Preparation and Crystal Structure of the Ternary Uranium Rare Earth Antimonides $(U_{2/3}R_{1/3})Sb_2$ and $(U_{1/2}R_{1/2})_3Sb_7$ with Mixed U/*R* Occupancy of the Metal Sites and a Variety of Antimony Polyanions

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The ternary antimonides $(U_{2/3}R_{1/3})Sb_2$ (R = Y, Ce−Nd, Sm, Gd−Tm) and $(U_{1/2}R_{1/2})_3Sb_7$ (R = Y, Gd−Ho) have been prepared by reaction of the uranium antimonide USb_2 with the corresponding rare earth antimonides RSb_2 and an excess of elemental antimony at high temperatures. The crystal structure of the isotypic series $(U_{2/3}R_{1/3})Sb_2$ has been determined from single-crystal X-ray data of $(U_{0.675(9)}Gd_{0.325(9)})Sb_2$. It is isotypic with $PbCl_2$: *Pnma*, $Z = 4$, $a = 754.6(1)$, $b = 419.6(1)$, $c = 1025.7(3)$ pm. The compounds of the other series crystallize with a new structure type, which has been determined for $(U_{0.49(1)}Ho_{0.51(1)})_3Sb_7$: *Immm*, $Z = 4$, $a = 410.1(1)$, $b = 1447.7(3)$, $c = 1821.2(5)$ pm. In both structures, the metal positions have mixed occupancy and high coordination numbers. Both structures contain numerous weak Sb−Sb bonds, thus forming a band of antimony atoms in the structure of $(U_{2/3}Gd_{1/3})Sb_2$ and a chain and a three-dimensionally infinite network of antimony atoms in the structure of $(U_{1/2}Ho_{1/2})_3Sb_7$. Analyses of the Sb−Sb bonding within the antimony polyanions on the basis of bond-length bond-strength considerations indicate that the uranium atoms have mixed or intermediate +3/+4 valence in these compounds. The structure of $(U_{1/2}Ho_{1/2})_3Sb_7$ may be considered as a defect variant of the structure of Ce_6MnSb_{15}.

Introduction

Solid-state antimonides are attracting increasing interest in recent years because of their potential as thermoelectric materials.[1−5] Some 10 years ago, the pseudo-binary section USb_2−$GdSb_2$ of the phase diagram uranium−gadolinium−antimony was studied, resulting in two ternary compounds, which were designated at that time with the formulas U_2GdSb_6 and $UGdSb_4$.[6] In the course of our investigations of binary and ternary antimonides, e.g., R_2Sb_5 (R = Sm, Gd−Dy),[7] $Nd_{9-x}Sb_{20-y}$,[8] AT_4Sb_{12} (A = Ca, Sr, Ba, and rare earth elements; T = Fe, Ru, Os),[9] U_3TSb_5 (T = Ti, V, Cr, Mn),[10] $RTSb_2$ (R = rare earth elements and uranium; T = Mn, Co, Cu, Ag, Au, Zn, Cd),[11] $RTSb_3$ (R = rare earth elements; T = V, Cr),[12] $RTSb$ (R = rare earth elements; T = Rh, Ir, Ni),[13] and $ARu_{2-x}Sb_2$ (A = lanthanoids and actinoids),[14] we became interested in the crystal structures of the compounds "U_2GdSb_6" and "$UGdSb_4$", which are reported here. Somewhat to our surprise, they turned out as pseudobinaries with mixed occupancy of all metal positions. We have also prepared the corresponding series of isotypic antimonides with other rare earth metals. A brief account of the present work has been presented at a conference.[15]

Experimental Section

Sample Preparation and Lattice Constants. The ternary uranium rare earth antimonides were prepared by reaction of the binaries USb_2 and RSb_2 with an excess of elemental antimony in an arc-melting furnace. Starting materials were turnings of uranium (Merck, "nuclearrein"), ingots of the rare earth elements (Heraeus, nominal purity 99.9%), and shots of antimony (Johnson Matthey, 99.5%). The uranium turnings were treated with diluted nitric acid to remove oxide impurities, the rare earth ingots were cut into small pieces, and the antimony shots were ground to powder. The components, in the ideal atomic ratio U:Sb and R:Sb = 1:2, were cold pressed into pellets and sealed in evacuated silica tubes. These were placed in a cold furnace, rapidly heated to 850 °C, kept at this temperature for 5 days, and cooled to room temperature in the furnace. The resulting binary compounds, USb_2 and RSb_2, were in the form of porous solids. They were ground to powders and mixed with an excess of antimony powder in the ratios USb_2:RSb_2:Sb of 2:1:0.6 and 1:1:1.2, corresponding to the overall formal compositions "$(U_{2/3}R_{1/3})Sb_{2.2}$" and "$(U_{1/2}R_{1/2})_3Sb_{7.8}$", respectively. The excess antimony was added to compensate for the loss by evaporation

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Table 1. Lattice Constants of the Orthorhombic Compounds $(U_{2/3}R_{1/3})Sb_2$ and $(U_{1/2}R_{1/2})_3Sb_7$ Obtained from Guinier Powder Data[a]

compound	a (pm)	b (pm)	c (pm)	V (nm^3)
$(U_{2/3}Y_{1/3})Sb_2$	754.4(2)	418.6(1)	1025.7(2)	0.3239
$(U_{2/3}Ce_{1/3})Sb_2$	758.2(1)	423.7(1)	1034.8(2)	0.3324
$(U_{2/3}Pr_{1/3})Sb_2$	758.2(1)	423.1(1)	1032.4(2)	0.3312
$(U_{2/3}Nd_{1/3})Sb_2$	758.0(1)	422.6(1)	1031.7(3)	0.3305
$(U_{2/3}Sm_{1/3})Sb_2$	755.4(1)	420.3(1)	1027.5(2)	0.3263
$(U_{2/3}Gd_{1/3})Sb_2$	754.6(1)	419.6(1)	1025.7(3)	0.3248
$(U_{2/3}Tb_{1/3})Sb_2$	754.7(1)	418.7(1)	1024.3(2)	0.3237
$(U_{2/3}Dy_{1/3})Sb_2$	754.3(1)	418.2(1)	1023.6(2)	0.3229
$(U_{2/3}Ho_{1/3})Sb_2$	754.0(1)	418.0(1)	1023.1(2)	0.3224
$(U_{2/3}Er_{1/3})Sb_2$	753.4(1)	417.9(1)	1022.0(2)	0.3217
$(U_{2/3}Tm_{1/3})Sb_2$	753.2(1)	417.3(1)	1020.9(2)	0.3209
$(U_{1/2}Y_{1/2})_3Sb_7$	411.2(2)	1452.0(2)	1824.1(2)	1.0891
$(U_{1/2}Gd_{1/2})_3Sb_7$	411.4(1)	1453.2(4)	1825.2(5)	1.0912
$(U_{1/2}Tb_{1/2})_3Sb_7$	411.0(1)	1451.7(3)	1823.4(5)	1.0879
$(U_{1/2}Dy_{1/2})_3Sb_7$	410.3(1)	1450.0(3)	1825.8(6)	1.0862
$(U_{1/2}Ho_{1/2})_3Sb_7$	410.1(1)	1447.7(3)	1821.2(5)	1.0812

[a] Standard deviations in the positions of the least significant digits are given in parentheses throughout the paper.

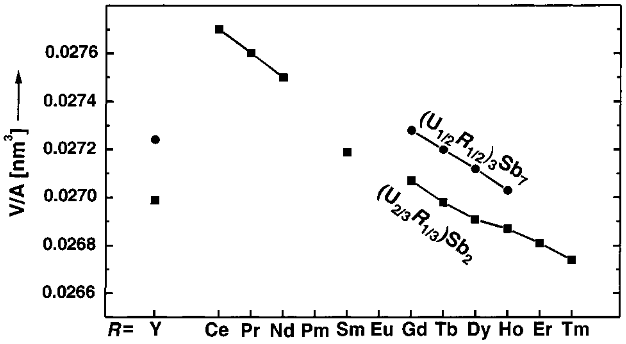

Figure 1. Average atomic volumes of the compounds $(U_{2/3}R_{1/3})Sb_2$ and $(U_{1/2}R_{1/2})_3Sb_7$.

during the arc melting. The arc melting was carried out under 0.6 bar argon (99.996%), which was (further) purified in a titanium sponge furnace. The arc-melted pellets werde turned over and remelted at least twice to enhance their homogeneity. It is also possible to obtain the ternary compounds by reaction of cold-pressed mixtures of powders of the binaries USb_2 and RSb_2 in stoichiometric amounts in evacuated silica tubes for 7 days at 800 °C. The single crystals used for the structure determinations were isolated from crushed samples prepared by the latter preparation technique.

Compact samples are gray with some luster, comparable to ingots of elemental silicon. Powdered samples are dark gray. They are stable in air for long periods of time. Energy-dispersive X-ray fluorescence analyses in a scanning electron microscope did not reveal any impurity elements heavier than sodium.

The samples were characterized by Guinier powder X-ray diagrams and recorded with Cu Kα_1 radiation using α-quartz (a = 491.30, c = 540.46 pm) as an internal standard. The observed diffraction diagrams were identified by comparison with diagrams calculated[16] using the positional parameters of the refined structures. The lattice constants listed in Table 1 were obtained by least-squares fits. The average atomic volumes of these compounds are plotted in Figure 1.

Table 2. Crystal Data for $(U_{2/3}Gd_{1/3})Sb_2$ and $(U_{1/2}Ho_{1/2})_3Sb_7$[a]

emirical formula	$(U_{2/3}Gd_{1/3})Sb_2$	$(U_{1/2}Ho_{1/2})_3Sb_7$
space group	*Pnma* (No. 62)	*Immm* (No. 71)
a (pm)	754.5(1)	410.1(1)
b (pm)	419.5(1)	1447.7(3)
c (pm)	1025.2(2)	1821.2(4)
V (nm^3)	0.3245	1.0813
Z	4	4
composition	$(U_{0.675(9)}Gd_{0.325(9)})Sb_2$	$(U_{0.49(1)}Ho_{0.51(1)})_3Sb_7$
fw	456	1454
T (°C)	21	21
λ (pm)	71.07	71.07
ρ_{calc} (g/cm^3)	9.33	8.93
μ (cm^{-1})	564	500
$R(F)$[b]	0.022	0.020
$R_w(F^2)$[b]	0.057	0.050

[a] The lattice constants were obtained on the four-circle diffractometer. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma\, w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (\mathrm{Max}\,(F_o^2) + 2F_c^2)/3$, $a = 0.0410$, and $b = 0$ for $(U_{0.675(9)}Gd_{0.325(9)})Sb_2$; $a = 0.0341$ and $b = 46.714$ for $(U_{0.49(1)}Ho_{0.51(1)})_3Sb_7$.

Structure Determinations. The single crystals of $(U_{2/3}Gd_{1/3})Sb_2$ and $(U_{1/2}Ho_{1/2})_3Sb_7$ isolated from the crushed samples had the shape of needles, with the needle axes extending in the direction of the short translation periods. They were examined in a Buerger precession camera to establish their suitability for the intensity data collection. These data were recorded on a four-circle diffractometer (Enraf-Nonius CAD4) with graphite-monochromated Mo Kα radiation, a scintillation counter with pulse-height discrimination, and background counts at both ends of each $\theta/2\theta$ scan. Empirical absorption corrections were applied from ψ scan data. Additional details of the data collections are listed in Table 2 and in the Supporting Information.

The structures were determined and refined using the program packages SDP[17] and SHELX-97.[18] The positions of most heavy atoms were determined by direct methods, and the remaining atoms were located by difference Fourier syntheses. The structures were refined with a full-matrix least-squares program using atomic scattering factors, corrected for anomalous dispersion, as provided by the program.[18] The weighting schemes reflected the counting statistics, and a parameter, correcting for isotropic secondary extinction, was optimized as a least-squares variable. It was found that in both structures, all uranium and rare earth atoms are located at sites with mixed occupancy. Therefore, these sites were refined with constrained full occupancy. We also checked for deviations from the ideal occupancies for any of the antimony sites by fixing the just determined U/R ratios and refining the occupancy values of all antimony atoms together with their displacement parameters. These refinements resulted in occupancy values of 100.4(4) and 100.5(3)% for the Sb1 and Sb2 positions of $(U_{2/3}Gd_{1/3})Sb_2$, respectively. For $(U_{1/2}Ho_{1/2})_3Sb_7$, the occupancy parameters of the antimony atoms varied between 99.4(6) % for Sb6 and 101.2(6) % for Sb5. Hence, within two of the rather small standard deviations, no indications were found for deviations from the ideal occupancy values for the antimony positions. Therefore, during the final refinement cycles, the ideal occupancy values were assumed for all antimony sites. These refinements with anisotropic displacement parameters for all atoms resulted in the compositions $(U_{0.675(9)}Gd_{0.325(9)})Sb_2$ and $(U_{0.49(1)}Ho_{0.51(1)})_3Sb_7$. The positional parameters and equivalent isotropic displacement parameters are listed in Table 3. The structures and the near-neighbor coordinations are shown in Figures 2−5. The anisotropic displacement parameters are listed in a table in the Supporting Information.

Discussion

The new ternary compounds are represented by their volume per atom ratios, V/A, in Figure 1, together with the average atomic volumes determined by us for the previously reported[6] gadolinium containing compounds, "U_2GdU_6" and "$UGdSb_4$". The V/A ratio of the cerium compound $(U_{2/3}Ce_{1/3})Sb_2$ is somewhat greater than that of the corresponding praseodymium compound, indicating that cerium is trivalent. If cerium were tetravalent, a considerably smaller V/A ratio would be expected. On the other hand, the V/A ratio of the samarium compound

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Table 3. Atomic Parameters of $(U_{0.675(9)}Gd_{0.325(9)})Sb_2$ and $(U_{0.49(1)}Ho_{0.51(1)})_3Sb_7$[a]

		occupancy	*x*	*y*	*z*	B_{eq}
		$(U_{0.675(9)}Gd_{0.325(9)})Sb_2$ (*Pnma*, $PbCl_2$ type)				
U/Gd	4*c*	0.675(9)/0.325(9)	0.21576(3)	1/4	0.34875(2)	0.55(1)
Sb1	4*c*	1	0.09365(5)	1/4	0.66414(4)	0.73(1)
Sb2	4*c*	1	0.12190(5)	1/4	0.04894(4)	0.62(1)
		$(U_{0.49(1)}Ho_{0.51(1)})_3Sb_7$ (*Immm*, own type)				
U/Ho(1)	8*l*	0.458(9)/0.542(9)	0	0.14131(2)	0.36826(1)	0.57(1)
U/Ho(2)	4*i*	0.56(1)/0.44(1)	0	0	0.16960(2)	0.56(1)
Sb(1)	8*l*	1	0	0.21156(3)	0.19775(2)	0.61(1)
Sb(2)	8*l*	1	0	0.36031(3)	0.41093(2)	0.79(1)
Sb(3)	4*j*	1	1/2	0	0.30047(3)	0.61(1)
Sb(4)	4*g*	1	0	0.33745(4)	0	0.75(1)
Sb(5)	2*c*	1	1/2	1/2	0	0.89(1)
Sb(6)	2*a*	1	0	0	0	1.17(1)

[a] The last column contains the equivalent isotropic values B_{eq} of the anisotropic displacement parameters ($\times 10^{-4}$, pm^2), as defined by $B_{eq} = 8\pi^2 U_{eq}$, where U_{eq} is one-third of the orthogonalized U_{ij} tensor. The positional parameters were standardized with the program STRUCTURE TIDY.[19] Occupancy parameters of the mixed atomic positions U/Gd and U/Ho were refined with constrains. Therefore, only one of the two standard deviations listed for each combined occupancy parameter is independent.

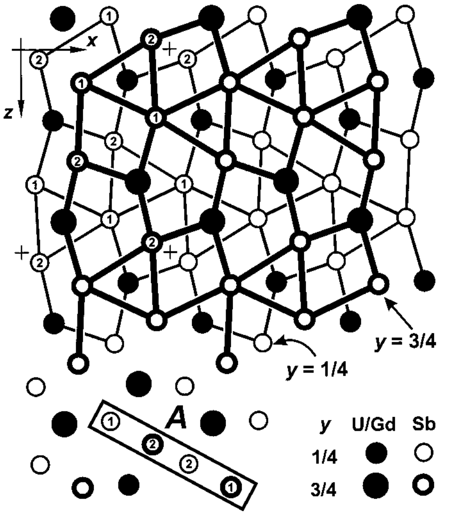

Figure 2. Crystal structure of the $PbCl_2$ type antimonide $(U_{2/3}Gd_{1/3})Sb_2$. All atoms are situated on mirror planes, which are separated from each other by half a translation period of the projection direction. These atoms are connected by heavy ($y = 3/4$) and light lines ($y = 1/4$), which do not necessarily correspond to chemical bonds. The four antimony atoms enframed and designated with the letter *A* form a band which is shown from a different point of view in Figure 5.

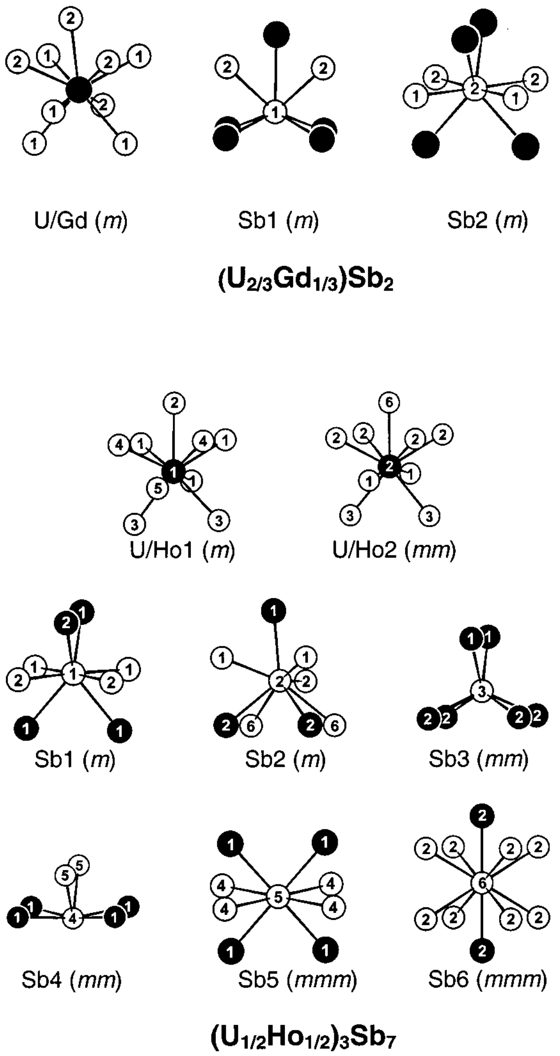

Figure 3. Near-neighbor coordinations in the structures of $(U_{2/3}Gd_{1/3})Sb_2$ and $(U_{1/2}Ho_{1/2})_3Sb_7$. The site symmetries of the central atoms are given in parentheses. Single-digit numbers correspond to the atom designations.

$(U_{2/3}Sm_{1/3})Sb_2$ somewhat deviates from the smooth function. This is probably due to a slightly different U/*R* ratio. The V/A ratios of the yttrium compounds $(U_{2/3}Y_{1/3})Sb_2$ and $(U_{1/2}Y_{1/2})_3Sb_7$ fit between those of the corresponding gadolinium and terbium compounds. This is also the case for several series of rare earth (*R*) transition metal (*T*) aluminides, e.g., the series with the compositions RT_2Al_{10}.[20,21] For the antimonides RAgSb$_2$[11] and aluminides $R_6Cr_4Al_{43}$[22] and $R_6Mo_4Al_{43}$,[22] the cell volumes of the yttrium compounds fit between those of the terbium and dysprosium compounds. For ternary rare earth transition metal carbides and phosphides, the cell volumes of the yttrium compounds were found to be between those of the terbium and dysprosium compounds or between those of the dysprosium and holmium compounds; for oxides, it usually is between those of the dysprosium and holmium or holmium and erbium compounds.[23,24] Thus, there is a tendency for the atomic volume of yttrium to decrease relative to the atomic volume of the other

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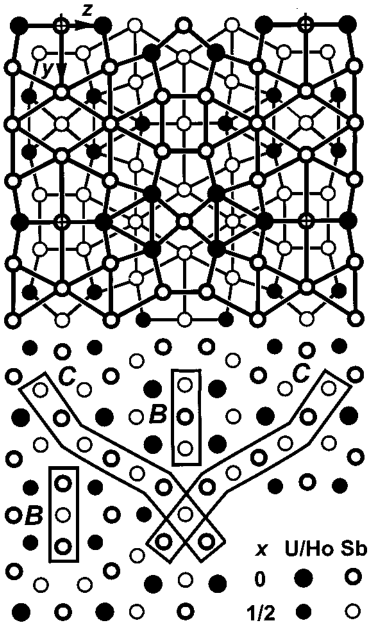

Figure 4. Crystal structure of $(U_{1/2}Ho_{1/2})_3Sb_7$. All atoms are situated on mirror planes at $x = {}^1/_2$ and $x = 0$ as indicated by heavy and light lines, respectively. These lines do not necessarily correspond to chemical bonds. Single-digit numbers indicate atom designations. The structure contains antimony chains and a three-dimensionally infinite network of antimony atoms. Fragments of the chains (*B*) and the network (*C*) are outlined and shown from different viewpoints in Figure 5.

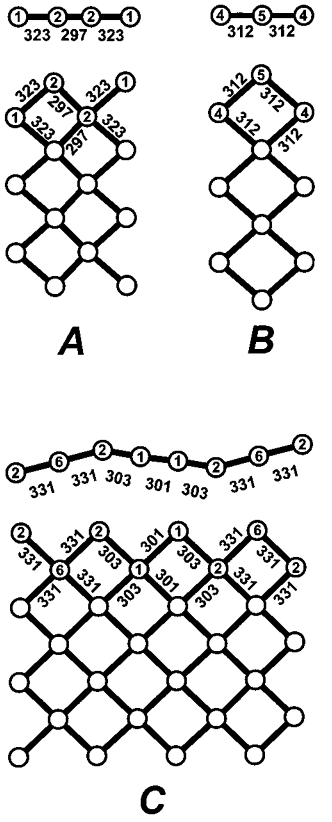

Figure 5. Cutouts of the polyanionic antimony band *A* in the structure of $(U_{2/3}Gd_{1/3})Sb_2$, the chain *B*, and the net *C* of $(U_{1/2}Ho_{1/2})_3Sb_7$ shown in Figures 2 and 4. In the upper parts of the three partial figures *A*, *B*, and *C*, the antimony atoms are shown as in the Figures 2 and 4; below, these polyanions are shown in projections perpendicular to their infinite extensions. Interatomic Sb−Sb distances are given in pm units.

rare earth elements in going from aluminides and antimonides via carbides and phosphides to oxides.

The compounds $(U_{2/3}R_{1/3})Sb_2$ crystallize with the orthorhombic $PbCl_2$ type structure, which has almost 500 representatives.[25] This simple structure has already been observed for the binary pnictides with typically tetravalent metals: TiP_2,[26−28] ZrP_2,[26,28] HfP_2,[26] ThP_2,[29] $ZrAs_2$,[30] $HfAs_2$,[31,32] $ThAs_2$,[29] and β-$ZrSb_2$.[33] The compounds $(U_{2/3}R_{1/3})Sb_2$ also belong to the same branch of the $PbCl_2$ type structure as these binary dipnictides with similar axial ratios, a/c and $(a+c)/b$.[34] The structure is shown in Figure 2, with $(U_{2/3}Gd_{1/3})Sb_2$ as an example. The uranium and gadolinium atoms statistically occupy one site, which is surrounded only by (nine) antimony atoms (Figure 3). Hence, there are no metal−metal bonds. The antimony atoms occupy two sites, one (Sb2) with four metal neighbors in approximately tetrahedral coordination, the other (Sb1) with five metal neighbors in approximately square-pyramidal arrangement. In addition, both antimony atoms have antimony neighbors. The Sb1 atom has two very weak Sb1−Sb2 bonds, with a distance of 322.6 pm. The Sb2 atoms form a zigzag chain, with Sb2−Sb2 distances of 296.5 pm. In addition, they have two Sb1 neighbors (at 322.6 pm). The resulting antimony polyanion is one-dimensionally infinite in the form of a band (Figure 5).

In a recent paper, the Zintl−Klemm concept was combined with bond-length bond-strength relationships in order to rationalize antimony−antimony bonds in rare earth polyantimonides.[35] For an Sb−Sb bond of 280 pm, a bond order of one (corresponding to one two-electron bond) was assumed. Assuming the octet rule to be valid, an antimony atom with one Sb−Sb bond thus obtains an oxidation number of −2.[41] For longer bonds, the bond order is lower. When the Sb−Sb distances exceed 350 pm, the antimony atoms are considered to be isolated from each other. They obtain the oxidation number −3. Using this relationship,[35] we obtain for the Sb−Sb bonds of 322.6 and 296.5 pm in $(U_{2/3}Gd_{1/3})Sb_2$ bond orders of 0.316 and 0.640, corresponding to oxidation numbers of $(2 \times 0.316 - 3.00 =) -2.37$ for the Sb1 atoms and $(2 \times 0.640 + 2 \times 0.316 - 3.00 =) -1.09$ for the Sb2 atoms. Since the gadolinium atoms are normally trivalent, we can calculate the valency (corresponding to the oxidation number) of the uranium atoms by using the occupancy parameters of the uranium and gadolinium atoms of 0.675 and 0.325 and balancing the formal charges. This results in the formula $[(U^{+3.69})_{0.675}]^{+2.49}[(Gd^{+3})_{0.325}]^{+0.97}$-$[Sb1^{-2.37}Sb2^{-1.09}]^{-3.46}$, which indicates that the uranium atoms have a mixed (+3/+4) or intermediate valency (+3.69). In any case, their valency is greater than +3, and this may be the reason the $PbCl_2$ type structure has not been observed for binary antimonides of the (trivalent) rare earth elements. On the other hand, $PbCl_2$ type pnictides are known for many typically tetravalent metals, which we have enumerated in the preceding paragraph. Only for β-$ZrSb_2$ has this structure been refined with great accuracy.[33] Interestingly, an extended Hückel calculation for this compound showed occupied antibonding states close to the Fermi level.[33] This, in turn, allows one to rationalize why

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Scheme 1

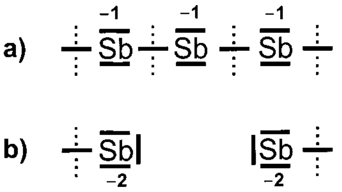

Table 4. Interatomic Distances in $(U_{0.675(9)}Gd_{0.325(9)})Sb_2$ and $(U_{0.49(1)}Ho_{0.51(1)})_3Sb_7$[a]

				$(U_{0.675(9)}Gd_{0.325(9)})Sb_2$				
U/Gd:	2Sb1	314.2	Sb1:	2U/Gd	314.2	Sb2:	2Sb2	296.5
	1Sb2	315.6		2U/Gd	317.1		1U/Gd	315.6
	2Sb1	317.1		2Sb2	322.6		2U/Gd	318.1
	2Sb2	318.1		1U/Gd	336.4		2Sb1	322.6
	1Sb2	323.9		[1Sb2	395.3]		1U/Gd	323.9
	1Sb1	336.4		[2Sb2	396.3]		[1Sb1	395.3]
							[2Sb1	396.3]

		$(U_{0.49(1)}Ho_{0.51(1)})_3Sb_7$			
U/Ho1:	2Sb3	314.9	Sb2:	2Sb1	303.4
	1Sb5	315.3		2U/Ho2	323.2
	2Sb4	317.1		1Sb2	324.4
	2Sb1	319.2		1U/Ho1	326.4
	1Sb2	326.4		2Sb6	330.5
	1Sb1	326.8		[2Sb4	387.7]
U/Ho2:	1Sb6	308.9	Sb3:	2U/Ho2	314.4
	2Sb1	310.5		4U/Ho1	314.9
	2Sb3	314.4	Sb4:	2Sb5	312.1
	4Sb2	323.2		4U/Ho1	317.1
Sb1:	2Sb1	301.1		[4Sb2	387.7]
	2Sb2	303.4	Sb5:	4Sb4	312.1
	1U/Ho2	310.5		4U/Ho1	315.3
	2U/Ho1	319.2	Sb6:	2U/Ho2	308.9
	1U/Ho1	326.8		8Sb2	330.5

[a] The distances were calculated with the lattice constants obtained from the Guinier powder data. All distances shorter than 400 pm are listed. Standard deviations are all 0.1 pm or smaller than that. Atoms with distances listed in brackets are not shown in Figure 3.

in $(U_{2/3}Gd_{1/3})Sb_2$ the uranium atoms are not purely tetravalent. Apparently, with mixed (or intermediate) valent $U^{3+/4+}$ atoms, no antibonding Sb−Sb states need to be occupied in $(U_{2/3}Gd_{1/3})$-Sb_2. In this context it is also fitting that the antimony sites in the zirconium antimonide β-$ZrSb_2$ were found to deviate from the full occupancy. The exact composition was found to be $ZrSb_{1.956(4)}$.[33] Unoccupied Sb sites allow antibonding Sb−Sb interactions to be turned into nonbonding states, which are energetically more favorable. The latter can readily be demonstrated by comparing three antimony atoms in a chain with single Sb−Sb bonds, as compared to the situation when the antimony atom in the middle of the chain is taken out. For this demonstration we use the Lewis formalism, where two electrons are represented by a solid line. In the following scheme the three antimony atoms of the chain obtain a) a total formal charge of −3 as compared to b) the formal charge of −4 for the two antimony atoms of the broken chain. Thus, a larger formal charge can be accommodated if some antimony sites remain unoccupied.

The structure of the compounds $(U_{1/2}R_{1/2})_3Sb_7$, determined for $(U_{0.49(1)}Ho_{0.51(1)})_3Sb_7$, is of a new type with a total of eight atomic sites. Both of the two metal sites are coordinated by nine antimony atoms forming a trigonal prism, where the three rectangular faces of the prism are capped by three additional antimony atoms. The U/Ho1−Sb distances cover the range from 314.9 to 326.8 pm; for the U/Ho2 sites this range extends between 308.9 and 323.2 pm (Table 4). The average U/Ho−Sb distances amount to 319.0 and 316.8 pm, respectively. Thus, despite the longer spread of the distances (which should result in a longer average distance), the average distance for the U/Ho2 atoms is shorter. This suggests a higher formal charge for the U/Ho2 sites, which conforms with the higher U/Ho ratio of 0.56(1)/0.44(1) for the U/Ho2 site as compared to the U/Ho ratio of 0.458(9)/0.542(9) for the U/Ho1 site. (For comparison, the metallic radii for the coordination number 12 are 176.6 pm for holmium and 156 pm for uranium.[36] In the elemental structures the holmium atoms are certainly trivalent, whereas the average uranium atom in the structure of elemental uranium[37] almost certainly has a valency higher than three.)

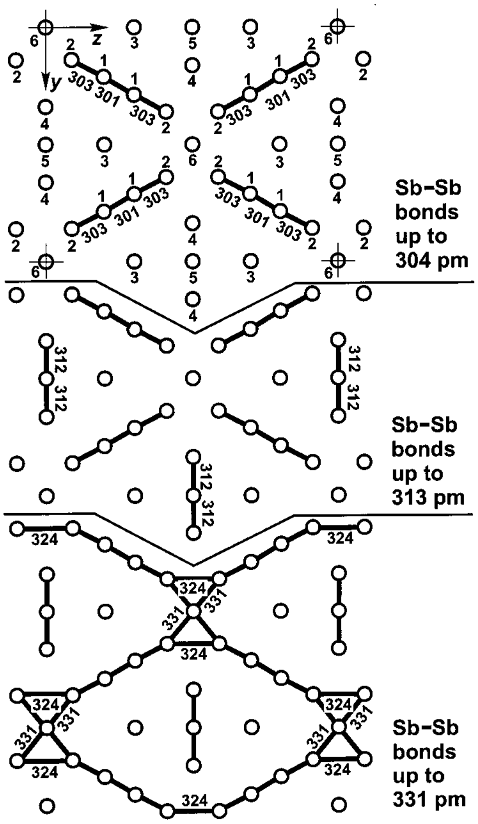

Figure 6. Bond distances within the polyanionic antimony network and antimony bands in the structure of $(U_{1/2}Ho_{1/2})_3Sb_7$. Single-digit numbers in the upper part of the drawing correspond to the designations of the antimony atoms. The Sb3 atoms do not form Sb−Sb bonds.

The structure of $(U_{1/2}Ho_{1/2})_3Sb_7$ has six antimony sites, with total coordination numbers (Figure 3) varying between 6 for the Sb3 and Sb4 atoms and 10 for the Sb6 atoms. The Sb6 atoms have two metal neighbors, the Sb2 atoms have three metal neighbors, the Sb1, Sb4, and Sb5 atoms have four metal neighbors, and the Sb3 atom is somewhat exceptional in that it has six metal and no antimony neighbors. Thus, with the exception of the Sb3 atom, all antimony atoms form Sb−Sb bonds with bond lengths varying between 301.1 pm for the Sb1−Sb1 bond and 330.5 pm for the Sb2−Sb6 interactions. The Sb1, Sb2, and Sb6 atoms form a three-dimensional network with the somewhat arbitrarily outlined building element *C* shown in Figures 4, 5, and in the lower part of Figure 6. The cavities of this network contain one-dimensionally infinite bands *B* of Sb4 and Sb5 atoms, the isolated Sb3 atoms, and (of course) also the metal atoms. The Sb−Sb bonding is outlined in Figure

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Table 5. Antimony−Antimony Distances d_{ij} (pm), Bond Orders (Bond Strengths, Bond Valencies) v_{ij}, and Formal Charges *ch* in $(U_{1/2}Ho_{1/2})_3Sb_7$ as Calculated from the Equation $v_{ij} = \exp[(280 - d_{ij})/37]$[a]

atom		d_{ij}	v_{ij}	$\sum v_{ij}$	*ch*/Sb	*ch*/cell
Sb1:	2Sb1	301.1	2 × 0.565	1.13		
	2Sb2	303.4	2 × 0.531	1.06	−0.81/Sb1	−6.48/8Sb1
Sb2:	2Sb1	303.4	2 × 0.531	1.06		
	1Sb1	324.4	1 × 0.301	0.30		
	2Sb6	330.5	2 × 0.255	0.51	−1.13/Sb2	−9.04/8Sb2
Sb3:	−	−	−	−	−3.00/Sb3	−12.00/4Sb3
Sb4:	2Sb5	312.1	2 × 0.420	0.84	−2.16/Sb4	−8.64/4Sb4
Sb5:	4Sb4	312.1	4 × 0.420	1.68	−1.32/Sb5	−2.64/2Sb5
Sb6:	8Sb2	330.5	8 × 0.255	2.04	−0.96/Sb6	−1.92/2Sb6
total formal charge per unit cell:						−40.72/28Sb

[a] The last two columns contain the formal charge per antimony atom (*ch*/Sb) and the formal charge of the antimony atoms per unit cell (*ch*/cell).[35]

6. We have used the previously optimized bond-length bond-strength relationship[35] to assign bond orders and formal charges to the Sb−Sb bonds in $(U_{1/2}Ho_{1/2})_3Sb_7$, as outlined above for $(U_{2/3}Gd_{1/3})Sb_2$ and shown in Table 5. This analysis results in a total formal charge of −40.72 for the 28 antimony atoms of the unit cell. For a formula unit, this corresponds to a formal charge of −10.18. By compensation of the formal charges one obtains formal charges (valencies) for the uranium atoms, assuming a formal charge of +3 for the holmium atoms. The corresponding formula for the compound then is $[[(U^{+3.80})_{0.49}(Ho^{+3})_{0.51}]^{+3.39}]_3[Sb_7]^{-10.18}$. It can be seen that the average uranium atom of this compound obtains a valency of 3.80. Again, as already discussed for $(U_{2/3}Gd_{1/3})Sb_2$, this allows one to rationalize why this structure has not been found for binary rare earth antimonides.

In Figure 7, we demonstrate that the structure of $(U_{1/2}Ho_{1/2})_3Sb_7$ has great similarity with the structures reported for the compounds La_6TSb_{15} (*T* = Mn, Cu, Zn) and Ce_6MnSb_{15}.[38] For the latter compound the structure has been determined independently in our laboratory, resulting in the composition $Ce_6Mn_{0.800(4)}Sb_{14.80(1)}$.[39] The difference between the structure of the series Ln_6TSb_{15} and the presently reported structure of $(U_{1/2}Ho_{1/2})_3Sb_7$ is emphasized in the projections of the two structures shown in the lower part of Figure 7. It can be seen that the positions of the manganese atoms of Ce_6MnSb_{15} are unoccupied in $(U_{1/2}Ho_{1/2})_3Sb_7$ and that two adjacent antimony atoms of Ce_6MnSb_{15} are substituted by a single antimony atom in $(U_{1/2}Ho_{1/2})_3Sb_7$. These substitutions may be expressed by the crystal chemical formulas $Ce_6MnSb_{13}Sb_2\square$ and $(U/Ho)_6\square Sb_{13}\square_2Sb$, where the squares $\square$ indicate vacant sites. In reality this coupled formation of vacancies and substitutions is more complicated, since the manganese atoms are situated on a four-fold position with an occupancy of only 40%.

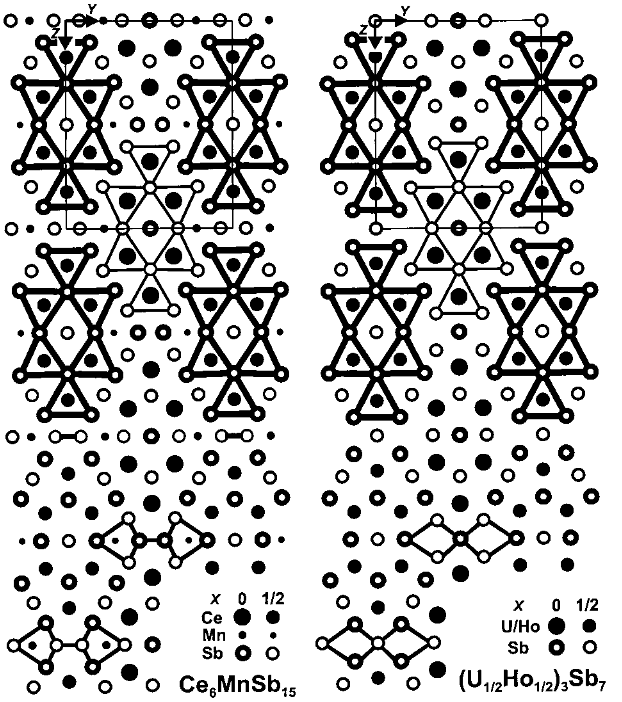

Figure 7. Comparison of the $(U_{1/2}Ho_{1/2})_3Sb_7$ and Ce_6MnSb_{15} structures. In the upper parts of the drawings, the trigonal prisms of antimony atoms surrounding the uranium and lanthanoid atoms are outlined. In the lower left-hand part of the figure, the Sb_2 pairs in Ce_6MnSb_{15} substituting for the Sb6 atoms of $(U_{1/2}Ho_{1/2})_3Sb_7$ are shown. The antimony environments of the manganese atoms in Ce_6MnSb_{15} are emphasized.

The recently reported structure of $Pr_{12}Ga_4Sb_{23}$ also has some similarity to the structures of $(U_{1/2}Ho_{1/2})_3Sb_7$ and $Ce_6Mn_{1-x}Sb_{15-y}$. The reader is referred to Figure 10 of the paper by Mills and Mar[40] for a comparison of the structures of $Pr_{12}Ga_4Sb_{23}$ and La_6MnSb_{15} (the latter being isotypic with Ce_6MnSb_{15}).

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Supporting Information Available: Further crystallographic details and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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