

# The Crystal Chemistry of Zirconium Sulphates

## Part VII. Structural Relationships and Transformations among the $Zr(SO_4)_2$ -Hydrates

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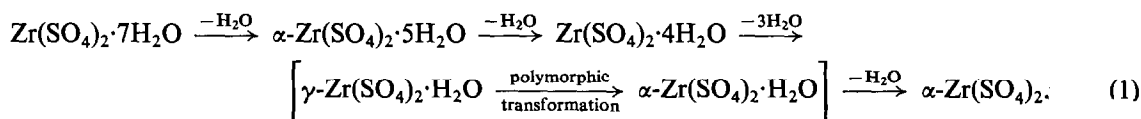
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The structural relationships between the hepta-,  $\alpha$  and  $\beta$ -penta, tetra-, and  $\gamma$  and  $\alpha$ -monohydrates of  $Zr(SO_4)_2$  and of  $\alpha$ - $Zr(SO_4)_2$  are summarized, and transformations among them are discussed. The observed dehydration and hydration sequences support the view that, in transformations resulting in polymorphic forms, the modification which is structurally closest to its precursor is likely to be formed first.

### Introduction

Structural knowledge of the members of a reaction series can provide a basis for the prediction of the mechanism involved in each step particularly when more than one polymorph can exist at a specific composition (1), (2), (3), and (4). Such knowledge can also assist in the understanding of the behaviour of metastable compounds. Parts I-V of this series of papers have described the crystal structures of the hepta,  $\alpha$  and  $\beta$ -penta and  $\gamma$  and  $\alpha$ -monohydrates of  $Zr(SO_4)_2$  (5), (6), (7), (8), and (9), while Part VI (10) described that of  $\alpha$ - $Zr(SO_4)_2$ . The structure of the tetrahydrate has been reported by Singer and Cromer (11). These compounds, with the exception of  $\beta$ -pentahydrate, can be formed as consecutive products of the controlled thermal decomposition of zirconium sulphate heptahydrate. The observed reaction sequence is:



$\beta$ -pentahydrate, which is a hydration product of  $\beta$ - $Zr(SO_4)_2$  (12) could not be obtained by dehydration of the heptahydrate. However, like  $\alpha$ -pentahydrate it decomposes to the tetrahydrate.

In the present paper the relationships between the skeletal sulphate lattices of the  $Zr(SO_4)_2$ -hydrates are considered and possible mechanisms of transformation proposed. It is shown that when more than one polymorph can exist at a given composition, then in either hydration or dehydration reactions leading to that composition the polymorph which

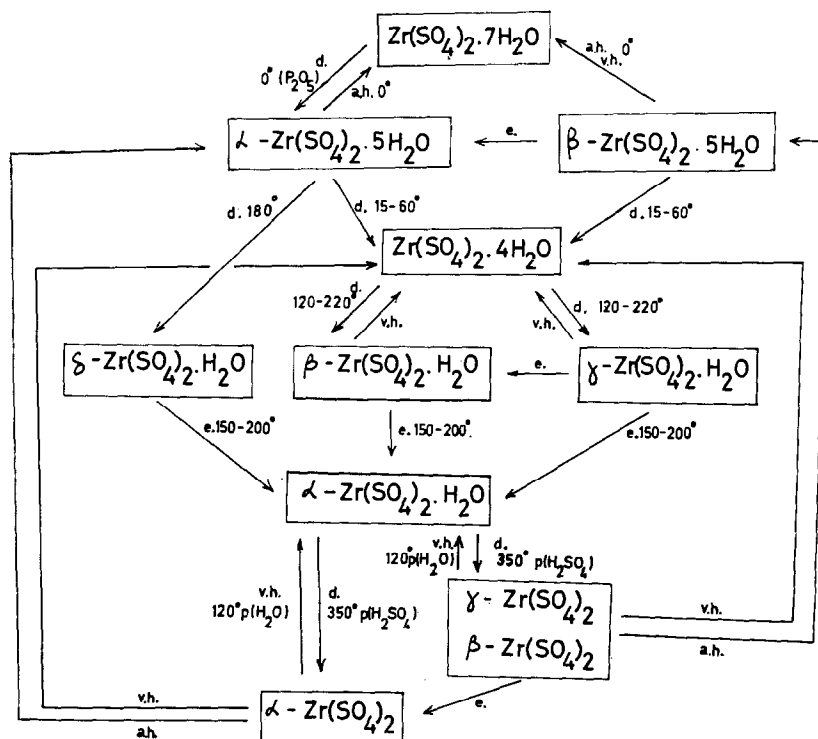
is closest in structure to its precursor is likely to be formed initially.

### Description of the Hydrates of $Zr(SO_4)_2$

The chemical interrelationships of phases in the  $Zr(SO_4)_2$ - $H_2O$  system are summarized in Fig. 1. These relationships have been discussed in detail elsewhere (2), (12), (13), (14), (15), and (16).

Crystallographic data for these phases are summarized in Table I, and schematic representations of their skeletal  $Zr(SO_4)_2$  lattices are shown in Fig. 3. Unless otherwise stated, oxygen atoms are omitted but oxygen bridges, not necessarily linear, are indicated by lines joining the zirconium and sulphur atoms. These diagrams emphasize a striking feature of all of these structures, namely that they contain the same general arrangement of zirconium and sulphur atoms in their three-dimensional arrays.

In each structure zirconium atoms are surrounded by an array of at least six sulphur atoms. This is most clearly seen in the cases of the  $\alpha$ -monohydrate and the  $\alpha$ -anhydrate, where there are six sulphate groups actually attached to each zirconium atom. In discussing these structures we have depicted them as identical regular lattices with each zirconium atom central to an hexagonal array of sulphur atoms. While this gives a slight distortion of the true structures, the correct bonding relationships are maintained. Depending on the packing in the layer

FIG. 1. Chemical inter-relationships in the  $Zr(SO_4)_2 \cdot H_2O$  system.

a.h.—aqueous hydration.  
 v.h.—vapor hydration.  
 e.—equilibration.  
 d.—decomposition.

TABLE I  
 $Zr(SO_4)_2 \cdot H_2O$  SYSTEM

Compound	Symmetry and Space Group	<i>a</i>	<i>b</i>	<i>c</i>	$\alpha$	$\beta$	$\gamma$	Volume ( $\text{\AA}^3$ )	Density $\text{g cm}^{-3}$	<i>Z</i>
$\alpha\text{-Zr(SO}_4)_2$ <sup>a</sup>	Orthorhombic <i>Pnma</i>	8.61	5.44 <sub>3</sub>	10.89	90	90	90	511	3.71	4
$\beta\text{-Zr(SO}_4)_2$ <sup>b</sup>	—									
$\gamma\text{-Zr(SO}_4)_2$	Orthorhombic	7.41	5.86	11.84	90	90	90	514	(3.66)	(4)
$\alpha\text{-Zr(SO}_4)_2 \cdot H_2O$	Monoclinic <i>P2<sub>1</sub>/c</i>	7.32	8.54	11.82	90.0	106.0	90.0	710	2.84	4
$\beta\text{-Zr(SO}_4)_2 \cdot H_2O$	Triclinic	7.86	5.34	8.97	91.0	100.7	109.4	348	(2.87)	(2)
$\gamma\text{-Zr(SO}_4)_2 \cdot H_2O$	Triclinic $P\bar{1}$	7.89	5.21	8.96	95.2	99.8	109.2	339	2.93	2
$\delta\text{-Zr(SO}_4)_2 \cdot H_2O$ <sup>b</sup>	—									
$Zr(SO_4)_2 \cdot 4H_2O$	Orthorhombic	25.92	5.53	11.62	90	90	90	1666	2.80	8
$\alpha\text{-Zr(SO}_4)_2 \cdot 5H_2O$	Triclinic $P\bar{1}$	11.90	6.17	7.75	106.5	95.7	104.6	507	2.41	2
$\beta\text{-Zr(SO}_4)_2 \cdot 5H_2O$	Triclinic $P\bar{1}$	8.55	7.60	7.71	101.4	98.6	89.9	486	2.55	2
$Zr(SO_4)_2 \cdot 7H_2O$	Triclinic $P\bar{1}$	12.04	6.36	8.28	93.0	92.4	95.9	629	2.25	2

<sup>a</sup> Structures known (5), (6), (7), (8), (9) (10), and (11).

<sup>b</sup> Powder data not yet indexed (see Fig. 1).

structures the atoms may lie up to 2 Å above or below the mean plane of the layer. However this has not been indicated except in the case of  $\alpha$ -monohydrate where the relative positions of the atoms will be referred to in considering the mechanism of its transformation to  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>. In  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub> the zirconium and sulphur atoms are situated at the special positions,  $y = \frac{1}{2}$  and  $y = \frac{3}{4}$ , required by the space group *Pnma* and this has been indicated in the schematic diagram of the structure viewed in (010) projection [Fig. 3(e)].

#### A. The Dimeric Sulphates, Zr(SO<sub>4</sub>)<sub>2</sub>·7H<sub>2</sub>O and $\alpha$ and $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O

The three dimeric sulphates Zr(SO<sub>4</sub>)<sub>2</sub>·7H<sub>2</sub>O,  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O and  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O, are derived from isolated dimeric units, of composition Zr<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>8</sub> (5), (6), and (7). Each zirconium atom in a dimer is bonded to four oxygen atoms belonging to a total of three sulphate groups, as well as to oxygen atoms of four water molecules, giving the metal a coordination number of eight. The three-dimensional array which these units form appears to be held together by hydrogen bonds. These dimeric units have two noteworthy features.

One is the bidentate or Zr—O—S bonding of the two



terminal sulphate groups; the second is the manner in which the other two sulphate tetrahedra form a double bridge between the two zirconium atoms, resulting in an eight-membered ring structure which we have referred to as the *dimeric ring* (7). Figure 2 is a diagram of this ring structure, with atoms omitted which are not part of the ring. Table II gives Zr—Zr, S—S, and O—O distances across the centre of the unit for the three hydrates. The structural individuality of these hydrates resides in differences in these dimensions, the disposition of the dimer in the unit cell and in the number and position of the nonbonded water molecules.

Figure 3(a) depicts the array of isolated dimeric units which form the basis of the structures of the heptahydrate and the  $\alpha$ - and  $\beta$ -pentahydrates. The heptahydrate is structurally equivalent to the  $\beta$ -pentahydrate except that its lattice contains two additional water molecules not bonded to zirconium. The two pentahydrates differ in the relative disposition of the terminal groups and ring structure within the unit cell. The  $\beta$ -form, which is the less stable, has a very short O<sub>1</sub>—O<sub>1</sub> distance across the dimeric ring (Fig. 2 and Table II) and we believe that its instability results in part from repulsion between these very close oxygen atoms (7).

#### B. Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O

This hydrate is the stable phase under atmospheric conditions, and is the phase which co-exists with saturated zirconium sulphate solution under equilibrium conditions at 0–60°C. It has a layer structure with, presumably, hydrogen bonding providing

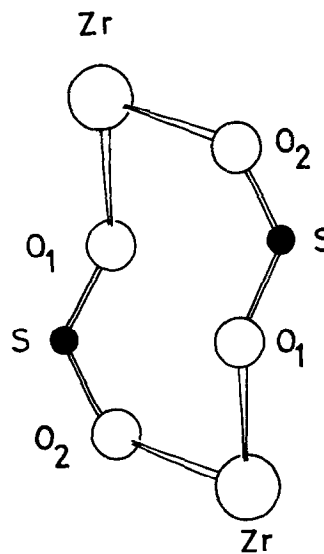


FIG. 2. Dimeric ring structure consisting of two zirconium atoms joined by two O—S—O bridges.

Large open circles—Zirconium atoms.  
Full black circles—Sulphur atoms.  
Medium open circles—Oxygen atoms.

TABLE II

DIMENSION OF THE DIMERIC RINGS IN Zr(SO<sub>4</sub>)<sub>2</sub>-HYDRATE STRUCTURES IN Å

Compound	Zr—Zr	S—S	O <sub>1</sub> —O <sub>1</sub>	O <sub>2</sub> —O <sub>2</sub>
Zr(SO <sub>4</sub> ) <sub>2</sub> ·7H <sub>2</sub> O	5.38	4.47	2.98	4.45
$\alpha$ -Zr(SO <sub>4</sub> ) <sub>2</sub> ·5H <sub>2</sub> O	5.53	4.46	2.95	4.29
$\beta$ -Zr(SO <sub>4</sub> ) <sub>2</sub> ·5H <sub>2</sub> O	5.55	4.28	2.78	4.16
$\gamma$ -Zr(SO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	<i>a</i>	5.60	4.20	2.87
	<i>b</i>	5.12	4.31	3.15
	<i>c</i>	5.25	4.41	3.06
	<i>d</i>	5.69	3.91	2.76
	<i>e</i>	5.12	4.31	3.15
	<i>f</i>	5.26	4.52	3.14
$\alpha$ -Zr(SO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O				
Ring containing	5.07	4.68	3.52	3.92
Zr—O—S linkages only				
$\alpha$ -Zr(SO <sub>4</sub> ) <sub>2</sub>	<i>a = f</i>	5.52	4.34	3.08
	<i>b = e</i>	5.45	4.06	3.66
	<i>c = d</i>	5.62	4.19	2.87



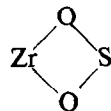
cohesion between the layers. However, it does not contain dimeric ring units within its layers, unlike all the other zirconium sulphate hydrates and anhydrides for which the structures are known, Table II. Instead, it has the arrangement shown in skeletal form in Fig. 3(b). Each zirconium atom is bonded to oxygen atoms of four sulphate groups and also to four water molecules giving a coordination number of eight as in the dimeric sulphates. As in the hepta- and pentahydrates, all sulphate groups have two terminal oxygens.

### C. $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O

Like the tetrahydrate, the metastable  $\gamma$  monohydrate has a layer structure; the layers of composition [Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O]<sub>n</sub> are again held together with hydrogen bonds. However the coordination number of the metal is only seven; zirconium is bonded to one oxygen atom from each of six sulphate groups, Fig. 3(c), and to one water molecule not shown in the figure. As in the penta- and heptahydrates the structure is based on dimeric rings, but here the rings are interconnected in a planar network and six rings may be discerned, five of them non-equivalent [*a*, (*b*  $\equiv$  *e*), *c*, *d*, *f* in Table II and Fig. 3(c)]. Each zirconium atom can be regarded as being situated at the intersection of three chains of rings.

### D. $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O

The stable monohydrate again has a layer structure with zirconium in sevenfold coordination, which is attained in this case by each zirconium atom bonding to five sulphate groups but forming a



Zr—O—S linkage with one of them. As in

$\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, each sulphate group has only one terminal oxygen. A layer unit of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O [Fig. 3(d)] is thus composed of cross-linked zig-zag chains of dimeric rings with each alternate ring

containing two Zr—O—S linkages.



### E. $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>

In contrast to its hydrates the equilibrium anhydrous zirconium sulphate,  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>, is a three-dimensional network of sulphate-bridged zirconium polyhedra (10). The structure viewed in (010) projection is represented by Fig. 3(e), where the dotted lines indicate oxygen bridges from sulphur atoms to adjacent zirconium atoms one unit cell

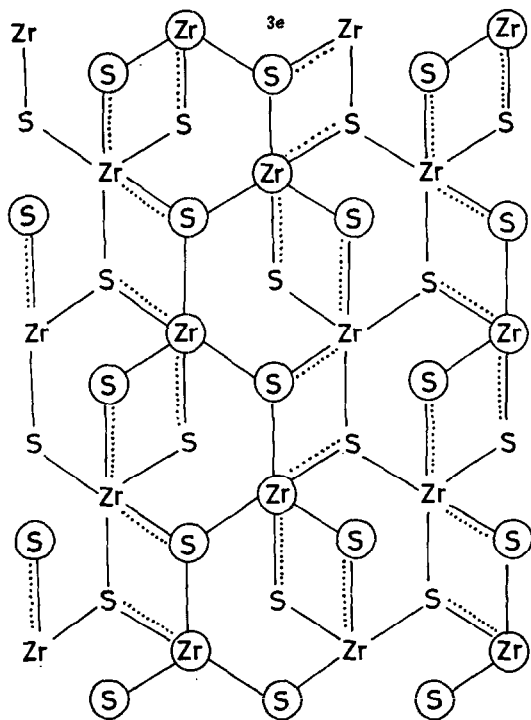


FIG. 3. Schematic representation of the skeletal sulphate lattices of the hydrates and  $\alpha$ -anhydrate of Zr(SO<sub>4</sub>)<sub>2</sub>. Lines joining sulphur and zirconium atoms represent oxygen bridges which are not necessarily linear. Oxygen atoms including terminal oxygens of sulphate groups and oxygens of water molecules are omitted. Dotted lines indicate oxygen bridges to overlying or underlying zirconium atoms. (a) An array of isolated dimeric units common to the structures of the three dimeric sulphates—Zr(SO<sub>4</sub>)<sub>2</sub>·7H<sub>2</sub>O,  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O and  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O. (b) A layer of the Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O structure. (c) A layer of the  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O structure, equivalent to the  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub> structure viewed in (001) projection. (d) A layer of the  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O structure. Ringed atoms lie above the mean plane of the layer, others lie below. (e) The  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub> structure viewed in (010) projection. Ringed atoms situated at the special position of  $y = \frac{3}{4}$ , others at  $y = \frac{1}{4}$ .

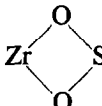
length above or below those shown. Each zirconium atom is in sevenfold coordination, with bonds to one oxygen atom from each of seven attached sulphate tetrahedra. This arrangement results in the formation of sheets, normal to [001], which are composed entirely of dimeric rings and which are held together by Zr-O-S linkages. Thus the structure of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub> viewed in [001] projection can be represented by the same schematic diagram as a layer of  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O [Fig. 3 (c)]. There are three nonequivalent dimeric rings in the structure [Figure 3 (c) and Table II]. There are two types of sulphate tetrahedra; one is bonded to four zirconium atoms while the other is bonded to three zirconium atoms and has one terminal oxygen.

### Postulated Structural Transformations of Zr(SO<sub>4</sub>)<sub>2</sub> Lattices

#### A. The Consecutive Decomposition Reactions

1. *The Transformation of Zr(SO<sub>4</sub>)<sub>2</sub>·7H<sub>2</sub>O to  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O.* This decomposition (5) involves the migration of two nonbonded water molecules from the heptahydrate lattice. No zirconium-oxygen bonds are broken and, although the unit cell contracts, the disposition of the dimer within the unit cell is changed only slightly.

2. *The Transformation of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O to Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O.* This reaction involves the loss of a single nonbonded water molecule together with a rearrangement of the skeletal structure. Four water molecules remain bonded to each zirconium atom, and the coordination number of the latter is unchanged. The isolated dimers [Fig. 3 (a)] link up in two dimensions to form the layers of the Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O structure [Figure 3 (b)]. The proposed mechanism is depicted in Fig. 4 (a). Not only must one or both

oxygen bridges forming the Zr  S linkages be

broken and remade to another zirconium atom, but one oxygen bridge of each dimeric ring must be broken and remade elsewhere. An infinite network formed from two intersecting -Zr-O-S-O-Zr- chains results, and the ring structure of the parent compound is completely destroyed.

3. *The Transformation of Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O to  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O.* Thermal decomposition of Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O in air at temperatures between 120 and 220°C generally results in the formation of metastable  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O as the initial product (Fig. 1) (14), (16), and (8). This reaction involves the loss of three of the four water molecules which

were coordinated to zirconium in the parent Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O structure. Two of the coordination positions thus made vacant are filled by terminal oxygen atoms of neighbouring sulphate groups which so far have not been involved in coordination with zirconium. This is shown in Fig. 4b where the broken lines indicate the new oxygen bridges between zirconium and sulphur atoms. During this transformation and in all the following transformations of one layer structure to another there is a change in the relative positions of the zirconium and sulphur atoms above and below the mean plane of the layer. As this movement of the atoms is in a direction normal to the plane of each layer it is thought that it can occur without causing any disruption of the lattices.

When the dimensions of the five different rings which make up the structure of  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O are considered (Table II), it is seen that the O<sub>1</sub>-O<sub>1</sub> distance in ring d is very short, a factor which, as in the case of  $\beta$ -pentahydrate, can be expected to contribute to the metastability of the  $\gamma$ -monohydrate.

4. *The Conversion of  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O to  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O.* When  $\gamma$ -zirconium sulphate monohydrate is heated in a sealed tube at temperatures between 150 and 200°C it transforms to stable  $\alpha$ -monohydrate (Fig. 1) either directly or via the  $\beta$  phase which is also metastable under these conditions. As the structure of  $\beta$ -zirconium sulphate monohydrate has not yet been determined, only the direct transformation of  $\gamma$  to  $\alpha$ -monohydrate will be considered.

Of the six dimeric rings in the  $\gamma$  modification only two associated with each zirconium atom are not disrupted [Fig. 3 (d)] and these have relatively long (> 3.0 Å) O<sub>1</sub>-O<sub>1</sub> distances. A schematic representation illustrating this proposed transformation is shown in Fig. 4 (c). It should be noted that for convenience the representation of the  $\gamma$ -monohydrate structure in this diagram has been rotated so that the chain of dimeric rings *a* and *d* is horizontal.

5. *Transformation of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O to  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>.* The product from the complete dehydration of the tetrahydrate or monohydrates of zirconium sulphate in air is generally one of the metastable anhydrous phases with, as yet, unknown structure, but under high partial pressure of H<sub>2</sub>SO<sub>4</sub> (2), (14) the equilibrium alpha anhydrate is formed directly.

If the schematic diagram for a layer of  $\alpha$ -zirconium sulphate monohydrate is compared with that for the structure of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub> viewed in (010) projection [Fig. 3 (d) and (e)] the similarity between the

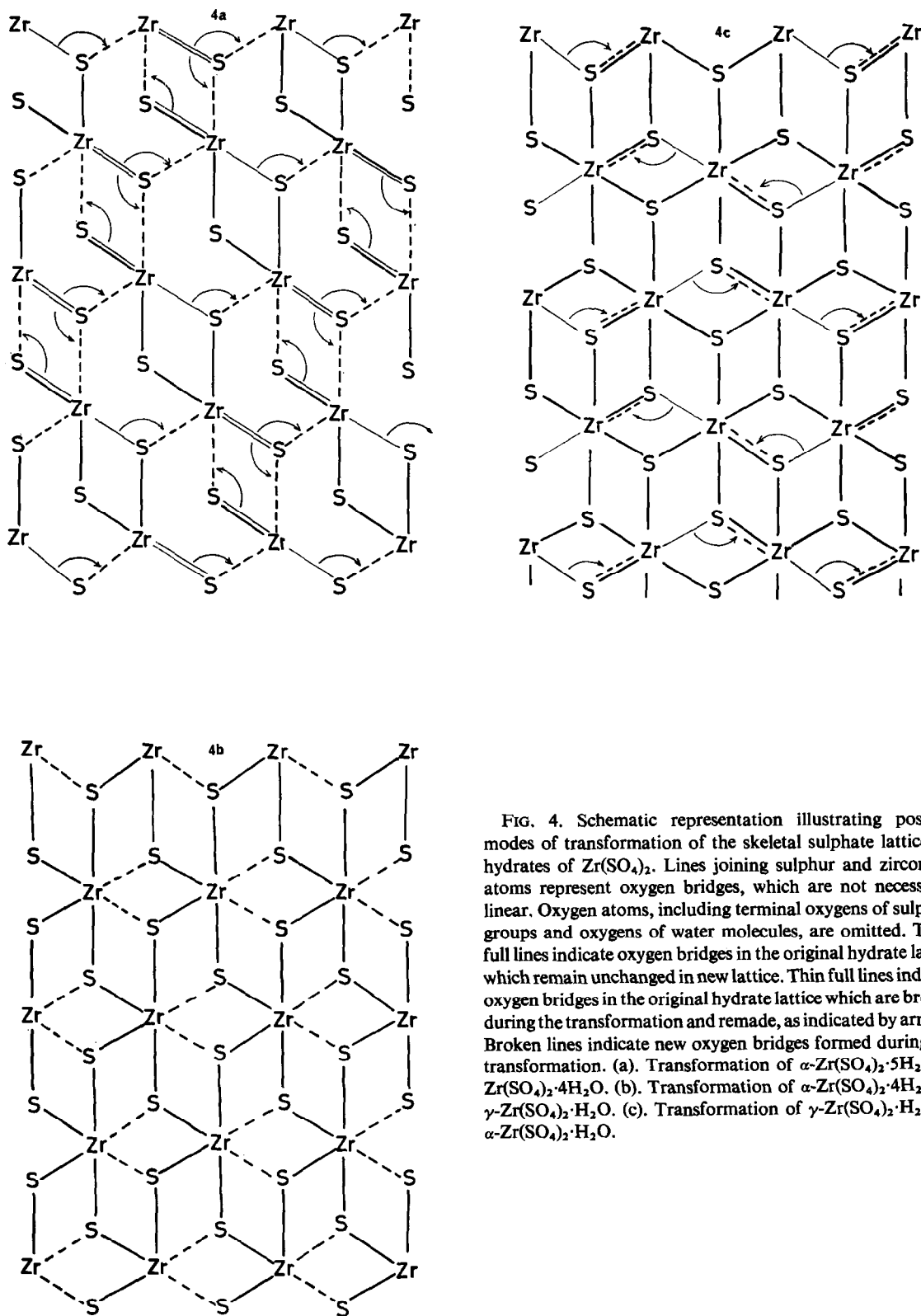
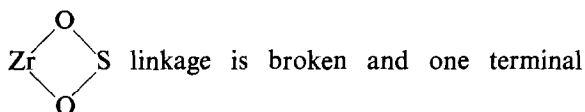


FIG. 4. Schematic representation illustrating possible modes of transformation of the skeletal sulphate lattices of hydrates of  $Zr(SO_4)_2$ . Lines joining sulphur and zirconium atoms represent oxygen bridges, which are not necessarily linear. Oxygen atoms, including terminal oxygens of sulphate groups and oxygens of water molecules, are omitted. Thick full lines indicate oxygen bridges in the original hydrate lattice which remain unchanged in new lattice. Thin full lines indicate oxygen bridges in the original hydrate lattice which are broken during the transformation and remade, as indicated by arrows. Broken lines indicate new oxygen bridges formed during the transformation. (a). Transformation of  $\alpha-Zr(SO_4)_2 \cdot 5H_2O$  to  $Zr(SO_4)_2 \cdot 4H_2O$ . (b). Transformation of  $\alpha-Zr(SO_4)_2 \cdot 4H_2O$  to  $\gamma-Zr(SO_4)_2 \cdot H_2O$ . (c). Transformation of  $\gamma-Zr(SO_4)_2 \cdot H_2O$  to  $\alpha-Zr(SO_4)_2 \cdot H_2O$ .

two equilibrium phases can be seen. The zig-zag chains of dimeric rings are still present in  $\alpha$ - $\text{Zr}(\text{SO}_4)_2$  and their manner of cross-linking is similar. Thus, on the loss of the one water molecule which was coordinated to each zirconium atom, the layers of the monohydrate lattice move closer together with the zirconium and sulphur atoms adjusting to the special positions  $y = \frac{1}{4}$  and  $y = \frac{3}{4}$  of the space group  $Pnma$ . This movement of the zirconium and sulphur atoms is in effect only a change in tilt of the dimeric rings and is unlikely to disrupt the original layers in the monohydrate structure. However, in order to connect the layers one oxygen bridge of each



oxygen atom of each sulphate group coordinates to a zirconium atom in a neighbouring layer of the structure, forming the sheets of dimeric rings normal to the [001] direction of the  $\alpha$ - $\text{Zr}(\text{SO}_4)_2$  structure [Fig. 3(c)].

## B. Hydration Reactions

1. *Aqueous Hydration.* Under the conditions of aqueous hydration liquid water is present during the reaction (13). Thus the hydration proceeds via the species in solution (17). We have pointed out elsewhere (15) that in concentrated solutions of zirconium sulphate [ $> 60\%$  by weight  $\text{Zr}(\text{SO}_4)_2$ ] the preferred solution species is probably closely related to the isolated dimeric unit of the solid hepta and  $\alpha$ -pentahydrates. Solubility and saturated solution vapour pressure data for the higher hydrates of  $\text{Zr}(\text{SO}_4)_2$  (12), (15) suggest that a metastable dimeric species, related structurally to the isolated dimeric unit of the solid  $\beta$ -pentahydrate, can also exist transiently in these very concentrated solutions. The same data indicate further that these dimeric solution species differ markedly from the species present in the more dilute solutions saturated with respect to the stable tetrahydrate.

The initial solid product of the aqueous hydration of the  $\alpha$ -anhydrate and the  $\alpha$ - and  $\gamma$ -monohydrates is either the  $\alpha$ -pentahydrate or the heptahydrate depending on the temperature of the reaction (15). These three reactants all contain dimeric rings in their structures so that on dissolution in a limited quantity of water (13) they can break down readily to form the preferred dimeric species. For example, in the aqueous hydration of  $\alpha$ -monohydrate it is only necessary for two water molecules to displace from each zirconium atom the oxygen atoms connecting to each of two sulphate groups in order to

isolate the skeletal dimeric unit, Fig. 3 (a) and (d). As one water molecule was already bonded to each zirconium atom in the solid monohydrate only one more now needs to be coordinated to each to complete the unit. Crystallization of a solid product would then involve the hydrogen bridging of such solution dimers in orientations dependent on the number of non-bonded water molecules filling the spaces of the three-dimensional structure. The initial solid product subsequently transforms to the stable tetrahydrate as described under sections 1 and 2 above.

The structure of the  $\beta$ -anhydrate is not yet known but presumably on solvation it breaks down to form the metastable dimeric species in solution and so yield  $\beta$ -pentahydrate as the initial solid product (Fig. 1).

2. *Vapour Hydration.* The experimental conditions for vapour hydration limit the rate of absorption of water by the sample so that deliquescence does not occur and the rate of formation of the hydrate product is restricted. Therefore, metastable products are not usually observed during such hydrations unless their equilibration rates are very low. Consequently, the processes involved in vapour hydrations and the parent-product relationships are often obscure. For example, on vapour hydration of the  $\text{Zr}(\text{SO}_4)_2$  anhydrides at room temperature only the stable tetrahydrate can be recovered. However, if the reaction proceeds at  $0^\circ\text{C}$  where the equilibration rates are low the solid dimeric sulphates, unstable with respect to the tetrahydrate, can be isolated.

## Discussion

Polymorphic transitions represent the simplest type of transformation in crystalline solids and the structural and energy changes involved in such transitions have been studied extensively (3), (4). Some of the findings relating to polymorphic transitions may be applicable to more complex reactions such as the decomposition of a salt hydrate or anhydrate (1), (2). In any transition between crystalline solids there is a potential energy barrier opposing the change in structure which we can assess from the postulated reconstructive atom movements. If the reaction product obtained from a crystalline solid can exist in a number of structural configurations under the same conditions of temperature and pressure, its initial form is likely to be that which is closest in structure to the parent compound and thus separated from it by the lowest potential energy barrier. Such a polymorph is not necessarily the structure with the lowest free energy



but it is the least stable of the forms appearing in the particular reaction. The present series of dehydrations and hydrations provide a number of examples of this behaviour, Fig. 1.

For instance, the disposition of the terminal sulphate groups and the dimeric ring in the unit cells of the heptahydrate and  $\alpha$ -pentahydrate are similar, and different from that in  $\beta$ -pentahydrate. As a consequence, metastable  $\beta$ -pentahydrate does not appear as a dehydration product of the heptahydrate.

There are four known monohydrate polymorphs, of which the structures of two have been defined (8), (9). To transform the skeletal sulphate lattice of the parent tetrahydrate directly to that of the stable  $\alpha$ -monohydrate, not only would one terminal oxygen on every sulphate group need to link up to a zirconium atom, as occurs in the transformation to  $\gamma$ -Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O [Fig. 4(b)] but for a quarter of the sulphate groups an oxygen bridge to a zirconium atom would need to be broken and remade to a different zirconium atom. If we assume that the potential energy barrier in linking an oxygen atom to a zirconium is the same in both cases then, in the transformation to  $\alpha$ -monohydrate, there is an additional potential barrier for the breaking and remaking of the oxygen bridge. Thus the metastable  $\gamma$ -monohydrate, closer structurally to the tetrahydrate than is the stable monohydrate, is the form initially produced.

The  $\alpha$ -pentahydrate is the initial solid product from the aqueous hydration of the  $\alpha$ -anhydrate because it is closer structurally both to the species in solution and to the parent solid than is the stable tetrahydrate. Likewise, although the structure of the  $\beta$ -anhydrate is still unknown, we can conclude that  $\beta$ -pentahydrate is the initial solid product of the aqueous hydration of  $\beta$ -anhydrate because it is closer structurally to the latter than is the more stable  $\alpha$ -pentahydrate or the equilibrium tetrahydrate.

The present work has emphasized that if any given parent compound is decomposed in the stability field of a product composition, e.g., the monohydrates, then the polymorph of that composition, which is nearest in structure to the parent, is most likely to be formed initially. In this respect, we can regard the stable  $\alpha$ -monohydrate as derivable from either of two independent *parent* compounds, i.e. the tetrahydrate which forms under specific conditions from the  $\alpha$ -pentahydrate, or the  $\alpha$ -pentahydrate itself. Considering the relationship between the  $\alpha$ -pentahydrate and the known monohydrate polymorphs, we noted that the parent compound was crystallographically closer to the

stable  $\alpha$ -monohydrate than to the metastable  $\gamma$ -modification [cf., Fig. 3(a), (c), and (d)]. Therefore, we could expect that either the stable  $\alpha$ -monohydrate would be the initial product of this decomposition or a new metastable monohydrate intermediate, even closer in structure to the  $\alpha$ -pentahydrate, would be formed first.

These conclusions prompted a further investigation of the decomposition of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O and a new intermediate metastable monohydrate, which we have designated  $\delta$ -Zr(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O, was indeed formed, Fig. 1. X-ray powder data only have been collected to date; single crystals of this phase suitable for X-ray structure analysis have yet to be obtained. However, on the basis of the present concepts we expect that its structure will be intermediate between those of  $\alpha$ -pentahydrate and  $\alpha$ -monohydrate.

The general conclusion to be drawn from our observations of the entire series of hydrates is that, provided the existence conditions for the appropriate compounds are met (2), the initial product of a decomposition is likely to be the polymorph which is closest in structure to the parent compound.

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