The Magnetic Field Induced Ferromagnetism in EuPd$_2$Sn$_4$ Novel Compound

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Crystal structure, magnetic and thermal physical properties of EuPd$_2$Sn$_4$ stannide are reported on. From the magnetic susceptibility measurements, a divalent state of Eu rare earth element is determined together with an antiferromagnetic (AFM) order at 11 K. By applying magnetic field, the magnetic behavior variation reveals a complex magnetic structure. Above a critical field $B_c$, a ferromagnetic (FM)-like character starts to prevail. AFM and FM regimes are separated by a metamagnetic region. Heat capacity measurements confirm this behavior.

1. Introduction

Eu, as well as Sm, Tm, Yb, and Ce intermetallic compounds, constitutes an interesting class of materials, due to the different configurations of their $4f$ electrons, which can lead to the phenomenon of valence instability, where valence fluctuates between integer values. In these systems, a wealth of fascinating properties has emerged, such as heavy fermion behavior, magnetic frustration, and quantum criticality. Concerning Eu and Yb compounds, the phenomenon of valence instability is one of the most intensively studied and it consists of the possibility for these two ions to fluctuate between divalent (Eu$^{2+}$ and Yb$^{2+}$) and trivalent (Eu$^{3+}$ and Yb$^{3+}$) ground states.

In the past, we conducted a systematic investigation on R–Pd–X (R = Eu, Yb, Ce; X = In, Sn) ternary compounds, among which a certain number of them exhibited anomalous physical behavior. Concerning the Eu–Pd–Sn system, novel compounds have been discovered, such as Eu$_3$Pd$_2$Sn$_3$ and EuPdSn$_2$, showing a stable Eu$^{2+}$ magnetic state and complex magnetic structures. This last feature, together with magnetic anisotropy, seems to characterize many compounds belonging to Eu–T–X systems (T = transition metals; X = p-block elements). In fact, magnetic properties measured on a single crystal of EuRh$_2$Si$_2$ exhibit a marked magnetic anisotropy with the easy plane perpendicular to the $c$ axis, whereas a single-crystal study on EuRhGe$_3$ revealed significant anisotropy and incommensurate antiferromagnetic (AFM) structures with amplitude-modulated character. These elaborated magnetic scenarios require to be verified by microscopic techniques, like neutron diffraction. A careful neutron scattering study was indeed conducted on EuPdSn, confirming the complex magnetic structure occurring in these compounds. In fact, EuPdSn exhibits a noncollinear sine-wave modulated structure below $T = 15.5$ K, which evolves into a planar helimagnetic structure at lower temperatures.

These scenarios of complex and strongly anisotropic magnetism are not expected for Eu$^{2+}$ because of its spin $S = 7/2$ and orbital $L = 0$ numbers precluding the presence of crystal electric field effects.

Following the same line of study of Eu-based compounds, in this work, we report on the physical properties of EuPd$_2$Sn$_4$, a new ternary member of the Eu–Pd–Sn system.

2. Experimental Results

2.1. Crystal Structure Analysis

From scanning electron microscopy (SEM)/EPMA analyses, the sample prepared on nominal composition EuPd$_2$Sn$_4$ resulted in an almost single phase with some traces of Eu$_3$Pd$_2$Sn$_3$ (crystallizing in the Yb$_3$Rh$_4$Sn$_3$ structure type) and an unknown phase of atomic composition of 5% Eu, 40% Pd, and 55%Sn.

The XRD pattern of the EuPd$_2$Sn$_4$ phase (shown in Figure 1) was successfully indexed by analogy with the corresponding already known orthorhombic phase RAl$_2$In$_x$ (R = La, Ce, Pr, Nd) which crystallizes in NdRh$_2$Sn$_4$-structure type (oP28). Its crystal structure was established as orthorhombic...
space group Pnma (No. 62). The crystal structures of RAu$_2$In$_4$ are composed of a complex [Au$_2$In$_4$]$^{3-}$ 3D polyanion network in which R ions are embedded. This network is formed by In tetramer units, which is characteristic of the polyindide nature of the compounds.\(^{[17]}\)

The atomic positions of NdAu$_2$In$_4$ were taken as starting values and the structure was successfully refined in the XRD dataset using FULLPROF software.\(^{[19]}\) The number of used data points was 2268, whereas the number of refined parameters was 50. Final reliability factors of $R_p = 19\%$, $R_w = 19\%$, and $\chi^2 = 3.71$ were obtained in the Rietveld refinement (see Figure 1).

The atomic positions of EuPd$_2$Sn$_4$ are shown in Table 1. The structure is composed of four crystallographically distinct Sn atoms, two Pd atoms, and a unique Eu atom (Table 1). Rietveld refinement was done including around 7% mass of a second phase indexed as Eu$_3$Pd$_4$Sn$_{13}$, on the base of SEM results and using the atomic position of Yb$_3$Pd$_4$Sn$_{13}$ (see Figure 1).

### 2.2. Magnetic Properties

Figure 2 shows the temperature dependence of the inverse magnetic susceptibility $1/\chi(T)$ of EuPd$_2$Sn$_4$ in the temperature range of 2 – 400 K measured in the applied magnetic field of 1 T. The compound exhibits Curie–Weiss (CW) behavior above 11 K. To evaluate the basic magnetic characteristics, we fit $1/\chi(T)$ dependence in this temperature range following the equation

$$1/\chi(T) = \left[\chi_0 + C/(T - \Theta_p)\right]^{-1}$$

where $\chi_0$, $C$, and $\Theta_p$ represent the Pauli susceptibility, Curie constant, and paramagnetic Curie temperature, respectively. The obtained value of the effective magnetic moment $\mu_{\text{eff}} = 7.95$ $\mu_B$ is close to the theoretical Eu$^{2+}$ free ion value (7.94 $\mu_B$), indicating that Eu ions are in the magnetic state. The small but positive value of the paramagnetic Curie temperature $\Theta_p = 4.98$ K denotes some ferromagnetic (FM) exchange interactions between magnetic moments. The Pauli susceptibility $\chi_0$ obtained from the fit is negligible ($\approx$10$^{-10}$ m$^3$ mol$^{-1}$). For comparison, we fit also the $1/\chi(T)$ dependence in applied magnetic field 9 T. The resulting values ($\Theta_p = 3.34$ K, $\mu_{\text{eff}} = 7.98$ $\mu_B$) reveal

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**Table 1.** Atomic fractional coordinates of the novel compound EuPd$_2$Sn$_4$.

| atom | Wyckoff position | x/a | y/b | z/c |
|------|------------------|-----|-----|-----|
| Sn1  | c4               | 0.0316(3) | 1/4 | 0.366(1) |
| Sn2  | c4               | 0.1817(4) | 1/4 | 0.816(1) |
| Sn3  | c4               | 0.1966(5) | 1/4 | 0.235(1) |
| Sn4  | c4               | 0.4327(4) | 1/4 | 0.486(1) |
| Pd1  | c4               | 0.0346(5) | 1/4 | 0.741(1) |
| Pd2  | c4               | 0.2913(5) | 1/4 | 0.538(1) |
| Eu   | c4               | 0.3601(5) | 1/4 | 0.009(1) |
negligible changes in comparison with those obtained from measurements in 1 T.

The inset of Figure 2 shows at low temperature details of the \( \chi(T) \) dependence of EuPd\(_2\)Sn\(_4\) with a peak at \( T_N = 11 \) K, indicating a phase transition from paramagnetic to magnetically ordered state. Notably, such a sharp cusp is characteristic for AFM ordering. As one can see, there is no obvious difference between zero-field cooling (ZFC) and field cooling (FC) dependencies (in analogy with the results observed in EuPdSn\(_4\)\(^{[13]}\)), suggesting an AFM order. However, taking into account the positive \( \theta_p \) value, a more complex magnetic structure cannot be excluded. Complex magnetic structures were already described in EuPdSn, where the neutron diffraction experiment revealed incommensurate magnetic structures (sinusoidally modulated versus planar helimagnetic) in different temperature ranges well below the \( T_N \) transition.\(^{[16]}\)

To proceed with a detailed investigation of the ground-state magnetic properties of EuPd\(_2\)Sn\(_4\), a series of \( \chi(T) \) measurements were carried out, focusing on the low-temperature range 2 – 30 K in different applied magnetic fields up to 9 T. The \( \chi(T) \) dependencies were measured in the FC regime, where magnetic field was gradually increased by steps of 0.05 T for every consecutive measurement. Resultant dependencies are presented on a and b panels of Figure 3. For applied fields up to around 1 T, \( \chi(T) \) shows a cusp characteristic for AFM ordering (the blue curves in Figure 3a). With increasing \( B \) up to 2 T, the transition temperature \( T_N \) shifts to lower values and the peak broadens. For \( B > 2 \) T, the \( \chi(T) \) dependencies change their character, the AFM maximum disappears, and \( \chi(T) \) continuously increases with lowering temperature (black curves on Figure 3b). The displayed set of \( \chi(T) \) measurements shows the trend of magnetic saturation effect with increasing \( B \). It seems that FM-like correlations become prevalent in the system. This could explain also the positive \( \theta_p \) calculated from the fitting. Within the \( B \) range of \( \approx 2 – 2.3 \) T (red curves in both a, b panels of Figure 3), the absolute values of \( \chi(T) \) measurements are progressively higher, and this is typical for a progressive FM field-induced alignment from an AFM state. A similar switching of the prevailing type of magnetic interactions between AFM and FM was found in EuPdSn\(_2\) measurements\(^{[13]}\) whereas AFM EuRh\(_2\)Si\(_2\) was found to be on the verge of ferromagnetism above barely 0.1 T.\(^{[20,21]}\)

This scenario of field-induced ferromagnetism in EuPd\(_2\)Sn\(_4\) is corroborated by the \( M(B) \) magnetization dependencies at temperatures from 2 to 100 K (Figure 4). In the \( M(B) \) isotherms measured above the ordering temperature \( T_N = 11 \) K, the curves show the typical field dependence described by a Brillouin function expected for a paramagnetic compound, whereas below \( T_N \), a metamagnetic-like behavior in the \( M(B) \) takes place for the values of critical magnetic field \( B_c \) between 1 and 2 T. \( B_c \) was evaluated as the maximum of \( dM/dB \) derivative (see the inset of Figure 4), which represents the magnetic field for which the AFM regime is destroyed and the metamagnetic processes predominate. The inset of Figure 4 shows the maxima corresponding to \( B_c \) for different \( M(B) \) isotherms, where, with increasing temperature, \( B_c \) assumes smaller values (shown later in Figure 6 with orange pentagons). Far above the metamagnetic transition at \( B = 9 \) T and \( T = 2 \) K, the magnetization saturates at

\[ \text{Figure 3. A set of temperature-dependent } \chi(T) \text{ susceptibilities for EuPd}_2\text{Sn}_4 \text{ compound measured in the temperature range } 2–30 \text{ K in magnetic fields within the range a) } 0.075–2.3 \text{ T and b) } 2.05–9.0 \text{ T. According to the characteristic AFM/FM-like shape, the } \chi(T) \text{ dependencies are shown on the corresponding a/b panel of the figure.} \]

\[ \text{Figure 4. Isothermal } M(B) \text{ magnetization of EuPd}_2\text{Sn}_4 \text{ for the magnetic field } 0–9 \text{ T measured at selected temperatures within the range } 2–100 \text{ K. Inset of the figure shows the field dependencies of the } dM/dB \text{ derivative in the } 0–3 \text{ T range for selected isotherms.} \]
Low-temperature dependence of specific heat $C_p(T)$ of EuPd$_2$Sn$_4$ in different magnetic fields in the range 0–9 T. The inset shows the $C_p(T)$ measurements in zero field up to high temperatures.

6.95 $\mu_B$ Eu$^{-1}$, which is very close to the free Eu$^{2+}$ saturation moment $gJ = 7\mu_B$ Eu$^{-1}$.

### 2.3. Specific Heat

The specific heat $C_p(T)$ of EuPd$_2$Sn$_4$ in the temperature range of $2 - 230$ K for zero magnetic field is shown in the inset of Figure 5. In the low-temperature region, a $\lambda$ anomaly at $\approx 11$ K is observed, indicating the transition into AFM state. The main panel of Figure 5 shows the detail of this anomaly in accordance with different applied magnetic fields up to 9 T. For magnetic field $B < 2$ T, the $C_p(T)$ jump is reduced both in the temperature and in the height. This behavior is a typical feature of antiferromagnetically ordered systems in agreement with the $\chi(T)$ results (see Figure 3). In comparison with the magnetic measurements, the $T_N$ values extracted from $C_p(T)$ dependencies equally match with the Neél temperatures obtained from the $\chi(T)$ and tend to the same AFM trend below $B_c$. The $C_p(T)$ dependencies on Figure 5 also confirm the progressive FM-like character for $B > 2.5$ T, where the maximum shifts to higher $T$ and broadens with the strength of $B$ (characteristic for FM polarization). At lower temperatures (around 5 K), a shoulder-like anomaly is observed. Such a broad shoulder, seen at around one-fourth of $T_N$, is typical for $4f^7$ systems (Eu$^{2+}$ and Gd$^{3+}$) and is related to the large degeneracy of the $J = 7/2$ local moment within the mean-field theory for a $(2J + 1)$-fold degenerate multiplet.\[^{[13,21,22]}\]

### 2.4. Magnetic Phase Diagram

Figure 6 shows the analysis of the transition temperature as a function of applied magnetic field from the series of $\chi(T)$ curves (Figure 3), $M(B)$ magnetization (Figure 4) and the $C_p(T)$ specific heat measurements (Figure 5). For values of magnetic field ranging from zero up to $\approx 2$ T, the $T_N$ values, taken from maxima of $\chi(T)$ curves, decrease in agreement with typical AFM ordering (blue circles). The same trend of $T_N$ variation with magnetic field results from the analysis of $C_p(T)$ dependencies measured at $B \leq 1.5$ T (cyan triangles). For magnetic fields above 2.5 T, the magnetic evolution of the system can be described by tracing the temperature of the maximum $d\chi/dT$ slope: $T_{Nc}(B) = (d\chi/dT)_{max}$ (blue squares in Figure 6). This field-induced FM behavior is consistent with the isothermal $M(B)$ magnetization measurements (inset of Figure 4), where the critical magnetic field $B_c$ was evaluated for different temperatures. In Figure 6, we present this $T_N$ versus $B_c$ dependence (orange pentagons). The graphic is divided in two areas depending on the dominating type of interaction (AFM versus FM). On the magnetic field axis, the AFM/FM-like regimes are separated by the region of metamagnetic behavior left bounded by the critical magnetic field $B_c$. Such an explanation congruent with the $\chi(T)$ susceptibility (Figure 3) and $M(B)$ magnetization (Figure 4) measurements is supported also by the results for the analogous system, EuPtIn, where two metamagnetic transitions between AFM and FM spin alignment were observed.\[^{[23]}\]

### 3. Conclusion

The EuPd$_2$Sn$_4$ compound was synthesized by induction melting, and magnetic and thermal physical properties have been studied. In this stannide, Eu was found in the divalent state, which makes EuPd$_2$Sn$_4$ a magnetic compound. The series of $\chi(T)$ magnetic susceptibilities measured in low magnetic field reveal an AFM ordering at 11 K, but by increasing the strength of $B$, a more complex magnetic nature was observed. A typical AFM ground state was observed for values lower than $B < 2$ T and a further increase in the magnetic field induces FM-like behavior. These two regimes are separated by a metamagnetic region revealed by $M(B)$ measurements. The complexity and variation of magnetic mechanisms in EuPd$_2$Sn$_4$ are supported by the specific heat experiment, where $C_p(T)$ dependencies in $B > 2.5$ T are characterized by field-induced FM behavior, possibly due to a noncollinear ordering of magnetic moments in the AFM state. As a consequence, the increasing magnetic field $B$ would cause the rearrangement of...
magnetic moments toward an FM-like state. However, a change in the magnetic structure should be confirmed by neutron powder diffraction measurements.

4. Experimental Section

EuPd$_2$Sn$_4$ polycrystalline sample was prepared by weighing the stoichiometric amount of elements with the following nominal purity: Eu: 99.99 mass% (foil, Chimet, Arezzo, Italy), and Sn: 99.999 mass% (bar, Smart Elements GmbH, Vienna, Austria). Due to Eu element being prone to high oxidation reaction in air, the EuPd$_2$Sn$_4$ sample was weighed inside a glove box. To avoid the loss of europium during melting because of its high vapor pressure, all the weighed elements (total weight of 1.2 g) were enclosed in a small tantalum crucible sealed by arc welding in inert atmosphere inside the glove box.

The sample was subsequently melted in an induction furnace under a stream of pure argon. To ensure homogeneity, the crucible was continuously shaken during melting. The sample was then annealed in a resistance furnace for 2 weeks at 600 °C and finally quenched in cold water.

The sample was characterized by scanning electron microscopy (EVO 40, Carl Zeiss, Cambridge, England) equipped with a quantitative electron probe microanalysis system based on energy-dispersive X-ray spectroscopy (EPMA—EDX). For the quantitative and qualitative analysis, an acceleration voltage of 20 keV for 100 s was applied, and a cobalt standard was used for calibration. The crystal structure was determined by powder X-ray diffraction (XRD) using the vertical diffractometer X’Pert MPD (Philips, Almelo, The Netherlands) equipped with a graphite monochromator installed in the diffractometer beam (Bragg Brentano, CuK$_\alpha$ radiation). The theoretical powder pattern was calculated with the help of the Powder-Cell software,[24] and for Rietveld refinements the FULLPROF program was used.[19]

The thermodynamic and magnetic physical properties measurements were carried out using a Physical Property Measurement System Dynacool (Quantum Design) in the temperature range of 2–400 K under applied magnetic field up to 9 T. SPECIFIC heat was determined by means of the relaxation 2$\tau$ method.

Acknowledgements

This work was supported by the projects VEGA 1/0956/17, VEGA 1/0611/18, VEGA 1/0705/20, and APVV-16-0079, University Science Park TECHNICOM for Innovation Applications Supported by Knowledge Technology II Phase (ITMS: 313011D232), and Research & Development Operational Programme funded by the ERDF.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

antiferromagnetic ordering, europium, Eu–Pd–Sn compounds, ferromagnetism, metamagnetism

Received: December 30, 2020
Revised: March 15, 2021
Published online: April 15, 2021

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