

## Synthesis and Structure of YbIrIn<sub>5</sub>

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The new ternary indium-rich compound YbIrIn<sub>5</sub> was synthesized from the elements via an indium flux technique. A mixture with the starting composition 1:1:7 was heated at 1300 K in a tantalum tube for 6 h and cooled to room temperature at a rate of 5 K/h. The structure was refined from X-ray single crystal diffractometer data: HoCoGa<sub>5</sub> type, *P4/mmm*, *a* = 461.96(7), *c* = 740.21(15) pm, *wR*<sup>2</sup> = 0.0616, 222 *F*<sup>2</sup> values, and 12 variable parameters. The iridium atoms have eight indium neighbors in square prismatic coordination at Ir—In distances of 274 pm. The square prisms are condensed via common edges forming layers which are separated by the ytterbium and further indium atoms. Ytterbium has a cuboctahedral indium coordination. The cell volume is suggestive for divalent or intermediate-valent ytterbium.

**Key words:** Indium, Crystal Structure, Solid State Synthesis

### Introduction

Ternary indides with tetragonal HoCoGa<sub>5</sub> or Ho<sub>2</sub>CoGa<sub>8</sub> type structure [1] are the ternary intermetallics with the so far highest indium content. The preparation and crystal structures of RECoIn<sub>5</sub> and RE<sub>2</sub>CoIn<sub>8</sub> indides (*RE* = rare earth element) have already been reported by Kalychak *et al.* in 1989 [2]. The corresponding rhodium based indides RERhIn<sub>5</sub> (*RE* = Y, La—Sm, Gd—Yb) have first been presented at a conference [3]. These intermetallics have then attracted considerable interest in recent years due to their outstanding physical properties. Discovery of the heavy fermion state and superconductivity in these materials [4–8] initiated large research programs, especially on the cerium based compounds. To give some examples, CeCoIn<sub>5</sub> [6] is a 2.3 K heavy-fermion su-

perconductor and CeRhIn<sub>5</sub> [8] is a heavy-fermion antiferromagnet with an ordering temperature of 3.8 K.

So far, only compounds with a stable trivalent oxidation state of the rare earth metal have been investigated [9, 10]. The neodymium, samarium, and gadolinium compounds show long-range magnetic ordering in the susceptibility and specific heat data. Recently we synthesized the ytterbium based compounds YbCoIn<sub>5</sub> and YbRhIn<sub>5</sub> [11]. The course of the cell volumes indicates intermediate-valent or divalent ytterbium. We have now obtained the isotypic iridium compound from an indium flux. The synthesis and structure determination of YbIrIn<sub>5</sub> are reported herein.

### Experimental Section

#### Synthesis

Starting materials for the preparation of YbIrIn<sub>5</sub> were ytterbium ingots (Johnson Matthey), iridium powder (Degussa-Hüls, 200 mesh), and indium tear drops (Johnson Matthey), all with stated purities better than 99.9%. Small ytterbium and indium pieces were mixed with the iridium powder in the atomic ratio 1:1:7 and sealed in a small tantalum tube under an argon atmosphere of about 800 mbar [12]. The argon was purified over titanium sponge (900 K), silica gel, and molecular sieves. The tantalum tube was subsequently sealed in an evacuated silica ampoule to prevent oxidation, first heated to 1300 K and annealed for 6 h at this temperature in a resistance furnace followed by slow cooling to room temperature at a rate of 5 K/h. After the annealing procedure the sample could easily be separated from the tantalum tube. No reactions with the tube could be detected. Compact pieces of YbIrIn<sub>5</sub> are light gray with metallic luster. The sample is stable in moist air. No decomposition was observed after several months.

The YbIrIn<sub>5</sub> single crystals investigated on the imaging plate diffractometer have been analyzed by an EDX measurement using a LEICA 420 I scanning electron microscope with YbF<sub>3</sub>, iridium, and indium arsenide as standards. No impurity elements were detected. The analyses 15 ± 1 at.-% Yb : 15 ± 1 at.-% Ir : 70 ± 1 at.-% In is in good agreement with the ideal compositions of 14.3 at.-% Yb : 14.3 at.-% Ir : 71.4 at.-% In.

#### X-ray film data and structure refinement

The YbIrIn<sub>5</sub> sample was characterized through its Guinier powder pattern using Cu-K<sub>α1</sub> radiation and α-quartz (*a* = 491.30, *c* = 540.46 pm) as an internal standard. The experimental Guinier pattern was compared with a theoretical one

Table 1. Crystal data and structure refinement for YbIrIn<sub>5</sub>.

Empirical formula	YbIrIn <sub>5</sub>
Formula weight	939.34 g/mol
Unit cell dimensions	$a = 461.96(7)$ pm $c = 740.21(15)$ pm $V = 0.1580$ nm <sup>3</sup>
Pearson symbol	tP7
Structure type	HoCoGa <sub>5</sub>
Space group	$P4/mmm$
Formula units per cell	$Z = 1$
Calculated density	9.87 g/cm <sup>3</sup>
Crystal size	20 × 50 × 80 μm <sup>3</sup>
Transmission ratio (max/min)	1.47
Absorption coefficient	53.4 mm <sup>-1</sup>
$F(000)$	392
Detector distance	60 mm
Exposure time	12 min
$\omega$ Range; increment	0–180°, 1.0°
Integration parameters A, B, EMS	15.0, 4.5, 0.018
$\theta$ Range for data collection	4° to 34°
Range in $hkl$	±7, ±7, ±11
Total no. of reflections	2244
Independent reflections	222 ( $R_{\text{int}} = 0.1062$ )
Reflections with $I > 2\sigma(I)$	222 ( $R_{\sigma} = 0.0405$ )
Data / restraints / parameters	222 / 0 / 12
Goodness-of-fit on $F^2$	1.100
$R$ indices (all data)	$R1 = 0.0246$ ; $wR2 = 0.0616$
Extinction coefficient	0.013(1)
Largest diff. peak and hole	3.72 and $-2.56$ e/Å <sup>3</sup>

[13] and it clearly revealed the fingerprint of the HoCoGa<sub>5</sub> type structure for YbIrIn<sub>5</sub>. Additional lines indicated the presence of binary IrIn<sub>3</sub> [14] and elemental indium. Due to the high indium content, the sample showed a high ductility and it was not possible to get high quality X-ray powder data for a refinement of the lattice parameters. The structure refinement was therefore performed with the lattice parameters determined on the single crystal diffractometer.

Platelet like single crystals were isolated from the annealed sample by mechanical fragmentation and first examined on a Buerger precession camera (equipped with an imaging plate system Fujifilm BAS-1800) in order to establish suitability for intensity data collection. Single crystal intensity data were collected at room temperature on a Stoe IPDS-II diffractometer with graphite monochromatized Mo-K $\alpha$  radiation. All relevant crystallographic data for the data collection and evaluation are listed in Table 1.

The atomic positions of YbRhIn<sub>5</sub> [11] were taken as starting values and the structure was successfully refined using SHELXL-97 (full-matrix least-squares on  $F_o^2$ ) [15] with anisotropic atomic displacement parameters for all sites. As a check for the correct composition, the occupancy parameters were refined in a separate series of least-squares cycles. The occupancy parameters varied between 99.1(9)% for In1 and 100.5(6)% for Ir. Thus, all sites were fully occupied within two standard deviations. In the last cycles, the ideal occupan-

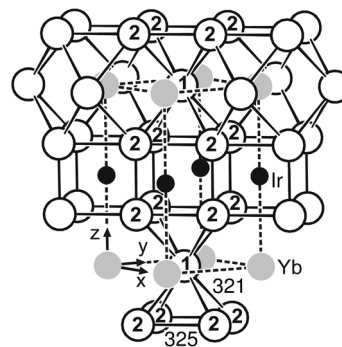


Fig. 1. The crystal structure of YbIrIn<sub>5</sub>. Large gray, black filled, and open circles represent ytterbium, iridium, and indium, respectively. The layers of condensed distorted IrIn<sub>8</sub> cubes and YbIn<sub>12</sub> cuboctahedra are emphasized.

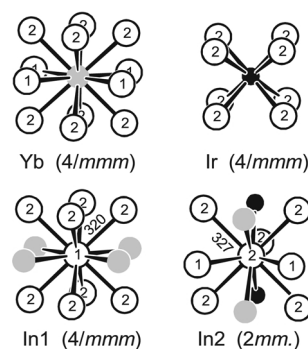


Fig. 2. The coordinations in the YbIrIn<sub>5</sub> structure. Some relevant interatomic distances [pm] and the site symmetries are given.

cies were assumed again. A final difference Fourier synthesis revealed no significant residual peaks (see Table 1). The positional parameters and interatomic distances are listed in Tables 2 and 3. Listings of the observed and calculated structure factors are available.\*

## Discussion

The YbIrIn<sub>5</sub> structure is presented in Fig. 1 and the coordination polyhedra in Fig. 2. Each iridium atom has a square prismatic indium coordination at Ir–In distances of 275 pm, close to the sum of the covalent radii for iridium and indium of 276 pm [16]. The Ir–In distance is comparable to those in CaIrIn<sub>2</sub> (271–280 pm) [17], SrIrIn<sub>2</sub> (277–279 pm) [18], CaIrIn<sub>4</sub> (261–287 pm) [19], and binary IrIn<sub>3</sub> (265–277 pm)

\*Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), E-Mail: crysdata@fiz-karlsruhe.de, by quoting the Registry No. CSD-413163.

Atom	W.-pos.	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{eq}$
Yb	1a	0	0	0	92(2)	$U_{11}$	67(4)	84(2)
Ir	1b	0	0	1/2	75(2)	$U_{11}$	85(3)	78(2)
In1	1c	1/2	1/2	0	111(3)	$U_{11}$	90(6)	104(3)
In2	4i	1/2	0	0.2997(1)	86(2)	173(3)	67(4)	109(2)

Table 2. Atomic coordinates and anisotropic displacement parameters ( $\text{pm}^2$ ) for  $\text{YbIrIn}_5$ .  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.  $U_{12} = U_{13} = U_{23} = 0$ .

Table 3. Interatomic distances (pm) of  $\text{YbIrIn}_5$  (standard deviations in parentheses).

Yb:	8	In2	320.3(1)	In2:	2	Ir	274.5(1)
	4	In1	326.7(1)		1	In2	296.5(2)
Ir:	8	In2	274.5(1)		2	Yb	320.3(1)
In1:	8	In2	320.3(1)		2	In1	320.3(1)
	4	Yb	326.7(1)		4	In2	326.7(1)

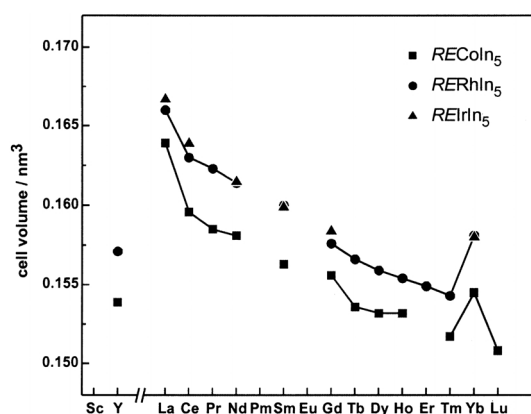


Fig. 3. Plot of the cell volumes of the  $RET\text{In}_5$  ( $T = \text{Co}, \text{Rh}, \text{Ir}$ ) compounds (extended version from ref. [11]).

[14]. The square prisms are condensed *via* common edges within the *ab* plane forming a layer. Within this layer, only every other square prism is filled with iridium.

The ytterbium atoms are located at the origin of the unit cell. They have a slightly distorted cuboctahedral coordination by eight In2 (320 pm) and four In1 (327 pm) atoms. This coordination is realized in undistorted form in binary  $\text{YbIn}_3$  [20] with the well known  $\text{Cu}_3\text{Au}$  type structure (Yb–In 326 pm). Also the cuboctahedra in  $\text{YbIrIn}_5$  are condensed and they form a layer around  $z = 0$ . The layers of the  $\text{RhIn}_8$  square prisms and the  $\text{YbIn}_{12}$  cuboctahedra are condensed via the common In2 atoms.

Finally we briefly discuss the coordination of the two crystallographically independent indium atoms.

In1 has eight In2 neighbors at 320 pm, a coordination that is similar to tetragonal body-centered indium ( $8 \times 325$  pm and  $4 \times 338$  pm) [21]. Such structural motifs often occur in indium rich intermetallics [19, 22]. The coordination sphere of In1 is completed by four additional ytterbium atoms at an Yb–In1 distance of 327 pm. This way, In1 also has coordination number 12 in a slightly distorted cuboctahedral form. The In2 atoms on site 4i have the lowest site symmetry ( $2mm$ ). They have the lower coordination number 11 formed by two iridium, two ytterbium, and seven indium atoms (see Fig. 2).

A plot of the cell volumes of all  $RET\text{In}_5$  ( $T = \text{Co}, \text{Rh}, \text{Ir}$ ) is shown in Fig. 3. As expected from the lanthanoid contraction, the cell volumes decrease from the early to the late rare earth elements. Since rhodium and iridium have similar atomic (Rh: 134 pm, Ir: 136 pm) and covalent (Rh: 125 pm, Ir: 126 pm) radii [16], the cell volumes of the  $RERh\text{In}_5$  and  $REIr\text{In}_5$  compounds are similar. For the three series, the cell volume of the ytterbium compounds show a pronounced positive deviation from the smooth curve, indicating intermediate-valent or divalent ytterbium. So far it was not possible to get bulk samples of  $\text{YbCoIn}_5$ ,  $\text{YbRhIn}_5$ , and  $\text{YbIrIn}_5$  which are free of contaminations, mostly from elemental indium (crystal growth from an indium flux). Further investigations are in progress in order to shed light on the valence behavior of ytterbium in these intermetallics.

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