Acta Cryst. (1965). **18**, 1028

Probability Distribution of the Phases in a Crystal with Heavy Atoms
II. Non-Centrosymmetric Crystal: Probability Distribution of the Phase Angle

BY S. PARTHASARATHY

Department of Physics, University of Madras, Madras 25, *India*

(*Received* 24 *March* 1964 *and in revised form* 11 *September* 1964)

The probability distribution of the difference between the phase of the structure factor due to all the atoms in the unit cell and that due to the heavy atoms alone has been worked out. The cumulative function of this phase difference is worked out for the various cases, namely, a non-centrosymmetric crystal containing, besides a large number of light atoms, one, two and many heavy atoms in the unit cell. The results of the theory are used to compare the heavy-atom phased Fourier of the centrosymmetric and non-centrosymmetric crystals. The theory is also applied to a discussion of the determination of the phase angle of a reflexion by the anomalous-dispersion method. The theoretical results have been tested with the data from hypothetical as well as actual two-dimensional models.

Introduction

In part I, the expressions for the fractional number of reflexions having the same sign as the heavy-atom contribution were worked out for a centrosymmetric crystal for different numbers of heavy atoms in the unit cell. In this paper it is proposed to consider the corresponding problem for a non-centrosymmetric crystal, namely the distribution of $\alpha_N-\alpha_P=\theta$, where α_N and α_P are respectively the phases of the structure factors of a reflexion, contributed by all the atoms in the unit cell and by the heavy atoms alone. The notation used here is the same as in part I (Parthasarathy, 1965).

Derivation of the probability density function of $\alpha_N\alpha_P=\theta$

We consider a non-centrosymmetric crystal containing P heavy atoms and Q light atoms in the unit cell so that the total number of atoms in the unit cell is $P+Q=N$. The structure factor of a reflexion $H(=hkl)$ can be written in terms of the contributions from the P atoms and the Q atoms as

$$F_N(H)=F_P(H)+F_Q(H)\,. \tag{1}$$

The vector triangle formed by F_N, F_P and F_Q is shown in an Argand diagram in Fig. 1. The probability density function of F_Q is known to be

$$P(F_Q)=(1/\pi\sigma_Q^2)\exp(-|F_Q|^2/\sigma_Q^2)\,. \tag{2}$$

From (1) and (2), the probability density function of F_N for a given F_P is given by

$$P(F_N;F_P)=(1/\pi\sigma_Q^2)\exp[-(|F_N|-|F_P|)^2/\sigma_Q^2]\,. \tag{3}$$

However, the function $P(F_N;F_P)$ is related to the joint probability of $|F_N|$ and θ for a given F_P, namely the function $P(|F_N|,\theta;F_P)$ by the equation

$$P(|F_N|,\theta;F_P)=|F_N|P(F_N;F_P)\,. \tag{4}$$

From (3) and (4), the conditional joint probability of $|F_N|$ and θ for a given F_P is given by

$$P(|F_N|,\theta;\mathrm{F}_P)=(|F_N|/\pi\sigma_Q^2)\exp[-\{|F_N|^2+|F_P|^2-2|F_N||F_P|\cos\theta\}/\sigma_Q^2]\,. \tag{5}$$

Hence the conditional density function of θ for a given F_P is given by

$$P(\theta;F_P)=\int_0^\infty P(|F_N|,\theta;F_P)d|F_N|$$
$$=\frac{1}{\pi\sigma_Q^2}\exp[-|F_P|^2\sin^2\theta/\sigma_Q^2]\int_0^\infty|F_N|\exp[-\{|F_N|-|F_P|\cos\theta\}^2/\sigma_Q^2]d|F_N|\,,$$

which, after integration becomes

$$P(\theta;F_P)=\frac{1}{2\pi}\exp(-|F_P|^2/\sigma_Q^2)+ + \frac{|F_P|\cos\theta}{2\sqrt{\pi}\sigma_Q}\exp(-|F_P|^2\sin^2\theta/\sigma_Q^2][1+\operatorname{erf}(|F_P|\cos\theta/\sigma_Q)]\;.^{*} \tag{6}$$

Since (6) is an even function of θ, the density function of $|\theta|$ for a particular F_P is given by

$$P(|\theta|;F_P)=2P(\theta;F_P)=(1/\pi)\exp(-|F_P|^2/\sigma_Q^2)+ + \frac{|F_P|\cos\theta}{\sqrt{\pi}\sigma_Q}\exp(-|F_P|^2\sin^2\theta/\sigma_Q^2)[1+\operatorname{erf}(|F_P|\cos\theta/\sigma_Q)]\,. \tag{7}$$

From (7), the density function of $|\theta|$ (independent of F_P) is given by

$$P(|\theta|)=\int_{F_P}P(|\theta|;F_P)P(F_P)dF_P\,. \tag{8}$$

It is evident from (8) that the density function of $|\theta|$ depends on the density function of F_P, which in turn

---

* *Note added in proof:* Equation (6) has also been derived by Mr C. M. Venkatachalam of this Department in connection with another problem by an entirely independent method.

depends on the number of heavy atoms in the unit cell. Accordingly we may consider four important cases, namely, a non-centrosymmetric crystal containing 1, 2, and many heavy atoms (P-atoms), in addition to a large number of light atoms (Q-atoms). In the particular case of many heavy atoms, the P-group of atoms may be either centrosymmetric or non-centrosymmetric.

(*a*) *One-atom case*

If the origin is chosen on the heavy atom, the probability density function of F_P is given by,

$$P(F_P)=\delta(F_P-f_P)=\delta(F_P-\sigma_P)\,, \qquad (9)$$

since $\sigma_P^2=f_P^2$. Using (9) and (7) in (8), the density function of $|\theta|$ is given by

$$\begin{aligned} P(|\theta|) &= \int_0^\infty P(|\theta|;\,F_P)\delta(F_P-\sigma_P)dF_P=P(|\theta|,\,\sigma_P) \\ &= \frac{1}{\pi}\exp\,(-\sigma_P^2/\sigma_Q^2) \\ &+\frac{\cos\theta}{\sqrt{\pi}}\,\frac{\sigma_P}{\sigma_Q}\exp\,(-\sigma_P^2\sin^2\theta/\sigma_Q^2)[1+\operatorname{erf}\,(\sigma_P\cos\theta/\sigma_Q)] \\ &= \frac{1}{\pi}\exp\,(-\sigma_1^2/\sigma_2^2) \\ &+\frac{\cos\theta}{\sqrt{\pi}}\,\frac{\sigma_1}{\sigma_2}\exp\,(-\sigma_1^2\sin^2\theta/\sigma_2^2)[1+\operatorname{erf}\,(\sigma_1\cos\theta/\sigma_2)]\,. \end{aligned} \qquad (10)$$

(*b*) *Two atom case*

In this case if we choose the origin midway between the two heavy atoms, the density function of F_P is given by

$$P(F_P)=(1/\pi\sqrt{2}\sigma_P)/\sqrt{1-(F_P^2/2\sigma_P^2)}\,; \quad |F_P|\le\sqrt{2}\sigma_P\,, \qquad (11)$$

since $\sigma_P^2=2f_P^2$. Using (11) and (7) in (8), the density function of $|\theta|$ is given by

$$\begin{aligned} P(|\theta|)=\int_{-\sqrt{2}\sigma_P}^{\sqrt{2}\sigma_P}\Bigg[&\frac{1}{\pi}\exp\,(-F_P^2/\sigma_Q^2) \\ &+\frac{\cos\theta}{\sqrt{\pi}}\,\frac{|F_P|}{\sigma_Q}\exp\,(-F_P^2\sin{}^2\theta/\sigma_Q^2)\{1 \\ &+\operatorname{erf}\,(|F_P|\cos\theta/\sigma_Q)\}\Bigg]\frac{dF_P}{\pi\sqrt{2}\sigma_P\sqrt{1-(F_P^2/2\sigma_P^2)}} \end{aligned} \qquad (12)$$

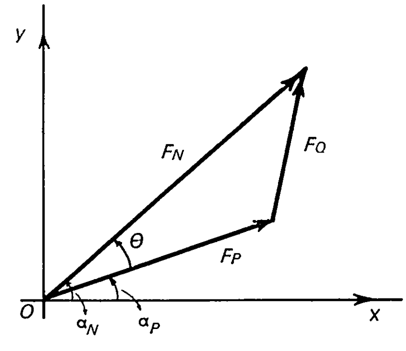


Fig. 1. The Argand diagram representing the structure factor of a reflexion $H(=hkl)$ in terms of the contributions from the P- and the Q-atoms.

Since the integrand involves $|F_P|$ and F_P^2, it is an even function of F_P and hence (12) can be written

$$\begin{aligned} P(|\theta|)=\ &\frac{2}{\pi^2\sqrt{2}\sigma_P}\int_0^{\sqrt{2}\sigma_P}\frac{\exp\,(-F_P^2/\sigma_Q^2)dF_P}{\sqrt{1-(F_P^2/2\sigma_P^2)}} \\ &+\frac{2\cos\theta}{\pi^{3/2}\sqrt{2}\sigma_P\sigma_Q}\int_0^{\sqrt{2}\sigma_P}\frac{|F_P|\exp\,(-F_P^2\sin^2\theta/\sigma_Q^2)}{\sqrt{1-(F_P^2/2\sigma_Q^2)}}\Bigg)\Bigg[1 \\ &+\operatorname{erf}\left(\frac{|F_P|\cos\theta}{\sigma_Q}\right)\Bigg]dF_P=I_1+I_2\,,\ \text{say}\,. \end{aligned} \qquad (13)$$

Using (A-1) (Appendix A) for the first integral I_1 and substituting $(F_P/\sqrt{2}\sigma_P)=x$ in the second integral I_2 in the right hand side of (14), we obtain

$$\begin{aligned} P(|\theta|)=\ &\frac{1}{\pi}\exp\,(-\sigma_1^2/\sigma_2^2)I_0(\sigma_1^2)/\sigma_2^2 \\ &+\frac{2b}{\pi^{3/2}}\int_0^1\frac{x\exp\,(-a^2x^2)}{\sqrt{1-x^2}}\,[1+\operatorname{erf}\,(bx)]dx\,, \end{aligned} \qquad (14)$$

where for simplicity we have put

$$a=\sqrt{2}\sigma_1\sin\theta/\sigma_2 \quad \text{and} \quad b=\sqrt{2}\sigma_1\cos\theta/\sigma_2\,. \qquad (15)$$

On integration, (14) gives [see Appendix A, equations (A-2), (A-4) and (A-9)]

$$\begin{aligned} P(|\theta|)=\ &\frac{1}{\pi}\exp\,(-\sigma_1^2/\sigma_2^2)I_0(\sigma_1^2/\sigma_2^2)+\frac{2b}{\pi^{3/2}}\,{}_1F_1(1\,;\tfrac{3}{2};\,-a^2) \\ &+\frac{2b^2}{\pi^2}\sum_{n=0}^{\infty}\frac{(-c)^n}{n!}\,\beta(n+\tfrac{3}{2},\,\tfrac{1}{2})\,{}_2F_2(1,\,n+\tfrac{3}{2};\,{}^3/_2,\,n+2;\,b^2)\,, \end{aligned} \qquad (16)$$

where $c=a^2+b^2=2\sigma_1^2/\sigma_2^2$. Expanding the hypergeometric function in the form of a series, (16) becomes

$$\begin{aligned} P(|\theta|)=\ &\frac{1}{\pi}\exp\,(-\sigma_1^2/\sigma_2^2)I_0(\sigma_1^2/\sigma_2^2)+\frac{b}{\pi}\sum_{n=0}^{\infty}\frac{(-a^2)^n}{\Gamma(n+\frac{3}{2})} \\ &+\frac{b^2}{\pi}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{(-c)^n\Gamma(m+n+\frac{3}{2})b^{2m}}{\Gamma(n+1)\Gamma(m+n+2)\Gamma(m+\frac{3}{2})}\,. \end{aligned} \qquad (17)$$

The series on the right hand side of (17) can be easily evaluated for small values of σ_1^2, say $\sigma_1^2\simeq 0{\cdot}2$. However, the convergence of the series rapidly decreases as σ_1^2 increases, so that it is not convenient to use (17) for moderate and large values of σ_1^2. For such values of σ_1^2 it is more convenient to obtain $P(|\theta|)$ by numerical integration. However, (14) is not convenient for numerical integration since the integrand has a singularity at $x=1$. To make it suitable for numerical integration, (14) can be modified and written as follows (see Appendix A, equations (A-2) and (A-12)]:

$$\begin{aligned} P(|\theta|)=\ &\frac{1}{\pi}\exp\,(-\sigma_1^2/\sigma_2^2)I_0(\sigma_1^2/\sigma_2^2) \\ &-\frac{2a^2b}{\pi^{3/2}}\int_0^1\sqrt{1-y}\exp\,(-a^2y)[1+\operatorname{erf}(b\sqrt{y})]dy \\ &+\frac{2b}{\pi^{3/2}}+\frac{4b^2}{\pi^2}\int_0^1\sqrt{1-y^2}\exp\,(-2\sigma_1^2y^2/\sigma_2^2)dy\,. \end{aligned} \qquad (18)$$

To obtain $P(|\theta|)$ these integrals were evaluated by a numerical method for particular values of σ_1^2, say $\sigma_1^2=0{\cdot}4$, $0{\cdot}6$ and $0{\cdot}8$.

(*c*) *Many-atom case* (*P-group centrosymmetric*)

If we choose the origin at the centre of inversion of the P-group, F_P will be real and the density function of F_P will be given by

$$P(F_P)=(1/\sqrt{2\pi\sigma_P^2})\exp(-F_P^2/2\sigma_P^2)\ ;\quad |F_P|\le\infty\ . \tag{19}$$

Using (19) and (7) in (8), the density function of $|\theta|$ is given by

$$P(|\theta|)=\int_{-\infty}^{+\infty}\frac{\exp(-F_P^2/2\sigma_P^2)}{\sqrt{2\pi\sigma_P^2}}\left\{\frac{1}{\pi}\exp(-F_P^2/\sigma_Q^2)+\frac{|F_P|\cos\theta}{\sqrt{\pi}\sigma_Q}\exp(-F_P^2\sin^2\theta/\sigma_Q^2)\left[1+\operatorname{erf}\left(\frac{|F_P|\cos\theta}{\sigma_Q}\right)\right]\right\}dF_P\ . \tag{20}$$

It is now convenient to use the simplifying substitutions

$$\frac{1}{\varrho_0^2}=\frac{1}{2\sigma_P^2}+\frac{1}{\sigma_Q^2}=\frac{1+\sigma_1^2}{2\sigma_1^2\sigma_2^2\sigma_N^2}\ , \tag{21a}$$

and

$$\frac{1}{\varrho^2}=\frac{1}{2\sigma_P^2}+\frac{\sin^2\theta}{\sigma_Q^2}=\frac{1+\sigma_1^2-2\sigma_1^2\cos^2\theta}{2\sigma_1^2\sigma_2^2\sigma_N^2}\ . \tag{21b}$$

Since the integrand in (20) involves only $|F_P|$ and F_P^2, it is an even function of the real variable F_P. Hence from (20) and (21), the density function of $|\theta|$ can be shown to be

$$P(|\theta|)=\frac{\sqrt{2}}{\pi^{3/2}\sigma_1\sigma_N}\int_0^\infty\exp(-F_P^2/\varrho_0^2)dF_P+\frac{\sqrt{2}\cos\theta}{\pi\sigma_1\sigma_2\sigma_N^2}\int_0^\infty|F_P|\exp(-F_P^2/\varrho^2)[1+\operatorname{erf}(|F_P|\cos\theta/\sigma_2\sigma_N)]dF_P=I_3+I_4\ ,\quad\text{say}\ . \tag{22}$$

This gives on integration (see Appendix B, equation (B-1) and (B-5)]

$$P(|\theta|)=\frac{\sigma_2}{\pi\sqrt{1+\sigma_1^2}}+\frac{\sqrt{2}\sigma_1\sigma_2\cos\theta}{\pi(1+\sigma_1^2-2\sigma_1^2\cos^2\theta)}\left[1+\frac{\sqrt{2}\sigma_1\cos\theta}{\sqrt{1+\sigma_1^2}}\right]\ . \tag{23}$$

(*d*) *Many-atom case* (*P-group non-centrosymmetric*)

Contrary to the previous cases where F_P was a real structure factor, (because the P-group was centrosymmetric with the origin at the inversion centre), the structure factor F_P is here complex. The density function of F_P is given by

$$P(F_P)=(1/\pi\sigma_P^2)\exp(-|F_P|^2/\sigma_P^2)\ ;\quad 0\le|F_P|\le\infty\quad\text{and}\quad-\pi\le\operatorname{Arg}F_P\le\pi\ . \tag{24}$$

In this case dF_P in (8) represents an element of area, namely $|F_P|d|F_P|d\theta_P$. Hence substituting (24) and (7) in (8), the density function of $|\theta|$ will be given by

$$P(|\theta|)=\frac{1}{\pi\sigma_P^2}\int_{|F_p|=0}^{\infty}\int_{-\pi}^{\pi}\exp\left(-\frac{|F_P|^2}{\sigma_P^2}\right)\left[\frac{\exp(-|F_P|^2/\sigma_Q^2)}{\pi}+\frac{|F_P|\cos\theta}{\sqrt{\pi}\sigma_Q}\exp\left(-\frac{|F_P|^2\sin^2\theta}{\sigma_Q^2}\right)\left\{1+\operatorname{erf}\left(\frac{|F_P|\cos\theta}{\sigma_Q}\right)\right\}\right]|F_P|d|F_P|d\theta_P\ . \tag{25}$$

Since the integrand in (25) is not an explicit function of θ_P, the integration over θ_P gives 2π. Further if we use the simplifying notations,

$$\frac{1}{k_0^2}=\frac{1}{\sigma_P^2}+\frac{1}{\sigma_Q^2}=\frac{1}{\sigma_1^2\sigma_2^2\sigma_N^2}\ , \tag{26a}$$

and

$$\frac{1}{k^2}=\frac{1}{\sigma_P^2}+\frac{\sin^2\theta}{\sigma_Q^2}=\frac{1-\sigma_1^2\cos^2\theta}{k_0^2}\ , \tag{26b}$$

in (25), the density function of $|\theta|$ will be given by

$$P(|\theta|)=\frac{2}{\pi\sigma_1^2\sigma_N^2}\int_0^\infty\left[\exp(-|F_P|^2/k_0^2)+\frac{\sqrt{\pi}|F_P|\cos\theta}{\sigma_2\sigma_N}\exp(-|F_P|^2/k^2)\left\{1+\operatorname{erf}\left(\frac{|F_P|\cos\theta}{\sigma_2\sigma_N}\right)\right\}\right]|F_P|d|F_P|\ , \tag{27}$$

which on integration gives [see Appendix C, equations (C-2), (C-3) (C-4) and (C-9)]

$$P(|\theta|)=\frac{\sigma_2^2}{\pi}+\frac{\sigma_1^2\sigma_2^2\cos^2\theta}{\pi(1-\sigma_1^2\cos^2\theta)}+\frac{\sigma_1\sigma_2^2\cos\theta}{(1-\sigma_1^2\cos^2\theta)^{3/2}}\left[\tfrac{1}{2}+\frac{1}{\pi}\tan^{-1}\left(\frac{\sigma_1\cos\theta}{\sqrt{(1-\sigma_1^2\cos^2\theta)}}\right)\right]. \tag{28}$$

It is possible to show that the density functions (10), (18), (23) and (28) are in the normalized form, since they satisfy the normalization integral

$$\int_0^\pi P(|\theta|)d\theta=1\ . \tag{29}$$

However, the integral (29) was not evaluated by an analytical method since the integrand is a complicated function of $|\theta|$ in each case. The integration was performed by a numerical method which was necessary to evaluate the cumulative function $N(\theta)$ (see below). This established that the integral (29) is unity. Further the density function must satisfy two other physical conditions, namely that $P(|\theta|)=1/\pi$ when there is no heavy atom in the unit cell and that $P(|\theta|)=\delta(\theta)$ when the light atom contribution tends to zero. This means that the following limits should hold:

$$P(|\theta|)\to 1/\pi\quad\text{as}\quad\sigma_1^2\to 0\quad\text{and}\quad\sigma_2^2\to 1\ , \tag{30}$$

$$P(|\theta|)\to\delta(\theta)\quad\text{as}\quad\sigma_1^2\to 1\quad\text{and}\quad\sigma_2^2\to 0\ . \tag{31}$$

It is readily shown that both results are satisfied by all the density functions.

Discussion of the theoretical results

The cumulative function of $|\theta|$, namely $N(|\theta|) = \int_0^{|\theta|} P(|\theta|)d\theta$, has been evaluated by numerical integration corresponding to $\sigma_1^2 = 0{\cdot}2$, 0·4, 0·6 and 0·8 for the various cases and results are given in Table 1. However, only the values for the two-atom case are plotted in Fig. 2 in order to show the general nature of the function $N(\theta)$. The horizontal line $N(\theta) = 1$ represents the cumulative function for $\sigma_1^2 = 1{\cdot}0$ while the line $N(|\theta|) = |\theta|/\pi$ represents that for $\sigma_1^2 = 0$. For any intermediate values of σ_1^2 the corresponding curve should lie between these two straight lines.

Table 1. *Cumulative function* $N(|\theta|)$ *for the different cases at different heavy-atom contributions* σ_1^2

The four cases are those in which the known *P*-group consists of (*A*) one-atom, (*B*) two atoms, (*C*) many atoms, non-centrosymmetric, (*D*) many atoms, centrosymmetric.

$\sigma_1{}^2$	$\lvert\theta\rvert$	0°	30°	60°	90^c	120°	150°	180°
0·2	*A*	0	33·7	59·4	76·0	86·6	94·0	100
	B	0	31·5	56·6	73·0	84·0	92·5	100
	C	0	31·2	56·0	72·0	83·7	92·0	100
	D	0	30·0	53·5	69·5	81·5	91·0	100
0·4	*A*	0	46·2	75·5	88·5	94·4	98·0	100
	B	0	43·3	69·2	82·3	90·0	95·5	100
	C	0	42·5	68·0	81·5	89·5	95·0	100
	D	0	39·5	63·5	77·5	86·5	93·2	100
0·6	*A*	0	62·0	88·5	96·0	98·1	99·0	100
	B	0	56·5	80·1	89·0	94·0	97·6	100
	C	0	55·0	78·9	88·5	93·8	97·2	100
	D	0	50·0	72·3	83·0	90·2	95·0	100
0·8	*A*	0	83·0	98·7	99·8	99·9	99·9	100
	B	0	72·5	88·6	93·5	96·3	98·0	100
	C	0	71·5	89·3	94·5	97·1	98·5	100
	D	0	63·2	81·6	89·0	93·7	97·0	100

The results of the theory can be used to discuss the general nature of the heavy-atom method from the point of view of the number (P) and fractional contribution σ_1^2 of the heavy atoms in the unit cell. In general, a larger value of $N(|\theta|)$ for a given $|\theta|$ will be more favourable for the determination of a structure by the heavy-atom method. This is so because the larger the value of $N(|\theta|)$, the larger will be the probable number of reflexions for which the phase-angle error $\theta(=\alpha_N - \alpha_P)$ will be smaller in magnitude than $|\theta|$ and the more nearly will the Fourier synthesis using the phases α_P resemble the true electron-density diagram (see *e.g.* Sim, 1961). However, as we have seen, $N(|\theta|)$ for a given $|\theta|$ and σ_1^2 depends on the number of heavy atoms. To have a direct comparison of the different cases, the function $N(|\theta|)$ for the four cases is plotted on a single diagram (Fig. 3) for a particular value of $\sigma_1^2 = 0{\cdot}6$. From Fig. 3 and Table 1 it is easy to see that, for a given value of σ_1^2,

$$\langle\theta\rangle_1 < \langle\theta\rangle_2 \simeq \langle\theta\rangle_{M\cdot A} < \langle\theta\rangle_{M\cdot C}$$

where the subscripts to the expectation symbol refer to the number of heavy atoms in the unit cell. Since the case in which the mean phase angle error, *i.e.* $\langle\theta\rangle$, is smaller would be more favourable for structure determination by the heavy-atom method, the cases with $P=1$ or 2 seem to be more favourable than the many-atom case. However, from the point of view of interpreting the γ'-synthesis, the many-atom case with a non-centrosymmetric P-group is more favourable than the others. This is because the spurious duplication of the structure about the centre of symmetry of the P-group, occurring in the cases with $P=1$ or 2 will not arise in the many-atom case with a non-centrosymmetric P-group. Further, since the terms for which $|F_P| \simeq 0$ are omitted in the pratical computing of the γ'-syntheses, the actual distribution of $|F_P|$ is also important in determining the success of the heavy-atom method as this depends on the number of terms that can be put in the early Fourier syntheses. The percentage of reflexions for which $y_P(=|F_P|/\sigma_P)$ is less than say 0·1 is larger when the P-group of atom is centrosymmetric than when it is non-centrosymmetric (the case $P=1$ being an exception). Thus from a practical point of view of including more terms (obviously when $P=1$, every term can be included), and from the point of view of interpreting the heavy-atom-phased Fourier syntheses, the many-atom case with a non-centrosym-

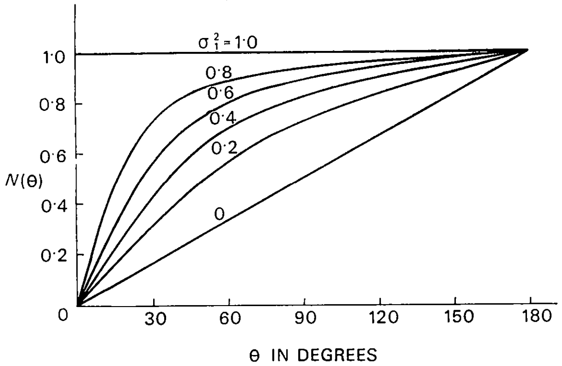


Fig. 2. The cumulative function of $|\theta| = |\alpha_N - \alpha_P|$ for the two-atom case. The number given near each curve represents the value of $\sigma_1{}^2$.

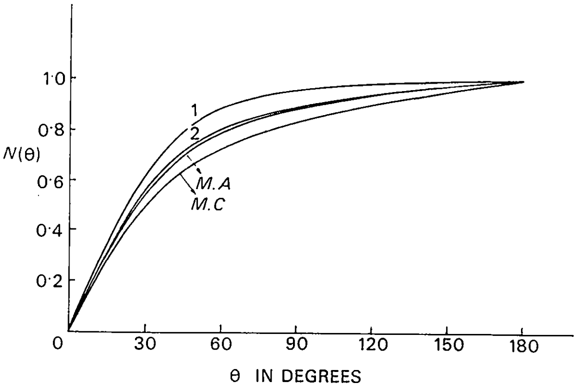


Fig. 3. The cumulative function of $|\theta| = |\alpha_N - \alpha_P|$ for the various cases corresponding to $\sigma_1{}^2 = 0{\cdot}6$. The symbols 1, 2, *MA* and *MC* near the curves respectively represent the one-, two-, many-atom (*P*-group non-centrosymmetric) and many-atom (*P*-group centrosymmetric) cases.

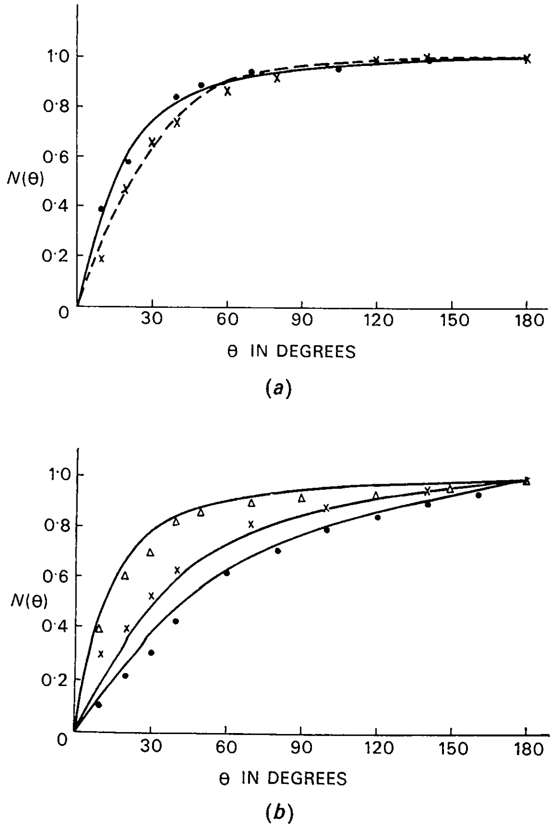
metric P-group is more favourable than the others. It may, however, be noted that all terms can be included in the γ'-synthesis by employing a simple weighting function which becomes useful in improving the resolution of the unknown atoms, especially when the heavy-atom contribution is small (For details see Blow & Crick, 1959 and Sim, 1960).

From Fig. 3 and Table 1 it is easily seen that the mean phase-angle error $\langle\theta\rangle_P$ for a given number (P) of heavy atoms in the unit cell decreases as σ_1^2 increases. Thus, α_P would become closer to α_N as σ_1^2 increased. Since better phase information leads to better resolution of the unknown atoms, it follows from the above that the resolution of the Q-atoms improves with increasing value of σ_1^2. This result deduced qualitatively is in agreement with that obtained by Luzzati (1953), who has considered the question of resolution of the unknown atoms in a quantitative way using statistical methods.

It would be worth while comparing the cases of a centrosymmetric and a non-centrosymmetric crystal having the same value of σ_1^2 and the same number of heavy atoms. This could be done by comparing the values of $P(+)$ in Table 1 of part I with the values of $N(\theta)$ in Table 1 of this part. For example, we may take the case of one heavy atom having the value of $\sigma_1^2=0{\cdot}6$. From part I we see that 89% of the reflexions are likely to have the same phase as the heavy atoms. On the other hand, as shown in Table 1 of this part, only 62% of the reflexions have a phase-angle error $\theta\leq 30°$ in this case. Consequently, it is clear the centrosymmetric case is much more favourable for solution by the heavy-atom technique. This is true not only because $P(+)$ is appreciably higher than $N(30°)$, but also because in the centrosymmetric case when the sign is positive the phase is *exactly* correct and equal to the heavy-atom phase. A similar relation is found for the other values of σ_1^2 and with other types of P-atom groups. It may be stated as a general proposition that a centrosymmetric crystal (or projection) will be much easier to solve than a non-centrosymmetric crystal (or projection) under similar conditions. This broadly agrees with the experience of structure analyses (see also Sim, 1957). This also agrees with Luzzati's result (1953) that in the γ'-synthesis the expected height of an atomic peak corresponding to an atom of the Q-type is greater when the crystal is centrosymmetric than when it is non-centrosymmetric, under similar conditions.

It was mentioned in part I that, in connection with the resolution of the twofold ambiguity in the process of phase determination by the anomalous-dispersion method, it would be useful to know the frational number of reflexions for which $\theta\leq 90°$ for a given σ_1^2 corresponding to the various cases. The required data are now available in the middle column of Table 1. From this table it is clear that, if we choose the acute angle (say θ_0) out of the two possibilities, namely θ and $\pi-\theta$, then the percentage of reflexions whose phases are correctly determined will be a maximum when P is just one in number and is least when the P-group consists of many atoms with a centrosymmetric configuration. However, the few reflexions for which the true phase is actually equal to the obtuse angle $\pi-\theta_0$ would lead to wrong Fourier coefficients if we choose the acute angle for all the reflexions and such wrong coefficients will lead to spurious details in the Fourier map. In such cases, it seems useful to use a weighting function in which both the possible phases are given weights according to the probabilities with which they occur. Such a weighting function has been derived in this department. This weighting function is under test and the results will be published separately (Parthasarthy, Ramachandran & Srinavasan, 1964).

The results of the theory have been tested with the data from actual crystals as well as hypothetical two-dimensional models. The complete data regarding the tests are given in Table 2. In each case the mean value of σ_1^2, say $\langle\sigma_1^2\rangle$, was obtained as described in part I and the theoretical curve corresponding to the value of $\langle\sigma_1^2\rangle$ was drawn by interpolation. The experimental data in each case are seen to agree with the corresponding theoretical curve, as is evident from Fig. 4.



(a)

(b)

Fig. 4. Verification of the cumulative functions $N(\theta)$ for (a) the one-atom and many-atom (P-acentric) cases and (b) the two-atom case respectively.
In (a) ● = P_4S_5 and × = the one-atom case; in (b) ▲ = L-tyrosine HBr, × = L-tyrosine HCl and ● = cellobiose plus two chlorine atoms.

The author wishes to express his thanks to Professor G. N. Ramachandran and Dr R. Srinivasan for the useful discussion he had with them during the course of this work. He wishes to thank Dr K. Venkatesan for having suggested the problem. He also wishes to thank the referees for their useful comments. Finally, his thanks are due to the Council of Scientific and Industrial Research for the award of a Junior Research Fellowship during the tenure of which this work was done.

APPENDIX A

If we substitute $F_P/\sqrt{2}\sigma_P = \cos(\varphi/2)$ in the first term on the right hand side of (13), we get

$$I_1 = \frac{1}{\pi^2}\int_0^\pi \exp[-2\sigma_1^2 \cos^2(\varphi/2)/\sigma_2^2]d\varphi$$

$$= \frac{1}{\pi^2}\exp(-\sigma_1^2/\sigma_2^2)\int_0^\pi \exp(-\sigma_1^2 \cos\varphi/\sigma_2^2)d\varphi$$

$$= \frac{1}{\pi}\exp(-\sigma_1^2/\sigma_2^2)I_0(\sigma_1^2/\sigma_2^2)\,, \qquad (A\text{-}1)$$

where $I_0(x)$ is the Bessel function of imaginary argument, of order zero. The second term on the right-hand side of (14) can be written

$$\frac{2b}{\pi^{3/2}}\int_0^1 \frac{x\exp(-a^2x^2)}{\sqrt{1-x^2}}dx$$
$$+\frac{2b}{\pi^{3/2}}\int_0^1 \frac{x\exp(-a^2x^2)}{\sqrt{1-x^2}}\operatorname{erf}(bx)dx = I'+I''\,,\ \text{say.} \qquad (A\text{-}2)$$

If we expand $\exp(-x)$ in terms of hypergeometric series (Sneddon, 1961; problem 11(i) p. 46), then I' becomes

$$I' = \frac{2b}{\pi^{3/2}}\int_0^1 \frac{x\,{}_1F_1(\alpha;\alpha;-a^2x^2)}{\sqrt{1-x^2}}dx\,. \qquad (A\text{-}3)$$

Making the substitution $x^2=y$ in (A-3) we get

$$I' = \frac{b}{\pi^{3/2}}\int_0^1 (1-y)^{-\frac{1}{2}}\,{}_1F_1(\alpha;\alpha;-a^2y)dy\,,$$

which on integration becomes (Sneddon, 1961; p. 47, problem 16(i)]

$$I' = \frac{b}{\pi^{3/2}}\beta(1,\tfrac{1}{2})\,{}_2F_2(\alpha,1;\alpha,\tfrac{3}{2};-a^2)$$

$$= \frac{2b}{\pi^{3/2}}\,{}_1F_1(1;\tfrac{3}{2};-a^2). \qquad (A\text{-}4)$$

If erf (x) is represented by the hypergeometric function, I'' in (A-2) can be written (Erdelyi, 1954, Vol. 2, p. 295)

$$I'' = \frac{2b}{\pi^{3/2}}\int_0^1 \frac{x\exp(-a^2x^2)}{\sqrt{1-x^2}}\times$$
$$\frac{2bx}{\sqrt{\pi}}\exp(-b^2x^2)\,{}_1F_1(1;\tfrac{3}{2};b^2x^2)dx\,. \qquad (A\text{-}5)$$

On substitution $x^2=y$, (A-5) becomes

$$I'' = \frac{2b^2}{\pi^2}\int_0^1 y^{\frac{1}{2}}(1-y)^{-\frac{1}{2}}\exp(-cy)\,{}_1F_1(1;\tfrac{3}{2};b^2y)dy\,, \qquad (A\text{-}6)$$

where

$$a^2+b^2=(2\sigma_1^2/\sigma_2^2)(\cos^2\theta+\sin^2\theta)=2\sigma_1^2/\sigma_2^2=c\,. \qquad (A\text{-}7)$$

Expanding $\exp(-cy)$ into a power series, (A-7) can be written

$$I'' = \frac{2b^2}{\pi^2}\sum_{n=0}^{\infty}\frac{(-c)^n}{n!}\int_0^1 y^{n+\frac{1}{2}}(1-y)^{-\frac{1}{2}}\,{}_1F_1(1;\tfrac{3}{2};b^2y)dy\,, \qquad (A\text{-}8)$$

which on integration becomes [Sneddon, 1961; p. 47, problem 16(i)]

$$I'' = \frac{2b^2}{\pi^2}\sum_{n=0}^{\infty}\frac{(-c)^n}{n!}\beta(n+\tfrac{3}{2},\tfrac{1}{2})\,{}_2F_2(1,n+\tfrac{3}{2};\tfrac{3}{2},n+2;b^2)\,. \qquad (A\text{-}9)$$

Table 2. *Details of the crystals used for the verification of the theoretical results*

No.*	Type	Crystal	Plane Plane	$\sigma_1{}^2$	$N(90°)$ Theoretical	Experimental
1	One-atom case	Hypothetical (C_9Cl)	*p*1	0·615	96·0 %	94·7 %
2	Two-atom case	L-tyrosine HBr $C_9H_{11}NO_3HBr$	*pg*	0·843	94·8	91·3
3	Two-atom case	L-tyrosine HCl $C_9H_{11}NO_3HCl$	*pg*	0·474	84·8	88·1
4	Two-atom case	Hypothetical– Cellobiose+2Cl $C_{12}O_{11}H_{22}Cl$	*pg*	0·3	77·0	75·8
5	Many-atom case (*P*-group non-centrosymmetric)	Based on phosphorus pentasulphide $P_4S_2(3S)_3$	*pg*	0·82	94·8	93·8

* 1. This 2-dimensional hypothetical structure (C_9Cl) consists of 9 carbon atoms and 1 chlorine atom randomly distributed in a rectangular cell.
2. This crystal was solved by Srinivasan (1959*a*).
3. This crystal was solved by Srinivasan (1959*b*).
4. Into the structure of cellobiose (Jacobson, Wunderlich & Lipscomb, 1961) two chlorine atoms were introduced to make it a hypothetical structure with heavy atoms.
5. In the structure of P_4S_5 (van Houten & Wiebinga, 1957) three of the sulphur atoms in the asymmetric unit were assumed to scatter three times as strongly as a 'real' sulphur atom (see Ramachandran & Ayyar, 1963) and this makes the structure a suitable hypothetical crystal with heavy atoms.

In (A-2), if we put $x^2=y$, we get

$$I'+I''=\frac{b}{\pi^{3/2}}\int_0^1(1-y)^{-\frac{1}{2}}\exp(-a^2y)[1+\operatorname{erf}(b\sqrt{y})]dy$$

$$=-\frac{2b}{\pi^{3/2}}\int_0^1\exp(-a^2y)[1+\operatorname{erf}(b\sqrt{y})]d\sqrt{1-y}\,,$$

which on integration by parts gives

$$I'+I''=-\frac{2b}{\pi^{3/2}}\left[\exp(-a^2y)\{1+\operatorname{erf}(b\;\sqrt{y})\}\sqrt{1-y}\right]_0^1$$

$$+\frac{2b}{\pi^{3/2}}\int_0^1\sqrt{1-y}\;d[\exp(-a^2y)\{1+\operatorname{erf}(b\sqrt{y})\}]\;. \quad (A\text{-}10)$$

Since the first term on the right-hand side vanishes, and since

$$d[\operatorname{erf}(b\sqrt{y})]=b\exp(-b^2y)/\sqrt{\pi y}\,, \quad (A\text{-}10)$$

can be written

$$I'+I''=\frac{2b}{\pi^{3/2}}$$

$$-\frac{2a^2b}{\pi^{3/2}}\int_0^1(1-y)^{\frac{1}{2}}\exp(-a^2y)\;[1+\operatorname{erf}(b\sqrt{y})]dy$$

$$+\frac{2b^2}{\pi^2}\int_0^1 y^{-\frac{1}{2}}(1-y)^{\frac{1}{2}}\exp[-(a^2+b^2)y]dy\;. \quad (A\text{-}11)$$

Putting $\sqrt{y}=z$, the last term in (A-11) becomes

$$\frac{4b^2}{\pi^2}\int_0^1\sqrt{1-z^2}\exp(-2\sigma_1^2z^2/\sigma_2^2)dz\;.$$

However, z is a dummy variable so that for uniformity of representation it can be replaced by y. Hence (A-11) becomes

$$I'+I''=\frac{2b}{\pi^{3/2}}$$

$$-\frac{2a^2b}{\pi^{3/2}}\int_0^1\sqrt{1-y}\exp(-a^2y)[1+\operatorname{erf}(b\sqrt{y})]dy$$

$$+\frac{4b^2}{\pi^2}\int_0^1\sqrt{1-y^2}\exp(-2\sigma_1^2y^2/\sigma_2^2)dy\;. \quad (A\text{-}12)$$

APPENDIX B

We shall first work out the integral I_3 in (22). This is

$$I_3=\frac{\sqrt{2}}{\pi^{3/2}}\frac{\varrho_0}{\sigma_1\sigma_N}\int_0^\infty\exp(-F_P^2/\varrho_0^2)d(F_P/\varrho_0)$$

$$=\frac{\varrho_0}{\pi\sqrt{2}\,.\,\sigma_1\sigma_N}\,,$$

which, on making the substitution from (21a), becomes

$$I_3=\sigma_2/\pi\sqrt{1+\sigma_1^2}\,. \quad (B\text{-}1)$$

The second integral in (22) is I_4, namely

$$I_4=\frac{\sqrt{2}\cos\theta}{\pi\sigma_1\sigma_2\sigma_N^2}\int_0^\infty|F_P|\exp(-|F_P|^2/\varrho^2)[1$$
$$+\operatorname{erf}(|F_P|\cos\theta/\sigma_2\sigma_N)]dF_P$$

$$=-\frac{\varrho^2\cos\theta}{\pi\sqrt{2}\sigma_1\sigma_2\sigma_N^2}\int_0^\infty[1$$
$$+\operatorname{erf}(|F_P|\cos\theta/\sigma_2\sigma_N)]d[\exp(-|F_P|^2/\varrho^2)]\,,$$

which, on integration by parts, gives

$$I_4=-k_1^2[\{1+\operatorname{erf}(k_2F_P)\}\exp(-F_P^2/\varrho^2)]_0^\infty+$$
$$+k_1^2\int_0^\infty\exp(-F_P^2/\varrho^2)d[1+\operatorname{erf}(k_2F_P)]\,. \quad (B\text{-}2)$$

Here

$$k_1^2=\frac{\varrho^2\cos\theta}{\pi\sqrt{2}\sigma_1\sigma_2\sigma_N^2}=\frac{\sqrt{2}\sigma_1\sigma_2\cos\theta}{\pi(1+\sigma_1^2-2\sigma_1^2\cos^2\theta)}\,,$$

and

$$k_2=\cos\theta/\sigma_2\sigma_N\,, \quad (B\text{-}3)$$

where (21b) has been used. Since $d[\operatorname{erf}(k_2F_P)]=(2k_2/\sqrt{\pi})\exp(-k_2^2F_P^2)$, ($B$-2)simplifies to

$$I_4=k_1^2+\frac{2k_1^2k_2}{\sqrt{\pi}}\int_0^\infty\exp\left[-\left(\frac{1}{\varrho^2}+k_2^2\right)F_P^2\right]dF_P$$
$$=k_1^2+\left\{k_1^2k_2/\sqrt{k_2^2+(1/\varrho^2)}\right\}\cdot \quad (B\text{-}4)$$

Substituting for k_1, k_2 and ϱ from (B-3) and (21b), (B-4) gives

$$I_4=\frac{\sqrt{2}\,.\,\sigma_1\sigma_2\cos\theta}{\pi(1+\sigma_1^2-2\sigma_1^2\cos^2\theta)}\left[1+\frac{\sqrt{2}\sigma_1\cos\theta}{\sqrt{1+\sigma_1^2}}\right]. \quad (B\text{-}5)$$

APPENDIX C

If we put

$$\frac{2\cos\theta}{\sqrt{\pi\sigma_1^2\sigma_2\sigma_N^3}}=p_1 \text{ and } \frac{\cos\theta}{\sigma_2\sigma_N}=p_2 \quad (C\text{-}1)$$

in (27), we have

$$P(|\theta|)=\frac{2}{\pi\sigma_1^2\sigma_N^2}\int_0^\infty|F_P|\exp(-|F_P|^2/k_0^2)d|F_P|$$
$$+p_1\int_0^\infty|F_P|^2\exp(-|F_P|^2/k^2)d|F_P|$$
$$+p_1\int_0^\infty|F_P|^2\exp(-|F_P|^2/k^2)\operatorname{erf}(p_2|F_P|)d|F_P|$$
$$=I_5+I_6+I_7\,,\text{ say}\;. \quad (C\text{-}2)$$

On integration, I_5 gives

$$I_5=(k_0^2/\pi\sigma_1^2\sigma_2^2)=\sigma_2^2/\pi\,, \quad (C\text{-}3)$$

since

$$k_0^2=\sigma_1^2\sigma_2^2\sigma_N^2 \text{ (equation 26}a\text{)}.$$

Using equation 381, p. 820 of Korn & Korn (1961), I_6 becomes $\sqrt{\pi}p_1k^3/4$, which on substitution for p_1 and k from (C-1) and (26b), gives

$$I_6=\frac{\sigma_1\sigma_2^2\cos\theta}{2(1-\sigma_1^2\cos^2\theta)^{3/2}}\,. \quad (C\text{-}4)$$

From (C-2), I_7 can be written

$$I_7=-\frac{k^2p_1}{2}\int_0^\infty|F_P|\operatorname{erf}(p_2|F_P|)d[\exp(-|F_P|^2/k^2)]\,,$$

which on integration by parts gives

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

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

$$I_7 = \frac{k^2p_1}{2}\int_0^\infty \exp(-|F_P|^2/k^2) \operatorname{erf}(p_2|F_P|)d|F_P|$$
$$+\frac{k^2p_1p_2}{\sqrt{\pi}}\int_0^\infty |F_P| \exp[-(1/k^2+p_2^2)|F_P|^2]d|F_P|$$
$$= I_7^1 + I_7^{11} \text{, say} \,. \qquad (C\text{-}6)$$

Now

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

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

$$I_7 = \frac{p_1k^3}{2}\int_0^\infty \exp(-y^2) \operatorname{erf}(p_2ky)dy$$
$$+\frac{p_1p_2k^2k_0^2}{2\sqrt{\pi}}\int_0^\infty \exp(-|F_P|^2/k_0^2)d(|F_P|^2/k_0^2)$$
$$= \frac{p_1k^3}{2}\frac{1}{\sqrt{\pi}}\tan^{-1}(p_2k)+\frac{p_1p_2k^2k_0^2}{2\sqrt{\pi}} \,, \qquad (C\text{-}8)$$

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 26a, b), the equation (C-8) gives

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

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-