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# Refinement of the crystal structure of gibbsite, $Al(OH)_3$

By H. SAALFELD and M. WEDDE

Mineralogisch-Petrographisches Institut der Universität Hamburg

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**Auszug**

Mit Hilfe neuer Diffraktometerdaten wurde eine Strukturverfeinerung von Gibbsit nach der Methode der kleinsten Quadrate durchgeführt. Die Strukturbestimmung von MEGAW (1934) konnte bestätigt werden. Die verfeinerten Atomabstände sowie die Wasserstofflagen werden mitgeteilt.

**Abstract**

On the basis of new diffractometer data the structure of gibbsite has been refined by least-squares calculations. The structure determination by MEGAW (1934) was confirmed. The revised interatomic distances as well as the hydrogen positions are reported.

## Introduction

Gibbsite (hydrargillite), $Al(OH)_3$, is a sheet structure crystallizing usually in pseudohexagonal platelets or prisms with monoclinic symmetry. Occasionally it may also crystallize with triclinic symmetry (SAALFELD, 1960). PAULING (1930) first proposed a crystal structure. The monoclinic structure was originally determined by MEGAW (1934). Gibbsite consists of double layers of OH ions with Al ions occupying two thirds of the octahedral interstices within the layers. Each double layer is located with respect to its neighbors so that OH ions of adjacent layers are situated directly opposite each other. Thus, a layer sequence AB—BA—AB— · · · results. Hydrogen bondings operate between the OH ions of adjacent double layers. A proposal concerning the hydrogen positions in the gibbsite structure was made by BERNAL and MEGAW (1935). KROON and STOLPE (1959) deduced a scheme of the spatial distribution of the hydrogen bonds based upon proton magnetic resonance measurements. This, however, does not agree with the suggestion of BERNAL and MEGAW.

The present structure refinement of gibbsite was undertaken to revise the interatomic distances and to establish the locations of the hydrogen atoms.

Table 1. *Final positional parameters*
(standard deviations in brackets)

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Al(1) | 0.1679(1) | 0.5295(2) | − 0.0023(1) |
| Al(2) | 0.3344(1) | 0.0236(2) | − 0.0024(1) |
| O(1) | 0.1779(2) | 0.2183(4) | − 0.1115(2) |
| O(2) | 0.6692(2) | 0.6558(4) | − 0.1023(2) |
| O(3) | 0.4984(2) | 0.1315(4) | − 0.1044(2) |
| O(4) | − 0.0205(2) | 0.6293(4) | − 0.1068(2) |
| O(5) | 0.2971(2) | 0.7178(4) | − 0.1052(2) |
| O(6) | 0.8194(2) | 0.1491(4) | − 0.1015(2) |
| H(1) | 0.101(6) | 0.152(10) | − 0.124(5) |
| H(2) | 0.595(6) | 0.573(10) | − 0.098(5) |
| H(3) | 0.503(5) | 0.137(10) | − 0.190(5) |
| H(4) | − 0.029(5) | 0.801(10) | − 0.107(4) |
| H(5) | 0.293(6) | 0.724(11) | − 0.196(6) |
| H(6) | 0.815(5) | 0.160(9) | − 0.190(5) |

Table 2a. *Thermal parameters* ($\times 10^4$) *of the non-hydrogen atoms*
The anisotropic temperature factors are of the form:
$T = \exp - (h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2klB_{23} + 2hlB_{13})$
(Standard deviations in brackets)

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| Al(1) | 12(1) | 47(3) | 23(1) | − 1(1) | 5(1) | 2(1) |
| Al(2) | 12(1) | 48(3) | 23(1) | 1(1) | 4(1) | 0(1) |
| O(1) | 13(3) | 83(8) | 29(2) | − 8(4) | − 1(2) | − 3(3) |
| O(2) | 12(3) | 89(8) | 29(2) | − 8(4) | 0(2) | − 3(3) |
| O(3) | 18(2) | 86(8) | 24(2) | 0(4) | 2(2) | 5(3) |
| O(4) | 15(2) | 79(8) | 30(2) | − 3(4) | 2(2) | 5(3) |
| O(5) | 22(2) | 85(8) | 24(2) | − 4(4) | 5(2) | − 1(3) |
| O(6) | 19(2) | 82(8) | 23(2) | − 2(4) | 2(2) | − 2(3) |

Table 2b
*Isotropic temperature parameters of the hydrogen atoms with standard deviations*

| Atom | H(1) | H(2) | H(3) | H(4) | H(5) | H(6) |
|---|---|---|---|---|---|---|
| $B$ | 1(1) | 1(1) | 1(1) | 0(1) | 2(1) | 1(1) Å$^2$ |

## Experimental

A crystal plate (diameter 0.2 mm) from Langesundfjord, Norway, was used for the determination of the lattice constants and for the intensity measurements. The following unit-cell parameters were obtained by a least squares adjustment of high-angle Cu$K\alpha$ reflections:

$$a = 8.684 \pm 0.001 \text{ Å},$$
$$b = 5.078 \pm 0.001 \text{ Å},$$
$$c = 9.736 \pm 0.002 \text{ Å},$$
$$\beta = 94.54 \pm 0.01^\circ.$$

There are eight formula weights per unit cell. The intensity measurements of 816 reflections were carried out on an automated Siemens diffractometer with Cu$K\alpha$ radiation. Corrections for absorption and extinction were applied. The statistical $N(z)$ test (HOWELL, PHILLIPS

Table 3. *Interatomic distances*
In brackets are listed the distances given by MEGAW (1934)

| | | |
|---|---|---|
| a) Al—Al distances in the double layer | | |
| Al(1)—Al(2′) | 2.896(1) Å | |
| Al(1)—Al(1′) | 2.936(2) | |
| Al(1)—Al(2) | 2.948(1) | |
| Al(2)—Al(2′) | 2.883(2) | |
| Mean | 2.92(3) Å | |
| b) Al—O distances (octahedral groups) | | |
| Al(1)—O(5) | 1.831(2) | [1.73] |
| —O(4′) | 1.906(2) | [1.98] |
| —O(1) | 1.911(2) | [1.91] |
| —O(6′) | 1.918(2) | [1.73] |
| —O(2′) | 1.922(2) | [1.85] |
| —O(4) | 1.926(2) | [1.95] |
| Mean | 1.90(4) | [1.86(11)] |
| Al(2)—O(5′) | 1.862(2) | [1.90] |
| —O(3) | 1.882(2) | [1.94] |
| —O(3′) | 1.889(2) | [1.80] |
| —O(2′) | 1.923(2) | [1.97] |
| —O(1) | 1.930(2) | [1.87] |
| —O(6) | 1.947(2) | [2.14] |
| Mean | 1.91(3) | [1.94(12)] |

Table 3. *(Continued)*

c) O—O *distances*. The types I—V are identical with those given by MEGAW (1934)

| | This work | MEGAW (1934) | | This work | MEGAW (1934) |
|---|---|---|---|---|---|
| | I | | | III | |
| O(1) —O(2′) | 2.463(3) Å | 2.47 Å | O(4) —O(5) | 2.793(3) Å | 2.72 Å |
| O(1′)—O(2) | 2.463(3) | 2.47 | O(5) —O(1) | 2.739(3) | 2.76 |
| O(4) —O(4′) | 2.462(3) | 2.51 | O(1) —O(4) | 2.709(3) | 2.76 |
| O(3) —O(3′) | 2.431(4) | 2.52 | O(1) —O(3) | 2.814(3) | 2.90 |
| O(5) —O(6′) | 2.419(3) | 2.48 | O(3) —O(5′) | 2.733(3) | 2.88 |
| O(5′)—O(6) | 2.419(3) | 2.48 | O(5′)—O(1) | 2.743(3) | 2.78 |
| Mean | 2.44(2) | 2.49(3) | O(3) —O(6) | 2.787(3) | 2.84 |
| | | | O(6) —O(2′) | 2.824(3) | 2.84 |
| | II | | O(2′)—O(3) | 2.834(3) | 2.76 |
| O(4) —O(6′) | 2.805(3) | 2.64 | O(6) —O(2) | 2.885(3) | 2.92 |
| O(4′)—O(6) | 2.805(3) | 2.64 | O(2) —O(4) | 2.701(3) | 2.66 |
| O(5) —O(2′) | 2.770(3) | 2.75 | O(4) —O(6) | 2.810(3) | 2.66 |
| O(5′)—O(2) | 2.770(3) | 2.75 | Mean | 2.78(6) | 2.79(8) |
| O(1) —O(4′) | 2.728(3) | 2.81 | | | |
| O(1′)—O(4) | 2.728(3) | 2.81 | | IV | |
| O(2) —O(3′) | 2.793(3) | 2.96 | O(5) —O(2) | 3.245(3) | 3.32 |
| O(2′)—O(3) | 2.793(3) | 2.96 | O(2) —O(3) | 3.047(3) | 3.10 |
| O(3) —O(5′) | 2.707(3) | 2.65 | O(3) —O(5) | 3.453(3) | 3.46 |
| O(3′)—O(5) | 2.707(3) | 2.65 | O(6) —O(1) | 3.142(3) | 2.94 |
| O(6) —O(1′) | 2.788(3) | 2.79 | O(1) —O(4′) | 3.454(3) | 3.38 |
| O(6′)—O(1) | 2.788(3) | 2.79 | O(4′)—O(6) | 2.985(3) | 2.98 |
| Mean | 2.77(4) | 2.77(11) | Mean | 3.2(2) | 3.2(2) |
| | | | | V | |
| | | | O(1) —O(5″) | 2.785(3) | 2.82 |
| | | | O(2) —O(6″) | 2.894(3) | 2.82 |
| | | | O(3) —O(4″) | 2.833(3) | 2.72 |
| | | | Mean | 2.84(5) | 2.79(10) |

and ROGERS, 1950) confirmed the centrosymmetric space group $P2_1/n$. The refinement was initially based upon the atomic coordinates derived by MEGAW. Some cycles of least-squares refinement (BUSING, MARTIN and LEVY, 1962) with anisotropic thermal parameters and isotropic extinction corrections (ZACHARIASEN, 1967, 1968) reduced the residual discrepancy index $R$ to 0.032 (observed reflections only). The weighted value $R_w$ (omitting non-observed reflections) is 0.037 with $W = 1/\sigma^2(F)$ [1].

[1] $\sigma(F) = \dfrac{(I_{\text{peak}} + I_{\text{backgr}})^{1/2}}{2F}$ .

Table 4. *Interatomic distances* D—H · · · A *and bond angles* (D = donor, A = acceptor)

| D—H | | H · · · A | |
|---|---|---|---|
| O(1) —H(1) | 0.75(5) Å | H(1) · · · O(6) | 2.48(5) Å |
| O(2) —H(2) | 0.78(5) | H(2) · · · O(3) | 2.38(5) |
| O(3) —H(3) | 0.84(5) | H(3) · · · O(4′) | 2.00(5) |
| O(4′)—H(4) | 0.88(5) | H(4′) · · · O(6) | 2.21(5) |
| O(5) —H(5) | 0.88(5) | H(5) · · · O(1) | 1.91(6) |
| O(6) —H(6) | 0.86(5) | H(6) · · · O(2) | 2.04(5) |

| D—H · · · A | |
|---|---|
| O(1) —H(1)—O(6) | 149(5)° |
| O(2) —H(2)—O(3) | 144(5) |
| O(3) —H(3)—O(4′) | 177(4) |
| O(4′)—H(4)—O(6) | 148(4) |
| O(5) —H(5)—O(1) | 170(5) |
| O(6) —H(6)—O(2) | 173(4) |

The hydrogen atoms were found by subsequent difference syntheses considering the criteria concerning the location of hydrogen atoms recently given by BAUR (1972). The refinement of these positions was then carried out with isotropic thermal parameters. The atomic parameters of all atoms are listed in Table 1 using the oxygen notation of MEGAW. The thermal parameters of the heavy atoms are given in Table 2a. The isotropic *B* values of the hydrogen atoms are to be found in Table 2b. The resulting interatomic distances are collected in Table 3a—c. Distances and bond angles of the hydrogen-bond system are shown in Table 4.

## Discussion

The original structure determination carried out by MEGAW has been completely confirmed. The refined interatomic distances show that the distortions of the Al-O octahedra are not as large as assumed previously. The cycles produced coordinate shifts of up to 0.09 Å for aluminum and 0.23 Å for oxygen. The hydrogen positions are in fairly good agreement with the proposal made by BERNAL and MEGAW forty years ago. Figure 1 shows the arrangement of the oxygen and hydrogen atoms according to BERNAL and MEGAW. The selected OH groups form an irregular trigonal prism. O(1), O(4′), O(6) belong to the top of one layer and O(2), O(3), O(5) to the bottom of the next. The result of the structure refinement is shown in Fig. 2. Three of the hydrogen atoms

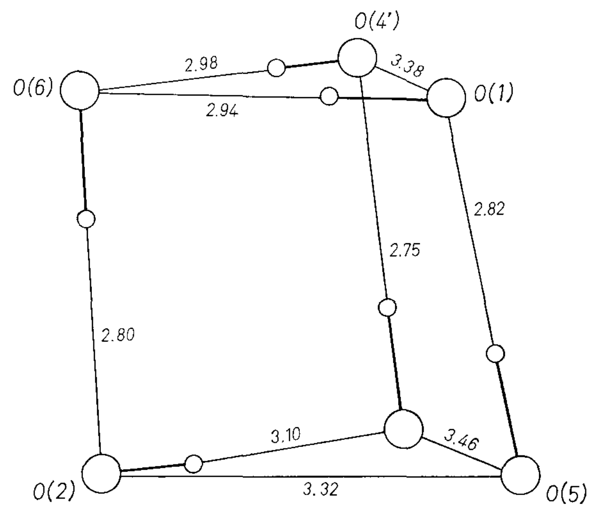


Fig. 1. Arrangement of the hydrogen bonds in gibbsite proposed by BERNAL and MEGAW (1935)

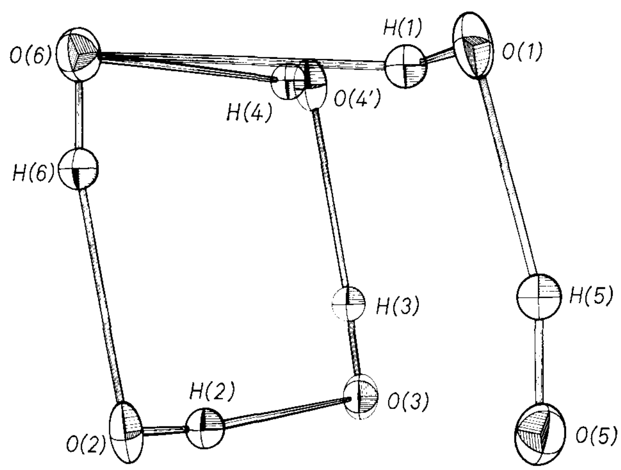


Fig. 2. Arrangement of the hydrogen bonds in gibbsite after structure refinement

are located within the oxygen layers whereas the three others are placed between the $Al(OH)_3$ layers giving rise to hydrogen bonds which link the double layers. The O—H · · · O values of 2.781, 2.829 and 2.888 Å are likewise in good agreement with the hydrogen-bridge distances found in many other compounds containing hydrogen bonds. The angular deviation D—H · · · A varies from 3—36°. The O—H distances vary from 0.75 up to 0.88 Å. These distances are shorter than those usually found with neutron-diffraction. It is, however, a well-known fact that x-ray determinations yield shorter D—X-distances.

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