

Investigation of the Crystal Structure of γ -CaSO₄, CaSO₄ · 0.5 H₂O, and CaSO₄ · 0.6 H₂O by Powder Diffraction Methods

C. Bezou, A. Nonat, and J.-C. Mutin

Laboratoire de Recherche sur la Réactivité des Solides, URA CNRS No. 23, Université de Bourgogne, B.P. 138, F-21004 Dijon, France

A. Nørslund Christensen

Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

and

M. S. Lehmann

Institut Max von Laue-Paul Langevin, 156 X Centre de Tri, F-38042 Grenoble Cedex, France

Received August 24, 1994; in revised form November 29, 1994; accepted December 5, 1994

INTRODUCTION

The crystal structures of soluble anhydrite, γ -CaSO₄, and the two calcium sulfate subhydrates, CaSO₄ · 0.5 H₂O and CaSO₄ · 0.6 H₂O, were investigated by powder diffraction methods, using synchrotron X ray radiation and neutron powder diffraction, and the positions of the water molecules in the structure were determined. γ -CaSO₄ is orthorhombic, space group C222 (N°21) with $a = 12.0777(7)$, $b = 6.9723(4)$, $c = 6.3040(2)$ Å (from the neutron diffraction data), and $Z = 6$. The structure contains two different chains of CaO₈ coordination polyhedra (mean Ca–O = 2.460 Å) held together by SO₄²⁻ ions. CaSO₄ · 0.5 H₂O (SH1) is monoclinic, space group I121 (No. 5) with $a = 12.0317(4)$, $b = 6.9269(2)$, $c = 12.6712(3)$ Å, $\beta = 90.27(1)^\circ$ (from the neutron diffraction data), and $Z = 12$. The structure contains chains of alternating CaO₈ and CaO₉ coordination polyhedra held together by the SO₄²⁻ ions. The average Ca–O distances in the CaO₈ and in the CaO₉ coordination polyhedra are 2.469 and 2.500 Å, respectively. A monoclinic structure is proposed for CaSO₄ · 0.6 H₂O (SH2), space group I121 (No. 5) with $a = 11.9845(4)$, $b = 6.9292(2)$, $c = 12.7505(3)$ Å, $\beta = 90^\circ$ (from the neutron diffraction data), and $Z = 12$. The structure contains chains of CaO₈ and chains of CaO₉ coordination polyhedra, both held together by the SO₄²⁻ ions. The average Ca–O distances in the CaO₈ and in the CaO₉ coordination polyhedra are 2.538 and 2.494 Å, respectively. All of the three structures have channels where the water molecules associated with the CaO₉ polyhedra are located in the case of subhydrates. In the case of the hemihydrate, the water molecules form hydrogen bonds with oxygen atoms of the sulfate tetrahedra of 2.85–3.03 Å. In the case of CaSO₄ · 0.6 H₂O, two adjacent water molecules in the channels are linked by a strong hydrogen bond (O–H = 1.9 Å). © 1995 Academic Press, Inc.

Several studies have been published on the crystal structures of calcium sulfate and its hydrates with composition CaSO₄ · x H₂O, where $2 \geq x \geq 0$. The structures of gypsum, CaSO₄ · 2 H₂O (1), and of insoluble anhydrite, β -CaSO₄ (2), are well established.

The thermal decomposition of CaSO₄ · 2 D₂O (3) and CaSO₄ · 2 H₂O (4) studied as a function of temperature by neutron powder diffractometry and in equilibrium with the ambient water vapor pressure shows that gypsum decomposes thermally to a subhydrated compound CaSO₄ · x H₂O, then to γ -CaSO₄, and finally to insoluble anhydrite, β -CaSO₄. The subhydrated dehydration product formed in this investigation (4) had the composition CaSO₄ · 0.74 H₂O. Other studies by thermogravimetric methods (5–7) reveal that the degree of hydration varies with the experimental conditions like the water vapor pressure and the surface area of the sample.

The structure of soluble anhydrite, γ -CaSO₄, was investigated by single-crystal diffractometry (8) and by time of flight (TOF) neutron powder diffraction analysis (9), and structures of different subhydrated compounds, CaSO₄ · x H₂O with $0.8 \geq x \geq 0.5$, have been reported by several authors (8, 10–14).

All these compounds have structures with channels where water molecules may be situated. However, ambiguities exist concerning some of the structures due to uncertainty with respect to the number of water mole-

cules in the channels, and several of them have a water content higher than the steric limit of 0.66.

Investigation of the thermodynamic diagram $P_{\text{H}_2\text{O}}-T$ of the calcium sulfate (15) from a hydrothermally crystallized sample of subhydrated calcium sulfate instead of a dehydration product of gypsum shows that two subhydrated phases exist, $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$ (SH1) and $\text{CaSO}_4 \cdot 0.6 \text{H}_2\text{O}$ (SH2). These are, together with $\gamma\text{-CaSO}_4$, the three different phases with which it is possible to get by the dehydration of gypsum in the fabrication of plaster of Paris. It is not possible to relate these compositions to the structures proposed previously, since in no cases in the previously reported diffraction analysis was the pressure of water vapor over the sample controlled during the data collection.

Table 1 displays a selection of crystallographic data for some calcium sulfate hydrates, $\text{CaSO}_4 \cdot x \text{H}_2\text{O}$, $2 \geq x \geq 0$. The volume of a formula unit of $\text{CaSO}_4 \cdot x \text{H}_2\text{O}$ for $x = 0, 0.5, 0.6,$ and 2 are displayed in Fig. 1. The compounds with channels in the structures, $\gamma\text{-CaSO}_4$, SH1, and SH2 have almost identical volumes for one formula unit of $\text{CaSO}_4 \cdot x \text{H}_2\text{O}$, showing that the water molecules can be readily distributed in the channels.

In order to overcome this ambiguity concerning the water content and structures of the subhydrates attempts were made to make X ray single-crystal diffraction measurements with crystals grown by the procedure reported by Caspari (17). However, the crystals obtained were twinned, and subsequent structure analyses were performed with X ray and neutron powder diffraction data. The X ray powder patterns of $\gamma\text{-CaSO}_4$ and the subhydrates resemble each other; thus the structures must have common features. According to Flörke (8), the structures have chains of CaO_8 polyhedra connected by SO_4 tetrahedra forming large channels where water molecules may be situated. In this work, the positions of the

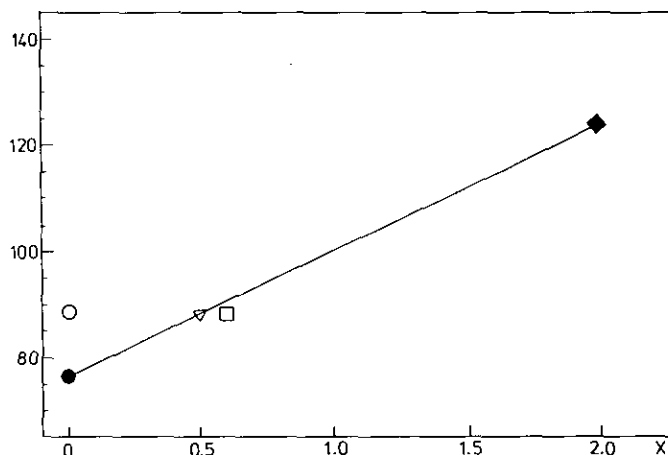


FIG. 1. Volume in \AA^3 per formula unit of $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ vs x . The symbols represent (○) $\gamma\text{-CaSO}_4$; (▽) SH1, $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$; (□) SH2, $\text{CaSO}_4 \cdot 0.6 \text{H}_2\text{O}$; (●) CaSO_4 insoluble anhydrite; and (◆) $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$.

water molecules in the structures of the subhydrate SH1 have been determined by neutron powder diffraction analysis, and the structure is compared with that of soluble anhydrite and SH2.

EXPERIMENTAL

Sample preparation. All the diffraction studies were made on samples prepared by autoclave treatment of a very pure sample of the mineral gypsum, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ from Maurienne, France. The conditions of thermolysis were $T = 134^\circ\text{C}$ ($P = 3$ bars) for four hours. The sample obtained in this treatment was a subhydrate of excellent crystal quality that was used in the preparation of the pure phases. Hydration degree of samples was checked by thermogravimetric analysis under controlled vapor

TABLE 1
Crystallographic Data for $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$, $2 \geq x \geq 0$

Compound	a (Å)	b (Å)	c (Å)	β (°)	Space group	Ref.
$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$	5.679	15.202	6.522	118.43	$I2/a$	(1)
$\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$	11.94	6.83	12.70	90.60	$C121$	(10)
$\text{CaSO}_4 \cdot 0.67 \text{H}_2\text{O}$	12.028	6.927	12.67	90.21	$I2$	(12)
$\text{CaSO}_4 \cdot 0.53 \text{H}_2\text{O}$	12.0275(4)	6.9312(3)	12.6919(5)	90.18(1)	$I2$	(14)
$\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$	12.0344(1)	6.9294(1)	12.6757(2)	90.265(3)	$I121$	This work
$\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$	6.9372		6.345		$P3_121$	(16)
$\text{CaSO}_4 \cdot 0.8 \text{H}_2\text{O}$	6.968		6.410		$P3_121$	(13)
$\text{CaSO}_4 \cdot 0.62 \text{H}_2\text{O}$	13.861(3)		12.7391(6)			(14)
$\text{CaSO}_4 \cdot 0.6 \text{H}_2\text{O}$	11.988	6.930	12.753	90	$I121$	This work
$\gamma\text{-CaSO}_4$	6.982		6.340		$P6_222$	(8)
$\gamma\text{-CaSO}_4$	6.9694		6.3033		$P6_222$	(9)
$\gamma\text{-CaSO}_4$	12.0777(7)	6.9723(4)	6.3040(2)		$C222$	This work
CaSO_4 insoluble	7.006	6.998	6.245		$Amma$	(2)

pressure. Determination of the equilibrium curve SH2/SH1 in the $P_{\text{H}_2\text{O}}-T$ diagram of the system CaSO₄-H₂O (18), and of the equilibrium curve SH1/ γ -CaSO₄ (19), permits the preparation of the three phases as pure samples. SH1, CaSO₄ · 0.5 H₂O, was made at 50°C and $P_{\text{H}_2\text{O}} = 20$ Torr, and the samples used for diffraction analysis were sealed in capillaries for the X ray measurements and in a vanadium container with indium gaskets for the neutron measurements. A sample of SH2, CaSO₄ · 0.6 H₂O, was prepared at room temperature (25°C) at a relative humidity of 95%. The sample of soluble anhydrite, γ -CaSO₄, was made at 120°C at $P_{\text{H}_2\text{O}} = 20$ Torr and sealed in containers for the diffraction experiments as described above.

X ray diffraction analysis. The purity of the samples was checked with X ray powder diffractograms measured on a laboratory diffractometer equipped with a position sensitive detector (INEL LPS 50) using CuK β radiation, $\lambda = 1.3923$ Å. The full-width at half-maximum (FWHM) of these patterns was typically 0.1° at $2\theta = 40^\circ$. To obtain better resolution of the powder patterns of SH1 and SH2 and to study in detail the differences between the patterns, additional data were obtained by the use of synchrotron radiation, giving a FWHM of 0.04° at $2\theta = 40^\circ$. These data were collected with 0.7-mm diameter Lindeman capillary samples of SH1 and SH2, using the diffractometer at the X7A beam line at the Brookhaven National Synchrotron Light Source (NSLS). The wavelength used was 1.3075 Å. The patterns were measured in the 2θ ranges SH1, 11.50°–77.00°, SH2, 11.50°–90.00°, at step intervals of 0.01°, and the capillary samples were oscillated 10° at each step to ensure particle randomization.

The powder pattern of SH1 can be indexed with a monoclinic cell similar to that published previously (12, 14). The powder pattern of SH2 had a higher symmetry than monoclinic, and three programs, FZON (20), TREOR (21), and DICVOL91 (22) were used to autoindex the pattern. The results listed in Table 2 show that orthorhombic as well as hexagonal unit cells may index the powder pattern. A hexagonal unit cell with $a =$

TABLE 2
Indexing of the X Ray Powder Pattern of SH2, NSLS Data

Program	a	b	c	M_{20}
FZON	12.006	6.931	6.368	327
	12.006	6.932	12.735	263
	13.863	13.863	6.368 ^a	
	13.863	13.863	12.735 ^a	
TREOR	13.8633(1)	13.8633(1)	6.3678(1)	245
DICVOL91	6.00281(3)	6.93135(4)	6.36794(3)	1578

^a Solutions from FZON using hexagonal setting.

13.8615 and $c = 12.7391$ Å has been reported for a subhydrate that is possibly of the SH2 type (14).

Neutron diffraction analysis. The neutron powder diffraction patterns was obtained at room temperature on the D2B diffractometer at the Institut Laue-Langevin, Grenoble, with a neutron wavelength of 1.594 Å. The powder was loaded in a vanadium container. The experimental conditions were as follows: γ -CaSO₄, soluble anhydrite, 2θ range 15°–130°, 8-mm diameter container; CaSO₄ · 0.5 H₂O, 2θ range 15°–130°, 11-mm diameter container; CaSO₄ · 0.6 H₂O, 2θ range 12°–130°, 8-mm diameter container, with a step interval of 0.05° in each case. The background level for the subhydrates was quite high due to the hydrogen content of the samples, but that for γ -CaSO₄ was low.

STRUCTURE ANALYSIS

The structures were refined by the least-squares profile method developed by Rietveld (23). A function for modeling the peak shape and four parameters for describing the FWHM were used: $(U \tan^2\theta + V \tan\theta + W)^{1/2} + S \tan\theta + T/\cos\theta$. The least-squares program EDINP (24, 25) was used for the refinement, with weights taken as 1/counts. In the X ray structure analysis the scattering factors derived by Cromer and Mann (26) were used, and in

TABLE 3
Refined Parameters for the Structure of γ -CaSO₄, Space Group C222

Atom	x/a	y/b	z/c	B (Å ²)
S2	0	0	$\frac{1}{2}$	0.73(36)
S4	$\frac{1}{2}$	$\frac{1}{2}$	0.1648(25)	0.56(19)
Ca2	$\frac{1}{2}$	$\frac{1}{2}$	0.6664(26)	1.60(18)
Ca4	0	0	0	0.62(19)
O12	0.0713(7)	-0.1158(10)	0.3548(12)	0.69(14)
O41	0.2267(7)	0.4152(13)	0.3049(14)	0.18(15)
O42	0.3494(5)	0.2740(10)	0.0292(12)	1.01(15)

Refined parameters: Zero = -1.0421(1)^o, $U = 0.067(5)$, $V = -0.139(10)$, $W = 0.160(5)$, $T = 0.070(7)$, $S = -0.040(11)$; $R_p = 7.6\%$, $R_{wp} = 10.9\%$, $R_F = 4.8\%$, $R_I = 6.5\%$, $R_E = 6.5\%$.

The FWHM is calculated from the profile parameters as $\text{FWHM} = (U \tan^2\theta + V \tan\theta + W)^{1/2} + S \tan\theta + T/\cos\theta$. $a = 12.0777(7)$, $b = 6.9723(4)$, $c = 6.3040(2)$ Å.

Atoms	Distances (Å)	Number of distances	Atoms	Distances (Å)	Number of distances
Ca2-O12	2.356(9)	2	S2-O12	1.49(1)	4
Ca2-O41	2.358(9)	2	S4-O41	1.48(1)	2
Ca2-O41	2.569(9)	2	S4-O42	1.48(1)	2
Ca2-O42	2.588(16)	2			
Ca4-O42	2.414(6)	4			
Ca4-O12	2.529(8)	4			

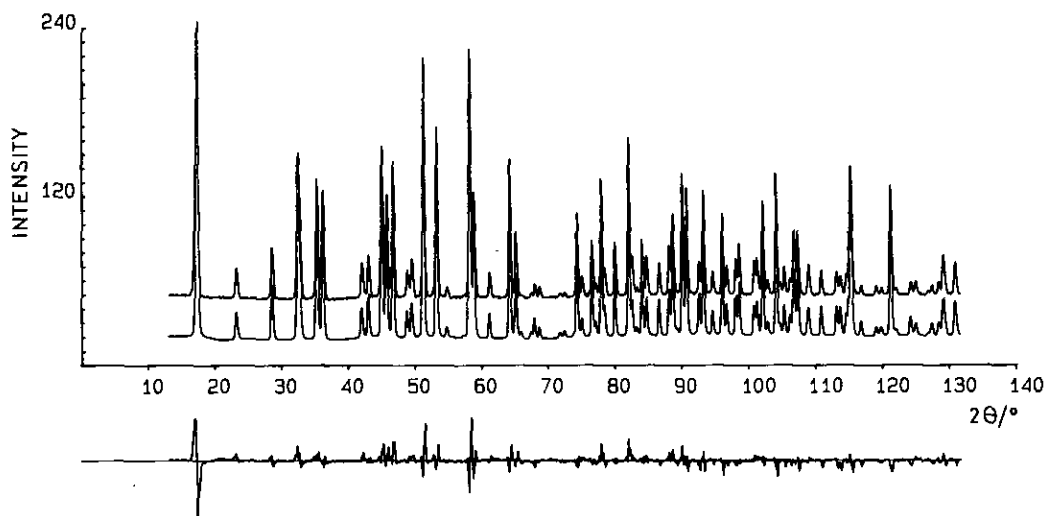


FIG. 2. Observed and calculated neutron diffraction powder pattern of γ -CaSO₄: A difference plot is shown below the abscissa.

the neutron structure analysis the scattering lengths tabulated by Koester and Rauch (27).

γ -CaSO₄ soluble anhydrite. The structure has been reported by Lager *et al.* (9) as hexagonal with space group $P6_222$ and $a = 6.9694(8)$, $c = 6.3033(4)$ Å. This model has Ca in 3c sites at $(\frac{1}{2}, 0, 0)$, S in 3d at $(\frac{1}{2}, 0, \frac{1}{2})$, and O in 12k at $(0.4458(3), 0.1347(3), 0.3578(3))$ with $Z = 3$ as determined from TOF neutron powder diffraction data, confirming one of the two possible models for the structure suggested previously by Flörke (8). The γ -CaSO₄ sample used in the TOF experiment was prepared from synthetic gypsum by dehydration at 373 K. The profile was notably broadened and it was necessary to vary three peak shape parameters of the resolution function and five for the definition of the functional dependence of the background. Despite these actions, the fit was not very good ($R_p = 12.1$, $R_E = 2.43$), which, according to the authors, may reflect the inability of the resolution function to properly model the peak shape broadening. The use of the results of the above study as starting parameters to fit the present neutron diffraction powder pattern which is practically free of sample broadening does not give a better fit ($R_p = 13.6$, $R_E = 6.5$) with the following similar structural parameters: $a = 6.9705(8)$, $c = 6.3041(3)$ Å, $B(\text{Ca}) = 1.51(12)$, $B(\text{S}) = 0.58(15)$, $B(\text{O}) = 0.905(4)$ Å² and the positional parameters for the oxygen atom $x/a = 0.4533(4)$, $y/b = 0.1409(3)$, $z/c = 0.3600(4)$. The R values are rather high, and a difference plot showed also an unacceptable agreement between the observed and calculated patterns. The lack of fit in the previous study is not solely due to the sample broadening but also to the structural model. In the proposed model, three sulfate ions are built from one oxygen atom and show severe asymmetries. We tried to fit the pattern with the

same cell and a lower symmetric space group such as $P32$. In this case, sulfate ions are built from four independent oxygen atoms, and calcium and S atoms are in general positions. The fit is not better and leads to the same R factors. The only way to get a better fit was to consider a larger cell; an orthorhombic model of the structure was then tested, using space group $C222$, and the unit cell $a = 12.0780(7)$, $b = 6.9720(4)$, $c = 6.3040(2)$ Å. This cell is related to the hexagonal cell above as $a_o = \sqrt{3} a_h$, $b_o = a_h$, and $c_o = c_h$.

This model gave a considerably better fit ($R_p = 7.6\%$, $R_E = 6.5\%$). The refined parameters are listed in Table 3, and Fig. 2 is a plot of the pattern. Figure 3 shows a projection of the model after [001] direction. The structure of soluble anhydrite is built of CaO₈ polyhedra con-

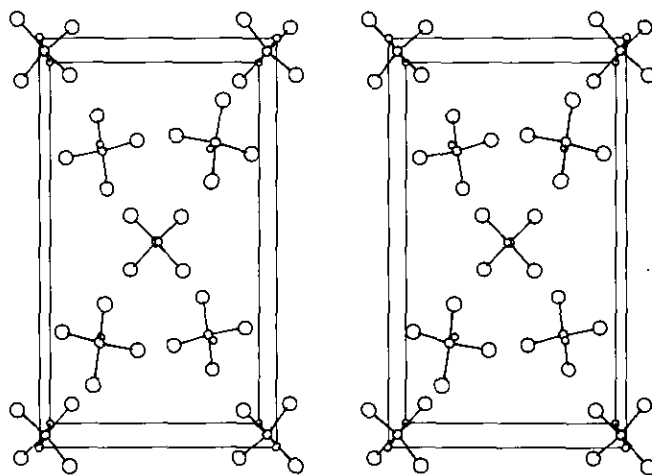


FIG. 3. Stereoscopic projection of the structure of γ -CaSO₄ along [001]. The b axis is along the page.

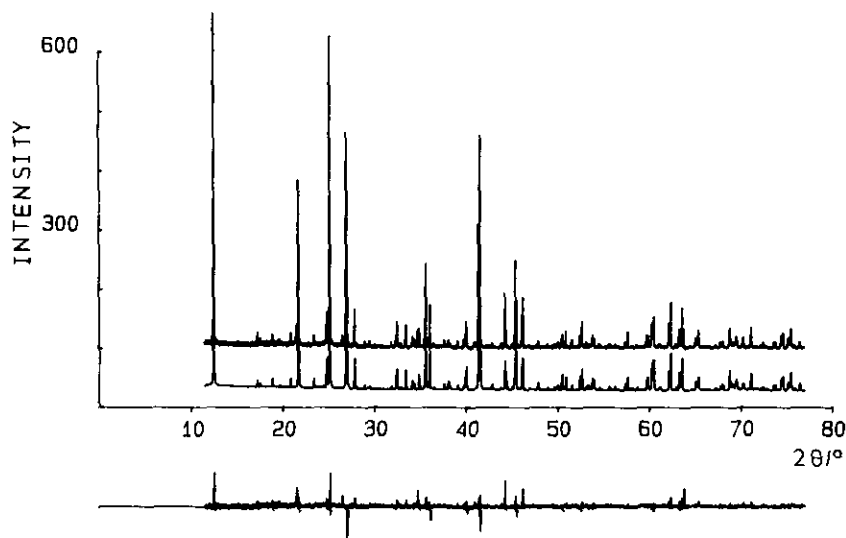


FIG. 4. Observed and calculated synchrotron X ray diffraction powder pattern of SH1, CaSO₄ · 0.5 H₂O.

nected with SO₄ tetrahedra. In the $P6_222$ and $P32$ models, the polyhedra form chains parallel to the [001] direction which are all equivalent. In the $C222$ model, the structure is built of two types of chains: the chains building the cell edges and the chains inside the cell. In the first chain, the Ca–O bond in the CaO₄ plane is Ca–O = 2.414(6) Å, and the Ca–O bond out of the plane is 2.529(8) Å. The CaO₄ plane of the polyhedra of the other chains has shorter Ca–O bonds (2.358(9) Å), and the Ca–O length out of the plane is longer (2.57(1) Å).

SH1: CaSO₄ · 0.5 H₂O. Gallitelli (10) carried out an X ray single-crystal analysis of CaSO₄ · 0.5 H₂O based on space group $C121$ (No. 5). However, the crystals investigated were twinned and showed a rhombohedral pseudo-

symmetry consistent with space group $P3_121$. For this reason, the positions of the atoms could not be determined with great precision. Another analysis was made by Bushuev (12) on untwinned single crystals grown by hydrothermal synthesis from “chemically pure” grade gypsum. The unit cell was found to be monoclinic $I121$ (No. 5) with $\beta = 90.21^\circ$, and the composition was determined to be CaSO₄ · 0.67 H₂O from refinement of the occupancy of the oxygen atoms of the water molecules. This composition is not in agreement with thermogravimetric analysis (18).

A comparison of the X ray powder pattern of γ -CaSO₄ with that of SH1 shows certain similarities. The transformation from γ -CaSO₄ to SH1 is connected with a symmetry reduction from orthorhombic to monoclinic. The syn-

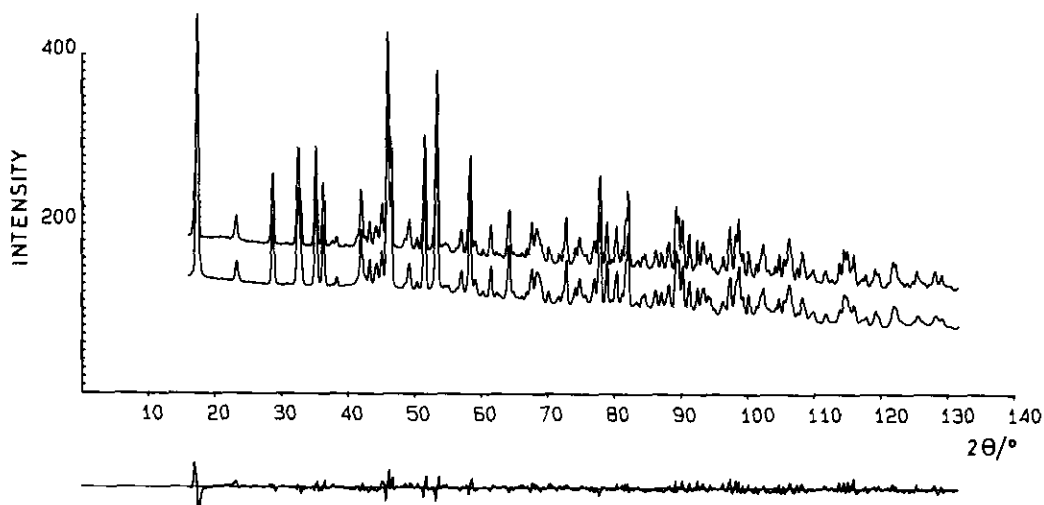


FIG. 5. Observed and calculated neutron diffraction powder pattern of SH1, CaSO₄ · 0.5 H₂O.

TABLE 4
Structure Parameters for SH1, $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$ X Ray and Neutron Data

Atom	x/a	y/b	z/c	B (Å ²)	Atoms	Distances (Å)
S2	0.001(1)	0.003(2)	0.254(1)	0.8(1)	S2-O22	1.482
	-0.002(1)	0.024(3)	0.253(1)	0.9(1)	S2-O12	1.492
S3	0.724(1)	0.172(2)	0.418(1)	0.8(1)	S2-O11	1.495
	0.723(1)	0.191(3)	0.417(1)	1.0(1)	S2-O21	1.496
S4	0.275(1)	0.183(2)	0.086(1)	0.9(1)	S3-O32	1.485
	0.276(1)	0.204(3)	0.087(1)	1.0(1)		
Ca1	0.000(0)	0.003(2)	0.500(0)	0.5(1)	S3-O31	1.489
	0.000(0)	0.015(4)	0.500(0)	0.5(1)	S3-O33	1.503
Ca2	0.720(1)	0.164(2)	0.158(1)	0.5(1)	S3-O34	1.509
	0.718(1)	0.177(3)	0.157(1)	0.6(1)	S4-O42	1.480
Ca3	0.263(1)	0.206(2)	0.336(1)	0.4(1)		
Ca4	0.263(1)	0.218(3)	0.337(1)	0.7(1)	S4-O41	1.481
	0.000(0)	0.000(0)	0.000(0)	0.3(1)	S4-O44	1.490
O11	0.000(0)	0.000(0)	0.000(0)	0.7(1)	S4-O43	1.496
	0.076(1)	0.144(3)	0.309(2)	1.0(1)	Ca1-O33	2.400
0.072(1)	0.156(3)	0.315(1)	1.3(1)			
O12	0.066(2)	-0.130(3)	0.186(2)	0.9(2)	Ca1-O33	2.400
	0.063(1)	-0.102(3)	0.181(1)	1.3(1)	Ca1-O42	2.414
O21	-0.069(2)	0.108(3)	0.176(1)	1.0(2)	Ca1-O42	2.414
	-0.079(1)	0.130(3)	0.180(1)	1.1(2)	Ca1-O22	2.487
O22	-0.063(2)	-0.111(3)	0.331(2)	0.9(2)	Ca1-O22	2.489
	-0.065(1)	-0.105(3)	0.325(1)	1.1(1)	Ca1-O11	2.686
O31	0.737(2)	0.306(3)	0.330(1)	0.9(1)	Ca1-O11	2.688
	0.738(1)	0.338(3)	0.333(1)	1.3(1)	Ca2-O43	2.346
O32	0.635(1)	0.227(4)	0.495(1)	1.0(2)		
O33	0.629(1)	0.232(3)	0.489(1)	1.2(1)	Ca2-OW2	2.365
	0.824(1)	0.157(4)	0.485(2)	1.0(2)	Ca2-O22	2.398
O34	0.825(1)	0.180(4)	0.486(1)	1.3(1)	Ca2-O34	2.409
	0.700(2)	-0.016(3)	0.365(2)	1.0(1)	Ca2-O31	2.410
O41	0.706(1)	-0.003(3)	0.365(1)	1.3(1)	Ca2-O21	2.480
	0.236(2)	0.349(3)	0.147(2)	1.1(2)	Ca2-O31	2.508
O42	0.226(1)	0.364(3)	0.148(1)	1.3(1)	Ca2-O42	2.573
	0.378(1)	0.241(3)	0.028(2)	0.6(2)	Ca2-O34	2.930
O43	0.376(1)	0.244(3)	0.022(1)	1.2(1)	Ca3-O11	2.357
	0.196(2)	0.099(3)	0.009(1)	0.7(2)		
O44	0.194(1)	0.131(3)	0.007(1)	1.2(1)	Ca3-O44	2.368
	0.300(2)	0.043(3)	0.169(1)	0.8(1)	Ca3-O12	2.445
OW2	0.299(1)	0.042(3)	0.161(1)	1.2(1)	Ca3-O41	2.461
	0.044(2)	0.481(4)	0.650(2)	2.5(4)	Ca3-O33	2.505
OW1	0.049(1)	0.503(3)	0.650(1)	2.6(3)	Ca3-O32	2.555
	0.000(0)	0.347(5)	0.000(0)	2.2(6)	Ca3-O44	2.583
H1	0.000(0)	0.349(2)	0.000(0)	2.5(2)	Ca3-O41	2.642
	-0.049(2)	0.436(5)	0.039(3)	5.3(4)	Ca4-OW1	2.419
H2	-0.021(2)	0.567(4)	0.659(3)	5.6(4)		
H3	0.049(3)	0.400(4)	0.703(2)	5.5(4)	Ca4-O32	2.425
					Ca4-O32	2.425
					Ca4-O43	2.510
					Ca4-O43	2.510
					Ca4-O12	2.518
					Ca4-O12	2.518
					Ca4-O21	2.627
					Ca4-O21	2.627

Note. For each atom the coordinates listed are from the synchrotron X-ray powder diffraction data, and from the neutron diffraction powder data. The latter coordinates are assumed to be the most accurate. Profile parameters, unit cell parameters, and R values were obtained from the program EDINP and are listed from the neutron diffraction powder data. $U = 0.094(1)$, $V = -0.149(1)$, $W = 0.159(1)$, $T = 0.151(3)$, $S = -0.291(5)$, $a = 12.0317(4)$, $b = 6.9269(2)$, $c = 12.6712(3)$ Å, $\beta = 90.27(1)$, $R_E = 3.0\%$, $R_P = 2.0\%$, $R_{WP} = 2.9\%$, $R_F = 5.4\%$, $R_I = 8.2\%$.

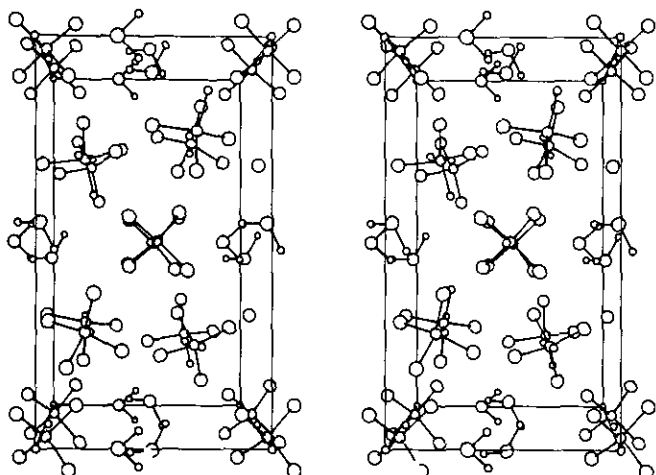


FIG. 6. Stereoscopic projection of the structure of SH1, CaSO₄ · 0.5 H₂O along [001]. The *b* axis is along the page.

chrotron X ray powder pattern of SH1 was indexed with a monoclinic cell, and the pattern was decomposed into the integrated intensities using the program PAWSYN (28). The resulting 354 individually resolved reflections all had Miller indices ($h + k + l = 2n$) confirming the space group *I*121, and with unit cell parameters $a = 12.0317(4)$, $b = 6.9272(2)$, $c = 12.6711(3)$ Å, $\beta = 90.27(1)^\circ$ with an *R* factor of 7.7%. The unit cell of SH1 has a volume about twice that of γ -CaSO₄ since the *c* axis of the former is twice that of the latter. The positional parameters of the atoms in γ -CaSO₄ were used to calculate a starting set of positional parameters for the atoms in the structure of SH1, and the latter was then refined using the program EDINP (25). The values of the refined parameters are listed in Table 4. Figure 4 shows a plot of the synchrotron X ray powder pattern of SH1, and Fig. 5 shows a plot of the neutron pattern.

A projection of the structure along [001] is displayed in Fig. 6. The symmetry is different from that in Fig. 3, but the structure retains channels that probably accommodate the water molecules, which have van der Waals radii of 2.4 Å (29). The composition of SH1 is CaSO₄ · 0.5 H₂O, and hence six water molecules must be contained in the unit cell, corresponding to one set of oxygen atoms in general positions and one set in special positions. Packing considerations (29–31) were used to estimate the starting parameters for the atoms of the water molecules, and the refined positional parameters are listed in Table 4.

The structure has two independent water molecules, one with the oxygen atom OW1 in a special position and bonded to H1, and the other with the oxygen atom OW2 in a general position, and bonded to the hydrogen atoms H2 and H3. The bond angles for the two water molecules

are H1–OW1–H1 = 103.75° and H2–OW2–H3 = 104.6°, and the oxygen–hydrogen distances are OW1–H1 = 0.97(3), OW2–H2 = 0.96(3), and OW2–H3 = 0.98(4) Å. The structure has channels directed along the [001] direction, and the water molecules are located within these with the sequence OW1–OW2–OW2 and with distances OW1–OW2 = 5.8 Å, and OW2–OW2 = 4.0 Å. The channels are formed by the calcium–oxygen coordination polyhedra CaO₈ and CaO₉ stacked on top of each other and held together by the sulfate ions with the sequence CaO₈–S–CaO₉ (see Fig. 7).

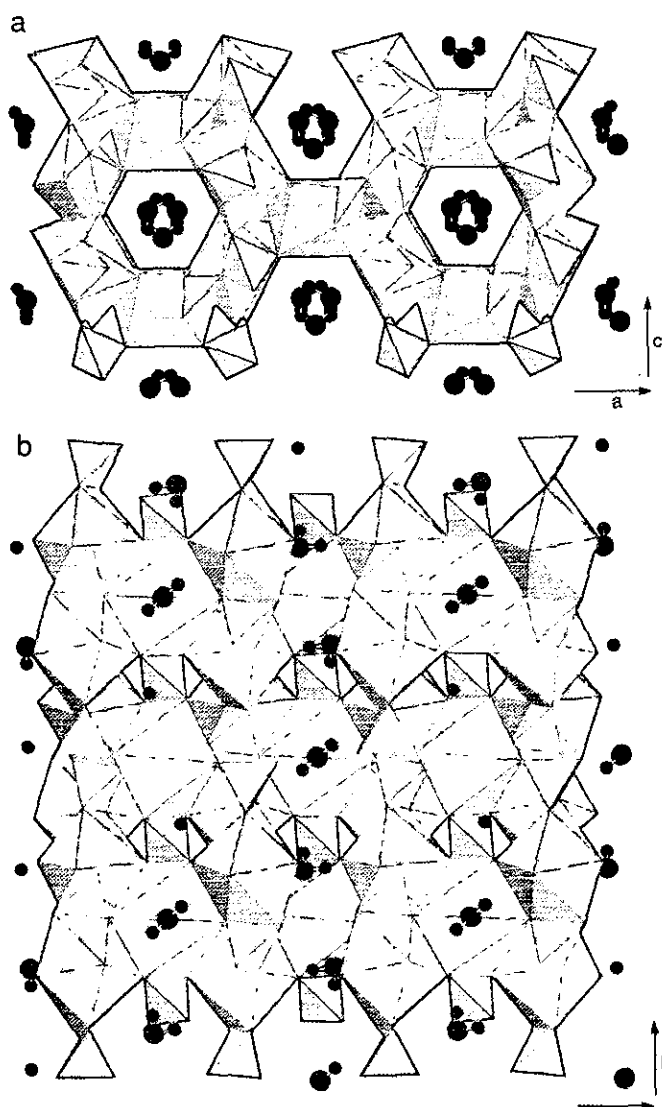


FIG. 7. Packing of the water molecules in the channels formed by the CaO₈ polyhedra in the SH1 structure. The *a* axis is along the page: (a) projection along [001]; (b) projection along [010]. Each water molecule enters the coordination of every second calcium atom in a chain parallel to the *c* axis.

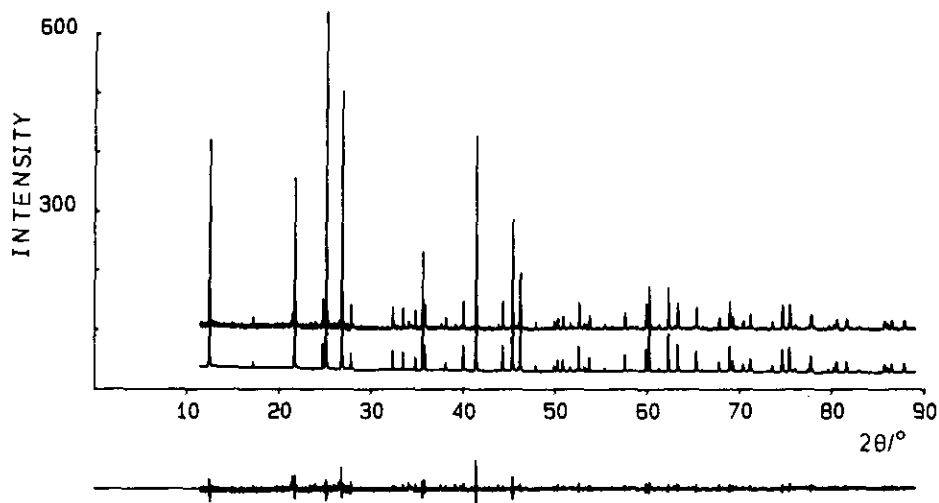


FIG. 8. Observed and calculated synchrotron X ray diffraction powder pattern of SH2 using a hexagonal cell $a = 6.932$, $c = 6.368$ Å and the program PAWSYN.

Calcium coordination polyhedra are less regular than in the case of soluble anhydrite. In the CaO_8 polyhedra, the mean Ca–O distance in the CaO_4 plane is 2.47(2) Å; in the case of CaO_9 polyhedra, the mean Ca–O distance in the CaO_4 plane is 2.51(2) Å; the out-of-plane mean Ca–O distance is 2.58(2) Å in both CaO_8 and CaO_9 polyhedra. The water molecule H1–OW1–H1 is bonded to Ca_4 by the oxygen atom OW1, the bond is directed along the bisector of the HOH plane (Ca_4 –OW1 = 2.42(2) Å) corresponding to a trigonal coordination (type D according to (31)). The water molecule forms weak hydrogen bonds with O32 through H1 (H1–O32 = 2.23 Å and OW1–O32 = 3.03 Å). The water molecule H2–OW2–H3 is

bonded to Ca_2 by the oxygen atom OW2 (Ca_2 –OW2 = 2.37(2) Å). The H2 atom is situated in the mean CaO_5 plane, and the H3 atom is situated above corresponding to a tetrahedral coordination (type J according to (29)). The water molecule forms weak hydrogen bonds with O11 through H3 (H3–O11 = 2.24 Å and OW2–O11 = 2.85 Å) and with O44 through H2 (H2–O44 = 2.17 Å and OW2–O44 = 3.03 Å).

The existence of two types of water molecules are in agreement with the hypothesis emitted by Lager *et al.* (9) from the IR spectrum of deuterated hemihydrate (32). However, the actual locations of water molecules are different from those proposed by them and Abriel and

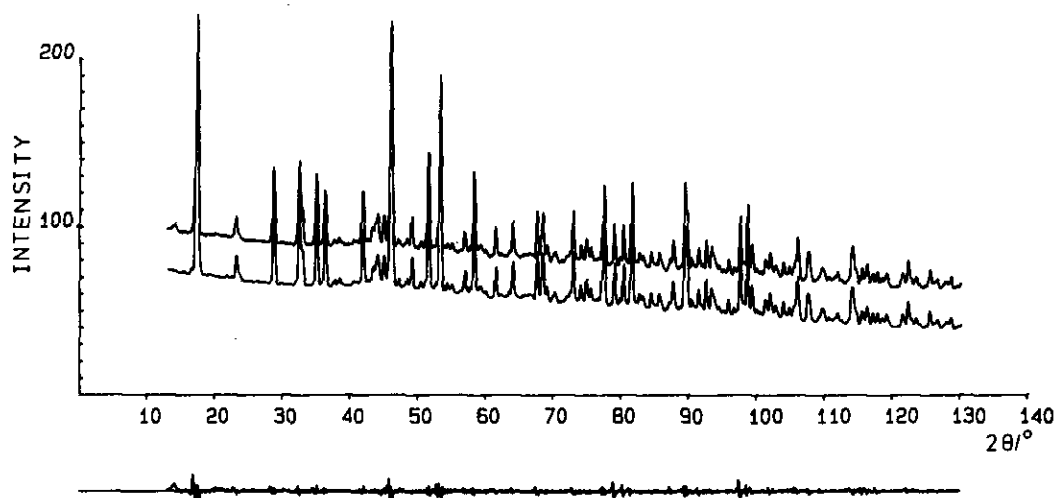


FIG. 9. Observed and calculated neutron diffraction powder pattern of SH2 using a hexagonal cell $a = 13.846$, $c = 12.748$ Å and the program PAWSYN.

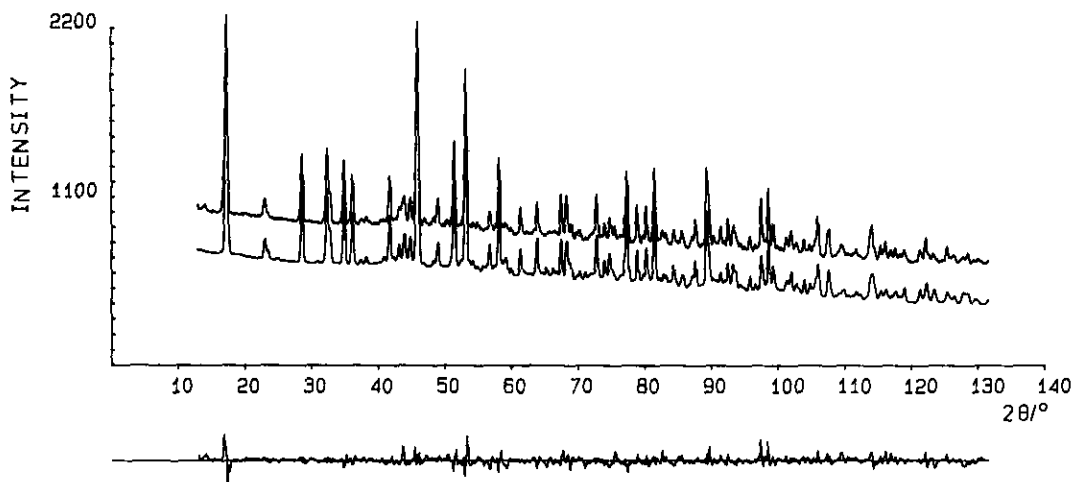


FIG. 10. Observed and calculated neutron diffraction powder pattern of SH2 with the model (Table 6) and the space group $I121$. A difference plot is shown below the abscissa.

Nesper (16) essentially due to the fact that water molecules enter the coordination of calcium ions.

SH2: CaSO₄ · 0.6 H₂O. The indexing of the synchrotron X ray powder pattern of SH2 gave orthorhombic or hexagonal unit cells with volumes from 265 to 2120 Å³. The density of SH2 is assumed to be close to that of SH1, which is 2.74 g cm⁻³, and the small orthorhombic cell with the volume 265 Å³ thus corresponds to three formula units in the cell. This cell is thus rather a trigonal cell with $a = 6.932$ and $c = 6.368$ Å, which was also reported previously for a calcium sulfate subhydrate (13). To test the orthorhombic and hexagonal unit cells found in indexing of the synchrotron X ray powder pattern of SH2, the pattern was decomposed using the program PAWSYN (28). The results found are listed in Table 5. The orthorhombic as well as the hexagonal cells tested all gave acceptable agreements between observed and calculated powder patterns. The unit cell that gave the lowest R value 7.6% and fitted all reflections was an orthorhombic I -centered cell with $a = 12.008$, $b = 6.931$, $c = 12.737$ Å. However, a hexagonal cell with $a = 6.932$ and $c = 6.368$ Å gave an R value of 7.8%, and this fit is displayed in Fig. 8. From the indexing of the synchrotron X ray powder pattern an ambiguity thus exists concerning the size and symmetry of the unit cell. The neutron diffraction powder pattern of SH2 was also decomposed using the program PAWSYN (28). In this case, orthorhombic or hexagonal cells with a unit cell volume of 1060 Å³ gave acceptable agreements between observed and calculated powder patterns. Cells with unit cell volumes of 265 or 530 Å³ could not index two significantly observed reflections at $2\theta = 43^\circ$ and 71° , respectively. These two reflections are not due to an impurity since they are not observed in the neutron diffraction powder patterns of

γ -CaSO₄ and SH1, which are synthesized from the same sample as SH2. The most likely unit cells for SH2 is thus an orthorhombic cell with the unit cell volume 1060 Å³ ($R = 1.6\%$) or a hexagonal cell with the unit cell volume 2120 Å³ ($R = 1.8\%$), and this latter fit is displayed in Fig. 9.

The three compounds γ -CaSO₄, SH1, and SH2 have most likely related structures with channels that may accommodate water molecules. In the structure of SH1 the water molecules are ordered in well-defined positions (see above). This results in a monoclinic cell with a β angle only slightly different from 90° and cell dimensions comparable with the orthorhombic cell that can index the powder pattern of SH2. The hypothesis that the structure of SH2 is similar to that of SH1 but with the water mole-

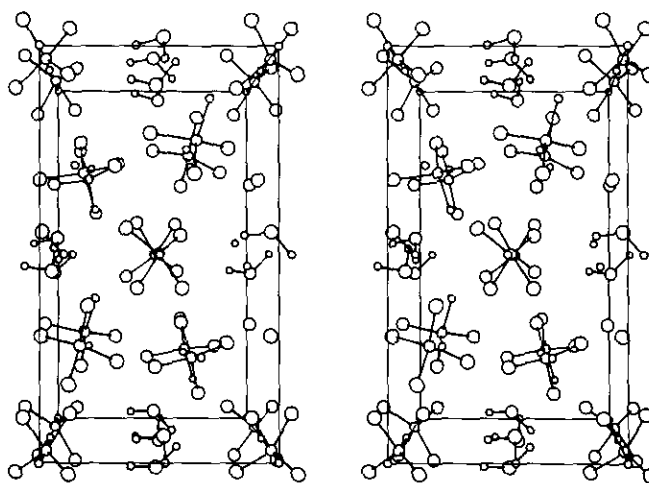


FIG. 11. Stereoscopic projection of the structure of SH2, CaSO₄ · 0.6 H₂O along [001]. The b axis is along the page.

TABLE 5
Unit Cells Obtained by Decomposition of the Synchrotron X Ray and Neutron Powder Diffraction Patterns of SH2, Using the Program PAWSYN

<i>a</i>	<i>b</i>	<i>c</i>	Cell volume (Å ³)	<i>R_w</i> (%)
NSLS synchrotron X ray data				
Hexagonal cells				
6.932		6.368	265	7.7
13.864		6.368	1060	8.3
13.864		12.736	2120	8.5
Orthorhombic P-cells				
6.003	6.931	6.368	265	8.0
12.007	6.931	6.389	530	8.0
12.006	6.931	12.737	1060	8.2
Orthorhombic I-cell				
12.008	6.931	12.737	1060	7.6
ILL neutron diffraction data				
Hexagonal cells				
6.926		6.373	265	4.4
13.849		6.373	1059	2.9
13.846		12.748	2117	1.8
Orthorhombic P-cells				
5.995	6.925	6.374	265	3.4
11.981	6.929	6.373	529	3.8
11.988	6.930	12.753	1059	1.6
Orthorhombic I-cell				
11.988	6.930	12.753	1059	2.0

cules arranged in another way in the channels of the structure is discussed. The model to be tested has a monoclinic *I*121 cell with $\beta = 90^\circ$, $a = 11.988$, $b = 6.930$, $c = 12.753$ Å and atomic coordinates similar to the atomic coordinates listed in Table 4.

A set of positional parameters for the calcium atoms and the atoms in the sulfate ions from the SH1 model was used as starting parameters in a profile refinement of the neutron powder diffraction pattern with the program EDINP (24), and the space group *I*121. Fourier and difference Fourier maps calculated from the refined parameters did not show any clear scattering density that could be interpreted as water molecules. Instead packing considerations were involved to give the positions of some water molecules, and with these water molecules included in the model the profile refinement gave the

atomic coordinates listed in Table 6. Figure 10 is a plot of the observed and calculated neutron diffraction powder pattern of SH2, and Fig. 11 is a projection of the model of the structure along the [001] direction.

The structure of SH2 is built from CaO₈ polyhedra chains which constitute the vertical edges of the cell and are perpendicular to the middle of the *ab* plane, and CaO₉ polyhedral chains which are inside the cell. The position of the water molecules in the channels were defined from two independent molecules in general positions H11-OW1-H12 and H21-OW2-H22 with the sequence W1-W2-W2-W1 and with the distances OW1-OW2 = 2.42 Å

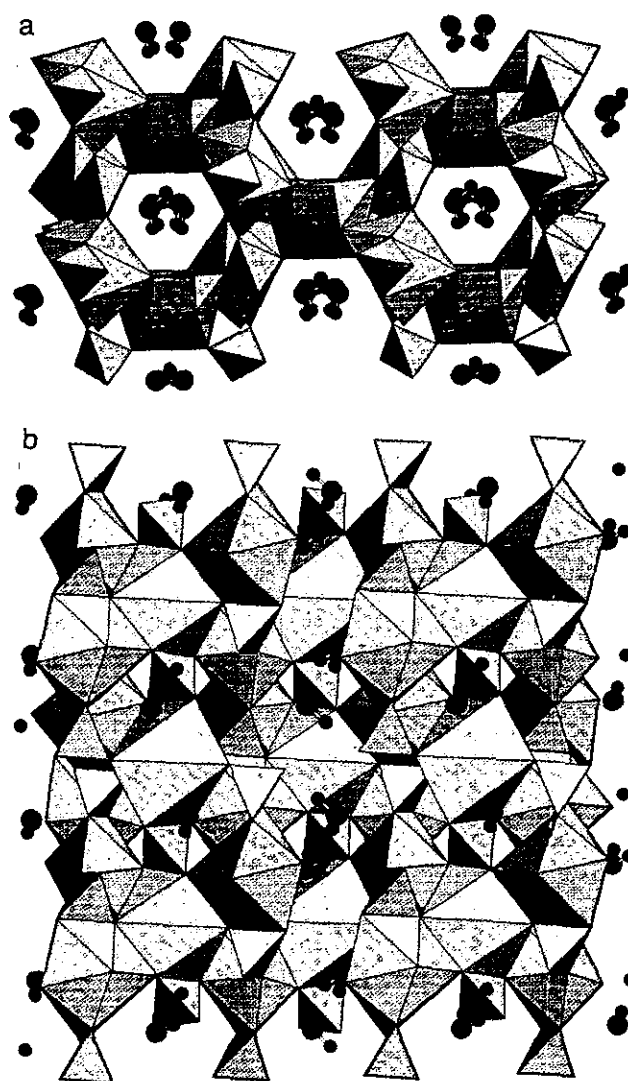


FIG. 12. Packing of the water molecules in the channels formed by the CaO₈ polyhedra in the SH2 structure. The *a* axis is along the page: (a) projection along [001]; (b) projection along [010]. The water molecules enter the coordination of each calcium atom in two of the three chains building the channel; they are grouped by two molecules linked by a strong hydrogen bond.

TABLE 6
Structure Parameters for SH2, CaSO₄ · 0.6 H₂O X Ray and Neutron Data

Atom	x/a	y/b	z/c	B (Å ²)	Atoms	Distances (Å)
S2	0.007(1)	0.009(3)	0.247(1)	0.7(1)	S2-O21	1.452
	-0.001(2)	0.007(4)	0.244(2)	0.7(1)	S2-O11	1.462
S3	0.724(1)	0.168(4)	0.408(9)	0.7(1)	S2-O12	1.533
	0.718(2)	0.163(4)	0.405(2)	0.7(1)	S2-O22	1.557
S4	0.273(1)	0.177(3)	0.085(1)	0.7(1)		
	0.276(1)	0.162(4)	0.091(2)	0.7(1)	S3-O31	1.497
Ca1	0.000(0)	0.026(3)	0.500(0)	0.8(1)	S3-O34	1.499
	0.000(0)	0.000(6)	0.500(0)	0.6(1)	S3-O33	1.503
Ca2	0.722(9)	0.178(3)	0.166(8)	0.2(1)	S3-O32	1.509
	0.723(2)	0.139(3)	0.141(2)	0.7(1)		
Ca3	0.270(1)	0.187(3)	0.322(8)	0.4(1)	S4-O42	1.492
	0.259(2)	0.189(5)	0.341(2)	0.7(1)	S4-O41	1.500
Ca4	0.000(0)	0.000(0)	0.000(0)	0.7(1)	S4-O44	1.504
	0.000(0)	0.000(0)	0.000(0)	0.3(1)	S4-O43	1.507
O11	0.074(3)	0.121(6)	0.304(2)	1.0(1)		
	0.087(2)	0.109(4)	0.301(2)	1.6(1)	Ca1-O33	2.561
O12	0.058(8)	-0.101(6)	0.182(3)	1.0(1)	Ca1-O33	2.561
	0.089(2)	-0.088(3)	0.177(3)	1.7(1)	Ca1-O42	2.585
O21	-0.082(3)	0.113(5)	0.187(2)	1.0(1)	Ca1-O42	2.585
	-0.049(2)	0.110(3)	0.156(1)	1.7(1)	Ca1-O22	2.680
O22	-0.044(3)	-0.125(5)	0.324(2)	1.0(1)	Ca1-O22	2.680
	-0.066(2)	-0.139(3)	0.314(2)	1.7(1)	Ca1-O11	2.846
O31	0.743(3)	0.344(4)	0.343(2)	0.9(1)	Ca1-O11	2.846
	0.732(2)	0.308(3)	0.319(2)	1.7(1)		
O32	0.629(2)	0.236(6)	0.479(2)	1.0(1)	Ca2-O43	2.239
	0.621(2)	0.214(3)	0.474(2)	1.6(1)	Ca2-OW2	2.262
O33	0.813(2)	0.174(5)	0.489(2)	1.0(1)	Ca2-O31	2.403
	0.804(2)	0.147(3)	0.490(1)	1.6(1)	Ca2-O34	2.457
O34	0.697(3)	-0.022(5)	0.354(3)	1.0(1)	Ca2-O42	2.467
	0.697(2)	-0.035(2)	0.360(2)	1.7(1)	Ca2-O22	2.501
O41	0.183(2)	0.312(5)	0.124(2)	1.1(1)	Ca2-O31	2.554
	0.232(2)	0.320(2)	0.161(2)	1.6(1)	Ca2-O21	2.739
O42	0.368(2)	0.248(6)	0.018(2)	0.6(1)	Ca2-O34	3.059
	0.376(1)	0.199(4)	0.025(2)	1.6(1)		
O43	0.199(2)	0.147(5)	-0.007(2)	0.7(1)	Ca3-O11	2.199
	0.186(1)	0.120(4)	0.012(1)	1.6(1)	Ca3-O44	2.201
O44	0.296(2)	0.053(4)	0.181(5)	0.9(1)	Ca3-O33	2.312
	0.295(2)	-0.008(3)	0.163(1)	1.7(1)	Ca3-O12	2.402
OW1	0.426(3)	-0.001(7)	0.345(3)	1.7(1)	Ca3-O41	2.488
	0.455(2)	0.024(3)	0.329(2)	1.9(2)	Ca3-O41	2.555
OW2	0.542(3)	-0.023(6)	0.129(2)	1.2(1)	Ca3-OW1	2.617
	0.556(2)	-0.004(4)	0.167(2)	2.3(3)	Ca3-O44	2.678
H11	0.515(3)	0.031(8)	0.382(3)	3.6(5)	Ca3-O32	2.770
H12	0.469(5)	-0.095(4)	0.288(4)	4.4(5)		
H21	0.500(3)	0.087(5)	0.191(3)	1.4(5)	Ca4-O21	2.207
H22	0.548(4)	-0.116(5)	0.212(4)	6.7(5)	Ca4-O21	2.207
					Ca4-O43	2.386
					Ca4-O43	2.386
					Ca4-O32	2.476
					Ca4-O32	2.476
					Ca4-O12	2.566
					Ca4-O12	2.566

Note. For each atom the coordinates listed are from the synchrotron X-ray powder diffraction data, and from the neutron diffraction powder data. Profile parameters, unit cell parameters, and R values were obtained from the program EDINP and are listed from the neutron diffraction powder data. $U = 0.083(1)$, $V = -0.180(1)$, $W = 0.176(1)$, $T = 0.028(3)$, $S = 0.034(5)$, $a = 11.9845(4)$, $b = 6.9292(2)$, $c = 12.7505(3)$ Å, $\beta = 90.0$, $R_E = 4.3\%$, $R_p = 2.8\%$, $R_{wp} = 4.0\%$, $R_F = 9.1\%$, $R_I = 13.8\%$.

and OW2–OW2 = 6.5 Å. The short length between OW1 and OW2 reveals a strong hydrogen bond between them. The water molecule H11–OW1–H12 is bonded to Ca₃ by the oxygen atom OW1, the bond is directed along a lone pair of the oxygen atom (Ca₃–OW1 = 2.63(2) Å). The H11 and H12 atoms are situated above and below the CaO₅ plane, respectively. The second lone pair of OW1 is directed toward the H21 atom of W2 water molecules to form a strong hydrogen bond (OW1–H21 = 1.9 Å), that is, a tetrahedral coordination of type D according to (31). The water molecule W1 forms another weaker hydrogen bond with O32 through H11 (H11–O32 = 2.11 Å and OW1–O32 = 1.99 Å). The water molecule H21–OW2–H22 is bonded to Ca₂ by the oxygen atom OW2 (Ca₂–OW2 = 2.3(2) Å). The H21 atom is situated in the mean CaO₅ plane and the H22 atom is situated above corresponding to a tetrahedral coordination (type J according to (31)). The water molecule exchanges a polybifurcated hydrogen bond with O31 and O34 through H22 (H22–O31 = 2.69 Å, OW2–O31 = 2.85 Å, H22–O34 = 2.60 Å, and OW2–O34 = 2.96 Å). The occupancy of the four sites per channel, or two water pairs as illustrated in Fig. 12, corresponds to a stoichiometry CaSO₄ · 0.66 H₂O. To account for the actual stoichiometry previously reported (15), corresponding to the occupancy of seven sites out of eight, an occupation factor of 0.875 has been used for the water molecules during the fit. However, as mentioned above, an ambiguity exists concerning the space group for the structure of SH2. The packing of the calcium and sulfate ions show an apparent threefold symmetry, but this could not be found with respect to the packing of the water molecules. The proposed structure for SH2 is thus only tentative at this stage and single crystal data are necessary to resolve the uncertainty.

ACKNOWLEDGMENTS

This investigation was supported by a grant from Lafarge Coppee Recherche. We thank the Institut Max von Laue–Paul Langevin, Grenoble, for the use of the neutron powder diffractometer. A.N.C. and M.S.L. thank NATO for Grant 86/0551 which supported the synchrotron part of this work. Dr. D. E. Cox is thanked for fruitful discussions.

REFERENCES

1. B. F. Pedersen and D. Semmingsen, *Acta Crystallogr. Sect. B* **38**, 1074 (1982).
2. A. Kirfel and G. Will, *Acta Crystallogr. Sect. B* **36**, 2881 (1980).
3. A. N. Christensen, M. S. Lehmann, and J. Pannetier, *J. Appl. Crystallogr.* **18**, 170 (1985).
4. W. Abriel, K. Reisdorf, and J. Pannetier, *J. Solid State Chem.* **85**, 23 (1990).
5. M. Frick and H. J. Kuzel, *Fortschr. Mineral.* **60**, 80 (1982).
6. J. J. Gardet, B. Guilhot, and M. Soustelle, *Bull. Soc. Chim. Fr.* **10**, 549 (1970).
7. C. Bezou, thesis, University of Bourgogne, Dijon, 1991.
8. O. W. Flörke, *Neues Jahrb. Mineral. Monatsh.* **84**, 189 (1952).
9. G. A. Lager, Th. Armbruster, F. J. Rotella, J. D. Jorgensen, and G. H. Hinks, *Am. Mineral.* **69**, 910 (1984).
10. P. Gallitelli, *Period. Mineral.* **4**, 1 (1933).
11. N. N. Bushuev and V. M. Borisov, *Russ. J. Inorg. Chem.* **27**, 341 (1982).
12. N. N. Bushuev, *Russ. J. Inorg. Chem.* **27**, 344 (1982).
13. W. Abriel, *Acta Crystallogr. Sect. C* **39**, 956 (1983).
14. H. J. Kuzel and M. Hauner, *Zem. Kalk Gips, Ed. B* **40**, 628 (1987).
15. C. Bezou, J.-C. Mutin, and A. Nonat, *J. Chim. Phys.* **87**, 1257 (1990).
16. W. Abriel and R. Nesper, *Z. Kristallogr.* **205**, 99 (1993).
17. W. A. Caspari, *Cryst. Proc. R. Soc. London*, **155A**, 41 (1936).
18. C. Bezou, J. C. Mutin, and A. Nonat, *C.R. Acad. Sci. Paris Ser. II*, 1493 (1990).
19. J. J. Gardet, B. Guilhot, and M. Soustelle, *Bull. Soc. Chim. Fr.* **10**, 827 (1970).
20. J. W. Visser, *J. Appl. Crystallogr.* **2**, 89 (1969).
21. P.-E. Werner, *Z. Kristallogr.* **120**, 375 (1964).
22. A. Boulitif and D. Louër, *J. Appl. Crystallogr.* **24**, 987 (1991).
23. H. M. Rietveld, *J. Appl. Crystallogr.* **2**, 65 (1969).
24. G. A. Mackenzie, G. S. Pawley, and O. W. Dietrich, *Acta Crystallogr. Sect. A* **31**, 851 (1975).
25. G. S. Pawley, *J. Appl. Crystallogr.* **13**, 630 (1980).
26. D. T. Cromer and J. B. Mann, *Acta Crystallogr. Sect. A* **24**, 321 (1968).
27. L. Koester and H. Rauch, "Summary of Neutron Scattering Lengths." KFS Jülich, 1981.
28. G. S. Pawley, *J. Appl. Crystallogr.* **14**, 357 (1981).
29. G. Chiari and G. Ferraris, *Acta Crystallogr. Sect. B* **38**, 2331 (1982).
30. R. Chidambaram, A. Sequira, and S. K. Sikka, *J. Chem. Phys.* **41**, 3616 (1964).
31. G. Ferraris and M. Franchini-Angela, *Acta Crystallogr. Sect. B* **28**, 3572 (1991).
32. R. J. Morris Jr, *Anal. Chem.* **35**, 1489 (1963).