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The Crystal Structure of Sr_2Sb

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Sr_2Sb crystallizes in the tetragonal system, space group $I4/mmm$, with four formula units in a cell of dimensions $a=5{\cdot}002\pm0{\cdot}003$ and $c=17{\cdot}405\pm0{\cdot}008$ Å. The calculated density is 4·528 g cm^{-3}. The structure of Sr_2Sb has been solved by three-dimensional Patterson synthesis. The positional parameters and isotropic thermal coefficients were refined by the least-squares method based on 674 reflexions. The final conventional R index is 0·095. There are uncommonly short Sr–Sr distances in layers perpendicular to the c axis.

Introduction

Preliminary results on the Sr–Sb system obtained by Shchukarev, Morozova & Kan Kho-in (1957*a*, *b*) indicated the existence of four compounds in the system, $SrSb_3$, SrSb, Sr_3Sb_2 and Sr_2Sb. Later, Brauer & Müller (1961) reported on a compound with formula Sr_2Sb and tetragonal symmetry.

A recent investigation undertaken by Martinez-Ripoll & Brauer (1973) demonstrated the existence of a new compound in the system with hexagonal symmetry, whose formula Sr_5Sb_3 was deduced from the study of its crystal structure.

The present paper reports on the crystal structure of the compound Sr_2Sb, whose single crystals grow together with those of Sr_5Sb_3.

Experimental

Single crystals of Sr_2Sb are prepared by the method described in the case of Sr_5Sb_3 (Martinez-Ripoll & Brauer, 1973). The crystals of Sr_2Sb are black and have laminar shape, the c axis being perpendicular to the plate. Because of their extreme sensitivity to air they had to be kept under argon atmosphere.

Precession photographs taken with Mo $K\alpha$ radiation were used to determine the symmetry, space group and approximate lattice parameters. Sr_2Sb was found to be tetragonal with four formula units in the cell. The systematic absences correspond to four space groups, $I4mm$, $I\bar{4}m2$, $I\bar{4}2m$ and $I4/mmm$. The statistics of the normalized structure factors showed the existence of a centre of symmetry; no piezoelectric properties were found and analysis of the Patterson function led to a centrosymmetric arrangement of atoms. As a consequence, the space group $I4/mmm$ was assumed.

Accurate measurement on a diffractometer of the θ values for several reflexions led to the lattice parameters $a=5{\cdot}002\pm0{\cdot}003$ and $c=17{\cdot}405\pm0{\cdot}008$ Å. The calculated density is 4·528 g cm^{-3}. These data agree well with the results of Brauer & Müller (1961) and Müller (1960): $a=5{\cdot}00$, $c=17{\cdot}41$ Å and experimental density 4·52 g cm^{-3}.

Intensity data were measured for a complete octant of reciprocal space using a single crystal (0·025 × 0·030 × 0·006 cm) mounted on a Weissenberg-geometry single-crystal Huber diffractometer (RHD 402) on line to a PDP-8 computer. Pulse-height analysis was used with Mo $K\alpha$ radiation in conjunction with a monochromating graphite crystal. Symmetry-related reflexions were averaged to produce 674 independent reciprocal points. All intensity data were corrected for the Lorentz–polarization factor. For the purpose of the present work absorption corrections were not considered to be necessary ($\mu R\simeq1{\cdot}6$). In any case, such corrections would be tedious because of the irregular form of the crystals.

Determination of the structure

Structure factors based on the coordinates obtained from the three-dimensional Patterson function and isotropic temperature factors of 1·21 Å^2 gave an R index of 0·20. The f curves for neutral atoms (Thomas & Umeda, 1957) corrected for anomalous dispersion were used.

Refinement was done by the full-matrix least-squares procedure using the program *ORFLS* (Busing, Martin & Levy, 1962) and assuming unit weights. The final conventional R index is 0·095 based on the parameters given in Table 1.*

Table 1. *Positional and thermal parameters*

Standard deviations, multiplied by 10^5, are given in parentheses.

	x/a	y/b	z/c	B
Sr(1)	0	½	0	0·85 Å^2
Sr(2)	0	0	0·32825 (10)	1·24
Sb	0	0	0·13666 (5)	0·94

* A list of observed and calculated structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30114. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

This structure agrees with the one given by Müller (1960), who used single crystals to propose a space group. He used powder patterns to calculate by trial-and-error methods atomic parameters of the compound Sr_2Bi believed to be isomorphous with the compound Sr_2Sb.

Description and discussion of the structure

This crystal structure can be visualized as being built up from atomic layers perpendicular to the **c** direction, similar to those of the PbFCl structure, as shown in Fig. 1. There are layers (*A*) containing only Sr(1) atoms in a cubic arrangement. Between two successive *A* layers there are two more layers (*B*), each one containing Sr(2) and Sb atoms. To a first approximation, the Sr(2) and Sb atoms in a *B* layer form a closest-packed sheet, one of these layers being translated by a vector (**a**/2+**b**/2) with respect to the other, in such a way that each Sr(2) atom has an Sb atom as nearest neighbour on the adjacent layer of the same kind. The strontium atoms of the *A* layers, Sr(1), are all coplanar. However, the atoms of the *B* layers are not exactly in the same plane; the Sr(2) atoms are shifted 0·61 Å from the plane built up by the Sb atoms in the direction of the adjacent *B* layer.

Each strontium atom of the *A* layers, Sr(1), has twelve neighbours [4Sr(1)+4Sr(2)+4Sb] arranged as shown in Fig. 2. The four antimony atoms are each at a distance of 3·451 Å and the four Sr(2) atoms at 3·898 Å. The other four neighbours are Sr(1) atoms, and their arrangement implies four very short Sr(1)–Sr(1) distances of 3·537 Å.

The atomic distribution around the strontium atoms of the *B* layers, Sr(2), is shown in Fig. 3. Each one of these atoms has thirteen neighbours [4Sr(1)+4Sr(2)+5Sb]. Four Sb atoms on the same *B* layer are situated at the corners of a square, at distances of 3·589 Å; the fifth antimony atom at a distance of 3·335 Å belongs to the neighbouring *B* layer and completes a pyramidal arrangement. The four Sr(1) atoms belong to an *A* layer and are at 3·898 Å from the Sr(2) atom. The remaining four neighbours of Sr(2) are also Sr(2) atoms but situated in the parallel *B* layer and at distances appreciably greater (4·464 Å).

Each antimony atom has nine neighbours only, forming a unit $SbSr_9$ as shown in Fig. 4. Four of the neighbours are Sr(1) atoms, each at a distance of 3·451 Å. Four Sr(2) atoms are at 3·589 Å and one Sr(2) atom is at 3·335 Å. Each Sr(1) atom is shared among four $SbSr_9$ groups and each Sr(2) atom is shared among five groups. A similar arrangement of strontium atoms around the Sb atom (tetrakaidecahedron) has been found in the structure of Sr_5Sb_3 (Martinez-Ripoll & Brauer, 1973).

A list of all interatomic distances is given in Table 2. Several valence angles are reported in Table 3.

The average Sb–Sr distance of 3·499 Å is appreciably short compared with the value of 3·70 Å obtained from the sum of metallic radii given by Pauling (1947) and assuming coordination numbers of 9, 12 and 13 for Sb, Sr(1) and Sr(2) respectively. A similar result has been found in the structure of Sr_5Sb_3 (Martinez-Ripoll & Brauer, 1973), where the mean value of

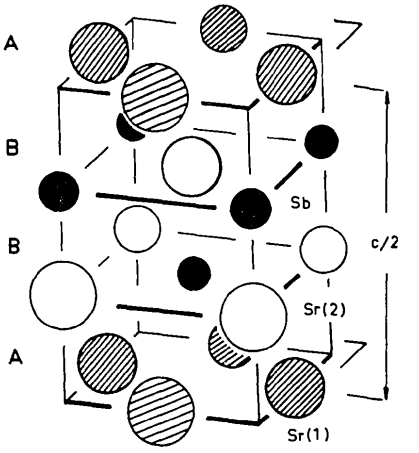

Fig. 1. The structure of Sr_2Sb showing the plane atom layers of atom perpendicular to the *c* axis.

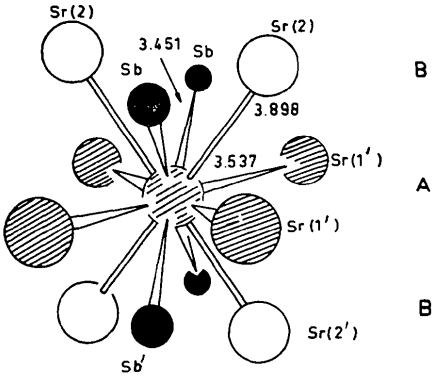

Fig. 2. Arrangement of atoms around Sr(1). The bond lengths are given in Å. Three mirror planes pass through the central atom, containing the four Sb, the four Sr(2) and the four Sr(1') atoms.

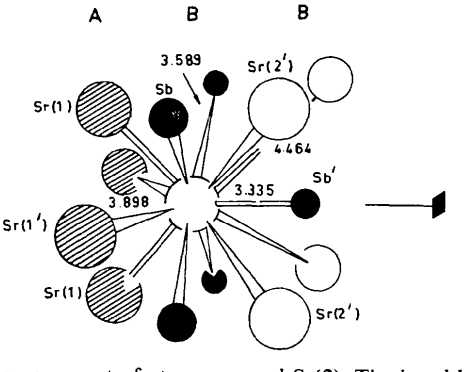

Fig. 3. Arrangement of atoms around Sr(2). The bond lengths are given in Å.

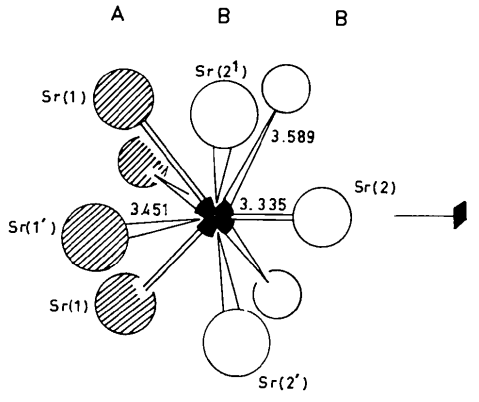

Fig. 4. Arrangement of atoms around Sb. The bond lengths are in Å.

Table 2. *Interatomic distances*

Estimated standard deviation ±0·008 Å

			Averages	
Sr(1)–Sb	3·451 Å	(×4)	Sr(1)–Sr(1)	3·537 Å
Sr(1)–Sr(1)	3·537	(×4)	Sr(1)–Sr(2)	3·898
Sr(1)–Sr(2)	3·898	(×4)	Sr(1)–Sr	3·718
Sr(2)–Sb	3·335 Å	(×1)	Sr(2)–Sr(1)	3·898 Å
Sr(2)–Sb	3·589	(×4)	Sr(1)–Sr(2)	4·464
Sr(2)–Sr(1)	3·898	(×4)	Sr(2)–Sr	4·181
Sr(2)–Sr(2)	4·464	(×4)		
Sb—Sr(2)	3·335 Å	(×1)	Sb—Sr(1)	3·451 Å
Sb—Sr(1)	3·451	(×4)	Sb—Sr(2)	3·538
Sb—Sr(2)	3·589	(×4)	Sb—Sr	3·499

the Sb–Sr distances is 3·516 Å. These results and the short Sr(1)–Sr(1) distances of 3·537 Å mentioned above (3·711 Å in Sr_5Sb_3) indicate a pronounced deviation from metallic behaviour, probably in the direction of a partial ionic character of these atoms.

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Table 3. *Valence angles*

Estimated standard deviation ±0·2°

Around Sr(1)			
Sr(2)	Sr(2)	79·8°	(×2)
Sr(2)	Sr(2')	100·2	(×2)
Sr(2)	Sr(1')	63·0	(×8)
Sr(2)	Sb	58·1	(×8)
Sr(1')	Sr(1')	90·0	(×4)
Sb	Sb	92·9	(×2)
Sb	Sb'	87·1	(×2)
Around Sr(2)			
Sr(1)	Sr(1)	79·8°	(×2)
Sr(1)	Sr(1')	54·0	(×4)
Sr(1)	Sb	54·7	(×8)
Sr(2')	Sr(2')	68·1	(×4)
Sr(2')	Sb'	52·4	(×4)
Sr(2')	Sb	47·4	(×4)
Sb	Sb	88·3	(×4)
Around Sb			
Sr(1)	Sr(1)	92·9°	(×2)
Sr(1)	Sr(2')	67·2	(×8)
Sr(1)	Sr(1')	61·6	(×4)
Sr(2)	Sr(2')	80·2	(×4)
Sr(2')	Sr(2')	88·3	(×4)

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