

**$\beta$ -Rubidium antimonide,  $\text{Rb}_4\text{Sb}_4$** 

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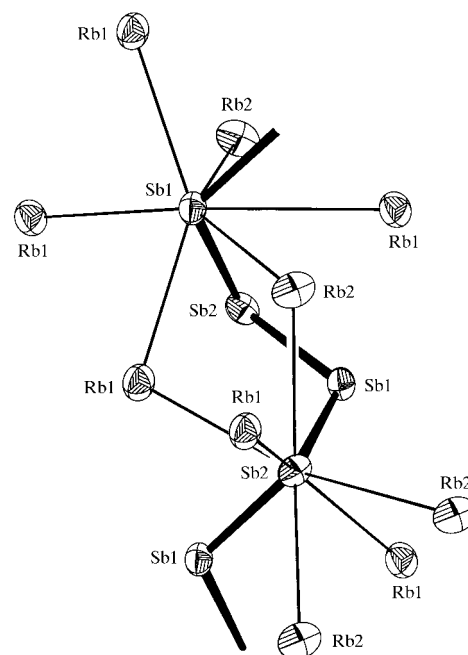
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$\beta$ -RbSb crystallizes with the LiAs structure type. As in the  $\alpha$  phase (NaP type),  $\text{Sb}^-$  forms approximate  $4_1$  helical chains ( $2_1$  crystallographic symmetry), with Sb—Sb distances of 2.838 (1) and 2.862 (1) Å. In contrast to the  $\alpha$  phase, the helices have different chirality.

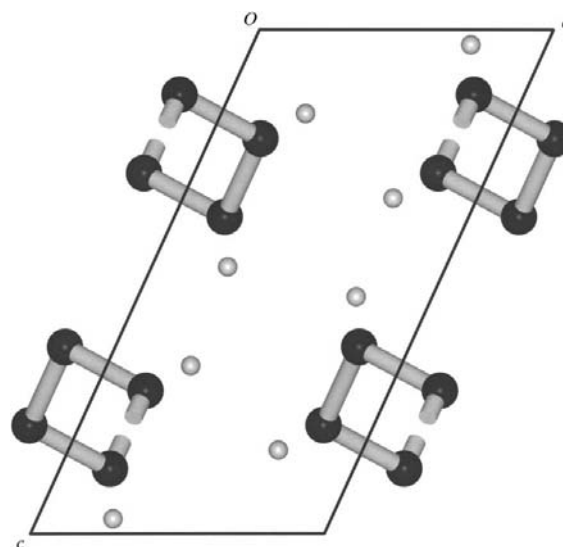
**Comment**

The monopentelides  $A^1M^V$  of the alkali metals  $A$  have been known for a long time and are well characterized. They crystallize in two structure types, which both contain infinite helical chains of  $M^-$  as common building units. In each pentelide series, the compounds having a smaller ratio of cation to anion radius, *i.e.* LiP (Hönle & von Schnering, 1981), LiAs (Cromer, 1959*a*), NaSb (Cromer, 1959*b*) and KSb (Hönle & von Schnering, 1981) form the LiAs structure type, whereas higher ionic radius ratios, for example, in NaP, KP (von Schnering & Hönle, 1979), NaAs, KAs, RbAs (Hönle & von Schnering, 1978), RbSb and CsSb (von Schnering *et al.*, 1979), give rise to the formation of the NaSb structure type. As already expected by von Schnering & Hönle (1979), both structure types may be stable at the border of the ratio ranges.

The second form of RbSb,  $\beta$ -RbSb, crystallizes with the LiAs structure type (Cromer, 1959*a*).  $\text{Sb}^-$  atoms form infinite chains arranged around crystallographic  $2_1$  screw axes with approximate  $4_1$  symmetry (Fig. 1) running parallel to the [010] direction (Fig. 2). The distances and angles within the chains are in accordance with those observed in KSb (LiAs structure type) and  $\alpha$ -RbSb (NaP structure type). The Sb—Sb distances are of two lengths, 2.838 (1) and 2.862 (1) Å [KSb: 2.829 (1) and 2.852 (1) Å;  $\alpha$ -RbSb: 2.852 (3) and 2.864 (3) Å]. The interbond angles at the two crystallographically independent Sb atoms are 115.59 (3) [Sb1] and 110.36 (3)° [Sb2], respectively, [KSb: 113.95 (4) and 109.38 (4)°;  $\alpha$ -RbSb: 116.93 (8) and 109.72 (6)°]. The values of the dihedral angles [56.9 (1) and 71.6 (1)°] are also in the same range as in KSb and the  $\alpha$  form of the title compound. The further coordination of the Sb atoms consists of six Rb cations with Sb—Rb distances ranging from 3.641 (2) to 3.794 (2) Å. The main difference of the two forms of RbSb is the chirality of the  $\text{Sb}^-$  screw chains. While in



**Figure 1**  
ORTEP (Johnson, 1968) view of the  ${}_{\infty}[\text{Sb}]^-$  chains (75% probability ellipsoids) with the coordination polyhedra of one Sb1 and one Sb2 atom.



**Figure 2**  
Unit cell of  $\beta$ -RbSb (light gray spheres are Rb atoms and dark gray balls are Sb atoms).

the  $\alpha$  form only one chirality is present (non-centrosymmetric space group), the  $\beta$  form described here contains both screw directions side by side, *i.e.* the Sb chains at  $(0, y, \frac{1}{4})$  and  $(0, y, \frac{3}{4})$  are of different chirality (Fig. 2). We have observed a related form of dimorphism for the corresponding Cs compound, but the  $\beta$  form of CsSb (Hirschle & Röhr, 2000) crystallizes with a superstructure of the LiAs structure. In the series of ASb structures, the Sb bond angle and the rise per turn of the helical chains increases with the radius of the  $A$  cation [NaSb: 6.34 (2) Å; CsSb: 7.32 (2) Å], where the  $\beta$  forms show smaller

values [RbSb:  $\alpha$  7.197 (4),  $\beta$  7.134 (1) Å; CsSb:  $\alpha$  7.345 (5),  $\beta$  7.32 (2) Å]. Both the  $\alpha$  and  $\beta$  phases were prepared below the melting point of RbSb at 883 K (Dorn & Klemm, 1961). While the  $\alpha$  phase (von Schnering *et al.*, 1979) was synthesized by treatment of Sb with Rb at 843 K for 140 h, the  $\beta$  phase was formed at a lower temperature of 793 K. For this reason, we assume that the new modification reported here is the low-temperature form of RbSb. This is in accordance with the unit-cell volumes per formula unit ( $\alpha$ : 84.3 Å<sup>3</sup>;  $\beta$ : 82.5 Å<sup>3</sup>). Details concerning the thermodynamic and kinetic aspects of the formation of the two phases are currently being studied.

## Experimental

Liquid rubidium (Alkalimetallhandels-gesellschaft Bonn, 99.9%) (678.8 mg, 7.93 mmol) was reacted with Sb (ABCR, 99.999%) (322.0 mg, 2.64 mmol) in tantalum crucibles under an argon atmosphere. The mixture was heated to 793 K over a period of 5 h and cooled to 733 K at a rate of 2 K h<sup>-1</sup> and after that to room temperature by switching off the furnace. Almost black metallic crystals in the form of flattened needles of  $\beta$ -RbSb up to a length of 0.3 mm grew in the matrix of elemental Rb.

### Crystal data

Rb <sub>4</sub> Sb <sub>4</sub>	$D_x = 4.172 \text{ Mg m}^{-3}$
$M_r = 828.88$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 7.3566$ (8) Å	$\theta = 12.3\text{--}26.9^\circ$
$b = 7.1341$ (9) Å	$\mu = 22.696 \text{ mm}^{-1}$
$c = 13.7930$ (13) Å	$T = 293$ (2) K
$\beta = 114.28$ (2)°	Prism, dark metallic
$V = 659.86$ (13) Å <sup>3</sup>	$0.30 \times 0.10 \times 0.08 \text{ mm}$
$Z = 2$	

### Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.048$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 29.0^\circ$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 10$
$T_{\text{min}} = 0.051$ , $T_{\text{max}} = 0.163$	$k = 0 \rightarrow 9$
1863 measured reflections	$l = -18 \rightarrow 17$
1740 independent reflections	3 standard reflections
	frequency: 120 min
	intensity decay: none

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.127$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.022$	$\Delta\rho_{\text{max}} = 1.97 \text{ e \AA}^{-3}$
1627 reflections	$\Delta\rho_{\text{min}} = -3.01 \text{ e \AA}^{-3}$
37 parameters	

**Table 1**

Selected geometric parameters (Å, °).

Sb1–Sb2 <sup>i</sup>	2.8383 (13)	Rb1–Sb2 <sup>v</sup>	3.8417 (15)
Sb1–Sb2	2.8617 (12)	Rb2–Sb1 <sup>vi</sup>	3.6788 (17)
Rb1–Sb1 <sup>ii</sup>	3.6414 (17)	Rb2–Sb1 <sup>iii</sup>	3.6921 (15)
Rb1–Sb2	3.6605 (15)	Rb2–Sb1 <sup>iiii</sup>	3.7364 (16)
Rb1–Sb2 <sup>iii</sup>	3.7097 (16)	Rb2–Sb2 <sup>ii</sup>	3.7793 (16)
Rb1–Sb1	3.7894 (17)	Rb2–Sb2 <sup>iiii</sup>	3.7817 (17)
Rb1–Sb1 <sup>iv</sup>	3.7943 (17)	Rb2–Sb2 <sup>v</sup>	4.0207 (18)
<hr/>			
Sb2 <sup>i</sup> –Sb1–Sb2	115.59 (3)	Sb1 <sup>iii</sup> –Sb2–Sb1	110.36 (3)

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* (Spek, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1968) and *DRAWxtl* (Finger & Kroeker, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1316). Services for accessing these data are described at the back of the journal.

## References

- Cromer, D. T. (1959a). *Acta Cryst.* **12**, 36–40.  
 Cromer, D. T. (1959b). *Acta Cryst.* **12**, 41–45.  
 Dorn, F. W. & Klemm, W. (1961). *Z. Anorg. Allg. Chem.* **309**, 189–203.  
 Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.  
 Finger, L. & Kroeker, M. (1999). *DRAWxtl*. Home page, <http://www.lwfinger.net/drawxtl.html>.  
 Hirschle, Ch. & Röhr, C. (2000). *Z. Kristallogr. Suppl.* **17**, 164–164.  
 Hönle, W. & von Schnering, H. G. (1978). *Acta Cryst.* **A34**, S152–156.  
 Hönle, W. & von Schnering, H. G. (1981). *Z. Kristallogr.* **155**, 307–314.  
 Johnson, C. K. (1968). *ORTEP*. Oak Ridge National Laboratory, Tennessee, USA. [Openwindows Version (1991) of Norimasa Yamazaki, Tokyo, Japan.]  
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.  
 Schnering, H. G. von & Hönle, W. (1979). *Z. Anorg. Allg. Chem.* **456**, 194–206.  
 Schnering, H. G. von, Hönle, W. & Krogull, G. (1979). *Z. Naturforsch. Teil B*, **34**, 1678–1682.  
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.  
 Spek, A. L. (1993). *HELENA*. Utrecht University, The Netherlands.