Intermetallic Compounds $RETMg_2$ (RE = La, Pr, Nd; T = Ni, Pd, Pt) with $MgCuAl_2$-type Structure

Marcel Kersting and Rainer Pöttgen

Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstraße 30, 48149 Münster, Germany

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

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The magnesium-rich intermetallic compounds $RETMg_2$ (RE = La, Pr, Nd; T = Ni, Pd, Pt) were obtained by melting of the elements in sealed tantalum ampoules and subsequent annealing. Their structures have been characterized on the basis of powder X-ray diffraction. The $RETMg_2$ phases crystallize with the orthorhombic $MgCuAl_2$-type structure, space group *Cmcm*. The crystal chemical peculiarities are briefly discussed.

Key words: Magnesium, Intermetallics, Crystal Chemistry

Introduction

Among the large family of more than 200 reported intermetallic $RE_xT_yMg_z$ (RE = rare earth element; T = transition metal) compounds [1], so far only $LaNiMg_2$ [2, 3] and $LaPdMg_2$ [4] were shown to have the $MgCuAl_2$-type structure [5, 6]. From a crystal chemical point of view these intermetallics are somehow unique. The magnesium atoms build up orthorhombically distorted, three-dimensional networks of tetrahedra, closely related to the indium network of the well known Zintl phase $CaIn_2$ and the transition metal-filled variants $SrTIn_2$ [7]. Also some cadmium-containing compounds $RETCd_2$ have been reported [8, 9]. A COHP analysis (crystal orbital Hamilton population) of $LaNiCd_2$ reveals a Cd-Cd ICOHP bonding energy comparable with that of cadmium metal. A similar situation was observed for $LaNiMg_2$ [8].

$LaNiMg_2$ [3] and $LaPdMg_2$ [4] absorb hydrogen under mild conditions (200 °C, *ca.* 10 bar) forming the hydrides $LaNiMg_2H_7$ and $LaPdMg_2H_7$. The structures have been determined from powder neutron diffraction data of the respective deuterides. These hydrides contain discrete $[NiH_4]^{4-}$ and $[PdH_4]^{4-}$ hydridometalate units besides three H^- per formula unit, leading to an electron precise description $La^{3+}(2Mg^{2+})^{4+}[TH_4]^{4-}(3H^-)^{3-}$ with a count of 18 electrons for the transition metals.

Based on these pioneering results from the Yvon group [3, 4], the hydrogen-uptake behavior of $LaNiMg_2$ has thoroughly been studied with respect to its high hydrogen absorption capacity and cycling behavior [9 – 16]. The influence of reactive milling and the microstructure of the hydrogenated $LaNiMg_2$ samples have intensively been investigated.

$LaNiMg_2$ can directly be prepared by induction melting of the elements, while $LaPdMg_2$ had to be synthesized in a two-step procedure, *i. e.* (i) LaPd was prepared by melting lanthanum and palladium, and (ii) $LaPdMg_2$ was obtained from the precursor compound LaPd with the adequate amount of magnesium with a final annealing step at 873 K.

During our systematic phase analytical studies of $RE_xT_yMg_z$ intermetallics we obtained a series of seven new isotypic compounds $RETMg_2$ (RE = La, Pr, Nd; T = Ni, Pd, Pt), extending the work on $MgCuAl_2$-type intermetallics. The synthesis conditions and powder X-ray data of these phases are reported herein.

Experimental Section

Synthesis

The $RETMg_2$ samples were synthesized by a two-step procedure. Starting materials were pieces of the rare earth elements (Smart Elements, > 99.9 %), nickel powder (Merck, > 99.9 %), palladium and platinum foil (Allgemeine Gold- und Silberscheideanstalt, Pforzheim, > 99.9 %), and a magnesium rod (alpha Aesar, > 99.8 %). To avoid oxydic impurities, the surface of the magnesium rod was carefully removed on a turning lathe. Pieces of the elements were weighed in the ideal atomic 1 : 1 : 2 ratios and arc-welded [17] in small tantalum tubes under an argon pressure of about 700 mbar. The argon was purified before with titanium sponge (870 K), silica gel and molecular sieves. The tubes were subsequently placed in a water-cooled quartz sample chamber of an induction furnace (Hüttinger Elektronik, Freiburg, type TIG 1.5/300) [18], and first heated to *ca.* 1500 K and kept at that temperature for 5 min under flowing argon. The temperature was then lowered rapidly to 900 K, and the ampoules were annealed for another two hours followed by quenching. The temperature was controlled through a Sensor Therm Methis MS09 pyrometer with an accuracy of ±30 K. All samples

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Compound	a (pm)	b (pm)	c (pm)	V (nm^3)	Reference
$LaNiMg_2$	422.66(6)	1030.3(1)	836.0(1)	0.3640	[3]
$PrNiMg_2$	414.95(9)	1011.1(3)	832.7(3)	0.3494	this work
$NdNiMg_2$	413.6(1)	1009.3(2)	832.0(2)	0.3473	this work
$LaPdMg_2$	432.28(1)	1052.89(2)	830.95(1)	0.3782	[4]
$PrPdMg_2$	426.59(9)	1037.7(2)	829.7(2)	0.3673	this work
$NdPdMg_2$	424.20(5)	1034.1(1)	829.4(1)	0.3638	this work
$LaPtMg_2$	429.57(4)	1050.7(1)	826.09(7)	0.3729	this work
$PrPtMg_2$	425.14(5)	1034.0(1)	825.0(1)	0.3627	this work
$NdPtMg_2$	423.77(4)	1030.22(7)	824.82(6)	0.3601	this work

Table 1. Lattice parameters (Guinier powder data) of $RETMg_2$ compounds.

could easily be separated from the tantalum tube by mechanical fragmentation.

Guinier powder patterns of these samples showed a phase mixture, in which the $RETMg_2$ compounds were definitely not the main phase. The polycrystalline samples were subsequently ground to fine powders in an agate mortar under dried n-hexane and pressed to pellets (∅ 6 mm). The latter were again sealed in tantalum ampoules which were in turn sealed in quartz tubes for oxidation protection. Finally the ampoules were annealed in a muffle furnace at 823 K for three weeks, resulting in X-ray-pure $RETMg_2$ samples which are stable in air over weeks.

Powder X-ray diffraction

The polycrystalline $RETMg_2$ samples were characterized after each synthesis step by powder X-ray diffraction on a Guinier camera (equipped with a Fuji-film image plate system, BAS-1800) using Cu$K_{\alpha 1}$ radiation and α-quartz (a = 491.30, c = 540.46 pm) as an internal standard. The orthorhombic lattice parameters (Table 1) were deduced from least-squares refinements of the powder data. To ensure correct indexing, the experimental patterns were compared to calculated ones [19] using the positional parameters of $LaNiMg_2$ [3] and the adequate scattering factors for each sample. The experimental patterns showed excellent agreement with the simulated ones.

Discussion

Seven new $MgCuAl_2$-type intermetallic compounds $RETMg_2$ (RE = La, Pr, Nd; T = Ni, Pd, Pt) have been synthesized and structurally characterized on the basis of powder X-ray diffraction. Although we obtained X-ray pure phases, after the annealing procedures the samples remained polycrystalline, and no single crystals suitable for structure refinements have become available. For the three series with T = Ni, Pd, Pt, the lattice parameters decrease from the lanthanum to the neodymium compound (Fig. 1), in agreement with the lanthanoid contraction. Under our synthesis conditions, no 1-1-2 compound was obtained with cerium. The origin of this behavior is not yet clear, but a valence instability of cerium might be a reason, since Ce_2Ni_2Mg [20, 21] and $CeNi_4Mg$ [20] both show a tendency towards tetravalent cerium. Also with samarium, no 1-1-2 compound was obtained. Most likely samarium and intermediate-valent

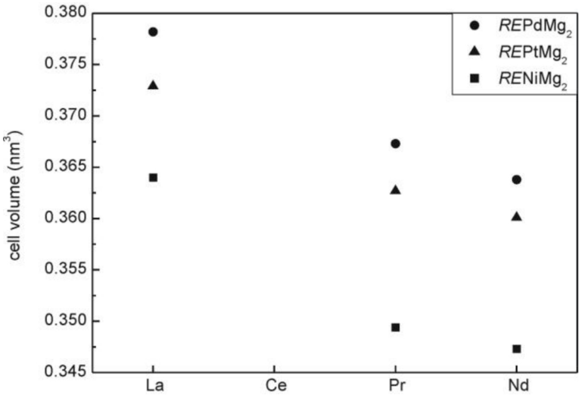

Fig. 1. Course of the cell volume in the series of $RETMg_2$ compounds.

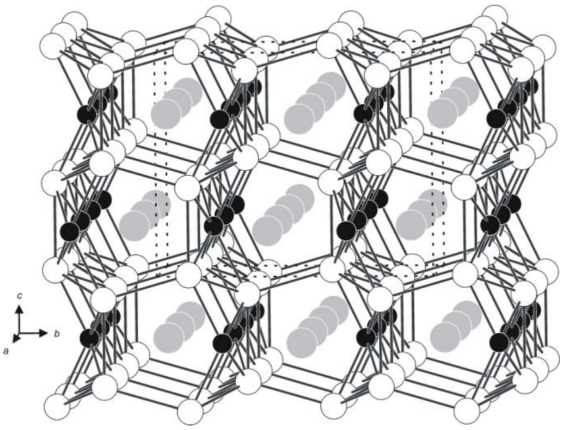

Fig. 2. View of the $LaPtMg_2$ structure approximately along the a axis. Lanthanum, platinum, and magnesium atoms are drawn as medium grey, black filled, and open circles, respectively. The three-dimensional [$PtMg_2$] network is emphasized.

cerium are too small to stabilize such an atomic arrangement. At this point it is worthwhile to note that isothermal sections of the La-Ni-Mg (723 K) [22, 23], Ce-Ni-Mg (673 and 1123 K) [24], and Pr-Ni-Mg (773 and 1123 K) [25] phase diagrams have been studied, however, $PrNiMg_2$ was not observed during that investigation.

For the three series with *RE* = La, Pr, and Nd, the cell volumes increase from the nickel to the palladium compounds and then slightly decrease on going to the platinum ones. This behavior has also been observed for the series $CaNiIn_2$ [26] $\rightarrow$ $CaPdIn_2$ $\rightarrow$ $CaPtIn_2$ [27] and might be ascribed to the relativistic contraction of platinum. As emphasized in a recent review article [6], the positional parameters show no pronounced changes for the many $MgCuAl_2$-type compounds, however, the lattice parameters vary anisotropically, allowing changes in chemical bonding. As an example we present the structure of $LaPtMg_2$ in Fig. 2, using the positional parameters of the nickel compound [3]. The platinum and magnesium atoms build up a three-dimensional $[PtMg_2]$ network which leaves larger cavities of coordination number 13 for the lanthanum atoms. The crystal chemical peculiarities of the $RETMg_2$ compounds presented here are similar to those of $LaNiMg_2$. For further details we refer to previous work [3, 6, 8].

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