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Key indicators

Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{Yb}-\text{Cu}) = 0.0013$ Å
Disorder in main residue
 R factor = 0.014
 wR factor = 0.036
Data-to-parameter ratio = 10.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.On the stoichiometry breadth of $\text{YbIn}_{1-x}\text{Rh}_x\text{Cu}_4$ [$x = 0.19$ (3)]

Ytterbium indium rhodium tetracopper, $\text{YbIn}_{1-x}\text{Rh}_x\text{Cu}_4$ [$x = 0.19$ (3)], an Rh-substituted version of the compound YbInCu_4 , has been synthesized from the corresponding elements using a Cu/In flux. Its structure is a substitutional derivative of the AuBe_5 type (Pearson code cF24). All atoms occupy special positions: Yb (site symmetry $\bar{4}3m$), In/Rh ($\bar{4}3m$) and Cu ($.3m$). A greater Rh content in the solid solutions, although possible, could not be confirmed by structure analyses due to poor quality of the single crystals.

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Comment

The ternary intermetallic compound YbInCu_4 with the ordered AuBe_5 type (Villars & Calvert, 1991) is known for its first-order valence transition (Felner & Nowik, 1986), in which the Yb state changes from a high-temperature local-moment trivalent state (smaller ionic size) to a low-temperature mixed-valent state (Lawrence *et al.*, 1996; Fritsch *et al.*, 2006). This behavior is clearly expressed in the unusual temperature dependence of the unit-cell volume (Lawrence *et al.*, 1996). As a result of systematic studies on the mixed-valency of Yb in a variety of Yb-based intermetallics, we recently discovered a limited solid solubility of Rh on the In site – Wyckoff letter 4c, site symmetry $\bar{4}3m$ (Fritsch *et al.*, 2006). The partial displacement of In by Rh evidently results in shifting the valence transitions towards higher temperature, as evidenced from

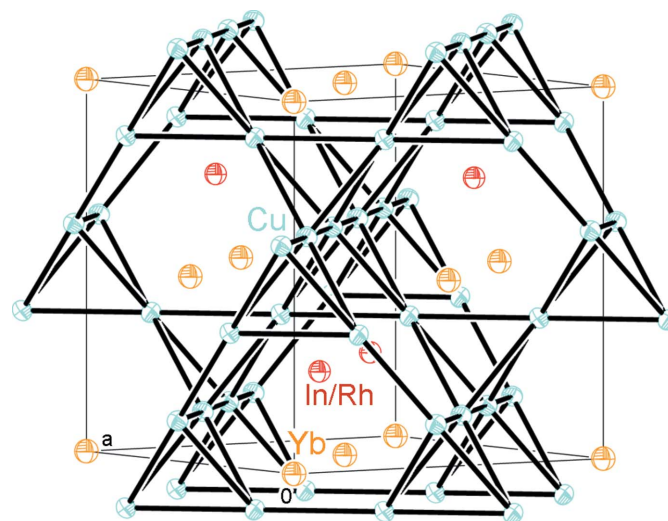


Figure 1

A view of the $\text{YbIn}_{1-x}\text{Rh}_x\text{Cu}_4$ [$x = 0.19$ (3)] structure. Displacement ellipsoids are drawn at the 98% probability level. Yb atoms are drawn as orange ellipsoids, Cu and In/Rh atoms are shown as blue and as red ellipsoids, respectively. The unit cell is outlined.

magnetic susceptibility, resistivity and heat-capacity measurements (Fritsch *et al.*, 2006). Therefore, we have undertaken further experiments in the Yb–In–Rh–Cu system aimed at establishing this trend and mapping the phase boundaries. The results of these studies indicate that the In–Rh solid solubility could extend beyond 20%. However, at above 20% at Rh content, the crystal quality deteriorates significantly and hinders further structural work by single-crystal X-ray diffraction (Fritsch *et al.*, 2006).

YbIn_{0.81(3)}Rh_{0.19(3)}Cu₄ (Fig. 1) is the Rh-richest phase that has been structurally characterized. Although the size of Rh is slightly smaller than that of In [Pauling's (1960) radii: In 1.421, Rh 1.252 Å], the unit-cell parameter of YbIn_{0.81(3)}Rh_{0.19(3)}Cu₄ [$a = 7.1469(2)$ Å] is almost 0.015 Å larger than that of the end member YbInCu₄ [$a = 7.1319(3)$ Å; Lawrence *et al.*, 1996]. In both cases, the cell parameters were determined at the same temperature, 100 K, which is reportedly above the transition temperature for YbInCu₄ (Lawrence *et al.*, 1996). We also note that the data for YbInCu₄ were obtained from neutron powder diffraction using polycrystalline samples, whereas our data are from single-crystal work on flux-grown crystals. A possible explanation is that the presence of geometric frustration (the magnetic ions are in a tetrahedral lattice) is relieved through Rh-doping, which, in turn, introduces more long-range interactions and drives the systems to a thermodynamically more stable non-magnetic state (Fritsch *et al.*, 2006).

Experimental

A mixture of the reactants (all 99.99%+), in a 1:5:0.6:1.4 stoichiometric ratio of Yb (Ames), Cu (Alfa), Rh (Alfa) and In (Alfa), was placed in a 5 ml alumina crucible which was subsequently enclosed in a fused-silica ampoule and flame-sealed under vacuum (below *ca* 50 mTorr). The ampoule was heated at 1373 K for 2 h, and cooled at a rate of 20 K h⁻¹ to 1073 K, when it was removed from the furnace. The excess of the molten Cu–Rh–In eutectic was removed by centrifugation.

Crystal data

YbIn _{0.81} Rh _{0.19} Cu ₄	$D_x = 9.820$ Mg m ⁻³
$M_r = 539.73$	Mo $K\alpha$ radiation
Cubic, $F\bar{4}3m$	$\mu = 53.84$ mm ⁻¹
$a = 7.1469(2)$ Å	$T = 100(2)$ K
$V = 365.05(2)$ Å ³	Irregular fragment, grey
$Z = 4$	$0.06 \times 0.05 \times 0.04$ mm

Data collection

Bruker SMART APEX diffractometer	1381 measured reflections
ω scans	96 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	96 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.040$, $T_{\max} = 0.115$	$R_{\text{int}} = 0.054$
	$\theta_{\text{max}} = 33.0^\circ$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.014$	$\Delta\rho_{\text{max}} = 1.09$ e Å ⁻³
$wR(F^2) = 0.036$	$\Delta\rho_{\text{min}} = -0.93$ e Å ⁻³
$S = 1.21$	Extinction correction: SHELXTL
96 reflections	Extinction coefficient: 0.0118 (7)
9 parameters	Absolute structure: Flack (1983), 40
$w = 1/[\sigma^2(F_o^2) + (0.0202P)^2]$	Friedel pairs
where $P = (F_o^2 + 2F_c^2)/3$	Flack parameter: 0.04 (3)

Table 1

Selected bond lengths (Å).

Yb–Cu ⁱ	2.96371 (13)	Cu–Cu ⁱⁱ	2.5197 (10)
In/Rh–Cu ⁱⁱ	2.96219 (14)		

Symmetry codes: (i) $x - 1, -y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x, -y + 1, -z + 1$.

Initial refinement assuming a fully stoichiometric formula led to convergence with very good residuals, yet two of the In sites had slightly larger displacement parameters than the rest. Refinement by freeing the site-occupation factor for an individual atom, while other remaining parameters were kept fixed, proved that the In site is *ca* 90% occupied. The occupancy factors for all other sites did not deviate from unity by more than 2σ upon free refinement. Therefore, it was assumed that Rh and In occupy statistically the same crystallographic site. Subsequent refinement suggests an In:Rh ratio of 0.81(3):0.19(3), which is in relatively good agreement with the nominal composition. However, it needs to be pointed out that, as the Rh-content increases, the departures between the nominal composition and the stoichiometry of the product become larger. The highest peak in the final difference map is located 0.96 Å from Yb.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2001); program(s) used to refine structure: SHELXTL (Sheldrick, 2001); molecular graphics: XP in SHELXTL; software used to prepare material for publication: SHELXTL.

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