Rare Earth-rich Magnesium Compounds RE_4PdMg (RE = Y, Sm, Gd) and RE_4PtMg (RE = Y, Nd, Sm, Gd)

Selcan Tuncel[a], Bernard Chevalier[b], and Rainer Pöttgen[a]

[a] Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstraße 30, D-48149 Münster, Germany
[b] Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB), CNRS [UPR 9048], Université Bordeaux 1, 87 avenue du Docteur Albert Schweitzer, 33608 Pessac Cedex, France

Reprint requests to R. Pöttgen.
E-mail: pottgen@uni-muenster.de

Z. Naturforsch. **2008**, *63b,* 600 – 602; received December 10, 2007

The rare earth-rich intermetallic magnesium compounds RE_4PdMg (RE = Y, Sm, Gd) and RE_4PtMg (RE = Y, Nd, Sm, Gd) were prepared by melting of the elements in sealed tantalum tubes in an induction furnace. These new Gd_4RhIn-type compounds were characterized by X-ray powder diffraction. The structures of the gadolinium compounds were refined from single crystal X-ray diffractometer data: space group $F\bar{4}3m$, Z = 16, a = 1388.1(2) pm, $wR2$ = 0.0392, 381 F^2 values and 20 variables for $Gd_4Pd_{1.14}Mg_{0.86}$ and a = 1387.6(2) pm, $wR2$ = 0.0519, 409 F^2 values, BASF = 0.47(4) and 21 variables for $Gd_4Pt_{1.07}Mg_{0.93}$. The gadolinium atoms build up palladium (platinum) centered trigonal prisms which are condensed *via* common corners and edges, leading to three-dimensional networks. The magnesium atoms form Mg_4 tetrahedra which show slight mixing with the platinum metal.

Key words: Intermetallics, Magnesium, Crystal Chemistry

Introduction

The rare earth-rich parts of the rare earth (RE)-transition metal (T)-magnesium systems are characterized by the series of compounds RE_2T_2Mg ([1] and refs. therein), $RE_{23}Ir_7Mg_4$ [2], and RE_4TMg [3 – 5]. The common structural motifs of these intermetallics are transition metal centered trigonal prisms of the rare earth metals. These prisms are condensed *via* common rectangular faces in RE_2T_2Mg, but *via* common edges and corners in $RE_{23}Ir_7Mg_4$ and RE_4TMg.

Cubic Gd_4RhIn-type [6] compounds RE_4TMg have so far been reported with cobalt, ruthenium, and rhodium as transition metal component [3 – 5]. Members of this series exist with almost all rare earth elements. The chemical bonding peculiarities have been studied in detail for La_4CoMg [3] and La_4RuMg [5]. Depending on the valence electron concentration, the transition metal centered trigonal prisms exhibit different geometries and bond strengths. Keeping these bonding properties in mind, we have extended our investigations on the RE_4TMg compounds with respect to the transition elements of the nickel group.

The RE_4NiMg compounds [7] exist with RE = Y, Pr–Nd, Sm, Gd–Tm, Lu. First property investigations on Gd_4NiMg revealed antiferromagnetic ordering at 92 K. Gd_4NiMg absorbs large amounts of hydrogen up to a composition Gd_4NiMgH_{11}. The hydride remains paramagnetic down to 2 K. Herein we report on the RE_4PdMg and RE_4PtMg compounds. In contrast to all other RE_4TMg series, the palladium and platinum series exist only for few rare earth elements.

Experimental Section

Synthesis

Starting materials for the synthesis of the RE_4PdMg and RE_4PtMg samples were ingots of the rare earth metals (Johnson Matthey or smart elements, $>$ 99.9 %), palladium and platinum powder (Degussa-Hüls, 200 mesh, $>$ 99.9 %), and a magnesium rod (Johnson Matthey, ∅ 16 mm, $>$ 99.95 %). Surface impurities on the magnesium rod were removed on a turning lathe. Pieces of the rare earth ingots were first arc-melted [8] to small buttons under an argon atmosphere. The argon was purified before with molecular sieves, silica gel, and titanium sponge (900 K). Subsequently the rare earth buttons, palladium (platinum) powder and pieces of the magnesium rod (4 : 1 : 1 atomic ratio) were sealed in tantalum tubes under an argon pressure of *ca.* 700 mbar. The tubes were placed in a water-cooled sample chamber of an induction furnace (Hüttinger Elektronik, Freiburg, and type TIG 1.5/300) under flowing argon [9] and first heated for 2 min to about 1300 K, followed by another 2 h annealing time at *ca.* 920 K. Finally the tubes were quenched to room temperature. The temperature was controlled through a Sensor Therm Methis MS09 pyrometer with an accuracy of $\pm$30 K. All samples could easily be separated from the crucible material. No reaction with the container was observed. The polycrystalline samples are stable in air over weeks.

EDX data

Semiquantitative EDX analyses on the crystals investigated on the diffractometer were carried out by use of a

Table 1. Lattice parameters (Guinier powder data) of the ternary magnesium compounds RE_4TMg (T = Pd, Pt).

Compound	a (pm)	V (nm^3)
Y_4PdMg	1382.4(4)	2.6418
Sm_4PdMg	1402.1(1)	2.7564
Gd_4PdMg	1389.5(3)	2.6827
$Gd_4Pd_{1.14}Mg_{0.86}$ [a]	1388.1(2)	2.6746
Y_4PtMg	1380.11(8)	2.6287
Nd_4PtMg	1405.6(2)	2.7771
Sm_4PtMg	1396.5(4)	2.7235
Gd_4PtMg	1391.3(2)	2.6932
$Gd_4Pt_{1.07}Mg_{0.93}$ [a]	1387.6(2)	2.6717

[a] Single crystal data.

Table 2. Crystal data and structure refinement for $Gd_4Pd_{1.14}Mg_{0.86}$ and $Gd_4Pt_{1.07}Mg_{0.93}$.

Empirical formula	$Gd_4Pd_{1.14}Mg_{0.86}$	$Gd_4Pt_{1.07}Mg_{0.93}$
Molar mass, g·mol^{-1}	771.46	859.82
Crystal system	cubic	cubic
Space group	$F\bar{4}3m$	$F\bar{4}3m$
Unit cell dimensions	Table 1	Table 1
Calculated density, g cm^{-3}	7.66	8.55
Crystal size, μm^3	$20 \times 30 \times 90$	$20 \times 40 \times 50$
Transm. ratio (max/min)	2.86	2.47
Absorption coeff., mm^{-1}	42.1	61.4
Detector distance, mm	60	60
Exposure time, min	5	5
ω range; increment	0 – 180°, 1.0°	0 – 180°, 1.0°
Integr. param. A, B, EMS	13.5; 3.5; 0.012	13.5; 3.5; 0.012
F(000), e	5102	5607
θ range, deg	2 – 29	2 – 30
Range in hkl	±18, ±18 ±18	±19, ±19 ±19
Total no. reflections	3361	3333
Independent reflections	381	409
R_{int}	0.0620	0.0818
Reflections with $I \geq 2\sigma(I)$	313 ($R_\sigma = 0.0540$)	317 ($R_\sigma = 0.0691$)
Data/parameters	381 / 20	409 / 21
Goodness-of-fit on F^2	0.788	0.797
Final R indices [$I \geq 2\sigma(I)$]	$R1 = 0.0214$	$R1 = 0.0270$
	$wR2 = 0.0381$	$wR2 = 0.0499$
R indices (all data)	$R1 = 0.0310$	$R1 = 0.0406$
	$wR2 = 0.0392$	$wR2 = 0.0519$
Extinction coefficient	0.000125(9)	0.000082(7)
x (Flack) parameter / BASF	−0.07(5)	0.47(4)
Largest diff. peak	2.01	2.38
and hole, e Å^{-3}	−1.27	−1.35

Leica 420i scanning electron microscope with GdF_3, palladium, platinum, and MgO as standards. The experimentally observed compositions were close to the ideal one. No impurity elements heavier than sodium (detection limit of the instrument) were found.

X-Ray diffraction

The polycrystalline samples were characterized through X-ray powder diffraction (Guinier technique, imaging plate detector, Fujifilm BAS-1800) using Cu$K_{\alpha1}$ radiation and α-quartz (a = 491.30 and c = 540.46 pm) as an internal standard. The cubic lattice parameters (Table 1) were refined from the powder data by a least-squares routine. The correct indexing was ensured through intensity calculations [10] taking the atomic positions from the structure refinements.

Single crystals of Gd_4PdMg and Gd_4PtMg were selected from the annealed samples, and their quality was checked

Table 3. Atomic coordinates and isotropic displacement parameters (pm^2) of $Gd_4Pd_{1.14}Mg_{0.86}$ and $Gd_4Pt_{1.07}Mg_{0.93}$ [a]. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff site	x	y	z	U_{eq}
$Gd_4Pd_{1.14}Mg_{0.86}$					
Gd1	24g	0.56685(7)	1/4	1/4	109(2)
Gd2	24f	0.18951(8)	0	0	88(2)
Gd3	16e	0.34995(6)	x	x	87(3)
Pd1	16e	0.14345(10)	x	x	111(5)
86(2) % Mg / 14(2) % Pd2	16e	0.5821(3)	x	x	306(36)
$Gd_4Pt_{1.07}Mg_{0.93}$ [a]					
Gd1	24g	0.43429(10)	3/4	3/4	164(3)
Gd2	24f	0.81013(11)	0	0	133(3)
Gd3	16e	0.65144(7)	x	x	118(3)
Pt1	16e	0.85768(6)	x	x	129(3)
93(1) % Mg / 7(1) % Pt2	16e	0.4170(6)	x	x	388(52)

[a] It should be noted that the refined coordinate set of the platinum-containing compound formally had the opposite absolute structure with respect to the palladium-containing compound. Absolute-structure refinement revealed inversion twinning of the Pt compound (see Table 2).

Table 4. Interatomic distances (pm) in the structures of $Gd_4Pd_{1.14}Mg_{0.86}$ and $Gd_4Pt_{1.07}Mg_{0.93}$. Standard deviations are given in parentheses. All distances within the first coordination spheres are listed. Note that the magnesium sites show transition metal-magnesium mixing (see Table 3).

$Gd_4Pd_{1.14}Mg_{0.86}$				**$Gd_4Pt_{1.07}Mg_{0.93}$**			
Gd1:	2	Mg	330.3(7)	Gd1:	2	Mg	328.6(11)
	2	Pd	359.1(1)		2	Pt	357.7(1)
	2	Gd3	359.4(1)		2	Gd3	358.1(1)
	4	Gd1	359.5(2)		4	Gd1	361.6(2)
	4	Gd2	368.9(1)		4	Gd2	368.3(1)
Gd2:	2	Pd	288.8(2)	Gd2:	2	Pt	287.0(1)
	2	Mg	355.7(2)		2	Mg	354.8(2)
	4	Gd1	368.9(1)		4	Gd1	368.3(1)
	2	Gd3	369.3(1)		2	Gd3	369.9(1)
	4	Gd2	372.0(2)		4	Gd2	372.6(2)
Gd3:	3	Pd	286.9(1)	Gd3:	3	Pt	286.7(1)
	3	Mg	348.8(2)		3	Mg	352.0(3)
	3	Gd1	359.4(1)		3	Gd1	358.1(1)
	3	Gd2	369.3(1)		3	Gd2	369.9(1)
	3	Gd3	392.4(2)		3	Gd3	386.8(3)
Pd:	3	Gd3	286.9(1)	Pt:	3	Gd3	286.7(1)
	3	Gd2	288.8(2)		3	Gd2	287.0(1)
	3	Gd1	359.1(1)		3	Gd1	357.7(1)
Mg:	3	Mg	322(1)	Mg:	3	Mg	326(2)
	3	Gd1	330.3(7)		3	Gd1	328.6(11)
	3	Gd3	348.7(2)		3	Gd3	352.0(3)
	3	Gd2	355.7(2)		3	Gd2	354.8(2)

by Laue photographs on a Buerger camera (white Mo radiation). Intensity data were collected at room temperature by use of a Stoe IPDS-II imaging plate diffractometer in oscillation mode (graphite monochromatized MoK_α radiation). Numerical absorption corrections were applied to the data sets. All relevant details concerning the data collections and evaluations are listed in Table 2.

Structure refinements

The isotypy of Gd_4PdMg and Gd_4PtMg with the cubic Gd_4RhIn type [6], space group $F\bar{4}3m$ (No. 216), was already evident from the Guinier patterns. The atomic parameters of La_4RuMg [5] were taken as starting values, and both structures were refined using SHELXL-97 [11] (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for all atoms. Similar to $Sm_{3.92}Ru_{1.16}Mg_{0.92}$ [5], the two gadolinium-based crystals also revealed too small displacement parameters for the magnesium sites, indicating transition metal-magnesium mixing. In the final cycles, these 16e sites were refined with Mg/Pd and Mg/Pt mixing, leading to the compositions $Gd_4Pd_{1.14}Mg_{0.86}$ and $Gd_4Pt_{1.07}Mg_{0.93}$ for the investigated crystals. All other sites were fully occupied within two standard deviations. Refinement of the correct absolute structure was ensured through calculation of the Flack parameter [12, 13]. The $Gd_4Pt_{1.07}Mg_{0.93}$ crystal revealed twinning by inversion. The final difference Fourier syntheses were flat (Table 2). The positional parameters and interatomic distances are listed in Tables 3 and 4.

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, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforde rung.html) on quoting the deposition numbers CSD-418861 ($Gd_4Pd_{1.14}Mg_{0.86}$) and CSD-418862 ($Gd_4Pt_{1.07}Mg_{0.93}$).

Discussion

The series of rare earth-rich magnesium intermetallics RE_4TMg has been extended with the synthesis of new compounds RE_4PdMg (RE = Y, Sm, Gd) and RE_4PtMg (RE = Y, Nd, Sm, Gd). For both series of compounds, the course of the unit cell volumes is compatible with the lanthanoid contraction, and the smallest cell volume is observed for the yttrium compounds.

The single crystal data of the gadolinium compounds showed a small degree of magnesium-palladium (platinum) mixing on one of the 16e sites (Table 3). This behavior has so far only been observed for $Sm_{3.92}Ru_{1.16}Mg_{0.92}$ [5]. Since the palladium and platinum atoms are slightly smaller than magnesium [14], the cell parameters of the single crystals are slightly smaller than those determined from the bulk samples (Table 1). The Mg-Pd (Pt) mixing is not surprising. Similar solid solutions have been observed for $CeRh_{1.262}Mg_{0.738}$ [15] or $YbAg_{1.053}Mg_{0.947}$ [16].

The crystal chemistry of the RE_4TMg compounds has been discussed in detail for the series RE_4CoMg, RE_4RuMg, and RE_4RhMg [3 – 5]. For drawings and the discussion of chemical bonding we refer to our previous contributions.

Acknowledgements

We thank Dipl.-Ing. U. Ch. Rodewald for the intensity data collections. This work was financially supported by the Deutsche Forschungsgemeinschaft. S. T. is grateful to the DAAD for a PhD stipend. B. C. and R. P. are indebted to EGIDE and DAAD for research grants within the PROCOPE programs (11457RD and D/0502176). Finally, B. C. thanks the European Science Foundation (ECOM_COST action P16) for financial support.

[1] M. Lukachuk, R. Pöttgen, *Z. Kristallogr.* **2003**, *218*, 767.
[2] U. Ch. Rodewald, S. Tuncel, B. Chevalier, R. Pöttgen, *Z. Anorg. Allg. Chem.* **2008**, submitted.
[3] S. Tuncel, R.-D. Hoffmann, B. Chevalier, S. F. Matar, R. Pöttgen, *Z. Anorg. Allg. Chem.* **2007**, *633*, 151.
[4] S. Tuncel, U. Ch. Rodewald, B. Chevalier, R. Pöttgen, *Z. Naturforsch.* **2007**, *62b*, 642.
[5] S. Tuncel, B. Chevalier, S. F. Matar, R. Pöttgen, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2019.
[6] R. Zaremba, U. Ch. Rodewald, R.-D. Hoffmann, R. Pöttgen, *Monatsh. Chem.* **2007**, *138*, 523.
[7] S. Tuncel, J. G. Roquefère, C. Stan, J.-L. Bobet, B. Chevalier, E. Gaudin, R.-D. Hoffmann, U. Ch. Rodewald, R. Pöttgen, unpublished results.
[8] R. Pöttgen, Th. Gulden, A. Simon, *GIT Labor-Fachzeitschrift* **1999**, *43*, 133.
[9] D. Kußmann, R.-D. Hoffmann, R. Pöttgen, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1727.
[10] K. Yvon, W. Jeitschko, E. Parthé, *J. Appl. Crystallogr.* **1977**, *10*, 73.
[11] G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen (Germany) **1997**.
[12] H. D. Flack, G. Bernadinelli, *Acta Crystallogr.* **1999**, *A55*, 908.
[13] H. D. Flack, G. Bernadinelli, *J. Appl. Crystallogr.* **2000**, *33*, 1143.
[14] J. Emsley, *The Elements*, Oxford University Press, Oxford, **1999**.
[15] Th. Fickenscher, R.-D. Hoffmann, R. Kraft, R. Pöttgen, *Z. Anorg. Allg. Chem.* **2002**, *628*, 667.
[16] Th. Fickenscher, R. Pöttgen, *J. Solid State Chem.* **2001**, *161*, 67.