

MgCuAl₂-type Intermetallics REPdCd₂ (RE = Ce, Pr, Nd, Sm)

Michael Johnscher and Rainer Pöttgen

Institut für Anorganische und Analytische Chemie,
Universität Münster, Corrensstrasse 30, D-48149
Münster, Germany

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

Z. Naturforsch. **2012**, 67b, 1221–1224

DOI: 10.5560/ZNB.2012-0224

Received August 22, 2012

The cadmium-rich intermetallic compounds REPdCd₂ (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 REPdCd₂ phases crystallize with the orthorhombic MgCuAl₂-type structure, space group *Cmcm*. The structure of NdPdCd₂ was refined from single-crystal X-ray diffractometer data: *a* = 421.9(3), *b* = 995.4(7), *c* = 834.5(6) pm, *wR* = 0.0286, 451 structure factors, 16 variables. The palladium and cadmium atoms build up a three-dimensional [PdCd₂] network (281–283 pm Pd–Cd; 298–335 pm Cd–Cd) in which the neodymium atoms fill cavities. They are connected to the [PdCd₂] network via shorter Nd–Pd bonds of 286 pm.

Key words: Cadmium, Intermetallics, Crystal Chemistry

Introduction

The MgCuAl₂-type structure [1, 2] has more than 100 representatives [3]. Geometrically it can be considered as a ternary ordered version of the Re₃B type [4], however, both structure types differ distinctly in chemical bonding. Ternary compounds with this structure type with the general formula ATX₂ (*A* = alkali, alkaline earth, or rare earth metal; *T* = Co, Ni, Rh, Pd, Ir, Pt, Au; *X* = Mg, Al, Ga, In, Tl, Sn, Cd) are known for valence electron concentrations per formula unit varying from 17 (e. g. LaPdMg₂) to 20 (e. g. CaPdSn₂). As emphasized in Fig. 1, the *X* atoms build up orthorhombically distorted networks of corner-sharing tetrahedra which derive from the structure of hexagonal diamond, lonsdaleite. Together with the *A* atoms, one obtains a distorted representative of the well known Zintl phase CaIn₂. Consequently, one can describe the ATX₂ intermetallics as transition metal-filled versions of AX₂. Detailed electronic structure investigations [5–8] have re-

vealed 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, Tl, and Sn, it was surprising that the MgCuAl₂-type structure is also formed with magnesium [9–13] as part of a tetrahedral network. Especially LaNiMg₂ 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 RE_{*x*}T_{*y*}Mg_{*z*} [21] and RE_{*x*}T_{*y*}Cd_{*z*} [22] intermetallic compounds, one can also consider RETCd₂ compounds in this context. So far only LaNiCd₂ [12], PrNi_{0.951}Cd₂ and LaPdCd₂ [23] have been reported. During our systematic phase analytical studies of RE_{*x*}T_{*y*}Cd_{*z*} intermetallics we have now obtained the remaining members of the REPdCd₂ (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 REPdCd₂ 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 1 : 1 : 2 always led to the equiatomic phases 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 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

Table 1. Refined lattice parameters (Guinier powder data) of the intermetallic compounds $REPdCd_2$ ($RE = La, Ce, Pr, Nd, Sm$). Standard deviations are given in parentheses.

| Compound | <i>a</i> (pm) | <i>b</i> (pm) | <i>c</i> (pm) | <i>V</i> (nm ³) | Reference |
|---------------------|---------------|---------------|---------------|-----------------------------|-----------|
| LaPdCd ₂ | 431.9(1) | 1015.7(4) | 835.7(2) | 0.3666 | [23] |
| CePdCd ₂ | 428.1(3) | 1006.7(7) | 836.5(6) | 0.3605 | this work |
| PrPdCd ₂ | 425.7(2) | 1003.5(7) | 837.0(6) | 0.3576 | this work |
| NdPdCd ₂ | 421.9(3) | 995.4(7) | 834.5(6) | 0.3505 | this work |
| SmPdCd ₂ | 417.6(4) | 990.0(4) | 835.6(3) | 0.3455 | this work |

MS09 pyrometer with an accuracy of ± 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 $REPdCd_2$ samples are slightly sensitive to moisture. They were kept in Schlenk tubes under argon. The powdered samples are dark gray, and single crystals exhibit metallic luster.

X-Ray diffraction

The polycrystalline $REPdCd_2$ samples were characterized by powder X-ray diffraction on a Guinier camera (equipped with a Fuji-film image plate system, BAS-1800) using $CuK\alpha_1$ radiation and α -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 NdPdCd₂ 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 $MoK\alpha$ 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 NdPdCd₂

Careful examination of the data set revealed a *C*-centered orthorhombic lattice, and the systematic extinctions were compatible with space group *Cmcm*, in agreement with our earlier work on LaPdCd₂ [23]. The atomic sites of the lanthanum compound were taken

Table 2. Crystallographic data and structure refinement of NdPdCd₂.

| | |
|--|-----------------------|
| Empirical formula | NdPdCd ₂ |
| Molar mass, g mol ⁻¹ | 475.48 |
| Crystal size, μm^3 | 20 × 30 × 50 |
| Space group; <i>Z</i> | <i>Cmcm</i> ; 4 |
| Structure type | MgCuAl ₂ |
| Lattice parameters (powder data) | |
| <i>a</i> , pm | 421.9(3) |
| <i>b</i> , pm | 995.4(7) |
| <i>c</i> , pm | 834.5(6) |
| Cell volume <i>V</i> , nm ³ | 0.3505 |
| Calculated density, g cm ⁻³ | 9.01 |
| <i>F</i> (000), e | 808 |
| Radiation; λ , pm | Mo $K\alpha$; 71.073 |
| Absorption coefficient, mm ⁻¹ | 31.3 |
| Transmission (max/min) | 0.595/0.490 |
| Detector distance, mm | 60 |
| Irradiation time, min | 6 |
| ω -range; step width, deg | 0–180/1.0 |
| Integr. param. A/B/EMS | 12.9/2.9/0.012 |
| θ range, deg | 4–35 |
| <i>hkl</i> range | ±6, ±16, ±13 |
| Total no. reflections | 2695 |
| Independent reflections/ <i>R</i> _{int} | 451/0.0291 |
| Reflections with $I > 2\sigma(I)/R_\sigma$ | 328/0.0220 |
| Data/ref. parameters | 451/16 |
| <i>R</i> / <i>wR</i> for $I > 3\sigma(I)$ | 0.0128/0.0247 |
| <i>R</i> / <i>wR</i> for all data | 0.0320/0.0286 |
| Goodness-of-fit (<i>F</i> ²) | 0.80 |
| Extinction coefficient | 187(6) |
| Largest diff. peak/hole, e Å ⁻³ | 1.86/−2.16 |

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.

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-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD-425064.

Crystal chemistry

Four new representatives of the MgCuAl₂-type structure have been synthesized. The $REPdCd_2$ series

| Atom | Wyckoff site | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> ₁₁ | <i>U</i> ₂₂ | <i>U</i> ₃₃ | <i>U</i> ₂₃ | <i>U</i> _{eq} |
|------|--------------|----------|------------|------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Nd | 4 <i>c</i> | 0 | 0.06419(3) | 1/4 | 98(1) | 72(1) | 128(2) | 0 | 99(1) |
| Pd | 4 <i>c</i> | 0 | 0.77723(5) | 1/4 | 109(2) | 96(2) | 101(2) | 0 | 102(1) |
| Cd | 8 <i>f</i> | 0 | 0.35630(3) | 0.04934(4) | 112(1) | 100(1) | 98(1) | 6(1) | 103(1) |

Table 3. Atomic coordinates and anisotropic displacement parameters (pm²) for NdPdCd₂. *U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor. *U*₁₂ = *U*₁₃ = 0.

Table 4. Interatomic distances (pm) in the structure of NdPdCd₂. All distances of the first coordination spheres are listed. Standard deviations are all smaller or equal than 0.1 pm.

| | | | | | | | |
|-----|---|----|-------|-----|----|-------|-------|
| Nd: | 1 | Pd | 285.6 | Cd: | 2 | Pd | 280.6 |
| | 2 | Pd | 299.1 | | 1 | Pd | 283.0 |
| | 2 | Cd | 335.5 | | 1 | Cd | 297.7 |
| | 4 | Cd | 336.4 | | 2 | Cd | 309.9 |
| | 4 | Cd | 339.6 | | 1 | Cd | 334.9 |
| | 2 | Nd | 421.9 | | 1 | Nd | 335.6 |
| Pd: | 2 | Nd | 436.4 | 2 | Nd | 336.4 | |
| | 4 | Cd | 280.6 | 2 | Nd | 339.6 | |
| | 2 | Cd | 283.0 | | | | |
| | 1 | Nd | 285.6 | | | | |
| | 2 | Nd | 299.1 | | | | |

exists with $RE = \text{La}$ [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 $RE\text{PdCd}_2$ 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 NdPdCd₂ 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) [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 [30] of 269 pm. This is indicative of strong Pd–Cd bonding, as also evident from the electronic structure calculations [12]. The neodymium atoms bind to the three-dimensional $[\text{PdCd}_2]$ 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

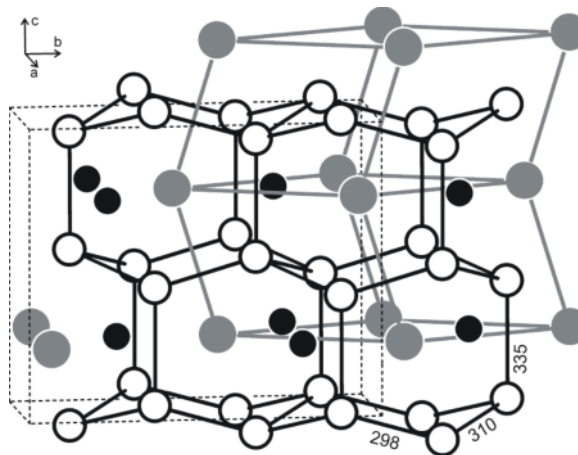


Fig. 1. View of the NdPdCd₂ structure approximately along the crystallographic *a* axis. Neodymium, palladium, and cadmium atoms are drawn as medium grey, black filled, and open circles, respectively. The lonsdaleite-related cadmium network and the distorted hexagonal neodymium subcell are emphasized.

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 [3].

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 Ca_4AgMg and Ca_4AuMg [31].

Acknowledgement

This work was financially supported by the Deutsche Forschungsgemeinschaft. We thank Dipl.-Ing. U. Ch. Rodewald for collecting the single-crystal diffraction data.

- [1] H. Perlitz, A. Westgren, *Ark. Kemi, Mineral. Geol.* **1943**, *16*, 1.
- [2] B. Heying, R.-D. Hoffmann, R. Pöttgen, *Z. Naturforsch.* **2005**, *60b*, 491.
- [3] R. Pöttgen, M. Lukachuk, R.-D. Hoffmann, *Z. Kristallogr.* **2006**, *221*, 435.
- [4] B. Aronsson, M. Bäckman, S. Rundqvist, *Acta Chem. Scand.* **1960**, *14*, 1001.
- [5] R.-D. Hoffmann, U. Ch. Rodewald, R. Pöttgen, *Z. Naturforsch.* **1999**, *54b*, 38.
- [6] R.-D. Hoffmann, D. Kußmann, U. Ch. Rodewald, R. Pöttgen, C. Rosenhahn, B. D. Mosel, *Z. Naturforsch.* **1999**, *54b*, 709.
- [7] R.-D. Hoffmann, R. Pöttgen, *Chem. Eur. J.* **2001**, *7*, 382.
- [8] S. Liu, J. D. Corbett, *Inorg. Chem.* **2003**, *42*, 4898.
- [9] M. E. Kost, A. L. Shilov, N. T. Kuznetsov, *Russ. J. Inorg. Chem.* **1988**, *33*, 467.
- [10] G. Renaudin, L. Guénée, K. Yvon, *J. Alloys Compd.* **2003**, *350*, 145.
- [11] K. Yvon, J.-Ph. Rapin, N. Penin, Z. Ma, M. Y. Chou, *J. Alloys Compd.* **2007**, *446–447*, 34.
- [12] A. Doğan, D. Johrendt, R. Pöttgen, *Z. Anorg. Allg. Chem.* **2005**, *631*, 451.
- [13] M. Kersting, R. Pöttgen, *Z. Naturforsch.* **2011**, *66b*, 651.
- [14] K. Yvon, G. Renaudin, C. M. Wie, M. Y. Chou, *Phys. Rev. Lett.* **2005**, *94*, 066403.
- [15] M. Di Chio, L. Schiffini, S. Enzo, G. Cocco, M. Baricco, *J. Alloys Compd.* **2007**, *434–435*, 734.
- [16] M. Di Chio, A. Ziggotti, M. Baricco, *Intermetallics* **2008**, *16*, 102.
- [17] M. Di Chio, L. Schiffini, S. Enzo, G. Cocco, M. Baricco, *Renewable Energy* **2008**, *33*, 237.
- [18] S. F. Parker, J. W. Taylor, H. Herman, J.-Ph. Rapin, N. Penin, K. Yvon, *J. Alloys Compd.* **2009**, *470*, 80.
- [19] L. Z. Ouyang, L. Yao, H. W. Dong, L. Q. Li, M. Zhu, *J. Alloys Compd.* **2009**, *485*, 507.
- [20] A. Teresiak, M. Uhlemann, A. Gebert, J. Thomas, J. Eckert, L. Schultz, *J. Alloys Compd.* **2009**, *481*, 144.
- [21] U. Ch. Rodewald, B. Chevalier, R. Pöttgen, *J. Solid State Chem.* **2007**, *180*, 1720.
- [22] F. Tappe, R. Pöttgen, *Rev. Inorg. Chem.* **2011**, *31*, 5.
- [23] A. Doğan, U. Ch. Rodewald, R. Pöttgen, *Z. Naturforsch.* **2007**, *62b*, 610.
- [24] R. Pöttgen, Th. Gulden, A. Simon, *GIT Laborfachzeitschrift* **1999**, *43*, 133.
- [25] R. Pöttgen, A. Lang, R.-D. Hoffmann, B. Künnen, G. Kotzyba, R. Müllmann, B. D. Mosel, C. Rosenhahn, *Z. Kristallogr.* **1999**, *214*, 143.
- [26] K. Yvon, W. Jeitschko, E. Parthé, *J. Appl. Crystallogr.* **1977**, *10*, 73.
- [27] V. Petříček, M. Dušek, L. Palatinus, JANA2006, The Crystallographic Computing System, Institute of Physics, University of Prague, Prague (Czech Republic) **2006**.
- [28] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **2007**, *40*, 786.
- [29] J. Donohue, *The Structures of the Elements*, Wiley, New York **1974**.
- [30] J. Emsley, *The Elements*, Oxford University Press, Oxford **1999**.
- [31] M. Kersting, S. F. Matar, C. Schwickert, R. Pöttgen, *Z. Naturforsch.* **2012**, *67b*, 61.