

## Single crystal investigation of the $\text{EuAg}_x\text{Ga}_{3-x}$ ( $x = 0.13$ ) and $\text{Eu}_4\text{Ag}_{11+x}\text{Ga}_{6-x}$ ( $x = 0.27$ ) phases

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Received April 30, 2013; accepted June 19, 2013; available on-line November 4, 2013

Two new ternary gallides,  $\text{EuAg}_x\text{Ga}_{3-x}$  ( $x = 0.13$ ) and  $\text{Eu}_4\text{Ag}_{11+x}\text{Ga}_{6-x}$  ( $x = 0.27$ ), have been prepared by arc-melting mixtures of the elements. Their crystal structures were determined by direct methods from single crystal X-ray diffraction data. The refined structural parameters are: space group *Cmcm*, Pearson symbol *oS16*,  $Z = 4$ , lattice parameters  $a = 4.3154(10)$  Å,  $b = 18.411(8)$  Å,  $c = 4.3781(10)$  Å,  $V = 347.84(19)$  Å<sup>3</sup>, reliability factors  $R1 = 0.0540$ ;  $wR = 0.0999$ ,  $\chi = 1.024$  for  $\text{EuAg}_x\text{Ga}_{3-x}$ , and space group *Pnma*, Pearson symbol *oP168*,  $Z = 8$ , lattice parameters  $a = 9.784(3)$  Å,  $b = 9.3026(16)$  Å,  $c = 37.246(18)$  Å,  $V = 3390.0(19)$  Å<sup>3</sup>, reliability factors  $R1 = 0.0560$ ;  $wR = 0.0878$ ,  $\chi = 1.000$  for  $\text{Eu}_4\text{Ag}_{11+x}\text{Ga}_{6-x}$ .

Intermetallics / Crystal structure / X-ray diffraction

### Introduction

Europium – transition metal (*T*) – gallides have been intensively studied in recent years due to their synthesis behavior and crystal chemistry, as well as their great variety of magnetic, thermal and electrical properties. Some of this information can be found in [1-4].

According to our best knowledge, isothermal sections have been constructed, in part of or in the whole concentration range, only for five systems: Eu–Mn–Ga [5], Eu–Fe–Ga [6], Eu–Co–Ga [7], Eu–Cu–Ga [8] and Eu–Zn–Ga [9]. 17 ternary  $\text{Eu}_x\text{T}_y\text{Ga}_z$  phases with established crystal structure are known [10]. They represent a multitude of compositions and structure types:  $\text{BaAl}_4$ ,  $\text{BaZn}_5$ ,  $\text{CeCu}_2$ ,  $\text{CeFe}_2\text{Al}_8$ ,  $\text{CeNiSi}_2$ ,  $\text{CeNi}_{8.5}\text{Si}_{4.5}$ ,  $\text{EuAu}_2\text{Ga}_5$ ,  $\text{Eu}_5\text{Co}_5\text{Ga}_{3.5}$ ,  $\text{Na}_3\text{Pt}_4\text{Ge}_4$ ,  $\text{NaZn}_{13}$ , and  $\text{TiNiSi}$ .

The present work is part of a systematic investigation of ternary europium-based ternary alloy systems and compounds. Herein, we report on the synthesis and structure determination of two new Eu–Ag–Ga ternary phases.

### Experimental details

Starting materials for the preparation of the samples were ingots of europium, silver plate and gallium

tear drops, all with stated purities better than 99.95%. The original large europium ingots were re-melted, cut into small pieces and stored in inert atmosphere before the reactions. The samples, with a total weight  $\leq 1.0$  g, were prepared by arc-melting the elements under argon atmosphere (with titanium/zirconium as a getter) on a water-cooled copper hearth. The products were re-melted three-five times in order to ensure homogeneity. Due to partial evaporation of europium metal during the synthesis, up to 0.5 at.% Eu was added in excess to the nominal composition in each sample. Finally, the alloys were crushed into small pieces, sealed in quartz tubes under vacuum ( $10^{-5}$  Torr) and annealed at 500°C for one month. After the heat treatment, the samples were quenched, by submerging the quartz tubes in cold water, and analyzed.

Single crystal diffraction data were collected at room temperature using a four-circle Enraf-Nonius Mach III diffractometer with graphite monochromatized  $\text{Mo K}\alpha$ -radiation and a scintillation counter with pulse height discrimination. Scans were performed in the  $\omega/2\theta$  mode. Empirical absorption corrections were applied on the basis of  $\psi$ -scan data. The crystal structure was successfully refined using Jana2006 [11] and SHELXL-97 [12] (full-matrix least-squares on  $F^2$ ).

## Results and discussion

### The $\text{EuAg}_x\text{Ga}_{3-x}$ ( $x = 0.13$ ) phase

During the X-ray phase analysis of as-cast alloys and alloys annealed at 500°C containing 25 at.% Eu, a new ternary phase of general composition  $\text{EuAg}_x\text{Ga}_{3-x}$  with small amounts of Ag (less than 5 at.%) was detected. Preliminary studies based on powder X-ray diffraction data indicated a structure close to the  $\text{CeNiSi}_2$  type [13]. Further X-ray diffraction studies were performed on single crystals.

Block-like single crystals were isolated from a sample with nominal composition  $\text{Eu}_{25}\text{Ag}_5\text{Ga}_{70}$  by mechanical fragmentation and used in the X-ray diffraction measurements. Careful examination of the data sets revealed a *C*-centered orthorhombic lattice, and the additional systematic extinctions  $h0l$ , only observed for  $h, l = 2n$ , led to space groups

$Cmcm$ ,  $C2cm$  and  $Cmc2_1$ , of which the centrosymmetric group was found to be correct during the structure refinements. The starting atomic parameters were deduced from an automatic interpretation of direct methods. Refinement with anisotropic displacement parameters showed extremely large  $U_{11}$  values for the  $M3$  position, indicating that the atoms are displaced from the mirror plane perpendicular to  $[100]$ . We subsequently introduced split positions with an occupancy of 50%, *i.e.* Wyckoff position  $8g$  ( $x y \frac{1}{4}$ ) instead of  $4c$  ( $0 y \frac{1}{4}$ ). From the refinement, Ag/Ga mixing was found for the  $M2$  site. The  $M1$  position is fully occupied by Ga atoms. Refinement of the occupation factors resulted in the final composition  $\text{EuAg}_{0.13}\text{Ga}_{2.87}$ . Crystallographic data and experimental details for the data collection are listed in Table 1. The positional parameters and interatomic distances are given in Tables 2 and 3.

**Table 1** Crystal data and experimental details for  $\text{EuAg}_x\text{Ga}_{3-x}$ .

Phase	$\text{EuAg}_{0.13}\text{Ga}_{2.87}$
Refined composition	$\text{Eu}_{25}\text{Ag}_{3.3}\text{Ga}_{71.7}$
Relative molar mass	366.23
Crystal system	Orthorhombic
Space group	$Cmcm$ (No. 63)
Pearson symbol	$oS16$
Unit cell dimensions	
<i>a</i>	4.3154(10) Å
<i>b</i>	18.411(8) Å
<i>c</i>	4.3781(10) Å
<i>V</i>	347.84(19) Å <sup>3</sup>
Formula units per cell	4
Calculated density	6.993 g/cm <sup>3</sup>
Crystal shape and color	Block, Silvery
Diffractometer	Enraf-Nonius Mach III
Radiation	Mo $K\alpha$ ( $\lambda = 0.71073$ Å)
Monochromator	Graphite
Temperature	293(2) K
Absorption coefficient	40.194 mm <sup>-1</sup>
$F(000)$	633
$\theta$ range for data collection	2.21° to 43.21°
Scan type	$\omega$ -2 $\theta$
Range in $hkl$	$-5 \rightarrow 5, -20 \rightarrow 20, -5 \rightarrow 5$
Total no. reflections	2418
Independent reflection	368
Reflections with $I > 2\sigma(I)$	267
$R_\sigma, R_{eq}$	0.0636, 0.1406
Structure refinement	SHELXL-97 [12]
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	368/1/22
Goodness-of-fit on $F^2$	1.024
Final $R$ indices <sup>a</sup>	$R1 = 0.0540, wR2 = 0.0999$
Weighting scheme <sup>b</sup>	$a = 0.0379, b = 0$
Extinction coefficient	0.0023(5)
Largest diff. peak/hole	5.703/-4.011 e/Å <sup>3</sup>

<sup>a</sup>  $R1 = \sum(|F_o| - |F_c|) / \sum|F_o|$ ,  $wR2 = \{\sum w[(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}$ ;

<sup>b</sup>  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = (F_o^2 + 2F_c^2)/3$ .

**Table 2** Atom coordinates and isotropic displacement parameters for  $\text{EuAg}_x\text{Ga}_{3-x}$ .

Site	Wyckoff position	$x$	$y$	$z$	$U_{\text{eq}} (\text{\AA}^2)$	$G$
Eu	4c	0	0.39147(7)	1/4	0.0072(4)	1Eu
M1	4c	0	0.16801(17)	1/4	0.0075(6)	1Ga
M2	4c	0	0.75048(15)	1/4	0.0091(8)	0.13(4)Ag+0.87(4)Ga
M3	8g	0.050(2)	0.0309(2)	1/4	0.014(2)	0.5Ga

Anisotropic displacement parameters for  $\text{EuAg}_x\text{Ga}_{3-x}$  ( $\text{\AA}^2$ ).

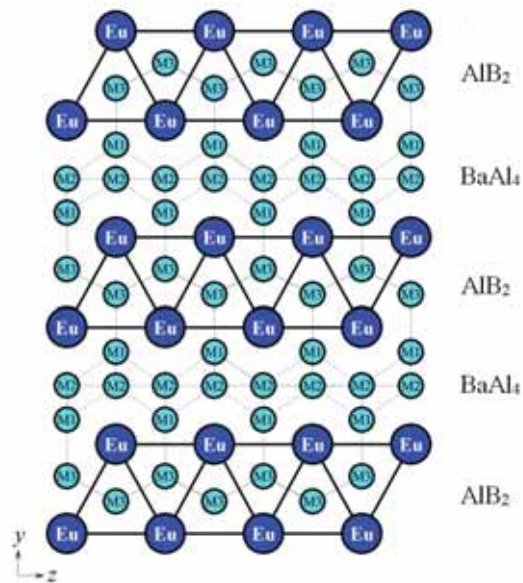
Site	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Eu1	0.0046(6)	0.0090(7)	0.0080(6)	0	0	0
M1	0.0049(11)	0.0084(15)	0.0092(12)	0	0	0
M2	0.0066(12)	0.0100(17)	0.0108(13)	0	0	0
M3	0.025(7)	0.006(2)	0.0105(16)	0	0	0.0011(16)

**Table 3** Interatomic distances in the structure of  $\text{EuAg}_x\text{Ga}_{3-x}$ .

	Atoms		$\delta$ ( $\text{\AA}$ )		Atoms		$\delta$ ( $\text{\AA}$ )	
Eu:	2	M3	3.219(6)	M2:	2	M1	2.638(2)	
	4	M3	3.257(5)		2	M1	2.654(2)	
	4	M1	3.263(1)		4	M2	3.074(1)	
	2	M2	3.375(3)		2	Eu	3.375(3)	
	2	M2	3.409(3)		2	Eu	3.409(3)	
	2	M3	3.496(7)		M3:	2	M3	2.467(2)
	4	M3	3.531(6)			2	M3	2.505(3)
	2	Eu	4.315(1)			1	M1	2.534(5)
	2	Eu	4.378(1)			1	Eu	3.219(6)
	2	Eu	4.557(2)			2	Eu	3.257(5)
M1:	1	M3	2.534(5)	1		Eu	3.496(7)	
	2	M2	2.638(2)	2		Eu	3.531(6)	
	2	M2	2.654(2)					
	4	Eu	3.263(1)					

The structure of  $\text{EuAg}_{0.13}\text{Ga}_{2.87}$  can be described as a disordered variant of the  $\text{CeNiSi}_2$  structure type, which is an intergrowth of  $\text{BaAl}_4$ - and  $\text{AlB}_2$ -like slabs (Fig. 1). The splitting of the M3 position in  $\text{EuAg}_{0.13}\text{Ga}_{2.87}$  makes the difference with the  $\text{CeNiSi}_2$  type. However, the next nearest neighbor coordinations of the atoms in  $\text{EuAg}_{0.13}\text{Ga}_{2.87}$  are similar to those observed in  $\text{CeNiSi}_2$ . The Eu atoms are situated inside 16-vertex polyhedra. The coordination polyhedra of the M1 atoms have the form of one-capped square antiprisms. The M2 atoms are situated inside distorted cubooctahedra. The coordination polyhedra of the M3 atoms are equatorially capped trigonal prisms.

Interatomic distances are listed in Table 3. The Eu–Eu distances are much longer than the Eu–Eu distances of 4.04  $\text{\AA}$  between the atoms in elementary europium [14]. The Eu–M distances range from 3.219 to 3.531  $\text{\AA}$ . Most of these distances are shorter than the sum of the metallic radii (3.41  $\text{\AA}$ ) [14]. Besides the strong Eu–M bonds, a variety of interactions can be observed between the M atoms. The M–M distances cover a broad range from 2.467 to 3.074  $\text{\AA}$ . They agree well with the Ga–Ga (2.78  $\text{\AA}$ ) and Ag–Ga (2.83  $\text{\AA}$ ) distances considering metallic radii [14], and the strongest contacts are reduced by appr. 11%.


**Fig. 1** Projection of the structure of  $\text{EuAg}_x\text{Ga}_{3-x}$  onto the  $YZ$  plane. The  $\text{AlB}_2$ - and  $\text{BaAl}_4$ -like fragments and the three-dimensional  $[M_3]$  network are indicated.

$\text{EuAg}_{0.13}\text{Ga}_{2.87}$  is the first representative among compounds from  $R\text{-Ag-Ga}$  systems with a structure related to the  $\text{CeNiSi}_2$  type. It should also be noted that  $\text{EuMn}_{0.3}\text{Ga}_{2.7}$ ,  $\text{EuCo}_{0.2}\text{Ga}_{2.8}$ , and  $\text{EuCu}_{0.2}\text{Ga}_{2.8}$  are the only known  $\text{EuT}_1\text{Ga}_{3-x}$  compounds with  $\text{CeNiSi}_2$  structure type, and that these crystal structures were studied on the basis of powder X-ray diffraction data. Due to the similar chemistry of europium and metals from group IIa of the periodic table, formation of structures related to the  $\text{CeNiSi}_2$  type can be expected in ternary  $\{\text{Ca}, \text{Ba}, \text{Sr}\}$  – transition metal – gallium systems.

#### The $\text{Eu}_4\text{Ag}_{11+x}\text{Ga}_{6-x}$ ( $x = 0.27$ ) phase

In the alloys annealed at  $500^\circ\text{C}$  with compositions along the  $\text{EuGa}_4\text{-EuAg}_4$  cross-section, a new ternary phase ( $\sim\text{EuAg}_{2.7}\text{Ga}_{1.3}$ ) was found. Small plate-like single crystals were extracted from the  $\text{Eu}_{20}\text{Ag}_{54}\text{Ga}_{26}$  alloy. The single crystal X-ray diffraction data set

showed a primitive orthorhombic cell, the systematic extinctions being compatible with the centrosymmetric space group  $Pnma$ . Seven europium positions ( $\text{Eu1-Eu7}$ ) and twenty-two Ag/Ga sites ( $M1\text{-}M22$ ) were obtained from the direct methods. The occupancy parameters of the atoms were verified step-by-step in separate fittings. Full occupancy of all the positions was observed. Ga and Ag atoms occupy the  $M6$  and  $M7$ , and the  $M12$ ,  $M16$ ,  $M19$ ,  $M21$  and  $M22$  sites, respectively. For the other positions Ag/Ga mixtures were revealed. In the final cycles, the occupancy parameters of all the atom sites were fixed, and the atom positions were refined isotropically. Crystallographic data and details on the data collection are shown in **Table 4**. Atomic coordinates and isotropic displacement parameters are presented in **Table 5**.

The structure of  $\text{Eu}_4\text{Ag}_{11+x}\text{Ga}_{6-x}$  can be viewed as consisting of the alternate stacking of **A** and **B** atomic layers (**Figs. 2** and **3**) along the  $y$ -axis. The **A** type

**Table 4** Crystal data and experimental details for  $\text{Eu}_4\text{Ag}_{11+x}\text{Ga}_{6-x}$ .

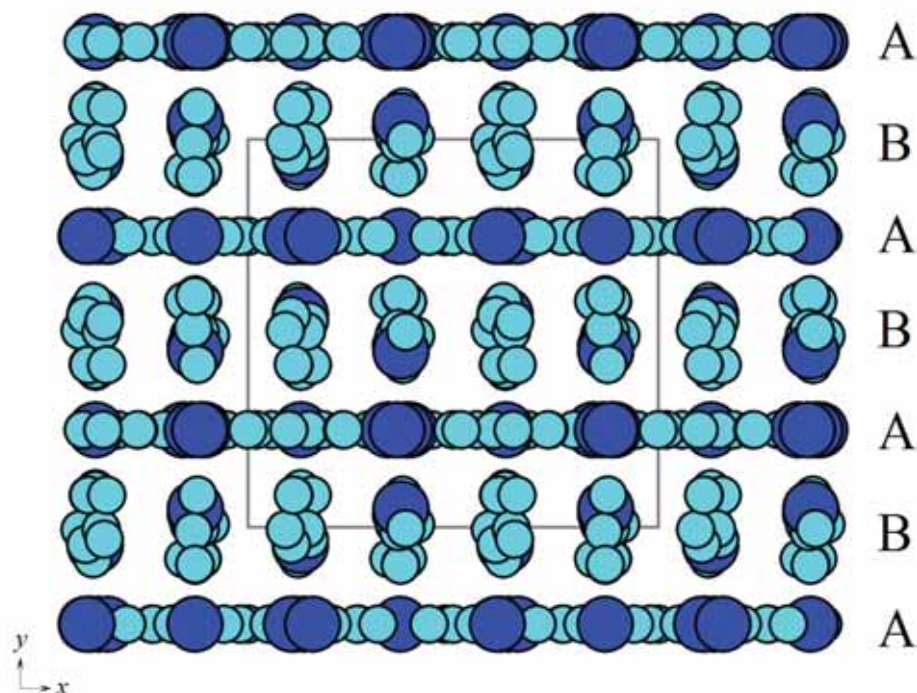
Phase	$\text{Eu}_4\text{Ag}_{11.27}\text{Ga}_{5.73}$
Refined composition	$\text{Eu}_{19}\text{Ag}_{53.7}\text{Ga}_{27.3}$
Relative molar mass	2223.03
Crystal system	Orthorhombic
Space group	$Pnma$ (No. 62)
Pearson symbol	$oP168$
Unit cell dimensions	
$a$	9.784(3) Å
$b$	9.3026(16) Å
$c$	37.246(18) Å
$V$	3390.0(19) Å <sup>3</sup>
Formula units per cell	8
Calculated density	8.711 g/cm <sup>3</sup>
Crystal shape and colour	Plate, Silvery
Diffractometer	Enraf-Nonius Mach III
Radiation	Mo $K\alpha$ ( $\lambda = 0.71073$ Å)
Monochromator	Graphite
Temperature	293(2) K
Absorption coefficient	36.121 mm <sup>-1</sup>
$F(000)$	7675
$\theta$ range for data collection	1.09° to 29.91°
Scan type	$\omega$ -2 $\theta$
Range in $hkl$	$-12 \rightarrow 12, -12 \rightarrow 12, -40 \rightarrow 35$
Total no. reflections	8701
Independent reflection	1481
Reflections with $I > 2\sigma(I)$	409
$R_\sigma, R_{eq}$	0.0639, 0.1623
Structure refinement	SHELXL-97 [12]
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	1481/0/102
Goodness-of-fit on $F^2$	1.000
Final $R$ indices <sup>a</sup>	$R1 = 0.0560, wR2 = 0.0878$
Weighting scheme <sup>b</sup>	$a = 0.0195, b = 0$
Extinction coefficient	0.000018(3)
Largest diff. peak/hole	2.012/−1.835 e/Å <sup>3</sup>

<sup>a</sup>  $R1 = \sum(|F_o| - |F_c|) / \sum|F_o|$ ,  $wR2 = \{\sum w[(F_o^2 - F_c^2)^2] / \sum w[(F_o^2)^2]\}^{1/2}$ ;

<sup>b</sup>  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = (F_o^2 + 2F_c^2)/3$ .

**Table 5** Atom coordinates and isotropic displacement parameters for  $\text{Eu}_4\text{Ag}_{11+x}\text{Ga}_{6-x}$ .

Site	Wyckoff position	$x$	$y$	$z$	$U_{\text{iso}} (\text{\AA}^2)$	$G$
Eu1	4c	0.1290(9)	¼	0.1322(3)	0.015(2)	1Eu
Eu2	4c	0.3420(9)	¼	0.4647(3)	0.015(3)	1Eu
Eu3	4c	0.3633(10)	¼	0.7146(3)	0.018(3)	1Eu
Eu4	4c	0.3821(10)	¼	0.5688(2)	0.008(3)	1Eu
Eu5	4c	0.3912(8)	¼	0.0149(2)	0.008(3)	1Eu
Eu6	4c	0.3938(10)	¼	0.2441(2)	0.010(3)	1Eu
Eu7	8d	0.1277(7)	0.5473(4)	0.36542(19)	0.011(2)	1Eu
M1	4c	0.0005(15)	¼	0.6986(4)	0.018(4)	0.66Ag+0.34Ga
M2	4c	0.0206(14)	¼	0.5726(4)	0.012(4)	0.60Ag+0.40Ga
M3	4c	0.0588(15)	¼	0.4126(5)	0.014(5)	0.29Ag+0.71Ga
M4	4c	0.0996(19)	¼	0.8628(5)	0.017(5)	0.13Ag+0.87Ga
M5	4c	0.1474(16)	¼	0.6365(4)	0.011(4)	0.46Ag+0.64Ga
M6	4c	0.1828(16)	¼	0.3144(5)	0.011(5)	1Ga
M7	4c	0.2310(20)	¼	0.8030(5)	0.017(5)	1Ga
M8	4c	0.2950(17)	¼	0.3785(6)	0.018(5)	0.12Ag+0.88Ga
M9	4c	0.4476(15)	¼	0.1518(5)	0.017(5)	0.36Ag+0.64Ga
M10	4c	0.7344(14)	¼	0.5708(4)	0.011(4)	0.68Ag+0.32Ga
M11	8d	0.1164(9)	0.0040(9)	0.4498(2)	0.014(2)	0.92Ag+0.08Ga
M12	8d	0.1228(10)	0.5815(8)	0.1425(2)	0.011(2)	1Ag
M13	8d	0.1281(11)	0.0957(10)	0.0520(3)	0.018(3)	0.41Ag+0.59Ga
M14	8d	0.1289(13)	0.0983(11)	0.2115(4)	0.017(4)	0.09Ag+0.91Ga
M15	8d	0.1327(10)	0.0124(8)	0.2800(2)	0.016(2)	0.92Ag+0.08Ga
M16	8d	0.1563(9)	0.0819(9)	0.5224(2)	0.010(2)	1Ag
M17	8d	0.3500(10)	0.0313(7)	0.0947(3)	0.015(3)	0.91Ag+0.09Ga
M18	8d	0.3576(11)	0.0051(11)	0.1803(3)	0.016(3)	0.45Ag+0.55Ga
M19	8d	0.3875(11)	0.5826(10)	0.2539(3)	0.018(2)	1Ag
M20	8d	0.3945(10)	0.0450(7)	0.3232(3)	0.018(3)	0.92Ag+0.08Ga
M21	8d	0.4087(8)	0.0068(9)	0.4048(2)	0.013(2)	1Ag
M22	8d	0.6113(10)	0.0821(9)	0.5181(2)	0.018(2)	1Ag


**Fig. 2** Projection of the structure of  $\text{Eu}_4\text{Ag}_{11+x}\text{Ga}_{6-x}$  onto the  $XY$  plane, emphasizing the A- and B-layers (europium: blue balls; Ag/Ga atoms: cyan balls).

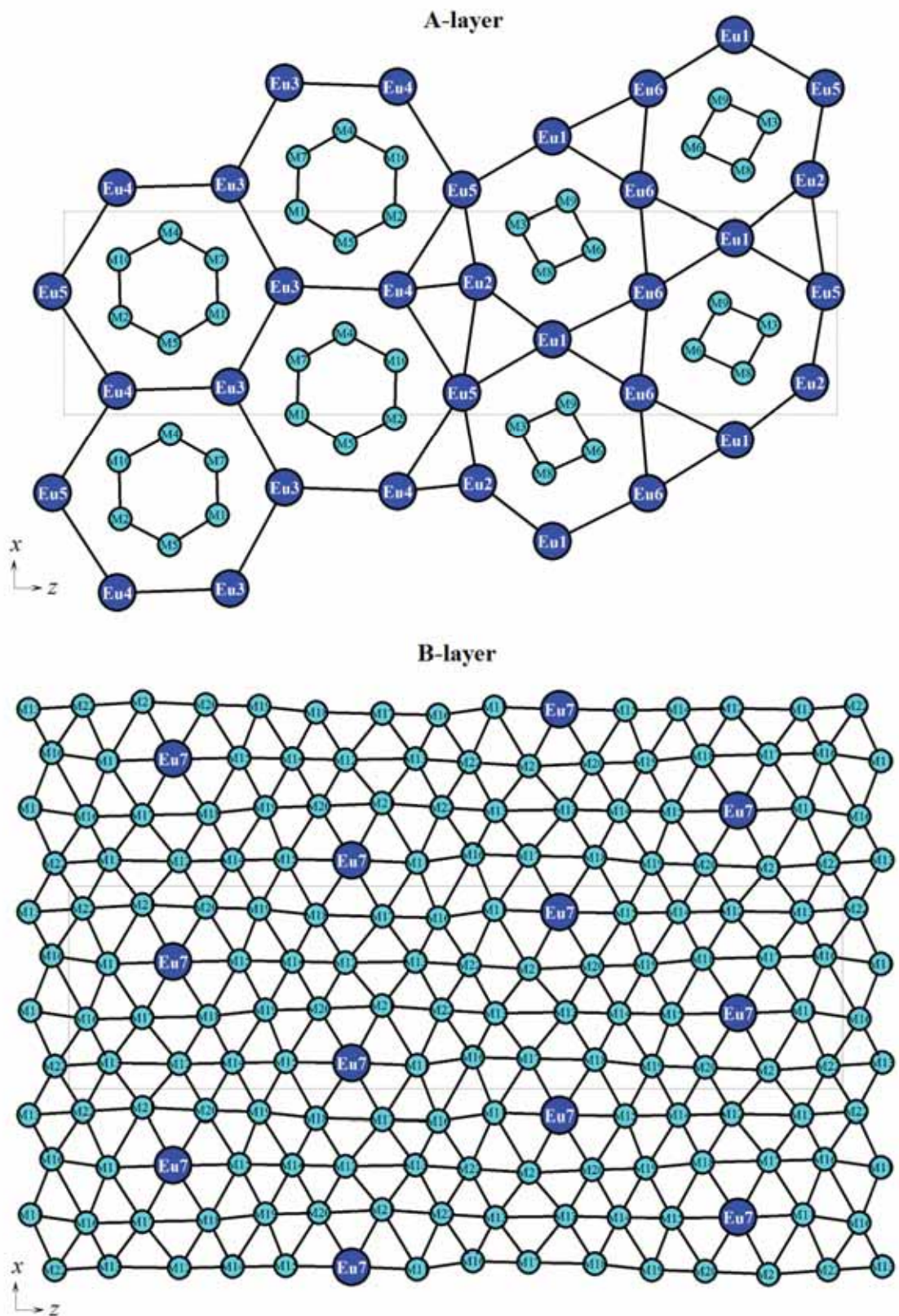


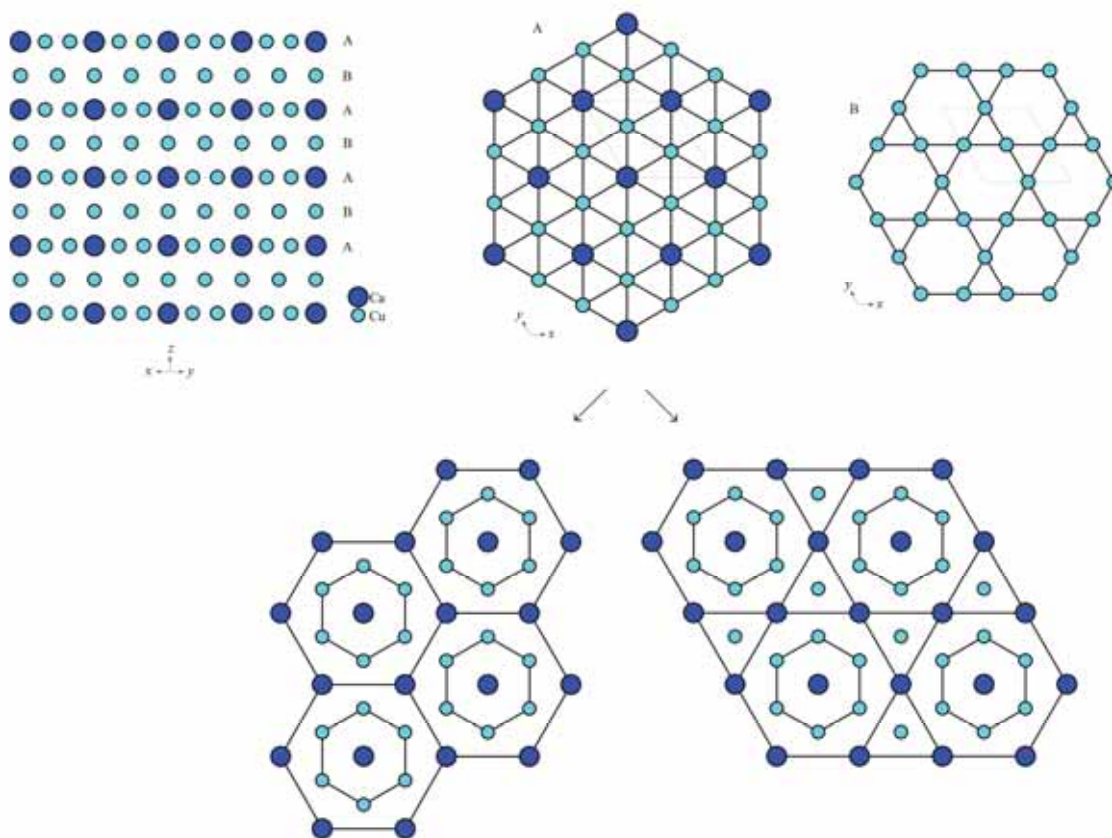
Fig. 3 A- and B-layers in  $\text{Eu}_4\text{Ag}_{11+x}\text{Ga}_{6-x}$  viewed along the y-axis.

layer, containing europium and Ag/Ga atoms, is completely flat. The arrangement of the atoms in this layer is similar to that found in the  $\text{CaCu}_5$  structure type [13] (Fig. 4). The slightly puckered B-layers also consist of Eu and Ag/Ga atoms, resembling hexagonal atomic motifs of the Laves phases [13] (Fig. 5). It should be noted that, in the  $R\text{-}T\text{-Ga}$  systems, layer-like structures have also been established and well described for the  $\text{Y}_2\text{Co}_3\text{Ga}_9$ ,  $\text{CeOsGa}_4$ ,  $\text{Ho}_3\text{Ru}_4\text{Ga}_{15}$ , and  $\text{U}_2\text{Mn}_3\text{Si}_5$  phases [13].

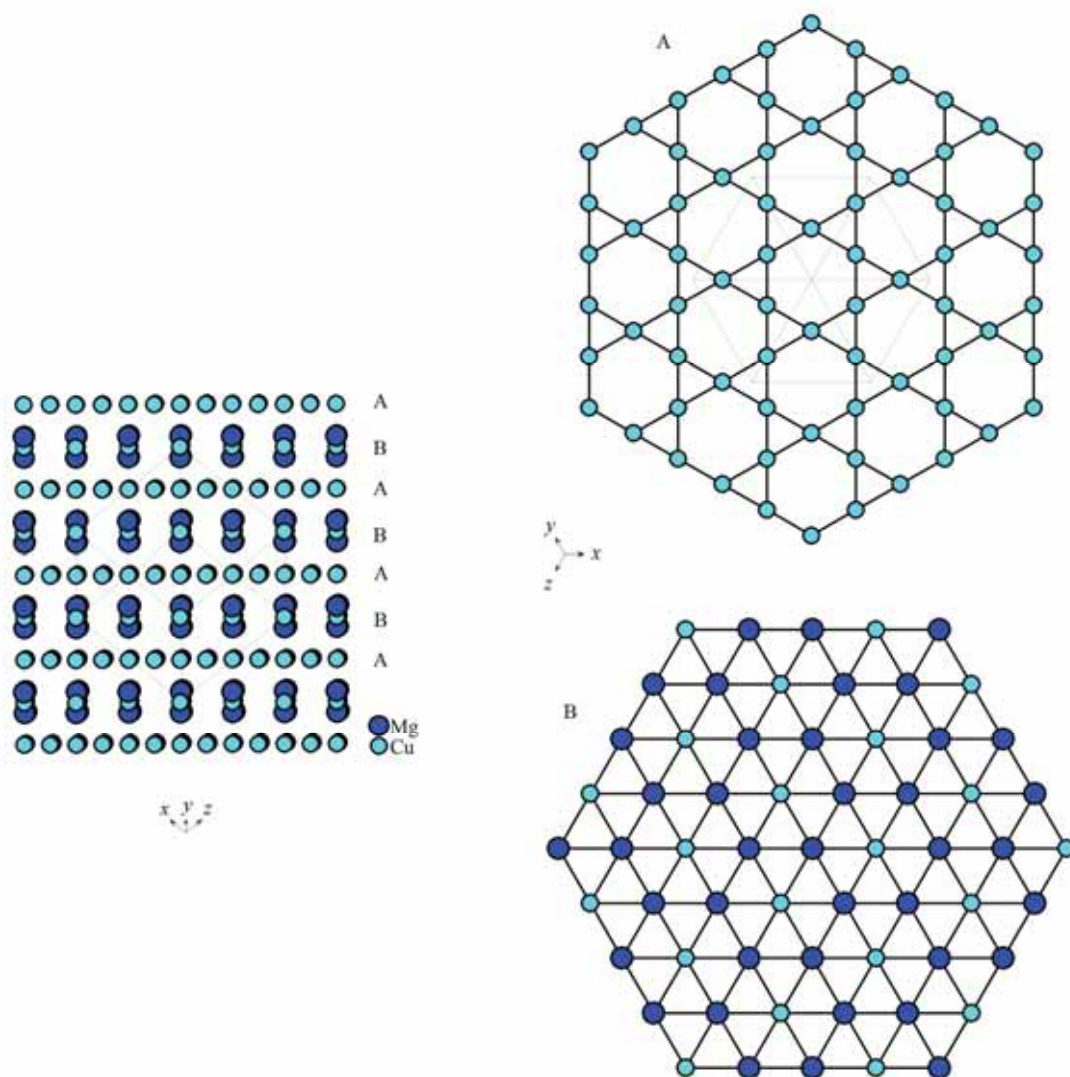
Nearest neighbors and interatomic distances in the structure of  $\text{Eu}_4\text{Ag}_{11+x}\text{Ga}_{6-x}$  are given in Table 6. The coordination environments of the europium atoms usually contain 17 or 18 atoms. The number of nearest neighbors of the small Ag/Ga atoms varies between 10 and 13. The coordination polyhedra formed by 12 atoms can be considered as distorted icosahedra. The shortest Eu–M distances vary within wide ranges (3.108–3.695 Å), but indicate strong interactions between these atoms. Strong interactions can also be deduced from the M–M distances. The shortest M–M distances, of 2.572 Å, were calculated for the M4–M7 atoms.

The only Eu–Eu distances shorter than the sum of the atomic radii in pure europium metal are 3.771 and 3.897 Å. The shortest one corresponds to Eu7–Eu7 dumbbells, which can indicate partial ionisation of these atoms. The hexagon-like coordination observed for the Eu7–Eu7 dumbbells shows similarities with the coordination of the europium atoms in the binary  $\text{EuAg}_5$  compound [2] with  $\text{CaCu}_5$  structure type (see Fig. 6). The stacking of the polyhedra (orange color) of the Eu7 atoms along the y-axis and their location within the  $\text{Eu}_4\text{Ag}_{11+x}\text{Ga}_{6-x}$  structure are also shown in Fig. 7 (some interatomic connections are not shown for simplification). The resulting structure is similar to a honeycomb one, where deformations of the complex atomic network can easily be seen.

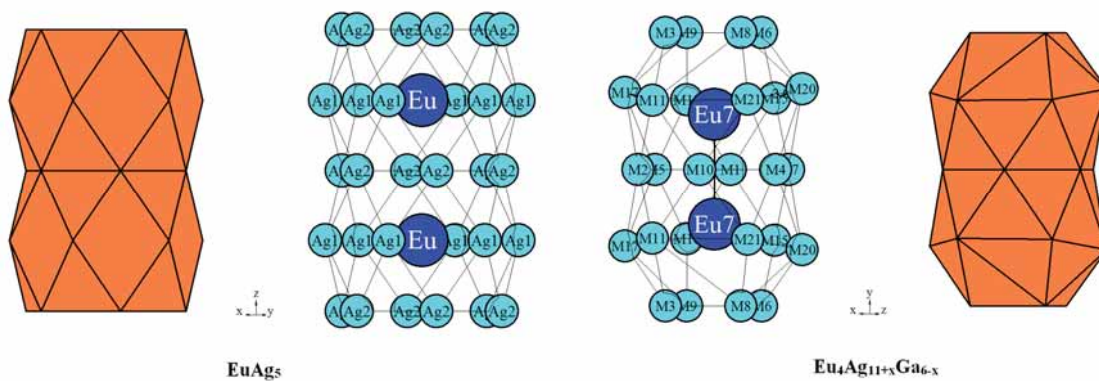
To conclude, the studied  $\text{Eu}_4\text{Ag}_{11+x}\text{Ga}_{6-x}$  phase represents a unique structure, which can be constructed on the basis of structural units of the  $\text{CaCu}_5$  type and the Laves phases. Other  $R_x\text{Ag}_y\text{Ga}_z$  phases derived from the  $\text{CaCu}_5$  type structure are known only for Yb:  $\text{YbAg}_{3.6}\text{Ga}_{1.9}$  (own type) and  $\text{YbAg}_{2.5}\text{Ga}_{2.1}$  (own type) [15].



**Fig. 4** Flat A- and B-layers along the [001] direction in the structure of the  $\text{CaCu}_5$  type. Selected Ca–Ca and Cu–Cu connections of the simplified B-layer are shown at the bottom.

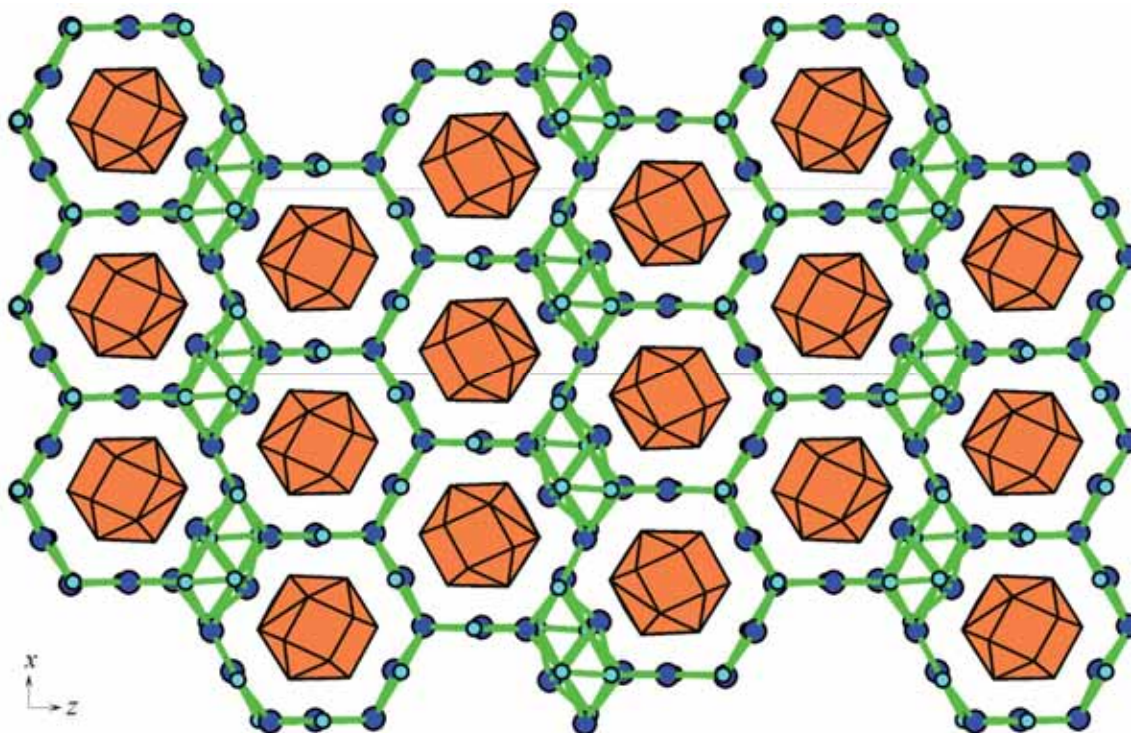


**Fig. 5** Flat **A**- and slightly puckered **B**-layers along the [111] direction in the structure of the cubic Laves phase.



**Fig. 6** Coordination of the  $\text{Eu7-Eu7}$  dumbbells in  $\text{Eu}_4\text{Ag}_{11+x}\text{Ga}_{6-x}$  and of the  $\text{Eu}$  atoms in the binary  $\text{EuAg}_5$  compound.





**Fig. 7**  $\text{Eu}_4\text{Ag}_{11+x}\text{Ga}_{6-x}$  viewed along the  $y$ -axis. Selected interatomic connections are shown by bold green lines.

**Table 6** Interatomic distances in the structure of  $\text{Eu}_4\text{Ag}_{11+x}\text{Ga}_{6-x}$ .

Atoms			$\delta$ (Å)	Atoms			$\delta$ (Å)
Eu1:	2	M12	3.108(8)	Eu2:	2	M22	3.189(9)
	1	M9	3.202(17)		2	M13	3.207(13)
	2	M14	3.273(17)		2	M16	3.219(12)
	2	M17	3.281(12)		2	M11	3.228(11)
	1	M8	3.292(19)		1	M8	3.243(25)
	2	M13	3.314(15)		2	M21	3.244(11)
	2	M18	3.661(13)		1	M3	3.383(19)
	2	M21	3.415(11)		2	M22	3.650(13)
	2	M20	3.415(12)		1	Eu4	3.897(14)
	1	Eu2	4.573(15)		1	Eu5	4.476(12)
				1	Eu1	4.573(15)	
Eu3:	2	M12	3.112(12)	Eu4:	2	M12	3.161(10)
	2	M19	3.122(14)		2	M16	3.211(11)
	2	M14	3.243(10)		2	M13	3.278(10)
	2	M19	3.254(14)		2	M21	3.296(10)
	2	M15	3.449(11)		1	M4	3.319(20)
	2	M18	3.455(13)		2	M22	3.324(12)
	1	M1	3.501(19)		1	M5	3.410(18)
	1	M7	3.538(22)		1	M10	3.448(17)
	1	M5	3.595(19)		1	M2	3.540(17)
	1	M1	3.599(18)		2	M17	3.597(11)
	1	M7	3.657(22)		1	Eu2	3.897(14)
	1	M4	3.695(21)				

**Table 6** (continued)

Atoms		$\delta$ (Å)	Atoms		$\delta$ (Å)				
Eu5:	2	M16	3.135(8)	Eu6:	2	M19	3.116(9)		
	1	M3	3.159(19)		2	M14	3.165(15)		
	2	M13	3.255(13)		2	M14	3.191(15)		
	2	M16	3.332(11)		2	M18	3.311(12)		
	2	M22	3.382(12)		1	M6	3.334(19)		
	2	M11	3.386(10)		2	M15	3.340(11)		
	2	M11	3.438(10)		1	M9	3.478(20)		
	1	M2	3.496(17)		2	M20	3.510(12)		
	1	M10	3.542(17)		1	M6	3.570(19)		
	2	M17	3.624(12)		2	M15	3.633(11)		
	1	Eu2	4.476(12)		M1:	1	M7	2.637(24)	
	Eu7:	1	M21			3.156(10)	1	M5	2.723(21)
		1	M20			3.166(12)	2	M19	2.805(16)
		1	M18			3.181(13)	2	M18	2.833(13)
1		M11	3.181(10)	2		M15	2.880(11)		
1		M17	3.182(12)	2		Eu7	3.289(14)		
1		M15	3.230(10)	1		Eu3	3.501(19)		
1		M8	3.250(10)	1		Eu3	3.599(18)		
1		M4	3.269(16)	M2:		1	M5	2.684(21)	
1		M5	3.287(14)			2	M16	2.776(14)	
1		M1	3.289(14)			1	M10	2.801(19)	
1		M7	3.297(17)			2	M11	2.842(11)	
1		M2	3.315(13)			2	M17	3.021(10)	
1		M10	3.320(14)			2	Eu7	3.315(13)	
1		M9	3.341(10)		1	Eu5	3.496(17)		
1	M3	3.345(11)	1		Eu4	3.540(17)			
1	M6	3.399(12)	M4:		1	M7	2.572(27)		
1	Eu7	3.771(5)			2	M12	2.689(18)		
M3:	1	M9			2.634(25)	1	M10	2.803(24)	
	1	M8			2.637(25)	2	M21	2.857(13)	
	2	M11			2.734(13)	2	M20	3.116(12)	
	2	M17			2.896(13)	2	Eu7	3.269(16)	
	1	Eu5		3.159(19)	1	Eu4	3.319(20)		
	2	Eu7		3.345(11)	1	Eu3	3.695(21)		
	1	Eu2		3.383(19)	M6:	2	M15	2.601(12)	
M5:	1	M2		2.684(21)		1	M9	2.623(23)	
	1	M1		2.723(21)		1	M8	2.628(28)	
	2	M12		2.750(16)		2	M20	2.834(14)	
	2	M18		2.880(14)		1	Eu6	3.334(19)	
	2	M17		3.045(11)		2	Eu7	3.399(12)	
	2	Eu7	3.287(14)	1		Eu6	3.570(19)		
	1	Eu4	3.410(18)	M8:		1	M6	2.628(28)	
	1	Eu3	3.595(19)		1	M3	2.637(24)		
M7:	1	M4	2.572(27)		2	M21	2.705(13)		
	1	M1	2.637(24)		2	M20	2.971(19)		
	2	M19	2.667(19)		1	Eu2	3.243(25)		
	2	M15	2.910(13)		2	Eu7	3.250(10)		
	2	M20	3.099(12)		1	Eu1	3.292(19)		
	2	Eu7	3.297(17)						
	1	Eu3	3.538(22)						
	1	Eu3	3.657(22)						

**Table 6** (continued)

Atoms			$\delta$ (Å)	Atoms			$\delta$ (Å)	
<i>M9:</i>	1	<i>M6</i>	2.623(23)	<i>M10:</i>	2	<i>M22</i>	2.785(15)	
	1	<i>M3</i>	2.634(25)		1	<i>M2</i>	2.801(19)	
	2	<i>M18</i>	2.663(14)		1	<i>M4</i>	2.803(24)	
	2	<i>M17</i>	3.094(16)		2	<i>M11</i>	2.881(12)	
	1	Eu1	3.202(17)		2	<i>M21</i>	2.914(11)	
	2	Eu7	3.341(10)		2	Eu7	3.320(14)	
	1	Eu6	3.478(20)		1	Eu4	3.448(17)	
	1				1	Eu5	3.542(17)	
<i>M11:</i>	1	<i>M3</i>	2.734(13)	<i>M12:</i>	1	<i>M4</i>	2.689(18)	
	1	<i>M16</i>	2.827(11)		1	<i>M5</i>	2.750(16)	
	1	<i>M2</i>	2.842(11)		1	<i>M18</i>	2.812(14)	
	1	<i>M10</i>	2.881(12)		1	<i>M20</i>	2.830(13)	
	1	<i>M16</i>	2.971(12)		1	<i>M21</i>	2.858(12)	
	1	<i>M22</i>	3.029(13)		1	<i>M17</i>	3.035(13)	
	1	<i>M17</i>	3.099(13)		1	<i>M14</i>	3.067(16)	
	1	Eu7	3.181(10)		1	Eu3	3.112(12)	
	1	Eu2	3.228(11)		1	Eu1	3.108(8)	
	1	Eu5	3.386(10)		1	<i>M12</i>	3.135(11)	
	1	Eu5	3.438(10)		1	Eu4	3.161(10)	
<i>M13:</i>	1	<i>M22</i>	2.615(13)	<i>M14</i>	1	<i>M18</i>	2.666(17)	
	1	<i>M17</i>	2.757(15)		1	<i>M15</i>	2.674(16)	
	1	<i>M21</i>	2.807(13)		1	<i>M20</i>	2.679(17)	
	1	<i>M13</i>	2.871(13)		1	<i>M14</i>	2.822(14)	
	1	<i>M16</i>	2.897(13)		1	<i>M12</i>	3.067(16)	
	1	<i>M22</i>	3.135(14)		1	Eu6	3.165(15)	
	1	Eu2	3.207(13)		1	<i>M19</i>	3.173(16)	
	1	Eu5	3.255(13)		1	Eu6	3.191(15)	
	1	Eu4	3.278(10)		1	Eu3	3.243(10)	
	1	Eu1	3.314(15)		1	Eu1	3.273(17)	
	<i>M15:</i>	1	<i>M6</i>		2.601(12)	<i>M16:</i>	1	<i>M2</i>
1		<i>M14</i>	2.674(16)	1	<i>M11</i>		2.827(11)	
1		<i>M19</i>	2.818(14)	1	<i>M17</i>		2.892(13)	
1		<i>M19</i>	2.851(14)	1	<i>M13</i>		2.897(13)	
1		<i>M1</i>	2.880(11)	1	<i>M11</i>		2.971(12)	
1		<i>M7</i>	2.910(13)	1	<i>M22</i>		3.124(12)	
1		<i>M20</i>	3.040(14)	1	<i>M16</i>		3.128(12)	
1		<i>M18</i>	3.072(14)	1	Eu5		3.135(8)	
1		Eu7	3.230(10)	1	Eu4		3.211(11)	
1		Eu6	3.340(11)	1	Eu2		3.219(12)	
1		Eu3	3.449(11)	1	Eu5		3.332(11)	
1		Eu6	3.633(11)					
<i>M17:</i>		1	<i>M13</i>	2.757(15)	<i>M18:</i>		1	<i>M9</i>
	1	<i>M16</i>	2.892(13)	1		<i>M14</i>	2.666(17)	
	1	<i>M3</i>	2.896(13)	1		<i>M12</i>	2.812(14)	
	1	<i>M2</i>	3.021(10)	1		<i>M1</i>	2.833(13)	
	1	<i>M12</i>	3.035(13)	1		<i>M19</i>	2.875(16)	
	1	<i>M5</i>	3.045(11)	1		<i>M5</i>	2.880(14)	
	1	<i>M9</i>	3.094(16)	1		<i>M15</i>	3.072(14)	
	1	<i>M11</i>	3.099(13)	1		Eu7	3.181(13)	
	1	Eu7	3.182(12)	1		<i>M17</i>	3.198(16)	
	1	<i>M18</i>	3.198(16)	1		Eu6	3.311(12)	
	1	Eu1	3.281(12)	1		Eu3	3.455(13)	
	1	Eu4	3.597(11)	1		Eu1	3.661(13)	
	1	Eu5	3.624(12)					

**Table 6** (continued)

Atoms			$\delta$ (Å)	Atoms			$\delta$ (Å)
M19:	1	M7	2.667(19)	M20:	1	M14	2.679(17)
	1	M1	2.805(16)		1	M12	2.830(13)
	1	M15	2.818(14)		1	M6	2.834(14)
	1	M20	2.842(15)		1	M19	2.842(15)
	1	M15	2.851(14)		1	M8	2.971(19)
	1	M18	2.875(16)		1	M15	3.040(14)
	1	M19	3.115(13)		1	M21	3.063(13)
	1	Eu6	3.116(9)		1	M7	3.099(12)
	1	Eu3	3.122(14)		1	M4	3.116(12)
	1	M14	3.173(16)		1	Eu7	3.166(12)
	1	Eu3	3.254(14)	1	Eu1	3.415(12)	
				1	Eu6	3.510(12)	
M21:	1	M8	2.705(13)	M22:	1	M13	2.615(13)
	1	M13	2.807(13)		1	M10	2.785(15)
	1	M4	2.857(13)		1	M22	2.979(13)
	1	M12	2.858(12)		1	M21	2.998(11)
	1	M10	2.914(11)		1	M11	3.029(13)
	1	M22	2.998(11)		1	M16	3.124(12)
	1	M20	3.063(13)		1	M22	3.124(12)
	1	Eu7	3.156(10)		1	M13	3.135(14)
	1	Eu2	3.244(11)		1	Eu2	3.189(9)
	1	Eu4	3.294(10)		1	Eu4	3.324(12)
	1	Eu1	3.415(11)	1	Eu5	3.382(12)	
				1	Eu2	3.650(13)	

**Acknowledgements**

This work was partially supported by FCT, Portugal, under contract № PTDC/CTM/102766/2008.

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