

## The Crystal Structure of the Potassium Aluminate



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The structure of the potassium aluminate  $\text{K}_2[\text{Al}_2\text{O}(\text{OH})_6]$  has been determined from three-dimensional X-ray data. The symmetry is orthorhombic, the space group is No. 41:  $Aba2$  and the unit cell dimensions are

$$a = 10.23 \text{ \AA}, \quad b = 7.58 \text{ \AA}, \quad \text{and } c = 10.04 \text{ \AA}$$

The structure contains discrete aluminium-oxygen groups  $[(\text{OH})_3\text{AlOAl}(\text{OH})_3]^{2-}$  built up from two  $\text{AlO}_4$  tetrahedra sharing an oxygen. These groups are held together by means of the potassium ions.

Investigations on alkaline aluminum salt solutions have shown that the aluminum ion probably occurs mainly as a complex with one negative charge per aluminum atom.<sup>1</sup> It has been suggested that the coordination number of aluminum in these solutions is 4 rather than 6 and Raman spectra are consistent with a  $T_d$  symmetry although in the absence of an infrared spectrum a unique interpretation has not been possible.<sup>2</sup> In order to get more information on the bonding characteristics of the aluminum ion under these conditions it would be of value to know the structures of some water-containing aluminates. Two such sodium aluminates and one potassium aluminate have been described<sup>3-5</sup> but their structures have not been investigated. In the present paper the determination of the crystal structure of the potassium aluminate  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  will be given.

## EXPERIMENTAL

For the preparation of crystals a 43 % KOH solution was saturated at about 50°C with potassium aluminate obtained by dissolving aluminum metal (99.99 %) in 50 % KOH (*p.a.*). Precautions were taken to protect the solutions from the carbon dioxide of the air. After filtering and cooling to room temperature well formed crystals separated in a few hours. Because of their extreme water solubility they could not be washed free from the mother liquor. They could, however, be washed with absolute alcohol and then seemed to be somewhat less unstable in air, but no reproducible results could be obtained when crystals treated in this way were analyzed, indicating an incomplete removal of the mother liquor or a slight decomposition of the crystals.

For the analysis aluminum was precipitated with 8-hydroxy-quinoline. Water was determined by means of Brush and Penfield's method as described by Kolthoff and Sandell<sup>6</sup> and potassium was precipitated with sodium tetraphenyl boron. The averages of the values found were 39.6 %  $\text{Al}_2\text{O}_3$ , 38.2 %  $\text{K}_2\text{O}$ , and 21.2 %  $\text{H}_2\text{O}$  which are in approximate agreement with the values 40.75 %  $\text{Al}_2\text{O}_3$ , 37.65 %  $\text{K}_2\text{O}$ , and 21.6 %  $\text{H}_2\text{O}$  calculated for the composition  $\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ . This formula was suggested by Fricke and Jucaitis<sup>4,5</sup> on the basis of the results of a large number of analyses carried out by various methods and is confirmed by the present structure determination.

All preparations were carried out in glass-ware made of Pyrex or Jena glass and some silica may therefore have been present in the solutions. No silicon could, however, be detected in the crystals when tested by means of ammonium molybdate.

For the collection of intensity data a crystal was transferred directly from the mother liquor into a thin-walled glass capillary. A small amount of mother liquor was also transferred into the capillary which was then sealed by means of lacquer. Weissenberg and rotation photographs showed the crystals to be orthorhombic with the unit cell dimensions:

$$a = 10.2, \text{ \AA} \quad b = 7.6, \text{ \AA} \quad c = 10.0, \text{ \AA}$$

In order to get more precise values for the unit cell dimensions powder photographs were taken of crystals which had been washed with absolute alcohol. Apparently this treatment did not cause any noticeable change in the structure since the photographs taken in a Guinier focussing camera could be completely indexed on the basis of the unit cell determined from the Weissenberg photographs (Table 1).  $\text{CuK}\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ )

Table 1. Powder photograph of  $\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ . Guinier camera  $\text{CuK}\alpha$  radiation.

<i>h k l</i>	$10^4 \sin^2\theta$ calc	$10^4 \sin^2\theta$ obs	<i>I</i> obs
1 1 1	219	218	vw
0 2 0	413	414	vvw
2 0 2	462	461	vs
2 2 0	640	640	s
0 2 2	648	648	s
3 1 1	672	673	vs
1 1 3	689	689	vw
1 2 2	705	705	vvw
2 1 3	859	859	m
2 2 2	875	876	m
0 0 4	941	940	vs
1 3 1	1045	1045	w
4 1 1	1069	1070	w
4 0 2	1142)	1142	m
3 1 3	1143)		
1 2 4	1411	1412	vvw
3 3 1	1498	1499	w
5 1 1	1579)	1582	s
2 2 4	1581)		
1 1 5	1631	1629	w
0 4 0	1653	1649	vvw
4 0 4	1848	1849	vvw
1 4 2	1945	1945	vvw
3 3 3	1969	1968	vvw

radiation was applied and KCl ( $a_0 = 6.2929 \text{ \AA}$ ) was used as internal standard. By means of a least squares procedure the unit cell dimensions were found to be:

$$a = 10.23, \text{ \AA} \quad b = 7.57, \text{ \AA} \quad c = 10.04, \text{ \AA}$$

The density determined by means of flotation was found to be 2.11. That calculated assuming four formula weights in the unit cell is 2.135.

Weissenberg photographs were taken along the  $a$  axis (0 to 3rd layer line), along [011] (0 to 3rd layer line) and along [101] (0 to 7th layer line). The systematic absences were such that

$$\begin{array}{l} hkl \text{ occurred only for } k + l = 2n \\ 0kl \quad \text{»} \quad \text{»} \quad \text{»} \quad k = 2n \text{ and } l = 2n \\ h0l \quad \text{»} \quad \text{»} \quad \text{»} \quad h = 2n \text{ and } l = 2n \end{array}$$

This is characteristic of the space groups No. 64: *Acam* (the setting differs from that given in the *International Tables*) and No. 41: *Aba2*.

Intensities were estimated by means of a scale prepared by timed exposures of one of the reflections of the crystal. Only the two sets of photographs taken around the diagonals were used for the intensity measurements. Since a small amount of mother liquor always adhered to the crystals the absorption conditions were not specified and no correction for absorption could be applied. The shapes of the crystals were rather irregular with the largest dimension about 0.2 mm.

The intensities were put on a common scale by means of reflections occurring on more than one photograph. 380 independent reflections were observed corresponding to about 80 % of those within the sphere of reflection.

### STRUCTURE DETERMINATION

Table 2 lists those peaks in the three dimensional Patterson function

Table 2. Peaks ( $> 15$ ) in the three-dimensional Patterson function (expected heights for single K—K, K—Al, and Al—Al vectors are 10, 7, and 5, respectively).

$u$	$v$	$w$	Peak height	Number of vectors		
				K—K	K—Al	Al—Al
0.11	0.5	0	46	4		
0.39	0	0	21	2 + 2		
0.5	0.09	0	28			4
0.5	0.5	0	84	4 + 4		4 + 4
0	0.41	0	18			2 + 2
0.205	0.25	0.25	26		2 + 2 + 2 + 2	
0.31	0.235	0.25	29		2 + 2 + 2 + 2	

which have a height larger than 15. On this scale the expected heights are 10, 7, and 5 for a single K—K, K—Al, and Al—Al vector, respectively. No peaks occur at  $00\frac{1}{2}$ ,  $0\frac{1}{2}0$ , or  $00w$  which limits the possible positions for the 8 potassium and the 8 aluminum atoms in the unit cell to  $8(f)$  in *Acam* or  $8(b)$  in *Aba2*. These positions have the coordinates  $(0,0,0; 0, \frac{1}{2}, \frac{1}{2}) + x,y,z; \bar{x}, \bar{y}, z; \frac{1}{2} - x, \frac{1}{2} + y, z; \frac{1}{2} + x, \frac{1}{2} - y, z$  where  $z = 0$  if the space group is the centrosymmetric *Acam*. Possible  $x$  and  $y$  parameters can be calculated from the peak positions given in Table 2 using the Harker vectors  $\frac{1}{2} - 2x, \frac{1}{2}, 0$  and  $\frac{1}{2}, \frac{1}{2} - 2y, 0$ , each of which has a fourfold weight. The possible parameters are then found to be  $0, \frac{1}{2}, \pm 0.195$ , and  $\pm 0.305$  for  $x$ , and  $0, \frac{1}{2}, \pm 0.205$ , and  $\pm 0.295$  for  $y$ .

The heights of the peaks listed in Table 2 indicate that the first and the fourth of the vectors are most likely to correspond to K—K vectors. The parameters for the K atoms should then be  $x = 0.195$  and  $y = 0$ . The  $z$  para-

meter must be 0 if the space group is *Acam* and can be chosen to be 0 if the space group is *Aba2*. Other possible positions are equivalent to this. From the remaining vectors in Table 2 the parameters of the Al atoms can be calculated to be  $x = 0.5$  and  $y = 0.205$ . As shown in Table 2 the vectors  $2x, 2y, 0$  when calculated from the deduced parameter values are found to correspond to peaks in the Patterson function which supports the correctness of the assumed parameters.

The  $\bar{K}$ -Al vectors do not correspond to peaks in the Patterson function, if the space group is assumed to be *Acam*, where the  $z$  parameter can only have the values 0 or  $\frac{1}{2}$ . For the non-centrosymmetric *Aba2*, however, these vectors can be unambiguously related to peaks in the plane  $w \approx 1/4$ , indicating a value of  $z \approx 0.25$  for the Al atom.

According to the interpretation of the Patterson function, therefore, the structure is non-centrosymmetric and the space group is No. 41: *Aba2*. Both the potassium and the aluminum atoms are in positions 8(*b*) with the following parameter values:

$$\begin{array}{lll} \text{K: } x = 0.195 & y = 0 & z = 0 \\ \text{Al: } x = 0.50 & y = 0.205 & z = 0.25 \end{array}$$

All resulting K-K, K-Al, and Al-Al vectors are compared with observed peaks in Table 2. Many of the vectors overlap partly (indicated in the table by 2+2 *etc*) which results in an apparent discrepancy between observed and calculated heights.

The parameters of the potassium and the aluminum atoms were refined by means of 9 least squares cycles \* which lowered the  $R$  factor ( $R = \sum ||F_{\text{obs}}| - |F_{\text{calc}}|| / \sum |F_{\text{obs}}|$ ) from 0.31 in the first cycle to 0.27 in the last cycle. The resulting parameters were used to calculate a three-dimensional electron density map. Although the phases of the structure factors were based only on the contributions from the potassium and the aluminum atoms the positions of three sets of oxygens in positions 8(*b*) and one set of oxygens in 4(*a*) were clearly indicated. This accounts for all of the oxygens in the unit cell if the formula  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  is assumed to be correct.

All atoms were now included for a new series of least squares refinements. The  $R$  factor decreased from 0.26 to 0.125 in 12 cycles. Individual, isotropic temperature factors were also refined. Hughes' weighting scheme <sup>7</sup> was used. In the last cycle no shift in any of the parameters exceeded 1/20 of the calculated standard deviation. Observed and calculated structure factors obtained in the last cycle are compared in Table 3.

\* The calculations were carried out on a Facit EDB computer. The least squares program by Åsbrink and Brändén (*IUCr World List of Cryst. Computer Programs*, No. 6023 FACIT (1962)) and the structure factor and Fourier programs by Liminga and Olovsson (*Acta Polytechn. Scand.* (1964) Ma 10) were used.

Table 3. Observed and calculated structure factors.

<i>h</i>	<i>k</i>	<i>l</i>	$F_{obs}$	$F_{calc}$	$\alpha/360$	<i>h</i>	<i>k</i>	<i>l</i>	$F_{obs}$	$F_{calc}$	$\alpha/360$
2	0	0	42	39	0	7	1	3	46	51	0.479
4			31	31	0	8			13	13	0.230
6			76	89	0	9			22	23	0.152
8			22	20	0	10			24	27	0.318
10			98	78	0	11			15	17	0.165
12			—	9	0.5	12			30	34	0.239
0	0	2	38	28	0.542	1	1	5	49	43	0.962
2			110	166	0.496	2			56	52	0.131
4			24	24	0.276	3			60	55	0.571
6			58	68	0.544	4			42	37	0.784
8			88	138	0.550	5			80	75	0.029
10			26	18	0.921	6			53	54	0.776
12			39	48	0.465	7			47	41	0.544
0	0	4	149	192	0.084	8			15	15	0.616
2			45	41	0.406	9			23	16	0.882
4			86	80	0.966	10			14	9	0.448
6			97	102	0.979	11			21	19	0.980
8			< 9	5	0.733	12			18	16	0.704
10			59	63	0.022	1	1	7	20	20	0.084
12			—	8	0.753	2			35	42	0.927
0	0	6	34	36	0.244	3			45	42	0.527
2			96	115	0.512	4			30	25	0.166
4			26	26	0.507	5			63	59	0.037
6			18	19	0.441	6			39	40	0.224
8			—	50	0.505	7			48	42	0.543
10			—	35	0.056	8			—	9	0.365
0	0	8	110	108	0.945	9			—	9	0.192
2			41	44	0.683	10			—	5	0.071
4			37	40	0.054	11			—	17	0.064
6			62	61	0.013	1	1	9	—	18	0.107
8			27	26	0.762	2			17	16	0.338
10			—	45	0.010	3			54	56	0.574
0	0	10	—	37	0.305	4			< 10	11	0.934
2			—	62	0.506	5			34	30	0.034
4			19	15	0.209	6			—	15	0.939
6			32	34	0.351	7			34	32	0.548
8			56	68	0.465	8			12	10	0.676
1	1	1	41	38	0.909	9			—	8	0.016
2			24	21	0.776	1	1	11	—	20	0.048
3			103	110	0.624	2			—	13	0.283
4			76	74	0.636	3			—	21	0.485
5			103	113	0.940	4			19	18	0.340
6			32	29	0.655	5			41	49	0.091
7			46	48	0.528	6			12	11	0.155
8			< 9	4	0.560	0	2	0	36	37	0.500
9			17	17	0.887	1			40	48	0
10			25	28	0.851	2			122	152	0.500
11			31	28	0.879	3			14	11	0.500
12			32	30	0.819	4			41	34	0
13			22	29	0.577	5			12	11	0
1	1	3	35	34	0.063	6			< 8	4	0
2			77	75	0.683	7			41	43	0
3			108	112	0.463	8			65	78	0.500
4			21	19	0.565	9			< 10	5	0.500
5			65	64	0.088	10			29	31	0
6			45	46	0.106	11			< 10	3	0

<i>h</i>	<i>k</i>	<i>l</i>	$F_{\text{obs}}$	$F_{\text{calc}}$	$\alpha/360$	<i>h</i>	<i>k</i>	<i>l</i>	$F_{\text{obs}}$	$F_{\text{calc}}$	$\alpha/360$
12	2	0	38	38	0.500	5	3	1	74	74	0.123
0	2	2	121	177	0.975	6			45	45	0.083
1			48	40	0.173	7			44	41	0.545
2			88	72	0.616	8			18	18	0.422
3			52	41	0.323	9			18	19	0.064
4			55	50	0.905	10		<	10	13	0.376
5			16	13	0.918	11			30	32	0.178
6			82	81	0.006	12			12	14	0.181
7			13	14	0.698	1	3	3	25	22	0.519
8			14	11	0.179	2			45	37	0.124
9			35	37	0.486	3			94	86	0.632
10			56	62	0.008	4			39	34	0.474
11			11	11	0.130	5			73	75	0.921
12			19	21	0.631	6			30	25	0.972
0	2	4	37	36	0.983	7			68	67	0.567
1			65	64	0.980	8			21	21	0.633
2			96	108	0.507	9			32	34	0.685
3			14	14	0.882	10			22	21	0.730
4			48	48	0.348	11			29	25	0.828
5			33	29	0.403	12			20	21	0.821
6			58	54	0.380	1	3	5	72	71	0.174
7			17	16	0.137	2			13	12	0.151
8			76	82	0.478	3			62	56	0.369
9			19	17	0.871	4			51	43	0.446
10			25	26	0.114	5			75	75	0.071
11			27	28	0.939	6			34	31	0.140
12			38	45	0.483	7			18	20	0.365
0	2	6	132	152	0.989	8		<	11	9	0.381
1			16	16	0.482	9			46	46	0.158
2			41	35	0.822	10		<	9	9	0.122
3			48	48	0.519	11			25	30	0.145
4			75	65	0.982	1	3	7	49	43	0.784
5			12	11	0.061	2		<	9	4	0.033
6			63	58	0.978	3			90	88	0.621
7			20	15	0.091	4			39	42	0.582
8			32	26	0.652	5			40	31	0.913
9			36	33	0.513	6			19	16	0.901
10			58	51	0.001	7			50	37	0.641
0	2	8	—	52	0.245	8			13	14	0.628
1			34	31	0.072	9			38	33	0.820
2			77	79	0.488	10			8	7	0.777
3			< 10	4	0.344	1	3	9	—	19	0.203
4			27	24	0.491	2			14	13	0.963
5			19	16	0.656	3			40	37	0.322
6			40	33	0.482	4			23	20	0.577
7			20	17	0.896	5			69	72	0.127
8			83	69	0.507	6			—	21	0.087
0	2	10	—	87	0.029	7			28	28	0.454
1			—	13	0.998	1	3	11	—	12	0.922
2			—	12	0.735	2			—	14	0
3			< 7	11	0.695	3			—	57	0.669
4			35	29	0.010	4			17	20	0.656
5			7	2	0.425	5			25	28	0.904
6			44	45	0.978	0	4	0	106	119	0
1	3	1	73	74	0.982	1			33	33	0
2			53	48	0.036	2			10	7	0
3			99	104	0.359	3			47	46	0.500
4			33	29	0.338	5			21	21	0.500

<i>h</i>	<i>k</i>	<i>l</i>	$F_{obs}$	$F_{calc}$	$\alpha/360$	<i>h</i>	<i>k</i>	<i>l</i>	$F_{obs}$	$F_{calc}$	$\alpha/360$
6	4	0	40	39	0	3	5	1	85	96	0.692
7			< 10	12	0.500	4			51	54	0.507
8			21	26	0.500	5			73	81	0.868
9			33	43	0.500	6			37	42	0.961
10			34	50	0	7			32	30	0.650
11			15	26	0	8			17	19	0.615
0	4	2	52	55	0.082	9			22	29	0.806
1			59	65	0.941	10			< 8	6	0.376
2			81	84	0.502	11			23	36	0.803
3			46	44	0.661	1	5	3	38	36	0.165
4			40	35	0.589	2			48	49	0.038
5			17	10	0.499	3			69	74	0.360
6			29	22	0.616	4			43	41	0.563
7			45	44	0.047	5			75	65	0.186
8			55	57	0.522	6			27	21	0.956
9			< 10	5	0.826	7			44	43	0.339
10			< 10	12	0.984	8			19	21	0.431
11			24	31	0.983	9			39	42	0.206
0	4	4	81	83	0.047	10			11	14	0.153
1			16	17	0.147	1	5	5	62	52	0.819
2			28	23	0.427	2			38	36	0.869
3			49	45	0.510	3			78	59	0.677
4			45	38	0.063	4			33	32	0.560
5			25	24	0.870	5			32	35	0.907
6			41	37	0.003	6			49	42	0.078
7			18	15	0.933	7			40	39	0.602
8			21	15	0.667	8			17	18	0.570
9			52	57	0.477	9			26	27	0.745
10			42	47	0.015	10			12	15	0.658
0	4	6	16	14	0.095	1	5	7	50	43	0.166
1			73	69	0.023	2			35	30	0.165
2			64	62	0.523	3			37	32	0.301
3			21	21	0.978	4			33	26	0.536
4			< 9	6	0.145	5			56	47	0.111
5			8	7	0.630	6			45	38	0.997
6			12	11	0.035	7			33	26	0.447
7			23	19	0.979	8			12	11	0.482
8			38	36	0.542	1	5	9	< 9	8	0.788
9			10	7	0.795	2			34	28	0.049
10			18	19	0.046	3			60	56	0.629
0	4	8	50	43	0.020	4			29	24	0.519
1			22	15	0.030	5			27	23	0.795
2			37	29	0.627	6			20	15	0.083
3			24	23	0.547						
4			27	24	0.940	0	6	0	78	78	0
5			16	16	0.188	1			61	63	0
6			29	23	0.016	2			25	23	0.500
7			20	19	0.209	3			< 9	0	0.500
8			14	13	0.523	4			17	14	0.500
0	4	10	—	30	0.069	5			18	17	0
1			—	26	0.092	6			31	26	0
2			—	34	0.518	7			—	41	0
3			16	15	0.459	8			—	10	0
4			21	19	0.340	9			—	17	0.500
5			—	—	—	10			—	23	0
6			14	17	0.270	0	6	2	32	29	0.735
1	5	1	58	54	0.738	1			37	42	0.044
2			13	10	0.992	2			34	35	0.563

<i>h</i>	<i>k</i>	<i>l</i>	$F_{\text{obs}}$	$F_{\text{calc}}$	$\alpha/360$	<i>h</i>	<i>k</i>	<i>l</i>	$F_{\text{obs}}$	$F_{\text{calc}}$	$\alpha/360$
3	6	2	29	31	0.432	8	7	3	12	13	0.556
4			27	25	0.080	1	7	5	50	41	0.220
5			10	9	0.283	2			42	39	0.133
6			< 11	2	0.241	3			42	39	0.270
7			13	9	0.051	4			41	38	0.548
8			31	36	0.567	5			55	49	0.136
9			30	52	0.516	6			26	30	0.918
10			12	22	0.968	7			16	18	0.220
0	6	4	46	41	0.091	1	7	7	27	38	0.686
1			52	49	0.034	2			35	30	0.941
2			30	26	0.486	3			49	46	0.674
3			20	19	0.450	4			33	30	0.522
4			< 11	9	0.938	5			29	30	0.826
5			9	8	0.280						
6			19	18	0.075	0	8	0	28	22	0.500
7			35	33	0.017	1			31	29	0
8			22	27	0.411	2			22	21	0.500
9			14	14	0.666	3			44	46	0.500
0	6	6	48	41	0.030	4			18	9	0
1			26	24	0.063	5			17	15	0.500
2			13	13	0.620	6			—	10	0.500
3			49	42	0.511	7			—	19	0
4			14	9	0.847	0	8	2	45	41	0.011
5			19	14	0.473	1			41	39	0.026
6			< 15	2	0.795	2			7	7	0.817
7			12	10	0.132	3			24	21	0.521
8			10	10	0.542	4			16	13	0.803
0	6	8	31	28	0.966	5			13	13	0.788
1			41	34	0.031	6			24	21	0.958
2			29	23	0.537	7			21	27	0.957
3			24	20	0.616	0	8	4	16	11	0.452
4			18	15	0.306	1			41	45	0.987
5			10	9	0.728	2			25	24	0.463
						3			19	22	0.639
1	7	1	56	49	0.183	4			19	17	0.359
2			40	38	0.003	5			13	13	0.515
3			37	32	0.287	6			17	19	0.424
4			43	39	0.543	0	8	6	37	32	0.964
5			38	30	0.135	1			30	29	0.029
6			29	29	0.005	2			17	12	0.883
7			31	29	0.371	3			18	17	0.580
8			—	20	0.460	4			18	20	0.980
1	7	3	23	23	0.756	1	9	1	52	42	0.753
2			21	14	0.881	2			24	23	0.999
3			44	46	0.635	3			20	16	0.658
4			34	40	0.481	4			28	32	0.464
5			32	36	0.768	1	9	3	24	20	0.335
6			44	50	0.058	2			23	24	0.052
7			30	40	0.676	3			17	14	0.231

Seven more cycles were carried out using the weighting scheme suggested by Cruickshank<sup>8</sup> but no significant changes in the parameters occurred. The largest differences from the previous results were all well below the calculated standard deviations.

In order to check the results of the least squares refinement and to confirm that no other atoms were present in the unit cell a three-dimensional electron



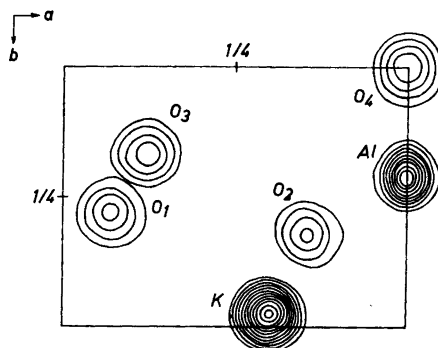


Fig. 1. A composite drawing of the final three-dimensional electron density map. Contours are drawn at intervals of  $4 \text{ e.}\text{\AA}^{-3}$ , beginning with the  $4 \text{ e.}\text{\AA}^{-3}$  contour.

density map and a three-dimensional difference map were calculated with the use of the parameters obtained in the least squares refinement and with all observed reflections included. All peaks in the difference map were within  $\pm 1.5 \text{ e}/\text{\AA}^3$  except for some spurious peaks close to the heavy atoms which were slightly higher than  $2 \text{ e}/\text{\AA}^3$ . These are probably due to the lack of correction for absorption and extinction. No remaining shifts were indicated. A summary of the three-dimensional electron density map is given in Fig. 1.

Table 4. Final parameters.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
8 K in 8 ( <i>b</i> )	0.1986	0.9743	0.0062	$1.2 \text{ \AA}^2$
8 Al » 8 »	0.5092	0.2078	0.2444	0.7
8 O <sub>1</sub> » 8 »	0.0685	0.2824	0.0813	1.5
8 O <sub>2</sub> » 8 »	0.3569	0.3202	0.2483	1.4
8 O <sub>3</sub> » 8 »	0.1199	0.1694	0.3416	0.5
4 O <sub>4</sub> » 4 <i>a</i>	0	$\frac{1}{2}$	0.3153	1.2

Table 5. Interatomic distances.

Distances within an  $AlO_4$  tetrahedron:

Al—O <sub>1</sub>	1.75 Å	O <sub>1</sub> —O <sub>2</sub>	2.85 Å	O <sub>2</sub> —O <sub>3</sub>	2.85 Å
—O <sub>2</sub>	1.78	—O <sub>3</sub>	2.80	—O <sub>4</sub>	2.91
—O <sub>3</sub>	1.76	—O <sub>4</sub>	2.95	O <sub>3</sub> —O <sub>4</sub>	2.80
—O <sub>4</sub>	1.73				

Short O—O distances:

O <sub>2</sub> —O <sub>3</sub>	2.82 Å
O <sub>2</sub> —O <sub>3</sub>	2.85 Å

Other O—O distances < 4 Å:

O <sub>1</sub> —O <sub>1</sub>	3.58 Å	O <sub>1</sub> —O <sub>2</sub>	3.44 Å	O <sub>1</sub> —O <sub>4</sub>	3.49 Å
—O <sub>2</sub>	3.41	—O <sub>3</sub>	3.83	O <sub>2</sub> —O <sub>4</sub>	3.96
—O <sub>3</sub>	3.96	—O <sub>4</sub>	3.11	O <sub>3</sub> —O <sub>3</sub>	3.55

K—O distances < 4 Å:

K—O <sub>1</sub>	2.79 Å	K—O <sub>3</sub>	2.89 Å	K—O <sub>2</sub>	3.93 Å
—O <sub>1</sub>	2.89	—O <sub>4</sub>	2.80	—O <sub>2</sub>	3.73
—O <sub>2</sub>	2.76	—O <sub>1</sub>	3.44	—O <sub>3</sub>	3.76
—O <sub>3</sub>	2.95	—O <sub>2</sub>	3.27		

## DESCRIPTION OF THE STRUCTURE

Final parameters are given in Table 4. Bond lengths are given in Table 5. The calculated standard deviations are about 0.006 Å for K, 0.007 Å for Al, 0.017 Å for O<sub>1</sub>, O<sub>2</sub>, and O<sub>3</sub> and 0.024 Å for O<sub>4</sub>. This leads to standard deviations of about 0.01<sub>8</sub> Å in K—O and Al—O distances and about 0.02<sub>4</sub> Å in O—O distances.

Projections of the structure along the three axes of the unit cell are shown in Fig. 2. Each Al atom is tetrahedrally surrounded by four O atoms at an average distance of 1.76 Å, which is close to the sum of the crystal radii 1.78 Å.<sup>10</sup> In a review of Al—O tetrahedral distances Smith and Bailey<sup>9</sup> have found values for these between 1.75 and 1.80 Å in well refined structures.

The coordination around the potassium ion is rather irregular with six oxygens at distances between 2.76 and 2.95 Å and two more oxygens at 3.27 and 3.44 Å. The sum of the crystal radii for K<sup>+</sup> and O<sup>2-</sup> is 2.73 Å.<sup>10</sup>

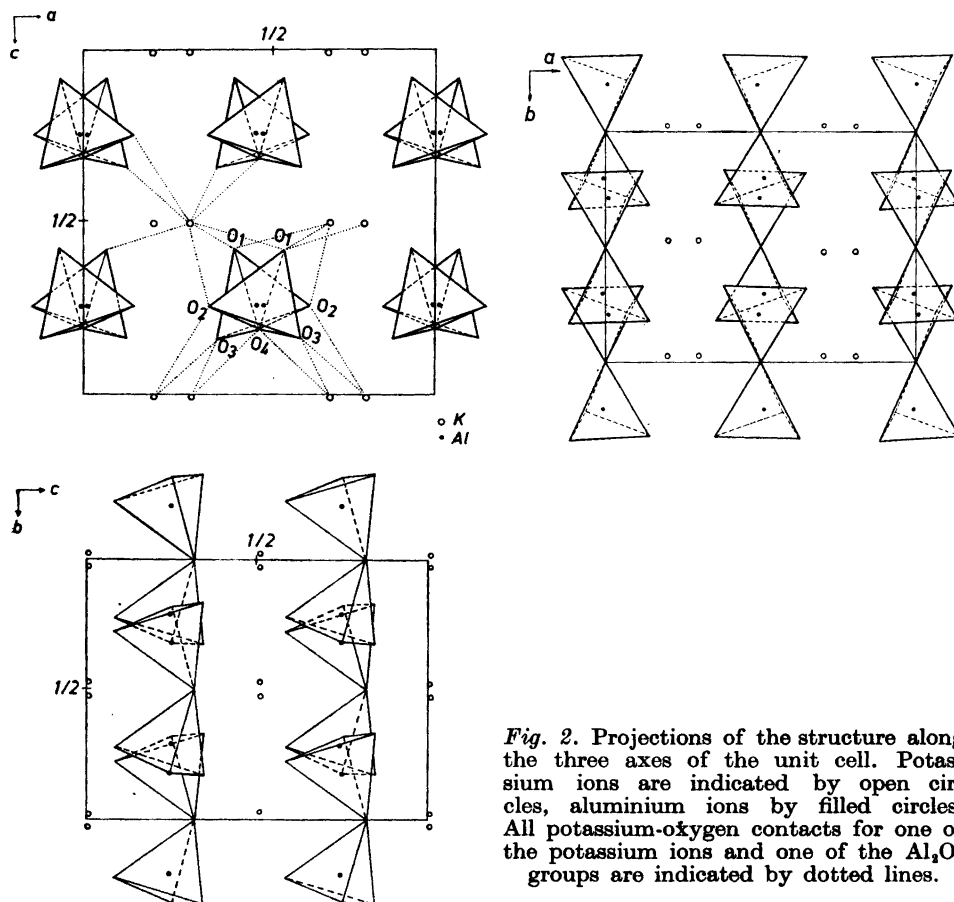


Fig. 2. Projections of the structure along the three axes of the unit cell. Potassium ions are indicated by open circles, aluminium ions by filled circles. All potassium-oxygen contacts for one of the potassium ions and one of the Al<sub>2</sub>O<sub>4</sub> groups are indicated by dotted lines.

A surprising feature in the structure is the presence of discrete aluminium-oxygen complexes built up from two  $AlO_4$  tetrahedra having an oxygen in common (Fig. 2). The Al—O—Al angle is  $132^\circ$ . These negative  $Al_2O_7$  groups are held together in the structure by the potassium ions as shown in Fig. 2 where some of the K—O contacts are indicated.

It seems reasonable to assume that the 24 hydrogen atoms in the unit cell are bonded to those oxygens which belong to only one aluminum atom, although no direct proof of this can be given. The formula for the aluminium-oxygen group should then be  $[Al_2O(OH)_6]^{2-}$ . The short distances between the  $O_2$  and  $O_3$  atoms (Table 5) probably indicate the presence of hydrogen bonds. This assumption is supported by the size of the angles  $O_3—O_2—O_3$  and  $O_2—O_3—O_2$  which are  $110^\circ$  and  $101^\circ$ , respectively.

An estimate of the charge distribution in the unit cell also supports the assumed arrangement of the hydrogen atoms. Since the Al—O bonds have a large amount of ionic character the sum of the bond strengths for each oxygen atom should be close to two as has been found to be the case for other aluminum-oxygen compounds.<sup>10,11</sup> By applying the formula  $D(n) = D(1) - 0.60 \log n$  suggested by Pauling<sup>10</sup> the bond lengths  $D(n)$  can be related to a bond number  $n$ . If the electrostatic valences of the potassium ion and the aluminium ion are divided among their bonds according to this relation, the sum of the bond strengths for the oxygen atoms are found to be 2.09, 1.92, 1.98, and 2.02 for the  $O_1$ ,  $O_2$ ,  $O_3$ , and  $O_4$  atoms, respectively. These values are all close to two, as expected, and the bridging oxygen does not differ from the oxygens assumed to be associated with hydrogen atoms. It seems very likely, therefore, that the discrete aluminum-oxygen complexes have a structure corresponding to the formula  $[(OH)_3AlOAl(OH)_3]^{2-}$ .

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