

Synthesis and crystal structures of $\text{Nd}_6\text{Pt}_{13}\text{In}_{22}$, $\text{Sm}_6\text{Pt}_{12.30}\text{In}_{22.70}$, and $\text{Gd}_6\text{Pt}_{12.48}\text{In}_{22.52}$

Vasyl I. Zaremba^a, Vitaliy P. Dubenskiy^a, Ute Ch. Rodewald^b, Birgit Heying^b,
Rainer Pöttgen^{b,*}

^a*Inorganic Chemistry Department, Ivan Franko National University of Lviv, Kyryla and Mephodiya Street 6, 79005 Lviv, Ukraine*

^b*Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstrasse 36, D-48149 Münster, Germany*

Received 26 October 2005; received in revised form 6 December 2005; accepted 10 December 2005

Available online 20 January 2006

Abstract

The rare earth-platinum-indides $\text{Nd}_6\text{Pt}_{13}\text{In}_{22}$, $\text{Sm}_6\text{Pt}_{12.30}\text{In}_{22.70}$, and $\text{Gd}_6\text{Pt}_{12.48}\text{In}_{22.52}$ were synthesized from the elements by arc-melting of the components. Single crystals were grown using special annealing sequences. The three indides were investigated by X-ray powder and single crystal diffraction: $\text{Tb}_6\text{Pt}_{12}\text{In}_{23}$ type, $C2/m$, $Z = 2$, $a = 2811.9(6)$, $b = 441.60(9)$, $c = 1486.6(3)$ pm, $\beta = 112.10(3)^\circ$, $wR_2 = 0.0629$, 3645 F^2 values, 126 variables for $\text{Nd}_6\text{Pt}_{13}\text{In}_{22}$, $a = 2821.9(6)$, $b = 443.06(9)$, $c = 1481.0(3)$ pm, $\beta = 112.39(3)^\circ$, $wR_2 = 0.0543$, 3679 F^2 values, 127 variables for $\text{Sm}_6\text{Pt}_{12.30}\text{In}_{22.70}$, and $a = 2818.5(6)$, $b = 439.90(9)$, $c = 1480.9(3)$ pm, $\beta = 112.29(3)^\circ$, $wR_2 = 0.0778$, 3938 F^2 values, 127 variables for $\text{Gd}_6\text{Pt}_{12.48}\text{In}_{22.52}$. Most platinum atoms in these structures have a distorted trigonal prismatic coordination by rare earth metal and indium atoms. Together, the platinum and indium atoms build up a complex three-dimensional $[\text{Pt}_{12+x}\text{In}_{23-x}]$ polyanionic network in which the rare earth metal atoms fill distorted pentagonal and hexagonal channels. The $2c$ Wyckoff site in these structures plays a peculiar role. This site is occupied by indium in the prototype $\text{Tb}_6\text{Pt}_{12}\text{In}_{23}$, while platinum atoms fill the $2c$ site in $\text{Nd}_6\text{Pt}_{13}\text{In}_{22}$, leading to a linear Pt_3 chain with Pt–Pt distances of 275 pm. The crystals with samarium and gadolinium as rare earth metal component show mixed Pt/In occupancies.

© 2005 Elsevier Inc. All rights reserved.

Keywords: Intermetallic compounds; Crystal structure; Indium

1. Introduction

High-quality single crystals of indium-rich (more than 50 at% per formula unit) rare earth (RE)-transition metal (T)-indides can be grown via indium flux techniques. Either the elements are reacted directly with an excess of indium, or a precursor alloy is re-crystallized from liquid indium via a special temperature program. The excess indium can softly be removed with diluted acetic acid. An overview on the different compounds and metal flux techniques is given in [1] and [2].

In the RE –Pt–In systems, the indium-rich compounds $RE\text{PtIn}_3$ ($RE = \text{La, Ce, Pr, Nd, Sm}$) [3], $RE_3\text{Pt}_4\text{In}_{12}$

($RE = \text{Gd, Tb}$) [4], $RE_3\text{Pt}_4\text{In}_{13}$ ($RE = \text{La, Ce}$) [5], $\text{Dy}_2\text{Pt}_7\text{In}_{16}$ and $\text{Tb}_6\text{Pt}_{12}\text{In}_{23}$ [6], LaPtIn_4 and YbPtIn_4 [3,7], and $RE_4\text{Pt}_{10}\text{In}_{21}$ ($RE = \text{La, Ce, Pr, Nd}$) [8] have been synthesized via the indium-flux technique or through special annealing procedures. All these compounds have complex crystal structures, where the platinum and indium atoms build up three-dimensional polyanionic networks. Within the polyanionic networks, the platinum atoms are well separated from each other. The shortest Pt–Pt distances observed are in $\text{Gd}_3\text{Pt}_4\text{In}_{12}$ (338 pm) [4] and $\text{Tb}_6\text{Pt}_{12}\text{In}_{23}$ (320 pm) [6], however, these Pt–Pt distances are considerably longer than the Pt–Pt distance of 277 pm in fcc platinum [9]. Further phase analytical investigations in the RE –Pt–In systems revealed a peculiar crystal chemical situation for the $\text{Tb}_6\text{Pt}_{12}\text{In}_{23}$ structure type. The $2c$ In3 site can also be occupied by platinum (leading to a Pt_3 cluster unit) or one observes Pt/In mixing. Both

*Corresponding author. Fax: +49 251 83 36002.

E-mail addresses: vazar@franko.lviv.ua (V.I. Zaremba),
pottgen@uni-muenster.de (R. Pöttgen).

Table 1
Lattice parameters of the monoclinic indides $RE_6Pt_{12+x}In_{23-x}$

Compound	<i>a</i> (pm)	<i>b</i> (pm)	<i>c</i> (pm)	β (deg)	<i>V</i> (nm ³)	Ref.
Nd ₆ Pt ₁₃ In ₂₂ ^a	2811.9(6)	441.60(9)	1486.6(3)	112.10(3)	1.7104	This work
Nd ₆ Pt ₁₃ In ₂₂	2812.7(5)	441.7(1)	1487.2(3)	112.11(2)	1.7119	This work
Sm ₆ Pt _{12.30} In _{22.70} ^a	2821.9(6)	443.06(9)	1481.0(3)	112.39(3)	1.7121	This work
Sm ₆ Pt ₁₂ In ₂₃	2820.5(5)	443.3(1)	1480.7(3)	112.36(1)	1.7121	This work
Gd ₆ Pt _{12.48} In _{22.52} ^a	2818.5(6)	439.90(9)	1480.9(3)	112.29(3)	1.6990	This work
Gd ₆ Pt ₁₂ In ₂₃	2814.2(3)	437.82(6)	1479.9(1)	112.035(9)	1.6902	This work
Tb ₆ Pt ₁₂ In ₂₃	2834.6(4)	440.05(7)	1477.1(3)	112.37(1)	1.7038	[6]

^aSingle crystal data.

Table 2
Crystal data and structure refinement for $RE_6Pt_{12+x}In_{23-x}$ (*RE* = Nd, Sm and Gd) with Tb₆Pt₁₂In₂₃-type structure, space group *C2/m*; *Z* = 2

Empirical formula	Nd ₆ Pt ₁₃ In ₂₂	Sm ₆ Pt _{12.30(1)} In _{22.70(1)}	Gd ₆ Pt _{12.48(1)} In _{22.52(1)}
Molar mass (g/mol)	5927.65	5964.31	6005.71
Unit cell dimensions	Table 1	Table 1	Table 1
Calculated density (g/cm ³)	11.51	11.57	11.74
Crystal size (μm ³)	15 × 15 × 170	15 × 20 × 80	15 × 15 × 140
Detector distance (mm)	70	70	70
Exposure time (min)	8	12	5
ω range; increment	24–166°; 1.0°	0–180°; 1.0°	0–180°; 1.0°
Integr. param. <i>A</i> , <i>B</i> , EMS	14.0; 4.0; 0.012	14.5; 4.5; 0.012	13.5; 3.5; 0.012
Transm. ratio (max/min)	5.12	6.67	7.72
Absorption coefficient (mm ⁻¹)	76.3	77.4	79.3
<i>F</i> (000)	4904	4928	4952
θ range (deg)	3–34	3–34	3–35
Range in <i>hkl</i>	–43/+25, ±6, ±22	±43, ±6, ±22	±44, ±6, ±23
Total no. reflections	8537	11 660	12 855
Independent reflections	3645 (<i>R</i> _{int} = 0.0490)	3679 (<i>R</i> _{int} = 0.0670)	3938 (<i>R</i> _{int} = 0.0652)
Reflections with <i>I</i> > 2σ(<i>I</i>)	2873 (<i>R</i> _σ = 0.0515)	2552 (<i>R</i> _σ = 0.0781)	3266 (<i>R</i> _σ = 0.0530)
Data/parameters	3645/126	3679/127	3938/127
Goodness-of-fit on <i>F</i> ²	0.942	0.889	1.001
Weighting scheme ^a	<i>a</i> = 0.0296 <i>b</i> = 0	<i>a</i> = 0.0157 <i>b</i> = 0	<i>a</i> = 0.0397 <i>b</i> = 0
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0326 w <i>R</i> ₂ = 0.0595	<i>R</i> ₁ = 0.0362 w <i>R</i> ₂ = 0.0488	<i>R</i> ₁ = 0.0367 w <i>R</i> ₂ = 0.0734
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0495 w <i>R</i> ₂ = 0.0629	<i>R</i> ₁ = 0.0710 w <i>R</i> ₂ = 0.0543	<i>R</i> ₁ = 0.0485 w <i>R</i> ₂ = 0.0778
Extinction coefficient	0.00045(1)	0.000235(7)	0.00041(2)
Largest diff. peak and hole (e/Å ³)	2.66/–3.73	2.91/–4.74	3.33/–5.83

^aWeight = 1/[σ² (*F*_o²) + (*aP*)² + *bP*] where *P* = 1/3 max (0, *F*_o²) + 2/3 *F*_c².

situations have been observed in the indides Nd₆Pt₁₃In₂₂, Sm₆Pt_{12.30}In_{22.70}, and Gd₆Pt_{12.48}In_{22.52}. The synthesis, structure refinements, and crystal chemistry of these compounds are reported herein.

2. Experimental

2.1. Synthesis

Starting materials for the preparation of Nd₆Pt₁₃In₂₂, Sm₆Pt_{12.30}In_{22.70}, and Gd₆Pt_{12.48}In_{22.52} were ingots of the rare earth metals (Kelpin, Chempur or Johnson-Matthey), platinum powder (ca. 200 mesh, Degussa-Hüls), and

indium tear drops (Johnson-Matthey), all with stated purities better than 99.9%.

In the first step the larger rare earth ingots were cut into smaller pieces under paraffin oil. They were subsequently washed with *n*-hexane and kept under argon atmosphere prior to use. The paraffin oil and *n*-hexane were dried over sodium wire. The argon was purified before over titanium sponge (900 K), silica gel, and molecular sieves.

The rare earth pieces were then arc-melted to small buttons under an argon atmosphere of ca. 600 mbar argon in a small arc-melting furnace [10]. Subsequently, the melted rare earth buttons were mixed with cold-pressed pellets of the platinum powder and pieces of

the indium tear drops in the ideal 6:12:23 or 6:13:22 atomic ratios and arc-melted. Each sample was re-melted three times in order to ensure good homogeneity. Weight losses after the melting procedures were always smaller than 0.5 wt%. After the arc-melting procedure the $RE_6Pt_{12}In_{23}$ indides were obtained only as polycrystalline powders.

Single crystals were grown using special heat treatment. First, the alloys were powdered and cold-pressed into pellets. Next, the samples were put in small tantalum containers that have been sealed in evacuated silica tubes as an oxidation protection. The ampoules were first heated to 1300 K for the Nd compound (to 1320 K for the Sm and Gd compounds) within 6 h and held at that temperature for another 6 h. Subsequently, the temperature was lowered at a rate of 4 K/h to 900 K for the Nd compound (to 920 K for the Sm and Gd compounds), then at a rate of 10 K/h to 700 K, and finally cooled to room temperature within 10 h. After cooling, the samples could easily be separated from the tantalum container. No reaction of the samples with tantalum could be detected. The brittle samples were all stable in air as compact pieces as well as fine-grained powders. The needle-shaped single crystals exhibit metallic luster.

2.2. X-ray powder diffraction

The indides were investigated via Guinier powder patterns (imaging plate technique, Fujifilm BAS-1800) using $CuK\alpha_1$ radiation and α -quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The monoclinic lattice parameters (Table 1) were obtained from least-square fits of the Guinier powder data using a self-written computer program. The indexing of the complex powder patterns was facilitated through intensity calculations [11] using the positional parameters of the structure refinements. The lattice parameters determined from the powders and the single crystals showed reasonable agreement within two combined standard uncertainties. The course of the lattice parameters with respect to the rare earth metal component is discussed below.

2.3. Scanning electron microscopy

The crystals investigated on the diffractometer have been analyzed in a scanning electron microscope (LEICA 420i) through energy dispersive analyses of X-rays using NdF_3 , SmF_3 , GdF_3 , platinum metal, and InAs were used as standards. No impurity elements heavier than sodium have been observed. The experimentally determined compositions of 14 ± 2 at% Nd: 33 ± 2 at% Pt: 53 ± 2 at% In for $Nd_6Pt_{13}In_{22}$ (14.6:31.7:53.7), 15 ± 2 at% Sm: 30 ± 2 at% Pt: 55 ± 2 at% In for $Sm_6Pt_{12.3}In_{22.7}$ (14.6:30.0:55.4), and 15 ± 2 at% Gd: 30 ± 2 at% Pt: 55 ± 2 at% In for $Gd_6Pt_{12.48}In_{22.52}$ (14.6:30.4:55.0) were close to the compositions calculated from the structure refinements (in

parentheses). The uncertainties of the measurements of ± 2 at% arise from the irregular surface of the single crystals.

2.4. Structure refinements

Needle-shaped single crystals of the three indides were selected from the crushed samples and examined on a Buerger precession camera (white Mo radiation, Fujifilm BAS-1800 imaging plate system) in order to check the quality. The intensity data sets were recorded in oscillation mode by use of a Stoe IPDS-II diffractometer with graphite monochromatized $MoK\alpha$ radiation. The absorption corrections for these crystals were numerical (X-Shape/X-Red). All relevant crystallographic data and experimental details for the data collections are listed in Table 2.

The close structural relationship of the three new compounds with the $Tb_6Pt_{12}In_{23}$ type was already evident from the X-ray powder data. Analyses of the diffractometer data sets were compatible with space group $C2/m$. The atomic parameters of $Tb_6Pt_{12}In_{23}$ [6] were taken as starting values and the structures were refined with SHELXL-97 (full-matrix least-squares on F^2) [12] with anisotropic displacement parameters for all atoms. The refinements revealed very small equivalent isotropic displacement parameters for the $2c$ Wyckoff site, indicating a larger scattering power. From a crystal chemical point of view, it is only possible to substitute the indium atoms of the $Tb_6Pt_{12}In_{23}$ type by platinum. Refinement of the occupancy parameters of the $2c$ sites revealed full platinum occupancy for the neodymium crystal and Pt/In mixing for the samarium and the gadolinium crystals, leading to the refined compositions $Nd_6Pt_{13}In_{22}$, $Sm_6Pt_{12.30}In_{22.70}$, and $Gd_6Pt_{12.48}In_{22.52}$ for the crystals investigated. The final difference Fourier syntheses were flat for all three data sets (Table 2). The highest residual peaks were close to the platinum sites and most likely resulted from incomplete absorption corrections of these highly absorbing compounds. The positional parameters and interatomic distances of the refinements are listed in Tables 3 and 4. Further data on the structure refinements are available.¹

3. Discussion

The three new indides $Nd_6Pt_{13}In_{22}$, $Sm_6Pt_{12.30}In_{22.70}$, and $Gd_6Pt_{12.48}In_{22.52}$ have a close structural relationship with the recently reported structure of $Tb_6Pt_{12}In_{23}$ [6]. As an example we present a projection of the $Nd_6Pt_{13}In_{22}$ structure onto the xz plane in Fig. 1a. The unit cell is formed by two identical networks situated

¹Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry Nos. CSD-415864 ($Nd_6Pt_{13}In_{22}$), CSD-415865 ($Sm_6Pt_{12.30}In_{22.70}$), and CSD-415866 ($Gd_6Pt_{12.48}In_{22.52}$).

Table 3
Atomic coordinates and isotropic displacement parameters (pm^2) of $RE_6\text{Pt}_{12+x}\text{In}_{23-x}$ ($RE = \text{Nd}, \text{Sm}$ and Gd)

Atom	Wyck.	Occ.	x	y	z	U_{eq}
Nd₆Pt₁₃In₂₂						
Nd1	4i	1.00	0.45324(3)	0	0.30004(5)	84(1)
Nd2	4i	1.00	0.82120(3)	0	0.91931(5)	82(1)
Nd3	4i	1.00	0.83717(3)	0	0.46918(5)	81(1)
Pt1	4i	1.00	0.25147(2)	0	0.36333(3)	79(1)
Pt2	4i	1.00	0.38141(2)	0	0.84816(3)	83(1)
Pt3	4i	1.00	0.32036(2)	0	0.08900(3)	78(1)
Pt4	4i	1.00	0.90101(2)	0	0.36453(3)	95(1)
Pt5	4i	1.00	0.96735(2)	0	0.13891(4)	95(1)
Pt6	4i	1.00	0.39324(2)	0	0.63812(3)	83(1)
Pt7	2c	1.00	0	0	1/2	161(2)
In1	4i	1.00	0.40842(4)	0	0.04752(6)	78(2)
In2	4i	1.00	0.71263(4)	0	0.43517(6)	76(2)
In4	4i	1.00	0.76225(4)	0	0.08371(6)	77(2)
In5	4i	1.00	0.14323(4)	0	0.28181(6)	84(2)
In6	4i	1.00	0.04265(4)	0	0.33970(7)	90(2)
In7	4i	1.00	0.94468(4)	0	0.93590(6)	92(2)
In8	4i	1.00	0.32556(4)	0	0.27999(6)	102(2)
In9	4i	1.00	0.87577(4)	0	0.16870(6)	80(2)
In10	4i	1.00	0.47078(4)	0	0.82143(6)	88(2)
In11	4i	1.00	0.43497(4)	0	0.49771(6)	95(2)
In12	4i	1.00	0.72748(4)	0	0.24700(6)	83(2)
Sm₆Pt_{12.30(1)}In_{22.70(1)}						
Sm1	4i	1.00	0.45384(3)	0	0.30123(6)	95(2)
Sm2	4i	1.00	0.82103(3)	0	0.92033(6)	93(2)
Sm3	4i	1.00	0.83509(3)	0	0.46980(6)	104(2)
Pt1	4i	1.00	0.25192(2)	0	0.36348(4)	87(1)
Pt2	4i	1.00	0.38150(2)	0	0.84887(4)	88(1)
Pt3	4i	1.00	0.32044(2)	0	0.09017(4)	89(1)
Pt4	4i	1.00	0.90060(2)	0	0.36520(4)	106(1)
Pt5	4i	1.00	0.96696(2)	0	0.13908(5)	103(1)
Pt6	4i	1.00	0.39235(2)	0	0.64141(4)	98(1)
Pt7	2c	0.30(1)	0	0	1/2	138(5)
In1	4i	1.00	0.40768(4)	0	0.04810(8)	89(2)
In2	4i	1.00	0.71267(4)	0	0.43431(8)	90(1)
In3	2c	0.70	0	0	1/2	138
In4	4i	1.00	0.76219(4)	0	0.08352(8)	88(2)
In5	4i	1.00	0.14465(4)	0	0.28019(8)	91(2)
In6	4i	1.00	0.04421(4)	0	0.33298(8)	114(2)
In7	4i	1.00	0.94407(4)	0	0.93705(8)	99(2)
In8	4i	1.00	0.32552(4)	0	0.28111(8)	117(2)
In9	4i	1.00	0.87620(4)	0	0.16946(8)	93(2)
In10	4i	1.00	0.47191(4)	0	0.82561(8)	94(2)
In11	4i	1.00	0.42752(5)	0	0.49530(9)	165(3)
In12	4i	1.00	0.72735(4)	0	0.24589(8)	91(2)
Gd₆Pt_{12.48(1)}In_{22.52(1)}						
Gd1	4i	1.00	0.45386(2)	0	0.30101(5)	95(1)
Gd2	4i	1.00	0.82141(2)	0	0.92061(5)	92(1)
Gd3	4i	1.00	0.83570(2)	0	0.46935(5)	102(1)
Pt1	4i	1.00	0.25268(2)	0	0.36376(4)	83(1)
Pt2	4i	1.00	0.38104(2)	0	0.84920(4)	85(1)
Pt3	4i	1.00	0.32048(2)	0	0.08867(4)	86(1)
Pt4	4i	1.00	0.90097(2)	0	0.36479(4)	98(1)
Pt5	4i	1.00	0.96767(2)	0	0.14085(4)	100(1)
Pt6	4i	1.00	0.39168(2)	0	0.63869(4)	95(1)
Pt7	2c	0.48(1)	0	0	1/2	142(3)
In1	4i	1.00	0.40822(3)	0	0.04866(7)	82(1)
In2	4i	1.00	0.71311(3)	0	0.43502(6)	81(1)
In3	2c	0.52	0	0	1/2	142
In4	4i	1.00	0.76223(3)	0	0.08366(7)	81(1)
In5	4i	1.00	0.14473(4)	0	0.28086(7)	88(1)

Table 3 (continued)

Atom	Wyck.	Occ.	x	y	z	U_{eq}
In6	4i	1.00	0.04401(4)	0	0.33668(7)	116(2)
In7	4i	1.00	0.94415(3)	0	0.93713(7)	94(2)
In8	4i	1.00	0.32645(4)	0	0.28114(7)	106(2)
In9	4i	1.00	0.87633(3)	0	0.16950(7)	86(1)
In10	4i	1.00	0.47076(3)	0	0.82274(7)	90(2)
In11	4i	1.00	0.42976(5)	0	0.49548(7)	168(2)
In12	4i	1.00	0.72752(4)	0	0.24553(7)	87(1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

at the heights $y = 0$ and $1/2$, and are displaced relative to each other along the $[100]$ direction by the distance of $a/2$ (C -centered unit cell). The layers are built up by three-, four- and five-membered rings. Thus, the atoms of the largest size (RE) are situated only in pentagonal prisms, the atoms of medium size (In) are distributed in pentagonal and tetragonal ones, and the atoms of the smallest size (Pt) are placed in part of the trigonal prisms, while the other part of trigonal prisms remains empty. Two platinum atoms in $\text{Nd}_6\text{Pt}_{13}\text{In}_{22}$ (Pt7 in the $2c$ site) are placed in distorted square prisms. The latter are substituted by two indium atoms (In3 in the $2c$ site) in $\text{Tb}_6\text{Pt}_{12}\text{In}_{23}$. Similar layers, which are built up by three-, four- and five-membered rings, are characteristic of other ternary indides in the $RE\text{-Pt-In}$ systems— $RE_4\text{Pt}_{10}\text{In}_{21}$ [8], $\text{Ce}_6\text{Pt}_{11}\text{In}_{14}$ [13], or $RE\text{Pt}_2\text{In}_2$ [14]. The most similar structure is $\text{Yb}_2\text{Pd}_6\text{In}_{13}$ [15], in which we can single out fragments identical to those in the $\text{Nd}_6\text{Pt}_{13}\text{In}_{22}$ structure (Fig. 1b).

On the other hand, we can describe the structure of $\text{Nd}_6\text{Pt}_{13}\text{In}_{22}$ as a packing of trigonal prisms, which form columns along the $[010]$ direction (Fig. 2a). Therein we can single out two different types of chains formed by trigonal prisms, which differ in the way they are connected within the chain—either by means of double empty trigonal prisms or by means of distorted empty octahedra. The latter connect the adjoining chains at various heights. A similar type of packing trigonal prisms can also be observed in the $\text{Yb}_2\text{Pd}_6\text{In}_{13}$ structure (Fig. 2b).

The shortest interatomic distances in the $\text{Nd}_6\text{Pt}_{13}\text{In}_{22}$ structure occur for Pt-In (269–307 pm) and In-In (294–372 pm). Each platinum atoms has at least 4–7 indium neighbors at Pt-In distances smaller than 287 pm. These Pt-In bond lengths are close to the sum of the covalent radii of 279 pm [16]. Also, the 12 crystallographically independent indium atoms have between 2 and 6 shorter In-In contacts that are equal or shorter than the shortest In-In distance of 325 pm in tetragonal body-centered indium [9]. Together, the platinum and indium atoms build up a complex three-dimensional $[\text{Pt}_{13}\text{In}_{22}]$ polyanionic network in which the neodymium atoms fill distorted pentagonal and hexagonal channels (Fig. 3). This is the typical structural arrangement

Table 4

Interatomic distances (pm), calculated with the single crystal lattice parameters of Nd₆Pt₁₃In₂₂

Nd1:	2	Pt4	300.2	Pt3:	2	In9	270.5	In2:	1	Pt6	275.8	In8:	1	Pt3	278.8
	1	In11	316.8		2	In4	273.0		1	Pt1	277.8		1	Pt1	279.6
	2	In9	319.9		1	In4	273.9		2	Pt1	284.4		2	Pt4	299.2
	2	In6	322.9		1	In1	276.8		1	In12	298.0		2	In9	337.1
	1	In10	327.5		1	In8	278.8		2	In2	315.6		2	In12	342.1
	2	Pt5	338.9		2	Nd2	335.9		2	Nd3	321.8		1	Nd1	348.9
	1	In11	343.6	Pt4:	1	In9	272.5		2	In5	324.6		2	Nd3	349.3
	1	In1	348.2		1	Pt7	275.4		1	Nd3	334.5		1	In11	352.8
	1	In8	348.9		1	Nd3	278.3	In4:	2	Pt3	273.0		2	In4	355.7
	2	Pt7	353.6		2	In11	287.8		1	Pt3	273.9	In9:	2	Pt3	270.5
Nd2:	2	Pt2	319.5		2	In8	299.2		1	In12	293.9		1	Pt4	272.5
	2	In4	321.0		2	Nd1	300.2		1	In9	295.8		1	Pt5	277.2
	2	In12	321.2	Pt5:	2	In10	273.4		2	In4	320.2		1	In4	295.8
	2	In1	331.8		1	In9	277.2		2	Nd2	321.0		2	In1	319.5
	2	Pt3	335.9		2	In1	278.8		1	Nd2	343.1		2	Nd1	319.9
	1	In7	338.7		1	In7	284.0		2	In8	355.7		2	In8	337.1
	1	In4	343.1		1	In6	293.9	In5:	1	Pt1	282.1		1	Nd2	343.8
	1	In9	343.8		1	In7	307.0		2	Pt2	284.3	In10:	1	Pt2	268.8
	1	In5	349.1		2	Nd1	338.9		2	Pt6	287.4		2	Pt5	273.4
Nd3:	1	Pt4	278.3	Pt6:	1	In11	275.3		2	In2	324.6		1	Pt6	277.7
	2	Pt1	321.0		1	In2	275.8		1	In7	325.1		2	In7	304.1
	2	In2	321.8		1	In10	277.7		1	In6	325.1		2	In6	317.4
	2	Pt6	326.9		2	In6	279.1		2	In12	341.7		1	In1	321.8
	1	In2	334.5		2	In5	287.4		1	Nd2	349.1		1	Nd1	327.5
	2	In11	342.7		1	Pt2	326.2		1	Nd3	353.2		2	In5	371.6
	2	In8	349.3		2	Nd3	326.9		2	In10	371.6	In11:	1	Pt6	275.3
	1	In6	350.3	Pt7:	2	Pt4	275.4	In6:	2	Pt6	279.1		2	Pt7	285.9
	1	In5	353.2		4	In11	285.9		1	Pt5	293.9		2	Pt4	287.8
	1	In12	357.2		2	In6	304.4		1	Pt7	304.4		2	In6	315.7
Pt1:	2	In12	272.8		4	Nd1	353.6		2	In11	315.7		1	Nd1	316.8
	1	In2	277.8	In1:	1	Pt3	276.8		2	In10	317.4		2	Nd3	342.6
	1	In8	279.6		1	Pt2	276.9		2	Nd1	322.9		1	Nd1	343.7
	1	In5	282.1		2	Pt5	278.8		1	In5	325.1		1	In8	352.8
	2	In2	284.4		2	In7	315.3		1	Nd3	350.3		1	In11	363.2
	2	Nd3	321.0		2	In9	319.5	In7:	2	Pt2	282.8	In12:	2	Pt1	272.8
Pt2:	1	In10	268.8		1	In10	321.8		1	Pt5	284.0		1	Pt2	284.9
	1	In1	276.9		2	Nd2	331.8		1	In7	297.5		1	In4	293.9
	2	In7	282.8		1	Nd1	348.2		2	In10	304.1		1	In2	298.0
	2	In5	284.3						1	Pt5	307.0		2	Nd2	321.2
	1	In12	284.9						2	In1	315.3		2	In5	341.7
	2	Nd2	319.5						1	In5	325.0		2	In8	342.1
	1	Pt6	326.2						1	Nd2	338.7		1	Nd3	357.2

Standard deviations are all equal or less than 0.2 pm. All distances within the first coordination spheres are listed.

observed for a whole family of rare earth-transition metal-indides [1].

The three crystallographically independent neodymium sites have high coordination numbers, i.e. CN 15 (6 Pt + 9 In) for Nd1, CN 14 (4 Pt + 10 In) for Nd2, and CN 15 (5 Pt + 10 In) for Nd3 (Fig. 4). This is the typical coordination for rare earth metal atoms in such inter-metallic rare earth indides [1]. Nd1 and Nd3 have a distorted penta-capped pentagonal-prismatic coordination. The Nd2 coordination sphere is similar, but the In8 atoms (the 15th neighbor), coordinating the fifth rectangular site of the pentagonal prisms have the long Nd2–In8 distance of 408 pm. The shortest Nd–Nd distance is at 442 pm and corresponds to the *b* lattice parameter. In view of the average Nd–Nd distance of 367 pm in the ABAC stacking

variant of neodymium [9], we do not consider the Nd–Nd distances in Nd₆Pt₁₃In₂₂ as bonding.

The difference between the structures of Nd₆Pt₁₃In₂₂ presented here and Tb₆Pt₁₂In₂₃ [6] is the occupancy of the 2*c* site. The latter is fully occupied by indium in Tb₆Pt₁₂In₂₃, but with platinum in Nd₆Pt₁₃In₂₂. The crystals with samarium and gadolinium as rare earth metal component revealed mixed Pt–In occupancies, leading to the refined compositions Sm₆Pt_{12.30}In_{22.70}, and Gd₆Pt_{12.48}In_{22.52} for the crystals investigated.

This situation of transition metal and/or indium/gallium occupancy has also been observed in the series of U₄Ni₁₁Ga₂₀ [17] and Ho₄Ni₁₀Ga₂₁ [18]-type gallides and indides [8,19–21]. In Fig. 5 we present cutouts of these structures in order to elucidate the crystal chemical

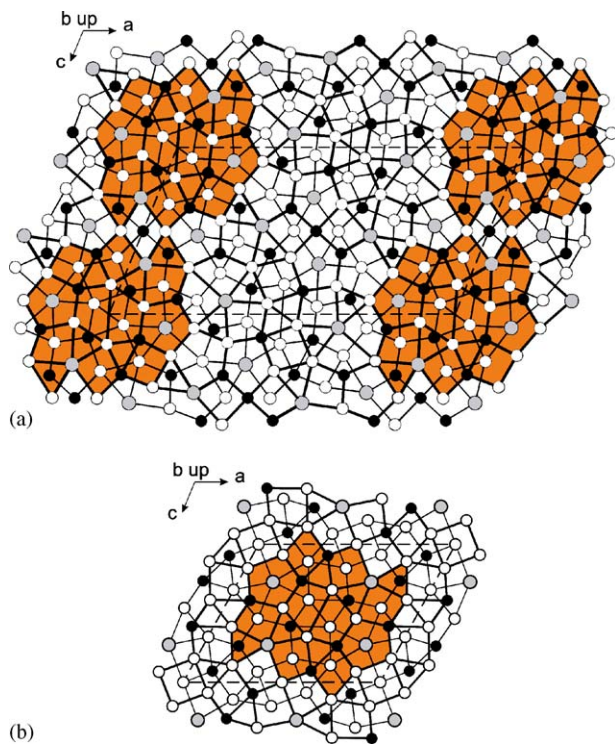


Fig. 1. (a). Projection of the $\text{Nd}_6\text{Pt}_{13}\text{In}_{22}$ structure onto the xz plane. Neodymium, platinum, and indium atoms are drawn as gray, black filled, and open circles, respectively. All atoms lie on mirror planes at $y = 0$ (thin lines) and $y = 1/2$ (thick lines), respectively. (b). Projection of the $\text{Yb}_2\text{Pd}_6\text{In}_{13}$ structure onto the xz plane. Common fragments of these structures are emphasized.

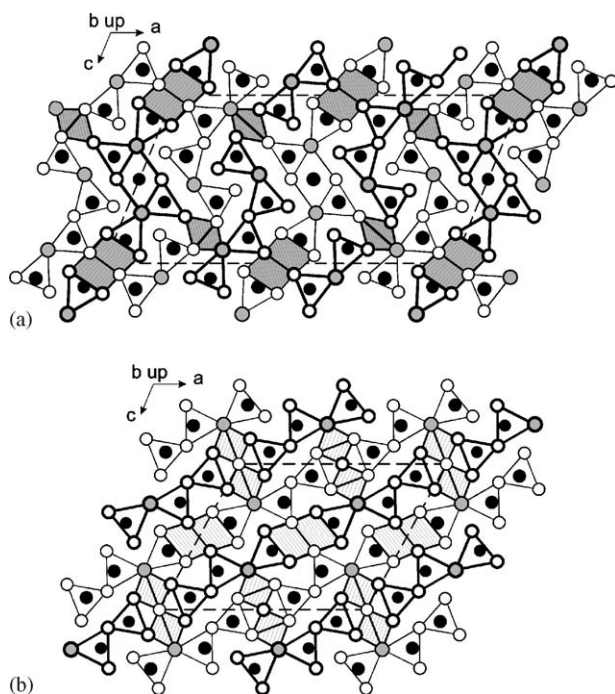


Fig. 2. Packing of the trigonal prisms and octahedra in the $\text{Nd}_6\text{Pt}_{13}\text{In}_{22}$ (a) and $\text{Yb}_2\text{Pd}_6\text{In}_{13}$ (b) structures. The empty trigonal double prisms and octahedra are shaded.

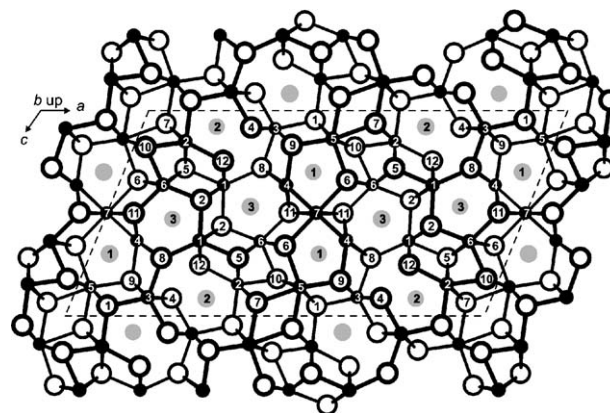


Fig. 3. View of the $\text{Nd}_6\text{Pt}_{13}\text{In}_{22}$ structure along the short unit cell axis. Neodymium, platinum, and indium atoms are drawn as gray, black filled, and open circles, respectively. The three-dimensional $[\text{Pt}_{13}\text{In}_{22}]$ network is emphasized. For clarity, only the Pt–In and Pt–Pt bonds are drawn.

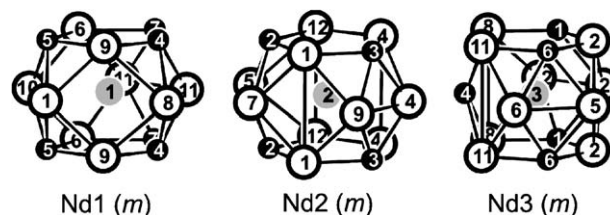


Fig. 4. Coordination polyhedra of the neodymium atoms in $\text{Nd}_6\text{Pt}_{13}\text{In}_{22}$. Neodymium, platinum, and indium atoms are drawn as gray, black filled, and open circles, respectively. Nd1, Nd2, and Nd3 have site symmetry m .

consequences of the different occupancies. In the $\text{Nd}_6\text{Pt}_{13}\text{In}_{22}$ structure the platinum atoms build a linear chain with a Pt–Pt distance of 275 pm, close to the Pt–Pt distance of 277 pm in fcc platinum [9]. We can thus assume a significant degree of Pt–Pt bonding in $\text{Nd}_6\text{Pt}_{13}\text{In}_{22}$. The linear Pt_3 chains (one-dimensional clusters) are connected via the In11 atoms. In the structures of $\text{Y}_4\text{Ni}_{11}\text{In}_{20}$ [21] and $\text{Nd}_4\text{Pd}_{10}\text{In}_{21}$ [20], the different occupancy in the nickel compound leads to a one-dimensional cluster unit. The Ni6 atoms are condensed with two Ni_2 pairs, while the In1 atoms in $\text{Nd}_4\text{Pd}_{10}\text{In}_{21}$ connect the Pd_2 dumb-bells.

Finally we need to discuss the course of the lattice parameters a , b , and c (Table 1). Since platinum (129 pm) and indium (150 pm) [16] have significantly different covalent radii, the occupancy of the $2c$ site strongly influences the a and c lattice parameters. The b lattice parameter, on the other hand, is more or less determined by the size of the rare earth element (Table 1). If the $2c$ site is occupied by the larger indium atoms, as in the case of $\text{Tb}_6\text{Pt}_{12}\text{In}_{23}$, the a lattice parameter significantly expands, in order to realize longer In3–In11 distances of 304 pm, as compared to the smaller Pt7–In11 distances of 286 pm in $\text{Nd}_6\text{Pt}_{13}\text{In}_{22}$. As a consequence to this enlargement, the c lattice parameter contracts, in order to retain the other distances.

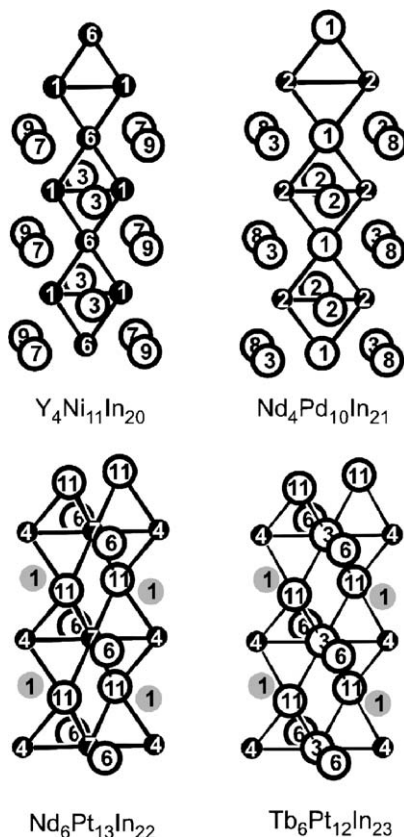


Fig. 5. Coordination of the $2c$ site in the $Nd_6Pt_{13}In_{22}$ and $Tb_6Pt_{12}In_{23}$ structure and of the $2b$ and $2d$ sites of $Nd_4Pt_{10}In_{21}$ and $Y_4Ni_{11}In_{20}$, respectively. The rare earth metal, transition metal, and indium atoms are drawn as grey, black filled, and open circles, respectively. For details see text.

Acknowledgments

We are grateful to Dr. R.-D. Hoffmann for help with the intensity data collections. This work was supported by the Deutsche Forschungsgemeinschaft. V.I.Z. is indebted to the Alexander-von-Humboldt Foundation for a research stipend.

References

- [1] Ya.M. Kalychak, V.I. Zaremba, R. Pöttgen, M. Lukachuk, R.-D. Hoffmann, Rare earth-transition metal-indides, in: K.A. Gschneider Jr., V.K. Pecharsky, J.-C. Bünzli (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 34, Elsevier, Amsterdam, 2005, pp. 1–133 (Chapter 218).
- [2] M.G. Kanatzidis, R. Pöttgen, W. Jeitschko, *Angew. Chem.* 117 (2005) 7156.
- [3] Ya.V. Galadzhun, R. Pöttgen, *Z. Anorg. Allg. Chem.* 625 (1999) 481.
- [4] U.Ch. Rodewald, V.I. Zaremba, Ya.V. Galadzhun, R.-D. Hoffmann, R. Pöttgen, *Z. Anorg. Allg. Chem.* 628 (2002) 2293.
- [5] M.F. Hundley, J.L. Sarrao, J.D. Thompson, R. Movshovich, M. Jaime, C. Petrovic, Z. Fisk, *Phys. Rev. B* 65 (2002) 024401.
- [6] V.I. Zaremba, Ya.M. Kalychak, V.P. Dubenskiy, R.-D. Hoffmann, U. Ch. Rodewald, R. Pöttgen, *J. Solid State Chem.* 169 (2002) 118.
- [7] V.I. Zaremba, U.Ch. Rodewald, R.-D. Hoffmann, Ya.M. Kalychak, R. Pöttgen, *Z. Anorg. Allg. Chem.* 629 (2003) 1157.
- [8] V.I. Zaremba, V. Hlukhyy, U.Ch. Rodewald, R. Pöttgen, *Z. Anorg. Allg. Chem.* 631 (2005) 1371.
- [9] J. Donohue, *The Structures of the Elements*, Wiley, New York, 1974.
- [10] R. Pöttgen, Th. Gulden, A. Simon, *GIT-Laborfachzeitschrift* 43 (1999) 133.
- [11] K. Yvon, W. Jeitschko, E. Parthé, *J. Appl. Crystallogr.* 10 (1977) 73.
- [12] G.M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [13] J. Stepień-Damm, Z. Bukowski, V.I. Zaremba, A.P. Pikul, D. Kaczorowski, *J. Alloy Compd.* 379 (2004) 204.
- [14] V.I. Zaremba, Ya. Galadzhun, Ya. Kalychak, D. Kaczorowski, J. Stepień-Damm, *J. Alloy Compd.* 296 (2000) 280.
- [15] V.I. Zaremba, V.P. Dubenskiy, Ya.M. Kalychak, R.-D. Hoffmann, R. Pöttgen, *Solid State Sci.* 4 (2002) 1293.
- [16] J. Emsley, *The Elements*, Oxford University Press, Oxford, 1999.
- [17] Yu.N. Grin, P. Rogl, *J. Nucl. Mater.* 137 (1986) 89.
- [18] Yu.N. Grin, Ya.P. Yarmolyuk, E.I. Gladyshevskii, *Dokl. AN SSSR* 245 (1979) 1102 (in Russian).
- [19] L. Vasylechko, W. Schnelle, U. Burkhardt, R. Ramlau, R. Niewa, H. Borrmann, K. Hiebl, Z. Hu, Yu. Grin, *J. Alloy Compd.* 350 (2003) 9.
- [20] V.I. Zaremba, U.Ch. Rodewald, Ya.M. Kalychak, Ya.V. Galadzhun, D. Kaczorowski, R.-D. Hoffmann, R. Pöttgen, *Z. Anorg. Allg. Chem.* 629 (2003) 434.
- [21] V. Hlukhyy, V.I. Zaremba, Ya.M. Kalychak, R. Pöttgen, *J. Solid State Chem.* 177 (2004) 1359.