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The Crystal Structure of Ca_5Sb_3

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Ca_5Sb_3 crystallizes in the orthorhombic system, space group *Pnma*, with 4 formula units in a cell of dimensions $a=12{\cdot}502\pm0{\cdot}008$, $b=9{\cdot}512\pm0{\cdot}007$ and $c=8{\cdot}287\pm0{\cdot}007$ Å. The calculated density is 3·81 g cm^{-3}. The structure of Ca_5Sb_3 has been solved by three-dimensional Patterson synthesis. Least-squares refinement of positional and isotropic thermal parameters led to a final R index of 0·062 for 1755 reflexions. The interatomic distances indicate some ionic character of bonds.

Introduction

Preliminary investigation on the binary system Ca–Sb undertaken by Donski (1908) indicated a eutectic at *ca.* 8·5 wt.% Ca. On the basis of the existence of a maximum in the heat-of-formation curve, Kubaschewski & Walter (1939) reported on a compound with stoichiometry Ca_3Sb_2. Later, investigations by Brauer & Müller (1961) indicated the existence of a compound with a composition near to Ca_7Sb_4 with orthorhombic symmetry.

As a part of a programme of investigation of intermetallic compounds, we have solved the crystal structure of the last compound. Its correct formula, Ca_5Sb_3, was deduced from this study.

Experimental

Single crystals of Ca_5Sb_3 can be prepared by cooling a melt of stoichiometry 3Ca+2Sb with a small excess of calcium from 1350 °C to room temperature in an argon atmosphere (Müller, 1960). Isolated single crystals are obtained by subsequent leaching of the alloy with anhydrous ammonia. They are black and have nearly prismatic shape, the *a* axis being parallel to the needle axis. Because of their extreme sensitivity to air they had to be kept under an argon atmosphere.

The space group and approximate lattice parameters were obtained from precession and Weissenberg photographs taken with Mo $K\alpha$ radiation. Ca_5Sb_3 was found to be orthorhombic with 4 formula units in the cell. The systematic absences correspond to the space groups *Pnma* or $Pn2_1a$. 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 *Pnma* was assumed.

Precise lattice parameters were obtained by least-squares fit of the θ values for several reflexions. The following dimensions were found: $a=12{\cdot}502\pm0{\cdot}008$, $b=9{\cdot}512\pm0{\cdot}007$, $c=8{\cdot}287\pm0{\cdot}007$ Å. The calculated density is 3·81 g cm^{-3}. These data compare with the results of Brauer & Müller (1961) and Müller (1960): 12·50, 9·57, 8·32 Å and experimental density 3·74 g cm^{-3}.

The intensity data from 18 reciprocal layers perpendicular to the *a* axis were obtained from a prismatic single crystal with nearly circular cross section (0·25 mm diameter) mounted on a Weissenberg-geometry single-crystal Huber diffractometer (RHD 402) on line to a PDP-8 computer. Graphite-monochromated Mo $K\alpha$ radiation was used in connection with a scintillation detector and pulse-height discrimination. 2057 reflexions were collected in the range $3°<\theta<40°$. Of this total, 1755 reflexions were considered 'observed' according to the criterion $I>2\,.\,\sigma(I)$ and used in the calculations. Absorption corrections ($\mu\,.\,R=1{\cdot}30$) were made assuming cylindric shape. The structure amplitudes were obtained after the usual Lorentz and polarization reduction.

Determination of the structure

All maxima of the three-dimensional Patterson function could be explained in terms of the two space

Table 1. *Positional and thermal parameters*

Standard deviations are given in parentheses.

	x	*y*	*z*	*B*
Ca(1)	0·07531 (15)	0·04248 (19)	0·69297 (21)	0·75 (2) Å^2
Ca(2)	0·22749 (22)	¼	0·32130 (31)	0·76 (3)
Ca(3)	0·28942 (22)	¼	0·85151 (31)	0·79 (3)
Ca(4)	0·50630 (20)	¼	0·46446 (29)	0·60 (3)
Sb(1)	0·17042 (5)	−0·01461 (6)	0·06680 (6)	0·67 (1)
Sb(2)	−0·01675 (6)	¼	0·42152 (9)	0·60 (1)

groups *Pnma* and $Pn2_1a$, and in both cases the same centrosymmetric arrangement of atoms was found. Therefore, the centrosymmetric space group *Pnma* was assumed.

Structure factors based on the Patterson coordinates, assuming isotropic temperature factors of 0·87 Å^2 gave $R=\sum||F_o|-|F_c||/\sum|F_o|=0{\cdot}27$. Scattering factors were those for neutral atoms (Hanson, Herman, Lea & Skillman, 1964).

Refinement was carried out 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 0·062 based on the parameters given in Table 1. A table listing the observed and calculated structure factors is available.*

Description and discussion of the structure

The unit-cell contents are shown in Fig. 1 as viewed along the c axis. There are four Ca atoms and two Sb atoms in the asymmetric unit. Sb(1) and Ca(1) are located in general positions, while the remaining atoms occupy special positions corresponding to the point symmetry m (Table 1).

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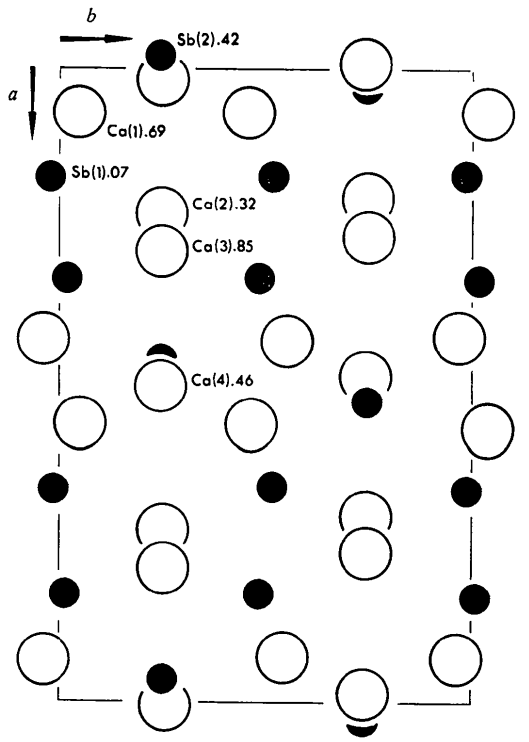

Fig. 1. The structure of Ca_5Sb_3 as viewed along the c axis.

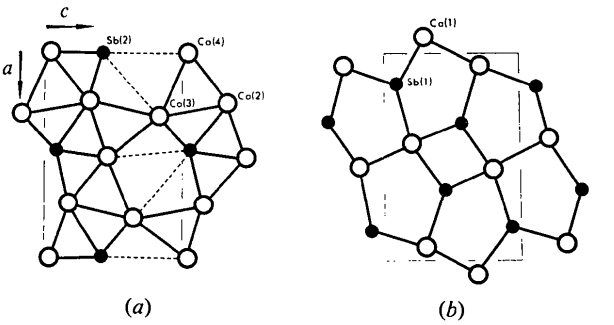

Fig. 2. The atomic layers perpendicular to the b axis. (*a*) At $y=\frac{1}{4}$. [The identical layer at $y=\frac{3}{4}$ is obtained through the centre of symmetry at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.] (*b*) At $y\simeq 0,\frac{1}{2}$.

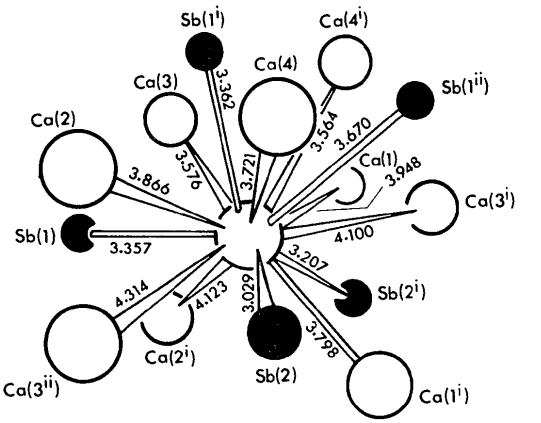

Fig. 3. Arrangement of atoms around Ca(1). The bond lengths are given in Å.

This crystal structure can be visualized as being built up from atomic layers perpendicular to the **b** direction. The layers at $y=\frac{1}{4},\frac{3}{4}$ contain Sb(2), Ca(2), Ca(3) and Ca(4) atoms, are exactly plain, and form, to a first approximation, a distorted closest-packed sheet [Fig. 2(*a*)]. The atomic layers at $y\simeq 0,\frac{1}{2}$ contain Sb(1) and Ca(1) atoms, and are also shown in Fig. 2(*b*).

The Ca(1) atom has 14 neighbours [3Sb(1)+2Sb(2)+2Ca(1)+2Ca(2)+3Ca(3)+2Ca(4)] arranged as shown in Fig. 3. The average values of the Ca(1)–Sb and Ca(1)–Ca distances are 3·325 and 3·890 Å respectively. The atomic distribution around the Ca(2) atom is shown in Fig. 4. Each Ca(2) atom is surrounded by 14 neighbours [4Sb(1)+2Sb(2)+4Ca(1)+2Ca(3)+2Ca(4)], the averages of the Ca(2)–Sb and Ca(2)–Ca distances being 3·371 and 3·967 Å respectively. The Ca(3) atom has 15 neighbours [4Sb(1)+1Sb(2)+6Ca(1)+2Ca(2)+2Ca(4)] distributed as shown in Fig. 5, and implying average values for the Ca(3)–Sb and Ca(3)–Ca distances of 3·300 and 4·047 Å respectively. The arrangement of atoms around the Ca(4) atom is shown in Fig. 6. Each Ca(4) atom has 13

neighbours [4Sb(1)+1Sb(2)+4Ca(1)+2Ca(2)+2Ca(3)] and the average values of the Ca(4)–Sb and Ca(4)–Ca distances are 3·249 and 3·743 Å respectively. In counting the number of neighbouring atoms around the calcium atoms, a criterion was used similar to that proposed by Brunner & Schwarzenbach (1971). If the distances from the considered atom to all other atoms are ordered in a series according to increasing value,

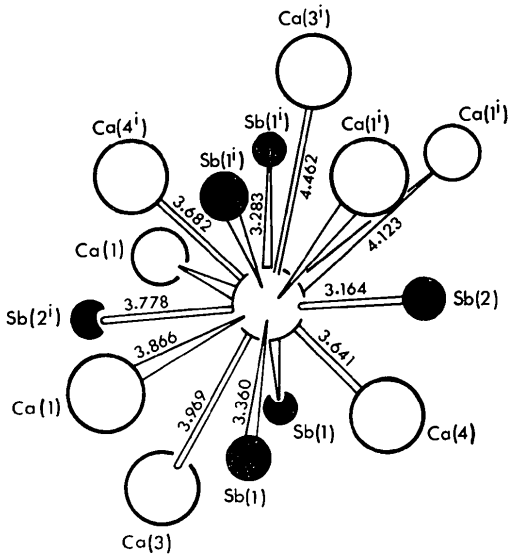

Fig. 4. Arrangement of atoms around Ca(2). The bond lengths are given in Å. A mirror plane passes through the central atom, containing the two Sb(2), the two Ca(3) and the two Ca(4) atoms.

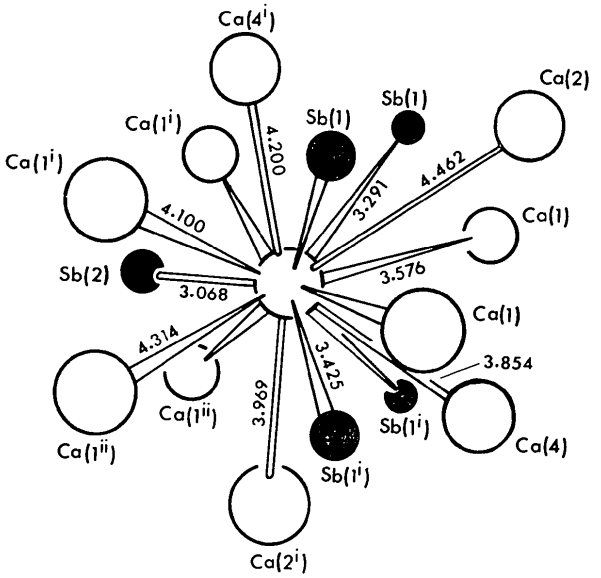

Fig. 5. Arrangement of atoms around Ca(3). The bond lengths are given in Å. A mirror plane passes through the central atom, containing the Sb(2), the two Ca(2) and the two Ca(4) atoms.

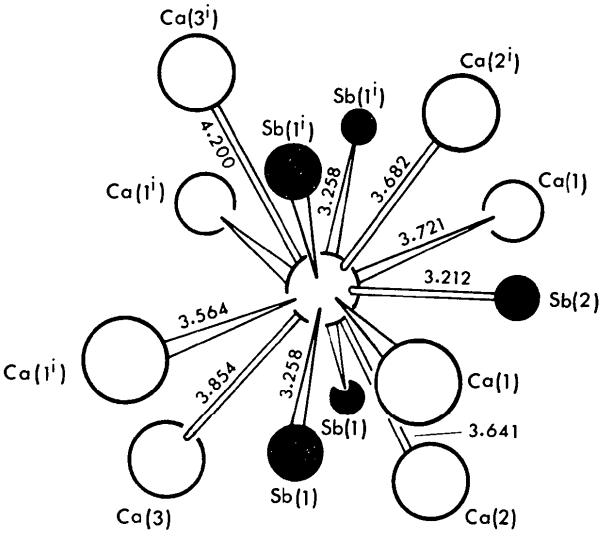

Fig. 6. Arrangement of atoms around Ca(4). The bond lengths are given in Å. A mirror plane passes through the central atom, containing the Sb(2), the two Ca(2) and the two Ca(3) atoms.

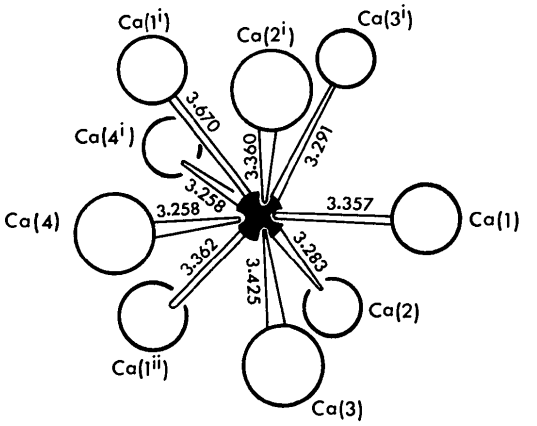

Fig. 7. Arrangement of atoms around Sb(1). The bond lengths are given in Å.

there is generally a striking gap or minimum in this series which limits the area of the neighbours. As a consequence, any distance greater than 4·5 Å should be disregarded.

Each Sb(1) atom has 9 neighbours forming a unit $SbCa_9$ as shown in Fig. 7. The average Sb(1)–Ca distance is 3·363 Å. A similar atomic arrangement around the antimony atoms is present in the $SbSr_9$ units found in the structures of Sr_2Sb (Martinez-Ripoll, Haase & Brauer, 1973) and Sr_5Sb_3 (Martinez-Ripoll & Brauer, 1973). The Sb(2) atoms have 8 neighbours only, arranged in the form shown in Fig. 8. The average value of the Sb(2)–Ca distances is 3·212 Å.

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

Table 2. *Interatomic distances*

Estimated standard deviation ±0·002 Å

Around Ca(1)			Around Ca(2)		
Ca(1)–Sb(2)	3·029 Å	(×1)	Ca(2)–Sb(2)	3·164 Å	(×1)
–Sb(2)	3·207	(×1)	–Sb(1)	3·283	(×2)
–Sb(1)	3·357	(×1)	–Sb(1)	3·360	(×2)
–Sb(1)	3·362	(×1)	–Sb(2)	3·778	(×1)
–Sb(1)	3·670	(×1)	–Ca(4)	3·641	(×1)
–Ca(4)	3·564	(×1)	–Ca(4)	3·682	(×1)
–Ca(3)	3·576	(×1)	–Ca(1)	3·866	(×2)
–Ca(4)	3·721	(×1)	–Ca(3)	3·969	(×1)
–Ca(1)	3·798	(×1)	–Ca(1)	4·123	(×2)
–Ca(2)	3·866	(×1)	–Ca(3)	4·462	(×1)
–Ca(1)	3·948	(×1)			
–Ca(3)	4·100	(×1)			
–Ca(2)	4·123	(×1)			
–Ca(3)	4·314	(×1)			

Around Ca(3)			Around Ca(4)		
Ca(3)–Sb(2)	3·068 Å	(×1)	Ca(4)–Sb(2)	3·212 Å	(×1)
–Sb(1)	3·291	(×2)	–Sb(1)	3·258	(×2)
–Sb(1)	3·425	(×2)	–Sb(1)	3·258	(×2)
–Ca(1)	3·576	(×2)	–Ca(1)	3·564	(×2)
–Ca(4)	3·854	(×1)	–Ca(2)	3·641	(×1)
–Ca(2)	3·969	(×1)	–Ca(2)	3·682	(×1)
–Ca(1)	4·100	(×2)	–Ca(1)	3·721	(×2)
–Ca(4)	4·200	(×1)	–Ca(3)	3·854	(×1)
–Ca(1)	4·314	(×2)	–Ca(3)	4·200	(×1)
–Ca(2)	4·462	(×1)			

Around Sb(1)			Around Sb(2)		
Sb(1)–Ca(4)	3·258 Å	(×1)	Sb(2)–Ca(1)	3·029 Å	(×2)
–Ca(4)	3·258	(×1)	–Ca(3)	3·068	(×1)
–Ca(2)	3·283	(×1)	–Ca(2)	3·164	(×1)
–Ca(3)	3·291	(×1)	–Ca(1)	3·206	(×2)
–Ca(1)	3·357	(×1)	–Ca(4)	3·212	(×1)
–Ca(2)	3·360	(×1)	–Ca(2)	3·778	(×1)
–Ca(1)	3·362	(×1)			
–Ca(3)	3·425	(×1)			
–Ca(1)	3·670	(×1)			
–Sb(1)	4·412	(×1)			
–Sb(1)	4·478	(×1)			

Averages

Ca(1)–Sb	3·325 Å	Ca(4)–Sb	3·249 Å
Ca(1)–Ca	3·890	Ca(4)–Ca	3·743
Ca(2)–Sb	3·371	Sb(1)–Ca	3·363
Ca(2)–Ca	3·967	Sb(2)–Ca	3·212
Ca(3)–Sb	3·300		
Ca(3)–Ca	4·047		

Table 3. *Valence angles*

Estimated standard deviation = ±0·1°.

Around Ca(1)

Ca(2)	Ca(3)	79·6°	Ca(4)	$Sb(1^{ii})$	52·3°
Sb(1)	Ca(2)	54·9	$Ca(4^i)$	$Sb(1^{ii})$	53·5
Ca(2)	$Ca(3^{ii})$	57·7	$Ca(4^i)$	Ca(1)	56·4
Ca(3)	$Ca(2^i)$	70·4	$Sb(1^{ii})$	Ca(1)	94·1
$Ca(3^{ii})$	$Ca(2^i)$	68·8	$Sb(1^{ii})$	$Ca(3^i)$	49·7
Sb(1)	$Ca(3^{ii})$	51·2	Ca(1)	$Ca(3^i)$	61·2
Sb(1)	$Ca(2^i)$	50·8	$Ca(3^i)$	$Sb(2^i)$	47·7
Sb(1)	Ca(3)	56·6	$Sb(2^i)$	$Ca(1^i)$	50·4
Ca(2)	$Sb(1^i)$	53·5	$Sb(2^i)$	Sb(2)	105·0
Ca(3)	$Sb(1^i)$	59·1	Sb(2)	$Ca(1^i)$	54·6
$Sb(1^i)$	Ca(4)	54·5	$Sb(1^{ii})$	$Ca(1^i)$	91·5
$Sb(1^i)$	$Ca(4^i)$	56·0	Sb(2)	$Ca(3^{ii})$	45·3
Ca(4)	$Ca(4^i)$	82·3	$Sb(2^i)$	$Ca(2^i)$	49·2

Table 3 (*cont.*)

Around Ca(2)

Ca(1)	Ca(1)	92·0°	$Sb(1^i)$	$Ca(3^i)$	47·3°
Ca(1)	$Sb(2^i)$	46·7	$Sb(1^i)$	$Ca(1^i)$	52·4
$Sb(2^i)$	$Ca(4^i)$	51·0	$Ca(1^i)$	$Ca(1^i)$	57·2
Ca(1)	$Ca(4^i)$	59·0	$Ca(1^i)$	Sb(2)	50·1
Ca(1)	$Sb(1^i)$	55·4	$Ca(1^i)$	Ca(4)	97·8
Ca(1)	Ca(3)	66·8	Sb(2)	Ca(4)	55·8
$Sb(2^i)$	Ca(3)	46·6	Sb(2)	Sb(1)	87·7
Ca(1)	Sb(1)	54·8	Sb(1)	Ca(4)	55·3
$Sb(2^i)$	Sb(1)	81·1	Ca(3)	Sb(1)	55·0
Sb(1)	Sb(1)	97·0	$Ca(3^i)$	$Ca(1^i)$	49·0
Sb(1)	$Sb(1^i)$	87·7	$Ca(4^i)$	$Ca(3^i)$	61·2
$Sb(1^i)$	$Sb(1^i)$	86·0	$Ca(3^i)$	Sb(2)	84·8

Around Ca(3)

$Ca(1^i)$	$Ca(1^i)$	57·6°	Ca(1)	Ca(4)	57·2°
Sb(2)	$Ca(1^i)$	50·7	Ca(1)	$Sb(1^i)$	57·4
$Ca(1^i)$	$Ca(1^{ii})$	53·6	Ca(4)	$Sb(1^i)$	52·8
Sb(2)	$Ca(1^{ii})$	44·6	$Sb(1^i)$	$Sb(1^i)$	94·6
$Ca(1^{ii})$	$Ca(1^{ii})$	80·3	$Sb(1^i)$	$Ca(2^i)$	53·4
$Ca(4^i)$	Sb(1)	49·8	$Ca(2^i)$	$Ca(1^{ii})$	55·5
Sb(1)	Sb(1)	85·7	Sb(1)	$Sb(1^i)$	86·5
Sb(1)	Ca(2)	47·2	$Ca(4^i)$	Ca(2)	50·2
Ca(2)	Ca(1)	60·5	Sb(2)	$Ca(4^i)$	87·6
Ca(1)	Ca(1)	67·0	Ca(1)	Ca(4)	103·3

Around Ca(4)

$Ca(1^i)$	$Ca(1^i)$	67·3°	Ca(1)	Ca(2)	79·3°
$Ca(1^i)$	$Ca(3^i)$	63·1	Sb(1)	Sb(1)	101·2
$Ca(1^i)$	$Sb(1^i)$	64·9	Sb(1)	Ca(2)	58·0
$Ca(3^i)$	$Sb(1^i)$	50·5	Sb(1)	Ca(3)	56·8
$Sb(1^i)$	$Sb(1^i)$	86·8	Ca(3)	$Ca(1^i)$	57·5
$Sb(1^i)$	$Ca(2^i)$	56·1	Sb(1)	$Sb(1^i)$	85·2
$Ca(2^i)$	Ca(1)	63·0	Ca(3)	$Ca(3^i)$	106·9
$Ca(2^i)$	Sb(2)	66·1	$Ca(3^i)$	$Ca(2^i)$	68·6
Ca(1)	Sb(2)	51·2	Sb(2)	Ca(2)	54·6
Ca(1)	Ca(1)	96·8	Ca(2)	Ca(3)	63·9

Around Sb(1)

$Ca(1^i)$	$Ca(1^{ii})$	102·4°	Ca(3)	$Ca(1^{ii})$	63·6°
Ca(4)	$Ca(4^i)$	94·8	Ca(2)	$Ca(1^{ii})$	71·1
Ca(4)	$Ca(1^i)$	64·6	Ca(3)	Ca(2)	90·5
$Ca(4^i)$	$Ca(1^i)$	61·6	$Ca(2^i)$	Ca(1)	70·3
Ca(4)	$Ca(1^{ii})$	65·1	$Ca(3^i)$	Ca(1)	65·1
$Ca(4^i)$	$Ca(1^{ii})$	68·4	Ca(2)	Ca(1)	76·8
$Ca(1^i)$	$Ca(2^i)$	83·8	Ca(3)	Ca(1)	79·0
$Ca(1^i)$	$Ca(3^i)$	71·9	Ca(4)	Ca(1)	133·0
$Ca(2^i)$	$Ca(3^i)$	91·6	$Ca(4^i)$	Ca(1)	132·0
$Ca(2^i)$	Ca(3)	71·6	$Ca(1^{ii})$	Ca(1)	129·4
Ca(4)	$Ca(2^i)$	66·7	$Ca(1^i)$	Ca(1)	128·2
Ca(4)	Ca(3)	70·4			

Around Sb(2)

$Ca(1^i)$	$Ca(1^i)$	76·0°	Ca(3)	Ca(2)	70·0°
$Ca(1^i)$	$Ca(2^i)$	80·7	Ca(1)	$Ca(2^i)$	98·7
$Ca(1^i)$	Ca(3)	81·6	Ca(4)	$Ca(2^i)$	69·6
$Ca(1^i)$	Ca(1)	75·0	Ca(4)	Ca(1)	73·1
Ca(1)	Ca(1)	133·4	Ca(1)	Ca(2)	68·2
Ca(1)	Ca(3)	90·1	Ca(3)	Ca(4)	133·0

The average Sb(1)–Ca [Sb(2)–Ca] distance of 3·363 Å (3·212 Å) is somewhat short compared with the value of 3·54 Å (3·53 Å) obtained from the sum of metallic radii given by Pauling (1947) and assuming coordination numbers of 8, 9 and ~14 for Sb(1), Sb(2) and Ca, respectively. The minimum Ca–Ca distances of 3·564 Å are also shorter than the Ca–Ca distances of 3·94 Å in

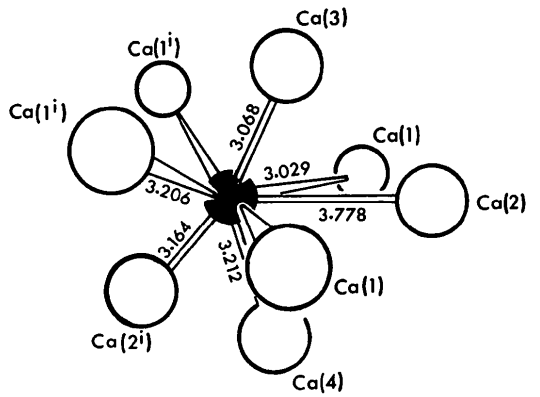

Fig. 8. Arrangement of atoms around Sb(2). The bond lengths are given in Å. A mirror plane passes through the central atom, containing the Ca(3), the Ca(4) and the two Ca(2) atoms.

metallic calcium. This can be due to an electron transfer or partial ionic character of bonds (Pauling, 1950). Similar deviation from metallic behaviour were also found in the structures of Sr_2Sb (Martinez-Ripoll, Haase & Brauer, 1973) and Sr_5Sb_3 (Martinez-Ripoll & Brauer, 1973), where the minimum Sr–Sr distances (3·537 and 3·711 Å respectively) are also shorter than the Sr–Sr distance of 4·31 Å in metallic strontium.

The numerical computations required in the analysis were performed using the X-RAY 70 System of crystallographic programs (Stewart, Kundell & Baldwin, 1970) on the 1108 UNIVAC computer of the University of Freiburg, Germany. Thanks are due to Huber Diffraktions-Technik for the facilities given in order to obtain the intensity data.

Dr Müller kindly allowed us to use a sample used in the work for his Thesis. The authors are grateful to Mr A. Haase for his aid in isolating the crystals suitable for this crystal analysis.

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Note added in proof:–Professor Bärnighausen drew our attention to the similarity between the Ca_5Sb_3 and the Rh_5Ge_3 structures (Geller, 1955). The space group *Pbnm* which can also be used to describe the crystal structure of Ca_5Sb_3 is a same-class maximal sub-group of index 2 to the space group *Pbam* of Rh_5Ge_3.

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