

COMPUTATION OF ABSORPTION CORRECTIONS,
AND THE SIGNIFICANCE OF END EFFECTCHARLES W. BURNHAM, *Geophysical Laboratory, Carnegie
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ABSTRACT

A method of computing transmission factors using Gaussian quadrature numerical integration for crystals whose shape can be described by plane faces has been programmed specifically for equi-inclination Weissenberg diffraction geometry. This program is readily adaptable to single-crystal orienter geometry and will compute transmission factors at rates varying from about 60 to 350 *hkl* reflections per minute on the IBM 7090 computer. The method has been used to investigate the magnitude of end effect inherent in cylindrical absorption corrections for non-equatorial, or upper-level reflections. For cylindrical crystals with $\mu\nu$ values of 0.5 or greater, end effect introduces errors into transmission factors for reflections measured at equi-inclination angles greater than 20° when the length/diameter ratio of the cylinder is 20 or less.

INTRODUCTION

The techniques now available for crystal-structure refinement allow very precise determination of atomic positional and thermal parameters. If full advantage is to be taken of these techniques, intensity data obtained by *x*-ray diffraction must be properly corrected for physical and geometrical effects which otherwise lead to systematic errors. The correction for absorption of *x* radiation by the specimen is particularly important unless the experimental conditions are such that there is very little (<5 per cent) variation in the correction from one measured intensity to another.

The mathematical form for the transmission factor (*i.e.*, the percentage of incident intensity not absorbed) is well known (*International Tables for X-ray Crystallography*, vol. II, 291):

$$T = \frac{I}{I_0} = \frac{1}{V} \int^V e^{-\mu_i \rho} dV \quad (1)$$

Equation 1 has been evaluated for spherical crystals by Evans and Ekstein (1952). For spheres the transmission factor, *T*, is a function only of the diffraction angle θ , linear absorption coefficient μ_i , and crystal volume *V*. The ease of applying this correction is, in most cases, offset by the difficulty of preparing spherical specimens and orienting them without morphological aids. Attempts to grind crystals possessing pronounced cleavages to truly spherical shape frequently fail, and in many cases the result is, at best, an ellipsoid. Computation of *T* for ellipsoids has, however, been performed by Fitzwater (1961).

Claassen (1930) and later Bradley (1935) evaluated transmission factors for cylindrical crystals for zero-level Weissenberg geometry.

Buerger and Niizeki (1958) extended the treatment to equi-inclination Weissenberg geometry. This correction assumes that the crystal, whose entire volume is irradiated, has a very large length/diameter ratio and, hence, that end effect caused by abnormally short path lengths near the ends of the crystal is negligible.

Graphical methods of computing transmission factors for prismatic crystals have been presented by Hendershot (1937), Albrecht (1939), Howells (1950), Evans (1952) and Rogers and Moffett (1956). These techniques are extremely time consuming and are, in most cases, not applicable to equi-inclination upper-level reflections. Because of these limitations, the cylindrical absorption correction is sometimes used as an approximation for prismatic crystals.

The only practical method of applying an accurate absorption correction to arbitrarily shaped crystals is to solve equation 1 on a high-speed digital computer using any one of several numerical integration techniques. Busing and Levy (1957) have described a method employing the Gaussian quadrature technique; this same general method has been used in a program, written for the IBM 7090 computer, that computes transmission factors for crystals of essentially arbitrary shape for equi-inclination Weissenberg geometry.¹

The intent of this paper is to describe very briefly the method used to compute transmission factors, and to report the results of an investigation of the errors to be expected due to end effect when using cylindrical absorption corrections.

MATHEMATICAL METHOD

The analytic description of the crystal consists of a set of equations of the form

$$A_n x + B_n y + C_n z + D_n = 0, \quad (2)$$

each of which represents one of the n crystal faces. The equations are derived relative to an orthogonal coordinate system that is fixed with respect to the crystal and bears the following relation to the equi-inclination single-crystal diffractometer: The x axis is parallel to the primary x -ray beam with its positive sense away from the x -ray source when ϕ , the crystal-rotation angle, and μ , the equi-inclination angle, are both zero; the z axis is coincident with the crystal-rotation axis, ϕ , with its positive

¹ This program consists of a set of subroutines which, when incorporated in a main data-processing program, allow absorption corrections to be made while intensities are being converted to observed structure factors. Two primary subroutines are written in Fortran, while two subsidiary subroutines involving no input-output are written in FAP language. Operational instructions and symbolic card decks are available from the author.

direction away from the diffractometer spindle; the positive y axis is oriented so as to make the coordinate system right-handed.

To determine the coefficients A_n through D_n for each plane, one measures the coordinates x_i, y_i, z_i of three non-colinear points on each face; the required coefficients are the cofactors of the first row terms in the determinant

$$\begin{vmatrix} x & y & z & 1 \\ x_1 & y_1 & z_1 & 1 \\ x_2 & y_2 & z_2 & 1 \\ x_3 & y_3 & z_3 & 1 \end{vmatrix} \quad (3)$$

If equation 2 for each plane is adjusted so that D_n is positive (by multiplication by -1 if necessary), then any point x, y, z , lies inside or on the surface of the crystal if the inequality

$$A_n x + B_n y + C_n z + D_n \geq 0 \quad (4)$$

is satisfied for all n planes, provided that (a) there are no reentrant angles in the crystal model, and (b) the origin of the coordinate system is inside the crystal.

Equation 1 may be expanded as a triple integral:

$$T = \frac{1}{V} \int_a^b dx \int_{c(x_i)}^{d(x_i)} dy \int_{e(x_i, y_i)}^{f(x_i, y_i)} e^{-\mu_l r} dz \quad (5)$$

To apply the Gaussian quadrature method, the triple integral (5) is approximated by a triple sum (Busing and Levy, 1957):

$$T = \frac{1}{V} \sum_{i=1}^m \sum_{j=1}^m \sum_{k=1}^m [b-a][d(x_i) - c(x_i)][f(x_i, y_j) - e(x_i, y_j)] W_i W_j W_k e^{-\mu_l r_{ijk}} \quad (6)$$

where x_i, y_j, z_k are coordinates of sample points inside the crystal, given by

$$\begin{aligned} x_i &= a + (b-a)u_i \\ y_j &= c(x_i) + [d(x_i) - c(x_i)]u_j \\ z_k &= e(x_i, y_j) + [f(x_i, y_j) - e(x_i, y_j)]u_k \end{aligned} \quad (7)$$

The volume of the crystal is given by

$$V = \sum_{i=1}^m \sum_{j=1}^m \sum_{k=1}^m [b-a][d(x_i) - c(x_i)][f(x_i, y_j) - e(x_i, y_j)] W_i W_j W_k \quad (8)$$

and P_{ijk} is the total path length of incident and diffracted beams to the sample point x_i, y_j, z_k . The fractional intervals, u_i , and their associated weights, W_i , depend on the number of terms, m , in the summation. Values of these constants have been tabulated by Lowan *et al.* (1942) for values of m from 2 to 16. The program allows a choice of m of 4, 6, or 8.

To determine the limits of integration, the coordinates of all possible

intersections of three planes (2) are found. From those intersections whose coordinates satisfy the inequalities (4) (and hence represent intersections of crystal faces) the smallest and largest x coordinates are selected as the limits a and b . Similarly, the smallest and largest y coordinates of valid intersections of two planes occurring at the m intervals along x (computed with (7)) are selected as the set of limits $c(x_i)$ and $d(x_i)$. Finally, for each combination $x_i y_j$, the limits $e(x_i y_j)$ and $f(x_i y_j)$ are the two values of z , found by solving each of the plane equations (1), which also satisfy the inequalities (4).

The total path length, P_{ijk} , associated with the point $x_i y_j z_k$ inside the crystal, is the sum of the primary beam path length, $P_{p(ijk)}$, and the diffracted beam path length, $P_{d(ijk)}$. The length of a vector, r_{pn} , parallel to the primary beam from point $x_i y_j z_k$ to any crystal face, n , is given by

$$r_{pn} = \frac{-A_n x_i - B_n y_j - C_n z_k - D_n}{A_n \cos \alpha_p + B_n \cos \beta_p + C_n \cos \gamma_p} \quad (9)$$

where $\cos \alpha_p$, $\cos \beta_p$, and $\cos \gamma_p$ are the direction cosines of the vector with respect to the orthogonal coordinate system previously described. Since the positive sense of r_{pn} is away from the point $x_i y_j z_k$, and opposite to the direction of travel of the primary beam, the required direction cosines are not equal to those of the primary beam itself. The signs of equation 9 dictate that r_{pn} will be positive only if plane n is between $x_i y_j z_k$ and the primary-beam source, provided that D_n for each plane is zero or positive. Thus the primary beam length, $P_{p(ijk)}$, to point $x_i y_j z_k$ is the smallest positive value of the set of r_{pn} .

In an analogous manner the diffracted beam path length, $P_{d(ijk)}$, is the smallest positive value of the set of r_{dn} , computed according to

$$r_{dn} = \frac{-A_n x_i - B_n y_j - C_n z_k - D_n}{A_n \cos \alpha_d + B_n \cos \beta_d + C_n \cos \gamma_d} \quad (10)$$

where $\cos \alpha_d$, $\cos \beta_d$, and $\cos \gamma_d$ are direction cosines of a vector parallel to the diffracted beam with positive sense in the direction of travel of the beam.

The direction cosines of the primary and diffracted beams depend on the geometry of the diffractometer and the orientation of the coordinate system used to describe the crystal. The direction cosines for equi-inclination geometry relative to the previously defined coordinate system are listed in Table 1. A similar coordinate system may be employed with single-crystal orienters, in which case the positive x axis is parallel to and in the same direction as the primary x -ray beam when ϕ , χ , and θ are zero, and the positive z axis is coincident with the ϕ axis and directed away from the goniometer head. Again y is selected to complete a right-handed

TABLE 1. DIRECTION COSINES OF PRIMARY AND DIFFRACTED BEAMS RELATIVE TO THE ORTHOGONAL COORDINATE SYSTEM DESCRIBED IN THE TEXT

	Equi-inclination Weissenberg	Single-Crystal Orienter ¹
$\cos \alpha_p$	$\cos (\pi - \phi) \cos \mu$	$-\cos \theta \cos \phi - \sin \theta \cos \chi \sin \phi$
$\cos \beta_p$	$\sin (\pi - \phi) \cos \mu$	$-\cos \theta \sin \phi + \sin \theta \cos \chi \cos \phi$
$\cos \gamma_p$	$\sin \mu$	$\pm \sin \theta \sin \chi$
$\cos \alpha_d$	$\cos (T - \phi) \cos \mu$	$\cos \theta \cos \phi - \sin \theta \cos \chi \sin \phi$
$\cos \beta_d$	$\sin (T - \phi) \cos \mu$	$\cos \theta \sin \phi + \sin \theta \cos \chi \cos \phi$
$\cos \gamma_d$	$\sin \mu$	$\pm \sin \theta \sin \chi$

¹ The sign of terms containing $\sin \chi$ is determined as follows: If increasing the value of χ moves the goniometer head toward the $+y$ axis of the coordinate system as determined with ϕ , χ , and θ zero, the sign is $-$; if the goniometer head moves toward the $-y$ axis, the sign is $+$ (C. T. Prewitt, 1965, pers. comm.).

system. Direction cosines for this geometry are also listed in Table 1 (R. B. Roof, Jr., 1962, pers. comm.; B. J. Wuensch and C. T. Prewitt, 1964, pers. comm.).

Table 2 lists the approximate computing speed and estimates of the integration precision as a percentage of the computed transmission factor for the three choices of the number of integration points, m , in each direction. Since the precision decreases with increasing linear absorption coefficients, the estimated values in Table 2 are valid only within the stated range of transmission factors. The high speed of the IBM 7090/7094 computers makes it practical and economical to use values of m of 6 or 8 for processing the hundreds of reflections needed for complete three-dimensional structure analyses. Using these higher values of m , the effective limits of transmission factor precision depend primarily on the precision with which a crystal can be measured under the microscope and on uncertainties in the linear absorption coefficient.

TABLE 2. SPEED AND PRECISION ESTIMATES FOR TRANSMISSION FACTOR COMPUTATION ON THE IBM 7090 COMPUTER

m	Integration Points	Approximate Processing Time (reflections/minute)	Estimated Precision, % (for $T > 0.1$)
4	64	350	± 4
6	216	125	± 2
8	512	60	± 0.5

THE SIGNIFICANCE OF END EFFECT

Transmission factors for reflections from cylindrical or prismatic crystals completely bathed in radiation are subject to end effect whenever the primary and diffracted beams are not normal to the prism or cylinder axis. This effect is due to shortening of path lengths to and from volume elements near the ends of the crystal and is neglected by graphical methods of transmission factor computation and by the cylindrical approximation method (Buerger and Niizeki, 1958). Since the numerical integration technique considers the entire crystal shape, it automatically takes account of any end effect. It is thus possible using this method to evaluate the magnitude of errors due to end effect in the cylindrical approximation.

When primary and diffracted beams are normal to the cylinder axis, the transmission factor depends on the product $\mu_l r$, where μ_l is the linear absorption coefficient and r is the cylinder radius, and on θ ($=\Upsilon/2$ when μ , the equi-inclination angle, is 0°). Buerger and Niizeki (1958) showed that for equi-inclination geometry, when $\mu = -\nu \neq 0$, all path lengths must be modified by $1/\cos \mu$, and that for a given value of Υ ($\neq 2\theta$ when $\mu \neq 0$) the transmission factor must be found for $\mu_l(r/\cos \mu)$ rather than $\mu_l r$. The magnitude of end effect will thus depend on $\mu_l r$, Υ , the equi-inclination angle μ , and the length/diameter ratio of the cylinder.

To compute end effect, transmission factors were first computed for a cylinder having a length/diameter ratio of 100 for three values of Υ (0° , 60° , 120°), and values of μ ranging from 0° to 60° . Computations were carried out using two values of $\mu_l r$, 0.5 and 1.0. These two values are typical of those encountered with the small single crystals used on modern diffractometers.

Cylinders were approximated by 16-sided prisms, since the transmission factor program requires crystal descriptions in terms of plane faces. In the prism approximation the normal to each face from the prism axis to the face had length r , where r is the radius of the cylinder being approximated.¹ To change the length/diameter ratio, only the equations for the ends of the prism had to be altered. The computed transmission factors were compared with those obtained from the *International Tables for X-ray Crystallography* (vol. II, pages 295–298) using $\mu_l r/\cos \mu$ for upper-level conditions. This comparison provided assurance that a length/diameter ratio of 100 was large enough to eliminate end effect over the entire range of μ and Υ values. It also demonstrated that the prism approximation was extremely precise.

¹ The cross-section area of the prism is 1.3 per cent greater than that of the cylinder. The effect of this error on transmission factors is insignificant, at least in the range of transmission factors encountered in this investigation.

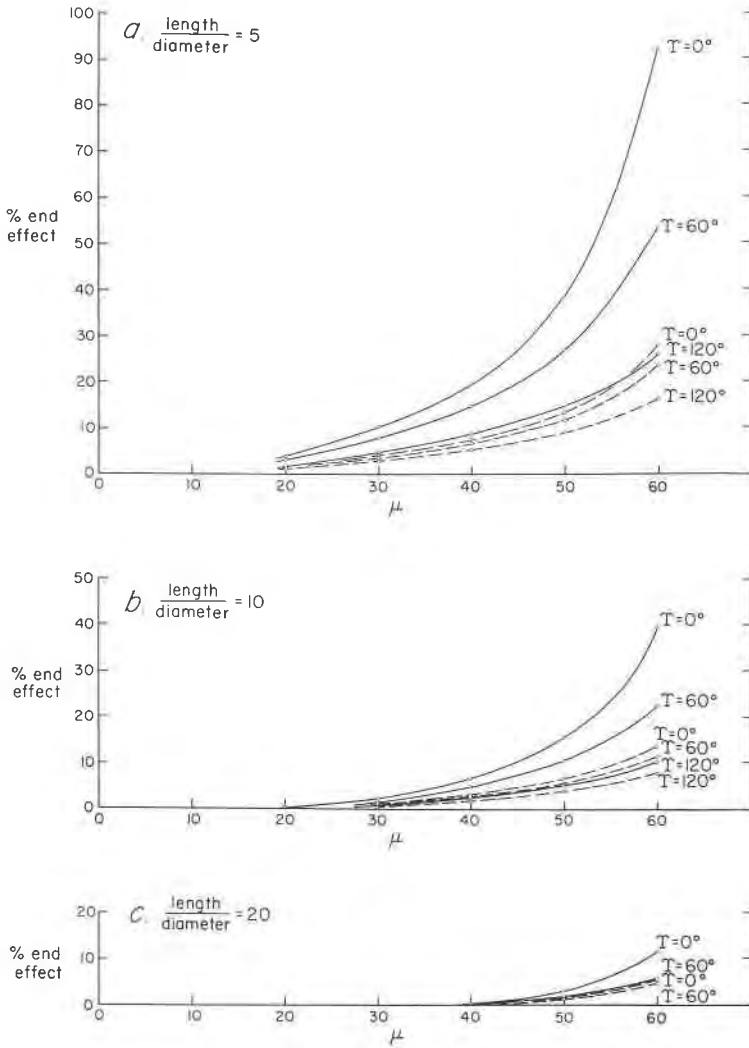


FIG. 1. Percentage of end effect in transmission factors, T , for cylinders with equi-inclination Weissenberg geometry. Solid lines are for $\mu r = 1.0$; dashed lines are for $\mu r = 0.5$. Three groups of curves show end effect in cylinders having length/diameter ratios of 5 (case a), 10 (case b), and 20 (case c).

The computations were repeated for cylinders having length/diameter ratios of 5, 10, 20, and 30. The percentage of end effect was computed according to

$$\% \text{ end effect} = 100 \left[\frac{\Delta T}{T_{U/d=100}} \right] \tag{11}$$

where ΔT is the difference between the transmission factor for a particular length/diameter ratio and that computed for the length/diameter ratio of 100. The term ΔT is ≥ 0 because end effect, if present, tends to increase transmission factors.

Results of these computations are shown in Fig. 1. When the length/diameter ratio is 30 or greater, end effect is negligible for all combinations of τ , μ , and $\mu_0 r$ investigated. The curves of Fig. 1 show that end effect may introduce significant errors in cylindrical absorption corrections for upper-level reflections when length/diameter ratios are 20 or less. By illustrating the behavior of end effect for a limited set of conditions, these curves afford the experimenter a general indication of whether or not he is liable to encounter end effect, and hence whether or not the cylindrical approximation correction can be employed safely. Under suitable experimental conditions, one could use the curves to obtain an end effect correction for transmission factors computed by the cylindrical approximation method.

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