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Crystal Structure and Magnetic Properties of new Eu–Pd–Sn Compounds

I. ČURLÍK^{a,*}, F. GASTALDO^b, M. GIOVANNINI^{b,c}, A.M. STRYDOM^d AND M. REIFFERS^{a,e}

^aFaculty of Humanities and Natural Sciences, University of Prešov, 17. novembra 1, 081 16 Prešov, Slovakia

^bDepartment of Chemistry, University of Genova, Via Dodecaneso 31, 16146 Genova, Italy

^cCNR-SPIN, Corso Ferdinando Maria Perrone 24, 16152, Genova, Italy

^dHighly Correlated Matter Research Group, Department of Physics, University of Johannesburg,
PO Box 524, Auckland Park 2006, South Africa

^eInstitute of Experimental Physics, SAS, Watsonova 47, 040 01 Košice, Slovakia

We report on the synthesis, crystal structure determination, and magnetic susceptibility measurements of $\text{Eu}_3\text{Pd}_2\text{Sn}_2$, EuPd_2Sn_4 , and EuPdSn_2 . For all three compounds a divalent state of Eu ions was obtained from the fitting of the magnetic susceptibilities. At low temperatures $\text{Eu}_3\text{Pd}_2\text{Sn}_2$, EuPd_2Sn_4 , and EuPdSn_2 order magnetically at 23, 12, and 13 K, respectively.

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1. Introduction

The lanthanide elements Eu and Yb can exist in intermetallic compounds in the trivalent or in the divalent state. In the case of Yb these two states are Yb^{3+} ($4f^{13}$)/ Yb^{2+} ($4f^{14}$), and for Eu intermetallics Eu^{3+} ($4f^6$) / Eu^{2+} ($4f^7$). Moreover, a certain number of Yb and Eu compounds show strong correlation between electrons, due to hybridization of f -electrons and conduction electrons. Owing to this fact, ternary compounds of europium and ytterbium show a great variety of anomalous physical phenomena ranging from quantum phase transitions to absence of magnetic order due to magnetic frustration [1–4].

In a previous paper the isothermal section at 600 °C of the Yb–Pd–Sn system was studied [5]. Among the various intermetallic compounds present in this system, the crystal structure of $\text{Yb}_3\text{Pd}_2\text{Sn}_2$ was determined *ab initio* and YbPdSn_2 was confirmed to crystallize in the MgCuAl_2 -type [5, 6]. In a systematic search for new ternary compounds in the analogous Eu–Pd–Sn system, we have discovered the compounds $\text{Eu}_3\text{Pd}_2\text{Sn}_2$, EuPdSn_2 , and EuPd_2Sn_4 . A comparison between crystal structures of $\text{Eu}_3\text{Pd}_2\text{Sn}_2$ and $\text{Yb}_3\text{Pd}_2\text{Sn}_2$ was made through their polyanionic networks [7].

In this paper we report on the crystal structure of EuPdSn_2 and EuPd_2Sn_4 and on magnetic data of the three compounds, including $\text{Eu}_3\text{Pd}_2\text{Sn}_2$.

2. Experimental details

Polycrystalline samples of the new compounds $\text{Eu}_3\text{Pd}_2\text{Sn}_2$, EuPdSn_2 , and EuPd_2Sn_4 have been prepared by weighing the stoichiometric amount of elements

with the following nominal purity (mass%): Eu — 99.99 (pieces), Pd — 99.95 (foil) and Sn — 99.999 (bar). Due to Eu being prone to slow oxidation in air, all the elements were weighed in a controlled atmosphere in a glovebox and afterwards enclosed and sealed in a small tantalum crucible by arc welding under pure argon. The samples were melted in an induction furnace under a stream of pure argon. To ensure homogeneity during the melting, the crucible was shaken continuously. Samples were then annealed in a resistance furnace ($\text{Eu}_3\text{Pd}_2\text{Sn}_2$ — three weeks at 600 °C, EuPdSn_2 — two weeks at 650 °C, EuPd_2Sn_4 — two weeks at 600 °C) and finally quenched in cold water. The crystal structure was examined by X-ray powder diffraction using the vertical diffractometer X'Pert MPD (Philips, Almelo, The Netherlands), with $\text{Cu } K_\alpha$ radiation and electronic microscopy and quantitative electron probe microanalysis (EPMA). The magnetic measurements were performed by a PPMS Dynacool (Quantum Design) device. The magnetic properties for all the three Eu–Pd–Sn compounds were measured in the temperature range of 2–300 K. The measurement in zero field cooling regime for EuPdSn_2 ($m = 15$ mg) and EuPd_2Sn_4 ($m = 18.3$ mg) were performed in applied magnetic field $H = 1000$ Oe, whereas for $\text{Eu}_3\text{Pd}_2\text{Sn}_2$ ($m = 4$ mg) an applied magnetic field of 200 Oe was used.

3. Results and discussion

The results of the crystal structures for the three compounds are presented in Table I. The three compounds crystallize in orthorhombic lattices. $\text{Eu}_3\text{Pd}_2\text{Sn}_2$ [7] was found to be isotypic to $\text{La}_3\text{Ni}_2\text{Ga}_2$ -type ($Pbcm$ space group), whereas XRD patterns of EuPdSn_2 and EuPd_2Sn_4 were successfully indexed in this work within MgCuAl_2 -type ($Cmcm$ space group) and NdRh_2Sn_4 -type ($Pnma$ space group), respectively. The obtained magnetic results for $\text{Eu}_3\text{Pd}_2\text{Sn}_2$, EuPdSn_2 , and EuPd_2Sn_4 are

*corresponding author; e-mail: ivan.curlik@unipo.sk

shown in Figs. 1–3, and summarized in Table II. Well above the characteristic ordering temperatures all the $\chi(T)$ dependences follow the modified Curie–Weiss (C–W) law $\chi(T) = \chi_0 + \frac{C}{T - \theta_P}$. From the fitting of $1/\chi(T)$ with the inverse modified C–W function (see the insets of the corresponding figures) we obtained the values of temperature independent susceptibility χ_0 , paramagnetic Weiss temperature θ_P and effective magnetic moment μ_{eff} shown in Table II. In all the three compounds the obtained values of μ_{eff} are ascribable to Eu^{2+} , since this

is the only magnetic element in the three studied compounds. The μ_{eff} are close to the theoretical Eu^{2+} free-ion value $7.94 \mu_B$, indicating that Eu ions are in the magnetic and stable-moment state for all the compounds. It is worth noting the very small values of χ_0 indicating very low Pauli susceptibilities for the three compounds. The observed values of paramagnetic Weiss temperatures are small and negative in case of $\text{Eu}_3\text{Pd}_2\text{Sn}_2$, whereas the θ_P is positive in EuPdSn_2 and EuPd_2Sn_4 pointing to ferromagnetic correlations in the latter two compounds.

Crystallographic data on the novel Eu compounds.

TABLE I

Compound	Pearson symbol/ prototype	Lattice parameters [nm]			Ref.
		<i>a</i>	<i>b</i>	<i>c</i>	
$\text{Eu}_3\text{Pd}_2\text{Sn}_2$	<i>oP28</i> / $\text{La}_3\text{Ni}_2\text{Ga}_2$	0.6033(5)	0.8755(4)	1.4108(7)	[7]
EuPdSn_2	<i>oS16</i> / MgCuAl_2	0.4451(4)	1.1587(2)	0.7455(2)	this work
EuPd_2Sn_4	<i>oP28</i> / NdRh_2Sn_4	1.8592(2)	0.4592(2)	0.7264(8)	work

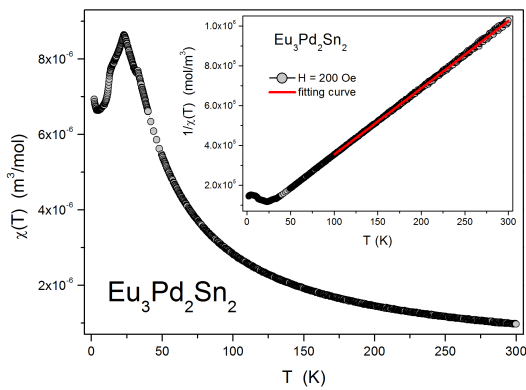


Fig. 1. Temperature dependence $\chi(T)$ for $\text{Eu}_3\text{Pd}_2\text{Sn}_2$ measured in the temperature range 2–300 K in a magnetic field of 200 Oe. In the inset the $1/\chi(T)$ dependence and fitting of the paramagnetic part as explained in the text is shown.

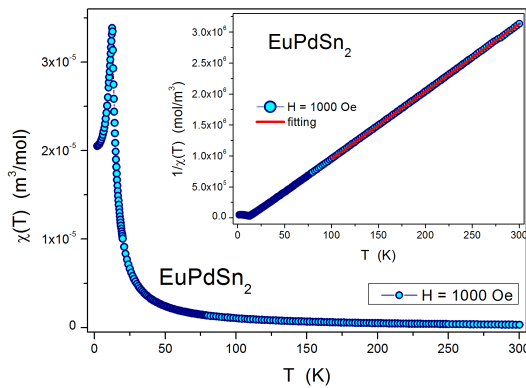


Fig. 2. Temperature dependence $\chi(T)$ for EuPdSn_2 measured in the temperature range 2–300 K in a magnetic field of 1000 Oe. In the inset the $1/\chi(T)$ dependence and a theoretical fit are shown.

At low temperatures, for all the studied compounds distinct cusps are observed in the magnetic susceptibilities $\chi(T)$ indicating that the compounds are magnetically

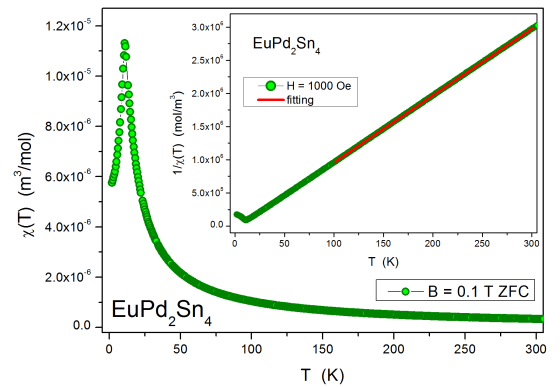


Fig. 3. Temperature dependence $\chi(T)$ for EuPd_2Sn_4 measured in the temperature range 2–300 K in magnetic field of 1000 Oe. In the inset the $1/\chi(T)$ dependence together with a fit to extract magnetic parameters is shown.

TABLE II

Magnetic characteristics of the three Eu–Pd–Sn compounds (T_M = magnetic order temperature).

Compound	χ_0 [$\frac{\text{m}^3}{\text{mol}}$]	θ_P [K]	$\mu_{\text{eff}}/\text{Eu}$ [μ_B]	T_M [K]
$\text{Eu}_3\text{Pd}_2\text{Sn}_2$	5×10^{-9}	–5	7.95	23
EuPdSn_2	4×10^{-10}	12.2	7.7	13
EuPd_2Sn_4	2.4×10^{-10}	4.5	7.95	12

ordered. A sharp cusp such as this in dc-magnetic susceptibility is indicative of long-range antiferromagnetic type ordering, although a more complex magnetic structure cannot be excluded (see e.g. [3]). In the case of EuPdSn_2 and EuPd_2Sn_4 where positive Weiss temperature values were observed we note that the orthorhombic crystal structure of both structure types may plausibly have anisotropy in the magnetic exchange of the lanthanide ions, and that antiferromagnetic order at low temperature may be the outcome of one type of exchange dominating over another. Further measurements of magnetic, specific heat and transport properties are in progress in order to ascertain the nature of the ground state.

The low-temperature magnetic behaviour of $\text{Eu}_3\text{Pd}_2\text{Sn}_2$ (see Fig. 1) is characterized by the presence of a main cusp at 23 K with two shoulders at about 13 K and 33 K which might be due to spurious phases. In fact, the effect at 13 K is probably due to the presence in the compound of a minor phase of EuPdSn (as confirmed by XRD and EPMA analysis) which orders at $T_N = 16$ K [8].

4. Conclusions

The novel Eu compounds $\text{Eu}_3\text{Pd}_2\text{Sn}_2$, EuPdSn_2 , and EuPd_2Sn_4 were synthesized and their crystal structures were derived from powder X-ray diffraction data. In the paramagnetic state the magnetic susceptibilities follow the Curie–Weiss behaviour with a divalent, magnetic state of Eu ions and very small Pauli susceptibilities. At low temperatures phase transitions to magnetically ordered states occur for all three compounds with ordering temperatures $T_M < 23$ K. Further studies involving a full suite of physical properties are in progress on these compounds and will be reported in due course.

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