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On the Structures of Alkali Polyaluminates

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Besides the so-called β-Al_2O_3 ($R_2O{\cdot}11Al_2O_3$; R=Na or K), there have been found two kindred compounds with approximate formulas, $R_2O{\cdot}7Al_2O_3$ (β'-Al_2O_3) and $R_2O{\cdot}5Al_2O_3$ (β''-Al_2O_3). The structure determination of the latter two compounds was undertaken; the results are compared with the structure of β-Al_2O_3 in the present paper. These three structures are composed of spinel layers of the same configuration. The structures of β and β' are very similar to each other, both equally bearing a layer-stacking according to a two-fold screw symmetry, while β'' differs from these two in exhibiting another way of layer-stacking, according to a three-fold screw symmetry.

It has been established that the so-called β-Al_2O_3 is in fact an alkali polyaluminate with the chemical formula of $Na_2O{\cdot}11Al_2O_3$ or $K_2O{\cdot}11Al_2O_3$. In 1943 one of the present authors (G. Y.)[1] studied its formation during a sintering reaction between Al_2O_3 and alkali carbonate; he thus found a new substance whose X-ray powder diffraction pattern displayed a close resemblance to that of β-Al_2O_3. However, a few lines in the pattern, such as the strong 1.954A and 1.382A lines, failed to be properly indexed unless the c-axis of the crystal was assumed to be 3/2 or 3 times as long as that of β-Al_2O_3. He also pointed out that the above two lines coincide in spacings with the 400 and 440 reflections, respectively, from the spinel structure.

About ten years later, Yamaguchi[2] reinvestigated the material by chemical as well as X-ray methods. and reported that two phases were revealed, one with the approximate composition, $Na_2O{\cdot}8Al_2O_3$ or $K_2O{\cdot}8Al_2O_3$, and the other, with $Na_2O{\cdot}5A\ {}_2O_3$ or $K_2O{\cdot}5Al_2O_3$. The former was designated β'-Al_2O_3 (β'_{Na}, β'_K), and the latter, β''-Al_2O_3 (β''_{Na}, β''_K). He then reported in another paper[3] that the experimental formulas were $Na_2O{\cdot}8.1Al_2O_3$ for β'_{Na}, $Na_2O{\cdot}5.8Al_2O_3$ for β''_{Na}, and $K_2O{\cdot}5.6Al_2O_3$ for β'_K, and that the way of oxygen packing in the β' structure might be similar to that in β, both being reflection-symmetrical across planes perpendicular to the c-axis, while that in

1) G. Yamaguchi, *Elect. Chem. Soc. Japan*, **11**, 260 (1943).

2) G. Yamaguchi, Preprint for the 7th Annual Meeting of the Chemical Socity of Japan (April, 1954), p. 192.

3) G. Yamaguchi, Doctor Thesis, University of Tokyo (1954).

β'' was after the manner of cubic closest-packing, with some layers replaced by those bearing less oxygen and some alkali ions. He thus explained the fact that the two lines characteristic of β'' coincide in spacings with the 400 and 440 lines from spinel, and gave the lattice parameters reproduced in Table 1.

TABLE 1. LATTICE PARAMETERS (IN Å) OF β'-Al_2O_3 AND β-Al_2O_3[3]

	β'_{Na}	β''_{Na}	β''_{K}
a	5.594	5.595	5.596
c or 2c	22.56	67.86	68.01

Recently, Théry *et al.*[4] have published a report on substances which are probably the same as the alkali polyaluminates under consideration; one is $Na_2O{\cdot}5Al_2O$ with the lattice parameters of $a=5.61$ Å and $c=33.95$Å, and the other, $Na_2O{\cdot}7.02Al_2O_3$, with $a=5.595$Å and $c=34.02$Å.

In the present paper, the authors will describe the structures of these alkali polyaluminates.

TABLE 2. SYNTHETIC DATA AND PROPERTIES OF β'- AND β''-Al_2O_3

Species	Experimental formula	Ideal formula	Mixing ratio R_2CO_3 : $2Al(OH_3)$	Heating temp., °C	Heating period	Density
β'_{Na}	$Na_20.7.02Al_2O_3$	$Na_20.7.22Al_2O_3$	1 : 3	1400	20 min	3.22
β'_{K}	$K_20.6.8Al_2O_3$	$K_20.7.22Al_2O_3$	1 : 3	1400	20 min	3.35
β''_{K}	$K_20.5.1Al_2O_3$	$K_20.5.34Al_2O_3$	1 : 1	1380	8 hr	3.50—3.39

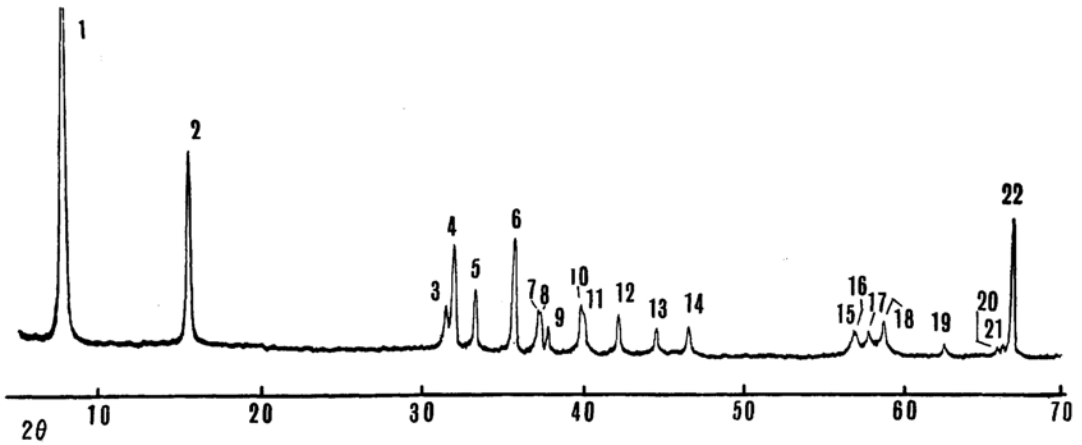

Fig. 1. X-Ray powder diffraction pattern of β'-Al_2O_3 (Cu$K\alpha$).

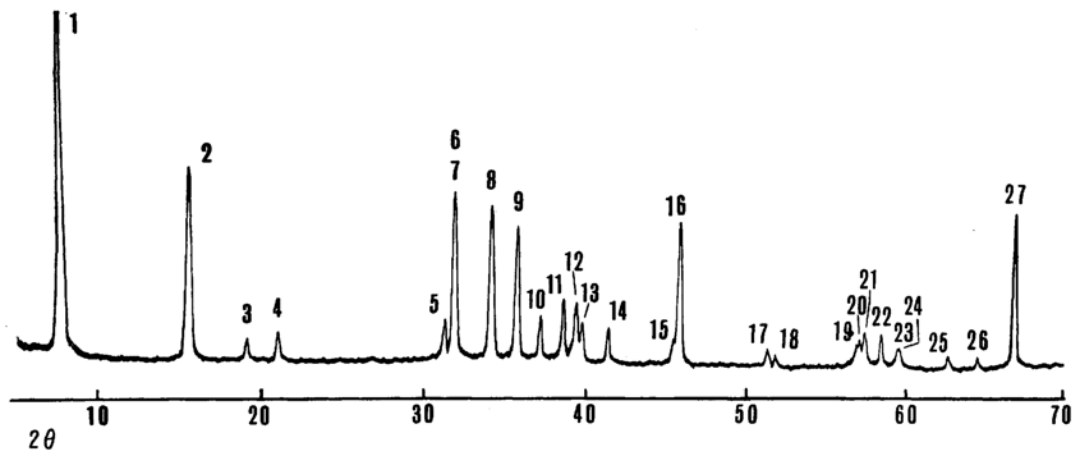

Fig. 2. X-Ray powder diffraction pattern of β''-Al_2O_3 (Cu$K\alpha$).

4) J. Théry *et al.*, *Compt. Rend. Acd. Sci. (Paris)*, **254**, 2782 (1962); *Rev. Temper. et Refract.*, 221 (1964).

Since no single crystal had yet been obtained for any of these materials, we were obliged to carry out this work using their powder data only. Therefore, we cannot claim that the results we deduce here are highly accurate, but we still believe them to be essentially correct.

Experimental

Mixtures of aluminum hydroxide and alkali carbonate in appropriate ratios were heated. The products were then washed with dilute HCl and water, and their chemical compositions and densities examined. The results, together with the suitable conditions for their preparations, are listed in Table 2. Though both sodium and potassium are capable of forming β' and β'', the former tends to favor the production of β', while the latter favors β''. The X-ray powder diffraction patterns shown in Figs. 1 and 2 were obtained with β'_{Na} and β''_{K} respectively. The observed lines were indexed with the aid of the lattice parameters given in Table 1, and their peak intensities were measured for a fixed exposure time. The results are tabulated in Tables 3 and 4, where the relative values of intensities have been put onto such a scale as to minimize the *R*-factors and where the calculated values for the strongest lines are taken to be 100. The lattice parameters newly derived from these two sets of data are given in Table 5.

Table 3. X-Ray powder diffraction data of β'_{Na}
$a=5.592$ Å, $c=22.711$ Å

Peak No.	*hk l*	Observed *d* (Å)	Observed *I*	Calculated *d* (Å)	Calculated *I*
1	00 2	11.3651	127	11.3631	100
2	00 4	5.6815	46	5.6815	33
3	00 8	2.8408	11	2.8408	7
4	11 0	2.8034	28	2.8034	20
5	01 7	2.6955	18	2.6955	30
6	11 4	2.5157	35	2.5140	38
7	02 0	2.4165	14	2.4278	—
8	02 1			2.4141	14
9	02 2	2.3840	6	2.3742	10
10	00,10	2.2631	15	2.2726	6
11	11 6	2.2533	14	2.2533	7
12	02 5	2.1441	15	2.1415	18
13	02 6	2.0342	8	2.0440	9
14	02 7	1.9513	10	1.9443	11
15	00,14	1.6233	6	1.6233	3
16	03 0	1.6195	3	1.6185	1
17	12 7	1.5924	7	1.5976	4
18	02,11	1.5722	11	1.5734	13
19	12 9	1.4890	3	1.4847	5
20	00,16	1.4204	1	1.4204	—
21	02,13	1.4193	1	1.4187	11
22	22 0	1.4012	41	1.4017	40

Table 4. X-Ray powder diffraction data of β''_{K}
$a=5.595$ Å, $c=34.226$ Å

Peak No.	*hk l*	Observed *d* (Å)	Observed *I*	Calculated *d* (Å)	Calculated *I*
1	00 3	11.4080	142	11.4088	100
2	00 6	5.7044	111	5.7044	69
3	01 2	4.5679	10	4.5681	2
4	01 4	4.2214	12	4.2162	1
5	00,12	2.8507	16	2.8522	14
6	11 0	2.7975	98	2.7974	66
7	01,10			2.7955	45
8	01,11	2.6184	60	2.6181	46
9	11 6	2.5114	56	2.5118	118
10	02 1	2.4164	20	2.4166	11
11	02 4	2.3304	32	2.3310	34
12	00,15	2.2800	22	2.2818	6
13	11 9	2.2635	12	2.2534	4
14	02 7	2.1753	12	2.1708	32
15	11,12	1.9897	8	1.9972	15
16	02,10	1.9781	84	1.9774	74
17	02,13	1.7829	4	1.7827	—
18	11,15	1.7692	8	1.7681	—
19	03 0	1.6132	12	1.6151	11
20	01,20			1.6136	1
21	02,16	1.6029	20	1.6035	30
22	12,11	1.5782	16	1.5787	—
23	03 6	1.5525	19	1.5540	13
24	02,17			1.5484	13
25	01,22	1.4836	5	1.4813	3
26	02,19	1.4465	6	1.4455	1
27	22 0	1.3987	97	1.3987	95

Table 5. Lattice parameters newly obtained in this experiment

	a (Å)	*c* (Å)
β'_{Na}	5.592	22.711
β'_{K}	5.594	22.728
β''_{K}	5.595	34.226

Structure Analysis

At the onset of the structure determination of these two crystals, the diffraction pattern of β-Al_2O_3 was produced for comparison; the results are given in Fig. 3 and Table 6. On the base of the structure of this material as worked out by Beevers and Ross[5] and reproduced here in Fig. 4 and Table 7, the calculated intensities were deduced and compared with the observed intensities, shown in Table 6. The *R*-factor was found to be 0.30. It may be noted in Fig. 4 that the structure is composed of layers of the spinel structure, and that each layer is flanked by a pair of planes perpendicular to the c-axis and containing alkali ions (R in

5) C. A. Beevers and M. A. S. Ross, *Z. Krist.*, **97**, 59 (1937).

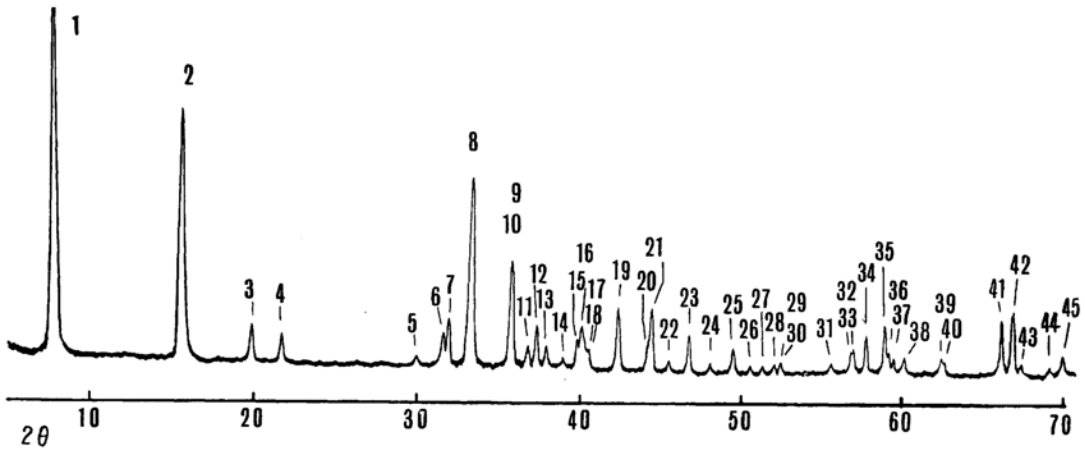

Fig. 3. X-Ray powder diffraction pattern of β-Al_2O_3 (Cu$K\alpha$).

TABLE 6. X-RAY POWDER DIFFRACTION DATA OF β_{Na} $a=5.593$ Å, $c=22.610$ Å

Peak No.	hk l	Observed d (Å)	Observed I	Calculated d (Å)	Calculated I	Peak No.	hk l	Observed d (Å)	Observed I	Calculated d (Å)	Calculated I
1	00 2	11.3136	120	11.2891	100	24	01,11	1.8926	1	1.8902	—
2	00 4	5.6570	51	5.6446	24	25	02 8	1.8404	5	1.8391	4
3	01 2	4.4579	7	4.4556	11	26	11 2	1.8074	1	1.8088	1
4	01 3	4.0800	6	4.0764	3	27	12 3	1.7797	2	1.7805	—
5	01 6	2.9714	1	2.9729	—	28	01,12	1.7539	1	1.7541	—
6	00 8	2.8228	6	2.8223	3	29	02 9	1.7439	2	1.7434	1
7	11 0	2.7991	8	2.7997	13	30	12 4			1.7429	—
8	01 7	2.6895	44	2.6856	28	31	02,10	1.6533	2	1.6524	3
9	00 9	2.5089	23	2.5087	—	32	03 0	1.6159	6	1.6164	2
10	11 4			2.5087	29	33	00,14	1.6121	6	1.6127	2
11	01 8	2.4345	4	2.4392	—	34	12 7	1.5933	10	1.5936	7
12	02 1	2.4101	10	2.4108	9	35	02,11	1.5658	11	1.5666	12
13	02 2	2.3707	6	2.3706	4	36	11,12	1.5622	4	1.5616	3
14	02 3	2.3084	1	2.3074	2	37	03 4	1.5526	1	1.5540	6
15	00,10	2.2611	8	2.2578	1	38	12 8	1.5374	4	1.5372	—
16	11 6	2.2476	11	2.2462	11	39	03 6	1.4851	4	1.4853	3
17	01 9	2.2290	7	2.2282	—	40	12 9	1.4809	4	1.4800	—
18	02 4			2.2278	4	41	02,13	1.4133	14	1.4119	14
19	02 5	2.1359	15	2.1362	14	42	22 0	1.4002	17	1.3999	30
20	00,11	2.0491	6	2.0526	—	43	22 2	1.3897	1	1.3892	2
21	02 6	2.0380	15	2.0382	17	44	22 4	1.3592	1	1.3587	2
22	11 8	1.9918	2	1.9875	—	45	14 1	1.3428	6	1.3430	2
23	02 7	1.9392	10	1.9381	10						

the figure). These planes shall hereafter be called "alkali layers," and the part, within a unit cell, of a spinel layer, a "spinel block."

Structure of β'-Al_2O_3. The powder pattern of β'_{Na} was used for this purpose. As will be recognized upon comparisons of Fig. 4 with Fig. 3 and of Table 3 with Table 6, the powder pattern of β'-Al_2O_3 closely resembles that of β-Al_2O_3. This fact, together with the similarity in lattice parameters between these two substances, strongly suggests that both structures have the same principle. In fact, the pattern of β'-Al_2O_3 is completely in harmony with the space group of β-Al_2O_3, $P6_3/mmc$; namely, the $hh\bar{2}hl$ reflections are missing when l is odd. Therefore, it was assumed at the beginning of the analysis that the structure of β'-Al_2O_3 consists of spinel blocks which have the same configuration and mode of arrangement as in the structure of β-Al_2O_3.

Next, if we compare the experimental formula of the substance, shown in Table 2, with the composition of β-Al_2O_3, we shall find that the former

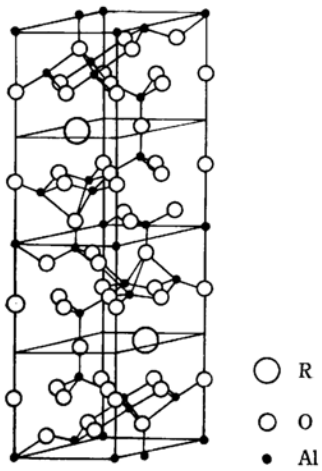

Fig. 4. Structure of β-Al_2O_3.

contains one and a half times as much alkali as the latter, both against a certain amount of oxygen. Therefore, $R_{1.50}Al_{10.83}O_{17}$ or $R_2O{\cdot}7.22Al_2O_3$ was tentatively adopted as the ideal formula for this phase. The theoretical values of density from this formula are 3.26 for β'_{Na} and 3.38 for β'_{K}, in good agreement with the observed values, 3.22 and 3.35 respectively.

Then, taking into account the fact that the spinel block is so densely constituted that no alkali ion is admitted into it, we could restrict the probable positions for excessive alkali ions in or near the alkali layers. Trial-and-error procedures carried out with the aid of an electronic computer then led us to the final structure, shown in Fig. 5.

In this structure, two sites for alkali ions per spinel block are statistically occupied by 1.5 ions, while the positions for Al ions (two per block) nearest the alkali layers are occupied by 1.83 such ions. The atomic coordinates are listed in Table 8, while the calculated intensities for the structure are given in Table 3. The *R*-factor for I deduced from this table is 0.26. It has also been confirmed that the intensities calculated for unobserved reflections are all less than 1 on the intensity scale of the table.

Structure of β''-Al_2O_3. Potassium-bearing β''-Al_2O_3 was chosen for this study; its powder data are given in Table 4. Since in every observed reflection there holds, between its indices, a $-h+k+l\equiv 0 \pmod 3$ relation, no other condition being associated, the only conclusion deducible is that the crystal lattice is rhombohedral. However, there are five space groups altogether, each based upon the rhombohedral lattice and satisfying the above relation, so from the powder data alone it is impossible to identify the space group of the crystal further. Accordingly, we had to search for the structure on the base of the knowledge of the crystal lattice and by assuming the structure also to be built up of spinel blocks.

Next, a comparison of the experimental formula of this phase with the composition of β-Al_2O_3 suggests that a spinel block contains nearly two alkali ions in the present case. Therefore, $R_2Al_{10.67}O_{17}$ or $R_2O{\cdot}5.34Al_2O_3$ was considered as the ideal formula, for which the calculated density was 3.45.

The procedures described above were then employed for the derivation of the probable solution; the final result obtained is a structure based upon the $R\bar{3}m$ space group and illustrated in Fig. 6.

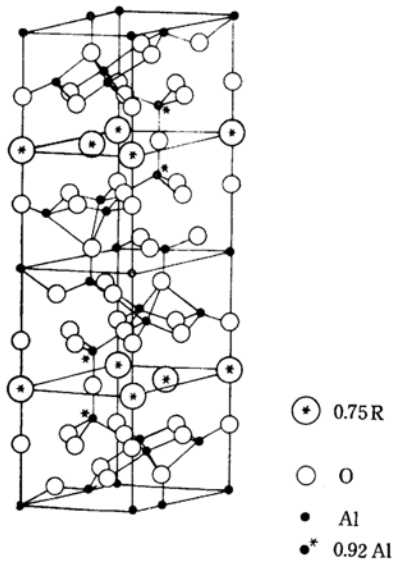

Fig. 5. Structure of β'-Al_2O_3.

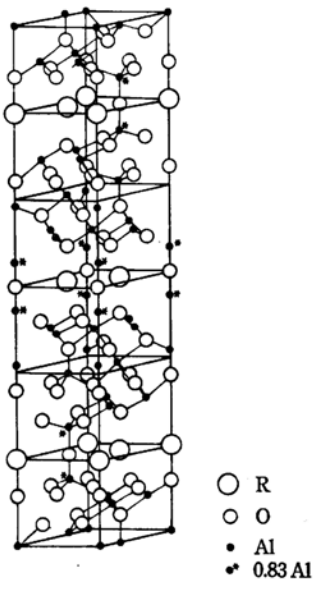

Fig. 6. Probable atomic arrangement in β''-Al_2O_3.

TABLE 7. ATOMIC PARAMETERS OF β_{Na} (SPACE GROUP, $P6_3/mmc$)

Atom	Number of atom	x	y	z
Na	2	0.667	0.333	0.250
Al_1	2	0	0	0
Al_2	4	0.333	0.667	0.022
Al_3	12	0.333	0.167	0.106
Al_4	4	0.333	0.667	0.178
O_1	12	0.167	0.333	0.050
O_2	4	0.667	0.333	0.050
O_3	4	0	0	0.144
O_4	12	0.500	0.500	0.144
O_5	2	0.333	0.667	0.250

TABLE 8. ATOMIC PARAMETERS OF β'_{Na} (SPACE GROUP, $P6/mmc$)

Atom	Number of atom	x	y	z
Na_1	2×0.75	0	0	0.250
Na_2	2×0.75	0.667	0.333	0.250
Al_1	4	0.333	0.667	0.170
Al_2	2	0	0	0
Al_3	4	0.333	0.667	0.030
Al_4	12	0.333	0.167	0.105
O_1	12	0.167	0.333	0.050
O_2	4	0.667	0.333	0.050
O_3	12	0.500	0	0.144
O_4	4	0	0	0.144
O_5	2	0.333	0.667	0.250

TABLE 9. ATOMIC PARAMETERS OF β''_K (SPACE GROUP, $R\bar{3}m$)

Atom	Number of atom	x	y	z
K	6	0	0	0.184
Al_1	3	0	0	0
Al_2	6	0	0	0.346
Al_3	18	0.333	0.167	0.073
Al_4	6×0.83	0	0	0.443
O_1	18	0.167	0.333	0.040
O_2	6	0	0	0.293
O_3	6	0	0	0.092
O_4	13	0.167	0.333	0.241
O_5	3	0	0	0.500

In this structure, a statistical distribution is observed only over the positions of the Al ions, two per block, nearest the alkali layers; they are occupied by 1.67 such ions. The coordinates are tabulated in Table 9, and the calculated intensities, in Table 4. The R-factor for I is 0.28; the statement given above concerning the unobserved reflections of β'-Al_2O_3 also applies in this case.

Discussion

According to the results of analysis so far described, some conclusions may now be reached. The three phases, β, β', and β'', are all composed of spinel layers of the same configuration. The former two are almost identical structurally, but are different in the amounts of alkali and aluminum present. On the other hand, the last one has its own way of layer-stacking. Thus, the former two structures may be looked upon as characterized by layer-stacking according to a two-fold screw symmetry, shown in Fig. 7, while the

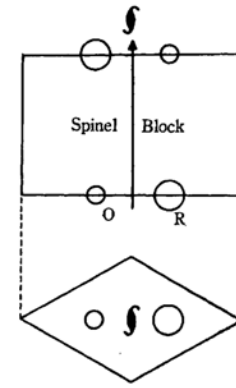

Fig. 7. Mode of stacking of spinel blocks in the β and β'-Al_2O_3 structures.

last, by that according to a three-fold screw symmetry, given in Fig. 8. These findings, together with the fact previously mentioned that sodium and potassium favor the formation of β' and β'' respectively, seem to suggest that the mode of layer-stacking in this series of structures depends upon the amount and kind of alkali.

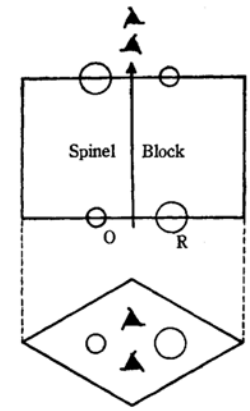

Fig. 8. Probable mode of stacking of spinel blocks in the β''-Al_2O_3 structure.

From the view-point of ionic distribution, β-Al_2O_3 may be considered an ordered phase, while β' and β'' are disordered phases, exhibiting a

statistical distribution of cations over sites in and near the alkali layers. An example of such a distribution has been found in an imperfect spinel, $RO \cdot nAl_2O_3$.[6]

Finally, it should be noted that, because of the restriction imposed upon the present work, namely, the difficulty of obtaining a single crystal for any of the substances under investigation, our results are liable to be some what inaccurate with regard to the atomic coordinates. For example, a position for excess alkali given above to β' or β'' in all probability indicates only the center of gravity of a more dispersed statistical distribution of the ion. However, the authors believe that, in spite of such minute uncertainties, the structural principles of this series of compounds have now been established satisfactorily.

6) G. Yamaguchi, *J. Ceram. Assoc. Japan*, **61**, 500 (1953).