Ternary Gallides *RE*MgGa (*RE* = Y, La, Pr, Nd, Sm–Tm, Lu) – Synthesis and Crystal Chemistry

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The title compounds have been synthesized by reacting the elements in sealed niobium or tantalum tubes in a high-frequency furnace. They crystallize with the hexagonal ZrNiAl type structure, space group $P\bar{6}2m$. All gallides have been characterized through their X-ray powder diffractogram. The cell volume decreases from the lanthanum to the lutetium compound as expected from the lanthanoid contraction. The structures of LaMgGa, PrMgGa, NdMgGa, SmMgGa and TmMgGa have been refined from single crystal diffractometer data. The structures contain two crystallographically independent gallium sites which both have a trigonal prismatic coordination: Ga1 by six *RE* and Ga2 by six Mg atoms. These trigonal prisms are capped on the rectangular sites by three Mg (*RE*) atoms, leading to coordination number 9 for each gallium atom. Together, the gallium and magnesium atoms form a three-dimensional [MgGa] network in which the rare earth atoms fill distorted hexagonal channels. Within the network the magnesium atoms have short Mg–Mg contacts, *i. e.* 312 pm in SmMgGa. The Mg–Ga distances in that gallide range from 284 to 287 pm. Bonding in the network is thus governed by strong Mg–Ga and Mg–Mg bonding. EuMgGa crystallizes with the orthorhombic TiNiSi type: *Pnma*, a = 783.1(2), b = 472.8(1), c = 829.8(2) pm.

Key words: Rare Earth Compounds, Magnesium, Crystal Chemistry

Introduction

Many equiatomic *RETX* (*RE* = rare earth element, *T* = transition metal, *X* = element of the 3rd, 4th or 5th main group) [1] crystallize with the orthorhombic TiNiSi [2] or hexagonal ZrNiAl [3 – 5] type structure. Both structure types are built up from three-dimensional [*TX*] networks. Chemical bonding is governed by strong covalent *T*–*X* interactions within these networks, and the rare earth atoms fill two different kinds of distorted hexagonal channels left by the network. The compounds with a non-magnetic rare earth metal are sometimes superconducting, however, with very low transition temperatures, *e. g.* LaRhSn 1.7 K [6]. If the rare earth atoms are paramagnetic, a variety of different magnetic phenomena occur, such as long-range ferro- or antiferrromagnetic ordering, intermediate valence, heavy Fermion, or Kondo behaviour. The nature of the magnetic behaviour mainly depends on two factors, (i) the *RE*–*RE* distance in a given *RETX* compound and (ii) the hybridisation of the *RE* 4*f* states with the transition metal *d* states.

The magnetic behaviour can be influenced, if the *d*-element component is substituted by a light main group element such as lithium or magnesium. Such substitutions are known from compounds like YLiSi [7], YLiSn [8], or GdMgIn and GdMgGa [9]. The gadolinium compounds show long-range ordering at 15.3 K (GdMgGa) while GdMgIn remains paramagnetic. However, compared with the very large family of *RETX* intermetallics, only little information on *REXX'* compounds is available in the literature [1]. We have recently started a systematic investigation on *REXX'* compounds in order to study the similarities and differences with respect to *RETX* intermetallics. Within the series *RE*MgGa, so far only the gadolinium compound has been reported [9]. Our recent investigations revealed the existence of CeMgGa, a 3.1 K antiferromagnet that undergoes a metamagnetic transition at a critical field of 1 T [10]. Herein we report on the synthesis and structure refinements on the remaining compounds within the *RE*MgGa series.

Experimental Section

Starting materials for the synthesis of the *RE*MgGa compounds were ingots of the rare earth metals (Johnson Matthey, >99.9 %), a magnesium rod (Johnson Matthey,

Table 1. Lattice parameters of the hexagonal gallides *RE*MgGa (space group $P\bar{6}2m$, ZrNiAl type).

Compound	a (pm)	c (pm)	V (nm^3)	Reference
YMgGa	726.8(4)	441.3(2)	0.2019	this work
LaMgGa	760.2(2)	459.6(1)	0.2300	this work
CeMgGa	752.7(2)	454.8(1)	0.2232	[10]
PrMgGa	747.9(2)	453.10(8)	0.2195	this work
NdMgGa	744.4(2)	451.00(9)	0.2164	this work
SmMgGa	737.6(2)	447.5(1)	0.2108	this work
GdMgGa	732.7(3)	444.8(1)	0.2068	this work
GdMgGa	730.7(1)	444.1(2)	0.2053	[9]
TbMgGa	728.2(3)	442.6(1)	0.2033	this work
DyMgGa	726.1(3)	441.6(2)	0.2016	this work
HoMgGa	723.8(3)	440.9(2)	0.2000	this work
ErMgGa	720.5(3)	439.6(1)	0.1976	this work
TmMgGa	718.5(3)	437.9(2)	0.1958	this work
LuMgGa	714.6(2)	436.6(1)	0.1931	this work

>99.5 %), and gallium pieces (Wacker, >99.9 %). In a first step the larger rare earth metal pieces and the magnesium rod were mechanically cut into smaller pieces and parts of the larger gallium ingots were crushed in a steel mortar under liquid nitrogen into smaller fragments.

The elements were then weighted in the ideal 1:1:1 atomic ratio (total weight between 500 and 1000 mg) and sealed in small tantalum or niobium containers under an argon pressure of about 800 mbar. Details about the arc-welding equipment are given elsewhere [11]. The argon was purified before over titanium sponge (600 K), molecular sieves, and silica gel.

The sealed metal ampoules were then placed in a water-cooled sample chamber made of quartz [12] which itself has been placed in the center of an induction coil of a high-frequency generator (Hüttinger Elektronik, Freiburg, TIG 1.5/300). The tubes were first heated with the maximum power output in order to get a homogeneous melt. The reaction between the three elements was visible as a short heat flash. The ampoules were then annealed at about 800 K for another 2 h and finally cooled to r. t. by switching off the high-frequency generator.

The *RE*MgGa compounds could readily be separated from the metal ampoules. No reaction with the crucible material has been observed. Compact pieces of the *RE*MgGa compounds are stable in air. Fine-grained powders slowly deteriorate in moist air. Single crystals exhibit silvery metallic lustre.

The polished but unetched samples have been analysed in a scanning electron microscope (Leica 420 I) in backscattering mode by energy dispersive analyses of X-rays. The anal-

Table 2. Crystal data and structure refinement for LaMgGa, PrMgGa, NdMgGa, SmMgGa and TmMgGa (space group $P\bar{6}2m$; Z = 3).

Empirical formula	LaMgGa	PrMgGa	NdMgGa	SmMgGa	TmMgGa
Molar mass	232.94 g/mol	234.94 g/mol	238.27 g/mol	244.38 g/mol	262.96 g/mol
Unit cell dimensions	Table 1	Table 1	Table 1	Table 1	Table 1
Calculated density	5.05 g/cm^3	5.33 g/cm^3	5.48 g/cm^3	5.77 g/cm^3	6.69 g/cm^3
Crystal size	$10 \times 15 \times 20$ μm^3	$10 \times 25 \times 40$ μm^3	$15 \times 20 \times 25$ μm^3	$15 \times 20 \times 20$ μm^3	$20 \times 25 \times 40$ μm^3
Transmission ratio (max/min)	1.43	1.44	1.21	1.45	2.08
Absorption coefficient	22.4 mm^{-1}	25.5 mm^{-1}	27.0 mm^{-1}	30.1 mm^{-1}	43.9 mm^{-1}
$F(000)$	300	306	309	315	336
Detector distance	60 mm	–	60 mm	–	–
Exposure time	28 min	–	15 min	–	–
ω Range, increment	$0-180°$; 1.0°	–	$0-180°$; 1.5°	–	–
Integr. parameters A, B, EMS	14.4, 4.5, 0.020	–	11.2, 1.9, 0.016	–	–
θ Range	5° to 35°	3° to 30°	3° to 35°	3° to 35°	3° to 40°
Range in *hkl*	$-4 \le h \le 12$,	±9,	±11,	±11,	±11,
	$-12 \le k \le 6$,	±9,	$-9 \le k \le 12$,	±11;	±11;
	$-3 \le l \le 7$	±6	±7	$0 \le l \le 7$	±7
Total no. reflections	924	716	3252	2031	3224
Independent reflections	395 (R_{int} = 0.090)	273 (R_{int} = 0.097)	385 (R_{int} = 0.085)	377 (R_{int} = 0.094)	423 (R_{int} = 0.081)
Reflections with $I > 2\sigma(I)$	321 (R_{sigma} = 0.105)	242 (R_{sigma} = 0.090)	347 (R_{sigma} = 0.044)	351 (R_{sigma} = 0.051)	382 (R_{sigma} = 0.041)
Data/parameters	395 / 14	273 / 14	385 / 14	377 / 15	423 / 15
Goodness-of-fit on F^2	1.008	0.84	1.854	1.090	1.154
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.048	$R1$ = 0.043	$R1$ = 0.044	$R1$ = 0.031	$R1$ = 0.028
	$wR2$ = 0.074	$wR2$ = 0.096	$wR2$ = 0.054	$wR2$ = 0.045	$wR2$ = 0.055
R Indices (all data)	$R1$ = 0.065	$R1$ = 0.055	$R1$ = 0.055	$R1$ = 0.036	$R1$ = 0.037
	$wR2$ = 0.078	$wR2$ = 0.103	$wR2$ = 0.056	$wR2$ = 0.046	$wR2$ = 0.058
Extinction coefficient	0.007(2)	0.004(2)	0.012(1)	0.0148(9)	0.020(2)
Flack parameter	0.2(1)	0.3(2)	0.1(1)	–	–
BASF	–	–	–	0.49(9)	0.28(5)
Largest diff. peak and hole	2.01 and −2.30 e/Å^3	2.10 and −1.71 e/Å^3	2.58 and −4.33 e/Å^3	1.55 and −1.89 e/Å^3	3.09 and −2.15 e/Å^3

Table 3. Atomic coordinates and isotropic displacement parameters (pm^2) for LaMgGa, PrMgGa, NdMgGa, SmMgGa, and TmMgGa (space group $P62m$). U_{eq} is defined as a third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff site	*x*	*y*	*z*	U_{eq}
LaMgGa					
La	3*f*	0.5783(1)	0	0	91(2)
Mg	3*g*	0.2415(7)	0	1/2	97(13)
Ga1	2*d*	1/3	2/3	1/2	97(6)
Ga2	1*a*	0	0	0	104(7)
PrMgGa					
Pr	3*f*	0.4232(2)	0	0	79(4)
Mg	3*g*	0.757(1)	0	1/2	82(19)
Ga1	2*d*	1/3	2/3	1/2	77(8)
Ga2	1*a*	0	0	0	92(11)
NdMgGa					
Nd	3*f*	0.4236(1)	0	0	100(2)
Mg	3*g*	0.7558(7)	0	1/2	113(12)
Ga1	2*d*	1/3	2/3	1/2	95(4)
Ga2	1*a*	0	0	0	105(6)
SmMgGa					
Sm	3*f*	0.57582(9)	0	0	88(1)
Mg	3*g*	0.2444(6)	0	1/2	79(9)
Ga1	2*d*	1/3	2/3	1/2	91(4)
Ga2	1*a*	0	0	0	103(5)
TmMgGa					
Tm	3*f*	0.57157(8)	0	0	70(1)
Mg	3*g*	0.2433(6)	0	1/2	81(9)
Ga1	2*d*	1/3	2/3	1/2	64(3)
Ga2	1*a*	0	0	0	84(5)

Table 4. Interatomic distances (pm), calculated from single crystal data using the lattice parameters taken from X-ray powder data of SmMgGa. Standard deviation are all equal or smaller than 0.7 pm.

Sm:	1	Ga2	312.9	Mg:	2	Ga1	284.4
	4	Ga1	313.9		2	Ga2	287.3
	2	Mg	331.4		2	Mg	312.2
	4	Mg	352.2		2	Sm	331.4
	4	Sm	381.3		4	Sm	352.2
Ga1:	3	Mg	284.4	Ga2:	6	Mg	287.3
	6	Sm	313.9		3	Sm	312.9

yses were in agreement with the ideal composition and no impurity elements have been detected.

The polycrystalline products have been characterized through their Guinier powder pattern. The Guinier cameras were equipped with an image plate system (Fujifilm, Basread-1800) and monochromated Cu-$K_{\alpha 1}$ radiation. α-quartz (a = 491.30, c = 540.46 pm) was used as an internal standard. All patterns could be indexed on the basis of small hexagonal unit cells with the lattice parameters listed in Table 1. The correct indexing was ensured through intensity calculations [13], using the positional parameters of the struture refinements. For the gadolinium compound, our lattice parameters are in good agreement with the data of Canepa *et al.* [9].

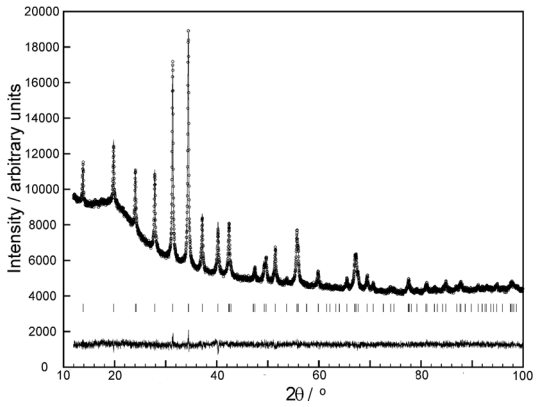

Fig. 1. Rietveld refinement plot for SmMgGa, in which the observed intensites are indicated with open circles and the calculated pattern with a line on top of the circles. The vertical lines indicate the Bragg positions. The difference y(obs)-y(calc) is drawn below the Bragg indicators.

Some of the *RE*MgGa gallides have also been studied on a powder diffractometer (Stoe Stadi P, $CuK_{\alpha 1}$ radiation) in order to perform full profile Rietveld refinements. As an example we present the data for SmMgGa. The measurement was performed in Debye-Scherrer transmission geometry using $CuK_{\alpha 1}$ radiation (λ = 154.0598 pm, Ge monochromator) within the 2θ range 12 – 100° in steps of 0.02° (2θ).

Single crystal X-ray diffractometer data for LaMgGa and NdMgGa were collected on a Stoe IPDS II image plate diffractometer with monochromatized Mo-K_α radiation. Intensity for PrMgGa, SmMgGa, and TmMgGa were collected on a Nonius CAD4 four-circle diffractometer equipped with a scintillation detector and graphite monochromatized Mo-K_α radiation. All relevant crystallographic data and details for the data collections are listed in Table 2.

Structure refinements

Irregularly shaped single crystals of *RE*MgGa (*RE* = La, Pr, Nd, Sm, and Tm) were isolated from the crushed samples and first investigated on a Buerger precession camera equipped with an imaging plate system (Fujifilm, Basread-1800). Only single crystals with high quality Laue photographs were selected for the intensity data collections.

The isotypy with hexagonal ZrNiAl was already evident from the powder data. The atomic parameters of CeMgGa were taken as starting values and the five structures have successfully been refined with anisotropic displacement parameters for all atoms using SHELXL-97 [14] (full-matrix least-squares on F^2). As a check for the correct site assignment and possible mixed occupancies (Mg-Ga mixing), the occupancy parameters have been refined in separate least-squares cycles for all compounds. All sites were fully occupied within two standard deviations, and in the final cycles,

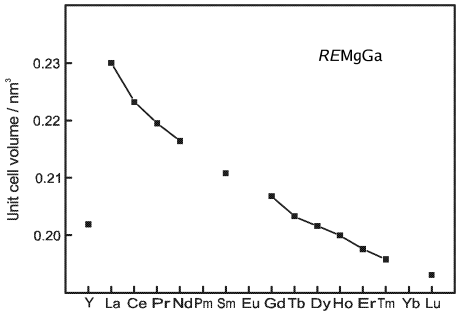

Fig. 2. Plot of the cell volumes of the *RE*MgGa compounds.

the ideal occupancy parameters were assumed again. Refinement of the correct absolute structures was ensured through refinement of the Flack parameters [15, 16]. In some cases, the positional parameters have been inverted. The crystals of the samarium and the thulium compound showed twinning by inversion. This is a rare case for ZrNiAl type intermetallics. The final difference Fourier analyses showed no significant residual peaks (Table 2). The refined atomic positions and the interatomic distances for SmMgGa are listed in Tables 3 and 4. Listings of the anisotropic displacement parameters and structure factor tables are available.*

The Rietveld calculations for the SmMgGa data set were performed with the FULLPROF [17] software. The background was set manually and the profiles were modelled using the Pseudo-Voigt function (No. 5). The limit of peak asymmetry was set to 60 degrees (2θ) and an arbitrary absorption value of μR = 1.4 was used. 75 reflections could be observed, to which 16 parameters were fitted: 2 fractional coordinates, 4 isotropic displacement parameters, the scale factor, 2 cell parameters, the zero-position, 4 peak profile parameters, and 2 peak asymmetry parameters. The standard deviations of the refined parameters have been multiplied with the Bérar-Lelann factor [18]. The refinement smoothly converged to the residuals R_{Bragg} = 0.0425, R_{F} = 0.0343, and a goodness-of-fit of 1.05. The resulting positional *x* parameters for the samarium and magnesium atoms are *x*(Sm) = 0.5763(2) and *x*(Mg) = 0.248(2). While the coordinate for samarium is in good agreement with the single crystal data (one combined standard deviation), there is a small deviation for the magnesium *x* coordinate: 0.248(2) for the powder data as compared to 0.2444(6) for the single crystal data. We attribute this effect to the lower precision of the powder data (peak/parameter ratio = 4.7 as compared to 25.1 for the single crystal data). The plot of the experimental and calculated intensity data is presented in Fig. 1.

*Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No's. CSD-413276 (LaMgGa), CSD-413285 (PrMgGa), CSD-413277 (NdMgGa), CSD-413286 (SmMgGa), and CSD-413278 (TmMgGa).

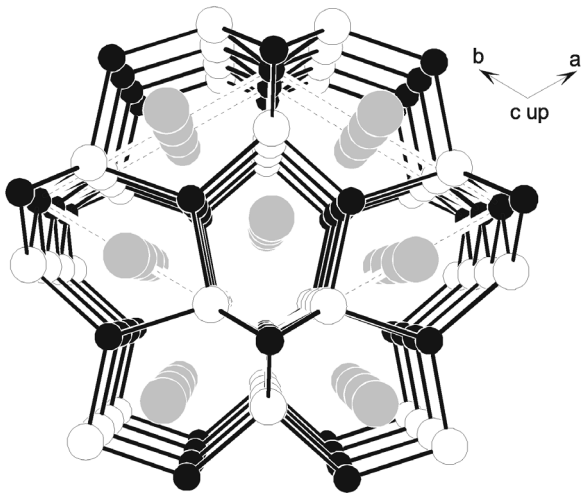

Fig. 3. Perspective view of the SmMgGa unit cell along the *z* axis. The samarium, magnesium, and gallium atoms are drawn as gray, open and filled circles, respectively. The three-dimensional [MgGa] network is emphasized.

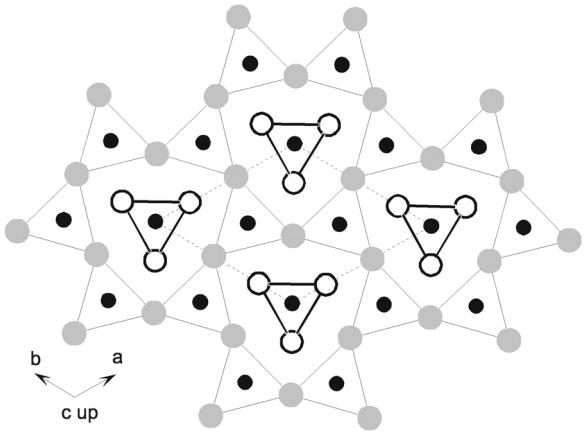

Fig. 4. Projection of the SmMgGa structure onto the *xy* plane. All atoms lie on mirror planes at *z* = 0 (thin lines) and *z* = 1/2 (thick lines), respectively. The samarium, magnesium, and gallium atoms are drawn as gray, open and filled circles, respectively.

Results and Disscussion

Crystal Chemistry

Twelve new members of the *RE*MgGa series have been synthesized and structurally characterized. As depicted in Fig. 2, the cell volumes of these intermetallics decrease from the lanthanum to the lutetium compound as expected from the lanthanoid contraction. The volume of CeMgGa fits perfectly into the smooth curve, indicating trivalent cerium, as is clearly evident also

from the magnetic data [10]. As is frequently the case for such intermetallics, the YMgGa cell volume fits between those for TbMgGa and DyMgGa (Fig. 2).

As an example for the series of *RE*MgGa compounds we briefly discuss the structure of SmMgGa. Within the three-dimensional [MgGa] network the magnesium atoms have four gallium neighbors at Mg–Ga distances ranging from 284 to 287 pm (Fig. 3), close to the sum of the covalent radii for Mg and Ga of 261 pm [19]. Besides the Mg–Ga interaction we also observe a significant degree of Mg–Mg bonding within the network. Each magnesium atom has two magnesium neighbours at 312 pm, shorter than the average Mg–Mg distance of 320 pm in *hcp* magnesium [20]. The samarium atoms fill distorted hexagonal channels within the [MgGa] network. The structure has two crystallographically independent gallium positions. Ga1 and Ga2 both have a trigonal prismatic coordination (Fig. 4); Ga1 by six samarium and Ga2 by six magnesium atoms. The rectangular faces of these prisms are capped with magnesium atoms for Ga1 and by samarium atoms for Ga2, leading to coordination number 9 for each gallium atom.

EuMgGa crystallizes with the orthorhombic TiNiSi type: *Pnma*, a = 783.1(2), b = 472.8(1), c = 829.8(2) pm. So far we obtained no single crystals suitable for a structure refinement. The volume per formula unit (fu) EuMgGa is 76.8 $Å^3$, even slightly larger than the volume of 76.7 $Å^3$/fu for LaMgGa. This is indicative of divalent europium. Detailed magnetic susceptibility and ^{151}Eu Mössbauer spectroscopic investigations are in progress.

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