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STRUCTURE REFINEMENT OF DEUTERATED BOEHMITE

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Abstract—The crystal structure of a deuterated synthetic boehmite powder, γ-AlOOD, has been determined by time-of-flight neutron diffraction and Rietveld profile refinement in space group *Cmcm* to a weighted profile R of 3.71%. Cell dimensions are $a = 2.868(1)$, $b = 12.2336(4)$, and $c = 3.6923(1)$ Å. Alternate space groups for the boehmite structure suggested in the recent literature were found to be unacceptable. Atom positions, bond distances, and angles, with the exception of those involving hydrogen, were nearly identical to those determined by R. J. Hill in 1981 who studied a single crystal of boehmite by X-ray diffraction. All atoms were refined with anisotropic thermal parameters. The *b* value is 0.013 Å larger, and the thermal ellipsoids of oxygen are slightly more anisotropic than those reported by Hill and may reflect the different samples studied.

Key Words—Boehmite, Crystal structure, Deuterium, Hydrogen position, Neutron diffraction, Rietveld refinement.

INTRODUCTION

The positions of the aluminum and oxygen atoms in boehmite, γ-AlOOH, have been known with reasonable certainty since the original structure determination by Reichertz and Yost (1946). The positions of the hydrogen atoms are less well known, and consequently the correct space group has been a subject of conjecture. Single crystals of boehmite are rare and all structural studies to date except that of Hill (1981) have used powders.

X-ray and neutron diffraction studies have shown the O–H . . . O interlayer distance is about 2.7 Å, too long for a symmetrical location for the hydrogen. All previous powder X-ray diffraction studies (see Hill, 1981, for a literature review) were unable to locate the hydrogen atoms and concluded that the space group *Cmcm* was the best description of the structure. A *Cmcm* space group and an asymmetrical hydrogen atom position imply that the asymmetry of each O–H . . . O chain is unrelated to the asymmetry of neighboring chains or that the hydrogen displacements are not uniform within each chain. From a single crystal X-ray diffraction study, Hill (1981) located the hydrogen atom, determined the bonded O–H distance to be 0.75 Å, and gave the O–H . . . O bond angle as 176°. Hill concluded that the overall space group is *Cmcm* and that the structure is disordered at room temperature with regard to adjacent hydrogen-bond chains. He was able to refine his data with anisotropic thermal parameters for all atoms but hydrogen, but did not refine the hydrogen atom coordinates.

Christensen *et al.* (1982) studied the structure of a partially deuterated boehmite at 4.7°K by powder neutron diffraction and Rietveld profile-refinement techniques. The structure refined to an R of about 11.5% in both *Cmcm* and $Cmc2_1$ space groups. Both refinements used overall thermal parameters. They chose to describe the structure in space group *Cmcm*. The hydrogen position was found to be 0.14 Å off the line connecting the oxygen atoms in the hydrogen bond. The O–(D,H) . . . O distance was found to be 2.73 Å; the O–(D,H) distance, 0.94 Å.

Christensen *et al.* (1982) tested the suggestions of Farmer (1980) who, from Raman and infrared spectra, proposed additional centrosymmetric space groups, *Pnma* and $P2_1/c$, in which the hydrogen atoms were ordered and displaced from the symmetry center. They also tested the hypothesis of Slade and Halstead (1980) who suggested, on the basis of a nuclear magnetic resonance study, that the hydrogen atoms occupied two 8f sites in space group *Cmcm* with a 0.25 occupancy. No evidence of these structural arrangements was found. Hill (1981) also examined his data for evidence bearing on Farmer's suggestions but found none.

The objective of the present study was to utilize the superior intensity and resolution afforded by the Intense Pulsed Neutron Source at Argonne National Laboratory to provide the best experimental powder diffraction data to date to decide the space group of boehmite and to determine the hydrogen (deuterium) positions with certainty. The Argonne facility also provided the capability of performing the structure analysis with profile refinement methods. Our results differ from those of Christensen *et al.* (1982) because we refined all atoms with anisotropic thermal values. Also, our *refined* hydrogen position differs significantly from that determined by Hill (1981) from X-ray Fourier difference plots, because nuclear positions rather than

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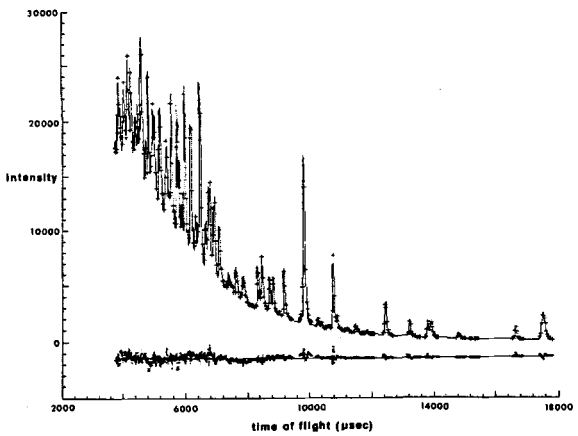


Figure 1. Neutron time-of-flight data for deuterated boehmite at 18°C. Upper plot: Observed data shown by + symbols; calculated data for space group *Cmcm* shown by solid line. Lower plot shows observed minus calculated. Regions excluded from refinement shown by absence of observed data points. Range is from 3660 μsec (0.49 Å) to 18,000 μsec (2.41 Å) and includes 350 possible Bragg reflections. Neutron time of flight is linearly proportional to d-value with a constant of proportionality of 7470 μsec/Å for the instrument used in this study.

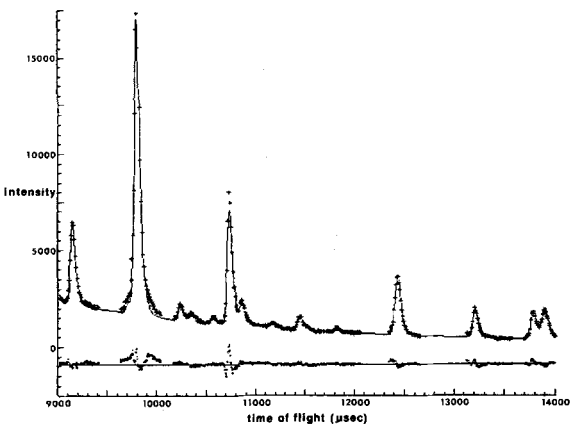


Figure 2. Enlargement of a portion of Figure 1 from 9000 μsec (1.20 Å) to 14,000 μsec (1.87 Å).

electron densities are detected in neutron diffraction studies.

EXPERIMENTAL

Deuterated boehmite was prepared as follows: About 15 g of reagent grade $Al(OH)_3$ powder, pure gibbsite as shown by X-ray powder diffraction (XRD), was dehydrated for two days at 250°C. Boehmite was the only crystalline phase recognized by XRD after the dehydration. The boehmite was reacted in a silver-lined hydrothermal pressure vessel with an excess of 99.8% pure heavy water at 325 ± 15°C at ~120 bars for two weeks, after which it was removed, dried, and then reintroduced into the pressure vessel with an additional excess of heavy water and equilibrated at the same temperature for two more weeks. It is likely that no more than 97% of the hydrogen atoms were replaced by deuterium atoms, based on the relative weights for boehmite and heavy water, and a suitable partitioning coefficient and complete equilibrium for H/D. An infrared pattern of the final product showed an essentially pure deuterated boehmite, AlOOD. Chemical analyses were made by X-ray fluorescence for 14 elements which could be expected as impurities. One-half weight percent of Mg and 0.15 wt. % Ag were detected; no other element was detected above 0.06 wt. %.

Approximately 7 g of the deuterated boehmite powder was packed into an Ar-filled, thin-walled vanadium cylinder (11 mm diameter by 55 mm long), and the sample and container were exposed to the pulsed neutron flux for ~22 hr at 18.3 ± 2.7°C. The neutron flux at the sample was about 4×10^5 n-cm^{-2}sec^{-1}. The high-resolution time-of-flight powder diffractometer used in this study is similar to that described by Jorgensen and Rotella (1982). Banks of ^{3}He detectors were placed at $\pm 145°2\theta$; observed data used in the refinement included 350 possible reflections whose d-values ranged from 0.49 to 2.40 Å. The influence of the background on the final results was minimized by excluding from the refinement portions of the observed data where there are no observed or expected diffraction peaks (see Figures 1 and 2). Data reduction and Rietveld refinement were accomplished with the program described by von Dreele *et al.* (1982). Coherent scattering lengths were taken from the International Tables for X-ray Crystallography, vol. IV, 1973, Kynoch Press, Birmingham, p. 229.

RESULTS AND DISCUSSION

Neutron diffraction profile

All of the observed peaks in the neutron diffraction pattern except one are consistent with a C-centered space group which confirms the findings of Hill (1981) and Christensen *et al.* (1982). The origin of a diffuse, weak peak at about 1.74 Å remains uncertain (see discussion below). Preliminary computer-simulated patterns (Corbató and Tettenhorst, 1982) for Farmer's proposed space groups were distinguishable from each other and from a simulated pattern for boehmite in space group *Cmcm*. No evidence, however, was found in the experimental pattern to support the space groups proposed by Farmer (1980).

The difference profile (observed minus calculated, Figures 1 and 2) shows small variations only, the largest of which are associated with intense peaks such as 200 shown at 10,700 μsec. The boehmite crystals are small,

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Table 1. Parameters for deuterated boehmite.

Space group: *Cmcm* (#63)
Weighted profile R: 3.71%
Cell parameters:
$a = 2.8681(1)$ Å
$b = 12.2336(4)$
$c = 3.6923(1)$

Cell volume and density:
$V = 129.55(1)$ Å^3
$D_c = 3.075$ g/cm^3
Site occupancy:
D 0.967 (8)
H 0.033

Position and thermal parameters:

Atom	Wyckoff site	x	y	z	β_{11}	β_{22}	β_{33}	β_{23}
Al	4c	0	−.3178 (2)	¼	100 (16)	8 (1)	87 (9)	0
O (1)	4c	0	.2901 (1)	¼	188 (13)	18 (1)	42 (7)	0
O (2)	4c	0	.0810 (1)	¼	151 (15)	9 (1)	165 (9)	0
½ (D, H)	8f	0	.0236 (2)	.0687 (5)	566 (26)	32 (2)	194 (13)	−32 (3)

Thermal parameters are times 10^4; anisotropic temperature factor is of the form: $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{23}kl)]$.

Refinement included factors for background (4), peak shape (3), absorption (1), extinction (1), and scale (1).
Weighted profile R is of the form:

$$\{\Sigma\, w_i[y_i(\text{obs}) - (1/c)y_i(\text{calc})]^2/\Sigma\, w_i[y_i(\text{obs})]^2\}^{1/2} \cdot 100\%.$$

have a highly anisotropic shape, and the (200) plane is perpendicular to the direction of maximum growth (Tettenhorst and Hofmann, 1980). Peaks such as 200, additional h00 reflections, and other reflections from planes which make a small angle with the (200) plane are narrow compared with most of the other peaks. The largest deviations on the difference profile reflect the inability of the refinement program to model correctly peaks having different shapes. A similar observation was made by Adams and Hewat (1981) for the neutron diffraction pattern of dickite.

Space group Cmcm

The best refinement was made in space group *Cmcm* which gave a weighted profile R of 3.71%. Initial parameters were taken from Hill (1981). Cell dimensions, fractional coordinates, and thermal parameters for this model are listed in Table 1. Final refinement included parameters for (number in parentheses) cell (3), position (5), thermal (13), peak shape (3), background (4), site-occupancy (1), scale (1), absorption (1), and extinction (1). In general, these data agree well with those of Hill (1981). Cell parameters are nearly identical except for *b*, for which we obtained a value 0.013 Å larger, possibly due to the substitution of deuterium for hydrogen or to the presence of the magnesium impurity in place of aluminum. Fractional coordinates for aluminum and oxygen and thermal vibration ellipsoid parameters for aluminum are nearly identical. Thermal vibration ellipsoids for the oxygen atoms are slightly more anisotropic than those of Hill (1981). All of these differences may reflect the differences between our synthetic deuterated powder and the natural single crystal used by Hill (1981).

The (D,H)–O distance determined here (Table 2) is about 0.97 Å compared with 0.75 Å for Hill (1981); our value agrees better with the approximately 1.0 Å value determined for the hydrogen-oxygen distance for many other substances, as should be expected for a technique which yields nuclear positions. The O–(D,H) . . . O bond angle is about 179°; the (D,H) atom centroid is only about 0.01 Å off the O . . . O line. The deuterium site occupancy refined to 0.967(8), in excellent agreement with the maximum of 0.97 expected for complete deuterium exchange.

The Slade and Halstead (1980) model was refined in space group *Cmcm* with two (D,H) sites with a 0.25 occupancy per site. This model did not refine as well as the model discussed above, but the obtained cell dimensions and fractional coordinates were nearly identical to those given in Table 1 with the exception of the (D,H) atom. This refinement converged to a weighted profile R of 3.86% with anisotropic thermal values for all atoms except (D,H). We were unable to confirm the results of Christensen *et al.* (1982) on the site occupancies of the two sets of (D,H) atoms. The refinement showed essentially no change in the 0.25 site occupancies when all other parameters were held constant, indicating no statistical preference between the sites. Another refinement diverged when both the deuterium site occupancy and (D,H) isotropic thermal value were allowed to vary, with all other parameters constant.

The estimated average relative precision of the measurements of Hill (1981) and Christensen *et al.* (1982) are compared with those found in this study in Table 3. This comparison shows that the present study provides an improvement in the relative precision of the results. The improvement with respect to Christiansen *et al.* (1982) is believed to be the result of the superior intensity and resolution of the time-of-flight facility at Argonne National Laboratory. The improvement with

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Table 2. Pertinent bond distances and angles for boehmite.

Deuterium-hydrogen distances:		
(D,H)–O(2) ∥ *b*–*c*	0.970	(2)
(D,H) . . . O(2) ∥ *b*–*c*	1.738	(2)
(D,H) . . . (D,H) × 2 ∥ *b*–*c*	1.934	(3)
Aluminum bond lengths:		
Al–O(1) × 2 ∥ *b*–*c*	1.877	(1)
Al–O(2) × 2 ∥ *a*–*b*	1.894	(2)
Al–O(1) × 2 ∥ *a*–*b*	1.949	(2)
Octahedral lengths:		
O(1) . . . O(1) × 4 s	2.535	(1)
O(1) . . . O(2) × 2 s ∥ *b*	2.558	(2)
O(1) . . . O(2) × 4	2.818	(1)
O(1) . . . O(1) = *a*	2.8681	(1)
O(2) . . . O(2) = *a*	2.8681	(1)
Other distances:		
Al . . . Al × 4	2.866	(2)
Al . . . Al × 2 = *a*	2.8681	(1)
Al . . . Al × 2 = *c*	3.6923	(1)
Al . . . O(2) × 2 ∥ *b*–*c*	3.435	(2)
O(1) . . . O(1) × 2 = *c*	3.6923	(1)
O(1) . . . O(2) × 2 ∥ *a*–*b*	3.837	(2)
O(2) . . . O(2) × 2 ∥ *b*–*c*	2.709	(1)
Interior octahedral angles:		
O(1)–Al–O(1) × 4 s	82.98	(6)
O(1)–Al–O(2) × 2 s ∥ *a*–*b*	83.43	(8)
O(1)–Al–O(2) × 4	96.78	(6)
O(1)–Al–O(1) ∥ *a*–*b*	94.74	(8)
O(2)–Al–O(2) ∥ *a*–*b*	98.39	(8)
Transoctahedral angles:		
O(1)–Al–O(1) ∥ *b*–*c*	159.20	(12)
O(1)–Al–O(2) × 2 ∥ *a*–*b*	178.18	(9)
Other angles:		
O(2)–(D,H) . . . O(2)	178.97	(16)
(D,H)–O(2)–Al × 2	118.23	(16)
Al–O(1)–Al × 4	97.02	(6)

Distances are given in Å, angles are given in degrees; shared edges between AlO_6 octahedra are indicated by s.

Table 3. Estimated average relative precision of results for structure refinements of boehmite.

	Hill (1981)	Christensen *et al.* (1982)	This study
Method:	X-ray diffraction	Neutron diffraction	Neutron time of flight
Sample:	Crystal	Powder	Powder
Parameters			
Cell:	1:4000	1:1000	1:30,000
Position:	1:900 (without hydrogen)	1:600	1:1200
Thermal:	1:6	1:4	1:12
Number:	9	1	13
Type:	anisotropic	isotropic	anisotropic

respect to Hill (1981) is less marked but is believed to be due to a combination of the differences in the scattering of neutrons in comparison to X-rays and the whole-pattern profile-refinement technique.

Space group $Cmc2_1$

The structure refined in space group $Cmc2_1$ to a weighted profile R of 4.91% with anisotropic thermal parameters for all atoms. Aluminum and oxygen atoms were given initial z values slightly different than z = 0.25; the refinement did not move the atoms further away from the special positions. Christensen *et al.* (1982), using 52 reflections, refined boehmite in space groups *Cmcm* and $Cmc2_1$ and obtained a slightly lower R value for space group $Cmc2_1$; because of the limited data, an overall isotropic thermal value was used for both refinements. Our more extensive data refined to a lower R in space group *Cmcm*. Furthermore, the estimated errors for all parameters in space group $Cmc2_1$, i.e., cell dimensions, fractional coordinates, and thermal values, were equal to or larger for the $Cmc2_1$ space-group refinement than for space group *Cmcm*. The deuterium site occupancy factor in space group $Cmc2_1$ refined to 0.840, which is lower than expected. A $Cmc2_1$ space group for boehmite in localized domains cannot be ruled out, but the evidence favors space group *Cmcm*.

Space group $P222_1$

A very small peak with a d-value of 1.74 Å, partially shown at ~13,100 μsec on Figure 2, cannot be accounted for with the C-centered space groups. The peak may be due to an impurity, correspond to an (070) reflection (d = 1.748 Å) of a primitive cell which is nearly C-centered, or be due to some unknown factor. $P222_1$ is the only orthorhombic space group which allows an (070) reflection and retains special positions for the aluminum and oxygen atoms [2c and 2d, respectively, at (0 y ¼) and (½ y ¼) instead of 4c at (0 y ¼) in space group *Cmcm* or 4a at (0yz) in space group $Cmc2_1$]. Two independent groups of atoms are thus produced. Attempts to refine in this space group produced no shift from a C-centered arrangement and no significant (070) reflection. An exhaustive search for an impurity which matched this peak was also unsuccessful. No satisfactory explanation for the presence of this weak peak can therefore be offered.

CONCLUSIONS

The results show that the (D,H) atoms in boehmite are distributed with a site occupancy of 0.50 each on two positions on either side of the symmetry center at 0.97 Å from the oxygen atoms. The structure is described best in space group *Cmcm*. These neutron diffraction data and the X-ray diffraction data of Hill (1981) represent the average structure taken over many unit cells over a large time. Small domains of lower

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symmetry may exist in boehmite to explain the infrared results of Farmer (1980).

The boehmite has also been studied by infrared, Raman spectroscopy, and inelastic scattering techniques, and the data will be correlated with the neutron diffraction results and reported elsewhere. Also, neutron diffraction data have been taken on a hydrogen boehmite at Argonne National Laboratory and the H and D varieties at Los Alamos National Laboratory for a comparison of the two systems and two varieites of boehmite.

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Резюме—Кристаллическая структура дейтерированного синтетического беметового порошка, γ-AlOOD, определялась при помощи дифракции нейтронов и уточнения профиля Ретвельда в пространственной гпуппе *Cmcm* до весового профиля P равного 3,71%. Размеры ячейки равны: a = 2,868 (1), b = 12,2336 (4), и c = 3,6923 (1) Å. Другие варианты пространственных групп для структур бемита, принятые в литературе, не могут быть признаны. Положения атомов, межатомные расстояния и углы, исключая связи, содержащие водород, были такие же самые как величины, определенные в 1981 году P. Y. Гиллом, который исследовал одиночный кристалл бемита при помощи рентгеновской порошковой дифракции. Все атомы были уточнены при использовании анизотропных термических параметров. Величина b является 0,013 Å большой, а термические эллипсоиды кислорода—немного более анизотропные, чем величины, определенные Гиллом, и могут отображать различные исследованные образцы. [E.G.]

Resümee—Die Kristallstruktur von deuteriertem, synthetischem Boehmitpulver, γ-AlOOD, wurde durch time-of-flight Neutronendiffraktion und durch Rietveldprofil-Verfeinerung in der Raumgruppe *Cmcm* auf ein gewichtetes Profil R-Wert 3,71% bestimmt. Die Zelldimensionen sind a = 2,868(1), b = 12,2336(4), und c = 3,6923(1) Å. Alternierende Raumgruppen, die in der jüngsten Literatur für die Boehmitstruktur vorgeschlagen werden, erwiesen sich als nicht haltbar. Die Atomladung, Bindungsabstände und -winkel waren mit Ausnahme derer, die den Wasserstoff betreffen, nahezu identisch mit denen, die von R. J. Hill in 1981 anhand eines Einzelkristalls von Boehmit mittels Röntgendiffraktion bestimmt wurden. Alle Atome wurden mit anisotropen thermischen Parametern verfeinert. Der b-Wert ist 0,013 Å größer, und die thermischen Ellipsoide von Sauerstoff sind etwas mehr anisotrop als die, die von Hill berichtet werden, was vielleicht auf die verschiedenen untersuchten Proben zurückgeht. [U.W.]

Résumé—La structure cristalline d'une poudre boéhmite synthétique deutérée, γ-AlOOD, a été déterminée par le temps de vol de la diffraction de neutrons et par le rafinement de profile Rietveld dans le groupe d'espace *Cmcm* à un profile appesanté R de 3,71%. Les dimensions de maille sont a = 2,868(1), b = 12,2336(4), et c = 3,6923(1) Å. Des espaces de groupe alternatifs pour la structure de la boéhmite suggérés dans la littérature récente n'ont pas été trouvés être acceptables. Les positions des atomes, les distances des liaisons, et les angles, avec l'exception de ceux impliquant l'hydrogène, étaient pratiquement identiques à ceux déterminés en 1981 par R. J. Hill qui a étudié un seul cristal de boéhmite par la diffraction des rayons-X. Tous les atomes étaient rafinés avec des paramètres thermiques anisotropiques. La valeur b est plus élevée de 0,013 Å, et les éllipsoïdes thermiques d'oxygène sont légèrement plus anisotropiques que ceux rapportés par Hill et pourraient refléter les differents échantillons étudiés. [D. J.]

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