Polycrystal x-ray diffraction modelling: grazing incidence versus Bragg-Brentano

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Abstract. Diffraction-based texture analysis plays a significant role in the investigation of the physical properties of materials. The development of computer-aided tools for this research area facilitates quantitative validation of proposed orientation distribution models. We analyze the differences between Bragg-Brentano and grazing-incidence diffraction experiments from the point of view of texture characterization. New software packages for modelling Bragg-Brentano and grazing-incidence (one- and two-dimensional) XRD patterns produced by axially-textured polycrystals are presented. A case study based on a virtual experiment with a BaTiO₃ sample is presented. The effect of texture on the diffraction patterns obtained by application of the different techniques considered differs significantly.

1. Introduction

Nowadays investigation on nanostructured materials such as thin films leads towards diffraction experiments with the grazing incidence method. This type of experiment happens often on synchrotrons and laboratory diffractometers.

One of the most often interpretation practices of diffractograms comes from modelling. In modelling various methods, such as Rietveld refinement, provide quantitative descriptions of crystallographic phenomena. Several software packages serve the purpose of polycrystal diffraction modelling and refinement. Fullprof [1] and PowderCell [2] are among popular crystal diffraction programs. Mentioned software packages model the effect of texture on the intensities of diffraction peaks, under the consideration of symmetric q-2q, Bragg-Brentano (B-B), geometry. The role of texture on grazing-incidence experiments is scarcely considered in available programs.

Here we focus on providing the modelling of 1D- and 2D-XRD patterns, while taking into consideration the effects of texture on different geometries of diffraction experiments.

Texture describes the phenomenon where crystallites are preferentially oriented toward some direction. The basic statistical descriptors of texture are the direct and inverse pole figures (PF, IPF) and the orientation distribution function (ODF) [3]. In the special case of axial sample symmetry, the IPF of the symmetry axis plays the role of the ODF.

In the present report we introduce two software codes: “grazing”, for 1D-XRD (grazing incidence and B-B) and a Windows version of the 2D-XRD program “ANAELEU” (ANAlytical Emulator Laue Utility (ANAELEU)) [4].

2. 1D-XRD: Bragg Brentano vs Grazing incidence

The integrated intensities of x-rays diffraction peaks are affected by crystallographic texture, differently, depending on the measurement geometry.

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\[ I = I_0 K |F|^2 |\rho(LP)| AD/v^2 | T \]  

(1)

\[ T = \begin{cases} Ph[\varphi(Bragg)] & \text{Bragg-Brentano} \\ Ph[\varphi(Grazing)] & \text{Grazing incidence} \end{cases} \]  

(2)

I = Incident beam intensity, \( K \) = Instrumental constant, \(|F|\) = Structure factor, \( \rho \) = Multiplicity factor, \( (LP) \) = Lorentz-polarization factor, \( A \) = Absorption, \( D \) = Debye-Waller factor, \( v \) = Cell volume and \( T \) = texture factor. In Bragg-Brentano configuration, the intensities are modulated by the inverse pole figure of the normal to the sample surface direction. In grazing incidence experiments, the modulating factors are the corresponding direct pole figures, evaluated at the Bragg angles.

The model applied in the present work consists in proposing a Gaussian-shaped inverse pole figure and proceeding with further calculations on dependence of the considered case.

Model texture:

\[ R(h) = R_0 e^{-0.5(\varphi/\sigma)^2} \]  

(3)

\( \varphi \) denotes the polar angle, measured from the location of the IPF maximum, \( \sigma \) is the standard deviation of the orientation distribution and \( R_0 \) is a normalization constant, such that the integral of \( R(h) \) over the whole unitary sphere has a value of \( 4\pi \).

Calculation of direct pole figures from the symmetry axis inverse pole figure proceeds by application of the Fundamental Equation of Fiber Textures [5], eq. (4):

\[ P_h(\varphi) = \frac{1}{2\pi} \int_0^{2\pi} R(\varphi, \psi) d\psi \]  

(4)

Figure 1 shows a hypothetical Cu-K\( \alpha \) diffraction experiment with a BaTiO\(_3\) thin film exhibiting an extremely sharp (0, 0, 1) texture. The difference in results obtained by the two considered experimental methods is striking. Bragg-Brentano would produce significantly intense 0, 0, 1 peaks. On the other hand, in the grazing incidence experiment, the 0, 0, 1 peaks would practically disappear. The crystal planes (0, 1, 2) form an angle of approximately 26° with the sample surface. They would be so oriented that the Bragg condition would be fulfilled with very good approximation. The grazing incidence experiment would show this lone peak with very high intensity.

3. Program “Grazing”

In Grazing, the modeling is systematized to obtain 1D-XRD patterns for Bragg-Brentano and grazing incidence methods. In this software diffractograms are based on the intensities obtained from equation (1) shown above. Required input data are the crystal structure (space group, lattice parameters, atomic positions), experimental parameters (e.g. wavelength) and proposed texture characteristics.
Texture data are preferred orientation indexes \((h,k,l)\) and IPF width \((\sigma)\). Based on these data, \textit{Grazing} obtains intensities without textures and applies the correct modulations for each method. For Bragg-Brentano method, the inverse pole figure, eq. (3), modulates the intensities of peaks. In grazing incidence, the intensities’ modulation is produced by the direct pole figures, calculated by eq. (4).

The software has been developed with language Python 3. It utilizes modules such as Matplotlib [6], NumPy [7] and SciPy [8]. \textit{Grazing} offers a representation of 1D-XRD patterns of materials such as thin films and surfaces under the effect of texture measured with the Bragg-Brentano and grazing incidence methods. Given the preferential orientation \textit{Grazing} determines the 1-D XRD pattern for both methods, this in order to demonstrate the quantitative difference of crystallites orientation at the same distribution width.

4. **ANAELU**

For the interpretation of bidimensional diffractograms, program \textit{ANAELU} is used. The 2D diffraction pattern displayed by \textit{ANAELU} shows the intensity distribution within the so-called Debye rings. The modulation of intensities, in the 2-dimensional case, is characterized by eq. (5)

\[
I_{h}^{\text{textured}}(2\theta, \alpha) = I_{h}^{\text{random}} \ast P_{h}[\phi(\theta, \alpha)]
\]

Angle \(\alpha\) represents the azimuth in a 2D-XRD Debye ring. \textit{ANAELU} is an open source, Rietveld-inspired [9], software package. It is programmed in two languages: Fortran and Python. Given the crystalline structure and the inverse pole figure, \textit{ANAELU} models and represent graphically 2D-XRD pattern for texture analysis. \textit{ANAELU} works by utilizing the Crystallographic Fortran Modules Library [10] (CrysFML) for the determination of crystallographic parameters. Afterwards it reads and handles data from two-dimensional X-ray detectors employing FabIO [11] module. Moreover, \textit{ANAELU} can perform texture analysis on grazing incidence and transmission methods [12]. The contribution to \textit{ANAELU} that is reported in the present article is the creation of a version that is functional on Windows. It can be downloaded at: https://gitlab.com/Vidal95/anaelu2.

5. **Case of Study (BaTiO3 textured thin film)**

5.1. **1D-XRD**

To illustrate the proposed methodology, a representative study of case is presented. Hypothetical films of BaTiO3 are presented with different textures and the differences between Bragg-Brentano and grazing incidence results are shown. The XRD peaks of the perovskite BaTiO3 with an orientation \((001)\) modeled in virtual experiments were obtained using \textit{Grazing}. Figures 2-4 show the modelled diffractograms corresponding to distribution widths \(\sigma = 3^\circ\), 30° and 300°. Inverse pole figures are modelled as functions of polar and azimuthal angles. Figure 2 represents the case of an extremely sharp 001 texture. Peaks with the form \(00l\) are very intense while peaks of the form \(h00\) are not visible in Bragg Brentano. The 012 peak is hardly observable. In the grazing incidence experiment, the 012 peak is very intense and 00l don’t appear. Figure 3 shows the case for \(\sigma = 30^\circ\). Peaks start to appear on both methods, the distribution of intensities obeys different rules according to the assumed experimental geometry. As the distribution width becomes broader, both diffractograms tend to be similar as it is shown in figure 4.

![Figure 2. Virtual experiment of BaTiO3. A) Inverse pole figure \(\sigma = 3^\circ\). B) Bragg-Brentano modelled diffractogram. C) Grazing incidence modelled diffractogram.](image)
Figure 3. Virtual experiment of BaTiO₃. A) Inverse pole figure $\sigma = 30^\circ$. B) Bragg-Brentano modelled diffractogram. C) Grazing incidence modelled diffractogram.

Figure 4. Virtual experiment of BaTiO₃. A) Inverse pole figure $\sigma = 300^\circ$. B) Bragg-Brentano modelled diffractogram. C) Grazing incidence modelled diffractogram.

5.2. 2D-XRD
Using ANAELU 2.0, 2D-XRD patterns were obtained with the same distribution widths as in Figures 2-4. The intensity distributions along the Debye rings, evaluated at $\alpha = 0$ (vertical cuts), lead to the unidimensional diffractograms obtained with Grazing.V.

Figure 5. 2D-XRD patterns on ANAELU for $\alpha = 3^\circ$, $30^\circ$ and $300^\circ$ respectively.

6. Summary
X-rays diffraction patterns produced by textured polycrystals show distinguishing characteristics on dependence of the measurement geometry.
In particular, Bragg-Brentano and grazing incidence experiments from sharp textures lead to strikingly different diffraction effects. Proper algorithms and computer programs have been developed to facilitate the interpretation of considered measurements. The presented particular case study illustrates some peculiarities that are observed in both 1D and 2D essays.

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References
[1] Rodriguez J 1990 A program for Rietveld refinement and pattern matching analysis XV congress of the IUCr
[2] Kraus W and Nolze G 1996 A program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. J Appl Crystallogr 29(3) 1-3
[3] Bunge H 2013 Texture analysis in materials science: mathematical methods. Elsevier
[4] Burciaga Valencia D C, Villalobos Portillo E E, Marín Romero J A, del Río M S, Montero-Cabrera M E and Fuentes Cobas L E 2018 Recent developments in the texture analysis program ANAELU Journal of Materials Science: Materials in Electronics 29(18) 15376-82
[5] Fuentes L 1989 Anomalous Scattering and Null-Domain Ghost Corrections for Fibre Textures. Texture, Stress, and Microstructure 10(4) 347-60
[6] Hunter JD 2007 Matplotlib: A 2D graphics environment Computing in science & engineering 9(3) 90-5
[7] Oliphant T 2006 A guide to NumPy Trelgol Publishing
[8] Virtanen P, Gommers R, Oliphant T E, Haberland M, Reddy T and Cournapeau D 2020 1.0: fundamental algorithms for scientific computing in Python SciPy 17(3) 261-72
[9] Rietveld HM 2014 The rietveld method. Physica Scripta 89(9) 098002
[10] Rodriguez Carvajal J and González Platas J 2003 Crystallographic Fortran 90 Modules Library (CrysFML): a simple toolbox for crystallographic computing programs Commission on Crystallographic Computing of IUCr, Newsletter
[11] Knudsen E B, Sørensen H O, Wright J P, Goret G and Kieffer J 2013 FabIO: easy access to two-dimensional X-ray detector images in Python. J Appl Crystallogr. 46(2) 537-9
[12] Gruner S, Eikenberry E and Tate M 2006 Comparison of X-ray detectors. International Tables for Crystallography Volume F: Crystallography of biological macromolecules Springer 143-7