Order and disorder in the lamellar hydrated tetracalcium monocarboaluminate compound

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Abstract

A single crystal X-ray diffraction study was performed on the cementitious phase 3CaO · Al₂O₃ · CaCO₃ · 11H₂O (C₄AкровH₁₁, using cement chemistry shorthand) prepared by hydrothermal synthesis. This layered compound crystallizes with pseudohexagonal symmetry (centrosymmetric space group P1) with parameters a = 5.7422(4) Å, b = 5.7444(4), c = 15.091(3) Å, α = 92.29(1)°, β = 87.45(1)°, γ = 119.55(1), Dx = 2.182 g/cm³, and F(000) = 294. Refinement of 1444 independent reflections led to a residual factor R of 0.0468. The structure is disordered; the carbonate group and three of the five water molecules in the interlayer are distributed statistically among general positions. Where the carbonate group is absent, its O-atoms are replaced by three water molecules. The structure is built by stacking of slabs parallel to (001) in the sequence ½(CO₃²⁻ · 6H₂O) – [Ca₄Al₂(OH)₁₂]²⁺ – ½(CO₃²⁻ · 6H₂O) – 2H₂O – [Ca₄Al₂(OH)₁₂]²⁺ – 2H₂O. Hydrogen atoms of the three disordered water molecules are not localized. This structure is the second modification found for this AFm phase. The first, completely ordered in the interlayer region thus has the composition [Ca₄Al₂(OH)₁₂]²⁺ · 6H₂O.

Keywords: X-ray diffraction; Crystal structure; Carbonation; Ca₄Al₂O₆; Hydration

Hydrated tetracalcium aluminate and derived basic salts are of special interest because they occur in the chemistry of many kinds of cement. The hydrated tetracalcium monocarboaluminate 3CaO · Al₂O₃ · CaCO₃ · 11H₂O (or C₄AкровH₁₁ using cement chemistry shorthand) is a frequently encountered structure which is based on distorted brucite-like main layers of composition [Ca₄Al₂(OH)₁₂]²⁺. The interlayer region thus has the composition [CO₃²⁻ · 5H₂O]²⁻. In this nonrefined model the carbonate group was supposed to be parallel to the layers. Allmann [2] made a more detailed study of another AFm phase, C₄ASH₁₂. In 1982, Fischer and Kuzel [3] proposed a triclinic lattice for this monocarboaluminate, but they did not improve the model proposed by Ahmed and Taylor. A complete structural determination of this compound was made in 1998 by François et al. [4]. The C₄AкровH₁₁ was formed by hydrothermal synthesis at 2Kbar and 120°C. It crystallizes in the noncentrosymmetric space group P1 with the triclinic lattice parameters a = 5.7747 Å, b = 8.4689 Å, c = 9.923 Å, α = 64.77°, β = 82.75°, and γ = 81.43°. The structure is fully ordered and could be described by the stacking sequence [Ca₄Al₂(OH)₁₂]²⁺ – (2H₂O) – (CO₃²⁻ · 3H₂O) – [Ca₄Al₂(OH)₁₂]²⁺ – (2H₂O) – (CO₃²⁻ · 3H₂O) – etc. parallel to (011). It was found that the carbonate group is bonded to Ca atoms and tilted through an angle of 21.8° from the parallel layers.

This article presents an X-ray diffraction study using a single crystal obtained in the same conditions as described previously [4] but at a temperature of 100°C. The “100°C-structure” was solved and showed major differences from the “120°C-structure.” The new results are presented here and both structures are compared.

1. Experimental and results

1.1. Sample preparation

The C₄AкровH₁₁ single crystals were prepared by hydrothermal synthesis. The starting powder (Ca(OH)₂, Al(OH)₃, and CaCO₃ in mole ratio 3.5/2/0.5) was mixed with water.
The preparation was examined by X-ray powder diffraction. The major phase C₃A(CH₁₁)$_{11}$ was (platy pseudohexagonal crystals) with minor C₃A₅H₆ and residual CaCO₃ and Al(OH)$_3$.

1.3. Single crystal X-ray diffraction

X-ray diffraction study was performed on a single crystal mounted in an automatic Nonius diffractometer. Recording and refinement parameters are summarized in Table 1. Lattice parameters were refined using 25 reflections in the 0 range 20° to 70° with CAD-4 software [6].

Data reduction was performed using programs of Blessing’s system [7]. Absorption corrections were made using the ABSORB program [7], with maximum and minimum transmission factors of 0.85(5) and 0.34(3). The structure was then solved by direct methods (SHELXS program [8]) in the centrosymmetric space group P1. The scattering factors used for the structure factor calculation and transformed Fourier analysis were those of the neutral atoms H, O, C, Al, and Ca. These values were taken from International Tables [9].

The positions of Al, Ca, O, and C atoms were determined in a first run and the model tested by least squares refinement (SHELX97 program [10]) by using 1444 independent reflections. This led to a residual factor of about 10%. Refinement of occupancy factors for the interlayer oxygen and carbon sites gave values of 0.5, allowing the R factor to decrease to 0.06. The ordered hydrogen sites are found by difference syntheses. The positions of these eight hydrogen atoms were refined and temperature factors were held to 1.2 for 0.95(1) Å and angles H-O-H in the noncentrosymmetric space group P1 did not increase the goodness of fit. Investigations on localization of the six missing hydrogen atoms by Fourier difference maps did not lead to reasonable results. Subsequent Raman spectroscopy experiments on the same single crystal permitted us to place these last hydrogen atoms [11].

The atomic parameters are represented in Tables 2 and 3. The Al-atoms are situated on symmetry centers, whereas all other atoms are on general positions. Twelve hydroxyl groups OH(1-6) formed by O(1)-H(1) . . . etc. are contained in the main layer; five water molecules H₂O(7-10) formed by C(7a)-O(7w)-H(7b), O(8w) . . . etc. and one carbonate group CO₃$^{2-}$ formed by C, O(8c), O(9c), and O(10c) are contained in the interlayer. The carbonate group and the three H₂O(8), H₂O(9), and H₂O(10) water molecules have occupancy factors of 50%, implying that the structure is partially disordered.

2. Discussion

2.1. Interatomic distances and coordination

This structure will be called the D-C₃A(CH₁₁)$_{11}$ structure (disordered structure) by comparison with the O-C₃A(CH₁₁)$_{11}$ structure (ordered structure) determined previously [4]. Selected interatomic distances are reported on Table 4. They are not significantly different from those reported for the O-C₃A(CH₁₁)$_{11}$ structure. The oxygen coordination of the Al and Ca cations are six and seven, respectively, as is usual in AFm phases. The seventh neighbor of the Ca(2) atoms is the water molecule H₂O(7), whereas the seventh neighbor of 50% of the Ca(2) atoms is the water molecule H₂O(8) and that of the other 50% are O(8c) atoms of the carbonate.
Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å² × 10⁴) for D-C₆H₁₃

<table>
<thead>
<tr>
<th>Group</th>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>Ueq</th>
<th>Occup.</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Al(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.74</td>
<td>1</td>
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<tr>
<td></td>
<td>Al(2)</td>
<td>0.0</td>
<td>1/2</td>
<td>1/2</td>
<td>18.3</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Ca(1)</td>
<td>0.1669(1)</td>
<td>0.3294(1)</td>
<td>0.9629(1)</td>
<td>18.9</td>
<td>1</td>
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<tr>
<td></td>
<td>Ca(2)</td>
<td>0.6648(1)</td>
<td>0.8385(1)</td>
<td>0.5375(1)</td>
<td>21.2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>OH(1)</td>
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<td>0.8079(5)</td>
<td>0.5648(2)</td>
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<td>1</td>
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<td>0.9429(5)</td>
<td>0.9327(2)</td>
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<td>1</td>
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<td>OH(3)</td>
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<td>0.7456(5)</td>
<td>0.9324(2)</td>
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<tr>
<td></td>
<td>OH(4)</td>
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<td>0.5664(2)</td>
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<tr>
<td></td>
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<td>0.291(10)</td>
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<tr>
<td></td>
<td>OH(7)</td>
<td>0.66833(5)</td>
<td>0.45165(5)</td>
<td>0.55678(2)</td>
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<td>1</td>
</tr>
<tr>
<td></td>
<td>H₂O(7)</td>
<td>0.69678(6)</td>
<td>0.32066(6)</td>
<td>0.7945(3)</td>
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<td>0.1659(2)</td>
<td>0.7674(4)</td>
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<td>1</td>
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<td></td>
<td>H₂O(9)</td>
<td>0.1067(1)</td>
<td>0.98371(1)</td>
<td>0.7425(5)</td>
<td>31.2</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>H₂O(10)</td>
<td>0.2584(4)</td>
<td>0.3733(3)</td>
<td>0.7452(5)</td>
<td>46.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>CO₂⁻</td>
<td>C</td>
<td>0.363(1)</td>
<td>0.661(1)</td>
<td>0.7393(7)</td>
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</tr>
<tr>
<td>bonded to Ca(2)</td>
<td>O(8c)</td>
<td>0.600(2)</td>
<td>0.839(2)</td>
<td>0.710(1)</td>
<td>29.3</td>
<td>0.5</td>
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<tr>
<td></td>
<td>O(9c)</td>
<td>0.177(1)</td>
<td>0.722(1)</td>
<td>0.7496(5)</td>
<td>30.2</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>O(10c)</td>
<td>0.323(3)</td>
<td>0.429(2)</td>
<td>0.760(2)</td>
<td>35.4</td>
<td>0.5</td>
</tr>
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</table>

Ueq is defined as one third of the trace of the orthogonalized Uij tensor.

Table 3
Anisotropic displacement parameters (Å² × 10⁴) for D-C₆H₁₃

<table>
<thead>
<tr>
<th>Atom</th>
<th>U₁₁</th>
<th>U₁₂</th>
<th>U₂₂</th>
<th>U₂₃</th>
<th>U₃₃</th>
<th>U₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(1)</td>
<td>7.5(8)</td>
<td>5.1(7)</td>
<td>41(1)</td>
<td>1.4(7)</td>
<td>0.4(8)</td>
<td>3.8(1)</td>
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<tr>
<td>Al(2)</td>
<td>9.8(8)</td>
<td>7.1(7)</td>
<td>38(1)</td>
<td>0.0(7)</td>
<td>-0.6(8)</td>
<td>4.0(6)</td>
</tr>
<tr>
<td>Ca(1)</td>
<td>8.4(5)</td>
<td>7.5(4)</td>
<td>41(1)</td>
<td>0.1(4)</td>
<td>-1.1(4)</td>
<td>3.9(3)</td>
</tr>
<tr>
<td>Ca(2)</td>
<td>10.7(5)</td>
<td>7.9(4)</td>
<td>45(1)</td>
<td>0.3(4)</td>
<td>-0.6(4)</td>
<td>4.9(3)</td>
</tr>
<tr>
<td>O(1)</td>
<td>15(1)</td>
<td>11(1)</td>
<td>40(2)</td>
<td>-2(1)</td>
<td>0(1)</td>
<td>6(1)</td>
</tr>
<tr>
<td>O(2)</td>
<td>10(1)</td>
<td>11(1)</td>
<td>36(2)</td>
<td>0(1)</td>
<td>1(1)</td>
<td>6(1)</td>
</tr>
<tr>
<td>O(3)</td>
<td>10(1)</td>
<td>8(1)</td>
<td>40(2)</td>
<td>3(1)</td>
<td>0(1)</td>
<td>3(1)</td>
</tr>
<tr>
<td>O(4)</td>
<td>12(1)</td>
<td>9(1)</td>
<td>35(2)</td>
<td>-1(1)</td>
<td>2(1)</td>
<td>6(1)</td>
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<tr>
<td>O(5)</td>
<td>12(1)</td>
<td>9(1)</td>
<td>45(3)</td>
<td>3(1)</td>
<td>0(1)</td>
<td>6(1)</td>
</tr>
<tr>
<td>O(6)</td>
<td>16(1)</td>
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<td>40(2)</td>
<td>2(1)</td>
<td>2(1)</td>
<td>9(1)</td>
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<tr>
<td>O(7w)</td>
<td>20(2)</td>
<td>20(2)</td>
<td>50(3)</td>
<td>-1(2)</td>
<td>0(2)</td>
<td>6(1)</td>
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<tr>
<td>O(8w)</td>
<td>43(8)</td>
<td>29(5)</td>
<td>62(8)</td>
<td>12(5)</td>
<td>27(9)</td>
<td>0(6)</td>
</tr>
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<td>O(8c)</td>
<td>21(6)</td>
<td>15(5)</td>
<td>40(6)</td>
<td>7(4)</td>
<td>15(6)</td>
<td>2(5)</td>
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<tr>
<td>O(9c)</td>
<td>27(3)</td>
<td>26(3)</td>
<td>40(5)</td>
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<td>14(3)</td>
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<td>O(9c)</td>
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<td>25(3)</td>
<td>47(5)</td>
<td>1(3)</td>
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<td>15(3)</td>
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<td>O(10w)</td>
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<td>64(9)</td>
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<td>-2(9)</td>
<td>-9(7)</td>
<td>26(7)</td>
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<tr>
<td>O(10c)</td>
<td>30(8)</td>
<td>25(5)</td>
<td>52(11)</td>
<td>-6(6)</td>
<td>-7(7)</td>
<td>15(5)</td>
</tr>
<tr>
<td>C</td>
<td>20(5)</td>
<td>17(4)</td>
<td>34(7)</td>
<td>-6(4)</td>
<td>-1(4)</td>
<td>3(4)</td>
</tr>
</tbody>
</table>

The anisotropic displacement factor exponent takes the form: −2π²

\[ \ln a^2 U_{11} + \ldots + 2 h k a^* b^* U_{12} \].

Table 4
Selected bond lengths [Å] and angles [deg] for D-C₆H₁₃

<table>
<thead>
<tr>
<th>Atom to atom</th>
<th>Distance</th>
<th>Atom to atom</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(1)-O(4)</td>
<td>2 × 1.900(3)</td>
<td>Ca(2)-O(6)</td>
<td>2.353(3)</td>
</tr>
<tr>
<td>Al(2)-O(4)</td>
<td>2 × 1.911(3)</td>
<td>O(5)-O(6)</td>
<td>2.951(3)</td>
</tr>
<tr>
<td>Al(2)-O(5)</td>
<td>2 × 1.894(3)</td>
<td>O(5)-O(6)</td>
<td>2.951(3)</td>
</tr>
<tr>
<td>Al(2)-O(5)</td>
<td>2 × 1.909(3)</td>
<td>O(6)-O(6)</td>
<td>2.951(3)</td>
</tr>
<tr>
<td>Ca(1)-O(4)</td>
<td>3.247(3)</td>
<td>O(8c)-O(8c)</td>
<td>2.540(4)</td>
</tr>
<tr>
<td>Ca(1)-O(4)</td>
<td>3.247(3)</td>
<td>O(8c)-O(8c)</td>
<td>2.540(4)</td>
</tr>
</tbody>
</table>

The anisotropic displacement factor exponent takes the form: −2π²

\[ \ln a^2 U_{11} + \ldots + 2 h k a^* b^* U_{12} \].

group. Atoms of the carbonate group, situated on O(8c), O(9c), O(10c), and C sites, as shown by C-O distances in the range of 1.23–1.30 Å and O-C-O angles in the range of 119–122°, are found by refinement without applying restraint. In the final refinement, C-O distances are constrained to 1.29(1) Å and angles O-C-O were restrained at the value of 120.0(1)° found for the carbonate group in the O-C₆H₁₃ structure. The carbonate group (which was also restrained to
be flat) is tilted by an angle of 20.5° from the planes of the layers. The tilt is slightly less but comparable to that of 21.8° measured in the O-C₄ACh₁₁ structure. The other constraints applied for the final refinement are the distance O-H of 0.95(1) Å for hydroxyl anions and water molecule O(7w), with an angle H(7a)-O(7w)-H(7b) of 104.5(1.0)°.

2.2. Comparison with the O-C₄ACh₁₁ structure

D-C₄ACh₁₁ and O-C₄ACh₁₁ structures have identical main layers [Ca₄Al₂(OH)₁₂]₂⁺, but they have different arrangements of water molecules and carbonate groups forming the interlayer region of composition [CO₃ · 5H₂O]²⁻. This leads to major differences with regard to the stacking of the slabs into the structures.

Optical measurements showed different birefringence values for these two modifications. The birefringence normal to the layers was approximately 0.007 (Table 1). For the ordered structure in the same orientation, it was =0.003.

2.2.2. Order and disorder

The ordering of the various species contained in the interlayer of the C₄ACh₁₁ triclinic structure, i.e., five water molecules and one carbonate group per unit cell, results in loss of the symmetry center. The arrangement of an odd number of identical molecules around a symmetry center cannot be done without generating disorder, i.e., with statistical occupancy of some atoms in general positions.

The disordered part of the D-C₄ACh₁₁ structure is shown in Fig. 2. This concerns only atoms belonging to carbonate groups and water molecules (H₂O(8–10)).

In the interlayer region only the O(7w) site is fully occupied. All the other sites in this part of the structure have an occupancy of 50%. When H₂O(8), H₂O(9) and H₂O(10) are present, their oxygen atoms are on the O(8w), O(9w), and O(10w) sites, respectively, whereas the carbonate group is absent and the O(8c), O(9c), O(10c), and C sites are empty (and vice versa). The splitting of the averaged sites O(8) (in the two sites O(8w) and O(8c)), O(9) (in the two sites O(9w) and O(9c)), and O(10) (in the two sites O(10w) and O(10c)) have respective values of 0.54(1) Å, 1.332(8) Å, and 0.42(3) Å. The coordinates of the O(8), O(9), and O(10) sites calculated from their average positions are as follows:

O(8):  x = 0.6531, y = 0.8599, z = 0.7087 midway between O(8w) and O(8c)sites,
O(9):  x = 0.1221, y = 0.7992, z = 0.7461 midway between O(9w) and O(9c) sites
O(10): x = 0.2906, Y = 0.4009, z = 0.7526 midway between O(10w) and O(10c) sites.

In summary, when the carbonate group is absent, it is replaced by three water molecules. The sites O(8) and O(10) are split in O(8w), O(8c), and O(10w), O(10c) for the oxygen atoms of the water molecules and carbonate group, respectively. Finally, the O(9w) and O(9c) sites are also occupied as alternatives, with a larger split around the hypothetical O(9) averaged site.

2.2.3. Geometrical relations between O- and D-lattice

D-C₄ACh₁₁ can be considered as having a distorted hexagonal structure as can be seen by the triclinic lattice parameters: a = b, α = 90°, and γ = 120°. The relation between the triclinic O-C₄ACh₁₁ lattice and the hexagonal system is less evident. Nevertheless, the O- and D-structures are very close; as seen earlier, they differ only in their interlayer organization. It follows that the two triclinic lattices must be linked by geometrical relations. Indeed, the triclinic O-unit cell can be converted into a pseudohexagonal lattice by the following transformation:

\[
\begin{pmatrix}
a'\cdot_o & = & -1/2a_o - 1/2b_o + 1/2c_o \\
b'\cdot_o & = & -1/2a_o + 1/2b_o - 1/2c_o \\
c'\cdot_o & = & b_o + c_o
\end{pmatrix}
\]

where \(a_o, b_o, \) and \(c_o\) are the basis vectors of the O-lattice and, and \(a'\cdot_o, b'\cdot_o, \) and \(c'\cdot_o\) are those of the pseudohexagonal lattice. The transformation matrix thus is as follows:

\[
M_0' = \begin{pmatrix}
-1/2 & -1/2 & 1/2 \\
1/2 & 1/2 & -1/2 \\
0 & 1 & 1
\end{pmatrix}
\]
The parameters of the transformed O-lattice called “O-lattice” and those of the D-lattice are reported in Table 4 for comparison. Deviation from hexagonal symmetry as indicated by the values of the parameters \((a-b)/(a+b)\), \(\gamma - 120^\circ\), and the split (angle between the pseudohexagonal axis and the normal to the (001) plane, i.e., \(\varepsilon^*)\) also are reported.

It is evident that the O-lattice is deviates further from hexagonal lattice. The (a,b) basal planes remain approxi-
mately hexagonal in both O- and D-structures, as seen by
a – b/a + b and γ – 120° values near zero, whereas the de-
VIATION appears mainly in the split parameter (2.8° in D- and
13.7° in O-structure). This fact can be explained by the mode
of construction of the AFm phases in general. They are
formed by substitution of one third of Ca²⁺ by Al³⁺ cations
in the trigonal structure of Ca(OH)₂ (space group R3). The re-
suiting main layers of composition [Ca₂Al(OH)₆]⁺ keep the
hexagonal symmetry. Following the constraints induced by
the interlayer region, i.e., by anionic species and molecular
water, the stacking of main layers and interlayers may or
may not partially or wholly destroy the hexagonal symmetry.
For example, in the monosulfate C₄ASH₁₂ structure [3] (trigo-
nal space group R3), the hexagonal lattice is preserved. This
structure is disordered; the sulfate groups have two possible
orientations and are not directly connected to Ca cations.
Thus, it is reasonable to suppose the increase in the deviation
from hexagonal parameter when going from C₄ASH₁₂ to
D-C₄ACH₁₁ and to O-C₄ACH₁₁ structures is due to the in-
crease of constraints induced by the various intercalated species.

2.3. Superstructure in the direction normal to the
layer stacking

A crystallographic study of hydrocalumite (a natural car-
bonated AFm phase) was made by Buttler et al. [12] in
1959. The authors pointed out the “difficult problem of de-
termining the true value or values of c axis” in this com-
pound and they supposed “this structural element proves to
be the key of the structure.” To explain the oscillation, rota-
tion, and Weissenberg photographs, Buttler et al. proposed a
superstructure in the direction of the pseudohexagonal lat-
tice. Various works on single crystals of AFm phases also
indicate superstructures in the same direction [1,13,14],
with generally the parameter c = 6 c’, or sometimes c = 12
(‘c’ is the layer thickness).

In the present work, we do not find a true superstructure
for the C₄ACH₁₁ compound along the layer stacking. In the
case of the D-C₄ACH₁₁, the pseudohexagonal lattice has a
parameter c = 15.091 Å. This value corresponds to the dou-
bled-layer thickness. The disorder localized in the interlayer
part does not introduce superstructure in the direction. On
the other hand, rotation and Weissenberg photographs
clearly show a superstructure along the direction. This su-
perstructure corresponds to an arrangement in this direction
of the interlayer molecules. A carbonate ion in the (X, Y, Z)
cell alternates with three water molecules in the following
(X + 1, Y, Z) cell. So, the disorder localized in the inter-
layer part is only along the direction. The order in the direc-
tion is understandable because of the shortest distance of
2.18(2) Å between a water molecule set in the O(8w) site of
the (X, Y, Z) cell and another water molecule located on the
O(9w) site in the next (X + 1, Y, Z) cell.

### Table 4

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>(a – b)/(a + b)</th>
<th>γ – 120° (°)</th>
<th>Split (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O'-lattice</td>
<td>5.7447</td>
<td>5.7398</td>
<td>15.5509</td>
<td>103.36</td>
<td>86.08</td>
<td>119.63</td>
<td>0.04</td>
<td>–0.37</td>
<td>13.7</td>
</tr>
<tr>
<td>D-lattice</td>
<td>5.7422</td>
<td>5.7444</td>
<td>15.091</td>
<td>92.290</td>
<td>87.450</td>
<td>119.54</td>
<td>0.02</td>
<td>–0.45</td>
<td>2.8</td>
</tr>
</tbody>
</table>

* Explanation for the term “split” is given in the text.
The triclinic lattice of O-C₄AH₁₁ also does not have a true superstructure. However, Weissenberg and precession photographs are generally taken with crystals oriented in the nonequivalent pseudohexagonal O'-lattice (because the O-C₄AH₁₁ compound faces of the platy hexagonal crystal do not give any indication on the real O-lattice orientation). Such photographs seem to show superstructure in a direction normal to the layers, but this in fact arises simply because of a rotation or precession around a direction that is not a main crystallographic one.

3. Conclusion

We have shown that two modifications of C₄AH₁₁ exist. Both were obtained by hydrothermal synthesis. The only experimental parameter that differed was the temperature: O-C₄AH₁₁ was obtained at 120°C, and D-C₄AH₁₁ at 100°C.

Our X-ray diffraction study was based on one single crystal extracted from each preparation and did not relate to the whole sample. Moreover, the X-ray powder diffraction patterns of both preparations showed no visible differences, which was to be expected as the diffraction patterns (not shown here) simulated from structural data presented in this paper for the D- and in [4] for the O-modification showed only slight differences related to weak Bragg peaks. The existence of a single modification in each preparation was checked by Raman microspectrometry.

The main geometrical difference between these two modifications is the presence or otherwise of the symmetry center. When the structure is centrosymmetric P1, the compound is disordered and pseudohexagonal. When the structure is noncentrosymmetric P1, the structure is ordered with a unit cell further removed from the hexagonal lattice. The origin of the difference lies in the stacking sequences of the layers in the O- and D-C₄AH₁₁ layer structures. Superstructure along the layer stacking in these two modifications of C₄AH₁₁ structure were not observed.

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References