Deuteration of Crystalline Hydroxides. Hydrogen Bonds of γ-AlOO(H,D) and γ-FeOO(H,D)

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The hydrogen deuterium exchange between D_2O and the crystalline hydroxides α-CrOOH, γ-AlOOH, γ-FeOOH, $In(OH)_3$ and $Y(OH)_3$ was studied in the temperature range 20−120 °C by neutron diffraction. Only the compounds γ-AlOOH and γ-FeOOH showed a measurable H−D exchange.

The hydrogen bonds of γ-AlOO($H_{0.33}D_{0.67}$) with the unit cell parameters $a = 2.876(3)$, $b = 12.24(1)$, $c = 3.709(3)$ Å and γ-FeOO($H_{0.04}D_{0.96}$) with the unit cell parameters $a = 3.070(2)$, $b = 12.53(2)$, $c = 3.876(3)$ Å were measured from neutron diffraction powder patterns using the space group Cmcm, No. 63. The hydrogen bond distances are 2.73(2) Å for γ-AlOO($H_{0.33}D_{0.67}$) and 2.65(2) Å for γ-FeOO($H_{0.04}D_{0.96}$).

In investigations of structures containing hydroxy groups, water molecules or other hydrogen-containing groups by neutron diffraction it is preferable to have deuterated specimens instead of hydrogen-containing specimens, as these yield high scattering backgrounds in contrast to deuterated compounds. For the cases of hydroxides or oxide hydroxides of the transition metals or the group III elements such deuterated compounds have been made by hydrothermal synthesis where all solutions were made with D_2O and where NaOD for the precipitation of the hydroxides was made by reaction of sodium with D_2O.[1,2]

The rate of crystallization of amorphous iron(III) hydroxide to α-Fe_2O_3 and α-FeOOD was recently investigated at hydrothermal conditions by measurements of neutron powder diffraction diagrams simultaneously with the hydrothermal crystallization treatment of the specimens.[3] It was found that the crystallizations of amorphous iron(III) hydroxide in D_2O to α-Fe_2O_3 and α-FeOOD were fast processes that in the temperature range 100−180 °C were complete within 1−4 h. The hydrothermal deuteration of crystalline hydroxides may also be a relatively fast process that may be dependent upon reaction temperature, crystallite size of specimen, structure and hydrogen bonding of the compounds. If this was the case, such deuterated compounds could be made by hydrothermal deuteration of the crystalline hydroxides instead of by the rather tedious method of preparation described above. The reaction kinetics of such hydrothermal deuterations of crystalline hydroxides have not been investigated previously, and five compounds, α-CrOOH, γ-AlOOH, γ-FeOOH, $In(OH)_3$ and $Y(OH)_3$ with different structures and degrees of hydrogen bonding were selected for this investigation.

EXPERIMENTAL

Sample preparation and characterization. The compounds α-CrOOH,[1] γ-AlOOH,[4] $In(OH)_3$[5] and $Y(OH)_3$,[6] were all made by hydrothermal synthesis as described previously. In addition, two samples of γ-AlOOH were obtained from *Haldor Topsøe A/S* and the sample of γ-FeOOH was obtained from Minnesota Mining and Manufacturing Company. X-Ray powder patterns of all specimens were measured on a Philips powder diffractometer. Some of the patterns showed a broadening of the powder lines. The instrumental broadening of the powder lines was estimated from powder patterns taken of Si and NaCl and used in a calculation of the apparent crystal size of the hydroxides and oxide hydroxides using the methods described by

Table 1. Average crystallite size (Å) of compounds investigated.

γ-AlOOH	500	In(OH)$_3$	700
γ-AlOOH	500[a]	Y(OH)$_3$	1000
γ-AlOOH	1650[a]	γ-FeOOH	200
α-CrOOH	500		

[a] Suppliers values.

Drenck,[7] and by Lipson and Steeple.[8] The results of these investigations are listed in Table 1.

Determination of the H − D exchange rate by on-line neutron diffraction. In a typical experiment 1.00 g of the crystalline compound was mixed with 3.0 ml D$_2$O in an 11 mm diameter vanadium container. The container was closed, so that no D$_2$O was lost during the experiment. The neutron diffraction powder pattern of the container was measured using a 400 cell multidetector covering 80° in 2θ at the powder diffractometer D1B at the Laue-Langevin Institute. The container was placed in a thermostated vanadium oven with a temperature stability of ± 1.0 °C.[3] Each experiment was started by a fast heating of the container in hot water. The container was then transferred to the oven at the spectrometer table when it had reached the same temperature as that of the oven or 100 °C in the case when the temperature of the oven was greater than 100 °C. The neutron diffraction powder patterns were recorded repeatedly and were extracted at 6, 12 and 18 min intervals dependent upon the H − D exchange rate. The specimens of γ-AlOOH were investigated in the temperature range 31 − 110 °C and showed a measurable H − D exchange rate. The specimen of γ-FeOOH was measured at room temperature and at 100 °C. The exchange rate was so fast that the H − D exchange was complete within 6 min. The specimens of α-CrOOH, In(OH)$_3$ and Y(OH)$_3$ were measured at the temperatures 120, 130 and 130 °C, respectively. At these temperatures none of the compounds showed a measurable H − D exchange rate over a 1 − 2 h period.

Neutron diffraction powder pattern of γ-AlOO(H,D). A sample of crystalline γ-AlOOH (crystallite size 500 Å) was partly deuterated by treatment with D$_2$O. Approximately 5 g γ-AlOOH was kept at 100 °C with 30 ml D$_2$O for 6 h. After this treatment the product was dried in air and used for the neutron diffraction experiments.

A neutron diffraction powder pattern of γ-AlOO(H,D) was measured at 4.7 K at the D1A spectrometer at the Laue-Langevin Institute in Grenoble, using neutrons of wave length λ = 1.9145 Å. The diagram was measured in the 2θ interval 10.0 to 145.95° in steps of 0.05°.

Neutron diffraction powder pattern of γ-FeOO(H,D). A sample of crystalline γ-FeOOH was deuterated by treatment with D$_2$O. The powder was so fine that it was difficult to wet it with D$_2$O. 10 g γ-FeOOH was treated with 30 ml D$_2$O and 5 drops of a liquid detergent that reduces the surface tension of D$_2$O so much that γ-FeOOH was wetted by the liquid. The suspension was kept at room temperature for 24 h. The product was then dried at 95 °C and used for the neutron diffraction experiment. The neutron diffraction powder pattern of γ-FeOO(H,D) was measured at room temperature at the spectrometer TAS5 at Risø, using 1.82 Å neutrons over the 2θ interval 11.0 to 90.8° in steps of 0.2°. The powder was housed in a 15 mm diameter vanadium container.

RESULTS AND DISCUSSIONS

Deuteration of γ-AlOOH. In the structure of γ-AlOO(H,D) the structure factor F$_{020}$ is very sensitive to the H − D ratio of the specimen. Fig. 1 shows the variation in I$_{020}$ with the H − D ratio normalized to 100 for I$_{020}$ of γ-AlOOH and calculated using the Rietveld programme[9] and the structure data obtained for γ-AlOO(H,D), see below. The rate of exchange of hydrogen with deuterium in γ-AlOOH was followed by the variation of the intensity of the 020 reflection. For each recorded powder pattern I$_{020}$ was measured by fitting the 020 peak to a Gaussian function.[10] For each series of measurements I$_{020}$ for t = 0 was found by extrapolation and all intensities of the 020 reflections were normalized after the value I$_{020, t=0}$ = 100. The normalized intensities of a series showed decreasing values with time and using Fig. 1 the variation of hydrogen contents (% H = 100 for γ-AlOOH) was found. Figs. 2, 3 and 4 show the variation of the hydrogen contents in γ-AlOO(H,D) with the square root of time. It is characteristic that
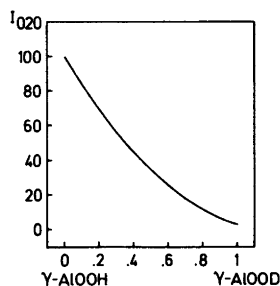
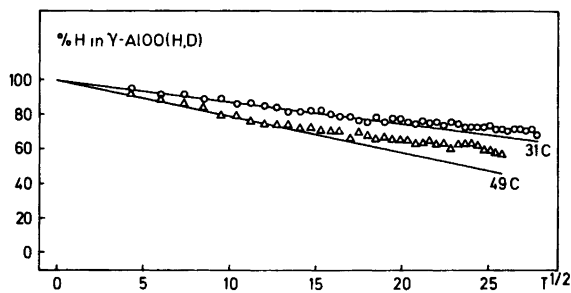*Fig. 1.* The intensity of the 020 reflection of γ-AlOO(H,D) *vs.* the H − D ratio.

Fig. 2. The hydrogen contents in γ-AlOO(H,D) *vs.* the square root of time in minutes. 1650 Å particle size of γ-AlOOH.
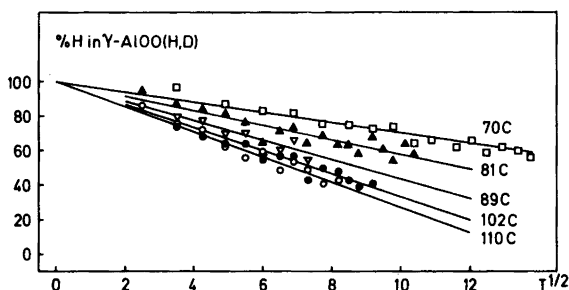

Fig. 3. The hydrogen contents in γ-AlOO(H,D) *vs.* the square root of time in minutes. 1650 Å particle size of γ-AlOOH.
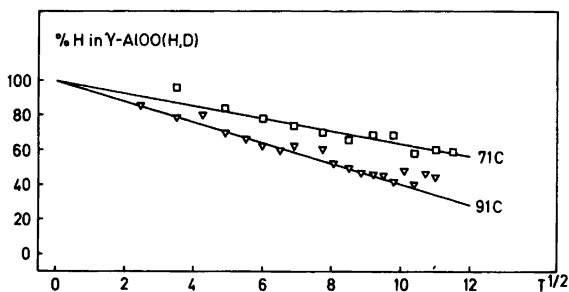

Fig. 4. The hydrogen contents in γ-AlOO(H,D) *vs.* the square root of time in minutes. 500 Å particle size of γ-AlOOH.

this variation over a long period of time is linear, indicating that the rate determining step for H−D exchange is diffusion.[11,12] This explains also that the exchange rate for γ-AlOOH with 500 Å crystallites is greater than the specimen for the same compound with 1650 Å crystallites. The investigation shows also that the exchange rate increases with temperature, and Table 2 lists the time necessary to exchange 25% of H in γ-AlOOH

with D. The rates of exchange for γ-AlOOH at the crystallite sizes used are thus relatively high.

Deuteration of γ-FeOOH, α-CrOOH, In(OH)$_3$ and Y(OH)$_3$. The rate of deuteration of γ-FeOOH was extremely high. As γ-FeOOH and γ-AlOOH have the same structure and the specimen of γ-FeOOH has a very small crystallite size, the origin of the high rate of deuteration is assumed to be the small crystallite size of the specimen. The other three

Table 2. Time in min necessary to exchange 25 % of H in γ-AlOOH with D using 1 g of solid and 3 ml of D_2O. Uncertainty in parentheses.

γ-AlOOH particle size 1650 Å		500 Å	
Temp. °C	Time min	Temp. °C	Time min
31	400(40)		
49	145(15)		
70	72(10)	71	50(8)
81	35(7)		
89	20(4)	91	18(5)
102	14(2)		
110	12(2)		

compounds showed no measurable H − D exchange rate. They all have crystallite sizes comparable to those of the γ-AlOOH samples.

The investigation thus shows that the rate determining step in the first part of the H − D exchange between crystalline hydroxides and D_2O is diffusion, and that the rate depends upon the crystallite size of the solid and on the temperature. The investigation does not give a clear picture concerning a relation between the length of the hydrogen bonds in the solids and the rate of H − D exchange of the solid with D_2O. α-CrOOH[1] has short hydrogen bonds of 2.47 Å, γ-AlOOH has hydrogen bonds of 2.73 Å (this work), In(OH)$_3$[5] has hydrogen bonds of 2.733 and 2.892 Å, and Y(OH)$_3$[6] has no hydrogen bonds.

Hydrogen bonds in γ-AlOO(H,D). The structure was refined and the degree of deuteration was determined by least-squares refinements using the Rietveld refinement programme for powder intensities[9] and the scattering lengths (in 10^{-12} cm units): $b_{Al} = 0.345$, $b_O = 0.580$, $b_D = 0.667$ and $b_H = -0.374$.[13] The structure was refined in the space groups *Cmcm* (No. 63) and *Cmc2$_1$* (No. 36). Farmer[14] has suggested, based on interpretation of Raman and infrared spectra of γ-AlOOH, that the structure could be described in the space groups *Pnma* (No. 62) and *P2$_1$/c* (No. 14). With the special positions of the atoms in the structure with $x = 0$ and 1/2, and $z = 1/4$ and 3/4, the coordinates arrived at in No. 62 are identical with the coordinates from No. 63. For the space group *P2$_1$/c* the hydrogen atoms are described with two sets of coordinates instead of one set for the space group *Cmcm*. When the structure is refined in the space group *P2$_1$/c* the coordinates arrived at are not significantly different from the coordinates found when the structure is refined in the space group *Cmcm*. In this space group the hydrogen atoms are placed in site 8*f* with 1/2 H atom in the site, and thus on each side of the centre of symmetry of the hydrogen bond. In the noncentrosymmetric space group *Cmc2$_1$* the hydrogen atom is placed in site 4*a*. Slade and Halstead[15] have suggested, from interpretation of NMR absorption spectra, a centrosymmetric hydrogen bond in γ-AlOOH in space group *Cmcm* with four 1/4 H atoms in the bond. When such a model is refined including refinement of the occupancy of the hydrogen atoms one set of the 1/4 H atoms gets an occupancy close to zero and the other set gets an occupancy close to 0.5. This model can thus be ruled out.

The results of the refinement of the structure of γ-

Table 3. Results of refinement of the structure of γ-AlOO(H,D). $a = 2.876(3)$, $b = 12.24(1)$, $c = 3.709(3)$ Å.

Atom	x	y	z	$B(\text{Å}^2)$	Occupancy
Space group *Cmcm*, $R = 11.55\%$, 52 reflections					
Al	0	−0.3172(4)	1/4	0.14(4)	1
O1	0	0.2902(2)	1/4	0.14(4)	1
O2	0	0.0820(2)	1/4	0.14(4)	1
H,D [a]	0.5	0.5186(11)	0.3924(24)	0.14(4)	0.246(6) [b]
Space group *Cmc2$_1$*, $R = 11.46\%$, 52 reflections					
Al	0	−0.3166(4)	1/4	0.16(4)	1
O1	0	0.2901(2)	0.2313(40)	0.16(4)	1
O2	0	0.0818(2)	0.2344(39)	0.16(4)	1
H,D [a]	0.5	0.5202(11)	0.3804(36)	0.16(4)	0.242(7) [b]

[a] 67.4 % D, 32.6 % H. [b] for a D-atom.

Fig. 5. Projection of the structure of γ-AlOO(H,D) along the 100-direction. Interatomic distances are in Å with standard deviations 0.01 Å.
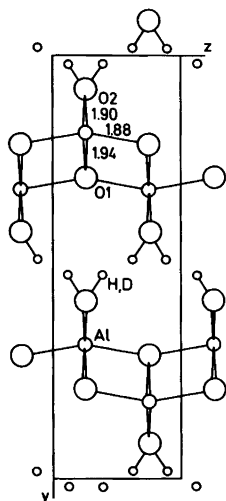

Fig. 6. Projection of the structure of γ-FeOO(H,D) along the 100-direction. Interatomic distances are in Å with standard deviations 0.02 Å.

AlOO(H,D) in space group *Cmcm* and *Cmc2₁* are listed in Table 3. The *R*-value obtained in space group *Cmc2₁* is not significantly better than that obtained in space group *Cmcm*, that is chosen as the space group for describing the structure of γ-AlOO(H,D). From the occupancy value listed in Table 3 the degree of deuteration is calculated to be 67.4%. Fig. 5 is a projection of the structure of γ-AlOO(H,D) along the 100-direction. The hydrogen atom is placed approximately 0.14 Å off the line connecting the oxygen atoms in the hydrogen bond. The distances found in the hydrogen bond are: O
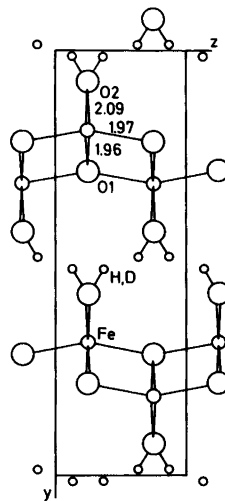
$-$H,D$\cdots$O: 2.73(2) Å, and O$-$H,D: 0.94(2) Å, in agreement with the O$-$H$\cdots$O distance 2.71(1) Å found in γ-AlOOH.[4]

Hydrogen bonds in γ-FeOO(H,D). The structure was refined in the space groups *Cmcm* and *Cmc2₁* using the same programme and scattering lengths for O, H, and D as described above. In addition, the scattering length $b_{Fe} = 0.951 (10^{-12}$ cm units)[13] was used. The coordinates arrived at are listed in Table 4. The hypothesis that the *R*-value 8.21% obtained in the space group *Cmc2₁* is better than the *R*-value 9.99% obtained in the space group *Cmcm* can only

Table 4. Results of the refinement of the structure of γ-FeOO(H,D). $a = 3.070(2)$, $b = 12.53(2)$, $c = 3.876(3)$ Å.

Atom	x	y	z	$B(Å^2)$	Occupancy
Space group *Cmcm*, $R = 9.99\%$, 27 reflections					
Fe	0	−0.3137(9)	1/4	0.67(14)	1
O1	0	0.2842(12)	1/4	0.67(14)	1
O2	0	0.0724(13)	1/4	0.67(14)	1
H,D[a]	0.5	0.5143(32)	0.3663(63)	0.67(14)	0.471(27)[b]
Space group *Cmc2₁*, $R = 8.21\%$, 27 reflections					
Fe	0	−0.3140(10)	1/4	0.49(16)	1
O1	0	0.2852(13)	0.2926(101)	0.49(16)	1
O2	0	0.0738(14)	0.2902(87)	0.49(16)	1
H,D[a]	0.5	0.5186(32)	0.3850(67)	0.49(16)	0.472(26)[b]

[a] 96.4% D, 3.6% H. [b] for a D-atom.

be accepted on a 20% confidence level.[16] It is preferred to describe the structure in the centrosymmetrical space group instead of in the non-centrosymmetrical space group.[17] The structure of γ-FeOO(H,D) projected along the 100-direction is shown in Fig. 6. The distances found in the hydrogen bond are: $O-H,D\cdots O$: 2.65(2) Å, and $O-H,D$: 0.86(2) Å, and the hydrogen atom is placed approximately 0.22 Å off the line connecting the oxygen atoms in the hydrogen bond. For γ-FeOOH the corresponding distances are 2.68(2) and 0.83(2) Å, respectively.[17]

A list of observed and calculated neutron intensities for γ-AlOO(H,D) and γ-FeOO(H,D) can be obtained from one of us (ANC).

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