

Short Communication

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Unit cell and crystal structure of nordstrandite, $\text{Al}(\text{OH})_3$. By HERMAN J. BOSMANS, *Faculteit der Landbouwwetenschappen, Katholieke Universiteit te Leuven Heverlee, Belgium*

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The X-ray powder pattern of synthetic nordstrandite, $\text{Al}(\text{OH})_3$, has been indexed by the Ito-de Wolff method on the basis of a triclinic unit cell with $Z=2$. $a=5.114$, $b=5.082$, $c=5.127$ Å; $\alpha=70^\circ 16'$, $\beta=74^\circ 0'$, $\gamma=58^\circ 28'$. A structural model based on space group $P\bar{1}$ was refined by least squares; a suggested superstructure was not taken into account. Dioctahedral $\text{Al}(\text{OH})_3$ layers similar to those in the other known $\text{Al}(\text{OH})_3$ polymorphs, are displaced with respect to one another. The hydroxyl groups of adjacent layers approach superposition. This suggests hydrogen bonding between the layers as in the case of gibbsite, but here it is a result of the shift and not of the reversal of the layers.

Nordstrandite, an uncommon crystalline $\text{Al}(\text{OH})_3$ phase, has been identified as such by van Nordstrand, Hettinger & Keith (1956) in synthetic products. Since then it has also been found to occur in nature (Wall, Wolfenden, Beard & Deans, 1962; Hathaway & Schlanger, 1962, 1965).

Two powder samples were prepared in a pure state according to the methods of Hauschild (1963). One sample was obtained by reacting slightly amalgamated Al plates in a 5% aqueous ethylenediamine solution for six weeks at room temperature, and the second sample was prepared by allowing an amorphous precipitated aluminum hydroxide gel to stand in an ethylenediamine solution at 58°C for six weeks. The X-ray powder patterns of the two samples were nearly identical, the sample prepared from the gel showing a somewhat higher degree of crystallinity. The chemical composition was found to correspond to $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (by chemical analysis $\text{Al}_2\text{O}_3 \cdot 2.93\text{H}_2\text{O}$ or 34.0% H_2O and 65.7% Al_2O_3 by weight).

The 2θ values of the nordstrandite X-ray powder pattern were measured with $\text{Cu } K\alpha$ radiation ($\lambda=1.5418$ Å) on a diffractometer with quartz powder (25%) as an internal standard. The intensities were recorded by integrating the whole peak, and subtracting the background. By using a sufficiently thick layer, the need for an absorption correction was obviated (Cullity, 1956).

All the observed peaks of the powder pattern could be indexed on the basis of a triclinic unit cell, by use of the general indexing method of Ito (1949) as extended by de Wolff (1957). The parameters, calculated from three sets of six unequivocally indexed lines, are

$$\begin{array}{lll} a=5.114 & b=5.082 & c=5.127 \text{ \AA} \\ \alpha=70^\circ 16' & \beta=74^\circ 0' & \gamma=58^\circ 28' \end{array}$$

The cell content $Z=2$ was calculated from the measured density which was 2.51 g.cm^{-3} according to Hauschild (1963), or 2.436 g.cm^{-3} according to Young as quoted by Hathaway & Schlanger (1962). The calculated density with two formula units per unit-cell is 2.400 g.cm^{-3} .

Following the standard Bravais-Buerger method (Buerger, 1957), a reduced unit cell was derived. The transform-

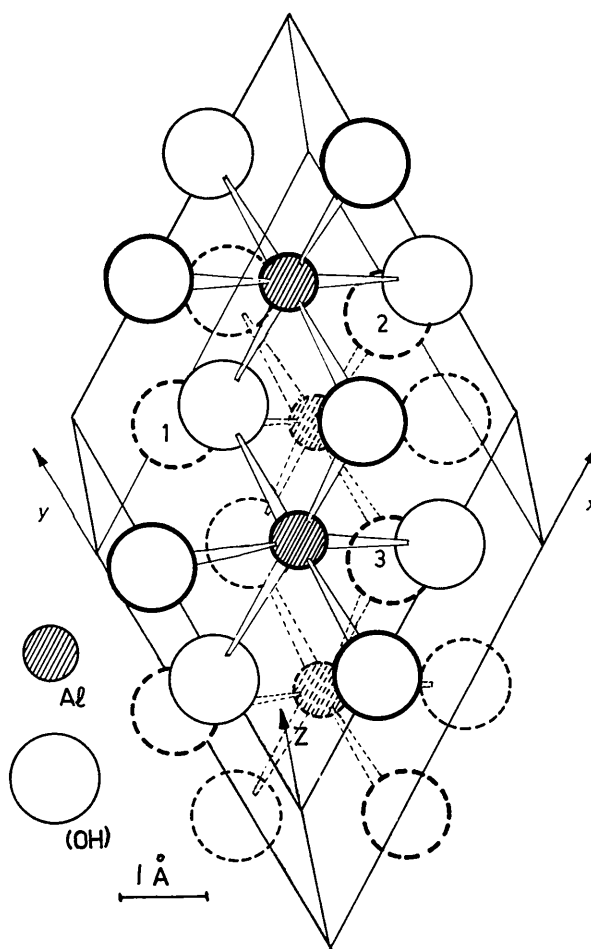


Fig. 1. Structure of nordstrandite, $\text{Al}(\text{OH})_3$, projected on the xy plane.

mation matrix for obtaining the conventional cell from the given cell is $[010/001/1\bar{1}0]$.

The reduced unit cell has the following parameters:

$$\begin{array}{lll} a_r = 5.082 & b_r = 5.127 & c_r = 4.980 \text{ \AA} \\ \alpha_r = 93^\circ 40' & \beta_r = 118^\circ 55' & \gamma_r = 70^\circ 16' \end{array}$$

Following a preliminary paper, Saalfeld & Mehrotra (1966) have reported X-ray data obtained from a natural single crystal, in samples originating from Sarawak (Wall *et al.*, 1962). They have obtained a triclinic unit-cell with $Z=8$. The original parameters of Saalfeld & Mehrotra are

$$\begin{array}{lll} a_s = 8.893 & b_s = 5.004 & c_s = 10.237 \text{ \AA} \\ \alpha_s = 92^\circ 56' & \beta_s = 110^\circ 23' & \gamma_s = 90^\circ 32' \end{array}$$

On application of a linear transformation using the matrix

$$\begin{bmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{2} \end{bmatrix}$$

it is seen that their unit cell is a quadruple of our unit cell. The transformed parameters are

$$\begin{array}{lll} a'_s = 5.122 & b'_s = 5.082 & c'_s = 5.119 \text{ \AA} \\ \alpha'_s = 69^\circ 47' & \beta'_s = 73^\circ 45' & \gamma'_s = 58^\circ 44' \end{array}$$

All 23 spacings d_{hkl} published by Saalfeld & Mehrotra (1966) agree with our values for the corresponding reflexions (in line no. 43 the indices (332) of Saalfeld & Mehrotra are in error). It should be noted that every index triple hkl of Saalfeld & Mehrotra has $(h+k)$ even and l even. Presumably the reciprocal lattice points corresponding to the superlattice give rise to unobservably weak structure lines in our material. Electron diffraction on selected areas of the sample revealed only a doubling of the c axis (unpublished data of H. Bosmans & C. de Kimpe).

We proceeded to derive a structure based on the subcell described above, ignoring the existence of a superstructure. A model based on the assumed space group $P\bar{1}$ refined satisfactorily.

The a , b and γ parameters (5.114 and 5.082 \AA , and $58^\circ 28'$) of the simple unreduced triclinic cell appear to represent a deformation of the basal plane of the ideal trigonal (hexagonal) layer-structure which has $a=5.1 \text{ \AA}$ and $\gamma=60^\circ$, as in the bayerite structure (*e.g.* Montoro, 1942; Yamaguchi & Sakamoto, 1958) and as first proposed for the structure of gibbsite (Pauling, 1930).

The basal spacing d_{001} of nordstrandite is intermediate between those of the other $\text{Al}(\text{OH})_3$ polymorphs: $d_{001}=4.72 \text{ \AA}$ for bayerite, $d_{001}=4.79 \text{ \AA}$ for nordstrandite, and $d_{002}=4.85 \text{ \AA}$ for the two gibbsite polymorphs (monoclinic and triclinic forms), the latter two containing two layers per unit cell as calculated from the data of Saalfeld (1960).

The acute angle $\alpha=70^\circ 16'$ and $\beta=74^\circ 0'$ suggest a displacement of one layer with respect to the other. Because of this shift, the hydroxyl groups of one layer are no longer directly above the interstices of the adjacent layer as in the case of bayerite, but are close to being imposed on the hydroxyl groups of adjacent layers. This suggests hydrogen bonding between the layers as in gibbsite (Bernal & Megaw, 1935), but in this case it is a result of a displacement of the layers and not of their reversal. In this way the Al atoms in neighbouring layers are shifted with respect to one another in contrast to the situation in bayerite and the two gibbsites.

An ideal trial structure with $z_{\text{OH}}=0.288$ and a mean shortening of the shared edges in the xy plane of 0.020 relative to the a and b parameters gave a reliability index $[R = \sum(|kF_o| - |F_c|) / \sum |kF_o|]$ of 23.2% for 28 non-overlapping powder reflexions. Application of the least-squares refinement program of G.S.D. King (*ERA 301*) on the

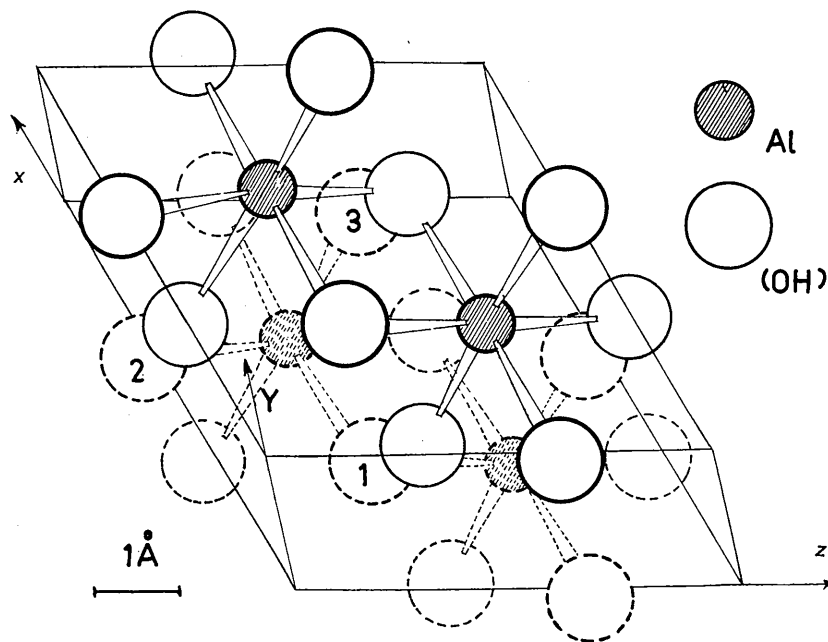


Fig. 2. Structure of nordstrandite, $\text{Al}(\text{OH})_3$, reduced cell, projected on the xz plane.

IBM 1620 computer resulted in a drop of the reliability index R to 15.1% after five cycles. The projection of the structure, based on the non-reduced cell – to permit easy comparison with the simple structure of bayerite (Yamaguchi & Sakamoto, 1958), for example – is given in Fig. 1 and the atomic coordinates are listed in Table 1. The temperature factor B was put equal to zero, because it did not refine satisfactorily.

Table 1. Atomic coordinates of nordstrandite, $\text{Al}(\text{OH})_3$

	x	y	z
Al	0.337 ± 0.005	0.333 ± 0.007	0.010 ± 0.005
(OH) (1)	0.319 ± 0.011	0.933 ± 0.012	0.242 ± 0.010
(OH) (2)	0.943 ± 0.009	0.591 ± 0.010	0.203 ± 0.009
(OH) (3)	0.622 ± 0.010	0.285 ± 0.013	0.208 ± 0.009

To conform with the conventional presentation of triclinic cells, the structure is described in terms of the reduced cell. The projection of this cell is given in Fig. 2 and the atomic coordinates are listed in Table 2.

Table 2. Atomic coordinates of nordstrandite (reduced cell)

	x_r	y_r	z_r
Al	0.670 ± 0.006	0.010 ± 0.005	0.337 ± 0.005
(OH) (1)	0.252 ± 0.014	0.242 ± 0.010	0.319 ± 0.011
(OH) (2)	0.534 ± 0.010	0.203 ± 0.009	-0.057 ± 0.009
(OH) (3)	0.908 ± 0.011	0.208 ± 0.009	0.622 ± 0.010

The reasonable agreement between the observed and calculated intensities (Table 3) suggests that the basic features of the structure of nordstrandite are probably correct,

Table 3. Powder data for nordstrandite, $\text{Al}(\text{OH})_3$

No. (Hauschild)	This work					Saalfeld <i>et al.</i>	
	d_{hkl} obs.	d_{hkl} calc.	hkl_r	I_{obs}	I_{calc}	hkl	d_{hkl} obs.
1	4.791	4.789	010	100.0	111.0	002	4.790
2	4.320	4.326	001	27.0	18.3	1 $\bar{1}$ 0	4.330
3	4.205	4.209	10 $\bar{1}$	{ 18.0	{ 14.2	110	4.220
4	4.160	4.163	100	{ 12.0	{ 13.4	200	4.162
5	3.888	3.894	110	11.0	14.6	20 $\bar{2}$	3.896
6	3.609	3.612	1 $\bar{1}$ $\bar{1}$	8.0	15.1	1 $\bar{1}$ $\bar{2}$	3.604
7	3.427	3.427	011	5.0	4.8	1 $\bar{1}$ 2	3.446
8	3.028	3.029	01 $\bar{1}$	3.3	4.2	1 $\bar{1}$ 2	3.022
9	2.848	2.845	1 $\bar{1}$ 1	3.0	5.5	112	2.867
10	2.710	2.705	1 $\bar{1}$ 0	2.5	2.2		
12	(2.501)	2.502	21 $\bar{1}$	{ 1.0	{ 1.7		
13	2.480	{ 2.489	{ 120	{	{ 0.2		
		{ 2.484	{ 1 $\bar{0}$ 2	{	{ 0.4		
		{ 2.483	{ 111	{ 12.0	{ 8.8	3 $\bar{1}$ 2	2.481
14	2.455	2.456	101	{ 8.0	{ 6.8	3 $\bar{1}$ 0	2.454
15	2.393	{ 2.394	{ 020	{ 27.0	{ 4.5	004	2.393
		{ 2.391	{ 201	{	{ 34.6	310	
16	2.333	2.331	12 $\bar{1}$	5.0	4.4		
17	2.271	2.269	11 $\bar{2}$	29.0	37.9	02 $\bar{2}$	2.265
18	2.217	{ 2.216	{ 210	{ 3.0	{ 0.1		
		{ 2.214	{ 021	{	{ 0.3		
		2.163	002	{ 0.7	{ 1.0		
19	2.146	2.146	1 $\bar{1}$ 2	{ 2.5	{ 2.0		
20	2.113	{ 2.120	{ 21 $\bar{2}$	{	{ 0.7		
		{ 2.104	{ 20 $\bar{2}$	{ 1.6	{ 1.1		
		{ 2.081	{ 200	{	{ 0.9		
21	2.074	{ 2.077	{ 22 $\bar{1}$	{ 3.0	{ 0.6		
		{ 2.069	{ 012	{	{ 0.0		
22	2.016	2.017	121	{ 24.0	{ 36.0	3 $\bar{1}$ 4	2.015
23	(1.991)	1.993	02 $\bar{1}$	{ 2.0	{ 1.5		
24	1.975	1.973	1 $\bar{1}$ 1	{ 1.0	{ 0.9		
25	1.945	1.947	220	5.0	1.6		
26	1.902	1.889	2 $\bar{1}$ 1	{ 19.0	{ 31.6	312	1.904
		1.897	1 $\bar{2}$ 1	{	{ 0.5		
27	(1.877)	1.886	01 $\bar{2}$	{ 2.0	{ 2.0		
28	1.821	1.817	1 $\bar{2}$ 0	2.0	2.0		
(28')	1.804	1.806	22 $\bar{2}$	3.0	1.7		
29	1.784	{ 1.786	{ 120	{ 13.0	{ 23.0	024	1.781
		{ 1.778	{ 212	{	{ 2.2		
30	1.715	1.714	022	1.0	0.6		
31	1.704	{ 1.705	{ 130	{ 2.0	{ 0.0		
		{ 1.702	{ 2 $\bar{1}$ 0	{	{ 1.2		
		{ 1.679	{ 211	{	{ 0.1		
32	1.668	{ 1.671	{ 31 $\bar{1}$	{ 4.0	{ 0.8		
		{ 1.668	{ 1 $\bar{2}$ 2	{	{ 6.1		
33	1.653	{ 1.655	{ 112	{ 3.0	{ 2.7		
		{ 1.652	{ 31 $\bar{2}$	{	{ 1.3		
34	1.632	1.634	1 $\bar{0}$ 3	1.5	0.3		

Table 3 (cont.)

No. (Hauschild)	This work					Saalfeld <i>et al.</i>	
	d_{hkl} obs	d_{hkl} calc	hkl_r	I_{obs}	I_{calc}	hkl	d_{hkl} obs
35	1.616	1.625	13 $\bar{1}$	1.0	0.4	31 $\bar{6}$	1.595
		1.620	102		0.3		
		1.614	202		0.6		
		1.599	23 $\bar{1}$		6.7		
		1.597	21 $\bar{3}$		1.0		
36	1.598	1.596	030	5.0	0.1		
		1.594	201		0.1		
		1.591	32 $\bar{1}$		0.0		
		1.576	221		1.1		
		1.571	30 $\bar{3}$		1.4		
37	1.572	1.564	30 $\bar{1}$	4.0	1.6		
		1.561	031		1.1		
		1.560	230		4.2		
38	1.560	1.552	32 $\bar{2}$	1.0	0.2		
		1.550	131		5.9		
		1.547	1 $\bar{1}$ 3		0.3		
		1.546	11 $\bar{3}$		0.7		
		1.516	1 $\bar{2}$ 1		11.2		
39	1.547	1.515	02 $\bar{2}$	6.0	0.7	3 $\bar{1}$ 4	1.513
		1.513	122		3.3		
		1.479	310		8.9		
40	1.517	1.471	2 $\bar{1}$ 3	7.0	0.1	60 $\bar{2}$	1.478
		1.463	2 $\bar{2}$ 1		1.5		
41	1.479	1.447	23 $\bar{2}$	2.0	0.4	60 $\bar{2}$	1.478
		1.442	003		7.6		
		1.441	31 $\bar{3}$		10.5		
		1.441	320		6.1		
		1.441	03 $\bar{1}$		0.5		
		1.438	1 $\bar{1}$ 2		0.1		
		1.431	22 $\bar{3}$		1.0		
42	1.465	1.430	013	14.0	7.5	330 33 $\bar{2}$ (332)*	1.440
		1.423	222		0.7		
		1.403	30 $\bar{3}$		3.9		
43	1.441	1.388	33 $\bar{1}$	5.0	0.1	224	1.431
		1.388	1 $\bar{3}$ 1		0.0		
		1.388	300		0.6		
		1.387	2 $\bar{1}$ 1		0.8		
		1.387	13 $\bar{2}$		0.7		
44	1.430	1.373	312	3.0	0.7	330	1.403
		1.368	032		0.9		
		1.365	231		0.6		
45	1.404	1.388	33 $\bar{1}$	1.5	0.1	600	1.388
		1.388	1 $\bar{3}$ 1		0.0		
46	1.388	1.388	300	1.0	0.6		
		1.387	2 $\bar{1}$ 1		0.8		
		1.370	13 $\bar{2}$		0.7		
47	1.370	1.373	312	0.6	0.7		
		1.368	032		0.9		
48	1.365	1.363	231	0.6	0.6		
		1.363	231		0.6		

* A misprint in Saalfeld & Mehrotra.

but in view of a superstructure revealed by the single-crystal work of Saalfeld & Mehrotra (1966) these coordinates should clearly be considered as mean values.

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