Acta Cryst. (1957). **10**, 574

The Crystal Structure of P_4S_3

By Yuen Chu Leung and Jürg Waser
Chemistry Department, The Rice Institute, Houston, Texas, U.S.A.

and S. van Houten, Aafje Vos, G. A. Wiegers and E. H. Wiebenga
Laboratorium voor Anorganische en Fysische Chemie, Rijksuniversiteit, Groningen, The Netherlands

(*Received* 3 *October* 1956 *and in revised form* 14 *January* 1957)

The crystal structure of P_4S_3 has been determined by X-ray diffraction. Space group *Pmnb*, 8 molecules per unit cell. Two independent structure determinations are described; one by the application of inequalities and two-dimensional least-squares refinement and another by means of a three-dimensional Patterson synthesis and refinement by successive two-dimensional Fourier syntheses. The final coordinates were obtained by three-dimensional least-squares refinement. The crystal consists of P_4S_3 molecules having the same structure as that derived by Hassel & Pettersen in an electron-diffraction study of gaseous P_4S_3. The average P–S and P–P distances are 2·090 and 2·235 Å respectively.

1. Introduction

Of the various sulfides of phosphorus described in the literature (Stock, 1910*a*, *b*, *c*), the existence of P_4S_{10}, P_4S_7, P_4S_5 and P_4S_3 is well established. The crystal structures of P_4S_{10} and P_4S_7 are described by Vos & Wiebenga (1955), and that of P_4S_5 has been determined recently (Van Houten & Wiebenga, 1957).

P_4S_3 was discovered in 1864 by Lemoine and was more fully examined by Stock and later by Treadwell & Beeli (1935). Hassel & Pettersen (1941) found, by electron diffraction of the vapor, a molecular structure with an average bond length of 2·15 Å, which is shown in Fig. 1(*b*). It will be referred to as Hassel's model.

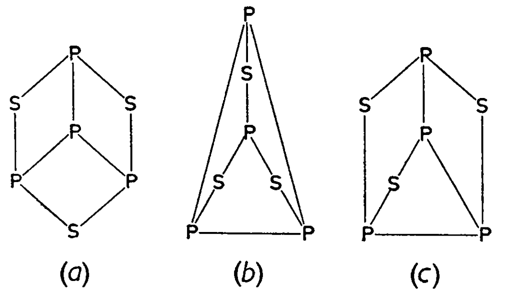

Fig. 1. Proposed structures for P_4S_3.

From theoretical considerations Pernert & Brown (1949) proposed, however, two other structures for the P_4S_3 molecule, which are represented by Figs. 1(*a*) and 1(*c*).

The structure of one of the crystalline modifications of P_4S_3 was determined independently in two laboratories (Leung, Waser & Roberts, 1955; van Houten, Vos & Wiegers, 1955). It was shown that this modification consists of molecules of P_4S_3, the molecules having the structure observed by Hassel & Pettersen (1941).

In the present paper the results of the two preliminary structure determinations are compared, and a three-dimensional least-squares refinement is described which was carried out by Waser and Leung using van Houten's intensity data.

2. Experimental

(*a*) *Material*

The compound was prepared following the procedure of Stock (1910*a*), and was crystallized first from carbon disulfide and then from benzene. By differential thermal analysis, dilatometry and by observation under the polarizing microscope, the crystals were found to have a transition point at 39°±1° C. The heat of transition amounts to *ca.* 3·4 kcal./mol. Only the low-temperature modification was further investigated.

Crystals of this modification were obtained by cooling a solution of P_4S_3 in a mixture of carbon disulfide and benzene from room temperature to 0° C. Crystals were also grown by slow evaporation of a solution in acetone. Most crystals were laths along the *a* axis showing the orthorhombic habit, faces parallel to (100), (010) and (001) being predominant.

For the X-ray work crystals were used having a diameter of approximately 0·1 mm. perpendicular to the crystal axis about which the photographs were made. To avoid oxidation by air, the crystals were sealed in pyrex capillaries.

(*b*) *Unit cell and space group*

Weissenberg and oscillation photographs about the *a* and *b* axes showed the crystals to be orthorhombic. The systematic absences observed were $h0l$ with $h+l$ odd and $hk0$ with k odd which indicated as probable space groups D_{2h}^{16}–$Pmnb$ and C_{2v}^{9}–$P2_1nb$. The statistical method of Howells, Phillips & Rogers (1950) indicated the presence of a center of symmetry, which is compatible with the absence of a pyro- and a piezoelectric effect*. The space group *Pmnb* was therefore tentatively adopted; it was confirmed by the result of the structure determination.

Accurate lattice constants were obtained by means of a special back-reflection camera, using copper radiation. With $\lambda(\mathrm{Cu}K\alpha_2)=1{\cdot}54433$ Å and $\lambda(\mathrm{Cu}K\alpha_1) = 1{\cdot}54051$ Å the following values were found:

$$a = 9{\cdot}660,\quad b = 10{\cdot}597,\quad c = 13{\cdot}671\ \text{Å}\,.$$

The accuracy of these values may be represented by a standard deviation of 0·005 Å.

With eight molecules per unit cell the density was calculated to be 2·08 g.cm.$^{-3}$; the experimental value is 2·03 g.cm.$^{-3}$ (Stock, 1910*a*).

(*c*) *Structure factors*

The intensities of most reflections were measured on integrated equi-inclination Weissenberg photographs (Wiebenga & Smits, 1950) about the *a* axis, using Ni-filtered copper radiation. The weak intensities were visually estimated on ordinary Weissenberg photographs of long exposure time. Use was made of the multiple-film technique.

In this way the intensity data for 954 independent *hkl* reflections were obtained. Lorentz and polarization factors were taken into account and an approximate correction for absorption was applied, assuming the crystal to be a cylindrical rod. The data obtained from different layer lines were related by photographs about the *c* axis. In the course of the structure determination the scaling factors thus obtained were slightly adjusted by comparing calculated and observed structure factors.

3. Determination of the approximate structure

The approximate structure was found by Leung & Waser by application of inequalities and two-dimensional least-squares refinement and independently by van Houten, Vos & Wiegers from a three-dimensional-Patterson synthesis and refinement by means of successive two-dimensional Fourier syntheses. For these two structure determinations two independently measured sets of zonal intensity data were used.

(*a*) *Application of inequalities and two-dimensional least-squares refinement of the coordinates*

The first attempt at solving the structure centered around the zone (0*kl*) since it corresponds to a projection of the electron density which has symmetry centers in either space group. The signs of a number of structure factors were found by the inequalities $(U_H \pm U_{H'}) \le (1\pm U_{H+H'})(1\pm U_{H-H'})$ introduced by Harker & Kasper (1948), and derived in an especially compact way by MacGillavry (1950). These inequalities were applied systematically by using a scheme described by Grison (1951), and were supplemented by more complex inequalities derived by utilizing all symmetry elements of the (100) projection.

To obtain experimental values for the unitary structure factors U_H, the observed structure factors were first put on an approximately absolute scale (Wilson, 1942; Harker, 1948). No corrections for the temperature effect were attempted at this stage. Since the resulting U values were too small, so that very few sign relations were obtained, they were artificially boosted by multiplication by $a \exp(b \sin^2\theta/\lambda^2)$. The constants *a* and *b* were chosen by trial and error so as to lead to as many non-contradictory sign relations as possible. In this way 35 out of the 86 observed structure factors could be provided with signs. A (100) Fourier synthesis using these 35 signs was calculated; in this projection the asymmetric unit showed only nine major peaks to which 14 atoms had to be fitted. Calculations of structure factors with various peaks accounted for by superimposing two or three atoms, however, failed to give reasonable agreement with the experimental values.

The many superpositions suggested the existence of mirror planes parallel to (100), corresponding to space-group *Pmnb*. This was supported by the evidence from the statistical test described previously and the space group was at this point assumed to be *Pmnb*.

Inequalities were then derived with U_{h0l} values which had been boosted in a way similar to the U_{0kl}, and for these reflections 26 of 35 signs could be determined. On a Fourier synthesis based on these 26 reflections Hassel's model (Fig. 2) could easily be fitted. The resulting coordinates were improved somewhat by a second (010) Fourier synthesis. Once these coordinates were available it became clear how the two crystallographically different molecules could be fitted to the preliminary (100) projection.

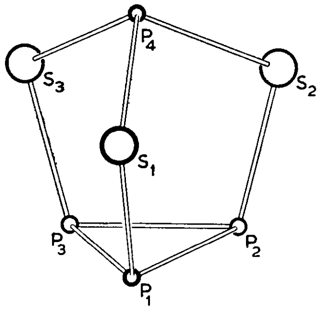

Fig. 2. Molecule of P_4S_3.

The approximate parameters were refined by six least-squares cycles involving the zonal data by the procedure used in the three-dimensional refinement described later. During this refinement the same tem-

---

* The absence of the piezo-electric effect was kindly demonstrated for us by Dr W. G. Perdok, Crystallographic Institute, Groningen, The Netherlands.

perature factor was used for all atoms and only the diagonal terms in the coefficient matrix of the normal equations were calculated. Although this procedure is justifiable when three-dimensional data are employed and the axes are all at right angles, it is less acceptable when only zonal reflections are used. Indeed, it was found that in these two-dimensional refinements the convergence could be improved by permitting the corrections to the atomic parameters to be only one-half of the actually computed amounts.

With a temperature factor $\exp(-2{\cdot}89 \sin^2\theta/\lambda^2)$ a disagreement index $R = 0{\cdot}16$ was obtained. The final parameters are listed in Table 1, with their standard deviations, the r.m.s. value of which is 0·028 Å. These deviations should, however, be viewed with caution because they were computed without taking into account the non-diagonal terms in the coefficient matrix of the normal equations.

(b) *Three-dimensional Patterson synthesis and successive Fourier syntheses of the three projections*

The Patterson synthesis showed a large number of peaks near the plane $(0, y, z)$, which indicated that many atoms had approximately the same x coordinate. Many of the peaks in the section $(\frac{1}{2}, y, z)$, which is a Harker section for the two possible space groups *Pmnb* and $P2_1nb$, are therefore non-Harker maxima, and an examination of this section did not look very promising. An attempt was made to obtain information from the Harker lines $(\frac{1}{2}, y, \frac{1}{2})$ and $(0, \frac{1}{2}, z)$. As on these lines the Harker maxima overlapped to a great extent, it was not possible to determine their positions directly. Use could be made, however, of the fact that vectors between bonded atoms, as represented by peaks around the origin, have to be found also between Harker maxima and general peaks in the Patterson synthesis. In this way some of the maxima on the Harker lines could be located. This procedure gave the y and z coordinates and the relative x coordinates of four atoms. It was now tentatively assumed that these four atoms were repeated in the structure, because the Patterson synthesis showed a remarkably high peak around $x = 0{\cdot}15$, $y = 0{\cdot}00$, $z = 0{\cdot}50$, which was surrounded by other peaks in a similar way as the peak at the origin. Therefore coordinates $x = 0{\cdot}15$, $y = 0{\cdot}00$, $z = 0{\cdot}50$ relative to the known set of four atoms were assigned to a second set of four atoms. The positions of the eight atoms found so far were proved to be approximately correct by comparing the vector diagram of these eight atoms and the atoms symmetrically related to them with the Patterson synthesis. From the positions of some of the remaining peaks relative to the maxima already used, it was now noticed that a further atom connected two of the four atoms of the second set. These five atoms (E, F, G, H and K in Fig. 3), appeared—within the limits of error—to be a part of Hassel's model (Fig. 2), with one of its symmetry planes parallel to the plane $(0, y, z)$.

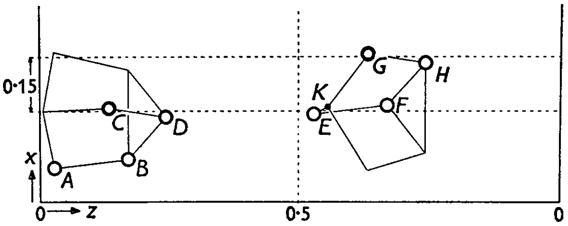

Fig. 3. The first nine atoms deduced from the Patterson map, schematically shown in [010] projection. This figure may be compared with Fig. 5(*b*) giving the [010] projection of the final structure.

Another Hassel molecule could be fitted to the first set of four atoms (A, B, C, and D in Fig. 3) such that one of its symmetry planes coincided with the symmetry plane of the first molecule parallel to $(0, y, z)$. It was then concluded that the space group was *Pmnb*.

The coordinates were refined by successive Fourier syntheses of the three projections. 'Back-shift' corrections for the termination of the series (Booth, 1946)

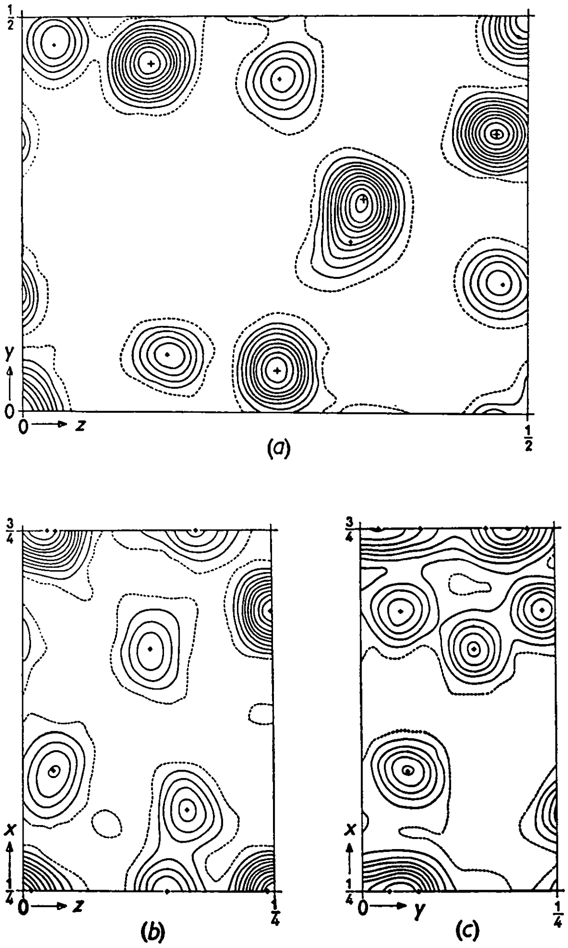

Fig. 4. Electron-density projections along (*a*) [100], (*b*) [010] and (*c*) [001]. Contour lines are at intervals of 4 e.Å^{-2}; the broken line is at 4 e.Å^{-2}. Crosses indicate final atomic coordinates.

were applied in the later stages of this refinement. After the final structure-factor calculation, the signs of 11 out of the 244 observed zonal structure factors remained uncertain. Using for P and S the scattering factors from the *Internationale Tabellen zur Bestimmung von Kristallstrukturen,* and a temperature factor $\exp(-3{\cdot}5 \sin^2 \theta/\lambda^2)$, a value of 0·13 was obtained for the disagreement index R for the observed $0kl$, $h0l$ and $hk0$ reflections. The final electron-density maps are shown in Fig. 4. The atomic coordinates deduced from these maps are given in Table 1; some of these values are averages of independent values obtained from different projections.

Table 1. *Coordinates for the atoms of the asymmetric unit**

Atom	Coordinate	Two-dimensional Fouriers	Least squares on three zones	σ	Three-dimensional least squares	σ
S_1	x	0·584	0·586	0·0034	0·5853	0·00076
	y	0·147	0·149	22	0·1474	58
	z	0·970	0·971	19	0·9711	48
S_3	y	−0·073	−0·068	22	−0·0699	58
	z	0·857	0·857	16	0·8580	48
P_1	x	0·636	0·636	35	0·6341	80
	y	0·232	0·232	23	0·2324	62
	z	0·837	0·840	22	0·8376	51
P_3	y	0·078	0·076	22	0·0801	63
	z	0·756	0·759	20	0·7580	51
P_4	y	0·024	0·019	22	0·0219	62
	z	0·992	0·992	19	0·9934	50
S_1'	x	0·084	0·081	34	0·0851	75
	y	0·560	0·558	21	0·5613	58
	z	0·872	0·874	19	0·8728	48
S_3'	y	0·337	0·334	22	0·3347	59
	z	0·977	0·971	16	0·9709	47
P_1'	x	0·136	0·140	31	0·1345	81
	y	0·448	0·446	23	0·4456	63
	z	0·753	0·755	23	0·7536	50
P_3'	y	0·285	0·288	23	0·2873	62
	z	0·825	0·822	17	0·8223	50
P_4'	y	0·534	0·533	22	0·5301	64
	z	0·968	0·966	17	0·9683	49

* For numbering of atoms see Fig. 2. Corresponding atoms in the two independent molecules are distinguished by the use of a prime. Atoms S_3, P_3 and P_4 lie on the mirror plane at $x = \frac{3}{4}$, atoms S_3', P_3' and P_4' on the mirror plane at $x = \frac{1}{4}$.

The accuracy of the final atomic coordinates was estimated by comparing the values obtained for 11 coordinates from different projections. The estimated standard deviation is 0·015 Å for all directions. Since, however, during the refinement each cycle was started with the mean values of the atomic parameters, obtained from two projections in the preceding cycle, the coordinates derived from the three projections are not entirely independent. For this reason the value 0·015 Å for the standard deviation must be considered as a lower limit. The standard deviation calculated with Cruickshank's formula (1949) was 0·02 Å. This latter value was taken for the standard deviation in the atomic coordinates.

4. Three-dimensional least-squares refinement

As starting parameters for the least-squares refinement, using all available hkl-reflections, the averages between the final parameters of the two independent two-dimensional refinements were taken. For the calculations a digital computer (the Datatron, built by the Electrodata Corporation of Pasadena, California) was employed. The computer not only furnished the coefficients of the normal equations involving corrections to the atomic coordinates as well as to the temperature parameters, but also solved these equations. The computer program used was that developed by Lavine & Rollett (1956). In this program the observational equations are weighted automatically in a manner similar to the one suggested by Hughes (1941):

When $F_o > 4F_{\text{min.}}$ $\quad w = 1/F_o^2$.
When $F_{\text{min.}} < F_o < 4F_{\text{min.}}$ $\quad w = 1/(4F_{\text{min.}})^2$.
When $F_o = 0$; $F_c > F_{\text{min.}}$ $\quad w = 1/(4F_{\text{min.}})^2$ and F_o is replaced by $F_{\text{min.}}$
When $F_o = 0$; $F_c < F_{\text{min.}}$ $\quad w = 0$.

Here F_o and F_c are the observed and computed structure factors for a given reflection, w is the weight of the corresponding observational equation, and $F_{\text{min.}}$ is the magnitude of the smallest observed structure factor. Though the minimum observed intensity actually varies with θ, a constant value $F_{\text{min.}}$ was used. The computer program provided for individual temperature factors for all atoms. The same temperature factor was, however, used for all atoms in the refinements discussed here, but in every cycle individual atomic shifts in the temperature parameter were computed. Since most of the experimental data used had been obtained from equi-inclination Weissenberg photographs about the a axis, reflections with different values of h were given different scale factors; these scale factors were readjusted after each cycle.

Altogether five refinement cycles were completed. The constant $F_{\text{min.}}$ was chosen to be 4·0. The value of R decreased from 0·222 for the initial parameters to 0·159 for the parameters resulting from the fourth cycle, while $\Sigma w(\Delta F)^2$ decreased from 736 to 304. In Table 4 the observed and calculated structure factors are listed; the latter are based on the parameters computed in the fourth cycle, and a temperature parameter $B = 3{\cdot}66$ Å². The ratio $\Sigma|F_o|/\Sigma|F_c|$ is 1·017. The averaged shifts of the fifth cycle would change

Table 2. *Comparison of the different sets of coordinates*

	R.m.s. differences	
	Obs.	Calc.
Two-dimensional Fouriers and two-dimensional least squares	0·033 Å	0·034 Å
Two-dimensional Fouriers and three-dimensional least squares	0·023 Å	0·021 Å
Two-dimensional least squares and three-dimensional least squares	0·027 Å	0·029 Å

B to 3·83 Å^2, indicating an average r.m.s. displacement of the atoms of the order of 0·2 Å. The final atomic coordinates and their standard deviations are given in Table 1. The latter were obtained from the residual $\Sigma w(\Delta F)^2$ and the diagonal coefficients of the normal equations.

5. Accuracy of the atomic coordinates

Table 2 gives the r.m.s. differences between the coordinates derived from the two independent two-dimensional structure determinations and those obtained from the three-dimensional least-squares refine-

Table 3. *Bond lengths and angles in the* P_4S_3 *molecule*

P_1–P_2	2·240 Å	P_1'–P_2'	2·232 Å	P_1–P_2–P_3 P_3–P_1–P_2	60·1°	P_1'–P_2'–P_3' P_3'–P_1'–P_2'	59·9°
P_2–P_3 P_3–P_1	2·246	P_2'–P_3' P_3'–P_1'	2·223	P_2–P_3–P_1	59·8	P_2'–P_3'–P_1'	60·3
P_1–S_1 P_2–S_2	2·089	P_1'–S_1' P_2'–S_2'	2·095	P_1–S_1–P_4 P_2–S_2–P_4	103·3	P_1'–S_1'–P_4' P_2'–S_2'–P_4'	102·7
P_3–S_3	2·097	P_3'–S_3'	2·092	P_3–S_3–P_4	103·0	P_3'–S_3'–P_4'	102·7
P_4–S_1 P_4–S_2	2·096	P_4'–S_1' P_4'–S_2'	2·087	S_1–P_1–P_2 S_2–P_2–P_1	103·0	S_1'–P_1'–P_2' S_2'–P_2'–P_1'	103·2
P_4–S_3	2·091	P_4'–S_3'	2·070	S_1–P_1–P_3 S_2–P_2–P_3	103·0	S_1'–P_1'–P_3' S_2'–P_2'–P_3'	103·1
				S_3–P_3–P_2 S_3–P_3–P_1	103·2	S_3'–P_3'–P_2' S_3'–P_3'–P_1'	103·3
				S_1–P_4–S_2	98·8	S_1'–P_4'–S_2'	99·5
				S_2–P_4–S_3 S_3–P_4–S_1	99·6	S_2'–P_4'–S_3' S_3'–P_4'–S_1'	99·7

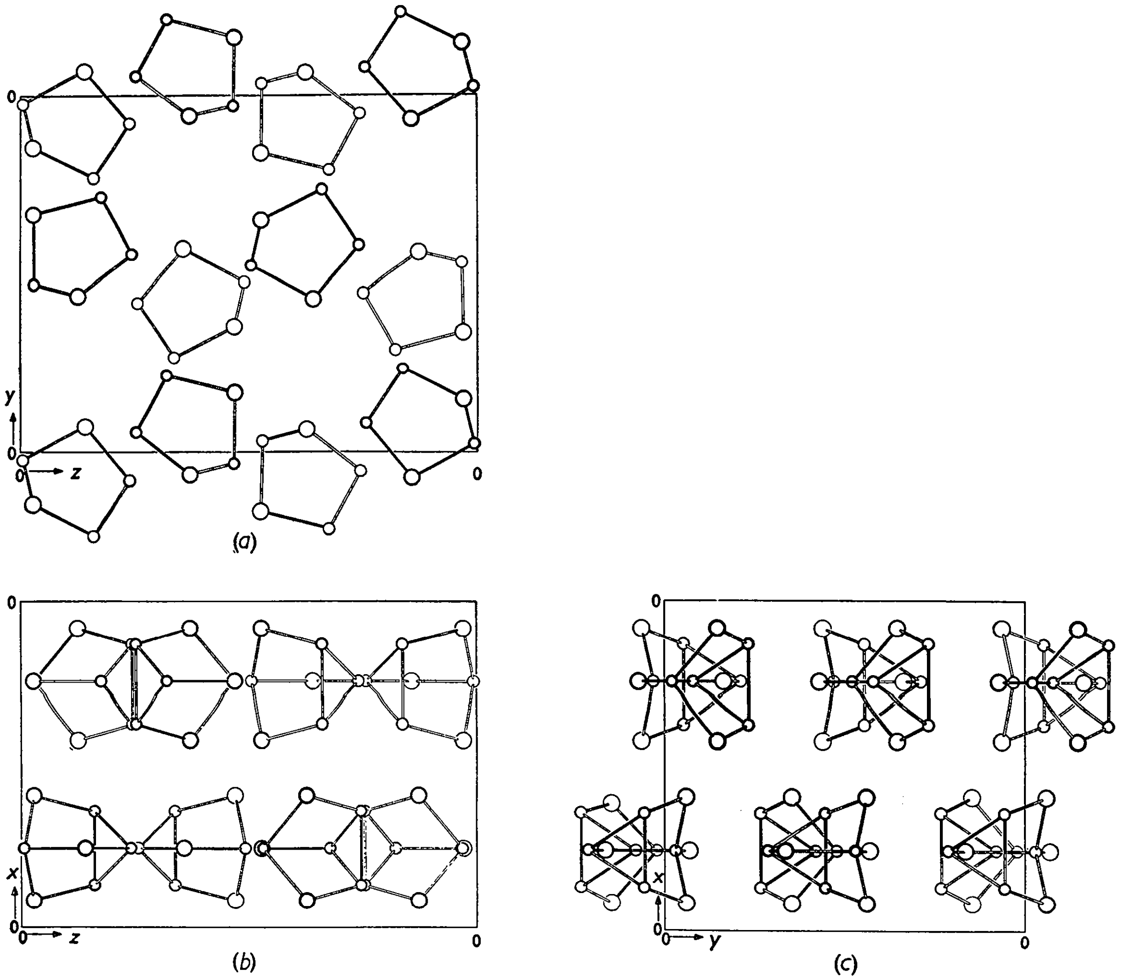

Fig. 5. Projections of the structure along (*a*) [100], (*b*) [010] and (*c*) [001]. Small circles: P; large circles: S.

Table 4. *Observed and computed structure factors*

This table contains 12 sub-tables, each for a different *h* and each containing three sets of four columns. In these four columns are listed, in order: *k*, *l*, 2·5 F_o, 2·5 F_c.

h = 0

00	02	010	021
00	04	311	265
00	06	311	301
00	08	393	360
00	10	290	-278
00	12	069	046
00	14	136	-137
00	16	000	002
00	18	079	-062
01	01	000	000
01	02	296	291
01	03	177	-167
01	04	095	-083
01	05	198	-172
01	06	321	304
01	07	046	-039
01	08	247	262
01	09	010	016
01	10	036	-029
01	11	074	-072
01	12	069	083
01	13	095	-093
01	14	126	126
01	15	000	-001
01	16	030	-044
02	00	293	289
02	01	043	-034
02	02	010	-011
02	03	218	-215
02	04	216	195
02	05	036	-033
02	06	272	-272
02	07	066	-065
02	08	383	381
02	09	077	-099
02	10	056	-037
02	11	090	-115
02	12	010	-050
02	13	000	002
02	14	010	028
02	15	000	-009
02	16	079	090
03	01	169	145
03	02	507	-513
03	03	010	011
03	04	234	235
03	05	046	-039
03	06	270	265
03	07	010	013
03	08	216	-202
03	09	036	-022
03	10	048	044
03	11	092	-109
03	12	010	026
03	13	059	-050
03	14	051	041
03	15	046	-048
04	00	159	136
04	01	010	018
04	02	177	-167
04	03	187	-179
04	04	136	-121
04	05	054	065
04	06	172	145
04	07	043	-033
04	08	036	-031
04	09	010	022
04	10	000	-000
04	11	154	-141
04	12	095	116
04	13	046	035
05	01	010	020
05	02	177	-175
05	03	010	023
05	04	301	-284
05	05	036	049
05	06	051	-016
05	07	064	-067
05	08	164	-159
05	09	048	-037
05	10	244	-253
05	11	059	-033
05	12	077	-076
05	13	041	-038
05	14	046	063
06	00	131	-151
06	01	059	053
06	02	414	428
06	03	154	-169
06	04	303	259
06	05	172	167
06	06	082	077
06	07	033	-020
06	08	090	-096
06	09	000	008
06	10	141	122
06	11	059	-048
06	12	051	-072
06	13	038	058
07	01	133	-123
07	02	131	-115
07	03	115	-087
07	04	079	074
07	05	010	-025
07	06	097	079
07	07	010	-024
07	08	061	-038
07	09	069	-074
07	10	033	024
07	11	000	-006
07	12	041	029
07	13	043	067
08	00	154	-175
08	01	043	059
08	02	144	156
08	03	139	-123
08	04	061	031
08	05	033	-021
08	06	121	126
08	07	113	-117
08	08	118	-151
08	09	033	-009
08	10	051	071
08	11	079	-103
08	12	023	022
09	01	077	-080
09	02	084	089
09	03	033	047
09	04	000	007
09	05	010	018
09	06	059	-026
09	07	056	-057
09	08	064	081
09	09	010	-023
09	10	038	036
10	00	187	-218
10	01	033	-021
10	02	059	-027
10	03	059	-048
10	04	010	-041
10	05	010	-011
10	06	000	-003
10	07	082	-101
10	08	061	-085
10	09	056	-056
10	10	056	067
10	11	036	000
11	01	041	034
11	02	041	043
11	03	010	023
11	04	066	-061
11	05	041	034
11	06	077	-111
12	00	000	004
12	01	010	020
12	02	010	020
13	01	030	-046

h = 2

00	00	566	-550
00	02	049	020
00	04	263	-247
00	06	151	-141
00	08	080	-050
00	10	075	065
00	12	088	-095
00	14	049	033
01	01	015	012
01	02	098	-102
01	03	237	-239
01	04	106	102
01	05	072	-096
01	06	057	-033
01	07	122	127
01	08	033	-008
01	09	132	113
01	10	036	034
01	11	010	-014
01	12	010	-025
01	13	127	090
01	14	000	-009
01	15	091	079
01	16	010	026
02	00	122	-131
02	01	122	-118
02	02	143	-142
02	03	218	-212
02	04	234	-228
02	05	080	087
02	06	041	015
02	07	130	-128
02	08	122	-124
02	09	088	-098
02	10	010	025
02	11	088	-074
02	12	010	-020
02	13	010	011
02	14	010	-023
02	15	010	-016
02	16	000	008
03	01	268	268
03	02	114	096
03	03	070	072
03	04	036	-042
03	05	138	134
03	06	062	050
03	07	106	115
03	08	132	130
03	09	036	031
03	10	067	-050
03	11	036	017
03	12	010	023
03	13	000	-008
03	14	010	011
03	15	000	000
04	00	174	-175
04	01	010	014
04	02	151	-142
04	03	057	-063
04	04	093	-085
04	05	255	260
04	06	132	-137
04	07	156	169
04	08	010	012
04	09	010	025
04	10	010	-034
04	11	057	040
04	12	010	-013
04	13	106	114
05	01	088	-090
05	02	028	-030
05	03	112	113
05	04	057	051
05	05	010	-016
05	06	049	025
05	07	000	-003
05	08	052	044
05	09	039	042
05	10	000	002
05	11	067	050
05	12	000	-007
05	13	010	028
05	14	000	001
06	00	010	017
06	01	096	-091
06	02	166	-173
06	03	010	031
06	04	070	-024
06	05	164	159
06	06	065	-058
06	07	075	067
06	08	000	004
06	09	039	047
06	10	085	-068
06	11	052	048
06	12	033	035
06	13	044	031
07	01	104	-120
07	02	010	-010
07	03	000	-004
07	04	000	-001
07	05	065	036
07	06	010	020
07	07	067	-057
07	08	000	001
07	09	010	-023
07	10	010	-011
07	11	101	107
07	12	010	-011
07	13	010	013
08	00	083	063
08	01	000	-000
08	02	026	-037
08	03	010	020
08	04	010	047
08	05	078	-079
08	06	000	-009
08	07	010	037
08	08	000	-002
08	09	026	-043
08	10	052	-046
08	11	000	-000
09	01	026	019
09	02	010	020
09	03	132	134
09	04	054	026
09	05	054	049
09	06	093	066
09	07	010	-016
09	08	010	017
09	09	000	004
09	10	010	025
10	00	054	-042
10	01	000	006
10	02	000	003
10	03	080	086
10	04	000	007
10	05	010	-013
10	06	010	-015
10	07	010	038
10	08	000	-004
10	09	062	058
10	10	000	-009
10	11	036	037
11	01	010	018
11	02	000	-007
11	03	010	012
11	04	046	036
11	05	010	028
11	06	010	012
12	00	010	-016
12	01	041	036
12	02	000	013
12	03	010	041
12	04	026	-010
13	01	000	-001

h = 1

00	01	047	-031
00	03	010	016
00	05	224	-189
00	07	058	046
00	09	000	-001
00	11	095	-082
00	13	010	-017
00	15	098	084
01	01	095	-084
01	02	423	-415
01	03	010	023
01	04	061	-056
01	05	000	004
01	06	070	-075
01	07	070	-060
01	08	193	-190
01	09	000	006
01	10	232	-211
01	11	010	024
01	12	010	-010
01	13	010	-035
01	14	081	-043
01	15	010	022
01	16	010	-011
02	00	336	346
02	01	145	-141
02	02	033	-018
02	03	010	-018
02	04	434	425
02	05	047	-028
02	06	058	-038
02	07	033	031
02	08	030	024
02	09	098	-096
02	10	044	-051
02	11	010	040
02	12	117	090
02	13	010	-016
02	14	106	-101
02	15	010	016
02	16	000	-009
03	01	106	-098
03	02	056	052
03	03	201	-181
03	04	010	-012
03	05	070	-052
03	06	106	113
03	07	030	044
03	08	086	091
03	09	103	-098
03	10	044	-040
03	11	000	-009
03	12	061	051
03	13	075	072
03	14	010	024
03	15	000	-004
04	00	308	-262
04	01	047	-041
04	02	243	-246
04	03	047	028
04	04	291	299
04	05	162	-147
04	06	311	-314
04	07	010	021
04	08	126	092
04	09	044	-046
04	10	010	010
04	11	010	-034
04	12	151	128
04	13	000	-008
05	01	156	-150
05	02	075	-057
05	03	058	-023
05	04	010	016
05	05	044	-044
05	06	131	-113
05	07	092	-078
05	08	112	-108
05	09	000	-008
05	10	042	049
05	11	000	-003
05	12	100	-075
05	13	000	001
05	14	010	-031
06	00	081	071
06	01	126	-098
06	02	204	-207
06	03	000	-002
06	04	086	087
06	05	033	074
06	06	000	-000
06	07	070	-063
06	08	000	-009
06	09	075	-051
06	10	000	-004
06	11	010	051
06	12	120	140
06	13	010	-013
07	01	056	-042
07	02	193	173
07	03	134	-108
07	04	207	-201
07	05	000	001
07	06	134	-133
07	07	044	-026
07	08	010	-010
07	09	044	-053
07	10	010	-046
07	11	000	-007
07	12	103	-074
07	13	010	023
08	00	000	-005
08	01	072	094
08	02	134	137
08	03	000	003
08	04	106	091
08	05	010	022
08	06	010	-011
08	07	010	021
08	08	114	073
08	09	010	047
08	10	010	028
08	11	000	004
09	01	168	-143
09	02	010	023
09	03	010	-033
09	04	098	084
09	05	086	-083
09	06	000	-003
09	07	095	-079
09	08	000	007
09	09	010	032
09	10	112	104
10	00	075	056
10	01	010	026
10	02	010	-014
10	03	010	-038
10	04	072	-119
10	05	072	067
10	06	081	107
10	07	092	-082
10	08	000	-001
10	09	010	041
10	10	010	014
10	11	000	-003
11	01	070	-036
11	02	042	059
11	03	081	-075
11	04	010	-024
11	05	010	-022
11	06	000	005
12	00	033	-045
12	01	047	071
12	02	010	025
12	03	010	-035
13	01	000	-007
13	03	042	011

h = 3

00	01	208	-193
00	03	218	199
00	05	152	159
00	07	524	577
00	09	067	-064
00	11	131	112
00	13	084	130
00	15	050	051
00	17	058	-076
01	01	373	-411
01	02	084	-070
01	03	101	092
01	04	000	-009
01	05	131	-134
01	06	140	133
01	07	172	-168
01	08	063	051
01	09	104	101
01	10	010	-036
01	11	010	022
01	12	000	-000
01	13	065	051
01	14	058	056
01	15	010	047
01	16	000	008
02	00	038	021
02	01	417	-457
02	02	109	114
02	03	000	-003
02	04	118	113
02	05	131	128
02	06	060	045
02	07	026	012
02	08	050	-042
02	09	167	-169
02	10	067	-057
02	11	065	050
02	12	000	000
02	13	063	-048
02	14	010	-013
02	15	010	019
02	16	046	-054
03	01	084	-078
03	02	000	-006
03	03	055	038
03	04	121	123
03	05	208	211
03	06	131	131
03	07	118	-115
03	08	121	116
03	09	072	-080
03	10	065	063
03	11	097	108
03	12	065	036
03	13	094	061
03	14	048	049
03	15	072	-075
04	00	055	-049
04	01	101	103
04	02	063	-055
04	03	072	-079
04	04	089	085
04	05	152	-172
04	06	000	004
04	07	046	-026
04	08	118	-105
04	09	065	-074
04	10	063	-041
04	11	101	-107
04	12	010	037
04	13	010	-011
04	14	050	-027
04	15	010	-022
04	16	046	-024
05	01	126	126
05	02	065	050
05	03	434	466
05	04	075	056
05	05	235	227
05	06	077	070
05	07	092	-085
05	08	067	055
05	09	055	035
05	10	060	036
05	11	000	001
05	12	089	077
05	13	024	-034
05	14	010	-011
05	15	063	-076
06	00	099	-096
06	01	160	166
06	02	114	-104
06	03	087	075
06	04	029	036
06	05	133	136
06	06	084	-088
06	07	010	-021
06	08	010	-021
06	09	184	205
06	10	080	-073
06	11	072	066
06	12	041	039
06	13	000	005
07	01	010	011
07	02	010	017
07	03	036	024
07	04	000	001
07	05	058	061
07	06	089	-105
07	07	033	011
07	08	048	-035
07	09	010	-019
07	10	010	013
07	11	029	037
07	12	010	-015
07	13	010	032
07	14	033	-026
08	00	080	078
08	01	143	188
08	02	010	-017
08	03	036	021
08	04	128	097
08	05	065	-038
08	06	060	-049
08	07	082	-073
08	08	010	-014
08	09	116	125
08	10	048	-031
08	11	024	-020
09	01	033	026
09	02	033	037
09	03	010	-026
09	04	000	-000
09	05	010	-013
09	06	010	-026
09	07	010	043
09	08	038	-024
09	09	024	018
09	10	010	029
10	00	072	074
10	01	033	054
10	02	010	014
10	03	048	-037
10	04	010	010
10	05	084	-077
10	06	038	-017
10	07	065	-096
10	08	010	015
10	09	046	-019
10	10	038	-035
10	11	038	-033
11	01	143	139
11	02	063	052
11	03	072	044
11	04	000	006
11	05	010	014
11	06	000	003
11	07	097	084
11	08	031	031
11	09	021	019
12	00	070	-045
12	01	021	-018
12	02	031	-019
12	03	010	012
12	04	050	-054
12	05	010	015
12	06	038	-031
13	01	065	056

Table 4 (*cont.*)

h = 4

00	00	030	−006
00	02	232	235
00	04	120	127
00	06	109	111
00	08	057	−040
00	10	086	093
00	12	049	−036
00	14	044	025
01	01	000	−002
01	02	083	−082
01	03	180	186
01	04	060	046
01	05	093	076
01	06	049	033
01	07	070	−081
01	08	101	−095
01	09	117	−128
01	10	039	022
01	11	036	033
01	12	036	044
01	13	112	−087
01	14	044	−044
01	15	062	−063
01	16	000	−000
02	00	130	126
02	01	031	018
02	02	161	167
02	03	242	278
02	04	033	−014
02	05	185	−185
02	06	216	213
02	07	187	202
02	08	010	−014
02	09	010	038
02	10	010	−015
02	11	120	098
02	12	010	030
02	13	036	−034
02	14	057	045
02	15	057	039
02	16	054	−054
03	01	229	−249
03	02	067	057
03	03	000	−009
03	04	062	−066
03	05	156	−136
03	06	091	−082
03	07	107	−114
03	08	000	−005
03	09	000	−009
03	10	010	−022
03	11	000	−008
03	12	010	−025
03	13	010	−010
03	14	010	015
03	15	010	018
04	00	057	−016
04	01	193	−203
04	02	208	211
04	03	180	184
04	04	112	117
04	05	266	−293
04	06	062	040
04	07	096	−082
04	08	000	−003
04	09	112	−107
04	10	101	089
04	11	060	052
04	12	036	−048
04	13	117	−158
04	14	000	−002
04	15	041	028
05	01	122	110
05	02	080	−068
05	03	169	−161
05	04	062	053
05	05	049	035
05	06	028	−021
05	07	010	033
05	08	101	−084
05	09	080	−071
05	10	036	030
05	11	060	−038
05	12	044	035
05	13	000	−006
05	14	033	−043
05	15	041	−038
06	00	130	128
06	01	057	035
06	02	062	048
06	03	088	077
06	04	028	010
06	05	234	−283
06	06	078	078
06	07	080	048
06	08	036	013
06	09	088	−089
06	10	000	−000
06	11	044	−027
06	12	010	021
06	13	057	−047
06	14	023	−013
07	01	083	076
07	02	062	070
07	03	104	065
07	04	039	−046
07	05	046	−046
07	06	039	−036
07	07	010	012
07	08	052	051
07	09	091	069
07	10	010	−023
07	11	091	−110
07	12	000	007
08	00	046	−027
08	01	093	−088
08	02	010	−021
08	03	010	013
08	04	060	051
08	05	096	091
08	06	080	−095
08	07	036	−039
08	08	046	066
08	09	010	010
08	10	026	020
08	11	033	047
09	01	010	016
09	02	080	−054
09	03	167	−179
09	04	000	003
09	05	010	−019
09	06	046	−054
09	07	036	035
09	08	026	−041
09	09	026	−027
09	10	010	−010
10	00	088	125
10	01	036	050
10	02	036	−066
10	03	093	−085
10	04	010	030
10	05	010	−014
10	06	000	−008
10	07	010	−013
10	08	026	037
10	09	054	−035
11	01	052	−038
11	02	026	020
11	03	026	025
11	04	033	−044
11	05	026	−036
11	06	000	−006
11	07	023	−018
12	00	010	026
12	01	062	−033
12	02	010	−020
12	03	049	−068
12	04	010	032
12	05	049	052

h = 6

00	00	480	−545
00	02	219	−234
00	04	074	−075
00	06	172	−169
00	08	142	−141
00	10	023	032
00	12	090	088
00	14	032	037
01	01	000	−005
01	02	020	008
01	03	102	084
01	04	093	−071
01	05	116	100
01	06	179	−181
01	07	000	−001
01	08	072	−065
01	09	010	017
01	10	041	−032
01	11	037	025
01	12	072	−075
01	13	079	068
01	14	037	−032
02	00	160	−158
02	01	093	083
02	02	046	−048
02	03	027	013
02	04	088	077
02	05	125	124
02	06	079	−050
02	07	048	−048
02	08	118	−121
02	09	125	110
02	10	016	016
02	11	037	043
02	12	016	021
02	13	025	021
02	14	041	−043
03	01	065	−045
03	02	125	148
03	03	062	−054
03	04	037	−040
03	05	051	045
03	06	135	−121
03	07	000	005
03	08	034	023
03	09	000	−003
03	10	039	036
03	11	076	064
03	12	013	−013
03	13	055	050
03	14	062	−052
04	00	069	072
04	01	153	168
04	02	020	008
04	03	027	−020
04	04	030	029
04	05	027	029
04	06	023	−015
04	07	055	−042
04	08	010	013
04	09	069	068
04	10	053	−057
04	11	000	006
04	12	010	−017
04	13	046	030
04	14	030	−024
05	01	039	−043
05	02	205	191
05	03	058	046
05	04	088	081
05	05	058	−050
05	06	016	010
05	07	023	013
05	08	165	146
05	09	060	056
05	10	128	133
05	11	020	015
05	12	027	022
05	13	016	006
06	00	062	−043
06	01	000	008
06	02	142	−167
06	03	000	005
06	04	144	−153
06	05	016	031
06	06	081	−074
06	07	107	−092
06	08	046	044
06	09	053	041
06	10	023	−020
06	11	013	016
06	12	000	−004
07	01	116	105
07	02	010	014
07	03	000	−002
07	04	000	−001
07	05	044	029
07	06	039	−033
07	07	062	053
07	08	020	−025
07	09	000	001
07	10	010	017
07	11	010	018
08	00	083	084
08	01	046	047
08	02	046	−046
08	03	046	048
08	04	100	−111
08	05	000	−006
08	06	016	018
08	07	086	082
08	08	023	036
08	09	041	033
08	10	037	−025
08	11	023	022
09	01	010	019
09	02	023	−023
09	03	025	026
09	04	030	−031
09	05	027	−035
09	06	013	012
09	07	016	017
09	08	020	−028
09	09	041	038
09	10	037	−036
10	00	062	057
10	01	027	−040
10	02	067	080
10	03	032	039
10	04	000	−009
10	05	039	033
10	06	020	024
10	07	044	046
10	08	025	024
11	01	000	−001
11	02	051	−042
11	03	055	−051
11	04	058	052
11	05	010	−011
11	06	044	069

h = 5

00	01	022	024
00	03	238	−224
00	05	286	235
00	07	268	−264
00	09	110	095
00	11	085	−061
00	13	022	005
00	15	032	−008
01	01	080	083
01	02	193	−188
01	03	198	−189
01	04	067	−067
01	05	085	070
01	06	050	−035
01	07	085	073
01	08	153	−138
01	09	117	−127
01	10	148	−128
01	11	055	046
01	12	035	−031
01	13	020	019
01	14	000	−008
01	15	010	−025
01	16	020	−024
02	00	000	005
02	01	268	279
02	02	128	133
02	03	165	−151
02	04	145	158
02	05	040	−044
02	06	032	040
02	07	010	015
02	08	067	−056
02	09	060	059
02	10	047	048
02	11	138	−131
02	12	020	−001
02	13	087	083
02	14	027	−034
03	01	153	−157
03	02	022	−019
03	03	077	076
03	04	045	023
03	05	110	−117
03	06	092	086
03	07	037	−033
03	08	000	006
03	09	037	020
03	10	000	004
03	11	010	−011
03	12	010	031
03	13	010	−013
03	14	000	007
03	15	060	051
04	00	245	−261
04	01	153	−131
04	02	010	−010
04	03	057	−027
04	04	000	−009
04	05	082	069
04	06	010	−011
04	07	097	−101
04	08	065	−062
04	09	047	−029
04	10	110	070
04	11	035	034
04	12	057	050
04	13	020	−028
04	14	037	042
05	01	032	−033
05	02	032	032
05	03	153	−153
05	04	062	−050
05	05	015	−008
05	06	077	−091
05	07	022	033
05	08	022	−020
05	09	117	−106
05	10	000	−000
05	11	012	030
05	12	060	−063
05	13	010	021
06	00	165	−168
06	01	037	−039
06	02	045	032
06	03	062	066
06	04	010	−012
06	05	107	−127
06	06	037	035
06	07	082	067
06	08	072	−072
06	09	057	−064
06	10	097	098
06	11	010	011
06	12	010	014
06	13	000	−005
06	14	017	025
07	01	095	−079
07	02	037	037
07	03	037	016
07	04	067	−066
07	05	020	−039
07	06	097	−086
07	07	080	−051
07	08	057	−049
07	09	012	004
07	10	010	−011
07	11	000	−005
07	12	042	−030
08	00	030	030
08	01	072	−098
08	02	080	101
08	03	075	089
08	04	010	−024
08	05	010	−012
08	06	077	093
08	07	045	050
08	08	000	005
08	09	040	−037
08	10	010	013
08	11	072	078
09	01	082	−074
09	02	072	076
09	03	067	−068
09	04	010	011
09	05	040	−042
09	06	010	−020
09	07	020	−032
09	08	055	064
09	09	027	−007
09	10	010	033
10	00	000	−009
10	01	010	−025
10	02	000	000
10	03	042	044
10	04	035	−032
10	05	042	−037
10	06	000	009
10	07	010	016
10	08	027	024
11	01	045	−040
11	02	010	−010
11	03	027	−036
11	04	020	027
11	05	020	−020
11	06	000	005
11	07	047	−033
12	00	042	052
12	01	020	012
12	02	020	−038
12	03	000	000
12	04	017	−026

h = 7

00	01	014	006
00	03	026	032
00	05	031	018
00	07	010	016
00	09	026	−017
00	11	043	043
01	01	033	020
01	02	160	161
01	03	035	025
01	04	031	032
01	05	010	−010
01	06	040	032
01	07	038	014
01	08	086	100
01	09	033	018
01	10	107	112
01	11	010	−019
01	12	014	010
01	13	000	009
01	14	043	017
02	00	086	−108
02	01	000	003
02	02	023	−020
02	03	031	035
02	04	184	−181
02	05	016	014
02	06	000	005
02	07	019	−014
02	08	021	002
02	09	033	032
02	10	010	012
02	11	000	007
02	12	059	−036
02	13	000	−008
02	14	035	049
03	01	083	064
03	02	031	−014
03	03	059	049
03	04	000	−002
03	05	040	036
03	06	047	−063
03	07	000	−008
03	08	052	−041
03	09	047	038
03	10	010	013
03	11	000	002
03	12	031	−029
03	13	033	−030
04	00	138	144
04	01	028	036
04	02	093	092
04	03	016	−003
04	04	117	−113
04	05	059	049
04	06	141	125
04	07	021	011
04	08	021	−021
04	09	019	027
04	10	010	−017
04	11	010	011
04	12	062	−064
04	13	019	009
05	01	050	060
05	02	010	015
05	03	026	024
05	04	000	000
05	05	021	012
05	06	083	061
05	07	026	027
05	08	057	046
05	09	019	023
05	10	028	−021
05	11	000	−004
05	12	040	041
06	00	000	007
06	01	026	042
06	02	079	078
06	03	028	−014
06	04	010	−032
06	05	000	006
06	06	000	−004
06	07	010	012
06	08	019	019
06	09	023	027
06	10	010	−015
06	11	031	−026
06	12	045	−063
07	01	026	032
07	02	100	−077
07	03	047	040
07	04	093	094
07	05	019	005
07	06	079	075
07	07	016	020
07	08	014	015
07	09	010	022
07	10	010	021
07	11	019	002
08	00	000	−005
08	01	019	−024
08	02	074	−076
08	03	019	−020
08	04	035	−036
08	05	000	−005
08	06	010	−012
08	07	010	−017
08	08	059	−031
08	09	010	−016
08	10	016	−013
09	01	059	073
09	02	010	−026
09	03	050	028
09	04	031	−037
09	05	047	043
09	06	000	006
09	07	031	038
10	00	045	−024
10	01	000	−007
10	02	000	006
10	03	000	008
10	04	057	056
10	05	010	−017
10	06	040	−046
11	01	016	018
11	02	011	−024
11	03	026	037

ment. In column 2 are listed the actually observed r.m.s. differences between these coordinates; column 3 gives the r.m.s. differences as expected from the standard deviations estimated for the individual sets of coordinates. For the two-dimensional Fourier refinement and the least-squares refinement the latter have been cited in § 3; they amount to 0·02 and 0·028 Å respectively. For the three-dimensional least-squares

Table 4 (*cont.*)

h = 8

00	00	348	322	03	06	000	−004	06	06	017	014
00	02	099	−090	03	07	038	−042	06	07	071	−069
00	04	127	115	03	08	094	−097	06	08	000	−008
00	06	056	062	03	09	017	−020	06	09	000	−002
00	08	086	053	03	10	046	047	06	10	063	053
00	10	069	−085	04	00	109	126	06	11	023	−026
00	12	099	087	04	01	081	060	07	01	051	060
01	01	010	−006	04	02	017	021	07	02	010	−019
01	02	092	091	04	03	043	−022	07	03	033	−022
01	03	084	081	04	04	028	016	07	04	010	019
01	04	107	−084	04	05	081	−079	07	05	010	−010
01	05	040	036	04	06	086	087	07	06	000	−001
01	06	010	013	04	07	092	−094	07	07	035	039
01	07	076	−061	04	08	028	−008	07	08	020	−020
01	08	048	043	04	09	025	021	07	09	023	−008
01	09	043	−037	04	10	028	−007	07	10	017	018
01	10	025	−034	04	11	058	−051	08	00	025	−038
01	11	000	−002	04	12	030	029	08	01	035	033
01	12	000	003	05	01	010	023	08	02	025	037
01	13	038	−037	05	02	079	045	08	03	010	−021
02	00	023	036	05	03	010	−022	08	04	051	−055
02	01	071	063	05	04	048	−059	08	05	010	025
02	02	033	032	05	05	000	−000	08	06	035	043
02	03	030	038	05	06	010	−011	09	01	015	−021
02	04	166	159	05	07	010	−010	09	02	015	005
02	05	030	004	05	08	000	−002	09	03	025	−035
02	06	104	−090	05	09	000	−005	09	04	023	−022
02	07	020	018	05	10	010	−015	09	05	030	−030
02	08	092	099	05	11	023	−024	09	06	051	−031
02	09	066	058	06	00	066	−060	10	00	010	−015
03	01	384	−083	06	01	043	053	10	01	023	−024
03	02	094	−086	06	02	094	111	10	02	015	021
03	03	043	−044	06	03	048	−051	10	03	020	−035
03	04	048	054	06	04	033	016	10	04	012	−017
03	05	020	−045	06	05	020	−013				

h = 9				h = 10				h = 12			
00	05	207	−213	00	00	204	−143	00	00	088	102

refinement the standard deviations of the individual coordinates are given in Table 1 and their r.m.s. value is 0·007 Å. They mainly result from inaccuracies in the observed intensities.

It is seen that the expected and observed values are in agreement.

The standard deviation in the final coordinates, which is 0·007 Å, corresponds to a standard deviation of $\sqrt{2}\times0{\cdot}007 = 0{\cdot}01$ Å in the bond lengths. The effect of the inaccuracies in the lattice constants, amounting to approximately 0·001 Å, is negligible. The standard deviation in the bond angles is 0·5° (Cruickshank & Robertson, 1953).

6. Discussion

The structure consists of molecules of P_4S_3, with shortest intermolecular distances of approximately 3·6 Å. The arrangement of the molecules in the crystal is shown in Fig. 5. Their packing resembles that of hexagonal closest packing. The distinction between phosphorus and sulfur atoms has been based on chemical arguments exclusively.

One of the mirror planes of a molecule coincides with a mirror plane of the crystal and the 6 atoms S_3, S_3', P_3, P_3', P_4, and P_4' (numbered as indicated in the footnote of Table 1) and 18 symmetry-related atoms lie in the special fourfold sets of positions (*c*) of the space group *Pmnb* (*International Tables*, 1952). The remaining 4 atoms of the asymmetric unit and the 28 symmetry-related atoms take up positions of the general eightfold set (*d*). There are thus 24 positional parameters and the asymmetric unit consists of halves of two different molecules.

The intramolecular atomic distances and bond angles are listed in Table 3. Two types of bonds can be distinguished in the molecule, P–P with an average value of 2·235 Å and P–S with an average value of 2·090 Å. When the individual values are considered to be equivalent, a standard deviation of about 0·005 Å is calculated for the mean values. The four types of bond angles in the molecule and their average values are as follows:

S–P–S (99·4°), P–S–P (103·0°), S–P–P (103·1°),
P–P–P (60·0°).

The bond lengths 2·235 Å (weight in radial distribution function 3/2·235 = 1·34) and 2·090 Å (weight 6/2·090 = 2·87), average 2·14 Å, agree with the reported electron-diffraction value 2·15 Å (Hassel & Pettersen, 1941). The non-bonded distances are in fair agreement with the single peak of the radial distribution function at 3·38 Å. They fall into three groups of different weights: 3·19 Å (0·94), 3·27 Å (0·92), 3·39 Å (1·77).

The values for the bond lengths may be compared with those observed in P_4S_7 and P_4S_{10} (Vos & Wiebenga, 1955, 1956), which are 2·35 Å and 2·08 Å for P–P and P–S respectively; with those in P_4S_5 (Van Houten & Wiebenga, 1957), which are 2·21 Å for P–P and 2·08–2·19 Å for P–S; and with the P–P distance of 2·21 Å in P_2I_4 (Leung & Waser, 1956). As is seen, these distances are essentially equivalent, with the exception of the remarkably long P–P distance in P_4S_7.

The liberal help of Dr John S. Rollett in the least-squares refinement using the zonal data, and the assistance of Mr H. Schürer during the Fourier refinements, are gratefully acknowledged. The Patterson and Fourier syntheses were computed on IBM machines, which were generously put at our disposal by Theodorus Niemeyer N. V., Groningen. We also are grateful to the Robert A. Welch Foundation of Houston, Texas, for its financial assistance, making possible the use of a high-speed electronic computer for the least-squares refinements.

References

Booth, A. D. (1946). *Proc. Roy. Soc.* A, **188**, 74.
Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.
Cruickshank, D. W. J. & Robertson, A. P. (1953). *Acta Cryst.* **6**, 698.
Grison, E. (1951). *Acta Cryst.* **4**, 489.
Harker, D. (1948). *Amer. Min.* **33**, 764.
Harker, D. & Kasper, J. S. (1948). *Acta Cryst.* **1**, 70.
Hassel, O. & Pettersen, A. (1941). *Tids. Kjemi Bergv. Met.* **1**, 57.
Houten, S. van, Vos, A. & Wiegers, G. A. (1955). *Rec. Trav. Chim. Pays-Bas*, **74**, 1167.
Houten, S. van & Wiebenga, E. H. (1957). *Acta Cryst.* **10**, 156.
Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210.

HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
International Tables for X-ray Crystallography (1952), p. 151. Birmingham: Kynoch Press.
LAVINE, L. R. & ROLLETT, J. S. (1956). *Acta Cryst.* **9**, 269.
LEUNG, Y. C., WASER, J. & ROBERTS, L. R. (1955). *Chem. Ind.* p. 948.
LEUNG, Y. C. & WASER, J. (1956). *J. Phys. Chem.* **60**, 539.
MACGILLAVRY, C. H. (1950). *Acta Cryst.* **3**, 214.
PERNERT, J. C. & BROWN, J. H. (1949). *Chem. Engng. News*, **27**, 2143.
STOCK, A. (1910*a*). *Ber. dtsch. chem. Ges.* **43**, 150.
STOCK, A. (1910*b*). *Ber. dtsch. chem. Ges.* **43**, 414.
STOCK, A. (1910*c*). *Ber. dtsch. chem. Ges.* **43**, 1223.
STOCK, A. & THIEL, K. (1905). *Ber. dtsch. chem. Ges.* **38**, 2719.
TREADWELL, W. D. & BEELI, CH. (1935). *Helv. chim. Acta*, **18**, 1161.
VOS, A. & WIEBENGA, E. H. (1955). *Acta Cryst.* **8**, 217.
VOS, A. & WIEBENGA, E. H. (1956). *Acta Cryst.* **9**, 92.
WIEBENGA, E. H. & SMITS, D. W. (1950). *Acta Cryst.* **3**, 265.
WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

Acta Cryst. (1957). **10**, 582

The Choice of the Standard Unit Cell in a Triclinic Lattice

BY V. BALASHOV AND H. D. URSELL
The University, Leeds 2, England

(*Received* 22 *August* 1956 *and in revised form* 13 *May* 1957)

An algorism for the reduction of the experimental data directly to the three shortest non-coplanar translations (Dirichlet triplet) is given. A method is also given for deriving the Dirichlet triplet from the Delaunay reduced cell, and analysis of the latter concept shows that the Delaunay cell can have interaxial angles arbitrarily near to 180°. For the Dirichlet triplet, in contrast, the interaxial angles can never deviate by more than 30° from right angles.

1. Introduction

In crystallography the choice of a unit cell in a lattice is, by convention, governed by the properties of symmetry. This applies to all crystallographic systems except the triclinic, where symmetry gives us no guidance.

Delaunay (1933) has given a profound and illuminating discussion of the geometry of crystal lattices, basing his work on the work of Selling (1874) and Voronoi (1908) on the reduction of positive definite quadratic forms. Delaunay makes great use of the 'Voronoi domains' (for definition see below, following equation (1·6)).

The lack of uniformity in the presentation of the lattice parameters of triclinic substances was realised long ago, and a number of suggestions were brought forward for a unique choice of the unit cell (Balashov, 1956; Barth & Tunell, 1933; Buerger, 1937, 1942, chap. 19, 1956, pp. 107–8); Crowfoot, 1935; Donnay & Melon, 1933; Donnay, Tunell & Barth, 1934; Donnay, 1943*a*, *b*, 1952; Peacock, 1937; Tunell, 1933). A particular cell, called the 'Delaunay reduced cell', brought to the attention of crystallographers by Ito (1950, p. 189), was later described in *International Tables* (1952, p. 530) and used by Donnay & Nowacki (1954) as a standard reference cell.

This cell is obtained from an arbitrary primitive cell by a simple and elegant algorism given by Delaunay (1933) and applied to the parameters of Selling. These refer to a quartet

$$\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{d} \qquad (1\cdot1)$$

of lattice translations, satisfying

$$\mathbf{a}+\mathbf{b}+\mathbf{c}+\mathbf{d} = \mathbf{0}\,, \qquad (1\cdot2)$$

and such that any three of them form a primitive triplet. The Selling parameters are the six scalar products

$$\mathbf{a}\,.\,\mathbf{b},\ \mathbf{a}\,.\,\mathbf{c},\ \mathbf{a}\,.\,\mathbf{d},\ \mathbf{b}\,.\,\mathbf{c},\ \mathbf{b}\,.\,\mathbf{d},\ \mathbf{c}\,.\,\mathbf{d}\,, \qquad (1\cdot3)$$

which are sufficient to determine the lengths of **a**, **b**, **c**, **d** and the angles between them: for

$$a^2 = \mathbf{a}\,.\,\mathbf{a} = -\mathbf{a}\,.\,\mathbf{b}-\mathbf{a}\,.\,\mathbf{c}-\mathbf{a}\,.\,\mathbf{d}\,, \qquad (1\cdot4)$$

$$ab\cos\gamma = \mathbf{a}\,.\,\mathbf{b}\,. \qquad (1\cdot5)$$

Selling's reduction theory shows that there is a particular quartet (1·1) of lattice vectors satisfying (1·2) and such that all the numbers (1·3) are negative or zero. In general the reduced quartet is unique (save for a possible *simultaneous* change of sign of all four) and gives Selling parameters all negative.

The so-called Delaunay reduced cell is formed from the reduced quartet ($\mathbf{a}_r$, $\mathbf{b}_r$, $\mathbf{c}_r$, $\mathbf{d}_r$) by discarding one of them, say $\mathbf{d}_r$, and taking the other three as concurrent edges of a parallelepiped. Whichever one of