

Starting with  $\text{ord}(2) = \{3, 4, 6\}$  and observing from Table 1 that  $\text{ord}^-(4) = \{5\}$ , we get

$$\begin{aligned}\text{ord}^+(4) &= 2 \text{ord}^-(4) \cup 4 \text{ord}^-(2) \cup 8 \text{ord}^-(0) \\ &= \{8, 10, 12\}.\end{aligned}$$

Hence

$$\begin{aligned}\text{ord}(4) &= \text{ord}^+(4) \cup \text{ord}^-(4) \\ &= \{5, 8, 10, 12\}.\end{aligned}$$

This result is consistent with the enumeration of the four-dimensional space groups given by Brown *et al.* (1978).

Continuing in this fashion one can generate the values for dimensions  $n \leq 100$  using Table 1 alone. We have done this for  $n \leq 23$  in Table 2.

It is interesting to observe that the first example

where the maximum of the allowable new orders does not increase occurs in going from dimensions 20 to 22.

It is a pleasure to thank the referee for numerous helpful suggestions and R. L. E. Schwarzenberger for his encouragement to write up these results.

#### References

- BROWN, H., BÜLOW, R., NEUBÜSER, J., WONDRATSCHEK, H. & ZASSENHAUS, H. (1978). *Crystallographic Groups of Four-Dimensional Space*. New York: John Wiley.
- COXETER, H. M. S. (1973). *Regular Polytopes*. New York: Dover.
- HERMANN, C. (1949). *Acta Cryst.* **2**, 139–145.
- LANG, S. (1971). *Algebra*. Reading: Addison-Wesley.
- PLEASANTS, P. A. B. (1985). *Quasicrystallography: Some Interesting New Patterns*. Preprint (Cardiff). To appear in *Semester Proc. Banach Int. Math. Center, Warsaw*.
- REES, E. (1983). *Notes on Geometry*. Berlin: Springer.
- SCHWARZENBERGER, R. L. E. (1980). *N-dimensional Crystallography*. London: Pitman.

*Acta Cryst.* (1985). **A41**, 544–551

## Direct Methods and Superstructures. I. Effects of the Pseudotranslations on the Reciprocal Space

BY G. CASCARANO, C. GIACOVAZZO AND M. LUIĆ\*

*Dipartimento Geo-Mineralogico, Università, Piazza Umberto I, 70121 Bari, Italy*

(Received 29 October 1984; accepted 1 May 1985)

### Abstract

The effects on the reciprocal space of one or more pseudotranslations occurring in a crystal structure are studied. A quantitative theory is described, which gives full account of the subsets of pseudonormalized structure factors whose mean intensity significantly deviates from unity. Conversely, statistical criteria are suggested aiming at facilitating the recognition of the nature of the superstructure. The theory has been implemented into a computer program that, from 72 different pseudotranslational symmetries, chooses the most probable one, estimates the number of atoms suffering pseudosymmetry and renormalizes structure factors.

### Symbols and abbreviations

$\mathbf{h} = (h, k, l)$ : vectorial index of a reflection.  
 $f$ : atomic scattering factor. The thermal factor is included; anomalous dispersion is not.  
 $F_{\mathbf{h}}, E_{\mathbf{h}}$ : structure factor and normalized structure factor respectively with vectorial index  $\mathbf{h}$ .

$C_s = (\mathbf{R}_s, \mathbf{T}_s)$ :  $s$ th symmetry operator.  $\mathbf{R}_s$  is the rotational part,  $\mathbf{T}_s$  the translational part.

$m$ : order of the space group (it coincides with the number of symmetry operators).

$\mathbf{u}_i$ :  $i$ th pseudotranslation in the unit cell.

$p$ : number of atoms (symmetry-equivalent included) whose positions are related by the pseudotranslations  $\mathbf{u}$ .

$n_i$ : order of the pseudotranslation  $\mathbf{u}_i$  (see § 2a).

$F_p, E_p$ : structure factor and normalized structure factor relative to the  $p$  atoms.

$q$ : number of atoms (symmetry-equivalent included) whose positions are not related by any pseudotranslation.

$t_p$ : number of independent atoms that generate the  $p$  atoms when the pseudotranslations  $\mathbf{u}_i$  and the symmetry operators  $C_s$ ,  $s = 1, \dots, m$ , are applied.

$t_q$ : number of independent atoms that generate the  $q$  atoms by application of the symmetry operators  $C_s$ ,  $s = 1, \dots, m$ .

$\rho(\mathbf{r})$ : electron density function in the unit cell.

$\rho_p(\mathbf{r})$ : electron density function corresponding to the  $p$  atoms.

$\sum_{t_p}, \sum_{t_q}, \sum_p, \sum_q, \sum_N \equiv \sum f_j^2$  (thermal factor included) where the summation is extended to the  $t_p, t_q, p, q, N$  atoms respectively.

\* Present address: 'Rudjer Bošković' Institute, Bijenička 54, 41000 Zagreb, Yugoslavia.

$\sum_{i_p}^0, \sum_{i_q}^0, \sum_{i_p}^0, \sum_{i_q}^0, \sum_N^0 \equiv \sum (f_j^0)^2$  (no thermal factor included).

$$s = \sin \theta / \lambda.$$

cs, ncs: centrosymmetric, noncentrosymmetric.

## 1. Introduction

*A priori* information, when available, facilitates crystal structure solution. Successful procedures (Karle, 1970; Beurskens & Noordik, 1974; Main, 1976; Heinerman, 1977; Giacovazzo, 1983) have been described for the following four kinds of information: (a) randomly positioned atoms; (b) randomly positioned and randomly oriented atomic groups; (c) randomly positioned but correctly oriented atomic groups; (d) correctly positioned atoms.

Sometimes the *a priori* information is only indirectly available. For example, it is provided by inspection of the Patterson map or of the intensity distribution. Indeed, when pseudosymmetry occurs (a non-negligible part of the atoms approximately satisfies a higher symmetry than the whole structure) the mean intensities of the measured structure factors are different for distinct classes of reflexions.

Often difficulties arise for the solution of structures showing pseudosymmetry. Attempts to solve such structures usually lead to solutions containing several structural images related by the pseudosymmetry. Hauptman & Karle (1959) suggested the *E* values of the various classes of reflections should be rescaled. This procedure sometimes succeeds but it proved unable to solve other crystal structures. Qurashi (1963) and Takéuchi (1972) suggested the use of special Patterson functions and Ito (1973) attempted to solve structures by a special use of least-squares refinement.

An important kind of pseudosymmetry occurs when a non-negligible amount of the electron density, say  $\rho_p(\mathbf{r})$ , fulfils a pseudotranslation  $\mathbf{u}: \rho_p(\mathbf{r}) \sim \rho_p(\mathbf{r} + \mathbf{u})$ . Buerger (1956, 1959) suggested that such structures should be treated as the sum of a substructure and the complement structure. Consequently, the reflections have to be divided into the set of substructure reflections with high mean intensity and the set of superstructure reflections, giving information about the complement structure. From a different point of view Lipson & Woolfson (1952) and Rogers & Wilson (1953) noticed that the reflection of a subunit along a line introduces a modulation factor, which increases the dispersion of the intensities: therefore the cumulative distribution of the *E* values approximates to the characteristic cs or hypercentrosymmetric cumulative functions even if the space group is ncs.

More recently, some important contributions by Fan Hai-fu, Yao Jia-xing, Main & Woolfson (1983), Böhme (1982, 1983) and Gramlich (1975, 1984) gave more insight into the theoretical reasons, which sug-

gest the substructure and the superstructure reflections should be treated differently. In particular, Böhme observed that substructure and superstructure reflections have to be described by different forms of the structure-factor equation so that the probabilistic formulas derived with the assumption that the functional form of the structure factor equation does not change cannot hold.

Gramlich interpreted the mean squares of the sets of normalized structure factors that significantly deviate from unity in terms of correlation coefficients of the atom coordinates. He derived also an asymptotic formula, which provides a basis for the use of triplet phase relationships of the type 'super-sub-super'.

In this paper we describe a new statistical approach that is able to obtain normalized structure factors by taking into account explicitly the structural regularities arising from the presence of one or more pseudotranslations. It will also be shown that the type of pseudotranslational symmetry and the percentage of electron density that is pseudotranslated may be in favourable circumstances readily guessed *via* statistics of the diffraction magnitudes. In a following paper (Cascarano, Giacovazzo & Luić, 1985) a probabilistic theory of triplet invariants particularly devoted to the solution of crystal structures having superstructure effects, experimental procedures and results will be described.

## 2. Algebraic results for pseudotranslations

(a) A general pseudotranslation may be expressed as

$$\mathbf{u} = \nu'_1 \mathbf{a} / \mu'_1 + \nu'_2 \mathbf{b} / \mu'_2 + \nu'_3 \mathbf{c} / \mu'_3,$$

where  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$  are the vectors of the unit cell,  $\nu'_i$  and  $\mu'_i$  are integer numbers whose greatest common divisor is unity, and

$$0 \leq \nu'_i < \mu'_i, \quad i = 1, 2, 3.$$

The index  $n$  of the pseudotranslation is the smallest integer for which  $n\mathbf{u}$  is a lattice vector: it coincides with the least common multiple of  $\mu'_1, \mu'_2, \mu'_3$ . In  $P1$   $n$  gives the number of sites related by  $\mathbf{u}$  to a given positional vector  $\mathbf{r}$ . For example,  $n = 6$  for  $\mathbf{u} = \frac{1}{2}\mathbf{a} + \frac{1}{3}\mathbf{b} + \frac{2}{3}\mathbf{c}$ .

If the crystal structure has symmetry higher than  $P1$ , the condition  $\rho_p(\mathbf{r} + \mathbf{u}) = \rho_p(\mathbf{r})$  must also satisfy the space-group symmetry. In that case  $mn$  is the overall number of sites in the cell related to a given positional vector  $\mathbf{r}$ . Then the structure-factor equation (for simplicity, no atom is assumed to be on a special crystallographic position) will be

$$F_{\mathbf{h}} = \sum_{j=1}^{t_p} f_j \sum_{s=1}^m \sum_{\nu=0}^{n-1} \exp 2\pi i \mathbf{h} \mathbf{C}_s(\mathbf{r}_j + \nu \mathbf{u}) \\ + \sum_{j=t_p+1}^{t_p+t_q} f_j \sum_{s=1}^m \exp 2\pi i \mathbf{h} \mathbf{C}_s \mathbf{r}_j.$$

In this case  $N = nmt_p + mt_q$ . As a consequence of the space-group symmetry, the pseudotranslations  $\mathbf{R}_s \mathbf{u}$ ,  $s = 1, \dots, m$ , will coexist in the unit cell.

(b) A pseudotranslation is independent of some others if its presence is not the necessary consequence of the presence of the others. Let us suppose that more than one independent pseudotranslation  $\mathbf{u}_i$ ,  $i = 1, 2, 3, \dots$ , are contemporaneously present in a  $P1$  unit cell. Then, for each atom in  $\mathbf{r}_j$ ,  $n_1 n_2 n_3 \dots$  equivalent atoms can be found, given by

$$(\mathbf{r}_j + \nu_1 \mathbf{u}_1 + \nu_2 \mathbf{u}_2 + \nu_3 \mathbf{u}_3 + \dots), \quad 0 < \nu_i < n_i - 1. \quad (1')$$

Then, in a space group of order  $m$ , the structure factor may be defined as ( $N = mt_p n_1 n_2 n_3 \dots + mt_q$ )

$$F_{\mathbf{h}} = \sum_{j=1}^{t_p} f_j \sum_{s=1}^m \sum_{\nu_1=0}^{n_1-1} \sum_{\nu_2=0}^{n_2-1} \sum_{\nu_3=0}^{n_3-1} \dots \exp [2\pi i \mathbf{h} \mathbf{C}_s \times (\mathbf{r}_j + \nu_1 \mathbf{u}_1 + \nu_2 \mathbf{u}_2 + \nu_3 \mathbf{u}_3 + \dots)] \\ + \sum_{j=t_p+1}^{t_p+t_q} f_j \sum_{s=1}^m \exp 2\pi i \mathbf{h} \mathbf{C}_s \mathbf{r}_j, \quad (2)$$

In accordance with (A1)-(A4) (Appendix), (2) may be written as

$$F_{\mathbf{h}} = \sum_{j=1}^{t_p+t_q} f_j g_j, \quad (3)$$

where

$$g_j = \sum_{s=1}^m \frac{\sin n_1 \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_1}{\sin \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_1} \frac{\sin n_2 \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_2}{\sin \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_2} \\ \times \frac{\sin n_3 \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_3}{\sin \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_3} \dots \exp \{2\pi i \mathbf{h} \mathbf{C}_s \\ \times [\mathbf{r}_j + (n_1 - 1) \mathbf{u}_1 / 2 + (n_2 - 1) \mathbf{u}_2 / 2 \\ + (n_3 - 1) \mathbf{u}_3 / 2 + \dots]\} \quad (4a)$$

if  $j \leq t_p$ ;

$$g_j = \sum_{s=1}^m \exp 2\pi i \mathbf{h} \mathbf{C}_s \mathbf{r}_j \quad (4b)$$

if  $j > t_p$ .

The above results suggest that: (1) the number of independent atomic positions are only  $t_p + t_q$ . These positions will be the primitive random variables in our probabilistic approach; (2) the algebraic form of the structure factor assumes two different expressions according to whether  $j \leq t_p$  or  $j > t_p$ . Our probabilistic approach will take specific account of this fact.

(c) If the reciprocal vector  $\mathbf{h}$  is assumed to be fixed and the  $t_p + t_q$  primitive random variables  $\mathbf{r}_j$  sweep the asymmetric unit of the cell, then the expected value of  $\langle |F_{\mathbf{h}}|^2 \rangle$  is

$$\langle |F_{\mathbf{h}}|^2 \rangle = \sum_{j=1}^{t_p+t_q} f_j^2 \langle |g_j|^2 \rangle = \varepsilon_{\mathbf{h}} \left( \sum_{t_p} \delta + \sum_q \right), \quad (5)$$

where

$$\delta = \left\{ \sum_{s=1}^m \frac{\sin^2 n_1 \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_1}{\sin^2 \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_1} \frac{\sin^2 n_2 \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_2}{\sin^2 \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_2} \times \frac{\sin^2 n_3 \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_3}{\sin^2 \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_3} \dots \right\}$$

and  $\varepsilon_{\mathbf{h}}$  is the statistical weight of the reflection  $\mathbf{h}$ . If  $n_1 = n_2 = n_3 = 1$  then no pseudotranslation occurs and

$$\langle |F_{\mathbf{h}}|^2 \rangle = \varepsilon_{\mathbf{h}} (\sum_{t_p} m + \sum_q) = \varepsilon_{\mathbf{h}} (\sum_p + \sum_q) = \varepsilon_{\mathbf{h}} \sum_N,$$

which is the well known Wilson relationship.

If  $\mathbf{h} \mathbf{u} \equiv 0 \pmod{1}$  then also  $-\mathbf{h} \mathbf{u} \equiv 0 \pmod{1}$ . Therefore in the  $cs$  space groups (5) may be written as

$$\langle |F_{\mathbf{h}}|^2 \rangle = 2\varepsilon_{\mathbf{h}} \sum_{j=1}^{t_p} f_j^2 \sum_{s=1}^{m/2} \frac{\sin^2 n_1 \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_1}{\sin^2 \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_1} \\ \times \frac{\sin^2 n_2 \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_2}{\sin^2 \pi \mathbf{h} \mathbf{R}_s \mathbf{u}_2} \dots + \varepsilon_{\mathbf{h}} \sum_q,$$

where  $s$  varies over the set of symmetry operators not related by the inversion center.

(d) In order to have more insight into the above equations let us first consider the space groups  $P1$  and  $P\bar{1}$ . If one pseudotranslation  $\mathbf{u}$  of order  $n$  is present then

$$(P1): \quad \langle |F_{\mathbf{h}}|^2 \rangle = \frac{\sin^2 n \pi \mathbf{h} \mathbf{u}}{\sin^2 \pi \mathbf{h} \mathbf{u}} \sum_{t_p} + \sum_q$$

$$(P\bar{1}): \quad \langle |F_{\mathbf{h}}|^2 \rangle = 2 \frac{\sin^2 n \pi \mathbf{h} \mathbf{u}}{\sin^2 \pi \mathbf{h} \mathbf{u}} \sum_{t_p} + \sum_q.$$

Since  $\sin n \pi \mathbf{h} \mathbf{u} \equiv 0$  for every  $\mathbf{h}$ , we have two cases of interest:

(i)  $\mathbf{h} \mathbf{u} \not\equiv 0 \pmod{1}$ ; then  $\sin^2 n \pi \mathbf{h} \mathbf{u} / \sin^2 \pi \mathbf{h} \mathbf{u} = 0$  and

$$(P1, P\bar{1}): \quad \langle |F_{\mathbf{h}}|^2 \rangle = \sum_q; \quad (6)$$

(ii)  $\mathbf{h} \mathbf{u} \equiv 0 \pmod{1}$ ; then  $\sin^2 n \pi \mathbf{h} \mathbf{u} / \sin^2 \pi \mathbf{h} \mathbf{u} = n^2$  and

$$(P1): \quad \langle |F_{\mathbf{h}}|^2 \rangle = n^2 \sum_{t_p} + \sum_q = n \sum_p + \sum_q \quad (7a)$$

$$(P\bar{1}): \quad \langle |F_{\mathbf{h}}|^2 \rangle = 2n^2 \sum_{t_p} + \sum_q = n \sum_q. \quad (7b)$$

The case (i) corresponds to superstructure reflections, for which  $\langle |F_{\mathbf{h}}|^2 \rangle \leq \sum_N$ , the case (ii) to the substructure reflections for which  $\langle |F_{\mathbf{h}}|^2 \rangle \geq \sum_N$ .

Let us now suppose that more than one independent pseudotranslation exist. Then, for the superstructure reflections, we obtain (6) again and for the substructure reflections

$$(P1), (P\bar{1}): \quad \langle |F_{\mathbf{h}}|^2 \rangle = (n_1 n_2 n_3 \dots) \sum_p + \sum_q. \quad (8)$$

It is worthwhile observing that the substructure reflections are those that satisfy all the conditions  $\mathbf{h} \mathbf{u}_i \equiv 0 \pmod{1}$  for every  $i$ . For example, if (pseudo  $F$  cell)  $\mathbf{u}_1 = (\mathbf{a}/2 + \mathbf{b}/2)$ ,  $\mathbf{u}_2 = (\mathbf{a}/2 + \mathbf{c}/2)$ , then the substructure reflections are the two parity groups with indices  $h, k, l$  all even or all odd.

The relation (9)

$$\langle |F_{\mathbf{h}}|^2 \rangle = \varepsilon \{ n_1 n_2 n_3 \dots \sum_p + \sum_q \} \quad (9)$$

does not always hold for the substructure reflections. In a given space group (9) holds if

$$\mathbf{hR}_s \mathbf{u} \equiv 0 \pmod{1} \text{ for all } s \text{ when } \mathbf{hu} \equiv 0 \pmod{1}. \quad (10)$$

However, condition (10) is not always verified. For example, in  $P4$  when  $\mathbf{u} = \mathbf{a}/4$ , the expected average intensity of the substructure reflections calculated according to (5) agrees with the following table

$$\begin{array}{ll} (hkl) \text{ with } h \equiv 0 \pmod{4} & \langle |F_{\mathbf{h}}|^2 \rangle = 2 \sum_p + \sum_q \\ (hkl) \text{ with } h \equiv 0 \pmod{4}, k \equiv 0 \pmod{4} & \\ & \langle |F_{\mathbf{h}}|^2 \rangle = 4 \sum_p + \sum_q \\ (00l) & \langle |F_{\mathbf{h}}|^2 \rangle = 4(4 \sum_p + \sum_q). \end{array}$$

In that case (9) is a poor simplification of (5).

(e) From the considerations made in § 2(c) it may be concluded that (5) may be written as

$$\langle |F_{\mathbf{h}}|^2 \rangle = \varepsilon_{\mathbf{h}} (\alpha_{\mathbf{h}} \sum_p + \sum_q), \quad (11)$$

where

$$\alpha_{\mathbf{h}} = (n_1 n_2 n_3 \dots) \gamma_{\mathbf{h}} / m$$

and  $\gamma_{\mathbf{h}}$  is the number of times for which algebraic congruences

$$\mathbf{hR}_i \mathbf{u}_i \equiv 0 \pmod{1} \text{ for } i = 1, 2, 3, \dots$$

are simultaneously satisfied when  $s$  varies from 1 to  $m$ . If  $\gamma_{\mathbf{h}} = 0$  we say that  $F_{\mathbf{h}}$  is a superstructure reflection: then  $\langle |F_{\mathbf{h}}|^2 \rangle = \varepsilon \sum_q$ . Otherwise  $F_{\mathbf{h}}$  is a substructure reflection. The maximum value of  $\gamma$  is  $m$ ; consequently the maximum value of  $\alpha$  is  $n_1 n_2 n_3 \dots$ .

The above definitions do not agree with but have several advantages over previous definitions given by other authors (Buerger, 1956, 1959; Jeffery, 1964; Taxer, 1981). Indeed, reflections are divided into two subsets according to whether their intensities are or are not influenced by the substructure.

Details about this point can be found in a recent paper (Cascarano, Giacobozzo & Luić, 1984).

(f) The normalized structure factor  $E_{\mathbf{h}}$  is defined by

$$E_{\mathbf{h}} = F_{\mathbf{h}} / \langle |F_{\mathbf{h}}|^2 \rangle^{1/2} \quad (12)$$

where  $\langle |F_{\mathbf{h}}|^2 \rangle$  is given by (11). The fact may be stressed that  $q < N$  atoms is the apparent content of the unit cell when superstructure reflections are normalized, while  $\alpha_{\mathbf{h}} p + q \cong N$  is the apparent content of the cell involved in the normalization of the reflection  $\mathbf{h}$ . The usefulness of this observation should be appreciated when the reliability of triplet relations will be estimated (Cascarano, Giacobozzo & Luić, 1985).

(g) In accordance with Böhme (1982), pseudotranslations in a crystal structure can be recognized by the unequal distributions of the normalized structure factors if normalization has been

executed without taking pseudotranslation effects into account.  $E'$  will denote such pseudonormalized structure factors. If we correctly distinguish between substructure and superstructure reflections we can obtain estimates of the  $p$  and  $q$  values. Indeed we have

$$\langle |E'_{\mathbf{h}}|^2 \rangle = (\alpha_{\mathbf{h}} \sum_p + \sum_q) / \sum_N. \quad (13)$$

If  $p$  and  $q$  atoms are supposed to have the same unitary scattering factor and the same temperature factor then (13) reduces to

$$\langle |E'_{\mathbf{h}}|^2 \rangle = (\alpha_{\mathbf{h}} p + q) / N, \quad (14)$$

from which

$$q/N \sim (\langle |E'_{\mathbf{h}}|^2 \rangle - \alpha_{\mathbf{h}}) / (1 - \alpha_{\mathbf{h}}). \quad (15)$$

The averages are calculated by allowing  $\mathbf{h}$  to vary over a statistically homogeneous ( $\alpha_{\mathbf{h}} \equiv \alpha$ ) set of reflections.  $p/N$  ( $q/N$ ) is the percentage of electrons in the unit cell that can be considered to be affected (not affected) by the pseudotranslations. If  $\alpha_{\mathbf{h}} \equiv 0$  then (15) reduces to

$$q/N \sim \langle |E'_{\mathbf{h}}|^2 \rangle_{\text{sup}}, \quad (16)$$

where  $\mathbf{h}$  is allowed to vary over the set of superstructure reflections.

(h) When nothing is known about the crystal structure the number of primitive random variables (*i.e.* the atomic positions of symmetry-independent atoms) is correctly assumed to be equal to  $N/m$ . According to § 2(g), normalizing reflections in the usual way provides information about pseudotranslations if they exist. The identification of the pseudotranslations occurring in the structure leads to a new definition of the primitive random variables, which are now the  $t_p + t_q$  positional vectors. The distribution of the new  $E$ 's will lose the centric or the hypercentric character and will approach the ncs or cs distribution according to whether the space group is ncs or cs respectively.

(i) Real crystal structures usually do not exactly obey the mathematical model described in this paper. Often atomic positions roughly comply with (1'); sometimes pseudotranslated atoms have different atomic number.

It should be concluded that the values of  $p$  and  $q$  found by our approach have only a statistical meaning. People working on direct methods usually consider  $N_{\text{eff}} = (\sum Z_j^2)^3 / (\sum Z_j^3)^2$  as the 'effective' number of atoms in the cell. In the same way,  $p$  (and  $q$ ) may be considered the corresponding 'effective' number of atoms that are (are not) affected by pseudotranslations. Thus  $N_{\text{eff}}$  will replace  $N$  in (14)–(16). This point of view will prove useful when triplet relationships by structures having superstructure effects will be estimated (Cascarano, Giacobozzo & Luić, 1985).

### 3. The normalization procedure

Our normalization program has been modified to handle structures having pseudotranslational symmetry. The number of different pseudotranslations having index  $n < 16$  is 64 (the lattice translations included) provided in (1)  $\mu'_i \leq 4$  for  $i = 1, 2, 3$ . The set of substructure reflections characterized by the condition

$$\mathbf{h}\mathbf{u} \equiv 0 \pmod{1} \quad (17)$$

has been associated with each pseudotranslation.

The seven different pairs and the unique triple of independent pseudotranslations of order two have also been considered. To each of them the set of substructure reflections characterized by the condition

$$\mathbf{h}\mathbf{u}_1 \equiv 0 \pmod{1} \text{ and } \mathbf{h}\mathbf{u}_2 \equiv 0 \pmod{1} \quad (18)$$

or

$$\mathbf{h}\mathbf{u}_1 \equiv 0 \pmod{1} \text{ and } \mathbf{h}\mathbf{u}_2 \equiv 0 \pmod{1}$$

and

$$\mathbf{h}\mathbf{u}_3 \equiv 0 \pmod{1} \quad (19)$$

is associated according to whether two or three independent pseudotranslations are assumed to coexist.

The indices of each reflection are analyzed in order to construct tables such as Tables 1, 2, where, for each of the 72 cases:

(a) the number of reflections satisfying (17) or (18) or (19) is given and their average intensity  $\langle |E|^2 \rangle_a$  is calculated. In addition, the user can input one or more index relationships and obtain the corresponding statistics.

(b) the values of  $p$  and  $q$  are calculated according to (15) and (16). In particular, (15) is calculated at maximum for two homogeneous sets of reflections having  $\alpha \neq 1$  and (16) is calculated for the set having  $\alpha = 0$ . Such a procedure allows us to estimate  $q/N$  also when reflections having  $\alpha = 1$  do not exist (for example, in a pseudo-cubic  $F$  cell);

(c) the figure of merit

$$R = \langle |E'^2| \rangle_a / \langle |E'^2| \rangle_b \quad (20)$$

is calculated for each of the 72 cases. In (20)  $\langle |E'^2| \rangle_a$  is the average intensity calculated for the set of reflections (17) or (18) or (19),  $\langle |E'^2| \rangle_b$  is calculated for the complementary set. The maximum value of (20) is expected to indicate the true pseudotranslational symmetry.

A new Wilson plot and renormalized structure factor  $E$  according to (12) are calculated. The simplest Wilson plot is given by

$$\lg \{ \langle |F_h|^2 \rangle / \langle \alpha_h \sum_p^0 + \sum_q^0 \rangle \} = -2Bs^2 - \lg K. \quad (21)$$

On the assumption that

$$\langle \alpha_h \sum_p^0 + \sum_q^0 \rangle \sim \sum_N^0$$

for every shell, (21) should produce the same  $B$  and  $K$  values provided by the usual Wilson method. In that case the  $E$ 's can be directly obtained according to

$$|E_h|^2 = |E'_h|^2 \sum_N^0 / (\alpha_h \sum_p^0 + \sum_q^0). \quad (22)$$

It is often advisable (e.g. when  $p$  atoms are heavy and  $q$  atoms are light) to refine simultaneously the temperature factors of the  $p$  and  $q$  atoms separately. Then a non-linear iterative least-squares procedure may be adopted (for an analogous approach, valid when a partial structure is known, see Parthasarathy, 1966; Gould, van den Hark & Beurskens, 1975), according to which the quantity to be minimized is

$$\sum_{\text{shells}} (G - G_p - G_q)^2,$$

where

$$G = \langle |F_h|^2 \rangle$$

$$G_p = K \alpha_h \sum_p^0 \exp(-2B_p s^2)$$

$$G_q = K \sum_q^0 \exp(-2B_q s^2).$$

The parameters to be refined are  $K$ ,  $B_p$  and  $B_q$ .

It is worthwhile observing that we do not normalize super- and substructure reflections separately as done by Böhme (1982). The separate normalization was the consequence of the separation of  $\rho(\mathbf{r})$  into  $\rho_p(\mathbf{r})$  and  $\rho(\mathbf{r}) - \rho_p(\mathbf{r})$ , which allowed the author to provide an empirical scheme for weighting the reliability of the various types of triplets. The probabilistic theory for triplet phase relationships to be described in the next paper (Casarano, Giacobuzzo & Luić, 1985) exempts us from using the separate normalization of super- and substructure reflections.

### 4. Experimental tests

Our normalization procedure has been tested over a large number of random equal-atom structures showing different kinds of pseudotranslational symmetry. The correct symmetry was always identified *via* (18) and accurate estimates of  $q/N$  were also provided (13% has been the maximum error in our tests). In Fig. 1 the cumulative distributions of  $z = |E|^2$  and  $z' = |E'|^2$  are compared with the theoretical cs and ncs Wilson distributions for a random  $P2$  structure characterized by

$$p = 40, q = 30, u = (\mathbf{a} + \mathbf{b})/4.$$

The program estimates are  $\mathbf{u} = (\mathbf{a} + \mathbf{b})/4$ ,  $p$ ,  $q = 39.2$ ,  $30.8$ . The curve  $N(z')$  in Fig. 1 has a centric character while  $N(z)$  reveals the non-centrosymmetric nature of the space group.

Table 1. A non-real P2 structure (20 Cl, 20 O, 50 C): the average  $\langle |E|^2 \rangle$  for 72 sets of reflections

The program indicates the correct pseudotranslation by a double arrow.

	number	$\langle E^{*2} \rangle$		number	$\langle E^{*2} \rangle$		number	$\langle E^{*2} \rangle$
1) all	= 1n	5322 1.000	2) h	= 2n	2635 .969	3) k	= 2n	2656 1.868 <<
4) l	= 2n	2662 .988	5) h+k+l	= 2n	2661 .992	6) h+k	= 2n	2665 .959
7) h+l	= 2n	2667 .992	8) k+l	= 2n	2680 .983	9) h	= 3n	1747 .966
10) k	= 3n	1764 .862	11) l	= 3n	1768 .954	12) h+k	= 3n	2961 1.059
13) h+l	= 3n	1778 .984	14) k+l	= 3n	2974 1.037	15) h+k+l	= 3n	2956 1.032
16) h+k+2l	= 3n	2974 1.015	17) h+2k+l	= 3n	2956 1.032	18) 2h+k+l	= 3n	2974 1.015
19) h+2k	= 3n	2961 1.059	20) h+2l	= 3n	1760 1.012	21) k+2l	= 3n	2974 1.037
22) l	= 4n	1316 .978	23) k	= 4n	1313 3.105	24) h	= 4n	1296 .915
25) h+k	= 4n	2009 .651	26) h+l	= 4n	1333 1.010	27) k+l	= 4n	2013 .686
28) h+k+l	= 4n	2010 .714	29) 2h+2k+l	= 4n	1335 .961	30) 2h+k+2l	= 4n	1332 1.864
31) h+2k+2l	= 4n	1316 .956	32) 2h+k+l	= 4n	2008 .683	33) h+2k+l	= 4n	1337 1.001
34) h+k+2l	= 4n	2005 .667	35) h+2k	= 4n	1306 .911	36) h+2l	= 4n	1318 .954
37) k+2l	= 4n	1335 1.842	38) 2h+k	= 4n	1338 1.817	39) 2h+l	= 4n	1331 .964
40) 2k+l	= 4n	1336 .970	41) 3h+3k+l	= 4n	1994 .717	42) 3h+k+3l	= 4n	2010 .714
43) h+3k+3l	= 4n	1994 .717	44) h+2k+3l	= 4n	1325 1.058	45) h+3k+2l	= 4n	2005 .667
46) 3h+k+2l	= 4n	2005 .667	47) h+3k	= 4n	2009 .651	48) h+3l	= 4n	1345 1.036
49) k+3l	= 4n	2013 .686	50) 3k+2l	= 6n	878 1.779	51) 2k+3l	= 6n	884 .940
52) 2h+3k	= 6n	871 1.796	53) 3h+2k	= 6n	867 .824	54) 3h+2l	= 6n	881 .924
55) 2h+3l	= 6n	873 .938	56) 2h+2k+3l	= 6n	1475 1.020	57) 3h+2k+3l	= 6n	887 .827
58) 3h+3k+2l	= 6n	891 .916	59) 4k+3l	= 12n	436 .916	60) 4h+3l	= 12n	423 .886
61) 4h+3k	= 12n	436 2.940	62) 3k+4l	= 12n	431 2.969	63) 3h+4k	= 12n	428 .740
64) 3h+4l	= 12n	434 .983						
			65) h = 2n & k = 2n	1317 1.803				
			66) h = 2n & l = 2n	1321 .949				
			67) k = 2n & l = 2n	1338 1.833				
			68) h = 2n & k+l = 2n	1327 .945				
			69) k = 2n & h+l = 2n	1331 1.850				
			70) l = 2n & h+k = 2n	1333 .940				
			71) h+k = 2n & h+l = 2n	1345 .935				
			72) h=2n & k=2n & l=2n	665 1.751				

The procedure has been tested also for unequal-atom structures. The risk was that structures with pseudotranslational symmetry between two atoms with different atomic numbers  $Z_1$  and  $Z_2$  respectively should be interpreted as produced by an equal-atom superposition structure (Takéuchi's substructure) with an intermediate  $Z$  factor (see Fig. 2). In Table 1 the statistical analysis over the 72 classes of reflections is given for a random P2 structure with  $N = 90$  (20 Cl, 20 O, 50 C). While C atoms are randomly

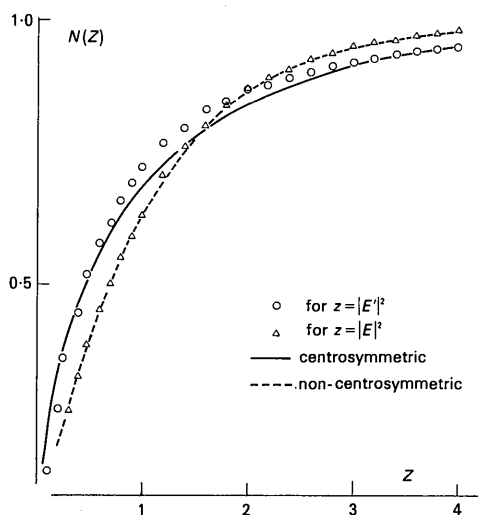


Fig. 1. Cumulative distributions for a non-real equal-atom P2 structure with  $t_p = 5$ ,  $t_o = 15$ ,  $\mathbf{u} = (\mathbf{a} + \mathbf{b})/4$ , before and after renormalization, compared with theoretical cs and ncs distributions.

dispersed in the cell, two symmetry-independent Cl atoms are related by  $\mathbf{u} = \mathbf{b}/2$ . Halfway between them an O atom is located in order to simulate the pseudotranslational symmetry  $\mathbf{u} = \mathbf{b}/4$  (see Fig. 2i). Our procedure correctly finds  $\mathbf{u} = \mathbf{b}/2$  (our  $R$  figure of merit is 13.70 for  $k = 2n$  and 9.92 for  $k = 4n$  reflections) in spite of the fact that  $\langle |E|^2 \rangle_{k=4n}$  is much larger than  $\langle |E|^2 \rangle_{k=2n}$ . The other parameters we chose for the structure were

$$N_{\text{eff}} \sim \left( \sum_{j=1}^N Z_j^2 \right)^3 / \left( \sum_{j=1}^N Z_j^3 \right)^2 = 48.87$$

$$(p/N)_{\text{eff}} = \left( \sum_{j=1}^p f_j^2 \right) / \left( \sum_{j=1}^N f_j^2 \right) = 0.80.$$

Our procedure calculates  $p/N = 0.87$ .

The large value of  $R$  for  $k = 4n$  suggests the additional presence of the pseudotranslation  $\mathbf{u} = \mathbf{b}/4$ . In this case the procedure calculates for  $p/N$  the value 0.69, which corresponds to the Takéuchi substructure.

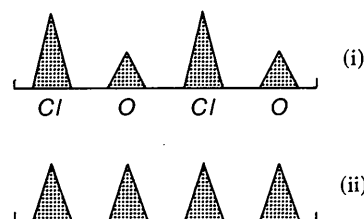


Fig. 2. (i) Translational symmetry with  $\mathbf{u} = \mathbf{b}/2$  relating Cl-Cl and O-O atoms. A pseudotranslational symmetry with  $\mathbf{u} = \mathbf{b}/4$  is also present relating Cl-O atoms. (ii) Takéuchi's superposition structure.

Table 2. *Freieslebenite*: the average  $\langle |E|^2 \rangle$  for 72 sets of reflections

The program indicates the correct pseudotranslation by a double arrow.

	number	$\langle E^{**2} \rangle$		number	$\langle E^{**2} \rangle$		number	$\langle E^{**2} \rangle$
1) all	= 1n	2000 1.000	2) h	= 2n	1026 1.665	3) k	= 2n	978 .960
4) l	= 2n	1006 1.057	5) h+k+l	= 2n	1010 .990	6) h+k	= 2n	1024 .917
7) h+l	= 2n	996 1.031	8) k+l	= 2n	1008 .986	9) h	= 3n	649 1.055
10) k	= 3n	631 2.022	11) l	= 3n	671 .976	12) h+k	= 3n	1128 .835
13) h+l	= 3n	662 .970	14) k+l	= 3n	1126 .810	15) h+k+l	= 3n	1121 .787
16) h+k+2l	= 3n	1129 .803	17) h+2k+l	= 3n	1121 .787	18) 2h+k+l	= 3n	1129 .803
19) h+2k	= 3n	1128 .835	20) h+2l	= 3n	654 .964	21) k+2l	= 3n	1126 .810
22) l	= 4n	496 1.051	23) k	= 4n	458 .923	24) h	= 4n	512 1.685
25) h+k	= 4n	768 .707	26) h+l	= 4n	488 1.024	27) k+l	= 4n	760 .964
28) h+k+l	= 4n	764 .989	29) 2h+2k+l	= 4n	506 1.070	30) 2h+k+2l	= 4n	484 .966
31) h+2k+2l	= 4n	508 2.402	32) 2h+k+l	= 4n	758 .965	33) h+2k+l	= 4n	500 1.012
34) h+k+2l	= 4n	772 .680	35) h+2k	= 4n	512 1.664	36) h+2l	= 4n	508 1.618
37) k+2l	= 4n	492 .958	38) 2h+k	= 4n	510 .852	39) 2h+l	= 4n	492 1.051
40) 2k+l	= 4n	506 1.084	41) 3h+3k+l	= 4n	758 .979	42) 3h+k+3l	= 4n	764 .984
43) h+3k+3l	= 4n	758 .979	44) h+2k+3l	= 4n	510 1.000	45) h+3k+2l	= 4n	772 .680
46) 3h+k+2l	= 4n	772 .680	47) h+3k	= 4n	768 .707	48) h+3l	= 4n	490 1.027
49) k+3l	= 4n	760 .964	50) 3k+2l	= 6n	325 .926	51) 2k+3l	= 6n	313 2.107
52) 2h+3k	= 6n	323 .949	53) 3h+2k	= 6n	339 3.684 <<	54) 3h+2l	= 6n	343 1.631
55) 2h+3l	= 6n	323 1.104	56) 2h+2k+3l	= 6n	570 .883	57) 3h+2k+3l	= 6n	313 2.081
58) 3h+3k+2l	= 6n	345 .896	59) 4k+3l	= 12n	157 2.057	60) 4h+3l	= 12n	159 1.079
61) 4h+3k	= 12n	151 .842	62) 3k+4l	= 12n	153 .852	63) 3h+4k	= 12n	171 3.685
64) 3h+4l	= 12n	169 1.593						
			65) h = 2n & k = 2n	514 1.543				
			66) h = 2n & l = 2n	514 1.749				
			67) k = 2n & l = 2n	496 1.004				
			68) h = 2n & k = 2n	522 1.630				
			69) k = 2n & h+l = 2n	492 .981				
			70) l = 2n & h+k = 2n	520 .963				
			71) h+k = 2n & h+l = 2n	514 .933				
			72) h=2n & k=2n & l=2n	262 1.593				

ture described in Fig. 2(ii). Indeed

$$(p/N)_{\text{eff}} = \sum (f_0 + f_{Cl})^2 / 2 \sum f_j^2 = 0.70.$$

In § 2(h) it has been pointed out that real crystal structures usually do not show 'exact' pseudotranslational symmetry. In order to introduce such a situation in our model we shifted every second Cl atom along the  $b$  axis by  $0.4 \text{ \AA}$ . Even if corresponding Patterson peaks were not resolved, the statistics proved to be affected. Our procedure finds  $\mathbf{u} = \mathbf{b}/4$  (our  $R$  figure of merit is 3.38 for  $k = 4n$  and 1.96 for  $k = 2n$  reflections) with  $(p/N) = 0.58$ . The outcome agrees well with the observation that the additional translation of  $0.4 \text{ \AA}$  degrades the pseudotranslation  $\mathbf{u} = \mathbf{b}/2$  more efficiently than  $\mathbf{u} = \mathbf{b}/4$  (see Fig. 2).

The outcome of our procedure for a real structure [Freieslebenite; Ito & Novacki (1974); PbAgSbS, space group  $P2_1/a$ ,  $Z = 4$ ] is shown in Table 2 and in Fig. 3. Our procedure correctly identifies the presence of two pseudotranslations;  $\mathbf{u}_1 = \mathbf{a}/2$  and  $\mathbf{u}_2 = \mathbf{b}/3$  relating atoms of different types (Sb, Pb, Ag) and calculates  $(p/N)_{\text{eff}} = 0.55$ , which is a reasonable value. In Fig. 3 it may be seen that after renormalization the  $N(z)$  curve loses the hypercentric character and approximates quite well the cs distribution.

## 5. Concluding remarks

The mathematical model of non-crystallographic pseudotranslational symmetry described in this paper cannot give a full account of all the situations that can occur in real crystals [see Cascarano, Giocovazzo

& Luić, (1984) for a detailed analysis]. However it seems a reasonable tool for handling the statistical properties of diffraction intensities. It is worthwhile mentioning that information on the presence and the nature of pseudotranslational symmetry can be directly obtained by a qualitative inspection of the Patterson map. If a partial interpretation of the map reveals the positions of some atoms then the full structure may be recovered by methods such as those described by Karle (1970), Beurskens, Prick, Doeburg & Gould (1979), Main (1976) and Giocovazzo (1983).

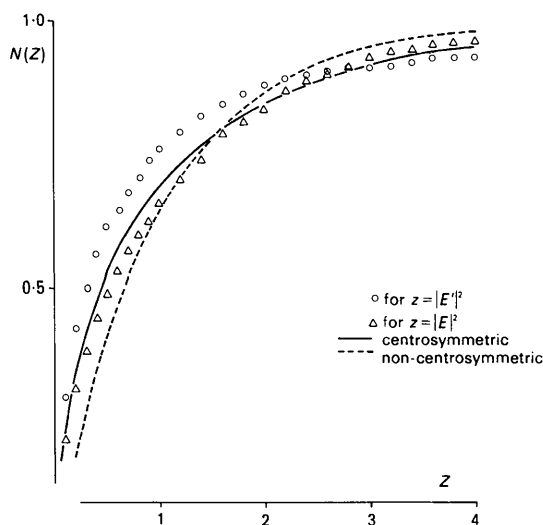


Fig. 3. Cumulative distribution for Freieslebenite before and after renormalization, compared with theoretical cs and ncs distributions.

If a partial structure is not available because: (1) the Patterson synthesis is not calculated; (2) the map is calculated but it is difficult to solve; (3) a light-atom structure is studied; then the mere information on the pseudotranslational symmetry may be used in order to normalize the structure factors correctly. In the second paper of this series (Cascarano, Giacovazzo & Luić, 1985) the same information will be used in order to estimate triplet invariants.

## APPENDIX

It is well known that

$$\sum_{k=0}^{n-1} \sin(x+ky) = \sin[x+(n-1)y/2] \sin[ny/2] / \sin[y/2], \quad (\text{A.1})$$

$$\sum_{k=0}^{n-1} \cos(x+ky) = \cos[x+(n-1)y/2] \sin[ny/2] / \sin[y/2]. \quad (\text{A.2})$$

From (A.1) and (A.2), (A.3) follows:

$$F_{ph} = \sum_{j=1}^{t_p} f_j \sum_{\nu=0}^{n-1} \exp 2\pi i h(\mathbf{r}_j + \nu \mathbf{u}) = \frac{\sin n\pi h \mathbf{u}}{\sin \pi h \mathbf{u}} \sum_{j=1}^{t_p} f_j \exp 2\pi i h \left( \mathbf{r}_j + \frac{n-1}{2} \mathbf{u} \right). \quad (\text{A.3})$$

From (A.3) the following factorization rule follows:

$$\sum_{\nu_1=0}^{n_1-1} \sum_{\nu_2=0}^{n_2-1} \exp 2\pi i h(\mathbf{r}_j + \nu_1 \mathbf{u}_1 + \nu_2 \mathbf{u}_2) = \sum_{\nu_1=0}^{n_1-1} \exp(2\pi i h \nu_1 \mathbf{u}_1) \sum_{\nu_2=0}^{n_2-1} \exp 2\pi i h(\mathbf{r}_j + \nu_2 \mathbf{u}_2)$$

*Acta Cryst.* (1985). **A41**, 551-556

## Use of the Fast Differentiation Algorithm for Phase Refinement in Protein Crystallography

BY V. YU. LUNIN

Research Computing Centre, USSR Academy of Sciences, 142292 Pushchino, Moscow Region, USSR

(Received 29 October 1984; accepted 7 May 1985)

### Abstract

Additional information of various kinds on the structure, such as 'atomicity', noncrystallographic symmetry, known molecular boundaries, nonnegativity of the electron density and so forth, may be described

$$\begin{aligned} &= \frac{\sin n_2 \pi h \mathbf{u}_2}{\sin \pi h \mathbf{u}_2} \exp \left[ 2\pi i h \left( \frac{n_2-1}{2} \right) \mathbf{u}_2 \right] \\ &\quad \times \sum_{\nu_1=0}^{n_1-1} \exp 2\pi i h(\mathbf{r}_j + \nu_1 \mathbf{u}_1) \\ &= \frac{\sin n_1 \pi h \mathbf{u}_1}{\sin \pi h \mathbf{u}_1} \frac{\sin n_2 \pi h \mathbf{u}_2}{\sin \pi h \mathbf{u}_2} \\ &\quad \times \exp 2\pi i h \left[ \mathbf{r}_j + \frac{1}{2}(n_1-1)\mathbf{u}_1 + \frac{1}{2}(n_2-1)\mathbf{u}_2 \right]. \end{aligned} \quad (\text{A.4})$$

### References

- BEURSKENS, P. T. & NOORDIK, J. H. (1971). *Acta Cryst.* **27**, 187-188.
- BEURSKENS, P. T., PRICK, A. J., DOESBURG, H. M. & GOULD, R. O. (1979). *Acta Cryst.* **A35**, 765-772.
- BÖHME, R. (1982). *Acta Cryst.* **A38**, 318-326.
- BÖHME, R. (1983). *Z. Naturforsch.* **38**, 304-307.
- BUERGER, M. (1956). *Proc. Natl Acad. Sci. USA*, **42**, 776-781.
- BUERGER, M. (1959). *Vector Space*. New York: Wiley.
- CASCARANO, G., GIACOVAZZO, C. & LUIĆ, M. (1984). In *Statistical Crystallography*. New York: Adenine Press. In the press.
- CASCARANO, G., GIACOVAZZO, C. & LUIĆ, M. (1985). In preparation.
- FAN HAI-FU, YAO JIA-XING, MAIN, P. & WOOLFSON, M. M. (1983). *Acta Cryst.* **A39**, 566-569.
- GIACOVAZZO, C. (1983). *Acta Cryst.* **A39**, 685-692.
- GOULD, R. O., VAN DEN HARK, TH. E. M. & BEURSKENS, P. T. (1975). *Acta Cryst.* **A31**, 813-817.
- GRAMLICH, V. (1975). *Acta Cryst.* **A31**, S90.
- GRAMLICH, V. (1984). Submitted to *Acta Cryst.*
- HAUPTMAN, H. & KARLE, J. (1959). *Acta Cryst.* **12**, 846-850.
- HEINERMAN, J. J. L. (1977). *Acta Cryst.* **A33**, 100-106.
- ITO, T. (1973). *Z. Kristallogr.* **137**, 399-411.
- ITO, T. & NOVACKI, W. (1974). *Z. Kristallogr.* **139**, 85-102.
- JEFFERY, J. W. (1964). *Acta Cryst.* **17**, 776-777.
- KARLE, J. (1970). In *Crystallographic Computing*. Copenhagen: Munksgaard.
- LIPSON, H. & WOOLFSON, M. M. (1952). *Acta Cryst.* **5**, 680-682.
- MAIN, P. (1976). *Crystallographic Computing Techniques*, edited by F. R. AHMED, pp. 97-105. Copenhagen: Munksgaard.
- PARTHASARATHY, S. (1966). *Z. Kristallogr.* **123**, 27-50.
- QURASHI, M. M. (1963). *Acta Cryst.* **16**, 307-310.
- ROGERS, D. & WILSON, A. J. C. (1953). *Acta Cryst.* **6**, 439-449.
- TAKÉUCHI, Y. (1972). *Z. Kristallogr.* **135**, 120-136.
- TAXER, K. (1981). *Z. Kristallogr.* **155**, 1-25.

by an equation  $\rho = \tau[\rho]$  or by the corresponding system of equations for structure factors. To use this information, one tries generally to solve the 'phase' part of the structure-factor equations by simple iterations. The complete system of equations can, however, be used for phase refinement if the latter is