

The Use of Karle–Hauptman Determinants in Small-Structure Determinations. II

BY R. A. G. DE GRAAFF AND W. J. VERMIN

X-ray Department, Gorlaeus Laboratories, PO Box 9502, 2300 RA Leyden, The Netherlands

(Received 25 August 1981; accepted 27 January 1982)

Abstract

This paper presents the results of an investigation into the usefulness of Karle–Hauptman determinants for the solution of the phase problem in small structures. The algorithm is discussed in some detail. Results for five test structures are given. For all test structures starting sets of about 25 reflexions with an acceptable phase error of 25° or less could be obtained. Various attempts to extend these starting sets in order to solve the structures are reported. In the writing of the program compatibility with the *MULTAN* system has been the authors' intention.

Introduction

The basis of most program systems designed to solve the phase problem by direct methods is the \sum_2 relation. Various attempts have been made to include higher-order phase relations (Gilmore, 1977; Freer & Gilmore, 1980).

In 1977 we decided to try a hitherto neglected approach suggested much earlier by Karle & Hauptman (1950). These authors discussed various properties of Hermitian determinants having structure factors as elements.

Since then, much work has been done to use these determinants in large-structure determinations, with some considerable success (de Rango, Mauguen & Tsoucaris, 1975; de Rango, Mauguen, Tsoucaris, Dodson, Dodson & Taylor, 1979). Applications to small structures have been rare, which is why we decided on a thorough investigation into the applicability of known theory to the solution of the phase problem in intractable small structures.

In 1978 we published a preliminary report (Vermin & de Graaff, 1978). The present paper contains our results, together with a description of the methods of building the matrix and maximizing the determinants we have used.

Also in 1978 a paper by Taylor, Woolfson & Main appeared reporting on their work in this field. We have developed algorithms differing significantly from the ones given by Taylor *et al.* Where this seemed relevant we have compared results.

This introduction is followed by a few definitions and

a discussion of some relevant properties of Karle–Hauptman (henceforth KH) determinants. Next we will describe the algorithms necessary to construct and maximize the determinant. We conclude by reporting the results and the conclusions we have drawn from them. The routines described below are available on request, in Fortran for IBM and IBM compatible systems. A CDC version will be available at a later date. The programs cannot be used independently of the *MULTAN* system.

Karle–Hauptman determinants

Definitions

- A the KH matrix with elements $E(hkl)$
- m the order of A
- B the inverse of A
- a_{ij} an element of A ($i, j = 1, 2, \dots, m$)
- α_{ij} the phase of a_{ij} ($i, j = 1, 2, \dots, m$)
- b_{ij} an element of B ($i, j = 1, 2, \dots, m$)
- β_{ij} the phase of b_{ij} ($i, j = 1, 2, \dots, m$)
- n the number of independent reflexions in A
- a_i the i th independent reflexion ($i = 1, 2, \dots, n$)
- b_i the element of B having the same row and column number as a_i
- α_i the phase of a_i
- β_i the phase of b_i
- a** a vector of elements a_1, a_2, \dots, a_n
- b** a vector of elements b_1, b_2, \dots, b_n
- α** a vector of elements $\alpha_1, \alpha_2, \dots, \alpha_n$
- β** a vector of elements $\beta_1, \beta_2, \dots, \beta_n$
- π** a vector of elements π
- det A the value of the determinant of A

We now give a short and necessarily incomplete survey of relevant properties of the KH matrices. For further details the reader is referred to the literature given.

1. A is Hermitian, *i.e.* $a_{ij} = a_{ji}^*$.
2. A is positive semi-definite, *i.e.* all eigenvalues are greater than or equal to zero (Goedkoop, 1952).
3. $\det A > 0$ if $m \leq N$, $\det A = 0$ if $m > N$; N is the number of atoms in the unit cell (Goedkoop, 1952; Kitaigorodsky, 1950).
4. The maximum determinant rule formulated by Tsoucaris (1970).

When a given KH matrix A of order m , containing structure factors with known phases, is bordered – to obtain a KH matrix A_1 of order $m + 1$ – by a row and a column containing elements, the phases of which are unknown, the most probable set of phases in this column maximizes $\det A_1 / \det A$.

This rule has been generalized by Tsoucaris (1970) to read that for a given KH matrix A the most probable set of phases will maximize $\det A$. Heinermann, Kroon & Krabbendam (1979) have been able to prove this generalized rule neglecting terms of fifth and higher orders.

5. Main (1975) has published an interesting method to optimize the phases in a KH matrix containing approximate values for these phases. The essence of the method is the maximization of a few of the largest eigenvalues of the KH matrix *via* an iterative procedure. Practical tests of this method are discussed extensively by Taylor and coworkers (Taylor *et al.*, 1978).

6. A simple expression exists for the derivative of $\det A$ with respect to a given phase:

$$\partial \det A / \partial \alpha_{ij} = 2 |a_{ij}| |b_{ij}| \sin(\beta_{ij} - \alpha_{ij}) \det A. \quad (1)$$

The derivation is given in the Appendix.

For a KH matrix to be useful in *ab initio* phase determination three criteria have to be met. The matrix A must have large off-diagonal elements (to minimize $\det A$) to increase the selectivity of the local maxima. Similar considerations make it imperative for the determinant to contain as few independent reflexions as possible. The matrix A may not contain any independent columns or groups of columns.

The program designed to obtain *ab initio* phases using KH determinants consists of two main blocks: (i) the construction of the matrix; (ii) finding a starting point and refining the phases until a local maximum is obtained.

Construction of the matrix

A general algorithm to construct useful KH matrices in an automatic way is not easy to design. We have tried the method given by Main (1975). This method was used in practice by Taylor and coworkers (Taylor *et al.*, 1978). We met with obstacles similar to those met by these authors, the main problem being the unsuitability for extension of the starting sets contained in the matrices obtained. Frequently, reflexions belonging to a particular parity group did not occur in the matrix at all.

We have developed an algorithm that approaches the problem from a different angle. Instead of building a very large matrix and trying to chip the best possible block from it, we construct a matrix of the desired dimensions immediately. This matrix is then optimized iteratively.

The algorithm consists of the following steps:

1. A convergence map is produced by the program *CONVERGE* of the *MULTAN* system.

2. Each reflexion is assigned a weight $W_i = |E| G_i$ ($i = 1, 2, \dots, nc$; nc is the number of reflexions in the convergence list).

$$G_i = \text{MAX}\{10, 100 \exp[-(i-1)^2 \ln(10)/59^2]\} \quad (2)$$

($i = 1, 2, \dots, nc$).

The program *CONVERGE* attempts to find a path in reciprocal space. Following this path, starting from the reflexions *CONVERGE* has identified as critical to a continuous phase extension process, *FASTAN* (the tangent refinement program of the *MULTAN* system) is best able to arrive at a complete phase set.

By giving the critical reflexions a high weight in the matrix optimization, the chance of successful extension of the phase set contained in the optimized matrix is maximized. G equals 100 for the first reflexion in the convergence list, dropping to 10 for $i = 60$. Therefore, the reflexions selected by the convergence procedure as suitable choices for inclusion in the starting set get the highest weights. All reflexions not in the list are given a weight of one.

3. A top row is constructed, containing the reflexions with the highest weights. While symmetry-dependent reflexions are used as well, due care is taken to ensure that all origin-defining and symbolic reflexions occur at least once in the top row of the matrix.

4. For each column a figure of merit (Kolfom) is calculated (see below).

5. A combined figure of merit (Matfom) is assigned to the matrix: $\text{Matfom} = (\prod \text{Kolfom}_i)$ ($i = 1, 2, \dots, m$).

6. Matfom is now maximized by changing individual columns one after the other until convergence (see below).

The figure of merit of column i is given by

$$\text{Kolfom}_i = \exp \left\{ -(N'_i 5/m)^2 \right\} \left(\frac{1}{2} \right)^{N''_i} \\ \times \exp \left\{ - \sum_{j=0}^7 (1 - 8P_j / \sum_{l=0}^7 P_l)^2 \right\} \sum_{k=0}^m w_k, \quad (3)$$

in which N'_i is the number of reflexions unique to this column; N''_i is the number of non-observed reflexions in the column; P_l equals $\sum |E|$ of all the reflexions present in the matrix belonging to parity group l ($ooo = 0$, $ooe = 1$, ..., $eee = 7$). $\sum_{k=1}^m W_k$ is the sum of the weights of the reflexions in the column.

The first exponential in (3) controls the number of independent reflexions in the column, the second reaches a maximum if all parity groups are represented evenly in the matrix. The term $(\frac{1}{2})^{N''_i}$ suppresses columns with an unacceptably high number of non-observed reflexions.

An individual column is optimized by permuting the reflexions with the highest weights already in the column, with their symmetry dependents, over all the

positions in the column. The exact number of reflexions to be permuted is controlled by the user. For each permutation the new top row element is calculated, from which the new Kolfom is determined.

If the new value is greater than the old one, Matfom is redetermined. If the new value of Matfom is higher than the old one, the new column is accepted and the optimization continues with the next column. If not, the next permutation is started.

Should Matfom no longer increase in one complete pass through the matrix, then the optimization is finished.

A typical KH matrix of order 20 takes about 1 min to construct on an Amdahl V7B. The matrix would contain about 80 independent reflexions and 110 relations. Excluding non-observed reflexions is no problem (usually no more than one or two are present). In general the reflexions are evenly distributed over the parity groups. The starting set of strong E 's contained in the matrix would number about 25.

Determination of the phases

In order to obtain useful phase information from the KH determinants a starting point of the maximization process has to be provided. By constructing matrices containing the origin-defining and symbolic reflexions chosen by *CONVERGE* we were able to generate starting phases for most of the reflexions by applying the \sum_2 relations contained in the matrix. The phases are then optimized by one of the two following algorithms. Note that in the beginning all the phase sums of the three-phase invariants are set at zero. This does not imply that on completion of the maximization of the determinant all strong triplets have the value zero still.

The NAG (1978) subroutine library contains a 'quasi Newton' algorithm written to optimize an arbitrary function with respect to all the variables, when the first-order derivatives are known. The program calculates improved estimates of the second-order derivatives in each cycle. The number of iterations necessary to reach convergence is roughly proportional to n , the number of variables. The matrix inversion, necessary to obtain $\partial \det A / \partial \alpha_{ij}$, is an m^3 -order process, while n is roughly proportional to m . The optimizing process using this routine is therefore of the order m^5 .

The second method, the one we use routinely, is rather more empirical in nature. In the maximum $\partial \det A / \partial \alpha_{ij} \approx 0$ or

$$|a_{ij}| |b_{ij}| \sin(\alpha_{ij} - \beta_{ij}) \det A \approx 0 \quad (i, j = 1, \dots, m). \quad (4)$$

These partial derivatives cannot be zero exactly because symmetry relations exist between various α_{ij} 's. ($\partial \det A / \partial \alpha_i$, $i = 1, \dots, n$, must be exact, for obvious reasons.)

According to Knossow the function

$$\tau(r) = -\sum_{i,j} b_{ij} \exp[-2\pi i(h_i - h_j) r] \quad (i, j = 1, 2, \dots, m), \quad (5)$$

the negative Fourier transform of the elements of the inverse of A , contains maxima on the atomic positions (Knossow, de Rango, Mauguén, Sarrazin & Tsoucaris, 1977). The Fourier transform of the matrix elements a_{ij} has maxima on the same positions, implying for the correct phases the relation $\beta_{ij} \approx \alpha_{ij} + \pi$. This deduction is consistent with (1), albeit only strictly if A contains a sufficient number of terms, e.g. in large matrices used in protein crystallography. A further condition is, of course, that Tsoucaris's rule holds.

The foregoing considerations led us to formulate the following iterative scheme: $\alpha_{\text{new}} = \alpha_{\text{old}} + \Delta\alpha$ with the following possibilities: [1] $\Delta\alpha = \alpha - \beta + \pi$; or [2] $\Delta\alpha = \beta - \alpha + \pi$, resulting in $\Delta\alpha = 0$ if $\beta - \alpha = \pi$.

Close to the maximum only [1] is consistent with expression (1), giving

$$\Delta\alpha \approx \sin(\Delta\alpha) = \sin(\alpha - \beta + \pi) = \sin(\beta - \alpha). \quad (6)$$

We calculate the elements of the actual shift vector $\Delta\alpha_i$ from

$$\Delta\alpha_i = (\Delta\alpha'_i + SS'_i) F_i \quad (7)$$

in which

$$\Delta\alpha'_i = \omega_i \{(\alpha_i - \bar{\beta}_i + \pi), \text{mod } 2\pi\} \quad (8)$$

and

$$\bar{\beta}_i = \tan^{-1} \left\{ \frac{\sum_i^{N_i} \sin(S_{pq} \beta_{pq} - \varphi_{pq})}{\sum_i^{N_i} \cos(S_{pq} \beta_{pq} - \varphi_{pq})} \right\}. \quad (9)$$

$\Delta\alpha'_i$ is the shift given by [1] averaged over the N symmetry equivalents and the variable α_i itself. S_{pq} and φ_{pq} describe the symmetry relation between parameter i and one symmetry equivalent, element p , q of the matrix. ω_i is a weight given by

$$\omega_i = \sin\{(\bar{\beta}_i - \alpha_i), \text{mod } 2\pi/2\} \left| \sum_i^{N_i} S_{pq} b_{pq} e^{i\varphi_{pq}} \right| \left| \sum_i^{N_i} |b_{pq}| \right|. \quad (10)$$

The effect of ω_i is to tone down large shifts as well as to account for the consistency of the indications for symmetry-related reflexions. S'_i is the sign of $\partial \det A / \partial \alpha_i$, calculated from (1). S is given by $\sum_{i=1}^N |\Delta\alpha'_i| / n$. Should S'_i and $\Delta\alpha'_i$ of a given parameter i have a different sign, then $\Delta\alpha'_i$ is set to zero. F_i is a 'fudge factor'; it is multiplied by $\frac{1}{2}$ if the sign of the shift is the same from one cycle to the next, if not F_i is divided by 2. The starting values are 0.3. If, during maximization,

the value $\det A$ decreases, all values of F_i are divided by 2, and the determinant is recalculated, this is repeated if necessary.

This rather complicated and, admittedly, artificial scheme converges to essentially the same points in parameter space as the Newton method. However, the number of iterations required is a very weak function of the number of parameters, *i.e.* the order of the process is m^3 to m^4 , a very significant improvement on the quasi Newton method.

Both methods suffer from the same handicap, namely that special reflexions cannot change their phases gradually. In $P2_1$ structures a separate treatment proved to be unnecessary, $h0l$ reflexions arrived on or very near to their allowed values (0 or π). In $P2_12_12_1$ a separate treatment of the special reflexions was essential. If during two consecutive cycles a shift of more than $\pi/3$ was calculated for a given special reflexion, π was added to the phase.

Recognizing the best set of phases

In the foregoing sections a procedure is outlined which will supply the user with a number of phase sets (dependent on the number of permutations generated by *MULTAN*). These phase sets can then be used as starting points for phase extension.

We have attempted to find a suitable figure of merit, enabling us to discriminate between the sets generated. Obvious choices are the value of the determinant and a measure of the way in which the relation $\beta_{ij} - \alpha_{ij} = \pi$ holds.

A less obvious but possibly better choice is a criterion not directly related to the target function. Considering the theory given by Main (see *Introduction*), the highest eigenvalue of A might be such a criterion. Furthermore we have tested various criteria derived from the paper by Navaza & da Silva (1979).

Regrettably none of these possibilities provided us with a figure of merit discriminating between the various sets obtained from smaller matrices of order 20 or thereabouts. This is in accordance with the conclusions of Baggio & Woolfson (1978) that it is impossible to define a useful figure of merit for a small (20 to 30) set of high E values, even if a similar number of weak reflexions is also known.

However, in the one example we have of a partially successful phase extension using KH matrices alone, we found the product of the determinant value and the highest eigenvalue to be a good figure of merit.

The multi matrix method

Working on not very large structures imposes severe restrictions on the size of the determinants as the

maximum determinant rule is not valid for determinants of order $N/2$ or larger (N is the number of atoms in the unit cell) (Heinermann *et al.*, 1979).

Therefore, the procedure outlined in the previous sections cannot be applied to a determinant containing sufficient information to define the structure in the case of structures with $N < 150$. To circumvent this problem we have provided the option of maximizing several determinants concurrently. The construction procedure strongly links the matrices to avoid the possibility of the maximizing producing phase sets related to different origin settings in different determinants.

An example of this technique, which is essentially a phase extension procedure, is discussed in the section on test structures. The implementation of this option provides the user with an opportunity to develop sufficiently large phase sets to obtain structural information directly, bypassing the tangent refinement.

Test structures

We have tested the program based on the procedures given in the previous sections by trying to solve the phase problem for five test structures. All of these structures were not, or were only partially, solved by *MULTAN* 78.

We tried to solve the structures automatically, that is using the default options of the *MULTAN* system as input to the determinant program. A 20×20 matrix was then constructed using default values again to control the construction procedure. The starting sets of phases obtained from the maximizing routine were fed into *FASTAN*, and the map of the final solution with the highest combined figure of merit (FOM) was calculated.

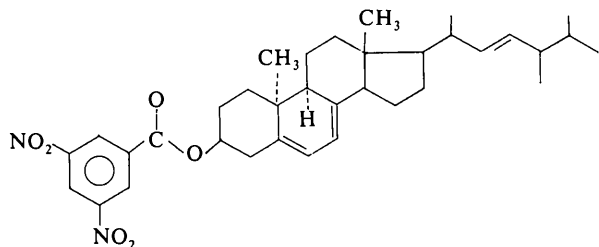
Only if this map or any other maps calculated from this set of solutions was not interpretable did we use our familiarity with the program to produce different, larger or possibly better matrices, different phase permutations, *etc.* The interpretation of the maps was done 'fairly', *i.e.* known atomic coordinates were not used and peaks were treated in descending order of strength. In order to verify if the inclusion of the KH step into the system was indeed a useful one we also attempted to solve the structures with *MULTAN* directly.

The first test structure was also used for a few experiments involving phases calculated from the known structure.

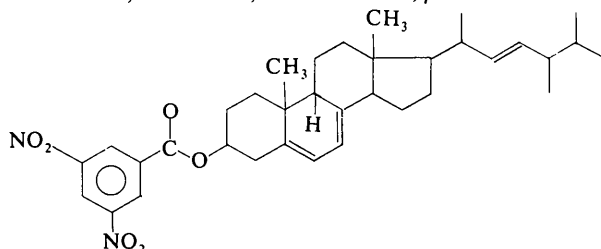
The compounds

1. PYROC: $C_{35}H_{46}N_2O_6$ (de Kok & Romers, 1975), 10α -ergosta-5,7,22-trien-3 β -yl 3',5'-dinitro-

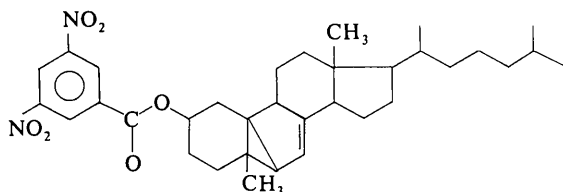
benzoate, $N = 86$, space group $P2_1$, $Z = 2$, $a = 11.28$,
 $b = 11.27$, $c = 12.537$ Å, $\beta = 93.25^\circ$.



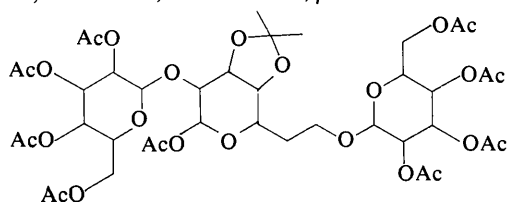
2. ISOPYR: $C_{35}H_{46}N_2O_6$ (de Kok, Romers & Hoogendorp, 1975), 9 β -ergosta-5,7,22-trien-3 β -yl 3',5'-dinitrobenzoate, $N = 86$, space group $P2_1$, $Z = 2$, $a = 18.364$, $b = 5.955$, $c = 14.568$ Å, $\beta = 94.03^\circ$.



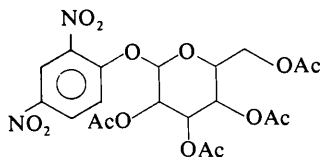
3. TOX: $C_{34}H_{46}N_2O_6$ (de Kok, Boomsma & Romers, 1976), 6,10-cyclo-5 α -methyl-19-norcholest-7-en-2 α -yl 3',5'-dinitrobenzoate, $N = 84$, space group $P2_1$, $Z = 2$, $a = 8.912$, $b = 7.3136$, $c = 24.889$ Å, $\beta = 98.93^\circ$.



4. TRIGAL: $C_{40}H_{56}O_{25}$ (Hoogendorp & Romers, 1982), methyl 3,4-*O*-isopropylidene-2,6-di-*O*-(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)- α -D-galactopyranoside, $N = 124$, space group $P2_1$, $Z = 2$, $a = 12.480$, $b = 8.821$, $c = 21.18$ Å, $\beta = 98.46^\circ$.



5. GLUCOPYR: $C_{20}H_{22}N_2O_{14}$ (Koeners, de Kok, Romers and van Boom, 1980), 2',4'-dinitrophenyl 2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranoside, $n = 144$, space group $P2_12_12_1$, $Z = 4$, $a = 8.16$, $b = 17.05$, $c = 17.05$ Å.



Results

PYROC

Using the available structural information (the shape of the dinitrobenzoic group is known), phasing 500 reflexions with *MULTAN* 78 resulted in a partial solution. In the best map about half the structure could be located.

Following the automatic procedure sketched above, three sets of 20 strong reflexions with an average phase error of less than 25° were obtained. Phase extension using *FASTAN* with defaults and calculating the *E* map of the solution with the highest combined figure of merit resulted in a map showing 41 out of 43 atoms. The 272 highest *E*'s were used, the highest peak not corresponding to an atom was number 41.

We also tried maximizing the same determinant with the phases calculated from the actual structure as starting point. The phase error on convergence was 17° , phase extension again proceeded smoothly. Optimizing the largest eigenvalue using the iterative procedure given by Main (1975), again starting with the calculated phases, resulted in a significantly larger deviation from the true values, 30° . Also in later stages of this optimizing process the value of the determinant decreased. It is probably necessary to use more than one eigenvalue to obtain satisfactory results. [See Taylor *et al.* (1978) for further illustrations of this procedure.]

ISOPYR

As in the case of PYROC using *MULTAN* 78 yields no more than a partial solution, which in this case was shifted over 1 Å with respect to the screw axis.

A run using default options of the *MULTAN* system and starting sets of 26 reflexions obtained from a 20×20 KH matrix produced a map containing a fragment of 32 atoms not shifted with respect to the symmetry element. The corresponding phase set (which had the highest combined figure of merit) was obtained by extending a starting set with an average error of 45° . Extension of phase sets with a smaller error (28°) yielded smaller fragments of the structure.

TOX

MULTAN 78 does not solve the phase problem, not even partially. An automatic run of *MULTAN* combined with the determinant program produced a map from which the ester group could be recognized. The 20×20 KH matrix contained 29 strong reflexions. After the maximizing procedure there were 12 sets with an average phase error of less than 35° , two of which had an error of 25° . Clearly the phase extension by tangent refinement was not very successful. However, the best

map coincided with the highest combined figure of merit.

TRIGAL

The structure could not be determined using the *MULTAN* system. Maximizing a 20×20 KH determinant containing 23 strong *E*'s resulted in a starting set with an average phase error of 22° . Phase extension of this and other sets did not result in interpretable *E* maps.

Using an order 30×30 matrix 29 strong reflexions could be phased with an average error of 28° . Again extension by tangent refinement was not successful. The phases obtained from this matrix were used as input in the concurrent optimization of ten 15×15 determinants. Calculating the Fourier transform of the 192 unique reflexions contained in these matrices produced a map containing a recognizable fragment of the structure. The figure of merit described earlier proved to be useful: the phase set giving the fragment was second in the list.

It is noteworthy that calculating the Fourier transform of the 192 reflexions using correct phases gave the same fragment and no more.

GLUCOPYR

This structure has up to now resisted all attempts to solve the phase problem by direct methods. Using KH matrices, starting sets with a small phase error could be obtained. The best of these had an average phase error of 20° in 20 strong reflexions. However, extension proved to be impossible with both the tangent refinement and the multi matrix approach.

We have looked into the correct phase values of the three-phase invariants. Many strong triplets have phases differing greatly from zero. Interestingly this does not interfere unduly with our attempts to produce starting sets. The solution quoted reproduced several of these invariants fairly well.

Conclusions

Four out of five of the 'problem structures' we have tested could be solved using a combination of *MULTAN* 78 and the procedure given in this paper. In one case phase extension *via* the multi matrix method gave a useful result not obtainable using the tangent refinement as carried out in the *MULTAN* program. The conclusion must be that a program such as ours can be a useful addition to the *MULTAN* package.

With regard to the various possibilities of maximizing the determinant, we would like to make the following comments.

Our experiments with theoretical phases in the case of PYROC seem to indicate that optimizing the highest eigenvalue of the matrix does not converge to the same point in parameter space as the two other methods we have tested. Moreover, convergence is less rapid than in the case of the empirical iterative scheme. Therefore if one wishes to use the maximum-determinant rule to obtain *ab initio* phases we think our method is of more general use.

The computer time required to set up and maximize a determinant large enough to produce a suitable starting set for *FASTAN* is of the same order as a conventional *MULTAN* run.

The authors are indebted to Professor C. Romers for his unflagging interest in this project. The algorithms described were developed and tested on the CDC computer of the ECN in Petten. The calculations on the test structures were done on the Amdahl V7 computer of the computing centre of Leyden State University, CRI.

APPENDIX

Definitions

- C* a complex matrix
- m* the order of *C*
- c_{ij} an element of *C* ($i, j = 1, 2, \dots, m$)
- F* the inverse of *C*
- f_{ij} an element of *F*
- γ_{ij} the phase of c_{ij} ($i, j = 1, 2, \dots, m$)
- φ_{ij} the phase of f_{ij} ($i, j = 1, 2, \dots, m$)
- Δ the determinant of *C*
- Δ_{ij} the determinant of the matrix obtained from *C* by deleting row *i* and column *j*

Derivation of expression (1) for $\partial \det A / \partial a_{ij}$

Expanding along row *k* we obtain

$$\Delta = \sum_{j=1, j \neq i}^m (-1)^{k+j} c_{kj} \Delta_{kj} + (-1)^{k+i} c_{ki} \Delta_{ki}. \quad (A1)$$

Differentiation with respect to c_{kl} gives

$$\partial \Delta / \partial c_{kl} = -1^{k+l} \Delta_{kl}. \quad (A2)$$

Application of Cramers' rule gives

$$\partial \Delta / \partial c_{kl} = f_{lk} \Delta, \quad (A3)$$

$$\partial c_{kl} = i c_{kl} \partial \varphi_{kl}. \quad (A4)$$

Combining (A3) and (A4) gives

$$\partial \Delta / \partial \varphi_{kl} = i c_{kl} f_{lk} \Delta. \quad (A5)$$

Applying this to the Hermitian matrix A,

$$\partial \det A / \partial a_{kl} = ia_{kl} b_{lk} \det A - ia_{lk} b_{kl} \det A, \quad (A6)$$

which after some simplification becomes

$$\partial \det A / \partial a_{kl} = 2|a_{kl}| |b_{kl}| \sin(\beta_{kl} - \alpha_{kl}) \det A. \quad (A7)$$

References

- BAGGIO, R. & WOOLFSON, M. M. (1978). *Acta Cryst.* **A34**, 883–892.
- FREER, A. A. & GILMORE, C. J. (1980). *Acta Cryst.* **A36**, 470–475.
- GILMORE, C. J. (1977). *Acta Cryst.* **A33**, 712–716.
- GOEDKOOP, J. A. (1952). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, edited by R. PEPINSKY, pp. 61–83. The Pennsylvania State College.
- HEINERMANN, J. J. L., KROON, J. & KRABBENDAM, H. (1979). *Acta Cryst.* **A35**, 101–105.
- HOOGENDORP, J. & ROMERS, C. (1982). *Acta Cryst. B*. In the press.
- KARLE, J. & HAUPTMAN, H. (1950). *Acta Cryst.* **3**, 181–187.
- KITAIGORODSKY, A. I. (1950). *X-ray Structure Analysis*, Vol. III, p. 61. Moscow: Gostekhizdat.
- KNOSSOW, M., RANGO, C. DE, MAUGUEN, Y., SARRAZIN, M. & TSOUCARIS, G. (1977). *Acta Cryst.* **A33**, 119–125.
- KOENERS, H. J., KOK, A. J. DE, ROMERS, C. & BOOM, J. H. VAN (1980). *Recl Trav. Chim. Pays-Bas*, pp. 355–362.
- KOK, A. J. DE, BOOMSMA, F. & ROMERS, C. (1976). *Acta Cryst.* **B32**, 2492–2496.
- KOK, A. J. DE & ROMERS, C. (1975). *Acta Cryst.* **B31**, 1535–1542.
- KOK, A. J. DE, ROMERS, C. & HOOGENDORP, J. (1975). *Acta Cryst.* **B31**, 2818–2823.
- MAIN, P. (1975). *Crystallographic Computing Techniques*, edited by F. R. AHMED, pp. 165–175. Copenhagen: Munksgaard.
- NAG: NUMERICAL ALGORITHMS GROUP (1978). *NAG Fortran Library Manual*, Mark 7. Oxford Univ. Press.
- NAVAZA, J. & SILVA, A. M. (1979). *Acta Cryst.* **A35**, 266–275.
- RANGO, C. DE, MAUGEN, Y. & TSOUCARIS, G. (1975). *Acta Cryst.* **A31**, 227–233.
- RANGO, C. DE, MAUGUEN, Y., TSOUCARIS, G., DODSON, G. G., DODSON, E. J. & TAYLOR, D. J. (1979). *J. Chim. Phys. Phys. Chim. Biol.* **76**, 811–812.
- TAYLOR, D. J., WOOLFSON, M. M. & MAIN, P. (1978). *Acta Cryst.* **A34**, 870–883.
- TSOUCARIS, G. (1970). *Acta Cryst.* **A26**, 492–494.
- VERMIN, W. J. & GRAAFF, R. A. G. DE (1978). *Acta Cryst.* **A34**, 892–894.

Acta Cryst. (1982). **A38**, 470–476

Crystalline Modifications and Structural Phase Transitions of NaOH and NaOD

BY H.-J. BLEIF AND H. DACHS

Hahn-Meitner-Institut für Kernforschung, Glienicker Strasse 100, D-1000 Berlin 39, Federal Republic of Germany

(Received 10 February 1981; accepted 4 February 1982)

Abstract

Structural work on the three modifications of sodium hydroxide is reviewed. The monoclinic and cubic modifications were determined with neutron and X-ray diffraction, respectively. The phase-transition temperatures were determined by specific-heat measurements. The cubic to monoclinic transition is a first-order transition with a freezing of the rotational motion of the OH (and OD) groups. The monoclinic axes **a**, **b** and **c*** tend to be oriented parallel to the original cubic directions $[\bar{1}\bar{1}2]$, $[1\bar{1}0]$ and $[111]$, respectively. The orthorhombic to monoclinic transition is a nearly continuous displacive phase transition with a soft acoustic shear mode. The order parameter is the homogeneous shear of the crystal in the **a** direction. Its

temperature dependence is described within Landau theory.

1. Introduction

The low-temperature orthorhombic modification of NaOH was determined by Ernst (1946) with some speculations on the position of the hydrogen atom. Stehr (1967) determined the H positions with neutron scattering and found a monoclinic modification $P2_1/m$ at higher temperatures. Bleif (1971) found from specific-heat measurements and X-ray diffraction patterns that there are three different modifications as a function of temperature, the high-temperature phase being cubic $Fm\bar{3}m$, as suggested by West (1935). The