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Crystal chemistry and magnetic properties of ternary stannides R_2M_2Sn (R = rare earth or uranium, M = Ni, Pd)

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Abstract

We have synthesized a great number of ternary stannides R_2Ni_2Sn, $R_2Pd_{2+x}Sn_{1-x}$ (R = rare earth) and U_2M_2Sn (M = Fe, Co, Ni, Ru, Rh, Pd, Ir, Pt). They crystallize either in the orthorhombic W_2CoB_2-type or in the tetragonal U_3Si_2-type. A structural relationship exists between these types and those of binary RNi and ternary RNiSn or RPdSn equiatomic compounds. Attention is also focused on the wide range of their magnetic properties [complex (B, T)-magnetic phase diagram, antiferromagnetic ⇒ ferromagnetic transition,...]. © 1997 Elsevier Science S.A.

Keywords: Uranium; Rare earth; Stannides; Crystal structure; Magnetic properties

1. Introduction

The ternary uranium U_2M_2Sn stannides (M = Fe, Co, Ni, Ru, Rh, Pd, Ir, Pt) have been extensively investigated during the past 3 years due to their wide range of physical properties [1,2]. The existence of this family of uranium compounds allows us to study the influence of 5*f*(U)-ligand hybridization effects on the electronic and magnetic properties. These stannides except U_2Ir_2Sn and U_2Pt_2Sn crystallize in the tetragonal ordered version of the U_3Si_2-type structure [3]. U_2Ir_2Sn and U_2Pt_2Sn adopt the tetragonal Zr_3Al_2-type which is a superstructure of the U_3Si_2-type [4].

Recently, some investigations have been carried out on some similar stannides based on cerium such as Ce_2Ni_2Sn [5,6] and $Ce_2Pd_{2+x}Sn_{1-x}$ [6–8]. Isotypic compounds can be obtained with other rare earth elements. A survey of their structural and magnetic properties is the subject of this present paper.

2. Results and discussion

All ternary stannides were prepared by melting of the constituent elements under a purified argon atmosphere. The samples were then annealed under vacuum at 800°C for 2–3 weeks. Their purity and chemical composition homogeneity were checked by microprobe analysis and X-ray powder diffraction.

2.1. Formation of the stannides

The ternary compounds R_2Ni_2Sn are obtained for R = Ce, Nd, Gd, Tb and Dy. Our attempts to synthesize Ho_2Ni_2Sn and Er_2Ni_2Sn have failed. Moreover the microprobe analysis performed on Tb_2Ni_2Sn and Dy_2Ni_2Sn samples reveals the presence of parasitic phases such as equiatomic stannide TbNiSn or DyNiSn and binary compound $TbNi_2$ or $DyNi_2$. It is certain that the stability of R_2Ni_2Sn stannides is governed by the size of the R-element.

Nowadays, the $R_2Pd_{2+x}Sn_{1-x}$ compounds can be obtained with R = Ce, Nd, Gd, Tb, Dy, Ho, Er and U

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and present a large range of homogeneity on the palladium rich side [6–10]. For instance these stannides exist with R = Ce and U, respectively, for $0.04(3) \leq x \leq 0.21(4)$ [7] and $0 \leq x \leq 0.44(2)$ [9].

2.2. Crystal structure

All the R_2Ni_2Sn compounds based on rare earths crystallize in the orthorhombic structure related to the W_2CoB_2-type. R atoms form a three-dimensional network (Fig. 1) and constitute a [R_8] prism surrounding either Sn atoms or Ni–Ni pairs. These last atoms are located inside a distorted [R_6] trigonal prism. An interesting structural comparison concerns CeNi (CrB-type), Ce_2Ni_2Sn and CeNiSn (TiNiSi-type) (Fig. 1) which contain trigonal prisms [$NiCe_6$] more or less distorted. The formation of Ce_2Ni_2Sn and CeNiSn stannides arises from the insertion of Sn atoms into the [Ce_6] prisms which are unoccupied in CeNi. According to the sequence $Ce_2Ni_2Sn \Rightarrow$ CeNiSn, Sn fills a double [Ce_6] prism so forming a [$SnCe_8$] prism then a simple [$SnCe_6$] trigonal prism.

The unit cell parameters of R_2Ni_2Sn compounds decrease with the size of the rare earth (Table 1). This variation leads to a decrease of d_{Ni-Sn} distance which varies from 0.2734(1) nm to 0.2642(1) nm following the sequence $Ce_2Ni_2Sn \Rightarrow Dy_2Ni_2Sn$. These values, much smaller than the metallic radii sum ($r_{Ni} + r_{Sn} = 0.2869$ nm), suggest a strong $3d$(Ni)–$5p$(Sn) bond in these compounds.

All the $R_2Pd_{2+x}Sn_{1-x}$ compounds crystallize in the tetragonal $Ce_2Pd_{2+x}Sn_{1-x}$-type structure (Fig. 1) where Pd excess atoms occupy one split position surrounding the replaced Sn atoms [7]. This structure is

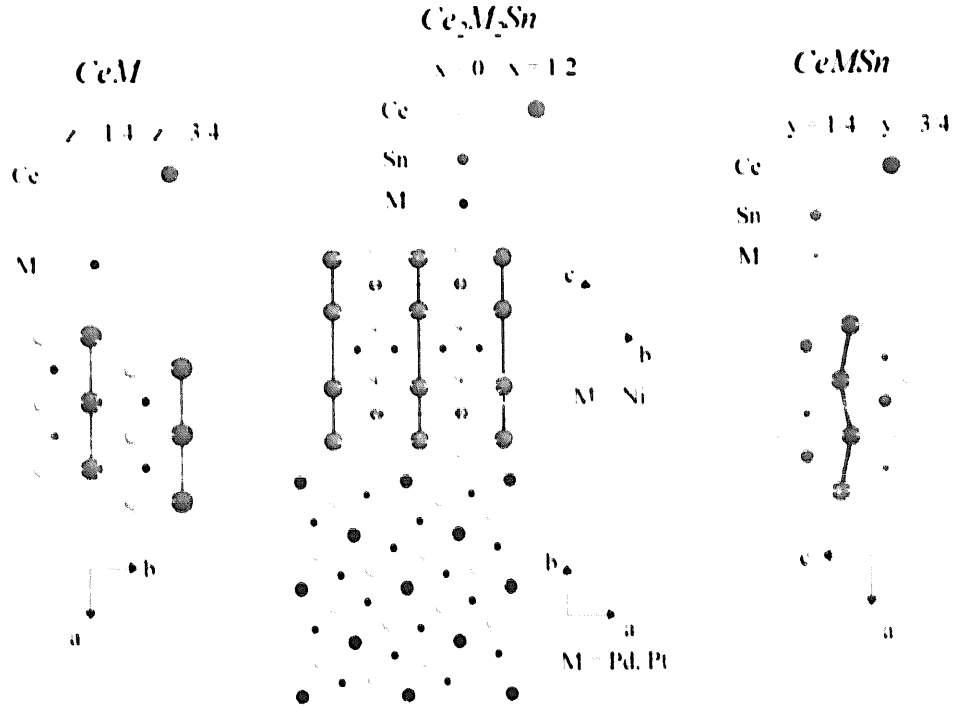

Fig. 1. Comparison of the crystal structure of CeM (M = Ni), Ce_2Ni_2Sn, Ce_2M_2Sn (M = Pd, Pt) and CeMSn (M = Ni, Pd, Pt).

Table 1
Crystallographic data relative to R_2Ni_2Sn stannides

R	Lattice parameters (nm)			Volume (nm^3)	Reference
	a	*b*	*c*		
Ce	0.4391(1)	0.5735(2)	0.8591(3)	0.2163	[6]
Ce	0.43936(9)	0.57396(9)	0.85967(13)	0.2168	[5]
Nd	0.4360(1)	0.5695(2)	0.8498(2)	0.2110	[11]
Gd	0.4294(1)	0.5638(1)	0.8390(1)	0.2031	[a]
Tb	0.4278(1)	0.5614(1)	0.8332(1)	0.2001	[a]
Dy	0.4247(1)	0.5615(1)	0.8273(1)	0.1973	[a]

[a] This work.

characterized by infinite columns of $[Ce_6]$ trigonal prisms surrounding Pd atoms and infinite columns of $[Ce_8]$ tetragonal prisms where Sn or Pd excess atoms take position.

2.3. Magnetic properties

Our recent investigations indicate that: (i) the magnetic properties of Ce_2Ni_2Sn appear to be governed by a strong competition between the Kondo and RKKY magnetic interactions; it exhibits the behaviour of a magnetically ordered Kondo system having $T_K \cong 8$ K and $T_N = 4.7$ K, respectively, as Kondo and Néel temperatures [5]; (ii) at low fields, Nd_2Ni_2Sn shows three ordering transitions, one antiferromagnetic occuring at 21 K and the others appearing, respectively, at 17.7 K and 14–15 K; the complex magnetic phase diagram of Nd_2Ni_2Sn suggests a competition between the magnetocrystalline anisotropy produced by CEF effect and the oscillatory character of the RKKY exchange interactions [11].

As claimed previously, the purity of Tb_2Ni_2Sn and Dy_2Ni_2Sn samples is not good and their investigation by magnetization measurements confirm this statement. Three maximums are clearly visible on the Mag. = f(T) curve concerning the temperature dependence of the magnetization of Tb_2Ni_2Sn (Fig. 2): (i) the first appearing at 65(1) K could be attributed to the occurrence of antiferromagnetic ordering for this stannide; (ii) on the contrary, the others peaks around 42(1) K and 7(1) K, respectively, characterize the presence of $TbNi_2$ (ferromagnet at $T_c = 45$ K) [12] and TbNiSn (antiferromagnet at $T_N = 20$ K but exhibiting a canted structure at 7 K) [13]. The susceptibility of Tb_2Ni_2Sn exhibits Curie–Weiss behaviour above 80 K: the parameters obtained by fitting are

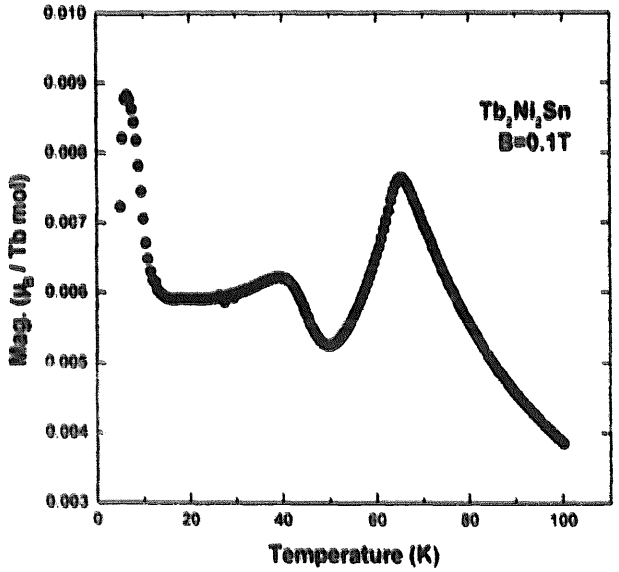

Fig. 2. Temperature dependence of the magnetization of Tb_2Ni_2Sn.

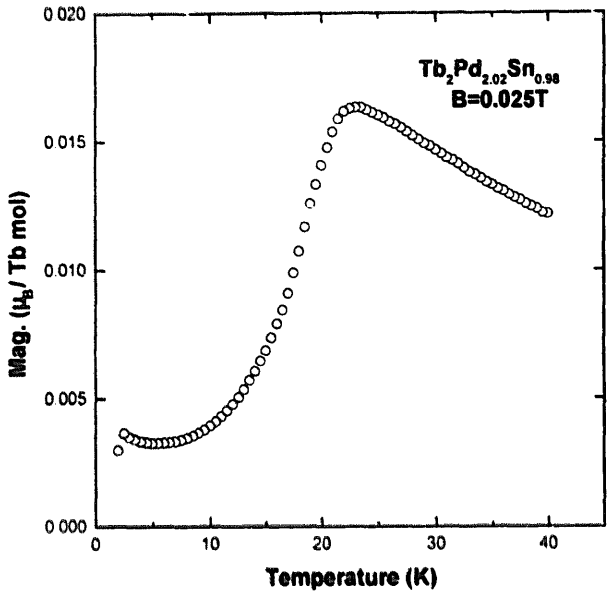

Fig. 3. Temperature dependence of the magnetization of $Tb_2Pd_{2.02}Sn_{0.98}$.

$\mu_{eff} = 10.23\ \mu_B$/Tb and $\theta_p = 39$ K. Neutron diffraction experiments are now in progress in order to establish the intrinsic magnetic properties of Tb_2Ni_2Sn.

Various magnetic properties are observed for $R_2Pd_{2+x}Sn_{1-x}$ stannides: (i) a phase transition between an incommensurate antiferromagnetic structure and a simple ferromagnetic one appears around 2.8–3.4 K for $Ce_2Pd_{2.04}Sn_{0.96}$ [14]; (ii) $Nd_2Pd_{2+x}Sn_{1-x}$ compounds order antiferromagnetically but the T_N temperature decreases with increasing x ($T_N = 8.8(3)$ K and 6.5(3) K, respectively, for $x = 0.02$ and 0.12). Moreover, these stannides exhibit several step-like field induced metamagnetic transitions [15]; (iii) neutron powder diffraction yields for $U_2Pd_{2+x}Sn_{1-x}$ non-collinear $k = (0, 0, 0)$ ($x = 0$) and collinear $k = (0, 0, 1/2)$ ($x = 0.35$) antiferromagnetic structures with magnetic moments at 1.5 K equal to 2.20(5) and 0.90(2) μ_B/U, respectively; the reduced U-magnetic moment observed for $x = 0.35$ can be correlated to an increase of the number of Pd atoms surrounding U ones and favouring the $5f$(U)–$4d$(Pd) hybridization [16].

All the $R_2Pd_{2+x}Sn_{1-x}$ stannides with R = Gd, Tb, Dy, Ho and Er order antiferromagnetically. For instance, the magnetization of $Tb_2Pd_{2.02}Sn_{0.98}$ as a function of the temperature (Fig. 3) exhibits a maximum, indicating the onset of antiferromagnetic ordering at $T_N = 22(1)$ K. Also, at 2 K the field dependence of its magnetization evidences metamagnetic-like behaviour with a critical field of approx. 3.5 T. Similar measurements performed on $R_2Pd_{2.02}Sn_{0.98}$ compounds indicate that T_N is equal to 27.5(5), 13(1), 6(1) and 8(1) K for R = Gd, Dy, Ho and Er, respectively.

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