Solid-State Chemistry

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How Much Water Does Calcined Gypsum Contain?**

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Gypsum has been used in construction since antiquity. Currently stucco, screed, plasterboard, filler, and many more products for the construction industry are based on this binder. Gypsum, $CaSO_4·2H_2O$, is typically named dihydrate in construction chemistry. In different calcination processes, $CaSO_4·2H_2O$ is heated above 100 °C, thus removing some of the crystal water, and hemihydrate $CaSO_4·0.5H_2O$, or so-called plaster of Paris or stucco is formed. It may also be found as the rare mineral bassanite.[1] In nature, some deep-sea medusa use single crystals of hemihydrate for orientation.[2] By the calcination of gypsum at higher temperatures, all the crystal water is removed and anhydrate, $CaSO_4$, is formed. Huge deposits of gypsum and anhydrate occur naturally and are mined industrially.[3] Most products are colloquially called gypsum, but are chemically hemihydrate, which is the most-produced inorganic compound worldwide. The structure and water content of hemihydrate is thus of huge scientific and economic interest.[4]

Numerous publications and entries in databases exist on the structure and symmetry of hemihydrate. Initial contributions were made by Gallitelli in 1933.[5] His interpretation of Weissenberg photographs lead to the structure that still holds true today. He realized that the trigonal symmetry is only slightly distorted, and thus stated $P3_121$ as being the space group. Subsequent publications deal with the symmetry of hemihydrate; an overview is given in Table 1.

The basic structure of hemihydrate is reproduced well in all models, but discussions are still ongoing regarding the arrangement of water molecules in the structure. Whereas structure analyses with Rietveld methods in powder samples give good models, single-crystal structure analyses suffer from the hexagonal pseudosymmetry that is present. The models contain split positions for the water molecules; their occupancies have to be refined with free parameters, which might suggest a water content of more than 0.5 per sum formula. However, experimental evidence that the structure really contains more than 0.5 water molecules has not been seen to date.

Table 1: Literature overview of published hemihydrate structures.[a]

H_2O	a [Å]	b [Å]	c [Å]	β [°]	SG	Year	Ref.
0.5	6.84	$=a$	12.72		$P3_121$	1933	[5]
0.5	6.82	$=a$	6.24		$P\bar{3}m1$	1936	[6]
0	6.99	$=a$	6.34		$P6_222$	1952	[7]
0.5	6.85	11.88	12.60	ca. 90	$I2$	1965	[8]
0.67	12.028	6.927	12.674	90.21	$I2$	1982	[9]
0.5	6.977	$=a$	12.617		$P3_112$	1982	[10]
0.52	13.865(1)	$=a$	12.718(2)		hex.	1982	[11]
0.48	12.061(2)	6.933(1)	12.670(2)		orth.	1982	[11]
0.8	6.968(8)	$=a$	6.410(4)		$P3_121$	1982	[12]
0	6.9694(8)	$=a$	6.3033(4)		$P6_222$	1984	[13]
0.5	12.0275(4)	6.9312(3)	12.6919(5)	90.18(1)	$I2$	1987	[14]
0.66	13.8615(3)	$=a$	12.7391(6)		$P3_121$	1987	[14]
0	6.9719(2)	$=a$	6.3124(4)		$P6_222$	1987	[14]
0.53	12.0275(4)	6.9312(3)	12.6919(5)	90.18(1)	$I2$	1993	[15]
0	12.0777(7)	6.9723(4)	6.3040(2)		$C222$	1995	[16]
0.5	12.0317(1)	6.9272(2)	12.6711(3)	90.27(1)	$I2$	1995	[16]
0.5	12.0350(5)	6.9294(3)	12.6705(4)	90.266(3)	$I2$	2001	[17]

[a] H_2O: water content relative to the formula $CaSO_4·xH_2O$; SG: space group.

For the investigation described herein, some well-formed crystals were taken from a technical process for the production of hemihydrate. The measurement on a single-crystal image-plate detection system shows the same pattern for all crystals, so that the following symmetry considerations are systematic.

The observation of the reciprocal space reconstructed from the single-crystal measurement shows the pseudo-hexagonal symmetry (Figure 1). The indexation with a

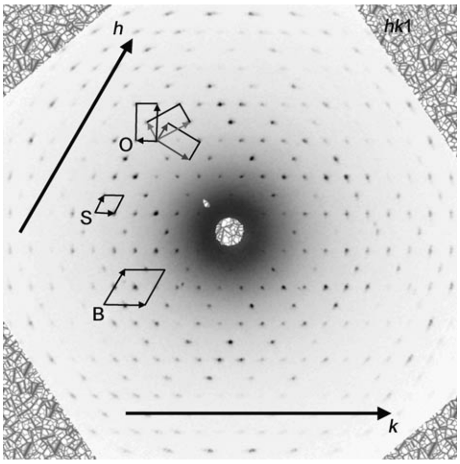

Figure 1. A cut $hk1$ through the reciprocal space, reconstructed from a single-crystal measurement, indexed by the pseudo-hexagonal setting of the basic cell (B). The super cell (S) indexes all reflections, but has unusual extinctions. The basis vectors of three pseudo-orthorhombic cells (O) give a reasonable indexation.

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hexagonal cell ($a=b=6.9$ Å, $c=12.6$ Å) is successful for about 50 % of the observed reflections. All reflections can be indexed with a doubled cell in a and b. Figure 1 shows a slice through the reciprocal space and the cell vectors of the two hexagonal cells. The uncommon extinctions can not be explained by any space group. As previously reported, the reciprocal space can be indexed properly by three pseudo-orthorhombic cells $a=12.0$ Å, $b=6.9$ Å, $c=12.6$ Å, $\alpha=\beta=\gamma=90°$[12] whose vectors are also given in Figure 1. This setting fulfills only monoclinic symmetry and can be described in $I2$. Herein, the standard setting in $C2$ is used, with $a=17.559(3)$ Å, $b=6.9619(7)$ Å, $c=12.071(2)$ Å and $\beta=133.56(1)°$.

The structure was solved and refined in one of the three monoclinic indexed cells. The structure shown in Figure 2 has channels in which the differential Fourier synthesis gives four electron residual maxima in this stage of refinement, which can be accounted for with four partly occupied oxygen sites. However, the refinement results in large R values, and the anisotropic displacement parameters of most sites are refined to meaningless values. To introduce the obvious twinning, all reflections have to be determined that have contributions by more than one individual. These reflections are reindexed by the twinning matrices and listed in the reflection list for each individual separately. With this list in the hklf5 format, a threefold twin can be refined with SHELX97.[18] The anisotropic displacement parameters of the $CaSO_4$ framework can then be refined to reasonable values. But the description of the residual electron density in the channels still has to be carried out with four oxygen sites that are not fully occupied and can not be refined anisotropically.

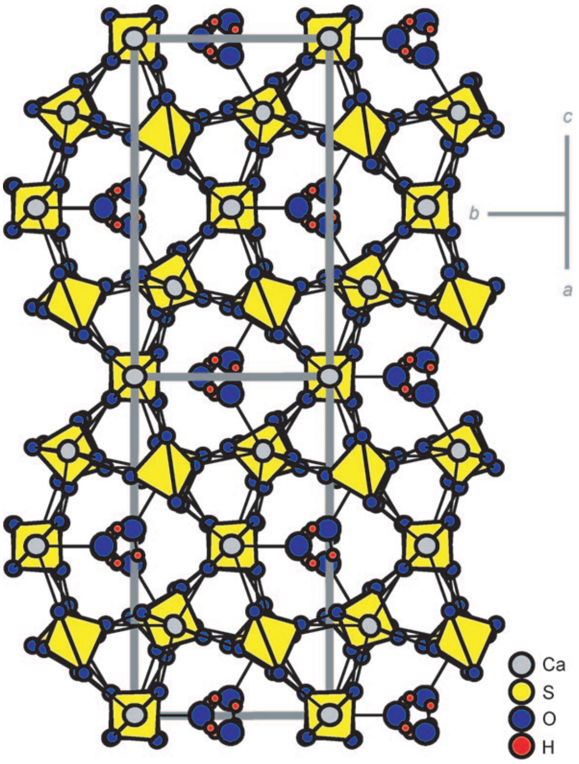

Figure 2. Part of the structure of $CaSO_4{\cdot}0.5\,H_2O$. The SO_4 tetrahedra (dashed) form, together with calcium atoms, alternate columns that arrange in a trigonal pattern. The crystal water orders itself in the free channels in between. Anisotropic displacement parameters are set at 80 % probability.

To gain further insight into the symmetry problem, the reduction from the highest possible to the true monoclinic symmetry is observed in a Bärnighausen tree (Figure 3).[19]

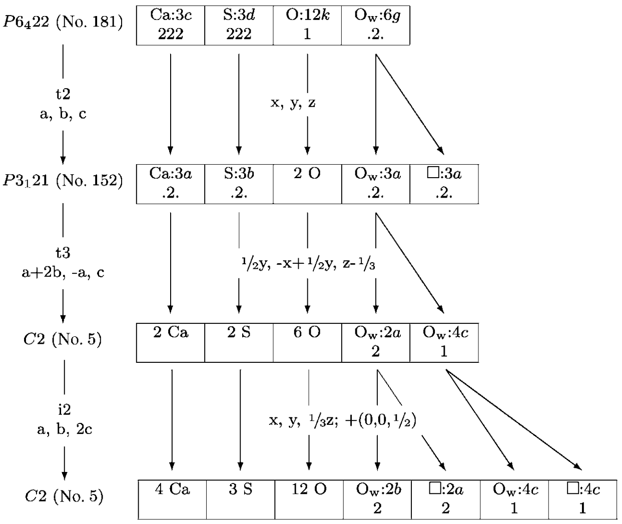

Figure 3. Bärnighausen tree with the symmetry reduction in $CaSO_4{\cdot}0.5\,H_2O$.[19] The hexagonal pseudosymmetry can be reduced to the real monoclinic symmetry in three steps.[20] The translation-equivalent transitions $t2$ and $t3$ indicate that the structure must be refined as twin of a threefold twin, which is in this case a sixfold twin. The splitting of the oxygen sites inside the channels O_W can be clearly seen. The site continuation for the $CaSO_4$ framework is condensed for clarity.

Taking only the $CaSO_4$ framework into account and ignoring minor distortions, the structure fulfills $P6_422$ (No. 181). The symmetry can be reduced in three steps to the space group $C2$ (No. 5), two translation-equivalent transitions and one isomorphic transition are needed.[20] Apart from this reported symmetry reduction, others are also possible, and can easily be found at the Bilbao Crystallographic Server, for example.[21] Translation-equivalent transitions always indicate twinning, and the partial merohedric threefold twinning can be discovered in the diffraction pattern in this case. This observation correlates well with the $t3$ transition from $P3_121$ to $C2$; the $t2$ transition from $P6_422$ to $P3_121$ is not represented in the refinement so far. The twin combined with a threefold twin is in this case a sixfold twin. The orientation matrices of the three additional individuals in the reciprocal space can be revealed by inversion of each individual of the threefold twin. The site continuation in Figure 3 shows the splitting and closure of the sites occupied with oxygen inside the channels. For the refinement, all reflections with contributions of more than one individual have to be reindexed and listed for each individual separately. With the reflection list in hklf5 format the refinement for a sixfold twin can be carried out. The split positions for the oxygen sites in the channel then disappear and only two fully occupied sites remain that refine with meaningful anisotropic displacement parameters. The discussion about split positions in the hemihydrate can thus be traced back to an overseen twinning. Details of the refinement can be found in reference [22].

The refinement as sixfold twin results in an ordered structure model for $CaSO_4\cdot 0.5\,H_2O$. By ignoring the twinning, a model with multiple oxygen split positions is revealed. By refining the occupancy of these sites with a free parameter, compositions with $x > 0.5$ for $CaSO_4\cdot x\,H_2O$ can be obtained. One example for this can be found in reference [15]. To date, there is no experimental proof that the structure is able to absorb more than 0.5 water molecules per formula. Most production routines yield hemihydrate in fine powders with large external surfaces, which can easily adsorb water, making it difficult to differentiate between crystal water and adsorbed water. The crystal water can easily be removed by heating without transformation into the anhydrate structure. This very soluble but water-free form is called anhydrate III, or soluble anhydrate.

To clarify the exact positions of the hydrogen atoms and the orientation of the water molecules inside the channels, the structure was optimized using three-dimensional periodic constraints.[23] To evaluate the accuracy of the method (functional, pseudopotentials, number of plane waves, plane-wave energy cutoff), the well-known structures of gypsum and anhydrate were geometry-optimized. The convergence of the plane-wave cutoff was evaluated by independent test calculations at 70, 80, 100, and 120 Ry; the results are given in Table 2.

Table 2: Independent test optimizations of the anhydrate structure.[a]

	Ref. [24]	120 Ry	100 Ry	80 Ry	70 Ry
a [Å]	7.006	6.998	6.994	6.975	6.952
b [Å]	6.998	6.997	6.994	6.975	6.952
c [Å]	6.245	6.244	6.241	6.224	6.203
β [°]	90	90	90	90	90
Volume [Å^3]	306.18	305.76	305.29	302.82	299.75
Deviation [%]		0.137	0.154	0.809	1.013
d(Ca–O) [Å]	2.471	2.45	2.448	2.44	2.435
d(S–O) [Å]	1.472	1.503	1.501	1.492	1.481

[a] Data from the published structure of Kirfel and Will.[24] The results of the DFT calculations (BLYP) are taken after the stated cutoff (Ry).

At a cutoff as low as 70 Ry, the agreement of the lattice parameters is excellent. The resulting deviation is about 1%. At a cutoff of 100 Ry, the calculation is converged and the resulting deviation less than 0.2%. The deviations of the bond distances are remarkable. The description of the Ca–O bond improves with increasing quality of the calculation, but is always slightly too short. The difference at 120 Ry (0.021 Å) is better than at 70 Ry (0.036 Å). In contrast, the S–O distance is overestimated at each level. The overestimation at 70 Ry (0.009 Å) is better than at 100 Ry, for which it is about 0.029 Å longer. The excellent agreement of the calculated lattice constants compared to the measured values reflects the error compensation of both effects.

The starting parameters for gypsum were taken from work by Cole and Lancucki.[25] The agreement between DFT calculations and experiment are again very good. The volume deviation at 100 Ry is 0.163% (Table 3), and the deviation of the bond distances is comparable to the calculation of anhydrate.

Table 3: Optimization of the gypsum structure.[a]

	Ref. [25]	100 Ry
a [Å]	5.670	5.680
b [Å]	15.201	15.203
c [Å]	6.533	6.520
β [°]	118.6	118.4
Volume [Å^3]	494.37	495.18
Deviation [%]		0.163
d(Ca-O) [Å]	2.471	2.439
d(S-O) [Å]	1.472	1.505

[a] From DFT calculations (BLYP) with a cutoff of 100 Ry. The experimental data are taken from reference [25].

From the structure of hemihydrate mentioned above, the optimization results show a slightly smaller deviation than the structures of gypsum and anhydrate. The results are summarized in Table 4.

Table 4: Optimization of the hemihydrate structure.[a]

		100 Ry
a [Å]	17.559	17.561
b [Å]	6.962	6.963
c [Å]	12.071	12.072
β [°]	133.56	133.55
Volume [Å^3]	1069.23	1069.67
Deviation [%]		0.04
d(Ca–O) [Å]	2.471	2.462
d(S–O) [Å]	1.472	1.503

[a] From DFT calculations (BLYP) after a cutoff of 100 Ry. Values are compared to those obtained from the structure of the twin refinement of this work.

The calculations do not impose symmetry constraints, and all lattice parameters can be varied freely. It is for this reason that the good agreement of the lattice constants provides independent evidence for the proposed structure.

A comparison of the optimized structure and the one calculated from single-crystal data shows that the $CaSO_4$ framework and the position and orientation of the water molecules inside the channels are in good agreement. Additionally, DFT calculations allow for the calculation of bond distances between hydrogen and other atoms with the same level of accuracy, namely better than 0.03 Å. This accuracy is impossible using the data from the X-ray diffraction experiment because of the low electron density at the hydrogen atoms. Subsequently the discussion on the distances between the water molecules and the framework must be carried out with respect to the calculated structure. Owing to the distances between and orientation of the water molecules, no interaction between them can be assumed (Figure 4).

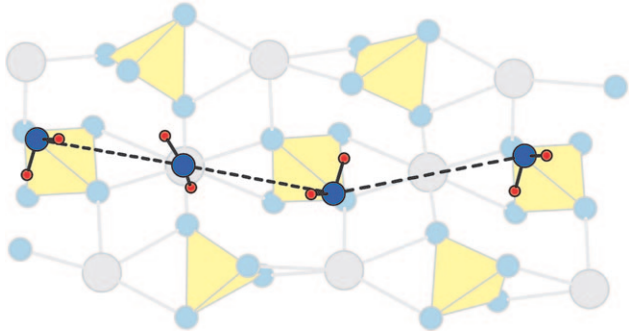

Figure 4. View perpendicular to the channels of the optimized structure. As the structure is optimized without symmetry restrictions, the distances $d(O_{water}-O_{water})$ vary over the cell content from 5.08 Å to 3.98 Å, with the average of 4.30 Å. S yellow, Ca gray, O blue, H red.

The distances between the water molecules are short enough that no further water can be inserted. Each water molecule is coordinated to the atoms around the channels, which can be seen in the short distances between the oxygen atoms of the water molecules and the calcium atoms at the edge of the channels (Figure 5). The distances $d(Ca-O_{water})$ are between 2.3 Å and 2.4 Å, implying a coordinative bond. Furthermore, the hydrogen atoms of the water molecules point towards the nearby oxygen atoms of the sulfate ions. Figure 5 shows the hydrogen bonds that can be assumed from the relative atomic distances, which vary between 1.95 and 2.40 Å.

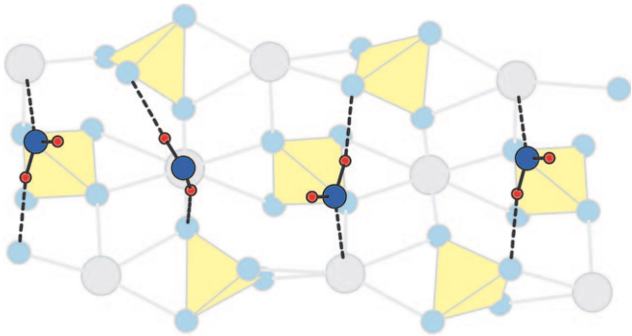

Figure 5. The oxygen atoms of the water molecules point to calcium atoms, and the hydrogen atoms form hydrogen bonds to the sulfate ions. The average distance $d(O_{water}-Ca)$ is 2.37 Å, the minimum distance is 2.34 Å, maximum distance is 2.39 Å. In comparison, the distance $d(O_{sulfate}-Ca)$ is only slightly longer (maximum 2.49 Å, minimum 2.35 Å). The average hydrogen bond length $d(O_{sulfate}-H)$ is 2.05 Å, with strong (1.95 Å) and weak bonds (2.40 Å). S yellow, Ca gray, O blue, H red.

In conclusion, from the results of the single-crystal refinement and the structure optimization by DFT calculations, it must be assumed that hemihydrate contains exactly 0.5 water molecules per formula. They are tightly bound to the $CaSO_4$ framework, and so it must be presumed that it is not possible to insert more water into the channels, and subhydrates with a crystal water content of more than 0.5 per $CaSO_4$ is unlikely.

Experimental Section

The crystals for this investigation were taken from a technical process for the hydrothermal production of crystalline hemihydrate. In large autoclaves, dihydrate that is pressed into porous molds is heated to temperatures between 120 °C and 180 °C. During this treatment regularly shaped crystals form with sizes of up to several millimeters. From this process, appropriate crystals of the size of 0.05 × 0.05 × 0.1 mm were selected under a light microscope and measured with a STOE IPDS I diffractometer.[22]

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[22] The measurements were conducted on a Stoe IPDS I diffractometer using $Mo_{K\alpha}$ radiation. The analysis, integration, and construction of the reciprocal space were carried out with the program package X-Area 1.35 from Stoe. Integration was performed in the hexagonal super cell, with subsequent reindexation and multiple listing of all reflections of each individual. Owing to the complex twinning and the low absorption coefficient for $CaSO_4{\cdot}0.5\,H_2O$ (2.23 mm^{-1}) no absorption correction was conducted. Refinement with the reflections in the hklf5 format was carried out with SHELX97.[18] Hydrogen atom sites were taken from reference [16] and were not refined. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-380286.

[23] DFT calculations[26] with gradient corrections on exchange and correlation from Becke–Lee–Yang–Parr (BLYP)[27] were conducted with the periodic Car–Parrinello[28] program CPMD 3.9.1.[29] Calcium atoms were treated with norm-conserving Troullier–Martins pseudopotentials[30] with semi-core states. 3s and 3p states of the calcium atoms are treated as valence states. Plane-wave basis sets with energy cutoffs of 70–120 Ry for the expansion of the valence orbitals were used (see Tables 2–4). The Brillouin zone was sampled applying a Monkhorst package with 2×2×2 sampling.[31] Static minimizations were performed with a steepest descent algorithm to minimize the cell parameters, and no constraints were applied. The optimization was conducted until stationary pressure of less than 1 MPa.

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