a simple numerical method. Any combination of **k** and **k**′ implies some q value by energy conservation, and the distribution of crystallite orientations means that if the vectors **κ**, **τ** and **q** can form a triangle then there are some crystal grains which can produce phonon scattering. For a single crystal, the restriction of the fixed crystal orientation means that the allowed (**k**,**k**′) values will not necessarily be represented by points on the grid which we use. In addition, a study of TDS in a single crystal requires a knowledge of the resolution function of the spectrometer.

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Progress in Representations Theory. The Concept of Generalized Representations

BY CARMELO GIACOVAZZO

Istituto di Mineralogia, Palazzo Ateneo, Università, 70121 Bari, Italy

(*Received* 9 *January* 1980; *accepted* 18 *February* 1980)

Abstract

The concept of generalized representation for structure seminvariants is introduced. When a structure seminvariant is estimated *via* a generalized representation an amount of *a priori* information can be exploited larger than that accessible *via* the mere representation.

1. Introduction*

Hauptman (1975) first suggested that a s.i. or a s.s. can be estimated with increasing reliability *via* a sequence of sets of diffraction magnitudes (sequence of nested neighbourhoods) each contained within the succeeding one. Independently, Giacovazzo (1975) had already applied the idea to the one-phase s.s.'s in $P\bar{1}$, whose estimation was performed *via* the magnitudes in their second neighbourhoods. Hauptman (1976) described heuristic methods of finding sequences of nested neighbourhoods for certain s.i.'s or s.s.'s.

A more general method for estimating s.s.'s was described by Giacovazzo (1977) (from now on, paper I). For any s.s. Φ, the method arranges in a general way the set of reflections in a sequence of subsets whose order is that of the expected effectiveness (in the statistical sense) for the estimation of Φ. These subsets do not coincide in general with the corresponding nested-neighbourhood sequence given by Hauptman and were called phasing shells in order to stress this difference. Giacovazzo's method introduces the idea that any s.i. or s.s. Φ can be represented by one or

* Symbols and abbreviations are defined in the Appendix.

0567-7394/80/040704-08$01.00

more sets $\{\Psi\}$ of s.i.'s Ψ whose values are related to Φ by constants which arise because of translational symmetry. If the Ψ's are evaluated then Φ is evaluated too. Any set $\{\Psi\}$ is called a representation of Φ.

A general comparison between neighbourhood and representation concepts has been made (Giacovazzo, 1980*a*; from now on, paper II). New theoretical aspects of the representation theory were there presented. In particular: (*a*) some algebraic properties of the s.s.'s of first and of second rank are described which make practical application easier and the probabilistic estimations of the s.s.'s more reliable; (*b*) the concepts of generalized first representation and of generalized first phasing shell are introduced which enable one, in favourable cases, to exploit new information into probabilistic calculations. In the present paper we introduce the concept of generalized upper representations and apply it to the probabilistic estimation of the s.s.'s of first rank.

It was recognized in paper II that the concept of generalized first representation is of minor importance in the procedures for the estimation of the s.i.'s. Therefore in this paper no attempt to apply the concept of generalized representations to s.i.'s is made.

In order to make the reading of this paper easier, we recall in § 2 some basic definitions in representation theory. In §§ 3 and 4 the generalized representations of the one-phase s.s.'s of first rank are defined. The same is done in § § 5 and 6 for the two-phase and the three-phase s.s.'s of first rank. The definition of the generalized representations for s.s.'s of higher order is strictly recursive and does not present any difficulty.

2. Some basic definitions in representations theory

Let

$$\Phi = A_1\varphi_{\mathbf{h}_1} + A_2\varphi_{\mathbf{h}_2} + \ldots + A_n\varphi_{\mathbf{h}_n} \quad (1)$$

be the general expression for a s.s.

2.1. *The rank of the s.s. Φ*

If at least one phase $\varphi_{\mathbf{h}}$ and two symmetry operators $\mathbf{C}_p$ and $\mathbf{C}_q$ exist ($R_{\mathbf{h}}$ may or may not be experimentally measured) such that

$$\begin{aligned}\Psi_1 &= \Phi' + \varphi_{\mathbf{hR}_p} - \varphi_{\mathbf{hR}_q}\\ &= A_1\varphi_{\mathbf{h}_1\mathbf{R}_s} + A_2\varphi_{\mathbf{h}_2\mathbf{R}_t} + \ldots + A_n\varphi_{\mathbf{h}_n\mathbf{R}_v} + \varphi_{\mathbf{hR}_p} - \varphi_{\mathbf{hR}_q}\end{aligned} \quad (2)$$

is a s.i., then Φ is a s.s. of first rank. If Φ is a s.s. for which (2) does not hold, then two phases $\varphi_{\mathbf{h}}$ and $\varphi_{\mathbf{l}}$ four symmetry operators $\mathbf{C}_p$, $\mathbf{C}_q$, $\mathbf{C}_i$, $\mathbf{C}_j$ exist ($R_{\mathbf{h}}$ and $R_{\mathbf{l}}$ may or may not be experimentally measured) such that

$$\begin{aligned}\Psi_1 &= \Phi' + \varphi_{\mathbf{hR}_p} - \varphi_{\mathbf{hR}_q} + \varphi_{\mathbf{lR}_i} - \varphi_{\mathbf{lR}_j}\\ &= A_1\varphi_{\mathbf{h}_1\mathbf{R}_s} + \ldots + A_n\varphi_{\mathbf{h}_n R_v} + \varphi_{\mathbf{hR}_p} - \varphi_{\mathbf{hR}_q} + \varphi_{\mathbf{lR}_i}\\ &\quad - \varphi_{\mathbf{lR}_j}\end{aligned} \quad (3)$$

is a s.i. In this case Φ is said to be a s.s. of the second rank.

Thus, $\Phi = \varphi_{246}$ is a s.s. of the first rank in $P\bar{1}$, of the second rank in $P2_12_12_1$.

2.2. *The first representation of the s.s. Φ*

The first representation of Φ is the collection of the s.i.'s Ψ_1 as given by (2) or (3) according to whether Φ is a s.s. of the first or of the second rank. In both cases the first representation of Φ will be denoted by $\{\Psi\}_1$. Since

$$\varphi_{\mathbf{hR}} = \varphi_{\mathbf{h}} - 2\pi\mathbf{hT}, \quad (4)$$

any Ψ_1 differs from Φ by a constant which arises because of the translational symmetry.

2.3. *The first phasing shell*

The collection of the $|E|$ magnitudes which are basis or cross magnitudes of at least one s.i. $\Psi_1 \in \{\Psi\}_1$ is the first phasing shell of Φ and is denoted by $\{B\}_1$.

2.4. *The upper representations of Φ*

For any Ψ_1 belonging to $\{\Psi\}_1$ we construct the s.i.'s

$$\Psi_2 = \Psi_1 + \varphi_{\mathbf{k}} - \varphi_{\mathbf{k}},$$

where $\mathbf{k}$ is a free vector. The collection of the s.i. Ψ_2's is denoted by $\{\Psi\}_2$ and is said to be the second representation of Φ. Likewise, the collections of the s.i.'s $\Psi_3 = \Psi_2 + \varphi_{\mathbf{l}} - \varphi_{\mathbf{l}}$, where $\mathbf{l}$ is a free vector, is the third representation of Φ. The procedure and the definitions are recursive.

2.5. *The upper phasing shells of Φ*

The collection of the $|E|$ magnitudes which are basis or cross magnitudes of at least one s.i. $\Psi_n \in \{\Psi\}_n$ is the nth phasing shell of Φ and is denoted by $\{B\}_n$.

A general procedure which is able to obtain $\{B\}_n$ for any Φ is described in paper II.

2.6. *The generalized first phasing shell of Φ*

Let Φ, Φ', Φ'', ... be a set of s.s.'s for which one or more sequences

$$\Phi = \Phi' + \Phi'' + \ldots$$

can be found. The set theoretic union

$$\{B\}_1^g = \{B\}_1 \cup \{B'\}_1 \cup \{B''\}_1 \cup \ldots \quad (5)$$

is said to be the generalized first phasing shell of Φ provided that Φ, Φ', Φ'', ... constitute a multipole whose order with respect to Φ is the same as that of the phase relationship associated with Φ.

In order to give a numerical example in $P\bar{1}$, let $\Phi = \varphi_{240} + \varphi_{668}$. Its first representation is the collection of the special quartets

$$\Psi_1 = \varphi_{240} + \varphi_{668} - \varphi_{454} - \varphi_{454}$$
$$\Psi_1' = \varphi_{240} - \varphi_{668} + \varphi_{214} + \varphi_{214}$$

and its first phasing shell is

$$\{B\}_1 = \{R_{240}, R_{668}, R_{454}, R_{214}, R_{8,10,8}, R_{428}\}.$$

Since $\Phi' = \varphi_{240}$ and $\Phi'' = \varphi_{668}$ are one-phase s.s.'s of first rank, the first phasing shells $\{B'\}_1 = \{R_{240}, R_{120}\}$ and $\{B''\}_1 = \{R_{668}, R_{334}\}$ arise. Then, in accordance with (5),

$$\{B\}_1^g = \{R_{240}, R_{668}, R_{454}, R_{214}, R_{8,10,8}, R_{428}, R_{120}, R_{334}\}.$$

In paper II, the concept of the generalized first phasing shell was further enlarged by observing that information about Φ can be obtained by means of very special s.i.'s which estimate 2Φ. Thus, if $\Phi = \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2}$, then (see also Hauptman & Green, 1978)

$$\Psi' = \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_1\mathbf{R}_p} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_2\mathbf{R}_p}, \quad (\mathbf{h}_1 + \mathbf{h}_2)(\mathbf{I} + \mathbf{R}_p) = 0, \tag{6}$$

is a quartet and its value equals $2\Phi + a$, where a is a constant which arises because of translational symmetry. Since a is a known quantity the value of Ψ' can fix (with some ambiguity) that of Φ. As a further example, let $\Phi = \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3}$. Then

$$\Psi' = \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_1\mathbf{R}_p} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_2\mathbf{R}_p} + \varphi_{\mathbf{h}_3} + \varphi_{\mathbf{h}_3\mathbf{R}_p}, \tag{7}$$

with $(\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3)(\mathbf{I} + \mathbf{R}_p) = 0$, is a sextet whose value, because of (4), is $2\Phi + a$.

We are therefore justified in assuming that the generalized first phasing shell of Φ contains also the magnitudes belonging to the first phasing shells of the s.i.'s Ψ' as given by (6) or (7) when Φ is a two- or three-phase s.s. respectively. The conclusion may be generalized to the n-phase s.s.'s.

3. The generalized second phasing shell for one-phase s.s.'s of first rank

$\Phi = \varphi_{2\mathbf{h}}$ is a s.s. in $P\bar{1}$. In accordance with § 2 its first and second representations are given by

$$\{\Psi\}_1 = \varphi_{2\mathbf{h}} - \varphi_{\mathbf{h}} - \varphi_{\mathbf{h}}$$
$$\{\Psi\}_2 = \{\varphi_{2\mathbf{h}} - \varphi_{\mathbf{h}} - \varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} + \varphi_{\mathbf{k}}\},$$

from which

$$\{B\}_1 = \{R_{2\mathbf{h}}, R_{\mathbf{h}}\},$$
$$\{B\}_2 = \{R_{2\mathbf{h}}, R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{h}\pm\mathbf{k}}, R_{2\mathbf{h}\pm\mathbf{k}}\}.$$

However, the quintets in the set

$$\{\Psi'\}_2 = \{\varphi_{2\mathbf{h}} - \varphi_{\mathbf{h}-\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{k}}\}$$

also give information about $\varphi_{2\mathbf{h}}$, which now depends on

$$\{B'\}_2 = \{R_{2\mathbf{h}}, R_{\mathbf{h}}, R_{\mathbf{h}\pm\mathbf{k}}, R_{\mathbf{k}}, R_{2\mathbf{h}-\mathbf{k}}, R_{2\mathbf{h}-2\mathbf{k}}, R_{2\mathbf{k}}\}.$$

If $\mathbf{k}$ and $-\mathbf{k}$ are used in $\{\Psi'\}_2$ then $\varphi_{2\mathbf{h}}$ may be estimated *via* the generalized second phasing shell

$$\{B\}_2^g = \{B\}_2 \cup \{B'\}_2$$
$$= \{R_{2\mathbf{h}}, R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{h}\pm\mathbf{k}}, R_{2\mathbf{h}\pm\mathbf{k}}, R_{2\mathbf{k}}, R_{2\mathbf{h}\pm2\mathbf{k}}\}. \tag{8}$$

The procedure may be extended to any space group in the following way. Denoting a general one-phase s.s. by $\Phi = \varphi_{\mathbf{H}} = \varphi_{\mathbf{h}(\mathbf{I}-\mathbf{R}_n)}$, its first and second representations are the sets

$$\{\Psi\}_1 = \{\varphi_{\mathbf{H}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{h}\mathbf{R}_n}\}, \tag{9}$$

$$\{\Psi\}_2 = \{\varphi_{\mathbf{H}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{h}\mathbf{R}_n} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{k}}\}, \tag{10}$$

from which

$$\{B\}_1 = \{R_{\mathbf{H}}, R_{\mathbf{h}}\},$$
$$\{B\}_2 = \{R_{\mathbf{H}}, R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{H}\pm\mathbf{k}} R_{\mathbf{h}\pm\mathbf{k}} R_{\mathbf{h}\mathbf{R}_n\pm\mathbf{k}}\}.$$

It may be noted that when $\mathbf{R}_n \neq -\mathbf{I}$, $\mathbf{h}$ is a free vector under the condition (Giacovazzo, 1978*a*)

$$\mathbf{h}(\mathbf{I} - \mathbf{R}_n) = \mathbf{H}. \tag{11}$$

Thus, in $P2_1$ if $\mathbf{H} = (408)$ then $\mathbf{h} = (2k4)$, where k is a free index. We will denote by $\{\mathbf{h}\}$ the set of the vectors $\mathbf{h}$ which satisfy (11) and by $\{R_{\mathbf{h}}\}$ the corresponding set of observable magnitudes.

Let us now recall a more useful expression for $\{\Psi\}_2$ and $\{B\}_2$. In a centrosymmetric space group of order m for fixed $\mathbf{h} \in \{\mathbf{h}\}$ and $\mathbf{k}$, one may construct the set of special quintets

$$\Psi_2 = \varphi_{\mathbf{H}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{h}\mathbf{R}_n} - \varphi_{\mathbf{k}\mathbf{R}_j} + \varphi_{\mathbf{k}\mathbf{R}_j}, \quad j = 1, \ldots, m/2. \tag{12}$$

In (12), j varies over the subset of matrices not related by the centre of symmetry. The second representation of $\varphi_{\mathbf{H}}$ is then the collection of the special quintets (12) obtained when $\mathbf{h}$ varies over $\{\mathbf{h}\}$ and $\mathbf{k}$ only over the asymmetric region of reciprocal space. The cross magnitudes of any Ψ_2 are then

$$R_{\mathbf{H}\pm\mathbf{k}\mathbf{R}_j}, R_{\mathbf{h}\pm\mathbf{k}\mathbf{R}_j}, R_{\mathbf{h}\mathbf{R}_n\pm\mathbf{k}\mathbf{R}_j}, \quad j = 1, \ldots, m/2.$$

Since $E_{\mathbf{h}\mathbf{R}_p\pm\mathbf{k}\mathbf{R}_q}$ is symmetry equivalent to $E_{\mathbf{h}\pm\mathbf{k}\mathbf{R}_j}$, where $\mathbf{R}_j = \mathbf{R}_q\mathbf{R}_p^{-1}$, the second phasing shell of $\varphi_{\mathbf{H}}$ reduces to

$$\{B\}_2 = \{R_{\mathbf{H}}, R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{h}\pm\mathbf{k}\mathbf{R}_j}, R_{\mathbf{H}+\mathbf{k}\mathbf{R}_j}, \quad j = 1, \ldots, m\}. \tag{13}$$

In a non-centrosymmetric space group, for fixed $\mathbf{h} \in \{\mathbf{h}\}$ and $\mathbf{k}$ the quintets

$$\Psi_2 = \varphi_{\mathbf{H}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{h}\mathbf{R}_n} - \varphi_{\mathbf{k}\mathbf{R}_j} + \varphi_{\mathbf{k}\mathbf{R}_j}, \quad j = 1, \ldots, m$$

may be constructed, whose second phasing shell is

$$\{B\}_2 = \{R_{\mathbf{H}}, R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{h}\pm\mathbf{kR}_j}, R_{\mathbf{H}\pm\mathbf{kR}_j}, \quad j=1,\ldots,m\}. \tag{13'}$$

If the fictitious (not belonging to the space group) symmetry operators $\mathbf{C}_{m+j} = (-\mathbf{R}_j, -\mathbf{T}_j)$, $j = 1, \ldots, m$ are introduced, then (13′) can be written down as (13) provided $m' = 2m$ replaces m.

The study of the joint probability distribution

$$P(E_{\mathbf{H}}, \{E_{\mathbf{h}}\}, \{E_{\mathbf{k}}\}, \{E_{\mathbf{h}+\mathbf{kR}_j}\}, \{E_{\mathbf{h}+\mathbf{kR}_j}\}, \quad j=1,\ldots,m'), \tag{14}$$

is therefore suggested by (13) and (13′), where $m' = m$ for centrosymmetric and $m' = 2m$ for non-centrosymmetric space groups. Giacovazzo [1978*a*; see equations (36) and (40)] obtained from (14) probabilistic expressions which estimate $\varphi_{\mathbf{H}}$ in all the space groups. Practical applications of these formulae (Burla, Nunzi, Polidori, Busetta & Giacovazzo, 1980) showed that the estimates obtained *via* the second representation are remarkably more accurate than those *via* the well known $\sum_1$ relationships.

We observe now that, besides (10), the special quintets

$$\Psi_2' = \varphi_{\mathbf{H}} - \varphi_{\mathbf{h}+\mathbf{k}} + \varphi_{(\mathbf{h}+\mathbf{k})\mathbf{R}_n} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{kR}_n}$$

also give information about $\varphi_{\mathbf{H}}$. The important structural difference between the quintets Ψ_2 and Ψ_2' is that the Ψ_2's are constructed by adding and subtracting to the triplets in the first representation of $\varphi_{\mathbf{H}}$ the phases $\varphi_{\mathbf{k}}$, whereas the Ψ_2''s are the sum of a special three-phase s.s. and of a constant arising because of translational symmetry (*i.e.* $\varphi_{\mathbf{k}} - \varphi_{\mathbf{kR}_n}$). The phasing shell which arises from $\{\Psi'\}_2$ is the set

$$\{B'\}_2 = \{R_{\mathbf{H}}, R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{H}+\mathbf{k}}, R_{\mathbf{hR}_n+\mathbf{k}}, R_{\mathbf{h}+\mathbf{kR}_n}, R_{\mathbf{H}-\mathbf{kR}_n}, R_{\mathbf{H}+\mathbf{k}(\mathbf{I}-\mathbf{R}_n)}, R_{\mathbf{h}+\mathbf{k}(\mathbf{I}+\mathbf{R}_n)}, R_{\mathbf{hR}_n+\mathbf{k}(\mathbf{I}+\mathbf{R}_n)}, R_{\mathbf{k}(\mathbf{I}-\mathbf{R}_n)}\}.$$

Let us now find more useful expressions for $\{\Psi'\}_2$ and $\{B'\}_2$. In a centrosymmetric space group, for fixed $\mathbf{h} \in \{\mathbf{h}\}$ and $\mathbf{k}$, one may construct the set

$$\{\Psi'\}_2 = \{\varphi_{\mathbf{H}} - \varphi_{\mathbf{h}+\mathbf{kR}_j} + \varphi_{(\mathbf{h}+\mathbf{kR}_j)\mathbf{R}_n} + \varphi_{\mathbf{kR}_j} - \varphi_{\mathbf{kR}_j\mathbf{R}_n}, \quad j=1,\ldots,m/2\}. \tag{15}$$

In (15), j varies over the subset of matrices not related by the centre of symmetry. After suitable algebriac treatment, the set of magnitudes in the phasing shells of the quintets in (15) may be written as

$$\{B'\}_2 = \{R_{\mathbf{H}}, R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{h}+\mathbf{kR}_j}, R_{\mathbf{H}+\mathbf{kR}_j}, R_{\mathbf{k}(\mathbf{I}-\mathbf{R}_n)}, R_{\mathbf{h}+\mathbf{kR}_j(\mathbf{I}+\mathbf{R}_n)}, R_{\mathbf{H}+\mathbf{kR}_j(\mathbf{I}-\mathbf{R}_n)}, \quad j=1,\ldots,m\}. \tag{16}$$

In a non-centrosymmetric space group, for fixed $\mathbf{h} \in \{\mathbf{h}\}$ and $\mathbf{k}$, one may construct the set of quintets

$$\{\Psi'\}_2 = \{\varphi_{\mathbf{H}} - \varphi_{\mathbf{h}+\mathbf{kR}_j} + \varphi_{(\mathbf{h}+\mathbf{kR}_j)\mathbf{R}_n} + \varphi_{\mathbf{kR}_j} - \varphi_{\mathbf{kR}_j\mathbf{R}_n}, \quad j=1,\ldots,m\}.$$

The set of magnitudes in their phasing shells is

$$\{B'\}_2 = \{R_{\mathbf{H}}, R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{h}\pm\mathbf{kR}_j}, R_{\mathbf{H}\pm\mathbf{kR}_j}, R_{\mathbf{k}(\mathbf{I}-\mathbf{R}_n)}, R_{\mathbf{h}\pm\mathbf{kR}_j(\mathbf{I}+\mathbf{R}_n)}, R_{\mathbf{H}\pm\mathbf{kR}_j(\mathbf{I}-\mathbf{R}_n)}, \quad j=1,\ldots,m\}. \tag{17}$$

As for the second representation, we introduce the fictitious (not belonging to the space group) symmetry operators $\mathbf{C}_{m+j} = (-\mathbf{R}_j, -\mathbf{T}_j)$, $j = 1, \ldots, m$. Then, (17) can be written as (16) provided $m' = 2m$ replaces m.

The set theoretic union

$$\begin{aligned}\{B\}_2^g &= \{B\}_2 \cup \{B'\}_2 \\ &= \{R_{\mathbf{H}}, R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{h}+\mathbf{kR}_j}, R_{\mathbf{H}+\mathbf{kR}_j}, R_{\mathbf{k}(\mathbf{I}-\mathbf{R}_n)}, \\ &\quad R_{\mathbf{h}+\mathbf{kR}_j(\mathbf{I}+\mathbf{R}_n)}, R_{\mathbf{H}+\mathbf{kR}_j(\mathbf{I}-\mathbf{R}_n)}, j=1,\ldots,m'\}\end{aligned} \tag{18}$$

is defined to be the generalized second phasing shell of $\varphi_{\mathbf{H}}$. In (18), $m' = m$ or $m' = 2m$ according to whether the space group is centro- or non-centro-symmetric.

In accordance with this definition, the generalized second representation of $\varphi_{\mathbf{H}}$ is the set theoretic union

$$\{\Psi\}_2^g = \{\Psi\}_2 \cup \{\Psi'\}_2.$$

This result suggests the study of the joint probability distribution

$$P(E_{\mathbf{H}}, \{E_{\mathbf{h}}\}, \{E_{\mathbf{k}}\}, \{E_{\mathbf{h}+\mathbf{kR}_j}\}, \{E_{\mathbf{H}+\mathbf{kR}_j}\}, \{E_{\mathbf{k}(\mathbf{I}-\mathbf{R}_n)}\}, \{E_{\mathbf{h}+\mathbf{kR}_j(\mathbf{I}+\mathbf{R}_n)}\}, \{E_{\mathbf{H}+\mathbf{kR}_j(\mathbf{I}-\mathbf{R}_n)}\}, \quad j=1,\ldots,m'), \tag{19}$$

where $\{E_{\mathbf{h}}\}$ is the set of structure factors whose indices belong to $\{\mathbf{h}\}$, $\{E_{\mathbf{k}}\}$ is any chosen set in the asymmetric region of reciprocal space, and $\{E_{\mathbf{h}+\mathbf{kR}_j}\}, \ldots, \{E_{\mathbf{H}+\mathbf{kR}_j(\mathbf{I}-\mathbf{R}_n)}\}$ are sets obtainable according to the specified conditions on $\mathbf{h}$ and $\mathbf{k}$.

Distribution (19) is able to exploit the knowledge of a number of magnitudes larger than that considered in (14). Since the information is of order $1/N^{3/2}$ in both cases (we deal always with quintets), we can expect that conclusive formulae arising from (19) will give more accurate estimates for Φ than those arising from (14).

The reader can generalize the above method to the cases in which, for a given $\mathbf{H}$, (11) can be satisfied by more matrices $\mathbf{R}_n$ and more sets $\{\mathbf{h}\}$. Thus, in $P2_12_12_1$, when $\mathbf{H} = (008)$ the two matrices

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

and, correspondingly, the two sets $\{h04\}$ and $\{0k4\}$ satisfy (11).

A probabilistic approach for the estimation of the one-phase s.s.'s *via* the magnitudes contained in their generalized second phasing shells is described in the next paper (Giacovazzo, 1980*b*).

4. The generalized upper phasing shells for one-phase s.s.'s of first rank

The generalized third representation is the collection of the special septets in

$$\{\Psi\}_3 = \{\Psi_2 + \varphi_{\mathbf{lR}_p} - \varphi_{\mathbf{lR}_p}, \quad j, p = 1, \ldots, m'/2\}$$

and in

$$\{\Psi'\}_3 = \{\Psi'_2 + \varphi_{\mathbf{lR}_p} - \varphi_{\mathbf{lR}_p}, \quad j, p = 1, \ldots, m'/2\}.$$

The generalized third phasing shell is then the set of magnitudes which are basis or cross terms of at least one septet in the generalized third representation.

The definition of the upper phasing shells is now trivial.

5. The generalized second phasing shell for two-phase s.s.'s of first rank

$\Phi = \varphi_{\mathbf{h}+\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}$ is a s.s. in $P\bar{1}$. In accordance with § 2 its first representation is given by the collection of quartets

$$\Psi_1 = \varphi_{\mathbf{h}+\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}} - \varphi_{\mathbf{h}} - \varphi_{\mathbf{h}},$$

$$\Psi'_1 = \varphi_{\mathbf{h}+\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{k}},$$

from which

$$\{B\}_1 = \{R_{\mathbf{h}\pm\mathbf{k}}, R_{\mathbf{h}}, R_{\mathbf{k}}, R_{2\mathbf{h}}, R_{2\mathbf{k}}\}.$$

In accordance with § 2.6, if $\varphi_{\mathbf{h}+\mathbf{k}}$ and $\varphi_{\mathbf{h}-\mathbf{k}}$ are themselves s.s.'s, then

$$\{B\}_1^g = \{R_{\mathbf{h}+\mathbf{k}}, R_{\mathbf{h}}, R_{\mathbf{k}}, R_{2\mathbf{h}}, R_{2\mathbf{k}}, R_{\frac{1}{2}(\mathbf{h}\pm\mathbf{k})}\}.$$

The second representation is the collection of sextets

$$\Psi_2 = \varphi_{\mathbf{h}+\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}} - \varphi_{\mathbf{h}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{l}} - \varphi_{\mathbf{l}}, \tag{20}$$

$$\Psi'_2 = \varphi_{\mathbf{h}+\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} - \varphi_{\mathbf{l}}, \tag{20'}$$

where $\mathbf{l}$ is a free vector in reciprocal space. Then,

$$\{B\}_2 = \{R_{\mathbf{h}\pm\mathbf{k}}, R_{\mathbf{h}}, R_{\mathbf{k}}, R_{2\mathbf{h}}, R_{2\mathbf{k}}, R_{\mathbf{l}}, R_{\mathbf{h}\pm\mathbf{k}\pm\mathbf{l}}, R_{\mathbf{h}\pm\mathbf{l}}, R_{\mathbf{k}\pm\mathbf{l}}, R_{2\mathbf{h}\pm\mathbf{l}}, R_{2\mathbf{k}\pm\mathbf{l}}\}.$$

In conclusion, 6 and 19 magnitudes are in the first and second phasing shells of Φ respectively.

However, besides the sextets in (20) and (20′), the sextets

$$\Psi''_2 = \varphi_{\mathbf{h}+\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{l}} - \varphi_{\mathbf{h}+\mathbf{l}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{l}}, \tag{20''}$$

$$\Psi'''_2 = \varphi_{\mathbf{h}+\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}} - \varphi_{\mathbf{k}+\mathbf{l}} - \varphi_{\mathbf{k}+\mathbf{l}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{l}} \tag{20'''}$$

also give information about Φ. If besides $\mathbf{l}$, $-\mathbf{l}$ is also used in (20″) and (20‴), then we say that the generalized second representation of Φ is the collection of sextets Ψ_2, Ψ'_2, Ψ''_2, Ψ'''_2, when $\mathbf{l}$ varies over the asymmetric region of reciprocal space. The generalized second phasing shell of Φ is then

$$\{B\}_2^g = \{R_{\mathbf{h}\pm\mathbf{k}}, R_{\mathbf{h}}, R_{\mathbf{k}}, R_{2\mathbf{h}}, R_{2\mathbf{k}}, R_{\mathbf{l}}, R_{\mathbf{h}\pm\mathbf{k}\pm\mathbf{l}}, R_{\mathbf{h}\pm\mathbf{l}}, R_{\mathbf{k}\pm\mathbf{l}}, R_{2\mathbf{h}\pm\mathbf{l}}, R_{2\mathbf{k}\pm\mathbf{l}}, R_{2\mathbf{l}}, R_{2(\mathbf{h}\pm\mathbf{l})}, R_{2(\mathbf{k}\pm\mathbf{l})}, R_{\mathbf{h}\pm\mathbf{k}\pm 2\mathbf{l}}\}.$$

As we see, 28 magnitudes are contained in the generalized second phasing shell of Φ in $P\bar{1}$.

If $\varphi_{\mathbf{h}+\mathbf{k}}$ and $\varphi_{\mathbf{h}-\mathbf{k}}$ are themselves s.s.'s, the set $\{B\}_2^g$ will include the magnitudes $R_{\frac{1}{2}(\mathbf{h}\pm\mathbf{k})}$ too.

The above procedure may be extended to any space group in the following way. $\Phi = \varphi_{\mathbf{u}} + \varphi_{\mathbf{v}} = \varphi_{\mathbf{h}_1-\mathbf{h}_2} + \varphi_{-\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2\mathbf{R}_q}$ is the more general expression of a two-phase s.s. of first rank (Giacovazzo, 1979). Its first representation is the collection of the quartets

$$\Psi_1 = \varphi_{\mathbf{v}} + \varphi_{\mathbf{uR}_p} + \varphi_{\mathbf{h}_2\mathbf{R}_p} - \varphi_{\mathbf{h}_2\mathbf{R}_q},$$

$$\Psi'_1 = \varphi_{\mathbf{v}} + \varphi_{\mathbf{uR}_q} + \varphi_{\mathbf{h}_1\mathbf{R}_p} - \varphi_{\mathbf{h}_1\mathbf{R}_q},$$

where $\mathbf{h}_1$ and $\mathbf{h}_2$ are free vectors under the condition

$$\begin{cases} \mathbf{h}_1 - \mathbf{h}_2 = \mathbf{u} \\ -\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2\mathbf{R}_q = \mathbf{v}. \end{cases}$$

The sets of the vectors $\mathbf{h}_1$ and $\mathbf{h}_2$ will be denoted by $\{\mathbf{h}_1\}$ and $\{\mathbf{h}_2\}$ and the sets of corresponding magnitudes by $\{R_{\mathbf{h}_1}\}$ and $\{R_{\mathbf{h}_2}\}$. Then,

$$\{B\}_1 = \{R_{\mathbf{u}}, R_{\mathbf{v}}, \{R_{\mathbf{h}_1}\}, \{R_{\mathbf{h}_2}\}, \{R_{\mathbf{h}_1(\mathbf{R}_q-\mathbf{R}_p)}\}, \{R_{\mathbf{h}_2(\mathbf{R}_q-\mathbf{R}_p)}\}, \{R_{\mathbf{uR}_q+\mathbf{h}_1\mathbf{R}_p}\}, \{R_{\mathbf{v}+\mathbf{h}_2\mathbf{R}_p}\}\},$$

where $\{R_{\mathbf{h}_1(\mathbf{R}_q-\mathbf{R}_p)}\{, \ldots, \{R_{\mathbf{v}+\mathbf{h}_2\mathbf{R}_p}\}$ are sets defined according to the specified conditions on $\mathbf{h}_1$ and $\mathbf{h}_2$.

Joint probability distributions involving all the E's in $\{B\}_1$ have been studied by Giacovazzo (1979). The conclusive formulae, estimating Φ given $\{B\}_1$, were tested in all the space groups up to orthorhombic: they can secure a good estimate of several two-phase s.s.'s (Giacovazzo, Spagna, Vickovič & Viterbo, 1979).

If $\varphi_{\mathbf{u}}$ and $\varphi_{\mathbf{v}}$ are themselves one-phase s.s.'s, then, in accordance with § 2.6,

$$\{B\}_1^g = \{R_{\mathbf{u}}, R_{\mathbf{v}}, \{R_{\mathbf{h}_1}\}, \{R_{\mathbf{h}_2}\}, \{R_{\mathbf{h}_1(\mathbf{R}_q-\mathbf{R}_p)}\}, \{R_{\mathbf{h}_2(\mathbf{R}_q-\mathbf{R}_p)}\}, \{R_{\mathbf{uR}_q+\mathbf{h}_1\mathbf{R}_p}\}, \{R_{\mathbf{v}+\mathbf{h}_2\mathbf{R}_p}\}, \{R_{\mathbf{k}_1}\}, \{R_{\mathbf{k}_2}\}\}, \tag{21}$$

where $\{R_{\mathbf{k}_1}\}$ and $\{R_{\mathbf{k}_2}\}$ are the sets of the magnitudes belonging to the first phasing shells of $\varphi_{\mathbf{u}}$ and $\varphi_{\mathbf{v}}$ respectively.

If at least one of $\varphi_{\mathbf{u}}$ and $\varphi_{\mathbf{v}}$ is non-centrosymmetric, then the cross vectors of the quartets which estimate 2Φ must also be included in $\{B\}_1^g$. The algebra of these very special quartets in all the non-centrosymmetric space groups up to orthorhombic is described by Giacovazzo & Vickovič (1980).

By means of the quartets in the first representation, the collection of the sextets

$$\varphi_{\mathbf{v}} + \varphi_{\mathbf{u}\mathbf{R}_p} + \varphi_{\mathbf{h}_2\mathbf{R}_p} - \varphi_{\mathbf{h}_2\mathbf{R}_q} + \varphi_{\mathbf{l}} - \varphi_{\mathbf{l}}, \qquad (22)$$

$$\varphi_{\mathbf{v}} + \varphi_{\mathbf{u}\mathbf{R}_q} + \varphi_{\mathbf{h}_1\mathbf{R}_p} - \varphi_{\mathbf{h}_1\mathbf{R}_q} + \varphi_{\mathbf{l}} - \varphi_{\mathbf{l}} \qquad (22')$$

can be constructed. In a centrosymmetric space group and for fixed $\mathbf{h}_1$, $\mathbf{h}_2$ and $\mathbf{l}$, one may obtain the sets of sextets

$$\Psi_2 = \varphi_{\mathbf{v}} + \varphi_{\mathbf{u}\mathbf{R}_p} + \varphi_{\mathbf{h}_2\mathbf{R}_p} - \varphi_{\mathbf{h}_2\mathbf{R}_q} + \varphi_{\mathbf{l}\mathbf{R}_j} - \varphi_{\mathbf{l}\mathbf{R}_j}, \quad j = 1, \ldots, m/2, \qquad (23)$$

$$\Psi_2' = \varphi_{\mathbf{v}} + \varphi_{\mathbf{u}\mathbf{R}_q} + \varphi_{\mathbf{h}_1\mathbf{R}_p} - \varphi_{\mathbf{h}_1\mathbf{R}_q} + \varphi_{\mathbf{l}\mathbf{R}_j} - \varphi_{\mathbf{l}\mathbf{R}_j}, \quad j = 1, \ldots, m/2. \qquad (23')$$

In (23) and (23′), j varies over the subset of matrices not related by the centre of symmetry. The second representation of Φ is then the collection of the special sextets (23) and (23′) obtained when $\mathbf{h}_1$ and $\mathbf{h}_2$ vary over $\{\mathbf{h}_1\}$ and $\{\mathbf{h}_2\}$ respectively and $\mathbf{l}$ only over the asymmetric region of reciprocal space. The second phasing shell is then

$$\begin{aligned}\{B\}_2 = \{R_{\mathbf{u}}, R_{\mathbf{v}}, &\{R_{\mathbf{h}_1}\}, \{R_{\mathbf{h}_2}\}, \{R_{\mathbf{h}_1(\mathbf{R}_q-\mathbf{R}_p)}\}, \{R_{\mathbf{h}_2(\mathbf{R}_q-\mathbf{R}_p)}\},\\ &\{R_{\mathbf{u}\mathbf{R}_q+\mathbf{h}_1\mathbf{R}_p}\}, \{R_{\mathbf{v}+\mathbf{h}_2\mathbf{R}_p}\}, \{R_{\mathbf{u}\pm\mathbf{l}\mathbf{R}_j}\}, \{R_{\mathbf{v}\pm\mathbf{l}\mathbf{R}_j}\},\\ &\{R_{\mathbf{h}_1\pm\mathbf{l}\mathbf{R}_j}\}, \{R_{\mathbf{h}_2+\mathbf{l}\mathbf{R}_j}\}, \{R_{\mathbf{h}_1(\mathbf{R}_q-\mathbf{R}_p)\pm\mathbf{l}\mathbf{R}_j}\},\\ &\{R_{\mathbf{h}_2(\mathbf{R}_q-\mathbf{R}_p)\pm\mathbf{l}\mathbf{R}_j}\}, \{R_{\mathbf{u}\mathbf{R}_q+\mathbf{h}_1\mathbf{R}_p\pm\mathbf{l}\mathbf{R}_j}\},\\ &\{R_{\mathbf{v}+\mathbf{h}_2\mathbf{R}_p\pm\mathbf{l}\mathbf{R}_j}\}, \quad j = 1, \ldots, m/2\}. \end{aligned} \qquad (24)$$

In a way strictly analogous to that used for the one-phase s.s.'s, (24) is shown to represent the second phasing shell for non-centrosymmetric space groups too, provided m replaces $m/2$ in the algebraic expression.

We observe now that, besides (22) and (22′), the sextets

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

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

also give information about Φ. The important structural difference between the above sextets and those in (22) and (22′) is the following: the sextets in (22) and (22′) are constructed by adding and subtracting to the quartets in the first representation of Φ the phase $\varphi_{\mathbf{l}}$, whereas the above sextets are the sum of a special four-phase s.s. and of a constant arising because of translational symmetry. In a centrosymmetric space group of order m and for fixed $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{l}$, we may construct the sets

$$\Psi_2'' = \varphi_{\mathbf{v}} + \varphi_{\mathbf{u}\mathbf{R}_p} + \varphi_{(\mathbf{h}_2+\mathbf{l}\mathbf{R}_j)\mathbf{R}_p} - \varphi_{(\mathbf{h}_2+\mathbf{l}\mathbf{R}_j)\mathbf{R}_q} + \varphi_{\mathbf{l}\mathbf{R}_j\mathbf{R}_q} - \varphi_{\mathbf{l}\mathbf{R}_j\mathbf{R}_q}, \quad j = 1, \ldots, m/2, \qquad (25)$$

$$\Psi_2''' = \varphi_{\mathbf{v}} + \varphi_{\mathbf{u}\mathbf{R}_q} - \varphi_{(\mathbf{h}_1+\mathbf{l}\mathbf{R}_j)\mathbf{R}_p} - \varphi_{(\mathbf{h}_1+\mathbf{l}\mathbf{R}_j)\mathbf{R}_a} + \varphi_{\mathbf{l}\mathbf{R}_j\mathbf{R}_q} - \varphi_{\mathbf{l}\mathbf{R}_j\mathbf{R}_p}, \quad j = 1, \ldots, m/2. \qquad (25')$$

The generalized second representation of Φ is now the collection of the special sextets (23), 23′), (25) and (25′) obtained when $\mathbf{h}_1$ and $\mathbf{h}_2$ vary over $\{\mathbf{h}_1\}$ and $\{\mathbf{h}_2\}$ respectively and $\mathbf{l}$ only over the asymmetric region of reciprocal space. The generalized second phasing shell is then

$$\begin{aligned}\{B\}_2^g = \{R_{\mathbf{u}}, R_{\mathbf{v}}, &\{R_{\mathbf{h}_1}\}, \{R_{\mathbf{h}_2}\}, \{R_{\mathbf{h}_1(\mathbf{R}_q-\mathbf{R}_p)}\}\\ &\{R_{\mathbf{h}_2(\mathbf{R}_q-\mathbf{R}_p)}\}, \{R_{\mathbf{u}\mathbf{R}_q+\mathbf{h}_1\mathbf{R}_p}\}, \{R_{\mathbf{v}+\mathbf{h}_2\mathbf{R}_p}\},\\ &\{R_{\mathbf{u}\pm\mathbf{l}\mathbf{R}_j}\}, \{R_{\mathbf{v}+\mathbf{l}\mathbf{R}_j}\}, \{R_{\mathbf{h}_1\pm\mathbf{l}\mathbf{R}_j}\}, \{R_{\mathbf{h}_2\pm\mathbf{l}\mathbf{R}_j}\},\\ &\{R_{\mathbf{h}_1(\mathbf{R}_q-\mathbf{R}_p)\pm\mathbf{l}\mathbf{R}_j}\}, \{R_{\mathbf{h}_2(\mathbf{R}_q-\mathbf{R}_p)\pm\mathbf{l}\mathbf{R}_j}\},\\ &\{R_{\mathbf{u}\mathbf{R}_q+\mathbf{h}_1\mathbf{R}_p\pm\mathbf{l}\mathbf{R}_j}\}, \{R_{\mathbf{v}+\mathbf{h}_2\mathbf{R}_p\pm\mathbf{l}\mathbf{R}_j}\}, \{R_{\mathbf{l}(\mathbf{R}_p-\mathbf{R}_q)}\},\\ &\{R_{\mathbf{h}_1(\mathbf{R}_p-\mathbf{R}_q)\pm\mathbf{l}(\mathbf{R}_p-\mathbf{R}_q)\mathbf{R}_j}\}, \{R_{\mathbf{h}_2(\mathbf{R}_p-\mathbf{R}_q)\pm\mathbf{l}(\mathbf{R}_p-\mathbf{R}_q)\mathbf{R}_j}\},\\ &\{R_{\mathbf{h}_1\pm\mathbf{l}(\mathbf{R}_p+\mathbf{R}_q)\mathbf{R}_j}\}, \{R_{\mathbf{h}_2\pm\mathbf{l}(\mathbf{R}_p+\mathbf{R}_q)\mathbf{R}_j}\},\\ &\{R_{\mathbf{u}+\mathbf{l}(\mathbf{R}_p-\mathbf{R}_q)\mathbf{R}_j}\}, \{R_{\mathbf{v}+\mathbf{l}(\mathbf{R}_p-\mathbf{R}_q)\mathbf{R}_j}\},\\ &\{R_{\mathbf{v}+\mathbf{h}_2\mathbf{R}_p\pm\mathbf{l}(\mathbf{R}_p+\mathbf{R}_q)\mathbf{R}_j}\}, \{R_{\mathbf{u}\mathbf{R}_q+\mathbf{h}_1\mathbf{R}_p\pm\mathbf{l}(\mathbf{R}_p+\mathbf{R}_q)\mathbf{R}_j}\},\\ &j = 1, \ldots, m/2\}, \end{aligned} \qquad (26)$$

which is able to exploit much more information than $\{B\}_2$.

As previously suggested, (26) represents the second phasing shell for non-centrosymmetric space groups too, provided m replaces $m/2$ in the algebraic expression.

If $\varphi_{\mathbf{u}}$ and $\varphi_{\mathbf{v}}$ are themselves s.s.'s, then $\{B\}_2^g$ will include the same sets of magnitudes $\{R_{\mathbf{k}_1}\}$ and $\{R_{\mathbf{k}_2}\}$ included in (21). If at least one of $\varphi_{\mathbf{u}}$ and $\varphi_{\mathbf{v}}$ is non-centrosymmetric then also the cross vectors of the quartets which estimate 2Φ must be included in $\{B\}_2^g$.

The procedure so far described may be generalized to the cases in which, for given $\mathbf{u}$ and $\mathbf{v}$, more pairs of matrices $(\mathbf{R}_p, \mathbf{R}_q)$ and more pairs of sets $(\{\mathbf{h}_1\}, \{\mathbf{h}_2\})$ satisfy the equations

$$\begin{cases}\mathbf{h}_1 - \mathbf{h}_2 = \mathbf{u}\\ -\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2\mathbf{R}_q = \mathbf{v}.\end{cases}$$

Upper phasing shells of Φ can be found on the basis of § 4.

6. The generalized phasing shells of the s.s.'s of high order

The algebraic procedure so far described enables one to obtain the generalized phasing shells of the s.s.'s of high order. With a view to making the reading of this paper easy we briefly deal only with the case of the three-phase s.s.'s.

The first representation of $\Phi = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{h}+\mathbf{k}+2\mathbf{l}}$ in $P\bar{1}$ is the collection of the quintet invariants

$$\Psi_1' = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{k}+2\mathbf{l}} + 2\varphi_{\mathbf{l}}, \qquad (27')$$

$$\Psi_1'' = -\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{k}+2\mathbf{l}} + 2\varphi_{\mathbf{h}+\mathbf{l}}, \qquad (27'')$$

$$\Psi_1''' = \varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h+k+2l}} + 2\varphi_{\mathbf{k+l}}, \qquad (27''')$$

$$\Psi_1'''' = -\varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h+k+2l}} - 2\varphi_{\mathbf{h+k+l}}, \qquad (27'''')$$

whose first phasing shell is

$$\{B\}_1 = \{R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{h+k+2l}}, R_{\mathbf{l}}, R_{\mathbf{h+l}}, R_{\mathbf{k+l}}, R_{\mathbf{h+k+l}}, R_{\mathbf{h+k}}, R_{\mathbf{h-k}}, R_{\mathbf{h+2l}}, R_{\mathbf{k+2l}}, R_{\mathbf{h+2k+2l}}, R_{\mathbf{2h+k+2l}}, R_{\mathbf{2l}}, R_{\mathbf{2h+2l}}, R_{\mathbf{2k+2l}}, R_{\mathbf{2h+2k+2l}}\}. \qquad (28)$$

A probabilistic formula which estimates Φ *via* its first phasing shell has been described by Giacovazzo (1978*b*).

The generalized first phasing shell $\{B\}_1^g$ may be constructed *via* the procedure described in § 2.6 [see also Giacovazzo (180*a*) for some practical examples]. The second representation of Φ is the collection of the septets

$$\Psi_2' = \Psi_1' + \varphi_{\mathbf{p}} - \varphi_{\mathbf{p}'}, \qquad (29')$$

$$\vdots \qquad \vdots$$

$$\Psi_2'''' = \Psi_1'''' + \varphi_{\mathbf{p}} - \varphi_{\mathbf{p}'}, \qquad (29'''')$$

where $\mathbf{p}$ is a free vector in reciprocal space.

Besides (29), the following septets may also be formed, all giving information about Φ:

$$\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h+k+2l}} + 2\varphi_{\mathbf{l+p}} - 2\varphi_{\mathbf{p}}, \qquad (30')$$

$$-\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h+k+2l}} + 2\varphi_{\mathbf{h+l+p}} - 2\varphi_{\mathbf{p}}, \qquad (30'')$$

$$\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h+k+2l}} + 2\varphi_{\mathbf{k+l+p}} - 2\varphi_{\mathbf{p}}, \qquad (30''')$$

$$-\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h+k+2l}} + 2\varphi_{\mathbf{h+k+l+p}}\ 2\varphi_{\mathbf{p}}. \qquad (30'''')$$

The generalized second representation is the collection of the septets (29) and (30). Consequently, the generalized second phasing shell is the set of magnitudes which are basis or cross terms of at least one septet (29) or (30). In accordance with the preceding paragraph, if $\varphi_{\mathbf{h}}$, $\varphi_{\mathbf{k}}$, $\varphi_{\mathbf{h+k+2l}}$ or their combinations are themselves s.s.'s, then $\{B\}_2^g$ contains also the magnitudes belonging to their first phasing shells.

In space groups with symmetry higher than $P\bar{1}$ it was shown (Giacovazzo, 1980*a*) that the more general expression for a three-phase s.s. of first rank is

$$\Phi = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2} + \varphi_{\mathbf{u}_3} = \varphi_{\mathbf{h}_1-\mathbf{h}_2\mathbf{R}_\beta} + \varphi_{\mathbf{h}_2-\mathbf{h}_3\mathbf{R}_\gamma} + \varphi_{\mathbf{h}_3-\mathbf{h}_1\mathbf{R}_\alpha},$$

where $\mathbf{R}_\beta$, $\mathbf{R}_\gamma$, $\mathbf{R}_\alpha$ are suitable rotation matrices and $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{h}_3$ are free vectors in reciprocal space which satisfy the condition

$$\begin{cases} \mathbf{h}_1 - \mathbf{h}_2\,\mathbf{R}_\beta = \mathbf{u}_1 \\ \mathbf{h}_2 - \mathbf{h}_3\,\mathbf{R}_\gamma = \mathbf{u}_2 \\ \mathbf{h}_3 - \mathbf{h}_1\,\mathbf{R}_\alpha = \mathbf{u}_3. \end{cases} \qquad (31)$$

We will denote by $\{\mathbf{h}_1\}$, $\{\mathbf{h}_2\}$, $\{\mathbf{h}_3\}$ the sets described by $\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{h}_3$ respectively.

A formula which estimates Φ in $P2_1$ *via* suitable subsets of its first representation has been secured by Hauptman & Potter (1979). It may be noted that more trios of rotation matrices ($\mathbf{R}_\alpha$, $\mathbf{R}_\beta$, $\mathbf{R}_\gamma$) can satisfy (31) so that more trios of sets ($\{\mathbf{h}_1\}$, $\{\mathbf{h}_2\}$, $\{\mathbf{h}_3\}$) can correspondingly be derived.

The first representation is the collection of the special quintets (32):

$$\varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2\mathbf{R}_\beta} + \varphi_{\mathbf{u}_3\mathbf{R}_\gamma\mathbf{R}_\beta} - \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_1\mathbf{R}_\alpha\mathbf{R}_\gamma\mathbf{R}_\beta}, \qquad (32')$$

$$\varphi_{\mathbf{u}_1\mathbf{R}_\alpha\mathbf{R}_\gamma} + \varphi_{\mathbf{u}_2} + \varphi_{\mathbf{u}_3\mathbf{R}_\gamma} - \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_2\mathbf{R}_\beta\mathbf{R}_\alpha\mathbf{R}_\gamma}, \qquad (32'')$$

$$\varphi_{\mathbf{u}_1\mathbf{R}_\alpha} + \varphi_{\mathbf{u}_2\mathbf{R}_\beta\mathbf{R}_\alpha} + \varphi_{\mathbf{u}_3} - \varphi_{\mathbf{h}_3} + \varphi_{\mathbf{h}_3\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\alpha}. \qquad (32''')$$

The first phasing shell is the collection of the magnitudes which are basis or cross terms of at least one s.i. in (32). For the generalized first phasing shell see § 2.6. The second representation of Φ is the collection of the septets obtained by adding and subtracting to each s.i. in (32) the same phase $\varphi_{\mathbf{p}}$, where $\mathbf{p}$ is a free vector in reciprocal space:

$$\{\Psi\}_2 = \{\Psi_1 + \varphi_{\mathbf{p}} - \varphi_{\mathbf{p}}\}. \qquad (33)$$

Besides (33),

$$\varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2\mathbf{R}_\beta} + \varphi_{\mathbf{u}_3\mathbf{R}_\gamma\mathbf{R}_\beta} - \varphi_{(\mathbf{h}_1+\mathbf{p})} + \varphi_{(\mathbf{h}_1+\mathbf{p})\mathbf{R}_\alpha\mathbf{R}_\gamma\mathbf{R}_\beta} + \varphi_{\mathbf{p}} - \varphi_{\mathbf{p}\mathbf{R}_\alpha\mathbf{R}_\gamma\mathbf{R}_\beta}, \qquad (34')$$

$$\varphi_{\mathbf{u}_1\mathbf{R}_\alpha\mathbf{R}_\gamma} + \varphi_{\mathbf{u}_2} + \varphi_{\mathbf{u}_3\mathbf{R}_\gamma} - \varphi_{(\mathbf{h}_2+\mathbf{p})} + \varphi_{(\mathbf{h}_2+\mathbf{p})\mathbf{R}_\beta\mathbf{R}_\alpha\mathbf{R}_\gamma} + \varphi_{\mathbf{p}} - \varphi_{\mathbf{p}\mathbf{R}_\beta\mathbf{R}_\alpha\mathbf{R}_\gamma}, \qquad (34'')$$

and

$$\varphi_{\mathbf{u}_1\mathbf{R}_\alpha} + \varphi_{\mathbf{u}_2\mathbf{R}_\beta\mathbf{R}_\alpha} + \varphi_{\mathbf{u}_3} - \varphi_{(\mathbf{h}_3+\mathbf{p})} + \varphi_{(\mathbf{h}_3+\mathbf{p})\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\alpha} + \varphi_{\mathbf{p}} - \varphi_{\mathbf{p}\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\alpha} \qquad (34''')$$

also give information about Φ. The collection of the septets (33) and (34), when $\mathbf{l}$ varies over reciprocal space and ($\mathbf{R}_\alpha$, $\mathbf{R}_\beta$, $\mathbf{R}_\gamma$), ($\mathbf{h}_1$, $\mathbf{h}_2$, $\mathbf{h}_3$) over the corresponding sets of rotation matrices and vectors satisfying (31), is defined to be the generalized second representation of Φ. The generalized second phasing shell is consequently defined. For upper representations the technique described in § 4 can be applied.

7. Conclusions

The generalized representations of the s.s.'s of first rank have been defined together with an algebraic method for obtaining them. When generalized representations are used instead of the mere representations, a new amount of *a priori* information is available: it is therefore expected that more accurate estimates of the s.s.'s can be obtained.

So far, the idea of generalized representation has been applied to: (*a*) the estimation of the centrosymmetric two-phase s.s.'s of first rank *via* their generalized first representations (Burla, Nunzi, Giacovazzo & Polidori, 1980); (*b*) The estimation of the non-centrosymmetric two-phase s.s.'s of first rank *via* their generalized first representations (Busetta, Giacovazzo, Spagna & Viterbo, 1980); (*c*) The estimation of the one-phase s.s.'s of first rank *via* their generalized second representations (Giacovazzo, 1980*b*).

The results obtained in (*a*) and (*b*) improve previous results (Giacovazzo, Spagna, Vicković & Viterbo, 1979). It may be expected that the application of the probabilistic theory in (*c*) will be successful too. The application of the generalized upper representations to two- and three-phase s.s.'s is a difficult but not prohibitive task.

APPENDIX
Symbols and abbreviations

m = number of symmetry operators in the space group
N = number of atoms in the unit cell
$E_{\mathbf{h}}$ = normalized structure factor
$R_{\mathbf{h}}$ = magnitude of the normalized structure factor
$\mathbf{C}_p \equiv (\mathbf{R}_p, \mathbf{T}_p)$ = pth symmetry operator
$\mathbf{R}_p$ = pth rotation matrix of the point group
$\mathbf{T}_p$ = translation vector associated with the pth rotation matrix of the point group
$\mathbf{I}$ = identity 3×3 matrix
s.i. = structure invariant
s.s. = structure seminvariant

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The Estimation of the One-Phase Structure Seminvariants of First Rank by means of their Generalized Second Representations

BY CARMELO GIACOVAZZO

Istituto di Mineralogia, Palazzo Ateneo, Università, 70121 *Bari, Italy*

(*Received* 9 *January* 1980; *accepted* 18 *February* 1980)

Abstract

The concept of generalized second representation [Giacovazzo (1980). *Acta Cryst.* A**36**, 704–711] has been used in order to estimate the one-phase structure seminvariants of first rank.

1. Introduction*

In a preceding paper (Giacovazzo, 1978; from now on paper I), the estimation of the one-phase s.s.'s of first rank was carried out by means of the joint probabiilty distribution method. The *a priori* information exploited in the calculations was chosen according to the theory of representations of the s.s.'s (Giacovazzo, 1977). In particular, any one-phase s.s. Φ was estimated *via* its second representation: that is to say, the knowledge of the diffraction magnitudes belonging to the second phasing shell of Φ was exploited in order to give a probabilistic estimate of Φ.

Burla, Nunzi, Polidori, Busetta & Giacovazzo (1980) showed that the estimates of the one-phase s.s.'s *via* their second representation are in general considerably more accurate than the corresponding estimates *via* the $\sum_1$ relationships (Hauptman & Karle, 1953; Cochran

* Symbols and abbreviations are defined in the Appendix.

0567-7394/80/040711-05$01.00