Acta Cryst. (1979). A**35**, 401–412

A Probabilistic Theory of Two-Phase Seminvariants of First Rank *via* the Method of Representations. IV. Practical Aspects and Applications

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(*Received* 21 *July* 1978; *accepted* 7 *December* 1978)

Abstract

An algorithm is devised to calculate the expected values of two-phase seminvariants of first rank in space groups up to orthorhombic. This algorithm is based on the probabilistic theory [Giacovazzo (1979). *Acta Cryst.* A**35**, 296–305]. The method has been tested on several known structures using the probabilistic formulae obtained *via* the Gram–Charlier expansion of the characteristic function. We report here the results of the calculations which show how the method can secure a good estimate of a limited number of two-phase seminvariants. These estimates can certainly be of great help in the initial stages of phase determination. In addition, the estimated values of the two-phase seminvariants can be used as a figure of merit to discriminate among the several sets of phases generated in a multisolution process. The use of two-phase seminvariants for enantiomorph discrimination in space groups of class 222 is also illustrated. A detailed comparison with the coincidence method shows the noticeable improvement attained by the present algorithm.

1. Introduction

Two-phase seminvariants are those linear combinations of two phases

$$\Phi = \varphi_{\mathbf{u}} + \varphi_{\mathbf{v}} \tag{1}$$

whose indices satisfy the condition

$$\mathbf{u} + \mathbf{v} \equiv 0 \pmod{\omega_s}, \tag{2}$$

where ω_s is the seminvariant modulus of the given space group. The first attempt at evaluating, by means of the coincidence method, the values of these relationships, for centrosymmetric structures, was described by Grant, Howells & Rogers (1957). The idea of coincidence was extended to noncentrosymmetric space groups by Debaerdemaeker & Woolfson (1972); Giacovazzo (1977*a*,*b*) derived a generalized probabilistic theory of the coincidence method which is valid for all space groups. More recently Green & Hauptman (1976, 1978*a*,*b*) and Hauptman & Green (1978), using the neighborhood concept, have derived conditional probability distributions for two-phase seminvariants in space groups $P\bar{1}$ and $P2_1$.

In this paper we describe some practical aspects of the application of a probabilistic theory recently described by Giacovazzo (1979) which uses the idea of representation (Giacovazzo, 1977*c*).

We recall here that Φ is a two-phase seminvariant of first rank, if two rotation matrices $\mathbf{R}_p$ and $\mathbf{R}_q$ and at least a vector $\mathbf{h}$ exist in principle (in the sense that $|E_{\mathbf{h}}|$ may or may not be experimentally measured) such that

$$\psi_1 = \Phi' + \varphi_{\mathbf{hR}_p} - \varphi_{\mathbf{hR}_q} \tag{3}$$

is a structure invariant. In (3) Φ' is a symmetry equivalent of Φ, *i.e.*

$$\Phi' = \varphi_{\mathbf{uR}_\mu} + \varphi_{\mathbf{vR}_\nu} \tag{4}$$

and

$$\mathbf{uR}_\mu + \mathbf{vR}_\nu + \mathbf{h}(\mathbf{R}_p - \mathbf{R}_q) = 0. \tag{5}$$

Comparing (5) with (2), the condition

$$\mathbf{h}(\mathbf{R}_p - \mathbf{R}_q) \equiv 0 \pmod{\omega_s} \tag{6}$$

0567-7394/79/030401-12$01.00

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follows. In Table 1, for symmetry classes up to orthorhombic, the rotation matrices $\mathbf{R}_i$ and the possible $\mathbf{D}_{pq} = (\mathbf{R}_p - \mathbf{R}_q)$ matrices are given, together with the seminvariant moduli ω_s. We shall see below how this table is used to define the two-phase seminvariants in all the space groups of the first three symmetry systems.

The structure invariant ψ_1 in (3) differs from the seminvariant Φ by a constant angle. We have in fact

$$\psi_1 - \Phi' = \varphi_{\mathbf{hR}_p} - \varphi_{\mathbf{hR}_q} = 2\pi\mathbf{h}(\mathbf{T}_q - \mathbf{T}_p),$$

where $\mathbf{T}_p$ and $\mathbf{T}_q$ are the translation vectors corresponding to the rotation matrices $\mathbf{R}_p$ and $\mathbf{R}_q$. Therefore, the evaluation of ψ_1 is at the same time an estimate of Φ.

The *first representation* of the seminvariant Φ is defined by the collection of all invariants ψ_1 obtained when $\mathbf{h}$ ranges over reciprocal space and $\mathbf{R}_p$, $\mathbf{R}_q$ range over the set of the rotation matrices. The *first phasing shell* of Φ comprises the set of diffraction amplitudes which are basis or cross magnitudes of at least one invariant ψ_1. We shall denote this set $\{B\}_1$.

Below, reference is made to paper III of this series (Giacovazzo, 1979) and the equations denoted (III.*xx*) refer to it.

2. An algorithm for the estimation of two-phase seminvariants in space groups up to orthorhombic

Proposition 4 of paper III warrants that, if $\varphi_{\mathbf{u}} + \varphi_{\mathbf{v}}$ is a structure seminvariant of first rank, there are at least two reciprocal vectors $\mathbf{h}_1$ and $\mathbf{h}_2$ and two rotation matrices $\mathbf{R}_p$ and $\mathbf{R}_q$ for which the system

$$\begin{cases} \mathbf{u} = \mathbf{h}_1 - \mathbf{h}_2 & (8a) \\ \mathbf{v} = -\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2\mathbf{R}_q & (8b) \end{cases}$$

holds. If $\{\mathbf{h}_1\}$ and $\{\mathbf{h}_2\}$ denote the collections of vectors $\mathbf{h}_1$ and $\mathbf{h}_2$ which satisfy (8), then the set of quartet invariants

$$\varphi_{\mathbf{v}} + \varphi_{\mathbf{uR}_p} + \varphi_{\mathbf{h}_2\mathbf{R}_p} - \varphi_{\mathbf{h}_2\mathbf{R}_q}, \quad (9a)$$

$$\varphi_{\mathbf{v}} + \varphi_{\mathbf{uR}_q} + \varphi_{\mathbf{h}_1\mathbf{R}_p} - \varphi_{\mathbf{h}_1\mathbf{R}_q}, \quad (9b)$$

may be constructed as $\mathbf{h}_1$ varies within $\{\mathbf{h}_1\}$ and $\mathbf{h}_2 = \mathbf{h}_1 - \mathbf{u}$ varies correspondingly within $\{\mathbf{h}_2\}$. The expected values of the quartets (9*a*) and (9*b*) depend also on the magnitudes of the cross reflexions:

$$\mathbf{h}_2(\mathbf{R}_q - \mathbf{R}_p);\ \mathbf{v} + \mathbf{h}_2\mathbf{R}_p;\ \mathbf{h}_1\mathbf{R}_p, \quad (10a)$$

$$\mathbf{h}_1(\mathbf{R}_q - \mathbf{R}_p);\ \mathbf{h}_2\mathbf{R}_q;\ \mathbf{uR}_q + \mathbf{h}_1\mathbf{R}_p. \quad (10b)$$

Table 1. *Rotation matrices* $\mathbf{R}_i$, *their possible differences* $\mathbf{D}_{pq}$ (*only the diagonal elements of the matrices are given, the off-diagonal terms being all equal to zero*) *and seminvariant moduli* ω_s *for the eight symmetry classes up to orthorhombic*

Class number and $\mathbf{R}_i$ matrices	Class symbol	ω_s	Types of $\mathbf{D}_{pq} = \mathbf{R}_p - \mathbf{R}_q$ matrices						
			(200)	(020)	(002)	(220)	(202)	(022)	(222)
1 $\mathbf{R}_1 = (111)$	1	(000)	–	–	–	–	–	–	–
2 $\mathbf{R}_1 = (111)$ $\mathbf{R}_2 = (\bar{1}\bar{1}\bar{1})$	$\bar{1}$	(222)	–	–	–	–	–	–	$\mathbf{D}_{12} = (222)$
3 $\mathbf{R}_1 = (111)$ $\mathbf{R}_2 = (\bar{1}1\bar{1})$	2	(202)	–	–	–	–	$\mathbf{D}_{12} = (202)$	–	–
4 $\mathbf{R}_1 = (111)$ $\mathbf{R}_2 = (1\bar{1}1)$	m	(020)	–	$\mathbf{D}_{12} = (020)$	–	–	–	–	–
5 $\mathbf{R}_1 = (111)$ $\mathbf{R}_2 = (\bar{1}\bar{1}\bar{1})$ $\mathbf{R}_3 = (\bar{1}1\bar{1})$ $\mathbf{R}_4 = (1\bar{1}1)$	$2/m$	(222)	–	$\mathbf{D}_{14} = (020)$	–	–	$\mathbf{D}_{13} = (202)$	–	$\mathbf{D}_{12} = (2\bar{2}2)$ $\mathbf{D}_{34} = (\bar{2}2\bar{2})$
6 $\mathbf{R}_1 = (111)$ $\mathbf{R}_2 = (1\bar{1}\bar{1})$ $\mathbf{R}_3 = (\bar{1}11)$ $\mathbf{R}_4 = (\bar{1}\bar{1}1)$	222	(222)	–	–	–	$\mathbf{D}_{14} = (2\bar{2}0)$ $\mathbf{D}_{23} = (\bar{2}20)$	$\mathbf{D}_{13} = (20\bar{2})$ $\mathbf{D}_{24} = (\bar{2}02)$	$\mathbf{D}_{12} = (022)$ $\mathbf{D}_{34} = (0\bar{2}2)$	–
7 $\mathbf{R}_1 = (111)$ $\mathbf{R}_2 = (\bar{1}\bar{1}1)$ $\mathbf{R}_3 = (\bar{1}11)$ $\mathbf{R}_4 = (1\bar{1}1)$	$mm2$	(220)	$\mathbf{D}_{13} = (200)$	$\mathbf{D}_{14} = (020)$	–	$\mathbf{D}_{12} = (2\bar{2}0)$ $\mathbf{D}_{34} = (\bar{2}20)$	–	–	–
8 $\mathbf{R}_1 = (11\bar{1})$ $\mathbf{R}_2 = (1\bar{1}\bar{1})$ $\mathbf{R}_3 = (\bar{1}1\bar{1})$ $\mathbf{R}_4 = (\bar{1}\bar{1}1)$ $\mathbf{R}_5 = (\bar{1}11)$ $\mathbf{R}_6 = (\bar{1}1\bar{1})$ $\mathbf{R}_7 = (1\bar{1}1)$ $\mathbf{R}_8 = (111)$	mmm	(222)	$\mathbf{D}_{16} = (200)$	$\mathbf{D}_{17} = (020)$	$\mathbf{D}_{18} = (002)$	$\mathbf{D}_{14} = (2\bar{2}0)$ $\mathbf{D}_{67} = (\bar{2}20)$	$\mathbf{D}_{13} = (20\bar{2})$ $\mathbf{D}_{68} = (\bar{2}02)$	$\mathbf{D}_{12} = (022)$ $\mathbf{D}_{78} = (0\bar{2}2)$	$\mathbf{D}_{15} = (222)$ $\mathbf{D}_{37} = (2\bar{2}2)$ $\mathbf{D}_{48} = (\bar{2}\bar{2}2)$ $\mathbf{D}_{26} = (2\bar{2}\bar{2})$

The third cross vector of the quartet (9*a*) and the second cross vector of the quartet (9*b*) are crystallographically equivalent to one of the basis vectors of the quartets (9*b*) and (9*a*) respectively.

These results suggested (paper III) the study of the distribution

$$P(E_{\mathbf{h}_1}, E_{\mathbf{h}_2}, E_{\mathbf{u}}, E_{\mathbf{v}}, E_{\mathbf{h}_1(\mathbf{R}_q-\mathbf{R}_p)}, E_{\mathbf{h}_2(\mathbf{R}_q-\mathbf{R}_p)}, E_{\mathbf{u}\mathbf{R}_q+\mathbf{h}_1\mathbf{R}_p}, E_{\mathbf{v}+\mathbf{h}_2\mathbf{R}_p}). \quad (11)$$

As $\mathbf{h}_1$ is allowed to vary within $\{\mathbf{h}_1\}$, it will assume, in space groups up to orthorhombic (*cf.* corollary *b* of proposition 6 in paper III), the value $-\mathbf{h}_1\mathbf{R}_p\mathbf{R}_q$.

Then, also, the vectors

$$\mathbf{h}_1' = -\mathbf{h}_1\mathbf{R}_p\mathbf{R}_q, \quad \mathbf{h}_2' = -(\mathbf{u}\mathbf{R}_q + \mathbf{h}_1\mathbf{R}_p)\mathbf{R}_q$$

satisfy the system (8) (*cf.* proposition 6 of paper III) and the following quartets can be constructed

$$\varphi_{\mathbf{v}} + \varphi_{\mathbf{u}\mathbf{R}_p} - \varphi_{(\mathbf{u}\mathbf{R}_q+\mathbf{h}_1\mathbf{R}_p)\mathbf{R}_q\mathbf{R}_p} + \varphi_{\mathbf{u}\mathbf{R}_q+\mathbf{h}_1\mathbf{R}_p}, \quad (12a)$$

$$\varphi_{\mathbf{v}} + \varphi_{\mathbf{u}\mathbf{R}_q} - \varphi_{\mathbf{h}_1\mathbf{R}_q} + \varphi_{\mathbf{h}_1\mathbf{R}_p}, \quad (12b)$$

whose cross vectors are

$$\mathbf{h}_2(\mathbf{R}_q - \mathbf{R}_p);\ \mathbf{v} - \mathbf{u}\mathbf{R}_p - \mathbf{h}_1\mathbf{R}_q;\ -\mathbf{h}_1\mathbf{R}_q, \quad (13a)$$

$$\mathbf{h}_1(\mathbf{R}_q - \mathbf{R}_p);\ \mathbf{u}\mathbf{R}_q + \mathbf{h}_1\mathbf{R}_p;\ \mathbf{h}_2\mathbf{R}_q. \quad (13b)$$

Similarly, as $\mathbf{h}_2$ is allowed to vary within $\{\mathbf{h}_2\}$, it will assume the value $-\mathbf{h}_2\mathbf{R}_p\mathbf{R}_q$.

Again, it is easily verified that

$$\mathbf{h}_1'' = -(\mathbf{v} + \mathbf{h}_2\mathbf{R}_p)\mathbf{R}_p, \quad \mathbf{h}_2'' = -\mathbf{h}_2\mathbf{R}_p\mathbf{R}_q$$

satisfy the system (8) and that the following quartets can be set up

$$\varphi_{\mathbf{v}} + \varphi_{\mathbf{u}\mathbf{R}_p} - \varphi_{\mathbf{h}_2\mathbf{R}_q} + \varphi_{\mathbf{h}_2\mathbf{R}_p}, \quad (14a)$$

$$\varphi_{\mathbf{v}} + \varphi_{\mathbf{u}\mathbf{R}_q} - \varphi_{\mathbf{v}+\mathbf{h}_2\mathbf{R}_p} + \varphi_{(\mathbf{v}+\mathbf{h}_2\mathbf{R}_p)\mathbf{R}_p\mathbf{R}_q}, \quad (14b)$$

whose cross vectors are

$$\mathbf{h}_2(\mathbf{R}_q - \mathbf{R}_p);\ \mathbf{h}_1\mathbf{R}_p;\ \mathbf{v} + \mathbf{h}_2\mathbf{R}_p, \quad (15a)$$

$$\mathbf{h}_1(\mathbf{R}_q - \mathbf{R}_p);\ -\mathbf{h}_2\mathbf{R}_p;\ -\mathbf{v} + \mathbf{u}\mathbf{R}_q - \mathbf{h}_2\mathbf{R}_p. \quad (15b)$$

From (12) and (13) and from (14) and (15) the distributions

$$P(E_{\mathbf{h}_1}, E_{\mathbf{u}\mathbf{R}_q+\mathbf{h}_1\mathbf{R}_p}, E_{\mathbf{u}}, E_{\mathbf{v}}, E_{\mathbf{h}_1(\mathbf{R}_q-\mathbf{R}_p)}, E_{\mathbf{h}_2(\mathbf{R}_q-\mathbf{R}_p)}, E_{\mathbf{h}_2}, E_{\mathbf{v}-\mathbf{u}\mathbf{R}_p-\mathbf{h}_1\mathbf{R}_q}), \quad (16)$$

and

$$P(E_{\mathbf{v}+\mathbf{h}_2\mathbf{R}_p}, E_{\mathbf{h}_2}, E_{\mathbf{u}}, E_{\mathbf{v}}, E_{\mathbf{h}_1(\mathbf{R}_q-\mathbf{R}_p)}, E_{\mathbf{h}_2(\mathbf{R}_q-\mathbf{R}_p)}, E_{-\mathbf{v}+\mathbf{u}\mathbf{R}_q-\mathbf{h}_2\mathbf{R}_p}, E_{\mathbf{h}_1}) \quad (17)$$

are indicated, in the same way as (11) follows from (9) and (10). If in (11), (16) and (17) the variables, in the given order, are labeled as E_1, E_2, ..., E_8, the expression for $P(E_1, E_2, \ldots, E_8)$ is given in (III.21) for the centrosymmetric case and in (III.47) for the non-centrosymmetric (both derived *via* the Gram–Charlier expansion of the characteristic function). In these expressions we use $\varepsilon_i = (|E_i|^2 - 1)$.

Referring to these equations we note that:

(*a*) contributions labeled ε_7 and ε_8 when (III.21) applies to (11) reappear as ε_2 and ε_1 when it refers to (16) and (17) respectively (*cf.* proposition 6 of paper III);

(*b*) the contributions denoted $2\varepsilon_1\varepsilon_7$ and $2\varepsilon_2\varepsilon_8$ when (III.21) is calculated with respect to distribution (11) are labeled $2\varepsilon_1\varepsilon_2$ when (III.21) applies to distributions (16) and (17) respectively;

(*c*) contributions denoted $\varepsilon_6\varepsilon_7$ and $\varepsilon_5\varepsilon_8$ when (III.21) applies to distribution (11) reappear as $\varepsilon_2\varepsilon_6$ and $\varepsilon_1\varepsilon_5$ when it refers to distributions (16) and (17) respectively. Similar considerations hold for the terms $\frac{1}{4}H_4(E_7)\varepsilon_6$ and $\frac{1}{4}H_4(E_8)\varepsilon_5$.

These considerations allow us to calculate the expected value of the two-phase seminvariant of first rank $\varphi_{\mathbf{u}} + \varphi_{\mathbf{v}}$ in space groups up to orthorhombic by means of a six-variate distribution of the type

$$P(E_{\mathbf{h}_1}, E_{\mathbf{h}_2}, E_{\mathbf{u}}, E_{\mathbf{v}}, E_{\mathbf{h}_2(\mathbf{R}_q-\mathbf{R}_p)}), \quad (18)$$

provided that the following conditions are satisfied:

(*a'*) the contributions $\varepsilon_5\sum'\varepsilon_1$ and $\varepsilon_6\sum'\varepsilon_2$ are calculated by allowing $\mathbf{h}_1$ and $\mathbf{h}_2$ to vary within the asymmetric region of the sets $\{\mathbf{h}_1\}$ and $\{\mathbf{h}_2\}$;

(*b'*) The contributions $\sum' 2\varepsilon_1\varepsilon_2$ are calculated by allowing $\mathbf{h}_1$ (or $\mathbf{h}_2$) to vary within the complete set $\{\mathbf{h}_1\}$ (or $\{\mathbf{h}_2\}$) (*i.e.* $\mathbf{h}_1$ assumes both values $\mathbf{h}_1$ and $-\mathbf{h}_1\mathbf{R}_p\mathbf{R}_q$) provided that $\mathbf{h}_1 \neq -\mathbf{h}_1\mathbf{R}_p\mathbf{R}_q$ (or $\mathbf{h}_2 \neq -\mathbf{h}_2\mathbf{R}_p\mathbf{R}_q$).

In paper III it was shown how the system of equations (8) could be written in the form

$$\mathbf{h}_1 = \mathbf{h}_2 + \mathbf{u} \quad (19a)$$

$$\mathbf{h}_2(\mathbf{R}_q - \mathbf{R}_p) = \mathbf{v} + \mathbf{u}\mathbf{R}_p, \quad (19b)$$

and how this could be solved for the unknown vectors $\mathbf{h}_1$ and $\mathbf{h}_2$ in a general way. When considering only the space groups up to orthorhombic, the solution of (19) becomes rather simple. We shall now consider an example to illustrate the procedure we have devised and, at the same time, to confirm that we are allowed to use the six-variate distribution (18) under the conditions (*a'*) and (*b'*). Reference will be made to Table 1.

Let us consider, in class 2, the reflexions

$$\mathbf{u} = 312 \quad \text{and} \quad \mathbf{v} = \bar{1}\bar{1}\bar{4},$$

forming the two-phase seminvariant

$$\Phi = \varphi_{312} + \varphi_{\bar{1}\bar{1}\bar{4}} = \varphi_{312} - \varphi_{114}. \quad (20)$$

Substituting in equation (19*b*) we obtain

$$\mathbf{h}_2\begin{pmatrix}200\\000\\002\end{pmatrix} = (\bar{1}\bar{1}\bar{4}) + (\bar{3}1\bar{2}) = (\bar{4}0\bar{6}). \quad (21)$$

The matrix $\mathbf{D}_{qp} = \mathbf{D}_{12}$ is singular and there will not be a unique solution for $\mathbf{h}_2$; the set $\{\mathbf{h}_2\}$ of all vectors lying on the reciprocal-lattice row $(\bar{2}k\bar{3})$ will, in fact, satisfy equation (21). From (19*a*) we can then derive

$$\{\mathbf{h}_1\} = (\bar{2}k\bar{3}) + (312) = (1,k+1,\bar{1}). \quad (22)$$

On assuming that the maximum value of the index k for the measured data is 8, we have

$\{\mathbf{h}_1\}$	$\{\mathbf{h}_2\}$	$\{\mathbf{h}_1\}$	$\{\mathbf{h}_2\}$
$1\bar{7}\bar{1}$*	$\bar{2}8\bar{3}$*	$12\bar{1}$	$\bar{2}1\bar{3}$
$16\bar{1}$*	$\bar{2}7\bar{3}$*	$13\bar{1}$	$\bar{2}2\bar{3}$
$15\bar{1}$*	$\bar{2}6\bar{3}$*	$14\bar{1}$	$\bar{2}3\bar{3}$
$14\bar{1}$*	$\bar{2}5\bar{3}$*	$15\bar{1}$	$\bar{2}4\bar{3}$
$13\bar{1}$*	$\bar{2}4\bar{3}$*	$16\bar{1}$	$\bar{2}5\bar{3}$
$12\bar{1}$*	$\bar{2}3\bar{3}$*	$17\bar{1}$	$\bar{2}6\bar{3}$
$11\bar{1}$*	$\bar{2}2\bar{3}$*	$18\bar{1}$	$\bar{2}7\bar{3}$
$10\bar{1}$	$\bar{2}1\bar{3}$*	–	$\bar{2}8\bar{3}$,
$11\bar{1}$	$\bar{2}0\bar{3}$		

(23)

where we have marked with asterisks those reflexions which are symmetry equivalent to other reflexions in the set. From these values of $\mathbf{h}_1$ and $\mathbf{h}_2$ we can set up several pairs of quartets whose general expressions are [*cf.* equations (9)]:

$$\begin{aligned}&\varphi_{\bar{1}\bar{1}\bar{4}} + \varphi_{\bar{3}1\bar{2}} + \varphi_{2k3} + \varphi_{2\bar{k}\bar{3}},\\ &\varphi_{\bar{1}\bar{1}\bar{4}} + \varphi_{312} + \varphi_{\bar{1},k+1,1} + \varphi_{\bar{1},\overline{k+1},1},\end{aligned} \tag{24}$$

with cross vectors

$$(\bar{4}0\bar{6});\ (1,k-1,\bar{1});\ (\bar{1},k+1,1),$$
$$(20\bar{2});\ (\bar{2}k\bar{3});\ (2,k+2,3).$$

We see that the cross term $\mathbf{v}+\mathbf{h}_2\mathbf{R}_p = (1,k-1,\bar{1})$ belongs to the same reciprocal-lattice row as $\mathbf{h}_1$ and the term $-(\mathbf{u}\mathbf{R}_q+\mathbf{h}_1\mathbf{R}_p) = (\bar{2},\overline{k+2},\bar{3})$ belongs to the same row as $\mathbf{h}_2$ (*cf.* proposition 6, paper III). As $\mathbf{h}_1$ varies within $\{\mathbf{h}_1\}$ and $\mathbf{h}_2$ varies within $\{\mathbf{h}_2\}$, they assume the values

$$\mathbf{h}_1' = -\mathbf{h}_1\mathbf{R}_p\mathbf{R}_q = (1,\overline{k+1},\bar{1})$$

and

$$\mathbf{h}_2' = -(\mathbf{u}\mathbf{R}_q + \mathbf{h}_1\mathbf{R}_p)\mathbf{R}_q = (\bar{2},\overline{k+2},\bar{3}),$$

giving the quartets

$$\begin{aligned}&\varphi_{\bar{1}\bar{1}\bar{4}} + \varphi_{\bar{3}1\bar{2}} + \varphi_{2,\overline{k+2},3} + \varphi_{2,k+2,3},\\ &\varphi_{\bar{1}\bar{1}\bar{4}} + \varphi_{312} + \varphi_{\bar{1},\overline{k+1},1} + \varphi_{\bar{1},k+1,1},\end{aligned} \tag{25}$$

with cross vectors

$$(\bar{4}0\bar{6});\ (1,\overline{k+3},\bar{1});\ (\bar{1},\overline{k+1},1),$$
$$(20\bar{2});\ (\bar{2},\overline{k+2},\bar{3});\ (2\bar{k}3).$$

Finally, $\mathbf{h}_1$ and $\mathbf{h}_2$ will also assume the values

$$\mathbf{h}_1'' = -(\mathbf{v}+\mathbf{h}_2\mathbf{R}_p)\mathbf{R}_p = 1,\overline{k-1},1$$

and

$$\mathbf{h}_2'' = -\mathbf{h}_2\mathbf{R}_p\mathbf{R}_q = \bar{2}\bar{k}\bar{3},$$

giving the quartets

$$\begin{aligned}&\varphi_{\bar{1}\bar{1}\bar{4}} + \varphi_{\bar{3}1\bar{2}} + \varphi_{2\bar{k}\bar{3}} + \varphi_{2k3},\\ &\varphi_{\bar{1}\bar{1}\bar{4}} + \varphi_{312} + \varphi_{\bar{1},\overline{k-1},1} + \varphi_{\bar{1},k-1,1},\end{aligned} \tag{26}$$

with cross vectors

$$(\bar{4}0\bar{6});\ (1,\overline{k+1},\bar{1});\ (1,k-1,\bar{1}),$$
$$(20\bar{2});\ (\bar{2}\bar{k}\bar{3});\ (2,\overline{k-2},3).$$

An analysis of the terms in the pairs of quartets (24), (25) and (26) shows that considerations (*a*), (*b*) and (*c*) apply. In fact:

– the term $\varepsilon_7 = \varepsilon_{2,k+2,3}$ in (24) is identical to $\varepsilon_2 = \varepsilon_{\bar{2},\overline{k+2},\bar{3}}$ in (25);

– the term $\varepsilon_8 = \varepsilon_{1,k-1,\bar{1}}$ in (24) is identical to $\varepsilon_1 = \varepsilon_{1,\overline{k-1},\bar{1}}$ in (26);

– as a consequence of the above identities also:

$2\varepsilon_1\varepsilon_7$ in (24) is identical to $2\varepsilon_1\varepsilon_2$ in (25),

$\varepsilon_6\varepsilon_7$ in (24) is identical to $\varepsilon_6\varepsilon_2$ in (25),

$\frac{1}{4}H_4(E_7)\varepsilon_6$ in (24) is identical to $\frac{1}{4}H_4(E_2)\varepsilon_6$ in (25),

and

$2\varepsilon_2\varepsilon_8$ in (24) is identical to $2\varepsilon_1\varepsilon_2$ in (26),

$\varepsilon_6\varepsilon_7$ in (24) is identical to $\varepsilon_5\varepsilon_1$ in (26),

$\frac{1}{4}H_4(E_8)\varepsilon_5$ in (24) is identical to $\frac{1}{4}H_4(E_1)\varepsilon_5$ in (26).

We can therefore conclude that the unique magnitudes in the first phasing shell contributing to the evaluation of the two-phase seminvariant (20) are

$$\{B\}_1 \equiv \{|E_{114}|, |E_{312}|, |E_{2k3}|, |E_{1,k+1,\bar{1}}|, |E_{20\bar{2}}|, |E_{406}|\}.$$

3. The role of the symmetry class in the estimation of two-phase seminvariants of first rank

The set of magnitudes of the first phasing shell for a two-phase seminvariant of first rank is defined by the symmetry class of the crystal. Two examples will immediately prove this statement and show how the proper use of symmetry can strengthen the estimate of the two-phase seminvariants.

Let us first consider

$$\Phi = \varphi_{123} + \varphi_{541}, \tag{27}$$

which is a seminvariant of first rank in classes $\bar{1}$, $2/m$ and *mmm*. From Table 1 we can see that in class $\bar{1}$ there is only one $\mathbf{D}_{pq}$ matrix of type (222), in class $2/m$ there are two $\mathbf{D}_{pq}$ matrices of this type and in class *mmm* there are four such matrices, yielding, respectively, one, two and four pairs of quartets such as (9). The two-phase seminvariant (27) will be defined by:

(1) 6 phasing magnitudes in class $\bar{1}$:

$$\{B\}_1 \equiv \{|E_{123}|, |E_{541}|, |E_{332}|, |E_{21\bar{1}}|, |E_{42\bar{2}}|, |E_{664}|\}; \tag{28}$$

(2) 10 phasing magnitudes in class $2/m$:

$$\{B\}_1 \equiv \{|E_{123}|, |E_{541}|, |E_{332}|, |E_{21\bar{1}}|, |E_{42\bar{2}}|, |E_{664}|, |E_{312}|, |E_{23\bar{1}}|, |E_{624}|, |E_{46\bar{2}}|\}; \tag{29}$$

(3) 18 phasing magnitudes in class *mmm*:

$$\{B\}_1 \equiv \{|E_{123}|, |E_{541}|, |E_{332}|, |E_{211}|, |E_{422}|, |E_{664}|, |E_{312}|, |E_{231}|, |E_{624}|, |E_{462}|, |E_{331}|, |E_{212}|, |E_{662}|, |E_{424}|, |E_{232}|, |E_{311}|, |E_{464}|, |E_{622}|\}; \quad (30)$$

and the statistical accuracy of its evaluation will correspondingly increase.

As a second example let us consider

$$\Phi = \varphi_{123} + \varphi_{\bar{5}\bar{2}\bar{3}}, \quad (31)$$

which is a two-phase seminvariant in all the classes given in Table 1. We shall compare here the first phasing shells of (31) in the three classes $\bar{1}$, 2 and *mm*2.

In the first class there is only one $\mathbf{D}_{pq}$ matrix of type (222) and Φ is defined by the six phasing magnitudes

$$\{B\}_1 \equiv \{|E_{123}|, |E_{523}|, |E_{200}|, |E_{323}|, |E_{400}|, |E_{646}|\}. \quad (32)$$

In class 2 there is only one $\mathbf{D}_{pq}$ matrix of type (202) and the first phasing shell is now

$$\{B\}_1 \equiv \{|E_{123}|, |E_{523}|, |E_{400}|, |E_{606}|, |E_{3k3}|, |E_{2,k+2,0}|\}, \quad (33)$$

where k is a free integer. Unlike in $P\bar{1}$, the vectors $\mathbf{h}_2$ and $\mathbf{h}_1$ are not uniquely defined; Φ depends on the distribution of the independent magnitudes (usually *several tens*) on the two reciprocal-lattice rows ($3k3$) and ($2k0$).

Finally, in class *mm*2, the most general $\mathbf{D}_{pq}$ matrix is of type (200) [the use of the matrices of type (220) would in fact yield a subset of the phasing magnitudes obtained by means of the (200) matrix] and the first phasing shell is

$$\{B\}_1 \equiv \{|E_{123}|, |E_{523}|, |E_{400}|, |E_{600}|, |E_{3kl}|, |E_{2,k+2,l+3}|\}, \quad (34)$$

where k and l are free integers. The vectors $\mathbf{h}_2$ and $\mathbf{h}_1$ now belong to the two reciprocal-lattice planes ($3kl$) and ($2kl$) and from these we select the independent terms (usually *several hundreds*) forming the phasing magnitudes of Φ.

The number of phasing magnitudes of the first shell of Φ thus increases by an order of magnitude on going from one class to the other and the estimate becomes more and more accurate in a statistical sense.

4. Use of the estimated cosines and enantiomorph discrimination

If $\cos(\varphi_\mathbf{u} + \varphi_\mathbf{v})$ or $\cos(\varphi_\mathbf{u} - \varphi_\mathbf{v})$ is reliably estimated and $\varphi_\mathbf{v}$ is a known phase then there is, for noncentrosymmetric reflexions, a sign ambiguity for $\varphi_\mathbf{u}$.

A more favorable condition occurs for space groups belonging to symmetry class 222 (*cf.* proposition 7, paper III), for which one is able to obtain information about both $\cos(\varphi_\mathbf{u} + \varphi_\mathbf{v})$ and $\cos(\varphi_\mathbf{u} - \varphi_\mathbf{v})$.

If we assume that c_1 and c_2 are equally accurate estimates of $\cos(\varphi_\mathbf{u} + \varphi_\mathbf{v})$ and $\cos(\varphi_\mathbf{u} - \varphi_\mathbf{v})$, respectively, we have as particular cases:

(*a*) $c_1 \simeq 1, c_2 \simeq 1$ giving $(\varphi_\mathbf{u}, \varphi_\mathbf{v}) \simeq (0,0)$ or (π,π)

(*b*) $c_1 \simeq -1, c_2 \simeq -1$ giving $(\varphi_\mathbf{u}, \varphi_\mathbf{v}) \simeq (0,\pi)$ or $(\pi,0)$

(*c*) $c_1 \simeq 1, c_2 \simeq -1$ giving

$$(\varphi_\mathbf{u}, \varphi_\mathbf{v}) \simeq \left(\frac{\pi}{2}, -\frac{\pi}{2}\right) \text{or} \left(-\frac{\pi}{2}, \frac{\pi}{2}\right)$$

(*d*) $c_1 \simeq -1, c_2 \simeq 1$ giving

$$(\varphi_\mathbf{u}, \varphi_\mathbf{v}) \simeq \left(\frac{\pi}{2}, \frac{\pi}{2}\right) \text{or} \left(-\frac{\pi}{2}, -\frac{\pi}{2}\right). \quad (35)$$

The last two cases are particularly important because $\varphi_\mathbf{u} + \varphi_\mathbf{v}$ and $\varphi_\mathbf{u} - \varphi_\mathbf{v}$ can both be assigned simultaneously in order to fix the enantiomorph.

Examples will be given when discussing the actual applications (*cf.* Table 8).

5. Some practical tests

A computer program has been implemented which can generate the two-phase seminvariants of first rank in all space groups up to orthorhombic and, by means of the algorithm described above, can define the corresponding magnitudes of the first phasing shell.

The evaluation of the two-phase seminvariants is performed, for centrosymmetric space groups, by means of a sign probability distribution of the type

$$P_+ = \tfrac{1}{2} + \tfrac{1}{2}\tanh(\text{ARG}), \quad (36)$$

while for noncentrosymmetric space groups the formula

$$\langle \cos \Phi \rangle = \frac{I_1(G)}{I_o(G)} \quad (37)$$

was used, with $G = 2\times\text{ARG}$.

In both (36) and (37) the value of ARG is defined as

$$\text{ARG} = \frac{\sum\limits_{(p,q)} A_{pq}}{1 + \sum\limits_{(p,q)} C_{pq}}, \quad (38)$$

where

$$A_{pq} = \frac{1}{2N} |E_3 E_4| \sum_j{}' a_j \Delta_j \quad (39)$$

and

$$C_{pq}=\frac{1}{2N}\{\varepsilon_3\varepsilon_4(\varepsilon_5+\varepsilon_6)+(\varepsilon_3+\varepsilon_4)\sum_j{}'b_j+\sum_j{}'r_j\}, \quad (40)$$

with

$$a=\varepsilon_1+\varepsilon_2+\varepsilon_5\varepsilon_1+\varepsilon_6\varepsilon_2+2\varepsilon_1\varepsilon_2 \quad (41)$$

$$\Delta=\cos\{2\pi(\mathbf{h}_1\mathbf{T}_p-\mathbf{h}_2\mathbf{T}_q)\},$$

$$b=\varepsilon_1\varepsilon_2 \quad (42)$$

$$r=\tfrac{1}{4}\{H_4(E_1)\varepsilon_5+H_4(E_2)\varepsilon_6\}$$

for centrosymmetric structures, or

$$r=\tfrac{1}{4}\{L_4(E_1)\varepsilon_5+L_4(E_2)\varepsilon_6\}$$

for noncentrosymmetric structures.

The summation in (38) is over all matrices $\mathbf{D}_{pq}$ contributing to the first representation of the given seminvariant. The summations over j in (39) and (40) are over all pairs $(\mathbf{h}_1,\mathbf{h}_2)$ and the primes indicate that duplicated contributors have been included only once. The numerical indices of the terms ε and E refer to the order of appearance in the six-variate distribution (18). All other terms have the same meaning as in paper III.

G as used in (37) differs from Q which appears in (III.56); in fact, the general definition given in (III.54), for space groups up to orthorhombic, reduces to

$$Q=\frac{|E_3E_4|}{N}\frac{\sum_{(p,q)}\sum_j{}'A_{j,p,q}}{\sum_{(p,q)}\sum_j{}'(1+C_{j,p,q}/N)}, \quad (43)$$

$A_{j,p,q}$ and $C_{j,p,q}$ being single contributors to (39) and (40). Equation (43) differs from (38) in the denominator; the modification is an empirical one and it was introduced after noticing that, in practice, quite often some of the terms C_j in (III.47), and consequently in (III.55) and (III.56), become negative. A negative C_j gives too high a weight to the corresponding term in the summation. Re-setting all negative C_j's to zero did not completely eliminate this problem and the empirical modification given in (38) proved to be most suitable.

The method was tested on 13 known structures of different complexity covering all different symmetry classes of the first three crystallographic systems.

Table 2 shows the reference and the most relevant features of the test structures whose results are discussed in this paper.

In Table 3 the 20 two-phase seminvariants with $|\mathrm{ARG}|\geq 1\cdot0$ ($P_+\geq 0\cdot891$ or $P_+\leq 0\cdot109$) for TETRA ($N=34$, $P\bar{1}$) are given. It is remarkable that a negative two-sign product (No. 11 in the table) has been correctly evaluated. Only the last two relations are incorrectly estimated as positive. Among the 50 relationships with $|\mathrm{ARG}|\geq 0\cdot75$ ($P_+\geq 0\cdot818$ or $P_+\leq 0\cdot182$) there are seven wrong indications all incorrectly estimated as positive while in fact negative. On the other hand the five negative indications are all correct.

The present results in $P\bar{1}$ confirm those obtained by Giacovazzo (1978) on a model structure with $N=40$. It is interesting to compare the estimates obtained *via* the first representation with those obtained from the probability distribution $P(E_{\mathbf{h}_1}, E_{\mathbf{h}_2}, E_{\mathbf{h}_1+\mathbf{h}_2}, E_{\mathbf{h}_1-\mathbf{h}_2})$

Table 2. *Abbreviations, references, space groups, formulae, types of normalized amplitudes (obs. meaning $|E|$'s computed from the observed intensities and calc. $|E|$'s calculated from the atomic coordinates) and minimum values of $|E|$ for the reflexions forming the two-phase seminvariants, for the 13 test structures*

	Reference	Space group	Formula	Z	E	$E_{\min}$
TETRA: tetrabenzyltetrazine	Spagna & Vaciago (1978)	$P\bar{1}$	$C_{30}H_{32}N_4$	1	obs.	1·9
KENNA: 3-methyl-mono-*o*-benzyl-autumnaline	Shakked & Kennard (1977)	$P\bar{1}$	$C_{30}H_{37}NO_5$	2	calc.	2·0
PICRY: 2,2-diphenyl-1-picrylhydrazyl (DPPH modification)	Kiers, de Boer, Olthof & Spek (1976)	$P\bar{1}$	$C_{18}H_{12}N_5O_6$	4	calc.	1·4
RIBO: 1,2,3,4-tetra-*o*-acetyl-α-D-ribopyranose	James & Stevens (1977)	$P2_1$	$C_{13}H_{18}O_9$	4	calc.	2·0
HEPTA: heptahelicene	Beurskens, Beurskens & Van den Hark (1976)	$P2_1$	$C_{30}H_{18}$	4	calc.	1·9
DIMER: dimer from 1-phenyl-3,3-biphenylene-allene	Dreissig, Luger & Rewicki (1974)	Cc	$C_{42}H_{28}$	4	calc.	1·8
METHOX: (±)-3-methoxy-7-nor-9β-estra-1,3,5(10)-trien-17-one	Hanson & Nordman (1975)	$P2_1/c$	$C_{18}H_{22}O_2$	4	calc.	1·8
PANBE: *p*-nitrobenzoic acid	Colapietro & Domenicano (1977)	$A2/a$	$C_7H_5NO_4$	8	obs.	1·7
TOLY: tolypomycinone	Brufani, Cellai, Cerrini, Fedeli & Vaciago (1978)	$P2_12_12_1$	$C_{37}H_{43}NO_{13}$	4	obs.	1·85
TOXE: fusicoccin A's aglycone	Cerrini, Fedeli, Gavuzzo & Mazza (1978)	$P2_12_12_1$	$C_{21}H_{35}O_5$	4	obs.	1·95
KARLE: photolysis product	Karle, Karle & Estlin (1967)	$P2_12_12_1$	$C_{12}H_{13}NO_4$	4	obs.	1·2
AZET: 3-chloro-1,3,4-triphenylazetidin-2-one	Colens, Declercq, Germain, Putzeys & Van Meerssche (1974)	$Pca2_1$	$C_{21}H_{16}ClNO$	8	obs.	1·6
PERYL: tetrabenzo[*a,cd,j,lm*]perylene	Kohno, Konno, Saito & Inokuchi (1975)	$Pcab$	$C_{34}H_{18}$	8	calc.	2·6

derived in two different ways by Giacovazzo (1974) and Green & Hauptman (1976). Fig. 2 of the first paper and, in more detail, Table 1 of the latter, computed for a model structure with $N = 90$, show how the four-magnitude formulae can also predict negative two-sign products. Table 1 of Green & Hauptman shows at the top (relationships 8 and 9) two wrong positive indications. Our results by means of the six-variate distribution, suggested by the representation theory, for TETRA as well as for KENNA ($N = 72$, $P\bar{1}$) and PICRY ($N = 110$, $P\bar{1}$), seem to make this problem less critical in the sense that the incorrect positive indications occur at rather low values of the probability. As we have seen in § 3, two-phase seminvariants in class $\bar{1}$ have only six magnitudes in the first phasing shell and therefore their estimate becomes less accurate as the number of atoms in the unit cell increases. This is confirmed by the trend of our results, giving for KENNA 22 two-phase seminvariants with $|\text{ARG}| \geq 1{\cdot}0$, but for PICRY only four such relations, in both cases all correctly indicated as positive. The first wrong indication for KENNA is a positive estimate with ARG = 0·95 and for PICRY is a positive estimate with ARG = 0·92.

In this class we believe that the use of upper representations and, in the case when both $\varphi_{\mathbf{u}}$ and $\varphi_{\mathbf{v}}$ are of the type (e,e,e), the use of the magnitudes in the first phasing shells of the one-phase seminvariants should also improve the estimates for rather large structures. Work in this field is in progress.

In Table 4 the results of our calculation for HEPTA ($N = 120$, $P2_1$) are shown. The first three indications are centrosymmetric pairs (*i.e.* relations in which both phases have restricted values) with $|\text{ARG}| \geq 0{\cdot}8$. They are all correct and it is our experience (*cf.* also Tables 7, 8, 9) that these indications are also correct in almost all cases when we consider values of |ARG| as low as 0·6. In the table are also given the 15 general two-phase seminvariants with $|G| \geq 1{\cdot}0$. All cosine signs are correct, and the average phase error is $\langle|\Delta\Phi|\rangle = 37°$.

For RIBO ($N = 88$, $P2_1$), which is a smaller structure, in the same space group, we have obtained better estimates. In fact, for the 16 general two-phase seminvariants with $|G| \geq 1{\cdot}0$ the average phase error is $\langle|\Delta\Phi|\rangle = 22°$.

Table 5 shows the 28 estimates of the general two-phase seminvariants with $G \geq 1{\cdot}0$ for DIMER ($N = 88$, Cc) (the C centering positions were not considered

Table 3. *TETRA: indices, |E|'s and actual signs of the reflexions forming the two-phase seminvariants, together with the computed argument of the hyperbolic tangent formula* (36) *and the corresponding probability*

The asterisks indicate incorrect evaluations.

	u			E_u	s_u	v			E_v	s_v	ARG	P_+
1)	4	0	5	2.70	+	6	0	-3	2.64	+	1.33	.935
2)	6	-7	-5	2.13	+	4	-7	5	1.93	+	1.32	.933
3)	2	4	-7	2.08	-	4	4	-11	1.90	-	1.27	.927
4)	4	-3	4	2.30	-	2	-3	8	1.92	-	1.25	.924
5)	1	-2	-5	2.21	-	3	-2	-9	2.18	-	1.25	.924
6)	0	0	3	2.26	+	2	0	-7	2.11	+	1.24	.923
7)	1	0	9	2.39	+	1	-4	7	2.07	+	1.20	.917
8)	2	-2	3	2.38	-	4	-2	-1	2.01	-	1.19	.915
9)	5	-7	-1	3.76	+	5	1	3	2.75	+	1.18	.914
10)	4	-7	1	2.76	+	6	-7	-3	1.97	+	1.17	.912
11)	7	-4	-4	2.71	-	5	-10	0	2.50	+	-1.15	.091
12)	3	5	4	3.56	-	1	5	8	3.28	-	1.15	.909
13)	1	5	8	3.28	-	1	-9	6	2.83	-	1.14	.907
14)	5	-10	0	2.50	+	5	0	0	1.95	+	1.12	.904
15)	4	-7	1	2.76	+	6	1	1	2.37	+	1.10	.900
16)	2	-3	11	3.21	-	6	-11	-1	3.10	-	1.07	.895
17)	5	-5	0	3.11	-	5	5	2	2.10	-	1.07	.895
18)	8	-1	-1	3.13	-	2	3	-3	2.23	-	1.06	.893
19)	5	-6	2	2.90	+	7	-4	-4	2.71	-	1.05	.891*
20)	6	-6	-3	1.94	+	6	-4	1	1.91	-	1.05	.891*

Table 4. *HEPTA: centrosymmetric pairs given as in Table* 3; *values of G, the calculated cosine, the true cosine, their absolute difference and the absolute phase error* $|\Delta\Phi| = |\cos^{-1}(\cos\Phi)_c - \cos^{-1}(\cos\Phi)_t|$ *of the estimate* (°) *for the general two-phase seminvariants*

	u			E_u	φ_u	v			E_v	φ_v	ARG			P_+
(1)	5	0	7	3·03	180	1	0	−5	2·81	0	−1·22		0·080	
(2)	11	0	0	2·66	0	7	0	2	1·93	180	−0·86		0·152	
(3)	6	0	7	4·02	180	10	0	−5	2·30	0	−0·82		0·162	
											G	$(\cos\Phi)_c$	$(\cos\Phi)_t$	$\lvert\Delta(\cos\Phi)\rvert$	$\lvert\Delta\Phi\rvert$
(1)	3	2	1	3·00	−153	5	2	7	2·22	−171	2·36	0·748	0·951	0·203	24
(2)	6	7	−6	2·60	170	8	7	6	2·10	−57	−1·58	−0·610	−0·682	0·072	5
(3)	12	2	1	2·38	−152	14	2	1	2·10	−158	1·50	0·591	0·995	0·404	48
(4)	3	7	−6	2·34	158	1	7	−6	2·09	142	1·44	0·576	0·961	0·385	39
(5)	3	2	0	2·90	23	11	2	0	2·36	16	1·43	0·573	0·993	0·420	48
(6)	6	9	−6	2·02	160	2	9	6	1·90	−16	−1·26	−0·527	−0·998	0·471	55
(7)	9	11	1	2·37	17	3	11	1	2·05	−8	1·25	0·524	0·906	0·382	33
(8)	9	7	1	3·60	−28	11	7	1	2·69	−18	1·24	0·521	0·985	0·464	49
(9)	3	2	7	3·00	−153	7	2	7	2·37	−143	1·19	0·507	0·985	0·478	50
(10)	3	11	−1	2·24	145	5	11	1	1·98	11	−1·18	−0·503	−0·695	0·192	14
(11)	11	4	0	1·99	66	11	4	2	1·95	−134	−1·18	−0·503	−0·940	0·437	40
(12)	8	7	6	2·10	−57	4	7	8	2·05	153	−1·16	−0·497	−0·866	0·369	30
(13)	0	6	7	2·71	−171	10	6	7	1·95	−138	1·14	0·491	0·839	0·348	28
(14)	5	9	6	2·08	−28	5	9	−8	1·93	0	1·04	0·459	0·883	0·424	35
(15)	6	5	−6	2·46	126	2	5	6	2·12	−57	−1·04	−0·459	−0·999	0·540	60

as they only determine the absent reflexions, which were not included among the phasing magnitudes). There are no centrosymmetric pairs, but this is not surprising in symmetry class *m*. Three estimated cosines (marked with an asterisk) show an incorrect sign: the 2nd, 9th and 22nd. Nevertheless, the average phase error is $\langle|\Delta\Phi|\rangle = 33°$.

For both test structures in class $2/m$, METHOX ($N = 80$, $P2_1/c$) and PANBE ($N = 96$, $A2/a$), all the estimates with $|ARG| \geq 1{\cdot}0$ are correct, and Table 6 shows an analysis of the number of correct sign indications for different limits of the argument of the hyperbolic tangent in (38).

In Table 7 the results for KARLE ($N = 68$, $P2_12_12_1$) are reported. Debaerdemaeker & Woolfson (1972) (D & W), in their paper on the extension of the coincidence method to noncentrosymmetric structures, have also used this compound as a test structure and a direct comparison of the two methods is therefore possible.

As far as the centrosymmetric pairs are concerned, in Table 7 there are four correct indications, while in Table 1 of D & W, of the four relationships of this type (only the first is in common with our list) one is incorrect; this particular seminvariant is also incorrectly evaluated by our method, but with ARG = 0·62, and this is one of only two cases for which we have a wrong indication with $|ARG| \geq 0{\cdot}6$ for centrosymmetric pairs in all the noncentrosymmetric structures we have considered.

The comparison of the results for the general two-phase seminvariants shows in a clearer way the advantage of the representation method over the coincidence method.

The total average phase error for the top 52 relations with smallest variance given in Table 1 of D & W is $\langle|\Delta\Phi|\rangle = 48°$, while it is $\langle|\Delta\Phi|\rangle = 32°$ for the 105 relations with $|G| \geq 1{\cdot}0$ shown in Table 7 [four relations, for which both $\cos(\varphi_{\mathbf{u}} - \varphi_{\mathbf{v}})$ and $\cos(\varphi_{\mathbf{u}} + \varphi_{\mathbf{v}})$ were evaluated, have been grouped together]. Moreover, of the 52 coincidences given by D & W, 30 are not present in our list, and the average phase error for these relations, as evaluated by the coincidence method, is rather large $\langle|\Delta\Phi|\rangle = 55°$. Also, for the 22 seminvariants in common (the order of appearance in the two lists is completely different) there is an improvement in their estimate: the average phase error reduces from 39 to 33°. These results show the ability of the representation method not only to give better estimates for the two-phase seminvariants, but also to take care of most of the bad estimates obtained by the coincidence method, by assigning them low $|G|$ values.

When we group the relations given in Table 7 in different intervals of increasing $|G|$ we have:

Interval	*NR*	$\langle\|\Delta\Phi\|\rangle$
1·0–1·5	37	38°
1·5–2·0	25	36
>2·0	43	23.

Table 5. *DIMER: general two-phase seminvariants given as in Table* 4

The asterisks indicate the cosines for which the sign is incorrectly evaluated.

	u	E_u	φ_u	v	E_v	φ_v	G	$(\cos\Phi)_c$	$(\cos\Phi)_t$	$\|\Delta(\cos\Phi)\|$	$\|\Delta\Phi\|$
(1)	13 17 −3	2·34	−7	13 9 −3	2·07	168	−3·54	−0·839	−0·996	0·157	28
(2)	0 8 3	2·00	−2	0 10 3	1·98	64	−3·00	−0·810	0·407*	1·217	78
(3)	3 1 −8	1·99	88	3 3 −8	1·84	−150	−2·95	−0·806	−0·530	0·276	22
(4)	8 2 −8	2·18	−161	8 0 −8	2·03	−4	−2·92	−0·804	−0·921	0·117	14
(5)	0 10 2	2·19	−101	0 4 2	1·84	48	−2·76	−0·791	−0·857	0·066	7
(6)	0 12 5	2·14	−18	0 14 5	1·91	134	−2·49	−0·764	−0·883	0·119	12
(7)	1 17 −5	1·88	144	1 11 −5	1·83	−40	−2·10	−0·711	−0·998	0·287	41
(8)	8 14 2	2·12	−60	8 20 2	2·07	170	−2·09	−0·710	−0·643	0·067	5
(9)	10 4 4	2·53	88	10 2 4	1·85	177	−1·88	−0·673	0·017*	0·690	43
(10)	14 16 −6	1·90	−149	14 14 −6	1·83	32	−1·84	−0·666	−1·000	0·334	48
(11)	10 0 4	3·50	−18	10 2 4	1·85	177	−1·84	−0·666	−0·966	0·300	33
(12)	8 14 −4	2·66	6	8 16 −4	1·81	−147	−1·82	−0·662	−0·891	0·229	22
(13)	14 0 −6	2·59	−129	14 6 −6	1·90	86	−1·69	−0·635	−0·819	0·184	16
(14)	6 0 −8	2·56	85	6 2 −8	1·89	−99	−1·64	−0·624	−0·998	0·374	48
(15)	7 15 1	2·94	48	7 13 1	1·84	−113	−1·63	−0·622	−0·946	0·324	33
(16)	9 19 −2	2·44	169	9 11 −2	2·00	−7	−1·61	−0·617	−0·998	0·381	48
(17)	13 1 −3	2·20	−173	13 9 −3	2·07	168	1·51	0·594	0·946	0·352	35
(18)	18 2 −4	2·80	−157	18 0 −4	2·43	−4	−1·43	−0·573	−0·891	0·318	28
(19)	3 1 1	2·45	172	3 19 1	1·85	38	−1·43	−0·573	−0·695	0·122	9
(20)	13 17 −3	2·34	−7	13 1 −3	2·20	−173	−1·42	−0·571	−0·970	0·399	41
(21)	0 12 5	2·14	−18	0 16 5	1·88	164	−1·42	−0·571	−0·999	0·428	53
(22)	14 0 −6	2·59	−129	14 16 −6	1·90	−149	−1·36	−0·555	0·940*	1·495	104
(23)	9 19 −2	2·44	169	9 1 −2	2·26	144	1·34	0·550	0·906	0·356	32
(24)	3 1 −7	2·02	−165	3 5 −7	1·90	69	−1·33	−0·547	−0·588	0·041	3
(25)	3 1 −7	2·02	−165	3 7 −7	1·91	35	−1·23	−0·518	−0·940	0·422	39
(26)	15 3 −5	2·95	−114	15 1 −5	1·82	−6	−1·22	−0·515	−0·309	0·206	13
(27)	1 13 5	2·00	10	1 17 5	1·87	25	1·12	0·485	0·966	0·481	46
(28)	15 3 −1	2·37	−38	15 13 −1	1·84	173	−1·11	−0·482	−0·857	0·375	30

A comparison of this table with Fig. 2 of D & W, where for the range of minimum variance $\langle |\Delta\Phi| \rangle \simeq 32°$, also illustrates the improvement obtained by our method.

In Table 7 only four seminvariants (3, 25, 42 and 61) have both $\cos(\varphi_u - \varphi_v)$ and $\cos(\varphi_u + \varphi_v)$ estimated with $|G| \geq 1{\cdot}0$; the actual values of the phases, for the relations 25, 42 and 61, approximately comply with the deduction of case (*d*) in § 4, while for the seminvariant 3, for which $\cos(\varphi_u - \varphi_v)$ is incorrectly evaluated as negative, the true phases contradict the deduction of the indicated case (*b*) of § 4.

More favorable, in this respect, are the results obtained for TOXE ($N = 108$, $P2_12_12_1$) shown in Table 8, where only the 12 seminvariants for which both $\cos(\varphi_u - \varphi_v)$ and $\cos(\varphi_u - \varphi_v)$ are evaluated with $|G| \geq 1{\cdot}0$ are given, together with the seven centrosymmetric pairs with $|\text{ARG}| \geq 0{\cdot}8$. The last column shows how the deductions of § 4 are complied with quite well for all but one case. For TOXE we have estimated 58 two-phase seminvariants with $|G| \geq 1{\cdot}0$ and the average phase error is $\langle |\Delta\Phi| \rangle = 34°$. The results for TOLY ($N = 104$, $P2_12_12_1$) are similar; we have correctly estimated 13 centrosymmetric pairs with $|\text{ARG}| \geq 0{\cdot}8$ and the average phase error for the 33 general seminvariants with $|G| \geq 1{\cdot}0$ is 32°. All five cases for which both $\cos(\varphi_u - \varphi_v)$ and $\cos(\varphi_u + \varphi_v)$ are given agree with the deductions of § 4.

The results for AZET ($N = 384$, $Pca2_1$), given in Table 9, qualitatively prove the arguments of § 3. In fact, some of the values of $|G|$ are very large and they correspond to the cases in which the first phasing shell is defined by $\mathbf{D}_{pq}$ matrices of type (200) or (020) and it includes several hundred magnitudes. The 13 centrosymmetric pairs with $|\text{ARG}| \geq 1{\cdot}0$ are all correctly evaluated and the average phase error for the 44 general two-phase seminvariants with $|G| \geq 1{\cdot}0$ is $\langle |\Delta\Phi| \rangle = 31°$.

Finally we quote the results for PERYL ($N = 272$, *Pcab*): of the 23 two-sign products with $|\text{ARG}| \geq 1{\cdot}0$ only the last is incorrectly evaluated.

Table 6. *The number of two-phase seminvariants and the percentage of correct estimates for different limits of the argument of the hyperbolic tangent formula* (36), *for two test structures in class* 2/*m* (*METHOX and PANBE*)

	METHOX		PANBE	
ARG	*NR*	% correct	*NR*	% correct
0·4	277	76·5	201	80·6
0·6	139	83·5	118	94·1
0·8	73	91·8	86	96·5
1·0	30	100·0	53	100·0
1·2	11	100·0	27	100·0
1·4	6	100·0	5	100·0
1·6	3	100·0		
2·0	1	100·0		

6. Concluding remarks

The results of § 5 indicate that the use of the representation theory allows those magnitudes to be defined which are most effective in determining, in a probabilistic way, the values of the two-phase semin-

Table 7. *KARLE: centrosymmetric pairs and general two-phase seminvariants given as in Tables* 4 *and* 5

The column 'type' indicates whether the estimate is for $\cos(\varphi_u - \varphi_v)$ or $\cos(\varphi_u + \varphi_v)$.

	u			E_u	φ_u	v			E_v	φ_v		ARG	P_+		
1)	5	4	0	2.31	90	1	2	0	1.44	-90		-1.65	.036		
2)	5	4	0	2.31	90	1	6	1	1.48	-90		-1.48	.049		
3)	4	5	0	1.63	0	8	3	0	1.21	180		-1.13	.094		
4)	0	5	7	2.44	-90	0	3	7	2.16	90		-.98	.123		

											Type	G	$(\cos\varphi)_c$	$(\cos\varphi)_t$	$\lvert\Delta(\cos\varphi)\rvert$	$\lvert\Delta\varphi\rvert$
1)	4	5	5	2.13	94	0	3	5	1.36	-90	u--	-4.04	-.356	-.998	.142	28
2)	3	4	3	1.95	-35	7	6	3	1.36	95	u-v	-3.57	-.840	-.643	.197	17
3)	8	5	2	2.31	-173	4	3	2	1.23	-85	u-v	-3.18	-.821	.035°	.856	57
											u-v	-1.01	-.449	-.208	.241	15
4)	0	5	7	2.44	-90	4	3	7	1.35	134	u-v	-3.13	-.818	-.719	.099	9
5)	2	4	1	2.23	160	6	2	1	1.39	-30	u-v	-3.09	-.816	-.985	.169	25
6)	0	4	14	1.95	0	4	2	14	1.37	165	u-v	-2.99	-.809	-.966	.157	21
7)	2	1	13	1.42	108	6	3	13	1.40	14	u-v	-2.94	-.806	-.070	.736	50
8)	6	4	1	1.93	155	2	2	1	1.53	-14	u-v	-2.88	-.801	-.982	.181	26
9)	4	5	7	2.22	-93	0	3	7	2.16	90	u-v	-2.80	-.795	-.999	.204	35
10)	4	2	12	1.74	-25	0	4	12	1.46	180	u-v	-2.77	-.792	-.906	.114	13
11)	5	4	12	2.19	-128	1	2	12	1.65	67	u-v	-2.57	-.773	-.966	.193	24
12)	1	1	14	1.53	178	3	1	14	1.30	-140	u-v	2.51	.766	-.743	.023	2
13)	8	4	6	1.93	92	4	6	6	1.35	-40	u-v	-2.49	-.764	-.669	.095	8
14)	1	4	14	1.92	93	5	6	14	1.29	-171	u-v	-2.46	-.761	-.105	.656	44
15)	8	4	3	1.40	-116	4	6	3	1.30	-36	u-v	-2.46	-.761	.174°	.935	60
16)	2	4	5	1.98	-12	6	2	5	1.54	95	u-v	-2.43	-.759	-.292	.467	32
17)	4	4	7	2.01	148	8	2	7	1.82	-74	u-v	-2.41	-.755	-.743	.012	1
18)	0	1	15	2.60	-90	4	1	15	1.24	-75	u-v	2.39	.752	.966	.214	26
19)	2	5	12	1.87	52	2	3	12	1.38	-46	u-v	2.39	.752	.995	.243	36
20)	1	3	12	1.68	-162	5	5	12	1.65	1	u-v	-2.37	-.750	-.956	.206	24
21)	0	0	12	2.43	180	4	2	12	1.74	-25	u-v	-2.36	-.748	-.906	.158	17
22)	8	6	2	1.66	89	4	4	2	1.23	-162	u-v	-2.35	-.747	-.326	.421	29
23)	2	6	8	2.18	170	6	4	8	1.47	-50	u-v	-2.34	-.746	-.766	.020	2
24)	6	3	5	1.31	46	2	5	5	1.21	88	u-v	-2.34	-.746	.743°	1.489	96
25)	2	5	7	1.52	-102	2	3	7	1.51	64	u-v	2.34	.745	.788	.043	4
											u-v	-1.50	-.590	-.970	.380	40
26)	1	3	12	1.68	-162	3	1	12	1.52	42	u-v	-2.29	-.740	-.500	.240	18
27)	5	4	14	1.08	30	1	2	14	1.48	-147	u-v	-2.26	-.735	-.999	.264	40
28)	5	6	4	1.51	94	1	4	4	1.41	-109	u-v	-2.22	-.729	-.921	.192	20
29)	3	3	12	1.69	174	1	5	12	1.40	-28	u-v	-2.21	-.727	-.829	.102	9
30)	7	3	1	1.35	87	3	5	1	1.27	-57	u-v	-2.20	-.726	-.809	.083	7
31)	7	4	7	1.95	-177	3	2	7	1.33	18	u-v	-2.19	-.725	-.966	.241	29
32)	4	4	13	1.57	-20	0	6	13	1.50	180	u-v	-2.17	-.722	-.940	.218	24
33)	6	5	12	1.66	164	2	3	12	1.38	-46	u-v	-2.16	-.721	-.866	.145	14
34)	2	3	7	1.51	64	6	5	7	1.49	-81	u-v	-2.14	-.718	-.819	.101	9
35)	2	6	8	2.18	170	2	4	8	1.76	19	u-v	-2.07	-.707	-.988	.281	36
36)	5	4	13	1.59	178	1	6	13	1.52	-52	u-v	-2.07	-.706	-.643	.063	5
37)	4	0	7	2.35	90	8	2	7	1.82	-74	u-v	-2.07	-.706	-.961	.255	29
38)	5	2	14	1.89	-179	1	4	14	1.30	71	u-v	-2.06	-.705	-.342	.363	25
39)	0	4	8	2.23	0	6	8	8	1.99	151	u-v	-2.05	-.703	-.875	.172	16
40)	8	0	7	1.69	90	4	2	7	1.43	-32	u-v	-2.04	-.702	-.530	.172	13
41)	5	4	7	1.45	-140	1	6	7	1.25	88	u-v	-2.02	-.698	-.669	.029	2
42)	2	3	14	1.29	147	2	5	14	1.26	-101	u-v	2.02	.699	.695	.004	0
											u-v	-1.36	-.555	-.375	.180	12
43)	2	4	18	1.63	-161	2	2	18	1.43	16	u-v	-2.00	-.694	-.858	.125	11
44)	0	6	11	1.36	0	4	4	11	1.36	-154	u-v	-1.98	-.691	-.899	.208	20
45)	6	4	4	1.88	-158	2	2	4	1.38	12	u-v	-1.97	-.690	-.985	.295	36
46)	0	3	14	2.05	90	4	5	14	1.39	-13	u-v	-1.97	-.690	-.225	.465	31
47)	1	6	15	1.52	151	5	4	15	1.42	-13	u-v	-1.97	-.690	-.961	.271	30
48)	6	3	14	1.50	113	2	5	14	1.26	-101	u-v	-1.96	-.688	-.829	.141	13
49)	0	2	10	1.34	0	4	4	10	1.26	171	u-v	-1.93	-.682	-.988	.306	38
50)	4	5	5	2.13	94	8	3	5	1.42	-134	u-v	-1.93	-.682	-.669	.013	1
51)	1	6	15	1.52	151	3	4	15	1.26	140	u-v	1.91	.679	.358	.321	22
52)	1	0	8	1.60	180	5	2	8	1.37	-35	u-v	-1.86	-.669	-.819	.150	13
53)	4	4	8	2.51	16	0	2	8	2.05	180	u-v	-1.84	-.666	-.961	.295	32
54)	2	4	1	2.23	160	2	2	1	1.53	-14	u-v	-1.80	-.657	-.829	.172	15
55)	8	4	3	1.40	-116	4	2	3	1.38	40	u-v	-1.77	-.652	-.914	.262	25
56)	1	1	14	1.53	178	3	3	14	1.22	49	u-v	-1.73	-.644	-.682	.038	3
57)	0	4	12	1.46	180	4	6	12	1.30	-146	u-v	-1.70	-.637	.859°	1.496	96
58)	0	6	10	1.35	180	4	4	10	1.26	171	u-v	-1.69	-.635	.988°	1.623	121
59)	5	4	0	2.31	90	5	4	14	2.08	30	u-v	1.68	.633	.500	.133	9
60)	1	4	6	1.26	71	3	6	6	1.22	-81	u-v	1.68	.633	.985	.352	41
61)	2	3	5	1.38	-89	2	5	5	1.21	88	u-v	1.66	.628	1.000	.372	51
											u-v	-1.26	-.528	-.999	.471	56
62)	1	2	14	1.47	-147	3	4	14	1.26	62	u-v	1.61	.618	.087	.531	33
63)	1	2	2	1.42	-22	3	4	2	1.36	-147	u-v	1.58	.611	-.982°	1.593	117
64)	1	4	9	1.32	143	3	2	9	1.24	-124	u-v	1.56	.606	.946	.340	34
65)	4	4	8	2.51	16	0	4	8	2.23	0	u-v	1.52	.597	.961	.364	37
66)	2	6	15	1.62	-36	2	2	1	1.53	-14	u-v	1.52	.596	.927	.331	31
67)	4	4	8	2.51	16	4	6	8	1.99	151	u-v	-1.50	-.592	-.707	.115	9
68)	4	5	0	1.63	0	4	5	14	1.39	-13	u-v	1.41	.567	.974	.407	42
69)	2	4	5	1.98	-12	4	6	5	1.81	-147	u-v	-1.40	-.564	-.707	.143	11
70)	2	4	10	2.09	-141	6	4	4	1.88	-158	u-v	1.38	.560	.956	.396	39
71)	3	4	7	1.33	118	1	6	7	1.25	88	u-v	1.35	.560	-.899°	1.459	98
72)	2	4	13	2.02	-22	2	4	1	2.23	160	u-v	-1.38	-.559	-.743	.184	14
73)	2	2	14	1.85	169	2	6	0	1.24	180	u-v	1.35	.553	.982	.429	46
74)	1	6	0	1.48	-90	1	2	14	1.47	-147	u-v	1.30	.540	.545	.005	0
75)	4	4	8	2.51	16	2	6	8	2.18	170	u-v	-1.23	-.520	-.899	.379	33
76)	5	4	14	2.08	30	5	6	14	1.29	-171	u-v	-1.22	-.515	-.934	.419	38
77)	6	6	2	1.46	129	6	2	12	1.20	-64	u-v	1.22	.515	.423	.092	6
78)	4	5	7	2.22	-93	4	3	7	1.35	134	u-v	-1.21	-.512	-.682	.170	12
79)	6	4	4	1.88	-158	6	6	4	1.32	-28	u-v	-1.18	-.503	-.643	.140	10
80)	2	1	1	1.89	-56	2	1	15	1.38	-73	u-v	1.16	.498	.956	.458	43
81)	4	0	7	2.35	90	4	4	7	2.01	148	u-v	1.16	.497	.530	.033	2
82)	0	5	7	2.44	-90	4	5	5	2.13	94	u-v	-1.14	-.490	-.998	.508	57
83)	0	3	7	2.16	90	4	3	9	1.84	11	u-v	1.13	.487	.191	.296	18
84)	2	4	17	1.83	-166	2	6	9	1.77	24	u-v	1.13	.487	-.985°	1.472	109
85)	6	2	7	1.78	-91	4	2	7	1.42	-32	u-v	1.11	.482	.515	.033	2
86)	8	5	2	2.31	-173	4	5	0	1.63	0	u-v	1.09	.476	-.993°	1.469	112
87)	4	4	8	2.51	16	6	4	8	1.47	-50	u-v	1.09	.475	.829	.354	28
88)	2	3	9	1.53	131	2	3	7	1.51	64	u-v	-1.09	-.475	-.966	.491	47
89)	2	3	6	1.94	-100	2	5	14	1.26	-101	u-v	1.08	.472	1.000	.528	62
90)	8	5	7	2.91	0	4	5	2	1.43	154	u-v	1.07	.469	-.899°	1.368	92
91)	4	2	0	2.54	180	4	2	14	1.37	165	u-v	1.07	.468	.966	.498	47
92)	2	5	12	1.87	52	2	5	10	1.48	149	u-v	-1.07	-.468	-.934	.466	41
93)	4	5	7	2.22	-93	6	5	7	1.49	-81	u-v	-1.04	-.459	-.995	.536	57
94)	5	2	6	1.89	-179	5	2	8	1.37	-35	u-v	-1.03	-.458	-.809	.351	27
95)	2	4	8	1.76	19	6	4	8	1.47	-50	u-v	1.03	.457	.358	.099	6
96)	5	4	12	2.19	-128	5	4	14	2.08	30	u-v	1.02	.454	-.139°	.593	35
97)	2	5	7	1.52	-102	6	5	7	1.49	-81	u-v	-1.02	-.453	-.999	.546	61
98)	2	1	13	1.42	108	2	1	15	1.38	-73	u-v	1.01	.450	.819	.369	28
99)	4	6	10	1.31	35	4	4	10	1.26	171	u-v	-1.01	-.450	-.719	.269	19
100)	5	4	7	1.45	-140	3	4	7	1.33	118	u-v	1.00	.447	.927	.480	41
101)	0	4	11	1.83	0	8	4	3	1.40	-116	u-v	1.00	.445	-.438°	.883	52

Table 8. *TOXE: centrosymmetric pairs and general two-phase seminvariants for which both* $\cos(\varphi_{\mathbf{u}} - \varphi_{\mathbf{v}})$ *and* $\cos(\varphi_{\mathbf{u}} + \varphi_{\mathbf{v}})$ *are estimated with* $|G| \geq 1{\cdot}0$

The last columns refer to the cases illustrated in § 4 when assuming $(\cos \Phi)_c = \pm 1{\cdot}0$. Δ_- and Δ_+ are the deviations of the actual phase differences or sums from the values indicated by the four cases in (35).

	u	E_u	φ_u	v	E_v	φ_v	ARG	P_+
1)	10 0 3	2.53	90	8 0 3	2.28	-90	-1.39	.058
2)	2 0 0	2.00	180	8 0 2	1.98	180	1.38	.940
3)	7 0 8	3.11	180	11 0 10	2.58	0	-1.26	.074
4)	3 5 0	2.65	90	1 3 0	2.33	-90	-1.22	.080
5)	6 0 2	2.89	0	2 0 0	2.00	180	-1.20	.083
6)	6 0 2	2.89	0	8 0 2	1.98	180	-0.92	.137
7)	3 16 0	2.58	90	9 2 0	2.27	-90	-0.86	.152

		Type	G	$(\cos\varphi)_c$	$(\cos\varphi)_t$	$\lvert\Delta(\cos\varphi)\rvert$	$\lvert\Delta\varphi\rvert$	Case	Δ_- / Δ_+
1)	2 9 2 2.37 -19 10 9 2 2.14 1	u-v	3.35	.831	.940	.109	14	a)	20
		u+v	1.58	.610	.951	.341	34		18
2)	3 9 1 2.70 98 5 9 1 1.95 -90	u-v	-3.28	-.827	-.990	.163	26	c)	8
		u+v	1.34	.550	.990	.440	49		8
3)	4 2 1 2.31 -2 2 2 1 1.95 -165	u-v	-2.06	-.705	-.956	.251	28	b)	17
		u+v	-1.53	-.538	-.974	.376	40		13
4)	2 16 1 2.44 169 2 2 1 1.95 -165	u-v	1.97	.690	.899	.209	20	a)	26
		u+v	1.06	.466	.998	.532	59		4
5)	7 1 7 2.29 61 1 1 5 2.07 83	u-v	1.91	.679	.927	.248	25	d)	22
		u+v	-1.41	-.568	-.809	.241	19		36
6)	7 4 3 3.02 83 9 4 1 2.06 100	u-v	1.54	.601	.956	.355	36	d)	17
		u+v	-1.25	-.524	-.999	.475	56		3
7)	10 8 1 2.60 161 4 10 1 2.10 11	u-v	-1.38	-.560	-.866	.306	26	b)	30
		u+v	-1.50	-.591	-.990	.399	46		8
8)	4 2 1 2.31 -2 4 10 1 2.10 11	u-v	1.37	.558	.974	.416	43	a)	13
		u+v	1.35	.552	.988	.436	48		9
9)	7 11 13 2.21 128 1 11 15 2.19 81	u-v	1.23	.518	.682	.164	12	d)	47
		u+v	-1.26	-.527	-.875	.348	29		29
10)	4 10 8 2.42 0 2 10 6 2.30 9	u-v	1.22	.515	.988	.473	50	a)	9
		u+v	1.35	.552	.988	.436	48		9
11)	4 9 3 2.12 100 10 9 3 2.01 -172	u-v	-1.16	-.497	.035*	.532	32	c)	92
		u+v	1.31	.541	.309	.232	15		72
12)	3 16 8 2.45 -168 3 16 6 2.32 -28	u-v	-1.05	-.463	-.766	.303	22	b)	32
		u+v	-1.94	-.684	-.961	.277	31		16

variants. The method also allows a generalized use of space-group symmetry and its extension to systems higher than orthorhombic is a practical computing problem and not a theoretical one.

Our calculations show that it is possible to have quite good estimates of some tens of two-phase seminvariants, which can be very important in the process of phase determination. When we use triple-phase invariants we assume that we know two of the phases in order to determine the third. If the known phases are in error, a rapid propagation of errors is possible, and, as pointed out by Gilmore (1977), the situation becomes worse for quartets where three known phases are needed to define the fourth. On the other hand, if we reduce the number of phases to two, the propagation of error is greatly reduced. The price we have to pay for this is that the number of reliably estimated relationships is greatly reduced. For this reason we believe that two-phase seminvariants should be especially useful in the initial stages of phase determination.

Debaerdemaeker & Woolfson (1972) suggested the use of two-phase seminvariants to enlarge the starting set or to reduce the number of permuted phases which must be introduced at the beginning of the phasing process by the multisolution method.

When using magic integers to represent the phases in the starting set, the use of two-phase seminvariants in defining a *secondary set* of phases (Declercq, Germain & Woolfson, 1975) would greatly reduce the effects of error propagation. Two-phase seminvariants, whose cosine is evaluated near $\pm 1{\cdot}0$, could form a set of very useful relations for use in the calculation of ψ maps (White & Woolfson, 1975); in this case negative indications in symmorphic space groups could play an essential role.

Phase expansion could also benefit by the use of two-phase seminvariants, when performed by a least-squares procedure such as that described by Woolfson (1977) or that, using the estimated cosine invariants and seminvariants, proposed by Gilmore (1977).

Finally, Giacovazzo (1977*a*) also suggested the use of two-phase seminvariants as a figure of merit to select the correct phase set among those produced by a multisolution procedure. Again, in this respect, the ability of correctly evaluating, in space groups with no translation symmetry, the relations for which $\varphi_{\mathbf{u}} + \varphi_{\mathbf{v}} \simeq \pi$ is very important.

The results described in this paper have been obtained using the linearized formulae derived by means of the Gram–Charlier expansion of the characteristic function. As a further attempt at improving the estimates of the two-phase seminvariants, we intend to use the exponential formulae described in paper III; in this way we expect to be able to obtain

Table 9. *AZET: centrosymmetric pairs and general two-phase seminvariants as in Tables 4 and 5*

	u			E_u	φ_u	v			E_v	φ_v	ARG	P_+
1)	9	5	0	1.97	0	9	1	0	1.85	0	23.90	1.000
2)	2	7	0	3.16	0	2	3	0	1.83	0	21.05	1.000
3)	9	3	0	1.95	180	9	1	0	1.85	0	−9.46	0.000
4)	7	6	0	2.01	180	7	2	0	2.00	180	7.44	1.000
5)	8	2	0	2.79	180	8	4	0	2.32	0	−6.00	0.000
6)	7	2	0	2.00	180	7	8	0	1.98	0	−4.44	0.000
7)	0	4	0	3.47	0	0	6	0	2.68	180	−2.37	0.009
8)	2	7	0	3.16	0	6	7	0	2.26	0	1.82	0.974
9)	2	7	0	3.16	0	16	7	0	2.21	180	−1.35	0.063
10)	7	6	0	2.01	180	7	8	0	1.98	0	−1.18	0.086
11)	16	7	0	2.21	180	14	7	0	2.14	180	1.17	0.912
12)	6	7	0	2.26	0	2	3	0	1.83	0	1.12	0.904
13)	7	1	0	1.95	0	9	1	0	1.85	0	1.06	0.893

											G	$(\cos\varphi)_c$	$(\cos\varphi)_t$	$\lvert\Delta(\cos\varphi)\rvert$	$\lvert\Delta\varphi\rvert$
1)	16	0	7	1.91	-26	16	4	7	1.87	-23	28.64	.970	.999	.029	12
2)	19	3	5	2.16	103	19	1	5	1.78	-102	-25.88	-.970	-.906	.064	11
3)	27	1	2	2.00	-118	27	3	2	1.99	60	-21.19	-.970	-.999	.029	12
4)	14	7	3	2.28	-158	14	5	3	1.85	51	-3.90	-.852	-.375	.023	3
5)	17	3	7	2.18	155	13	3	7	2.09	153	3.13	.818	.999	.181	33
6)	11	3	2	2.31	-110	15	3	2	1.89	-110	3.06	.814	1.000	.186	36
7)	10	5	6	2.19	178	14	5	6	2.11	149	2.68	.784	.875	.091	9
8)	1	3	10	2.02	-137	5	3	10	1.90	-165	2.53	.768	.883	.115	12
9)	25	3	3	2.26	100	29	3	3	2.22	35	2.38	.751	.423	.328	24
10)	18	5	5	1.81	-91	4	5	5	1.77	60	-2.33	-.744	-.875	.131	13
11)	20	5	1	2.38	4	16	5	1	2.26	6	2.05	.703	.999	.296	43
12)	9	8	2	2.49	50	5	8	2	1.94	35	2.02	.698	.966	.268	31
13)	21	3	3	2.32	51	25	3	3	2.26	100	1.78	.654	.656	.002	0
14)	16	5	5	2.23	87	4	5	5	1.77	60	1.77	.652	.891	.239	22
15)	6	2	3	2.19	51	22	2	3	1.81	-117	-1.77	-.652	-.978	.326	37
16)	17	3	3	2.63	25	29	3	3	2.22	35	1.64	.624	.985	.361	41
17)	4	5	6	2.53	-3	10	5	6	2.19	178	-1.61	-.617	-1.000	.383	52
18)	22	0	7	2.06	170	26	0	7	2.04	154	1.55	.603	.961	.358	37
19)	17	3	3	2.63	25	31	3	3	2.20	-132	-1.53	-.598	-.921	.323	30
20)	18	5	1	1.95	-176	22	5	1	1.92	-175	1.47	.584	1.000	.416	54
21)	17	3	3	2.63	25	21	3	3	2.32	51	1.47	.584	.899	.315	28
22)	1	3	4	2.15	-138	5	3	4	2.08	-32	1.47	.584	-.276*	.860	52
23)	22	2	7	2.22	-55	8	2	7	1.79	149	-1.45	-.579	-.914	.335	31
24)	9	3	4	2.34	-72	13	3	4	1.80	-75	1.45	.579	.999	.420	52
25)	1	8	2	2.01	64	5	8	2	1.94	35	1.44	.576	.875	.299	26
26)	15	3	1	2.56	-3	29	3	1	1.94	-177	-1.36	-.555	-.995	.440	51
27)	4	5	6	2.53	-3	0	5	6	2.53	-21	1.36	.555	.951	.396	38
28)	9	3	4	2.34	-72	5	3	4	2.08	-32	1.34	.550	.766	.216	17
29)	29	3	3	2.22	35	31	3	3	2.20	-132	-1.34	-.550	-.974	.424	44
30)	4	5	2	1.96	-138	26	1	2	1.90	-152	1.28	.533	.970	.437	44
31)	0	5	6	2.53	-21	14	5	6	2.11	149	-1.24	-.521	-.985	.464	49
32)	15	3	1	2.56	-3	31	3	1	2.15	40	1.23	.518	.731	.213	16
33)	11	3	2	2.31	-110	27	3	2	1.99	60	-1.23	-.518	-.985	.467	49
34)	24	0	7	2.43	-35	16	0	7	1.91	-26	1.22	.515	.988	.473	50
35)	5	8	2	1.94	35	13	2	2	1.83	-104	-1.18	-.503	-.755	.252	19
36)	25	3	3	2.26	100	31	3	3	2.20	-132	-1.16	-.497	-.616	.119	8
37)	9	8	2	2.49	50	1	8	2	2.01	64	1.15	.494	.970	.476	46
38)	9	8	2	2.49	50	13	2	2	1.83	-104	-1.10	-.479	-.899	.420	35
39)	7	1	1	1.87	-168	23	5	1	1.86	157	1.09	.476	.819	.343	27
40)	22	0	7	2.06	170	16	0	7	1.91	-26	-1.08	-.472	-.961	.489	46
41)	5	3	4	2.08	-32	13	3	4	1.80	-75	1.05	.463	.731	.268	19
42)	26	5	1	1.98	144	18	5	1	1.95	-176	1.04	.459	.766	.307	23
43)	2	5	4	2.84	-48	14	5	4	2.76	168	-1.01	-.449	-.809	.360	27
44)	24	0	7	2.43	-35	16	4	7	1.87	-23	1.01	.449	.978	.529	51

two-phase seminvariant estimates in the vicinity of $\pi/2$ also, with the corresponding variances. A more direct comparison with the results obtained by Green & Hauptman (1978*a*) (G & H) in the space group $P2_1$ will then be possible.

Here we restrict our attention to an important difference between our method and that of G & H. As we have seen [*cf.* equation (22)] in space group $P2_1$ the vectors corresponding to the phasing magnitudes lie on a reciprocal-lattice row with a free index k (b unique axis). In our formulation the contributions of all independent magnitudes are summed in the probability formula, while in that of G & H the magnitudes are considered in sets of six terms, one for each value of k (q in the paper of G & H), and the distribution yielding the minimum variance is assumed as the best estimate. We did not try the formulae of G & H, but the calculations of the values of ARG for each individual term j, show, for HEPTA, that the maximum value alone is too small to give reliable estimates. In one or two cases, when the indication of the maximum ARG is wrong, the other contributors tend to lower the weight of the relationship. We believe, therefore, that the inclusion of all the terms contributing to a certain seminvariant can improve its estimate.

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Rotation-Function Study of Flavocytochrome b_2

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(*Received* 13 *June* 1978; *accepted* 5 *December* 1978)

Abstract

A rotation-function study of flavocytochrome b_2 has been carried out using X-ray data from crystals which contain one tetramer of 230 000 Dalton per asymmetric unit. The function computed from 10–5·5 Å resolution data clearly shows the orientation of the molecular 222 symmetry axes. The presence of these symmetry elements is consistent with previous structural and biochemical studies of the molecule.

I. Introduction

Bakers yeast flavocytochrome b_2 [L-(+)-lactate cytochrome *c* oxidoreductase, EC 1.1.2.3) contains four identical subunits and has a molecular weight of 230 000 Dalton (Jacq & Lederer, 1974). It contains one protoheme IX and one flavin mononucleotide prosthetic group per subunit. It catalyzes the oxidation of lactate to pyruvate in mitochondria with the reducing equivalents passing to oxygen *via* the cytochrome *c*–cytochrome oxidase pathway (Pajot & Claisse, 1974).

When flavocytochrome b_2 is digested exhaustively with trypsin a small trypsin-resistant heme peptide, cytochrome b_2 core, remains intact (Labeyrie, Groudinsky, Jacquot-Armand & Naslin, 1966). The amino-acid sequence of the 96 residues of cytochrome b_2 core is remarkably homologous to that of microsomal cytochrome b_5 (Guiard & Lederer, 1976). Comparison of the two sequences with the atomic model of cytochrome b_5 (Mathews, Argos & Levine, 1971) indicates a possible structural similarity of the two molecules, as supported by other chemical and spectroscopic evidence (Guiard, Groudinsky & Lederer, 1974).

Large single crystals of flavocytochrome b_2 have been prepared which diffract to about 2·5 Å resolution (Mathews & Lederer, 1976). These crystals are trigonal and contain one tetramer in the asymmetric unit cell. The tetramer is expected to possess 222 symmetry (Olive, Barbotin & Risler, 1973). As part of the structural investigation of flavocytochrome b_2 it is

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