# On the Application of Phase Relationships to Complex Structures. XXIII. Automatic Determination of Crystal Structures having Pseudo-Translational Symmetry by a Modified *MULTAN* Procedure

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## Abstract

The *MULTAN*-80 program has been modified to handle structures having pseudo-translational symmetry. In this case the intensities of reflexions belonging to some index groups are systematically much weaker than others. The program can classify reflexions in groups in the usual way or according to certain index relationships specified by the user. The temperature factor and the scaling factor can then be calculated for each index group separately. The program recognizes the index groups with systematically weak reflexions; phase triplets involving three such reflexions will be eliminated in the SIGMA2 list. Each starting phase set is developed in two stages. During the first stage only the phases of the 'strong' reflexions are generated while in the second stage the phases of the 'weak' reflexions will be derived from phase relationships of the type 'weak–strong–weak'. Finally, an $E$ map using $E$ values before rescaling, rather than the rescaled ones, is calculated. Tests on typical known structures show that the procedure is a very effective one.

## Introduction

Crystal structures having pseudo-translational symmetry, such as superstructures and some heavy-atom-containing structures with the arrangement of the heavy atoms possessing certain subperiodicity, are notoriously difficult to solve. Attempts to solve such structures by the Patterson method or by conventional direct methods often lead to solutions containing several structural images related by the pseudo-translational symmetry. Normally there is no straightforward way to go from such a false solution to the true one. Fan, He, Qian & Liu (1978) have proposed a procedure by which the phases of the superstructure (systematically weak) reflexions can be derived by

making use of the phases of the subcell structure (systematically strong) reflexions. This procedure has now been made automatic and incorporated into the *MULTAN*-80 program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980).

## Theory

For a crystal having pseudo-translational symmetry the true structure can be described by superimposing a difference structure on to a subcell structure, in which the atoms are related exactly by the pseudo-translational symmetry. We write

$$\rho(\mathbf{r}) = \rho_p(\mathbf{r}) + \Delta\rho(\mathbf{r}), \qquad (1)$$

where $\rho(\mathbf{r})$ is the electron-density function of the true structure, $\rho_p(\mathbf{r})$ is that of the subcell structure and $\Delta\rho(\mathbf{r})$ is the difference electron density function between the true structure and the subcell structure. Fourier transforming both sides of the above equation gives

$$F(\mathbf{H}) = F_p(\mathbf{H}) + \Delta F(\mathbf{H}) \qquad (2)$$

where $F(\mathbf{H})$ is the structure factor of the true structure, $F_p(\mathbf{H})$ is the structure factor of the subcell structure and $\Delta F(\mathbf{H})$ denotes the Fourier transform of the difference structure. If a reciprocal vector $\mathbf{H}$ does not fall on a grid point of the reciprocal lattice of the subcell structure then it must correspond to a superstructure (systematically weak) reflexion. In this case $F_p(\mathbf{H})$ in (2) is zero. The structure factor of a superstructure reflexion is denoted by $F_s(\mathbf{H})$ and (2) becomes

$$F_s(\mathbf{H}) = \Delta F(\mathbf{H}). \qquad (3)$$

If both sides of (1) are squared and the term $\Delta\rho_2(\mathbf{r})$ is neglected it follows that

$$\rho^2(\mathbf{r}) = \rho_p^2(\mathbf{r}) + 2\rho_p(\mathbf{r})\,\Delta\rho(\mathbf{r}), \qquad (4)$$

from which, by Fourier transformation, one finds

$$F^{sq}(\mathbf{H}) = F_p^{sq}(\mathbf{H}) + (2/V) \sum_{\mathbf{H'}} F_p(\mathbf{H'}) \, \Delta F(\mathbf{H} - \mathbf{H'}), \quad (5)$$

where $F^{sq}(\mathbf{H})$ denoted the Fourier transform of $\rho^2(\mathbf{r})$. If $\mathbf{H}$ is a vector corresponding to one of the super-structure reflexions then (5) becomes

$$F_s^{sq}(\mathbf{H}) = \frac{2}{V} \sum_{\mathbf{H'}} F_p(\mathbf{H'}) \, F_s(\mathbf{H} - \mathbf{H'}). \quad (6)$$

Assuming that the crystal consists of nearly identical atoms or that the contributions of heavy atoms to the superstructure reflexions are either nearly zero or approximately as weak as those of the light atoms, we have

$$F_s^{sq}(\mathbf{H}) \sim f^{sq} \sum_{j=1}^{N} \exp 2\pi i \mathbf{H} . \mathbf{r}_j$$

$$= (f^{sq}/f) \sum_{j=1}^{N} f \exp 2\pi i \mathbf{H} . \mathbf{r}_j = \frac{1}{\varphi} F_s(\mathbf{H}) \quad (7)$$

where $f$ is the averaged atomic scattering factor, $f^{sq}$ is the averaged scattering factor of the 'squared' atoms and $\varphi = f/f^{sq}$. Substituting (7) into (6), we finally obtain

$$F_s(\mathbf{h}) = \frac{2\varphi}{V} \sum_{\mathbf{H'}} F_p(\mathbf{H'}) \, F_s(\mathbf{H} - \mathbf{H'}). \quad (8)$$

Equation (8) gives the phase relationship between the systematically strong reflexions and the systematically weak reflexions. With the help of this equation, a crystal structure having pseudo-translational symmetry can be determined in two stages; the phases of the systematically strong reflexions $F_p(\mathbf{H})$ can first be found by conventional direct methods and then the phases of the systematically weak reflexions $F_s(\mathbf{H})$ can be derived from the known phases of $F_p(\mathbf{H})$ by making use of (8).

### The modification on the MULTAN-80 program

In order to incorporate the above procedure into the MULTAN-80 program, the subroutines NORMAL and MULTAN have been modified to accommodate the following features:

1. The user can input index relationships for the classification of reflexions in up to 20 groups. This is needed in handling intensity data of structures having pseudo-translational symmetry since the 'strong' and 'weak' reflexion groups may have to be classified in ways not accepted in the original MULTAN-80 program.

2. The temperature and scaling factors are calculated for different index groups separately or the user

may specify the values of these factors for different index groups independently. In the event that the structure possesses pseudo-translational symmetry, atoms of different kinds and/or in different sites may have varying average contributions to different reflexion groups. For this reason, in order to obtain a better set of $E$ values, it is worth while to let different reflexion groups have their own temperature and scaling factors.

3. The program determines which groups have average intensities ($\langle E^2 \rangle$ before rescaling) lower than some given limit, the default value being 0·30. Reflexions in such groups will be treated by the program as 'systematically weak reflexions' and are distinguished from the 'strong' reflexions in further processing.

4. If there exist phase relationships involving three systematically weak reflexions then these will be disregarded and the tangent refinement for each starting phase set will be carried out in two stages. In the first stage, phases of reflexions other than the systematically weak ones are developed in the usual way. Then, in the second stage, those phases previously derived and having their weight greater than 0·9 will be treated as known phases and the phases of the systematically weak reflexions together with those of the remaining strong reflexions are developed.

5. For the calculation of $E$ maps the values before rescaling rather than the rescaled ones are output to the subroutine EXFFT. If the scaling factors of different index groups differ greatly from each other, the $E$ map calculated with rescaled $E$ values would have no proper physical basis; $E$ maps calculated with $E$ values before rescaling usually give a much better result.

### Practical examples

*Example* 1. $AsF_2(C_6H_5)_2$ (*Zheng, Xu & Fan*, 1981)

The structure belongs to space group Pbcn with unit-cell parameters $a = 6·272$, $b = 16·575$, $c = 14·511$ Å and $Z = 8$. The heavy atom, As, has coordinates approximately $(0\frac{11}{44})$ leading to the pseudo-translational symmetry with additional translation vectors $\mathbf{t}_1 = (\mathbf{a} - \mathbf{c})/2$ and $\mathbf{t}_2 = (\mathbf{b} - \mathbf{c})/2$. Hence the heavy atoms contribute to only the two parity groups with indices $h$, $k$ and $l$ either all even or all odd. Consequently a Patterson analysis or a heavy-atom phased Fourier map will result in a fourfold multiple solution, in which four structure images of the light-atom portion, related by $\mathbf{t}_1$ and $\mathbf{t}_2$, superimpose together. MULTAN-80 (unmodified) could solve this structure without too much difficulty. However, the heavy atom does not appear as the first but rather as the sixth strongest peak in the best $E$ map. On the other hand, a better, and more easily interpreted, result was obtained using the modified MULTAN-80 (Table 1).

Table 1. *Comparison of results from modified and unmodified MULTAN-80 for* $AsF_2(C_6H_5)_3$

| | From the best $E$ map by MULTAN-80 | | From the best $E$ map by the modified MULTAN-80 | |
|---|---|---|---|---|
| Atom | Peak no. | Height | Peak no. | Height |
| As | 6 | 1042 | 1 | 2170 |
| F | 1 | 1403 | 2 | 1576 |
| C1–C10 | 2–5 | 1359–1056 | 3–12 | 1262–666 |
| | 7–12 | 964–701 | | |

*Example* 2. $PbAgSbS_3$, *freielebenite* (*Ito & Nowacki*, 1974)

This is a typical superstructure and had been a test structure of the 'key shift method' (Ito, 1973). The superstructure belongs to space group $P2_1/a$ with unit-cell parameters $a = 7.518$, $b = 12.809$, $c = 5.940$ Å, $\beta = 92.25°$ and $Z = 4$. There are two pseudo-translation vectors $t_1 = a/2$ and $t_2 = b/3$ in the unit cell so that reflexions having $h \neq 2n$ or $k \neq 3n$ are

Table 2. *Comparison of results for* $PbAgSbS_3$

Shifts in the wrong direction are underlined.

Parameter shifts in the superstructure

| | Atomic parameters in the pseudo-structure | | | Final values | | | From the best $E$ map by the modified MULTAN-80 | | | | | From the best $E$ map by MULTAN-80 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Atom | $x$ | $y$ | $z$ | $\Delta x$ | $\Delta y$ | $\Delta z$ | $\Delta x$ | $\Delta y$ | $\Delta z$ | Peak | Height | $\Delta x$ | $\Delta y$ | $\Delta z$ | Peak | Height |
| Pb | 0.375 | 0.417 | 0.250 | −0.025 | −0.002 | −0.003 | −0.012 | −0.004 | +0.011 | 1 | 3266 | −0.005 | −0.002 | −0.014 | 1 | 4236 |
| Ag | 0.375 | 0.750 | 0.250 | +0.003 | +0.010 | −0.038 | +0.012 | +0.001 | −0.030 | 2 | 3264 | −0.001 | +0.008 | −0.006 | 2 | 2880 |
| Sb or As | 0.375 | 0.083 | 0.250 | −0.010 | +0.004 | +0.022 | −0.009 | +0.004 | +0.016 | 3 | 3148 | +0.012 | −0.004 | +0.029 | 3 | 2114 |
| S (1) | 0.125 | 0.250 | 0.250 | +0.013 | −0.031 | +0.096 | +0.012 | −0.029 | +0.095 | 5 | 791 | +0.018 | −0.028 | +0.079 | 5 | 857 |
| S (2) | 0.125 | 0.583 | 0.250 | +0.010 | +0.039 | −0.119 | −0.002 | +0.038 | −0.109 | 6 | 684 | | | | | |
| S (3) | 0.125 | 0.917 | 0.250 | +0.023 | +0.025 | +0.016 | +0.024 | +0.035 | +0.016 | 4 | 870 | +0.015 | +0.035 | +0.034 | 4 | 969 |

Table 3. *Comparison of results for* $BaCeF(CO_3)_2$

| | Pseudo-structure | | | | | | | | | Superstructure | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | From heavy-atom method | | | Final result | | | From the modified MULTAN-80 | | | | | From MULTAN-80 | | | | |
| Atom | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ | Peak | Height | $x$ | $y$ | $z$ | Peak | Height |
| Ce(1) | 0 | 0 | 0.25 | 0 | 0 | 0.25 + 0.0053 | 0 | 0 | 0.25 + 0.0073 | 1 | 5250 | 0 | 0 | 0.25 + 0.0136 | 4 | 2516 |
| Ce(2) | 0 | 0 | 0.75 | 0 | 0 | 0.75 − 0.0049 | 0 | 0 | 0.75 − 0.0068 | 2 | 4831 | 0 | 0 | 0.75 + 0.0005 | 2 | 4994 |
| Ba(1) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 | 4104 | 0 | 0 | 0 | 1 | 5102 |
| Ba(2) | 0 | 0 | 0.50 | 0 | 0 | 0.50 + 0.0009 | 0 | 0 | 0.50 + 0.0004 | 3 | 4132 | 0 | 0 | 0.50 + 0.0096 | 3 | 2995 |
| F(1) | 0 | 0 | 0.3151 | 0 | 0 | 0.3170 | 0 | 0 | 0.3149 | 7 | 734 | 0 | 0 | 0.3240 | 14 | 428 |
| * | 0 | 0 | 0.5651 | | | | 0 | 0 | 0.5655 | 10 | 624 | 0 | 0 | 0.5708 | 13 | 456 |
| * | 0 | 0 | 0.8151 | | | | 0 | 0 | 0.8237 | 17 | 511 | 0 | 0 | 0.8092 | 31 | 297 |
| * | 0 | 0 | 0.0651 | | | | 0 | 0 | 0.0654 | 9 | 645 | | | | | |
| F(2) | 0 | 0 | 0.6863 | 0 | 0 | 0.6849 | 0 | 0 | 0.6849 | 8 | 676 | 0 | 0 | 0.6524 | 9 | 692 |
| * | 0 | 0 | 0.9352 | | | | 0 | 0 | 0.9345 | 11 | 623 | 0 | 0 | 0.9392 | 16 | 407 |
| * | 0 | 0 | 0.1862 | | | | 0 | 0 | 0.1756 | 22 | 466 | 0 | 0 | 0.1787 | 12 | 497 |
| * | 0 | 0 | 0.4362 | | | | 0 | 0 | 0.4349 | 12 | 610 | 0 | 0 | 0.4280 | 25 | 325 |
| C(1) | 0 | 0 | 0.11 ~ 0.14 | 0 | 0 | 0.1272 | 0 | 0 | 0.1260 | 5 | 796 | 0 | 0 | 0.1347 | 8 | 736 |
| C(2) | 0 | 0 | 0.36 ~ 0.39 | 0 | 0 | 0.3936 | 0 | 0 | 0.3895 | 15 | 571 | 0 | 0 | 0.3945 | 39 | 264 |
| C(3) | 0 | 0 | 0.61 ~ 0.64 | 0 | 0 | 0.6086 | 0 | 0 | 0.6154 | 19 | 495 | 0 | 0 | 0.6087 | 7 | 822 |
| C(4) | 0 | 0 | 0.86 ~ 0.89 | 0 | 0 | 0.8735 | 0 | 0 | 0.8747 | 6 | 752 | 0 | 0 | 0.8649 | 36 | 275 |
| O(1) | 0.1426 | 0.2851 | 0.1248 | 0.1482 | 0.2964 | 0.1268 | 0.1308 | 0.2661 | 0.1326 | 13 | 599 | 0.1630 | 0.2947 | 0.1148 | 20 | 360 |
| * | 0.2891 | 0.1446 | 0.1251 | | | | 0.2653 | 0.1397 | 0.1243 | 20 | 494 | | | | | |
| O(2) | 0.1425 | 0.2849 | 0.3748 | 0.1489 | 0.2977 | 0.3947 | 0.1204 | 0.2550 | 0.3773 | 18 | 495 | | | | | |
| * | 0.2891 | 0.1446 | 0.3751 | | | | 0.2549 | 0.1290 | 0.3830 | 23 | 352 | | | | | |
| O(3) | 0.2890 | 0.1445 | 0.6251 | 0.2816 | 0.1408 | 0.6082 | 0.2593 | 0.1370 | 0.6235 | 16 | 519 | | | | | |
| * | 0.1425 | 0.2850 | 0.6248 | | | | 0.1184 | 0.2524 | 0.6175 | 25 | 303 | 0.1537 | 0.2854 | 0.5933 | 23 | 342 |
| O(4) | 0.2896 | 0.1448 | 0.8751 | 0.2926 | 0.1463 | 0.8724 | 0.2651 | 0.1399 | 0.8733 | 14 | 572 | 0.2870 | 0.1654 | 0.8584 | 29 | 299 |
| * | 0.1433 | 0.2865 | 0.8748 | | | | 0.1300 | 0.2646 | 0.8764 | 21 | 486 | 0.1489 | 0.2839 | 0.8576 | 34 | 283 |

\* Denotes a pseudo-translation image of a true atom.

systematically much weaker than those reflexions with $h = 2n$ and $k = 3n$. Conventional Patterson analysis leads only to a subcell structure with a sub unit cell six times smaller than that of the superstructure. Starting from the pseudo-structure Ito's key shift method determined the shift of heavy-atom positional parameters from the subcell structure to the superstructure and finally solved the whole structure. While *MULTAN*-80 failed to determine the superstructure correctly, the best $E$ map from the modified *MULTAN*-80 reveals not only all the shifts of the heavy-atom parameters but also shifts of the light-atom parameters with only the $x$ parameter of atom S(2) in the wrong direction. Furthermore, there is no need to make use of any preliminary knowledge of the subcell structure. Results from different methods are compared in Table 2.

*Example* 3. $BaCeF(CO_3)_2$, *hwangheite (Qian, Fu & Kung, 1982)*

The structure belongs to space group $R3m$ with unit-cell parameters $a = 5\cdot070$, $c = 38\cdot408$ Å and $Z = 6$. The two independent Ba atoms have their sites close to (000) and (00$\frac{1}{2}$), while the two Ce atoms are close to (00$\frac{1}{4}$) and (00$\frac{3}{4}$). Hence there is a pseudo-translation vector $t = c/4$ in the unit cell. Consequently, all reflexions with $l \neq 4n$ are systematically much weaker than those with $l = 4n$. Patterson analysis or the heavy-atom method could not determine the exact positional parameters of the heavy atoms. Moreover, in the heavy-atom-phased Fourier map there are eight rather than two independent F atoms and there are six instead of three O atoms surrounding each C atom. In order to determine the complete structure the following problems must be solved:

1. Determine the small shifts of the heavy-atom positional parameters.
2. Distinguish the two true F atoms from their pseudo-translational images.
3. Make a choice between the two sets of O atoms for each $CO_3$ group.

There is no straightforward way to solve all these problems. However, the modified *MULTAN*-80 solves the structure automatically and easily even without making use of knowledge about the heavy atoms. In the best $E$ map the largest four peaks correspond to the four heavy atoms with the correct positional parameter shifts. Among the next eighteen largest peaks eight correspond to the light atoms and the others correspond to pseudo-translation images of the light

atoms. Furthermore, the peak heights of true atoms have evidently larger values than those of the corresponding pseudo-atoms. The result is given in Table 3 in comparison with those from other methods.

The modification to *MULTAN*-80 is an option which does not prevent its usual operation. The modified version of the program will be available for distribution in the near future.

## Discussion

A recent paper by Böhme (1981) describes a procedure which is basically the same as that of Fan *et al.* (1978) and differs only in detail. Böhme gives a lengthy account of the meaning of $E$ values when there is a subcell structure and a related superstructure. Her conclusion is that you can make $\langle |E|^2 \rangle = 1$ for both strong and weak reflexions separately but the estimates of $E$'s should be made with different scattering factors, temperature factors, *etc.* for the different groups of reflexions. Fan *et al.* use the same scattering factors and just apply different scale and temperature factors to obtain the required averages. This has proved to be necessary in the *MULTAN* implementation since the *NORMAL* subroutine, which estimates the $E$'s, has no facility for completely independently scaling two or more groups of reflexions in the same data set. Most of the time the two methods of scaling will make little difference but on the whole the procedure of Böhme is probably to be preferred.

In the phase-determining process Böhme first determines phases for the strong reflexions alone and then uses these in a second calculation to determine phases for the superstructure reflexions. This is similar to the procedure of Fan *et al.* However, *MULTAN* carries out these operations automatically and the user is insulated from the need either to know or to understand the strategy.

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