II have very large limits of error, they may be taken only to represent the relative magnitudes of the values.

Discussion

The data in Table II show that $\Delta G_1°$, $\Delta G_2°$, and $\Delta G_3°$ are largely unaffected by the chain length except in the case of the mono(methylamino)silver(I) complex. The effect seen in $\Delta G_1°$ for the monomethylamino complex is of course seen again in the overall free energy change ($\Delta G_3°$). The $\Delta H_3°$ values increase negatively as methyl groups are substituted in the hydrocarbon chain and this increase continues through the bis(*n*-propylamino)silver(I) complex. The $\Delta H_3°$ values then decrease slightly for the *n*-butyl- and *n*-pentylamino complexes followed by an increase for the *n*-hexylamino complex. The $T\Delta S_3°$ values follow the same general pattern of variations with chain length as do the $\Delta H_3°$ values. With the exception of the anomalous $\Delta G_1°$ value for the monomethylamino complex and the decrease in $\Delta H_3°$ and $T\Delta S_3°$ for the *n*-butyl- and *n*-pentylamino complexes, the same trends in $\Delta G°$, $\Delta H°$, and $\Delta S°$ values with increasing hydrocarbon chain length have previously been observed for protonation of the *n*-alkylamines.[4]

It is interesting that the difference in the $\Delta H°$ values (between methyl and propyl) for protonation of *n*-alkylamines is ~0.6 kcal/mol[4] while the difference in the $\Delta H_3°$ values (between methyl and propyl) for formation of the bis(*n*-alkylamino)silver(I) complexes is ~1.0 kcal/mol. The protonation reaction involves only one ligand, whereas formation of bis(*n*-alkylamino)silver(I) complexes involves two. Therefore, assuming the difference in $\Delta H°$ for the addition of one amine ligand to be half of the difference observed for the formation of the bis(*n*-alkylamino)silver(I) complexes, it follows that the enthalpic effect on an alkyl group of the silver ion (~0.5 kcal/mol) is approximately the same as the effect of the proton (~0.6 kcal/mol).

The difference in the $T\Delta S°$ values (between methyl and propyl) for protonation of the *n*-alkylamines is ~0.7 kcal/mol[4] while the difference in $T\Delta S_3°$ values is ~0.3 kcal/mol. If $T\Delta S°$ for the addition of one amine ligand is again assumed to be half the difference observed for the formation of the bis-amino complexes, the entropic effect of the silver ion on an alkyl chain (~0.15 kcal/mol) is much smaller than the effect of the proton (~0.7 kcal/mol), in contrast to what was found in the case of the $\Delta H°$ values. The difference in behavior of the $\Delta H°$ and $T\Delta S°$ values results primarily from the anomalously large negative $T\Delta S_3°$ value (in comparison to $T\Delta S°$ values for protonation) for formation of the bis(methylamino)silver(I) complex ion.

The $\Delta H_3°$ and $T\Delta S_3°$ values in Table II indicate that anomalous effects are operating in the formation of the *n*-butyl- and *n*-pentylamino complexes of Ag^+ in comparison with the protonation reactions. A possible explanation for these anomalies is that there may be some hydrophobic interaction between the two ends of the hydrocarbon chains. In this regard it is disappointing that accurate stepwise $\Delta H°$ and $T\Delta S°$ values could not be obtained, since these data would probably have shown whether or not the above anomalies are the result of having two alkyl groups present in the complex.

In conclusion, the similarities in the trends in $\Delta G°$, $\Delta H°$, and $T\Delta S°$ for formation of bis(*n*-alkylamino)silver(I) complexes and protonation of *n*-alkylamines with hydrocarbon chain length suggest that the major cause of these trends is of a general electrostatic nature and not dependent on the nature of the metal ion involved.

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On the Structure of $Na_2O \cdot 4MgO \cdot 15Al_2O_3$, a Variant of β-Alumina

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A new phase has been found in the ternary system Na_2O–MgO–Al_2O_3, similar in structure to β-alumina. It is hexagonal, with $a = 5.62$ Å and $c = 31.8$ Å. Qualitative examination of some single-crystal X-ray intensities and quantitative measurement of powder intensities suggest the following structure. The space group is probably $P6_3/mmc$. The basal mirror planes are 15.9 Å apart, very loosely packed, and contain the sodium ions. Between these planes are spinel-like blocks, consisting of six layers of cubic-close-packed oxygens with Mg and Al in their interstices, in a typical spinel-like M_3O_4 alternation. The spinel blocks are spaced apart by linear Al–O–Al columns. These spacers, together with the loose packing, provide for an extraordinarily high two-dimensional sodium ion mobility. This differs from β-alumina only in that the latter has shorter blocks, containing only four oxygen layers.

Introduction

β-Alumina was originally reported by Rankin and Merwin,[1] who thought they were dealing with a crystallographic modification of pure alumina and thus adopted the designation which has persisted. It was soon recognized, however, a that a small admixture of an alkali oxide was necessary to produce this crystal

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(1) G. A. Rankin and H. E. Merwin, *J. Amer. Chem. Soc.*, **38**, 568 (1916).

structure. The X-ray work of Bragg, Gottfried, and West[2] and of Beevers and Ross[3] established the structure, placed the sodium ions, and established the idealized, defect-free composition to be $Na_2O \cdot 11Al_2O_3$. Recent work indicates,[4,5] however, that the composition is somewhat variable and that one is most apt to encounter samples which are about 25% richer in sodium than the ideal formula indicates.

Kummer and Weber[6] discovered that β-alumina has a high sodium ion conductivity. By hindsight, this fact is not surprising in view of the crystal structure. Yao and Kummer[7] discovered that many ions could be substituted for sodium in this structure and published extensive data on ion-exchange equilibria and on self-diffusion and interdiffusion coefficients.

Yamaguchi and Suzuki[8] described a compound designated as β'-alumina, which is supposed to be unusually rich in sodium oxide. It is questionable whether this is anything other than an example of the nonstoichiometric nature of β-alumina. In the same publication, however, Yamaguchi and Suzuki also described a new crystal structure designated as β''-alumina, which is a rhombohedral variant of β-alumina, consisting of three 11.2-Å spinel blocks related by a threefold screw axis. This compound had also been reported as $Na_2O \cdot 5Al_2O_3$ by Théry and Briançon,[9] who published its characteristic X-ray powder diagram but did not propose a structure. It is also referred to as "3-Block" Beta.[5] Bettman and Peters[10] found some single crystals of an MgO-containing ternary version of β''-alumina and did the first single-crystal determination of this structure. They described the idealized, defect-free formula as $Na_2O \cdot MgO \cdot 5Al_2O_3$. Interestingly, there is no ideal formula for the binary version of this structure, which is inherently an omission solid solution. There is also some evidence[4] that it is metastable, *i.e.*, that it does not exist as a thermodynamically stable compound anywhere in the Na_2O–Al_2O_3 phase diagram. This is not true of the MgO-containing ternary.

While attempting to grow more β''-alumina crystals we accidentally discovered the new phase which is the subject of this paper. We feel impelled, for the sake of consistency, to designate the new structure as β'''-alumina, even though this system of nomenclature perpetuates the original misconception of Rankin and Merwin. X-Ray work indicates that the new structure has alkali ion conduction planes essentially identical with those in β-alumina, separated by spinel blocks containing six oxygen layers, *vs.* the four layer blocks of β and β''. The idealized (*i.e.*, defect-free) formula of the new compound is $Na_2O \cdot 4MgO \cdot 15Al_2O_3$.

Very shortly after our discovery of this phase, Weber and Venero[11] began finding it in their work on the ternary Na_2O–MgO–Al_2O_3 phase diagram. They found that this new phase, at 1700°, has a narrow compositional area, which can be considered a point to within the limits of uncertainty of their work. This point corresponds to the composition $(Na_2O)_{1.275}(MgO)_{4.0}(Al_2O_3)_{14.91}$. As in the case of binary β-alumina, there appears a tendency toward an excess of sodium and a deficiency of aluminum. Weber and Venero made some approximate conductivity measurements on moderately well-sintered powder compacts of the material. They found a resistivity of about 100 ohm cm at 300°, with an activation energy of about 5 kcal/mol. These values are not far removed from what one expects, by experience, of similarly sintered compacts of β-alumina. For the sake of completeness, it should be mentioned here that Weber and Venero also found the corresponding rhombohedral structure, consisting of three spinel blocks of six oxygen layers each. They refer to this phase as β''''-alumina. It bears the same relation to β'''-alumina as β''-alumina does to β-alumina.

There exist many analogous and similar structures based on Ga_2O_3 or Fe_2O_3 in place of Al_2O_3, the Fe_2O_3 variations having received much more attention. The compounds of $K_2O \cdot 11Fe_2O_3$ and $K_2O \cdot 5Fe_2O_3$, described by Rooymans, Langereis, and Schulkes,[12] are probably isostructural with β- and β''-alumina, respectively. A somewhat similar type of compound is magnetoplumbite, $PbO \cdot 6Fe_2O_3$, whose structure was determined by Adelsköld.[13] This is similar to β-alumina, except that the mirror plane is very fully packed. A new series of structures similar to magnetoplumbite was found by Braun[14] among the hexagonal magnetic ferrites in the ternary system BaO–FeO–Fe_2O_3. Braun's structure "W" consists of two six-layer spinel blocks, separated by a fully packed mirror plane. It thus bears the same relation to β'''-alumina as magnetoplumbite does to β-alumina. It might be mentioned here that Braun's structural blocks "M" (essentially magnetoplumbite) and "Y" (no previously known analog) can stack in various combinations and permutations to form a large series of polytypes. These were further investigated by Kohn and Eckart,[15] who found many more polytypes. At present, there is no analog to Y and no evidence of polytypism in the β-aluminas of the MgO–Na_2O–Al_2O_3 system.

Experimental Section

The starting composition consisted of the following weight percentages: 85.5% Al_2O_3, 4.5% MgO, and 10% Na_2O. The last was added in the form of sodium carbonate. These components were well mixed and prereacted at 1200° in a platinum crucible in an air furnace. They were then ground up and mixed again. The final heating was carried out in a small, conical (for easy mold release), covered iridium crucible. The latter was supported on a zirconia cylinder inside a tungsten crucible which was inductively heated to the desired temperatures in a nitrogen atmosphere. A thick, porous zirconia heat reflector was placed over the tungsten susceptor, which in turn rested on a similar zirconia base.

The temperature *vs.* time profile to be described next is rather arbitrary and probably not the only or the optimum way to grow β'''-alumina crystals. However, casual variations in this procedure are not recommended. Starting with the same mixture, different temperature histories can produce slugs which contain, as the major phase, β-alumina, β''-alumina, β'''-alumina, spinel,

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[2] W. L. Bragg, C. Gottfried, and J. West, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **77**, 255 (1931).

[3] C. A. Beevers and M. A. Ross, *ibid.*, **97**, 59 (1937).

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[13] V. Adelsköld, *Ark. Kemi, Mineral. Geologi*, **12A**, No. 29 (1938).

[14] P. B. Braun, *Phillips Res. Rep.*, **12**, 491 (1957).

[15] J. A. Kohn and D. W. Eckart, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **124**, 69 (1967).

or mixtures of these. The procedure is as follows: (a) Heat to 1960° and hold for about 20 min. This should produce complete melting. (b) Slowly reduce temperature to 1860° at about 5°/hr. (c) Quickly reduce temperature to 1760°. We used no insulation on the cylindrical surfaces of the susceptor and therefore could lower the temperature quite quickly. (d) Hold at 1760° for 24 hr and then shut off the furnace. Nominal temperatures were measured with an optical pyrometer trained on the hottest part of the susceptor. These temperatures were then calibrated at 1773°, the melting point of platinum, by placing platinum wire inside a small zirconia crucible inside of the iridium crucible. The same ΔT, *i.e.*, 1773 − 1713°, the nominal pyrometer reading at this temperature, was then applied to all the other pyrometer readings.

Reproducibility was checked by making two such runs with essentially identical results. The slugs had a rather glassy appearance, with an occasional reflection from a flat face. X-Ray powder diffraction showed an appreciable amount of β-alumina and a small amount of spinel, as well as β'''-alumina. Upon light crushing, one can distinguish under a low-power microscope quite a number of single-crystal chips of almost millimeter size. They are recognizable by their flat cleavage faces (presumably the basal plane) and their optical clarity. Many, quite possibly all of these, are of the β'''-alumina phase.

The single-crystal X-ray work was limited to Polaroid precession photographs of the ($hk0$), ($h0l$), ($h1l$), and (hhl) nets using molybdenum radiation. Some of these were duplicated with copper radiation. Further, Laue photographs were taken along the three major symmetry directions. The intensities were very qualitatively estimated.

These qualitative single-crystal data were helpful in suggesting a trial structure, as explained later. Limitations of time and apparatus precluded a single-crystal refinement. Since Weber and Venero[11] had, by now, developed methods of producing powders of the essentially pure β''' phase by subsolidus sintering techniques, it was decided to justify our trial structure by measuring and calculating powder pattern intensities. Powder samples were treated by the method of Bloss, Frenzel, and Robinson[16] to avoid preferred orientation. A thick sample was used to obviate absorption corrections, and integrated intensities were obtained on a powder diffractometer, using monochromatic copper Kα radiation, to about 77° in 2θ. Beyond this, the clustering and overlapping of geometrically possible Bragg reflections becomes very bad, due to the long c axis.

The diffractometer had an LiF monochromator. The polarization factor for a monochromated beam is of the form $(1 + k \cos^2 2\theta)/(1 + k)$. We chose $k = 0.6$ as a compromise between the value of 0.5 which applies to an ideally mosaic LiF crystal and the value of 0.72 found by Jennings[17] for one of his crystals. Our compromise value should lead to an error in calculated intensity of no more than 10% in the worst cases, at low angles.

Below $2\theta = 20°$ the diffractometer intensities were rather poorly reproducible from one experiment to another, possibly due to surface roughness of the sample. It was therefore decided to obtain the intensities of the (002), (004), and (006) lines by integrating photometer traces of Debye–Scherrer photographs. These were taken with polychromatic copper radiation. They were brought to the same basis as the monochromatic diffractometer values by correcting them by the factor $(1 + 0.6 \cos^2 2\theta)/(1 + \cos^2 2\theta)$ and experimentally scaling them to the latter.

Crystal Data.—The primitive hexagonal unit cell has a = 5.63 Å and c = 31.85 Å. The Laue symmetry is $6/mmm$. The only systematic extinction is that of the (hhl)'s with $l = 2n + 1$. This leads to the possible space groups $P6_3mc$, $P\bar{6}2c$, or $P6_3/mmc$. The last corresponds to the actual trial structure which we have adopted.

One of the crystals examined showed what appeared to be weak (117) reflections, apparently violating the extinction rule. The possibility of double diffraction was carefully considered and ruled out as unlikely. When another, very clear, crystal was selected, it did not show these reflections. The explanation seems to be that the apparent (117) reflections are actually (311) type reflections from epitaxially aligned regions of cubic spinel phase; with (111) and $[1\bar{1}0]$ or $[\bar{1}10]$ of spinel parallel to (001) and [100] of β'''-alumina, respectively.

The Approximate Structure.—The compilation by Donnay and Donnay[18] was checked for materials with similar unit cell dimensions and space groups, in the hope of finding an isostructural prototype. This led to the compound $BaFe_{18}O_{27}$, of structural type "W," as described by Braun[14] and previously mentioned in the Introduction. Braun's intensities, however, did not correlate well with those of β'''-alumina. Even when they were recalculated, using the atomic scattering factors of sodium and aluminum in place of barium and iron, the correlation was still quite poor. At this point, the phase diagram work of Weber and Venero suggested the possible idealized formula $Na_2O \cdot 4MgO \cdot 15Al_2O_3$. This in turn suggested a loosely packed mirror plane, like that of β-alumina, combined with the six-layer spinel block of Braun's structure "W." The calculated structure factors now correlated quite well with the qualitatively observed intensities. Weber's resistivity measurements lend further qualitative support to the proposed structure. A schematic of this structure, along with that of β-alumina for comparison, is given in Figure 1.

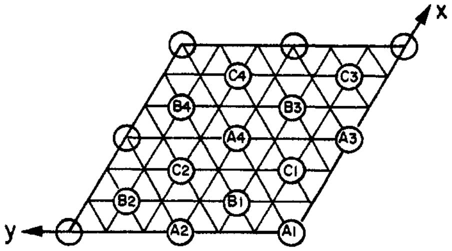

Figure 1.—Key to the x, y positions of ideally close-packed spheres; to be used with Figures 2 and 3. The letters A, B, and C have the usual close-packing connotation. Labels 1–4 are necessary because of the doubling of the a, b axes relative to the simplest type of close-packed structure.

The structure was refined in a limited way, using the least-squares program ORFLS. The limitation consisted of reducing the number of variables because of the rather small number of observations. The resulting parameters are given in Table I, and they lead to the calculated intensities of Table II. The latter includes all possible hkl values out to d = 1.23 Å. We stopped at this point because the degree of clustering was becoming ridiculous. Even before this, there are a considerable number of large clusters, indicated by braces in Table II. In such cases, the sum of the calculated intensities in a cluster should equal the measured value. Keeping this in mind, the agreement between calculated and observed intensities in Table

TABLE I

POSITIONS OF ATOMS IN β'''-ALUMINA

No./unit cell, Wykoff notation, atom type[a,b]	x[c]	z[f]	No./unit cell, Wykoff notation, atom type[a,b]	x[c]	z[f]
6, g, Al	$^1/_2$	0	12, k, Al	$-^1/_6$	0.1474 (3)
12, k, O	$-^1/_6$	0.0334 (4)	12, k, O	$^1/_6$	0.1765 (5)
4, f, O	$^1/_3$	0.0334 (4)	4, f, O	$^2/_3$	0.1765(5)
4, e, Al	0	0.0577 (7)	4, f, Al	$^1/_3$	0.1972 (7)
4, f, Al	$^2/_3$	0.0701 (7)	2, c, O	$^1/_3$	$^1/_4$
4, f, Al	$^1/_3$	0.0932 (6)	1.91 (12),[d] b, Na	0	$^1/_4$
12, k, O	$^1/_2$	0.1109 (4)	0.98 (11),[d] d, Na	$^2/_3$	$^1/_4$
4, e, O	0	0.1109 (4)	0.96 (12),[e] h, Na	$-^1/_6$	$^1/_4$

[a] "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1952, p 304. [b] We cannot differentiate between Al and Mg. All are listed as Al. [c] $y = -x$ for the asymmetric unit used in this table. [d] Twofold site, but the actual occupation number was varied. [e] Sixfold site, but the actual occupation number was varied. Some of these atoms could well be oxygens. [f] Standard deviations, in parentheses, apply to last digit(s).

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(17) L. D. Jennings, *Acta Crystallogr., Sect. A*, **24**, 472 (1968).

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TABLE II[f]

POWDER PATTERN FOR β‴-ALUMINA. OBSERVED AND CALCULATED ANGLES AND INTENSITIES FOR COPPER $K\alpha_1$ RADIATION

hkl	$2\theta_c$*	$2\theta_o$*	I_o**	I_c†
002	5.55	5.56	100	118
004	11.10	11.17	29.3	28.4
006	16.69	16.68	21.3	21.3
100	18.17	18.24	2.7	.86
101	18.39			1.14
102	19.01	19.12	3.0	.54
103	20.02	20.04	15.4	8.29
104	21.35	21.40	2.9	.98
008	22.31	a	a	.70
105	22.95	22.98	1.1	.82
106	24.77	a	a	.25
107	26.77	a	a	.79
0.0.10	27.99	27.95	.8	.90
108	28.92	a	a	.10
109	31.20	31.09	13.0	11.6
110	31.75	31.83	23.6	21.6
112	32.25	a	a	.05
1.0.10	33.58	33.58	29.9	26.6
114	33.73	a or b		1.55
0.0.12	33.74	a or b		1.96
1.0.11	36.04	36.05	49.8	14.4
116	36.07			44.1
200	36.82	36.90	29.1[c]	.25
201	36.94			8.14
202	37.27	37.30		15.5
203	37.82	37.90	9.1	7.58
204	38.58	38.55	5.6	.60
1.0.12	38.59			1.74
118	39.15	39.12	c	17.1
205	39.53	39.50	19.4	.15
0.0.14	39.58			2.57
206	40.68	40.66	10.8	9.12
1.0.13	41.20	41.10	1.4	3.45
207	42.00	a	a	.02
1.1.10	42.83	a	a	.18
208	43.48	43.46	20.4	21.2
1.0.14	43.88	a	a	.92
209	45.11	45.09	23.2	27.7
0.0.16	45.53	a	a	.25
1.0.15	46.61	a or b	14.6	.83
2.0.10	46.82	46.85		14.3
1.1.12	47.01			.29
2.0.11	48.78	48.77	3.2	3.60
210	49.39	49.5	.5	.90
1.0.16	49.41			.02
211	49.43			.11
212	49.75	a	a	.09
213	50.18	50.2	.4	1.14
214	50.79	a	a	.15
2.0.12	50.80	a	a	.06
215	51.57	51.6	1.2	.13
1.1.14	51.60			1.23
0.0.18	51.61			.03
1.0.17	52.26	a	a	.24
216	52.50	a or b	1.8	.07
2.0.13	52.93	52.93		1.11
217	53.59	53.5	.3	.17
218	54.83	a or b	.6	.03
2.0.14	55.16	55.0		.02
1.0.18	55.17			.38
219	56.21	~56.4 b,d	9.4	4.21
300	56.56			3.76
1.1.16	56.57			3.06
301	56.64			.00
302	56.88			.00
303	57.28	57.6 b,d	24.7	.00
2.0.15	57.50			9.16
2.1.10	57.73			10.7
304	57.83			.25
0.0.20	57.85			1.82
1.0.19	58.14			1.69
305	58.54	a	a	.00
2.1.11	59.38	59.35	27.2 c	6.59
306	59.40			9.52
2.0.16	59.93	59.85	c	9.66
307	60.41			.00
2.1.12	61.16	61.1	10.5 c	.86
1.0.20	61.17			.07
308	61.57	~61.5	c	4.57
1.1.18	61.88	~61.7	c	.78
2.0.17	62.46	62.4	.9	.63
309	62.85	63.0	2.0	.00
2.1.13	63.05			1.53
1.0.21	64.26	64.25	.3	.02
3.0.10	64.27			.08
0.0.22	64.29			.03
2.1.14	65.07	64.98	16.6	.05
2.0.18	65.07			17.1
3.0.11	65.32	a or b		.00
220	66.33	66.30 b	48.9	47.9
222	66.62			1.00
2.1.15	67.19	b 67.71	25.8	.51
1.0.22	67.42			.11
224	67.50			.98
3.0.12	67.50			.07
1.1.20	67.51			.17
2.0.19	67.78			22.6
226	68.94	68.95	3.1	1.69
3.0.13	69.30	a or e		.00
310	69.42	a or e		.03
2.1.16	69.43	a or e		.01
311	69.49	a or e		.03
312	69.70	a	a	.03
313	70.06	b	2.2	.39
314	70.56	70.46		.05
2.0.20	70.57			1.47
1.0.23	70.65			.09
228	70.94	a	a	.12
0.0.24	70.96	a	a	.19
315	71.20	a	a	.04
3.0.14	71.23	a	a	.39
2.1.17	71.77	a	a	.19
316	71.97	a	a	.02
317	72.89	a	a	.06
3.0.15	73.27	73.44	2.5	.00
2.0.21	73.46			1.15
2.2.10	73.47			.34
1.1.22	73.49			1.16
318	73.94			.01
1.0.24	73.96			.53
2.1.18	74.22			.31
319	75.12	75.18	1.7	1.72
3.0.16	75.42			1.16
3.1.10	76.43	76.4	c 6.8	4.38
2.0.22	76.45			.14
2.2.12	76.52			1.16
2.1.19	76.79	d		1.40
1.0.25	77.35			1.07

[a] Not observed. [b] Unresolved. [c] Cluster sufficiently resolved into individual reflections or subclusters to estimate positions of latter but not sufficiently resolved for separating their integrated intensities. [d] Very broad. [e] Unresolved from α_2 peak of preceding reflection. [f] Single asterisks indicate units of degrees. Double asterisks indicate the observed intensity in arbitrary units, assigning 100 to the strongest. Daggers indicate $I_c = SM[\exp(-2B(\sin^2\theta)/\lambda^2)]F^2(1 + 0.6\cos^2 2\theta)/(\sin^2\theta\cos\theta)$. I_c is the calculated intensity, scaled to the arbitrary observed intensity by scale factor S and M is the multiplicity. The temperature factor is $B = 0.774 \pm 0.103$. Structure factor F is calculated according to Table I.

II is quite respectable, which supports the essential correctness of the proposed structure.

The refinement contained the following restrictions and assumptions, all for the purpose of reducing the number of variables: (1) a single, overall isotropic temperature factor; (2) assuming the same columnar structure as in the other β's, all x and y parameters are assumed to be exactly of the types $m/6$, and $n/6$ and were not varied; (3) the z parameters of approximately coplanar oxygen layers were kept precisely equal. The usual experience with similar structures is that (2) is a very good approximation and (3) only a fair one. Unit weights were assigned to most reflections, except for down-weighting the three film-measured $(00l)$'s, as well as a few intensities extracted from overlapping clusters. There is one additional matter that needs discussion. The (002) line has the largest intensity because of an enormous Lp factor, yet the experimental value was still only about half of the calculated value, based on the idealized model and formula. It appeared that the only reasonable scheme for reducing its calculated intensity was to put extra atoms into the mirror planes at $z = {}^1/_4$ and ${}^3/_4$, where there is much extra room.

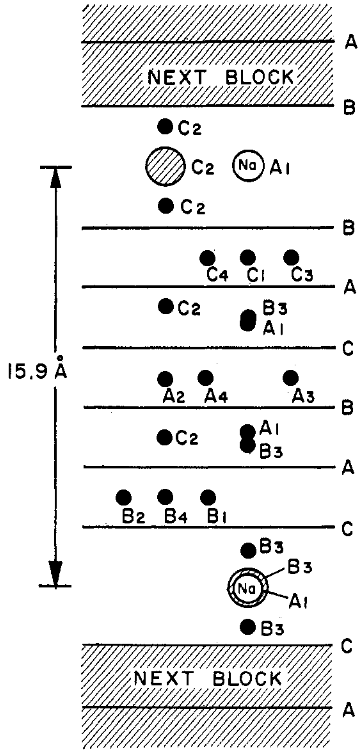

Figure 2.—Schematic projection of β‴-alumina onto the b–c plane. Oxygen layers are indicated only by a horizontal line marked A, B, or C, since they fill all four positions associated with a letter. Aluminums (and/or magnesiums) are small, solid circles, whose x, y positions are labeled according to the key of Figure 1. The "spacer column" oxygens are large, shaded circles, and the sodiums are open circles labeled "Na." The actual structure is likely to be somewhat distorted from this idealized scheme; *e.g.*, the oxygen planes will be somewhat puckered.

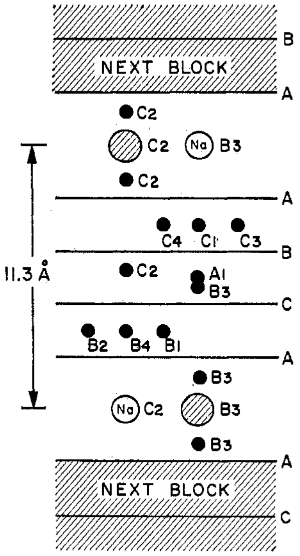

Figure 3.—Schematic of β-alumina, for comparison, using the same labeling scheme as for Figure 2.

It was therefore deemed necessary to adjust three more parameters, namely, the occupation numbers of equipoints 2b, 2d, and 6h. These comprise the most reasonable available interstices in the mirror planes. By comparison, the idealized model of Figures 1–3 has two sodiums in equipoints 2b, chosen because their nearest-neighbor coordination is identical with that of the sodiums in the Beevers–Ross[3] model for β-alumina.

The results left the "Beevers–Ross" positions, 2b, nearly full, distributed nearly one more atom between equipoints 2d, and distributed another 0.96 atom among equipoints 6h. All are listed as sodiums in Table I. They add up to 3.9 sodiums per unit cell *vs.* only 2 for the idealized model and about 2.6 suggested by the chemical analyses carried out for Weber and Venero (see Introduction). The possibility that a fraction of these extra atoms in the mirror planes may be oxygens, rather than sodiums, must be kept in mind.

A suspicion that the extra scattering matter in the mirror planes might be water was tested experimentally by dehydrating a sample by heating to 700° under vacuum and then quickly sealing the sample into an X-ray type capillary. The ratios of the (002), (004), and (006) intensities were measured again, photographically, but they had not changed by more than 10%.

We conclude either that the (00*l*)'s and particularly (002) are affected by some unrecognized systematic error or that there are more atoms in the mirror plane than what one expects from chemical analysis and experience with other β-aluminas. These extra atoms are listed in Table I but are not indicated in the schematics of the idealized structures in Figures 2 and 3.

The idealized formula $Na_2O \cdot 4MgO \cdot 15Al_2O_3$ is obtained from the following considerations. The 2 spinel blocks of 6 oxygen layers, with 4 oxygens per layer, call for 48 oxygens. The 10 interstitial layers of 3 (Al or Mg) each, demanded by an ideal spinel arrangement, call for 30 (Al or Mg)'s. The two spacer columns, one across each basal mirror plane, call for 4 more (Al or Mg)'s and 2 more oxygens. The number of sodium ions per unit cell must be even, and 2 is by far the closest even integer to the analyses of Weber and Venero. One thus arrives at a total of 50 oxygens, 34 (Al or Mg)'s, and 2 Na's. Assigning standard valences then leads to 4 Mg's and 30 Al's.

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Inversion and Ligand-Exchange Kinetics of Tetrahedral Bis-Chelate Complexes of Zinc(II) and Cadmium(II)

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A series of bis(β-aminothionato)zinc(II) and -cadmium(II) complexes, $M(R\text{–}SC_6H_5HR_\alpha)_2$ (1), has been prepared by a nonaqueous chelation procedure for the purpose of investigating inversion rates of the tetrahedral enantiomers (Δ, Λ). The chirality of the molecular configuration renders the methyl groups of the *N*-isopropyl substituent diastereotopic and permits determination of the rates and activation parameters for the process of diastereotopic averaging (inversion) without prior separation of enantiomers. Kinetic data for this process were obtained for $Zn(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)(C_6H_5CH_2\text{–}SC_6H_5HH)$ and $Zn(i\text{-}C_3H_7\text{–}SC_6H_5HH)(C_6H_5CH_2\text{–}SC_6H_5HH)$ (formed by ligand exchange in solution) in chlorobenzene and for $Cd(i\text{-}C_3H_7\text{–}SC_6H_5HR_\alpha)_2$ (R_α = H, CH_3) in deuteriochloroform by line shape analysis of the exchange-broadened isopropyl methyl region of the pmr spectra. The inversion rates of the zinc(II) complexes are slower than those of the cadmium(II) complexes and the activation energies are 21 (Zn) and *ca.* 12–15 (Cd) kcal/mol. Ligand exchange was found to be slow relative to inversion for zinc(II) complexes, which undergo inversion by an intramolecular process. For cadmium(II) complexes thermodynamic parameters for diastereotopic averaging and ligand exchange are similar, suggesting that the former process may follow a bond rupture pathway. A "twist" mechanism is provisionally proposed for the inversion of zinc(II) complexes. Qualitiative comparison of the isopropyl methyl pmr spectra of the pair $Zn(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)_2$ and $Zn(i\text{-}C_3H_7\text{–}C_6H_5HCH_3)_2$ (2) indicates that replacement of oxygen by sulfur in the coordination sphere increases the inversion rate. Methyl pmr signals of $Zn[(+)CH_3CHC_6H_5\text{–}SC_6H_5HH]_2$ reveal that the stabilities of the $\Delta(+,+)$, $\Lambda(+,+)$ diasteromers are essentially equal in $CDCl_3$ at ~30°

Introduction

Tetrahedral bis-chelate complexes derived from unsymmetrical ligands are enantiomeric with absolute configurations Δ and Λ.[2] Although partial resolution of various metal(II) complexes of this type have been reported, little quantitative information regarding rates of inversion at the metal center is available. A tabulation of optically active tetrahedral chelate complexes reported prior to 1958 is given by Basolo and Pearson.[3] Since that time there have been only four reports of partial resolution of other bis-chelate complexes,[4–8] and in one such case, a bis(formazyl)nickel(II) complex,[5] the optical isomerism does not arise from a tetrahedral structure.[9] Partially resolved complexes of Be(II), Cu(II), and Zn(II) as brucine and strychnine salts are reported to mutarotate to constant rotation within 15–25 min in chloroform solution.[10] Rapid mutarotation of the quinine salt of bis(salicylato)-

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