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Crystal and electronic structure of LaPdSn and $RE_3Pd_4Sn_6$ (RE = La, Ce)

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ABSTRACT

The stannide LaPdSn has been synthesized by arc-melting and the structure has been refined from X-ray single crystal diffractometer data: TiNiSi type, *Pnma*, a = 763.8(1), b = 473.47(7), c = 799.4(1) pm, $wR2 = 0.0417$, 548 F^2 values, 20 variables. The electronic structures of LaPdSn, $La_3Pd_4Sn_6$ and $Ce_3Pd_4Sn_6$ (own type) were investigated through scalar relativistic all-electron calculations within the DFT framework. The three stannides show a weakly metallic behavior with itinerant states crossing the Fermi level. The chemical bonding strength is such that Pd–Sn > La(Ce)–Sn > La(Ce)–Pd with a relevant feature of significant Sn–Sn bonding in $La_3Pd_4Sn_6$, in agreement with the interatomic distances in the [PdSn], respectively $[Pd_4Sn_6]$ polyanions. Spin polarized calculations on $Ce_3Pd_4Sn_6$ show spin polarization on all three crystallographically independent cerium sites, leading to ferrimagnetism.

1. Introduction

The rare earth metal (*RE*)–palladium–tin systems have thoroughly been investigated with respect to phase formation and crystal structure determination [[1–26], and ref. therein]. The ternary systems display a variety of different compounds, *i. e.* the series of equiatomic stannides *RE*PdSn, the Heusler phases $REPd_2Sn$, stannides $REPd_{1-x}Sn_2$ with partially filled $ZrSi_2$ type, $CaBe_2Ge_2$ type compounds $REPd_2Sn_2$, rare earth rich stannides RE_2Pd_2Sn, $Ce_8Pd_{24}Sn$, $Y_{13}Pd_{40}Sn_{31}$, and $YbPdSn_2$.

Besides the crystal chemical data, the physical properties of these ternary stannides have been in the focus of solid state chemists and physicists. To give some examples, superconductivity has been observed for several of the Heusler phases $REPd_2Sn$ [4] and the *RE*PdSn stannides with the magnetic rare earth elements showing magnetic ordering at low temperatures, *e. g.* $T_N = 4.2$ K for NdPdSn [26] or $T_N = 23$ K for TbPdSn [9]. Dimorphism occurs for CePdSn and YbPdSn. The cerium compound shows pressure-driven dimorphism, NP-CePdSn with orthorhombic TiNiSi type structure and HP-CePdSn with the hexagonal ZrNiAl type [24], while α-YbPdSn transforms to β-YbPdSn [17] by annealing. Whereas cerium remains trivalent in both modifications of CePdSn one observes a valence change for YbPdSn with trivalent ytterbium in the low- and divalent ytterbium in the high-temperature modification [17,23].

In view of the many property investigations, chemical bonding within these exciting materials has only little been investigated. The electronic structure of the solid solution $CeNi_{1-x}Pd_xSn$ and the series La*T*Sn (T = Ni, Cu, Pd) has been studied by photoemission spectroscopy in comparison with LMTO calculations [15], revealing strong hybridization of the *f* orbitals with the conduction band. For Ce_2Pd_2Sn, DFT calculations revealed a significant moment on the *f* element site, in good agreement with the experimental data [27].

In the course of our systematic studies of cerium based stannides [[18,22,24,28–30], and ref. therein] and their non-magnetic isotypic counterparts with lanthanum we are investigating also the bonding peculiarities of these stannides. Herein we report on single crystal X-ray data of equiatomic LaPdSn and a detailed study of chemical bonding of LaPdSn, $La_3Pd_4Sn_6$, and $Ce_3Pd_4Sn_6$ [18] which contain similar structural motifs.

2. Experimental

2.1. Synthesis

Starting materials for the preparation of LaPdSn were ingots of lanthanum (smart elements), pieces of a palladium sheet (Heraeus), and tin granules (Merck), all with stated purities better than 99.9%. Pieces of the lanthanum ingot were first arc-melted [31] to a small button under an argon atmosphere. The argon was purified before with molecular sieves, silica gel, and titanium sponge (900 K). The

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lanthanum button was then mixed with pieces of the palladium sheet and the tin granules in the ideal 1:1:1 atomic ratio and the elements were reacted by arc-melting. The product button was remelted three times to ensure homogeneity. The total weight loss was smaller than 0.5%. This way we obtained pure polycrystalline LaPdSn. The silvery polycrystalline sample is stable in air over weeks.

2.2. *EDX data*

Semiquantitative EDX analyses of the single crystal investigated on the diffractometer were carried out with a Leica 420i scanning electron microscope using LaF_3, Pd, and Sn as external standards. The experimentally observed composition was close to the ideal one and no impurity elements have been detected.

2.3. *X-Ray diffraction*

The polycrystalline LaPdSn sample was characterized by a Guinier pattern (imaging plate detector, Fujifilm BAS-1800) with $CuK\alpha_1$ radiation and α-quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The orthorhombic lattice parameters were deduced from a least-squares fit. Correct indexing was ensured by comparison with a calculated pattern [32] using the atomic positions obtained from the structure refinement. Our data (Table 1) are in good agreement with those previously published, i. e. $a = 763.9(1)$, $b = 473.94(7)$, $c = 799.7(1)$ pm [24] and $a = 763.1$, $b = 473.2$, $c = 798.6$ pm [12].

Single crystals of LaPdSn were picked from the crushed sample. Their quality was checked by Laue photographs on a Buerger precession camera (white Mo radiation). Intensity data were collected at room temperature by use of a four-circle diffractometer (CAD4) with graphite monochromatized Mo-Kα (71.073 pm) radiation and a scintillation counter with pulse height discrimination. Scans were taken in the $\omega/2\theta$ mode in the whole Ewald sphere. A numerical absorption correction was applied to the data set. All relevant details concerning the data collection and evaluation are listed in Table 1.

2.4. *Structure refinement*

Isotypism of LaPdSn with the orthorhombic TiNiSi type was already evident from the Guinier powder data and our previous work on HP-LaPdSn [24]. In line with the X-ray powder data the systematic extinctions of the single crystal data set were in agreement with space group *Pnma*. The atomic parameters of NP-CePdSn [22] were taken as starting values and the structure was refined using SHELXL-97 [33] (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for all atoms. As a check for a deviation from the ideal composition, the occupancy parameters were refined in a separate series of least-squares cycles. All sites were fully occupied within two standard deviations. The final difference Fourier synthesis revealed no significant residual peaks (Table 1). The final atomic positions, displacement parameters and distances (the refinement was carried out with the lattice parameters determined from the powder X-ray data) are given in Tables 2 and 3. Further details on the structure refinement may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD–422484.

Table 1
Crystal data and structure refinement for LaPdSn with TiNiSi type structure; space group *Pnma*; $Z = 4$.

Lattice parameters, pm (Guinier powder data)	$a = 763.8(1)$ $b = 473.47(7)$ $c = 799.4(1)$ $V = 0.2891$ nm^3
Molar mass, g mol^{-1}	364.00
Calc. density, g cm^{-3}	8.36
Abs. coefficient, mm^{-1}	28.9
$F(000)$, e	612
Crystal size, μm^3	10 × 20 × 80
Transm. ratio (max/min)	1.26
θ range, deg	3–32
Range in *hkl*	±11, ±7, ±11
Total no. reflections	3349
Independent reflections/R_{int}	548/0.0914
Reflections with $I \geq 2\sigma(I)/R_\sigma$	369/0.0487
Data/parameters	548/20
Goodness-of-fit on F^2	1.019
$R1/wR2$ for $I \geq 2\sigma(I)$	0.0295/0.0367
$R1/wR2$ for all data	0.0603/0.0417
Extinction coefficient	0.0017(2)
Largest diff. peak /hole, e Å^{-3}	1.64/−2.03

2.5. *Electronic structure calculations*

Using the crystal structure data of LaPdSn (this work), $La_3Pd_4Sn_6$, and $Ce_3Pd_4Sn_6$ [18], we carried out scalar relativistic all-electron calculations within the well established quantum theoretical DFT [34,35] framework. The effects of exchange and correlation are treated based on the gradient approximation GGA functional [36]. Geometry relaxations had been carried out in preliminary calculations but they showed only little deviation from the experimental data and the latter have been used for the final calculations.

The computations were performed using the full potential scalar relativistic augmented spherical wave (ASW) method [37,38]. In the ASW method, the wave function is expanded in atom-centered augmented spherical waves, which are *Hankel* functions and numerical solutions of Schrödinger's equation, respectively, outside and inside the so-called augmentation spheres. In the minimal ASW basis set, we chose the outermost shells to represent the valence states and the matrix elements were constructed using partial waves up to $l_{\max} + 1 = 4$ for La and Ce, *i. e.* 4*f* (La, Ce) were considered within the basis set; $l_{max} + 1 = 3$ for Pd and Sn. Self-consistency was achieved by a highly efficient algorithm for convergence acceleration [39]. The Brillouin zone integrations were performed using the linear tetrahedron method with up to 1088 k-points within the irreducible wedge. The calculations were started for an assumed spin degenerate non-magnetic (NSP) configuration for all stannides. But due to the presence of a partly filled 4*f* subshell, a magnetic instability related with a trivalent state of Ce could result; then complementary calculations allowing for spin polarization (SP) were carried out for $Ce_3Pd_4Sn_6$. The efficiency of this method in treating magnetism and chemical bonding properties in transition metal, lanthanide and actinide compounds has been well demonstrated in recent years [40,41].

The relative magnitude of the chemical bonding is obtained based on the overlap population analysis: S_{ij}, i and j being two chemical species. The crystal orbital overlap population (COOP) criterion is used [42]. In the plots positive, negative and zero COOP magnitudes indicate bonding, antibonding and non-bonding interactions respectively.

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

Atom	Wyckoff site	x	y	z	U_{eq}
La	4*c*	0.01307(9)	1/4	0.70033(7)	91(1)
Pd	4*c*	0.30077(12)	1/4	0.41481(17)	105(2)
Sn	4*c*	0.18525(10)	1/4	0.08675(15)	89(2)