

Advances in Texture Analysis from Diffraction Spectra

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Abstract

The orientation distribution of a textured polycrystal has been traditionally determined from a few individual pole figures of lattice planes *hkl*, measured by X-ray or neutron diffraction. A new method is demonstrated that uses the whole diffraction spectrum, rather than extracted peak intensities, by combining ODF calculation with Rietveld crystal structure refinement. With this method, which is illustrated for a synthetic calcite texture, it is possible to obtain quantitative texture information from highly incomplete pole figures and regions of the diffraction spectrum with many overlapping peaks. The approach promises to be advantageous for low-symmetry compounds and composites with complicated diffraction spectra. The method is particularly elegant for time-of-flight neutron diffraction, saving beam time by using small pole-figure regions and many diffractions.

1. Introduction

Traditionally, texture analysis has relied on pole-figure measurements (Wenk, 1985). Pole figures of a few individual lattice planes are measured with monochromatic X-ray or neutron diffraction by positioning of a detector on the center of a diffraction peak and rotation of the sample into various orientations. This is efficient if only a few pole figures are required to calculate the orientation distribution function (ODF) with a sufficient resolution and if diffraction peaks are reasonably strong (relative to background) and well separated, such as in pure face-centered-cubic and body-centered-cubic metals.

This method becomes increasingly unsatisfactory for complex diffraction spectra of low-symmetry compounds with many closely spaced and partially overlapped peaks, or if the peak maxima cannot be referred to a unique position as in the case of strong residual stresses. It is still difficult to measure quantitative pole figures for such materials, including polyphase composites, intermetallic compounds, many ceramics, minerals and polymers. At the same time, novel methods of data collection have become available. With position-sensitive detectors, or with time-of-flight (TOF) analysis of polychromatic neutrons, whole

spectra, containing signals from a large number of diffraction peaks, are recorded simultaneously (Will, Schaefer & Merz, 1989). It would be useful to use the whole spectrum, rather than a few isolated peaks to determine the texture.

As texture researchers are becoming concerned with complex diffraction spectra, crystallographers have developed a comprehensive new approach to crystal structure analysis. Originally, crystal structure determinations relied mainly on diffraction information from single crystals. However, in many cases, large single crystals are not available and powders have to be used. In a powder pattern, many peaks are overlapped and Rietveld (1969) introduced a method that relies on the whole spectrum. It has been highly successful and is included in several software packages (Wiles & Young, 1987; Larson & Von Dreele, 1986). In the last few years, powder patterns have been used to solve *ab initio* the crystal structures of novel compounds (Werner, 1991; Benard, Louër & Louër, 1991), using peak extraction routines like the Le Bail one (Le Bail, Duroy & Fourquet, 1988) and the Rietveld method.

It appeared that texture analysis could take advantage of these advances in crystallography and in 1993 the authors outlined a general iterative procedure to combine the Rietveld method with quantitative texture analysis (Wenk, Matthies & Lutterotti, 1994). In this paper, we test the method with an example and demonstrate its feasibility. By combination of the two approaches, some of the limitations of each individual method can be overcome and new possibilities become available for quantitative characterization of polycrystals. In the main part of the paper, we try only to describe and visually to demonstrate the general aspects, steps and testing results of the method, avoiding too many (sometimes rather complicated) mathematical details. For some mathematical aspects of the algorithms used and additional numerical data quantitatively characterizing the iterative process, we refer to the Appendix.

2. The main features of the Rietveld method

The objective of the Rietveld method (RM) is to determine or refine the crystal structure of a material. An X-ray or neutron diffraction spectrum of a polycrystalline sample with many individual or overlapping

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diffraction peaks hkl serves as experimental data and it is generally assumed that crystallites have a random orientation distribution. In such a case, the form of the spectrum, such as that of a calcite powder in Fig. 1(a), is determined by the crystal structure (mainly lattice parameters, atomic coordinates, occupancy), the physics of the scattering process (atomic form factors or scattering widths, Debye–Waller factors), the microstructure of the sample and instrumental details of the spectrometer.

The general idea of the RM is that a spectrum can be expressed as a nonlinear function of a finite number of parameters and that these parameters (commonly fewer than 100) can be deduced if that function is known.

A major limitation of the RM is the difficulty of obtaining a truly isotropic sample. If the polycrystalline sample is textured, the peak intensities are not only a function of crystal structure and instrument but also a

function of the texture, and can no longer be directly related to atomic parameters (Fig. 1b).

If structural and instrumental parameters are refined from such a diffraction spectrum, it is not possible to obtain a good fit and there are positive and negative deviations in intensity, which are illustrated in the lower curve of Fig. 1(b). For structural information, the deviations due to texture are undesirable and a semiempirical texture correction based on the concept of rigid platelets or needles floating in a viscous medium (March, 1932) is often applied (Dollase, 1986). Such texture corrections are not very sophisticated (Fig. 1c) compared with the capabilities of modern quantitative texture analysis. First attempts to introduce aspects of modern quantitative texture analysis into the RM (Berard & Garnier, 1992; Popa, 1992; Ferrari & Lutterotti, 1994) are still connected with limitations or simplifications like special fibre textures, high crystal symmetry and the use of the harmonic method (Bunge, 1982) that may be burdened by series-truncation effects.

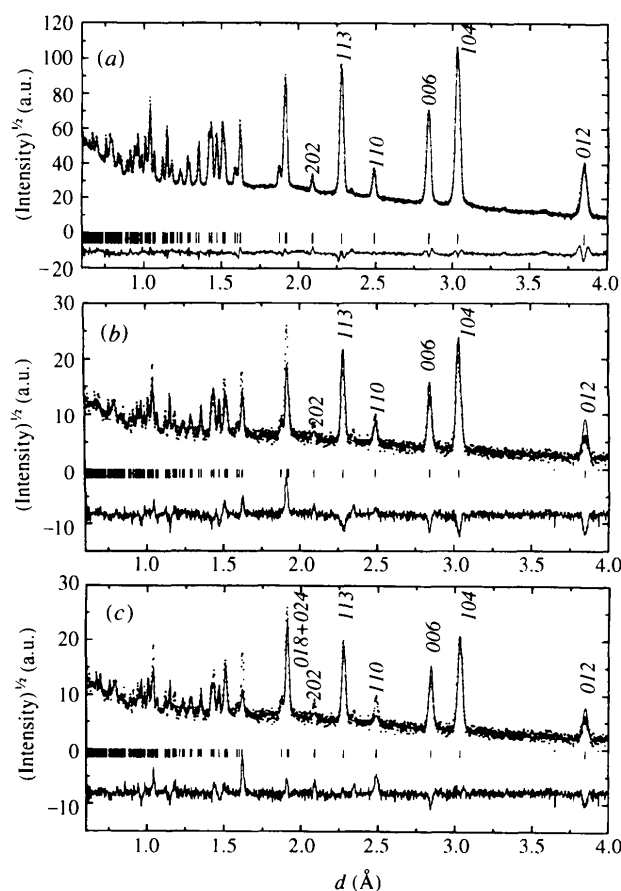


Fig. 1. TOF neutron diffraction spectrum of calcite, measured with the powder diffractometer at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory, USA. The upper line is the measured intensity curve and the lower line is the deviation between the experimental curve and a Rietveld fit, with the assumption that the material has no preferred orientation. (a) Randomized sample, averaging over all orientations. (b) Textured sample. (c) With application of the March and Dollase texture correction.

3. The main features of quantitative texture analysis

The objective of quantitative texture analysis (QTA) is to determine orientation characteristics of a polycrystalline sample from diffraction experiments. It is assumed that the crystal structure is known and that diffraction peaks can be assigned to individual hkl . A commonly used description of the texture is by the orientation distribution function (ODF) $f(g)$. An orientation g can be described by three orientation variables, *e.g.* Euler angles. For the commonly used angular grid of 5° , the three-dimensional orientation space contains about 200000 cells or nodes. Depending on crystal and sample symmetry, the number of nonredundant ODF values reduces (*e.g.* to about 2000 for the most symmetric case of cubic crystal and orthorhombic sample symmetry; except for the special case of cyclic fibre textures this number is always greater). Note that the number of data necessary to describe the orientation distribution of a sample for a given resolution is the same whether direct methods working with ODF values at discrete orientations (Matthies & Vinel, 1994) or Fourier methods (Bunge, 1982) are used, expressing the ODF by a sum of weighted continuous functions. In either case, QTA deals with a number of unknown parameters that is much greater than in the RM. This requires more experimental data (*i.e.* not only one single diffraction profile) and complex procedures for data processing.

The diffraction intensity of a textured sample with orientation $\mathbf{y}$ (direction of the scattering vector in a sample coordinate system) belonging to a lattice plane hkl ($\cong \mathbf{h}_i$) is proportional to the pole-figure value $PF(\mathbf{h}_i, \mathbf{y})$. For isolated diffraction peaks hkl pole-figure values can be extracted directly from peak intensities (after proper corrections and normalization).

Mathematically, an ('unreduced') pole-figure value is the sum of all ODF intensities along an hkl and y -dependent one-dimensional path through the orientation space. In other words, pole figures are two-dimensional projections of the ODF given in the three-dimensional orientation space. Commonly, the expression 'pole figures' means 'reduced' pole figures. Owing to Friedel's law, only reduced pole-figure data can be derived by normal scattering. A reduced hkl pole figure is the mean of the unreduced hkl and $\bar{h}\bar{k}\bar{l}$ figures (Matthies, 1979). There are powerful algorithms of 'pole-figure inversion', *i.e.* of reconstruction of the ODF from pole figures (Matthies, Wenk & Vinel, 1988). In all the applications below, we used the WIMV method (Matthies & Vinel, 1982). It is an iterative direct algorithm with well defined ghost corrections. There are universal PC-adapted versions available for any crystal symmetry.

4. General features of a combination of the Rietveld method and quantitative texture analysis

Suppose we have two samples of the same material, one isotropic (uniform orientation distribution) and the second one textured. From each we have a d spectrum that includes many diffraction peaks. For the isotropic sample, the Rietveld method is able to reproduce the spectrum SP_0 (peak positions, intensity, shape, width and background) by structural and spectrometer-related parameters (Fig. 1a). If the same parameters are used to fit the spectrum SP_y of the textured sample (with sample orientation y), deviations are observed (Fig. 1b). These deviations can be reduced by the application of texture factors $TF_{hkl}(y)$ to each peak hkl . Obviously for well separated peaks the texture factors TF_{hkl} are proportional to the corresponding pole-figure values PF . If such texture factors are applied, the spectrum SP_y can be described with the same fit quality as SP_0 .

There is a texture factor value for each peak hkl and for each sample orientation y . Therefore, the well defined RM system of equations appears to become rank-deficient. Physically the texture factors TF_{hkl} are not independent, but in the sense of pole-figure values they are related by the ODF. In other words, if a sufficient number of spectral data SP_y (*i.e.* spectra from more than one sample orientation y) is available, the equation system, containing the ODF values as unknown parameters, is again defined.

In principle, one could refine structural and textural parameters simultaneously, but with the large number of unknowns in the common case this would require formidable mathematical apparatus with results of questionable value. At least at this point it is more efficient to separate structure (RM) and texture (QTA) using already existing and well tested algorithms.

The working scheme which we chose is as follows. First, the 'structural' parameters (for brevity we include in this below all other fit parameters not connected with

texture) are refined with the RM using the isotropic SP_0 spectrum. Then, with the help of the known and fixed structural parameters and using the same RM peak-extraction algorithms (Le Bail, 1988) the pole-figure related TF_{hkl} can be determined from a sufficient number of SP_y of the textured sample. Finally, by pole-figure inversion methods of QTA the unknown ODF can be determined.

Unfortunately, there are some difficulties with the realization of this ideally straightforward scheme. First, there is the abovementioned problem with the preparation of ideally isotropic powder samples. The difficulties in getting the SP_0 spectrum can in principle be solved by measurement of the textured sample at a sufficiently large number of polar angles θ_y [$y = (\theta_y, \varphi_y)$] up to 90° with simultaneous azimuthal rotation of the sample around the Z axis of the sample coordinate system during the measurement (φ_y averaging). By averaging (weight $\sin\theta_y$) of these (cyclic) SP_y over all polar angles θ_y mathematically, an isotropic spectrum SP_0 can be constructed. For example, the new TOF texture spectrometer at the JINR at Dubna (Heinitz, Isakov, Nikitin, Shukarov & Walther, 1994) automatically covers the whole pole hemisphere, permitting a direct averaging over all y . It would be desirable not to have to perform special experiment(s) or steps connected with obtaining an isotropic standard SP_0 .

Our future plans for combining RM and QTA algorithms will explore the possibility of avoiding the SP_0 step using a special iterative cycle of structure refinement, analogous to the scheme described below, for the determination of the texture characteristics from a known structure – the main object of the present paper. We therefore make the assumption from now on that the crystal structure and spectrometer-related parameters are known and were, for instance, derived by the RM explaining an available isotropic SP_0 spectrum.

5. The iterative RM-QTA scheme for texture determination

The second nontrivial difficulty is connected with the fact that only for well separated diffraction peaks is there a direct (unique) relationship between the pole figures (the input quantities of the QTA algorithms) and the TF_{hkl} (fitted with the help of RM algorithms). For example, in Fig. 2 the two schematically indicated sets of TF_{hkl} for three closely overlapped bell-shaped peaks $hkl/1$, $hkl/2$ and $hkl/3$ may provide a visually identical profile.

The χ^2 surface in the space of the unknown parameters TF_{hkl} , where χ is the deviation between the model and real spectra, is very complicated in the vicinity of overlapping peaks and may contain many local minima. Which minimum of the χ^2 surface (*i.e.* set of TF_{hkl}) the computer finds depends on the TF_{hkl} starting values for the RM fit procedure (estimates H_{hkl}). Therefore, in

order to get values close to the 'true' set of TF_{hkl} , good estimates are indispensable. By combining RM and QTA algorithms, we hope to improve iteratively the quality of the estimates and the resulting TF_{hkl} .

At the beginning, nothing is known about texture and as starting estimate of the parameters TF_{hkl} for the first iteration step of the scheme we assume an isotropic sample ($H_{hkl}^{(0)} = 1$). The Rietveld cycle extracts in each spectrum independently the texture weights TF_{hkl} according to the Le Bail algorithm. The resulting texture factors $TF_{hkl}^{(1)}$ are in general highly incompatible, *i.e.* can hardly be interpreted as projections of an ODF. Nevertheless, they are used as pole-figure input for WIMV providing a first approximation of the ODF $f^{(1)}(g)$. Pole figures (projections) recalculated from $f^{(1)}(g)$, and therefore internally compatible with $H_{hkl}^{(1)}$, serve now as starting values for the second RM iteration, providing $TF_{hkl}^{(2)}$, which should be more compatible and closer to the true pole-figure values. The adjacent WIMV step provides $f^{(2)}(g)$ and $H_{hkl}^{(2)}$. The procedure is repeated to convergence.

6. Peak variances

As has already been explained, the fitted texture factors must not be unique in regions of peak overlaps and different values of initial estimates H_{hkl} may lead to different TF_{hkl} , always describing the given spectrum with the same quality. A necessary condition for the convergence of the above RM-QTA scheme is that this 'degree of freedom' is not constrained by any details of the RM fit algorithm. In the case that inner constraints of the RM algorithm lead always to the same set of TF_{hkl} independent of the starting values, the higher quality (compatibility) of new estimates H_{hkl} resulting from the WIMV step is lost again in the next RM step.

We have tested the reliability of our RM algorithm using the so-called 'variance' parameter V_{hkl} . This parameter can be considered for a given hkl peak as a quantitative measure of the ambiguity of its blind (without ODF correlations) fitted texture factor TF_{hkl} , or as a measure indicating the degree of peak overlap.

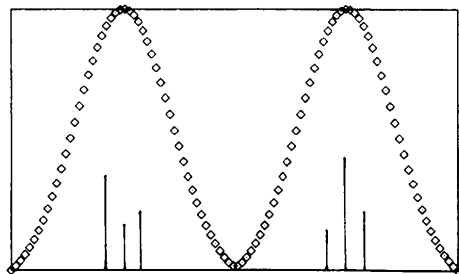


Fig. 2. Sketch illustrating the situation for a fit of highly overlapped peaks.

V_{hkl} is introduced as follows. All 'true' texture factors TF_{hkl} are identically equal to 1 for a spectrum SP0 of an isotropic sample. When the TF_{hkl} are fitted to such a spectrum, the results may differ because of the ambiguity of the TF_{hkl} for overlapped peaks and will depend on their starting values H_{hkl} if these are chosen not equal to 1. Of course, for a great number of trials (we analysed the Le Bail method always using 100 different sets of H_{hkl} with random values in the range of 0.6–1.4), the mean values of the fitted TF_{hkl} must be close to 1 for each peak hkl and for a 'clean' fit algorithm in the above sense. Correspondingly, the common variance of these TF_{hkl} (multiplied by 100 to express values in percent) can be considered.

As a test example, we used a constructed TOF spectrum of an isotropic calcite sample (for more details on the sample see below). The results of this ambiguity test are given for some reflections in Table 1 and a summary is given in Fig. 3, which compares intensities, means and variances. Note that for an infinite number of trials and an absolute ambiguity of a TF_{hkl} in the above numerical H_{hkl} region, the corresponding theoretical variance value is equal to 23%. 'Coupled' (marked by stars in Table 1) reflections of different order on the same lattice plane hkl (*e.g.* 00.6, 00.12, 00.18 – reflections 3, 18 and 55) possess the same V_{hkl} values. Their structure factors F are different but their texture factors should be the same.

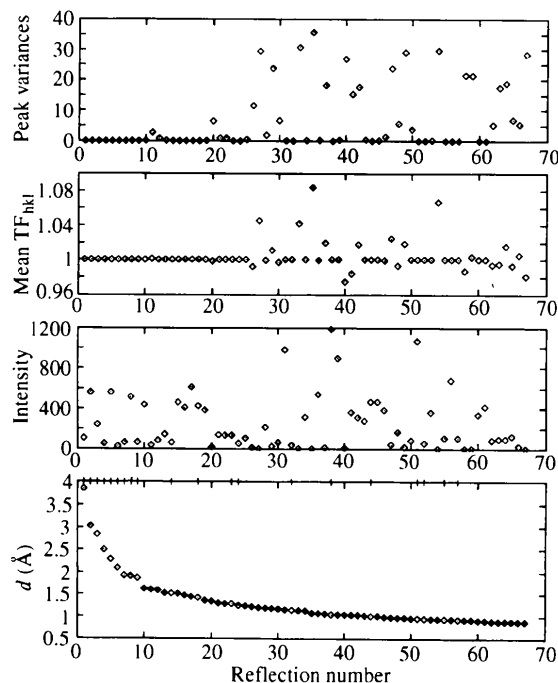


Fig. 3. Intensities (relative units), TF means and variances of the 67 considered calcite reflections. Isotropic sample. The open diamonds and corresponding marks at the top of the bottom diagram indicate coupled reflections.

Table 1. *Characteristic data of some of the 67 considered calcite reflections, with mean values of texture factors, variances for the 67 and 44 reflection models, neutron structure factor (F) and multiplier (M)*

Key: * coupled reflections; # reflections used in 'conventional' variant; + reflections selected for pole-figure representations.

Nr.	h	k	l	d_{hkl} (Å)	$TF_{hkl}(\text{mean})$	$V_{hkl}(67)$	F_{hkl}	M	$V_{hkl}(44)$
67	1	3	13	0.8850	0.981	28.5	0.382	12	20.7
66	1	1	18	0.8860	1.005	5.4	1.501	12	22.8
65	2	1	16	0.8929	0.993	6.9	3.241	12	22.8
64+	4	1	6	0.8950	1.016	18.9	2.863	12	23.3
63+	1	4	6	0.8950	0.995	17.5	2.863	12	22.7
62	2	3	8	0.8990	0.994	5.2	2.675	12	23.1
61	4	0	10	0.9127	1.000	0.0	8.341	6	23.8
60	3	2	7	0.9183	1.000	0.0	5.299	12	22.7
59	1	4	3	0.9303	1.003	21.4	0.513	12	22.7
58	4	1	3	0.9303	0.987	21.5	0.513	12	22.9
57	2	2	12	0.9377	1.000	0.0*	2.980	12	24.6
56	4	1	0	0.9430	1.000	0.0	7.526	12	23.2
55	0	0	18	0.9478	1.000	0.0*	7.391	2	24.2
54	3	1	11	0.9483	1.067	29.7	0.408	12	22.7
53	2	3	5	0.9520	1.000	0.2	5.479	12	22.3
52	0	2	16	0.9562	1.000	0.0*	3.135	6	21.9
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30	0	1	14	1.1729	0.997	6.6	3.298	6	24.3
29	2	1	10	1.1798	1.011	23.7	1.520	12	23.1
28	3	1	2	1.1868	0.999	1.9	4.227	12	24.3
27+	1	3	1	1.1955	1.045	29.5	0.483	12	23.0
26	2	2	3	1.2184	0.992	11.5	1.012	12	25.2
25	1	1	12	1.2352	1.000	0.5	2.994	12	22.4
24+	2	2	0	1.2474	1.000	0.0*	3.039	6	23.1
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23	0	3	6	1.2849	1.000	0.0*	4.769	6	
22	3	0	6	1.2849	1.000	1.0	4.769	6	
21	1	2	8	1.2967	1.000	0.9	3.416	12	
20	0	2	10	1.3390	0.998	6.4	1.828	6	
19	2	1	7	1.3568	1.000	0.1	5.656	12	
18	0	0	12	1.4217	1.000	0.0*	14.583	2	
17	3	0	0	1.4404	1.000	0.0	10.136	6	
16	1	2	5	1.4732	1.000	0.0	5.848	12	
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8	0	1	8	1.9124	1.000	0.0*	9.275	6	
7	0	2	4	1.9274	1.000	0.0*	3.270	6	
6	2	0	2	2.0944	1.000	0.0*	2.122	6	
5#	1	1	3	2.2846	1.000	0.0*	6.854	12	
4#	1	1	0	2.4948	1.000	0.0*	3.001	6	
3#	0	0	6	2.8435	1.000	0.0*	10.956	2	
2#	1	0	4	3.0356	1.000	0.0*	9.703	6	
1#	0	1	2	3.8548	1.000	0.0*	4.247	6	

Obviously, for well separated peaks  $V_{hkl}$  is close to 0%. Large variance values must appear and are indeed observed, for reflections in regions of overlap, *i.e.* for exact overlaps (such as 03.6 and 30.6 – reflections 22 and 23) as well as for partial overlaps (*e.g.* 30.0 and 00.12 – reflections 17 and 18). The variance test confirms that the used RM refinement algorithm does not constrain the freedom of fit for texture factors and is sensitive to the  $TF_{hkl}$  estimates  $H_{hkl}$  provided from the corresponding WIMV step.

## 7. Demonstration of the iterative RM-QTA scheme

As a test material for the proposed RM-QTA method, we used a sample of trigonal calcite, deformed in plane strain compression, which displays a moderately strong texture with considerable complexity. It was used in a round robin for a recent project to evaluate the quality of neutron diffraction texture analysis (Wenk, 1991).

The  $d$  spectra containing diffraction information of many peaks for a single sample orientation  $y$  can be obtained by neutron time-of-flight (TOF) measurements. When this project was started, such experimental data were not available. Furthermore, we found it more prudent to establish first with idealized synthetic data that the proposed procedure is feasible, and to quantitatively assess uncertainties, resolution and errors linked to the method, rather than to work 'blind' with real experimental data.

We therefore constructed our 'experimental data' by first expressing the texture of the calcite standard sample (Fig. 4a) with a set of 12 Gaussian standard components (Matthies, Vinel & Helming, 1987), obtaining a similar pattern (Fig. 4b). Finally, this distribution was additionally sharpened in order to give a model with more pronounced details for testing and analytical activities (Fig. 4c).

The next step was to cover the pole hemisphere with a hexagonal equal-area grid of  $7.6^\circ$  resolution (Matthies & Wenk, 1992). Orthorhombic sample symmetry was assumed and the central quadrant of the pole figure out to  $40^\circ$  was covered with 37 'hexagonal'  $y$  positions. For each of these 37  $y$  and the 67 reflections  $hkl$ , in the  $d$  range 3.85 to 0.88 Å, pole-figure values PF were calculated from the model ODF. Now, using these PF values as texture weights  $TF_{hkl}$ , assuming the crystal structure of calcite (Effenberger, Mereiter & Zemmann, 1981), we calculated three parameters for the background polynomial and five parameters for instrument resolution, applicable to the LANSCE and IPNS TOF neutron diffraction facilities. 37  $d$  spectra were calculated which then served as 'experimental' data, with no further knowledge about the texture.

For comparison (in order to evaluate the results of the RM-QTA scheme as well as of the use of small covered pole hemisphere areas) we also calculated complete pole figures, covering the whole pole hemisphere by the

conventional  $5 \times 5^\circ$  grid. For the given orientation distribution, the PF data at the 37  $y$  positions are sufficient to reconstruct by cubic splines the PF values at the  $5^\circ$  grid points up to a polar angle of  $40^\circ$ .

First, we used 63 ( $5 \times 5^\circ$  grid) complete pole figures (with four pairs of ideally overlapped reflections – 'doubles'; see below) as input data of our QTA (WIMV) procedure in order to establish the 'optimum' ODF resolution that can be derived exploiting the full (hypothetically available) information from the considered  $d$  range.

For comparison with the conventional procedure, we also calculated the ODF from the first five pole figures (complete;  $5 \times 5^\circ$  grid) with large  $d$  spacing, corresponding to the current experimental strategy to obtain the ODF from a few well separated pole figures, with many sample orientations.

Then, in order to demonstrate effects connected with highly incomplete PF input data and to establish the 'maximum variant' of ODF resolution we can achieve with the RM-QTA scheme, the data of 63 PFs (with four doubles) at the 37 hexagonal  $y$  positions were used as input data for WIMV.

In the subsequent analysis of the RM-QTA scheme, two cases are considered: the first case (A) with the whole  $d$  spectrum from 3.9 to 0.88 Å (67 peaks) and the second case (B) using only the highly overlapping region from  $d = 1.25$  to 0.88 Å (44 peaks).

Table 1 lists  $d$  spacings, neutron structure factors and variances defined above in order to facilitate the discussion of the results. Of particular interest are the marked four pairs ('doubles') of reflections {03.6, 30.6}, {03.12, 30.12 – reflections 44 and 45}, {14.3, 41.3} and {14.6, 41.6}, which are completely overlapped but not equivalent in the space group  $R\bar{3}c$ .

The texture data in this paper are represented as pole figures in equal-area projection and as ODFs using oblique  $\sigma$  sections, which show a minimum of distortion, also in polar coordinates (Matthies, Helming & Kunze, 1990). Pole figures show the distribution of poles to lattice planes whereas an ODF section gives the  $c$ -axis distribution of those crystallites which have their  $a$  axes at a certain position characterized by the  $\gamma$  angle (Wenk & Kocks, 1987). Owing to the orthorhombic sample symmetry, it is sufficient to display the ODF by  $\sigma$  sections at 0, 5, 10 and  $15^\circ$  (Fig. 4). For pole figures, we choose four representative reflections from the strongly overlapping region, including one pair of complete overlaps (Table 1, Figs. 5 and 6).

The results of conventional ODF calculations from 63 or five complete pole figures with the WIMV method (Figs. 4d and e) agree well with the model ODF (Fig. 4c). Slight differences are due to the inherent ambiguity of reduced pole-figure inversions ['ghost effects' (Matthies, 1979; Matthies, Wenk & Vinel, 1988)]. The differences seen in the 'maximum variant' (Fig. 4f) demonstrate the loss of information quality connected

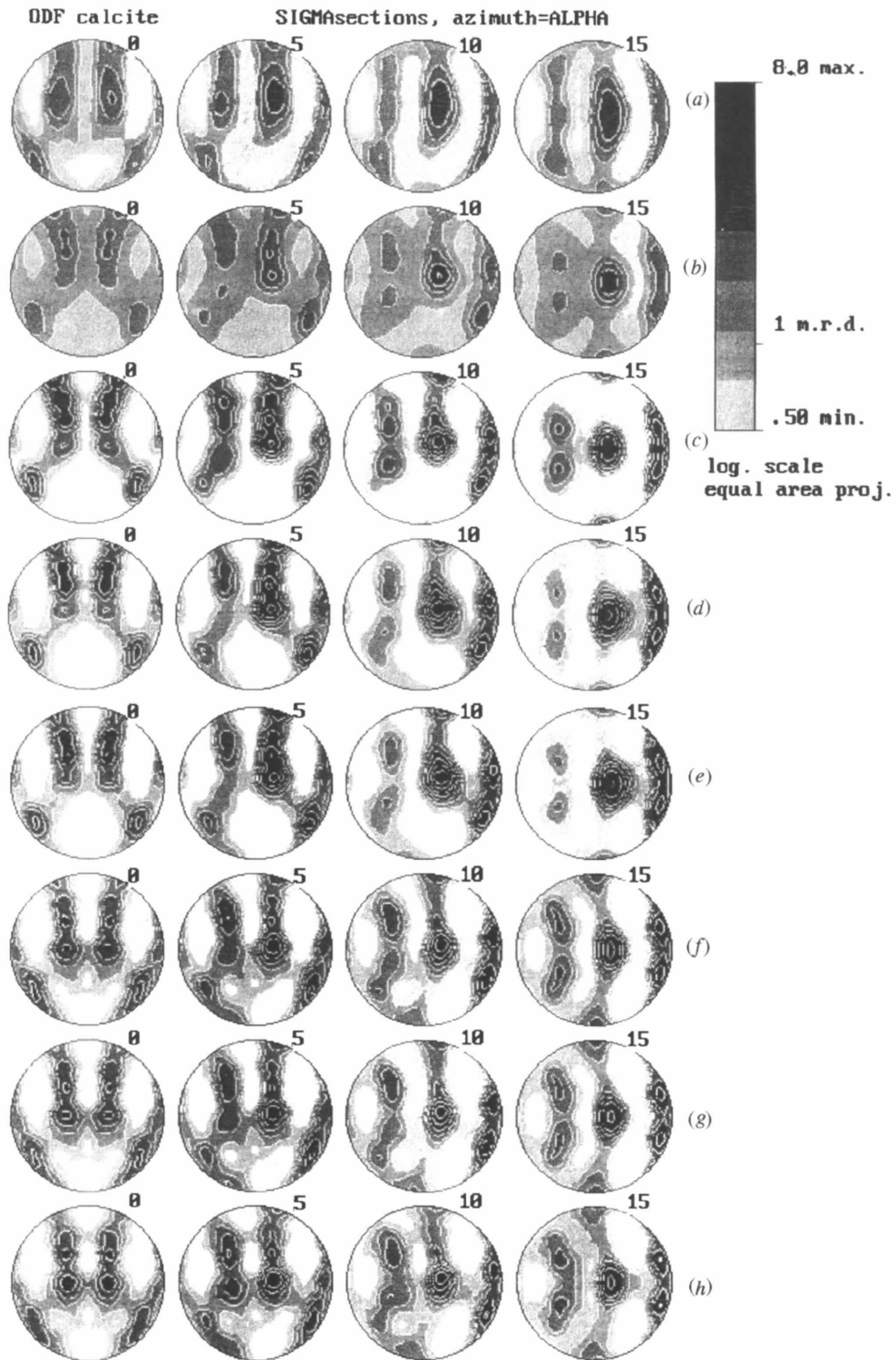


Fig. 4. Orientation distributions of calcite, displayed in oblique  $\sigma$  sections in equal-area projection. (a) Texture of experimentally deformed limestone measured by neutron diffraction. (b) Similar texture approximated by 12 Gaussian texture components. (c) The model ODF 'experiment' – a sharpened variant of (b). (d) Texture reconstructed with the WIMV algorithm from 63 (four doubles) complete pole figures – optimum variant. (e) Reconstructed from five complete pole figures – conventional variant. (f) Reconstructed from 63 (four doubles) incomplete pole figures given at 37 hexagonal  $y$  points – maximum variant. (g) ODF obtained with the RM-QTA scheme from 37 diffraction spectra with 67 peaks – case A. (h) RM-QTA results based on the overlapped region with 44 peaks – case B.

with the use of only incomplete pole figures with open normalization factors that are also to be determined.

Also shown are the ODFs that are based on the iterative RM-QTA procedure and a highly incomplete pole-figure coverage to  $40^\circ$ ; Fig. 4(g) relies on data from the spectral region between 3.9 and  $0.88 \text{ \AA}$  with 67 reflections – case A – and Fig. 4(h) on data from the highly overlapped region between 1.25 and  $0.88 \text{ \AA}$  with 44 reflections – case B. The similarity of the RM-QTA ODFs and the ‘maximum variant’ (Fig. 4f) is striking, considering the completely different methodology and different data.

The same applies to pole figures. Fig. 5(a) shows pole figures that belong to the model distribution. Fig. 5(b) shows pole figures recalculated from the ODF based on 63 (four doubles) complete pole figures – optimum variant (cf. Fig. 4d), Fig. 5(c) shows pole figures recalculated

from the ODF based on 63 (four doubles) incomplete pole figures – maximum variant (cf. Fig. 4f) (the inner circle indicates the extent of incomplete pole figures), Fig. 5(d) shows pole figures recalculated from the 67 reflections RM-QTA ODF (corresponding to Fig. 4g) and Fig. 5(e) those recalculated from the ODF derived from the 44 highly overlapped reflections (Fig. 4h). Again, there is a great similarity of the corresponding data, including the originally overlapped pole figures (14.6, 41.6) that have been separated.

We will use pole figures to illustrate the convergence of the RM-QTA scheme for overlapping reflections (Fig. 6) in case A (use of all 67 reflections). After the first RM step (Fig. 6b) fairly isolated pole figures such as 22.0 (22.0 is additionally coupled to the isolated 11.0 reflection) are well resolved; highly overlapped ones such as 13.1 are poor compared with the pole figures

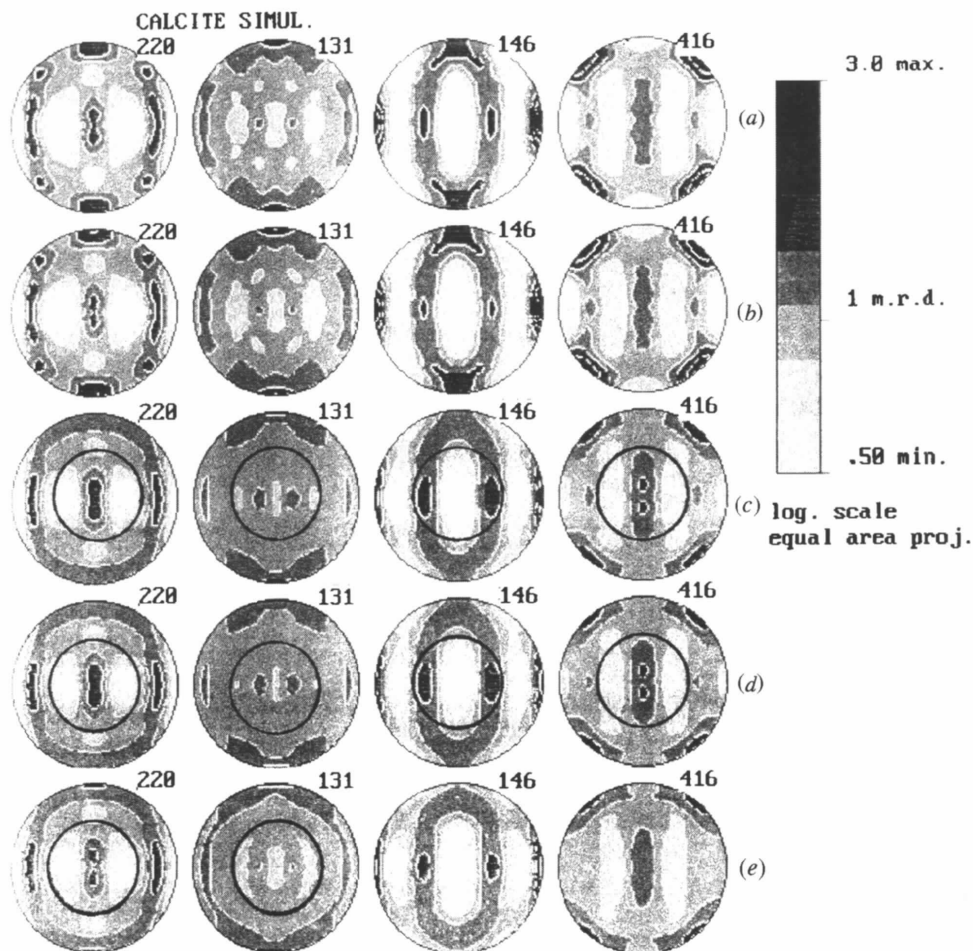


Fig. 5. Selected pole figures in equal-area projection. (a) Standard pole figures belonging to the model ODF represented by 12 Gaussian texture components. (b) Recalculated from the ODF based on 63 complete pole figures [cf. Fig. 4(d) – optimum variant]. (c) Recalculated from the ODF based on 63 incomplete pole figures [cf. Fig. 4(f) – maximum variant]. (d) Recalculated from the ODF based on the RM-QTA scheme from 37 diffraction spectra with 67 reflections (cf. Fig. 4g). (e) RM-QTA results based on the overlapped region with 44 peaks (cf. Fig. 4h). The outer PF regions in (c), (d) and (e) as well as for (e) the separated 14.6, 41.6 figures were not connected at all with experimental data inputs.

of the maximum variant (Fig. 6a) or model pole figures (cf. Figs. 5c and a).

Complete overlaps (doubles) cannot be distinguished by the RM {14.6, 41.6}. The first WIMV step (Fig. 6c) improves the situation greatly, including for highly overlapped pole figures that were omitted from the first WIMV cycle because of their high variance ( $>5\%$ ). The results from the second RM step (Fig. 6d) confirm our expectation that good initial estimates from WIMV provide better results. After the third RM-QTA step, the system has practically converged (Fig. 6e) and the pole figures only differ in minor details from those of the maximum variant (Fig. 6a).

The convergence process of the RM is highlighted in Fig. 7 using a one-dimensional array of texture factors  $TF_{hkl}$  for the 37 hexagonal  $y$  data points of the reflection 13.1. The values of the first RM fit results may be quite

wrong, but after WIMV provides better estimates RM quickly converges towards the correct values.

## 8. Conclusions

We have been astonished by the high resolution and rapid convergence of the procedure. Even for the spectral range with only overlapped peaks (case B – all reflections with variances greater than 20%!) the convergence to the basically correct ODF was obtained after three RM-QTA iteration steps. For more details, see Appendix C. In our tests, we used only 37  $y$  spectra out to  $40^\circ$ ; it is likely that fewer orientations would be sufficient but we have not explored the limits.

The results suggest that RM-QTA profile analysis, where few diffraction spectra consisting of many diffraction peaks are measured, is a real alternative to the

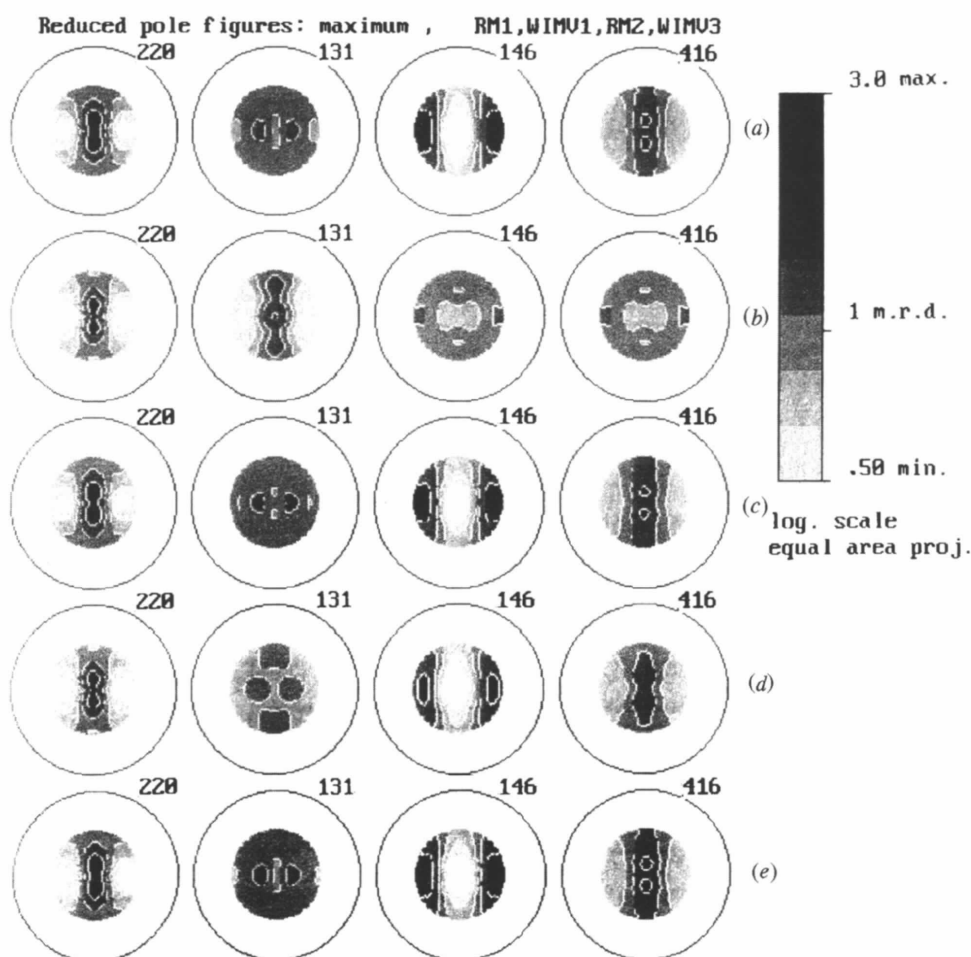


Fig. 6. Selected pole figures of calcite represented in equal-area projection documenting the refinement process in case A. (a) Pole figures recalculated from the ODF of the maximum variant [cf. Figs. 4(f) and 5(c)]. (b) Rietveld, first iteration step –  $TF_{hkl}^{(1)}$ . (c) WIMV first iteration step –  $H_{hkl}^{(1)}$ . (d) Rietveld second step –  $TF_{hkl}^{(2)}$ . (e) WIMV final third step –  $H_{hkl}^{(3)}$  (cf. Fig. 5d).

conventional method, which relies on intensities of a few reflections in many sample orientations. The method is particularly useful for monochromatic radiation with position-sensitive detectors or polychromatic radiation (e.g. TOF of neutrons or energy-dispersive X-ray detectors). With these techniques, continuous spectra are recorded but presently only a few diffraction peaks are extracted and used in the analysis.

We have completed a test of methodological procedures for general profile analysis (Rietveld) and ODF analysis (WIMV) for TOF neutron diffraction. A next step will be application to real experimental data (which have since then been collected at IPNS) and streamlining of the procedure to make it available for users. First, we will use single-detector TOF neutron diffraction data because of the simple geometry and minimal corrections. For neutrons, RM-QTA is attractive because of the vastly reduced amount of necessary experimental data. But the method can later be extended to X-ray diffraction and position-sensitive detectors too, applying appropriate corrections and introducing new experimental variables. The method offers possibilities for quantitative texture analysis of low-symmetry and polyphase materials that presently elude any quantitative analysis if only partially overlapped diffraction peaks are present.

Also, since whole diffraction spectra are available for different sample orientations, lattice parameters can be refined, leading to simultaneous determination of residual stresses in textured materials, which is becoming increasingly important for technological applications (Hutchings & Krawitz, 1993; Ferrari & Lutterotti, 1994). Finally, the method provides the possibility of an automatic texture correction for the Rietveld method, which has long been one of its main deficiencies.

## APPENDIX A

### *d*-Spectrum model and the Le Bail algorithm

The structure of the test spectra was chosen according to the common RM expressions for neutron TOF measurements. The intensity  $Y$  at the  $n$ th  $d$  channel  $d_n$  for

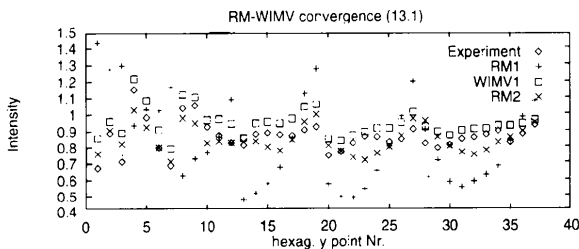


Fig. 7. One-dimensional representation of the texture factors at the 37 hexagonal  $y$  pole positions for reflection 27 (13.1), illustrating the convergence during the RM-QTA cycle. RM1  $\hat{=}$   $TF_{hkl}^{(1)}$ ; WIMV1  $\hat{=}$   $H_{hkl}^{(1)}$ ; RM2  $\hat{=}$   $TF_{hkl}^{(2)}$ .

the  $j$ th spectrum  $SP_{y_j}$  reads ( $\mathbf{h}_i \hat{=}$   $hkl$ )

$$Y(y_j, d_n) = bkg(y_j, d_n) + \sum_i I_{h_i}(y_j) S(d_{h_i}, y_j; d_{h_i} - d_n) \quad (1)$$

with

$$I_{h_i}(y_j) = I_{h_i}^{\text{random}} \text{PF}(h_i, y_j); I_{h_i}^{\text{random}} = C m_{hkl} |F_{hkl}|^2. \quad (2)$$

The sum includes all reflections (position at  $d_{h_i}$ ) of interest at  $d_n$ .

$S$  describes the peak form and  $bkg$  a background. The scattering intensity for the  $i$ th reflection of an isotropic sample is described by a scaling factor  $C$  that may yet contain (nonstructural or non-texture-related)  $d_{h_i}$  dependencies.  $m_{hkl}$  is the multiplicity and  $F$  the structure factor (inclusive of the Debye-Waller factor) of the  $hkl$  reflection. The principal formula of the Le Bail algorithm (iterative scheme – originally for peak-intensity extraction from powder spectra), applied to a textured spectrum  $SP_{y_j}$  reads for the  $(m + 1)$ th iteration (for brevity, background details are omitted):

$$\begin{aligned} TF_{h_i}^{(m+1)}(y_j) &= TF_{h_i}^{(m)}(y_j) \\ &\times \sum_n \left\{ Y^{\text{exp}}(y_j, d_n) S(d_{h_i}, y_j; d_{h_i} - d_n) \right. \\ &\times \left[ \sum_k I_{h_k}^{\text{random}} TF_{h_k}^{(m)}(y_j) \right. \\ &\times \left. \left. S(d_{h_k}, y_j; d_{h_k} - d_n) \right]^{-1} \right\} \end{aligned} \quad (3)$$

with  $TF_{h_i}^{(0)}(y_j) = 1$  and  $\sum_n S(d_{h_i}, y_j; d_{h_i} - d_n) = 1$ . For ‘coupled’ reflections (cf. §6), the corresponding TF are to be set equal.

## APPENDIX B

### QTA-related mathematical expressions

Below, we explain terms used in the main part of the paper by mathematical expressions, without going into full detail. The explicit consideration of such elements as the various symmetries important in QTA, the degree of completeness of the pole figures, corresponding normalization operations, the control of the velocity of convergence in iterative algorithms and conditional ghost-correction concepts would result in sometimes much more complicated and less transparent expressions. For more details, see for instance Matthies, Wenk & Vinel (1988). The orientation  $g$  of a crystallite relative to a sample fixed (right-handed, Cartesian) coordinate system  $K_A$  is described by the orientation of a crystal fixed coordinate system  $K_B$  relative to  $K_A$ . With the help of three well defined rotations, characterized by the Eulerian angles  $0 \leq \alpha, \gamma \leq 2\pi$ ,  $0 \leq \beta \leq \pi$ ,  $K_A$  can be oriented parallel to  $K_B$ .  $g$  can be represented

as  $g = \{\alpha, \beta, \gamma\} = \{\mathbf{r}, g\}$ . The direction  $\mathbf{r} = [\alpha, \beta]$  describes the  $Z_B$  axis in regard of  $K_A$ , with  $\alpha$  the azimuthal angle and  $\beta$  the polar angle correspondingly. All possible orientations  $g$  form the orientation space  $G$ . The orientation distribution function  $f(g) \geq 0$  (density of probability) characterizes the orientation distribution of the crystallites (of one crystalline phase) in a polycrystalline sample, with

$$\int_G f(g) dg = 1, \quad dg = (1/8\pi^2) \sin \beta d\alpha d\beta d\gamma. \quad (4)$$

Because of the nontrivial metrics of the  $G$  space, the ODF representation by two-dimensional  $G$ -space sections (one Euler angle is fixed) can often be remarkably distorted. These distortions can be reduced by the introduction of the  $\sigma$  variable and work with  $\sigma$  sections.

$$\sigma = (\alpha + \gamma)/2; \quad g = [\alpha, \beta, \sigma], \quad \gamma = 2\sigma - \alpha. \quad (5)$$

An (unreduced) pole figure  $P_{\mathbf{h}}(\mathbf{y})$  describes the frequency of the crystallites for which the crystal direction  $\mathbf{h}$  (given in  $K_B$ ) lies parallel to a sample direction  $\mathbf{y}$  (given in  $K_A$ ):

$$P_{\mathbf{h}}(\mathbf{y}) = \int_0^{2\pi} f(\{\mathbf{h}, \tilde{\varphi}\}^{-1} \cdot \{\mathbf{y}, 0\}) d\tilde{\varphi}/2\pi. \quad (6)$$

Owing to Friedel's law, normal scattering gives only reduced pole figures

$$\begin{aligned} \text{PF}(\mathbf{h}, \mathbf{y}) &= \tilde{P}_{\mathbf{h}}(\mathbf{y}) = [P_{\mathbf{h}}(\mathbf{y}) + P_{-\mathbf{h}}(\mathbf{y})]/2 \\ &= [P_{\mathbf{h}}(\mathbf{y}) + P_{\mathbf{h}}(-\mathbf{y})]/2. \end{aligned} \quad (7)$$

The central problem of QTA consists in the approximative reconstruction of the ODF from experimental pole-figure data  $\text{PF}(\mathbf{h}_i, \mathbf{y}_j)$  given for a limited set of reflections  $\mathbf{h}_i$  ( $hkl$ ) and sample directions  $\mathbf{y}_j$  on the pole hemisphere. With the experimental data  $\text{PF}^{\text{exp}}(\mathbf{h}_i, \mathbf{y}_j)$  (6) and (7) form a set of integral equations for  $f(g)$ . In the harmonic method (Bunge, 1982; Dahms & Bunge, 1988), it is approximately solved by a Fourier transformation using spherical functions:

$$\begin{aligned} f(g) &= \sum_{l=0}^{\infty} \sum_{m,n=-l}^l C_l^{m,n} D_{mn}^l(g^{-1}); \\ P_{\mathbf{h}}(\mathbf{y}) &= \sum_{l=0}^{\infty} \sum_{m,n=-l}^l C_l^{m,n} D_{m0}^l(\{\mathbf{h}, 0\}) D_{n0}^{l*}(\{\mathbf{y}, 0\}). \end{aligned} \quad (8)$$

The unknown  $C_l^{m,n}$  up to a series truncation at  $l = L$  are determined from the experimental PF values.

'Direct methods' try to solve (6) and (7) directly. This can be done by the introduction of, for instance,  $G$  space and  $Y$  space cells, *i.e.* by transformation of (5) and (6) into a set of algebraic equations (Ruer & Baro, 1977; Imhof, 1982; Pawlik, 1986; Schaeben, 1988).

The WIMV method (Matthies & Vinel, 1982) exactly considers (6) and (7), but works numerically with ODF and PF values only at fixed  $G$  space and  $Y$  space nodes ( $g_k, \mathbf{y}_j$ ), additionally using interpolation operations. The starting ODF approximation is given by ( $\mathbf{y}_{kim} \equiv g_k^{-1} \cdot \mathbf{h}_{im}$ ):

$$f^{(0)}(g_k) \simeq \prod_{i,m} [\text{PF}^{\text{exp}}(\mathbf{h}_i, \mathbf{y}_{kim})]^{E_k}, \quad (9)$$

where all physically equivalent reflection directions  $\mathbf{h}_{im}$  for the given set of  $\mathbf{h}_i$  pole figures are to be taken into account.  $E_k$  depends on the volume of the available experimental PF information connected with the ODF value at  $g_k$ . For missing experimental data at  $\mathbf{y}_{kim}$  (incomplete pole figures)  $\text{PF} = 1$  can always be formally set. The iteration scheme reads

$$\begin{aligned} f^{(n+1)}(g_k) &\simeq f^{(n)}(g_k) \prod_{i,m} \left( [\text{PF}^{\text{exp}}(\mathbf{h}_i, \mathbf{y}_{kim})] \right. \\ &\quad \times \left. \{ [\text{PF}^{(n)}(\mathbf{h}_i, \mathbf{y}_{kim})]^{-1} \}^{E_k^{(n)}} \right). \end{aligned} \quad (10)$$

The quality by which a reconstructed ODF  $f^{(n)}(g)$  explains the experimental data  $\text{PF}^{\text{exp}}(\mathbf{h}_i, \mathbf{y}_j)$  can quantitatively be characterized using the so-called RP values:

$$\begin{aligned} \text{RP}(\varepsilon) &= 100\% \left\{ \sum_{i,j} \Theta(\varepsilon) |\text{PF}^{(n)}(\mathbf{h}_i, \mathbf{y}_j) - \text{PF}^{\text{exp}}(\mathbf{h}_i, \mathbf{y}_j)| \right. \\ &\quad \times \left. [\text{PF}^{\text{exp}}(\mathbf{h}_i, \mathbf{y}_j)]^{-1} \right\} / \sum_{i,j} \Theta(\varepsilon; ij), \end{aligned}$$

with

$$\Theta(\varepsilon; ij) = \begin{cases} 0 & \text{PF}^{\text{exp}}(\mathbf{h}_i, \mathbf{y}_j) \leq \varepsilon \\ 1 & \text{PF}^{\text{exp}}(\mathbf{h}_i, \mathbf{y}_j) > \varepsilon \end{cases}. \quad (11)$$

Large RP values indicate bad results of the ODF reconstruction due to incorrect algorithms, as well as due to incompatibilities in the experimental data. The last ones disappear for model data constructed with standard precision. In Appendix C, some data are given characterizing the convergence and quality of ODF reconstruction for the test examples described in the main part of the paper in §7. RP means  $\text{RP}(\varepsilon)$  for  $\varepsilon = 0.005$  and RP1 for  $\varepsilon = 1$ .

## APPENDIX C

### Some numerical characteristics on the WIMV tests and RM-QTA calculations

The 'variants' and 'cases' are described in §7 of the main part. The WIMV iteration is truncated after saturation (velocity of convergence  $\leq 0.3\%$ ). For case A and the first iteration step, WIMV considered only the 45 reflections (from 67) with  $hkl \leq 5\%$ . See Table 2.

Table 2. Summary of RM-QTA calculations

Calculating variants	Number of WIMV iterations	RP (%)	RP1 (%)	Relevant figures
Optimum	12	2.10	1.53	4(d), 5(b)
Conventional	12	1.40	1.21	4(e)
Maximum	9	3.27	2.44	4(f), 5(c), 6(a)
Case A (67 reflections)				
RM-QTA first step	8	3.30	2.40	6(c)
RM-QTA second step	8	3.94	2.88	
RM-QTA third step	8	3.64	2.67	4(g), 5(d), 6(e)
Case B (44 reflections)				
RM-QTA first step	9	10.93	7.11	
RM-QTA second step	7	5.37	4.17	
RM-QTA third step	8	4.37	3.53	4(h), 5(e)

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