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## Hydroxyl Orientations in Gibbsite and Bayerite

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The hydrogen positions in bayerite and gibbsite [both Al(OH)<sub>3</sub>] have been determined by minimizing the electrostatic energy as a function of hydroxyl orientation for a fixed O–H distance. The hydrogen positions in gibbsite are known from an accurate X-ray refinement and one of the H–H distances is short (2.122 Å). The point charge model (fully ionized atoms) separates these hydrogens resulting in deviations from the observed OH orientations of approximately 18°. Several models with reduced charges on the ions were refined with no improvement in the hydroxyl orientations. The addition of a modifying function to simulate *sp*<sup>3</sup> hybridization of the oxygens resulted in hydrogen positional parameters which are within two standard deviations (X-ray) of the X-ray refinement for 16 of the 18 positional parameters. Hydrogen positions have been determined for all six geometrically possible hydroxyl orientations and the correct one has the lowest electrostatic energy. There are three geometrically possible hydroxyl orientations for bayerite and all three have been refined. The model with the lowest energy has, between the layers, one hydroxyl nearly normal to the hydroxide layer, (001), participating in a single hydrogen bond, a second hydroxyl inclined at 58.3° to (001) participating in a single hydrogen bond and a third hydroxyl in the surface of the hydroxide layer participating in a bifurcated bond.

### Introduction

The naturally occurring polymorphs of Al(OH)<sub>3</sub> are the minerals gibbsite, bayerite and nordstrandite. Gibbsite is readily found in nature; but both bayerite and

nordstrandite are extremely rare and yet bayerite, and to a lesser extent nordstrandite, are readily precipitated under alkaline conditions while gibbsite forms very slowly (Schoen & Roberson, 1970). Several mechanisms have been proposed to explain the appearance of one

or the other of these polymorphs during precipitation of aluminum hydroxide. These include screw dislocations (van Nordstrand, Hettinger & Keith, 1956), crystal growth upon substrates of other minerals (Barnhisel & Rich, 1965) and the influence of rates of precipitation (Hsu, 1966). More recently, Schoen & Roberson (1970) have proposed that the hydroxyl orientations on the surfaces of the hydroxide layers will determine the mode of stacking of the layers and hence the polymorph formed. These hydroxyl orientations are determined by the type of cationic aluminum complex in the precipitating solution which in turn is governed by  $pH$ .

The crystal structures of gibbsite and bayerite have been determined, but not nordstrandite. A recent X-ray refinement of the gibbsite structure which included the location and refinement of all the hydrogen atoms has been published by Saalfeld & Wedde (1974). The refinement of the bayerite structure (Rothbauer, Zigan & O'Daniel, 1967) using both X-ray and neutron powder diffraction data was not very definitive in locating the hydrogen atoms. Their positions have been criticized by Baur (1972) who has proposed two alternative arrangements of the hydroxyls based on geometrical arguments and the assumption that all hydrogens lie between the layers.

Hydroxyl hydrogen positions in inorganic structures have been determined by several methods other than the normal X-ray or neutron diffraction procedures. These are summarized in Baur (1972) and Hamilton & Ibers (1968). One approach has been to determine the hydrogen positions for which the total electrostatic energy of the crystal is a minimum with the constraint that the O-H distance is fixed at some reasonable value. This procedure has been used for hydrogens belonging to water molecules (Baur, 1965; Ladd, 1968) as well as hydroxyl hydrogens (Giese, 1971; Giese, Weller & Datta, 1971). In all of the hydroxyl studies, the number of hydroxyl groups was small with usually only one in the asymmetric part of the unit cell. The aluminum hydroxides are a much more difficult problem because of the large number of hydroxyls relative to the other atoms in the structures (six for gibbsite and three for bayerite) and the fact that there are a number of different geometrically reasonable arrangements for the hydroxyls. In view of these difficulties, the present study was undertaken to determine if the correct OH arrangement can be determined by using the electrostatic energy method for gibbsite and, if so, to determine the hydrogen positions for bayerite.

### Calculations

The electrostatic energy calculations were made with a modified version of the computer program *MANIOC* (Baur, 1965). The procedure for minimizing the energy for structures with more than one hydroxyl is described in detail elsewhere (Giese & Datta, 1973).

### Gibbsite

The *AB* closest packed arrangement of hydroxyls in each layer has  $\frac{2}{3}$  of the octahedral sites occupied by aluminum to form a dioctahedral structure. The layers are in an  $-AB-BA-AB-$  sequence so that a hydroxyl in one layer is close to only one hydroxyl in the next layer. Therefore, if one OH is oriented perpendicular to the hydroxide layer, the neighboring OH must be oriented in the plane of its hydroxide layer. There are three unique hydroxyls on one surface and three on the other surface of the layer so that a total of six different arrangements is geometrically possible.

As a check on the accuracy of the approach, the hydrogen positions of Saalfeld & Wedde were used as initial positions for the energy calculations and two cycles of refinement yielded the positions listed in Table 1 along with the angles  $H(X)-O-H(EE)$  where  $H(X)$  is the hydrogen determined from the X-ray study of Saalfeld & Wedde and  $H(EE)$  is the electrostatic energy hydrogen position. These angles indicate that

Table 1. *Positional parameters ( $\times 10^3$ ) for the hydrogen atoms in gibbsite*

The angles in the last column for the second set of positions are H-O-H angles between corresponding hydrogens determined by Saalfeld & Wedde and those determined by the electrostatic energy minimization.

	<i>x</i>	<i>y</i>	<i>z</i>	Angle
From Saalfeld & Wedde (1974)				
H(1)	101	152	-124	
H(2)	595	573	-98	
H(3)	503	137	-190	
H(4)	-29	801	-107	
H(5)	293	724	-196	
H(6)	815	160	-190	
Initial electrostatic energy calculation (two cycles) with unmodified electrostatic energy function				
H(1)	71	185	-142	18.2°
H(2)	575	557	-94	2.4
H(3)	496	128	-208	4.9
H(4)	-63	805	-112	18.0
H(5)	294	713	-205	3.5
H(6)	808	162	-201	3.2

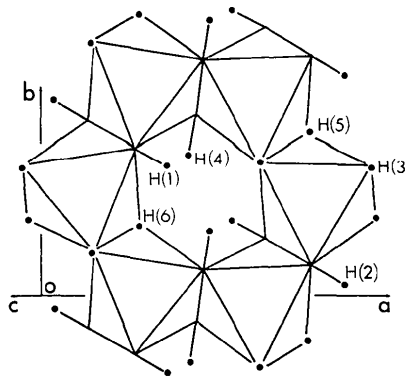


Fig. 1. A projection of one layer of the gibbsite structure onto (001). The oxygen octahedra coordinating the aluminum ions are outlined with solid lines joining the hydrogens (small dots) and oxygens of the hydroxyl groups.

the hydrogen positions determined by the energy minimization are in close agreement with the actual structure except for H(1) and H(4) which are misoriented by  $18.2$  and  $18.0^\circ$  respectively. The explanation for this error is seen in Fig. 1, a projection of the X-ray structure onto (001). Both H(1) and H(4) are horizontal and are oriented with the hydrogens toward the same empty octahedral site which brings them close to each other ( $2.122 \text{ \AA}$ ). The point charge model tries to reduce the electrostatic repulsion by rotating the OH's away from each other and moving the hydrogens slightly away from the hydroxide layer thus increasing the H-H distance. This repulsion might be reduced if the true charges on the ions were less than the full charges used for the calculation. Several recent estimates of true anion and cation charges in inorganic compounds have been made (Bartenev, Varisov, Gol'danskii, Prokop'ev & Tsyganov, 1972; Urusov, 1967) and show that the true charges are less than the ideal, fully ionized charges. There is, however, little agreement among different experimental techniques as to the values of the real charges, so three charge combinations were chosen for refinement: (1)  $+1.5, -1.0,$

$+0.5$ ; (2)  $+3.0, -1.5, +0.5$ ; (3)  $+3.0, -2.0, +0.5$  for aluminum, oxygen and hydrogen respectively. The hydroxyl orientations were refined for each charge combination and the resulting H(EE)-O-H(X) angles were calculated. None of the three was substantially better than the full charge refinement. The angular deviations ranged from a minimum of  $15.7^\circ$  [H(1), charge set No. 1] to a maximum of  $21.1^\circ$  [H(4), charge set No. 2]. This suggested that another approach was needed. The assumptions inherent in the ionic model do not take account of such things as bond hybridization of the  $sp^3$  type for the hydroxyl oxygen. Such hybridization tends to keep the Al-O-H angles near the tetrahedral angle of  $109.47^\circ$  and since there are two aluminum ions coordinating each oxygen the tendency is also to keep both angles equal. The ionic model can be readily altered to account for the hybridization by adding a modifying function to the calculated electrostatic energy. The empirical function used is the simple relation  $-cax^2$  - where  $x$  is the difference between the angles,  $a$  is a constant, and  $c$  is a weighting factor which varies linearly from 1 when the average Al-O-H angle is  $109.47^\circ$  to 0 when the

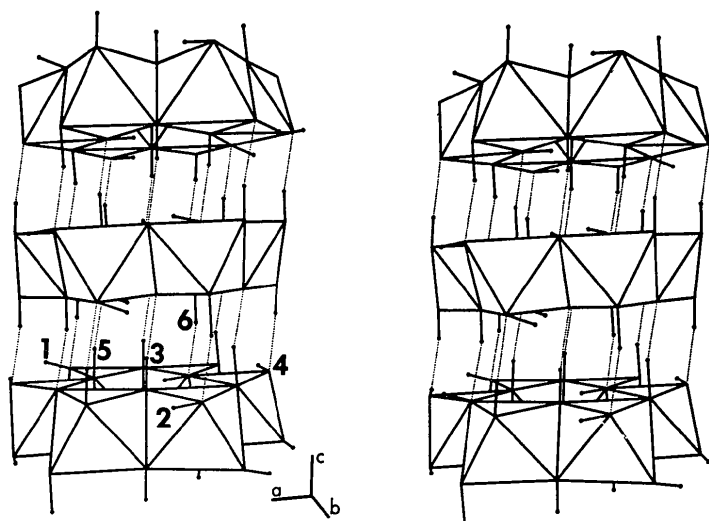


Fig. 2. A stereoscopic view of the gibbsite structure viewed down the  $b$  axis. The origin of the unit cell is at the lower rear right hand corner and the axial orientations are as shown in the insert.

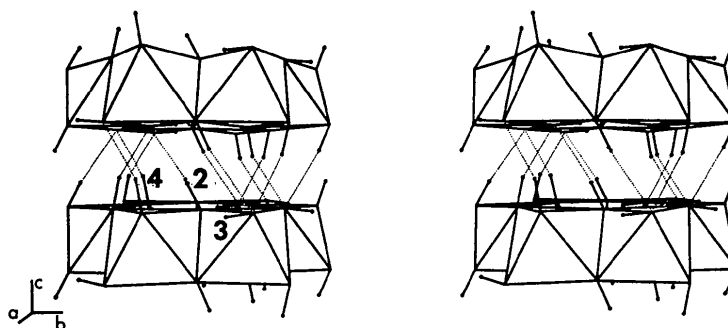


Fig. 3. A stereoscopic view of the bayerite structure viewed down the  $a$  axis. The origin of the unit cell is at the lower rear left-hand corner and the axial orientations are as shown in the insert.

average angle is  $124$  or  $92.94^\circ$  (vertical OH). The new function to be minimized is:

$$-\frac{e^2}{2} \sum_r^N \sum_s^\infty \frac{Z_r Z_s}{R_{rs}} + cax^2$$

where

$e$  = electron charge

$Z$  = ion charge

$R$  = interionic distance

$N$  = number of atoms in the unit cell

$x$  = difference between the two Al–O–H angles

$y$  = average of the two Al–O–H angles

$a$  = numerical constant

$c = -0.0605y + 7.6230$  ( $109.47 \leq y \leq 126.00$ )

$= 0.0605y - 5.6225$  ( $92.94 \leq y \leq 109.47$ )

$= 0.0$  ( $y < 92.94$ ;  $y > 126.00$ ).

When this modification was added to the computer program, the refined positions were in better agreement with the observed structure. Too large a value for  $a$  led to poor results for several hydrogens because the real structure does not have all pairs of angles exactly equal. A satisfactory weight was found by trial and error for  $a=0.01$  and this was used for all subsequent calculations of gibbsite and bayerite.

Table 2. Hydrogen positions ( $\times 10^3$ ) as determined by electrostatic energy minimization

The last column contains angles as described in Table 1 and the standard deviations (in parentheses) for the second set of data are those of the X-ray structure of Saalfeld & Wedde.

	$x$	$y$	$z$	Angle
O–H distance for all hydrogens = $0.97 \text{ \AA}$				
H(1)	79	142	-141	$8.3^\circ$
H(2)	573	561	-94	3.5
H(3)	495	122	-204	6.7
H(4)	-40	817	-122	5.9
H(5)	296	714	-205	3.6
H(6)	806	158	-201	4.5

O–H distances adjusted to agree with those of Saalfeld & Wedde

	$x$	$y$	$z$
H(1)	101 (0.02)	159 (0.69)	-135 (2.10)
H(2)	592 (0.47)	580 (0.66)	-96 (0.46)
H(3)	492 (2.24)	123 (1.42)	-191 (0.14)
H(4)	-39 (1.90)	800 (0.12)	-112 (1.13)
H(5)	296 (0.50)	714 (0.88)	-196 (0.07)
H(6)	807 (1.52)	157 (0.38)	-190 (0.00)

Initial coordinates were generated for all six sets of hydroxyl orientations and each model went through three cycles of refinement. The structure with the largest electrostatic energy corresponds to that of Saalfeld & Wedde and the resulting positional parameters and angular deviations from the experimentally determined structure are listed in Table 2. The small angular deviations between the refined electrostatic model and the X-ray hydrogen positions indicate the essential success of the modifying function. Another way of comparing the two sets of positional parameters is to recalculate those for the electrostatic model so that the OH orientations are unchanged but the O–H distances are identical with the experimentally determined values of Saal-

feld & Wedde. These recalculated hydrogen positions are listed as the last group in Table 2. Following each positional parameter is the number of standard deviations (X-ray) difference between the two sets of parameters. Only two exceed two s.d.'s and most are within one s.d. indicating that at the 99% confidence level the two sets of parameters are identical. Fig. 2 is a stereoscopic view of the gibbsite structure looking along the  $b$  axis.

### Bayerite

The stacking arrangement of the oxygens in bayerite is  $-AB-AB-$  so that each hydroxyl is close to three oxygens in the adjacent layer allowing the formation of one or more hydrogen bonds to any of these oxygens. Baur (1972) assumed in his geometrical calculation that all three hydrogens were situated between the hydroxide layers participating in hydrogen bonds. Therefore, an initial calculation was made with all three hydroxyls oriented approximately at  $90^\circ$  to (001). The refined parameters, however, corresponded to two perpendicular (or nearly so) hydroxyls and the third oriented in the (001) plane with the hydrogen near the vacant octahedral site. There are three geometrically different ways of arranging the hydroxyls in this manner and each of these models went through three cycles of refinement with the weighting scheme as described in an earlier section. The resulting positional parameters for the model with the largest electrostatic energy are listed in Table 3 along with the two proposed hydroxyl orientations of Baur (1972) transformed to agree with the positions reported here. The major difference, H(3), is due to Baur's assumption that the hydrogen atoms lie between the layers where they contribute to the interlayer bonding. The repulsion between adjacent hydrogens and the existence of a vacant octahedral site nearby make it energetically advantageous for one of the hydroxyls to be in the (001) plane with the hydrogen end toward the vacant site. Subsequently, the hydroxyl orientations were redetermined using the unmodified electrostatic energy function and the resulting average difference between the positional parameters of both sets is  $0.0018$ . Thus in the case of bayerite where there is no difficulty due to the close approach of hydrogens, both the unmodified and modified energy functions yield essentially the same hydroxyl orientations and either could be used for similar structures. Fig. 3 is a stereoscopic view of the bayerite structure looking along the  $a$  axis.

Table 4 is a listing of distances about the hydrogen atoms in gibbsite and bayerite based on the models with minimum electrostatic energy. Studies of the interlayer bonding in the kaolin minerals (Giese, 1973) have indicated that  $H \cdots O(A)$  distances less than  $2.6 \text{ \AA}$  represent long hydrogen bonds with the strength increasing as the distance decreases. Assuming that this limiting distance is applicable to bayerite and gibbsite, all hydrogens in gibbsite are participating in single hydrogen bonds except H(2) which is bifurcated with

Table 3. *Hydrogen positions* ( $\times 10^3$ ) *for bayerite as proposed by Baur (1972) and as calculated by the electrostatic energy minimization*

	x	y	z	Angle with Baur II
Arrangement I (Baur)				
H(2)	200	490	589	
H(3)	751	280	593	
H(4)	478	370	326	
Arrangement II (Baur)				
H(2)	184	490	584	
H(3)	551	372	684	
H(4)	297	264	413	
Electrostatic energy model				
H(2)	198	535	610	3.2°
H(3)	612	421	800	45.6
H(4)	323	287	430	14.8

Table 4. *The environment about the hydrogen atoms in gibbsite and bayerite*

A hydrogen bond donor (or potential donor) is designated *D* and the acceptor is *A*. The angle  $\varrho$  is the angle between the OH and (001) and a positive value indicates that the hydrogen lies between the hydroxide layers.

	<i>D</i>	<i>A</i>	<i>D-A</i>	<i>H-A</i>	<i>D-H...A</i> angle	$\varrho$ (OH)
Gibbsite						
H(1)	O(1)	O(6)	3.143 Å	2.315 Å	142.8°	17.4°
H(2)	O(2)	O(5)	3.245	2.523	131.2	-4.7
		O(3)	3.047	2.277	135.7	
H(3)	O(3)	O(4)	2.834	1.873	170.4	85.5
H(4)	O(4)	O(6)	2.986	2.087	153.3	3.0
H(5)	O(5)	O(1)	2.784	1.820	172.0	85.5
H(6)	O(6)	O(2)	2.894	1.942	166.4	86.1
Bayerite						
H(2)	O(2)	O(2)	3.014	2.512	112.1	58.3
		O(3)	3.214	2.255	169.9	
		O(4)	3.237	2.766	110.6	
H(3)	O(3)	O(2)	3.218	2.486	132.1	-6.3
		O(4)	3.201	2.362	144.4	
H(4)	O(4)	O(2)	3.237	2.605	123.0	77.2
		O(3)	3.157	2.545	121.1	
		O(3)	2.915	1.994	157.8	

one bond [to O(5)] being rather weak. Bayerite has all hydrogens participating in more complicated hydrogen bonds. H(2) (between the layers) forms a hydrogen bond to O(3) and possibly, using the criteria above, a weak interaction to O(2) but the O-H...O angle of 112.1° is smaller than one would expect for a hydrogen bond. The hydrogen pointing towards the empty octahedron (in the layer), H(3), forms a bifurcated hydrogen bond and the last hydrogen, H(4), (between the layers) forms a strong hydrogen bond with O(3) and is moderately near two other oxygens, O(2) and O(3). The possible contribution of these longer H...O distances cannot be assessed at the present time.

### Conclusions

The determination of hydroxyl hydrogen positions in polyhydroxy structures such as gibbsite and bayerite by minimizing the electrostatic energy is a useful technique in that it allows one to investigate many pos-

sible hydroxyl configurations and evaluate them quantitatively in terms of their electrostatic energy. The correct hydroxyl configuration is the one with minimum energy.

In cases where the structure is such that two or more hydroxyl hydrogens are in close proximity, as in gibbsite, so that the H...H distances are of the order of 2.1 Å or less and the hydroxyls have some orientational freedom, the simple electrostatic model must be modified to account for  $sp^3$  hybridization of the hydroxyl oxygen. Even with this inexact modification, the accuracy of the hydroxyl orientations is very good and the OH orientations are not statistically different from the very accurate X-ray refinement of gibbsite. Use of the modified electrostatic energy function to determine hydroxyl orientations in structures where there are no close H...H distances produces essentially the same hydrogen positions as the unmodified function.

The hydroxyl orientations in gibbsite and bayerite are very different with the former having OH's nearly normal to or in the plane of the hydroxide layer. Bayerite has one hydroxyl nearly normal to the hydroxide layer, a second at an inclined angle (58.3°) and a third in the layer. The interlayer hydrogen bonds in gibbsite are single and relatively short while in bayerite they are longer and more complex. These differences support the mechanism proposed by Schoen & Roberson (1970) which links the OH orientations to the mode of stacking of the hydroxide layers.

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