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About Symmetry-Inconsistent Three-Phase Structure Invariants

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Abstract

In a recent paper [Han & Langs (1988). *Acta Cryst.* A**44**, 563–566], the 230 space groups were examined to identify conditions which permit symmetry-inconsistent triplets. A careful analysis of the paper shows that results are incomplete, several wrong statements have been made and that a great deal of literature on the subject has been missed. In the present paper new conditions allowing the existence of symmetry-consistent and -inconsistent triplets are also given.

1. Symbols and abbreviations

$\phi_{\mathbf{h}}$; phase of $F_{\mathbf{h}}$.

$\mathbf{C}_s = (\mathbf{R}_s, \mathbf{T}_s)$: sth symmetry operator. $\mathbf{R}_s$ is its rotational part, $\mathbf{T}_s$ its translational part.

Some of the papers here quoted will be referred to as: HL: Han & Langs (1988); G1: Giacovazzo (1974*a*); G2: Giacovazzo (1974*b*); G3: Giacovazzo (1976); G4: Giacovazzo (1977); G5: Giacovazzo (1980); PK: Pontenagel & Krabbendam (1983).

2. Introduction

Inconsistent phase relationships are identified by HL with those particular phase invariants for which, as a consequence of space-group translational symmetry, a known phase shift is absorbed in a phasing loop involving a number of phase invariants. Two $\sum_1$ invariants which indicate contradictory signs or inconsistent quadrupoles (Viterbo & Woolfson, 1973) were suggested as familiar examples of such relationships.

Inconsistent three-phase invariants are introduced by HL in the following way: 'The question may be raised whether, given the triple invariant $\mathbf{h}+\mathbf{k}+\mathbf{l}=0$, the same three vectors may be combined in a non-identical manner, $\mathbf{h}+\mathbf{k}\,.\,\mathbf{R}_j+\mathbf{l}\,.\,\mathbf{R}_k=0$'. Accordingly, the following working definition arises: symmetry-inconsistent triplets are those triplets

$$\Phi_1 = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} \quad (\mathbf{h}+\mathbf{k}+\mathbf{l}=0) \qquad (1a)$$

for which at least a second triplet Φ_2

$$\Phi_2 = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}\mathbf{R}_j} + \varphi_{\mathbf{l}\mathbf{R}_k} = \Phi_1 - 2\pi(\mathbf{k}\mathbf{T}_j + \mathbf{l}\mathbf{T}_k) \qquad (1b)$$

can be formed with non-zero phase shift $2\pi(\mathbf{k}\mathbf{T}_j + \mathbf{l}\mathbf{T}_k)$.

Of course (1*a*) and (1*b*) can coexist only if

$$\mathbf{k}(\mathbf{R}_j - \mathbf{I}) + \mathbf{l}(\mathbf{R}_k - \mathbf{I}) = 0. \qquad (2)$$

Equation (2) was applied by HL [equation (HL11)] to all 230 space groups using Burzlaff & Hountas's (1982) equivalent-position-generation routine to determine if solutions to (2) exist. The results for all space groups satisfying (2) were given in Table HL1, where conditions for symmetry-related triplets (consistent and inconsistent ones) are collected.

A careful analysis of the HL paper shows that:

(*a*) contrarily to HL's statement, Table HL1 is incomplete. Indeed, several symmetry-related triplets can be found besides those fulfilling HL conditions. In § 3 an algorithm is described which is able to obtain both the conditions in Table HL1 and some supplementary ones;

(*b*) a great deal of literature has been completely missed by HL. Therefore in § 4 some papers on the subject are referred to in order to confute wrong or misleading HL sentences.

3. Some algorithms for finding symmetry-related triplets

HL analysed the possible solutions of (2). Their conclusion was: 'clearly no *independent* solutions

$$\mathbf{k}\,.\,(\mathbf{R}_j - \mathbf{I}) + \mathbf{l}\,.\,(\mathbf{R}_k - \mathbf{I}) = 0$$

exist if $\mathbf{R}_j$ and $\mathbf{R}_k$ both represent parent transformations, as $\mathbf{k}$ would be forced to be a symmetry transformation of $\mathbf{l}$, and define a $\sum_1$ invariant'.

In the (unusual) HL terminology, a parent transformation affects only the signs of the h, k, l components of a lattice vector, while a daughter operation transforms a vector as a mixed function of the h, k and l components. Accordingly, no space group up to the orthorhombic system is present in Table HL1.

The above HL conclusion is wrong. In order to prove that, let us consider in $P2_12_12_1$ the following triplets:

$$\Phi_1 = \varphi_{h_1,k_1,0} + \varphi_{-h_1,0,l_1} + \varphi_{0,-k_1,-l_1}. \qquad (3a)$$

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A simple rearrangement of the indices gives rise to

$$\begin{aligned}\Phi_2 &= \varphi_{h_1,k_1,0} + \varphi_{-h_1,0,-l_1} + \varphi_{0,-k_1,l_1} \\ &= \Phi_1 + \pi(h_1 + k_1 + l_1).\end{aligned} \quad (3b)$$

Thus Φ_1 and Φ_2 are symmetry related: they are inconsistent for odd values of $(h_1 + k_1 + l_1)$.

Triplets such as $(3a)$ and $(3b)$ are enantiomorphically related by a mirror operation on the l index and are restricted to the imaginary phase. It could be thought that they are of different nature with respect to the triplets described in the HL paper. Such a conclusion is wrong: inconsistency between $(3a)$ and $(3b)$ in $P2_12_12_1$ is due to the space-group symmetry (no inconsistency occurs in $P222$ or $P2_122$ *etc.*, where the same enantiomorphically related triplet pairs exist).

The existence of inconsistent triplets such as $(3a)$ and $(3b)$ was pointed out by Karle & Hauptman (1956) and discussed in papers G1 and G2. The obvious consequences are:

(a) Table HL1 does not provide all the conditions for symmetry-related or inconsistent triplets, contrary to the HL sentence, according to which in Table HL1, 'the reciprocal-lattice conditions for generating and computing the phase-shift inconsistency for all such possible triples in the 230 space groups' are reported;

(b) the HL statement 'Hitherto, single three-phase invariants, apart from pairs of contradictory $\sum_1$ relationships, had not been shown to be inconsistent within phasing loops smaller than a quadrupole' is wrong. These aspects will be more extensively discussed in § 3.

As may be expected, (3) is not the only case of inconsistent triplets not quoted by HL. Indeed, the complete class of symmetry-consistent or -inconsistent triplets with restricted phase value have been completely missed in the HL paper (they do not obey the rules stated by HL). Information on them (space-group dependent) is useful as well as the information on consistent or inconsistent triplets with unconstrained phase values. In order to give a practical example, diffraction data of APAPA [Suck, Manor & Saenger (1976); $P4_12_12$; $C_{30}H_{35}N_{15}O_{16}P_2$] were tested: 21 inconsistent triplets with restricted phase values have been found among the 426 largest $|E| > 1{\cdot}44$.

Such triplets can have phases not constrained to the imaginary plane, and do not obey the rules stated by HL for $P4_12_12$. It is immediately realized how prior knowledge about them can deeply modify the phasing process since the *CONVERGENCE* procedure.

The question may be raised now whether a general rule can be fixed in order to state, for any space group, the conditions for the symmetry inconsistency of those triplets [such as $(3a)$ and $(3b)$] which are formed by reflections with symmetry-restricted phase value. The usual way to test if a reflection $\mathbf{h}$ has a symmetry-restricted phase value is to look for the existence of a rotation matrix $\mathbf{R}_\alpha$ such that $\mathbf{hR}_\alpha = -\mathbf{h}$. Then

$$\begin{aligned}\varphi_{\mathbf{hR}_\alpha} &= \varphi_{\mathbf{h}} - 2\pi\mathbf{hT}_\alpha \\ \varphi_{-\mathbf{h}} &= \varphi_{\mathbf{h}} - 2\pi\mathbf{hT}_\alpha \\ -2\varphi_{\mathbf{h}} &= -2\pi\mathbf{hT}_\alpha \\ \varphi_{\mathbf{h}} &= \pi\mathbf{hT}_\alpha + n\pi.\end{aligned}$$

Let us denote by $(1a)$ a triplet formed by symmetry-restricted phase values. Its allowed values are therefore

$$\Phi_1 = \pi(\mathbf{hT}_\alpha + \mathbf{kT}_\beta + \mathbf{lT}_\gamma) + n\pi, \quad (4)$$

where $\mathbf{C}_\alpha, \mathbf{C}_\beta, \mathbf{C}_\gamma$ are the symmetry operators for which

$$\mathbf{hR}_\alpha = -\mathbf{h}, \quad \mathbf{kR}_\beta = -\mathbf{k}, \quad \mathbf{lR}_\gamma = -\mathbf{l}$$

and n is an integer value.

Besides $(1a)$, the triple phase

$$\Phi_2 = \varphi_{-h} + \varphi_{-k} + \varphi_{-l} = \Phi_1 - 2\pi(\mathbf{hT}_\alpha + \mathbf{kT}_\beta + \mathbf{lT}_\gamma)$$

also exists, which is symmetry inconsistent with Φ_1 if $(\mathbf{hT}_\alpha + \mathbf{kT}_\beta + \mathbf{lT}_\gamma)$ is not an integer value. Because of (4) the following working rule may be fixed: triple phases symmetry restricted to values different from $(0, \pi)$ characterize inconsistent triplet invariants (obviously, the reverse is not true; special care is needed for some special triplets in the 11 pairs of enantiomorph space groups, as suggested by PK). This working rule is routinely applied in the package for phase solution *SIR*88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989) for singling out this type of inconsistent triplet.

The question may be raised now whether an algorithm more effective than the mere application of (2) can be identified in order to obtain all the conditions reported in Table HL1. To this end, we first assume in (2)

$$\mathbf{R}_k = \mathbf{R}_j^{-1}.$$

Then (2) becomes

$$\mathbf{k}(\mathbf{R}_j - \mathbf{I}) + \mathbf{l}(\mathbf{R}_j^{-1} - \mathbf{I}) = 0 \quad (5)$$

with $\mathbf{R}_j^{-1} \neq \mathbf{R}_j$.

Suppose now that, besides $(1a)$ and $(1b)$, a third triplet can be found such as

$$\varphi_{\mathbf{k}} - \varphi_{\mathbf{lR}_j^{-1}} + \varphi_{\mathbf{w}} \quad (\mathbf{w} = \mathbf{lR}_j^{-1} - \mathbf{k}), \quad (6)$$

where $\mathbf{w}$ is the vectorial index of a special reflection with statistical (Wilson's) weight equal to n $(n > 1)$. $\{\mathbf{R}_\alpha\}$ then denotes the subset of the n rotation matrices for which

$$\mathbf{w}(\mathbf{R}_\alpha - \mathbf{I}) = 0, \quad (7)$$

or, more explicitly,

$$\mathbf{k}(\mathbf{R}_\alpha - \mathbf{I}) - \mathbf{lR}_j^{-1}(\mathbf{R}_\alpha - \mathbf{I}) = 0. \quad (8)$$

If $\mathbf{R}_\alpha = \mathbf{R}_j$, then (8) coincides with condition (5), which is thus satisfied. The above considerations suggest that possible symmetry-related or inconsistent triplets can be found according to the following two-step algorithm:

(*a*) A triplet is found, say

$$\Psi = \varphi_{\mathbf{w}} + \varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} \quad (\mathbf{w}+\mathbf{h}-\mathbf{k}=0), \tag{9}$$

where $\mathbf{w}$ is a reflection satisfying (7) for $\mathbf{R}_\alpha \neq \mathbf{I}$ and $\mathbf{w}$ is not an extinction, *i.e.* $2\pi\mathbf{w}\mathbf{T}_\alpha = 0$.

(*b*) Two triplets are constructed *via* the two reflections $\mathbf{h}$ and $\mathbf{k}$ appearing in (9):

$$\Phi_1 = \varphi_{\mathbf{h}} + \varphi_{\mathbf{kR}_j} + \varphi_{-(\mathbf{h}+\mathbf{kR}_j)} \tag{10}$$

$$\Phi_2 = \varphi_{\mathbf{h}} + \varphi_{\mathbf{kR}_j^{-1}} + \varphi_{-(\mathbf{h}+\mathbf{kR}_j^{-1})} \tag{11}$$

under the condition $\mathbf{R}_j \in \{\mathbf{R}_\alpha\}$.

Proof

Equations (10) and (11) are symmetry related if a matrix $\mathbf{R}_p$ can be found such that

$$(\mathbf{h}+\mathbf{kR}_j) = (\mathbf{h}+\mathbf{kR}_j^{-1})\mathbf{R}_p, \tag{12}$$

or, in another form,

$$\mathbf{h}(\mathbf{I}-\mathbf{R}_p) - \mathbf{k}(\mathbf{R}_j^{-1}\mathbf{R}_p - \mathbf{R}_j) = 0. \tag{13}$$

On assuming $\mathbf{R}_p = \mathbf{R}_j$, (13) becomes

$$(\mathbf{h}-\mathbf{k})(\mathbf{I}-\mathbf{R}_j) = \mathbf{w}(\mathbf{I}-\mathbf{R}_j) = 0, \tag{14}$$

which is satisfied because of the hypotheses.

Let us now calculate the difference $\Phi_2 - \Phi_1$. Because of (12), triplets (10) and (11) can be written as

$$\Phi_1 = \varphi_{\mathbf{h}} + \varphi_{\mathbf{kR}_j} + \varphi_{-(\mathbf{h}+\mathbf{kR}_j)} \tag{15}$$

$$\Phi_2 = \varphi_{\mathbf{h}} + \varphi_{\mathbf{kR}_j^{-1}} + \varphi_{-(\mathbf{h}+\mathbf{kR}_j)\mathbf{R}_j^{-1}} \tag{16}$$

so that

$$\begin{aligned}\Phi_2 - \Phi_1 &= \varphi_{\mathbf{kR}_j^{-1}} - \varphi_{\mathbf{kR}_j} + \varphi_{(\mathbf{h}+\mathbf{kR}_j)} - \varphi_{(\mathbf{h}+\mathbf{kR}_j)\mathbf{R}_j^{-1}} \\ &= 2\pi[\mathbf{k}(\mathbf{T}_j - \mathbf{T}_j') + (\mathbf{h}+\mathbf{kR}_j)\mathbf{T}_j'],\end{aligned}$$

where $\mathbf{T}_j'$ is the translational part of the symmetry operator $\mathbf{C}_j^{-1}$. Since $\mathbf{C}_j^{-1} = (\mathbf{R}_j^{-1}, -\mathbf{R}_j^{-1}\mathbf{T}_j)$, we have

$$\begin{aligned}\Phi_2 - \Phi_1 &= 2\pi[\mathbf{kT}_j + \mathbf{kR}_j^{-1}\mathbf{T}_j - \mathbf{hR}_j^{-1}\mathbf{T}_j - \mathbf{kR}_j\mathbf{R}_j^{-1}\mathbf{T}_j] \\ &= 2\pi[(\mathbf{k}-\mathbf{h})\mathbf{R}_j^{-1}\mathbf{T}_j] = 2\pi\mathbf{w}\mathbf{R}_j^{-1}\mathbf{T}_j. \end{aligned} \tag{17}$$

If (17) is different from zero then Φ_1 and Φ_2 are symmetry inconsistent.

From $\mathbf{wR}_j = \mathbf{w}$ it follows that $\varphi_{\mathbf{w}} = \varphi_{\mathbf{w}} - 2\pi\mathbf{wT}_j$, which means that reflection $\mathbf{w}$ is an extinction except when $2\pi\mathbf{wT}_j = 0$. So if $\mathbf{R}_j^{-1} \equiv \mathbf{R}_j$ and $\mathbf{w}$ is not an extinction then

$$\Phi_2 - \Phi_1 = 2\pi\mathbf{wT}_j = 0 \quad \text{and} \quad \Phi_2 = \Phi_1.$$

Therefore, the algorithm can find useful triplets only if $\mathbf{w}$ is a reflection which is special because of the presence of a symmetry axis of order larger than two. This explains why in Table HL1 the space groups with symmetry lower than orthorhombic are absent.

Let us now use triplets (9), (15) and (16) in order to obtain the conditions specified in Table HL1.

For space groups with point group 4, a reflection with statistical weight larger than 1 is $\mathbf{w} = (00l)$, so that

$$\Psi = \varphi_{0,0,l} + \varphi_{h_1,k_1,l_1} - \varphi_{h_1,k_1,l_2} \quad (l = l_2 - l_1). \tag{18}$$

If $\mathbf{R}_j$ corresponds to the fourfold symmetry axis then (15) and (16) become

$$\Phi_1 = \varphi_{h_1,k_1,l_1} + \varphi_{-k_1,h_1,l_2} + \varphi_{k_1-h_1,-(h_1+k_1),-(l_1+l_2)}$$

$$\Phi_2 = \varphi_{h_1,k_1,l_1} + \varphi_{k_1,-h_1,l_2} + \varphi_{-(h_1+k_1),h_1-k_1,-(l_1+l_2)},$$

respectively, which satisfy the condition $HK-A-B$ found for these space groups by HL.

The supplementary condition $HK-C-D$ can be trivially found by choosing in (18) $l = -(l_1+l_2)$ instead of $l = l_2 - l_1$. Then (9), (15) and (16) become

$$\Psi = \varphi_{0,0,l} + \varphi_{h_1,k_1,l_1} - \varphi_{h_1,k_1,-l_2}$$

$$\Phi_1 = \varphi_{h_1,k_1,l_1} + \varphi_{-k_1,h_1,-l_2} + \varphi_{k_1-h_1,-(h_1+k_1),l_2-l_1}$$

$$\Phi_2 = \varphi_{h_1,k_1,l_1} + \varphi_{k_1,-h_1,-l_2} + \varphi_{-(h_1+k_1),h_1-k_1,l_2-l_1},$$

respectively. As a further example, for space groups with point group 6, $\mathbf{w} = (00l)$ may be chosen, so that (18) still holds. This time two different symmetry operators can be exploited, corresponding to the sixfold and to the threefold axes respectively. In the first case,

$$\Phi_1 = \varphi_{h_1,k_1,l_1} + \varphi_{h_1+k_1,-h_1,l_2} + \varphi_{-(2h_1+k_1),h_1-k_1,-(l_1+l_2)}$$

$$\Phi_2 = \varphi_{h_1,k_1,l_1} + \varphi_{-k_1,h_1+k_1,l_2} + \varphi_{k_1-h_1,-(h_1+2k_1),-(l_1+l_2)},$$

which agree with condition $HK-G-H$.

In the second case,

$$\Phi_1 = \varphi_{h_1,k_1,l_1} + \varphi_{k_1,-(h_1+k_1),l_2} + \varphi_{-(h_1+k_1),h_1,-(l_1+l_2)}$$

$$\Phi_2 = \varphi_{h_1,k_1,l_1} + \varphi_{-(h_1+k_1),h_1,l_2} + \varphi_{k_1,-(h_1+k_1),-(l_1+l_2)}$$

are obtained, which agree with condition $HK-E-F$ found by HL. As we have already seen, the supplementary conditions $HK-K-L$ and $HK-I-J$ can be trivially obtained by the algorithm.

The reader will easily see that all the conditions quoted in Table HL1 can be readily obtained by applying (9), (15) and (16).

On the other hand, not all the conditions provided by our algorithm can be found in Table HL1. For example, let us consider the space groups with point group 432. Four conditions are quoted by HL:

(1) $HK-A-B$ and $HK-C-D$, owing to the fourfold axis along $\mathbf{c}$;

(2) $HL-M-N$ and $HL-O-P$, owing to the presence of the fourfold axis along $\mathbf{b}$.

Thus the conditions due to the presence of the fourfold axis along $\mathbf{a}$ were omitted. In this case (9),

(15) and (16) become

$$\Psi = \varphi_{h,0,0} + \varphi_{h_1,k_1,l_1} - \varphi_{h_2,k_1,l_1} \quad (h_2 = h_1 + h)$$

$$\Phi_1 = \varphi_{h_1,k_1,l_1} + \varphi_{h_2,-l_1,k_1} + \varphi_{-(h_1+h_2),l_1-k_1,-(k_1+l_1)}$$

$$\Phi_2 = \varphi_{h_1,k_1,l_1} + \varphi_{h_2,l_1,-k_1} + \varphi_{-(h_1+h_2),-(k_1+l_1),(k_1-l_1)},$$

respectively.

In addition, the conditions due to the presence of the four threefold axes along [111], [$\bar{1}$11], [1$\bar{1}$1] and [11$\bar{1}$] were also omitted. As an example, let us choose $\mathbf{w} = (h, h, h)$ corresponding to the threefold axis along [111]. Then (9), (15) and (16) become:

$$\Psi = \varphi_{h,h,h} + \varphi_{h_1,k_1,l_1} - \varphi_{h_1+h,h_1+k,l_1+h}$$

$$\Phi_1 = \varphi_{h_1,k_1,l_1} + \varphi_{k_1+h,l_1+h,h_1+h} + \varphi_{-(h_1+k_1+h),-(k_1+l_1+h),-(h_1+l_1+h)}$$

$$\Phi_2 = \varphi_{h_1,k_1,l_1} + \varphi_{l_1+h,h_1+h,k_1+h} + \varphi_{-(h_1+l_1+h),-(h_1+k_1+h),-(k_1+l_1+h)}.$$

The obvious consequence for Table HL1 is:

(1) for all the cubic space groups with fourfold axes the conditions due to the fourfold axis along [100] are omitted;

(2) for all the cubic space groups the conditions due to the presence of the four threefold axes are omitted;

(3) also from point (2), the conditions for the space groups *P*23, *F*23, *I*23, *P*2$_1$3, *I*2$_1$3, *Pm*3, *Pn*3, *Fm*3, *Fd*3, *Im*3, *Pa*3, *Ia*3 are also omitted. Such space groups do not appear in Table HL1.

This is in spite of the fact that Table HL1 provides conditions for both symmetry-consistent and -inconsistent triplets (numerals from 0 to 19 are used for the phase shifts as the last item in the symbol specifying the condition).

4. Concluding remarks

In HL's paper, the following concept may be found: 'An inherent weakness of cosine-invariant estimation techniques, both algebraic methods and those derived from probability distributions, is that they generally assume only *P*1 or *P*$\bar{1}$ symmetry. Algebraic triples formulae, for example, will produce the same three-phase cosine estimates from a monoclinic data set, regardless of the space group assumed within the lattice type for the structure....; space-group-specific information such as phase relationships... are not utilized'.

This statement reveals that a great deal of literature has been missed by HL. Indeed:

(*a*) The possible coexistence of symmetry-related triplets and the possible existence of symmetry-inconsistent ones were studied in papers G1 and G2.

It was shown that, when space-group symmetry is taken into account, the triplet reliability parameter

$$G = 2|E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}|/N^{1/2}$$

is replaced by [equation G2.10)]

$$G = [\langle\xi(\mathbf{h}_1)\xi(\mathbf{h}_2)\xi(\mathbf{h}_3)\rangle/(p_{\mathbf{h}_1}p_{\mathbf{h}_2}p_{\mathbf{h}_3})^{1/2}] \times 2|E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}|/N^{1/2}, \qquad (19)$$

where ξ is the trigonometric part of the structure-factor expression.

Since [equation (G1.*A*2)]

$$\xi(h_1)\xi(h_2)\xi(h_3) = \sum_{s=1}^{m}\sum_{r=1}^{m} \xi[\mathbf{h}_1(\mathbf{C}_s - \mathbf{I}) + \mathbf{h}_2(\mathbf{C}_r - \mathbf{I})]$$

$$= \sum_{s,r=1}^{m} a_s(\mathbf{h}_1)a_r(\mathbf{h}_2) \times \xi[\mathbf{h}_1(\mathbf{R}_s - \mathbf{I}) + \mathbf{h}_2(\mathbf{R}_r - \mathbf{I})],$$

where $a_s(\mathbf{h}) = \exp(2\pi i\mathbf{h}\mathbf{T}_s)$, (19) is able to take into account both the effects of the space-group lattice and the possible presence of symmetry-related triplets. Indeed, it was clearly stated that the mean value $\langle\xi(\mathbf{h}_1)\xi(\mathbf{h}_2)\xi(\mathbf{h}_3)\rangle$ is different from zero for all $\mathbf{C}_r$, $\mathbf{C}_s$ operations for which

$$\mathbf{h}_1(\mathbf{R}_s - \mathbf{I}) + \mathbf{h}_2(\mathbf{R}_r - \mathbf{I}) = 0,$$

which is identical to condition (HL11).

(*b*) Results obtained in papers G1 and G2 were generalized by PK, who, among other things, found that in the eleven pairs of enantiomorphously related space groups there are triple products for which the most probable phase angle assumes a value different from zero.

(*c*) A general point of view for the study of the coexistence of symmetry-related invariants (and seminvariants) was provided by the method of representations in paper G4. On assuming

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

as the most general expression for a structure invariant, a number of symmetry operators may be found in favourable cases such that one or more structure invariants,

$$\Psi_1 = A_1\varphi_{\mathbf{h}'_1} + A_2\varphi_{\mathbf{h}'_2} + \ldots + A_n\varphi_{\mathbf{h}'_n}$$

$$= A_1\varphi_{\mathbf{h}_1\mathbf{R}_s} + A_2\varphi_{\mathbf{h}_2\mathbf{R}_t} + \ldots + A_n\varphi_{\mathbf{h}_n\mathbf{R}_\nu}$$

arise in which at least one of the $\mathbf{h}'_j$ vectors does not coincide with $\mathbf{h}_j$. Because of (7), $\Psi_1 - \Phi$ is a constant if the geometrical form of the structure factor has been fixed. The collection of the distinct structure invariants Ψ_1 obtained when $\mathbf{R}_s, \mathbf{R}_t, \ldots, \mathbf{R}_\nu$ vary in 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 $\{\Psi\}_1$. According to this point of view, (1*a*) and (1*b*) are nothing but a subset $\{\Psi\}_1$ if Φ is a triplet.

Quartet invariants which may also be seen to be inconsistent are also signalized by HL and an example is given [equations (HL9) and (HL10)] characterized by a cross term which is a space-group extinction.

Since again no reference is given by HL, the reader might assume that no previous work has been done on the subject. On the contrary, several references must be quoted: the problem of the influence of the space-group symmetry in the quartet relationships was first treated in paper G3 from both the algebraic and the probabilistic points of view and the implementation of the theory in a procedure for phase solution was described by Busetta, Giacovazzo, Burla, Nunzi, Polidori & Viterbo (1980).

(*d*) An effective implementation in the *MULTAN* package of the results previously quoted for triplets has been described by Main (1985). The correct space-group weight for a triplet relationship is given by

$$w_{\mathbf{h},\mathbf{k}} = \varepsilon_{-\mathbf{h}}\varepsilon_{\mathbf{k}}\varepsilon_{\mathbf{h}-\mathbf{k}} \sum_{p,q} \delta_{p,q} \exp[2\pi i(-\mathbf{h}\mathbf{T}_p + \mathbf{k}\mathbf{T}_q)]$$

where

$$\delta_{p,q} = 1 \text{ when } \mathbf{h}(\mathbf{I}-\mathbf{R}_p) = \mathbf{k}(\mathbf{I}-\mathbf{R}_q)$$
$$= 0 \text{ otherwise.}$$

The summations are over all the space-group symmetry operations. Main's algorithm is clearly able to single out symmetry-consistent and -inconsistent triplets and to provide relative weights for their use in the phasing process. The last consideration introduces a final remark. Tables 1-3 in HL's paper are of limited use in direct-methods practice because:

(1) the method used by HL to derive the list of equivalent or inconsistent triplets can fail to recognize some special combinations of indices producing multiple solutions for (2). The supplementary rules derivable by means of the algorithm described in the present paper and those concerning triplets with restricted phase values are only two examples, but others could exist in principle.

(2) the use of large tables in routine programs is not advisable. Main's algorithm is an effective example of how relatively simple in practice the use of symmetry in such types of problems may be.

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Space Groups of Quasicrystallographic Tilings

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Abstract

A method is described for producing tilings with various quasicrystallographic space groups, paying particular attention to the two-dimensional space groups *pnm*1 and *pn*1*m* that can exist as distinct possibilities when the order of rotational symmetry *n* is a power of an odd prime number.

I. Introduction

Rokhsar, Wright and Mermin have discussed the definition and classification of lattices and space groups with crystallographically forbidden point-group symmetries, taking the view that such quasi-crystallographic concepts are best formulated in Fourier space. For any material whose diffraction

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