

## Ca<sub>7</sub>Au<sub>3</sub> and Ca<sub>5</sub>Au<sub>4</sub>, Two Structures Closely Related to the Th<sub>7</sub>Fe<sub>3</sub> and Pu<sub>5</sub>Rh<sub>4</sub> Types

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Two new intermetallic compounds have been synthesized and structurally studied by single crystal diffractometric data: Ca<sub>7</sub>Au<sub>3</sub> (*oP*80, space group *Pbca*,  $a = 20.742(8)$ ,  $b = 18.036(8)$ ,  $c = 6.665(2)$  Å,  $Z = 8$ ,  $R = 0.051$ ) and Ca<sub>5</sub>Au<sub>4</sub> (*mP*18, space group *P2<sub>1</sub>/c*,  $a = 8.028(3)$ ,  $b = 8.019(6)$ ,  $c = 7.727(3)$  Å,  $\beta = 109.16(6)^\circ$ ,  $Z = 2$ ,  $R = 0.104$ ). Both atomic arrangements, which represent new structural types, are based on Au-centered Ca trigonal prisms and are geometrically related to the Th<sub>7</sub>Fe<sub>3</sub> and Pu<sub>5</sub>Rh<sub>4</sub> structures. © 1985 Academic Press, Inc.

### Introduction

The Ca–Au system was investigated many years ago (1). In more recent times Notin *et al.* (2), in the potentiometric determination of the free enthalpies of formation of Ca–Au phases, came to the conclusion that in the Ca-rich side many more compounds probably exist than the two actually present with Ca<sub>2</sub>Au and Ca<sub>4</sub>Au<sub>3</sub> stoichiometry.

For a systematic study of this region we prepared alloys covering the range 24–50 at.% Au; in previous works the structure of CaAu (CrB type) (3) and Ca<sub>5</sub>Au<sub>3</sub> (Cr<sub>5</sub>B<sub>3</sub> type) (4) were reported. In this paper we give the results obtained for phases with compositions Ca<sub>7</sub>Au<sub>3</sub> and Ca<sub>5</sub>Au<sub>4</sub>.

### Experimental and Structure Determinations

Alloys were prepared on the two compo-

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sitions Ca<sub>7</sub>Au<sub>3</sub> and Ca<sub>56.5</sub>Au<sub>43.5</sub> using calcium (99.9% pure) from Fluka, Buchs, Switzerland, and gold (99.999% pure) from Koch–Light, Coinbrook, England. The elements were melted in Ta containers sealed by arc-welding under an argon atmosphere, and annealed 1 month at 923 and 1023 K, respectively. Owing to the brittleness of the phase Ca<sub>5</sub>Au<sub>4</sub>, only the alloy Ca<sub>7</sub>Au<sub>3</sub> could be checked by micrographic examination, turning out to be a homogeneous phase.

The single crystals, sealed in glass capillaries under vacuum, were mounted on a four-circle Enraf–Nonius CAD-4 automatic diffractometer, using graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71069$  Å). The lattice constants were determined by least squares from 25 diffractometer-measured reflections.

For the crystal of Ca<sub>7</sub>Au<sub>3</sub> (0.07 × 0.15 × 0.24 mm) 5745 intensities were collected in the  $\omega$  scan mode up to  $2\theta = 54^\circ$ , corresponding to 2838 independent reflections; for the crystal of Ca<sub>5</sub>Au<sub>4</sub> (0.03 × 0.13 ×

0.18 mm) 2141 intensities were collected in the  $\omega$ - $2\theta$  scan mode up to  $2\theta = 54^\circ$ , corresponding to 1074 independent reflections.

The intensity data of the two crystals were processed for  $Lp$  and absorption effects ( $\mu = 39.0$  and  $66.8 \text{ mm}^{-1}$  for  $\text{Ca}_7\text{Au}_3$  and  $\text{Ca}_5\text{Au}_4$ , respectively), applying both the correction for spherical specimens and a semiempirical correction based on the azimuthal scan data of some top reflections. The ratio between maximum and minimum transmission factor was 4 for  $\text{Ca}_7\text{Au}_3$  and 15 for  $\text{Ca}_5\text{Au}_4$ .

The crystal of  $\text{Ca}_7\text{Au}_3$  showed orthorhombic symmetry with  $a = 20.742(8)$ ,  $b = 18.036(8)$ ,  $c = 6.665(2) \text{ \AA}$ , and the following conditions for observed reflections:  $0kl$  only with  $k = 2n$ ,  $h0l$  only with  $l = 2n$  and  $kh0$  only with  $h = 2n$ . Symmetry and extinctions were confirmed also by precession photographs of another crystal. The space group is uniquely determined as  $Pbca$ . The structure was solved by direct methods and refined with SHELX 76 (5). Strong indication that this structure could be closely related to the  $\text{Th}_7\text{Fe}_3$  type (6) came from the cell relationships

$$a = 2a_{\text{Th}_7\text{Fe}_3}, \quad b = \sqrt{3}a_{\text{Th}_7\text{Fe}_3}, \\ c \approx c_{\text{Th}_7\text{Fe}_3},$$

and helped in the identification of seven Ca and three Au general positions in the  $E$  map. For the full matrix least-squares refinement, based on  $F_s$ , the atomic scattering factors and corrections for anomalous dispersion were taken from (7). The final refinement with anisotropic thermal parameters for the Au atoms gave  $R = 0.051$ ,  $wR = 0.052$  (1280 reflections with  $F_o > 6\sigma(F_o)$ , weights  $w = 1/\sigma^2(F_o)$ , 56 parameters).

The crystal of  $\text{Ca}_5\text{Au}_4$  showed monoclinic symmetry with  $a = 8.028(3)$ ,  $b = 8.019(6)$ ,  $c = 7.727(3) \text{ \AA}$ ,  $\beta = 109.16(6)^\circ$ , and the conditions  $h0l$  only with  $l = 2n$  and  $0k0$  only with  $k = 2n$ , corresponding to the unique space group  $P2_1/c$ . Direct methods

TABLE I  
ATOMIC COORDINATES AND ISOTROPIC  
THERMAL PARAMETERS

	x	y	z	$U$ ( $\text{\AA}^2$ )
$\text{Ca}_7\text{Au}_3$ , space group $Pbca$ , all atoms in equipoint 8(c)				
Ca(1)	0.2174(4)	0.1839(5)	0.960(1)	0.025(2)
Ca(2)	0.0301(4)	0.1873(5)	0.948(1)	0.025(2)
Ca(3)	0.1246(5)	0.1257(4)	0.458(1)	0.027(2)
Ca(4)	0.3733(8)	0.2092(4)	0.248(1)	0.026(2)
Ca(5)	0.2832(6)	0.0219(8)	0.266(1)	0.025(3)
Ca(6)	0.4724(6)	0.0210(7)	0.251(1)	0.023(3)
Ca(7)	0.3727(8)	0.0825(4)	0.755(1)	0.023(2)
Au(1)	0.1195(1)	0.0602(1)	0.0306(3)	0.029(1)*
Au(2)	0.2680(1)	0.1596(1)	0.5292(3)	0.031(1)*
Au(3)	0.4810(1)	0.1547(1)	0.9722(3)	0.028(1)*
$\text{Ca}_5\text{Au}_4$ , space group $P2_1/c$				
Ca(1) in 4(e)	0.692(2)	0.320(1)	0.069(1)	0.019(2)
Ca(2) in 4(e)	0.255(2)	0.332(1)	0.252(1)	0.023(2)
Ca(3) in 2(a)	0.0	0.0	0.0	0.019(3)
Au(1) in 4(e)	0.9884(4)	0.1301(3)	0.3712(3)	0.019(1)*
Au(2) in 4(e)	0.4192(4)	0.0329(3)	0.1433(3)	0.020(1)*

Note. The thermal factors are defined by  $T = \exp[-8\pi^2 U (\sin \theta/\lambda)^2]$ . Values marked with an asterisk correspond to equivalent  $U_s$  derived from the anisotropic parameters by the expression  $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \hat{a}_i \cdot \hat{a}_j$ .

followed by difference Fourier map allowed two Au and three Ca positions to be located, respectively. In the last cycles of refinement anisotropic thermal factors were applied to the Au atoms and convergence was obtained at  $R = 0.104$ ,  $wR = 0.080$  (858 reflections with  $F_o > 2\sigma(F_o)$ , weights  $w = 1/\sigma^2(F_o)$ , 43 parameters). The high value of the residuals may be attributed to the severe absorption of the crystal.

Table I lists the positional and thermal parameters of the two compounds.<sup>1</sup>

Powder patterns of  $\text{Ca}_7\text{Au}_3$  and  $\text{Ca}_5\text{Au}_4$  were indexed on the basis of the respective structures with the aid of LAZY PULVERIX (8) and confirmed the crystals have the same compositions as the bulk material.

## Discussion

Figure 1 shows the  $\text{Ca}_7\text{Au}_3$  structure,

<sup>1</sup> Lists of observed and calculated structure factors can be obtained from the authors on request.

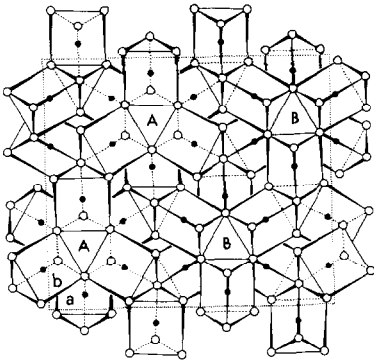


FIG. 1. Structure of Ca<sub>7</sub>Au<sub>3</sub> projected along the *c* axis. Ca trigonal prisms surrounding the Au atoms are outlined. Open circles: Ca; full circles: Au. The A and B symbols indicate Ca octahedra in the two possible orientations.

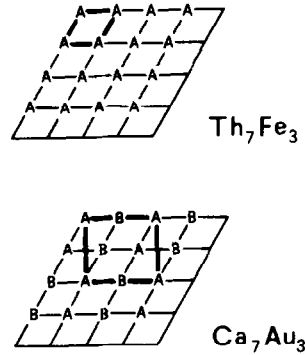


FIG. 2. Arrangement of the Th or Ca columns of octahedra along the short axis in Th<sub>7</sub>Fe<sub>3</sub> and Ca<sub>7</sub>Au<sub>3</sub>. The B columns are rotated 60° relative to the A columns.

which is closely related to the Th<sub>7</sub>Fe<sub>3</sub> type (6). Columns of face-sharing octahedra formed by Ca(1), Ca(2), and Ca(3), and columns of tetrahedra alternately joined by a face formed by Ca(4), Ca(5), Ca(6), and a vertex occupied by Ca(7), run parallel to the short *c* axis. This arrangement allows Au atoms located in between the columns to be surrounded by Ca trigonal prisms. If the columns of octahedra were all identical, we would obtain the simple structure of Th<sub>7</sub>Fe<sub>3</sub>. On the contrary, in Ca<sub>7</sub>Au<sub>3</sub> one of every two columns is rotated 60° relative to the other around the short axis, giving rise to a new structure. These two possible orientations are called A and B in Fig. 1.

Other structures can be derived for different sequences of the two types of columns. Arrangements which maintain the same stoichiometry and trigonal prismatic coordination of the minority atoms are already known in the literature for the trigonal Cr<sub>7</sub>C<sub>3</sub> and the orthorhombic Mn<sub>7</sub>C<sub>3</sub> phases (9). Recently, in (Cr,Fe)<sub>7</sub>C<sub>3</sub> carbides several polytypes have been observed by electron microscopy (10); the simplest member of the series should correspond to the structure of Ca<sub>7</sub>Au<sub>3</sub>. In Fig. 2, following the procedure of Bouchaud and Fruchart

(11) is given a schematic representation of the structure of Ca<sub>7</sub>Au<sub>3</sub> compared with the parent structure Th<sub>7</sub>Fe<sub>3</sub>.

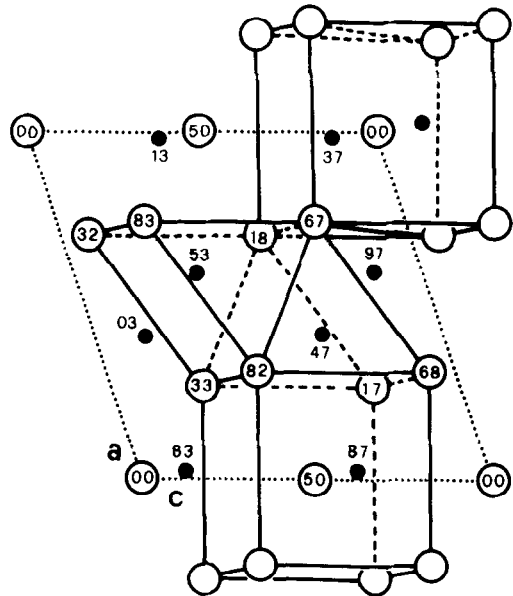


FIG. 3. Structure of Ca<sub>5</sub>Au<sub>4</sub> projected along the *b* axis. The characteristic motifs are outlined: two Ca double prisms centered by the Au(1) and Au(2) atoms, and a Ca cube centered by the Ca(3) atom. Open circles—Ca; full circles—Au. The heights of the atoms are multiplied by 100.

Distances in  $\text{Ca}_7\text{Au}_3$  are reported in Table II. The Au atoms have nine Ca neighbors: six Ca belong to the surrounding trigonal prism at distances in the range 2.97–3.09 Å, and three other Ca emerge from the lateral faces at larger distances 3.45–4.04 Å. The same coordination is found for the Fe atom in  $\text{Th}_7\text{Fe}_3$ . The Ca atoms always have 15 neighbors. The coordination polyhedron of the atoms forming octahedra, namely Ca(1), Ca(2), and Ca(3), is identical to that around Th(2) in  $\text{Th}_7\text{Fe}_3$ . For Ca(4), Ca(5), Ca(6), and Ca(7), which form columns of tetrahedra, different coordinations are found. Ca(4) and Ca(6) have the same polyhedron; Ca(5) presents the same polyhedron like Th(3) in  $\text{Th}_7\text{Fe}_3$ ; Ca(7), the apical

TABLE II  
INTERATOMIC DISTANCES IN  $\text{Ca}_7\text{Au}_3$  UP TO 5 Å

Ca(1)– Au(2)	3.05(1)	Ca(2)– Au(1)	3.00(1)
– Au(1)	3.05(1)	– Au(3)	3.04(1)
– Au(2)	3.09(1)	– Au(3)	3.07(1)
– Ca(4)	3.79(2)	– Ca(6)	3.80(1)
– Ca(5)	3.82(1)	– Ca(4)	3.85(2)
– Ca(2)	3.89(1)	– Ca(1)	3.89(1)
– Ca(5)	3.93(2)	– Ca(3)	3.90(1)
– Ca(3)	3.94(1)	– Ca(3)	3.97(1)
– Ca(7)	3.95(2)	– Ca(4)	3.97(2)
– Au(2)	3.96(1)	– Ca(6)	3.98(1)
– Ca(3)	3.98(1)	– Ca(7)	4.01(2)
– Ca(3)	4.00(1)	–2Ca(2)	4.03(1)
– Ca(4)	4.02(2)	– Au(3)	4.04(1)
–2Ca(1)	4.10(1)	– Ca(3)	4.08(1)
Ca(3)– Au(3)	3.06(1)	Ca(4)– Au(2)	3.01(1)
– Au(2)	3.07(1)	– Au(3)	3.06(1)
– Au(1)	3.09(1)	– Au(2)	3.54(1)
– Ca(6)	3.86(1)	– Au(3)	3.64(1)
– Ca(5)	3.87(1)	–2Ca(4)	3.64(1)
– Ca(2)	3.90(1)	– Ca(7)	3.76(1)
– Ca(6)	3.93(1)	– Ca(1)	3.79(2)
– Ca(1)	3.94(1)	– Ca(2)	3.85(2)
– Ca(2)	3.97(1)	– Ca(5)	3.86(2)
– Ca(1)	3.98(1)	– Ca(6)	3.97(2)
– Ca(7)	3.99(1)	– Ca(2)	3.97(2)
– Ca(5)	4.00(2)	– Ca(7)	4.00(1)
– Au(1)	4.00(1)	– Ca(1)	4.02(2)
– Ca(1)	4.00(1)	– Ca(7)	4.08(1)
– Ca(2)	4.08(1)		

TABLE II—Continued

Ca(5)– Au(2)	3.06(1)	Ca(6)– Au(1)	3.04(1)
– Au(1)	3.06(1)	– Au(3)	3.05(1)
–2Ca(5)	3.69(1)	– Au(1)	3.45(1)
– Ca(7)	3.74(2)	– Ca(6)	3.59(1)
– Au(2)	3.79(1)	– Ca(6)	3.62(1)
– Au(1)	3.80(1)	– Au(3)	3.63(1)
– Ca(1)	3.82(1)	– Ca(7)	3.72(2)
– Ca(4)	3.86(2)	– Ca(2)	3.80(1)
– Ca(3)	3.87(1)	– Ca(3)	3.86(1)
– Ca(7)	3.91(1)	– Ca(5)	3.93(2)
– Ca(6)	3.93(2)	– Ca(3)	3.93(1)
– Ca(1)	3.93(2)	– Ca(4)	3.97(2)
– Ca(3)	4.00(2)	– Ca(2)	3.98(1)
– Ca(7)	4.03(1)	– Ca(7)	4.05(1)
		– Ca(7)	4.10(1)
Ca(7)– Au(3)	2.97(1)		
– Au(1)	2.98(1)	Au(1)– Ca(7)	2.98(1)
– Au(2)	2.99(1)	– Ca(2)	3.00(1)
– Ca(6)	3.72(2)	– Ca(6)	3.04(1)
– Ca(5)	3.74(2)	– Ca(1)	3.05(1)
– Ca(4)	3.76(1)	– Ca(5)	3.06(1)
– Ca(5)	3.91(1)	– Ca(3)	3.09(1)
– Ca(1)	3.95(2)	– Ca(6)	3.45(1)
– Ca(3)	3.99(1)	– Ca(5)	3.80(1)
– Ca(4)	4.00(1)	– Ca(3)	4.00(1)
– Ca(2)	4.01(2)		
– Ca(5)	4.03(1)	Au(3)– Ca(7)	2.97(1)
– Ca(6)	4.05(1)	– Ca(2)	3.04(1)
– Ca(4)	4.08(1)	– Ca(6)	3.05(1)
– Ca(6)	4.10(1)	– Ca(4)	3.06(1)
Au(2)– Ca(7)	2.99(1)	– Ca(3)	3.06(1)
– Ca(4)	3.01(1)	– Ca(2)	3.07(1)
– Ca(1)	3.05(1)	– Ca(6)	3.63(1)
– Ca(5)	3.06(1)	– Ca(4)	3.64(1)
– Ca(3)	3.07(1)	– Ca(2)	4.04(1)
– Ca(1)	3.09(1)		
– Ca(4)	3.54(1)		
– Ca(5)	3.79(1)		
– Ca(1)	3.96(1)		

atom from which rise three trigonal prisms, has the shortest Ca–Au distances.

Figure 3 gives the projection of the  $\text{Ca}_5\text{Au}_4$  structure along the monoclinic unique axis. Two characteristic motifs are outlined: Ca trigonal prisms centered by Au(1) and Au(2) and joined two by two through a rectangular face, and Ca cubes centered by Ca(3) atoms. As reported by Parthé (12), these construction elements,

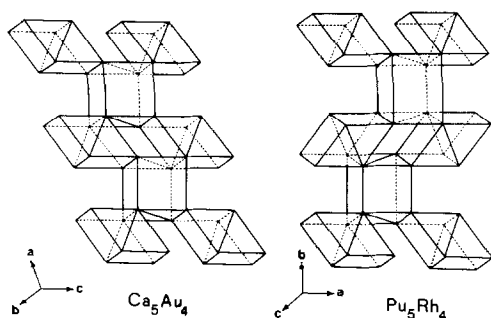


FIG. 4. Arrangements of double prisms in the two related structures Ca<sub>5</sub>Au<sub>4</sub> and Pu<sub>5</sub>Rh<sub>4</sub>.

TABLE III

INTERATOMIC DISTANCES IN Ca<sub>5</sub>Au<sub>4</sub> UP TO 4.9 Å  
FOR DISTANCES INVOLVING Ca AND UP TO 4.2 Å  
FOR Au–Au DISTANCES

Ca(1)– Au(1)	3.13(1)	Ca(3)–2Au(1)	3.08(1)
– Au(2)	3.16(1)	–2Au(1)	3.12(1)
– Au(2)	3.25(1)	–2Au(2)	3.19(1)
– Au(1)	3.25(1)	–2Ca(2)	3.50(1)
– Au(2)	3.35(1)	–2Ca(2)	3.53(1)
– Au(1)	3.49(1)	–2Ca(1)	3.72(1)
– Au(2)	3.50(1)	–2Ca(1)	3.73(1)
– Ca(3)	3.72(1)		
– Ca(3)	3.73(1)	Au(1)– Au(1)	2.85(1)
– Ca(2)	3.76(2)	– Ca(2)	3.03(1)
– Ca(2)	3.85(1)	– Ca(2)	3.04(1)
–2Ca(1)	4.02(1)	– Ca(2)	3.06(1)
– Ca(1)	4.10(2)	– Ca(3)	3.08(1)
– Ca(2)	4.13(1)	– Ca(3)	3.12(1)
– Ca(2)	4.19(2)	– Ca(1)	3.13(1)
– Ca(2)	4.27(2)	– Ca(1)	3.25(1)
– Ca(2)	4.31(1)	– Ca(1)	3.49(1)
Ca(2)– Au(2)	2.95(1)		
– Au(2)	2.99(1)	Au(2)– Ca(2)	2.95(1)
– Au(1)	3.03(1)	– Au(2)	2.96(1)
– Au(1)	3.04(1)	– Ca(2)	2.99(1)
– Au(1)	3.06(1)	– Ca(2)	3.07(1)
– Au(2)	3.07(1)	– Ca(1)	3.16(1)
– Ca(3)	3.50(1)	– Ca(3)	3.19(1)
– Ca(3)	3.53(1)	– Ca(1)	3.25(1)
– Ca(1)	3.76(2)	– Ca(1)	3.35(1)
– Ca(1)	3.85(1)	– Ca(1)	3.50(1)
–2Ca(2)	4.08(1)		
– Ca(1)	4.13(1)		
– Ca(1)	4.19(2)		
– Ca(1)	4.27(2)		
– Ca(1)	4.31(1)		

double prisms and cubes, are present in structure types like U<sub>3</sub>Si<sub>2</sub>, Er<sub>3</sub>Ni<sub>2</sub>, Pu<sub>5</sub>Rh<sub>4</sub>, and Zr<sub>5</sub>Si<sub>4</sub>, occurring for compounds of the rare earths with transition metals. Ca<sub>5</sub>Au<sub>4</sub> belongs to the same family and its close relationship with the orthorhombic Pu<sub>5</sub>Rh<sub>4</sub> type (13) appears in Fig. 4, where a slab of double prisms is drawn for each structure.

Distances in Ca<sub>5</sub>Au<sub>4</sub> are listed in Table III. The coordination polyhedra look like those of the Pu<sub>5</sub>Rh<sub>4</sub> structure. Besides the six Ca forming the trigonal prism, the Au atoms have three waist contacts through the lateral faces of the prism with another Au and two Ca, i.e., similar coordination to that of the Rh atoms. Ca(1) with 7 Au and 11 Ca neighbors has an environment very similar to Pu(3), but with an additional Ca atom; the polyhedra around Ca(2) and Ca(3) are identical to those around Pu(2) and Pu(1), respectively. In particular, Ca(3) is surrounded by a cube of Ca interpenetrated with an octahedron of Au atoms. It can be noted that the cube is more regular in Ca<sub>5</sub>Au<sub>4</sub>, since all edges correspond to Ca–Ca bonds ranging from 4.02 to 4.31 Å.

A last remark can be made about the influence of valence on the stability of intermetallic phases. Taking into account the structural results, a close resemblance is actually found between the Ca–Au and Yb–Au systems, especially concerning the Ca- and Yb-rich intermediate compounds. In the Yb–Au system (14) there exist Yb<sub>7</sub>Au<sub>3</sub>, Yb<sub>5</sub>Au<sub>3</sub>, and Yb<sub>5</sub>Au<sub>4</sub> phases crystallizing in the structure types Th<sub>7</sub>Fe<sub>3</sub>, Cr<sub>5</sub>B<sub>3</sub>, and Sm<sub>5</sub>Ge<sub>4</sub>, respectively. In these three phases, which are structurally identical or closely related to the corresponding Ca–Au phases with the same stoichiometries, magnetic measurements showed that Yb behaves as divalent element, like an alkaline earth.

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