Acta Cryst. (1980). A**36**, 1017–1025

The Theory of Representations: its Application to the Estimation of the Two-Phase Variants and Seminvariants

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(*Received* 26 *March* 1980; *accepted* 6 *May* 1980)

Abstract

The theory of representations has been used to obtain probabilistic estimates of the two-phase variants and seminvariants for the non-centrosymmetric space groups up to orthorhombic. Some practical applications show that the phase estimations can be useful in direct procedures, mostly for those crystal structures in which the enantiomorph definition is difficult.

Notation

$\mathbf{h}_1, \mathbf{h}_2$ = reciprocal vectors
N = number of atoms in the unit cell
t = number of atoms in the asymmetric unit
$E_{\mathbf{h}}$ = normalized structure factor
$\mathbf{I}$ = identity 3 × 3 matrix
$\varepsilon = E^2 - 1$
$R_{\mathbf{h}}$ = magnitude of the normalized structure factor
$\mathbf{R}_p$ = pth rotation matrix of the point group
$\mathbf{T}_p$ = translation vector associated with the pth rotation matrix in the space group.

1. Introduction

Special quartets are those for which some algebraic relations can be found among the basis vectors in addition to the condition $\sum_j \mathbf{h}_j = 0$. Examples of special quartets (Giacovazzo, 1980*a*) are given in (i)–(iv).

(i) $\Psi = \varphi_{\mathbf{h}_1} - \varphi_{\mathbf{h}_1\mathbf{R}} + \varphi_{\mathbf{h}_2} - \varphi_{\mathbf{h}_1(\mathbf{I}-\mathbf{R})+\mathbf{h}_2}$.

This type of quartet is characterized by the property that two basis vectors are related by symmetry operations. From

$$\varphi_{\mathbf{hR}} = \varphi_{\mathbf{h}} - 2\pi\mathbf{hT} \qquad (1)$$

it follows that $\Psi = \varphi_{\mathbf{h}_2} - \varphi_{\mathbf{h}_1(\mathbf{I}-\mathbf{R})+\mathbf{h}_2} + 2\pi\mathbf{h}_1\mathbf{T}$. So Ψ is the sum of a constant arising from translational symmetry and a two-phase structure seminvariant of first rank. The role played by this type of quartet in the estimation of the two-phase structure seminvariants of first rank is well established (Giacovazzo, 1977*b*,*c*; Green & Hauptman, 1978; Giacovazzo, 1979; Giacovazzo, Spagna, Vicković & Viterbo, 1979).

(ii) $\Psi = \varphi_{\mathbf{h}_1(\mathbf{I}-\mathbf{R})} - \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_1\mathbf{R}+\mathbf{h}_2}$.

Because of (1), $\Psi = \varphi_{\mathbf{h}_1(\mathbf{I}-\mathbf{R})} - \varphi_{\mathbf{h}_1\mathbf{R}} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_1\mathbf{R}-\mathbf{h}_2} - 2\pi\mathbf{h}_1\mathbf{T}$. So Ψ is the sum of a constant arising from translational symmetry, a one-phase structure seminvariant of first rank, and a triplet invariant. The estimation of Ψ is therefore able to give an estimation for $\varphi_{\mathbf{h}_1(\mathbf{I}-\mathbf{R})}$ provided the $|E|$'s are sufficiently large. The role played by quartets (ii) in direct procedures for phase estimation has been described (Giacovazzo, 1975; Giacovazzo, 1978; Burla, Nunzi, Polidori, Busetta & Giacovazzo, 1980).

(iii) $\Psi = \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_1\mathbf{R}} + \varphi_{\mathbf{h}_2} - \varphi_{\mathbf{h}_1(\mathbf{I}+\mathbf{R})+\mathbf{h}_2}$.

Because of (1), $\Psi = 2\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} - \varphi_{\mathbf{h}_1(\mathbf{I}+\mathbf{R})+\mathbf{h}_2} - 2\pi\mathbf{h}_1\mathbf{T}$. Categories (i) and (iii) are quite different and play very different roles in direct procedures. Even if formulae for the estimation of quartets (iii) have been given (Giacovazzo, 1980*a*), no specific application has been tried so far. If $\mathbf{h}_2$ is chosen so that $\mathbf{h}_1(\mathbf{I} + \mathbf{R}) = -\mathbf{h}_2(\mathbf{I} + \mathbf{R})$ category (iii) reduces to

(iv) $\Psi = \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_1\mathbf{R}} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_2\mathbf{R}}$. (2)

Because of (1), $\Psi = 2(\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2}) - 2\pi(\mathbf{h}_1 + \mathbf{h}_2)\mathbf{T}$. So, if Ψ is estimated, some information about $\Phi = \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2}$ can be derived. Of course it does not make sense to calculate Ψ in centrosymmetric space groups, where Ψ is always a constant.

Formulae which give information about Φ in $P2_1$, when Φ is a structure seminvariant of first rank, were given by Hauptman & Green (1978). No practical

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0567-7394/80/061017-09$01.00

application of those formulae has been tried so far. In this paper we shall discuss the role of the quartets (iv) in direct procedures for phase estimation (§ 2) and describe probabilistic formulae which give information about Φ in all the non-centrosymmetric space groups up to orthorhombic (§§ 4 and 5). Formulae hold when Φ is a structure seminvariant, and when it is not (then it is a two-phase variant). To do that we shall make full use of the space-group symmetry (§ 3) as suggested by representation theory (Giacovazzo, 1977*a*). In particular we shall estimate Φ *via* the first representation of Ψ. According to the symmetry class, Ψ can depend on more than three cross magnitudes (Giacovazzo, 1976; Busetta, Giacovazzo, Burla, Nunzi, Polidori & Viterbo, 1980). To involve all the available cross magnitudes some algebraic considerations are useful, which are described in § 3. Practical applications are presented in § 6.

2. The role of the Ψ quartets in direct procedures

In § 1 we showed that $\Psi = 2\Phi - 2\pi(\mathbf{h}_1 + \mathbf{h}_2)\mathbf{T}$. Since $(\mathbf{h}_1 + \mathbf{h}_2)\mathbf{R} = -(\mathbf{h}_1 + \mathbf{h}_2)$, $E_{\mathbf{h}_1+\mathbf{h}_2}$ is a reflection with restricted phase values: in particular, $\varphi_{\mathbf{h}_1+\mathbf{h}_2} = \pi[n + (\mathbf{h}_1 + \mathbf{h}_2)\mathbf{T}]$ where n is an integer. Therefore if $\varphi_{\mathbf{h}_1+\mathbf{h}_2}$ assumes only values 0 or π, then $\Psi = 2\Phi$. For example, in $P2_1$,

$$\Psi = \varphi_{125} + \varphi_{12\bar{5}} + \varphi_{627} + \varphi_{62\bar{7}} = 2(\varphi_{125} + \varphi_{62\bar{7}}).$$

In this case if Ψ is estimated to be 0, the minimal useful information is obtained for Φ: in fact $\Phi \simeq 0, \pi$. If Ψ is estimated to be π, then $\Phi \simeq \pm\pi/2$ which is an enantiomorph-sensitive relation.

If $\varphi_{\mathbf{h}_1+\mathbf{h}_2}$ assumes only values $\pm\pi/2$, then $\Psi = 2\Phi + \pi$. For example, in $P2_12_12_1$,

$$\Psi = \varphi_{125} + \varphi_{125} + \varphi_{6\bar{2}4} + \varphi_{6\bar{2}4} = 2(\varphi_{125} + \varphi_{624}) \pm \pi.$$

In this case if Ψ is estimated to be 0 then $\Phi \simeq \pm\pi/2$; if Ψ is estimated to be π then $\Phi \simeq 0, \pi$.

The less useful situation occurs when $|\Psi|$ is estimated to be $|\alpha|$, with $\alpha \neq 0, \pm\pi/2$; then four values ensue for Φ: $\pm\alpha/2, \pm\alpha/2 + \pi$.

What is the role of the quartets Ψ in direct procedures? Without loss of generality we discuss the question in space groups up to orthorhombic following some recent ideas (Giacovazzo, 1980*b*). Let

$$R_{\mathbf{h}_1}, R_{\mathbf{h}_2}, R_{\mathbf{h}_1(\mathbf{I}+\mathbf{R})}, R_{\mathbf{h}_1+\mathbf{h}_2}, R_{\mathbf{h}_1\mathbf{R}+\mathbf{h}_2}$$

be the five magnitudes contained in the first phasing shell of Ψ. Four triplet relations ensue from them:

$$\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} \simeq \varphi_{\mathbf{h}_1+\mathbf{h}_2}, \tag{3}$$

$$\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} \simeq \varphi_{\mathbf{h}_1\mathbf{R}+\mathbf{h}_2} + 2\pi\mathbf{h}_1\mathbf{T}, \tag{4}$$

$$2\varphi_{\mathbf{h}_1} \simeq \varphi_{\mathbf{h}_1(\mathbf{I}+\mathbf{R})} + 2\pi\mathbf{h}_1\mathbf{T}, \tag{5}$$

$$2\varphi_{\mathbf{h}_2} \simeq -\varphi_{\mathbf{h}_1(\mathbf{I}+\mathbf{R})} + 2\pi\mathbf{h}_2\mathbf{T}. \tag{6}$$

Let E_t be the minimum value of $|E|$ chosen for carrying out phase determination by means of triplets and, for simplicity, let

$$\varphi_{\mathbf{h}_1+\mathbf{h}_2} = \varphi_{\mathbf{h}_1\mathbf{R}+\mathbf{h}_2} = 0, \pi,$$

$$2\pi(\mathbf{h}_1 + \mathbf{h}_2)\mathbf{T} = 2\pi\mathbf{h}_1\mathbf{T} = 2\pi\mathbf{h}_2\mathbf{T} = 0.$$

If all the R's in the first phasing shell of Ψ are large, then Φ is estimated to be 0 or π, in agreement with triplets (3) and (4) and with the relation sum between (5) and (6). The correlation between information provided by Ψ and that provided by triplets is very high.

If $R_{\mathbf{h}_1(\mathbf{I}+\mathbf{R})}$, $R_{\mathbf{h}_1+\mathbf{h}_2}$, $R_{\mathbf{h}_1\mathbf{R}+\mathbf{h}_2}$ are all smaller than E_t, then none of the four triplets (3)–(6) is estimated in the direct procedure. The information provided by Ψ is now quite new.

If $R_{\mathbf{h}_1+\mathbf{h}_2} > E_t$ and moderately large, and $R_{\mathbf{h}_1(\mathbf{I}+\mathbf{R})}$, $R_{\mathbf{h}_1\mathbf{R}+\mathbf{h}_2}$ are moderately small, then Φ can be estimated near $\pm\pi/2$, at variance with the information provided by (3).

In conclusion, the estimation of the quartets Ψ can be a useful tool for checking the validity of special triplets such as (3)–(6) or for introducing new phase information not provided by the triplets. On the other hand, quartets are relations of order $1/N$ whereas triplets are of order $1/\sqrt{N}$. That suggests that the reliability of the quartet information rapidly falls when N increases. A way of opposing this effect is to make full use of the crystal symmetry. To do that we shall describe in § 3 the circumstances in which more than five magnitudes are in the first phasing shell of Ψ.

3. Algebraic considerations

It is possible to search in different ways for quartets such as (2). Trivially, the subset (2) can be picked out from the overall set of quartets obtainable by a general quartet routine. We preferred to search for (2) by the following *ad hoc* procedure.

The condition $(\mathbf{I} + \mathbf{R})(\mathbf{h}_1 + \mathbf{h}_2) = 0$ holds for (2). When $\mathbf{h}_1$ and $\mathbf{R}$ are chosen, then $\mathbf{h}_2$ is determined by means of

$$\mathbf{D}\mathbf{h}_2 = \mathbf{H} \tag{7}$$

where $\mathbf{D} = (\mathbf{I} + \mathbf{R})$ and $\mathbf{H} = -\mathbf{D}\mathbf{h}_1$. However, $(\mathbf{I} + \mathbf{R})$ may be a singular matrix; therefore $\mathbf{h}_2$ may not be uniquely determined by (7). The more general way of dealing with this problem is to introduce the concept of the reflexive generalized inverse of a matrix. Then (see Giacovazzo, 1980*c* for the background and applications to structure seminvariants)

$$\mathbf{h}_2 = \mathbf{D}^*\mathbf{H} + (\mathbf{I} - \mathbf{D}^*\mathbf{D})\mathbf{Z}, \tag{8}$$

where $\mathbf{D}^*$ is the reflexive generalized inverse of $\mathbf{D}$ and $\mathbf{Z}$ is a free vector in reciprocal space. When considering

only the space groups up to orthorhombic the calculations on the right-hand side of (4) are rather simple. In fact any $\mathbf{D} = [d_{ij}]$ is a matrix for which $d_{ij} = 0$ for $i \neq j$. Then $\mathbf{D}^* = [d^*_{ij}]$ is a matrix for which $d^*_{ij} = 0$ for $i \neq j$, $d^*_{ii} = 0$ if $d_{ii} = 0$, otherwise $d^*_{ii} = 1/d_{ii}$. As an example, consider the case

$$\mathbf{h}_1 = \begin{vmatrix} 1 \\ 2 \\ 3 \end{vmatrix}, \quad \mathbf{R} = \begin{vmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{vmatrix}.$$

Then,

$$\mathbf{H} = \begin{vmatrix} 0 \\ \bar{4} \\ 0 \end{vmatrix}, \quad \mathbf{D}^* = \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0{\cdot}5 & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

and

$$\mathbf{h}_2 = \begin{vmatrix} 0 \\ \bar{2} \\ 0 \end{vmatrix} + \begin{vmatrix} h \\ 0 \\ l \end{vmatrix} = \begin{vmatrix} h \\ \bar{2} \\ l \end{vmatrix},$$

where h and l are free indices. On assuming that the maximum values of the indices h and l are known, we are immediately able to define all the $\mathbf{h}_2$ vectors which form the quartets (2) with $\mathbf{h}_1$. The application of these considerations to point groups 2, m and 222 is immediate. A situation particularly favorable occurs in $mm2$. Let us denote

$$\mathbf{R}_1 = \mathbf{I}, \quad \mathbf{R}_2 = \begin{vmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}, \quad \mathbf{R}_3 = \begin{vmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{vmatrix},$$

$$\mathbf{R}_4 = \begin{vmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{vmatrix}.$$

Then the search for all the vectors $\mathbf{h}_2$ which form quartets such as (2) with a chosen $\mathbf{h}_1$ may be made merely by means of the rotation matrix $\mathbf{R}_4$. In fact if (8) is applied to $\mathbf{h}_1 = 123$, then:

(*a*) $\mathbf{h}_2 = hk\bar{3}$ for $\mathbf{R} = \mathbf{R}_4$,
(*b*) $\mathbf{h}_2 \equiv h\bar{2}\bar{3}$ for $\mathbf{R} = \mathbf{R}_2$,
(*c*) $\mathbf{h}_2 \equiv \bar{1}k\bar{3}$ for $\mathbf{R} = \mathbf{R}_3$,

where h and k are free indices in reciprocal space. As we see, the vectors $\mathbf{h}_2$ in (*b*) and (*c*) constitute subsets of that obtained *via* $\mathbf{R} = \mathbf{R}_4$.

It should be useful to note that less than five magnitudes may be contained in the first phasing shell of Φ. As an example, in $P2_1$,

$$\Psi = \varphi_{040} + \varphi_{040} + \varphi_{3\bar{4}8} + \varphi_{\bar{3}\bar{4}\bar{8}}$$

depends only on two cross magnitudes, R_{080} and R_{308}. In the symmetry class 2 this situation occurs only when $\mathbf{h}_1$ or $\mathbf{h}_2$ is a $0k0$ reflection. Owing to similar considerations, in the symmetry class m, Φ depends on two cross magnitudes when $\mathbf{h}_1$ or $\mathbf{h}_2$ is a $h0l$ reflection. Analogous situations may be found in the symmetry classes 222 and $mm2$.

We come now to the problem of identifying quartets which depend on more than three cross magnitudes. They are characterized by the following property (Giacovazzo, 1976): at least one of the cross vectors satisfies, for a given rotation matrix $\mathbf{R}$, the condition

$$\mathbf{h}(\mathbf{I} - \mathbf{R}) = 0, \quad \mathbf{R} \neq \mathbf{I}. \tag{9}$$

For example,

$$\Psi = \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3} - \varphi_{\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3}$$

depends on the three cross magnitudes $R_{\mathbf{h}_1+\mathbf{h}_2}$, $R_{\mathbf{h}_1+\mathbf{h}_3}$, $R_{\mathbf{h}_2+\mathbf{h}_3}$. If $(\mathbf{h}_1 + \mathbf{h}_2)\mathbf{R} = 0$, then

$$\begin{aligned} \Psi' &= \varphi_{\mathbf{h}_1\mathbf{R}} + \varphi_{\mathbf{h}_2\mathbf{R}} + \varphi_{\mathbf{h}_3} - \varphi_{\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3} \\ &= \Psi' - 2\pi(\mathbf{h}_1 + \mathbf{h}_2)\mathbf{T} \end{aligned}$$

is a quartet too, with cross magnitudes $R_{\mathbf{h}_1+\mathbf{h}_2}$, $R_{\mathbf{h}_1\mathbf{R}+\mathbf{h}_3}$, $R_{\mathbf{h}_2\mathbf{R}+\mathbf{h}_3}$. If no other special condition occurs, then Ψ depends on five cross magnitudes.

Let us apply these considerations to

$$\Psi = \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_1\mathbf{R}_p} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_2\mathbf{R}_p}, \tag{10}$$

which depends on

$$R_{\mathbf{h}_1(\mathbf{I}+\mathbf{R}_p)}, R_{\mathbf{h}_1+\mathbf{h}_2}, R_{\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2}.$$

Since $\mathbf{h}_1(\mathbf{I} + \mathbf{R}_p)$ satisfies (9) for $\mathbf{R} = \mathbf{R}_p$, the quartet

$$\Psi' = \varphi_{\mathbf{h}_1\mathbf{R}_p} + \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_2\mathbf{R}_p}$$

can be constructed. In this case, however, Ψ' coincides with Ψ. It may be concluded that in symmetry classes 2 and m all the quartets such as (10) depend on three cross magnitudes at the most. A different situation occurs in class 222, where the reflections $E_{\mathbf{h}_1+\mathbf{h}_2}$ and (or) $E_{\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2}$ can satisfy (9) by a rotation matrix $\mathbf{R}_q \neq \mathbf{R}_p$. As an example, suppose that $\mathbf{h} = \mathbf{h}_1\mathbf{R}_p + h_2$ satisfies (9) for $\mathbf{R} = \mathbf{R}_q \neq \mathbf{R}_p$. Then

$$\Psi' = \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_1\mathbf{R}_p\mathbf{R}_q} + \varphi_{\mathbf{h}_2\mathbf{R}_q} + \varphi_{\mathbf{h}_2\mathbf{R}_p}$$

may be constructed, whose cross vectors are $\mathbf{h}_1(\mathbf{I} + \mathbf{R}_p\mathbf{R}_q) = \mathbf{h}_1(\mathbf{I} + \mathbf{R}_i)$ where $\mathbf{R}_i = \mathbf{R}_p\mathbf{R}_q$, $\mathbf{h}_1 + \mathbf{h}_2\mathbf{R}_q$, $\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2$.

In a similar way, if $\mathbf{h} = \mathbf{h}_1 + \mathbf{h}_2$ satisfies (9) by $\mathbf{R} = \mathbf{R}_q \neq \mathbf{R}_p$, then

$$\Psi' = \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_1\mathbf{R}_p\mathbf{R}_q} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_2\mathbf{R}_p\mathbf{R}_q}$$

may be constructed whose cross vectors are $\mathbf{h}_1(\mathbf{I} + \mathbf{R}_p\mathbf{R}_q) = \mathbf{h}_1(\mathbf{I} + \mathbf{R}_i)$ where $\mathbf{R}_i = \mathbf{R}_p\mathbf{R}_q$, $\mathbf{h}_1 + \mathbf{h}_2$ and $\mathbf{h}_1\mathbf{R}_i + \mathbf{h}_2$.

In conclusion, in both cases Ψ depends on the five cross magnitudes

$$R_{\mathbf{h}_1(\mathbf{I}+\mathbf{R}_p)}, R_{\mathbf{h}_1+\mathbf{h}_2}, R_{\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2}, R_{\mathbf{h}_1(\mathbf{I}+\mathbf{R}_i)}, R_{\mathbf{h}_1\mathbf{R}_j+\mathbf{h}_2}, \tag{11}$$

where: (*a*) $\mathbf{R}_i = \mathbf{R}_p\mathbf{R}_q$; (*b*) $\mathbf{R}_j = \mathbf{R}_q$ if $\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2$ satisfies (9) for $\mathbf{R} = \mathbf{R}_q$ and $\mathbf{R}_j = \mathbf{R}_i$ if $\mathbf{h}_1 + \mathbf{h}_2$ satisfies (9) for $\mathbf{R} = \mathbf{R}_q$.

To give a numerical example denote

$$\mathbf{R}_2 = \begin{vmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{vmatrix}, \quad \mathbf{R}_3 = \begin{vmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{vmatrix},$$

$$\mathbf{R}_4 = \begin{vmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{vmatrix}.$$

Then, by means of $\mathbf{R}_p = \mathbf{R}_3$ the quartet

$$\begin{aligned} \Psi &= \varphi_{123} + \varphi_{\bar{1}2\bar{3}} + \varphi_{1\bar{2}5} + \varphi_{\bar{1}\bar{2}\bar{5}} \\ &= 2(\varphi_{123} + \varphi_{1\bar{2}5}) \end{aligned} \tag{12}$$

is constructed, with cross vectors (040), (208), (002). Since $\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2 = (002)$ satisfies (9) for $\mathbf{R}_q = \mathbf{R}_4$, then

$$\Psi' = \varphi_{123} + \varphi_{\bar{1}2\bar{3}} + \varphi_{\bar{1}2\bar{5}} + \varphi_{\bar{1}\bar{2}\bar{5}},$$

which depends, in accordance with (11), on R_{200}, R_{048}, R_{002}. A last observation is that in the point group 222, besides $\Psi_1 = 2(\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2}) - 2\pi(\mathbf{h}_1 + \mathbf{h}_2)\mathbf{T}_p$, $\Psi_2 = 2(\varphi_{\mathbf{h}_1} - \varphi_{\mathbf{h}_2}) - 2\pi(\mathbf{h}_1 - \mathbf{h}_2)\mathbf{T}_p$ may also be calculated. For example, besides (12),

$$\varphi_{123} + \varphi_{\bar{1}23} + \varphi_{1\bar{2}\bar{5}} + \varphi_{125} = 2(\varphi_{123} + \varphi_{125})$$

also exists, which depends on R_{040}, R_{202}, R_{008}, R_{200}, R_{042}. A consequence is that in the symmetry class 222 information about both $\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2}$ and $\varphi_{\mathbf{h}_1} - \varphi_{\mathbf{h}_2}$ may be achieved.

A more favorable symmetry class is $mm2$ because quartets such as (10) depend always on at least five cross magnitudes. As an example choose $\mathbf{h}_1 = (123)$ and $\mathbf{R}_p = \mathbf{R}_4$ (see notation at the beginning of this paragraph). We obtain

$$\Psi = \varphi_{123} + \varphi_{1\bar{2}3} + \varphi_{hk3} + \varphi_{\bar{h}\bar{k}\bar{3}}$$

whose cross vectors are (006), $(1 + h, 2 + k, 0)$, $(\bar{1} + h, \bar{2} + k, 0)$. Since (006) satisfies (9) for $\mathbf{R} = \mathbf{R}_2$ and $\mathbf{R} = \mathbf{R}_3$, the following quartets arise

$$\Psi^{\mathrm{i}} = \varphi_{\bar{1}23} + \varphi_{123} + \varphi_{hk\bar{3}} + \varphi_{\bar{h}\bar{k}\bar{3}},$$

$$\Psi^{\mathrm{ii}} = \varphi_{123} + \varphi_{123} + \varphi_{hk\bar{3}} + \varphi_{h\bar{k}\bar{3}},$$

whose cross vectors are (006), $(\bar{1} + h, 2 + k, 0)$, $(1 + h, \bar{2} + k, 0)$. In conclusion any quartet such as (9) with $\mathbf{R}_p = \mathbf{R}_4$ depends on the five cross magnitudes

$$R_{\mathbf{h}_1(\mathbf{I}+\mathbf{R}_4)}, R_{\mathbf{h}_1+\mathbf{h}_2}, R_{\mathbf{h}_1\mathbf{R}_4+\mathbf{h}_2}, R_{\mathbf{h}_1\mathbf{R}_2+\mathbf{h}_2}, R_{\mathbf{h}_1\mathbf{R}_3+\mathbf{h}_2}. \tag{13}$$

However, when $h = 1$ or $k = 2$ the cross reflection $E_{\bar{1}+h,\bar{2}+k,0}$ satisfies (9) by means of $\mathbf{R} = \mathbf{R}_2$ or $\mathbf{R} = \mathbf{R}_3$. Then the supplementary quartets

$$\Psi^{\mathrm{iii}} = \varphi_{123} + \varphi_{1\bar{2}3} + \varphi_{\bar{1}k\bar{3}} + \varphi_{\bar{1}\bar{k}\bar{3}}$$

or

$$\Psi^{\mathrm{iv}} = \varphi_{123} + \varphi_{123} + \varphi_{\bar{h}23} + \varphi_{\bar{h}\bar{2}\bar{3}}$$

arise which introduce the supplementary cross magnitude R_{206} or R_{046} respectively. The results can be summarized: in $mm2$ any quartet such as (10) depends on the five cross reflections (13) when $\mathbf{R}_p = \mathbf{R}_4$. When $\mathbf{R}_p = \mathbf{R}_2$ or $\mathbf{R}_p = \mathbf{R}_3$ the additional cross magnitude $R_{\mathbf{h}_1(\mathbf{I}+\mathbf{R}_p)}$ is to be added to (13).

4. Probabilistic formulae (in the exponential Bessel function form) estimating Φ

In accordance with § 3 we have calculated the joint probability distributions $P(R_1, R_2, \ldots, R_n, \varphi_1, \varphi_2, \ldots, \varphi_n)$ proper for each symmetry class. The method requires the calculation of the characteristic function of the distribution:

$$C(\rho_1, \ldots, \rho_n, \psi_1, \ldots, \psi_n) = \exp\left[\sum_{\nu=2}^{\infty} S_\nu / t^{\nu/2}\right],$$

where ρ_j and ψ_j are carrying variables associated with R_j and φ_j, and the S_ν are functions which depend on the standardized cumulants of the distribution.

We shall use two different methods to derive the probability densities. The first obtains them by calculating the Fourier transform of the Gram–Charlier expansion of the characteristic function (Klug, 1958): conclusive formulae are described in § 5. The second method directly derives the probability densities by calculating the Fourier transform of the characteristic function: the corresponding formulae are here described. The reader will find exhaustive information about both methods in earlier papers (Giacovazzo, 1977*b*,*c*).

In both methods the standardized cumulants of low order have to be calculated. The value of any cumulant depends on the actual space group, on the statistical weights of the reflections involved in the cumulant and on the mutual correlation among the indices of those reflections (Giacovazzo, 1974*a*,*b*). The exact estimation of the cumulants may be too time consuming. On the other hand, our previous experience suggests that the effects of the statistical weights of the reflections and the mutual correlation among their indices can be neglected without compromising the estimation of Φ too much. We have followed this strategy in our mathematical approach.

In the symmetry classes 2 and m fix the five numbers R_i, $i = 1, \ldots, 5$ such that

$$R_1 = R_{\mathbf{h}_1}; \quad R_2 = R_{\mathbf{h}_2}; \quad R_3 = R_{\mathbf{h}_1(\mathbf{I}+\mathbf{R}_p)};$$
$$R_4 = R_{\mathbf{h}_1+\mathbf{h}_2}; \quad R_5 = R_{\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2}.$$

$\mathbf{R}_p$ represents the non-identity rotation matrix. Then the conditional probability distribution $P(\Phi | R_i, i = 1, \ldots,$

5) is given by

$$P(\Phi|\ldots) \simeq \frac{1}{L}\exp\left\{\frac{R_1^2R_2^2}{4N} \times [\,w_{1,2} - 2w_3^2 - w_4^2 - w_5^2\,]\cos 2\Phi\right\} \times I_0(X)\cosh\left(w_4\frac{R_1R_2R_4}{\sqrt{N}}\cos\Phi\right) \times \cosh\left(w_5\frac{R_1R_2R_5}{\sqrt{N}}\cos\Phi\right),$$

where

$$X = \frac{w_3R_3}{\sqrt{N}}\{R_1^4 + R_2^4 + 2R_1^2R_2^2\cos 2\Phi\}^{1/2}.$$

I_0 is the modified Bessel function of order zero and L is a normalization factor obtained by numerical techniques. The weight w_j is assumed to be 1 unless the corresponding R_j is not in the measurements. $w_{1,2}$ is assumed always to be unity. Hauptman & Green (1978) suggested a similar formula with different weights, which holds when Φ is a structure seminvariant and when all three cross vectors are in the measurements.

In the symmetry class 222 fix the seven numbers R_i, $i = 1, \ldots, 7$ such that

$$R_1 = R_{\mathbf{h}_1};\quad R_2 = R_{\mathbf{h}_2};\quad R_3 = R_{\mathbf{h}_1(\mathbf{I}+\mathbf{R}_p)};$$
$$R_4 = R_{\mathbf{h}_1+\mathbf{h}_2};\quad R_5 = R_{\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2};$$
$$R_6 = R_{\mathbf{h}_1(\mathbf{I}+\mathbf{R}_l)};\quad R_7 = R_{\mathbf{h}_1+\mathbf{h}_2\mathbf{R}_j};$$

where $\mathbf{R}_p$, $\mathbf{R}_l$, $\mathbf{R}_j$ have the meaning defined in § 3. Then the conditional probability distribution $P(\Phi|R_i,\ i = 1, \ldots, 7)$ is given by

$$P(\Phi|\ldots) \simeq \frac{1}{L}\exp\left\{\frac{R_1^2R_2^2}{4N}[\,w_{1,2}\cos S_p - 2w_3^2\cos S_p - w_4^2\cos(2a_4) - w_5^2\cos(2a_5) - 2w_6^2\cos S_r - w_7^2\cos(2a_7)\,]\cos 2\Phi\right\} \times I_0(X_3)\cosh\left[w_4\frac{R_1R_2R_4}{\sqrt{N}}\cos(\Phi + a_4)\right] \times \cosh\left[w_5\frac{R_1R_2R_5}{\sqrt{N}}\cos(\Phi + a_5)\right] \times I_0(X_6)\cosh\left[w_7\frac{R_1R_2R_7}{\sqrt{N}}\cos(\Phi + a_7)\right],$$

where

$$X_3 = \frac{w_3R_3}{\sqrt{N}}[R_1^4 + R_2^4 + 2R_1^2R_2^2\cos(2\Phi - S_p)]^{1/2},$$

$$X_6 = \frac{w_6R_6}{\sqrt{N}}[R_1^4 + R_2^4 + 2R_1^2R_2^2\cos(2\Phi - S_r)]^{1/2},$$

$$S_p = 2\pi(\mathbf{h}_1 + \mathbf{h}_2)\mathbf{T}_p,$$
$$S_r = 2\pi(\mathbf{h}_1 + \mathbf{h}_2)(\mathbf{T}_p + \mathbf{T}_q).$$

E_4, E_5, E_7 are centrosymmetric reflections and a_4, a_5, a_7 symbolize any one of the two permitted phase values of φ_4, φ_5, φ_7 respectively. $w_{1,2}$ is assumed (Giacovazzo, 1976, Appendix *A*) to be 1 if $\cos S_p = \cos S_r$, otherwise $w_{1,2} = 0$. The condition $w_{1,2} = 0$ occurs when one of the cross reflections corresponds to a space-group extinction.

The weight w_i is assumed to be 1 if R_i is in the measurements otherwise $w_i = 0$.

In the symmetry class *mm*2 fix the eight numbers $R_i = 1, \ldots, 8$ such that

$$R_1 = R_{\mathbf{h}_1};\quad R_2 = R_{\mathbf{h}_2};\quad R_3 = R_{\mathbf{h}_1(\mathbf{I}+\mathbf{R}_4)};$$
$$R_4 = R_{\mathbf{h}_1+\mathbf{h}_2};\quad R_5 = R_{\mathbf{h}_1\mathbf{R}_4+\mathbf{h}_2};\quad R_6 = R_{\mathbf{h}_1(\mathbf{I}+\mathbf{R}_9)};$$
$$R_7 = R_{\mathbf{h}_1\mathbf{R}_2+\mathbf{h}_2};\quad R_8 = R_{\mathbf{h}_1\mathbf{R}_3+\mathbf{h}_2};$$

where (see § 3) $\mathbf{R}_q = \mathbf{R}_2$ or $\mathbf{R}_q = \mathbf{R}_3$ according to whether quartets Ψ can be found by means of the rotation matrices $\mathbf{R}_2$ or $\mathbf{R}_3$. Then the conditional probability distribution $P(\Phi|R_i,\ i = 1, \ldots, 8)$ is given by

$$P(\Phi|\ldots) \simeq \frac{1}{L}\exp\left\{\frac{R_1^2R_2^2}{4N}[\,w_{1,2}\cos S_p - 2w_3^2\cos S_p - w_4^2 - w_5^2 - 2w_6^2\cos S_q - w_7^2 - w_8^2\,]\cos 2\Phi\right\} \times I_0(X_3)\cosh\left(w_4\frac{R_1R_2R_4}{\sqrt{N}}\cos\Phi\right) \times \cosh\left(w_5\frac{R_1R_2R_5}{\sqrt{N}}\cos\Phi\right) \times I_0(X_6)\cosh\left(w_7\frac{R_1R_2R_7}{\sqrt{N}}\cos\Phi\right) \times \cosh\left(w_8\frac{R_1R_2R_8}{\sqrt{N}}\cos\Phi\right),$$

where $p = 4$ and

$$X_3 = \frac{w_3R_3}{\sqrt{N}}[R_1^4 + R_2^4 + 2R_1^2R_2^2\cos(2\Phi - S_p)]^{1/2},$$

$$X_6 = \frac{w_6R_6}{\sqrt{N}}[R_1^4 + R_2^4 + 2R_1^2R_2^2\cos(2\Phi - S_q)]^{1/2},$$

$$S_p = 2\pi(\mathbf{h}_1 + \mathbf{h}_2)\mathbf{T}_4,$$
$$S_q = 2\pi(\mathbf{h}_1 + \mathbf{h}_2)\mathbf{T}_q.$$

$w_{1,2}$ is assumed to be 1 if $\cos S_p = \cos S_q$, otherwise $w_{1.2} = 0$. If the first phasing shell of Φ contains R_6 and R_6 is in the measurements, then $w_6 = 1$; otherwise $w_6 = 0$. The weight w_i, $i \neq 6$ is assumed to be 1 unless R_i is not in the measurements.

We note now that in the symmetry classes 2, m and $mm2$ the permitted phase values for the centrosymmetric reflections are always 0 or π. That suggests the following general formula:

$$P(\Phi|\ldots) \simeq \frac{1}{L}\exp\left\{\frac{R_1^2R_2^2}{4N}\left[w_{1,2}\cos S_p - 2w_3^2\cos S_p - w_4^2\cos(2a_4) - w_5^2\cos(2a_5) - 2w_6^2\cos S_r - w_7^2\cos(2a_7) - w_8^2\cos(2a_8)\right]\cos 2\Phi\right\} \times I_0(X_3)\cosh\left[w_4\frac{R_1R_2R_4}{\sqrt{N}}\cos(\Phi + a_4)\right] \times \cosh\left[w_5\frac{R_1R_2R_5}{\sqrt{N}}\cos(\Phi + a_5)\right] \times I_0(X_6)\cosh\left[w_7\frac{R_1R_2R_7}{\sqrt{N}}\cos(\Phi + a_7)\right] \times \cosh\left[w_8\frac{R_1R_2R_8}{\sqrt{N}}\cos(\Phi + a_8)\right]. \quad (14)$$

Equation (14) holds in all the non-centrosymmetric space groups up to orthorhombic provided: (*a*) the w_i corresponding to the reflections which are not in the phasing shell of Φ are assumed to be zero; (*b*) the meaning of S_p, S_r, w_i, ... assumes the meaning above defined for each symmetry class.

The mode of the distribution $P(\Phi|\ldots)$, the expected value of Φ and its reliability may be calculated by numerical techniques. A measure of reliability is the variance, calculated by

$$\int_0^{\pi/2} P(\Phi|\ldots)(\Phi - \langle\Phi\rangle^2)\,\mathrm{d}\Phi.$$

The limits $(0, \pi/2)$ of the integral are due to the unsolvable ambiguity among $\pm\Phi$, $\pi \pm \Phi$.

5. Exponential probabilistic formulae estimating Φ

If the Gram–Charlier expansion of the characteristic function is used, we obtain for Φ the following conditional probability distribution

$$P(\Phi|\ldots) \simeq \frac{1}{2\pi I_0(G)}\exp\left[G\cos 2\Phi\right], \quad (15)$$

where $G = A/(1 + B)$. The expressions for A and B for the various point groups are defined below.

(*a*) In point groups 2 and m:

$$A = \frac{R_1^2R_2^2}{4N}\left(w_{1,2} + 2w_3^2\varepsilon_3 + w_4^2\varepsilon_4 + w_5^2\varepsilon_5\right),$$
$$B \simeq \{w_4^2\varepsilon_1\varepsilon_2\varepsilon_4 + w_5^2\varepsilon_1\varepsilon_2\varepsilon_5 + \tfrac{1}{4}w_3^2\,[L_4(E_1) + L_4(E_2)]\}/2N,$$

where

$$L_4(E) = E^4 - 4E^2 + 2.$$

(*b*) In 222:

$$A = \frac{R_1^2R_2^2}{4N}\left[w_{1,2}\cos S_p + 2w_3^2\varepsilon_3\cos S_p + w_4^2\varepsilon_4\cos 2a_4 + w_5^2\varepsilon_5\cos 2a_5 + 2w_6^2\varepsilon_6\cos S_r + w_7^2\varepsilon_7\cos 2a_7\right],$$
$$B = \{w_4^2\varepsilon_1\varepsilon_2\varepsilon_4 + w_5^2\varepsilon_1\varepsilon_2\varepsilon_5 + \tfrac{1}{4}w_3^2\varepsilon_3[L_4(E_1) + L_4(E_2)] + \tfrac{1}{4}w_6^2\varepsilon_6[L_4(E_1) + L_4(E_2)] + w_7^2\varepsilon_1\varepsilon_2\varepsilon_7\}/2N.$$

If E_1 or E_2 are centrosymmetric reflections, $L_4(x)$ may be replaced by the Hermite polynomial of order four $H_4(x) = x^4 - 6x^2 + 3$.

(*c*) In $mm2$:

$$A = \frac{R_1^2R_2^2}{4N}\left\{w_{1,2}\cos S_p + 2w_3^2\varepsilon_3\cos S_p + w_4^2\varepsilon_4 + w_5^2\varepsilon_5 + 2w_6^2\varepsilon_6\cos S_q + w_7^2\varepsilon_7 + w_8^2\varepsilon_8\right\},$$
$$B = \{w_4^2\varepsilon_1\varepsilon_2\varepsilon_4 + w_5^2\varepsilon_1\varepsilon_2\varepsilon_5 + \tfrac{1}{4}w_3^2\varepsilon_3[L_4(E_1) + L_4(E_2)] + \tfrac{1}{4}w_6^2\varepsilon_6[L_4(E_1) + L_4(E_2)] + w_7^2\varepsilon_1\varepsilon_2\varepsilon_7 + w_8^2\varepsilon_1\varepsilon_2\varepsilon_8\}/2N.$$

In (*a*), (*b*), (*c*) the symbols have the meaning defined in § 4 for the various point groups. The same considerations which led us to suggest the general formula (14) suggest now the following general expressions for A and B:

$$A = \frac{R_1^2R_2^2}{4N}\left[w_{1,2}\cos S_p + 2w_3^2\varepsilon_3\cos S_p + w_4^2\varepsilon_4\cos 2a_4 + w_5^2\varepsilon_5\cos 2a_5 + 2w_6^2\varepsilon_6\cos S_r + w_7^2\varepsilon_7\cos 2a_7 + w_8^2\varepsilon_8\cos 2a_8\right],$$
$$B = \{w_4^2\varepsilon_1\varepsilon_2\varepsilon_4 + w_5^2\varepsilon_1\varepsilon_2\varepsilon_5 + \tfrac{1}{4}w_3^2\varepsilon_3[L_4(E_1) + L_4(E_2)] + \tfrac{1}{4}w_6^2\varepsilon_6[L_4(E_1) + L_4(E_2)] + w_7^2\varepsilon_1\varepsilon_2\varepsilon_7 + w_8^2\varepsilon_1\varepsilon_2\varepsilon_8\}/2N.$$

Equation (15) is a bimodal Von Mises type angular distribution. The modes are in 0 or π if G is positive, in $\pm\pi/2$ if G is negative.

6. Practical applications

A computer program has been implemented which estimates the various Φ's in all the non-centrosymmetric space groups up to orthorhombic (except $P1$) *via* their complete first phasing shell. The method was tested on five known structures covering the symmetry classes 2, 222, $mm2$. Table 1 shows the references and the most relevant features of the test structures whose

results are discussed in this paper. For each structure we used the first 100 reflections, arranged in decreasing order of $|E|$, to form the two-phase variants and seminvariants. Therefore, in Table 1, E_{min} is the $|E|$ value corresponding to the 100th reflection.

The use of the exponential Bessel formulae (§ 4) requires more computing time than the pure exponential functions (§ 5); however they proved slightly more accurate when enantiomorph-sensitive variants or seminvariants were estimated. Therefore, in this section we only refer to the application of the exponential Bessel functions.

For HEPTA ($N = 120$, $P2_1$) we have calculated 279 variants or seminvariants. The 15 of them which are estimated as enantiomorph sensitive (*i.e.* with $\Phi_m \geq 30°$) with the smallest variance are shown in Table 2. Their e.s.d.'s lie in the range 25–26°.

Table 1. *Abbreviations, references, space groups, formulae and minimum values of $|E|$ for the reflections forming the two-phase variants and seminvariants, for the five test structures*

	Reference	Space group	Formula	Z	E_{min}
HEPTA	Beurskens, Beurskens & van den Hark (1976)	$P2_1$	$C_{30}H_{18}$	4	2·02
RIBO	James & Stevens (1977)	$P2_1$	$C_{13}H_{18}O_9$	4	2·05
TOXE	Cerrini, Fedeli, Gavuzzo & Mazza (1975)	$P2_12_12_1$	$C_{21}H_{35}O_5$	4	1·98
KARLE	Karle, Karle & Estlin (1967)	$P2_12_12_1$	$C_{12}H_{13}NO_4$	4	1·50
AZET	Colens, Declercq, Germain, Putzeys & van Meerssche (1974)	$Pca2_1$	$C_{21}H_{16}ClNO$	8	1·80

Table 2. *HEPTA: indices, $|E|$'s, true values of $\Phi(\Phi_t)$ reduced to the first quadrant of the trigonometric circle and corresponding mode values (Φ_m) for the two-phase variants and seminvariants which are estimated enantiomorph sensitive*

The mode is calculated according to the exponential Bessel functions. The Φ's are arranged in decreasing reliability.

$\mathbf{h}_1$	$E_{\mathbf{h}_1}$	$\mathbf{h}_2$	$E_{\mathbf{h}_2}$	Φ_t (°)	Φ_m (°)
040	3·64	12,4,1	2·41	78	40
040	3·64	646̄	2·15	89	50
040	3·64	141	2·07	70	30
337	2·91	836̄	2·74	12	90
10,3,2	2·18	632̄	2·16	58	90
231	2·23	536	2·13	56	90
836̄	2·74	737̄	2·24	18	90
337	2·91	737̄	2·24	30	90
296̄	2·76	691	2·16	6	90
836̄	2·74	536	2·13	81	90
330	2·24	536	2·13	83	90
636̄	2·23	632̄	2·16	87	90
11,3,1	2·66	737̄	2·24	79	90
737̄	2·24	536	2·13	81	90
3,11,1̄	2·24	3,11,1	2·06	27	90

For RIBO ($N = 88$, $P2_1$) 261 variants or seminvariants were calculated. The 15 of them which are estimated enantiomorph sensitive with the smallest variance are in Table 3. Their e.s.d.'s are in the range 26–27°.

For AZET ($N = 192$, $Pca2_1$) we have calculated 403 variants or seminvariants. The 15 of them which are estimated enantiomorph sensitive with the smallest variance are shown in Table 4. The corresponding e.s.d.'s are in the range 26–27°.

The number of two-phase variants and seminvariants estimated near 0 or π is much higher than the number of enantiomorph-sensitive pairs. In addition their variance can be smaller, so that their estimation may be more accurate. In HEPTA 20 pairs of phases estimated 0 or π have calculated e.s.d.'s between 14 and 20°: their experimental average error (as a difference between Φ_m^0 and Φ_t^0) is 12°. In RIBO, 20 pairs estimated 0 or π have a calculated e.s.d. between 23 and 25° with an experimental average error of 30°. In AZET 20 pairs of phases are estimated 0 or π with a calculated e.s.d. between 24 and 25°, and an experimental average error of 20°.

In the structures which crystallize in the space group $P2_12_12_1$ the definition of the enantiomorph usually is not a difficult problem because numerous phases can assume values near $\pm\pi/2$ merely by application of triplet relations. Therefore the quality of the information provided by the two-phase variants or seminvariants should be considered in the general terms described in § 2 rather than only with respect to the enantiomorph definition. We estimated for KARLE and TOXE 2336 and 1262 variants or seminvariants respectively. The efficiency of our probabilistic approach may be checked by comparing the true values of the 40 pairs of phases estimated with the smallest variance with the corresponding mode values. We have found for KARLE an average error of 17° and for TOXE an average error of 27°. We also applied the Hauptman & Green [1978; equation (5.1)] formula valid in $P2_1$ to HEPTA and RIBO. This formula does not give better results than those presented in this paper, and often overestimates the reliabilities of the phase relations. So one should be careful when applying this formula.

Execution time for our program is about 30 s per crystal structure such as HEPTA, RIBO and AZET on a Univac 1110 computer, about 1·20 min for TOXE and KARLE, which is reasonably fast considering the nature of the problem.

7. Conclusions

The representations theory enabled us to estimate two-phase variants and seminvariants Φ *via* the first phasing shells of very special quartets estimating 2Φ.

Table 3. *RIBO: indices, $|E|$'s true values of $\Phi(\Phi_t)$ reduced to the first quadrant of the trigonometric circle and corresponding mode values (Φ_m) for the two-phase variants and seminvariants which are estimated enantiomorph sensitive*

The mode is calculated according to the exponential Bessel functions. The Φ's are arranged in decreasing reliability.

$\mathbf{h}_1$	$E_{\mathbf{h}_1}$	$\mathbf{h}_2$	$E_{\mathbf{h}_2}$	Φ_t (°)	Φ_m (°)
48$\bar{5}$	2·58	98$\bar{1}$	2·45	57	90
98$\bar{1}$	2·45	78$\bar{2}$	2·27	79	90
16,2,$\bar{3}$	2·85	11,2,$\bar{6}$	2·10	61	90
12,7,0	3·06	176	2·39	85	50
16,2,$\bar{3}$	2·85	5,2,$\overline{10}$	2·07	36	90
246	3·22	14,4,$\bar{2}$	2·05	23	40
246	3·22	16,4,$\bar{2}$	2·18	60	90
18$\bar{6}$	2·70	78$\bar{2}$	2·27	74	90
12,3,0	2·13	13$\bar{8}$	2·06	41	90
1,2,$\overline{10}$	2·19	20,2,$\bar{7}$	2·13	69	90
10,3,$\bar{7}$	2·11	735	2·11	76	90
48$\bar{5}$	2·58	5,8,$\overline{10}$	2·08	76	90
8,3,$\overline{10}$	2·23	63$\bar{8}$	2·09	15	90
735	2·11	23,3,$\bar{3}$	2·08	26	90
10,3,$\bar{7}$	2·11	23,3,$\bar{3}$	2·08	78	90

Table 4. *AZET: indices, $|E|$'s, true values of $\Phi(\Phi_t)$ reduced to the first quadrant of the trigonometric circle and corresponding mode values (Φ_m) for the two-phase variants or seminvariants which are estimated enantiomorph sensitive*

The mode is calculated according to the exponential Bessel functions. The Φ's are arranged in decreasing reliability.

$\mathbf{h}_1$	$E_{\mathbf{h}_1}$	$\mathbf{h}_2$	$E_{\mathbf{h}_2}$	Φ_t (°)	Φ_m (°)
254	2·83	14,5,4	2·75	36	90
14,5,4	2·75	534	2·07	20	90
15,3,1	2·55	13,3,1	2·09	75	90
134	2·14	534	2·07	74	90
422	2·17	452	1·95	84	90
254	2·83	364	1·86	54	90
14,5,4	2·75	364	1·86	90	90
254	2·83	134	2·14	90	90
14,5,4	2·75	934	2·33	60	90
15,3,1	2·55	18,2,1	1·82	36	90
11,3,2	2·30	622	1·83	60	90
13,3,1	2·09	711	1·86	90	90
31,3,1	2·14	13,3,1	2·09	62	90
422	2·17	15,3,2	1·88	68	90
422	2·17	27,1,2	1·99	76	90

The probabilistic formulae described in this paper seem able to give useful enantiomorph-sensitive and -insensitive information which may be useful in the phase-determination processes. It may be guessed that, owing to the very special nature of the quartets belonging to the first representation of 2Φ, the estimation of Φ is rather sensitive to the structural regularities. Thus for a sufficiently large number of quartets with the same value of the variance a reliable measure of the e.s.d. is obtained. But in the group we have a great number of well estimated and a number of badly estimated phases in such a way that the averaged experimental e.s.d. is almost equal to the theoretical deviation. The situation is very similar to that described by Busetta *et al.* (1980) for negative quartets.

What are the prospects of these phase relations in direct procedures? Giacovazzo (1980*c*) showed that when Φ is a structure seminvariant, the information contained in the first phasing shell of Φ may be associated with that provided by the quartets estimating 2Φ. In particular the concept of a generalized first representation was introduced which is the collection (in the non-centrosymmetric space groups) of the quartets estimating Φ and 2Φ. We shall show in a later paper how a two-phase seminvariant Φ may be estimated *via* its generalized first representation. Our first results suggest that a two-phase seminvariant can be estimated with higher accuracy *via* its generalized first representation than *via* the mere first representation (Giacovazzo, Spagna, Vicković & Viterbo, 1979). That should allow their active use after the first stages of the phase determination process.

As regards the two-phase variants, the accuracy of the present estimates are not so high as for the two-phase seminvariants: therefore their active use in direct procedures must be considered carefully, whereas they may be successfully used as a figure of merit. However, the estimates of the two-phase variants can be remarkably improved when joint probability distributions containing supplementary *a priori* information are used. We are now devoting our efforts to developing this new probabilistic procedure: our first tests in $P2_1$ are very encouraging.

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Measurement of X-ray *Pendellösung* Intensity Beats in Diffracted White Radiation from Silicon Wafers

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(*Received* 21 *March* 1980; *accepted* 8 *July* 1980)

Abstract

Pendellösung intensity beats of white radiation diffracted from parallel-sided single-crystal wafers of silicon were measured by a solid-state detector. After a few corrections, the extremum positions in the beat were measured to evaluate the atomic scattering factors for various reflections. The scattering factor shows a dependence on wavelength, λ, which can be interpreted by the anomalous dispersion term, f', as calculated by Cromer [*Acta Cryst.* (1965), **18**, 17–23]. The obtained values of the atomic scattering factor expressed as linear functions of wavelength are listed with those at $\lambda = 0{\cdot}5594$ Å for comparison with the data so far obtained with Ag $K\alpha_1$ and wedge crystals. The values for 111 and 220 reflections in the present experiment, 10·59 and 8·40, were almost the same as Tanemura & Kato's [*Acta Cryst.* (1972), A**28**, 69–80], $10{\cdot}66_4$ and $8{\cdot}46_3$, respectively.

1. Introduction

A striking example of the dynamical diffraction effect of X-rays is the *Pendellösung* fringe appearing in the topographic image of perfect wedge crystals. Kato & Lang (1959) first observed the fringes for silicon and quartz using characteristic radiation. The fringes are produced by the interaction between two wave fields with slightly different wave vectors in the crystal, and the fringe spacing can be expressed as a function of the structure factor of the crystal. Many workers have measured the fringe spacing in topographs for the purpose of obtaining the structure factors of silicon (Hattori, Kuriyama, Katagawa & Kato, 1965; Hart, 1966; Hart & Milne, 1969; Tanemura & Kato, 1972), germanium (Batterman & Patel, 1968; Persson, Zielińska-Rohozińska & Gerward, 1970) and others (Yamamoto, Homma & Kato, 1968; Yasuda, Hondoh & Higashi, 1979). This method requires accurate collimation of characteristic X-rays and precise shaping of the wedge specimen.

The *Pendellösung* fringes have also been observed in the topographic images of white radiation (Hashimoto, 1965; Kozaki, Ohkawa & Hashimoto, 1968; Aristov, Shmytko & Shulakov, 1977*a*,*b*). These fringes are apparently produced by the change in extinction distance with the wavelength of diffracted X-rays. Aristov *et al.* (1977*a*,*b*) tried to measure the atomic scattering factors of silicon and germanium using white X-ray topographs from parallel-sided and wedge-shaped specimens. It seems rather difficult in this case to determine the accurate value of the wavelength corresponding to the position on the topographic film.

In the present experiment an attempt is made to measure the *Pendellösung* intensity beat of white radiation directly with a solid-state detector. X-ray intensities in *hkl* Laue spots from silicon single-crystal wafers are successively measured at different Bragg angles. One observes the clear *Pendellösung* intensity beat following the variation in wavelength. The values of the atomic scattering factor of silicon are obtained with their wavelength dependence for various reflections by measuring the extremum positions in the intensity beats. Measured values and their wavelength dependence are discussed and compared with the previous data from topographic methods (Hattori *et al.*,

0567-7394/80/061025-06$01.00