

Synthesis and Crystal Structures of REAgMg (RE = La, Ce, Nd, Eu, Gd, Tb, Ho, Tm, and Yb)

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The title compounds were synthesized by reacting the elements in sealed tantalum tubes in a high-frequency furnace. They were investigated by X-ray diffraction on both powders and single crystals. With the trivalent rare earth elements they adopt the ZrNiAl-type structure, space group $P\bar{6}2m$: $a = 782.5(3)$ pm, $c = 432.8(1)$ pm, $wR2 = 0.0420$, and $277 F^2$ values for CeAgMg and $a = 775.7(3)$ pm, $c = 426.1(1)$ pm, $wR2 = 0.0387$, and $271 F^2$ values for NdAgMg with 15 parameters for each refinement. Geometrical motifs in CeAgMg are two types of silver-centered tricapped trigonal prisms: $[Ag1Mg_3Ce_6]$ and $[Ag2Mg_6Ce_3]$. The silver and magnesium atoms form a three-dimensional $[AgMg]$ network in which the cerium atoms fill distorted hexagonal channels. With divalent europium and ytterbium the orthorhombic TiNiSi-type occurs, space group $Pnma$: $a = 777.4(2)$ pm, $b = 463.0(1)$ pm, $c = 898.8(2)$ pm, $wR2 = 0.0430$, and $401 F^2$ values for EuAgMg and $a = 753.66(7)$ pm, $b = 446.49(7)$ pm, $c = 887.2(1)$ pm, $wR2 = 0.0742$, and $485 F^2$ values for YbAgMg with 21 parameters for each refinement. The europium(ytterbium) and magnesium atoms form zigzag chains of edge- and face-sharing trigonal prisms which are centered by the silver atoms. Also in EuAgMg and YbAgMg a three-dimensional $[AgMg]$ network occurs in which the europium(ytterbium) atoms are embedded. The magnesium positions of the cerium, neodymium, europium, and ytterbium compound show a small mixed magnesium/silver occupancy, leading to the refined compositions $CeAg_{1.034(7)}Mg_{0.966(7)}$, $NdAg_{1.035(6)}Mg_{0.965(6)}$, $EuAg_{1.032(6)}Mg_{0.968(6)}$, and $YbAg_{1.053(8)}Mg_{0.947(8)}$ for the crystals investigated. The crystal chemistry and chemical bonding in these intermetallics is briefly discussed. © 2001 Academic Press

Key Words: intermetallic compounds; magnesium; crystal structure.

investigated in recent years (1–15) with respect to crystal chemistry, chemical bonding, and physical properties. Besides the series RE_2T_2Mg ($T = Ni$ and Cu) (4, 8, 14), RE_2Au_2Cd ($RE = La, Ce, Pr, Nd, Sm$) (7, 12) and Ce_2Ni_2Cd (10) with tetragonal Mo_2FeB_2 -type structure (16) and also the equiatomic compounds $RETMg$ ($T = Pd, Ag, Au$) (3, 4, 9) and $RETCd$ ($T = Cu, Pd, Au$) (2, 6, 12) have recently been studied. The latter crystallize with the orthorhombic TiNiSi-type structure (17) when the rare earth element is divalent and with the hexagonal ZrNiAl-type structure (18–20) in the case of trivalent rare earth metals.

These magnesium- and cadmium-based intermetallics exhibit a wide range of physical properties. Magnetic susceptibility measurements revealed mixed-valent behavior for the cerium atoms in Ce_2Ni_2Mg (4) and Ce_2Ni_2Cd (10), a nonmagnetic ground state for the ytterbium atoms in $YbAuMg$ and $YbAuCd$ (12) and antiferromagnetic ordering in Gd_2Ni_2Mg (13). Comparatively high Curie temperatures of 28 and 62 K were observed for $EuAuCd$ (12) and $GdPdCd$ (15), respectively.

In view of the promising properties of such intermetallics, we have now extended our investigations with respect to the systems with silver as the transition-metal component. So far, only some Heusler-type phases $RE_yAg_xMg_{1-x-y}$ (1) and the equiatomic compounds $REAgMg$ ($RE = Y, La, Ce, Pr, Sm, Gd, Dy, Er$) with ZrNiAl-type structure have been reported. These investigations were based exclusively on X-ray powder data. We could synthesize new compounds $REAgMg$ ($RE = Nd, Eu, Tb, Ho, Tm, Yb$) and grow single crystals of CeAgMg, NdAgMg, EuAgMg, and YbAgMg. The structure refinements and crystal chemistry of these intermetallics are reported herein.

INTRODUCTION

The ternary systems rare earth metal (RE)–transition metal (T)–magnesium (cadmium) have been intensively in-

EXPERIMENTAL

Starting materials for the synthesis of the $REAgMg$ compounds were ingots of the rare earth elements (Johnson Matthey, > 99.9%), silver wire (Degussa-Hüls, > 99.9%, $\varnothing 2$ mm), and a magnesium rod (Johnson Matthey,

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Ø 16 mm, > 99.95%). The larger rare earth metal pieces were mechanically cut into smaller pieces and first arc-melted to small buttons (about 400 mg) under an argon atmosphere of about 600 mbar. Details on the arc-melting technique are given in (21). The argon was purified before over titanium sponge (900 K), silica gel, and molecular sieves.

The rare earth metal buttons were subsequently mixed with pieces of the silver wire and the magnesium rod in the ideal 1 : 1 : 1 atomic ratio and sealed in small tantalum tubes (ca. 1 cm³) under an argon atmosphere of about 800 mbar. The tantalum tubes were placed in a water-cooled quartz glass sample chamber of a high-frequency generator (KONTRON Roto-Melt, 1.2 kW) under purified flowing argon (22). They were first heated for 2 min with the maximum power output (about 1500 K) and subsequently annealed at about 900 K for another 4 h. The tubes were finally quenched by radiative heat loss within the water-cooled sample chamber. The reaction between the three elements was visible by a short heat flash. After the annealing procedures, the light-gray samples could readily be separated from the tantalum tubes. No reactions of the samples with the tubes could be detected. All samples were obtained in amounts of about 1 g. They are stable against air and moisture as compact buttons as well as fine-grained powders. Single crystals exhibit metallic luster.

The samples were characterized through powder diffractograms (Stoe Stadi P) using CuK α_1 radiation and silicon ($a = 543.07$ pm) as an external standard. The hexagonal and orthorhombic lattice parameters (Table 1) were obtained from least-squares fits of the powder data. The correct

indexing of the patterns was ensured by intensity calculations (23), taking the atomic positions from the structure refinements. The lattice parameters determined from the powders and the single crystals agreed well. For LaAgMg, CeAgMg, and GdAgMg, our X-ray powder data compared well with the previously published data by Iandelli (3).

Single-crystal intensity data were collected at room temperature by use of a four-circle diffractometer (CAD4) with graphite-monochromatized MoK α (71.073 pm) radiation and a scintillation counter with pulse height discrimination. The scans were taken in the $\omega/2\theta$ mode and empirical absorption corrections were applied on the basis of ψ -scan data, followed by spherical absorption corrections. All relevant details concerning the data collections are listed in Table 2.

RESULTS AND DISCUSSION

Structure Determination and Refinement

Irregularly shaped single crystals of CeAgMg, NdAgMg, EuAgMg, and YbAgMg were isolated from the annealed samples and examined by use of a Buerger camera equipped with an image plate system (Fujifilm BAS-2500) to establish both symmetry and suitability for intensity data collection. The isotypy of CeAgMg and NdAgMg with the ZrNiAl-type (18–20), space group $P\bar{6}2m$, and of EuAgMg and YbAgMg with the TiNiSi-type (17), space group $Pnma$, was already evident from the X-ray powder data. The relevant crystallographic data are listed in Table 2.

The starting atomic parameters were deduced from automatic interpretations of direct methods with SHELXS-97 (24). The structures were then successfully refined using SHELXL-97 (25) (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for all atoms. The correct absolute structure of CeAgMg and NdAgMg was ensured through refinement of the Flack parameters (26, 27).

As a check for the correct composition and the correct site assignment, the occupancy parameters were refined in separate series of least-squares cycles along with the displacement parameters. With the exception of the magnesium positions, all sites were fully occupied within three standard deviations (Table 3) and in the final cycles the ideal occupancy parameters were assumed for these sites. All magnesium sites showed elevated occupancy parameters, indicating mixed magnesium/silver occupancy. These sites were subsequently refined with mixed magnesium/silver occupancy, leading to the refined compositions CeAg_{1.034(7)}Mg_{0.996(7)}, NdAg_{1.035(6)}Mg_{0.965(6)}, EuAg_{1.032(6)}Mg_{0.968(6)}, and YbAg_{1.053(8)}Mg_{0.947(8)} for the crystals investigated.

The final difference Fourier syntheses were flat (Table 2). The positional parameters and interatomic distances of the

TABLE 1
Lattice Parameters of REAgMg Compounds with Hexagonal ZrNiAl and Orthorhombic TiNiSi-Type Structure

Compound	a (pm)	b (pm)	c (pm)	c/a	V (nm ³)	Reference
YAgMg	766.1(2)	a	413.8(1)	0.540	0.2103	(3)
LaAgMg	788.8(3)	a	437.4(1)	0.555	0.2357	This work
LaAgMg	785.3(2)	a	437.0(2)	0.556	0.2334	(3)
CeAgMg	782.5(3)	a	432.8(1)	0.553	0.2295	This work
CeAgMg	782.3(2)	a	433.1(1)	0.554	0.2295	(3)
PrAgMg	779.7(3)	a	429.3(3)	0.551	0.2260	(3)
NdAgMg	775.7(3)	a	426.1(1)	0.549	0.2220	This work
SmAgMg	773.0(1)	a	422.4(1)	0.546	0.2186	(3)
EuAgMg	777.4(2)	463.0(1)	898.8(2)	—	0.3235	This work
GdAgMg	767.9(2)	a	419.9(1)	0.547	0.2144	This work
GdAgMg	767.9(1)	a	418.9(1)	0.546	0.2139	(3)
TbAgMg	763.9(3)	a	416.5(1)	0.545	0.2105	This work
DyAgMg	764.5(2)	a	413.0(2)	0.540	0.2090	(3)
HoAgMg	763.32(8)	a	411.62(4)	0.539	0.2077	This work
ErAgMg	762.6(1)	a	407.4(1)	0.534	0.2052	(3)
TmAgMg	759.9(2)	a	408.2(1)	0.537	0.2041	This work
YbAgMg	753.66(7)	446.49(7)	887.2(1)	—	0.2986	This work

TABLE 2
Crystal Data and Structure Refinement for CeAgMg, NdAgMg, EuAgMg, and YbAgMg

Empirical formula	CeAgMg	NdAgMg	EuAgMg	YbAgMg
Molar mass (g/mol)	272.30	276.42	284.14	305.22
Space group, <i>Z</i>	$P\bar{6}2m$, 3	$P\bar{6}2m$, 3	$Pnma$, 4	$Pnma$, 4
Pearson symbol	<i>hP9</i>	<i>hP9</i>	<i>oP12</i>	<i>oP12</i>
Unit cell dimensions	Table 1	Table 1	Table 1	Table 1
Calculated density (g/cm ³)	5.91	6.20	5.83	6.79
Crystal size (μm^3)	30 × 35 × 60	20 × 20 × 80	10 × 20 × 100	10 × 60 × 60
Transm. ratio (max/min)	1.37	1.17	1.27	2.01
Abs. coefficient (mm ⁻¹)	21.0	23.8	25.1	37.6
<i>F</i> (000)	351	357	488	516
θ range for data collection	2° to 30°	2° to 30°	2° to 30°	2° to 30°
Range in <i>hkl</i>	± 10, ± 10, + 6	± 10, ± 10, + 5	± 10, + 5, + 12	± 10, + 6, ± 12
Total no. of reflections	1476	1445	1472	1815
Independent reflections	277 ($R_{\text{int}} = 0.0665$)	271 ($R_{\text{int}} = 0.0704$)	401 ($R_{\text{int}} = 0.0869$)	485 ($R_{\text{int}} = 0.0994$)
Reflections with $I > 2\sigma(I)$	260 ($R_{\text{sigma}} = 0.0358$)	251 ($R_{\text{sigma}} = 0.0400$)	297 ($R_{\text{sigma}} = 0.0638$)	376 ($R_{\text{sigma}} = 0.0652$)
Data/restraints/parameters	277/0/15	271/0/15	401/0/21	485/0/21
Goodness-of-fit on F^2	1.185	1.014	0.962	1.017
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R1 = 0.0232$ $wR2 = 0.0408$	$R1 = 0.0231$ $wR2 = 0.0372$	$R1 = 0.0345$ $wR2 = 0.0387$	$R1 = 0.0334$ $wR2 = 0.0669$
<i>R</i> indices (all data)	$R1 = 0.0277$ $wR2 = 0.0420$	$R1 = 0.0290$ $wR2 = 0.0387$	$R1 = 0.0616$ $wR2 = 0.0430$	$R1 = 0.0545$ $wR2 = 0.0742$
Extinction coefficient	0.0061(7)	0.0046(6)	0.0024(2)	0.0026(5)
Flack parameter	0.01(5)	− 0.05(4)	—	—
Largest diff. peak and hole	1.29 and − 0.87 e/Å ³	0.86 and − 0.71 e/Å ³	1.58 and − 1.73 e/Å ³	2.12 and − 2.99 e/Å ³

four refinements are listed in Tables 3 and 4. Listings of the observed and calculated structure factors are available.²

Crystal Chemistry and Chemical Bonding

The series REAgMg (3) has been extended by synthesis of the neodymium, europium, terbium, holmium, thulium, and ytterbium compounds. The structures of CeAgMg, NdAgMg, EuAgMg, and YbAgMg have been refined on the basis of single-crystal X-ray data. If the rare earth element is trivalent, the REAgMg compounds crystallize with the ZrNiAl structure (18–20), a ternary ordered version of the Fe₂P-type (28). The cell volumes of these REAgMg compounds decrease monotonically from the lanthanum to the thulium compound (Fig. 1), as expected from the lanthanoid contraction. The volume of the yttrium compound fits between those of the terbium and the dysprosium compound.

As an example for the hexagonal compounds, we present a projection of the CeAgMg structure in Fig. 2. CeAgMg contains two crystallographically different silver sites. The Ag1 atoms have a trigonal prismatic coordination of cerium atoms, while the Ag2 atoms are located in trigonal prisms formed by the magnesium atoms. These different trigonal

²Details may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No's. CSD-411768 (CeAgMg), CSD-411766 (NdAgMg), CSD-411767 (EuAgMg), and CSD-411769 (YbAgMg).

TABLE 3
Atomic Coordinates and Isotropic Displacement Parameters (pm²) for CeAgMg, NdAgMg, EuAgMg, and YbAgMg

Atom	Wyckoff site	Occup.	x	y	z	U_{eq}
CeAgMg (space group $P\bar{6}2m$)						
Ce	3 <i>f</i>	1.007(7)	0.5842(1)	0	0	158(2)
Ag1	2 <i>d</i>	0.984(8)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$	165(3)
Ag2	1 <i>a</i>	1.01(1)	0	0	0	169(4)
Mg/Ag	3 <i>g</i>	0.966(7)/0.034(7)	0.2402(6)	0	$\frac{1}{2}$	186(18)
NdAgMg (space group $P\bar{6}2m$)						
Nd	3 <i>f</i>	0.991(7)	0.4152(1)	0	0	158(2)
Ag1	2 <i>d</i>	1.001(8)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$	162(3)
Ag2	1 <i>a</i>	1.03(1)	0	0	0	165(4)
Mg/Ag	3 <i>g</i>	0.965(6)/0.035(6)	0.7564(6)	0	$\frac{1}{2}$	184(17)
EuAgMg (space group $Pnma$)						
Eu	4 <i>c</i>	1.000(6)	0.03323(9)	$\frac{1}{4}$	0.67834(8)	196(2)
Ag	4 <i>c</i>	0.996(6)	0.2721(1)	$\frac{1}{4}$	0.3754(1)	209(3)
Mg/Ag	4 <i>c</i>	0.968(6)/0.032(6)	0.1393(6)	$\frac{1}{4}$	0.0602(5)	217(16)
YbAgMg (space group $Pnma$)						
Yb	4 <i>c</i>	0.998(6)	0.03401(9)	$\frac{1}{4}$	0.67591(8)	169(2)
Ag	4 <i>c</i>	1.002(6)	0.2654(2)	$\frac{1}{4}$	0.3711(1)	176(3)
Mg/Ag	4 <i>c</i>	0.947(8)/0.053(8)	0.1393(6)	$\frac{1}{4}$	0.0605(6)	198(18)

Note. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. The occupancy parameters were refined in a separate series of least-squares cycles. In the final cycles only the mixed Mg/Ag occupancies were refined as a least-squares variable.

TABLE 4
Interatomic Distances (pm), Calculated with the Lattice Parameters Taken from X-ray Powder Data of CeAgMg, NdAgMg, EuAgMg, and YbAgMg

CeAgMg					
Ce: 4 Ag1	319.7(1)	Ag1: 3 Mg	303.9(4)	Mg: 2 Ag2	286.6(3)
1 Ag2	325.4(2)	6 Ce	319.7(1)	2 Ag1	303.9(4)
2 Mg	345.4(4)			2 Mg	325.6(9)
4 Mg	356.2(1)	Ag2: 6 Mg	286.6(3)	2 Ce	345.4(4)
4 Ce	407.6(2)	3 Ce	325.4(2)	4 Ce	356.2(1)
2 Ce	432.8(1)				
NdAgMg					
Nd: 4 Ag1	316.0(1)	Ag1: 3 Mg	299.5(3)	Mg: 2 Ag2	284.8(3)
1 Ag2	322.0(2)	6 Nd	316.0(1)	2 Ag1	299.5(3)
2 Mg	339.8(4)			2 Mg	327.3(8)
4 Mg	352.1(1)	Ag2: 6 Mg	284.8(3)	2 Nd	339.8(4)
4 Nd	404.3(2)	3 Nd	322.0(2)	4 Nd	352.1(1)
2 Nd	426.1(1)				
EuAgMg					
Eu: 2 Ag	328.5(1)	Ag: 1 Mg	291.2(4)	Mg: 1 Ag	291.2(4)
1 Ag	329.5(2)	2 Mg	293.1(3)	2 Ag	293.1(3)
2 Ag	335.1(1)	1 Mg	301.5(5)	1 Ag	301.5(5)
1 Mg	353.0(5)	2 Eu	328.5(1)	2 Mg	335.0(6)
2 Mg	356.1(3)	1 Eu	329.5(2)	1 Eu	353.0(5)
2 Mg	360.1(4)	2 Eu	335.1(1)	2 Eu	356.1(3)
1 Mg	373.9(4)			2 Eu	360.1(4)
2 Eu	398.8(1)			1 Eu	373.9(4)
2 Eu	409.5(1)				
YbAgMg					
Yb: 2 Ag	320.1(1)	Ag: 1 Mg	288.3(5)	Mg: 1 Ag	288.3(5)
2 Ag	320.4(1)	2 Mg	288.5(3)	2 Ag	288.5(3)
1 Ag	321.8(1)	1 Mg	291.5(5)	1 Ag	291.5(5)
2 Mg	347.8(4)	2 Yb	320.1(1)	2 Mg	324.7(7)
2 Mg	348.7(4)	2 Yb	320.4(1)	2 Yb	347.8(4)
1 Mg	350.3(5)	1 Yb	321.8(1)	2 Yb	348.7(4)
1 Mg	364.0(5)			1 Yb	350.3(5)
2 Yb	387.2(1)			1 Yb	364.0(5)
2 Yb	399.1(1)				

Note. All distances within the first coordination sphere are listed. The magnesium sites of all four compounds show mixed Mg/Ag occupancy with about 3 to 5% silver (see Table 3).

prisms are condensed via common edges and faces. The rectangular faces of these prisms are capped by further cerium and magnesium atoms, leading to coordination number 9, i.e., $[\text{Ag}_1\text{Mg}_3\text{Ce}_6]$ and $[\text{Ag}_2\text{Mg}_6\text{Ce}_3]$.

The shortest interatomic distances in the CeAgMg structure occur for the Ag–Mg contacts, ranging from 287 to 304 pm. Although these distances are larger than the sum of Pauling's single-bond radii (29) of 270 pm for silver and magnesium, we can assume at least medium Ag–Mg bonding in CeAgMg. The magnesium atoms forming the trigonal prisms around the Ag2 atoms have Mg–Mg distances of 326 pm within the triangular faces. In view of the average Mg–Mg distance of 320 pm in *hcp* magnesium (30), also these contacts may be considered as bonding.

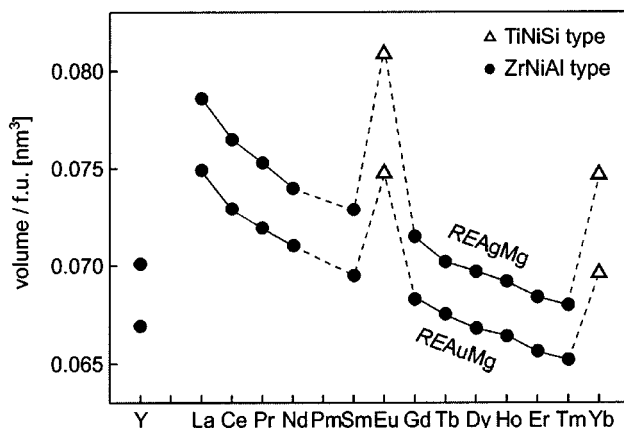


FIG. 1. Plot of the cell volumes (per formula unit) of the REAgMg and REAuMg (9) compounds. The solid and broken lines only serve as a guide for the eye.

In Fig. 3 we emphasize the three-dimensional $[\text{AgMg}]$ network in which the cerium atoms fill the distorted hexagonal channels. According to Pauling's electronegativity scale (Ce, 1.12; Ag, 1.93; Mg, 1.31) (31), cerium is the least electronegative component in CeAgMg. We can therefore assume an electron transfer from the cerium atoms to the more electronegative silver and magnesium atoms, enabling the Ag–Mg bonding.

The plot of the cell volumes shows a strong positive deviation from the linear behavior for the europium and the ytterbium compounds. This anomaly is due to the divalent character of the europium and ytterbium atoms in EuAgMg and YbAgMg, as is evident from magnetic susceptibility investigations. These data will be published elsewhere together with detailed ^{151}Eu Mössbauer spectroscopic and electrical resistivity studies on EuAgMg and EuAuMg (32).

The silver atoms in EuAgMg and YbAgMg have also a nearly trigonal prismatic coordination as outlined for EuAgMg in Fig. 2. The prisms are formed by four europium and two magnesium atoms. The rectangular faces are capped by further europium and magnesium atoms, leading to coordination number 9 for each silver atom, similar to the CeAgMg structure discussed above.

The Ag–Mg distances in EuAgMg and YbAgMg range from 288 to 302 pm. This range is similar to the hexagonal compounds. Each silver atom in EuAgMg has four magnesium neighbors in the form of a strongly distorted tetrahedron.

The EuAgMg structure may be considered as an orthorhombically distorted variant of the AlB_2 -type (33). This relation is readily visible from the perspective view presented in Fig. 3. The silver and magnesium atoms build puckered Ag_3Mg_3 hexagons and the europium atoms fill the distorted hexagonal channels of the three-dimensional $[\text{AgMg}]$ network. Due to the large distortions of the

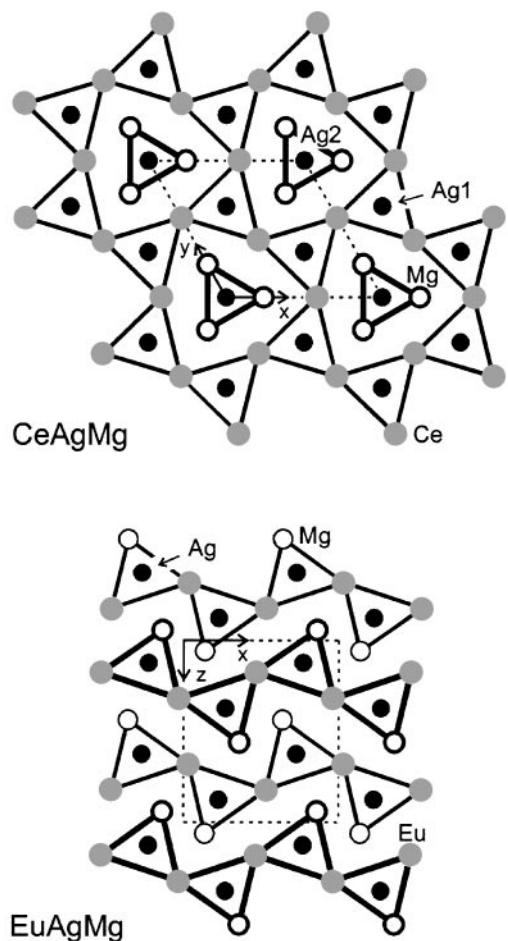


FIG. 2. Projection of the $CeAgMg$ and $EuAgMg$ structures onto the xy and xz planes, respectively. All atoms lie on mirror planes at $z = 0$ (thin lines) and $z = \frac{1}{2}$ (thick lines) for $CeAgMg$ and at $y = \frac{3}{4}$ (thick lines) for $EuAgMg$, respectively. The silver-centered trigonal prisms are emphasized.

$[AgMg]$ network, the magnesium atoms come closer together at $Mg-Mg$ distances of 335 pm in $EuAgMg$ and 325 pm in $YbAgMg$, slightly larger than those in *hcp* magnesium (320 pm) (30). We can therefore assume $Ag-Mg$ as well as $Mg-Mg$ bonding between the Ag_3Mg_3 layers. The structures of $CeAgMg$ and $EuAgMg$ have only briefly been described here. The crystal chemistry and chemical bonding in $ZrNiAl$ - and $TiNiSi$ -type compounds have been discussed in detail elsewhere (33–38).

A common feature of the four crystal structures is the mixed magnesium/silver occupancy which was also observed for the series $REAuMg$ (9). In contrast, no cadmium/gold mixing occurs for the $REAuCd$ compounds (12), most likely due to the smaller single-bond radius of magnesium (29). The degree of magnesium/silver mixing is slightly larger than the magnesium/gold mixing in the $REAuMg$ compounds (9). The larger standard deviation for the occu-

pancy parameters of the silver compounds is due to the smaller difference in the scattering power between magnesium and silver as compared to magnesium and gold. The mixed occupancies are indicative for homogeneity ranges $REAg_{1+x}Mg_{1-x}$; however, these were not investigated in detail.

The homogeneity range of isotypic $YbAuIn$ was studied thoroughly (39–42). A solid solution $YbAu_{1+x}In_{1-x}$ up to $YbAu_{1.27}In_{0.73}$ was evident from X-ray powder and single-crystal data (41, 42). With an increasing gold content it is possible to partially oxidize the ytterbium atoms in $YbAu_{1.27}In_{0.73}$ with respect to $YbAuIn$. Consequently, the absolute susceptibility values and the ytterbium valence increase (42).

Finally, we draw back to the course of the cell volumes presented in Fig. 1. Although the metallic single-bond radius (29) of silver (133.9 pm) and gold (133.6 pm) and the

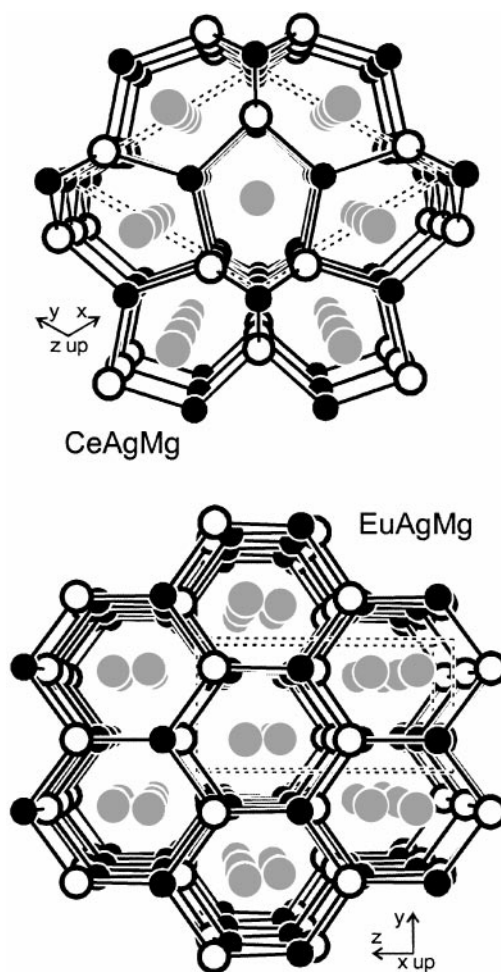


FIG. 3. Perspective views of the $CeAgMg$ (upper drawing) and $EuAgMg$ structures approximately along the z and x axis, respectively. The cerium(europium), silver, and magnesium atoms are drawn as gray, filled, and open circles, respectively. The three-dimensional $[AgMg]$ networks are emphasized.

lattice parameters (30) of *fcc* silver (408.57 pm) and gold (407.8 pm) are very similar, the cell volumes per formula unit are about 5% smaller for the hexagonal and even 7% smaller for the orthorhombic gold compounds. The contraction of the REAuMg unit cells is more or less isotropic. Similar behavior is observed in various other Eu(Ag/Au)*X* and Yb(Ag/Au)*X* intermetallics (43, 44). This behavior can most likely be attributed to the relativistic contraction of the gold 6s orbitals. A detailed investigation of the EuAgMg and EuAuMg band structures is in progress. These results will be presented together with the physical property data (32).

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