*Acta Cryst.* (1952). **5**, 68

# A New Analytical Method for Solving Complex Crystal Structures*

By W. H. Zachariasen

*Department of Physics, University of Chicago and Argonne National Laboratory, Chicago, Illinois, U.S.A.*

(*Received* 29 *May* 1951)

With the aid of an identity it is shown that relationships between signs of structure factors for centro-symmetrical crystals can be obtained even when the Harker–Kasper inequality considerations yield no useful information. It is shown that a structure determination can be formulated as a self-consistency problem with respect to these relationships, and it is indicated how the solution can be found.

The new method is successfully tested on a structure where other methods had failed. The test consisted in finding the twenty-seven degrees of freedom for oxygen and boron atoms in the structure of the monoclinic form of metaboric acid. The results of the structure determination are briefly given.

## *Introduction*

A new analytical procedure for the determination of crystal structures with many degrees of freedom is developed and described in this paper. The discussion is restricted to centro-symmetrical crystals. The possibility of extending the method to structures without inversion center is being investigated; but it is too early to express a definitive opinion as to how successful this attempt is going to be.

It should be emphasized at the outset that the method developed in this article is not be be regarded merely as still another mathematical formulation of a 'solution in principle' of the phase problem. The method has been tested as to its practical use in solving structures, neither on potassium dihydrogen phosphate, nor on oxalic acid dihydrate, but on metaboric acid which paradoxically provides a far more acid test. This latter structure involves 27 degrees of freedom (actually 36, but in the early stages of the structure determination one is not concerned with the 9 degrees of freedom associated with the hydrogen atoms), and all attempts to find the structure by means of known methods had failed in spite of the expenditure of much time and effort. Within a period of two weeks the new method led to a direct determination of the 27 degrees of freedom. The ease with which the solution was obtained indicates that the method may be successfully used on structures of far greater complexity.

The relationshop of the new procedure to the recent method of Sayre (1952) and its modification by Cochran (1952) will be discussed in §3 of this paper. Since Sayre's paper is scheduled to appear at the same time as this article it is proper to record that the general principles of Sayre's method were described to this writer before the investigation reported in this paper was begun, and the influence of Sayre's work on the present one is gratefully acknowledged.

## 1. Preliminary considerations

It will be supposed for the sake of generality that the space-group symmetry is $P\bar{1}$. Simplifications resulting from additional symmetry are readily taken into account. The expression for the unitary structure factor $U_H \equiv F_H / \sum_1^N f_i$ is thus

$$U_H = 2 \sum_1^{\frac{1}{2}N} n_j \cos \mathbf{H}.\mathbf{r}_j, \tag{1}$$

where

$$n_j \equiv f_j / \sum_1^N f_j, \quad \mathbf{H} = 2\pi(H_1\mathbf{b}_1 + H_2\mathbf{b}_2 + H_3\mathbf{b}_3)$$

and

$$\mathbf{r}_j = x_j\mathbf{a}_1 + y_j\mathbf{a}_2 + z_j\mathbf{a}_3.$$

Let $\sigma$ represent the root-mean-square value of the unitary structure factors. As is well known, $\sigma^2 = \sum_1^N n_j^2$, or $\sigma = N^{-\frac{1}{2}}$ if all atoms are equal (Hughes, 1949). The distribution function for the unitary factors is for all practical purposes the error curve.

The method of inequality relations can be used to solve structures of moderate complexity. The most powerful inequality relation deduced by Harker & Kasper (1948) is

$$|U_H \pm U_K|^2 \leqslant (1 \pm U_{H+K})(1 \pm U_{H-K}). \tag{2}$$

Suppose that $|U_H| = |U_K| = |U_{H+K}|$ and $U_{H-K} = 0$. Under these conditions the inequality yields information about signs only if $|U_H| > (17^{\frac{1}{2}} - 1)/8 = 0{\cdot}39$. It is estimated on the basis of such conclusions that the method of inequalities usually will lead to a structure determination if 20 % or more of the structure factors satisfy the condition $|U_H| > 0{\cdot}30$, and this implies $\sigma > 0{\cdot}22$. The considerations of this paper will be

---

* The results contained in this article were presented at a symposium held at Pennsylvania State College in April 1951.

restricted to structures which cannot be solved by the method of inequalities. Hence it may be assumed that $\sigma$ is of the order of 0·2 or less.

Experience shows that a Fourier synthesis based upon the stronger 15 % of the reflections usually gives a sufficiently detailed picture of the actual electron distribution so that the accurate structure can be obtained in straightforward manner by means of successive approximations. Hence it may be said that the difficult part of the crystal-structure problem consists in determining the signs for the larger 15 % of the structure factors. Since 13 % of the structure factors may be expected to fall in the range $|U_H| > 1{\cdot}5\sigma$, it is convenient to define a structure factor as large (and the corresponding reflection as strong) by the requirement $|U_H| \geqslant 1{\cdot}5\sigma$. Whether this lower limit is chosen as $1{\cdot}4\sigma$, $1{\cdot}5\sigma$ or $1{\cdot}6\sigma$ is of little importance for the arguments of the next section.

In determining complex crystal structures it is often useful first to consider a two-dimensional projection of the structure which involves only two-thirds as many degrees of freedom. The method to be developed in the following can, of course, be used for such projections. In the interest of generality it is, however, assumed that the method is to be used for a frontal attack directly on the three-dimensional structure. As a consequence it is presupposed that all reflections in the observational range $|\mathbf{H}| < 4\pi/\lambda$ have been measured.

## 2. The basic equations

The following identity, from which the Schwarz inequality directly follows, is well known and easily verified:

$$|\textstyle\sum a_j b_j|^2 = \sum |a_j|^2 \sum |b_k|^2 - \frac{1}{2} \sum_j \sum_k \begin{vmatrix} a_j & a_k \\ b_j & b_k \end{vmatrix}^2. \quad (3)$$

The considerations of this paper are based upon a special case of this identity,* namely,

$$(|U_H| + |U_K|)^2 = 1 - D_{HK} + S_H S_K (U_{H+K} + U_{H-K}) + U_{H+K} U_{H-K}, \quad (4)$$

where $U_H$ is given by (1), $S_H$ is the sign of $U_H$, and where

$$D_{HK} = 8 \sum_1^{\frac{1}{2}N} \sum_1^{\frac{1}{2}N} n_j n_k \begin{vmatrix} \cos(\mathbf{H}+\mathbf{K}).\mathbf{r}_j & \cos(\mathbf{H}+\mathbf{K}).\mathbf{r}_k \\ \cos(\mathbf{H}-\mathbf{K}).\mathbf{r}_j & \cos(\mathbf{H}-\mathbf{K}).\mathbf{r}_k \end{vmatrix}^2. \quad (5)$$

As an immediate consequence of the identity one has

$$(|U_H| + |U_K|)^2 \leqslant 1 + S_H S_K (U_{H+K} + U_{H-K}) + U_{H+K} U_{H-K}, \quad (6)$$

which the reader will recognize as the useful form of the inequality relationship given in (2).

It is of interest to examine the term $D_{HK}$ which is defined by (5). Clearly $D_{HK} = 1$ if

$$U_H = U_K = U_{H+K} = U_{H-K} = 0.$$

Also, $\bar{D}_{HK} = 1$ if the average is taken over all triplets $H$ and $K$. If $\sigma \leqslant 0{\cdot}2$, as assumed above, the distribution function for values $D_{HK}$ has a sharp maximum at unity. The assumption $D_{HK} \approx 1$ for given $H$ and $K$ is thus a good approximation except in the rare instances where large fluctuations from the mean occur. In other words the equation

$$(|U_H| + |U_K|)^2 \approx S_H S_K (U_{H+K} + U_{H-K}) + U_{H+K} U_{H-K} \quad (7)$$

usually holds for any set $H$ and $K$, but will on occasion break down. Were this equation always valid, it would represent a most powerful means of determining the signs of structure factors. Suppose, as an illustration of the potential power of (7), that

$$|U_H| + |U_K| = 0{\cdot}40, \quad |U_{H+K}| = 0{\cdot}30$$

and $|U_{H-K}| = 0{\cdot}10$. The inequality relation (6) gives no information in this case, but (7), were it valid for this particular combination of indices, would have given $S_{H+K} = S_H S_K = -S_{H-K}$.

If $U_H$, $U_K$ and $U_{H+K}$ all correspond to strong reflections, one concludes from (7) that the following relation is probably, but not necessarily, correct:

$$S_{H+K} = S_H S_K. \quad (8)$$

Most analytical procedures for the determination of signs of structure factors involve a chain process. An incorrect sign introduced at an early stage will therefore have produced a large number of incorrect signs by the time an advanced stage in the chain process has been reached. For this reason one may be led far astray if a structure determination is based upon equations (7) and (8) without regard for their fallibility.

In (4) let $K$ be replaced by $K_i$ and $H$ by $H + K_i$. Let $U_H$ be a particular structure factor, and let it be stipulated that $U_{K_i}$, $U_{H+K_i}$ be pairs of large structure factors. Imagine next that (4), for given $H$, is averaged over all $K_i$. It is to be supposed that there are enough pairs of the specified type to justify the equation $\overline{D_{K_i H+K_i}} = 1$. The averaged equation (4) becomes

$$\overline{(|U_{K_i}| + |U_{H+K_i}|)^2} = \overline{S_{K_i} S_{H+K_i}}\, U_H + \overline{S_{K_i} S_{H+K_i} U_{H+2K_i}} + \overline{U_{H+2K_i}}\, U_H. \quad (9)$$

The left member of this equation is known from the observed data. Since $U_{K_i}$ and $U_{H+K_i}$ are large structure factors, the value of the left member exceeds $9\sigma^2$, the probable value being about $12\sigma^2$.

Some of the structure factors $U_{H+2K_i}$ occurring in the last two terms of the right member of (9) will usually correspond to reflections outside the observational range, i.e. $|\mathbf{H} + 2\mathbf{K}_i| > 4\pi/\lambda$. Hence one would not in general be in position to evaluate these two terms.

---

* The writer is indebted to Prof. J. E. Mayer for the suggestion of using identities rather than inequalities for establishing useful relationships.

It is, however, possible to set upper limits for the various terms of the right member:

$$\left.\begin{aligned} \overline{S_{K_i}S_{H+K_i}U_H} &\leqslant |U_H|, \\ \overline{S_{K_i}S_{H+K_i}U_{H+2K_i}} &\leqslant \overline{|U_{H+2K_i}|}, \\ \overline{U_{H+2K_i}U_H} &\leqslant \overline{|U_{H+2K_i}|}\,|U_H|. \end{aligned}\right\} \quad (10)$$

Since one may set $\overline{|U_{H+2K_i}|}\,|U_H| \approx \sigma^2$, it is seen that the last term of the right member of (9) is always small compared with the left member.

Suppose that $U_H$ is a large structure factor. One may then set $|U_H| \approx 1{\cdot}5\sigma$ and $\overline{|U_{H+2K_i}|} \approx 0{\cdot}7\sigma$. Table 1 shows the value of the left member compared with the maximum values of the various terms of the right member. There are several noteworthy facts showing up in this table. In the first place one can conclude that the first term of the right member must be positive if $\sigma > 0{\cdot}07$. Secondly, one sees that the maximum values indicated in (10) are practically attained when $\sigma \geqslant 0{\cdot}20$.

Table 1

| | Value of left member | Maximum values of terms of right member | | |
|---|---|---|---|---|
| $\sigma$ | $12\sigma^2$ | $1{\cdot}5\sigma$ | $0{\cdot}7\sigma$ | $\sigma^2$ |
| 0·20 | 0·48 | 0·30 | 0·14 | 0·04 |
| 0·15 | 0·27 | 0·23 | 0·11 | 0·02 |
| 0·10 | 0·12 | 0·15 | 0·07 | 0·01 |
| 0·07 | 0·06 | 0·11 | 0·05 | — |

The equation

$$S_H = S(\overline{S_{K_i}S_{H+K_i}}), \quad (11)$$

which is the statistical equivalent of (8), is thus reliable at least for $\sigma > 0{\cdot}07$. If one makes the reasonable assumption that the actual values of the various terms of the right member of (9) are proportional to their maximum values, then (11) should be valid even for $\sigma < 0{\cdot}07$. On the basis of this same assumption it also becomes possible to estimate the numerical values of the quantity $|\overline{S_{K_i}S_{H+K_i}}|$. The result is

| $\sigma$ | $\lvert\overline{S_{K_i}S_{H+K_i}}\rvert$ |
|---|---|
| 0·20 | 1·0 |
| 0·15 | 0·75 |
| 0·10 | 0·5 |
| 0·07 | 0·35 |

One finds, in other words, that (8) is almost always valid if $\sigma = 0{\cdot}20$, while it holds only two out of three times if $\sigma = 0{\cdot}07$.

The procedure for determining signs of structure factors proposed in this article is based upon (11) rather than upon the too unreliable (8). The discussion just given indicates that the suggested procedure is valid at least for $\sigma > 0{\cdot}07$, i.e. for structures with up to 200 atoms in the primitive cell.

The general principle of the method is simply to give all large structure factors signs such that self-consistency with respect to (11) is attained. Some general remarks as to a practical procedure for solving this self-consistency problem should be made at this stage.

As the obvious first step towards the solution the inequality relation (6) should be used to deduce as many unique signs as can be found. Next one expresses the signs for a suitable chosen set of the largest structure factors by means of letter symbols *a*, *b*, *c*, *d*, .... The inequality relation is then used again to deduce the signs of further structure factors in terms of these letter symbols. In this manner a list of large structure factors will have been prepared with the signs either uniquely known or expressed in terms of the letter symbols *a*, *b*, *c*, *d*, .... It is to be presumed that a sufficient number of letter symbols have been introduced, so that this initial list is fairly extensive.

Equation (11) is next used in connection with this initial list both for the purpose of expanding the list and to determine which letter symbols represent $+1$ and which $-1$. In the final stage the initial list has been augmented to such an extent that it includes all large structure factors, and all letter symbols have been eliminated. The example discussed in § 4 illustrates the practical procedure.

## 3. The relationship to other methods

The relationship of the method discussed in this paper to the method of inequality relations has been referred to a number of times. The method of Harker & Kasper is based upon the inequality (6) which is a direct consequence of the identity in (4). The method of inequalities may thus be said to be a special case of the method proposed in this paper. Whenever the inequality relation (6) gives unique information about amplitude signs, the result is obtained in the form of (8) with assurance that the correctness of the result is proved. If the inequality relation is capable of yielding the desired information, then, of course, there is no point in using the new method. Indeed, the considerations of this article have been restricted to structures which cannot be solved by means of inequalities.

Recently, Sayre (1952) has found a relation between structure factors for a centro-symmetrical crystal containing equal atoms. Sayre's equation is

$$VfF_H = \sum_i F_{K_i}F_{H+K_i},$$

where $V$ is the volume of the unit cell. Clearly the only important terms in the sum are those for which both structure factors $F_{K_i}$ and $F_{H+K_i}$ are large. By applying a large temperature factor it is thus possible from Sayre's equation to obtain relations involving a small number of structure factors. In this manner Sayre has used his equation to obtain information about the signs of the structure factors.

The similarity of Sayre's equation to results obtained in this paper is brought out if his equation is divided by $Nf^2$. Introducing unitary structure factors one finds

$$VU_H = N\sum_i U_{K_i}U_{H+K_i}.$$

It is seen that (11) results when the signs of the two sides of the above equation are made to agree.

Quite recently Cochran (1952) has investigated the condition which must be imposed if the distribution function for point atoms is to make greater excursions in the positive than in the negative direction. Using Sayre's equation Cochran finds that the condition can be expressed as the probable validity of (8), which again implies (11).

## 4. Application of the method to the structure of metaboric acid

The unit cell of the monoclinic form of metaboric acid, $HBO_2$, has dimensions

$$a_1=7\cdot132\pm0\cdot002,\quad a_2=8\cdot852\pm0\cdot003,$$
$$a_3=6\cdot772\pm0\cdot002\ \text{Å}$$
with $$\alpha_2=93\cdot253\pm0\cdot005°.$$

The space group is $P2_1/a$, and twelve stoechiometric molecules are in the unit cell.

About one thousand distinct reflections can be observed with Cu $K\alpha$ radiation. The intensities of all but about twenty of these reflections were carefully measured with a General Electric X-Ray Geiger Counter Spectrometer which had been modified for single-crystal work. The absolute scale factor and the temperature factor were approximately determined by means of the usual averaging process.

The root-mean-square value for the unitary structure factor is about 0·17 in agreement with the equation $\sigma^2=\Sigma n_j^2$, and the largest observed numerical value for the unitary structure factor is 0·56. In agreement with the suggestion given in § 1 of this paper, it was found convenient to define a structure factor as large when $|U_H|\geqslant1\cdot5\sigma=0\cdot25$. A total of 138 of the 1000 reflections fall in this category.

Since the origin may be shifted from one inversion center to another, it is possible to choose the signs of three structure factors at will. Thus the positive sign was chosen for the reflections (201), $(35\bar{3})$ and (017). The signs of fourteen additional structure factors can be uniquely deduced from the inequality relation. If the signs of five further structure factors are expressed by letter symbols $b$, $c$, $h$, $x$ and $y$, the inequality relations lead to the determination of the signs of eighteen more structure factors in terms of these letter symbols. Table 2 lists the forty reflections for which the signs in this manner are either justifiably assumed or determined by means of inequality relations. Since five of the signs in Table 2 are unknown, there are, of course, $2^5$ distinct sign combinations. Table 3 lists the 138 strong reflections.

The problem is now, with the aid of equation (11),

(1) to expand Table 2 so as to include all large structure factors with the signs expressed either in terms of the symbols $b, c, h, x, y$ or as $+1$ and $-1$; and

(2) to find which of the letter symbols represent $+1$ and which $-1$.

In carrying out this task one should make use of the known symmetry properties. For $P2_1/a$ these are:

$$U_{H_1H_2H_3}=U_{H_1\bar{H}_2H_3}\quad\text{if}\quad H_1+H_2\quad\text{is even,}$$
$$U_{H_1H_2H_3}=-U_{H_1\bar{H}_2H_3}\quad\text{if}\quad H_1+H_2\quad\text{is odd.}$$

The method used to solve the self-consistency problem will now be illustrated by means of a series of examples.

Table 2. *Initial list*

| $H_1H_2H_3$ | $\|U_H\|$ | Sign | $H_1H_2H_3$ | $\|U_H\|$ | Sign |
|---|---|---|---|---|---|
| $20\bar{5}$ | 0·55 | + | $12\bar{3}$ | 0·35 | ($x$) |
| 006 | 0·53 | + | $16\bar{3}$ | 0·48 | ($y$) |
| 201 | 0·50 | (+) | $28\bar{1}$ | 0·50 | $bh$ |
| $19\bar{4}$ | 0·47 | + | $22\bar{2}$ | 0·46 | $b$ |
| $35\bar{3}$ | 0·44 | (+) | $17\bar{2}$ | 0·46 | $b$ |
| 017 | 0·44 | (+) | 275 | 0·44 | $-hy$ |
| 207 | 0·43 | + | $46\bar{3}$ | 0·43 | $h$ |
| 040 | 0·43 | + | $26\bar{4}$ | 0·42 | $h$ |
| $55\bar{2}$ | 0·41 | + | 571 | 0·40 | $b$ |
| 218 | 0·41 | + | 173 | 0·39 | $b$ |
| $21\bar{6}$ | 0·40 | − | 480 | 0·38 | $bh$ |
| 402 | 0·39 | + | 141 | 0·35 | $-bx$ |
| 195 | 0·38 | + | $33\bar{1}$ | 0·34 | $bh$ |
| 241 | 0·37 | + | $64\bar{1}$ | 0·34 | $c$ |
| 151 | 0·35 | + | 352 | 0·34 | $h$ |
| $39\bar{3}$ | 0·32 | + | 164 | 0·34 | $-y$ |
| 046 | 0·30 | + | 370 | 0·30 | $b$ |
| 023 | 0·45 | ($b$) | 224 | 0·28 | $b$ |
| $60\bar{1}$ | 0·48 | ($c$) | $47\bar{1}$ | 0·27 | $hy$ |
| 312 | 0·45 | ($h$) | 111 | 0·25 | $h$ |

As a first example consider the reflection $(15\bar{4})$ which is found in Table 3, but not in Table 2. Table 2 contains five pairs of the type $K_i$ and $H+K_i$ corresponding to $H=(15\bar{4})$. For each of the pairs one finds $S_{K_i}S_{H+K_i}=+1$. Hence, by (11), $S_{15\bar{4}}=+1$ and the structure factor $U_{15\bar{4}}$ can be added to Table 2.

In the second illustration let $H=(133)$. It is possible to find nine pairs $K_i$, $H+K_i$ in Table 2 corresponding to this choice for $H$. For five of these pairs one finds $S_{K_i}S_{H+K_i}=b$ and for the remaining four $S_{K_i}S_{H+K_i}=hb$. Since the numerical value of the quantity $\overline{S_{K_i}S_{H+K_i}}$ should be near unity it must accordingly be required that $h=+1$. Thus $S_{133}=b$ and $U_{133}$ can be transferred from Table 3 to Table 2 which now contains only four unknown quantities, namely, $b$, $c$, $x$ and $y$.

By repetition of the procedure illustrated in these two examples Table 2 is gradually expanded to include all large structure factors, and the unknown quantities $b$, $c$, $x$ and $y$ are reduced one by one until all letter symbols are eliminated. The final results as to the signs of large structure factors are given in Table 3.

Having thus deduced the signs of all structure factors for which $|U_H|\geqslant0\cdot25$, equation (11) was next used to find the signs of additional structure factors. For instance, the signs were deduced for all structure factors for which $|F_H|\geqslant20$, and for all structure factors for which $0\cdot20\leqslant|U_H|<0\cdot25$. Such reflections are listed in Table 4. As an example consider the reflection $H=(001)$ for which $|F_H|=29$ and $|U_H|=0\cdot11$. For $H=(001)$, there are twenty-one pairs of the type $K_i, H+K_i$ in Table 3. The quantity $\overline{S_{K_i}S_{H+K_i}}$

Table 3. *Large structure factors*

| $H_1H_2H_3$ | $\lvert U_H\rvert$ | Sign |
|---|---|---|
| $40\bar{8}$ | 0·56 | + |
| $20\bar{5}$ | 0·55 | + |
| 006 | 0·53 | + |
| 201 | 0·50 | + |
| $60\bar{1}$ | 0·48 | + |
| 207 | 0·43 | + |
| 402 | 0·39 | + |
| 603 | 0·34 | + |
| 401 | 0·33 | − |
| $40\bar{7}$ | 0·30 | − |
| $40\bar{2}$ | 0·28 | + |
| 404 | 0·27 | + |
| 400 | 0·25 | + |
| $20\bar{6}$ | 0·25 | − |
| | | |
| 312 | 0·45 | + |
| $31\bar{5}$ | 0·32 | − |
| $31\bar{3}$ | 0·29 | + |
| 117 | 0·29 | + |
| 114 | 0·26 | − |
| 111 | 0·25 | + |
| | | |
| 017 | 0·44 | + |
| $41\bar{5}$ | 0·42 | − |
| 218 | 0·41 | + |
| $21\bar{6}$ | 0·40 | − |
| $61\bar{4}$ | 0·33 | − |
| $41\bar{1}$ | 0·27 | + |
| | | |
| $22\bar{2}$ | 0·46 | − |
| 023 | 0·45 | − |
| 422 | 0·42 | − |
| $62\bar{3}$ | 0·35 | − |
| $22\bar{6}$ | 0·34 | − |
| 425 | 0·30 | − |
| 623 | 0·29 | − |
| 224 | 0·28 | − |
| | | |
| $12\bar{3}$ | 0·35 | + |
| 124 | 0·28 | − |
| $12\bar{2}$ | 0·26 | − |
| | | |
| $33\bar{1}$ | 0·34 | − |
| 730 | 0·28 | + |
| $73\bar{1}$ | 0·27 | − |
| $33\bar{5}$ | 0·26 | − |
| 133 | 0·25 | − |
| 530 | 0·25 | − |
| | | |
| $83\bar{3}$ | 0·45 | + |
| $23\bar{6}$ | 0·40 | + |
| 235 | 0·35 | − |
| $43\bar{4}$ | 0·32 | − |
| $43\bar{5}$ | 0·30 | + |
| $63\bar{3}$ | 0·30 | − |
| $63\bar{2}$ | 0·29 | + |
| 037 | 0·26 | − |
| $63\bar{4}$ | 0·25 | + |
| 031 | 0·25 | − |
| 034 | 0·25 | − |
| | | |
| 040 | 0·43 | + |
| 241 | 0·37 | + |
| $64\bar{1}$ | 0·34 | + |
| 046 | 0·30 | + |
| $24\bar{5}$ | 0·27 | + |
| $44\bar{2}$ | 0·25 | + |
| | | |
| 141 | 0·35 | + |
| 345 | 0·30 | + |
| $14\bar{7}$ | 0·30 | + |
| 343 | 0·29 | − |
| $54\bar{5}$ | 0·25 | + |
| | | |
| $35\bar{3}$ | 0·44 | + |
| $55\bar{2}$ | 0·41 | + |
| 151 | 0·35 | + |
| 352 | 0·34 | + |
| $75\bar{1}$ | 0·33 | + |
| 156 | 0·31 | + |
| $15\bar{5}$ | 0·28 | + |
| $35\bar{4}$ | 0·26 | + |
| $15\bar{4}$ | 0·25 | + |
| | | |
| 850 | 0·38 | − |
| $25\bar{3}$ | 0·33 | − |
| 453 | 0·32 | + |
| 454 | 0·31 | − |
| 655 | 0·30 | − |
| $65\bar{1}$ | 0·28 | − |
| $25\bar{2}$ | 0·27 | + |
| | | |
| $46\bar{3}$ | 0·43 | + |
| $26\bar{4}$ | 0·42 | + |
| 065 | 0·34 | + |
| 266 | 0·29 | + |
| 262 | 0·28 | + |
| $66\bar{2}$ | 0·28 | + |
| $26\bar{5}$ | 0·27 | − |
| 064 | 0·25 | − |
| | | |
| $16\bar{3}$ | 0·48 | + |
| $16\bar{2}$ | 0·40 | − |
| $56\bar{2}$ | 0·39 | − |
| 364 | 0·38 | + |
| $36\bar{3}$ | 0·37 | − |
| 164 | 0·34 | − |
| 363 | 0·32 | − |
| 163 | 0·31 | + |
| $36\bar{5}$ | 0·31 | − |
| $16\bar{6}$ | 0·31 | − |
| 565 | 0·30 | + |
| $36\bar{4}$ | 0·28 | + |
| $36\bar{1}$ | 0·25 | − |
| | | |
| $17\bar{2}$ | 0·46 | − |
| 571 | 0·40 | − |
| 173 | 0·39 | − |
| $37\bar{1}$ | 0·32 | − |
| 370 | 0·30 | − |
| 170 | 0·29 | + |
| 374 | 0·25 | − |
| | | |
| 275 | 0·44 | − |
| 273 | 0·39 | + |
| 072 | 0·32 | + |
| $27\bar{2}$ | 0·32 | + |
| $47\bar{1}$ | 0·27 | + |
| 071 | 0·27 | − |
| $27\bar{1}$ | 0·25 | − |
| 074 | 0·25 | − |
| | | |
| $28\bar{1}$ | 0·50 | − |
| 480 | 0·38 | − |
| 282 | 0·30 | + |
| 080 | 0·28 | − |
| 081 | 0·26 | + |
| | | |
| $18\bar{1}$ | 0·35 | − |
| 580 | 0·32 | + |
| $18\bar{4}$ | 0·32 | + |
| 185 | 0·29 | − |
| 582 | 0·26 | − |
| | | |
| $19\bar{4}$ | 0·47 | + |
| 590 | 0·39 | + |
| 195 | 0·38 | + |
| $39\bar{1}$ | 0·31 | + |
| 393 | 0·31 | + |
| $39\bar{3}$ | 0·31 | + |
| $19\bar{1}$ | 0·25 | + |
| 190 | 0·25 | + |
| | | |
| 290 | 0·35 | − |
| 491 | 0·30 | − |
| 095 | 0·27 | − |

Table 4. *Additional structure factors*

| $H_1H_2H_3$ | $\lvert U_H\rvert$ | Sign |
|---|---|---|
| 007 | 0·24 | − |
| $21\bar{2}$ | 0·24 | + |
| $31\bar{4}$ | 0·24 | + |
| $45\bar{1}$ | 0·24 | + |
| $45\bar{2}$ | 0·24 | − |
| $36\bar{2}$ | 0·24 | + |
| 541 | 0·24 | + |
| $16\bar{4}$ | 0·24 | − |
| 022 | 0·23 | − |
| 0,10,2 | 0·23 | + |
| 340 | 0·23 | + |
| 680 | 0·23 | + |
| 1,11,0 | 0·23 | + |
| 231 | 0·23 | − |
| $35\bar{1}$ | 0·23 | + |
| 334 | 0·23 | − |
| 264 | 0·23 | − |
| 632 | 0·23 | + |
| $40\bar{4}$ | 0·22 | + |
| 800 | 0·22 | + |
| 004 | 0·22 | + |
| $20\bar{4}$ | 0·22 | + |
| $20\bar{1}$ | 0·22 | + |
| 602 | 0·22 | − |
| $20\bar{8}$ | 0·22 | − |
| $13\bar{2}$ | 0·22 | − |
| 324 | 0·22 | + |
| $32\bar{5}$ | 0·22 | − |
| 254 | 0·22 | + |
| $51\bar{4}$ | 0·22 | − |
| 130 | 0·21 | − |
| 140 | 0·21 | − |
| 123 | 0·21 | + |
| $44\bar{1}$ | 0·21 | + |
| $51\bar{3}$ | 0·21 | + |
| $42\bar{5}$ | 0·21 | − |
| 063 | 0·20 | − |
| 027 | 0·20 | − |
| 540 | 0·20 | + |
| 470 | 0·20 | − |
| 710 | 0·20 | + |
| 380 | 0·20 | − |
| $32\bar{2}$ | 0·20 | + |
| $33\bar{2}$ | 0·20 | + |
| $42\bar{4}$ | 0·20 | − |
| 116 | 0·20 | + |
| 016 | 0·19 | − |
| $31\bar{1}$ | 0·19 | − |
| $21\bar{3}$ | 0·19 | − |
| 411 | 0·19 | − |
| 150 | 0·18 | + |
| 330 | 0·17 | − |
| 310 | 0·16 | − |
| 121 | 0·16 | + |
| 210 | 0·15 | − |
| $11\bar{1}$ | 0·15 | − |
| 200 | 0·15 | − |
| 001 | 0·12 | − |
| 212 | 0·10 | + |

evaluated over these twenty-one pairs gives the value $-0{\cdot}90$, and hence $S_{001} = -1$.

At this stage in the investigation the signs had been determined for 198 of the largest Fourier coefficients $F_H$, and it was felt that a three-dimensional Fourier synthesis based upon these terms would give a good approximation to the correct structure.

The results of this synthesis showed the presence of 24 maxima per unit cell corresponding to between nine and ten contour lines, and twelve maxima per unit cell corresponding to between five and six contour lines. All other maxima corresponded to less than three contour lines. The 24 largest maxima were assumed to represent oxygen atoms, the twelve next largest boron atoms.

Table 5 gives the coordinates for boron and oxygen atoms as obtained from the synthesis, while the corresponding B–O distances are listed in Table 6. It is to be expected that the inclusion of the more than eight hundred Fourier coefficients not yet used will lead to moderate revision in atomic co-ordinates and interatomic distances, without altering the main features of the structure.

The boron and oxygen atoms are bonded together to form endless chains parallel to the $a_2$ axis. The constituents of a chain are $BO_4$ tetrahedra and $B_2O_5$ groups, a $B_2O_5$ group being composed of two $BO_3$ triangles having one corner in common. These endless chains are presumably linked together by hydrogen bonds. The presence of such hydrogen bonds is indicated by the short O–O separations between chains noted in Table 6.

Structure factor calculations are now in progress and the detailed structure will be reported later.

Table 5. *Parameter values for metaboric acid*

| | $x$ | $-y$ | $z$ |
|---|---|---|---|
| $B_I$ | 0·261 | 0·295 | 0·478 |
| $B_{II}$ | 0·403 | 0·335 | 0·169 |
| $B_{III}$ | 0·241 | 0·544 | 0·335 |
| $O_I$ | 0·210 | 0·198 | 0·619 |
| $O_{II}$ | 0·229 | 0·444 | 0·498 |
| $O_{III}$ | 0·353 | 0·238 | 0·316 |
| $O_{IV}$ | 0·374 | 0·492 | 0·189 |
| $O_V$ | 0·489 | 0·287 | 0·019 |
| $O_{VI}$ | 0·046 | 0·550 | 0·236 |

Table 6. *Interatomic distances*

| | | | |
|---|---|---|---|
| $B_I$–$O_I$ | 1·35 Å | $B_{III}$–$O_I$ | 1·44 Å |
| $B_I$–$O_{II}$ | 1·35 | $B_{III}$–$O_{II}$ | 1·42 |
| $B_I$–$O_{III}$ | 1·40 | $B_{III}$–$O_{IV}$ | 1·48 |
| $B_{II}$–$O_{III}$ | 1·38 | $B_{III}$–$O_{VI}$ | 1·51 |
| $B_{II}$–$O_{IV}$ | 1·41 | $O_{II}$–H–$O_{VI}$ | 2·73 |
| $B_{II}$–$O_V$ | 1·29 | $O_{IV}$–H–$O_V$ | 2·63 |
| | | $O_V$–H–$O_{VI}$ | 2·71 |

I am deeply indebted to Prof. R. Pepinsky for the use of his computer in evaluating the three-dimensional Fourier synthesis.

## References

Cochran, W. (1952). *Acta Cryst.* **5**, 65.
Harker, D. & Kasper, J. S. (1948). *Acta. Cryst.* **1**, 70.
Hughes, E. W. (1949). *Acta Cryst.* **2**, 34.
Pepinsky, R. & Cochran, W. (1951). *Phys. Rev.* **83**, 226.
Sayre, D. (1952). *Acta Cryst.* **5**, 60.