

Some crystallographic studies in the system
 $\text{CaSO}_4\text{--CaSO}_4 \cdot 2\text{H}_2\text{O}$

II. The hydrous forms

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Summary. The existence and relationships of hydrated forms both to one another and to anhydrous CaSO_4 have been studied by X-ray methods. Detailed study of the hemi-hydrate reveals its true cell to be monoclinic and does not confirm the previously suggested polymorphism.

Dehydration studies of the dihydrate and hemi-hydrate are reported; cyclic dehydration and hydration of single crystals of the latter show a variable temperature interval between the formation of $\gamma\text{-CaSO}_4$ and the reconstitution of the hemi-hydrate at approximately constant humidity. An explanation of this behaviour is offered, and the structural implications of the results of the dehydration studies are discussed.

THERE remain some doubts as to whether or not there are two distinct hydrated forms of calcium sulphate. Most of the physical and chemical properties of the dihydrate (gypsum) have been fully investigated, and the essential features of its structure have been long known. There is, however, considerable literature on other hydrated forms and the main differences have been summarized by Deer, Howie, and Zussman (1962). In general, one group maintains that constitutions $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ occur, with n continuously variable from 0 to 1, without essential structural change; they regard such materials as having essentially the anhydrous $\gamma\text{-CaSO}_4$ structure with variable amounts of zeolitic water. On the other hand, some workers believe that $n = \frac{1}{2}$ has a distinctive structure different from that of $\gamma\text{-CaSO}_4$; this hemi-hydrate structure (bassanite) is to be regarded as the second stable hydrated form.

It is difficult to summarize the evidence against the existence of a distinct hemi-hydrate, but as pointed out by Deer, Howie, and Zussman, the structure proposed for the hemi-hydrate and that of $\gamma\text{-CaSO}_4$ are so similar that the differences between them can easily be overlooked if they are examined by X-ray powder methods. In addition, $\gamma\text{-CaSO}_4$ rehydrates so readily that unless experimental conditions are carefully controlled, confusion as to whether anhydrous or hydrous forms are

present may result (see McConnell, 1965). If the hydrated form is prepared from γ -CaSO₄, the existence of nuclei of the β -CaSO₄ (anhydrite) structure, which does not readily hydrate (p. 352), can give misleading values for the water content. Thermal dehydration studies on gypsum clearly support the distinct existence of a hemi-hydrate stage in the isobaric dehydration of the dihydrate. Further, most significant work on this subject was carried out by Flörke (1952). He prepared specimens most carefully from analysed gypsum (by controlled dehydration) and from analysed β -CaSO₄ (by controlled hydration); in all cases, analysis of the products revealed water contents corresponding to the hemi-hydrate constitution. Moreover, he grew crystals of the hemi-hydrate large enough for goniometric and single-crystal X-ray examination. He found that there are distinctive, reproducible changes in the single-crystal patterns when the water is expelled to give γ -CaSO₄. These general observations have been entirely confirmed in the present work. All hemi-hydrate single-crystal patterns are substantially identical, though there may be slight differences from one crystal to another due to the development of a sub-structural intergrowth; this will be discussed fully later. All hemi-hydrate single-crystal patterns show the same characteristic changes when heated sufficiently to expel the remaining water. The evidence quite clearly favours the separate existence of a hemi-hydrate phase; the probable causes of other confusing observations have already been outlined.

However, even among those who have accepted the existence of the hemi-hydrate, there has been dispute as to its symmetry and structure; it has been variously described as hexagonal, orthorhombic, and monoclinic and differing structures have been proposed. From an optical and X-ray examination, Flörke suggests that both orthorhombic and trigonal varieties can exist. This suggestion has been examined in the present work, and the heating attachment for the Unicam single goniometer has been used to obtain more data on the transformations between the hydrous forms and γ -CaSO₄.

Experimental results

CaSO₄ · 2H₂O. All specimens examined from natural sources gave results consistent with the normal monoclinic gypsum structure. On heating, specimens began to dehydrate at about 75–80° C; details of observations on the dehydration process are given later.

CaSO₄ · $\frac{1}{2}$ H₂O. Before describing the present results, it is relevant to summarize the conclusions of the single-crystal study by Flörke (1952).

He suggests that there are two structural forms of the hemi-hydrate. In one modification the structure has a *C*-face centred orthorhombic cell with dimensions $a \approx 6.8$, $b \approx 11.5$, $c \approx 12.7$ Å; however for hemi-hydrate crystals formed above 45° C, the symmetry is truly trigonal with $a \approx 6.8$, $c \approx 12.7$ Å. Owing to the ortho-hexagonal character of the cell ($b \approx \sqrt{3}a$), the orthorhombic crystals may have an intimate triplet intergrowth; such crystals show pseudo-trigonal diffraction effects. On structural grounds, Flörke rejects a monoclinic structure proposed by Gallitelli (1933). In support of such polymorphism for the hemi-hydrate, he observed optically an indistinct triplet structure in sections of the orthorhombic form perpendicular to the pseudo-triad *c*-axis; after heating at about 70° C for two or three days, such sections became uniaxial and homogeneous, whilst on cooling undulose extinction and the triplet structure reappeared.

In the present work, crystals of the hemi-hydrate were prepared by the method of Caspari (1936). Very small crystals that were first deposited were decanted, and subsequently crystals of a size suitable for X-ray examination were formed. The crystals were acicular with elongation parallel to the 12.7 Å *c*-axis of the hemi-hydrate. It was clear from preliminary observations about this rotation axis, that all crystals had only pseudo-hexagonal or pseudo-trigonal symmetry about this direction, due to the intergrowth of a sub-structure of lower symmetry; these crystals were probably identical with those described by Flörke as orthorhombic. A number of crystals were then carefully examined by oscillation and Weissenberg methods to establish the nature of the intergrowth and the symmetry of the hemi-hydrate. The effects of marked pseudo-symmetry, as shown by the hemi-hydrate cell, need extended and careful analysis. The full interpretation of the patterns cannot be given here, but the present investigation suggests that the true symmetry is monoclinic with a 6.85, b 11.88, c 12.60 Å, $\beta \doteq 90^\circ$; systematic absences suggest that the lattice is body-centred. That the true symmetry of the sub-individuals within these crystals is not orthorhombic can be seen from a typical oscillation photograph about the common *c*-axis (fig. 1). In this pattern, there are discrepancies between the intensities of maxima on the +1 and -1 layer lines related across the zero layer line and the spots on these layer lines have slightly different ζ values. If the orthorhombic triplet structure suggested by Flörke were correct, such pairs of related reflexions would be due to the same individual; thus with a true mirror plane of an orthorhombic cell perpendicular to the oscillation axis, no intensity discrepancies could

exist. With the monoclinic cell, no such relationship need exist, though if the monoclinic sub-components were all equally present within the crystal, the plane perpendicular to the oscillation axis would be an apparent mirror plane; in general the unheated hemi-hydrate crystals do not contain equal amounts of the various sub-components. Further for a true orthorhombic cell, the ζ values for the layer lines from each orientation of the sub-structure would be identical. However, if the



FIG. 1. Enlarged section of a c -axis photograph (15° oscillation, $\text{Cu-K}\alpha$ radiation) of an unheated hemi-hydrate crystal. Note intensity discrepancies for maxima on $+1$ and -1 layer lines and slightly variable ζ values for spots on these layer lines.

cell is monoclinic, with β slightly different from 90° , the ζ values for different components would be slightly different depending on whether the positive or the negative sense of the c -axis of the hemi-hydrate sub-component is vertical and parallel to the oscillation axis. Such observations together with the more detailed data obtained from other photographs suggest that the pseudo-trigonal crystals contain six orientations of monoclinic sub-components, which all have their c -axes parallel to the pseudo-triad direction; one set of three orientations rotated through 120° about this direction have their positive c -axis directions parallel to it, whilst the other set of three orientations is obtained by reflexion across a plane perpendicular to the pseudo-triad direction. Such an intergrowth would be expected from a monoclinic pseudo-trigonal structure. Some confirmation of this interpretation is provided by optical examination of crystal sections perpendicular to the common c -axis direction. Within the three sectors developed within the hexagonal outline of the crystal, thin lamellae ($\approx 1 \mu$ width) in two slightly different orientations are present (fig. 2).

Occasionally hemi-hydrate crystals were found for which strongly exposed oscillation photographs about the c -axis showed additional diffraction effects. Weak streaks along lines of constant ξ joining maxima

on odd layer lines were observed, often with some weak but relatively sharp diffraction spots superposed; the spacing corresponding to the separation of these spots is about 90–100 Å. These effects, suggesting some stacking disorder in the water molecules, disappeared when the crystal was heated to 40–50° C without any other significant changes in the diffraction pattern.

The suggestion that at higher temperatures the hemi-hydrate structure becomes truly trigonal was examined by heating a number of

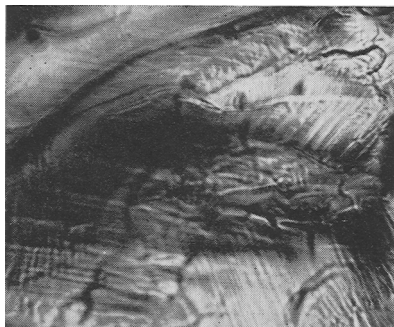


FIG. 2. Section of a microphotograph ($\times 650$) of a section of an unheated hemihydrate crystal perpendicular to the *c*-axis, crossed nicols.

crystals for varying periods (from a few hours up to ten days) at temperatures from 50° to 100° C upon the heating single-crystal camera. In no case was there detectable change in the diffraction pattern of any crystal; none of the intensity discrepancies that preclude higher symmetry disappeared. Similar experiments were carried out with a heated stage on a microscope; no changes were observed in the sectorized appearance of basal sections.

Thus the present examination provides no new evidence for the existence of a truly trigonal hemi-hydrate form. Two additional observations may be briefly mentioned here. Hemi-hydrate crystals can be dehydrated to give the hexagonal γ -CaSO₄ structure. If this γ -CaSO₄ crystal is then rehydrated, the six orientations of monoclinic hemi-hydrate structure due to symmetry degeneration are formed in equal amounts. The true symmetry then becomes more difficult to detect for the intensity discrepancies mentioned above are not apparent; a routine examination of the diffraction pattern might result in the attribution of higher symmetry. Secondly, it is found that under more or less constant

humidity conditions for a given hemi-hydrate crystal, the temperature of dehydration falls with successive hydration-rehydration cycles. The most convincing evidence for the trigonal polymorph is the disappearance of optical inhomogeneity in basal sections heated at 70°C , noted by Flörke. The variability of dehydration temperature due to the cyclic effect and its sensitivity to humidity suggest the possibility of a change from the hemi-hydrate to the uniaxial $\gamma\text{-CaSO}_4$ at such temperatures. Flörke considered this possibility and rejected it on two counts; firstly, he considered that the conditions of his heating experiments were such that escaping water molecules would have had to overcome considerable confining pressures, and secondly, he observed no marked increase in the double refraction of sections of the homogeneous crystals cut parallel to the c -axis.

It has been impossible to obtain additional evidence for polymorphism of the hemi-hydrate. Despite the fact that some of the observations recorded in Flörke's careful study are unresolved, it must be concluded that the balance of probability is against a second structural modification.

The transformations

Dihydrate to hemi-hydrate and anhydrous forms. No dehydration of the dihydrate is strictly oriented, but it is valuable to study these changes on the single-crystal goniometer to see if information concerning the structural mechanism can be obtained.

Photographs from single crystals of natural gypsum were taken at temperature intervals of 10°C . Up to the temperature range $75\text{--}80^\circ\text{C}$, no change was observed for any crystal. At slightly higher temperatures, little or no trace of the original dihydrate single crystal patterns remains. They are replaced by sharp powder patterns with rather poor orientation textures. Detailed examination of these patterns shows that they are usually due to an aggregation of hemi-hydrate crystals with a tendency to a fibre-texture in which the c -axes of the hemi-hydrate crystallites are parallel to the c -axis of the original dihydrate crystal, though there is often considerable orientation spread. Occasionally the product appears to be $\gamma\text{-CaSO}_4$ rather than the hemi-hydrate, but otherwise there is little difference. In all cases there is no premonitory sign of the impending dehydration; the dihydrate patterns remain sharp up to the temperature of transformation. Optically, the dihydrate crystals become milky in appearance after dehydration, due to minute irregular cracks that appear on the surface of the original single crystal.

With crossed nicols, the extinction becomes shadowy and ill-defined, but it was not possible to resolve any sub-structure. On returning the crystal to room temperature, there is no rehydration under normal circumstances, unless it contains γ -CaSO₄, which changes to the hemi-hydrate.

As the temperature is raised, γ -CaSO₄ patterns are more commonly observed; at 100–110° C this anhydrous form is invariably obtained. At about 150° C the presence of β -CaSO₄ is usually detectable, becoming more dominant as the temperature is raised; this form shows similar poor fibre texture, with a tendency for parallelism of the *c*-axes of the β crystallites to that of the original dihydrate crystal. These crystallites do not readily rehydrate when returned to room temperature. Optically such crystals are similar to those dehydrated at lower temperatures.

Hemi-hydrate to γ -CaSO₄. As mentioned in Part I, this transformation is strictly oriented, and has been used to produce single crystals of the unstable γ -CaSO₄ structure.

When the hemi-hydrate crystal with its multiple sub-structure is first dehydrated, the odd layer lines and intensity discrepancies disappear between 100–105° C; the resultant pattern shows the true hexagonal symmetry of γ -CaSO₄. Slight structural readjustments take place with the *c*-axes remaining parallel and the six *a*-axes of the monoclinic sub-structure becoming the other axial directions of the hexagonal structure. Optically this change is accompanied by the disappearance of the sectorial appearance of the basal section.

The γ -CaSO₄ crystal so produced can be rehydrated to the hemi-hydrate by lowering the temperature; under approximately the same humidity conditions there is, however, a lag before the water molecules are taken back into the structure and usually a drop in temperature to 80–85° C is required. For the rehydrated hemi-hydrate crystal, as noted earlier, the pseudo-symmetry is more marked owing to the development of equal amounts of the sub-structure, though the monoclinic character is still apparent from the slightly irregular character of the layer lines on *c*-axis oscillation photographs. Attempts to rehydrate the γ -CaSO₄ crystal at higher temperatures (90–100° C) in longer times were unsuccessful, and the interval between the temperatures of dehydration and the reconstitution of the hemi-hydrate must be regarded as significant. Indeed both the interval and the temperature appear to vary slightly with further cycles. For example, the second dehydration of the hemi-hydrate crystal usually takes place 5–10° C lower than the first, with the subsequent rehydration 2–3° C lower than the first recorded value. In the limit, the temperature interval becomes small

(two or three degrees) whilst the temperature for the formation of $\gamma\text{-CaSO}_4$ is lowered by 20–30° C. Such results stress the critical nature of the physico-chemical conditions in determining the retention of water molecules in the hemi-hydrate structure. In the present experiments there is no control upon the humidity conditions obtaining within the camera, though there is no reason to suspect that they vary significantly; of course, if a quantity of a silica gel is introduced into the camera, the temperature ranges for these effects are changed.

Discussion

The observations on the dehydration processes again stress the structural importance of the chains of Ca and SO_4 ions running parallel to the *c*-axes of all structures in this system. Even when water molecules are removed from the dihydrate structure and there is considerable general structural reorganization, the fibre texture of the resultant hemi-hydrate or anhydrous forms suggests that such chains play an important part in the nucleation of the crystallites. The collapse of the dihydrate structure must permit the recrystallization to occur from nuclei growing rapidly from sections of chains that are preserved.

Apart from this general parallelism of the *c*-axes, development of other phases from the dihydrate is consistent with the normal features of recrystallization. There are no warning signs of structural collapse, and the resultant crystallites must be relatively undistorted equi-axed particles of about 10^{-3} – 10^{-4} cm diameter; the contraction of the crystal due to the water loss leads to the irregular crack system.

In contrast, dehydration of the hemi-hydrate to $\gamma\text{-CaSO}_4$ requires no basic structural change, with water molecules leaving and reoccupying their particular sites relatively easily.

The variable temperature interval for cyclic dehydration of single crystals requires further comment. It seems probable that water molecules do not re-enter the crystal after the first dehydration unless the temperature is significantly lowered; the extended heating experiments at 90–100° C appear to preclude the possibility that at such temperatures the water molecules are present but in a disordered arrangement. If this is so, the water molecule positions in the hemi-hydrate structure must be energetically less favourable for the retention of these molecules if the hemi-hydrate is formed from the $\gamma\text{-CaSO}_4$ structure. This could be due to imperfections introduced into the original crystal by the dehydration. Apart from any inhomogeneities introduced by the dehydration mechanism (e.g. Dent Glasser, Glasser, and Taylor, 1963), it

has previously been noted that all $\gamma\text{-CaSO}_4$ crystals produced in this way contain embryonic nuclei of the markedly different $\beta\text{-CaSO}_4$ structure (p. 352). Further, until the structural irregularities, which lead to a micropore system throughout the crystal for water migration, are fully developed, there can be a lag between dehydration and rehydration. Eventually this interval becomes very small as the maximum surface area is approached after several cycles, at the same time as the binding energy of the water molecules in the imperfect structure approaches a minimum limiting value; there is no evidence that the $\beta\text{-CaSO}_4$ nuclei are significantly altered by the subsequent heat treatment.

These experiments, and the possible explanation suggested above, illustrate again that unless great caution is exercised in interpreting further experiments on the unstable $\gamma\text{-CaSO}_4$ and hemi-hydrate structures, the present confusion in the literature will be increased.

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References, see Part I, this vol., p. 353.

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