$$I_7 = -\frac{k^2 p_1}{2}[|F_P| \operatorname{erf}(p_2|F_P|) \exp(-|F_P|^2/k^2)]_0^\infty + \frac{k^2 p_1}{2}\int_0^\infty \exp(-|F_P|^2/k^2) d[|F_P| \operatorname{erf}(p_2|F_P|)] . \quad (C\text{-}5)$$

Since, on applying the limits the first term in the right-hand side of (C-5) vanishes, we have

$$I_7 = \frac{k^2 p_1}{2}\int_0^\infty \exp(-|F_P|^2/k^2) \operatorname{erf}(p_2|F_P|) d|F_P| + \frac{k^2 p_1 p_2}{\sqrt{\pi}}\int_0^\infty |F_P| \exp[-(1/k^2+p_2^2)|F_P|^2] d|F_P| = I_7^1 + I_7^{11} , \text{ say} . \quad (C\text{-}6)$$

Now

$$\frac{1}{k^2} + p_2^2 = \frac{1-\sigma_1^2\cos^2\theta}{\sigma_1^2\sigma_2^2\sigma_N^2} + \frac{\cos^2\theta}{\sigma_2^2\sigma_N^2} = \frac{1}{\sigma_1^2\sigma_2^2\sigma_N^2} = \frac{1}{k_0^2} . \quad (C\text{-}7)$$

If we put $|F_P|/k = y$ in (C-6) and use (C-7), we get

$$I_7 = \frac{p_1 k^3}{2}\int_0^\infty \exp(-y^2) \operatorname{erf}(p_2 k y) dy + \frac{p_1 p_2 k^2 k_0^2}{2\sqrt{\pi}}\int_0^\infty \exp(-|F_P|^2/k_0^2) d(|F_P|^2/k_0^2) = \frac{p_1 k^3}{2}\frac{1}{\sqrt{\pi}}\tan^{-1}(p_2 k) + \frac{p_1 p_2 k^2 k_0^2}{2\sqrt{\pi}} , \quad (C\text{-}8)$$

where equations (25) and (28) of part I have been used. If we substitute for p_1, p_2, k and k_0 from equations (C-1) and 26*a*, *b*), the equation (C-8) gives

$$I_7 = \frac{\sigma_1^2\sigma_2^2\cos^2\theta}{\pi(1-\sigma_1^2\cos^2\theta)} + \frac{\sigma_1\sigma_2^2\cos\theta}{\pi(1-\sigma_1^2\cos^2\theta)^{3/2}}\tan^{-1}\left[\frac{\sigma_1\cos\theta}{\sqrt{1-\sigma_1^2\cos^2\theta}}\right] . \quad (C\text{-}9)$$

References

BLOW, D. & CRICK, F. H. C. (1959). *Acta Cryst.* **12**, 794.

ERDELYI, A. (Editor) (1954). *Tables of Integral Transforms*, Vol. II. New York: McGraw-Hill.

HOUTEN, S. VAN & WIEBENGA, E. H. (1957). *Acta Cryst.* **10**, 156.

JACOBSON, R. A., WUNDERLICH, J. A. & LIPSCOMB, W. N. (1961). *Acta Cryst.* **14**, 598.

KORN, G. A. & KORN, T. M. (1961). *Mathematical Handbook for Scientists and Engineers*. New York: McGraw-Hill.

LUZZATI, V. (1953). *Acta Cryst.* **6**, 142.

PARTHASARATHY, S. (1965). *Acta Cryst.* **18**, 1022.

PARTHASARATHY, S., RAMACHANDRAN, G. N. & SRINIVASAN, R. (1964). *Curr. Sci.* **33**, 637.

RAMACHANDRAN, G. N. & AYYAR, R. R. (1963). In *Crystallography and Crystal Perfection* E,d. G. N. Ramachandran, p. 25, London: Academic Press.

SIM, G. A. (1957). *Acta Cryst.* **10**, 536.

SIM, G. A. (1960). *Acta Cryst.* **13**, 511.

SIM, G. A. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, Eds. R. Pepinsky, J. M. Robertson & J. C. Speakman, p. 227. London: Pergamon Press.

SNEDDON, I. N. (1961). *Special Functions of Mathematical Physics and Chemistry*. London: Oliver and Boyd.

SRINIVASAN, R. (1959*a*). *Proc. Indian Acad. Sci.* **A49**, 340.

SRINIVASAN, R. (1959*b*). *Proc. Indian Acad. Sci.* **A50**, 19.

Acta Cryst. (1965). **18**, 1035

Calculation of Absorption Corrections for Camera and Diffractometer Data

BY P. COPPENS, L. LEISEROWITZ AND D. RABINOVICH

Department of X-ray Crystallography, Weizmann Institute of Science, Rehovoth, Israel

(*Received* 24 *August* 1964)

A method is described for the calculation of absorption corrections for Weissenberg and precession camera, and three- and four-circle diffractometer data. The method has been successfully applied to a number of crystals.

Introduction

Several procedures for computation of absorption corrections have been described. Busing & Levy (1957) have first outlined a method suitable for high-speed computers and valid for crystals having no re-entrant angles between bounding planes. However, they did not derive the components along the crystal axes of the incident and diffracted beams for upper level reflexions. Such an extension for both Weissenberg and precession camera data has been given by Wells (1960). Here we propose an alternative procedure which makes extensive use of vector algebra and has also been applied to three- and four-circle cone diffractometers, since these are now widely used for collection of X-ray and neutron diffraction data.

A FORTRAN program has been written for the CDC 1604 computer which in its present form calcul-

ates absorption corrections for three-circle cone diffractometer, equi-inclination Weissenberg and precession camera data.

For the evaluation of the absorption integral we use the numerical method of Gauss, as described by Busing & Levy (1957). The Gaussian quadrature constants are now also available for values of $m > 16$ (Davis & Rabinowitz, 1956), and for inorganic crystals we have used values of m up to 32. The coordinates of the sampling points along the crystal axes and the associated weights are first evaluated. We then derive the components of the incident and diffracted beams for each reflexion. These are used to calculate the path length inside the crystal for each of the sampling points. Finally, the absorption correction is obtained as the weighted average over all the points.

In the following paragraphs we only describe the derivation of the components of the incident and diffracted beams and the calculation of the path lengths. A description of the other steps can be found in Busing & Levy's article.

The directions of the incident and diffracted rays

Diffractometer data

The four-circle cone diffractometer comprises four circles designated as φ, χ, Ω and 2θ (Fig. 1), the Ω circle being absent in the three-circle cone diffractometer. We shall assume that the **a*** axis has been set parallel to the φ axis of the diffractometer and that at $\varphi = 0$ the **c** axis is parallel to the χ axis. The crystal axes form a right-handed coordinate system and φ increases by clockwise rotation.

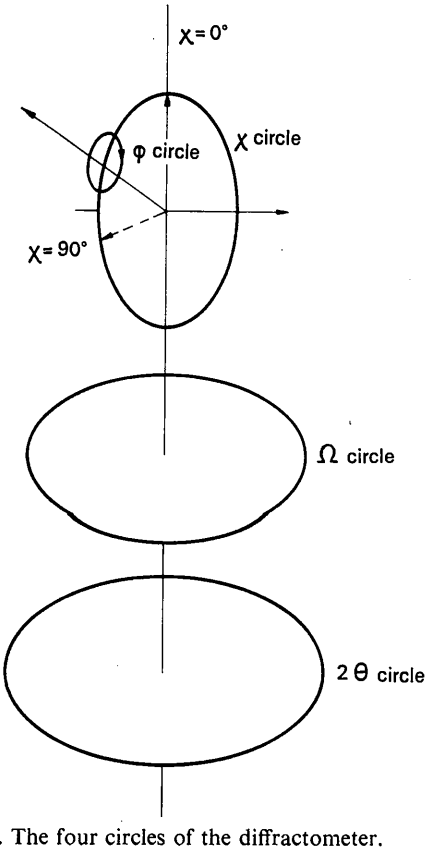

Fig. 1. The four circles of the diffractometer.

(1) *Three-circle cone diffractometer*

For each reflexion *hkl*, we choose unit vectors $\mathbf{s}_0$ and **s** in the directions of the incident and diffracted rays.

Let $\mathbf{D} = \mathbf{s} - \mathbf{s}_0 = \lambda(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) = D_1\mathbf{a} + D_2\mathbf{b} + D_3\mathbf{c}$. The components D_1, D_2, and D_3 are obtained by the transformation

$$\lambda g\{h, k, l\} = \{D_1, D_2, D_3\} \qquad (1)$$

where g is the matrix

$$\begin{pmatrix} \mathbf{a}^* \cdot \mathbf{a}^* & \mathbf{a}^* \cdot \mathbf{b}^* & \mathbf{a}^* \cdot \mathbf{c}^* \\ \mathbf{b}^* \cdot \mathbf{a}^* & \mathbf{b}^* \cdot \mathbf{b}^* & \mathbf{b}^* \cdot \mathbf{c}^* \\ \mathbf{c}^* \cdot \mathbf{a}^* & \mathbf{c}^* \cdot \mathbf{b}^* & \mathbf{c}^* \cdot \mathbf{c}^* \end{pmatrix}$$

and the curled brackets indicate column vectors.

Let $\mathbf{T} = \mathbf{s} + \mathbf{s}_0 = T_1\mathbf{a} + T_2\mathbf{b} + T_3\mathbf{c}$; $T = 2\cos\theta$.

We shall first determine the components of **T** and **D**. Once these are known we can obtain those of $\mathbf{s}_0$ and **s** with the relations

$$\mathbf{s}_0 = (\mathbf{T} - \mathbf{D})/2 \qquad (2)$$

$$\mathbf{s} = (\mathbf{T} + \mathbf{D})/2 \quad \text{(Fig. 2).} \qquad (3)$$

The geometry of the three-circle cone diffractometer assures us that

$$\mathbf{s} \cdot \mathbf{a}^* = -\mathbf{s}_0 \cdot \mathbf{a}^*$$

$$T_1 = (\mathbf{s} + \mathbf{s}_0) \cdot \mathbf{a}^* = 0 .$$

Further $\mathbf{D} \cdot \mathbf{T} = 0$, from which it follows that

$$(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \cdot (T_2\mathbf{b} + T_3\mathbf{c}) = kT_2 + lT_3 = 0 .$$

Also $T^2 = T_2^2b^2 + T_3^2c^2 + 2T_2T_3bc\cos\alpha = 4\cos^2\theta$.

Combining these last two equations, we find

$$T_2^2 = 4\cos^2\theta/(b^2 + k^2c^2/l^2 - 2kbc\cos\alpha/l) .$$

This expression leaves the sign of T_2 and, correspondingly, that of T_3 undetermined. But a reversal of the sense of **T** corresponds simply to a substitution of $-\mathbf{s}$ and $-\mathbf{s}_0$ for $\mathbf{s}_0$ and **s** respectively, which interchanges the incident and diffracted rays but leaves the total path length unchanged. We can therefore resolve this ambiguity in **T** by arbitrarily choosing the positive root of T_2.

We now have the components of **D** and **T**, from which we obtain those of $\mathbf{s}_0$ and **s**.

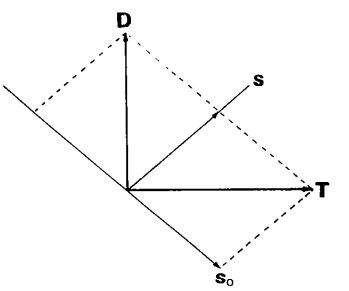

Fig. 2. The definition of the vectors **T** and **D**.

The intensities of $h00$ reflexions ($\chi=90°$) can be recorded at any value of φ and consequently the formulae for T_2 and T_3 derived above are not applicable. The vector **T** makes an angle of $180-\varphi$ with the **c** axis and therefore (Fig. 3)

$$\mathbf{T}\cdot\mathbf{b}=-Tb\cos(\alpha+\varphi)$$
$$=-2b\cos\theta\cos(\alpha+\varphi)=-(T_2b^2+T_3bc\cos\alpha)$$
$$\mathbf{T}\cdot\mathbf{c}=-Tc\cos\varphi$$
$$=-2c\cos\theta\cos\varphi=-(T_2bc\cos\alpha+T_3c^2)\,.$$

From these two equations T_2 and T_3 can be determined for a given value of φ.

(2) *Four-circle cone diffractometer*

The additional degree of freedom on a four-circle diffractometer allows the arbitrary setting of one of the angles. This angle, which we choose to be φ, has therefore to be specified for every reflexion, just as φ had to be specified for $h00$ reflexions on the three-circle goniometer. The vector **T** is no longer perpendicular to **a*** and it is convenient to introduce a unit vector **T'**, perpendicular to **a*** and coinciding with the χ axis after the rotation over φ. We have:

$$\mathbf{T}'=T_2'\mathbf{b}+T_3'\mathbf{c}$$
$$\mathbf{T}'\cdot\mathbf{b}=b\cos(\alpha+\varphi)=T_2'b^2+T_3'bc\cos\alpha$$
$$\mathbf{T}'\cdot\mathbf{c}=c\cos\varphi\qquad=T_2'bc\cos\alpha+T_3'c^2$$

from these equations we can determine T_2' and T_3'.

The crystal is brought into the reflecting position by rotations around the χ and Ω axes. These rotations do not remove **T'** from the horizontal plane of the Ω and 2θ circles. Therefore the vectors **T**, **D**, and **T'** are coplanar. Hence the following relation exists between the direct space components of the three vectors:

$$\begin{vmatrix} T_1 & T_2 & T_3 \\ D_1 & D_2 & D_3 \\ 0 & T_2' & T_3' \end{vmatrix} = 0$$

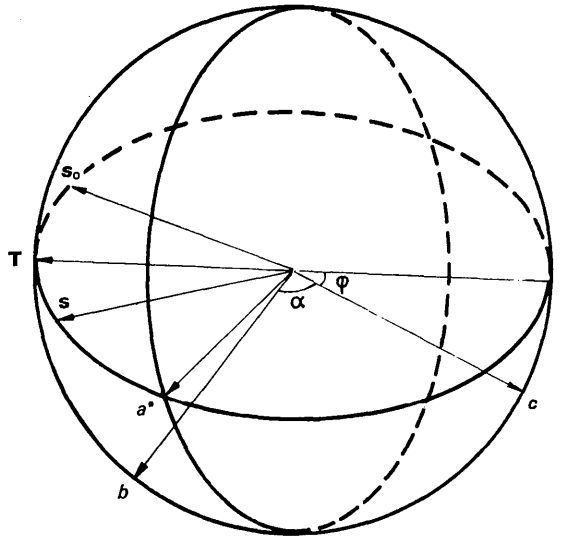

Fig. 3. The three-circle diffractometer at $\chi=90°$.

Therefore $T_1(D_2T_3'-D_3T_2')-T_2D_1T_3'+T_3D_1T_2'=0$.
Also $\mathbf{T}\cdot\mathbf{D}=0$ which gives $T_1h+T_2k+T_3l=0$.
Also $T=2\cos\theta$.

Since the components of **T'** and **D** are known the three components of **T** can be determined from these three equations.

Photographic data

(1) *Equi-inclination Weissenberg technique*

The method employed for the equi-inclination Weissenberg technique is very similar to that for the three-circle cone diffractometer.

The equi-inclination geometry is such that $\mathbf{s}_0\cdot\mathbf{a}=-\mathbf{s}\cdot\mathbf{a}$ assuming the **a** axis to be aligned parallel to the spindle axis of the camera.

This gives $(\mathbf{s}+\mathbf{s}_0)\cdot\mathbf{a}=0$.

Let $\mathbf{T}=\mathbf{s}+\mathbf{s}_0=t_1\mathbf{a}^*+t_2\mathbf{b}^*+t_3\mathbf{c}^*$.
Then $\mathbf{T}\cdot\mathbf{a}=t_1=0$.
Also $\mathbf{D}=\lambda\mathbf{d}^*=\lambda(h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*)$.
Since $\mathbf{T}\cdot\mathbf{D}=0$ it follows that

$$(h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*)\cdot(t_2\mathbf{b}^*+t_3\mathbf{c}^*)=0.$$

Also $T^2=t_2^2b^{*2}+t_3^2c^{*2}+2t_2t_3b^*c^*\cos\alpha^*=4\cos^2\theta$.

The components t_2 and t_3 can be derived in the same way as T_2 and T_3 were obtained for the three-circle cone diffractometer. With formulae (2) and (3) we determine the components of **s**, and $\mathbf{s}_0$ in reciprocal space. The corresponding components in real space are obtained by applying transformation (1).

(2) *Precession camera*

We assume the precession axis to be parallel to **a**, so that

$$\mathbf{s}_0\cdot\mathbf{a}=-a\cos\mu,$$

where μ is the precession angle.

Let $$\mathbf{s}_0=s_1^0\mathbf{a}^*+s_2^0\mathbf{b}^*+s_3^0\mathbf{c}^*$$

$$\mathbf{s}_0\cdot\mathbf{a}=s_1^0=-a\cos\mu$$

$$\mathbf{s}_0\cdot\mathbf{D}=s_0D\cos(90+\theta)=-D\sin\theta=-2\sin^2\theta$$

and

$$\mathbf{s}_0\cdot\mathbf{D}=s_1^0D_1+s_2^0D_2+s_3^0D_3$$

or

$$s_2^0D_2+s_3^0D_3=-2\sin^2\theta-s_1^0D_1=aD_1\cos\mu-2\sin^2\theta. \quad (4)$$

Since

$$\mathbf{s}_0\text{ is a unit vector }\mathbf{s}_0\cdot\mathbf{s}_0=1\,. \quad (5)$$

The components D_1, D_2 and D_3, and s_1^0 are known; therefore we have two equations (4) and (5) with two unknowns. As equation (5) is quadratic we obtain two sets of values of the components s_2^0 and s_3^0. These two sets correspond to the same reflexion on the film and the absorption correction to be applied is the arithmetic mean of the two individual corrections. The components of **s** can be derived from the equation

$$\mathbf{s}=\mathbf{s}_0+\mathbf{D}\,.$$

Calculation of the absorption correction

For each point in the crystal we have to determine the length of the path traversed inside the crystal by incident and diffracted rays. The distance $L_q(r)$ from the point r, defined by the radius vector $\mathbf{r}=r_1\mathbf{a}+r_2\mathbf{b}+r_3\mathbf{c}$, to the face q (with Miller indices h_q, k_q, l_q and reciprocal lattice vector $\mathbf{d}^*_q$) is given by $L_q(r)=B_q-\mathbf{N}_q\,.\,\mathbf{r}=B_q-(h_qr_1+k_qr_2+l_qr_3)/d^*_q$ (Fig. 4) where B_q is the distance from a chosen origin inside or on the surface of the crystal to the bounding face q and $\mathbf{N}_q$ is a unit vector along the outward normal to face q.

The distance travelled by the incident ray to the point r after crossing the plane of the face q is $P_q(r)=L_q(r)/(-\mathbf{s}_0\,.\,\mathbf{N}_q)$. But the face through which the incident ray actually enters the crystal on its way to $\mathbf{r}$ is that for which $P_q(r)$ has its smallest positive value. This is, then, the actual length $P_0(r)$ of the path, inside the crystal, of the incident ray to r. Similarly the distance $P(r)$ travelled inside the crystal by the diffracted ray from r is the smallest positive value of

$$P_q(r)=L_q(r)/(\mathbf{s}\,.\,\mathbf{N}_q)\,.$$

The absorption factor for the scattering point $\mathbf{r}$ is

$$a(r)=\exp\,(-\mu[P_0(r)+P(r)])$$

where μ is the linear absorption coefficient.

The total absorption is obtained as the weighted average over all the sampling points.

Experimental

A number of tests were performed to check the procedure:

(1) A crystal of dimethyl *trans-trans*-muconate was mounted along **b*** on the three-circle cone diffractometer. The crystal has six faces and its dimensions are about $0{\cdot}3\times0{\cdot}26\times0{\cdot}1$ mm. The $0k0$ reflexions were recorded every 20° in φ with Cu $K\alpha$ radiation ($\mu=9{\cdot}17$ cm^{-1}). The computation of the absorption corrections using a $10\times10\times8$ grid took about 5 seconds per intensity reading.

A similar experiment was done on a needle-shaped crystal of $YFeO_3$ ($\mu=879$ cm^{-1} for Cu $K\alpha$ radiation) mounted along the needle axis (**c***) and having six faces and a cross section of $0{\cdot}060\times0{\cdot}054$ mm^2. The absorption correction was calculated using a two-dimensional grid $\perp$ **c*** containing 32×32 points. The observed and corrected values for the 020 reflexion of dimethyl *trans-trans*-muconate and the 002 reflexion of $YFeO_3$ are given in Table 1. Remaining variations of the intensity as a function of φ could be due to errors in the absorption coefficient, in the measured dimensions of the crystal, to secondary extinction, and to some extent to Renninger effects.

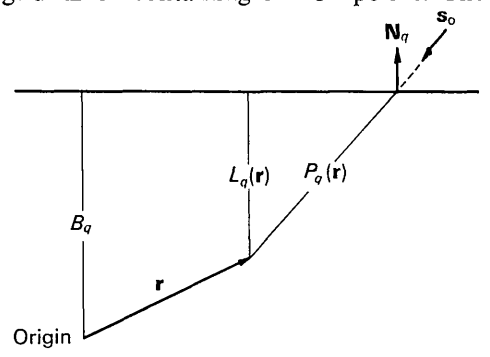

Fig. 4. The path length of the incident beam.

Table 1. *Observed and corrected intensities (counts sec^{-1}) of dimethyl trans-trans-muconate and* $YFeO_3$.

The intensities were measured on the General Electric goniostat at $\chi=90°$ at 20° intervals in φ.

Dimethyl *trans-trans*-muconate (020 reflexion)

φ	I_{obs}	I_{corr}
0°	6436	7000
20	6495	7080
40	6467	7120
60	6281	7090
80	5852	7070
100	5486	7200
120	5979	7170
140	6299	7080
160	6415	7030

$YFeO_3$ (002 reflexion)

φ	I_{obs}	I_{corr}
0°	147	29400
20	473	24510
40	869	26560
60	938	28250
80	635	28450
100	338	30130
120	832	32250
140	984	31620
160	698	29960

(2) A cylindrical crystal was approximated by defining 36 bounding planes, 10° apart and parallel to the needle axis. For $\mu R=5$ the absorption was computed at intervals of 5° in θ up to 85°. We used a two-dimensional grid perpendicular to the needle axis, which contained 256 sampling points. Absorption corrections computed agreed to better than ½% with the values listed in *International Tables for X-Ray Crystallography* (1959).

The program has also been applied successfully to Cu $K\alpha$ diffractometer data on β-chloro-*trans*-cinnamic acid ($\mu=36{\cdot}2$ cm^{-1}) and to Co $K\alpha$ and $K\beta$ Weissenberg data collected on $YFeO_3$ (μ 647 and 1002 cm^{-1} respectively).

We are indebted to Mr. S. Filippakis and to Mr M. Eibschütz for supplying intensity data on the dimethyl *trans-trans*-muconate and $YFeO_3$ respectively, and to the Computer Division of the Applied Mathematics Department for the use of the CDC 1604 computer.

References

BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.
DAVIS, P. & RABINOWITZ, P. (1956). *J. Res. Nat. Bur. Stands.* **56**, 35.
International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.
WELLS, M. (1960). *Acta Cryst.* **13**, 722.