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HYDROGEN ATOMS IN BOEHMITE: A SINGLE CRYSTAL X-RAY DIFFRACTION AND MOLECULAR ORBITAL STUDY

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Abstract—The crystal structure of natural boehmite, AlOOH, from Tveidalen, Langesundsfjorden, Norway, with a = 3.693(1), b = 12.221(2) and c = 2.865(1) Å, was refined from single crystal X-ray diffraction data (MoKα; maximum $2\theta = 120°$) to an R_w value of 0.032 in space groups *Amam* and $A2_1am$. In both cases the proton was found to occupy positions of the type (x, 0.038, 0), where x = 0.104 and 0.396, about 0.75 Å from the donor oxygen atom. This arrangement corresponds to the presence of chains of asymmetric hydrogen bonds with random polarity parallel to the a axis, and indicates that the effective space group is *Amam*. No significant electron density was observed either at the center (0, 0, 0) or at the position (1/4, y, 0), corresponding to symmetric and bifurcated hydrogen bonds, respectively, between the layers of octahedra.

Calculations of the total energy of a representative portion of the boehmite structure as a function of hydroxyl orientation, using semiempirical molecular orbitals of the Hückel type, are in agreement with the observed electron density distribution and suggest a preference for (1) sp^3, rather than sp^2, hybridization of the donor oxygen atom orbitals, and (2) asymmetric, rather than symmetric hydrogen bonds. Disorder of the hydrogen atom positions within individual hydrogen bond chains is shown to be much less likely than disorder between adjacent fully coherent chains.

Key Words—Aluminum hydroxide, Boehmite, Crystal structure, Electron density, Hydrogen positions, Molecular orbitals, Single crystal.

INTRODUCTION

Although the positions of the nonhydrogen atoms in boehmite, γ-AlOOH, and its isomorphs lepidocrocite, γ-FeOOH, and γ-ScOOH are known with some certainty, the detailed positions of the hydrogen atoms and therefore the exact space group of the structure type remain a subject of considerable debate.

In the first and only single crystal diffraction study of any of the three compounds, Ewing (1935) determined the space group of lepidocrocite to be *Amam*[1] and proposed a structure based on double layers of edge-sharing $MO_4(OH)_2$ octahedra with adjacent sheets held together by hydrogen bonds of length 2.7 Å (Figure 1). In order to preserve the space-group symmetry, Ewing proposed that the hydrogen atom was positioned in site 4a (0, 0, 0), midway between peripheral sp^3-hybridized oxygen atoms in adjacent layers, thereby producing zig-zag chains parallel to the a-axis of *symmetric* hydrogen bonds (Figure 2a). The possibility of placing the hydrogen in the site 4c (1/4, y, 0) of the same space group to produce a corresponding chain of *bifurcated* hydrogen bonds as in Figure 2b has not received attention, in spite of the fact that this position appears to be the most favorable electrostatically and is consistent with sp^2 hybridization of oxygen.

It is now known that truly symmetric O–H–O hydrogen bonds are limited to the O. . .O distance range below 2.40 Å, with a gradual transition taking place to completely asymmetric O–H. . .O bonds at 2.50 Å (Thomas and Liminga, 1978). With an O. . .O distance of 2.70 Å across the interlayer gap, the hydrogen bonds in boehmite are therefore almost certainly asymmetric, with the proton occupying site 4a (x, y, 0) of space group $A2_1am$ to produce chains of *asymmetric* hydrogen bonds parallel to the a-axis (Figure 2c). Where all the chains have similar polarity the symmetry falls to $A2_1am$, but if the structure is disordered in such a way that the polarity of each chain bears no relation to the polarity of the neighboring chains in the b- or c-axis directions, or if the proton displacements are not coherent within each chain itself, the *effective* space group remains as *Amam*, with half occupancy of site 8f (x, y, 0). A structure in which the hydrogen atom occupies the site 4b (1/4, y, z) of space group *Ama*2 to produce chains of hydrogen bonds in the c-axis direction along the exposed edges of the octahedra, rather than across the interlayer region, has also not been discussed in previous studies, probably because no hydrogen bonds are provided between adjacent sheets and because repulsion between Al and H is enhanced.

Reichertz and Yost (1946) and later Milligan and McAtee (1956) confirmed the isostructural relationship between lepidocrocite and boehmite suggested earlier from measurements of cell parameters, but their X-ray

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[1] For those more recent studies in which a unit-cell definition has been used corresponding to the standard *Cmcm* setting of space group D_{2h}^{17}, the results will be transformed into the original and more commonly used *Amam* setting.

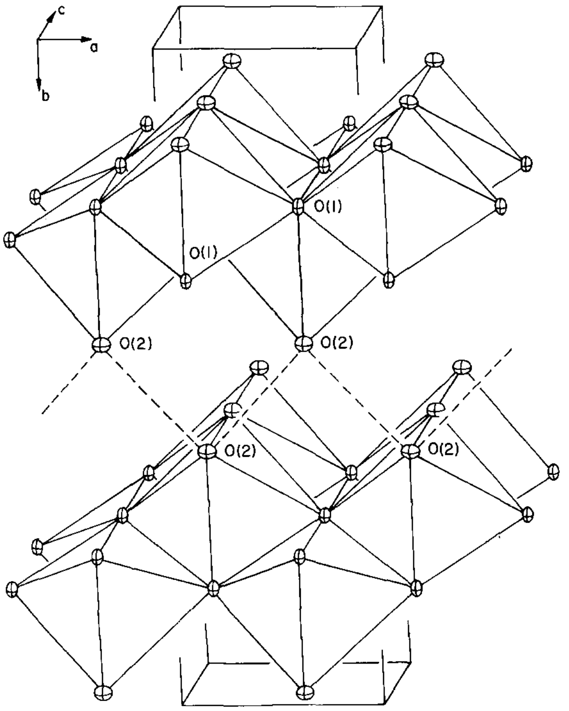

Figure 1. Unit-cell diagram of the boehmite crystal structure drawn with the atomic parameters determined in the present study but with the hydrogen atoms omitted. Thermal ellipsoids shown for oxygen atoms represent 75% probability surfaces. The AlO_6 octahedra are indicated as opaque polyhedra and possible hydrogen-bond interactions between nearest donor oxygen atoms as dashed lines.

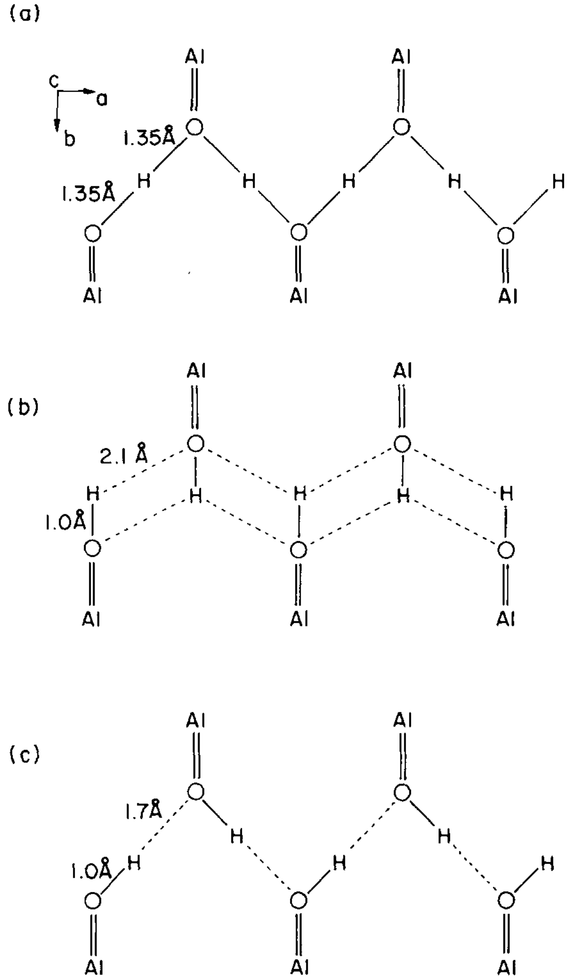

Figure 2. Alternative hydrogen-atom configurations in the z = 0.0 plane of the boehmite structure type: (a) symmetric bonds with H in site 4a (0, 0, 0) of space group *Amam*, (b) bifurcated bonds with H in site 4c (1/4, y, 0) of space group *Amam*, (c) asymmetric bonds with H in site 4a (x, y, 0) of space group $A2_1am$. In each case the Al–O (out of the plane of the paper) and O–H bonds are indicated by solid lines and the hydrogen bonds by short dashed lines.

powder diffraction data did not permit a detailed consideration of the hydrogen atom position. The first firm evidence for the existence of an asymmetric series of hydrogen bonds was obtained by Holm *et al.* (1958) from second-moment proton nuclear magnetic resonance (NMR) data, but in a similar study, Kroon and van der Stolpe (1959) were unable to distinguish between parallel (ordered) asymmetric O–H bonds in successive chains and antiparallel (disordered) bonds. More recently, Slade and Halstead (1980) reinterpreted NMR data in terms of the presence of "proton pairs" corresponding to the occupation of two sites (with 25% occupancy due to chain disorder) in the centrosymmetric space group.

The situation was further complicated by Kolesova and Ryskin (1962) who observed that the O-H-stretching frequencies in boehmite infrared (IR) spectra changed markedly with preparative technique and with time, indicating the presence of a variety of O–H bond lengths and O–H. . .O bond angles. On the other hand, Wickersheim and Korpi (1965) and Fripiat *et al.* (1967) explained the observed doubling of the stretching bands and their intensity loss with increasing temperature, respectively, in terms of direct coupling between equivalent hydroxyls arranged in a highly regular way within each chain (of space group *Amam* or $A2_1am$) and the probability of proton tunneling through potential energy barriers corresponding to anharmonic vibrational modes and/or reversal of chain dipole moments. An IR lattice-vibration study by Russell *et al.* (1978) concluded that the space group is noncentrosymmetric within an entire double layer of octahedra, but that "the weak coupling between different double sheets permits a random arrangement of OH orientations in the structure as a whole." However, using arguments based on Raman and IR activities, Farmer (1980) determined that the $A2_1am$ structure is inadmissible and that the true structure is consistent with ordered arrangements of protons in the centrosymmetric space groups *Pnam* or $P2_1/c11$.

Further X-ray powder diffraction studies of boehmite (Bezjak and Jelenic, 1964; Bosmans, 1966; Farkas *et al.*, 1977; Christoph *et al.*, 1979) all failed to locate the hydrogen atom, but, in spite of this, concluded that space group *Amam* was the most probable. Indeed, a low-temperature neutron powder diffraction study of lepidocrocite by Oles *et al.* (1970) concluded that the proton is centered in the hydrogen bond, although the possibility was admitted that the determined position may represent the mean of two asymmetric sites. However, a neutron powder diffraction study of lepidocrocite by Christensen and Christensen (1978), using profile refinement methods, concluded that a physically meaningful model could only be obtained if the proton were placed in site 4a of the noncentrosymmetric space group $A2_1am$.

It is clear, therefore, that the exact positions of the hydrogen atoms in the boehmite structure type have not been determined unequivocally. Consequently, when crystals of boehmite from Tveidalen, Langesundsfjorden, Norway, were made available by W. D. Birch of the National Museum of Victoria (specimen number M34896), the opportunity was taken to perform the first single crystal diffraction study of this mineral and to compare the results with a detailed molecular orbital study of the relative energies of the alternative hydrogen-atom configurations.

EXPERIMENTAL

Boehmite crystals from Tveidalen line the walls of cavities in massive natrolite/wairakite rock and are, in all respects, very similar in appearance to material from Ceylon described by Sahama *et al.* (1973). Several fragments were examined in a scanning electron microscope fitted with an X-ray energy dispersive analyzer and were found to contain aluminum and a very small amount of iron (equivalent to $<0.3\%$ Fe_2O_3).

To resolve the question of the presence of a center of symmetry prior to the refinement of the structure in alternative space groups, some of the boehmite crystals were subjected to a test for the generation of an optical second harmonic (Dougherty and Kurtz, 1976). Although a signal was detected it cannot be concluded with certainty that a center of symmetry is absent from the boehmite structure with this method due to the presence of nonocentrosymmetric natrolite.

X-ray diffraction data

The crystal selected for data collection was a pale brown, transparent, essentially equilateral triangular (010) platelet of thickness 0.05 mm and edge length 0.12 mm. Precession and Weissenberg photographs displayed the diffraction symmetry mmmA-a-, consistent with space groups *Amam*, *Ama*2 and $A2_1am$. The specimen was mounted on a Rigaku-AFC four-circle diffractometer in an arbitrary orientation, and the unit-cell parameters were refined by a least-squares technique from the observed 2θ values of 44 automatically centered reflections in the range $2\theta = 22\text{–}65°$, measured at 18°C with $MoK\alpha_1$ radiation ($\lambda = 0.70930$ Å). The resultant cell dimensions, a = 3.693(1), b = 12.221(2), c = 2.865(1) Å, agree with values reported previously. No evidence was found in support of a violation of the A-face-centering or of a doubling of the unit-cell dimensions and so no further consideration was given to the lower symmetry space groups proposed by Farmer (1980).

X-ray intensity data for the structure analysis were collected at 18°C with $MoK\alpha$ radiation monochromated by a flat graphite crystal ($2\theta_m = 12.0°$) using a θ–2θ scan technique and a 2θ scan rate of 1°/min. Backgrounds were determined from 15-sec stationary counts at both ends of each dispersion-corrected ($0.5 \tan \theta$) scan range (minimum width = $1.3°2\theta$). Three noncoplanar reflections measured after every fifty regular reflections showed no significant variation in either intensity or position. All reciprocal lattice points consistent with an A-face-centered lattice were sampled to a maximum 2θ value of 120°, but only those reflections for which a preliminary 1-sec count accumulated more than 2 counts were subsequently scanned in detail. The resultant 4104 reflections were corrected for background, Lorentz, and polarization (Lp) effects during data collection where

$$(Lp)^{-1} = \sin 2\theta(1 + \cos^2 2\theta_m)/(\cos^2 2\theta + \cos^2 2\theta_m).$$

Absorption corrections were applied to the data with the Gaussian quadrature method as coded in the XRAY76 system of programs (Stewart, 1976) using a $4 \times 4 \times 4$ grid and a μ value of 8.84 cm^{-1}: the minimum and maximum transmission factors were 0.918 and 0.961, respectively. Multiply-measured and symmetry-equivalent reflections consistent with point group mmm (or 2mm for the noncentrosymmetric structure refinement) were averaged to yield a set of 580 (1041) structure factors, F_o, each with a standard deviation estimated from the equation

$$\sigma_{F_o} = [\sigma_I^2 + (0.03I)^2]^{0.5}/2I^{0.5},$$

where I is the corrected raw intensity and σ_I is derived from counting and averaging statistics.[2] The overall internal consistency factor between averaged intensities [defined as $\Sigma(I - \bar{I})/\Sigma I$] was 0.051 (0.045), but only those 243 (405) observations with $I > 3\sigma_I$ were included in the subsequent least-squares analyses (five reflections severely affected by extinction were also later removed): the large number of data excluded in this process was a function both of the high proportion of high

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[2] A list of observed structure factors and estimated standard deviations is available from the author upon request.

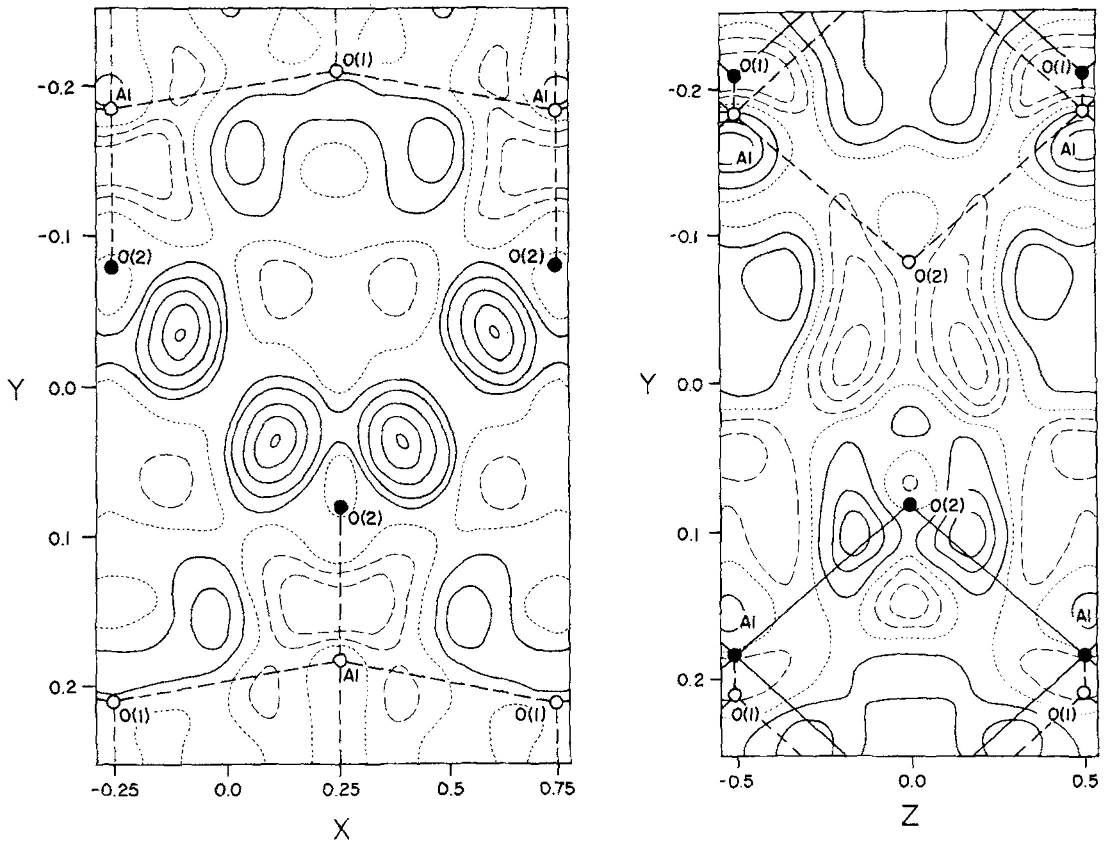

Figure 3. Fourier difference ($|F_o| - |F_c|$) map for the (a) z = 0.0, and (b) x = 0.25 planes in boehmite, calculated using only those data with $\sin\theta/\lambda < 0.65$ Å^{-1} and with no contribution from hydrogen to the value of F_c. The contour interval is 0.16 e/Å^3: zero and negative contours are indicated by dotted and dashed curves respectively. Bonds and atoms in the depicted planes are indicated by solid lines and filled circles, while broken lines and open circles represent bonds and atoms above or below the plane.

angle data and the small volume of the crystal used for data collection.

STRUCTURE REFINEMENT

Space group Amam

Refinement of the nonhydrogen atom positions and isotropic temperature factors was initiated in space group *Amam* with the atomic coordinates determined by Christoph *et al.* (1979). Scattering factors for Al and O (neutral atoms) were obtained from International Tables for X-ray Crystallography (1974) and were corrected for both real and imaginary anomalous dispersion components. Hydrogen was included in later models with the spherical scattering factor suggested by Stewart *et al.* (1965) but was not refined because of the low precision obtained for the derived parameters.

Least squares minimization[3] of the function $\Sigma w(|F_0| - |F_c|)^2$, where F_0 and F_c are the observed and calculated structure factors, and $w = 1/\sigma_{F_0}{}^2$, resulted in convergence at a conventional R_w factor of 0.086. Conversion to anisotropic temperature factors and the inclusion of an isotropic secondary-extinction parameter (type I, Lorentzian), as defined and scaled by Coppens and Hamilton (1970), further reduced R_w to 0.0342 with the error in an observation of unit weight, S = 2.687.

The z = 0 section of a difference-Fourier synthesis, calculated at this stage of the refinement but using only those data with $\sin\theta/\lambda < 0.65$ Å^{-1}, is given in Figure 3a. The map clearly shows a zigzag chain of mirror- and center-related electron-density peaks (maximum density = 0.80 e/Å^3) occurring in pairs about 0.75 Å from each hydroxyl oxygen atom O(2) in the interlayer region. These peaks are the largest positive residual density features in the unit cell (the calculated error in electron density is 0.2 e/Å^3) and may be interpreted in terms of the random occupation of hydrogen atom positions of the types (x, y, 0) corresponding to the presence of a-axis chains of asymmetric hydrogen bonds of mixed

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[3] Structure refinement and Fourier and geometry calculations were performed with local modifications of the well-known computer programs ORFLS, FORDAP, and ORFFE respectively: the crystal drawings were produced by ORTEP.

polarity. As with all of the electron density features discussed, these peaks are essentially unchanged when all data are included in the synthesis. The mean distance of the peaks from O(2) is ~0.20 Å shorter than the average O–H bond length (0.96 Å) measured in crystalline hydroxides and hydrates by neutron diffraction (Ferraris and Franchini-Angela, 1972), but may be ascribed to the relatively large distortion of electron density which takes place during formation of the O–H bond (Coppens, 1974). The peaks in Figure 3a may therefore be seen as overlaps of O–H covalent bond density and lone-pair density associated with the O(2) atom acceptor sites in the disordered chains. Figure 3b is a section calculated through the plane x = 0.25 in Figure 3a and shows a pair of peaks of maximum density 0.57 e/Å^3, a distance of 0.55 Å from O(2) along the Al–O(2) bonds. These peaks are the second largest positive electron-density features in the unit cell and may be considered to represent the occupation of the remaining two sp^3 hybrid orbitals of the O(2) atom.

Note that there is no residual density at the center (0, 0, 0) corresponding to a chain of symmetric hydrogen bonds, and very little density at the point (1/4, 0.025, 0) corresponding to a chain of bifurcated hydrogen bonds: both of these models for the boehmite structure may therefore be rejected. Indeed, while a refinement undertaken with a half-proton (U = 0.04 Å^2) positioned at the center of the residual peak in Figure 3a, i.e., at (0.396, 0.038, 0), resulted in R_w and S values of 0.0318 and 2.496 (for all 580 data the values are 0.0468 and 2.892), respectively, refinements with the hydrogen atom at (0, 0, 0) and at (1/4, 0.025, 0) raised the agreement indices to 0.0335, 2.629, and 0.0325, 2.547, respectively.

Although the absence of significant electron delocalization out of the plane z = 0 in the interlayer region (Figure 3b) eliminates space group *Ama*2 from contention, the distribution of residual electron density in Figure 3a does little to resolve the ambiguity between *Amam* and *A*2$_1$*am*. The presence of density significantly displaced from the mirror plane at x = 0.25 and the origin (0, 0, 0) requires that the hydroxyl chains (or portions within individual chains) have asymmetric hydrogen bonds and therefore local *A*2$_1$*am* symmetry, but if these asymmetric chains are of random polarity the effective space group is *Amam* in the X-ray diffraction experiment.

Of course, the electron density distribution about the plane x = 0.25 in Figure 3a must have mirror symmetry, because the refinement and Fourier synthesis were both undertaken in space group *Amam*. However, any deviation of the structure from this symmetry must be small because the thermal ellipsoids of all three non-hydrogen atoms are not markedly anisotropic (Table 1), and only for O(2) is the major axis of thermal vibration perpendicular to the mirror plane in question. These observations are consistent with the results obtained by Christensen and Christensen (1978) in their refinement of lepidocrocite in space group *A*2$_1$*am*, wherein none of the atoms showed a significant or consistent departure of their x-coordinates from the high-symmetry values. Indeed, their determination of the space group was primarily based on a consideration of the relative values of the proton thermal vibration parameter, a variable which is considered unreliable in powder diffraction studies.

Space group A2$_1$am

Nevertheless, an attempt was made to refine the boehmite structure in space group *A*2$_1$*am* using the 405 observed reflections consistent with point group 2*mm* and with the x-coordinate of aluminum held at 0.25 to define the unit-cell origin. Despite the introduction of a variety of small initializing shifts to the x-coordinates of both anions (with and without constraints on the variation of the temperature factors), all parameters except U_{11} and/or x of O(2) returned to within three standard deviations of their high-symmetry values. However, in no case was the asymmetry of electron-density about the plane at x = 0.25 significant in relation to the random fluctuations of density observed in other portions of the unit cell. Moreover, the inclusion of a hydrogen atom at various 4a sites did not result in a significant lowering of the R factors relative to the increased number of variables and observations (Hamilton, 1965).

Atoji and Lipscomb (1954) found a similar zig-zag chain of asymmetric hydrogen bonds (hydrogen atom peak height = 1.7 e/Å^3) in their study of crystalline HF in space group *Bmmb*. Attempts to refine the structure in the polar sub-group *Bm*2$_1$*b* also failed to produce a significant departure from the disordered chain model.

It is therefore concluded that the *overall* space group of the boehmite crystal structure is *Amam*, with the hydrogen atoms disordered over positions of the types (x, y, 0) where x = 0.104 and 0.396 and y = 0.038. Atomic coordinates along with their standard deviations estimated from the inverted full matrix are given in Table 1. Bond distances and angles, together with other relevant nonbonded distances, are collected in Table 2.

DISCUSSION OF THE STRUCTURE

Each AlO_6 octahedron (Figure 1) shares six of its twelve edges asymmetrically with adjacent octahedra and, as a consequence, is considerably distorted. The shared edges (marked with an s in Table 2) are ~0.30 Å shorter, and the angles they subtend at the central Al atom are ~14° narrower than those not involved in edge sharing. On the other hand, the Al. . .Al distances and

Table 1. Fractional atomic coordinates and temperature factor coefficients.

Atom	x	y	z	U_{11}	U_{22}	U_{33}
Al	0.25	−0.3178(2)[1]	0.0	0.0032(5)[2]	0.0043(5)	0.0047(6)
O(1)	0.25	0.2897(3)	0.0	0.0027(10)	0.0062(11)	0.0066(11)
O(2)	0.25	0.0809(3)	0.0	0.0064(11)	0.0055(11)	0.0047(11)
½H	0.396[3]	0.038	0.0	0.04		

[1] Parenthesized numbers here and in all other tables represent the e.s.d. in terms of the least significant figure to the left.

[2] The anisotropic ellipsoids are of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2}]$.

[3] Hydrogen atom position determined from Fourier synthesis.

Al–O–Al angles across the shared edges average 0.17 Å and 7.0° larger than those corresponding to a completely regular octahedron.

Because four of the six shared edges are on the O(1) side of the octahedron, the axial O(1)–Al–O(1) angle is considerably distorted from linearity to a value of 158.9(2)° (Figure 5b). Some of the steric constraints on the four-coordinated O(1) atom in the interior of the layer are reduced thereby, but its valence angles still display a significant departure from the tetrahedal arrangement expected for sp^3 hybridization; five of the angles are less than 98°, whereas one is 159°. In fact, the appearance of a peak or residual electron density (with maximum density 0.54 e/Å^3) 0.6 Å from O(1) near the center of the 159° angle (Figure 3b) suggests that this anion may be closer to a state of trigonal-bipyramidal hybridization. The situation for the O(2) atom on the exterior of the layers is a little clearer because it is coordinated by only two Al atoms and a proton at angles of 98° and 117°: the fourth sp^3 hybrid (a lone pair) then accepts the hydrogen bond from an equivalent proton 1.95 Å away in an adjacent sheet. Both anions in boehmite are completely charge balanced (Pauling, 1960), and as a result the three independent Al–O bonds are relatively uniform in length.

MOLECULAR ORBITAL CALCULATIONS

Although exact solutions to the Schrödinger equation are in general not realized for large molecules or solids, approximate semiempirical molecular-orbital theory has been successfully applied to the study of the geometrics and energetics of a large number of moderately complex systems (Allen, 1970; Dewar, 1975; Johnson, 1973; Pople and Beveridge, 1970; Tossell and Gibbs, 1977). Of these methods, extended Hückel theory, EHT, continues to be one of the most popular, especially in cases where the electronegativity difference between adjacent atoms is small, and where an appropriate choice of angular coordinate can be made for the comparison of related species (Allen, 1970). Moreover, recent work has established a relationship between the approximate total energy obtained from EHT and that from *ab initio* self-consistent field calculations (Boyd, 1977) and has also suggested that EHT may be superior to other semiempirical methods in modeling repulsive

Table 2. Interatomic distances and angles.

Al–O(1)	1.878(1) × 2	O(1)...O(1) s	2.530(3) × 4	O(1)–Al–O (1) s	82.90(7) × 4
O(2)	1.893(3) × 2	O(2) a	2.552(5) × 2	O(2) s	83.36(11) × 2
O(1)	1.944(3) × 2	O(2)	2.822(3) × 4	O(2)	96.87(7) × 4
		O(1)	2.865(1)	O(1)	94.95(16)
average = 1.905		O(2)...O(2)	2.865(1)	O(2)–Al–O(2)	98.33(18)
H–O(2)					
H...O(2)	0.752(2)	O(1)...O(1)	3.693(1)	O(1)–Al–O(1)	158.92(22)
O(2)...O(2)	1.955(3)	O(2)	3.837(2) × 2	O(2)	178.31(14) × 2
H...H	2.705(5)				
O(2)–H...O(2)	2.067	Al...Al	3.693(1)	Al–O(1)–Al	158.92(22)
	176.17(11)	Al	2.865(2) × 4	Al	97.10(7) × 4
H–O(2)–Al	117.12(6)	Al	2.865(1)	Al	94.95(16)
		Al	2.865(1)	Al–O(2)–Al	98.33(18)

Distances and angles are quoted in Å and degrees, respectively: those involved in the sharing of edges between AlO_6 octahedra are indicated by s, and those describing the hydrogen atom have been calculated with a contribution to the e.s.d. from the O and/or Al atom(s) alone.

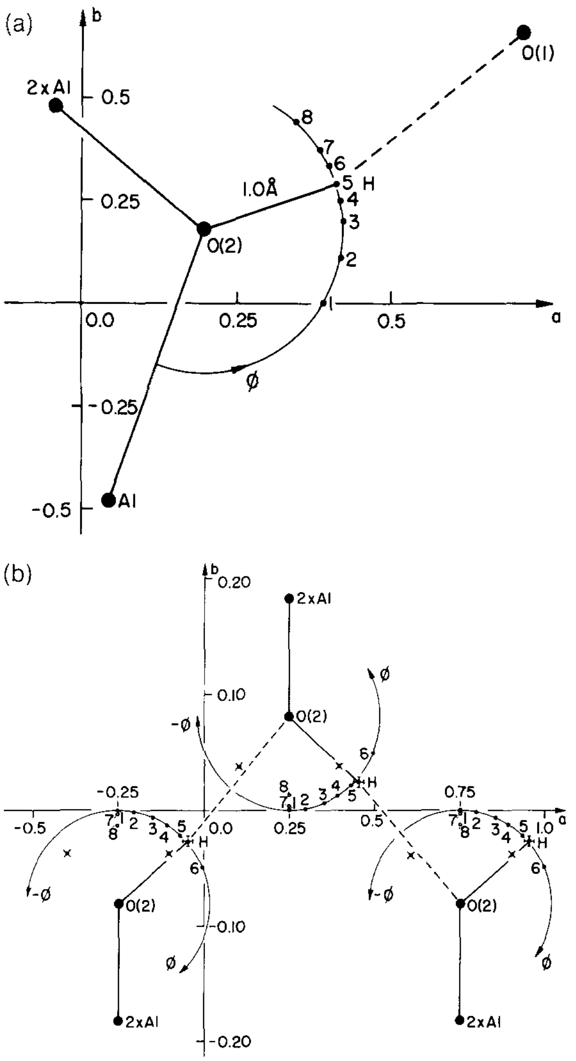

Figure 4. Angular coordinate diagrams for the (a) diaspore and (b) boehmite structures projected on to (001) and used to calculate the relative energies of various hydrogen atom configurations. In each diagram, the circle drawn about O(2) has a radius of 1.0 Å and represents the locus of all possible hydrogen atom positions in the mirror planes parallel to (001). The angular coordinate ϕ is the angle between the O(2)–H bond and (a) the Al–O(2) bond, or (b) the direction [010], measured in the plane (001) or (400). Positions 1 through 8 are the particular points for which the energy of the cluster was calculated [points 7 and 8 in (b) are respectively 20° and 32° above the plane of the paper in the planes (400)]. The observed hydrogen atom position in diaspore (Hill, 1979) is at position 5 in (a). In (b) the positions marked with crosses represent the centers of the difference-Fourier proton peaks determined for boehmite, while the sites indicated by the error bars correspond to the proton positions in lepidocrocite (Christensen and Christensen, 1978).

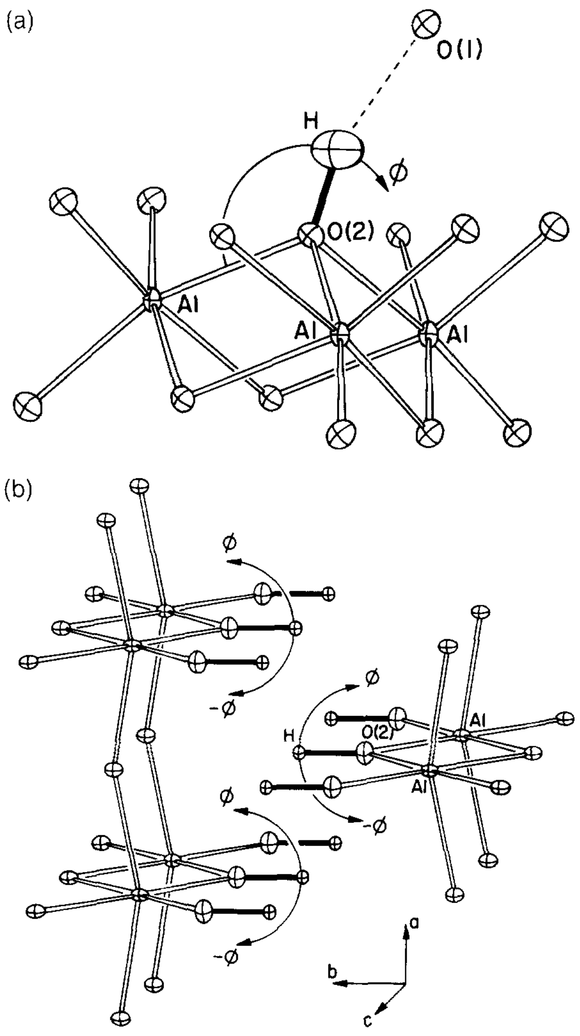

Figure 5. Coordination diagrams of the (a) $Al_3O(OH)F_{12}^{6-}$ and (b) $Al_6(OH)_9F_{19}^{10-}$ cluster used for Hückel calculations of total energy as a function of hydroxyl (filled bond) orientation for diaspore and boehmite, respectively. The circles drawn about the O(2) atoms have the same meaning as defined in Figure 4, but have only been drawn for the central chain of hydroxyl groups in (b).

potentials in the van der Waals contact region between molecules (Boyd, 1978).

Because the hydrogen bond problem in boehmite can be reduced to a consideration of various interlayer hydrogen atom positions in the presence of an essentially invariant, but extensive, aluminum and oxygen sheet structure, an attempt was made to determine the relative energies of these alternative proton configurations within the framework of EHT. As a check on the ability of the method to predict hydrogen-bond configurations, a parallel series of calculations was also performed on boehmite's polymorph, diaspore, for which the proton position is known with some precision (Busing and Levy, 1958; Hill, 1979).

Procedure

In both structures the donor and acceptor oxygen atoms and hydrogen all lie on mirror planes, and there-

Table 3. Valence-orbital ionization potentials (VOIP) and Slater exponents (ξ).

Atom	Oribtal	VOIP (eV)	ξ
Al	3s	11.26	1.372
	3p	5.93	1.355
F	2s	40.12	2.564
	2p	18.65	2.550
O	2s	32.33	2.246
	2p	15.79	2.227
H	1s	13.60	1.200

Ionization potentials are from Basch *et al.* (1965). Exponents for Al, F, and O are from Clementi and Raimondi (1963); for H, from Bartell *et al.* (1970).

fore the appropriate angular coordinates may be represented by a series of points on circles of radius 1.0 Å about the donor atom O(2) (Figure 4). In an attempt to account for the effect of as much of the surrounding structure as possible, the 'first coordination sphere' of octahedra around the relevant O(2) atom(s) was included in each calculation. For diaspore this arrangement resulted in a relatively small cluster containing only 18 atoms (Figure 5a), but in boehmite, O(2) is both the donor and acceptor of the hydrogen bond, necessitating the incorporation of a total of 43 atoms spread over portions of three hydrogen-bond chains (Figure 5b). In both clusters all distances and angles involving the non-hydrogen atoms were maintained at their observed values (Hill, 1979 and Table 2), but oxygen atoms and hydroxyl groups on the periphery of the clusters were replaced by fluorine to keep the overall charge and number of atoms at a minimum. All calculations were performed with the EHT program originally written by Hoffmann (1963) assuming a minimum-valence sp-basis for Al, O and F, and an s-basis for H, with the valence-orbital ionization energies and Slater orbital exponents listed in Table 3.

Results

The calculated relative energy for the diaspore cluster, plotted as a function of the angle ϕ between the Al–O(2) and O(2)–H bonds in the plane $z = 0.25$ (Figure 4a), is given in Figure 6a. The energy minimum occurs at an angle of 125.5°, very close to the observed value of 128.8(1)°. Note that the line of centers between O(2) and the hydrogen-bond acceptor atom O(1) occurs at 141°, the three Al. . .H distances are equal when ϕ is 118°, and the tetrahedral angle is 109.5°: as expected, the minimum energy configuration appears to represent a compromise among these three arrangements.

Relative energies calculated for boehmite as a function of the angle between the O(2)–H bonds and [010] in the plane $z = 0.0$ are given as filled circles connected by a solid line in Figure 6b. These energies were calculated for clusters in which the angular displacements,

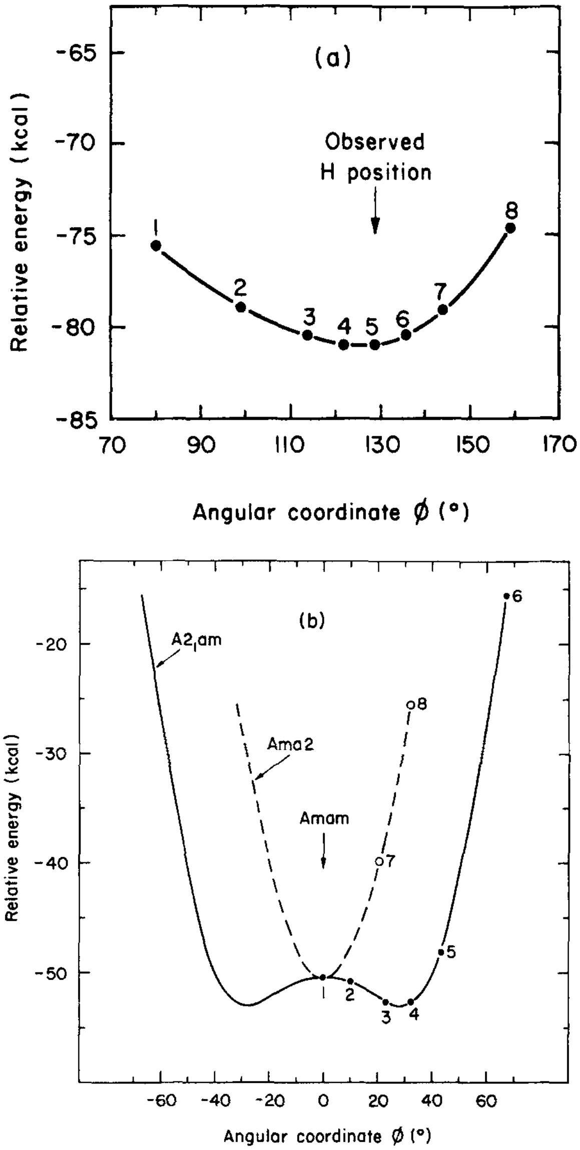

Figure 6. Relative energy of (a) the diaspore cluster in Figure 5a plotted as a function of ϕ, the angle between the hydroxyl group and the Al–O(2) bond in the plane (001), and (b) the boehmite cluster in Figure 5b, plotted as a function of ϕ, the angle between the hydroxyl group and [010]. For solid circles the angle is measured in the plane (001) corresponding to structures in space group $A2_1am$, and for open circles the angle is in the plane (400) of space group *Ama*2. Point 1 represents the proton position in space group *Amam*.

ϕ, of all nine hydrogen atoms were of the same magnitude and the same sign relative to +a. At $\phi = 0°$ and 180° the cluster has *Amam* symmetry, and at all other values the symmetry is $A2_1am$. The energy profile is, of course, symmetric about $\phi = 0°$, with positive and negative displacements corresponding merely to a reversal of the polarity of the structure in the a-axis direction. The open circles connected by a dashed line in

Figure 6b represent the relative energies calculated for a series of clusters in which the O(2)–H bonds were again rotated through various angles from [010], but this time the rotations were executed in planes of the type (400) rather than (001): for $\phi \neq 0°$, these clusters therefore have *Ama*2 symmetry.

Comparison of the relative energy profiles of the three structural models (Figure 6b) shows that space groups *Amam* (represented by a single point at $\phi = 0°$) and $A2_1am$ both permit the attainment of more stable proton configurations than *Ama*2. This result is in agreement with the observed confinement of the interlayer electron density to the plane z = 0.0 (Figure 3) and with the resultant earlier rejection of space group *Ama*2. Furthermore, a distinction can be made between the two remaining structures because an energy gain of some 2.2 kcal can be achieved in $A2_1am$, relative to the solitary *Amam* configuration, by a 28° rotation of the hydroxyl group in the z = 0.0 plane. The energy minimum in this case represents a compromise between a tendency to achieve sp^2 ($\phi = 0°$) and sp^3 ($\phi = 54.7°$) hybridization of the valence orbitals of the donor oxygen atom O(2).

For comparison, the proton positions determined from the electron density maps in Figure 3 correspond to ϕ values of ±44°, the position determined for lepidocrocite by Christensen and Christensen (1978) is at $\phi = 48°$, and the line of centers between the two O(2) atoms across the interlayer region is at $\phi = \pm 43°$. In fact, because one terminal hydrogen atom in each chain of the cluster in Figure 5b is left 'dangling' with no acceptor oxygen atom, it is likely that the calculated minimum-energy position would move to a somewhat higher ϕ value if larger segments of the chains could be included. The energy calculations therefore suggest that a structure with asymmetric chains of hydrogen bonds is significantly more stable than one containing chains of bifurcated bonds, consistent with the observed electron-density distribution.

Furthermore, the energy of a cluster with all protons positioned midway between O(2) atoms at the centers of symmetry was calculated to be 51 kcal/mole higher than at position 4 in Figures 4b and 5b, indicating that there should be no electron density near (0, 0, 0), consistent with the earlier rejection of the symmetrical hydrogen-bond model. Fripiat *et al.* (1967) calculated a similar value of 26 kcal for the potential energy barrier and suggested that this value was sufficiently low to permit proton tunneling between corresponding positions on either side of the center of symmetry. However, the separation between proton positions on opposite sides of the mirror plane at x = 0.25 is only 1.08 Å (compared to 1.20 Å across the center), and the EHT energy barrier in this direction is more than an order of magnitude smaller (i.e., 2.2 kcal). It therefore seems much more likely that coherent reversal of chain dipole moments would occur by a process of proton tunneling across the mirror plane rather than across the center.

It is clear from the above discussion that very little energy is required to reverse the dipole moment of a coherent chain of asymmetric hydrogen bonds, but the question remains as to whether the observed distribution of hydrogen-atom electron density is a reflection of disorder *within* or *between* individual chains. To test the former possibility a calculation was performed in which the orientation of one hydroxyl group in each of the three chains in Figure 5b was reversed relative to the others. The resultant total energy was ~10 kcal higher for each reversed hydroxyl group, suggesting that the disordering of hydrogen atom positions within individual chains is highly unfavorable. On the other hand, reversal of the orientation of all three hydroxyl groups in the central chain of Figure 5b to produce a cluster with antiparallel-chain dipole moments resulted in a destabilization of less than 0.2 kcal, indicating an essentially negligible level of interaction across the 2.865-Å gap separating adjacent chains. The EHT calculations therefore admit the possibility that at room temperature the boehmite structure is disordered in regard to the polarity of adjacent hydrogen-bond chains, thereby producing an overall *Amam* space group as observed in diffraction experiments.

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Резюме—Кристаллическая структура натурального бемита, AlOOH, Твейдалена, Лангезундсфьерден, Норвегия, с a = 3,693(1), b = 12,221(2), и c = 2,865(1) Å была усовершенствована на основе данных по рентгеновской однокристальной дифракции (MoKα; максимум 2θ = 120°) до величины R_w = 0,032 в пространственных группах *Amam* и $A2_1am$. В обоих случаях было обнаружено, что протон занимает положения типа (x, 0,038, 0), где x = 0,104 и 0,396, около 0,75 Å от донатора кислорода, соответственно присутствию цепных асимметрических водородных связей со случайной полярностью параллельной оси a и указывая на то, что эффективной пространственной группой является *Amam*. Значительная плотность электронов не наблюдалась ни в центре (0, 0, 0), ни в положении (1/4, y, 0), соответствующем симметрическим и раздвоённым водородным связям, соответственно, между слоями октаэдра.

Расчёты полной энергии характерной части структуры бемита, как функции ориентации гидроокиси, при использовании полуэмпирических молекулярных орбит типа Глюкла находятся в согласии с наблюдаемым распределением плотности электронов, указывая преимущественно на: (1) скорее sp^3, чем sp^2, гибридизацию орбит донатора кислорода, и (2) скорее асимметрические, чем симметрические водородные связ. Показано, что неупорядоченность положений атомов водорода внутри индивидуальных цепей водородных связей, вероятно, при комнатной температуре, намного меньше, чем неупорядоченность между соседними вполне когерентными цепями. [E.C.]

Resümee—Die Kristallstruktur von natürlichem Boehmit, AlOOH, von Tveidalen, Langesundsfjord, Norwegen, mit a = 3,693(1), b = 12,221(2), und c = 2,865(1) Å, wurde anhand von Einzelkristalldiffraktometerdaten (MoKα, Maximum 2θ = 120°) auf einen R_w-Wert von 0,032 in den Raumgruppen *Amam* und $A2_1am$ verfeinert. In beiden Fällen besetzt das Proton die Position (x, 0,038, 0), wobei x = 0,104 und 0,396 ist und etwa 0,75 Å vom Donor-Sauerstoffatom entfernt ist. Dies stimmt damit überein, daß Ketten von assymmetrischen Wasserstoffbrücken vorhanden sind, deren ungefähre Polarität parallel zur a-Achse liegt, was darauf hindeutet, daß die tatsächliche Raumgruppe *Amam* ist. Es wurde keine bemerkenswerte Elektronendichte beobachtet, weder im Zentrum (0, 0, 0) noch in der Position (1/4, y, 0), entsprechend symmetrischen bzw. sich gabelnden Wasserstoffbrücken zwischen den Oktaederschichten.

Berechnungen der Gesamtenergie eines repräsentativen Teils der Boehmitstruktur als eine Funktion der Hydroxyl-Orientierung mittels halbempirischer MO-Rechnungen (Hückel-Methode) stimmen mit der beobachteten Verteilung der Elektronendichte überein. Dies deutet darauf hin, daß (1) eher eine sp^3—als eine sp^2—Hybridisierung des Donor-Sauerstofforbitals erfolgt, und (2) eher assymmetrische als symmetrische Wasserstoffbrücken vorhanden sind. Es zeigt sich, daß eine Unordnung von Wasserstoffatom-Positionen innerhalb bestimmter Ketten von Wasserstoffbrücken bei Raumtemperatur weniger wahrscheinlich ist als eine Unordnung zwischen benachbarten koherenten Ketten. [U.W.]

Résumé—La structure cristalline d'une boéhmite naturelle AlOOH de Tveidalen, Langesundsfjorden, Norvège, avec a = 3,693(1), b = 12,221(2), et c = 2,865(1) Å a été rafinée à partir de données de diffraction aux rayons-X d'un seul cristal (MoKα; 2θ maximum = 120°) à une valeur R_w de 0,032 dans les groupes d'espacement *Amam* et $A2_1am$. Dans les deux cas on trouve le proton occupant les positions de type (x, 0,038, 0), où x = 0,104 et 0,0396, à à peu près 0,75 Å de l'atome d'oxygène donateur, correspondant à la présence de chaînes de liens d'hydrogène assymétriques avec une polarité au hasard parallèles à l'axe a, et indiquant que le groupe d'espacement éffectif est *Aman*. Aucune densité d'électron significative n'a été observée ni au centre (0, 0, 0) ni à la position (1/4, y, 0), correspondant aux liens d'hydrogène symmétriques et bifurqués, respectivement, entre les couches d'octaèdres.

Des calculs de l'énergie totale d'une portion représentative de la structure de la boéhmite en tant que fonction de l'orientation hydroxyl, utilisant des orbites moléculaires semi-empiriques de type Hückel, s'accordent avec la distribution de densité d'électrons observée en suggérant une préférence pour (1) l'hybridisation sp^3, plutôt que sp^2, des orbites d'atome d'oxygène donateur, et (2) des liens d'hydrogène assymétriques plutôt que symmétriques. Le désordre des positions de l'atome d'hydrogène dans des chaînes individuelles de liens d'hydrogène a été montré être beaucoup moins probable à température ambiante que le désordre entre des chaînes adjacentes totalement cohérentes. [D.J.]