$$G_q \exp(i\theta_q) = 2|E_q| \sum_{p\neq q=1}^{n} \Lambda_{pq} E_p.$$

Equations (2.2.5.31) and (2.2.5.32) generalize (2.2.5.11) and (2.2.5.7), respectively, and reduce to them for $n = 3$. Fourth-order determinantal formulae estimating triplet invariants in cs. and ncs. crystals, and making use of the entire data set, have recently been secured (Karle, 1979, 1980).

Advantages, limitations and applications of determinantal formulae can be found in the literature (Heinermann *et al.*, 1979; de Rango *et al.*, 1975, 1985). Taylor *et al.* (1978) combined K–H determinants with a magic-integer approach. The computing time, however, was larger than that required by standard computing techniques. The use of K–H matrices has been made faster and more effective by de Gelder *et al.* (1990) (see also de Gelder, 1992). They developed a phasing procedure (*CRUNCH*) which uses random phases as starting points for the maximization of the K–H determinants.

2.2.5.8. *Algebraic relationships for structure seminvariants*

According to the representations method (Giacovazzo, 1977*a*, 1980*a*,*b*):

(i) any s.s. Φ may be estimated *via* one or more s.i.'s $\{\psi\}$, whose values differ from Φ by a constant arising because of symmetry;

(ii) two types of s.s.'s exist, first-rank and second-rank s.s.'s, with different algebraic properties:

(iii) conditions characterizing s.s.'s of first rank for any space group may be expressed in terms of seminvariant moduli and seminvariantly associated vectors. For example, for all the space groups with point group 422 [Hauptman–Karle group $(h+k, l)$ $P(2, 2)$] the one-phase s.s.'s of first rank are characterized by

$$(h, k, l) \equiv 0 \bmod (2, 2, 0) \text{ or } (2, 0, 2) \text{ or } (0, 2, 2)$$
$$(h \pm k, l) \equiv 0 \bmod (0, 2) \text{ or } (2, 0).$$

The more general expressions for the s.s.'s of first rank are

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

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

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

$$\begin{aligned}(d)\ \Phi &= \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2} + \varphi_{\mathbf{u}_3} + \varphi_{\mathbf{u}_4}\\ &= \varphi_{\mathbf{h}_1-\mathbf{h}_2\boldsymbol{R}_\beta} + \varphi_{\mathbf{h}_2-\mathbf{h}_3\boldsymbol{R}_\gamma} + \varphi_{\mathbf{h}_3-\mathbf{h}_4\boldsymbol{R}_\delta} + \varphi_{\mathbf{h}_4-\mathbf{h}_1\boldsymbol{R}_\alpha}\end{aligned}$$

for four-phase s.s.'s; *etc.*

In other words:

(*a*) $\varphi_{\mathbf{u}}$ is an s.s. of first rank if at least one $\mathbf{h}$ and at least one rotation matrix $\boldsymbol{R}_\alpha$ exist such that $\mathbf{u} = \mathbf{h}(\boldsymbol{I} - \boldsymbol{R}_\alpha)$. $\varphi_{\mathbf{u}}$ may be estimated *via* the special triplet invariants

$$\{\psi\} = \varphi_{\mathbf{u}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{h}\boldsymbol{R}_\alpha}. \qquad (2.2.5.33)$$

The set $\{\psi\}$ is called the *first representation* of $\varphi_{\mathbf{u}}$.

(*b*) $\Phi = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2}$ is an s.s. of first rank if at least two vectors $\mathbf{h}_1$ and $\mathbf{h}_2$ and two rotation matrices $\boldsymbol{R}_\alpha$ and $\boldsymbol{R}_\beta$ exist such that

$$\begin{cases}\mathbf{u}_1 = \mathbf{h}_1 - \mathbf{h}_2\boldsymbol{R}_\beta\\ \mathbf{u}_2 = \mathbf{h}_2 - \mathbf{h}_1\boldsymbol{R}_\alpha.\end{cases} \qquad (2.2.5.34)$$

Φ may then be estimated *via* the special quartet invariants

$$\{\psi\} = \varphi_{\mathbf{u}_1\boldsymbol{R}_\alpha} + \varphi_{\mathbf{u}_2} - \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_2\boldsymbol{R}_\beta\boldsymbol{R}_\alpha} \qquad (2.2.5.35a)$$

and

$$\{\psi\} = \{\varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2\boldsymbol{R}_\beta} - \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_1\boldsymbol{R}_\alpha\boldsymbol{R}_\beta}\}. \qquad (2.2.5.35b)$$

For example, $\Phi = \varphi_{123} + \varphi_{\bar{7}2\bar{5}}$ in $P2_1$ may be estimated *via*

$$\{\psi\} = \varphi_{123} + \varphi_{\bar{7}\bar{2}\bar{5}} - \varphi_{\bar{3}K\bar{1}} + \varphi_{3K1}$$

and

$$\{\psi\} = \varphi_{123} + \varphi_{\bar{7}2\bar{5}} - \varphi_{4K4} + \varphi_{\bar{4}K\bar{4}},$$

where K is a free index.

The set of special quartets (2.2.5.35*a*) and (2.2.5.35*b*) constitutes the *first representations* of Φ.

Structure seminvariants of the second rank can be characterized as follows: suppose that, for a given seminvariant Φ, it is not possible to find a vectorial index $\mathbf{h}$ and a rotation matrix $\boldsymbol{R}_\alpha$ such that $\Phi - \varphi_{\mathbf{h}} + \varphi_{\mathbf{h}\boldsymbol{R}_\alpha}$ is a structure invariant. Then Φ is a structure seminvariant of the second rank and a set of structure invariants ψ can certainly be formed, of type

$$\{\psi\} = \Phi + \varphi_{\mathbf{h}\boldsymbol{R}_p} - \varphi_{\mathbf{h}\boldsymbol{R}_q} + \varphi_{\mathbf{l}\boldsymbol{R}_i} - \varphi_{\mathbf{l}\boldsymbol{R}_j},$$

by means of suitable indices $\mathbf{h}$ and $\mathbf{l}$ and rotation matrices $\boldsymbol{R}_p, \boldsymbol{R}_q, \boldsymbol{R}_i$ and $\boldsymbol{R}_j$. As an example, for symmetry class 222, φ_{240} or φ_{024} or φ_{204} are s.s.'s of the first rank while φ_{246} is an s.s. of the second rank.

The procedure may easily be generalized to s.s.'s of any order of the first and of the second rank. So far only the role of one-phase and two-phase s.s.'s of the first rank in direct procedures is well documented (see references quoted in Sections 2.2.5.9 and 2.2.5.10).

2.2.5.9. *Formulae estimating one-phase structure seminvariants of the first rank*

Let $E_{\mathbf{H}}$ be our one-phase s.s. of the first rank, where

$$\mathbf{H} = \mathbf{h}(\boldsymbol{I} - \boldsymbol{R}_n). \qquad (2.2.5.36)$$

In general, more than one rotation matrix $\boldsymbol{R}_n$ and more than one vector $\mathbf{h}$ are compatible with (2.2.5.36). The set of special triplets

$$\{\psi\} = \{\varphi_{\mathbf{H}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{h}\boldsymbol{R}_n}\}$$

is the first representation of $E_{\mathbf{H}}$. In cs. space groups the probability that $E_{\mathbf{H}} > 0$, given $|E_{\mathbf{H}}|$ and the set $\{|E_{\mathbf{h}}|\}$, may be estimated (Hauptman & Karle, 1953; Naya *et al.*, 1964; Cochran & Woolfson, 1955) by

$$P^+(E_{\mathbf{H}}) \simeq 0.5 + 0.5 \tanh \sum_{\mathbf{h},\, n} G_{\mathbf{h},\, n} (-1)^{2\mathbf{h}\cdot\mathbf{T}_n}, \qquad (2.2.5.37)$$

where

$$G_{\mathbf{h},\, n} = |E_{\mathbf{H}}|\varepsilon_{\mathbf{h}}/(2\sqrt{N}), \text{ and } \varepsilon = |E|^2 - 1.$$

In (2.2.5.37), the summation over n goes within the set of matrices $\boldsymbol{R}_n$ for which (2.2.5.35*a*,*b*) is compatible, and $\mathbf{h}$ varies within the set of vectors which satisfy (2.2.5.36) for each $\boldsymbol{R}_n$. Equation (2.2.5.36) is actually a generalized way of writing the so-called $\sum_1$ relationships (Hauptman & Karle, 1953).

If $\varphi_{\mathbf{H}}$ is a phase restricted by symmetry to $\theta_{\mathbf{H}}$ and $\theta_{\mathbf{H}} + \pi$ in an ncs. space group then (Giacovazzo, 1978)

$$P(\varphi_{\mathbf{H}} = \theta_{\mathbf{H}}) \simeq 0.5 + 0.5 \tanh\left\{\sum_{\mathbf{h},\, n} G_{\mathbf{h},\, n} \cos(\theta_{\mathbf{H}} - 2\pi\mathbf{h}\cdot\mathbf{T}_n)\right\}. \qquad (2.2.5.38)$$

If $\varphi_{\mathbf{H}}$ is a general phase then $\varphi_{\mathbf{H}}$ is distributed according to

$$P(\varphi_{\mathbf{H}}) \simeq \frac{1}{L}\exp\{\alpha\cos(\varphi_{\mathbf{H}} - \theta_{\mathbf{H}})\},$$

where

 references