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The calculation of absorption factors for highly absorbing crystals with rectangular cross-sections.

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We have been working on the crystal structures of substances with high absorption and have found it necessary to develop a simple method for working out the absorption integral,

$$A = \int_S \exp(-\mu l)\,dS ,$$

for the special case in which S refers to a rectangular or square cross-section of the crystal. The method is essentially the same as that suggested by Hendershot (1937) and developed by Grdenić (1949, 1952, 1956), Howells (1950) and Evans (1952). The crystal section is divided into areas over which the integral can be evaluated directly and the contributions of these areas are simply added together to give the required correction. In order for the method to be used in a systematic way, however, the conditions governing each reflection first must be determined since the proper sub-division of the crystal varies with the directions of the incident and diffracted beams. The absorption corrections for highly absorbing crystals then can be calculated directly by the use of simple formulae.

To derive these formulae we assume that the section of the crystal lies in the xy plane of a cartesian coordinate system. Let i and d be two sets of straight lines representing the incident and diffracted rays respectively. These two sets will be inclined to one another at an angle of $180°-2\theta$ where θ is the Bragg angle. The bisector QN of the angle between them is the normal to a $hk0$ plane and makes an angle ψ with some convenient arbitrary line.

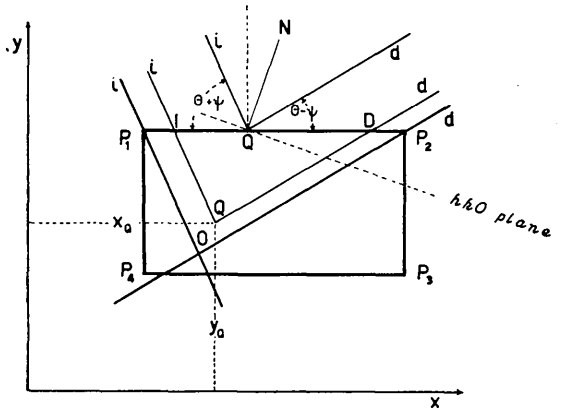

Fig. 1.

From Fig. 1 the path of an X-ray diffracted at Q, the centre of a small area dS, is: $l = l_i + l_d = IQ + QD$, where Q may be any point inside the section.

The points Q, I and D are related by

$$\begin{aligned}(y_Q - y_I)/(x_Q - x_I) &= -\tan(\theta+\psi)\\ (y_Q - y_D)/(x_Q - x_D) &= \tan(\theta-\psi) .\end{aligned} \qquad (1)$$

The path of the ray diffracted at the point Q is given by

$$l = l_i + l_d = [(x_Q - x_I)^2 + (y_Q - y_I)^2]^{\frac{1}{2}} + [(x_Q - x_D)^2 + (y_Q - y_D)^2]^{\frac{1}{2}} . \qquad (2)$$

These expressions may be transformed conveniently by combining (1) and (2) with the equations of the sides of the rectangle by which the rays enter or leave the crystal, e.g. $x_I = x_{P_1}$.

After this transformation the path l will depend only on the variables x_Q, y_Q. Hence

$$A = \int_S \exp[-\mu f(x_Q, y_Q)]\,.\,dx_Q dy_Q .$$

The possible values of $(\theta+\psi)$ and $(\theta-\psi)$ have been divided into groups. Each group contains reflections which give rise to integrals of the same type, i.e. with the equations for the same sides substituted into (1) and (2) and with the same limits. The values of θ and ψ which determine the change from one group to another are listed in Table 1. The lines of the sets i and d which pass through the corners of the section are the leading ones for this choice, e.g. P_1O and P_2O in Fig. 1.

Table 1. *Conditions for the assignment of the reflections to the proper groups*

Group	$\theta+\psi$	$\theta-\psi$	Other conditions
1	$\leqslant 90°$	$\geqslant 0°$	$\cot(\theta+\psi)+\cot(\theta-\psi) \geqslant L/L'$
2	$\leqslant 90°$	$\geqslant 0°$	$\cot(\theta+\psi)+\cot(\theta-\psi) \leqslant L/L'$
3	$\leqslant 90°$	$\leqslant 0°$	—
4	$\geqslant 90°$	$\geqslant 0°$	$\tan(\theta-\psi) \leqslant L'/L$
5	$\geqslant 90°$	$\geqslant 0°$	$\tan(\theta-\psi) \geqslant L'/L$
6	$\geqslant 90°$	$\leqslant 0°$	$\tan(\theta+\psi)+\tan(\theta-\psi) \geqslant L'/L$
7	$\geqslant 90°$	$\leqslant 0°$	$\tan(\theta+\psi)+\tan(\theta-\psi) \leqslant L'/L$

The integrals obtained for the various groups can be resolved. The expressions obtained are functions of $(\theta+\psi)$ and $(\theta-\psi)$ and of the products $\mu\mathscr{L}=L$ and $\mu\mathscr{L}'=L'$. Here μ is the absorption coefficient of the substance and $\mathscr{L}$, $\mathscr{L}'$ are the sides of the real section of the crystal in cm. The evaluation of such integrals for every value of L and L' is cumbersome and could be performed only with the aid of automatic computers.

If, however, the values of L and L' exceed a certain value (L and $L' \gtrsim 4$), the exponential functions can be simplified and the formulae assume a simple form of the general type:

$$A = (1/\mu^2)\{K_1 L + K_2 + K_3 L'\} . \qquad (3)$$

These simplified formulae are quoted in Table 2. They can be used to calculate the absorption factor in a section of the crystal. The calculation can be easily extended to the entire volume by a summation of the absorption factors calculated for different sections of the crystal.

We have used these expressions to calculate the absorption factors in a section of a crystal having $L=15$. The results obtained are in good agreement with the data

Table 2. *Coefficients* K_1, K_2, K_3 *for the formula*: $A=(1/\mu^2)\{K_1L+K_2+K_3L'\}$ (valid for L and $L'\gtrsim 4$)

Group	K_1	K_2	K_3
1–2	$\frac{1}{m'+q'}$	$\frac{1}{(m'+q')^2}\left[\frac{m'}{nq'}+\frac{q'}{rm'}\right]$ when $\psi=0°$	0
	$\frac{1}{2q'}$	$\frac{1}{2qq'}$	0
3	0	$\frac{1}{qm'}+\frac{1}{mq'}=\sin 2\psi$ when $\psi=45°$	0
	0	1	0
4–5	$\frac{1}{m'+q'}$	$\frac{(n-r)}{r(m+q)(m'+q')}-\frac{1}{r(m'+q')^2}-\frac{n}{(m+q)^2}$ when $\psi=45°$	$\frac{1}{m+q}$
	$\frac{1}{m+q}$	$\frac{n-1}{q(m+q)}-\frac{2n}{(m+q)^2}$	$\frac{1}{m+q}$
6–7	0	$\frac{1}{(m+q)^2}\left[\frac{nm}{q}+\frac{rq}{m}\right]$ when $\psi=90°$	$\frac{1}{m+q}$
	0	$\frac{1}{2qq'}$	$\frac{1}{2q}$

$L=\mu\mathscr{L}$ $n=|\tan(\theta+\psi)|$ $m=|\sec(\theta+\psi)|$ $m'=|\mathrm{cosec}(\theta+\psi)|$
$L'=\mu\mathscr{L}'$ $r=|\tan(\theta-\psi)|$ $q=|\sec(\theta-\psi)|$ $q'=|\mathrm{cosec}(\theta-\psi)|$

evaluated graphically by the method of Henshaw (1958). The method has been successfully applied to the study of the crystal structure of aluminium periodate dodecahydrate, $Al(IO_4)_3.12\,H_2O$.

The agreement between our formulae and those proposed by Grdenić (1952, 1956) is exact for groups 1–2 and 6–7 of Table 2 (Reflections of the face-type). The discrepancies for the group 3 and 4–5 seem due to incompleteness of the Grdenić formulae.

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An explicit expression for the lattice parameters of cubic crystals for the ratio method.

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In the ratio method of determining lattice parameters only the ratio of diameters of two back reflection lines is necessary to determine a cell dimension, assuming of course that the lines have been indexed and the wavelength of the radiation is known (Rovinskij & Kostjukova, 1958; M. Černohorský, 1960). In this paper the camera geometry is introduced into the simultaneous Bragg equations in order to obtain an explicit expression for the lattice parameter, a, of a cubic crystal. An extension to crystals of lower symmetry can be made.

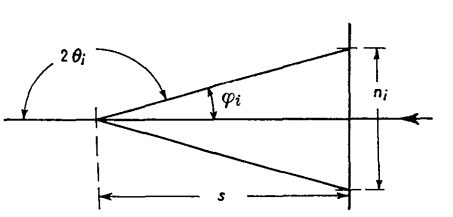

Fig. 1. Camera geometry of flat back reflection camera.