軌道放射X線粉末回折における選択配向の影響

井田　隆

名古屋工業大学先進セラミックス研究センター
〒 507-0071　岐阜県多治見市旭ヶ丘 10-6-29

Effect of Preferred Orientation in Synchrotron X-ray Powder Diffraction

Takashi Ida

Advanced Ceramics Research Center, Nagoya Institute of Technology,
10-6-29 Asahigaoka, Tajimi, Gifu 507-0071, JAPAN

Abstract

The capillary transmission or asymmetric reflection method is usually applied in synchrotron powder diffraction measurements, while the symmetric reflection method has conventionally been applied in laboratory powder diffraction measurements with the Bragg-Brentano geometry. Although Dollase [*J. Appl. Cryst*. **19**, 267–272 (1986)] has already pointed out that the formula of the preferred orientation factor for the capillary transmission mode should be different from that for the symmetric reflection mode, no appropriate implementation in Rietveld programs is currently available. In this study, an analytical expression and an efficient numerical algorithm to evaluate the preferred orientation factor based on the pole density profile of the March-Dollase model for capillary transmission and asymmetric reflection methods have been derived.

Key-words

Preferred orientation, Synchrotron powder diffraction, Rietveld method

1. Introduction

It is well known that observed powder diffraction intensities are often affected by preferred orientation of crystallites, particularly in the case of a collection of platy or rod-like crystallites [1, 2]. Most of the application programs for the Rietveld refinement implement some models for the preferred orientation factor, which are intended to simulate the change caused by the preferred orientation in the diffraction peak intensities measured in the symmetric reflection mode.

However, (i) a capillary transmission or (ii) an asymmetric reflection method is usually applied in synchrotron powder diffraction measurements, because the efficiency of detecting the diffracted x-ray photons is greatly enhanced by those methods accompanied with a position-sensitive detector or multiple point-detectors. Dollase has suggested an integral formula for the preferred orientation factor based on the March model for the capillary transmission mode [2], but no implementation about capillary transmission or asymmetric reflection method in Rietveld programs is currently available, to the author's knowledge.

In this study, the author has derived an analytical expression of the preferred orientation factor for the capillary transmission mode in powder diffraction, and also an effective numerical algorithm to evaluate the preferred orientation factor for the asymmetric reflection mode, both of which are based on the March-Dollase model for the pole density profile function.

2. Pole density profile and preferred orientation factor

2.1 Pole density profile of March-Dollase model

Dollase has proposed a formula for the pole density profile based on the March function, given by

$$P_{\mathbf{p}^*}(r,\rho)=\left(r^2\cos^2\rho+\frac{\sin^2\rho}{r}\right)^{-3/2}, \qquad (1)$$

where $\mathbf{p}^*$ represents the preferred orientation direction, which may be defined by $\mathbf{p}^* = H\mathbf{a}^* + K\mathbf{b}^* + L\mathbf{c}^*$ for the reciprocal lattice vectors $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$, r is the parameter for the preferred orientation, $r > 1$ for platy crystallites , $r < 1$ for rod-like crystallites, and $r = 1$ for random orientation of crystallites in a powder sample [2]. Note that the numbers of index (H K L) may be

non-integer values for rod-like ($r < 1$) crystallites, when the crystal structure belongs to the monoclinic or triclinic crystal system, while it is likely that they are integer values for platy ($1 < r$) crystallites. The angle ρ is the polar angle between the preferred orientation direction **p*** and the direction **s*** that specifies the direction of the specimen. Rotational symmetry of the preferred orientation about **s*** is assumed in the March-Dollase model, which can be ensured by spinning the sample about the direction **s*** during the acquisition of diffraction intensity data. Since it is essential to keep spinning the sample during the synchrotron powder diffraction measurements in most cases, the direction **s*** should naturally be identified to the rotation axis of the spinning attachment of the measurement system.

The general formula of preferred orientation factor, which should be proportional to the observed diffraction intensity, is given by

$$f_{\mathbf{d}^*}(r,\alpha,\Delta)=\frac{1}{2\pi}\int_0^{2\pi} g(r,\alpha,\Delta,\varphi')\,\mathrm{d}\varphi', \tag{2}$$

$$g(r,\alpha,\Delta,\varphi')=P_{\mathbf{p}^*}(r,\rho), \tag{3}$$

$$\cos\rho=\cos\alpha\cos\Delta-\sin\alpha\sin\Delta\sin\varphi', \tag{4}$$

where α is the angle between the diffraction vector $\mathbf{d}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ and the preferred orientation direction **p***, and Δ is the angle between the vectors **d*** and **s***. The angle Δ is equal to zero in the symmetric reflection mode, $\pi / 2$ in the capillary transmission mode, and is equal to the difference between the Bragg angle θ and the incident glancing angle Ω for the flat-plate reflection measurement, $\Delta = |\theta - \Omega|$.

2.2 Preferred orientation factor for symmetric reflection mode

Equations (2)-(4) are reduced to the following formula:

$$f_{\mathbf{d}^*}(r,\rho)=\left(r^2\cos^2\alpha+\frac{\sin^2\alpha}{r}\right)^{-3/2}, \tag{5}$$

for the symmetric reflection mode ($\Delta = 0$). It should be emphasized that the formula of eq. (5) is identical to that of eq. (1), but the meanings are definitely different. Note that the argument ρ in eq. (1) means the angle between **p*** and **s***, while α in eq. (5) means the angle between **p*** and **d***.

2.3 Preferred orientation factor for capillary transmission mode

Dollase has also suggested that the preferred orientation factor for the capillary transmission mode can numerically be evaluated by the formula given by eqs. (2)–(4) with $\Delta = \pi / 2$, that is,

$$f_{d^*}\left(r,\alpha,\frac{\pi}{2}\right)=\frac{r^{3/2}}{\pi}\int_{-\pi/2}^{\pi/2}\left[1+\left(r^3-1\right)\sin^2\alpha\sin^2\varphi'\right]^{-3/2}\mathrm{d}\varphi' \ . \tag{6}$$

In fact, an analytical solution of eq. (6) is available, which is given by the following formula:

$$f_{d^*}\left(r,\alpha,\frac{\pi}{2}\right)=\begin{cases}\dfrac{2r^{3/2}\,\mathrm{E}\left(\sqrt{1-r^3}\,\sin\alpha\right)}{\pi\left[1-\left(1-r^3\right)\sin^2\alpha\right]} & \left[r\le 1\right]\\[2ex] \dfrac{2r^{3/2}\,\mathrm{E}\left(\left(1+\dfrac{\mathrm{cosec}^2\alpha}{r^3-1}\right)^{-1/2}\right)}{\pi\sqrt{1+\left(r^3-1\right)\sin^2\alpha}} & \left[1<r\right]\end{cases}, \tag{7}$$

where

$$\mathrm{E}(k)\equiv\int_0^{\pi/2}\sqrt{1-k^2\sin\varphi}\,\mathrm{d}\varphi, \tag{8}$$

is the Legendre complete elliptic integral of the second kind. As an efficient algorithm to evaluate the elliptic integral is well known (Appendix A), there will be no reason for applying numerical integral suggested by Dollase, instead of the analytical solution given by eq. (7).

Figure 1 compares the preferred orientation factors for symmetric reflection and capillary transmission modes on variation of the values of r and α. Note that the values for $r = 0.8$ in the symmetric reflection mode are very close to the values for $r = 2$ in the capillary transmission mode within the range $45° < \alpha < 90°$, but clearly different in the range $0° < \alpha < 45°$. Since the March-Dollase pole density profile function $P_{\mathbf{p}^*}(r, \rho)$ satisfies the normalization condition:

$$\int_0^{2\pi}\int_0^{\pi} P_{\mathbf{p}^*}(r,\rho)\sin\rho\,\mathrm{d}\rho\,\mathrm{d}\varphi=4\pi, \tag{9}$$

it is expected that the application of the symmetric-reflection formula $f_{\mathbf{d}^*}(r, \alpha, 0)$ to the data measured in a symmetric reflection mode will be consistent with the requirement of normalization about the probability

density function. On the contrary, application of $f_{d^*}(r, \alpha, 0)$ to the data measured in a capillary transmission mode will violate the normalization condition, which will lead systematic errors in quantitative phase analysis. It is concluded that the correct formula of $f_{d^*}(r, \alpha, \pi/2)$ should be used for the data measured in a capillary transmission mode, even if the difference between $f_{d^*}(r, \alpha, 0)$ for $r < 1$ and $f_{d^*}(r, \alpha, \pi/2)$ for $1 < r$ could not clearly be distinguished on application to the observed powder diffraction pattern.

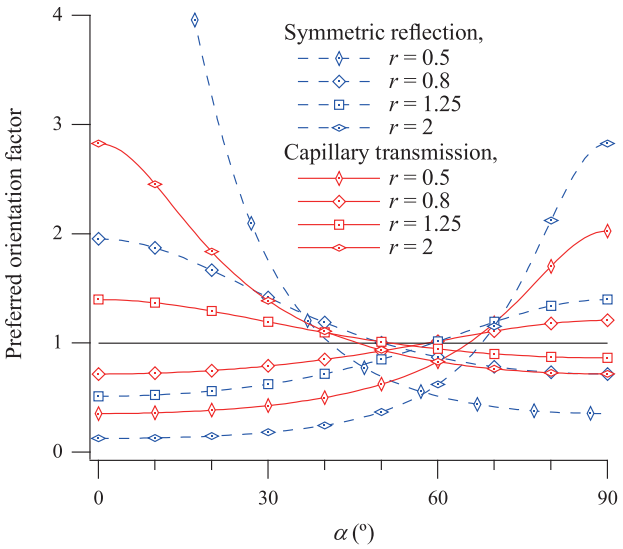

Fig. 1. Comparison of the preferred orientation factors calculated for symmetric reflection and capillary transmission methods.

2.4 Preferred orientation factor for asymmetric reflection mode

The formula of the preferred orientation factor for the asymmetric reflection mode may numerically be calculated straightforwardly by eqs. (2)–(4), as suggested by Dollase [2]. And it is generally recommended that sampling points for numerical integral should be evenly spaced, when the integrand is a periodic function [3]. Then the formula for numerical integral would be given by the following equation,

$$f_{d^*}(r,\alpha,\Delta) \approx \frac{1}{N}\sum_{j=0}^{N-1} g\left(r,\alpha,\Delta,\frac{j+0.5}{N}\pi\right), \qquad (10)$$

where the definition of the function $g(r,\alpha,\Delta,\varphi')$ is given by eqs. (1), (3) and (4).

However, when the degree of preferred orientation is strong ($1 << r$), the integrand in eq. (2) behaves almost singularly for the variable φ' in the case:

$$\cos\alpha\cos\Delta - \sin\alpha\sin\Delta\sin\varphi' \approx 0,$$

and accurate evaluation of the preferred orientation factor by numerical integral will become difficult with an ordinary computing system.

In order to avoid the above quasi-singularity, the author proposes an alternative formula of numerical integral given by the following equations,

$$f_{d^*}(r,\alpha,\Delta) \approx \frac{r^{3/2}}{\pi}(\xi_1-\xi_0)\sum_{j=0}^{N-1} w_j h(\xi_j), \qquad (11)$$

$$h(\xi) = \frac{1}{\sqrt{\sin^2\alpha\sin^2\Delta - \left[\cos\alpha\cos\Delta + \dfrac{\xi}{\sqrt{1-(r^3-1)\xi^2}}\right]^2}}, \qquad (12)$$

$$w_j = \frac{\pi}{2N}\sin\frac{(j+0.5)\pi}{N}, \qquad (13)$$

$$\xi_j = \frac{\xi_1+\xi_0}{2} + \frac{\xi_1-\xi_0}{2}\cos\frac{(j+0.5)\pi}{N}, \qquad (14)$$

$$\xi_0 = -\frac{\cos(\alpha-\Delta)}{\sqrt{1+(r^3-1)\cos^2(\alpha-\Delta)}}, \qquad (15)$$

$$\xi_1 = -\frac{\cos(\alpha+\Delta)}{\sqrt{1+(r^3-1)\cos^2(\alpha+\Delta)}}. \qquad (16)$$

The above formula corresponds to the application of the Chebyshev quadrature to the integral formula modified by variable transformation (Appendix B).

Tables 1 – 3 compare the values obtained by finite-term numerical integrals applying the two different formulas, the formula (I) given by eq. (10) and the formula (II) given by eqs. (11)–(16).

As shown in Tables 1 and 2, the formula (II) converges to the correct value by increasing the number of sampling points (N) more rapidly than the formula (I), particularly in the cases $1 << r$. They also confirm the validity of the analytical formula given by eq. (7) derived for the capillary transmission mode. Furthermore, numerical instability of the formula (I) for the nearly symmetric reflection case ($\Delta \approx 0$), as seen in Table 3, seems to be reduced by application of the formula (II). It is expected that the formula (II) is always more efficient and stable than the formula (I). The formula (II) becomes singular just in the case of

Table 1. Numerical values of preferred orientation factors for $\Delta = 90°$, $\alpha = 30°$, and $r = 0.5$ and 2, calculated by finite-term numerical integrals ($N = 1, 2, 4, 8, 16$) based on the formulas (I) and (II). The exact solutions calculated by eq. (7) are 0.42668 and 1.38810 for $r = 0.5$ and 2, respectively.

Formula	(I)	(II)	(I)	(II)
r	0.5	0.5	2	2
$N = 1$	0.51200	0.40000	0.62022	1.70561
$N = 2$	0.42064	0.42708	1.10165	1.40836
$N = 4$	0.42665	0.42668	1.36347	1.38850
$N = 8$	0.42668	0.42668	1.38798	1.38810
$N = 16$	0.42668	0.42668	1.38810	1.38810

Table 2. Numerical values of preferred orientation factors for $\Delta = 90°$, $\alpha = 30°$, and $r = 0.25$ and 4, calculated by the formulas (I) and (II). The exact solutions calculated by eq. (7) are 0.15508 and 1.33115 for $r = 0.25$ and 4, respectively.

Formula	(I)	(II)	(I)	(II)
r	0.25	0.25	4	4
$N = 1$	0.19096	0.14396	0.11670	1.95471
$N = 2$	0.15221	0.15527	0.30258	1.42285
$N = 4$	0.15506	0.15508	0.73815	1.34181
$N = 8$	0.15508	0.15508	1.20927	1.33164
$N = 16$	0.15508	0.15508	1.32802	1.33116

exactly symmetric reflection, $\Delta = 0$, but it can easily be treated by eq. (5) as an exceptional case in a practical computer application.

Figure 2 shows the dependence of the preferred orientation factor (POF) on the diffraction angle 2θ, expected for the asymmetric reflection mode with the fixed incident glancing angle of Ω. Note that the POF have maximum or minimum at the diffraction angle 2θ of just twice the incident glancing angle Ω, $2\theta = 2\Omega$, while the POF is expected to be constant and independent of the measured diffraction angle 2θ in the symmetric reflection mode. It is likely that the misuse of the symmetric formula will cause systematic errors on evaluation of atomic displacement parameters.

3. Discussion

The author would like to emphasize that this article is not intended to insist that the March-Dollase model should always be used as the model for preferred orientation. The validity of a preferred orientation model should be examined by well-controlled experiments. The author has already found such experimental data that cannot be well modeled by the March-Dollase pole density profile, and the study on extension or modification of the March-Dollase preferred orientation model is currently in progress.

Table 3. Numerical values of preferred orientation factors for $\Delta = 0.01°$, $\alpha = 30°$, and $r = 0.5$ and 2, calculated by the formulas (I) and (II). The solutions for $\Delta = 0°$ and $\alpha = 30°$ calculated by eq. (5) are 1.75425 and 0.18102 for $r = 0.5$ and 2, respectively.

Formula	(I)	(II)	(I)	(II)
r	0.5	0.5	2	2
$N = 1$	1.75324	1.75426	0.18107	0.18102
$N = 2$	1.75353	1.75426	0.18105	0.18102
$N = 4$	1.75359	1.75426	0.18105	0.18102
$N = 8$	1.75360	1.75426	0.18105	0.18102

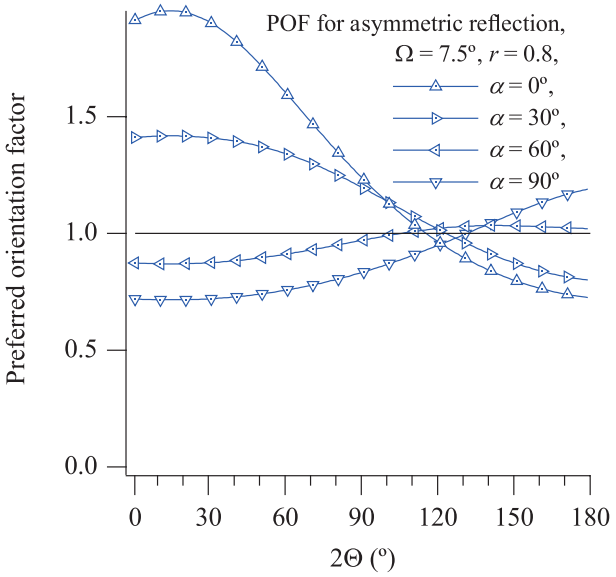

Fig. 2. An example of preferred orientation factors for an asymmetric reflection mode measurement.

4. Conclusion

An analytical expression of the preferred orientation factor for the capillary transmission mode and an efficient numerical algorithm to evaluate the preferred orientation factor for the asymmetric reflection mode in powder diffraction measurements have been derived. It is shown that the formulas of the preferred orientation factors for the capillary transmission and asymmetric reflection modes are definitely different from that for the conventional symmetric reflection mode. It is recommended to Rietveld programmers to implement the correct formulas for preferred orientation factor, applicable to the data collected with synchrotron powder diffraction measurements.

Appendix A. Computational method for elliptic integral

The Legendre complete elliptic integral of the second kind is calculated by

$$\mathrm{E}(k)=\mathrm{R}_{\mathrm{F}}\left(0,1-k^2,1\right)-\frac{k^2}{3}\mathrm{R}_{\mathrm{D}}\left(0,1-k^2,1,1\right), \qquad \text{(A1)}$$

where the functions $\mathrm{R_F}(x,y,z)$ and $\mathrm{R_J}(x,y,z,p)$ are the Carlson's elliptic integral of the first and second kinds, respectively, defined by

$$\mathrm{R}_{\mathrm{F}}(x,y,z)\equiv\frac{1}{2}\int_0^\infty\frac{\mathrm{d}t}{\sqrt{(t+x)(t+y)(t+z)}}, \qquad \text{(A2)}$$

$$\mathrm{R}_{\mathrm{J}}(x,y,z,p)\equiv\frac{3}{2}\int_0^\infty\frac{\mathrm{d}t}{(t+p)\sqrt{(t+x)(t+y)(t+z)}}. \qquad \text{(A3)}$$

An efficient algorithm for evaluation of the Carlson's elliptic integral is known [4].

Appendix B. Transformation of variable in numerical integral

As shown in sec. 2.1, the general formula of the preferred orientation factor is given by the following equations,

$$f_{d^*}(r,\alpha,\Delta)=\frac{1}{\pi}\int_{-\pi/2}^{\pi/2}g(r,\alpha,\Delta,\varphi')\,\mathrm{d}\varphi', \qquad \text{(B1)}$$

$$g(r,\alpha,\Delta,\varphi')=\left[\frac{1}{r}+\left(r^2-\frac{1}{r}\right)\cos^2\rho\right]^{-3/2}, \qquad \text{(B2)}$$

$$\cos\rho=\cos\alpha\cos\Delta-\sin\alpha\sin\Delta\sin\varphi'. \qquad \text{(B3)}$$

It is suggested by the relation :

$$\frac{\mathrm{d}}{\mathrm{d}x}\left[\frac{x}{\sqrt{a^2+x^2}}\right]=a^2\left(a^2+x^2\right)^{-3/2}, \qquad \text{(B4)}$$

that the quasi-singularity of the integrand $g(r,\alpha,\Delta,\varphi')$ in eq. (B1) at

$$\varphi'\approx\arcsin(\cot\alpha\cot\Delta), \qquad \text{(B5)}$$

can be removed by the transformation :

$$\xi=\frac{\sin\alpha\sin\Delta\sin\varphi'-\cos\alpha\cos\Delta}{\sqrt{1+\left(r^3-1\right)\left(\sin\alpha\sin\Delta\sin\varphi'-\cos\alpha\cos\Delta\right)^2}}, \qquad \text{(B6)}$$

which is equivalent to

$$\sin\varphi'=\frac{\cos\alpha\cos\Delta+\xi/\sqrt{1-\left(r^3-1\right)\xi^2}}{\sin\alpha\sin\Delta}. \qquad \text{(B7)}$$

This transformation leads the following relations,

$$\begin{array}{ccccc}\varphi' & : & -\pi/2 & \rightarrow & \pi/2\\ \xi & : & \xi_0 & \rightarrow & \xi_1\end{array}$$

$$\xi_0=-\frac{\cos(\alpha-\Delta)}{\sqrt{1+\left(r^3-1\right)\cos^2(\alpha-\Delta)}}, \qquad \text{(B8)}$$

$$\xi_1=-\frac{\cos(\alpha+\Delta)}{\sqrt{1+\left(r^3-1\right)\cos^2(\alpha+\Delta)}}. \qquad \text{(B9)}$$

However, the above transformation from φ' to ξ introduces other singularities at the edge points, $\xi=\xi_0$ and $\xi=\xi_1$.

It is found that another transformation from ξ to φ'' given by

$$\xi=\frac{\xi_1+\xi_0}{2}-\frac{\xi_1-\xi_0}{2}\cos\varphi'', \qquad \text{(B10)}$$

$$\begin{array}{ccccc}\xi & : & \xi_0 & \rightarrow & \xi_1\\ \varphi'' & : & 0 & \rightarrow & \pi\end{array},$$

can remove the singularities at the edge points, keeping the smooth behavior of the integrand almost unchanged. The second transformation of the variable given by eq. (B10) is equivalent to the method known as the Gauss-Chebyshev quadrature [4].

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