stippled or left clear. The idealized unit-cell ratios are listed in the lower part of Fig. 2. Table 1 compares idealized point positions with experimental point positions for all three structure types. Table 4 lists all the different structure types built up of centred trigonal prisms which can be derived using the concept of periodic unit-cell twinning of close-packed base structures. The different stackings of the close-packed base structures are denoted using Jagodzinski–Wyckoff symbols (Jagodzinski, 1954a,b). Twelve structure types can at present be derived using this concept; however, for those enclosed in parentheses only a very idealized version can be obtained.

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The Space Group and Structure of α-K₂SO₄

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The structure of the high-temperature form of K_2SO_4 was solved from powder diffraction data at 630°C. The space group appears to be $P6_3/mmc$, with $a = 5.90$ (2), $c = 8.11$ (3) Å and $Z = 2$. The structure was refined with a simplex method from 50 powder diffraction lines. The structure is disordered: For a SO_4^{2-} tetrahedron two orientations are possible, in which a S—O direction is pointing either along the positive c axis or in the opposite direction. The anions are evenly distributed among these two orientations. The structure is closely related to that of the low-temperature form.

Introduction

Two modifications of K_2SO_4 are known: β-K_2SO_4 is stable below 587°C and α-K_2SO_4 above. The structures of both forms have played the roles of structure models for a series of compounds of the type A_2BX_4. The structure of the β form is well established (Robinson, 1958; McGinnety, 1972).

Surprisingly, a complete structure analysis of α-K_2SO_4 has never been reported. Even the choice of

space group for α-K_2SO_4 is controversial. On the basis of X-ray powder data Pannetier (1966) proposed the space group $P\bar{3}m1$. Later, Eysel & Hahn (1970) proposed a hexagonal structure model for α-K_2SO_4 and its isomorphs; in this model the SO_4 tetrahedra are all oriented with a S—O radius in the same sense along the c axis; the corresponding space group is $P6_3mc$. Iwai, Sakai & Watanabe (1973) confirmed this structure using a high-temperature Weissenberg technique. Eysel (1971) showed the space group $P\bar{3}m1$ to be highly

improbable. Van den Berg, Tuinstra & Warczewski (1973), on the other hand, proposed a nonpolar hexagonal structure for the high-temperature form of K_2MoO_4, which is one of the structures assumed to be isostructural with α-K_2SO_4. According to them, the anion tetrahedra are randomly distributed among two orientations in which Mo—O radii point in the opposite sense along the c axis; the space group is $P6_3/mmc$. From a study of twin-domain-wall dynamics in K_2SO_4 and K_2SeO_4 Shiozaki, Sawada, Ishibashi & Takagi (1977) conclude that the space group is most probably $P6_3/mmc$ for the high-temperature forms of both compounds. The main issue, therefore, is whether the structure is of the polar or of the nonpolar type.

In the present work we show that the nonpolar structure with space group $P6_3/mmc$ is in far better agreement with our powder data than is the polar structure.

Experimental

A long quartz capillary (∅ = 0·4 mm) was filled with finely ground K_2SO_4 (Merck, Darmstadt). The capillary was mounted in a Simon–Guinier powder camera for high-temperature X-ray diffraction (Enraf–Nonius, Delft). The sample was heated to 630°C. At this temperature, diffraction patterns were obtained using Cu $K\alpha_1$ radiation. During the exposure the capillary moves periodically along its axis with an amplitude of 0·5 cm. At the same time the sample is rotated around its axis, in order to let as many crystallites as possible contribute to the pattern. An Al foil (50 μm thick) was kept in front of the films to suppress the fluorescence radiation. Two singly coated films (Kodirex) were put in the film cassette, one in front of the other. The resulting diffraction line profiles were perfectly smooth. The density on the film was measured with a micro-densitometer. From the results, integrated line intensities were derived using the program PEAK (Son-neveld & Visser, 1975). The intensities were corrected for the 2θ-dependent factors, i.e. the absorption in the specimen and in the Al foil, the oblique incidence factor and the geometric factor (see, for instance, Sas & de Wolff, 1966). In this way we collected integrated intensities of 28 lines, in the range of 0 to 110° (2θ). In the same range 21 calculated lines were not detectable on the films; they were given half the intensity of the weakest observable lines. These intensities were fed into a structure-search simplex computer program (Bassi, 1968). The program minimizes a residual R defined by $R = 100 \sum w(I_o - I_c)^2 / \sum w I_o^2$. The intensities of the reflections were grouped into five classes. To each of these classes a weight w was assigned such that $1/w$ is proportional to the square of an estimated error in I_o. For the two very strong reflections ($I = 95-100$) we took w to be 0·0025, for the next class of three

reflections ($I = 22-36$), $w = 0·04$; for six medium intensities ($I = 5-8$), $w = 0·15$, while for the rest of the reflections ($I < 3$, including the unobserved), $w = 1$. The atomic form factors for K⁺, S and O were those given by Moore (1963).[*] For the simplex program, initial structure models may be quite far from the final structure without disrupting the process of the refinement. In our simplex program no standard deviations (σ) are produced. In order to obtain σ's for the atomic coordinates, we carried out the following procedure. One atomic coordinate is changed stepwise. After each step a refinement is performed in which this particular parameter is kept constant while the remaining parameters are left free. All free atomic coordinates are subsequently treated in this way. The resulting R factors are then plotted as a function of the coordinate. In the resulting plot a significance level can be indicated as discussed by Hamilton (1965). A significance level at $R = 1·1 R_{min}$ was taken to correspond to 2σ; R_{min} is the value at the final refinement. In order to gain some insight into the structural change at the phase transitions from the α-K_2SO_4 to the β-K_2SO_4 phase we also recorded the diffraction pattern as a function of temperature in a range encompassing the transition temperature. The diffraction pattern changes discontinuously at 587°C typically for a first-order transition. The change consists mainly of small shifts since the lattices of both phases are closely similar. In particular, the $hk0$ lines of the α phase are a smooth continuation of the corresponding β lines. Neither the positions nor the intensities of those reflections change notably, so the two structures have the same c-axis projection.

Results

The lattice of α-K_2SO_4 can be described on a hexagonal basis. After refinement the cell parameters at 630°C are $a = 5·90$ (2), $c = 8·11$ (3) Å. The systematic absences of the hhl reflections with $l = 2n + 1$ indicate the space groups $P31c$, $P\bar{3}1c$, $P6_3mc$, $P\bar{6}2c$ or $P6_3/mmc$. The simplex structure-search program was run using each of these five space groups.

In order to keep the number of free parameters (N) low we assumed that the sulphate ion forms a regular tetrahedron, in which the S—O distance was the only parameter. Extrapolation from the low-temperature structure (as justified above) allows us to postulate the following essential features: (i) $Z = 2$; (ii) two potassium ions should be situated on the line $0,0,z$ of the cell (or distributed among equivalent positions around that line); (iii) the other two K ions and the

sulfate ions should occupy positions on the threefold axes $\frac{1}{3},\frac{2}{3},z$ and $\frac{2}{3},\frac{1}{3},z$.

Keeping this structure [called the basic structure by Eysel (1971)] in mind we used the starting positions listed in Table 1 in the simplex program. The values of z_1 and z_2 are determined by the x and y coordinates of O(2), the z values of S and the ideal form of the SO_4^{2-} ion. All other parameters were left free except for the x and y coordinates of K(2), S and O(1), while in $P6_3/mmc$ O(2) was kept in the mirror plane $y = 2x$. An overall isotropic temperature factor was also refined together with a scale factor. With the initial positions given in Table 1, the symmetry elements of the various space groups generate more positions in the unit cell than the number that would result from $Z = 2$, i.e. split atoms are introduced; the weight of each atom is given in Table 1. In $P\bar{3}1c$, for instance, the general position of O(2) is twelvefold, over which 12 O(2) atoms are distributed with weight $\frac{1}{2}$.

First we shall try to discern between the 'polar' structures (space groups $P31c$ and $P6_3mc$) on the one hand and the 'nonpolar' structures ($P\bar{3}1c$, $P\bar{6}2c$ and $P6_3/mmc$) on the other. Refinement in the space groups $P31c$ and $P6_3mc$, using the 50 reflection intensities, resulted in the same structure. The S—O distance of 1·39 Å is about 10% shorter than that reported in the literature; the final R factor is 11·3. Since in the

nonpolar space groups $P\bar{3}1c$, $P\bar{6}2c$ and $P6_3/mmc$ the structure refines to $R = 3·4$, the polar structures have to be rejected. In these nonpolar space groups, $P6_3/mmc$ yields the same structure as its subgroups $P\bar{3}1c$ and $P\bar{6}2c$. Details of the latter structure are given in Table 2. We conclude that the space group $P6_3/mmc$ displays the correct symmetry of the structure of α-K_2SO_4.

In order to obtain some indication of a rotation of the SO_4^{2-} ion around the threefold axis, we refined the structure again in $P6_3/mmc$, this time, however, putting O(2) at a general position ($y \neq 2x$). This causes O(2) to be split in positions of weight $\frac{1}{4}$ on either side of the mirror plane $y = 2x$. The simplex program now indeed refines to a structure in which O(2) is distributed over two positions as shown in Table 2 and Fig. 1. The atomic parameters were subjected to the procedure discussed above to obtain the σ's. The plots of $(R/R_{min})^{1/2}$ for some coordinates are shown in Fig. 2.

Discussion

The final structure is depicted in Fig. 1. The structure shows two sites for K(2) at $z = 0·796$ and at $z = 0·704$, each of these sites being half occupied. The two positions are 0·75 Å apart. Since the structure was refined using an isotropic temperature factor, the split position could also be the forced simulation of a strongly anisotropic thermal motion of a single K(2).
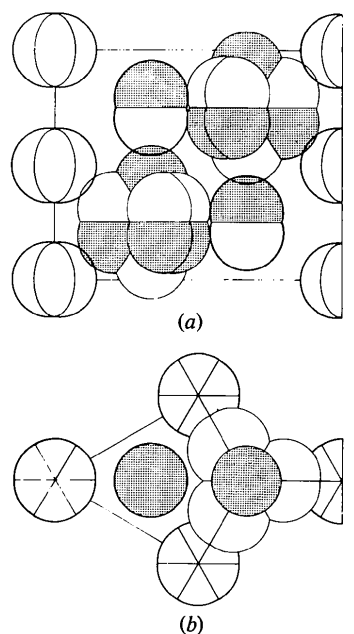
Table 1. *Starting positional parameters and weights assigned to the atoms in the different space groups*

Coordinates

	x	y	z
K(1)	0·002	0·040	0·010
K(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·755
S	$\frac{1}{3}$	$\frac{2}{3}$	0·245
O(1)	$\frac{1}{3}$	$\frac{2}{3}$	z_1
O(2)	0·205	0·410	z_2

Weights

	$P31c$	$P6_3mc$	$P\bar{3}1c$ and $P\bar{6}2c$	$P6_3/mmc$
K(1)	$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{12}$
K(2), S, O(2), O(1)	1	1	$\frac{1}{2}$	$\frac{1}{2}$

Table 2. *Final positional parameters*

	x	y	z
K(1)	0·002*	−0·037*	−0·019 (7)
K(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·797 (3)
S	$\frac{1}{3}$	$\frac{2}{3}$	0·252 (4)
O(1)	$\frac{1}{3}$	$\frac{2}{3}$	0·424 (2)
O(2)	0·185 (13)	0·411 (5)	0·195 (2)

* The K(1) atom is located at a distance $r = 0·037$ (9) from 0, 0, 0 (see Fig. 2). The S—O radius is 1·39 (2) Å. An overall temperature factor $\exp(-B \sin^2 \theta/\lambda^2)$ with $B = 9·3$ Å^2 has been found. $R = 3·45$. The number of free parameters is 7.

(a)

(b)

Fig. 1. The structure of α-K_2SO_4 projected on (a) (110) and (b) (001). Hatched and non-hatched atoms represent the two configurations which are statistically distributed among the cells. The O and K ions are depicted with the correct radius; the O ions are thinly drawn, the K ions thickly.

We subjected this hypothesis to a Hamilton test [see Hamilton (1965), example 3, and *International Tables for X-ray Crystallography* (1974)]. In both the single- and the split-atom models we allowed K(2) to have an anisotropic temperature factor. The result was strongly in favour of truly split-atom positions ($R = 3\cdot0$). The single position at $z = 0\cdot75$ ($R = 3\cdot6$) has to be rejected at the $0\cdot005$ level (*i.e.* the chance that we reject this hypothesis correctly is $99\cdot5\%$).

The sulphate ion shows two orientations, with the apices of the tetrahedra pointing in opposite directions along the c axis. The centres of both anions, the S atoms, appear to coincide. The distances from K(2) to the neighbouring S atoms, on the same threefold axis, are $3\cdot68$ and $4\cdot43$ Å. These distances are much longer than the corresponding distances ($3\cdot30$ and $4\cdot18$ Å) in the β-K$_2$SO$_4$ structure. However, only the longer distance is compatible with an O(1) atom between S and K(2). There must be a strong correlation in the **c** direction between the position chosen by K(2) and the orientation of the neighbouring SO$_4^{2-}$ ions. So at least in the short range there are two configurations, as depicted in Fig. 1. In an initial refinement the K(1) ion was kept at the origin exactly. The R factor dropped considerably when K(1) was allowed to move freely to a position $0\cdot2$ Å off the axis (it is almost independent of the direction of the displacement). The significance of this shift is demonstrated in Fig. 2, where the distance of K(1) to the axis is $a \times r$ Å. This small shift generates a 'pumpkin' around 0,0,0, which indicates that the thermal motion of the K(1) ion in the direction perpen-

dicular to the c axis is appreciably larger than is represented by the overall temperature factor B. it should be noted that in the structure of the β phase the corresponding cation positions form a zigzag chain along the c axis with an amplitude of $0\cdot46$ Å.

As mentioned above, Iwai, Sakai & Watanabe (1973) have carried out a structure analysis of α-K$_2$SO$_4$ based on three-dimensional Weissenberg data taken at 665 °C. They state that they have refined the structure, with anisotropic temperature factors, in the space group $P6_3mc$, obtaining a final (unspecified) R factor of $8\cdot7\%$. According to a figure, their final structure must be essentially the same as the polar structure we had to reject. They did not try a model with the symmetry $P6_3/mmc$. Unfortunately, all the information on the measured and calculated intensities is missing; a table of atomic positions is not provided; and cell dimensions at 665 °C are not mentioned. We do not even know how many reflections were used in the refinement. We are thus in a poor position to judge the validity of their statements.

Furthermore, Iwai, Sakai & Watanabe introduce a third modification of K$_2$SO$_4$ which they presume to exist over a temperature range of 15 °C in the neighbourhood of 587 °C. Our diffraction patterns do not show the slightest indication of such a phase, neither does the optical work of Shiozaki, Sawada, Ishibashi & Takagi (1977) nor the thermal work of Eysel (1971). Finally, Iwai, Sakai & Watanabe (1973) provide us with some thermal data. The ΔS at the phase transition is found to be $2\cdot3$ cal mol^{-1} K^{-1} which is in accordance with an order–disorder transition in which two equivalent configurations are involved (as they oddly enough state themselves).

The disordered structure of α-K$_2$SO$_4$ (which we propose, with a strong correlation in the direction of the c axis) is strongly supported by the work of Shiozaki, Sawada, Ishibashi & Takagi (1977) on the ferro-elasticity of K$_2$SO$_4$ at elevated temperatures. They observed moving domain walls in β-K$_2$SO$_4$ just below the phase-transition temperature of 587 °C. According to them, a number of tetrahedra flip over in the moving domain walls. Above 587 °C the domain-wall structure could no longer be observed. Their observations indicate a vanishing threshold energy for the flipping-over process as the temperature approaches 587 °C.

We conclude that the α-K$_2$SO$_4$ structure is most probably a dynamically disordered structure. A disorder in the orientation of SO$_4^{2-}$ ions has also been reported by Höfer, von Alpen & Eysel (1977) for Na$_2$SO$_4$(I) stabilized with Y$_2$(SO$_4$)$_3$. Complete rotational freedom has already been excluded on stereochemical grounds (Fischmeister, 1962). Our analysis provides some indications of large rotational vibrations of the anion. We find an S—O distance in the $P6_3/mmc$ structure which is 6% shorter than the value at room temperature (McGinnety, 1972); this could be accoun-
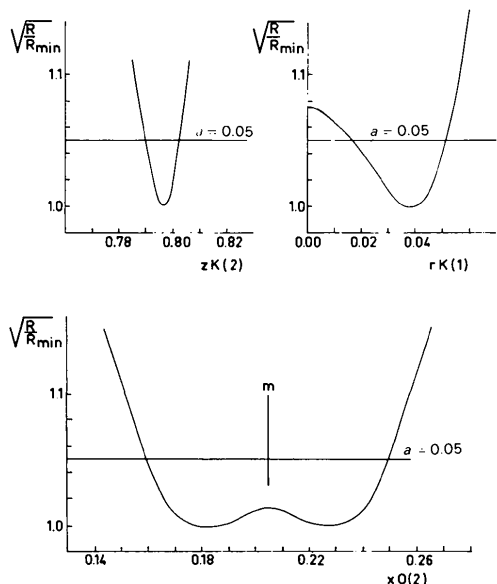

Fig. 2. $(R/R_{\min})^{1/2}$ as a function of three positional parameters. A significance level a of $0\cdot05$ from Hamilton (1965) shows the confidence intervals as not being symmetric for all parameters. The distance of K(1) to the line $00z$ is $5\cdot90r$ Å.

ted for by a root-mean-square amplitude of rotation of about 15°. This agrees well with the fact that the distance of O(2) to the mirror plane $y = 2x$ can be changed from 0 to 0·25 Å without significantly changing the value of $(R/R_{min})^{1/2}$, as the plot of x for O(2) in Fig. 2 shows.

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The Crystal Structure of Li₂Cu₅(Si₂O₇)₂ and the Proposal of New Values for the Effective Ionic Radii of Cu²⁺

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Synthetic copper lithium silicate, Li₂Cu₅(Si₂O₇)₂, is triclinic, $P\bar{1}$, with $a = 7·404$ (3), $b = 7·754$ (2), $c = 5·455$ (1) Å, $\alpha = 90·52$ (2), $\beta = 106·27$ (2), $\gamma = 114·64$ (3)°, $Z = 1$. The structure was deduced from Patterson syntheses and refined to $R = 0·040$ for 1203 observed reflexions. The structure contains Si₂O₇ pyrosilicate groups, three kinds of Cu²⁺ coordination polyhedra and one kind of trigonal bipyramidal coordinated Li⁺ ions. Cu(1) is in a square coplanar site, Cu(2) in an intermediate site between tetrahedral and square coplanar and Cu(3) in a distorted square pyramidal site. Based on the interionic distances between Cu²⁺ and O²⁻ in the recently determined structures, the following new values for the effective ionic radii are proposed: Cu²⁺(IV), 0·65 Å; (IV in IV + I or IV + II), 0·67 Å; (I or II in IV + I or IV + II), >0·9 Å.

Introduction

It is important, from the viewpoint of the coordination of divalent Cu ions, to investigate the crystal structure of copper silicates. Since natural specimens are frequently polycrystalline and very small, it is difficult to study them by X-ray single-crystal methods. Accordingly, the syntheses of these crystals are of substantial importance. Kawamura, Kawahara & Henmi (1976) first succeeded in synthesizing plancheite and shattuckite, and also obtained two new phases of anhydrous sodium copper silicates. These new phases have been found neither as natural minerals nor as synthetic products. The structure of the one of the phases (Na₂Cu₃Si₄O₁₂) was reported as a chain silicate (Kawamura & Kawahara, 1976), and that of the other