The LaPdIn₄ indide and elementary properties of the LaTIn₄ ($T = \text{Ni, Pd, Pt}$) materials family

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Abstract

The indium-rich intermetallic compound LaPdIn₄ is reported, prepared by arc-melting and annealing at 600 °C. Single crystal X-ray diffraction found the material to be orthorhombic, space group *Cmcm* (No. 63), with lattice parameters $a = 4.5462(3) \text{ \AA}$, $b = 16.9208(10) \text{ \AA}$, and $c = 7.3100(5) \text{ \AA}$. This previously unreported indide is isostructural with LaNiIn₄ and LaPtIn₄. It is demonstrated that all three compounds in the LaTIn₄ ($T = \text{Ni, Pd, Pt}$) family display metallic behavior with resistivity values between 20-30 $\mu\Omega\text{-cm}$ at 250 K. In addition, temperature and field-dependent magnetization measurements between 2 and 250 K show all to be weak paramagnets or diamagnets, with very small amounts of spin-bearing impurities present. The field-dependent magnetization showed evidence of de Haas-van Alphen quantum oscillations in the Pd and Pt containing compounds near applied fields of 5 Tesla.

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1. Introduction

Indium, unlike many other main group elements, has an electronegativity value that is similar to those of transition metals, a property that likely plays a role in the fact that RuIn_3 displays semiconducting properties even though this compound is not a Zintl phase and does not follow 18 electron counting rules.¹⁻² As a Group 13 element, indium is known in solid state chemistry for its tendency to form compounds based on indium clusters,³⁻⁶ just like gallides.⁷⁻⁸ In order to induce greater charge-transfer interactions in indides to manipulate their properties, elements that are electropositive, like rare earths, can be introduced into the system. Thus, indium-rich ternary intermetallic compounds containing rare earths (RE) and transition metals (T) have been widely studied due to their structural variety and interesting magnetic and electrical properties.⁹⁻¹⁵ For example, EuPtIn_4 displays two antiferromagnetic transitions and has a high Sommerfeld coefficient (γ),¹⁶ YbPdIn_2 and YbAuIn_2 are both Pauli paramagnets,¹⁷ CeCoIn_5 and CeIrIn_5 are heavy fermion superconductors,¹⁸ and YbNiIn_4 displays a valence instability.¹⁹ While ternary indium-rich intermetallics have been extensively studied for the rare earth elements cerium, europium and ytterbium, there has not been a comparable degree of study performed on materials based on non-magnetic rare earths such as lanthanum.²⁰⁻²¹

We report here the synthesis and structure of the previously unreported indide LaPdIn_4 , whose structure we have determined by single crystal diffraction. We also compare the temperature-dependent resistivity and magnetic properties in the LaTIn_4 ($T = \text{Ni, Pd, Pt}$) family. While the Ni and Pt containing compounds have been previously reported,²⁰⁻²¹ their physical properties have not been studied to the best of our knowledge. The LaTIn_4 family contains all basic paramagnets, with the Pd and Pt containing compounds displaying de Haas-van Alphen quantum oscillations, even in the polycrystalline materials studied here.

2. Experiment

Starting materials for the synthesis of LaTIn_4 ($T = \text{Ni, Pd, Pt}$) were lanthanum (>99.9%, chunk), nickel powder (99.9 %, 325 mesh, CERAC), palladium powder (99.9 %, 60 mesh, Alfa), platinum powder (99.99 %, 22 mesh, Alfa), and indium tear drops (99.9 %, Alfa). The individual metals nickel, palladium, and platinum were first arc-melted to minimize mass loss during reactions with lanthanum and indium. Lanthanum, the pre-melted transition metal, and indium were then arc-melted in a 1:1:4 ratio under approximately 600 mbar of argon pressure. Each

button was melted three times and flipped over between melts to ensure homogeneity. The total mass loss was $< 1\%$. Samples were sealed in an evacuated quartz tube and annealed at $600\text{ }^{\circ}\text{C}$ for 10 days. LaNiIn_4 , LaPdIn_4 , and LaPtIn_4 are all stable in air and do not decompose over time.

The sample purity for all compounds was checked using powder X-ray diffraction (Bruker D8 Advance Eco, $\text{Cu K}\alpha$ radiation) using a LynxEye-XE detector. Single crystal X-ray diffraction was performed only on the Pd-containing compound. Crystals selected from the arc-melted button were mounted on the tips of kapton loops. Intensity data were collected at 100 K on a Bruker Apex II diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5406\text{ \AA}$) radiation. Data were collected over a full sphere of reciprocal space with 0.5° scans in ω with an exposure time of 5 s per frame. The 2θ range extended from 4° to 80° . The SMART²² software was used for data acquisition. Intensities were extracted and corrected for Lorentz and polarization effects with the SAINT²² program. Numerical absorption corrections²³ were accomplished with XPREP with $I > 2\sigma(I)$. The crystal structures were solved with the SHELXTL²⁴ package using direct methods and refined by full-matrix least-squares on F^2 . All crystal structure drawings were produced using the program VESTA.²⁵ Rietveld refinement was performed for LaPdIn_4 using the FullProf Suite with Thompson-Cox-Hastings pseudo-Voigt peak shapes. The parameters from the single crystal refinement were used as a starting point. The powder refinement was consistent with the single crystal refinement and is therefore not discussed here.

Physical property measurements were performed on the annealed polycrystalline samples. Measurements of temperature-dependent electrical resistivity (ρ) using a four probe method were performed on a Quantum Design Physical Property Measurement System (PPMS) Dynacool. Field-dependent magnetization measurements were performed using the VSM option at 2 K with a sweep from -9 T to 9 T . All three compounds showed linear magnetization (M) with applied field (H) up to 1000 Oe . The magnetic susceptibility (χ) is therefore defined as $\chi = M/H$ at $H = 1000\text{ Oe}$. Zero-field cooled (ZFC), temperature-dependent magnetic susceptibility data were collected from 2 to 250 K in an applied field of 1000 Oe for LaTIn_4 .

3. Results and Discussion

The single crystal structure determination showed that LaPdIn_4 is orthorhombic and adopts the YNiAl_4 structure type (The single crystal crystallographic data for LaPdIn_4 is given in

Table 1 and the atomic coordinates are given in Table 2), which has previously been observed for LaNiIn₄ and LaPtIn₄.²⁰⁻²¹

Table 1. Single crystal crystallographic data for LaPdIn₄ at 100 K.

Empirical Formula	LaPdIn ₄
F.W. (g/mol);	704.59
Space group;	<i>Cmcm</i> (No.63)
<i>Z</i>	4
<i>a</i> (Å)	4.5462 (3)
<i>b</i> (Å)	16.9208 (10)
<i>c</i> (Å)	7.3100 (5)
<i>V</i> (Å ³)	562.32 (6)
Radiation	Cu (Kα)
Absorption Correction	Numerical
θ range (deg)	8.01-72.21
<i>hkl</i> ranges	$-5 \leq h \leq 5$
	$-20 \leq k \leq 20$
	$-8 \leq l \leq 9$
No. reflections; <i>R</i> _{int}	2874; 0.0338
No. independent reflections	338
No. parameters	24
<i>R</i> ₁ ; <i>wR</i> ₂	0.0408; 0.0956
Goodness of fit	1.133
Diffraction peak and hole (e ⁻ /Å ³)	3.258; -4.087

Table 2. Atomic coordinates and equivalent isotropic displacement parameters of LaPdIn₄. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor ($\text{\AA}^2$).

Atom	Wyckoff.	Occupancy.	x	y	z	U_{eq}
La	4c	1	0	0.1194(3)	$\frac{1}{4}$	0.0130(5)
Pd	4c	1	0	0.7746(6)	$\frac{1}{4}$	0.0139(5)
In1	4c	1	0	0.9299(3)	$\frac{1}{4}$	0.0129(5)
In2	4b	1	0	$\frac{1}{2}$	0	0.0126(5)
In3	8f	1	0	0.3160(5)	0.0498(8)	0.0131(4)

The ambient temperature powder diffraction pattern of LaPdIn₄ and the corresponding fit are shown in Figure 1. The crystal structure of LaPdIn₄, including the local coordination environment of each atom, is shown in Figure 2. LaPd₂In₄,²⁶ La₂Pd₃In₄,²⁷ LaPd₂In,²⁸ La₄Pd₁₀In₂₁,²⁹ LaPdIn₂³⁰ are also known in the La-Pd-In ternary system but the new LaPdIn₄ indide is the most indium-rich compound reported. The distorted bcc substructure, adopted by LaPdIn₄, is the common structural aspect among indium-rich ternary intermetallic compounds despite elemental indium displaying distorted cubic closest-packing.²⁰⁻²¹

Figure 1

The atomic coordination environments for each element in the LaPdIn₄ structure are given in the bottom of Figure 2. The structure has unique La and Pd sites and three In sites (In1, In2, and In3). Lanthanum is 7-coordinated, forming a monocapped distorted square antiprism

while palladium is 9-coordinated in an irregular polyhedron. In1 resides in the center of the distorted bcc substructure and has ten nearest neighbors including In2, In3, Pd, and La. Both In2 and In3 occupy the corners of the distorted body-centered cubes in the polyanionic network. The chemical bonding of the compounds CeNiIn_4 ³¹ and CaPdIn_4 ³² were previously investigated, which showed that the strongest bonding interactions were found for the *T*-In (*T* = Ni or Pd) bonds and the In-In bonds. Since LaPdIn_4 is analogous to both CeNiIn_4 and CaPdIn_4 , the structure as shown in Figure 2 can be written as $\text{La}^{+3}[\text{PdIn}_4]^{3-}$ with a covalently bonded polyanionic network, which forms a separate cage around each of the electropositive lanthanum atoms. The main panel in Figure 2 emphasizes the $[\text{PdIn}_4]^{3-}$ network: each lanthanum atom donates its three valence electrons to the network.

Figure 2

The previously reported compounds LaNiIn_4 ²⁰ and LaPtIn_4 ²¹ were prepared to analyze the physical properties of the LaTIn_4 family. Figure 3 shows the comparison of the the PXRD patterns for LaNiIn_4 , LaPdIn_4 , and LaPtIn_4 . All compounds are isostructural. The resistivities of LaNiIn_4 , LaPdIn_4 , and LaPtIn_4 are shown in Figure 4. All have resistivity values of $\sim 20 - 30 \mu\Omega\text{-cm}$ at 250 K; the three compounds show metallic conductivity behavior with low residual resistivity values of $\sim 2.5 \mu\Omega\text{-cm}$ at 2 K. In addition, the residual resistivity ratios ($\rho_{250\text{K}}/\rho_{2\text{K}}$) are quite high for polycrystalline samples with values of 11, 10.4, and 8.4 for the Ni, Pd, and Pt-containing compounds, respectively. A low residual resistivity value and high residual resistivity ratio has also been observed in the indium-rich intermetallic EuAuIn_4 .³³⁻³⁴ The low electrical resistivity values shown in Figure 4 are on the same order of magnitude as those typically seen for elemental indium,³⁵⁻³⁶ which is consistent with this family being indium-rich.

Figure 3.

Figure 4.

Figure 5 shows the field-dependent magnetizations for LaNiIn_4 , LaPdIn_4 , and LaPtIn_4 at selected temperatures. All display nearly linear field-dependent magnetization at both 50 K and 100 K. However, the sign and magnitude of the slope differs for each of the three compounds. Figure 5a and b show that dM/dH for the Ni and Pd-containing compounds is slightly negative at

100 K. This negative susceptibility results from the core magnetism. However, Figure 5c shows that dM/dH for LaPtIn_4 is positive, tentatively attributed to the conduction electrons, which give enough of a contribution to dominate the effects of the core electrons on the susceptibility. Figure 5a shows that the sign of the slope changes from slightly negative to positive for LaNiIn_4 on decreasing the temperature from 100 K to 50 K. Figure 5b shows no change in either the sign or the magnitude of the slope upon decreasing temperature for LaPdIn_4 , whereas dM/dH for LaPtIn_4 becomes more positive from 100 K to 50 K. The low field low temperature susceptibilities are dominated by impurity spins and positive susceptibility is seen in all cases at 2 K or 4 K. Impurity peaks do not appear in the PXRD patterns (except for non-magnetic LaPtIn_3 or In impurities; LaPtIn_4 was measured at 4 K rather than 2 K since there was a small amount of indium impurity present that has a superconducting transition at 3.4 K.), and thus the paramagnetic contributions to the susceptibility at low temperatures most likely came from magnetic impurity ions in the crystal. Figure 5b and c show the presence of de Haas-van Alphen (dHvA) quantum oscillations at high applied fields and low temperatures for LaPdIn_4 . These oscillations are less pronounced for LaPtIn_4 but still apparent. Typically, dHvA oscillations are not seen in polycrystalline samples since electrons will usually undergo nontrivial scattering in such samples.³⁷ De Haas-van Alphen measurements have been carried out on pure indium³⁸ in addition to cerium, ytterbium, and lutetium transition metal indium-rich compounds.³⁸⁻⁴¹ To the best of our knowledge, quantum oscillations have only been measured in LaIn_3 ⁴² and not in other indium-rich, ternary intermetallic compounds containing lanthanum. The frequency of dHvA oscillations can be used to map out the geometry of the Fermi surface,⁴³ which is extremely important in predicting electrical, thermal or other properties. Further study of the current materials in that context may therefore be of interest.

Figure 5.

Figure 6 shows the plot of the temperature-dependent magnetic susceptibility for polycrystalline samples of LaNiIn_4 , LaPdIn_4 , and LaPtIn_4 . All have a Curie tail at low temperature, which, as described above, results from small amounts of paramagnetic impurity spins. The data from the main panel in Figure 6 were used to construct the temperature-dependent inverse susceptibilities, $1/(\chi - \chi_0)$ vs. T , shown in the inset. The magnetic susceptibilities for each compound were fit to the Curie-Weiss law ($\chi - \chi_0 = C/(T - \theta_{\text{CW}})$), where χ is the susceptibility, χ_0 is the temperature-independent susceptibility, C is the Curie constant, T is temperature (K) and θ_{CW} is the Curie-Weiss temperature. (The fits were performed from 2 – 10 K for LaNiIn_4 and from 2 – 20 K for both LaPdIn_4 and LaPtIn_4 .) The effective magnetic moments for each compound (determined by $\mu_{\text{eff}} = \sqrt{8C}$) were found to be $0.043 \mu_B/\text{mol}$, $0.066 \mu_B/\text{mol}$, and $0.072 \mu_B/\text{mol}$, respectively; as are expected for metals with small amounts of magnetic ion impurities, which, assuming spin half impurity ions ($S = 1/2$), can be estimated as 0.1 %, 0.1 %, and 0.2 % for LaNiIn_4 , LaPdIn_4 , and LaPtIn_4 . The Curie-Weiss temperatures θ_{CW} are 0.24 K, 0.16 K, and -1.8 K for the Ni, Pd, and Pt containing compounds, respectively, consistent with the presence of essentially isolated impurity spins.

Figure 6.

4. Conclusions

The new indide LaPdIn₄ was prepared by arc-melting and subsequent annealing. Analysis of single crystal X-ray diffraction data indicates that LaPdIn₄ is isostructural with LaNiIn₄ and LaPtIn₄, which all crystalize in the orthorhombic YNiAl₄ structure type. The resistivity of the LaTIn₄ ($T = \text{Ni, Pd, Pt}$) family shows metallic behavior with resistivity values of $\sim 20 - 30 \mu\Omega\text{-cm}$ at 250 K. No superconductivity was observed in these materials down to 1.8 K. The materials are weakly diamagnetic or paramagnetic, with both the Pd and Pt polycrystalline samples displaying quantum oscillations at low temperature and high applied magnetic fields. The dHvA quantum oscillations are not often seen and therefore further study is needed on LaPdIn₄ to try to map the Fermi surface of this material.

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7. References

- [1] D. Bogdanov, K. Winzer, I. A. Nekrasov, T. Pruschke, Electronic properties of the semiconductor RuIn_3 , *J. Phys.: Condens. Matter.* 19 (2007) 232202. DOI: 10.1088/0953-8984/19/23/232202.
- [2] M. Wagner, R. Cardoso-Gil, N. Oeschler, H. Rosner, Yu. Grin, $\text{RuIn}_{3-x}\text{Sn}_x$, $\text{RuIn}_{3-x}\text{Zn}_x$ and $\text{Ru}_{1-y}\text{In}_3$ – new thermoelectrics based on the semiconductor RuIn_3 , *J. Mater. Res.* 26 (2011) 1886-1893. DOI: 10.1557/jmr.2011.153.
- [3] J. T. Zhao, J. D. Corbett, Square pyramidal clusters in La_3In_5 and Y_3In_5 . La_3In_5 as a metallic Zintl phase, *Inorg. Chem.* 34 (1995) 378-383. DOI: 10.1021/ic00105a057.
- [4] S. C. Sevov, J. D. Corbett, Synthesis, characterization, and bonding of indium clusters: $\text{Na}_7\text{In}_{11.8}$, a novel network structure containing closo- In_{16} and nido- In_{11} clusters, *Inorg. Chem.* 31 (1992) 1895-1901. DOI: 10.1021/ic00036a032.
- [5] C. Staudt, A. Wucher, Generation of large indium clusters by sputtering, *Phys. Rev. B.* 66 (2002) 075419. DOI: 10.1103/PhysRevB.66.075419.
- [6] S. C. Sevov, J. D. Corbett, Synthesis, characterization, and bonding of indium clusters: $\text{A}_3\text{Na}_{26}\text{In}_{48}$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) with a novel cubic network of arachno- and closo- In_{12} clusters, *Inorg. Chem.* 32 (1993) 1612-1615. DOI: 10.1021/ic00061a016.
- [7] W. Xie, H. Luo, B. F. Phelan, T. Klimczuk, F. A. Cevallos, R. J. Cava, Endohedral gallide cluster superconductors and superconductivity in ReGa_5 , *Proc. Natl. Acad. Sci.* 112 (2015) E7048- E7054. DOI:10.1073/pnas.1522191112.
- [8] N. Drebov, F. Weigend, R. Ahlrichs, Structures and properties of neutral gallium clusters: A theoretical investigation, *J. Chem. Phys.* 135 (2011) 044314. DOI: 10.1063/1.3615501.
- [9] Ya. M. Kalychak, Peculiarities of the composition and structure of the compounds of the rare-earth—Ni-In systems, *J. Alloys Compd.* 262-263 (1997) 341-345. DOI:10.1016/S0925-8388(97)00402-7.
- [10] M. Pustovoychenko, Y. Tyvanchuk, I. Hayduk, Y. Kalychak, Crystal structure of the $\text{RE}_{11}\text{Ni}_4\text{In}_9$ compounds ($\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}$ and Y), *Intermetallics.* 18 (2010) 929-932. DOI:10.1016/j.intermet.2010.01.003.
- [11] Ya. M. Kalychak, Composition and crystal structure of the rare-earths-Co-In compounds, *J. Alloys Compd.* 291 (1999) 80-88. DOI:10.1016/S0925-8388(99)00290-X.

- [12] S. Sarkar, M. J. Gutmann, S. C. Peter, Crystal Structure and Magnetic Properties of Indium Flux Grown EuAu_2In_4 and EuAuIn_4 , *Cryst. Growth Des.* 13 (2013) 4285-4294.
DOI: 10.1021/cg400619p.
- [13] M. Lukachuk, Y. V. Galadzhun, R. I. Zaremba, M. V. Dzevenko, Y. M. Kalychak, V. I. Zaremba, U. Ch. Rodewald, R. J. Pöttgen, New rare earth metal-rich indides $\text{RE}_{14}\text{Ni}_3\text{In}_3$ (RE = Sc, Y, Gd-Tm, Lu) – synthesis and crystal chemistry, *J. Solid State Chem.* 178 (2005) 2724-2733. DOI:10.1016/j.jssc.2005.06.021.
- [14] Yu. Tyvanchuk, R. Duraj, T. Jaworska-Golab, S. Baran, Ya. M. Kalychak, J. Przewoznik, A. Szytula, Structural chemistry and magnetic properties of $\text{R}_{11}\text{M}_4\text{In}_6$ (R = Gd, Tb, Dy, Ho, Er, Y; M = Si, Ge) compounds, *Intermetallics*. 25 (2012) 18-26.
DOI:10.1016/j.intermet.2012.02.005.
- [15] Ya. M. Kalychak, V. I. Zaremba, R. Pöttgen, M. Lukachuk, R.-D. Hoffmann, Rare earth-transition metal-indides, in: K.A. Gschneidner Jr., V.K. Pecharsky, J.-C. Bünzli (Eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Elsevier, Amsterdam, 2004, pp. 1–133. DOI:10.1016/S0168-1273(04)34001-8.
- [16] P. Kushwaha, A. Thamizhavel, A. K. Nigam, S. Ramakrishnan, Crystal Growth and Crystal Structure of EuPtIn_4 , *Cryst. Growth Des.* 14 (2014) 2747-2752. DOI: 10.1021/cg401864p.
- [17] Ya. V. Galadzhun, R.-D. Hoffmann, G. Kotzyba, B. Kunnen, R. Pöttgen, EuPdIn_2 , YbPdIn_2 , and YbAuIn_2 : Syntheses, Structures, and Properties of New Intermetallic Compounds with Ordered Re_3B -Type Structure, *Eur. J. Inorg. Chem.* 1999 (1999) 975-979.
DOI: 10.1002/(SICI)1099-0682(199906)1999:6<975::AID-EJIC975>3.0.CO;2-6.
- [18] R. Movshovich, M. Jaime, J. D. Thompson, C. Petrovic, Z. Fisk, P. G. Pagliuso, J. L. Sarrao, Unconventional Superconductivity in CeIrIn_5 and CeCoIn_5 : Specific Heat and Thermal Conductivity Studies, *Phys. Rev. Lett.* 86 (2001) 5152-5155. DOI: 10.1103/PhysRevLett.86.5152.
- [19] M. D. Koterlin, B. S. Morokhivskii, I. D. Shcherba, Ya. M. Kalychak, Transport and magnetic properties of the compounds YbNi_4In and YbNiIn_4 with valence-unstable Yb, *Phys. Solid State*. 41 (1999) 1759-1762. DOI: 10.1134/1.1131092
- [20] Y. M. Kalychak, V. I. Zaremba, Y. V. Galadzhun, K. U. Miliyanchuk, R.-D. Hoffmann, R. Pöttgen, A New $^1\infty[\text{Ni}_7]$ Cluster in LaNi_7In_6 and Distorted bcc Indium Cubes in LaNiIn_4 , *Chem.*

Eur. J. 7 (2001) 5343-5349. DOI: 10.1002/1521-3765(20011217)7:24<5343::AID-CHEM5343>3.0.CO;2-#.

[21] Y. V. Galadzhun, R. Pöttgen, Platinum-Indium Polyanions in the Structures of LaPtIn_4 and LnPtIn_3 ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$) and Structure Refinement of $\text{Ce}_2\text{Pt}_2\text{In}$, *Z. anorg. Allg. Chem.* 625 (1999) 481-487. DOI: 10.1002/(SICI)1521-3749(199903)625:3<481::AID-ZAAC481>3.0.CO;2-0.

[22] G. M. Sheldrick, SADABS; University of Gottingen: Gottingen, Germany, 2001.

[23] J. de Meulenaer, H. Tompa, The absorption correction in crystal structure analysis, *Acta Cryst.* 19 (1965) 1014-1019. DOI: 10.1107/S0365110X65004802.

[24] G. M. Sheldrick, A short history of SHELX, *Acta Cryst. Sect. A.* 64 (2008) 112–122. DOI:10.1107/S0108767307043930.

[25] K. Momma, F. Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, *J. Appl. Cryst.* 44 (2011) 1272–1276. DOI: 10.1107/S0021889811038970.

[26] A. Tursina, S. Nesterenko, E. Murashova, Z. Kurenbaeva, Yu. Seropegin, H. Noel, T. Roisnel, D. Kaczorowski, Synthesis, crystal structure and magnetic properties of the new ternary indides REPd_2In_4 ($\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$), *Intermetallics.* 19 (2011) 1864-1872. DOI:10.1016/j.intermet.2011.07.029.

[27] S. N. Nesterenko, A. I. Tursina, H. Noel, Y. D. Seropegin, D. Kaczorowski, New ternary indide $\text{La}_2\text{Pd}_3\text{In}_4$, *J. Alloys Compd.* 579 (2013) 112-116. DOI:10.1016/j.jallcom.2013.05.039.

[28] B. Xue, H. Schwer, F. Hulliger, Structure of LaPd_2In , *Acta Cryst. Sect. C.* 48 (1992) 2064-2065. DOI: 10.1107/S0108270192007303.

[29] V. I. Zaremba, U. Ch. Rodewald, Ya. M. Kalychak, Ya. V. Galadzhun, D. Kaczorowski, R.-D. Hoffmann, R. Pöttgen, Ternary Indides $\text{RE}_4\text{Pd}_{10}\text{In}_{21}$ ($\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$) – Synthesis, Structure, and Physical Properties, *Z. anorg. Allg. Chem.* 629 (2003) 434-442. DOI: 10.1002/zaac.200390072.

[30] V. I. Zaremba, D. Kaczorowski, U. Ch. Rodewald, R.-D. Hoffmann, R. Pöttgen, LaPdIn_2 with MgCuAl_2 and REPdIn_2 ($\text{RE} = \text{Y}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd} - \text{Tm}, \text{Lu}$) with HfNiGa_2 -Type Structure: Synthesis, Structure, and Physical Properties, *Chem. Mat.* 16 (2004) 466- 476. DOI: 10.1021/cm031139m.

[31] R. Pöttgen, Crystal structure and physical properties of CeNiIn_4 , *J. Mater. Chem.* 5 (1995) 769-772. DOI: 10.1039/JM9950500769.

- [32] R.-D. Hoffmann, R. Pöttgen, Distorted *bcc* Indium Cubes as Structural Motifs in Ca[TIn₄] (T = Rh, Pd, Ir), *Chem. Eur. J.* 6 (2000) 600-607. DOI: 10.1002/(SICI)1521-3765(20000218)6:4<600::AID-CHEM600>3.0.CO;2-9.
- [33] S. Sarkar, M. J. Gutmann, S. C. Peter, Crystal Structure and Magnetic Properties of Indium Flux Grown EuAu₂In₄ and EuAuIn₄, *Cryst. Growth Des.* 13 (2013) 4285-4294. DOI: 10.1021/cg400619p.
- [34] T. Sasakawa, T. Suemitsu, J. Kitagawa, O. Sologub, P. Salamakha, T. Takabatake, Magnetic and transport properties of a new valence-fluctuating compound, CeRhP, *J. Phys.: Condens. Matter.* 14 (2002) L267-L272. PII: S0953-8984(02)33105-9.
- [35] Y. Xi, F. Q. Zu, X. F. Li, J. Yu, L. J. Liu, Q. Li, Z. H. Chen, High-temperature abnormal behavior of resistivities for Bi-In melts, *Phys. Lett. A* 329 (2004) 221–225. DOI:10.1016/j.physleta.2004.06.089.
- [36] R. Fogelholm, O. Rapp, G. Grimvall, Electrical resistivity of indium: Deviation from linearity at high temperatures, *Phys. Rev. B* 23 (1981) 3845- 3851. DOI: 10.1103/PhysRevB.23.3845.
- [37] S. Ishiwata, Y. Shiomi, J. S. Lee, M. S. Bahramy, T. Suzuki, M. Uchida, R. Arita, Y. Taguchi, Y. Tokura, Extremely high electron mobility in a phonon-glass semimetal, *Nature Materials* 12 (2013) 512-517. DOI: 10.1038/NMAT3621.
- [38] A. J. Hughes, J. P. G. Shepherd, de Haas-van Alphen measurements and the band structure of indium, *J. Phys. C: Solid State Phys.* 2 (1969) 661-672. DOI: 0022-3719/2/4/310.
- [39] M. L. Sutherland, S. K. Goh, E. C. T. O'Farrell, C. Bergemann, J. Paglione, T. A. Sayles, M. B. Maple, Observation of de Haas-van Alphen oscillations across the phase diagram of CeRh_{1-x}Co_xIn₅, *J. Phys.: Conf. Ser.* 150 (2009) 042193. DOI:10.1088/1742-6596/150/4/042193.
- [40] R. Settai, H. Shishido, S. Ikeda, Y. Murakawa, M. Nakashima, D. Aoki, Y. Haga. H. Harima, Y Onuki, Quasi-two-dimensional Fermi surfaces and the de Haas-van Alphen oscillation in both the normal and superconducting mixed states of CeCoIn₅, *J. Phys.: Condens. Matter.* 13 (2001) L627-L634. PII: S0953-8984(01)23852-1.
- [41] R. Pöttgen, D. Johrendt, Equiatomic Intermetallic Europium Compounds: Syntheses, Crystal Chemistry, Chemical Bonding, and Physical Properties, *Chem. Mater.* 12 (2000) 875-897. DOI: 10.1021/cm991183v.

[42] Z. Kletowski, M. Glinski, A. Hasegawa, Magnetoresistance and the Fermi surface of the intermetallic compound LaIn_3 , *J. Phys. F: Met. Phys.* 17 (1987) 993-998. DOI: 0305-4608/17/4/024.

[43] L. Onsager, Interpretation of the de Haas-van Alphen effect, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 43 (1952) 1006-1008. DOI: 10.1080/14786440908521019.

Figures

Figure 1. Room-temperature PXRD pattern of LaPdIn₄. Bragg reflections are shown in green, observed data are shown in red, calculated data in black, and the difference between the calculated and observed intensities is shown in blue.

Figure 2. Crystal structure of LaPdIn₄. Lanthanum is shown in yellow, palladium in pink, and indium in blue. The irregular coordination polyhedra of lanthanum and palladium are shown at the bottom; La is 7-coordinated and Pd is 9-coordinated. In1 has 6 nearest neighbors including In2, In3, Pd, and La. In2 is only surrounded by In3 and In1. In3 has 10 nearest neighbors including In1, In2, In3, Pd, and La.

Figure 3. Comparison of the PXRD patterns of LaNiIn₄ (top), LaPdIn₄ (middle), and LaPtIn₄ (bottom). The asterisks in the bottom panel indicate the presence of a LaPtIn₃ impurity.

Figure 4. Temperature-dependent resistivity (ρ) from 2 to 250 K for polycrystalline LaNiIn₄ (Δ), LaPdIn₄ ($\bullet$), and LaPtIn₄ ($+$). All three compounds show metallic conductivity.

Figure 5. Field-dependent magnetizations for (a) LaNiIn₄, (b) LaPdIn₄, and (c) LaPtIn₄. Temperatures are indicated on the figure. DHvA quantum oscillations are especially visible for LaPdIn₄.

Figure 6. Main panel - Temperature-dependent magnetic susceptibility (χ), in an applied magnetic field of 1000 Oe, for polycrystalline LaNiIn₄ (Δ), LaPdIn₄ ($\bullet$), and LaPtIn₄ ($+$), at temperatures below 70 K. Inset – the inverse susceptibilities at low temperatures; in this plot a temperature independent term (χ_0), 1.5×10^{-5} emu/Oe mol for Ni, -5.0×10^{-6} emu/Oe mol for Pd, and 7.8×10^{-6} emu/Oe mol for Pt, has been subtracted from the raw data in conformance with the Curie-Weiss fit described in the text.