

# One-dimensional Gold Clusters in HP-Ce<sub>7</sub>Au<sub>13+x</sub>Ge<sub>10-x</sub>

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Single crystals of the high-pressure phase Ce<sub>7</sub>Au<sub>13+x</sub>Ge<sub>10-x</sub> were obtained by treating CeAuGe at 9.5 GPa and 1473–1523 K in a multi-anvil press. The structure of Ce<sub>7</sub>Au<sub>13.35</sub>Ge<sub>9.65</sub> was refined on the basis of single-crystal X-ray diffractometer data: new type, *Pbam*, *a* = 1571.9(3), *b* = 1780.3(4), *c* = 443.58(9) pm, *wR*<sub>2</sub> = 0.0470, 2017 *F*<sup>2</sup> values, 96 variables. Two of the five germanium sites show a small degree of Ge/Au mixing. The gold and germanium atoms build up a complex three-dimensional, covalently bonded [Au<sub>13.35</sub>Ge<sub>9.65</sub>] network with Au–Ge distances ranging from 249 to 293 pm. The [Au<sub>13.35</sub>Ge<sub>9.65</sub>] network also exhibits a one-dimensional gold cluster with Au–Au distances of 275–301 pm and a weakly bonded germanium dumb-bell with a Ge4–Ge5 bond length of 271 pm. The four crystallographically independent cerium atoms fill cavities of coordination numbers 19 and 20 within the [Au<sub>13.35</sub>Ge<sub>9.65</sub>] network. These coordinations are known from other structure types. Consequently one can describe the Ce<sub>7</sub>Au<sub>13.35</sub>Ge<sub>9.65</sub> structure as an intergrowth variant of EuAuGe, HP-CeAuGe (TiNiSi), CeAu<sub>2</sub>Ge<sub>2</sub> (CePt<sub>2</sub>Ge<sub>2</sub>), and Ce<sub>3</sub>Ag<sub>4</sub>Ge<sub>4</sub> (Gd<sub>3</sub>Cu<sub>4</sub>Sn<sub>4</sub>) related slabs.

**Key words:** High-pressure Synthesis, Cerium, Germanide, Crystal Structure, Gold

## Introduction

The ternary system Ce–Au–Ge is characterized by the germanides CeAuGe [1–8], CeAu<sub>2</sub>Ge<sub>2</sub> [9–13], Ce<sub>5</sub>Au<sub>0.43</sub>Ge<sub>3.57</sub> [14], Ce<sub>2</sub>AuGe<sub>6</sub> [15], and the solid solutions CeAu<sub>x</sub>Ge<sub>2-x</sub> [16, 17] with AlB<sub>2</sub>- or α-ThSi<sub>2</sub>-related structures. Some of these compounds show ordering of the cerium magnetic moments at low temperature. Ferromagnetic ordering has been detected at 6 and 8 K for CeAu<sub>0.75</sub>Ge<sub>1.25</sub> [16] and CeAu<sub>0.28</sub>Ge<sub>1.72</sub> [17], respectively. Equiatomic CeAuGe [2] has the higher Curie temperature of 10 K with an alignment of the moments approximately along the *a* axis of the hexagonal cell [4]. Antiferromagnetic ordering occurs in CeAu<sub>2</sub>Ge<sub>2</sub> [9–13]. Néel temperatures between 13.5 and 16 K have been reported from susceptibility and neutron diffraction experiments. The magnetic ordering of this germanide seems to depend strongly on the conditions of sample preparation, *e. g.*

arc-melting or different flux techniques for crystal growth.

Under normal-pressure conditions, CeAuGe [1–3] crystallizes with the hexagonal NdPtSb-type structure, a superstructure variant of the aristotype AlB<sub>2</sub> [18]. The gold and germanium atoms build up puckered layers of fully ordered Au<sub>3</sub>Ge<sub>3</sub> hexagons in AB stacking sequence, which are separated by the cerium atoms. *In-situ* high-pressure experiments in a diamond anvil cell showed a phase transition at 8.7 GPa [5]. CeAuGe shows a drastic orthorhombic distortion and its [AuGe] polyanionic network is three-dimensional (TiNiSi type). From a group-theoretical point of view, the phase transition is of a reconstructive type. The normal- and high-pressure modifications crystallize with different AlB<sub>2</sub> superstructures in the hexagonal, respectively orthorhombic branch [18].

Based on these *in-situ* high-pressure results we started synthesis experiments for HP-CeAuGe in a multi-anvil cell, in order to get a bulk amount of

the high-pressure phase for magnetic susceptibility and electrical resistivity studies. Instead of HP-CeAuGe we obtained a new phase, HP-Ce<sub>7</sub>Au<sub>13.35</sub>Ge<sub>9.65</sub>, under HP-HT conditions of 9.5 GPa and 1473–1523 K. The structure determination and crystal chemistry of this new germanide are reported herein.

## Experimental

### Synthesis

The synthesis of the new high-pressure phase Ce<sub>7</sub>Au<sub>13.35</sub>Ge<sub>9.65</sub> started from the precursor compound CeAuGe. Starting materials for the syntheses of CeAuGe were sublimed cerium pieces (Johnson Matthey), pieces of a gold bar (Heraeus), and germanium pieces (Chempur), all with stated purities better than 99.9%. A polycrystalline CeAuGe sample was prepared *via* arc-melting [19] of the elements under an argon atmosphere of *ca.* 700 mbar. The argon was purified over titanium sponge (900 K), silica gel, and molecular sieves. The CeAuGe sample was remelted three times in order to ensure homogeneity. The phase purity of the CeAuGe precursor was checked through a Guinier powder pattern.

The high-pressure/high-temperature treatments were carried out in a multi-anvil assembly. Details concerning the construction of the assembly can be found in references [20–23]. A boron nitride crucible of a 14/8-assembly was loaded with carefully milled CeAuGe, compressed within 2.5 h to 9.5 GPa and heated to 1473–1523 K for the following 15 min. After holding this temperature for 10 min

the sample was cooled down to 1173 K within a minute. To enhance the crystallinity of the sample, an annealing period of 420 min followed, accompanied by a slow decrease of the temperature from 1173 to 823 K. Afterwards, the sample was cooled to room temperature within 1 min. After decompression (8 h), the sample was carefully sep-

Table 1. Crystal data and structure refinement for Ce<sub>7</sub>Au<sub>13.35</sub>Ge<sub>9.65</sub>.

Empirical formula	Ce <sub>7</sub> Au <sub>13.35</sub> Ge <sub>9.65</sub>
Formula weight, g mol <sup>-1</sup>	4310.21
Unit cell dimensions, pm	<i>a</i> = 1571.9(3) <i>b</i> = 1780.3(4) <i>c</i> = 443.58(9)
Cell volume, nm <sup>3</sup>	<i>V</i> = 1.2413
Space group, <i>Z</i>	<i>Pbam</i> , 2
Pearson code	oP60
Calculated density, g cm <sup>-3</sup>	11.53
Crystal size, μm <sup>3</sup>	20 × 20 × 30
Absorption correction	multi-scan [24]
Absorption coefficient, mm <sup>-1</sup>	102.5
<i>F</i> (000), e	3538
$\theta$ range for data collection, deg	3–30
Range in <i>hkl</i>	±22, ±25, ±6
Total no. of reflections	3501
Independent reflections / <i>R</i> <sub>int</sub>	2017 / 0.0240
Reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> ) / <i>R</i> <sub><math>\sigma</math></sub>	1770 / 0.0272
Data / parameters	2017 / 96
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.047
<i>R</i> 1 / <i>wR</i> 2 for <i>I</i> > 2 $\sigma$ ( <i>I</i> )	0.0207 / 0.0455
<i>R</i> 1 / <i>wR</i> 2 for all data	0.0271 / 0.0470
Extinction coefficient	0.00007(2)
Largest diff. peak / hole, e Å <sup>-3</sup>	1.87 / -2.47

Table 2. Atomic coordinates and anisotropic displacement parameters (pm<sup>2</sup>) of Ce<sub>7</sub>Au<sub>13.35</sub>Ge<sub>9.65</sub>. *U*<sub>13</sub> = *U*<sub>23</sub> = 0. *U*<sub>eq</sub> is defined as one third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>eq</sub>
Ce1	4g	0.33792(3)	0.18209(3)	0	79(2)	103(3)	72(3)	10(2)	85(1)
Ce2	4h	0.15895(3)	0.95867(3)	1/2	65(2)	96(3)	66(3)	5(2)	76(1)
Ce3	4g	0.41515(3)	0.75895(3)	0	75(2)	123(3)	109(3)	6(2)	102(1)
Ce4	2c	0	1/2	0	89(3)	147(4)	102(4)	-31(3)	113(2)
Au1	4h	0.19614(3)	0.14983(2)	1/2	117(2)	136(2)	169(2)	-25(1)	141(1)
Au2	4h	0.43005(3)	0.27717(2)	1/2	134(2)	107(2)	119(2)	-11(1)	120(1)
Au3	4g	0.24582(2)	0.85711(2)	0	133(2)	121(2)	89(2)	20(1)	114(1)
Au4	4h	0.36733(2)	0.89163(2)	1/2	84(2)	129(2)	224(2)	8(2)	145(1)
Au5	4h	0.35034(3)	0.04985(2)	1/2	103(2)	105(2)	99(2)	-15(1)	102(1)
Au6	2a	0	0	0	216(3)	559(5)	169(3)	183(3)	315(2)
Au7	4h	0.03149(3)	0.09674(3)	1/2	93(2)	187(2)	512(3)	24(1)	264(1)
Ge1 <sup>a</sup>	4g	0.42783(6)	0.35868(6)	0	125(5)	113(6)	90(6)	21(4)	109(4)
Ge2	4h	0.52170(7)	0.86089(6)	1/2	72(4)	95(5)	248(6)	0(4)	139(2)
Ge3	4h	0.24939(7)	0.28351(6)	1/2	113(5)	80(5)	75(5)	1(4)	90(2)
Ge4	4g	0.29410(7)	0.99691(6)	0	114(5)	133(5)	80(5)	-50(4)	109(2)
Ge5 <sup>b</sup>	4g	0.15257(6)	0.08395(5)	0	181(5)	124(5)	81(5)	-12(3)	129(3)

<sup>a</sup> 97.2(3) % Ge + 2.8(3) % Au; <sup>b</sup> 85.7(4) % Ge + 14.3(4) % Au.

arated from the surrounding assembly parts. The resulting Ce<sub>7</sub>Au<sub>13.35</sub>Ge<sub>9.65</sub> crystals have metallic lustre and are stable in air over months.

After the HP-HT experiments a sample of the starting composition 7 Ce : 10 Au : 13 Ge was also prepared by arc-melting and subsequent annealing at 970 K for 5 d in order to check whether or not the new phase is also formed under ambient pressure conditions.

#### EDX data

EDX analyses were carried out in variable pressure mode with a Zeiss EVO<sup>®</sup> MA10 scanning electron microscope (SEM) with CeO<sub>2</sub>, Au, and Ge as standards. A small piece of the HP sample was embedded in a methylmetacrylate matrix and the surface was polished using different silica and diamond pastes. This polished surface was then analyzed in the SEM in backscattering mode (Fig. 1). EDX analyses revealed three different phases. One major phase with an average composition of 34 ± 2 at-% Ce : 31 ± 2 at-% Au : 35 ± 2 at-% Ge can be related to the precursor CeAuGe. Of the two minor, (i) with 22 ± 1 at-% Ce : 45 ± 1 at-% Au : 33 ± 1 at-% Ge corresponds to the phase Ce<sub>7</sub>Au<sub>13.35</sub>Ge<sub>9.65</sub> (23.3 : 44.5 : 32.3), and (ii) as another new phase with an approximate composition ~Ce<sub>5</sub>Au<sub>15</sub>Ge<sub>3</sub>, probably also a HP-HT phase. Further investigations on that phase are in progress.

#### X-Ray diffraction

The polycrystalline sample was characterized by a Guinier pattern (Huber G670 powder diffractometer) with CuK<sub>α1</sub> radiation. For powder diffraction measurements, the sample was carefully crushed in a hardened steel mortar and subsequently grinded in an agate mortar. A comparison of the powder pattern recorded from the bulk material with the simulation derived from the single-crystal structure determination revealed that Ce<sub>7</sub>Au<sub>13.35</sub>Ge<sub>9.65</sub> is only a minor phase. The structure of the main product of this experiment is still unknown.

Powder diffraction analyses of the 7-13-10 sample prepared by arc-melting under ambient conditions showed CeAuGe and CeAu<sub>2</sub>Ge<sub>2</sub> as the main products, directly after arc-melting as well as after the annealing sequence. Both powder patterns showed an additional new phase. The remaining lines could not be associated with one of the known ternary phases listed in the Introduction. EDX analyses of that phase were close to 24 ± 1 at-% Ce : 42 ± 1 at-% Au : 34 ± 1 at-% Ge. This composition is similar to that of the new HP phase, however, the powder patterns are distinctly different. Further phase analytical studies are in progress.

Two independently selected and irregularly shaped single crystals were taken from the high-pressure treated sam-

ple by mechanical fragmentation. The crystals were first investigated by Laue photographs in a Buerger camera (white molybdenum radiation; imaging plate technique, Fujifilm, BAS-1800) in order to check the quality for intensity data collection. Subsequently, intensity data of a suit-

Table 3. Interatomic distances (pm) for Ce<sub>7</sub>Au<sub>13.35</sub>Ge<sub>9.65</sub> calculated with the powder lattice parameters. Standard deviations are equal or smaller than 0.1 pm. All distances of the first coordination spheres are listed. Note the mixed occupancies of Ge1 and Ge5 (Table 2).

Ce1:	2	Au2	314.4	Au1:	1	Ge3	252.3	Ge1:	2	Au2	265.1
	2	Ge3	318.1		2	Ge5	260.1		1	Au3	273.0
	2	Au1	319.6		1	Au7	275.5		1	Au6	276.0
	2	Ge2	322.1		1	Au5	300.7		2	Au7	286.4
	2	Au5	324.0		2	Ce1	319.6		2	Ce2	315.4
	1	Ge4	336.8		2	Ce3	342.8		1	Ce3	323.7
	1	Au3	338.3		1	Ce2	343.3		1	Ce1	344.7
	1	Ge5	339.7	Au2:	1	Ge2	257.2	Ge2:	1	Au4	248.7
	1	Ge1	344.7		2	Ge1	265.1		1	Au5	256.3
	1	Ce3	402.1		1	Au7	275.3		1	Au2	257.2
	1	Ce4	412.3		1	Ge3	284.2		2	Ce1	322.1
	1	Ce3	420.7		2	Ce1	314.4		2	Ce3	331.9
	2	Ce1	443.6		2	Ce3	335.5		2	Ce4	334.2
Ce2:	2	Ge4	314.6		1	Ce2	352.1	Ge3:	1	Au1	252.3
	2	Ge5	314.7	Au3:	2	Ge3	257.7		2	Au3	257.7
	1	Au7	315.2		1	Ge4	260.2		1	Au4	265.9
	2	Ge1	315.4		1	Ge1	273.0		1	Au2	284.2
	2	Au3	317.1		2	Au4	299.1		2	Ce1	318.1
	1	Au7	317.1		2	Ce2	317.1		2	Ce3	343.5
	1	Au5	341.8		1	Ce3	318.4		1	Ce2	343.5
	2	Au6	342.1		1	Ce1	338.3	Ge4:	2	Au5	256.7
	1	Ge3	343.5	Au4:	1	Ge2	248.7		1	Au3	260.2
	1	Au1	345.3		1	Ge3	265.9		1	Ge5	271.1
	1	Au4	348.6		1	Au5	282.9		2	Au4	312.4
	1	Au2	352.1		2	Au3	299.1		2	Ce2	314.6
	2	Ce2	443.6		2	Ge4	312.4		1	Ce4	323.7
Ce3:	1	Au3	318.4		2	Ce3	332.6		1	Ce1	336.8
	1	Ge1	323.7		1	Ce2	348.6	Ge5:	2	Au1	260.1
	1	Ge5	329.2		2	Ce4	360.4		1	Ge4	271.1
	2	Ge2	331.9	Au5:	1	Ge2	256.3		1	Au6	282.6
	2	Au4	332.6		2	Ge4	256.7		2	Au7	293.1
	2	Au2	335.5		1	Au4	282.9		2	Ce2	314.7
	2	Au1	342.8		1	Au1	300.7		1	Ce3	329.2
	2	Ge3	343.5		2	Ce1	324.0		1	Ce1	339.7
	2	Au7	373.7		2	Ce4	335.3				
	1	Ce1	402.1		1	Ce2	341.8				
	1	Ce1	420.7	Au6:	2	Ge1	276.0				
	2	Ce3	443.6		2	Ge5	282.6				
	1	Ce4	449.4		4	Au7	285.1				
Ce4:	2	Ge4	323.7	Au7:	1	Au2	275.3				
	4	Ge2	334.2		1	Au1	275.5				
	4	Au5	335.3		2	Au6	285.1				
	4	Au4	360.4		2	Ge1	286.4				
	2	Ce1	412.3		2	Ge5	293.1				
	2	Ce4	443.6		1	Ce2	315.2				
	2	Ce3	449.4		1	Ce2	317.1				

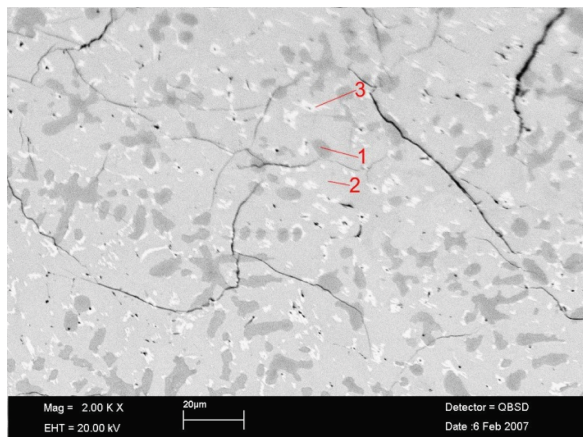


Fig. 1 (color online). Electron micrograph in backscattering mode of the polished surface of a small piece of the HP-HT-treated sample. The phases marked with 1 (medium grey), 2 (light grey), and 3 (white) correspond to Ce<sub>7</sub>Au<sub>13.35</sub>Ge<sub>9.65</sub>, CeAuGe, and a new phase with the approximate composition  $\sim$ Ce<sub>5</sub>Au<sub>15</sub>Ge<sub>3</sub>. The many micro cracks in the sample are readily visible.

able crystal of Ce<sub>7</sub>Au<sub>13.35</sub>Ge<sub>9.65</sub> were collected at room temperature by use of a Kappa CCD diffractometer (Bruker AXS / Nonius, Karlsruhe) equipped with a rotating anode. An absorption correction based on multi-scans [24] was applied to the data set. All relevant crystallographic data and details of the data collections are listed in Table 1.

#### Structure refinement

The Ce<sub>7</sub>Au<sub>13.35</sub>Ge<sub>9.65</sub> data set showed a primitive orthorhombic lattice, and the systematic extinctions were in agreement with space group *Pbam*. The starting atomic parameters were derived from Direct Methods with SHELXS-97 [25, 26], and the structure was refined with anisotropic displacement parameters for all atoms with SHELXL-97 (full-matrix least-squares on  $F_o^2$ ) [27, 28]. To check for deviations from the ideal composition, the occupancy parameters were refined in separate series of least-squares cycles. Except the Ge1 and Ge5 sites, all sites were fully occupied within three standard deviations. The course of the displacement parameters for Ge1 and Ge5 indicated mixed occupancy with more strongly scattering gold atoms. In the subsequent cycles these sites were refined with Ge/Au mixing, leading to the composition Ce<sub>7</sub>Au<sub>13.35</sub>Ge<sub>9.65</sub> for the investigated crystal. The final difference Fourier synthesis revealed no residual peaks. The refined atomic positions, anisotropic displacement parameters, and interatomic distances are given in Tables 2 and 3.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de), [http://www.fiz-karlsruhe.de/request\\_for\\_deposited\\_data.html](http://www.fiz-karlsruhe.de/request_for_deposited_data.html)) on quoting the deposition number CSD-426309.

#### Discussion

The high-pressure phase Ce<sub>7</sub>Au<sub>13+x</sub>Ge<sub>10-x</sub> crystallizes with a new structure type. Although the Ge1 and Ge5 sites show small degrees of Ge/Au mixing, we first discuss the ideal structure and draw back to the homogeneity range later. A projection of the Ce<sub>7</sub>Au<sub>13</sub>Ge<sub>10</sub> structure along the *c* axis is presented in Fig. 2. The gold and germanium atoms build up a complex three-dimensional [Au<sub>13</sub>Ge<sub>10</sub>] network with Au–Ge distances ranging from 249 to 293 pm, in close agreement with the sum of the covalent radii of 256 pm [29] and the Au–Ge distances within the puckered [AuGe] network of the equiatomic germanides REAuGe [3]. We can therefore assume substantial covalent Au–Ge bonding in Ce<sub>7</sub>Au<sub>13</sub>Ge<sub>10</sub>.

A striking structural feature of the Ce<sub>7</sub>Au<sub>13</sub>Ge<sub>10</sub> structure is the one-dimensional gold cluster (Fig. 3) within the [Au<sub>13</sub>Ge<sub>10</sub>] network which extends along 0 0 *z* and 1/2 1/2 *z* (Fig. 2). The Au7 atoms have slightly distorted tetrahedral gold coordination with Au–Au distances of 275–285 pm close to the Au–Au distance in *fcc* gold (288 pm) [30]. Two such tetrahedra share a common edge *via* the Au6 atoms and further condense in *c* direction *via* common corners. Double tetrahedra also occur in the germanide K<sub>4</sub>Au<sub>7</sub>Ge<sub>2</sub> (273–277 pm Au–Au) [31], however, these tetrahedra exclusively share common corners, and the Au substructure of K<sub>4</sub>Au<sub>7</sub>Ge<sub>2</sub> can be considered as a cutout of the cubic Laves phase.

The Ge1 and Ge2 atoms are directly bonded to the gold clusters. Refinement of the occupancy parameters revealed 2.8 and 14.3 % gold on the Ge1 and Ge5 sites, respectively. Thus one can assume a small homogeneity range Ce<sub>7</sub>Au<sub>13+x</sub>Ge<sub>10-x</sub>. The Au6 and Au7 atoms react on the Ge/Au mixing. Keeping the differences in the covalent radii for Au (134 pm) and Ge (122 pm) in mind, the enhanced displacement parameters *U*<sub>22</sub> and *U*<sub>33</sub> for Au6 and Au7 are comprehensible.

The [Au<sub>13</sub>Ge<sub>10</sub>] network leaves larger cavities that are filled by the four crystallographically independent cerium atoms. They have high coordination numbers of 19 (Ce1 and Ce2) and 20 (Ce3, Ce4) with differ-



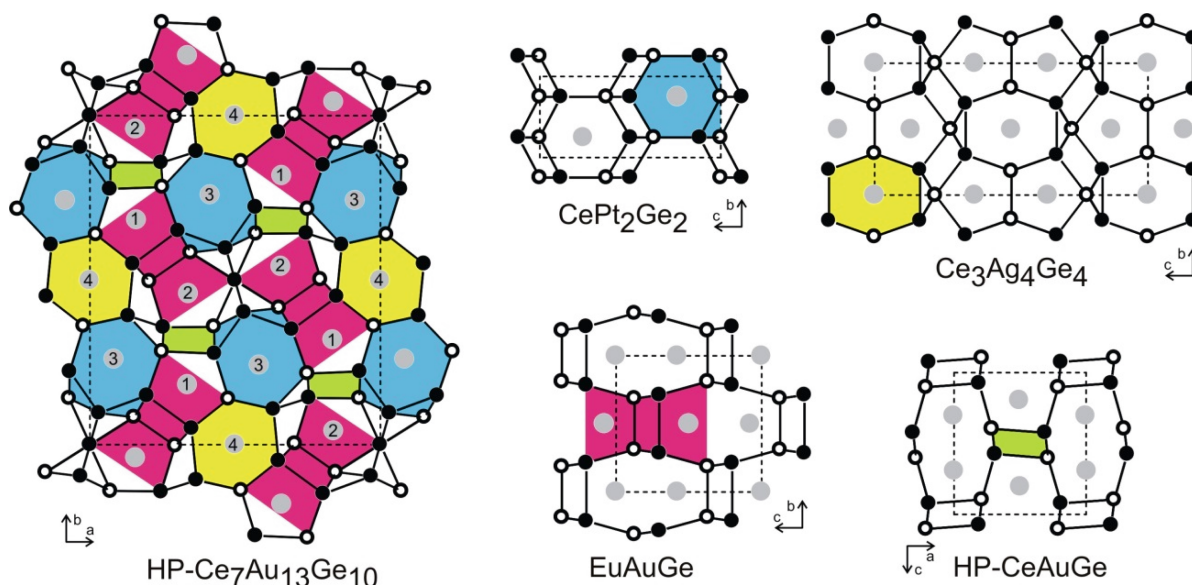


Fig. 2 (color online). Projection of the crystal structures of HP-Ce<sub>7</sub>Au<sub>13</sub>Ge<sub>10</sub>, CePt<sub>2</sub>Ge<sub>2</sub>, Ce<sub>3</sub>Ag<sub>4</sub>Ge<sub>4</sub>, EuAuGe, and HP-CeAuGe along the short unit cell axis. Rare earth, transition metal and germanium atoms are drawn as medium grey, black filled and open circles, respectively. The three-dimensional polyanionic networks built up by the transition metal and germanium atoms and the four crystallographically independent cerium sites in HP-Ce<sub>7</sub>Au<sub>13</sub>Ge<sub>10</sub> are emphasized. Characteristic structural slabs are underlined in color.

ent amounts of gold, germanium, and cerium atoms in their coordination shells: 7 Au + 7 Ge + 5 Ce for Ce1, 10 Au + 7 Ge + 2 Ce for Ce2, 9 Au + 6 Ge + 5 Ce for Ce3, and 8 Au + 6 Ge + 6 Ce for Ce4. The shortest Ce–Ce distance of 402 pm is well above the Hill limit [32] for *f* electron localization of 340 pm. This also suggests trivalent cerium in Ce<sub>7</sub>Au<sub>13</sub>Ge<sub>10</sub>. The Ge4 and Ge5 atoms are at a distance of 271 pm. In view of the Ge–Ge distances of 256 in the Zintl phase Eu<sub>5</sub>Ge<sub>3</sub> with a Ge<sub>2</sub><sup>6-</sup> dumb-bell and of 257 pm in EuIrGe<sub>2</sub> [33] with an infinite germanium zig-zag chain, the Ge4–Ge5 bonding in Ce<sub>7</sub>Au<sub>13</sub>Ge<sub>10</sub> can only be considered as weak.

Although the cerium atoms have almost equal coordination numbers, their coordination geometry is different. As emphasized in Fig. 2, one can describe the Ce<sub>7</sub>Au<sub>13</sub>Ge<sub>10</sub> structure as an intergrowth of different slabs that are known from other basic structure types. The Ce1 and Ce2 atoms are part of a slab that is known for the EuAuGe type [34]. Ce4 has similar coordination to Ce<sub>3</sub>Ag<sub>4</sub>Ge<sub>4</sub> [35], two planar hexagons built up from four transition metal and two germanium atoms each. The coordination of the Ce3 atoms is similar to the pattern in ordered BaAl<sub>4</sub> phases. It is related with the structures of CePt<sub>2</sub>Ge<sub>2</sub> [36] and CeAu<sub>2</sub>Ge<sub>2</sub> [9].

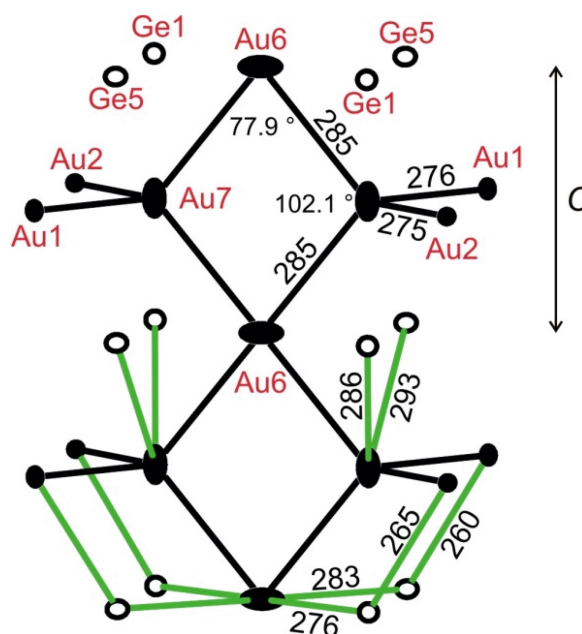


Fig. 3 (color online). Cutout of the one-dimensional gold cluster in HP-Ce<sub>7</sub>Au<sub>13</sub>Ge<sub>10</sub>. Gold and germanium atoms are drawn as black filled and open circles, respectively. Atom designations and relevant interatomic distances are indicated. The *c* lattice period is emphasized at the right-hand part of the drawing.

The condensation of these slabs leaves Au<sub>2</sub>Ge<sub>2</sub> rhombs which are known from HP-CeAuGe [5]. We can then describe all atoms of the Ce<sub>7</sub>Au<sub>13</sub>Ge<sub>10</sub> structure by a tessellation of these four basic slabs.

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- [1] D. Rossi, R. Marazza, R. Ferro, *J. Alloys Compd.* **1992**, 187, 267.
- [2] R. Pöttgen, H. Borrmann, R. K. Kremer, *J. Magn. Magn. Mater.* **1996**, 152, 196.
- [3] R. Pöttgen, H. Borrmann, C. Felser, O. Jepsen, R. Henn, R. K. Kremer, A. Simon, *J. Alloys Compd.* **1996**, 235, 170.
- [4] B. J. Gibson, R. Pöttgen, R. K. Kremer, *Physica B* **2000**, 276–278, 734.
- [5] V. Brouskov, M. Hanfland, R. Pöttgen, U. Schwarz, *Z. Kristallogr.* **2005**, 220, 122.
- [6] C. Lee, M.-H. Whangbo, J. Köhler, *Z. Anorg. Allg. Chem.* **2007**, 633, 2631.
- [7] B. M. Mhlungu, A. M. Strydom, *Physica B* **2008**, 403, 862.
- [8] B. M. Sondezi-Mhlungu, D. T. Adroja, A. M. Strydom, S. Paschen, E. A. Goremychkin, *Physica B* **2009**, 404, 3032.
- [9] A. Loidl, K. Knorr, G. Knopp, A. Krimmel, R. Caspary, A. Böhm, G. Sparr, C. Geibel, F. Steglich, A. P. Murrani, *Phys. Rev. B* **1992**, 46, 9341.
- [10] D. A. Joshi, A. K. Nigam, S. K. Dhar, A. Thamizhavel, *J. Magn. Magn. Mater.* **2010**, 322, 3363.
- [11] V. Fritsch, P. Pfundstein, P. Schweiss, E. Kampert, B. Pilawa, H. v. Löhneysen, *Phys. Rev. B* **2011**, 84, 104446.
- [12] S. D. Singh, A. Thamizhavel, J. W. Lynn, S. K. Dhar, T. Hermann, *Phys. Rev. B* **2012**, 86, 060405.
- [13] C. L. Huang, V. Fritsch, W. Kittler, H. v. Löhneysen, *Phys. Rev. B* **2012**, 86, 214401.
- [14] S. Bobev, E. D. Bauer, *Acta Crystallogr.* **2005**, E61, i73.
- [15] O. Sologub, K. Hiebl, P. Rogl, O. I. Bodak, *J. Alloys Compd.* **1995**, 227, 37.
- [16] C. D. W. Jones, R. A. Gordon, F. J. DiSalvo, R. Pöttgen, R. K. Kremer, *J. Alloys Compd.* **1997**, 260, 50.
- [17] C. P. Sebastian, M. G. Kanatzidis, *J. Solid State Chem.* **2010**, 183, 878.
- [18] R.-D. Hoffmann, R. Pöttgen, *Z. Kristallogr.* **2001**, 216, 127.
- [19] R. Pöttgen, Th. Gulden, A. Simon, *GIT Labor-Fachzeitschrift* **1999**, 43, 133.
- [20] H. Huppertz, *Z. Kristallogr.* **2004**, 219, 330.
- [21] D. Walker, M. A. Carpenter, C. M. Hitch, *Am. Mineral.* **1990**, 75, 1020.
- [22] D. Walker, *Am. Mineral.* **1991**, 76, 1092.
- [23] D. C. Rubie, *Phase Trans.* **1999**, 68, 431.
- [24] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, 276, 307.
- [25] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.
- [26] G. M. Sheldrick, *Acta Crystallogr.* **1990**, A46, 467.
- [27] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.
- [28] G. M. Sheldrick, *Acta Crystallogr.* **2008**, A64, 112.
- [29] J. Emsley, *The Elements*, Oxford University Press, Oxford **1999**.
- [30] J. Donohue, *The Structures of the Elements*, Wiley, New York **1974**.
- [31] U. Zachwieja, *Z. Anorg. Allg. Chem.* **1995**, 621, 975.
- [32] H. H. Hill in *Plutonium and other Actinides*, (Ed.: W. N. Mines), *Nuclear Materials Series, AIME*, **1970**, 17, 2.
- [33] R. Pöttgen, A. Simon, *Z. Anorg. Allg. Chem.* **1996**, 622, 779.
- [34] R. Pöttgen, *J. Mater. Chem.* **1995**, 5, 505.
- [35] A. Szytuła, D. Kaczorowski, S. Baran, J. Hernández-Velasco, B. Penc, N. Stüßer, E. Wawrzyńska, K. Gofryk, *Intermetallics* **2006**, 14, 702.
- [36] A. Dommann, F. Hulliger, H. R. Ott, V. Gramlich, *J. Less-Common Met.* **1985**, 110, 331.