A Structural Description of β-K_2SO_4

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A simple description of the structure of β-K_2SO_4 is given. It consists of a packing of tetrahedra, Edshammar 11-polyhedra (Edshammar, L.-E. *Thesis*, University of Stockholm, Sweden 1969), and a new type of polyhedron, a 'centaur' formed by joining an icosahedron and an Edshammar 11-polyhedron.

Dedicated to Professor Sten Andersson on the occasion of his 60th birthday.

The β-K_2SO_4 structure type (Strukturbericht-type $H1_6$) is widespread. Wyckoff[1] list no less than 48 sulfates, selenates, tellurates, phosphates, arsenates, vanadates, chromates, titanates and halides chiefly of the alkali metals, but also of thallium, barium etc. Despite these numerous examples, no simple, satisfactory description of the coordination of the potassium atoms has been given.

A structural model

We propose the use of the Edshammar 11-polyhedron[2] to describe the structure. (Edshammar introduced a number of polyhedra: here we will use the 11-polyhedron exclusively, and refer to it simply as the Edshammar polyhedron.) The Edshammar polyhedron is the 11-membered

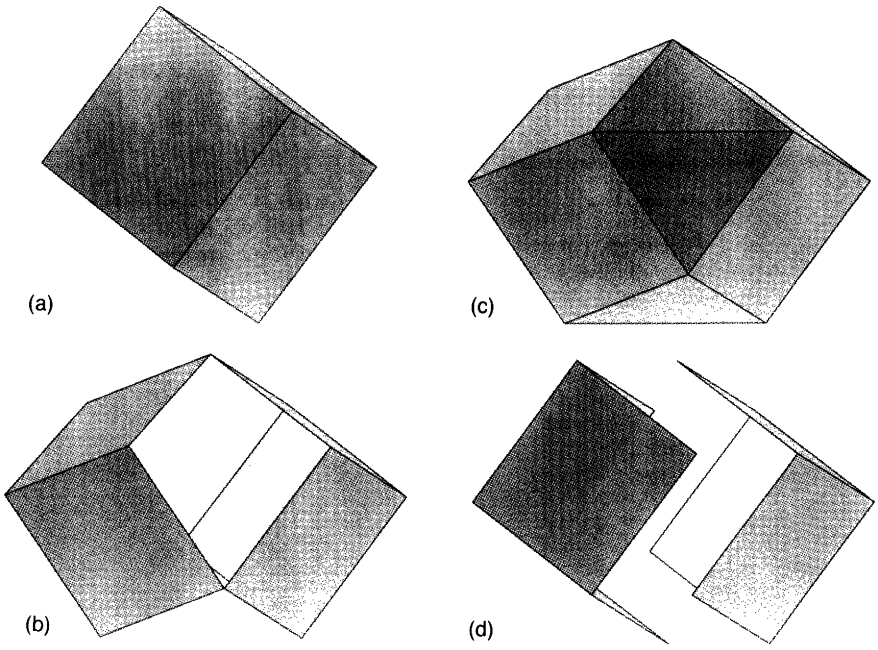

Fig. 1. A construction of the Edshammar polyhedron. (a) A cube viewed with the [111] direction vertical. (b) The cube is pulled apart into two halves. (c) The upper half is rotated by $2\pi/3$. (d) The completed Edshammar polyhedron.

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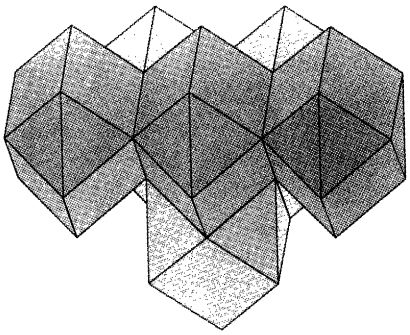

Fig. 2. An assembly of close-packed Edshammar polyhedra.

coordination polyhedron of As in Na_3As. A description can be constructed by pulling a cube apart along the [111] direction, twisting one of the halves by $2\pi/3$ around the three-fold axis and joining the halves again (Fig. 1).

In the Na_3As structure, layers of As-filled Edshammar polyhedra whose vertices are Na alternate with layers of empty Na cubes. It is easy to show[3] that a close packing of Edshammar polyhedra supports an AB_2 stoichiometry. There is, however, to our knowledge no compound with this structure. To understand the packing in the β-K_2SO_4 structure it is advantageous to invoke an imaginary K_2O_4 structure, consisting of a close-packing of K-filled Edshammar polyhedra (Fig. 2). That the Edshammar polyhedron is space-filling is clear from the following considerations: The equatorial triangles of the polyhedron all meet at dihedral angles of $2\pi/3$. Thus the polyhedra may be packed in planes, three coming together at each vertex, sharing triangular faces. The layers will expose only square faces, and the puckered surfaces will be identical to these presented by a [111] surface in a simple cubic packing. Thus layers may be stacked on top of each other in a space-filling fashion. When this is done for the imaginary K_2O_4 structure, the projection along the *b*-axis of the oxygen positions will form a hexagonal grid (Fig. 3).

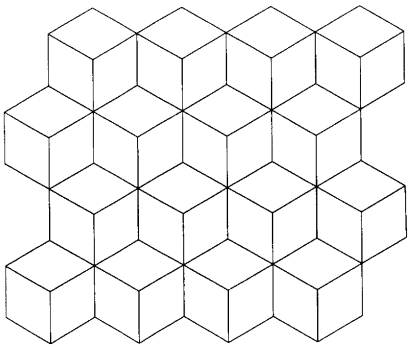

Fig. 3. The hexagonal grid formed by close-packed Edshammar polyhedra.

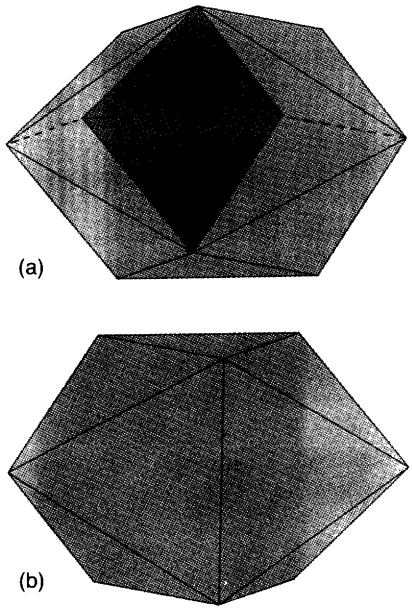

Fig. 4. The centaur polyhedron (light grey) and the tetrahedron (dark grey) formed by a budding process. (a) The centaur and the tetrahedron before the deformation due to the idealization of tetrahedra. The dashed lines indicate the connections that are broken in the budding process. (b) The centaur before deformation.

On examining the Edshammar polyhedron closer, it is clear that it contains three flattened tetrahedra arranged around the equator. These tetrahedra contain three different vertex-to-vertex distances. if the edge length of the original cube is set to unity, there are four unit distances, one of $2/\sqrt{3}$ and one of $\sqrt{2}$. The distorted tetrahedra contain a twofold axis of rotation along the direction of compression, whereas an ideal tetrahedron contains an axis of fourfold rotoinversion. Filling one of these equatorial tetrahedra with a sulfur atom and making that tetrahedron ideal will cause a dramatic deformation of the Edshammar polyhedron. the tetrahedron will bud off, leaving a new kind of coordination polyhedron. This polyhedron is a hybrid between an icosahedron and an Edshammar polyhedron, joined perpendicularly to a common twofold axis (Fig. 4). In this thesis Raschke[4] describes a hybrid between a cube and an icosahedron, using the term 'centaur' to emphasize the schizophrenic nature of the polyhedron. We will employ the same terminology here to underline the duality of the composite polyhedron. The centaur in β-K_2SO_4 is different from that of Raschke, and they should not be confused, but they share the common feature of being hybrids. The term 'centaur' used thus refers not to a single polyhedron, but to a group of polyhedra, distinguished by their hybrid nature. There need be no cause for confusion if it is made clear what particular centaur the text refers to. The centaur in β-K_2SO_4 has nine vertices, all of which were present in the original Edshammar polyhedron. In

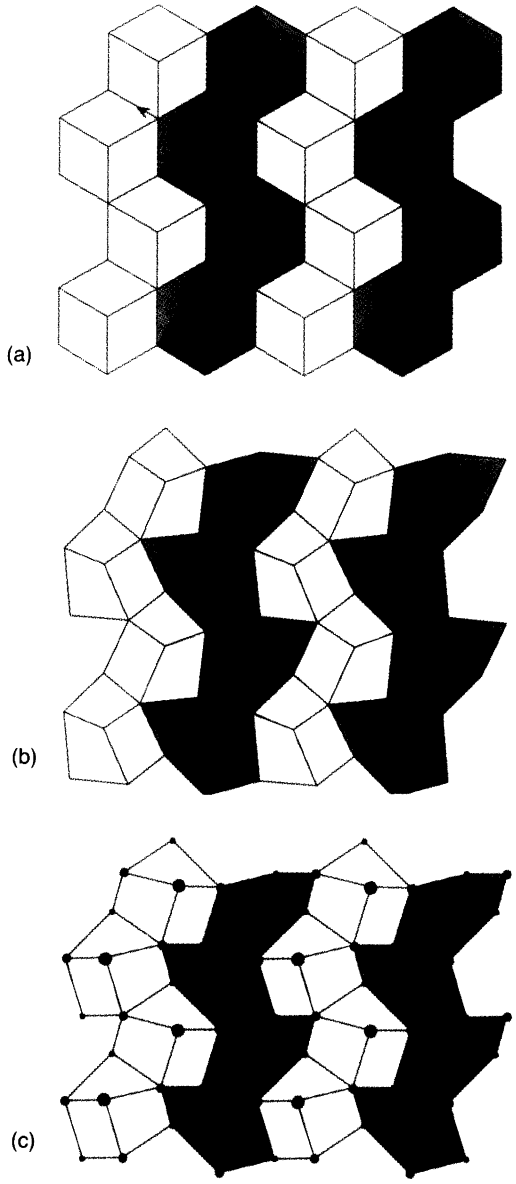

Fig. 5. One layer of the β-K_2SO_4 structure projected onto the *a,c*-plane. The Edshammar polyhedra in the picture are white, the tetrahedra light grey, and the centaur polyhedra are dark grey. the vertices of all polyhedra are oxygen atoms. The tetrahedra contain the sulfur atoms and the centaur- and Edshammar polyhedra contain the potassium atoms. (a) A model containing undistorted Edshammar polyhedra and heavily distorted tetrahedra. (b) The same model after idealizing the tetrahedra. (c) The real structure of β-K_2SO_4. The cell parameters *(Pnma)* are: a = 7.476, b = 5.763, c = 10.071(5) Å and the heights of the oxygen atoms relative to a reference mirror plane are: 0 (small discs), 0.209 or 0.291 (medium discs, the smaller value is valid for the oxygen atoms that form vertices to the tetrahedra in the reference mirror plane) and 1/2 (large discs).

Fig. 4(a), one equatorial flattened tetrahedron is distinguished in darker grey. When the vertical edge of this tetrahedron is disconnected from the rest of the Edshammar polyhedron, two polyhedra are formed; a flattned tetrahedron and a centaur. The two share a common edge. In Fig. 4(b) the tetrahedron is removed and the centaur is shown by itself. The icosahedron-like part is facing the reader. In the process, two additional, empty, tetrahedra are formed above and below the SO_4 tetrahedron.

The formation of the SO_4 tetrahedron forces deformations not only of the Edshammar polyhedron from which it is formed, but also of the surrounding centaur polyhedra and intact Edshammar polyhedra. By considering the budding process in projection for an ensemble of several unit cells, it is clear how the lattice will be affected. In Fig. 5(a) the original hexagonal grid is depicted with additional lines to indicate the tetrahedra-to-be (light grey) and the centaur polyhedra (dark grey). The tetrahedra are then allowed to bud off, forced to increasing regularity by the sulfur atoms. The arrows in Fig. 5(a) indicate how the lattice should deform if all SO_4 tetrahedra are made ideal. Apart from the rearrangements of atoms, it is clear that the structure must expand in the c-direction. The c/a ratio for the close-packed Edshammar polyhedral structure is in fact about 15 % less than that of β-K_2SO_4. In Fig. 5(b) the oxygens from Fig. 5(a) are moved according to the arrows, and the result can be compaired with the actual structure of β-K_2SO_4 in Fig. 5(c). It is clear that the major differences between the model and the real structure can be explained by the fact that the SO_4 tetrahedra are slightly smaller in the real structure than in the model. The distortion of the Edshammar lattice goes even further than in the model. We have, however, chosen not to develop the model further, but to keep it as simple as possible. We still get a striking similarity between model and reality.

Summary

This description is naturally not an attempt to furnish a mechanism for the formation of β-K_2SO_4, but only to show how the structure can be understood in terms of two competing principles. On one hand, the oxygen atoms are trying to form perfect tetrahedra around the sulfur atoms, while on the other hand, they are trying to form ideal Edshammar polyhedra around the potassium atoms. The resulting compromise is the structure of β-K_2SO_4. It is interesting to note that the sulfates in the structure group are considerably more ideal with respect to the tetrahedra, while the halides are more ideal with respect to the Edshammar polyhedra. Thus we see that the tug-of-war between the two structural principles ends with different victors depending on the species that build the structure.

A principal advantage of this model is that it provides a description of the coordination of potassium. Many previous descriptions[1,5] discuss only the coordination of sulfur by oxygen, while others[6] concentrate on the coordination of sulfur and oxygen by potassium. Our approach is complementary to the earlier descriptions and should lend itself easily to bond-length refinement calculations.

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References

1. Wyckoff, R. W. G. *Crystal Structures*, Wiley, New York 1965, Vol. 3.
2. Edshammar, L.-E. *Thesis*, University of Stockholm, Sweden 1969.
3. Lidin, S., Somer, M., Popp, T. and von Schnering, H.-G. *To be published.*
4. Raschke, D. *Thesis*, University of Stuttgart, Germany 1985.
5. McGinnety, J. A. *Acta Crystallogr., Sect. B 28* (1972) 2845.
6. O'Keeffe, M. and Hyde, B. G. *Struct. Bonding (Berl.) 61* (1985) 77.

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