

Transition Metal-Indium Substitution in Y_3Rh_2 -type Compounds

Roman Zaremba^a, Ute Ch. Rodewald^a, Vasyl' I. Zaremba^b, and Rainer Pöttgen^a

^a Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 30, 48149 Münster, Germany

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

Reprint requests to R. Pöttgen. E-mail: pottgen@uni-muenster.de

Z. Naturforsch. **2007**, 62b, 1397 – 1406; received May 25, 2007

New rare earth metal-rich indium compounds $RE_3T_{2-x}In_x$ ($RE = Gd, Tb, Dy, Ho, Er, Tm$; $T = Rh, Pd, Ir$) were synthesized from the elements *via* high-frequency melting and subsequent annealing in sealed silica ampoules. These intermetallics crystallize with substitution variants of the tetragonal Y_3Rh_2 -type structure, space group $I4/mcm$, $Z = 28$. All samples were studied by powder and single crystal X-ray diffraction: $a = 1164.2(2)$, $c = 2486.5(5)$ pm, for $Tb_3Rh_{1.25}In_{0.71}$, $a = 1139.4(2)$, $c = 2480.8(5)$ pm for $Er_3Rh_{1.48}In_{0.52}$, $a = 1153.7(2)$, $c = 2465.4(5)$ pm for $Tm_3Rh_{1.25}In_{0.71}$, $a = 1146.4(2)$, $c = 2498.4(5)$ pm for $Tb_3Ir_{1.62}In_{0.33}$, $a = 1154.9(2)$, $c = 2500.1(5)$ pm for $Tb_3Ir_{1.52}In_{0.44}$, $a = 1187.8(2)$, $c = 2559.2(5)$ pm for $Gd_3Pd_{1.27}In_{0.71}$, and $a = 1169.1(2)$, $c = 2530.3(5)$ pm for $Ho_3Pd_{1.27}In_{0.71}$. The indium atoms show different site occupancies on the transition metal positions, and for most crystals small defects occur for one transition metal site. $Gd_3Rh_{1.30}In_{0.64}$ ($a = 1166.3(2)$, $c = 2512.0(5)$ pm) and $Dy_3Rh_{1.31}In_{0.64}$ reveal complete rhodium–indium ordering. These two indides crystallize with the *translationengleiche* subgroup $I4/m$. The rare earth atoms in these $RE_3T_{2-x}In_x$ indides have coordination numbers between 13 and 15. A striking structural motif is the tetrahedral indium coordination in the first coordination sphere of the $RE5$ position (305 pm Gd–In in $Gd_3Rh_{1.30}In_{0.64}$). The transition metal atoms show trigonal prismatic or square anti-prismatic rare earth coordination. In all compounds investigated, the indium atoms substitute these metals only at the square prismatic sites and at one site of coordination number 10. The crystal chemical consequences of the different ordered and statistical transition metal–indium substitutions are discussed.

Key words: Indium, Intermetallics, Crystal Chemistry

Introduction

During our recent phase analytical investigations of the rare earth metal-rich parts of the rare earth metal (RE)-rhodium-indium systems we characterized the series of RE_4RhIn (Gd_4RhIn -type, space group $F\bar{4}3m$) [1] and $RE_{14}Rh_3In_3$ ($Lu_{14}Co_3In_3$ -type, space group $P4_2/nmc$) [2] indides. In both structure types, the rhodium atoms have trigonal prismatic rare earth coordination. These $RhRE_6$ prisms are condensed *via* common edges and corners, leading to three-, respectively two-dimensional networks. Such trigonal prismatic units also occur in the RE_2Rh_2In indides (Mo_2Fe_2B -type, space group $P4/mbm$) [3,4]. The trigonal prisms in these indides are condensed *via* a common rectangular face, leading to an AlB_2 related slab with Rh–Rh bonds.

In the rhodium-based systems, the RE_4RhIn , $RE_{14}Rh_3In_3$, and RE_2Rh_2In indides are pure ternary compounds. There are no binary rare earth–rhodium

compounds with related structures which would allow a substitution by indium. This is different for the palladium series. The RE_2Pd_2In indides [5] are derived from the binary compounds RE_3Pd_2 [6] by an ordered substitution at the $2a$ rare earth position by indium. Herein we report on a different substitution pattern. The binary compounds RE_3Rh_2 [7] and RE_3Ir_2 [8] (all Y_3Rh_2 -type, space group $I4/mcm$) have six crystallographically independent transition metal sites with trigonal prismatic, square prismatic, and square antiprismatic rare earth coordination. The square prismatic and one of the square antiprismatic sites show significant rhodium (iridium)/indium substitution, leading to ternary indides $RE_3Ir_{2-x}In_x$. Although the RE_3Pd_2 compounds crystallize with another structure type, the Y_3Rh_2 -type has also been observed for some indides $RE_3Pd_{2-x}In_x$. The preparation and structure refinements of $Gd_3Rh_{1.30}In_{0.64}$, $Tb_3Rh_{1.25}In_{0.71}$, $Dy_3Rh_{1.31}In_{0.64}$, $Er_3Rh_{1.48}In_{0.52}$, $Tm_3Rh_{1.25}In_{0.71}$, $Tb_3Ir_{1.62}In_{0.33}$, $Tb_3Ir_{1.52}In_{0.44}$,

Gd₃Pd_{1.27}In_{0.71}, and Ho₃Pd_{1.27}In_{0.71} are reported herein.

Experimental Section

Synthesis

Starting materials for the preparation of the RE₃Rh_{2-x}In_x, RE₃Pd_{2-x}In_x and RE₃Ir_{2-x}In_x samples were ingots of the rare earth metals (smart elements, Johnson Matthey), rhodium, palladium, and iridium powder or granules (Heraeus or Degussa-Hüls), and indium tear drops (Chempur), all with stated purities better than 99.9%. Pieces of the respective rare earth and transition metal and pieces of the indium tear drops were mixed in the atomic ratios listed in Table 1 and arc-melted [9] three times under argon pressure of *ca.* 600 mbar. The argon was purified over molecular sieves, silica gel and titanium sponge (900 K). Alternatively the elements can be inductively melted in small glassy carbon crucibles (Sigradur® G) in a high-frequency furnace (Hüttinger Elektronik, Freiburg, Typ TIG 1.5/300) [10]. Light-gray polycrystalline samples were obtained which are stable in air over months.

Single crystals of the compounds RE₃Rh_{2-x}In_x (RE = Gd–Dy, Tm), Gd₃Pd_{1.27}In_{0.71}, and Ho₃Pd_{1.27}In_{0.71} were grown *via* a special heat treatment. First, the induction-melted samples were powdered and cold-pressed into pellets of 6 mm diameter. Next, the samples were placed in small tantalum containers that were sealed in evacuated silica tubes as an oxidation protection. The ampoules were first heated within 6 h to a maximum value of 1295–1355 K and kept at that temperature for another 6 h. Subsequently, the temperature was lowered at a rate of 5 K h⁻¹ to 970 K in all cases, then at a rate of 15 K h⁻¹ to 670 K, and finally the samples were cooled to r. t. by switching off the furnace. After cooling, the samples could easily be separated from the tantalum containers. No reaction of the samples with tantalum was detected. Single crystals of irregular shape were selected. The single crystals of Er₃Rh_{1.48}In_{0.52}, Tb₃Ir_{1.62}In_{0.33}, and Tb₃Ir_{1.52}In_{0.44} were selected directly from the samples obtained by high-frequency melting.

The single crystals investigated on the diffractometer and the bulk samples were analyzed semiquantitatively by EDX in a LEICA 420 I scanning electron microscope using the lanthanoid trifluorides, rhodium, palladium, iridium, and InAs as standards. The EDX analyses revealed no impurity elements, and the results were in agreement with the compositions refined from the single crystal data.

X-Ray powder and single crystal data

The RE₃Rh_{2-x}In_x, RE₃Pd_{2-x}In_x and RE₃Ir_{2-x}In_x samples were studied by X-ray powder diffraction (Guinier technique) using CuK_{α1} radiation and α -quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The Guinier camera was

Table 1. Lattice parameters for RE₃T_{2-x}In_x compounds with tetragonal Y₃Rh₂-type and related structures.

| Compound | <i>a</i> (pm) | <i>c</i> (pm) | <i>V</i> (nm ³) | Reference |
|--------------------------------------------------------------------------|---------------|---------------|-----------------------------|-----------|
| <i>Rhodium compounds:</i> | | | | |
| Gd ₃ Rh _{1.30(1)} In _{0.64(1)} ^a | 1166.3(2) | 2512.0(5) | 3.4170 | this work |
| 6Gd : 2Rh : 1In ^b | 1171(5) | 2514(9) | 3.4473 | this work |
| Gd ₃ Rh ₂ | 1127(1) | 2532(2) | 3.2160 | [7] |
| Tb ₃ Rh _{1.25(1)} In _{0.71} ^a | 1164.2(2) | 2486.5(5) | 3.3701 | this work |
| 4Tb : 1Rh : 1In ^b | 1170.5(8) | 2491(2) | 3.4128 | this work |
| Tb ₃ Rh ₂ | 1125(1) | 2520(2) | 3.1893 | [7] |
| Dy ₃ Rh _{1.31(1)} In _{0.64(1)} ^a | 1156.6(2) | 2485.3(5) | 3.3246 | this work |
| 6Dy : 2Rh : 1In ^b | 1155(2) | 2491(3) | 3.3230 | this work |
| Dy ₃ Rh ₂ | 1116(1) | 2507(2) | 3.1224 | [7] |
| Er ₃ Rh _{1.48(2)} In _{0.52(2)} ^a | 1139.4(2) | 2480.8(5) | 3.2207 | this work |
| 21Er : 9Rh : 5In ^b | 1145.6(2) | 2478.0(2) | 3.2521 | this work |
| Er ₃ Rh ₂ | 1109(1) | 2488(2) | 3.0599 | [7] |
| Tm ₃ Rh _{1.25(1)} In _{0.71} ^a | 1153.7(2) | 2465.4(5) | 3.2815 | this work |
| 4Tm : 1Rh : 1In ^b | 1151.6(5) | 2458(2) | 3.2597 | this work |
| <i>Iridium compounds:</i> | | | | |
| Tb ₃ Ir _{1.62(1)} In _{0.33(1)} ^a | 1146.4(2) | 2498.4(5) | 3.2835 | this work |
| 6Tb : 3Ir : 1In ^b | 1153.7(8) | 2508(2) | 3.3382 | this work |
| Tb ₃ Ir _{1.52(1)} In _{0.44(1)} ^a | 1154.9(2) | 2500.1(5) | 3.3346 | this work |
| 21Tb : 9Ir : 5In ^b | 1164.5(5) | 2503(1) | 3.3942 | this work |
| Tb ₃ Ir ₂ | 1120.6(3) | 2504(1) | 3.1444 | [8] |
| <i>Palladium compounds:</i> | | | | |
| Gd ₃ Pd _{1.27(1)} In _{0.71} ^a | 1187.8(2) | 2559.2(5) | 3.6107 | this work |
| 5Gd : 2Pd : 1In ^b | 1189(1) | 2552(3) | 3.6078 | this work |
| Ho ₃ Pd _{1.27(1)} In _{0.71} ^a | 1169.1(2) | 2530.3(5) | 3.4584 | this work |
| 5Ho : 2Pd : 1In ^b | 1169.5(5) | 2530.4(9) | 3.4609 | this work |

^a Single crystal data; ^b starting composition for the samples investigated by Guinier powder data.

equipped with an imaging plate system (Fujifilm BAS-1800). The tetragonal lattice parameters (Table 1) were obtained from least-squares refinements of the Guinier data. To ensure correct indexing, the experimental patterns were compared to calculated ones [11] using the atomic positions obtained from the structure refinements.

Irregularly shaped single crystals were selected from the samples after the crystal growth procedure or directly from the melted ones (see above) and first examined by Laue photographs on a Buerger precession camera (equipped with an imaging plate system Fujifilm BAS-1800) in order to establish the crystal quality. Single crystal intensity data were collected at r. t. on a Stoe IPDS-II diffractometer with graphite monochromatized MoK_α radiation (71.073 pm) in oscillation mode. Numerical absorption corrections were applied to the data sets. All relevant crystallographic data and details for the data collections and evaluations are listed in Tables 2 and 3.

The nine data sets revealed the systematic extinctions expected for a body-centered tetragonal lattice and were in agreement with the centrosymmetric space group *I4/mcm*. The starting atomic parameters were deduced from automatic interpretations of Direct Methods with SHELXS-97 [12], and the structures were refined using SHELXL-97 (full-matrix

Table 2. Crystal data and structure refinement for Gd₃Rh_{1.30(1)}In_{0.64}, Tb₃Rh_{1.25(1)}In_{0.71}, Dy₃Rh_{1.31(1)}In_{0.64}, Er₃Rh_{1.48(2)}In_{0.52(2)}, and Tm₃Rh_{1.25(1)}In_{0.71}, *Z* = 28.

| Empirical formula | Gd ₃ Rh _{1.30(1)} In _{0.64} | Tb ₃ Rh _{1.25(1)} In _{0.71} | Dy ₃ Rh _{1.31(1)} In _{0.64} | Er ₃ Rh _{1.48(2)} In _{0.52(2)} | Tm ₃ Rh _{1.25(1)} In _{0.71} |
|-----------------------------------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|-------------------------------------------------------------|----------------------------------------------------------|
| Molar mass, g mol ⁻¹ | 679.86 | 687.38 | 695.65 | 713.83 | 717.23 |
| Crystal size, μm ³ | 30 × 40 × 70 | 40 × 100 × 250 | 20 × 70 × 70 | 20 × 20 × 100 | 20 × 50 × 70 |
| Space group | <i>I4/m</i> | <i>I4/mcm</i> | <i>I4/m</i> | <i>I4/mcm</i> | <i>I4/mcm</i> |
| Unit cell dimensions | see Table 1 | | | | |
| Calculated density, g cm ⁻³ | 9.25 | 9.48 | 9.73 | 10.31 | 10.16 |
| <i>F</i> (000), e | 7902 | 8015 | 8071 | 8291 | 8350 |
| Detector distance, mm | 60 | 60 | 55 | 80 | 80 |
| Exposure time, min | 12 | 5 | 12 | 4 | 8 |
| ω range; increment, deg | 0–180; 1.0 | 0–180; 1.0 | 0–180; 1.0 | 0–180; 1.0 | 0–180; 1.0 |
| Integr. param. A; B; EMS | 14.5; 4.5; 0.014 | 14; 4; 0.018 | 14.0; 4.0; 0.012 | 13; 3.5; 0.014 | 14; 3.5; 0.012 |
| Abs. coefficient, mm ⁻¹ | 47.3 | 50.9 | 53.9 | 61.7 | 63.7 |
| Transm. ratio (max/min) | 2.58 | 6.32 | 6.63 | 4.14 | 10.70 |
| θ range, deg | 3–35 | 3–30 | 3–32 | 2–30 | 2–32 |
| Range in <i>hkl</i> | ±18, ±18, ±40 | ±15, ±15, ±34 | ±17, ±17, ±36 | ±16, ±16, ±34 | ±17, ±17, ±36 |
| Total no. reflections | 24843 | 16840 | 19264 | 16064 | 19107 |
| Indep. refl.; <i>R</i> _{int} | 3674; 0.053 | 1341; 0.043 | 2804; 0.044 | 1287; 0.094 | 1529; 0.061 |
| Refl. with <i>I</i> ≥ 2σ(<i>I</i>); <i>R</i> _σ | 2930; 0.028 | 1113; 0.024 | 2509; 0.024 | 771; 0.075 | 1144; 0.038 |
| Data/parameters | 3674/90 | 1341/54 | 2804/90 | 1287/55 | 1529/54 |
| Goodness-of-fit on <i>F</i> ² | 0.976 | 0.974 | 1.013 | 0.694 | 0.867 |
| Final <i>R</i> ₁ ; <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)] | 0.028; 0.053 | 0.023; 0.045 | 0.024; 0.043 | 0.024; 0.043 | 0.024; 0.045 |
| Final <i>R</i> ₁ ; <i>wR</i> ₂ (all data) | 0.043; 0.057 | 0.033; 0.047 | 0.029; 0.044 | 0.058; 0.046 | 0.043; 0.047 |
| Extinction coefficient | 0.000135(5) | 0.000231(7) | 0.000110(4) | 0.000044(3) | 0.000131(4) |
| Δρ _{fin} (max/min), e Å ⁻³ | 2.23/–2.00 | 2.10/–2.78 | 1.46/–1.61 | 1.89/–1.85 | 2.13/–2.53 |

Table 3. Crystal data and structure refinement for Tb₃Ir_{1.62(1)}In_{0.33(1)}, Tb₃Ir_{1.52(1)}In_{0.44(1)}, Gd₃Pd_{1.27(1)}In_{0.71}, and Ho₃Pd_{1.27(1)}In_{0.71}, space group *I4/mcm*, *Z* = 28.

| Empirical formula | Tb ₃ Ir _{1.62(1)} In _{0.33(1)} | Tb ₃ Ir _{1.52(1)} In _{0.44(1)} | Gd ₃ Pd _{1.27(1)} In _{0.71} | Ho ₃ Pd _{1.27(1)} In _{0.71} |
|-----------------------------------------------------------------------------------|-------------------------------------------------------------|-------------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|
| Molar mass, g mol ⁻¹ | 825.69 | 819.40 | 689.12 | 711.97 |
| Crystal size, μm ³ | 10 × 40 × 70 | 40 × 40 × 280 | 10 × 50 × 160 | 20 × 40 × 100 |
| Unit cell dimensions | see Table 1 | | | |
| Calculated density, g cm ⁻³ | 11.69 | 11.43 | 8.87 | 9.57 |
| <i>F</i> (000), e | 9402 | 9341 | 7995 | 8244 |
| Detector distance, mm | 60 | 100 | 60 | 60 |
| Exposure time, min | 5 | 5 | 4 | 4 |
| ω range; increment, deg | 0–180; 1.0 | 0–180; 1.0 | 0–180; 1.0 | 0–180; 1.0 |
| Integr. param. A; B; EMS | 13.5; 3.5; 0.012 | 12.5; 3.5; 0.014 | 13.5; 3.5; 0.012 | 13.5; 3.5; 0.012 |
| Absorption coefficient, mm ⁻¹ | 91.8 | 88.1 | 45.3 | 55.1 |
| Transm. ratio (max/min) | 8.72 | 18.50 | 6.32 | 5.74 |
| θ range, deg | 3–30 | 1–30 | 2–30 | 2–30 |
| Range in <i>hkl</i> | ±16, ±16, ±34 | ±15, ±15, ±34 | ±16, ±16, ±36 | ±16, ±16, ±35 |
| Total no. reflections | 16433 | 15524 | 18087 | 17381 |
| Indep. reflections; <i>R</i> _{int} | 1304; 0.149 | 1243; 0.079 | 1433; 0.076 | 1382; 0.092 |
| Refl. with <i>I</i> ≥ 2σ(<i>I</i>); <i>R</i> _σ | 768; 0.099 | 976; 0.039 | 1023; 0.048 | 897; 0.069 |
| Data/parameters | 1304/56 | 1243/56 | 1433/54 | 1382/54 |
| Goodness-of-fit on <i>F</i> ² | 0.708 | 0.908 | 0.789 | 0.718 |
| Final <i>R</i> ₁ ; <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)] | 0.030; 0.044 | 0.026; 0.053 | 0.024; 0.041 | 0.023; 0.037 |
| Final <i>R</i> ₁ ; <i>wR</i> ₂ (all data) | 0.074; 0.049 | 0.041; 0.056 | 0.045; 0.044 | 0.052; 0.039 |
| Extinction coefficient | 0.000055(3) | 0.000081(5) | 0.000102(4) | 0.000143(3) |
| Δρ _{fin} (max/min), e Å ⁻³ | 2.67/–2.46 | 2.06/–2.57 | 1.68/–1.84 | 1.73/–2.29 |

least-squares on *F*_o²) [13] with anisotropic atomic displacement parameters for all sites. Comparison of the structures with the TYPX database [14] readily revealed isotypism with Y₃Rh₂ [7]. All atomic parameters were then transformed to the setting originally used for the yttrium compound.

The final task of the refinements was the correct site assignment for the transition metal and indium atoms. Considering the large size of indium, occupancy of the trigonal prismatic site is unlikely. Indeed, except for Er₃Rh_{1.48}In_{0.52}, all *T*1 sites show only small defects. Since indium has a stronger

Table 4. Atomic coordinates and isotropic displacement parameters (pm^2) of Gd₃Rh_{1.30(1)}In_{0.64}, Tb₃Rh_{1.25(1)}In_{0.71}, Dy₃Rh_{1.31(1)}In_{0.64}, Er₃Rh_{1.48(2)}In_{0.52(2)}, and Tm₃Rh_{1.25(1)}In_{0.71}. (U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor).

| Atom | Wyck. | Occupancy % | x | y | z | U_{eq} |
|--------------------------------------------------------------------------|-------|---------------|-------------|-------------|-------------|-----------------|
| <i>Gd₃Rh_{1.30(1)}In_{0.64} in I4/m:</i> | | | | | | |
| Gd1 | 16i | 100 | 0.20512(10) | 0.07769(12) | 0.07169(5) | 146(2) |
| Gd1a | 16i | 100 | 0.79518(10) | 0.07710(11) | 0.42798(5) | 148(2) |
| Gd2 | 16i | 100 | 0.07919(11) | 0.20324(10) | 0.19281(5) | 178(2) |
| Gd2a | 16i | 100 | 0.92155(12) | 0.20775(10) | 0.30859(5) | 187(2) |
| Gd3 | 8h | 100 | 0.34817(15) | 0.84853(15) | 0 | 142(1) |
| Gd4 | 8g | 100 | 0 | 1/2 | 0.10437(2) | 171(1) |
| Gd5 | 4d | 100 | 0 | 1/2 | 1/4 | 311(2) |
| Rh1 | 16i | 90.8(4) | 0.3170(2) | 0.8149(2) | 0.10727(2) | 198(2) |
| Rh2 | 8h | 100 | 0.0970(2) | 0.5953(2) | 0 | 143(1) |
| Rh3 | 4e | 100 | 0 | 0 | 0.13219(18) | 139(6) |
| Rh3a | 4e | 100 | 0 | 0 | 0.36876(18) | 144(6) |
| Rh4 | 4e | 100 | 0 | 0 | 0.2509(2) | 150(2) |
| Rh5 | 2b | 100 | 0 | 0 | 1/2 | 101(7) |
| In2 | 2a | 100 | 0 | 0 | 0 | 174(8) |
| In1 | 16i | 100 | 0.15606(15) | 0.65687(12) | 0.18495(2) | 175(1) |
| <i>Tb₃Rh_{1.25(1)}In_{0.71} in I4/mcm:</i> | | | | | | |
| Tb1 | 32m | 100 | 0.20597(3) | 0.07708(3) | 0.07196(1) | 85(1) |
| Tb2 | 32m | 100 | 0.07832(3) | 0.20469(3) | 0.19203(1) | 98(1) |
| Tb3 | 8h | 100 | 0.34731(4) | $x+1/2$ | 0 | 81(1) |
| Tb4 | 8g | 100 | 0 | 1/2 | 0.10320(2) | 97(1) |
| Tb5 | 4b | 100 | 0 | 1/2 | 1/4 | 179(2) |
| Rh1 | 16i | 93.8(5) | 0.31489(6) | $x+1/2$ | 0.10752(3) | 129(3) |
| Rh2 | 8h | 100 | 0.09561(7) | $x+1/2$ | 0 | 77(2) |
| Rh3 | 8f | 100 | 0 | 0 | 0.13128(3) | 73(2) |
| Rh4 | 4a | 100 | 0 | 0 | 1/4 | 73(3) |
| In1 | 16i | 100 | 0.15689(4) | $x+1/2$ | 0.18495(2) | 92(1) |
| In2 | 4c | 100 | 0 | 0 | 0 | 88(3) |
| <i>Dy₃Rh_{1.31(1)}In_{0.64} in I4/m:</i> | | | | | | |
| Dy1 | 16i | 100 | 0.20423(7) | 0.07658(6) | 0.07132(3) | 145(2) |
| Dy1a | 16i | 100 | 0.79445(7) | 0.07754(7) | 0.42813(3) | 150(1) |
| Dy2 | 16i | 100 | 0.07667(7) | 0.20613(7) | 0.19210(3) | 179(2) |
| Dy2a | 16i | 100 | 0.91989(7) | 0.20433(7) | 0.30803(3) | 171(2) |
| Dy3 | 8h | 100 | 0.34813(9) | 0.84772(9) | 0 | 142(1) |
| <i>Er₃Rh_{1.48(2)}In_{0.52(2)} in I4/mcm:</i> | | | | | | |
| Er1 | 32m | 100 | 0.20440(5) | 0.07637(5) | 0.07142(2) | 90(1) |
| Er2 | 32m | 100 | 0.07827(5) | 0.20601(5) | 0.19234(2) | 138(1) |
| Er3 | 8h | 100 | 0.34817(7) | $x+1/2$ | 0 | 83(2) |
| Er4 | 8g | 100 | 0 | 1/2 | 0.10486(4) | 116(2) |
| Er5 | 4b | 100 | 0 | 1/2 | 1/4 | 220(4) |
| Rh1 | 16i | 100 | 0.31666(9) | $x+1/2$ | 0.10712(5) | 150(3) |
| Rh2 | 8h | 100 | 0.09617(12) | $x+1/2$ | 0 | 70(4) |
| Rh3 | 8f | 100 | 0 | 0 | 0.13139(7) | 81(4) |
| Rh4 | 4a | 100 | 0 | 0 | 1/4 | 87(5) |
| In1/Rh5 | 16i | 79(6)/21(6) | 0.15616(7) | $x+1/2$ | 0.18516(5) | 117(4) |
| In2/Rh6 | 4c | 46(11)/54(11) | 0 | 0 | 0 | 75(8) |
| <i>Tm₃Rh_{1.25(1)}In_{0.71} in I4/mcm:</i> | | | | | | |
| Tm1 | 32m | 100 | 0.20675(3) | 0.07740(3) | 0.07209(1) | 94(1) |
| Tm2 | 32m | 100 | 0.07695(3) | 0.20394(3) | 0.19194(1) | 84(1) |
| Tm3 | 8h | 100 | 0.34838(5) | $x+1/2$ | 0 | 95(1) |
| Tm4 | 8g | 100 | 0 | 1/2 | 0.10290(3) | 97(1) |
| Tm5 | 4b | 100 | 0 | 1/2 | 1/4 | 120(2) |
| Rh1 | 16i | 93.5(6) | 0.31490(6) | $x+1/2$ | 0.10750(4) | 131(4) |
| Rh2 | 8h | 100 | 0.09555(8) | $x+1/2$ | 0 | 78(2) |
| Rh3 | 8f | 100 | 0 | 0 | 0.13045(5) | 78(2) |
| Rh4 | 4a | 100 | 0 | 0 | 1/4 | 75(3) |
| In1 | 16i | 100 | 0.15756(5) | $x+1/2$ | 0.18553(3) | 77(1) |
| In2 | 4c | 100 | 0 | 0 | 0 | 92(3) |

| Atom | Wyck. | Occupancy % | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} |
|--------------------------------------------------------------------------|-------------|-----------------|-------------|----------------|------------|------------------------|
| <i>Tb₃Ir_{1.62(1)}In_{0.33(1)} in I4/mcm:</i> | | | | | | |
| Tb1 | 32 <i>m</i> | 100 | 0.20503(6) | 0.07542(7) | 0.07196(3) | 115(2) |
| Tb2 | 32 <i>m</i> | 100 | 0.07903(8) | 0.20781(7) | 0.19287(4) | 199(2) |
| Tb3 | 8 <i>h</i> | 100 | 0.34807(10) | <i>x</i> + 1/2 | 0 | 117(3) |
| Tb4 | 8 <i>g</i> | 100 | 0 | 1/2 | 0.10658(7) | 167(4) |
| Tb5 | 4 <i>b</i> | 100 | 0 | 1/2 | 1/4 | 219(6) |
| Ir1 | 16 <i>l</i> | 90.8(5) | 0.31778(7) | <i>x</i> + 1/2 | 0.10689(5) | 160(4) |
| Ir2 | 8 <i>h</i> | 100 | 0.09484(7) | <i>x</i> + 1/2 | 0 | 84(3) |
| Ir3 | 8 <i>f</i> | 100 | 0 | 0 | 0.13299(5) | 82(3) |
| Ir4 | 4 <i>a</i> | 100 | 0 | 0 | 1/4 | 96(4) |
| In1/Ir5 | 16 <i>l</i> | 51(1)/49(1) | 0.15541(6) | <i>x</i> + 1/2 | 0.18544(6) | 140(5) |
| In2/Ir6 | 4 <i>c</i> | 25(3)/75(3) | 0 | 0 | 0 | 93(8) |
| <i>Tb₃Ir_{1.52(1)}In_{0.44(1)} in I4/mcm:</i> | | | | | | |
| Tb1 | 32 <i>m</i> | 100 | 0.20539(5) | 0.07583(5) | 0.07206(2) | 127(1) |
| Tb2 | 32 <i>m</i> | 100 | 0.07897(5) | 0.20592(5) | 0.19260(2) | 180(2) |
| Tb3 | 8 <i>h</i> | 100 | 0.34793(7) | <i>x</i> + 1/2 | 0 | 121(2) |
| Tb4 | 8 <i>g</i> | 100 | 0 | 1/2 | 0.10458(4) | 165(2) |
| Tb5 | 4 <i>b</i> | 100 | 0 | 1/2 | 1/4 | 272(4) |
| Ir1 | 16 <i>l</i> | 93.1(4) | 0.31675(5) | <i>x</i> + 1/2 | 0.10710(2) | 160(2) |
| Ir2 | 8 <i>h</i> | 100 | 0.09509(5) | <i>x</i> + 1/2 | 0 | 94(2) |
| Ir3 | 8 <i>f</i> | 100 | 0 | 0 | 0.13273(3) | 95(2) |
| Ir4 | 4 <i>a</i> | 100 | 0 | 0 | 1/4 | 111(2) |
| In1/Ir5 | 16 <i>l</i> | 66.4(9)/33.6(9) | 0.15559(6) | <i>x</i> + 1/2 | 0.18504(3) | 146(3) |
| In2/Ir6 | 4 <i>c</i> | 44(2)/56(2) | 0 | 0 | 0 | 104(5) |
| <i>Gd₃Pd_{1.27(1)}In_{0.71} in I4/mcm:</i> | | | | | | |
| Gd1 | 32 <i>m</i> | 100 | 0.20694(4) | 0.07776(4) | 0.07313(2) | 84(1) |
| Gd2 | 32 <i>m</i> | 100 | 0.07778(4) | 0.20840(4) | 0.19350(2) | 108(1) |
| Gd3 | 8 <i>h</i> | 100 | 0.34967(5) | <i>x</i> + 1/2 | 0 | 78(2) |
| Gd4 | 8 <i>g</i> | 100 | 0 | 1/2 | 0.10732(3) | 100(2) |
| Gd5 | 4 <i>b</i> | 100 | 0 | 1/2 | 1/4 | 177(3) |
| Pd1 | 16 <i>l</i> | 97.6(6) | 0.31583(6) | <i>x</i> + 1/2 | 0.10728(4) | 107(3) |
| Pd2 | 8 <i>h</i> | 100 | 0.09362(8) | <i>x</i> + 1/2 | 0 | 83(3) |
| Pd3 | 8 <i>f</i> | 100 | 0 | 0 | 0.13360(5) | 99(3) |
| Pd4 | 4 <i>a</i> | 100 | 0 | 0 | 1/4 | 88(3) |
| In1 | 16 <i>l</i> | 100 | 0.15850(5) | <i>x</i> + 1/2 | 0.18507(4) | 102(2) |
| In2 | 4 <i>c</i> | 100 | 0 | 0 | 0 | 119(3) |
| <i>Ho₃Pd_{1.27(1)}In_{0.71} in I4/mcm:</i> | | | | | | |
| Ho1 | 32 <i>m</i> | 100 | 0.20768(4) | 0.07743(4) | 0.07314(2) | 69(1) |
| Ho2 | 32 <i>m</i> | 100 | 0.07747(4) | 0.20760(4) | 0.19363(2) | 92(1) |
| Ho3 | 8 <i>h</i> | 100 | 0.34946(6) | <i>x</i> + 1/2 | 0 | 63(2) |
| Ho4 | 8 <i>g</i> | 100 | 0 | 1/2 | 0.10674(4) | 80(2) |
| Ho5 | 4 <i>b</i> | 100 | 0 | 1/2 | 1/4 | 148(3) |
| Pd1 | 16 <i>l</i> | 97.3(6) | 0.31580(7) | <i>x</i> + 1/2 | 0.10741(5) | 100(4) |
| Pd2 | 8 <i>h</i> | 100 | 0.09362(10) | <i>x</i> + 1/2 | 0 | 64(3) |
| Pd3 | 8 <i>f</i> | 100 | 0 | 0 | 0.13289(6) | 72(3) |
| Pd4 | 4 <i>a</i> | 100 | 0 | 0 | 1/4 | 66(4) |
| In1 | 16 <i>l</i> | 100 | 0.15781(6) | <i>x</i> + 1/2 | 0.18550(4) | 87(2) |
| In2 | 4 <i>c</i> | 100 | 0 | 0 | 0 | 90(4) |

Table 5. Atomic coordinates and isotropic displacement parameters (pm²) of Tb₃Ir_{1.62(1)}In_{0.33(1)}, Tb₃Ir_{1.52(1)}In_{0.44(1)}, Gd₃Pd_{1.27(1)}In_{0.71}, and Ho₃Pd_{1.27(1)}In_{0.71}. (*U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor).

scattering power than palladium and rhodium, these defects are unambiguous for the rhodium- and palladium-based compounds. For the iridium compounds, a mixed Ir/In occupancy was also possible, however, in view of the short distances to the rare earth atoms, and of the analogy to the rhodium and palladium compounds, the refinements with Ir1 defects are the correct ones.

From the other five crystallographically independent transition metal sites with higher coordination number, indium occupancy has only been observed on the 16*l* and 4*c* sites (Rh2 and Rh5) of the Y₃Rh₂-type. For the different crystals investigated we have observed mixed *T*/In occupancy and also full indium occupancy. A special situation occurred for the crystals of Gd₃Rh_{1.30}In_{0.64} and Dy₃Rh_{1.31}In_{0.64}.

| | | | | | | | | | | | |
|-------|--------|-------|-------|--------|-------|------|--------|-------|-------|--------|-------|
| Gd1: | 1 Rh1 | 293.9 | Gd2: | 1 Rh1 | 281.1 | Gd3: | 2 Rh1 | 274.7 | Rh2: | 2 Gd1a | 294.3 |
| | 1 Rh2 | 295.1 | | 1 Rh4 | 293.2 | | 1 Rh2 | 295.2 | | 2 Gd1 | 295.1 |
| | 1 Rh3 | 297.6 | | 1 Rh3 | 296.5 | | 1 Rh2 | 297.2 | | 1 Gd3 | 295.2 |
| | 1 In1 | 312.8 | | 1 In1 | 313.3 | | 2 Gd4 | 362.4 | | 1 Gd3 | 297.2 |
| | 1 In1 | 339.4 | | 1 In1 | 319.8 | | 2 Gd1 | 362.9 | | 2 Gd4 | 306.4 |
| | 1 Rh1 | 344.9 | | 1 Gd2a | 344.1 | | 2 Gd1a | 363.5 | Rh3: | 4 Gd2 | 296.5 |
| | 1 Gd2 | 355.0 | | 1 Gd1 | 355.0 | | 2 Gd1 | 368.6 | | 4 Gd1 | 297.6 |
| | 1 Gd1a | 359.0 | | 1 Gd2a | 355.8 | | 2 Gd1a | 369.8 | | 1 Rh4 | 298.1 |
| | 1 Gd1 | 360.2 | | 1 Gd2a | 358.1 | Gd4: | 2 Rh1 | 303.7 | | 1 In2 | 332.1 |
| | 2 Gd1 | 361.8 | | 1 In1 | 359.8 | | 2 Rh2 | 306.4 | Rh3a: | 4 Gd1a | 295.4 |
| | 1 Gd3 | 362.9 | | 2 Gd2 | 359.8 | | 2 In1 | 328.0 | | 1 Rh4 | 296.2 |
| | 1 Gd4 | 365.0 | | 1 Gd1 | 368.2 | | 2 Gd3 | 362.4 | | 4 Gd2a | 299.9 |
| | 1 Gd2 | 368.2 | | 1 Gd5 | 385.9 | | 2 Gd1a | 365.0 | | 1 Rh5 | 329.7 |
| | 1 Gd3 | 368.6 | Gd2a: | 1 Rh1 | 274.1 | | 2 Gd1 | 365.0 | Rh4: | 4 Gd2 | 293.2 |
| Gd1a: | 1 Rh1 | 292.2 | | 1 Rh4 | 296.8 | | 1 Gd5 | 365.8 | | 1 Rh3a | 296.2 |
| | 1 Rh2 | 294.3 | | 1 Rh3a | 299.9 | Gd5: | 4 In1 | 305.4 | | 4 Gd2a | 296.8 |
| | 1 Rh3a | 295.4 | | 1 In1 | 315.7 | | 2 Gd4 | 365.8 | | 1 Rh3 | 298.1 |
| | 1 Rh5 | 312.9 | | 1 In1 | 317.5 | | 4 Gd2a | 382.4 | Rh5: | 8 Gd1a | 312.9 |
| | 1 In1 | 339.8 | | 1 Gd2 | 344.1 | | 4 Gd2 | 386.0 | | 2 Rh3a | 329.7 |
| | 1 Rh1 | 341.1 | | 1 Gd1a | 350.5 | Rh1: | 1 Gd2a | 274.1 | In1: | 1 Gd5 | 305.4 |
| | 1 Gd2a | 350.5 | | 1 Gd2 | 355.8 | | 1 Gd3 | 274.7 | | 1 Gd2 | 313.3 |
| | 1 Gd1 | 359.0 | | 1 Gd2 | 358.1 | | 1 Gd2 | 281.1 | | 1 Gd2a | 315.7 |
| | 2 Gd1a | 361.0 | | 1 In1 | 360.0 | | 1 Gd1a | 292.2 | | 1 Gd2a | 317.5 |
| | 1 Gd1a | 361.8 | | 2 Gd2a | 366.3 | | 1 Gd1 | 293.9 | | 1 Gd2 | 319.8 |
| | 1 Gd3 | 363.5 | | 1 Gd1a | 367.3 | | 1 Gd4 | 303.7 | | 1 Rh1 | 327.5 |
| | 1 Gd4 | 365.0 | | 1 Gd5 | 382.4 | | 1 In1 | 327.5 | | 1 Gd4 | 328.0 |
| | 1 Gd2a | 367.3 | | | | | 1 Gd1a | 341.1 | | 1 Gd1 | 339.4 |
| | 1 Gd3 | 369.8 | | | | | 1 Gd1 | 344.9 | | 1 Gd1a | 339.8 |
| | | | | | | | | | | 1 Gd2 | 359.8 |
| | | | | | | | | | | 1 Gd2a | 360.0 |
| | | | | | | | | | In2: | 8 Gd1 | 312.8 |
| | | | | | | | | | | 2 Rh3 | 332.1 |

Table 6. Interatomic distances (pm), calculated with the powder lattice parameters of Gd₃Rh_{1.30}(1)In_{0.64} in space group *I4/m*. (Standard deviations are all equal to or less than 0.3 pm. All distances within the first coordination spheres are listed).

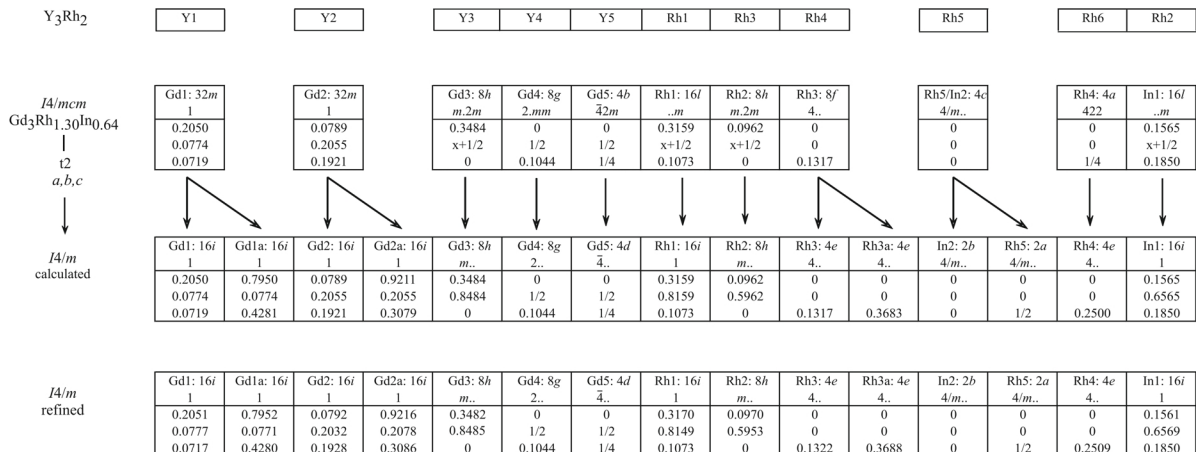


Fig. 1. Group-subgroup scheme in the Bärnighausen formalism [16–18] for the structures of Y₃Rh₂ [7] and Gd₃Rh_{1.30}In_{0.64}. The index for the *translationengleiche* symmetry reduction (t) and the evolution of the atomic parameters are also shown.

Refinement of the occupancy parameters revealed a 50% Rh/50% In occupancy for the 4c site. This allows an ordering in a lower symmetry space group. Consequently we have refined both structures in the *translationengleiche* subgroup of index 2 (t2) *I4/m* [15]. While switching from

high to low Laue symmetry, we observed twinning *via* the matrix (0 1 0, 1 0 0, 0 0 –1) and batch scale factors of *ca.* 0.5. The corresponding group-subgroup scheme in the Bärnighausen formalism [16–18] and the evolution of the atomic parameters are presented in Fig. 1.

All other sites were fully occupied within two standard uncertainties. Final difference Fourier syntheses revealed no significant residual peaks (see Tables 2 and 3). The positional parameters and interatomic distances (exemplary for Gd₃Rh_{1.30}In_{0.64}) are listed in Tables 4, 5, and 6.

Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-418098 (Gd₃Rh_{1.30}In_{0.64}), CSD-418099 (Tb₃Rh_{1.25}In_{0.71}), CSD-418100 (Dy₃Rh_{1.31}In_{0.64}), CSD-418101 (Er₃Rh_{1.48}In_{0.52}), CSD-418097 (Tm₃Rh_{1.25}In_{0.71}), CSD-418104 (Tb₃Ir_{1.62}In_{0.33}), CSD-418105 (Tb₃Ir_{1.52}In_{0.44}), CSD-418102 (Gd₃Pd_{1.27}In_{0.71}), and CSD-418103 (Ho₃Pd_{1.27}In_{0.71}).

Discussion

Nine new ternary indides RE₃T_{2-x}In_x with T = Rh, Pd, Ir with differently substituted variants of the tetragonal Y₃Rh₂-type structure [7], space group *I4/mcm*, have been synthesized and structurally characterized on the basis of single crystal diffractometer data. This structural arrangement has so far only been observed for a series of gallides RE₃(Ga_xNi_{1-x})₂ with RE = Dy, Ho, Er, Tm, Lu [19]. The structures of the gallides have been studied on the basis of powder X-ray diffraction, and nickel-gallium mixing has been reported at five sites for the Er₃(Ga_xNi_{1-x})₂ structure with *x* = 0.35–0.50.

The coordination polyhedra for this series of compounds are exemplarily shown for Tm₃Rh_{1.25}In_{0.71} in Fig. 2. The structure contains five crystallographically independent thulium sites with coordination numbers ranging from 13 to 15. Only the Tm3 atoms have exclusively thulium and rhodium atoms in their coordination shell. All other thulium atoms have also indium neighbors. A peculiar situation occurs for the Tm5 coordination. Four In1 atoms in tetrahedral coordination at Tm5–In1 of 302 pm are the nearest neighbors. These Tm–In distances are even slightly shorter than the sum of the covalent radii of 306 pm [20]. We can thus consider a first and a second coordination sphere for the Tm5 atoms.

The Tm–Tm distances cover the large range from 337 to 416 pm. In contrast to *hcp* thulium (Tm–Tm distances: 6 × 354 and 6 × 366 pm) [21], we observe even shorter Tm–Tm distances in this ternary compound, indicating strong Tm–Tm bonding. Similar short Tm–Tm contacts also occur in

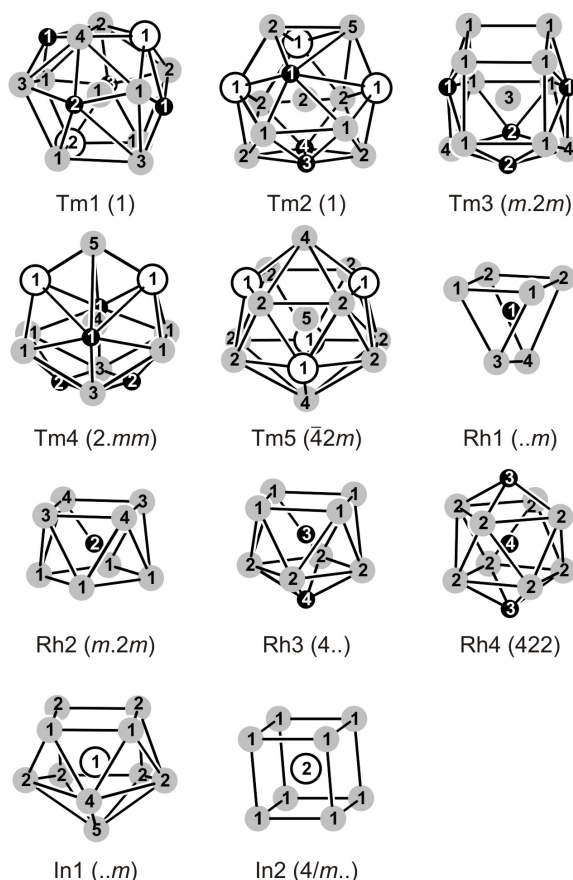


Fig. 2. Coordination polyhedra in the structure of Tm₃Rh_{1.25}In_{0.71}. The thulium, rhodium, and indium atoms are drawn as grey, filled, and open circles, respectively. Atom designations and site symmetries are indicated.

the thulium-rich compounds Tm₁₄Rh₃In₃ (340 pm) [2] and Tm₄RhIn (341 pm) [1]. The Tm–Rh distances in Tm₃Rh_{1.25}In_{0.71} cover a broad range (271 to 302 pm). The shorter ones are even shorter than the sum of the covalent radii of 281 pm [20], indicating strong covalent Tm–Rh bonding, similar to Tm₁₄Rh₃In₃ (270–281 pm Tm–Rh) [2] and Tm₄RhIn (278 pm Tm–Rh) [1]. In the indium-rich compound Tm₁₀Rh₉In₂₀ [22], the Tm–Rh distances are slightly longer (290–305 pm).

The smallest coordination number is observed for the Rh1 atoms. These atoms have a distorted trigonal prismatic thulium coordination with Rh1–Tm distances ranging from 271 to 302 pm. In general, prismatic sites are larger than antiprismatic ones. It is thus likely that the indium atoms will preferably substitute the rhodium atoms in the square prisms. This is the

in between is filled by the Tm₅In₁₄ tetrahedra and the two-dimensional networks of condensed trigonal prisms and square antiprisms around Rh1 and Rh2, respectively. This network is emphasized at the right-hand part of Fig. 3. The condensation of the trigonal prisms and square antiprisms proceeds *via* common edges.

The nine crystals investigated differ in the occupancy of the *T*1 site and the *T*/In occupancy in the square prismatic sites at the origin of the unit cells and at 0 0 1/2. In view of the short *T*1–*RE* distances, the defects on the *T*1 sites are not unusual. Many structures of ternary rare earth–transition metal–indides feature defects for transition metal atoms on trigonal prismatic sites and this has been discussed in more detail in [22] and [23].

The different occupancy variants within the columns of condensed square prisms and antiprisms are shown in Fig. 4. While all prisms are filled with rhodium in binary Y₃Rh₂ [7], the square prisms are filled with indium in Tm₃Rh_{1.25}In_{0.71}. This is also the case for the two palladium-based indides. In the structure of Er₃Rh_{1.48}In_{0.25} we observe a statistical occupancy by rhodium and indium on these sites. For Gd₃Rh_{1.30}In_{0.64} and Dy₃Rh_{1.31}In_{0.64}, refinement in space group *I4/mcm* revealed occupancy of the 4*c* site by 50 % Rh and 50 % In. These statistics could be resolved by an ordering of rhodium and indium in the

lower symmetry space group *I4/m* as discussed above, leading to a new ordered version of the Y₃Rh₂-type. In this ordered version we observe discrete stuffed cubes for the Rh5 and In2 sites which are close to a CsCl related arrangement. These coordinations also occur for the binary equiatomic compounds GdRh [24, 25] and GdIn [26–28]. The Gd–Rh (298 pm) and Gd–In (329 pm) distances in the binary compounds, however, are somewhat smaller and longer (both 313 pm in Gd₃Rh_{1.30}In_{0.64}) than in the ternary compound (Table 6). In the ordered structures of Gd₃Rh_{1.30}In_{0.64} and Dy₃Rh_{1.31}In_{0.64} we observe a small shift of the Rh3 atoms leading to Rh3–Rh4 distances of 298 pm between two stuffed antiprisms, only slightly longer than in *fcc* rhodium (269 pm) [21]. For comparison, the rhodium atoms in CsCl-type GdRh [24, 25] are well separated (344 pm). We can thus assume some weak Rh3–Rh4 bonding in the ternary compound.

Summing up, we were able to show that at two of the six crystallographically different rhodium sites in the Y₃Rh₂-type *T*/In substitution may occur, giving rise to homogeneity ranges for all of these ternary compounds. With a 50/50 occupancy of the square prisms a new ordering variant with lower symmetry is observed.

Acknowledgement

This work was financially supported by the Deutsche Forschungsgemeinschaft.

-
- [1] R. Zaremba, U. Ch. Rodewald, R.-D. Hoffmann, R. Pöttgen, *Monatsh. Chem.* **2007**, 138, 523.
 - [2] R. Zaremba, R. Pöttgen, *J. Solid State Chem.* **2007**, in press.
 - [3] F. Hulliger, *J. Alloys Compd.* **1995**, 221, L11.
 - [4] D. Kaczorowski, P. Rogl, K. Hiebl, *Phys. Rev. B* **1996**, 54, 9891.
 - [5] M. Lukachuk, R. Pöttgen, *Z. Kristallogr.* **2003**, 218, 767.
 - [6] O. Loebich Jr., E. Raub, *J. Less-Common Met.* **1973**, 30, 47.
 - [7] J.-M. Moreau, D. Paccard, E. Parthé, *Acta Crystallogr.* **1976**, B32, 1767.
 - [8] J. Le Roy, J. M. Moreau, D. Paccard, E. Parthé, *J. Less-Common Met.* **1980**, 76, 131.
 - [9] R. Pöttgen, Th. Gulden, A. Simon, *GIT Labor Fachzeitschrift* **1999**, 43, 133.
 - [10] D. Kußmann, R.-D. Hoffmann, R. Pöttgen, *Z. Anorg. Allg. Chem.* **1998**, 624, 1727.
 - [11] K. Yvon, W. Jeitschko, E. Parthé, *J. Appl. Crystallogr.* **1977**, 10, 73.
 - [12] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.
 - [13] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen (Germany) **1997**.
 - [14] E. Parthé, L. Gelato, B. Chabot, M. Penzo, K. Cen-zual, R. Gladyshevskii, TYPX-Standardized Data and Crystal Chemical Characterization of Inorganic Structure Types, in *Gmelin Handbook of Inorganic and Organometallic Chemistry*, 8th ed., Springer, Berlin, **1993**.
 - [15] *International Tables for Crystallography*, Vol. A1, *Symmetry relations between space groups*, (Eds: H. Wondratschek, U. Müller), Kluwer Academic Publishers, Dordrecht, **2004**.
 - [16] H. Bärnighausen, *Commun. Math. Chem.* **1980**, 9, 139.
 - [17] H. Bärnighausen, U. Müller, *Symmetriebeziehungen*

- zwischen den Raumgruppen als Hilfsmittel zur straffen Darstellung von Strukturzusammenhängen in der Kristallchemie, Universities of Karlsruhe and Kassel, **1996**.
- [18] U. Müller, *Z. Anorg. Allg. Chem.* **2004**, 630, 1519.
- [19] Yu.N. Grin, Ya.P. Yarmolyuk, E.I. Gladyshevsky, *Dopov. Akad. Nauk Ukr. RSR, Ser. A* **1980**, 42, 80.
- [20] J. Emsley, *The Elements*, Oxford University Press, Oxford, **1999**.
- [21] J. Donohue, *The Structures of the Elements*, Wiley, New York, **1974**.
- [22] M. Lukachuk, U.Ch. Rodewald, V.I. Zaremba, R.-D. Hoffmann, R. Pöttgen, *Z. Anorg. Allg. Chem.* **2004**, 630, 2253.
- [23] M. Lukachuk, V.I. Zaremba, R.-D. Hoffmann, R. Pöttgen, *Z. Naturforsch.* **2004**, 59b, 182.
- [24] A.E. Dwight, R.A. Conner Jr., J.W. Downey, *Acta Crystallogr.* **1965**, 18, 837.
- [25] K.A. Gschneidner Jr., *Acta Crystallogr.* **1965**, 18, 1082.
- [26] N.C. Baenziger, J.L. Moriarty Jr., *Acta Crystallogr.* **1961**, 14, 948.
- [27] S. Delfino, A. Saccone, R. Ferro, *Z. Metallkd.* **1983**, 74, 674.
- [28] H.B. Lal, *J. Magn. Magn. Mater.* **1982**, 30, 192.