

Synthesis and Structure of RE_2Rh_2Cd ($RE = La, Ce, Pr, Nd, Sm$)

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New intermetallic cadmium compounds RE_2Rh_2Cd ($RE = La, Ce, Pr, Nd, Sm$) were synthesized from the elements in sealed tantalum tubes in a high-frequency furnace. They were characterized through X-ray powder data: Mo_2FeB_2 type, space group $P4/mbm$, $Z = 2$. Single crystal data of the cerium compound ($a = 762.8(1)$, $c = 377.8(1)$ pm, $wR2 = 0.0662$, 199 F^2 values, and 13 variable parameters) revealed small defects on the rhodium position leading to the composition $Ce_2Rh_{1.86(3)}Cd$ for the investigated crystal. According to the course of the cell volumes Ce_2Rh_2Cd may be classified as a mixed-valent compound. The Ce_2Rh_2Cd structure is an intergrowth of slightly distorted AlB_2 and $CsCl$ related slabs of compositions $CeRh_2$ and $CeCd$. Within the $CeRh_2$ slab short Ce-Rh contacts (284–300 pm) are indicative of strong Ce-Rh bonding. The Rh-Rh distance within the AlB_2 related slab is 289 pm.

Introduction

Recently we started a systematic investigation of intermetallic rare earth metal (RE) – transition metal (T) – magnesium(cadmium) compounds RE_2T_2Mg and RE_2T_2Cd with tetragonal Mo_2FeB_2 [1] structure. These studies resulted in the series RE_2Au_2Cd ($RE = La-Sm$) [2], RE_2Cu_2Mg ($RE = Y, La-Sm, Gd-Tm, Lu$) [3], Ce_2T_2Mg ($T = Ni, Cu, Pd$) [4, 5], Ce_2T_2Cd ($T = Ni, Pd, Pt, Au$) [5], RE_2Ni_2Mg ($RE = Y, La-Sm, Gd-Tm$) [6, 7] and $Ce_2Ni_{1.88}Cd$ [8]. First physical property measurements showed a mixed cerium valency for Ce_2Ni_2Mg [4] and $Ce_2Ni_{1.88}Cd$ [8], while antiferromagnetic ordering at $T_N = 49$ K was observed for Gd_2Ni_2Mg [7]. The related cadmium compound Gd_2Ni_2Cd with the orthorhombic Mn_2AlB_2 structure [9] shows the higher Néel temperature of 65 K [10].

These magnesium and cadmium compounds complement a larger family of Mo_2FeB_2 intermetallics, *i. e.* indides, stannides, and plumbides $R_2T_2In(Sn, Pb)$, where R is a rare earth or actinoid metal. The cerium and uranium based compounds have been investigated most intensively with respect to their greatly varying physical properties. Some of the recent literature is given in ref. [5] and [11]. Besides the size of the atoms in this structure type, also the electron count per formula (f.u.) unit plays an important role for the magnetic behavior of these materials.

The plumbide Ce_2Au_2Pb [5] has the so far highest electron count of 32 e⁻/f.u. With the syntheses of Ce_2Rh_2Cd and the isotypic lanthanum, praseodymium, neodymium, and samarium compounds, we were now able to reduce the electron count to 26 e⁻/f.u., the so far lowest electron count among the rare earth metal based Mo_2FeB_2 intermetallics. The preparation, structure refinement, and crystal chemistry of these intermetallics are reported herein.

Experimental

Synthesis

Starting materials for the preparation of the RE_2Rh_2Cd compounds were ingots of the rare earth metals (Johnson Matthey), rhodium powder (Degussa-Hüls, 200 mesh), and a cadmium rod (Johnson Matthey, \varnothing 8 mm), all with stated purities better than 99.9%. The rare earth metal pieces were first arc-melted [12] to small buttons (about 400 mg) under an argon pressure of about 600 mbar. The argon was purified over titanium sponge (900 K), silica gel, and molecular sieves. The rare earth metal buttons and cadmium pieces were mixed with the rhodium powder in the ideal 2:2:1 atomic ratio and sealed in small tantalum tubes (tube volume about 1 cm³) under an argon atmosphere of about 800 mbar. The tantalum tube was placed in a water-cooled quartz glass sample chamber in a high-frequency furnace (HÜTTINGER TIG 1.5 / 300, 1.5 kW) under flowing argon [13]. It was first heated for 1 min with the maximum power output (about 1500 K) and subsequently annealed at about 800 K for another 4 h. After the annealing procedure the sample could easily be separated from the tantalum tube. No reactions with the tube could be detected. Compact pieces are light gray with metallic luster. The samples are slightly moisture and oxidation sensitive. The sil-



very surface of some samples becomes brass yellow after some time, most likely due to surface oxidation.

X-ray powder and single crystal data

The RE_2Rh_2Cd compounds were characterized through powder diffractometer patterns (Stoe StadiP) using $Cu-K_{\alpha 1}$ radiation and silicon ($a = 543.07$ pm) as an external standard. The lattice parameters (Table 1) were obtained from least-squares fits of the powder data. The correct indexing of the patterns was facilitated by intensity calculations [14] taking the atomic positions from the structure refinement. The lattice parameters of the cerium compound determined from the powder and the single crystal agreed well.

Table 1. Lattice parameters of the tetragonal compounds RE_2Rh_2Cd .

compound	<i>a</i> (pm)	<i>c</i> (pm)	<i>c/a</i>	<i>V</i> (nm ³)
La_2Rh_2Cd	775.2(2)	390.0(2)	0.503	0.2343
Ce_2Rh_2Cd	762.8(1)	377.8(1)	0.495	0.2198
Pr_2Rh_2Cd	761.9(2)	387.2(1)	0.508	0.2247
Nd_2Rh_2Cd	757.7(2)	385.4(2)	0.509	0.2212
Sm_2Rh_2Cd	754.9(2)	379.8(3)	0.503	0.2164

Irregularly shaped single crystals of Ce_2Rh_2Cd were isolated from the annealed sample by mechanical fragmentation. They were first examined by Laue photographs on a Buerger precession camera in order to establish their quality. Single crystal intensity data were collected at room temperature by use of a four-circle diffractometer (CAD4) with graphite monochromatized $Mo-K_{\alpha}$ radiation (71.073 pm) and a scintillation counter with pulse height discrimination. The scans were performed in the $\omega/2\theta$ mode. An empirical absorption correction was applied on the basis of ψ -scan data. All relevant crystallographic data and experimental details for the data collection are listed in Table 2.

An analysis of the data set revealed $P4/mbm$ as the correct space group in agreement with previ-

Table 2. Crystal data and structure refinement for $Ce_2Rh_{1.86(3)}Cd$.

Empirical formula	$Ce_2Rh_{1.86(3)}Cd$
Molar mass	598.46 g/mol
Unit cell dimensions	Table 1
Space group	$P4/mbm$ (No. 127)
Calculated density	9.04 g/cm ³
Crystal size	10 × 30 × 30 μm ³
Transm. ratio (max/min)	1.18
Absorption coefficient	32.2 mm ⁻¹
θ Range	2° to 30°
Range in <i>hkl</i>	±10, ±10, +5
Total no. reflections	1337
Independent reflections	199 ($R_{int} = 0.1607$)
Reflections with $I > 2\sigma(I)$	132 ($R_{sigma} = 0.0770$)
Data/parameters	199 / 13
Goodness-of-fit on F^2	1.075
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R1 = 0.0398$ $wR2 = 0.0542$
<i>R</i> Indices (all data)	$R1 = 0.0893$ $wR2 = 0.0662$
Extinction coefficient	0.0010(5)
Largest diff. peak and hole	3.24 and -2.22 e/Å ³

ous investigations [5–8]. The atomic positions of $Ce_2Ni_{1.88}Cd$ [8] were taken as starting values and the structure was successfully refined using SHELXL-97 (full-matrix least-squares on F_o^2) [15] with anisotropic atomic displacement parameters for all sites. This refinement showed an elevated equivalent isotropic displacement parameter for the rhodium site, indicating defects on this position, since the rhodium atoms have the smallest scattering power in this compound. As a check for the correct composition, the occupancy parameters were refined in a separate series of least-squares cycles. The cerium and cadmium sites were fully occupied within two standard deviations, while the rhodium site showed an occupancy of only 93.1(14)%, leading to the composition $Ce_2Rh_{1.86(3)}Cd$ for the investigated crystal. In the final cycles this occupancy parameter was refined as a least-squares variable. A final difference Fourier synthesis revealed no significant residual peaks (see Table 2). The positional parameters and

Table 3. Atomic coordinates and anisotropic displacement parameters (pm²) for $Ce_2Rh_{1.86(3)}Cd$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. $U_{23} = U_{13} = 0$.

* The rhodium position is occupied only by 93.1(14)%.

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11} = U_{22}$	U_{33}	U_{12}	U_{eq}
Ce	4 <i>h</i>	0.1694(2)	1/2 + <i>x</i>	1/2	134(5)	99(7)	-5(7)	123(4)
Rh*	4 <i>g</i>	0.3660(2)	1/2 + <i>x</i>	0	194(13)	337(18)	4(10)	242(11)
Cd	2 <i>a</i>	0	0	0	112(9)	214(17)	0	146(7)

interatomic distances are listed in Tables 3 and 4. Listings of the observed and calculated structure factors are available.*

Table 4. Interatomic distances (pm), calculated with the lattice parameters taken from X-ray powder data of $Ce_2Rh_{1.86(3)}Cd$. All distances within the first coordination sphere are listed. Standard deviations are equal or less than 0.5 pm.

Ce: 2	Rh	284.0	Rh: 2	Ce	284.0	Cd: 4	Rh	297.3
4	Rh	300.0	1	Rh	289.1	8	Ce	340.6
4	Cd	340.6	2	Cd	297.3			
1	Ce	365.5	4	Ce	300.0			
2	Ce	377.8						
4	Ce	400.7						

Discussion

Five new intermetallic cadmium compounds RE_2Rh_2Cd ($RE = La, Ce, Pr, Nd, Sm$) with Mo_2FeB_2 type structure [1] have been synthesized and the crystal structure was exemplarily refined for the cerium compound. Refinement of the occupancy parameter indicated defects for the rhodium site resulting in the composition $Ce_2Rh_{1.86(3)}Cd$ for the investigated crystal. A similar situation was recently also observed for the isotopic nickel compound [8] which shows mixed-valent behavior.

In Fig. 1 we present a plot of the lattice parameters vs the rare earth metal component. While the a parameters decrease from the lanthanum to the samarium compound, the c parameters show a dif-

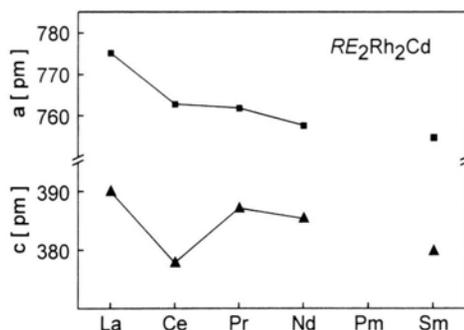


Fig. 1. Plot of the lattice parameters of the RE_2Rh_2Cd compounds with tetragonal Mo_2FeB_2 structure. The solid lines serve as a guide to the eye.

* Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD-412098.

ferent behavior. In the RE_2Rh_2Cd series the cerium compound shows the smallest c parameter, resulting from a partial tetravalency of cerium (and thus a smaller radius). From this plot it is evident, that the lattice parameter c is mainly influenced by the size of the rare earth atom.

At this point the question arises, whether or not the RE_2Rh_2Cd compounds with the other rare earth elements also show defects on the rhodium site. So far it was not possible to get suitable single crystals from the other compounds. Parallel work in the RE_2Ni_2Cd series [16] showed only defects for mixed valent $Ce_2Ni_{1.88}Cd$ [8], while Nd_2Ni_2Cd and Dy_2Ni_2Cd showed full nickel occupancies. Most likely the defects occur only for the mixed valent cerium compounds.

A projection of the Ce_2Rh_2Cd structure onto the xy plane is presented in Fig. 2. It may be considered an intergrowth of distorted AlB_2 and $CsCl$ related slabs of compositions $CeRh_2$ and $CeCd$. While a high-temperature (HT) modification of $CeCd$ with $CsCl$ type structure is known [17], $CeRh_2$ [18] adopts the structure of the cubic Laves phase $MgCu_2$. In HT- $CeCd$ the Ce-Cd distance is 333.5 pm. At low temperatures a tetragonal distortion to LT- $CeCd$ occurs with a c/a ratio of 1.03 and Ce-Cd distances of 332.4 pm [17]. In contrast, the c/a ratio in the compressed $CeCd$ slab of Ce_2Rh_2Cd is 0.94 and the Ce-Cd distances of 341 pm are slightly longer.

The Ce-Rh distances of 284 pm in Ce_2Rh_2Cd are even shorter than the sum of the covalent radii of 290 pm for cerium and rhodium [19, 20]. In the Laves phase $CeRh_2$ [18] the cerium atoms have coordination number 12 at the much longer Ce-Rh distance of 313 pm. We can thus assume a significant degree of Ce-Rh bonding in Ce_2Rh_2Cd .

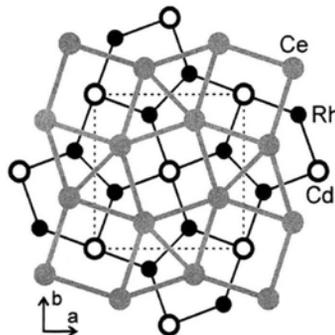


Fig. 2. Projection of the Ce_2Rh_2Cd structure onto the xy plane. The Rh-Cd network at $z = 0$ and the square- and trigonal-prismatic cerium slabs at $z = 1/2$ are emphasized.

This is consistent with a recent electronic structure calculation on isotopic $\text{Sc}_2\text{Ni}_2\text{In}$ [11], where the strongest bonding interactions were found for the Sc-Ni contacts followed by Sc-In and Ni-In. In the cerium compound the Rh-Rh (289 pm) and Rh-Cd (297 pm) distances are all longer than in *fcc* rhodium (269 pm) [21] and the sum of the covalent radii for rhodium and cadmium of 266 pm [19, 20], indicating only weak Rh-Rh and Rh-Cd interactions in $\text{Ce}_2\text{Rh}_2\text{Cd}$. The same holds true for the Ce-Cd contacts.

Summing up, we could synthesize five new $\text{RE}_2\text{Rh}_2\text{Cd}$ compounds among which the cerium compound shows mixed valency. Investigations of the physical properties of these interesting materials are in progress.

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