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Deuterium β-Alumina, $DAl_{11}O_{17}$: Atom Location and Structure Refinement by Powder Neutron Diffraction

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The crystal structure of anhydrous deuterium β-alumina at 4.5°K has been determined by powder neutron diffraction. The location of the deuterium atoms was revealed by Fourier methods associated with a profile analysis refinement routine; the data collection for this compound could only be performed by using powder neutron diffraction. The mirror plane sites normally occupied by metal ions in other β-aluminas are empty and the deuterium is bonded to the spacer oxygen in a hydroxyl linkage. This unusual β-alumina structure is a new (deutero) oxyhydroxide of aluminum. The deuterium occupation of about unity and the observation of moisture evolution during preparation indicates that deuterium β-alumina is likely to be stoichiometric $DAl_{11}O_{17}$, in contrast to the sodium and silver precursors. The atomic arrangement in deuterium β-alumina gives rise to a c-axis expansion compared with sodium and silver β-aluminas. This is directly reflected in a microstructural sense at low temperature in an abnormally long bond from Al(3) to the spacer oxygen, a consequence of the presence of the O(5)–D bond. There is a slight contraction of the c-axis on heating to 550°C. The diffraction analysis at this temperature does not permit an unequivocal location of the deuterium atoms, but is suggestive of considerable delocalization away from the position occupied at 4.5°K. This conclusion is strongly supported by the Al(3)–O(5) bond length which is contracted by 0.08 Å relative to that at 4°K and is in the "normal" range as found in the alkali metal β-aluminas. The still-expanded c-axis relative to sodium and silver β-aluminas suggests that the primary cause of the expansion observed in deuterium β-alumina may be the absence of cations on fixed sites in the mirror plane shielding oxygen–oxygen repulsions. The deuterium delocalization at high temperature implies the possibility of high-temperature proton conduction, with breaking of hydroxyl bonds, in framework oxyhydroxides.

Introduction

We recently reported (*1*) brief details of the structure of deuterium β-alumina at 4.5 and 828°K. The refinement of the data at 4.5°K has now been completed and is reported here. The structure at 823°K appears to be more complicated than previously indicated but is discussed from the point of view of the best refinement possible with the present data set.

Sodium β-alumina is claimed to have an ideal composition $NaAl_{11}O_{17}$, although the sodium-to-aluminum ratio found in real samples is invariably higher by, typically, 25%. The extra oxygen required to charge-compensate the extra sodium is found (*2*) in the mirror planes at the midoxygen position

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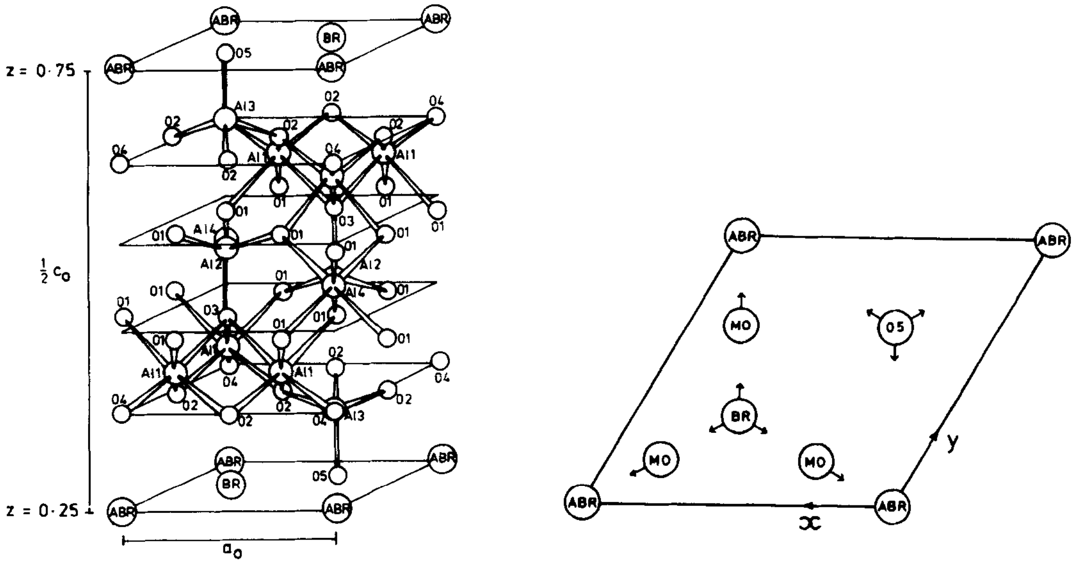
(Fig. 1) and is coordinated by interstitial aluminum displaced from Al(1) positions in the spinel blocks. Silver is readily completely exchanged for sodium by immersion in molten silver nitrate. The *c*-axis lattice spacings of sodium and silver β-alumina single crystals have been reported (*3*, *4*) to be 22.53 and 22.488 Å, respectively.

Replacement of sodium or silver by hydrogen or hydroxonium ions was reported by Saalfeld *et al.* (*5*), Nishikawa *et al.* (*6*), and Kummer (*7*). Saalfeld *et al.* exposed sodium β-alumina to hot concentrated sulfuric acid to give hydroxonium β-alumina, ideally $(H_3O)Al_{11}O_{17}$. One molecule of water was lost, reversibly, by 300°C to give, apparently, $HAl_{11}O_{17}$. A second molecule of water, marking irreversible decomposition of $HAl_{11}O_{17}$ to Al_2O_3, was not lost until 700°C, a high decomposition temperature for an oxyhydroxide. A more recent study of the production of hydroxonium β-alumina from the sulfuric acid route, and the thermogravimetric characterization of the products has been given (*8*, *9*).

Kummer (*7*) treated silver β-alumina with hydrogen gas at 300°C to give hydrogen β-alumina directly. Silver metal plated out on to the crystallite surfaces. The oxygen atom of H_3O^+ in hydroxonium β-alumina has



(a) (b)

FIG. 1. A schematic diagram of the β-alumina structure. (a) One-half of a unit cell is shown. Four close-packed layers of oxygen atoms lie between two mirror plane layers at $z = 0.25$ and $z = 0.75$. The oxygen atom density in the mirror planes is only one-quarter of that within the spinel blocks. The interior aluminum atoms, Al(4) and Al(2) are, respectively, octahedrally and tetrahedrally coordinated by oxygen. Octahedral Al(1) and tetrahedral Al(3) are coordinated by oxygen atoms which border the mirror plane (O(2) and O(4) to Al(1) and O(2) to Al(3)). The coordination of Al(3) is completed by the oxygen atom, O(5), located in the mirror plane. The Beevers–Ross (BR) and anti-Beevers–Ross (ABR) positions in the mirror planes are shown. (b) The conducting plane with the mid-oxygen (MO) positions also shown. The ideal BR, ABR, and O(5) positions are the 2*d*, 2*b*, and 2*c* sites in space group $P6_3/mmc$. Small displacements to 6*h* positions $(x, 2x, \frac{1}{4})$ are generally found and the directions of these displacements are indicated. The ideal MO position is the 6*h* site $(\frac{5}{6}, \frac{2}{3}, \frac{1}{4})$ but displacements (indicated) are again generally observed. The ideal BR and MO sites are in trigonal prismatic coordination by oxygen, whereas the ABR site has two closer O(4) neighbors. All these positions are to a greater or lesser extent occupied by metal ions in the metal β-aluminas, with silver in particular preferring the ABR location.

been found (*10*) to lie close to the Beevers–Ross site in $1.79H_2O:11Al_2O_3$; the *c*-axis lattice spacing was 22.702 Å, higher than for sodium or silver β-aluminas, in agreement with the larger size of H_3O^+. The hydrogen atom location is not known in either the H_3O^+ or H^+ compounds. Surprisingly, however, the lattice constant of hydrogen β-alumina was reported (*7*) to be 22.677 Å, also larger than for the sodium and silver compounds, in spite of the small effective size of a proton.

The present study was directed at the structure of deuterium β-alumina and, particularly, the deuterium location. The structure has been studied both at low temperature and at 550°C, reasonably close to the decomposition temperature. A polycrystalline sample was used to ensure that the ion exchange could be carried out, and the sample then maintained, under rigidly anhydrous conditions. Deuterium was used because of its favorable properties relative to hydrogen for neutron diffraction work, particularly the absence of the very high background resulting from the large incoherent scattering cross section of hydrogen. This is the first part of a study of hydrogen-containing β-aluminas by powder and single-crystal diffraction.

Experimental

The starting material was a high-soda ceramic of composition $1.45\,Na_2O:11Al_2O_3$[1] prepared by reacting sodium carbonate and aluminum oxide (both Analar). The initial sodium-to-aluminum ratio corresponded to the eutectic composition (37 wt% Na_2CO_3). After initial firing of the powder at 1100°C in a platinum crucible, the mixture was pelletized and fired at 1600–1700°C in a graphite crucible under vacuum using inductive heating. The product contained sodium aluminate in addition to β-alumina, indicating maintenance of excess soda during the reaction firing. A final firing at 1590°C for 1 min followed by leaching for 1 hr in dilute hydrochloric acid and drying at 400°C yielded pure β-alumina with no reflections of Al_2O_3, β″-alumina, or $NaAlO_2$ observable on an X-ray diffractometer trace (CuKα, graphite monochromator) with all the strong reflections run well off-scale. Silver exchange was performed twice in molten silver nitrate, followed by drying at 200°C. Neutron diffraction patterns were taken of the sodium β-alumina at 10°K and the silver β-alumina at 10°K and room temperature. Refinements of these data will be reported elsewhere.

Conversion to deuterium β-alumina was achieved by equilibration of the silver β-alumina with deuterium gas in a vacuum line of known volume at 450°C. The reaction tube was silica and the line was evacuated for several hours at temperature before admitting the deuterium. The reaction was monitored by observing the pressure change at fixed volume and temperature. After completion the deuterium was pumped off, the silica tube sealed under vacuum and opened in a nitrogen-filled drybox, and the deuterium β-alumina (coloured brown by the surface deposit of silver) transferred to a vanadium neutron diffraction sample can and sealed in with a gold wire O-ring. Although the sample had been thoroughly dried prior to the deuteration a certain amount of moisture evolution was observed after the D_2 gas was admitted. We interpret this as marking the loss of interstitial oxygen in a transformation to stoichiometric β-alumina, $DAl_{11}O_{17}$.

Neutron diffraction was performed on the PANDA diffractometer in PLUTO reactor, Harwell, using 1.512 Å neutrons

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[1] This composition is considerably higher in soda than the single crystals ($\sim 1.26Na_2O:11Al_2O_3$) used for previous structural investigations (*2*). We are grateful to A. Morton, Environmental and Medical Sciences Division, Harwell, for determining the sodium-to-aluminum ratio by atomic absorption analysis. The composition was confirmed by the weight change on conversion to silver β-alumina.

(germanium (331) monochromator, 70° take-off angle). A first pattern was taken at 4.5°K in an Oxford Instruments variable-temperature cryostat and the sample then transferred to a tantalum-heated vacuum furnace for a second experiment at 550°C. No changes were made to the instrumental parameters between the runs so that good significance can be placed on differences in the lattice parameters determined from the profile refinements. In agreement with this expectation the 2θ zero error, also determined as a variable from the profile refinement, was the same for the two experiments to within 0.01°.

A modified version of the Rietveld (*11*) profile analysis routine in which the output data could be converted to structure factors for Fourier and difference Fourier synthesis[2] was used for data refinement. The scattering density at regular points in the unit cell could be stored on file and plotted by the Calcomp General Purpose Contouring Package.

The least-squares refinement is based on the weighted counts at each point; a weighted profile R index ($\mathrm{w}R_{\mathrm{pr}}$) is minimized. An unweighted R_{pr} is given also, and after each refinement the observed and calculated profiles are deconvoluted into individual peak intensities using the half-width parameters determined; an R_{I} index is then calculated.

Results: 4.5°K Data

The space group is $P6_3/mmc$, $Z = 2$; the scattering lengths used were 6.67, 3.45, and 5.83 for deuterium, aluminum, and oxygen, respectively (all $\times 10^{-15}$ m).

Refinement of the 4.5°K data was first tried with the deuterium atom distributed among the Beevers–Ross (BR) and anti-Beevers–Ross (ABR) sites (Fig. 1). The data below 34.2° 2θ (involving the first 10 reflections) were excluded from the refinement because of the deviation of the peak shapes from symmetrical Gaussians. Also excluded were the regions (5° total) containing the six silver metal reflections occurring in the region scanned (up to 107° 2θ). These were clearly seen in an initial difference profile calculated using only the aluminum and oxygen atoms to generate the calculated profile. One hundred sixty-one intensities contributed to the remaining profile. The agreement could not be improved beyond $R_{\mathrm{I}} = 0.091$, weighted profile $\mathrm{w}R_{\mathrm{pr}} = 0.104$.

A total Fourier synthesis of the calculated structure factors and phases for a mirror plane section revealed scattering density in three equivalent extended locations around the spacer oxygen atom, O(5), and about 1 Å distant from it, and little at all near the BR and ABR positions. The Fourier synthesis revealed the deuterium location in spite of the incorrect model used. The β-alumina lattice provides a favorable situation for Fourier methods with powder diffraction because of the heavy phase weighting by the spinel block atoms of known position. In retrospect, we might have started with a difference Fourier map based on the aluminum and oxygen atoms only. The deuterium location is clearly revealed in such a plot (Fig. 2), although it is necessary to constrain the spacer oxygen to lie on the $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ site in the initial cycles of refinement for if the displacement which actually occurs is allowed without fixing O(5), the oxygen will move off its own site toward the deuterium site in an attempt to compensate for these absent atoms.

Clearly, therefore, the deuterium atom in deuterium β-alumina at low temperature was not structurally analogous to the alkali or silver atoms in the metal β-aluminas but was bound to the spacer oxygen in a hydroxyl linkage. Subsequent refinement confirmed this model. Until the final structural details were clear, the occupation number and

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[2] The Fourier routine utilizes the FORDAP program originally written by A. Zalkin and includes modifications made up to 1969.

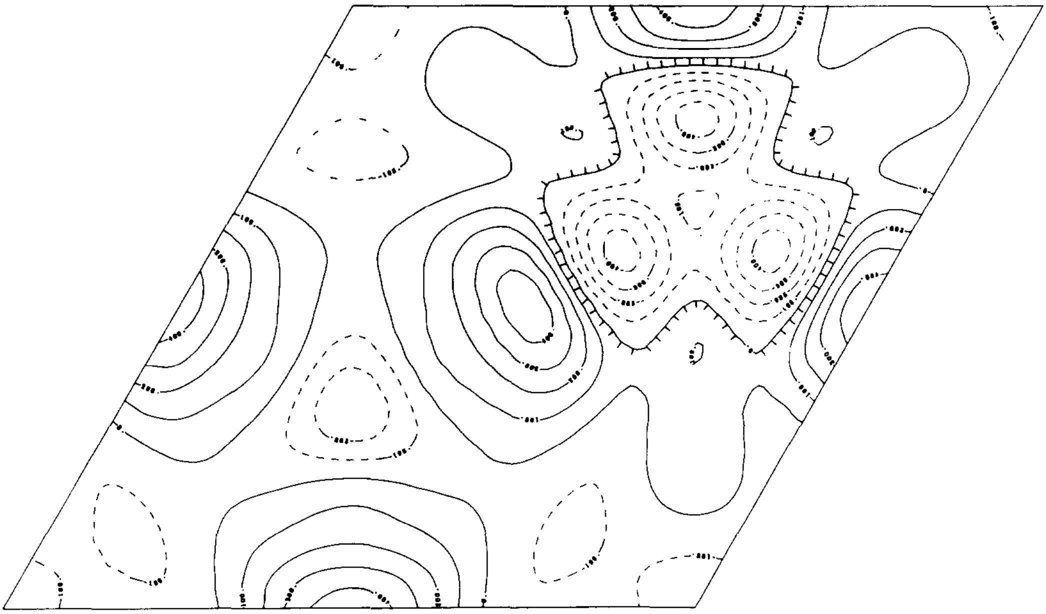

FIG. 2. Difference Fourier map in the mirror plane for $DAl_{11}O_{17}$ at 4.5°K with deuterium excluded from the refinement. Positive density indicating the presence of deuterium is found in locations with threefold symmetry around the O(5) position (constrained on $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$). The axes and origin are as for Fig. 1b.

temperature factor of the deuterium atom were both treated as variables. With the general deuterium location determined, other points to be settled were the exact nature of the deuterium and spacer oxygen sites, the possibility of refinement with anisotropic temperature factors, and any other occupation in the mirror plane. The lattice parameters determined in the refinement were $a = 5.6062(5)$ and $c = 22.6192(8)$ Å, the latter value confirming the expansion relative to sodium β-alumina observed (7) in the previous work.

The sausage-like nuclear density observed at the deuterium positions in the Fourier map (Fig. 3) indicated the possibility that the deuterium was not sited exactly on threefold $(x, 2x, \frac{1}{4})$ $6h$ positions, but rather on $12j$ $(x, y, \frac{1}{4})$ positions with mirror symmetry across the $6h$ sites. The least-squares refinement did not permit an unequivocal decision between these two possibilities, and although we have chosen $12j$ positions for D and O(5) as the basis for the structure discussion, as detailed below, the very small differences between the various possibilities are not significant to the general structural conclusions.

With the deuterium and O(5) in $6h$ positions, O(5) was found at $x = 0.2995(27)$ and D at $x = 0.4647(22)$. The temperature factor and occupation number for deuterium were 3.71(84) Å^2 and 1.09(8), respectively, and the R factors were $R_I = 0.0407$, $R_{pr} = 0.0997$, and $wR_{pr} = 0.0735$, respectively (the expected wR_{pr} determined from counting statistics was 0.114). The nearest D–O distance was 1.15 Å.

With the deuterium only allowed to shift to a $12j$ position, the deuterium temperature factor decreased slightly to 3.18(97) Å^2, but the occupation was very similar (1.08(8)). The oxygen position and the agreement factors were identical to the previous results. The D–O distance was 1.13 Å. However, when O(5) was also allowed to shift to a $12j$

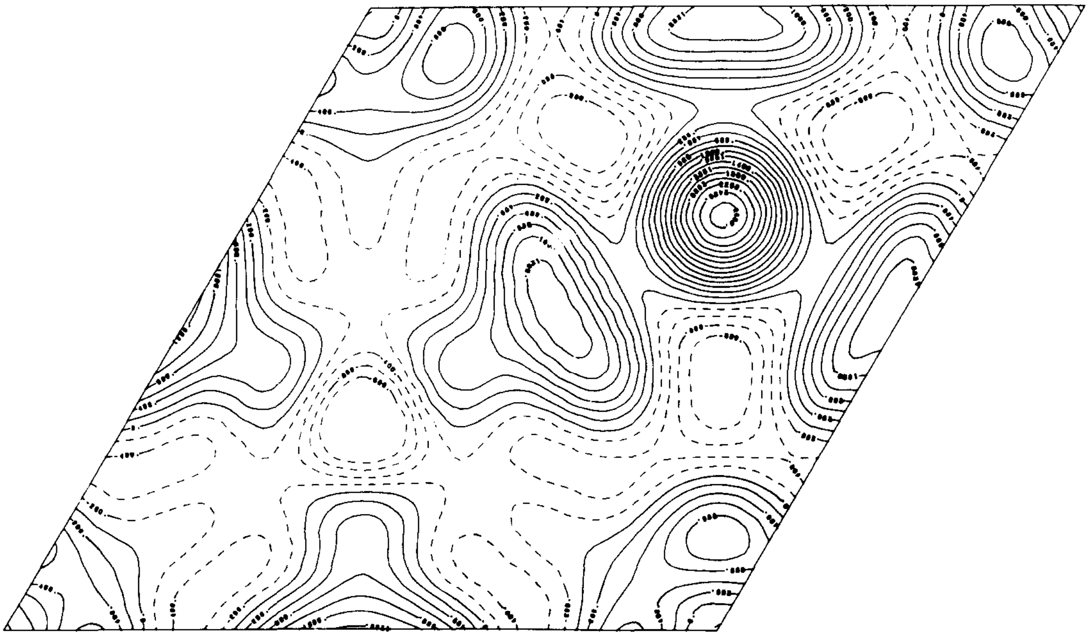

FIG. 3. Total Fourier map in the mirror plane for $DAl_{11}O_{17}$ at 4.5°K after the best refinement (Tables I and II). The axes and origin are as for Fig. 1b. The maximum at $(\frac{1}{3}, \frac{2}{3})$ is O(5), and the sausage-like locations of scattering due to the deuterium are clearly evident.

position, the agreement improved to give R values of 0.0338, 0.0974, and 0.0721. The deuterium temperature factor dropped further to 1.26(97) $Å^2$ and the occupation to 0.87(8), and the O(5) temperature factor was slightly negative (−0.91(59) $Å^2$). The D–O bond length was now 0.982(49) Å.

An infrared spectrum has not yet been taken of the sample, as it is still sealed in the vanadium can. However, O–H stretching frequencies have been observed (*12*) at 3546, 3520, and 3390 cm^{-1} for a single crystal of silver β-alumina subjected to prolonged exposure to hydrogen gas. No precautions were taken to exclude moisture from the sample after the hydrogenation, but the highest-frequency line in particular is the strongest before hydrogenation is quite complete and might be expected, therefore, to be least influenced by the effects of moisture absorption. From published curves of O–H stretching frequencies versus bond lengths (*13*) we see that this frequency (and indeed the other two) correspond to bond lengths of less than 1.0 Å. We take this as fairly strong support in favour of a D–O bond length of less than 1.0 Å, and thus of the $12j$ site symmetry for D and O(5), in spite of the negative temperature factor for O(5). The decreased temperature factor for deuterium also supports this model.

A refinement was attempted with the deuterium in the general $24l$ position of the space group to assess the possibility of displacement off the mirror plane. No significant improvement of the agreement was obtained and the z parameter (0.241(2)) was highly correlated with the temperature factor which became negative (−2.5(1.6) $Å^2$). The deuterium was constrained thereafter to lie in the mirror plane.

Attempts to continue the refinement using anisotropic temperature factors were largely unsuccessful, divergence usually being obtained even with a relaxation parameter of 0.05 for all variables (the relaxation parameter is the ratio of the shift given after a least squares cycle to the calculated shift). Only with O(5) at a 6*h* position could refinement be obtained, and the positional parameters were then very similar to those found for the isotropic refinements. The D–O bond length was 1.27 Å, rather longer than before because, although the O(5) atom was very close to the position found for the isotropic 6*h* position refinements, the deuterium was very close to the position found in isotropic refinements with O(5) at 12*j* (a shift of about 0.15 Å). This is perhaps some further evidence that the O(5) atom is better placed at a 12*j* position. The deuterium occupation was 0.85 (14), also very similar to the value obtained previously. The success with this particular refinement, and the values of the parameters obtained, makes it unlikely that any significant positional or occupational errors are concealed by the use of isotropic temperature factors. Several of the thermal ellipsoid parameters were smaller than their estimated standard deviations; basically, the number and quality of the present data set are not quite sufficient to allow meaningful refinement with anisotropic thermal parameters.

The best refinement with O(5) at a 12*j* position gave a deuterium occupation, as discussed above, of 0.87(0.08). This value, and indeed the range of values derived under various assumptions, indicated that the real occupation was probably unity and that the correct empirical formula for deuterium β-alumina was $DAl_{11}O_{17}$, in contrast to the composition of metal β-aluminas which are always metal rich and particularly to the immediate precursors in this work.[1] This conclusion is supported by the observed moisture evolution during the preparation, indicative of the reaction:

$$Ag_{1.45}Al_{11}O_{17.225}+0.725D_2\rightarrow DAl_{11}O_{17}+0.225D_2O+1.45Ag.$$

To test the sensitivity of the refinement to the deuterium occupation this was fixed at 0.87 (as previously found), 1.00, and 1.25, and refinements carried out with the other parameters varied as before. The weighted profile agreement indices were 0.0721, 0.0722, and 0.0733 for the three cases, respectively—a significant worsening for the highest occupation in accord with the hypothesis of a stoichiometric material. As expected, a slight increase in the deuterium temperature factor was observed (1.2(7) Å^2 to 2.5(7) Å^2) as the occupation changed from 0.87 to 1.00 (these parameters were 74% correlated in the original refinement); for an occupation of 1.25, the temperature factor had doubled again (4.6(7) Å^2). The intensity index, R_I, for the three cases increased from 0.034 to 0.036 to 0.040. Unfortunately, it is not straightforward to convert such data to a form suitable for applying statistical significance tests, because, on the one hand, the least-squares process minimizes the weighted profile index and, on the other, when regions of the diffraction pattern are excluded, as was the case here, the intensity index is affected by any reflections only partially included in the pattern. Suitable statistical tests for profile indices do not seem to have been derived yet.

One factor which could lower the apparent deuterium occupation is contamination by hydrogen which has a negative neutron scattering length. Considerable precautions were taken during the preparation, however, and 8% contamination would be required to reduce the apparent occupation from 1.00 to 0.87. Although an isotopic analysis of the sample has not yet been carried out, significant contamination would, because of the large incoherent scattering cross section of hydrogen, be expected to give rise to a noticeably greater background count level than was in fact observed.

Finally, we found no anomalously large temperature factor for Al(1) (which could have reflected partial vacancies on this lattice, arising from excitation of Al(1) atoms to interstitial sites next to mirror plane

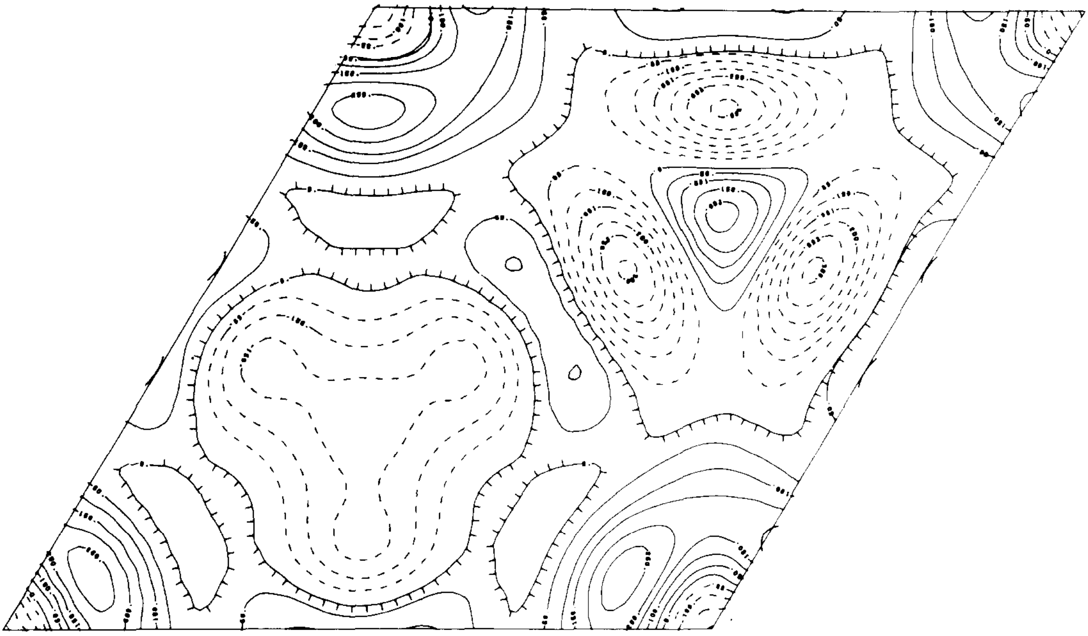

FIG. 4. Difference Fourier map corresponding to Fig. 3 and produced at the same scale. The maximum contour is 10% of the maximum observed at O(5) in Fig. 3.

midoxygen positions occupied by interstitial oxygen in nonstoichiometric sodium β-alumina (2)), and no extra scattering density in difference Fourier syntheses, which could have reflected either interstitial atoms resulting from nonstoichiometry or deuterium atoms located elsewhere than around O(5). Figures 3 to 6 show total Fourier and difference Fourier maps in the mirror plane and in the $[\bar{1}10]$ plane through the BR and ABR sites. The difference Fourier maps have no features greater than 10% of the maximum scattering density at the O(5) position, which is thought to be very satisfactory for a system of this complexity. Because of the rather spread-out location of O(5) the maximum scattering density at its position is only about one-third of that at the spinel block oxygens.

The final refinement with O(5) at a 12*j* position and the deuterium occupation varied is documented in Table I, and the observed and calculated intensities determined by deconvolution of the observed profile (after refinement of the Gaussian half-width parameters, lattice parameters, and zero-point error) in Table II.[3] Plots of the observed and calculated profiles are given in Fig. 7.

550°C Data

The data for the higher temperature have not been so straightforwardly analyzed as those at 4.5°K. Distinct changes in the unit cell parameters are observed, however, and a_0 increases from 5.6062(5) to 5.6216(6) Å

[3] See NAPS document No. 03480 for 11 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10017. Remit in advance for each NAPS Accession number. Institutions and organizations may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are $5.00. Microfiche are $3.00. Outside of the U.S. and Canada, postage is $3.00 for a photocopy or $1.00 for a fiche.

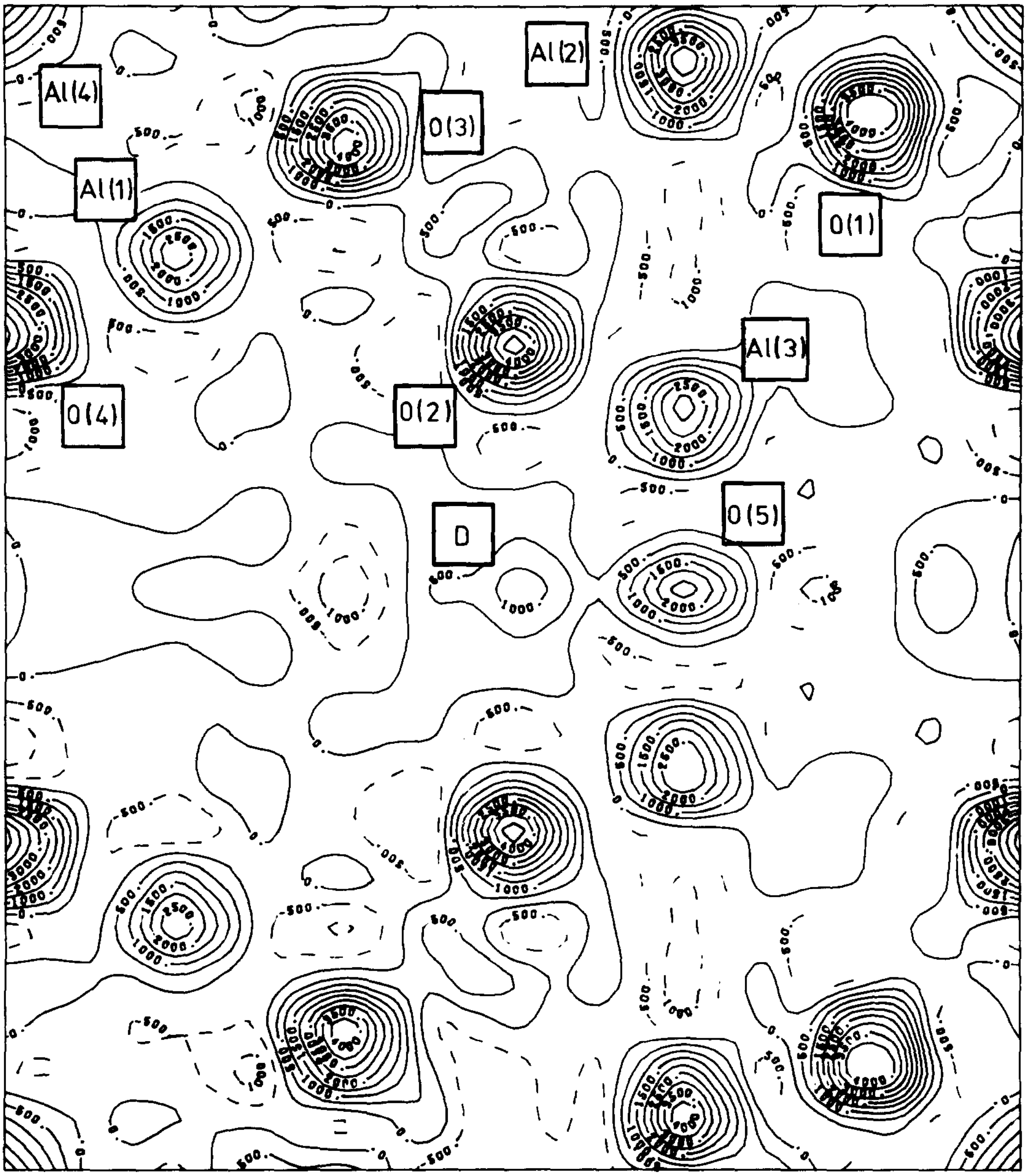

FIG. 5. Total Fourier map in the $\bar{1}10$ plane from $z = 0$ to $z = 0.50$ for $DAl_{11}O_{17}$ at 4.5°K after the best refinement. The identities of the various atomic peaks are indicated.

while c_0 decreases from 22.6192(8) to 22.6110(9) Å. Thus, although there is an increase in the unit cell volume of 0.5% this is associated with a net negative thermal expansion perpendicular to the mirror plane. Other work on the expansion of alkali metal β-aluminas and β-ferrites (*14*) indicates roughly linear thermal expansion up to about 600°C. The present result might, therefore, indicate some motion of the deuterium

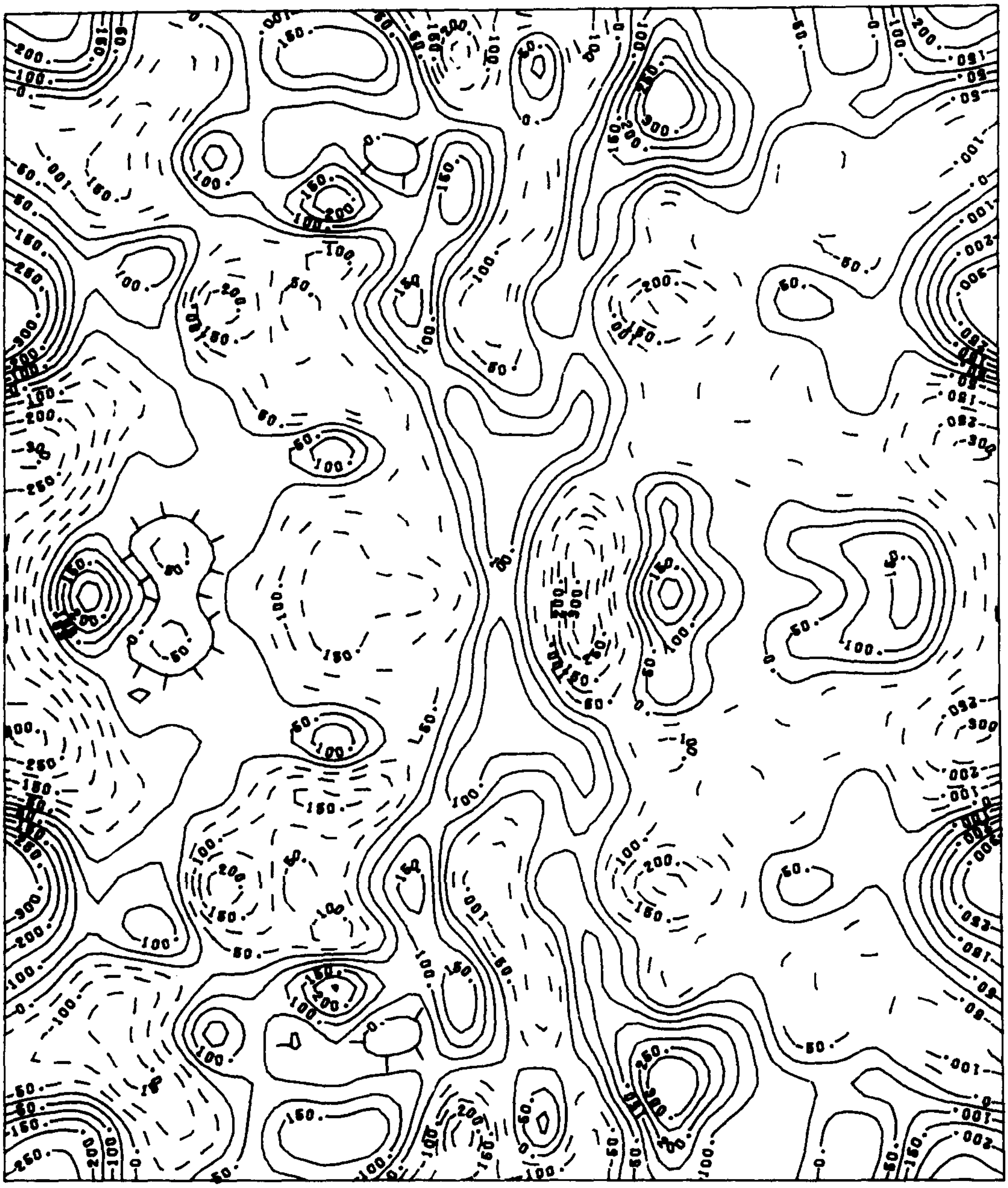

FIG. 6. Difference Fourier map corresponding to Fig. 5 and produced at the same scale. The maximum contour is 10% of the maximum observed in Fig. 5.

atoms away from sites close to O(5) toward positions normally occupied by metal ions, and such an interpretation is supported by the Al(3)–O(5) bond lengths (see below).

Our initial refinements (*1*) indicated a roughly equal population of deuterium in the BR and ABR positions. It thus appeared that the deuterium atoms had completely migrated from the low-temperature sites to

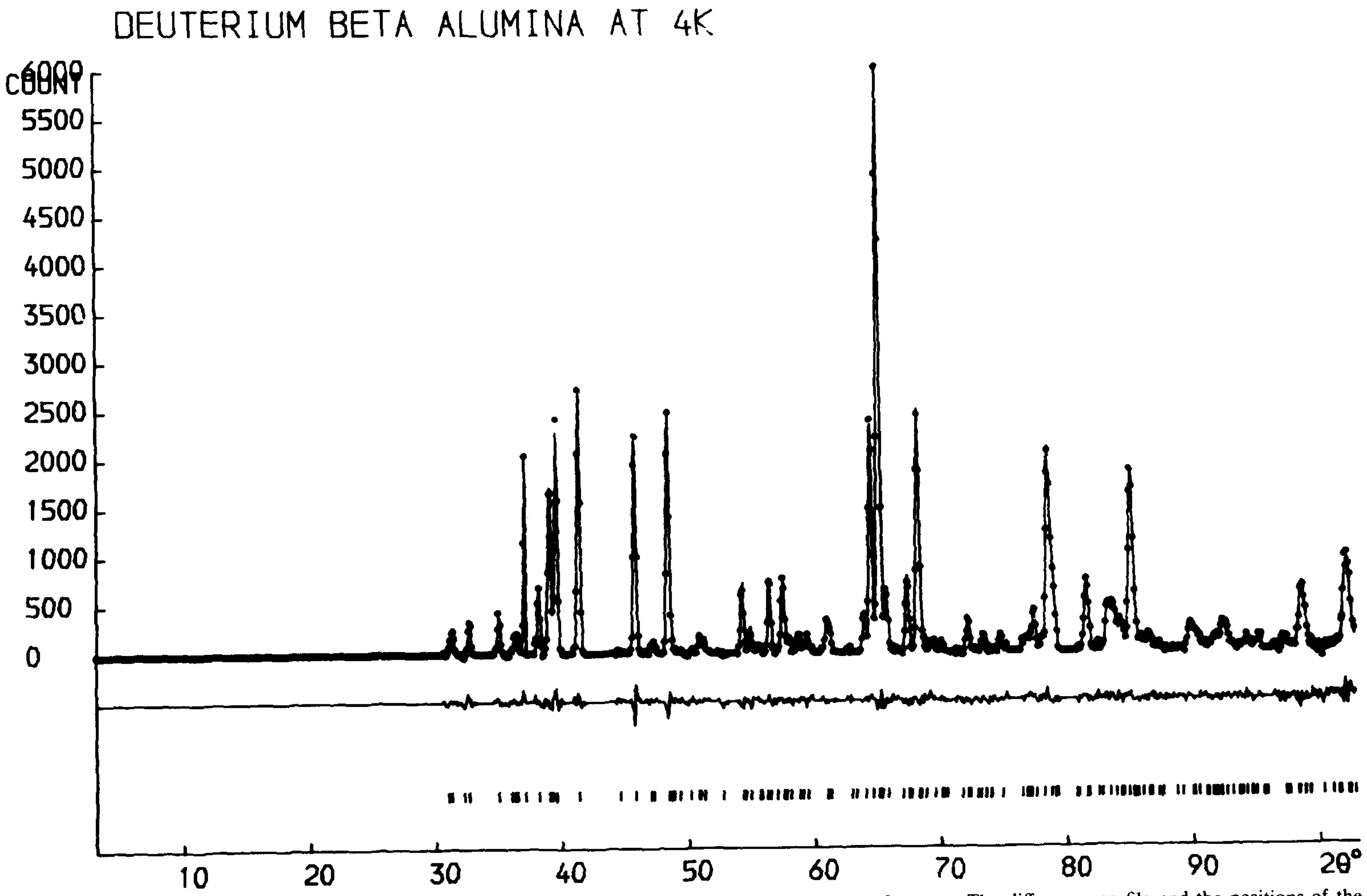

FIG. 7. Observed (dots) and calculated diffraction pattern for $DAl_{11}O_{17}$ at 4.5°K after the best refinement. The difference profile and the positions of the reflections are also shown.

TABLE I

ATOM POSITIONS IN DEUTERIUM β-ALUMINA AT 4.5°K[a,b]

Atom	Position	x	y	z	B	Occupation per cell
O(1)	12k	0.15518(61)	2x	0.04966(16)	−0.15(8)	12
O(2)	12k	0.50199(74)	2x	0.14549(18)	0.11(8)	12
O(3)	4f	$\frac{2}{3}$	$\frac{1}{3}$	0.05588(38)	0.18(22)	4
O(4)	4e	0.0	0.0	0.14099(51)	0.48(18)	4
O(5)	12j	0.3994(59)	0.6475(68)	$\frac{1}{4}$	−0.91(59)	2
Al(1)	12k	0.83299(109)	2x	0.10718(23)	0.25(9)	12
Al(2)	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.02376(57)	0.38(22)	4
Al(3)	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.17295(65)	0.33(22)	4
Al(4)	2a	0.0	0.0	0.0	−0.04(28)	2
D	12j	0.5202(87)	0.5673(55)	$\frac{1}{4}$	1.26(97)	1.744(90)

Preferred orientation factor: 0.039(6) $R_I = 0.0338$
Cell parameters: $a = 5.6062(5)$ Å, $c = 22.6191(8)$ Å $R_{pr} = 0.0974$
Correlations greater than 70%: O(5)x − O(5)y: 86%; D(B) − D(occ): 74% $wR_{pr} = 0.0721$

[a] Atom positions are in fractions of the unit cell edge.
[b] B values are in (Å)^2.

positions quite distant from the framework oxygens (~2.5 Å separation), which we presumed might be an indicator of hydrogen conductivity. A total Fourier map taken at this stage was not particularly revealing as to the mirror plane occupation.

Since then we have excluded the low-angle reflections as in the low-temperature case, optimized the background counts, and excluded a very few spurious counts arising from electrical pickup from the furnace power controller. Deuterium atoms were tested at 6h sites close to ABR and BR and in the low temperature refinement. A slight refinement variations pointed to a low ABR occupation and this site was then excluded. To attempt to avoid problems associated with excessive correlation between temperature factors, occupation numbers and positions it was necessary to fix at least the temperature factors of the deuteriums and O(5) (we recall that this was not necessary with the low-temperature form where there was a well-defined site). Values of 1.4 Å^2 for O(5) and 5.0 Å^2 for the deuteriums were considered reasonable. O(5) was at a 6h position in all the refinements. Allowing the occupation numbers of O(5) and the deuteriums to vary gave occupations of 1.04(6) for O(5), 0.63(7) for deuterium near BR, and 0.41(10) for deuterium at 12j (total deuterium occupation 1.04(12)). This was encouraging; the total occupation numbers of both species were effectively unity, the total deuterium occupation thus being in agreement with the low-temperature result. The R factors were R_I: 0.054, R_{pr}: 0.097 and wR_{pr}: 0.074 (expected wR_{pr} from counting statistics was 0.071) and were thus reasonably close to those obtained for the low structure refinement. A slight improvement was obtained when the total deuterium occupation was constrained to be unity (without any deuterium included R factors were 0.062, 0.104, and 0.082).

This could be thought a satisfactory result from the point of view of the customarily accepted (*15*) standards of comparison of wR_{pr} and the expected wR_{pr} in profile refinement. However, the profile R factors

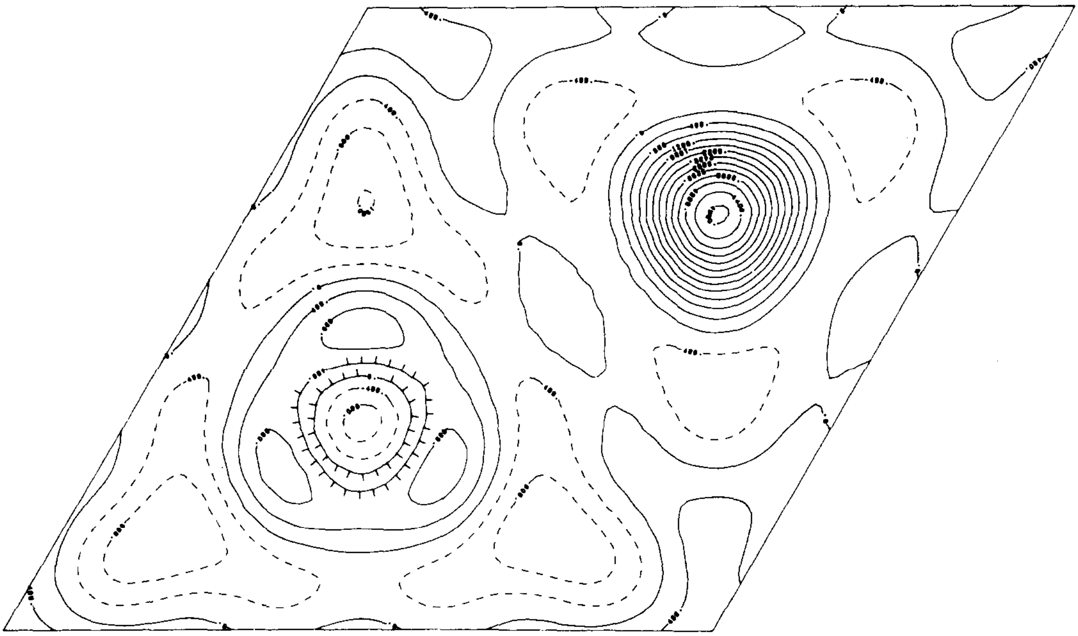

FIG. 8. Total Fourier map in the mirror plane for $DAl_{11}O_{17}$ at 550°C after the best refinement. The comparison with Fig. 3 is striking; there is no evidence now for the presence of scattering due to deuterium, and the only peak revealed in the mirror plane is due to O(5).

are no better than those for the low-temperature refinement, although the statistical accuracy of the 550°C data is higher (the counting time was 4 days compared to 2 days at 4.5°K as reflected in the expected wR_{pr} factors), and we feel that in a structure of this complexity such a result cannot necessarily be accepted unless supported by a Fourier or difference Fourier synthesis. A superficially acceptable refinement may give quite misleading populations and positions for atoms with a small occupancy. For the 550°C refinement, in contrast to the low-temperature data, we find no support in a Fourier map of the mirror plane (Fig. 8) for the occupation pattern determined in the best refinement (above) so far obtained. Indeed, there is no obvious peak at all apart from O(5). A difference Fourier map was also rather unenlightening, although there was some indication of a continuous distribution of scattering density around O(5) and about 1 Å from it, as though the deuterium had undergone a rotational delocalization around O(5). An attempt was made to simulate such a situation by introducing a second $12j$ site at 60° to the first. However, as already found in the initial refinements of the 550°C data, the quality of the data is not sufficient to allow a very satisfactory test to be made of models involving more than one type of position for the deuterium, and correlation between the parameters describing the deuterium atoms places a severe limitation on the number that can be refined independently. We were unable to obtain any improvement on the refinement already described, and we are presently unable to describe the deuterium location at high temperature.

One possible explanation of the high-temperature results is that the deuterium has become smeared out in the mirror plane. This is consistent with the change in c-axis spacing and would imply, as previously mentioned (*1*), that hydrogen β-alumina is a proton ionic conductor at high temperature. The loosening of the deuterium from its coordination to O(5) is supported by the change in Al(3)–O(5) bond length as we discuss below.

An alternative possibility would be that a reverse exchange had taken place with the silver metal to reform silver β-alumina. Although at 550°C the silver metal reflections can no longer be observed in the diffraction pattern with any confidence, this probably reflects thermal motion effects, for we have neither observed any scattering density at the anti-Beevers–Ross position, preferentially occupied by silver in silver β-alumina, nor a decrease in the *c*-axis spacing to a value characteristic of silver β-alumina (22.48 Å). Also, as mentioned below, the rather large O(2)–Al(3)–O(5) bond angle is uncharacteristic of metal β-aluminas.

The details of the best refinement already described are given in Table III, and the observed and calculated intensities in Table IV.[4] Plots of observed and calculated profiles are given in Fig. 9.

Discussion

We have demonstrated that the anhydrous deuterium analog of hydrogen β-alumina can be prepared and that it has a novel β-alumina structure with the hydrogen (deuterium) coordinated to the spacer oxygen, and the Beevers–Ross, anti-Beevers–Ross or midoxygen sites, occupied by the mobile cations in other β-aluminas, empty. The final refinement of the structure at 4.5°K detailed here confirms the model originally

TABLE III

ATOM POSITIONS IN DEUTERIUM β-ALUMINA AT 550°C[a,b]

Atom	Position	*x*	*y*	*z*	B	Occupation per cell
O(1)	12*k*	0.15675(54)	2*x*	0.04989(15)	0.65(8)	12
O(2)	12*k*	0.50109(58)	2*x*	0.14639(16)	0.83(8)	12
O(3)	4*f*	$\frac{2}{3}$	$\frac{1}{3}$	0.05539(36)	1.10(20)	4
O(4)	4*e*	0.0	0.0	0.14229(53)	1.62(20)	4
O(5)	6*h*	0.3087(17)	2*x*	$\frac{1}{4}$	1.4	2
Al(1)	12*k*	0.83203(104)	2*x*	0.10679(24)	1.12(10)	12
Al(2)	4*f*	$\frac{1}{3}$	$\frac{2}{3}$	0.02545(53)	0.44(18)	4
Al(3)	4*f*	$\frac{1}{3}$	$\frac{2}{3}$	0.17486(53)	0.24(20)	4
Al(4)	2*a*	0.0	0.0	0.0	0.64(30)	2
D(1)	12*j*	0.469(17)	0.611(19)	$\frac{1}{4}$	5.0	0.776 (84)
D(2)	6*h*	0.7451(31)	2×	$\frac{1}{4}$	5.0	1.224

Preferred orientation factor: 0.064(5)
Cell parameters: *a* = 5.6216(6) Å, *c* = 22.6110(9) Å
Correlations greater than 70%: D(1)*x* − D(1)*y*: 83%

$R_I = 0.0529$
$R_{pr} = 0.0973$
$wR_{pr} = 0.0738$

[a] Atom positions are in fractions of the unit cell edge.
[b] B values are in (Å)^2.

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[4] See NAPS document No. 03480 for 11 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10017. Remit in advance for each NAPS Accession number. Institutions and organizations may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are $5.00. Microfiche are $3.00. Outside of the U.S. and Canada, postage is $3.00 for a photocopy or $1.00 for a fiche.

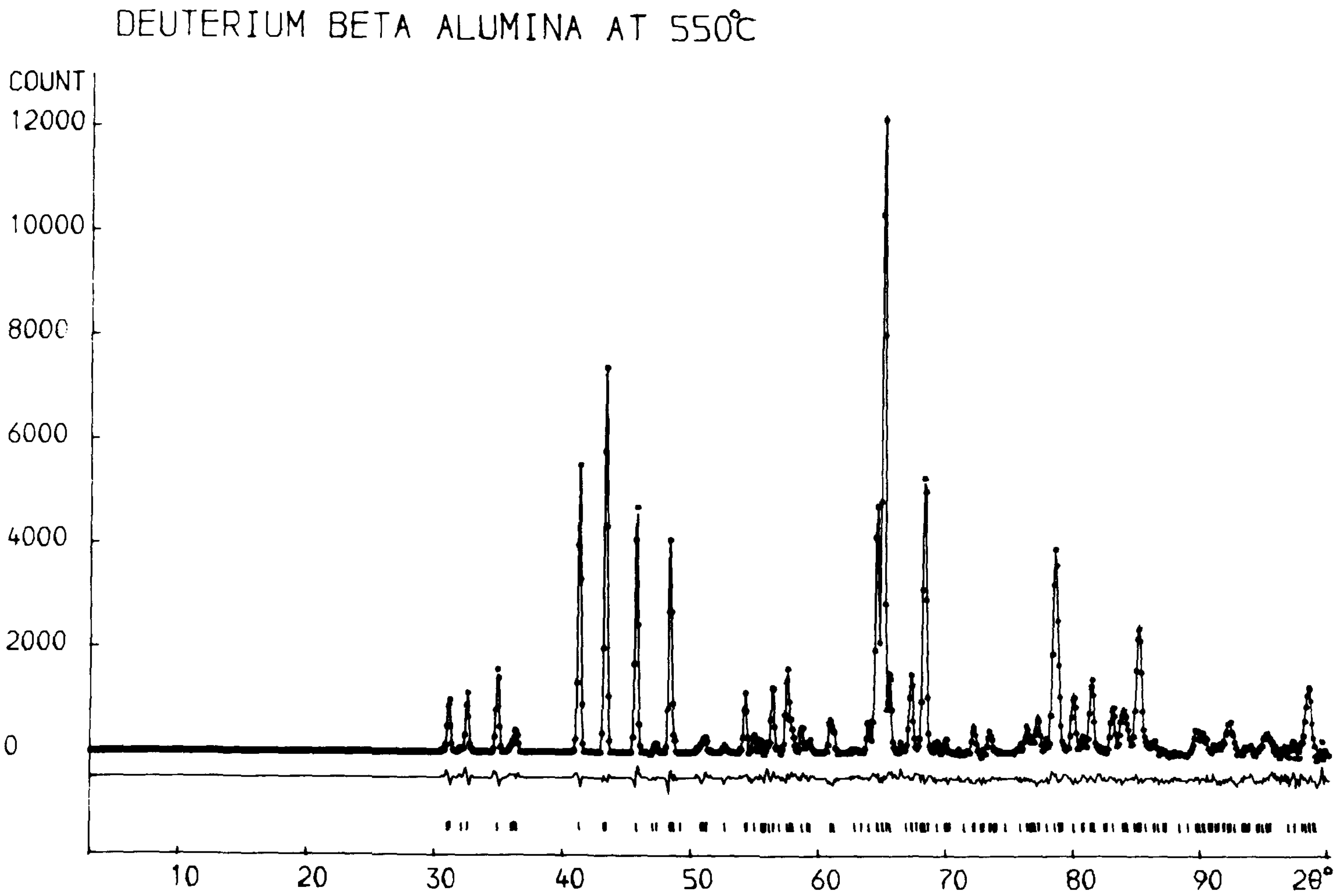

FIG. 9. Observed (dots) and calculated diffraction patterns for $DAl_{11}O_{17}$ at 550°C after the best refinement. The difference profile and the positions of the reflections are also shown.

presented (*1*). Although Colomban *et al.* have found (*16*) water-like species to be present in materials prepared by them from ammonium β-alumina or from the action of sulfuric acid on sodium β-alumina, we are not clear why they assert (*16*) that our material, and by extension presumably all hydrogenated or deuterated materials, should also contain water. We have no evidence for the presence of oxygen (or any other atom) near the Beevers–Ross site as is found in hydrated β-aluminas (*9, 17*). Our work, therefore, describes the first confirmed preparation of an anhydrous alkali-free hydrogen β-alumina. $D_2O \cdot 11Al_2O_3$, or $DAl_{11}O_{17}$, is thus both a novel β-alumina structure and a novel (deuterated) aluminum oxyhydroxide.

Our determination from the crystal structure refinement that $DAl_{11}O_{17}$ is probably stoichiometric provided (*1*) an indication that stoichiometric β-aluminas could be prepared, and this possibility has been positively confirmed by the spectroscopic and crystallographic investigation of Colomban *et al.* (*17*) on the deammoniation of ammonium β-alumina. We have recently prepared single crystals of hydrogen β-alumina from the thermal decomposition of ammonium β-alumina and a data set collected on the D9 neutron diffractometer at the I.L.L., Grenoble, is in the process of refinement. This work, a study of the decomposition of ammonium β-alumina crystals, and conductivity measurements on large crystals, will be presented later and will permit a clearer picture of the relation between hydrogen β-aluminas prepared by different routes.

The structural investigation we have carried out has been uniquely possible by neutron powder diffraction using profile analysis. We have found single crystals (Union Carbide) to be effectively disintegrated, at least from the point of view of neutron single-crystal diffraction, before hydrogen exchange is completed. The silver deposition on the surface precludes X-ray diffraction, and even without it the hydrogen location would be difficult to determine with any certainty using X-rays, particularly at elevated temperatures. Moreover, removal of the silver would involve exposure to moisture, and studies on hydrogen-containing β-aluminas prepared by other routes indicate that once incorporated in the structure, the water molecule of H_3O^+ β-alumina can be difficult to remove. Only about half of the water in H_3O^+ β-alumina prepared from the sulfuric acid reaction on sodium β-alumina was reported (*8, 9*) to be lost on heating, although the reason for the apparent discrepancy between these results and those of Saalfeld *et al.* (*5*) is not clear, and absorption of atmospheric moisture was implied (*17*) by the results describing the decomposition of ammonium β-alumina.

The use of Fourier methods to locate the deuterium atom indicates that this technique can be successfully used to locate atoms as well as to refine already approximately known structures. The β-alumina structure is, of course, rather favorable for Fourier analysis because the unchanging arrangement of the spinel block atoms acts as an effective "heavy atom" in determining phases. Perhaps for this reason we were initially successful in locating the deuterium using a total Fourier rather than a difference Fourier synthesis, but we have at present little experience of the range of applicability of Fourier methods for solving structures by powder diffraction. Nevertheless, although the determination of structure factors from profile analysis data is biased by the model used, a problem not encountered in single-crystal work, it seems clear that Fourier methods will constitute a useful extension of the powder diffraction armoury, already so dramatically strengthened by the use over the last few years of profile refinement (*15*). In particular, even if Fourier methods are not used in atom location, it seems useful, as shown for $DAl_{11}O_{17}$ at 550°C, to calculate

Fourier and difference Fourier maps to provide a check on refined structural models.

Bond Lengths and Angles, 4°K Refinement

Bond lengths and angles observed both in the present work and in previous studies on other β-aluminas are given in Tables V and VI. Although the 550°C refinement is incomplete insofar as the deuterium has not been located, we believe this has only a very minor effect on the aluminum–oxygen bond lengths and angles. The bond angle set is the more restricted, as not all studies have calculated them. Although the overall impression is of the similarity of the several compounds, as would be expected from the presence of the relatively unchanging spinel block, two interesting features may be discerned. In order of structural significance these are (a) the variations in Al(3)–O(5) bond lengths and O(2)–Al(3)–O(5) bond angles, and (b) variations in Al(1)-to-oxygen bond lengths. These are mentioned in turn, and the significance of the deuterium location in the plane is then discussed.

It is striking that the Al(3)–O(5) bond length in D^+ β-alumina at low temperature is about 0.08 Å longer than found in all the other materials except for H_3O^+ β-alumina prepared from the action of sulfuric acid on sodium β-alumina. We have shown that in D^+ β-alumina, O(5) is chemically bonded to a deuterium atom and a lengthening of other bonds involving O(5) is the expected consequence. A similar effect is observed (*18*) in diaspore, AlOOH, although the observation of bond lengthening in D^+ β-alumina is perhaps a more unequivocal demonstration in that the bond length can be measured with and without the attached deuterium.

The almost identical Al(3)–O(5) bond length observed in H_3O^+ β-alumina by Kato and Saalfeld (*10*) argues strongly that one proton in that structure is bonded directly to O(5). Ideally, one sees this as being consistent with the original observation of Saalfeld *et al.* (*5*) that H_3O^+ β-alumina, for which Kato and Saalfeld observed (*10*) the oxygen atom to be located at the Beevers–Ross position, can be reversibly dehydrated to a hydrogen β-alumina, presumably isostructural with $DAl_{11}O_{17}$. The more recent work of Breiter *et al.* (*8*) and Roth *et al.* (*9*), however, indicated that only about half of the H_2O content could be lost, so that some more complicated structural rearrangements may be involved, or differences in the stoichiometry of the sodium β-alumina starting materials might have an effect on the extent of dehydration.

The effect of the D–O or H–O bond is transferred, apparently, to the Al(3)–O(2) bonds in D^+ β and H_3O^+ β, for these are shorter by 0.02 to 0.03 Å than those in other β-aluminas. The net result is to leave the average Al(3)–O bond length more or less unchanged relative to NH_4^+, K^+, Rb^+, and Tl^+ β-aluminas. Interestingly, the average bond length for the small, most mobile, Ag^+ and Na^+ β-aluminas is about 0.02 Å smaller again. These compounds, presumably, most closely represent the optimum, unstrained Al(3)–O tetrahedron. As the size of the conducting ion is increased the Al(3)–O(5) bond length increases from about 1.675 Å to about 1.72 Å for K^+, Rb^+, Tl^+, and NH_4^+ β-aluminas. Except in the case of hydrogen-to-O(5) bonding, any further lattice expansion is taken up by an expansion of the O(2)–Al(3)–O(5) bond angle which increases from just over 111° in Ag^+ β-alumina to just over 113° in Rb^+ and Tl^+ β-aluminas. The latter value is almost identical with that observed for D^+ β-alumina at 4°K.

In this context the O(2)–Al(3)–O(5) bond angle in H_3O^+ β-alumina determined by Kato and Saalfeld is quite anomalous. They did not comment on this, and any explanation must await the determination of the proton positions. Bond angles were not given for the hydroxonium β-alumina obtained by Colomban *et al.* (*17*) from ammonium β-

TABLE V

BOND LENGTHS IN β-ALUMINAS[a]

	Number of bonds	D(4°K)[b]	D(550°C)[b]	H_3O[c]	$H_3O(N)$[d]	NH_4[d]	Ag[e]	Na[f]	K[g]	Rb[h]	Tl[i]
Octahedra											
Al(1)–O(1)	2	2.037(5)	2.040(6)	2.034	2.039	2.022	2.017	2.022	2.023	2.019	2.026
–O(2)	2	1.826(6)	1.843(4)	1.829	1.826	1.834	1.839	1.837	1.841	1.841	1.852
–O(3)	1	1.989(7)	1.986(7)	1.975	1.988	1.968	1.973	1.970	1.968	1.976	1.966
–O(4)	1	1.793(7)	1.822(7)	1.803	1.808	1.815	1.821	1.819	1.823	1.824	1.822
Average Al(1)–O	6	1.918	1.929	1.917	1.921	1.916	1.918	1.918	1.920	1.920	1.924
Al(4)–O(1)	6	1.879(5)	1.898(5)	1.890	1.905	1.891	1.893	1.895	1.896	1.897	1.899
Tetrahedra											
Al(2)–O(1)	3	1.826(7)	1.806(6)	1.803	1.798	1.800	1.806	1.801	1.802	1.800	1.790
–O(3)	1	1.801(15)	1.828(14)	1.812	1.807	1.811	1.800	1.809	1.811	1.802	1.814
Average Al(2)–O	4	1.820	1.816	1.803	1.800	1.803	1.805	1.803	1.804	1.801	1.796
Al(3)–O(2)	3	1.751(5)	1.756(5)	1.753	1.784	1.778	1.762	1.768	1.775	1.782	1.774
–O(5)	1	1.796(16)	1.716(12)	1.794	1.687	1.717	1.675	1.677	1.716	1.719	1.720
Average Al(3)–O	4	1.762	1.746	1.764	1.760	1.763	1.740	1.745	1.760	1.766	1.761
Lattice constants											
a_0 (Å)		5.606	5.6216	5.600	5.614	5.592	5.595	5.594	5.591	5.600	5.608
c_0 (Å)		22.619	22.611	22.702	22.62	22.808	22.488	22.53	22.711	22.87	22.96

[a] Bond lengths are in angstroms. The errors calculated in this work do not include correlation effects.

[b] This work.

[c] Reference (*10*).

[d] Reference (*17*).

[e] Reference (*4*).

[f] Reference (*3*).

[g] P. D. Dernier and J. P. Remeika, *J. Solid State Chem.* **17**, 245 (1976).

[h] T. Kodama and G. Muto, *J. Solid State Chem.* **19**, 35 (1976).

[i] T. Kodama and G. Muto, *J. Solid State Chem.* **17**, 61 (1976).

alumina (denoted $H_3O^+(N)$ to distinguish it from the crystal of Kato and Saalfeld), but an inspection of lattice parameters and bond lengths shows that the mirror plane structure must be different in the two crystals of nominally the same material. The c-axis spacings are considerably different and $H_3O^+(N)$ has a normal Al(3)–O(5) bond length, arguing against a hydroxyl linkage involving O(5), and a rather long bond from Al(3) to O(2). Clearly, the mirror-plane microstructure of hydrogen or hydrated metal-free β-aluminas is complicated and varied and awaits a proper unraveling.

The average Al(1)–oxygen bond length of $DAlO_{17}$ at 4°K is very similar to all the other β-aluminas studied previously. However, we notice a feature common only to $D^+\beta$, $H_3O^+\beta$, and $H_3O^+(N)\beta$, that the Al(1)–O(2) and the Al(1)–O(4) bonds are slightly shorter than those in the metal β-aluminas and in $NH_4^+\beta$. This is compensated by a slight increase in the Al(1)–O(1) and Al(1)–O(3) bond lengths. The changes are significant in

TABLE VI

BOND ANGLES IN β-ALUMINAS[a]

	D (4°K)[b]	D (550°C)[b]	Rb[c]	Tl[d]	Ag[e]	H_3O[f]
Octahedra						
O(1)–Al(1)–O(1)	79.7(3)	80.8(3)	—	81.9	—	80.7
O(1)–Al(1)–O(2)	90.4(2)	90.1(2)	90.3	90.4	90.7	90.1
O(1)–Al(1)–O(3)	88.5(3)	88.7(3)	89.1	89.2	89.2	88.8
O(1)–Al(1)–O(4)	83.5(3)	83.9(3)	84.4	84.5	84.0	83.5
O(2)–Al(1)–O(2)	98.7(4)	98.5(4)	—	97.0	—	98.5
O(2)–Al(1)–O(3)	85.1(2)	86.0(2)	85.9	86.2	86.1	85.5
O(2)–Al(1)–O(4)	101.6(3)	100.2(3)	—	99.3	—	—
O(1)–Al(4)–O(1)	88.0(2)	88.3(2)	88.2	88.7	—	88.4
	92.1(3)	91.7(3)	91.8	91.3	92.1	91.6
Tetrahedra						
O(1)–Al(2)–O(1)	110.2(5)	111.1(5)	110.6	110.6	110.4	110.6
O(1)–Al(2)–O(3)	108.7(4)	107.8(4)	108.4	108.3	108.6	108.3
O(2)–Al(3)–O(2)	108.1(6)	107.4(4)	105.6	105.5	107.6	107.5
O(2)–Al(3)–O(5)	113.1(11)	119.6(7)	113.2	113.2	111.3	98.5

[a] Bond angles are in degrees.

[b] This work.

[c] T. Kodama and G. Muto, *J. Solid State Chem.* **19**, 35 (1976).

[d] T. Kodama and G. Muto, *J. Solid State Chem.* **17**, 61 (1976).

[e] Reference (*4*).

[f] Reference (*10*).

that O(2) and O(4) will coordinate any interstitial aluminum, which is displaced Al(1), in nonstoichiometric β-aluminas, and thus we might expect longer average bond lengths from Al(1) to these atoms in nonstoichiometric than in stoichiometric β-aluminas. Colomban *et al.* (*17*) gave structural and spectroscopic support for $H_3O^+(N)$ β-alumina being stoichiometric, and we take the similar features in Al(1)-to-oxygen bond lengths in $D^+\beta$ at 4°K as support for our conclusion, derived from the deuterium occupation number and the observation of moisture evolution during preparation, that $DAl_{11}O_{17}$ is also a stoichiometric material. By analogy, it would appear that $H_3O^+\beta$, made from sulfuric acid on Na^+ β-alumina by Kato and Saalfeld (*10*), is also stoichiometric.

We have commented in the section on the structure solution on the nature of the deuterium position—whether it is strictly on a threefold 6*h* site or is slightly displaced to a 12*j* position. We chose the 12*j* position as being the more probable in the light of the D–O(5) bond length. A projection of the 12*j*, O(5), and O(2) sites is shown in Fig. 10. Any reason for a displacement of the 6*h* sites is not obvious, but the displacement from a 6*h* to a 12*j* site is only small; the distance between two mirror-plane-related 12*j* sites is 0.46 Å, but the next-nearest distance is 2.14 Å. The shift, if real, may just reflect the weakness of the O(5)–D–O(2) "hydrogen bond" which is presumably responsible for locating the deuteriums in (approximately) threefold symmetry around O(5) rather than in sixfold symmetry in the first place. The deuterium-to-O(2) distance, 2.39 Å, is not affected by the shift from a 6*h* to a 12*j* position and is so long compared to the D–O(5) distance (0.98 Å) that any D–O(2)

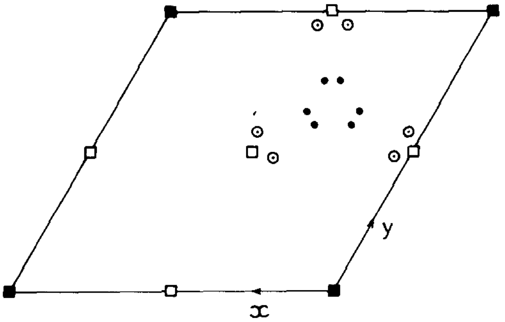

FIG. 10. The O(5) (●) and D (⊙) sites in the mirror plane. There are six equivalent sites in each mirror plane of the unit cell for atoms on 12*j* positions. Only one of these will be occupied in stoichiometric $DAl_{11}O_{17}$. As discussed in the text, a final decision on whether the atoms are on 12*j* sites, or on 6*h* sites with threefold symmetry around the ideal O(5) position $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$, could not be made. The displacements away from 6*h* sites are small, however; the distance between the nearest-neighbor equivalent deuterium 12*j* sites is only 0.46 Å. The closest D–O(5) distance for the arrangement shown is 0.98 Å, characteristic of a D–O interaction without associated hydrogen bonding. The projections of the O(2) (□) and the O(4) (■) atoms which border the mirror plane are shown. The next-nearest D–O distance, 2.39 Å to O(2), much longer than to O(5), is not affected by the uncertainty in the deuterium location. This long distance and the almost 90° O(2)–D–O(5) bond angle ensures that any hydrogen bonding between deuterium and O(2) must be very weak.

interaction must be extremely weak. Although we have no ir data for our compound, the data collected on single crystals, and mentioned above, support the idea of a very weak hydrogen bond, as, of course, does the fact that the deuterium is located in the mirror plane rather than between O(2) and O(5). Possibly, a 6*h*-to-12*j* displacement might reflect a partial tendency toward sixfold symmetry or greater delocalization around O(5), even at 4.5°K, or alternatively a partial freezing-in of such a situation—the cooling rate of the sample from room temperature was quite rapid. We are collecting more accurate data on this sample on the D1A powder diffractometer at the I.L.L. Grenoble, and it will be interesting to observe the deuterium disposition at room temperature. We are not aware of any known examples of 360° proton delocalization around an oxygen atom to which it is bonded.

Bond Lengths and Angles, 550°C Refinement

No structural details on other β-aluminas at temperatures above ambient seem to have been published, so that comparisons are restricted. However, all the bond angles, except O(2)–Al(3)–O(5) are very similar to the room-temperature values. The latter has increased to 119.6°, compared to the maximum of just over 113° in all other materials. As mentioned, we believe that, although the deuterium location is not unequivocally established, the oxygen and aluminum positions are not seriously in error, so the expansion seems a real effect.

The most dramatic change, however, is the 0.08-Å contraction of the Al(3)–O(5) bond length back to a value characteristic of other β-aluminas. This change is not affected if deuteriums are omitted from the refinement. We take this as strong evidence to support our proposition that the deuterium has become delocalized from the 4.5°K position. As the Al(3)–O(2) bond length is little changed, the average Al(3)–O bond length is also contracted. Otherwise, there is an expansion in the average bond lengths in the Al–O octahedra and virtually no change in the Al(2)–O tetrahedral average distance.

We must ask why at 550°C, with the deuteron delocalization and the shortening of the Al(3)–O(5) bond, although there is a small reduction in *c*-axis lattice spacing compared to 4°K (from 22.619 to 22.611 Å), this is still higher than in sodium and silver β-aluminas. It seems most likely that the primary cause of the lattice expansion in D^+ β-alumina, both at low and high temperatures, is the lack of large cations in the mirror plane to screen O(2)–O(2) and O(4)–O(4) *trans*-plane repulsions. The variations in lengths and angles reflect, therefore, the mirror plane chemistry but do not primarily determine the lattice constant, and the delocalized proton would appear to be relatively inefficient in screening the oxygen–oxygen repulsions. This could be understood, for example, if deuterium motion occurred via jumps from O(5) to other oxygen atoms in, or bordering, the mirror plane with a covalent bond being formed at each site. The magnitude of any associated ionic conductivity will depend, inter alia, on the relative time scales for residence and hopping. Sadly, it seems unlikely that ionic conductivity data can readily be collected on anhydrous β-aluminas prepared from silver β-alumina, for the coating of silver will provide an electronically conducting pathway and can only be removed from a powder by action of nitric acid. As already discussed, it seems (*8, 9, 17*) that water, once present in the lattice, may be difficult to remove. With single crystals, we find there are double disadvantages in that the complete exchange of hydrogen for silver causes a severe disintegration and also that the silver plates out in internal cracks, fissures, and grain boundaries as well as on the surface so that it cannot all be effectively removed even by nitric acid.

Conclusions

We have determined the structure of deuterium β-alumina at 4.5°K from powder neutron diffraction data and have shown, with the aid of Fourier methods, that the deuterium atom is bonded to the O(5) spacer oxygen in a hydroxyl linkage. The D–O(5) bond causes an increase in the Al(3)–O(5) bond length over that found in other β-aluminas. A similar effect is seen in H_3O^+ β-alumina prepared by the action of sulfuric acid on sodium β-alumina (*10*), but not in H_3O^+ β-alumina prepared by the thermal decomposition of ammonium β-alumina (*17*). The mirror plane sites normally occupied by cations are empty in $DAl_{11}O_{17}$, and we believe the unscreened *trans*-plane oxygen repulsions cause the lattice constant increase perpendicular to the mirror plane relative to sodium and silver β-aluminas.

The deuterium occupation number, and the Al(1)–O(2) and Al(1)–O(4) bond lengths support the hypothesis that the material studied is stoichiometric $DAl_{11}O_{17}$, a new (deutero) oxyhydroxide of aluminum with a novel β-alumina structure. At 550°C, the deuterium can no longer be observed and is presumed to be delocalized within the mirror plane. The Al(3)–O(5) bond length is significantly shortened relative to the value at 4.5°K, and there is a small decrease in the c-axis lattice spacing.

Further data are being collected on the high-resolution powder diffractometer, DlA, at the I.L.L. Grenoble, in an attempt to resolve outstanding structural questions, in particular, the deuterium location at high temperature, the possibility of an intermediate temperature phase with the deuterium rotationally delocalized about, but still bonded to, O(5), and whether satisfactory refinements with anisotropic temperature factors can be made.

The 550°C results imply that, in anhydrous deuterium β-alumina, the deuterium is delocalized within the mirror plane. This is a rather interesting conclusion because proton mobility in nonhydrated, non-hydrogen-bonded, oxyhydroxides is not a well-known phenomenon. In hydrated or hydrogen-bonded systems such as the recently reported hydrogen uranyl phosphate (*19*) quite high proton conductivities are well known; the field has been recently reviewed (*20*). These systems all decompose to lose water below 200°C, and generally below 100°C. Hydrogen β-alumina does not lose water irreversibly until about 700°C (*5*) and the structure of $DAl_{11}O_{17}$ at 550°C implies that hydrogen mobility is possible by the breaking (and presumably making) of covalent O–H bonds. We are not aware that such a mechanism has previously been established, although the high-temperature catalytic properties of hydrogen-containing zeolites could imply a similar phenomenon. The requirements to permit such a process would seem to be a stable framework, incorporating all the oxygen atoms to which the hydrogen can bond, and a path of suitable potential so that the primary O–H bond can be weakened by minimal thermal excitation, allowing the proton to "roll" along the internal surfaces of tunnels or planar spaces in otherwise close-packed structures.

We hope that calculations of lattice potentials might throw some light on the criteria for such conductivity. If the effect proves to be a real one, and solids can be engineered to have high proton conductivity in the 300–500°C temperature region, they will be interesting candidates for electrolytes in medium-temperature fuel cells where the temperature is such that precious metal catalysts are no longer necessary.

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