Determination of a Centrosymmetric Crystal Structure using Physically Estimated X-Ray Phases

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The program MULTAN 78 has been modified to accept physically estimated triplet phases with weights to be specified by the user. When the weights are increased, these triplets will appear further down in the convergence map. The subsequent development of phases may then proceed by a very different path through the set of reflections. Changing the path of the phase development in direct methods may sometimes be essential in order to solve the phase problem with difficult structures. Different weights have been tested with a mosaic, organic and centrosymmetric crystal with unit cell volume ~3000 Å^3 and unknown structure. In one test-run, 21 reflections from the experimental triplets were at the bottom of the convergence map. The starting set included seven of these 21 reflections and, in addition, two reflections from Σ_1-relations. It was used to generate 32 phase models, of which the correct one led to significantly better figures of merit than the others. All the non-H atoms were located in the parent *E*-map. Of the 17 experimental triplet phases included, 16 proved to be correct.

In early work, Post[1] observed phase signals in three-beam diffraction experiments with a "relatively imperfect" crystal of α-Al_2O_3. Later, Colella and coworkers,[2] on the basis of studies involving the so-called "forbidden" 222 reflection in a perfect Si crystal, were led to propose that phase effects should be observable under multiple-diffraction conditions also in mosaic crystals. In recent years, X-ray phase information has been obtained from various *n*-beam experiments with mosaic crystals (see, e.g., Refs. 3–8). These experiments were carried out with crystals of moderate mosaic character and, in most cases, relatively small unit cells. Han and Chang[9] have demonstrated that the structure of the known intermetallic compound $Cs_{10}Ga_6Se_{14}$ with unit cell volume ~2160 Å^3 could be solved using experimental triplet phases in a direct-method approach. This cell appears to be the largest tackled so far in *n*-beam diffraction experiments. The degree of mosaic character of the crystal was not stated, however.

In a preceding paper we have reported successful measurements of triplets for a mosaic, organic crystal with unknown structure and assumed chemical composition $C_{18}H_{15}N_3O$.[10] The unit cell volume was ~3000 Å^3, space group *I2/a* with $Z = 8$. The diffracted intensity profiles for this crystal had full widths at half maximum (~15°) in θ.

We present here a scheme for early and efficient introduction of the measured triplets in a structure solution by direct methods.

Experimental

A data set was collected from a mosaic, organic crystal (in the following denoted EHM III). The crystal, with dimensions 0.42×0.48×0.42 mm, was mounted on a Picker FACS-I diffractometer; Nb-filtered Mo$K\bar{\alpha}$ radiation (λ = 0.71073 Å) was employed. A total of 4426 reflections were measured to a limit in $(\sin\theta)/\lambda$ of 0.704 Å^{-1}, using the $\omega/2\theta$ scan mode. The unit cell is monoclinic, space group *I2/a*, with $Z = 8$, a = 17.820(1), b = 14.857(1), c = 11.299(1) Å, β = 99.17(1)° and V = 2953.2(4) Å^3 at 86 K. Lattice parameters were determined from the Mo$K\alpha_1$ peaks of 21 reflec-

Table 1. The 17 measured triplet phases used for structure solution with the experimental three-phase structure invariant, Φ_3, and the estimated probabilities.

H	−L	L−H	Φ_3	Prob.
$\bar{3}\,\bar{4}\,5$	$3\,2\,\bar{3}$	$0\,2\,\bar{2}$	0	1.00
$8\,\bar{4}\,4$	$0\,2\,\bar{2}$	$\bar{8}\,2\,2$	180[a]	0.99
$4\,\bar{2}\,\bar{2}$	$0\,2\,2$	$\bar{4}\,0\,0$	0	1.00
$4\,\bar{2}\,\bar{2}$	$\bar{2}\,0\,0$	$\bar{2}\,2\,2$	180	1.00
$5\,2\,3$	$\bar{4}\,0\,\bar{0}$	$\bar{1}\,2\,3$	0	1.00
$3\,3\,2$	$\bar{1}\,\bar{3}\,\bar{2}$	$2\,0\,\bar{0}$	180	1.00
$3\,3\,\bar{2}$	$\bar{4}\,0\,0$	$1\,\bar{3}\,\bar{2}$	0	0.99
$3\,3\,\bar{2}$	$\bar{4}\,0\,0$	$1\,\bar{3}\,2$	0	1.00
$3\,3\,\bar{2}$	$\bar{1}\,\bar{3}\,2$	$\bar{2}\,0\,0$	180	1.00
$1\,5\,\bar{4}$	$\bar{2}\,2\,2$	$1\,\bar{3}\,\bar{2}$	0	1.00
$2\,3\,3$	$4\,0\,\bar{0}$	$\bar{2}\,\bar{3}\,\bar{3}$	0	1.00
$2\,3\,3$	$0\,\bar{3}\,\bar{3}$	$\bar{2}\,0\,0$	180	1.00
$2\,\bar{3}\,\bar{3}$	$2\,2\,2$	$\bar{4}\,\bar{1}\,\bar{1}$	180	0.99
$4\,2\,\bar{2}$	$0\,\bar{3}\,3$	$\bar{4}\,1\,1$	180	1.00
$4\,4\,\bar{2}$	$0\,\bar{4}\,2$	$\bar{4}\,0\,0$	0	1.00
$1\,4\,\bar{3}$	$\bar{2}\,\bar{2}\,\bar{2}$	$\bar{1}\,\bar{2}\,1$	0	0.99
$2\,2\,0$	$0\,4\,\bar{2}$	$\bar{2}\,\bar{2}\,2$	0	1.00

[a]After refinement of the structure, this triplet phase was 0°.

tions with 2θ in the range 55–61°. The data were corrected for long-term variations, coincidence loss, Lorentz and polarization effects and absorption. Reflections in the 2θ-range 6.5–12.5° were remeasured with reduced low-angle scans to minimize the effect of the Nb K absorption edge. Intensities influenced by β-peaks of higher-order reflections were corrected.

A second crystal of EHM III with edges ≤0.5 mm was used for the experimental estimation of triplet phases. Intensity profiles were mapped out during ψ step-scans; details of the experimental strategy are given elsewhere.[10]

On the basis of the observed asymmetry in the background tails of the primary diffracted intensities, phases were assigned to 17 of the 22 triplets examined. In four of the 17 profiles the asymmetry was smaller, and these triplets were assigned a lower probability than the remaining 13 (see Table 1). Table 2 gives the 25 reflections (11 primary and 14 secondary, and coupling beams) that participate in the triplets of Table 1, along with their structure factors (s.f.), normalized s.f. and the phases after termination of the refinement.

The aim was to use the measured triplets to solve the unknown structure by direct methods. For this purpose, the MULTAN 78 program[11] was modified as follows: Firstly, the new version recognizes the experimental triplets and assigns to them the estimated phases. Secondly, the weighting of the measured triplets is changed. In the standard application of the program each triplet has the weight:

$$G_{H,L} = 2\sigma_3\sigma_2^{-3/2}|E_H E_{-L} E_{L-H}| \qquad (1)$$

where

$$\sigma_n = \sum_{j=1}^{N} Z_j^n,$$

Table 2. Observed structure factors, F_o, normalized structure factors, E, and final phases for the 25 reflections appearing in the triplets given in Table 1. For comparison with Table 1, observe that $\varphi_{\bar{h}k\bar{l}} = \varphi_{h\bar{k}l} = \varphi_{hkl} - \pi h$.

Reflection	F_o	E	Phase
(a) Primary reflections			
$1\,4\,\bar{3}$	25.49	0.37	0
$1\,5\,4$	116.32	2.06	0
$2\,2\,0$	65.57	0.71	0
$2\,3\,\bar{3}$	46.77	0.66	180
$3\,3\,\bar{2}$	10.88	0.14	0
$3\,3\,\bar{2}$	72.30	1.00	180
$3\,4\,\bar{5}$	108.65	2.09	180
$4\,2\,\bar{2}$	25.01	0.32	0
$4\,4\,\bar{2}$	39.70	0.58	0
$5\,2\,3$	63.68	0.93	180
$8\,4\,4$	26.44	0.82	180
(b) Secondary and coupling reflections			
$0\,2\,2$	207.98	2.27	180
$0\,3\,3$	205.75	2.69	0
$0\,4\,\bar{2}$	171.18	2.21	180
$1\,2\,\bar{3}$	137.07	1.73	0
$1\,2\,\bar{1}$	142.99	1.49	0
$1\,3\,\bar{2}$	174.53	2.08	180
$1\,3\,2$	252.21	3.14	0
$2\,0\,\bar{0}$	135.94	0.99	0
$2\,2\,\bar{2}$	256.52	2.98	180
$2\,3\,\bar{3}$	178.10	2.38	0
$3\,2\,3$	216.44	2.79	0
$4\,0\,0$	218.91	1.77	180
$4\,1\,1$	141.84	1.68	180
$8\,2\,2$	195.46	3.68	0

Table 3. Parameter variations in the different tests of phase determination involving experimental triplets.

	Run		
	I	II	III
s	1.0	10.0	10.0
14 16 $\bar{6}$ included in starting set	Yes	Yes	No
Number of refl. in starting set	8	10	9

N is the number of atoms in the unit cell, Z is the atomic number, and E is the normalized s.f.

Triplets measured with assumed probability $= 1.00$, type A triplets, were given the weight:

$$G_{H,L} = s2\sigma_3\sigma_2^{-3/2}|E^3_{max}| \quad (2)$$

where E_{max} is the maximum normalized s.f. in the set and s is a scaling parameter that can be varied.

For the triplets measured with assumed probability < 1.00, type B, one obtains from (1), with $P_+ = 1/2 + 1/2 \tanh(\sigma_3\sigma_2^{-3/2}|E_H E_{-L} E_{L-H})$:

$$G_{H,L} = \left| \ln \frac{P_+}{1-P_+} \right| . \quad (3)$$

In Table 1, P_+ and P_- are given according to whether the measured phase is 0 or 180°. The program applies the higher weight from (1) or (3).

By increasing the weights of the experimental triplets, through s in (2) or P_+ in (3), it should be possible to move them further down in the convergence map. A starting set different from that preferred in the standard application of MULTAN 78 may then be selected, and the development of phases will then take a different path through the set of reflections. For a given starting set, the individual phases are determined from the triplets according to the standard procedures of MULTAN 78. By perturbing the variable phases in the starting set, different solution sets are found, and the most reliable ones are associated with the best figures of merit.

The calculations were performed on a SPERRY 1100 computer.

Table 4. The number of undetermined phases in the refinements of the correct phase model. Parameters of the different tests are given in Table 3.

Cycle	Number of reflections considered	Number of undetermined phases		
		I	II	III
1	60	0	2	21
2	60	0	0	19
7	60	0	0	19
8	203	3	2	113
9	203	1	1	5
10	203	1	1	1
Final	203	0	0	0

Results

A total of 203 reflections, including the 25 in Table 2, were used in the test calculations. Note that ten of the reflections involved in experimental triplets have $E \leq 1.00$. The number of unique Σ_2-relations was 1320. The phases of 0160 and 4 10 $\bar{10}$ were indicated from Σ_1-relations with probability ≥ 0.99, and they were included in the starting set in all tests. Table 3 shows the parameter variations in the different calculations. In runs I and II, the starting set consisted of reflections from the experimental triplets, the two Σ_1-reflections, and 14 16 $\bar{6}$. This reflection has the largest E-value, 5.04, and participates in many Σ_2-relations. In run III, 14 16 $\bar{6}$ was deleted from the starting set. In all three runs, the program used 033 and 33$\bar{2}$ to define the origin. The number of reflections with variable phases in the starting set was 4 (run I), 6 (II) and 5 (III), respectively, which implies 16, 64 and 32 different solution sets.

In runs II and III, all 21 reflections involved in the triplets of type A appeared at the bottom of the convergence map. With $s = 1.0$ (run I), only 11 of these reflections were involved in the starting stages of the phase determination. This shows how an increase in s moves the reflections of the type A triplets down in the convergence map.

MULTAN 78 calculates several different figures of merit (FOM): absolute FOM, the criterion ψ_0, a crystallographic residual R, and, in addition, a combination of the three criteria, i.e. a combined FOM. Both runs I and II gave two

solution sets with considerably better combined FOM than the others. The starting sets of these solutions differed only in the phase for 14 16 6̄. In both runs, $\varphi_{14\,16\bar{6}} = 0°$ gave the best combined FOM, viz. 2.68 (Ia) and 2.91 (IIa), respectively. $\varphi_{14\,16\bar{6}} = 180°$ led to the values 2.55 (Ib) and 2.82 (IIb). FOM for the other solutions were <1.94 (run I) and <2.58(II). When 14 16 6̄ was deleted from the starting set in run III, one solution (IIIa) had a combined FOM, 2.88, significantly higher than the next, 2.64. In model IIIa the refined phase for 14 16 6̄ was 180°. The correct phase is 180°, and the phase sets Ib, IIb and IIIa all gave the correct solution.

Table 4 presents the number of undetermined phases at different stages in the refinements based on the correct starting set. In the first seven cycles, only the 60 reflections at the bottom of the convergence map are considered. From cycle eight, all phases are developed and refined. The phases of the starting set are always kept fixed. Table 4 shows that the convergence was much slower in run III, where 14 16 6̄ was not included in the starting set. A closer investigation of this case showed that reflections with index $h \geq 11$ did not enter in the first eight cycles. Clearly, 14 16 6̄ is important for linking these reflections with the starting set for which $h \leq 10$. However, in spite of the much slower progress in run III, phases were assigned to all reflections, and the correct phase model had significantly better FOM than the others.

The final phases for the reflections appearing in the measured triplets are given in Table 2. For this space group, the following relation exists between the phases of symmetry-equivalent reflections:

$$\varphi_{\bar{h}k\bar{l}} = \varphi_{hk\bar{l}} = \varphi_{hkl} - \pi h.$$

Combinations of the phases show that only one experimental triplet, viz. 8̄4̄4/022/8̄2̄2̄, was incorrect, the refined and estimated values being 0 and 180°, respectively. This triplet is of type *B*.

The positions of all the non-H atoms except one C atom in one of the phenyl rings corresponded to the highest maxima in the *E*-map. In addition, an O atom in a water molecule was localized in a special position. The lacking C atom was located as a peak of lower height. The chemical composition of EHM III is $C_{18}H_{15}N_3O \cdot {}^1/_2 H_2O$, and its formal structure is depicted in Fig. 1. A discussion of the molecular structure will be given elsewhere.[12]

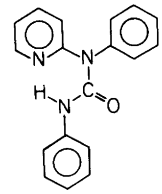

Fig. 1. The EHM III molecule.

It was possible to solve the structure of EHM III by standard direct methods. In this case the starting set did not involve any of the reflections included in the type *A* triplets, and the pathway of the Σ_2-process was very different from those employed in the test-runs.

Concluding remarks

To our knowledge, this is the first reported case of the solution of an unknown structure based on physically estimated phases. By applying appropriate weights, all the reflections involved in the triplets with secured phases could be moved to the bottom of the convergence map. In effect, this means a larger and more stable starting set than with the standard procedure of MULTAN 78. The progress of the phase development and refinement is also changed. This may sometimes be essential in order to solve the phase problem.

Structures that are difficult to solve are frequently characterized by groups of reflections which interact very little or late in the normal Σ_2-process. Molecules with pseudo-translation symmetry constitute one example. From an analysis of the data in such cases, it should be possible to identify triplets connecting these subsets of reflections with the bulk of the data. By a combination of measurements and weighting, the phase development may then be modified in its early stages to involve the critical triplet relationships.

The present work provides an example of how the absence of one reflection in the starting set can lead to the exclusion of a large group of reflections ($h \geq 11$) during the primary extension of the phase set. This situation can be avoided if the reflection in question participates in a triplet suitable for measurement.

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