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Acta Cryst. (1980). **A36**, 442–450

Absorption Correction for Weissenberg Diffractometers

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(Received 28 August 1979; accepted 19 December 1979)

Abstract

Formulas are derived extending several semi-empirical absorption-correction methods to diffractometers operating in Weissenberg geometries, with particular attention paid to flat-cone geometry. These formulas are useful for a variety of instruments using both area and linear position-sensitive detectors. While a complete data set can sometimes be corrected using a single absorption reflection, it was found that the best corrections are usually obtained by considering two absorption reflections rather than one. A discussion of the optimum choice of absorption correction when a crystal has at least a twofold symmetry axis is presented. The accuracy of the methods and the limits of applicability have been examined by computer simulations.

Introduction

Intensities observed in X-ray and neutron single-crystal diffraction experiments will be, in most cases, significantly modified by absorption. For a typical protein crystal of size $1 \times 0.5 \times 0.5$ mm and $\mu = 1.0$ mm⁻¹, transmission of X-rays varies between 69 and 48%.

The same range of transmission is observed with neutrons in a crystal which has $\mu = 0.25$ mm⁻¹ and is four times as large in each dimension. The methods for evaluation of the absorption correction that are based on accurate measurements of external dimensions of the crystals (Busing & Levy, 1957; Coppens, Leiserowitz & Rabinovich, 1965; de Meulenaer & Tompa, 1965; Wells, 1960; Santoro, 1969) are seldom applicable to crystals of proteins and other macromolecules, owing to the usually complex shape of the sample and mounting. While semi-empirical corrections have been used successfully in macromolecular crystallography, their application has been described so far only for the geometries of three- and four-circle diffractometers, linear diffractometers (Arndt & Phillips, 1961) and five-circle diffractometers (Banner, Evans, Marsh & Phillips, 1977). Recently, considerable gains in the speed of data collection have been achieved by the use of area detectors (Xuong, Freer, Hamlin, Nielsen & Vernon, 1978) and linear detectors (Cain, Norvell & Schoenborn, 1975; Prince, Wlodawer & Santoro, 1978). Since these diffractometers measure the reflections with one of the Weissenberg geometries, such as normal-beam or flat-cone (Buerger, 1942), it seems desirable to

generalize and extend the existing semi-empirical absorption-correction methods to these cases.

The immediate aim of our work was to provide formulas and procedures for the absorption-correction measurement for a flat-cone diffractometer equipped with a linear position-sensitive detector (Prince, Wlodawer & Santoro, 1978). The formulas derived below are, however, completely general and should be equally applicable to diffractometers equipped with linear or area detectors and operating with the normal-beam geometry (Cain, Norvell & Schoenborn, 1975; Xuong *et al.*, 1978) or indeed with any arbitrary Weissenberg configuration.

Summary of existing methods

Let us consider a reciprocal-lattice point

$$\mathbf{h} = \begin{pmatrix} h \\ k \\ l \end{pmatrix}. \quad (1)$$

The Bragg condition for \mathbf{h} can be satisfied by orienting the crystal with respect to the primary beam in an infinite number of ways. The rotations required to achieve any of these orientations depend on several factors (lattice parameters and initial crystal orientation, technique being used, azimuth of the reflecting planes at which the measurement is to be made, *etc.*), but they can always be expressed in terms of the three Eulerian angles ω , χ , ϕ . The observed intensity of \mathbf{h} , because of absorption, is related to its true intensity $I_0(\mathbf{h})$ by the equation

$$I_{\text{obs}}(\mathbf{h}, \omega, \chi, \phi) = T(\mathbf{h}, \omega, \chi, \phi) I_0(\mathbf{h}), \quad (2)$$

where $T(\mathbf{h}, \omega, \chi, \phi)$ is the transmission factor. It has been shown (Flack, 1974) that $T(\mathbf{h}, \omega, \chi, \phi)$ can be split into two factors according to the expression

$$T(\mathbf{h}, \omega, \chi, \phi) = T'(\mathbf{h}, \omega, \chi, \phi) \langle T(\mathbf{h}, \omega, \chi, \phi) \rangle_{2\theta}, \quad (3)$$

where

$$\langle T(\mathbf{h}, \omega, \chi, \phi) \rangle_{2\theta} = \frac{1}{8\pi^3} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} T(\mathbf{h}, \omega, \chi, \phi) d\omega d\chi d\phi \quad (4)$$

and where the subscript 2θ indicates that $\langle T(\mathbf{h}, \omega, \chi, \phi) \rangle$ is a function of 2θ only. It has also been shown (Flack, 1974) that the factor T' is shape dependent.

The approximation most commonly adopted for the 2θ -dependent factor is the spherical correction; *i.e.* it is assumed that the variation of $\langle T \rangle$ with 2θ , for any given linear absorption coefficient μ , is the same as that of a sphere whose radius is related in some way to the volume or to the linear dimensions of the crystal under study. We may write then

$$\langle T(\mathbf{h}, \omega, \chi, \phi) \rangle_{2\theta} = S(\mu r, 2\theta) \quad (5)$$

and, since S is known and tabulated (*International Tables for X-ray Crystallography*, 1959), the outstanding problem is the determination of $T'(\mathbf{h}, \omega, \chi, \phi)$. This quantity may be evaluated empirically from the intensities of several standard reflections \mathbf{k} , each measured at regular intervals of the angle Ψ of the rotation about the corresponding scattering vector. For simplicity in this paper, we will call *absorption reflections* the reflections \mathbf{k} selected for the correction; *absorption curve* the curve describing the variation of intensity of \mathbf{k} as a function of Ψ ; and *absorption plane* the plane perpendicular to the central reciprocal row on which \mathbf{k} is located.

The procedures proposed so far for the empirical evaluation of T' can be summarized as follows.

(A) Method of North, Phillips & Mathews (1968)

In this method (designated NPM), T' is approximated by the expression

$$T'(\mathbf{h}, \omega, \chi, \phi) \simeq \frac{I_1(\mathbf{k}) + I_2(\mathbf{k})}{2I_{\text{max}}(\mathbf{k})} C, \quad (6)$$

where $I_{\text{max}}(\mathbf{k})$ is the maximum intensity observed on the absorption curve of \mathbf{k} . $I_1(\mathbf{k}) [\equiv I(\mathbf{k}, \omega_1, \chi_1, \phi_1)]$ and $I_2(\mathbf{k}) [\equiv I(\mathbf{k}, \omega_2, \chi_2, \phi_2)]$ are the intensities of \mathbf{k} measured for those orientations of the crystal for which the mean directions* of \mathbf{k} are coincident with the projections† of the incident and diffracted beams of the reflection \mathbf{h} , respectively (Fig. 1). In the Weissenberg methods, and

* We designate as mean direction of a reflection the resultant of the unit vectors along incident and diffracted beams.

† Unless otherwise indicated, as projection of a vector we indicate the projection of the vector on the absorption plane.

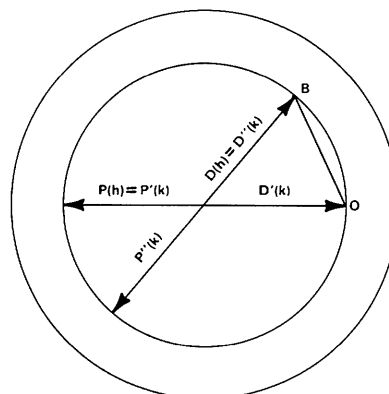


Fig. 1. Method of NPM for the equi-inclination geometry. The rotation axis of the crystal is perpendicular to the plane of the figure at O . $P(\mathbf{h})$ and $D(\mathbf{h})$ are the primary and diffracted beams of the reflection \mathbf{h} under study, corresponding to the reciprocal node B . $P'(\mathbf{k})$ and $D'(\mathbf{k})$ and $P''(\mathbf{k})$ and $D''(\mathbf{k})$ are the projections on the absorption plane of the primary and diffracted beams of the absorption reflection \mathbf{k} for the two orientations of the crystal for which the intensities $I_1(\mathbf{k})$ and $I_2(\mathbf{k})$ are measured (see text).

in those methods which have similar geometry (Phillips, 1964), \mathbf{k} is chosen so that the corresponding reciprocal-lattice point lies on the rotation axis of the crystal, if this is coincident with a reciprocal row, or on a reciprocal row as close as possible to the rotation axis, and so that \mathbf{h} and \mathbf{k} lie on the same level (the levels considered here are those perpendicular to the rotation axis). As noted by NPM, the transmission factor (6) is evaluated relative to the direction of least absorption in any one level. Consequently, the intensities in one level differ from those in another by a constant factor, the unknown ratio between the minimum absorptions suffered by the two axial reflections. This factor is taken into consideration in (6) by the scale factor C , constant for each level.

Equation (6) is an extension of the simplified (and less accurate) expression for T' proposed originally by Furnas (1957):

$$T'(\mathbf{h}, \omega, \chi, \varphi) \simeq [I_m(\mathbf{k})/I_{\max}(\mathbf{k})] C, \quad (7)$$

where $I_m(\mathbf{k})$ is the intensity of the absorption reflection \mathbf{k} measured for that orientation of the crystal for which the mean direction of \mathbf{k} is coincident with the mean direction of \mathbf{h} .

(B) Method of Kopfman & Huber (1968)

In this method (designated KH),

$$T'(\mathbf{k}, \omega, \chi, \varphi) \simeq R_I R_R, \quad (8)$$

where

$$R_I = (1/V) \sum_j \exp(-\mu l_j') \Delta V_j, \\ R_R = (1/V) \sum_j \exp(-\mu l_j'') \Delta V_j. \quad (9)$$

In the above expression V is the volume of the crystal and l_j' and l_j'' are the path lengths of incident and diffracted beams corresponding to the volume element ΔV_j .

(C) Method of Flack (1974)

$$T'(\mathbf{k}, \omega, \chi, \varphi) \simeq \frac{I(\mathbf{k}, \omega, \chi, \varphi)}{\langle I(\mathbf{k}, \omega, \chi, \varphi) \rangle}, \quad (10)$$

where

$$\langle I(\mathbf{k}, \omega, \chi, \varphi) \rangle = \frac{1}{8\pi^3} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} I(\mathbf{k}, \omega, \chi, \varphi) d\omega d\chi d\varphi. \quad (11)$$

The procedures of KH and Flack are limited in their present form to four-circle diffractometers. In addition, they require rather complex interpolation schemes for evaluating, from the values of $T'(\mathbf{k}, \omega, \chi, \varphi)$ of a limited number of absorption reflections, the transmission factors $T'(\mathbf{h}, \omega, \chi, \varphi)$ to be applied to intensities measured during a routine data-collection run. The choice of the reflections \mathbf{k} needed in the last two

procedures is not as restricted as in the method of NPM. The evaluation of $I(\mathbf{k}, \omega, \chi, \varphi)$, however, requires the use of at least four general equivalent reflections.

(D) Method of Lee & Ruble (1977)

This method (designated LR) is restricted to crystals having at least twofold symmetry and the adopted strategy is such that intensity measurements are made for those orientations of the crystal for which the optical paths of incident and diffracted beams of the absorption reflection and of the reflections to be corrected are the same. The procedure is based on the approximation proposed by KH and its application is limited to four-circle diffractometers.

(E) Methods not based on azimuthal scans

Katayama, Sakabe & Sakabe (1972) have reported a method for evaluating the three-dimensional transmission of the crystal based on statistical analysis of intensity differences of equivalent reflections. Xuong *et al.* (1978) used the intensities of equivalent reflections to correct data measured with an area detector. These methods, as well as that of Flack (1974), are limited to crystals with symmetry higher than monoclinic.

The method of NPM is very simple from the experimental point of view, does not need elaborate and time-consuming computations and, in most cases, provides fairly accurate corrections. For these reasons, it has been extensively and successfully applied to protein data collection using four-circle and linear diffractometers. The validity of the corrections calculated from (6) and (7), however, is limited to those cases in which the sample shape has approximately twofold symmetry about the rotation axis. If this condition is not satisfied, and if the crystal possesses at least one axis of twofold crystallographic symmetry, the problem can be quite well circumvented by applying the procedure proposed by LR.

The main disadvantage of the other methods is that they require the use of a large number of absorption reflections and/or elaborate interpolation schemes to evaluate the transmission factors of general reflections. We have, therefore, limited our analysis to the absorption corrections evaluated according to NPM and LR. These procedures have been extended specifically to the flat-cone geometry. However, they can also be applied, with little or no modification, to the normal-beam method or to the general Weissenberg case. This should prove particularly useful for diffractometers equipped with area detectors.

Corrections in flat-cone geometry

The main problem in extending empirical corrections to Weissenberg methods other than the equi-inclination

arises because, in these configurations, incident and diffracted beams of a general reflection \mathbf{h} do not lie on the same diffraction cone. In these cases, we may adopt two strategies to make the beam directions of the absorption reflection \mathbf{k} as close as possible to the beam directions of the reflection \mathbf{h} under study: (i) we may choose as reflection \mathbf{k} one for which incident and diffracted beams lie on diffraction cones between those of the incident and diffracted beams of \mathbf{h} ; or (ii) we may use two reflections \mathbf{k} to make the correction, one, \mathbf{k}_i , such that its diffraction cone is the same as that of the incident beam of \mathbf{h} (or as close as possible to it), and the other, \mathbf{k}_j , such that its diffraction cone is the same as that of the diffracted beam of \mathbf{h} (or as close as possible to it). For the flat-cone geometry, therefore, \mathbf{k}_i is located on the level twice that of \mathbf{h} , and \mathbf{k}_j is located on a level as close as possible to the zero level.

The geometry involved in these choices is illustrated in Fig. 2 for the method of NPM. The extension of this method to case (i) is trivial and does not require any modifications of the equations previously derived. For case (ii), (6) is rewritten

$$T'(\mathbf{h}, \omega, \chi, \varphi) \simeq \left[\frac{I_1(\mathbf{k}_i)}{2I_{\max}(\mathbf{k}_i)} + \frac{I_2(\mathbf{k}_j)}{2I_{\max}(\mathbf{k}_j)} \right] C, \quad (12)$$

where $I_1(\mathbf{k}_i)$ and $I_2(\mathbf{k}_j)$ are the intensities of \mathbf{k}_i and \mathbf{k}_j measured for those orientations of the crystal for which the projections of the mean directions of \mathbf{k}_i and \mathbf{k}_j are coincident with the projections of the incident and diffracted beams of \mathbf{h} respectively. The factor C appearing in (12) is constant for each level and does not need to be determined if the intensities in only one reciprocal-lattice level are being considered. However, if three-dimensional data are corrected with different combinations of \mathbf{k}_i and \mathbf{k}_j , then the resulting intensities have to be put on the same scale. This can be accomplished with the following procedure.

Let us indicate with $\mathbf{h}_1, \mathbf{h}_2, \dots, \mathbf{h}_n$ reflections located on levels 1, 2, \dots, n . By combining equations (2), (3) and (5), we may write*

$$I_{\text{obs}}(\mathbf{h}_s) = T'(\mathbf{h}_s) S(\mathbf{h}_s) I_0(\mathbf{h}_s) = T''(\mathbf{h}_s) C_s S(\mathbf{h}_s) I_0(\mathbf{h}_s), \quad (13)$$

i.e.

$$I_0(\mathbf{h}_s) C_s = b_s = I_{\text{obs}}(\mathbf{h}_s) / \{T''(\mathbf{h}_s) S(\mathbf{h}_s)\}. \quad (14)$$

The quantities b_1, b_2, \dots, b_n are known. If we put

$$C_{1r} = C_1/C_r, \dots, C_{nr} = C_n/C_r, \quad (15)$$

* The angles ω, χ, φ at which a reflection \mathbf{h} is measured are fixed once the crystal is oriented on the diffractometer and the technique and rotation axis are selected. $T'(\mathbf{h}_s) = T''(\mathbf{h}_s) C_s$ and $I_{\text{obs}}(\mathbf{h}_s)$, therefore, should be taken to imply $T'(\mathbf{h}_s, \omega, \chi, \varphi)$ and $I_{\text{obs}}(\mathbf{h}_s, \omega, \chi, \varphi)$ restricted to the values of ω, χ, φ imposed by the experimental conditions. Similarly, $S(\mathbf{h}_s)$ implies that $S(\mu R, \mathbf{h}_s)$ is restricted to the value of μR of the experiment.

equation (14) can be written

$$C_r I_0(\mathbf{h}_s) = b_s / C_{sr}. \quad (16)$$

In (16), r indicates some convenient level chosen as a reference for the whole set of intensities. Therefore, C_r is a factor by which all intensities are multiplied and which, consequently, can be included in the overall scale factor. The quantity C_{sr} , characteristic of level s , can be estimated experimentally with the procedure outlined in Appendix I.

As mentioned in the previous section, LR have proposed a method of absorption correction which is particularly valuable in those cases in which the procedure of NPM fails because the sample shape does not have twofold symmetry about the rotation axis. This method is restricted to crystals possessing at least a twofold axis of crystallographic symmetry and is applicable to the Weissenberg geometry only if the symmetry axis is selected as the rotation axis. The principle of the method is illustrated in Fig. 3 in which AS and SB are the projections on the absorption plane (coincident with the plane of figure) of incident and diffracted beams for a reflection \mathbf{h} represented by the reciprocal node B . The projections of incident and diffracted beams of the reflection \mathbf{h}' , related to \mathbf{h} by the operation of the twofold axis, are DS and SC , respectively. If we adopt the approximation of KH given in (8), we may write

$$\left. \begin{aligned} I_{\text{obs}}(\mathbf{h}) &= R(AS) R(SB) S(\mathbf{h}) I_0(\mathbf{h}) \\ I_{\text{obs}}(\mathbf{h}') &= R(DS) R(SC) S(\mathbf{h}) I_0(\mathbf{h}) \end{aligned} \right\} \quad (17)$$

Let us now choose as absorption reflection \mathbf{k}_i the axial reflection whose beam directions lie on the diffraction cone of AS and SD and let us measure its

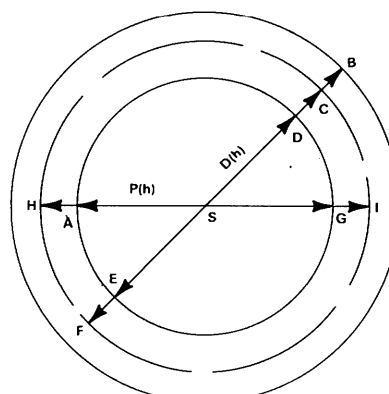


Fig. 2. Method of NPM for the flat-cone geometry. The rotation axis of the crystal is perpendicular to the plane of the figure at G . AS and SB are the incident and diffracted beams of the reflection \mathbf{h} under study, located on level l . The empirical transmission is evaluated from the intensities of two absorption reflections. AS and SG are the incident and diffracted beams of the first of them, located on level $2l$, and FS and SC are those of the second, located on a level as close as possible to level zero.

intensity for that orientation of the crystal for which we may write

$$I_{\text{obs}}(\mathbf{k}_i) = R(AS) R(DS) S(\mathbf{k}_i) I_0(\mathbf{k}_i). \quad (18)$$

As absorption reflection \mathbf{k}_j , let us select the axial reflection located on the closest level to the level zero, and let us measure its intensity, so that we may write

$$\begin{aligned} I_{\text{obs}}(\mathbf{k}_j) &= R(ES) R(SF) S(\mathbf{k}_j) I_0(\mathbf{k}_j) \\ &\simeq R(SC) R(SB) S(\mathbf{k}_j) I_0(\mathbf{k}_j). \end{aligned} \quad (19)$$

Combining equations (17), (18) and (19), we obtain

$$\begin{aligned} I_0^2(\mathbf{h}) &= [I_{\text{obs}}(\mathbf{h}) I_{\text{obs}}(\mathbf{h}') / I_{\text{obs}}(\mathbf{k}_i) I_{\text{obs}}(\mathbf{k}_j)] \\ &\times [S(\mathbf{k}_i) S(\mathbf{k}_j) / S^2(\mathbf{h})] I_0(\mathbf{k}_i) I_0(\mathbf{k}_j). \end{aligned} \quad (20)$$

Equation (20) is the equivalent, in flat-cone geometry, of equation (6) in the paper by LR. The factor $I_0(\mathbf{k}_i) \times I_0(\mathbf{k}_j)$ is unknown, but is constant for each level. If the intensities to be corrected belong to different levels, this factor has to be evaluated. The procedure to do this experimentally is given in Appendix II. It should be stressed that the scale factors determined experimentally with NPM or LR methods should be treated as refinable parameters since they could introduce systematic errors in the corrected intensities.

Equations (12) and (20) show that two absorption curves per level are required to evaluate the corrections. One of them is the same for all levels, while the other changes from level to level. For crystals with large unit cells (*i.e.* with reciprocal nets close to one another), protein crystals in particular, two or three absorption curves may suffice for the whole data set. Thus, in general, the number of curves required by this method is not larger than that of NPM and LR.

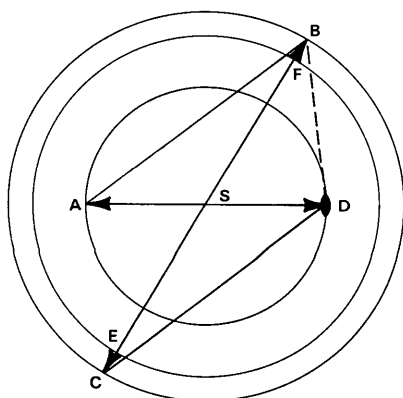


Fig. 3. Method of LR for flat-cone geometry. AS and SB are incident and diffracted beams of reflection \mathbf{h} , and DS and SC those of \mathbf{h}' , symmetrically equivalent to \mathbf{h} . AS and SD are the incident and diffracted beams of the first absorption reflection, and ES and SF those of the second. The levels of the absorption reflections are chosen as in the previous case.

The rotations needed to orient the crystal for the intensity measurements required for evaluating (12) and (20) can be calculated with the methods summarized in Appendix III.

Tests of the methods

The transmission factors evaluated by employing the methods previously described have been tested by comparison with the results obtained analytically with the Gauss method of numerical integration (Busing & Levy, 1957). The crystal adopted in the tests is a right cylinder with an elliptical cross section of large eccentricity ($e = 0.85$ and more) and dimensions of 7.5, 2.5 and 5 mm for the height of the cylinder and the minor and major axes of the ellipse. The conditions chosen for the tests were supposed to approximate those found in the neutron data collection on proteins. In most of the cases analyzed, the crystal size and the linear absorption coefficient were chosen to give $\mu r \simeq 1.5$.* The reflections for which absorption corrections were calculated covered the range of resolution from 2.8 to 1.8 Å ($\theta = 17.5$ to 27.6°, $\lambda = 1.68$ Å). Lattice parameters were arbitrarily chosen as $a = 35.00$, $b = 37.16$, $c = 38.27$ Å, $\alpha = \beta = \gamma = 90^\circ$, but their actual choice is immaterial in the application of the methods.

Following the procedure of NPM, the 'experimental' absorption curves used to evaluate the empirical transmission factors were calculated with the Gaussian quadrature method in steps of 10° of the rotation about the scattering vectors of the absorption reflections.

To test the method of NPM, the empirical transmission factors were evaluated by means of the expression

$$\left[\frac{t_1(\mathbf{k}_i)}{2t_{\text{max}}(\mathbf{k}_i)} + \frac{t_2(\mathbf{k}_j)}{2t_{\text{max}}(\mathbf{k}_j)} \right] S(\mathbf{h}), \quad (21)$$

where $t_1(\mathbf{k}_i)$, $t_2(\mathbf{k}_j)$, $t_{\text{max}}(\mathbf{k}_i)$ and $t_{\text{max}}(\mathbf{k}_j)$ are the transmissions of the absorption reflections \mathbf{k}_i and \mathbf{k}_j read from the corresponding absorption curves at the appropriate values of the angle about the scattering vectors. The ratio, a , of these empirical values to those calculated with the Gaussian quadrature should be constant for each level.

The method of LR was tested by evaluating the expression

$$\left[\frac{t(\mathbf{h}) t(\mathbf{h}')}{t(\mathbf{k}_i) t(\mathbf{k}_j)} \frac{S(\mathbf{k}_i) S(\mathbf{k}_j)}{S^2(\mathbf{h})} \right]^{1/2}, \quad (22)$$

where \mathbf{h} and \mathbf{h}' are two reflections related by the two-fold axis of crystallographic symmetry chosen as rotation axis of the crystal, $t(\mathbf{k}_i)$ and $t(\mathbf{k}_j)$ are, again,

* $r = (1/2)\bar{x}$ or $r = (3V/4\pi)^{1/3}$, where \bar{x} is the mean linear dimension of the crystal and V the crystal volume (Flack, 1974).

read from the absorption curves of k_i and k_j at the appropriate angles, and $t(h)$ and $t(h')$ are the true transmissions of h and h' calculated analytically for the geometrical situations under which the reflections were measured. The quantity (22) can be easily derived from (20). Its value should be equal to unity.

The number of reflections used in each test varied between 30 and 60. As a measure of the dispersion from the average, \bar{a} , of the ratios evaluated by means of (21), or from unity in the case of expression (22), we adopted the mean absolute deviation divided by the mean and expressed as a percentage. Some results of these calculations are given in Table 1.

Case (A) shows that, when the beam paths in the crystal are a smooth and slow-varying function of the angle μ (the angle μ is defined in Prince, Wlodawer & Santoro, 1978), reasonable values of the correction are obtained for all methods employed. The results show, however, that the procedure employing the two absorption reflections $0,0,2l + 001$ has to be preferred to the ones making use of $0,0,2l$ or 001 only. On the other hand, the reflection $00l$ with a diffraction cone located between those of $0,0,2l$ and 001 , gives results as good as $0,0,2l + 001$. This is no longer true if the crystal orientation is such that the beam paths are not a slow-varying and smooth function of μ , as illustrated by case (B). In this case, the use of a single absorption reflection $00l$ gives unacceptably high deviations, while

the use of $0,0,2l + 001$ gives corrections comparable to those obtained for the same method in case (A).

The method of NPM gives satisfactory results in all situations in which the sample has exact or approximate twofold symmetry about the rotation axis of the crystal. This is true even if the rotation axis and the reciprocal row on which the nodes of the absorption reflections are located do not coincide. The results of case (C) were obtained by assuming an angle of 15° between the two axes. If this angle is decreased, the mean and maximum deviations decrease from the values of 7.2 and 16.8% reported in Table 1.

If the sample does not possess even approximate twofold symmetry about the rotation axis, as in case (D) reported in Table 1, the method of NPM cannot be used any longer, and the method of LR, if applicable, becomes the best alternative.

In all previous calculations, the effect of the 2θ -dependent factor is small because the maximum change of 2θ for the reflections considered does not exceed about 20° . This situation is typical in the study of crystals with large unit cells.

Expressions (21) and (22) have been derived by making use of approximations and assumptions which are valid only if the linear absorption coefficient and the size of the crystal are small. The values of the mean and maximum deviations reported in Table 1 were calculated with $\mu = 0.3 \text{ mm}^{-1}$. For the geometry of case (A), and with $\mu = 0.6 \text{ mm}^{-1}$, the mean deviation becomes 6.5% for the method of NPM and 14.3% for the method of LR, and with $\mu = 0.8 \text{ mm}^{-1}$ these values become 10.9 and 24.5%, respectively. Similar results are obtained when the eccentricity of the cylinder is increased. In these cases, as expected, the empirical transmission factors are particularly poor for those reflections whose beams travel along the long direction of the crystal.

In all cases in which the sample has twofold symmetry about the rotation axis, the method of NPM gives better results than those obtained with the method of LR. This is almost certainly due to the fact that the approximation of KH, used in the method of LR, is valid only for low values of μr .

The previous discussion on the results of the calculations of empirical absorption corrections in flat-cone geometry permits us to draw the following conclusions.

(i) It is always preferable to evaluate the transmission factors of the reflections located on each level of the reciprocal lattice by using two properly selected absorption reflections rather than one. This conclusion applies also to those cases in which the shape of the sample does not vary abruptly with μ .

(ii) The sample should be prepared so that it has, at least approximately, a twofold axis of symmetry, and it should be mounted on the diffractometer in such a way that the crystal can be rotated about a zone axis coincident with that axis, or about a zone axis as close as possible to it.

Table 1. Tests of the methods for evaluating empirically the absorption correction in the flat-cone geometry

Method	Absorption reflections	Mean deviation (%)	Maximum deviation (%)
NPM ^(A)	0,0,2l + 001	1.3	5.3
NPM ^(A)	0,0,2l	5.0	14.2
NPM ^(A)	001	4.3	11.2
NPM ^(A)	00l	1.3	4.9
LR ^(A)	0,0,2l + 001	3.3	16.4
NPM ^(B)	0,0,2l + 001	2.1	8.6
NPM ^(B)	00l	17.6	40.0
NPM ^(C)	0,0,2l + 001	7.2	16.8
NPM ^(D)	0,0,2l + 001	16.1	30.7
LR ^(D)	0,0,2l + 001	3.4	16.6

In all cases the rotation axis of the crystal was assumed to be [001].

(A) Cylinder axis coincident with [001].

(B) Cylinder axis perpendicular to [001]; short axis of ellipse along [001].

(C) Cylinder axis coincident with [001]. The interaxial angles, in this case were assumed to be $\alpha = 105.0$, $\beta = \gamma = 90^\circ$, so that the angle between [001] and the reciprocal row of the absorption reflections is 15° .

(D) Cylinder axis at approximately 45° from [001].

In cases (A), (B) and (D) the reciprocal row of the absorption reflections is coincident with [001].

In cases (A), (B) and (C) the sample has exact or approximate twofold symmetry about the rotation axis.

(iii) If the crystal possesses at least a twofold axis of crystallographic symmetry, it is not necessary to satisfy the conditions outlined in (ii). In this case, however, the sample should be mounted on the diffractometer so that the Weissenberg rotation can take place about the axis of symmetry.

The above conclusions were derived for flat-cone geometry. They are valid, however, for all the Weissenberg methods in which the diffraction cones of incident and diffracted beams are different (normal-beam, equal-cone and the general case). In fact, even the corrections in the equi-inclination method can be considered as particular cases of the general treatment given previously.

The use of a three-circle goniometer to provide the needed rotation of the crystal confers considerable flexibility on a diffractometer operating in flat-cone or any other Weissenberg geometry. In fact, with such a device it is possible to change the rotation axis without having to dismount the crystal, which is a great advantage in selecting the best geometrical conditions for absorption corrections. If the diffractometer does not have a three-circle goniometer, and the crystal is rotated by means of a single circle, as in some diffractometers equipped with area detectors, the measurements needed for evaluating absorption corrections cannot be carried out. In this case it is necessary to make such measurements with a conventional four-circle diffractometer before or after collecting the data with the area detector. This procedure may be followed in any case to avoid inefficient use of diffractometers equipped with position-sensitive detectors.

All computer programs used in this study, including programs for application of absorption correction to experimental data, are available upon request from the authors.

APPENDIX I

Evaluation of C_{sr}

Let us consider a reciprocal net t , intersecting the parallel nets s and r and let us call \mathbf{k}_t the absorption reflection of t (according to our definitions, the node \mathbf{k}_t belongs to t and it lies on a central reciprocal row perpendicular to t , if such a row exists, or on a row as close as possible to the zone axis perpendicular to t). Let us consider the nodes \mathbf{m}_{st} and \mathbf{m}_{rt} chosen so that \mathbf{m}_{st} belongs to both levels s and t and \mathbf{m}_{rt} to both r and t . If we measure these two reflections with the equi-inclination method when the crystal is being rotated about the zone axis perpendicular to s and r , we may use the correction given by (6) and write

$$I'_{\text{obs}}(\mathbf{m}_{\alpha t}) = \frac{I_1(\mathbf{k}_{\alpha}) + I_2(\mathbf{k}_{\alpha})}{2I_{\text{max}}(\mathbf{k}_{\alpha})} C_{\alpha} I_0(\mathbf{m}_{\alpha t}) S(\mathbf{m}_{\alpha t}). \quad (A1)$$

In the above expression, α represents s or r ; \mathbf{k}_{α} are the absorption reflections of s and r ; and the meaning of the other symbols has been given previously. Let us now re-measure the intensities of \mathbf{m}_{st} and \mathbf{m}_{rt} , again with the equi-inclination method, but by rotating the crystal about the zone axis perpendicular to the level t . By applying once more the transmission given by (6), we obtain

$$I'_{\text{obs}}(\mathbf{m}_{\alpha t}) = \frac{I_1(\mathbf{k}_{t, m_{\alpha t}}) + I_2(\mathbf{k}_{t, m_{\alpha t}})}{2I_{\text{max}}(\mathbf{k}_t)} C_t I_0(\mathbf{m}_{\alpha t}) S(\mathbf{m}_{\alpha t}), \quad (A2)$$

where $I_1(\mathbf{k}_{t, m_{\alpha t}})$ and $I_2(\mathbf{k}_{t, m_{\alpha t}})$ are the intensities of \mathbf{k}_t measured for those orientations of the crystal for which the mean direction of \mathbf{k}_t is coincident with the projections of the incident and diffracted beams of $\mathbf{m}_{\alpha t}$ respectively. Calling

$$A(\mathbf{k}_s) = \frac{I_1(\mathbf{k}_s) + I_2(\mathbf{k}_s)}{2I_{\text{max}}(\mathbf{k}_s)} \quad \text{etc.}, \quad (A3)$$

we obtain

$$C_{\alpha t} = C_{\alpha} / C_t = \frac{I'_{\text{obs}}(\mathbf{m}_{\alpha t}) A(\mathbf{k}_{t, m_{\alpha t}})}{I'_{\text{obs}}(\mathbf{m}_{\alpha t}) A(\mathbf{k}_{\alpha})}. \quad (A4)$$

It follows that

$$\begin{aligned} C_{sr} &= C_{st} / C_{rt} \\ &= [I'_{\text{obs}}(\mathbf{m}_{st}) I'_{\text{obs}}(\mathbf{m}_{rt}) / I'_{\text{obs}}(\mathbf{m}_{st}) I'_{\text{obs}}(\mathbf{m}_{rt})] \\ &\quad \times [A(\mathbf{k}_{t, m_{st}}) A(\mathbf{k}_r) / A(\mathbf{k}_s) A(\mathbf{k}_{t, m_{rt}})]. \end{aligned} \quad (A5)$$

Equation (A5) is the desired expression for evaluating C_{sr} since all quantities in the right member can be measured with the described procedures. If \mathbf{m}_{st} and \mathbf{m}_{rt} are symmetrically equivalent, then

$$I_0(\mathbf{m}_{st}) = I_0(\mathbf{m}_{rt}), \quad S(\mathbf{m}_{st}) = S(\mathbf{m}_{rt}) \quad (A6)$$

and from equations (A2), we obtain

$$\frac{I'_{\text{obs}}(\mathbf{m}_{rt})}{I'_{\text{obs}}(\mathbf{m}_{st})} = \frac{A(\mathbf{k}_{t, m_{rt}})}{A(\mathbf{k}_{t, m_{st}})}. \quad (A7)$$

From equation (A5) we have, then,

$$C_{sr} = \frac{I'_{\text{obs}}(\mathbf{m}_{st}) A(\mathbf{k}_r)}{I'_{\text{obs}}(\mathbf{m}_{rt}) A(\mathbf{k}_s)}, \quad (A8)$$

i.e., in this case the use of the intersecting net t is not necessary for determining C_{sr} .

Since the method of NPM should be applied for samples with twofold symmetry about the rotation axis, the previous method will give reliable results only for samples having this symmetry about axes coincident with \mathbf{k}_{α} and \mathbf{k}_t .

APPENDIX II

Evaluation of $I_0(k_i) I_0(k_j)$

Let us consider a reciprocal net t intersecting both nets i and j and perpendicular to these nets and let us call l the absorption reflection of t . With reference to Fig. 2 in the paper by LR, let us consider the intensity measurements made for those orientations of the crystal for which we may write

$$\begin{aligned} I_c(k_i) &= R(1) R(1') S(k_i) I_0(k_i), \\ I_c(\bar{k}_i) &= R(\bar{1}) R(\bar{1}') S(k_i) I_0(k_i), \\ I_1(l) &= R(1) R(\bar{1}) S(l) I_0(l), \\ I_1(l') &= R(1') R(\bar{1}') S(l) I_0(l), \end{aligned} \quad (A9)$$

and similar equations for level j . From the first set of equations we may derive $I_0(k_i)$ and from the second $I_0(k_j)$. From these solutions, we readily obtain

$$\begin{aligned} I_0(k_i) I_0(k_j) &= [I_c(k_i) I_c(\bar{k}_i) / I_1(l) I_1(l')]^{1/2} \\ &\times [I_c(k_j) I_c(\bar{k}_j) / I_2(l) I_2(l')]^{1/2} \\ &\times [S^2(l) / S(k_i) S(k_j)] I_0^2(l). \end{aligned} \quad (A10)$$

The factor $I_0^2(l)$ is unknown. However, it is the same for all reflections and it can be incorporated in the overall scale factor.

APPENDIX III

Diffractometer settings for absorption corrections

A flat-cone diffractometer utilizing a linear position-sensitive detector has been described by Prince, Wlodawer & Santoro (1978), designated PWS in what follows. In this instrument, use is made of a four-circle assembly to produce the conditions required by the flat-cone geometry. Procedures for calculating the settings of the instrument required for rotating the crystal about a zone axis or a scattering vector have been described by PWS and by Busing & Levy (1967). Here we give only concepts and expressions useful in the evaluation of the empirical absorption corrections.

In addition to the reference systems defined in PWS, it is convenient to introduce here a new Cartesian reference system $(OXYZ)_A$ attached to the reciprocal lattice and defined in the following way. Consider an absorption reflection with components, on the reciprocal axes, given by

$$\mathbf{k} = \begin{pmatrix} k_1 \\ k_2 \\ k_3 \end{pmatrix}. \quad (A11)$$

Select a second reflection

$${}_0\mathbf{k} = \begin{pmatrix} {}_0k_1 \\ {}_0k_2 \\ {}_0k_3 \end{pmatrix} \quad (A12)$$

noncollinear with \mathbf{k} . This second reflection is used to fix the zero of the rotation about the reciprocal-lattice vector \mathbf{k} . Now we may define the reference system by means of the equations

$$\begin{aligned} \mathbf{OX}_A &= \mathbf{k} / |\mathbf{k}|, \\ \mathbf{OZ}_A &= (\mathbf{k} \times {}_0\mathbf{k}) / (|\mathbf{k} \times {}_0\mathbf{k}|), \\ \mathbf{OY}_A &= \mathbf{OZ}_A \times \mathbf{OX}_A. \end{aligned} \quad (A13)$$

Clearly, each absorption reflection has its own reference system associated with it, except when these reflections are collinear. The absorption plane defined in one of the previous sections is the plane defined by the vectors \mathbf{OY}_A and \mathbf{OZ}_A . A point of coordinates

$$\mathbf{x} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} \quad (A14)$$

on the reciprocal axes, is transformed in $(OXYZ)_A$ by the equation

$$\mathbf{x}_A = \mathbf{U}' \mathbf{B} \mathbf{x}, \quad (A15)$$

where matrix \mathbf{B} is the same as that used in PWS and its expression has been given elsewhere (Santoro & Zocchi, 1964; Busing & Levy, 1967). Matrix \mathbf{U}' can be easily derived, with a method similar to that described by Busing & Levy (1967), by finding the components of the vectors \mathbf{OX}_A , \mathbf{OY}_A and \mathbf{OZ}_A in the Cartesian reference system $(OXYZ)_C$ attached to the reciprocal lattice as described by Busing & Levy (1967) or Santoro & Zocchi (1964).

Let us consider a point of coordinates

$$\mathbf{x}_L = \begin{pmatrix} x_{1L} \\ x_{2L} \\ x_{3L} \end{pmatrix} \quad (A16)$$

in a Cartesian system attached to the laboratory. The coordinates \mathbf{x}_A in the system $(OXYZ)_A$ are then given by

$$\mathbf{x}_A = \begin{pmatrix} x_{1A} \\ x_{2A} \\ x_{3A} \end{pmatrix} = \mathbf{U}' \tilde{\mathbf{U}} \tilde{\Phi} \tilde{\chi} \tilde{\Omega} \tilde{\mathbf{M}} \mathbf{x}_L. \quad (A17)$$

Suppose now that the direction cosines of the incident and diffracted beams of a reflection \mathbf{h} are $\boldsymbol{\eta}_L$ and $\boldsymbol{\delta}_L$, respectively, in the reference system attached to the laboratory. By means of (A17) we can readily obtain

the corresponding direction cosines η_A and δ_A in the reference system $(OXYZ)_A$. The projections on the absorption plane of the two beams and of their mean direction are characterized by the angles

$$\tan \varepsilon_{\text{inc.}}(\mathbf{h}) = \frac{\eta_{3A}(\mathbf{h})}{\eta_{2A}(\mathbf{h})}, \quad (A18)$$

$$\tan \varepsilon_{\text{diffr.}}(\mathbf{h}) = \frac{\delta_{3A}(\mathbf{h})}{\delta_{2A}(\mathbf{h})} \quad (A19)$$

and

$$\tan \varepsilon_{\text{mean}}(\mathbf{h}) = \frac{\eta_{3A}(\mathbf{h}) + \delta_{3A}(\mathbf{h})}{\eta_{2A}(\mathbf{h}) + \delta_{2A}(\mathbf{h})}. \quad (A20)$$

From these angles we may easily calculate the values of the azimuth at which the absorption reflection \mathbf{k} has to be measured to carry out the absorption correction with one of the methods analyzed and, from these, the settings of the diffractometer required for the measurement.

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X-ray and Neutron Investigations of the $P\bar{1}-I\bar{1}$ Transition in Pure Anorthite

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(Received 10 July 1979; accepted 14 November 1979)

Abstract

The temperature dependence of sharp and diffuse c and d reflections in pure anorthite was investigated by X-ray and neutron measurements from room temperature up to 700 K. At 513 ± 4 K a complete, reversible and continuous phase transition $P\bar{1}-I\bar{1}$ can be observed. Here the diffuse scattering reaches a maximum. It has a remarkable anisotropy along the \mathbf{b}^* and $(\mathbf{a}^* - \mathbf{b}^*)$ directions. All experimental findings as well as the formation of an antiphase domain structure can be explained by a simple dynamical model.

0567-7394/80/030450-11\$01.00

I. Introduction

Feldspars have been investigated very frequently and many publications exist on this topic (see, for example, Smith, 1974). In the case of plagioclases ($\text{Ca}_x\text{Na}_{1-x}[\text{Al}_{1+x}\text{Si}_{3-x}\text{O}_8]$), which are the subject of our investigation, the structure of the end members, anorthite ($x = 1$) and albite ($x = 0$), are rather well known. Yet with the intermediate members new structures and disorder structures occur, e.g. antiphase domains and exsolutions, which considerably complicate the structural interpretation (Jagodzinski & © 1980 International Union of Crystallography