (⊥OICP|O)

Fissurella oriens (ν, 20|ICoCL|*<110>)

Scutus antipodes (⊥ICCL|*a, 90)

Nerita polita (∠, 25|ICCL|*a)
Nerita scabricota (⊥ICoCL|O)
Viana regina (⊥ICCL|O) (⊥OCCL|O) (∠, 15|OHC|O)
Phylogenetic interest: nacre = ancestral (Carter & Clarck, 1985)

19 evolutionary events, from cladistics character analysis
nacre not ancestral

9 events
## Calcitic fossils: trichites

<table>
<thead>
<tr>
<th></th>
<th>Layer type</th>
<th>ODF Max (mrd)</th>
<th>ODF min (mrd)</th>
<th>RP0 (%)</th>
<th>RP1 (%)</th>
<th>c-axis</th>
<th>a-axis</th>
<th>{001} Max (mrd)</th>
<th>F^2 (mrd^2)</th>
<th>- S</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pinna nobilis</strong></td>
<td>OP</td>
<td>303</td>
<td>0</td>
<td>50</td>
<td>29</td>
<td>// N</td>
<td>random</td>
<td>68</td>
<td>29</td>
<td>2.3</td>
</tr>
<tr>
<td><strong>Pteria penguin</strong></td>
<td>OP</td>
<td>84</td>
<td>0</td>
<td>29</td>
<td>15</td>
<td>// N</td>
<td>random</td>
<td>31</td>
<td>13</td>
<td>1.9</td>
</tr>
<tr>
<td><strong>Amussium parpiraceum</strong></td>
<td>OP</td>
<td>330</td>
<td>0</td>
<td>53</td>
<td>33</td>
<td>// G</td>
<td>&lt;110&gt; // M</td>
<td>20</td>
<td>31</td>
<td>2.6</td>
</tr>
<tr>
<td><strong>Bathymodiolus thermophilus</strong></td>
<td>OP</td>
<td>63</td>
<td>0</td>
<td>25</td>
<td>18</td>
<td>// G</td>
<td>// M</td>
<td>27</td>
<td>13</td>
<td>1.9</td>
</tr>
<tr>
<td><strong>Mytilus edulis</strong></td>
<td>OP</td>
<td>207</td>
<td>0</td>
<td>41</td>
<td>25</td>
<td>75° from N</td>
<td>&lt;110&gt; // M</td>
<td>23</td>
<td>21</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>Trichites</strong></td>
<td>P</td>
<td>390</td>
<td>0</td>
<td>52</td>
<td>28</td>
<td>15° from N</td>
<td>random</td>
<td>56</td>
<td>41</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>Crassostrea gigas</strong></td>
<td>IF</td>
<td>908</td>
<td>0</td>
<td>45</td>
<td>31</td>
<td>35° from N</td>
<td>// M</td>
<td>&gt;100</td>
<td>329</td>
<td>5.1</td>
</tr>
</tbody>
</table>

No DNA is available on fossils like Trichites, but Trichite's textural parameters are close to the ones of *pinnoids* or *pterioids*: interesting for the classification of extinct species.
Belemnita mucronatus

Calcitic fossils: *Belemnites*

**c-axes perp. to the shell: as in other cephalopods: nacre ancestral?**
Aragonitic fossils: *Baculities sp.*

\[ \text{c-axes perp. to the shell: as in other cephalopods,} \]
\[ \text{strong c-calcite to c-aragonite fossils interaction} \]
- Predict macroscopic anisotropic properties: Elastic

Arithmetic average
\[
\langle \mathcal{T} \rangle = \int_{g} \mathcal{T}(g) \, f(g) \, dg
\]
\[
\langle (\mathcal{T})^{-1} \rangle \neq \langle \mathcal{T} \rangle^{-1}
\]

Voigt average
Homogeneous strain
\[
C_{ijk\ell}^{M} = \langle C_{ijk\ell} \rangle
\]
Upper bound

Reuss average
Homogeneous stress
\[
S_{ijk\ell}^{M} = \langle S_{ijk\ell} \rangle
\]
Lower bound

Geometric average
\[
[b] = \prod_{k=1}^{N} b_k^{w_k} = \exp(\langle \ln b \rangle)
\]
scalar
\[
\langle \ln b \rangle = \sum_{k=1}^{N} w_k \ln b_k
\]
\[ [T]_{ij} = \exp(<\ln T>_{i'j'}) \]

tensor

\[ [\lambda_1] = 1/ [1/\lambda_1] = [\lambda_1^{-1}]^{-1} \]

Eigenvalues of \( T_{ij} \)

\[ \left\langle (C_{ijk\ell})^{-1} \right\rangle = \left\langle C_{ijk\ell} \right\rangle^{-1} \]

- Predict macroscopic anisotropic properties: Electric polarisation

\[ \left\langle p_h \right\rangle = \frac{\iint p_h \rho_h(y) \, dy}{\iint \rho_h(y) \, dy} \]
- Predict macroscopic anisotropic properties: BAW

Propagation equation

$$\rho \frac{\partial^2 u^i}{\partial t^2} = \left[ C^{i\ell mn} \right] \frac{\partial^2 u_n}{\partial x^m \partial x^\ell}$$

Propagation direction

<table>
<thead>
<tr>
<th>Propagation direction</th>
<th>( V_P )</th>
<th>( V_{S1} )</th>
<th>( V_{S2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>( \sqrt{\frac{c^{M,11}}{\rho}} )</td>
<td>( \sqrt{\frac{c^{M,44}}{\rho}} )</td>
<td>( \sqrt{\frac{c^{M,44}}{\rho}} )</td>
</tr>
<tr>
<td>[110]</td>
<td>( \sqrt{\frac{c^{M,11} + 2c^{M,44} + c^{M,12}}{2\rho}} )</td>
<td>( \sqrt{\frac{c^{M,11} - c^{M,12}}{2\rho}} )</td>
<td>( \sqrt{\frac{c^{M,44}}{\rho}} )</td>
</tr>
<tr>
<td>[111]</td>
<td>( \sqrt{\frac{c^{M,11} + 4c^{M,44} + 2c^{M,12}}{3\rho}} )</td>
<td>( \sqrt{\frac{c^{M,11} + c^{M,44} - c^{M,12}}{3\rho}} )</td>
<td>( \sqrt{\frac{c^{M,11} + c^{M,44} - c^{M,12}}{3\rho}} )</td>
</tr>
</tbody>
</table>

Cubic crystal system
<table>
<thead>
<tr>
<th></th>
<th>$c_{11}$ or $c_{11}^M$</th>
<th>$c_{12}$ or $c_{12}^M$</th>
<th>$c_{13}$ or $c_{13}^M$</th>
<th>$c_{14}$ or $c_{14}^M$</th>
<th>$c_{33}$ or $c_{33}^M$</th>
<th>$c_{44}$ or $c_{44}^M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single crystal</td>
<td>201</td>
<td>54.52</td>
<td>71.43</td>
<td>8.4</td>
<td>246.5</td>
<td>60.55</td>
</tr>
<tr>
<td>LiNbO$_3$/Si</td>
<td>206.4</td>
<td>68.5</td>
<td>67.6</td>
<td>0.48</td>
<td>216.5</td>
<td>64</td>
</tr>
<tr>
<td>LiNbO$_3$/Al$_2$O$_3$</td>
<td>204</td>
<td>65.7</td>
<td>69.7</td>
<td>1.1</td>
<td>219.9</td>
<td>63.2</td>
</tr>
</tbody>
</table>

**Single crystal**

LiNbO$_3$/Si

LiNbO$_3$/Al$_2$O$_3$
- Predict macroscopic anisotropic properties: Magnetisation

\[
\frac{M_\perp}{M_S} = 2\pi \int_0^{\pi/2} \left(1 - \rho_0 \right) PV(\theta_g) \sin \theta_g \cos(\theta_g - \theta) \, d\theta_g + \rho_0 M_{\text{random}}
\]

max \{001\}: 3.9 mrd
min: 0.5 mrd

\textbf{ErMn}_3\textbf{Fe}_9\textbf{C}: ODF + micros. \to macros.
- Correlate macroscopic anisotropic properties: Thermoelectric PF

9.8 MPa for 2 h
19.6 MPa for 6 h
19.6 MPa for 20 h

Electrical conductivity \( \sigma_{ab} \) (10^4 S/m)

Uniaxial Pressing duration time (h)

Power Factor PF_{ab} (mW/mK^2)
- Correlate macroscopic anisotropic properties: **Pyroelectric coefficient**

Enhancement of <001> texture
- Correlate macroscopic anisotropic properties: Tauc gap in nano-Si
-Correlate macroscopic anisotropic properties: Bi-2223 / Bi-2212 superconducting Jc’s

<table>
<thead>
<tr>
<th>Sinter-forging dwell time (h)</th>
<th>Orientation Distribution Max (m.r.d.)</th>
<th>RP0 (%)</th>
<th>RP1 (%)</th>
<th>Jc (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bi2212</td>
<td>Bi2223</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>21.8</td>
<td>20.7</td>
<td>17.74</td>
<td>10.56</td>
</tr>
<tr>
<td>50</td>
<td>24.1</td>
<td>24.4</td>
<td>17.05</td>
<td>11.04</td>
</tr>
<tr>
<td>100</td>
<td>31.5</td>
<td>25.2</td>
<td>13.54</td>
<td>9.31</td>
</tr>
<tr>
<td>150</td>
<td>65.4</td>
<td>27.2</td>
<td>16.24</td>
<td>12.25</td>
</tr>
</tbody>
</table>

Texture strength

% Bi2223

Crystallite Size
- Correlate macroscopic anisotropic properties: **Levitation force** and trapped flux in MTG-YBCO

Neutron pole figures (D1B-ILL)

Levitation force and trapped flux
Why needing combined analysis

- Solve the peak-overlap problems (intra- and inter-phases)

Resolved during ODF refinement
Polyphased Mylonite (Palm Canyon, CA)

Using 0D detector hardly manageable

<table>
<thead>
<tr>
<th>Space group</th>
<th>C2/m</th>
<th>R3</th>
<th>C-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Theta (°)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intensity (x 10^6)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Plasma-treated polypropylene films

Large broadening + overlaps + amorphous phase
**PCT ferroelectric films**

**Substrate influence:**
Interphase overlaps of reflections from the film and the substrate

**Intraphase overlaps**

![Graph showing X-ray diffraction patterns with peaks labeled for PCT thin film and Pt reflections.](image)
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

Belemnitė sp.
1D CPS + 2 Ips + XRF

With 2 sources (Mo + Cu)
Calibration

ω = 20°

ω = 40°

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

- **X-Ray specular Reflectivity**
  - Roughness, electron Density & EDP, Thickness
  - pole figures, inverse pole figures
  - Structural parameters
    - atomic positions, substitutions, vibrations
    - cell parameters
  - Multiphased, layered samples:
    - Thickness
    - Anisotropic Sizes and $\mu$-strains (Popa),
    - Stacking faults (Warren),
    - Distributions, Turbostratism (Ufer)

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

- **Matrix (Parrat), DWBA**

- **Fresnel, WIMV, E-WIMV, Harmonics, components, ADC**

- **Le Bail, Voigt, Reuss, Geometric mean**

- **TEM, XRF, GIXRF, PDF**
Why not more?

- Electrons
- Muons
- Neutrons
- Photons
  \((X, \gamma, IR \ldots)\)

- Magnetic Nuclear (isotopic) scattering
- SANS, n-Tomography, PDF

- MAUD, Jana
- Fullprof

- Macroscale
  - Magnetic structure
  - Magnetic Texture
  - Magnetic roughness
  - Vacancies
  - Atomic scale

- Structure
  - Local environment
  - Texture
  - Residual Stresses
  - Phases
  - Thickness
  - Roughness
  - Porosity
  - Size and shape
  - Amorphization

- Composition
- Interfaces
- Nanoscales
- Misorientations
- Dislocations
- Twins, Faults

- Open Databases

- XRD, DAFS, Reflectivity
- XAFS, PDF, SAXS
- Raman, Mössbauer, XANES
- X-Tomography

- SEM, TEM, HRTEM
- EBSD, e-Tomography
- PDF, EDX
- RHEED, \(\mu\)SR

- \(T, \vec{\nabla}T\)
- \(\vec{H}\)
- \(p, \sigma_{ij}\)
- \(\vec{E}\)
- \(\mu\)
- Don't want or can't powderise your sample:
  . Rare: Ice from deep cores, meteorite rocks ...
  . Expensive: high-tech materials
  . Impossible: hard materials, polymers, thin structures ...

- Decreases instrument time:
  . $5^\circ \times 5^\circ$ grid = 1368 points / pole figure
  . ODF: needs as much pole figures as possible

- Access to other parameters:
  . crystal sizes, micro-strains, stacking faults + twins (QMA)
  . residual strains and stresses (QSA)
  . Structure determination
  . Phase proportions (QPA)
  . Thicknesses, roughnesses (XRR)
- Avoid false minima due to parameter correlation:
  . phase and texture
  . Structure and texture
  . Structure and strains
  . Thickness and phase
  ...

- Benefit of these correlation to access "true" values
  Textured materials: between powder and single-crystal, angular discrimination

- Easier to practice!