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YPdSn and YPd₂Sn: Structure, ⁸⁹Y solid state NMR and ¹¹⁹Sn Mössbauer spectroscopy

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ABSTRACT

The stannides YPdSn and YPd₂Sn were synthesized by high-frequency melting of the elements in sealed tantalum tubes. Both structures were refined on the basis of single crystal X-ray diffractometer data: TiNiSi type, *Pnma*, $a=715.4(1)$, $b=458.8(1)$, $c=789.1(1)$ pm, $wR2=0.0461$, 510 F^2 values, 20 variables for YPdSn and MnCu₂Al type, *Fm $\bar{3}m$* , $a=671.44(8)$, $wR2=0.0740$, 55 F^2 values, 5 parameters for YPd₂Sn. The yttrium atoms in the new stannide YPdSn are coordinated by two tilted Pd₃Sn₃ hexagons (ordered AlB₂ superstructure). In the Heusler phase YPd₂Sn each yttrium atom has octahedral tin coordination and additionally eight palladium neighbors. The cubic site symmetry of yttrium is reflected in the ¹¹⁹Sn Mössbauer spectrum which shows no quadrupole splitting. In contrast, YPdSn shows a single signal at $\delta=1.82(1)$ mm/s subjected to quadrupole splitting of $\Delta E_Q=0.93(1)$ mm/s. Both compounds have been characterized by high-resolution ⁸⁹Y solid state NMR spectroscopy, which indicates the presence of strong Knight shifts. The spectrum of YPd₂Sn is characterized by an unusually large linewidth, suggesting the presence of a Knight shift distribution reflecting local disordering effects. The range of ⁸⁹Y Knight shifts of several binary and ternary intermetallic yttrium compounds is briefly discussed.

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1. Introduction

Modern high-resolution solid state nuclear magnetic resonance spectroscopy is an excellent complementary tool for structure determination in many cases where X-ray diffraction is at its limits. In particular its element selectivity, inherently quantitative character, and its focus on local atomic environments make it uniquely suitable for the study of order/disorder phenomena in crystalline solid solution systems, the identification of local defects in non-stoichiometric materials, and the study of phase transitions and formation of superstructures. If crystals are not available for single-crystal diffractometry, NMR spectra give the number of crystallographically distinct sites and in favorable cases can provide sufficient constraints for developing a structure solution based entirely on spectroscopic data (NMR crystallography). Finally, even in the absence of a periodic lattice, or in the case of multiphase systems with high compositional complexity, structural models can be developed based on the quantification of local and medium-range order by complementary spectroscopic approaches. While applications abound for a wide range of solid inorganic structures (salts, oxides, semiconductors), organic and inorganic molecular crystals, polymers, inorganic–organic hybrid materials, nanocomposites, ceramics and

glasses, high-resolution NMR techniques focusing on local structural issues have been applied to a much lesser extent to intermetallic systems. This is particularly true for rare earth (RE) based intermetallic materials, where the strong Curie paramagnetism of unpaired 4f electrons renders the direct observation of the rare-earth atomic nuclei by NMR spectroscopy impossible. Exceptions are ⁴⁵Sc, ⁸⁹Y, ¹³⁹La, ¹⁷⁵Lu, and – for intermetallic compounds containing divalent rare-earth species – ¹⁷¹Yb. Of these nuclei, the high-resolution solid state NMR spectroscopy of the ⁴⁵Sc isotope has by now been broadly developed in both the fields of intermetallics [1] and oxide based materials [2]. Prominent examples in the field of intermetallics are the superstructure determinations of ScAgSn [3], ScAuSi [4], and the series of carbides Sc₃TC₄ (T=Ni, Co, Ru, Rh, Os, Ir) [5]. While continuing our systematic exploration of ⁴⁵Sc NMR interaction parameters in relation to the local environments and electronic structures of ternary Sc_xT_yX_z (T=transition metal; X=element of the 3rd, 4th, and 5th main group) intermetallic compounds [6] we are now also pursuing parallel ⁸⁹Y investigations on structurally related yttrium compounds. While high-resolution solid state ⁸⁹Y NMR spectroscopy of diamagnetic insulators has been well-developed by now [7–14], NMR applications to metallic systems have thus far been limited mostly to low-resolution work on the electronic and magnetic properties of yttrium hydrides [15–19], yttrium–iron based alloys [20–22] and borocarbides [23]. The only structurally focused high-resolution

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^{89}Y NMR applications to metallic systems appear to be a studies of $\text{Y}_5\text{Si}_2\text{B}_8$ [24] and YB_4 [25]. Based on our knowledge on stannides and intermetallic tin compounds [26] we have started our studies with the cubic Heusler compound YPd_2Sn and the new TiNiSi type stannide YPdSn . The 4.9 K superconductor YPd_2Sn has intensively been studied in the 1980s with respect to solid solutions and the pressure dependence of the transition temperature [27–32]. Although the series of equiatomic REPdSn stannides has repeatedly been studied with respect to the structural behavior and the magnetic properties [33–37], YPdSn has not been reported so far. Here we present the crystal structure refinements of YPd_2Sn and YPdSn by single crystal X-ray crystallography as well as their structural characterization via ^{89}Y solid state NMR and ^{119}Sn Mössbauer spectroscopy.

2. Experimental

2.1. Synthesis

Starting materials for the preparation of the YPdSn and YPd_2Sn samples were yttrium ingots (smart elements), palladium powder (Degussa-Hüls), and tin drops (Merck), all with stated purities better than 99.9%. The elements were weighed in the ideal 1:1:1 and 1:2:1 atomic ratios and arc-welded [38] in tantalum tubes under 800 mbar argon. Argon was purified with titanium sponge (900 K), silica gel, and molecular sieves. The tantalum tubes were then placed in the water-cooled sample chamber of an induction furnace [39] (Hüttinger Elektronik, Freiburg, Germany, Typ TIG 2.5/300). The tubes were subsequently annealed for 30 min at 1600 K and finally for 90 min at 900 K, followed by quenching. Both samples could easily be separated mechanically from the tubes. No reaction with the crucible material could be detected. The silvery polycrystalline samples are stable in air over weeks.

2.2. Scanning electron microscopy

The YPd_2Sn and YPdSn single crystals investigated on the diffractometers were studied by EDX using a Zeiss EVO MA10 scanning electron microscope with Y, Pd and Sn as standards for the semi-quantitative measurements. The experimentally observed compositions of 26 ± 2 at% Y: 50 ± 2 at% Pd: 24 ± 2 at% Sn and 35 ± 2 at% Y: 33 ± 2 at% Pd: 32 ± 2 at% Sn were close to the ideal values. The standard deviations account for the irregular surface of the crystals (conchoidal fracture). No impurity elements have been detected.

2.3. X-ray powder and single crystal data

The polycrystalline YPdSn and YPd_2Sn samples were characterized through Guinier powder patterns (imaging plate technique, Fujifilm BAS-1800) with $\text{CuK}_{\alpha 1}$ radiation and α -quartz ($a=491.30$ and $c=540.46$ pm) as an internal standard. The lattice parameters (Table 1) were deduced from the powder data by a least-squares routine. Correct indexing of the patterns was ensured by intensity calculations [40].

Irregularly-shaped single crystals of YPd_2Sn and YPdSn were selected from the crushed samples and glued to quartz fibers. They were investigated by Laue photographs on a Buerger camera (white molybdenum radiation, Fuji-film image plate technique) in order to check the quality for intensity data collection. The YPdSn data set was collected at room temperature by use of a four-circle diffractometer (CAD4) with graphite monochromatized AgK_{α} (56.083 pm) radiation and a scintillation counter with pulse height discrimination. Scans were taken in the $\omega/2\theta$ mode. An empirical absorption correction was applied on the basis of Ψ -scan data, accompanied by spherical absorption corrections. Intensity data of the YPd_2Sn crystal were

Table 1
Crystallographic data and structure refinement for YPdSn and YPd_2Sn .

Empirical formula	YPdSn	YPd_2Sn
Structure type	TiNiSi	MnCu_2Al
Space group; Z	$Pnma$; 4	$Fm\bar{3}m$; 4
M mass (g mol^{-1})	314.0	420.40
Lattice parameters (pm) (Guinier data)	$a=715.4(1)$ $b=458.8(1)$ $c=789.1(1)$	$a=671.44(8)$
Cell volume (nm^3)	0.2590	0.3027
ρ (g cm^{-3})	8.05	9.23
Crystal size (μm^3)	$20 \times 20 \times 40$	$20 \times 40 \times 80$
Radiation	Ag-K_{α} ($\lambda=56.083$ pm)	Mo-K_{α} ($\lambda=71.073$ pm)
Abs. coeff., μ (mm^{-1})	20.6	38.5
$F(0\ 0\ 0)$, (e)	540	724
θ range (deg.)	3–25	5–35
hkl range	$\pm 10, \pm 6, -2-10$	$\pm 10, \pm 10, \pm 10$
Total no. refl.	2140	1143
Independent reflections/ R_{int}	510/0.0617	55/0.0309
Reflections with $I \geq 2\sigma(I)/R_{\sigma}$	322/0.0439	55/0.0174
Data/ parameters	510/20	55/5
Goodness-of-fit	1.025	1.340
$R1/ wR2$ for $I \geq 2\sigma(I)$	0.0293/0.0406	0.0367/0.0740
$R1/ wR2$ for all data	0.0636/0.0461	0.0367/0.0740
Extinction coeff.	0.0160(7)	0.0074(15)
Largest diff. peak/hole ($\text{e } \text{\AA}^{-3}$)	2.00/−1.38	2.46/−3.45

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (pm^2) for the stannides YPdSn and YPd_2Sn . U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff site	x	y	z	U_{eq}
YPdSn					
Y	4c	−0.0075(2)	1/4	0.70615(9)	95(2)
Pd	4c	0.20371(14)	1/4	0.0837(2)	104(3)
Sn	4c	0.30468(12)	1/4	0.41212(17)	92(2)
YPd₂Sn					
Y	4b	1/2	1/2	1/2	292(11)
Pd	8c	1/4	1/4	1/4	131(8)
Sn	4a	0	0	0	150(9)

collected at room temperature by use of a Stoe IPDS-II imaging plate diffractometer in oscillation mode (graphite monochromatized MoK_{α} radiation). A numerical absorption correction was applied to the data set. All relevant crystallographic data and details of the data collections and evaluations are listed in Table 1.

The Guinier patterns of YPdSn and YPd_2Sn indicated isotypism with TiNiSi [41] and MnCu_2Al [42]. In agreement with the powder X-ray data, the diffractometer data sets were compatible with space groups $Pnma$ and $Fm\bar{3}m$. The starting atomic parameters were deduced from Direct Methods with SHELXS-97 [43,44] and both structures were refined with SHELXL-97 [45,46] (full matrix least squares on F_o^2) with anisotropic displacement parameters for all sites. The occupancy parameters have been refined in a separate series of least squares cycles. All sites were fully occupied within three standard deviations. Final difference Fourier synthesis revealed no significant residual peaks. The refined atomic parameters and interatomic distances are listed in Tables 2 and 3.

Further details on the structure refinements are available. Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No's. CSD-424012 (YPdSn) and CSD-424011 (YPd_2Sn).

2.4. ^{119}Sn Mössbauer spectroscopy

A $\text{Ca}^{119\text{m}}\text{SnO}_3$ source was available for the ^{119}Sn Mössbauer spectroscopic investigations. The samples were placed within

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