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Stoichiometry and Structure of the Super Ionic Conductor Silver Beta-Alumina

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Beta-alumina is a crystalline nonstoichiometric compound highly permeable to sodium and silver ions. The mobile ions are statistically distributed among a manifold of nearly equivalent sites in widely separated planes perpendicular to the hexagonal axis and two-dimensional ionic conduction results from the interchange of ions between sites in these planes. Sodium and silver beta-alumina are isomorphous but at room temperature there is a different distribution of potential mobile cations among the conduction sites.

There is at present considerable experimental and theoretical interest in the properties and understanding of solids with exceptionally high ionic conductivity. Such solids, which may be called super ionic conductors, exhibit ionic conductivities that can be as large as inverse ohm-centimeters at temperatures ranging from near room temperature to 1200°C (*1*). Examples are the cation disordered phases of the silver halides and chalcogenides, which have been discussed by Wiedersich and Geller (*2*), defect stabilized mixed oxides such as calcia stabilized zirconia (*3*), and the ismorphous series of hexagonal compounds with the so-called "beta-alumina" structure (*4*). Efforts to understand the properties of these solids have demonstrated a need for more rigorous characterization of their structures, particularly with regard to stoichiometry, defects, and disorder.

"Beta-alumina" is the commonly accepted name in the literature for a complex sodium aluminate which originally was considered to be an allotropic modification of alumina (*5*). Many compounds crystallize with this structure and beta-alumina has come to refer to the atomic arrangement which characterizes a large family of isomorphs with an "ideal" composition near $AM_{11}O_{17}$, where A may be Na, K, Rb or Ag and M may be Al, Fe or Ga. A recent review of the literature data on beta-alumina type phases has been given by DeVries and Roth (*4*).

Although beta-alumina has been the subject of several structure investigations, its composition and structure are still not clear. The first single crystal X-ray study was by Hendricks and Pauling (*6*) who established that the crystal was hexagonal with cell dimensions $a = 5.61$ Å and $c = 22.459$ Å and with probable space group $P\bar{6}2c$, $P6_3mc$ or $P6_3/mmc$. At this time, beta was thought to be a polymorph of α-Al_2O_3. The first structure analysis by Bragg, Gottfried, and West (*7*) utilized a limited number of $00l$ and $hk0$ reflections which had been measured with an ionization spectrometer. The observation of etch figures and the absence of a piezoelectric effect was used to rule out the noncentrosymmetric space groups, leaving only $P6_3/mmc$. The significance of sodium was now recognized and an attempt was made to incorporate sodium in the structure. An inconsistency was noted between the X-ray data and chemical analysis which persists to the present. According to the chemical analysis, crystal density and lattice parameters, there should have been 35 O, 0.991 Na and 23.07 Al atoms per unit cell, a composition which is not compatible with the number of equivalent sites in the space group.

The structure adopted by Bragg *et al.* is similar to that which has been found in subsequent investigations. Parallel to the basal plane of the hexagonal cell are sheets of atoms such that four layers of oxygens are in cubic closest packing. Aluminum atoms, which occupy octahedral and tetrahedral interstices, are distributed as in spinel, $MgAl_2O_4$, with Mg atoms replaced by Al. The spinel-like blocks are bound together by layers of sodium and oxygen atoms which lie on mirror planes. Bragg *et al.* commented that the calculated intensities did not agree with those observed as well as expected for quantitative work. They believed the spinel-like portion of the structure was definitely established but that the arrangement of atoms in the mirror planes was uncertain and that the structure was probably disordered.

Improved chemical analysis (*8*), combined with lattice parameters and crystal density, led Beevers and Broult (*9*) to conclude that the formula of beta-alumina was $Na_2Al_{22}O_{34}$. Beevers and Ross (*10*) then undertook the redetermination of the structure. The original spectrometer measurements of Bragg *et al.* were combined with intensities obtained from oscillation photographs to complete the data required for a projection of the electron density on the *a–c* plane. The only point considered doubtful was the position of the sodium atoms in the horizontal mirror planes. The main thrust of the investigation was choosing between the (b) and (d) positions in $P6_3/mmc$ and it was concluded the agreement of calculated and observed intensities was better for sodium in the (d) sites: 2/3, 1/3, 1/4 and 1/3, 2/3, 3/4.

The atomic arrangement described by Beevers and Ross has become the accepted structure for beta-alumina. The analysis was based on a combination of accurately measured spectrometer intensities and film data. There have been two recent refinements of the structure utilizing spectrometer data and least-squares methods. The first redetermination by Felsche (*11*) confirmed the general aspects of the Beevers–Ross structure but found the sodium sites only 1/3 occupied and the cation deficiency compensated by oxygen vacancies. Suspecting the crystal that Felsche worked on was atypical (it was obtained from a beta-alumina refractory block which had been used in a tank for making sheet glass), Peters *et al.* (*12*) repeated the refinement using a crystal which contained a "typical" excess of sodium. The latter study found about 3/4 sodium atoms near the normal (d) positions, and the remaining sodium in elongated ellipsoids centered near positions which are halfway between the oxygens of the basal mirror planes.

Two other sodium aluminates, β' and β'', are reported to give diffraction patterns that are very similar to that obtained from beta-alumina. Beta-alumina, or β, the compound studied by Beevers and Ross, has a composition near $Na_2O \cdot 11Al_2O_3$ to $Na_2O \cdot 9Al_2O_3$. It is characterized by a hexagonal cell with two spinel-like blocks in the crystallographic repeat unit. β'' (*13*, *14*) is rhombohedral with three spinel blocks in the crystallographic repeat unit; the composition is near $Na_2O \cdot 5Al_2O_3$–$Na_2O \cdot 7Al_2O_3$ and the phase is isomorphous with the ternary compound $Na_2O \cdot MgO \cdot 5Al_2O_3$ investigated by Bettman and Peters (*15*). Yamaguchi and Suzuki (*14*) have reported there is a third phase, β', which has a structure similar to that of β but with the composition near $Na_2O \cdot 7Al_2O_3$.

It is clear that the structure of beta-alumina is variable and highly defective. Since the stoichiometry and defect structure are undoubtedly of major importance in determining the mobility of sodium and ionic conductivity, the present work was undertaken in an effort to elucidate the nature of these defects. This paper describes an investigation of an isomorph of beta-alumina in which sodium has been replaced by silver. The silver isomorph was selected to take advantage of the large silver form factor for determining the concentration, positions and thermal vibrations of the mobile cations.

Synthesis

Crystals of sodium beta-alumina were grown from a sintered mixture of Linde-A Al_2O_3 and CP Baker sodium aluminate by resistance heating with carbon electrodes at a temperature of about 2000°C. The crystals grew as thin plates parallel to (00.1), about 1 mm in diameter and 0.1–0.2 mm thick. Specimens for study were selected under a microscope to eliminate obvious impurities, imperfections, and second-phase material.

Sodium was replaced by silver using the procedure described by Yao and Kummer (*16*). Crystals were enclosed in a basket constructed from 80-mesh platinum screen and immersed, with occasional agitation, in molten silver nitrate at 370°C for 48–95 hr. Analysis showed less than 0.1% sodium remained in the exchanged beta-alumina. These crystals were removed from the melt, most of the silver nitrate drained off, and the small excess which remained was washed off with water. A surface stain, probably silver, was removed by a short immersion in dilute nitric acid. Exposure of the crystals to water and acid was kept as small as possible (3–5 min in all) to minimize the replacement of silver by hydrogen or hydronium ions.

X-Ray diffraction showed the crystals were hexagonal with $a_0 = 5.595$ Å and $c_0 = 22.488$ Å, which agrees well with the results of Yao and Kummer (*16*) (5.594 and 22.498 Å) and Whittingham and Huggins (*17*) (5.596 and 22.47 Å).

Stoichiometry

In view of the history of conflicting chemical analyses the stoichiometry was investigated by physical methods which could be applied to small crystals that could be characterized by X-ray diffraction. Several methods were used: (1) the change in weight when sodium was replaced by silver, (2) the lattice parameters and density of sodium beta crystals and silver beta crystals, and (3) least-squares refinement of site occupation parameters. The first method can give only the percentage of M^+ ion in the crystal, whereas (2) gives information about the molecular formula, and (3) can in addition locate the position of the M^+ ions in the structure.

Weight change. In the first experiment, 12 "optically good" crystals with weights which varied from 223 to 978 × 10^{-6} g were weighed individually on a microbalance, exchanged as a group for 16 hr at 370°C, then reweighed. The second exchange used 10 crystals with weights ranging from 215 to 2032 × 10^{-6} g and a time of 45 hr. The third experiment was a "batch" operation in which 1.2 g of "fair quality" crystals were exchanged for 4 days at 360°C.

Stoichiometry was calculated assuming the reaction

$$Na_2O \cdot nAl_2O_3 + 2Ag^+ = Ag_2O \cdot nAl_2O_3 + 2Na^+.$$

The results of the first two experiments are plotted in Fig. 1 which shows the increase in weight of individual crystals is directly proportional to their initial weight. Several conclusions may be derived from this result. First, that replacement of sodium by silver is complete; second, that the composition of crystals of different size was the same, and third, the crystals contained sodium in excess of the stoichiometric formula. The experimental data are compared with calculated values for different compositions and with the possible exception of the smallest crystal, all points fall significantly above 1:11 and near composition 1:9.

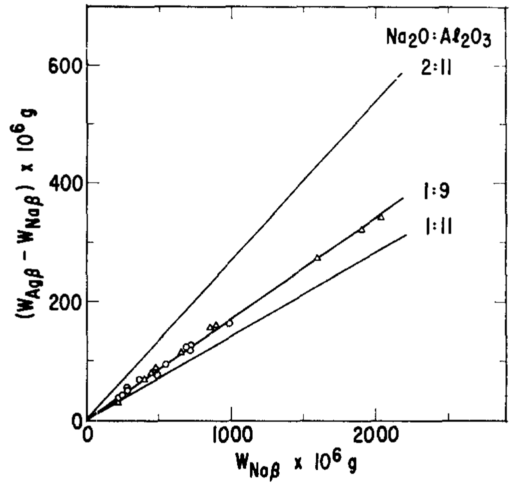

FIG. 1. Increase in weight of beta-alumina crystals exchanged with silver nitrate at 370°C: O 16 hr; △ 45 hr.

Values of n, calculated from the total change in weight of the three batches, are given in Table I. The average value of n is 9.16.

X-Ray density. The formula weights per unit cell of the original and exchanged crystals in experiment 3, Table I were calculated from the unit cell volumes and crystal densities. Lattice parameters were obtained from single crystal rotation photographs ($CuK\alpha_1 = 1.5405$ Å) and Debye–Sherrer photographs ($CrK\alpha_1 = 2.2896$ Å). Pycnometric densities were determined by displacement of toluene to avoid reaction with water. Table II gives the formula weights per unit cell calculated from the equation

$$\rho = 1.66020 \Sigma A / V$$

where ρ is the density, ΣA is the sum of the atomic weights in the unit cell, and V is the volume in $Å^3$ of the unit cell. The formula weights found were

$\Sigma A = 1200$ for sodium beta-alumina.

$\Sigma A = 1400$ for silver beta-alumina.

TABLE I

ISOMORPHOUS SUBSTITUTION OF SILVER FOR SODIUM IN BETA-ALUMINA: CHANGE IN WEIGHT OF BETA-ALUMINA CRYSTALS EXCHANGED IN MOLTEN SILVER NITRATE

Exp.	Temperature and time of exchange (°C/hr)	No. of crystals	Initial weight in grams	% increase in weight	$Ag_2O \cdot nAl_2O_3$ (n)	$mAg_2O \cdot 11Al_2O_3$ (m)
1	370, 16	12	0.00553	17.22	9.13	1.20
2	370, 45	10	0.00940	17.26	9.11	1.21
3	360, 96	>1000	1.1940	17.04	9.23	1.19

TABLE II[a]

COMPOSITION OF UNIT CELLS OF SODIUM AND SILVER BETA-ALUMINA

M	a (Å)	c (Å)	V (Å^3)	ρ (g cm^{-3})	ΣA	$mM_2O \cdot 11Al_2O_3$ (m)
Na	5.594	22.603	612.5	3.253	1200	1.23
Ag	5.595	22.488	609.6	3.813	1400	1.20

[a] The formula weight per cell is calculated from $\Sigma A = \rho V/1.6602$.

Assuming that all of the ions are in their normal oxidation states, conservation of mass and charge requires the number of sodium or silver atoms N_M, aluminum atoms N_{Al}, and oxygen atoms N_O satisfy the equations:

$$23.0\,N_M + 27.0\,N_{Al} + 16.0\,N_O = 1200,$$

$$107.9\,N_M + 27.0\,N_{Al} + 16.0\,N_O = 1400,$$

$$1.0\,N_M + 3.0\,N_{Al} - 2.0\,N_O = 0.$$

Two sets of allowed ranges of values for N_M and N_{Al} can be obtained by eliminating N_O from the above relations. The result, plotted in Fig. 2, shows that the curves intersect and therefore are uniquely satisfied at point b, $N_M = 2.44$, $N_{Al} = 22.04$, $N_O = 34.28$. This stoichiometry is in excellent agreement with that obtained from the increase in weight of crystals when Na was replaced by Ag since the 1:9.16 composition corresponds to $N_M = 2.40$ and $N_O = 34.2$ when N_{Al}, the number of aluminum atoms per cell, is taken equal to 22.

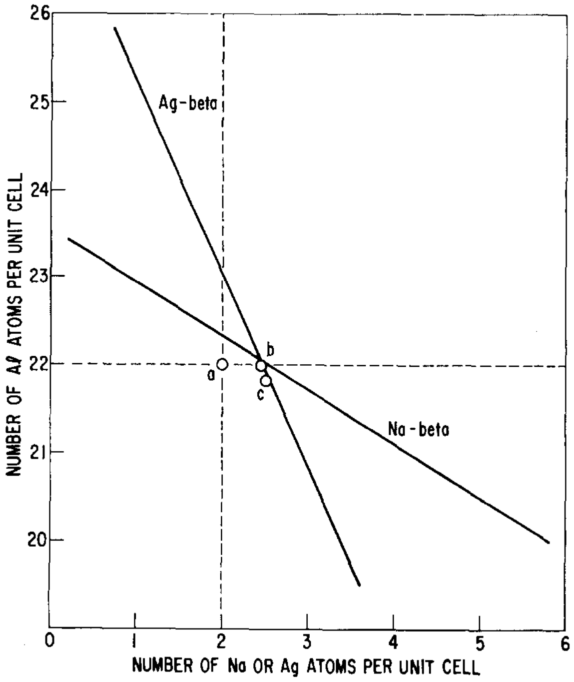

FIG. 2. Unit cell content from crystal parameters and density: a = stoichiometric $M_2Al_{22}O_{34}$; b = nonstoichiometric with compensation by interstitial oxygen, $M_{2.44}Al_{22.04}O_{34.28}$; c = nonstoichiometric with compensation by aluminum vacancies, $M_{2.50}Al_{21.83}O_{34}$.

Impurities. The calculation of stoichiometry implicitly assumes that the identity of all the chemical species is known. No significant concentrations of impurities were observed by spectrographic and X-ray fluorescence analysis, which leaves only H or OH as likely undetected contaminants.

Untreated beta-alumina crystals usually exhibit broad infrared absorption bands near 3220 cm^{-1} due to O–H stretching by H_2O (or strongly hydrogen bonded oxygen atoms). The intensity of the band can be increased by heating in water vapor at 100°C or reduced to negligible levels by heating in air to 450°C. When examined under a microscope, most crystals are seen to have micro-cleavages or fissures parallel to (00.1) (Fig. 3a). A scanning electron micrograph of a cleavage crack in an otherwise sound crystal is shown in Fig. 3b. Crystals easily cleave parallel to these layers and it is believed the infrared bands are due to water molecules adsorbed on the surfaces of the cleavage cracks. Taking the extinction coefficient for water as 62.7 cm^{-1} mole^{-1} (*18*), the intensity of the infrared band in a typical untreated beta-alumina crystal corresponded to about 0.63×10^{18} molecules H_2O cm^{-3}. A characteristic average separation between the cracks observed in many crystals is about 5×10^{-4} cm. If water were adsorbed at the layer interfaces, there would be about $0.63 \times 10^{18} \times 5 \times 10^{-4} = 3 \times 10^{14}$ molecules per cm^2 of surface. This is a reasonable density for a few monolayers and supports the view that water is adsorbed on the crystal surfaces and is not incorporated in the structure.

In contrast to the broad water band seen in sodium beta crystals, the infrared spectra of some of the crystals of silver beta-alumina exhibited a

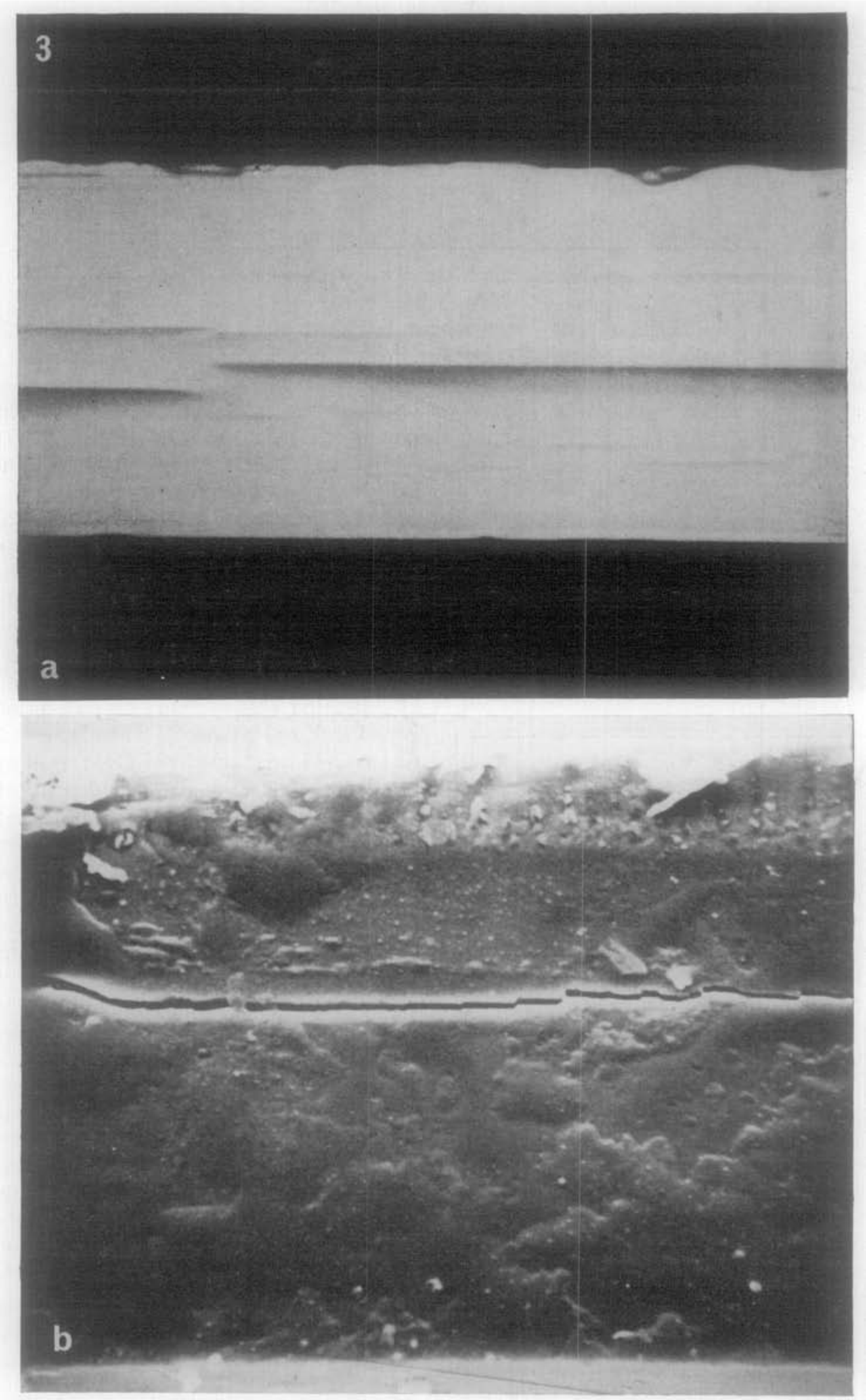

FIG. 3a. Photomicrograph of polished edge of a beta-alumina crystal showing cleavage cracks parallel to (00.1). Polarized light. Magnification 230×. 3b. Scanning electron micrograph of edge of a beta-alumina crystal showing a crack or fissure parallel to the (00.1) plane. Magnification 2300×.

sharp peak at 3540 cm^{-1}. Because of the sharpness of the peak, it is attributed to hydroxyl ions which were produced on the cleavage crack interfaces by reaction of the adsorbed water in the molten silver nitrate. In the unlikely event the OH ions are incorporated within the structure, the concentration is estimated to be less than 0.07 OH per unit cell.

Structure Analysis

A clear, transparent crystal of excellent optical quality was selected for X-ray study. Silver beta crystals cleave easily and since it was not feasible to grind a sphere, the crystal was cut with a razor blade to a nearly equiaxed parallelopiped with edges equal to 7×10^{-3} cm.

Laue and precession photographs taken with the X-ray beam parallel to the principal axes were in agreement with the space group $P6_3/mmc$. Heavily exposed photographs were searched for diffuse scattering, superstructure peaks, or peaks forbidden by the space group, but no evidence for disorder was observed.

The intensity data were collected with a General Electric Datex–Automated Diffractometer using filtered Cu*Kα* radiation and a scintillation counter. Integrated intensities of six sets of independent reflections hkl, $h \gg k \gg 0$ and $l \gg 0$ were measured by the θ, 2θ scan technique. One set was repeated with three thicknesses of Ni filter. The seven segments, which should be equivalent except for absorption and extinction, were averaged to give a final set in which the deviation of individual values from the mean was usually less than 10%.

The final set of 302 independent reflections were corrected for Lorentz, polarization, and absorption effects. Absorption corrections were made by representing the crystal as a sphere of equivalent volume, with $\mu/\rho = 66.03$, $R = 4.34 \times 10^{-3}$ cm, and $\mu R = 1.093$. The structure was refined by differential fourier syntheses and least-squares adjustment of parameters using the ORFLS program of Busing, Martin and Levy, as modified by W. C. Hamilton and S. J. LaPlaca at the Brookhaven National Laboratory. The silver form factor was that tabulated by Cromer and Waber (*20*), aluminum and oxygen form factors were taken from the International Tables for Crystallography (*21*), and corrections for anomalous dispersion were made with the terms given by Cromer (*22*).

Weights. Since the structure analysis was expected to be concerned with problems of partial site occupations, complicated by position and displacement disorder, and large thermal parameters, unit weights were used initially to avoid unwittingly prejudicing the course of the analysis. R dropped initially to 0.14 and was reduced below 0.12 by subsequent refinement. The final calculations were carried out with a semiempirical set of weights derived from a plot of σ_{obsd} vs. F_{obsd}: $\sigma = 0.50 + (20/1.4F) + 3.7 \times 10^{-4} F^2_{\text{obsd}}$.

Refinement of the Structure

It was clear from the outset that the aluminum and oxygen atoms were close to the positions in the spinel block originally assigned by Bragg *et al.* and that the principal problem would be accounting for the nonstoichiometry. The departure of the composition from $AgAl_{11}O_{17}$ could be due (a) to excess Ag in the mirror planes at $z = 1/4$, $3/4$ or (b) to partial substitution of silver for aluminum in the spinel blocks. Furthermore, electrical neutrality imposes the restriction that the positive charge associated with the excess silver be neutralized, either by aluminum vacancies, or additional oxygen. Three-dimensional anisotropic least-square refinements of various models resulted in only small shifts of the atomic parameters in the spinel block but there were large changes in the site occupation, position, and thermal parameters of the atoms in the mirror planes.

Calculations which assumed beta-alumina had the structure proposed by Beevers and Ross for beta-alumina (two molecules per cell and silver atoms in the (d) sites) resulted in completely unsatisfactory intensity agreement with $R(F) > 25\%$. The R value improved, but still was unsatisfactory, when the two silver atoms were distributed equally (each site 1/2 occupied) among the (d) and (b) sites. There was further improvement when the silver occupation parameters were treated as variables and it was gratifying, at this stage, to find the X-ray intensities required that the crystal contain a nonstoichiometric excess of silver in approximate agreement with that found by weight change and density. A complete refinement indicated the silver sites were only partially occupied with about 0.69 Ag in (d) and 0.55 Ag in (b). The silver thermal parameters were extremely anisotropic with $\beta_{11}/\beta_{33} \sim 1000$. The agreement between calculated and observed intensities still was unsatisfactory ($R = 14.6\%$) and a search for the origin of the difficulty was undertaken by fourier analysis.

The electron density sections $\rho(\bar{x}, x, 0)$ and $\rho(x, y, 1/4)$ shown in Figs. 4 and 5 confirmed the approximate correctness of the structure with the exception that the contours about the silver in (d)

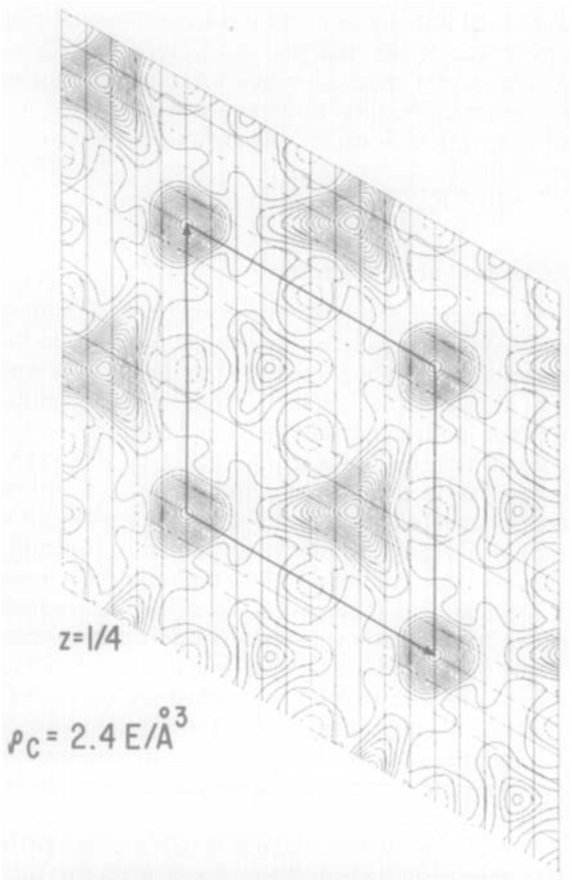

FIG. 4. Electron density in mirror plane of Ag beta-alumina. Ag(1) and Ag(2) are centered about 2/3, 1/3, 1/4 and 0, 0, 1/4, O(5) about 1/3, 2/3, 1/4. The negative contour is dotted.

were elongated into spikes such that a continuous bridge of electron density extended between the atoms in the (b) and (d) sites. The minimum density between the silver atoms was about $2E/A^3$. There was a similar distortion of the electron density about O(5).

The electron density in the spike was approximated by a Ag(3) atom in 6(h) with $x \sim .75$. Variation of the three Ag occupation parameters and the position coordinate of the "bridging" silver atom resulted in considerably improved intensity agreement ($R = 10.9\,\%$). However, the sum of the occupation parameters gave a total silver concentration significantly larger than had been measured by the exchange experiments. In addition, there were several unacceptable discrepancies when F_{obsd} was compared with F_{calcd}. Numerous modifications of the model were explored: (a) neutral atom form factors were substituted for ionic form factors; (b) the silver in excess of the stoichiometric composition was substituted for aluminum in the spinel block; (c) the bridging silver atoms were placed in (j) sites to allow them to move off the vertical mirror planes; (d) the occupation parameter of O(5) was varied; (e) O(5) was placed in the (h) sites and the site occupation and position parameters were varied. None of these modifications resulted in significant improvement.

At this stage, electron density difference fouriers were computed and these suggested the Ag(1) and Ag(2) atoms should be displaced from the 3-fold axis and moved toward each other. This was accomplished by removing Ag(3) and placing Ag(1) and Ag(2) in 6(h) positions. There was a significant improvement in the refinement and R dropped to $8\,\%$. The adjusted values of the parameters showed the displacement of Ag(1) was considerably larger than that of Ag(2) and that the distribution of silver between the sites was approximately (d):(b) = 2:1. Although the R factor now was about that expected

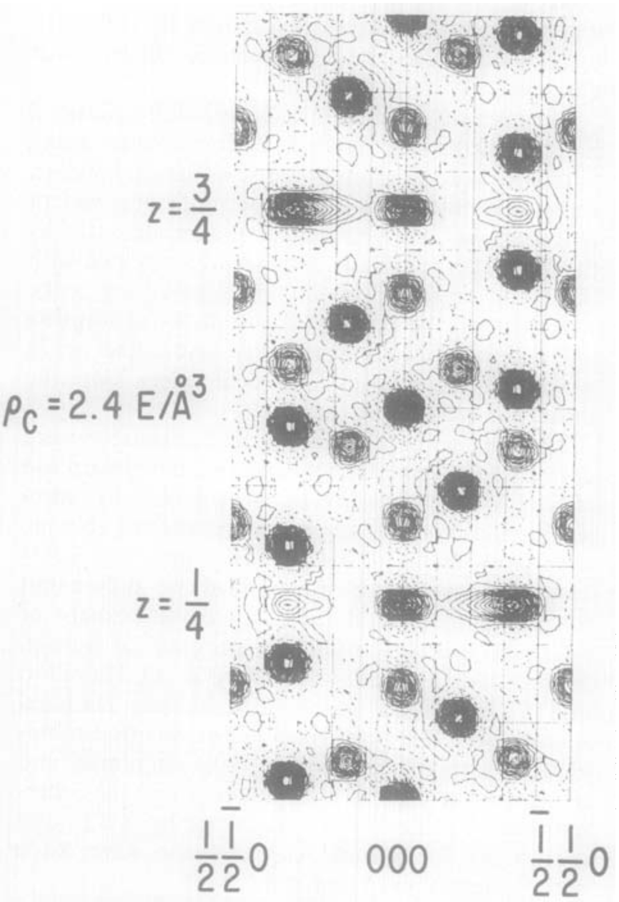

FIG. 5. Electron density in ($\bar{x}$, x, z) section of Ag beta-alumina. The anisotropic electron density about Ag(1), Ag(2), and O(5) in the mirror planes at $z = 1/4$, $3/4$ is due to both thermal vibrations and displacement disorder.

from the variation of the intensities of equivalent reflections in the same form, there were several discrepancies between F_{obsd} and F_{calcd} that were beyond reasonable estimates of the probable errors.

Difference maps computed with the new phases showed that additional electron density was required in the bridge, i.e., the density could not be accounted for by the position and thermal parameters of only two silver atoms. A third atom again was introduced between Ag(1) and Ag(2). When this atom was assumed to be oxygen, the R factor improved to 7.5% and adjustment of the occupation parameters gave 0.4 oxygen in the bridge. However, the sum of the adjusted silver occupation parameters corresponded to only 2.14 silver atoms in the cell, appreciably less than that found by the weight change and crystal density measurements. The alternative interpretation, that the bridging density was due to silver, resulted in further improvement of R to 7.2% and 0.057 for the probability the bridge site was occupied by silver. The total silver content of the unit cell was 2.55, in reasonable agreement with that found by weight change and X-ray density, and there were no disturbing disagreements between F_{obsd} and F_{calcd}.

Final calculations were made to see whether a decision could be made between charge compensation by cation vacancies or interstitial anions in the mirror planes. R was unchanged when the multiplicity factors of Al(1), Al(2), Al(3), Al(4) were varied and the shifts in site occupation factors were less than the estimated errors.

Structure of the Spinel Block

The crystallographic structure parameters of Ag beta-alumina are tabulated in Tables III and IV. The final values of $R_1 = 7.2\%$ and $R_2 = 6.5\%$ are about that expected from the variations observed in the measurement of symmetry equivalent reflections. The observed and calculated structure factors

TABLE III

SILVER BETA ALUMINA CRYSTALLOGRAPHIC DATA

Hexagonal, space group $P6_3/mmc$

$a = 5.595$ Å

$c = 22.488$ Å

$Z = \mathrm{Ag}_{2.4}\mathrm{Al}_{22}\mathrm{O}_{34.2}$

$\rho_{\mathrm{obs}} = 3.813\ \mathrm{g\ cm^{-3}}$

$\rho_{\mathrm{calc}} = 3.813$

Radiation, Cu$K\alpha$ = 1.5418 Å

$\mu = 252\ \mathrm{cm^{-1}}$

Number of independent reflections = 302

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.072$

$R_2 = (\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^{\,2})^{1/2} = 0.065$

TABLE IV[a]

SILVER BETA-ALUMINA, POSITION AND THERMAL PARAMETERS [a,b]

	Position	Number per unit cell	$x \times 10^4$	$z \times 10^4$	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^6$	$\beta_{13} \times 10^6$
Al(1)	12(k)	12	8321 (2)	1064 (1)	50 (6)	44 (8)	233 (31)	34 (62)
Al(2)	4(f)	4	3333	248 (1)	16 (8)	β_{11}	−24 (46)	0
Al(3)	4(f)	4	3333	1755	55 (9)	β_{11}	10 (50)	0
Al(4)	2(a)	2	0	0	34 (11)	β_{11}	−24 (54)	0
O(1)	12(k)	12	1566 (5)	503 (11)	31 (13)	88 (17)	62 (71)	−74 (141)
O(2)	12(k)	12	5027 (5)	1470 (2)	8 (11)	10 (15)	274 (63)	−117 (166)
O(3)	4(f)	4	6666	553 (3)	7 (20)	β_{11}	94 (125)	0
O(4)	4(e)	4	0	1428 (3)	14 (19)	β_{11}	122 (99)	0
O(5)	6(h)	1.913 (.070)	3074 (32)	2500	294 (103)	498 (258)	222 (283)	0
Ag(1)	6(h)	1.344 (.014)	7097 (7)	2500	528 (30)	927 (87)	699 (66)	0
Ag(2)	6(h)	0.865 (.011)	9753 (13)	2500	519 (23)	1236 (32)	329 (53)	0
Ag(3)	6(h)	0.336 (.013)	8072 (20)	2500	138 (41)	421 (116)	149 (280)	0

[a] Estimated standard deviations in parentheses.

[b] The x, z are fractions of the unit cell edges and thermal parameters are of the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. $\beta_{12} = \frac{1}{2}\beta_{22}$; $\beta_{23} = 2\beta_{31}$.

TABLE V

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SILVER BETA-ALUMINA

K	L	F_{obsd}	F_{calcd}
		$H = 0$	
0	2	14	15
0	4	23	23
0	6	69	72
0	8	128	136
0	10	147	156
0	12	55	52
0	14	152	156
0	16	52	45
0	18	18	17
0	20	126	139
0	22	48	49
0	24	36	37
0	26	65	64
0	28	93	96
		$H = 1$	
0	0	9	7
0	1	26	27
0	2	23	23
0	3	10	10
0	4	4	2
0	5	29	30
0	6	28	28
0	7	119	126
0	8	44	41
0	9	6	5
0	10	24	24
0	11	30	27
0	12	1	1
0	13	13	12
0	14	18	18
0	15	38	37
0	16	25	24
0	17	6	6
0	18	23	22
0	19	35	36
0	20	50	50
0	21	63	62
0	22	13	14
0	23	5	4
0	24	16	16
0	25	3	2
0	26	18	18
0	27	3	4
0	28	16	17
1	0	92	124
1	2	40	43
1	4	114	130
1	6	29	26
1	8	42	39
1	10	65	63
1	12	83	83
1	14	42	39
1	16	59	58
1	18	57	56
1	20	23	22
1	22	16	16
1	24	35	35
1	26	50	54
		$H = 2$	
0	0	31	28
0	1	58	58
0	2	52	56
0	3	31	32
0	4	40	38
0	5	91	98
0	6	93	100
0	7	72	76
0	8	63	58
0	9	28	25
0	10	55	54
0	11	105	110
0	12	33	33
0	13	129	131
0	14	127	129
0	15	3	5
0	16	5	1
0	17	29	29
0	18	56	55
0	19	39	37
0	20	25	24
0	21	15	14
0	22	27	26
0	23	7	8
0	24	13	13
0	25	59	63
0	26	31	33
0	27	64	67
1	0	5	5
1	1	2	2
1	2	1	2
1	3	4	1
1	4	0	1
1	5	6	5
1	6	28	28
1	7	89	93
1	8	52	52
1	9	15	14
1	10	26	25
1	11	9	7
1	12	14	13
1	13	17	17
1	14	11	10
1	15	20	19
1	16	23	22
1	17	12	11
1	18	13	12
1	19	18	19
1	20	44	42
1	21	44	44
1	22	2	5
1	23	3	1
1	24	14	14
1	25	6	7
2	0	180	286
2	2	42	46
2	4	49	50
2	6	11	3
2	8	53	54
2	10	28	22
2	12	11	5
2	14	83	80
2	16	4	2
2	18	43	40
2	20	72	73
2	22	12	13
		$H = 3$	
0	0	64	71
0	1	10	11
0	2	4	3
0	3	3	2
0	4	75	79
0	5	20	21
0	6	52	52
0	7	2	2
0	8	9	6
0	9	6	6
0	10	28	28
0	11	5	6
0	12	49	48
0	13	3	2
0	14	14	14
0	15	15	15
0	16	32	31
0	17	2	2
0	18	33	32
0	19	2	4
0	20	33	33
0	21	7	7
0	22	4	2
0	23	0	1
0	24	18	19
0	25	7	7
1	0	2	1
1	1	9	9

TABLE V—*cont.*

K	L	F_{obsd}	F_{calcd}	K	L	F_{obsd}	F_{calcd}	K	L	F_{obsd}	F_{calcd}
						$H = 4$		2	9	7	4
1	2	15	16	0	0	19	17	2	10	28	27
1	3	19	19	0	1	48	48	2	11	54	53
1	4	7	6	0	2	36	38	2	12	16	16
1	5	6	5	0	3	36	38	2	13	74	76
1	6	13	13	0	4	6	4	2	14	69	73
1	7	62	63	0	5	49	49	3	0	2	2
1	8	26	25	0	6	42	45	3	1	5	6
1	9	21	20	0	7	42	45	3	2	1	2
1	10	23	23	0	8	42	41	3	3	1	0
1	11	4	2	0	9	15	14	3	4	4	3
1	12	3	2	0	10	47	46				
1	13	29	29	0	11	74	76			$H = 5$	
1	14	19	18	0	12	32	31	0	0	6	5
1	15	11	10	0	13	95	93	0	1	15	16
1	16	14	14	0	14	84	83	0	2	3	0
1	17	24	22	0	15	2	1	0	3	8	8
1	18	21	20	0	16	10	7	0	4	7	7
1	19	10	11	0	17	23	21	0	5	11	11
1	20	35	33	0	18	49	46	0	6	12	12
1	21	34	33	0	19	27	27	0	7	47	47
1	22	13	15	0	20	26	26	0	8	32	31
1	23	10	11	0	21	12	11	0	9	23	23
2	0	10	8	1	0	38	41	0	10	27	26
2	1	4	3	1	1	2	1	0	11	7	6
2	2	11	13	1	2	13	11	0	12	7	7
2	3	12	11	1	3	7	7	0	13	18	20
2	4	3	3	1	4	45	47	0	14	11	11
2	5	4	4	1	5	7	7	0	15	4	1
2	6	17	17	1	6	50	49	0	16	9	9
2	7	60	61	1	7	0	3	1	0	3	1
2	6	21	20	1	8	0	6	1	1	7	5
2	9	8	8	1	9	0	1	1	2	0	0
2	10	8	7	1	10	11	11	1	3	8	6
2	11	5	6	1	11	1	0	1	4	3	1
2	12	3	1	1	12	25	25	1	5	3	1
2	13	21	21	1	13	4	3	1	6	13	14
2	14	11	12	1	14	2	2	1	7	43	44
2	15	16	16	1	15	7	6	1	8	26	27
2	16	19	18	1	16	14	15	1	9	15	13
2	17	17	15	1	17	6	6	1	10	16	15
2	18	17	18	1	18	17	17	1	11	1	0
2	19	15	17	1	19	1	0	1	12	7	7
2	20	34	36	2	0	24	22				
3	0	37	40	2	1	43	42			$H = 6$	
3	2	9	8	2	2	17	18	0	0	119	143
3	4	44	44	2	3	26	24	0	1	2	0
3	6	42	40	2	4	2	5	0	2	36	36
3	8	6	3	2	5	31	29	0	3	2	1
3	10	15	14	2	6	40	42	0	4	40	38
3	12	23	24	2	7	35	37	0	5	2	0
3	14	2	4	2	8	23	21	0	6	15	11

TABLE VI

ALUMINUM-OXYGEN DISTANCES IN β-ALUMINA AND RELATED COMPOUNDS

	Number of bonds	Distances (Å)			
		Ag-β	Na-β [Felsche (11), (Kato (23)]	Na-β [Peters *et al.* (12)]	$CaAl_{12}O_{19}$ (23)
Octahedra					
Al(1)-O(1)	2	2.017	2.026	2.022	1.995
O(2)	2	1.839	1.841	1.837	1.818
O(3)	1	1.973	1.947	1.970	1.970
O(4)	1	1.821	1.818	1.819	1.860
Al(4)-O(1)	6	1.893	1.885	1.895	1.833
Tetrahedra					
Al(2)-O(1)	3	1.806	1.798	1.801	1.801
Al(2)-O(3)	1	1.800	1.777	1.809	1.828
Al(3)-O(2)	3	1.762	1.758	1.768	
Al(3)-O(5)	1	1.675	1.685	1.677	

are given in Table V and the agreement is generally satisfactory. The only discrepancy beyond a reasonable estimate of the error is (22.0) which is observed too weak because of extinction. A small improvement in the intensity agreement could probably be achieved by correcting the intensities for extinction.

The atomic arrangement within the spinel block differs only slightly from that reported originally by Bragg *et al.* The spinel block consists of a distorted cubic close-packed arrangement of oxygens with Al(1), Al(4) atoms occupying octahedral interstices and Al(2), Al(3) atoms occupying tetrahedral interstices. The principal interatomic distances and angles are given in Tables VI, VII. It is instructive to compare these distances and angles with those of sodium beta-alumina and $CaAl_{12}O_{19}$. Calcium aluminate crystallizes in the related magnetoplumbite structure in which the $[AgO]^-$ layer is replaced by a $[CaAlO_3]^-$ layer. The mirror plane in $CaAl_{12}O_{19}$ is essentially a dense close-packed layer of three oxygens and one calcium. The structure is completely ordered and exhibits none of the conducting properties of beta-alumina.

It is to be noted that the distortions from ideal octahedral and tetrahedral coordination in the spinel portion of the structure are remarkably similar in the different compounds despite extensive changes in the composition and structure in the mirror plane. The distortions of the aluminum coordination polyhedra are probably the result of the small size and large positive charge of the Al^{+3} ions in tetrahedral coordination. This may be seen by comparing the interatomic distances with those in the normal spinel, $MgAl_2O_4$. The metal-oxygen distances in spinel, calculated from the parameters given by Willis (*24*), are nearly the same for the two sites: 1.924 Å for the aluminum atoms which are in octahedral coordination and 1.919 Å for the magnesium atoms which are in tetrahedral coordination. The average Al-O distance for octahedrally coordinated aluminum in silver beta-alumina is 1.912 Å, approximately the same as it is in spinel. On the other hand, the average Al-O distance in the tetrahedral sites of silver beta-alumina is 1.760 Å,

TABLE VII

ALUMINUM-OXYGEN BOND ANGLES IN Ag-β AND RELATED COMPOUNDS

	Angles in degrees		
	Ag-β	Na-β (11, 23)	$CaAl_{12}O_{19}$ (23)
Octahedra			
O(1)-Al(1)-O(2)	90.70	90.45	90.93
O(1)-Al(1)-O(3)	89.19	88.55	89.28
O(1)-Al(1)-O(4)	84.04	84.18	85.13
O(2)-Al(1)-O(3)	86.09	86.41	86.52
O(1)-Al(1)-O(2′)	96.86	97.55	96.94
O(1)-Al(4)-O(1′)	92.06	91.41	93.22
O(1)-Al(4)-O(1″)	92.06	91.41	93.22
Tetrahedra			
O(1)-Al(2)-O(1′)	110.37	110.93	111.58
O(1)-Al(2)-O(3)	108.56	107.97	107.23
O(2)-Al(3)-O(2′)	107.55	107.03	
O(2)-Al(3)-O(5)	111.33	111.82	

much shorter than the corresponding Mg–O distance in spinel.

The principal amplitudes of thermal vibration are given in Table VIII. The vibrations of Al(1), Al(2), Al(3), Al(4) and O(1), O(2), O(3), O(4) are small and nearly isotropic. (The negative values in Table IV for β_{33} of Al(2) and Al(4) are less than the estimated errors, and only their magnitudes were used in the calculation.) No significance is attributed to the small differences in the thermal vibrations of the atoms in the spinel block, but they clearly are differentiated as a group from the extraordinarily large anisotropic vibrations of atoms in the mirror plane.

Structure in the Mirror Plane

There are three striking features of the structure in the mirror plane: the partial occupation of (b) and (d) sites, the displacement of Ag(1) from the 3-fold axis, and the bulges in electron density about the (d) site (Fig. 4). The structure in these planes is highly disordered and, in fact, is approaching a semiliquid state. There are several types of disorder that are involved: (1) disorder due to partial occupation of sites, (2) two-dimensional disorder due to the displacements of atoms from a single set of regular positions, and (3) thermal disorder due to the large anisotropic vibrations of the highly mobile silver ions. Observations at different temperatures would be necessary to separate the contributions of the different types of disorder but, it is believed, the present analysis shows that all are significant and must be taken into consideration.

The electron density sections of Figs. 4 and 5 give an overall picture of the disorder. The total concentration of silver in the mirror plane was estimated from the fourier maps by summing the electron density in trapezodial section defined by the points $0, 0, 1/4; \overline{1/3}, 1/3, 1/4; \overline{1/2}, 0, 1/4; \overline{1/3}, \overline{1/6}, 1/4$ and normalizing with respect to similar summations for aluminum atoms in the spinel block. The ratio of the number of electrons attributed to Ag(1) + Ag(2) + Ag(3) to Al was 4.58. Taking the number of electrons per silver and aluminum as 47 and 13, respectively, the concentration of silver in the plane is $4.58 \times (13/47) = 1.27$, or 2.54 Ag per cell, in agreement with the value 2.55 found from the multiplicity factors.

The allocation of silver to the different sites in the mirror plane is more difficult. The parameters in Table IV give 43 % for the probability that a particular (b) site is occupied by a silver atom. The interpretation of the multiplicity parameters for the remaining silver is less clear. If the total amount of silver associated with Ag(1) and Ag(3) is attributed to (d) sites, there is an 84 % chance each (d) site is occupied. If, on the other hand, the silver in the bridge is not included, the occupation probability is reduced to 67 %. In either case, the total probability is greater than unity and there must be silver-rich regions in the plane. The following discussion is based on the assumption the excess silver exists in the form of small two-dimensional clusters. An alternative description, in which the excess silver is concentrated in domain walls, will be given in a later section.

Clusters of Ag(1)–Ag(1′) or Ag(2)–Ag(2′) are unlikely because the distance between them, 0.72 and 0.42 Å, is small compared to 2.8 Å which is the separation expected for nonbonded silver atoms. The most probable type of cluster would be Ag(1)–Ag(2) pairs which are separated by 2.574 to 3.220 Å. Trigonal symmetry requires there be random orientations of the pairs among the equivalent sites.

The unequal occupation densities and displacements of silver in (b) and (d) sites are due to their different crystallographic environment. If a particular (b) site is occupied by silver, the neighboring (d) sites will tend to be unoccupied and the silver will be coordinated to two O(4) and three O(5) atoms in a pentagonal bipyramid. The Ag(2)–O(5) separations are extremely large, two at 3.117 Å and one at 3.470 Å, but there are two short bonds to O(4) at 2.424 Å. Short Ag–O bonds have been observed in various other compounds of silver and is attributed to covalency effects (*25*). Conversely, if a particular (d) site is occupied, the adjacent (b) sites will tend to be vacant and the silver is octahedrally coordinated to six O(2) atoms. If the silver were in the center of the octahedron, the closest approach to oxygen would be 2.809 Å. This distance is large compared to 2.66 Å expected for octahedrally coordinated silver and Ag(1) is displaced from the center to form four shorter bonds with O(2) at 2.720 Å and two longer bonds at 3.064 Å.

The displacements may also reflect dynamic effects associated with the diffusion of silver. The large amplitudes of vibration along the Ag(1)–Ag(2) bond, and the excess electron density within the bond, suggest the vibrations may be anharmonic and the Ag(1) atom spends appreciable time in the region between occupied Ag(1) and vacant Ag(2) sites. This is consistent with the spikes in the electron density which lie along the lowest energy path silver atoms could take in moving between the close-packed oxygen layers. A diffusive "jump" takes place when the amplitude of vibration is sufficient for the silver to surmount the potential barrier at the saddle point between oxygens.

The most recent refinement of the structure of sodium beta-alumina also found the cations smeared out in a complex pattern in the mirror plane (*12*). The sodium and silver atoms are found among the same sites but the distribution is different. Approximately 0.75 Na were found near the (d) sites, which may be compared with 0.67 Ag(1) found near the same sites in this study. The remaining Na was found at the Ag(3) "bridge" position, and none was found near the (b) or Ag(2) site.

Since the source of beta-alumina was not the same in the two investigations, it is of course possible that the original structures were different. It is more likely the difference arises from the different electronic structure of Na^{+1} and Ag^{+1} ions. Silver is a highly polarizable ion and is probably stabilized in (b) sites by the strong covalent bonds it forms with O(4) atoms above and below the mirror plane.

Charge Compensation

The principal mechanisms for neutralization of the positive charge due to excess silver are aluminum vacancies, Al^{+2} and foreign M^{+2} ions, or interstitial oxygen. Aluminum^{+2} can be eliminated on energetic grounds and foreign divalent ions in sufficient concentration were not observed by X-ray emission or spectrographic analysis. Whittingham and Huggins (*26*) have suggested that electrical neutrality is probably achieved by aluminum ion vacancies in the spinel block. Because of the structural disorder, only limited conclusions about the compensation mechanism can be drawn. The present analysis did not show aluminum vacancies but suggested that compensation is achieved by the incorporation of extra oxygen in the conduction plane.

Two sets of experimental results bear on the question of compensation. First the unit cell volumes and and crystal densities of silver beta- and sodium beta-alumina are better satisfied by the formula $M_{2.40}Al_{22}O_{34.20}$ than $M_{2.40}Al_{21.83}O_{34}$ (Fig. 2). Second, the total aluminum calculated from the site occupation parameters is 22.04 atoms of aluminum per unit cell, compared to 22.00 if all sites are occupied, or 21.83 if the excess monovalent cation is compensated by Al^{+3} vacancies. Neither of these results is considered to be beyond the experimental uncertainty. There is a comparable uncertainty in the fourier maps, because the background fluctuations in electron density corresponded to about 0.1 oxygen and excess oxygen in the plane, if present, can not be resolved.

Domain Model for Nonstoichiometry

The absence of evidence for disorder in the X-ray photographs, and the statistical distribution of silver atoms among the (b) and (d) sites can be explained by Ag(1)–Ag(2) pairs randomly distributed in the plane. An alternative interpretation of the silver disorder will now be suggested.

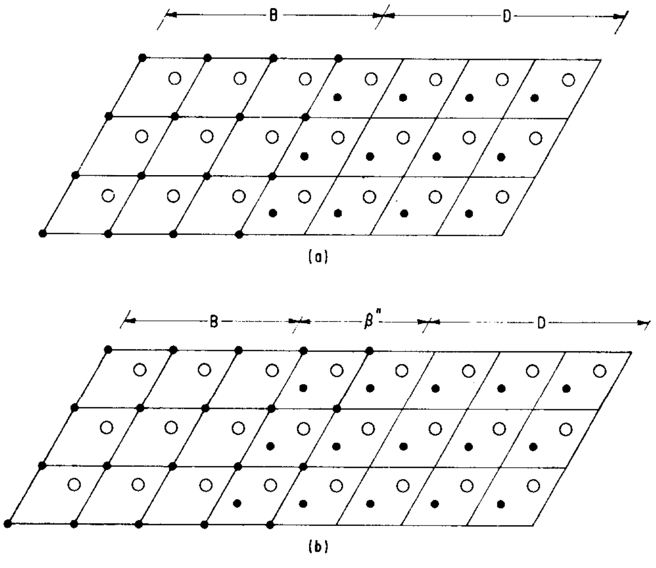

FIG. 6. Domain structures in beta-alumina. The open circles are oxygens and silver atoms occupy (0, 0) sites in the B domain and (2/3, 1/3) sites in the D domain. (a) The wall shown contains 1.5 Ag atoms per spinel block. (b) The wall contains 2 Ag per spinel block arranged as in the β″ beta-alumina structure.

The model is based on two primary assumptions: first, that the silver atoms are distributed in domains, each of which has the stoichiometric composition, $AgAl_{11}O_{17}$, and second, that nonstoichiometry arises from the transition region between domains. Two ways in which this might occur are shown in Fig. 6a, b which represents sections through the mirror plane of beta-alumina. The domains co-exist in what may appear to be a single crystal, but actually is a syntactic intergrowth of phases which have the same composition though slightly different structure. The only difference in structure is the distribution of silver atoms. The structure formed when the silver atoms occupy (b) sites will be called a B domain; similarly, D domains are formed when silver atoms occupy (d) sites in the mirror plane. The remainder of the atoms are assumed to occupy identical positions in both structures. (The B and D domains are the structures Beevers and Ross considered when they decided the sodium atoms in beta-alumina occupied the (d) sites.) If the atomic arrangement in the mirror plane does not repeat periodically in a direction perpendicular to the plane, the imperfection in effect is a stacking fault.

Figure 6a shows an abrupt transition or "domain wall" between B and D domains. The transition region is one unit cell thick and the concentration of silver in the wall is 1.5 times that in the B or D domains. Figure 6b illustrates a thicker wall which contains two silver atoms. The structure in the wall is identical with the atomic arrangement of β'' beta-alumina (*14*) and $Na_2O\cdot MgO\cdot 5Al_2O_3$ (*15*). Domain walls of different thickness would account for the variable stoichiometry observed in beta-alumina. There probably would be small displacements of the atoms in the wall relative to those in the domains. These are not shown in order to simplify the description but they would account, in this model, for the distorted electron density about Ag(1) and O(5). Substructures are frequently seen in grossly nonstoichiometric solids and beta-alumina may be another example of the growing list of extended defect solids (*2*).

The possibility of observing the postulated domains depends on their size and whether they are three-dimensionally periodic. Large domains (>100 Å) diffract independently and the intensities will be proportional to $x_B F_B^2 + (1 - x_B) F_D^2$, where x_B is the fraction of B domains, and F_B, F_D are the structure factors of the B and D structures. It may be shown that $F_B = F_D$ when $h - k = 3n$, $F_B \neq F_D$ when $h - k = 3n \pm 1$ and, consequently, the structures can be differentiated, in principle, by X-ray diffraction and diffraction contrast electron microscopy. The difference in structure factor will be very small since the structures differ only in the positions of a few atoms. As the size of the domains decreases, the $F_B \cdot F_D$ cross terms will become increasingly important and, in the limit, the intensities will be given by the statistical model used in this paper. If the average size of the B and D domains are the same, and if the domain wall is of the type illustrated in Figure 6a, the 25% excess M^{+1} found in beta-alumina would be accounted for by domains only 5–10 Å wide. Larger domains would be formed if the walls were thicker and contained more silver.

The proposed model for extended defects or domains is equally appropriate for the other isomorphs, including sodium beta-alumina. The variable stoichiometries and different structures that have been found are easily understood because, according to this model, the defect structure will depend on the thermal history of the specimen, and, in particular, on the quenching or cooling rate. It should also be noted that since the substitution of M^{+1} ions (Na by Ag in the present study) only requires equivalence of the average structures of the two compounds, the distribution of cations among the sites need not be the same.

Transport Properties

The conductivity of silver beta-alumina is due to silver ions moving in the mirror planes and the electron transference number is less than 10^{-6} at temperatures below 500°C (*26*). The electron density in the mirror plane (Figs. 4 and 5) shows that the conduction mechanism is probably interchange of silver ions between occupied and vacant (b) and (d) sites. The diffusing silver atoms follow zig-zag paths along the valleys between oxygen atoms in the layers above and below the conducting plane.

The large silver mobility is associated with extreme disorder and the structure in the plane is approximately that of a two-dimensional liquid. The cation sites are only partially occupied and each potentially mobile cation has several vacant sites into which it can move; the atoms in the plane are vibrating with exceptionally large anisotropic amplitudes of motion and their centers are displaced from positions of high symmetry on the 3-fold axes. It is instructive to consider the liquid-like nature of the structure in the conducting plane in relation to the Lindemann law of melting (*27*). Lindemann assumed that a solid melts when the mean square amplitude of vibration of atoms about their equilibrium positions becomes larger than a certain fraction of the atomic spacing. The value of this constant has been found to be near

0.1 for a large number of metals (*25*). If a similar relation applied to silver in beta-alumina, the mean-square amplitude of vibration would be

$$\begin{aligned}[\langle u^2\rangle]^{1/2} &= 0.1\ \mathrm{D}_{\mathrm{Ag(1)-Ag(2)}}\\ &= 0.32\ \text{Å}\end{aligned}$$

Table VIII shows that the average amplitude of vibration of silver atoms in the plane at room temperature is 0.28 Å, about that calculated from the Lindemann formula. The concept that beta-alumina behaves in some respects like a two-dimensional liquid conductor is also supported by calculations made in the framework of a new theory of super ionic conduction (*1*).

It was previously noted that the electron density in the bond between Ag(1) and Ag(2) might be due to positional disorder or hopping. A simple calculation indicates the density is probably due to defect clusters or domain walls. The fraction of silver ions in the conducting state at room temperature is approximately

$$\exp(-E/RT) = 1.2 \times 10^{-3},$$

where $E = 4050$ cal mole^{-1} is the activation energy for tracer diffusion. The observed electron density in the bridge is about 13% that in (b) and (d) sites, which is a factor of 10^2 larger than that calculated for hopping.

TABLE VIII

COMPONENTS OF PRINCIPAL AMPLITUDES OF THERMAL VIBRATION OF ATOMS IN SILVER BETA-ALUMINA[a]

Atoms in the spinel block	$(\bar{U}_{11}^2)^{1/2}$ (Å)	$(\bar{U}_{22}^2)^{1/2}$ (Å)	$(\bar{U}_{33}^2)^{1/2}$ (Å)	$(\bar{U}_{\mathrm{av}}^2)^{1/2}$ (Å)
Al(1)	0.077	0.072	0.077	0.080
Al(2)	.044	.044	.024	.041
Al(3)	.081	.081	.014	.072
Al(4)	.063	.063	.025	.057
O(1)	.061	.102	.040	.050
O(2)	.032	.035	.084	.056
O(3)	.028	.028	.048	.040
O(4)	.041	.041	.056	.048
Atoms in the mirror plane				
Ag(1)	.250	.332	.134	.287
Ag(2)	.249	.383	.092	.262
Ag(3)	.128	.224	.062	.265
O(5)	.187	.243	.075	.193

[a] $\bar{U}_{11}$, $\bar{U}_{22}$, $\bar{U}_{33}$ are the root-mean square displacements of vibration parallel to a^*, b^*, and c^*.

The tracer diffusion measurements of Yao and Kummer (*16*) and conductivity data of Whittingham and Huggins (*26*) obey the Nernst–Einstein equation with a correlation factor $D(\sigma)/D(\mathrm{t}) = 1.64$. Whittingham and Huggins show the correlation factor can be interpreted by an interstitialcy mechanism in which all silver ions are completely free. The silver ions on normal lattice sites are Ag(1) and the interstitial ions are Ag(2). Correlation factors calculated for interstitial silvers in clusters or in domains will probably be similar if the domains are sufficiently small, since in both cases the mechanism of ion motion is interchange of silver between occupied and vacant (b) and (d) sites. However, differences are expected if the domains are large and the conductivity may then become sensitive to the presence of structural defects and crystal imperfections.

Whittingham and Huggins attempted to measure the oxygen partial pressure dependence of the total conductivity and concluded that the dominant conduction process was essentially independent of oxygen partial pressure from that of air to about 10^{-24} atmospheres at temperatures from 600 to 800°C. They suggest the absence of an oxygen effect might be explained if the compensation mechanism for the excess monovalent ions involved aluminum vacancies which were frozen into the structure at high temperature when the samples are crystallized. Compensation by oxygen interstitials was considered less likely since they are expected to diffuse rapidly at 800°C.

The evidence in this paper slightly favors oxygen interstitials in the conducting plane. The choice between the vacancy and interstitial compensation mechanisms might be possible if the sensitivity of the X-ray analysis were improved to 0.2 $E/\text{Å}^3$. Further refinement of the present data was not considered justified, first, because of the slight possibility that the silver beta-alumina crystal might contain some OH, and second, it is believed that more detailed analysis requires the development of methods for dealing simultaneously with anharmonic vibrations and position disorder of atoms in the mirror plane.

Summary

The sodium in beta-alumina crystals has been isomorphously substituted by silver and the structure and stoichiometry investigated. The principal results of the study are:

1. Beta-alumina is a nonstoichiometric compound which contains approximately 25% more

sodium than the stoichiometric composition $NaAl_{11}O_{17}$.

2. All of the silver in silver beta-alumina is in the horizontal mirror planes of the crystal and there is negligible substitution of silver in the spinel blocks.

3. The spinel block portion of the structure is distorted and the interatomic distances and angles are nearly identical with those of sodium beta-alumina and $CaAl_{12}O_{19}$. The distortion is attributed to the small size and large positive charge of aluminum ions in tetrahedral sites.

4. The silver atoms are distributed statistically among the (b) and (d) sites in the horizontal mirror planes and an average of 84% of the (d) sites and 43% of the (b) sites were occupied by silver atoms.

5. The distribution of sodium and silver among the sites in the conducting plane of beta-alumina is not the same and the difference is attributed to covalent Ag–O bonding.

6. Some evidence was obtained to suggest that the excess positive charge is compensated by interstitial oxygen.

7. A domain model is proposed to explain the deviation from stoichiometry and the partial occupation of cation sites in the horizontal mirror planes.

8. The thermal motions of the atoms in the mirror planes are anomalously large and may involve anharmonic terms associated with the passage of silver ions over the activation barrier between (b) and (d) sites.

Note added in proof: The possibility ionic motion contributes to the electron density between (b) and (d) sites is supported by wide line NMR studies being carried out by D. Kline and H. S. Story at the State University of New York at Albany which shows the onset of strong motional narrowing of the sodium lines in beta alumina well below room temperature.

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