

Ternary Arsenides $ACuAs_2$ and Ternary Antimonides $AAsb_2$ ($A =$ Rare-Earth Elements and Uranium) with $HfCuSi_2$ -Type Structure

Markus Brylak, Manfred H. Möller, and Wolfgang Jeitschko

Anorganisch-Chemisches Institut der Universität Münster, Wilhelm-Klemm-Strasse 8, D-48149 Münster, Germany

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The arsenides $ACuAs_2$ ($A = Y, La-Nd, Sm, Gd-Lu$) and the isotypic antimonides $AAsb_2$ ($A = Y, La-Nd, Sm, Gd-Tm, U$) were prepared for the first time and their lattice constants are reported. Single crystals of $CeAgSb_2$ were obtained from a $NaCl/KCl$ flux and their structure was determined from four-circle diffractometer X-ray data: $P4/nmm$, $a = 436.3(1)$ pm, $c = 1069.9(4)$ pm, $Z = 2$, $R = 0.017$ for 381 structure factors and 12 variable parameters. $CeAgSb_2$ is isotypic with $HfCuSi_2$, $CaMnBi_2$, and $ZrCuSiAs$. In contrast to other ternary lanthanoid transition metal antimonides with $HfCuSi_2$ -type structure, the silver site is fully occupied. Chemical bonding in $CeAgSb_2$ can be rationalized by the formula $Ce^{3+}Ag^+Sb^3-$, where the superscripts indicate oxidation numbers. © 1995 Academic Press, Inc.

INTRODUCTION

A "filled" $PbFCl$ type structure was first reported for the quaternary silicide arsenide $ZrCuSiAs$ (1). The first ternary compound with the corresponding atomic positions was $ZrCuSi_2$ (2), however, its structure was not determined at that time. It was communicated for the isotypic silicide $HfCuSi_2$ shortly thereafter (3). $UCuAs_2$ was the first arsenide (4) and $CaMnBi_2$ was the first bismuthide (5) with this structure. Consequently, in the following years this simple tetragonal structure with only eight atoms per cell was referred to as $ZrCuSiAs$, $ZrCuSi_2$, $HfCuSi_2$, $UCuAs_2$, and $CaMnBi_2$ type by various authors. We prefer $HfCuSi_2$ as the prototype name for the ternary compounds, while we reserve $ZrCuSiAs$ as the prototype for quaternaries.

In contrast to $CaMnBi_2$, where the manganese position seems to be fully occupied, the isotypic rare-earth compounds $LaMn_{0.7}Sb_2$ (6), $NdFe_{0.6}Sb_2$ (7), $LaCo_{0.68}Sb_2$ (6), $LaCu_{0.85}Sb_2$ (6), and $LaZn_{0.52}Sb_2$ (6) were found with considerable defects for the transition metal sites. $ZrCuGe_2$ and $HfCuGe_2$ were the first germanides with this structure (3) and the series $LnNiSb_2$ ($Ln = Ce-Sm$) has been known for some time (8). The uranium compounds $UTPn_2$ ($T = Fe, Co, Ni, Cu$, and $Pn = P, As, Sb, Bi$) are known (9), and it seems that this structure type may have almost as

many representatives as the related $ThCr_2Si_2$ ($BaAl_4$) type structure for which more than 700 isotypic compounds are listed in "Pearson's Handbook" (10). Here we report 27 new arsenides and antimonides with $HfCuSi_2$ type structure.

SAMPLE PREPARATION, PROPERTIES, AND LATTICE CONSTANTS

Starting materials were ingots of the rare-earth metals (Kelpin, 99.9%), platelets of uranium (Merck, "nuklearrein"), silver wire (Alfa, m3N), and powders of copper (Ventron, 99.99%), arsenic (Serva, 99.999%), and antimony (Johnson Matthey, 325 mesh, M2N5). Filings of the rare-earth ingots were prepared under dried paraffin oil. Adhering iron particles were removed using a magnet. The uranium platelets were cleaned with nitric acid to remove oxide impurities. Prior to the reaction the arsenic was purified by fractional sublimation and the copper was reduced in a stream of hydrogen at about 300°C. A variety of slightly different reaction procedures was used. Most samples were prepared by reaction of the starting composition $A : T : Pn = 1 : 1 : 2$ ($Pn = As, Sb$) in sealed, evacuated silica tubes for 3 days at 500°C. All reaction products were then ground to powders, cold-pressed, sealed again in silica tubes, melted in a high frequency furnace, and annealed for 1–2 weeks at 800–900°C. The uranium-containing samples were prepared by arc-melting the elemental components under argon with a somewhat higher amount of antimony to compensate for the losses during the arc-melting. These samples were subsequently annealed at 800°C for 10 days in alumina crucibles, which were sealed in silica tubes under argon.

Single crystals of $CeAgSb_2$ were obtained by reaction of the elemental components in a $NaCl/KCl$ flux. The starting ratio was $Ce : Ag : Sb : NaCl/KCl = 1 : 1 : 2 : 20$. The sample was annealed in a sealed, evacuated silica tube for 2 weeks at 800°C, cooled to 690°C at a rate of 3°C/hr, and quenched in ice water. The $NaCl/KCl$ flux was dissolved in H_2O using an ultrasonic bath. The energy-dispersive X-ray fluorescence analysis of these crys-

TABLE 1
Lattice Constants of Arsenides and Antimonides with the
Tetragonal HfCuSi₂-Type Structure^a

Compound	<i>a</i> (pm)	<i>c</i> (pm)	<i>c/a</i>	<i>V</i> (nm ³)
YCuAs ₂	388.62(8)	987.10(3)	2.540	0.1491
LaCuAs ₂	404.8(3)	1027(1)	2.537	0.1683
CeCuAs ₂	401.81(7)	1010.4(2)	2.515	0.1631
PrCuAs ₂	399.42(8)	1006.8(3)	2.521	0.1606
NdCuAs ₂	396.7(1)	1005.5(5)	2.535	0.1582
SmCuAs ₂	393.50(6)	997.2(2)	2.534	0.1544
GdCuAs ₂	391.05(4)	992.9(2)	2.549	0.1518
TbCuAs ₂	389.42(4)	987.9(2)	2.537	0.1498
DyCuAs ₂	388.20(4)	984.8(2)	2.537	0.1484
HoCuAs ₂	387.24(9)	982.2(3)	2.536	0.1473
ErCuAs ₂	385.83(7)	978.9(3)	2.537	0.1457
TmCuAs ₂	384.87(7)	976.9(3)	2.538	0.1447
YbCuAs ₂	384.5(1)	974.5(5)	2.535	0.1441
LuCuAs ₂	383.42(7)	974.2(3)	2.541	0.1432
UCuAs ₂ ^b	394.8(2)	953.3(5)	2.415	0.1486
YAgSb ₂	427.65(3)	1048.8(1)	2.452	0.1918
LaAgSb ₂	439.03(6)	1084.0(2)	2.469	0.2089
CeAgSb ₂	436.3(1)	1069.9(4)	2.452	0.2037
PrAgSb ₂	434.99(6)	1067.0(3)	2.453	0.2019
NdAgSb ₂	433.53(3)	1063.0(2)	2.452	0.1998
SmAgSb ₂	431.2(1)	1055.5(5)	2.448	0.1962
GdAgSb ₂	429.52(7)	1050.6(2)	2.446	0.1938
TbAgSb ₂	428.33(7)	1047.6(2)	2.446	0.1922
DyAgSb ₂	427.43(5)	1044.2(3)	2.443	0.1908
HoAgSb ₂	426.62(9)	1042.2(3)	2.443	0.1897
ErAgSb ₂	425.65(8)	1039.0(3)	2.441	0.1883
TmAgSb ₂	425.29(7)	1039.0(3)	2.443	0.1880
UAgSb ₂	432.40(6)	1031.8(2)	2.386	0.1929

^a Standard deviations in the place values of the last listed digits are given in parentheses throughout the paper.

^b From Ref. (4).

tals in a scanning electron microscope showed no impurities of elements with atomic numbers equal to or greater than sodium. The detectability limits were at about 1 at. %.

The compounds are stable in air over long periods of time. Compact samples have metallic luster; the powders are black. They were characterized through Guinier powder patterns with α -quartz ($a = 491.30$ pm, $c = 540.46$ pm) as internal standard. The lattice constants (Table 1) were refined by least-squares fits. The plot of the cell volumes (Fig. 1) shows the expected lanthanoid contraction.

STRUCTURE REFINEMENT OF CeAgSb₂

Single crystals of CeAgSb₂ were examined in a Buerger precession camera to establish their symmetry and suitability for the intensity data collection. Intensity data were recorded in a four-circle diffractometer with graphite-monochromated MoK α radiation, a scintillation counter with pulse-height discriminator, and background counts

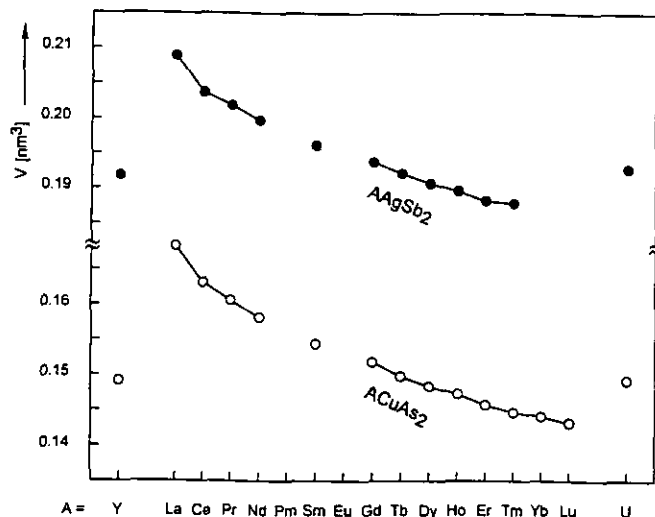


FIG. 1. Cell volumes of ACuAs₂ and AAgSb₂ compounds.

at both ends of each $\theta/2\theta$ scan. An absorption correction was made from ψ scan data. The crystallographic data are summarized in Table 2.

The starting parameters for the structure determination were taken from CaMnBi₂ (5). The structure was refined by full-matrix least-squares cycles with atomic scattering factors (11), corrected for anomalous dispersion (12). A parameter accounting for isotropic secondary extinction was optimized and the weighting scheme included a term which accounted for the counting statistics. All atoms were refined with anisotropic displacement parameters. To check for deviations from the ideal composition, occupancy parameters were varied in one series of least-squares cycles together with variable thermal parameters and a fixed scale factor. The results (in % with standard

TABLE 2
Crystal Data for CeAgSb₂

Space group	<i>P4/nmm</i> (No. 129)
Formula units/cell	<i>Z</i> = 2
Formula weight	491.5
Calculated density (g/cm ³)	8.01
Linear absorption coefficient (mm ⁻¹)	$\mu(\text{MoK}\alpha) = 28.8$
Crystal dimensions (μm^3)	44 × 66 × 22
$\theta/2\theta$ scans up to	$2\theta = 90^\circ$
Range in <i>h, k, l</i>	±8, ±8, 0–18
Total number of reflections	3484
Highest/lowest transmission	2.17
Unique reflections	570
Inner residual	$R_i = 0.031$
Reflections with $I_o > 3\sigma(I_o)$	381
Number of variables	12
Conventional residual	$R = 0.017$
Weighted residual	$R_w = 0.018$

TABLE 3
Atomic Parameters of CeAgSb₂^a

Atom	<i>P4/nmm</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Ce	2 <i>c</i>	1/4	1/4	0.23815(4)	0.545(3)
Ag	2 <i>b</i>	3/4	1/4	1/2	0.971(5)
Sb1	2 <i>a</i>	3/4	1/4	0	0.696(4)
Sb2	2 <i>c</i>	1/4	1/4	0.67368(5)	0.670(5)

Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Ce	72.0(8)	72.0(8)	63(1)	0	0	0
Ag	134(1)	134(1)	100(2)	0	0	0
Sb1	94(1)	94(1)	76(1)	0	0	0
Sb2	71.9(9)	71.9(9)	111(2)	0	0	0

^a The equivalent isotropic thermal parameters *B*_{eq} are listed in units of 10⁻² nm². The anisotropic thermal parameters *U* (×10⁴) are defined by exp[-2π²(h²*a*²*U*₁₁ + . . .)]. The positional parameters are standardized using the program STRUCTURE TIDY (13).

deviations in parentheses) of 99.6(1) for Ce, 99.6(2) for Ag, 100.2(1) for Sb1, and 100.3(2) for Sb2 showed no significant deviations from the full occupancies, and in the final least-squares cycles the ideal occupancies were assumed. The final conventional and weighted residuals are *R* = 0.017 and *R*_w = 0.018 for 12 variable parameters and 381 structure factors. The atomic parameters and interatomic distances are given in the Tables 3 and 4. A listing of the structure factors is available from the authors.

DISCUSSION

In the crystal structure of CeAgSb₂ (Fig. 2) the cerium atoms are coordinated by eight antimony atoms forming a distorted square antiprism. The silver atoms have four antimony neighbors forming a slightly distorted tetrahedron with Sb–Ag–Sb angles of 114.9° (4×) and 99.2° (2×). The four silver atoms at 308.5 pm may be counted as belonging to the coordination sphere of the silver atoms, although these Ag–Ag interactions are rather weak, considering the Ag–Ag distance of 288.9 pm in elemental silver with coordination number 12. The antimony atoms occupy two different sites with entirely different coordina-

TABLE 4
Interatomic Distances (pm) in the Structure of CeAgSb₂^a

Ce: 4Sb2 322.6	Ag: 4Sb2 286.6	Sb1: 4Sb1 308.5	Sb2: 4Ag 286.6
4Sb1 335.4	4Ag 308.5	4Ce 335.4	4Ce 322.6
4Ag 355.1	4Ce 355.1		

^a All distances shorter than 400 pm are listed. The standard deviations are all equal to or less than 0.1 pm.

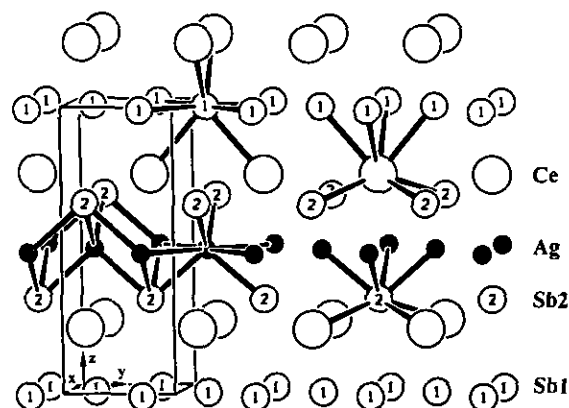


FIG. 2. Crystal structure and near-neighbor environments of CeAgSb₂.

tions. The Sb1 atoms have four cerium neighbors at 335.4 pm forming a considerably stretched tetrahedron with Ce–Sb1–Ce angles of 125.2° (4×) and 81.1° (2×). The coordination is completed by four Sb1 atoms forming a square. The corresponding bond distances of 308.5 pm are greater than the three short (“two-electron bond”) Sb–Sb distances of 290.8 pm in the α-modification of elemental antimony, but they are shorter than the three next nearest neighbors in α-Sb at the (“van der Waals”) distance of 335.5 pm (14). The Sb2 atoms are coordinated by four cerium atoms at 322.6 pm and four silver atoms at 286.6 pm in distorted square-antiprismatic arrangement.

Chemical bonding in CeAgSb₂ can be rationalized to some extent on the basis of a simple model. The cerium atoms are essentially trivalent since the cell volume of CeAgSb₂ fits almost smoothly in between those of LaAgSb₂ and PrAgSb₂. For tetravalent cerium a much smaller cell volume would be expected. For the Sb2 atoms the oxidation number (formal charge) has to be –3, since the antimony atoms are the most electronegative component in the compound and since the Sb2 atoms do not form any Sb–Sb bonds. For the Ag and Sb1 atoms the oxidation numbers are not quite as obvious, however, a formula with the oxidation numbers (where the bonding electrons are counted at the more electronegative partner) of Ce³⁺Ag⁺(Sb1)[–](Sb2)^{3–} seems to be reasonable. The four Sb1 atoms surrounding each Sb1 atom then need to be considered bonded by one-electron bonds (four one-electron bonds are equivalent to two two-electron bonds). This assignment is supported by the fact that the isotopic compounds LaCu_{0.85}Sb₂ and LaZn_{0.52}Sb₂ (where the Sb1–Sb1 distances are of similar lengths as in CeAgSb₂) have defects at the transition metal sites (6). The formation of these defects correlates with the tendency of copper and zinc for the divalent state. Thus, the zinc compound could be written with the formula La³⁺(Zn_{0.5}²⁺)⁺(Sb1)[–](Sb2)^{3–} and an intermediate oxidation

number may be assigned to the copper atoms in $\text{LaCu}_{0.85}\text{Sb}_2$. Similarly some defects seem to be possible for the copper sites in the isotypic arsenides LnCuAs_2 reported here.

The silver atoms in CeAgSb_2 have larger thermal parameters than the other atoms (Table 3). Since we found this position to be fully occupied, the somewhat higher thermal parameters of the silver atoms indicate that the silver atoms are not as strongly bonded in the structure as the other atoms. We considered the possibility for an ion exchange and we boiled some CeAgSb_2 powder in an aqueous solution of CuSO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ for 1 hr. After this treatment the energy dispersive analysis of the crystals in a scanning electron microscope, however, showed a copper content of only a few percent, possibly only at the surface of the crystals. Similarly, boiling a polycrystalline sample of CeAgSb_2 in an aqueous solution of KCN for 1 hr did not result in a noticeable exchange of silver for potassium ions.

We were not successful in preparing the isotypic compounds YbAgSb_2 and LuAgSb_2 . In this context we note that the cell volume of the corresponding thulium compound shows a positive deviation from the smooth function observed for the cell volumes of the other LnAgSb_2 compounds (Fig. 1). This suggests that the thulium compound may have a slightly different composition. Apparently the thulium atoms are somewhat too small for an optimal bonding arrangement. Similar upturns of the cell volumes of the last compound (the one with the heaviest lanthanoid) of an isotypic series of rare-earth compounds were found for $\text{ErNi}_{2-x}\text{Sb}_2$ (15), ErPd_2P_2 (16), and TmNi_2Sb_2 (17).

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