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The crystal structure of $Ca_5(HAsO_4)_2(AsO_4)_2.4H_2O$ (Sainfeldite)

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Résumé. — La sainfeldite, dihydrogène arséniate diarséniate de calcium tétrahydraté, appartient au système monoclinique, groupe spatial *C2/c*. La maille, de paramètres $a_o = 18{,}781\ (7)$ Å, $b_o = 9{,}820\ (4)$ Å, $c_o = 10{,}191\ (4)$ Å, $\beta = 97^\circ\ 1'\ (3')$, contient quatre groupements moléculaires. La structure a été résolue à l'aide des mesures de diffraction des rayons X faites sur un diffractomètre automatique à trois cercles avec la radiation $K\alpha$ du cuivre. Les 1 909 réflexions indépendantes non nulles ont été corrigées des effets de l'absorption, de l'extinction secondaire et de la dispersion anomale. Le facteur de reliabilité obtenu après affinement anisotrope (par moindres carrés) est de 0,039. Les atomes d'hydrogène ont pu être localisés par une série différence de Fourier. Dans la structure de la sainfeldite on retrouve des groupes $(AsO_4)^{3-}$ et des groupes $(HAsO_4)^{2-}$; les cations Ca^{2+}, entourés de 6 atomes d'oxygène, ont une coordination octaédrique déformée. La structure est caractérisée par la répétition de groupements de cinq polyèdres de coordination du Ca dans lesquels les octaèdres partagent des arêtes ; ces unités se lient mutuellement par mise en commun de sommets des octaèdres, en formant une connexion tridimensionnelle. Des liaisons hydrogène forment une chaîne infinie parallèle à l'axe *z* ; une de ces liaisons est bifide.

The crystal structure of $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 4H_2O$ *(Sainfeldite).*

Abstract. — Sainfeldite, calcium bis-hydrogen-arsenate bis-arsenate tetrahydrate, crystallizes in the monoclinic system, space group *C2/c*. Unit-cell parameters are : $a_o = 18.781\ (7)$, $b_o = 9.820\ (4)$, $c_o = 10.191\ (4)$ Å, $\beta = 97^\circ\ 1'\ (3')$; Z = 4. The crystal structure was solved and refined anisotropically, to R = 0.039, using 1909 non-zero reflexions measured on an automatic three-circle diffractometer ($CuK\alpha$ radiation). Corrections for absorption, secondary extinction and anomalous scattering were applied. The hydrogen atoms were located from a difference map. In the structure of sainfeldite there are $(AsO_4)^{3-}$ and $(HAsO_4)^{2-}$ groups ; the three crystallographically independent calcium atoms are coordinated by 6 oxygen atoms according to distorted octahedra which, by sharing sides and vertices, link themself in a three-dimensional framework where compact groups of five polyhedra stand out. Infinite chains of hydrogen bonds, one of which is bifurcated, run along the *z* axis.

Introduction.

Sainfeldite, $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 4H_2O$ (calcium bis-hydrogen-arsenate bis-arsenate tetrahydrate), was described the first time by Pierrot (1964) in 1964 ; it has been found in old specimens from Jachymov (Bohemia) and in fresh material from Sainte-Marie-aux-Mines (Alsatia). Sainfeldite is the least hydrated member of the group including vladimirite, $Ca_5H_2(AsO_4)_4 \cdot 5H_2O$, and guérinite, $Ca_5H_2(AsO_4)_4 \cdot 9H_2O$.

We carried out the X-ray crystal structure determination of sainfeldite as a part of a programme of structural research on acidic and hydrated arsenates (cf. Chiari *et al.* (1971) and references therein quoted).

PREPARATION AND CRYSTAL DATA.

$Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 4H_2O$ crystals, suitable for an X-ray study, were grown by the method of Guérin (1941); the material was checked by comparison with X-ray powder spectrum data given by Pierrot (1964).

We obtained needle crystals elongated in the z direction and with a roughly equidimensional cross-section; they were limpid and colourless. CuKα X-ray diffraction analysis (Weissenberg and precession photographs, single-crystal diffractometry) confirmed the monoclinic symmetry found by Pierrot (1964); the space group $C2/c$ has been chosen on the basis of the systematic absences (Cc or $C2/c$), of the absence of the piezoelectric effect and of the examination of the Harker sections of the Patterson function. The successful refinement of the structure confirmed the validity of the choice.

By measurements on a few crystals we detected the following forms: $a = \{100\}$, $b = \{110\}$ (the most developed), $c = \{210\}$, $d = \{111\}$, $e = \{\bar{3}11\}$.

Unit-cell parameters, from θ values measured on a single-crystal diffractometer (CuKα radiation), were extrapolated against $1/2\,(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$; their values are: $a_o = 18.781\,(7)$ Å, $b_o = 9.820\,(4)$ Å, $c_o = 10.191(4)$ Å, $\beta = 97^\circ 1'\,(3')$. They are in agreement with the values given by Pierrot (1964).

Other physical data are: M. W. 850.120, $V = 1865.4$ Å^3, $D_m = 3.04$ gr cm^{-3} (Pierrot, 1964), $Z = 4$, $D_c = 3.027$ gr cm^{-3}, $F(000) = 808\,e$, linear absorption coefficient for CuKα radiation, $\mu = 221$ cm^{-1}.

INTENSITY MEASUREMENT.

Intensities, all on the same relative scale, were collected on an automatic three-circle General Electric diffractometer ($\theta - 2\theta$ scanning, 2° per minute; 0.5° background on both sides of each peak).

We mounted a needle crystal with its z axis along the instrumental φ axis and collected 2033 independent reflexions; 124 of them were rejected during the refinement because very weak and $|F_c| < |F_o|$.

Absorption correction was applied using the program GONO9 by Hamilton (1966); the dimensions of the slightly idealised crystal were: 0.060 mm, 0.054 mm and 0.50 mm across the opposite faces of $\{100\}$, $\{110\}$ and $\{001\}$ respectively. The range of the transmission factor was between 0.52 and 0.66.

A secondary extinction correction was introduced towards the end of the refinement; with a least-squares procedure we deduced, for the function

1) $|F_c|/|F_o| = k\,(1 + g\,I_c)$,
$k = 0.992$ and $g = 49.10^{-8}$.

The atomic scattering factors, including the real and the imaginary correction for anomalous scattering, were a linear interpolation of the values reported, for neutral atoms, in International Tables for X-ray Crystallography (1962).

SOLUTION AND REFINEMENT OF THE STRUCTURE.

The structure was solved by the heavy atom method. In a three-dimensional Patterson function we were able to locate the two independent As-atoms and Ca(1); a subsequent difference synthesis (R = 0.48) showed all the oxygen atoms except W (2) which came up from the successive Fourier synthesis (R = 0.14). In the unit cell there are four formula units; however all the atoms, except Ca (1), are on a general position.

A least-squares refinement was then started with isotropic temperature factors; subsequent cycles, including anisotropic vibrational parameters, reduced R to 0.043. At this stage, after correcting for the secondary extinction effect, a three-dimensional difference synthesis was computed from which it was possible to deduce the coordinates of all the five independent hydrogen atoms. Since the total number of maxima ($0.5 \div 1\,e$ Å^{-3}) was greater than the number of possible hydrogen atoms, a selection was made after calculation of the bond distances and angles for all of them. After trying to refine the positional and vibrational parameters of the hydrogen atoms, we decided to keep the coordinates deduced from the Fourier synthesis deeming their least-squares shifts meaningless. The refinement was successfully completed with R = 0.039; in the list (1) of the structure factors excluding a few reflexions, marked with an asterisk, the

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(1) A list of $|F_o|$ and F_c is available either from the authors or from the editorial office.

TABLE I.

Fractional atomic coordinates and vibrational parameters (Å^2) with the significant figures of the estimated standard deviations in parentheses.

	x/a_o	y/b_o	z/c_o	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
As (1)............	0.41471 (2)	0.31962 (5)	0.41581 (4)	0.67 (2)	0.64 (2)	0.62 (2)	— 0.02 (1)	— 0.03 (1)	— 0.03 (1)
As (2)............	0.65932 (2)	0.24002 (5)	0.62295 (4)	0.61 (2)	0.39 (2)	0.58 (2)	0.05 (1)	0.02 (1)	— 0.02 (1)
Ca (1)............	1/2	0.39531 (13)	3/4	0.71 (4)	0.79 (4)	0.71 (4)	0	— 0.02 (3)	0
Ca (2)............	0.32106 (5)	0.08094 (9)	0.18553 (9)	0.95 (3)	0.68 (3)	0.97 (3)	— 0.06 (2)	0.12 (2)	0.09 (2)
Ca (3)............	0.32375 (5)	0.46774 (9)	0.14044 (9)	0.82 (3)	0.67 (3)	1.00 (3)	— 0.07 (2)	0.08 (2)	— 0.20 (2)
O (1)............	0.4829 (2)	0.2007 (4)	0.4305 (4)	1.89 (15)	1.77 (14)	1.87 (16)	1.11 (12)	— 0.41 (12)	— 0.43 (12)
O (2)............	0.4250 (2)	0.4313 (4)	0.2970 (3)	1.41 (13)	1.25 (12)	1.01 (12)	— 0.28 (10)	0.13 (10)	0.50 (10)
O (3)............	0.3388 (2)	0.2324 (4)	0.3657 (4)	0.96 (13)	1.63 (14)	1.46 (13)	— 0.74 (10)	0.02 (10)	— 0.42 (11)
O (4)............	0.4128 (2)	0.3940 (4)	0.5635 (3)	1.32 (13)	1.54 (13)	0.45 (11)	0.31 (10)	— 0.08 (9)	— 0.39 (9)
O (5)............	0.6624 (2)	0.2583 (3)	0.4591 (3)	1.51 (13)	0.96 (12)	0.73 (12)	0.01 (10)	— 0.00 (9)	0.01 (9)
O (6)............	0.7029 (2)	0.0956 (3)	0.6740 (3)	1.14 (12)	0.52 (11)	1.62 (13)	0.38 (9)	0.38 (10)	0.44 (9)
O (7)............	0.7017 (2)	0.3747 (3)	0.7009 (3)	0.81 (12)	1.01 (12)	1.69 (13)	— 0.33 (9)	0.15 (10)	— 0.54 (10)
O (8)............	0.5726 (2)	0.2339 (3)	0.6523 (3)	0.85 (12)	0.86 (12)	1.38 (13)	— 0.05 (9)	0.23 (10)	— 0.05 (9)
W (1)............	0.2383 (3)	0.4115 (3)	0.4725 (4)	1.54 (14)	0.75 (12)	1.33 (13)	0.03 (10)	0.37 (10)	0.01 (10)
W (2)............	0.5708 (3)	0.0207 (6)	0.8395 (6)	2.05 (19)	3.94 (25)	4.68 (26)	1.23 (18)	0.97 (18)	0.81 (21)
H (1)............	0.515 (6)	0.230 (10)	0.500 (11)	B = 2.4					
H (2)............	0.258 (6)	0.358 (11)	0.438 (10)	1.4					
H (3)............	0.212 (6)	0.358 (11)	0.520 (10)	2.1					
H (4)............	0.564 (5)	0.110 (11)	0.780 (10)	7.2					
H (5)............	0.532 (6)	— 0.030 (11)	0.820 (11)	5.6					

R value is 0.037. These reflexions, probably affected by some measurement errors, were given zero weight throughout the refinement.

The full-matrix least-squares program by Busing *et al.* (1962), with minor modifications, was used. In the final cycles the following weighting scheme (with $|F_o|$ 1.02 times the absolute scale) has been employed :

$$2)\quad w = \frac{\left(110 + 100\,\frac{\sin^2\theta}{\lambda^2}\right)}{(0.01\,|F_o|^2 + 2\,|F_o| + 40)} \qquad if\,|F_o| \leq 40$$

$$3)\quad w = 0.025\,|F_o| \qquad if\,|F_o| > 40.$$

The weighted R value was 0.047 ; the standard error of an observation of unit weight was 2.60.

The final values of the fractional coordinates and the B_{ij} coefficients of the expression

$$4)\quad \exp\left(-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3} B_{ij}h_ih_ja^*_ia^*_j\right)$$

are listed in table I with, in parentheses, the estimated standard deviations obtained, for all the atoms, from the least-squares refinement.

Description and discussion of the structure

In the crystal structure of sainfeldite we found $(HAsO_4)^{2-}$ and $(AsO_4)^{3-}$ groups, which, obviously, are crystallographically independent ; their interatomic distances and bond angles are reported in table II which shows also the As-O distances corrected for the thermal motion assuming a riding model (Busing *et al.*, 1964).

Table II.

Interatomic distances (corrected (B) and uncorrected (A) for the thermal motion) and angles (O-As-O) in the two AsO_4 group. The estimated standard deviations are 0.003 Å and 0.005 Å for As-O and O-O distances respectively ; 0.2° for the angle values.

	A (Å)	B (Å)		A (Å)	B (Å)
As (1)-O (1).....	1.726	1.735	As (2)-O (5)......	1.688	1.693
As (1)-O (2).....	1.663	1.668	As (2)-O (6)......	1.688	1.693
As (1)-O (3).....	1.689	1.694	As (2)-O (7)......	1.691	1.694
As (1)-O (4).....	1.678	1.684	As (2)-O (8)......	1.693	1.696
Average......	1.689	1.695	Average.......	1.690	1.694
	(Å)	(°)		(Å)	(°)
O (1)-O (2)......	2.793	111.0	O (5)-O (6).......	2.743	108.7
O (1)-O (3)......	2.725	105.9	O (5)-O (7).......	2.735	108.1
O (1)-O (4)......	2.759	108.3	O (5)-O (8).......	2.755	109.2
O (2)-O (3)......	2.685	106.5	O (6)-O (7).......	2.756	109.3
O (2)-O (4)......	2.778	112.5	O (6)-O (8).......	2.785	110.9
O (3)-O (4)......	2.798	112.5	O (7)-O (8).......	2.783	110.6
Average.......	2.756		Average.......	2.759	
O (1)-H (1)......	0.92 (11) Å				
As (1)-O (1)-H (1)	105 (6)°				

It seems to us that $Ca_5\,(HAsO_4)_2\,(AsO_4)_2 \cdot 4H_2O$ is the first compound, investigated by X-rays, showing simultaneously the above anionic groups ; vladimirite and guerinite could be other examples.

The acidic hydrogen atom H (1) (1) is attached

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(1) The notation is as in the figures 1 and 3. Number 1...8 are for crystallographycally independent atoms; wherever two

to O (1); it was located on the basis of a difference synthesis, of a survey of the As-O distances (Cruickshank, 1961; Ferraris, 1970) [As (1)-O (1) = 1.726 (4) Å] and of the O...O contacts [O (1)...O (8) = 2.670 (5) Å]. The As (1) and As (2)-tetrahedra are linked in pairs through the hydrogen bond involving H (1).

The presence of $(HAsO_4)^{2-}$ and $(AsO_4)^{3-}$ groups in the same structure allows to test, independently from whatever kind of errors, the constancy, in different AsO_4 groups, of the average As-O value; the average values for the two chemically and crystallographically different tetrahedra in sainfeldite are 1.689 Å and 1.690 Å, in agreement with previous experimental and theoretical results (Ferraris, 1970; Kálmán, 1971). The four As (2)-O distances do not deviate significantly from their average value; this result is plausible since O (5), O (6) and O (7), contacting two Ca-atoms, have the same environment; O (8), which has the longest As (2)-O distance, contacts one calcium atom and is engaged in two hydrogen bonds. The O-As-O angles are very near to the tetrahedral value and so $As(2)O_4$ is an almost regular tetrahedron.

Into the As (1)-tetrahedron, excluding O (1), which is not calcium-coordinated but is bound to the acidic hydrogen atom, the longest As-O distance is As (1)-O (3) since O (3), coordinating Ca (2) and being acceptor in two hydrogen bonds, has the highest coordination (cf. Ferraris (1970)); moreover it is quite close to an extra calcium atom [Ca (3)-O (3) = 3.246 Å]. Unexpectedly O (2), which coordinates two calcium atoms and has the same environment as O (4), forms with As a significantly shorter bond than the latter oxygen (1.663 against 1.678 Å). That could be a consequence of a steric hindrance with the Ca (1) atom; in fact Ca (1) contacts two O (2) connected by a twofold axis [Ca (1)-O $(2,2)^{II}$ = Ca (1)-O $(2,8)^{III}$ = 2.297 (3) Å]. The « short » As-O (2) distance causes a partial failure of the empiric rule (Ferraris, 1970) stating that to oxygen atoms without acidic hydrogen correspond O-As-O angles larger than the tetrahedral value.

TABLE III.

Interatomic distances (Å) and angles (deg.) involving hydrogen atoms and hydrogen bonds; the significative figure of the estimated standard deviations are below.

A	B	C	D	E	AB	BC	AC	CD	CE	DE	BD	BCD	ACD	ABC	CDE
O $(3,3)^{VIII}$.....	H (3)-	W (1)-	H (2)...	O (3)	1.82 10	0.90 11	2.720 5	0.76 11	2.889 5	2.16 11	1.27 15	100 11	109.5 2	172 10	165 11
O (1,8).....					2.28 12		2.948 7						144.1 3	133 9	
	H (5)-	W (2)-	H (4)...	O (8)		0.86 11		1.06 11	2.836 7	1.80 10	1.57 16	107 9			162 8
W $(2,5)^{I}$.....					2.42 11		3.035 8						71.2 3	127 9	
		O (1)-	H (1)...	O (8)				0.92 11	2.670 5	1.78 11					162 10

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numbers separated by a comma are included in brackets, the second (2...8) denotes the equivalent positions generated by $\bar{x}, \bar{y}, \bar{z}$; $\pm$ $(1/2 - x, 1/2 - y, \bar{z})$; $\pm$ $(\bar{x}, 1/2 - y, 1/2 - z)$; $\pm$ $(1/2 + x, 1/2 - y, 1/2 + z)$. Roman numbers have the following meaning: I: $+ a_0, + c_0$; II: $+ a_0, + b_0, + c_0$; III: $+ b_0$; IV: $+ a_0$; V: $- a_0, - c_0$; VI: $- b_0$; VII: $+ b_0, - c_0$; VIII: $+ c_0$.

TABLE IV.

Interatomic distances and angles (O-Ca-O) concerning the three crystallographically independent Ca-polyhedra. The estimated standard deviations are 0.003-0.004 and 0.005 Å for Ca-O and O-O distances respectively; 0.1-0.2° for the angle values.

	(Å)		(Å)		(Å)
Ca (1)-O (4)	2.254	Ca (2)-O (3)	2.355	Ca (3)-O (2)	2.356
Ca (1)-O (4,5)$^{\mathrm{I}}$		Ca (2)-O (6,2)$^{\mathrm{I}}$	2.327	Ca (3)-O (7,2)$^{\mathrm{II}}$	2.330
Ca (1)-O (8)	2.386	Ca (2)-O (5,5)$^{\mathrm{IV}}$	2.327	Ca (3)-O (5,5)$^{\mathrm{IV}}$	2.323
Ca (1)-O (8,5)$^{\mathrm{I}}$		Ca (2)-O (7,7)$^{\mathrm{V}}$	2.308	Ca (3)-O (6,7)$^{\mathrm{V}}$	2.418
Ca (1)-O (2,2)$^{\mathrm{II}}$	2.297	Ca (2)-W (2,2)$^{\mathrm{I}}$	2.306	Ca (3)-O (4,8)$^{\mathrm{VII}}$	2.361
Ca (1)-O (2,8)$^{\mathrm{III}}$		Ca (2)-W (1,6)$^{\mathrm{VI}}$	2.483	Ca (3)-W (1,8)$^{\mathrm{VII}}$	2.499
Average	2.346	Average	2.351	Average	2.381

	(Å)	(°)		(Å)	(°)		(Å)	(°)
O (4,5)$^{\mathrm{I}}$-O (8,5)$^{\mathrm{I}}$	3.412	92.1	O (5,5)$^{\mathrm{IV}}$-O (3)	3.318	90.2	O (5,5)$^{\mathrm{IV}}$-O (6,7)$^{\mathrm{V}}$	3.339	89.5
O (4)-O (8)			O (5,5)$^{\mathrm{IV}}$-O (7,7)$^{\mathrm{V}}$	3.450	96.2	O (5,5)$^{\mathrm{IV}}$-W (1,8)$^{\mathrm{VII}}$	3.765	102.6
O (4)-O (8,5)$^{\mathrm{I}}$	3.278	74.7	O (5,5)$^{\mathrm{IV}}$-W (1,6)$^{\mathrm{VI}}$	3.689	100.1	O (5,5)$^{\mathrm{IV}}$-O (4,8)$^{\mathrm{VII}}$	3.691	104.0
O (4,5)$^{\mathrm{I}}$-O (8)			O (5,5)$^{\mathrm{IV}}$-W (2,2)$^{\mathrm{I}}$	3.382	93.7	O (5,5)$^{\mathrm{IV}}$-O (2)	3.369	92.1
O (4)-O (2,2)$^{\mathrm{II}}$	3.632	102.7	O (6,2)$^{\mathrm{I}}$-O (3)	3.328	90.6	O (7,2)$^{\mathrm{II}}$-O (6,7)$^{\mathrm{V}}$	2.998	78.3
O (4,5)-O (2,8)$^{\mathrm{III}}$			O (6,2)$^{\mathrm{I}}$-O (7,7)$^{\mathrm{V}}$	2.998	80.6	O (7,2)$^{\mathrm{II}}$-W (1,8)$^{\mathrm{VII}}$	3.402	89.5
O (4)-O (2,8)$^{\mathrm{III}}$	2.920	77.8	O (6,2)$^{\mathrm{I}}$-W (1,6)$^{\mathrm{VI}}$	3.035	78.2	O (7,2)$^{\mathrm{II}}$-O (4,8)$^{\mathrm{VII}}$	3.420	93.6
O (4,5)$^{\mathrm{I}}$-O (2,2)$^{\mathrm{II}}$			O (6,2)$^{\mathrm{I}}$-W (2,2)$^{\mathrm{I}}$	3.251	89.1	O (7,2)$^{\mathrm{II}}$-O (2)	3.051	81.2
O (8)-O (8,5)$^{\mathrm{I}}$	3.567	96.7	O (3)-O (7,7)$^{\mathrm{V}}$	3.083	82.8	O (6,7)$^{\mathrm{V}}$-W (1,8)$^{\mathrm{VII}}$	2.857	71.5
O (8)-O (2,2)$^{\mathrm{II}}$	3.328	90.5	O (3)-W (2,2)$^{\mathrm{I}}$	3.783	108.5	W (1,8)$^{\mathrm{VII}}$-O (4,8)$^{\mathrm{VII}}$	3.300	85.5
O (2,2)$^{\mathrm{II}}$-O (2,8)$^{\mathrm{III}}$	3.084	84.3	W (2,2)$^{\mathrm{I}}$-W (1,6)$^{\mathrm{VI}}$	3.337	88.3	O (4,8)$^{\mathrm{VII}}$-O (2)	2.920	76.5
O (2,8)$^{\mathrm{III}}$-O (8,5)$^{\mathrm{I}}$	3.328	90.5	W (1,6)$^{\mathrm{VI}}$-O (7,7)$^{\mathrm{V}}$	3.048	78.9	O (2)-O (6,7)$^{\mathrm{V}}$	4.216	124.0
O (4)-Ca (1)-O (4,5)$^{\mathrm{I}}$		179.4	O (5,5)$^{\mathrm{IV}}$-Ca (2)-O (6,2)$^{\mathrm{I}}$		176.6	O (5,5)$^{\mathrm{IV}}$-Ca (3)-O (7,2)$^{\mathrm{II}}$		159.2
O (2,8)$^{\mathrm{III}}$-Ca (1)-O (8)		167.3	O (7,7)$^{\mathrm{V}}$-Ca (2)-W (2,2)$^{\mathrm{I}}$		165.0	W (1,8)$^{\mathrm{VII}}$-Ca (3)-O (2)		159.1
O (2,2)$^{\mathrm{II}}$-Ca (1)-O (8,5)$^{\mathrm{I}}$		167.3	W (1,6)$^{\mathrm{VI}}$-Ca (2)-O (3)		159.8	O (4,8)$^{\mathrm{VII}}$-Ca (3)-O (6,7)$^{\mathrm{V}}$		155.5

The three crystallographically independent calcium atoms are coordinated by six oxygen atoms belonging to different As-tetrahedra or to the water molecules. The resulting octahedra are quite distorted (table IV), in part because they share some sides and in part owing to the spread of the values of the Ca-O distances [2.297 (3) Å ÷ 2.499 (4) Å]. As a consequence of the Ca-Ca repulsion the smallest values among the O-O octahedral distances are those of the shared sides, O (4)-O $(2,8)^{III}$ between Ca (1) and Ca (3)-polyhedra and O $(6,2)^{I}$-O $(7,7)^{V}$ between Ca (2) and Ca (3)-polyhedra. Through the shared sides, the Ca-octahedra gather, along the x axis, in short five members chains (fig. 1 and 2) ; a Ca (1)-octahedron, on a twofold axis, is in the

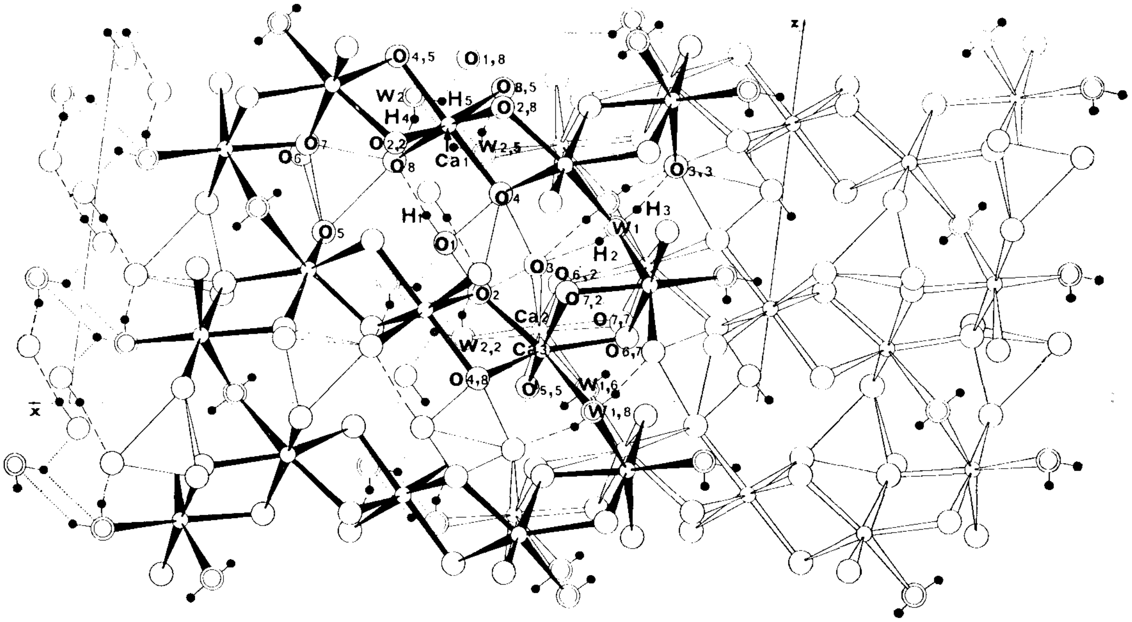

FIG. 1. — View of two contiguous strips of Ca-octahedron chains ; the contents of about two thirds of one unit cell are projected onto the xz plane. The double circles are the oxygen atoms (W) of the water molecules.

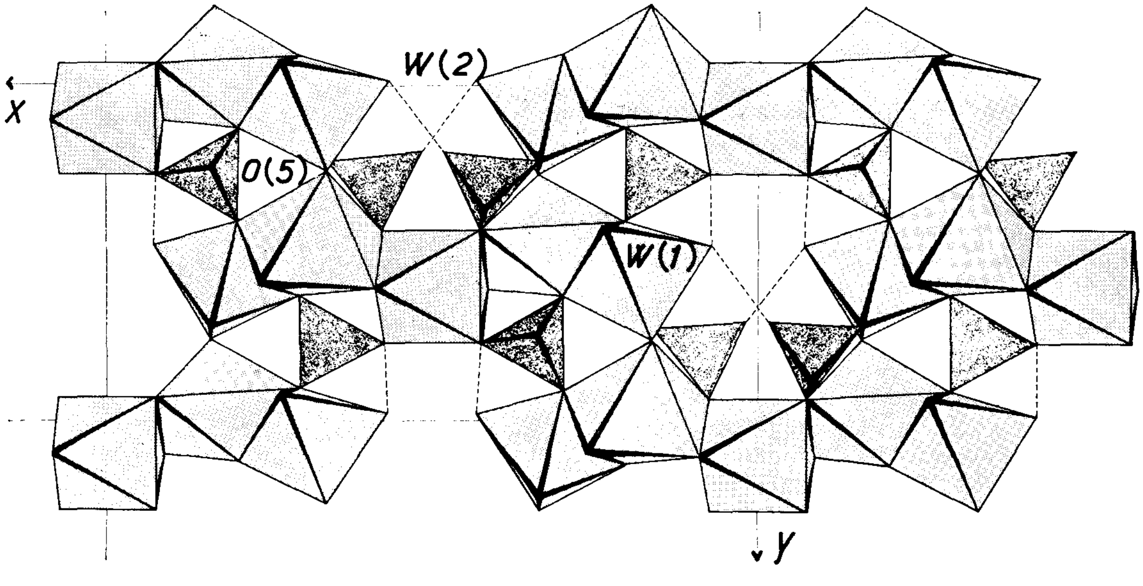

FIG. 2. — Packing of Ca-polyhedra projected along [001].

middle of the chains and links itself to two Ca (3)-polyhedra which, in their turn, share an edge with a Ca (2)-octahedron. In the unit cell there is a second chain, produced by the *c* operation and a b_0 shift, « parallel » to the first one and at about the same height on *y* ; these chains share, on both sides, their vertices occupied by W (1) and generate, along the *z* axis, a corrugated strip (fig. 1). An analogous strip is produced, $a_0/2$ and $b_0/2$ away, by the *C* operation ; these two strips are partly superimposed and Ca (2) and Ca (3)-polyhedra of different strips share their O (5) vertices (see figure 2 and O (5,5) in fig. 1). On the basis of the above description we can see that the Ca-octahedra are linked in a three-dimensional framework where compact groups of five polyhedra stand out.

We remark that the Ca (1)-octahedron is repeated, along *y*, only by the lattice vector b_0 (fig. 2) ; therefore we can see, between two Ca (1)-octahedra, a break of the three-dimensional connection where the water molecules W (2) and, on the borders, W (1) are accomodated. These molecules, which are Ca-coordinated, are involved in two series of hydrogen bonds. W (2), together with O (1), forms an infinite O (1)...H (5)-W (2)-H (4)...O (8)...H (1)-O (1) hydrogen bonding (dashed-dotted lines in fig. 1 and 3) on both sides of the Ca-polyhedron strips ; these hydrogen bonds link both chains of the same strip and chains of one strip with those of the next, along *y*, strip. On the basis of the values of the bond angles and distances (table III) it seems plausible that W (2) forms a bifurcated hydrogen bond with O (1,8) and W (2,5) (dotted lines in figures 1 and 3) ; the bond W (2)...W (2,5) would be across two strips along *x*. W (1) is donor in two hydrogen bonds linking, along *y*, two contiguous strips; in these hydrogen bonds only the anionic oxygen atom O (3) is involved, in such a way that four W...O directions are the sides of a rhombus (fig. 1). The structure of sainfeldite, as described, seems to preclude the existence of good cleavages.

If we suppose that each oxygen atom receives a formal charge 5/4 from As and 1/3 from Ca, it is easy to verify that for O (2), O (4), O (5), O (6) and O (7) the Pauling rule is quite satisfied ; however in order to satisfy the rule for the other oxygen atoms, including water molecules, it would be necessary to make more or less arbitrary hypotheses on the formal charge of the hydrogen bonds, one of which is bifurcated.

Table V shows the parameters characteri-

TABLE V.

Parameters characterizing the principal directions 1, 2, 3 of thermal vibration for As, Ca, and O-atoms : root-mean-square displacements (A) and angles which the principal directions make with the *x* (B), *y* (C) and *z* (D) axes.

		A (Å)	B (°)	C (°)	D (°)
As (1)...........	1	0.090	103	19	101
	2	0.100	36	87	133
	3	0.082	57	71	45
As (2)...........	1	0.083	59	86	38
	2	0.092	34	78	128
	3	0.069	102	13	85
Ca (1)...........	1	0.100	90	0	90
	2	0.102	138	90	41
	3	0.089	48	90	49
Ca (2)...........	1	0.110	25	96	73
	2	0.113	111	71	25
	3	0.090	77	20	107
Ca (3)...........	1	0.103	14	104	98
	2	0.118	94	115	25
	3	0.084	77	29	67
O (1)............	1	0.14	76	68	31
	2	0.21	47	54	121
	3	0.10	133	44	92
O (2)............	1	0.13	38	73	63
	2	0.15	124	45	60
	3	0.08	105	130	42
O (3)............	1	0.14	119	82	24
	2	0.17	115	35	109
	3	0.07	40	56	76
O (4)............	1	0.12	35	123	87
	2	0.16	55	39	109
	3	0.06	88	73	19
O (5)............	1	0.11	90	4	86
	2	0.14	7	89	103
	3	0.10	83	94	14
O (6)............	1	0.12	28	80	123
	2	0.15	69	69	36
	3	0.06	108	24	103
O (7)............	1	0.11	40	122	117
	2	0.16	86	120	32
	3	0.08	50	46	75
O (8)............	1	0.11	121	32	78
	2	0.13	83	96	15
	3	0.10	32	58	99
W (1)...........	1	0.12	125	90	28
	2	0.14	35	88	62
	3	0.10	92	2	91
W (2)...........	1	0.22	107	133	46
	2	0.26	74	53	45
	3	0.13	24	114	97

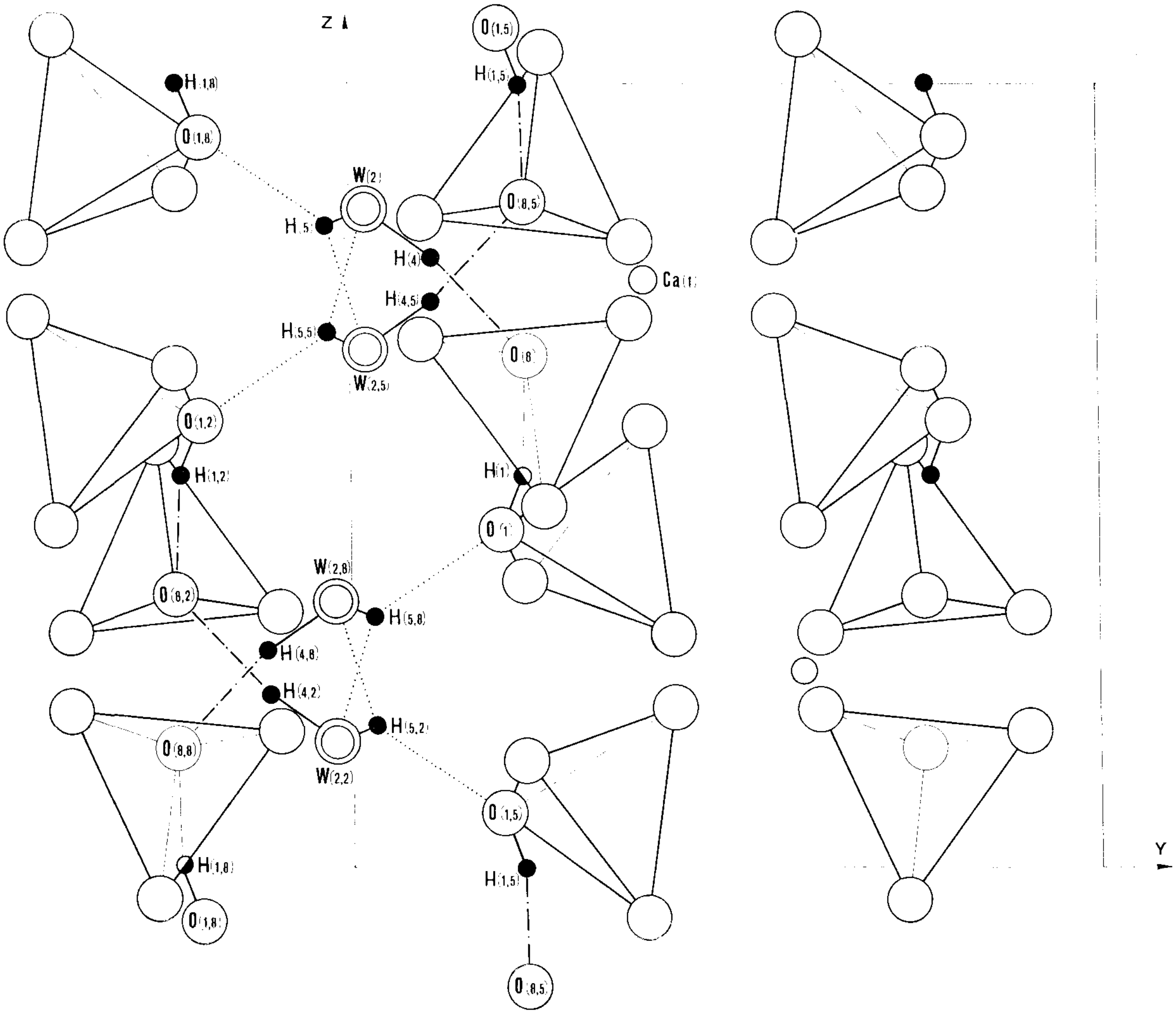

FIG. 3. — Projection, onto the *yz* plane, of a part of the contents of one unit cell to show the infinite chains of hydrogen bonds (dotted and dashed lines).

zing the principal directions of thermal vibration for As, Ca and O-atoms. It seems to us that, as usual in essentially ionic structures, the orientation of the thermal ellipsoids is random.

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