

Alternative algorithm for the correction of preferred orientation in Rietveld analysis

J. Bergmann,^a T. Monecke^{b*} and R. Kleeberg^b

^aLudwig-Renn-Allee 14, D-01217 Dresden, Germany, and ^bUniversity of Mining and Technology, Institute of Mineralogy, Brennhausgasse 14, D-09596 Freiberg, Germany. Correspondence e-mail: tmonecke@mineral.tu-freiberg.de

Texture effects caused by preferred orientation can be corrected in Rietveld analysis by an alternative algorithm presented in this contribution. This algorithm is equivalent to models using symmetrized linear combinations of spherical harmonic functions, but it is unique to all Laue classes and to all orders. Positive definiteness of the polar-axis density is achieved by the exponential method. The outlined algorithm was tested during Rietveld refinement of selected polycrystal samples. The algorithm was proven to be numerically robust and satisfactorily described deviations from the ideal intensity ratios of the Bragg reflections caused by the texture of the samples.

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1. Introduction

Rietveld refinement of polycrystal diffraction patterns is a powerful tool for the determination of crystalline structures as well as for quantitative phase analysis. However, the texture of samples can be a serious drawback because a preferred orientation (PO) of the grains (or crystallites) causes deviations from the ideal intensity ratios of the reflections. Unfortunately, a random orientation of the crystallites can usually not be achieved during sample preparation. Therefore, the effects of PO have to be corrected during Rietveld refinement by applying appropriate analytical texture models.

The texture model most commonly applied in Rietveld analysis is based on the March function (Dollase, 1986). However, because this method assumes that the crystallites are axially symmetrical, the model is unable to describe complicated PO that may be caused by *e.g.* multiple cleavages of the investigated materials. Moreover, the crystal symmetry is not taken into account. Although the reduced number of parameters required for the texture description by the March function is attractive, more general texture models have to be developed.

The most general description of the PO of crystallites in polycrystal samples is the orientation distribution function (ODF) that gives the probability of each of the possible crystallite orientations with respect to a suitably chosen coordinate system (Bunge, 1991, 1993, 1997, 1998, 1999). This function is most commonly represented by series expansion into generalized spherical harmonics, although alternative methods, such as the texture component model (Helming & Eschner, 1990), have been proposed. Except for simple cases [*e.g.* cubic crystal system plus rotational sample symmetry (DeWolff & Sas, 1969)], the information required for construction of the ODF cannot be obtained from a single angular scan. However, the problem simplifies to the deter-

mination of the inverse pole figure, called polar-axis density in the context of Rietveld analysis, if the orientation of the diffraction vector is fixed in sample coordinates. This function is usually expanded in a series of symmetrized spherical harmonics (Järvinen *et al.*, 1970; Popa, 1992; Järvinen, 1993, 1998; Ferrari & Lutterotti, 1994; Von Dreele, 1997). In Rietveld programs, the symmetrized spherical harmonics are either explicitly encoded up to some maximum order *n* (Järvinen, 1993) and/or generated using selection rules depending on the crystal symmetry of the phase under investigation (Popa, 1992; Von Dreele, 1997).

In the present study, an alternative algorithm based on a different series expansion is introduced that is unique to all Laue classes and to all orders. The algorithm can easily be implemented in Rietveld programs and does not require explicit tabulation and/or generation rules for the coefficients. In analogy to the texture description by a finite series expansion into symmetrized spherical harmonics, positive definiteness of the polar-axis density is not ensured for all arguments. Therefore, the exponential method proposed by Van Houtte (1991) was adapted. It has been experimentally shown that this algorithm is numerically robust and satisfactorily describes texture effects in powder diffraction patterns.

2. Theory

2.1. Mathematical formulation of preferred-orientation correction

In the original Rietveld method (Rietveld, 1969), the integrated intensity of a Bragg reflection in a polycrystal diffraction pattern was described by crystal-structure-dependent parameters and a one-dimensional PO model was proposed. A

correction factor has to be introduced when the sample is not randomly oriented; the intensity of a Bragg reflection is then given by

$$I_{\text{obs}}(\mathbf{h}) = T(\mathbf{h})LPS|F(\mathbf{h})|^2 = T(\mathbf{h})I_{\text{id}}(\mathbf{h}), \quad (1)$$

where $I_{\text{obs}}(\mathbf{h})$ is the observed diffracted intensity of a Bragg reflection, $I_{\text{id}}(\mathbf{h})$ is the ideal diffracted intensity of a Bragg reflection, $T(\mathbf{h})$ is the correction factor for preferred orientation, L is the Lorentz factor, P is the polarization factor, S is the scale factor of the phase causing the Bragg reflection, $F(\mathbf{h})$ is the structure factor of the Bragg reflection, and $\mathbf{h} = h_i$, the Miller indices of a Bragg reflection.

Supposing that the measurement of the polycrystal sample is made in Bragg–Brentano measuring geometry, the polar-axis density can be approximated by a finite series of spherical harmonic functions,

$$T(\mathbf{h}) = T(\vartheta, \varphi) = \sum_{l=0,2,4,\dots}^n \sum_{m=-l}^l a_{l,m} Y_{l,m}(\vartheta, \varphi), \quad (2)$$

where the polar and azimuthal angles ϑ and φ describe the direction of the normal to the lattice-plane family given by \mathbf{h} in a Cartesian coordinate system $\mathbf{r} = x_i$ with

$$\begin{aligned} x_1 &= r \cos \varphi \sin \vartheta, \\ x_2 &= r \sin \varphi \sin \vartheta, \\ x_3 &= r \cos \vartheta. \end{aligned} \quad (3)$$

The coefficients $a_{l,m}$ in equation (2) are adjustable parameters. The first term $a_{0,0}Y_{0,0}$ in the expansion is independent of angle and, therefore, describes a random orientation of crystallites, whereas the other terms represent the deviation from this ideal case. In X-ray powder diffraction, only symmetrized spherical harmonic functions of even order need to be considered because only these functions fulfil the symmetry $\bar{1}$ that is common to all Laue classes (Friedel's law). To derive an algorithm that is unique to all Laue classes and to all orders n , equation (2) can be expressed as

$$T(\vartheta, \varphi) = \left(\sum_{i_1=1}^3 \sum_{i_2=1}^3 \dots \sum_{i_n=1}^3 \mathbf{G}_{i_1, i_2, \dots, i_n}^0 x_{i_1} x_{i_2} \dots x_{i_n} \right) / r^n, \quad (4)$$

where \mathbf{G}^0 is a fully symmetric tensor of even order n . In contrast to equation (2), the terms in equation (4) are not orthogonal. However, orthogonality is not required in Rietveld analysis. Therefore, the application of equation (4) for texture correction is fully equivalent to the use of equation (2). The vector \mathbf{r} can be written in lattice and in reciprocal-lattice coordinates as

$$\mathbf{r} = x_i = \sum_{i=1}^3 u_i \mathbf{a}_i = \sum_{i=1}^3 h_i \mathbf{a}_i^* \quad (5)$$

and equation (4) can be rewritten in terms of the unit vector $\mathbf{h}/|\mathbf{h}|$ as

$$T(\mathbf{h}) = \left(\sum_{i_1=1}^3 \sum_{i_2=1}^3 \dots \sum_{i_n=1}^3 \mathbf{G}_{i_1, i_2, \dots, i_n} h_{i_1} h_{i_2} \dots h_{i_n} \right) / |\mathbf{h}|^n \quad (6)$$

with a new tensor \mathbf{G} .

2.2. Symmetry considerations

The symmetry of the phase under investigation has not yet been taken into account in equation (6). This can be done in the following way. If the A_{ij}^k with $i, j = 1 \dots 3$ are the transformation matrices of the point group of the phase under investigation in the polycrystal sample, \mathbf{G} should be replaced by a tensor $\hat{\mathbf{G}}$ that is invariant to the transformation

$$\hat{\mathbf{G}}_{i_1, i_2, \dots, i_n} = \sum_{j_1=1}^3 \dots \sum_{j_n=1}^3 \hat{\mathbf{G}}_{j_1, j_2, \dots, j_n} A_{i_1, j_1}^k \dots A_{i_n, j_n}^k \quad (7)$$

for each k . This expression may be written as

$$\hat{\mathbf{G}} = \mathcal{A}^k \hat{\mathbf{G}} \quad (8)$$

in a symbolic notation. An invariant tensor $\hat{\mathbf{G}}$ can be constructed by applying the Γ_1 -projection operator

$$\bar{\mathcal{A}} = (1/m) \sum_{k=1}^m \mathcal{A}^k \quad (9)$$

to a non-invariant tensor \mathbf{G} ,

$$\hat{\mathbf{G}} = \bar{\mathcal{A}} \mathbf{G}. \quad (10)$$

The polar-axis density is then given by

$$T(\mathbf{h}) = \left(\sum_{i_1=1}^3 \sum_{i_2=1}^3 \dots \sum_{i_n=1}^3 \hat{\mathbf{G}}_{i_1, i_2, \dots, i_n} h_{i_1} h_{i_2} \dots h_{i_n} \right) / |\mathbf{h}|^n. \quad (11)$$

The tensor $\hat{\mathbf{G}}$ can be derived using the general positions

$$\mathbf{X}^k = (X_1^k, X_2^k, X_3^k) \quad (12)$$

given in the *International Tables for Crystallography* and tabulated in Rietveld programs. The matrices A_{ij}^k are given by

$$A_{ij}^k = \partial X_i^k / \partial x_j \quad (13)$$

and $\hat{\mathbf{G}}$ is then obtained by a simple algorithm without tabulation or generation of symmetrized linear combinations of spherical harmonic functions specific to each Laue class and to each order n , which is especially complicated in the case of the two cubic Laue classes (Popa, 1992; Bunge, 1993).

2.3. Positive definiteness and normalization

The ODF as well as the polar-axis density are probability functions and must, therefore, be positive. The problem of positive definiteness is well discussed for ODFs (Matthies & Helming, 1982). Different ways to achieve a positive definiteness of the ODF are given by Van Houtte (1991). In analogy to his exponential method, a new polar-axis density is defined by the non-linear transformation

$$\tilde{T}(\mathbf{h}) = \exp[T(\mathbf{h})], \quad (14)$$

conserving the degree of completeness of $T(\mathbf{h})$.

The exponential function was chosen instead of the quadratic method because no additional minima are introduced into the Rietveld refinement. Following Van Houtte (1991), this new polar-axis density has to be normalized:

$$\tilde{T}(\mathbf{h}) / \bar{\tilde{T}} \quad (15)$$

Table 1
Effective number of parameters introduced into the Rietveld refinement depending on the order n of the texture model and the Laue class of the phase under investigation (Bunge, 1993).

Crystal system	Laue class	$n = 2$	$n = 4$	$n = 6$	$n = 8$	$n = 10$
Triclinic	$\bar{1}$	6	15	28	45	66
Monoclinic	$2/m$	4	9	16	25	36
Orthorhombic	mmm	3	6	10	15	21
Tetragonal	$4/m$	2	5	8	13	18
	$4/mmm$	2	4	6	9	12
Rhombohedral	$\bar{3}$	2	5	10	15	22
	$\bar{3}m$	2	4	7	10	14
Hexagonal	$6/m$	2	3	6	9	12
	$6/mmm$	2	3	5	7	9
Cubic	$m\bar{3}$	1	2	4	5	7
	$m\bar{3}m$	1	2	3	4	5

with

$$\bar{T} = (1/4\pi) \int_{-1}^1 d\cos\vartheta \int_0^{2\pi} d\varphi \tilde{T}(\mathbf{h}). \tag{16}$$

However, \bar{T} does not have to be determined in each step of the Rietveld refinement process. \bar{T} is part of the scale factor S , which has to be calculated only once at the end of the refinement. Hence, equation (1) may be rewritten as

$$\begin{aligned} I_{\text{obs}}(\mathbf{h}) &= [4\pi\tilde{T}(\mathbf{h})] / \int_{-1}^1 d\cos\vartheta \int_0^{2\pi} d\varphi \tilde{T}(\mathbf{h}) \\ &\times \underbrace{(1/4\pi) \int_{-1}^1 d\cos\vartheta \int_0^{2\pi} d\varphi \tilde{T}(\mathbf{h}) LP|F(\mathbf{h})|^2}_S \\ &= \tilde{T}(\mathbf{h}) LP|F(\mathbf{h})|^2. \end{aligned} \tag{17}$$

This expression is unique to all Laue classes and to all orders n of the texture model. During Rietveld refinement, the $(n + 1)(n + 2)/2$ independent elements of the tensor \mathbf{G} are refined in each iterative step. In this way the refinement algorithm is independent of the Laue class of the investigated phase. The tensor $\hat{\mathbf{G}}$ is determined numerically in each step by applying the Γ_1 -projection to the tensor \mathbf{G} in order to compute the intensities of the Bragg reflections of the simulated X-ray diffraction pattern. The number of independent components of the symmetrized tensor $\hat{\mathbf{G}}$ depends on the order n as well as on the Laue class of the phase under investigation (Table 1).

3. Experimental

Initially, the outlined algorithm was implemented in the Rietveld program *BGMN* (Bergmann *et al.*, 1998; see also www.bgm.de). The numerical stability of the applied texture correction was tested during routine quantitative phase analysis of various multiphase materials. In all investigated cases, the exponential method resulted in correct approximations of

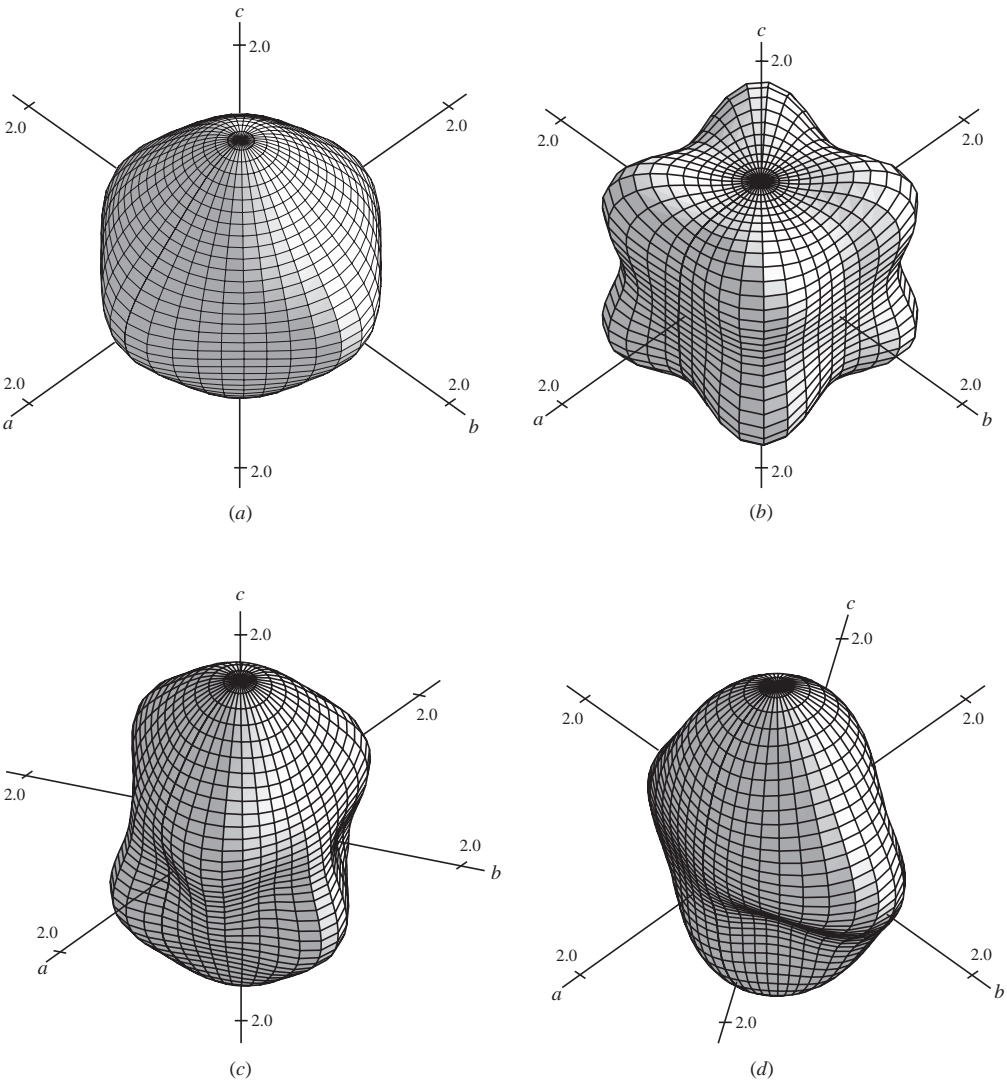


Figure 1
Shapes of the normalized polar-axis densities of (a) halite, (b) fluorite, (c) calcite and (d) oligoclase. The order of the texture model was defined prior to the Rietveld refinement and was $n = 4$ for oligoclase, $n = 6$ for calcite and $n = 8$ for halite and fluorite. The shapes of the polar-axis densities clearly reflect the orientations of the perfect cleavages in the different materials: $\{100\}$ for halite, $\{111\}$ for fluorite, $\{104\}$ for calcite, as well as $\{001\}$ and $\{010\}$ for oligoclase.

the PO even in the cases of strong textures ($I_{\text{obs}}/I_{\text{id}}$ up to approximately 4) and low orders n of the texture model.

As examples, the application of the texture correction is demonstrated by investigating four different powdered samples consisting of halite, fluorite, calcite and oligoclase, respectively. Because Rietveld analysis cannot be performed on strongly textured samples, the powders were carefully pressed in conventional front-packed holders, without a shearing motion. Step-scan data ($15\text{--}130^\circ 2\theta$, $0.02^\circ 2\theta$ step, 10 s step^{-1}) were collected on the spinning sample using an XRD 3000 TT (Seifert, Germany) diffractometer equipped with a diffracted-beam graphite monochromator. A Cu tube was used and operated at 40 kV and 40 mA.

The texture model of each of the four minerals was refined numerically as a part of the Rietveld refinement of the four diffraction patterns. The order n of the applied texture model was defined prior to the Rietveld refinement. Owing to the careful sample preparation, the texture of the phases was so smooth that texture correction up to the eighth order was sufficient for correction of the effects of preferred orientation. The low orders of the applied texture models are also of advantage because significant parameter correlations can be avoided by using only a restricted number of independent texture parameters (Table 1).

The polar-axis densities were also plotted, with the help of the software package *MAPLE V*, using the elements of the tensors $\hat{\mathbf{G}}$ determined during the Rietveld refinement. In analogy to work by Järvinen (1998), the polar-axis densities of the four minerals were constructed in spherical coordinates. The resulting shapes of the normalized polar-axis densities of halite, fluorite, calcite and oligoclase are presented in Fig. 1. The figure shows that the PO of each of the four investigated phases primarily resulted from the perfect and partially multiple cleavages of the materials. The applied PO correction model yields physically reasonable results for moderately textured samples.

4. Summary

In the present contribution, an algorithm is presented that allows the correction of preferred orientation in polycrystal samples during Rietveld refinement. The proposed algorithm is positive definite. The method is unique to all Laue classes and orders of the texture model. Therefore, the algorithm is numerically robust and not limited to special applications. The

method has been implemented in a Rietveld computer program. As examples, samples of halite, fluorite, calcite and oligoclase were refined. The resulting shapes of the polar-axis densities of these phases are physically reasonable. Application of the mathematical model can particularly improve the accuracy of quantitative phase analysis by the Rietveld method. Moreover, implementation of the proposed algorithm in Rietveld computer programs may be of particular advantage because the maximum order of the texture model can be rapidly enlarged without changes of the algorithm if necessary.

We express our gratitude to J. Monecke and W. Cordts (Institute of Theoretical Physics, Freiberg University of Mining and Technology) for valuable comments and remarks that fundamentally improved the manuscript. TM and RK thank P. Herzig and S. Köhler (Institute of Mineralogy, Freiberg University of Mining and Technology) for the discussion of the applicability of the texture model. TM gratefully acknowledges a grant provided by the Studienstiftung des Deutschen Volkes and RK acknowledges financial support by the Deutsche Forschungsgemeinschaft.

References

- Bergmann, J., Friedel, P. & Kleeberg, R. (1998). *CPD Newsl.* **20**, 5–8.
- Bunge, H. J. (1991). *Mater. Sci. Forum*, **79–82**, 169–178.
- Bunge, H. J. (1993). *Texture Analysis in Material Science: Mathematical Methods*. Göttingen: Cuvillier.
- Bunge, H. J. (1997). *Textures Microstruct.* **29**, 1–26.
- Bunge, H. J. (1998). *Mater. Sci. Forum*, **278–281**, 200–213.
- Bunge, H. J. (1999). *Defect and Microstructure Analysis by Diffraction*, pp. 406–519. IUCr Monographs. Oxford University Press.
- DeWolff, P. M. & Sas, W. H. (1969). *Acta Cryst.* **A25**, 206–209.
- Dollase, W. A. (1986). *J. Appl. Cryst.* **19**, 267–272.
- Ferrari, M. & Lutterotti, L. (1994). *J. Appl. Phys.* **76**, 7246–7255.
- Helming, K. & Eschner, T. (1990). *Cryst. Res. Technol.* **25**, K203–K208.
- Järvinen, M. (1993). *J. Appl. Cryst.* **26**, 525–531.
- Järvinen, M. (1998). *Mater. Sci. Forum*, **278–281**, 184–199.
- Järvinen, M., Merisalo, M., Pesonen, A. & Inkinen, O. (1970). *J. Appl. Cryst.* **3**, 313–318.
- Matthies, S. & Helming, K. (1982). *Phys. Status Solidi B*, **113**, 569–582.
- Popa, N. C. (1992). *J. Appl. Cryst.* **25**, 611–616.
- Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
- Van Houtte, P. (1991). *Textures Microstruct.* **13**, 199–212.
- Von Dreele, R. B. (1997). *J. Appl. Cryst.* **30**, 517–525.