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*Acta Cryst.* (1980). B36, 3084–3085

## Room-Temperature Phase of Lithium Rubidium Sulphate

BY SIGETOSI TANISAKI AND HIROYUKI MASHIYAMA

*Department of Physics, Faculty of Science, Yamaguchi University, Yamaguchi 753, Japan*

KATSUHIKO HASEBE

*Department of Physics, Faculty of Liberal Arts, Yamaguchi University, Yamaguchi 753, Japan*

YOSHIHIRO SHIROISHI

*Hitachi Central Laboratory, Kokubunji, Tokyo 185, Japan*

AND SHOZO SAWADA

*Department of Engineering Physics, Chubu Institute of Technology, Kasugai, Aichi 487, Japan*

(Received 1 May 1980; accepted 14 July 1980)

**Abstract.** LiRbSO<sub>4</sub> (phase V), monoclinic,  $P2_1/n$ ,  $a = 5.288$  (1),  $b = 9.105$  (1),  $c = 8.731$  (1) Å (unique axis),  $\gamma = 90.09$  (2)°,  $V = 420.4$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 2.89$ ,  $D_x = 2.978$  (2) Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 11.815$  mm<sup>-1</sup>. The parameters were refined by full-matrix least-squares calculations. The final  $R$  was 0.047 for 1544 independent reflections. The SO<sub>4</sub><sup>2-</sup> anion is an almost regular tetrahedron, and each SO<sub>4</sub> tetrahedron shares all of its corners with LiO<sub>4</sub> distorted tetrahedra.

**Introduction.** LiRbSO<sub>4</sub> is one of the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-type ferroelectric crystals. The crystal undergoes successive transitions at 439, 458, 475 and 477 K. These phases are denoted (I) ( $Pm\bar{c}n$ ), (II) (incommensurate,  $c \simeq 5c_0$ ), (III) ( $c = 2c_0$ ), (IV) (ferroelectric,  $c = 5c_0$ ) and (V) in the order of decreasing temperature. Another ferroelectric phase (VI) ( $c = 3c_0$ ) is induced by the application of an electric field (Shiroishi, Nakata & Sawada, 1976; Shiroishi & Sawada, 1979; Mashiyama, Hasebe, Tanisaki, Shiroishi & Sawada, 1979*a,b*). The lattice parameters of the room-temperature phase (V) were given by Hahn, Lohre & Chung (1969). The axial ratios are very close to those of LiNH<sub>4</sub>SO<sub>4</sub> (Dollase, 1969) and this suggests that the structure of LiRbSO<sub>4</sub> is similar to that of LiNH<sub>4</sub>SO<sub>4</sub>.

The monoclinic space group  $P2_1/n$  reported by Hahn *et al.* (1969) was confirmed by the systematic absences ( $00l$ ,  $l = 2n + 1$ ;  $hk0$ ,  $h + k = 2n + 1$ )

observed on rotation and Weissenberg photographs. The first setting of the crystallographic axes, chosen by Shiroishi *et al.* (1976), was adopted in this paper. The reflection data were collected on a Philips PW 1100 four-circle diffractometer with Mo  $K\alpha$  graphite-monochromated radiation from a roughly spherical specimen (radius 0.1 mm) obtained from an untwinned transparent part of a crystal. Measurements were carried out for  $2\theta < 90^\circ$  by the  $\theta$ - $2\theta$  scanning method with a scan speed 0.05° s<sup>-1</sup> in  $\theta$ , and the scan width in  $\theta$  was  $1.2^\circ + 0.3^\circ \tan \theta$ . The reflections were omitted if  $I_{\text{top}} - 2\sqrt{I_{\text{top}}} < I_{\text{bck}}$ , where  $I_{\text{top}}$  is the intensity in counts s<sup>-1</sup> at the top of the reflection, and  $I_{\text{bck}}$  is the mean intensity of the background on each side of the reflection. Absorption, Lorentz and polarization corrections were made for 1544 independent reflections (Kato, Miura & Kawano, 1974).

Parameters of all independent atoms [except O(4)] of a starting model were taken directly from those of LiNH<sub>4</sub>SO<sub>4</sub> (Dollase, 1969). Parameters of O(4) were obtained from O(2) of LiNH<sub>4</sub>SO<sub>4</sub> by the  $n$ -glide operation in order to form an SO<sub>4</sub> tetrahedron. All  $x$  parameters were increased by 0.25 so as to make the origin a center of symmetry. The structure was refined by full-matrix least-squares calculations with anisotropic thermal factors using UNICS (1967). The scattering factors for the neutral atoms and the dispersion corrections for Rb, S and O were taken from *International Tables for X-ray Crystallography* (1968).

At the final stage of the refinement, five reflections (200, 112,  $\bar{1}12$ , 022 and 004) were omitted from the calculations because they seemed to be affected by secondary extinction, and a correction for the anomalous scattering was taken into account. Finally,  $R$  reduced to the stationary value of 0.046 for 1539 reflections. The  $R$  value was 0.047 when the five previously omitted reflections were included. A difference Fourier map revealed no peaks larger than  $-1.5$  and  $+0.9$  e  $\text{\AA}^{-3}$ . Final parameters are given in Table 1.\*

**Discussion.** The calculated bond lengths and bond angles are given in Table 2. The  $\text{SO}_4^{2-}$  anion is an almost regular tetrahedron and each  $\text{SO}_4$  tetrahedron shares all of its corners with  $\text{LiO}_4$  distorted tetrahedra.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35547 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\times 10^2$ ) with *e.s.d.'s* in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$ ( $\text{\AA}^2$ )
Rb	7355 (1)	2225 (1)	5043 (1)	181 (3)
Li	2434 (20)	4103 (11)	3242 (10)	185 (32)
S	2466 (2)	778 (1)	2064 (1)	86 (3)
O(1)	2556 (8)	932 (6)	408 (4)	270 (16)
O(2)	1491 (7)	2132 (4)	2739 (5)	223 (i4)
O(3)	5035 (6)	482 (4)	2655 (4)	180 (13)
O(4)	794 (7)	-448 (4)	2477 (5)	198 (13)

Table 2. Interatomic distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) for  $\text{SO}_4$  and  $\text{LiO}_4$  tetrahedra

S—O(1)	1.453 (4)	Li—O(1 <sup>III</sup> )	1.891 (9)
S—O(2)	1.461 (4)	Li—O(2 <sup>I</sup> )	1.913 (11)
S—O(3)	1.478 (3)	Li—O(3 <sup>II</sup> )	1.950 (11)
S—O(4)	1.468 (4)	Li—O(4 <sup>II</sup> )	1.928 (11)
Average	1.465 (4)	Average	1.921 (11)
O(1)—S—O(2)	109.4 (3)	O(1 <sup>III</sup> )—Li—O(2 <sup>I</sup> )	102.4 (5)
O(1)—S—O(3)	109.6 (2)	O(1 <sup>III</sup> )—Li—O(3 <sup>II</sup> )	114.5 (5)
O(1)—S—O(4)	109.7 (3)	O(1 <sup>III</sup> )—Li—O(4 <sup>II</sup> )	109.1 (5)
O(2)—S—O(3)	109.8 (2)	O(2 <sup>I</sup> )—Li—O(3 <sup>II</sup> )	110.1 (5)
O(2)—S—O(4)	109.2 (2)	O(2 <sup>I</sup> )—Li—O(4 <sup>II</sup> )	111.3 (5)
O(3)—S—O(4)	109.2 (2)	O(3 <sup>II</sup> )—Li—O(4 <sup>II</sup> )	109.4 (5)
Average	109.5 (2)	Average	109.5 (5)

#### Symmetry code

(i)	<i>x</i> , <i>y</i> , <i>z</i>	(ii')	$-\frac{1}{2} + x$ , $\frac{1}{2} + y$ , $\frac{1}{2} - z$
(ii)	$\frac{1}{2} + x$ , $\frac{1}{2} + y$ , $\frac{1}{2} - z$	(iii)	$\frac{1}{2} - x$ , $\frac{1}{2} - y$ , $\frac{1}{2} + z$

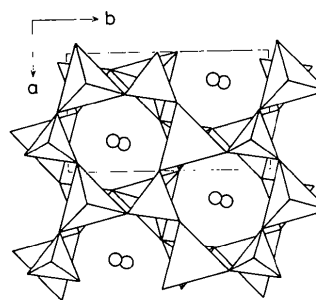


Fig. 1. Projection of the structure of  $\text{LiRbSO}_4$  along [001]. The pseudo-hexagonal rings of  $\text{SO}_4$  (small tetrahedra) and  $\text{LiO}_4$  (large tetrahedra) are shown. The  $\text{Rb}^+$  ions are shown as circles.

As shown in Fig. 1,  $\text{LiRbSO}_4$  has a pseudo-hexagonal network of six-membered rings of  $\text{SO}_4$  and  $\text{LiO}_4$  tetrahedra. In a similar network observed in  $\text{LiNH}_4\text{SO}_4$ , the successive layers of the network are almost exactly eclipsed when viewed along the  $c$  axis. On the other hand, the structure of  $\text{LiRbSO}_4$  is characterized by the alternate rotation in opposite directions of each tetrahedron layer by layer.

The authors are indebted to Professor H. Shima, Dr A. Kitakaze and Dr T. Mizota for the use of the automatic four-circle diffractometer and for invaluable help in the data collection. This study was partly supported by the Scientific Research Fund of the Ministry of Education. The computations were carried out at Kyushu University Computer Center.

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