Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Cerium copper diantimonide, $CeCu_{0.93(1)}Sb_2$

Paul H. Tobash and Svilen Bobev*

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA

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

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(Ce–Sb) = 0.002 Å
Disorder in main residue
R factor = 0.045
wR factor = 0.119
Data-to-parameter ratio = 12.8

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

Received 22 July 2005
Accepted 1 August 2005
Online 6 August 2005

$CeCu_{0.93(1)}Sb_2$, synthesized in the presence of an Sn flux, crystallizes in the $ZrCuSi_2$-type structure, but with a partial occupancy of the Cu site.

Comment

Ternary intermetallics containing cerium have attracted increased interest over the last few decades because low-temperature studies have indicated the occurrence of phenomena such as superconductivity, heavy fermion behavior, and valence fluctuations (Koyama *et al.*, 2001; Lakshmi *et al.*, 1996; Muro *et al.*, 1997; Skolozdra *et al.*, 1994; Thamizhavel *et al.*, 2003). Our systematic investigation of ternary *RE*–Cu–Sb and *RE*–Mn–Sb systems (*RE* = rare earth) has led to the synthesis of large crystals of $CeCu_{0.93}Sb_2$, which crystallizes with the tetragonal $ZrCuSi_2$-type structure (Villars & Calvert, 1991). Its structure can be viewed as consisting of infinite corrugated CuSb-layers of PbO-type, which are separated by the Ce atoms and square nets of Sb atoms (Fig. 1). The Ce atoms have a coordination number of 12 and relevant distances are given in Table 1. Previous work on polycrystalline samples of $CeCuSb_2$ reports refined atomic positions (Skolozdra *et al.*, 1994), presumably from powder data, which are in good agreement with the ones reported here. However, the former study does not mention refinement of the Cu occupancy or anisotropic displacement parameters. Our single-crystal work suggests that the refined occupancy for the Cu site is 0.93 (1). The La counterpart, $LaCu_{1-x}Sb_2$, takes on a phase range from $LaCu_{0.82}Sb_2$ to $LaCu_{0.87}Sb_2$ (Cordier *et al.*, 1985).

The unit-cell parameters for $CeCu_{0.93}Sb_2$ are in close agreement with those from previous studies on presumably fully stoichiometric $CeCuSb_2$ (Koyama *et al.*, 2001; Lakshmi *et al.*, 1996; Muro *et al.*, 1997; Skolozdra *et al.*, 1994; Thamizhavel *et al.*, 2003). These similarities could indicate that the homogeneity range in $CeCu_{1-x}Sb_2$ is small, with x varying only slightly. Samples prepared by techniques different from the Sn flux method used here may lead to different values of x. There is precedence for non-stoichiometry in related compounds, such as $CeT_{1-x}Sb_2$ (T = Ni, Cu, Pd, Ag) (Muro *et al.*, 1997), and $CeCd_{1-x}Sb_2$ (Tkachuk & Mar, 2004). The small but detectable phase range in $CeCu_{1-x}Sb_2$ may account for some discrepancies in the electrical and magnetic properties of these materials.

Experimental

Starting materials (Ce pieces, 99.99%, Aldrich; Cu, Sb, Sn, >99.99%, Alfa) were used as received. A mixture of reactants, in the stoichiometry Ce:Cu:Sb = 1:1.78:1.78 with a nearly 20-fold excess of Sn,

was placed in a 2 cm^3 alumina crucible within an evacuated fused-silica ampule. The ampule was heated at 1273 K for 8 h and 1073 K for 60 h, and cooled at 20 K h^{-1} to 773 K, at which point it was removed from the furnace. The molten Sn was removed by centrifugation.

Crystal data

$CeCu_{0.93}Sb_2$	Mo $K\alpha$ radiation
M_r = 442.71	Cell parameters from 154 reflections
Tetragonal, $P4/nmm$	θ = 2.0–26.6°
a = 4.3424 (15) Å	μ = 30.26 mm^{-1}
c = 10.221 (7) Å	T = 120 (2) K
V = 192.73 (16) Å^3	Block, silver
Z = 2	0.04 × 0.04 × 0.03 mm
D_x = 7.629 Mg m^{-3}	

Data collection

Bruker SMART APEX diffractometer	154 independent reflections
ω scans	133 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	R_{int} = 0.056
T_{min} = 0.328, T_{max} = 0.404	θ_{max} = 26.6°
958 measured reflections	$h = -5 \rightarrow 3$
	$k = -5 \rightarrow 5$
	$l = -7 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0679P)^2 + 5.731P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.045	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.120	$\Delta\rho_{max}$ = 4.37 e Å^{-3}
S = 1.14	$\Delta\rho_{min}$ = −2.95 e Å^{-3}
154 reflections	Extinction correction: *SHELXTL*
12 parameters	Extinction coefficient: 0.006 (2)

Table 1
Selected bond distances (Å).

Ce—Sb1^{i}	3.2299 (14)	Sb2—Sb2^{iii}	3.0705 (11)
Ce—Cu	3.351 (2)	Sb2—Sb2^{iv}	3.0705 (11)
Ce—Sb2^{ii}	3.356 (2)	Cu—Sb1^{ii}	2.6675 (18)

Symmetry code: (i) $-x, -y, -z+1$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+2, -y+1, -z+1$; (iv) $-x+1, -y, -z+1$.

Initial refinement assuming a fully stoichiometric formula led to displacement parameters for Cu that were 50% greater than for the other sites, suggesting a partial occupancy for the Cu site. The occupancies for all sites were verified by freeing the site-occupation factor for an individual atom, while other remaining parameters were kept fixed. The refined occupancy for the Cu site was 0.93 (1). The maximum peak and deepest hole are located 1.54 Å from the Cu atom and 0.82 Å from Sb2, respectively.

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: *SHELXTL*.

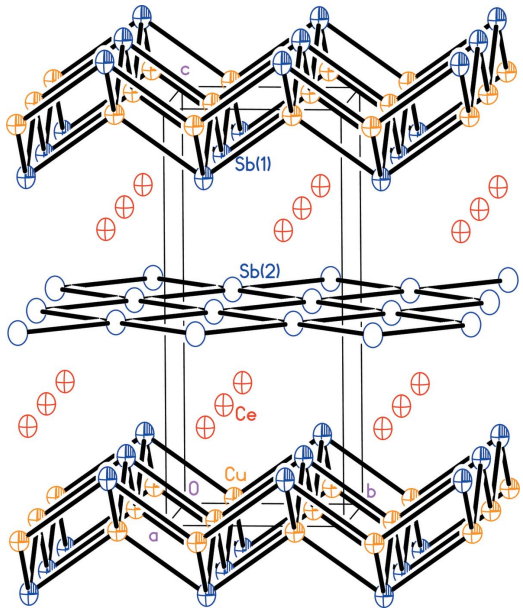

Figure 1
A view of $CeCu_{0.93}Sb_2$ projected approximately along [100]. Displacement ellipsoids are drawn at the 95% probability level. Ce atoms are drawn as red crossed ellipsoids, Cu atoms as yellow shaded ellipsoids, and Sb1 and Sb2 atoms as blue full and open displacement ellipsoids, respectively.

This work was funded by a University of Delaware start-up grant.

References

Bruker (2002). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cordier, G., Schäfer, H. & Woll, P. (1985). *Z. Naturforsch. Teil B*, **40**, 1097–1099.
Koyama, T., Matsumoto, M., Wada, S., Muro, Y. & Ishikawa, M. (2001). *J. Phys. Soc. Jpn*, **70**, 3667–3672.
Lakshmi, K. V., Menon, L., Nigam, A. K., Das, A. & Malik, S. K. (1996). *Physica B*, **223–224**, 289–291.
Muro, Y., Takeda, N. & Ishikawa, M. (1997). *J. Alloys Compd*, **257**, 23–29.
Sheldrick, G. M. (2001). *SHELXTL*. University of Göttingen, Germany.
Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
Skolozdra, R. V., Mikhalski, Ja. F., Kaczmarska, K. & Pierre, J. (1994). *J. Alloys Compd.* **206**, 141–146.
Thamizhavel, A., Takeuchi, T., Okubo, T., Yamada, M., Asai, R., Kirita, S., Galatanu, A., Yamamoto, E., Ebihara, T., Inada, Y., Settai, R. & Onuki, Y. (2003). *Phys. Rev. B*, **68**, 0544271–0544278.
Tkachuk, A. V. & Mar, A. (2004). *Acta Cryst.* E**60**, i82–i83.
Villars, P. & Calvert, L. D. (1991). *Pearson's Handbook of Crystallographic Data for Intermetallic Compounds*, 2nd ed. Materials Park, Ohio, USA: American Society for Metals.