The Phase Transition of K_2SO_4 at about 850 K

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Dedicated to Professor Dr H. Jagodzinski on the occasion of his 65th birthday

Abstract

The crystal structure of K_2SO_4 was investigated by neutron diffraction in the region of the phase transition at 853 K. The β-K_2SO_4 structure was determined at 832 K. The high- or α-K_2SO_4 structure was studied at 847 and 913 K. At 832 K, $a = 5.927$ (4), $c = 7.882$ (4) Å, $R = 0.071$ for 469 observed reflections; at 847 K, $a = 5.886$ (4), $c = 8.118$ (4) Å, $R = 0.090$ for 70 observed reflections; at 913 K, $a = 5.917$ (4), $c = 8.182$ (4) Å, $R = 0.055$ for 100 observed reflections. The X-ray data obtained by Miyake, Morikawa & Iwai [*Acta Cryst.* (1980), B**36**, 532–536] at 1073 K were also included in the structure calculations. α-K_2SO_4 has the space group $P6_3/mmc$ and can be described by two models: the 'apex' model in which one apex of the SO_4 tetrahedron is oriented statistically 'up' and 'down' with respect to [001]; the 'edge' model in which one edge of the tetrahedron is parallel to [001] and three SO_4 groups are statistically superposed. It seems that the edge model is more likely at 847 and 913 K while the apex model is more likely at 1073 K. In the region of the phase transition the orientation of the tetrahedra is still correlated as can be deduced from the observation of diffuse reflections. Crystals grown at room temperature from aqueous solution incorporate OH_3^+ ions. They decay in the temperature region from 573 to 723 K. Single crystals are usually destroyed by this process.

Introduction

The crystal structure of β-K_2SO_4 at room temperature was investigated by Ehrenberg & Hermann (1929),

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Robinson (1958) and McGinnety (1972). The β phase transforms into the α phase at a transition temperature of ~853 K. This value is obtained by DTA (differential thermal analysis) of powder samples (Eysel, 1971). However, El-Kabbany (1980) has reported a hysteresis with a transition temperature of 844 K at heating and 839 K at cooling. The high or α phase is the representative for a structure type into which a great number of chemical compounds transform at high temperatures. Iwai, Sakai & Watanabe (1973) first investigated the α-K_2SO_4 structure using single crystals and the X-ray photographic Weissenberg technique, but no atomic position parameters were reported. They confirmed the structure model proposed by Hahn & Eysel (1970) and Eysel (1971). According to these authors the α-K_2SO_4 structure belongs to the space group $P6_3mc$ and all tetrahedra have one apex pointing in the same direction, [001]. During our investigation van den Berg & Tuinstra (1978) reported X-ray diffraction studies. They used powder samples and took photographs with a Simon–Guinier camera. They determined for α-K_2SO_4 the centrosymmetric space group $P6_3/mmc$. In their structure model, the SO_4 tetrahedra are disordered in such a way that, in the mean, one apex is statistically pointing up and one down the [001] direction. In our paper this is called the 'apex' model. Furthermore, they determined a split position for the potassium atom above and below the SO_4 tetrahedra. The apex model has been discussed by many authors: Fischmeister (1962) and Bernard & Hocart (1961) derived this model by discussing the lattice parameters as a function of temperature. Shiozaki, Sawada, Ishibashi & Tagagi (1977) observed twin domains in β-K_2SO_4. When this paper had already been submitted for publication, Miyake, Morikawa & Iwai (1980) published the results of their structure determination of α-K_2SO_4. They confirmed the apex model without the split position of the potassium atoms.

We included their measured data in our structure calculations.

In the region of the phase transition at 853 K several anomalies were observed with different physical methods. Watanabe, Sakai & Iwai (1973) investigated the dielectric constants, Miyake, Minato & Iwai (1977, 1979) and El-Kabbany (1980) the specific heat. The Japanese group observed also an 'intermediate phase' under the microscope in the temperature range 843–860 K. Kolontsova, Kulago, Byakhova & Mihailenko (1973) detected an increase of the diffuse intensity of X-rays below the β–α phase transition. Majumdar & Roy (1965) and Arnold, Kurtz & Grimm (1980) concluded from the temperature dependence of the lattice constants that the phase transition is of first order with a large contribution of second-order terms. Using inelastic neutron scattering, Arnold *et al.* (1980) investigated the phonon dispersion of the β and α phases. In the direction of the hexagonal axis of α-K_2SO_4 a 'soft longitudinal acoustic mode' was observed, but there is no indication of an incommensurate phase transition at low temperatures similar to that of K_2SeO_4. The latter was observed by Aiki (1970) at 77 K.

The purpose of the present investigation was to study the crystal structure of K_2SO_4 in the temperature range of the β–α phase transition to obtain an insight into the underlying mechanism. In particular, we are interested in a structural basis for a model of the soft longitudinal acoustic mode which was observed for the first time in the case of K_2SO_4.

Experimental

K_2SO_4 (*p.a.* Merck company) was used for the growth of single crystals from aqueous solution. The crystals, which were obtained from a solution at room temperature, burst into pieces when they were heated to ~ 570 K. This effect had already been reported by Mallard (1882) and Retgers (1890). They ruled out the incorporation of water. However, under a hot-stage microscope one can observe the growth of small bubbles in the crystal. These bubbles are filled with water. When the vapour pressure becomes too high the crystal explodes. Apparently the reaction

$$[K_{1-x}(OH_3)_x]_2SO_4 \xrightarrow{570\ K} (K_{1-x}H_x)_2SO_4 + 2xH_2O\uparrow$$
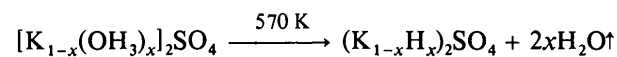
occurs. The amount of water is small ($x \ll 1$). From 50 g K_2SO_4 dried in vacuum three small drops were collected after the dehydration. At about 720 K a recombination of hydrogen occurs:

$$(K_{1-x}H_x)_2SO_4 \xrightarrow{720\ K} (K_{1-x}\square_x)_2SO_4 + xH_2\uparrow.$$
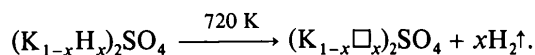
The fragments become opaque and electrically charged.

It takes about five minutes for the charge to be compensated, possibly by a reaction like

$$2(K_{1-x}\square_x)_2SO_4 \xrightarrow{720\ K} (2 - 2x)K_2SO_4$$
$$+ 2xSO_3\uparrow + xO_2\uparrow.$$
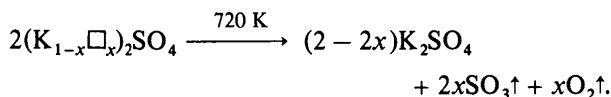
The resulting sample can be cooled and reheated without showing the effects just described. Large crystals grown from aqueous solution at 350–360 K contain less OH_3^+ and can survive the heat treatment. Bernard & Hocart (1961) have observed an anomaly in the lattice expansion of K_2SO_4 powder in the temperature range 570 to 720 K. They interpreted their observation as an additional phase transition.

Out of clear and transparent regions of large crystals, cubes of approximately $4 \times 4 \times 4$ mm were cut according to the orthorhombic axes. Neutron diffraction measurements were performed on the four-circle instrument P32 of the Kernforschungszentrum Karlsruhe. A monochromatic neutron beam ($\lambda = 1\cdot0237$ Å) was obtained from a focusing Cu (311) crystal. The integrated intensities were measured by ω scans with 27 or 31 steps and a range of $1\cdot62$ to $2\cdot17°$ depending on the resolution of the instrument. The standard deviation of each reflection intensity I was estimated to be $\sigma(I) = [\sigma^2(\text{counting statistics}) + (0\cdot02I)^2]^{1/2}$. Absorption effects were not taken into account.

The β phase was studied at $832 \pm 0\cdot5$ K. The lattice constants were obtained by a least-squares fit of eight reflections. One quarter of reciprocal space in the range $5 \leq 2\theta \leq 60°$ was measured containing 758 reflections (including standard reflections). After the measurement at 832 K the crystal was heated up to 847 K. At this temperature the neighbourhood of strong reflections was checked for satellite reflections, but new reflections were not observed. The reflections with $h + k = 2n$ slowly disappeared. After three days at 847 K the crystal was totally transformed into the α phase. Again, one quarter of reciprocal space in the range of $5 \leq 2\theta \leq 60°$ was measured. From the resulting 412 reflections the intensity in 186 cases did not exceed the 2σ limit (unobserved reflections). The lattice parameters were obtained from eight reflections. At 913 K a second crystal was measured in the range $5 \leq 2\theta \leq 70°$. In one eighth of reciprocal space 228 reflections (98 unobserved) were taken. The lattice parameters were obtained from six reflections. During the measurement of the α phase the indices hkl of the β phase were maintained.

Symmetry and unit cell

A phase transition is conventionally described in terms of the structure with highest symmetry. The crystal structure of α-K_2SO_4 belongs to the space group

$P6_3/mmc$. The symmetry of the room-temperature structure can be deduced by the following subgroup relations:

$$P6_3/mmc \xleftrightarrow{\;3\;} Cmcm \xleftrightarrow{\;2\;} Pmcn = Pnma.$$

The number above the arrows indicates the index of the related symmetry reduction.

In order to compare the different structures a common unit cell is used, i.e. the orthohexagonal cell. This is an orthorhombic unit cell with a_o, b_o, c_o obtained from the hexagonal basis vectors a_h, b_h, c_h by $a_o = a_h$, $b_o = a_h + 2b_h$, $c_o = c_h$. The origin is chosen at the point which has the point symmetry $\bar{3}m$ in the α phase. The symmetry operations in this unit cell are listed in Table 1. The first eight operations given are those of the space group $Pmcn$. The space group $Cmcm$ is derived from $Pmcn$ by introducing a C centring within the unit cell. $P6_3/mmc$ is obtained from $Cmcm$ by adding a threefold rotation axis at $0,0,z$. The relations between the special positions in these space groups are given in Table 2.

In Fig. 1 is shown the room-temperature structure of K_2SO_4 with the different unit cells in use. The details of the transformations are given in the Appendix.

Lattice parameters are listed in Table 3. The lattice expands from room temperature to 832 K by 11%, 2%

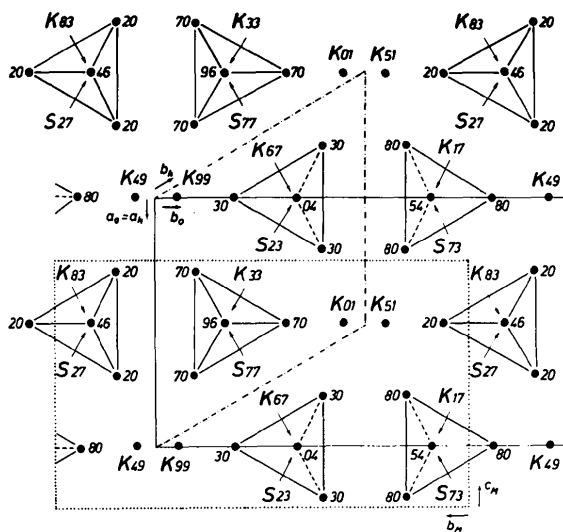with the phase transition, and another 5% between 847 and 1073 K.

Fig. 1. The K_2SO_4 structure at room temperature according to McGinnety (1972). (——) Orthohexagonal unit cell with basis vectors a_o, b_o, c_o as used in this paper. (—·—·—) Hexagonal unit cell with basis vectors a_h, b_h, c_h as used in *International Tables for X-ray Crystallography* (1969). (..........) Orthorhombic unit cell with the basis vectors a_M, b_M, c_M as used by McGinnety (1972).

Table 1. *Symmetry operations of space group $P6_3/mmc$ (No. 194), Wyckoff position (1), referring to an orthohexagonal unit cell with basis vectors a, $b = a\sqrt{3}$, c; $\alpha = \beta = \gamma = 90°$*

The origin is at $\bar{3}2/mc$. The first two rows contain the symmetry operations of the space group $Pmcn$ (No. 62) with origin at $mc2_1$. To these operations the symmetry element of a threefold rotation axis at $0, 0, z$ is applied. The orthohexagonal cell is C centred.

$(0,0,0; \frac{1}{2},\frac{1}{2},0) +$

x,y,z;	$\bar{x},\bar{y},\frac{1}{2}+z$;	$\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$;	$\frac{1}{2}+x,\frac{1}{2}-y,\bar{z}$;
$\frac{1}{2}-x,\frac{1}{2}-y,\bar{z}$;	$\frac{1}{2}+x,\frac{1}{2}+y,\frac{1}{2}-z$;	$x,\bar{y},\frac{1}{2}+z$;	$\bar{x},y,z$;
$\frac{1}{2}(-x-3y,x-y,2z)$;	$\frac{1}{2}(x+3y,-x+y,1+2z)$;	$\frac{1}{2}(x-3y,-x-y,1-2z)$;	$\frac{1}{2}(-x+3y,x+y,2\bar{z})$;
$\frac{1}{2}(x+3y,-x+y,2\bar{z})$;	$\frac{1}{2}(-x-3y,x-y,1-2z)$;	$\frac{1}{2}(-x+3y,x+y,1+2z)$;	$\frac{1}{2}(x-3y,-x-y,2z)$;
$\frac{1}{2}(-x+3y,-x-y,2z)$;	$\frac{1}{2}(x-3y,x+y,1+2z)$;	$\frac{1}{2}(1+x+3y,1+x-y,1-2z)$;	$\frac{1}{2}(1-x-3y,1-x+y,2\bar{z})$;
$\frac{1}{2}(1+x-3y,1+x+y,2\bar{z})$;	$\frac{1}{2}(1-x+3y,1-x-y,1-2z)$;	$\frac{1}{2}(-x-3y,-x+y,1+2z)$;	$\frac{1}{2}(x+3y,x-y,2z)$.

Table 2. *Relation between the Wyckoff positions in the space groups $P6_3/mmc$, $Cmcm$ and $Pmcm$, orthohexagonal unit cell*

Model	Edge		Apex				Room temperature	
Space group	$P6_3/mmc$		$P6_3/mmc$		$Cmcm$		$Pmcm$	
K(1)	$2(a)$ $\bar{3}m$	$0,0,0$	$2(a)$ $\bar{3}m$	$0,0,0$	$4(a)$ $2/m$	$0,0,0$	$4(c)$ m	$0,y,z$
K(2)	$2(d)$ $\bar{6}m2$	$0,\frac{1}{3},\frac{3}{4}$	$2(d)$ $\bar{6}m2$	$0,\frac{1}{3},\frac{3}{4}$	$4(c)$ $m2m$	$0,y,\frac{3}{4}$	$4(c)$ m	$0,y,z$
S	$2(c)$ $\bar{6}m2$	$0,\frac{1}{3},\frac{1}{4}$	$2(c)$ $\bar{6}m2$	$0,\frac{1}{3},\frac{1}{4}$	$4(c)$ $m2m$	$0,y,\frac{1}{4}$	$4(c)$ m	$0,y,z$
O(1)	$6(h)$ $m2m$	$0,y,\frac{1}{4}$	—		—		—	
			$4(f)$ $3m$	$0,\frac{1}{3},z$	$8(f)$ m	$0,y,x$	$4(c)$ m	$0,y,z$
O(2)	$12(k)$ m	$0,y,z$	$12(k)$ m	$0,y,z$	$8(f)$ m	$0,y,z$	$4(c)$ m	$0,y,z$
O(3)	—		*		$16(h)$ 1	x,y,z	$8(d)$ 1	x,y,z

$* x[O(3)]_{ortho} = \frac{1}{3}\bar{y}[O(2)]_{hex}$, $y[O(3)]_{ortho} = \frac{1}{3}\bar{y}[O(2)]_{hex}$, $z[O(3)]_{ortho} = z[O(2)]_{hex}$,

$x[O(3)]_{hex} = 2\bar{x}[O(2)]_{hex}$, $y[O(3)]_{hex} = \bar{x}[O(2)]_{hex}$, $z[O(3)]_{hex} = z[O(2)]_{hex}$.

Table 3. *Unit-cell constants, pseudohexagonal angle γ and density*

T (K)	a (Å)	b (Å)	c (Å)	γ† (°)	V (Å³)	D_{cell} (Mg m⁻³)	D_{bulk} (Mg m⁻³)	References
293	5·776 (5)	10·08 (1)	7·456 (6)	119·81 (10)	434 (1)	2·658 (5)	2·621 (4)	Robinson (1958)
293	5·763 (2)	10·071 (4)	7·476 (3)	119·78 (3)	433·9 (5)	2·667 (2)	2·662*	McGinnety (1972)
832	5·927 (4)	10·318 (4)	7·882 (4)	119·87 (3)	482 (1)	2·401 (4)	—	This work
847‡	5·886 (4)	10·209 (4)	8·118 (4)	119·97 (3)	488 (1)	2·372 (4)	—	This work
913	5·917 (4)	10·240 (4)	8·182 (4)	120·02 (3)	496 (1)	2·334 (4)	—	This work
1073	5·947 (2)	10·301	8·375 (3)	120	513·02	2·26	—	Miyake *et al.* (1980)

* *Handbook of Chemistry and Physics* (1975).

† $\gamma = 90° + \arctan(a/b)$.

‡ After the phase transition.

Structure determination

For the structure calculations the computer program XRAY 72 of Stewart, Kruger, Ammon, Dickinson & Hall (1972) was used. The scattering lengths S = 2·847, K = 3·71 and O = 5·803 fm were listed by Koester (1977). Statistical tests applied to the data sets gave no convincing support for the existence of a centre of symmetry.

The β-K_2SO_4 structure at 832 K was refined from the parameters of the room-temperature structure published in McGinnety (1972). The resulting parameters are in close agreement with those at room temperature and slightly shifted towards the special positions of the α-K_2SO_4 structure. In the β structure the apices of the SO_4 tetrahedra are ordered owing to symmetry. Half of them are pointing up and the other half down the c axis. At 832 K the thermal motion of the atoms is increased but no anomaly was detected. The structure parameters are given in Tables 4 and 5.

The derivation of the α-phase structure was more tedious. There are only three times more observed independent reflections than parameters to be determined. There were difficulties in the refinement based on F. When the reliability factor based on F decreased, the reliability factor based on I increased. The refinement based on F tended to give better agreement for reflections with medium or low intensity and worse agreement for strong reflections. The refinement based on F encouraged the introduction of split positions for the atoms without a convincing gain in the agreement factors. As the measured quantities are the intensities I the refinement was finally based on I. This gave an overall better agreement favouring the special positions of the unit cell. For the weighting scheme the experimental standard deviations of I were used. A refinement in space group Cmcm was attempted with no success. Finally, the intensities of symmetrical equivalent reflections were averaged according to the symmetry of space group $P6_3/mmc$.

Table 4. *Positional parameters*

The oxygen atoms O(2) and O(3) of the apex model belong to the same special position.

Temperature (K)		293	832	847	913	1073	847	913	1073
Model		McGinnety	*Pmcm*	Apex	Apex	Miyake *et al.*	Edge	Edge	Edge
K(1)	x	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0
	y	0·04594 (10)	0·0364 (5)	0·0	0·0	0·0	0·0	0·0	0·0
	z	−0·01104 (13)	−0·0081 (9)	0·0	0·0	0·0	0·0	0·0	0·0
K(2)	x	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0
	y	0·33938 (11)	0·3362 (7)	0·3333	0·3333	0·3333	0·3333	0·3333	0·3333
	z	0·67377 (15)	0·6920 (11)	0·75	0·75	0·75	0·75	0·75	0·75
S	x	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0
	y	0·33029 (10)	0·3322 (7)	0·3333	0·3333	0·3333	0·3333	0·3333	0·3333
	z	0·23298 (15)	0·2401 (10)	0·25	0·25	0·25	0·25	0·25	0·25
O(1)	x	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0
	y	0·3334 (4)	0·3345 (7)	0·3333	0·3333	0·3333	0·1981 (33)	0·1966 (5)	0·1970 (28)
	z	0·0379 (5)	0·0596 (8)	0·066 (10)	0·0718 (27)	0·089 (5)	0·25	0·25	0·25
O(2)	x	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0
	y	0·1918 (2)	0·1988 (4)	0·2038 (14)	0·2041 (5)	0·213 (2)	0·250 (5)	0·2552 (10)	0·267 (4)
	z	0·2963 (5)	0·2942 (8)	0·303 (6)	0·2983 (37)	0·311 (3)	0·384 (7)	0·3900 (13)	0·376 (4)
O(3)	x	0·2098 (11)	0·1996 (5)	0·1943 (14)	0·1938 (5)	0·181 (2)	—	—	—
	y	0·3978 (3)	0·3967 (3)	0·3981 (14)	0·3979 (5)	0·394 (2)	—	—	—
	z	0·3009 (4)	0·2973 (6)	0·303 (6)	0·299 (4)	0·311 (3)	—	—	—

Table 5. Mean square displacement (Å²)

$$U = (p_{11}U_{11} + p_{22}U_{22} + p_{33}U_{33})/(p_{11} + p_{22} + p_{33}) \text{ with } p_{ll} = 1/\sigma_{ll}^2(U_{ll}).$$

The anisotropic thermal parameters are expressed in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$

Temperature (K)	293	832	847	813	1073	847	913	1073
Model	McGinnety	*Pmcn*	Apex	Apex	Miyake *et al.*	Edge	Edge	Edge
K(1)	0·0207 (10)	0·070 (5)	0·132 (4)	0·127 (10)	0·139 (6)	0·133 (11)	0·132 (13)	0·132 (9)
K(2)	0·0230 (8)	0·077 (13)	0·074 (46)	0·105 (39)	0·080 (8)	0·075 (53)	0·109 (36)	0·091 (11)
S	0·0148 (4)	0·038 (2)	0·047 (3)	0·047 (10)	0·098 (9)	0·044 (2)	0·044 (12)	0·088 (4)
O(1)	0·0257 (56)	0·129 (38)	0·310 (47)	0·211 (89)	0·104 (33)	0·074 (25)	0·081 (28)	0·075 (34)
O(2)	0·0229 (54)	0·082 (20)	0·095 (13)	0·111 (18)	0·097 (2)	0·241 (3)	0·239 (9)	0·069 (11)
O(3)	0·0264 (51)	0·084 (19)	—	—	—	—	—	—

The observed structure factors published by Miyake *et al.* (1980) were also refined. They reported only observed F values without standard deviations. Therefore, we refined the 1073 K X-ray data in the same manner as the authors, with unit weights. Our refinement of the apex model confirmed the published parameters within one standard deviation.

The main features of the structure can be seen on the Fourier maps of the mirror planes $0,y,z$, Fig. 2, and x, $y,\frac{1}{4}$, Fig. 3. At 832 K the positions of the atoms are well resolved. The thermal motion of the K(1) and S atoms is large in the direction towards their position in the α phase. The SO_4 tetrahedron oscillates in the mirror plane. At 913 K the signs of the F values are independent of the edge and apex models (see below). Owing to the reduced number of observed structure factors contributing to the map, the scale of the neutron scattering density is reduced by half. The potassium and sulphur atoms occupy special positions with fixed

coordinates. The anisotropic temperature factors are still large in the direction of the shift associated with the phase transition. In particular, the elongation of the K(2) atom towards the SO_4 tetrahedron in [001] is extremely large. At 1073 K the electron density map was computed with the signs of the apex model. The edge model differs in the signs of eight very weak reflections. The differences in the Fourier maps of 913 and 1073 K are mainly due to the difference between nuclear density and electron density. However, it can be seen that the elongation of the K(2) position in [001] is reduced.

The structure determination at 913 K gave, in general, a better fit to the measured data than that at 847 K. The region of measurement at 913 K was larger; of the 30 additional reflections in the sphere only six were observable. It seems that after annealing for three days the crystal had not reached its equilibrium state. Although the results have larger standard
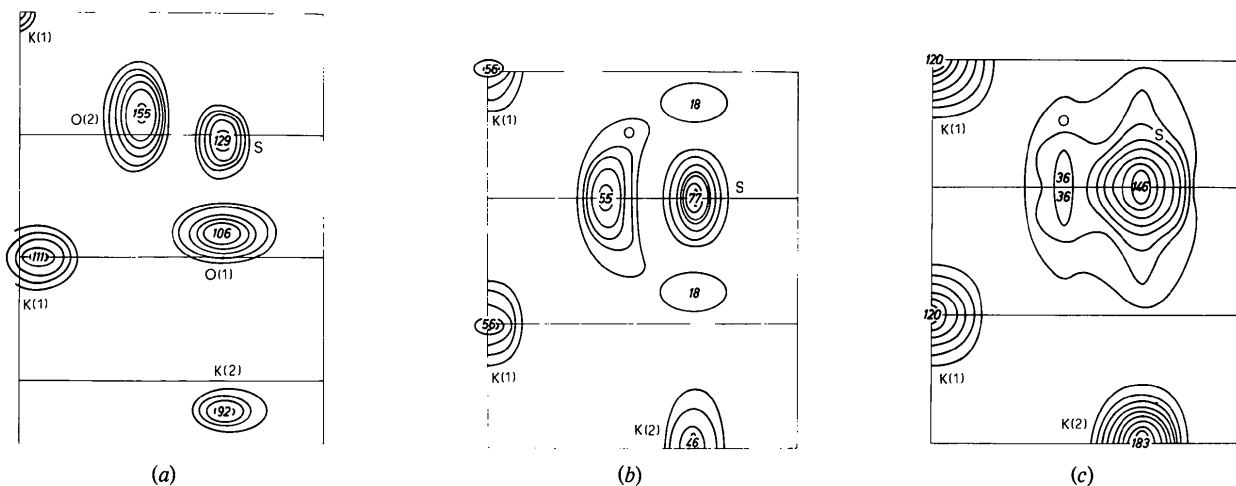

Fig. 2. Fourier map of the mirror plane $0,y,z$ with $0 \le y \le \frac{1}{2}$ and $-0·4 \le z \le \frac{1}{2}$. (*a*) Low-$K_2SO_4$ structure at 832 K, neutron scattering mass density. (*b*) High-K_2SO_4 structure at 913 K, neutron scattering mass density. (*c*) High-K_2SO_4 structure at 1073 K, electron density. The signs of the F values were obtained from the apex model in accordance with Miyake *et al.* (1980).
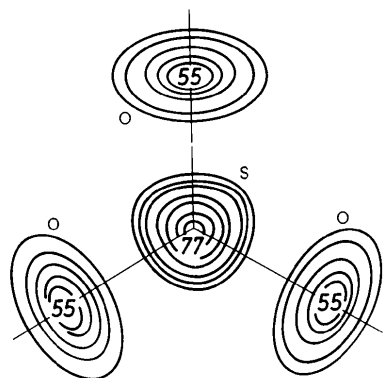
Fig. 3. Fourier map of the mirror plane at x, y,$\frac{1}{4}$ of high-K$_2$SO$_4$ at 913 K, neutron scattering mass density: section through the disordered SO$_4$ group.

deviations they follow the trend and therefore they are reported here also.

The α-K$_2$SO$_4$ structure can be described by two models. Schematic drawings are given in Fig. 4. The two models can be roughly explained as follows.

Apex model

In this model the centres of the SO$_4$ tetrahedra remain at the position of the low-temperature structure. One of their apices points up and down randomly with respect to [001]. The symmetry common to a position of a particular tetrahedron and to the lattice is $3m$. The model can also be described by assuming that owing to the new mirror plane at x,y,$\frac{1}{4}$ the room-temperature structure is statistically superimposed.

Edge model

This model differs from the apex model only in the orientation of the SO$_4$ tetrahedra. In this case, three

tetrahedra are statistically superimposed. One edge of the tetrahedron is parallel to the threefold axis, the remaining two apices lie in the mirror plane x,y,$\frac{1}{4}$. The symmetry common to a particular tetrahedron and the lattice is $mm2$.

Discussion

The reliability factors are summarized in Table 6.* For the α phase the apex and edge models each gave good agreement with the measured data. If we consider the small differences of the R values as significant then the edge model seems to be more likely at 847 and 913 K and the apex model seems to be favoured at 1073 K. This can be supported by the discussion of the interatomic distances. However, the anisotropic temperature factors indicate large fluctuations in the structure. The average distances of the bulk structure are not necessarily those of a local configuration.

At 874 and 913 K the tetrahedra in the apex model have S–O distances 1·69 (8) and 1·65 (2) Å, Table 7, which exceed the values of all other sulphates which were listed by Louisnathan, Hill & Gibbs (1977). In contrast, the K(2)–O(1) distances of 2·57 (8) and 2·63 (2) Å are too short. These distances, however, are coupled with large mean square displacements U_{33} of 0·5 and 0·3 Å^2 for K(2). These displacements are five times larger than the displacements normal to the [001] direction (Table 8). Apparently the position of the K(2) atom is not well defined. If an SO$_4$ tetrahedron comes into an up position the potassium atom above the tetrahedron may move upwards. If the next tetrahedron is in a down position the displacement of the
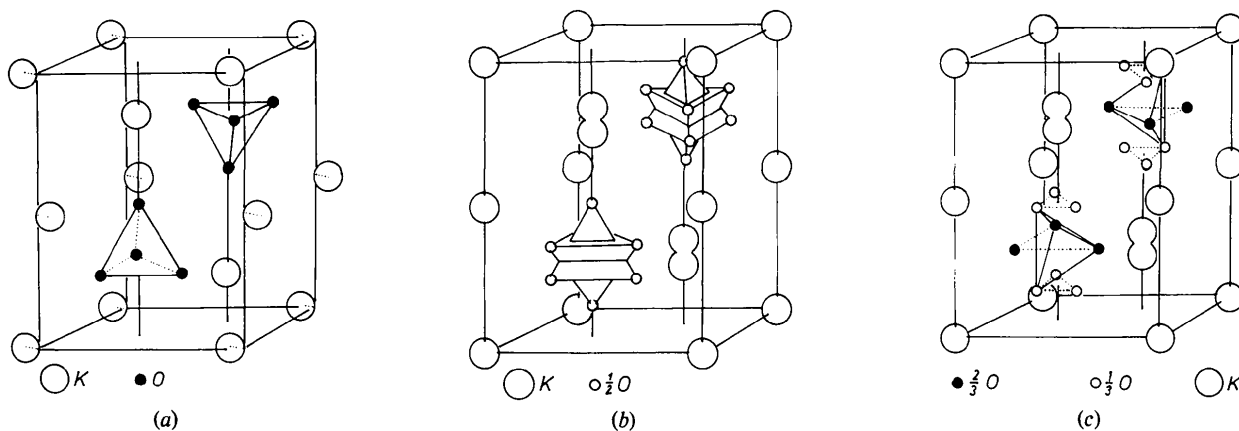
Fig. 4. Schematic drawing of the K$_2$SO$_4$ structure model. (a) Low-K$_2$SO$_4$, half of the unit cell. (b) High-K$_2$SO$_4$, apex model. (c) High-K$_2$SO$_4$, edge model.

Table 6. *Statistics and agreement factors*

Temperature (K)	832	847	913	1073	847	913	1073
				Miyake			
Model	Pmcn	Apex	Apex	et al.	Edge	Edge	Edge
Number of observations	469	70	100	66	70	100	66
Number of contributing reflections	392	55	61	66	53	65	66
Number of variables	40	16	16	16	17	17	17
Number of unobserved	187	26	38	—	26	38	—
R factors:							
F omitting unobserved	0·071	0·090	0·055	0·089	0·065	0·050	0·106
Weighted F omitting unobserved	0·114	0·115	0·098	0·074	0·094	0·095	0·082
F^2 omitting unobserved	0·093	0·092	0·063	—	0·070	0·046	—
I omitting unobserved	0·079	0·068	0·046	—	0·051	0·031	—

Table 7. *Interatomic distances* (Å)

	Temperature (K)	293	832	847	913	1073
						Miyake
	Model	McGinnety	Pmcn	Apex	Apex	et al.
S—O(1)	0,y,z	1·446 (4)	1·423 (10)	1·491 (79)	1·457 (22)	1·348 (45)
—O(2)	0,y,z	1·460 (4)	1·440 (9)	1·389 (14)	1·382 (9)	1·343 (9)
—O(3)	±x,y,z	1·464 (4)	1·430 (5)			
K(1)—O(1)	0,y,z	2·918 (7)	3·122 (9)	3·443 (13)	3·466 (4)	3·514 (10)
—O(1)	±½,½ − y, −z	3·149 (7)	3·275 (4)			
—O(2)	0,y,z	2·727 (5)	2·914 (9)	3·220 (34)	3·213 (23)	3·408 (18)
—O(3)	±½ ∓ x,½ − y, −z	2·795 (6)	2·974 (7)			
—O(2)	0, −y, z − ½	2·844 (5)	2·884 (8)	2·624 (27)	2·663 (19)	2·702 (14)
—O(3)	±½ ∓ x,y − ½,½ − z	2·737 (6)	2·830 (6)			
K(2)—O(1)	0, y, 1 + z	2·723 (3)	2·898 (11)	2·568 (79)	2·631 (22)	2·840 (45)
—O(2)	±½,½ − y, −z	2·907 (5)	2·987 (2)	3·000 (11)	3·009 (5)	3·055 (13)
—O(2)	0,y,z	3·190 (5)	3·440 (11)	3·862 (36)	3·920 (22)	3·877 (22)
—O(3)	±x,y,z	3·095 (8)	3·386 (9)			
—O(3)	±x, 1 − y,½ + z	3·061 (8)	3·112 (8)	3·000 (11)	3·009 (5)	3·055 (10)
—O(3)	±½ ∓ x,½ − y, −z	2·922 (8)	2·992 (6)			
S—O(1)*		1·459 (4)	1·526 (10)	1·688 (79)	1·654 (22)	1·42 (4)
—O(2)*		1·473 (4)	1·499 (9)	1·447 (14)	1·452 (9)	1·43 (2)
—O(3)*		1·477 (4)	1·474 (5)			

Table 7 (*cont.*)

		847	913	1073
Temperature (K)		Edge	Edge	Edge
Bond	Multiplicity			
S—O(1)	2	1·379 (1)	1·401 (1)	1·4044 (5)
—O(2)	2	1·381 (42)	1·397 (9)	1·256 (26)
K(1)—O(1)	4	2·864 (1)	2·870 (1)	2·916 (1)
—O(2)	4	2·719 (18)	2·766 (4)	2·938 (11)
K(2)—O(1)	4	2·962 (20)	2·974 (4)	2·990 (17)
—O(2)	2	3·088 (51)	3·051 (10)	3·210 (30)
—O(2)	2	3·254 (31)	3·299 (7)	3·318 (22)
S—O(1)*	2	1·423 (1)	1·437 (1)	1·439 (1)
—O(2)*	2	1·54 (4)	1·518 (9)	1·27 (3)

* Corrected values according to the riding-atom model of Busing & Levy (1964).

potassium atom may trigger a flipping of the tetrahedron from the down into the up position. Thus at these temperatures there must be a correlation between the tetrahedra which lie on a particular threefold axis.

At 1073 K the edge model has the more distorted tetrahedra. This is seen by comparing the S—O distances in Table 7 and the O—S—O angles in Table 9. The mean square displacement U_{33} of K(2) is decreased considerably. The K(2)—O(1) distance is still small but tolerable.

One can calculate the K(2)—K(2) distance on the threefold axis with one SO_4 tetrahedron in between, with the normal ion radii (O = 1·40 and K = 1·33 Å) and distances (S—O = 1·46 Å). In the ordered arrangement 'one apex up' the K—K distance becomes 7·22 Å, in the edge model 7·89 Å, and in the apex model, i.e. tetrahedra simultaneously up and down, 8·38 Å. These correspond to the c lattice constants at about 0, 832 and 1050 K respectively. One can discuss the phase transition by referring to the volume of the cage defined by the atoms K(1). At low temperatures the space allows only an ordered arrangement of the tetrahedron in the cage. When the c axis becomes large enough the tetrahedra may flip. However, the edge model is more likely since the tetrahedra fit better into the cage. When the c axis becomes large enough the apex model becomes more probable. The α-K_2SO_4 structure is in dynamical equilibrium, i.e. the tetrahedra do not have a

Table 8. *Mean square displacement* ($Å^2$) *of the potassium atom* K(2)

The anisotropic thermal parameters are expressed in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2})]$.

Temperature (K)	293	832	847	913	1073	847	913	1073
Model	McGinnety	*Pmcn*	Apex	Apex	Miyake *et al.*	Edge	Edge	Edge
U_{11}	0·0214 (5)	0·069 (5)	0·06 (3)	0·088 (12)	0·076 (5)	0·06 (3)	0·095 (8)	0·086 (6)
U_{22}	0·0243 (5)	0·066 (5)	0·06 (3)	0·088 (12)	0·076 (5)	0·06 (3)	0·095 (8)	0·086 (6)
U_{33}	0·0232 (5)	0·112 (7)	0·48 (12)	0·283 (27)	0·112 (10)	0·50 (11)	0·30 (2)	0·144 (14)

Table 9. *Bonding angles in the* SO_4 *tetrahedron* (°)

Temperature (K)		293	832	847	913	1073
Model		McGinnety	*Pmcn*	Apex	Apex	Miyake *et al.*
Bond	Multiplicity					
O(1)–S–O(2)	1	110·0	108·2 (6)			
O(1)–S–O(3)	2	109·6	107·9 (4)	108·0 (18)	106·6 (12)	112·5 (9)
O(2)–S–O(3)	2	109·1	110·6 (4)			
O(3)–S–O(3)	1	109·6	111·6 (5)	110·9 (13)	112·2 (8)	106·2 (9)

Table 9 (*cont.*)

Temperature (K)		847	913	1073
Model		Edge	Edge	Edge
Bond	Multiplicity			
O(1)–S–O(1)	1	120·0 (12)	120·0 (2)	120·0 (10)
O(1)–S–O(2)	4	107·9 (13)	106·7 (3)	105·9 (10)
O(2)–S–O(2)	1	104·2 (19)	110·0 (4)	113·7 (11)

fixed position but oscillate with large amplitudes and the models just described are only special positions in this motion.

With rising temperature some of the S—O distances seem to decrease. The distances were corrected according to the riding-atom model of Busing & Levy (1964). It seems that this correction is insufficient.
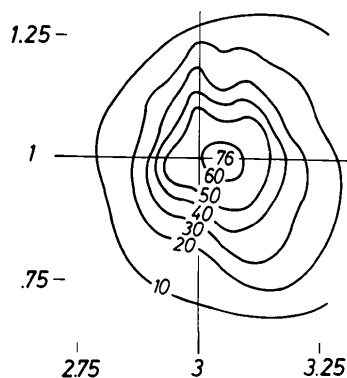

Fig. 5. Diffuse neutron scattering intensity at 867 K measured on a triple-axis spectrometer with energy transfer $v = 0$: the region in the 0*kl* plane around the position 013. The diffuse scattering is mainly due to fluctuations and correlations in the high-K_2SO_4 structure.

The structure fluctuations and resulting short-range-order effects can be observed. The strong reflection 013 should vanish at the phase transition, but a broad diffuse peak remains. This has been measured with a triple-axis neutron spectrometer. The distribution of intensity is shown in Fig. 5. The inelastic scattering, *i.e.* the influence of the thermal diffuse background, was suppressed.

The phenomenon of the soft longitudinal acoustic mode can be discussed as follows. The K(1) atoms form an ordered chain on the 6_3 axes; the K(2) atoms together with the SO_4 tetrahedra form a disordered chain on the 3 axes. The energy of waves is absorbed by increasing the oscillations and the disorder of the K(2)–SO_4 chains. Thus all waves are damped, especially the longitudinal acoustic mode in [001]. In this direction the crystal acts like a shock absorber.

Höfer (1979) has investigated the Na_2SO_4 I structure and came to similar conclusions to those reported in this paper.

APPENDIX

The different unit cells and choices of axes are shown in Fig. 1. The transformation from one system to the others is achieved by the following matrices.

Orthohexagonal to hexagonal unit cell:

$$P = \begin{pmatrix} 1 & -\frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad Q = \begin{pmatrix} 1 & 1 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

Orthohexagonal to orthorhombic unit cell as used by McGinnety (1972):

$$P = \begin{pmatrix} 0 & 0 & \bar{1} & \frac{1}{4} \\ 0 & \bar{1} & 0 & \frac{3}{4} \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad Q = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & \bar{1} & 0 & \frac{3}{4} \\ \bar{1} & 0 & 0 & \frac{1}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

The matrix P is applied to the row matrix $(\mathbf{a},\mathbf{b},\mathbf{c},0)$, *i.e.* $(\mathbf{a},\mathbf{b},\mathbf{c},0)P$. The matrix Q is applied to the column matrix $(x,y,z,1)$, *i.e.*

$$Q \begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix}.$$

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