

The modified α -synthesis employs the coefficient $\alpha_{\text{mod}} = \{|F_N|^2 - |F_P|^2 - \sum f_Q^2\} F_P$ and contains all the peaks of Table 1 with the elimination, however, of the known atoms and the known background, i.e., the peaks 1·1, 1·2, 1·3, 1·4 and 2·1. The isomorphous α -synthesis employs the coefficient

$$\alpha_{\text{is}} = \{|F_N^1|^2 - |F_N^2|^2 - |F_P^1|^2 + |F_P^2|^2\} F_P$$

and gives only the peaks under term III viz., the required peaks 3·1, with only the peaks in 3·2, 3·3 and 3·4 as background. The anomalous α -synthesis does not exist for centrosymmetric structures.

5. The β -class and the γ -class

We will now briefly outline the properties of the other types of syntheses. The β -class of syntheses employs the coefficient $(1/F_P^*)|F_N|^2$ which is the same as $(1/F_P)|F_N|^2$, while the γ -class employs the coefficient $|F_N|^2 \exp i\alpha_P$. (It is to be noted that $\exp i\alpha_P$ is just plus or minus unity in the present case.) The detailed results are not given here to conserve space. The most interesting result is that the isomorphous β -synthesis gives only the structure with no background at all in the case of a centrosymmetric structure. The coefficient β_{is} of equation (37) Part II now reduces to $2F_Q$ since $\exp i2\alpha_P = 1$, and the synthesis gives just the structure alone. The weights are, however, doubled with respect to the non-centrosymmetric case. The anomalous β -synthesis does not exist. The γ -synthesis has properties intermediate between those of α and β .

6. Comparison of centrosymmetric and non-centrosymmetric cases

It is worthwhile to compare the properties of the various syntheses in the centrosymmetric and non-centrosymmetric cases. Two important features emerge in this connection. The first is that the number of distinct background peaks is much less in the centro-

symmetric case as compared with that in the non-centrosymmetric case. The reason for this is that the Patterson of the latter contains many fewer peaks than the former. Since the background peaks arise because of the modulation of the non-origin peaks of the Patterson with the peaks of the deconvoluting agent, the background is considerably reduced in the centrosymmetric case. This particular point is best appreciated by considering the β_{is} -synthesis. Whereas with a non-centrosymmetric crystal the above synthesis gives the structure against a small background, for a centro-symmetric crystal it gives just the structure and the background is nil.

The second point to be noted is that the ratio of the strengths of the unknown atoms to known atoms is higher when centrosymmetry is present than when it is not present. This again is due to the fact that all the non-origin peaks of the Patterson, except those at $\pm 2\mathbf{r}_j$, are double peaks. An exact result can be obtained in the case of the α -synthesis. Here the ratio works out to be $2S_P^2 f_{Qj} / (S_N^2 + 2S_P^2) f_{Pj}$ in the centrosymmetric and $S_P^2 f_{Qj} / (S_N^2 + S_P^2) f_{Pj}$ in the non-centrosymmetric case, which leads to an increase by a factor of 2 when the number of P atoms is small (i.e., $S_P \ll S_N$). In the case of β - and γ -syntheses also there is an increase in the strength, but the exact value is not worked out here. It is found that the value depends on the approximations employed in working out the modulus, phase, reciprocal etc., syntheses. Higher-order approximations are being worked out in this laboratory and these will be presented in a later part.

The author is indebted to Prof. G. N. Ramachandran for helpful discussions.

References

- RAMACHANDRAN, G. N. & RAMAN, S. (1959). *Acta Cryst.* **12**, 957.
RAMAN, S. (1959). *Acta Cryst.* **12**, 964.

Acta Cryst. (1961). **14**, 150

Absorption Corrections for Diffraction Measurements from Large Single Crystals

BY A. HARGREAVES AND R. A. L. SULLIVAN

Physics Department, College of Science and Technology, Manchester 1, England

(Received 12 February 1960)

General expressions are derived for the absorption corrections required in evaluating the intensities of beams diffracted from large crystal blocks.

1. Introduction

An account of the absorption corrections used in evaluating the intensities of beams diffracted from

crystal specimens is given in the new edition of Vol. II of the *International Tables for X-ray Crystallography* (1959). Formulae are included for the absorption cor-

rections required with most of the commonly used experimental arrangements. Amongst these are two, particularly useful in the field of neutron diffraction, in which a narrow beam falls on a large crystal block; in one the diffracted beam is reflected from the extended face of the block and in the other it is transmitted through the block. Unfortunately the formulae given in the *International Tables for X-ray Crystallography* (1959) are of restricted application since they have been developed only for the special case in which the normal to the crystal face is in the plane of the incident and diffracted beams. In this paper formulae are derived for the general case in which the plane of the incident and diffracted beams makes any angle with the normal to the surfaces of the block.

The symbols used in § 2 and § 3 correspond, as far as possible, with those used in the *International Tables for X-ray Crystallography* (1959) for the special cases. The effect of absorption will be expressed by a quantity A_c (*International Tables for X-ray Crystallography*, 1959, p. 291) which is given by

$$A_c = \frac{1}{S_0} \int \exp \{-\mu(p+q)\} dV, \quad (1)$$

where

μ is the linear absorption coefficient,
 p and q are the lengths of the paths, in the crystal,
of the incident and diffracted beams respectively,
 S_0 is the cross-sectional area of the incident beam,
 dV is a volume element in the crystal, at a depth x
below the surface, such that $dV = (\text{area of surface of crystal irradiated}) \times dx$.

2. Reflection from extended face of crystal block

It will be assumed that both the reflecting crystal planes and the plane of the incident and reflected beams are inclined to the face of the block at general angles. The directions of the following are represented in the stereogram, Fig. 1:

M , the normal to the reflecting plane,
 N , the normal to the plane containing the incident and reflected rays,
 Q , the normal to the crystal surface in the direction pointing away from the block,
 I , the incident beam,
 R , the reflected beam.

The stereogram is used to determine α , the angle $I \wedge Q$, and β , the angle $R \wedge Q$, in terms of the angles θ , φ and ψ , where

θ is the Bragg angle,

$\varphi = Q \wedge M$ is the angle between the normal to the reflecting planes and the normal to the crystal face,

$\psi = Q \wedge N$ is the angle between the normal to the plane containing the incident and reflected rays, and the normal to the crystal face.

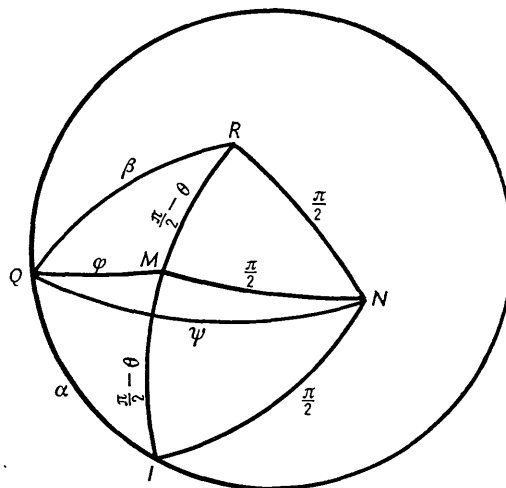


Fig. 1. Stereogram used to determine the angles α and β in terms of the angles θ , φ and ψ for reflection from the extended face of a crystal block.

In spherical triangle QMN , $\cos \widehat{QMN} = \cos \psi / \sin \varphi$.
Also $\cos \widehat{QMN} = \cos (\widehat{QMI} + \frac{1}{2}\pi) = -\sin \widehat{QMI}$

$$\therefore \cos \widehat{QMI} = \pm [1 - (\cos^2 \psi / \sin^2 \varphi)]^{\frac{1}{2}}.$$

Whence, from triangle QIM ,

$$\cos \alpha = \cos \varphi \sin \theta \pm \cos \theta (\sin^2 \varphi - \cos^2 \psi)^{\frac{1}{2}}. \quad (2)$$

And, since $\widehat{QMR} = \pi - \widehat{QMI}$, from triangle QMR we obtain

$$\cos \beta = \cos \varphi \sin \theta \mp \cos \theta (\sin^2 \varphi - \cos^2 \psi)^{\frac{1}{2}}. \quad (3)$$

It is easily shown that in equations (2) and (3) the upper signs are required when $\beta > \alpha$ and the lower signs when $\beta < \alpha$.

Equation (1) can now be written as

$$A_c = \frac{1}{S_0} \int_0^t \exp \{-\mu x (\sec \alpha + \sec \beta)\} \cdot S_0 \sec \alpha \cdot dx \\ = \frac{\sec \alpha}{\mu (\sec \alpha + \sec \beta)} \cdot [1 - \exp \{-\mu t (\sec \alpha + \sec \beta)\}],$$

where t is the thickness of the block, i.e.

$$A_c = \frac{1 - \exp \left\{ -\mu t \left[\frac{2 \cos \varphi \cdot \sin \theta}{\cos^2 \varphi - \sin^2 \psi \cos^2 \theta} \right] \right\}}{\mu \left(1 + \frac{\cos \varphi \cdot \sin \theta \pm \cos \theta [\sin^2 \varphi - \cos^2 \psi]^{\frac{1}{2}}}{\cos \varphi \cdot \sin \theta \mp \cos \theta [\sin^2 \varphi - \cos^2 \psi]^{\frac{1}{2}}} \right)}. \quad (5)$$

When the crystal is of sufficient thickness to give negligible transmission the numerator of the right-hand side of equation (5) becomes unity. If, in addition, $\varphi = \frac{1}{2}\pi$ and $\beta > \alpha$ we find that equation (5) reduces to the equation for the special case given in the *International Tables for X-ray Crystallography* (1959) (equation (6), p. 291).

3. Transmission through crystal block of thickness t

Again we consider the case in which both the reflecting crystal planes and the plane of the incident and reflected beams are inclined at general angles to the face of the block.

Angular relationships are indicated in Fig. 2.

N , M , Q , I , R , θ and ψ are defined as in § 2.

Q' represents the normal to the surface from which the transmitted beam emerges.

$Q \wedge M$, the angle between the normal to the reflecting planes and the normal to the crystal face, is now defined as $(\frac{1}{2}\pi - \varphi)$ in order to conform with the nomenclature adopted in the *International Tables for X-ray Crystallography* (1959) (§ 5.3.4).

In spherical triangle QMN , $\cos \widehat{QMN} = \cos \psi / \cos \varphi$

$$\begin{aligned} \therefore \cos \widehat{QMI} &= \cos (\tfrac{1}{2}\pi - \widehat{QMN}) = \sin \widehat{QMN} \\ &= [1 - (\cos^2 \psi / \cos^2 \varphi)]^{\frac{1}{2}} \end{aligned}$$

(the choice of the positive sign to precede the root is easily justified).

Whence, from triangle QIM ,

$$\cos \alpha = \sin \varphi \sin \theta + \cos \theta (\cos^2 \varphi - \cos^2 \psi)^{\frac{1}{2}}. \quad (6)$$

And, since $R\widehat{M}Q' = Q\widehat{M}I$, from triangle MRQ' we obtain

$$\cos \beta = \cos \theta (\cos^2 \varphi - \cos^2 \psi)^{\frac{1}{2}} - \sin \varphi \sin \theta. \quad (7)$$

Equation (1) now becomes

$$\begin{aligned} A_c &= \frac{1}{S_0} \int_0^t \exp \{-\mu(x \sec \alpha + [t-x] \sec \beta)\} S_0 \sec \alpha \cdot dx \\ &= \frac{\sec \alpha \cdot \exp \{-\mu t \sec \beta\}}{\mu (\sec \alpha - \sec \beta)} [1 - \exp \{-\mu t (\sec \alpha - \sec \beta)\}] \end{aligned}$$

i.e.

$$A_c = \frac{\exp \left\{ -\mu t \left[\frac{1}{\cos \theta [\cos^2 \varphi - \cos^2 \psi]^{\frac{1}{2}} - \sin \varphi \sin \theta} \right] \right\} - \exp \left\{ -\mu t \left[\frac{1}{\cos \theta [\cos^2 \varphi - \cos^2 \psi]^{\frac{1}{2}} + \sin \varphi \sin \theta} \right] \right\}}{\mu \left(1 - \frac{\cos \theta [\cos^2 \varphi - \cos^2 \psi]^{\frac{1}{2}} + \sin \varphi \sin \theta}{\cos \theta [\cos^2 \varphi - \cos^2 \psi]^{\frac{1}{2}} - \sin \varphi \sin \theta} \right)}. \quad (8)$$

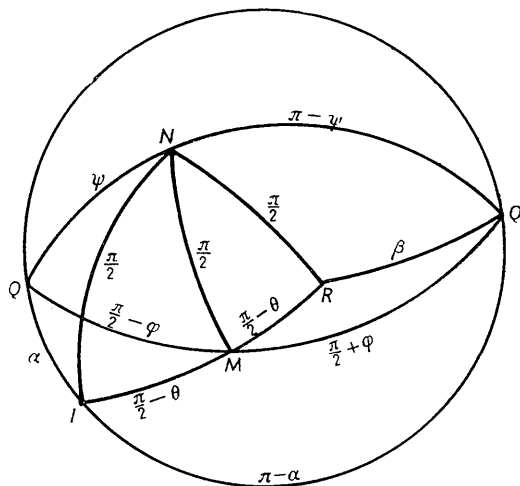


Fig. 2. Stereogram used to determine the angles α and β in terms of the angles θ , φ and ψ for transmission through a crystal block.

For the special case $\psi = \frac{1}{2}\pi$, equation (8) reduces to equation (8) on p. 291 of the *International Tables for X-ray Crystallography* (1959).

We wish to thank Dame Kathleen Lonsdale and Dr J. S. Kasper for drawing our attention to this problem. One of us (R. A. L. S.) acknowledges with thanks a maintenance grant from the Department of Scientific and Industrial Research.

Reference

International Tables for X-ray Crystallography (1959). Birmingham: Kynoch Press.