THE CRYSTAL STRUCTURES OF SALT HYDRATES: A DETERMINATION OF THE STRUCTURE OF SODIUM THIOSULPHATE PENTAHYDRATE BY X-RAY DIFFRACTION.

Thesis for the degree of Ph.D.
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August 1951.

Contents.

Chapter 1.

Introduction

(1) General.

The determination of the structure of sodium thiosulphate pentahydrate is a problem possessing three principal points of interest.

No structure determination of a compound containing the S_2O_3'' group has yet been reported. Its shape, however, has been predicted, and confirmation would complete our knowledge of the structures of all the sulphur-oxygen groups by X-ray diffraction.

It will, in addition to this, provide a further example of the way in which water of crystallisation is utilised in crystal structures.

Thirdly, the problem will be of interest purely in relation to the technique of structure-determination. The relative positions of the atoms in such a compound cannot be predicted, with the exception of the thiosulphate group. In other words, no chemical knowledge of the shape of the molecule is available to assist the crystallographer, apart from interatomic distances found in other structures.

It was decided at the commencement of this work that a solution by purely crystallographic means would be attempted. X-ray analysis is obviously a more powerful tool in the elucidation of the structure of matter if it can succeed without the assistance of other evidence.

This thesis provides some evidence of the possibility of such work.

(2) Sulphur-oxygen Groups.

In 1927, when Sidgwick's "Electronic Theory of Valency" was published, structure determination by X-ray diffraction was in its infancy. The comprehensive picture given by Sidgwick of chemical bonding in all types of compounds is based on the theory of the simple Bohr atom, with resulting conceptions of ionic, normal-covalent and dative-covalent bonds. The nature of these conceptions is well known. It will be remembered that the structure of the sulphate group was represented by Sidgwick in these terms as consisting of the central sulphur atom bonded to two oxygen atoms by single normal-covalent bonds, and to the remaining two by dative-covalent bonds--- i.e. $(S^{+4}\ 2O^{-2}\ 2O^{-1})^{-2}$.

This complies with the "octet" rule limiting the number of electrons round sulphur to eight. The earlier double-bonded structure of Lewis was thus discarded.

The theory of resonance arose shortly after this as a result of the necessity of reconciling the Bohr atom with the findings of structural chemistry, primarily in the case of carbon. The simple Bohr theory pictured one of the four valence electrons of the carbon atom as having spatial properties differing from those of the other three. But it has always been obvious that chemically the four bonds were equivalent, and the famous stereochemical theory of Kekule had shown that they are arranged tetrahedrally. So arose the "hybridisation" theories of the wave mechanical treatment of Schrodinger, Heitler, London and others. The one 2s and the three 2p unpaired electron orbits, are hybridised to give four equivalent tetrahedrally arranged σ orbitals.

Stereochemical work of the same nature as that for carbon had shown that the valencies of sulphur were arranged tetrahedrally.

Compounds of the type $R_1R_2R_3SX$ were shown to have a similar tetrahedral distribution, where X is the anion of a strong acid, optical isomerism existing in ionised solution. In addition to this $R_1R_2S = O$ was discovered to be optically active. Thus the sulphur's four bonds have a tetrahedral distribution even if one is unoccupied.

L. Pauling in 1931 (1) gave a summary of the extension of the hybridisation theories over a wider field. W. H. Zachariasen (6) later put forward an electronic structure for SO_4'' and the related ions on the lines laid down by Pauling. Two electrons are gained ionically from the metallic ion or ions; the group is then represented as $(S^{+2}O_4^{-1})^{-2}$. The sulphur's four remaining electrons are supposed one 3s and three 3p; these hybridise tetrahedrally.

This implies that the bonds are single and not dative.

The results of X-ray analysis began shortly afterwards to contribute to molecular theories.

Salts containing the sulphate ion became early the subject of many investigations. James & Wood gave an analysis of $BaSO_4$ & $CaSO_4$ in 1925 but they assume rather than confirm the tetrahedral nature of the SO_4'' group. An analysis of Na_2SO_4 by Gossner & Mussgnug in 1929 was even less convincing. However, in 1930 a series of investigations was commenced by W.H. Zachariasen which established the structure of nearly all the sulphur-oxygen groups.

In chronological order these are:-

	reference no.
Na_2SO_3	(2)
Na_2SO_4	(3)
$K_2S_2O_6$ (by Helwig)	(4)
$K_2S_2O_5$	(5)
$Cs_2S_2O_8$ & $(NH_4)_2S_2O_8$	(6)
$K_2S_3O_6$	(7)

From the crystallographic point of view these investigations show the early developments of the

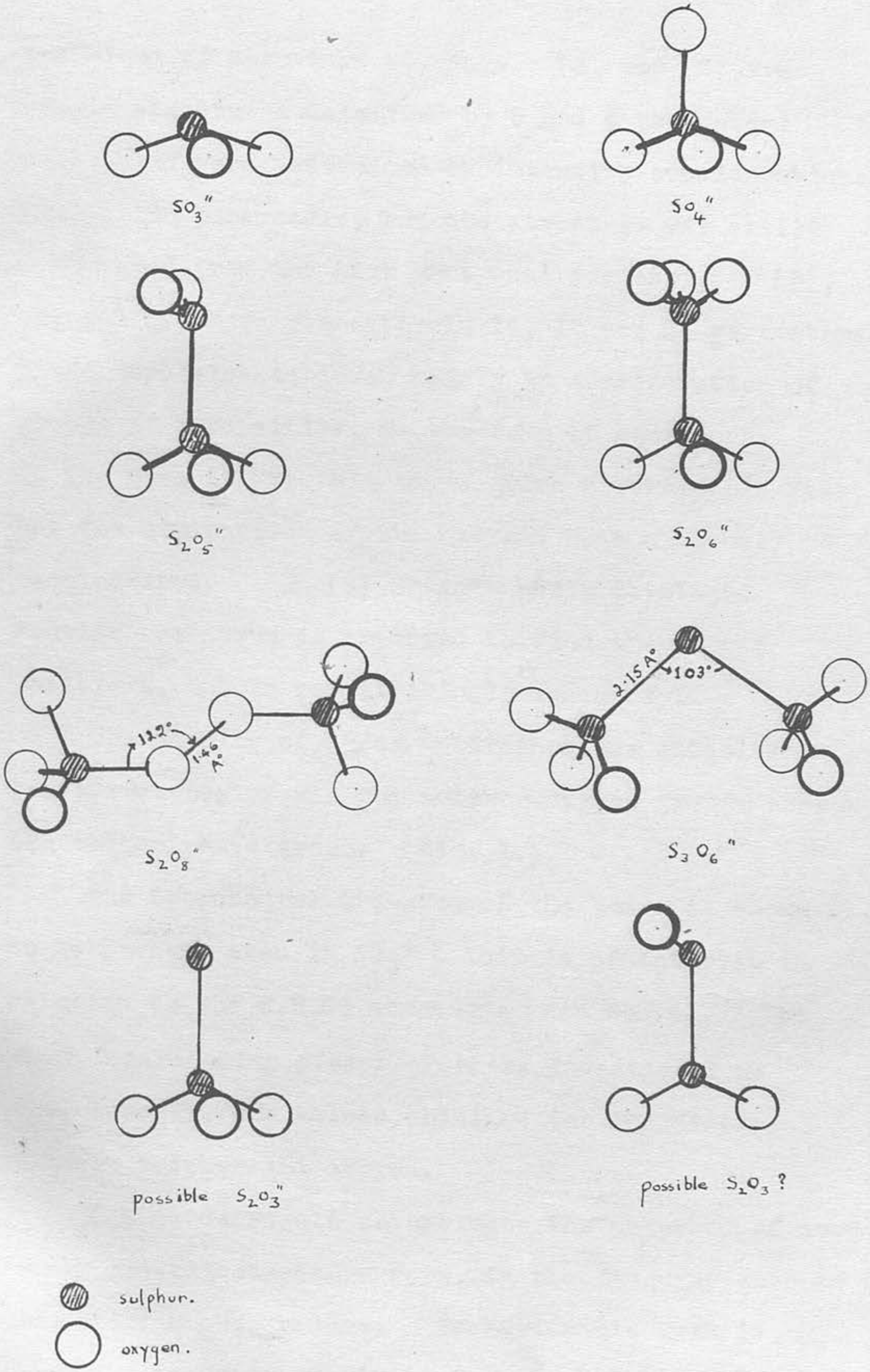

Fig. 1. Sulphur-Oxygen anion structures.

technique of structure solving. (2) and (3) are simple structures described by 5 and 4 parameters only; they were determined by intensity considerations. (4) has 20 parameters, but the structure was easily postulated from the high trigonal symmetry. (5), (6) and (7) have respectively 16, 18 and 20 parameters; these were also achieved mainly by consideration of groups of intensities, in the form of equations. In the case of (7) this seems quite a remarkable feat; but the limitations of the methods have obviously been reached. In (6) Bragg's newly developed Fourier technique is employed to find the oxygen positions, but is not strikingly successful.

The results of these determinations established the structures of all the sulphur-oxygen groups except the thiosulphate group. (Fig. 1.)

The tetrahedral grouping of the bonds is shown to be present even in SO_3'' - this is of interest in relation to the R_1R_2SO compounds (see above). The most far-reaching effect of these investigations was, however, the values obtained for the distances between sulphur and oxygen.

(It is difficult to estimate the accuracy of such early crystal-structure work, in the frequent absence of numerical F obs. values. Zachariasen's work is probably accurate to within 0.1 A^{o}, but the $K_2S_2O_6$ oxygen parameters must be considered (see over) still in doubt.)

Table 1.

Compound	S-O distance (A°)	S-S distance (A°)
Na_2SO_3	1.39	-
Na_2SO_4	1.49	-
$K_2S_2O_5$	1.47	2.18
$(NH_4)_2S_2O_8$	1.50	-
$K_2S_2O_6$	1.81* 1.39†	2.04
$K_2S_3O_6$	1.50	2.15
FeS_2	-	2.14

(*from the parameters given by Helwig. The oxygen parameter is possibly inaccurate.)

The S-O angles of the tetrahedral groups are in all cases approximately 109°. Other special distances and angles are shown in Fig 1.

It will be remembered that the S-O bonds were considered to be single dative-covalent, in accordance with the octet theory. Pauling summarised the bond length data of a large number of compounds whose bond nature is considered definite, in order to establish values for the single, double and triple bond radii of the commoner elements (8). These quantities he discovered to be additive in general.

(see over)

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† From Huggin's parameters of a similar structure.

Table 2.

(A°)	Sulphur	Oxygen
single-bond radius	1.04	0.66
double-bond radius	0.94	0.55
triple-bond radius	0.87	0.50

A comparison with table 1 shows immediately that the S-O bond in the sulphate group does not correspond to the single bond length. In the case of SO_3'' it is in fact shorter even than the double-bond value.

Thus the SO_4'' ion is now described as a resonance hybrid of partial double-bond character. Pauling suggests that the d-orbitals of the sulphur are involved.

The position is summed up by Phillips, Hunter and Sutton (9), 1945 who combine the X-ray evidence with their dipole moment observations and heats of formation values. They support the view that the S-O bond is double. Pauling attributes shortening of the bond length from his double-bond value to the fact that structures containing one or more co-ordinate S- O links contribute to the resonance picture; the resulting "formal charge" on sulphur reduces the length. The latter authors disagree, saying that bond lengths should be interpreted less rigidly.

It will be observed (tables 1 & 2) that the S-S in the complex ions appear by contrast to be single, by the length criteria. In S_3O_6'' and S_2O_6'' they are presumably covalent but not dative; but in S_2O_3'', supposing it to have the left-hand structure of figure 1, the bond may be dative to the exterior sulphur. Some evidence of molar refraction has been said to indicate no double negative charge on this atom (10).

The electron density picture which the crystal analysis will achieve, in addition to the values obtained for bond-lengths, should help to elucidate these matters. Previous authors have not in general made reference to the apparent height of sulphur in S-O compounds though some record that an f-curve for neutral S gives better agreement than S^{+6} in sulphates.

(3) Salt Hydrate Structures.

The composition of hydrates was the object of much speculation before X-ray analysis could reveal any actual crystal structures. Werner attempted to reconcile them with his general theories of coordination complexes and ~~co~~valency maxima.

He had established the following values for the latter quantity, from a consideration of all types of compounds:-

Hydrogen : 2 (i.e. 4 shared electrons)
1st short period : 4
2nd " " : 6
1st long period : 6
subsequent elements : 8, possibly 10 after 2nd long period.

Many hydrated salts obviously contain a number of water molecules which represent this covalency maximum for their metallic ion component. But many also have either a greater or a lesser number. An example of this is the existence of both $NiSO_4 6H_2O$ and $NiSO_4 7H_2O$. Werner had no satisfactory theory for explaining these anomalies.

Subsequent writers pointed out that other influences must be taken into account. N. V. Sidgwick in "The Electronic Theory of Valency" points out that some water molecules may be attached to the anion; in this case a hydrogen atom sets as an electron acceptor, whereas in cation hydration the oxygen will act as a donor. The latter tendency is, however, stronger, and consequently cation hydration is more notable. Sidgwick accordingly concludes that the number of water molecules round a paticular ion is in fact limited by the ion's covalency maximum; but he does not give a satisfactory explanation of the situation when the number of water molecules is less than this quantity. He points out however, that there is a general agreement with Fajan's theory, which stated that tendency to form maximum covalency groups increased in accordance with the following rules:-

(1) when the ionic charge is large

(2) when small, if a cation

(3) when large, if an anion.

The advent of X-ray crystallography clarified the position immensely. Some notable structure determinations of hydrates are the following:-

reference no.

(1) $CaSO_4 2H_2O$. Wooster, 1929. (10)

(2) $NiSO_4 6H_2O$. Beevers & Lipson, 1932. (11)

(3) $BeSO_4 4H_2O$. " " " " (12)

(4) $CuSO_4 5H_2O$. Beevers & Lipson, 1934. (13)

(5) $NiSO_4 7H_2O$. Beevers & Schwartz, 1935. (14)

(6) the alums. Beevers & Lipson, 1935. (15)

(7) $Nd(BrO_3)_3 9H_2O$. Helmholtz, 1939. (16)

(8) $NaK(COOH)_2 4H_2O$ (Rochelle Salt) Beevers & Hughes, 1941. (17) $(C_4H_4O_6)$

To summarise this work crystallographically, it might be said to show how structure-solving was now making full use of the methods beginning to be employed at the time of Zachariasen. Isomorphous replacement methods were also used here, in (4).

Structure (5), $NiSO_4 7H_2O$ contained 39 parameters. This is obviously a problem of a much more advanced nature. Indeed it marks one of the first occasions when the Patterson synthesis (18) was used in structure determination. This, as in Zachariasen's first Fourier work, was used with hesitation, and isomorphous replacement methods were used to check the results for the Ni parameters. It did, however, prove of service in locating the sulphur positions. Fourier work then revealed the remaining atomic locations. In structure (8) the Patterson method was again employed.

The effect on chemical theory of this information must now be discussed. It becomes immediately obvious that the coordination group of the metallic ion is always complete even although the number of water molecules is less than the number required; atoms belonging to the anion in such cases complete the group. A comparison with the structures solved by Zachariasen shows that in the case of these non-hydrates the coordination group is in fact the same in number, though formed now by oxygen atoms of sulphate and related groups, entirely. The tendency for the metallic ion to use water of crystallisation to complete its group may still be said to conform generally to Fajan's rules; no hard and fast predictions can be made in such a complicated problem of molecular packing.

It is also found that some water molecules do not take part in the coordination group.

The nature of the water molecule itself was a topic also under discussion at this time. Pauling in his 1931 paper (1) mentions that the structure of the water molecule is obviously not collinear, from the large electric moment. He suggests that in the water molecule the angle formed between the three atoms is little more than 90°, the oxygen atom's two unpaired p electrons forming bonds with the hydrogen atoms at this angle.

Bernal and Fowler in 1933 (19) proposed a quartz-like four-coordinated structure for water at ordinary temperatures after a consideration of all the existing physical-chemical evidence. They express this as follows:- "The net electronic density distribution will resemble a tetrahedron, with two corners of positive and two of negative charge". The negative areas are the "lone pairs" and the positive areas are bonded to the hydrogens, which can "receive" by contrast to the "donation" powers of the pairs.

One should consequently expect to find that water molecules in crystal structures make four tetrahedrally arranged contacts. It is found that this is not always so; some have this disposition but some form three planar contacts roughly at 120° to each other. Coordination group water molecules may have either disposition; but "odd" waters, bonded only to other waters and oxygen, appear to be always tetrahedral.

Beevers and Lipson (15) pointed out the connection this must have with the central coordinating ion. In the structure of the alums the Al^{+++} ion holds six tri-bonded waters. K^+ in the same structure holds six tetra-bonded waters. Ni^{++} in $NiSO_4 6$(or 7)H_2O has a composite group of two tetra-bonded and four tri-bonded waters. They interpret this as meaning that Al^{+++} is able to hold 12 negative bonds, Ni^{++} 10 and K^+ only 6. The two "negative areas" of the water have coalesced, by these assumptions, into a donation group of four electrons, or two coordinate links.

The nature of the bonds of non-water oxygens must be contrasted with this. In the case of the sulphate ions, these can only be single, since the S-O bond is already double and at least one other contact is always made. Thus sulphate oxygens will only contribute a single bond to the coordination group. This will be the case for most oxy-acid groups.

A survey of negative-bond or electron-pair content of coordination groups, with their distances, compiled on those assumptions, might be of interest;

but the true picture is probably much less definite.

Table 3.

ion	compound	distance (A^o)	coord. No.	electron pair content.
Ca^{++}	in $CaSO_4 2H_2O$	2.4 - 2.6	8	10
Ni^{++}	in $NiSO_4 6H_2O$ & $7H_2O$	2.0	6	10
Be^{++}	in $BeSO_4 4H_2O$	1.65	4	8
Cu^{++}	in $CuSO_4 5H_2O$	2.4 - 2.8	6	6
Al^{+++}	in the alums	2.0	6	12
K^{+}	" " "	2.9	6	6
Na^{+}	in Rochelle salt	2.4	6	7
K^{+}	" " "	2.8	4 or 8	4 or 8
Li^{+}	in $LiClO_3 3H_2O$	3.1	6	6
Zn^{++}	in $Zn(BrO_3)_2 6H_2O$	2.1	6	12
Na^{+}	in $Na_2CO_3H_2O$	2.3 - 2.6	6	7

It can be seen that the assumed "coordination maxima" break down frequently. But Fajan's rules have obviously a good deal of application. Not enough evidence exists to compare the behaviour of any one ion in different compounds, though the behaviour of Na^{+} above remains the same in two examples. It will be of interest to compare the coordination group of Na^{+} in the structure under consideration.

Chapter 2.

Determination of Unit Cell Dimensions and Space-Group.

Preparation of specimens.

Sodium thiosulphate pentahydrate is described by Groth (20) as monoclinic prismatic, with a : b : c = 0.3508 : 1 : 0.2745, and $\beta = 103^\circ\ 58'$. The crystals are prismatic about the c axis and tabular on the 010 face, grown from aqueous or alcoholic solution. The following faces are listed:- 010, 110, 120, 001, 011, $11\bar{1}$, $13\bar{1}$,

Crystals were grown for the present work by slow evaporation of saturated aqueous solution at 18°C, and were found to correspond to the above description. From specimens of a few millimetres in dimensions it was found possible to identify all three principal axes without accurate optical goniometry, due to the characteristic features described above.

Photography.

A standard Metropolitan-Vickers crystallographic X-ray unit provided the copper K -α radiation used for this work, the K -β being removed by the use of nickel windows. Ilford double-coated X-ray film was employed throughout, with the manufacturers recommended developing and fixing procedure. The camera was a normal-beam vertical-travel Weissenberg, of crystal-to-film radius 5 cm., the travel rate being 0.74 mm./degree.

Trial photographs were first taken using cylindrical crystals of various diameters. The compound has a high absorption, and it was found that a specimen of no more than 0.2 mm. diameter was required before the spots near the meridian of the film were free from absorption "gaps" in their centres. This condition was considered desirable for the eventual measurement of intensity at all angles of reflection by comparison with a single multipully exposed reflection. Consequently specimens of such dimensions were prepared parallel to each principal axis and rendered as uniformly cylindrical as possible. Exposures of 30-50 hours were required for intense Weissenberg photographs.

These were taken of the three zero layer lines about the principal axes, together with an exposure of about one eighth the time in each case. Oscillation photographs of an arbitrary range and time were taken for each axis to show the layer line spacing. A Weissenberg of the first upper layer line was also taken to show general intensities for space-group considerations.

The later systematic recording of the general intensities will also be described here.

The oscillation photographs about the two short axes (a & c) show three and two recordable layer lines above the zero line. These were recorded by Weissenberg photographs. As the cell is monoclinic, both hkl and $hk\bar{l}$ spots must be included as these are not equivalent; they will record on a single Weissenberg if the crystal is oriented so that a 200° oscillation includes the necessary reflections.

About the b axis 12 recordable layer lines occur. Weissenberg photography would take a great deal of time in such circumstances, so five oscillation photographs, of equal range, covering 200° were taken.

All photographs recording general intensities were taken once only for considerations of time. It was felt that great accuracy in intensity measurement was more necessary for the zero layer line Weissenbergs already described, since these would provide the most convenient data for the refinement of the structure, though the general intensities might be necessary for its first rough derivation.

This procedure does not record every intensity in the limiting sphere. This will be discussed later.

Indexing of Photographs.

All Weissenberg photographs were indexed by inspection; on transparencies are drawn lines of reflections of constant h, k or l indices. Bernal charts are of assistance.

Oscillation photographs require a knowledge of the unit cell dimensions to be indexed. This was accordingly done after the latter had been determined from the earlier photographs (see later).

Methods employing the reciprocal lattice are most convenient. A diagram of the latter for h0l reflections was constructed, a suitable scale being 1 reciprocal lattice unit = 10 cm.

$$a^* = \frac{\lambda}{a \sin\beta}$$

$$c^* = \frac{\lambda}{c \sin\beta}$$

$$\beta^* = 180 - \beta.$$

Indexing may now be carried out by measuring the value of ξ for every spot, that is the horizontal component of the distance in the reciprocal lattice of the plane in question to the origin. A Bernal chart (21) will now give the variation of this quantity for a normal beam, 5 cm. radius film. In correlating film spots with their reciprocal lattice analogues unambiguously, the following procedure is most convenient.

When the axis of oscillation is perpendical to the zero layer of the reciprocal lattice (which is fortunately the case here for the b axis) the oscillation of the crystal may be represented for every layer line at once on the stationary h0l lattice diagram, as the pairs of lunes resulting from the oscillation of the corresponding level of the reflecting sphere. These levels are defined by a knowledge of the reciprocal lattice translation in the vertical direction, here $\frac{\lambda}{b}$; the circles representing them are concentric but diminish in size with each higher layer line. The reflecting sphere oscillates about an axis perpendicular to its equatorial level passing through the lattice origin. The diagram of lunes is thus pivoted about the latter, and the correct position with respect to the photographs found by inspection. The various lunes are marked in different colours and it is found convenient to construct tables showing the prescence or absence of any reflection on each photograph in a systematic way. Subsequent intensity measurements may then be recorded on the tables by direct inspection of the photographs.

Space Group Determination.

On examination of the three zero layer Weissenbergs, that given by Groth as b is found perpendicular to the other two, which are inclined; this is in accordance with convention.

Using Groth's nomenclature further, 0k0 reflections are present with only k = 2n and h0l's with only h = 2n. hkl's are present in all orders.

This shows that the axes given by Groth as a & c must be interchanged, in accordance with the nomenclature in Internationale Tabellen. We then have h0l's present with only k = 2n, and the space-group is $P2_1/c$, or $C2h^5$.

Unit Cell Dimensions.

These were obtained first for previous work from the layer line spacings about the three principal axes by the relation:-

$$a^* = \frac{\lambda}{a \sin \beta} = \frac{\sin \tan^{-1} \frac{y_n}{r}}{n \sin \beta} \qquad (1)$$

where y_n is the height of the nth layer line above the equatorial line. β was measured from the separation of the 001 and h00 lines of reflections on the h0l Weissenberg. These methods are, however, limited in accuracy by the nature of the measurements to about 1%. The values obtained were:-

$$a^* = 0.268$$
$$b^* = 0.0713$$
$$c^* = 0.212$$
$$\beta = 103^\circ\ 55'.$$

Farquhar & Lipson (22) have suggested a method wherebye greater accuracy can be obtained.

If ξ (= 2 sin θ) is obtained, then for zero layer line reflections,

$$\xi^2 = h^2a^{*2} + K^2b^{*2} \quad \text{(for hk0's)} \quad (2)$$
$$\xi^2 = K^2b^{*2} + l^2c^{*2} \quad \text{(for 0kl's)} \quad (3)$$
$$\xi^2 = h^2a^{*2} - 2hla^*c^* + l^2c^{*2} \quad \text{(for h0l's)} \quad (4)$$

If x is the horizontal film coordinate of any spot, the rate of change of sinθ with x is greatest as $\theta \longrightarrow 90^\circ$, that is amongst the reflections nearest the limit of recording. Farquhar & Lipson suggest recording the K - α doublets of such spots near the centre of the film by reversing it so that the beam passes through it, and adjusting the crystal so that each spot is recorded on both sides.

Then $90^\circ - \theta = \frac{S.\ 180^\circ}{4R.\ \pi}$ where S is the distance between the α doublets, and R the camera radius.

This procedure is carried out for all reflections showing K - α doublets, and error due to film shrinkage eliminated by extrapolating the results obtained to a value at $\sin^2\theta = 1$, solution being commenced from a rough value of one cell edge, followed by successive approximation.

An adaption of the method was used here. The collimator support acts as a "knife-edge" and throws a shadow on the film at the recordable limit, near $\sin\theta = 90^{\circ}$. If x, the horizontal distance of a spot from this is measured, (preferably on both sides of the film) and if ϕ, the angle subtended by this edge at the film's centre with the beam direction, be found by measurement then

$$90^{\circ} - \theta - \phi = \frac{x.\ 18^{0}}{R.\ \pi}$$

Using the rough values of a^* and c^* already obtained, equations (2) and (3) were solved using the above data obtained from hk0 and 0kl reflections having k high but h & l low. The resulting extrapolated value for b^{*2} at $\sin^2\theta = 1$ was then used to give new accurate values of a^{*2} and c^{*2} from the same equations, but using now reflections having h & l high with respect to k. Recalculation of b^{*2} with these new values gave a smoother plot but the same value. (see fig. 2)

The h0l reflections with $K\alpha$ doublets were then used in the same way to calculate $\cos\beta$ from equation (4). This zone contains much fewer spots than the other two, so the plot is less satisfactory; and limits of error greater.

The resulting values are, with limits of error judged from the graphs (fig. 2):-

$$a^{*2} = 0.07097 \pm 0.00003 \quad \therefore \quad a = 5.944 \text{ A}^{\circ} \pm 0.03\%$$

$$b^{*2} = 0.00578 \pm 0.00003 \quad \therefore \quad b = 21.57 \text{ A}^{\circ} \pm 0.2\%$$

$$c^{*2} = 0.04435 \pm 0.00003 \quad \therefore \quad c = 7.525 \text{ A}^{\circ} \pm 0.04\%$$

$$\cos\beta = 0.2420 \pm 0.002, \quad \therefore \quad \beta = 103^{\circ}58' \pm 5'.$$

Taking a value given for the density of the substance as 1.729, z, the number of molecules in the unit cell, is given by these dimensions as 3.94 $\sim$ 4.

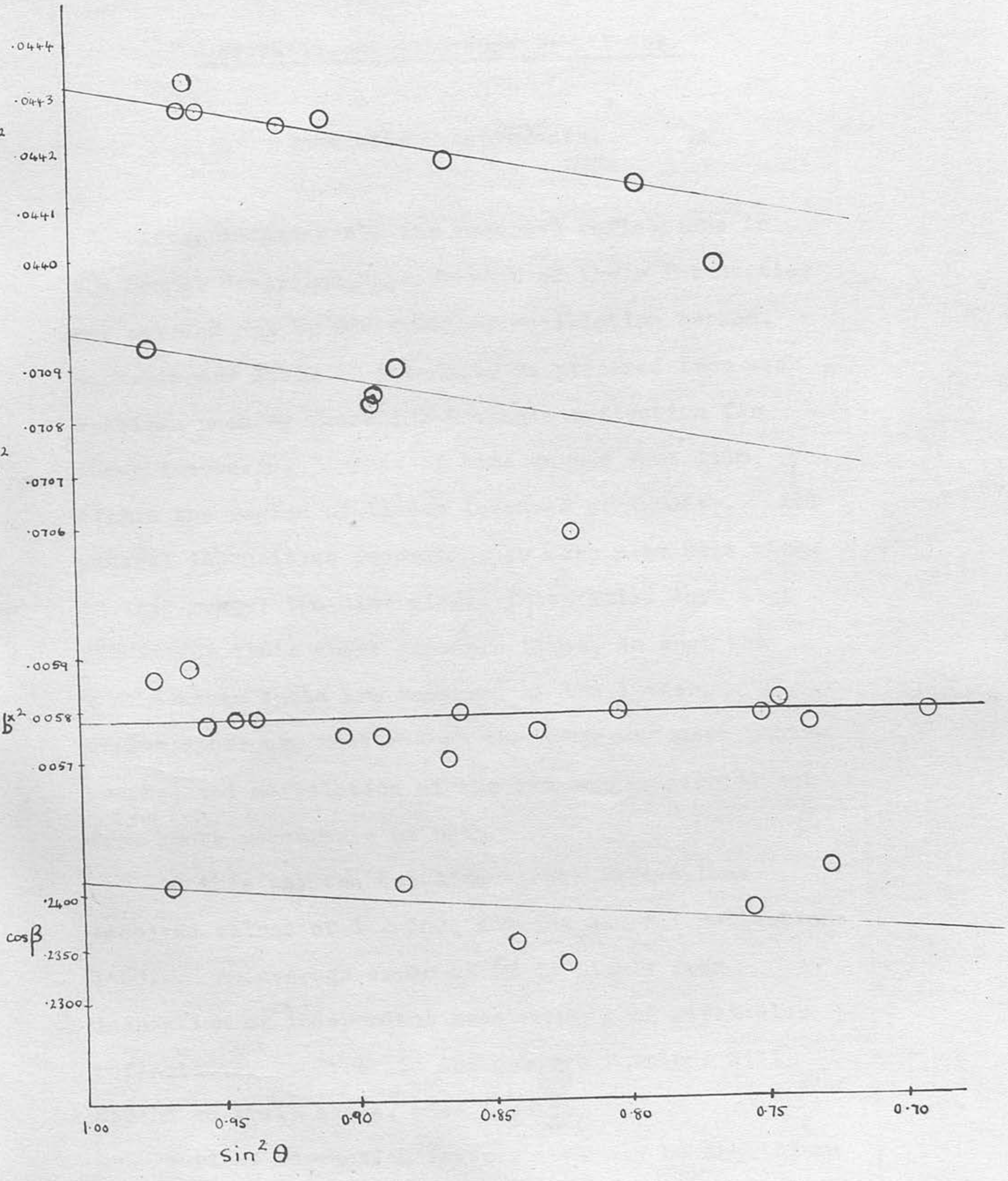


Fig. 2. Derivation of unit cell dimensions.

Chapter 3.

Derivation of Structure Amplitudes.

Intensity Measurements.

After indexing all the recorded reflections in the manner described, measurement of their intensities was carried out by the multiple oscillation method. An arbitrary scale of intensity is prepared from each specimen used by recording a single reflection for known increasing periods of time on the same film, within the region of linear increase of density. All general intensities recorded once were also kept within this range; two-dimensional intensities were kept within for their short exposure times, so that the more intense spots are measured on the latter. Weaker spots are measured on the longer-exposed photographs, and correlation of the two ranges carried out from spots measurable on both.

In this way the two-dimensional reflections received values of 1 - 300, and the general reflections 1-50. An average error of 5% is likely from inspection of independent measurements of particular reflections. Error in the derived F values will depend on their scale. (See later).

Various correction factors must now be applied to the direct intensity figures, to render them proportional to F^2 values.

Equatorial zone reflections require only the combined Lorentz and polarisation factor Θ, that is they must be multiplied by $\frac{\sin 2\theta}{1 + \cos^2 2\theta}$ i.e. Θ^{-1}.

Intensities on non-equatorial layer lines require in addition to this factor, The Cox and Shaw geometrical factors D_1 and D_2. The first allows for time spent in the reflecting position and is dependent on $\sin\theta$, the second corrects for obliquity of incidence and is constant for any one layer line.

No corrections were made for absorption or thermal motion.

The convenient method suggested by Cochran (23) was employed to apply Θ, D_1 and D_2 in one operation. He shows that these factors can be combined as

$$D = \frac{(\sin^2 2\theta - \xi)^{\frac{1}{2}}}{1 + \cos^2 2\theta}$$

for normal beam photographs and gives charts showing the location of this function in reciprocal space. Correction of intensities on any one layer line is then carried out by preparing a transparent scale showing variation of the function to the edge of the limiting sphere, at the corresponding height above the equatorial plane.

Correlation of Intensities.

The corrected intensity values require now to be correlated amongst themselves. At the same time it is desirable for eventual comparison of calculated and observed Fs to obtain the observed values on the same scale as that used for calculation; namely the "absolute" scale where the diffracting power of one electron is unity.

This cannot be done at this stage by comparison as the calculated Fs are not known. A method has been suggested by A.J.C. Wilson for obtaining the observed F's on this scale directly (24).

He shows that $\overline{I}_{hkl} = \Sigma f^{2}$ where $\overline{I}$ is the average absolute intensity in a given range of $\sin\theta$, and Σf^{2} is the sum of the squares of the atomic scattering factors over all the atoms at the centreof this range. Thus if the relative intensities are averaged in groups, a plot of the ratio of this to Σf^{2} for every group will give a correction curve against $\sin\theta$.

This process was employed to correlate all intensities to the absolute scale in the following way.

Separate correction curves were derived for the arbitrarily measured hk0, 0kl, and h0l F's. (See fig.3) Five equal ranges of $\sin^{2}\theta$ were used in each case, this ensuring a roughly equal number of intensities in each range. James and Brindley scattering curves for S^{-1}, Na^{+1} and O (neutral) were used.

Wilson points out that if thermal motion is the only factor not corrected for, the logarmithic plot against $\sin^2\theta$ should be a straight line. Absorption was also not corrected in this case; but for a cylindrical crystal it should be dependent only on $\sin\theta$. Consequently the curves will not show linearity but should be expected to correct the effect of absorption in any one specimen.

On examination of the 0k0 reflections which are common to the okl and hk0 zones it was felt that this assumption was justified. The relative F^2 values from the two crystals show a decidedly differing absorption effect; but the absolute F and F^2 values, derived quite arbitarily, are in good agreement.

(ID - relative F^2)

k	ID from c-axis	ID from a-axis	$F^2/100$ abs. c-axis	$F^2/100$ abs. a-axis	F abs. c-axis	F abs. a-axis
2	2	1	2	2	16	16
4	54	21	67	55	81	71
6	17	10	20	22	45	46
8	1	2	1	3	11	17
10	40	24	43	38	59	62
12	4	6	4	8	22	28
14	42	32	45	37	67	60
16	3	5	3	5	15	22
18	14	19	15	17	35	41
20	2	4	2	3	16	18
22	0	1	0	1	0	9
24	14	20	25	21	50	45
26	0	0	0	0	0	0

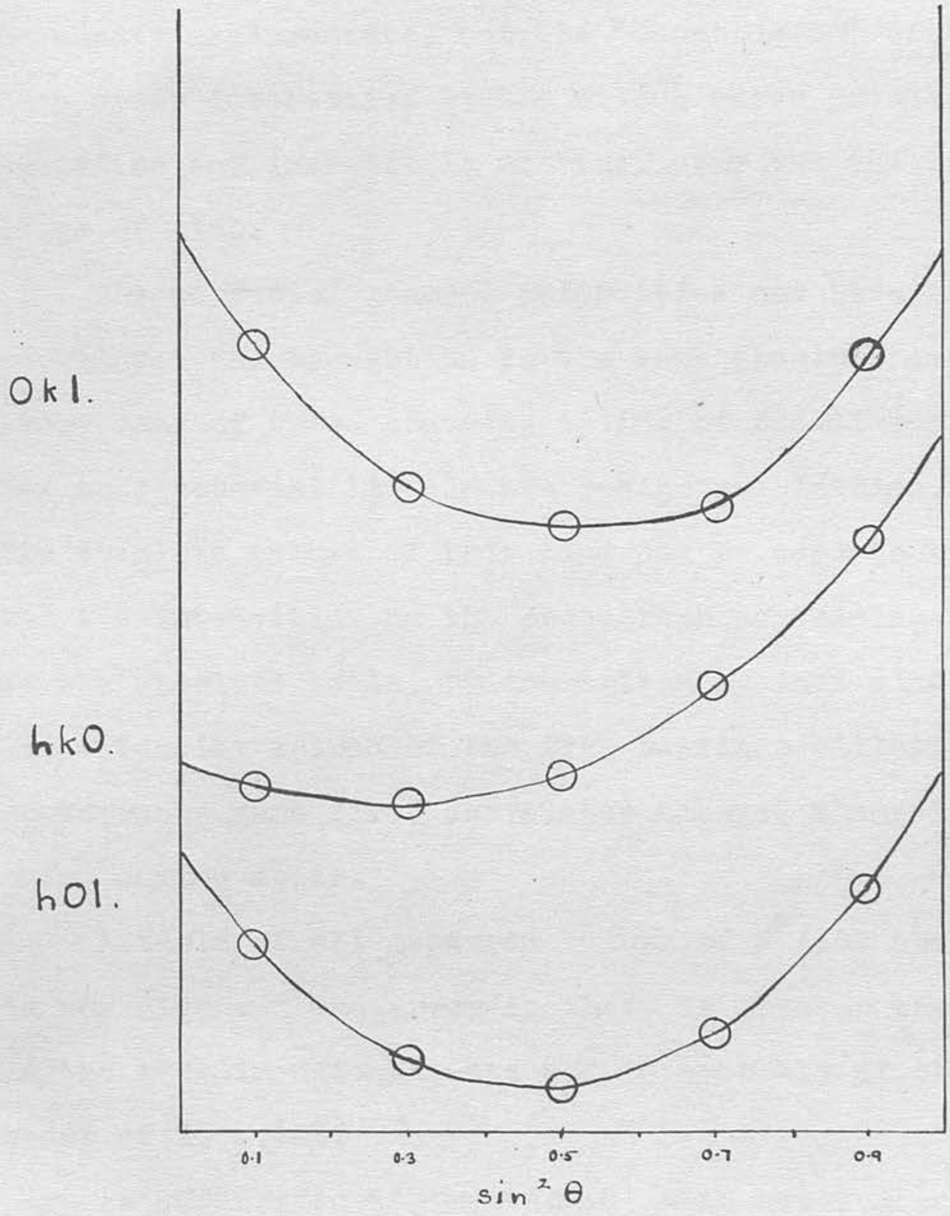


Fig. 3, showing relative shape of $\sum\frac{\overline{f}^2}{I}$ curves for each zone.

The quantity $\dfrac{\left|\sum F\,(\text{a-axis}) - \sum F\,(\text{c-axis})\right|}{\sum F \text{ average}}$ is 0.15 for the above 0k0 reflections.

The error in the two-dimensional F's as a whole is thus considered to be of the order of half of this. Their range is only one-third that of the original intensity measurements, but the "boosting-up" of the high order intensities by the Wilson curve probably nullifies any increase in accuracy over the whole range of sinθ.

The corrected general intensities now have to be correlated and brought on to the same absolute scale. Every zone of these contains a line of two-dimensional Fs- an equatorial line in the reciprocal lattice. The absolute values of this line can be used to bring all the intensities on the photograph containing it to the absolute scale, by comparison against sinθ. The intensity values of the five b-axis oscillation photographs were first correlated amongst themselves using common spots.

A table of all measured values of $F^2/100$ absolute is now given. The error in these is greater than in the two-dimensional data and is probably of the order of 10 - 15%.

As was previously mentioned, this table does not contain every reflection in the reflecting sphere. The layer lines measured extend roughly half way up the radius of the sphere along positive and negative directions of the three principal axes. Consequently there are small wedge-shaped volumes in the outer regions of the sphere in which reflections have not been recorded. It can however, be seen by construction that these are all above the level $\sin\theta = 0.70$, and it was found in fact that any measured above this never exceeded in value 1/6 of the maximum and were usually much less.

Consequently F^2 computation was carried through ignoring the missing regions.

The values of the two-dimensional F's used in refinement are given later (see F obs. - F calc agreement.)

$F^2/100$ absolute values. h = 0.

k l	0	1	2	3	4	5	6	7	8	9
0	/	0	87	0	11	0	25	0	0	0
1	0	15	23	1	24	13	9	9	1	0
2	3	22	0	1	0	0	3	1	5	0
3	0	19	13	7	2	1	4	9	6	0
4	50	13	18	30	2	7	3	7	1	0
5	0	9	80	28	22	23	1	8	12	0
6	22	2	29	21	24	13	1	0	4	0
7	0	44	22	23	17	5	3	13	0	7
8	4	29	5	55	21	7	0	0	1	1
9	0	18	40	2	25	1	3	0	5	
10	38	33	22	24	19	22	9	0	0	
11	0	7	35	2	33	5	10	8	8	
12	8	34	0	7	0	4	3	10	0	
13	0	0	4	13	10	17	17	6	2	
14	37	2	6	2	3	6	6	1	3	
15	0	19	0	13	9	7	0	2		
16	5	31	3	4	12	7	0	6		
17	0	11	2	14	0	3	13	13		
18	17	13	26	19	17	5	0	9		
19	0	17	10	5	0	8	1			
20	3	11	10	0	6	5	2			
21	0	2	13	8	4	0	0			
22	1	10	22	7	26	0				
23	0	7	4	4	2	2				
24	21	5	12	9	2					
25	0	7	6	7						
26	0	25	7	2						
27	0	4	0							

$F^2/100$ absolute values. h = 1.

k l	0	1	2	3	4	5	6	7	8	$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$	$\bar{5}$	$\bar{6}$	$\bar{7}$	$\bar{8}$	$\bar{9}$
0	57	0	20	0	33	0	8	0	0	0	45	0	40	0	17	0	12	0
1	33	18	65	37	55	10	10	3	3	20	47	90	10	15	10	7	0	0
2	5	60	20	0	55	50	5	0	10	23	60	0	20	15	0	10	5	2
3	49	53	40	15	27	25	40	0	0	38	65	15	7	10	0	0	5	0
4	38	0	40	13	27	22	5	0	0	0	17	00	0	25	22	15	7	7
5	12	0	60	0	35	18	0	5	10	17	0	7	10	3	3	5	5	0
6	3	0	0	3	10	0	23	0	17	85	50	55	5	3	7	5	10	7
7	32	42	0	47	0	31	1	0	0	3	0	18	10	13	8	0	0	5
8	99	35	12	0	23	3	6	0	6	3	20	0	0	0	0	6	0	
9	107	13	0	13	15	13	3	3		35	24	10	0	0	6	6	3	
10	21	41	12	8	0	4	4	4		25	33	45	0	8	4	0	15	
11	6	45	12	46	5	19	6	6		15	12	0	0	6	6	0	20	
12	1	35	0	8	0	8				20	3	8	8	17	2	8	0	
13	10	0	20	0	3					0	10	6	2	3	0	1	0	
14	15	0	2	5	3					3	0	10	0	7	20	1	0	
15	0	12	15	0	2					50	0	2	0	10	0	1		
16	4	12	5	2	3					15	3	0	3	5	10	18		
17	30	1	15	5	0					0	2	0	10	0	0	2		
18	2	2	18	2	2					0	0	15	10	10	2	2		
19	12	0	40	1	15					0	5	5	20	1	0			
20	2	8	0	1	2					10	7	35	0	0	2			
21	5	5	2	15	2					7	0	2	2	2	5			
22	1	1	0	1						0	12	0	20	0				
23	7	0	10	1						12	2	0	2	2				
24	14	7	5	2						2	0	20	0					
25	3	0	0							0	0	0	5					
26	0	7	0							5	0							
27	15	0								10								

$F^2/100$ absolute values. h = 2.

k	0	1	2	3	4	5	6	7	8	$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$	$\bar{5}$	$\bar{6}$	$\bar{7}$	$\bar{8}$	$\bar{9}$
0	80	0	10	0	60	0	33	0	0	0	40	0	15	0	0	0	12	0
1	105	10	80	0	5	0	15	3	0	58	0	8	3	3	3	35	3	1
2	0	95	22	5	0	20	0	7	0	38	0	63	10	35	0	5	5	1
3	1	50	50	43	40	4	5	5	3	13	10	10	3	0	0	5	5	0
4	29	55	3	20	30	20	12	3	0	3	5	25	5	22	3	0	8	8
5	1	5	53	10	5	0	3	10	0	5	3	22	38	10	0	5	3	12
6	2	0	0	3	5	0	2	10	2	27	37	25	5	0	7	3	10	9
7	3	15	22	104	0	18	0	3		0	0	78	23	23	0	0	0	4
8	2	12	6	29	6	0	0	9		0	6	29	3	0	15	3	0	
9	1	3	9	3	0	3	3	3		6	24	27	42	18	18	8	3	
10	4	12	16	0	8	4	8			12	11	16	8	0	0	0	4	
11	10	5	5	5	16	12	12			12	17	6	0	6	12	2	0	
12	2	17	8	8	0	15				0	17	8	0	25	0	10	0	
13	5	2	0	0						35	20	0	0	2	2	15	10	
14	0	3	1	1						45	10	0	0	0	5	0		
15	11	15	5	0						5	0	0	2	0	5	0		
16	10	0	5	0						2	0	0	5	2	15	8		
17	37	1	1	15						1	30	25	8	15	2			
18	2	2	12	0						30	0	5	0	0	15			
19	0	1	20	0						0	0	0	0	3	0			
20	5	2	8	0						0	0	8	2	0	0			
21	0	0	0							0	5	8	0	15				
22	1	0	30							7	5	3	0					
23	7	2	20							0	10	10	10					
24	1	0	0							7	3	10						
25	20	5								5	0							
26	0																	

$F^2/100$ absolute values. h = 3.

k l	0	1	2	3	4	5	6	7	$\overline{1}$	$\overline{2}$	$\overline{3}$	$\overline{4}$	$\overline{5}$	$\overline{6}$	$\overline{7}$	$\overline{8}$	$\overline{9}$
0	0	0	3	0	30	0	18	0	0	45	0	15	0	25	0	0	0
1	0	28	0	8	0	15	0	0	8	12	0	5	3	35	10	10	3
2	0	22	35	0	10	0	5	3	32	10	38	25	3	0	0	3	3
3	0	0	0	8	40	15	0	3	38	53	30	0	5	25	0	3	17
4	2	60	3	13	22	8	15	10	12	75	10	25	22	0	3	10	0
5	2	65	0	5	5	5	0	0	55	3	10	25	12	22	3	10	0
6	2	40	0	15	5	0	3	17	3	20	5	4	16	0	0	3	1
7	28	3	3	8	0	8	0	0	19	0	42	0	13	10	0	0	
8	29	12	12	0	0	3	3	0	0	0	0	43	4	0	6	3	
9	2	0	0	0	0	3	0		3	13	6	35	0	4	6	2	
10	4	8	0	16	8	4	8		16	53	0	16	6	6	0		
11	23	0	6	6	6	6			12	0	15	3	0	20	0		
12	6	8	8	0	17	17			17	8	8	21	0				
13	8	3	12	0					2	0	8						
14	8	0	0	10					14	25	0						
15	0	8	12	15					0	0	15						
16	2	5	0	0					18	0	0						
17	4	1	5	5					0	0	15						
18	4	7	12	0					0	0	0						
19	10	0	0	0					0	0	0						
20	4	10	10	15					2	0	4						
21	3	2	0						0	0	15						
22	3	0	30						5	0	0						
23	3	0	0						0	0	5						
24	8	0							15								
25	14																

$F^2/100$ absolute values. $h = 4$.

l \ k	0	1	2	3	4	5	6	$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$	$\bar{5}$	$\bar{6}$	$\bar{7}$	$\bar{8}$	$\bar{9}$
0	54	0	0	0	10	0	10	0	4	0	0	0	1	0	20	0
1	5	0	15	10	8	5	10	27	0	40	8	5	70	0	4	1
2	2	18	15	5	0	10	3	58	3	14	8	20	8	8	0	0
3	3	5	5	15	20	0	8	30	5	14	0	20	20	0	0	1
4	0	5	5	0	5	0	3	5	4	4	20	5	0	12	1	
5	22	5	63	0	5	0	3	5	48	5	0	0	0	8	12	
6	0	7	53	0	10	0	3	8	25	28	55	22	0	0	0	
7	4	8	0	10	0	0	3	3	0	0	0	5	0	3	0	
8	3	3	9	0	0	3	0	9	13	20	26	12	4	0	0	
9	10	3	20	6	0	3		3	0	0	6	6	6	2		
10	24	5	0	4	4	0		0	15	10	9	9	0	0		
11	0	6	6	6	6			0	3	0	0	12	6	3		
12	8	0	0	8	0			15	0	0						
13	0	8	0	2				5	5	3						
14	17	2	0	0				15	10	0						
15	9	1	5	2				0	0	3						
16	23	5	0	0				10	0	5						
17	3	6	0	0				0	3	0						
18	3	0	0	5				0	0	3						
19	9	0	20					0	3	3						
20	2	2						0	0	8						
21	2	20						2	0							
22	0							4								
23								8								

$F^2/100$ absolute values. $h = 5$.

k l	0	1	2	3	4	5	$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$	$\bar{5}$	$\bar{6}$	$\bar{7}$	$\bar{8}$
0	15	0	10	0	8	0	0	5	0	5	0	31	0	0
1	4	17	0	0	5	5	6	0	5	0	5	0	0	0
2	3	0	0	5	3	5	5	0	0	10	0	9	8	0
3	0	45	25	25	0	3	0	15	15	0	10	0	0	3
4	5	30	3	0	5	0	0	0	30	10	0	3	0	0
5	35	5	10	0	3	8	18	3	5	3	0	8	0	1
6	0	0	0	0	0	1	9	3	8	10	0	0	0	1
7	1	17	0	5	3		3	0	0	10	4	1	0	
8	12	0	5	3	3		4	3	20	4	4	0	1	
9	15	0	6	0	3		4	8	2	13	5	1		
10	4	0	4	0			0	0	11	0	0	0		
11	7	12	0	0			0	20	0	0	0			
12	5	0	0	0			8	0	3					
13	12	0	0	0			0	25	10					
14	4	0	0				0	0	3					
15	3	0	0				10	0	0					
16	0	0					2	0	0					
17	2	0					4	0	2					
18	4	0					0	0	3					
19	0	0					2							
20	0	0					1							

$F^2/100$ absolute values. h = 6.

k l	0	1	2	3	4	$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$	$\bar{5}$	$\bar{6}$	$\bar{7}$
0	3	0	0	0	16	0	0	0	0	0	0	0
1	4	0	0	0	0	18	10	0	0	0	3	6
2	0	1	0	8		33	0	5	0	0	0	0
3	4	0	0	0		0	15	0	0	8	0	4
4	0	5	5	5		3	5	17	0	0	0	5
5	0	0	8	0		3	5	0	3	3	0	0
6	6	6	20			3	3	0	0	0	0	
7	3	4	0			0	0	16	0	21	0	
8	13	0	2			0	0	0	0	0	4	
9	4	0	5			3	3	3	0	0		
10	1	2	10			2	2	2	2			
11	2	5				12	6	6				
12	11	0				0	0	0				
13	3	5				10	0	0				
14	1	5				0	10	0				
15	3					15	10					
16	0					2						

k $F^2/100$ absolute values. h = 7

k ↓ \ l →	0	1	$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$	$\bar{5}$	$\bar{6}$
0	0	0	0	5	0	5	0	4
1	0	1	0	0	1	3	0	
2	0	0	3	4	10	1	0	
3	4	4	0	0	0	0	0	
4	8	4	0	12	0	8	10	
5	5	0	0	0	1	8	0	
6	1	4	1	3	3	0		
7	0		0	1	1			
8	0		0	1	1			
9	21		10					

Chapter 4.

The Determination of the Sulphur Parameters.

(1) Two-dimensional Attempts.

The fundamental problem of determining a crystal structure from X-ray diffraction data is that the phases of the structure factors cannot be found experimentally. Before 1935 only indirect methods of approaching this problem were in use; the whole or part of the structure had to be postulated, and such possibilities tested for successful agreement with the numerical values of the structure factors. This is possible where only a few distinct atoms require to be found, or in highly symmetrical cases. It might also be possible where the shape and dimensions of the molecule are previously partly or completely known.

The advent of the Fourier method extended the power of such indirect approaches to more complex structures, by enabling unknown parts of a structure to be found directly from the parts already determined by indirect methods; the most common possibility of this sort is that where one or two heavy atoms sufficiently dominate the phases to determine the remaining positions by refinement. But the problem of establishing the initial information still exists.

The structure under consideration here might be determined by such methods if the sulphur positions can be found, though it is not intended to make any assumptions about molecular shape. Projections on the planes 001 and 100, containing the long b axis, should be expected to show most of the atoms resolved from one another; Fourier work could be done therefore with the 0kl and hk0 F's using phases suggested by the sulphur positions.

The latter cannot however be in the special positions on the centres of symmetry, due to the probable nature of the thiosulphate group. The problem of finding one or both in general positions by indirect intensity considerations would be a very formidable if not impossible one. But the method suggested by A. L. Patterson in 1935 (18) has opened up extensive new possibilities.

Patterson showed that a synthesis of F^2 values, independent of phases, had the following direct relation to the real electron density distribution. If such a function be computed in the real cell, maxima occur at vectorial distance from the origin corresponding to vectors between every pair of atoms in the cell. Such maxima will have heights proportional to the product of the heights of the two atoms concerned.

This function has been of immense use in the solution of unknown structures. It was first employed, computed in projection, (18) to determine the positions of heavy atoms alone. More recently it has been employed, also in projection, in searching for molecules of known shape lacking heavy atoms; (25,) 23); and methods are now being suggested for the complete solution of structures from the function. (26,) 25).

It was decided to employ this synthesis to determine the sulphur positions by computing it in projection on the planes 001, 100 and 010. (See Appendix).

The resulting maps are shown on Fig. 4.

The peaks produced in the Patterson function by the space-group $P\,2_1/c$ must now be considered.

The general equivalent positions are (30):-

$x,y,z;\;\; x,\frac{1}{2}-y,\frac{1}{2}+z;\;\; \bar{x},\bar{y},\bar{z};\;\; \bar{x},\frac{1}{2}+y,\frac{1}{2}-z.$

The Patterson will contain peaks corresponding to two types of vector.

(1) Vectors between crystallographically related atoms - special vectors.

(2) Vectors between non-related atoms - general vectors.

The special vectors can be derived from one set of equivalent positions, as above. They reduce to:-

(see over)

(a) $0, \frac{1}{2} + 2y, \frac{1}{2}$. occurring 2 times - weight 2.
(b) $2x, 2y, 2z$. occurring 4 times - weight 1.
(c) $2x, \frac{1}{2}, \frac{1}{2} + 2z$. occurring 2 times - weight 2.

together with the origin peak, which has weight $\sum f_r^2$, over all the atoms. The symmetry elements repeating these vectors throughout the cell are a mirror plane in the ac plane at $y = \frac{1}{2}b$ and centres of symmetry at 0 and $\frac{1}{2}$ on each axis.

General vectors between $x_1 y_1 z_1$ and $x_2 y_2 z_2$ are, with the same symmetry elements:-

$$x_1 - x_2;\ \ y_1 - y_2;\ \ z_1 - z_2.$$
$$x_1 - x_2;\ \ \tfrac{1}{2} + y_1 + y_2;\ \ \tfrac{1}{2} + z_1 - z_2$$
$$x_1 + x_2;\ \ y_1 + y_2;\ \ z_1 + z_2.$$
$$x_1 + x_2;\ \ \tfrac{1}{2} + y_1 - y_2;\ \ \tfrac{1}{2} + z_1 + z_2.$$

These each occur 4 times being in general positions like (b) above. It is found that they have, however, double the weight of the (b) peaks and thus correspond in weight to (a) and (c), which become double on account of their position on symmetry elements.

A systematic search was therefore commenced for the sulphur parameters by attempting to locate the special sulphur vectors as follows.

The peaks $0, \frac{1}{2} + 2y, \frac{1}{2}$ will appear along one edge of the unique quarter of each projection shown. Since they are double-weight it should be possible to derive likely y parameters. The peaks of type (b) will appear on the two short edges. All possible combinations of y with z and x parameters suggesting heavy atoms are listed. These possibilities are then tested by searching for resulting 2x, 2y, 2z peaks. This should suggest the most likely y and x and y and z combinations, though it will not decide between a combination of y and 30-y with z and vice versa. But these ambiguities will be removed by identifying general peaks $x_1 - x_2$, etcetera.

A likely solution was quickly found (fig. 4) for the projection on 100. This gave the y and z parameters of the two sulphur atoms as

y(60ths)		z(60ths)
9	-	4
4	-	17

The y parameters seemed definitely indicated by the 0, $\frac{1}{2}+2y$, $\frac{1}{2}$ peaks on both projections. A solution for y and x was then attempted on 001. The most obvious was

y		x
9	-	39
4	-	9

The heavy peak at y = 5, z = 11, seems to appear at x = 30. (See fig. 4). This peak is being interpreted as the $x_1 - x_2$; $y_1 - y_2$; $z_1 - z_2$; vector. But this will necessitate a distance of 3 - 4A° between the sulphur atoms. This seems extremely unlikely in view of chemical theory, and it was

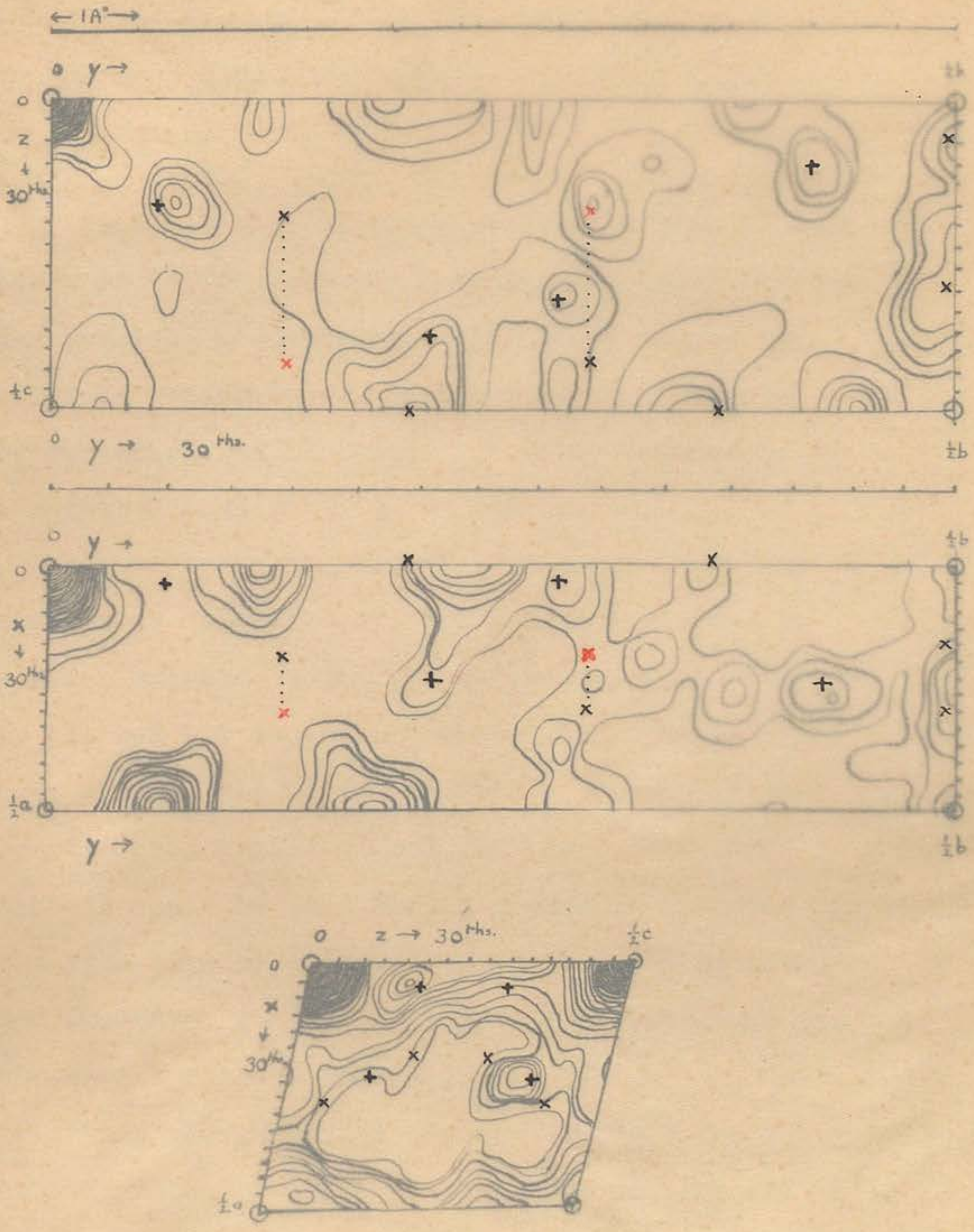


Fig. 4. Patterson projections on 100, 001 and 010 (downwards).

Overlay shows correct positions of sulphur vectors, (general-+, special-x,) in black. Incorrect positions chosen are in red.

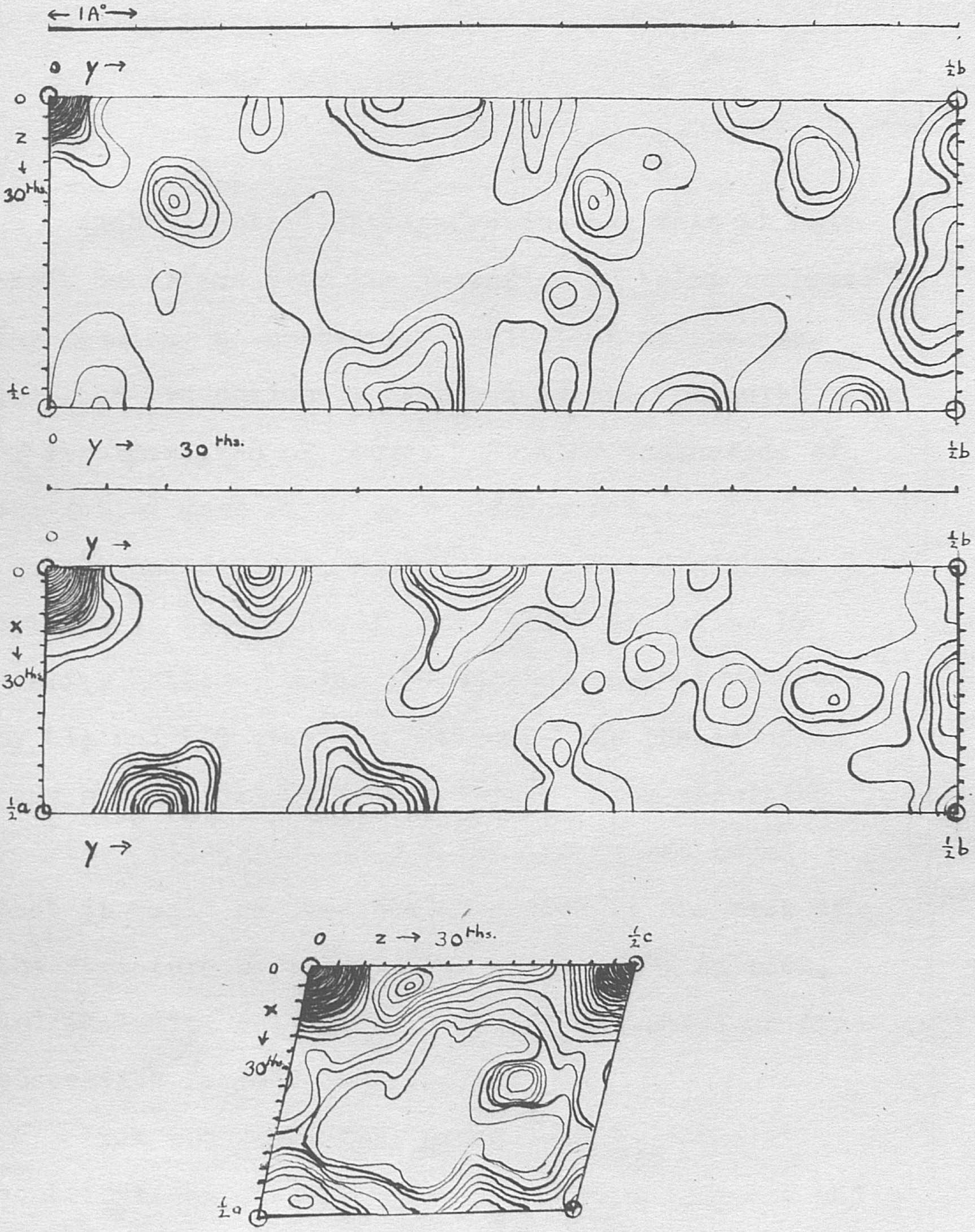


Fig. 4. Patterson projections on 100, 001 and 010

(downwards).

Overlay shows correct positions of sulphur vectors, (general-+, special-x,) in black. Incorrect positions chosen are in red.

decided that the interpretation, on 001 at least, could not be correct. Another solution was found for this projection placing the vector at $y = 5$, $x = 3$. This gave

y		x
9	-	6
4	-	9

Considerable dissatisfaction was felt at this early departure from the intention to solve without any chemical assumptions. Solutions of the projections are obviously hampered by the ambiguity caused by superposition of peaks. Further weaknesses of the method were still to be discovered.

It was decided, however, to proceed with an attempt to determine all the atomic positions by Fourier methods, using the sulphur parameters given by (1) and (3) above to determine the phases of as many hk0 and 0kl Fs as possible. From resulting Fourier projections on 001 and 100 it was hoped that it would be possible to arrive at the rest of the structure by correlating extra peaks on both, and including them gradually in F calculations for successive Fourier refinements.

This procedure failed completely. The contributions of the two sulphurs were computed using the scattering curve for neutral sulphur given by James and Brindley. Large contributions were present in general for large Fs and this was felt to be encouraging. Values of the factor

$$R = \frac{\sum(F\ \text{obs.} - |F\ \text{calc.}|)}{\sum F\ \text{obs.}}$$

roughly 0.60 for both zones.

The Fs were then assigned the phases of these sulphur contributions where the latter totalled more than an absolute value of 15 units., and Fourier projections on 001 and 100 were computed. (See Appendix).

However, on examining these it was found extremely difficult to identify corresponding extra peaks. The glide plane at $y = \frac{1}{4}$ & $\frac{3}{4}b$ appears in projection on 001 as a mirror plane, confusing y with 30-y. Finally four extra peaks were selected and the F calc. values altered by adding their contributions, carrying oxygen weight, to those of the sulphurs. The value of R worsened slightly, and further Fourier work with the new phases made the peaks less convincing and failed to suggest further possible positions.

Attempts to solve the 100 projections alone in the same way led eventually to an apparently likely picture containing the correct number of peaks and giving R = 0.50, but further attempted refinement worsened the agreement.

It was decided that the only satisfactory method of solving the structure lay in the use of three-dimensional methods. Even if the sulphur positions were correct, which now seems doubtful, their derivation from the projections was not satisfactory. The Patterson function in three dimensions should enable the necessary peaks to be identified with certainty.

(2) Three-dimensional Patterson Work.

The unique quarter of the Patterson function was computed in three dimensions in sections parallel to the plane of the a & b axes, at z = 0, 3, 7, 10, 13, 17, 20, 23, 27, and 30 60ths. Each section was computed in 60ths. of y and 30ths. of x. (See Appendix — collected formulae and methods of calculation). The "Patterson-Harker" (32) section at $y = \frac{1}{2}b$ was also computed. This section and five of the general sections are shown.

Derivation of the Sulphur Parameters.

The interatomic vectors of type (b) (see p. 41) $2x, \frac{1}{2}, \frac{1}{2} + 2z$ appear on the Harker section. They are double-weight, so that those corresponding to the two sulphurs should exceed the weight of any other peak, except a chance general sulphur peak.

It is in fact found on examination of the Patterson-Harker section that two predominantly heavy peaks are present.(See fig. 5). An interpretation of their positions gives the following possible combinations of x and z parameters for the sulphurs, listing crystallographically distinct possibilities only:-

	x (60ths)		z (60ths)
(1)	6 or 36	with	6
(2)	9 or 39	with	17

The single-weight 2x, 2y, 2z, peaks corresponding to these will however, appear along the lines $x = 12$, $z = 12$, and $x = 42$, $z = 26$ in this unique quarter of the function, whatever combination of these parameters is present. These lines were accordingly examined on the corresponding sections, in order to derive the y parameters. Any likely peaks can be compared with the line $x = 0$, $z = \frac{1}{2}$, containing the special vectors $0, \frac{1}{2} + 2y, \frac{1}{2}$.

An examination of fig. 5 will show how striking is the agreement. The values of 2y suggested are 8 and 17. These give the sulphur parameter combinations in the first quarter as

(all 60ths)	x	y	z			x	y	z
(1) (a & b)	6	(4 or 26)	6	or	(2) (a & b)	36	(4 or 26)	6
(3)	9	9	17	or	(4)	39	9	17

(other combinations of y correspond only to a change of origin to $y = \frac{1}{2}b$).

Scale ½" = 1A°, Figs. 5-7, 9.

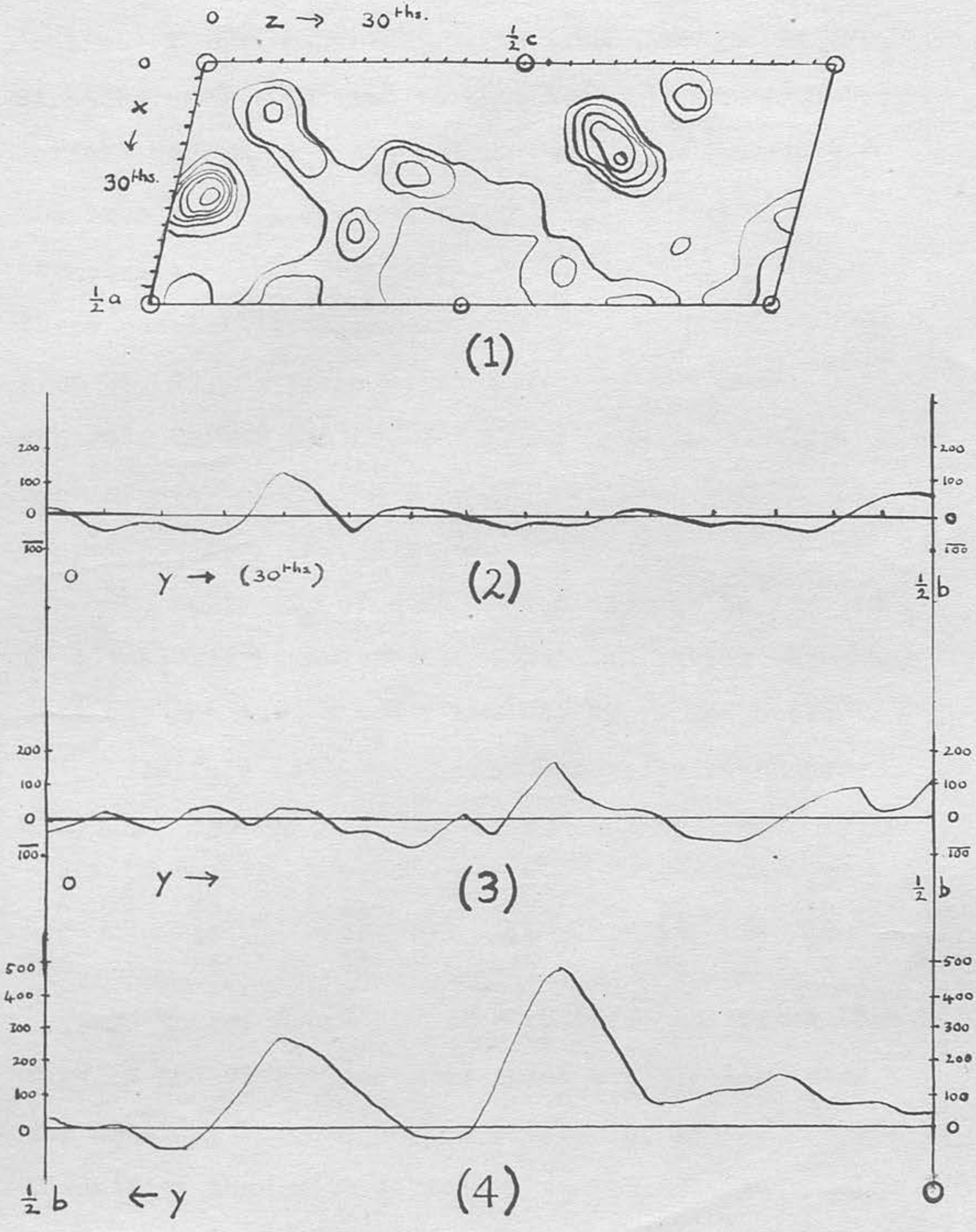


Fig. 5. Derivation of the sulphur parameters.

(1) Patterson-Harker section at y = ½b.
(2) " line section at x = 12, z = 12 (60ths).
(3) " " " " x = 42, z = 26 (").
(4) " " " " x = 0, z = ½c.

The mistake made in the solution of the projections is now apparent. The single-weight 2x, 2y, 2z peaks were misplaced so that the sulphur parameters derived were x_1, y_2, z_1, and x_2, y_1, z_2, instead of the true x_1, y_1, z_1, and x_2; y_2, z_2,. Due to the symmetries of the Patterson, a distinction between these possibilities can only be made by locating the true 2x, 2y, 2z peaks since they give the same general, Harker and (0, $\frac{1}{2}$ + 2y, $\frac{1}{2}$) peaks. Only a much heavier atom than S could have made the 2x, 2y, 2z peaks clear. (See fig. 4).

The ambiguity of combination may now be removed by identifying the general vectors. Taking parameter sets (1) (a) (i.e. y = 4) and (3) above we obtain

in full cell			in unique quarter shown		
x/60a	y/60b	z/60c	x/60a	y/60b	z/60c
3	5	11	3	5	11
3	43	41	57	17	19
15	13	23	15	13	23
15	35	53	45	25	7

Peaks are found to occur at these positions (See figs. 6 and 7) and in three cases are heavier than any other peak found in the entire function. This identifies them with certainty as the general sulphur vectors. No other set of vectors between any two sets of (1) (a & b), (2) (a & b), (3) or (4) above gives such agreement; ~~(~~ (2)(a) and (4) give the same set but their parameters correspond to a change of origin to x = $\frac{1}{2}$a).

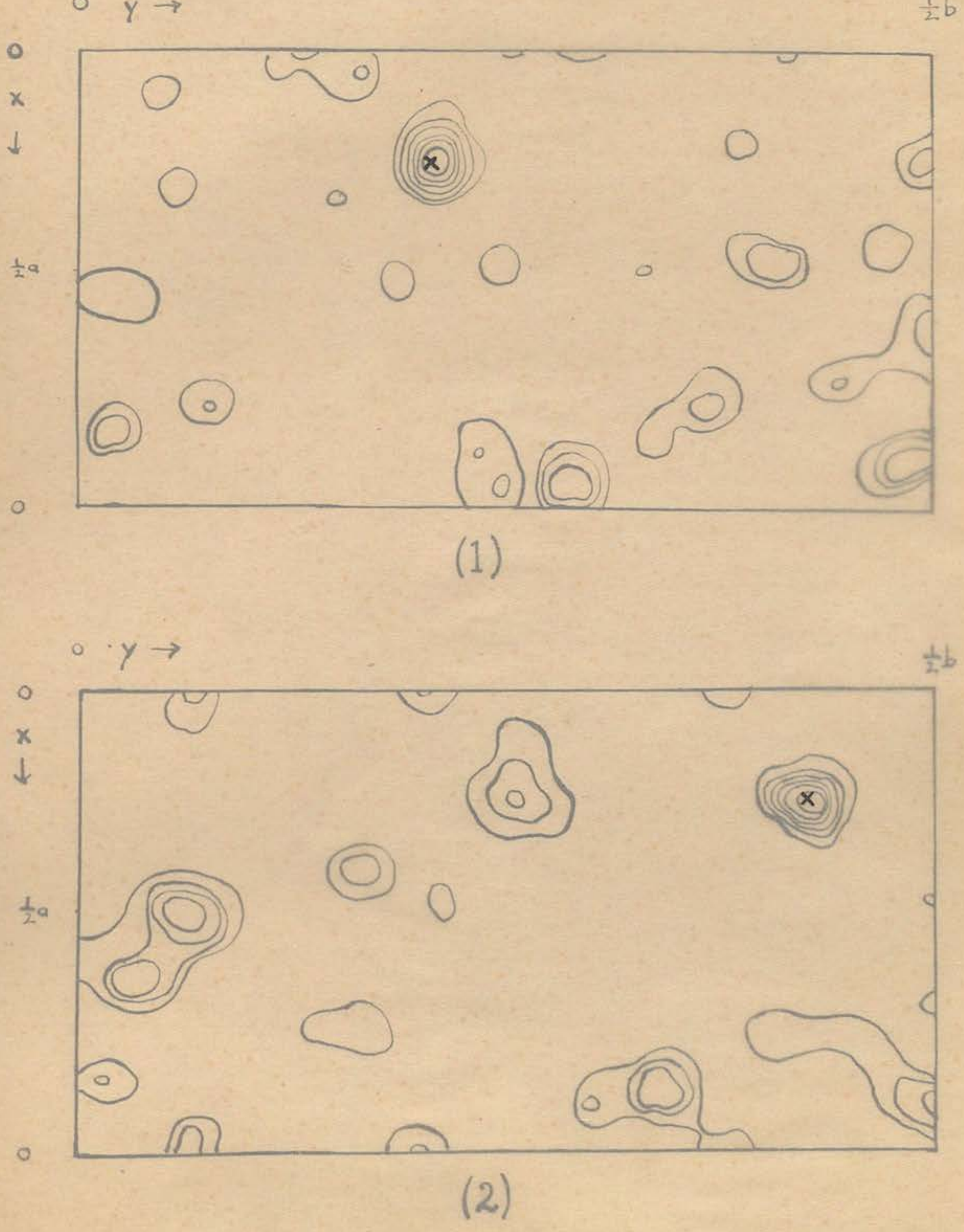


Fig. 6. (1) Patterson section at z = 23/60c.
(2) " " " z = 53/60c.
(General sulphur vectors marked on overlay).

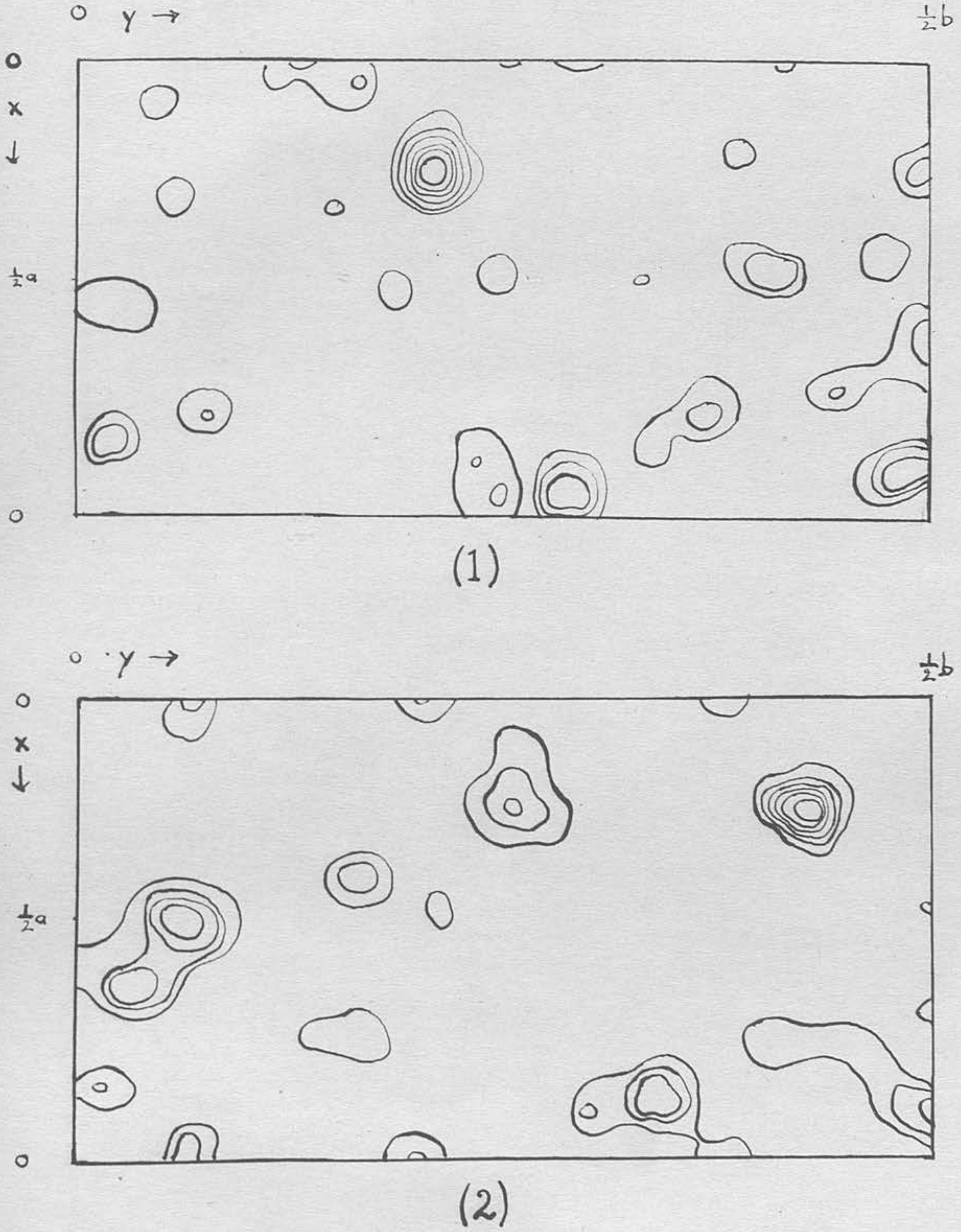
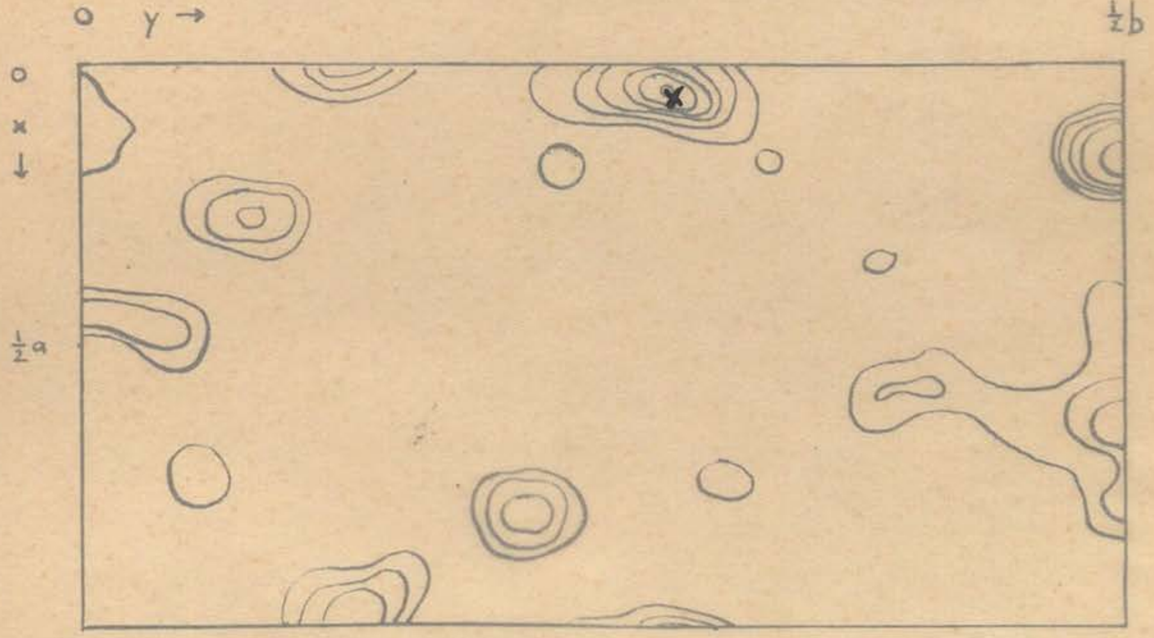


Fig. 6. (1) Patterson section at z = 23/60c.
(2) " " " z = 53/60c.
(General sulphur vectors marked on overlay).

(3)



(4)

Fig. 7. (3) Patterson section at $z = 10/60c$.
(4) " " $z = 40/60c$
(General sulphur vectors marked on overlay).

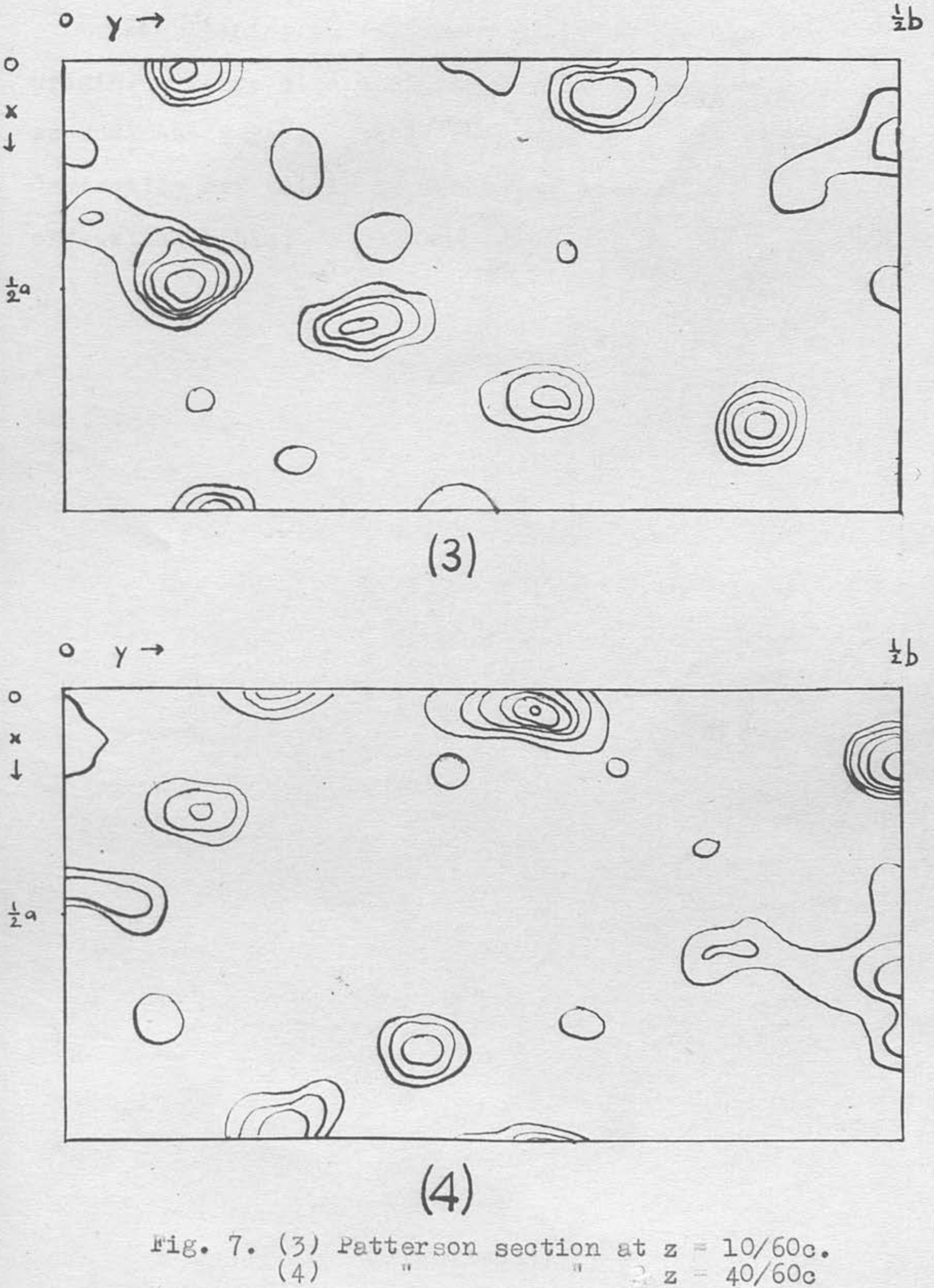


Fig. 7. (3) Patterson section at z = 10/60c.
(4) " " at z = 40/60c
(General sulphur vectors marked on overlay).

Thus the approximate sulphur parameters are

$x/60a$	$y/60b$	$z/60c$
6	4	6
9	9	17

establishing an arbitrary position for the origin. These give a distance between the two of approximately 2A$^{\circ}$. It is felt however, that their derivation may fairly be described as purely crystallographic.

Chapter 5.

The Complete Solution of the Structure.

The remaining ten atomic positions could now be searched for by the Fourier means already attempted with incorrect sulphur positions. But a more convincing, quicker and more elegant solution might be got from an analysis of the Patterson in three dimensions, by using the sulphurs to "search" out the other atoms. This will be free from the weakness of two-dimensional work, where overlapping may give rise to ambiguities.

A method of this sort called the use of the "Vector Convergence" function has been used in the analysis of strychnine hydrobromide by Beevers and Robertson (26) and by the latter was later applied to rubidium benzoyl penicillin (26). The method depends upon the presence of a heavy atom in a multiple space-group. The origin of the Patterson is placed on each related position of the heavy atom in the real cell, correctly oriented with respect to the latter. The remaining atom positions are then marked by the convergence of vectors upon them from each "searcher" atom. If these are in general positions, as here, the function has the symmetry of the real cell. The method is thus one of deducing the interpretation of part of the Patterson function and using this to solve the rest. Methods bearing a relation to this have been suggested by Buerger (27) in aseries of papers dealing with the properties of vector sets.

The operation used here is effectively an addition of the values of the Patterson function obtained when the eight-point polygon of the sulphur atoms in the complete unit cell ranges through Patterson space.

This was carried out in practice as follows. Fig. 8 shows on a small scale the positions of the eight sulphurs in the unit cell (heavy line) with Patterson space (dotted line) placed with its origin upon them. These serve as guiding diagrams. Taking searcher atom (1) all peaks above an arbitrary level occurring in the Patterson were marked as they fall in the unique quarter of the real cell when the origin of the Patterson is so placed. The process was then repeated for the remaining seven searcher atoms, but for each one a different colour of symbol was used. The resulting function thus mapped the unique quarter of the real cell at the intervals at which the Patterson was originally calculated. The level above which peaks were marked was chosen as one well below the expected height of a sulphur-oxygen vector. Some indication of differing height above this was imparted

Scale $\frac{1}{10}$" = 1A°.

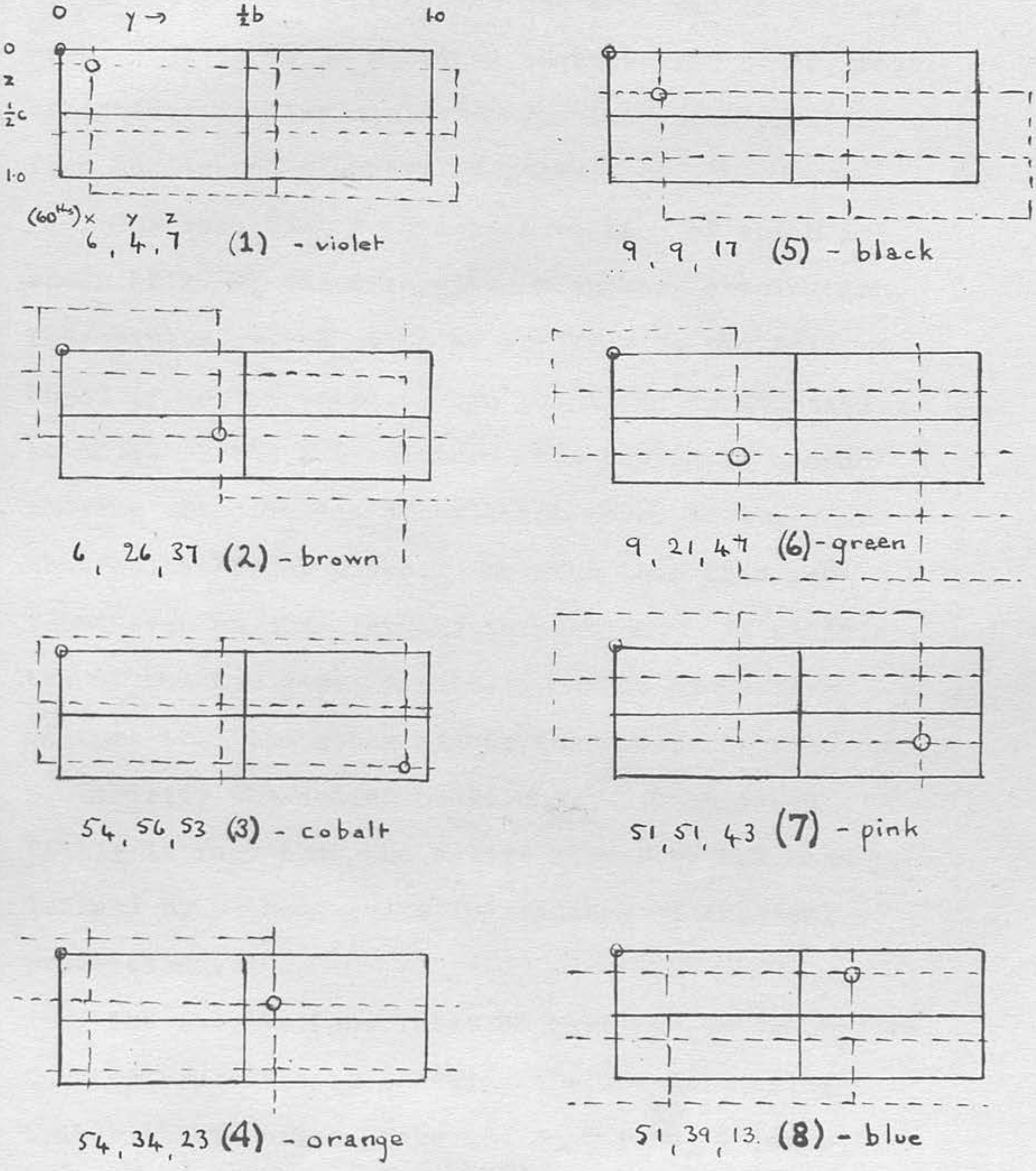


Fig. 8. The positions of the eight "searcher" atoms (sulphurs) in the unit cell.

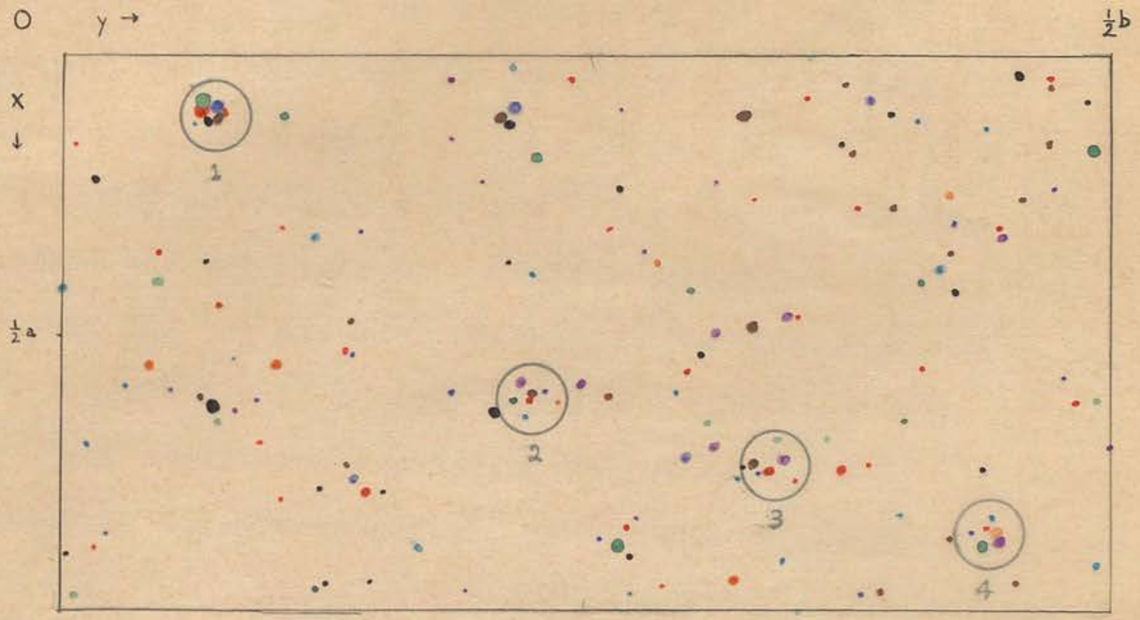
to the function by marking the peaks with three sizes of symbol. (See fig. 9).

It is now to be expected that the atomic positions will be visible as clusters of eight peaks, one of each colour. Such a method of distinguishing the different searcher atoms was not employed in previous work. It is to be expected that it will be of great assistance in distinguishing genuine coincidences from accidental clusters of peaks.

The resulting function, a section of which is shown (fig. 9) was then given a cursory examination. The results proved quite as striking as had been hoped if not expected. Ten positions in addition to those of the two sulphurs were instantly noted showing coincidences of at least seven of the theoretical eight peaks. No more than this were found even on more lengthy inspection. In addition, two of the ten were definitely marked by heavier vectors than the other eight; these were in all probability the sodium positions. It appeared likely in fact that the entire structure had been defined by methods quite independant of chemical predictions.

The results (see Table 3) were now tested before further procedure by checking the resulting distribution of Harker peaks and $0, \frac{1}{2} + 2y, \frac{1}{2}$ peaks, and subsequently by building a model. The peaks

Fig. 9. (Above.) The section at z = 7/60c of the complete vector convergence function. This shows three extra coincidences marking atomic locations (ringed.) (1) A searcher atom S_1, (sevenfold as origin peak not marked.) (2) H_2O_4 - eightfold. (3) Na_1 - eightfold. (4) H_2O_7 - sevenfold.



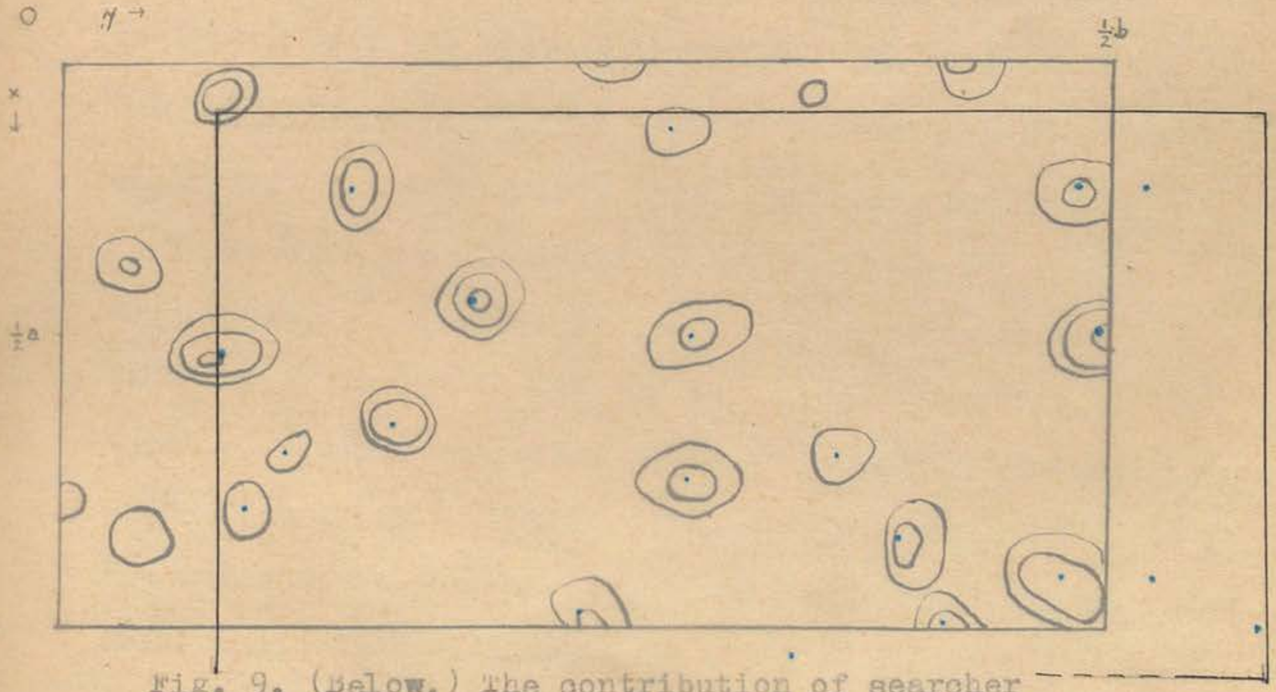
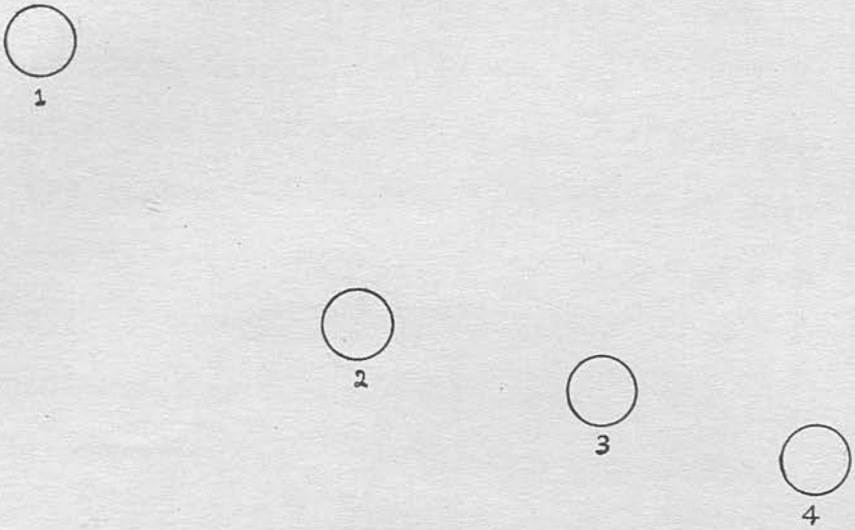


Fig. 9. (Below.) The contribution of searcher atom 3 to the above complete section - i. e. the section at z = 13/60c of the Patterson shown in position to illustrate the method.

Fig. 9. (Above.) The section at $z = 7/60c$ of the complete vector convergence function. This shows three extra coincidences marking atomic locations (ringed.) (1) A searcher atom S_1, (sevenfold as origin peak not marked.) (2) H_2O_4 - eightfold. (3) Na_1 - eightfold. (4) H_2O_7 - sevenfold.



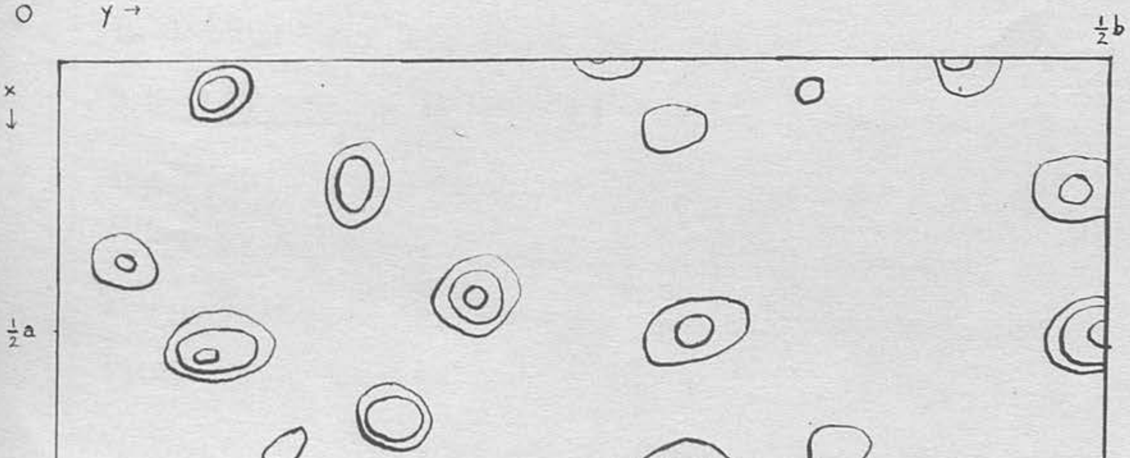


Fig. 9. (Below.) The contribution of searcher atom 3 to the above complete section - i. e. the section at $z = 13/60c$ of the Patterson shown in position to illustrate the method.

showed good agreement, particularily those of the line section.

The model showed instantly that the structure seemed highly probable, for every atomic location. The expected tetrahedral thiosulphate group was present, with three oxygens at roughly 1.5 A° from the central sulphur; one of the sodiums was surrounded octahedrally by six water and thiosulphate oxygens and the other by a similar octahedron of five oxygens and the exterior sulphur. The Na-O distance was roughly 2.5 A° in both cases.

The conculsive crystallographic test of the structure was now commenced, namely the calculation of Fs for comparison with the observed values.

The hk0 and 0kl Fs were first calculated, as before, from the vector convergence structure expressed in 120ths of b and 60ths of a and c. The values of

$$R = \frac{\Sigma | F\ \text{obs.} - |F\ \text{calc.}||}{\Sigma F\ \text{obs.}}$$

were respectively 0.48 and 0.49. This is fairly high, but agreement of large Fs with small sulphur contributions was encouraging. Fourier projections were computed from these results on 001 and 100. All the atoms appeared clearly, no extra peaks of comparable height being brought up. The Fs were re-calculated with the refinements suggested. R was now 0.38 and 0.39. This substantial fall was good proof of the structure's correctness in every respect. As a final check, a

Table 3.

Parameters from the Vector Convergence Maps, with final parameters (see later) shown in brackets.

	x (60ths)		y (60ths)		z (60ths)	
S_1	6	($6\frac{1}{2}$)	$4\frac{1}{2}$	($4\frac{1}{6}$)	7	($6\frac{1}{2}$)
S_2	9	(9)	$8\frac{1}{2}$	($8\frac{3}{6}$)	17	($16\frac{1}{2}$)
Na_1	44	(43)	$20\frac{1}{2}$	($20\frac{3}{6}$)	5	($4\frac{1}{2}$)
Na_2	15	(15)	$24\frac{1}{2}$	($24\frac{3}{6}$)	12	($12\frac{1}{2}$)
O_1	21	(20)	8	($7\frac{2}{6}$)	26	(26)
O_2	55	(55)	$8\frac{1}{2}$	($9\frac{1}{6}$)	20	($20\frac{1}{2}$)
O_3	11	(12)	$11\frac{1}{2}$	($11\frac{4}{6}$)	10	(11)
H_2O_4	37	(37)	$13\frac{1}{2}$	(14)	7	(7)
H_2O_5	5	(6)	$18\frac{1}{2}$	($18\frac{4}{6}$)	17	(17)
H_2O_6	38	($37\frac{1}{2}$)	$21\frac{1}{2}$	($22\frac{1}{6}$)	23	($21\frac{1}{2}$)
H_2O_7	51	(52)	$26\frac{1}{2}$	($26\frac{4}{6}$)	7	(7)
H_2O_8	39	(39)	$\frac{1}{2}$	($\frac{5}{6}$)	15	(15)

line of general hkl Fs was calculated from the original structure. This gave highly satisfactory agreement (see Table 4). The value of R is 0.35. This would probably be lower with more refined parameters, and better general F measurements.

The Fourier refinement of the projections on 001 and 100 was then continued. Three further successive refinements in each case reduced the values of R to 0.35 and 0.32 respectively; no fresh changes of sign were produced by the last refinement, so it was assumed that the limit of accuracy had been reached, by the means employed so far.

h0l Fs were now calculated, with the parameters attained from the last refinement. These gave R = 0.38. It was felt that in the case of this small zone, the Wilson method of obtaining absolute Fs was probably not as satisfactory as in the case of the larger zones. The quantity $\frac{\Sigma F\text{ calc.}}{\Sigma F\text{ obs.}}$ for F obs. >0, was computed for five equal ranges of $\sin^2\theta$, for each zone. On plotting the three sets of points, it was in fact discovered that the departure from unity was only significant in the case of the h0ls. Correction of these Fs was accordingly made using the curve suggested by this means. R now fell to 0.32.

The Fourier syntheses on 001 and 100 from which the final parameters above were derived are shown (figs. 10 and 11). Note that here the unique quarter

Table 4.

General F agreement from original structure.

	($h = 2$, $l = 3$)		($h = 2$, $l = \overline{3}$)	
k	F obs.	F calc.	F obs.	F calc.
0	0	0	0	0
1	0	$\overline{1}$	28	$\overline{20}$
2	22	10	79	84
3	63	$\overline{54}$	32	12
4	45	46	50	$\overline{37}$
5	32	31	47	26
6	17	12	50	35
7	102	120	89	$\overline{97}$
8	54	$\overline{57}$	54	60
9	17	20	52	$\overline{52}$
10	0	$\overline{5}$	40	$\overline{30}$
11	22	$\overline{24}$	24	15
12	28	32	28	$\overline{42}$
13	0	$\overline{4}$	0	$\overline{8}$
14	10	$\overline{21}$	0	$\overline{11}$
15	0	5	0	7
16	0	$\overline{19}$	0	19
17	39	$\overline{47}$	55	59
18	0	25	0	18
19	0	7	0	$\overline{9}$
20	0	$\overline{10}$	0	9
21			22	$\overline{32}$
22			22	27
23			32	$\overline{29}$
24			17	$\overline{38}$

Scale 1" = 1A°, in Figs. 10 - 13.

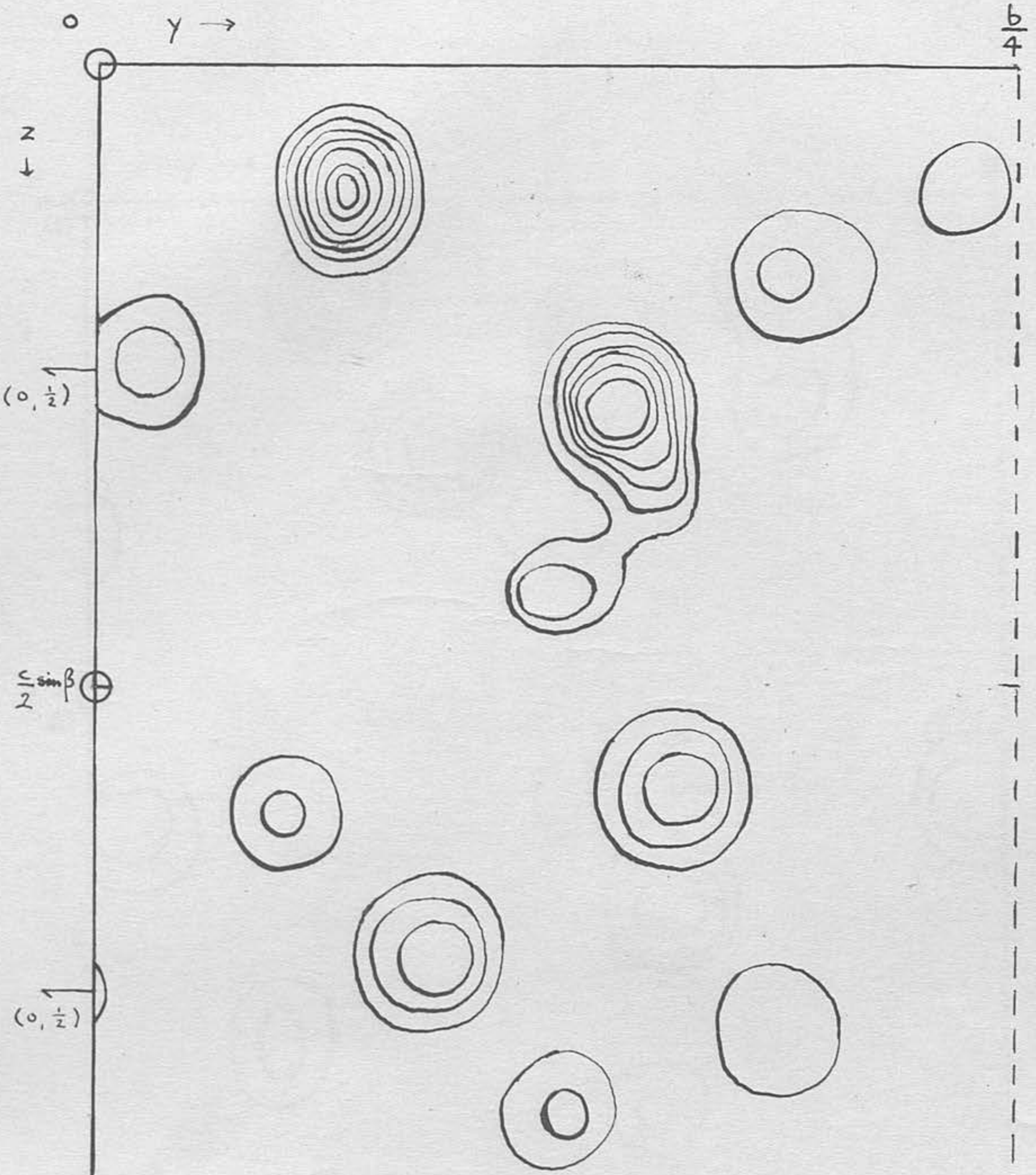


Fig. 10. Fourier projection on 100.
(Contours at 10, 15...40 electrons/A°^{2}.)

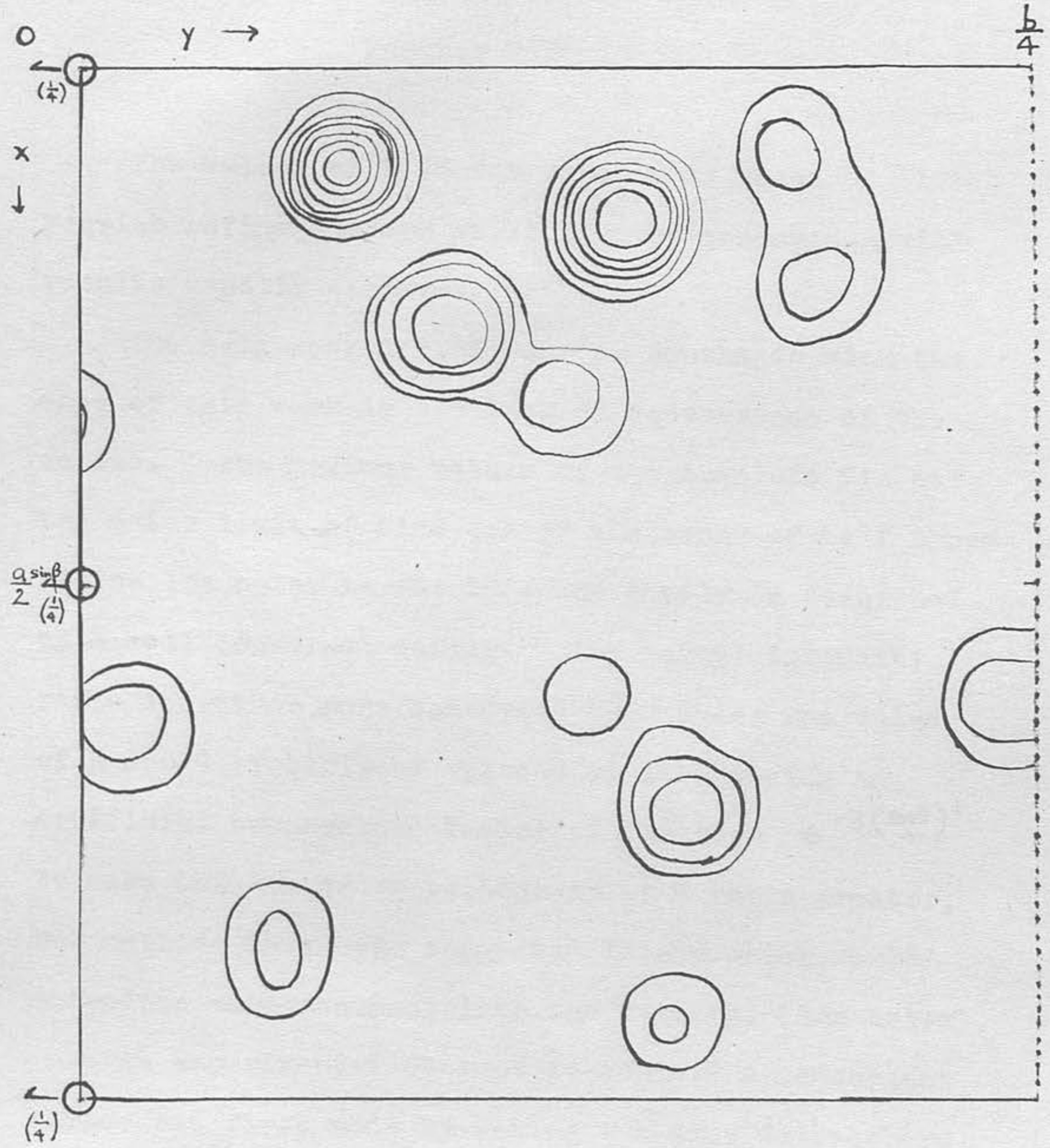


Fig. 11. Fourier projection on 001.

(Contours at 10. 15....40 electrons/A^{o2}.)

of the cell x- 0-1, y- 0-$\frac{1}{4}$, z- 0-1, has been used for convenience of representation.

There is a lack of evenness in the heights of the oxygen atoms which leaves much to be desired.

Further Refinement.

The values of R so far reached by means of direct Fourier refinement are still high by comparison with results usually achieved.

The main weakness of Fourier synthesis with the data of this work is the lack of convergence of the series. The maximum values of the absolute F's at the outer limit of sinθ are of the order of half those of the low order terms; this can hardly be described as a well converged series. The actual intensity ratio is rather more converged than this; the value of R could probably be reduced by introducing an artificial temperature factor of the form $e^{-B\left(\frac{\sin\theta}{\lambda}\right)^2}$ to make the low-order to high-order F ratio greater, but methods have been suggested lately which would introduce more accuracy into the results. (See below).

An experimental attempt to achieve a convergent series was first made by taking a c-axis Weissenberg photograph with Molybdenum K-α radiation. It was found however, that while more than twice the number of reflections than given by Copper K-α are theoretically recordable, the intensity falls off so rapidly with sinθ that no~~w~~ more information is in fact attained even on prolonged exposure.

The question of obtaining the greatest possible accuracy in atomic positions by Fourier and other methods has been very fully discussed by Cochran (28). He shows that all such methods are in fact a process of minimising a function related to $\sum(F_o-F_c)2$. Where the series is convergent and the projection resolved, direct Fourier synthesis minimises $\sum \frac{1}{f_r}(F_o-F_c)^2$. These conditions are however, not usually realised in practice. For an overlapped projection the least-squares method of minimising the function $\sum(F_o-F_c)^2$ has been of service (29). This process would also correct for lack of convergence as it is a means of increasing the agreement between F obs. and F calc. which is mechanical, and does not involve choosing atomic positions from a synthesis affected by the lack of convergence. Cochran however, shows that the minimising process correcting for the latter could also be carried out by computing Fourier projections using as coefficients (F obs. - F calc.). The gradient of this function at the positions used to give F calc. values will determine the shift necessary for atomic positions giving a minimum $\sum \frac{1}{f_r}(F_o-F_c)^2$, from the relation

$$\Delta = \frac{\left(\frac{dD}{dr}\right)_{r=0}}{2p\,\rho_o(0)}$$

(see over)

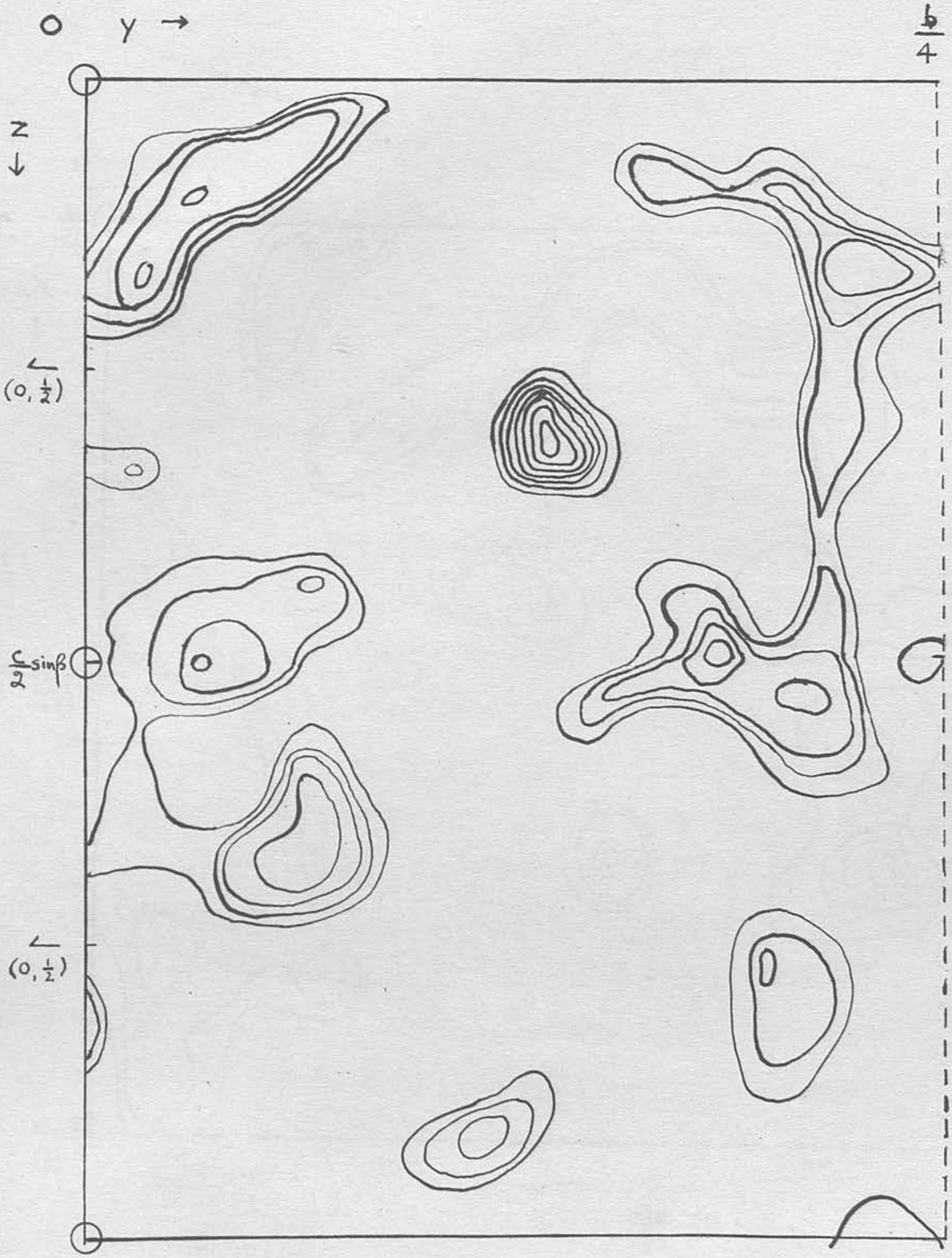


Fig. 12. (Fo - Fc) synthesis on 100.

(Contours at 1,2,3......electrons/A$^{0\,2}$.)

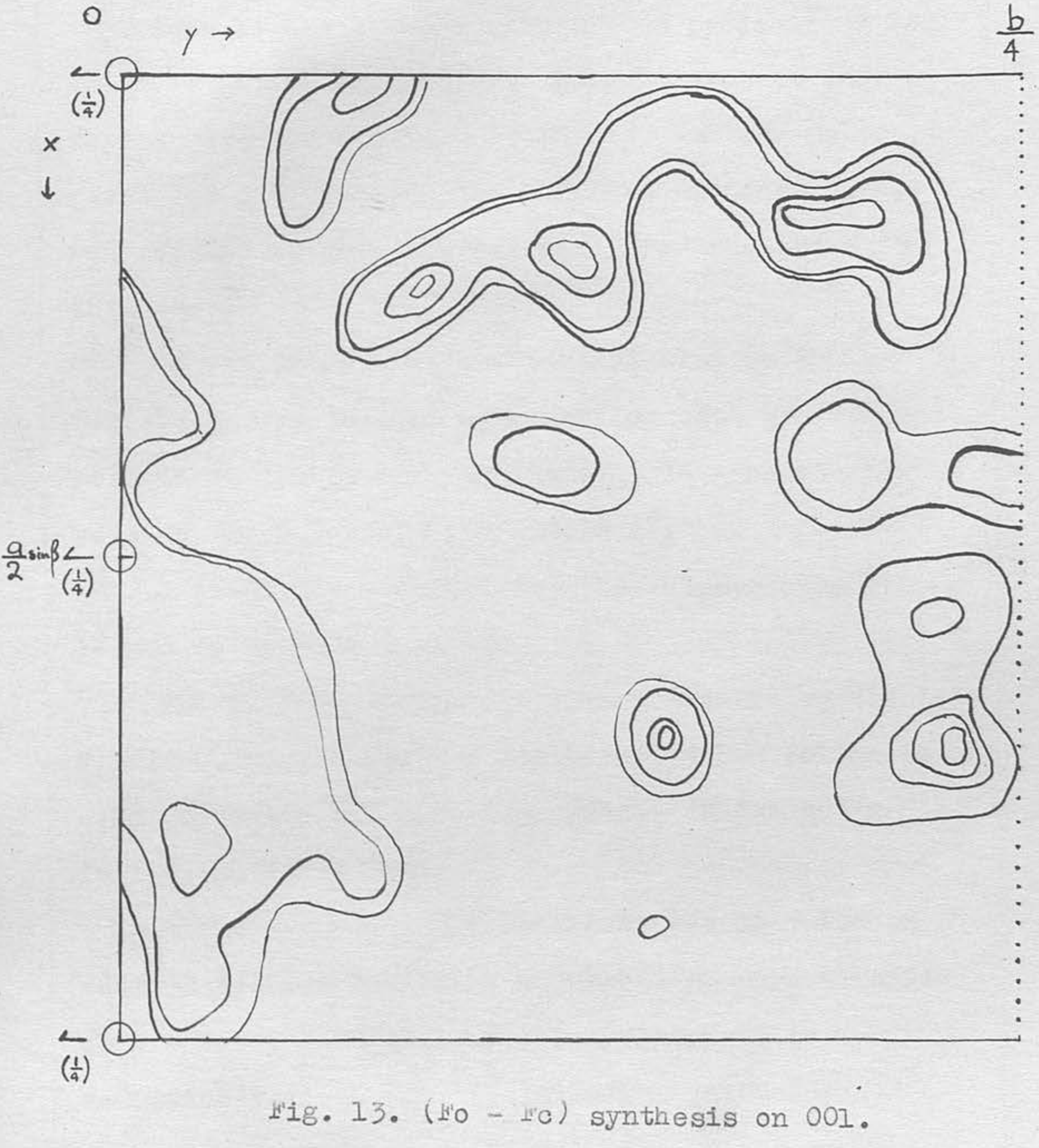


Fig. 13. (Fo - Fc) synthesis on 001.

(Contours at 1,2,3.... electrons /A°^{2}.)

where Δ is the shift required, $\frac{dD}{dr}$ the slope at the atomic centre, $\rho_0(0)$ the height of the atom concerned and p a constant giving the height at small distances (r) from the centre in terms of an exponential function of r, and $\rho_0(0)$.

Such syntheses were computed on projections 100 and 001; (Figs. 12 and 13). $\rho_0(0)$ was taken as the values given by the full syntheses, and the value given for p by Cochran for nitrogen and carbon, 4.9, was assumed to hold approximately for the atoms in this case.

It was found that shifts indicated in the y direction were in good agreement on both projections, both in direction and magnitude. In general they were of the order of 0.05 - 0.10 A^o.

A shift was obtained for the sulphur atom overlapped by an oxygen on 100.

The resulting parameters were used to recalculate F values, and it was now found that R had fallen to 0.26 for 0kl's and 0.29 for hk0's. R for h0l's fell slightly to 0.31.

A further $(F_o - F_c)$ synthesis was computed on each projection but these suggested no more significant shifts. F obs. - F calc. agreement is accordingly given for the following parameters:-

(see over)

Final Structure.

(Parameters in A^{o}, but derived from x and z in 120ths, y in 360ths, as in Table 3.)

	x	y	z
S_1	0.62	1.50	0.82
S_2	0.86	3.06	2.07
Na_1	4.13	7.38	0.56
Na_2	1.44	8.83	1.57
O_1	1.92	2.64	3.26
O_2	5.28	3.30	2.57
O_3	1.15	4.20	1.38
H_2O_4	3.55	5.04	0.88
H_2O_5	0.58	6.72	2.13
H_2O_6	3.60	7.97	2.69
H_2O_7	4.98	9.60	0.88
H_2O_8	3.74	0.30	1.88

The positions are considered correct to the nearest unit of cell edge above, shifts of such magnitude being sufficient to worsen the agreement. This gives a maximum error of 0.03 in the positions and 0.06 A^{o} in the resulting bond lengths. The maximum bond angle error is estimated at 5^{o}.

Fobs. - Fcalc. agreement.*

Okl F's.

k	l	Fo	Fc
0	2	87	102
	4	33	34
	6	50	62
	8	0	17
1	1	38	17
	2	48	34
	3	8	4
	4	49	39
	5	36	39
	6	30	28
	7	29	39
	8	9	2
	9	0	8
2	0	16	6
	1	47	46
	2	0	2
	3	12	13
	4	0	1
	5	0	4
	6	16	21
	7	9	19
	8	22	25
	9	0	7
3	1	43	44
	2	31	21
	3	26	18
	4	15	4
	5	9	6
	6	18	13
	7	31	45
	8	23	25
	9	13	4
4	0	76	130
	1	37	31
	2	42	19
	3	55	57
	4	15	2
	5	26	22
	6	16	16
	7	22	34
	8	12	20
	9	0	6
5	1	31	7
	2	89	116
	3	53	36
	4	46	46
	5	48	66
	6	9	16
	7	28	41
	8	34	37
	9	0	5
6	0	45	31
	1	13	3
	2	54	36
	3	46	34
	4	48	54
	5	36	39
	6	9	7
	7	0	5
	8	19	29
	9	0	5
7	1	66	79
	2	47	24
	3	48	29
	4	41	42
	5	22	18
	6	18	13
	7	35	41
	8	0	5
	9	26	28
8	0	14	4
	1	54	49
	2	22	11
	3	74	101
	4	45	40
	5	26	15
	6	0	10
	7	0	12
	8	8	3
	9	8	11
9	1	43	18
	2	64	73
	3	15	14
	4	50	48
9	5	9	13
	6	20	16
	7	0	11
	8	23	31
10	0	60	53
	1	57	51
	2	47	36
	3	48	39
	4	43	47
	5	46	61
	6	9	24
	7	0	4
	8	0	20
11	1	26	14
	2	59	61
	3	15	4
	4	57	68
	5	23	16
	6	32	37
	7	29	23
	8	27	26
12	0	25	23
	1	58	60
	2	0	4
	3	26	24
	4	0	1
	5	21	0
	6	18	13
	7	31	27
	8	0	0
13	1	0	1
	2	27	10
	3	45	30
	4	39	25
	5	41	69
	6	41	44
	7	35	30
	8	14	16
14	0	64	73
	1	13	0
	2	24	16
	3	13	10
	4	16	14
	5	24	31

---

* S^{-1}, Na^{+1}, O neutral.

Fobs. - Fcalc agreement.

0kl F's continued.

k	l	Fo	Fc
14	6	25	$\overline{30}$
	7	8	20
	8	16	27
15	1	43	$\underline{37}$
	2	0	$\underline{15}$
	3	35	$\underline{30}$
	4	29	$\underline{31}$
	5	26	$\underline{19}$
	6	0	5
	7	14	1
16	0	19	$\underline{24}$
	1	57	56
	2	16	11
	3	21	$\underline{28}$
	4	34	$\underline{32}$
	5	27	$\underline{19}$
	6	0	10
	7	24	25
17	1	33	27
	2	13	$\underline{8}$
	3	37	$\underline{36}$
	4	0	2
	5	18	18
	6	36	$\underline{34}$
	7	36	23
18	0	38	$\overline{\underline{40}}$
	1	35	33
	2	50	$\underline{69}$
	3	43	$\underline{51}$
	4	40	$\underline{42}$
	5	22	$\underline{21}$
	6	0	2
	7	30	34
19	1	41	$\overline{\underline{46}}$
	2	32	30
	3	23	$\underline{27}$
	4	0	7
	5	28	33
	6	11	21
20	0	17	$\underline{12}$
	1	9	$\underline{2}$
	2	32	$\underline{36}$
	3	0	3
	4	25	30
	5	22	8
	6	13	14
21	1	16	$\overline{\underline{13}}$
	2	35	28
	3	29	$\underline{25}$
	4	19	$\underline{23}$
	5	0	3
	6	00	6
22	o	5	$\overline{\underline{2}}$
	1	32	$\underline{28}$
	2	47	47
	3	27	31
	4	51	40
	5	0	2
23	1	26	$\overline{12}$
	2	20	9
	3	19	$\underline{15}$
	4	13	4
	5	17	3
24	0	48	$\overline{44}$
	1	24	19
	2	34	31
24	3	30	$\underline{28}$
	4	13	4
25	1	0	$\overline{7}$
	2	26	$\underline{25}$
	3	20	21
	4	27	34
26	0	0	10
	1	50	38
	2	25	18
	3	15	8
27	1	19	$\underline{18}$
	2	0	3

Fobs. - Fcalc. agreement.

hko F's.

k	h	Fo	Fc
0	1	75	81
	2	90	90
	3	5	7
	4	73	84
	5	38	55
	6	16	11
	7	11	7
1	1	58	39
	2	103	96
	3	0	8
	4	22	30
	5	21	20
	6	19	18
	7	0	3
2	0	16	6
	1	22	18
	2	0	4
	3	5	3
	4	13	9
	5	18	24
	6	0	6
	7	0	0
3	1	70	57
	2	9	8
	3	6	10
	4	18	4
	5	0	1
	6	19	21
	7	15	28
4	0	76	130
	1	62	45
	2	54	52
	3	14	5
	4	0	5
	5	22	33
	6	0	2
	7	29	21
5	1	11	8
	2	9	12
	3	15	20
5	4	47	55
	5	59	60
	6	0	11
	7	37	32
6	0	45	31
	1	20	5
	2	13	13
	3	14	15
	4	0	3
	5	0	1
	6	25	32
	7	14	6
7	1	57	42
	2	16	15
	3	53	42
	4	19	25
	5	11	9
	6	19	21
	7	0	3
8	0	14	4
	1	99	94
	2	13	13
	3	54	56
	4	17	16
	5	35	39
	6	35	45
	7	0	4
9	1	103	89
	2	11	7
	3	15	11
	4	32	39
	5	38	35
	6	20	9
	7	46	49
10	0	60	53
	1	46	29
	2	20	13
	3	20	17
	4	49	50
	5	19	30
	6	11	15
11	1	26	32
	2	31	23
	3	48	39
	4	0	10
	5	25	34
	6	16	8
12	0	25	23
	1	8	10
	2	14	12
	3	24	10
	4	28	24
	5	22	27
	6	35	41
13	1	31	21
	2	22	16
	3	28	21
	4	0	0
	5	37	37
	6	19	20
14	0	64	73
	1	37	44
	2	0	0
	3	27	32
	4	41	56
	5	20	28
	6	10	7
15	1	0	4
	2	33	43
	3	0	1
	4	30	40
	5	20	15
	6	17	14
16	0	19	24
	1	22	16
	2	32	28
	3	15	15
	4	48	62
	5	0	8
	6	0	16
17	1	55	51

Fobs. - Fcalc. agreement.

hk0 F's continued.

k	h	Fo	Fc	k	h	Fo	Fc	k	h	Fo	Fc
17	2	61	$\overline{\underline{78}}$	20	0	17	12	23	1	26	$\overline{\underline{15}}$
	3	19	$\underline{29}$		1	15	$\underline{21}$		2	27	24
	4	16	11		2	22	$\underline{24}$		3	19	26
	5	15	9		3	19	28		4	8	16
					4	15	23				
18	0	38	$\overline{\underline{40}}$		5	0	6	24	0	48	$\overline{\underline{44}}$
	1	15	24						1	37	$3\underline{8}$
	2	15	14	21	1	22	31		2	11	4
	3	19	35		2	0	$\underline{6}$		3	26	36
	4	16	$\underline{14}$		3	16	11		4		
	5	19	13		4	15	18	25	1	19	16
									2	45	36
19	1	33	41	22	0	5	$\overline{\underline{2}}$		3	37	38
	2	0	$\underline{1}$		1	11	$\underline{13}$				
	3	32	$\underline{30}$		2	11	$\underline{12}$	26	0	0	10
	4	30	$3\underline{4}$		3	16	12		1	0	7
	5	0	9		4	0	1		2	0	8
								27	1	39	31

hol F's.

h	l	Fo	Fc	h	l	Fo	Fc	h	l	Fo	Fc
0	2	87	$\overline{\underline{102}}$	2	$\overline{\underline{2}}$	54	76	4	$\overline{\underline{6}}$	15	$\underline{8}$
	4	33	$\underline{34}$		$\underline{4}$	36	$\underline{35}$		8	57	51
	6	50	62		$\underline{6}$	11	18				
	8	0	17		8	34	39	5	0	38	$\overline{\underline{53}}$
									2	34	30
1	0	75	$\underline{81}$	3	0	5	$\overline{7}$		$\underline{4}$	40	47
	2	39	39		2	10	$\underline{18}$		$\underline{2}$	21	$\underline{8}$
	4	50	59		4	57	64		$\underline{4}$	24	16
	6	21	$\underline{10}$		$\underline{6}$	50	41		$\underline{6}$	58	$\underline{73}$
	$\underline{8}$	19	$\underline{8}$		$\underline{2}$	60	69		8	30	39
	$\underline{2}$	47	$\underline{35}$		$\underline{4}$	42	$\underline{53}$				
	$\underline{4}$	64	$\underline{78}$		$\underline{6}$	46	63	6	0	16	$\overline{\underline{15}}$
	$\underline{6}$	39	27		8	0	7		2	22	15
	8	49	41						$\underline{4}$	49	45
				4	0	73	$\overline{85}$		$\underline{2}$	0	4
2	0	90	$\overline{\underline{90}}$		2	15	16		$\underline{4}$	0	13
	2	33	$\underline{22}$		4	35	46		6	19	18
	4	70	73		$\underline{6}$	49	40				
	6	59	84		$\underline{2}$	29	18	7	$\underline{0}$	11	$\underline{9}$
	8	0	7		4	0	14		$\underline{2}$	29	29
									$\underline{4}$	22	$\underline{9}$
									6	17	21

Chapter 6.

(1) Discussion of the Results.

A diagram of the structure in a full unit cell is shown in projection on the 100 plane, (see end). The main features have already been mentioned in chapter 5; to enlarge on this it seems best to give first the values of all bond lengths and angles. A schematic diagram of the bonds is given. (Fig. 14).

The Thiosulphate Group.

(Distances in A^o; angles in degrees.)

$S_1 — S_2$ 1.97
$S_2 — O_1$ 1.46
$S_2 — O_2$ 1.59
$S_2 — O_3$ 1.40

(Bond angles all between 104° and 115°, average 110°.)

(non-bonded) $S_1 — O$ 2.74, 2.74, 2.85.
$O — O$ 2.43, 2.44, 2.48.

Na_1 Group.

$Na_1 — O_2$ 2.39
$— H_2O_7$ 2.38
$— H_2O_4$ 2.45
$— H_2O_6$ 2.38
$— O_1$ 2.39
$— H_2O_5$ 2.53

(adjacent angles range from 84°— 107°, average 89°.)

Na_2 Group.

Na_2 — H_2O_5 2.41
— H_2O_6 2.40
— H_2O_7 2.33
— H_2O_8 2.36
— O_1 2.35
— S_1 3.36

(adjacent angles 73° — 103° average 89°.)

S_1 Group.

S_1 — S_2 1.97
— H_2O_7 3.35
— H_2O_8 3.35
— H_2O_8 3.38
— H_2O_6 3.31
— Na_2 3.36

(Angles S_2-S_1-X range from 97°-118°. Angles X-S_1-X range from 57°-84° (where X is any H_2O))

Remaining bond lengths.

O_3 — H_2O_4 2.77
O_3 — H_2O_5 2.74
O_3 — H_2O_5 2.94
H_2O_4 — O_2 2.79
H_2O_4 — H_2O_6 2.99
H_2O_7 — H_2O_8 2.92

Na_1 — Na_2 distances ---3.49, 3.43.

Bond angles of oxygen atoms.

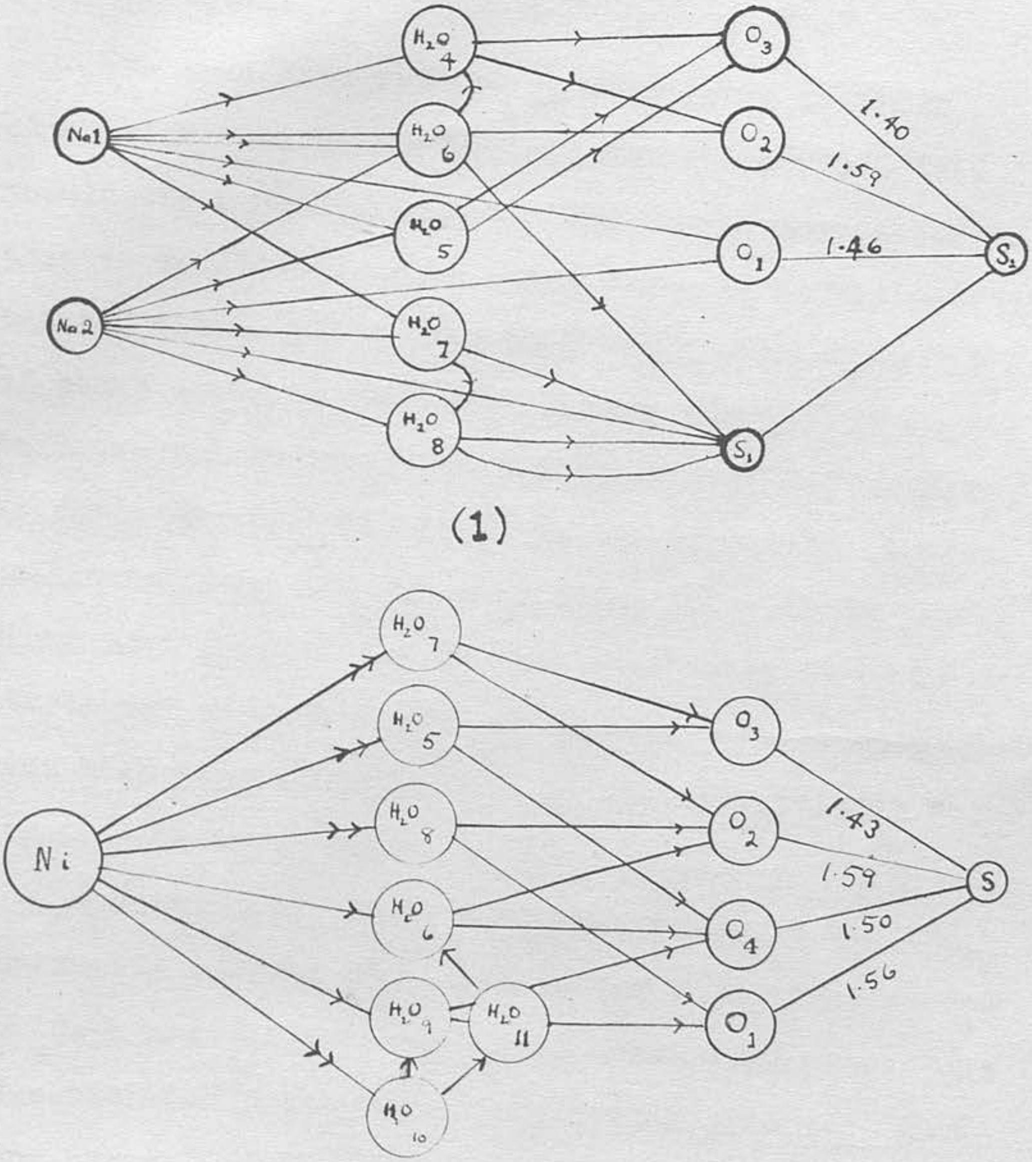
O_1	95,* 122, 146°.
O_2	93, 151, 113°.
O_3	116, 122, 92, 80, 129, 109°.
H_2O_4	101, 91, 78, 122, 124, 127°.
H_2O_5	88,* 109, 107, 127, 128, 106°.
H_2O_6	94,* 104, 134, 115, 116, 94°.
H_2O_7	91, 126, 93,* 141, 101, 110°.
H_2O_8	123, 101, 126, 112, 83, 102°.

(* angle subtended by Na_1 and Na_2.)

The structure of the thiosulphate group is of primary interest. Considering first the role of the sulphurs, the electron density on both 100 and 001 gives that of S_1 rather higher than S_2, the ratio being about 1.07 : 1. This might indicate some tendency to coordinate bond formation from the central sulphur. The bond length, 1.97, is about 0.1 A° shorter than the Pauling single bond radius.

The differing length of the sulphur-oxygen bonds is difficult to explain, though after allowance for possible maximum error it is not perhaps highly significant.

It will be appreciated that in most structure determinations so far carried out of sulphate and related ion salts, whether hydrated or non-hydrated, the group has been situated upon a symmetry element so that the sulphur-oxygen distances are invariant.



(1)

(2)

Fig. 14. Schematic diagram showing bonds in (1) $Na_2S_2O_3 5H_2O$; (2) $NiSO_4 7H_2O$. Directions shown give water molecules two incoming and two outgoing (hydrogen) bonds.

An exception to this is nickel sulphate heptahydrate (Beevers and Schwartz, 14) in which the four bond lengths are 1.56, 1.59, 1.43 and 1.50 A° (Fig. 14). The authors however, claim an accuracy in atomic position of only 1 A^{O}, and make no comment upon the variations.

The bond structure of this compound is shown along with that of the present structure (Fig. 14). Should the nickel sulphate structure be more accurate than it is claimed to be there seems no correspondence between the length of the S — O bonds and the number of other contacts that each oxygen makes. It would be reasonable however, to attribute such differences to environmental effects. In the hypo case it seems unexpected that the oxygen holding three other bonds shows most shortening, if such shortening is to be attributed to double bond character. It is concluded that much more accurate data is required to give any significant information.

A distinctive feature of the structure are the continuous columns of linked sodium octahedral groups in the a axis direction. Each octahedron shares one edge with the preceding and following groups. Thus four oxygen or water atoms form direct links between the two sodiums; O_1 and H_2O_6, then H_2O_5 and H_2O_7. Now the distance between the two sodiums is 3.50 or roughly the square root of twice the square of the sodium coordination distance. Consequently the linking oxygen atoms are constrained to form squares with the sodiums, and the O-Na- O angles are roughly 90°. The other bonds formed by the oxygens depart from the average tetrahedral or trigonal angle in consequence.

The contacts made by the external sulphur atom (1) are six in number but not octahedrally disposed. The five long contacts, to Na_2, and to water oxygens (a new type of hydrogen bond) are inclined roughly equally away from the S-S bond at about 110°. Between each other they make angles of about 75°. Thus the group resembles a parasol "inside out"; two such inverted parasols face each other, stems, i.e. S-S bonds, pointing outwards, across the centres of symmetry.

The water molecules all make four contacts though all show angles much deformed from a tetrahedral disposition, for reasons already mentioned. Oxygen-water and water-water distances (hydrogen bonds) are all of the usual length, 2.7 - 2.9 A°.

The electron-pair content of the sodium coordination groups, following the ideas suggested in the introduction, will approximate to 6 in each case. The average coordination distance is that usually found.

(2) Discussion of methods used.

Some consideration of the general applicability of the methods used to derive the structure seems appropiate.

The vast majority of space-groups of complex structures are multiple; it is therefore to be expected that the special-vector methods used here could in general be successful to find particular atoms. Unless these are of outstanding weight it will of course be desirable to calculate the Patterson function in three dimensions. The possible use of the special vector and vector-convergence methods with searcher atoms no heavier than those of the rest of the structure (e.g. in the case of an organic compound) is an interesting question. Any prophecies must obviously await experimental confirmation, but it seems possible that, given the Patterson function calculated with greater refinement and at a shorter interval than that employed here, success is feasible. It has been shown (Fig. 5) (table 3) that Patterson peaks show a high degree of accuracy in position, provided resolution is obtained. It is now felt that for this purpose it is important to include as many terms as possible, particularily when dealing with lighter vectors.

The methods of Buerger (27) are similar in some respects. They involve the isolation of one or more single vectors followed by a multiplication of the Patterson function at the ends of a vector as it ranges through the whole volume of the function.

Such methods might well be more advantageous when dealing with a smaller number of searcher atoms, as multiplication will not produce so much spurious height as addition. Experimental contrasting of the two approaches is not yet available.

Appendix.

Collected structure factor and electron density formulae.

All such formulae employed in the course of the work are given here.

The origin and axes given in the 'Internationale Tabellen zur Bestimmung von Kristallstrukturen', were used throughout. $\cos 2\pi \frac{hx}{a}$, $\sin 2\pi \frac{ky}{b}$ etc., will be abbreviated to cos hx, sin ky, etc.

Structure Factor Calculations.

The space group $P2_1/c$ is centro-symmetric, so B' is 0 throughout where $|F^2 hkl| = A'^2 + B'^2$.

Then $Fhkl = A' = \sum f_r A$, the summation extending over all crystallographically distinct atoms in the cell.

Lonsdale (31) gives

(1) $A = 4\cos(hx + lz).\cos ky$ where $k + l = 2n$.

(2) $A = -4\sin(hx + lz).\sin ky$ where $k + l = 2n + 1$.

In (1) $F(hkl) = F(h\bar{k}l)$; in (2) $F(hkl) = -F(h\bar{k}l)$

but $F(\bar{h}kl) = \underset{=-F(hk\bar{l})_{(2)}}{F(hk\bar{l})^{(1)}} \neq F(hkl)$ in both cases.

Then for $F(hk0)$, $A = 4\cos hx.\cos ky$, where $k = 2n$,

$A = -4\sin hx.\sin ky$, " $k = 2n + 1$;

for $F(0kl)$, $A = 4\cos.ky.\cos lz$, " $k + l = 2n$,

$A = -4\sin ky.\sin lz$, " $k + l = 2n+1$;

for $F(h0l)$, $A = 4\cos hx.\cos lz - 4\sin hx.\sin lz$,

for $F(h0\bar{l})$, $A = 4\cos hx.\cos lz + 4\sin hx.\sin lz$.

Electron Density Formulae.

Lonsdale's formulae for ρ, the electron density for $P2_1/c$ is:-

$$\rho_{xyz} = \frac{4}{V_c}\left\{\overset{k+l=2n}{\sum_0^\infty\sum_0^\infty\sum_0^\infty}\left[F(hkl)\cos(hx+lz)+F(\bar{h}kl)\cos(-hx+lz)\right]\cos ky - \overset{k+l=2n+1}{\sum_0^\infty\sum_0^\infty\sum_0^\infty}\left[F(hkl)\sin(hx+lz)+F(\bar{h}kl)\sin(-hx+lz)\right]\sin ky.\right\}$$

Using this or reduced versions, $F(0k0)$, $F(00l)$, $F(h00)$ and $F(h0l)$ must be divided by 2. In such a way the formulae

$$\rho_{oyz} = \frac{4a}{V_c}\left[\overset{k+l=2n}{\sum_0^\infty\sum_0^\infty} F(0kl)\cos ky.\cos lz - \overset{k+l=2n+1}{\sum_0^\infty\sum_0^\infty} F(0kl)\sin ky,\sin lz,\right]$$

and

$$\rho_{xy0} = \frac{4c}{V_c}\left[\overset{k=2n}{\sum_0^\infty\sum_0^\infty} F(hk0)\cos hx.\cos ky - \overset{k=2n+1}{\sum_0^\infty\sum_0^\infty} F(hk0)\sin hx.\sin ky.\right]$$

were used.

The Patterson Synthesis.

The general formula is

$$P_{xyz} = |F^2hkl| \cos(hx+ky+lz).$$

In the following expansions of this formula used, $F^2(0k0)$, $F^2(00l)$, $F^2(h00)$ and $F^2(h0l)$ were divided by 2.

$$P_{xyo} = 4\sum_0^\infty\sum_0^\infty F^2(hk0)\cos hx.\cos ky, \text{ since } F^2(hk0)=F^2(\bar{h}k0)$$

$$P_{Oyz} = 4\sum_0^\infty\sum_0^\infty F^2(0kl)\cos ky.\ \cos lz, \text{ since } F^2(0kl)=F^2(0k\bar{l})$$

$$P_{xOz} = 4\left\{\sum_0^\infty\sum_0^\infty\left[F^2(h0l)+F^2(h0\bar{l})\right]\cos hx.\cos lz - \sum_0^\infty\sum_0^\infty\left[F^2(h0l)-F^2(h0\bar{l})\right]\sin hx.\sin lz,\right\}\text{since } F^2(h0l)\neq F^2(h0\bar{l}).$$

and for three-dimensional work,

$$P_{xyz} = 4\left\{\sum_0^\infty\sum_0^\infty\sum_0^\infty\left[F^2(hkl)+F^2(hk\bar{l})\right]\cos hx.\cos ky.\ \cos lz - \sum_0^\infty\sum_0^\infty\sum_0^\infty\left[(F^2(hkl)-F^2(hk\bar{l})\right]\sin hx.\cos ky.\ \sin lz\right\}$$

-as $F^2(hkl) = F^2(h\bar{k}l)$.

but $F^2(hkl) \neq F^2(hk\bar{l})$.

(2) Methods of Calculation.

Fourier projections and all Patterson sections and projections were calculated in 60ths of b, and 30ths of a andc. All summations necessitated for this were very conveniently carried out on the machine built for such work, in one dimensions, by Dr. F. Stern (31). This machine was constructed of telephone equipment on the Hägg-Laurent type, and is capable of summing a complete set of sin and cosine waves, with wave-numbers up to 15 and amplitudes of

0-100, over all four quadrants, with one setting of amplitudes. Wave-numbers of 0 - 30 can be summed with two settings of amplitudes, for even and odd 60ths. Tests show a maximum error of 4 units in all readings.

The immense assistance provided by this machine need not be stressed. The work involved in the average two-dimensional summation, a matter of some 20 hours using the Beevers-Lipson strips, is reduced to four hours. The possibility of obtaining all four quadrants of a full sine-cosine summation without re-arranging additions etc., is very valuable in this connection. Using maximum amplitude values the accuracy is quite sufficient for work utilising visually-measured intensities.

F. Calculations were done in the units given from prepared tables of $\sin 2\pi hx$ and $\cos 2\pi hx$ etc., in such units. For summing the eight oxygen atoms with respect to x and z, the Beevers-Lipson strips in 3° intervals were used. It might also be mentioned that for earlier F calculations where the coordinates were expressed in 60ths of a and c, the Stern machine was employed to sum the oxygens with respect to x and y.

Acknowledgements.

The writer wishes to record her sincere gratitude to Dr. C. A. Beevers for the advice and encouragement given by him at all times during the course of this work.

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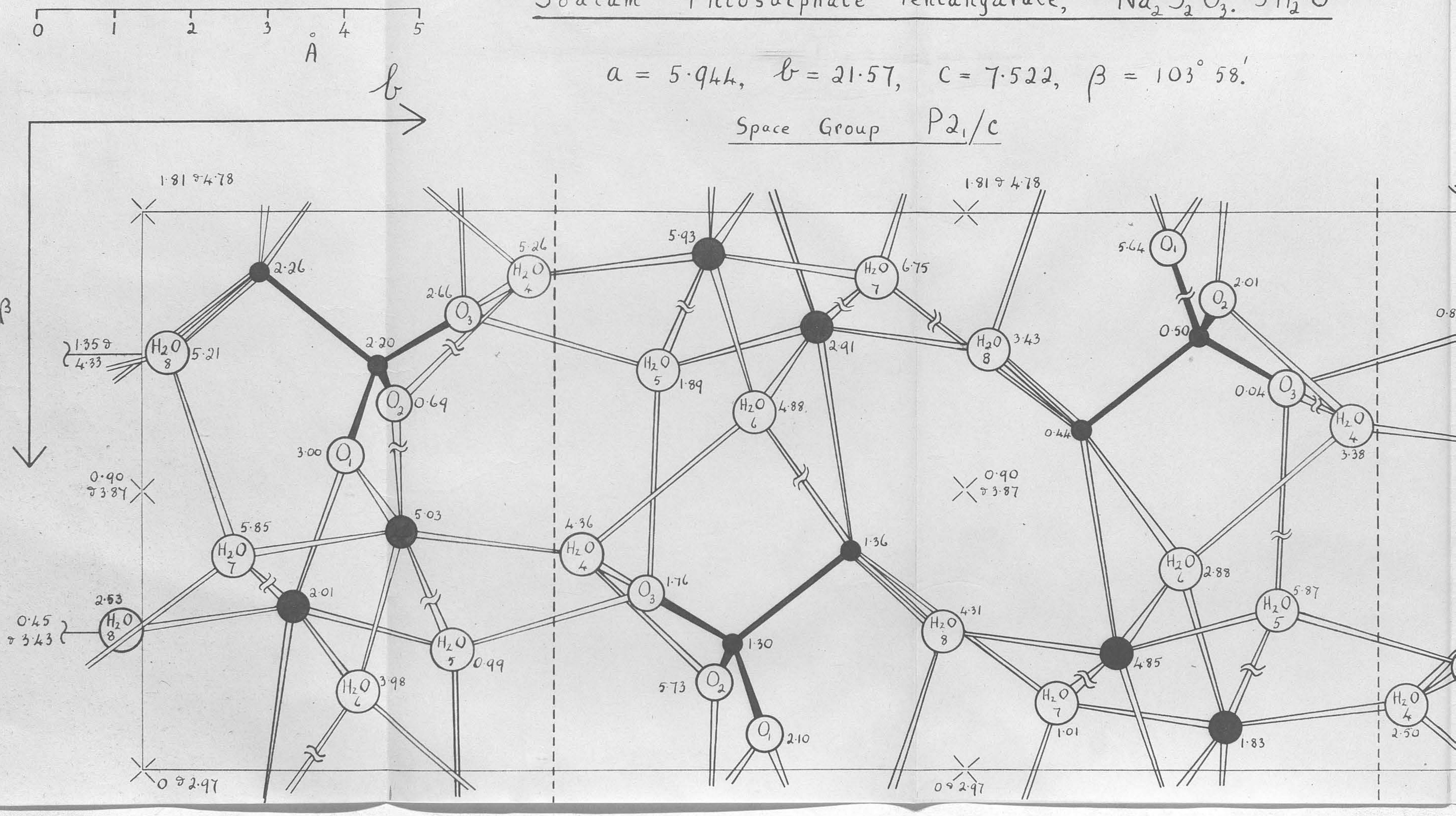
Sodium Thiosulphate Pentahydrate, $Na_2S_2O_3 . 5H_2O$

$a = 5·944$, $b = 21·57$, $c = 7·522$, $\beta = 103° 58'$

Space Group $P2_1/c$



ahydrate, $Na_2S_2O_3.\ 5H_2O$

= 7·522, β = 103° 58′.

$2_1/c$

● = Sulphur

● = Sodium

○ = Oxygen

○ = Water

Heights of Atoms in Å above a plane perpendicular to a.