finite but small gaps. Since the coupling between first-order modes becomes important near the crossing, the normal modes in this region have elliptical polarization varying with the angle of incidence, and a more careful analysis is needed to obtain accurate fields and intensities. In particular, the polarization composition of reflected intensities from unpolarized sources becomes very complex around $x=-1$, and simple conceptual interpretations of three-beam effects using plane polarized modes and based on unpolarized incident radiation become inadequate.

As the details of the various crossings, such as in Fig. 6, depend intricately on the parameters of every specific three-beam case, it is unlikely that next-order perturbation solutions can be cast in the same universal form as the solutions discussed here.

In any case, since higher-order effects become important only in the region $|x|\lesssim 1$, they in no way obscure the major asymmetries at the heart of the first-order solutions that should be observable under good experimental conditions at much larger x.

This work was partly supported by Joint Services Electronics Program Contract No. F49620-82-C-0084. We also thank the referee for calling our attention to the paper by Watanabe *et al.*

References

AFANAS'EV, A. M. & PERSTNEV, I. P. (1969). *Acta Cryst.* **A25**, 520–523.
BATTERMAN, B. W. & COLE, H. (1964). *Rev. Mod. Phys.* **36**, 681–717.
BETHE, H. A. (1928). *Ann. Phys. (Leipzig)*, **87**, 55–129.
BONSE, U. & HART, M. (1965). *Appl. Phys. Lett.* **6**, 155–156.
BORRMANN, G. (1950). *Z. Phys.* **42**, 157–162.
CHANG, S. L. (1982). *Phys. Rev. Lett.* **48**, 163–166.
CHAPMAN, L. D., YODER, D. R. & COLELLA, R. (1981). *Phys. Rev. Lett.* **46**, 1578–1581.
COLELLA, R. (1974). *Acta Cryst.* **A30**, 413–423.
COWAN, P. L., GOLOVCHENKO, J. A. & ROBBINS, M. F. (1980). *Phys. Rev. Lett.* **44**, 1680–1683.
EWALD, P. P. (1916). *Ann. Phys. (Leipzig)*, **49**, 1–38.
EWALD, P. P. & HÉNO, Y. (1968). *Acta Cryst.* **A24**, 5–15.
FUES, E. (1938). *Z. Phys.* **109**, 236–259.
GJØNNES, J. (1962). *Acta Cryst.* **15**, 703–707.
GONG, P. P. (1983). PhD Thesis, Polytechnic Institute of New York.
HILDEBRANDT, G. (1967). *Phys. Status Solidi*, **24**, 245–261.
HILDEBRANDT, G. (1982). *J. Phys. E*, **15**, 1140–1155.
HÜMMER, K. & BILLY, H. W. (1982). *Acta Cryst.* **A38**, 841–848.
JAMES, R. W. (1963). *Solid State Phys.* **15**, 53–220.
JURETSCHKE, H. J. (1982*a*). *Phys. Rev. Lett.* **48**, 1487–1489.
JURETSCHKE, H. J. (1982*b*). *Phys. Lett.* **92A**, 183–185.
JURETSCHKE, H. J. & WASSERSTEIN-ROBBINS, F. (1982). *Phys. Rev. B*, **26**, 4262–4268.
KAMBE, K. & MIYAKE, S. (1954). *Acta Cryst.* **7**, 218–219.
KOHN, V. G. (1979). *Phys. Status Solidi A*, **54**, 375–384.
LAUE, M. VON (1960). *Roentgenstrahl-Interferenzen.* Frankfurt (Main): Akademische Verlagsgesellschaft.
LEROUX, S. D., COLELLA, R. & BRAY, R. (1975). *Phys. Rev. Lett.* **35**, 230–234.
MILLS, D. & BATTERMAN, B. W. (1980). *Phys. Rev. B*, **22**, 2887–2897.
NICOLOSI, J. (1982). PhD Thesis, Polytechnic Institute of New York.
POST, B. (1979). *Acta Cryst.* **A35**, 17–22.
STERN, R. M., PERRY, J. J. & BOUDREAUX, D. S. (1969). *Rev. Mod. Phys.* **41**, 275–295.
UEBACH, W. (1973). *Z. Naturforschung. Teil A*, **28**, 1214–1220.
WATANABE, D., UYEDA, R. & KOGISO, M. (1968). *Acta Cryst.* **A24**, 249–250.

Acta Cryst. (1984). A**40**, 389–394

The Distribution of $\alpha_{\mathbf{h}}$

BY G. CASCARANO AND C. GIACOVAZZO

Dipartimento Geomineralogico, Università, 70121 *Bari, Italy*

M. C. BURLA AND A. NUNZI

Istituto di Mineralogia dell'Università, 06100 *Perugia, Italy*

AND G. POLIDORI

Centro di Calcolo Elettronico dell'Università, 06100 *Perugia, Italy*

(*Received* 13 *October* 1983; *accepted* 25 *January* 1984)

Abstract

The asymptotic distribution of $\alpha_{\mathbf{h}}$ is calculated *via* the distribution of the resultant of complex random vectors whose phase values are distributed according to Von Mises distributions. The statistical results suggest that the phase of the resultant, say $\theta_{\mathbf{h}}$, is distributed around the phase $\varphi_{\mathbf{h}}$, approximately according to a Von Mises distribution.

Introduction

When several pairs of phases $\varphi_{\mathbf{k}_j}$, $\varphi_{\mathbf{h}-\mathbf{k}_j}$ are known, the conditional probability distribution of the phase

0108-7673/84/040389-06$01.50 © 1984 International Union of Crystallography

$\varphi_{\mathbf{h}}$ given the set $\{\varphi_{\mathbf{k}_j}, \varphi_{\mathbf{h}-\mathbf{k}_j}, G_j\}$ is a Von Mises distribution (Karle & Hauptman, 1956):

$$P(\varphi_{\mathbf{h}}|\{\varphi_{\mathbf{k}_j}, \varphi_{\mathbf{h}-\mathbf{k}_j}, G_j\}) \simeq [2\pi I_0(\alpha_{\mathbf{h}})]^{-1} \exp[\alpha_{\mathbf{h}} \cos(\varphi_{\mathbf{h}} - \theta_{\mathbf{h}})], \quad (1)$$

where $G_j = 2|E_{\mathbf{h}}E_{\mathbf{k}_j}E_{\mathbf{h}-\mathbf{k}_j}|/N^{1/2}$. $\theta_{\mathbf{h}}$ is the most efficient value for $\varphi_{\mathbf{h}}$ and is given by (Karle & Karle, 1966)

$$\tan\theta_{\mathbf{h}} = \frac{\sum_j |E_{\mathbf{k}_j}E_{\mathbf{h}-\mathbf{k}_j}| \sin(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j})}{\sum_j |E_{\mathbf{k}_j}E_{\mathbf{h}-\mathbf{k}_j}| \cos(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j})} = \frac{T_{\mathbf{h}}}{B_{\mathbf{h}}}, \quad (2)$$

where

$$\alpha_{\mathbf{h}} = 2N^{-1/2}|E_{\mathbf{h}}|(T_{\mathbf{h}}^2 + B_{\mathbf{h}}^2)^{1/2}. \quad (3)$$

Equation (1) will be represented by the symbol $M[\varphi_{\mathbf{h}}; \theta_{\mathbf{h}}, \alpha_{\mathbf{h}}]$, where the variable is in the first position, its expected value in the second and the concentration parameter $\alpha_{\mathbf{h}}$ in the third.

The parameter α plays a central role in the phasing procedures since the discovery (Karle & Karle, 1966) that the variance of a phase angle determined *via* (2) may be expressed as a function of α. To give some examples we notice:

(*a*) the expected value of α^2, that is

$$\alpha_E^2 = \sum_j G_{\mathbf{h},\mathbf{k}_j}^2 + \sum_{i\neq j} G_{\mathbf{h},\mathbf{k}_j} G_{\mathbf{h},\mathbf{k}_i} D_1(G_{\mathbf{h},\mathbf{k}_i}) D_1(G_{\mathbf{h},\mathbf{k}_j}), \quad (4)$$

where $D_i(x) = I_i(x)/I_0(x)$ and I_i is the modified Bessel function of order i, is used in the convergence procedure (Germain, Main & Woolfson, 1970) for choosing the starting reflexions;

(*b*) in the weighted tangent formulas (Germain, Main & Woolfson, 1971) such as

$$\tan\varphi_{\mathbf{h}} = \frac{\sum_j W_{\mathbf{k}_j} W_{\mathbf{h}-\mathbf{k}_j} |E_{\mathbf{k}_j}E_{\mathbf{h}-\mathbf{k}_j}| \sin(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j})}{\sum_j W_{\mathbf{k}_j} W_{\mathbf{h}-\mathbf{k}_j} |E_{\mathbf{k}_j}E_{\mathbf{h}-\mathbf{k}_j}| \cos(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j})} = \frac{T'_{\mathbf{h}}}{B'_{\mathbf{h}}}, \quad (5)$$

the correct weight to use should be inversely proportional to the variance and, to a good approximation, this is proportional to $\alpha_{\mathbf{h}}$:

$$W_{\mathbf{h}} = \min(0{\cdot}2\alpha_{\mathbf{h}}, 1{\cdot}0). \quad (6)$$

In the weighted tangent formula suggested by Hull & Irwin (1978) a weight is suggested which assumes its maximum (=1) when $\alpha_{\mathbf{h}}^2 = \alpha_E^2$; thus supporting a more realistic agreement between the calculated and the expected value of $\alpha_{\mathbf{h}}$;

(*c*) several figures of merit, based on the α values [*i.e.* the residual R proposed by Karle & Karle (1966); the M criterion proposed by Germain, Main & Woolfson (1971);...) are widely used to predict which solutions are worth examining in the multisolution approaches.

In spite of the very important role of $\alpha_{\mathbf{h}}$ no attempt has been made so far at obtaining the distribution function of $\alpha_{\mathbf{h}}$. The only known characteristic of this distribution used in practice is α_E^2, while equally useful would be information about the variance of α. This paper is devoted to the calculation of the probability distribution of α.

2. The distribution of $\alpha_{\mathbf{h}}$ in non-centrosymmetric space groups

A general technique for deriving the distribution of $\alpha_{\mathbf{h}}$ involves the use of the characteristic function. Suppose that $\theta_j = \theta_{\mathbf{k}_j} + \theta_{\mathbf{h}-\mathbf{k}_j}$, $j = 1, \ldots, r$, are a random sample and they are independently distributed with probability density function $f_j(\theta_j)$, $j = 1, \ldots, r$. For fixed G_j values, $j = 1, \ldots, r$, let us denote

$$A = \sum_{j=1}^r G_j \cos\theta_j, \qquad B = \sum_{j=1}^r G_j \sin\varphi_j,$$

$$\alpha_{\mathbf{h}} = (A^2 + B^2)^{1/2}, \cos\theta_{\mathbf{h}} = A/\alpha_{\mathbf{h}}, \sin\theta_{\mathbf{h}} = B/\alpha_{\mathbf{h}}. \quad (7)$$

The joint characteristic function of (A, B) is

$$C(u, v) = \langle \exp i(uA + vB)\rangle = \prod_{j=1}^r C_j(u, v), \quad (8)$$

where $C_j(u, v)$ is the joint characteristic function of $(G_j \cos\theta_j, G_j \sin\theta_j)$.

From the change of variables

$$u = \rho\cos\psi, \qquad v = \rho\sin\psi, \quad (9)$$

the following useful expression for C_j arises:

$$C_j(\rho, \psi) = \int_0^{2\pi} \exp\{i\rho G_j \cos(\theta_j - \psi)\} f_j(\theta_j)\, d\theta_j. \quad (10)$$

The Fourier transform of (8) *via* (10) gives

$$P(\alpha_{\mathbf{h}}, \theta_{\mathbf{h}}) \simeq 1/(2\pi)^2 \alpha_{\mathbf{h}} \int_0^{+\infty} \int_0^{2\pi} \rho \exp\{-i\alpha_{\mathbf{h}}\rho\cos(\psi - \theta_{\mathbf{h}})\} \times \prod_{j=1}^r C_j(\rho, \psi)\, d\rho\, d\psi. \quad (11)$$

Integrating over $\theta_{\mathbf{h}}$ in (11) gives

$$P(\alpha_{\mathbf{h}}) = 1/(2\pi)\alpha_{\mathbf{h}} \int_0^{+\infty} \int_0^{2\pi} \rho J_0(\rho\alpha_{\mathbf{h}}) \prod_{j=1}^r C_j(\rho, \psi)\, d\rho\, d\psi, \quad (12)$$

where J_0 is the Bessel function of order zero.

Relation (12) is basic for our subsequent applications. We will study (12) under two different assumptions:

(1) the variables θ_j are uniformly and independently distributed in the interval $(0, 2\pi)$. This case will clearly reveal the connexions of the present problem with the classical problem of isotropic random walk (Pearson, 1905);

(2) the variables θ_j are distributed around $\varphi_{\mathbf{h}}$ according to the Von Mises distributions $M[\theta_j; \varphi_{\mathbf{h}}, G_j]$. When every G_j goes to zero this case reduces to case 1).

3.1. Let the random variables φ_j be isotropically and independently distributed on the circle. Then $f_j(\varphi_j) = 1/2\pi$, and $C_j(\rho, \psi) = J_0(\rho G_j)$. Therefore (Kluyver, 1905):

$$P(\alpha_{\mathbf{h}}) = \alpha_{\mathbf{h}} \int_0^{+\infty} \rho J_0(\rho\alpha_{\mathbf{h}}) \prod_{j=1}^{r} J_0(\rho G_j)\, d\rho. \quad (13)$$

It is difficult to evaluate (13) for $r > 2$. It is possible to obtain a simple expression when r is sufficiently large by using the asymptotic expression

$$\prod_{j=1}^{r} J_0(\rho G_j) \simeq \exp\left(-\frac{\rho}{4}\Sigma_2\right), \quad (14)$$

where $\Sigma_i = \sum_{j=1}^{r} G_j^i$, from which (Rayleigh, 1905)

$$P(\alpha_{\mathbf{h}}) = \frac{2\alpha_{\mathbf{h}}}{\Sigma_2} \exp\left(-\alpha_h^2/\Sigma_2\right). \quad (15)$$

The density (15) represents Wilson's distribution (Wilson, 1942) if G_j is the atomic scattering of the jth atom and $\alpha_{\mathbf{h}} = |F|$.

3.2. Let every θ_j be distributed around $\varphi_{\mathbf{h}}$ according to $M[\theta_j; \varphi_{\mathbf{h}}, G_j]$. The distribution function $f_j(\theta_j) = M[\theta_j; \varphi_{\mathbf{h}}, G_j]$ may be introduced in (10) giving rise to

$$P(\alpha_{\mathbf{h}}) = \frac{\alpha_{\mathbf{h}}}{2\pi \prod_{j=1}^{r} I_0(G_j)} \int_0^{+\infty} \int_0^{2\pi} \rho J_0(\rho\alpha_{\mathbf{h}})$$
$$\times \prod_{j=1}^{r} J_0\{G_j[\rho^2 - 1$$
$$-2i\rho \cos(\varphi_{\mathbf{h}} - \psi)]^{1/2}\}\, d\rho\, d\psi. \quad (16)$$

Since it is difficult to evaluate (16) for finite values of r, we try to obtain a compact expression when r is sufficiently large by using again the approximation (14). Then we have

$$\prod_{j=1}^{r} J_0\{G_j[\rho^2 - 1 - 2i\rho \cos(\varphi_{\mathbf{h}} - \psi)]^{1/2}\}$$
$$\simeq \exp\left\{\frac{\Sigma_2}{4} - \frac{\rho^2}{4}\Sigma_2 + \frac{i}{2}\rho\, \Sigma_2 \cos(\varphi_h - \psi)\right\}.$$

Integrating with respect to ψ in (16) and introducing (14) gives

$$P(\alpha_{\mathbf{h}}) \simeq \frac{2\alpha_{\mathbf{h}}}{\Sigma_2} I_0(\alpha_{\mathbf{h}}) \exp\left\{-\frac{\alpha_{\mathbf{h}}^2}{\Sigma_2} - \frac{\Sigma_2}{4}\right\}. \quad (17)$$

The expected value of $\alpha_{\mathbf{h}}^2$ according to (17) is

$$\langle\alpha_{\mathbf{h}}^2\rangle = \Sigma_2\left(1 + \frac{\Sigma_2}{4}\right)$$

and the variance of $\alpha_{\mathbf{h}}$ is given by

$$\langle\alpha_{\mathbf{h}}^2\rangle - \langle\alpha_{\mathbf{h}}\rangle^2 = \Sigma_2\left\{\left(1 + \frac{\Sigma_2}{4}\right) - \frac{\pi}{4}\exp\left(-\frac{\Sigma_2}{2}\right)\left[{}_1F_1\left(\frac{3}{2}; 1; \frac{\Sigma_2}{4}\right)\right]^2\right\}, \quad (18)$$

where ${}_1F_1$ is the confluent hypergeometric function.

In order to obtain (17) from (16) we used the same approximations introduced for the derivation of (15) from (13). While (15) is satisfactory when applied as a Wilson's distribution, (17) is not very useful for our purposes.

As an example, let us suppose that seven G_j values concur to fix a given $\theta_{\mathbf{h}}$:

$G_1 = 2{\cdot}81$; $G_2 = 1{\cdot}86$; $G_3 = 1{\cdot}73$; $G_4 = 1{\cdot}67$;

$G_5 = 1{\cdot}63$; $G_6 = 1{\cdot}48$; $G_7 = 1{\cdot}33$.

The value of $\langle\alpha_{\mathbf{h}}^2\rangle$ according to (17) is about 160, while it is 80 according to (4). Thus (17) appears too rough for practical purposes and we prefer to introduce a new point of view.

4. The asymptotic distribution of $R_{\mathbf{h}}$ and $\varphi_{\mathbf{h}}$

The estimation of a statistical parameter from large samples may be obtained by calculating the value of the parameter in the sub-population composed by the sample. It is well known that for samples of size r a valid measure of precision is provided by the standard error provided that:

(a) the sampling distribution of the statistic under discussion approaches normality;

(b) r is large enough.

In this sense,

$$C = \frac{1}{\Sigma_1}\sum_{j=1}^{r} G_j \cos\theta_j,$$
$$S = \frac{1}{\Sigma_1}\sum_{j=1}^{r} G_j \sin\theta_j \quad (19)$$

are statistical parameters for the population of the θ_j variables: in particular they may be considered weighted averages of independent random variables.

In accordance with the central limit theorem, for r sufficiently large, C and S will be distributed according to normal distributions. Let us assume that any θ_j is distributed according to $M[\theta_j; \varphi_{\mathbf{h}}, G_j]$: then

$$\langle C\rangle = \frac{1}{\Sigma_1}\sum_{j=1}^{r} G_j D_1(G_j) \cos\varphi_{\mathbf{h}},$$
$$\langle S\rangle = \frac{1}{\Sigma_1}\sum_{j=1}^{r} G_j D_1(G_j) \sin\varphi_{\mathbf{h}}, \quad (20a)$$

$$\sigma_1^2 = \operatorname{var} C = \frac{1}{2\Sigma_1^2}\sum_{j=1}^{r} G_j^2[1 + D_2(G_j)\cos 2\varphi_{\mathbf{h}} - 2D_1^2(G_j)\cos^2\varphi_{\mathbf{h}}], \quad (20b)$$

$$\sigma_2^2 = \operatorname{var} S = \frac{1}{2\sum_1^2} \sum_{j=1}^{r} G_j^2 [1 - D_2(G_j) \cos 2\varphi_{\rm h} - 2D_1^2(G_j) \sin^2 \varphi_{\rm h}]. \quad (20c)$$

Further information about C and S is provided by application of the bidimensional central limit theorem. According to this theorem the joint probability distribution of C and S is asymptotically normal, and is completely defined if, besides the parameters $\langle C\rangle$, $\langle S\rangle$, var C, var S, cov (C, S) is also calculated:

$$\operatorname{cov}(C, S) = \frac{1}{2\sum_1^2} \sum_{j=1}^{r} G_j^2 [D_2(G_j) - D_1^2(G_j)] \sin 2\varphi_h.$$

In conclusion:

$$P(C, S) \simeq \frac{1}{2\pi\sigma_1\sigma_2\sqrt{1-\rho^2}} \times \exp\left\{-\frac{1}{2(1-\rho^2)}\left[\frac{(C-\langle C\rangle)^2}{\sigma_1^2} - 2\frac{(C-\langle C\rangle)(S-\langle S\rangle)}{\sigma_1\sigma_2} + \frac{(S-\langle S\rangle)^2}{\sigma_2^2}\right]\right\},$$

where $\rho = \operatorname{cov}(C, S)/(\sigma_1\sigma_2)$ is the correlation coefficient of C and S.

More useful for our purposes are the distributions of

$$R_{\rm h} = (C^2 + S^2)^{1/2}, \qquad \theta_{\rm h} = \arctan(S/C). \quad (21)$$

Since $R_{\rm h}$ and $\theta_{\rm h}$ are differentiable functions of C and S, which in their turn have variances of order $1/r$, the following well-known lemma may be used (Kendall & Stuart, 1977).

Lemma: Suppose that x_i has mean ξ_i and that the variances and covariances of the m variates $x_1, x_2, \ldots, x_m$ are of order r^{-1}. Consider the function $g(\mathbf{x}) = g(x_1, x_2, \ldots, x_m)$: if $g_i'(\boldsymbol{\xi}) = g_i'(\xi_1, \xi_2, \ldots, \xi_m)$ is $\delta g(\mathbf{x})/\delta x_i$ evaluated at $\mathbf{x} = \boldsymbol{\xi}$, $g_{ij}''(\boldsymbol{\xi}) = g_{ij}''(\xi_1, \xi_2, \ldots, \xi_m)$ is $\delta^2 g(\mathbf{x})/(\delta x_i\, \delta x_j)$ evaluated at $\mathbf{x} = \boldsymbol{\xi}$, then

$$\langle g\rangle \simeq g(\boldsymbol{\xi}) + \frac{1}{2}\left[\sum_{i=1}^{m} g_i''(\boldsymbol{\xi}) \operatorname{var} x_i + \sum_{i\neq j=1}^{m} g_{ij}''(\boldsymbol{\xi}) \operatorname{cov}(x_i, x_j)\right] \quad (22)$$

and

$$\operatorname{var} g \simeq \sum_{i=1}^{m} [g_i'(\boldsymbol{\xi})]^2 \operatorname{var} x_i + \sum_{i\neq j=1}^{m} g_i'(\boldsymbol{\xi}) g_j'(\boldsymbol{\xi}) \operatorname{cov}(x_i, x_j), \quad (23)$$

provided not all the $g_i'(\boldsymbol{\xi}) = 0$.

The above lemma may be applied to our problem by assuming $\mathbf{x}$ as a random vector with two components $x_1 = C$, $x_2 = S$, while $R_{\rm h}$ and $\theta_{\rm h}$ take in turn the role of g. After some calculation we obtain (see Appendix):*

$$\langle R_{\rm h}\rangle \simeq \left[\sum_{j=1}^{r} G_j D_1(G_j)\right] \Big/ \textstyle\sum_1, \quad (24)$$

$$\sigma_R^2 = \operatorname{var} R_{\rm h} \simeq \frac{1}{\sum_1^2} \sum_{j=1}^{r} G_j^2 \left[1 - \frac{1}{G_j} D_1(G_j) - D_1^2(G_j)\right] \quad (25)$$

$$\langle \theta_{\rm h}\rangle \simeq \arctan \langle S\rangle/\langle C\rangle = \varphi_{\rm h} \quad (26)$$

$$\sigma_\theta^2 = \operatorname{var} \theta_{\rm h} \simeq \left[\sum_{j=1}^{r} G_j D_1(G_j)\right]^{-1}. \quad (27)$$

Correctly, $\sigma_\theta^2 \simeq 0$ if the G_j are large enough.

The above equations have the following meaning. From the population of the random variables θ_j we select by a random method m independent collections of r elements with r sufficiently large. For the qth of these collections we observe the average values R_q and θ_q and from them we calculate the average values:

$$R_{\rm av} = \frac{1}{m} \sum_{q=1}^{m} R_q; \quad \theta_{\rm av} = \frac{1}{m} \sum_{q=1}^{m} \theta_q. \quad (28)$$

Our results suggest that $R_{\rm av}$ and $\theta_{\rm av}$ are dispersed around

$$\langle R_{\rm h}\rangle = \frac{1}{\sum_1} \sum_{j=1}^{r} G_j D_1(G_j)$$

and $\langle \theta_{\rm h}\rangle = \varphi_{\rm h}$, respectively, according to normal distributions. If all G_j's tend to zero then $\langle R_{\rm h}\rangle \simeq 0$ and $\langle \theta_{\rm h}\rangle$ is not defined. In this case the distribution of $R_{\rm h}$ is related to a χ^2 distribution (Mardia, 1972).

The following lemma helps us to calculate the asymptotic joint probability distribution function of $R_{\rm h}$ and $\theta_{\rm h}$.

Lemma: Suppose that x_i has mean ξ_i and that the variances and covariances of the m variates $x_1, x_2, \ldots, x_m$ are of order r^{-1}. If $g(\mathbf{x}) = g(x_1, x_2, \ldots, x_m)$, $h(\mathbf{x}) = h(x_1, x_2, \ldots, x_m)$ are two differentiable functions of $x_1, x_2, \ldots, x_m$, then

$$\operatorname{cov}(g, h) \simeq \sum_{i=1}^{m} g_i'(\boldsymbol{\xi}) h_i'(\boldsymbol{\xi}) \operatorname{var} x_i + \sum_{i\neq j=1}^{m} g_i'(\boldsymbol{\xi}) h_j'(\boldsymbol{\xi}) \operatorname{cov}(x_i, x_j). \quad (29)$$

The joint probability distribution of g and h is asymptotically bivariate normal.

In accordance with the above lemma we obtain (see Appendix) for the covariance of $R_{\rm h}$ and $\theta_{\rm h}$: cov $(R_{\rm h}, \theta_{\rm h}) = 0$.

---

* The Appendix has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39167 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Finally, the asymptotic joint probability distribution of $R_{\mathbf{h}}$ and $\theta_{\mathbf{h}}$ is the product of two uncorrelated normal distributions.

The asymptotic validity of the previous results should be stressed. Indeed, according to the normal distribution, the value of $R_{\mathbf{h}}$ may theoretically range from $-\infty$ to $+\infty$, in spite of the algebraically strict limits $0 \leq R_{\mathbf{h}} \leq 1$. However, if r is sufficiently large and G_j, $j=1, \ldots, r$, do not vanish, the contribution to the integral $\int_{-\infty}^{+\infty} P(R_{\mathbf{h}})\,dR_{\mathbf{h}}$ from the intervals $(-\infty, 0)$ and $(1, +\infty)$ could be neglected.

In its turn the theoretical distribution obtained for $\theta_{\mathbf{h}}$ is not a Von Mises distribution.

5. The asymptotic distribution of $C_{\mathbf{h}}$ in a centrosymmetric case

Let us define

$$C_{\mathbf{h}} = \frac{1}{\sum_1} \sum_{j=1}^{r} G_j \cos \theta_j \tag{30}$$

and suppose that the variables θ_j are distributed according to two-point distributions of type $\mathrm{CW}(\theta_j; \varphi_{\mathbf{h}}, G_j)$, where

(a) θ_j may assume the values 0 or π so that $\cos \theta_j$ is the sign of the product $E_{\mathbf{k}_j} E_{\mathbf{h}-\mathbf{k}_j}$;

(b) $\varphi_{\mathbf{h}}$ is the phase value (0 or π) of $E_{\mathbf{h}}$;

(c) $G_j = |E_{\mathbf{h}} E_{\mathbf{k}_j} E_{\mathbf{h}-\mathbf{k}_j}|/\sqrt{N}$;

(d) CW is the Cochran & Woolfson (1955) probability density for $\cos \theta_j$:

$$P_j(\cos \theta_j) \simeq 0{\cdot}5 + 0{\cdot}5 \tanh (G_j \cos \theta_j \cos \varphi_{\mathbf{h}}).$$

$C_{\mathbf{h}}$ is the sum of independent random variables. If r is sufficiently large the central limit theorem may be applied, according to which

$$\langle C_{\mathbf{h}} \rangle = \frac{1}{\sum_1} \left(\sum_{j=1}^{r} G_j \tanh G_j \right) \cos \varphi_{\mathbf{h}}, \tag{31}$$

$$\sigma_C^2 = \mathrm{var}\, C_{\mathbf{h}} = \frac{1}{\sum_1^2} \sum_{j=1}^{r} G_j^2 [1 - \tanh^2 G_j].$$

Then

$$P(C_{\mathbf{h}}) \frac{1}{\sigma_C \sqrt{2\pi}} \exp \left[-\frac{(C_{\mathbf{h}} - \langle C_{\mathbf{h}} \rangle)^2}{2\sigma_C^2} \right]. \tag{32}$$

6. The distributions of $\alpha_{\mathbf{h}}$ and $\theta_{\mathbf{h}}$

Let us denote by $N[x; y, z]$ the normal distribution of the variable x, with expected value y and variance z. In accordance with § 4 the distribution of $\alpha_{\mathbf{h}} = \sum_1 R_{\mathbf{h}}$ is

$$P(\alpha_{\mathbf{h}}) = N[\alpha_{\mathbf{h}}; \langle \alpha_{\mathbf{h}} \rangle, \sigma_{\alpha_{\mathbf{h}}}^2], \tag{33}$$

where

$$\langle \alpha_{\mathbf{h}} \rangle = \sum_{j=1}^{r} G_j D_1(G_j), \tag{34}$$

$$\sigma_{\alpha_{\mathbf{h}}}^2 = \tfrac{1}{2} \sum_{j=1}^{r} G_j^2 [1 + D_2(G_j) - 2D_1^2(G_j)]. \tag{35}$$

For the centrosymmetric case $\alpha_{\mathbf{h}} = \sum_1 C_{\mathbf{h}}$, where $C_{\mathbf{h}}$ is given by (30). In accordance with § 5, $P(\alpha_{\mathbf{h}})$ is again given by (33) with

$$\langle \alpha_{\mathbf{h}} \rangle = \left(\sum_{j=1}^{r} G_j \tanh G_j \right) \cos \varphi_{\mathbf{h}}, \tag{36}$$

$$\sigma_{\alpha_{\mathbf{h}}}^2 = \sum_{j=1}^{r} G_j^2 [1 - \tanh^2 G_j]. \tag{37}$$

In seeming contrast with (1) the distribution of $\theta_{\mathbf{h}}$ [see (26) and (27)] is a normal distribution, *i.e.* $N[\theta_{\mathbf{h}}; \varphi_{\mathbf{h}}, \langle \alpha_{\mathbf{h}} \rangle^{-1}]$. However, if $\langle \alpha_{\mathbf{h}} \rangle$ is large enough (≥ 2), $N[\theta_{\mathbf{h}}; \varphi_{\mathbf{h}}, \langle \alpha_{\mathbf{h}} \rangle^{-1}]$ may be approximated by $M[\theta_{\mathbf{h}}; \varphi_{\mathbf{h}}, \langle \alpha_{\mathbf{h}} \rangle]$, which is really the expected asymptotic form of the distribution (1).

7. Experimental

Because of their asymptotic nature our results hold for r sufficiently large. What such an assumption means in our case is not easy to state. In general some statistics tend to normality more rapidly than others and a given r may be large for some purposes but not for others. For the usual applications of the tangent formula the value of r ranges from 1 to about 50. Therefore our theoretical results, even if useful for practical purposes, cannot have strict validity.

We have checked the correctness of the distribution $P(\alpha)$ *via* its first moments by generating p random samples of θ values (Best & Fisher, 1979), each sample consisting of q events θ, distributed according to the Von Mises distribution $M[\theta; 0, G]$. In Table 1 the theoretical values $\langle \alpha_{\mathbf{h}} \rangle$ and $\sigma_{\alpha_{\mathbf{h}}}$ are compared with the experimental ones (in parentheses). A satisfactory agreement is found: for large values of p and q the small discrepancies are mainly due to the approximations caused by the analytical estimation of the function D_1; for small values of p and q the relatively larger discrepancies are mainly due to the sampling effects. There is experimental evidence that $P(\alpha)$ may usefully be applied to tangent procedures provided the θ_j's are random samples from Von Mises populations.

From $P(\alpha)$ some related distributions may be calculated:

(a) if $y = \alpha/\langle \alpha \rangle$, then

$$P(y) = N[y; 1, \sigma'], \tag{38}$$

where $\sigma' = \sigma/\langle \alpha \rangle$;

(b) if $x = \alpha^2/\langle \alpha^2 \rangle$ then

$$P(x) = \frac{1}{2\sigma'' \sqrt{2\pi x}} \exp \left\{ -\frac{[\sqrt{x} - m]^2}{2\sigma''^2} \right\}, \tag{39}$$

where $\sigma''^2 = \sigma^2/\langle \alpha^2 \rangle$, $m = \langle \alpha \rangle / \langle \alpha^2 \rangle^{1/2}$.

Table 1. *Theoretical and experimental (in parentheses) values of $\langle\alpha_h\rangle$ and σ_{α_h} from p samples of q events distributed according to the Von Mises distribution* $M[\theta; 0, G]$

p, q	50, 5000	20, 2000	10, 10	5, 5
G	1·5	3	1·5	1·5
$\langle\alpha\rangle$	4451	4864	9·69	4·45
	(4479)	(4848)	(10·0)	(4.18)
σ	53·2	36·2	2·38	1·68
	(59·8)	(36·0)	(2·23)	(1·61)

Equation (39) is shown for some selected cases in Fig. 1. The distribution $P(x)$ was invoked by Hull & Irwin in order to justify their weight

$$w'_h = \psi\, e^{-x^2} \int_0^x \exp t^2\, dt. \tag{40}$$

In particular they supposed that (40) (the dotted line in Fig. 1) roughly corresponds to $P(x)$. Our results show that:

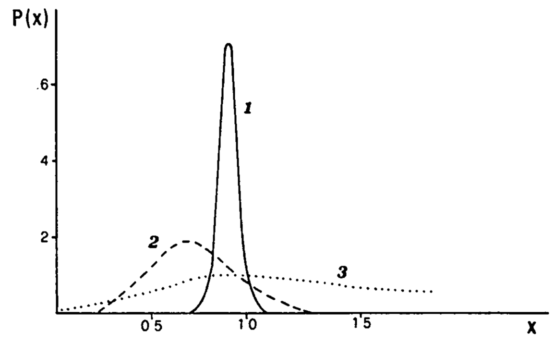

Fig. 1. The distribution $P(x)$ given by (43) is shown for selected values of parameters m and σ''. Line 1: $m = 0{\cdot}95$, $\sigma'' = 0{\cdot}03$. Line 1 represents the distribution of x for a sample of ten complex vectors $2\,e^{i\theta_j}$ distributed according to $M[\theta_j; 0, 2]$. Line 2: $m = 0{\cdot}84$, $\sigma'' = 0{\cdot}13$. Line 2 represents the distribution of x for a sample of ten complex vectors $e^{i\theta_j}$ distributed according to $M[\theta_j; 0, 1]$. Line 3: The distribution (6).

(1) $P(x)$ depends on the two parameters m and σ'' while no parameter is in (40);

(2) the distribution (40) does not agree with $P(x)$. In particular the maximum of $P(x)$ is usually not at 1.

8. Conclusions

The asymptotic distribution of the resultant of the complex vectors $G_j \exp(i\theta_j)$, $j = 1, \ldots, r$, where $\theta_j = \theta_{\mathbf{k}_j} + \theta_{\mathbf{h}-\mathbf{k}_j}$ is distributed according to $M[\theta_j; \varphi_{\mathbf{h}}, G_j]$, is calculated. The statistical results suggest that the phase of the resultant is distributed around $\varphi_{\mathbf{h}}$ approximately according to a Von Mises distribution with concentration parameter equal to $\langle\alpha_{\mathbf{h}}\rangle$, while the modulus of the resultant is normally distributed around $\langle\alpha_{\mathbf{h}}\rangle$ [given by (34) and (36) for non-centrosymmetric and centrosymmetric structures, respectively].

One of the authors (CG) would like to thank Professor G. Girone for helpful discussions.

References

BEST, D. J. & FISHER, N. I. (1979). *Appl. Statist.* **28**, 2, 152–157.
COCHRAN, W. & WOOLFSON, M. M. (1955). *Acta Cryst.* **8**, 1–12.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274–285.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
HULL, S. E. & IRWIN, M. J. (1978). *Acta Cryst.* **A34**, 863–870.
KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635–651.
KARLE, J. & KARLE, I. (1966). *Acta Cryst.* **21**, 849–859.
KENDALL, M. & STUART, A. (1976). *The Advanced Theory of Statistics.* Vol. I, p. 246. London: Charles Griffin.
KLUYVER, J. C. (1905.) *Proc. K. Ned. Akad. Wet.* **8**, 341–350.
MARDIA, K. V. (1972). *J. R. Stat. Soc.* **B34**, Part 1, 112–208.
PEARSON, K. (1905). *Nature (London)*, **72**, 294, 318.
RAYLEIGH, LORD (1905). *Nature (London)*, **72**, 318.
WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151.

Acta Cryst. (1984). **A40**, 394–398

Polarization Phenomena of X-rays in the Bragg Case

BY O. BRÜMMER, CH. EISENSCHMIDT AND H. R. HÖCHE

Martin-Luther-Universität Halle-Wittenberg, Sektion Physik, Friedemann-Bach-Platz 6, 4020 *Halle, German Democratic Republic*

(*Received* 2 *September* 1983; *accepted* 30 *January* 1984)

Abstract

Using a double crystal diffractometer with an additional crystal between the two crystals used as X-ray-optical polarizer and analyzer the phase relation between mutually perpendicularly polarized wave fields is examined in the Bragg case. The additional crystal is a (110)-surface oriented silicon crystal adjusted for the symmetric 220 Cu $K\alpha_1$ Bragg case. In the case of coherent excitation of both σ- and π-polarized wave fields in the silicon crystal it is experimentally shown that a unique phase relation

0108-7673/84/040394-05$01.50 © 1984 International Union of Crystallography