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Decomposition of EuPdIn and EuPtIn at high temperature and high pressure—formation of the hexagonal Laves phases $\text{EuPd}_{0.72}\text{In}_{1.28}$ and $\text{EuPt}_{0.56}\text{In}_{1.44}$

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Dedicated to Marie-Christine

Abstract

$\text{EuPd}_{0.72}\text{In}_{1.28}$ and $\text{EuPt}_{0.56}\text{In}_{1.44}$ were prepared under multianvil high-pressure (10.5 GPa) high-temperature (1500 and 1400 K) conditions from the precursor compounds EuPdIn and EuPtIn. They were investigated by X-ray diffraction on both powders and single crystals: MgZn₂-type, space group $P6_3/mmc$, $a = 578.7(1)$ pm, $c = 944.9(3)$ pm, $wR2 = 0.0734$, 263 F^2 values for $\text{EuPd}_{0.72}\text{In}_{1.28}$ and $a = 591.1(2)$ pm, $c = 933.8(2)$ pm, $wR2 = 0.0853$, 151 F^2 values for $\text{EuPt}_{0.56}\text{In}_{1.44}$ with 13 variable parameters per refinement. Both structures are built up from face- and corner-sharing tetrahedra of palladium (platinum) and indium atoms. The europium cations are located in cavities within the three-dimensional $[\text{Pd}_{0.72}\text{In}_{1.28}]$ and $[\text{Pt}_{0.56}\text{In}_{1.44}]$ networks. The $2a$ and $6h$ positions of the tetrahedral networks show mixed Pd/In and Pt/In occupancy in $\text{EuPd}_{0.72}\text{In}_{1.28}$ and $\text{EuPt}_{0.56}\text{In}_{1.44}$, respectively. The crystal chemistry of these indides is briefly discussed.

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1. Introduction

In two recent reviews [1,2] we summarized the crystal chemistry, chemical bonding, and the various physical properties of equiatomic intermetallic EuTX and YbTX (T = transition metal; X = element of the 3rd, 4th or 5th main group) compounds. Due to the special electronic situation of europium and ytterbium, i.e., $\text{Eu}^{\text{II}}[\text{Xe}]4f^7 \rightleftharpoons \text{Eu}^{\text{III}}[\text{Xe}]4f^6$ and $\text{Yb}^{\text{II}}[\text{Xe}]4f^{14} \rightleftharpoons \text{Yb}^{\text{III}}[\text{Xe}]4f^{13}$, such intermetallics are potential candidates when screening for mixed-valent compounds. Mixed-valent europium has only been observed for the pnictides EuTP (T = Ni, Pd, Pt) and EuPdAs [1, and references therein]. With ytterbium as rare-earth metal component mixed-valent YbCuAl , YbPtAs , and YbNiSb have been reported [2, and references therein]. So far, more than 150 EuTX and

YbTX intermetallics are known; however, only seven of these show mixed-valent behavior. In most EuTX and YbTX compounds, however, europium and ytterbium are divalent.

There seem to be two factors, a chemical and a physical one, that might allow an oxidation of europium and ytterbium from +II to +III or at least to an intermediate oxidation state. Chemically we can use T and X components with high electronegativity, i.e., late transition metals and elements of the 5th main group. Physically we can apply high pressure to the compounds in order to achieve a further europium (ytterbium) oxidation. Since the chemical influence on the oxidation is limited to the combination of the T and X components, we have now started a systematic investigation of the EuTX and YbTX intermetallics under high-pressure high-temperature conditions. Herein, we report on high-pressure high-temperature reactions of EuPdIn and EuPtIn which decomposed to the hexagonal Laves phases $\text{EuPd}_{0.72}\text{In}_{1.28}$ and $\text{EuPt}_{0.56}\text{In}_{1.44}$.

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2. Experimental

2.1. Synthesis

Starting materials for the synthesis of the precursor compounds EuPdIn [3] and EuPtIn [4,5] were ingots of europium (Johnson Matthey), palladium/platinum powder (Degussa-Hüls, 200 mesh), and indium tear drops (Chempur), all with stated purities better than 99.9%. The moisture-sensitive europium ingots were cut under paraffin oil, washed with *n*-hexane and stored in Schlenk tubes under argon. The paraffin oil and *n*-hexane have been dried over sodium wire and the argon was purified before over titanium sponge (900 K), silica gel, and molecular sieves.

Europium pieces were subsequently mixed with palladium (platinum) powder and indium tear drops in the ideal 1:1:1 atomic ratio and arc-welded in small tantalum tubes (ca. 1 cm³) under an argon atmosphere of about 800 mbar. The tantalum tubes were placed in a water-cooled quartz glass sample chamber of a high-frequency generator (KONTRON Roto-Melt, 1.2 kW) under purified flowing argon. Details on the arc-melting technique and the high-frequency setup are given in Refs. [6,7]. They were first heated for 2 min at about 1500 K, annealed at about 900 K for another 4 h and finally quenched by radiative heat loss within the sample chamber. The moisture stable samples were obtained in amounts of about 1 g. For more details concerning the preparation we refer to the original work [3–5].

2.2. High-pressure high-temperature treatment

The precursor compounds EuPdIn and EuPtIn were filled into cylindrical capsules made of hexagonal boron nitride (length: 4.0 mm, outer diameter: 2.70 mm, wall thickness: 0.35 mm) which were capped by BN plates. Cylindrical graphite resistance heaters with variable wall thickness were placed around the capsules. The space at the top and bottom of the samples was filled with MgO disks. The furnaces were surrounded by cylindrical zirconia sleeves providing thermal insulation. Cr₂O₃-doped MgO octahedra (Ceramic Substrates and Components Ltd., Isle of Wight) with an edge length of 14 mm were used as pressure media. The cylindrical assemblies were positioned inside the drilled octahedrons and contacted with a molybdenum ring at the top and a molybdenum plate at the bottom. Pt/Pt₈₇Rh₁₃ thermocouples were inserted axially into the octahedral assemblies monitoring the experimental temperatures. Each octahedron was compressed by eight tungsten carbide cubes (Plansee, Reutte, TSM 10, edge length: 32 mm) with truncations of 8 mm. The cubes were separated by pyrophyllite gaskets. Compression of the cubes was accomplished via a modified Walker-style split-cylinder multianvil apparatus [8]. For further

details concerning the Walker-type module technique and multianvil experiments see Refs. [8–11].

For the decomposition of EuPdIn and EuPtIn the assemblies were compressed to a pressure of 10.5 GPa within 3 h. In the case of EuPdIn the probe was heated up to 1500 K in the following 30 min. The temperature was hold for 15 min and lowered to 1000 K in another 15 min. Afterwards the probe was quenched by turning off the power with a quench rate of > 500°C/s.

EuPtIn was heated up to 1400 K in 30 min, kept at this temperature for 15 min, followed by quenching the sample to room temperature. Both experiments were decompressed within 9 h to normal pressure. The recovered octahedrons were broken apart and the probes carefully separated from the surrounding BN.

2.3. X-ray diffraction

The samples were characterized through powder diffractograms (Stoe Stadi P) using CuK α ₁ radiation and silicon (*a* = 543.07 pm) as an external standard. The hexagonal lattice parameters (Table 1) were obtained from least-squares fits of the powder data. The correct indexing of the patterns was verified through intensity calculations [12] taking the atomic positions from the structure refinements. The lattice parameters determined from the powders and the single crystals agreed well.

Single crystal intensity data of EuPt_{0.56}In_{1.44} were collected at room temperature by use of a four-circle diffractometer (CAD4) with graphite monochromatized MoK α (71.073 pm) radiation and a scintillation counter with pulse height discrimination. The scans were taken in the $\omega/2\theta$ mode and empirical absorption corrections were applied on the basis of psi-scan data, followed by a spherical absorption correction. The data collection for EuPd_{0.72}In_{1.28} was performed on a Stoe IPDS-II image plate diffractometer at a detector distance of 40 mm, an exposure time of 40 min, and an omega range from 0° to 165° ($\Delta\omega = 1^\circ$). The integration parameters were *A* = 11.9, *B* = 2.1, and EMS = 0.01. A numerical absorption correction was applied to the data. All relevant details concerning the data collections are listed in Table 1.

2.4. Structure refinements

Small, irregularly shaped single crystals of EuPd_{0.72}In_{1.28} and EuPt_{0.56}In_{1.44} were examined by use of a Buerger camera equipped with an image plate system (Fujifilm BAS-2500) in order to establish both symmetry and suitability for intensity data collection. The isotypy of both indium compounds with the hexagonal Laves phase MgZn₂ [13,14], space group *P*6₃/*mmc* was already evident from the X-ray powder data.

Table 1

Crystal data and structure refinements for $\text{EuPd}_{0.72}\text{In}_{1.28}$ and $\text{EuPt}_{0.56}\text{In}_{1.44}$ (space group $P6_3/mmc$; $Z = 4$)

Empirical formula	$\text{EuPd}_{0.72}\text{In}_{1.28}$	$\text{EuPt}_{0.56}\text{In}_{1.44}$
Molar mass (g/mol)	375.52	461.87
Unit cell dimensions (powder data)	$a = 578.7(1)$ pm $c = 944.9(3)$ pm $V = 0.2741$ nm ³	$a = 591.1(2)$ pm $c = 933.8(2)$ pm $V = 0.2826$ nm ³
Calculated density (g/cm ³)	9.10	10.86
Crystal size (μm ³)	10 × 20 × 20	20 × 20 × 30
Transm. ratio (max/min)	0.678:0.386	0.434:0.234
Abs. coefficient (mm ⁻¹)	37.6	79.0
$F(000)$	635	760
θ range for data collection	4–35°	3–28°
Range in hkl	±9, ±9, +15	±7, ±7, +11
Total no. of reflections	3081	1296
Independent reflections	263 ($R_{\text{int}} = 0.0613$)	151 ($R_{\text{int}} = 0.1448$)
Reflections with $I > 2\sigma(I)$	214 ($R_{\sigma} = 0.0202$)	100 ($R_{\sigma} = 0.0536$)
Data/restraints/parameters	263/0/13	151/0/13
Goodness-of-fit on F^2	1.220	0.979
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0340$ $wR_2 = 0.0688$	$R1 = 0.0321$ $wR_2 = 0.0676$
R indices (all data)	$R1 = 0.0478$ $wR_2 = 0.0734$	$R1 = 0.0727$ $wR_2 = 0.0853$
Extinction coefficient	0.0010(5)	0.0015(6)
Largest diff. peak and hole	1.28 and -1.54 e/Å ³	2.28 and -2.63 e/Å ³

The starting atomic parameters were deduced from automatic interpretations of direct methods with SHELXS-97 [15] and both structures were successfully refined using SHELXL-97 [16] (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for all atoms.

As a check for the correct composition and the correct site assignment, the occupancy parameters were refined in separate series of least-squares cycles along with the displacement parameters. The europium sites of both crystals were fully occupied within two standard deviations. Refinement of the occupancy parameters of the $2a$ and $6h$ sites revealed mixed Pd/In and Pt/In occupancy. In the final cycles these sites have been refined with mixed occupancies. Both refinements were stable and lead to the compositions $\text{EuPd}_{0.72(7)}\text{In}_{1.28(7)}$ and $\text{EuPt}_{0.56(5)}\text{In}_{1.44(5)}$, for the investigated crystals assuming the absence of defects. The higher standard deviations for the occupancy parameters of the palladium compound are most likely due to the small difference of the scattering factors of palladium and indium. It is not possible to obtain a higher accuracy from the single crystal X-ray data. The final difference Fourier synthesis were flat (Table 1). The positional parameters and interatomic distances of the refinements are listed in Tables 2 and 3. Listings of the observed and calculated structure factors are available.¹

¹Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry Nos. CSD-391096 ($\text{EuPd}_{0.72}\text{In}_{1.28}$), and CSD-391097 ($\text{EuPt}_{0.56}\text{In}_{1.44}$).

Table 2

Atomic coordinates and isotropic displacement parameters (pm²) for $\text{EuPd}_{0.72}\text{In}_{1.28}$ and $\text{EuPt}_{0.56}\text{In}_{1.44}$

Atom	Wyckoff site	x	y	z	U_{eq}
<i>EuPd</i> _{0.72} <i>In</i> _{1.28}					
Eu	4 <i>f</i>	1/3	2/3	0.05814(8)	218(3)
M1	2 <i>a</i>	0	0	0	188(4)
M2	6 <i>h</i>	0.8325(1)	2 <i>x</i>	1/4	200(3)
<i>EuPt</i> _{0.56} <i>In</i> _{1.44}					
Eu	4 <i>f</i>	1/3	2/3	0.0580(2)	170(9)
M1	2 <i>a</i>	0	0	0	109(11)
M2	6 <i>h</i>	0.8319(3)	2 <i>x</i>	1/4	143(9)

Note: U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. $M1 = 0.35\text{Pd}1/0.65\text{In}1$ and $M2 = 0.37\text{Pd}2/0.63\text{In}2$ for $\text{EuPd}_{0.72}\text{In}_{1.28}$; $M1 = 0.54\text{Pt}1/0.46\text{In}1$ and $M2 = 0.20\text{Pt}2/0.80\text{In}2$ for $\text{EuPt}_{0.56}\text{In}_{1.44}$.

2.5. Scanning electron microscopy

Both crystals have been analyzed in a LEICA 420 I scanning electron microscope equipped with an OXFORD EDX analyzer. Since the crystals were mounted by beeswax on glass fibers, they have first been coated with a carbon film. InAs, EuF_3 , Pd, and Pt have been used as standards for the EDX measurements. The analyses (34 ± 3 at.% Eu: 19 ± 3 at.% Pt: 47 ± 3 at.% In and 32 ± 3 at.% Eu: 28 ± 3 at.% Pd: 40 ± 3 at.% In) were in reasonable agreement with the refined compositions of 33 ± 1 at.% Eu: 19 ± 2 at.% Pt: 48 ± 2 at.% In and 33 ± 1 at.% Eu: 24 ± 3 at.% Pd: 43 ± 3 at.% In. The

Table 3

Interatomic distances (pm), calculated with the lattice parameters taken from X-ray powder data of $\text{EuPd}_{0.72}\text{In}_{1.28}$ and $\text{EuPt}_{0.56}\text{In}_{1.44}$

			$\text{EuPd}_{0.72}\text{In}_{1.28}$	$\text{EuPt}_{0.56}\text{In}_{1.44}$
Eu:	3	<i>M2</i>	335.3(1)	333.6(2)
	3	<i>M1</i>	338.6(1)	345.5(1)
	6	<i>M2</i>	341.5(1)	345.7(1)
	3	Eu	351.7(1)	358.0(2)
	1	Eu	362.6(2)	358.7(4)
<i>M1</i> :	6	<i>M2</i>	289.8(1)	290.1(2)
	6	Eu	338.6(1)	345.5(1)
<i>M2</i> :	2	<i>M2</i>	287.9(2)	290.1(2)
	2	<i>M1</i>	289.8(1)	292.9(5)
	2	<i>M2</i>	290.8(2)	298.2(5)
	2	Eu	335.3(1)	333.6(2)
	4	Eu	341.5(1)	345.7(1)

Note: All distances within the first coordination sphere are listed. The *M* sites show a mixed Pd/In and Pt/In occupancy (see Table 2).

uncertainties of the EDX measurements result from the wax coating and the irregular shape of both crystals.

3. Results and discussion

$\text{EuPd}_{0.72}\text{In}_{1.28}$ and $\text{EuPt}_{0.56}\text{In}_{1.44}$ crystallize with the structure of the hexagonal Laves phase MgZn_2 [13,14]. A drawing of the structure is shown in Fig. 1. Although the MgZn_2 structure has two crystallographically independent zinc sites, no transition metal–indium ordering was observed. The *2a* and *6h* sites show different degrees of Pd/In and Pt/In mixing. Only the *M2* site of the platinum compound shows a site preference for indium (20% Pt + 80% In). The palladium (platinum) and indium atoms form rows of face- and corner-sharing tetrahedra along the *c*-axis (Fig. 1). These rows are interconnected via *M*–*M* contacts leading to a three-dimensional network of condensed tetrahedra.

The *M*–*M* distances within the tetrahedral network range from 288 to 291 pm in $\text{EuPd}_{0.72}\text{In}_{1.28}$ and from 290 to 298 pm in $\text{EuPt}_{0.56}\text{In}_{1.44}$. These distances are longer than those within the ordered three-dimensional [PdIn] and [PtIn] networks of EuPdIn [3] (282–283 pm) and EuPtIn [4] (280–282 pm). Nevertheless, we have to keep in mind that due to the mixed Pd/In and Pt/In occupancies the distances increase in $\text{EuPd}_{0.72}\text{In}_{1.28}$ and $\text{EuPt}_{0.56}\text{In}_{1.44}$ due to the larger indium atoms.

The europium atoms have coordination number 16 with 12 *M* and four Eu neighbors. Due to the Pd/In and Pt/In mixing, it is difficult to compare the Eu–*M* distances in $\text{EuPd}_{0.72}\text{In}_{1.28}$ and $\text{EuPt}_{0.56}\text{In}_{1.44}$ with those in EuPdIn and EuPtIn with TiNiSi -type structure. The

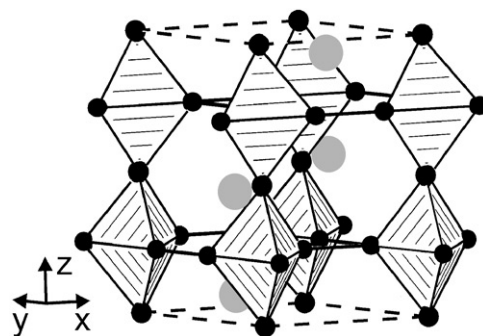


Fig. 1. Crystal structure of $\text{EuPt}_{0.56}\text{In}_{1.44}$. The europium and platinum/indium atoms are drawn as gray and filled circles, respectively. The tetrahedral $[\text{Pt}_{0.56}\text{In}_{1.44}]$ network is emphasized.

Eu–*M* distances in $\text{EuPd}_{0.72}\text{In}_{1.28}$ range from 335 to 342 pm. They are within the Eu–Pd (314–323 pm) and Eu–In distances (339–358 pm) of EuPdIn . A much more striking difference occurs for the Eu–Eu distances: 379–394 pm in EuPdIn [3] vs 352–363 pm in $\text{EuPd}_{0.72}\text{In}_{1.28}$ and 376–393 pm in EuPtIn [4] vs 358–359 pm in $\text{EuPt}_{0.56}\text{In}_{1.44}$. Magnetic susceptibility and ^{151}Eu Mössbauer spectroscopic studies [1,5] clearly revealed the divalent character of europium in EuPdIn and EuPtIn . One might speculate that the shorter Eu–Eu distances in the Laves phases might arise from an at least partial oxidation of europium. However, in view of the missing physical property measurements (two-phase samples) this remains an open question.

The decomposition of the precursor compounds EuPdIn and EuPtIn under high-pressure conditions leads to the major reaction products $\text{EuPd}_{0.72}\text{In}_{1.28}$ and $\text{EuPt}_{0.56}\text{In}_{1.44}$. Consequently, the further reaction products need to have a higher transition metal content. So far it was not possible to identify these phases. The reactions of EuRhIn [17] and EuAuIn [3] under the same high-pressure high-temperature conditions again gave different products. These investigations are still in progress.

Finally, it is interesting to compare the decomposition reactions observed for EuPdIn and EuPtIn with that observed for EuPdSi with cubic LaIrSi -type structure [18]. At 4 GPa and 1123 K EuPdSi decomposes into a silicon-rich phase $\text{EuPd}_{0.56(2)}\text{Si}_{1.44(2)}$ with AlB_2 structure and a palladium-rich phase $\text{EuPd}_{1.33(1)}\text{Si}_{0.67(1)}$ with MgZn_2 structure [18]. This parallels the present investigations. Based on size arguments, the silicon atoms are the smallest in the silicide and the palladium atoms are the smallest in the indide. Consequently, the Laves phase is formed for the silicon-poor compound $\text{EuPd}_{1.33(1)}\text{Si}_{0.67(1)}$ and for the palladium-poor compound $\text{EuPd}_{0.72}\text{In}_{1.28}$. The second phases observed for the indides are not of the AlB_2 -type like in the silicide system. Furthermore, we should note that under normal pressure conditions, the solid solutions $\text{EuT}_{1-x}\text{In}_{1+x}$

and $\text{EuT}_{1+x}\text{In}_{1-x}$ crystallize with ZrNiAl- or KHg₂-type structure [19].

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