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

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We report on the synthesis, crystal structure determination, and magnetic susceptibility measurements of Eu3Pd2Sn2, EuPd2Sn4, and EuPdSn2. For all three compounds a divalent state of Eu ions was obtained from the fitting of the magnetic susceptibilities. At low temperatures Eu3Pd2Sn2, EuPd2Sn4, and EuPdSn2 order magnetically at 23, 12, and 15 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 Yb3+(4f13)/Yb2+(4f14), and for Eu intermetallics Eu3+(4f6) / Eu2+(4f7). 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 Yb3Pd2Sn2 was determined ab initio and YbPdSn2 was confirmed to crystallize in the MgCuAl2-type [5, 6]. In a systematic search for new ternary compounds in the analogous Eu–Pd–Sn system, we have discovered the compounds Eu3Pd2Sn2, EuPdSn2, and EuPd2Sn4. A comparison between crystal structures of Eu3Pd2Sn2 and Yb3Pd2Sn2 was made through their polyanionic networks [7].

In this paper we report on the crystal structure of EuPdSn2 and EuPd2Sn4 and on magnetic data of the three compounds, including Eu3Pd2Sn2.

2. Experimental details

Polycrystalline samples of the new compounds Eu3Pd2Sn2, EuPdSn2, and EuPd2Sn4 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 (Eu3Pd2Sn2 — three weeks at 600°C, EuPdSn2 — two weeks at 650°C, EuPd2Sn4 — 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 XPert MPD (Philips, Almelo, The Netherlands), with Cu Kα 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 EuPd2Sn4 (m = 15 mg) and EuPd2Sn4 (m = 15 mg) were performed in applied magnetic field H = 1000 Oe, whereas for Eu3Pd2Sn2 (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. Eu3Pd2Sn2 [7] was found to be isotypic to La3Ni2Ga2-type (Pbcm space group), whereas XRD patterns of EuPd2Sn2 and EuPd2Sn4 were successfully indexed in this work within MgCuAl2-type (Cmcm space group) and NdRh2Sn4-type (Pnma space group), respectively. The obtained magnetic results for Eu3Pd2Sn2, EuPdSn2, and EuPd2Sn4 are
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 $\chi_0$, paramagnetic Weiss temperature $\Theta_P$ and effective magnetic moment $\mu_{\text{eff}}$ shown in Table II. In all the three compounds the obtained values of $\mu_{\text{eff}}$ are ascribable to Eu$^{2+}$, since this is the only magnetic element in the three studied compounds. The $\mu_{\text{eff}}$ 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 $\chi_0$ indicating very low Pauli susceptibilities for the three compounds. The observed values of paramagnetic Weiss temperatures are small and negative in case of Eu$_3$Pd$_2$Sn$_2$, whereas the $\Theta_P$ is positive in EuPdSn$_2$ and EuPd$_2$Sn$_4$ pointing to ferromagnetic correlations in the latter two compounds.

TABLE I Crystallographic data on the novel Eu compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pearson symbol/prototype</th>
<th>Lattice parameters [nm]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu$_3$Pd$_2$Sn$_2$</td>
<td>$oP28/La$_3$Ni$_2$Ga$_2$</td>
<td>a = 0.6033(5), b = 0.8755(4), c = 1.4108(7)</td>
<td>[7]</td>
</tr>
<tr>
<td>EuPdSn$_2$</td>
<td>SI$'$/MgCuAl$_2$</td>
<td>a = 0.4451(4), b = 1.1587(2), c = 0.7455(2)</td>
<td>this</td>
</tr>
<tr>
<td>EuPd$_2$Sn$_4$</td>
<td>oP$_2$8/NdRh$_2$Sn$_4$</td>
<td>a = 1.8592(2), b = 0.4592(2), c = 0.7264(8)</td>
<td>work</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\chi_0$ [m$^3$/mol]</th>
<th>$\Theta_P$ [K]</th>
<th>$\mu_{\text{eff}}$/[Eu $\mu_B$]</th>
<th>$T_M$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu$_3$Pd$_2$Sn$_2$</td>
<td>$5 \times 10^{-9}$</td>
<td>$-5$</td>
<td>-</td>
<td>23</td>
</tr>
<tr>
<td>EuPdSn$_2$</td>
<td>$4 \times 10^{-10}$</td>
<td>12.2</td>
<td>7.7</td>
<td>13</td>
</tr>
<tr>
<td>EuPd$_2$Sn$_4$</td>
<td>$2.4 \times 10^{-10}$</td>
<td>4.5</td>
<td>7.95</td>
<td>12</td>
</tr>
</tbody>
</table>

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$_2$Sn$_4$ 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 Eu₃Pd₂Sn₂ (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 Eu₃Pd₂Sn₂, EuPdSn₂, and EuPd₂Sn₄ 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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