of N_r, where N_r is the number of reflections with R_{calc} larger than a given threshold. In Fig. 1 the trend of RES_n is shown for the nine test structures: in accordance with our observations in Table 2, RES_n generally increases with N_r.

The above considerations suggest that estimating non-measured diffraction magnitudes is rather complicated. The statistical relationships which can be used are of order N^{-1} (and therefore rather weak) and do not offer a satisfactory solution of the problem, unless some supplementary structural information is available.

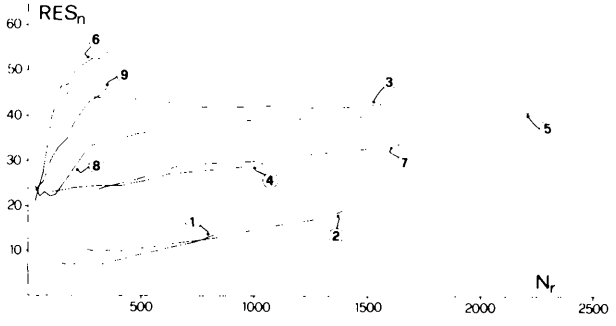

Fig. 1. RES_n is plotted as a function of N_r, where N_r is the number of reflections with R_{calc} larger than a given threshold. The curves correspond to the following test structures: (1) GEN1; (2) GEN2; (3) PGE2; (4) SKN1; (5) LOGANIN; (6) FEGAS; (7) SALEX; (8) PIC; (9) TIPORF.

The initial contribution by L. Favia is kindly acknowledged.

References

CASCARANO, G., DOGGUY-SMIRI, L. & NGUYEN-HUY DUNG (1987). *Acta Cryst.* C**43**, 2050-2053.
CHRISTENSEN, A. N., GRAND, A., LEHMANN, M. S. & COX, D. E. (1990). *Acta Chem. Scand.* **44**, 103.
CHRISTENSEN, A. N. & LEHMANN, M. S. (1989). *Acta Chem. Scand.* **43**, 19-25.
COCHRAN, W. (1955). *Acta Cryst.* **8**, 473-478.
DAVID, W. I. F. (1987). *J. Appl. Cryst.* **20**, 316-319
DETITTA, G. T., LANGS, D. A., EDMONDS, J. W. & DUAX, W. L. (1980). *Acta Cryst.* B**36**, 638-645.
GIACOVAZZO, C. (1976). *Acta Cryst.* A**32**, 91-99.
HAUPTMAN, H. & KARLE, J. (1953). *The Solution of the Phase Problem. I. The Centrosymmetric Crystal.* Am. Crystallogr. Assoc. Monogr. No 3. New York: Polycrystal Book Service.
JONES, P. G., SHELDRICK, G. M., GLÜSENKAMP, K.-H. & TIETZE, L. F. (1980). *Acta Cryst.* B**36**, 481-483.
NAYA, S., NITTA, I. & ODA, T. (1965). *Acta Cryst.* **19**, 734-747.
SAYRE, W. (1952). *Acta Cryst.* **5**, 60-65.
SCORDARI, F. & STASI, F. (1990). *Z. Kristallogr.* **190**, 47-62.
VAN DER PUTTEN, N., SCHENK, H. & TSOUCARIS, G. (1982). *Acta Cryst.* A**38**, 98-102.

Acta Cryst. (1991). A**47**, 484-490

TELS: Least-Squares Solution of the Structure-Invariant Equations

BY FUSEN HAN

Upjohn Laboratories, The Upjohn Company, Kalamazoo, MI 49001, *USA*

AND GEORGE DETITTA AND HERBERT HAUPTMAN

Medical Foundation of Buffalo, Inc., 73 *High Street, Buffalo, NY* 14203, *USA*

(*Received* 21 *June* 1990; *accepted* 6 *March* 1991)

Abstract

Procedures are described to extract the values of individual phases from estimated structure invariants. The linear-equation and least-squares methods are used as two separate techniques in these procedures. The linear-equation method uses a linearly independent set of equations, with arbitrarily assigned integers, which are sufficient in number to solve for values of an equal number of phases. The least-squares method uses a set of overdetermined equations in which an 'integer problem' has to be considered. The assembly of these two techniques with a novel integer-trial-and-error method shows a remarkable ability to overcome the 'integer problem'. As a test of the whole procedure, phases were extracted from three-phase structure invariants calculated from the theoretical data for the platinum chloride derivative of cytochrome c_{550}.

Introduction

The structure invariant continues to play a central role in the direct-methods approach to the phase problem. Over the past few years, several investigators have attempted to derive new probabilistic formulae to improve structure-invariant estimations (Hauptiman, 1982; Giacovazzo, 1983). Some of these formulae, for example the formula for anomalous-scattering data, yield unique estimates for the structure invariants themselves, as opposed to their cosines.

0108-7673/91/050484-07$03.00

A traditional approach to the phase problem employs the three-phase structure invariant or 'triple'

$$\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} = \omega_{\mathbf{h},\mathbf{k}}, \text{ where } \mathbf{h}+\mathbf{k}+\mathbf{l}=0.$$

The value of the sum, $\omega_{\mathbf{h},\mathbf{k}}$, is either implicitly assumed to be zero (modulo 2π) (*i.e.* $\omega_{\mathbf{h},\mathbf{k}} = 0\pi, 2\pi, 4\pi$ *etc.*) or is explicitly estimated, *e.g. via* anomalous-scattering data and probabilistic formulae (Hauptman, 1982), to be $\omega_{\mathbf{h},\mathbf{k}} = \omega'_{\mathbf{h},\mathbf{k}} + 2\pi N$ (*i.e.* $\omega_{\mathbf{h},\mathbf{k}} = \omega'_{\mathbf{h},\mathbf{k}}, \omega'_{\mathbf{h},\mathbf{k}} + 2\pi, \omega'_{\mathbf{h},\mathbf{k}} + 4\pi$ *etc.*). The terms $0\pi, 2\pi, 4\pi$ *etc.* appear when the values of the individual phases are allowed to range from zero to 2π. For example, when $\varphi_{\mathbf{h}} = 5\pi/4$, $\varphi_{\mathbf{k}} = 3\pi/4$ and $\varphi_{\mathbf{l}} = \pi/2$, the triple value $\omega_{\mathbf{h},\mathbf{k}} = 5\pi/2 = 2\pi + \pi/2$. In many direct-methods approaches to phase extraction, phase values are estimated by the tangent formula (Hauptman & Karle, 1956) or the modified tangent formula (Olthof & Schenk, 1982). Because trigonometric functions of the phases and the estimates $\omega'_{\mathbf{h},\mathbf{k}}$ are involved, the values of the modulo 2π parts of $\omega_{\mathbf{h},\mathbf{k}}$ are immaterial, *e.g.* $\cos(\omega_{\mathbf{h},\mathbf{k}}) = \cos(\omega'_{\mathbf{h},\mathbf{k}} + 2\pi N) = \cos(\omega'_{\mathbf{h},\mathbf{k}})$, no matter what the value of the integer N. However, in the sequel we will describe our efforts to further a distinct approach to phase extraction and in that approach the ability to estimate values for the modulo 2π portions of the phase sums, *i.e.* the integers N, is critical.

Woolfson (1977) pointed out an attractive alternative to the tangent formula in a paper describing a potential successor to *MULTAN* called *MAGLIN*. It described efforts to implement a solution of a set of simultaneous linear equations involving the structure invariants. The goal was to develop a large set of starting values and to refine, by least-squares techniques, the values of the phases. As Woolfson pointed out, the tangent formula can, on occasion, take a set of correctly calculated phases and 'refine' them away from their initial (correct) values. The least-squares approach he described, on the other hand, was quite stable and had a rather larger radius of convergence than the tangent formula. To make the least-squares approach feasible it was imperative to have a correct set of integers, N's, to associate with each of the structure invariants involving, say, $\varphi_{\mathbf{h}}$

$$\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}_i} + \varphi_{\mathbf{l}_i} = \omega'_{\mathbf{h},\mathbf{k}_i} + 2\pi N_i \qquad (1)$$

$$\varphi_{\mathbf{h}} = \omega'_{\mathbf{h},\mathbf{k}_i} + 2\pi N_i - \varphi_{\mathbf{k}_i} - \varphi_{\mathbf{l}_i} \qquad (2)$$

with $i = 1, 2, \ldots, q$, where q is the number of triples involving $\varphi_{\mathbf{h}}$. If the values of all the phases to be determined are constrained to be between 0 and 2π, then the values of $\omega_{\mathbf{h},\mathbf{k}_i}$ are constrained to be between 0 and 6π, *i.e.* $\omega_{\mathbf{h},\mathbf{k}_i} = \omega'_{\mathbf{h},\mathbf{k}_i} + 2\pi N_i$; $N_i = 0$, 1 or 2. If we must determine p phases using q triples then there are 3^{q-p} possible sets of integers that are associated with the estimates $\omega'_{\mathbf{h}_i,\mathbf{k}_i}$, if all of the integers are allowed to assume all of their possible values. Such a situation is computationally intractable. However, Woolfson pointed out a strategy that greatly reduced the number of values that the N_i could assume. Let us assume that we have abstracted from the complete set of triples available to us a very small independent subset that involves p phases and an equal number of triple relationships. A good place to find these would be at the bottom of a convergence map. The triples involved would presumably be the ones for which we have the most reliable estimates of the fractional parts $\omega'_{\mathbf{h}_i,\mathbf{k}_i}$ of the phase sums. Now, in the situation where the number of unknowns and the number of linear equations are exactly equal it is possible to arbitrarily assign the integer portions N_i, say $\{N_i = 0\}$. This requires that the subset of p equations is linearly independent and that it involves p equations in p unknowns. Our freedom to arbitrarily assign the p values of N_i comes about because, in this type of linearly independent set of equations, the addition of any multiple of 2π to the right-hand sides of (2) merely adds a like multiple of 2π to the individual phase $\varphi_{\mathbf{h}}$. Once we overdetermine the set of equations, however, we are no longer free to assign arbitrary values to the additional integers N_i introduced as additional equations (additional triples) enter the system.

With the subset of phases and triples in equal numbers and with the integer portions of (1) arbitrarily assigned, we can readily solve for the phases. Note, however, that any errors in the estimations of the fractional parts of the phase sums $\omega_{\mathbf{h},\mathbf{k}_i}$ are directly transferred to the calculated phases. Therefore, the size of the subset is a reflection of our confidence in the techniques for estimating the ω' values. We can afford to be conservative at this stage and restrict the subset to ten or fewer triples and unknown phases.

Given the values calculated for the small subset of phases, we can calculate the values of *all* triples involving those phases, inclusive of the original subset of triples that determined the starting phases, paying special attention to the calculation of the integer parts of any additionally determined triples. It will be the case that any errors introduced into the phase values from the initial fractional estimates $\omega'_{\mathbf{h}_i,\mathbf{k}_i}$ will cause the additionally determined triple equations to be approximations to equalities. For example, in the first step we might have determined the phases for reflections with serial numbers φ_1, φ_5 and φ_8 and furthermore it may transpire that $\varphi_1 + \varphi_5 + \varphi_8$ is a triple that did not enter into the initial estimates for φ_1, φ_5 and φ_8. We now have trial values for φ_1, φ_5 and φ_8, for example, $\varphi_1 = \pi/4$, $\varphi_5 = 3\pi/4$, $\varphi_8 = 5\pi/4$, and we may have, *via* a probabilistic approach, an estimate of $\omega'_{1,5} = 0\pi$. The additional relationship is

$$\varphi_1 + \varphi_5 + \varphi_8 = \omega'_{1,5} + 2\pi N$$

or

$$\pi/4 + 3\pi/4 + 5\pi/4 = 0\pi + 2\pi N$$

or

$$9\pi/4 = 2\pi N.$$

In this case, $N = 9/8$. The nearest integer to 9/8 is obviously $N = 1$.

We may now utilize a least-squares procedure to refine the values of the p phases using the original set of p equations with their arbitrarily assigned values of N_i, plus the additionally determined equations with their integer multiples of 2π set to the values of the nearest integers. The nearest integers are calculated as the integers nearest to

$$(\varphi_{\mathbf{h}_i} + \varphi_{\mathbf{k}_i} + \varphi_{\mathbf{l}_i} - \omega'_{\mathbf{h}_i,\mathbf{k}_i})/2\pi. \qquad (3)$$

The system is overdetermined and we assume that errors in the equations come from errors in the estimates for $\omega'_{\mathbf{h}_i,\mathbf{k}_i}$. We are free to adjust the phases to minimize that error. With those phases we may again calculate nearest integers for all the equations *etc.* and cycle between phase adjustment and integer adjustment. Such a procedure usually converges in one or two cycles.

The integer problem

With a small subset of p determined phases and q ($>p$) triples as described we might now endeavor to calculate the value of a single additional phase, $\varphi_{\mathbf{h}}$. That calculation will involve previously determined phases from the basis set and some small number of additional triples involving $\varphi_{\mathbf{h}}$ and the phases in the basis set. If the original basis set involved p phases and q triples, the new set of equations involves $p+1$ phases and $q+q_1$ triples (q_1 being the number of newly added triples). We do not know the value of $\varphi_{\mathbf{h}}$ but we can restrict it to the range 0–2π. We need to assign values for the q_1 additional integers introduced with the q_1 additional triples. One way to proceed would be to assume $\varphi_{\mathbf{h}} = \pi$ and calculate values of the nearest integers for the q_1 additional triples. There may be errors in these integers due to errors in the $\omega'_{\mathbf{h},\mathbf{k}_i}$ values and the assumption that $\varphi_{\mathbf{h}} = \pi$, but we have observed that we are rarely off by more than ± 1, *i.e.* if we calculate $N = 2{\cdot}4$, the true value of N is probably 2, but may possibly be 1 or 3. If q_1 additional triples are brought in with phase $\varphi_{\mathbf{h}}$ we might have to perform as many as 3^{q_1} least-squares calculations to be certain we have not introduced any substantial errors in the refinement process due to a miscue on the integers. Again, such a situation is computationally unattractive. A partial resolution to the integer problem comes about when we realize that the values of the additional integers are severely restricted, to q_1+1 values and not to 3^{q_1} values, because of their interconnectedness. We proceed as follows. Assume $\varphi_{\mathbf{h}} = 0$ [noted as $\varphi_{\mathbf{h}}(0)$] and calculate the nearest integer values for the q_1 additional triples. Now let $\varphi_{\mathbf{h}}$ increase to a certain point $\varphi_{\mathbf{h}}(1)$. One of the q_1 values of N_i will 'click' over to the next integer which must be larger than its previous value. For example, say that we introduce one new phase $\varphi_{\mathbf{h}}$ and four new invariants ω'_1, ω'_2, ω'_3 and ω'_4. Restrict the phase $\varphi_{\mathbf{h}}$ to the interval $(0, 2\pi)$. At $\varphi_{\mathbf{h}}(0) = 0$, say that we calculate $N_1 = 0{\cdot}1$, $N_2 = 1{\cdot}2$, $N_3 = 1{\cdot}3$ and $N_4 = 2{\cdot}9$. The nearest integers are 0, 1, 1, 3 respectively. As $\varphi_{\mathbf{h}}$ increases from 0 up to but not including $0{\cdot}4\pi$, the values of the nearest integers are not changed. However, at $\varphi_{\mathbf{h}}(1) = 0{\cdot}4\pi$ we calculate that $N_1 = 0{\cdot}1 + 0{\cdot}2 = 0{\cdot}3$, $N_2 = 1{\cdot}2 + 0{\cdot}2 = 1{\cdot}4$, $N_3 = 1{\cdot}3 + 0{\cdot}2 = 1{\cdot}5$ and $N_4 = 2{\cdot}9 + 0{\cdot}2 = 3{\cdot}1$. The nearest integers are now 0, 1, **2**, 3 respectively. Only the nearest integer for N_3 has changed and has increased by one from its previous value. Now increase $\varphi_{\mathbf{h}}(2)$ from $0{\cdot}4\pi$ to $0{\cdot}6\pi$. Calculated values for the N's remain unchanged until $\varphi_{\mathbf{h}}(2) = 0{\cdot}6\pi$, where $N_1 = 0{\cdot}1 + 0{\cdot}3 = 0{\cdot}4$, $N_2 = 1{\cdot}2 + 0{\cdot}3 = 1{\cdot}5$, $N_3 = 1{\cdot}3 + 0{\cdot}3 = 1{\cdot}6$ and $N_4 = 2{\cdot}9 + 0{\cdot}3 = 3{\cdot}2$. The nearest integers are 0, **2**, 2, 3. Again, a single integer, this time N_2, 'clicks' up to the next-higher value, *i.e.* from 1 to 2. Continue to increase $\varphi_{\mathbf{h}}(3)$ from $0{\cdot}6\pi$ to $0{\cdot}8\pi$, and now $N_1 = 0{\cdot}1 + 0{\cdot}4 = 0{\cdot}5$, $N_2 = 1{\cdot}2 + 0{\cdot}4 = 1{\cdot}6$, $N_3 = 1{\cdot}3 + 0{\cdot}4 = 1{\cdot}7$ and $N_4 = 2{\cdot}9 + 0{\cdot}4 = 3{\cdot}3$. The nearest integers are now **1**, 2, 2, 3. Again, just one integer, N_1, advances, from 0 to 1. Finally, increase $\varphi_{\mathbf{h}}(4)$ to $1{\cdot}2\pi$. We find that $N_1 = 0{\cdot}1 + 0{\cdot}6 = 0{\cdot}7$, $N_2 = 1{\cdot}2 + 0{\cdot}6 = 1{\cdot}8$, $N_3 = 1{\cdot}3 + 0{\cdot}6 = 1{\cdot}9$ and $N_4 = 2{\cdot}9 + 0{\cdot}6 = 3{\cdot}5$, with nearest integers 1, 2, 2, **4** respectively and only N_4 has increased. Notice that if we assume $\varphi_{\mathbf{h}}$ to have a value greater than $\varphi_{\mathbf{h}}(4) = 1{\cdot}2\pi$ (in fact any value up to 2π) the nearest integers allowable for the q_1 additional triples do not change. The only allowable sets of integers for any value of $\varphi_{\mathbf{h}}$ are then

N_1	N_2	N_3	N_4
0	1	1	3
0	1	2	3
0	2	2	3
1	2	2	3
1	2	2	4.

There are now q_1+1 ($4+1=5$) possible sets of integers which can enter into a least-squares determination of the phase $\varphi_{\mathbf{h}}$ and adjustment of the p original phases.

This process can clearly be repeated, adding a single unknown phase φ_{p+2}, thus generating q_2 new structure invariants, adjoining q_2 additional linear equations with q_2 new integers

$$N_{q+q_1+1}, N_{q+q_1+2}, \ldots, N_{q+q_1+q_2},$$

via (3), having precisely q_2+1 sets of values, which can be solved by iterative least squares *etc.*

As the procedure is repeated, the whole system follows the convergence map to reach new phases and improve estimates for all phases. This process we call the trial-and-error least-squares method – TELS. It works extremely well even in the presence

of a large mean error in the initial estimates of the structure invariants.

Implementation

The trial-and-error least-squares technique is implemented in the following steps.

(*a*) The data are separated into three reflection groups. Group one contains general reflections with large $|E|$ values. Group two consists of general reflections having moderate $|E|$ values. Because the structure-invariant formulas we use cannot reliably estimate invariants which involve special reflections, all special reflections are stored in group three.

(*b*) Three different groups of three-phase structure invariants are constructed and estimated: (1) all three phases lie in group one; (2) at least one phase lies in group one and at least one phase lies in group two; (3) precisely one phase lies in group three.

(*c*) A convergence map is calculated using group one reflections only. There are two critical requirements for the convergence map: it should have large A values on the bottom of the map and there must be no gaps in the map. Two criteria can be used to ensure these requirements. One is the use of the product of A values instead of the normally employed α values. This will give a good A-value distribution, but sometimes gaps occur in the map. The other maximizes the number of relations involved. It always shows a gap-free map, but frequently has a poor A distribution. Combining the two criteria, the product of A values is used for the bottom half of the map and the number-of-relations criterion is used for the top half. With this method a gap-free large-A-bottom convergence map can normally be constructed. At the extreme bottom of the map, a certain number of reflections will be left automatically for fixing the origin.

(*d*) From the bottom of the convergence map a small set (<ten) of independent linear equations is selected by checking that the determinant is not equal to zero. This equation set can be solved by straightforward means.

(*e*) A set of starting nearest integers is calculated with the phase solutions of step *d*. Then a trial-and-error least-squares procedure is carried out step by step. For each step, the best result is always among the smallest values of the residual, R.

$$R = \sum |(\varphi_{\mathbf{h}_i} + \varphi_{\mathbf{k}_i} + \varphi_{\mathbf{l}_i}) - (\omega'_{\mathbf{h}_i,\mathbf{k}_i} + 2\pi N_i)|/Q,$$

where $Q = q + q_1 + \ldots + q_p$ is the total number of equations involved in the least-squares calculation and $i = 1, 2, \ldots, Q$. To avoid missing the correct answer, a few (~five) sets with lowest R values are kept as the starting points for the next step. Within the first 100 steps, the typical number of additional triples per step, q_j, is less than ten. The number of trial sets will be $q_j + 1$ times the number of kept trial sets (~five) at each step, usually less than 50. It is not necessary to extend this calculation to a very large data set, because 100 steps will generate 100 high-quality phases which are enough to serve as the starting phases for the tangent formula.

(*f*) Starting with these 100 phases, at each step 50 additional phases can be estimated in the order established by the convergence map, employing the generalized tangent formula which incorporates non-zero estimates for the invariants. The phase results of every extension are used to calculate the nearest integers. Full-matrix least-squares phase refinement follows. Repetition of these steps will phase all the reflections in group one.

(*g*) The phases in group two can be extracted by the tangent formula alone or by step (*f*). This depends on the computing power available to treat very large matrix inversions.

(*h*) Since the only available estimate of the invariants containing a restricted phase (those in group three) is zero, the restricted phases can be estimated only by the regular tangent formula. Each phase of a special reflection has two possible values. Three reliability factors can be used as figures of merit to select the correct values of the restricted phases: (1) α; (2) the number of contributors; and (3) the difference between the calculated phase from the tangent formula and the closer of the two possible values of the restricted phase. The phases selected on the basis of all three figures of merit are, for the most part, correctly chosen.

Assembly of steps (*a*) to (*h*) yields a practical procedure for phasing an unknown structure of a very large size in reasonable computing time.

Table 1. *20 315 estimated ω' values from 616 Friedel pairs of anomalous-scattering data, ⟨error⟩ of $\omega' =$ 56·12°*

To see the unbiased feature of the estimation, the invariants are sorted into two groups, one contains all estimated values smaller than the true value ($0 < \omega'_{true} - \omega' < 180$), the other contains $0 < \omega' - \omega'_{true} < 180°$.

	$\omega' < \omega'_{true}$		$\omega' > \omega'_{true}$	
A	Number	⟨Error⟩ (°)	Number	⟨Error⟩ (°)
0·25–0·50	671	72·03	641	72·35
0·50–0·75	3621	63·98	3623	65·00
0·75–1·00	3141	55·47	2888	56·63
1·00–1·25	1632	48·10	1413	46·20
1·25–1·50	756	40·10	649	37·90
1·50–1·75	356	37·03	277	38·25
1·75–2·00	192	28·20	138	30·19
2·00–2·25	90	26·07	59	26·61
2·25–2·50	35	35·75	41	22·69
2·50–2·75	26	30·58	20	24·98
2·75–3·00	14	29·15	6	19·27
3·00–3·25	9	28·90	3	6·22
3·25–3·50	3	15·20	3	4·60
3·50–3·75	0	0·0	2	19·75
3·75–4·00	0	0·0	1	0·67
4·00–4·50	1	10·79	1	7·32
4·50–4·75	0	0·0	1	49·39

Table 2. *Bottom of the convergence map*; *reflection numbers are in bold type, single-digit numbers representing symmetry codes follow*; *the decimal numbers are A values of invariants*

11	0	**9**	1	**−3**	0	1·45	**11**	0	**−7**	1	**−6**	0	1·05	**11**	0	**−10**	0	**−8**	0	1·04
10	0	**9**	1	**1**	0	1·49	**10**	0	**−8**	0	**5**	0	1·19							
9	1	**8**	1	**6**	0	1·21														
−8	0	**3**	0	**1**	0	1·18														
7	0	**−4**	0	**−2**	0	1·18														
6	0	**−3**	0	**−2**	0	1·34	**6**	0	**5**	0	**−1**	1	1·18							
5	0	**4**	0	**3**	0	1·42														
4	1	**−2**	0	**1**	0	1·40														

1, 2, 3 are used as origin-fixing reflections and are considered as known phases. Hence there are only $p = 8$ unknown phases and a system of $q = 12$ equations, a suitably chosen subset of which, consisting of eight equations, is linearly independent.

The application

Tests were done using calculated structure factors for the known 134 amino acid protein structure of the $PtCl_4^{2-}$ derivative of cytochrome c_{550}, space group $P2_12_12_1$ with $a = 42{\cdot}70$, $b = 82{\cdot}17$, $c = 31{\cdot}56$ Å (Timkovich & Dickerson, 1973, 1976). The coordinates were obtained from the Protein Data Bank (Bernstein *et al.*, 1977). Group one has 616 general reflections with $|E| > 1{\cdot}2$. Group two contains 873 general reflections with $1{\cdot}2 > |E| > 0{\cdot}8$. Group three contains 539 special reflections. All three groups of data have a resolution of 1·5 Å. A VAX8600 computer was used for all the calculations.

Three-phase structure invariants were generated and estimated assuming anomalous-scattering data for reflections in group one (Hauptman, 1982). Table 1 shows that the quality of the estimation is extremely dependent on the A value and the errors are unbiased about the true values. There are 20 135 invariants in group one, 106 682 structure invariants involve reflections in groups one and two and 145 688 structure invariants involve precisely one restricted phase from group three.

A convergence map was generated using the group one data (CPU ~2·5 min). For the first 300 phases the criterion in the construction of the map was the product of the A values. The rest of the convergence map used the number-of-relations criterion. At the end of the map, three reflections were identified automatically for the unique origin choice. They are 3,13,6, $|E| = 2{\cdot}37$; 24,9,3, $|E| = 2{\cdot}39$ and 20,4,4, $|E| = 1{\cdot}81$. Each of them is allowed two possible initial phase estimations (45, 315° or 135, 225°) which correspond to an origin shift in each dimension. To be specific, choose for each origin-specifying phase the two possible values 45 and 315°, one of which will differ from the true value by less than 45°, the remaining two values (135, 225°) correspond to a different choice of origin and may therefore be ignored. Because the possible phases were undetermined, for each of them two values which differ by 90° from each other have to be considered. One of the two values will have an error less than 45°. For space groups which require three reflections to fix the origin, eight trials have to be carried out. If we denote a trial with a phase in error by less than 45° as * and one with phase error greater than 45° as ×, the eight trials will be:

1. ∗ × × 3. × ∗ × 5. × × ∗ 7. × × ×

2. × ∗ ∗ 4. ∗ × ∗ 6. ∗ ∗ × 8. ∗ ∗ ∗.

One of the two alternative sets in the same columns as above shows at least two of the three phases with an error less than 45°. Since the trial-and-error least-squares method is relatively error insensitive, the origin-fixing reflections can be assigned even with a large error. Therefore it is recommended that only two sets of origin-fixing phases (rather than eight) be tested. By employment of the residuals, R, the correct answer can be easily picked from the two solution sets.

For the initial linear-equation step eight equations were selected (Table 2). The trial-and-error least-squares program was run until 100 unknown phases were individually determined for the two phase sets corresponding to the two trial origin assignments. The two solutions have residuals equal to $R = 8{\cdot}68$ and $R = 27{\cdot}27\%$ respectively. The first one obviously is the correct one. This step gave 100 high-quality phases with a mean error of ~16° (Table 3).

The extension from 100 to 616 phases used the tangent formula and full-matrix least squares alternately. Firstly 30 new phases which are located close to the first 100 reflections on the convergence map were calculated by the tangent formula. Then all the 130 phases and three origin-fixing phases (which had not been refined previously) took part in the least-squares refinement. Experience showed second cycles were rarely necessary. It took about twenty alternations to reach all 616 phases (Table 4).

This procedure can be repeated until all general reflections are phased. For a practical implementation, however, the inversion of very large matrices can be a very high price for most computers. On the other hand, the mean error of the first 616 phases was only about 25° and the average number of triples per phase for the remaining 869 general reflections was about 122, no doubt good enough for the tangent formula. Tests showed that, using the tangent formula alone, the phases of group two could be well determined. The phase evaluation of all 1485 general reflec-

Table 3. *The* 103 φ*'s determined by the trial-and-error least-squares method* (454 *triples, CPU* ~10 min), $\langle error \rangle$ *of* $\varphi = 15{\cdot}45°$; $47\varphi < \varphi_{true}$, $\langle error \rangle = 14{\cdot}39°$; $56\varphi > \varphi_{true}$, $\langle error \rangle = 16{\cdot}34°$

Again, the results are in two groups to show their unbiased nature.

⟨Error⟩ (°)	Number of $\varphi < \varphi_{true}$	Number of $\varphi > \varphi_{true}$
0·0-10·0	22	24
10·0-20·0	15	17
20·0-30·0	6	8
30·0-40·0	2	4
40·0-50·0	0	1
50·0-60·0	1	1
70·0-80·0	1	0
90·0-100·0	0	1

Table 4. *The* 616 *phases estimated and refined by the tangent formula and least-squares methods* (20 315 *invariants, CPU* ~2 h 12 min) *using the phase of Table* 3; $\langle error \rangle$ *of* $\varphi = 24{\cdot}64°$; $316\varphi < \varphi_{true}$, $\langle error \rangle = 25{\cdot}57°$; $300\varphi > \varphi_{true}$, $\langle error \rangle = 23{\cdot}67°$

⟨Error⟩	Number of $\varphi < \varphi_{true}$	Number of $\varphi > \varphi_{true}$
0·0-10·0	115	107
10·0-20·0	90	86
20·0-30·0	37	41
30·0-40·0	21	26
40·0-50·0	11	9
50·0-60·0	5	6
60·0-70·0	7	3
70·0-80·0	5	5
80·0-90·0	3	3
90·0-100·0	3	3
100·0-110·0	4	2
110·0-120·0	4	1
120·0-130·0	1	2
130·0-140·0	4	2
140·0-150·0	4	1
150·0-160·0	1	0
160·0-170·0	1	2
170·0-180·0	0	1

Table 5. *The* 869 *phases estimated by the tangent formula alone* (126 997 *invariants, CPU* ~56 min)

1485 (616 + 869) φ's are sorted in this table which have: ⟨error⟩ = 28·26°; $787\varphi < \varphi_{true}$, ⟨error⟩ = 28·75°; $698\varphi > \varphi_{true}$, ⟨error⟩ = 27·70°.

⟨Error⟩	Number of $\varphi < \varphi_{true}$	Number of $\varphi > \varphi_{true}$
0·0-10·0	245	222
10·0-20·0	208	189
20·0-30·0	117	105
30·0-40·0	50	54
40·0-50·0	37	28
50·0-60·0	30	20
60·0-70·0	22	12
70·0-80·0	12	11
80·0-90·0	12	7
90·0-100·0	8	8
100·0-110·0	6	6
110·0-120·0	7	6
120·0-130·0	4	11
130·0-140·0	9	6
140·0-150·0	8	2
150·0-160·0	4	0
160·0-170·0	5	7
170·0-180·0	3	4

Table 6. 538 *restricted phases were calculated using normal tangent formula* (145 688 *invariants, CPU* ~40 min); *the phase results shown in this table are sorted in different weight ranges*

Weight range	Number of phases	Incorrect phases
0·9-1·0	211	28 13·3%
0·8-1·0	228	32 14·0%
0·7-1·0	258	40 15·5%
0·6-1·0	287	47 16·4%
0·5-1·0	316	53 16·8%
0·4-1·0	354	64 18·1%
0·3-1·0	393	75 19·1%
0·2-1·0	425	91 21·4%
0·1-1·0	467	109 23·3%
0·0-1·0	538	136 25·3%

tions in groups one and two is shown in Table 5. Most phases have a small error and all of them are unbiased compared to the true values.

The 539 special reflections were evaluated using the regular tangent formula (all $\omega'_{\mathbf{h},\mathbf{k}_i} = 0{\cdot}0$). The calculated results were forced to the closer of the two restricted values. Each result had a quality weight w_j:

$$w_j = w_\alpha w_r w_\varphi$$

$$w_\alpha = \min(1{\cdot}0, \alpha/10{\cdot}0)$$

$$w_r = \min(1{\cdot}0, \text{'redundancy'}/50)$$

$$w_\varphi = \min(1{\cdot}0, \cos \Delta\varphi).$$

Here, 'redundancy' means the number of structure invariants involving this phase and $\Delta\varphi$ is the difference between the calculated value of φ and the closer of the two restricted values. 538 phases had non-zero weight, of these 136 had the incorrect value. However, if we accept only those phases with weight $>0{\cdot}5$, only 53 are incorrect among 316 phases (Table 6).

The above procedures supply a total of 1801 reliable phases (1485 from Table 5 and 316 from Table 6) for an *E*- or *F*-map calculation.

Concluding remarks

Experience so far with this method has been very encouraging. At the core of this procedure, the trial-and-error least-squares method has a very practical nature. In the present paper the error of the estimated invariants based on error-free structure factors is in the range 30 to 40°. It is believed that the mean error will also be acceptable when a good measured data set is used.

It is also noteworthy that this is not an expensive operation, taking only a few hours on a minicomputer for the treatment of a thousand or more reflections. Except for the few origin-fixing phase sets, no multiple trials are necessary during the whole procedure. The figure-of-merit problem can normally be avoided.

The authors thank Drs D. Langs and H. King and Mr S. Potter for helpful discussions. This work was supported in part by NSF grants DMB-8610382 and CHE-8508724.

References

BERNSTEIN, F. C., KOETZLE, T. F., WILLIAMS, G. J. B., MEYER, E. F. JR, BRICE, M. D., ROGERS, J. R., KENNARD, O., SHIMANOUCHI, T. & TASUMI, M. (1977). *J. Mol. Biol.* **112**, 535-542.
GIACOVAZZO, C. (1983). *Acta Cryst.* A**39**, 585-592.
HAUPTMAN, H. (1982). *Acta Cryst.* A**38**, 632-641.
HAUPTMAN, H. & KARLE, J. (1956). *Acta Cryst.* **9**, 45-55.
OLTHOF, G. J. & SCHENK, H. (1982). *Acta Cryst.* A**38**, 117-122.
TIMKOVICH, R. & DICKERSON, R. E. (1973). *J. Mol. Biol.* **79**, 39-56.
TIMKOVICH, R. & DICKERSON, R. E. (1976). *J. Biol. Chem.* **251**, 4033-4046.
WOOLFSON, M. M. (1977). *Acta Cryst.* A**33**, 219-225.

Acta Cryst. (1991). A**47**, 490-497

Dynamical Treatment of the Splitting of HOLZ Lines from Dislocations in Silicon*

BY HUAMIN ZOU, XIFU YAO AND RENHUI WANG†

Department of Physics, Wuhan University, 430072 *Wuhan, People's Republic of China, and Beijing Laboratory of Electron Microscopy, Academia Sinica, PO Box* 2724, 100080 *Beijing, People's Republic of China*

(*Received* 25 *June* 1990; *accepted* 12 *March* 1991)

Abstract

The splitting of higher-order Laue-zone (HOLZ) lines of convergent-beam electron diffraction (CBED) due to the presence of dislocations in Si was investigated experimentally and theoretically. The parameters affecting the separation and relative positions of the fringes of split HOLZ lines were examined with experiments and/or computations. According to the results obtained, a method for identification of Burgers vector is discussed.

1. Introduction

The splitting of higher-order Laue-zone (HOLZ) lines in a convergent-beam electron diffraction (CBED) pattern from dislocations was first reported by Carpenter & Spence (1982). They found that a HOLZ line is split only if the value of $\mathbf{g}\cdot\mathbf{b}$ does not equal zero. By identifying lines that remain unsplit, implying $\mathbf{g}\cdot\mathbf{b}=0$, the direction of the Burgers vector of the dislocation can be determined. The intensity symmetry of Kikuchi bands reverses when the probe is moved from one side of the dislocation to the other, which can be used to identify the sense of $\mathbf{b}$. They also make a two-beam dynamical calculation to show that a line of the intensity minimum in the bright-field (BF) disc due to a HOLZ reflection can indeed split into two subsidiary minima due to the presence of a dislocation. Fung (1985) studied the HOLZ-line splitting from stacking faults and dislocations. He pointed out that the splitting and unsplitting of the reflections correspond to the visibility and invisibility of the defect in the kinematical theory of diffraction contrast of imperfect crystals. Preston & Cherns (1985) made a kinematical calculation of HOLZ rocking curves to show the splitting of HOLZ lines due to dislocations. When the whole strained area associated with a dislocation is illuminated by a defocus convergent beam, Cherns & Preston (1986) and Cherns, Kiely & Preston (1988) found that HOLZ deficiency lines close to the dislocation shadow image twist and split in the large-angle convergent-beam diffraction (LACBED) pattern (Tanaka pattern). Their simulation with kinematical approximation shows good qualitative agreement with the experiments. Tanaka, Terauchi & Kaneyama (1988) simulated LACBED patterns for dislocations with various characters (edge, screw and mixed) for different values of $\mathbf{g}\cdot\mathbf{b}$ and different depth of dislocation in the specimen with two-beam dynamical theory. They found that a HOLZ line generally splits into $n+1$ subsidiary fringes, where $n=\mathbf{g}\cdot\mathbf{b}$, around the intersection point of the HOLZ line and the shadow image of the dislocation and the HOLZ line twists in the opposite direction if the sign of $n=\mathbf{g}\cdot\mathbf{b}$ is changed. These results were successfully

* Project supported by the National Natural Science Foundation of China.

† To whom all correspondence should be addressed.

0108-7673/91/050490-08$03.00