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Structure of Na₂SO₄(I) at 693 K

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Abstract

The crystal structure of Na₂SO₄(I) at 693 K was investigated by X-ray diffraction and refined to an *R* value of 0.049 for 63 observed independent reflections. Na₂SO₄(I) has the space group *P6₃/mmc* with *a* = 5.444 (2), *c* = 7.347 (6) Å, *V* = 188.6(2) Å³ and *Z* = 2. *M_r* = 142.04, *D_x* = 2.501 Mg m⁻³, *F*(000) = 140 and *μ*(Mo *Kα*) = 0.9466 mm⁻¹. The SO₄ tetrahedron mainly adopts the apex model orientation with one of the apices pointing statistically up and down the *c* axis. Further, the apical O atom is not exactly on the threefold axis passing through the central S atom, but deviates slightly from it. A small fraction of SO₄ groups take the orientation of the edge model at 693 K.

Introduction

Five modifications designated as phases (I) to (V) have been reported for Na₂SO₄ crystals to date (Kracek & Gibson, 1930; Kracek & Ksanda, 1930; Saito, Kobayashi & Maruyama, 1982; Eysel, Höfer, Keester & Hahn, 1985). Among these modifications, Na₂SO₄(IV) is supposed to be metastable and the phase relation has not yet been well established. Precise structure determinations of the room-temperature

phase Na₂SO₄(V) and of the intermediate phase Na₂SO₄(III) were carried out by Nord (1973) and Mehrotra (1981), respectively. Since the stable temperature range of Na₂SO₄(II) is narrow, the structural details of Na₂SO₄(II) are unknown. Several structure models have been proposed for the high-temperature phase Na₂SO₄(I). The arrangement of Na⁺ and SO₄²⁻ ions is the same in all these models except for the orientation of SO₄²⁻ groups.

Recently, Eysel *et al.* (1985) carried out a detailed structure investigation of yttrium-stabilized Na₂SO₄(I) at room temperature, and revealed that the structure agrees well with the model proposed by Höfer (1979), where one of tetrahedral edges of the SO₄²⁻ group is parallel to the *c* axis of the hexagonal lattice and statistically the anion takes three crystallographically equivalent orientations in equal probability around the threefold rotation axis. However, the mode of the statistical distribution may change with temperature as pointed out by Eysel *et al.* (1985). Therefore, it is of interest to obtain the structural details of Na₂SO₄(I) at high temperatures where the modification is stable.

Amirthalingam, Karkhanavala & Rao (1977) reported that crystals of Na₂SO₄(III), which show topotactic transformation to Na₂SO₄(I), remain

transparent when they are heated to transform into Na₂SO₄(I) and cooled again to Na₂SO₄(III). A series of structural investigations were carried out on Na₂SO₄(I) and Na₂SO₄(III) by making use of crystals of Na₂SO₄(III). In the present paper, the crystal structure of Na₂SO₄(I) at 693 K is studied by the single-crystal X-ray diffraction method. The thermal change of anharmonic vibrations of O atoms in Na₂SO₄(III) will be reported in a forthcoming paper.

Experimental

Na₂SO₄ from Wako Pure Chemical Industries, Japan, was dissolved in distilled water. The aqueous solution was quickly evaporated at about 333 K, giving needles of Na₂SO₄(III) together with bipyramidal crystals of Na₂SO₄(V).

The crystal used for intensity measurements had dimensions 0.04 × 0.07 × 0.41 mm. It was set on the top of a fused-silica capillary (diameter 0.3 mm) with adhesive Sauereisen cement. A Pt-Pt13% Rh thermocouple (diameter 0.1 mm) was placed 0.3 mm below the sample through the capillary for temperature measurement. A heating apparatus for a four-circle diffractometer developed by Ishizawa & Kato (1983) was used to heat the specimen. The temperature stability was within ±3 K up to 1273 K.

Intensities were measured at 693 K on a four-circle diffractometer (Rigaku AFC-5UD) with Mo K α radiation ($\lambda = 0.71069$ Å) monochromated with pyrolytic graphite. The ω -scan mode was employed with a scanning speed of 2° min⁻¹ in ω . Because of the diffuseness of reflection spots, large scan widths were adopted according to the formula $(4.5 + \tan \theta)^\circ$. The intensities were corrected for Lorentz-polarization factors and for absorption effects, assuming a rectangular shape for the crystal. The absorption correction factors were in the range 1.012–1.041.

A total of 106 reflections which satisfied $|F_o| > 3\sigma(|F_o|)$ were obtained within the range $2\theta < 50^\circ$, $0 \leq h \leq 5$, $0 \leq k \leq 5$ and $-8 \leq l \leq 0$, and used for the subsequent refinements (176 reflections were measured, of which 70 were unobserved; there were 63 unique observed reflections). Here, $\sigma(|F_o|)$ is the estimated standard deviation due to counting statistics. The lattice parameters were obtained from 43 reflections in the range $14 < 2\theta < 30^\circ$ by the least-squares procedure. Dimensions of the hexagonal unit cell are $a = 5.444$ (2) and $c = 7.347$ (6) Å at 693 K. The observed systematic absences of hhl for l odd restricted the possible space groups to $P6_3/mmc$, $P\bar{6}2c$ and $P6_3mc$.

Structure refinement

The three-dimensional Patterson map showed Na at (0, 0, 0), (0, 0, $\frac{1}{2}$), ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{3}{4}$) and ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{4}$), and S at ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$) and ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{3}{4}$). These atomic positions are identical to

Table 1. Atomic parameters and anisotropic temperature factors (\AA^2) of Na₂SO₄(I) at 693 K

Standard deviations in parentheses refer to the last significant figures. The anisotropic temperature factors are expressed in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	x	y	z	U ₁₁ †	U ₂₂	U ₃₃	U ₁₃
Na (1)	0.0	0.0	0.0	0.083 (3)	U ₁₁	0.090 (5)	0.0
Na (2)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.082 (4)	U ₁₁	0.166 (8)	0.0
S	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.048 (2)	U ₁₁	0.069 (3)	0.0
O(1)	0.271 (5)	2x	0.450 (3)	0.25 (13)	0.14 (11)	0.08 (2)	0.03 (3)
O(2)	0.193 (1)	2x	0.226 (6)	0.12 (1)	0.08 (2)	0.31 (2)	-0.06 (2)

$$\dagger 2U_{12} = U_{11} \text{ and } U_{23} = 2U_{13}.$$

those in the structure models previously reported. The Fourier and difference Fourier maps synthesized with phases derived from Na and S atoms gave three peaks on the plane $z = \frac{1}{4}$ around the S atom at ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$), which were supposed to be O atoms. Besides them, two peaks were observed above and below the S atom, having heights a half of those for the peaks on the $z = \frac{1}{4}$ plane. Initially, structure refinement was tried by allotting O atoms to the three peaks on $z = \frac{1}{4}$ and to the peak above the S atom, assuming the space group $P6_3mc$. However, the peak below S did not disappear on the difference Fourier map after this refinement, suggesting the true space group $P6_3/mmc$ with statistical distribution of the SO₄ tetrahedron between the two orientations.

The structure was therefore refined with the full-matrix least-squares program *LINEX* (Becker & Coppens, 1974a,b, 1975) on the basis of symmetry $P6_3/mmc$, by taking into account the orientational disorder of the SO₄ tetrahedron over the two possible orientations. The refinement with anisotropic temperature factors gave a wR value of 0.054. At this stage, Fourier and difference Fourier maps were synthesized. These maps revealed that the O(1) atom has a triradiated electron cloud and O(2) an extraordinarily elongated electron cloud along the c axis. The final refinement was carried out by splitting the O(1) atom further into three located at positions deviating slightly from the threefold axis, giving R and wR values of 0.056 and 0.051 for the 106 observed reflections, and 0.049 and 0.044 for the unique reflections. The atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The function $\sum w(|F_o| - |F_c|)^2$ was minimized, assuming $w = 1$ for all reflections. The final positional and thermal parameters are given in Table 1.* Maximum $\Delta/\sigma = 0.032$. The final residual densities are between 0.23 and -0.53 e \AA^{-3} . Bond distances and angles are listed in Table 2 after correc-

* A list of observed and calculated structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43327 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances (Å) and angles (°) in Na₂SO₄(I) at 693 K*

S ⁱ -O(1 ⁱ)	(×1)	1.58 (2)	1.70 (2)*
S ⁱ -O(2 ⁱ)	(×3)	1.33 (1)	1.47 (1)*
	average	1.39	1.53
O(1 ⁱ)-O(2 ^v)	(×2)	2.13 (4)	
O(1 ⁱ)-O(2 ⁱⁱ)	(×1)	2.36 (4)	
O(2 ⁱ)-O(2 ^v)	(×2)	2.31 (1)	
O(2 ⁱ)-O(2 ⁱⁱ)	(×1)	2.28 (1)	
	average	2.25	
O(1 ⁱ)-S ⁱ -O(2 ⁱⁱ)	(×1)	108.0 (1.0)	
O(1 ⁱ)-S ⁱ -O(2 ^v)	(×2)	93.4 (1.1)	
O(2 ⁱ)-S ⁱ -O(2 ⁱⁱ)	(×1)	118.2 (0.8)	
O(2 ⁱ)-S ⁱ -O(2 ^v)	(×2)	120.6 (0.8)	
Na(1 ⁱ)-O(1 ^{iv})	(×1)	2.58 (2)	
Na(1 ⁱ)-O(1 ^v)	(×2)	3.49 (3)	
Na(1 ⁱ)-O(2 ⁱ)	(×3)	2.47 (3)	
Na(1 ⁱ)-O(2 ^{iv})	(×3)	2.72 (4)	
	average	2.79	
Na(2 ⁱ)-O(1 ⁱ)	(×1)	2.28 (2)	
Na(2 ⁱ)-O(1 ⁱⁱⁱ)	(×3)	3.25 (3)	
Na(2 ⁱ)-O(2 ⁱⁱⁱ)	(×6)	2.74 (1)	
Na(2 ⁱ)-O(2 ^{iv})	(×3)	3.74 (4)	
	average	3.05	

Symmetry code: (i) x, y, z ; (ii) $1-y, 1+x-y, z$; (iii) $1-x, 1-y, 1-z$; (iv) $x, y, \frac{1}{2}-z$; (v) $y-x, 1-x, \frac{1}{2}-z$.

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

tion for thermal vibrations according to the riding-motion model (Busing & Levy, 1964).

Discussion

Fig. 1 shows the cell relation between Na₂SO₄(I) and Na₂SO₄(III) together with the atomic arrangements in Na₂SO₄(III). The cell dimensions of Na₂SO₄(III) are $a = 5.607$, $b = 8.955 (= \sqrt{3} \times 5.170)$, $c = 6.967$ Å at 505 K (Mehrotra, 1981), while those of Na₂SO₄(I) are $a = 5.408$, $c = 7.216$ Å at 533 K (Mehrotra, 1973) and $a = 5.444$, $c = 7.347$ Å at 693 K (this work). With increase in temperature from 505 to 533 K through the phase-transition point, the cell dimensions decrease by 3.5% along the a axis and increase by 4.6% and 3.6% along the b and c axes, respectively. Above the transition point, both a and c increase with temperature (0.7% and 1.8% from 533 to 693 K along a and c , respectively).

Since the number of observed (independent) reflections is only about four times the number of parameters to be refined, the values obtained have large standard deviations. As a consequence, an unreasonably large distortion is observed in the shape of the SO₄ tetrahedron. However, several important features of the structure can be deduced from the final Fourier maps shown in Fig. 2. The maps suggest the following facts concerning the orientation of the SO₄ tetrahedron: (a) the SO₄ tetrahedron has one of its faces approximately parallel to (001); (b) the apex opposite to the face points up and down with equal probability; (c) the tri-radiated shape of the O(1) electron cloud indicates that O(1) is further split into three within

the (001) plane; (d) with a much smaller probability, the SO₄ tetrahedron seems to take the orientation where one of its edges is parallel to the c axis. The orientations of (a) and (d) correspond to the apex and edge models, respectively, proposed by Arnold, Kurtz, Richter-Zinnius, Bethke & Heger (1981) for the high-temperature form of K₂SO₄.

Refinement with the edge model gave a final wR value of 0.054 with anisotropic temperature factors. The positions of O atoms obtained by the refinements are indicated by the marks X in Figs. 2(b) and 2(c). The marks are located on the tails of O(2) peaks extending along the c direction as seen in Fig. 2(c). Therefore, the apex model should be the main arrangement in Na₂SO₄(I) at 693 K, and a smaller contribution is afforded by the edge model. A similar feature was observed in the high-temperature form of K₂SO₄ (Miyake, Morikawa & Iwai, 1980). It is noteworthy that the signs of the F values are

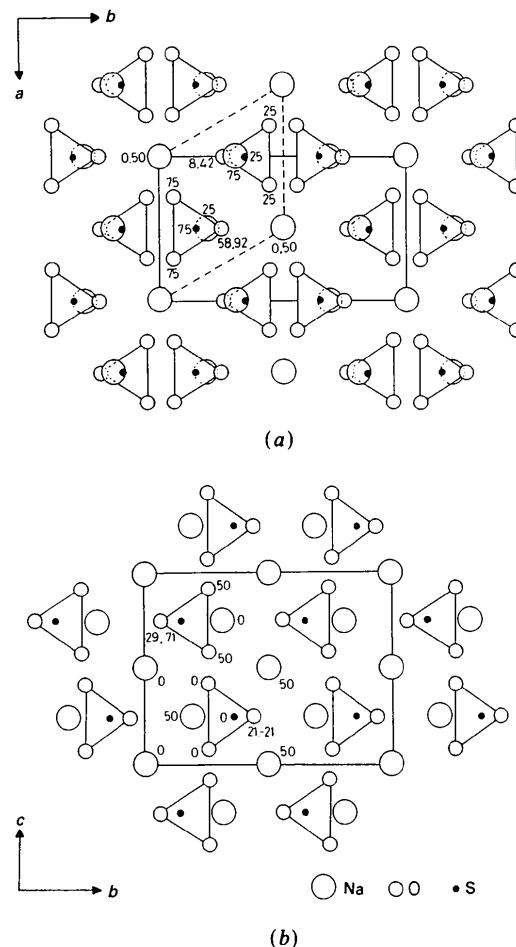


Fig. 1. The unit-cell relation between Na₂SO₄(III) and Na₂SO₄(I) with the atomic arrangements in Na₂SO₄(III) projected along (a) c and (b) a axes. The solid and dotted lines indicate unit cells of the phases (III) and (I), respectively.

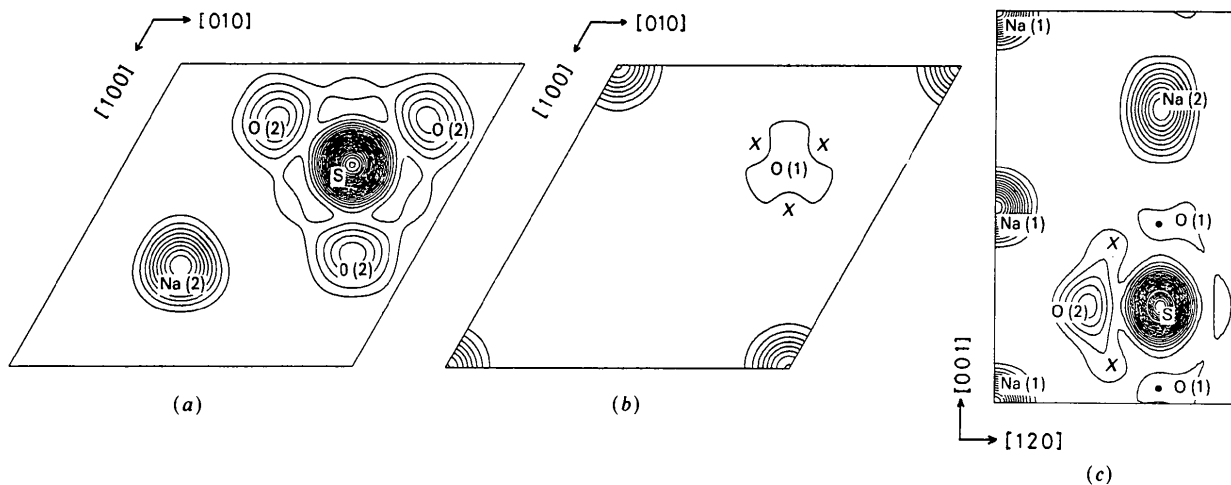


Fig. 2. Fourier maps of Na₂SO₄(I) at 693 K through the planes (a) $z=0.25$, (b) $z=0.05$ and (c) $y=2x$. O-atom positions in the edge and apex models are marked with crosses and dots, respectively.

independent of the structure model when it is restricted to the edge and apex types mentioned above, as already pointed out by Arnold *et al.* (1981) for the high-temperature form of K₂SO₄.

According to the structural investigation of yttrium-stabilized Na₂SO₄(I) by Eysel *et al.* (1985), the SO₄ group mainly takes the orientation of the edge model at room temperature. However, they predicted that the apex model gains more importance at higher temperatures. The present results accord well with their prediction.

The Na atoms in Na₂SO₄(V) and Na₂SO₄(III) form NaO₆ coordination octahedra with average Na–O distances of 2.431 Å (Nord, 1973) and 2.457 Å (Mehrotra, 1981), respectively. On average, the Na atoms in Na₂SO₄(I) are surrounded by seven O atoms, with mean Na(1)–O and Na(2)–O distances of 2.59 and 2.67 Å, respectively. The Na(1) atom has six O(2) atoms arranged octahedrally around it. There are six O(1) positions near Na(1) (2.58 Å), but each has a population of $\frac{1}{6}$. The Na(2) atom has six O(2) atoms roughly on the plane through Na(2) and parallel to (001). The O(1) positions, approximately on the line through Na(2) and parallel to the *c* axis, are at a distance of 2.28 Å. Since this distance is too short for an Na–O bond, the structure should have a static deviation of the Na(2) atom from the mean position along the *c* direction. Actually, the electron density

map shows elongation of the Na(2) electron cloud along the *c* direction.

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