The Choice of an Enantiomorph and its Consequence on Statistical Formulae for Triple-Product Phases

By W. M. G. F. Pontenagel*

Laboratorium voor Struktuurchemie, Rijksuniversiteit Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

Abstract

An enantiomorph-dependent probability distribution is derived by integrating the joint probability distribution of two related triple-product phases with respect to one of the variables over the range 0 to π. The result, which is correct up to and including terms of order N^{-1}, can be written as a Von Mises distribution, of which the mode can be anywhere between $-\frac{1}{2}\pi$ and $+\frac{1}{2}\pi$. Application of the results to the X-ray data of a P1 structure, which could not be solved by conventional direct methods, is discussed. It is shown that resolving the enantiomorph ambiguity by means of the new formula leads to a successful structure determination, provided some alterations are made in the usual tangent-formula algorithm. From the derived distribution function a new figure of merit (ENFOM) is also determined which indicates whether a given set of phases for the largest normalized structure factors corresponds to an E map dominated by only one enantiomorph, or to an E map in which both enantiomorphs are present. For the test structure, ENFOM correctly classifies the different phase sets obtained in a multi-solution approach.

Introduction

The joint probability distribution of a number of structure factors can only be a function of origin (sem)invariant quantities. If the amplitudes of the structure factors are known, conditional probability distributions for origin (sem)invariant phases can be derived that depend on the normalized amplitudes only. If the relatively small effects of anomalous dispersion are ignored, these amplitudes are insensitive to an inversion of the crystal structure, so all derived formulae will describe both enantiomorphs in the same way. In most of the non-centrosymmetric space groups this leads to conditional probability distributions of (sem)invariant phases which are either unimodal with their mode on 0 or π [*e.g.* the probability distribution of a triple-product phase (Cochran, 1955) or a quartet phase with three large cross terms or a quartet phase with three small cross terms (Hauptman, 1975*b*)], or bimodal with their modes on Φ and

---

* Present address: DSM Research, Geleen, The Netherlands.

$-\Phi$ [*e.g.* the distribution of a quartet phase with three intermediate cross terms (Hauptman, 1975*b*)]. In all cases the formulae are symmetric around zero, which is a direct consequence of the enantiomorph ambiguity. In direct methods, most procedures are based on these enantiomorph-independent distributions. This is often a serious source of trouble in the application of the procedures, resulting in electron density maps in which both enantiomorphs are present. Recently, it was shown by Pontenagel & Krabbendam (1983) that in the eleven pairs of chiral space groups enantiomorph-dependent distribution functions can be derived. In these special cases, the choice for one space group out of the two possible ones automatically implies the choice for one of the two enantiomorphs; the result is that then for certain triple-product phases a unimodal probability distribution is found of which the mode is not on zero. In the present paper we will show that also in P1 enantiomorph-dependent probability distributions may be obtained after the ambiguity is resolved by restricting an arbitrary triple-product phase to the range 0 to π.

Procedure

We start with the joint probability distribution $P(R_1, R_2, R_3, R_4, R_{12}, R_{23}, R_{31}; \varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_{12}, \varphi_{23}, \varphi_{31})$ of the magnitudes $|E_h|$, $|E_k|$, $|E_l|$, $|E_m|$, $|E_{h+k}|$, $|E_{k+l}|$, $|E_{l+h}|$ and the phases φ_h, φ_k, φ_l, φ_m, φ_{h+k}, φ_{k+l}, φ_{l+h} where $\mathbf{h, k, l}$ and $\mathbf{m}$ are the primitive random variables, subject to the condition $\mathbf{h + k + l + m = 0}$ (Hauptman, 1975*a*). It has been shown previously (Heinerman, 1976; Giacovazzo, 1977) that, under certain conditions for the reciprocal vectors, the same distribution is obtained if $\mathbf{h, k, l}$ and $\mathbf{m}$ are supposed to be fixed, while the atomic coordinates are considered to be the primitive random variables. The latter approach will be followed for the interpretation of our results. By integrating this distribution function with respect to the variables φ_1, φ_2, φ_3, φ_4, φ_{12}, φ_{23} and φ_{31}, subject to the conditions $\varphi_1 + \varphi_2 - \varphi_{12} = T_1$ and $\varphi_3 + \varphi_4 + \varphi_{12} = T_2$ and by fixing the seven magnitudes, we obtain the conditional joint probability distribution $P(T_1, T_2 | R_1, R_2, R_3, R_4, R_{12}, R_{23}, R_{31})$ of the two triple-product phases $\Phi_1 = \varphi_h + \varphi_k - \varphi_{h+k}$ and $\Phi_2 = \varphi_l + \varphi_{-h-k-l} + \varphi_{h+k}$. This distribution is integrated

with respect to T_2 over the range 0 to π, thus specifying $0 \le T_2 < \pi$ which implies the choice of an enantiomorph. The resulting $P^{(e)}(T_1|R_1, R_2, R_3, R_4, R_{12}, R_{23}, R_{31})$ is an enantiomorph-sensitive conditional probability distribution of the phase Φ_1 in which the superscript (e) is added to state explicitly that it is valid for only one of the two possible enantiomorphs, as will be shown in the sequel.

The conditional joint probability distribution of $\Phi_1 = \varphi_h + \varphi_k - \varphi_{h+k}$ and $\Phi_2 = \varphi_l + \varphi_{h+k} + \varphi_{-h-k-l}$

The desired distribution function is easily obtained from Hauptman's joint probability distribution of seven normalized structure factors (Hauptman, 1975a). The calculations are given in Appendix II and the result is

$$P(T_1, T_2|R_1, R_2, R_3, R_4, R_{12}, R_{23}, R_{31})$$

$$= C \exp [2N^{-1/2}R_1R_2R_{12}\cos{(T_1)} + 2N^{-1/2}$$

$$\times R_3R_4R_{12}\cos{(T_2)} + 2N^{-1}$$

$$\times (R_{23}^2 + R_{31}^2 - 2)R_1R_2R_3R_4\cos{(T_1 + T_2)}],$$

$$(1)$$

where

$$C = [4\pi^2 I_0(2N^{-1/2}R_1R_2R_{12})I_0(2N^{-1/2}R_3R_4R_{12})]^{-1}.$$

From (1) it follows that the most probable value for the phase pair (Φ_1, Φ_2) will always be $(0, 0)$ if $(R_{23}^2 + R_{31}^2) \ge 2$. An example of such a probability distribution is given in Fig. 1(a). If, on the other hand, $(R_{23}^2 + R_{31}^2) < 2$, the position of the maximum of (1) depends also on the relative values of the other five magnitudes. Especially when R_{12} is not too large, the most probable value for (Φ_1, Φ_2) can differ considerably from $(0, 0)$ (see Fig. 1b for an example). Note that if $R_{12} = 0$, (1) does not depend on T_1 and T_2 separately, but only on their sum. As in this case the amplitudes of the triple products $E_hE_kE_{-h-k}$ and $E_lE_{h+k}E_{-h-k-l}$ are both equal to zero, we cannot expect any information about their phases. The only possible phase information concerns the quartet $E_hE_kE_lE_{-h-k-l}$ with a phase equal to $(\Phi_1 + \Phi_2)$. Integrating (1) with respect to T_1 and T_2 both from 0 to 2π under the condition $T_1 + T_2 = Q$ leads to

$$P(Q|R_1, R_2, R_3, R_4, R_{12}, R_{23}, R_{31})$$

$$= K \exp [2N^{-1}(R_{12}^2 + R_{23}^2 + R_{31}^2 - 2)$$

$$\times R_1R_2R_3R_4\cos{(Q)}],$$

$$(2)$$

which was also obtained by Heinerman (1976) after rewriting Hauptman's results in exponential form.

The enantiomorph-dependent conditional probability distribution of the phase $\Phi_1 = \varphi_h + \varphi_k - \varphi_{h+k}$

From (1) we can calculate

$$\int_0^\pi P(T_1, T_2|R_1, R_2, R_3, R_4, R_{12}, R_{23}, R_{31})\,dT_2$$

$$= C'P^{(e)}(T_1|R_1, R_2, R_3, R_4, R_{12}, R_{23}, R_{31}),\quad (3)$$

in which C' is a suitable normalizing constant.

With the reciprocal-lattice vectors fixed and the atomic position vectors the primitive random variables, $C'P^{(e)}(T_1|R_1, R_2, R_3, R_4, R_{12}, R_{23}, R_{31})\,dT_1$ gives the fraction of the total number of possible structures with N atoms in the unit cell for which the following conditions are fulfilled:

$$T_1 \le \Phi_1 < T_1 + dT_1 \qquad (4)$$

$$0 \le \Phi_2 < \pi, \quad \text{where } \Phi_2 = \varphi_l + \varphi_{h+k} + \varphi_{-h-k-l} \quad (5)$$

$$|E_h| = R_1, |E_k| = R_2, |E_l| = R_3, |E_{h+k+l}| = R_4,$$

$$|E_{h+k}| = R_{12}, |E_{k+l}| = R_{23}, |E_{l+h}| = R_{31}. \qquad (6)$$

Condition (5) implies that this fraction does not contain two structures that are related by an inversion centre. Therefore, the integration in (3) implicitly means the choice of an enantiomorph as, of all pairs of enantiomorphously related structures, only one member remains in the sample space of $P^{(e)}$. The calculations are given in Appendix III and the result is

$$P^{(e)}(T_1|R_1, R_2, R_3, R_4, R_{12}, R_{23}, R_{31})$$

$$= K \exp [2N^{-1/2}R_1R_2R_{12}\cos{(T_1)}$$

$$- 4\pi^{-1}N^{-1}(R_{23}^2 + R_{31}^2 - 2)R_1R_2R_3R_4\sin{(T_1)}].$$

$$(7)$$

Integrating T_2 from π to 2π in (3) corresponds to the choice of the other enantiomorph. From Appendix III it is easily seen that the result is analogous to (7); the only difference appears in the sign of the enantiomorph-sensitive sine term.

Both situations can be described by a Von Mises distribution (Heinerman, Krabbendam & Kroon, 1977):

$$P^{(e)}(T_1|R_1, R_2, R_3, R_4, R_{12}, R_{23}, R_{31})$$

$$= K \exp [X \cos{(T_1 + \varepsilon)}], \qquad (8)$$

where $X^2 = A^2 + s^2 B^2$, $A = 2N^{-1/2}R_1R_2R_{12}$, $B = 2N^{-1}(R_{23}^2 + R_{31}^2 - 2)R_1R_2R_3R_4$, $X\cos{(\varepsilon)} = A$, $X\sin{(\varepsilon)} = sB$, $s = +2/\pi$ if T_2 has been integrated from 0 to π, $s = -2/\pi$ if T_2 has been integrated from π to 2π, $K = [2\pi I_0(X)]^{-1}$.

Equation (8) is unimodal in the range $0 \le T_1 < 2\pi$ and the maximum is found at

$$T_1^{mode} = -\varepsilon = -\arctan{[sB/A]}$$

$$= -\arctan{[sN^{-1/2}(R_{23}^2 + R_{31}^2 - 2)R_3R_4R_{12}^{-1}]}.$$

$$(9)$$

Interpretation of the derived distribution

The effect of the 'enantiomorph-dependent' integration of T_2 on the probability distribution of Φ_1 can be visualized in Fig. 1. Integrating T_2 from 0 to π (*i.e.* $s = +2/\pi$) is equivalent to projecting the posterior half of the figure on the axis T_1. It is obvious from the drawings that in Fig. 1(a) the resulting distribution function will have a mode at the left of the origin; in fact from (9) it follows that the mode is approximately at $-54°$. On the other hand, in Fig. 1(b) the mode of the resulting distribution function will be at

the right of the origin if the posterior half of the figure is projected on the axis T_1. For this example (9) leads to a mode in the vicinity of $+36°$.

It is of interest to compare (8) with the distribution obtained by projecting the whole figure on the axis T_1. This is equivalent to integrating (1) with respect to T_2 over the range 0 to 2π. After employing (I.1)–(I.3), (I.4) leads to

$$P(T_1|R_1, R_2, R_{12}) = L' \exp [A \cos (T_1)], \quad (10)$$

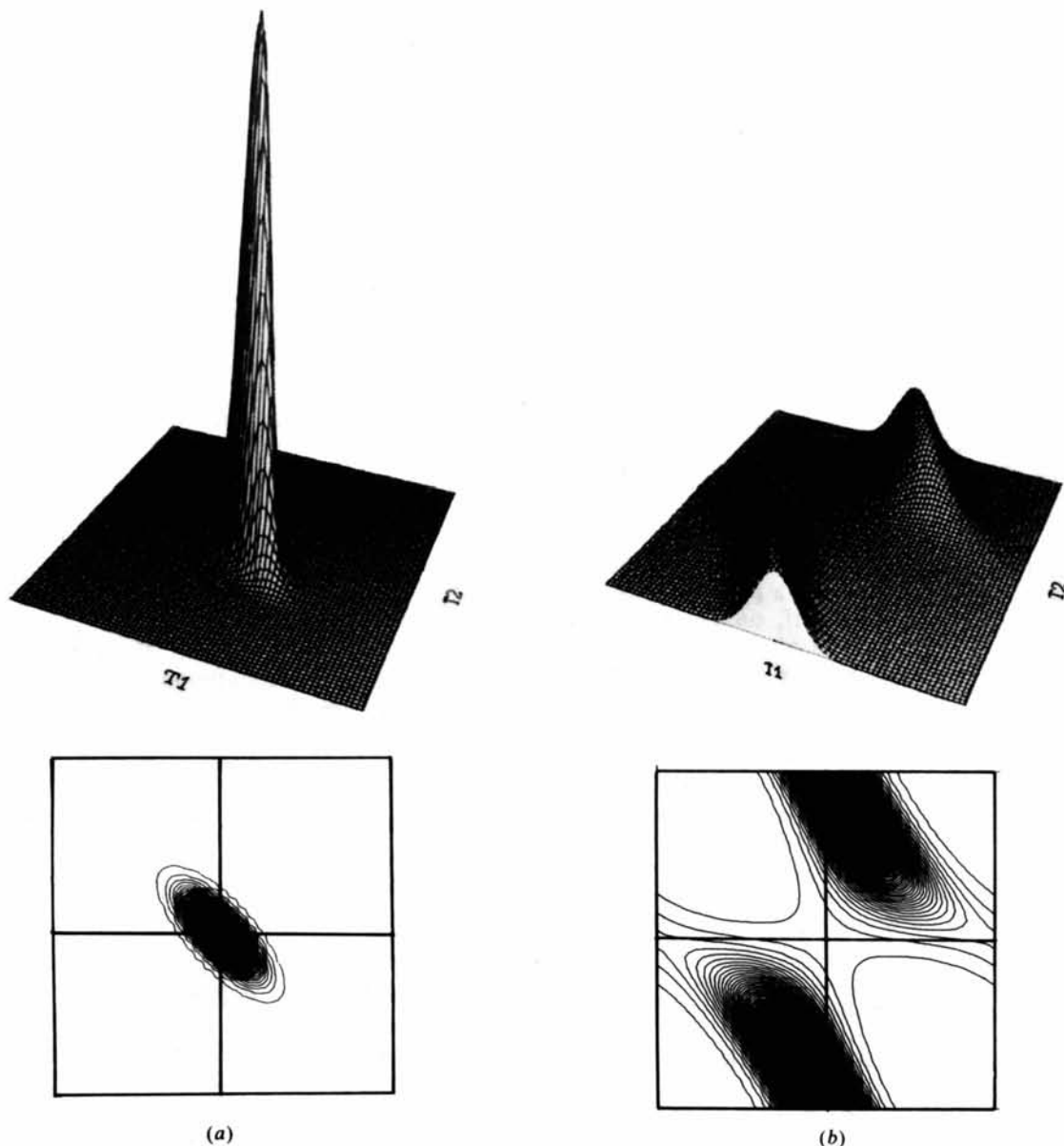where $L' = [2\pi I_0(A)]^{-1}$, which is identical to the well

Fig. 1. The conditional joint probability distribution of two triple-product phases. T_1 runs from left to right from $-\pi$ to $+\pi$; T_2 from the front to the back from $-\pi$ to $+\pi$. For the sake of clarity the contour diagrams, on an arbitrary scale, are also given. Both figures are calculated from equation (1) for an idealized structure in $P1$ with $N = 29$. The examples are taken from Hauptman (1975b). (a) $R_1 = 3·034$, $R_2 = 2·863$, $R_3 = 2·023$, $R_4 = 2·012$, $R_{12} = 1·732$, $R_{23} = 0·997$, $R_{31} = 2·454$; (b) $R_1 = 2·862$, $R_2 = 2·672$, $R_3 = 2·275$, $R_4 = 1·700$, $R_{12} = 1·106$, $R_{23} = 0·404$, $R_{31} = 0·222$.

known Cochran distribution (Cochran, 1955). Note that (8) reduces to (10) if we define $s = 0$ if Φ_2 can be anywhere between 0 and 2π. Distribution (10), correct up to and including terms of order N^{-1}, only depends on R_1, R_2 and R_{12} and always has its mode on zero, while (8) depends on all seven magnitudes and may have its mode anywhere between $-\frac{1}{2}\pi$ and $+\frac{1}{2}\pi$. [Note that $\cos(T_1^{\text{mode}})$ is always positive.] The larger the extra four magnitudes R_3, R_4, R_{23} and R_{31}, the more the variance decreases and the more the mode differs from zero. The latter effect is more pronounced if R_{12} (*i.e.* the amplitude of the structure factor involved in both triple products) is not too large.

In this context it is noted that the probability distributions used in this paper are only correct if they can be written as a converging series of powers of $N^{-1/2}$. Therefore, it follows that the order N^{-1} terms should be small compared to the order $N^{-1/2}$ terms, which leads to the conclusion that, strictly speaking, the use of (8) is limited to those cases for which $|B| < A$. The examples used in Fig. 1 do not fulfil this condition but they clearly show the two limiting characteristics of (1). The four magnitudes R_3, R_4, R_{23} and R_{31} corresponding to $|E_1|$, $|E_{-h-k-1}|$, $|E_{k+1}|$ and $|E_{1+h}|$, respectively, all belong to the second phasing shell of the triple product $E_h E_k E_{-h-k}$ as defined by Giacovazzo (1980). These amplitudes were thought to influence the probability distribution of the triple-product phase only in the terms of order $N^{-3/2}$, whereas the extra terms in (8) are of order N^{-1}; apparently the extra information about the related triple-product phase Φ_2 is sufficient to promote a part of the second phasing shell in such a way that it effects the order N^{-1} terms of the probability distribution of Φ_1. As the relation between Φ_1 and Φ_2 is only based on the common structure-factor phase φ_{h+k}, we conclude that choosing an enantiomorph *via* restrictions on the phase of $E_1 E_{-h-k-1} E_{h+k}$ influences the distributions of the phases of all triple products containing either E_1 or E_{-h-k-1} or E_{h+k}.

The choice of an enantiomorph in phase-determining procedures. A practical test

Equation (8) can be used in an active way in normal direct-methods procedures by first selecting a triple product to specify an enantiomorph and then calculating *via* (8) the modes and variances of the distributions of all triple products having one structure factor in common with the 'enantiomorph definer'. This was tested on the crystal structure of calcium trilactate trihydrate ($CaC_9O_9H_{16}.3H_2O$; space group $P1$ with $a = 5\cdot823$, $b = 8\cdot295$, $c = 8\cdot975$ Å, $\alpha = 78\cdot39$, $\beta = 73\cdot61$ and $\gamma = 75\cdot19°$). All attempts to solve this problem with conventional direct-methods procedures were unsuccessful. Only with the support of the measured Bijvoet differences caused by the

anomalous scattering of the calcium atom could the structure be determined. Details of this work will be published in a forthcoming paper. From the initial failures it was clear that the major problem concerned the definition and maintaining of an enantiomorph. In particular, the iterative use of the tangent formula for phase refinement drove all phase sets in a few cycles to (pseudo)centrosymmetric solutions of which the E maps could not be interpreted. Therefore this structure seemed to be a good example to test whether the application of (8) could restrain the phase refinement. With the *MULTAN*78 system (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) amplitudes of normalized structure factors were calculated from 1545 unique reflexions which were considered to be observed [$I \geq 2\frac{1}{2}\sigma(I)$]. Subsequently, the 188 largest E values were passed to the SIGMA-TWO routine, resulting in 1112 unique triple products. Each of these invariants could in principle be used to define an enantiomorph, but a sensible choice could be made keeping the following requirements in mind: (*a*) the chosen 'enantiomorph definer' must have many related triple products with one structure factor in common; (*b*) the phase of each of these related triple products should have a probability distribution of type (8) with a small variance and a mode considerably differing from zero. A small variance is obtained by using large normalized structure factors, as can be seen from (8), but from (9) it follows that the larger the value of R_{12}, the more the mode approaches to zero. As we aimed primarily at enantiomorph-sensitive phase indications, emphasis was put on the requirement concerning the mode. Equation (9) then led to the definition of the following parameter for a triple product $E_{h_1} E_{h_2} E_{h_3}$ ($\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 = 0$):

$$S = |E_{h_1}||E_{h_2}||E_{h_3}|^{-1} n_{h_3} + |E_{h_1}||E_{h_3}||E_{h_2}|^{-1} n_{h_2}$$

$$+ |E_{h_2}||E_{h_3}||E_{h_1}|^{-1} n_{h_1}, \tag{11}$$

where only the 188 largest E values were considered and where n_{h_i} ($i = 1, 2, 3$) means the number of large triple products containing E_{h_i}. The triple product $E_{510} E_{021} E_{\overline{531}}$ (with $A = 2N^{-1/2} EEE = 4\cdot22$ and $\Phi_{\text{true}} = -5°*$) resulted in the largest value of S and was therefore chosen to define an enantiomorph. Then, by employing (8) with $s = +2/\pi$, the modes and variances of the distributions $P^{(e)}$ of 105 related triple-product phases were calculated. In these calculations the unobserved E values were put equal to their expected values ($|E|^2 = 1\cdot0$). The remaining 1007 relations were processed in the usual way *via* the Cochran distribution (10).

---

* Φ_{true} was calculated from the parameters of the refined crystal structure with the correct absolute configuration.

In a convergence procedure, based on all 1112 $\sum_2$ relations, the order in which the phases were to be generated and refined by the tangent formula was determined. Noteworthy was the fact that most of the enantiomorph-dependent phase indications appeared in the bottom of the convergence map. The reason for this is that a variance calculated from the seven-magnitude distribution (8) tends to be smaller than a variance calculated from (10). In fact, for a given triple product, (8) can never lead to a variance larger than the one obtained from (10). After fixing an origin by assigning arbitrary phases to three linearly independent structure factors, 50 different starting sets of phases were generated by permuting five other phases *via* a magic-integer representation. After application of the *MULTAN*78 routine FASTAN it appeared that, in spite of the non-centrosymmetric phase indications in the early stages of the phase expansion, all 50 sets refined to the same over-consistent pseudo-centrosymmetric solution with figures of merit 1·36, 2·58 and 10·92 for ABS FOM, PSI-ZERO and RESID, respectively. In our local packet of direct-methods procedures (the *REDUC* system; to be published) a different algorithm is used for the application of the tangent formula. The alternative was developed especially for application in connection with a multi-solution approach of the phase problem and can best be seen as a restraint on the phase refinement which prevents a phase set refining to a solution which bears no relation to the chosen starting phases. More details of the procedure are given in Appendix IV. Application of the procedure to the enantiomorph-sensitive set of $\sum_2$ relations resulted in 18 different solutions out of 64 different starting points. Some relevant data of the 18 sets are given in Table 1. *E* maps were calculated for the six most promising sets as indicated by the COMBINED FOM. The numbers 3, 17, 36 and 9 again failed to show interpretable lactate fragments among the 30 highest peaks (set 3 is identical to the one found by *FASTAN*). Set 26, however, could be interpreted without many difficulties; apart from the calcium atom, three fragments were found, each consisting of five peaks and all three compatible with the expected lactate groups. From subsequent Fourier syntheses based on these parameters the complete structure was easily obtained. In Fig. 2 an outline of the refined structure is given. Inspection of the initial *E* map showed afterwards that 18 of the 22 atoms were present among the 30 highest peaks, while only six peaks appeared to belong to the inverted structure. The predominance of one enantiomorph compared to the other is clearly demonstrated in Table 2 where the 30 highest peaks of four relevant *E* maps are classified in three groups: (*a*) peaks belonging to the true enantiomorph as found from the Bijvoet differences [labelled as O(1), C(1) *etc.*]; (*b*) peaks belonging to the inverted structure (labelled as *i*O(1), *i*C(1) *etc.*)

Table 1. *Figures of merit for the* 18 *different solutions obtained after application of the tangent formula via the described modified algorithm*

The COMBINED FOM is calculated with unit weights for ABS FOM, PSI ZERO and RESID. The numbers between parentheses refer to classifications of the sets based on the individual figures of merit. The parameter ENFOM is described in detail in the main text.

Set No.	ABS FOM	PSI ZERO	RESID	COMB FOM	ENFOM
1	1·15 (16)	2·29 (3)	17·24 (18)	0·84 (18)	0·102 (5)
2	1·22 (6)	2·41 (10)	12·65 (7)	1·55 (7)	0·099 (7)
3	1·36 (1)	2·58 (18)	10·88 (1)	2·00 (1)	0·026 (18)
4	1·09 (18)	2·10 (1)	16·97 (16)	1·04 (16)	0·123 (1)
9	1·27 (2)	2·53 (17)	11·85 (3)	1·61 (4)	0·070 (17)
13	1·12 (17)	2·31 (4)	14·60 (14)	1·08 (15)	0·120 (2)
17	1·25 (3)	2·43 (12)	11·69 (2)	1·77 (2)	0·085 (15)
19	1·21 (9)	2·46 (13)	12·80 (8)	1·41 (11)	0·092 (13)
23	1·22 (7)	2·47 (14)	12·57 (6)	1·44 (10)	0·094 (11)
26	1·19 (13)	2·31 (5)	13·24 (10)	1·58 (5)	0·103 (4)
29	1·25 (4)	2·48 (15)	12·35 (5)	1·58 (6)	0·086 (14)
36	1·22 (8)	2·35 (7)	12·82 (9)	1·66 (3)	0·097 (9)
38	1·19 (11)	2·38 (8)	14·30 (13)	1·26 (13)	0·094 (12)
41	1·19 (12)	2·42 (11)	13·31 (11)	1·34 (12)	0·102 (6)
43	1·18 (14)	2·31 (6)	13·66 (12)	1·47 (9)	0·106 (3)
45	1·25 (5)	2·52 (16)	12·07 (4)	1·53 (8)	0·078 (16)
50	1·17 (15)	2·27 (2)	17·11 (17)	0·96 (17)	0·098 (8)
56	1·20 (10)	2·38 (9)	15·07 (15)	1·17 (14)	0·095 (10)

and (*c*) non-interpretable peaks (labeled as ?). The results of sets 3 and 36 are included to show the difficulties with the definition of an enantiomorph. In set 3 both enantiomorphs are almost equally well represented and it is clear that this pseudo-centrosymmetric solution could not be interpreted. In set 36 most of the highest peaks correspond to only one enantiomorph. The reason that this solution was rejected at first is that most of the carbon atoms, necessary to form a reasonable lactate fragment (see Fig. 2), are not present among the 30 highest peaks.

From set 3, *via* set 36, to set 26 the PSI ZERO figure of merit gradually drops while the preference for one enantiomorph appears to increase. The results related to the *E* map of set 4, being the one with the best PSI ZERO indication, are also given in Table 2, where it can be seen that the preference for the chosen enantiomorph is even more pronounced. In spite of the unpromising values for ABS FOM and RESID,
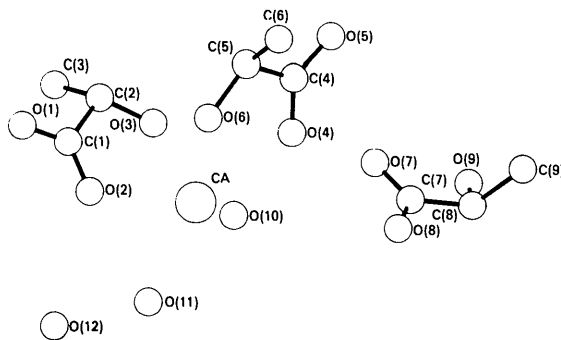

Fig. 2. Outline of the test structure projected approximately on the least-squares plane.

Table 2. *Interpretation of the 30 highest peaks in the calculated E maps*

In all sets the first peak is about two or three times as large as the second one. The heights of peaks 2 to 30 gradually decreases in all sets. Peaks labeled O(1), C(1) *etc.* correspond to atomic positions of the true enantiomorph as found from the Bijvoet differences. Peaks labeled *i*O(1), *i*C(1) *etc.* correspond to the (through the calcium atom) inverted structure.

Peak	Set 26	Set 3	Set 36	Set 4
1	Ca	Ca	Ca	Ca
2	*i*O(1)	O(5)	*i*O(1)	*i*O(5)
3	*i*O(8)	*i*O(5)	*i*O(5)	*i*O(1)
4	*i*O(5)	O(1)	*i*O(8)	*i*O(8)
5	O(5)	*i*O(3)	O(5)	*i*C(1)
6	?	O(8)	?	*i*O(4)
7	?	?	*i*O(3)	*i*O(3)
8	*i*C(1)	O(9)	*i*O(11)	*i*C(7)
9	*i*O(2)	*i*O(4)	*i*C(1)	?
10	O(9)	O(2)	*i*O(7)	?
11	O(3)	*i*O(9)	?	*i*C(2)
12	*i*C(5)	*i*O(11)	?	*i*O(7)
13	*i*O(3)	*i*O(8)	*i*O(9)	O(7)
14	*i*O(9)	*i*O(1)	O(4)	O(11)
15	*i*O(11)	O(11)	*i*C(2)	O(4)
16	O(11)	?	O(9)	*i*O(2)
17	*i*O(7)	?	?	*i*C(5)
18	O(4)	*i*O(7)	*i*O(6)	*i*O(11)
19	*i*O(4)	C(5)	*i*O(4)	*i*O(9)
20	?	C(1)	?	O(3)
21	?	O(7)	C(4)	*i*O(6)
22	?	?	O(11)	*i*C(4)
23	*i*O(12)	O(3)	O(7)	*i*O(12)
24	*i*O(6)	C(4)	?	*i*C(8)
25	*i*C(4)	*i*C(1)	?	?
26	*i*C(2)	?	*i*O(2)	?
27	*i*C(7)	?	O(2)	O(9)
28	O(7)	?	O(8)	?
29	?	C(9)	O(3)	?
30	*i*C(8)	*i*O(2)	*i*C(5)	?

this set appears to give the best solution. The three lactate fragments can easily be found among the highest peaks although the geometry is somewhat less accurate compared to the result of set 26. The predominant enantiomorph in the described solutions is in agreement with the choice for $s = +2/\pi$ in (8); *i.e.* the choice that the phase of $E_{510}E_{021}E_{\bar{5}\bar{3}\bar{1}}$ must lie between 0 and π.

Repetition of the described calculations with $s = -2/\pi$ led to results comparable to those obtained before, but now, as expected, the true enantiomorph dominated the final E maps. Although the single triple product $E_{510}E_{201}E_{\bar{5}\bar{3}\bar{1}}$ does not seem to be a very suitable invariant to resolve the ambiguity ($\Phi_{\text{true}} = -5°$), employing it *via* (8) clearly leads to satisfactory results. Apparently the simultaneous effect of the derived phase indications is sufficient to obtain a set of structure-factor phases which correspond to an E map dominated by the chosen enantiomorph.

The enantiomorph-sensitive figure of merit ENFOM

Apart from the active application, as described in the preceding section, (8) can also be used for the defini-

tion of an enantiomorph-sensitive figure of merit. If (8) is applied to triple products formed from the larger E values only, the parameter B is expected to be positive, no matter which pair of triple products is considered. Therefore, for any pair $E_h E_k E_{-h-k}$ and $E_{-h}E_l E_{h-l}$ of large triple products, the expected phases will be in opposite hemicycles of the Argand diagram. This leads to the conclusion that all large triple products $E_h E_k E_{-h-k}$ for fixed h and arbitrary k are expected to have a phase in the same hemicycle of the Argand diagram if the enantiomorph has been specified. This characteristic can be used to rank refined phase sets according to their ability to describe only one enantiomorph. If ENFOM is defined as

$$\text{ENFOM} = T^{-1}\left\{\sum_h \left| \sum_k \sin\left(\varphi_h + \varphi_k + \varphi_{-h-k}\right)\right|\right\}, \quad (12)$$

where only the T terms for which $E_h E_k E_{-h-k}$ is large are considered, ENFOM will always be between zero and unity; small values of the parameter indicate the absence of the described clustering of related triple-product phases in a hemicycle of the Argand diagram, while the larger values of ENFOM point to a phase set which follows (8). ENFOM was calculated for the 18 phase sets described in the preceding paragraph and the results are given in the last column of Table 1. Set 4 leads to the largest value of the figure of merit, which indicates that the corresponding E map will be dominated by only one enantiomorph. As described before, it can be seen in Table 2 that this is indeed the case. Also, set 26, which was the first one which revealed a large part of the structure, leads to a promising value of ENFOM.

By far the smallest value of ENFOM is found for set 3, which indicates the absence of the clustering of triple-product phases. The E map of this set is therefore expected to contain peaks belonging to both enantiomorphs.

From the results we conclude that ENFOM leads to a valuable indication for the correctness of a phase set in a non-centrosymmetric space group.

Concluding remarks

The derived enantiomorph-dependent conditional probability distribution of a triple-product phase (equation 8) was shown to be of practical importance in the determination of a P1 structure. Apart from the active use of the new formula, a passive application in the form of an enantiomorph-sensitive figure of merit was described. The basis of the new figure of merit ENFOM is (8) from which it was concluded that the phases of related large triple products are expected to cluster in the first or fourth quadrant of the Argand diagram. Qualitatively this effect can be explained from the fact that the number of positive

quartets (*i.e.* quartet invariants with an expected phase of 0) is far greater than the number of negative quartets (the expected phase is π). Therefore, it is anticipated that two triple products, which together form a quartet (*i.e.* $E_h E_k E_{-h-k}$ and $E_{-h} E_l E_{h-l}$), will have phases which tend to sum to zero; so if one phase is between 0 and π, the other one will be found between π and 2π more often than between 0 and π. This indicates that the enantiomorph-dependent formulae for triple-product phases, as derived in this paper, are strongly correlated to the distribution function of a quartet invariant.

Note

After the manuscript had been submitted, one of the referees pointed out a paper by Hauptman (1977) in which enantiomorph-dependent probability distributions are also derived. Starting from the 13 structure factors in the third neighbourhood of a quartet invariant, he derived an expression ($P_{2/13}$) for the joint probability distribution of two related quartet phases ($\Phi_{1m} = \varphi_h + \varphi_k + \varphi_l + \varphi_m$ and $\Phi_{pq} = \varphi_h + \varphi_k + \varphi_p + \varphi_q$). This $P_{2/13}$ is given in a mixed form containing both Bessel functions and exponentials. Hauptman concludes that $P_{2/13}$ has, in general, two maxima which are related by inversion through $(0,0)$. By choosing one or the other maximum, an enantiomorph may be selected which may lead to a number of enantiomorph-sensitive (conditional) probability distributions. However, the procedure is only appropriate if $P_{2/13}$ has a pronounced maximum on an enantiomorph-sensitive position [*i.e.* different from $(0,0)$, $(0,\pi)$, $(\pi,0)$ of (π,π)], which is in strong contrast to the possibilities of the present approach.

APPENDIX I

Some formulae

From elementary trigonometry (Hauptman, 1971),

$$\sum_i A_i \cos(\varphi + \alpha_i) = X \cos(\varphi + \varepsilon), \qquad (I.1)$$

where $X^2 = \sum_i \sum_j A_i A_j \cos(\alpha_i - \alpha_j)$ (I.2)

$$X \cos(\varepsilon) = \sum_i A_i \cos(\alpha_i) \qquad (I.3a)$$

$$X \sin(\varepsilon) = \sum_i A_i \sin(\alpha_i). \qquad (I.3b)$$

From (Abramowitz & Stegun, 1970, p. 376, formula 9.6.16)

$$\int_0^\pi \exp[z \cos(\varphi)]\, d\varphi = \pi I_0(z), \qquad (I.4)$$

it follows that

$$\int_0^{2\pi} \exp[z \cos(\varphi + \varepsilon)]\, d\varphi = 2\pi I_0(z),$$

where $I_0(z)$ is the modified Bessel function of the first kind of order zero. For an expression for $I_0(z)$ in the form of an ascending series of powers of z we obtain, from Abramowitz & Stegun (1970, p. 375, formula 9.6.12),

$$I_0(z) = 1 + \tfrac{1}{4}z^2 + \tfrac{1}{64}z^4 + \dots$$

$$= \exp(\tfrac{1}{4}z^2)(1 + \text{terms of order } z^4 + \dots). \qquad (I.5)$$

APPENDIX II

The derivation of (1)

For an expression of the joint probability distribution of the magnitudes and phases of the seven normalized structure factors E_h, E_k, E_l, E_{-h-k-l}, E_{h+k}, E_{k+l} and E_{l+h} we refer to formula (2.5) of Hauptman (1975a) which is correct up to and including terms of order N^{-1} that depend on the phases. The joint probability distribution of the two triple-product phases Φ_1 and Φ_2 can be obtained by integrating with respect to the seven variables φ_1, φ_2, φ_3, φ_4, φ_{12}, φ_{23} and φ_{31} subject to the conditions $\varphi_1 + \varphi_2 - \varphi_{12} = T_1$ and $\varphi_3 + \varphi_4 + \varphi_{12} = T_2$. This is most conveniently done by first collecting all terms in the exponent which depend on φ_{31}, and combining them using (I.1)–(I.3). We obtain

$$2N^{-1/2}R_1 R_3 R_{31} \cos(\varphi_1 + \varphi_3 - \varphi_{31})$$

$$+ 2N^{-1/2}R_2 R_4 R_{31} \cos(\varphi_2 + \varphi_4 + \varphi_{31})$$

$$- 2N^{-1}R_1 R_2 R_{23} R_{31} \cos(\varphi_1 - \varphi_2 + \varphi_{23} - \varphi_{31})$$

$$- 2N^{-1}R_3 R_4 R_{23} R_{31} \cos(\varphi_3 - \varphi_4 - \varphi_{23} - \varphi_{31})$$

$$- 2N^{-1}R_2 R_3 R_{31} R_{12} \cos(\varphi_2 - \varphi_3 + \varphi_{31} - \varphi_{12})$$

$$- 2N^{-1}R_1 R_4 R_{31} R_{12} \cos(\varphi_1 - \varphi_4 - \varphi_{31} - \varphi_{12})$$

$$= X_{31} \cos(\varphi_{31} + \varepsilon_{31}), \qquad (II.1)$$

where

$$X_{31}^2 = 4N^{-1}R_{31}^2[R_1^2 R_3^2 + R_2^2 R_4^2$$

$$+ 2R_1 R_2 R_3 R_4 \cos(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4)]$$

$$+ \text{terms of order } N^{-3/2}.$$

Because X_{31} and ε_{31} are independent of φ_{31} the

integration with respect to φ_{31} is easily obtained using (I.4):

$$P(\varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_{12}, \varphi_{23}; R_1, R_2, R_3, R_4, R_{12}, R_{23}, R_{31})$$
$$= 2\pi^{-6} R_1 R_2 R_3 R_4 R_{12} R_{23} R_{31}$$
$$\times \exp\left[-R_1^2 - R_2^2 - R_3^2 - R_4^2 - R_{12}^2 - R_{23}^2 - R_{31}^2\right.$$
$$+2N^{-1/2} R_1 R_2 R_{12} \cos(\varphi_1 + \varphi_2 - \varphi_{12})$$
$$+2N^{-1/2} R_3 R_4 R_{12} \cos(\varphi_3 + \varphi_4 + \varphi_{12})$$
$$+2N^{-1/2} R_2 R_3 R_{23} \cos(\varphi_2 + \varphi_3 - \varphi_{23})$$
$$+2N^{-1/2} R_1 R_4 R_{23} \cos(\varphi_1 + \varphi_4 + \varphi_{23})$$
$$-2N^{-1} R_1 R_3 R_{12} R_{23} \cos(\varphi_1 - \varphi_3 - \varphi_{12} + \varphi_{23})$$
$$-2N^{-1} R_2 R_4 R_{12} R_{23} \cos(\varphi_2 - \varphi_4 - \varphi_{12} - \varphi_{23})$$
$$\left. -4N^{-1} R_1 R_2 R_3 R_4 \cos(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4)\right]$$
$$\times I_0[X_{31}]. \tag{II.2}$$

Formula (II.2) is correct up to and including terms of order N^{-1} which depend on the phases. Because the argument of the Bessel function is independent of φ_{23} within the given order of accuracy, the integration with respect to φ_{23} can be performed using the same procedure. The result is

$$P(\varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_{12}; R_1, R_2, R_3, R_4, R_{12}, R_{23}, R_{31})$$
$$= 4\pi^{-5} R_1 R_2 R_3 R_4 R_{12} R_{23} R_{31}$$
$$\times \exp\left[-R_1^2 - R_2^2 - R_3^2 - R_4^2 - R_{12}^2 - R_{23}^2 - R_{31}^2\right.$$
$$+2N^{-1/2} R_1 R_2 R_{12} \cos(\varphi_1 + \varphi_2 - \varphi_{12})$$
$$+2N^{-1/2} R_3 R_4 R_{12} \cos(\varphi_3 + \varphi_4 + \varphi_{12})$$
$$\left. -4N^{-1} R_1 R_2 R_3 R_4 \cos(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4)\right]$$
$$\times I_0[X_{31}] I_0[X_{23}], \tag{II.3}$$

where

$$X_{23}^2 = 4N^{-1} R_{23}^2 [R_2^2 R_3^2 + R_1^2 R_4^2$$
$$+2R_1 R_2 R_3 R_4 \cos(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4)]$$
$$+\text{terms of order } N^{-3/2}.$$

After the substitutions $\varphi_1 = T_1 - \varphi_2 + \varphi_{12}$ and $\varphi_3 = T_2 - \varphi_4 - \varphi_{12}$ the distribution function appears to be independent of φ_2, φ_4 and φ_{12}, leading to a trivial factor of $(2\pi)^3$ when the integrations with respect to these three variables are performed. After fixing the seven magnitudes the conditional joint probability distribution of the phases Φ_1 and Φ_2 is obtained:

$$P(T_1, T_2 | R_1, R_2, R_3, R_4, R_{12}, R_{23}, R_{31})$$
$$= L I_0[Y_{31}] I_0[Y_{23}] \exp\left[2N^{-1/2} R_1 R_2 R_{12} \cos(T_1)\right.$$
$$+2N^{-1/2} R_3 R_4 R_{12} \cos(T_2)$$
$$\left. -4N^{-1} R_1 R_2 R_3 R_4 \cos(T_1 + T_2)\right], \tag{II.4}$$

where L is a suitable normalizing constant,

$$Y_{31}^2 = 4N^{-1} R_{31}^2 [R_1^2 R_3^2 + R_2^2 R_4^2$$
$$+2R_1 R_2 R_3 R_4 \cos(T_1 + T_2)]$$
$$+\text{terms of order } N^{-3/2}$$

and

$$Y_{23}^2 = 4N^{-1} R_{23}^2 [R_2^2 R_3^2 + R_1^2 R_4^2$$
$$+2R_1 R_2 R_3 R_4 \cos(T_1 + T_2)]$$
$$+\text{terms of order } N^{-3/2}.$$

Using (I.5) we rewrite the Bessel functions in exponential form leading to

$$P(T_1, T_2 | R_1, R_2, R_3, R_4, R_{12}, R_{23}, R_{31})$$
$$= C \exp\left[2N^{-1/2} R_1 R_2 R_{12} \cos(T_1)\right.$$
$$+2N^{-1/2} R_3 R_4 R_{12} \cos(T_2)$$
$$\left. +2N^{-1}(R_{23}^2 + R_{31}^2 - 2) R_1 R_2 R_3 R_4 \cos(T_1 + T_2)\right]. \tag{II.5}$$

The normalizing constant C can be obtained by integrating (II.5) with respect to T_1 and T_2 from 0 to 2π and setting the result equal to unity. Retention of terms up to and including order N^{-1} leads to

$$C = [4\pi^2 I_0(2N^{-1/2} R_1 R_2 R_{12}) I_0(2N^{-1/2} R_3 R_4 R_{12})]^{-1}. \tag{II.6}$$

APPENDIX III

The derivation of (7)

From (1) and (3) it follows that

$$P^{(e)}(T_1 | R_1 \ldots R_{31}) = C' \int_0^\pi \exp\left[A_1 \cos(T_1)\right.$$
$$\left. +A_2 \cos(T_2) + B \cos(T_1 + T_2)\right] dT_2, \tag{III.1}$$

where

$$A_1 = 2N^{-1/2} R_1 R_2 R_{12}, \quad A_2 = 2N^{-1/2} R_3 R_4 R_{12},$$
$$B = 2N^{-1}(R_{23}^2 + R_{31}^2 - 2) R_1 R_2 R_3 R_4$$

and C' is a normalizing constant.

Expanding the exponent in a power series we get

$$C' \int_0^\pi [1 + A_1 \cos(T_1) + A_2 \cos(T_2) + B \cos(T_1 + T_2)$$
$$+\tfrac{1}{2} A_1^2 \cos^2(T_1) + \tfrac{1}{2} A_2^2 \cos^2(T_2)$$
$$+A_1 A_2 \cos(T_1) \cos(T_2)$$
$$+\ldots + O(N^{-3/2})] dT_2$$
$$= C'\pi(1 + A_1 \cos(T_1) - 2\pi^{-1} B \sin(T_1)$$
$$+\tfrac{1}{2} A_1^2 \cos^2(T_1) + \tfrac{1}{4} A_2^2 + \ldots). \tag{III.2}$$

As $(1+x) = \exp[\ln(1+x)] = \exp(x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \ldots)$, the exponential form of the conditional probability distribution, correct up to and including terms of order N^{-1}, becomes

$$P^{(e)}(T_1|R_1 \ldots R_{31}) = L \exp[A_1 \cos(T_1) - 2\pi^{-1}B \sin(T_1)], \quad \text{(III.3)}$$

where L is a suitable normalizing constant. (III.3) can be written in the more familiar form of a von Mises distribution. As $\sin(T_1) = \cos(T_1 - \frac{1}{2}\pi)$, (I.1)–(I.3) lead to

$$P^{(e)}(T_1|R_1 \ldots R_{31}) = L \exp[x \cos(T_1 + \varepsilon)], \quad \text{(III.4)}$$

where $x^2 = A_1^2 + 4\pi^{-2}B^2$, $x \cos(\varepsilon) = A_1$ and $x \sin(\varepsilon) = 2\pi^{-1}B$.

The normalizing constant L now follows directly from (I.4):

$$L = [2\pi I_0(x)]^{-1}.$$

APPENDIX IV

An alternative algorithm for the application of the tangent formula

The weighted tangent formula, which is frequently used for phase expansion and refinement in direct methods, can be written as

$$\tan(\varphi_h) = \frac{\sum\limits_{k} w_k w_{h-k} Q_{hk} \sin(\varphi_k + \varphi_{h-k} + q_{hk})}{\sum\limits_{k} w_k w_{h-k} Q_{hk} \cos(\varphi_k + \varphi_{h-k} + q_{hk})}, \quad \text{(IV.1)}$$

where w_k and w_{h-k} are the weights associated with the phases φ_k and φ_{h-k}; q_{hk} is the most probable phase of the Σ_2 relation $(\varphi_h - \varphi_k - \varphi_{h-k})$ and Q_{hk} is the parameter associated with the variance of the phase indication $\varphi_h - \varphi_k - \varphi_{h-k} \simeq q_{hk}$. In a multi-solution approach several trials of numerical values for a small set of phases are put into (IV.1) as a starting point. After expansion to a complete set, the refinement can be seen as a search for a possible solution of the phase problem in a region around the starting phases. Such a solution is indicated by a reasonable correspondence between the left- and righthand side of (IV.1). The variable structure-factor phases are modified in such a way that they fit as well as possible to the assumed Σ_2 relations. To make full use of the multi-solution principle it is essential to find local extremes rather than the absolute best fit between the left- and righthand side of (IV.1). If the assumed Σ_2 relations are (almost) perfectly consistent with each other, the absolute best fit is so pronounced that nearly any starting point will lead to that solution if no special precautions are taken. Such a stabilization can be performed in numerous ways via

restrictions on the variable parameters, but then the available Σ_2 relations will remain, indicating that a better fit will be found if the restraints are relaxed. A good alternative is provided by the following reasoning.

If at some stage of the refinement a phase φ_h is calculated with unit weight, we accept this phase to be 'almost correct'. This means that, although its value can still be refined, it is already used as a reliable phase indication. If then the summation in (IV.1) contains terms for which simultaneously $w_k = 1 \cdot 0$ and $w_{h-k} = 1 \cdot 0$, the most probable phase for the Σ_2 relation $\varphi_h - \varphi_k - \varphi_{h-k}$ can be calculated from the current values of φ_h, φ_k and φ_{h-k}.

By ascribing this phase to the parameter q_{hk} in (IV.1) we are sure that the most predominant indications for φ_h are more or less consistent with the current value of φ_h. Therefore, we expect in the next cycle of refinement a relatively small change in the value of φ_h, thus decreasing the tendency of a gradual drift towards a solution far away from the starting point. The overall effect of the 'selective updating of triple-product phases' can now be seen as restricting the possible solution for a set of phases to be in the neighbourhood of the chosen starting point. If the multi-solution approach scans phase space effectively, we expect to find, besides the most pronounced solution (which is in $P1$ almost invariably wrong) a number of local extremes in the fulfilment of (IV.1). Calculations have shown that the rate of convergence of our procedure is very high; in a few cycles it ends at some point in the high-dimensional phase space. Next, all triple-product phases are reset to their initial values and the complete set of structure-factor phases is allowed to refine a few cycles in the ordinary way without updating the Σ_2 relations. The procedure has been tested extensively and was found to be a valuable alternative to the *MULTAN78* routine *FASTAN*. Especially in space groups like $P1$, $P2_1$ etc., the number of reasonable non-trivial solutions increases considerably, thus enhancing the chance of finding the correct one. For example, applying it to the test structure of the main text with all triple-product phases initially set equal to zero resulted in 16 different solutions out of 64 different starting points. Their figures of merit varied from 1·41 to 1·02 for ABS FOM, 2·70 to 1·20 for PSI ZERO and 27·34 to 10·45 for RESID. Unfortunately, the E maps calculated from he six most promising sets (based on the COMBINED FOM) did not contain any interpretable lactate fragment among the 30 highest peaks. The current version of the program still lacks the possibility of a magic-integer representation of the phases in the starting set and is only capable of employing the 'old fashioned' quadrant permutation. To limit the amount of computing time not more than three general structure-factor phases are normally permuted which results in 64 different starting sets.

References

ABRAMOWITZ, M. & STEGUN, I. A. (1970). *Handbook of Mathematical Functions*. New York: Dover.
COCHRAN, W. (1955). *Acta Cryst.* **8**, 473.
GIACOVAZZO, C. (1977). *Acta Cryst.* A33, 50–54.
GIACOVAZZO, C. (1980). *Direct Methods in Crystallography*, pp. 280–303. London: Academic Press.
HAUPTMAN, H. (1971). *Z. Kristallogr.* **134**, 28–43.
HAUPTMAN, H. (1975a). *Acta Cryst.* A31, 671–679.
HAUPTMAN, H. (1975b). *Acta Cryst.* A31, 680–687.
HAUPTMAN, H. (1977). *Acta Cryst.* A33, 556–564.

HEINERMAN, J. J. L. (1976). In *Proceedings of the Intercongress Symposium on Direct Methods in Crystallography*, edited by H. HAUPTMAN, pp. 177–194, Buffalo.
HEINERMAN, J. J. L., KRABBENDAM, H. & KROON, J. (1977). *Acta Cryst.* A33, 873–878.
MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univ. of York, England, and Louvain, Belgium.
PONTENAGEL, W. M. G. F. & KRABBENDAM, H. (1983). *Acta Cryst.* A39, 333–340.

Crystallography, Geometry and Physics in Higher Dimensions. I. Point-Symmetry Operations

BY D. WEIGEL, R. VEYSSEYRE, T. PHAN AND J. M. EFFANTIN*

Laboratoire de Chimie-Physique du Solide (Equipe de Recherche Associée au CNRS) and Laboratoire de Mathématiques de la Physique, Ecole Centrale des Arts et Manufactures, Grande Voie des Vignes, 92290 Châtenay-Malabry, France

AND Y. BILLIET†

Faculté des Sciences et Techniques, Université de Bretagne Occidentale, 6 Avenue Le Gorgeu, 29283 Brest CEDEX, France

Abstract

Physical phenomena such as incommensurate phases or diffraction enhancement of symmetry are interpreted by using symmetry groups in four, five or six dimensions. This first paper concerns the point-symmetry operations (PSO) in these Euclidean superspaces. Elementary, non-elementary, degenerate and non-degenerate PSOs are defined and their geometrical supports and geometrical symbols are specified. A geometrical description is thus given of nineteen types of PSO which are either the crystallographic rotations of the four-dimensional space or the crystallographic rotations and improper rotations of the five-dimensional space or the improper crystallographic rotations of the six-dimensional space. These PSOs are elements of crystallographic point groups of these spaces and the physical application to polar point groups is given.

* Present address: DRF–DN–CENG, 38041 Grenoble CEDEX, France.
† Present address: Recherches en Symétrie Cristallographique à Sétif A5, 35 Cité du 8 mai 1945, Sétif, Algeria.

General introduction

Regularities observed in the diffraction pattern of a crystal and not explained by the three-dimensional Euclidean symmetry – called external space symmetry – are interpreted as due to Euclidean symmetry in a $(3 + d)$-dimensional superspace involving d additional dimensions, called internal dimensions (Janner & Janssen 1980).

The following cases of incommensurate phases are well known; according to whether the incommensurability is parallel to a crystallographic direction, to a direction of a crystallographic plane or to any direction of the crystal, one, two or three additional (internal) d dimensions may be introduced (de Wolff, 1974; Comes, Lambert & Zeller, 1973; Janner & Janssen, 1977; Yamamoto, 1982).

The symmetry of diffraction patterns of some layered or intercalate crystals may be higher than that corresponding to the Friedel–Laue class (Sadanaga & Takeda, 1968; Marumo & Saito, 1972; Iwasaki, 1972). This phenomenon has been termed 'diffraction enhancement of symmetry' and two types – simple and double – have been analysed (Perez-Mato &