Rare Earth-rich Cadmium Compounds RE_4TCd (T = Ni, Pd, Ir, Pt)

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New intermetallic compounds RE_4TCd (RE = Y, La–Nd, Sm, Gd–Tm, Lu; T = Ni, Pd, Ir, Pt) were synthesized by melting of the elements in sealed tantalum tubes in a high-frequency furnace. They crystallize with the Gd$_4$RhIn-type structure, space group $F\bar{4}3m$, Z = 16. The four gadolinium compounds were characterized by single crystal X-ray diffractometer data: a = 1361.7(1) pm, $wR2$ = 0.062, 456 F^2 values, 19 variables for Gd$_4$NiCd; a = 1382.1(2) pm, $wR2$ = 0.077, 451 F^2 values, 19 variables for Gd$_4$PdCd; a = 1363.6(2) pm, $wR2$ = 0.045, 494 F^2 values, 19 variables for Gd$_4$IrCd; a = 1379.0(1) pm, $wR2$ = 0.045, 448 F^2 values, 19 variables for Gd$_4$PtCd. The rare earth atoms build up transition metal-centered trigonal prisms which are condensed *via* common corners and edges, leading to three-dimensional adamantane-related networks. The cadmium atoms form Cd$_4$ tetrahedra which fill voids left in the prisms' network.

Key words: Intermetallics, Cadmium, Crystal Chemistry

Introduction

The recently discovered structure type Gd$_4$RhIn [1] shows remarkable structural motifs and a certain variety in the valence electron concentration. The rhodium atoms have trigonal prismatic gadolinium coordination, and these prisms are condensed to a three-dimensional network with adamantane topology *via* common edges and corners. Voids within this rigid network are filled by In$_4$ tetrahedra, a structural building unit which is also known in molecular structures and some Zintl phases. With indium as the main group component, this structure type also exists for the series of RE_4IrIn compounds [2].

A remarkable result was the recent synthesis of isotypic magnesium [3 – 7] and even cadmium [8, 9] compounds with isolated Mg$_4$ and Cd$_4$ tetrahedra with Mg–Mg and Cd–Cd distances close to the distances in *hcp* magnesium and cadmium. Besides these structural features, the compounds show interesting properties. Preliminary magnetic studies revealed comparatively high ordering temperatures for some of these 4-1-1 compounds, *e. g.* 92 K for Gd$_4$NiMg [10]. Furthermore, the magnesium compounds show good hydrogen sorption at r. t. A recent study revealed an uptake of up to eleven hydrogen atoms per formula unit for Gd$_4$NiMg [10].

We have now systematically explored the existence ranges of the different 4-1-1 compounds. Herein we report on the synthesis and structural characterization of the four series RE_4TCd (RE = Y, La–Nd, Sm, Gd–Tm, Lu; T = Ni, Pd, Ir, Pt).

Experimental Section

Synthesis

Starting materials for the synthesis of the RE_4TCd samples were ingots of the rare earth metals (Johnson Matthey or smart elements), nickel wire (Johnson Matthey, ∅ 0.38 mm), palladium, iridium and platinum powder (Heraeus, *ca.* 200 mesh), and cadmium drops (Johnson Matthey), all with stated purities better than 99.9 %. Except thulium, pieces of the rare earth ingots were first arc-melted [11] 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, pieces of the nickel wire or palladium (iridium, platinum) powder and pieces of the cadmium drops were weighed in the ideal 4 : 1 : 1 atomic ratio and sealed in tantalum tubes under an argon pressure of *ca.* 700 mbar. The tubes were placed in a water-cooled sample chamber of a high-frequency furnace (Hüttinger Elektronik, Freiburg, and type TIG 1.5/300) under flowing argon [12] and first heated for 3 min at about 1370 K (La, Ce, Pr compounds), respectively 1420 K (Y, Nd–Lu compounds). The samples were then cooled to *ca.* 1020 K within 5 min and annealed for another 3 h at that temperature. Finally the tubes were quenched to r. t. The temperature was controlled through a Sensor Therm Methis MS09 pyrometer with an accuracy of ±30 K. All samples could easily be separated from the tantalum crucibles. No reaction with the container material was observed. The polycrystalline samples are stable in air over weeks.

For the growth of small single crystals, the elements were cold-pressed to small pellets (∅ 6 mm) and sealed in tantalum tubes. The latter were sealed into silica tubes for oxidation protection. The tubes were placed in a muffle furnace and heated to *ca.* 1420 K within 4 h and kept at that temperature for 6 h, followed by slow cooling to *ca.* 1020 K at a rate of 2 K h^{-1}. Finally the samples were annealed at 1020 K for six days and subsequently cooled to r. t. within 6 h.

EDX data

Semiquantitative EDX analyses on the crystals investigated on the diffractometer were carried out by use of a Leica 420i scanning electron microscope with GdF_3, nickel, palladium, iridium, platinum, and cadmium as standards. The experimentally observed compositions were close to the ideal ones. No impurity elements heavier than sodium (detection limit of the instrument) were found.

X-Ray diffraction

The powder samples were studied through Guinier patterns (imaging plate detector, Fujifilm BAS-1800 readout system) using Cu$K_{\alpha 1}$ radiation and α-quartz (a = 491.30, c = 540.46 pm) as an internal standard. The lattice parameters (Table 1) were obtained from the powder data by least-squares calculations. Proper indexing was ensured through intensity calculations [13].

Single crystals of Gd_4TCd (T = Ni, Pd, Ir, Pt) were picked from the crushed annealed samples, and their quality was ensured by Laue photographs on a Buerger camera (white Mo radiation). Intensity data were collected at r. t. 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_4TCd (T = Ni, Pd, Ir, Pt) with the cubic Gd_4RhIn type [1], space group $F\bar{4}3m$, was already obvious from the powder patterns. The atomic positions of isotypic Gd_4CoCd [9] were taken as starting parameters and the three structures refined using SHELXL-97 [14] (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for all atoms. As a check for deviations from the ideal composition, the occupancy parameters were refined in separate series of least-squares cycles. All sites were fully occupied within three standard deviations. Refinement of the correct absolute structure was ensured through calculation of the Flack parameter [15, 16]. 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 investigations 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) on quoting the deposition numbers CSD-419610 (Gd_4NiCd), CSD-419611 (Gd_4PdCd), CSD-419612 (Gd_4IrCd), and CSD-419613 (Gd_4PtCd).

Table 1. Lattice parameters (Guinier powder data) of the cubic ternary cadmium compounds RE_4TCd (T = Ni, Pd, Ir, Pt).

RE	T = Ni	T = Pd	T = Ir	T = Pt
Y	1356.0(2)	1373.6(1)	1359.9(1)	1367.4(1)
La	1427.4(4)	1445.9(2)	1427.3(1)	1442.1(2)
Ce	1397.6(3)	1423.0(3)	1404.8(1)	1416.1(1)
Pr	1390.2(2)	1411.6(2)	1398.4(1)	1409.5(2)
Nd	1384.0(2)	1409.9(1)	1391.0(1)	1400.7(1)
Sm	1368.9(2)	1397.5(2)	1378.5(1)	1388.7(1)
Gd	1361.7(1)	1382.1(2)	1363.6(2)	1379.0(1)
Tb	1353.4(3)	1371.7(1)	1359.6(1)	1364.9(1)
Dy	1343.2(2)	1366.3(2)	1354.4(2)	1357.3(1)
Ho	1339.6(3)	1357.6(1)	1348.0(3)	1355.2(1)
Er	1333.3(2)	1352.7(1)	1342.6(1)	1347.2(1)
Tm	1331.0(3)	1347.9(1)	1335.7(1)	1342.7(1)
Lu	1321.9(4)	1338.6(1)	1330.2(1)	1334.0(2)

Discussion

Systematic phase analytical studies in the ternary rare earth–transition metal–cadmium systems revealed the existence of four further series of RE_4TCd compounds, *i. e.* with T = Ni, Pd, Ir, Pt. As expected from the lanthanoid contraction, the cell volumes decrease from the lanthanum to the lutetium compounds for all four series. The four yttrium compounds fit between terbium and dysprosium. So far, in all series of RE_4TX compounds, no representative with europium or ytterbium has been observed. Most likely europium and ytterbium prefer the divalent state and do not satisfy the electronic requirements for a formation of RE_4TX compounds. Among the whole family of the compounds, those with cadmium as X component have the highest number of representatives. For a detailed discussion on the crystal chemistry and chemical bonding of these compounds we refer to our previous work [1 – 10].

The striking structural motifs of the RE_4TCd compounds are the transition metal-centered trigonal rare earth prisms with short RE–T distances and the isolated Cd_4 tetrahedra. Of the Gd_4TCd compounds discussed herein, the shortest Cd–Cd distances (307 pm) occur for Gd_4IrCd. They compare well with the Cd–Cd distances in *hcp* cadmium (6 × 298 and 6 × 329 pm) [17], and one can assume substantial Cd–Cd bonding within these units, similar to the observations

Table 2. Crystal data and structure refinement for Gd$_4T$Cd (T = Ni, Pd, Ir, Pt), Gd$_4$RhIn type, space group $F\bar{4}3m$, Z = 16.

Empirical formula	Gd$_4$NiCd	Gd$_4$PdCd	Gd$_4$IrCd	Gd$_4$PtCd
Molar mass, g mol^{-1}	800.11	847.80	933.60	936.49
Unit cell dimensions	Table 1	Table 1	Table 1	Table 1
Calculated density, g cm^{-3}	8.42	8.53	9.78	9.49
Crystal size, μm^3	10 × 15 × 40	10 × 40 × 50	10 × 20 × 50	10 × 20 × 50
Detector distance, mm	40	80	80	80
Exposure time, min	5	5	9	5
ω range; increment, deg	0 – 180; 1.0	0 – 180; 1.0	0 – 180; 1.0	0 – 180; 1.0
Integr. param. A, B, EMS	13.0, 3.0, 0.014	14.0, 4.0, 0.020	14.0, 4.0, 0.010	14.0, 4.0, 0.018
Transm. ratio (max/min)	0.106 / 0.025	0.192 / 0.101	0.578 / 0.103	0.379 / 0.113
Absorption coefficient, mm^{-1}	47.5	45.3	65.3	64.2
F(000)	5312	5600	6096	6112
θ range, deg	2 – 32	2 – 31	2 – 33	2 – 31
Range in *hkl*	±20, ±20, ±20	±19, ±19, ±19	±20, ±20, ±20	−18 / 19, ±19, ±19
Total no. reflections	4846	7172	15751	7093
Independent reflections / R_{int}	456 / 0.179	451 / 0.287	494 / 0.058	448 / 0.101
Reflections with $I \geq 2\sigma(I)/R_\sigma$	275 / 0.146	329 / 0.130	480 / 0.017	330 / 0.081
Data / parameters	456 / 19	451 / 19	494 / 19	448 / 19
Goodness-of-fit on F^2	0.643	0.696	1.111	0.751
Final $R1/wR2$ indices [$I \geq 2\sigma(I)$]	0.036 / 0.055	0.034 / 0.071	0.021 / 0.044	0.029 / 0.043
$R1/wR2$ indices (all data)	0.073 / 0.062	0.056 / 0.077	0.023 / 0.045	0.047 / 0.045
Extinction coefficient	0.000086(9)	0.000083(16)	0.000111(7)	0.000064(4)
Flack parameter	0.04(11)	0.03(7)	−0.002(18)	−0.01(3)
Largest diff. peak / hole, e Å^{-3}	2.51 / −1.86	4.28 / −1.80	4.80 / −1.70	4.61 / −1.83

Table 3. Atomic coordinates and isotropic displacement parameters (pm^2) of Gd$_4T$Cd (T = Ni, Pd, Ir, Pt). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Note that the Gd$_4$PtCd crystal had the opposite absolute structure.

	Atom	W. site	x	y	z	U_{eq}
Gd$_4$NiCd:	Gd1	24*g*	0.56395(15)	1/4	1/4	135(4)
	Gd2	24*f*	0.18999(17)	0	0	140(4)
	Gd3	16*e*	0.34920(11)	x	x	129(5)
	Ni	16*e*	0.1428(3)	x	x	169(13)
	Cd	16*e*	0.57983(15)	x	x	128(7)
Gd$_4$PdCd:	Gd1	24*g*	0.56592(9)	1/4	1/4	116(3)
	Gd2	24*f*	0.19005(10)	0	0	113(3)
	Gd3	16*e*	0.35153(8)	x	x	140(4)
	Pd	16*e*	0.14390(14)	x	x	176(6)
	Cd	16*e*	0.58315(17)	x	x	285(7)
Gd$_4$IrCd:	Gd1	24*g*	0.56256(5)	1/4	1/4	101(1)
	Gd2	24*f*	0.19053(5)	0	0	85(1)
	Gd3	16*e*	0.34891(3)	x	x	77(2)
	Ir	16*e*	0.14164(3)	x	x	87(1)
	Cd	16*e*	0.57957(6)	x	x	100(2)
Gd$_4$PtCd:	Gd1	24*g*	0.43517(9)	3/4	3/4	83(3)
	Gd2	24*f*	0.80882(11)	0	0	79(3)
	Gd3	16*e*	0.64859(9)	x	x	73(4)
	Pt	16*e*	0.85693(7)	x	x	66(3)
	Cd	16*e*	0.41866(15)	x	x	129(6)

Table 4. Interatomic distances (pm) in the structures of Gd$_4$NiCd, Gd$_4$PdCd, Gd$_4$IrCd, and Gd$_4$PtCd. Standard deviations are given in parentheses. All distances within the first coordination spheres are listed.

			Gd$_4$NiCd	Gd$_4$PdCd	Gd$_4$IrCd	Gd$_4$PtCd
Gd1:	2	Cd	328.4(3)	327.0(3)	329.5(1)	329.7(3)
	2	T	349.1(2)	356.5(1)	348.1(1)	354.5(1)
	2	Gd3	349.3(2)	356.6(1)	348.2(1)	354.6(1)
	4	Gd2	360.8(1)	366.8(1)	360.7(1)	365.3(1)
	4	Gd1	358.3(3)	359.8(2)	361.5(1)	361.1(2)
Gd2:	2	T	282.4(5)	288.4(2)	281.2(1)	286.8(1)
	2	Cd	349.1(2)	353.1(1)	349.0(1)	351.5(2)
	4	Gd1	360.8(1)	366.8(1)	360.7(1)	365.3(1)
	2	Gd3	362.4(1)	366.1(1)	362.7(1)	364.4(1)
	4	Gd2	365.9(3)	371.5(2)	367.4(1)	372.8(2)
Gd3:	3	T	281.5(4)	287.1(2)	283.2(1)	287.5(1)
	3	Cd	342.5(2)	344.6(2)	343.4(1)	343.1(2)
	3	Gd1	349.3(2)	356.6(1)	348.2(1)	354.6(1)
	3	Gd2	362.4(1)	366.1(1)	362.7(1)	364.4(1)
	3	Gd3	382.1(4)	396.9(2)	381.5(1)	395.6(4)
T:	3	Gd2	281.5(4)	288.4(2)	281.2(1)	286.8(1)
	3	Gd3	282.4(5)	287.1(2)	283.2(1)	287.5(1)
	3	Gd1	349.1(2)	356.5(1)	348.1(1)	354.5(1)
Cd:	3	Cd	307.5(6)	325.0(7)	306.9(1)	317.2(6)
	3	Gd1	328.4(3)	327.0(3)	329.5(1)	329.7(3)
	3	Gd3	342.5(2)	344.7(2)	343.4(1)	343.1(2)
	3	Gd2	349.1(2)	353.1(1)	349.0(1)	351.5(2)

made with the magnesium compounds [3,5]. Further investigations with gallium and zinc are in progress in order to check the formation of X_4 tetrahedra with these elements in RE_4TX compounds.

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