Cowan, 1985) for Bragg beams carry over to the thin-crystal case considered here. One important exception, however, occurs when the θ values of the Bragg and Laue diffracted beams are very close together (*i.e.* for $\Phi < \Phi_c$). In this case the strongly excited internal waves travelling towards the rear surface to generate the Laue exit beams are also partially reflected back towards the front surface. These waves can then contribute to the intensity of the Bragg exit beams, although in practice this effect is usually negligible. Calculating the magnitude of these 'internally reflected Laue waves' requires a method such as the n-beam theory which retains all of the solutions of the dynamical equations.

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References

AFANAS'EV, A. M. & MELKONYAN, M. K. (1983). *Acta Cryst.* A**39**, 207-210.

ALEKSANDROV, P. A., MELKONYAN, M. K. & STEPANOV, S. A. (1984). *Kristallografiya*, **29**, 376. Engl. transl: *Sov. Phys. Crystallogr.* **29**, 226.

ANDREEV, A. V., KOV'EV, E. K., MATVEEV, Y. A. & PONOMAREV, Y. V. (1982). *Pis'ma Zh. Eksp. Teor. Fiz.* **35**, 412. Engl. transl: *JETP Lett.* **35**, 508.

BARYSHEVSKII, V. G. (1976). *Pis'ma Zh. Tekh. Fiz.* **2**, 112. Engl. transl: *Sov. Tech. Phys. Lett.* **2**, 43.

BATTERMAN, B. W. & COLE, H. (1964). *Rev. Mod. Phys.* **36**, 681-717.

BEDYNSKA, T. (1973). *Phys. Status Solidi A*, **19**, 365-372.

BEDYNSKA, T. (1974). *Phys. Status Solidi A*, **25**, 405-411.

BERNHARD, N., BURKEL, E., GOMPPER, G., METZGER, H., PEISL, J., WAGNER, H. & WALLNER, G. (1987). *Z. Phys. B*, **69**, 303-311.

COLELLA, R. (1974). *Acta Cryst.* A**30**, 413-423.

COLELLA, R. & LUCCIO, A. (1984). *Opt. Commun.* **50**, 41-44.

COWAN, P. L. (1985). *Phys. Rev. B*, **32**, 5437-5439.

COWAN, P. L., BRENNAN, S., JACH, T., BEDZYK, M. J. & MATERLIK, G. (1986). *Phys. Rev. Lett.* **57**, 2399-2402.

EWALD, P. P. (1916*a*). *Ann. Phys. (Leipzig)*, **49**, 1-38.

EWALD, P. P. (1916*b*). *Ann. Phys. (Leipzig)*, **49**, 117-143.

EWALD, P. P. (1917). *Ann. Phys. (Leipzig)*, **54**, 519-597.

FARWIG, P. & SCHÜRMANN, H. W. (1967). *Z. Phys.* **204**, 489-500.

HÄRTWIG, J. (1976). *Phys. Status Solidi A*, **37**, 417-425.

HÄRTWIG, J. (1977). *Phys. Status Solidi A*, **42**, 495-500.

HÖCHE, H. R. & BRÜMMER, O. (1986). *Acta Cryst.* A**42**, 585-587.

JAMES, R. W. (1982). *The Optical Principles of the Diffraction of X-rays.* Woodbridge, Connecticut: Ox Bow Press.

KISHINO, S. (1971). *J. Phys. Soc. Jpn*, **31**, 1168-1173.

KISHINO, S., NODA, A. & KOHRA, K. (1972). *J. Phys. Soc. Jpn*, **33**, 158-166.

LAUE, M. VON (1931). *Ergeb. Exakten Naturwiss.* **10**, 133-158.

LORRAIN, P. & CORSON, D. (1970). *Electromagnetism and Waves.* San Francisco: Freeman.

MARRA, W. C., EISENBERGER, P. & CHO, A. Y. (1979). *J. Appl. Phys.* **50**, 6927-6933.

RUSTICHELLI, F. (1975). *Philos. Mag.* **31**, 1-12.

SCHMIDT, M. & COLELLA, R. (1985). *Phys. Rev. Lett.* **55**, 715-717.

TISCHLER, J. & BATTERMAN, B. W. (1986). *Acta Cryst.* A**42**, 510-514.

VINEYARD, G. (1982). *Phys. Rev. B*, **26**, 4126-4159.

ZACHARIASEN, W. H. (1945). *Theory of X-ray Diffraction in Crystals.* New York: John Wiley.

SHORT COMMUNICATIONS

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Acta Cryst. (1989). A**45**, 141-143

A new von Mises probabilistic formula for quartet invariants.

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Abstract

Von Mises formulas for quartet invariants [Giacovazzo (1976). *Acta Cryst.* A**32**, 91-99], even if useful in most cases of practical interest, suffer from some systematic errors. A new von Mises formula is suggested with better theoretical features.

Symbols

$\Phi = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} - \varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$

$R = |E|$

$\varepsilon = R^2 - 1$

$E_{\mathbf{l}} = R_{\mathbf{l}} \exp(i\varphi_{\mathbf{l}}) = E_{\mathbf{h}} \exp(i\varphi_{\mathbf{h}})$;

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$E_2 = R_2 \exp(i\varphi_2) = E_k \exp(i\varphi_k); \ldots;$

$E_5 = R_5 \exp(i\varphi_5) = R_{h+k} \exp(i\varphi_{h+k});$

$E_6 = R_6 \exp(i\varphi_6) = R_{h+l} \exp(i\varphi_{h+l});$

$E_7 = R_7 \exp(i\varphi_7) = R_{k+l} \exp(i\varphi_{k+l})$

$G_{ijl} = 2R_iR_jR_l/N^{1/2}$

$B = 2R_1R_2R_3R_4/N$

$D_1(x) = I_1(x)/I_0(x)$

= ratio of modified Bessel functions of order 1 and 0 respectively.

1. Introduction

After the early work of Schenk (1973, 1974) it was clear that reliable quartet invariant estimates could be obtained *via* the method of joint probability distributions of seven structure factors. Two types of probabilistic formulas are widely used today. The first was provided by Hauptman (1975):

$$P(\Phi) \simeq (1/L) \exp(-2B \cos \Phi) I_0(Z_5) I_0(Z_6) I_0(Z_7) \quad (1)$$

where

$$Z_5 = [G_{125}^2 + G_{345}^2 + 2G_{125}G_{345} \cos \Phi]^{1/2},$$

$$Z_6 = [G_{136}^2 + G_{246}^2 + 2G_{136}G_{246} \cos \Phi]^{1/2},$$

$$Z_7 = [G_{237}^2 + G_{147}^2 + 2G_{237}G_{147} \cos \Phi]^{1/2}.$$

L is a normalizing constant which may be calculated by a numerical study of (1).

The second kind of formula (of von Mises type) was suggested by Giacovazzo:

$$P(\Phi) = [2\pi I_0(G')]^{-1} \exp(G' \cos \Phi) \quad (2)$$

where

$$G' = B(1 + \varepsilon_5 + \varepsilon_6 + \varepsilon_7)/(1 + Q).$$

According to different considerations three expressions were proposed for Q (Giacovazzo, 1976, 1980*a*), the latest of which is

$$Q_3 = [(\varepsilon_1\varepsilon_2 + \varepsilon_3\varepsilon_4)\varepsilon_5 + (\varepsilon_1\varepsilon_3 + \varepsilon_2\varepsilon_4)\varepsilon_6 + (\varepsilon_1\varepsilon_4 + \varepsilon_2\varepsilon_3)\varepsilon_7]/2N.$$

In spite of different mathematical techniques used for their derivation (Hauptman regarded the reciprocal-lattice vectors as the primitive random variables while Giacovazzo considered the atomic positional vectors as primitive random variables), (1) and (2) are strictly connected (Giacovazzo, 1977*a*, 1980*a*; Heinerman, 1977): in particular the numerator of (2) (but not the denominator) may be obtained from (1) by expanding the Bessel function I_0 according to

$$I_0(z) = 1 + z^2/4 + \ldots \simeq \exp(z^2/4).$$

Apparently (1) seems more useful than (2). Indeed, estimates near 0 or π and in the middle range can in principle be obtained by (1); by contrast (2) can provide only estimates near 0 or π according to whether G' is positive or negative.

A more careful investigation of the properties of (1) and (2) shows on the contrary that:

(*a*) Estimates by (1) lying in the middle range are expected to be in poor agreement with the true values because of the large value of the variance. If N is large enough ($N \geq 150$) estimates in the middle range cannot occur and only estimates near 0 or π are in practice provided by (1).

(*b*) for N sufficiently large estimates obtained by (1) and by (2) coincide in most cases of practical interest.

Furthermore,

(*c*) (1) is more time consuming than (2): first, the scaling factor L has to be found by numerical methods, *via* the condition $\int_0^\pi P(\Phi)\, d\Phi = 1$; then

$$\langle|\Phi|\rangle = \int_0^\pi \Phi P(\Phi)\, d\Phi$$

and the variance

$$V = \int_0^\pi (\Phi - \langle|\Phi|\rangle)^2 P(\Phi)\, d\Phi \quad (3)$$

have to be calculated. The simplicity of the formula is of particular importance for quartets since they are phase relationships of order N^{-1}, and a very large number of them have to be estimated in order to select a reliable subset.

(*d*) Triplet invariants are considered to be distributed around 2π according to von Mises distributions with concentration parameter G_{ijl}. If quartets are used actively, they will cooperate with triplets: thus the variance calculated *via* (3) should conveniently be transformed in terms of a concentration parameter of a von Mises distribution.

Actually G' is a concentration parameter of a von Mises distribution, but it suffers from approximations used in the mathematical approach. In particular, a systematic error is produced which increases (in an average sense) as long as the magnitudes R increase to extreme limits. In order to give a simple example, let

$$R_1 = R_2 = R_3 = R_4 = 2 \quad \text{and} \quad R_5 = R_6 = R_7 = R_{\text{cross}}.$$

The calculation of (2) gives, for $N = 100$,

$$\Phi \simeq 0 \quad \text{with } G' = 1{\cdot}77 \quad \text{for } R_{\text{cross}} = 2$$

$$\Phi \simeq 0 \quad \text{with } G' = 0{\cdot}49 \quad \text{for } R_{\text{cross}} = 3$$

$$\Phi \simeq 0 \quad \text{with } G' = 0{\cdot}14 \quad \text{for } R_{\text{cross}} = 4$$

which is contrary to expectations (intuitive considerations suggest that G' should be an increasing function of R_{cross}). In the extreme hypothetical case in which $R_i = N^{1/2}$ for $i = 1, \ldots, 7$, the estimate is

$$\Phi \simeq 0 \quad \text{with } G' \simeq 2,$$

against the intuitive expectation $\Phi \simeq 0$ with $G' = \infty$.

The problem of obtaining a von Mises distribution from (1) can be solved according to the Appendix. Then (1) may be approximated by

$$P(\Phi) = [2\pi I_0(G)]^{-1} \exp(G \cos \Phi) \quad (4)$$

where

$$G = B + (q_5 - B) + (q_6 - B) + (q_7 - B) \quad (5)$$

and q_5, q_6, q_7 satisfy the equations

$$D_1(q_5) = D_1(G_{125}) D_1(G_{345}) \quad (6a)$$

$$D_1(q_6) = D_1(G_{136}) D_1(G_{246}) \quad (6b)$$

$$D_1(q_7) = D_1(G_{237}) D_1(G_{147}). \quad (6c)$$

Solution of (6) is very easy (and provides accurate results) if polynomial approximations of order three are introduced for D_1 and D_1^{-1}.

$(q_i - B)$ may be considered the contribution to the concentration parameter G arising from the prior information on the cross magnitude R_i. $(q_i - B) > 0$ strengthens the prediction of a positive quartet, $(q_i - B) < 0$ drives the quartet towards negativity. As an example, if all the cross magnitudes are equal to zero, then $G = -2B$ as in Hauptman's formulation.

If R_i is not in measurements no prior information on the ith cross magnitude is available: then $(q_i - B) = 0$. Thus special cases (Giacovazzo, 1977*a*; Heinerman, 1977) in which one or more cross reflections are out of measurements are easily handled by (4).

It is easy to see that (4) approximates (1) better than (2). As an example, let us consider, for a $P1$ structure with 29 atoms in the unit cell, the following data:

$(R_i,\ i = 1, \ldots, 7)$

$= (2{\cdot}918;\ 1{\cdot}733;\ 2{\cdot}863;\ 2{\cdot}276;\ 0{\cdot}323;\ 1{\cdot}331;\ 1{\cdot}440).$

While, according to (2), $G' > 0$, distributions (1) and (4) both provide a negative-cosine estimate for the quartet.

Previous observations allow us to generalize (4) to quartets with more than three cross reflections. Let us suppose, according to representation theory (Giacovazzo, 1977*b*, 1980*b*), that the first representation of Φ includes one or more additional quartets Φ_j which are referred to the first one by symmetry phase shifts

$$\Delta_j = \Phi - \Phi_j.$$

Then the new estimate is

$$\tan \Phi = \frac{\sum_i (q_i - B) \sin \Delta_i}{B + \sum_i (q_i - B) \cos \Delta_i} = \frac{N}{D} \qquad (7)$$

and

$$G = (N^2 + D^2)^{1/2}. \qquad (8)$$

The summation in (7) goes over all different cross vectors of Φ.

2. Concluding remarks

Triplet invariants, estimated *via* distributions of von Mises type, play a central role in most direct-methods procedures. Cooperation of quartet with triplet invariants in the phasing process is often easier if quartets too are estimated *via* von Mises distributions. A method has been described for obtaining the transformation of Hauptman's conditional probability distribution of a quartet phase into a von Mises distribution. The new formula requires less computational effort in practical applications and is an alternative to Giacovazzo's von Mises formulas for quartets.

APPENDIX

Some results in the theory of circular variables are briefly quoted.

Let us introduce the following notation:

(*a*)

$$M(\varphi; \theta, G) = [2\pi I_0(G)]^{-1} \exp[G \cos(\varphi - \theta)]. \qquad (A1)$$

M is the von Mises distribution, φ the variable, θ the most probable value of φ and G the concentration parameter of the distribution;

(*b*)

$$W_N(\varphi; \theta, \rho) = [1 + 2 \sum_{p=1}^{\infty} \rho^{p^2} \cos p(\varphi - \theta)]/2\pi \qquad (A2)$$

is the wrapped normal distribution, with $0 < \varphi \leq 2\pi$, $0 \leq \rho \leq 1$.

The following observations may be made.

(1) Von Mises and wrapped normal distributions can be made to approximate each other closely (Stephens, 1963) by assuming

$$\rho = D_1(G). \qquad (A3)$$

(2) Let φ_1, φ_2 be two mutually independent variables distributed according to $W_N(\varphi_1;\ \theta_1,\ \rho_1)$ and $W_N(\varphi_2;\ \theta_2,\ \rho_2)$ respectively. Then the variable sum $\Phi = \varphi_1 + \varphi_2$ has probability distribution

$$W_N(\Phi;\ \theta_1 + \theta_2,\ \rho_1\rho_2). \qquad (A4)$$

(3) If φ_1 and φ_2 are two mutually independent variables distributed according to $M(\varphi_1;\ \theta_1,\ G_1)$ and $M(\varphi_2;\ \theta_2,\ G_2)$ respectively, the probability distribution of $\Phi = \varphi_1 + \varphi_2$ is given by

$$P(\Phi) = [2\pi I_0(G_1) I_0(G_2)]^{-1} I_0 \times [G_1^2 + G_2^2 + 2G_1G_2 \cos(\Phi - \theta_1 - \theta_2)]^{1/2}. \qquad (A5)$$

(4) Equation (*A*5) may be approximated by a von Mises distribution in the following way: first $M(\varphi_1;\ \theta_1,\ G_1)$ and $M(\varphi_2;\ \theta_2,\ G_2)$ are approximated by $W_N[\varphi_1;\ \theta_1,\ D_1(G_1)]$ and $W_N[\varphi_2;\ \theta_2,\ D_1(G_2)]$ respectively.

According to point (2) the convolution of these two distributions is the wrapped normal distribution

$$W_N[\Phi;\ \theta_1 + \theta_2,\ D_1(G_1)D_1(G_2)],$$

which in turn [see point (2)] may be approximated by the von Mises distribution

$$M(\Phi;\ \theta_1 + \theta_2, \alpha)$$

where

$$D_1(\alpha) = D_1(G_1)D_1(G_2). \qquad (A6)$$

According to points (1)-(5) above, each function $I_0(Z_i)$ in (1) may be approximated (but for a scaling factor) by a von Mises function $M(\Phi;\ 0, \alpha_i)$ where α_i should satisfy equations such as (*A*6).

References

GIACOVAZZO, C. (1976). *Acta Cryst.* A**32**, 91-99, 100-104.

GIACOVAZZO, C. (1977*a*). *Acta Cryst.* A**33**, 50-54.

GIACOVAZZO, C. (1977*b*). *Acta Cryst.* A**33**, 933-944.

GIACOVAZZO, C. (1980*a*). *Direct Methods in Crystallography.* London: Academic Press.

GIACOVAZZO, C. (1980*b*). *Acta Cryst.* A**36**, 362-372.

HAUPTMAN, H. (1975). *Acta Cryst.* A**31**, 671-679, 680-687.

HEINERMAN, J. J. L. (1977). Thesis. Univ. of Utrecht, The Netherlands.

SCHENK, K. (1973). *Acta Cryst.* A**29**, 77-82, 480-481.

SCHENK, H. (1974). *Acta Cryst.* A**30**, 477-481.

STEPHENS, H. A. (1963). *Biometrika*, **50**, 385-390.