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The Crystal Structure of Potassium Palmitate (Form B)

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Form B of potassium palmitate, $C_{16}H_{31}O_2K$, is triclinic with $a=4\cdot15$, $b=5\cdot60$, $c=37\cdot82$ Å; $\alpha=93\cdot0$, $\beta=91\cdot4$, $\gamma=92\cdot4°$. The space group is $P\bar{1}$ with two molecules per unit cell. The hydrocarbon chains are all parallel to each other and are packed in accord with a somewhat distorted version of the usual triclinic sub cell. The ionic layers have essentially the same structure as those in form A of potassium caprate. The angle of tilt of the chain axes is 52°.

Introduction

Early work on the crystallography of potassium soaps was carried out by Piper (1929), who reported one form each for neutral and 1:1 acid potassium soaps. Later work by Vand, Lomer & Lang (1947) established the existence of three anhydrous forms A, B and C for neutral even-numbered potassium soaps, the B form being identical with that described by Piper. The unit-cell dimensions of potassium soaps in these three forms have been determined from powder photographs by Lomer (1952). Form A is monoclinic and occurs when soaps with from six to ten carbon atoms are crystallized from alcohol at room temperature; form B, which is triclinic, occurs in similar conditions for soaps of greater chain length. Both the A and B forms transform to the monoclinic C form at higher temperatures. The crystal structure of potassium caprate, form A, has been described by Vand, Lomer & Lang (1949). The determination of the structure of potassium palmitate, form B, is described below.

Experimental

Samples of potassium laurate, myristate, palmitate and stearate were prepared by neutralizing alcoholic solutions of the appropriate fatty acids with a solution of potassium hydroxide in alcohol which contained about 5% water. Phenolphthalein was used as an indicator. The solutions were then allowed to evaporate slowly in an evacuated desiccator containing calcium chloride. The solutions of the palmitate alone produced single crystals suitable for X-ray examination: as usual with these long-chain compounds the crystals were extremely thin plates, the large faces being (001). A crystal approximately 1 mm × 0·5 mm × 0·03 mm was mounted in a Weissenberg camera and rotation and moving film photographs were taken with the crystal rotating successively about [100] and [010]. The unit cell was found to be triclinic with $a=4\cdot15\pm0\cdot01$, $b=5\cdot60\pm0\cdot02$, $c=37\cdot82\pm0\cdot04$ Å, $\alpha=93\cdot0\pm0\cdot3$, $\beta=91\cdot4\pm0\cdot3$, $\gamma=92\cdot4\pm0\cdot3°$; the long spacing ($=1/c^*$) was 37·80 Å, and assuming two molecules of $C_{16}H_{31}O_2K$ per unit cell the calculated density was $1\cdot109\pm0\cdot008$ g.cm^{-3}, which agrees satisfactorily with the observed value of $1\cdot117\pm0\cdot01$ g.cm^{-3}. The cell dimensions agree well with those determined earlier by Lomer (1952).

The intensities of the *h*0*l* and 0*kl* reflexions were estimated visually: the multiple film technique was used in conjunction with a standard set of spots produced by timed exposures of one of the reflections from the crystal. Some difficulty was experienced in the intensity estimation because of the wide variation in spot shape; the average discrepancy between the estimates of the two authors was equivalent to an *R* index of about 10%. Cochran's (1948) method was used to calculate the Lorentz and polarization factors. The observed structure factors were subsequently brought to the absolute scale by comparison with calculated values. No absorption corrections were applied, since, apart from a very few reflexions which occur for nearly grazing incidence or emergence, the path length of the beam in the crystal does not greatly exceed the thickness of the crystal and thus for the great majority of reflections μt is less than 0·2.

Determination of the structure

The short cell dimensions of the A and B forms are almost exactly the same except that the *a* axis is twice as long in the A form as it is in the B form. This suggested that the crossing of the chain axis direction in alternate layers, perpendicular to the *a* axis, which occurs in the A form was absent in the B form. It was thus possible to visualize a trial structure for the B form in which the packing in the ionic double layer was the same as that in the A form, and in which all the hydrocarbon chains were arranged as those in one of the layers of the A form. This structure also explained the great observed intensity of the reflexions 014 and 104, and was consistent with the Patterson projections along [100] and [010]. The trial structure was refined in the initial stages by the usual method of electron density projections, and in the later stages by use of Curtis's (1959) least-squares program. The

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scattering factor data of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used for the heavy atoms and those of McWeeny (1951) for hydrogen atoms. After several cycles of refinement R was 15·5% for the *h*0*l* reflexions and 17·6% for the 0*kl* reflexions. At this stage the positional parameters of all the atoms, except the hydrogens, had been reliably determined but difficulty was experienced in deciding the best isotropic thermal motion parameters for the carbon and oxygen atoms. Values of B $(=8\pi^2\bar{\mu}_s^2)$ of 2, 3 or 4 Å^2 all gave roughly equal values for R. It was therefore decided to refine the three-dimensional data collected from the upper layer line photographs.

A separate scale factor for each layer was used to bring the observed structure factors to the absolute scale: these factors were revised once during the several cycles of least-squares refinement that were carried out. The program of Hodgson & Rollett (1963) was used and the computing was done on the Oxford University Mercury Computer. Towards the end of the refinement the hydrogen atoms, placed in calculated positions, were included in the calculation of the structure factors but their parameters were not refined. Isotropic temperature factors for each of the other atoms were used and refined simultaneously with the position parameters. The final R value was 11·6% and the total number of structure factors used was about 850. The parameters resulting from the last cycle of refinement are given in Table 1. The accuracy of these parameters may be judged from the standard deviations given in Table 2. The values of the observed and calculated structure factors are given in Table 3.

Discussion of the results

The general arrangement of the atoms in the crystal is illustrated in Fig. 1, which shows that, as in other soap structures, the potassium and oxygen atoms form double layers, parallel to (001), which are separated from each other by the hydrocarbon chains. The packing of the potassium and oxygen atoms in one half of a double layer is illustrated in Fig. 2; it differs from that found in the A form of potassium caprate chiefly in that the angle γ is 92·4° instead of 90°. Each potassium atom is surrounded by four oxygen atoms in the same half of the double layer and by two more in the other half of the double layer. The distances from a potassium atom to its four neighbours in the same half of the double layer are 2·71, 2·73, 2·73 and 2·78 Å and those to the two neighbours in the other half of the double layer are both 2·82 Å.

The carbon—oxygen bond lengths in the carboxyl group are respectively 1·21 ± 0·025 Å and 1·27 ± 0·025 Å and make an angle of 123° with each other. Both of these lengths are thus significantly shorter than the length of either a single bond or of a bond of partial double character and it is not clear why this should be so. The bond lengths between the carbon atoms were calculated and the average is 1·521 ± 0·010 Å; the average distance between alternate carbon atoms is 2·557 ± 0·005 Å and the C–C–C bond angle is 114·4 ± 1°. The carbon atoms are all co-planar within the limits of experimental error, but the oxygen atoms lie one on either side of this plane. The displacements may be regarded as resulting from a 16·4° rotation of the carboxyl group about the first carbon–carbon bond in the molecule. A similar rotation of the carboxyl group has been reported in the crystal structure of the A_1 form of lauric acid by Lomer (1963) and also in the crystal structure of tetradecanamide by Turner & Lingafelter (1955) and in 11-aminoundecanoic acid hydrobromide hemihydrate by Sim (1955). These results suggest that this rotation may be a property of the fatty acid radical rather than due to an effect of the end packing of the molecules, which is different, both physically and ge-

Table 1. *Atomic coordinates as fractions of the unit cells*

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*
K	0·23761	0·25687	0·02755	1·96
O(1)	0·76645	0·57339	0·04122	3·1
O(2)	0·72621	0·96148	0·04114	3·4
C(1)	0·71214	0·77592	0·05632	2·8
C(2)	0·61077	0·77670	0·09534	2·9
C(3)	0·50343	0·54146	0·11026	3·1
C(4)	0·43396	0·56098	0·14913	3·0
C(5)	0·31384	0·32458	0·16358	3·0
C(6)	0·23401	0·33782	0·20269	3·6
C(7)	0·12604	0·10154	0·21710	3·3
C(8)	0·03194	0·11470	0·25574	3·2
C(9)	0·93194	0·88061	0·27044	3·3
C(10)	0·84033	0·89108	0·30903	3·6
C(11)	0·73586	0·65645	0·32386	3·5
C(12)	0·64259	0·67219	0·36263	4·1
C(13)	0·53943	0·43008	0·37654	4·0
C(14)	0·44560	0·44556	0·41574	4·3
C(15)	0·34819	0·20426	0·42890	5·8
C(16)	0·25107	0·21069	0·46828	7·2
H(1)	0·837	0·827	0·1103	5
H(2)	0·430	0·911	0·0983	5
H(3)	0·287	0·496	0·0956	5
H(4)	0·694	0·412	0·1076	5
H(5)	0·661	0·611	0·1640	5
H(6)	0·254	0·695	0·1520	5
H(7)	0·097	0·272	0·1488	5
H(8)	0·504	0·188	0·1608	5
H(9)	0·459	0·389	0·2178	5
H(10)	0·051	0·473	0·2058	5
H(11)	0·910	0·051	0·2022	5
H(12)	0·317	0·967	0·2142	5
H(13)	0·254	0·167	0·2709	5
H(14)	0·847	0·251	0·2589	5
H(15)	0·712	0·830	0·2560	5
H(16)	0·110	0·746	0·2680	5
H(17)	0·064	0·943	0·3244	5
H(18)	0·657	0·027	0·3124	5
H(19)	0·510	0·608	0·3092	5
H(20)	0·917	0·524	0·3212	5
H(21)	0·871	0·721	0·3779	5
H(22)	0·465	0·805	0·3659	5
H(23)	0·315	0·377	0·3618	5
H(24)	0·722	0·293	0·3738	5
H(25)	0·676	0·495	0·4314	5
H(26)	0·269	0·578	0·4194	5
H(27)	0·127	0·152	0·4140	5
H(28)	0·534	0·068	0·4260	5

ometrically in the ionically bonded soaps and the hydrogen bonded acid and amides. The angle of tilt (*i.e.* the angle between the chain axes and the (001) plane) is 52·03 ± 0·20°. The individual bond lengths and angles, together with their calculated standard deviations are given in Fig. 4.

The side by side packing of the hydrocarbon chains can be described by a *subcell* (Vand & Bell, 1951; von Sydow, 1956) which has dimensions $a_s = 4{\cdot}15$, $b_s = 5{\cdot}30$,

Table 2. *Standard deviations of the atomic coordinates*

Atom	σ_x	σ_y	σ_z
K	0·0037 Å	0·0041 Å	0·0036 Å
O(1)	0·0104	0·0113	0·0102
O(2)	0·0107	0·0118	0·0106
C(1)	0·0157	0·0180	0·0156
C(2)	0·0157	0·0177	0·0156
C(3)	0·0160	0·0177	0·0159
C(4)	0·0160	0·0180	0·0159
C(5)	0·0160	0·0178	0·0158
C(6)	0·0170	0·0187	0·0167
C(7)	0·0167	0·0186	0·0162
C(8)	0·0164	0·0181	0·0160
C(9)	0·0166	0·0184	0·0161
C(10)	0·0170	0·0190	0·0167
C(11)	0·0172	0·0188	0·0166
C(12)	0·0179	0·0196	0·0177
C(13)	0·0177	0·0192	0·0173
C(14)	0·0185	0·0205	0·0182
C(15)	0·0212	0·0230	0·0209
C(16)	0·0255	0·0257	0·0240

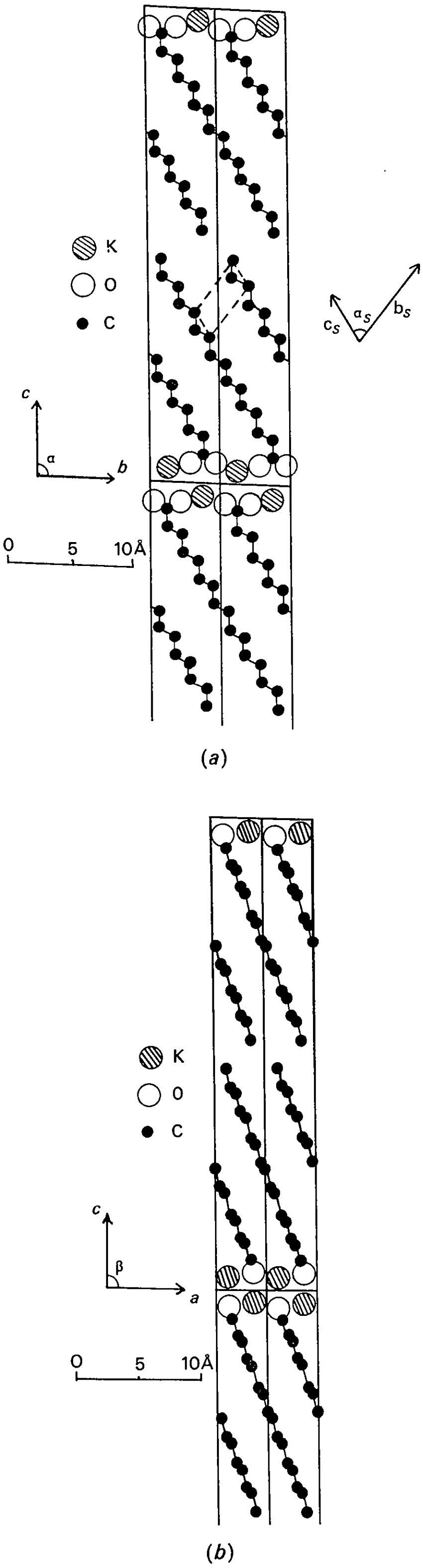

Fig. 1. Arrangement of the atoms in the crystal. (*a*) is the *a*-axis projection; the parallelogram in broken lines is the projection of the subcell; a_s is parallel to *a*. (*b*) is the *b*-axis projection of the structure.

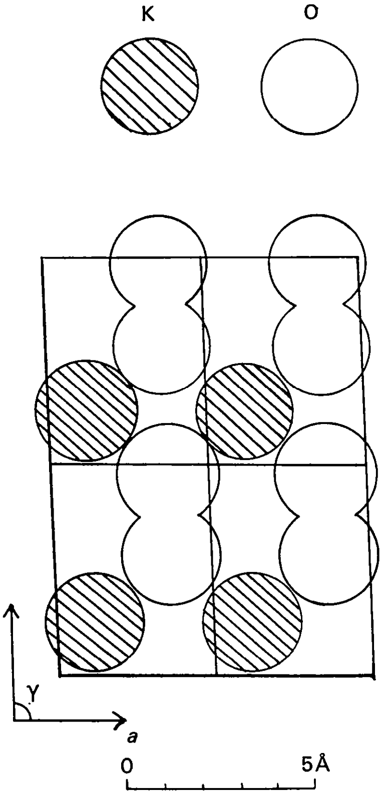

Fig .2. Arrangement of the atoms in one half of the ionic double layer.

Table 3. *Values of observed and calculated structure factors*

The structure factors are arranged in blocks of constant *h* and *k*; each block is headed with **hk*. The first column gives the *l* index, the second column gives the observed value and the third column gives the calculated value. The values given are fifty times the absolute values.

* 0 0		
1	0	2568
2	0	678
3	0	2209
4	0	329
5	0	1445
6	0	-185
7	358	428
8	-805	-766
9	-760	-628
10	-1431	-1363
11	-1521	-1518
12	-1834	-1740
13	-2057	-2056
14	-2102	-1876
15	-2326	-2290
16	-1968	-1785
17	-2549	-2405
18	-1476	-1353
19	2639	2139
20	-716	-700
21	-760	-654
22	-403	-268
23	-537	-418
* 0 1		
0	-939	-1075
1	0	-159
2	-939	-1017
3	0	661
4	6485	6086
5	-3220	-2666
6	-2549	-2353
7	-1700	-1329
8	-2013	-1772
9	-1476	-1261
10	-1521	-1467
11	-1342	-1155
12	-1118	-1190
13	-1073	-1070
14	-850	-921
15	-805	-903
16	-581	-617
17	-626	-688
18	0	-351
19	-537	-453
20	0	64
21	0	-224
22	1029	995
23	2862	2982
24	0	243
25	0	406
26	626	700
27	0	511
28	716	732
29	626	529
30	626	641
-1	0	-9
-2	-716	-760
-3	447	412
-4	0	-215
-5	850	848
-6	313	385
-7	1252	1162
-8	716	891
-9	1431	1378
-10	984	1201
-11	1342	1374
-12	984	1203
-13	939	1000
-14	537	736
-15	1789	2048
-16	671	924
-17	492	602
-18	403	409
-19	0	-31
-20	0	-26
-21	-447	-508
-22	-447	-478
-23	-716	-827
-24	-716	-755
-25	-850	-985
-26	-760	-851
-27	-850	-985
-28	-581	-756
-29	-716	-797
-30	0	-481
-31	0	-556
-32	0	105
-33	0	-24
-34	-939	-892
* 0 2		
0	-1118	-1126
1	-716	-634
2	-1118	-961
3	-760	-638
4	-805	-711
5	-581	-509
6	-716	-518
7	0	-125
8	0	510
9	-895	-890
10	-447	-437
11	0	-219
12	0	91
13	0	53
14	0	467
15	0	458
16	716	742
17	760	723
18	984	946
19	939	853
20	850	975
21	716	781
22	581	810
23	0	607
24	0	687
25	0	348
26	939	957
27	1297	1372
-1	-492	-614
-2	-939	-1182
-3	-403	-546
-4	-850	-1151
-5	0	-322
-6	-805	-907
-7	0	28
-8	-581	-592
-9	671	703
-10	1029	1053
-11	-1610	-1546
-12	-537	-475
-13	0	50
-14	0	161
-15	403	439
-16	537	589
-17	581	642
-18	716	787
-19	716	711
-20	805	863
-21	581	729
-22	760	875
-23	403	620
-24	716	785
-25	0	477
-26	716	714
-27	0	255
-28	984	1058
-29	1163	1024
-30	-1029	-967
-31	-447	-581
-32	-447	-501
-33	-4447	-626
-334	-447	-571
-35	-447	-634
-36	-447	-595
-37	-447	-626
-38	-4447	-594
* 0 3		
1	626	554
2	939	525
3	1208	1065
4	1342	1070
5	11789	1429
6	1789	1397
7	1789	1505
8	1700	1415
9	1386	1244
10	1297	1063
11	760	763
12	0	448
13	850	760
0	0	-175
-1	0	50
-2	-760	-818
-3	0	-328
-4	-1029	-1227
-5	0	-149
-6	984	1052
-7	-2236	-2673
-8	-1789	-2126
-9	-1386	-1614
-10	-1386	-1563
-11	-984	-1154
-12	-850	-1012
-13	-581	-727
-14	-447	-552
-15	0	-386
-16	0	-176
-17	0	-58
-18	0	210
-19	0	180
-20	447	466
-21	0	346
-22	537	700
-23	0	355
-24	939	1283
-25	1476	1932
* 0 4		
0	0	443
1	984	843
-1	1655	1243
-2	3354	2822
* 1 0		
0	-1565	-1524
1	0	57
2	-2415	-22621
3	0	1083
4	6932	6835
5	-895	-883
6	0	-31
7	-626	-564
8	-671	-692
9	-850	-789
10	-1029	-1103
11	-1029	-1074
12	-1163	-1283
13	-1208	-1231
14	-1297	-1321
15	-1118	-1220
16	-1029	-1083
17	-984	-1037
18	-805	-808
19	-850	-893
20	-492	-454
21	-895	-954
22	403	397
23	2192	2076
24	581	486
25	984	894
26	895	798
27	984	858
28	939	914
29	895	798
30	895	807
31	805	668
32	671	594
-1	0	32
-2	-984	-917
-3	224	143
-4	-492	-358
-5	313	227
-6	0	91
-7	492	381
-8	358	479
-9	716	543
-10	760	821
-11	895	791
-12	895	962
-13	850	828
-14	447	643
-15	4786	3865
-16	1521	1400
-17	0	62
-18	850	733
-19	0	-180
-20	0	198
-21	-581	-493
-22	0	-336
-23	-939	-718
-24	-760	-691
-25	-1029	-914
-26	-1029	-882
-27	-1118	-959
-28	-1029	-888
-29	-1029	-843
-30	-850	-710
-31	-805	-650
-32	-537	-430
-33	-537	-385
-34	-626	-548
-35	0	-235
-36	0	16
-37	0	133
-38	0	217
-39	403	357
-40	403	356
-41	403	410
-42	403	435
* 2 0		
0	-1834	-2013
1	-1744	-1845
2	-1968	-2171
3	-1655	-1684
4	-2013	-2113
5	-1208	-1190
6	-2236	-2469
7	492	613
8	2102	2276
9	0	-100
10	850	822
11	671	646
12	850	947
13	850	938
14	939	999
15	895	990
16	939	957
17	760	891
18	626	773
19	626	707
20	492	617
21	0	435
22	0	278
23	0	-28
24	0	-92
25	-716	-834
26	760	348
-1	-1655	-1751
-2	-1521	-1663
-3	-1297	-1311
-4	-984	-1048
-5	-626	-677
-6	0	-292
-7	0	107
-8	492	453
-9	760	745
-10	850	789
-11	1834	1862
-12	1610	1592
-13	537	715
-14	1297	1339
-15	760	848
-16	1029	1081
-17	581	665
-18	671	717
* 3 0		
0	0	-59
1	0	-84
2	0	-11
3	0	-36
4	0	73
5	0	35
6	0	46
7	0	77
8	0	8
9	0	117
10	0	-625
11	1029	1331
12	1297	1502
13	0	499
14	716	825
15	581	617
16	671	629
17	0	470
18	0	382
19	0	273
20	0	147
21	0	30
22	0	-117
23	0	-160
24	0	-283
25	0	-378
26	-537	-549
27	-671	-640
28	-939	-840
-1	0	-135
-2	0	-101
-3	0	-136
-4	0	-114
-5	0	-221
-6	0	-338
-7	0	-198
-8	0	-206
-9	-671	-781
-10	-581	-485
-11	-626	-669
-12	-581	-591
-13	-626	-663
-14	0	-597
-15	0	-465
-16	0	-358
-17	0	-223
-18	0	-98
-19	0	50
-20	0	171
-21	0	328
-22	0	426
-23	671	564
-24	581	548
-25	805	736
-26	0	38
-27	0	209
-28	895	781
-29	626	615
-30	626	545
-31	492	452
* 4 0		
0	0	772
1	671	745
2	671	732
3	671	675
4	0	639
5	0	534
6	0	457
7	0	309
8	0	244
9	0	7
10	0	-83
11	0	-291
12	0	-332
13	-492	-632
14	-671	-916
-1	0	646
-2	0	548
-3	0	419
-4	0	364
-5	0	104
-6	0	78
-7	0	-72
-8	0	-238
-9	0	-356
-10	0	-492
-11	0	-461
-12	0	-504
-13	0	-491
-14	0	-507
-15	0	-467
-16	0	-453
-17	0	-386
-18	0	-349
-19	0	-244
-20	0	-277
-21	0	-92
-22	-537	-493
-23	-537	-467
* 1 -1		
0	6485	7412
1	1968	1884
2	2370	2099
3	1521	1390
4	1252	1154
5	1163	918
6	537	491
7	447	396
8	0	-74
9	0	-78
10	-581	-547
11	-581	-497
12	-805	-800
13	-805	-716
14	-1029	-962
15	-1029	-941
16	-1163	-1098
17	-1342	-1267
18	-1208	-1097
19	0	-106
20	-805	-745
21	-581	-512
22	-716	-620
23	-626	-492
24	-581	-399
25	-492	-350
26	0	-233
27	0	-175
28	0	-60
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25	805	739
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Table 3 (*cont.*)

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-14	-403	-393
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3	760	704
4	581	611
5	537	568
6	403	429
7	358	377
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11	-1073	-820
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17	760	501
18	492	603
19	626	627
20	671	676
21	671	673
22	716	692
23	581	547
24	626	563
25	403	355
26	537	440
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29	1118	935
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33	-403	-476
34	-492	-505
35	-537	-551
36	-537	-528
37	-537	-543
38	-492	-521
39	-403	-490
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-17	537	592
-18	581	711
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-21	760	655
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6	671	678
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8	760	746
9	895	871
10	716	731
11	895	899
12	492	464
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26	-492	-498
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30	-537	-464
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-25	-850	-786
-26	-447	-425
-27	-537	-386
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-29	0	-17
-30	0	142
-31	0	246
-32	537	369
-33	537	476
-34	537	525
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-38	492	503
-39	537	536
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1	581	620
2	313	300
3	447	546
4	268	242
5	403	473
6	313	257
7	358	421
8	313	239
9	313	361
10	0	204
11	0	250
12	0	66
13	0	-102
14	0	-288
15	-671	-614
16	-716	-723
17	-358	-201
18	-537	-643
19	-760	-673
20	-760	-732
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-6	895	1029
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-8	1073	1029
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-10	939	930
-11	760	783
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-24	-492	-493
-25	-581	-480
-26	-447	-431
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1	-626	-728
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4	-403	-520
5	-581	-820
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9	-939	-912
10	-805	-898
11	-537	-731
12	-492	-646
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-3	0	-264
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-5	0	-222
-6	0	-161
-7	0	-132
-8	0	-78
-9	0	11
-10	0	34
-11	0	131
-12	0	80
-13	760	763
-14	0	174
-15	-537	-458
-16	0	248
-17	0	228
-18	492	389
-19	403	410
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-21	492	505
-22	492	458
-23	447	433
-24	447	374
-25	403	316
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3	0	-451
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-3	0	-314
-4	0	-389
-5	-447	-407
-6	-447	-464

$c_s=2\cdot557$ Å; $\alpha_s=65\cdot2°$, $\beta_s=108\cdot5°$, $\gamma_s=110\cdot4°$. The a_s axis of the subcell has the same orientation and length as the a axis of the crystal unit cell; the relation of the other subcell axes to those of the crystal cell is indicated in Fig. 1(*a*). These subcell dimensions differ considerably from those found in the hydrocarbon octadecane by Hayashida (1962). We attribute these differences to the effect of the strong binding in the ionic layers of the soap crystal, which must, to some extent, influence the packing of the chains. It would be interesting to measure the dimensions of the subcell in other triclinic soaps to see if this postulated influence of the ionic layers decreases as the length of the hydrocarbon chains increases. The packing of the methyl groups is illustrated in Fig. 3; each methyl group in the lower half of the cell is contact with four methyl groups in the upper half of the cell which are at distances from it of 4·35, 4·45, 4·01 and 4·02 Å.

The thermal vibration parameters show that the atoms nearer to the ionic layer have smaller vibration amplitudes than those at the farther end of the molecules. This effect is not unexpected since the movement of these atoms is restrained by the heavy potassium atom. This observation explains, at least partly, why the atoms near the methyl group end of a hydrocarbon chain often appear, on electron-density maps, as peaks of lower height than those corresponding to atoms nearer the other end of the chain. We had hoped to investigate the anisotropy of the thermal motions in this compound but as the final residual of 11·5% was already as low as could be expected from the estimated errors of our intensity estimation, it did not seem reasonable to expect to obtain reliable values for any such anisotropy.

We are indebted to I.C.I. Ltd for a grant to help cover our computing expenses.

We wish to thank Dr J. Rollett for his help with the computing described in this paper.

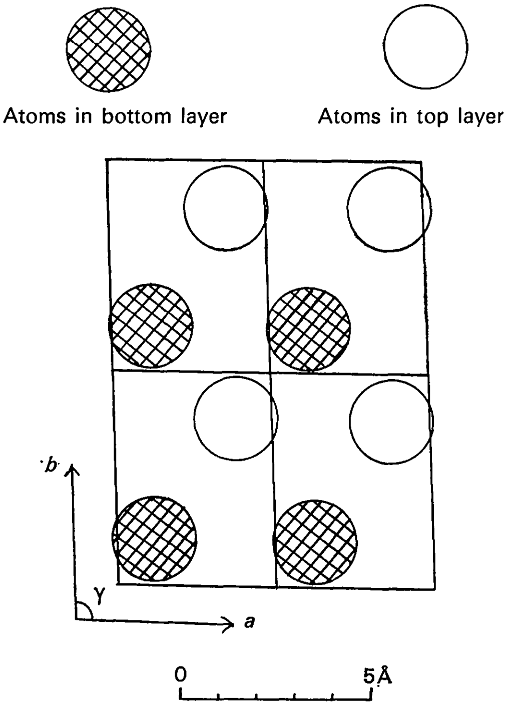

Fig. 3. Arrangement of methyl groups in the crystal.

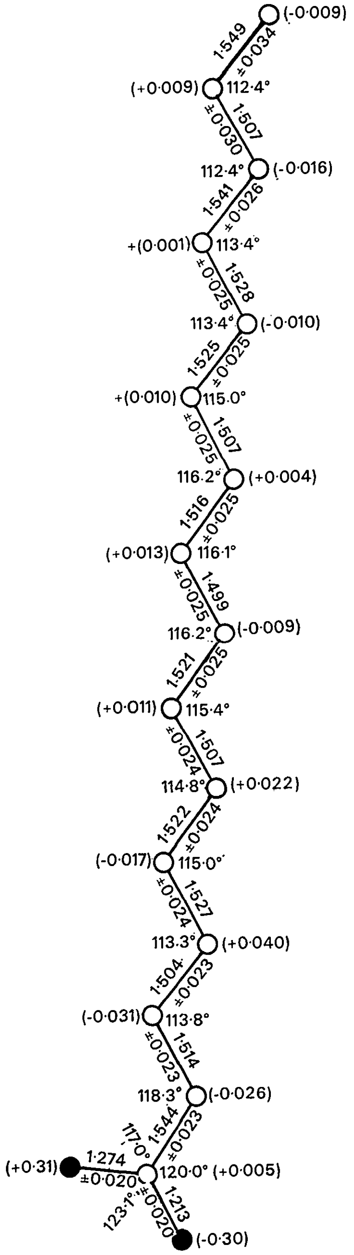

Fig. 4. Arrangement of atoms in the palmitate ion. Open circles are carbon atoms; full circles are oxygen atoms. The figures in parentheses are the deviations (Å) of the atoms from the best plane through the carbon atoms. The bond lengths and their calculated standard deviations are given in Å. The calculated standard deviations of the angles are all approximately 1·0°.

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A Refinement of the Crystal Structure of Yttria

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The crystal structure of yttria, Y_2O_3, has been refined using single-crystal X-ray diffraction data. The results confirm the general features of earlier analyses using powder diffraction data, but a considerable improvement in accuracy has been achieved.

Introduction

Yttria, Y_2O_3, is one of a series of metal oxides which have similar face-centered cubic structures conforming to the space group *Ia*3 (T_h^7)*. Eight metal ions are in the special positions $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; the remaining twenty-four occupy the sites $u, 0, \frac{1}{4}$. The forty-eight oxygen ions are in general positions x, y, z, and are arranged in distorted octahedra around the metal ions, the metal–oxygen bonding distances being unequal. This structure is generally referred to as the *C*-type metal oxide structure. All the sesquioxides of the rare earths belong to this system, as do Ga_2O_3, In_2O_3, Tl_2O_3 and the mineral bixbyite, $(Fe,Mn)_2O_3$.

The first basically correct determination of the structure of a *C*-type metal oxide was carried out by Pauling & Shappel (1932), using a trial-and-error method to analyse the powder-diffraction pattern of bixbyite. The accuracy of the analysis was low, for there are relatively few non-overlapping lines in the powder pattern. Moreover, the atomic scattering factor curves were quoted as having a possible error of twenty per cent. The oxygen positions were not determined directly, but from packing and bonding considerations they were deduced to be at sites equidistant from the metal ions. This structure was redetermined by Dachs (1956), who made a least-squares analysis of the powder-diffraction pattern. The parameters obtained were quite different from those found by Pauling & Shappel.

The first experimental determination of the structure of yttria itself was reported by Villian (1957) who examined the neutron-diffraction powder pattern. A similar study was made by Fert (1962) who used a least-squares method on sixteen reflexions to find the parameters x, y, z, u as well as the neutron scattering length of yttrium.

Table 1 shows the results of these independent determinations, and it can be seen that there is a large range in the atomic coordinates quoted. Standard deviations on neither the atomic coordinates nor thermal parameters have been reported.

Table 1. *Structure parameters from previous investigations*

	u	*x*	*y*	*z*
Pauling & Shappel	0·030	0·385	0·145	0·380
Dachs	0·034	0·375	0·162	0·400
Villian	0·034	0·396	0·155	0·383
Fert	0·034	0·389	0·150	0·377

In view of the importance of the *C*-type metal oxide structure in oxide chemistry an analysis has been carried out with three-dimensional X-ray diffraction data collected from a single crystal. Since there is no overlapping of non-equivalent reflexions the number of independent observations is much greater than can be

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* The space groups of several *C*-type crystals are reported incorrectly in the ASTM Card File as T_5. The systematic absences of the reflexions for this space group are similar to those of T_h^7 except that the condition $hk0\ h(k) = 2n+1$ is allowed.