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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 $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ ($C_4A\overline{C}H_{11}$ using cement chemistry shorthand) prepared by hydrothermal synthesis. This layered compound crystallizes with pseudohexagonal symmetry (centrosymmetric space group $P\bar{1}$) 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 $^1/_2(CO_3^{2-} \cdot 6H_2O)$– $[Ca_4Al_2(OH)_{12}]^{2+}$ – $^1/_2(CO_3^{2-} \cdot 6H_2O)$–$2H_2O$–$[Ca_4Al_2(OH)_{12}]^{2+}$–$2H_2O$. 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 noncentrosymmetric space group P1, was described previously. The two modifications, the ordered called "O-$C_4A\overline{C}H_{11}$" and the disordered called "D-$C_4A\overline{C}H_{11}$", are compared.

Keywords: X-ray diffraction; Crystal structure; Carbonation; $Ca_3Al_2O_6$; 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 $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ (or $C_4A\overline{C}H_{11}$ using cement chemistry shorthand) is a frequently encountered and important AFm phase in hydrated cement. This lamellar family of cement compounds forms platy hexagonal or pseudohexagonal crystals. AFm phases have the general formula $[Ca_2Al(OH)_6](X)_x \cdot yH_2O$, where $(X)_x$ represents OH^-, Cl^-, NO_3^-, $(CO_3^{2-})_{0.5}$, $(SO_4^{2-})_{0.5}$, or $Al(OH)_4^-$.

The $C_4A\overline{C}H_{11}$ compound has been the subject of various studies for many years. Ahmed and Taylor [1] in 1967 gave a trigonal model for its structure, which is based on distorted brucite-like main layers of composition $[Ca_4Al_2(OH)_{12}]^{2+}$. The interlayer region thus has the composition $[CO_3 \cdot 5H_2O]^{2-}$. 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, $C_4A\overline{S}H_{12}$. 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 $C_4A\overline{C}H_{11}$ 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 $[Ca_4Al_2(OH)_{12}]^{2+}$–$(2H_2O)$–$(CO_3^{2-} \cdot 3H_2O)$–$[Ca_4Al_2(OH)_{12}]^{2+}$–$(2H_2O)$– $(CO_3^{2-} \cdot 3H_2O)$–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 $C_4A\overline{C}H_{11}$ single crystals were prepared by hydrothermal synthesis. The starting powder ($Ca(OH)_2$, $Al(OH)_3$, and $CaCO_3$ in mole ratio 3.5/2/0.5) was mixed with water

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(weight ratio solid/water = 0.5) and loaded into a silver capsule (length 100 mm, diameter 5 mm, and thickness 0.5 mm). The $Ca(OH)_2$ was obtained by hydrating freshly calcined calcite in a wet CO_2-free atmosphere. The $Al(OH)_3$ was a freshly precipitated bayerite obtained by an electrochemical method [5]. The mother-mix (solid plus water) was placed in the hot side of the capsule and the crystallization took place in the "cold" side. The capsule was placed for 1 month in an autoclave at 2 Kbar isotropic pressure and 100°C.

1.2. Examination of product

The preparation was examined by X-ray powder diffraction. The major phase $C_4A\overline{C}H_{11}$ was (platy pseudohexagonal crystals) with minor C_3AH_6 and residual $CaCO_3$ 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 ϑ 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 $P\overline{1}$. 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].

Table 1
Crystal data and structure refinement for D-$C_4A\overline{C}H_{11}$

Chemical composition	$3CaO \cdot A1_2O_3 \cdot CaCO_3 \cdot 11H_2O$
Formula weight	568.47
Temperature	293(2) K
Wavelength	1.54180 Å
Scan mode	w-2θ
Crystal system	Triclinic
Space group	$P\overline{1}$
Unit cell dimensions	a = 5.7422(4) Å α = 92.29(1)°
	b = 5.7444(4) Å β = 87.45(1)°
	c = 15.091(3) Å γ = 119.547(7)°
Volume	432.52(10)$Å^3$
Z	1
Density (calculated)	2.182 g/cm^3
Briefringence (Dn)	0.007
Absorption coefficient	12.907 mm^{-1}
F(000)	294
Crystal size	Thickness = 0.025 mm, R sphere = 0.036 mm
Theta range for data collection	5.87 to 69.90 degree
Index ranges	−6 <= h <= 6, −6 <= k <= 6, 0 <= 1 <=18
Reflections collected	2402
ψ-Scan, (0-360°, δψ = 10°)	On 20 reflections
Independent reflections	1444
Reflections [Fo > 4 sigma (Fo)]	1256
Refinement method	Full-matrix least-squares on F^2
Number of refined parameters	182
Number of restraints	16
Goodness-of-fit on F2	1.076
Final R indices [I > 2 sigma (I)]	R1 = 0.0468, wR2 = 0.1318
Largest diff. peak and hole	0.79 and −0.64 $e.Å^{-3}$

The positions of Al, Ca, C, and O 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 factor was held to 1.20 U_{eq} of the corresponding oxygen atom (R value decreased to 0.05). Finally, some restraints on geometry of carbonate (distances C-O = 1.29(1) Å, angles O-C-O = 120(1)°), water molecules and hydroxyl anions (distances O-H = 0.95(1) Å and angles H-O-H = 104.5(1.0) °) were applied, leading to a final R value of 0.047. An attempt to refine the structure in the noncentrosymmetric space group P1 did not increase the goodness of fit. Investigations on localization of the six missing hydrogen atom 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 reported 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 H_2O(7-10) formed by H(7a)-O(7w)-H(7b), O(8w) . . . etc. and one carbonate group CO_3^{2-} formed by C, O(8c), O(9c), and O(10c) are contained in the interlayer. The carbonate group and the three H_2O(8), H_2O(9), and H_2O(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-$C_4A\overline{C}H_{11}$ structure (disordered structure) by comparison with the O-$C_4A\overline{C}H_{11}$ 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-$C_4A\overline{C}H_{11}$ 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(1) atom is the water molecule H_2O(7), whereas the seventh neighbor of 50% of the Ca(2) atoms is the water molecule H_2O(8) and that of the other 50% are O(8c) atoms of the carbonate

Table 2
Atomic coordinates and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for D-$C_4A\overline{C}H_{11}$

Group	Atom	X	Y	Z	U_{eq}	Occup.
	Al(1)	0	0	0	17.4 (5)	1
	Al(2)	0	1/2	1/2	18.3 (5)	1
	Ca(1)	0.6696 (1)	0.3294 (1)	0.9629 (1)	18.9 (3)	1
	Ca(2)	0.6648 (1)	0.8385 (1)	0.5375 (1)	21.2 (4)	1
OH(1)	O(1)	0.2440 (5)	0.8079 (5)	0.5648 (2)	22.2 (8)	1
	H(1)	0.213 (10)	0.811 (10)	0.6268 (9)	26.6 (−)	1
OH(2)	O(2)	0.2579 (5)	0.9429 (5)	0.9327 (2)	18.5 (8)	1
	H(2)	0.239 (10)	0.899 (10)	0.871 (1)	22.2 (−)	1
OH(3)	O(3)	0.7004 (5)	0.7456 (5)	0.9324 (2)	20.0 (8)	1
	H(3)	0.709 (10)	0.798 (10)	0.873 (1)	23.9 (−)	1
OH(4)	O(4)	0.0614 (5)	0.3029 (5)	0.9351 (2)	18.7 (8)	1
	H(4)	0.107 (10)	0.294 (10)	0.875 (1)	22.4 (−)	1
OH(5)	O(5)	0.0506 (5)	0.2532 (5)	0.5664 (2)	21.8 (8)	1
	H(5)	0.112 (10)	0.291 (10)	0.625 (1)	26.2 (−)	1
OH(6)	O(6)	0.6883 (5)	0.4516 (5)	0.5678 (2)	21.8 (8)	1
	H(6)	0.681 (10)	0.385 (10)	0.625 (1)	26.1 (−)	1
$H_2O(7)$	O(7w)	0.6987 (6)	0.3206 (6)	0.7945 (3)	31.7 (9)	1
bonded to Ca(1)	H(7a)	0.872 (5)	0.464 (5)	0.783 (4)	38.0 (−)	1
	H(7b)	0.695 (8)	0.169 (5)	0.767 (4)	38.0 (−)	1
$H_2O(8)$ bonded to Ca(2)	O(8w)	0.706 (2)	0.881 (3)	0.707 (1)	53 (4)	0.5
$H_2O(9)$ slightly bonded water	O(9w)	0.067 (1)	0.877 (1)	0.7425 (5)	31 (2)	0.5
$H_2O(10)$ slightly bonded water	O(10w)	0.258 (4)	0.373 (3)	0.745 (2)	46 (5)	0.5
CO_3^{2-}	C	0.363 (1)	0.661 (1)	0.7393 (7)	26 (2)	0.5
bonded to Ca(2)	O(8c)	0.600 (2)	0.839 (2)	0.710 (1)	29 (3)	0.5
	O(9c)	0.177 (1)	0.722 (1)	0.7496 (5)	30 (2)	0.5
	O(10C)	0.323 (3)	0.429 (2)	0.760 (2)	35 (4)	0.5

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

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-$C_4A\overline{C}H_{11}$ structure. The carbonate group (which was also restrained to

Table 3
Anisotropic displacement parameters ($Å^2 \times 10^3$) for D-$C_4A\overline{C}H_{11}$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Al(1)	7.5 (8)	5.1 (7)	41 (1)	1.4 (7)	0.4 (8)	3.8 (6)
Al(2)	9.8 (8)	7.1 (7)	38 (1)	0.0 (7)	−0.6 (8)	4.0 (6)
Ca(1)	8.4 (5)	7.5 (4)	41 (1)	0.1 (4)	−1.1 (4)	3.9 (3)
Ca(2)	10.7 (5)	7.9 (4)	45 (1)	0.3 (4)	−0.6 (4)	4.9 (3)
O(1)	15 (1)	11 (1)	40 (2)	−2 (1)	0 (1)	6 (1)
O(2)	10 (1)	11 (1)	36 (2)	0 (1)	1 (1)	6 (1)
O(3)	10 (1)	8 (1)	40 (2)	3 (1)	0 (1)	3 (1)
O(4)	12 (1)	9 (1)	35 (2)	−1 (1)	2 (1)	6 (1)
O(5)	12 (1)	9 (1)	45 (3)	3 (1)	0 (1)	6 (1)
O(6)	16 (1)	13 (1)	40 (2)	2 (1)	2 (1)	9 (1)
O(7w)	20 (2)	20 (2)	50 (3)	−1 (2)	0 (2)	6 (1)
O(8w)	43 (8)	29 (5)	62 (8)	12 (5)	27 (9)	0 (6)
O(8c)	21 (6)	15 (5)	40 (6)	7 (4)	15 (6)	2 (5)
O(9w)	27 (3)	26 (3)	40 (5)	−4 (3)	−2 (3)	14 (3)
O(9c)	22 (3)	25 (3)	47 (5)	1 (3)	−2 (3)	15 (3)
O(10w)	33 (8)	64 (9)	45 (10)	−2 (9)	−9 (7)	26 (7)
O(10c)	30 (8)	25 (5)	52 (11)	−6 (6)	−7 (7)	15 (5)
C	20 (5)	17 (4)	34 (7)	−6 (4)	−1 (4)	3 (4)

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \ldots + 2 h k a^* b^* U_{12}]$.

Table 4
Selected bond lenghts [Å] and angles [deg] for D-$C_4A\overline{C}H_{11}$

Atom to atom	Distance	Atom to atom	Distance
Al(1)-O(4)	2 × 1.900(3)	Ca(2)-O(6)	2.353(3)
O(2)	2 × 1.911(3)	-O(1)	2.355(3)
O(3)	2 × 1.922(3)	-O(5)	2.360(3)
Al(2)-O(1)	2 × 1.894(3)	-O(1)	2.432(3)
-O(5)	2 × 1.909(3)	-O(5)	2.442(3)
-O(6)	2 × 1.923(3)	-O(6)	2.481(3)
Ca(1)-O(4)	2.347(3)	-O(8w)	2.57(2)
-O(2)	2.359(3)	-O(8c)	2.62(2)
-O(3)	2.372(3)		
-O(4)	2.438(3)	C-O(9c)	1.280(7)
-O(2)	2.448(3)	-O(10c)	1.284(8)
-O(3)	2.459(3)	-O(8c)	1.300(8)
-O(7w)	2.540(4)		

Atom to atom	Angle
O(9c)-C-O(10c)	120.7(8)
O(9c)-C-O(8c)	120.1(7)
O(10c)-C-O(8c)	119.2(8)

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-$C_4A\overline{C}H_{11}$ 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-$C_4A\overline{C}H_{11}$ structure

D-$C_4A\overline{C}H_{11}$ and O-$C_4A\overline{C}H_{11}$ structures have identical main layers $[Ca_4Al_2(OH)_{12}]^{2+}$, but they have different arrangements of water molecules and carbonate groups forming the interlayer region of composition $[CO_3 \cdot 5H_2O]^{2-}$. 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.

2.2.1. Stacking sequences

The layer stacking of O-structure [projection on (100)] and D-structure [projection on (010)] is shown in Fig. 1. The structures can be described by the stacking of A = $[Ca_4Al_2(OH)_{12}]^{2+}$, B = $2H_2O$, and $C_O = CO_3^{2-} \cdot 3H_2O$ or $C_D = {}^1\!/_2(2CO_3^{2-} \cdot 6H_2O)$ sublayers in the following sequences:

O-$C_4A\overline{C}H_{11}$ structure:

$$\underbrace{C_O\ \ A\ \ B}_{[C_4A\overline{C}H_{11}]}\ \underbrace{C_O\ \ A\ \ B}_{[C_4A\overline{C}H_{11}]}\ \underbrace{C_O\ \ A\ \ B}_{[C_4A\overline{C}H_{11}]}$$

D-$C_4A\overline{C}H_{11}$ structure:

$$\underbrace{C_O\ \ A\ \ C_D}_{[C_4A\overline{C}_2H_{12}]^{2-}}\quad \underbrace{B\ \ A\ \ B}_{[C_4AH_{10}]^{2+}}\ \underbrace{C_D\ \ A\ \ C_D}_{[C_4A\overline{C}_2H_{12}]^{2-}}$$

The O-structure can be regarded as being built from a unique neutral layer $[Ca_4Al_2(OH)_{12} \cdot CO_3 \cdot 5H_2O]$ corresponding to B-A-C_O sequence, whereas the D-structure is built from two kinds of layers, one negatively charged $[Ca_4Al_2(OH)_{12} \cdot 2CO_3 \cdot 6H_2O]^{2-}$ corresponding to a C_D-A-C_D sequence, and the other positively charged $[Ca_4Al_2(OH)_{12} \cdot 4H_2O]^{2+}$ corresponding to a B-A-B sequence.

The distances between two adjacent main layers (called A in the stacking model) are closely similar in both structures, d = 7.554 Å in O-$C_4A\overline{C}H_{11}$ and d = 7.536 Å in D-$C_4A\overline{C}H_{11}$. They correspond to the interreticular distances of the (011) and (002) planes, respectively. Such a small difference is quite normal because the interlayer global compositions are the same: $[CO_3 \cdot 5H_2O]^{2-}$.

2.2.2. Order and disorder

The ordering of the various species contained in the interlayer of the $C_4A\overline{C}H_{11}$ 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-$C_4A\overline{C}H_{11}$ structure is shown in Fig. 2. This concerns only atoms belonging to carbonate groups and water molecules (H_2O(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 H_2O(8), H_2O(9) and H_2O(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-$C_4A\overline{C}H_{11}$ can be considered as having a distorted hexagonal structure as can be seen by the triclinic lattice parameters: a ≈ b, α and β ≈ 90°, and γ ≈ 120°. The relation between the triclinic O-$C_4A\overline{C}H_{11}$ 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:

$$\begin{cases} a'_O = -1/2a_O - 1/2b_O + 1/2c_O \\ b'_O = -1/2a_O + 1/2b_O - 1/2c_O \\ c'_O = b_O + c_O \end{cases}$$

where a_O, b_O, and c_O are the basis vectors of the O-lattice and, and a'_O, b'_O, and c'_O are those of the pseudohexagonal lattice. The transformation matrix thus is as follows:

$$M_O/ \ = \begin{pmatrix} -1/2 & -1/2 & 1/2 \\ -1/2 & 1/2 & -1/2 \\ 0 & 1 & 1 \end{pmatrix}$$

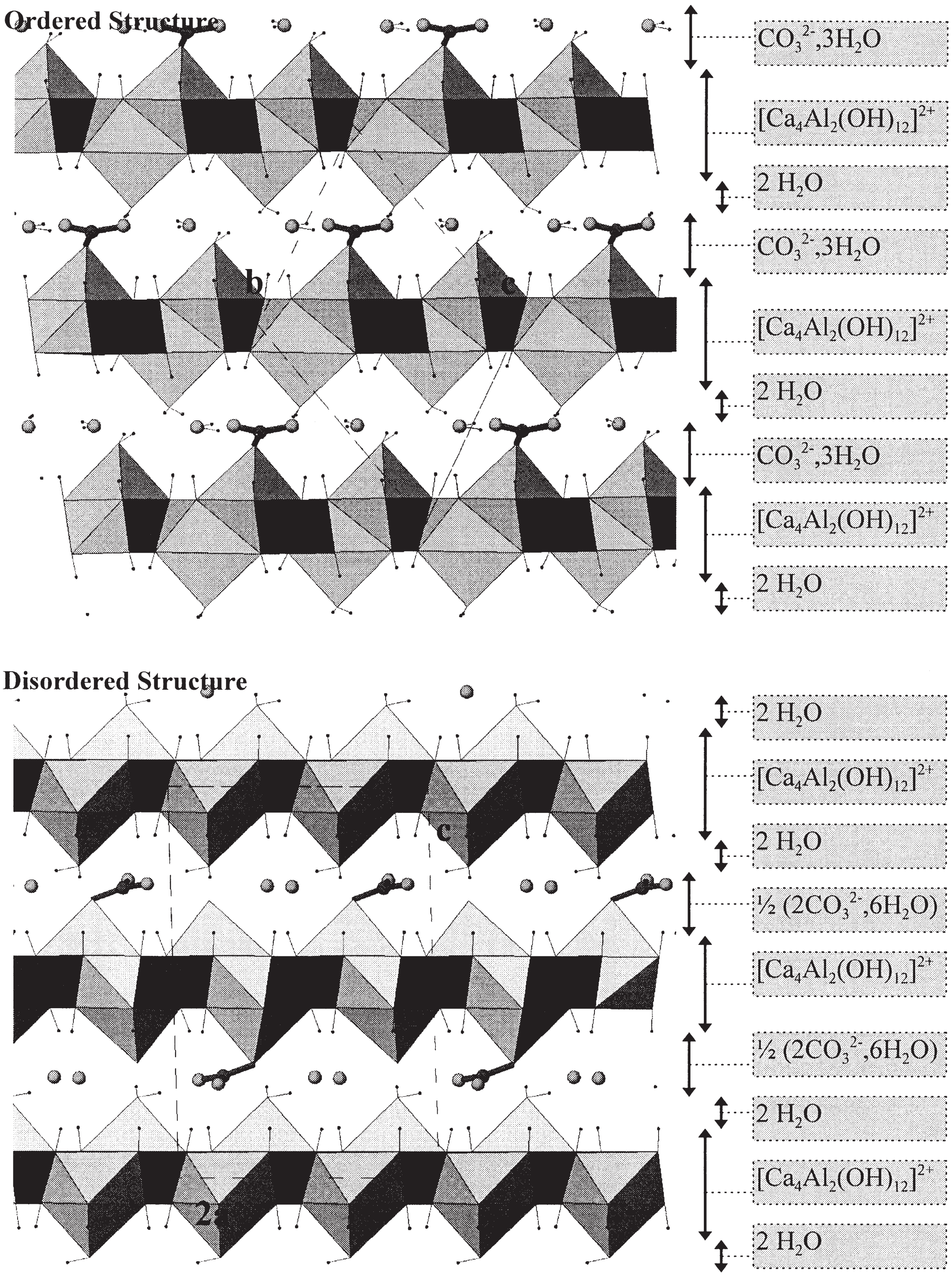

Fig. 1. Projections of the O-$C_4A\overline{C}H_{11}$ and D-$C_4A\overline{C}H_{11}$ structures on (100) and (010), respectively. The D-$C_4A\overline{C}H_{11}$ structure is represented in an ordered way with a double lattic $2\vec{a}, \vec{b}, \vec{c}$.

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), γ − 120°, and the split (angle between the pseudohexagonal axis and the normal to the (001) plane, i.e., $\vec{c}$ *) also are reported.

It is evident that the O-lattice is deviates further from hexagonal lattice. The (a,b) basal planes remain approxi-

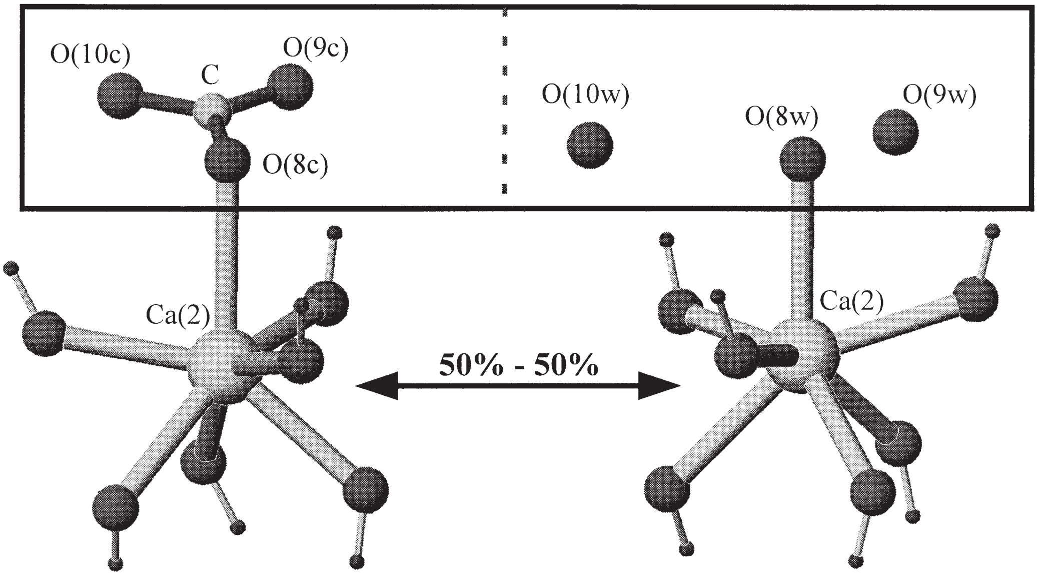

Fig. 2. Disordered positions of the D-structure.

mately hexagonal in both O- and D-structures, as seen by a − b/a + b and $\gamma - 120°$ values near zero, whereas the deviation 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 Ca^{2+} by Al^{3+} cations in the trigonal structure of $Ca(OH)_2$ (space group). The resulting main layers of composition $[Ca_2Al(OH)_6]^+$ 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 $C_4A\overline{S}H_{12}$ structure [3] (trigonal space group $R\overline{3}$), 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 $C_4A\overline{S}H_{12}$ to D-$C_4A\overline{C}H_{11}$ and to O-$C_4A\overline{C}H_{11}$ structures is due to the increase 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 carbonated AFm phase) was made by Buttler et al. [12] in 1959. The authors pointed out the "difficult problem of determining the true value or values of c axis" in this compound and they supposed "this structural element proves to be the key of the structure." To explain the oscillation, rotation, and Weissenberg photographs, Buttler et al. proposed a superstructure in the direction of the pseudohexagonal lattice. 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′ (c′ is the layer thickness).

In the present work, we do not find a true superstructure for the $C_4A\overline{C}H_{11}$ compound along the layer stacking. In the case of the D-$C_4A\overline{C}H_{11}$, the pseudohexagonal lattice has a parameter c = 15.091 Å. This value corresponds to the doubled-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 superstructure 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 interlayer part is only along the direction. The order in the direction 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
Comparison of the O′- and D-lattice parameters and the calculated deviation from hexagonal lattice

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	(a − b)/(a + b)	γ − 120 (°)	Split (°)*
O′-lattice	5.7447	5.7398	15.5509	103.36	86.08	119.63	0.04	−0.37	13.7
D-lattice	5.7422	5.7444	15.091	92.290	87.450	119.54	0.02	−0.45	2.8

* Explanation for the term "split" is given in the text.

The triclinic lattice of O-$C_4A\overline{C}H_{11}$ 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-$C_4A\overline{C}H_{11}$ compound faces of the platy hexagonal crystal do not gave 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 $C_4A\overline{C}H_{11}$ exist. Both were obtained by hydrothermal synthesis. The only experimental parameter that differed was the temperature: O-$C_4A\overline{C}H_{11}$ was obtained at 120°C, and D-$C_4A\overline{C}H_{11}$ 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 $P\overline{1}$, 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-$C_4A\overline{C}H_{11}$ layer structures. Superstructure along the layer stacking in these two modifications of $C_4A\overline{C}H_{11}$ structure were not observed.

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