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RhSn₃ and the Modifications of RhSn₄ – Structure and ¹¹⁹Sn Mössbauer spectroscopic characterization

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Abstract: Single crystals of the high-temperature modification of RhSn₄ were obtained from a tin flux (1:20 molar ratio; final annealing at 920 K; dissolution of the tin matrix in 2N HCl). The structure was refined from single-crystal X-ray diffractometer data: $I4_1/acd$, $a = 629.73(5)$, $c = 2288.36(18)$ pm, $wR2 = 0.0382$, 447 F^2 values and 14 variables. β -RhSn₄ is isotypic with β -IrSn₄. The rhodium atoms have slightly distorted square-antiprismatic tin coordination with Rh–Sn distances of 4×273.4 and 4×274.1 pm. The RhSn₈ units are condensed via common edges to layers that are staggered with respect to each other and stacked in ABCD sequence. A ¹¹⁹Sn Mössbauer spectroscopic characterization of β -RhSn₄ and the stannides RhSn₃ and α -RhSn₄ shows the typical isomer shifts for transition metal stannides. Only for α -RhSn₄ the three crystallographically independent tin sites could be resolved, a consequence of the different s-electron density. Treatment of α -RhSn₄ under high-pressure (up to 10 GPa)/high-temperature (up to $T = 1370$ K) conditions leads to decomposition into Rh_{1.5}Sn, RhSn₂ and β -Sn.

Keywords: crystal structure; Mössbauer spectroscopy; rhodium; stannide.

1 Introduction

Most transition metals react with liquid tin forming a variety of binary stannides [1, 2]. These stannides can be obtained through direct reaction of the elements, by classical ampoule reactions, via arc-melting or induction melting. The tin-rich phases can easily be grown via the self-flux technique [3]. So far, not all phase diagrams are completely known [4, 5]. No stannides have been reported for the tungsten and rhenium systems. Zinc, cadmium and mercury show low solubility for tin. The basic crystal chemical features of transition metal stannides have been summarized in a review article [2].

Besides phase-analytical studies and structure determination, property studies play an important role in stannide research. A major application concerns solder joints, where stannides form via interfacial reactions with cobalt, palladium, silver or gold substrates [2, 6]; even metastable stannides are formed, e.g. CoSn₄ [7]. Stannide formation is one of the major problems concerning brittleness of the joints.

Nb₃Sn is one of the technologically important superconducting materials ($T_c = 18.3$ K) [8, 9], used in most superconducting magnetic coils for application in NMR spectrometers, SQUID magnetometers, or magnetic resonance imaging apparatuses, operating at liquid helium temperature. β -IrSn₄ is a type-II superconductor with a much lower critical temperature of $T_c = 0.9$ K [10]. Other important electronic properties have been found for the topological insulator Ru₂Sn₃ which shows a semiconductor-metal transition along with a structural phase transition (tetragonal high- to orthorhombic low-temperature phase) [11–13]. The large linear magnetoresistance behavior of Ru₂Sn₃ is similar to that of the recently reported high-temperature modification of RhSn₄ [14]. The latter shows $\Delta\rho/\rho$ of ~600% at 2 K and 9 T.

The noble metal stannides are promising candidates for heterogeneous catalysis. They find application as thin films on SiO₂ or alumina supports, or in the form of nanoparticles. Typical catalysts are AuSn/SnO_x-Al₂O₃, Rh-Sn/Al₂O₃ or Pd-Sn/SiO₂ [15–17] for CO oxidation or hydrogenation reactions. The electronic state of the tin atoms in

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these catalysts was repeatedly studied by ¹¹⁹Sn Mössbauer spectroscopy.

From a crystal chemical point of view it is interesting to mention the polymorphism of several transition metal stannides. The first example was the tetragonal-to-orthorhombic phase transition of Ru₂Sn₃ [11], which is associated with drastic changes in the physical properties (*vide ultra*). CoSn₃ is dimorphic. The high-temperature β -modification crystallizes with its own structure type and transforms to α -CoSn₃ with a PdSn₃ type structure [18]. IrSn₄ is trimorphic [19, 20]: trigonal α -IrSn₄ (*P*3₁21) transforms to tetragonal β -IrSn₄ (*I*4₁/*acd*), and its high-pressure modification (6 GPa, *T* = 900–1100 K) is isotypic with orthorhombic PtSn₄ [21]. Under ambient pressure conditions, α -RhSn₄ [19] and β -RhSn₄ [14, 22] are isotypic with the corresponding iridium phases.

Herein we report on the first single crystal structure refinement of β -RhSn₄ along with an ¹¹⁹Sn Mössbauer spectroscopic study and high-pressure/high-temperature experiments on α -RhSn₄ samples.

2 Experimental

2.1 Synthesis

Starting materials for the syntheses of the rhodium stannides were pieces of rhodium sheet (Heraeus) and tin granules (Merck), both with stated purities better than 99.9%. Three different syntheses were conducted: (i) Rhodium and tin were mixed in a molar ratio of 1:20, sealed in an evacuated silica tube and rapidly heated to *T* = 1320 K. The temperature was kept for 2 h and then lowered to 920 K within 7 d, followed by switching off the furnace. The excess tin matrix was dissolved in 2N HCl at room temperature over a period of several days. The product crystals were rinsed with demineralized water. This sample contained well-shaped β -RhSn₄ crystals besides RhSn₃ as a by-product. Samples with different starting ratios of Rh to Sn > 1:4 gave similar results. (ii) α -RhSn₄ was obtained from a 1:10 molar mixture (sealed evacuated silica tube)

that was annealed for 2 d at *T* = 820 K, rapidly cooled to 570 K and kept at that temperature for another 7 d, followed by quenching in an ice/water mixture. The tin matrix was dissolved similar to synthesis protocol (i); (iii) polycrystalline RhSn₃ was synthesized from an ideal molar ratio of 1:3, again sealed in an evacuated silica tube. The mixture was rapidly heated to *T* = 820 K, kept at that temperature for 2 d and then cooled down to 600 K at a rate of 50 K h^{−1}. After an additional annealing at 600 K for 9 d the ampoule was quenched in an ice/water mixture. The product was additionally treated with 2N HCl for several days to remove tin inclusions at the grain boundaries. All samples are stable in moist air over several months.

2.2 X-ray diffraction

The RhSn₃ and various RhSn₄ samples were characterized by Guinier patterns (Enraf-Nonius FR552 camera, imaging plate detector, Fujifilm BAS-1800) with CuK α ₁ radiation and α -quartz (*a* = 491.30, *c* = 540.46 pm) as an internal standard. The tetragonal lattice parameters (Table 1) were deduced from standard least-squares refinements. Correct indexing of the patterns was ensured through intensity calculations [23].

Small platelet-like single crystal fragments of β -RhSn₄ were selected from the crushed annealed sample, glued to quartz fibers using beeswax and studied on a Buerger camera (using white Mo radiation) to check their quality. An intensity data set was collected on a Stoe IPDS-II diffractometer (graphite-monochromatized MoK α radiation; oscillation mode) and a numerical absorption correction was applied. Details about the data collection and the crystallographic parameters are summarized in Table 2.

2.3 Structure refinement

The β -RhSn₄ data set showed a body-centred tetragonal lattice, and the systematic extinctions were compatible

Table 1: Lattice parameters of RhSn₃ and RhSn₄.

Compound	Structure type	Space group	<i>a</i> (pm)	<i>c</i> (pm)	<i>V</i> (nm ³)	Reference
RhSn ₃	β -CoSn ₃	<i>I</i> 4 ₁ / <i>acd</i>	632.4(1)	3412(1)	1.3646	[19]
RhSn ₃	β -CoSn ₃	<i>I</i> 4 ₁ / <i>acd</i>	632.91(7)	3418.0(9)	1.3692	this work
α -RhSn ₄	IrGe ₄	<i>P</i> 3 ₁ 21	677.4(2)	861.4(2)	0.3423	[19]
α -RhSn ₄	IrGe ₄	<i>P</i> 3 ₁ 21	677.70(9)	861.62(9)	0.3427	this work
β -RhSn ₄	β -IrSn ₄	<i>I</i> 4 ₁ / <i>acd</i>	629.73(6)	2288.36(18)	0.9075	this work

Table 2: Crystal data and structure refinement for β -RhSn₄, β -IrSn₄ type, space group $I4_1/acd$, $Z=8$.

Empirical formula	RhSn ₄
Formula weight, g mol ⁻¹	577.7
Unit cell dimension (Guinier powder data)	
<i>a</i> , pm	629.73(6)
<i>c</i> , pm	2288.36(18)
Cell volume, nm ³	<i>V</i> =0.9075
Calculated density, g cm ⁻³	8.46
Crystal size, μ m ³	20×45×45
Transm. ratio (min/max)	0.447/0.851
Absorption coefficient, mm ⁻¹	25.1
Detector distance, mm	70
Exposure time, min	15
ω range/increment, deg	0–180/1
Integr. Param. A/B/EMS	15.0/–2.0/0.020
<i>F</i> (000), <i>e</i>	1960
θ range, deg	3.5–33.4
Range in <i>hkl</i>	±9, ±9, ±34
Total no. of reflections	11408
Independent reflections/ <i>R</i> _{int}	447/0.0461
Reflections with $I \geq 2 \sigma(I)/R_\sigma$	310/0.0093
Data/parameters	447/14
Goodness-of-fit on <i>F</i> ²	1.17
<i>R</i> ₁ / <i>wR</i> ₂ for $I \geq 2\sigma(I)$	0.0137/0.0323
<i>R</i> ₁ / <i>wR</i> ₂ for all data	0.0329/0.0382
Extinction coefficient	256(14)
Largest diff. peak/hole, <i>e</i> Å ⁻³	3.21/–3.08

with space group $I4_1/acd$, confirming isotypy with β -IrSn₄ (that was already evident from the X-ray powder diffraction data) [20]. The known atomic parameters of the iridium compound were taken as starting atomic parameters and the structure was refined with anisotropic displacement parameters for all atoms using the JANA2006 package (full-matrix least-squares on *F*_o²) [24]. Separate refinement of the occupancy parameters of all sites revealed full occupancy for all positions. The final difference Fourier synthesis showed no residual peaks. The refined atomic positions, displacement parameters, and interatomic distances are given in Tables 3 and 4.

CCDC 1868170 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3: Atomic coordinates and displacement parameters (pm²) for β -RhSn₄.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	<i>U</i> _{eq}
Rh	8 <i>b</i>	0	1/4	1/8	63(1)	<i>U</i> ₁₁	72(2)	3(2)	0	0	66(1)
Sn	32 <i>g</i>	0.17555(4)	0.57351(5)	0.06160(1)	98(1)	101(1)	92(1)	–21(1)	–5(1)	9(1)	97(1)

*U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Table 4: Interatomic distances (pm) for β -RhSn₄.

Rh:	4	Sn	273.4	Sn:	1	Rh	273.5
	4	Sn	274.1		1	Rh	274.1
					1	Sn	297.1
					1	Sn	313.5
					1	Sn	318.7
					2	Sn	328.2
					2	Sn	328.5
					2	Sn	365.2
					1	Sn	370.0

Standard deviations are equal or smaller than 0.1 pm. All distances of the first coordination spheres are listed.

2.4 EDX data and scanning electron microscopy

The β -RhSn₄ crystal studied on the diffractometer was semi-quantitatively analysed by EDX in variable pressure mode with a Zeiss EVO® MA10 scanning electron microscope using elemental Rh and Sn as standards. The measurement (20±1 at.% Rh:80±1 at.% Sn) confirmed the proposed composition. No impurity elements (e.g. silicon from the container material) were observed.

Figure 1 displays scanning electron micrographs. The main figure shows β -RhSn₄ crystals grown on a RhSn₃ matrix. The extremely large *c/a* ratios of the RhSn₃ and β -RhSn₄ unit cells lead to crystal growth of thin plates (mostly only several μ m thick). Selected square platelets of β -RhSn₄ are presented in the inset.

2.5 Mössbauer spectroscopy

The ^{119m}Sn Mössbauer spectroscopic measurements of the RhSn₃ and α -RhSn₄ samples were conducted with a Ca^{119m}SnO₃ source in usual transmission geometry at *T*=78 K. The samples were placed in thin PMMA containers with a sample thickness of about 10 mg Sn cm⁻². To reduce the *K* X-rays emitted by the ^{119m}Sn Mössbauer source a thin palladium foil (thickness 0.05 mm) was placed in front of the detector. Each spectrum was measured over a period of 1 day. Fitting of the spectra was done with the WINNORMOS for IGOR6 software package [25].

Fig. 1: Scanning electron micrographs of β -RhSn₄ crystals. The main figure shows β -RhSn₄ crystals grown on a RhSn₃ matrix. The inset shows selected β -RhSn₄ platelets.

2.6 High-pressure/high-temperature experiments

Starting materials for the high-pressure/high-temperature experiments were α -RhSn₄ and a mixture of α -RhSn₄ and β -RhSn₄ (ca. 1:1) prepared as described in Chapter 2.1. The experiments were performed on a multi-anvil device with a Walker-type module and octahedral pressure-cell geometry. For experimental details on the setup we refer to [26, 27] and the references therein. The powdered samples were filled in a crucible made of hexagonal boron nitride and compressed within 200 and 230 min to 8.5 and 10 GPa, respectively. Two different experiments were conducted: (i) α -RhSn₄ was compressed to 8.5 GPa and heated within 10 min to $T=1070$ K. The temperature was kept for 10 min and then lowered to 720 K within 120 min, followed by quenching to room temperature. (ii) At 10 GPa two syntheses were carried out, starting from α -RhSn₄ and a mixture of α -RhSn₄ and β -RhSn₄. Both samples were heated to 1370 K within 10 min and kept for another 10 min at this temperature. They were then cooled to 970 K during the next 90 min with subsequent quenching to room temperature. The pressure was finally released through a period of 600–700 min and the octahedral pressure medium could be recovered and broken apart. The surrounding crucible material could be easily removed from the polycrystalline samples, which appeared silvery with metallic lustre.

3 Crystal chemistry

β -RhSn₄ is isotypic with β -IrSn₄ [20], space group $I4_1/acd$, Pearson symbol *t*40 and Wyckoff sequence *gb*. The

synthesis and single crystal data of β -RhSn₄ were first reported in 2008 [22]. Recent work focused on the magnetoresistance behavior of β -RhSn₄ [14]. In the latter work, the crystals were only characterized on the basis of orientation photographs confirming the *c* axis of 2280 pm.

A view of the β -RhSn₄ unit cell is presented in Fig. 2. The rhodium atoms have slightly distorted square antiprismatic tin coordination with Rh–Sn distances of 4×273.4 and 4×274.1 pm, slightly longer than the sum of the covalent radii of Rh + Sn of 265 pm [28]. Similar ranges of Rh–Sn distances have been observed for α -RhSn₄ (270.1–273.8 pm) and RhSn₃ (273.7–277.3 pm) [19]. The many ternary rare earth-rhodium-stannides show comparable distances within the three-dimensional rhodium-tin substructures, e.g. 262–277 pm Rh–Sn in CeRhSn₂ [29].

The RhSn₈ square antiprisms in β -RhSn₄ form layers through a condensation via common edges. These layers are staggered and stacked in ABCD sequence. For comparison we present the structure of the tin-poorer phase RhSn₃ in Fig. 2. The lower tin content results in a condensation of RhSn₈ square antiprisms via common square faces. These double antiprisms also condense via common edges in the *ab* plane and with the same space group type ($I4_1/acd$) and stacking sequence ABCD. Due to the larger extension of the double antiprisms in *c* direction the *c*

Fig. 2: The crystal structures of RhSn₃ ($I4_1/acd$) and β -RhSn₄ ($I4_1/acd$). The condensed square Rh@Sn₈ antiprisms are emphasized.

lattice parameter of RhSn₃ (3412 pm) is distinctly larger than for β -RhSn₄ (2288 pm). RhSn₃ and β -RhSn₄ belong to a larger family of stannides which structurally consist of stacking sequences of mono or double square antiprisms. The structural relationships have been discussed for the stannides PdSn_n ($n=2, 3, 4$) [30, 31] and polymorphic IrSn₄ [20], including slightly distorted structural variants. Adjacent layers are connected via Sn–Sn bonds (297–370 pm Sn–Sn in β -RhSn₄). All these structures are prone to stacking disorder. A very detailed study was recently performed for metastable NiSn₄ [32].

β -RhSn₄ shows a reconstructive phase transition to the trigonal low-temperature phase α -RhSn₄ with IrGe₄-type structure ($P\bar{3}_121$). For the crystal chemical details we refer to the original work [19].

The individual coordination of the crystallographically independent atoms is important for the interpretation of the ¹¹⁹Sn Mössbauer spectra (*vide infra*). While the rhodium atoms in RhSn₃, α -RhSn₄ and β -RhSn₄ have slightly distorted square anti-prismatic tin coordination, the tin atoms have low site symmetry along with an irregular coordination sphere. The individual tin coordination polyhedra of RhSn₃, α -RhSn₄ and β -RhSn₄ are presented in Fig. 3 along with their site symmetries.

β -RhSn₄ has only one crystallographic tin site. Each tin atom has two rhodium and ten tin atoms in its coordination shell. This polyhedron is similar to that of the Sn2 atoms in RhSn₃. In contrast, the Sn1 atom of the latter stannide has four rhodium and eleven tin neighbors. The Sn1 and Sn2 sites in RhSn₃ occur in 1:2 ratio. α -RhSn₄ has three

Fig. 3: Coordination polyhedra in RhSn₃ and in the two modifications of RhSn₄. Rhodium and tin atoms are drawn as blue and magenta circles, respectively. The site symmetries are indicated.

crystallographically independent tin sites, all with two rhodium and twelve tin neighbors. These sites occur in a ratio of Sn1:Sn2:Sn3 of 2:1:1. The ranges of the interatomic distances show some differences and one can regroup the three tin sites in two types, i.e. Sn1 and Sn3 vs. Sn2. Sn1 (270.1 and 273.3 pm) and Sn3 (2×273.8 pm) show shorter Sn–Rh distances than Sn2 (2×286.2 pm). On the other hand, the average Sn–Sn distances for the twelve nearest tin atoms are longer for Sn1 (349.7 pm) and Sn3 (352.2 pm) as compared to Sn2 (340.8 pm). This fact is addressed below when discussing the ¹¹⁹Sn Mössbauer spectra.

4 ¹¹⁹Sn Mössbauer spectroscopy

The ¹¹⁹Sn Mössbauer spectra of RhSn₃, α -RhSn₄ and a mixture of RhSn₃ and β -RhSn₄ (as indicated in the Experimental Section, RhSn₃ was a by-product in all synthesis attempts) at $T=78$ K are presented in Fig. 4. The corresponding fitting parameters are listed in Table 5. Although RhSn₃ contains two crystallographically independent tin sites, the spectrum was well reproduced with a single signal at an isomer shift of 2.24(1) mm s^{−1} (Fig. 4, bottom). Both tin sites show comparable average Sn–Rh and Sn–Sn distances, indicating a similar electronic situation. We thus observe only the envelope of the two sub-signals

Fig. 4: ¹¹⁹Sn Mössbauer spectra of RhSn₃ (bottom), α -RhSn₄ (middle) and a sample containing a mixture of RhSn₃ and β -RhSn₄ (top).

which cannot be resolved. This is expressed in the slightly larger experimental line width of $\Gamma = 1.11(1) \text{ mm s}^{-1}$. The quadrupole splitting parameter for RhSn₃ of $0.82(1) \text{ mm s}^{-1}$ is distinctly larger than for the PdSn_{*n*} (*n* = 2, 3, 4) stannides [30], indicating larger structural distortion in the rhodium compound.

Figure 4 (top) shows the ¹¹⁹Sn spectrum of a sample containing RhSn₃ and β -RhSn₄. Again, it was not possible to resolve the separate sub-spectra. Since the tin coordination in β -RhSn₄ is similar to that of the Sn2 site of RhSn₃ (*vide supra*), the β -RhSn₄ signal fully overlaps with that of RhSn₃ and we can thus conclude a very similar electronic state for these tin sites.

The situation is different for α -RhSn₄ (Fig. 4, middle). The spectrum was well reproduced with a superposition of three sub-spectra in a ratio of 2:1:1 (Table 5) corresponding to the tin sites Sn1, Sn2 and Sn3. Keeping the discussion of the different tin environments in mind (*vide supra*), one can understand the similar isomer shift values for Sn1 and Sn3. The larger δ value of the Sn2 atoms is a consequence of the larger *s* electron density at the Sn2 nuclei, caused by the shorter average Sn–Sn contacts. This course of the isomer shifts as a function of the *s* electron density is comparable with that found in the series of CaTSn₂ (*T* = Rh, Pd, Ir) stannides [33].

The ¹¹⁹Sn spectrum of α -IrSn₄ [34, 35] is similar to our spectrum of α -RhSn₄. In the earlier work it was claimed that the α -IrSn₄ structure contains four tin sites (no further details were reported). This is only possible through a description in the *translationengleiche* subgroup *P*3₁ of *P*3₂₁ (the correct space group), where the 6*c* site splits into two 3*a* sites. The spectrum was wrongly reproduced by four superimposed singlets with isomer shifts covering the broad range from 1.47 to 2.98 mm s^{−1} and area percentages that strongly deviate from the possible site ratio of 1:1:1:1. The correct description would be a fit with three doublets, similar to α -RhSn₄.

Table 5: Fitting parameters of ¹¹⁹Sn Mössbauer spectroscopic measurements of RhSn₃, α -RhSn₄ and a sample containing a mixture of RhSn₃ and β -RhSn₄ at *T* = 78 K: δ = isomer shift, ΔE_Q = electric quadrupole splitting, Γ = experimental line width.

Compound	δ (mm · s ^{−1})	ΔE_Q (mm · s ^{−1})	Γ (mm · s ^{−1})	Area (%)
RhSn ₃	2.24(1)	0.82(1)	1.11(1)	100
α -RhSn ₄	2.17(1)	0.79(3)	1.14(3)	50* (Sn1)
	2.72(1)	0.79(4)	0.97(4)	25* (Sn2)
	2.28(1)	1.38(4)	0.89(3)	25* (Sn3)
	2.29(1)	0.83(1)	0.89(1)	100

Parameters marked with an asterisk were kept fixed during the fitting procedure.

5 High-pressure/high-temperature studies of RhSn₄ samples

Earlier studies in the Ir–Sn system under high-pressure (above 6 GPa)/high-temperature (*T* = 900–1100 K) conditions led to the metastable orthorhombic modification of IrSn₄ with PtSn₄ type structure [21]. Since iridium and rhodium have similar covalent and metallic radii, we attempted the high-pressure/high-temperature synthesis of a potential rhodium analogue under the experimental conditions listed in Chapter 2.6. The 10 GPa experiments of α -RhSn₄ and a mixture of α -RhSn₄ and β -RhSn₄ led to a decomposition to a mixture of RhSn₂ [36] and β -Sn while the 8.5 GPa experiment with α -RhSn₄ yielded Rh_{1.5}Sn [37] and β -Sn. These phases were unequivocally proven by X-ray powder diffraction. Under the present experimental conditions, there was no hint for the existence of a high-pressure phase of RhSn₄.

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