MgCuAl\textsubscript{2}-type Intermetallics

\textit{REPdCd\textsubscript{2}} (\textit{RE} = Ce, Pr, Nd, Sm)

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The cadmium-rich intermetallic compounds \textit{REPdCd\textsubscript{2}} (\textit{RE} = Ce, Pr, Nd, Sm) were obtained by high-frequency melting of the elements in sealed niobium ampoules and subsequent annealing in muffle furnaces. The \textit{REPdCd\textsubscript{2}} phases crystallize with the orthorhombic MgCuAl\textsubscript{2}-type structure, space group \textit{Cmcm}. The structure of NdPdCd\textsubscript{2} was refined from single-crystal X-ray diffractometer data: \textit{a} = 421.9(3), \textit{b} = 998.4(7), \textit{c} = 834.5(6) pm, \textit{wR} = 0.0286, 451 structure factors, 16 variables. The palladium and cadmium atoms build up a three-dimensional \textit{[PdCd\textsubscript{2}]} network (281 – 283 pm Pd–Cd; 298 – 335 pm Cd–Cd) in which the neodymium atoms fill cavities. They are connected to the \textit{[PdCd\textsubscript{2}]} network via shorter Nd–Pd bonds of 286 pm.

Key words: Cadmium, Intermetallics, Crystal Chemistry

Introduction

The MgCuAl\textsubscript{2}-type structure [1, 2] has more than 100 representatives [3]. Geometrically it can be considered as a ternary ordered version of the \textit{Re\textsubscript{2}B} type [4], however, both structure types differ distinctly in chemical bonding. Ternary compounds with this structure type with the general formula \textit{AX\textsubscript{2}} (\textit{A} = alkali, alkaline earth, or rare earth metal; \textit{T} = Co, Ni, Rh, Pd, Ir, Pt, Au; \textit{X} = Mg, Al, Ga, In, Ti, Sn, Cd) are known for valence electron concentrations per formula unit varying from 17 (e.g. LaPdMg\textsubscript{2}) to 20 (e.g. CaPdSn\textsubscript{2}). As emphasized in Fig. 1, the \textit{X} atoms build up orthorhombically distorted networks of corner-sharing tetrahedra which derive from the structure of hexagonal diamond, lonsdaleite. Together with the \textit{A} atoms, one obtains a distorted representative of the well known Zintl phase CaF\textsubscript{2}. Consequently, one can describe the \textit{AX\textsubscript{2}} intermetallics as transition metal-filled versions of \textit{AX\textsubscript{2}}. Detailed electronic structure investigations [5 – 8] have revealed that the bonding within the tetrahedral network is strongly modified upon the insertion of the transition metal.

While tetrahedral networks have been known for diverse intermetallic compounds with Al, Ga, In, Ti, and Sn, it was surprising that the MgCuAl\textsubscript{2}-type structure is also formed with magnesium [9 – 13] as part of a tetrahedral network. Especially LaNiMg\textsubscript{2} has intensively been studied with respect to its hydrogenation behavior [10, 14 – 20], when searching for new hydrogen storage materials. Given the close structural relationship between \textit{RE\textsubscript{2}T\textsubscript{2}Mg\textsubscript{2}} [21] and \textit{RE\textsubscript{2}T\textsubscript{2}Cd\textsubscript{2}} [22] intermetallic compounds, one can also consider \textit{RET\textsubscript{2}Cd\textsubscript{2}} compounds in this context. So far only LaNiCd\textsubscript{2} [12], PrNi\textsubscript{0.95}Cd\textsubscript{2} and LaPdCd\textsubscript{2} [23] have been reported. During our systematic phase analytical studies of \textit{RE\textsubscript{2}T\textsubscript{2}Cd\textsubscript{2}} intermetallics we have now obtained the remaining members of the \textit{REPdCd\textsubscript{2}} (\textit{RE} = Ce, Pr, Nd, Sm) series. The synthesis conditions and powder and single-crystal X-ray data of these phases are reported herein.

Experimental

Synthesis

The \textit{REPdCd\textsubscript{2}} samples were synthesized directly from the elements. Starting materials were pieces of the rare earth elements (Smart Elements), palladium powder (Allgemeine Gold- und Silberscheideanstalt, Pforzheim), and a cadmium rod (Johnson Matthey), all with stated purities better than 99.9%. The air-sensitive pieces of the rare earth elements were kept under argon in Schlenk tubes prior to the reactions. The argon was purified with titanium sponge (870 K), silica gel and molecular sieves. Starting compositions \textit{1 : 1 : 2} always led to the equiatomic phases \textit{REPdCd} as by-products (most likely small amounts of cadmium distilled to the top of the niobium ampoules). A small cadmium excess corresponding to an initial composition \textit{1 : 1 : 2.05} was used to obtain pure phases. Pieces of the elements were weighed in the latter ratio and arc-welded [24] in small niobium tubes under an argon pressure of about 700 mbar. The tubes were then placed in a water-cooled quartz sample chamber of an induction furnace (Hüttinger Elektronik, Freiburg, type TIG 1.5/300) [25], first heated to ca. 1400 K and kept at that temperature for 1 min under flowing argon. The temperature was then lowered to 900 K within 30 min, 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 \( \pm 30 \) K. Subsequently the niobium ampoules were sealed in evacuated silica tubes for oxidation protection and further annealed at 873 K for 7 d. At the end of the annealing sequence all samples could easily be separated from the niobium tube by mechanical fragmentation. The \( \text{REPdCd}_2 \) samples are slightly sensitive to moisture. They were kept in Schlenk tubes under argon.

**X-Ray diffraction**

The polycrystalline \( \text{REPdCd}_2 \) samples were characterized by powder X-ray diffraction on a Guinier camera (equipped with a Fuji-film image plate system, BAS-1800) using Cu-K\( \alpha \) radiation and \( \alpha \)-quartz (\( a = 491.30, c = 540.46 \) pm) as an internal standard. The orthorhombic lattice parameters (Table 1) were refined from the powder data by a standard least-squares routine. The experimental powder patterns were compared to calculated ones [26] in order to ensure correct indexing.

Small single crystals of \( \text{NdPdCd}_2 \) were selected from the crushed annealed sample. The crystals were glued to thin quartz fibers, and their quality was first 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 Mo-K\( \alpha \) radiation). A numerical absorption correction was applied to the data set. All relevant details concerning the data collection and evaluation are listed in Table 2.

**Results and Discussion**

**Structure refinement of \( \text{NdPdCd}_2 \)**

Careful examination of the data set revealed a \( C \) centered orthorhombic lattice, and the systematic extinctions were compatible with space group \( \text{Cmcm} \), in agreement with our earlier work on \( \text{LaPdCd}_2 \) [23]. The atomic sites of the lanthanum compound were taken as starting values, and the structure was refined using the JANA2006 package [27, 28] with anisotropic atomic displacement parameters (ADPs) for all atoms. In a separate refinement of the occupancy parameters no deviation from the ideal composition was observed. A final difference Fourier synthesis showed no significant residual peaks. The refined atomic positions, the ADPs, and the interatomic distances are given in Tables 3 and 4.

**Crystal chemistry**

Four new representatives of the MgCuAl\(_2\)-type structure have been synthesized. The \( \text{REPdCd}_2 \) series...
Table 3. Atomic coordinates and anisotropic displacement parameters (pm$^2$) for NdPdCd$_2$. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor. $U_{12} = U_{13} = 0$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd</td>
<td>4c</td>
<td>0</td>
<td>0.06419(3)</td>
<td>1/4</td>
<td>98(1)</td>
<td>72(1)</td>
<td>128(2)</td>
<td>0</td>
<td>99(1)</td>
</tr>
<tr>
<td>Pd</td>
<td>4c</td>
<td>0</td>
<td>0.77723(5)</td>
<td>1/4</td>
<td>109(2)</td>
<td>96(2)</td>
<td>101(2)</td>
<td>0</td>
<td>102(1)</td>
</tr>
<tr>
<td>Cd</td>
<td>8f</td>
<td>0</td>
<td>0.35630(3)</td>
<td>0.04934(4)</td>
<td>112(1)</td>
<td>100(1)</td>
<td>98(1)</td>
<td>6(1)</td>
<td>103(1)</td>
</tr>
</tbody>
</table>

Table 4. Interatomic distances (pm) in the structure of NdPdCd$_2$. All distances of the first coordination spheres are listed. Standard deviations are all smaller or equal than 0.1 pm.

<table>
<thead>
<tr>
<th>Nd:</th>
<th>1 Pd</th>
<th>285.6</th>
<th>Cd: 2 Pd</th>
<th>280.6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 Pd</td>
<td>299.1</td>
<td>1 Pd</td>
<td>283.0</td>
</tr>
<tr>
<td></td>
<td>2 Cd</td>
<td>335.5</td>
<td>1 Cd</td>
<td>297.7</td>
</tr>
<tr>
<td></td>
<td>4 Cd</td>
<td>336.4</td>
<td>2 Cd</td>
<td>309.9</td>
</tr>
<tr>
<td></td>
<td>4 Cd</td>
<td>339.6</td>
<td>1 Cd</td>
<td>334.9</td>
</tr>
<tr>
<td></td>
<td>2 Nd</td>
<td>421.9</td>
<td>1 Nd</td>
<td>335.6</td>
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<tr>
<td></td>
<td>2 Nd</td>
<td>436.4</td>
<td>2 Nd</td>
<td>336.4</td>
</tr>
<tr>
<td>Pd:</td>
<td>4 Cd</td>
<td>280.6</td>
<td>2 Nd</td>
<td>339.6</td>
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<tr>
<td></td>
<td>2 Cd</td>
<td>283.0</td>
<td>1 Nd</td>
<td>285.6</td>
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<tr>
<td></td>
<td>2 Nd</td>
<td>299.1</td>
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<td></td>
</tr>
</tbody>
</table>

exists with $RE = $La \cite{23}, Ce, Pr, Nd, and Sm. The samarium-based sample already showed some additional reflections which could not be assigned to one of the known phases. With gadolinium as rare earth metal a REPdCd$_2$ phase was not obtained under the present experimental conditions. Similar to the corresponding magnesium-based series, the cadmium compounds are obtained only with the larger rare earth elements. The cell volumes (Table 1) decrease from the lanthanum to the samarium compound as expected from the lanthanoid contraction. The CePdCd$_2$ cell volume nicely fits in between the lanthanum and praseodymium compounds, indicating trivalent cerium.

A view of the NdPdCd$_2$ structure approximately along the $a$ axis is presented in Fig. 1. The cadmium substructure shows Cd–Cd distances ranging from 298 to 335 pm, close to the range in hcp cadmium (6 × 298 and 6 × 329 pm) \cite{29}. The palladium atoms are bound to the cadmium network with Pd–Cd distances of 281 and 283 pm, slightly longer than the sum of the covalent radii \cite{30} of 269 pm. This is indicative of strong Pd–Cd bonding, as also evident from the electronic structure calculations \cite{12}. The neodymium atoms bind to the three-dimensional [PdCd$_2$] network via shorter Nd–Pd distances of 286 and 299 pm, in good agreement with the sum of the covalent radii of 292 pm and with the trend of the electronegativities.

The strongly distorted trigonal prismatic neodymium coordination of the cadmium atoms is also shown in Fig. 1 in order to emphasize the structural relationship with the Zintl phase CaIn$_2$. The palladium insertion strongly distorts the structure, and each cadmium atom has only five nearest neodymium neighbors at Cd–Nd distances of 336–340 pm. The sixth neodymium atom is at the much longer distance of 487 pm and thus, the description as a filled CaIn$_2$ substructure is only a geometrical one in order to emphasize the structural relationship. For further crystal chemical details on related phases we refer to a review article \cite{31}.

Finally we draw back to the stability range of the MgCuAl$_2$-type phases. Although such compounds have been observed with a valence electron concentration (VEC) ranging from 17 to 20, for the magnesium and cadmium containing samples only VEC = 17 has so far been observed. First synthetic attempts with gold did not show the orthorhombic phase. Probably one needs to keep VEC = 17 because the magnesium and cadmium networks might not accept additional electrons, and gold compounds with an alkaline earth ele-
ment might therefore offer the way out. The clear segregation of magnesium and heavier alkaline earth elements is possible as recently shown by the synthesis of $\text{Ca}_4\text{AgMg}$ and $\text{Ca}_4\text{AuMg}$ [31].

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