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The new complex lanthanum tetrelide $La_{55}Sn_{36.6}Ge_{24.4}$

Ines Dürr, Caroline Röhr*

Institut für Anorganische und Analytische Chemie, University of Freiburg, Albertstr. 21, D-79104 Freiburg, Germany

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ABSTRACT

The new ternary mixed lanthanum stannide/germanide $La_{55}Sn_{36.6}Ge_{24.4}$ (orthorhombic, space group $Cmcm$, $a = 2373.98(5)$, $b = 2375.52(6)$, $c = 2378.64(5)$ pm, $Z = 4$, $R1 = 0.0728$) was synthesized from stoichiometric melts of the three elements. Its complex structure contains a great variety of different tetrel anions, some known from the binary border compounds and new unusual Ge/Sn structural units: isolated Ge atoms (octahedrally coordinated by La), isolated Sn atoms (coordinated by 10 La cations), bent trimers $[Sn_3]$ and four-membered planar rings $[Sn_4]$ are also present in binary La germanides and stannides (*i.e.* $La_{11}Sn_{10}$, La_3Sn_4 or l.t.-LaSn). New tetrele anions are the eight-membered planar chain pieces $[M_8]$ (M = Ge, Sn), which exhibit both *cis*, *trans* and also linear conformation. Despite the presence of several mixed Ge/Sn sites, a tendency towards an alternation of Ge and Sn in the chain is apparent. The only extended structural elements of the title compound are polyanions $[M_{24}]$ consisting of eight-membered Ge rings, in which all atoms are bonded in a trigonal-planar geometry. In two directions, these rings are connected *via* two-bonded M pairs to form ribbons. In the orthogonal direction, two five-membered chain pieces are connected, which are similar in conformation and Ge/Sn distribution to the $[M_8]$ chains. The remaining four Ge atoms of the ring are connected to terminal tin atoms.

The diversity of the anions and particularly the different conformations of the planar chains in $La_{55}Sn_{36.6}Ge_{24.4}$ allows not only a comparison with the respective binary La germanides and stannides but also a study on the 'coloring' in tetrelides and a detailed analysis of the bond lengths of two-bonded Ge and Sn atoms.

Despite the complex structure and the variety of tetrelide anions, a simple electron count reveals the title compound to be an electron precise Zintl phase.

1. Introduction

Binary lanthanum tetrelides, particulary those in the 1:1 composition range, are interesting and variegated compounds not only because of their large structural diversity and polymorphism but also from the more general view on chemical bonding in polar intermetallics. Both border phases, LaGe and LaSn, are dimorphic exhibiting the simple FeB (LaGe [1–4]) and CrB (LaSn [5]) structure types at higher temperatures. Despite their simple crystal structures, which exhibit planar all-*trans* zig-zag chains in different orientations to each other, the chemical bonding in these compounds is still puzzling and has therefore been the topic of several recent experimental and theoretical studies [4,6–9]. The low-temperature (l.t.) form of LaGe [10] crystallizes with the l.t.-LaSi type, where the Ge chains show a *cis*/*trans* conformation and the Ge–Ge bonds are of alternating lengths. The low-temperature form of LaSn forms a rather complex structure [5,11] containing structural elements of the neighbour phase $La_{11}Sn_{10}$ ($Ho_{11}Ge_{10}$ structure type). Not only this 11:10 tetrelide is closely related in composition to the monotetrelides, but in the tin-rich part of the ternary system La–Sn–Ge compounds like La_5Sn_4 (which like the germanide crystallizes with the Sm_5Ge_4 structure type), La_4Ge_3 [12] and the new compound La_3Sn_4 (Er_3Ge_4 structure type [5]) all present different crystallographic positions applicable for a Ge/Sn substitution and thus for the exploration of the 'coloring' of tetrelides.

It is widely known, for instance for the rare-earth phases of the 5:4 composition [13,14], that the chemically similar elements germanium and silicon can replace each other in many tetrelides, frequently resulting in continuous solid solutions. In contrast, examples for the partial substitution of the less similar elements germanium and tin against each other are rare. The only systematic work reported in the literature concerns the M-rich mixed stannides/germanides of the late rare-earth elements: the nearly

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* Corresponding author.
E-mail address: caroline@ruby.chemie.uni-freiburg.de (C. Röhr).

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stoichiometric compounds RESnGe and RE_2Sn_4Ge [15,16] of the series REM_2 ($ZrSi_2$ type) – LnM_3 ($DyGe_3$ type) exhibit an almost complete ordering of the two tetrel element at the different crystallographic sites: the Ge atoms are exclusively forming the zig-zag chains of the CrB section in the structures of this series.

Herein we report on the complicated crystal structure of the new compound $La_{55}Sn_{36.6}Ge_{24.4}$, which could be obtained from stoichiometric melts in pure phase. Our findings about other compounds in the system La–Sn–Ge will be published elsewhere [17].

2. Experimental

2.1. Preparation and phase determination

The synthesis of several mixed La stannides/germanides was performed starting from the elements lanthanum, tin and germanium obtained from commercial sources and used without further purification (La: Aldrich, 99%; Sn and Ge: ABCR Karlsruhe). For the furnace preparations, the educts (*approx.* 1 g) were filled into tantalum crucibles under an argon atmosphere. The sealed containers were heated in corundum tubes under a static Ar atmosphere to maximum temperatures of 1200 °C with a constant rate of 200 K/h and subsequently cooled to room temperature with a rate of 20 K/h. For the arc-melted samples, about 100 mg of the three elements were weighed under argon, transfered to the water-cooled copper crucible plate of a vacuum arc melter, evacuated and arc-melted at low pressure helium atmosphere. After both preparations, representative parts of the reguli were ground in Ar atmosphere and sealed in capillaries with a diameter of 0.3 mm. X-ray powder diagrams were collected on a transmission powder diffractometer system (STADI P, linear PSD, Stoe & Cie, Darmstadt, $MoK_{\alpha 1}$ radiation, germanium monochromator).

The title compound was first detected in form of single crystals during a systematic study of the phase formation at the *pseudo*-binary section La_2Sn_3–La_2Ge_3 from Ge-rich samples like La_2SnGe_2 (513 mg/3.69 mmol La; 219 mg/1.84 mmol Sn; 268 mg/3.69 mmol Ge). The main reflections of the powder diagrams of these samples could be indexed by La_2SnGe_2 (Mo_2FeB_2 structure type), but in addition, minor amounts of $LaGe_{2-x}$ (α-$GdSi_2$ type, [18,19]) and $La_3Sn_3Ge_2$ (Th_3Pd_5 structure type [17]) are visible in the powder diffractogram. With the knowledge of the composition of the title compound from the X-ray single crystal structure analysis, phase pure samples of $La_{55}Sn_{36.6}Ge_{24.4}$ (La:Sn:Ge = 1:0.66:0.44) could be prepared in several directed syntheses from melts in the vicinity of this stoichiometry. For example, the somewhat La-richer sample composed of 121 mg (0.87 mmol) La, 56 mg (0.47 mmol) Sn and 23 mg (0.32 mmol) Ge and prepared in the arc-melter as described above contains the title compound in pure phase. Furnace and arc-melted samples with only slightly decreased lanthanum and increased tin contents like $LaSn_{0.77}Ge_{0.46}$ or $LaSnGe_{0.25}$ yielded two further new mixed Ge/Sn tetrelides $La_3Sn_{3.1}Ge_{0.9}$ (Er_3Ge_4 structure type) and $La_9Sn_{6.7}Ge_{3.3}$ (new structure type) [17].

2.2. Single crystal structure determination

For the crystal structure determination, the irregularly shaped single crystals of dark metallic lustre were selected using a stereo microscope and mounted in glass capillaries (diameter 0.1 mm) under dried paraffine oil. The crystals were centered on diffractometers equipped with an image plate area detector. After the data collection of several twinned crystals (*cf.* the tetragonal *pseudo* symmetry) one untwinned single crystal was obtained, enabling the smooth crystal structure solution *via* direct methods. The intensity data clearly exhibited only orthorhombic Laue symmetry with the integral extinction condition of a *C* centered Bravais lattice and the extra systematic absence condition 'reflections $h\,0\,l$ only present for $l = 2n$' leaving $Cmc2_1$ and *Cmcm* as only possible space groups. The structure was solved by direct methods (program SHELXS-97 [20,21]) in the centrosymmetric space group. This solution yielded all nineteen lanthanum sites and the positions exclusively occupied by tin. The remaining Ge and mixed Ge/Sn sites were found by successive refinements and difference electron density syntheses (program SHELXL-97 [20,21]). After applying and refining a mixed occupation for the respective (M) positions the equivalent isotropic displacement parameters converged to plausible values. Admittedly, in the vicinity of the isolated tin atoms Sn(11) three small extra maxima appear in the difference electron density map. In Fig. 3 bottom left this electron density is plotted at a level of 6 $e^- \, 10^{-6}\,pm^{-3}$ after the removal of the central Sn(11) position. The shape and the height of the maxima could be best described applying a statistic distribution of isolated tin atoms Sn(11) at the center (61%) and [Ge(12)–Ge(13)] dumbbells (39%), which are themselves affected by a further disorder (Ge(13): 20%, Fig. 3). This model is not only consistent with the occupation factors of all three M(3*X*) sites, it is also reasonable from a crystal chemical point of view, even if the Ge–Ge distance in the dumbbell is clearly underestimated (234(4) pm, compared to the single bond distance of 244 pm). The final crystallographic data and the refined atomic parameters are summarized in Tables 1 and 2, respectively. Selected interatomic distances M–M and M–La are collected in the two Tables 3 and 4 [22].

Table 1
Crystallographic data and details of the data collection, structure solution and refinement of $La_{55}Sn_{36.6}Ge_{24.4}$.

Crystal system		Orthorhombic
Space group		*Cmcm*, No. 63
Lattice constants [pm]	*a*	2373.98(5)
	b	2375.52(6)
	c	2378.64(5)
Unit cell volume [10^6 pm^3]		13414.2(5)
Z		4
Density (X-ray) [g/cm^3]		6.84
Diffractometer		Stoe Image Plate IPDS-2 (Mo-K_α radiation, graphite monochromator)
Absorption coeff. $\mu_{MoK\alpha}$ [mm^{-1}]		29.27
θ range [°]		1.48–29.25
No. of reflections collected		89921
No. of independent reflections		9472
R_{int}		0.1394
Corrections		Lorentz, polarisation, absorption ([31])
Structure solution		SHELXS-97 [20,21]
Structure refinement		SHELXL-97 [20,21]
No. of free parameters		320
Goodness-of-fit on F^2		1.167
R Values (for refl. with $I \geq 2\sigma(I)$)	*R*1	0.0725
	*wR*2	0.1051
R Values (all data)	*R*1	0.1083
	*wR*2	0.1150
Residual elect. density [$e^- 10^{-6}$ pm^{-3}]		+3.7/−3.6

3. Discussion

3.1. Structure description

The title compound $La_{55}Sn_{36.6}Ge_{24.4}$ crystallizes with a new complex orthorhombic structure type. Although the similarities of the lattice parameters suggest a cubic structure, the Laue class is only *mmm*. The large crystal structure contains several different Ge/Sn anions, which are – with the exception of the infinite chains formed by the atoms of the general label M(6*X*) – isolated by lanthanum cations. For the purpose of the following structure description, the unit cell is divided into two sets of overlapping slabs A and B. In Fig. 1 the unit cell is projected along the [0 1 0] direction. On the left hand side of this figure, the slabs A between the two mirror planes at $\frac{1}{4} < z < \frac{3}{4}$ are depicted in two orientations. On the right hand side, the slabs B between the two glide planes at $0 < z < \frac{1}{2}$ are shown in the same two views.

The first slab A contains four different structure elements (the Sn/Ge atoms (M) are labeled in accordance with these anionic building blocks):

- The tin atoms of the crystallographic positions Sn(41) and Sn(42) form four-membered rings around the special position 8(*e*) $(0.7465, 0, \frac{1}{2})$. The point group symmetry of the ring is thus 2.. and eight such rings are present in the unit cell (two per formula unit (f.u.)). These rings are shown together with their lanthanum surrounding in Fig. 2 top left. The rings are almost planar (mean deviation of the atoms from the best plane: 16 pm) with Sn–Sn distances *e*, *f* and *g* in the range of 291–298 pm (Table 3) and angles $\angle_{Sn-Sn-Sn}$ close to rectangular (88.68(4)° and 89.96(4)°). The coordination spheres of both these Sn atoms are completed by seven La cations, such that the typical tricapped trigonal pyramidal 2 + 7 coordination is reached (d_{La-Sn} = 328.2–395.8 pm, Table 3). Like the four-membered rings in the $Ho_{11}Ge_{10}$ structure type (as in $La_{11}Sn_{10}$ [5]) additional much longer Sn–Sn contacts of

Table 2
Atomic coordinates and equivalent isotropic displacement parameters [pm^2] for the crystal structure of $La_{55}Sn_{36.6}Ge_{24.4}$ (*disordered with Sn(11)).

Atom	Wyckoff position	Sn prop. [%]	*x*	*y*	*z*	$U_{equiv.}$
La(1)	4*c*		0	0.24786(11)	1/4	184(4)
La(2)	4*c*		0	0.91849(12)	1/4	261(5)
La(3)	4*c*		0	0.57724(9)	1/4	112(4)
La(4)	8*f*		0	0.30531(6)	0.62537(6)	94(3)
La(5)	8*f*		0	0.34064(6)	0.11795(6)	102(3)
La(6)	8*f*		0	0.15730(8)	0.10516(9)	283(4)
La(7)	8*g*		0.13081(6)	0.15114(6)	1/4	127(3)
La(8)	8*g*		0.37490(6)	0.19363(6)	1/4	90(3)
La(9)	8*g*		0.14591(7)	0.33504(6)	1/4	135(3)
La(10)	16*h*		0.27135(4)	0.08650(4)	0.16335(4)	103(2)
La(11)	16*h*		0.41448(4)	0.08886(4)	0.02029(4)	107(2)
La(12)	16*h*		0.26518(4)	0.41339(4)	0.15402(4)	109(2)
La(13)	16*h*		0.26108(4)	0.12541(4)	0.00953(4)	124(2)
La(14)	16*h*		0.23841(4)	0.24945(4)	0.13160(4)	121(2)
La(15)	16*h*		0.40753(5)	0.32459(4)	0.15784(5)	152(2)
La(16)	16*h*		0.11813(4)	0.24648(4)	0.01144(4)	128(2)
La(17)	16*h*		0.09064(4)	0.47087(4)	0.15895(4)	96(2)
La(18)	16*h*		0.09686(4)	0.08424(4)	0.51674(4)	118(2)
La(19)	16*h*		0.09094(5)	0.01434(5)	0.15920(5)	192(2)
Sn(1)	4*c*		0	0.40239(11)	1/4	161(5)
Sn(2)	4*c*		0	0.76299(15)	1/4	252(7)
Sn(11)	4*c*	61(1)	0	0.0933(2)	1/4	224(17)
Ge(12)*	4*c*	39(1)	0	0.03494(13)	1/4	905(11)
Ge(13)*	8*f*	39(1)	0	0.1240(13)	0.2094(18)	224(16)
Sn(21)	16*h*		0.14379(5)	0.35383(5)	0.10354(5)	107(2)
Sn(22)	16*h*		0.09673(5)	0.24705(5)	0.15308(5)	141(2)
Sn(23)	16*h*		0.14660(5)	0.13819(5)	0.10613(5)	113(2)
Ge(31)	8*d*		1/4	1/4	0	231(6)
Ge(32)	16*h*		0.31959(9)	0.33083(10)	0.07047(9)	215(4)
Sn(41)	16*h*		0.18501(5)	0.49468(5)	0.06094(5)	135(2)
Sn(42)	16*h*		0.19195(5)	0.00820(5)	0.06203(6)	160(3)
Ge(51)	8*f*		0	0.30560(12)	0.00059(11)	128(5)
Sn(52)	8*f*		0	0.18777(7)	0.54321(7)	125(3)
M(53)	8*f*	46(3)	0	0.08109(9)	0.61757(9)	136(8)
M(54)	8*f*	72(3)	0	0.01995(8)	0.05664(8)	131(7)
Ge(61)	8*f*		0	0.56132(11)	0.11913(11)	101(5)
Ge(62)	16*h*		0.40801(8)	0.10299(7)	0.15781(8)	107(3)
Ge(63)	8*g*		0.36938(11)	0.06010(11)	1/4	113(5)
M(64)	8*f*	29(3)	0	0.47419(10)	0.05597(10)	126(9)
Sn(65)	16*h*		0.35682(5)	0.18968(5)	0.10610(5)	142(2)
M(66)	8*f*	37(3)	0.19413(9)	0.47192(9)	1/4	120(8)
Sn(67)	8*f*		0.19355(8)	0.01690(8)	1/4	180(4)
M(68)	8*f*	44(3)	0.36693(9)	0.41728(9)	1/4	136(8)
Sn(69)	8*f*		0.29236(7)	0.30949(7)	1/4	110(3)
Ge(70)	8*f*		0.24799(11)	0.19125(11)	1/4	110(5)

343 (Sn(42)–Sn(23)) and 363 pm (Sn(41)–Sn(21)) loosely connect the four-membered rings with trimers [Sn(2*X*)$_3$].

- The angular Sn_3 trimers (or chain pieces) [Sn(21)–Sn(22)–Sn(23)] (Fig. 2 middle) are situated on a general position of the space group exhibiting no special point group symmetry. As a consequence, there are 16 such anions in the unit cell (4/f.u.). The Sn–Sn distances *b* (301.2 pm) and *c* (305.5 pm) are slightly longer than those in the four-membered rings, the Sn–Sn–Sn bond angle is 115.21(5)°. The overall coordination sphere of the central Sn(22) atom (2 + 7) is in accordance with that of the Sn atoms in LaSn (zig-zag chains of CrB structure type) and the Sn(4*X*) ring atoms. The terminating Sn(21) and Sn(23) atoms show a square antiprismatic surrounding by eight lanthanum cations ($d_{La–Sn}$ = 332.6–357.2 pm, Table 3). The La antiprisms are capped by the directly connected Sn(22) and the longer contact of the chain pieces with the four-membered rings [Sn(4*X*)$_4$].
- The linear chains [Ge(32)–Ge(31)–Ge(32)] with long Ge–Ge distances *d* of 303.7 pm are situated in the cages formed by the [Sn(4*X*)$_4$] rings and the angular [Sn(2*X*)$_3$] units. These Ge trimers exhibit the site symmetry $\overline{1}$ (Wyckoff position 8*d*: $\frac{1}{4}$, $\frac{1}{4}$,0) so that two such Ge_3 units are present in the formula unit. As expected, the distances to the La countercations ($d_{La–Ge}$ = 289.3–314.4 pm) as well as the coordination numbers (Ge(32): 6 + 1 and Ge(31): 6 + 2) are significantly smaller than for the tin atoms. The La octahedra around Ge(31) and Ge(32) are connected *via* common faces. A comparable octahedral surrounding of isolated Ge atoms is also observed in the La_3In_4Ge structure type, which occurs in the system La–Ge–Sn as well ($La_3Sn_{4.4}Ge_{0.6}$: $d_{La–Ge}$ = 302.9–322.6 pm [17]).
- The planar eight-membered chains (M(5*X*), Fig. 1 bottom) show $\frac{2}{m}..$ symmetry, their centers are located at 0,$\frac{1}{2}$, $\frac{1}{2}$ (Wyckoff position 4*b*; 1/f.u.). The six two-bonded M atoms of the chain section are arranged in a *cis*/*trans*/*cis* conformation with bond angles of 101.7(1)° (at M(54)) and 114.0(1)° (at Sn(53)). In contrast, the bond angle at Sn(52) next to the terminating germanium atoms is considerably larger and with 165.5° virtually linear. The conformation of the whole chain segment can thus be classified as linear(*h*)/bent(*i*)/*cis*(*j*)/*trans*(*k*)/*cis*/bent/linear. Concerning the tetrele distribution, only Ge(51) and Sn(52) are pure positions, the crystallographic positions M(53) and M(54) are statistically occupied by Ge and Sn atoms. As expected, the more electronegative bonding partner germanium occupies the terminal positions. Inside the chains, a clear tendency towards alternating Ge and Sn rich positions is noticeable. The terminating Ge(51) atoms show – similar to Ge(32) – a monocapped octahedral coordination by La cations and a Ge(51)–Sn(52) bond *h* of length 298.7 pm. The

Table 3
Selected interatomic distances [pm] in the crystal structures of $La_{55}Sn_{36.6}Ge_{24.4}$ (anions Sn(1), Sn(2), Ge(3*X*), Sn(4*X*) and M(5*X*); *: excluded due to disorder).

Atoms		Dist.	Bd.	Freq.	CN	Atoms		Dist.	Bd.	Freq.	CN	Atoms		Dist.	Bd.	Freq.	CN
Sn(1)	- La(17)	345.9(2)		4×		Sn(2)	- La(4)	337.9(2)		2×							
	- La(5)	346.7(2)		2×			- La(8)	339.6(2)		2×							
	- La(1)	367.1(4)					- La(15)	343.0(2)		4×							
	- La(9)	381.5(2)		2×			- La(2)	369.4(5)									
	- La(3)	415.3(3)			10		- La(3)	441.3(4)			10						
Sn(11)	- Ge(13)	123(3)*		2×		Ge(12)	- Sn(11)	141(3)*				Ge(13)	- Sn(11)	123(3)*			
	- Ge(12)	141(3)*					- Ge(13)	234(4)	*a*	2×			- Ge(12)	234(4)	*a*		
	- La(7)	339.6(3)		2×			- La(2)	274(3)					- Ge(13)	202(6)*			
	- La(19)	358.4(3)		4×			- La(19)	308.9(5)		4×			- La(6)	257(3)			
	- La(1)	367.2(6)					- La(7)	417(2)		2×			- La(1)	314(3)			
	- La(6)	376.6(3)		2×									- La(7)	333(1)		2×	
	- La(2)	415.2(6)			10								- La(19)	355(2)		2×	3 + 6
Sn(21)	- Sn(22)	301.2(2)	*b*			Sn(22)	- Sn(21)	301.2(2)	*b*			Sn(23)	- Sn(22)	305.5(2)	*c*		
	- La(17)	332.6(2)					- Sn(23)	305.5(2)	*c*				- La(18)	340.3(2)			
	- La(14)	341.2(2)					- La(1)	325.4(1)					- Sn(42)	343.4(2)			
	- La(16)	341.7(2)					- La(5)	330.4(2)					- La(7)	345.6(1)			
	- La(12)	342.8(2)					- La(9)	332.4(2)					- La(19)	346.4(2)			
	- La(5)	344.5(1)					- La(6)	333.4(2)					- La(14)	347.9(2)			
	- La(9)	351.3(1)					- La(7)	334.1(2)					- La(10)	348.3(2)			
	- La(11)	352.7(2)					- La(14)	340.2(2)					- La(16)	348.5(2)			
	- La(13)	354.6(2)			1 + 8		- La(16)	340.7(2)			2 + 7		- La(6)	351.0(1)			
													- La(13)	357.2(2)			1 + (1) + 8
Ge(31)	- Ge(32)	303.7(2)	*d*	2×		Ge(32)	- Ge(31)	303.7(2)	*d*								
	- La(13)	298.0(1)		2×			- La(13)	289.3(2)									
	- La(14)	314.3(1)		2×			- La(15)	294.9(3)									
	- La(16)	314.4(1)		2×	2 + 6		- La(16)	305.9(2)									
							- La(12)	307.6(2)									
							- La(14)	309.3(2)									
							- La(18)	310.5(2)			1 + 6						
Sn(41)	- Sn(41)	291.0(2)	*e*			Sn(42)	- Sn(41)	293.9(2)	*f*								
	- Sn(42)	293.9(2)	*f*				- Sn(42)	297.6(3)	*g*								
	- La(17)	328.2(2)					- La(12)	330.1(2)									
	- La(11)	339.4(2)					- La(18)	332.8(2)									
	- La(10)	343.0(2)					- La(19)	333.4(2)									
	- La(12)	350.1(2)					- La(18)	344.5(2)									
	- La(13)	354.8(2)					- La(13)	346.5(2)									
	- La(13)	357.5(2)					- La(10)	358.1(2)									
	- La(11)	364.0(2)			2 + 7		- La(13)	395.8(2)			2 + 7						
Ge(51)	- La(5)	291.3(3)				Sn(52)	- Ge(51)	298.7(3)	*h*								
	- Sn(52)	298.7(3)	*h*				- M(53)	309.0(3)	*i*								
	- La(4)	299.6(3)					- La(16)	339.1(1)		2×							
	- La(16)	314.7(2)		2×			- La(4)	340.8(2)									
	- La(11)	326.4(2)		2×	1 + 6		- La(18)	342.5(2)		2×							
							- La(15)	351.3(2)		2×							
							- La(6)	360.3(3)			2 + 8						
M(53)	- M(54)	280.4(3)	*j*			M(54)	- M(53)	280.4(3)	*i*								
	- Sn(52)	309.0(3)	*i*				- M(54)	285.7(4)	*k*								
	- La(2)	315.0(2)					- La(19)	326.0(2)		2×							
	- La(15)	328.0(2)		2×			- La(18)	326.6(2)		2×							
	- La(19)	328.3(2)		2×			- La(6)	346.1(3)									
	- La(18)	332.3(2)		2×	2 + 7		- La(18)	350.9(2)		2×	2 + 7						

pure tin site Sn(52) exhibits the largest coordination sphere of 2M + 8La, whereas the mixed positions M(53) and M(54) show again the typical tricapped trigonal prismatic coordination of the monotetrelides by two M and seven La atoms. For the detailed discussion of all M–M bond lengths (see below) the Ge/Sn ratio of both bonding partners have to be taken into account.

In addition, the Ge/Sn atoms M(64) are formally also part of the slabs A, as they are crosslinking the eight-membered rings of two adjacent slabs B to form infinite chains running along the *c* axis, *i.e.* through the slabs A (*cf.* Fig. 3 top right).

According to the structure description and number of different anions the formula of slab A sums up to

$$[Sn(4X)_4]_2[Sn(2X)_3]_4[Ge(3X)_3]_2[M(5X)_8]$$

The Ge/Sn anions of slab B are shown in two orientations on the right hand side of Fig. 1. They are depicted with their La coordination in more detail in Fig. 3. Slab B consists of four separated Ge/Sn anions:

- The atoms Sn(1) and Sn(2), which are located at special positions of type $0,y,\frac{1}{4}$ (4*c*) exhibiting *m*2*m* site symmetry, are coordinated by lanthanum cations only. This ten-fold coordination in the form of bicapped square antiprisms is depicted in Fig. 3 in a polyhedra representation. The Sn–La distances inside these polyhedra range from 337.9 to 441.3 pm (*cf.* Table 3). According to their site symmetry, four Sn(1) and four Sn(2) atoms are present in the unit cell.
- The atoms Sn(11) (see Fig. 3 bottom left) at the same Wyckoff position also show this ten-fold coordination by La atoms with comparable distances of $d_{La–Sn} = 339.6–415.2$ pm. As detailed in

Table 4
Selected interatomic distances [pm] in the crystal structure of $La_{55}Sn_{36.6}Ge_{24.4}$ (anion M(6*x*)).

Atoms		Dist.	Bd.	Freq.	CN	Atoms		Dist.	Bd.	Freq.	CN	Atoms		Dist.	Bd.	Freq.	CN
Ge(61)	- M(64)	255.8(3)	*l*			Ge(62)	- Ge(61)	256.8(2)	*m*			Ge(63)	- M(66)	258.1(3)	*p*		
	- Ge(62)	256.8(2)	*m*	2×			- Ge(63)	258.6(2)	*n*				- Ge(62)	258.6(2)	*n*	2×	
	- La(3)	313.6(3)					- Sn(65)	268.9(2)	o				- La(3)	312.7(3)			
	- La(4)	317.2(3)					- La(17)	313.9(2)					- La(10)	317.1(2)		2×	
	- La(11)	317.5(2)		2×			- La(3)	315.5(2)					- La(8)	317.5(3)			
	- La(17)	318.5(2)		2×	3 + 6		- La(8)	317.2(2)					- La(17)	317.6(2)		2×	3 + 6
							- La(4)	317.9(2)									
							- La(10)	327.1(2)									
							- La(11)	329.2(2)			3 + 6						
M(64)	- Ge(61)	255.8(3)	*l*			Sn(65)	- Ge(62)	268.9(2)	*o*			M(66)	- Ge(63)	258.1(3)	*p*		
	- M(64)	293.1(5)	*q*				- La(14)	320.7(2)					- Sn(67)	287.3(3)	*r*		
	- La(11)	310.7(2)		2×			- La(16)	323.6(2)					- La(12)	316.1(2)		2×	
	- La(17)	326.1(2)		2×			- La(11)	343.2(2)					- La(17)	327.5(2)		2×	
	- La(5)	349.8(3)					- La(4)	343.2(1)					- La(9)	344.7(3)			
	- La(11)	350.2(2)		2×	2 + 7		- La(8)	345.1(1)					- La(10)	351.1(2)		2×	2 + 7
							- La(10)	346.1(2)									
							- La(13)	357.4(2)									
							- La(15)	363.8(2)			1 + 8						
Sn(67)	- M(68)	276.8(3)	*s*			M(68)	- Sn(67)	276.8(3)	*r*			Sn(69)	- Ge(70)	300.0(3)	*u*		
	- M(66)	287.3(3)	*r*				- Sn(69)	311.3(3)	*t*				- M(68)	311.3(3)	*t*		
	- La(10)	322.4(2)		2×			- La(2)	315.9(2)					- La(8)	337.9(2)			
	- La(19)	325.6(2)		2×			- La(15)	325.3(2)		2×			- La(14)	340.7(1)		2×	
	- La(12)	349.5(2)		2×			- La(19)	331.4(2)		2×			- La(12)	342.3(2)		2×	
	- La(7)	352.0(2)			2 + 7		- La(12)	332.5(2)		2×	2 + 7		- La(15)	352.3(2)		2×	
													- La(9)	352.9(2)			2 + 8
Ge(70)	- Sn(69)	300.0(3)	*u*														
	- La(7)	294.0(3)															
	- La(8)	301.3(3)															
	- La(14)	314.5(2)		2×													
	- La(10)	327.9(2)		2×	1 + 6												

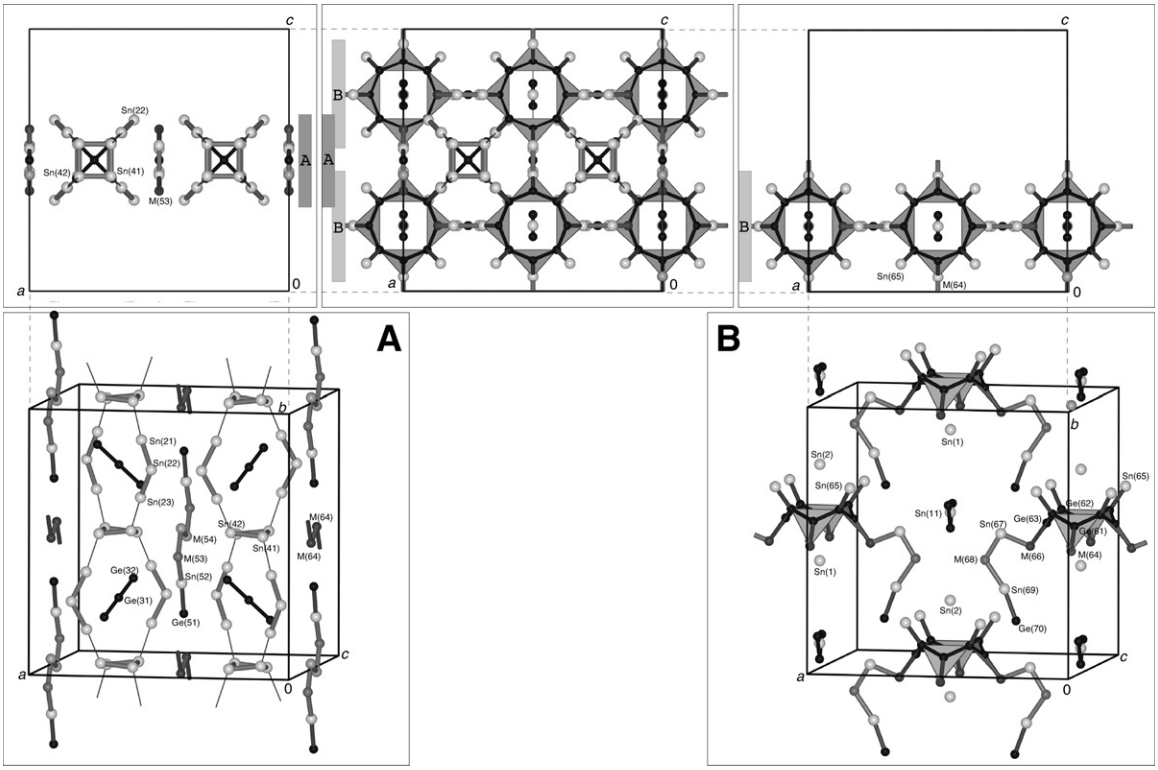

Fig. 1. Views of the unit cell of $La_{55}Sn_{36.6}Ge_{24.4}$ and its segmentation into two interpenetrating layers: above: projection of the whole structure along the [0 1 0] direction. Left and right: layers A and B in the same projection and in a perspective view (small dark balls: La; large light gray balls: Sn; dark gray balls: Ge; color and size of the M positions changing with the Ge/Sn ratio [44]).

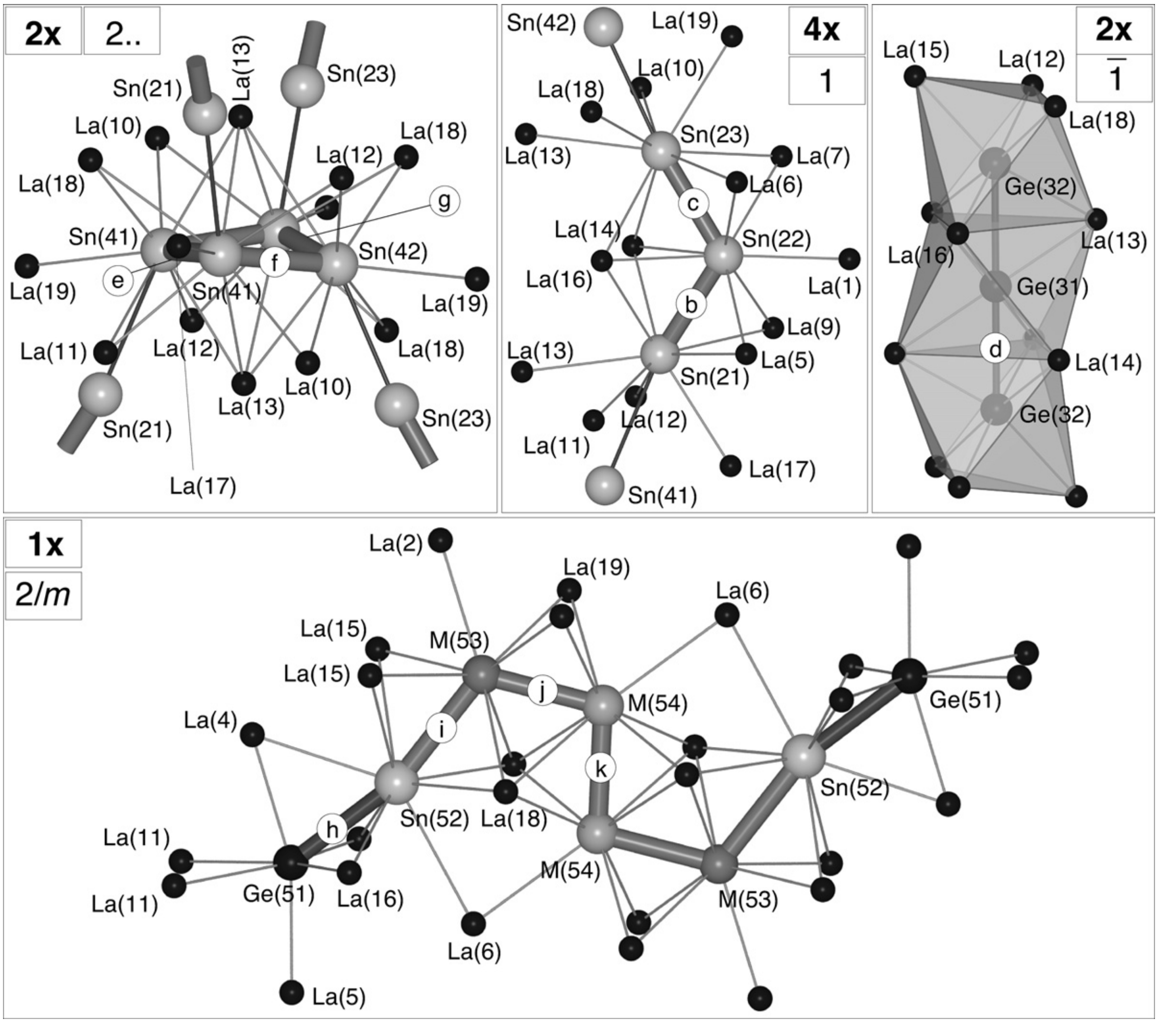

Fig. 2. Structure elements (tetrel anions) of the layers A together with their La coordination: four-membered rings $[\mathrm{Sn}(4X)_4]$; chain pieces $[\mathrm{Sn}(2X)_3]$; linear trimers $[\mathrm{Ge}(3X)_3]$ and planar chain pieces $[M(5X)_8]$.

the description of the structure refinement in the experimental section, the position Sn(11) is only partially occupied (61%) and the difference Fourier map reveals extra electron density, which is reconciled by disordered Ge_2 dumbbells formed by Ge(12) and Ge(13) atoms (Fig. 3 bottom left). Due to the disorder and the low occupation of only 39%, the Ge–Ge distance of 234 pm (*a*) inside these dumbbells is somewhat below the expected range.

- The most fascinating structure element in the crystal structure of the title compound is the complex polyanion formed by the Ge/Sn atoms of the positions M(6*X*). These building blocks are depicted in Fig. 2 top right in three different orientations. The germanium atoms Ge(61), Ge(62) and Ge(63) form eight-membered rings (site symmetry *m*2*m* (0,*y*,1/4), Wyckoff position 4*c*, 1/f.u.). The Ge–Ge distances *m* and *n* inside this ring amount to 256.8 and 258.6 pm (Table 4). These Ge atoms of the ring are additionally connected with the M(64), Sn(65) and M(66) atoms in a trigonal planar arrangement. As already mentioned above, direct M(64)–M(64) bonds *q* establish the connection to the equivalent adjacent anions through the tetrel anions of layer A. The Sn(65) atoms, which are connected to Ge(62) of the eight-membered ring by the comparatively short Sn–Ge distance *o*, are terminating the polyanion in the *b* direction. Connected to Ge(63) are planar chains segments Ge(66)–Sn(67)–M(68)–Sn(69)–Ge(70) in the conformation (starting from terminal Ge(70)) linear (*u*)/bent(*t*)/*cis*(*s*)/*trans*(*r*). This conformation and the alternating Sn/Ge distribution as well as the La coordinations of the chain atoms are very similar to those in the isolated eight-membered chains M(5*X*) of slab A (Fig. 2 top right and Table 4). The overall composition of this complex polyanion compiles to

$$[Ge(62)Sn(65)]_4[Ge(61)M(64)]_2[Ge(63)M(66\text{–}70)]_2 = [M_{24}].$$

Adding up all anions of slab B results in the overall composition of this layer:

$$[Sn(1)][Sn(2)][Sn(11)]_{0.61}[Ge(12/13)_2]_{0.39}[M(6X)_{24}]$$

Not only the size of the unit cell but also the four-membered, nearly planar rings $[\mathrm{Sn}(4X)_4]$ and the eight-membered rings $[\mathrm{Ge}(6X)_8]$ reflect the *pseudo*-four-fold symmetry of the crystal structure along [0 1 0], which also comes apparent from the overall arrangement of the tetrelide ions depicted in Fig. 1. In this view, the eight-membered chain pieces $[\mathrm{M}(6X)_8]$ of slab A and the long chains connected to the $[\mathrm{Ge}_8]$ rings of slab B are also related by this tetragonal *pseudo* symmetry.

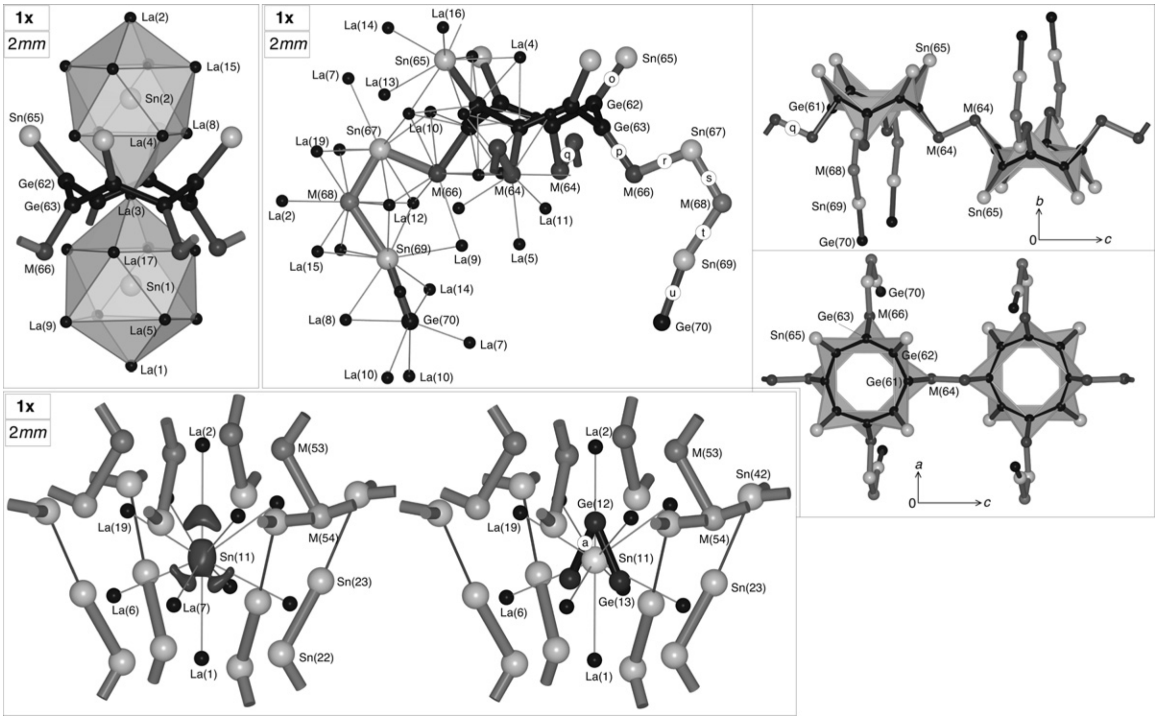

Fig. 3. Structure elements (tetrel anions) of the layers B together with their La coordination: La polyhedra around the isolated Sn(1) and Sn(2) atoms; eight-membered rings of trigonal-planar coordinated Ge atoms with long chain pieces $[M(6X)_{24}]$ in three different orientations; environment of Sn(11) with a difference electron density map at a level of 6 e^- 10^{-6} pm^{-3} and the refined Sn/Ge_2 positions.

3.2. Comparison of the anions with those of other binary stannides and germanides

Table 5 summarizes the structural chemistry of binary lanthanum germanides and stannides. For a comparison, the respective alkaline-earth tetrelides, which mostly satisfy Zintl's electron counting rule, are included in this survey.

Isolated, noble-gas isosteric Ge/Sn atoms (M^{4-} after Zintl) are widely known from the electron precise alkaline-earth (A^{II}) tetrelides A_2M forming the Co_2Si structure type and from the whole series of compounds A_5M_3 with the Cr_5B_3 type. With lanthanum as a countercation, the crystal structures of the stannides La_5Sn_3 (W_5Si_3 and Mn_5Si_3 structure type), $La_{11}Sn_{10}$ and l.t.-LaSn [5] exhibit isolated tin anions. Examples among the germanides are La_4Ge_3 (Th_3P_4 type [12]) and $La_3Sn_{4.4}Ge_{0.6}$ [17] (La_3In_4Ge type [23]). For the stannides, a nine-fold coordination by La cations, which form monocapped square antiprisms or tricapped trigonal prisms, is characteristic. In some cases, the isolated tin atoms are centers of La dodecahedra (CN = 8) or bicapped square antiprisms (CN = 10). The respective La–Sn distances of the binary stannides mentioned are in the range 337–421 pm. Against this background, the ten-fold coordination of Sn(1), Sn(2) and Sn(11) and the La–Sn distances in the crystal structure of $La_{55}Sn_{36.6}Ge_{24.4}$ are in full accordance with the situation in the binary La stannides. As expected, isolated germanium atoms exhibit a lower coordination number both in the title compound (Ge(31) and Ge(32)) and in $La_3Sn_{4.4}Ge_{0.6}$: six La cations are octahedrally coordinated with La–Ge distances between 289.3 and 322.6 pm. One (Ge(32)) and two (Ge(31)) further germanium atom(s) are arranged above the octahedral face(s) with large Ge–Ge distances *d*. A similar coordination sphere of six La and one M atom is also observed for the terminal germanium atoms Ge(51) and Ge(70) of the chains segments, in these cases indeed with standard Ge–M bond lengths.

$[M_2]$ *dumbbells* ($[M_2]^{6-}$) are very common in tetrel-poor germanides and stannides like $A_5^{II}M_3$, La_5M_4 (Sm_5Ge_4 type), $La_{11}Sn_{10}$, l.t.-LaSn and in the Ca-rich stannides $Ca_{36}Sn_{23}$ [24], $Ca_{31}Sn_{20}$ [25] and $Ca_7(Ge/Sn)_6$ [24]. In the title compound, only one [Ge–Ge] dumbbell, which is affected by both partial occupation and disorder, is present. Its Ge–Ge distance of 234(4) pm (*a*) is not too reliable but nevertheless within the expected range.

$[M]_x$ *-chain pieces* consisting of three to six Ge/Sn atoms are known both in linear and bent planar forms of different conformations in binary germanides and stannides: linear three-membered chains are found in l.t.-LaSn, bent ones in La_3Sn_4 [5]. The angular four-membered chain pieces in RE_5M_4, Ca_7Ge_6 and Ca_7Sn_6 are of *trans*, those in β-LaSn of *cis*/*trans* conformation. Longer chain pieces with five and six tin atoms are present in linear form in the Ca stannides $Ca_{31}Sn_{20}$ and $Ca_{36}Sn_{23}$. The mean Sn–Sn distances in angulated chain pieces (290–305 pm) are somewhat smaller compared to the linear conformation (302–315 pm). With bond lengths *b* and *c* of 301.2 and 305.3 pm, the three-membered bent $[Sn(2X)_3]$ units in $La_{55}Sn_{36.6}Ge_{24.4}$ are fully comparable to the binary stannides. The conformations and the related M–M distances of the longer Ge/Sn chain segments are discussed together with the distances in the infinite chains of the monotetrelides below.

Four-membered rings ($[M_4]^{8-}$) in planar conformation appear in the structures of $La_{11}Sn_{10}$ and the isotypic late lanthanoid germanides of the $Ho_{11}Ge_{10}$ type. They are also present in the structures of β-LaSn und La_2Sn_3 (in addition to chains with terminal three-membered rings, Sn_8^{14-} [26]). The Sn–Sn distances alternate in the range between 296 (in $La_{11}Sn_{10}$) and 316 pm (in β-LaSn) and thus the bond lengths in the $[Sn(4X)_4]$ ring of the title compound (*e*, *f* and g: 291.0–297.6 pm) are in the common range.

The *trigonal planar three-bonded* M atoms in $La_{55}Sn_{36.6}Ge_{24.4}$ are germanium atoms exclusively. In accordance, there are no examples for planar three-bonded tin atoms in binary stannides, whereas this coordination – due to the possibility for the formation of sp^2 hybrids in germanium – is common in germanides. The Ge–Ge distances *m* and *n* of the title compound (256.8 and 258.6 pm) are between the bond length in La_3Ge_5 (Y_3Ge_5 structure

Table 5
Comparison of the crystal structures of alkaline-earth (A) and lanthanum stannides and germanides in the composition range Ge/Sn:A/La = 0.5–3.0 (*: presumably only stuffed variants).

	A = Ca, Sr, Ba		*A* = La	
M:*A*	M = Ge	M = Sn	M = Ge	M = Sn
0.5	A_2Ge (Co_2Si)	A_2Sn (Co_2Si)	–	–
0.6	A_5Ge_3(Cr_5B_3)	A_5Sn_3(Cr_5B_3)	La_5Ge_3 ($Mn_5Si_3^*$)	La_5Sn_3 ($Mn_5Si_3^*$)
				La_5Sn_3 (W_5Si_3)
0.639	–	$Ca_{36}Sn_{23}$ [24]	-	-
0.645	–	$Ca_{31}Sn_{20}$ [32,25]	–	–
0.75	–	–	La_4Ge_3 (Th_3P_4) [12]	–
0.8	–	–	La_5Ge_4 (Sm_5Ge_4)	La_5Sn_4 (Sm_5Ge_4)
0.857	Ca_7Ge_6 [24]	Ca_7Sn_6 [33]	–	–
0.909	–	–	–	$La_{11}Sn_{10}$ ($Ho_{11}Ge_{10}$) [5]
1	*A*Ge (CrB)	*A*Sn (CrB)	ht-LaGe (FeB) [4]	ht-LaSn (CrB) [5]
			lt-LaGe (lt-LaSi) [10]	lt-LaSn [11,5]
1.11	–	–	$La_9Sn_{6.7}Ge_{3.3}$ [17]	
1.33	–	–	–	*La_3Sn_4 (Er_3Ge_4)* [5]
	–	–	$La_3Sn_{3.1}Ge_{0.9}$ (Er_3Ge_4) [17]	
1.5	–	–		La_2Sn_3 [26]
1.67	–	$(Sr/Ba)_3Sn_5$ (Pu_3Pd_5) [34]	La_3Ge_5 (Y_3Ge_5) [19]	La_3Sn_5 (Pu_3Pd_5) [35]
	$Ba_3Sn_{2.8}Ge_{2.2}$ (Pu_3Pd_5) [36]		$La_3Sn_{4.4}Ge_{0.6}$ (La_3In_4Ge) [17]	
	–	–	$La_3Sn_2Ge_3$ (Th_3Pd_5) [17]	
2	$CaGe_2$ ($EuGe_2$ [37,38])	$BaSn_2$ [39]	$LaGe_{2-x}$ (α-$GdSi_2$) [18,19]	$LaSn_2$ ($ZrGa_2$) [40]
2.33	–	–	–	La_3Sn_7 (Gd_3Sn_7) [28]
2.5	–	–	–	La_2Sn_5 (Ce_2Sn_5) [28]
3		$CaSn_3$, $SrSn_3$ (Cu_3Au) [41]	$LaGe_3$ ($TaCo_3$) [42]	$LaSn_3$ (Cu_3Au) [28]
		$BaSn_3$ (Ni_3Sn) [43,41]		

type: d_{Ge-Ge} = 267–279.6 pm) and the variants of the $ThSi_2$ structure type (d_{Ge-Ge} = 243–253 pm). Eight-membered rings of exclusively trigonal-planar coordinated M atoms are also observed in the mixed Al germanide $Yb_{17}Al_8Ge_{19}$ [27].

3.3. Analysis of the bond lengths in two-bonded tetrelides

The large variety of two-bonded germanium and tin atoms in the title compound allows a more detailed analysis of the bond lengths and conformations in infinite chains and large chain segments. Planar Ge/Sn chains of various conformation are common for the monotetrelides of lanthanum and the alkaline-earth elements: all-*trans* conformation is observed in the CrB and FeB structure types of the high-temperature forms of the binary phases, h.t.-LaSn (CrB, d_{Sn-Sn} = 299.1 pm [5]) and h.t.-LaGe (FeB, d_{Ge-Ge} = 266.7 pm [4]). These two bond lengths are used as a reference for our analysis of the M–M distances in pure and mixed germanides and stannides (*cf.* Fig. 4). The crystal structure of the low temperature form of LaGe [10] exhibits a similar Ge chain, but in this case with a *cis*/*trans* conformation, accompanied by a strong bond-length alternation (d_{Ge-Ge} = 262.1 (*cis*) and 279.9 pm (*trans*)). La_5Sn_3 (W_5Si_3-type) contains (beside isolated Sn atoms) linear tin chains with an increased Sn–Sn distance of 317 pm. All M–M bond lengths of two-bonded Ge/Sn atoms in the title compound can now be set into relation to these binary compounds, if the respective distances are plotted against the mean tin content of both bonding partners. Fig. 4 shows, that the bond lengths of the *trans* conformations (*b*, *c* and *r*) are very close to the line connecting the distances of the binary CrB and FeB type structures. Only the distance *q*, which forms the crosslink of the eight-membered Ge rings of adjacent layers B through the slabs A, is somewhat enlarged compared to the mean M–M distances of *trans* chains. The graph also shows, that bonds with a *cis* conformation (*j*, *k* and *s* of the title compound) exhibit bond lengths which are decreased by 15–20 pm. Also the *cisoid* distances in the four-membered ring (*e*, *f* and *g*) are lying below the CrB/FeB line. The shortest M–M bond lengths are those forming the connection to the three-bonded Ge atoms Ge(61), Ge(62) and Ge(63) of the eight-membered ring (*l*, *p* and *o*). These positions are preferentially occupied by germanium. In contrast, the linearly coordinated M atoms found at the ends of the chains pieces are mainly occupied by tin. Their bond distances *u*, *h*, *t* and *i* also form a line of typical slope, which is shifted above the FeB/CrB reference line, indicating the increased bond lengths of linearly connected tetrel atoms.

3.4. Electron count

Nearly all of the alkaline-earth germanides and stannides listed in Table 5 are electron precise Zintl compounds. In contrast,

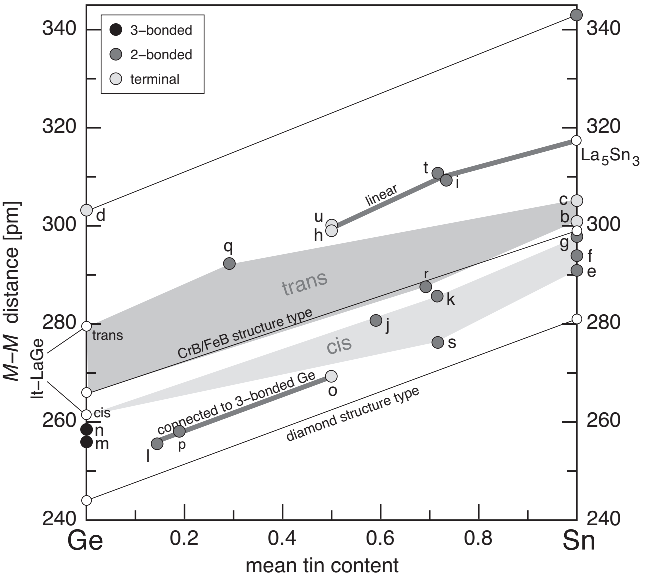

Fig. 4. Analysis of the Ge–Ge, Ge–Sn and Sn–Sn distances in the crystal structure of $La_{55}Sn_{36.6}Ge_{24.4}$ (distance labels *cf.* Tables 3 and 4).

most of the La tetrelides show a slight deviation from the Zintl electron count (*e.g.* +15:−14 in La_5M_4, +66:−64 in $La_{11}Sn_{10}$ or +90:−88 in l.t.-LaSn). The differences are always very small and towards a slight formal electron excess, indicating an incomplete charge transfer from lanthanum to the tetrelide anions. Band structure calculations on several La germanides [4] and stannides [5,28,29] substantiate the π-bonding contributions between La-d and M-p states. In accordance, the La–Sn and La–Ge distances are decreased when compared to those in the isotypic electron-precise alkaline-earth tetrelides and the calculated valence electron densities show distinct bond critical points at the respective short La–M contacts. Unfortunately, due to the large unit cell and the statistically occupied Ge/Sn positions a reliable band structure calculation of the title compound is not feasible. The charge balance can thus only be calculated by simply applying the Zintl concept taking the connectivity of all Ge/Sn atoms of all anions into account. By this means, the formal charge of all anions of one formula unit of the slab A

$$2 \times [Sn(4X)_4]^{8-} + 4 \times [Sn(2X)_3]^{8-} + 6 \times [Ge(3X)]^{4-} + [M(5X)_8]^{18-}$$

sums up to 90 negative charges. The corresponding charge balance for the anions of slab B is

$$[Sn(1)]^{4-} + [Sn(2)]^{4-} + [Sn(11)]^{4-}_{0.61}/[Ge(12/13)_2]^{6-}_{0.39} + [M(6X)_{24}]^{62-}$$

and thus results in an overall charge for this layer of −74.8. Adding the charges of all anions of both slabs results in a negative charge of −164.8/f.u., which is nicely compensated by the 55 lanthanum cations per formula unit, which provide an overall electron number of 165.

3.5. Aspects of ‘coloring’ in mixed tetrelides

According to the higher electronegativity of germanium (Ge: 2.02 and Sn: 1.72 according to Allred and Rochow), Ge atoms should occupy the M positions with a higher formal negative charge. Consistently, the isolated sites Ge(31) and Ge(32) (charge −4), the dumbbells [Ge(12)–Ge(13)] (−3) and the terminal Ge positions of the chain pieces (Ge(51) and Ge(70)) (−3) are occupied by germanium exclusively, whereas all mixed Ge/Sn and most Sn atoms occupy two-bonded (−2) sites in the anion(s). What might appear as a contradiction, all three-bonded positions in the eight-membered rings, which bear the low formal charge of −1, are also occupied by germanium atoms only (Ge(61), Ge(62) and Ge(63)). Here, the increased potential of the lighter element germanium to form s–p hybrid states and multiple bonds seems to be the crucial factor. In the chains of two-bonded M atoms, a trend towards an alternating occupation by Sn and Ge is noticeable. Positions within the chains showing a nearly linear M–M–M bond angle are occupied by tin only (Sn(52) and Sn(69)). This observation is rationalized by the propensity of the heavier element tin to form hypervalent bonds [30]. In all mixed lanthanum stannides/germanides, the smaller building blocks like dumbbells, trimers or four-membered rings are either formed by pure Ge or Sn [17]. In the late rare-earth mixed stannides/germanides *RE*SnGe and RE_2Sn_4Ge [15,16] of the general series REM_2 ($ZrSi_2$ type) – LnM_3 ($DyGe_3$ type) the Ge atoms are exclusively forming the zig-zag chains, whereas Sn occupies the positions of the square nets. In accordance, band structure calculations for the pure stannides of the closely related series $LaSn_2$ ($ZrGa_2$ type) – $LaSn_3$ (Cu_3Au type) [28] show, that the atoms in the zig-zag chains exhibit the higher negative charge when compared to the positions forming the Cu_3Au sections of the structure.

4. Summary and conclusion

The title compound $La_{55}Sn_{36.6}Ge_{24.4}$ is one of the rare examples of a mixed tetrelide of the chemically different elements germanium and tin. It forms from stoichiometric melts of the elements in pure phase and crystallizes with a complex *pseudo*-tetragonal structure. Despite some Sn/Ge mixed positions in the tetrel anions, no significant phase width could be observed by crystallography of multiple samples. The formation of a variety of different anions (isolated M atoms, dumbbells, trimers, four-membered rings, planar chain segments and complex ribbons of eight-membered rings) and thus the overall rather complicated crystal structure is evidently driven by the differences in size and electronegativity of the isovalence electronic elements Ge and Sn. In addition, germanium has the smaller separation energy between s and p states enabling hybridisation, multiple bonds and thus the trigonal-planar coordination observed in the three-bonded Ge-atoms in the title compound as well as in various binary germanides of the $ThSi_2/AlB_2$ structure family. In contrast, tin as the heavier element is able to contribute to hypervalent bonding, forming linear (*e.g.* chains) or square-planar (*e.g.* 2D nets) bonds within the anions.

Further mixed lanthanum stannides/germanides, which include ordered variants of binary lanthanum stannides (Er_3Ge_4 and $Ho_{11}Ge_{10}$ structure type), compounds of known structure types not present as border phases (La_3In_4Ge, Mo_2FeB_2 and Th_3Pd_5 type) and the new complex compound $La_9Sn_{6.7}Ge_{3.3}$ will be reported elsewhere [17]. Attempts to synthesize and characterize ternary variants of the binary stannides $LaSn_2$–La_2Sn_5 – in analogy to the related series of the smaller rare earth cations – are currently in progress.

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