

## Neutron Diffraction Determination of the Structures of Deuterium $\beta$ -Alumina at 4.5 and 823 K

By WILLIAM A. ENGLAND and ALLAN J. JACOBSON

(*Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR*)

and BRUCE C. TOFIELD\*

(*Materials Physics Division, A.E.R.E., Harwell, Oxfordshire OX11 0RA*)

**Summary** Refinements of powder neutron diffraction data show that deuterium  $\beta$ -alumina,  $D_2O \cdot 11Al_2O_3$ , has deuterium atoms bonded to the spacer oxygen at 4.5 K, but at 823 K the deuterium distribution in the mirror plane resembles that found for Na and K  $\beta$ -aluminas providing strong evidence for high deuterium conductivity.

$\beta$ -ALUMINA,<sup>1</sup> ideal composition  $M_2O \cdot 11Al_2O_3$ , has a structure which contains spinel-like  $Al_2O_3$  blocks with four oxygen layers per block, separated by spacer oxygens. The conducting  $M^+$  ions move in the inter-block (mirror) planes where the oxygen atom density is only one quarter of that within the spinel blocks. Single crystal *X*-ray studies of Na-,<sup>2</sup> K-,<sup>3</sup> Ag-,<sup>4</sup> and Tl-<sup>5</sup>  $\beta$ -aluminas have revealed the cation distribution in the mirror plane (Figure 1). In all cases, the majority of  $M^+$  cations are close to the Beevers-Ross (BR) position, with the remainder either close to the mid-oxygen position (MO) (Na and K) or the anti-Beevers-Ross (ABR) site (Ag and Tl). Excess cations, generally 0.2 to 0.3 atoms per formula unit, are found in the conducting plane.

Hydrogen may be exchanged for silver by reduction of silver  $\beta$ -alumina at 573 K to give hydrogen  $\beta$ -alumina<sup>1</sup> which is thermally remarkably stable, not losing water to leave  $Al_2O_3$  until *ca.* 1020 K.<sup>6</sup> Nothing has been known,

however, about either the structure or the magnitude of the H mobility in this compound. We report here a novel  $\beta$ -alumina structure for the deuterium compound at low temperature and present evidence for a high tem-

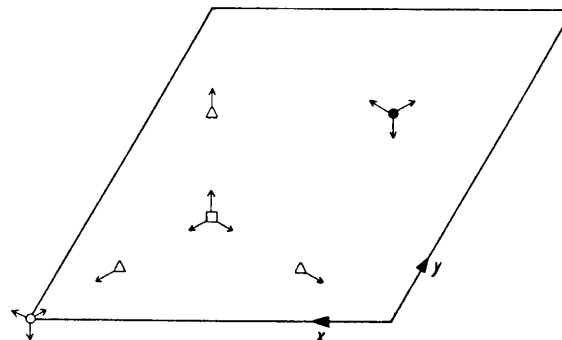


FIGURE 1. The conducting plane of  $\beta$ -alumina showing the Beevers-Ross (BR)  $\square$ , anti-Beevers-Ross (ABR)  $\circ$ , spacer oxygen, O(5)  $\bullet$ , and mid-oxygen (MO)  $\triangle$  positions. The former are at  $2d$ ,  $2b$  and  $2c$  positions, respectively, in the space group  $P6_3/mmc$  but small displacements of atoms to  $6h$  positions, as shown, are often found. The mid-oxygen position is at the  $6h$  position  $(-1/6, -1/3, 1/4)$ , but again, a small displacement is generally observed.

perature structure similar to those of the Na and K compounds with an abnormally long D-O distance.

Deuterium  $\beta$ -alumina was prepared by the action of  $D_2$  on polycrystalline silver  $\beta$ -alumina at 723 K in a silica tube. The silver  $\beta$ -alumina had been prepared by twice exchanging  $1.47Na_2O \cdot 11Al_2O_3$ , a pure  $\beta$  phase, in molten silver nitrate at 573 K. Structural work on the sodium and silver compounds will be reported elsewhere. The deuterium  $\beta$ -alumina was transferred under dry nitrogen to a vanadium sample can and sealed. Neutron diffraction patterns were taken on the PANDA diffractometer at Harwell at 4.5 and 823 K using a wavelength of 1.512 Å, in the range  $5^\circ < 2\theta < 105^\circ$  ( $0.1^\circ$  steps).

Profile refinement<sup>7</sup> of the 4.5 K data in space group  $P6_3/mmc$ ,  $a = 5.602(3)$ ,  $c = 22.604(5)$  Å,  $Z = 2$  with starting parameters for the positions of the atoms in the spinel blocks taken from the sodium  $\beta$ -alumina structure did not give satisfactory agreement with D in any of the MO, BR, or ABR sites. However, a Fourier map based on the spinel block positions revealed deuterium in  $12j$  sites close to the spacer [O(5)] oxygen (Figure 2). Least squares refinement of this model with isotropic temperature factors converged to give an  $R$  factor based on integrated intensities of 0.05. The Fourier analysis of the powder data is successful here because of heavy phase weighting by 28 of the 29 atoms in the asymmetric unit which are not changed significantly in position by ion exchange.

The occupation of the mirror plane at 823 K is substantially different. A refinement based on the 4.5 K model did not give satisfactory agreement and a Fourier map revealed occupancy of both the BR and MO positions. The least squares refinement [ $a = 5.618(3)$ , and  $c = 22.597(6)$  Å] with isotropic temperature factors gave  $R(I) = 0.09$  and occupancies of 0.49(3) (MO) and 0.53(3) (BR). The total deuterium content is in good agreement with that found at low temperature [0.98(7)].

The structure at low temperature, differing from that found for the other alkali metal  $\beta$ -aluminas, arises from the formation of O-D bonds; the shortest possible O-D bond length (Figure 2) of 1.19(11) Å is within the error

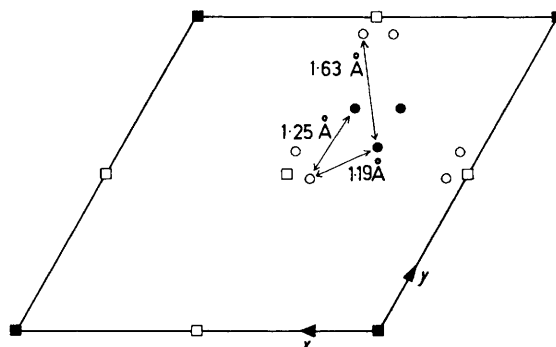


FIGURE 2. The location of deuterium in the conducting plane of deuterium  $\beta$ -alumina at 4.5 K.  $\circ$ , Deuterium  $12j$  sites;  $\bullet$ , O(5)  $6h$  sites;  $\square$ , O(2) projection on to the plane;  $\blacksquare$ , O(4) projection on to the plane. In any one mirror plane only one of the six equivalent deuterium positions per unit cell and one of the three equivalent O(5) positions will be occupied. The three possible D-O bond lengths are indicated; it seems likely that the atoms will arrange to permit the shortest of these to be achieved wherever possible. The positions of the neighbouring oxygen atoms O(2) and O(4) in the close-packed layers above and below the mirror plane are also indicated. The deuterium is not far displaced from a linear O(2)-D-O(2) situation [ $1/2$  of O(2)-O(2) = 2.353(1) Å, D-O(2) = 2.38(5) Å].

range expected. The high temperature structure reveals an unusual co-ordination for deuterium in oxides, with O-D distances of ca. 2.5 Å. This strongly suggests that deuterium is mobile at high temperatures and that hydrogen  $\beta$ -alumina may be a fast hydrogen ion conductor.

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