with the fact that the carboxyl group is ionized. No C–C bond lengths in the benzene ring deviate significantly from the mean value of 1.390 Å. The bond length of C(4)–O(10), 1·360 Å, accords with the corresponding one in *p*-hydroxybenzoic acid monohydrate. The angle O(10)–C(4)–C(5), 117·4°, is smaller than that of O(10)–C(4)–C(3), 123·3°, as observed in the monohydrate. The mean values of the C–C and C–N bond lengths in the piperidine ring are 1·519 and 1·498 Å, respectively. These values are in accordance with 1·505 and 1·497 Å in piperidine hydrochloride (Rérat, 1960), and 1·522 and 1·499 Å in 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl (Berliner, 1970), respectively. The bond angles in the piperidine ring are slightly larger than the regular tetrahedral angle.

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The Crystal Structure of Sr_5Sb_3

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Sr_5Sb_3 crystallizes as a Mn_5Si_3-type structure, space group $P6_3/mcm$, with two formula units in a cell of dimensions $a = 9{\cdot}496 \pm 0{\cdot}005$, $c = 7{\cdot}422 \pm 0{\cdot}005$ Å. The calculated density is 4·602 g cm^{-3}. The structure of Sr_5Sb_3 has been determined by three-dimensional Patterson synthesis. The positional and isotropic thermal parameters were refined by least-squares analysis, yielding a final R value of 0·056. There is one unusually short distance Sr–Sr in chains parallel to the c axis.

Introduction

The binary system Sr–Sb was treated by Shchukarev, Morozova & Kan Kho-in (1957*a*, *b*) in a preliminary study. Metallographic observations of cast alloys, thermal analysis and gram-formula volume *vs.* composition curves indicated the existence of four intermediate phases corresponding to the compounds $SrSb_3$, SrSb, Sr_3Sb_2 and Sr_2Sb. More recently, Brauer & Müller (1961) have reported on a compound with tetragonal symmetry and formula Sr_2Sb.

We prepared new samples of Sr-rich alloys in order to solve the crystal structure of the last compound. Powder X-ray diffraction patterns of those samples demonstrated the existence of two compounds in the alloys. One of them, in agreement with Brauer & Müller (1961), belongs to the tetragonal system. The other compound of the mixture is not tetragonal; the present paper reports on its crystal structure. From this study the formula Sr_5Sb_3 was deduced for this compound.

Experimental

Single crystals of Sr_5Sb_3 were prepared by cooling a melt of stoichiometry 4Sr + 1Sb from 1430 °C to room temperature in argon atmosphere with subsequent leaching of the alloy with anhydrous ammonia. Under these conditions the excess of Sr is removed and separated black crystals of Sr_5Sb_3 with nearly prismatic shape were obtained. They are hard and extremely sensitive to air. Thus they had to be kept under argon. The elements used for synthesis had stated purities of 99% (Sr) and 99·99% (Sb).

The symmetry, space group and approximate lattice parameters were determined from Weissenberg photographs taken with Cu $K\alpha$ radiation. Sr_5Sb_3 was found to be hexagonal with two formula units in the cell. The systematic absences correspond to three space groups, $P6_3cm$, $P\bar{6}c2$ and $P6_3/mcm$. No piezoelectric properties were found, and the results of the E-value distribution did not conclusively differentiate between centrosymmetric and non-centrosymmetric structures. Analysis of the Patterson function eliminated the space group $P\bar{6}c2$, but did not discern between the space groups $P6_3cm$ and $P6_3/mcm$. As discussed later, the space group $P6_3/mcm$ was assumed.

Precise lattice parameters were obtained by accurate measurements of θ on a diffractometer for several reflexions. The following dimensions were found: $a=9{\cdot}496\pm0{\cdot}005$ and $c=7{\cdot}422\pm0{\cdot}005$ Å. The calculated density is 4·602 g cm^{-3}.

The intensity data from eight reciprocal layers perpendicular to the c axis were obtained from a prismatic single crystal with nearly circular cross section (0·26 mm diameter). A two-circle diffractometer with 2θ scan and filtered Mo $K\alpha$ radiation were used. The intensities were corrected for Lorentz and polarization effects in the usual manner. As the crystal showed strong absorption effects ($\mu R=4{\cdot}0$) in spite of its small size, the due corrections were made assuming cylindrical shape.

Determination of the structure

The first step in the solution of this crystal structure was based on the interpretation of the three-dimensional Patterson function. As mentioned above, the peak distribution in the Patterson synthesis eliminated the space group $P\bar{6}c2$. All maxima could be explained in terms of the two remaining space groups $P6_3cm$ and $P6_3/mcm$, and in both cases the same centrosymmetric arrangement of atoms was found. Therefore, the centric space group $P6_3/mcm$ was assumed.

Structure factors based on the Patterson coordinates, assuming isotropic temperature factors of 0·83 $Å^2$ obtained from the Wilson plot, correspond to $R=0{\cdot}15$. The f curves for neutral Sr and Sb (Thomas & Umeda, 1957) corrected for anomalous dispersion were used. The difference electron-density map showed no peaks greater than 2 e $Å^{-3}$.

Since the structural arrangement obtained was reasonable from the crystal-chemistry point of view, this structure was refined by the use of the least-squares program *ORFLS* (Busing, Martin & Levy, 1962). Several cycles of isotropic refinement gave an R index of 0·056. A weight of one for each observation was used. The final positional and thermal parameters are shown in Table 1.*

Description and discussion of the structure

Fig. 1 shows a view of the structure with partial projection on the (001) plane. The strontium atoms occupy two different crystallographic sites corresponding to the point symmetries 32, Sr(1), and *mm*, Sr(2). There is one crystallographic independent Sb atom only, which corresponds to the point symmetry *mm*.

Sr_5Sb_3 crystallizes in the Mn_5Si_3-type structure (Aronsson, 1960). Although the principles of this structure have been repeatedly discussed (Parthé, Lux & Nowotny, 1955; Nowotny, Lux & Kudielka, 1956; Aronsson, 1960; Schubert, 1964; Bärnighausen, Knau-

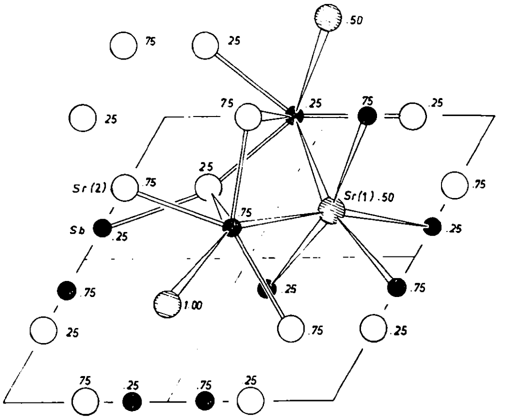

Fig. 1. The projection of one unit-cell on (001). The heights of the atoms are given as fractions of the c parameter.

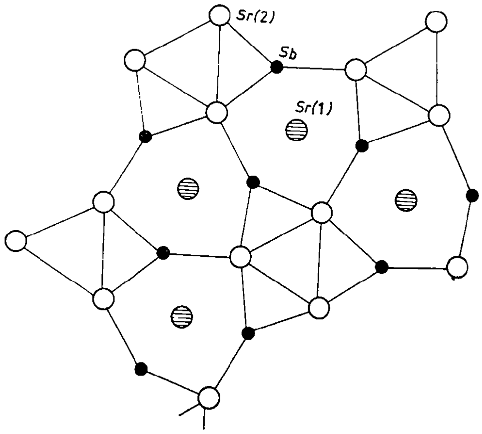

Fig. 2. The structure of Sr_5Sb_3 showing a plane atom layer perpendicular to the c axis. The Sr(1) atoms are between successive layers.

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)	0·33333 (0)	0·66667 (0)	0·50000 (0)	0·87 $Å^2$
Sr(2)	0·25337 (11)	0·00000 (0)	0·75000 (0)	0·98
Sb	0·39045 (6)	0·00000 (0)	0·25000 (0)	0·63

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* The table of observed and calculated structure factors has been deposited at the National Lending Library, England (Supplementary Publication No. SUP 30173). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

senberger & Brauer, 1965) we want to point to some peculiarities that may be relevant to the case of Sr_5Sb_3. This crystal structure contains plane atom layers which resemble the so-called *A* layers (Black, 1956) of most of the transition-metal atoms in the so-called *T*2 phases (Parthé, Lux & Nowotny, 1955), but an important difference is that the layers in Sr_5Sb_3, besides Sr metal atoms, contain antimony atoms (Fig. 2). In a first approximation the antimony atoms form a hexagonal closest-packed arrangement. Each strontium atom of the *A* layer, Sr(2), has fifteen-neighbours, whereas the Sr(1) atoms between two successive *A* layers have fourteen (Table 2). The octahedral voids (at 0,0,0 and 0,0,$\frac{1}{2}$) between two layers are empty.

The crystal structure of Sr_5Sb_3 can be also easily described in terms of $SbSr_9$ units. Each one of these units contains four strontium atoms Sr(1) and five Sr(2). These nine Sr atoms are arranged at the corners of a very distorted tetrakaidecahedron whose centre is occupied by the antimony atom. Such a unit is shown in Fig. 3. The four strontium atoms of type Sr(1) are at 3·470 Å from the Sb atom. However, the distances Sb–Sr(2) are not all equal; two Sr(2) atoms are at 3·258 Å and one is at 3·382 Å. The two remaining Sb–Sr(2) distances are significantly greater (3·933 Å) and correspond to an elongation of 0·536 Å (~16%) compared to the average of the other seven distances.

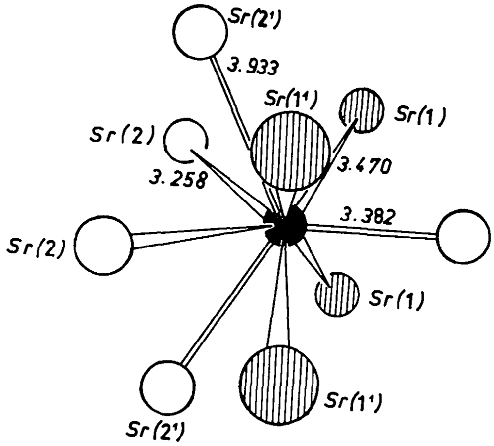

Fig. 3. Arrangement of strontium atoms around Sb. The bond lengths in Å are given. Two mirror planes pass through Sb, containing the two Sr(2) and the two Sr(2^1) atoms respectively.

Each $SbSr_9$ group shares its nine strontium atoms with other groups, but not all the Sr atoms are equally shared. The Sr(1) atoms are common to six groups and occupy the holes between two adjacent layers (Figs. 1 and 2). The six Sb–Sr(1) distances are 3·470 Å. This situation implies a very short Sr(1)–Sr(1) distance in the **c** direction (3·711 Å) compared with the value of 4·34 Å obtained from the metallic radius of this atom for coordination number 14 (Pauling, 1947). The Sr(2) atoms, on the other hand, are shared among five $SbSr_9$ groups only, corresponding to the arrangement shown in Fig. 4 and to an averaged Sr(2)–Sb distance of 3·553 Å.

The mean value of 3·516 Å for the Sb–Sr distance in the $SbSr_9$ group is certainly appreciably shorter than would be predicted (3·72 Å) from the sum of metallic radii given by Pauling (1947) and assuming coordination numbers of 9, 14 and 15 for Sb, Sr(1) and Sr(2) respectively. This result may be due to the possibility of significant effects resulting from electron transfer or from partial ionic character of bonds (Pauling, 1950), effects which are expected to give a large correcting term to the normal metallic radii of the elements in the case of alloys between hypoelectronic and hyperelectronic atoms. These effects could also explain the uncommon short distances Sr(1)–Sr(1) mentioned above (3·711 Å) with the assumption of a partial positive charge on these atoms. The results appearing in the structures of SrMgX (X = Si, Ge, Sn) (Eisenmann, Schäfer & Weiss, 1972) indicate also that the element strontium in those compounds must be considered as having a smaller radius than that expected.

Table 2. *Interatomic distances*

Estimated standard deviation ±0·006 Å.

Sr(1)–Sb	3·470 Å (×6)	Sb–Sr(2)	3·258 Å (×2)
Sr(1)–Sr(1)	3·711 (×2)	Sb–Sr(2)	3·382 (×1)
Sr(1)–Sr(2)	4·055 (×6)	Sb–Sr(1)	3·470 (×4)
		Sb–Sr(2)	3·933 (×2)
Sr(2)–Sb	3·258 Å (×2)	Sb–Sb	4·254 (×2)
Sr(2)–Sb	3·382 (×1)		
Sr(2)–Sb	3·933 (×2)		
Sr(2)–Sr(1)	4·055 (×4)		
Sr(2)–Sr(2)	4·167 (×2)		
Sr(2)–Sr(2)	4·423 (×4)		
Averages			
Sr(1)–Sr(1)	3·711 Å	Sb–Sr(1)	3·470 Å
Sr(1)–Sr(2)	4·055	Sb–Sr(2)	3·553
Sr(1)–Sr	3·969	Sb–Sr	3·516
Sr(2)–Sr(1)	4·055 Å		
Sr(2)–Sr(2)	4·337		
Sr(2)–Sr	4·225		

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

Table 3. *Valence angles around* Sb

Estimated standard deviation ±0·1°.

Sr(2^i)–Sb–Sr(2)	75·3°	(×4)
Sr(2^i)–Sb–Sr(2^i)	141·3	(×1)
Sr(2) –Sb–Sr(2)	79·5	(×1)
Sr(1) –Sb–Sr(1)	64·7	(×2)
Sr(1) –Sb–Sr(1^i)	104·4	(×2)
Sr(1) –Sb–Sr(2^i)	72·6	(×4)
Sr(2^i)–Sb–Sr(1)	66·1	(×4)

The numerical calculations were carried out on the 7040 IBM and 1108 UNIVAC computers of the University of Freiburg, Germany. We acknowledge the facilities given by Huber Diffraktions-Technik in order to obtain the intensity data. We also acknowledge the aid given by the Deutsche Forschungs-Gemeinschaft which made available several laboratory facilities.

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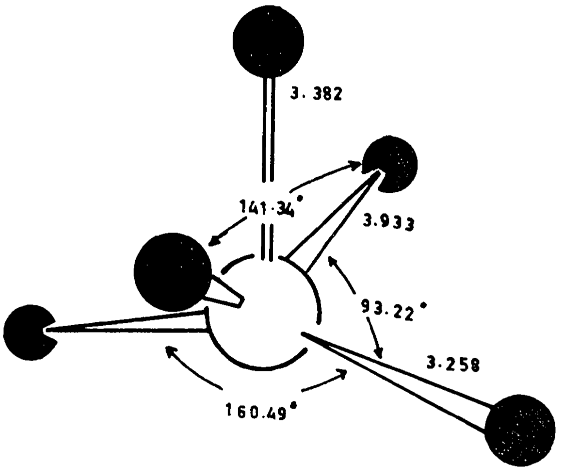

Fig. 4. The antimony atom arrangement around Sr(2). The bond lengths in Å, and the corresponding valence angles are given.

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