OH2(*A*) atom of $Pt_8Cd_{40}$. The *B* clusters of the two Pt–Cd structures are also very similar. The two OH(*B*)–CO(*B*) contacts are lost for one of the atoms [OH2(*B*)], reducing the CN for this atom from 13 to 11. Two of the CO(*B*) atoms in $Pt_8Cd_{41}$ have CO(*B*)–OH(*B*) contacts which are longer (2·739 Å) in the $Pt_8Cd_{40}$ structure.

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# Structure Reinvestigation of the High-Temperature Form of $K_2SO_4$

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## Abstract

The crystal structure of the high-temperature form of $K_2SO_4$ was redetermined from three-dimensional X-ray diffractometer data at 1073 K and refined to an *R* value of 0·086 for 66 observed reflexions. The structure belongs to the hexagonal space group $P6_3/mmc$, with $a = 5{\cdot}947$ (2), $c = 8{\cdot}375$ (3) Å, $Z = 2$, and $D_x = 2{\cdot}26$ Mg m$^{-3}$. The $SO_4^{2-}$ tetrahedron has two orientations with one of the apices of the $SO_4^{2-}$ tetrahedron pointing statistically in opposite directions along the *c* axis. The net entropy change, $\Delta S = 5{\cdot}02$ J mol$^{-1}$ K$^{-1}$ at the phase-transition point (860 K), was explained successfully by the configurational change of the $SO_4^{2-}$ tetrahedron in the low- and high-temperature forms. The $SO_4^{2-}$ tetrahedron is approximately undistorted with a corrected mean S–O distance of 1·43 Å. Two crystallographically independent K atoms are coordinated by 9 and 13 O atoms with mean K–O distances of 3·20 and 3·37 Å, respectively.

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## Introduction

Two modifications of potassium sulphate, $K_2SO_4$, were reported by Bredig (1942), Bernard & Hocart (1961) and Fischmeister (1962). The first-order phase transition between them occurs at 860 K. The space group and structure of the low-temperature form are well established (Robinson, 1958; McGinnety, 1972).

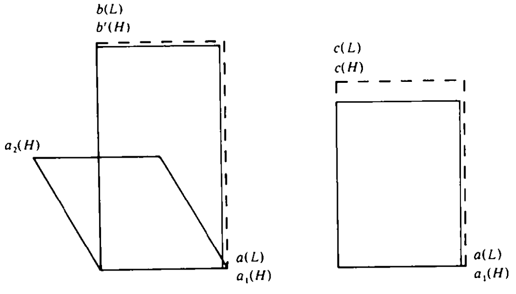
The space groups reported for the high-temperature form of $K_2SO_4$ were inconsistent. Bredig (1942) and Eysel & Hahn (1970) proposed the space groups $P\bar{3}m1$ and $P6_3mc$, respectively, from powder X-ray diffraction analyses. Iwai, Sakai & Watanabè (1973) carried out a structure analysis using a high-temperature Weissenberg technique. They concluded that the space group is $P6_3mc$, but ambiguity in the structure remains unexplored. The ferroelastic study of Shiozaki, Sawada, Ishibashi & Takagi (1977) suggests that the space group is $P6_3/mmc$.

Recently, van den Berg & Tuinstra (1978) refined the crystal structure of the high-temperature form on the basis of 50 powder diffraction data taken at 903 K. In the course of the structure refinement, the intensities of 21 undetectable reflexions were suitably estimated. They concluded that the space group was neither $P\bar{3}m1$ nor $P6_3mc$, but was $P6_3/mmc$. They also concluded that the $SO_4^{2-}$ tetrahedron was split into four positions around 0·333, 0·667, 0·25, and introduced a split-atom model for K atoms in place of anisotropic temperature factors. The theoretical entropy change for configurational change of the $SO_4^{2-}$ tetrahedra between this structure and the low-temperature form would be 11·51 J mol$^{-1}$ K$^{-1}$. However, the net entropy change was measured to be 5·02 J mol$^{-1}$ K$^{-1}$ (Miyake, 1979). This discrepancy suggests that the proposed structure is unsatisfactory.

In this paper, the crystal structure of the high-temperature form of $K_2SO_4$ was determined by means of single-crystal X-ray diffraction at 1073 K to clarify the many problems mentioned above.

## Experimental

The temperature dependence of the structure was investigated by a high-temperature Weissenberg camera (Iwai, Tagai, Kato & Shimamune, 1971) up to 1073 K using single crystals. From the high-temperature Weissenberg photographs rotated around the *a* and *c* axes, the crystal was found to have pseudohexagonal symmetry from about 860 to about 920 K and hexagonal symmetry above 920 K. The low-temperature form transforms topotaxially to the high-temperature form. The *a* and *c* axes of the low-temperature form are parallel to the *a* and *c* axes of the high-temperature form, respectively. Fig. 1 shows the lattice orientation between the low- and the high-temperature forms. Systematic absences of *hhl* for *l* odd restricted the possible space groups to $P6_3/mmc$ (centrosymmetric), $P\bar{6}2c$ (non-centrosymmetric), and $P6_3mc$ (non-centrosymmetric). This result rejects the space group $P\bar{3}m1$.



(*a*) (*b*)

Fig. 1. Lattice orientation between the low- and the high-temperature forms: *L*: the low-temperature form at room temperature; *H*: the high-temperature form at 1073 K. (*a*) Projection along the *c* axis; broken line: orthohexagonal lattice of the high-temperature form, $b'(H) = \sqrt{3}a_2\ (H)$. (*b*) Projection along the *b* axis of the low-temperature form; solid line: the low-temperature form; broken line: the high-temperature form.

Table 1. *Crystallographic data of the low- and high-temperature forms of* $K_2SO_4$

| Low-$K_2SO_4$* | High-$K_2SO_4$ (1073 K) |
|---|---|
| $a =$ 5·763 (2) Å | $a =$ 5·947 (2) Å |
| $b =$ 10·071 (4) | $c =$ 8·375 (3) |
| $c =$ 7·476 (3) | |
| $V =$ 433·90 Å$^3$ | $V =$ 256·51 Å$^3$ |
| $Z = 4$ | $Z = 2$ |
| $D_x =$ 2·67 Mg m$^{-3}$ | $D_x =$ 2·26 Mg m$^{-3}$ |

* McGinnety (1972).

Intensities were measured on a Rigaku automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite plate, equipped with a high-temperature apparatus (Ishizawa, Miyata, Minato & Iwai, 1978) and using a single crystal of dimensions 0·1 × 0·1 × 0·3 mm at 1073 K. The $2\theta$–$\omega$ scan technique was employed with a scanning speed of 8° min$^{-1}$ in $\omega$. Because of diffuse reflexion spots at elevated temperature, wide scan widths determined with the formula $(2{\cdot}0 + \tan\theta)^\circ$ were employed. The intensities were corrected for Lorentz and polarization factors.

A total of 108 independent reflexions were measured within the range $2\theta \leq 50°$, and 66 reflexion data, whose $|F|$'s were larger than $2\sigma(|F|)$, were used in the structure determination. Here, the $\sigma(|F|)$'s are the estimated standard deviations of the structure amplitudes due to counting statistics. There were few significant reflexions above background beyond the range $2\theta > 50°$. Corrections for absorption were carried out in the course of the structure refinement with a sphere 0·2 mm in diameter assumed for the crystal shape. Crystallographic data of the low- and high-temperature forms of $K_2SO_4$ are given in Table 1.

## Structure determination

The structure was solved by the heavy-atom method. The arrangements of K and S atoms were derived from the three-dimensional Patterson function based on the space groups $P6_3/mmc$, $P\bar{6}2c$ and $P6_3mc$. Fourier and difference Fourier maps synthesized with phases derived from K and S atoms indicated peaks due to O above and below the position of the S atom along the *c* axis. This suggests that the $SO_4^{2-}$ tetrahedra are statistically distributed between two orientations in which one of the apices of the $SO_4^{2-}$ tetrahedron points in opposite directions along the *c* axis.

Table 2. *R values for several kinds of structural models of the high-temperature form of* $K_2SO_4$

*A*, *B* and *C*: the $SO_4^{2-}$ tetrahedron has two orientations along the *c* axis; *D*: the $SO_4^{2-}$ tetrahedron has one orientation with one of the apices of the $SO_4^{2-}$ tetrahedron pointing upwards; *E*: the $SO_4^{2-}$ tetrahedron has one orientation with one of the apices of the $SO_4^{2-}$ tetrahedron pointing downwards; *F*: atomic parameters reported by van den Berg & Tuinstra (1978); *G*: the S atom is disordered along the *c* axis and O(2) is set at general positions $y \neq 2x$; *H*: the S atom is ordered and O(2) is set at general positions $y \neq 2x$.

| | *A* | *B* | *C* | *D* |
|---|---|---|---|---|
| Space group | $P6_3/mmc$ | $P\bar{6}2c$ | $P6_3mc$ | $P6_3mc$ |
| *R* value | 0·113 | 0·114 | 0·121 | 0·133 |

| | *E* | *F* | *G* | *H* |
|---|---|---|---|---|
| Space group | $P6_3mc$ | $P6_3/mmc$ | $P6_3/mmc$ | $P6_3/mmc$ |
| *R* value | 0·134 | 0·196 | 0·160 | 0·113 |

The structure was refined with the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) by assigning isotropic temperature factors to all atoms for the space groups $P6_3/mmc$, $P\bar{6}2c$ and $P6_3mc$ with the disordered $SO_4^{2-}$ tetrahedron taken into account. As shown in Table 2, conventional *R* values of 0·113, 0·114 and 0·121 were obtained for space groups $P6_3/mmc$ (model *A*), $P\bar{6}2c$ (model *B*) and $P6_3mc$ (model *C*), respectively. Significant differences could not be found between the three space groups from the results of Hamilton's (1965) *R* test at the 0·005 level. Since the converged positional parameters of O(2) in space group $P\bar{6}2c$ have the relation $y = 2x$ within the range of one standard deviation, there is a local mirror plane perpendicular to the *a* axis in the $K_2SO_4$ structure obtained. In space group $P6_3mc$, the disordered $SO_4^{2-}$ tetrahedron along the *c* axis gave rise to a local mirror plane perpendicular to the *c* axis at $z =$ 0·25, and the *z* parameter of K(2) converged near to $z = 0{\cdot}75$ within the range of one standard deviation. Thus, the results of refinements for the space groups $P\bar{6}2c$ and $P6_3mc$ agreed with that for the space group $P6_3/mmc$. Therefore, we adopted the space group $P6_3/mmc$ as the symmetry of the structure of the high-temperature form of $K_2SO_4$. The space group of the low-temperature form, *Pmcn*, belongs to one of the subgroups of space group $P6_3/mmc$.

With anisotropic temperature factors included, a final *R* value of 0·086 was obtained. Unit weights were allotted to all reflexions. The atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The final positional and thermal parameters are given in Table 3.*

Table 3. *Final positional and isotropic thermal parameters for the high-temperature form of* $K_2SO_4$

| | *x* | *y* | *z* | *B* ($\text{Å}^2$)* |
|---|---|---|---|---|
| K(1) | 0·0 | 0·0 | 0·0 | 10·63 |
| K(2) | 0·6667 | 0·3333 | 0·25 | 7·00 |
| S | 0·3333 | 0·6667 | 0·25 | 8·77 |
| O(1) | 0·3333 | 0·6667 | 0·410 (5) | 8·40 |
| O(2) | 0·212 (2) | −0·212 (2) | 0·188 (3) | 7·57 |

* Calculated from the anisotropic thermal parameters according to the expression: $B = 8\pi^2(U_{11} + U_{22} + U_{33}\sin^2\gamma + 2U_{12}\cos\gamma)/(3\sin^2\gamma)$.

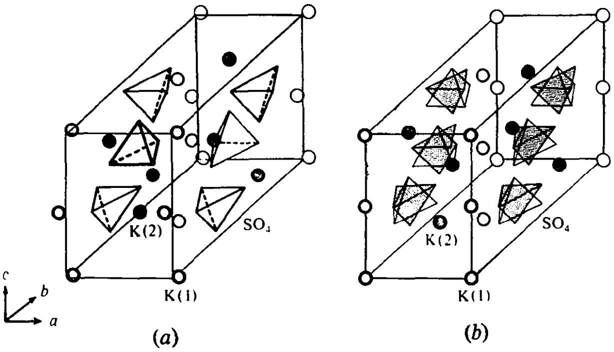


Fig. 2. Illustrations of the crystal structures of (*a*) the low-temperature form (McGinnety, 1972) and (*b*) the high-temperature form.

Illustrations of the crystal structures of the low- and the high-temperature forms are shown in Fig. 2.

## Discussion

The low-temperature form of $K_2SO_4$ (McGinnety, 1972) belongs to the orthorhombic space group *Pmcn*, with four formula units in a unit cell, and all atoms but one, which is present at general positions, are fixed by the mirror plane in the structure. The high-temperature form belongs to the hexagonal space group $P6_3/mmc$, with two formula units. K(1) and K(2) occupy $\bar{3}m$ (origin) and $\bar{6}m2$ positions, respectively. Isolated $SO_4^{2-}$ tetrahedra are present with S and O(1) atoms occupying $3m$ positions, whereas O(2) is fixed by the mirror plane $y = 2x$, resulting in $3m$ ($C_{3v}$) symmetry for the $SO_4^{2-}$ tetrahedron in the structure of the high-temperature form, while its symmetry is *m* ($C_s$) in that of the low-temperature form.

In the structure of the low-temperature form, K(1) atoms are arranged in a zigzag fashion along the *c* axis, and the $SO_4^{2-}$ tetrahedron has one orientation with one of the apices of the adjacent $SO_4^{2-}$ tetrahedron pointing alternately up and down along the *c* axis. In the high-temperature form, K(1) atoms form a line along

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34952 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the *c* axis, and the $SO_4^{2-}$ tetrahedron has two orientations with one of the apices of the $SO_4^{2-}$ tetrahedron pointing statistically in opposite directions along the *c* axis, as shown in Fig. 2.

The interatomic distances and bond angles calculated by the program *RSDA*-4 (Sakurai, 1967) are given in Table 4. The average value of the S—O distances is 1·35 (4) Å, which is much shorter than the mean S—O distances of 1·469 Å in the low-temperature form (McGinnety, 1972) and 1·473 Å in sulphate structures (Baur, 1970). This was ascribed to the very large values of the thermal vibrations for the S and O atoms (Table 3). The mean S—O distance corrected by the riding-motion model (Busing & Levy, 1964) becomes 1·43 (4) Å, which agrees with the mean S—O distances in the low-temperature form and in sulphate structures within the range of one standard deviation. In the high-temperature form, K(1) is surrounded by 9 O atoms, and K(2) by 13 O atoms. Three K—O bond distances were found in the $K(1)O_9$ polyhedron: 2·69 (2), 3·41 (2) and 3·52 (1) Å (mean value 3·21 Å). Similarly, four K—O bond distances appeared in the $K(2)O_{13}$ polyhedron: 2·85 (4), 3·05 (1), 3·69 (2) and 3·88 (2) Å (mean value 3·37 Å). In the low-temperature form, K(1) and K(2) are surrounded by 9 and 11 O atoms, and the mean K—O bond distances are 2·86 and 3·02 Å, respectively (McGinnety, 1972). The coordination number of K(2) increases from 11 to 13 at the phase transition. This is due to an increase in symmetry of the $SO_4^{2-}$ tetrahedron from *m* ($C_s$) to 3*m* ($C_{3v}$) at the phase transition. The mean K—O bond distance is longer in the high-temperature form than in the low-temperature form.

Table 4. *Interatomic distances* (Å) *and bond angles* (°)

The S—O distances in square brackets have been corrected for thermal vibrations according to the riding-motion model (Busing & Levy, 1964).

Symmetry code

| | | | |
|---|---|---|---|
| (0) | $x,y,z$ | (viii) | $1-x, \bar{y}, \frac{1}{2}+z$ |
| (i) | $\bar{y}, x-y, z$ | (ix) | $\bar{x}, \bar{y}, -\frac{1}{2}+z$ |
| (ii) | $y-x, \bar{x}, z$ | (x) | $y, y-x, \frac{1}{2}+z$ |
| (iii) | $x-y, x, \frac{1}{2}+z$ | (xi) | $x-y, x, -\frac{1}{2}+z$ |
| (iv) | $x, 1+y, z$ | (xii) | $1-x+y, 1-x, z$ |
| (v) | $1+x, y, z$ | (xiii) | $1-x, 1-y, \frac{1}{2}+z$ |
| (vi) | $1-y, x-y, z$ | (xiv) | $1+x, 1+y, \frac{1}{2}-z$ |
| (vii) | $1-x+y, \bar{x}, z$ | (xv) | $1-x+y, 1-x, \frac{1}{2}-z$ |

| | |
|---|---|
| The $SO_4^{2-}$ tetrahedron | |
| $S^0$—$O(1)^0$ | 1·34 (4) [1·42 (4)] |
| $S^0$—$O(2)^{i,iv,xii}$ | 1·35 (2) [1·43 (2)] (×3) |
| Average | 1·35 [1·43] |
| $O(1)^0$—$O(2)^{i,iv,xii}$ | 2·24 (4) (×3) |
| $O(2)^i$—$O(2)^{iv,xii}$ | 2·17 (2) (×2) |
| $O(2)^{iv}$—$O(2)^{xii}$ | 2·17 (2) |
| $O(1)^0$—$S^0$—$O(2)^{i,iv,xii}$ | 112·6 (10) (×3) |
| $O(2)^i$—$S^0$—$O(2)^{iv,xii}$ | 106·2 (10) (×2) |
| $O(2)^{iv}$—$S^0$—$O(2)^{xii}$ | 106·2 (10) |
| Environment of the K atoms | |
| $K(1)^0$—$O(1)^{ix,x,xi}$ | 3·52 (1) (×3) |
| $K(1)^0$—$O(2)^{0,i,ii}$ | 2·69 (2) (×3) |
| $K(1)^0$—$O(2)^{ix,x,xi}$ | 3·41 (2) (×3) |
| Average | 3·21 |
| $K(2)^0$—$O(1)^x$ | 2·85 (4) |
| $K(2)^0$—$O(1)^{0,ii,v}$ | 3·69 (2) (×3) |
| $K(2)^0$—$O(2)^{o,i,vi,vii,xiv,xv}$ | 3·05 (1) (×6) |
| $K(2)^0$—$O(2)^{iii,viii,xiii}$ | 3·88 (2) (×3) |
| Average | 3·37 |

In order to demonstrate the crystal structure of the high-temperature form of $K_2SO_4$ mentioned above, several kinds of structural models were built by referring to the structures proposed by Iwai *et al.* (1973) and van den Berg & Tuinstra (1978). Structural models were refined with isotropic temperature factors, and the results of the structure refinements were examined by Hamilton's (1965) *R* test at the 0·005 level. *R* values for several kinds of structural models are listed in Table 2.

In the space group $P6_3mc$, two polar structural models could be constructed. In these models, one of the apices of the $SO_4^{2-}$ tetrahedron is always orientated in the same direction along the *c* axis; namely it points either upwards (model *D*) or downwards (model *E*). These structural models could be rejected by Hamilton's *R* test at the 0·005 level as well as from the results of the Fourier and difference Fourier maps. In addition, the temperature dependence of the dielectric constants showed not a maximum but a discontinuous increase at the phase transition point. Measurement of the dielectric constants suggests that the high-temperature form has a disordered structure (Miyake, 1979). The above results clearly show that the polar structural models reported by Iwai *et al.* (1973) are incorrect.

In the space group $P6_3/mmc$, it is possible to array atoms at several positions by introducing split- or disordered-atom models. The S atom is split along the *c* axis, and O(2) in the mirror plane $y = 2x$ is transferred to general positions $y \neq 2x$. The split-atom models were not introduced since the difference Fourier map suggested that the K atoms are not split along the *a* and the *c* axes. Models *F* and *G* could be rejected at the 0·005 level. In model *H*, positional parameters of O(2) converged to positions $y = 2x$ within the range of one standard deviation when O(2) is set at general positions $y \neq 2x$. This result supports the proposal that O(2) is fixed by the mirror plane $y = 2x$; *i.e.* the $SO_4^{2-}$ tetrahedron has two configurations in which one of its apices points either along the positive *c* axis or in the opposite direction.

The $SO_4^{2-}$ tetrahedron has one configuration in the low-temperature form, while statistically it has two equivalent configurations in the high-temperature form, and K atoms are ordered in both structures. Configurational change in the $SO_4^{2-}$ tetrahedron only occurs at the phase transition. The theoretical entropy change calculated from Boltzmann's relation will give $\Delta S = 5 \cdot 77$ J mol$^{-1}$ K$^{-1}$, provided that the configuration of the $SO_4^{2-}$ tetrahedron in the high-temperature form has two orientational possibilities. The observed entropy change, $\Delta S = 5 \cdot 02$ J mol$^{-1}$ K$^{-1}$, agrees well with the calculation. The crystal structure of the high-temperature form of $K_2SO_4$ determined in this paper appears reasonable in respect of the entropy change.

We are grateful to Dr Ishizawa of Tokyo Institute of Technology for his assistance in the measurement of the intensity data at elevated temperature. The computations were carried out on the M-180 computer at the Computer Center of Tokyo Institute of Technology.

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