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

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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,  $\varnothing$  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 <sup>3</sup> ) |
|--|------------|------------------------|
| Y <sub>4</sub> PdMg  | 1382.4(4)  | 2.6418                 |
| Sm <sub>4</sub> PdMg   | 1402.1(1)  | 2.7564                 |
| Gd <sub>4</sub> PdMg   | 1389.5(3)  | 2.6827                 |
| Gd <sub>4</sub> Pd <sub>1.14</sub> Mg <sub>0.86</sub> <sup>a</sup> | 1388.1(2)  | 2.6746                 |
| Y <sub>4</sub> PtMg  | 1380.11(8) | 2.6287                 |
| Nd <sub>4</sub> PtMg   | 1405.6(2)  | 2.7771                 |
| Sm <sub>4</sub> PtMg   | 1396.5(4)  | 2.7235                 |
| Gd <sub>4</sub> PtMg   | 1391.3(2)  | 2.6932                 |
| Gd <sub>4</sub> Pt <sub>1.07</sub> Mg <sub>0.93</sub> <sup>a</sup> | 1387.6(2)  | 2.6717                 |

<sup>a</sup> Single crystal data.Table 2. Crystal data and structure refinement for Gd<sub>4</sub>Pd<sub>1.14</sub>Mg<sub>0.86</sub> and Gd<sub>4</sub>Pt<sub>1.07</sub>Mg<sub>0.93</sub>.

|  | Gd <sub>4</sub> Pd <sub>1.14</sub> Mg <sub>0.86</sub> | Gd <sub>4</sub> Pt <sub>1.07</sub> Mg <sub>0.93</sub> |
|--|---|---|
| Empirical formula                              | Gd <sub>4</sub> Pd <sub>1.14</sub> Mg <sub>0.86</sub> | Gd <sub>4</sub> Pt <sub>1.07</sub> Mg <sub>0.93</sub> |
| Molar mass, g·mol <sup>-1</sup>                | 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 <sup>-3</sup>         | 7.66  | 8.55  |
| Crystal size, μm <sup>3</sup>                  | 20 × 30 × 90  | 20 × 40 × 50  |
| Transm. ratio (max/min)                        | 2.86  | 2.47  |
| Absorption coeff., mm <sup>-1</sup>            | 42.1  | 61.4  |
| Detector distance, mm                          | 60  | 60  |
| Exposure time, min                             | 5   | 5   |
| $\omega$ 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  |
| $\theta$ 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 [ $I \geq 2\sigma(I)$ ]      | $R1 = 0.0214$<br>$wR2 = 0.0381$                       | $R1 = 0.0270$<br>$wR2 = 0.0499$                       |
| $R$ indices (all data)                         | $R1 = 0.0310$<br>$wR2 = 0.0392$                       | $R1 = 0.0406$<br>$wR2 = 0.0519$                       |
| Extinction coefficient                         | 0.000125(9)   | 0.000082(7)   |
| $x$ (Flack) parameter / BASF                   | –0.07(5)  | 0.47(4)   |
| Largest diff. peak and hole, e Å <sup>-3</sup> | 2.01<br>–1.27   | 2.38<br>–1.35   |

Leica 420i scanning electron microscope with GdF<sub>3</sub>, 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 CuK $\alpha_1$  radiation and  $\alpha$ -quartz ( $a = 491.30$  and  $c = 540.46$  pm) as an internal

Table 3. Atomic coordinates and isotropic displacement parameters (pm<sup>2</sup>) of Gd<sub>4</sub>Pd<sub>1.14</sub>Mg<sub>0.86</sub> and Gd<sub>4</sub>Pt<sub>1.07</sub>Mg<sub>0.93</sub><sup>a</sup>.  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

| Atom  | Wyckoff site | $x$         | $y$ | $z$ | $U_{eq}$ |
|---|--------------|-------------|-----|-----|----------|
| <b>Gd<sub>4</sub>Pd<sub>1.14</sub>Mg<sub>0.86</sub></b>             |              |             |     |     |          |
| 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 /<br>14(2) % Pd2   | 16e          | 0.5821(3)   | $x$ | $x$ | 306(36)  |
| <b>Gd<sub>4</sub>Pt<sub>1.07</sub>Mg<sub>0.93</sub><sup>a</sup></b> |              |             |     |     |          |
| 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 /<br>7(1) % Pt2  | 16e          | 0.4170(6)   | $x$ | $x$ | 388(52)  |

<sup>a</sup> 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<sub>4</sub>Pd<sub>1.14</sub>Mg<sub>0.86</sub> and Gd<sub>4</sub>Pt<sub>1.07</sub>Mg<sub>0.93</sub>. 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 <sub>4</sub> Pd <sub>1.14</sub> Mg <sub>0.86</sub> |       |          | Gd <sub>4</sub> Pt <sub>1.07</sub> Mg <sub>0.93</sub> |       |           |
|---|-------|----------|---|-------|-----------|
| 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)  |

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<sub>4</sub>PdMg and Gd<sub>4</sub>PtMg were selected from the annealed samples, and their quality was checked

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  $\text{MoK}\alpha$  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  $\text{Gd}_4\text{PdMg}$  and  $\text{Gd}_4\text{PtMg}$  with the cubic  $\text{Gd}_4\text{RhIn}$  type [6], space group  $F43m$  (No. 216), was already evident from the Guinier patterns. The atomic parameters of  $\text{La}_4\text{RuMg}$  [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  $\text{Sm}_{3.92}\text{Ru}_{1.16}\text{Mg}_{0.92}$  [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  $\text{Gd}_4\text{Pd}_{1.14}\text{Mg}_{0.86}$  and  $\text{Gd}_4\text{Pt}_{1.07}\text{Mg}_{0.93}$  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  $\text{Gd}_4\text{Pt}_{1.07}\text{Mg}_{0.93}$  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\\_anforderung.html](http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html)) on quoting the deposition numbers CSD-418861 ( $\text{Gd}_4\text{Pd}_{1.14}\text{Mg}_{0.86}$ ) and CSD-418862 ( $\text{Gd}_4\text{Pt}_{1.07}\text{Mg}_{0.93}$ ).

#### Discussion

The series of rare earth-rich magnesium intermetallics  $\text{RE}_4\text{TMg}$  has been extended with the synthesis of new compounds  $\text{RE}_4\text{PdMg}$  ( $\text{RE} = \text{Y}, \text{Sm}, \text{Gd}$ ) and  $\text{RE}_4\text{PtMg}$  ( $\text{RE} = \text{Y}, \text{Nd}, \text{Sm}, \text{Gd}$ ). 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  $\text{Sm}_{3.92}\text{Ru}_{1.16}\text{Mg}_{0.92}$  [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  $\text{CeRh}_{1.262}\text{Mg}_{0.738}$  [15] or  $\text{YbAg}_{1.053}\text{Mg}_{0.947}$  [16].

The crystal chemistry of the  $\text{RE}_4\text{TMg}$  compounds has been discussed in detail for the series  $\text{RE}_4\text{CoMg}$ ,  $\text{RE}_4\text{RuMg}$ , and  $\text{RE}_4\text{RhMg}$  [3–5]. For drawings and the discussion of chemical bonding we refer to our previous contributions.

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