

# Structural, magnetic, and spectroscopic studies of YAgSn, TmAgSn, and LuAgSn

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## Abstract

The rare earth–silver–stannides YAgSn, TmAgSn, and LuAgSn were synthesized from the elements by arc-melting and subsequent annealing. The three stannides were investigated by X-ray powder and single-crystal diffraction: NdPtSb type,  $P6_3mc$ ,  $Z = 2$ ,  $a = 468.3(1)$ ,  $c = 737.2(2)$  pm,  $wR_2 = 0.0343$ , 353  $F^2$  values, 12 variables for YAgSn, and ZrNiAl type,  $P\bar{6}2m$ ,  $a = 726.4(2)$ ,  $c = 443.7(1)$  pm,  $wR_2 = 0.0399$ , 659  $F^2$  values, 15 variables for TmAgSn, and  $a = 723.8(2)$ ,  $c = 442.47(9)$  pm,  $wR_2 = 0.0674$ , 364  $F^2$  values, 15 variables for LuAgSn. Besides conventional laboratory X-ray data with monochromatized Mo radiation, the structures were also refined on the basis of synchrotron data with  $\lambda = 48.725$  pm, in order to clarify the silver–tin ordering more precisely. YAgSn has puckered, two-dimensional [AgSn] networks with Ag–Sn distances of 278 pm, while the [AgSn] networks of TmAgSn and LuAgSn are three-dimensional with Ag–Sn distances of 279 and 284 pm for LuAgSn. Susceptibility measurements indicate Pauli paramagnetism for YAgSn and LuAgSn. TmAgSn is a Curie–Weiss paramagnet with an experimental magnetic moment of  $7.2 \mu_B/\text{Tm}$ . No magnetic ordering is evident down to 2 K. The local environments of the tin sites in these compounds were characterized by  $^{119}\text{Sn}$  Mössbauer spectroscopy and solid-state NMR (in YAgSn and LuAgSn), confirming the tin site multiplicities proposed from the structure solutions and the absence of Sn/Ag site disordering. Mössbauer quadrupolar splittings were found in good agreement with calculated electric field gradients predicted quantum chemically by the WIEN2k code. Furthermore, an excellent correlation was found between experimental  $^{119}\text{Sn}$  nuclear magnetic shielding anisotropies (determined via MAS-NMR) and calculated electric field gradients. Electronic structure calculations predict metallic properties with strong Ag–Sn bonds and also significant Ag–Ag bonding in LuAgSn.

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## 1. Introduction

The equiatomic rare earth (*RE*)–silver–stannides *REAgSn* have been intensively studied in recent years with respect to their crystal chemistry and physical properties [1–34]. Depending on the valence state and size of the rare

earth element, the *REAgSn* stannides crystallize with different structure types. With  $RE = \text{Y, La–Nd, Sm, Gd–Er}$  they crystallize with the hexagonal NdPtSb-type structure, space group  $P6_3mc$ , a slightly puckered, version of  $\text{AlB}_2$  [35] with ordered  $\text{Ag}_3\text{Sn}_3$  hexagons. The rare earth atoms are all in a stable trivalent state in the latter stannides.

$\text{EuAgSn}$  [7,12,26] and  $\text{YbAgSn}$  [1,10,13,20,21,28] contain divalent europium and ytterbium, and their crystal structures differ from those of the early rare earth elements.

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The europium compound crystallizes with the orthorhombic  $\text{KHg}_2$ -type structure, space group  $Imma$ , and  $\text{YbAgSn}$  adopts the  $\text{YbAgPb}$  type, space group  $P\bar{6}m2$ , with a planar and two puckered  $\text{Ag}_3\text{Sn}_3$  hexagons. Nevertheless, the three different structure types are all superstructures of the aristotype  $\text{AlB}_2$  [35].

Most of the  $\text{REAgSn}$  stannides show antiferromagnetic ordering at low temperatures and the magnetic structures have been determined from neutron powder data [4,17]. For the refinement of the nuclear structures, the fits of the neutron data were slightly better for the ordered  $\text{NdPtSb}$ -type arrangement. Magnetization data indicated interesting metamagnetic behavior for the neodymium, terbium [5], and holmium [6] compounds. A very interesting observation is noticed in the  $^{119}\text{Sn}$  Mössbauer spectra [7,20,23,26,29,31,33,34]. The isomer shift decreases from the lanthanum ( $\delta = 1.85 \text{ mm/s}$ ) to the erbium ( $\delta = 1.67 \text{ mm/s}$ ) compound, indicating a decrease of the  $s$  electron density at the tin nuclei. This is directly related to the trend of the electronegativities of the rare earth elements. At low temperatures, in the magnetically ordered regimes, the  $^{119}\text{Sn}$  spectra show significant transferred magnetic hyperfine fields.

With the smaller rare earth elements thulium, lutetium, and scandium, so far no  $\text{REAgSn}$  stannides have been reported. We were interested in these compounds in the course of our systematic  $^{119}\text{Sn}$  solid-state NMR investigations of ternary stannides with the diamagnetic rare earth elements [36]. Herein we report on the successful synthesis of  $\text{YAgSn}$ ,  $\text{TmAgSn}$ , and  $\text{LuAgSn}$  in X-ray pure form. The new stannides  $\text{TmAgSn}$  and  $\text{LuAgSn}$  crystallize with the  $\text{ZrNiAl}$  type, space group  $P\bar{6}2m$ . With the smallest rare earth element scandium, the  $\text{TiFeSi}$  type is formed [37]. The latter is a superstructure of the  $\text{ZrNiAl}$  type upon doubling of one subcell axis [38].

A common problem of all ternary silver stannides is the correct site assignment for the silver and tin atoms. Since silver and tin differ by only three electrons, it is difficult to distinguish the silver and tin sites even in high-quality single-crystal X-ray data sets. We have therefore investigated the stannides  $\text{YAgSn}$ ,  $\text{TmAgSn}$ , and  $\text{LuAgSn}$  also by single-crystal synchrotron data, using a radiation of  $48.725 \text{ pm}$ , near the silver edge. Together with  $^{119}\text{Sn}$  solid-state NMR data, a definite assignment of these sites was possible.

## 2. Experimental

### 2.1. Synthesis

The starting materials for the preparation of  $\text{YAgSn}$ ,  $\text{TmAgSn}$ , and  $\text{LuAgSn}$  were ingots of the rare earth elements (Johnson-Matthey and Kelpin), silver wire (Degussa-Hüls,  $\varnothing 1 \text{ mm}$ ), and tin granules (Merck), all with stated purities better than 99.9%. In a first step, small pieces of the rare earth ingots were arc-melted [39] to small buttons under an argon atmosphere of ca. 600 mbar. The

argon was purified before over titanium sponge (870 K), silica gel, and molecular sieves. The small rare earth buttons were then mixed with pieces of the silver wire and the tin granules in the ideal 1:1:1 atomic ratios and arc-melted three times in order to get homogenous samples. The total weight losses after the arc-melting procedures were always smaller than 0.5 wt%. In a second step the samples were sealed in evacuated silica tubes and annealed at 970 K for 10 days.  $\text{YAgSn}$ ,  $\text{TmAgSn}$ , and  $\text{LuAgSn}$  were obtained as light gray buttons in amounts of ca. 1 g. The samples are stable in moist air over a period of months. Single crystals of these stannides exhibit metallic lustre.

### 2.2. X-ray powder data

The samples were characterized through Guinier powder patterns with  $\alpha$ -quartz ( $a = 491.30$ ,  $c = 540.46 \text{ pm}$ ) as an internal standard and  $\text{Cu } K\alpha_1$  radiation. The Guinier camera was equipped with an imaging plate system (Fujifilm, BAS-1800). The experimental patterns were compared to calculated ones [40], taking the atomic sites derived from the single-crystal data. All samples were phase pure on the level of X-ray powder diffraction. After correct indexing, the hexagonal lattice parameters (Table 1) were refined by least-squares calculations. The lattice parameters determined on the single-crystal diffractometers were in good agreement with the powder data, however, only the powder data that have been refined with internal standard are listed.

### 2.3. Laboratory single-crystal X-ray data

Irregularly shaped crystals of  $\text{YAgSn}$ ,  $\text{TmAgSn}$ , and  $\text{LuAgSn}$  were directly selected from the crushed samples. They were glued to small quartz fibers using bees wax and then checked by Laue photographs on a Buerger camera, equipped with the same Fujifilm, BAS-1800 imaging plate technique. The good quality crystals were then used for the intensity data collections on a Nonius CAD4 four circle diffractometer, equipped with graphite monochromatized  $\text{Mo } K\alpha$  radiation and a scintillation counter with pulse-height discrimination. Scans were taken in the  $\omega/2\theta$  mode and empirical absorption corrections were applied on the basis of  $\psi$ -scan data, followed by spherical absorption corrections. All relevant crystallographic data for these data collections and evaluations are listed in Table 1.

### 2.4. Single-crystal synchrotron data

Silver and tin are difficult to distinguish by normal (non-resonant) X-ray diffraction, or by neutron diffraction (scattering lengths are  $b_{\text{Ag}} = 6.02$  and  $b_{\text{Sn}} = 6.22 \text{ fm}$ ). Resonant X-ray diffraction can provide a good contrast between similar elements by exploiting the large changes in anomalous dispersion coefficients close to elemental absorption edges. The Ag K and Sn K edges have energies of 25 514 and 29 200 eV, respectively, so an energy just

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