

*Some crystallographic studies in the system*  
*CaSO<sub>4</sub>-CaSO<sub>4</sub>.2H<sub>2</sub>O*

*I. The polymorphism of anhydrous CaSO<sub>4</sub>*

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[Read 11 March 1965]

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*Summary.* The existence and relationships of the polymorphs of CaSO<sub>4</sub> have been studied by X-ray methods. Only two distinct phases are found: no crystallographic evidence is available to support the suggestion that the  $\gamma$ -CaSO<sub>4</sub> structure can have two forms, and it is shown that most previous data on the existence of the high temperature  $\alpha$ -CaSO<sub>4</sub> polymorphs are likely to be due to decomposition of the sulphate.

Some observations on the  $\gamma$  to  $\beta$ -CaSO<sub>4</sub> transformation are reported. The structural implications of these results and their relevance to the nature of the transformation are discussed.

THE technical importance of this system has provided an extensive but confusing literature that leaves many basic problems unresolved. In particular, the number of anhydrous and hydrous phases that exist and the nature of the transformations between them cannot be regarded as finally established. The present crystallographic studies were undertaken to provide additional data on this aspect of the system.

The development of a controlled heating attachment for a Unicam single crystal goniometer by Rickson, Hall, and McConnell (1963) allows the examination of the X-ray diffraction patterns of single crystals of the various phases at different temperatures. This technique has provided most of the data to be described, though it has been supplemented by powder and optical methods where appropriate.

In the first paper, the results for anhydrous CaSO<sub>4</sub> are presented, whilst the second paper contains data for the hydrated forms.

*Nomenclature for anhydrous CaSO<sub>4</sub> phases*

It has become customary to use Greek prefixes to distinguish the various polymorphs; although objections to this can be raised on mineralogical grounds, this system will be retained in the present paper for clarity.

The existence of four distinct anhydrous forms has been postulated on a variety of evidence derived mainly from thermo-chemical, X-ray, and optical examination by different workers. In the most recent detailed study, Flörke (1952) reported evidence for two anhydrous phases; these were  $\gamma$ -CaSO<sub>4</sub> (sometimes called soluble anhydrite or dehydrated hemi-hydrate) and the commoner mineralogical variety  $\beta$ -CaSO<sub>4</sub> (insoluble anhydrite or dead-burned gypsum). Earlier Grahmann (1920) had suggested the existence of another polymorph,  $\alpha$ -CaSO<sub>4</sub>, stable at high temperatures; although Flörke carried out some more high-temperature experiments, he was unable to synthesize this phase. In addition, Kelly *et al.* (1941) suggested on thermo-chemical evidence that  $\gamma$ -CaSO<sub>4</sub> had two polymorphic forms; although no reference is made to this work, Flörke's data provide no confirmatory evidence on this point.

With the tentative nature of two of these phases, the relationships between the possible anhydrous phases are known only in general terms. It is generally agreed that  $\gamma$ -CaSO<sub>4</sub> is only metastable, and that under equilibrium conditions dehydration takes place directly to  $\beta$ -CaSO<sub>4</sub>; some observations on the transformation of the metastable  $\gamma$  form to the stable  $\beta$  form on heating have been given by Flörke.  $\alpha$ -CaSO<sub>4</sub> has been reported as the stable form from about 1200° to 1450° C, at which temperature decomposition of the sulphate takes place.

#### *Experimental results*

**$\gamma$ -CaSO<sub>4</sub>.** This is obtained by the slow dehydration of the dihydrate (gypsum) or the hemi-hydrate (bassanite). Dehydration of dihydrate single-crystals is not strictly topotactic, and the resultant  $\gamma$ -CaSO<sub>4</sub>, although showing a preferred orientation with respect to the original dihydrate crystals, is too finely crystalline for the present work. Powder records of such  $\gamma$ -CaSO<sub>4</sub> aggregates were indistinguishable from those prepared from dehydrated hemi-hydrate crystals.

Single crystals of the  $\gamma$  form can be obtained by dehydration of the hemi-hydrate, and all experiments on the heating camera were carried out on such crystals. The hemi-hydrate crystals were prepared according to the method used by Caspari (1936). Such hemi-hydrate crystals are multiply twinned on a very fine scale, and oscillation about the twin axis shows a repeat distance of about 12.70 Å; when  $\gamma$ -CaSO<sub>4</sub> is obtained by heating, this repeat distance is halved with the odd layer lines of the hemi-hydrate pattern disappearing. The instability of the  $\gamma$  form is demonstrated by the reappearance of the odd layer lines if the

temperature is lowered and atmospheric water is allowed to rehydrate the crystal. The temperature of dehydration depends critically on the conditions of the experiments, in particular the humidity; in the present experiments, where only the temperature can be carefully controlled,  $\gamma\text{-CaSO}_4$  has been formed at temperatures between  $75^\circ$  and  $105^\circ\text{C}$ . Moreover, it is found that even at approximately constant humidity, the temperature of formation of the  $\gamma$  form can vary significantly for the same crystal if it undergoes several cycles of dehydration and rehydration. Fuller details of the crystallography of the hemi-hydrate crystals and heating experiments on them will be given in the second paper.

The untwinned hexagonal  $\gamma\text{-CaSO}_4$  crystals produced in this way have the space-group and approximate cell dimensions quoted by Flörke (1952). However, careful examination of the diffraction patterns invariably reveals the presence of weak diffuse maxima in addition to the normal Bragg spots of the  $\gamma$  form; at lower temperatures ( $100\text{--}200^\circ\text{C}$ ) these maxima are of considerable extension in reciprocal space, and are elongated along the  $c^*$ -axis of the  $\gamma\text{-CaSO}_4$  crystal. If the crystal of the  $\gamma$  form is rehydrated, these diffuse regions remain and are seen in the hemi-hydrate pattern. At higher temperatures, the formation of  $\beta\text{-CaSO}_4$  is promoted; these diffuse regions become sharper, and it becomes apparent that they are in the position of strong maxima of the diffraction pattern of the  $\beta$  form. The significance of these maxima and the nature of the  $\gamma \rightarrow \beta$  transformation will be discussed in detail in a later section. At the moment, it need only be observed that as the crystal of the  $\gamma$  form is slowly converted into  $\beta\text{-CaSO}_4$ , there is no detectable change either in the positions or in the relative intensities of the Bragg spots of the  $\gamma\text{-CaSO}_4$  pattern, which gradually disappears. In so far as the present experiments are concerned, there is only crystallographic evidence for one  $\gamma\text{-CaSO}_4$  polymorph.

**$\beta\text{-CaSO}_4$ .** In addition to its widespread natural occurrence, this polymorph is the stable dehydration product of the dihydrate or hemi-hydrate. Again, the dehydration of a dihydrate crystal produces an aggregate of fine  $\beta$  crystals with a degree of preferred orientation. If dehydration of a hemi-hydrate crystal takes place through the unstable  $\gamma$  form as mentioned above, triplet crystals of twinned  $\beta\text{-CaSO}_4$  are formed (see below). All the materials examined, whether natural anhydrite crystals or the products of laboratory dehydration, show very similar diffraction patterns, which are unchanged on heating at temperatures up to  $1000\text{--}1100^\circ\text{C}$ .  $\beta\text{-CaSO}_4$  is stable over an extensive

temperature range, though at about 1000° C changes can take place, which are discussed in the next section.

**$\alpha$ -CaSO<sub>4</sub>.** Evidence of this high temperature modification comes from the presence of an endothermic peak on the heating and cooling curves of  $\beta$ -CaSO<sub>4</sub> above 1100° C (Masuda, 1932). This supports an earlier suggestion by Grahmann (1920), who claimed to have observed the transformation optically at 1183° C of orthorhombic  $\beta$ -CaSO<sub>4</sub> to monoclinic  $\alpha$ -CaSO<sub>4</sub>. Later Flörke (1952) melted CaSO<sub>4</sub> specimens at 1450° C; before examination, some specimens were quenched and others annealed for a short time at 1100° C. In all cases, the fine crystals present proved to be  $\beta$ -CaSO<sub>4</sub>, and he concluded that if the  $\beta \rightleftharpoons \alpha$  transformation exists, it must be unquenchable and experiments should be carried out at high temperatures. This suggests that the transformation is of a 'displacive' character, possibly associated with the onset of free rotation of the SO<sub>4</sub> groups. In turn, this would lead us to expect an oriented change from  $\beta \rightarrow \alpha$ -CaSO<sub>4</sub>, with a probable increase in symmetry in the  $\alpha$  form, which is contrary to Grahmann's observation.

In the present work, it was hoped that the single-crystal heating unit would allow the resolution of this problem.  $\beta$ -CaSO<sub>4</sub> crystals, either from natural sources or triplets from dehydration experiments were heated; for all specimens, at about 1150° C faint powder arcs were observed superposed upon the single crystal patterns. Unfortunately, such temperatures are the highest attainable with the furnace attachment, and although extended heating strengthens the powder arcs slightly, it was impossible to complete the change or to observe the powder pattern satisfactorily in reasonable times. It was clear that the finely crystalline product showed no preferred orientation with respect to the single crystal host.

Since the faint powder arcs remained after the  $\beta$ -CaSO<sub>4</sub> crystal had been returned to room temperature, it seemed reasonable to continue the experiments by quenching the crystals after heating in an external furnace. Again between 1150° and 1200° C a powder pattern is observed superposed upon the single crystal spots; conversion is complete at about 1300° C, when no trace of  $\beta$ -CaSO<sub>4</sub> remains. The resultant pattern is moderately complex; for different specimens line positions are constant but there is some variation in relative intensities. Measurement of line spacings shows that the powder pattern is due to a mixture of CaO and Ca(OH)<sub>2</sub>. The variation in intensities for the quenched specimens is due to a variable proportion of the hydroxide; the weak arcs seen on photographs taken of specimens at high temperature belong only to CaO.

The most reasonable interpretation of these results is that, under the present experimental conditions, crystals of  $\beta\text{-CaSO}_4$  decompose into  $\text{CaO}$  with the loss of  $\text{SO}_3$  at temperatures around  $1150^\circ\text{C}$ . The presence of the hydroxide is due to the variable partial hydration of some of the small  $\text{CaO}$  crystallites by atmospheric water after quenching. Additionally, later experiments showed that if  $\beta\text{-CaSO}_4$  powder specimens are examined at low pressure ( $\sim 10^{-5}$  mm) in a high-temperature powder camera, only  $\text{CaO}$  lines are observed; these begin to appear at about  $1050^\circ\text{C}$ , with completion of decomposition at about  $1200^\circ\text{C}$ .

These experiments demonstrate that the decomposition temperature of the sulphate is dependent on the experimental circumstances. If this temperature depends on the partial pressure of the  $\text{SO}_3$  vapour, its value will be determined by whether an open or closed system is used. With an effectively open system decomposition takes place below  $1100^\circ\text{C}$ ; the temperature of  $1450^\circ\text{C}$  often quoted in the literature probably represents the upper limit obtained from an effectively closed system. The rate of decomposition will also be determined by the experimental conditions, including the size of the sulphate crystals, so that the effects of decomposition may be apparent over a range of temperatures. Such considerations, together with the fact that there is no change in the  $\beta\text{-CaSO}_4$  single-crystal or powder X-ray patterns at temperatures just below those at which decomposition begins, can only strengthen doubts about the existence of the  $\alpha\text{-CaSO}_4$  polymorph. The thermal evidence for such a phase seems invalid, and only the optical observations of a monoclinic form reported by Grahmann remain. The weight of evidence is such that it must be concluded that he was misled in making very difficult optical observations.

#### *The $\gamma \rightarrow \beta\text{-CaSO}_4$ transformation*

The oriented nature of this transformation emphasizes the close structural relationship between the two polymorphs. A structure of the hexagonal  $\gamma$  form has been proposed by Flörke (1952), whilst the general features of that of the orthorhombic  $\beta$  form has been known for much longer (the axial relationships described in Deer, Howie, and Zussmann [1962] are used in this paper). When the  $\beta$  form develops from a crystal of  $\gamma\text{-CaSO}_4$ , multiply oriented sub-individuals develop due to the symmetry degeneration. Careful indexing of the diffraction pattern from a completely transformed  $\gamma$  crystal shows that three distinct orientations of  $\beta$  crystals are present. The  $c_\beta$ -axis is parallel to the  $c_\gamma$ -axis for all three; about this common axis, the  $\beta\text{-CaSO}_4$  crystallites are equally

inclined at  $120^\circ$  to each other, so that for each orientation the  $a_\beta$ -axis is parallel to an  $a_\gamma$ -axis of the host. A triplet structure of this kind was observed optically by Flörke for hemi-hydrate crystals heated at  $200^\circ\text{C}$ .

It has earlier been remarked that all  $\gamma$ - $\text{CaSO}_4$  crystals examined show diffuse maxima associated with this triplet structure. Such maxima become reasonably well-defined at temperatures around  $150^\circ\text{C}$ . As the temperature is raised, these identifiable  $\beta$  spots gradually become stronger and rather sharper, though the transformation is rather sluggish; if the crystal is heated only during the exposure period (8 hours), temperatures of about  $900^\circ\text{C}$  are required before all traces of the  $\gamma$  form have disappeared. The temperature scale varies slightly from specimen to specimen, but for all specimens the completed transformation produces triplet  $\beta$  crystals for which the diffraction spots are not completely sharp and further heating at higher or lower temperatures fails to sharpen their reflexions.

Considering first the orientation of the two polymorphs in the transformation, in common with all structures in this system the  $\gamma$  and  $\beta$  forms show a succession of Ca and  $\text{SO}_4$  ions in chains, which run parallel to the  $c$ -axes of both phases. The structural reason for the parallelism of the  $a$ -axes in the triplet structure is not so obvious. It has been said by Flörke that dimensionally similar  $\text{CaSO}_4$  layers occur in the (100) plane of the  $\beta$ - $\text{CaSO}_4$  structure and (10 $\bar{1}$ 0) plane of the  $\gamma$ - $\text{CaSO}_4$  structure. Whilst it is true that this plane of the  $\gamma$  structure is more suitable than any other ( $hki$ 0) section, the atomic correspondence is by no means perfect. In addition, even if the atomic distortions for one such layer were not too great, the three-dimensional construction of the  $\beta$ - $\text{CaSO}_4$  structure would necessitate considerable movement and closer packing of the chains of Ca and  $\text{SO}_4$  ions.

It is relevant to the mechanism of the transformation to consider the significance of the diffuse reflections found on all  $\gamma$ - $\text{CaSO}_4$  diffraction patterns. These reflections may be regarded as arising from embryonic nuclei of a disordered  $\beta$  structure within the  $\gamma$ - $\text{CaSO}_4$  structure. The nature of the reflections suggests that whilst the regularity of the Ca and  $\text{SO}_4$  ions in the chains is preserved, there is initially considerable disorder in their arrangement as they collapse from the more open  $\gamma$  structure. The relatively sluggish nature of the transformation reflects the necessity of the supply of appreciable thermal energy to allow the reconstruction of the embryonic nuclei into reasonably ordered domains of a recognizable  $\beta$ - $\text{CaSO}_4$  structure, which grow in size as increased temperature promotes the collapse of the remaining  $\gamma$  structure. It is clear

that in reasonable laboratory times it is not possible to produce perfectly ordered  $\beta$ - $\text{CaSO}_4$  crystallites and that some domain structure is retained. The existence of embryonic disordered  $\beta$ - $\text{CaSO}_4$  nuclei, which cannot be readily hydrated, within  $\gamma$ - $\text{CaSO}_4$  crystals must be taken into consideration in physico-chemical experiments on the stability and hydration of  $\gamma$ - $\text{CaSO}_4$ .

*Acknowledgements.* I wish to record my thanks to Prof. C. E. Tilley, F.R.S., for stimulating and encouraging the present work. I am indebted to my colleagues, Dr. J. D. C. McConnell and Dr. M. G. Bown, for helpful discussion and to Mr. K. O. Rickson for much technical assistance.

*References (for Parts I and II)*

- CASPARI (W. A.), 1936. Proc. Roy. Soc. Lond., ser. A, vol. 155, p. 4L.  
DEER (W. A.), HOWIE (R. A.), and ZUSSMAN (J.), 1962. Rock Forming Minerals, Longmans, London, vol. 5, p. 219.  
DENT GLASSER (L. S.), GLASSER (F. B.), and TAYLOR (H. F. W.), 1963. Min. Soc. Amer., Special Paper no. 1, p. 200.  
FLÖRKE (O. W.), 1952. Neues Jahrb. Min., Abh., vol. 84, p. 189.  
GALLITELLI (P.), 1933. Periodico Min., Roma, vol. 4, p. 132.  
GRAHMANN (W.), 1920. Neues Jahrb. Min., vol. 1, p. 1.  
KELLY (K. K.), SOUTHARD (J. C.), and ANDERSON (C. F.), 1941. U.S. Bureau Mines, Tech. Paper, 625.  
MCCONNELL (J. D. C.), 1965. Min. Mag., vol. 34, p. 327.  
MASUDA (M.), 1932. Proc. Imp. Acad. Tokyo, vol. 8, p. 436.  
RICKSON (K. O.), HALL (C. B.), and MCCONNELL (J. D. C.), 1963. Journ. Sci. Instr., vol. 40, p. 420.

[*Manuscript received 22 July 1964*]

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