The Stannides EuPdSn and EuPtSn
Rainer Pöttgen
Max-Planck-Institut für Festkörperforschung,
Heisenbergstrasse 1, D-70569 Stuttgart, Germany
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Europium Intermetallic Compounds, Crystal Structure

EuPdSn and EuPtSn were prepared from the elements in tantalum tubes at 1070 K and investigated by X-ray diffraction on both powder as well as single crystals. They crystallize with the TiNiSi type structure of space group Pnma and with Z = 4 formula units per cell. Both structures were refined from single-crystal diffractometer data: a = 751.24(9), b = 469.15(6), c = 804.31(9) pm, V = 0.2835(1) nm³ for EuPdSn, and a = 753.38(7), b = 467.72(4), c = 793.08(7) pm, V = 0.2795(1) nm³ for EuPtSn. The structures consist of three-dimensional [PdSn] and [PtSn] polyatomic networks in which the europium atoms are embedded. The crystal chemistry of these stannides is briefly discussed.

Introduction

The equiatomic intermetallic phases of rare-earth elements with a transition metal and an element of the p block have intensively been investigated in the past because of their greatly varying structural and physical properties. A detailed review of this large family of compounds was given recently by Szytula and Leciejewicz [1]. Today, more than 1000 of these equiatomic phases are known [2]. They crystallize in more than 30 different structure types [3].

Although such a large number of compounds has been synthesized, only little information is available on the europium containing intermetallics. This is certainly related to the more complicated synthesis conditions. Due to the low boiling temperature of europium (about 1870 K), a simple synthesis by arc-melting techniques always results in large weight losses due to evaporation of europium metal. These experimental difficulties were overcome for the pnictides EuTX (T = Cu, Pd, Ag; X = P, As, Sb, Bi) by a direct syntheses in alumina crucibles [4,5] and for the compounds EuTX (T = Zn, Cd; X = Si, Ge, Sn, Pb) by reacting the elements in closed tantalum tubes [6]. Using the latter technique, we were successful in preparing a series of germanides EuTGe (T = Cu, Zn, Pd, Ag, Pt, Au) [7 and references cited therein] and indides EuTIn (T = Pd, Ag, Pt, Au) [8]. Especially the germanides exhibit a large variety of interesting magnetic properties [7]. We have now extended our investigations to include the corresponding systems with tin as p block component. Herein we report on the synthesis and structure refinement of EuPdSn and EuPtSn. Powder data of the palladium compound have recently been published by Adroja and Malik [9].

Experimental

Starting materials for the preparation of EuPdSn and EuPtSn were ingots of europium (Johnson Matthey), palladium powder (Degussa), platinum powder (Degussa), and tin granules (Merck), all with stated purities greater than 99.9 %. The large europium ingots were cut into small pieces in a dry box and kept under argon prior to the reactions. The elemental components were mixed in the ideal atomic ratio and sealed in tantalum tubes under an argon pressure of about 800 mbar. The argon was purified over molecular sieves, titanium sponge (900 K) and an oxisorb catalyst [10]. The tantalum tubes were subsequently sealed in quartz glass ampoules to prevent oxidation and heated for two days at 1320 K. The temperature was then lowered by 50 K/day down to 970 K. The tubes were subsequently annealed at this temperature for two more weeks and finally quenched in air. The reactions resulted in small compact buttons which could easily be removed from the tantalum tubes.

Fine-grained powders of EuPdSn and EuPtSn are dark grey, while single crystals of these stannides are silvery with metallic lustre. Both compounds are stable in air over months. No decomposition, whatsoever, was observed.
Empirical formula

EuPdSn

EuPtSn

Formula weight

377.05 g/mol

465.74 g/mol

Temperature

293(2) K

293(2) K

Wavelength

56.068 pm

56.086 pm

Crystal system

orthorhombic

orthorhombic

Space group

Pnma (No. 62)

Pnma (No. 62)

Unit cell dimensions

\(a = 751.24(9)\) pm

\(a = 753.38(7)\) pm

\(b = 469.15(6)\) pm

\(b = 467.72(4)\) pm

\(c = 804.31(9)\) pm

\(c = 793.08(7)\) pm

\(V = 0.2835(1)\) nm\(^3\)

\(V = 0.2795(1)\) nm\(^3\)

Formula units per cell

\(Z = 4\)

\(Z = 4\)

Calculated density

8.84 g/cm\(^3\)

11.07 g/cm\(^3\)

Crystal size

25 \(\times\) 50 \(\times\) 50 \(\mu\)m\(^3\)

40 \(\times\) 40 \(\times\) 75 \(\mu\)m\(^3\)

Absorption correction

from \(\psi\)-scan data

from \(\psi\)-scan data

Transmission ratio (max/min)

1 : 0.838

1 : 0.635

Absorption coefficient

19.36 mm\(^{-1}\)

43.40 mm\(^{-1}\)

F(000)

636

764

\(\theta\) Range for data collection

2\(^\circ\) to 22\(^\circ\)

2\(^\circ\) to 22\(^\circ\)

Scan type

\(\omega/\theta\)

\(\omega/\theta\)

Range in \(hkl\)

\(0 < h < 9, -6 \leq k \leq 0, -10 \leq l \leq 10\)

\(0 < h < 1, -6 \leq k \leq 5, -10 \leq l \leq 0\)

Total no. reflections

756

671

Independent reflections

391 (\(R_{int} = 0.0474\))

387 (\(R_{int} = 0.0373\))

Refinement method

Full-matrix least-squares on \(F^2\)

Full-matrix least-squares on \(F^2\)

Data/restraints/parameters

390 / 0 / 20

387 / 0 / 20

Goodness-of-fit on \(F^2\)

1.143

1.220

Final \(R\) indices \([I \geq 2\sigma(I)]\)

\(R_1 = 0.0264, wR_2 = 0.0542\)

\(R_1 = 0.0285, wR_2 = 0.0686\)

\(R_1 = 0.0421, wR_2 = 0.0617\)

\(R_1 = 0.0323, wR_2 = 0.0711\)

Extinction coefficient

0.023(1)

0.028(2)

Largest diff. peak and hole

2416 and -1768 e/nm\(^3\)

2643 and -3734 e/nm\(^3\)

Table I. Crystal data and structure refinement for EuPdSn and EuPtSn.

Lattice constants

Modified Guinier powder patterns [11] of the samples were recorded with Cu K\(_{α1}\) radiation using 5N silicon (\(a = 543.07\) pm) as an internal standard. The powder patterns could easily be indexed on the basis of primitive orthorhombic cells with the lattice constants listed in Table I. To assure correct indexing, the observed patterns were compared with calculated ones [12] taking the atomic positions from the structure refinements. The lattice constants of EuPdSn (see Table I) are in agreement with the data reported previously by Adroja and Malik [9]:

\(a = 749.8, b = 468.2, c = 803.9\) pm, and \(V = 0.2822\) nm\(^3\).

Structure refinements

Irregular shaped single crystals of EuPdSn and EuPtSn were isolated from the annealed samples by mechanical fragmentation and were examined by Buerger precession photographs in order to establish both symmetry and suitability for intensity data collection. The photographs showed orthorhombic Laue symmetry \(mmm\) and the systematic extinctions were compatible with space group Pnma (No. 62) in agreement with the previous investigations on EuPdIn and EuAuIn [8]. Crystallographic data and experimental details for the data collections are listed in Table I.

Single crystal intensity data were collected by use of a four-circle diffractometer (CAD4) with graphite monochromatized Ag K\(_{α}\) radiation and a scintillation counter with pulse height discrimination.

The atomic parameters of EuPdIn [8] were taken as starting values and both structures were successfully refined using SHELXL-93 [13] with anisotropic atomic displacement parameters for all atoms. Within the refinement procedure of EuPdSn, one reflection (535) with \(F_2^2 < -2\sigma(F_2^2)\) was treated as unobserved [13]. Final difference Fourier synthesis showed no significant residual peaks. The positional parameters and interatomic distances of both refinements are listed in Tables II and III. Listings of the observed and calculated structure factors are available.*

Discussion

EuPdSn and EuPtSn are the first two compounds of the EuTSn family whose structures have

*Details may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No’s. CSD-404401 (EuPdSn) and CSD-404400 (EuPtSn).
Table II. Atomic coordinates and anisotropic displacement parameters (\( \text{pm}^2 \)) for EuPdSn and EuPtSn. \( u_{eq} \) is defined as one third of the trace of the orthogonalized \( U_{ij} \) tensor. The anisotropic displacement factor exponent takes the form:

\[-2\pi^2[(ha^*)^2U_{11} + ... + 2hka*b^*U_{12}]].

\( U_{12} = U_{23} = 0. \)

<table>
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<tr>
<th>Atom</th>
<th>Wyckoff site</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( U_{11} )</th>
<th>( U_{22} )</th>
<th>( U_{33} )</th>
<th>( U_{12} )</th>
<th>( U_{13} )</th>
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<td>1/4</td>
<td>0.67924(9)</td>
<td>105(4)</td>
<td>92(4)</td>
<td>85(4)</td>
<td>-8(3)</td>
<td>94(3)</td>
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<td>1/4</td>
<td>0.38771(15)</td>
<td>128(7)</td>
<td>86(6)</td>
<td>89(6)</td>
<td>12(5)</td>
<td>101(3)</td>
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<td>1/4</td>
<td>0.07005(13)</td>
<td>97(6)</td>
<td>77(5)</td>
<td>70(5)</td>
<td>14(4)</td>
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<td>80(5)</td>
<td>10(4)</td>
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Table III. Interatomic distances (\( \text{pm} \)) in the structures of EuPdSn and EuPtSn. Standard deviations are all equal or less than 0.2 pm.

<table>
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<th>EuPdSn</th>
<th>EuPtSn</th>
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<td>Eu:</td>
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<td>1 Pd</td>
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<td>2 Sn</td>
<td>329.4</td>
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<td>2 Eu</td>
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<tr>
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<tr>
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<td>276.5</td>
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<td>2 Sn</td>
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<td>345.9</td>
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<tr>
<td>2 Sn</td>
<td>351.1</td>
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</table>

been investigated by single crystal techniques. The structure refinements confirmed the TiNiSi-type structure for the two stannides with a complete order between the transition metal and tin atoms, as was recently also observed for the corresponding indides EuPdIn and EuAuIn [8]. This is different for the silver containing compounds EuAgIn and EuAgSn [14]. Our first structural investigations on single crystals showed that both compounds crystallize with the body-centered orthorhomic CeCu-type structure (Imma) with a statistical distribution of the silver and indium (tin) atoms on the copper position. These investigations further indicate homogeneity ranges EuAg\(_2\)-In\(_x\) and EuAg\(_2\)-Sn\(_y\). More detailed structural and magnetic studies of these systems are in progress.

A projection of the EuPdSn structure is shown in Fig. 1. The structure is built up from Eu-Eu zig-zag chains which extend along the \( x \) axis at two different heights. The intrachain distances amount to 373.7 (EuPdSn) and 374.1 pm (EuPtSn), while the interchain distances of 392.5 (EuPdSn) and 391.3 pm (EuPtSn) are about 20 pm longer. Here it is interesting to note that the intrachain (390.2) and interchain (394.1 pm) distances in EuAuIn [8] are more or less equal, while they differ significantly in EuAuGe (373.8 and 403.7 pm) [15].

Together with the tin atoms, the europium-europium zig-zag chains form trigonal [Eu\(_4\)Sn\(_2\)] prisms which are centered by the smaller palladium and platinum atoms, as shown in Fig. 1. The [Eu\(_4\)]
square and one \([\text{Eu}_2\text{Sn}_2]\) square are capped by tin atoms, while the second \([\text{Eu}_2\text{Sn}_2]\) square is capped by a europium atom. This nine-fold coordination for transition metal atoms is frequently observed in intermetallic compounds, e. g. for all compounds with structures derived from \(\text{AlB}_2\) and \(\text{Fe}_2\text{P}\).

It is interesting to note that the crystal chemistry in the series \(\text{LnPdSn}\) and \(\text{LnPtSn}\) is different. The palladium stannides, including \(\text{EuPdSn}\), adopt the orthorhombic \(\text{TiNiSi}\) structure. The plot of the cell volumes of the \(\text{LnPdSn}\) stannides \([9]\) shows a large positive deviation for the europium compound, indicating the tendency of the europium atoms towards the divalent state, as was also shown by magnetic susceptibility measurements \([9]\). The unit cell of \(\text{EuPdSn}\) is about 7\% larger than the one of \(\text{GdPtSn}\). In the \(\text{LnPtSn}\) series \([17,18]\), \(\text{EuPtSn}\) crystallizes with the \(\text{TiNiSi}\) structure, while all other stannides adopt the ordered hexagonal \(\text{Fe}_2\text{P}\) type. Here, the volume per \(\text{LnPtSn}\) formula unit is about 8\% larger for \(\text{EuPtSn}\) (0.06988 nm\(^3\)) when compared to \(\text{GdPtSn}\) (0.06486 nm\(^3\)), also indicating the tendency of the europium atoms towards the divalent state.

Alternatively, the structures of \(\text{EuPdSn}\) and \(\text{EuPtSn}\) may be described by the concept of polyanionic networks. Since the europium atoms are by far the most electropositive component of the compounds, they will largely have transferred their valence electrons to the \([\text{PdSn}]\) and \([\text{PtSn}]\) networks. To a first approximation, the formulae of both compounds may then be written as \(\text{Eu}^{2+}[\text{PdSn}]^{2-}\) and \(\text{Eu}^{2+}[\text{PtSn}]^{2-}\). The \([\text{PdSn}]\) and \([\text{PtSn}]\) polyanionic networks as shown in Fig. 2 are three-dimensional. They form large open tubes in which the europium atoms are embedded. The palladium and platinum atoms have four tin neighbors at average \(\text{Pd-Sn}\) and \(\text{Pt-Sn}\) distances of 277.5 and 275.6 pm, respectively. Both of these distances are only slightly larger than the sum of the covalent radii \((r_{\text{Pd}} + r_{\text{Sn}} = 268.2; r_{\text{Pt}} + r_{\text{Sn}} = 269.4 \text{ pm} [19])\), indicating strong \(\text{Pd-Sn}\) and \(\text{Pt-Sn}\) interactions within the three-dimensional networks. A more detailed description/discussion of this family of compounds was given in reference 8. Studies of the physical properties by magnetic susceptibility, electrical conductivity as well as \(^{151}\text{Eu}\) and \(^{119}\text{Sn}\) Mössbauer spectroscopy of these and other \(\text{EuTSn}\) stannides are in progress.

Acknowledgments

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