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Low-Temperature Rubidium Sulphate

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Abstract. β-Rb_2SO_4, orthorhombic, *Pnam*, $a=7·8128$ (5), $b=10·4255$ (7), $c=5·9694$ (5) Å (25°C); $Z=4$, calculated density 3·647 g cm^{-3}. Crystals were grown from a melt of Rb_2SO_4. The structure has been refined by least-squares methods to give an R value of 0·055 for 634 diffractometer-measured reflexions. The present work has confirmed the general features of the atomic arrangement reported by Ogg [*Phil. Mag.* (1928). **5**, 354–367]. The rubidium ions are surrounded by nine or eleven oxygen atoms. The SO_4^{2-} tetrahedra are regular with an average S–O distance of 1·474 Å.

Introduction. This work was undertaken as part of a study to provide additional information about the dimensions of the sulphate ion. The structure of β-Rb_2SO_4 was originally determined without any refinement (Ogg, 1928).

Crystals were grown from a melt of Rb_2SO_4 in *pro analysi* quality from Merck, Darmstadt. The unit-cell dimensions were refined from 32 distinct reflexions measured on a Guinier powder photograph (25°C) with KCl as internal standard.

A single-crystal fragment, roughly approximating a prismatic needle grown in the [111] direction and with the dimensions 0·02 × 0·02 × 0·12 mm, was used for the collection of single-crystal data. The intensities were obtained with an automatic Siemens AED diffractometer (graphite monochromator, θ–2θ scan) using Mo $K\alpha$ radiation, $\lambda=0·7107$ Å. From a total of about 1000 independent reflexions measured up to $\theta=35°$, 634 were considered to be observed with $\sigma(I)/I<0·5$. The net intensities were corrected for Lorentz, polarization and absorption ($\mu=214$ cm^{-1}) effects.

The systematic absences are: $h0l$, $h\neq 2n$, and $0kl$, $k+l\neq 2n$, which is characteristic of the space group $Pna2_1$ and its centrosymmetric equivalent *Pnam*. Since all statistical tests applied, *e.g.* the $N(z)$ test of Howells, Phillips & Rogers (1950), indicated a centric distribution, a centre of symmetry was assumed, *i.e.* space group *Pnam* (see below).

The structure was redetermined using Patterson and Fourier methods giving atom positions close to those reported by Ogg (1928). A few least-squares cycles, with anisotropic thermal parameters for all atoms,

Table 1. *Atomic coordinates and temperature factors*

Standard deviations are given in parentheses. The anisotropic temperature factors are of the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$. The B_{ij} values below are multiplied by 10^4.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rb(1)	0·6750 (2)	0·4097 (1)	$\frac{1}{4}$*	67 (2)	32 (1)	95 (1)	0 (2)	0*	0*
Rb(2)	−0·0116 (2)	0·7030 (1)	$\frac{1}{4}$*	59 (2)	37 (1)	134 (3)	6 (2)	0*	0*
S	0·2380 (3)	0·4191 (3)	$\frac{1}{4}$*	38 (4)	21 (3)	58 (5)	−4 (5)	0*	0*
O(1)	0·0471 (11)	0·4137 (10)	$\frac{1}{4}$*	44 (13)	53 (10)	196 (26)	−5 (17)	0*	0*
O(2)	0·2974 (12)	0·5532 (9)	$\frac{1}{4}$*	92 (15)	38 (10)	137 (23)	−61 (18)	0*	0*
O(3)	0·3030 (8)	0·3540 (7)	0·0497 (9)	100 (10)	37 (6)	111 (14)	−1 (12)	62 (21)	−50 (18)

* Parameter fixed by symmetry.

were computed. At this stage a correction for secondary extinction (isotropic) was applied as described by Åsbrink & Werner (1966) utilizing Zachariasen's (1963) formula: $F_{\text{corr}} \approx k\,.\,|F_{\text{obs}}|\,.\,[1+c\,.\,I_{\text{obs}}\,.\,\beta(2\theta)]$, (with $c = 2{\cdot}38 \times 10^{-4}$). The stiucture was then refined with a local modification (A. G. Nord) of the full-matrix least-squares program *LALS*. Atomic scattering factors for Rb^+, S^0, and O^-, with corrections for the real part ($\Delta f'$) of the anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1968). Weights according to Hughes (1941) were applied, with $h = 4$ and $F_{o,\min} = 45$.

The final atomic parameters, obtained after five cycles of refinement, are given in Table 1. These parameters gave an R value of 0·055.* The possibility of an error in the assignment of the space group was also tested by lowering the symmetry from *Pnam* to *Pna*2$_1$. The new refinement, however, did not give any significant improvement. This, together with the statistical tests and the reasonable interatomic distances obtained (Table 2), suggests that *Pnam* is the correct space group.

Discussion. The present work shows that Ogg's atom positions were broadly correct. β-Rb$_2$SO$_4$ is isomorphous with β-K$_2$SO$_4$ and (probably) with β-Cs$_2$SO$_4$ (Ogg, 1928). The cell constants for β-Rb$_2$SO$_4$ and β-K$_2$SO$_4$ [the latter from McGinnety (1972)] are a= 7·8128 (5), b= 10·4255 (7), c= 5·9694 (5) Å, and a= 7·476 (3), b= 10·071 (4), c= 5·763 (2) Å respectively.

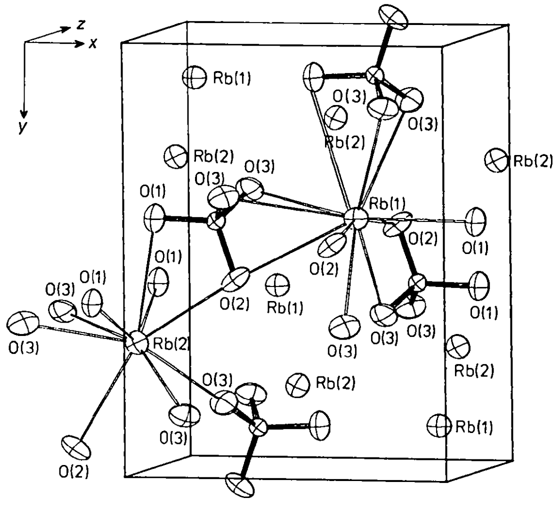

Fig. 1. Plot picture of the β-Rb$_2$SO$_4$ structure. The small ellipsoids represent sulphur atoms. For clarity only two rubidium–oxygen polyhedra are shown.

Interatomic distances and angles are listed in Table 2. The rubidium ions are surrounded in an irregular way by either 9 or 11 oxygen atoms. The average Rb–O distances are 3·003 Å (9-coordination) and 3·143 Å (11-coordination) respectively. The SO$_4^{2-}$ tetrahedra are fairly regular. They have a crystallographically imposed m symmetry. The average S–O distance in β-Rb$_2$SO$_4$ is 1·474 Å (uncorrected), which may be compared with the corresponding values 1·469 Å in β-K$_2$SO$_4$ (McGinnety, 1972), 1·476 Å in Na$_2$SO$_4$(V) (Nord, 1973*a*), and 1·473 Å in Li$_2$SO$_4$ (Nord, 1973*b*). The S–O distances have also been corrected for the thermal vibrations of the atoms by means of the riding-motion model (Busing & Levy, 1964). The character of the thermal motion may also be studied in Fig. 1, an *ORTEP* plot of the crystal structure.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Standard deviations in the last figures are quoted in parentheses. All Rb–O distances < 4 Å are given below. The S–O distances in square brackets have been corrected for thermal vibrations assuming the riding-motion model.

Rb(1)–O(1)	2·907 (9)		Rb(2)–O(2)	2·876 (9)	
Rb(1)–O(2)	3·017 (1)	(×2)	Rb(2)–O(3)	2·887 (7)	(×2)
Rb(1)–O(3)	3·050 (7)	(×2)	Rb(2)–O(2)	2·948 (9)	
Rb(1)–O(3)	3·160 (7)	(×2)	Rb(2)–O(3)	2·956 (7)	(×2)
Rb(1)–O(3)	3·196 (7)	(×2)	Rb(2)–O(1)	3·051 (10)	
Rb(1)–O(2)	3·308 (9)		Rb(2)–O(1)	3·235 (4)	(×2)
Rb(1)–O(1)	3·516 (9)		Average:	3·003	
Average:	3·143				

S–O(1)	1·492 (9)	[1·506]	
S–O(2)	1·473 (10)	[1·486]	
S–O(3)	1·466 (7)	[1·478]	(×2)
Average:	1·474	[1·487]	

O(1)–S–O(2)	110·6 (6)	
O(1)–S–O(3)	109·2 (3)	(×2)
O(2)–S–O(3)	109·3 (4)	(×2)
O(3)–S–O(3)	109·3 (6)	
Average:	109·47	

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* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Suplementary Publication No. SUP 30369 (5 pp.). Copies may be obtained from The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.