New Indides $\text{Sc}_6\text{Co}_{2.18}\text{In}_{0.82}$, $\text{Sc}_{10}\text{Ni}_9\text{In}_{19.44}$ and $\text{ScCu}_4\text{In}$ – Synthesis, Structure, and Crystal Chemistry

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New indides $\text{Sc}_6\text{Co}_{2.18}\text{In}_{0.82}$, $\text{Sc}_{10}\text{Ni}_9\text{In}_{19.44}$ and $\text{ScCu}_4\text{In}$ have been synthesized from the elements by arc-melting. Single crystals were grown by special annealing modes. The three indides were investigated via X-ray powder and single crystal diffraction: $\text{Ho}_6\text{Co}_{2}\text{Ga}$ type, $\text{Immm}$, $a = 886.7(3)$, $b = 878.0(2)$, $c = 932.1(3)$ pm, $wR_2 = 0.0517$, 711 $F^2$ values, 35 variables for $\text{Sc}_6\text{Co}_{2.18}\text{In}_{0.82}$, $\text{Ho}_{10}\text{Ni}_9\text{In}_{19}$ type, $P4/nmm$, $a = 1287.5(2)$, $c = 884.7(1)$ pm, $wR_2 = 0.0642$, 1221 $F^2$ values, 63 variables for $\text{Sc}_{10}\text{Ni}_9\text{In}_{19.44}$, and $\text{MgCu}_4\text{Sn}$ type, $F\bar{4}3m$, $a = 704.03(7)$ pm, $wR_2 = 0.2627$, 101 $F^2$ values, and 7 variables for $\text{ScCu}_4\text{In}$. The scandium rich indide $\text{Sc}_6\text{Co}_{2.18}\text{In}_{0.82}$ contains two Co dumb-bells at Co–Co distances of 221 and 230 pm. Each cobalt atom within these dumb-bells has a tricapped trigonal prismatic coordination. The In1 site has a distorted cube-like coordination by scandium and shows a mixed occupancy (36%) with cobalt. The In2 atoms have distorted icosahedral coordination. As a consequence of the small size of the scandium atoms, the In4 site in $\text{Sc}_{10}\text{Ni}_9\text{In}_{19.44}$ shows defects and was furthermore refined with a split model leading to a new distorted variant within the family of $\text{Ho}_{10}\text{Ni}_9\text{In}_{19}$ compounds. $\text{ScCu}_4\text{In}$ is an ordered version of the cubic Laves phase with scandium and indium atoms in the CN16 voids of the copper substructure. The Cu–Cu distances within the three-dimensional network of corner-sharing tetrahedra are 248.6 and 249.2 pm. The crystal chemical peculiarities of these three indide structures are briefly discussed.

Key words: Scandium, Intermetallics, Crystal Chemistry, Chemical Bonding

Introduction

Although scandium has a significantly smaller metallic radius (161 pm) than the smallest rare earth element lutetium (173 pm) [1], scandium sometimes forms intermetallic compounds that are isotopic with those of the rare earth elements [2]. So far, the indides $\text{ScNi}_4\text{In}$ (MgCu$_4$Sn type) [3], $\text{Sc}_2\text{T}_2\text{In}$ (T = Ni, Cu, Pd, Ag, Pt, Au) (MnCu$_2$Al type) [4–6], $\text{Sc}_2\text{T}_2\text{In}$ (T = Ni, Cu, Pd, Au) (Mo$_2$FeB$_2$ or U$_2$Pt$_2$Sn type) [7, 8], $\text{ScPtIn}$ with ZrNiAl structure [9], $\text{Sc}_3\text{Ni}_2\text{In}_4$ and $\text{Sc}_3\text{Rh}_2\text{In}_4$ with Lu$_3\text{Ni}_2\text{In}_4$ type [10], the Lu$_3\text{Co}_1\text{O}_7\text{In}_4$ related indides $\text{Sc}_3\text{Ni}_{2-x+y}\text{In}_x$ (x = 0.10, y = 0.24 and x = 0.30, y = 0.40), $\text{ScPd}_{0.981}\text{In}$, and $\text{ScRh}_{1.993}\text{In}_4$ [11], and a solid solution $\text{Sc}_{1–x}\text{Pd}_{x}$ [12] with CsCl structure have been reported.

Of all rare earth–transition metal–indium systems, however, those with scandium have only been scarcely investigated. We have now started a more systematic study of the scandium–transition metal–indium systems with respect to the crystal chemical peculiarities. The synthesis and structures of new indides $\text{Sc}_6\text{Co}_{2.18}\text{In}_{0.82}$, $\text{Sc}_{10}\text{Ni}_9\text{In}_{19.44}$ and $\text{ScCu}_4\text{In}$ are reported herein.

Experimental Section

Synthesis

Starting materials for the preparation of the $\text{Sc}_6\text{Co}_3\text{In}$, $\text{Sc}_{10}\text{Ni}_9\text{In}_{20}$ and $\text{ScCu}_4\text{In}$ samples were scandium ingots (Kelpin), cobalt powder (Sigma-Aldrich, 100 mesh), nickel wire (∅0.38 mm, Johnson Matthey), copper wire (Johnson Matthey, ∅1 mm), and indium tear drops (Johnson-Matthey), all with stated purities better than 99.9%. Small scandium pieces were arc-melted [13] in a first step under an argon pressure of ca. 600 mbar. This pre-melting procedure avoids shattering during the subsequent reactions with the other elements. The argon was purified over molecular sieves, silica gel and titanium sponge (900 K).
The small scandium buttons were then mixed with the transition metal and pieces of the indium tear drops in the ideal 6:2:1, 10:9:2, and 1:4:1 atomic ratios and the mixtures were subsequently melted in the same arc-melting furnace. The product pellets were turned over and remelted three times in order to ensure homogeneity. The weight losses after the different melting steps were always smaller than 0.5 weight-%. The samples are stable in air for months. No deterioration was observed. Powders of these indides are dark grey and the single crystals exhibit metallic lustre.

Single crystals of Sc₆Co₂In and Sc₁₀Ni₉In₂₀ were grown using special heat treatment. First, the alloys were powdered and cold-pressed into pellets. Next, the samples were put in tubes as an oxidation protection. The ampoules were first heated to 1290 K for the Co and to 1250 K for the Ni compound within 8 h and held at that temperature for 6 h. Subsequently, the temperature was lowered at rate 4 K/h to 970 K for the Co compound (to 870 K for the Ni compound), then at a rate of 10 K/h to 600 K for both compounds, and finally cooled to room temperature within 10 h. As a result, in both cases, single crystals of irregular shape were obtained. After cooling, the samples could easily be separated from tantalum containers. No reaction of the samples with tantalum could be detected. Sc₆Cu₄In crystals were obtained from the arc-melted button.
The isotypy of these scandium indides with the MgCu4Sn [15, 16], Ho6Co2Ga [17], and Ho10Ni9In20 [18] type structures was already evident from the X-ray powder data. The atomic positions of the latter compounds were then taken as starting values and the structures were refined using SHELXL-97 (full-matrix least-squares on \( F^2 \)) [19] with anisotropic atomic displacement parameters for all sites. For ScCu4In refinement of the Flack parameter [20, 21] ensured the correct site assignment and possible defects or mixed occupancies, the occupancy parameters were refined in separate series of least-squares cycles. For ScCu4In all sites were fully occupied within two standard uncertainties. The 2a In site was refined independently. Only the isotropic displacement parameter of both split sites was constrained at the same value. We have then obtained a stable refinement without significant residual peaks (see Table 1) in the final difference Fourier synthesis. The sum of the freely refined occupancy parameters of both split sites was similar to the occupancy obtained from the anisotropic refinement and we obtained the composition \( \text{Sc}10\text{Ni}9\text{In}19.44 \) for the investigated crystal. The crystal chemical consequences of the split model are discussed below. The positional parameters and interatomic distances of the three refinements are listed in Tables 2–4. Further details on the structure refinements are available.²

**EDX analyses**

The bulk samples and the single crystals measured on the diffractometer have been analyzed by EDX using a LEICA 420 I scanning electron microscope with scandium, cobalt, nickel, copper, and indium arsenide as standards. The single crystals mounted on the quartz fibre were coated with a thin carbon film. Pieces of the bulk samples were polished with different silica and diamond pastes and left unetched for the analyses in the scanning electron microscope in backscat-

²Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No’s. CSD–416529 (ScCu4In), CSD–416530 (Sc10Ni9In19.44), and CSD–416528 (ScCu4In).

### Table 2. Atomic coordinates and equivalent isotropic displacement parameters (pm²) of ScCu4In, Sc6Co218In0.82(1), and Sc10Ni9In19.44

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<thead>
<tr>
<th>Atom</th>
<th>Wyck.</th>
<th>Occ.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Ueq</th>
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<td>1/4</td>
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<td>0.38016(4)</td>
<td>x</td>
<td>0.40899(8)</td>
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Table 3. Interatomic distances (pm) of ScCu4In and Sc6Co2In18 calculated with the powder lattice parameters. Standard deviations are all equal or less than 0.2 pm. All distances within the first coordination spheres are listed. M denotes 64% In1 and 36% Co3 for Sc6Co2In18.

<table>
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<tr>
<td>Sc:</td>
<td>12 Cu 291.9</td>
<td>Cu: 3 Cu 248.6</td>
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<td>4 In 304.9</td>
<td>Cu: 3 Cu 249.2</td>
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<tr>
<td></td>
<td>4 Sc 304.9</td>
<td>Sc: 3 In 291.9</td>
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</tbody>
</table>

Table 4. Interatomic distances (pm), calculated with the single crystal lattice parameters of Sc10Ni9In19.44. The too short In-In distances that are affected by the In4 split positions are put in brackets. Standard deviations are all equal or less than 0.3 pm.

| Sc1: | 4 Ni2 286.3 | In2: 2 Ni2 269.7 |
|      | 4 In5 314.0 | 2 In4b 280.3 |
|      | 4 In3 318.3 | 2 In4a 286.6 |
| Sc2: | 4 Ni3 288.7 | 2 Sc4 310.4 |
|      | 4 In3 315.2 | 2 Sc3 314.3 |
|      | 4 In5 323.2 | 2 In5 317.7 |
| Sc3: | 4 Ni3 277.2 | 2 In2 337.7 |
|      | 2 In5 296.7 | In3: 2 Ni3 270.2 |
|      | 2 In1 297.4 | 1 Ni2 277.1 |
|      | 2 In4b 310.0 | 1 In4a 300.6 |
|      | 2 In2 314.3 | 2 Sc4 307.1 |
|      | 1 In3 321.6 | 1 In3 308.8 |
|      | 2 In4a 325.8 | 2 In1 313.9 |
|      | 2 Ni2 290.4 | 1 Sc1 318.3 |
|      | 2 In3 307.1 | 1 Sc3 321.6 |
|      | 2 In2 308.6 | 4 In4b 342.0 |
|      | 1 In5 318.3 | 1 Ni2 252.1 |
|      | 1 In5 325.5 | 1 Ni1 260.6 |
| Ni1: | 4 In4b 252.6 | 1 In4b [266.3] |
|      | 4 In4a 260.6 | 2 In2 286.6 |
|      | 4 In1 273.0 | 1 In1 289.1 |
| Ni2: | 1 In4a 252.1 | 1 In3 300.6 |
|      | 2 In5 264.4 | 1 In4a 304.9 |
|      | 2 In2 269.7 | 2 Sc3 325.8 |
|      | 1 In3 277.1 | 2 Sc4 349.2 |
|      | 1 In4b 278.2 | In4b: 2 In4a [39.4] |
|      | 1 Sc1 286.3 | 1 In4b [226.9] |
|      | 2 Sc4 290.5 | 1 Ni1 252.6 |
| Ni3: | 2 In1 266.6 | 1 In4a 266.3 |
|      | 2 In3 270.2 | 1 Ni2 278.2 |
|      | 1 In5 272.0 | 2 In2 280.2 |
|      | 2 Sc3 277.2 | 1 In1 307.5 |
|      | 1 Sc2 288.7 | 2 Sc3 310.0 |
|      | 1 Sc4 289.1 | 1 In3 342.0 |
| Sc10Ni9In19.44: | 2 Ni3 266.6 | In5: 2 Ni2 264.4 |
|      | 2 Ni1 273.0 | 1 Ni3 272.0 |
|      | 2 In4a 289.1 | 2 Sc3 296.7 |
|      | 2 Sc3 297.4 | 1 Sc1 314.0 |
|      | 2 In4b 307.5 | 2 In2 317.7 |
|      | 2 Sc4 308.6 | 1 Sc4 318.3 |
|      | 2 In3 313.9 | 1 Sc2 323.2 |
|      | 1 Sc2 323.2 | 1 Sc4 325.5 |
|      | 2 In5 335.2 | 2 In5 335.2 |

Discussion

Three new scandium-transition metal-indides, i.e. Sc6Co2In, Sc10Ni9In20 and ScCu4In were synthesized and their crystal structures were refined on the basis of single crystal diffractometer data. Among these compounds, ScCu4In adopts the simplest structure. The copper compound crystallizes with the cubic MgCu2Sn type structure [15,16], a ternary ordered variant of the cubic Laves phase MgCu2. This structure type was also observed for isotypic ScNi4In [3].

As emphasized in Fig. 1, the copper atoms in ScCu4In build up a three-dimensional network of corner-sharing Cu4/4 tetrahedra. The scandium and indium atoms show an ordering on the magnesium site of the Laves phase, resulting in a translationengleiche symmetry reduction of index 2 from space group Fd3m to F43m. Due to the symmetry reduction we observe a small distortion within the tetrahedral network, lead-
The crystal structure of \( \text{ScCu}_4\text{In} \). The scandium, copper, and indium atoms are drawn as medium gray, black filled, and open circles, respectively. The three-dimensional network of corner-sharing \([\text{Cu}_4]\) tetrahedra is emphasized.

Fig. 2. View of the \( \text{Sc}_6\text{Co}_{2.18}\text{In}_{0.82} \) structure approximately along the \( c \) axis. The scandium, cobalt, and indium atoms are drawn as medium gray, black filled, and open circles, respectively. The distorted cube-like \((\text{In}_1/\text{Co}_3)\) and icosahedral \((\text{In}_2)\) coordination polyhedra and the two crystallographically independent \( \text{Co}_2 \) dumb-bells are emphasized. For details see text.

Fig. 3. Cutout of the \( \text{Sc}_6\text{Co}_{2.18}\text{In}_{0.82} \) structure. The condensation of the distorted trigonal prisms around the cobalt atoms is emphasized.

Fig. 1. The crystal structure of \( \text{ScCu}_4\text{In} \). The scandium, copper, and indium atoms are drawn as medium gray, black filled, and open circles, respectively. The three-dimensional network of corner-sharing \([\text{Cu}_4]\) tetrahedra is emphasized.

The crystal structure of \( \text{Sc}_6\text{Co}_{2.18}\text{In}_{0.82} \) is presented in Fig. 2. This indide crystallizes with the orthorhombic \( \text{Ho}_6\text{Co}_2\text{Ga} \) type structure, space group \( \text{Immm} \). So far, this structure type has been observed for the series of gallides \( \text{RE}_6\text{Co}_{2.5}\text{Ga} \) and \( \text{RE}_6\text{Ni}_2\text{Ga} \) [28], some stan-nides \( \text{RE}_6\text{Ni}_2\text{Sn} \) [28] and the indides \( \text{RE}_6\text{Co}_{2.4}\text{In}_{1−x} \) \( \text{RE} = \text{Y, Sm, Gd–Tm, Lu} \) [22, 29, 30]. Similar to the holmium compound [23], also for the scandium compound we observed a small range of homogeneity \( \text{Sc}_6\text{Co}_{1+x}\text{In}_{1−x} \).

The complex structure is best described by the orthorhombic body-centered packing of two different motifs, \( i.e. \) distorted \( \text{In}_2\text{Sc}_{12} \) icosahedra and distorted \( \text{In}_1\text{Sc}_3 \) cubes. Each of these packings leaves voids that are filled by \( \text{Co}_2 \) dumb-bells: \( \text{Co}_1–\text{Co}_1 \) at 221 pm extending along \( c \) and \( \text{Co}_2–\text{Co}_2 \) at 230 pm extending along \( b \). Both \( \text{Co}–\text{Co} \) distances are significantly smaller than the average \( \text{Co}–\text{Co} \) distance of 250 pm in \( \text{hcp} \) cobalt [23], and we can assume strong \( \text{Co}–\text{Co} \) bonding within these units.

The most complex structure among these three scandium indides is \( \text{Sc}_{10}\text{Ni}_9\text{In}_{19.44} \). This compound crystallizes with the tetragonal \( \text{Ho}_{10}\text{Ni}_9\text{In}_{20} \) type, also observed for \( \text{RE} = \text{Tb, Dy, Er, Tm, Lu} \) [18, 34].
Fig. 4. Projection of the Sc$_{10}$Ni$_9$In$_{19.44}$ structure onto the $xy$ plane (left-hand drawing; for clarity, only half the structure along $c$ is shown). The scandium, nickel, and indium atoms are drawn as medium gray, black filled, and open circles, respectively. The split In$_4$ site is designated with $a$ and $b$. The local coordination of these sites is presented in the middle (split model) and right-hand (ellipsoidal presentation) drawing. The In$_4a/b$--In$_4a/b$ distances resulting from the split refinement are also given. The asterisk marked in the middle drawing indicates a position that can be occupied in some Ho$_{10}$Ni$_9x$In$_{20}$ type compounds. For details see text.

and the series of rhodium compounds $RE_{10}$Rh$_9$In$_{20}$ ($RE = Y$, Tb–Tm, Lu) [35]. However, Tb$_{10}$Ni$_9x$In$_{20}$ and Dy$_{10}$Ni$_9x$In$_{20}$ and the $RE_{10}$Rh$_9x$In$_{20}$ indides show a significant difference when compared with Sc$_{10}$Ni$_9$In$_{19.44}$ described herein. With the larger rare earth metals one observes one additional nickel or rhodium site within a trigonal prism. This position, marked with an asterisk in Fig. 4, is not occupied in Sc$_{10}$Ni$_9$In$_{19.44}$. This is a direct consequence of the small size of the scandium atoms. An occupancy of that position would result in very short Ni–In distances of 240 pm. The crystal chemistry of this structure type was described in detail already for the $RE_{10}$Rh$_9x$In$_{20}$ series [35]. Therefore, herein we focus only on the peculiarities of the Sc$_{10}$Ni$_9$In$_{19.44}$ structure.

Besides the non-occupied trigonal prism, the small size of the scandium atoms also has a drastic effect on the In$_4$ position. Refinement of the occupancy parameter revealed an occupancy of only 86%, and a small range of homogeneity Sc$_{10}$Ni$_9$In$_{20} - x$ is likely to exist. Furthermore, the In$_4$ atoms show an extremely anisotropic displacement (right-hand part of Fig. 4).

A reasonable refinement of this structure without significant residual peaks in the difference Fourier synthesis was only possible with an In$_4$ split position with free $y$ and $z$ parameters. The split positions In$_4a$ and In$_4b$ show shorter and longer In$_4a/b$--In$_4a/b$ distances. The In$_4b$ sites cannot simultaneously be occupied, since too short distances of 227 pm would result. The refined occupancy parameters of In$_4a$ (54%) and In$_4b$ (32%) are consistent with these findings. The In$_4b$ site shows the smaller occupancy.

The In$_4a$--In$_4b$ (266 pm) and In$_4a$--In$_4a$ (305 pm) distances are also shorter than the In--In distances in tetragonal body-centered indium (4 × 325 and 8 × 338 pm) [23]. Such shorter In--In distances have repeatedly been observed in ternary indides. Recent examples are the structures of La$_4$Pd$_9$In$_{21}$ [36] (286 and 289 pm), EuRh$_2$In$_8$ [37] (288 and 290 pm) or La$_3$In$_4$Ge [38] (287 pm).

Acknowledgements

We thank H.-J. Göcke for the work at the scanning electron microscope. This work was supported by the Deutsche Forschungsgemeinschaft.
