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Synthesis and crystal structures of the new indides Dy_5Pd_2In and Y_5Pd_2In

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The new ternary indides Dy_5Pd_2In and Y_5Pd_2In were prepared by arc-melting of compact metals under an argon atmosphere with subsequent annealing at 870 K for 720 h. The crystal structure of Dy_5Pd_2In was determined from X-ray single crystal data: Mo_5SiB_2 structure type, space group *I*4/*mcm*, Pearson symbol *tI*32, $Z = 4$, $a = 7.8490(11)$, $c = 13.492(3)$ Å, $R1 = 0.0399$, $wR2 = 0.0637$, for 201 independent reflections with $I > 2\sigma(I)$ and 16 variables. The crystal structure of the isotypic compound Y_5Pd_2In (refined composition $Y_{4.69(2)}Pd_2In_{1.31(2)}$, $a = 7.798(1)$, $c = 13.598(2)$ Å) with statistical distribution of part of the yttrium and indium atoms was investigated using X-ray powder diffraction. All the atoms in the title compounds have relatively low coordination numbers: 14 and 16 for dysprosium, 9 for palladium, and 10 for indium, similarly to other intermetallic compounds with high rare-earth content. No strong bonding was observed in the structures.

Dysprosium / Palladium / Indium / Intermetallic compounds / Crystal structure / X-ray diffraction

1. Introduction

The existence of more than 120 ternary compounds has been revealed in the *RE*–Pd–In (*RE* = rare-earth metal) systems [1]. They are characterized by different compositions, crystal structures and remarkable physical properties [2], like, for example those of the heavy-fermion compound Ce_2PdIn_8 [3-10]. Most of the compounds form at a rare-earth content of up to 33.3 at.%. Only compounds with the structure types Mo_2FeB_2, $Lu_5Ni_2In_4$, $Nd_{11}Pd_4In_9$, and $Lu_{14}Co_3In_3$ exist at higher rare-earth contents. Systematic investigations of the interaction of the components in the Y–Pd–In and Dy–Pd–In systems, among others, revealed the existence of ternary compounds with the composition RE_5Pd_2In (*RE* = Y, Dy). Compounds with similar composition and Mo_5B_2Si-type structure are known in *RE*–Ni–In systems (*RE* = Er, Tm) [11]. Recently a large group of isotypic compounds was discovered with cadmium and zinc (M_5T_2Cd, *M* = Ca, Yb, Eu, *T* = Cu, Ag, Au, and Yb_5Cu_2Zn) [12], and also for pnictides and tetraeles with iridium and rare earths (RE_5Ir_2X, *RE* = Y, Gd-Ho, *X* = Sn, Sb, Pb, Bi) [13].

In this work the results of a structural investigation of two new indides, Dy_5Pd_2In and Y_5Pd_2In, are presented. Preliminary data have been reported in [14,15].

2. Experimental

Compact metals with the following purities: lanthanides – 99.85 wt.%, palladium – 99.92 wt.%, indium – 99.99 wt.%, were used as starting materials for the synthesis. Samples of nominal composition $RE_{63.0}Pd_{25.0}In_{12.0}$ (*RE* = Dy, Y) were prepared by arc-melting under an argon atmosphere at a pressure of 0.7-0.8 atm. The argon was purified by melting titanium sponge. The samples were remelted twice to ensure homogeneity. The weight loss of the samples was less than 1%. The ingots were sealed in evacuated silica tubes and annealed at 870 K for 1 month, and subsequently quenched in cold water without breaking the ampoule. No reaction with the quartz tube was observed and irregularly shaped single crystals had grown on the surface of the $Dy_{63.0}Pd_{25.0}In_{12.0}$ specimen. The single crystals exhibit metallic lustre while the ground powders are gray. Single-crystal X-ray diffraction was performed at room temperature on a KM-4 CCD diffractometer with Mo *K*α radiation. The structure was solved by direct methods, and refined using the SHELXS-97 program package [16]. The yttrium polycrystalline sample was investigated at room temperature on a DRON-2.0 M diffractometer (Fe *K*α-radiation, interval $20 \leq 2\theta \leq 120°$, scan step mode, step size 0.02° 2θ).

Table 1 Experimental details and crystallographic data for Dy_5Pd_2In.

Compound	Dy_5Pd_2In
Chemical formula weight M, g·mol^{-1}	1140.12
Pearson symbol; Z	$tI32$; 4
Space group	$I4/mcm$
Unit-cell parameters: a; c, Å	7.8490(11); 13.492(3)
Unit-cell volume V, Å^3	831.2(2)
Density D_X, g·cm^{-3}	9.111
$F(000)$	1884
Diffractometer	KM-4 CCD
Radiation; wavelength, Å	Mo $K\alpha$; 0.71073
Absorbtion coefficient μ, mm^{-1}	51.179
Extinction coefficient	0.00019(4)
Range hkl	$-9 \leq h \leq 9$; $-9 \leq k \leq 9$; $-15 \leq l \leq 15$
Temperature, K	293(2)
θ_{min}-θ_{max}, °	3.67-24.63°
Total number of reflections	3151
Independent reflections	208
Reflections with $I > 2\sigma(I)$	201
R_{int}	0.0733
Size of the crystal, mm	0.07 × 0.03 × 0.03
Color of the crystal	grey
Data/parameters	201/16
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.384
$R[I > 2\sigma(I)]$: R_1; wR_2	0.0399; 0.0637
R[all]: R_1; wR_2	0.0432; 0.0645

Table 2 Experimental details and crystallographic data for $Y_{4.69}Pd_2In_{1.31}$.

Compound	$Y_{4.69(2)}Pd_2In_{1.31(2)}$
Chemical formula weight M, g·mol^{-1}	780.18
Unit-cell parameters: a; c, Å	7.798(1); 13.598(2)
Unit-cell volume V, Å^3	826.9(2)
Density D_X, g·cm^{-3}	6.286
Scale factor	$0.82(1)\cdot10^{-5}$
Texture parameter G [direction]	0.946(8) [001]
Number of reflections	101
Range 2θ, °	0.232(9)
Profile parameters U; V; W	0.22(7); -0.15(9); 0.12(3)
Mixing parameter η	1.20(4)
Asymmetry parameter C_M	0.01(2)
Number of refined parameters	17
Reliability factors R_B; R_p; R_{wp}	0.1341; 0.0483; 0.0654
Goodness of fit S	0.81

The FullProf.2k (version 4.40) program package [17] was used for phase analysis and Rietveld refinement. Experimental details and crystallographic data for the Dy_5Pd_2In and Y_5Pd_2In compounds are listed in Table 1 and Table 2, respectively.

3. Results and discussion

The crystallographic data and details of the data collection for the single crystal of Dy_5Pd_2In are listed in Table 1. Starting atomic parameters were derived by direct methods with SHELXS-97. The structure was refined in space group $I4/mcm$ with SHELXL-97 [16], using anisotropic atomic displacement parameters. The final electron-density difference map was flat and did not reveal any significant residual peaks. All the crystallographic positions are fully occupied. Final atomic positional and displacement parameters of Dy_5Pd_2In are presented in Table 3 and Table 4. The compound Dy_5Pd_2In crystallizes with the structure type Mo_5SiB_2 [18], which is a superstructure of the Cr_5B_3 type [19]. The crystal structure of the isotypic yttrium compound was refined from X-ray powder data (Fig. 1, Table 5) (a = 7.798(1), c = 13.598(2) Å, R_p = 0.0483, R_{wp} = 0.0654). Wyckoff position 4*c* in the yttrium compound is occupied by a mixture of Y and In atoms (Table 5) and the composition corresponds to the formula $Y_{4,69(2)}Pd_2In_{1,31(2)}$, similarly to $Tm_{4,83}Ni_2In_{1,17}$ [11]. In the Dy_5Pd_2In compound the same position is fully occupied by dysprosium atoms.

Table 3 Atomic coordinates, equivalent displacement parameters and site occupancies for Dy_5Pd_2In.

Atom	Site	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}, Å$^{2\ a}$
Dy1	4*c*	0	0	0	0.0201(6)
Dy2	16*l*	0.15701(10)	0.34299(10)	0.14252(7)	0.0189(5)
Pd	8*h*	0.3657(2)	0.1343(2)	0	0.0172(6)
In	4*a*	0	0	¼	0.0170(7)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 4 Anisotropic displacement parameters (Å^2) for Dy_5Pd_2In.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Dy1	0.0217(8)	U_{11}	0.017(1)	0	0	0
Dy2	0.0210(5)	U_{11}	0.0146(6)	0.0016(4)	0.0003(3)	-0.0003(3)
Pd	0.0187(9)	U_{11}	0.014(1)	0.001(1)	0	0
In	0.019(1)	U_{11}	0.014(1)	0	0	0

Table 5 Atom coordinates and isotropic displacement parameters for $Y_{4.69}Pd_2In_{1.31}$.

Atom	Site	*x*/*a*	*y*/*b*	*z*/*c*	Occ.	B_{iso}, Å^2
Y1/In1	4*c*	0	0	0	0.69(2)/0.31(2)	0.2(1)
Y2	16*l*	0.1595(6)	0.6595(6)	0.1422(4)	1	0.2(1)
Pd	8*h*	0.3694(9)	0.8694(9)	0	1	1.3(2)
In2	4*a*	0	0	¼	1	1.4(3)

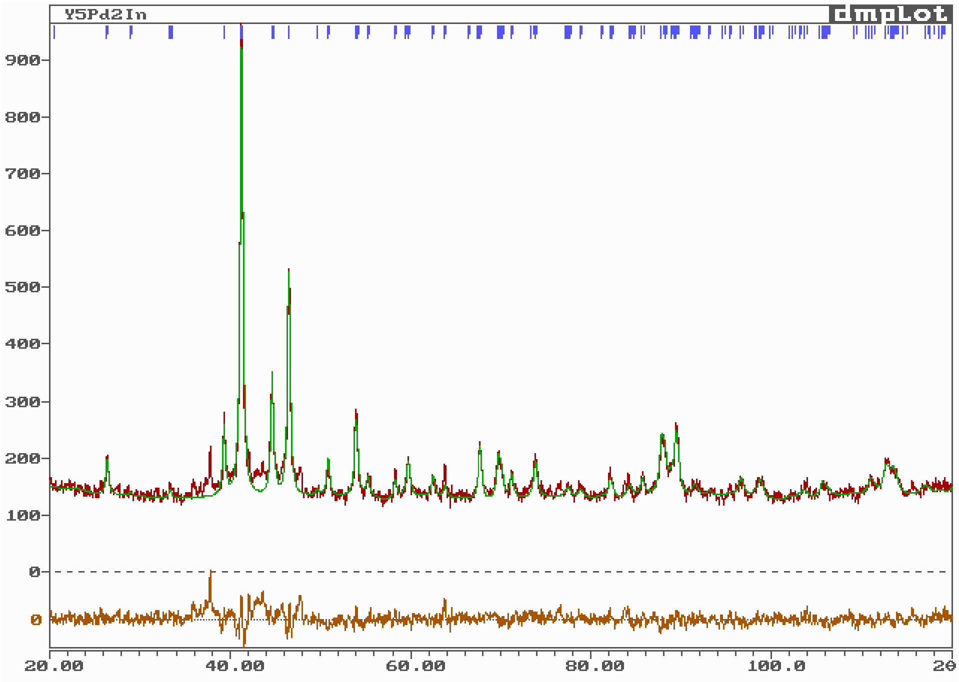

Fig. 1 Observed, calculated and difference X-ray powder diffraction patterns of $Y_{4.69}Pd_2In_{1.31}$ (DRON-2.0M, Fe *K*α radiation).

The interatomic distances (δ), reductions of the interatomic distances with respect to the sum of the atomic radii ($\Delta = 100(\delta - \Sigma r) / \Sigma r$, where Σr is the sum of the respective atomic radii), and the coordination numbers of the atoms in the Dy_5Pd_2In compound are listed in Table 6 (values of the atomic radii are taken from [20]: r(Dy) = 1.773 Å, r(Pd) = 1.376 Å, r(In) = 1.626 Å). The majority of the interatomic distances are in good agreement with the size of the atoms. Some Dy-Dy and Dy-Pd interatomic distances are slightly shorter than the sum of the atomic radii, but not more than 5% (Table 6).

The projection of the crystal structure of Dy_5Pd_2In onto the *xz* plane and the coordination polyhedra (CP) of the atoms can be seen in Fig. 2. The structure can be considered as an intergrowth of Al_2Cu- (composition Dy_2In) and U_3Si_2- (composition Dy_3Pd_2) related slabs, and belongs to a homological series of compounds with the general formula written as $RE_{2m+3n}T_{2n}X_m$, where T and X are transition metals and indium, respectively. The numbers $m = n = 1$ correspond to the numbers of Al_2Cu and U_3Si_2 blocks [21] (Fig. 2).

Table 6 Interatomic distances (δ), distance reductions (Δ; see text) and coordination numbers (CN) for the Dy_5Pd_2In compound.

Atoms		δ, Å	CN	Δ, %
Dy1	4 Pd	3.058(2)	14	-2.9
	2 In	3.3730(8)		-0.8
	8 Dy2	3.5304(9)		-0.4
Dy2	2 Pd	2.993(2)	16	-5.0
	Pd	3.011(2)		-4.4
	2 In	3.2968(9)		-3.0
	Dy2	3.486(1)		-1.7
	2 Dy1	3.5304(9)		-0.4
	Dy2	3.560(1)		+0.4
	2 Dy2	3.806(1)		+7.3
	Dy2	3.846(2)		+8.5
	4 Dy2	4.187(1)		+18.1
Pd	Pd	2.982(2)	9	+8.4
	4 Dy2	2.993(2)		-5.0
	2 Dy2	3.011(2)		-4.4
	2 Dy1	3.058(2)		-2.9
In	8 Dy2	3.2968(9)	10	-3.0
	2 Dy1	3.3730(8)		-0.8

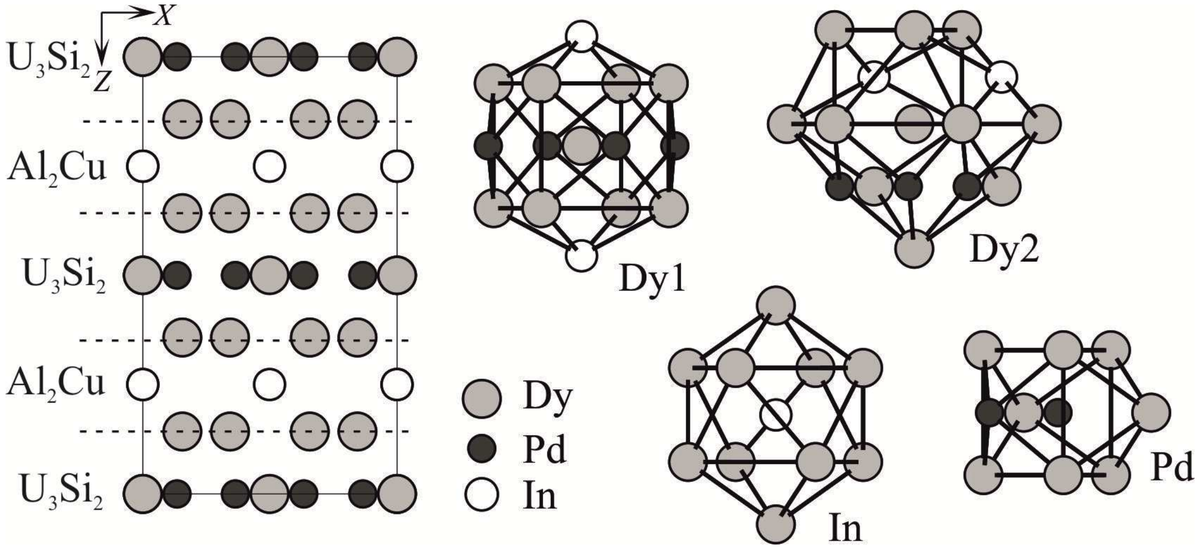

Fig. 2 Unit cell of the Dy_5Pd_2In compound, slabs of Al_2Cu and U_3Si_2 and coordination polyhedra of the atoms.

The coordination polyhedra (CP) of the Dy atoms have 14 and 16 vertices and consist of atoms of all sorts. The CP of the Dy1 atoms is a tetragonal prism with six additional atoms [$Dy1(Dy_8Pd_4In_2)$]. The CP of Dy2 can be described as a pentagonal prism with additional atoms [$Dy2(Dy_{11}Pd_2In_3)$]. It is interesting to note that the distances to the four Dy2 atoms, 4.187(1) Å, are considerably larger than the sum of the radii of the dysprosium atoms (3.546 Å). These CP are similar to the corresponding CP of the La1 atoms in the structure of $La_6Co_{13}In$ [22]. The Pd atoms are surrounded by trigonal prisms of Dy atoms with two Dy and one Pd capping lateral faces: [$Pd(Dy_8Pd_1)$]. Such polyhedra, centered by transition metal atoms, are typical for the structures of $RE_{12}Co_6In$ ($Sm_{12}Ni_6In$-type) [23], RE_6Co_2In (Ho_6Co_2Ga-type) [24,25], $RE_{12}Fe_2In_3$ ($Er_{12}Fe_2In_3$-type) [26], and $RE_{14}Co_3In_3$ ($Lu_{14}Co_3In_3$-type) [27,28] and many two-layered structures of ternary indides [1]. The coordination number of the indium atoms is equal to 10. Only dysprosium atoms form the base-capped tetragonal antiprisms, and this CP is similar to the CP of the indium atoms in the $La_6Co_{13}In$ compound [22]. Icosahedra (or distorted icosahedra) are typical CP for other *RE*-rich indides of transition metals [23-28].

The Dy_5Pd_2In compound belongs to a group of compounds, which are limited by the line RET_2–*RE*In on the concentration triangle *RE*–*T*–In, (*T* = transition metal) according to its stoichiometry [1]. The structure types are complex multilayer structures. The coordination numbers of all of the atoms are relatively low, which is not common for intermetallic compounds of rare earths with high transition-metal content [1].

It should be noted that the structures of this group of compounds is characterized by the existence of transition metal (T_2) dumb-bells with short interatomic distances: Co-Co ($\delta = 2.423$ Å) for $La_8Co_2In_3$ [29], Ni-Ni ($\delta = 2.463$ Å) for $Sm_{12}Ni_6In$ [23], Co-Co ($\delta = 2.227$ Å) for Ho_6Co_2In [25], Fe-Fe ($\delta = 2.294$ Å) for $Dy_6Fe_{1.72}In$ [30], and Fe-Fe ($\delta = 2.241$ Å) for $Er_{12}Fe_2In_3$ [26]. In Dy_5Pd_2In the distances between the Pd atoms within the dumb-bells are slightly longer than the sum of the atomic radii ($\delta = 2.982$ Å). Only rare-earth atoms form the coordination sphere of the *d*-metal dumb-bells in the structures of Dy_5Pd_2In, $Sm_{12}Ni_6In$, Ho_6Co_2Ga, $Dy_6Fe_{1.72}In$, and $Er_{12}Fe_2In_3$, whereas lanthanum and two indium atoms form the coordination sphere of the Co_2 dumb-bells in $La_8Co_2In_3$.

4. Conclusions

The crystal structure of the Dy_5Pd_2In compound, which crystallizes in the structure type Mo_5B_2Si, has been investigated on single-crystal X-ray diffraction data: space group *I*4/*mcm*, Pearson symbol *tI*32, $Z = 4$, $a = 7.8490(11)$, $c = 13.492(3)$ Å, $R1 = 0.0399$, $wR2 = 0.0637$, for 201 independent reflections with $I > 2\sigma(I)$ and 16 variables. No strong Pd-Pd bonding is observed in this structure. The structure of Dy_5Pd_2In belongs to the homological series with formula $RE_{2m+3n}M_{2n}X_m$, which is a combination of the Al_2Cu (*m*) and U_3Si_2 (*n*) types. The isotypic compound $Y_{4.69(2)}Pd_2In_{1.31(2)}$ with statistical distribution of part of yttrium and indium atoms, was discovered in the Y–Pd–In system. The crystal structure was refined from X-ray powder data.

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