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The Method of Representations of Structure Seminvariants. II.* New Theoretical and Practical Aspects

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Abstract

The fundamental ideas of representation given in a preceding paper [Giacovazzo (1977). *Acta Cryst.* A **33**, 933–944] are generalized further. Some algebraic properties of structure seminvariants are stated and their importance for practical applications is discussed. The concept of a generalized first phasing shell is introduced: it allows in some cases a better estimation of the seminvariants.

1. Introduction†

Hauptman (1975) first fixed the idea of defining a sequence of sets of reflections (sequence of nested neighbourhoods) each contained within the succeeding one and having the property that the cosine invariant or seminvariant may be estimated *via* the magnitudes constituting any neighbourhood. A practical application of the idea had already been performed independently by Giacovazzo (1975) who calculated in $P\bar{1}$ the one-phase s.s.'s *via* the magnitudes in their second neighbourhoods. Heuristic methods of finding sequences of nested neighbourhoods for certain s.i.'s or s.s.'s have been presented by Hauptman (1976). However, different sequences for the same s.s.'s exist.

A more general method for estimating s.s.'s was described by Giacovazzo (1977*a*, 1977*b*). The method is able, for any s.s., Φ, to arrange 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. In particular, the theory introduces the idea of the upper representations of a s.s. and organizes the set of reflections in a sequence of subsets, each contained in the succeeding one, which does not coincide in general with the corresponding nested-neighbourhood sequence given by Hauptman. These subsets were called phasing shells in order to stress this difference.

In general, a neighbourhood is an arbitrary (but appropriate) subset of a phasing shell. For instance, for $P\bar{1}$ 17 and 48 magnitudes are in the first phasing shells of the three-phase s.s. and the four-phase s.s. respectively. The first two neighbourhoods given by Hauptman (1976) for the same s.s.'s are subsets constructed by means of 13 and 24 magnitudes respectively. Again, 22 and 67 magnitudes are contained in the second and third phasing shells of a quartet invariant, while subsets with 13 and 21 magnitudes are in the third and fourth Hauptman's (1977*a*) neighbourhoods. In some cases magnitudes contained in Hauptman's neighbourhoods are not merely subsets of suitable phasing shells. For instance, the following six magnitudes (Hauptman, 1976)

$$|E_{2\mathbf{h}}|,\ |E_{\mathbf{h}}|,\ |E_{\mathbf{k}}|,\ |E_{\mathbf{h}\pm\mathbf{k}}|,\ |E_{2\mathbf{k}}|$$

are in the second neighbourhood of the one-phase s.s. $\Phi=\varphi_{2\mathbf{h}}$ in $P\bar{1}$. For the same s.s. the first phasing shell is constructed by means of the seven magnitudes

$$|E_{2\mathbf{h}}|,\ |E_{\mathbf{h}}|,\ |E_{\mathbf{k}}|,\ |E_{\mathbf{h}\pm\mathbf{k}}|,\ |E_{2\mathbf{h}\pm\mathbf{k}}|,$$

among which $|E_{2\mathbf{k}}|$ does not appear.

Methods of neighbourhoods and representations have quite different approaches to phase estimation. When methods were applied to the same practical cases, they required completely different procedures and did not give the same estimations. The case of two-phase s.s.'s is very instructive: Green & Hauptman (1978*a*,*b*) and Hauptman & Green (1978) used the neighbourhood concept and derived some conditional probability distributions for two-phase s.s's in $P2_1$. Different conditional probability distributions were suggested to Giacovazzo (1979) by the method of representations. In general, the number of reflections simultaneously involved in these distributions is much larger than that involved in distributions suggested by the neighbourhood method. A practical effect is that the representations method requires peculiar procedures for phase estimation (see Giacovazzo, Spagna, Vickovic & Viterbo, 1979).

An important quality of the representation theory is that it largely exploits space-group algebra. In fact,

* Part I: Giacovazzo (1977).

† Abbreviations: s.i. = structure invariant, s.s. = structure seminvariant.

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probability distributions and related conclusive formulae can be obtained which hold in any space group. This is quite useful from the practical point of view, because programs for automatic computing with general validity can be written.

So far the method has been applied to: (*a*) estimation of quartet invariants in any space group *via* their first representations (Giacovazzo, 1976; Busetta *et al.*, 1980); (*b*) estimation of one-phase s.s.'s *via* their first and second representations (Giacovazzo, 1978*a*; Burla *et al.*, 1980); (*c*) estimation of two-phase s.s.'s *via* their first representations (references already quoted). Practical tests were successful and proved that the method is an effective tool for phase estimation.

Basic ideas of representation theory were described in Giacovazzo's (1977*b*) paper I. However, not all the theoretical aspects were developed, and some propositions were not algebraically proved. The first aim of this paper is to complete the theoretical development begun in I. The second is to develop the theory further so as to make practical applications easier and the probabilistic estimations of s.s.'s more reliable.

2. Some basic definitions in representations theory

In order to make the reading of this paper easier we recall some basic definitions given in I to which we often refer in this paper. We again denote by $\mathbf{C}_p = (\mathbf{R}_p, \mathbf{T}_p)$, $p = 1, \ldots, m$, the m symmetry operators for a space group of order m ($\mathbf{R}_p$ rotational component, $\mathbf{T}_p$ translational component). Furthermore,

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

will be the general expression for a s.i. or a s.s.

2.1. *The first representation of a s.i. Φ*

If the crystal symmetry is higher than triclinic, a number of symmetry operators may be found in favourable cases such that one or more s.i.'s,

$$\begin{aligned}\Psi_1 &= A_1 \varphi_{\mathbf{h}'_1} + A_2 \varphi_{\mathbf{h}'_2} + \ldots + A_n \varphi_{\mathbf{h}'_n} \\ &= A_1 \varphi_{\mathbf{h}_1 \mathbf{R}_s} + A_2 \varphi_{\mathbf{h}_2 \mathbf{R}_t} + \ldots + A_n \varphi_{\mathbf{h}_n \mathbf{R}_v},\end{aligned}$$

arise in which at least one of the $\mathbf{h}'_j$ vectors does not coincide with $\mathbf{h}_j$. Since

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

$\Psi_1 - \varphi$ is a constant if the geometrical form of the structure factor has been fixed. The collection of the distinct s.i., Ψ_1, obtained when $\mathbf{R}_s, \mathbf{R}_t, \ldots, \mathbf{R}_v$ vary over the set of the m rotation matrices of the actual space group is defined to be the first representation of Φ and will be denoted by $\{\Psi\}_1$.

The first phasing shell is given by the collection of magnitudes which are basis magnitudes (*i.e.* $E_{\mathbf{h}_1}, \ldots, E_{\mathbf{h}_n}$) or cross magnitudes of at least one s.i., Ψ_1. In their turn, the cross vectors of any s.i., Ψ_1, are defined by the expressions

$$m_1 \mathbf{h}'_1 + m_2 \mathbf{h}'_2 + \ldots + m_n \mathbf{h}'_n \qquad (m_p = 0, \ldots, A_p),$$

which are all linear combinations of the vectors $\mathbf{h}'_1, \mathbf{h}'_2, \ldots, \mathbf{h}'_n$ with integer coefficients, $0 \le m_p \le A_p$ if $A_p > 0$; if $A_p < 0$, then the integer coefficients m_p satisfy $A_p \le m_p \le 0$.

The first phasing shell is denoted by $\{B\}_1$.

2.2. *The upper representations of a s.i. Φ*

For any Ψ_1 belonging to $\{\Psi\}_1$, let us 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 the second representation of Φ. The second phasing shell of Φ is the collection of magnitudes which are basis or cross magnitudes of at least one Ψ_2. Likewise, $\Psi_3 = \Psi_2 + \varphi_{\mathbf{l}} - \varphi_{\mathbf{l}}$, *etc.*

The procedure and the definitions are recursive.

The definitions given above are quite clear. Thus, the identification of the various phasing shells for any s.i., Φ, is a straightforward task.

2.3. *The first representation of a s.s. Φ*

It has been known for some time (Hauptman & Karle, 1953) that one-phase s.s.'s can be estimated *via* one or more special triplet invariants. Giacovazzo (1977*b*) first fixed the idea that, whatever the s.s. may be, it can be estimated *via* one or more s.i.'s and that with respect to the procedures for phase estimation, the s.s.'s should be split into two classes.

Let us suppose that Φ, as given by (1), is a s.s.: if there exists a phase $\varphi_{\mathbf{h}}$ and symmetry operators $\mathbf{C}_s, \mathbf{C}_t, \ldots, \mathbf{C}_v, \mathbf{C}_p, \mathbf{C}_q$ such that

$$\Psi_1 = A_1 \varphi_{\mathbf{h}_1 \mathbf{R}_s} + A_2 \varphi_{\mathbf{h}_2 \mathbf{R}_t} + \ldots + A_n \varphi_{\mathbf{h}_n \mathbf{R}_v} + \varphi_{\mathbf{hR}_p} - \varphi_{\mathbf{hR}_q} \qquad (3)$$

is a s.i., then Φ is, by definition, a s.s. of the first rank. Then Φ', defined by

$$\Phi' = A_1 \varphi_{\mathbf{h}_1 \mathbf{R}_s} + A_2 \varphi_{\mathbf{h}_2 \mathbf{R}_t} + \ldots + A_n \varphi_{\mathbf{h}_n \mathbf{R}_v},$$

is also a s.s. of the first rank. We note that, because of (2), Ψ_1 differs from Φ by a constant which arises because of the translational symmetry.

Suppose now that Φ is a s.s. for which (3) does not hold. If two phases $\varphi_{\mathbf{h}}$ and $\varphi_{\mathbf{l}}$ and four symmetry operators $\mathbf{C}_p$, $\mathbf{C}_q$, $\mathbf{C}_i$, $\mathbf{C}_j$ exist in principle ($|E_h|$ and

$|E_l|$ may or may not be experimentally measured) such that

$$\begin{aligned}\Psi_1 &= \Phi' + \varphi_{\mathbf{hR}_p} - \varphi_{\mathbf{hR}_q} + \varphi_{\mathbf{lR}_i} - \varphi_{\mathbf{lR}_j} \\ &= A_1\varphi_{\mathbf{h}_1\mathbf{R}_s} + \ldots + A_n\varphi_{\mathbf{h}_n\mathbf{R}_v} + \varphi_{\mathbf{hR}_p} - \varphi_{\mathbf{hR}_q} \\ &\quad + \varphi_{\mathbf{lR}_i} - \varphi_{\mathbf{lR}_j} \qquad (4)\end{aligned}$$

is a s.i., then Φ is said to be a s.s. of the second rank.

The first representation of a s.s. of the first rank, Φ, is the collection of the Ψ_1's as given by (3). If Φ is a s.s. of the second rank, the collection of the Ψ_1's as given by (4) is the first representation of Φ. In both cases the first representation of Φ will be denoted by $\{\Psi\}_1$, and $\{B\}_1$ will be the collection of the $|E|$ magnitudes which are basis or cross magnitudes of at least one s.i. $\Psi_1 \in \{\Psi\}_1$.

It is now clear that n-phase s.s.'s of first rank will be estimated *via* their first representation, by means of a collection of $(n + 2)$-phase s.i.'s; on the other hand, n-phase s.s.'s of second rank will be estimated by means of a collection of $(n + 4)$-phase s.i.'s.

2.4. *The upper representations of a s.s. Φ*

The first representation of any s.s., Φ, is a collection of s.i.'s; therefore the rules for constructing the upper representations of Φ do not differ from those described for the case in which Φ is a s.i.

Unlike s.i.'s, it is not always straightforward, for any s.s. Φ, to define its first phasing shell; however, when $\{B\}_1$ is known, $\{B\}_n$ is always readily obtainable.

3. Algebraic properties of the s.s.'s of first rank

The effective use of s.s.'s in direct procedures for phase solution requires that: (*a*) the linear combinations of phases which are s.s.'s are identified; (*b*) the rank of these s.s.'s is recognized; (*c*) the first phasing shell is readily found.

The operations for (*a*) do not present any difficulty. In fact, the algebraic conditions to be satisfied were clearly stated by Hauptman & Karle (1953, 1956, 1959) and were listed in a paper by Giacovazzo (1974). Although a table of s.s.'s of first rank for any Hauptman–Karle group has been given in I, the operations for (*b*) can present some difficulties. In particular, in I the algebraic criteria which led to the table were not given. The operations for (*c*) can present major difficulties. In fact, in I we only described some heuristic ways for solving this problem for one and two-phase s.s.'s of the first rank.

We present in this section some general algebraic properties which characterize the s.s.'s of first rank. Algebraic properties of s.s.'s of the second rank will be described in §6. We emphasize the fact that these properties are extremely useful for practical applications because they are the theoretical support for general programs devoted to the automatic estimation of s.s.'s in all the space groups.

Proposition 1. Let $\varphi_{\mathbf{u}_1}, \varphi_{\mathbf{u}_2}, \ldots, \varphi_{\mathbf{u}_n}$ be a set of phases for which the system

$$\begin{aligned}\mathbf{h}_1 - \mathbf{h}_2\mathbf{R}_\beta &= \mathbf{u}_1 && (5.1)\\ \mathbf{h}_2 - \mathbf{h}_3\mathbf{R}_\gamma &= \mathbf{u}_2 && (5.2)\\ \mathbf{h}_3 - \mathbf{h}_4\mathbf{R}_\delta &= \mathbf{u}_3 && (5.3)\\ &\vdots && \vdots\\ \mathbf{h}_{n-1} - \mathbf{h}_n\mathbf{R}_\nu &= \mathbf{u}_{n-1} && (5.n\text{-}1)\\ \mathbf{h}_n - \mathbf{h}_1\mathbf{R}_\alpha &= \mathbf{u}_n && (5.n)\end{aligned}$$

holds. Then $\Phi = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2} + \ldots + \varphi_{\mathbf{u}_n}$ is a s.s. of the first rank.

Proof. We multiply (5.2) by $\mathbf{R}_\beta$, (5.3) by $\mathbf{R}_\gamma\mathbf{R}_\beta$, ..., and we obtain

$$\begin{aligned}&\mathbf{h}_1 - \mathbf{h}_2\mathbf{R}_\beta = \mathbf{u}_1 && (6.1)\\ &\mathbf{h}_2\mathbf{R}_\beta - \mathbf{h}_3\mathbf{R}_\gamma\mathbf{R}_\beta = \mathbf{u}_2\mathbf{R}_\beta && (6.2)\\ &\mathbf{h}_3\mathbf{R}_\gamma\mathbf{R}_\beta - \mathbf{h}_4\mathbf{R}_\delta\mathbf{R}_\gamma\mathbf{R}_\beta = \mathbf{u}_3\mathbf{R}_\gamma\mathbf{R}_\beta && (6.3)\\ &\vdots && \vdots\\ &\mathbf{h}_n\mathbf{R}_\nu\ldots\mathbf{R}_\beta - \mathbf{h}_1\mathbf{R}_\alpha\mathbf{R}_\nu\ldots\mathbf{R}_\beta = \mathbf{u}_n\mathbf{R}_\nu\ldots\mathbf{R}_\beta. && (6.n)\end{aligned}$$

The addition of (6) gives

$$\begin{aligned}&\mathbf{u}_1 + \mathbf{u}_2\mathbf{R}_\beta + \mathbf{u}_3\mathbf{R}_\gamma\mathbf{R}_\beta + \ldots + \mathbf{u}_n\mathbf{R}_\nu\ldots\mathbf{R}_\beta\\ &\quad -\mathbf{h}_1(\mathbf{I} - \mathbf{R}_\alpha\mathbf{R}_\nu\ldots\mathbf{R}_\beta) = 0,\end{aligned}$$

which, compared with (3), proves the statement.

Proposition 2. If $\varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2} + \ldots + \varphi_{\mathbf{u}_n}$ is a s.s. of first rank, there are at least n vectors $\mathbf{h}_1, \mathbf{h}_2, \ldots, \mathbf{h}_n$ and n matrices $\mathbf{R}_\alpha, \mathbf{R}_\beta, \mathbf{R}_\gamma, \ldots, \mathbf{R}_\nu$ such that system (5) holds.

Proof. By hypothesis, at least $n + 2$ rotation matrices $\mathbf{R}_\eta, \mathbf{R}_\psi, \mathbf{R}_\xi, \ldots, \mathbf{R}_y, \mathbf{R}_p, \mathbf{R}_q$ and a vector $\mathbf{h}$ exist such that

$$\mathbf{u}_1\mathbf{R}_\eta + \mathbf{u}_2\mathbf{R}_\psi + \mathbf{u}_3\mathbf{R}_\xi + \ldots + \mathbf{u}_n\mathbf{R}_y + \mathbf{hR}_p - \mathbf{hR}_q = 0. \qquad (7)$$

Writing

$$\begin{aligned}\mathbf{R}_\psi &= \mathbf{R}_\beta\mathbf{R}_\eta\\ \mathbf{R}_\xi &= \mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\eta\\ &\vdots\\ \mathbf{R}_y &= \mathbf{R}_\nu\ldots\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\eta,\end{aligned}$$

we may write (7) as

$$\begin{aligned}&\mathbf{u}_1\mathbf{R}_\eta + \mathbf{u}_2\mathbf{R}_\beta\mathbf{R}_\eta + \mathbf{u}_3\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\eta + \ldots\\ &\quad + \mathbf{u}_n\mathbf{R}_\nu\ldots\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\eta = \mathbf{h}(\mathbf{R}_q - \mathbf{R}_p). \qquad (8)\end{aligned}$$

A more useful form of (8) is

$$\begin{aligned}&\mathbf{u}_1\mathbf{R}_\eta + \mathbf{u}_2\mathbf{R}_\beta\mathbf{R}_\eta + \mathbf{u}_3\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\eta + \ldots\\ &\quad + \mathbf{u}_n\mathbf{R}_\nu\ldots\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\eta = \mathbf{h}_1(\mathbf{R}_\eta - \mathbf{R}_\theta^{-1}\mathbf{R}_p), \qquad (9)\end{aligned}$$

where $\mathbf{h}_1$ and $\mathbf{R}_\theta$ are a suitable vector and matrix respectively for which $\mathbf{h}_1 = \mathbf{h}\mathbf{R}_\theta, \mathbf{R}_q = \mathbf{R}_\theta\mathbf{R}_\eta$. We observe now that for fixed $\mathbf{u}_1$, $\mathbf{h}_1$ and $\mathbf{R}_\beta$ it is always possible to find a vector $\mathbf{h}_2$ such that

$$\mathbf{h}_1 - \mathbf{h}_2\mathbf{R}_\beta = \mathbf{u}_1. \tag{10.1}$$

Again, for fixed $\mathbf{u}_2$, $\mathbf{R}_\gamma$ and $\mathbf{h}_2$, it is always possible to find a vector $\mathbf{h}_3$ such that

$$\mathbf{h}_2 - \mathbf{h}_3\mathbf{R}_\gamma = \mathbf{u}_2. \tag{10.2}$$

Again, for fixed $\mathbf{u}_{n-1}$, $\mathbf{R}_\nu$ and $\mathbf{h}_{n-1}$ it is always possible to find a vector $\mathbf{h}_n$ such that

$$\mathbf{h}_{n-1} - \mathbf{h}_n\mathbf{R}_\nu = \mathbf{u}_{n-1}. \tag{10.n-1}$$

Lastly, for fixed $\mathbf{u}_n$, $\mathbf{R}_\eta$ and $\mathbf{h}_n$ it is always possible to find a vector $\mathbf{k}$ such that

$$\mathbf{h}_n - \mathbf{k}\mathbf{R}_\eta = \mathbf{u}_n. \tag{10.n}$$

If (10.1), (10.2), ..., (10.n) are first multiplied by $\mathbf{R}_\eta$, $\mathbf{R}_\beta\mathbf{R}_\eta$, ..., $\mathbf{R}_\nu$ ... $\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\eta$ respectively and then summed, one obtains

$$\begin{aligned}\mathbf{u}_1\mathbf{R}_\eta + \mathbf{u}_2\mathbf{R}_\beta\mathbf{R}_\eta + \ldots + \mathbf{u}_n\mathbf{R}_\nu\ldots\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\eta \\ = \mathbf{h}_1\mathbf{R}_\eta - \mathbf{k}\mathbf{R}_\eta\mathbf{R}_\nu\ldots\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\eta.\end{aligned} \tag{11}$$

Comparison of (11) with (9) gives

$$\mathbf{h}_1\mathbf{R}_\theta^{-1}\mathbf{R}_p = \mathbf{k}\mathbf{R}_\eta\mathbf{R}_\nu\ldots\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\eta.$$

In other words, $\mathbf{k}$ denotes a reflexion symmetry equivalent to $\mathbf{h}_1$, so that (10.n) may be written as

$$\mathbf{h}_n - \mathbf{h}_1\mathbf{R}_\alpha = \mathbf{u}_n, \tag{12}$$

where $\mathbf{R}_\alpha = \mathbf{R}_\theta^{-1}\mathbf{R}_p\mathbf{R}_\eta^{-1}\mathbf{R}_\beta^{-1}\mathbf{R}_\gamma^{-1}\ldots\mathbf{R}_\nu^{-1}$. The proposition is now proved because (10.1), (10.2), ..., (10.n) form a system like (5).

Propositions 1 and 2 ensure that the more general expressions for the s.s.'s of first rank are:

(*a*) $\Phi = \varphi_\mathbf{u} = \varphi_{\mathbf{h}(\mathbf{I}-\mathbf{R}_\alpha)}$, for one-phase s.s.'s;

(*b*) $\Phi = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2} = \varphi_{\mathbf{h}_1-\mathbf{h}_2\mathbf{R}_\beta} + \varphi_{\mathbf{h}_2-\mathbf{h}_1\mathbf{R}_\alpha}$, for two-phase s.s's;

(*c*) $\Phi = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2} + \varphi_{\mathbf{u}_3} = \varphi_{\mathbf{h}_1-\mathbf{h}_2\mathbf{R}_\beta} + \varphi_{\mathbf{h}_2-\mathbf{h}_3\mathbf{R}_\gamma} + \varphi_{\mathbf{h}_3-\mathbf{h}_1\mathbf{R}_\alpha}$ for three-phase s.s.'s;

(*d*) $\Phi = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2} + \varphi_{\mathbf{u}_3} + \varphi_{\mathbf{u}_4} = \varphi_{\mathbf{h}_1-\mathbf{h}_2\mathbf{R}_\beta} + \varphi_{\mathbf{h}_2-\mathbf{h}_3\mathbf{R}_\gamma} + \varphi_{\mathbf{h}_3-\mathbf{h}_4\mathbf{R}_\delta} + \varphi_{\mathbf{h}_4-\mathbf{h}_1\mathbf{R}_\alpha}$ for four-phase s.s.'s; *etc.*

This result is not trivial. In fact it ensures that, whatever the space group may be and for any s.s. of the first rank, Φ, the set of vectors $\{\mathbf{U}\} = (\mathbf{u}_1, \mathbf{u}_2, \ldots, \mathbf{u}_n)$ can be expressed in terms of a fundamental set $\{\mathbf{h}\} = (\mathbf{h}_1, \mathbf{h}_2, \ldots, \mathbf{h}_n)$. Provided we are able, for any Φ, to express in terms of $\{\mathbf{h}\}$ the basis vectors of any $\Psi_1 \in \{\Psi\}_1$, then the conditional distribution $P(\Phi|\{B\}_1)$ may in principle be calculated in a form valid for all the space groups.

For example, $\Phi = \varphi_{\mathbf{u}_1} = \varphi_{\mathbf{h}(\mathbf{I}-\mathbf{R}_\eta)}$ is a s.s. of the first rank in any space group which contains the rotation matrix $\mathbf{R}_\eta$. Furthermore, $\Psi_1 = \varphi_{\mathbf{h}(\mathbf{I}-\mathbf{R}_\eta)} - \varphi_\mathbf{h} + \varphi_{\mathbf{h}\mathbf{R}_\eta}$ is the general expression of the s.i.'s, Ψ_1, belonging to the first representation of Φ. So the joint probability distribution, $P(E_{\mathbf{h}(\mathbf{I}-\mathbf{R}_\eta)}, \{E_\mathbf{h}\})$, may be used in order to estimate $\varphi_{\mathbf{u}_1}$ in any space group *via* its first representation. From them the conditional distribution $P(\varphi_{\mathbf{u}_1}| |E_{\mathbf{u}_1}|, \{|E_\mathbf{h}|\})$ may be derived. This conditional distribution may be specialized for a given space group just by assigning, according to point-group symmetry, the actual values of $\mathbf{R}_\eta$ and of the $|E_\mathbf{h}|$'s.

The problem is now that of obtaining, for a given s.s. of first rank, Φ, the set $\{\mathbf{h}\}$ from the set $\{\mathbf{U}\}$. Multiplying (5.1) by $\mathbf{I}$, (5.2) by $\mathbf{R}_\beta$, (5.3) by $\mathbf{R}_\gamma\mathbf{R}_\beta$, ..., (5.$n$) by $\mathbf{R}_\nu\ldots\mathbf{R}_\gamma\mathbf{R}_\beta$ and summing, one finds

$$\begin{aligned}\mathbf{h}_1(\mathbf{I} - \mathbf{R}_\alpha\mathbf{R}_\nu\ldots\mathbf{R}_\gamma\mathbf{R}_\beta) = \mathbf{u}_1 + \mathbf{u}_2\mathbf{R}_\beta + \mathbf{u}_3\mathbf{R}_\gamma\mathbf{R}_\beta \\ + \ldots + \mathbf{u}_n\mathbf{R}_\nu\ldots\mathbf{R}_\gamma\mathbf{R}_\beta.\end{aligned} \tag{13.1}$$

In a similar way one can obtain

$$\begin{aligned}&\mathbf{h}_2(\mathbf{I} - \mathbf{R}_\beta\mathbf{R}_\alpha\mathbf{R}_\nu\ldots\mathbf{R}_\delta\mathbf{R}_\gamma) \\ &= \mathbf{u}_2 + \mathbf{u}_3\mathbf{R}_\gamma + \mathbf{u}_4\mathbf{R}_\delta\mathbf{R}_\gamma + \ldots + \mathbf{u}_n\mathbf{R}_\nu\ldots\mathbf{R}_\delta\mathbf{R}_\gamma \\ &\quad + \mathbf{u}_1\mathbf{R}_\alpha\mathbf{R}_\nu\ldots\mathbf{R}_\delta\mathbf{R}_\gamma,\end{aligned} \tag{13.2}$$

$$\begin{aligned}&\mathbf{h}_3(\mathbf{I} - \mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\alpha\mathbf{R}_\nu\ldots\mathbf{R}_\delta) \\ &= \mathbf{u}_3 + \mathbf{u}_4\mathbf{R}_\delta + \ldots + \mathbf{u}_n\mathbf{R}_\nu\ldots\mathbf{R}_\delta \\ &\quad + \mathbf{u}_1\mathbf{R}_\alpha\mathbf{R}_\nu\ldots\mathbf{R}_\delta + \mathbf{u}_2\mathbf{R}_\beta\mathbf{R}_\alpha\mathbf{R}_\nu\ldots\mathbf{R}_\delta,\end{aligned} \tag{13.3}$$

$$\begin{aligned}&\mathbf{h}_n(\mathbf{I} - \mathbf{R}_\nu\ldots\mathbf{R}_\delta\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\alpha) \\ &= \mathbf{u}_n + \mathbf{u}_1\mathbf{R}_\alpha + \mathbf{u}_2\mathbf{R}_\beta\mathbf{R}_\alpha + \ldots + \mathbf{u}_{n-1}\mathbf{R}_{\nu-1}\ldots \\ &\quad \times \mathbf{R}_\delta\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\alpha.\end{aligned} \tag{13.n}$$

Equations (13) yield the set $\{\mathbf{h}\}$ from the set $\{\mathbf{U}\}$. However, $(\mathbf{I} - \mathbf{R}_i \ldots \mathbf{R}_j)$ may be a singular matrix. Therefore, depending on the values of $\mathbf{u}_1, \mathbf{u}_2, \ldots, \mathbf{u}_n, \mathbf{R}_\alpha, \mathbf{R}_\beta, \ldots, \mathbf{R}_\nu$, the set $(\mathbf{h}_1, \mathbf{h}_2, \ldots, \mathbf{h}_n)$ may not be uniquely determined by (13); instead, one or more sets $(\mathbf{h}_1, \mathbf{h}_2, \ldots, \mathbf{h}_n)$ may exist which satisfy (13), and consequently (5) too. The more general way of dealing with this problem is to introduce the concept of the reflexive generalized inverse of a matrix (see, for example, Ben-Israel & Greville, 1974).

Definition. If $\mathbf{A}$ is an $m \times n$ matrix, an $n \times m$ matrix $\mathbf{A}^*$ is said to be a reflexive generalized inverse of $\mathbf{A}$ provided $\mathbf{A}\mathbf{A}^*\mathbf{A} = \mathbf{A}$ and $\mathbf{A}^*\mathbf{A}\mathbf{A}^* = \mathbf{A}^*$.

Property. A system of linear equations

$$\mathbf{A}\mathbf{x} = \mathbf{b} \tag{14}$$

has a solution if and only if

$$\mathbf{A}\mathbf{A}^*\mathbf{b} = \mathbf{b}. \tag{15}$$

Furthermore, if (14) has a solution then

$$\mathbf{x} = \mathbf{A}^*\mathbf{b} + (\mathbf{I} - \mathbf{A}^*\mathbf{A})\,\mathbf{z}, \tag{16}$$

where $\mathbf{z}$ is an arbitrary vector.

From a formal point of view, (16) may be easily applied to (13): *i.e.* for (13.1),

$$\mathbf{A} = (\mathbf{I} - \tilde{\mathbf{R}}_\beta \tilde{\mathbf{R}}_\gamma \ldots \tilde{\mathbf{R}}_\nu \tilde{\mathbf{R}}_\alpha),$$

$$\mathbf{b} = \mathbf{u}_1 + \mathbf{u}_2 \mathbf{R}_\beta + \ldots + \mathbf{u}_n \mathbf{R}_\nu \ldots \mathbf{R}_\gamma \mathbf{R}_\beta.$$

In our case, however, $\mathbf{A}$ and $\mathbf{b}$ are an integral matrix and vector respectively; furthermore, we are interested only in integral solutions.

Hurt & Waid's (1970) theorem for diophantine systems may be used, according to which, if $\mathbf{A}$ and $\mathbf{b}$ are integral, then (14) has an integral solution if and only if

$$\mathbf{A}^*\mathbf{b} \equiv 0 \ (\mathrm{mod}\ 1). \tag{17}$$

In this case the general integral solution of (14) is given by (16), where $\mathbf{z}$ is an arbitrary integral vector. With this background, we are able to obtain, from (13), the general expressions for the vectors $\mathbf{h}_1, \mathbf{h}_2, \ldots, \mathbf{h}_n$, given $\mathbf{u}_1, \mathbf{u}_2, \ldots, \mathbf{u}_n$. Furthermore, (13) suggests, for a given s.s. of the first rank, Φ, the expression of the s.i. $\Psi_1 \in \{\Psi\}_1$:

$$\varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2\mathbf{R}_\beta} + \varphi_{\mathbf{u}_3\mathbf{R}_\gamma\mathbf{R}_\beta} + \ldots + \varphi_{\mathbf{u}_n\mathbf{R}_\nu\ldots\mathbf{R}_\gamma\mathbf{R}_\beta} - \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_1\mathbf{R}_\alpha\mathbf{R}_\nu\ldots\mathbf{R}_\gamma\mathbf{R}_\beta}, \tag{18.1}$$

$$\varphi_{\mathbf{u}_2} + \varphi_{\mathbf{u}_3\mathbf{R}_\gamma} + \varphi_{\mathbf{u}_4\mathbf{R}_\delta\mathbf{R}_\gamma} + \ldots + \varphi_{\mathbf{u}_n\mathbf{R}_\nu\ldots\mathbf{R}_\delta\mathbf{R}_\gamma} + \varphi_{\mathbf{u}_1\mathbf{R}_\alpha\mathbf{R}_\nu\ldots\mathbf{R}_\delta\mathbf{R}_\gamma} - \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_2\mathbf{R}_\beta\mathbf{R}_\alpha\mathbf{R}_\nu\ldots\mathbf{R}_\delta\mathbf{R}_\gamma}, \tag{18.2}$$

$$\varphi_{\mathbf{u}_3} + \varphi_{\mathbf{u}_4\mathbf{R}_\delta} + \ldots + \varphi_{\mathbf{u}_n\mathbf{R}_\nu\ldots\mathbf{R}_\delta} + \varphi_{\mathbf{u}_1\mathbf{R}_\alpha\mathbf{R}_\nu\ldots\mathbf{R}_\gamma} + \varphi_{\mathbf{u}_2\mathbf{R}_\beta\mathbf{R}_\alpha\mathbf{R}_\nu\ldots\mathbf{R}_\delta} - \varphi_{\mathbf{h}_3} + \varphi_{\mathbf{h}_3\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\alpha\mathbf{R}_\nu\ldots\mathbf{R}_\delta}, \tag{18.3}$$

$$\vdots$$

$$\varphi_{\mathbf{u}_n} + \varphi_{\mathbf{u}_1\mathbf{R}_\alpha} + \varphi_{\mathbf{u}_2\mathbf{R}_\beta\mathbf{R}_\alpha} + \ldots + \varphi_{\mathbf{u}_{n-1}\ldots\mathbf{R}_\delta\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\alpha} - \varphi_{\mathbf{h}_n} + \varphi_{\mathbf{h}_n\mathbf{R}_\nu\ldots\mathbf{R}_\delta\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\alpha}. \tag{18.n}$$

It is now a trivial task to write down the magnitudes in the first phasing shell of Φ: one only needs to write down the set of magnitudes which are basis or cross magnitudes of at least one s.i. (18).

We note again that every (13.i) can be satisfied by more than one vector $\mathbf{h}_i$. If we suppose that for every (13.i) we know the complete set of solutions $\{\mathbf{h}_i\}$, then the problem of finding a particular set $(\mathbf{h}_1, \mathbf{h}_2, \ldots, \mathbf{h}_n)$ which satisfies system (5) is trivial. In fact, if a value $\mathbf{h}_1 \in \{\mathbf{h}_1\}$ is arbitrarily chosen, then $\mathbf{h}_2 \in \{\mathbf{h}_2\}$ is fixed by (5.1), $\mathbf{h}_3$ by (5.2), *etc.* The following theorem enables one to obtain the complete set of solutions $(\mathbf{h}_1, \mathbf{h}_2, \ldots, \mathbf{h}_n)$ which satisify (5).

Proposition 3. Let $\mathbf{h}_1, \mathbf{h}_2, \ldots, \mathbf{h}_n$ be a solution of the system (5) for fixed matrices $\mathbf{R}_\alpha, \mathbf{R}_\beta, \ldots, \mathbf{R}_\nu$. Then also $\mathbf{h}_1 + \mathbf{k}_1, \mathbf{h}_2 + \mathbf{k}_2, \ldots, \mathbf{h}_n + \mathbf{k}_n$ satisfy (5) provided

$$\mathbf{k}_1(\mathbf{I} - \mathbf{R}_\alpha \mathbf{R}_\nu \ldots \mathbf{R}_\gamma \mathbf{R}_\beta) = 0,$$

$$\mathbf{k}_2(\mathbf{I} - \mathbf{R}_\beta \mathbf{R}_\alpha \mathbf{R}_\nu \ldots \mathbf{R}_\delta \mathbf{R}_\gamma) = 0,$$

$$\vdots$$

$$\mathbf{k}_n(\mathbf{I} - \mathbf{R}_\nu \ldots \mathbf{R}_\delta \mathbf{R}_\gamma \mathbf{R}_\beta \mathbf{R}_\alpha) = 0.$$

Proof. Because of the hypothesis, $\mathbf{h}_1 + \mathbf{k}_1, \mathbf{h}_2 + \mathbf{k}_2, \ldots, \mathbf{h}_n + \mathbf{k}_n$ is a solution of (5) if

$$\mathbf{k}_1 - \mathbf{k}_2 \mathbf{R}_\beta = 0 \tag{19.1}$$

$$\mathbf{k}_2 - \mathbf{k}_3 \mathbf{R}_\gamma = 0 \tag{19.2}$$

$$\mathbf{k}_3 - \mathbf{k}_4 \mathbf{R}_\delta = 0 \tag{19.3}$$

$$\vdots$$

$$\mathbf{k}_n - \mathbf{k}_1 \mathbf{R}_\alpha = 0. \tag{19.n}$$

Multiplying (19.1) by $\mathbf{I}$, (19.2) by $\mathbf{R}_\beta$, (19.3) by $\mathbf{R}_\gamma \mathbf{R}_\beta$, ..., (19.$n$) by $\mathbf{R}_\nu \ldots \mathbf{R}_\gamma \mathbf{R}_\beta$ and summing, one finds

$$\mathbf{k}_1(\mathbf{I} - \mathbf{R}_\alpha \mathbf{R}_\nu \ldots \mathbf{R}_\gamma \mathbf{R}_\beta) = 0.$$

Analogous conditions for $\mathbf{k}_2, \mathbf{k}_3, \ldots, \mathbf{k}_n$ are obtainable in a similar way.

4. First-rank seminvariant modulus vectors

The results in §3 enable us to describe a simple procedure which singles out the algebraic conditions which characterize the s.s.'s of the first rank. Without any loss of generality, we will first treat one-phase s.s.'s of the first rank: the results however are general.

According to §§2 and 3, $\varphi_{\mathbf{H}}$ is a s.s. of first rank if a vector $\mathbf{h}$ and a rotation matrix $\mathbf{R}_n$ exist such that $\mathbf{A}_n \mathbf{h} = (\mathbf{I} - \tilde{\mathbf{R}}_n)\mathbf{h} = \mathbf{H}$. Let us try to solve the system with respect to $\mathbf{h}$ for any $\mathbf{R}_n$ in $P312$. For this space group the symmetry relations are

$$(xyz);\ (\bar{y}\ x - y\ z);\ (y - x\ \bar{x}z);$$

$$(\bar{y}\bar{x}\bar{z});\ (x\ x - y\ \bar{z});\ (y - x\ y\bar{z}).$$

The matrices $\mathbf{A}_n$ are given by

$$\mathbf{A}_2 = \begin{vmatrix} 1 & \bar{1} & 0 \\ 1 & 2 & 0 \\ 0 & 0 & 0 \end{vmatrix}, \qquad \mathbf{A}_3 = \begin{vmatrix} 2 & 1 & 0 \\ \bar{1} & 1 & 0 \\ 0 & 0 & 0 \end{vmatrix},$$

$$\mathbf{A}_4 = \begin{vmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 2 \end{vmatrix}, \qquad \mathbf{A}_5 = \begin{vmatrix} 0 & \bar{1} & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{vmatrix},$$

$$\mathbf{A}_6 = \begin{vmatrix} 2 & 0 & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & 2 \end{vmatrix}$$

and their generalized inverses by

$$\mathbf{A}_2^* = \begin{vmatrix} 2/3 & 1/3 & 0 \\ -1/3 & 1/3 & 0 \\ 0 & 0 & 0 \end{vmatrix}; \qquad \mathbf{A}_3^* = \begin{vmatrix} 1/3 & -1/3 & 0 \\ 1/3 & 2/3 & 0 \\ 0 & 0 & 0 \end{vmatrix};$$

$$\mathbf{A}_4^* = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1/2 \end{vmatrix}; \qquad \mathbf{A}_5^* = \begin{vmatrix} 0 & 0 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1/2 \end{vmatrix};$$

$$\mathbf{A}_6^* = \begin{vmatrix} 0 & -1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1/2 \end{vmatrix}.$$

Let us apply conditions (15) and (17) to $\mathbf{A}_2$. Writing $\mathbf{H} \equiv (H_1, H_2, H_3)$ and $\mathbf{h} \equiv (h_1, h_2, h_3)$, we obtain

$$\mathbf{A}_2\,\mathbf{A}_2^*\,\mathbf{H} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{vmatrix} \times \begin{vmatrix} H_1 \\ H_2 \\ H_3 \end{vmatrix} = \begin{vmatrix} H_1 \\ H_2 \\ 0 \end{vmatrix} = \begin{vmatrix} H_1 \\ H_2 \\ H_3 \end{vmatrix},$$

$$\mathbf{A}_2^*\,\mathbf{H} = [(2H_1 + H_2)/3, (-H_1 + H_2)/3, 0] \equiv 0 \bmod (1, 1, 1),$$

from which

$$(H_1 - H_2, H_3) \equiv 0 \bmod (3,0).$$

The following generalized solution arises from (16)

$$\mathbf{h} = [(2H_1 + H_2)/3, (-H_1 + H_2)/3, l],$$

where l is a free index.

Let us now apply conditions (15) and (17) to $\mathbf{A}_3, \ldots, \mathbf{A}_n$. We obtain:

for A_3 $(H_1 - H_2, H_3) \equiv 0 \bmod (3,0)$,

$$\mathbf{h} = [(H_1 - H_2)/3, (H_1 + 2H_2)/3, l];$$

for A_4 $(H_1 - H_2, H_3) \equiv 0 \bmod (0,2)$,

$$\mathbf{h} = (H_1 - k, k, H_3/2);$$

for A_5 $(2H_1 + H_2, H_3) \equiv 0 \bmod (0,2)$,

$$\mathbf{h} = (h, -H_1, H_3/2);$$

for A_6 $(H_1 + 2H_2, H_3) \equiv 0 \bmod (0,2)$

$$\mathbf{h} = (-H_2, k, H_3/2).$$

It may be concluded that $\varphi_{\mathbf{H}}$ is a s.s. of first rank in $P312$ if $\mathbf{H}$ or any symmetry equivalent satisfies

$$(H_1 - H_2, H_3) \equiv 0 \bmod (3,0) \text{ or } (0,2). \qquad (20)$$

In an analogous way it may be shown that $\Phi = \varphi_{\mathbf{u}} + \varphi_{\mathbf{v}}$ is a s.s. of first rank in $P312$ if at least a pair of matrices $\mathbf{R}_p$ and $\mathbf{R}_q$ exist such that $\mathbf{uR}_p + \mathbf{vR}_q \equiv (H_1,H_2,H_3)$ satisfies condition (20).

The use of these results in practical applications may be simplified if, by a procedure analogous to that introduced by Hauptman & Karle (1953, 1956), we consider $(H_1 - H_2, H_3)$ as the first-rank vector seminvariantly associated with $\mathbf{H}$, and (3,0), (0,2) as the first-rank seminvariant modulus vectors.

For example, (H_1,H_2,H_3) is the first-rank vector seminvariantly associated with $\mathbf{H}$ for the symmetry class 222; (2,2,0), (2,0,2) and (0,2,2) are the first-rank seminvariant modulus vectors. A short list of the first-rank vectors seminvariantly associated with $\mathbf{H}$ and of the first-rank seminvariant modulus vectors was given in the Appendix of paper I.

5. Numerical applications

In order to clarify the algebraic procedures described above and the role of point-group symmetry we give some numerical examples in $P\bar{1}$, $P2_1$, $P2_12_12_1$ and $Pmmm$. The notation of symmetry operators in $P2_12_12_1$ and $Pmmm$ follows the following.

$P2_12_12_1$: (x,y,z), $(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z)$, $(\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z)$, $(\frac{1}{2} + x, \frac{1}{2} - y, \bar{z})$;

$Pmmm$: (x,y,z), $(\bar{x},\bar{y},\bar{z})$, $(\bar{x},\bar{y},z)$, $(x,\bar{y},\bar{z})$, $(\bar{x},y,\bar{z})$, $(x,y,\bar{z})$, $(\bar{x},y,z)$, $(x,\bar{y},z)$.

Example 1. $\Phi = \varphi_{\mathbf{u}} = \varphi_{600}$ is a s.s. of first rank in $P2_1$. According to previous results we can write $\mathbf{u} = \mathbf{h}(\mathbf{I} - \mathbf{R}_2)$. For $\mathbf{A} = \mathbf{A}_2 = (\mathbf{I} - \mathbf{R}_2)$, (16) gives

$$\mathbf{h} = \mathbf{A}_2^*\,\mathbf{u} + (\mathbf{I} - \mathbf{A}_2^*\,\mathbf{A}_2)\,\mathbf{z}, \qquad (21)$$

where $\mathbf{z}$ is an arbitrary integral vector and

$$\mathbf{A}_2^* = \begin{vmatrix} 1/2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1/2 \end{vmatrix}.$$

Then, $\mathbf{h} = (300) + (0k0) = (3k0)$, where k is a free index. According to (18), the first representation of Φ is the collection of the s.i.'s

$$\Psi_1 = \varphi_{\mathbf{h}(\mathbf{I}-\mathbf{R}_2)} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{hR}_2} = \varphi_{600} - \varphi_{3k0} + \varphi_{\bar{3}k0}.$$

In $P2_12_12_1$, (15) is satisfied, given $\mathbf{u} = (600)$, by both $\mathbf{A}_2^*$ and $\mathbf{A}_3^*$, where

$$\mathbf{A}_3^* = \begin{vmatrix} 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & 0 \end{vmatrix}.$$

Then, in addition to (21),

$$\mathbf{h}' = \mathbf{A}_3^*\,\mathbf{u} + (\mathbf{I} - \mathbf{A}_3^*\,\mathbf{A}_3)\,\mathbf{z} \qquad (22)$$

is a solution of the system $\mathbf{u} = \mathbf{h}(\mathbf{I} - \mathbf{R}_n)$. From (22) one obtains $\mathbf{h}' = (300) + (00l) = (30l)$ where l is a free index. Then, according to (18), the pair of s.i.'s,

$$\Psi_1 = \varphi_{\mathbf{u}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{hR}_2} = \varphi_{600} - \varphi_{3k0} + \varphi_{\bar{3}k0},$$

$$\Psi_1' = \varphi_{\mathbf{u}} - \varphi_{\mathbf{h}'} + \varphi_{\mathbf{h}'\mathbf{R}_3} = \varphi_{600} - \varphi_{30l} + \varphi_{\bar{3}0l},$$

constitute the first representation of Φ provided k and l range over the integers.

In *Pmmm*, (15) is satisfied also by $\mathbf{A}_7^*$, where

$$\mathbf{A}_7^* = \begin{vmatrix} 1/2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}.$$

Solving $\mathbf{h}'' = \mathbf{A}_7^*\,\mathbf{u} + (\mathbf{I} - \mathbf{A}_7^*\,\mathbf{A}_7)\,\mathbf{z}$ gives $\mathbf{h}'' = (3kl)$. Solutions obtained by means of the other rotation matrices are all subsets of $\mathbf{h}''$. Thus, according to (18), the s.i.'s

$$\Psi'' = \varphi_{600} - \varphi_{3kl} + \varphi_{\bar{3}kl}$$

constitute the first representation of φ_{600} in *Pmmm*.

Example 2. $\Phi = \Phi_{123} + \varphi_{7\bar{2}5}$ is a two-phase s.s. of the first rank in $P2_1$. According to previous results, we can write $\Phi = \varphi_{\mathbf{h}_1-\mathbf{h}_2\mathbf{R}_\beta} + \varphi_{\mathbf{h}_2-\mathbf{h}_1\mathbf{R}_\alpha}$. Then, because of (13), the solution of the system

$$\mathbf{h}_1 - \mathbf{h}_2\mathbf{R}_\beta = \mathbf{u}_1$$
$$\mathbf{h}_2 - \mathbf{h}_1\mathbf{R}_\alpha = \mathbf{u}_2$$

is given by

$$\mathbf{h}_1(\mathbf{I} - \mathbf{R}_\alpha\mathbf{R}_\beta) = \mathbf{u}_1 + \mathbf{u}_2\mathbf{R}_\beta,\ \mathbf{h}_2(\mathbf{I} - \mathbf{R}_\beta\mathbf{R}_\alpha) = \mathbf{u}_2 + \mathbf{u}_1\mathbf{R}_\alpha. \tag{23}$$

According to (15), the system (23) has no solution when $\mathbf{R}_\alpha\mathbf{R}_\beta = \mathbf{I}$. When $\mathbf{R}_\alpha = \mathbf{I}$, $\mathbf{R}_\beta = \mathbf{R}_2$, we obtain, according to (15) and (16),

$$\begin{aligned} \mathbf{h}_1 &= \mathbf{A}_2^*(\mathbf{u}_1 + \mathbf{u}_2\,\mathbf{R}_2) + (\mathbf{I} - \mathbf{A}_2^*\,\mathbf{A}_2)\mathbf{z} \\ &= (\bar{3}0\bar{1}) + (0k0) = (\bar{3}k\bar{1}), \\ \mathbf{h}_2 &= \mathbf{A}_2(\mathbf{u}_2 + \mathbf{u}_1) + (\mathbf{I} - \mathbf{A}_2^*\,\mathbf{A}_2)\mathbf{z} \\ &= (404) + (0k0) = (4k4). \end{aligned} \tag{24}$$

Equations (18) reduce then to

$$\Psi_1 = \varphi_{123} + \varphi_{\bar{7}2\bar{5}} - \varphi_{\bar{3}k\bar{1}} + \varphi_{3k1},$$
$$\Psi_1' = \varphi_{7\bar{2}5} + \varphi_{123} - \varphi_{4k4} + \varphi_{\bar{4}k\bar{4}}.$$

The combination $\mathbf{R}_\alpha = \mathbf{R}_2$, $\mathbf{R}_\beta = \mathbf{I}$ does not give further solutions. The first phasing shell is then

$$\{B\}_1 = \{R_{123}, R_{725}, R_{3k1}, R_{4k4}, R_{602}, R_{808}\}, \tag{25}$$

where k is a free index.

In $P2_12_12_1$, the two phases φ_{123} and φ_{725} give rise to two s.s.'s of the first rank of type $\Phi_1 = \varphi_{\mathbf{u}_1} - \varphi_{\mathbf{u}_2} = \varphi_{123} + \varphi_{\bar{7}\bar{2}5}$ and $\Phi_2 = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2} = \varphi_{123} + \varphi_{\bar{7}\bar{2}5}$ which can be estimated independently because they do not have identical phasing shells. If (24) is applied to Φ_1, the same solution as in $P2_1$ is obtained. Therefore, (25) is the first phasing shell of $\varphi_{123} + \varphi_{7\bar{2}5}$ in $P2_12_12_1$ too.

If (24) is applied to the pair $[\mathbf{u}_1 = (123), \mathbf{u}_2 = (\bar{7}\bar{2}5)]$, the following solutions arise: $\mathbf{h}_1 = (4k\bar{1})$, $\mathbf{h}_2 = (\bar{3}k4)$. The first representation of Φ_2 is then, according to (18),

$$\Psi_1 = \varphi_{123} + \varphi_{7\bar{2}\bar{5}} - \varphi_{4k\bar{1}} + \varphi_{\bar{4}k1},$$
$$\Psi_1' = \varphi_{\bar{7}\bar{2}5} + \varphi_{123} - \varphi_{\bar{3}k4} + \varphi_{3k\bar{4}}.$$

The first phasing shell of Φ_2 is therefore

$$\{B\}_1 = \{R_{123}, R_{725}, R_{3k4}, R_{4k1}, R_{802}, R_{608}\}.$$

Example 3. $\Phi = \varphi_{234} + \varphi_{858}$ is a two-phase s.s. in $P\bar{1}$ and in *Pmmm*. We apply (23) and (24) in $P\bar{1}$ for $\mathbf{R}_\alpha = \mathbf{I}$, $\mathbf{R}_\beta = \mathbf{R}_2 = -\mathbf{I}$. As

$$\mathbf{A}_2^* = \begin{vmatrix} 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & 1/2 \end{vmatrix},$$

(24) gives $\mathbf{h}_1 = (\mathbf{u}_1 - \mathbf{u}_2)/2 = (\bar{3}\bar{1}\bar{2})$, $\mathbf{h}_2 = (\mathbf{u}_1 + \mathbf{u}_2)/2 = (546)$. Then (18) leads to the first representation of Φ:

$$\Psi_1 = \varphi_{234} + \varphi_{\bar{8}\bar{5}\bar{8}} + \varphi_{312} + \varphi_{312},$$
$$\Psi_1' = \varphi_{858} + \varphi_{234} - \varphi_{546} - \varphi_{546}.$$

The first phasing shell of Φ is therefore

$$\{B\}_1 = \{R_{234}, R_{858}, R_{312}, R_{546}, R_{624}, R_{10,8,12}\}.$$

In *Pmmm*, (15) is satisfied when $\mathbf{A}_{\alpha,\beta} = \mathbf{A} = (\mathbf{I} - \mathbf{R}_\alpha\,\mathbf{R}_\beta)$ assumes the indices (1,2), (3,6), (4,7), (5,8). Then, according to (13) and (16),

$$\mathbf{h}_1 = \mathbf{A}_{\alpha,\beta}^*(\mathbf{u}_1 + \mathbf{u}_2\mathbf{R}_\beta) + (\mathbf{I} - \mathbf{A}_{\alpha,\beta}^*\,\mathbf{A}_{\alpha,\beta})\,\mathbf{z},$$
$$\mathbf{h}_2 = \mathbf{A}_{\beta,\alpha}^*(\mathbf{u}_2 + \mathbf{u}_1\mathbf{R}_\alpha) + (\mathbf{I} - \mathbf{A}_{\beta,\alpha}^*\,\mathbf{A}_{\beta,\alpha})\,\mathbf{z}.$$

For the matrix involved $\mathbf{A}_{\alpha,\beta}^*\,\mathbf{A}_{\alpha,\beta} = \mathbf{I}$. The following results are obtained:

$$\mathbf{A}_{1,2}: \mathbf{h}_1 = (\bar{3}\bar{1}\bar{2}),\ \mathbf{h}_2 = (546);$$
$$\mathbf{A}_{3,6}: \mathbf{h}_1 = (54\bar{2}),\ \mathbf{h}_2 = (316);$$
$$\mathbf{A}_{4,7}: \mathbf{h}_1 = (\bar{3}46),\ \mathbf{h}_2 = (512);$$
$$\mathbf{A}_{5,8}: \mathbf{h}_1 = (5\bar{1}6),\ \mathbf{h}_2 = (342).$$

The first representation of Φ is therefore the collection of the following eight s.i.'s:

$$\Psi_1 = \varphi_{234} + \varphi_{\bar{8}\bar{5}\bar{8}} + \varphi_{312} + \varphi_{312},$$
$$\Psi_1' = \varphi_{858} + \varphi_{234} - \varphi_{546} - \varphi_{546},$$
$$\Psi_1'' = \varphi_{234} + \varphi_{85\bar{8}} - \varphi_{54\bar{2}} + \varphi_{\bar{5}\bar{4}2},$$
$$\Psi_1''' = \varphi_{858} + \varphi_{\bar{2}\bar{3}4} - \varphi_{\bar{3}16} + \varphi_{\bar{3}\bar{1}\bar{6}},$$
$$\Psi_1^{\mathrm{IV}} = \varphi_{234} + \varphi_{\bar{8}58} - \varphi_{\bar{3}46} + \varphi_{3\bar{4}\bar{6}},$$
$$\Psi_1^{\mathrm{V}} = \varphi_{858} + \varphi_{\bar{2}3\bar{4}} - \varphi_{512} + \varphi_{\bar{5}\bar{1}\bar{2}},$$
$$\Psi_1^{\mathrm{VI}} = \varphi_{234} + \varphi_{8\bar{5}\bar{8}} - \varphi_{5\bar{1}6} + \varphi_{\bar{5}1\bar{6}},$$
$$\Psi_1^{\mathrm{VII}} = \varphi_{858} + \varphi_{\bar{2}3\bar{4}} - \varphi_{342} + \varphi_{\bar{3}\bar{4}\bar{2}}.$$

Lastly, the first phasing shell of Φ is

$$\begin{aligned} \{B\}_1 = \{&R_{234}, R_{858}, R_{312}, R_{546}, R_{624}, \\ &R_{10,8,12}, R_{345}, R_{512}, R_{6,8,12}, R_{10,2,4}, \\ &R_{516}, R_{342}, R_{10,2,12}, R_{684}, R_{542}, \\ &R_{316}, R_{10,8,4}, R_{6,2,12}\}. \end{aligned}$$

Example 4. $\Phi = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2} + \varphi_{\mathbf{u}_3} = \varphi_{123} + \varphi_{334} + \varphi_{6\bar{5}5}$ is a s.s. of first rank in $P2_1$. According to previous results, we can write $\Phi = \varphi_{\mathbf{h}_1 - \mathbf{h}_2\mathbf{R}_\beta} + \varphi_{\mathbf{h}_2 - \mathbf{h}_3\mathbf{R}_\gamma} + \varphi_{\mathbf{h}_3 - \mathbf{h}_1\mathbf{R}_\alpha}$. Because of (13), the solution of the system

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

is given by

$$\mathbf{h}_1(\mathbf{I} - \mathbf{R}_\alpha\mathbf{R}_\gamma\mathbf{R}_\beta) = \mathbf{u}_1 + \mathbf{u}_2\mathbf{R}_\beta + \mathbf{u}_3\mathbf{R}_\gamma\mathbf{R}_\beta,$$
$$\mathbf{h}_2(\mathbf{I} - \mathbf{R}_\beta\mathbf{R}_\alpha\mathbf{R}_\gamma) = \mathbf{u}_2 + \mathbf{u}_3\mathbf{R}_\gamma + \mathbf{u}_1\mathbf{R}_\alpha\mathbf{R}_\gamma,$$
$$\mathbf{h}_3(\mathbf{I} - \mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\alpha) = \mathbf{u}_3 + \mathbf{u}_1\mathbf{R}_\alpha + \mathbf{u}_2\mathbf{R}_\beta\mathbf{R}_\alpha.$$

According to (15) and (16) no solutions are obtained when $\mathbf{R}_\alpha\mathbf{R}_\beta\mathbf{R}_\gamma = \mathbf{I}$. Therefore, only the combinations

$$(\alpha,\beta,\gamma) = (1,1,2) \text{ or } (1,2,1) \text{ or } (2,1,1) \text{ or } (2,2,2)$$

are useful. The following solutions arise for the various values of (α,β,γ):

$$(\alpha,\beta,\gamma) = (1,1,2),\ \mathbf{h}_1 = (\bar{1}k1)\ \mathbf{h}_2 = (\bar{2}k\bar{2})\ \mathbf{h}_3 = (5k6);$$
$$= (1,2,1),\ \mathbf{h}_1 = (\bar{4}k\bar{3})\ \mathbf{h}_2 = (5k6)\ \mathbf{h}_3 = (2k2);$$
$$= (2,1,1),\ \mathbf{h}_1 = (5k6)\ \mathbf{h}_2 = (4k3)\ \mathbf{h}_3 = (1k\bar{1});$$
$$= (2,2,2),\ \mathbf{h}_1 = (2k2)\ \mathbf{h}_2 = (\bar{1}k1)\ \mathbf{h}_3 = (4k3).$$

According to (18), the s.i.'s belonging to the first representation of Φ are given, for fixed $\mathbf{R}_\alpha$, $\mathbf{R}_\beta$, $\mathbf{R}_\gamma$, by

$$\begin{aligned}
&\varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2\mathbf{R}_\beta} + \varphi_{\mathbf{u}_3\mathbf{R}_\gamma\mathbf{R}_\beta} - \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_1\mathbf{R}_\alpha\mathbf{R}_\gamma\mathbf{R}_\beta},\\
&\varphi_{\mathbf{u}_2} + \varphi_{\mathbf{u}_3\mathbf{R}_\gamma} + \varphi_{\mathbf{u}_1\mathbf{R}_\alpha\mathbf{R}_\gamma} - \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_2\mathbf{R}_\beta\mathbf{R}_\alpha\mathbf{R}_\gamma},\\
&\varphi_{\mathbf{u}_3} + \varphi_{\mathbf{u}_2\mathbf{R}_\alpha} + \varphi_{\mathbf{u}_2\mathbf{R}_\beta\mathbf{R}_\alpha} - \varphi_{\mathbf{h}_3} + \varphi_{\mathbf{h}_3\mathbf{R}_\gamma\mathbf{R}_\beta\mathbf{R}_\alpha}.
\end{aligned} \tag{26}$$

Specifying (26) for the useful combinations of α, β, γ gives the first representation of Φ:

$$\Psi_1 = \varphi_{123} + \varphi_{334} + \varphi_{\bar{6}\bar{5}\bar{5}} - \varphi_{\bar{1}k1} + \varphi_{1k\bar{1}},$$
$$\Psi_1' = \varphi_{334} + \varphi_{\bar{6}\bar{5}\bar{5}} + \varphi_{\bar{1}2\bar{3}} - \varphi_{\bar{2}k\bar{2}} + \varphi_{2k2},$$
$$\Psi_1'' = \varphi_{6\bar{5}5} + \varphi_{123} + \varphi_{334} - \varphi_{5k6} + \varphi_{\bar{5}k\bar{6}},$$
$$\Psi_1''' = \varphi_{123} + \varphi_{\bar{3}3\bar{4}} + \varphi_{\bar{6}\bar{5}\bar{5}} - \varphi_{\bar{4}k\bar{3}} + \varphi_{4k3}.$$

It is now a trivial task to write down the magnitudes in the first phasing shell (see Hauptman, 1977*b*, 1978; Hauptman & Potter, 1979 for an heuristic derivation).

6. The generalized first phasing shell

Let $\{B\}_1$ be the first phasing shell of the s.s. Φ defined by (1). We suppose that the linear combination of phases

$$\Phi' = \sum_{i=1}^{n'} A_i \varphi_{\mathbf{h}_i}\ (n' < n)$$

be a s.s. whose first phasing shell is $\{B'\}_1$. Then, $\Phi - \Phi'$ is also a s.s. whose first phasing shell is denoted by $\{B''\}_1$. If Φ' and $\Phi - \Phi'$ are estimated *via* their first representations then Φ is also evaluated. Because of the phase interrelationship principle stated in I (see §2), it is expected that the estimation of Φ *via* the set theoretical union $\{B\}_1 \cup \{B'\}_1 \cup \{B''\}_1$ is, in the statistical sense, more accurate than that *via* $\{B\}_1$ only.

A first rank s.s. with r phases is estimated *via* one or more s.i.'s with $r + 2$ phases. Thus, a phase relationship of order $N^{-1/2}$ is associated with the first-rank one-phase s.s.'s, a phase relationship of order N^{-1} is associated with the first-rank two-phase s.s.'s, *etc.*

Suppose now that Φ, Φ', $\Phi - \Phi'$ are s.s.'s of first rank with

$$r\left(r = \sum_{i=1}^{n} |A_i|\right),\ r'\left(r' = \sum_{i=1}^{n'} |A_i|\right) \text{ and } r - r'$$

phases respectively. The orders of the phase relationships associated with them are $(\sqrt{N})^{-r}$, $(\sqrt{N})^{-r'}$, $(\sqrt{N})^{-(r-r')}$. According to §14 of I, Φ, Φ' and $\Phi - \Phi'$ constitute a tripole whose order with respect to Φ is $(\sqrt{N})^{-r}$, which coincides with the order of the phase relationship associated with Φ. It is concluded that the information contained in $\{B'\}_1 \cup \{B''\}_1$ is of the same order as that contained in $\{B\}_1$. It is therefore useful to introduce the concept of *generalized first phasing shell*: '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 theoretical union

$$\{B\}_1^g = \{B\}_1 \cup \{B'\}_1 \cup \{B''\}_1 \cup \ldots$$

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. It is expected that the estimation of Φ *via* $\{B\}_1^g$ is more accurate in the statistical sense than *via* $\{B\}_1$.'

We give two examples in order to clarify the statement. In $P\bar{1}$ let $\Phi = \varphi_{\mathbf{h}+\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}$. The first phasing shell of Φ is

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

If both $\varphi_{\mathbf{h}+\mathbf{k}}$ and $\varphi_{\mathbf{h}-\mathbf{k}}$ are s.s., the multipole

$$\Phi = \varphi_{\mathbf{h}+\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}$$
$$\Phi' = \varphi_{\mathbf{h}+\mathbf{k}} - \varphi_{(\mathbf{h}+\mathbf{k})/2} - \varphi_{(\mathbf{h}+\mathbf{k})/2}$$
$$\Phi'' = \varphi_{\mathbf{h}-\mathbf{k}} - \varphi_{(\mathbf{h}-\mathbf{k})/2} - \varphi_{(\mathbf{h}-\mathbf{k})/2}$$

arises which is of order $1/N$ with respect to Φ. In conclusion, it is

$$\{B\}_1^g = \{R_{\mathbf{h}+\mathbf{k}}, R_{\mathbf{h}-\mathbf{k}}, R_{\mathbf{h}}, R_{\mathbf{k}}, R_{2\mathbf{h}}, R_{2\mathbf{k}}, R_{(\mathbf{h}+\mathbf{k})/2}, R_{(\mathbf{h}-\mathbf{k})/2}\}.$$

As a further example in $P\bar{1}$ let $\Phi = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{h}+\mathbf{k}+2\mathbf{l}}$. The four s.i.'s (Giacovazzo, 1978*b*),

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

constitute the first representation of Φ and

$$\{B\}_1 = \{R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{h}+\mathbf{k}+2\mathbf{l}}, R_{\mathbf{l}}, R_{\mathbf{h}+\mathbf{l}}, R_{\mathbf{k}+\mathbf{l}}, R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}, R_{\mathbf{h}+\mathbf{k}}, R_{\mathbf{h}-\mathbf{k}}, R_{\mathbf{h}+2\mathbf{l}}, R_{\mathbf{k}+2\mathbf{l}}, R_{\mathbf{h}+2\mathbf{k}+2\mathbf{l}}, R_{2\mathbf{h}+\mathbf{k}+2\mathbf{l}}, R_{2\mathbf{l}}, R_{2\mathbf{h}+2\mathbf{l}}, R_{2\mathbf{k}+2\mathbf{l}}, R_{2\mathbf{h}+2\mathbf{k}+2\mathbf{l}}\}$$

is its first phasing shell.

(*a*) If $\Phi' = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}}$ is a s.s., the tripole

$$\Phi = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{h}+\mathbf{k}+2\mathbf{l}}$$
$$\Phi' = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}}$$
$$\Phi'' = \varphi_{\mathbf{h}+\mathbf{k}+2\mathbf{l}} - \varphi_{(\mathbf{h}+\mathbf{k})/2+\mathbf{l}} - \varphi_{(\mathbf{h}+\mathbf{k})/2+\mathbf{l}}$$

arises which is of order $1/N\sqrt{N}$ with respect to Φ. Since

$$\{B'\}_1 = \{R_{\mathbf{h}}, R_{\mathbf{k}}, R_{(\mathbf{h}+\mathbf{k})/2}, R_{(\mathbf{h}-\mathbf{k})/2}, R_{\mathbf{h}+\mathbf{k}}, R_{\mathbf{h}-\mathbf{k}}\},$$
$$\{B''\}_1 = \{R_{\mathbf{h}+\mathbf{k}+2\mathbf{l}}, R_{(\mathbf{h}+\mathbf{k})/2+\mathbf{l}}\},$$

then $\{B\}_1^g$ will contain, besides the seventeen magnitudes in $\{B\}_1$, also $R_{(\mathbf{h}+\mathbf{k})/2}, R_{(\mathbf{h}-\mathbf{k}/2}, R_{(\mathbf{h}+\mathbf{k})/2+\mathbf{l}}$.

(*b*) If $\Phi' = \varphi_{\mathbf{h}} + \varphi_{\mathbf{h}+\mathbf{k}+2\mathbf{l}}$ is a s.s. then

$$\{B\}_1^g = \{B\}_1 \cup \{R_{\mathbf{h}+\mathbf{k}/2+\mathbf{l}}, R_{\mathbf{k}/2+\mathbf{l}}, R_{\mathbf{k}/2}\}.$$

(*c*) If $\Phi' = \varphi_{\mathbf{k}} + \varphi_{\mathbf{h}+\mathbf{k}+2\mathbf{l}}$ is a s.s. then

$$\{B\}_1^g = \{B\}_1 \cup \{R_{\mathbf{h}/2+\mathbf{k}+\mathbf{l}}, R_{\mathbf{h}/2+\mathbf{l}}, R_{\mathbf{h}/2}\}.$$

(*d*) If $\varphi_{\mathbf{h}}, \varphi_{\mathbf{k}}, \varphi_{\mathbf{h}+\mathbf{k}+2\mathbf{l}}$ are s.s.'s, the conditions (*a*), (*b*), (*c*) are simultaneously fulfilled. Then,

$$\{B\}_1^g = \{B\}_1 \cup \{R_{\mathbf{h}/2}, R_{\mathbf{k}/2}, R_{(\mathbf{h}+\mathbf{k})/2+\mathbf{l}}, R_{(\mathbf{h}+\mathbf{k})/2}, R_{(\mathbf{h}-\mathbf{k})/2}, R_{\mathbf{h}+\mathbf{k}/2+\mathbf{l}}, R_{\mathbf{k}/2+\mathbf{l}}, R_{\mathbf{h}/2+\mathbf{k}+\mathbf{l}}, R_{\mathbf{h}/2+\mathbf{l}}\}.$$

The concept of a generalized first phasing shell is of minor importance when Φ is a s.i. In fact, in this case, it is not possible to find a sequence $\Phi', \Phi'', \ldots$ such that the multipole $\Phi, \Phi', \Phi'', \ldots$ is of the same order with respect to Φ as the phase relationships associated with Φ unless $\Phi', \Phi'', \ldots$ are all s.i.'s. In this last case, however, $\{B\}_1^g \equiv \{B\}_1$. For example,

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

is a sextet invariant whose first phasing shell is

$$\{B\}_1 \equiv \{R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{h}+\mathbf{k}}, R_{\mathbf{l}}, R_{\mathbf{m}}, R_{\mathbf{l}+\mathbf{m}}, R_{\mathbf{h}+\mathbf{l}}, R_{\mathbf{h}+\mathbf{m}}, R_{\mathbf{h}-\mathbf{l}-\mathbf{m}}, R_{\mathbf{k}+\mathbf{l}}, R_{\mathbf{k}+\mathbf{m}}, R_{\mathbf{k}-\mathbf{l}-\mathbf{m}}, R_{\mathbf{h}+\mathbf{k}-\mathbf{l}}, R_{\mathbf{h}+\mathbf{k}-\mathbf{m}}, R_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}}, R_{\mathbf{h}+\mathbf{l}+\mathbf{m}}, R_{\mathbf{k}+\mathbf{l}+\mathbf{m}}, R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}, R_{\mathbf{h}+\mathbf{k}+\mathbf{m}}, R_{\mathbf{h}+\mathbf{k}-\mathbf{l}-\mathbf{m}}, R_{\mathbf{h}-\mathbf{l}}, R_{\mathbf{h}-\mathbf{m}}, R_{\mathbf{k}-\mathbf{l}}, R_{\mathbf{k}-\mathbf{m}}\}.$$

No additional cross terms arise from the fact that $\Phi = \Phi' + \Phi''$, where $\Phi' = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{k}}$, $\Phi'' = \varphi_{\mathbf{l}} + \varphi_{\mathbf{m}} - \varphi_{\mathbf{l}+\mathbf{m}}$. For a further example let us suppose that $\Phi = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{k}}$ is a s.i. in which $\Phi' = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}}$ and $\Phi'' = \varphi_{\mathbf{h}+\mathbf{k}}$ are s.s.'s of first rank. The tripole

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

is of order $1/N^{3/2}$ with respect to Φ. It is concluded that the phase information about Φ arising from the seminvariant nature of Φ' and Φ'' is of order $1/N$ higher than the order of the triplet relationship. In the same way, the phase information about $\Phi = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} - \varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ arising from the seminvariant nature of $\Phi' = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}}$, $\Phi'' = \varphi_{\mathbf{l}} - \varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$ is of order $1/N^2$, whereas Φ is a s.i. of order $1/N$.

The following observation can enlarge further on the concept of generalized first phasing shell: phase information about a s.s Φ, with the same order as the order of Φ, may be contained in the first phasing shell of special s.i.'s, Φ'. For example, let $\Phi = \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2}$ be a two-phase s.s. for a given space group. If

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

(with $\mathbf{h}_1\mathbf{R}_p \neq -\mathbf{h}_1$, $\mathbf{h}_2\,\mathbf{R}_q \neq -\mathbf{h}_2$) is a quartet, then 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 Φ' can fix that of Φ. It is therefore justified to assume that the generalized first phasing shell of Φ contains also the magnitudes belonging to the first phasing shell of the s.i. Φ'.

The procedure just described generalizes a previous observation of Hauptman & Green (1978), who use quartets such as Φ' in $P2_1$ in order to estimate Φ when Φ is a two-phase s.s. of first rank. In our approach, Φ may or may not be a s.s.

We give now two numerical examples in order to clarify the ideas described in this paragraph.

Example 1. From example 2 of §5, the reader will easily verify that the first representation of $\Phi = \varphi_{204} + \varphi_{606}$ in $P2_1$ is the collection of the s.i.'s

$$\Psi_1 = \varphi_{204} + \varphi_{\bar{6}0\bar{6}} - \varphi_{\bar{2}k\bar{1}} + \varphi_{2k1},$$
$$\Psi_2 = \varphi_{606} + \varphi_{204} - \varphi_{4k5} + \varphi_{\bar{4}k\bar{5}},$$

where k is a free index. Therefore, the first phasing shell of Φ is

$$\{B\}_1 = \{R_{204}, R_{606}, R_{2k1}, R_{4k5}, R_{402}, R_{8,0,10}\}.$$

However, φ_{204} and φ_{606} are themselves s.s.'s of first rank. Thus, the generalized first phasing shell is given by

$$\{B\}_1^g = \{R_{204}, R_{606}, R_{2k1}, R_{4k5}, R_{402}, R_{8,0,10}, R_{1k2}, R_{3k3}\}.$$

Example 2. From example 2 of §5, $\Phi = \varphi_{123} + \varphi_{7\bar{2}5}$ is a two-phase s.s. in $P2_1$. Its first phasing shell is given by (25). As $\mathbf{u}_1\mathbf{R}_2 \neq -\mathbf{u}_1$ and $\mathbf{u}_2\mathbf{R}_2 \neq -\mathbf{u}_2$, the quartet

$$\Phi' = \varphi_{123} + \varphi_{7\bar{2}5} + \varphi_{\bar{1}2\bar{3}} + \varphi_{\bar{7}\bar{2}\bar{5}}$$

may be constructed whose first phasing shell contains the five magnitudes $R_{123}, R_{725}, R_{808}, R_{040}, R_{602}$. Then the generalized first phasing shell of Φ is

$$\{B\}_1^g = \{R_{123}, R_{725}, R_{3k1}, R_{4k4}, R_{602}, R_{808}, R_{040}\}.$$

7. Algebraic properties of s.s.'s of second rank

A s.s. $\Phi = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2} + \ldots + \varphi_{\mathbf{u}_n}$ for which system (5) does not exist is a s.s. of second rank. Then, according to (4), at least one vector $\mathbf{h}$ and suitable rotation matrices $\mathbf{R}_\eta, \mathbf{R}_\psi, \ldots, \mathbf{R}_y, \mathbf{R}_p, \mathbf{R}_q$ can be found such that the combination of phases

$$\Phi' = \varphi_{\mathbf{u}_1\mathbf{R}_\eta} + \varphi_{\mathbf{u}_2\mathbf{R}_\psi} + \ldots + \varphi_{\mathbf{u}_n\mathbf{R}_y} + \varphi_{\mathbf{hR}_p} - \varphi_{\mathbf{hR}_q} \quad (27)$$

is a s.s. of first rank. Then, the same algebraic properties hold for Φ' as for the s.s.'s of first rank: in particular one or more systems such as

$$\mathbf{h}_1 - \mathbf{h}_2\mathbf{R}_\beta = \mathbf{u}_1 \quad (28.1)$$

$$\mathbf{h}_2 - \mathbf{h}_3\mathbf{R}_\gamma = \mathbf{u}_2 \quad (28.2)$$

$$\vdots \qquad\qquad \vdots$$

$$\mathbf{h}_{n-1} - \mathbf{h}_n\mathbf{R}_\nu = \mathbf{u}_{n-1} \quad (28.n-1)$$

$$\mathbf{h}_n - \mathbf{h}_{n+1}\mathbf{R}_l = \mathbf{u}_n \quad (28.n)$$

$$\mathbf{h}_{n+1} - \mathbf{h}_{n+2}\mathbf{R}_j = \mathbf{hR}_p \quad (28.n+1)$$

$$\mathbf{h}_{n+2} - \mathbf{h}_l\mathbf{R}_\alpha = -\mathbf{hR}_q \quad (28.n+2)$$

exist for suitable values of the rotation matrices. We note that $\mathbf{h}$ is now a free vector under the condition that Φ' is a s.s. of first rank. The general expressions for the s.i.'s $\Psi_1 \in \{\Psi\}_1$ can be derived from (28) in the same way as the s.i.'s (18) have been deduced from (5):

$$\varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2\mathbf{R}_\beta} + \ldots + \varphi_{\mathbf{u}_n\mathbf{R}_\nu\ldots\mathbf{R}_\gamma\mathbf{R}_\beta} + \varphi_{\mathbf{hR}_p\mathbf{R}_l\mathbf{R}_\nu\ldots\mathbf{R}_\gamma\mathbf{R}_\beta}$$
$$\varphi_{\mathbf{hR}_q\mathbf{R}_j\mathbf{R}_l\mathbf{R}_\nu\cdots\mathbf{R}_\gamma\mathbf{R}_\beta} - \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_1\mathbf{R}_\alpha\mathbf{R}_j\mathbf{R}_l\mathbf{R}_\nu\ldots\mathbf{R}_\gamma\mathbf{R}_\beta}, \quad (29.1)$$

$$\varphi_{\mathbf{u}_1\mathbf{R}_\alpha\mathbf{R}_j\mathbf{R}_l\mathbf{R}_\nu\ldots\mathbf{R}_\gamma} + \varphi_{\mathbf{u}_2} + \varphi_{\mathbf{u}_3\mathbf{R}_\gamma} + \ldots + \varphi_{\mathbf{u}_n\mathbf{R}_\nu\ldots\mathbf{R}_\gamma}$$
$$+ \varphi_{\mathbf{hR}_p\mathbf{R}_l\mathbf{R}_\nu\ldots\mathbf{R}_\gamma} - \varphi_{\mathbf{hR}_q\mathbf{R}_j\mathbf{R}_l\mathbf{R}_\nu\ldots\mathbf{R}_\gamma} - \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_2\mathbf{R}_\beta\mathbf{R}_\alpha\mathbf{R}_j\mathbf{R}_l\mathbf{R}_\nu\ldots\mathbf{R}_\gamma}, \quad (29.2)$$

$$\vdots$$

$$\varphi_{\mathbf{u}_1\mathbf{R}_\alpha} + \varphi_{\mathbf{u}_2\mathbf{R}_\beta\mathbf{R}_\alpha} + \ldots + \varphi_{\mathbf{u}_n\mathbf{R}_\nu\ldots\mathbf{R}_\beta\mathbf{R}_\alpha}$$
$$+ \varphi_{\mathbf{hR}_p\mathbf{R}_l\mathbf{R}_\nu\ldots\mathbf{R}_\beta\mathbf{R}_\alpha} - \varphi_{\mathbf{hR}_q} - \varphi_{\mathbf{h}_{n+2}} + \varphi_{\mathbf{h}_{n+2}\mathbf{R}_j\mathbf{R}_l\mathbf{R}_\nu\ldots\mathbf{R}_\beta\mathbf{R}_\alpha}. \quad (29.n+2)$$

In order to give an example let us deal with $\Phi = \varphi_{\mathbf{u}_1}$ in space group $P2_12_12_1$. In this case, the system (28) reduces to

$$\mathbf{h}_1 - \mathbf{h}_2\mathbf{R}_\beta = \mathbf{u}_1 \quad (30.1)$$

$$\mathbf{h}_2 - \mathbf{h}_3\mathbf{R}_j = \mathbf{hR}_p \quad (30.2)$$

$$\mathbf{h}_3 - \mathbf{h}_1\mathbf{R}_\alpha = -\mathbf{hR}_q. \quad (30.3)$$

From (13), the solution of (30) satisfies

$$\mathbf{h}_1(\mathbf{I} - \mathbf{R}_\alpha\mathbf{R}_j\mathbf{R}_\beta) = \mathbf{u}_1 + \mathbf{h}(\mathbf{R}_p\mathbf{R}_\beta - \mathbf{R}_q\mathbf{R}_j\mathbf{R}_\beta),$$
$$\mathbf{h}_2(\mathbf{I} - \mathbf{R}_\beta\mathbf{R}_\alpha\mathbf{R}_j) = \mathbf{u}_1\mathbf{R}_\alpha\mathbf{R}_j + \mathbf{h}(\mathbf{R}_p - \mathbf{R}_q\mathbf{R}_j), \quad (31)$$
$$\mathbf{h}_3(\mathbf{I} - \mathbf{R}_j\mathbf{R}_\beta\mathbf{R}_\alpha) = \mathbf{u}_1\mathbf{R}_\alpha + \mathbf{h}(\mathbf{R}_p\mathbf{R}_\beta\mathbf{R}_\alpha - \mathbf{R}_q),$$

where $\mathbf{h}$ is a free vector satisfying system (31).

For every combination $\mathbf{h}, \mathbf{R}_\beta, \mathbf{R}_j, \mathbf{R}_\alpha, \mathbf{R}_p, \mathbf{R}_q$ for which (31) holds the following Ψ_1's arise:

$$\varphi_{\mathbf{u}_1} + \varphi_{\mathbf{hR}_p\mathbf{R}_\beta} - \varphi_{\mathbf{hR}_q\mathbf{R}_j\mathbf{R}_\beta} + \varphi_{\mathbf{h}_1} - \varphi_{\mathbf{h}_1\mathbf{R}_\alpha\mathbf{R}_j\mathbf{R}_\beta},$$
$$\varphi_{\mathbf{u}_1\mathbf{R}_\alpha\mathbf{R}_j} + \varphi_{\mathbf{hR}_p} - \varphi_{\mathbf{hR}_q\mathbf{R}_j} - \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_2\mathbf{R}_\beta\mathbf{R}_\alpha\mathbf{R}_j},$$
$$\varphi_{\mathbf{u}_1\mathbf{R}_\alpha} + \varphi_{\mathbf{hR}_p\mathbf{R}_\beta\mathbf{R}_\alpha} - \varphi_{\mathbf{hR}_q} - \varphi_{\mathbf{h}_3} + \varphi_{\mathbf{h}_3\mathbf{R}_j\mathbf{R}_\beta\mathbf{R}_\alpha}.$$

As a numerical example in $P2_12_12_1$, let $\Phi = \varphi_{246}$. It is easily seen that

$$\varphi_{246} - \varphi_{hk3} + \varphi_{-h,k,3}$$

is a s.s. of first rank like (27). Then a quintet such as (29) can be constructed

$$\varphi_{246} - \varphi_{hk3} + \varphi_{-h,k,3} - \varphi_{1-k,2,l} + \varphi_{-1+h,-2,l}.$$

In a similar way the following quintets arise:

$$\varphi_{246} - \varphi_{hk3} + \varphi_{h,-k,-3} - \varphi_{1,2-k,l} + \varphi_{-1,2+k,l},$$
$$\varphi_{246} - \varphi_{h2l} + \varphi_{-h,-2,l} - \varphi_{1-h,k,3} + \varphi_{-1+h,k,-3},$$
$$\varphi_{246} - \varphi_{h2l} + \varphi_{h,-2,-l} - \varphi_{1,k,3-l} + \varphi_{-1,k,-3+l},$$
$$\varphi_{246} - \varphi_{1kl} + \varphi_{-1,k,-l} - \varphi_{h,2,3-l} + \varphi_{h,-2,-3+l},$$
$$\varphi_{246} - \varphi_{1kl} + \varphi_{-1,-k,l} - \varphi_{h,2-k,3} + \varphi_{h,-2+k,-3}.$$

In conclusion, the first phasing shell of φ_{246} is given by

$$\{B\}_1 = \{R_{hk3}, R_{h2l}, R_{1kl}, R_{2h,0,6}, R_{0,2k,6}, R_{2h,4,0}, R_{0,4,2l},$$
$$R_{2,0,2l}, R_{2,2k,0}\},$$

where h, k, l are free indices.

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Characterization of the Locally Ordered Regions in Short-Range Ordered α-Phase Cu–Al Alloys*†

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Abstract

The ordered domain structure present in the α-phase Cu–Al alloys investigated by Epperson, Fürnrohr & Ortiz [*Acta Cryst.* (1978), A**34**, 667–681] is determined by an extension of the computer method developed recently by Epperson [*J. Appl. Cryst.* (1979), **12**, 351–356] for analyzing a Gehlen–Cohen type simulated structure for a binary, f.c.c., locally ordered alloy in terms of nearest-neighbor atomic configurations. The dominant ordered feature of the more concentrated of these alloys is the existence of randomly dispersed Borie–Sparks tetrahedra; that is, four nearest-neighbor Al atoms arranged tetrahedrally about a Cu atom. The majority of these tetrahedra are isolated; however, as many as three or four are occasionally found to be joined in fragments of a Cu_3Au-type antiphase-shift structure. This extended ordered structure also incorporates the Cu_3Au-type ring configuration, another principal characteristic structural feature of these Cu–Al alloys. As a typical example, a Cu–14·76 at.% Al alloy quenched from 923 K and annealed for 1580 h at 423 K was found to contain 87 such locally ordered regions in an 8000-atom model. Of these 'domains', 74 were isolated tetrahedra and the remainder consisted of pairs of tetrahedra joined such that their central atoms were mutual second-nearest neighbors. For this alloy and heat treatment, the locally ordered regions of this type amount to about 14 volume % of the microstructure and contain 32% of the Al in the alloy. The average (spherical) domain size is only 3·4 Å. Not only are the locally ordered regions very small, but there are also perceptible imperfections in the packing sequence.

Introduction

One of the principal goals of diffuse-scattering investigations of concentrated alloys has been that of understanding locally ordered structures in terms of charac-

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