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A Probabilistic Theory of Two-Phase Seminvariants of First Rank *via* the Method of Representations. III

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Abstract

The estimation of two-phase seminvariants of first rank is carried out for all space groups. Representations theory [Giacovazzo (1977). *Acta Cryst.* A33, 933–944] is suitably combined with the joint probability distribution method. Formulae are obtained which exploit the knowledge of the diffraction magnitudes belonging to the first phasing shell of two-phase seminvariants both *via* the exponential form the characteristic function and *via* its Gram–Charlier expansion.

1. Introduction

In two recent papers [Giacovazzo, 1977*a*,*b*; hereafter (I) and (II) respectively] a probabilistic theory of coincidence relationships has been described which holds for all the space groups and improves on the results of Grant, Howells & Rogers (1957) and Debaerdemaeker & Woolfson (1972) and also on Hauptman's (1972) algebraic approach. In these papers the symmetry number of a given space group was denoted by m, and $\mathbf{C}_s \equiv (\mathbf{R}_s, \mathbf{T}_s)$. ($s = 1, \ldots, m$) denoted the m symmetry operators. $\mathbf{R}_s$ represents the sth rotation matrix and $\mathbf{T}_s$ the corresponding matrix of translation. The theory derives the expected value of the seminvariant cosine $\cos(\varphi_{\mathbf{h}_1+\mathbf{h}_2} - \varphi_{\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2\mathbf{R}_q})$ given $|E_{\mathbf{h}_1+\mathbf{h}_2}|$, $|E_{\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2\mathbf{R}_q}|$ and one or more pairs of magnitudes $(|E_{\mathbf{h}_1+\mathbf{k}}|, |E_{\mathbf{h}_2-\mathbf{k}}|)$, where $\mathbf{k}(\mathbf{R}_p - \mathbf{R}_q) = 0$. In particular, the theory is capable of giving in centrosymmetric symmorphic space groups sign relationships of the type

$$S(\mathbf{h}_1 + \mathbf{h}_2)\, S(\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2\mathbf{R}_q) = -1,$$

which are of great interest in direct procedures for phase determination. In noncentrosymmetric space groups it was shown that the most probable value of $\cos(\varphi_{\mathbf{h}_1+\mathbf{h}_2} - \varphi_{\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2\mathbf{R}_q})$ may lie anywhere between -1 and 1. In $P1$ the results were equivalent to those described by Giacovazzo (1974) and more recently by Green & Hauptman (1976).

The method of *representations* (Giacovazzo, 1977*c*) has given the author new insights into probabilistic methods for obtaining accurate estimates of the phase invariants or seminvariants. This theory is able, for any universal structure invariant or structure seminvariant Φ, to arrange in a general way the set of reflexions in a sequence of rested subsets, whose order is that of the expected effectiveness (in the statistical sense) for the estimation of Φ. For each subset $\{B\}_n$, which is called a *phasing shell* of nth order for Φ, one is able to estimate a collection of structure invariants [denoted in Giacovazzo (1977*c*) as $\{\psi\}_n$] whose values may differ from Φ by constants which arise because of the translational symmetry. The first aim of this paper is to estimate for any space group two-phase seminvariants of first rank by means of their first representation. We recall that $\Phi = \varphi_{\mathbf{u}} + \varphi_{\mathbf{v}}$ is a structure seminvariant of first rank if a vector $\mathbf{h}$ and two symmetry operators $\mathbf{C}_i$ and $\mathbf{C}_j$ exist such that

$$\begin{aligned}\psi_1 &= \Phi' + \varphi_{\mathbf{hR}_i} - \varphi_{\mathbf{hR}_j}\\ &= \varphi_{\mathbf{uR}_s} + \varphi_{\mathbf{vR}_n} + \varphi_{\mathbf{hR}_i} - \varphi_{\mathbf{hR}_j}\end{aligned} \qquad (1)$$

is a universal structure invariant ($\mathbf{R}_h$ may or may not be experimentally measured). As

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

ψ_1 differs from Φ by a constant which arises because of the translational symmetry:

$$\psi_1 - \Phi = -2\pi(\mathbf{uT}_s + \mathbf{vT}_n + \mathbf{hT}_i - \mathbf{hT}_j).$$

Therefore, if ψ_1 is estimated, Φ is consequently estimated. The collection of quartets ψ_1 is the first representation of Φ; its first phasing shell contains the basis and cross-magnitudes of quartets ψ_1. As an example, $\Phi = \varphi_{\mathbf{u}} + \varphi_{\mathbf{v}}$ is a structure seminvariant of first rank for the point group 222 if $\mathbf{uR}_s + \mathbf{vR}_n \equiv 0$ mod (0,2,2), (2,0,2) or (2,2,0), whereas Φ is a structure seminvariant of second rank when $\mathbf{uR}_s + \mathbf{vR}_n \equiv 0$ mod (2,2,2). The application of the method of representations to the two-phase structure seminvariants of first rank is able to give better estimates (in the statistical sense) than those provided by the coincidence method. For example, in $P\bar{1}$ the coincidence method evaluates $\Phi = \varphi_{\mathbf{h}_1+\mathbf{h}_2} + \varphi_{\mathbf{h}_1-\mathbf{h}_2}$ in terms of the four magnitudes (hereafter $R_{\mathbf{h}} = |E_{\mathbf{h}}|$): $R_{\mathbf{h}_1+\mathbf{h}_2}$, $R_{\mathbf{h}_1-\mathbf{h}_2}$,

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$R_{\mathbf{h}_1}$, $R_{\mathbf{h}_2}$. The representation method involves, *via* the two quartets

$$\psi_1 = \varphi_{\mathbf{h}_1+\mathbf{h}_2} + \varphi_{\mathbf{h}_1-\mathbf{h}_2} - \varphi_{\mathbf{h}_1} - \varphi_{\mathbf{h}_1},$$

$$\psi'_1 = \varphi_{\mathbf{h}_1+\mathbf{h}_2} - \varphi_{\mathbf{h}_1-\mathbf{h}_2} - \varphi_{\mathbf{h}_2} - \varphi_{\mathbf{h}_2},$$

the six magnitudes $R_{\mathbf{h}_1+\mathbf{h}_2}$, $R_{\mathbf{h}_1-\mathbf{h}_2}$, $R_{\mathbf{h}_1}$, $R_{\mathbf{h}_2}$, $R_{2\mathbf{h}_1}$, $R_{2\mathbf{h}_2}$. The sign probability of a two-phase seminvariant in $P\bar{1}$ given six magnitudes has recently been calculated by Giacovazzo (1978). The estimation of two-phase seminvariants will be carried out by means of the mathematical device of joint probability distribution functions. We shall assume that the reciprocal vectors are fixed and that the atomic coordinates are the primitive random variables. Two different mathematical methods will be used. The first involves a Gram–Charlier expansion of the characteristic function in terms of standardized cumulants. The second uses the same cumulants, but directly in the exponential expression of the characteristic function. Both methods require the ability to compute non-vanishing cumulants for every space group. Space-group algebra, by which this analysis may be performed, has already been described in (I) and (II). In particular, we emphasized there [see Appendix *B* of (I)] that mixed cumulants of the type $\lambda_{0..20.20..}$ do not always vanish for space groups with symmetry higher than $P\bar{1}$. For the sake of simplicity we neglect the weak effects of this type of cumulant on the distributions studied in this paper. Furthermore, we do not apply here the concept of 'generalized first phasing shell' which has recently been formulated (Giacovazzo, 1979*a*). We defer to a later paper (Giacovazzo, 1979*b*) the application of this concept to the probabilistic theory of the two-phase seminvariants of first rank.

2. Some algebraic properties of the two-phase seminvariants of first rank

In (I) and (II) we took the system

$$\varphi_{\mathbf{h}_1} - \varphi_{\mathbf{h}_2} \simeq \varphi_{\mathbf{h}_1-\mathbf{h}_2} = \varphi_{\mathbf{u}},$$

$$\varphi_{-\mathbf{h}_1\mathbf{R}_p} + \varphi_{\mathbf{h}_2\mathbf{R}_q} \simeq \varphi_{-\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2\mathbf{R}_q} \simeq \varphi_{\mathbf{v}}, \quad (3)$$

as a starting point for studying the two-phase structure seminvariants of first rank by the coincidence method. It was suggested that the algebraic properties of system (3) should be exploited in order to derive the nature of the vectors $\mathbf{h}_1$ and $\mathbf{h}_2$ which contribute to the estimation of $\varphi_{\mathbf{u}} + \varphi_{\mathbf{v}}$. The results should be very useful from both theoretical (they suggest suitable probability distribution functions which exploit the space-group symmetry) and practical points of view (they allow us to introduce a fast automatic procedure for the estimation of two-phase seminvariants). We intend to state these properties more rigorously than in (I) and (II).

Proposition 1. $\Phi = \varphi_{\mathbf{hR}_p} - \varphi_{\mathbf{hR}_q}$ is a structure seminvariant for each space group which presents the rotation matrices $\mathbf{R}_p$ and $\mathbf{R}_q$.

Proof. Since

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

then

$$\Phi = 2\pi\mathbf{h}(\mathbf{T}_q - \mathbf{T}_p),$$

which depends only on the fixed functional form of the structure factor.

This proposition helps to prove proposition 2.

Proposition 2. $\varphi_{\mathbf{h}(\mathbf{R}_p-\mathbf{R}_q)}$ is a structure seminvariant for each space group which presents the rotation matrices $\mathbf{R}_p$ and $\mathbf{R}_q$.

Proof. Since

$$\varphi_{\mathbf{h}(\mathbf{R}_p-\mathbf{R}_q)} + \varphi_{\mathbf{hR}_q} - \varphi_{\mathbf{hR}_p}$$

is a universal structure invariant, its value is a constant whatever the origin. From proposition 1, $\varphi_{\mathbf{hR}_q} - \varphi_{\mathbf{hR}_p}$ is a constant when the origin varies within an equivalence class. Consequently, $\varphi_{\mathbf{h}(\mathbf{R}_p-\mathbf{R}_q)}$ enjoys the same property.

Proposition 3. Let $\varphi_{\mathbf{u}}$ and $\varphi_{\mathbf{v}}$ be a pair of phases for which

$$\mathbf{u} = \mathbf{h}_1 - \mathbf{h}_2 \quad (5a)$$

$$\mathbf{v} = -\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2\mathbf{R}_q. \quad (5b)$$

Then $\varphi_{\mathbf{u}} + \varphi_{\mathbf{v}}$ is a structure seminvariant of first rank.

Proof. Let (5*a*) be multiplied by $\mathbf{R}_p$ and add it to (5*b*); this gives

$$\mathbf{uR}_p + \mathbf{v} = \mathbf{h}_2(\mathbf{R}_q - \mathbf{R}_p). \quad (6)$$

From proposition 2, $\varphi_{\mathbf{uR}_p} + \varphi_{\mathbf{v}}$ is a structure seminvariant. Furthermore, it is of first rank because

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

is a universal structure seminvariant of the same kind as those defined by (1).

Proposition 4. If $\varphi_{\mathbf{u}} + \varphi_{\mathbf{v}}$ is a structure seminvariant of first rank, there are at least two vectors $\mathbf{h}_1$ and $\mathbf{h}_2$ and two rotation matrices $\mathbf{R}_p$ and $\mathbf{R}_q$ for which (5) holds.

Proof. Because of the hypothesis, (1) holds. Therefore,

$$\mathbf{uR}_s + \mathbf{vR}_n + \mathbf{h}(\mathbf{R}_i - \mathbf{R}_j) = 0. \quad (7)$$

Without any loss of generality we can denote

$$\mathbf{uR}_s = (\mathbf{H}_1 - \mathbf{h})\mathbf{R}_i, \quad (8)$$

where $\mathbf{H}_1$ is a suitable vector. (7) then reduces to

$$\mathbf{vR}_n = \mathbf{hR}_j - \mathbf{H}_1\mathbf{R}_i. \quad (9)$$

If we denote

$$\mathbf{h}_1 = \mathbf{H}_1\mathbf{R}_i\mathbf{R}_s^{-1}, \quad \mathbf{h}_2 = \mathbf{hR}_i\mathbf{R}_s^{-1},$$

(8) then reduces to (5*a*). Next, denoting by $\mathbf{C}_v$ the symmetry operator for which $\mathbf{R}_j = \mathbf{R}_i\mathbf{R}_v$, (9) may be written as

$$\mathbf{v} = \mathbf{h}\mathbf{R}_i\mathbf{R}_v\mathbf{R}_n^{-1} - \mathbf{H}_1\mathbf{R}_i\mathbf{R}_n^{-1}$$
$$= \mathbf{h}_2\mathbf{R}_s\mathbf{R}_v\mathbf{R}_n^{-1} - \mathbf{h}_1\mathbf{R}_s\mathbf{R}_n^{-1},$$

which reduces to (5*b*) if $\mathbf{R}_p = \mathbf{R}_s\mathbf{R}_n^{-1}$, and $\mathbf{R}_q = \mathbf{R}_s\mathbf{R}_v\mathbf{R}_n^{-1}$.

Propositions 3 and 4 warrant that the probabilistic theory we describe holds for all two-phase seminvariants of first rank.

We now develop the conditions necessary and sufficient for the existence of system (5): for these the general expression of the solution $(\mathbf{h}_1,\mathbf{h}_2)$ is given. By combining (5*a*) with (5*b*) we have

$$\mathbf{h}_2(\mathbf{R}_q - \mathbf{R}_p) = \mathbf{v} + \mathbf{u}\mathbf{R}_p. \qquad (10)$$

For fixed $\mathbf{u}$, $\mathbf{v}$, $\mathbf{R}_p$ and $\mathbf{R}_q$, (10) may be considered a system of linear equations whose unknown is $\mathbf{h}_2$. If the solution of (10) is found, since $\mathbf{h}_1$ is fixed by (5*a*) the solution of system (5) is also found. Since $\mathbf{R}_q - \mathbf{R}_p$ is generally singular, in order to solve (10) the concept of a reflexive generalized inverse matrix has to be introduced.

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

$$\mathbf{A}\mathbf{A}^*\mathbf{A} = \mathbf{A} \quad \text{and} \quad \mathbf{A}^*\mathbf{A}\mathbf{A}^* = \mathbf{A}^*.$$

Property. A system of linear equations

$$\mathbf{A}\mathbf{x} = \mathbf{b} \qquad (11)$$

has a solution if and only if $\mathbf{A}\mathbf{A}^*\mathbf{b} = \mathbf{b}$. Furthermore, if it has a solution then

$$\mathbf{x} = \mathbf{A}^*\mathbf{b} + (\mathbf{I} - \mathbf{A}^*\mathbf{A})\mathbf{z}, \qquad (12)$$

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

However, in (10), $\mathbf{A} = (\mathbf{R}_q - \mathbf{R}_p)^+$ (the superscript indicates the transpose of the matrix) and $\mathbf{b} = \mathbf{v} + \mathbf{u}\mathbf{R}_p$ are the integral matrix and vector respectively; furthermore, we are only interested in integral solutions. We can then use Hurt's & Waid's (1970) theorem for diophantine systems; according to this, if $\mathbf{A}$ and $\mathbf{b}$ are integral, (11) has an integral solution if and only if

$$\mathbf{A}^*\mathbf{b} \equiv 0 \ (\mathrm{mod}\ \mathbf{1}). \qquad (13)$$

In this case the general integral solution of (11) is given by (12), where $\mathbf{z}$ is an arbitrary integral vector.

It is clear that from (10) and propositions 3 and 4 a new property of the two-phase seminvariants of first rank follows.

Property. $\varphi_{\mathbf{u}} + \varphi_{\mathbf{v}}$ is a structure seminvariant of first rank if (7) holds for at least one vector $\mathbf{h}_2$ and a pair of matrices $(\mathbf{R}_p,\mathbf{R}_q)$.

Let us now describe the consequences of the above theorems. For fixed $\mathbf{u}$ and $\mathbf{v}$ let $(\mathbf{R}_p,\mathbf{R}_q)$ be a pair of matrices which make (10) consistent and let $\{\mathbf{h}_2\}$ denote the set of reciprocal vectors which satisfy (10). Accordingly $\{\mathbf{h}_1\}$ denotes the collection of vectors $\mathbf{h}_1 = \mathbf{u} + \mathbf{h}_2$ which arise when $\mathbf{h}_2$ varies within $\{\mathbf{h}_2\}$. The sets of quartet invariants

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

and

$$E_{\mathbf{v}}, \quad E_{\mathbf{u}\mathbf{R}_q}, \quad E_{+\mathbf{h}_1\mathbf{R}_p}, \quad E_{-\mathbf{h}_1\mathbf{R}_q} \qquad (14b)$$

may then be constructed; these depend on the cross-magnitudes

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

and

$$|E_{\mathbf{h}_1(\mathbf{R}_q - \mathbf{R}_p)}|, \quad |E_{\mathbf{h}_2\mathbf{R}_q}|, \quad |E_{\mathbf{u}\mathbf{R}_q + \mathbf{h}_1\mathbf{R}_p}| \qquad (15b)$$

respectively. It is easy to see that one cross-vector of the quartets (14*a*) always coincides with a basis vector of the quartets (14*b*) and *vice versa* (*i.e.* $\mathbf{h}_1\mathbf{R}_p$ and $\mathbf{h}_2\mathbf{R}_q$ respectively). This observation suggests that the value of the seminvariant $\varphi_{\mathbf{u}} + \varphi_{\mathbf{v}}$ may be estimated by means of the joint probability distribution

$$P[E_{\mathbf{h}_1}, E_{\mathbf{h}_2}, E_{\mathbf{h}_1 - \mathbf{h}_2}, E_{-\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2\mathbf{R}_q}, E_{\mathbf{h}_1(\mathbf{R}_p - \mathbf{R}_q)}, E_{\mathbf{h}_2(\mathbf{R}_p - \mathbf{R}_q)},$$
$$E_{-\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2\mathbf{R}_q - \mathbf{h}_1\mathbf{R}_q}, E_{-\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2\mathbf{R}_q + \mathbf{h}_2\mathbf{R}_p}] \qquad (16)$$

more accurately (in the statistical sense) than by means of the two separate seven-variates distributions

$$P[E_{\mathbf{h}_1}, E_{\mathbf{h}_2}, E_{\mathbf{h}_1 - \mathbf{h}_2}, E_{-\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2\mathbf{R}_q}, E_{\mathbf{h}_1(\mathbf{R}_p - \mathbf{R}_q)},$$
$$E_{-\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2\mathbf{R}_q - \mathbf{h}_1\mathbf{R}_q}],$$
$$P[E_{\mathbf{h}_1}, E_{\mathbf{h}_2}, E_{\mathbf{h}_1 - \mathbf{h}_2}, E_{-\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2\mathbf{R}_q}, E_{\mathbf{h}_2(\mathbf{R}_p - \mathbf{R}_q)},$$
$$E_{-\mathbf{h}_1\mathbf{R}_p + \mathbf{h}_2\mathbf{R}_q + \mathbf{h}_2\mathbf{R}_p}].$$

This last approach, in fact treats the two quartets (14*a*) and (14*b*) as though they were statistically independent of one another; this is not strictly true. A study of distribution (16) is now made.

The following propositions can be very useful in automatic procedures because from a single element of $\{\mathbf{h}_2\}$ or $\{\mathbf{h}_1\}$ the generalized solution of system (5) is derivable.

Proposition 5. If $(\mathbf{h}_1,\mathbf{h}_2)$ is a solution of system (5), $(\mathbf{h}_1 + \mathbf{k}, \mathbf{h}_2 + \mathbf{k})$ is also, provided $\mathbf{k}(\mathbf{R}_p - \mathbf{R}_q) = 0$.

Proof. This is trivial: one only needs to replace $(\mathbf{h}_1,\mathbf{h}_2)$ in (5) by $(\mathbf{h}_1 + \mathbf{k}, \mathbf{h}_2 + \mathbf{k})$.

Proposition 6 will prove very useful in paper IV (Giacovazzo, Spagna, Vicković & Viterbo, 1979) where an algorithm has been formulated for deriving, for space groups up to the orthorhombic system, the conditional joint probability density of $\varphi_{\mathbf{u}} + \varphi_{\mathbf{v}}$, given all the magnitudes in (14) and (15).

Proposition 6. If the matrices $\mathbf{R}_p$ and $\mathbf{R}_q$ represent symmetry operators of order two, then $-(\mathbf{v} + \mathbf{h}_2\mathbf{R}_p)\mathbf{R}_p$ and $-(\mathbf{u}\mathbf{R}_q + \mathbf{h}_1\mathbf{R}_p)\mathbf{R}_q$ belong to the sets $\{\mathbf{h}_1\}$ and $\{\mathbf{h}_2\}$ respectively.

Proof. Because of propostion 5, proposition 6 holds if the difference between the elements $-(\mathbf{v} + \mathbf{h}_2\mathbf{R}_p)\mathbf{R}_p$ and any $\mathbf{h}_1$ and the difference between $-(\mathbf{u}\mathbf{R}_q +$

$\mathbf{h}_1\mathbf{R}_p)\mathbf{R}_q$ and any $\mathbf{h}_2$ are vectors $\mathbf{k}$ for which $\mathbf{k}(\mathbf{R}_p-\mathbf{R}_q)=0$. This is so because

$$[-(\mathbf{v}+\mathbf{h}_2\mathbf{R}_p)\mathbf{R}_p-\mathbf{h}_1]\times(\mathbf{R}_p-\mathbf{R}_q)=-\mathbf{h}_2(\mathbf{I}+\mathbf{R}_q\mathbf{R}_p)(\mathbf{R}_p-\mathbf{R}_q)=0,$$

$$[-(\mathbf{u}\mathbf{R}_q+\mathbf{h}_1\mathbf{R}_p)\mathbf{R}_q-\mathbf{h}_2]\times(\mathbf{R}_p-\mathbf{R}_q)=-\mathbf{h}_1(\mathbf{I}+\mathbf{R}_p\mathbf{R}_q)(\mathbf{R}_p-\mathbf{R}_q)=0.$$

Corollary (*a*). If $\mathbf{R}_p=-\mathbf{R}_q$, $\mathbf{v}+\mathbf{h}_2\mathbf{R}_p$ is symmetry equivalent to $\mathbf{h}_1$ and $\mathbf{u}\mathbf{R}_q+\mathbf{h}_1\mathbf{R}_p$ to $\mathbf{h}_2$.

In $P1$, this property suggests the study of the six-variates distribution

$$P(E_{\mathbf{h}_1}, E_{\mathbf{h}_1+\mathbf{h}_2}, E_{\mathbf{h}_1-\mathbf{h}_2}, E_{2\mathbf{h}_1}, E_{2\mathbf{h}_2}),$$

which has recently been described (Giacovazzo, 1978).

Corollary (*b*). If $\mathbf{R}_p$ and $\mathbf{R}_q$ correspond to symmetry operators of order two and $\mathbf{h}_1$ and $\mathbf{h}_2$ are elements of $\{\mathbf{h}_1\}$ and $\{\mathbf{h}_2\}$, respectively, then $-\mathbf{h}_1\mathbf{R}_p\mathbf{R}_q$ and $-\mathbf{h}_2\mathbf{R}_p\mathbf{R}_q$ also belong to $\{\mathbf{h}_1\}$ and $\{\mathbf{h}_2\}$ respectively.

Proof. As for proposition 6.

Proposition 7. Let $\varphi_\mathbf{u}+\varphi_\mathbf{v}$ be a structure seminvariant of first rank for which equations (5) hold. If $\varphi_{\mathbf{h}(\mathbf{R}_p+\mathbf{I})}$ and $\varphi_{\mathbf{h}(\mathbf{R}_q+\mathbf{I})}$ are structure seminvariants whatever $\mathbf{h}$ may be, then $\varphi_\mathbf{u}-\varphi_\mathbf{v}$ is also a structure seminvariant.

Proof. From equations (5) we obtain

$$\mathbf{u}-\mathbf{v}=\mathbf{h}_1(\mathbf{R}_p+\mathbf{I})-\mathbf{h}_2(\mathbf{R}_q+\mathbf{I}).$$

Because of the hypothesis, $\mathbf{h}_1(\mathbf{R}_p+\mathbf{I})\equiv 0 \pmod{\boldsymbol{\omega}_s}$ and $\mathbf{h}_2(\mathbf{R}_q+\mathbf{I})\equiv 0 \pmod{\boldsymbol{\omega}_s}$. Consequently $\mathbf{u}-\mathbf{v}\equiv 0 \pmod{\boldsymbol{\omega}_s}$.

Proposition 7 is trivial in centrosymmetric space groups because $\varphi_\mathbf{u}+\varphi_\mathbf{v}=\varphi_\mathbf{u}-\varphi_\mathbf{v}$. However, in non-centrosymmetric space groups it can enable one to obtain, in favourable circumstances, additional information about phase values. From our point of view the more favourable circumstances occur when both $\varphi_\mathbf{u}+\varphi_\mathbf{v}$ and $\varphi_\mathbf{u}-\varphi_\mathbf{v}$ are structure seminvariants of first rank. This occurs, for example, in space groups belonging to symmetry class 222. For these, let

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

$$\mathbf{R}_3=\begin{vmatrix}\bar{1}&0&0\\0&1&0\\0&0&\bar{1}\end{vmatrix};$$

and

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

be the rotation matrices and (Giacovazzo, 1977*c*, Appendix)

$$\mathbf{u}\pm\mathbf{v}\equiv 0 \bmod (2,2,0) \text{ or } (2,0,2) \text{ or } (0,2,2) \qquad (17)$$

be the condition which is satisfied if $\varphi_\mathbf{u}\pm\varphi_\mathbf{v}$ is a seminvariant of first rank. If a given pair $\varphi_\mathbf{u}+\varphi_\mathbf{v}$ satisfies (17), then since

$$\mathbf{h}(\mathbf{R}_2+\mathbf{I})=(0,0,2l),\quad \mathbf{h}(\mathbf{R}_3+\mathbf{I})=(0,2k,0),$$
$$\text{and}\quad \mathbf{h}(\mathbf{R}_4+\mathbf{I})=(2k,0,0),$$

$\varphi_\mathbf{u}-\varphi_\mathbf{v}$ also satisfies (17).

For a given two-phase seminvariant of first rank, $\varphi_\mathbf{u}+\varphi_\mathbf{v}$ more pairs $(\mathbf{R}_p,\mathbf{R}_q)$ can exist, each giving rise to integral solutions $(\mathbf{h}_1,\mathbf{h}_2)$ of system (5). Some of these solutions, however, may be equivalent in the crystallographic sense. Therefore, those properties may be useful which are able to reduce the number of solutions to non-equivalent ones.

Proposition 8. Let $(\mathbf{h}_1,\mathbf{h}_2)$ be the generalized solution of system (5). If system

$$\mathbf{h}'_1-\mathbf{h}'_2=\mathbf{u}, \qquad (18a)$$

$$-\mathbf{h}'_1\mathbf{R}_q+\mathbf{h}'_2\mathbf{R}_p=\mathbf{v} \qquad (18b)$$

has the generalized solution $(\mathbf{h}'_1,\mathbf{h}'_2)$, then this is crystallographically equivalent to $(\mathbf{h}_1,\mathbf{h}_2)$.

Proof. Combining (18*a*) with (18*b*) one obtains

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

which in turn may be combined with (10) to give

$$(\mathbf{h}'_2+\mathbf{h}_2)(\mathbf{R}_p-\mathbf{R}_q)=\mathbf{u}(\mathbf{R}_q-\mathbf{R}_p). \qquad (19)$$

Because of (5*a*), (19) may be written as $\mathbf{h}'_2(\mathbf{R}_p-\mathbf{R}_q)=-\mathbf{h}_1(\mathbf{R}_p-\mathbf{R}_q)$, which, because of proposition 5, gives $\mathbf{h}'_2=-\mathbf{h}_1+\mathbf{k}$ provided $\mathbf{k}(\mathbf{R}_p-\mathbf{R}_q)=0$. Next, from (5*a*) and (18*a*) $\mathbf{h}'_1=-\mathbf{h}_2+\mathbf{k}$.

Proposition 9. Let $(\mathbf{h}_1,\mathbf{h}_2)$ be the generalized solution of system (5). Then the system

$$\mathbf{h}'_1-\mathbf{h}'_2=\mathbf{u}\mathbf{R}_\nu, \qquad (20a)$$

$$-\mathbf{h}'_1\mathbf{R}_\alpha+\mathbf{h}'_2\mathbf{R}_\beta=\mathbf{v}\mathbf{R}_\psi \qquad (20b)$$

has the generalized solution $(\mathbf{h}'_1,\mathbf{h}'_2)$, which is crystallographically equivalent to $(\mathbf{h}_1,\mathbf{h}_2)$ provided $\mathbf{R}_\alpha=\mathbf{R}_\nu^{-1}\mathbf{R}_p\mathbf{R}_\psi$, $\mathbf{R}_\beta=\mathbf{R}_\nu^{-1}\mathbf{R}_q\mathbf{R}_\psi$.

Proof. Because of the hypothesis, (20*b*) becomes $-\mathbf{h}'_1\mathbf{R}_\nu^{-1}\mathbf{R}_p+\mathbf{h}'_2\mathbf{R}_\nu^{-1}\mathbf{R}_q=\mathbf{v}$. By denoting $\mathbf{h}_1=\mathbf{h}'_1\mathbf{R}_\nu^{-1}$, and $\mathbf{h}_1=\mathbf{h}'_2\mathbf{R}_\nu^{-1}$, (20) reduces to (5).

In addition to the preceding properties we note that because of proposition (8), proposition (9) also holds if the roles of $\mathbf{R}_\alpha$ and $\mathbf{R}_\beta$ are exchanged. Solutions crystallographically equivalent to $(\mathbf{h}_1,\mathbf{h}_2)$ are also found if $(-\mathbf{u},-\mathbf{v})$ replaces $(\mathbf{u},\mathbf{v})$ in (5), (18) and (20).

3. The estimation of two-phase seminvariants of first rank in centrosymmetric space groups when the Gram–Charlier expansion of the characteristic function is used

The joint probability distribution (16) was first studied *via* the Gram–Charlier expansion of its characteristic function. Denoting

$$E_1=E_{\mathbf{h}_1};\quad E_2=E_{\mathbf{h}_2};\quad E_3=E_{\mathbf{h}_1-\mathbf{h}_2};\quad E_4=E_{-\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2\mathbf{R}_q};$$
$$E_5=E_{\mathbf{h}_1(\mathbf{R}_p-\mathbf{R}_q)};\quad E_6=E_{\mathbf{h}_2(\mathbf{R}_p-\mathbf{R}_q)};$$
$$E_7=E_{-\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2\mathbf{R}_q-\mathbf{h}_1\mathbf{R}_q};$$

and $E_8=E_{-\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2\mathbf{R}_q+\mathbf{h}_2\mathbf{R}_p}$,

we obtain

$$P_+\simeq 0\cdot5+0\cdot5\tanh\left\{\frac{|E_3E_4|}{2N}\left(\frac{A}{1+C/2N}\right)\Delta_{p,q}\right\},\qquad(21)$$

where P_+ is the probability that the sign of $E_{\mathbf{h}_1-\mathbf{h}_2}E_{-\mathbf{h}_1\mathbf{R}_p+\mathbf{h}_2\mathbf{R}_q}$ is positive,

$$A=a_1+a_2,$$
$$a_1=\varepsilon_1+\varepsilon_2+\varepsilon_7+\varepsilon_8,$$
$$a_2=\varepsilon_1\varepsilon_5+\varepsilon_2\varepsilon_6+2\varepsilon_1\varepsilon_2+2\varepsilon_1\varepsilon_7+2\varepsilon_2\varepsilon_8,$$
$$C=\tfrac14H_4(E_1)\varepsilon_5+\tfrac14H_4(E_2)\varepsilon_6+(\varepsilon_1\varepsilon_2+\varepsilon_1\varepsilon_7+\varepsilon_2\varepsilon_8)(\varepsilon_3+\varepsilon_4)+\varepsilon_3\varepsilon_4(\varepsilon_5+\varepsilon_6),$$
$$H_4(E_i)=E_i^4-6E_i^2+3,$$
$$\varepsilon_i=E_i^2-1,$$

and

$$\Delta_{p,q}=(-1)^{2(\mathbf{h}_1\mathbf{T}_p-\mathbf{h}_2\mathbf{T}_q)}.$$

(21) does not take into account the statistical nature of the reflexions. A general way for making it do so is described in Appendix *A*.* Marginal probability densities of (21) can provide suitable formulae which estimate the sign of a two-phase seminvariant in cases for which not all the magnitudes of the reflexions in (16) are measured. The corresponding probability values can be derived from (21) by equating to zero the terms ε_i corresponding to the magnitudes $|E_i|$ which are not in the set of measurements. For example, if $|E_5|$, $|E_6|$, $|E_7|$ and $|E_8|$ are not measured, (21) reduces to equation (II.13) calculated for $\gamma=1$.

In $P\bar1$, $\mathbf{R}_p=\mathbf{I}$ and $\mathbf{R}_q=-\mathbf{I}$ or *vice versa*. (16) then reduces to $P(E_{\mathbf{h}_1}, E_{\mathbf{h}_2}, E_{\mathbf{h}_1-\mathbf{h}_2}, E_{\mathbf{h}_1+\mathbf{h}_2}, E_{2\mathbf{h}_1}, E_{2\mathbf{h}_2})$ which has been studied by Giacovazzo (1978).

In the conditions for which proposition 6 holds (for example, for all the space groups up to the orthorhombic system) a number of new non-vanishing cumulants (see Appendix *A*) arise. In these cases (21) still holds but A' and C' replace A and C respectively:

$$A'=A+\varepsilon_5\varepsilon_8+\varepsilon_6\varepsilon_7;$$

$$C'=C+\tfrac14H_4(E_8)\varepsilon_5+\tfrac14H_4(E_7)\varepsilon_6.$$

Again, algebraic considerations described in §2 suggest, for a given $\varphi_u+\varphi_v$, that $\mathbf{h}_1$ and $\mathbf{h}_2$ are, in general, free vectors under certain conditions [*i.e.* they must satisfy system (5)]. Furthermore, in favourable conditions more $(\mathbf{R}_p, \mathbf{R}_q)$ pairs can exist which give rise to generalized solutions $(\mathbf{h}_1, \mathbf{h}_2)$ of system (5), which are crystallographically non-equivalent to one another. This suggests the following generalized formula:

$$P_+\simeq 0\cdot5+0\cdot5\tanh\left\{\frac{|E_3E_4|}{2N}\,\frac{\sum'_{j,p,q}A''_{j,p,q}\Delta_{j,p,q}}{1+\sum'_{j,p,q}C''_{j,p,q}/2N}\right\},\qquad(22)$$

where (*a*) the primes on the summation symbols warn that precautions have to be taken in order to avoid duplicates in the contributions; (*b*) *j* is an index associated with the *j*th pair $(\mathbf{h}_1, \mathbf{h}_2)$; (*c*) A''_j and C''_j are suitable terms which take account of the space-group symmetry (in the sense that a choice must be made between factors A, C or A', C') and incidental non-measured reflexions.

Equation (21) [and (22) of course] may easily be generalized to cover structures with unequal atoms: *i.e.* (21) becomes

$$P_+\simeq 0\cdot5+0\cdot5\tanh\left\{\frac{|E_3E_4|}{2}\times\left[\frac{A'''}{1+(\sigma_3^2/2\sigma_2^3)C'''}\right]\Delta_{p,q}\right\},\qquad(23)$$

where

$$A'''=\frac{\sigma_4}{\sigma_2^2}a_1+\frac{\sigma_3^2}{\sigma_2^3}a_2,\quad C'''=C,\quad \sigma_n=\sum_{j=1}^{N}Z_j^n,$$

and Z_j is the atomic number of atom *j*.

* Appendices *A* and *B* have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33916 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

4. The estimation of $\varphi_{\mathbf{h}_1+\mathbf{h}_2} + \varphi_{\mathbf{h}_1-\mathbf{h}_2}$ in $P\bar{1}$ when the exponential form of the characteristic function is used

Formulae which estimate two-phase seminvariants in $P\bar{1}$ *via* their first representations have already been given by Giacovazzo (1978). We again use here the same mathematical approach but some integrations which are not exactly performable are achieved by more suitable techniques. We obtain

$$P_+ = \frac{P^0_+}{P^+_0 + P^-_0}, \qquad (24)$$

where

$$\begin{aligned} P^0_\pm = {} & \exp(\mp B) \\ & \times [\exp(+A^\pm_6 \pm A^\pm_{1,2} \mp A^\pm_{1,2,6}) \\ & \times \cosh(A^\pm_5 - A_{5,6} \mp A^\pm_{1,2,5}) \\ & + \exp(-A^\pm_6 \pm A^\pm_{1,2} \pm A^\pm_{1,2,6}) \\ & \times \cosh(A^\pm_5 + A_{5,6} \mp A^\pm_{1,2,5}) \\ & + \exp(+A^\pm_6 \mp A^\pm_{1,2} \pm A^\pm_{1,2,6}) \\ & \times \cosh(A^\pm_5 - A_{5,6} \pm A^\pm_{1,2,5}) \\ & + \exp(-A^\pm_6 \mp A^\pm_{1,2} \mp A^\pm_{1,2,6}) \\ & \times \cosh(A^\pm_5 + A_{5,6} \pm A^\pm_{1,2,5})], \end{aligned} \qquad (25)$$

where

$$B = (R_1^2 + R_2^2 - 1)R_3 R_4/N,$$

$$A^\pm_5 = \left(\frac{\varepsilon_1}{2} \pm R_3 R_4\right) R_5/N^{1/2},$$

$$A^\pm_6 = \left(\frac{\varepsilon_2}{2} \pm R_3 R_4\right) R_6/N^{1/2},$$

$$A^\pm_{1,2} = R_1 R_2 (R_3 \pm R_4)/N^{1/2},$$

$$A_{5,6} = R_5 R_6 (R_3^2 + R_4^2)/2N,$$

$$A^\pm_{1,2,5} = R_1 R_2 R_5 (R_3 \pm R_4)/N,$$

$$A^\pm_{1,2,6} = R_1 R_2 R_6 (R_3 \pm R_4)/N.$$

In (25) the terms $A_{1,2,6}$, $A_{5,6}$ and $A_{1,2,5}$ are of order $1/N$. If they are neglected in comparison with A_6, $A_{1,2}$ and A_5, (25) reduces to

$$P^0_\pm = \exp(\mp B) \cosh A^\pm_5 \cosh A^\pm_6 \cosh A^\pm_{1,2} \qquad (26)$$

which proved to be a useful approximation of (25). If we denote by $P_\pm(|R_i, R_j, \ldots)$ the marginal conditional sign probabilities for $E_3 E_4$ given $R_i, R_j, \ldots$, we obtain from (26)

$$P_\pm(|R_1, R_2, R_3, R_4) \simeq \exp\{\mp(R_1^2 + R_2^2) \times R_3 R_4/2N\} \cosh A^\pm_{1,2},$$

which coincides with (4.10) of Green & Hauptman (1976) or with (II.20) when (II.20) is calculated in $P\bar{1}$. See §5 for further marginal sign probabilities.

5. The estimation of two-phase seminvariants of first rank in centrosymmetric space groups when the exponential form of the characteristic function is used

By using the same notation as in §3 we obtain, for the conditions under which (21) holds,

$$\begin{aligned} & P^0_\pm(|R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8) \\ & \simeq \exp(\mp B\Delta_{p,q}) \cosh A^\pm_5 \cosh A^\pm_6 \cosh A^\pm_{1,2} \\ & \quad \times \cosh A^\pm_{1,7} \cosh A^\pm_{2,8}, \end{aligned} \qquad (27)$$

where

$$B = \frac{R_3 R_4}{2N} [4(R_1^2 + R_2^2 - 1) + R_7^2 + R_8^2], \qquad (28)$$

$$A^\pm_5 = \frac{1}{N^{1/2}} \left(\frac{\varepsilon_1}{2} \pm R_3 R_4 \Delta_{p,q}\right) R_5, \qquad (29)$$

$$A^\pm_6 = \frac{1}{N^{1/2}} \left(\frac{\varepsilon_2}{2} \pm R_3 R_4 \Delta_{p,q}\right) R_6, \qquad (30)$$

$$A^\pm_{1,2} = \frac{1}{N^{1/2}} (R_3 \pm R_4 \Delta_{p,q}) R_1 R_2, \qquad (31)$$

$$A^\pm_{1,7} = \frac{1}{N^{1/2}} (R_3 \pm R_4 \Delta_{p,q}) R_1 R_7, \qquad (32)$$

$$A^\pm_{2,8} = \frac{1}{N^{1/2}} (R_3 \pm R_4 \Delta_{p,q}) R_2 R_8. \qquad (33)$$

The marginal sign probabilities can be readily derived by integrating $P(E_3, E_4, R_1, R_2, R_5, R_6, R_7, R_8)$ with respect to the E_j's whose magnitudes are not measured. For example,

$$\begin{aligned} & P^0_\pm(|R_1, R_2, R_3, R_4, R_6, R_7, R_8) \\ & \simeq \exp\left[\mp \frac{R_3 R_4}{2N} (3R_1^2 + 4R_2^2 - 3 + E_7^2 + E_8^2)\Delta_{p,q}\right] \\ & \quad \times \cosh A^\pm_6 \cosh A^\pm_{1,2} \cosh A^\pm_{1,7} \cosh A^\pm_{2,8}; \end{aligned}$$

$$\begin{aligned} & P^0_\pm(|R_1, R_2, R_3, R_4, R_7, R_8) \\ & \simeq \exp\left[\mp \frac{R_3 R_4}{2N} (3R_1^2 + 3R_2^2 - 2 + E_7^2 + E_8^2)\Delta_{p,q}\right] \\ & \quad \times \cosh A^\pm_{1,2} \cosh A^\pm_{1,7} \cosh A^\pm_{2,8}; \end{aligned}$$

$$\begin{aligned} & P^0_\pm(|R_2, R_3, R_4, R_5, R_6, R_7, R_8) \\ & = P^0_\pm(|R_2, R_3, R_4, R_6, R_7, R_8) \\ & \simeq \exp\left[\mp \frac{R_3 R_4}{2N} (2R_2^2 - R_7^2 + R_8^2)\Delta_{p,q}\right] \\ & \quad \times \cosh A^\pm_6 \cosh A^\pm_{2,8}; \end{aligned}$$

$$\begin{aligned} & P^0_\pm(|R_2, R_3, R_4, R_6, R_7) \\ & \simeq \exp\left(\mp \frac{R_3 R_4}{2N} \varepsilon_7 \Delta_{p,q}\right) \cosh A^\pm_6. \end{aligned}$$

In Appendix B* the algebraic expression of $P_8 \equiv P(E_1, E_2, \ldots, E_8)$ is given in order to allow the reader to derive further marginal sign probabilities.

If $\mathbf{R}_p$ and $\mathbf{R}_q$ correspond to symmetry operators of order two, (27) becomes

$$P^0_\pm(|R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8) \simeq \exp(\mp B' \Delta_{p,q}) \cosh A'^{\pm}_5 \cosh A'^{\pm}_6 \cosh A^{\pm}_{1,2} \times \cosh A^{\pm}_{1,7} \cosh A^{\pm}_{2,8}, \quad (34)$$

where

$$B' = \frac{R_3 R_4}{2N}(4R_1^2 + 4R_2^2 + 2R_7^2 + 2R_8^2 - 6), \quad (35)$$

$$A'^{\pm}_5 = \frac{1}{N^{1/2}}\left(\frac{\varepsilon_1}{2} + \frac{\varepsilon_8}{2} \pm R_3 R_4 \Delta_{p,q}\right) R_5, \quad (36)$$

$$A'^{\pm}_6 = \frac{1}{N^{1/2}}\left(\frac{\varepsilon_2}{2} + \frac{\varepsilon_7}{2} \pm R_3 R_4 \Delta_{p,q}\right) R_6. \quad (37)$$

The following marginal sign probabilities can find frequent application:

$$P^0_\pm(|R_1, R_2, R_3, R_4, R_5, R_6) \simeq \exp\left[\mp (2R_1^2 + 2R_2^2 - 2)\frac{R_3 R_4}{2N} \Delta_{p,q}\right] \cosh A^{\pm}_5 \times \cosh A^{\pm}_6 \cosh A^{\pm}_{1,2}; \quad (38)$$

$$P^0_\pm(|R_1, R_2, R_3, R_4, R_i) \simeq \exp\left[\mp (2R_j^2 + R_n^2 - 1)\frac{R_3 R_4}{2N} \Delta_{p,q}\right] \cosh A^{\pm}_{1,2} \times \cosh A^{\mp}_i, \quad (39)$$

if $i = 5, 6$, $(j, n) = (1,2)$ or $(2,1)$ respectively;

$$P^0_\pm(|R_1, R_2, R_3, R_4) \simeq \exp\left[\mp (R_1^2 + R_2^2)\frac{R_3 R_4}{2N}\right] \Delta_{p,q} \quad \cosh A^{\pm}_{1,2}, \quad (40)$$

which coincides with (II.20);

$$P^0_\pm(|R_2, R_3, R_4, R_5, R_6) = P^0_\pm(|R_2, R_3, R_4, R_6) \simeq \cosh A^{\pm}_6; \quad (41)$$

$$P^0_\pm(|R_1, R_3, R_4, R_5, R_6) = P^0_\pm(|R_1, R_3, R_4, R_5) \simeq \cosh A^{\pm}_5; \quad (42)$$

$$P^0_\pm(|R_i, R_3, R_4, R_j) \simeq \exp\left(\pm \varepsilon_i \frac{R_3 R_4}{2N} \Delta_{p,q}\right)$$

for $(i,j) = (1,6)$ and $(2,5)$; (43)

* Appendix B has been deposited. See previous footnote.

$$P^0_\pm(|R_i, R_3, R_4) \simeq \exp\left(\pm \varepsilon_i \frac{R_3 R_4}{2N} \Delta_{p,q}\right) \quad \text{for} \quad i = 1,2 \quad (44)$$

$$P^0_\pm(|R_3, R_4, R_5, R_6) \simeq 0{\cdot}5. \quad (45)$$

It should be noted that equations (38)–(45) hold both when $\mathbf{R}_p$ and $\mathbf{R}_q$ do and do not represent symmetry operators of order two. Furthermore, equations (38)–(45) constitute the complete set of marginal sign probabilities for the case when $\mathbf{R}_p = -\mathbf{R}_q$. The generalization of (27) and (34) to cases in which more $(\mathbf{R}_p, \mathbf{R}_q)$ pairs exist, which gives rise to the crystallographically independent generalized solution $(\mathbf{h}_1, \mathbf{h}_2)$ of system (5), is not a trivial task. It may be expected that formulae such as

$$P^0_\pm \simeq \exp\left(\mp \sum_{(p,q)}{}' \sum_j{}' B''_j \Delta_{j,p,q}\right) \prod{}'_j \cosh A''^{\pm}_{j,p,q} \quad (46)$$

can be useful approximations of the 'true' sign probability, provided B''_j and $A''_{j,p,q}$ are suitably chosen. A general approach for obtaining such approximations will be given elsewhere (Giacovazzo, 1979b).

6. The estimation of two-phase seminvariants of first rank in noncentrosymmetric space groups when the Gram–Charlier expansion of the characteristic function is used

Let $\Phi = \varphi_{\mathbf{u}} + \varphi_{\mathbf{v}}$ be our seminvariant. After some calculations we obtain

$$P(\Phi|R_1, R_2, \ldots, R_8) \simeq [2\pi I_0(G)]^{-1} \exp\{G \cos(\Phi - \Delta_{p,q})\}, \quad (47)$$

which is a Von Mises distribution, where

$$G = \frac{R_3 R_4}{N}\left(\frac{A}{1 + C/N}\right),$$

$$C = +\tfrac{1}{4}L_4(E_1)\varepsilon_5 + \tfrac{1}{4}L_4(E_2)\varepsilon_6 + (\varepsilon_1\varepsilon_2 + \varepsilon_1\varepsilon_7 + \varepsilon_2\varepsilon_8) \times (\varepsilon_3 + \varepsilon_4) + \varepsilon_3\varepsilon_4(\varepsilon_5 + \varepsilon_6),$$

$$L_4(E_i) = E_i^4 - 4E_i^2 + 2,$$

$$\Delta_{p,q} = 2\pi(\mathbf{h}_1 \mathbf{T}_p - \mathbf{h}_2 \mathbf{T}_q).$$

A is the same quantity as occurs in (21). Useful expectation values are

$$\langle \cos \Phi \rangle \simeq \cos \Delta_{p,q} \frac{I_1(G)}{I_0(G)}, \quad (48)$$

$$\langle \sin \Phi \rangle \simeq \sin \Delta_{p,q} \frac{I_1(G)}{I_0(G)}, \quad (49)$$

$$\mathrm{var}[\cos\Phi]\simeq\frac{1}{2}+\left[\frac{1}{2}-\frac{I_1(G)}{GI_0(G)}\right]\cos 2\Delta_{p,q}$$
$$-\frac{1}{2}\frac{I_1^2(G)}{I_0^2(G)}-\frac{1}{2}\frac{I_1^2(G)}{I_0^2(G)}\cos 2\Delta_{p,q}, \quad (50)$$

$$\mathrm{var}[\sin\Phi]\simeq\frac{1}{2}-\left[\frac{1}{2}-\frac{I_1(G)}{GI_0(G)}\right]\cos 2\Delta_{p,q}$$
$$-\frac{1}{2}\frac{I_1^2(G)}{I_0^2(G)}+\frac{1}{2}\frac{I_1^2(G)}{I_0^2(G)}\cos 2\Delta_{p,q}. \quad (51)$$

We emphasize that the variance of $\cos\Phi$ is not always smaller than that of $\sin\Phi$ [*i.e.* if $\mathbf{h}_1\mathbf{T}_p-\mathbf{h}_2\mathbf{T}_q=(2n+1)/4$]. Furthermore, the variance of Φ depends on $|G|$ alone:

$$\mathrm{var}[\Phi]\simeq\frac{\pi^2}{3}+[I_0(|G|)]^{-1}\sum_{n=1}^{\infty}\frac{I_{2n}(|G|)}{n^2}$$
$$-4[I_0(|G|)]^{-1}\sum_{n=0}^{\infty}\frac{I_{2n+1}(|G|)}{(2n+1)^2}. \quad (52)$$

If $\mathbf{R}_p$ and $\mathbf{R}_q$ correspond to symmetry operators of order two, (47)–(52) still hold provided G' replaces G, where

$$G'=\frac{R_3R_4}{N}\frac{A'}{1+C'/N},\quad A'=A+\varepsilon_5\varepsilon_8+\varepsilon_6\varepsilon_7,$$
$$C'=C+\tfrac{1}{4}L_4(E_8)\varepsilon_5+\tfrac{1}{4}L_4(E_7)\varepsilon_6.$$

Marginal distributions are obtained from (48) and (49) in the same way as from (21) in centrosymmetric space groups. If more $(\mathbf{R}_p,\mathbf{R}_q)$ pairs exist, which give rise to the crystallographically independent generalized solution $(\mathbf{h}_1,\mathbf{h}_2)$ of system (5), we obtain

$$P(\Phi|\ldots)\simeq[2\pi I_0(Q)]^{-1}\exp[Q\cos(\Phi-\theta)], \quad (53)$$

where

$$Q=\left[\left(\sum_{(p,q)}{}'\sum_j{}'G_j''\cos\Delta_{j,p,q}\right)^2+\left(\sum_{(p,q)}{}'\sum_j{}'G_j''\sin\Delta_{j,p,q}\right)^2\right]^{1/2}, \quad (54)$$

$$\tan\theta=\frac{\sum_{(p,q)}{}'\sum_j{}'G_j''\sin\Delta_{j,p,q}}{\sum_{(p,q)}{}'\sum_j{}'G_j''\cos\Delta_{j,p,q}}. \quad (55)$$

The meanings of the symbols are analogous to those in (22). (53) is a unimodal distribution which has its maximum at $\Phi=\theta$, and the larger the value of Q, the higher this maximum will be. For up to orthorhombic space groups this is always $\theta=0,\pi$.

The variance of Φ is given by (52) if Q replaces $|G|$. Useful expectation values are:

$$\langle\cos\Phi\rangle\simeq\frac{I_1(Q)}{I_0(Q)}\cos\theta, \quad (56)$$

$$\langle\sin\Phi\rangle\simeq\frac{I_1(Q)}{I_0(Q)}\sin\theta, \quad (57)$$

$$\mathrm{var}[\cos\Phi]\simeq\left(\frac{1+\cos 2\theta}{2}\right)\left[1-\frac{I_1^2(Q)}{I_0^2(Q)}\right]-\frac{I_1(Q)}{QI_0(Q)}\cos 2\theta, \quad (58)$$

$$\mathrm{var}[\sin\Phi]\simeq\left(\frac{1-\cos 2\theta}{2}\right)\left[1-\frac{I_1^2(Q)}{I_0^2(Q)}\right]+\frac{I_1(Q)}{QI_0(Q)}\cos 2\theta. \quad (59)$$

If Q is large enough, the expected values of $\cos\Phi$ and $\sin\Phi$ are very close to $\cos\theta$ and $\sin\theta$ respectively. As, in these conditions, small variance values occur, θ should be a reliable estimate of Φ.

7. The estimation of two-phase seminvariants of first rank in noncentrosymmetric space groups when the exponential form of the characteristic function is used

Provided $\mathbf{R}_p$ and $\mathbf{R}_q$ do not correspond to symmetry operators of order two we obtain for $\Phi=\varphi_3+\varphi_4$,

$$P(\Phi|R_1,R_2,R_3,R_4,R_5,R_6,R_7,R_8)$$
$$\simeq\frac{1}{L}\exp\{-2B\cos(\Phi-\Delta_{p,q})\}$$
$$\times I_0(Z_5)I_0(Z_6)I_0(Z_{1,2})I_0(Z_{1,7})I_0(Z_{2,8}), \quad (60)$$

where

$$Z_5=\frac{2}{N^{1/2}}R_5[\tfrac{1}{4}\varepsilon_1^2+R_3^2R_4^2+\varepsilon_2R_3R_4\cos(\Phi-\Delta_{p,q})]^{1/2}, \quad (61)$$

$$Z_6=\frac{2}{N^{1/2}}R_6[\tfrac{1}{4}\varepsilon_2^2+R_3^2R_4^2+\varepsilon_2R_3R_4\cos(\Phi-\Delta_{p,q})]^{1/2}, \quad (62)$$

$$Z_{1,2}=\frac{2}{N^{1/2}}R_1R_2[R_2^3+R_4^2+2R_3R_4\cos(\Phi-\Delta_{p,q})]^{1/2}, \quad (63)$$

$$Z_{1,7}=\frac{2}{N^{1/2}}R_1R_7[R_3^2+R_4^2+2R_3R_4\cos(\Phi-\Delta_{p,q})]^{1/2}, \quad (64)$$

$$Z_{2,8}=\frac{2}{N^{1/2}}R_2R_8[R_3^2+R_4^2+2R_3R_4\cos(\Phi-\Delta_{p,q})]^{1/2}, \quad (65)$$

$$L=2\pi\sum_{m,n,\nu,\mu,\varrho=-\infty}^{+\infty}(-1)^{m+n+\nu+\mu+\varrho}I_{mn\nu\mu\varrho}I_{m+n+\nu+\mu+\varrho}(2B), \quad (66)$$

$$I_{mn\nu\mu\varrho}=I_m\left(\frac{2R_2R_3R_8}{N^{1/2}}\right)I_m\left(\frac{2R_2R_4R_8}{N^{1/2}}\right)I_n\left(\frac{2R_1R_3R_7}{N^{1/2}}\right)\times I_n\left(\frac{2R_1R_4R_7}{N^{1/2}}\right)I_\nu\left(\frac{2R_1R_2R_3}{N^{1/2}}\right)\times I_\nu\left(\frac{2R_1R_2R_4}{N^{1/2}}\right)I_\mu\left(\frac{\varepsilon_2R_6}{N^{1/2}}\right)I_\mu\left(\frac{2R_3R_4R_6}{N^{1/2}}\right)\times I_\varrho\left(\frac{\varepsilon_1R_5}{N^{1/2}}\right)I_\varrho\left(\frac{2R_3R_4R_5}{N^{1/2}}\right)$$

I_ν is the modified Bessel function of order ν and B is fixed by (28).

The conditional expected value of $\cos\Phi$ is found from (60):

$$\langle\cos(\Phi|R_1,R_2,R_3,R_4,R_5,R_6,R_7,R_8)\rangle\simeq\cos\Delta_{p,q}\frac{a}{b}, \quad (67)$$

where

$$a=\sum_{m,n,\nu,\mu,\varrho=-\infty}^{+\infty}(-1)^{m+n+\nu+\mu+\varrho+1}I_{mn\nu\mu\varrho}\times I_{m+n+\nu+\mu+\varrho+1}(2B),$$

$$b=\sum_{m,n,\nu,\mu,\varrho=-\infty}^{+\infty}(-1)^{m+n+\nu+\mu+\varrho}I_{mn\nu\mu\varrho}I_{m+n+\nu+\mu+\varrho}(2B).$$

It should be noted that in (60) L is a normalizing parameter which does not depend on Φ. Although an explicit expression for L is given, the conditional expected value of $\cos\Phi$ is more readily obtained by first calculating the distribution (60) and then computing numerically the value of L. The mode of the distribution may be calculated in the same way.

Marginal probability values for Φ are readily obtained by integrating (60) with respect to non-measured reflexions:

$$P(\Phi|R_1,R_2,R_3,R_4,R_5,R_6)\simeq\frac{1}{L}\exp\left[-(2R_1^2+2R_2^2-2)\frac{R_3R_4}{N}\cos(\Phi-\Delta_{p,q})\right]\times I_0(Z_5)I_0(Z_6)I_0(Z_{1,2}); \quad (68)$$

$$P(\Phi|R_1,R_2,R_3,R_4,R_i)\simeq\frac{1}{L}\exp\left[-(2R_j^2+R_n^2-1)\frac{R_3R_4}{N}\cos(\Phi-\Delta_{p,q})\right]\times I_0(Z_{1,2})I_0(Z_i), \quad (69)$$

if $i=5,6$, then $(j,n)=(1,2)$ or $(2,1)$ respectively;

$$P(\Phi|R_1,R_2,R_3,R_4)\simeq\frac{1}{L}\exp\left[-(R_1^2+R_2^2)\frac{R_3R_4}{N}\cos(\Phi-\Delta_{p,q})\right]\times I_0(Z_{1,2}), \quad (70)$$

which coincides with (III.31);

$$P(\Phi|R_2,R_3,R_4,R_5,R_6)=P(\Phi|R_2,R_3,R_4,R_6)\simeq\frac{1}{L}I_0(Z_6); \quad (71)$$

$$P(\Phi|R_1,R_3,R_4,R_5,R_6)=P(\Phi|R_1,R_3,R_4,R_5)=\frac{1}{L}I_0(Z_5); \quad (72)$$

$$P(\Phi|R_i,R_3,R_4,R_j)\simeq\exp\left[-\varepsilon_i\frac{R_3R_4}{N}\cos(\Phi-\Delta_{p,q})\right], \quad (73)$$

for $(i,j)=(1,6)$ and $(2,5)$;

$$P(\Phi|R_i,R_3,R_4)\simeq\exp\left[-\varepsilon_i\frac{R_3R_4}{N}\cos(\Phi-\Delta_{p,q})\right]\text{ for } i=1,2; \quad (74)$$

$$P(\Phi|R_3,R_4,R_5,R_6)\simeq 1/2\pi. \quad (75)$$

In each of (68)–(75) L is a normalizing factor whose formal expression can be readily derived from the general expression (66).

(60) may be a rough approximation of the 'true' distribution when some of the eight terms of the distribution are centrosymmetric reflexions. For example,

if $\mathbf{R}_p$ and $\mathbf{R}_q$ correspond to symmetry operators of order two, E_5 and E_6 are centrosymmetric reflexions. In fact, if $\mathbf{R}_m$ is a rotation matrix for which $\mathbf{R}_p\mathbf{R}_m = \mathbf{R}_q$ (then $\mathbf{R}_q\mathbf{R}_m = \mathbf{R}_p$ also), we have

$$\mathbf{h}(\mathbf{R}_p - \mathbf{R}_q)\mathbf{R}_m = \mathbf{h}(\mathbf{R}_q - \mathbf{R}_p) = -\mathbf{h}(\mathbf{R}_p - \mathbf{R}_q),$$

which in terms of phases gives, because of (4),

$$\varphi_{\mathbf{h}(\mathbf{R}_p-\mathbf{R}_q)\mathbf{R}_m} = \varphi_{\mathbf{h}(\mathbf{R}_p-\mathbf{R}_q)} - 2\pi\mathbf{h}(\mathbf{R}_p - \mathbf{R}_q)\mathbf{T}_m = -\varphi_{\mathbf{h}(\mathbf{R}_p-\mathbf{R}_q)}. \quad (76)$$

From (76),

$$\varphi_{\mathbf{h}(\mathbf{R}_p-\mathbf{R}_q)} = \pi\mathbf{h}(\mathbf{R}_p - \mathbf{R}_q)\mathbf{T}_m$$

is easily obtained, and gives the restricted phase values for $\varphi_{\mathbf{h}(\mathbf{R}_p-\mathbf{R}_q)}$. If E_5 and E_6 are centrosymmetric reflexions, (60) no longer holds; in fact, the modified Bessel function of zero order involving Z_5 and Z_6 has to be replaced by hyperbolic cosines of suitable arguments and a suitable B' value has to replace B. Furthermore, the problem of generalizing (60) to cases in which more $(\mathbf{R}_p, \mathbf{R}_q)$ pairs exist, which give rise to the crystallographically independent generalized solutions $(\mathbf{h}_1, \mathbf{h}_2)$ of system (5), needs to be solved. All these theoretical aspects are discussed elsewhere (Giacovazzo, 1979*b*) where a general distribution function is given, which in several cases can be considered a useful approximation of the 'true' distribution of Φ.

8. Concluding remarks

A theory has been described which is capable of deriving for any space group the value of a two-phase seminvariant of first rank, $\Phi = \varphi_{\mathbf{u}} + \varphi_{\mathbf{v}}$, given all or some of the magnitudes belonging to the first phasing shell of Φ. The probabilistic formulae are derived both by using the exponential forms of the characteristic functions of the joint probability distributions studied and *via* their Gram–Charlier expansion. A general algebra for two-phase seminvariants of first rank has been developed which makes their estimation easier in the automatic procedures for phase solution.

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The Elongated Rhombic Dodecahedron in Alloy Structures

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Abstract

With the space-filling elongated dodecahedron or its truncated form as a coordination polyhedron for larger atoms, structures like $BaAl_4$, $CeMg_2Si_2$, $BaHg_{11}$ and $ThMn_{12}$ can be accurately described.

Introduction

When an alloy contains atoms of very different sizes, it is often useful to describe the structure by a polyhedron of the smaller atoms coordinating the larger atom. An example of this is $NaZn_{13}$ (Shoemaker, Marsh, Ewing & Pauling, 1952). Zn atoms are at the corners of a regular snub cube which is centred by a Na atom, and such snub cubes form the structure by sharing square faces. When dissecting various alloy structures we came across some that could be described by the so-called elongated dodecahedron, one of Federov's five space-filling polyhedra.

The elongated dodecahedron is a polyhedron with 18 corners. It is obtained if the rhombic dodecahedron is elongated along one of its fourfold axes (Fig. 1). The

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