The Gold-rich Indide $Sr_5Au_{13.5}In_{8.5}$

Ihor Muts[a,b], Ute Ch. Rodewald[b], Vasyl' I. Zaremba[a], and Rainer Pöttgen[b]

[a] Inorganic Chemistry Department, Ivan Franko National University of Lviv,
Kyryla and Mephodiya Street 6, 79005 Lviv, Ukraine
[b] Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstraße 30,
48149 Münster, Germany

Reprint requests to R. Pöttgen. E-mail: pottgen@uni-muenster.de

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The orthorhombic indide $Sr_5Au_{13.5}In_{8.5}$ was obtained during phase-analytical studies of the Sr-Au-In system. This new indide is formed upon melting of the elements in a sealed tantalum tube. $Sr_5Au_{13.5}In_{8.5}$ was characterized on the basis of powder and single-crystal X-ray diffraction: *Pmmn*, $a = 476.37(9)$, $b = 2927.5(9)$, $c = 894.9(2)$ pm, $wR2 = 0.056$, 2355 F^2 values, 87 variables. The structure is of a new type. The gold and indium atoms build up a complex three-dimensional $[Au_{13.5}In_{8.5}]$ polyanionic network in which the strontium atoms fill channels which extend in the *a* direction. One site within the polyanion shows Au/In mixing. The $Sr_5Au_{13.5}In_{8.5}$ structure is composed of $SrAu_3In_3$- and SrAu-related slabs.

Key words: Crystal Structure, Indide, Intergrowth Structure, Gold, Strontium

Introduction

The ternary systems alkaline earth metal (*AE*)-transition metal (*T*)-indium have intensively been studied with respect to phase analyses and structure determination in the last twenty years. Today more than 70 ternary $AE_xT_yIn_z$ phases [1 – 42] are known (Fig. 1). The structural chemistry of these intermetallics is closely related to the rare earth (*RE*)-based phases [43], *i. e.* the *T* and In atoms build up complex three-dimensional $[T_yIn_z]$ polyanionic networks in which the *RE* or *AE* atoms fill cages or channels. Such crystal chemistry is not observed with magnesium, which does not play the role of a typical alkaline earth metal. Magnesium substitutes for indium, leading to extended solid solutions like $IrIn_{3-x}Mg_x$ [44] or $Ir_3Mg_{13-x}In_x$ [45], and the structure type of the binary intermetallic compound is maintained.

Of the many *AE*-*T*-In systems those with gold have most extensively been investigated (Fig. 1), especially with respect to searches for quasicrystals and approximants [41, and refs. therein]. Although already ten ternary phases with distinctly different crystal structures and compositions have been described, including the recently reported phases $SrAu_{4.76}In_{1.24}$ [34] and $SrAu_{4.3}In_{1.7}$ [41], our phase-analytical investigations of the Sr-Au-In system revealed the new gold-rich compound $Sr_5Au_{13+x}In_{9-x}$. The synthesis and crystal structure of this intermetallic phase are reported herein.

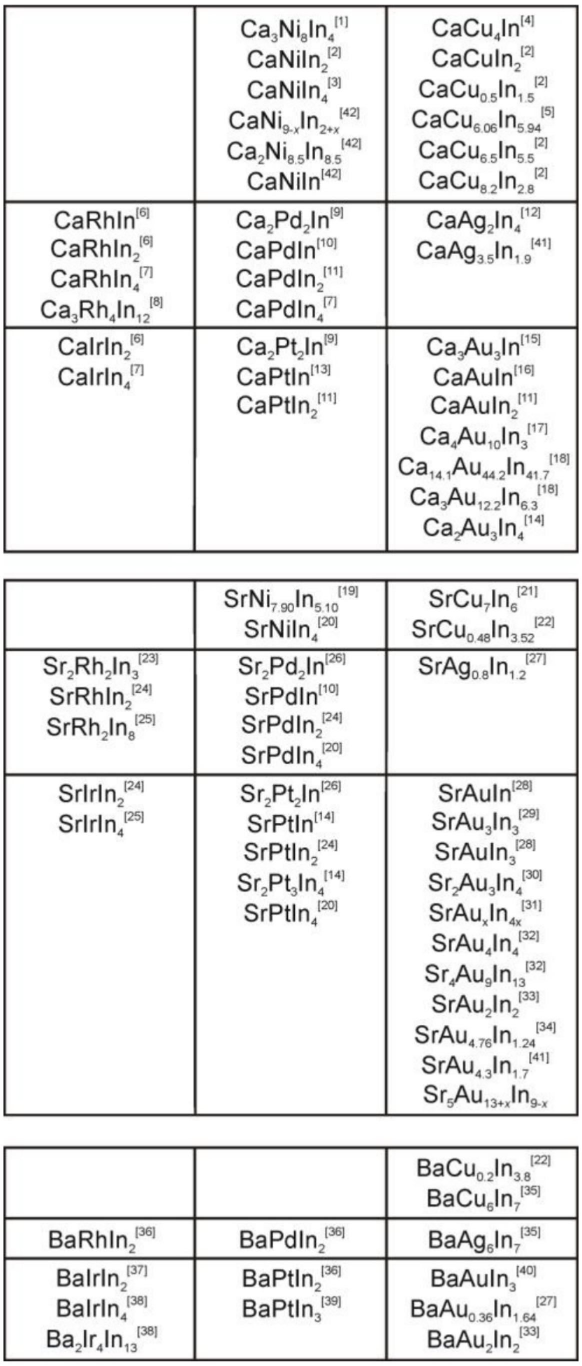
Experimental Section

Synthesis

Starting materials for the syntheses of $Sr_5Au_{13.5}In_{8.5}$ were a strontium rod (Johnson Matthey), pieces of a gold bar (Heraeus), and indium ingots (Johnson Matthey), all with stated purities better than 99.9 %. The strontium rod was cut into smaller pieces under dried (Na wire) paraffin oil, washed with *n*-hexane and kept in a Schlenk tube under argon. The argon was purified over titanium sponge (900 K), silica gel, and molecular sieves. Strontium, gold, and indium were weighed in a 10 : 27 : 17 atomic ratio and sealed in a tantalum tube [46]. This ampoule was placed in a water-cooled sample chamber [47] of a high-frequency furnace (Hüttinger Elektronik, Freiburg, type TIG 1.5/300) under flowing argon and first annealed at 1500 K for about one minute, followed by cooling to 900 K within three hours. Finally the sample was annealed for five hours at that temperature, followed by quenching. The temperature was controlled through a Sensor Therm Methis MS09 pyrometer with an accuracy of ±30 K. The sample was separated mechanically from the ampoule. No reaction with the crucible material was evident. Polycrystalline $Sr_5Au_{13.5}In_{8.5}$ is stable in air.

EDX data

Semiquantitative EDX analyses of the single crystal studied on the diffractometer were carried out in variable pres-



	$Ca_3Ni_8In_4$[1] $CaNiIn_2$[2] $CaNiIn_4$[3] $CaNi_{9-x}In_{2+x}$[42] $Ca_2Ni_{8.5}In_{8.5}$[42] $CaNiIn$[42]	$CaCu_4In$[4] $CaCuIn_2$[2] $CaCu_{0.5}In_{1.5}$[2] $CaCu_{6.06}In_{5.94}$[5] $CaCu_{6.5}In_{5.5}$[2] $CaCu_{8.2}In_{2.8}$[2]
$CaRhIn$[6] $CaRhIn_2$[6] $CaRhIn_4$[7] $Ca_3Rh_4In_{12}$[8]	Ca_2Pd_2In[9] $CaPdIn$[10] $CaPdIn_2$[11] $CaPdIn_4$[7]	$CaAg_2In_4$[12] $CaAg_{3.5}In_{1.9}$[41]
$CaIrIn_2$[6] $CaIrIn_4$[7]	Ca_2Pt_2In[9] $CaPtIn$[13] $CaPtIn_2$[11]	Ca_3Au_3In[15] $CaAuIn$[16] $CaAuIn_2$[11] $Ca_4Au_{10}In_3$[17] $Ca_{14.1}Au_{44.2}In_{41.7}$[18] $Ca_3Au_{12.2}In_{6.3}$[18] $Ca_2Au_3In_4$[14]

	$SrNi_{7.90}In_{5.10}$[19] $SrNiIn_4$[20]	$SrCu_7In_6$[21] $SrCu_{0.48}In_{3.52}$[22]
$Sr_2Rh_2In_3$[23] $SrRhIn_2$[24] $SrRh_2In_8$[25]	Sr_2Pd_2In[26] $SrPdIn$[10] $SrPdIn_2$[24] $SrPdIn_4$[20]	$SrAg_{0.8}In_{1.2}$[27]
$SrIrIn_2$[24] $SrIrIn_4$[25]	Sr_2Pt_2In[26] $SrPtIn$[14] $SrPtIn_2$[24] $Sr_2Pt_3In_4$[14] $SrPtIn_4$[20]	$SrAuIn$[28] $SrAu_3In_3$[29] $SrAuIn_3$[28] $Sr_2Au_3In_4$[30] $SrAu_xIn_{4x}$[31] $SrAu_4In_4$[32] $Sr_4Au_9In_{13}$[32] $SrAu_2In_2$[33] $SrAu_{4.76}In_{1.24}$[34] $SrAu_{4.3}In_{1.7}$[41] $Sr_5Au_{13+x}In_{9-x}$

		$BaCu_{0.2}In_{3.8}$[22] $BaCu_6In_7$[35]
$BaRhIn_2$[36]	$BaPdIn_2$[36]	$BaAg_6In_7$[35]
$BaIrIn_2$[37] $BaIrIn_4$[38] $Ba_2Ir_4In_{13}$[38]	$BaPtIn_2$[36] $BaPtIn_3$[39]	$BaAuIn_3$[40] $BaAu_{0.36}In_{1.64}$[27] $BaAu_2In_2$[33]

Fig. 1. Structurally characterized alkaline earth metal-transition metal indides.

Table 1. Crystal data and structure refinement for $Sr_5Au_{13.5(1)}In_{8.5(1)}$; space group *Pmmn*; $Z = 2$.

Unit cell dimensions	(Guinier powder data)
a, pm	476.37(9)
b, pm	2927.5(9)
c, pm	894.9(2)
Cell volume V, nm^3	1.2244
Molar mass, g mol^{-1}	4074.35
Calculated density, g cm^{-3}	11.05
Absorption coefficient, mm^{-1}	99.2
$F(000)$, e	3347
Crystal size, μm^3	$10 \times 30 \times 60$
Transm. ratio (max / min)	0.406 / 0.045
θ range, deg	2 – 32
Range in *hkl*	±6, ±43, ±13
Total no. reflections	28814
Independent reflections / R_{int}	2355 / 0.172
Reflections with $I \geq 2\sigma(I)$ / R_σ	1674 / 0.092
Data / parameters	2355/ 87
$R1$ / $wR2$ for $I \geq 2\sigma(I)$	0.045 / 0.050
$R1$ / $wR2$ for all data	0.085 / 0.056
Goodness-of-fit on F^2	0.956
Extinction coefficient	0.00051(2)
Largest diff. peak / hole, e Å^{-3}	3.62 / −3.02

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (pm^2) of $Sr_5Au_{13.5(1)}In_{8.5(1)}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff site	Occupancy %	x	y	z	U_{eq}
Sr1	4*e*	100	1/4	0.01451(7)	0.6844(2)	121(4)
Sr2	4*e*	100	1/4	0.62525(8)	0.8034(2)	162(4)
Sr3	2*a*	100	1/4	1/4	0.6666(3)	121(5)
Au1	4*e*	100	1/4	0.06170(3)	0.35575(8)	130(2)
Au2	4*e*	100	1/4	0.11477(3)	0.88758(10)	157(2)
Au3	4*e*	100	1/4	0.19623(3)	0.33399(9)	144(2)
Au4	4*e*	100	1/4	0.56078(3)	0.09795(10)	148(2)
Au5	4*e*	100	1/4	0.57678(3)	0.46549(10)	163(2)
Au6	4*e*	100	1/4	0.68514(3)	0.48977(9)	144(2)
Au7	2*b*	100	1/4	3/4	0.05290(14)	183(3)
In1	4*e*	100	1/4	0.03437(5)	0.06515(16)	99(3)
In2	4*e*	100	1/4	0.13168(5)	0.57239(16)	99(3)
In3/Au8	4*e*	74(1)/26(1)	1/4	0.19996(5)	0.02526(15)	176(5)
In4	2*b*	100	1/4	3/4	0.7287(3)	138(4)
In5	4*e*	100	1/4	0.66098(5)	0.19116(16)	138(3)

sure mode with a Zeiss EVO® MA10 scanning electron microscope with SrF_2, Au, and InAs as standards. The experimentally observed average composition (in at.-%) of 15 : 54 : 31 is close to the one refined from the single crystal X-ray data of 18.5 : 50.0 : 31.5. No impurity elements were detected.

X-Ray diffraction

The powder sample of starting composition 10Sr : 27Au : 17In was characterized by a Guinier pattern (imaging plate detector, Fujifilm BAS-1800) with Cu$K_{\alpha 1}$ radiation and α-quartz (a = 491.30, c = 540.46 pm) as an internal standard. The orthorhombic lattice parameters were obtained from a least-squares refinement. Correct

Table 3. Interatomic distances (pm), calculated with the powder lattice parameters of $Sr_5Au_{13.5(1)}In_{8.5(1)}$. Standard deviations are all equal or less than 0.2 pm.

Sr1:	1	Au1	324.9
	2	Au1	325.1
	2	Au5	325.3
	1	Au5	331.4
	2	Au4	333.0
	1	Au2	345.3
	1	In1	345.7
	2	In1	354.0
	1	In2	357.3
Sr2:	1	Au4	324.2
	2	Au1	330.9
	1	Au6	331.0
	1	Au5	334.0
	2	Au3	336.0
	2	In3/Au8	354.9
	1	In5	362.4
	2	Au2	363.3
	1	In4	371.3
	2	In1	373.1
Sr3:	4	Au6	332.0
	2	Au3	336.7
	2	Au7	343.0
	2	In3/Au8	352.8
	2	In2	356.5
	4	In5	372.5
Au1:	1	In1	272.1
	1	In2	282.0
	2	Au5	286.6
	1	Sr1	324.9
	2	Sr1	325.1
	2	Sr2	330.9
Au2:	1	In3/Au8	278.1
	2	In5	279.1
	2	Au4	282.4
	1	In1	284.0
	1	In2	286.4
	1	Sr1	345.3
	2	Sr2	363.3
Au3:	1	In3/Au8	276.5
	2	Au6	283.8
	1	In2	285.0
	2	In4	287.3
	1	Au3	314.8
	2	Sr2	336.0
	1	Sr3	336.7
Au4:	1	In1	280.1
	2	Au2	282.4
	2	In1	286.2
	1	In5	305.0
	1	Sr2	324.2
	1	Au5	332.2
	2	Sr1	333.0
Au5:	2	In2	285.6
	2	Au1	286.6
	1	Au6	318.0
	2	Sr1	325.3
	1	Sr1	331.3
	1	Au4	332.2
	1	Sr2	334.0
	1	In5	347.9
Au6:	1	In5	276.4
	2	Au3	283.8
	1	In4	286.0
	2	In2	286.7
	1	Au5	318.0
	1	Sr2	331.0
	2	Sr3	332.0
Au7:	4	In3/Au8	284.5
	2	In5	288.5
	1	In4	290.1
	2	Sr3	343.0
In1:	1	Au1	272.1
	1	Au4	280.1
	1	Au2	284.0
	2	Au4	286.2
	2	In1	329.7
	1	Sr1	345.7
	2	Sr1	354.0
	2	Sr2	373.1
In2:	1	Au1	282.0
	1	Au3	285.0
	2	Au5	285.6
	1	Au2	286.4
	2	Au6	286.7
	2	In5	326.7
	1	Sr3	356.5
	1	Sr1	357.3
In3/Au8:	1	Au3	276.5
	1	Au2	278.1
	2	Au7	284.6
	1	In3/Au8	293.0
	2	In5	324.2
	1	Sr3	352.8
	2	In4	352.9
	2	Sr2	354.9
In4:	2	Au6	286.0
	4	Au3	287.3
	1	Au7	290.1
	4	In3/Au8	352.9
	2	Sr2	371.3
In5:	1	Au6	276.4
	2	Au2	279.1
	1	Au7	288.5
	1	Au4	305.0
	2	In3/Au8	324.2
	2	In2	326.7
	1	Au5	347.9
	1	Sr2	362.4
	2	Sr3	372.5

indexing of the pattern was ensured through an intensity calculation [48].

Small singe crystals were selected from the crushed sample, glued to quartz fibres using bees wax and studied on a Buerger camera (using white Mo radiation). A data set of a well-shaped crystal was collected in oscillation mode on a Stoe IPDS II diffractometer using $\mathrm{Mo}K_\alpha$ radiation. A numerical absorption correction was applied to the data set. Details about the data collection and the crystallographic parameters are summarized in Table 1.

Structure determination and refinement

The diffractometer data set showed a primitive orthorhombic lattice, and the observed extinction conditions were in agreement with space group *Pmmn*. The starting atomic parameters were deduced from Direct Methods [49], and the structure was refined with anisotropic displacement parameters for all atoms with SHELXL-97 (full-matrix least-squares on F_o^2) [50]. One of the 4*e* sites was initially refined exclusively with the scattering power of indium. However, the equivalent isotropic displacement parameter was too small, indicating higher scattering power. Similar to the structures of $SrAu_{4.76}In_{1.24}$ [34] and $SrAu_{4.3}In_{1.7}$ [41], the investigated crystal also showed In/Au mixing. The In/Au mixed occupancy was then refined as a least-squares variable, leading to the composition $Sr_5Au_{13.5}In_{8.5}$ for the investigated crystal. Before the final refinement, the positional parameters were standardized with the STRUCTURE TIDY routine [51]. All other sites were fully occupied within two standard deviations. The final difference Fourier synthesis revealed no residual peaks. The refined atomic positions, equivalent isotropic displacement parameters, and interatomic distances are given in Tables 2 and 3.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-423679.

Discussion

The structure of $Sr_5Au_{13.5}In_{8.5}$ is of a new type. It is already the eleventh intermetallic compound in the ternary system Sr-Au-In (Fig. 1). A projection of the $Sr_5Au_{13.5}In_{8.5}$ structure along the short unit cell axis is presented in Fig. 2. The shortest interatomic distances occur between the gold and indium atoms. The Au–In distances range from 272 to 305 pm. The shorter ones are close to the sum of the covalent radii of 284 pm [52], indicating substantial Au–In bonding. Similar ranges of Au–In distances occur in EuAuIn

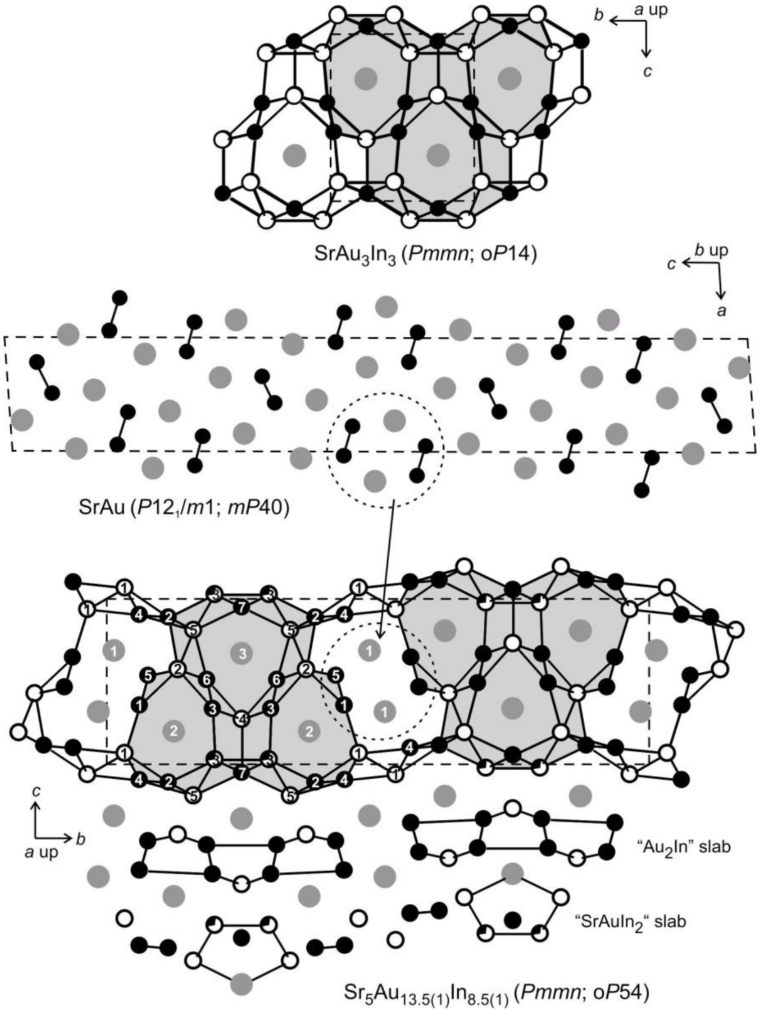


Fig. 2. Projection of the $SrAu_3In_3$ (top), SrAu (middle), and $Sr_5Au_{13.5}In_{8.5}$ (bottom) structures along the short unit cell axes. Strontium, gold, and indium atoms are drawn as medium grey, black filled, and open circles, respectively. The mixed occupied site in $Sr_5Au_{13.5}In_{8.5}$ (see Table 2) is emphasized by segments. Atom designations and characteristic structural slabs are outlined.

(283 – 288 pm) [53] and $EuAuIn_2$ (284 – 289 pm) [54]. Together, the gold and indium atoms build up a complex three-dimensional network. Due to the high gold content within this network, we observe a variety of Au–Au interactions. The shortest Au–Au distance (Au2–Au4 of 282 pm) is even shorter than in *fcc* gold (288 pm) [55]. Furthermore we observe a variety of shorter In–In distances, 330 pm In1–In1 and 327 pm In2–In5. The latter compare well with the tetragonal body-centered structure of elemental indium (a = 325.2 pm, c = 494.7 pm) [55], where each indium atom has four nearest neighbors at 325 pm and eight further neighbors at 338 pm. Much shorter In–In distances occur in the orthorhombically distorted tetrahedral indium network of $EuAuIn_2$ (298 – 312 pm In–In) [54]. Thus, the three-dimensional $[Au_{13.5}In_{8.5}]$ polyanionic network is stabilized by Au–In as well as Au–Au and In–In interactions.

The $[Au_{13.5}In_{8.5}]$ network leaves large channels that are filled by the three crystallographically independent strontium atoms. The bonding of strontium to the network proceeds *via* Sr–Au contacts. Each strontium atom has between seven and nine gold neighbors at Sr–Au distances ranging from 324 to 345 pm, in good agreement with the sum of the covalent radii of 326 pm [52]. A similar bonding situation has been observed also for the other $Sr_xAu_yIn_z$ phases listed in Fig. 1.

An interesting structural feature is the gold substructure of the $Sr_xAu_yIn_z$ phases. In the recently reported compound $SrAu_{4.76}In_{1.24}$ [34] the gold atoms form pronounced Au_4 squares that are condensed *via*

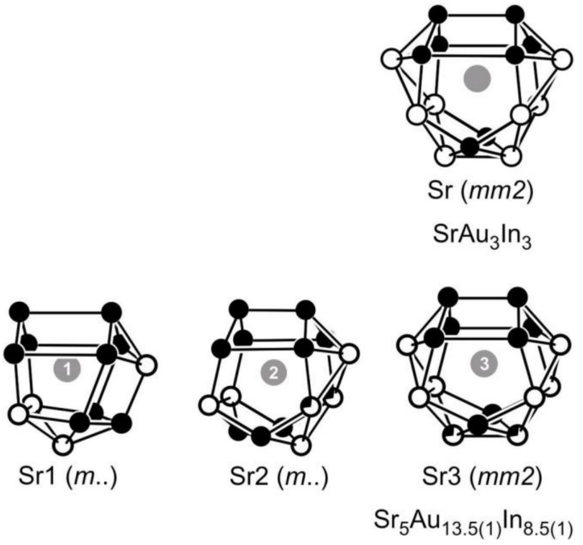


Fig. 3. Coordination of the strontium atoms in the structures of $SrAu_3In_3$ (top) and $Sr_5Au_{13.5}In_{8.5}$ (bottom). Strontium, gold, and indium atoms are drawn as medium grey, black filled, and open circles, respectively. The mixed occupied site (see Table 2) is emphasized by segments. Site symmetries are given.

weaker Au–Au contacts to a three-dimensional network. The structure of $SrAu_3In_3$ [29] contains isolated gold atoms (no Au–Au interactions) besides Au–Au zig-zag chains. As emphasized in Fig. 2, the structure of $Sr_5Au_{13.5}In_{8.5}$ also shows these features. The structural slabs that are similar to $SrAu_3In_3$ are shaded in medium grey. The Sr2 and Sr3 atoms lie within these slabs. They have similar coordination as the strontium atoms in $SrAu_3In_3$ (see Fig. 3). The $SrAu_3In_3$-related slabs in $Sr_5Au_{13.5}In_{8.5}$ are separated by the Sr1 atoms. The latter are coordinated by Au1–Au5 zig-zag chains. This kind of coordination is similar to that in SrAu (Fig. 2) which crystallizes with a stacking variant of FeB and CrB slabs [56].

In our earlier contribution on the structure of $SrAu_3In_3$ [29] we had already emphasized the 'Au_2In' and '$SrAuIn_2$' related slabs (Fig. 2). In this context it is interesting to note that $EuAuIn_2$ [54] and $EuAu_3In_3$ [29] exist, but a ternary indide '$SrAuIn_2$' with $MgCuAl_2$ structure is not known [57], and our recent phase analytical studies gave no hint to such a phase.

Finally we draw back to the Au/In mixed occupancy of the Au3/In8 site which is located within the $SrAu_3In_3$ related slabs. In the $SrAu_3In_3$ structure itself, the related site is fully occupied by indium. Nevertheless, most $Sr_xAu_yIn_z$ structures contain one or more Au/In mixed occupied sites. Thus, one can expect a small homogeneity range for $Sr_5Au_{13+x}In_{9-x}$.

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