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Magnetic ordering in the $RE_2Pd_{2+x}Sn_{1-x}$ ternary stannides (RE=Gd, Tb, Dy, Ho, Er)

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Abstract

Contrary to other compounds as RE_2Ni_2Sn, the ternary stannides $RE_2Pd_{2+x}Sn_{1-x}$ show a range of homogeneity on the palladium-rich side and crystallize in the structure deriving from the tetragonal U_3Si_2-type. Magnetization measurements reveal that these compounds order antiferromagnetically with Néel temperatures decreasing from 27.5 K ($Gd_2Pd_{2.02}Sn_{0.98}$) to 8 K ($Er_2Pd_{2.02}Sn_{0.98}$). Moreover some of them exhibit a complex magnetic phase diagram as, for instance, $Tb_2Pd_{2.05}Sn_{0.95}$ where two magnetic transitions occur respectively at T_N=27.5 and T_2=23.5 K. For this series, T_N varies roughly proportional to the De Gennes factor implying that a R.K.K.Y. mechanism is responsible for their magnetic properties. © 1998 Elsevier Science S.A.

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1. Introduction

The recent discovery of the ternary stannides U_2M_2Sn (M=Fe, Co, Ni, Ru, Rh, Pd, Ir, Pt) in which the magnetic state of uranium is strongly dependent on the nature of M transition element has stimulated the study of the lanthanide-based compounds [1,2]. For instance, we have shown both that the $Ce_2Pd_{2+x}Sn_{1-x}$ system exists for $0.04(3) \leq x \leq 0.21(4)$ and that $Ce_2Pd_{2.04}Sn_{0.96}$ stannide orders antiferromagnetically at T_N=4.8(2) K then ferromagnetically below T_C=3.0 K [3,4].

Similar compounds $RE_2Pd_{2+x}Sn_{1-x}$ can be obtained with RE=Nd, Gd, Tb, Dy, Ho and Er. Here, we report the structural and magnetic properties of some characteristics stannides. Many of them exhibit two magnetic transitions at low temperatures.

2. Experimental procedure

The samples were prepared by melting of the constituents under a purified argon atmosphere in an induction levitation furnace. Then the alloys buttons were annealed for 2–4 weeks at 800°C under vacuum.

Microprobe analysis was used to check both the homogeneity and the chemical composition of the annealed samples. The analysis was based on the measurements of the RE $L_{\alpha1}$, Pd $L_{\alpha1}$ and Sn $L_{\alpha1}$ X-ray emission lines, which were compared with those obtained for equiatomic compounds REPdSn (RE=Gd, Tb, Dy, Ho, Er) used as a reference. The structural properties of the stannides were characterized by X-ray powder diffraction (Guinier camera, Cu $K_{\alpha1}$ radiation).

Magnetization measurements were carried out between 1.8 and 300 K using a superconducting quantum device magnetometer. The electrical properties were investigated above 4.2 K by resistivity measurements using a four-probe d.c. technique.

3. Results and discussion

Microprobe analysis of these ternary stannides confirms that they exist and form a large range of homogeneity on the palladium-rich side. Contrary to the $Ce_2Pd_{2+x}Sn_{1-x}$ system where an excess of palladium is necessary for its stabilization [3], we note in consideration of the dubiousness of the microprobe analysis that the ideal RE_2Pd_2Sn formulae can be obtained (Table 1). We have not tried to determine the upper limit of these solid solutions in the present work.

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Table 1
Crystallographic and magnetic data concerning the $RE_2Pd_{2+x}Sn_{1-x}$ stannides

RE	Composition	Lattice parameters (nm)		Magnetic data				
	x	a	c	μ_{eff} (μ_B/RE) calc.	exp.	θ_p (K)	T_N (K)	T_2 (K)
Gd	0.02(2)	0.7672(2)	0.3768(1)	7.94	8.20(5)	8(1)	27.5(5)	
	0.09(2)	0.7642(1)	0.3781(1)		8.3(1)	5(1)	28(1)	
Tb	0.02(2)	0.7641(1)	0.3740(1)	9.70	10.2(1)	−2(1)	22	
	0.05(2)	0.7633(2)	0.3747(1)		10.13(5)	−10.5(5)	27.5(5)	23.5(5)
	0.11(2)	0.7618(1)	0.3748(1)		10.24(5)	−7(5)	23(1)	
Dy	0.02(2)	0.7617(1)	0.3703(1)	10.60	11.3(1)	0(1)	13.0(5)	11.0(5)
	0.04(2)	0.7613(1)	0.3710(1)		10.53(5)	−3(1)	13.7(5)	10.5(5)
	0.11(2)	0.7610(2)	0.3719(1)		11.11(5)	−9(1)	13.0(5)	11.5(5)
Ho	0.02(2)	0.7615(1)	0.3679(1)	10.60	10.59(5)	−7(1)	6.0(5)	
	0.04(2)	0.7608(1)	0.3689(2)		10.84(5)	−10(1)	6.5(5)	
	0.08(2)	0.7608(2)	0.3694(1)		9.9(1)	−8(1)	6.5(5)	
Er	0.02(2)	0.7600(1)	0.3682(1)	9.60	9.68(5)	−6(1)	8.0(5)	7.2(5)
	0.05(2)	0.7613(1)	0.3665(1)		9.58(5)	−5(1)	7.2(5)	5.0(5)
	0.06(2)	0.7598(2)	0.3663(1)		9.68(5)	−3(1)	7.5(5)	5.5(5)

Standard deviations of the least significant digit are given in parentheses.

The X-ray diffraction patterns of these compounds were indexed in the tetragonal $Ce_2Pd_{2+x}Sn_{1-x}$-type structure having P4/mbm as space group [3]. In this structure, deriving from the tetragonal U_3Si_2-type, Pd atoms occupy two inequivalent sites Pd1 and Pd2. The latter site, labelled 4e (0 0 $z \cong 0.31$), results from the existence of excess (x) of palladium in these stannides. In other words, the Pd2 atoms replace the Sn ones but occupy a different site: 2a (0 0 0) for Sn and 4e (0 0 $z \cong 0.31$) for Pd2. Moreover, RE atoms in $RE_2Pd_{2+x}Sn_{1-x}$ stannides form a three-dimensional network constituted by $[RE_6]$ trigonal prism surrounding Pd1 atom and $[RE_8]$ tetragonal prism where Sn and Pd2 are located. This RE-network is also described by a sequence of planes perpendicular to the c-axis. Each RE atom has seven RE nearest neighbours: five in the basal (ab)-plane and two along the c-axis.

The unit cell parameters of some $RE_2Pd_{2+x}Sn_{1-x}$ ternary stannides are given in Table 1. For the series with $x=0.02$, the parameters follow the lanthanide contraction expected for trivalent RE^{3+} ions. Also for compounds based on RE=Gd, Tb, Dy and Ho, we observe with increasing x a decrease of the a-parameter and an increase of the c-parameter. This behaviour described previously for $Ce_2Pd_{2+x}Sn_{1-x}$ and $U_2Pd_{2+x}Sn_{1-x}$ systems [3,5] can be explained considering that: (i) the replacement of Sn atom ($r_{Sn}=0.1623$ nm) by the smaller Pd2 one ($r_{Pd}=0.1376$ nm) involves a decrease in a-parameter, these atoms forming with Pd1 an atomic plane perpendicular to the c-axis; (ii) for a same RE element the interatomic distances d_{RE-Pd1} existing in the $[RE_6]$ trigonal prism are almost independent of the x-composition. As these distances depend on both the a- and c-parameters, any decrease of a by chemical substitution (Sn→Pd2) may be expected to be accompanied by an increase of the c-parameter.

The temperature dependence of the reciprocal magnetic susceptibility χ_m^{-1} is shown in Fig. 1 for two representatives stannides. These curves can be fitted by a Curie–Weiss law. The effective moment (μ_{eff}) and the paramagnetic Curie temperature (θ_p) deduced from this analysis are listed in Table 1. The μ_{eff} values are close to those calculated for a trivalent RE^{3+} free ion. All θ_p temperatures, excepted for the $Gd_2Pd_{2+x}Sn_{1-x}$ compounds, are

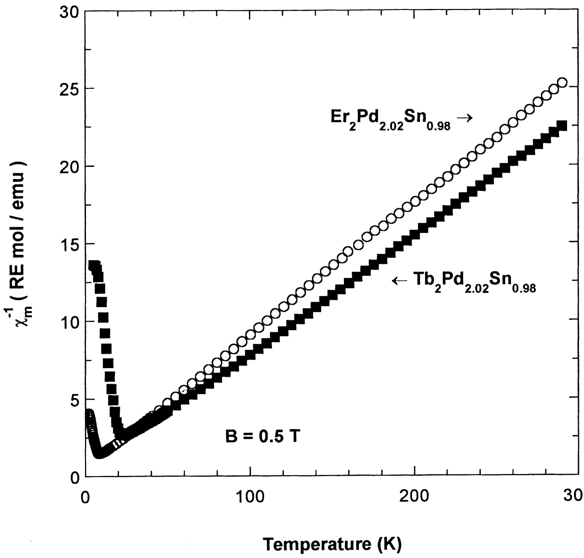

Fig. 1. Temperature dependence of the reciprocal magnetic susceptibility of $RE_2Pd_{2.02}Sn_{0.98}$ (RE=Tb, Er).

negative suggesting a predominance of antiferromagnetic interactions.

The temperature dependence of the magnetic susceptibility χ_m, measured down to 2 K in a field of 0.025 T, is presented for $RE_2Pd_{2.05}Sn_{0.95}$ (RE=Tb, Er) in Fig. 2. Two distinct features are observed: (i) a clear maximum at T_N indicating the occurrence of antiferromagnetic ordering; (ii) below T_N, χ_m decreases suddenly at (T_2) indicating a second magnetic transition. All the compounds studied in this work are antiferromagnets and many of them exhibit other transition at T_2-temperature (Table 1).

In Fig. 3, we present the thermal dependence of the reduced electrical resistivity of $Tb_2Pd_{2.05}Sn_{0.95}$. In the paramagnetic state, the resistivity increases practically linearly with temperature showing a metallic behaviour. A strong discontinuity of the slope is observed around 26–27 K corresponding to the Néel temperature T_N. No clear anomaly can be seen on the curve at T_2 where the second magnetic transition appears.

Recently, the investigation of $Tb_2Pd_{2.05}Sn_{0.95}$ by neutron powder diffraction confirms the existence of two magnetic transitions for this stannide [6]: (i) between T_N and T_2 its magnetic structure is characterized by an incommensurate wave vector $k_1=(k_x\ k_x\ \frac{1}{2})$ with for instance $k_x=0.115(5)$ at $T=26.3$ K; (ii) the low temperature structure is commensurate with $k_2=(0\ 0\ \frac{1}{2})$. In both cases, the Tb-magnetic moments are perpendicular to the c-axis and arranged along the [1 1 0] and [1 −1 0] directions.

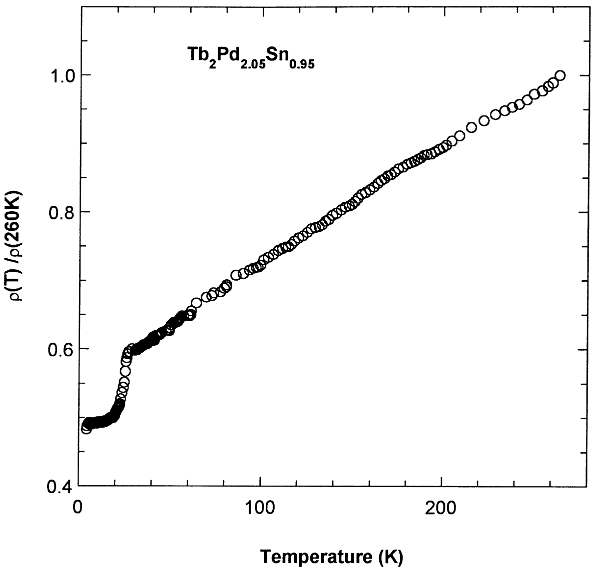

Fig. 3. Temperature dependence of the reduced electrical resistivity of $Tb_2Pd_{2.05}Sn_{0.95}$.

Isothermal magnetization curves obtained at 2 K are shown in Fig. 4 for $RE_2Pd_{2.02}Sn_{0.98}$ (RE=Tb, Er). The magnetization of $Tb_2Pd_{2.02}Sn_{0.98}$ varies in a first step linearly with magnetic field and jumps drastically at critical field of $B_1 \cong 3.2$ T. A two-step behaviour appears in the magnetization process of $Er_2Pd_{2.02}Sn_{0.98}$: the critical fields are 1.2 and 3.5 T. These metamagnetic transitions suggest a complex B–T magnetic phase diagrams for these stannides.

The magnetic properties of these intermetallic stannides result from the indirect exchange interaction between the 4f(RE) moments via conduction electrons. In this model proposed by Ruderman, Kittel, Kasuya and Yosida

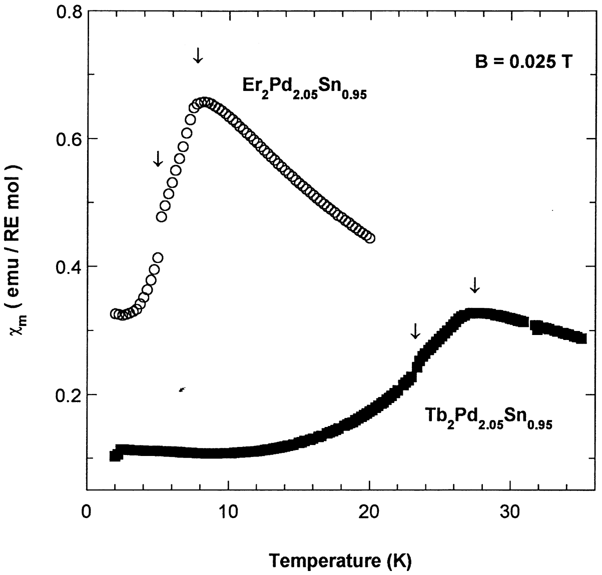

Fig. 2. Temperature dependence of the magnetic susceptibility of $RE_2Pd_{2.05}Sn_{0.95}$ (RE=Tb, Er). The arrows indicate T_N and T_2 temperatures.

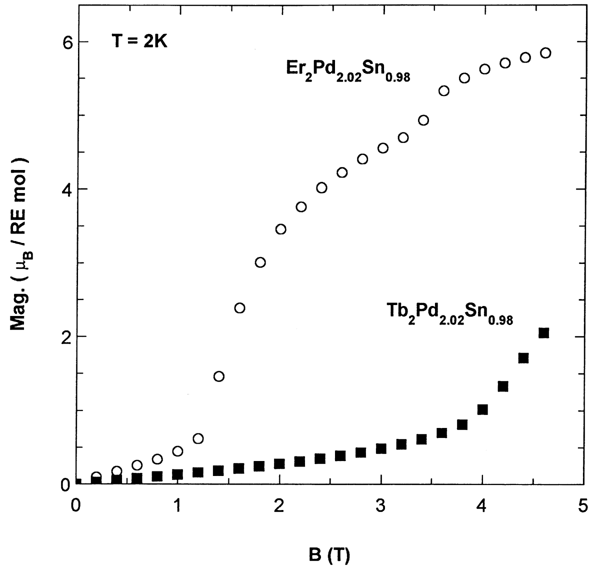

Fig. 4. Field dependence at 2 K of the magnetization of $RE_2Pd_{2.02}Sn_{0.98}$ (RE=Tb, Er).

(R.K.K.Y.) [7–9], the ordering temperature (T_N) is proportional to the de Gennes factor $G=(g_J-1)^2J(J+1)$ where g_J is the Landé factor and J the total angular momentum of the RE^{3+} ion [10]. The T_N temperature of $RE_2Pd_{2.02}Sn_{0.98}$ compounds is plotted as a function of G in Fig. 5. For this series, excepted for $Er_2Pd_{2.02}Sn_{0.98}$, the T_N value decreases with G implying that a R.K.K.Y. mechanism is responsible for their magnetic properties. Certainly the role played by the crystalline-electric-field (CEF) in these stannides is unimportant. This effect governs the magnetic properties of the other compounds REPdSn where the Néel temperature T_N of TbPdSn is seen to be greater than that of GdPdSn (Fig. 5) [11,12].

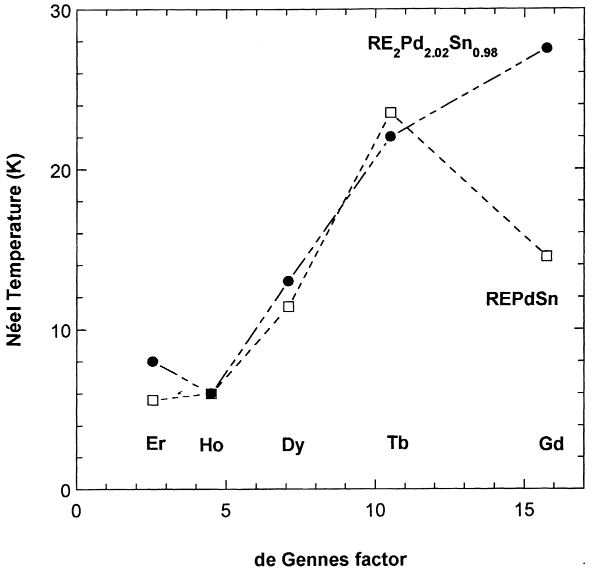

Fig. 5. T_N dependence versus de Gennes factor of $RE_2Pd_{2.02}Sn_{0.98}$ and REPdSn (taken from Ref. [11]) stannides (RE=Gd, Tb, Dy, Ho, Er).

This preliminary study concerning the $RE_2Pd_{2+x}Sn_{1-x}$ compounds indicates interesting magnetic properties. Neutron powder diffraction, already reported for $Ce_2Pd_{2.04}Sn_{0.96}$ and $Tb_2Pd_{2.05}Sn_{0.95}$ [4,6], are in progress in order to understand the nature of the two magnetic transitions appearing at T_N and T_2 temperatures.

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