Crystal structure and physical properties of the new intermetallics REPt$_4$In$_4$ (RE = Gd − Lu, Y)

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ABSTRACT

A new compound ErPt$_4$In$_4$ was synthesized by arc melting and its crystal structure was determined from the single crystal X-ray diffraction data: space group $P6_3/mmc$, $a = 4.5321(9)$ Å, $c = 19.807(13)$ Å, Pearson symbol hP18. The new structure type is composed of condensed via side edges Er-centered polyhedra [Pt$_8$In$_6$] and the corrugated slabs of In atoms alternating in the c-direction. A few isostructural compounds were found to form with Gd–Lu, and Y. The low-temperature physical properties of TbPt$_4$In$_4$, DyPt$_4$In$_4$ and YbPt$_4$In$_4$ were characterized by means of magnetic susceptibility and electrical resistivity measurements. All three compounds exhibit Curie−Weiss paramagnetism, due to the presence of well localized magnetic moments carried on trivalent rare-earth atoms, and metallic character of their electrical conductivity. The compounds TbPt$_4$In$_4$ and DyPt$_4$In$_4$ order magnetically below 8 and 5 K, respectively, whereas YbPt$_4$In$_4$ remains paramagnetic down to 1.7 K.

1. Introduction

In contrast to the well studied crystal chemistry of light rare-earths (RE) platinum indides, characterized by multitude of crystal structure types, the related field of late RE based compounds seems much less recognized. Fragmentary investigations into the ternary phase diagrams RE−Pt−In have yielded the following phases and structure types: RE$_6$Pt$_{12}$In$_{23}$ (RE = Nd, Sm, Gd) [1,2], REPtIn (RE = Eu−Tm, Lu) [3−5], R$_{12}$Pt$_7$In (R = Ce, Pr, Nd, Gd, Ho) [6], YbPtIn$_4$ [7], Dy$_2$Pt$_7$In$_{16}$ [2], Gd(Tb)$_3$Pt$_4$In$_{12}$ [8], GdPt$_2$In [9], RE$_5$Pt$_2$In$_4$ (RE = Sc, Y, La−Nd, Sm, Gd−Tm, Lu) [10]. Herein, we report on the new series of the late rare-earth indides REPt$_4$In$_4$ (RE = Gd − Lu, Y), which crystallize with a new structure type. A few representatives of this novel family of compounds have been characterized regarding their magnetic and electrical transport properties.

2. Experimental

The metals used for the sample preparation were rare-earths (Gd−Lu) and yttrium, platinum and indium ingots of the purity 99.8 and 99.8, 99.99 and 99.999 wt%, respectively. The elemental components were taken in the 1:4:4 and 1:4:5 atomic ratios and arc

melted several times under purified argon atmosphere. To compensate for the weight losses due to possible volatilization of rare-earth metals the masses were adjusted beforehand for the appropriate extra amounts of rare-earths. The total weight losses after final melting were always smaller than 1 wt%. The products were annealed in evacuated quartz ampoules at 1073 K for one month, and subsequently quenched in cold water. All the materials were stable against air and moisture.

The polycrystalline sample compositions were investigated by means of energy dispersive X-ray (EDX) spectroscopy using a scanning electron microscope Carl Zeiss LEO EVO 50XVP equipped with an EDX-spectrometer INCA Energy 450 (Oxford Instruments). For the REPt$_4$In$_4$ samples the EDX data revealed the composition RE11(±2)Pt44(±2)In45(±2), while for the REPt$_4$In$_5$ it was RE10(±2)Pt41(±2)In49(±2).

The X-ray examination of the obtained samples was carried out by both powder and single crystal methods. The powder data were collected with a Stoe Stadi-P transmission diffractometer (Cu Kα_1-radiation), equipped with curved Ge(111) primary beam monochromator and a linear PSD. Single crystals suitable for the data collection were obtained from the crashed samples of DyPt$_4$In$_4$, ErPt$_4$In$_4$ and HoPt$_4$In$_4$. The X-ray intensity data were collected on a CAD4 Enraf Nonius diffractometer (Ag Kα radiation, ω/θ-scan). An empirical absorption correction was done on the basis of Ψ-scan data [11].

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Table 1
Crystallographic data for REPt$_4$In$_4$ (RE = Dy, Ho, Er) (single crystal data).

Empirical formula	DyPt$_4$In$_4$	HoPt$_4$In$_4$	ErPt$_4$In$_4$
Space group	$P6_3/mmc$	$P6_3/mmc$	$P6_3/mmc$
a (Å)	4.5364(18)	4.5350(12)	4.5321(9)
c (Å)	19.792(11)	19.800(4)	19.807(13)
V (Å^3)	352.7(3)	352.66(15)	352.3(3)
Z	2	2	2
D (calc) (g/cm^3)	13.202	13.227	13.261
Abs coeff μ (mm^{-1})	55.187	55.510	55.959
Extinction coef	–	0.0053(3)	0.0089(3)
Range θ	1.62°–19.99°	1.62°–24.96°	1.62°–29.93°
Range $h\,k\,l$	$-4 \leq h \leq 5$	$-6 \leq h \leq 6$	$0 \leq h \leq 8$
	$-5 \leq k \leq 0$	$-6 \leq k \leq 6$	$-8 \leq k \leq 6$
	$0 \leq l \leq 24$	$-29 \leq l \leq 29$	$0 \leq l \leq 35$
Reflns collected/ unique/R_{int}	725/168/0.0656	2210/289/0.0503	2084/452/0.0613
Parameters/reflections with $I > 2\sigma(I)$	15/131	19/232	18/308
GooF on F^2	1.270	1.355	1.067
$R[F^2 > 2\sigma(F^2)]$	0.0490	0.0224	0.0219
$wR(F^2)$	0.1240	0.0425	0.0492

Some attempts to synthesize isotypic REPt$_4$In$_4$ compounds with light rare-earths (La–Sm) appeared unsuccessful.

The magnetic properties of TbPt$_4$In$_4$, DyPt$_4$In$_4$ and YbPt$_4$In$_4$ were studied on polycrystalline specimens in the temperature range 1.7–400 K and in external magnetic field up to 5 T using a Quantum Design MPMS-5 SQUID magnetometer. The electrical resistivity was measured on parallelepiped-shaped samples over the temperature interval 5–300 K employing a home-made setup and DC four-point technique. Current and voltage leads were attached to the specimens using silver epoxy paste.

3. Structure refinement

Details on the data collection and structure refinement made for the single crystal of ErPt$_4$In$_4$ are presented in Table 1. The obtained crystallographic data are gathered in Table 2 (the positional and thermal displacement parameters) and Table 3 (the interatomic distances). The starting atomic parameters in the structure determination were deduced by direct methods using SHELXS-97 [12] and were refined using SHELXL-97 [12] (full-matrix least-squares on F^2) with anisotropic displacement parameters for all atoms. As a check for correct composition and site assignment, the occupancy parameters were refined in a separate series of least squares cycles along with the displacement parameters. All sites were fully occupied within two standard deviations and in the final cycles the ideal occupancies were assumed. The final difference Fourier syntheses revealed a residual peak of 8.8 e/Å^3, located at (0, 0, 0). A refinement with indium on this position (In3) resulted in an occupancy of 2.6(7) at.% and led to the composition ErPt$_4$In$_{4.013}$. In spite of rather short In3–In1 distances of 2.7418(6) Å, we consider the refinement with the In atom on the 2a (In3) position as the most reliable one. This is because: (i) the coordination environment of the 2a position (CN = 14) would be unusual for Pt atom, and (ii) the presence of extra Er atom is not possible in view of the chemical composition revealed by the EDX analysis. On the other hand, the existence of a compound with the hypothetical composition ErPt$_4$In$_5$ was suggested by the EDX data, and such a phase could be formed if the 2a site is fully filled up by indium.

The positional parameters derived for ErPt$_4$In$_4$ were used in the refinements of the single-crystal X-ray diffraction data collected for DyPt$_4$In$_4$ and HoPt$_4$In$_4$ (see Table 1 and Table 2). The results indicated some In occupancy at the 2a site in the latter crystal, while in the former one this position was empty within the experimental accuracy. Because in each case the amount of the extra indium content was found very small (if finite), in the following, the ideal compositions REPt$_4$In$_4$ were assumed to label the investigated samples. Precise determination of the actual homogeneity range in the particular REPt$_4$In$_{4+x}$ compounds might become a subject of separate investigation.

For the other REPt$_4$In$_4$ compounds synthesized in this work (RE = Gd, Tb, Tm, Yb, Lu and Y), the lattice parameters were refined from the powder X-ray diffraction data (see Table 4). For the sake of completeness, the table comprises also the results obtained for powder samples of DyPt$_4$In$_4$, HoPt$_4$In$_4$ and ErPt$_4$In$_4$. Apparently, the unit cell volume systematically decreases on passing from the Gd-based to the Lu-based indide. No deviation from the lanthanide contraction is observed for YbPt$_4$In$_4$, hence suggesting that the Yb ions in this compound are trivalent. The volume of YPt$_4$In$_4$ fits between those of TbPt$_4$In$_4$ and DyPt$_4$In$_4$.

Table 2
Atomic coordinates and isotropic-equivalent displacement parameters (Å^2) for REPt$_4$In$_4$ (RE = Dy, Ho, Er).

Atom	Wyckoff position	x	y	z	Ueq	Occupancy
DyPt$_4$In$_4$						
Dy	2c	1/3	2/3	1/4	0.0025(9)	1.0
Pt1	4f	1/3	2/3	0.09555(11)	0.0024(7)	1.0
Pt2	4f	1/3	2/3	0.67971(10)	0.0018(7)	1.0
In1	4f	1/3	2/3	0.54132(18)	0.0029(10)	1.0
In2	4e	0	0	0.1419(2)	0.0025(9)	1.0
HoPt$_4$In$_4$						
Ho	2c	1/3	2/3	1/4	0.00412(18)	1.0
Pt1	4f	1/3	2/3	0.09584(3)	0.00563(15)	1.0
Pt2	4f	1/3	2/3	0.67973(2)	0.00467	1.0
In1	4f	1/3	2/3	0.54148(5)	0.0064(2)	1.0
In2	4e	0	0	0.14221(5)	0.0058(2)	1.0
In3	2a	0	0	0	0.010(7)	0.060(8)
ErPt$_4$In$_4$						
Er	2c	1/3	2/3	1/4	0.00195(13)	1.0
Pt1	4f	1/3	2/3	0.09613(2)	0.00280(10)	1.0
Pt2	4f	1/3	2/3	0.67989(2)	0.00219(9)	1.0
In1	4f	1/3	2/3	0.54134(4)	0.00361(13)	1.0
In2	4e	0	0	0.14247(4)	0.00337(14)	1.0
In3	2a	0	0	0	0.005(11)	0.026(7)