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# New compounds with $Nd_{11}Pd_4In_9$ structure type in the systems *RE*–Pd–In (*RE* = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy)

L. Sojka [a,b], M. Demchyna [a,*], B. Belan [a], M. Manyako [a], Ya. Kalychak [a]

[a] Faculty of Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, UA-79005 Lviv, Ukraine
[b] Andrey Krupynsky Lviv State Medical College, Doroshenka St. 70, UA-79000 Lviv, Ukraine

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ABSTRACT

$RE_{11}Pd_4In_9$ compounds (*RE* = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy) were synthesized by arc-melting of pure metals under an argon atmosphere with subsequent annealing at 870 K and characterized by X-ray powder diffraction. They belong to the $Nd_{11}Pd_4In_9$ structure type (space group *Cmmm*, $Z = 2$) with the following lattice constants: $a = 15.581(5)$, $b = 22.606(8)$, $c = 3.767(1)$ Å for $La_{11}Pd_4In_9$; $a = 15.431(6)$, $b = 22.516(9)$, $c = 3.763(2)$ Å for $Ce_{11}Pd_4In_9$; $a = 14.883(3)$, $b = 22.319(4)$, $c = 3.736(1)$ Å for $Pr_{11}Pd_4In_9$; $a = 14.825(6)$, $b = 22.269(8)$, $c = 3.779(1)$ Å for $Nd_{11}Pd_4In_9$; $a = 14.706(2)$, $b = 22.094(3)$, $c = 3.729(1)$ Å for $Sm_{11}Pd_4In_9$; $a = 14.701(3)$, $b = 22.046(5)$, $c = 3.722(8)$ Å for $Gd_{11}Pd_4In_9$; $a = 14.614(5)$, $b = 21.985(3)$, $c = 3.679(2)$ Å for $Tb_{11}Pd_4In_9$, $a = 14.606(4)$, $b = 21.896(6)$, $c = 3.626(9)$ Å for $Dy_{11}Pd_4In_9$. The structure is a member of the homological series $RE_{m+n}M_{2n}X_m$ based on $AlB_2$ (*m*) and CsCl (*n*) types.



## 1. Introduction

The compounds of rare earths, transition metals and indium form an important group of intermetallic compounds with very diverse compositions, crystal structures and interesting physical properties [1,2]. The interactions in the systems of rare earths-3*d* metal-indium, especially with Co, Ni, and Cu, have been studied the most extensively. The existence of approximately 300 ternary compounds has been revealed in these systems, whereas the exploration of the systems with platinum family is not systematical. However, it should be noted that the investigation of the systems with palladium is more comprehensive than for the other representatives of platinum family. The isothermal sections of Ce–Pd–In phase diagram over the whole concentration range at 1023 K [3] and at 773 K [4], and partly of Tb–Pd–In and Ho-Pd-In ternary systems at 1020 K [5] have been constructed for today. The $Mo_2FeB_2$-type phases with homogeneity ranges and solid solutions $RE_xPdIn_{1-x}$ based on PdIn binary compound with the CsCl-type [5] were synthesized in the systems with terbium and holmium. The existence of the series of ternary compounds $REPd_2In$ ($MnCu_2Al$-type) [6], *RE*PdIn (ZrNiAl-type) [7,8], $RE_2Pd_2In$ ($Mo_2FeB_2$-type) [9], $REPdIn_2$ ($MgCuAl_2$ or $HfNiGa_2$-type) [10] and $RE_4Pd_{10}In_{21}$ ($Ho_4Ni_{10}Ga_{21}$-type) [11,12] was established. Some compounds of *RE*-Pd-In system, such as $Yb_2Pd_6In_{13}$ [13], $CePd_3In_2$ [14], $Ce_{20}Pd_{36}In_{67}$ [15], $Ce_6Pd_{12}In_5$ [16], $Ce_2Pd_4In_5$ [17] (which was previously found at $CePd_2In_2$ composition [3]) are the first representatives of the new structure types. Physical properties of $RE_2PdIn_8$ (*RE* = Ce, Pr, Nd, Sm) compounds with the $Ho_2CoGa_8$-type were investigated [18,19]. Crystal structures, magnetic and electrical properties of several tetragonal compounds of Ce–Pd–In system have been determined recently: $Ce_2PdIn_8$, $Ce_3PdIn_{11}$ (own type) and $Ce_5Pd_2In_9$ (own type) [20]. These compounds are the representatives of the homological series $Ce_mPd_nIn_{3m+2n}$ based on the $AuCu_3$-type and $PtHg_2$-type units. The same coordination numbers for all the atoms and nearly equal values of the interatomic distances are inherent for the compounds of this homological series.

We have recently found a new compound with the composition $Nd_{11}Pd_4In_9$ (*Cmmm*, $a = 14.843(3)$, $b = 22.284(3)$, $c = 3.7857(6)$) [21] which is the first representative of a new structure type. It belongs to a series of compounds based on the $AlB_2$ and CsCl types with a general formula $RE_{m+n}M_{2n}X_m$. The representatives of the $Nd_{11}Pd_4In_9$ structure type were found in *RE*-Co-In (*RE* = Gd, Tb, Dy, Ho, Er) [22] and *RE*-Ni-In (*RE* = La, Ce, Pr, Nd, Sm, Gd, Tb and Y) systems [23]. In this paper, we present our results on the synthesis and crystal structure of the $RE_{11}Pd_4In_9$ (*RE* = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy) compounds. Preliminary data about these compounds were reported [24,25].

## 2. Experimental

The compact metals with the following purity: lanthanides – 99.85 wt%, palladium – 99.92 wt%, indium – 99.99 wt% were used as starting materials for the synthesis. The samples of the compositions $RE_{45.83}Pd_{16.67}In_{37.50}$ (*RE* = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy) were

* Corresponding author. Tel.: +380 322936676.
*E-mail address:* marta.dem.85@gmail.com (M. Demchyna).

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**Table 1**
Crystallographic data and results of the refinement of $RE_{11}Pd_4In_9$ compounds.

| $RE_{11}Pd_4In_9$ | La | Ce | Pr | Nd | Sm | Gd | Tb | Dy |
|---|---|---|---|---|---|---|---|---|
| Content of the main phase[a], wt.% | 70.8(1) | 76.9(1) | 80.1(2) | 100(0) | 80.7(3) | 62.3(2) | 100(0) | 53.8(1) |
| Cell parameters a, Å | 15.581(5) | 15.431(6) | 14.883(3) | 14.825(6) | 14.706(2) | 14.701(3) | 14.614(5) | 14.606(4) |
| *b*, Å | 22.606(8) | 22.516(9) | 22.319(4) | 22.269(8) | 22.094(3) | 22.046(5) | 21.985(3) | 21.896(6) |
| c, Å | 3.767(1) | 3.763(2) | 3.736(1) | 3.779(1) | 3.729(1) | 3.722(8) | 3.679(2) | 3.626(9) |
| *V*, Å$^3$ | 1326(1) | 1307(1) | 1264(4) | 1247.9(7) | 1211.7(4) | 1207.6(5) | 1182.6(4) | 1168.1(5) |
| $\rho$ [g/cm$^3$] | 7.48 | 7.75 | 7.91 | 8.11 | 8.14 | 8.74 | 9.12 | 9.33 |
| *RE*1 at 8*p* (*x y* 0) | $x = 0.212(1)$ | 0.242(3) | 0.242(1) | 0.233(1) | 0.237(1) | 0.240(1) | 0.237(1) | 0.241(1) |
| | $y = 0.162(1)$ | 0.164(1) | 0.169(8) | 0.165(1) | 0.172(7) | 0.175(8) | 0.174(3) | 0.178(8) |
| *RE*2 at 4*i* (0 *y* 0) | $y = 0.161(2)$ | 0.156(2) | 0.155(1) | 0.152(1) | 0.161(1) | 0.161(1) | 0.161(1) | 0.165(1) |
| *RE*3 at 4*i* (0 *y* 0) | $y = 0.380(2)$ | 0.373(1) | 0.375(1) | 0.370(1) | 0.371(1) | 0.365(9) | 0.375(5) | 0.363(9) |
| *RE*4 at 4*g* (*x* 0 0) | $x = 0.283(2)$ | 0.242(4) | 0.309(3) | 0.313(2) | 0.373(1) | 0.322(2) | 0.309(7) | 0.313(2) |
| *RE*5 at 2*a* (0 0 0) | | | | | | | | |
| Pd at 8*q* (*x y* 1/2) | $x = 0.368(2)$ | 0.381(4) | 0.344(3) | 0.337(2) | 0.345(3) | 0.335(2) | 0.339(7) | 0.338(2) |
| | $y = 0.091(1)$ | 0.106(2) | 0.098(1) | 0.097(1) | 0.099(8) | 0.112(9) | 0.097(5) | 0.115(8) |
| In1 at 8*q* (*x y* 1/2) | $x = 0.059(2)$ | 0.096(3) | 0.104(1) | 0.099(1) | 0.103(1) | 0.105(1) | 0.104(7) | 0.105(1) |
| | $y = 0.284(1)$ | 0.270(2) | 0.268(1) | 0.266(1) | 0.261(8) | 0.263(9) | 0.260(5) | 0.263(9) |
| In2 at 8*q* (*x y* 1/2) | $x = 0.139(3)$ | 0.149(3) | 0.143(1) | 0.148(2) | 0.148(4) | 0.148(2) | 0.139(7) | 0.138(2) |
| | $y = 0.071(1)$ | 0.066(1) | 0.069(1) | 0.073(1) | 0.071(7) | 0.069(9) | 0.074(4) | 0.066(8) |
| In3 at 2*c* (1/2 0 1/2) | | | | | | | | |
| Scale factor | $0.129(1)\cdot10^{-4}$ | $0.64(1)\cdot10^{-5}$ | $0.70(1)\cdot10^{-5}$ | $0.38(5)\cdot10^{-5}$ | $0.64(8)\cdot10^{-5}$ | $0.95(5)\cdot10^{-6}$ | $0.38(1)\ 10^{-4}$ | $0.87(5)\cdot10^{-6}$ |
| Texture parameter, *G* [010] | 0.98(2) | 0.82(2) | 0.73(1) | 0.84(1) | 0.91(1) | 1.39(8) | 0.379(7) | 0.92(1) |
| Total reflections | 510 | 440 | 630 | 620 | 581 | 582 | 552 | 536 |
| Zero parameter $2\theta$, ° | 0.0013(1) | 0.036(7) | 0.047(2) | 0.033(1) | −0.043(5) | 0.032(8) | 0 | 0.047(1) |
| Half width parameters *U* | 0.629(4) | 0.549(5) | 0.314(3) | 0.227(1) | 0.181(8) | 0.261(6) | 0.629(6) | 0.233(4) |
| *V* | 0 | 0 | 0 | 0 | 0 | 0.034(3) | −0.153(0) | 0.025(2) |
| *W* | 0.025(2) | 0.055(3) | 0.009(3) | 0.098(7) | 0.018(7) | | 0.0564(2) | |
| Mixing parameter, $\eta$ | 1.21(5) | 1.3(1) | 1.02(9) | 1.116(5) | 1.06(5) | 1.18(2) | 0.548(1) | 1.22(3) |
| Peak assym. parameter $C_M$ | 0 | 0.17(6) | 0 | 0 | 0 | 0.15(3) | 0.109(3) | 0 |
| $R_P$, % | 3.36 | 3.70 | 2.77 | 3.62 | 1.97 | 2.64 | 2.53 | 2.71 |
| $R_{wp}$, % | 4.57 | 4.91 | 3.67 | 4.76 | 2.52 | 3.57 | 3.46 | 3.77 |
| $R_f$, % | 4.14 | 4.77 | 4.30 | 5.21 | 4.31 | 5.65 | 3.15 | 5.12 |
| $R_B$, % | 8.80 | 8.25 | 8.32 | 8.67 | 7.01 | 9.09 | 5.81 | 8.33 |
| Goodness of fit *S* | 1.7 | 1.7 | 1.4 | 1.12 | 1.2 | 1.4 | 1.7 | 1.2 |

[a] Additional phase *RE*PdIn (ZrNiAl-type) is present in all samples except for Nd and Tb samples.

prepared by arc-melting under an argon atmosphere under a pressure of 0.7–0.8 atm. The argon was purified by melting of titanium sponge. The samples were remelted twice to ensure homogeneity. The loss of the samples weight were smaller than 1%. The buttons were sealed in evacuated silica tubes and annealed at 870 K for 1 month. After that the samples were quenched in cold water. The powdered polycrystalline samples were measured at room temperature using an STOE STADI P diffractometer (Cu $K\alpha_1$-radiation, linear position sensitive detector, curved Ge (111) monochromator, transmission geometry, measured interval $6.0 \le 2\theta \le 110.6°$, scan step mode, step size in $2\theta = 0.015°$, scanning time 350–750 s/step).

The FullProf.2k (version 4.40) [26] program package was used for X-ray phase and Rietveld analysis of collected data. Experimental details and crystallographic data for the $RE_{11}Pd_4In_9$ compounds are listed in Table 1.

## 3. Results and discussion

X-ray phase analysis of the $RE_{45.83}Pd_{16.67}In_{37.50}$ alloys revealed that single-phase samples were obtained only with Nd and Tb (Fig. 1a). Other samples contained two phases, namely, $RE_{11}Pd_4In_9$ and equiatomic compounds *RE*PdIn with the ZrNiAl structure type [27]. The spurious phase is in phase equilibrium with the studied compounds at the annealing temperature 870 K. Experimental, calculated and difference X-ray powder diffraction patterns of samples with terbium and samarium are presented on Fig. 1. Rietveld refinement confirmed that the $RE_{11}Pd_4In_9$ compounds belong to the $Nd_{11}Pd_4In_9$ type (Table 1).

The structure of the compounds with the $Nd_{11}Pd_4In_9$-type has two layers along the shortest direction [001]. Thus the larger *RE* atoms form nets of tetragons and triangles at $z = 0$; and smaller size atoms of indium and palladium are at $z = 1/2$ and form nets of

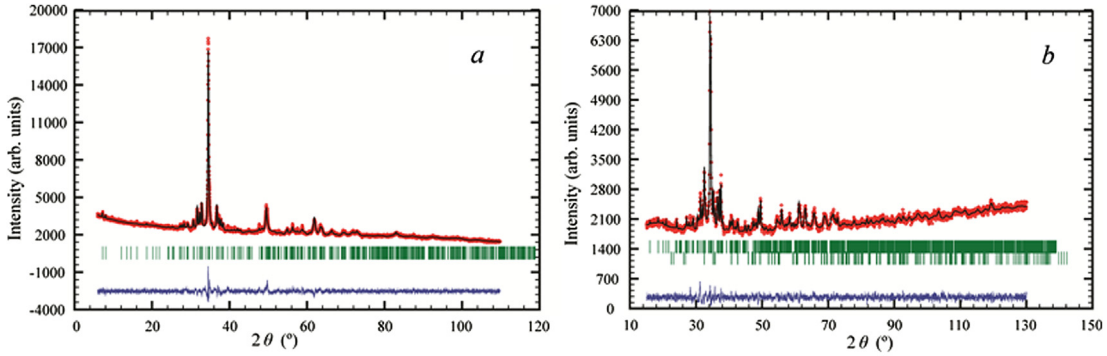


**Fig. 1.** Observed and calculated patterns and difference between them: *a* – $Tb_{11}Pd_4In_9$, *b* – $Sm_{11}Pd_4In_9$. Additional phase in alloy with Sm is SmPdIn (ZrNiAl-type).