Crystal structure and physical properties of the novel stannide $Yb_3Pd_2Sn_2$

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Abstract. The crystal structure and the physical properties at low temperatures of the novel stannide $Yb_3Pd_2Sn_2$ have been studied. The compound crystallizes in a new structure type, space group *Pbcm*, with Yb occupying four different positions in the lattice. Measurements of DC susceptibility and ^{170}Yb Mössbauer suggest a close to divalent Yb-ions behaviour, ruling out a scenario of heterogeneous mixed valence for the Yb-ions .

A large number of unusual low temperature features are found in Yb and Ce intermetallic compounds due to hybridization of *f*-electrons and conduction (*f-c*) electrons. A recent investigation on the Yb-Pd-Sn system was published [1], motivated by the intriguing physical properties of some of the ternary compounds in the system. As an example, in Yb_2Pd_2Sn magnetic order appears and then vanishes by applying increasing values of pressure, suggesting the existence of two quantum critical points within the same compound [2]. Similar behaviour occurs by doping Sn sites by In [3], Yb_2Pd_2In being isotypic to Yb_2Pd_2Sn [4]. Other interesting examples in this system are $YbPd_2Sn$, which is one of the few Yb-compound where superconductivity coexists with antiferromagnetism [5], and αYbPdSn where coexistence of localized and delocalized f-electrons seems to occur [6].

In the investigation of the Yb-Pd-Sn system, a new compound with the formula $Yb_3Pd_2Sn_2$ and an orthorhombic cell was found [1]. Here we present results on the study of the structure and the low temperature physical properties of this compound. The metals used were ytterbium (pieces, 99.993 % Yb/TREM purity, Smart Elements GmbH, Vienna, Austria), palladium (foil, 99.95 mass % purity, Chimet, Arezzo, Italy) and tin (bar, 99.999 mass% purity). The sample was prepared by weighing stoichiometric amounts of the elements. The elements were enclosed in a small tantalum crucible sealed by arc welding under pure argon, and melted in an induction furnace under a stream of pure argon. The alloy was then annealed in a resistance furnace at 600 °C for three weeks and finally quenched in cold water. After quenching, the sample was characterized by scanning electron microscopy (SEM) and electron probe micro-analysis (EPMA) based on energy dispersive X-ray spectroscopy. Since all the attempts to solve the structure of the compound from single crystal data have been unsuccessful, the crystal structure has been determined *ab initio* from powder X-ray diffraction (XRD) data. The structure solution was found in the direct space by global optimization of the parameters using the program FOX [7]. The trial model was tested and refined with the Rietveld method using the program FULLPROF [8]. (for details of crystal structure determination see [9]).

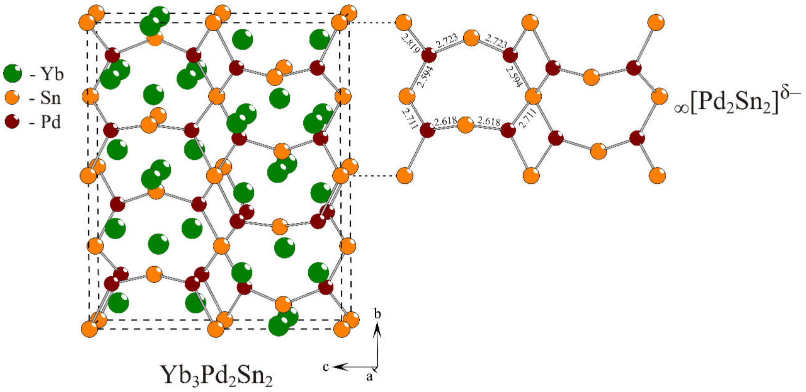


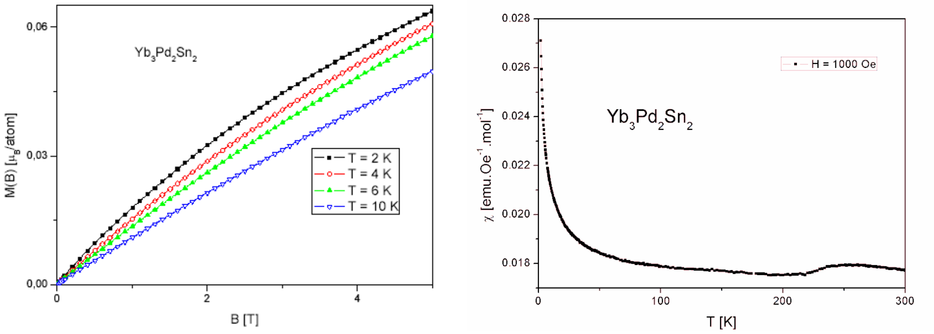
Figure 1. Crystal structure of $Yb_3Pd_2Sn_2$ with outlined polyanionic networks of $_{\infty}[Pd_2Sn_2]^{\delta-}$ composition. In the top right corner the distances of heterogeneous Pd–Sn contacts within $_{\infty}[Pd_2Sn_2]^{\delta-}$ network are indicated.

Atom	**Wyckoff position**	***x/a***	***y/b***	***z/c***	**CN**
Pd1	8*e*	0.019(2)	0.3517(5)	0.0903(10)	11
Pd2	8*e*	0.281(2)	0.1146(6)	0.0889(9)	10
Yb1	8*e*	0.196(1)	0.6778(4)	0.0981(7)	17
Yb2	8*e*	0.505(2)	0.4296(4)	0.0973(6)	17
Yb3	4*d*	0.004(3)	0.5108(6)	¼	17
Yb4	4*d*	0.295(2)	0.2437(7)	¼	17
Sn1	4*d*	0.503(3)	0.0650(8)	¼	12
Sn2	4*d*	0.209(2)	0.8275(8)	¼	12
Sn3	4*c*	0.308(2)	¼	0	16
Sn4	4*a*	0	0	0	14

Table 1. Crystallographic data of the $Yb_3Pd_2Sn_2$ structure refined in the space group *Pbcm*. R_F = 6.35%, R_B = 8.47%, R_{wp} = 15.2%

The compound crystallizes as a new structure type in the orthorhombic space group *Pbcm*. The refined lattice parameters are a = 0.58262(2) nm, b = 1.68393(8) nm and c = 1.38735(7) nm. $Yb_3Pd_2Sn_2$ is composed of a complex $_{\infty}[Pd_2Sn_2]^{\delta-}$ polyanionic network in which Yb ions are embedded (Fig.1). In the crystal structure of $Yb_3Pd_2Sn_2$ Yb ions occupy four inequivalent crystallographic sites. Furthermore, all these positions are characterized by similar coordination environments and interatomic distances within the first coordination sphere are comparables (Table 1). The DC magnetization was measured using a Quantum Design MPMS commercial device down to 2 K and up to 5 T. Measurements till 1000 K were performed in VSM in VERSALAB device. ^{170}Yb

Mössbauer spectrum was obtained with both the source and the sample located in a helium flow cryostat at the same temperature, whereas ^{119}Sn Mössbauer spectrum was taken at room temperature. Fig. 2(a) shows the magnetic field dependence of magnetization *M(B)* of $Yb_3Pd_2Sn_2$ for different temperatures. The dependencies are characteristic of paramagnetic behaviour without a tendency to saturation at lower temperatures. The DC susceptibility as a function of temperature (Fig. 2(b)) shows a Pauli paramagnetic contribution suggesting a close to divalent behaviour of Yb ions. The small increase of susceptibility shown at low temperatures is likely due to paramagnetic impurities, whereas a tiny broad bump above 200 K suggests some degree of *c-f* hybridization. Extended measurements till 1000 K confirmed this behaviour.

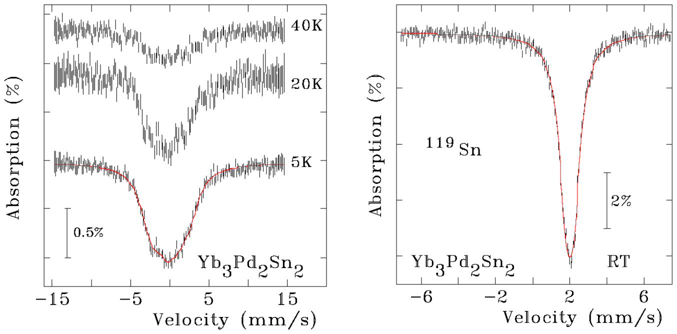


(a) (b)

Figures 2 (a) Field dependence of magnetization of $Yb_3Pd_2Sn_2$ at different temperatures

(b) DC magnetic susceptibility of $Yb_3Pd_2Sn_2$ at 1000 Oe.

The scenario of close to divalent Yb-ions is corroborated by the ^{170}Yb Mössbauer measurements (Fig. 3a). Only a broadened single feature centred on zero velocity appears, suggesting the existence of divalent ytterbium (Yb^{2+}) and ruling out the presence of trivalent ytterbium (Yb^{3+}) between 5 K and 40 K. A detailed fitting of the spectum is precluded by the multiple Yb-site occupation. However, a hightly constrained fit (shown in Fig.3(a)) yields quite reasonable values for linewidth and average magnitude for eQV_{zz}. The ^{119}Sn Mössbauer spectrum is shown in Fig.3(b). It fits well with a



(a) (b)

Figures 3 (a) ^{170}Yb Mössbauer spectrum of $Yb_3Pd_2Sn_2$ at 5, 20 and 40 K. (b) ^{119}Sn Mössbauer spectrum of $Yb_3Pd_2Sn_2$ at room temperature. The solid line is a fit described in the text.

single component, implying that the environments of the four tin sites in the structure are too similar to be resolved. The parameters are typical of tin in a metallic environment.

In summary, structure, magnetism and Mössbauer spectra (^{170}Yb and ^{119}Sn) of a novel polyanionic stannide have been studied. From the structural features, magnetic properties and ^{170}Yb Mössbauer spectra, a close to Yb^{2+} behavior arise for this compound, and a scenario of heterogeneous mixed-valence system, where Yb^{2+} and Yb^{3+} coexist, can be ruled out. Nevertheless, the high-T feature of magnetic susceptibility suggest a certain degree of hybridization of 4f- and conduction electrons. This is corroborated also by electron structure calculation and heat capacity measurements done for this compound [9].

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