

## A crystallographic study of the low-temperature dehydration products of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ : hemihydrate $\text{CaSO}_4 \cdot 0.50\text{H}_2\text{O}$ , and $\gamma\text{-CaSO}_4$

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### Abstract

The crystal structure of  $\gamma\text{-CaSO}_4$  [ $a = 6.9694(8)$ ,  $c = 6.3033(4)\text{\AA}$ ;  $Z = 3$ ; space group  $P6_222$ ] has been refined from time-of-flight neutron powder diffraction data to agreement factors of 4.92 (weighted profile  $R$ ) and 12.10 (Rietveld  $R$ ). The observed neutron powder profile for hemihydrate ( $\text{CaSO}_4 \cdot 0.50\text{D}_2\text{O}$ ) is qualitatively consistent with a model in which the water molecules occupy two different levels in the channels of a distorted  $\gamma\text{-CaSO}_4$  framework. Hemihydrates formed by dehydration of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or synthesized from concentrated solutions of  $\text{HNO}_3$  are monoclinic with space group  $I2$  [ $a = 12.062(4)$ ,  $b = 12.660(3)$ ,  $c = 6.930(1)\text{\AA}$ ;  $\gamma \approx 90^\circ$ ]. Experimental data do not support the existence of a high-temperature trigonal form. Hemihydrate crystals grown in saturated NaCl solution contain  $\sim 0.50$  wt.%  $\text{Na}_2\text{O}$ . The presence of Na stabilizes the structure and produces significant changes in the refractive indices and unit-cell parameters.

### Introduction

Hemihydrate ( $\text{CaSO}_4 \cdot 0.50\text{H}_2\text{O}$ ) and  $\gamma\text{-CaSO}_4$  (soluble anhydrite) are the low-temperature ( $T < 383$  K) dehydration products of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). Hemihydrate, which occurs in nature as the mineral bassanite, is a very important raw material in the building industry where it is used principally in the manufacture of plaster and plasterboard. Recent experimental evidence suggests that its formation in geologic environments may have important implications with regard to the partitioning of seawater cations during the gypsum–anhydrite transformation (Kushnir, 1982). Heating hemihydrate to  $\sim 373$ – $383$  K produces  $\gamma\text{-CaSO}_4$ , a metastable phase which rehydrates rapidly under normal atmospheric conditions.

The major contributions to the crystallography of these phases were made by Gallitelli (1933), Flörke (1952) and Gay (1965a,b) (Table 1). Gallitelli (1933) was the first to propose a structural model for hemihydrate based on single-crystal X-ray data. He determined the space group and unit-cell parameters from Weissenberg methods and demonstrated that the structure was characterized by pseudo-trigonal channels which house the water molecules. He also observed that the structure was only slightly distorted from trigonal symmetry and therefore approximated it in terms of the space group  $P3_121$ . Flörke (1952) expanded upon the work (Gallitelli, 1933) and considered all dehydrated phases in the system  $\text{CaSO}_4\text{-H}_2\text{O}$ . His principal conclusions with respect to hemihy-

Table 1. Unit cells proposed for hemihydrate  $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ \*

|   |                |  |
|---|----------------|--|
| <u>Gallitelli,</u><br><u>1933</u>         | C2             | 11.94, 6.83, 12.70; $\beta \approx 90$         |
|   | $P3_121$       | 6.83, 12.70 (approximation to C2 cell)         |
| <u>Caspari,</u><br><u>1936</u>            | $P\bar{3}m1$   | 6.82, 6.24                                     |
| <u>Flörke,</u><br><u>1952</u>             | C222           | 6.8, 11.5, 12.7 (T<318K)                       |
|   | $P3_221$       | 6.8, 12.7, (T>318K)                            |
| <u>Gay,</u><br><u>1965 b</u>              | I-monoclinic   | 6.85, 11.88, 12.60; $\beta \approx 90$         |
| <u>Frik and Kuzel,</u><br><u>1982</u>     | Orthorhombic** | 12.061, 6.933, 12.670 (n=0.48)                 |
|   | Hexagonal      | 13.865, 12.718 (n=0.52)                        |
| <u>Bushuev and Borisov</u><br><u>1982</u> | $I2^+$         | 12.028, 12.674, 6.927; $\gamma=90.21$ (n=0.67) |
|   | $P3_121$       | 6.977, 12.617 (n=0.50)                         |
| <u>Abriel,</u><br><u>1983</u>             | $P3_121$       | 6.968, 6.410 (n=0.80)                          |

\* Unit-cell parameters expressed in Angstroms and degrees. Unless otherwise indicated n=0.50.

\*\* The orthorhombic form is stable under low relative humidity (RH<5%).

+ Low-temperature form stable in the range 323-352K. Monoclinic first setting with the 2-fold axis parallel to  $c$ .

hydrate and  $\gamma\text{-CaSO}_4$  can be summarized as follows (for a good review of the literature prior to 1960, see Deer et al., 1962):

(1) Hemihydrate exhibits a unique crystal structure distinct from that of  $\gamma\text{-CaSO}_4$ .

(2) Based on single-crystal X-ray data, two models were proposed for the structure of  $\gamma\text{-CaSO}_4$ . In the preferred one, Ca and S occupied positions 3c and 3d in space group  $P6_222$ . This model was essentially the hexagonal analog of Gallitelli's  $P3_121$  hemihydrate structure with  $c_{\gamma\text{-CaSO}_4} = 1/2 c_{\text{Hemi}}$ .

(3) Hemihydrate exists in both low- and high-temperature forms. From optical data, Flörke (1952) suggests that the structure is trigonal above 318 K and orthorhombic below this temperature. The orthorhombic form is twinned on (001) which results in pseudotrigonal symmetry. Flörke's orthorhombic hemihydrate is similar to Gallitelli's C2 structure but with  $\text{H}_2\text{O}$  located at (0, 0, 0) and (0, 0, 1/3) rather than (0, 0, 1/6) and (0, 0, 1/2).

(4) In the dehydration of hemihydrate to  $\gamma\text{-CaSO}_4$ , only small changes occur in the crystal structure.

Gay (1965b) has suggested that the symmetry of hemihydrate is monoclinic  $I$ -centered. On the basis of oscillation and Weissenberg methods, he concludes that hemihydrate is multiply-twinned on a fine scale and consists of monoclinic subcrystals which differ in orientation but which have their  $c$  crystallographic axes parallel to the 3-fold axis of pseudosymmetry (Gay's triplet structure). Using high-temperature X-ray and optical techniques, he

was unable to prove the existence of Flörke's trigonal hemihydrate but he did observe a hexagonal form ( $\sim 378$  K) which had the space group symmetry and approximate cell parameters of  $\gamma\text{-CaSO}_4$ . Gay did not discuss his observations in terms of the structure of hemihydrate.

Teimurov et al. (1979) have proposed a structural model for hemihydrate based primarily on the steric details of the gypsum structure (Cole and Lancucki, 1974) and the mechanism of its dehydration (Weiser et al., 1936). Frik and Kuzel (1982) have suggested that the symmetry of hemihydrate is dependent on the vapor pressure of  $\text{H}_2\text{O}$  (Table 1). They recognized two forms of hemihydrate: an orthorhombic phase which is stable under low relative humidity (RH) conditions (RH < 5%) and a hexagonal phase (RH  $\sim$  40%). Bushuev and Borisov (1982) concluded that the existence of two hemihydrate forms is related to the amount of structural water in the channels. The symmetry can be either hexagonal ( $0 < n \leq 0.5$ ) or monoclinic ( $0.5 < n \leq 0.67$ ) (Table 1). Bushuev (1982) subsequently determined the crystal structure of the compound  $\text{CaSO}_4 \cdot 0.67\text{H}_2\text{O}$  from single-crystal X-ray intensity data. The water molecules are located within the coordination sphere of the  $\text{Ca}^{2+}$  ion (nine-coordinated) and exhibit long-range ordering which results in a supercell with a  $38\text{\AA}$  channel axis. To minimize the electrostatic repulsion only 67% of the available water sites are occupied on the average. If all sites are occupied then the hypothetical composition  $\text{CaSO}_4 \cdot 1\text{H}_2\text{O}$  would be reached and each channel would contain six water molecules separated by distances of  $\sim 2\text{\AA}$ . According to Bushuev (1982), the monoclinic distortion results from the close proximity of water molecules in the channels. This "steric hindrance," as he calls it, does not occur in stoichiometric hemihydrate because of the smaller water content and consequently it is believed to be trigonal. Although Bushuev (1982) considers  $\text{CaSO}_4 \cdot 0.67\text{H}_2\text{O}$  to be the limiting composition, Abriel (1983) has recently reported a structure determination of  $\text{CaSO}_4 \cdot 0.80\text{H}_2\text{O}$ . The Abriel and Bushuev structures are very similar; the latter is pseudotrigonal monoclinic whereas the former is trigonal. It is difficult to imagine, however, how 80% of the water positions could be occupied in a cell ( $Z = 3$ ) which has a dimension of only  $6.4\text{\AA}$  parallel to the channel axis (Table 1). Some channels would have to contain three molecules which is chemically unreasonable given the radius of the oxygen ion ( $1.30\text{\AA}$ ). In both of the published structures of hemihydrate, the water content has been determined from site occupation refinements.

Although a considerable amount of literature has been devoted to the crystallography of hemihydrate, there are still a number of unresolved problems. Recent work, for example, has suggested a relation between the water content and structure of hemihydrate. Because of the twinning observed in single crystals and the presence of hydrogen, it was thought that this problem was ideally suited to high-resolution neutron powder diffraction. In

addition, the structure would not have to be solved from first principles because a refinement model could be derived from the  $\gamma$ -CaSO<sub>4</sub> structure. As discussed below, this approach proved to be unsuccessful in practice because of the peak shape broadening and the small distortion from hexagonal symmetry ( $a - b\sqrt{3} = 0.06$ ). It was, however, possible to formulate a qualitative model for hemihydrate based on the refinement of the  $\gamma$ -CaSO<sub>4</sub> structure and the information gained from a variety of experimental techniques, including neutron and X-ray diffraction, infrared spectroscopy, DTA/DTG thermal analyses and polarized-light microscopy. The recent literature on hemihydrate is critically examined in terms of this model.

### Experimental

DTA/DTG thermal analyses of synthetic and natural gypsum were consistent with the dehydration reactions  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 0.50\text{H}_2\text{O} + 1.50\text{H}_2\text{O}$  and  $\text{CaSO}_4 \cdot 0.50\text{H}_2\text{O} \rightarrow \gamma\text{-CaSO}_4 + 0.50\text{H}_2\text{O}$ . Only slight departures from the stoichiometric compositions were noted ( $\pm 0.02 \text{ H}_2\text{O}$ ). Dehydrating gypsum under a variety of conditions (e.g., different temperatures, heating rates, atmospheres, etc.) always produced stoichiometric hemihydrate as determined by weight loss after heating. Guinier X-ray ( $\text{FeK}\alpha_1$ ;  $\lambda = 1.9359\text{\AA}$ ) powder patterns taken at regular intervals during the dehydration ( $\sim 363 \text{ K}$ ) showed increasing intensities for hemihydrate and decreasing intensities for gypsum until the reaction was complete. No additional phase was observed. It must be noted that it is extremely difficult to obtain precise data for structural water in  $\text{CaSO}_4 \cdot 0.50\text{H}_2\text{O}$  based on weight loss measurements. Water begins to escape from gypsum at  $\sim 363 \text{ K}$  which is the same temperature normally applied to determine the amount of surface water.

Time-of-flight neutron powder diffraction data were collected for  $\text{CaSO}_4 \cdot 2\text{D}_2\text{O}$  and  $\gamma\text{-CaSO}_4$  at  $295 \text{ K}^1$  and for hemihydrate ( $\text{CaSO}_4 \cdot 0.50\text{D}_2\text{O}$ ) at  $295 \text{ K}$  and  $378 \text{ K}$  on the special environment diffractometer at the Intense Pulsed Neutron Source (IPNS) located at Argonne National Laboratory. The  $\gamma\text{-CaSO}_4$  and hemihydrate samples used in the  $295 \text{ K}$  experiments were prepared from synthetic gypsum by dehydration. In the case of hemihydrate, gypsum ( $\text{CaSO}_4 \cdot 2\text{D}_2\text{O}$ ) synthesized from ultrapure  $\text{CaCO}_3$  and  $\text{D}_2\text{SO}_4$  was heated to  $350 \text{ K}$  in a closed system which had been previously evacuated (Fig. 1). An ice trap was used to collect the  $\text{D}_2\text{O}$  evolved during dehydration. After a period of  $\sim 36 \text{ hr}$ , the vapor pressure stabilized at  $P \sim 4.6 \text{ mm}$  and the measured volume of  $\text{D}_2\text{O}$  was within  $\sim 3\%$  ( $\pm 0.02 \text{ D}_2\text{O}$ ) of the value calculated from the sample mass.  $\gamma\text{-CaSO}_4$  was prepared at  $373 \text{ K}$  from  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  using the same procedure.

The  $\gamma\text{-CaSO}_4$  data (Table 2)<sup>2</sup> were refined using a Rietveld (1976) profile analysis which has been modified for spallation pulsed neutron sources (von Dreele et al., 1983). Starting

<sup>1</sup> Unless otherwise indicated, temperatures are believed to be accurate to  $\pm 1 \text{ K}$ .

<sup>2</sup> To receive a copy of Table 2, order Document AM-84-246 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N. W., Washington, D. C. 20009. Please remit \$5.00 in advance for the microfiche.

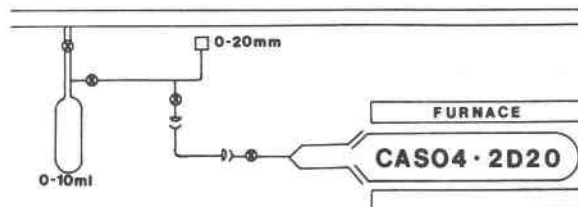


Fig. 1. Schematic drawing of the system used to produce  $\gamma\text{-CaSO}_4$  and hemihydrate ( $\text{CaSO}_4 \cdot 0.50\text{H}_2\text{O}$ ) from gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) by dehydration.

parameters in the refinement were those of Florke's model II in which Ca and S occupy positions  $3c (1/2, 0, 0)$  and  $3d (1/2, 0, 1/2)$  in space group  $P6_22$ . Model I of Florke (1952) was rejected in the data preparation step after a comparison of observed and calculated profiles. The refinement model included 233 allowed Bragg reflections and 17 variable parameters, five of which defined the functional dependence of the background. The profile was noticeably broadened and it was also necessary to vary three peak shape parameters of the resolution function. Final agreement factors were 4.92 (weighted profile  $R_{wp}$ ) and 12.10 (Rietveld  $R_p$ ) with an expected  $R_e$  of 2.43.<sup>3</sup> The structural parameters refined were the unit-cell dimensions ( $\text{\AA}$ ) [ $a = 6.9694(8)$ ,  $c = 6.3033(4)$ ], positional parameters of oxygen ( $x, y, z$ ) [ $0.4458(3)$ ,  $0.1347(3)$ ,  $0.3578(3)$ ] and isotropic thermal parameters ( $\text{\AA}^2$ ) for S [ $1.17(10)$ ], Ca [ $0.99(8)$ ] and O [ $1.44(6)$ ]. Selected interatomic distances and angles are presented in Table 3 and the final refinement profile is shown in Figure 2. The lack of fit, apparent in certain  $d$ -regions of the spectrum, may reflect the inability of the resolution function to properly model the peak shape broadening (5 times instrumental broadening). The fit could also be affected by the presence of an impurity phase such as anhydrite ( $\beta\text{-CaSO}_4$ ). X-ray single-crystal photographs of  $\gamma\text{-CaSO}_4$  all show weak diffuse maxima which have been attributed to the presence of small  $\beta\text{-CaSO}_4$  nuclei within  $\gamma\text{-CaSO}_4$  (Gay, 1965a).

Data were also taken on the gypsum powder ( $\text{CaSO}_4 \cdot 2\text{D}_2\text{O}$ ) which was eventually dehydrated to form hemihydrate. The structure was refined as a check on sample purity and to

$$R_{wp} = \left[ \frac{\sum_i w_i [Y_i(\text{obs}) - Y_i(\text{calc})]^2}{\sum_i w_i [Y_i(\text{obs})]^2} \right]^{1/2}$$

$$R_p = \frac{\sum_i |Y_i(\text{obs}) - Y_i(\text{calc})|}{\sum_i |Y_i(\text{obs}) - \text{bkg}_i|}$$

$$R_e = \frac{\sqrt{df}}{\sum_i w_i [Y_i(\text{obs})]^2}$$

where  $df$  is the number of degrees of freedom in the refinement,  $Y_i(\text{obs})$ ,  $Y_i(\text{calc})$  and  $\text{bkg}_i$  are the observed and calculated intensity and the background at the  $i$ th time channel, and  $w_i$  is the weight assigned to the  $i$ th channel.

Table 3. Selected interatomic distances (Å) and angles (degrees) for  $\gamma$ -CaSO<sub>4</sub>\*

|                    |          |                      |          |
|--------------------|----------|----------------------|----------|
| S-O                | 1.477(2) | O-S-O <sup>i</sup>   | 110.0(2) |
| O-O <sup>i</sup>   | 2.420(4) | O-S-O <sup>ii</sup>  | 113.2(1) |
| O-O <sup>ii</sup>  | 2.467(4) | O-S-O <sup>iii</sup> | 105.3(2) |
| O-O <sup>iii</sup> | 2.348(5) | S-Ca                 | 3.152(1) |
| Ca-O               | 2.543(2) | Ca-O <sup>iv</sup>   | 2.385(2) |

\* Symmetry code: i x-y, -y, -z  
 ii y-x, y, -z  
 iii -x, -y, z  
 iv -y, x-y, 2/3+z

determine the level of deuteration. Positional parameters and isotropic temperature factors were in good agreement with a recent single-crystal neutron study (Pederson and Semmingsen, 1982). Refinement of the H/D site occupation assuming  $n = 2$  revealed that the sample was >90% deuterated.

The 295 K hemihydrate profile could be indexed using either the hexagonal cell of Frik and Kuzel (1982) or an orthorhombic body-centered cell (Lager et al., 1983). Initially it was not clear whether the cell was hexagonal or whether the resolution and/or peak broadening did not permit observation of the orthorhombic distortion. As a result, Guinier-de Wolff X-ray data (FeK $\alpha_1$ ;  $\lambda = 1.9359\text{\AA}$ ) were collected from the same sample. The powder patterns showed considerable line broadening but from the splitting of several reflections indexed in the hexagonal cell, it was obvious that the symmetry was lower than hexagonal, probably orthorhombic or monoclinic. Because of the line broadening, these data were not used to determine the unit-cell parameters. A second photograph, identical in detail to the first, was obtained at standard conditions ( $T = 295\text{ K}$ ,  $\text{RH} = 40\%$ ) from a natural gypsum dehydrated at 363 K for 60 hr (% weight loss = 15.7). Although line broadening was still observed, it was considerably less than for the sample dehydrated from the

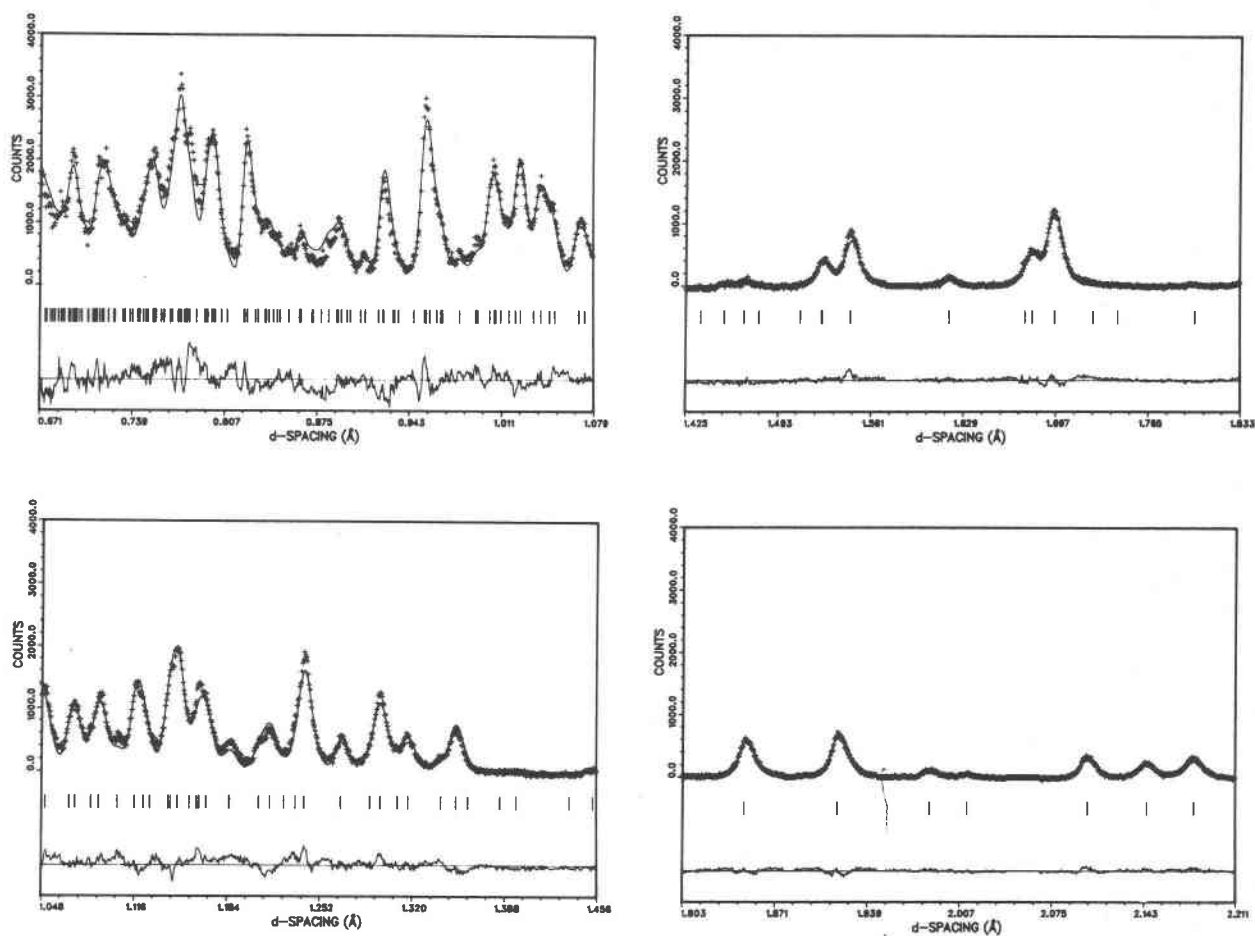


Fig. 2. Rietveld refinement profile for  $\gamma$ -CaSO<sub>4</sub> (145° detectors). Plus marks (+) are the raw data. The solid line is the best-fit profile. Tick marks below the profile indicate the positions of all allowed reflections. A difference curve (observed minus calculated) appears at the bottom. Background was fit as part of the refinement but has been subtracted before plotting.

synthetic material. Forty reflections were measured from this second film with an internal Si standard to  $2\theta = 82^\circ$  and submitted to the autoindexing program INDLSQ (Appleman and Evans, 1973). Of these data, 26 reflections were uniquely indexed ( $2\theta$  tolerance =  $0.047^\circ$ ) in a body-centered orthorhombic cell with dimensions ( $\text{\AA}$ )  $a = 12.062(4)$ ,  $b = 12.660(3)$  and  $c = 6.930(1)$  (Table 4).<sup>4</sup> The remaining 14 reflections were also consistent with the  $I$ -centered cell.

It was not possible to decide from the X-ray powder data alone if the symmetry was lower than orthorhombic. To resolve this problem and determine the space group symmetry, single crystals were grown according to the procedures described by Caspari (1936). Gypsum crystals were dissolved in a concentrated nitric acid solution maintained at  $353 \pm 5$  K for a period of several weeks. The hemihydrate crystals synthesized were of two types: large (100–300  $\mu\text{m}$ ) cigar-shaped crystals elongated parallel to the  $b$ -axis and smaller (50–100  $\mu\text{m}$ ) prismatic crystals terminated by trigonal pyramids. Guinier X-ray powder patterns of these crystals could be indexed in the "orthorhombic" cell refined from the dehydrated powders. Several ( $\sim 20$ ) of the single crystals described above were examined optically with the polarizing microscope. All crystals were pseudotrigonal and multiply-twinned on the (010) [twin plane (101)]. In the majority of crystals the twinning was observed optically as undulatory extinction on (010); in a few cases, sector twinning, similar to that observed in micas and cordierites, was well-developed. Heating in oil to 433 K produced no detectable change in the twinning, confirming the observation that optical data do not support the existence of a high-temperature trigonal form of hemihydrate (Gay, 1965b). Refractive indices were measured on a spindle stage (Bloss, 1981) to within 0.0005 by the oblique illumination technique ( $\lambda$ ,  $T$ -variation method). The final values (589.3 nm, 298 K) were obtained by least-squares refinements of the linearized Sellmeier equations (36 measurements per index). Due to the twinning, no difference could be resolved in the (010) plane ( $n_{\parallel b} = 1.5821$ ,  $n_{\perp b} = 1.5558$ ). If the crystals were heated in air for 2 h at  $373 \pm 5$  K and then rapidly quenched in oil, the refractive indices decreased significantly ( $n_{\parallel b} = 1.546$ ,  $n_{\perp b} < 1.500$ ) (Flörke, 1952), indicating that dehydration had occurred. After dehydration, cracks developed parallel to the prism faces and precise refractive index measurements were no longer possible. Although the crystal was stored with an oil film on its surface, it rehydrated within 24 hr. The cracks disappeared and the refractive indices were identical to those measured for hemihydrate.

Zero-level ( $h0l$ ) and ( $hk0$ ) precession photographs (MoK $\alpha$  radiation) of the above crystals exhibited pseudotrigonal symmetry. Analyses of upper level ( $h1l$ ) and ( $h2l$ ) Weissberg photographs established the space group as  $I2$  or  $I2_1$  for the unit cell setting  $a = 12.06$ ,  $b = 12.66$ ,  $c = 6.93 \text{\AA}$  and  $\gamma \cong 90^\circ$  (monoclinic first setting). An untwinned crystal suitable for structural analysis could not be obtained.

For some crystals, the pseudotrigonal symmetry observed in ( $h0l$ ) photographs was apparent only from the distribution of weak satellite reflections related to the twinning. These reflections could be resolved only at high angles ( $2\theta \sim 150^\circ$ ; CuK $\alpha$  radiation) on Weissberg photographs after long

Table 4. Observed and calculated interplanar distances ( $d$  in  $\text{\AA}$ ),  $hkl$  indices and relative intensities ( $I/I_0$ ) for "orthorhombic" Na-free hemihydrate and NaCl-grown hemihydrate  $[\text{Ca}_{0.98}\text{Na}_{0.03}\text{SO}_4 \cdot 0.47\text{H}_2\text{O}]$  ( $2\theta_{\text{max}} = 65^\circ$ )\*

|     |     |     | Na-free hemihydrate |                  |         | Na-containing hemihydrate |                  |         |
|-----|-----|-----|---------------------|------------------|---------|---------------------------|------------------|---------|
| $h$ | $k$ | $l$ | $d(\text{obs})$     | $d(\text{calc})$ | $I/I_0$ | $d(\text{obs})$           | $d(\text{calc})$ | $I/I_0$ |
| 2   | 0   | 0   |                     |                  |         | 6.051                     | 6.051            | 40      |
| 1   | 0   | -1  |                     |                  |         | 6.009                     | 6.013            | 40      |
| -1  | 0   | 1   |                     |                  |         |                           |                  |         |
| 1   | 0   | 1   | 6.012               | 6.009            | 90      | 5.980                     | 5.989            | 40      |
| -1  | 2   | 1   |                     |                  |         | 4.372                     | 4.369            | 15      |
| 1   | 2   | 1   | 4.361               | 4.358            | 5       |                           |                  |         |
| 2   | 1   | 1   | 4.279               | 4.281            | <5      |                           |                  |         |
| 1   | 3   | 0   | 3.983               | 3.983            | 5       | 3.994                     | 4.001            | <10     |
| 0   | 3   | 1   | 3.604               | 3.604            | 10      |                           |                  |         |
| -3  | 0   | 1   |                     |                  |         | 3.489                     | 3.491            | 25      |
| 3   | 0   | -1  |                     |                  |         |                           |                  |         |
| 3   | 0   | 1   |                     |                  |         | 3.476                     | 3.477            | 25      |
| 0   | 0   | 2   | 3.468               | 3.465            | 80      | 3.455                     | 3.455            | 25      |
| 1   | 1   | 2   | 3.220               | 3.221            | <5      |                           |                  |         |
| -3  | 2   | 1   |                     |                  |         | 3.061                     | 3.060            | <10     |
| 3   | 2   | 1   | 3.048               | 3.048            | 10      | 3.052                     | 3.050            | 10      |
| 0   | 2   | 2   | 3.039               | 3.039            | 20      |                           |                  |         |
| 4   | 0   | 0   |                     |                  |         | 3.025                     | 3.025            | 40      |
| -2  | 0   | 2   |                     |                  |         | 3.006                     | 3.007            | 40      |
| 2   | 0   | 2   | 3.004               | 3.004            | 90      | 2.994                     | 2.994            | 40      |
| 2   | 4   | 0   | 2.802               | 2.803            | 100     | 2.815                     | 2.815            | 100     |
| 4   | 2   | 0   |                     |                  |         | 2.733                     | 2.732            | <10     |
| -2  | 2   | 2   |                     |                  |         | 2.720                     | 2.718            | 10      |
| 2   | 2   | 2   | 2.713               | 2.714            | 20      | 2.710                     | 2.709            | 10      |
| -3  | 0   | 2   |                     |                  |         | 2.631                     | 2.630            | <10     |
| 1   | 3   | 2   | 2.612               | 2.614            | <5      |                           |                  |         |
| -3  | 4   | 1   |                     |                  |         | 2.349                     | 2.351            | <10     |
| 0   | 5   | 1   | 2.379               | 2.378            | <5      |                           |                  |         |
| 0   | 4   | 2   | 2.338               | 2.337            | 20      | 2.340                     | 2.340            | 15      |
| 0   | 1   | 3   | 2.271               | 2.272            | 20      |                           |                  |         |
| 3   | 3   | 2   | 2.230               | 2.229            | <5      |                           |                  |         |
| 2   | 5   | 1   | 2.211               | 2.212            | <5      |                           |                  |         |
| 2   | 4   | 2   | 2.179               | 2.179            | 20      |                           |                  |         |
| 3   | 5   | 0   |                     |                  |         | 2.152                     | 2.152            | <10     |
| 5   | 2   | 1   |                     |                  |         | 2.146                     | 2.147            | <10     |
| 4   | 2   | 2   |                     |                  |         | 2.139                     | 2.139            | 10      |
| 1   | 2   | 3   | 2.137               | 2.136            | 50      | 2.131                     | 2.130            | 10      |
| 0   | 6   | 0   | 2.112               | 2.110            | 40      | 2.119                     | 2.120            | 10      |
| -2  | 2   | 3   |                     |                  |         | 2.041                     | 2.042            | 25      |
| 0   | 3   | 3   | 2.027               | 2.026            | <5      |                           |                  |         |
| -5  | 3   | 1   |                     |                  |         | 2.014                     | 2.013            | <10     |
| 1   | 6   | 1   |                     |                  |         | 1.998                     | 1.998            | <10     |
| 3   | 0   | 3   | 2.003               | 2.003            | <5      |                           |                  |         |
| 2   | 6   | 0   | 1.992               | 1.992            | <5      |                           |                  |         |
| 5   | 1   | 2   | 1.954               | 1.956            | <5      |                           |                  |         |
| 6   | 1   | 1   | 1.908               | 1.909            | 20      |                           |                  |         |
| -3  | 2   | 3   |                     |                  |         | 1.912                     | 1.912            | <10     |
| 3   | 2   | 3   |                     |                  |         | 1.906                     | 1.905            | <10     |
| -6  | 2   | 1   |                     |                  |         | 1.855                     | 1.854            | 25      |
| 5   | 4   | 1   | 1.851               | 1.849            | 60      | 1.853                     | 1.853            | 25      |
| 1   | 4   | 3   | 1.843               | 1.844            | 85      |                           |                  |         |
| 6   | 2   | 1   |                     |                  |         | 1.849                     | 1.850            | 25      |
| 0   | 6   | 2   | 1.802               | 1.802            | <5      |                           |                  |         |

\* The intensities were visually estimated.

<sup>4</sup> The  $b$  crystallographic axis now becomes the pseudotrigonal axis parallel to the channels. The reasons for choosing this unit-cell setting will become clear in a later section of the paper.

exposure times (60–72 hr). In situ dehydration of one of these crystals at  $\sim 383$  K produced  $\gamma$ -CaSO<sub>4</sub> which was recognized in precession photographs by the disappearance of reflections of the type  $0kl$  with  $k + l = 2n$ . These are the reflections corresponding to the doubling of the channel axis in  $\gamma$ -CaSO<sub>4</sub>. The change from  $\bar{1}$  to  $mm$  symmetry in the  $hk0$  section at high temperature is also very striking and consistent with the hexagonal space group of  $\gamma$ -CaSO<sub>4</sub> ( $P6_222$ ). On rehydration at room temperature, the superstructure reflections reappeared but a subsequent examination of  $(h0l)$  and  $(h1l)$  Weissenberg photographs indicated that the crystal had diffraction symmetry  $6mm$  and the approximate cell parameters reported by Frik and Kuzel (1982) for their hexagonal cell (Table 1). It was still twinned as evidenced by the doublet at high angles but the twin-related reflections were now of equal intensity. These observations are consistent with the interpretation that after rehydration twin-related monoclinic domains in hemihydrate become equal in size (Gay, 1965b).

A second batch of crystals was grown in saturated NaCl solution (at  $337 \pm 5$  K for two weeks) according to the method described by Flörke (1952). The majority of these crystals were similar to those obtained in the HNO<sub>3</sub> synthesis. In addition, there were some larger crystals, milky-white in appearance, which were not examined in detail because of their skeletal growth habit. Zero through second-level single-crystal photographs were consistent with those taken of the HNO<sub>3</sub>-grown crystals, i.e., pseudotrigonal monoclinic- $I$  symmetry. Viewed optically with a spindle stage, the NaCl-grown crystals were characterized by well-developed cyclic sector twinning and significant birefringence in the (010) plane. Refractive indices ( $\lambda$ ,  $T$ -variation method) were smaller ( $n_{1b} = 1.5684$ ,  $n_{1a} = 1.5553$ ,  $n_{1c} = 1.5479$ ) than those measured for the HNO<sub>3</sub>-grown crystals and did not change in value after heating in air for 2 hr at  $393 \pm 5$  K. The X-ray data (Guinier geometry; program INDLSQ) obtained from the powdered single crystals could be indexed in a monoclinic- $I$  cell [ $a = 12.107(2)$ ,  $b = 12.718(2)$ ,  $c = 6.910(1)\text{\AA}$ ;  $\gamma = 90.27^\circ$ ;  $V = 1064(1)\text{\AA}^3$ ]. (Table 4). Due to the increase in the monoclinic angle, many of the lines indexed for "orthorhombic" hemihydrate were split (see also Powell, 1962).

Single crystals of hemihydrate (NaCl-grown) and gypsum (natural sample used in the dehydration experiments) were chemically analyzed for Ca, Cl, Na, Fe, and S with an electron microprobe. All chemical analyses totalled  $\sim 100$  wt.%, indicating that dehydration occurred during pumping of the sample chamber (vacuum  $\sim 2 \times 10^{-6}$  torr). The gypsum was found to be chemically pure. The hemihydrate contained  $\sim 0.50$  wt.% Na<sub>2</sub>O but no chlorine (Ca<sub>0.98</sub>Na<sub>0.03</sub>SO<sub>4</sub>). The water content [0.47(3) H<sub>2</sub>O] was determined from weight loss measurements carried out on a 150 mg sample of single crystals (after heating to 523 K).

Since neither the pseudo-orthorhombic nor monoclinic distortion could be resolved in the hemihydrate neutron profile, these data were not refined. However, a general knowledge of the structure could still be gained from a comparison of the observed profile with those calculated from models based on the refined  $\gamma$ -CaSO<sub>4</sub> structure. In this approach, the hexagonal coordinates of  $\gamma$ -CaSO<sub>4</sub> were transformed to the monoclinic cell ( $\gamma = 90^\circ$ ) noted previously. Several models were then formulated based on the distribution of water molecules within the channels. No distortions were introduced in the framework other than those already incorporated in the unit-cell parameters.

A high-temperature (378 K) data set for hemihydrate was also

collected to prove or disprove the existence of trigonal hemihydrate (Flörke, 1952). Gypsum (CaSO<sub>4</sub> · 2D<sub>2</sub>O) was dehydrated in situ for  $\sim 8$  hr after which data were collected at temperature for 12 hr. The 295 and 378 K patterns are almost identical in appearance and neither can be indexed in the cell proposed by Flörke (1952) (Table 1).

## Discussion

The crystal structure of  $\gamma$ -CaSO<sub>4</sub> is shown in projection in Figures 3 and 4. The basic structural unit common to all phases in the CaSO<sub>4</sub>-H<sub>2</sub>O system is the chain of edge-sharing sulfate tetrahedra and CaO<sub>8</sub> polyhedra. In  $\gamma$ -CaSO<sub>4</sub> these chains are related by a 6-fold screw-axis to form one-dimensional channels (diameter  $\sim 4\text{\AA}$ ) parallel to  $c$ . On the channel walls at intervals of  $1/6 c$ , oxygen atoms of four SO<sub>4</sub> groups are arranged in a near-planar configuration, equidistant ( $\sim 2.78\text{\AA}$ ) from the channel center. These oxygens lie approximately at the corners of a (00 $l$ ) rectangle whose sides (3.79 $\text{\AA}$  and 4.02 $\text{\AA}$ ) subtend angles of  $86^\circ$  and  $94^\circ$  with respect to a point at the center of the channel.

Assuming that only small atomic shifts occur during the transformation  $\gamma$ -CaSO<sub>4</sub>  $\rightarrow$  hemihydrate, an idealized  $I2$  structure for hemihydrate can be formulated. If the unit cells of  $\gamma$ -CaSO<sub>4</sub> and hemihydrate are related as shown in Figure 5, then the asymmetric unit for a hemihydrate with  $I2$  symmetry and  $Z = 12$  would contain  $3[\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}]^5$ . Two calcium atoms would occupy the special positions (1/2, 0,  $z$ ) and (0, 0,  $z$ ); all sulfur and framework oxygen atoms would be in general positions. In the simplest model, the water molecules (only oxygens considered) are located at (0, 1/6, 0) and (0, 1/2, 0) or (0, 0, 0) and (0, 1/3, 0) and do not interact with the Ca<sup>2+</sup> ions in the framework. Such an arrangement leads to a doubling of the  $c$ -dimension in  $\gamma$ -CaSO<sub>4</sub>. The  $y$ -coordinates are dictated by the steric details of the  $\gamma$ -CaSO<sub>4</sub> structure since at these levels along  $c$  the distance between the oxygen atom of the water molecule [O(w)] and its nearest neighbor on the channel wall would be  $\sim 2.8\text{\AA}$ , an ideal distance for an O(w)-H · · · O interaction. The existence of at least two water positions is consistent with the infrared spectrum (KBr disk media) recorded for the deuterated hemihydrate (Fig. 6). The spectrum shows three absorption maxima in the region 2600–2800 cm<sup>-1</sup> which can be assigned to D-O-D stretching modes (Morris, 1963). The above model was used to simulate a raw data plot for the 90° detector banks of the IPNS special

<sup>5</sup> The hemihydrate and  $\gamma$ -CaSO<sub>4</sub> unit cells are related by the transformation

$$\begin{bmatrix} a' \\ b' \\ c' \end{bmatrix} = \begin{bmatrix} 1 & 2 & 0 \\ 0 & 0 & 2 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix}$$

Hemi                       $\gamma$ -CaSO<sub>4</sub>  
 $\gamma = 90^\circ$

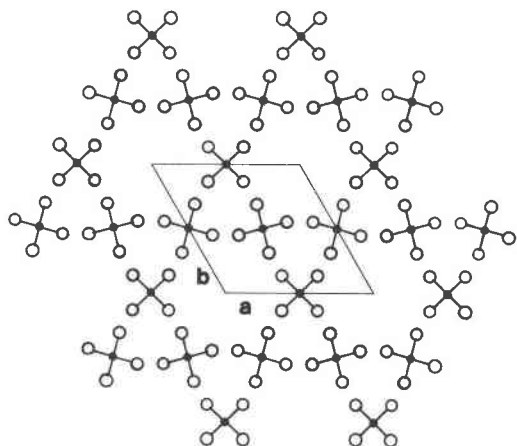


Fig. 3. [001] projection of the  $\gamma$ -CaSO<sub>4</sub> structure illustrating the sulfate tetrahedra and the channels developed parallel to *c*.

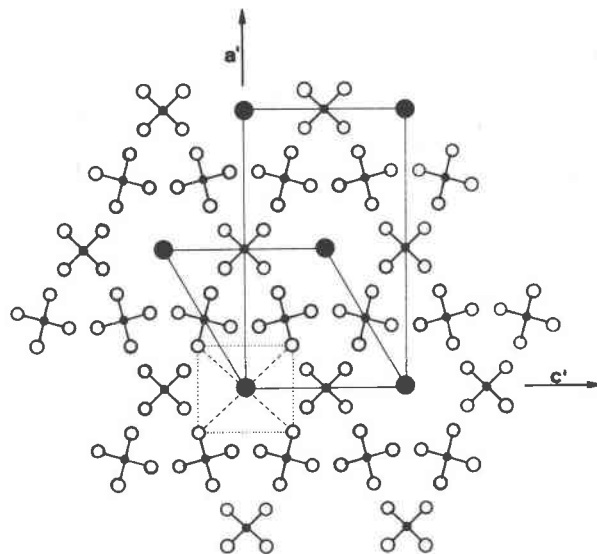


Fig. 5. [001] projection of the  $\gamma$ -CaSO<sub>4</sub> structure illustrating the relationship between the hexagonal and monoclinic ( $\gamma = 90^\circ$ ) unit cells of  $\gamma$ -CaSO<sub>4</sub> and hemihydrate. The asymmetric unit for *I*2 hemihydrate, 3[CaSO<sub>4</sub> · 0.50H<sub>2</sub>O], is contained within the subcell with dimensions  $a'/2$ ,  $b'/2$ ,  $c'$ . Possible positions for the water molecules in the hemihydrate structure are represented by large black circles. The dashed lines from the water molecule at (0, 1/2, 0) indicate the four oxygens which are located equidistant (2.78 Å) from the center of the channel in the undistorted hexagonal  $\gamma$ -CaSO<sub>4</sub> structure. These oxygens lie approximately in the plane (020) at the corners of a rectangle (dotted lines).

environment diffractometer using the FORTRAN computer program TOFSIMU (Rotella and Sabine, 1983). The poor agreement between observed and calculated profiles at low *d*-values (Fig. 7) suggests that additional distortions, not modelled by the monoclinic cell parameters are present in the hemihydrate structure. For example, the triplet at  $d \sim 2.1 \text{ \AA}$  in the calculated pattern has the approximate intensity distribution observed for  $\gamma$ -CaSO<sub>4</sub> (Fig. 7).

Several attempts were also made to include the deuterium atoms in the simulation. Approximate atomic positions can be calculated if the molecule is assumed to lie in the plane defined by the four oxygen atoms (described

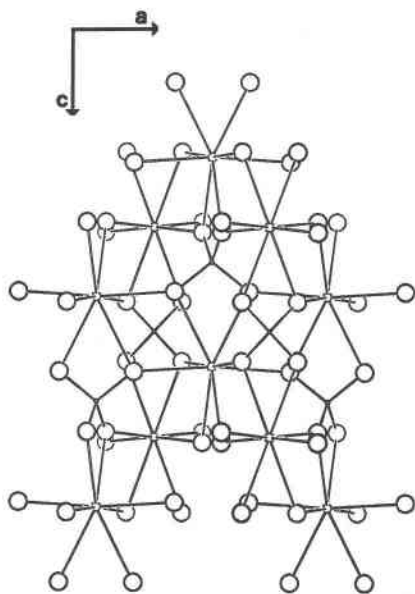


Fig. 4. [010] projection of the  $\gamma$ -CaSO<sub>4</sub> structure illustrating the chains of edge-sharing sulfate tetrahedra and CaO<sub>8</sub> polyhedra parallel to *c*.

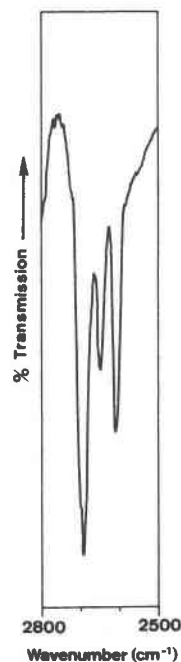


Fig. 6. Infrared spectrum of deuterated hemihydrate in the region 2500 and 2800  $\text{cm}^{-1}$ .

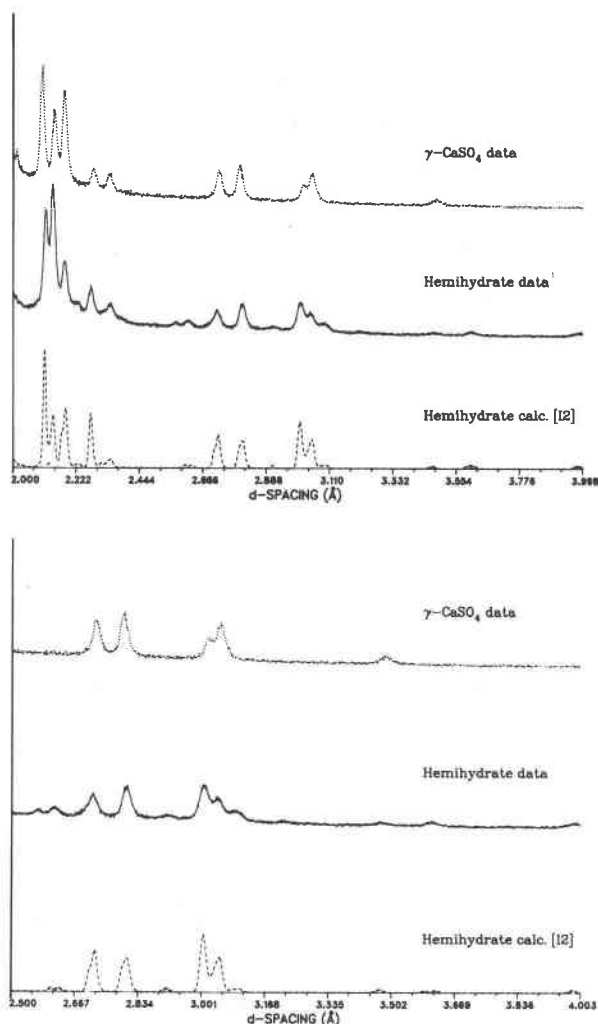


Fig. 7. Comparison of the observed and simulated (12) time-of-flight profiles for hemihydrate and the observed profile for  $\gamma$ -CaSO<sub>4</sub> for  $2\theta = 90^\circ$  and  $d$ -ranges of 2.5 – 4.0 Å and 2.0 – 4.0 Å.

earlier for  $\gamma$ -CaSO<sub>4</sub>). The O–D and D · · · O (channel wall) distances and the D–O–D angle can be constrained to the values observed for H in gypsum (Pederson and Semmingsen, 1982). A complication arises, however, because based on the  $\gamma$ -CaSO<sub>4</sub> structure and the positions assumed for O(w), the D<sub>2</sub>O molecule can have several possible orientations within the channel, i.e., the deuterium atoms would be disordered. For example, the molecule can be oriented with its O–D vectors pointing toward any one of the four sides of the “oxygen rectangle” (Fig. 5). There is no crystal-chemical reason to assume that one configuration would be preferred over another since the O (channel)–O(w)–O (channel) angles are approximately equal. For O(w)–H · · · O (channel) angles near 180° (as in gypsum), the H<sub>2</sub>O molecule should prefer environments in which the O–O(w)–O angles are close to ~110°.

Flörke (1952) rejected Gallitelli's C2 hemihydrate structure for precisely this reason; if water molecules are placed at (0, 1/6, 0) and (0, 1/2, 0), the O–O(w)–O angles are ~70°.

In the structure determined by Bushuev (1982), the water molecules in the channels are bonded to calcium ions resulting in a pseudotrigonal distortion of the framework. Of the six SO<sub>4</sub>–CaO<sub>8</sub> chains in  $\gamma$ -CaSO<sub>4</sub> that enclose each channel, every other one moves toward the center of one channel whereas the remaining three are displaced toward the center of adjacent channels. The water molecules, which are related by a pseudo 6<sub>1</sub> screw axis along [010], are located in Ca-centered oxygen pentagons oriented approximately parallel to (010). Two oxygens of a SO<sub>4</sub> group are situated above and below each pentagon to form a nine-vertex Ca-polyhedron. This irregular coordination results in a very distorted polyhedron; Ca–O bond distances in one polyhedron range from 2.35 to 2.87 Å. The latter distance is the longest (by ~0.2 Å) ever reported for a crystalline Ca-hydrate (Einspahr and Bugg, 1980).

The evidence presented by Bushuev (1982) and Bushuev and Borisov (1982) to support the existence of nonstoichiometric hemihydrate (CaSO<sub>4</sub> · 0.67H<sub>2</sub>O) is not convincing. The weight loss measured gravimetrically does not necessarily represent the loss of structural water. The low temperature of dehydration ( $T < 360$  K) makes it extremely difficult to differentiate between structural and surface water (e.g., in the form of inclusions); the latter could easily account for the apparent nonstoichiometry. The reliability of the water content refined from the X-ray intensity data is also questionable because of the high correlation between the site occupation and the temperature factor, both of which are unknown.

If the composition (0.67 H<sub>2</sub>O) is assumed to be correct, then for  $Z = 12$  each channel would contain four water molecules. Since the water is not distributed randomly in the channels, i.e., only levels of  $1/6 b$  are possible, some water-water distances will be unrealistically short (~2 Å). The same would be true in the structure of CaSO<sub>4</sub> · 0.80H<sub>2</sub>O (Abriel, 1983). If 50% of the water positions are occupied, as in CaSO<sub>4</sub> · 0.50H<sub>2</sub>O, the above distances lengthen to ~4 Å. Structural arguments simply do not favor the existence of a hemihydrate with excess water.

Powder intensities (Guinier geometry) calculated from the atomic parameters reported by Bushuev (1982) are in fair agreement with the estimated intensities in Table 3. However, a major discrepancy was noted between the calculated X-ray pattern and the Guinier data measured by Bushuev and Borisov (1982) for CaSO<sub>4</sub> · 0.67H<sub>2</sub>O. Estimated intensities for the lines at  $d = 1.8426, 1.851$  Å are given as 10 and 5, respectively (their Table 1); these are two of the most intense lines in the calculated pattern. The fit to the neutron powder data can be improved in the low  $d$ -region of the spectrum if Bushuev's model is used in the simulation (assuming 50% occupation of the water



positions, i.e.,  $\text{CaSO}_4 \cdot 0.50\text{H}_2\text{O}$ ). Although the overall structure determined by Bushuev (1982) may be correct, it has not been analyzed in further detail because of the poor accuracy in the bond distances, e.g., tetrahedral S–O distances range from 1.35 to 1.59 Å ( $\pm 0.01$  Å). It is very possible that the single crystal used in the structural analysis was twinned.

The  $I2$  structure described in the previous section is probably equivalent to the orthorhombic or monoclinic forms of Flörke (1952), Gay (1965b) and Frik and Kuzel (1982). The hexagonal cell described by Frik and Kuzel (1982), which is a  $2 \times 2 \times 2$  supercell of  $\gamma\text{-CaSO}_4$ , may be finely twinned monoclinic hemihydrate. Because the overall symmetry is hexagonal, this structure would be expected to exhibit short-range but not long-range order, i.e., the monoclinic domains would be distributed at random.

Bushuev and Borisov (1982) proposed a trigonal structure for stoichiometric hemihydrate on the basis of their high-temperature Guinier X-ray powder experiment. At  $\sim 353$  K they observed a change from monoclinic to hexagonal symmetry which they attributed to the dehydration reaction  $\text{CaSO}_4 \cdot 0.67\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 0.50\text{H}_2\text{O} + 0.17 \text{H}_2\text{O}$ . The powder pattern could be indexed with a cell which is remarkably similar to the  $\gamma\text{-CaSO}_4$  cell (Table 1). In fact, if the  $c$ -dimension is halved their unit cell closely corresponds to the one refined from the neutron diffraction data. Since it is always possible to index a powder pattern with a larger unit cell, the phase observed was probably not hemihydrate but  $\gamma\text{-CaSO}_4$ . Bushuev and Borisov (1982) also imply that all single crystals grown according to the method of Caspari (1936) are trigonal. This study and that of Gay (1965b) and Gallitelli (1933) have clearly demonstrated that these crystals are only *pseudotrigonal* (twinned) and that the true symmetry is monoclinic. Thus, there seems to be no evidence to support the existence of the trigonal structure proposed by Bushuev and Borisov (1982) and Bushuev (1982).

In the  $I2$  structure for hemihydrate, water molecules are located at two different levels along  $b$ :  $1/6$ ,  $1/2$ ,  $5/6$  and  $0$ ,  $1/3$ ,  $2/3$ . If the water molecules occupy only one level, then the lattice becomes  $C$ -centered and has the space group  $C2$  proposed by Gallitelli (1933). Although Gallitelli (1933) offers convincing proof for the  $C2$  structure in the form of upper level Weissenberg photographs, no single-crystal or powder data collected in this study could be indexed in this space group. Some of the hemihydrate single crystals examined by Gallitelli (1933) were grown in saturated NaCl solution. Hemihydrate formed in this way has been shown to contain significant amounts of  $\text{Na}_2\text{O}$  (up to 3% by weight) (Powell, 1962). It is conceivable that incorporation of Na in some form within the channels might have effected the distribution of the water molecules which in turn could have altered the symmetry ( $I \rightarrow C$ ). This supposition proved to be partially correct. The stoichiometry determined from chemical analysis of

the NaCl-grown hemihydrate suggests the substitution,  $2\text{Na}^+ \rightarrow \text{Ca}^{2+}$ , where half of the Na is in the framework and the remainder in the channels. The idea of channel Na is consistent with the greater thermal stability of NaCl-grown hemihydrate as observed in our optical experiments. The presence of Na in the channels could inhibit the movement of the water molecules and prevent dehydration. This stabilizing effect of Na could also explain the occurrence of the rare mineral bassanite in evaporite deposits. Although the substitution of Na for Ca produces significant changes in the lattice and optics of hemihydrate, it has no effect on the space group symmetry.

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