Combined Analysis: structure-texture-microstructure-phase-stresses-reflectivity determination by x-ray and neutron scattering
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Some typographical mistakes may have been introduced throughout this document. Suggestions and corrections are very welcome.
0 Introduction

Solid state chemistry and technology recent developments gave rise to the necessity of intensive structural analysis from single crystal diffraction. However for many solids, single crystal growth is not easy to manage and sometimes impossible. When this is the case, or when structural defects cannot be overcome, the corresponding phases have often been forsaken, due to the inherent difficulties to carry out crystallographic characterisations on polycrystals. But in the last decades powder diffraction techniques progressed significantly, notably due to the Rietveld approach (Rietveld, 1969) and computer science developments. Undoubtedly these developments are of prior importance in the study of solids that do not form large crystals, but also of all materials elaborated by classical solid state reactions, thin deposited structures, natural materials like clays and more recently nanomaterials in which the required properties are intimately linked to the stabilisation of small crystals.

Since the Rietveld method's birth, several ten thousands of structures have been refined and some thousands have been resolved ab-initio from the only diffraction data of powder samples. The number of laboratories and industries using this technique, still fairly new when dealing with the incorporation of various formalisms like in the combined approach, does not stop increasing. However, materials having specific properties are often elaborated from low symmetry phases, which are consequently anisotropic. Property's optimisation is then conditioned by the elaboration processes which have to keep the intrinsic microscopic anisotropy of the constituting crystals at the macroscopic level. These elaboration techniques are complex (alignment under uniaxial pressure, magnetic or electric fields, thermal gradients, flux or substrate growing ... and combinations) and often sample preparation is a hard, time consuming, matter. Naturally, non-destructive characterisations are then required. Unfortunately, when samples are oriented, which was not often the case until recently, most of the characterisation techniques (as the Rietveld analysis of concerns here) require samples grinding. Very often this grinding is not acceptable, for the previously described reasons, but also in the case of rare samples (fossils, comets ...) or simply when grinding modifies the physical behaviour of the samples themselves (thin films, residual stress materials ...). Sometimes grinding is simply not possible, imagine peeling off a 10 nm thick film on a substrate!

In all these cases, the combined analysis becomes essential.

The first part of this document is dedicated to some basic notions concerning diffraction by polycrystals. The various peak profiles used are described and some, most common combined analysis instrumental set-up detailed.

In the second part, powder diffraction data treatment is introduced. In particular, the Rietveld analysis is detailed, including treatment of all the information provided by diffraction diagrams, when texture is not present in the sample or simple to treat.

The third part deals with the automatic phase indexing, necessary step to solve a structure ab-initio. Since its effect prevails on real samples where textures are often stabilised, quantitative texture analysis is detailed in the fourth part.

The fifth part is dedicated to microstructural aspects (isotropic and anisotropic crystal sizes and microdistortions) of the powder diffraction profiles.

In part six, quantitative phase analysis from Rietveld analysis is introduced.
Part seven describes residual stress analysis for isotropic and anisotropic materials. The eighth part focuses on specular x-ray reflectivity and the various models associated. Part nine introduces the combined analysis concept, showing all the dilemma that show up when one looks at only one part of the analyses, and case examples are shown as illustration of the methodology. The 10th part is dedicated to the anisotropic and tensorial macroscopic properties and their simulations to account for the distribution of crystallite orientations in samples.

This book is not intended to provide the reader a complete description of all the approaches dealt within it, though quantitative texture analysis is more deeply detailed than others since texture appears to be the largest signal biaser, but a red wire to follow the many concepts introduced through so many years and necessary to understand scattering patterns.
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**Glossary**

- \( \rho \) Material density
- \( \rho_e \) Material electron density
- \( dS \) Surface element of the Pole Sphere
- \( a, b, c, \alpha_c, \beta_c, \gamma_c \) Unit-cell parameters
- \( a, b, c \) Unit vectors of the unit-cell
- \( \Delta k \) Scattering vector
- \( n \) Normal to the sample surface
- \( S \) Spectrometer (Diffractometer) space
- \( \delta_p \) Physical 3D space
- \( \delta_e \) External (reciprocal) 3D space
- \( \delta_i \) Internal (reciprocal) superspace orthogonal to \( \delta_e \)
- \( \chi \) Polar angle in the diffractometer space
- \( \phi \) Azimuthal angle in the diffractometer space
- \( \gamma \) Pole figure space
- \( \theta_y \) Polar angle in the pole figure space
- \( \phi_y \) Azimuth of pole figures
- \( h\ell \) Miller indices
- \( (h\ell) \) Crystallographic plane \( h\ell \)
- \( \{h\ell\} \) Crystallographic planes \( h\ell \) and diffracting equivalents
- \( [h\ell] \) Crystallographic direction \( h\ell \)
- \( [h\ell]^* \) Crystallographic direction \( h\ell \) of the reciprocal space
- \( <h\ell> \) Crystallographic direction \( h\ell \) and diffracting equivalents
- \( <h\ell>^* \) Crystallographic direction \( h\ell \) and diffracting equivalents of the reciprocal space
- \( \text{L}_{h\ell} \) Lotgering factor
- \( p, p_0 \) ratio entering the Lotgering factor for a textured and a random sample respectively
- \( h \) \( <h\ell>^* \) directions
- \( y \) \( \theta_y, \phi_y \) direction in \( \gamma \)
- \( I_m(y) \) Direct pole figure
- \( P_n(y) \) Normalised pole figure
- \( K_A \) Sample reference frame
- \( (x_A, y_A, z_A) \) Unit-vectors of the sample reference frame
- \( X_A, Y_A, Z_A \) Sample axes aligned with \( x_A, y_A, z_A \) respectively
- \( [XYZ] \) Vector of the sample reference frame
- \( K_B \) Crystal reference frame
- \( (x_B, y_B, z_B) \) Unit-vectors of the crystal reference frame
- \( X_B, Y_B, Z_B \) Crystal axes aligned with \( x_B, y_B, z_B \) respectively
- \( \mathcal{H} \) Orientation space
- \( g \) Set of three Euler angles defining one orientation
- \( g \) Orientation distance
- \( dg \) Orientation element in the \( \mathcal{H} \)-space
- \( \alpha, \beta, \gamma \) Euler angles in the \( \mathcal{H} \)-space in the Roe-Matthies convention
- \( \phi_1, \Phi, \phi_2 \) Euler angles in the \( \mathcal{H} \)-space in the Bunge convention
\( f(g) \)  
Orientation Distribution of crystallites

\( f_0(g) \)  
OD of ferroelectric domains

\( d_{hk\ell} \)  
Inter-reticular distance between \((hk\ell)\) planes

\( \omega \)  
Angle between the incident beam and the sample surface: incidence angle

\( \theta \)  
Angle between the incident beam and the scattering planes \(\{hk\ell\}\): Bragg angle

\( \delta \)  
Angle running along the Debye ring on a 2D detector

\( V \)  
Irradiated volume of the sample

\( dV(y) \)  
Volume of crystallites having \( h \) between \( y \) and \( y + dy \)

\( dV(g) \)  
Volume of crystallites which orientation is between \( g \) and \( g + dg \)

\( J_c \)  
Superconducting transport critical current density

\( F_d \)  
Damaged (amorphous) fraction of an irradiated sample

\( F_c \)  
Crystalline fraction of a sample

\( \gamma \)  
Microscopic tensor for a property

\( \gamma^M \)  
Macroscopic tensor

\( <\gamma> \)  
Arithmetic average of the tensor \( \gamma \)

\( \mathbf{p}_{h} \)  
electric polarisation vector of a ferroelectric domain

\( \varepsilon_{ij} \)  
strain tensor

\( \varepsilon_{ij}^M \)  
macroscopic strain tensor

\( \sigma_{ij} \)  
stress tensor

\( \sigma_{ij}^M \)  
macroscopic stress tensor

\( S_{ijkl} \)  
elastic compliance tensor

\( S_{ijkl}^M \)  
macroscopic elastic compliance tensor

\( S_{ijkl}^{V,R,H} \)  
macroscopic elastic compliance tensor calculated using the Voigt, Reuss, Hill models

\( C_{ijkl} \)  
elastic stiffness tensor

\( C_{ijkl}^M \)  
macroscopic elastic stiffness tensor

\( C_{ijkl}^{V,R,H} \)  
macroscopic elastic stiffness tensor calculated using the Voigt, Reuss, Hill models

\( \xi \)  
mixing parameter of the Hill model

\( \chi_{m,ij} \)  
Magnetic susceptibility tensor

\( \mu_{r,ij} \)  
Magnetic relative permeability tensor

\( \varepsilon_{r,ij} \)  
Dielectric relative permittivity tensor

\( \varepsilon_0 \)  
Dielectric permittivity of vacuum

\( L \)  
Atomic orbital angular momentum

\( S \)  
Atomic spin angular momentum

\( J \)  
Atomic total magnetic momentum

\( g_{ij} \)  
Anisotropic Landé factor

\( \mu_B \)  
Bohr magneton

\( k_B \)  
Boltzmann constant

\( c \)  
light speed

\( N \)  
Avogadro number
Abbreviations

14:24  (Sr,Ca)$_{14}$Cu$_{24}$O$_{41}$
BAW  Bulk Acoustic Waves
Bi2223  (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+x}$
Bi2212  (Bi,Pb)$_2$Sr$_2$Ca$_1$Cu$_2$O$_{8+x}$
CAPS  Curved-Area Position Sensitive detector
CCL  Comarginal Crossed Lamellar layer
CPS  Curved Position Sensitive detector
CSL  Coincidence Site Lattices
EBSD  Electron Back-Scattering Diffraction
EDX  Energy Dispersive X-ray
ESR  Electron Spin Resonance
FAp  Ca$_{10}$(PO$_4$)$_6$F$_2$
FWHM  Full Width at Half Maximum
HAp  Ca$_{10}$(PO$_4$)$_6$(OH)$_2$
HRTEM  High-Resolution TEM
HWHM  Half Width at Half Maximum
HWHD  Half Width at Half maximum of the distribution Density
ILL  Institut Laue-Langevin
LN  LiNbO$_3$
MPB  Morphotropic Phase Boundary
MQTA  Magnetic Quantitative Texture Analysis
m.r.d.  multiple of a random distribution
MTG  Melt Texture Growth
NMR  Nuclear Magnetic Resonance
ODF  Orientation Distribution Function
PSD  Position Sensitive Detector
PZT  Pb(Zr,Ti)O$_3$
PL  PhotoLuminescence
PLE  PhotoLuminescence Excitation
QMA  Quantitative Microstructure Analysis
QPA  Quantitative Phase Analysis
QTA  Quantitative Texture Analysis
RCL  Radial Crossed Lamellar layer
RSA  Residual Strain-stress Analysis
RTGG  Reactive Templated Grain-Growth
SBN  SrBi$_2$Nb$_2$O$_9$
SEM  Scanning Electron Microscope
TEM  Transmission Electron Microscope
TGG  Templating Grain Growth
TSMTG  Top-Seeded Melt Texture Growth
XRR  X-Ray specular Reflectivity
Y123  YBa$_2$Cu$_3$O$_{7.5}$
Y211  Y$_2$BaCuO$_5$
Constants

We used in this book the following values of the constants of physics:

- **Avogadro number** \( N = 6.022 \times 10^{23} \)
- **Electron charge** \( e = -1.6021892.10^{-19} \text{C} \)
- **Boltzmann constant** \( k_B = 1.380662.10^{-23} \text{J.K}^{-1} \)
- **Planck constant** \( h = 6.626176.10^{-34} \text{J.s} \)
- **Rydberg constant** \( R_H = 1.1 \times 10^7 \text{m}^{-1} \)
- **Electron mass** \( m_e = 9.109534.10^{-31} \text{kg} \)
- **Free-space permittivity** \( \varepsilon_0 = 8.8541878.10^{-12} \text{A.s.A}^{-1} \text{m}^{-1} \)
- **Free-space permeability** \( \mu_0 = 4\pi \times 10^{-7} \text{V.s.A}^{-1} \text{m}^{-1} \)
- **Free-space light speed** \( c = 299792458 \text{m.s}^{-1} \)

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**Warnings and comments**

This text is appended regularly. If you detect any incoherence, mistake, typos, lost or missing reference or whatsoever, or if you miss some explanation or development, please warn the author directly by email at daniel.chateigner@ensicaen.fr
Figures caption

Figure 1: Definitions of grains (green), crystallites (black and red) and crystallographic planes (dashes) in a polycrystalline sample.

Figure 2: Schematic illustration of Bragg's law.

Figure 3: Simulated x-ray diffraction diagrams for a Si powder, for $\lambda = 1.5406$ Å (a) and for $\lambda/2 = 0.7703$ Å (b). Intensities for the $\lambda/2$ contributions have been enhanced for visibility.

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**Table 18:** Results obtained from the combined analysis on a AlN/Pt/TiO$_2$/Al$_2$O$_3$/Ni-Co-Cr-Al-Y stack. Standard deviations in parenthesis for the last digit

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We took as reference unit-cell for non-biogenic crystals: $a = 4.9623(3)$ Å, $b = 7.968(1)$Å, $c = 5.7439(3)$Å (ICDD Card N° 41-1475)

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