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The Crystal Structure of Rubidium Metaphosphate

BY D. E. C. CORBRIDGE

Research Department, Albright and Wilson Limited, Oldbury, Birmingham, England

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The crystal structure of rubidium metaphosphate $(RbPO_3)_n$ has been determined by three-dimensional Fourier methods. The unit cell is monoclinic with $a = 12{\cdot}123 \pm 0{\cdot}002$, $b = 4{\cdot}228 \pm 0{\cdot}002$, $c = 6{\cdot}479 \pm 0{\cdot}002$ Å, $\beta = 96° \, 19' \pm 20'$. The space group is $P2_1/n$ and the unit cell contains 4 units of $RbPO_3$. The structure contains continuous chains of composition $(PO_3)_n^{n-}$, which spiral round the screw axes parallel to b with a repeat pattern every two PO_3 units. These chains are held laterally by the Rb^+ ions, each of which is sevenfold co-ordinated by oxygen. Bond lengths are P–O = $1{\cdot}46 \pm 0{\cdot}03$ Å, P–O (chain) = $1{\cdot}62 \pm 0{\cdot}03$ Å. Comparisons are made with similar chain structures in metasilicates and in sulphur trioxide.

Introduction

Anions of the metaphosphate composition are known to occur in several different polymeric forms. X-ray methods have established the tetrameric ring $(PO_3)_4^{4-}$ in several crystalline salts (Pauling & Sherman, 1937; Andress, Gehring & Fischer, 1949; Romers, Ketelaar & MacGillavry, 1951) and the trimeric ring $(PO_3)_3^{3-}$ has been indicated by X-ray measurements (Cagliotti, Giacomello & Bianchi, 1942; Raistrick, 1949).

The alkali metaphosphates, in addition to forming water-soluble salts containing finite ring anions, also exist in a number of insoluble varieties. Typical of these are the 'Kurrol salts' which often appear as long fibrous crystals and which, on the basis of their colloidal and other properties, are thought to contain long chains of high molecular weight (Topley, 1949; Pfansteil & Iler, 1952; Callis, Van Wazer & Arvan, 1954). The presence of such long chains has been indicated by a brief X-ray investigation of fibrous sodium metaphosphate (Pleith & Wurster, 1951), but no complete structure determination of any compound of this type has appeared in the literature. Unit-cell and space-group data for a number of Kurrol-type salts have already been given (Corbridge, 1955). In the present work the detailed structure of one of these has been determined.

Rubidium metaphosphate was prepared by heating rubidium dihydrogen phosphate:

$$n\mathrm{RbH_2PO_4} \rightarrow (\mathrm{RbPO_3})_n + n\mathrm{H_2O} \, .$$

Small, well formed needle crystals suitable for X-ray examination were obtained by slow cooling of the metaphosphate melt.

Unit cell and space group

The unit-cell dimensions, obtained by measurement of high-angle reflexions on oscillation photographs (Farquhar & Lipson, 1946) were

$$a = 12{\cdot}123 \pm 0{\cdot}002,\ b = 4{\cdot}228 \pm 0{\cdot}002,\ c = 6{\cdot}479 \pm 0{\cdot}002\ \text{Å};\quad \beta = 96° \, 19' \pm 20' \, .$$

The space group was determined from zero- and first-layer Weissenberg photographs taken about the three principal axes. Observed extinctions were $\{h0l\}$ for $h+l$ odd and $\{0k0\}$ for k odd, thus giving the space group unambiguously as $P2_1/n$. The density, determined by flotation was $\varrho_o = 3{\cdot}29$ g.cm.$^{-3}$, while that calculated, assuming 4 units of $RbPO_3$ per cell, was $3{\cdot}31$ g.cm.$^{-3}$.

Experimental

Intensity data were obtained by visual estimation from Weissenberg photographs taken with Cu $K\alpha$ radiation about the three principal axes. Three films were used for each photograph which was taken twice, with a long and a short exposure, to give a set of six films covering a wide range of intensities for each layer line. Sets of calibration spots were obtained from the actual crystals being examined, and the various photographs were related and corrected for geometrical and polarization factors by the usual methods.

Reflexions from 714 different planes were observed, of which 85 were too small to be measured. No corrections for absorption were made, but errors were minimized by using small equant crystals ~ 0·3 mm. The structure amplitudes were put on an absolute scale by comparison with the calculated values during later stages of the analysis.

The [*b*] *projection*

For general reasons, based on space-group and packing considerations, and the observed fibrous character of the crystal along the short axis, it seemed reasonable to suppose that a continuous chain, if present, would be arranged with its axis parallel to [*b*].

A Patterson synthesis (Fig. 1) was carried out for the symmetry-axis projection using 98 terms. Peak *A* can be interpreted as the Rb–Rb vector and peaks *B* and *C* as Rb–P vectors. Calculations of structure factors with the rubidium at position *A′* enabled the signs of 45 terms to be determined and a Fourier synthesis was carried out. Position *D′* for the Rb ion was rejected as it led to an unfavourable packing scheme. The approximate positions of the phosphorus atoms were given by the Fourier synthesis and these were in accord with the interpretation of the vectors *B* and *C*. After further trial-and-error work the (x, z) coordinates of the oxygen atoms were obtained; the final electron-density map is shown in Fig. 2.

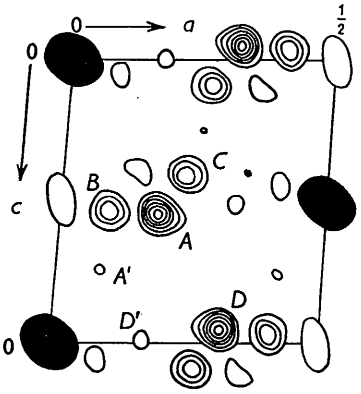

Fig. 1. Patterson synthesis, [*b*] projection.

The [*c*] *projection*

The approximate y coordinate of the Rb ion was obtained from a Patterson synthesis using 55 F^2_{hk0} terms. The approximate y coordinates of the remaining atoms were then obtained from packing considerations and two Fourier syntheses.

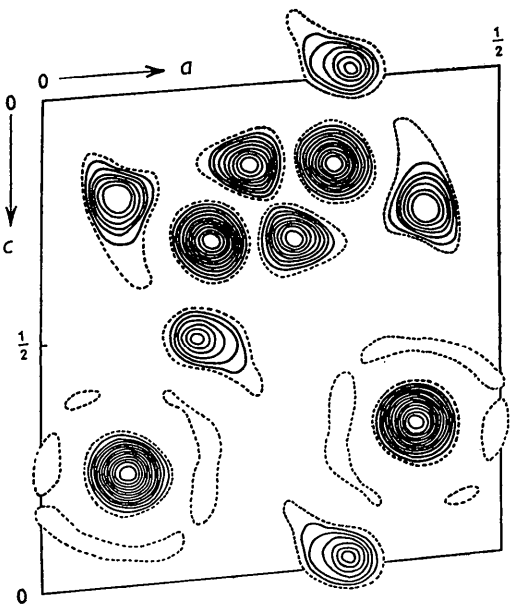

Fig. 2. Electron density, [*b*]-axis projection. Contours at arbitrary intervals.

The coordinates obtained from the final [*b*] and [*c*] projections were

	x	y	z
Rb	0·093	0·137	0·777
P	0·183	0·510	0·314
O_1	0·223	0·76	0·166
O_2	0·081	0·34	0·215
O_3	0·172	0·68	0·520

Three-dimensional refinement

Three successive three-dimensional section and line syntheses were computed, starting with the coordinates obtained from the projection syntheses. The line syntheses were carried out parallel to the [*b*] axis through each of the five atoms, and the sections were computed parallel to (010), in each case through the y coordinate indicated by the previous line synthesis.

The final electron-density functions shown in Figs. 3 and 4 were evaluated over a mesh of intervals of 1/120th of the cell edges in the region of the peak maxima. The atomic coordinates were obtained by an interpolation method (Booth, 1948).

Correction for termination-of-series errors was made from a three-dimensional synthesis computed with the F_c values, omitting terms where $F_o = 0$. The final observed and corrected coordinates are listed in Table 1.

Table 1. *Final atomic coordinates*

	x		y		z	
	Obs.	Corr.	Obs.	Corr.	Obs.	Corr.
Rb	0·0917	0·0914	0·1325	0·1323	0·7761	0·7764
P	0·179	0·179	0·495	0·495	0·320	0·320
O_1	0·219	0·219	0·748	0·744	0·150	0·153
O_2	0·076	0·079	0·338	0·348	0·218	0·210
O_3	0·181	0·181	0·632	0·636	0·528	0·522

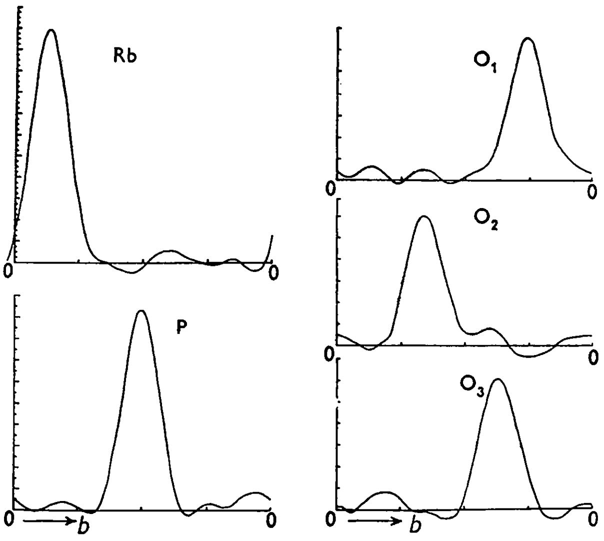

Fig. 3. Three-dimensional line synthesis: electron-density distribution along lines parallel to [*b*]. Ordinate scale intervals correspond to those taken for contours in Fig. 4.

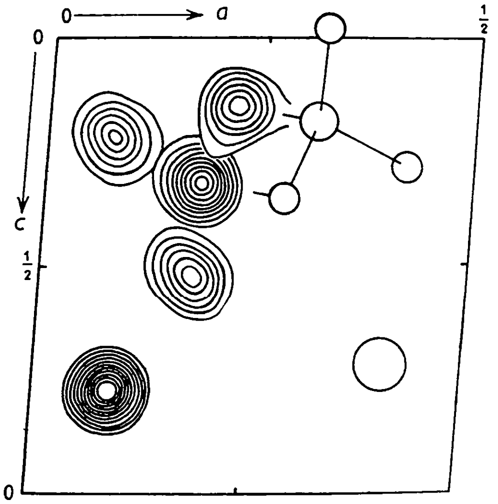

Fig. 4. Composite electron-density map from Fourier syntheses parallel to (010). Contours at intervals of approximately 1 e.Å^{-2} for oxygen, 2 e.Å^{-2} for phosphorus and 4 e.Å^{-2} for rubidium.

The value of the function $R = \Sigma||F_o| - |F_c|| \div \Sigma|F_o|$ was 14·5%, using a temperature factor of $B = 1{\cdot}0$ Å^2 and summing over all the non-zero $\{hkl\}$ terms (Table 5).

Description of structure

The structure consists of continuous chain anions of composition $(PO_3)_n^{n-}$, oriented with the chain axes lying parallel to [*b*] and the chain plane coinciding approximately with (101). Each unit cell contains a portion of two different chains which spiral in opposite ways round the screw axes, the pattern repeating itself every two PO_3 units. Diagrams of the structure are given in Figs. 5 and 6.

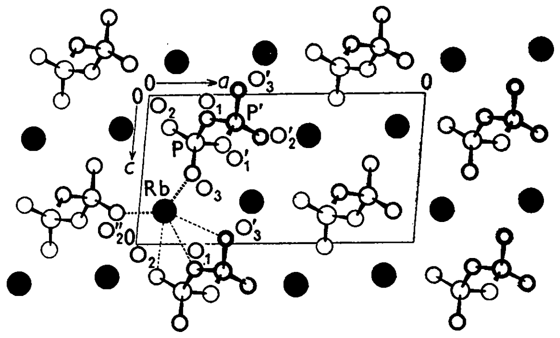

Fig. 5. Rubidium metaphosphate structure in [*b*] projection.

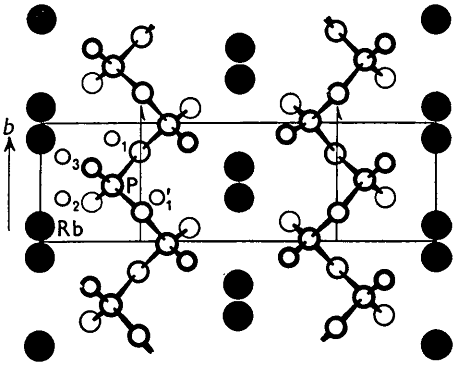

Fig. 6. Section of rubidium metaphosphate structure projected on to (101).

Table 2 lists interatomic distances and angles calculated from the data in Table 1. The standard deviation of the *x*, *y* and *z* parameters calculated according to Cruickshank (1949) are:

Table 2. *Interatomic distances and angles in rubidium metaphosphate*

$P-O_1 = 1{\cdot}621$ Å
$P-O_1' = 1{\cdot}624$
$P-O_2 = 1{\cdot}474$
$P-O_3 = 1{\cdot}438$

$O_1'-O_1 = 2{\cdot}53$ Å
$O_2-O_3 = 2{\cdot}56$
$O_1-O_3 = 2{\cdot}53$
$O_1-O_2 = 2{\cdot}44$
$O_1'-O_3 = 2{\cdot}41$
$O_1'-O_2 = 2{\cdot}55$

$P-P' = 2{\cdot}93$ Å

$P-O_1-P'$	129° 14′
O_1-P-O_1'	102 30
O_2-P-O_3	122 58
O_1-P-O_3	98 57
$O_1'-P-O_3$	95 49
O_1-P-O_2	95 48
$O_1'-P-O_2$	99 28

$\sigma = 0{\cdot}04$ Å for O, $\sigma = 0{\cdot}01$ Å for P, $\sigma = 0{\cdot}004$ Å for Rb.

These figures lead to a standard deviation of ±0·04 Å and a Gaussian probable error of ±0·03 Å in the P–O bond lengths. The difference between the P–O (chain) and the other P–O distances is significant, whereas the difference between the $P-O_2$ and $P-O_3$ bond lengths

Table 3. *Phosphorus–oxygen bond parameters*

	P–O (Å)	P–O–(P) (Å)	P–O–P (°)	Reference
Phosphorus pentoxide I, P_4O_{10}	1·39	1·62	123	(Hampson & Stosick, 1938)
Ammonium tetrametaphosphate, $(NH_4PO_3)_4$	1·46 (mean)	1·61 (mean)	132	(Romers *et al.*, 1951)
Rubidium metaphosphate, $(RbPO_3)_n$	1·46	1·62	129	This work

is probably not. In Table 3 similar P–O bond lengths found in other structures are listed for comparison.

In rubidium metaphosphate the phosphorus atoms are not in the centres of the PO_4 tetrahedra, but are displaced away from the oxygens common to two tetrahedra in a manner similar to that observed in ammonium tetrametaphosphate and the three forms of phosphorus pentoxide. The short P–O distances are close to those observed in these latter structures and are considerably less than those observed in simple tetrahedral phosphate groupings (e.g. 1·54 Å in KH_2PO_4, 1·51 Å in $NaHPO_3NH_2$, 1·51 Å in $NH_4H_2PO_2$ and 1·54 Å in BPO_4).

The chain anions are held laterally by the Rb^+ ions, each of which is coordinated by seven oxygen atoms according to the scheme indicated in Fig. 7. This unsymmetrical configuration may be regarded as a distorted octahedral arrangement with a mean arm length of Rb–O = 2·96 Å (sum of Pauling ionic radii $r_{Rb}+r_O$ = 2·98 Å) and with a seventh slightly longer arm of length 3·20 Å. While the chain oxygen atoms (O_1) are co-ordinated by only one rubidium ion, the remaining oxygens (O_2 and O_3) are each surrounded by three closest positive neighbours.

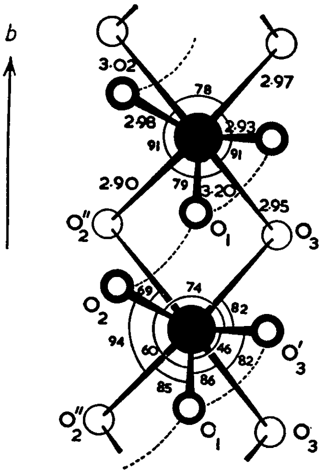

Fig. 7. Unsymmetrical co-ordination of Rb^+ ions viewed approximately normal to (101). All distances in Ångström units and all angles in degrees.

Comparison of chain structures of the meta composition

By sharing common corners, tetrahedral XO_4 units can link together to produce long chains of empirical composition $(XO_3)_n$. X-ray structural studies have shown this to be the case where X = Si, P, S and V. In Fig. 8 the metaphosphate chain is compared with the metasilicate chain as found in (*a*) enstatite, $MgSiO_3$ (Warren & Modell, 1930), (*b*) sodium metasilicate, Na_2SiO_3 (Grund & Pizy, 1952), (*d*) the chain structure in the asbestos form of sulphur trioxide (Westrik & MacGillavry, 1954), and (*e*) potassium metavanadate KVO_3H_2O (Christ, Clark & Evans, 1954).

A common feature of the five structures shown is that in each case the chain axis lies parallel to the shortest unit-cell axis, along which direction the crystals tend to develop a fibrous character. In each chain the pattern repeats every two XO_3 units, and, except in the case of enstatite, the chain axes are coincident with crystallographic axes of twofold screw symmetry. The greatest structural similarity is shown between the metaphosphate and the sulphur trioxide chains, which are more compact than the metasilicate chains, and which, unlike the others shown in the figure, form spiralling arrangements.

In all cases the external X–O bonds are considerably shorter than the X–O (chain) bonds. A progressive increase in covalent character of the latter is suggested by the closer approach to tetrahedral values of the angle X–O–X with increasing atomic number of X, but the experimental X–O (chain) distances all agree closely with the values calculated from the respective covalent radii (Pauling, 1944) after corrections for electronegativity difference have been made (Table 4).

Table 4. *Comparison of X–O bond lengths*

	Sodium meta-silicate, Na_2SiO_3	Rubidium meta-phosphate, $RbPO_3$	Sulphur tri-oxide SO_3
X–O (external)	1·57 Å	1·46 Å	1·41 Å
X–O (chain)	1·67	1·62	1·61
Sum of covalent radii, r_X+r_O	1·83	1·76	1·70
Sum of covalent radii with Schomaker–Stevenson electronegativity correction	1·68	1·63	1·61
X–O–X	137°	129°	121°

In the case of the metavanadate chain, where double sharing of oxygen produces a fivefold coordination round the vanadium, the chain V–O bonds are also found to be considerably longer than the remaining V–O bonds (Christ *et al.*, 1954).

Adjacent tetrahedral units in a meta chain may be mutually oriented in different ways, and Fig. 9 shows the idealized arrangements giving rise to the chains

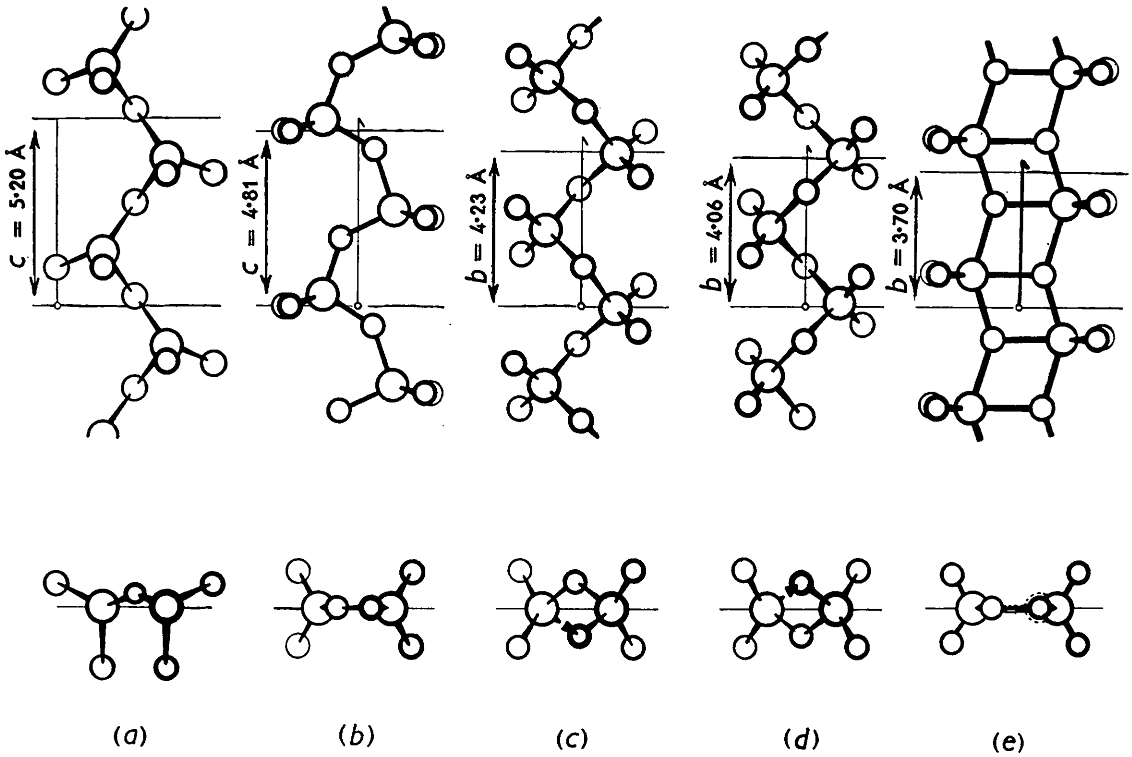

Fig. 8. Meta chain structures. In each case the upper diagram shows a section through the chain plane, while the lower diagram gives a view down the chain axis. Diagrams are drawn from the data given in the respective references, and positive ions are omitted: (*a*) enstatite, (*b*) sodium metasilicate, (*c*) rubidium metaphosphate (left-hand chain), (*d*) sulphur trioxide (right-hand chain), (*e*) potassium metavanadate monohydrate.

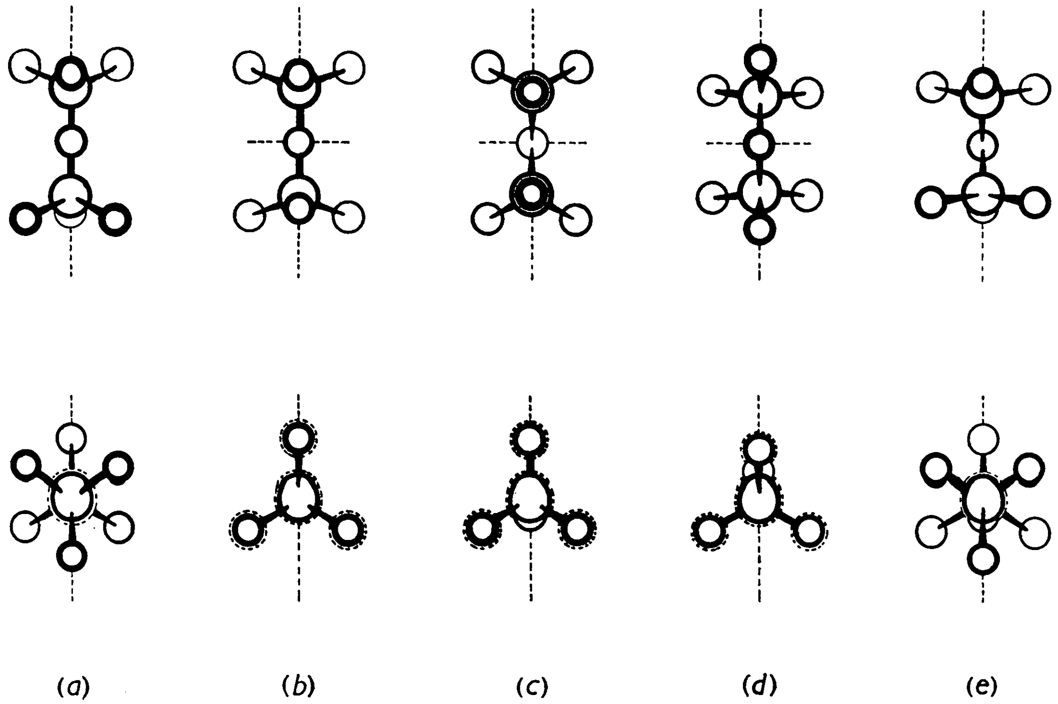

Fig. 9. Orientations of two corner linked tetrahedra: views with obscured atoms and mirror planes shown broken. (*a*) centrosymmetrical, (*b*) mirror plane, (*c*) as in enstatite, (*d*) as in rubidium metaphosphate and sulphur trioxide, (*e*) as in sodium metasilicate.

Table 5. *Observed and calculated structure amplitudes*

hkl	Fobs	Fcalc	hkl	Fobs	Fcalc	hkl	Fobs	Fcalc	hkl	Fobs	Fcalc	hkl	Fobs	Fcalc	hkl	Fobs	Fcalc	hkl	Fobs	Fcalc	hkl	Fobs	Fcalc
2 0 0	6	-13	7 0 7	13	+29	$\bar{4}$ 0 8	16	+22	3 1 3	60	+63	5 1 7	20	+27	$\bar{3}$ 1 4	45	+40	0 20	6	-6	7 2 3	17	-11
4	82	-82	0 0 8	<3	-1				4	7	-11	6	23	+32	$\bar{4}$	58	+55	1	78	+61	8	12	-16
6	78	-73	2	14	-26	1 1 0	32	+29	5	46	+51	0 1 8	23	-19	$\bar{5}$	5	-7	2	10	-11	9	16	-13
8	64	-66				2	88	+75	6	7	+9	1	<5	-7	$\bar{6}$	27	+21	3	82	+75	10	51	-56
10	83	+75	$\bar{1}$ 0 1	16	+14	3	51	+41	7	8	-5	$\bar{2}$	17	-20	$\bar{7}$	81	+72	4	8	-9	11	16	+16
12	87	+64	$\bar{3}$	88	-88	4	110	+102	8	55	+55	$\bar{1}$ 1 1	87	+73	$\bar{8}$	48	-50	5	6	+8	12	13	-17
14	24	-20	$\bar{5}$	56	-68	5	93	-97	9	33	-33	$\bar{2}$	130	-130	$\bar{9}$	9	+3	6	42	+41	0 2 4	9	-6
			$\bar{7}$	74	+70	6	27	-40	10	8	+8	$\bar{3}$	7	+4	$\overline{10}$	35	-32	7	36	-47	1	86	-82
1 0 1	2	0	$\bar{9}$	67	+67	7	22	-28	11	38	-40	$\bar{4}$	47	-43	$\overline{11}$	34	+29	8	17	-19	2	33	-26
3	149	+152	$\overline{11}$	22	-18	8	56	-55	12	36	-39	$\bar{5}$	57	-55	$\overline{12}$	<5	-2	9	46	-57	3	38	-38
5	13	-17	$\overline{13}$	24	-27	9	44	+48	13	9	+9	$\bar{6}$	19	+17	$\overline{13}$	<4	+11	10	<6	-3	4	46	+36
7	104	-103	$\overline{15}$	30	-36	10	36	-35	0 1 4	37	-33	$\bar{7}$	38	-38	$\overline{14}$	20	+28	11	<6	+6	5	33	+34
9	<8	-15	$\bar{2}$ 0 2	95	-84	11	7	+12	1	42	+40	$\bar{8}$	36	+28	$\bar{1}$ 1 5	53	+55	12	8	+9	6	19	-17
11	<5	-2	$\bar{4}$	71	+63	12	20	+24	2	44	-50	$\bar{9}$	26	+20	$\bar{2}$	25	-20	13	40	+46	7	53	+56
13	48	+50	$\bar{6}$	96	+108	13	18	+21	3	43	-52	$\overline{10}$	73	+58	$\bar{3}$	52	+47	14	19	-18	8	<7	0
15	22	+32	$\bar{8}$	28	+24	14	27	+34	4	27	-22	$\overline{11}$	32	+31	$\bar{4}$	73	-68	0 2 1	125	+117	9	22	+26
0 0 2	148	-146	$\overline{10}$	30	-28	15	8	-14	5	55	-62	$\overline{12}$	30	-23	$\bar{5}$	32	-29	1	32	-27	10	9	+9
2	11	-10	$\overline{12}$	102	-80	0 1 1	56	+46	6	35	+36	$\overline{13}$	30	+26	$\bar{6}$	14	+11	2	52	+45	11	24	-33
4	73	+76	$\overline{14}$	<5	-3	1	47	+46	7	25	+28	$\overline{14}$	37	-44	$\bar{7}$	33	-34	3	7	+10	0 2 5	50	+50
6	69	+76	$\bar{1}$ 0 3	24	-15	2	100	+92	8	40	+41	$\overline{15}$	25	-24	$\bar{8}$	12	+15	4	94	-83	1	17	-11
8	24	+17	$\bar{3}$	92	+73	3	47	-45	9	21	+22	$\bar{1}$ 1 2	36	-37	$\bar{9}$	25	-25	5	12	+11	2	17	-18
10	99	-85	$\bar{5}$	90	+74	4	14	+20	10	10	-10	$\bar{2}$	106	-106	$\overline{10}$	25	+27	6	71	-72	3	19	+17
12	19	-25	$\bar{7}$	24	-20	5	33	-46	11	21	+22	$\bar{3}$	34	-35	$\overline{11}$	21	+25	7	16	-14	4	57	-59
14	18	+18	$\bar{9}$	79	-77	6	11	+10	12	20	-18	$\bar{4}$	66	-57	$\overline{12}$	18	+22	8	<6	-4	5	17	-19
1 0 3	70	-70	$\overline{11}$	<8	-5	7	35	-40	0 1 5	58	+55	$\bar{5}$	42	+37	$\overline{13}$	21	+28	9	20	+17	6	17	-20
3	78	-76	$\overline{13}$	10	+13	8	57	-63	1	8	-5	$\bar{6}$	<5	-1	$\bar{1}$ 1 6	36	-43	10	48	+50	7	15	+19
5	30	+26	$\bar{2}$ 0 4	119	+103	9	42	+48	2	12	+12	$\bar{7}$	66	+64	$\bar{2}$	16	-15	11	<6	-2	8	16	+25
7	85	+97	$\bar{4}$	75	-52	10	40	-36	3	38	-38	$\bar{8}$	49	+49	$\bar{3}$	13	-14	12	42	+46	9	<7	+4
9	<6	+9	$\bar{6}$	67	-64	11	36	+36	4	14	+17	$\bar{9}$	28	-24	$\bar{4}$	36	-36	13	21	-20	10	33	+35
11	13	-16	$\bar{8}$	25	-32	12	46	+44	5	43	-47	$\overline{10}$	56	+53	$\bar{5}$	16	-11	14	8	-12	0 2 6	9	+14
13	55	-49	$\overline{10}$	<8	0	13	<6	+1	6	16	-22	$\overline{11}$	27	-30	$\bar{6}$	23	-23	0 2 2	4	+6	1	51	+57
0 0 4	71	+72	$\overline{12}$	99	+77	14	16	+19	7	12	+12	$\overline{12}$	23	-21	$\bar{7}$	40	+43	1	58	+55	2	9	0
2	41	-28	$\overline{14}$	12	+12	15	18	-22	8	47	-47	$\overline{13}$	9	-12	$\bar{8}$	21	+21	2	52	+38	3	25	+28
4	49	-50	$\bar{1}$ 0 5	18	-14	0 1 2	51	+44	9	34	+37	$\overline{14}$	30	-32	$\bar{9}$	25	+29	3	86	+74	4	20	-16
6	35	-48	$\bar{3}$	16	-13	1	52	-52	10	25	+23	$\overline{15}$	<5	0	$\overline{10}$	25	+31	4	38	-30	5	28	-40
8	10	+10	$\bar{5}$	98	-80	2	78	+74	11	18	+24	$\bar{1}$ 1 3	40	-40	$\overline{11}$	28	-30	5	10	-12	6	13	+14
10	73	+72	$\bar{7}$	17	-22	3	30	+33	0 1 6	32	+32	$\bar{2}$	75	+71	$\bar{1}$ 1 7	37	-39	6	6	-7	7	31	-50
1 0 5	102	+97	$\bar{9}$	85	+78	4	53	+49	1	16	-13	$\bar{3}$	45	-45	$\bar{2}$	10	-13	7	77	-75	0 2 7	9	-13
3	51	+50	$\overline{11}$	-	+19	5	79	+80	2	47	+39	$\bar{4}$	57	+56	$\bar{3}$	25	-30	8	12	+13	1	6	-8
5	61	-68	$\overline{13}$	7	-9	6	31	-30	3	57	+61	$\bar{5}$	30	-35	$\bar{4}$	40	+42	9	29	-30	2	26	+26
7	40	-46	$\bar{2}$ 0 6	103	-82	7	9	-6	4	13	-13	$\bar{6}$	8	-8	$\bar{5}$	<6	-3	10	8	-7	3	<8	+4
9	7	-8	$\bar{4}$	<8	-3	8	50	-51	5	13	+17	$\bar{7}$	46	+52	$\bar{6}$	12	+17	11	22	+22	4	19	+33
11	15	+23	$\bar{6}$	64	+58	9	30	+33	6	20	-22	$\bar{8}$	18	-24	$\bar{7}$	26	+36	12	6	+3	$\bar{5}$	<3	+3
0 0 6	<4	-2	$\bar{8}$	19	+26	10	20	-19	7	16	-16	$\bar{9}$	<7	+2	$\bar{8}$	12	-16	13	25	+42	$\bar{1}$ 2 1	9	+8
2	6	+10	$\overline{10}$	<3	+1	11	17	-24	8	21	-26	$\overline{10}$	51	-48	$\bar{9}$	25	+27	0 2 3	83	-77	$\bar{2}$	42	+44
4	35	+44	$\bar{1}$ 0 7	14	-21	12	27	+30	9	8	-17	$\overline{11}$	34	-32	$\bar{1}$ 1 8	22	+32	1	40	+40	$\bar{3}$	26	+23
6	28	+34	$\bar{3}$	19	+24	13	13	-12	0 1 7	34	-28	$\overline{12}$	6	-2	$\bar{2}$	11	-13	2	5	+2	$\bar{4}$	42	-45
8	38	-48	$\bar{5}$	67	+51	14	22	+29	1	10	+8	$\overline{13}$	21	-24	$\bar{3}$	9	+18	3	36	-34	$\bar{5}$	32	-36
1 0 7	77	-72	$\bar{7}$	19	+25	0 1 3	49	-47	2	8	-12	$\overline{14}$	40	+41	$\bar{4}$	22	+29	4	57	+56	$\bar{6}$	77	-92
3	<3	-10	$\bar{9}$	30	-34	1	51	-47	3	34	+38	$\bar{1}$ 1 4	23	+26	5	10	+8	5	22	+22	$\bar{7}$	29	+30
5	42	+50	2 0 8	46	+45	2	56	-59	4	6	-4	2	43	+39				6	54	+59	8	29	-30

hkl	Fobs	Fcalc	hkl	Fobs	Fcalc	hkl	Fobs	Fcalc	hkl	Fobs	Fcalc	hkl	Fobs	Fcalc	hkl	Fobs	Fcalc	hkl	Fobs	Fcalc	hkl	Fobs	Fcalc
$\bar{9}$ 2 1	15	-14	$\bar{7}$ 2 5	15	-10	2 3 2	62	+57	$\bar{9}$ 3 1	<10	+3	8 4 0	6	0	$\bar{1}$ 4 2	<10	-2	$\bar{3}$ 5 1	<6	+2			
$\overline{10}$	52	+56	$\bar{8}$	44	-48	3	67	-50	10	10	-18	9	8	+7	$\bar{2}$	47	+43	$\bar{4}$	37	+32			
$\overline{11}$	12	-10	$\bar{9}$	16	-12	4	<10	+7	11	29	+32	10	-	-33	$\bar{3}$	10	+8	$\bar{5}$	34	+31			
$\overline{12}$	48	+49	$\overline{10}$	20	+18	5	15	-22	$\overline{12}$	<10	+6	0 4 1	14	-13	$\bar{4}$	12	-11	$\bar{1}$ 5 2	38	+39			
$\overline{13}$	23	+21	$\overline{11}$	16	-10	6	11	-10	$\bar{1}$ 3 2	109	+84	1	67	-63	$\bar{5}$	<9	+4	$\bar{2}$	31	+29			
$\bar{1}$ 2 2	4	+3	$\overline{12}$	26	+40	7	23	-30	$\bar{2}$	33	-34	2	16	-10	$\bar{6}$	80	-68	$\bar{3}$	15	-9			
$\bar{2}$	7	-9	$\bar{1}$ 2 6	27	+31	8	29	-36	$\bar{3}$	21	-14	3	35	-41	$\bar{7}$	<8	-2	$\bar{4}$	34	+36			
$\bar{3}$	67	-73	$\bar{2}$	9	-8	9	26	+33	$\bar{4}$	42	-38	4	17	+11	$\bar{8}$	13	-18	$\bar{5}$	15	-17			
$\bar{4}$	37	+33	$\bar{3}$	25	-34	10	<9	-11	$\bar{5}$	32	-32	5	8	+8	$\bar{9}$	<6	-4	$\bar{1}$ 5 3	33	+38			
$\bar{5}$	52	-55	$\bar{4}$	<4	-2	11	39	+49	$\bar{6}$	<6	0	6	20	+12	$\overline{10}$	34	+40	$\bar{2}$	<7	-2			
$\bar{6}$	48	-47	$\bar{5}$	55	-62	12	19	+26	$\bar{7}$	8	-20	7	13	+24	$\bar{1}$ 4 3	<11	+10	3	<7	+8			
$\bar{7}$	33	+43	$\bar{6}$	10	+10	0 3 3	12	-9	$\bar{8}$	17	+31	8	<7	0	$\bar{2}$	<11	+7						
$\bar{8}$	10	+12	$\bar{7}$	8	-8	1	22	-13	$\bar{9}$	18	-19	9	30	+47	$\bar{3}$	74	-66						
$\bar{9}$	45	+52	$\bar{8}$	26	-22	2	82	+73	$\overline{10}$	16	+25	0 4 2	28	+37	$\bar{4}$	<11	-4						
$\overline{10}$	14	+12	$\bar{9}$	41	+39	3	24	+18	$\overline{11}$	44	+46	1	9	-10	$\bar{5}$	16	-18						
$\overline{11}$	8	+12	$\overline{10}$	20	+12	4	43	+32	$\bar{1}$ 3 3	42	-44	2	39	+35	$\bar{6}$	12	-12						
$\overline{12}$	11	-9	$\bar{1}$ 2 7	15	+16	5	37	+39	$\bar{2}$	16	-20	3	<7	-4	$\bar{7}$	14	+16						
$\overline{13}$	27	-26	$\bar{2}$	33	-49	6	57	-53	$\bar{3}$	<11	-7	4	53	-58	$\bar{8}$	<8	-5						
$\overline{14}$	12	+16	$\bar{3}$	4	-3	7	<11	0	$\bar{4}$	64	-52	5	<6	+3	$\bar{9}$	12	+21						
$\bar{1}$ 2 3	10	+10	$\bar{4}$	14	-14	8	11	-21	$\bar{5}$	13	+15	6	44	-55	$\bar{1}$ 4 4	<10	+6						
$\bar{2}$	81	-75	$\bar{5}$	18	-19	9	15	-24	$\bar{6}$	32	-28	7	5	+8	$\bar{2}$	15	-23						
$\bar{3}$	38	-34	$\bar{6}$	27	+30	10	7	-9	$\bar{7}$	42	+40	8	23	+29	$\bar{3}$	20	-9						
$\bar{4}$	40	+39	7	19	+16	11	15	-18	$\bar{8}$	69	+65	0 4 3	12	+10	$\bar{4}$	<10	-5						
$\bar{5}$	30	+27				0 3 4	11	-16	$\bar{9}$	<10	-1	1	53	+58	$\bar{5}$	-	-2						
$\bar{6}$	64	+76	1 3 0	61	-52	1	18	+11	$\overline{10}$	21	+29	2	10	+5	$\bar{6}$	38	+42						
$\bar{7}$	15	-14	2	46	+46	2	34	-35	$\overline{11}$	25	-25	3	22	+21	$\bar{1}$ 4 5	31	-29						
$\bar{8}$	25	+33	3	30	+28	3	31	+28	$\overline{12}$	9	-14	4	14	-8	$\bar{2}$	<8	-2						
$\bar{9}$	<4	-2	4	24	+31	4	<13	-11	$\bar{1}$ 3 4	43	-62	5	<7	-5	$\bar{3}$	43	+44						
$\overline{10}$	23	-26	5	26	+36	5	33	+39	$\bar{2}$	<10	-9	6	11	-8	4	<7	+1						
$\overline{11}$	20	+15	6	<6	-6	6	33	+28	$\bar{3}$	32	-34	0 4 4	50	-54									
$\overline{12}$	41	-57	7	16	+26	0 3 5	-	-16	$\bar{4}$	53	+47	1	16	+12	1 5 0	22	-27						
$\overline{13}$	10	-8	8	30	-45	1	<12	+4	$\bar{5}$	47	+39	2	-	+8	2	27	-37						
$\bar{1}$ 2 4	9	-10	9	<6	-10	2	54	-51	$\bar{6}$	<8	+7	3	<7	+2	3	15	+17						
$\bar{2}$	14	+14	10	<6	-11	3	40	-29	$\bar{1}$ 3 5	20	+35	4	47	+62	4	-	-36						
$\bar{3}$	55	+58	11	56	-48	4	<11	+1	$\bar{2}$	<11	+18	5	-	-4	5	<7	+13						
$\bar{4}$	20	-17	12	9	+11	5	16	-21	$\bar{3}$	16	+19	6	17	+19	0 5 1	<6	0						
$\bar{5}$	48	+50	0 3 1	<6	-4	6	44	+35	$\bar{4}$	49	+32	0 4 5	10	-9	1	18	-16						
$\bar{6}$	18	+14	1	23	+18	0 3 6	31	+28	$\bar{5}$	-	-9	1	33	-38	2	11	-16						
$\bar{7}$	<6	-11	2	47	-50	1	31	-17	$\bar{6}$	31	+29	2	-	0	3	7	+9						
$\bar{8}$	16	+12	3	<10	-1	2	13	+17	$\bar{1}$ 3 6	-	+42	3	17	-20	4	41	-29						
$\bar{9}$	47	-53	4	85	-70	3	27	-27	$\bar{2}$	<9	-8	$\bar{4}$	<5	+8	5	37	+35						
$\overline{10}$	19	-16	5	59	-51	4	<8	+1	3	48	+42	$\bar{1}$ 4 1	64	+44	0 5 2	<4	-5						
$\overline{11}$	26	-32	6	36	+34	$\bar{5}$	27	-30				$\bar{2}$	10	-7	1	10	+10						
$\overline{12}$	<4	0	7	10	-13	$\bar{1}$ 3 1	59	+47	0 4 0	45	-66	$\bar{3}$	54	+42	2	52	-46						
$\overline{13}$	15	+23	8	45	+57	2	40	+40	1	9	-8	$\bar{4}$	<11	+5	3	26	-19						
$\bar{1}$ 2 5	16	-16	9	15	+20	3	<7	+3	2	44	-42	$\bar{5}$	9	+15	4	17	-15						
$\bar{2}$	49	+50	10	<9	+6	4	102	+81	3	<6	-5	$\bar{6}$	29	+16	0 5 3	<6	-4						
$\bar{3}$	20	+16	11	24	+28	5	51	-43	4	37	+43	$\bar{7}$	11	-20	1	11	+13						
$\bar{4}$	<4	+3	12	<9	-9	6	17	-14	5	6	+2	$\bar{8}$	<8	+3	$\bar{2}$	20	+30						
$\bar{5}$	5	+5	0 3 2	5	+7	7	16	-17	6	49	+65	$\bar{9}$	50	-44	$\bar{1}$ 5 1	18	-41						
6	51	-53	1	20	+17	8	63	-63	7	<5	+2	$\overline{10}$	12	-9	2	<5	+7						

in Fig. 8. It is conceivable that chains derived from each of the arrangements (*a*)–(*e*) may exist in both the silicate and phosphate series although those involving 180° *X*–O–*X* angles may be restricted to the former. Preliminary work on α-sodium metaphosphate (Corbridge, 1955) suggests that this structure consists of alternate layers, parallel to ($\bar{1}01$), of sodium ions, and chains repeating every 4PO$_3$ units along the *b* axis.

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Short Communications

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The bond lengths in chrysene.

By D. M. Burns, *Physics Department, University College of the Gold Coast, Achimota, Gold Coast* and I. Iball,* *University of St. Andrews, Carnegie Laboratory of Physics, Queen's College, Dundee, Scotland*

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The crystal structure of chrysene has been re-investigated with a view to obtaining the C–C bond lengths. Starting from the approximate atomic coordinates given by Iball (1934), further ($h0l$) and ($0kl$) Fourier syntheses have been computed with Iball's structure factors (which were obtained by using an integrating photometer on Weissenberg photographs) together with some additional structure factors obtained by visual estimates of the intensity on photographs taken recently. The complete three-dimensional data for Cu $K\alpha$ radiation is being collected and it is hoped to improve on the accuracy obtained so far from two-dimensional Fourier syntheses. However, as the three-dimensional work will take some time to complete, this note gives the present position.

The atomic coordinates have been refined in the following way:

(*a*) Two-dimensional Fourier syntheses were computed on the ($0kl$) and ($h0l$) zones, all the observed structure factors being used in each case. The electron-density peaks were determined by the semi-analytical method of Burns & Iball (1955) modified slightly to take advantage of the suggestions put forward by Megaw (1954). The modification consists of using eleven points surrounding the highest recorded electron density and, from three linear combinations of these points, constructing three curves which should intersect at the true peak position. Usually the curves enclose a small triangle and the centroid is taken as the true position. In addition, the logarithms of the densities are used instead of the electron densities themselves.

(*b*) With the coordinates obtained from (*a*) all the structure factors for the two zones were calculated, including those too small to be observed. Errors due to series termination and overlapping were corrected by (i) computing new Fourier syntheses but now including the calculated value of the missing reflexions in the Cu $K\alpha$ reciprocal-lattice sphere (hydrogen atoms were taken into account in calculating the structure factors); (ii) determining the true electron peak positions by the above method again; and then (iii) correcting for the effect of nearest neighbours, as was done in the case of fluorene (Burns & Iball, 1955). In the case of fluorene, however, the table of corrections was obtained by the use of an atomic profile given by $\varrho(r) = A \exp[-pr^2]$, which does not have the diffraction ripples which cause series-termination errors. In the present work a table of corrections has been constructed from the atomic profile obtained by calculating the integral

$$\varrho'(r) = \int_0^{s_0} 2\pi s f(s) \, . \, J_0(2\pi r s) ds \, ,$$

where $f(s)$ is the Cu $K\alpha$ scattering curve for carbon, terminated at $\sin\theta = 1$. (It is desirable when one is using

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* British Empire Cancer Campaign Research Fellow.