profile data are sufficiently accurate and complete along the tail regions, this approach is preferred because additional information about the column-height distribution is obtained. This, of course, is made possible by the introduction of the variation coefficient and is illustrated by the following experimental example.

The line profiles from the 200 and 400 reflections were obtained from the wear debris of a partially stabilized zirconia sample. These profiles were used to determine the average column height, variation coefficient of the column-height distribution and the amount of microstrain present in the sample. The instrumental parameters, a_γ and a_β, were determined by least-squares fitting the line shape of the 110 and 211 reflections from an Mo powder standard to the Voigt function. A high-resolution diffractometer with a quartz monochromator was used to obtain the line shape experimentally. This effectively eliminated the $K\alpha_2$ component of the Cu $K\alpha$ doublet. A least-squares fit using (14) for the line broadening of the 200 and 400 reflections indicated that the average column length is 86 Å, the variation coefficient of the column-height distribution is 0·51 and the non-uniform r.m.s. strain component, $\langle \varepsilon_{1D}^2 \rangle^{1/2}$, which can be attributed to dislocations, is equal to 0·022 (see Fig. 1). The non-uniform strain component, $\langle \varepsilon_{1U}^2 \rangle^{1/2}$, was found to be insignificant or zero. The magnitude of the strain component, $\langle \varepsilon_{1D}^2 \rangle^{1/2}$, is surprisingly close to that found in cold-worked metals and metal films, indicating a high density of dislocations in partially stabilized zirconia wear debris. If it is assumed that the geometrical arrangement of dislocations is statistically spherical, a variation coefficient of 0·51 indicates that the dislocations that define the subgrains are not uniform in size. A least-squares fit of the experimental line shape with the single-sphere model (9) showed significant misfit in the first-order reflection, which is most influenced by subgrain size. Therefore, we must conclude that a distribution of spherical subgrains is in best agreement with the data. Also, it must be further concluded that the more complete analysis using (12) and (14) provides a more accurate analysis of subgrain size and strain. It was found that the particle size obtained using the single-sphere model is 12% larger while $\langle \varepsilon_{1D}^2 \rangle^{1/2}$ is 5% larger than the results obtained using the more complete analysis that includes the variation coefficient. For some applications these differences may not be important; however, information on subgrain-size distribution is lost.

The funding for the theoretical development of this paper was made available by National Science Foundation Grant No. DMR-8000933. Funding for the data collection of the partially stabilized wear debris as well as the sample preparation was derived from a DOE Energy Conversion and Utilization Technologies (ECUT) Program or subcontract 19B07733C.

The authors would like to thank Mary Colby for collecting the X-ray data.

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Acta Cryst. (1986). A42, 19–23

An Analytical Function for Absorption Correction

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(*Received* 1 *April* 1985; *accepted* 15 *May* 1985)

Abstract

A new analytical function is proposed for absorption correction. It is expressed by surface harmonics with polar angles that specify the primary and secondary beam directions. This function has an advantage over Fourier expansion because it is rotationally invariant. Two empirical methods are used to determine the expansion coefficients. One uses the intensity deviations of equivalent reflections, and the other uses the calculated intensities at the stage of structure refinement. The utility of the analytical function is demonstrated with a model and with actual data.

0108-7673/86/010019-05$01.50

1. Introduction

A proper treatment of the absorption effect, which largely influences the intensities of the diffraction beams, is of great importance in an accurate structure analysis. The absorption correction has usually been calculated by computer programs based on the Gaussian integration method (Busing & Levy, 1957). However, these procedures need the precise measurement of the crystal dimensions, which is not always easy when the crystal shape is complicated. It may be much more difficult when some additional absorber is attached to the crystal.

In order to overcome such difficulties, empirical methods have been developed by Furnas (1957), Kopfmann & Huber (1968), Huber & Kopfmann (1969), North, Phillips & Mathews (1968) and Flack (1974). Kopfmann & Huber (1968) made the first attempt to apply the functional analysis to the problem of absorption correction. These methods need the intensity measurements from azimuthal scanning with three- or four-circle diffractometers.

We proposed a convenient method (Katayama, Sakabe & Sakabe, 1972*a*), where the function of absorption correction, expressed by a Fourier series, is evaluated using the intensity deviations of the equivalent reflections. An alternative method (Katayama, Sakabe & Sakabe, 1972*b*) for the evaluation of the Fourier coefficients was also proposed using the calculated intensities at the stage of structure refinement. Walker & Stuart (1983) extended the latter method successfully for practical use. However, two-dimensional Fourier expansion with the polar angles is not proper mathematically because the function is not rotationally invariant, and causes errors in correction factors of the reflections at higher Bragg angles.

In this paper a new analytical function is proposed, which employs surface harmonics, and the results of its test with a model and with actual data are reported.

2. Analytical function

The absorption correction factor A is defined as

$$I_h = A(\mathbf{h})I_h^0, \qquad (1)$$

where I_h and I_h^0 are the corrected and the observed intensities of the reflection **h**, respectively. The factor A varies with the directions of the primary beam **p** and the secondary beam **s** if the crystal has an arbitrary shape. The absorption correction has been described as a product of two terms,

$$\begin{aligned} A(\mathbf{h}) &\simeq A^0(\theta_h)A^*(\mathbf{p}_h, \mathbf{s}_h) \\ &\simeq A^0(\theta_h)(A'(\bar{\mathbf{p}}_h) + A'(\mathbf{s}_h)), \qquad (2) \end{aligned}$$

where A^0 is the spherical part depending only on the Bragg angle θ_h and A^* is the part depending on the directions of the primary and secondary beams. The latter part is expressed by the sum of the contributions for the two directions, $A'(\bar{\mathbf{p}}_h)$ and $A'(\mathbf{s}_h)$. Empirically, this formulation has been used successfully for many applications (North, Phillips & Mathews, 1968; Katayama, Sakabe & Sakabe, 1972*a*, *b*, Walker & Stuart, 1983).

Instead of a Fourier series (Katayama, Sakabe & Sakabe, 1972*a*), we propose the following function for A^*:

$$\begin{aligned} A^*(\mathbf{p}, \mathbf{s}) = \sum_{n=0} \sum_{m=0}^{n} (&C_{nm}P_n^m(\sin \nu_{\bar{p}}) \cos m\varphi_{\bar{p}} \\ &+ S_{nm}P_n^m(\sin \nu_{\bar{p}}) \sin m\varphi_{\bar{p}} \\ &+ C_{nm}P_n^m(\sin \nu_s) \cos m\varphi_s \\ &+ S_{nm}P_n^m(\sin \nu_s) \sin m\varphi_s), \qquad (3) \end{aligned}$$

where P_n^m is the associated Legendre function, $\nu_{\bar{p}}$, $\varphi_{\bar{p}}$, ν_s and φ_s are the polar angles referring to the directions $\bar{\mathbf{p}}$ and **s** as shown in Fig. 1, and C_{nm} and S_{nm} are the expansion coefficients to be determined by either of the two methods mentioned below. The series will converge rapidly, since the absorption varies smoothly in these directions. This formula satisfies the physical requirement that the absorption does not change when the X-ray travels the reverse path.

The morphological symmetry of the crystal reduces the number of expansion terms; for example, $C_{nm} = S_{nm} = 0$ when $n + m = \text{odd}$ if there is a mirror perpendicular to the φ axis. Also $C_{nm} = S_{nm} = 0$ when $m = \text{odd}$ if there is a twofold symmetry parallel to the φ axis. Similarly, $C_{nm} = S_{nm} = 0$ when $n = \text{odd}$ if there is a center of symmetry. S_{n0} are always zero, and $S_{nm} = 0$ if there is a mirror parallel to the φ axis at $\varphi = 0°$.

When the above-mentioned conditions are expected, a transformation of the coordinate may be required to represent the morphological symmetry.

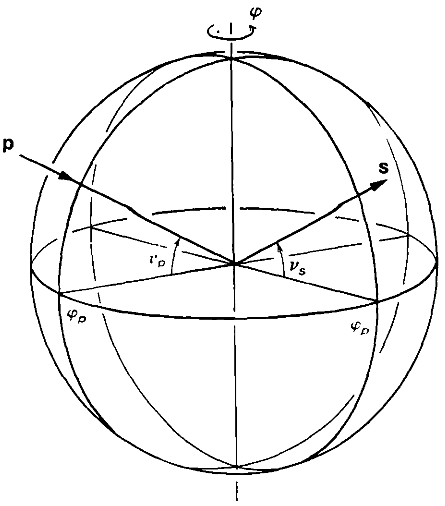

Fig. 1. Definition of the angles φ_p, ν_p, φ_s and ν_s.

The reduction of the expansion terms is more advantageous than keeping the angular symmetry of the primary and secondary beam directions.

The systematic lack of data, such as the diffraction data measured by Mo radiation within the limited 2θ angle, leads to correlations among the expansion terms since the orthogonality among the terms is not kept within the limited variable range. Therefore, when 2θ maximum is 60°, the terms, $C_{n,n}$, $C_{n+1,n}$, $C_{n+6,n}$, $C_{n+7,n}$, and the corresponding S_{nm} terms should be selected as the independent terms. If the diffraction data is collected in a hemisphere, a mirror symmetry or a center of symmetry should be assumed in order to extend the variable range of the function.

$A^0(\theta)$ is the correction factor corresponding to the effect that the mean path length decreases monotonically as the Bragg angle increases. This factor has a close resemblance with the isotropic thermal factor as is revealed by plotting both values. Therefore the factor is estimated simply from the lists of spherical absorption factors given in *International Tables for X-ray Crystallography* (1972) for a sphere whose volume is equal to that of the crystal.

Thus the absorption correction factor $A(\mathbf{h})$ could be expressed as a linear function of the expansion coefficients.

3. Determination of the expansion coefficients

The expansion coefficients are determined by a least-squares method, in which the squares of the differences between the corrected and true intensities are minimized. Since the true intensity is unknown, however, it can be approximated by the following two methods.

3.1. *Method* I

The averaged value of the corrected intensities over the equivalent reflections is assumed as the true intensity. Then the expansion coefficients are determined by minimizing the formula

$$\begin{aligned} R_1 &= \sum_h \sum_{i=1}^{N} \omega_{hi} \left\{ A(\mathbf{h}i) I_{hi}^0 - (1/N) \sum_{j=1}^{N} A(\mathbf{h}j) I_{hj}^0 \right\}^2 \\ &= \sum_h \sum_{i=1}^{N} \omega_{hi} \left\{ \sum_{j=1}^{N} A^*(\mathbf{p}_{hj}, \mathbf{s}_{hj}) J_{hj} \right\}^2, \end{aligned} \tag{4}$$

where

$$J_{hj} = \begin{cases} [(N-1)/N] A^0(\theta_{hj}) I_{hj}^0 & \text{when } j = i \\ -(1/N) A^0(\theta_{hj}) I_{hj}^0 & \text{when } j \neq i \end{cases}$$

and N is the total number of equivalent reflections. This formula is obtained from (2) in the previous paper (Katayama, Sakabe & Sakabe, 1972*a*) by considering the same weight for the equivalent reflections when they are measured under the same conditions. The function A^* defined by (3) is represented for brevity as

$$A^*(\mathbf{p}_h, \mathbf{s}_h) = \sum_q B_q T_q(\bar{\mathbf{p}}_h, \mathbf{s}_h), \tag{5}$$

where B_q is the qth expansion coefficient and $T_q(\bar{\mathbf{p}}_h, \mathbf{s}_h)$ is the corresponding expansion component. Then (4) becomes

$$R_1 = \sum_h \sum_{i=1}^{N} \omega_{hi} \left\{ \sum_q B_q \left[\sum_{j=1}^{N} T_q(\bar{\mathbf{p}}_{hj}, \mathbf{s}_{hj}) J_{hj} \right] \right\}^2. \tag{6}$$

The values in the brackets in (6) are all known. The normal equations can be solved as simultaneous equations by giving $C_{00} = 1$.

3.2. *Method* II

When a structure analysis is carried out without a correction for absorption, the omission will cause a systematic error in the structure factors, which is related to the directions $\mathbf{p}_h$ and $\mathbf{s}_h$. Therefore the function A^* can also be determined by minimizing the formula

$$\begin{aligned} R_2 &= \sum_h \omega_h (A(\mathbf{h}) I_h^0 - I_h^c\}^2 \\ &= \sum_h \omega_h \left\{ \sum_q B_q T_q(\bar{\mathbf{p}}_h, \mathbf{s}_h) J_h^0 - I_h^c \right\}^2, \end{aligned} \tag{7}$$

where I_h^c is the intensity calculated at the stage of structure refinement and $J_h^0 = A^0(\theta_h) I_h^0$. The expansion coefficients are determined by solving the normal equations and are used to correct the observed intensities. However, the calculated intensities may vary with further structure refinements after this correction, then this process must be repeated so as to give a self-consistent result.

4. Test calculation

The availability of the analytical function was tested by the following procedure in order to avoid complications due to experimental errors in measurement. The intensities, I_h^0's, are given as the products of the assumed intensities and the computed transmission factors of the model crystal. The intensities, thus prepared, are corrected by method I or II, and compared with the assumed intensities. The bisecting setting was employed for these test, since this setting has been used most frequently.

The transmission factors were calculated by the Gaussian integration of 6×6×6 points using a modification of the *INCOR* program in *UNICS* (1967). The shapes of four model crystals are shown in Fig. 2, and other assumptions are listed in Table 1. All the crystals have non-centrosymmetric shapes. Model *A* is a wedge-shaped crystal, *B* is a pyramidal one, *C* and *D* are rhombic crystals with the external absorber illustrated by shadowing in Fig. 2. The

Table 1. *Assumptions for the model crystals*

Model	*A*	*B*	*C*	*D*
Absorption coefficient (cm^{-1})	24	24	24	48
Laue symmetry	*mmm*	*mmm*	$\bar{3}$	$\bar{3}$
Directions of symmetry axes (φ, ν)(°, °)	(0, 35) (60, −35) (−60, −35)	(0, 73) (46, −12) (−46, −12)	(22, 13)	(22, 13)
Total number of reflections	1195×8	1195×8	1934×6	1934×6

Table 2. *Average errors (%) of the intensities corrected by using the* 64 *terms, which were determined with* 720 *reflections by method* I *or* II

Model	*A*	*B*	*C*	*D*
Method I	1·65	3·73	1·05	2·95
Method II	1·35	1·03	0·96	2·60

Table 3. *Coefficients C_{nm} (upper lines) and S_{nm} (lower lines) determined by method* II *for model D* (×1000)

n	*m* = 0	*m* = 1	*m* = 2	*m* = 3	*m* = 4	*m* = 5	*m* = 6	*m* = 7
0	1000							
1	51	−183						
		16						
2	298	−91	−103					
		50	65					
3	1	−49	1	4				
		18	0	−3				
4	59	−33	−8	1	0			
		13	5	−2	−1			
5	−26	−12	2	0	0	0		
		8	−1	0	0	0		
6	−17	−9	−1	0	0	0	0	
		4	1	0	0	0	0	
7	−17	−3	0	0	0	0	0	0
		3	0	0	0	0	0	0

absorption coefficient of the absorber is assumed to be the same as that of the crystal.

The accuracy of the correction is dependent on the number of the expansion terms and on the number of reflections used for the determination of the coefficients. Table 2 shows the result of the test calculation, in which 64 terms, namely $n = 0$-7, were employed. The 64 coefficients were determined with 720 reflections, which were randomly chosen from the lower-angle reflections. Table 3 shows the coefficients determined by method II for model *D*. Continuous lines in Fig. 3 are the contour plots of the transmission calculated with those coefficients over the reciprocal levels $\nu = -30$, 0 and 30°. The dotted lines are the plots of transmission obtained from a previous computation by Gaussian integration.

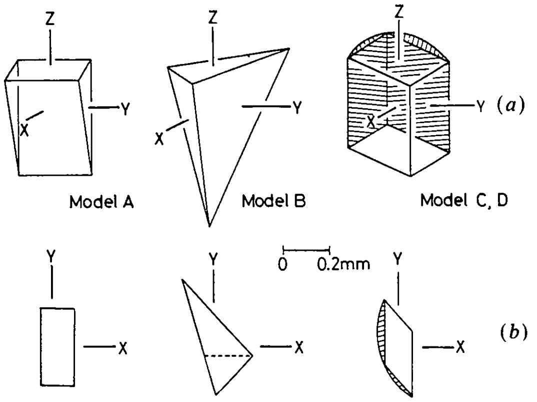

Fig. 2. (*a*) Composite clinographic projection of the model crystals. (*b*) View from the *z* direction. Shaded part shows the external absorber. Total volume of absorber is 0·012 mm^3 for each model. The *z* direction is parallel to the φ axis.

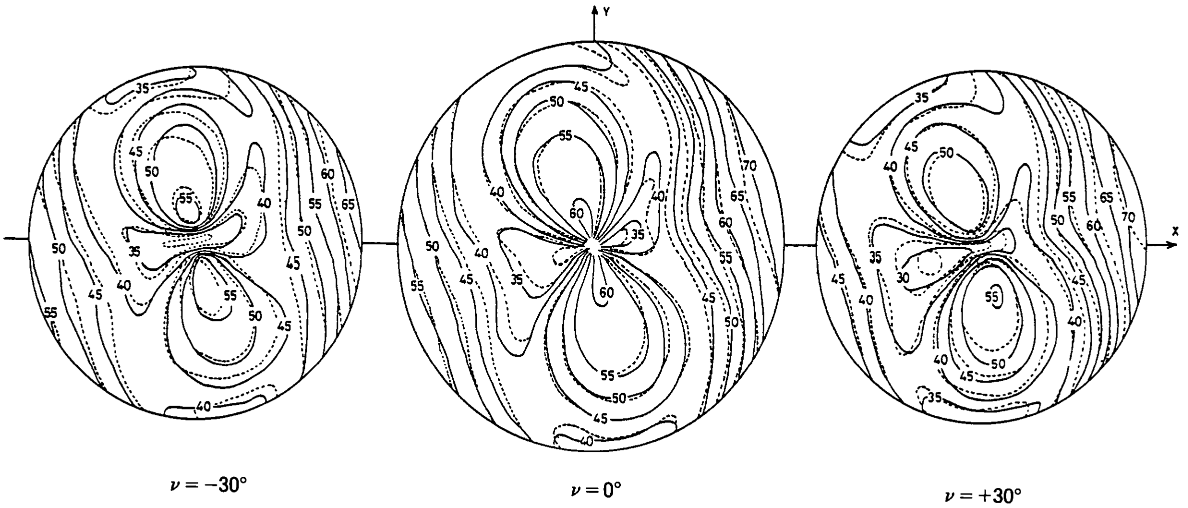

Fig. 3. Contour plots of transmission over the reciprocal levels $\nu = -30$, 0 and 30° for model *D*. Dotted lines are the plots of transmission of the model crystal. Continuous lines are those determined by method II and converted to the absolute scale. The numbers on the lines indicate the values of transmission in per cent.

Table 4. *Results of correction by the CRYSTAN program system*

Compound	Dimensions (mm)	μ (cm^{-1})	*R* factor (%) Before	*R* factor (%) After
$C_{22}H_{24}Se_8ReO_4$	0·2×0·05×0·4	205·6	12·8	5·52
$C_{21}H_{19}N_2O_2Cl_2I_3$	0·4×0·4×0·4	301·6	6·27	5·42
$C_{28}H_{16}S_8Cu_2Cl_6$	0·35×0·05×0·6	209·5	23·3	5·22
$C_{28}H_{16}S_8Cu_2Br_6$	0·13×0·05×0·02	138·7	6·61	4·31
$C_{20}H_{12}N_6S_4$	0·18×0·03×0·38	41·2	8·11	6·28
$C_{10}H_{12}S_8$	0·15×0·15×0·75	95·9	6·12	5·25
$C_{20}H_{12}N_6S_8$	0·09×0·02×1·1	64·9	6·85	5·87
$C_{20}H_{24}Te_8PF_6$	0·08×0·01×0·6	557·4	20·0	14·5

5. Discussion

In the previous paper (Katayama, Sakabe & Sakabe, 1972*a*) the average error, defined by

$$R = \sum |I_{\text{assum}} - I_{\text{corr}}| / \sum I_{\text{assum}}, \qquad (8)$$

was 1·4% by method I with 188×6 reflections for model *C*. In the present calculation the average error is improved to 1·05% with 120×6 reflections. This result is due to the improvement of the functional form. The correction for model *D*, in which the absorption is strong ($\mu = 48\ \text{cm}^{-1}$), can be performed with an accuracy of about 3% by method I or II.

The coefficients in Table 3 are determined by method II for model *D*, and these results indicate that the expansion is almost convergent by using finite series ($n = 0$–7). The contour plots, in Fig. 3, of the transmission calculated with these coefficients show an excellent agreement with those of model *D*.

In model *B*, with Laue symmetry *mmm*, a two-fold axis tilts only 17° from the φ axis, so that the beam directions of the equivalent reflections distribute in a narrow ν range. The application of method I to such a case is difficult, because the solution of (6) is not well defined concerning the ν dependence of the function. Therefore it is important to give particular attention to crystal mounting so that the ν values of the equivalent reflections are widely separated.

The applicability of method I is rather limited when the number of equivalent reflections is small. Therefore it is recommended to include Friedel pairs among the equivalent reflections even when anomalous effects are observed. The contributions of these effects will be non-systematic in (6), since these are independent of the beam directions.

On the other hand, method II is independent of the number of equivalent reflections. The calculated structure amplitude is a function of the atomic coordinates and thermal parameters. Such parameters, however, are not influenced by the absorption effect in the procedure of the structure refinement, since the functional forms are quite different from that of the absorption effect as illustrated in Fig. 3. Only the isotropic thermal factor may behave similarly to the absorption factor for a sphere, $A^0(\theta)$, in (2). Therefore the absorption effect may remain as a systematic error in the observed structure amplitudes, which are correlated with the directions of the primary and secondary beams.

In the program system *CRYSTAN* (Katayama & Honda, 1985), the transmission factor is expanded by surface harmonics in the same way as (2) and (3), and the expansion coefficients are determined at the stage of the atomic parameter refinement by minimizing R_3:

$$R_3 = \sum_{h} \{F^2_{\text{obs}} - T(\mathbf{h}) F^2_{\text{cal}}\}^2, \qquad (9)$$

where F_{obs} and F_{cal} are the observed and calculated structure amplitudes and $T(\mathbf{h})$ is the transmission factor. As a routine procedure, only ten terms up to $n = 6$ are employed by assuming the sample crystal has symmetry *mmm*. The results of several applications are shown in Table 4.

In practice a flat crystal is a serious problem for the absorption effect and the systematic error in the structure factors is very obvious. The results show that the applicability is satisfactory even for such a crystal with only ten terms by assuming the morphological symmetry *mmm*.

The author thanks Professor Jiro Tanaka for helpful discussions, Drs Noriyoshi Sakabe and Kiwako Sakabe for their valuable suggestions, and Miss Masako Honda for her kind assistance. All computation was done on the FACOM 382 computer at the computation center of Nagoya University. This work was supported by the grant in aids of special research project on properties of molecular assemblies (No. 59112003) from the Ministry of Education, Science and Culture, Japan.

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