

produkten kombiniert werden dürfen. Die Vorzeichenbestimmung der Reflexe der 2. Gruppe ist nun sogar besonders einfach, da in jedem Tripelprodukt stets ein Faktor zur 1. Gruppe gehört, von der viele Vorzeichen bereits bestimmt wurden. Man muss allerdings beachten, dass sich die Wahrscheinlichkeit geändert hat, mit der die Tripelprodukte positiv sind, da sich ja die neuen U -Werte nur auf die restliche Struktur beziehen und deshalb mit dem entsprechend veränderten N in der Wahrscheinlichkeitsformel zu rechnen ist (Woolfson, 1954).

Erwähnt sei noch, dass manchmal, auch ohne dass zusätzliche Auslöschungsbedingungen vorliegen, Schwierigkeiten in der Vorzeichenbestimmung auftreten können, zum Beispiel dann, wenn in einer Struktur einige schwere Atome vorhanden sind und deren Beitrag zu einer bestimmten Strukturamplitude zufällig sehr klein ist, während der der übrigen Atome

grösser ist. Die Begründung ist analog der im Beispiel am Anfang gegebenen.

Die hier beschriebene Methode wurde — anscheinend erfolgreich — auf ein Silberpolyphosphat angewendet. Die Strukturbestimmung ist jedoch noch nicht abgeschlossen (Jost, 1958).

H. Liebsch (im gleichen Institut) hat unabhängig von dieser Arbeit in ähnlicher Weise unitäre Struktur-faktoren für den Silikatanteil eines Bariumsilikats berechnet.

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An Equation between Structure Factors for Structures Containing Unequal or Overlapped Atoms. II. An Application to Structure Determination

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(Received 31 December 1957)

Oftentimes, when sign relationships are used as a method of solving crystal structures, there are found a large number of plausible sets of signs for the reflexions being considered. Mathematical criteria which have been used to narrow down further the choice of possible sign sets have always depended on the applicability of Sayre's equation to the structure or projection being considered. A new criterion (the Z test), based on the equation developed in Part I of this paper, has been suggested, and this may be applied under a wide range of conditions where Sayre's equation is no longer valid.

The potentialities of the criterion have been demonstrated by application to the projection of the known structure of α -glucose and also in the solution of a projection of an unknown structure, D-xylose.

A proposed programme for the Ferranti Mercury computer is described which, combining the use of sign relationships and the Z test, will start from the X-ray intensities and output from the machine a number of possible electron-density maps.

1. Structure determination by direct methods

Inequality or sign relationships applied as a means of structure determination rarely indicate a single solution as clearly correct; more often a number of almost equally probable sets of signs are found for the structure factors being considered. If this number is not too large, and computing facilities are available, it may be possible to examine the Fourier synthesis corresponding to each set of signs and to attempt to recognize the correct one. However, the success of such an operation does not depend only on the ease with which the syntheses can be calculated and contoured. In an attempt to solve the short-axis projection of

L-asparagine monohydrate the author has examined about 100 Fourier syntheses which were output by a computer in a form suitable for direct contouring. It seemed possible to interpret several of them in terms of the assumed molecule of L-asparagine plus a water molecule, but attempts at refinement have been completely unsuccessful and have taken a great deal of time.

It would clearly be useful to reduce further the number of possible sets of signs by means of some other discriminating mathematical criterion in addition to the sign relationships already used. The first example of such a criterion was given by Cochran & Penfold (1952) in the solution by direct methods of the c -axis

projection of L-glutamine. They used Sayre's equation (1952) in the modified form

$$U_{\mathbf{h}} = \alpha \sum_{\mathbf{h}'} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}, \quad (1)$$

where α was an empirically determined function of $\sin \theta$, and they found for each possible set of signs the value of

$$T = \sum |(|U_{\mathbf{h}}| - |\alpha \sum_{\mathbf{h}'} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}|)| \div \sum |U_{\mathbf{h}}|. \quad (2)$$

The modified Sayre's equation was best satisfied by the correct set of signs which gave the lowest value of T .

Another, and more systematic, criterion called the 'zero-check' has been developed by Cochran & Douglas (1957). For a structure containing equal resolved atoms the unitary structure factors are related by the equation

$$U_{\mathbf{h}} = N \overline{U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}}_{\mathbf{h}'}, \quad (3)$$

where N is the number of atoms in the unit cell and the average is taken over all values of \mathbf{h}' . When $U_{\mathbf{h}}=0$ this gives

$$\sum_{\mathbf{h}'} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'} = 0, \quad (4)$$

and if only the largest U 's are included in the summation its value should be small, if not zero. The 'zero-check' consists of evaluating

$$\sum_{\mathbf{h}} |(\sum_{\mathbf{h}'} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'})|$$

for each set of signs, the summations being over all available values of \mathbf{h}' and those \mathbf{h} for which $U_{\mathbf{h}} \neq 0$. A correct set of signs should give a low value for the zero-check. This criterion has been successfully applied in the solution of a projection of nitroguanidine but it has been found empirically that when the condition of equal resolved atoms is badly contravened the zero-check is quite useless; under such conditions Sayre's equation does not apply and any test related to Sayre's equation would likewise be invalid.

In Part I of the present paper (Woolfson, 1958) an equation was developed which applies reasonably well under a fairly wide range of conditions. A test function has been derived from this equation which may be applied to structures, or projections, containing unequal or overlapped atoms.

2. The test function

The function $\rho_{\mathbf{r}}$ given by the Fourier synthesis with only the terms corresponding to the largest U 's usually represents the atoms of a structure tolerably well as regards electron density and position. We should then expect the equation

$$F_{\mathbf{h}} = A_{\mathbf{s}} G'_{\mathbf{h}} + B_{\mathbf{s}} H'_{\mathbf{h}} \quad (5)$$

to be obeyed fairly well, where $G'_{\mathbf{h}}$ and $H'_{\mathbf{h}}$ are the Fourier coefficients of $(\rho_{\mathbf{r}})^2$ and $(\rho_{\mathbf{r}})^3$ respectively. Equation (5) is a modified form of equation (7) given in the first part of this paper.

The test function which has been developed from equation (5) is the value of

$$Z = \sum_{\mathbf{h}} |(|F_{\mathbf{h}}| - |A_{\mathbf{s}} G'_{\mathbf{h}} + B_{\mathbf{s}} H'_{\mathbf{h}}|)| \div \sum_{\mathbf{h}} |F_{\mathbf{h}}|. \quad (6)$$

The correct set of signs would be expected to give a low value for Z . It will be seen that the relationship of Z to equation (5) is similar to that of test function T to equation (1).

Table 1

$h k$	$A_{\mathbf{s}} G'_{\mathbf{h}} + B_{\mathbf{s}} H'_{\mathbf{h}}$								$ F_{\mathbf{h}} $
	1	2	3	4	5	6	7	8	
0 0	361	352	341	351	341	339	355	337	384
0 2	38	7	23	31	5	26	25	24	22
0 4	17	9	12	15	5	7	-2	23	29
0 6	2	-17	-2	6	-16	5	-16	-4	18
0 8	12	-2	-8	12	-10	8	-1	6	24
1 1	0	-15	-23	-3	6	27	27	6	16
1 2	-18	12	-14	1	25	-25	6	-25	35
1 3	-13	-6	4	1	6	16	16	-4	22
1 4	-16	5	14	-5	-13	-6	3	-4	20
1 5	12	-51	-23	48	25	40	17	-37	46
1 6	6	7	-10	-5	2	-6	-2	-14	25
1 7	-34	25	-15	18	-27	34	-6	9	36
1 8	-9	-3	-3	-13	-8	-15	-13	-3	11
2 0	6	38	45	0	-27	-4	0	-22	36
2 1	-7	-10	5	8	-5	-7	8	5	19
2 2	-9	-1	7	-5	4	4	8	-4	30
2 3	-11	17	-14	4	10	-1	-1	-15	23
2 4	16	6	6	1	-5	0	-4	-10	25
2 5	3	3	2	13	15	-11	-5	-6	16
2 6	0	-11	4	-6	7	-6	2	-7	41
2 7	-25	-29	19	-36	0	-34	-28	39	55
2 8	-4	1	-2	8	0	8	-12	2	0
3 1	-7	-2	-6	-4	-7	5	1	-8	26
3 2	67	-72	68	-63	60	-67	55	-69	90
3 3	1	-6	-6	-4	-9	0	-6	-12	19
3 4	-3	9	17	0	7	0	0	-10	36
3 5	-24	-32	-32	-28	-31	-35	-33	-25	37
3 6	-5	4	-4	6	-6	7	-7	-2	23
3 7	-29	30	-31	29	34	8	22	-38	41
3 8	-11	8	-4	-4	8	5	5	13	19
4 0	54	64	58	50	-56	-45	-49	-53	62
4 1	7	10	10	-5	0	4	-3	4	23
4 2	33	-27	-20	33	34	-41	-37	45	53
4 3	-36	-28	-8	33	24	-22	15	-29	49
4 4	7	4	-1	4	-7	-3	-8	-8	28
4 5	-2	9	2	14	4	21	-9	6	32
4 6	-30	-24	30	19	-14	-33	6	27	31
4 7	11	2	-9	-3	-2	-3	4	10	4
5 1	43	36	39	39	40	31	33	-39	56
5 2	6	4	2	10	-2	9	-2	2	30
5 3	36	30	41	33	-20	-35	-46	-35	48
5 4	-13	8	11	1	-1	1	-19	2	11
5 5	35	48	-35	28	29	-34	-26	40	41
5 6	13	-1	4	-3	0	10	-8	5	5
6 0	-4	-13	-5	-8	-2	-4	-11	-6	4
6 1	12	-16	11	-18	13	-14	15	-9	32
6 2	-11	0	-7	-15	-9	-13	-17	-14	32
6 3	-8	-4	-6	-4	-4	4	5	1	23
Z	0.479	0.476	0.511	0.515	0.525	0.493	0.573	0.446	

Table 2

h	k	$ U $	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
0	4	0.32	+	+	-	-	+	+	-	-	+	+	-	-	+	+	-	-
0	8	0.22	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1	2	0.27	+	+	-	-	+	+	-	-	+	+	-	-	+	+	-	-
1	12	0.22	-	+	+	-	?	+	+	-	-	?	+	-	-	+	+	-
1	13	0.28	-	?	+	?	-	?	-	?	?	?	?	-	?	?	?	-
2	2	0.24	+	+	+	+	-	-	-	-	+	+	+	+	-	-	-	-
2	4	0.33	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-
2	5	0.25	-	-	+	?	-	+	+	+	+	-	-	-	-	-	?	-
2	6	0.32	+	+	-	-	-	-	+	+	+	+	-	-	-	-	+	+
2	11	0.25	+	+	+	+	+	+	-	+	+	?	+	-	+	+	+	-
2	15	0.26	-	+	-	+	+	+	+	+	+	+	+	+	+	-	+	+
3	3	0.24	?	-	+	+	+	-	+	+	?	-	-	-	+	+	+	?
3	4	0.20	-	-	-	-	+	+	+	+	-	-	-	-	+	+	+	+
3	10	0.25	-	-	+	+	?	-	+	+	-	-	+	+	-	-	+	+
3	13	0.30	-	+	-	-	+	?	+	-	?	-	?	-	+	+	-	-
3	15	0.22	-	-	-	?	?	+	?	+	-	-	-	+	+	+	?	+
4	0	0.26	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	1	0.40	+	+	+	?	-	-	?	+	+	+	+	-	-	-	?	+
4	5	0.27	+	+	-	?	-	-	?	+	+	+	?	?	-	-	?	-
4	9	0.20	+	+	+	-	-	-	+	+	+	+	-	-	-	-	+	+
4	11	0.20	+	-	-	+	+	-	+	+	+	?	-	-	+	-	-	-
4	12	0.24	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	15	0.26	-	-	+	+	+	-	-	+	+	-	-	+	+	+	-	+
6	0	0.24	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-
6	6	0.23	-	-	+	+	+	+	-	-	-	-	+	+	+	+	-	-
6	7	0.44	+	+	-	+	+	+	+	+	+	+	+	+	+	+	+	+
7	5	0.32	-	-	-	?	?	-	+	-	+	-	-	-	-	+	?	+
7	6	0.26	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
7	11	0.29	-	-	+	+	?	+	+	-	-	-	?	+	+	+	+	+
8	0	0.22	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8	4	0.26	-	-	+	+	-	-	+	+	-	-	+	+	-	-	+	+
8	5	0.20	?	-	+	-	?	+	+	+	-	?	-	-	+	+	+	+
9	2	0.24	+	-	+	?	+	-	+	?	+	-	+	-	+	-	+	?
9	8	0.32	+	+	+	+	-	-	-	-	+	+	+	-	-	-	-	-
9	10	0.34	+	-	+	-	?	-	+	-	+	?	+	-	+	-	+	-
10	2	0.27	-	-	-	-	+	+	+	+	-	-	-	-	+	+	+	+
11	5	0.27	?	-	-	+	?	+	-	-	-	-	+	+	+	+	-	-
11	6	0.22	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

The summations involved in Z may be carried out over any convenient range of \mathbf{h} ; since ρ_r' shows atoms with limited positional accuracy it has been found convenient to restrict the range of \mathbf{h} to those values for which $\sin \theta$ is less than about 0.5.

The efficacy of the Z -test has been tried on the c -axis projection of the known structure of α -glucose (McDonald & Beevers, 1952). The systematic application of sign relationships (Woolfson, 1957) indicated that there were 8 possible sets of signs for 60 of the strongest U 's. The values of $|F_{\mathbf{h}}|$ and $A_s G_{\mathbf{h}}' + B_s H_{\mathbf{h}}'$ for reflexions within the range $0 \leq \sin \theta \leq 0.5$ for Cu $K\alpha$ radiation are given for each set of signs in Table 1. The values of Z , given at the foot of each column, favour set 8, which is in fact the correct set of signs. In assessing the values of Z due allowance has been made for the multiplicity of the various types of reflexion.

3. The solution of a projection of D-xylose

D-Xylose, $C_5H_{10}O_5$, crystallises in the orthorhombic space group $P2_12_12_1$ with $a = 9.1$, $b = 12.1$, $c = 5.6$ Å, the unit cell containing four molecules of the sugar. The c -axis projection would be expected to show

approximately equal atoms with any amount of overlap up to the complete overlap of a pair of atoms, a situation for which equation (5) can be made to hold fairly well. The systematic application of sign relationships gave the 16 possible sets of signs listed in Table 2. The values of Z are compared in Table 3

Table 3

Set no.	Z	T'	Set no.	Z	T'
1	0.536	0.611	9	0.581	0.586
2	0.545	0.617	10	0.564	0.627
3	0.493	0.458	11	0.626	0.651
4	0.634	0.734	12	0.605	0.674
5	0.548	0.559	13	0.543	0.545
6	0.433	0.522	14	0.535	0.588
7	0.561	0.588	15	0.591	0.696
8	0.656	0.700	16	0.520	0.571

for each of these, and indicate Set 6 as most probably correct. Fig. 1 shows the Fourier synthesis corresponding to Set 6 and it was easily interpreted in terms of the D-xylose molecule. One stage of refinement gave the Fourier synthesis shown in Fig. 2, and structure factors calculated at this stage gave a reliability index of 0.22.

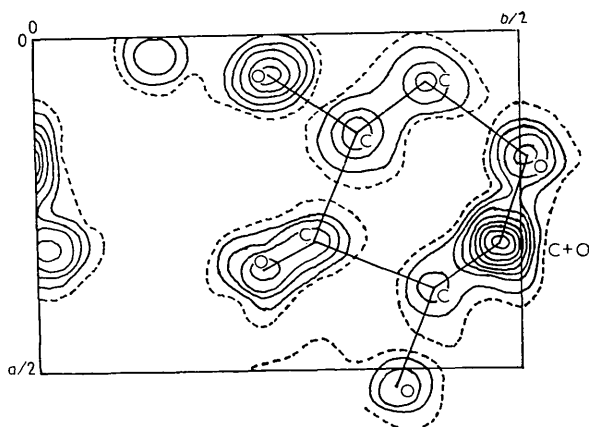


Fig. 1. ρ_r' for D-xylose with the signs indicated by the Z test. The dotted contour is at $3 \text{ e.}\text{\AA}^{-2}$ and the others at intervals of $2 \text{ e.}\text{\AA}^{-2}$.

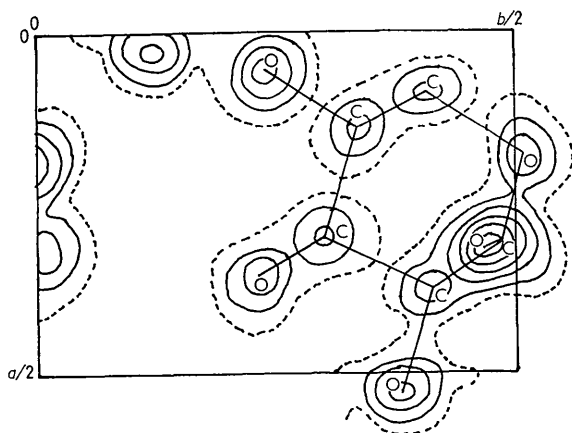


Fig. 2. The electron-density map for D-xylose after one stage of refinement. The dotted contour is at $3 \text{ e.}\text{\AA}^{-2}$ and the others at intervals of $2 \text{ e.}\text{\AA}^{-2}$.

Further work is being done on this structure and will be reported in due course.

4. Sayre's equation applied to D-xylose

The solution of the c -axis projection of L-glutamine involved the use of a test function which assumed the applicability of Sayre's equation. Since there is as much, if not more, overlap in this case as in the previously considered projection of D-xylose it is interesting to see how well a test function related to Sayre's equation can be made to work for D-xylose.

We therefore consider the statistical equation

$$F_{\mathbf{h}} = A_s' G_{\mathbf{h}}', \quad (7)$$

which is analogous to one described in § 3 of the first part of this paper and evolve the test function

$$T' = \frac{\sum_{\mathbf{h}} (|F_{\mathbf{h}}| - |A_s' G_{\mathbf{h}}'|)}{\sum_{\mathbf{h}} |F_{\mathbf{h}}|}. \quad (8)$$

Values of T' are compared in Table 3 for each of the

16 possible sets of signs and it can be seen from these values that Set 6 now appears as a rather poor second best to Set 3.

There can be no doubt of the superiority of Z over T' as a test function. The Z -test applied to a very large number of sets of signs may not favour the correct set of signs above all others; the Cochran-Douglas zero-check often works better for a few incorrect sets of signs than for the correct set. In such a case the additional inefficiency of T' could altogether prevent the correct set of signs from being found.

5. Some computing details

The calculations necessary for the previous sections were carried out on the Manchester University Ferranti Mark I computer. The methods of computing were conditioned by two factors, first the experimental nature of the work and secondly the limited life-expectancy of the machine, which is about to be replaced by the Ferranti Mercury computer. Consequently no attempt was made to design a complicated permanent programme; the work was broken up into a series of simple stages which were easy to programme and which enabled a close check to be kept on the progress of the calculations. The stages for D-xylose were:

- (i) The 16 Fourier syntheses were computed, the values of ρ_r' calculated at intervals of $1/30$ th of a cell edge being output on tape. This made use of an existing programme and took only 20 min.
- (ii) Values of $G_{\mathbf{h}}'$ and $H_{\mathbf{h}}'$ were computed by simple programmes which used the ρ_r' tape as data. The values of $G_{\mathbf{h}}'$ and $H_{\mathbf{h}}'$ were found by a sampling method similar to that described by Sayre (1951). Thus $G_{\mathbf{h}}$ was computed as

$$G_{\mathbf{h}}' = K \sum (\rho_r')^2 \cos 2\pi \mathbf{h} \cdot \mathbf{r}, \quad (9)$$

where the summation was taken over all the points for which ρ_r' was computed, and K is an easily determined numerical constant.

- (iii) Simple programmes using the $G_{\mathbf{h}}'$ and $H_{\mathbf{h}}'$ output tapes computed $A_s G_{\mathbf{h}}' + B_s H_{\mathbf{h}}'$ and $A_s' G_{\mathbf{h}}'$.

The whole process of computation probably took longer than a straightforward examination of the 16 original Fourier syntheses, but the values of Z did provide an objective test of the sets of signs which could certainly be carried out very quickly indeed by a more elegant programme.

6. Future proposals

A combination of the systematic method of obtaining plausible sets of signs backed up by the Z test does seem to provide a promising objective procedure for tackling centrosymmetrical structures of moderate

complexity. The availability of the Ferranti Mercury computer with its large storage facilities and high operational speed suggests the design of a programme for carrying out this procedure in which as much work as possible is done inside the machine and machine output is reduced to a minimum.

Work has begun on the design of a programme which will do the following:

- (i) Read in the following data: (a) unit-cell dimensions, (b) the number and relative weights of atoms in the unit cell, (c) all intensities, (d) the symmetry of the unit cell.
- (ii) Calculate the U 's and find all the sign and inequality relationships which inter-relate the largest of them. If the number of relationships is too small compared with the number of U 's then more U 's will be taken until there are about twice as many relationships as unknown signs.

At this stage the fraction of sign relationships expected to hold will be calculated (Cochran & Woolfson, 1955). This should be at least 85% if the method is to be successful.

- (iii) Find all plausible sets of signs for the largest U 's and then derive a number of additional signs for U 's of moderate magnitude by using the relationship

$$s(\mathbf{h}) = s\left(\sum_{\mathbf{h}'} U_{\mathbf{h}'} U_{\mathbf{h}+\mathbf{h}'}\right)$$

(§ 4.4, Cochran & Woolfson, 1955).

- (iv) Apply the Z test to each set of signs and output the best few sets in the form of Fourier syntheses.

Initially a pilot programme will be designed for two-dimensional work only. When this is working satisfactorily, and if the results seem to justify the step, a more ambitious programme to tackle three-dimensional problems will be developed.

The author is indebted to Prof. F. C. Williams, of the Manchester University Computing Machine Laboratory, for the computing facilities which made possible the work described in this paper.

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Surface Melt Patterns on Silicon

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(Received 8 October 1957 and in revised form 10 December 1957)

Surface melt patterns have been formed on silicon by heating to within a few degrees of the melting point (1412° C.), followed by a rapid quench. Localized melting occurs where specks of impurities reside on the surface. Straight-sided geometrical patterns several microns in extent are thus formed, and their shapes are uniquely determined by the surface crystal plane. Conclusive proof that these melt patterns are defined by {111} planes rather than any other system has been obtained through a study of their shapes on rational crystal surfaces presented by multi-twinned crystals. We have formed similar patterns on germanium, indium antimonide, gallium antimonide, and gallium arsenide crystals with this technique.

Introduction

Although thorough studies have been made on the detailed mechanisms of crystal growth, very little has been reported on the converse mechanisms involved in crystal melting. The present paper describes certain geometric patterns formed on the surfaces of silicon

single crystals following the initiation of melting. The shapes of these melt patterns are uniquely determined by the lattice orientation of the face on which they are formed, the contours being the intersections of the close-packed {111} planes with the surface. Nucleation of melting is effected by minute impurities residing on the surface which lower the melting point in their