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The Crystal Structure of $Ca_{31}Sn_{20}$

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The phase $Ca_{31}Sn_{20}$ has tetragonal symmetry with $a = 12{\cdot}542$, $c = 40{\cdot}00$ Å, space group $I4/mcm$, $Z = 4$ and $D_m = 3{\cdot}74$ g cm^{-3}. The structure was solved by direct methods and refined to a final R index of 0·092 for 274 observed reflexions. The close structural relation between $Ca_{31}Sn_{20}$ and W_5Si_3 and Y_3Rh_2 is pointed out. A discussion of the coordination polyhedra and a comparison with other phases of the Ca–Sn system are given.

Introduction

In the course of a general survey on the existence and structure of intermetallic M_5X_3 compounds formed by alkaline earths with Group I*b* through V*b* elements (Bruzzone, Franceschi & Merlo, private communication), a new tetragonal phase in the system Ca–Sn was identified whose structure could not be attributed to any one of the structural types usual for the M_5X_3 intermetallic phases.

A preliminary investigation by thermal analysis on the Ca–Sn system between 33 and 50 at.% Sn showed that this phase forms by peritectic reaction at 1156°C with a probable stoichiometry Ca_3Sn_2, intermediate between those of the compounds Ca_2Sn and CaSn, already present in the Ca–Sn diagram (Hansen, 1958).

The purpose of the present work was the structural determination of this new phase.

Experimental and structure resolution

From an alloy of nominal composition Ca_3Sn_2, prepared by melting and subsequent annealing of the two metals in a sealed iron crucible, a plate-like single crystal with approximate dimensions 0·18 × 0·11 × 0·04 mm was isolated and examined by X-ray methods, Laue, rotating and precession techniques being applied. The results are summarized in Table 1.

The lattice constants were measured on precession photographs. Laue group 4/*mmm* was established and systematic absences of reflexions *hkl* with $h + k + l$ odd and 0*kl* with l odd led to the three possible space groups $I4cm$, $I\bar{4}c2$ and $I4/mcm$. The centrosymmetric space group was chosen for the structure solution and was confirmed at the end of the work.

Table 1. *Crystal data of* $Ca_{31}Sn_{20}$

Tetragonal	$V = 6292$ Å^3
$a = 12{\cdot}542$ Å	$Z = 4$
$c = 40{\cdot}00$	$D_m = 3{\cdot}74$ g cm^{-3} (pycnometer)
Space group $I4/mcm$ (No. 140)	$D_c = 3{\cdot}82$
	μ(Mo $K\alpha$) = 102 cm^{-1}

By comparison of the cell volume with the sum of the elemental atomic volumes of Ca and Sn and with the experimental density taken into account, a content of 40 unit formulae in the elementary cell was assumed.

Intensities of 1075 reflexions recorded on integrated precession photographs (Mo $K\alpha$ radiation) and measured by a microdensitometer were corrected for Lorentz–polarization and absorption effects (the crystal being described as a nine-faced polyhedron) and put on a common scale by inter-layer correlation. The intensities of equivalent reflexions were averaged and the resulting 274 independent reflexions were scaled by Wilson statistics.

Inspection of the collected data showed an unusual intensity distribution with a large number of unobserved reflexions and a noticeable presence of strong reflexions for particular values of l, namely 0, 12 and 24. This could be due to the occurrence of layers densely populated and equally spaced along the z axis and this was confirmed at the end of the structure solution.

The symbolic addition method (Karle & Karle, 1966) was applied to a set of 145 reflexions with $|E| \geq 1{\cdot}50$. At the end of this procedure 123 reflexions were assigned phases and only one symbol remained undetermined. Two three-dimensional E-Fourier maps were calculated and one of these gave an acceptable arrangement of atoms allowing the immediate location of 76 atoms of Ca and 56 of Sn. After the analysis of the weaker peaks some spurious peaks were rejected and also, by the aid of geometrical considerations, a further 48 atoms of Ca and 24 of Sn were recognized. In conclusion, the unit cell contains 124 atoms of Ca in seven positions and 80 atoms of Sn in eight positions with a final stoichiometric formula $Ca_{31}Sn_{20}$.

Full-matrix least-squares refinement (Busing, Martin & Levy, 1962) of 21 atomic parameters, scale and overall temperature factor was made, applying the anomalous scattering correction (*International Tables for X-ray Crystallography*, 1962), and after three

Table 2. *Atomic parameters of* $Ca_{31}Sn_{20}$ [*space group I4/mcm; B* = 0·92 (8) Å^2]

	Equipoint	*x*	*y*	*z*
Ca(1)	8(*h*)	0·3405 (36)	$\frac{1}{2}+x$	0
Ca(2)	32(*m*)	0·2103 (24)	0·0519 (22)	0·0533 (6)
Ca(3)	8(*g*)	0	$\frac{1}{2}$	0·0716 (14)
Ca(4)	32(*m*)	0·0808 (36)	0·2161 (32)	0·1365 (6)
Ca(5)	8(*g*)	0	$\frac{1}{2}$	0·1678 (15)
Ca(6)	32(*m*)	0·2138 (27)	0·0861 (30)	0·2125 (9)
Ca(7)	4(*b*)	0	$\frac{1}{2}$	$\frac{1}{4}$
Sn(1)	4(*c*)	0	0	0
Sn(2)	8(*h*)	0·0859 (12)	$\frac{1}{2}+x$	0
Sn(3)	16(*l*)	0·3019 (7)	$\frac{1}{2}+x$	0·0748 (3)
Sn(4)	8(*f*)	0	0	0·0949 (5)
Sn(5)	16(*l*)	0·1617 (10)	$\frac{1}{2}+x$	0·1231 (3)
Sn(6)	8(*f*)	0	0	0·1733 (6)
Sn(7)	16(*l*)	0·3469 (9)	$\frac{1}{2}+x$	0·2087 (4)
Sn(8)	4(*a*)	0	0	$\frac{1}{4}$

cycles the refinement converged at an *R* index of 0·092 for 274 observed reflexions. This value is quite acceptable for photographically recorded diffraction data. The final parameters are given in Table 2.*

Powder patterns taken with Cu $K\alpha$ radiation could be indexed on the basis of the proposed structure and confirmed that the crystal had the same composition as the bulk material.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32737 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion

A comparison of the three compounds $Ca_{31}Sn_{20}$, Y_3Rh_2 (Moreau, Paccard & Parthé, 1976) and Eu_5Pb_3 with the W_5Si_3 structure (Franceschi, 1970) shows their close structural relation. They have the same space group *I4/mcm* and an *a* period of the same magnitude, whilst the *c* period of Y_3Rh_2 (25·16 Å) and of $Ca_{31}Sn_{20}$ (40·00 Å) is about four and six times that of Eu_5Pb_3 (6·214 Å) respectively. It is not surprising that intermetallic compounds which crystallize in the same space group with related lattice constants present a similar close-packed arrangement of atoms.

W_5Si_3 (Aronsson, 1955) is a four-layered structure formed by alternate nets with 2:1 (*A*) and 1:1 (*B*) stoichiometry, as shown in Fig. 1. If *A'* is the net obtained from *A* by a shift of $(\frac{1}{2}a + \frac{1}{2}b)$, the whole sequence along the *z* axis is *ABA'B*.

An analogous stacking of layers is found in the other two structures. Around $z = \frac{1}{4}$, Y_3Rh_2 shows the sequence *ABA'*, whilst $Ca_{31}Sn_{20}$ shows the sequence *ABA'BABA'*. Analogous sequences are found around $z = \frac{3}{4}$.

The comparison of the layers drawn for Y_3Rh_2 and $Ca_{31}Sn_{20}$ up to $z = \frac{1}{4}$ (Fig. 1) illustrates their close resemblance. Both structures show the same net with a 2:3 stoichiometry at $z = 0$ and a similar sequence of three other nets with atoms nearly in the same positions as in the *A* and *B* layers, but spread along the *z* axis.

Interatomic distances for $Ca_{31}Sn_{20}$ are given in Table 3 and are like those found in other Ca–Sn phases, such as Ca_2Sn (anti-$PbCl_2$-type) and CaSn (CrB-type). Only

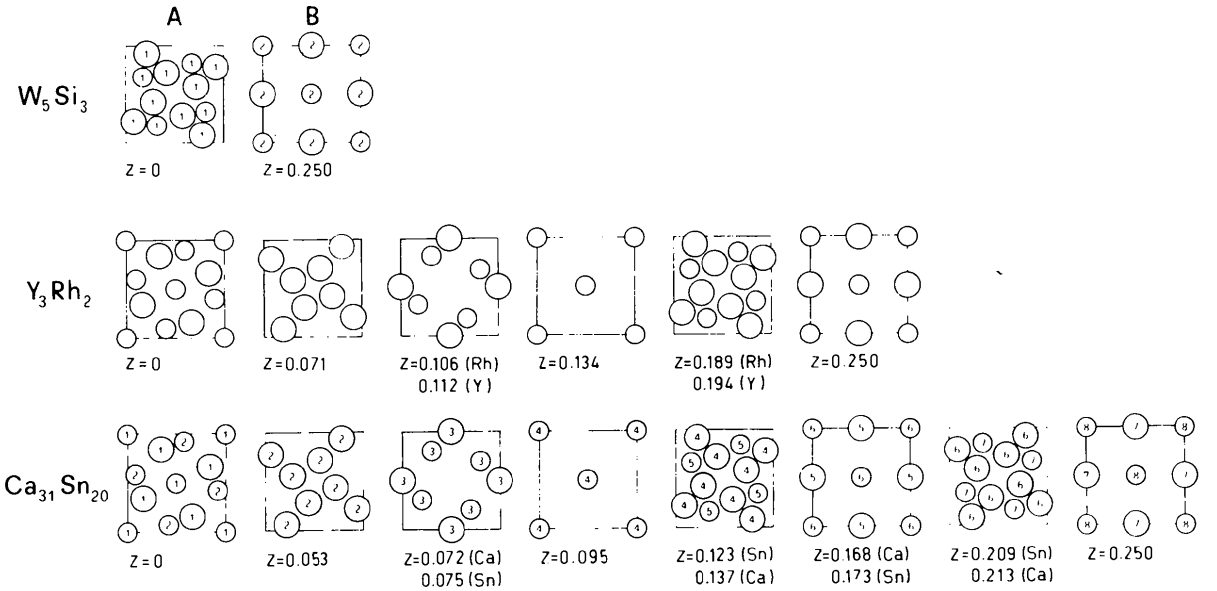

Fig. 1. Atomic arrangement in the *xy* sections from $z = 0$ to $z = \frac{1}{4}$ of the three compounds W_5Si_3 (a = 9·605, c = 4·964 Å), Y_3Rh_2 (a 11·232, c = 25·16 Å) and $Ca_{31}Sn_{20}$. Large circles: W, Y or Ca; small circles: Si, Rh or Sn. The numbers inside the circles refer to the corresponding atomic positions.

the distance Ca(5)–Ca(7), equal to 3·29 Å, shows a greater contraction (16%) compared with the metallic diameter of calcium, but this feature is common to compounds crystallizing in the W_5Si_3-type structure, where the corresponding M–M distance, equal to $c/2$, exhibits a remarkable contraction (in Eu_5Pb_3 such a distance between two Eu atoms is 3·11 Å, attaining a contraction of 24%).

The mean CN's (coordination numbers) of Ca and Sn are 15·0 and 9·7 respectively. The polyhedra of Ca(6) and Ca(4) formed by nine Ca and six Sn atoms are quite similar and correspond to the polyhedron of the W(1) atom in equipoint 16(k) of the W_5Si_3 type. Ca(2) also is surrounded by nine Ca and six Sn atoms and its polyhedron resembles in some respects Ca(6) and Ca(4).

Table 3. *Interatomic distances in* $Ca_{31}Sn_{20}$ (Å)

All e.s.d.'s are less than 0·02 Å.

Ca(1)–4 Ca(2) 3·77	Ca(5)–1 Ca(3) 3·85	Sn(4)–4 Ca(2) 3·19
–4 Ca(2) 4·25	–4 Ca(4) 3·91	4 Ca(4) 3·34
–2 Ca(3) 4·03	4 Ca(6) 4·15	–1 Sn(6) 3·14
–2 Sn(2) 3·21	–1 Ca(7) 3·29	
–2 Sn(3) 3·07	–2 Sn(5) 3·38	Sn(5)–2 Ca(2) 3·50
	–2 Sn(7) 3·17	–1 Ca(3) 3·53
Ca(2)–1 Ca(1) 3·77		–2 Ca(4) 3·35
–1 Ca(1) 4·25	Ca(6)–1 Ca(4) 3·69	–2 Ca(4) 3·45
–2 Ca(2) 3·84	–1 Ca(4) 3·83	1 Ca(5) 3·38
–1 Ca(2) 4·22	–1 Ca(5) 4·15	–2 Ca(6) 4·02
–1 Ca(2) 4·26	–1 Ca(6) 3·55	1 Sn(3) 3·15
–1 Ca(3) 3·76	–1 Ca(6) 3·70	
–1 Ca(4) 3·72	–1 Ca(6) 3·76	Sn(6)–4 Ca(4) 3·25
–1 Ca(4) 4·24	–2 Ca(6) 4·09	–4 Ca(6) 3·29
–1 Sn(1) 3·45	–1 Ca(7) 4·04	–1 Sn(4) 3·14
–1 Sn(2) 3·36	–1 Sn(5) 4·02	1 Sn(8) 3·07
–1 Sn(3) 3·26	–1 Sn(6) 3·29	
–1 Sn(3) 3·45	–1 Sn(7) 3·36	
–1 Sn(4) 3·19	–1 Sn(7) 3·44	Sn(7) 2 Ca(4) 3·44
–1 Sn(5) 3·50	–1 Sn(7) 3·66	–1 Ca(5) 3·17
	–1 Sn(8) 3·26	–2 Ca(6) 3·36
Ca(3)–2 Ca(1) 4·03		–2 Ca(6) 3·44
–4 Ca(2) 3·76	Ca(7)–2 Ca(5) 3·29	–2 Ca(6) 3·66
–4 Ca(4) 4·52	–8 Ca(6) 4·04	–1 Ca(7) 3·18
–1 Ca(5) 3·85	–4 Sn(7) 3·18	
–2 Sn(2) 3·25		Sn(8)–8 Ca(6) 3·26
–2 Sn(3) 3·52	Sn(1) 8 Ca(2) 3·45	–2 Sn(6) 3·07
–2 Sn(5) 3·53		
	Sn(2)–2 Ca(1) 3·21	
Ca(4)–1 Ca(2) 3·72	4 Ca(2) 3·36	
–1 Ca(2) 4·24	–2 Ca(3) 3·25	
–1 Ca(3) 4·52	–1 Sn(2) 3·05	
–1 Ca(4) 3·60		
2 Ca(4) 4·09		
–1 Ca(5) 3·91	Sn(3) 1 Ca(1) 3·07	
–1 Ca(6) 3·69	–2 Ca(2) 3·26	
–1 Ca(6) 3·83	2 Ca(2) 3·45	
–1 Sn(3) 3·07	–1 Ca(3) 3·52	
–1 Sn(4) 3·34	2 Ca(4) 3·07	
–1 Sn(5) 3·35	–1 Sn(5) 3·15	
–1 Sn(5) 3·45		
–1 Sn(6) 3·25		
–1 Sn(7) 3·44		

Ca(7) and Ca(5) both have ten Ca + four Sn neighbours which form a distorted CN 14 Frank & Kasper polyhedron, like that around the W(2) atom in equipoint 4(b) of the W_5Si_3 type. Very similar also is the polyhedron of Ca(3), save that one Ca atom is replaced by two Ca and two Sn, so that the CN becomes 17 (11 Ca + 6 Sn).

The crystallographic position of Ca(1) does not occur in the W_5Si_3 type. Nevertheless, out of 14 atoms belonging to its polyhedron, six Ca and four Sn form an arrangement common also to Ca(6) and Ca(3).

In $Ca_{31}Sn_{20}$ there are eight different positions for the Sn atoms. Sn(1), surrounded by a cube of eight Ca(2) atoms, has the same environment as the Sn atom in Mg_2Sn with the antifluorite structure. As regards the coordination, the other atoms can be divided into two groups: Sn(8), Sn(6), Sn(4) and Sn(2) on the one hand, and Sn(7), Sn(5) and Sn(3) on the other, similarly to the two Si atom positions in W_5Si_3.

The polyhedron around Sn(8), identical with that of Si(2) in equipoint 4(a) of the W_5Si_3 type, is a tetragonal antiprism with vertices occupied by Ca and square faces capped by Sn atoms. The same polyhedron is also found in the phases Sr_5Sn_3 and Ba_5Sn_3 with the Cr_5B_3 structure (Bruzzone, Franceschi & Merlo, private communication). On going from Sn(8) to Sn(6), Sn(4) and Sn(2), few changes occur. In Sn(6) the CN is still ten, but the Sn–Ca and Sn–Sn distances are no longer all equal; in Sn(4) one of the Sn atoms capping a face is removed and the number of neighbours becomes nine; finally, in Sn(2), surrounded by nine atoms, the antiprism is slightly distorted.

The polyhedron around Sn(7) is identical with that of Si(1) in equipoint 8(h) of the W_5Si_3 type, with ten Ca atoms coordinated to the central one. Here also, on going from Sn(7) to Sn(5) and Sn(3) some slight changes occur. In Sn(5) the number of neighbours rises to 11, because, in addition, a Sn(3) atom is coordinated at 3·15 Å and two Ca(6) atoms, although at a distance of 4·02 Å (greater than the appropriate sum of the metallic radii), still belong to the polyhedron. In contrast, these two Ca atoms are missing in the polyhedron of Sn(3), where the CN is lowered to nine and distances and angles are slightly rearranged.

Examining the coordination around the Sn atom in other phases of the Ca–Sn system, namely Ca_2Sn (anti-$PbCl_2$-type) and CaSn (CrB-type), one finds that the number of neighbours is nine and the corresponding polyhedra can be described as trigonal prisms of Ca atoms, with each lateral face capped by another atom.

It is interesting to note that, although the Si atoms in W_5Si_3 do not show such a coordination, in the polyhedra around Sn(2) and Sn(3) in $Ca_{31}Sn_{20}$ trigonal prisms are recognizable. In fact Fig. 2 shows that, save for the stoichiometry, the environments of Sn(2) and Sn(3) in $Ca_{31}Sn_{20}$, and those of the Sn atoms in Ca_2Sn and CaSn, are quite similar.

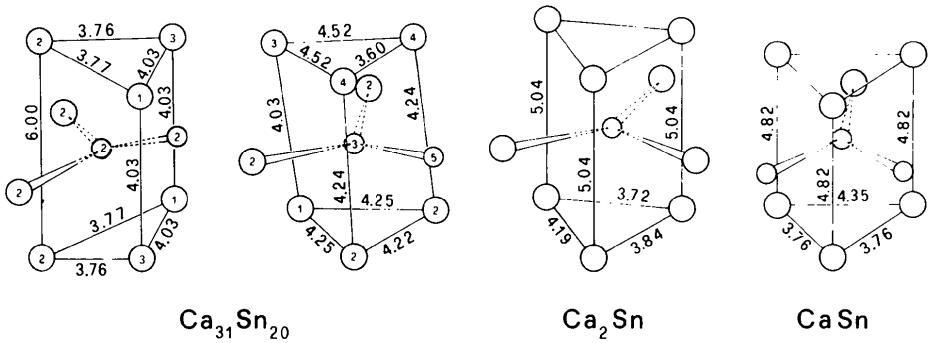

Fig. 2. Trigonal prismatic coordination around Sn(2) and Sn(3) in $Ca_{31}Sn_{20}$ and around the Sn atoms in Ca_2Sn (anti-$PbCl_2$-type) and CaSn (CrB-type). Large circles: Ca; small circles: Sn. The lengths of the prism edges are in Å.

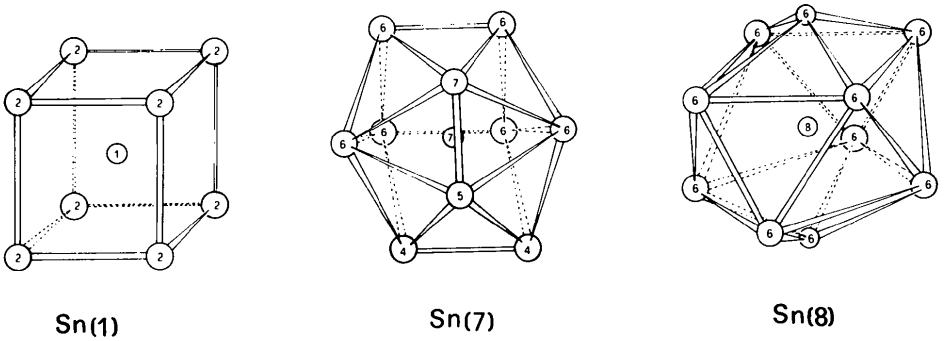

Fig. 3. Coordination polyhedra of Sn(1), Sn(7) and Sn(8) in $Ca_{31}Sn_{20}$. Large circles: Ca; small circles: Sn.

In Fig. 3 the most symmetrical polyhedra around the Sn atoms of $Ca_{31}Sn_{20}$ are drawn: a cube for Sn(1), a ten-coordination polyhedron for Sn(7) and a bicapped tetragonal antiprism for Sn(8).

In conclusion, the simultaneous presence in the same structure of several types of polyhedra, each occurring in other different structures, can account for the relative complexity of $Ca_{31}Sn_{20}$ and its particular stoichiometry.

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Note added in proof: Cromer & Larson (1977) have recently reported the crystal structure of $Pu_{31}Pt_{20}$. When the origin is shifted by $0,0,\frac{1}{2}$ the parameters of $Ca_{31}Sn_{20}$ are virtually identical with those of $Pu_{31}Pt_{20}$ and the two compounds must be considered as isotypic.

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