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$PrCu_{5-x}In_{1+x}$ [x = 0.24 (1)] with the orthorhombic $CeCu_6$ structure type

Svilen Bobev[a]* and
Eric D. Bauer[b]

[a]Department of Chemistry and Biochemistry, 304A Drake Hall, University of Delaware, Newark, DE 19716, USA, and [b]MST-10 Mail Stop K764, Los Alamos National Laboratory, NM 87545, USA

Correspondence e-mail:
sbobev@chem.udel.edu

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Large single crystals of the title compound were synthesized from the corresponding elements using an eutectic Cu/In mixture as a solvent. $PrCu_{5-x}In_{1+x}$ [x = 0.24 (1)] is a new ternary derivative of the orthorhombic $CeCu_6$ structure type [space group *Pnma* (No. 62)]. This result contradicts the findings of Kalychak *et al.* [(1988). *Dop. Akad. Nauk Ukr. RSR Ser. B*, **9**, 39–42], who found that $CeCu_{4.38}In_{1.62}$ belongs to a new structure type (space group *Pnnm*), derived from the parent $CeCu_6$ compound by doubling the *a* axis. In the present structure, all the atoms except one of the Cu species occupy special positions with mirror symmetry.

Key indicators

Single-crystal X-ray study
T = 93 K
Mean σ(n–Cu) = 0.001 Å
Disorder in main residue
R factor = 0.016
wR factor = 0.033
Data-to-parameter ratio = 15.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

We describe here the synthesis and structure of a new ternary Pr—Cu—In compound, $PrCu_{5-x}In_{1+x}$ [x = 0.24 (1)], (I), crystallizing with the $CeCu_6$ structure. While the existence of large stochiometry breadth in the $CeCu_{6-x}In_x$ system has been known for almost a decade (Kasaya *et al.*, 1995), detailed structural studies in these systems are still lacking. The heavy-fermion behavior of those solid solutions and of the parent $CeCu_6$ compound attracts much interest from the condensed matter community and prompted us to investigate Ce—Cu—In and Pr—Cu—In ternary systems in detail.

It is worth noting here that such intermetallic phases are typically synthesized by direct fusion of the corresponding elements in the desired stoichiometric ratios, often by means of arc-melters or induction furnaces. These techniques usually produce polycrystalline, often inhomogeneous, materials,

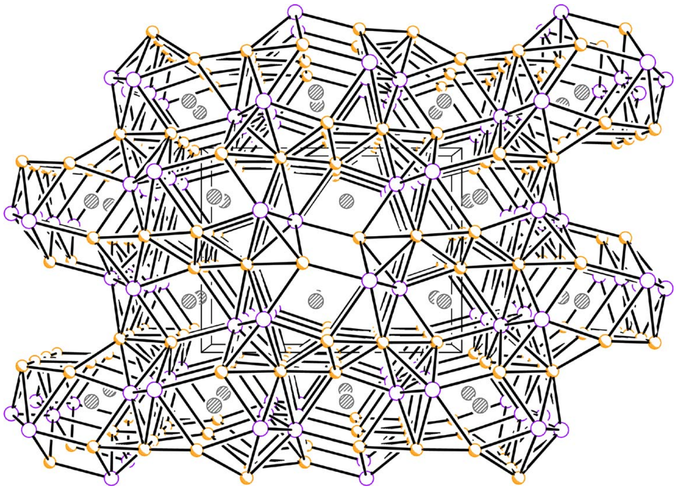

Figure 1
A ball-and-stick view down the *b* axis of the $PrCu_{5-x}In_{1+x}$ structure. In1 and In2/Cu2 are shown as purple open circles, and Cu3, Cu4 and Cu5 are drawn as shaded orange circles. Pr atoms are shown as isolated (not connected) hatched gray circles for clarity. The unit cell is outlined.

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which hamper interpretation of the data. Thus, the growth of large single crystals of such materials is highly desirable for unequivocal property measurements.

We employed a method commonly known as flux growth (Canfield & Fisk, 1992) to circumvent these experimental difficulties. This technique makes use of a (relatively) low-melting metal as a growth medium for the solute crystal and allows for substantially lower reaction temperatures. Using a eutectic Cu/In mixture as a solvent, we were successful in growing large single crystals of (I) (Fig. 1). The Pr atoms have a high coordination number of 19, as shown in Fig. 2. All interatomic distances are within the expected ranges for such intermetallic compounds.

The stoichiometry breadth displayed by (I) is not unusual for intermetallic compounds with this structure type, as evidenced by the studies on the properties of the non-stoichiometric $CeCu_{5-x}In_{1+x}$ [$0 < x < \frac{3}{4}$] and $CeCu_{5+x}In_{1-x}$ [$0 < x < 1$] (Kasaya *et al.*, 1995). However, we find no evidence for the existence of a superstructure with a doubled *a* axis as reported for $CeCu_{4.38}In_{1.62}$ (Kalychak *et al.*, 1988). This phase is said to belong to a new structure type with space group *Pnnm*, and can be derived from the archetype $CeCu_6$, which crystallizes in space group *Pnma* (Cromer *et al.*, 1960). The ordering in $CeCu_{4.38}In_{1.62}$ could arise from the different synthetic approaches, *viz*. arc-melting and subsequent annealing (Kalychak *et al.*, 1988) as opposed to flux-growth in Cu—In flux (this study). Further systematic investigations of the phase width and its dependence on the synthetic conditions are currently under way.

The physical properties of (I) will be reported later.

Experimental

All starting materials were used as received [Pr (Ames Laboratory, ingots, 99.99% metal basis), Cu (Alfa, granules, 99.999%) and In (Alfa, rods, 99.999%)]. Mixtures of the elements in a Pr/Cu/In ratio of 1:2:5 were loaded in alumina crucibles, which were subsequently enclosed in evacuated fused silica jackets by flame-sealing. The reaction was carried out at a temperature of 1373 K for 4 h; heating was followed by slow cooling ($3\ K\ h^{-1}$) down to 1073 K. At this point, the molten flux (Cu/In eutectic) was removed by centrifugation. The products of the reaction were relatively large and well defined crystals with silver metallic luster. These were later identified as non-stoichiometric $PrCu_{5-x}In_{1+x}$ [$x = 0.24\ (1)$], a new ternary derivative of the orthorhombic $CeCu_6$ structure. The corresponding unit-cell parameters determined at 93 (2) K are a = 8.4061 (7) Å, b = 5.0843 (4) Å, and c = 10.7278 (8) Å. The crystals are stable in air and moisture over extended periods of time (greater than *ca* three months), and decompose slowly in solutions of mineral acids.

Crystal data

$Cu_{4.76(1)}In_{1.24(1)}Pr$
$M_r = 585.74$
Orthorhombic, *Pnma*
$a = 8.4061\ (7)$ Å
$b = 5.0843\ (4)$ Å
$c = 10.7278\ (8)$ Å
$V = 458.50\ (6)$ Å^3
$Z = 4$
$D_x = 8.485$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 4154 reflections
$\theta = 3.1–28.3°$
$\mu = 37.98$ mm^{-1}
$T = 93\ (2)$ K
Block, metallic gray
0.06 × 0.06 × 0.05 mm

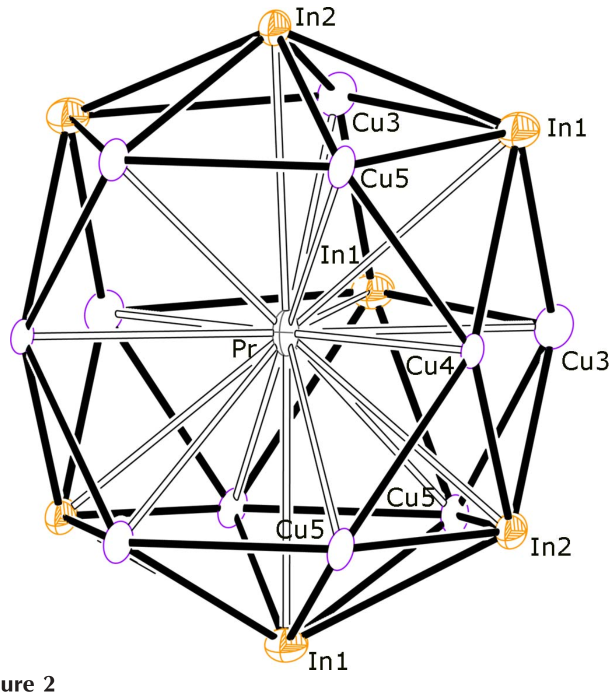

Figure 2
A view of the coordination polyhedron around the Pr atom in (I). Displacement ellipsoids are drawn at the 98% probability level. Color key: In1 and In2/Cu2 orange; Cu3, Cu4 and Cu5 purple.

Data collection

Bruker SMART APEX 1000 diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.124$, $T_{max} = 0.150$
4154 measured reflections
633 independent reflections
560 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 28.3°$
$h = -11 \rightarrow 11$
$k = -6 \rightarrow 6$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.033$
$S = 1.14$
633 reflections
42 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0056P)^2 + 1.7135P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.26$ e Å^{-3}
$\Delta\rho_{min} = -0.98$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00370 (14)

The initial refinement of (I) used the structure of $CeCu_6$ (Cromer *et al.*, 1960) as a starting point. However, this model failed to converge, and the Cu1 site was clearly occupied by a heavier atom. Therefore, in the next refinement cycles, In was assigned to the Cu1 site, and its occupation factor was allowed to vary. The refinement now converged, although at poor residuals ($R1 = 0.10$). The site occupation factor for In1 was virtually unchanged from its ideal value, and it appeared that the structure of (I) was $PrCu_5In$, an ordered ternary variant of the $CeCu_6$ type (Fig. 1). This situation is not without precedent; the ordered structures of UCu_5In (Zaremba *et al.*, 1998) and $CeCu_5Au$ (Ruck *et al.*, 1993) have already been reported. However, the anisotropic displacement parameters for Cu2 were notably smaller (*i.e.* nearly negative) than those for the other Cu sites. Thus, a model assuming In/Cu disorder at this site was developed, which led to the final model of 0.76 (1):0.24 (1) Cu/In occupancy. Refinement of the other Cu sites indicated no significant deviation (within 3σ) from full Cu occupancy, and these were fixed as such in the final refinement cycles. The highest peak is located 0.87 Å from atom In1.

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*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXL97* (Sheldrick, 2001).

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