OTANI, S., TANAKA, T. & ISHIZAWA, Y. (1983). *J. Cryst. Growth*, **62**, 211-218.
SAUVAGE, M. & PARTHÉ, E. (1972). *Acta Cryst.* A**28**, 607-616.
SAUVAGE, M. & PARTHÉ, E. (1974). *Acta Cryst.* A**30**, 239-249.
SAUVAGE, M., PARTHÉ, E. & YELON, W. B. (1974). *Acta Cryst.* A**30**, 597-599.
STORMS, E. K. (1967). *The Refractory Carbides.* New York: Academic Press.
TERAUCHI, H. & COHEN, J. B. (1979). *Acta Cryst.* A**35**, 646-652.
TOTH, L. E. (1971). *Transition Metal Carbides and Nitrides.* New York: Academic Press.
TOTH, L. E., ICHIKAWA, M. & CHANG, Y. A. (1968). *Acta Metall.* **16**, 1183-1187.
TOTH, L. E., WANG, C. P. & YEN, C. M. (1966). *Acta Metall.* **14**, 1403-1408.
TOTH, L. E. & ZBASNIK, J. (1968). *Acta Metall.* **16**, 1177-1182.
VENABLES, J. D. & LYE, R. G. (1969). *Philos. Mag.* **19**, 565-582.
WEBER, W. (1973). *Phys. Rev. B*, **8**, 5082-5092.
WILLIAMS, R. O. (1972). Report ORNL 4828. Oak Ridge National Laboratory, TN, USA.
WU, T. B., MATSUBARA, E. & COHEN, J. B. (1983). *J. Appl. Cryst.* **16**, 407-414.

Acta Cryst. (1988). A**44**, 176-183

Direct Methods and Structures Showing Superstructure Effects. III. A General Mathematical Model

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Abstract

A general mathematical model is presented which can describe a large variety of structures showing superstructure effects. In particular the model can take into account deviations, both of displacive and of replacive type, of the substructural part from ideal pseudotranslational symmetry. The formulation is used to predict statistical effects of deviations on diffraction data. It is shown that the scattering power of the substructural part may be estimated *via* a statistical analysis of diffraction data for ideal pseudotranslational symmetry or for displacive deviation from it, while it is not estimable in the case of replacive deviation.

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.
$F_{\mathbf{h}}$: structure factor with vectorial index $\mathbf{h}$.
$\mathbf{C}_s=(\mathbf{R}_s, \mathbf{T}_s)$: sth symmetry operator. $\mathbf{R}_s$ is the rotational part, $\mathbf{T}_s$ the translational part.
N: number of atoms in the cell.
m: order of the space group (it coincides with the number of symmetry operators).
$\mathbf{u}_i$: ith pseudotranslation in the unit cell.
n_i: order of the pseudotranslation $\mathbf{u}_i$.
p: number of atoms (symmetry-equivalent included) whose positions are related by the pseudotranslations $\mathbf{u}$.
q: number of atoms (symmetry-equivalent included) whose positions are not related by any pseudotranslation.
t_p: number of independent atoms which generate the p atoms when the pseudotranslations $\mathbf{u}_i$ and the symmetry operators $\mathbf{C}_s$, $s=1, \ldots, m$ are applied.
t_q: number of independent atoms which generate the q atoms by application of the symmetry operators $\mathbf{C}_s$, $s=1, \ldots, m$.
$\rho(\mathbf{r})$: electron density function in the unit cell.
$\rho_p(\mathbf{r})$, $\rho_q(\mathbf{r})$: electron density functions corresponding to the p atoms and q atoms respectively.
$\varepsilon_{\mathbf{h}}$: weight of the reflexion $\mathbf{h}$ in Wilson's statistics.
$\sum_{t_p}, \sum_{t_q}, \sum_p, \sum_q, \sum_N = \sum f_j^2$ (thermal factor included) where the summation is extended to the t_p, t_q, p, q, N atoms respectively.
$(F_{\mathbf{h}})_p$, $(F_{\mathbf{h}})_q$: structure factors relative to the p and to the q atoms respectively.
$E'_{\mathbf{h}}=F_{\mathbf{h}}/(\varepsilon_{\mathbf{h}}\sum_N)^{1/2}$: normalized structure factor in the absence of any information on pseudotranslational symmetry.
$E_{\mathbf{h}}$: normalized structure factor if prior information on pseudotranslational symmetry is taken into account.
$\varphi_{\mathbf{h}}, \varphi_{\mathbf{k}}, \ldots$: phase of $E_{\mathbf{h}}, E_{\mathbf{k}}, \ldots$.
$[\sigma_r]_p, [\sigma_r]_q, [\sigma_r]_N, \ldots = \sum Z_j^r$, where Z_j is the atomic

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number of the jth atom and the summation is made over the p, q, N, ... atoms.
$C_{\mathbf{h}}=\{\alpha_{\mathbf{h}}[\sigma_2]_p+[\sigma_2]_q\}^{-1/2}$.
I_0: modified Bessel function of order zero.

$$\sum_{\nu_1,\nu_2,\nu_3,\ldots,s}=\sum_{\nu_1=0}^{n_1-1}\sum_{\nu_2=0}^{n_2-1}\sum_{\nu_3=0}^{n_3-1}\cdots\sum_{s=1}^{m}.$$

Papers by Cascarano, Giacovazzo & Luić (1985, 1987) will be denoted respectively as papers I and II. The next paper of this series (Cascarano, Giacovazzo & Luić, 1988) will be referred to as paper IV.

Other symbols are defined in the text.

1. Introduction

The popularity of direct methods is mostly due to the fact that no structural information is strictly required for their success in solving crystal structures. In the absence of any information atoms are supposed to be uniformly distributed in the unit cell. If this condition is strongly violated, for example for crystal structures which have superstructure characteristics, then the crystal structure solution is usually difficult. The suggestion by Hauptman & Karle (1959) of rescaling normalized structure factors for the various classes of reflexions sometimes succeeds but it often proves unable to solve structures.

More recently some important contributions by Fan Hai-fu, Yao Jia-xing, Main & Woolfson (1983), Böhme (1982, 1983) and Gramlich (1984) have given important insights into the problem. In all these methods renormalization was combined with suitable probabilistic considerations in order to provide better estimations of triplet invariants.

The present paper aims at generalizing the mathematical model which was used in papers I and II to describe pseudotranslational symmetries so as to make it more suitable for real crystal structures. In paper IV a more robust probabilistic approach will be described which aims to determine at the same time the positions both of the substructural and of the superstructural atoms.

The practical procedure proposed in papers I and II may be summarized as follows:

(1) A mathematical model of the structure is constructed according to which one or more independent pseudotranslations $\mathbf{u}_i$, $i=1,2,3,\ldots$ may be simultaneously present. For each atom in $\mathbf{r}_j$ suffering pseudotranslational symmetry, $mn_1n_2n_3\ldots$ equivalent atoms can be found at

$$\mathbf{C}_s(\mathbf{r}_j+\nu_1\mathbf{u}_1+\nu_2\mathbf{u}_2+\nu_3\mathbf{u}_3+\ldots),$$

where

$$1\le s\le m,\qquad 0\le\nu_i\le n_i-1.$$

Then the structure factor equation may be defined as

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

Equation (1) may be rewritten as

$$F_{\mathbf{h}}=\sum_{j=1}^{t_p+t_q}f_jg_j, \quad (2)$$

where

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

if $j\le t_p$, and

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

if $j>t_p$.

(2) For a given $\mathbf{h}$

$$\langle|F_{\mathbf{h}}|^2\rangle=\varepsilon_{\mathbf{h}}\left(\alpha_{\mathbf{h}}\sum_p+\sum_q\right) \quad (3a)$$

where

$$\alpha_{\mathbf{h}}=(n_1n_2n_3\ldots)\gamma_{\mathbf{h}}/m.$$

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

$$\mathbf{h}\mathbf{R}_s\mathbf{u}_i\equiv 0\ (\mathrm{mod}\ 1)\quad \text{for } i=1,2,3,\ldots$$

are simultaneously satisfied when s varies from 1 to m. The fractional scattering powers $\sum_q/\sum_N$ and $\sum_p/\sum_N=(1-\sum_q/\sum_N)$ are calculated according to

$$\frac{\langle|E'_{\mathbf{h}}|^2\rangle-\alpha_{\mathbf{h}}}{1-\alpha_{\mathbf{h}}}=\frac{\sum_q}{\sum_N} \quad (3b)$$

or to

$$\frac{(\langle|E'_{\mathbf{h}}|^2\rangle-1)}{\alpha_{\mathbf{h}}-1}=\frac{\sum_p}{\sum_N} \quad (3c)$$

where the averages are taken over reflexions with a fixed value of α.

$F_{\mathbf{h}}$ is defined to be a superstructure reflexion if $\gamma_{\mathbf{h}}=0$ (for these $\langle|E'_{\mathbf{h}}|^2\rangle=\sum_q/\sum_N$), otherwise $F_{\mathbf{h}}$ is a substructure reflexion. The maximum value of γ is

m; consequently the maximum value of α is $n_1 n_2 n_3 \ldots$.

(3) Structure factors are renormalized according to

$$E_{\mathbf{h}} = F_{\mathbf{h}} \Big/ \left[\varepsilon_{\mathbf{h}} \left(\alpha_{\mathbf{h}} \sum_p + \sum_q \right) \right]^{1/2}.$$

Only the largest $E_{\mathbf{h}}$ are used in an active way in the phase determination process.

(4) The distribution of the triplet phase $\Phi = \varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}}$ is found to be of von Mises type: the maximum of the distribution occurs always at 2π, and the concentration parameter is given by

$$A(\mathbf{h}, \mathbf{k}, \mathbf{h}-\mathbf{k}) = 2|E_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}| / [N(\mathbf{h}, \mathbf{k}, \mathbf{h}-\mathbf{k})]^{1/2}$$

where

$$N(\mathbf{h}, \mathbf{k}, \mathbf{h}-\mathbf{k}) = \frac{(\alpha_{\mathbf{h}}[\sigma_2]_p + [\sigma_2]_q)(\alpha_{\mathbf{k}}[\sigma_2]_p + [\sigma_2]_q)(\alpha_{\mathbf{h}-\mathbf{k}}[\sigma_2]_p + [\sigma_2]_q)}{\{(\beta/m)[\sigma_3]_p (n_1^2 n_2^2 n_3^2 \ldots) + [\sigma_3]_q\}^2}. \quad (4)$$

β is the number of times for which

$$\begin{cases} \mathbf{h}\mathbf{R}_s\mathbf{u}_1 \equiv 0 \pmod 1, \mathbf{h}\mathbf{R}_s\mathbf{u}_2 \equiv 0 \pmod 1, \\ \quad \mathbf{h}\mathbf{R}_s\mathbf{u}_3 \equiv 0 \pmod 1, \ldots \\ \mathbf{k}\mathbf{R}_s\mathbf{u}_1 \equiv 0 \pmod 1, \mathbf{k}\mathbf{R}_s\mathbf{u}_2 \equiv 0 \pmod 1, \\ \quad \mathbf{k}\mathbf{R}_s\mathbf{u}_3 \equiv 0 \pmod 1, \ldots \\ (\mathbf{h}-\mathbf{k})\mathbf{R}_s\mathbf{u}_1 \equiv 0 \pmod 1, (\mathbf{h}-\mathbf{k})\mathbf{R}_s\mathbf{u}_2 \equiv 0 \pmod 1, \\ \quad (\mathbf{h}-\mathbf{k})\mathbf{R}_s\mathbf{u}_3 \equiv 0 \pmod 1, \ldots \end{cases}$$

are simultaneously satisfied when s varies from 1 to m. Obviously, $\beta \le m$: furthermore β cannot exceed the minimum of $\gamma_{\mathbf{h}}$, $\gamma_{\mathbf{k}}$ and $\gamma_{\mathbf{h}-\mathbf{k}}$.

Even if the procedure works quite well in most practical cases, it suffers some limitations:

(i) Real substructures often do not exactly comply with the mathematical model described in step 1 (*i.e.* atoms related by pseudotranslational symmetry are not exactly located or are of different nature). Such a situation involves a correlation between the superstructure and the substructure which was not taken into account by our model.

(ii) p atoms and q atoms may be of different type and may have different temperature factors: then the fractional scattering powers $\sum_q / \sum_N$ and $\sum_p / \sum_N$ are unknown functions of $(\sin^2\theta)/\lambda^2$. In this view their estimates through the average $\langle |E'|^2 \rangle$ as described in step 2 have different accuracy at the various $(\sin^2\theta)/\lambda^2$.

In spite of these limitations the renormalization procedure (step 3) may in principle almost always be satisfactorily performed. However, if some heavy atoms are present the method does not provide the species and the number of atoms suffering pseudotranslational symmetry. The unfavourable consequence is that $[\sigma_3]_p$ and $[\sigma_3]_q$ are not accessible *via* the statistical analysis of intensities so that $N(\mathbf{h}, \mathbf{k}, \mathbf{h}-\mathbf{k})$ is not exactly computable *via* (4).

For practical applications heavy atoms were supposed to be equally distributed in the substructural as well as in the superstructural part. In that case (4) was replaced by

$$N(\mathbf{h}, \mathbf{k}, \mathbf{h}-\mathbf{k}) = \frac{(\alpha_{\mathbf{h}} p + q)(\alpha_{\mathbf{k}} p + q)(\alpha_{\mathbf{h}-\mathbf{k}} p + q)}{[(\beta/m) p (n_1^2 n_2^2 n_3^2 \ldots) + q]^2}$$

where

$$p = \left[\frac{\sigma_2^3}{\sigma_3^2}\right]_N \frac{\sum_p}{\sum_N}, \quad q = \left[\frac{\sigma_2^3}{\sigma_3^2}\right]_N \frac{\sum_q}{\sum_N}. \quad (5)$$

In the present paper and in paper IV a more general mathematical model is proposed which can take into account a large variety of non-ideal substructures.

It will be shown that some parameters characterizing the nature of the superstructure will still remain unknown (namely the parameters $[\sigma_3]_p$ and $[\sigma_3]_q$ after the use of the new model) but some recipes will be obtained which make the phase determination process more robust.

2. The new mathematical model

Any crystal structure possessing spherical atoms can be described by means of the electron density distribution

$$\rho(\mathbf{r}) = \sum_{j=1}^{t_p + t_q} \sum_{\nu_1, \nu_2, \nu_3, \ldots, s} \rho_{j, \nu_1, \nu_2, \nu_3, \ldots} \times [\mathbf{r} - \mathbf{C}_s(\mathbf{r}_j + \nu_1\mathbf{u}_1 + \nu_2\mathbf{u}_2 + \nu_3\mathbf{u}_3 + \ldots + \Delta\mathbf{r}_{j, \nu_1, \nu_2, \nu_3, \ldots})] \quad (6)$$

if appropriate choices of the atomic densities $\rho_{j, \nu_1, \nu_2, \nu_3, \ldots}$ and of the shift parameters $\Delta\mathbf{r}_{j, \nu_1, \nu_2, \nu_3, \ldots}$ are made. The Fourier transform of (6) gives

$$F_{\mathbf{h}} = \sum_{j=1}^{t_p + t_q} \sum_{\nu_1, \nu_2, \nu_3, \ldots, s} (f_j + \Delta f_{j, \nu_1, \nu_2, \nu_3, \ldots}) \times \exp[2\pi i \mathbf{h}\mathbf{C}_s(\mathbf{r}_j + \nu_1\mathbf{u}_1 + \nu_2\mathbf{u}_2 + \nu_3\mathbf{u}_3 + \ldots + \Delta\mathbf{r}_{j, \nu_1, \nu_2, \nu_3, \ldots})], \quad (7)$$

where f_j is the scattering factor of the jth atom with position vector $\mathbf{r}_j$, $(f_j + \Delta f_{j, \nu_1, \nu_2, \nu_3, \ldots})$ is the scattering factor of the atom positioned at $(\mathbf{r}_j + \nu_1\mathbf{u}_1 + \nu_2\mathbf{u}_2 + \nu_3\mathbf{u}_3 + \ldots + \Delta\mathbf{r}_{j, \nu_1, \nu_2, \nu_3, \ldots})$. $\Delta f_{j, \nu_1, \nu_2, \nu_3, \ldots}$ may be positive or negative: without loss of generality it will always be assumed that $\Delta f_{j, \nu_1, \nu_2, \nu_3, \ldots} > (-f_j)$ in order to preserve the positivity of the electron density.

Specific cases are:

(a) No pseudotranslational symmetry occurs: then $\Delta\mathbf{r}_{j, \nu_1, \nu_2, \nu_3, \ldots}$ and/or $\Delta f_{j, \nu_1, \nu_2, \nu_3, \ldots}$ are sufficiently large and numerous.

An ideal pseudotranslational symmetry occurs: then both $\Delta\mathbf{r}_{j, \nu_1, \nu_2, \nu_3, \ldots}$ and $\Delta f_{j, \nu_1, \nu_2, \nu_3, \ldots}$ vanish for $j \le t_p$ and are sufficiently large for $j \ge (t_p + 1)$.

(*b*) If $p=(mt_pn_1n_2n_3\ldots)$ atoms related by pseudotranslational symmetry are ideally located but of different type and q atoms have uncorrelated positions, then the positional shifts $\Delta\mathbf{r}_{j,\nu_1,\nu_2,\nu_3,\ldots}$ vanish for $j\leq t_p$ while they are sufficiently large for $t_p<j\leq t_p+t_q$. In addition $\Delta f_{j,\nu_1,\nu_2,\nu_3,\ldots}$ do not all vanish for $j\leq t_p$ [the special case of missing atoms corresponds to $\Delta f_{j,\nu_1,\nu_2,\nu_3,\ldots}=(-f_j)$].

The following change of variables will prove useful: in (7), for $j\leq t_p$, $f_j+\Delta f_{j,\nu_1,\nu_2,\nu_3,\ldots}$ is replaced by $\hat{f}_j+\delta f_{j,\nu_1,\nu_2,\nu_3,\ldots}$, where $\hat{f}_j$ is the mean scattering factor obtained when the average (for fixed j) is calculated over the atomic positions

$$(\mathbf{r}_j+\nu_1\mathbf{u}_1+\nu_2\mathbf{u}_2+\nu_3\mathbf{u}_3+\ldots),$$
$$0\leq\nu_j\leq n_i-1,\ i=1,2,3,\ldots.$$

$\hat{f}_j$ is therefore the jth scattering factor of the so-called average or Takéuchi substructure $\hat{\rho}_p(\mathbf{r})$ (Takéuchi, 1972).

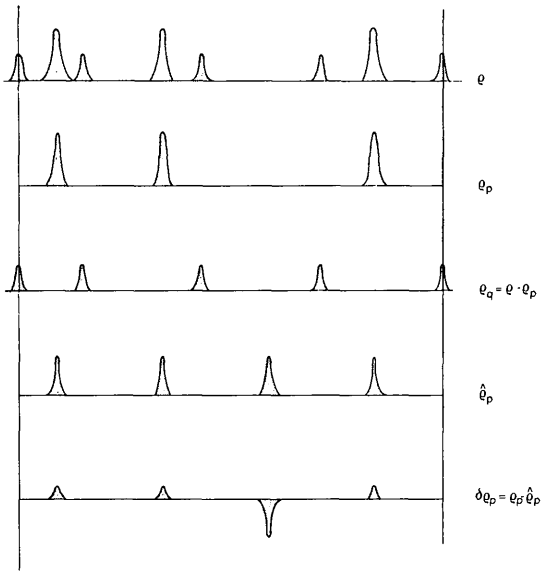

Fig. 1. Gaussian 'atoms' are located in a one-dimensional unit cell. Three heavy atoms satisfy the pseudotranslational vector $\mathbf{u}=\mathbf{a}/4$, the fourth has been missed. Four light atoms belong to ρ_q.

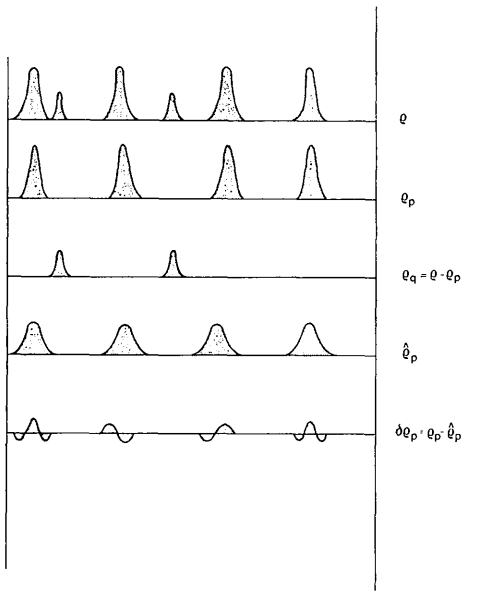

Fig. 2. Gaussian 'atoms' are located in a one-dimensional cell with a pseudotranslation $\mathbf{u}=\mathbf{a}/4$. Atoms related by $\mathbf{u}$ are of the same type but slightly shifted from ideal positions.

Under these conditions (7) may be written as

$$\begin{aligned}F_{\mathbf{h}}=&\sum_{j=1}^{t_p}\hat{f}_j\sum_{\nu_1,\nu_2,\nu_3,\ldots,s}\exp\left[2\pi i\mathbf{h}\mathbf{C}_s(\mathbf{r}_j+\nu_1\mathbf{u}_1\right.\\&\left.+\nu_2\mathbf{u}_2+\nu_3\mathbf{u}_3+\ldots)\right]\\&+\sum_{j=1}^{t_p}\delta f_{j,\nu_1,\nu_2,\nu_3,\ldots}\sum_{\nu_1,\nu_2,\nu_3,\ldots,s}\exp\left[2\pi i\mathbf{h}\mathbf{C}_s(\mathbf{r}_j+\nu_1\mathbf{u}_1\right.\\&\left.+\nu_2\mathbf{u}_2+\nu_3\mathbf{u}_3+\ldots)\right]\\&+\sum_{j=t_p+1}^{t_p+t_q}\sum_{s=1}^{m}f_j\exp\left(2\pi i\mathbf{h}\mathbf{C}_s\mathbf{r}_j\right)\\=&(F_{\mathbf{h}})_{\hat{p}}+(F_{\mathbf{h}})_{p-\hat{p}}+(F_{\mathbf{h}})_q\end{aligned}\tag{8}$$

where the meanings of the symbols are clear. $(F_{\mathbf{h}})_{\hat{p}}$ corresponds to the structure factor of the average structure according to Takéuchi (1972).

In Fig. 1 a unidimensional model structure $\rho(x)$ is shown: for the pseudotranslational vector $\mathbf{u}=\mathbf{a}/4$ (where $t_p=1$ and $t_q=4$) $\rho_p(x)$, $\hat{\rho}_p(x)$, $\rho_q(x)$ and $\delta\rho_p(x)=\rho_p(x)-\hat{\rho}_p(x)$ are given.

(*c*) Atoms related by pseudotranslational symmetry are equal but not ideally located (see Fig. 2). Then $\Delta f_{j,\nu_1,\nu_2,\nu_3,\ldots}\equiv 0$ for $j\leq t_p$, $\Delta\mathbf{r}_{j,\nu_1,\nu_2,\nu_3,\ldots}\neq 0$ but small for $j\leq t_p$, $\Delta\mathbf{r}_{j,\nu_1,\nu_2,\nu_3,\ldots}\neq 0$ and large for $t_p+1\leq j$. In this case (7) reduces to

$$\begin{aligned}F_{\mathbf{h}}=&\sum_{j=1}^{t_p}f_j\sum_{\nu_1,\nu_2,\nu_3,\ldots,s}\exp\left[2\pi i\mathbf{h}\mathbf{C}_s(\hat{\mathbf{r}}_j+\nu_1\mathbf{u}_1\right.\\&\left.+\nu_2\mathbf{u}_2+\nu_3\mathbf{u}_3+\ldots+\delta\mathbf{r}_{j,\nu_1,\nu_2,\nu_3,\ldots})\right]\\&+\sum_{j=t_p+1}^{t_q}f_j\sum_{s=1}^{m}\exp\left(2\pi i\mathbf{h}\mathbf{C}_s\mathbf{r}_j\right),\end{aligned}\tag{9}$$

where $\hat{\mathbf{r}}_j$ is the jth position vector of the average substructure $\hat{\rho}_p(\mathbf{r})$, and $\delta\mathbf{r}_{j,\nu_1,\nu_2,\nu_3,\ldots}$ satisfy

$$\hat{\mathbf{r}}_j+\delta\mathbf{r}_{j,\nu_1,\nu_2,\nu_3,\ldots}=\mathbf{r}_j+\Delta\mathbf{r}_{j,\nu_1,\nu_2,\nu_3,\ldots}.$$

(*d*) Atoms related by pseudotranslational symmetry are of different type and are also shifted from ideal positions. Then $\Delta f_{j,\nu_1,\nu_2,\nu_3,\ldots}$ and $\Delta\mathbf{r}_{j,\nu_1,\nu_2,\nu_3,\ldots}$ are not too large for $j\leq t_p$.

3. Pseudotranslational symmetry and statistical effects on the reciprocal space

3(*a*)

In paper I a procedure was described which, for ideal pseudotranslational symmetries, is able to

Table 1. *Main data for four randomly generated structures with space group P1 differing by a pseudotranslation vector* $\mathbf{u}=\mathbf{a}/3$ *(when* $\alpha_M=3$*)*

The values in the columns headed by $\sum_p/\sum_N$, $\sum_q/\sum_N$, $\sum_{\hat{p}}/\sum_N$ and $\sum_{p-\hat{p}}/\sum_N$ are true values, calculated *via* the integrals of the scattering factors for Na and C

Structure	$(\text{Type})_p$	t_p	p	$(\text{Type})_q$	q	$\sum_p/\sum_N$	$\sum_q/\sum_N$	$\sum_{\hat{p}}/\sum_N$	$\sum_{p-\hat{p}}/\sum_N$	$\langle\lvert E'_{\mathbf{h}}\rvert^2\rangle_{\text{super}}$
*S*1	C	6	18	C	18	0·50	0·50	0·50	0·0	0·49
*S*2	C	6	12	C	18	0·40	0·60	0·27	0·13	0·79
*S*3	Na	6	18	C	18	0·83	0·17	0·83	0·0	0·16
*S*4	Na	6	12	C	18	0·75	0·26	0·50	0·24	0·60

estimate the scattering powers $\sum_p$ and $\sum_q$ *via* a statistical analysis of diffraction data. The meaning of those estimates is unclear when that mathematical model is applied to real cases. In particular, it seems important to ascertain which relation exists between that estimate of $\sum_p$ and the scattering powers of the Takéuchi substructure or of the so-called reduced or Buerger (1956) substructure. While this problem does not exist for ideal pseudotranslational symmetries (when the two substructures coincide), for real ones it is of great importance because it can affect the efficiency of the phasing process.

Let us examine the various cases mentioned in § 2.

3(*b*) *Case* (*b*)

If atoms related by pseudotranslational symmetry are ideally located but of different type then the experimental values $\langle\lvert E'_{\mathbf{h}}\rvert^2\rangle$ for the various classes of reflexions provide estimates [see (*A*.8) of the Appendix] for

$$\left(\frac{\sum_{\hat{p}}}{\sum_N}-\frac{1}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}\right)$$

and

$$\left(\frac{\sum_q}{\sum_N}+\frac{\alpha_M}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}\right)$$

where α_M is the maximum value of $\alpha_{\mathbf{h}}$. More precisely

$$\begin{aligned}(1-\langle\lvert E'_{\mathbf{h}}\rvert^2\rangle_{\text{super}})&=\frac{\sum_{\hat{p}}}{\sum_N}-\frac{1}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N},\\ \langle\lvert E'_{\mathbf{h}}\rvert^2\rangle_{\text{super}}&=\frac{\sum_q}{\sum_N}+\frac{\alpha_M}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}.\end{aligned}\qquad(10)$$

It may be concluded that: (1) in the absence of supplementary information $\sum_{\hat{p}}/\sum_N$, $\sum_{p-\hat{p}}/\sum_N$, $\sum_q/\sum_N$ are in general not accessible from the statistical analysis of diffraction data; (2) $\sum_{\hat{p}}/\sum_N\geq(1-\langle\lvert E'_{\mathbf{h}}\rvert^2\rangle_{\text{super}})$ and $\sum_q/\sum_N\leq\langle\lvert E'_{\mathbf{h}}\rvert^2\rangle_{\text{super}}$.

In order to verify that our conclusions hold in practice four random *P*1 structures have been generated for which a pseudotranslation $\mathbf{u}=\mathbf{a}/3$ has been applied to $t_p=$ six atoms.

In Table 1 the main data for the four structures are shown: *S*1 and *S*2 are equal-atom structures, in *S*3 and *S*4 *p* atoms and *q* atoms are of different type. In order to generate a non-ideal pseudotranslational symmetry, one of three atoms related by **u** has been omitted in *S*2 and *S*4 (thus only 12 atoms of *p* type instead of 18 are present there). Data in Table 1 closely satisfy relations (10) and show how important the contribution of $\sum_{p-\hat{p}}/\sum_N$ may be in certain cases.

3(*c*) *Case* (*c*)

The case in which atoms related by pseudotranslational symmetry are equal but not ideally located (see Fig. 2) may be treated by squaring (9):

$$\begin{aligned}\langle\lvert F_{\mathbf{h}}\rvert^2\rangle\simeq\sum_{j=1}^{t_p}f_j^2\Bigg\langle\sum_{\substack{s,\nu_1,\nu_2,\nu_3,\ldots\\ \nu'_1,\nu'_2,\nu'_3,\ldots}}&\exp\left[2\pi i\mathbf{h}\mathbf{C}_s(\nu_1\mathbf{u}_1+\nu_2\mathbf{u}_2\right.\\ &+\nu_3\mathbf{u}_3+\ldots+\delta\mathbf{r}_{j,\nu_1,\nu_2,\nu_3,\ldots}-\nu'_1\mathbf{u}_1-\nu'_2\mathbf{u}_2\\ &\left.-\nu'_3\mathbf{u}_3-\ldots-\delta\mathbf{r}_{j,\nu'_1,\nu'_2,\nu'_3,\ldots})\right]\Bigg\rangle+\sum_q.\end{aligned}$$

If the shifts $\delta\mathbf{r}_{j,\nu_1,\nu_2,\nu_3,\ldots}$ are assumed to be equally and normally distributed then the quantity $(\alpha_{\mathbf{h}}\sum_p)$ in (3) has to be replaced (Mackay, 1953) by

$$\{\exp[-K\langle\lvert\delta\mathbf{r}\rvert^2\rangle(\sin^2\theta)/\lambda^2]\}\alpha_{\mathbf{h}}\sum_{\hat{p}},\qquad(11)$$

where K is a constant not defined here and $\langle\lvert\delta\mathbf{r}\rvert^2\rangle$ is the average square shift from ideal to actual atomic positions. According to (11) non-vanishing $\langle\lvert\delta\mathbf{r}\rvert^2\rangle$'s cause a transfer of intensity from substructure to superstructure reflexions, which varies with resolution. This transfer may be assumed to be linear in the permitted range of $(\sin\theta)/\lambda$ if $\langle\lvert\delta\mathbf{r}\rvert^2\rangle$ is small enough (large shifts should destroy the pseudotranslational symmetry).

Mathematical considerations presented in the Appendix for case (*b*) will hold in this case too: in particular (*A*.2) and (*A*.5) are still valid so that information may be obtained through (*A*.8*a*) and (*A*.8*b*) on

$$\left(\frac{\sum_{\hat{p}}}{\sum_N}-\frac{1}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}\right)$$

and

$$\left(\frac{\sum_q}{\sum_N}+\frac{\alpha_M}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}\right).$$

This time, however, as many values of

$$\frac{\sum_{\hat{p}}}{\sum_N}-\frac{1}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}$$

will be obtained as the number of ranges of $(\sin\theta)/\lambda$ into which reciprocal space has been divided. In Fig. 3 for three random structures (labelled *S*1, *S*1*M*, *S*1*MM*) the values of

$$\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}}=\left(\frac{\sum_q}{\sum_N}+\frac{\alpha_M}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}\right)$$

are shown at various $(\sin\theta)/\lambda$, together with corresponding least-squares straight lines. It may be observed that:

(1) *S*1 is a structure with ideal pseudotranslational symmetry (see Table 1), for which the value of $\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}}$ should not change on average with $(\sin\theta)/\lambda$.

(2) *S*1*M* and *S*1*MM* are obtained from *S*1 by randomly shifting p atoms by $\langle|\delta\mathbf{r}|\rangle=0{\cdot}2$ and $0{\cdot}3$ Å respectively. Different slopes of the least-squares straight lines are obtained for the two structures in accordance with expectations. Increasing values [with $(\sin\theta)/\lambda$] of $\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}}$ are due to the increasing contribution of $\sum_{p-\hat{p}}/\sum_N$.

(3) If a deviation from an ideal pseudotranslational symmetry is only due to positional shifts of equal atoms from ideal positions then an approximate estimate of $\sum_q/\sum_N$ (and therefore of $\sum_p/\sum_N$) is available, which is the value of the straight line at $(\sin\theta)/\lambda=0$.

3(*d*) *Case* (*d*)

If atoms related by pseudotranslational symmetry are of different type and are also shifted from ideal positions, then the effects described in §§ 3(*b*) and 3(*c*) will be present simultaneously. In particular, the slopes of the least-squares straight lines will again be defined by the average shifts $\langle|\delta\mathbf{r}|^2\rangle$, but their intercepts at $(\sin\theta)/\lambda=0$ will no longer coincide with $\sum_{\hat{p}}/\sum_N$, but with $(\sum_{\hat{p}}/\sum_N)-\Delta_s$, where Δ_s is the value of

$$\left(\frac{1}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}\right)$$

calculated in § 3(*b*).

In Fig. 4 the least-squares straight lines are shown for the real structures listed in Table 2. They appear to be affected in different ways by displacive deviations from ideal pseudotranslational symmetry (in good agreement with structural data to be described in § 4 of paper IV), while replacive deviations still remain unknown.

4. The renormalization procedure

In accordance with (*A*.7)

$$\begin{aligned}E_{\mathbf{h}}&=F_{\mathbf{h}}\Big/\left\{\varepsilon_{\mathbf{h}}\left[\alpha_{\mathbf{h}}\left(\sum_{\hat{p}}-\frac{1}{\alpha_M-1}\sum_{p-\hat{p}}\right)\right.\right.\\&\quad\left.\left.+\left(\frac{\alpha_M}{\alpha_M-1}\sum_{p-\hat{p}}+\sum_q\right)\right]\right\}^{1/2}\\&=E'_{\mathbf{h}}\Big/\left[\alpha_{\mathbf{h}}\left(\frac{\sum_{\hat{p}}}{\sum_N}-\frac{1}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}\right)\right.\\&\quad\left.+\left(\frac{\alpha_M}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}+\frac{\sum_q}{\sum_N}\right)\right]^{1/2}\\&=E'_{\mathbf{h}}/\langle|E'_{\mathbf{h}}|^2\rangle^{1/2}\end{aligned}\qquad(12)$$

where $\langle|E'_{\mathbf{h}}|^2\rangle$ is calculated at the $(\sin\theta)/\lambda$ corresponding to **h**.

Equation (12) justifies, from a theoretical point of view, the empirical Hauptman & Karle (1959) suggestion of renormalizing E' by simply rescaling $\langle|E'|^2\rangle$ to unity for the various classes of reflexions. In addition the present theory warns the reader that care of the $|\mathbf{h}|$ values has to be taken into the renormalization process; furthermore, paper II suggests that a record has to be taken also of the estimates for $\sum_p/\sum_N$

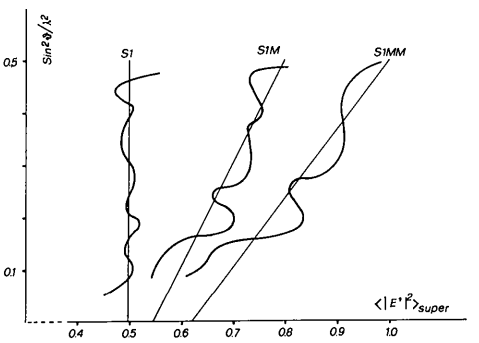

Fig. 3. $\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}}$ *versus* $(\sin^2\theta)/\lambda^2$ and least-squares straight lines for three random structures.

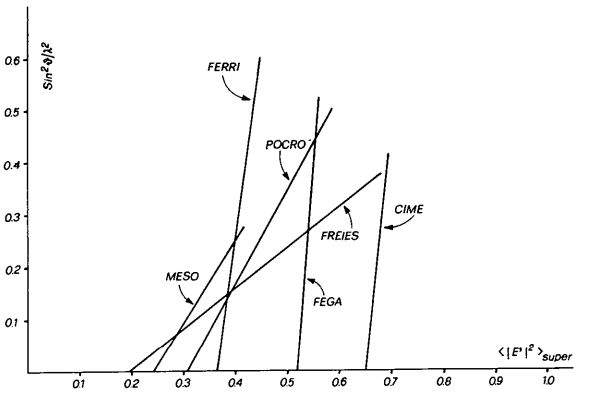

Fig. 4. $\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}}$ *versus* $(\sin^2\theta)/\lambda^2$ least-squares straight lines for structures listed in Table 2.

Table 2. *Real test structures: code title and chemical formula, space group, pseudotranslational vector* **u**, *references*

Crystal structure	Space group	**u**	References
Freieslebenite $PbAgSbS_3$	$P2_1/a$, $Z=4$	**a**/2+**b**/3	Ito & Novacki (1974)
Mesolite $Na_2Ca_2Al_6Si_9O_{30}.8H_2O$	$Fdd2$, $Z=16$	**a**/3	Adiwidjaja (1972)
Ferri $Fe_2(SO_4)_3$	$P2_1/n$, $Z=4$	(**a**+**b**)/2	Christidis & Rentzeperis (1975)
Fega $Fe_2Ga_2S_5$	$P6_3/mmc$, $Z=2$	**c**/3	Cascarano, Dogguy-Smiri & Nguyen-Huy Dung (1987)
Cimetidine $C_{10}H_{16}N_6S.H_2O$	Cc, $Z=4$	(**a**+**c**)/2	Kojić-Prodić, Ružić-Toroš, Bresciani-Pahor & Randaccio (1980)
Pocro KCr_5Se_8	$B2/m$, $Z=2$	**a**/6+**c**/2	Nguyen-Huy Dung, Vo-Van Tien, Behm & Beurskens (1987)

and $\sum_q/\sum_N$ in order to use them for triplet phase estimation.

In a more convenient way (12) may be written, according to (*A*.6*a*) and (*A*.6*b*), as

$$E_{\mathbf{h}} = E'_{\mathbf{h}}/[\alpha_{\mathbf{h}}(1-\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}})+\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}}]^{1/2}, \quad (13)$$

or, more generally, according to (*A*.8*a*) and (*A*.8*b*), as

$$E_{\mathbf{h}} = E'_{\mathbf{h}}\Big/\left[\alpha_{\mathbf{h}}\left(\frac{\langle|E'|^2\rangle-1}{\alpha_i-1}\right)+\left(\frac{\langle|E'|^2\rangle-\alpha_i}{1-\alpha_i}\right)\right]^{1/2}, \quad (14)$$

where the averages are made over reflexions with fixed α_i value. In practice the new normalization procedure may be described as follows:

(*a*) $|E'|$ moduli are calculated by the usual Wilson's plot and pseudotranslational symmetry is identified *via* statistical analysis of diffraction data (see paper I).

(*b*) $\langle|E'|^2\rangle_{\text{super}}$ is plotted as a function of $(\sin\theta)/\lambda$ and a least-squares straight line is calculated.

(*c*) Renormalization according to (13) and (14) is accomplished by use of least-squares straight-line values for each $(\sin\theta)/\lambda$.

The slope and intercept of the straight line are passed to a subsequent program for the estimation of triplet invariants (see paper IV).

APPENDIX

Let us derive an expression for $\langle|F_{\mathbf{h}}|^2\rangle$ for a crystal structure with a substructural unit having atoms (related by pseudotranslational symmetry) exactly located but of different nature [see point (*b*) of § 2]. For simplicity we shall assume that pseudotranslational symmetry divides reflexions into two homogeneous subsets, the substructure reflexions with $\alpha_{\mathbf{h}}=\alpha_M$ and superstructure reflexions with $\alpha_{\mathbf{h}}=0$. From equation (8)

$$\begin{aligned}\langle|F_{\mathbf{h}}|^2\rangle = {} & \langle|(F_{\mathbf{h}})_{\hat{p}}|^2\rangle+\langle|(F_{\mathbf{h}})_{p-\hat{p}}|^2\rangle+\langle|(F_{\mathbf{h}})_q|^2\rangle \\ & +2\langle(F_{\mathbf{h}})_{\hat{p}}(F_{-\mathbf{h}})_{p-\hat{p}}\rangle+2\langle(F_{\mathbf{h}})_{\hat{p}}(F_{-\mathbf{h}})_q\rangle \\ & +2\langle(F_{\mathbf{h}})_{p-\hat{p}}(F_{-\mathbf{h}})_q\rangle.\end{aligned}$$

If one assumes that the positions of the atomic peaks in ρ_p and $\hat{\rho}_p$ are uncorrelated with the atomic positions in ρ_q, one may obtain

$$\langle(F_{\mathbf{h}})_{\hat{p}}(F_{-\mathbf{h}})_q\rangle \simeq \langle(F_{\mathbf{h}})_{p-\hat{p}}(F_{-\mathbf{h}})_q\rangle \simeq 0.$$

Furthermore, in accordance with definitions, for substructure reflexions

$$(F_{\mathbf{h}})_p = (F_{\mathbf{h}})_{\hat{p}}, \quad (F_{\mathbf{h}})_{p-\hat{p}} = 0, \quad (A.1)$$

so that

$$\begin{aligned}\langle|F_{\mathbf{h}}|^2\rangle_{\text{sub}} &= \langle|(F_{\mathbf{h}})_{\hat{p}}|^2\rangle_{\text{sub}}+\langle|(F_{\mathbf{h}})_q|^2\rangle_{\text{sub}} \\ &= \varepsilon_{\mathbf{h}}[\alpha_M\textstyle\sum_{\hat{p}}+\sum_q]. \quad (A.2)\end{aligned}$$

Since $\sum_{\hat{p}}=\sum_N-\sum_q-\sum_{p-\hat{p}}$, then (*A*.2) becomes

$$\langle|F_{\mathbf{h}}|^2\rangle_{\text{sub}} = \varepsilon_{\mathbf{h}}[\alpha_M\textstyle\sum_N-\alpha_M\sum_{p-\hat{p}}+\sum_q(1-\alpha_M)], \quad (A.3)$$

from which

$$\frac{\sum_q}{\sum_N}+\frac{\alpha_M}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}=\frac{(\langle|E'_{\mathbf{h}}|^2\rangle_{\text{sub}}-\alpha_M)}{1-\alpha_M} \quad (A.4a)$$

or

$$\frac{\sum_{\hat{p}}}{\sum_N}-\frac{1}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}=\frac{\langle|E'_{\mathbf{h}}|^2\rangle_{\text{sub}}-1}{\alpha_M-1}. \quad (A.4b)$$

Similar observations for superstructure reflexions ($\alpha_{\mathbf{h}}=0$) lead to

$$\begin{aligned}\langle|F_{\mathbf{h}}|^2\rangle_{\text{super}} &= \langle|(F_{\mathbf{h}})_{p-\hat{p}}|^2\rangle_{\text{super}}+\langle|(F_{\mathbf{h}})_q|^2\rangle_{\text{super}} \\ &= \varepsilon_{\mathbf{h}}\left(\frac{\alpha_M}{\alpha_M-1}\textstyle\sum_{p-\hat{p}}+\sum_q\right), \quad (A.5)\end{aligned}$$

from which

$$\left(\frac{\sum_q}{\sum_N}+\frac{\alpha_M}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}\right)=\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}} \quad (A.6a)$$

or

$$\left(\frac{\sum_{\hat{p}}}{\sum_N}-\frac{1}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}\right)=1-\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}}. \quad (A.6b)$$

Finally the general relation (*A*.7) is obtained,

$$\langle|F_{\mathbf{h}}|^2\rangle = \varepsilon_{\mathbf{h}}\left(\alpha_{\mathbf{h}}\textstyle\sum_{\hat{p}}+\frac{\alpha_M-\alpha_{\mathbf{h}}}{\alpha_M-1}\sum_{p-\hat{p}}+\sum_q\right) \quad (A.7)$$

which replaces (3*a*). Accordingly (*A*.4*b*) and (*A*.6*b*) may be replaced by

$$\frac{\sum_{\hat{p}}}{\sum_N}-\frac{1}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}=\frac{(\langle|E_{\mathbf{h}}|^2\rangle-1)}{\alpha_{\mathbf{h}}-1}, \quad (A.8a)$$

and (*A*.4*a*) and (*A*.6*a*) by

$$\frac{\sum_q}{\sum_N}+\frac{\alpha_M}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}=\frac{\langle|E_{\mathbf{h}}|^2\rangle-\alpha_{\mathbf{h}}}{1-\alpha_{\mathbf{h}}}. \qquad (A.8b)$$

The average $\langle|E_{\mathbf{h}}|^2\rangle$ are made over subsets of reflexions with fixed α.

Equations (*A*.8) may be interpreted by observing that, while

$$\int_V \rho_p(\mathbf{r})\,d\mathbf{r}=\int_V \hat{\rho}_p(\mathbf{r})\,d\mathbf{r},$$

it holds that

$$\int_V \hat{\rho}_p^2(\mathbf{r})\,d\mathbf{r}\leq\int_V \rho_p^2(\mathbf{r})\,d\mathbf{r}.$$

The excess of scattering power of ρ_p with respect to $\hat{\rho}_p$ is completely transferred to the set of superstructure reflexions. Thus the averages $\langle|E'_{\mathbf{h}}|^2\rangle_{\text{sub}}$ and $\langle|E'_{\mathbf{h}}|^2\rangle_{\text{super}}$ will lead, through (*A*.4) and (*A*.6), to

$$\left(\frac{\sum_{\hat{p}}}{\sum_N}-\frac{1}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}\right)$$

and to

$$\left(\frac{\sum_{\hat{p}}}{\sum_N}+\frac{\alpha_M}{\alpha_M-1}\frac{\sum_{p-\hat{p}}}{\sum_N}\right)$$

rather than to the identification of $\sum_{\hat{p}}/\sum_N$, $\sum_{p-\hat{p}}/\sum_N$, $\sum_q/\sum_N$. Thus, even if the various subsets of reflexions may be renormalized by using the corresponding experimental values of $\langle|F_{\mathbf{h}}|^2\rangle$, the information (so useful for estimating triplet reliability) on $\sum_{\hat{p}}$, $\sum_{p-\hat{p}}$ and $\sum_q$ is not accessible.

References

ADIWIDJAJA, G. (1972). Dissertation. Univ. Hamburg, Federal Republic of Germany.

BÖHME, R. (1982). *Acta Cryst.* A**38**, 316-326.

BÖHME, R. (1983). *Z. Naturforsch.* **38**, 304-307.

BUERGER, M. (1956). *Proc. Natl Acad. Sci. USA*, **42**, 776-781.

CASCARANO, G., DOGGUY-SMIRI, L. & NGUYEN-HUY DUNG (1987). *Acta Cryst.* C**43**, 2050-2053.

CASCARANO, G., GIACOVAZZO, C. & LUIĆ, M. (1985). *Acta Cryst.* A**41**, 544-551.

CASCARANO, G., GIACOVAZZO, C. & LUIĆ, M. (1987). *Acta Cryst.* A**43**, 14-22.

CASCARANO, G., GIACOVAZZO, C. & LUIĆ, M. (1988). *Acta Cryst.* A**44**, 183-188.

CHRISTIDIS, P. C. & RENTZEPERIS, R. J. (1975). *Z. Kristallogr.* **141**, 233-245.

FAN HAI-FU, YAO JIA-XING, MAIN, P. & WOOLFSON, M. M. (1983). *Acta Cryst.* A**39**, 566-569.

GRAMLICH, V. (1984). *Acta Cryst.* A**40**, 610-616.

HAUPTMAN, H. & KARLE, J. (1959). *Acta Cryst.* **12**, 846-850.

ITO, T. & NOVACKI, W. (1974). *Z. Kristallogr.* **139**, 85-102.

KOJIĆ-PRODIĆ, B., RUŽIĆ-TOROŠ, Z., BRESCIANI-PAHOR, N. & RANDACCIO, L. (1980). *Acta Cryst.* B**36**, 1223-1225.

MACKAY, A. L. (1953). *Acta Cryst.* **6**, 214-215.

NGUYEN-HUY DUNG, VO-VAN TIEN, BEHM, H. J. & BEURSKENS, P. T. (1987). *Acta Cryst.* C**43**, 2258-2260.

TAKÉUCHI, Y. (1972). *Z. Kristallogr.* **135**, 120-136.

Acta Cryst. (1988). A**44**, 183-188

Direct Methods and Structures Showing Superstructure Effects. IV. A New Approach for Phase Solution

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Abstract

The mathematical model proposed in paper III of this series [Cascarano, Giacovazzo & Luić (1988). *Acta Cryst.* A**44**, 176-183] for describing structures with superstructure effects has been used to derive probabilistic formulas for estimating triplet invariants. The formulas obtained proved sufficiently robust to be applied successfully to a wide range of structures with superstructure effects, in which deviations both of replacive and of displacive type from ideal pseudotranslational symmetry occur.

Symbols and abbreviations

Symbols and abbreviations are as in paper III (Cascarano, Giacovazzo & Luić, 1988) of this series. Reference will also be made to papers I (Cascarano, Giacovazzo & Luić, 1985) and II (Cascarano, Giacovazzo & Luić, 1987).

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