

# Solid State Syntheses and Structure of $\text{LaPdCd}_2$ and $\text{PrNi}_{0.951(4)}\text{Cd}_2$

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The intermetallic cadmium compounds  $\text{LaPdCd}_2$  and  $\text{PrNi}_{0.951(4)}\text{Cd}_2$  were synthesized from the elements in sealed tantalum tubes in an induction furnace. Both phases were investigated by X-ray diffraction on powders and single crystals:  $\text{MgCuAl}_2$ -type, *Cmcm*,  $Z = 4$ ,  $a = 431.9(1)$ ,  $b = 1015.7(4)$ ,  $c = 835.7(2)$  pm,  $wR2 = 0.0436$ , 326  $F^2$  values, 16 variables for  $\text{LaPdCd}_2$  and  $a = 420.26(8)$ ,  $b = 981.0(2)$ ,  $c = 815.3(1)$  pm,  $wR2 = 0.0404$ , 604  $F^2$  values, 17 variables for  $\text{PrNi}_{0.951(4)}\text{Cd}_2$ . A small nickel deficit was observed for the  $\text{PrNi}_{0.951(4)}\text{Cd}_2$  crystal. The cadmium atoms build up orthorhombically distorted three-dimensional networks (Cd–Cd distances: 302–334 pm) that resemble the structure of hexagonal diamond, lonsdaleite. Together with the palladium (nickel) atoms,  $[\text{PdCd}_2]$  and  $[\text{Ni}_{0.951(4)}\text{Cd}_2]$  networks are formed which leave distorted hexagonal channels for the rare earth atoms.

**Key words:** Cadmium, Intermetallics, Crystal Chemistry

## Introduction

The orthorhombic  $\text{MgCuAl}_2$ -type structure [1–3] has a great flexibility for substitution on all three atomic sites. Besides aluminides, gallides, indides, and thallides [3], also some stannides and even  $\text{LaNiMg}_2$  [4] and  $\text{LaNiCd}_2$  [5] have been reported. The lonsdaleite (hexagonal diamond) related networks in this peculiar structure type can be formed by a variety of elements with different valence electron concentration.

In the course of our systematic phase analytical studies of rare earth metal-transition metal-cadmium compounds [5–8] we have obtained the new phases  $\text{LaPdCd}_2$  and  $\text{PrNi}_{0.951(4)}\text{Cd}_2$  with  $\text{MgCuAl}_2$ -type structure. The syntheses, structure refinements and crystal chemistry of both compounds are reported herein.

## Experimental

### Synthesis

Starting materials for the preparation of  $\text{LaPdCd}_2$  and  $\text{PrNi}_{0.951(4)}\text{Cd}_2$  were lanthanum and praseodymium ingots (Johnson Matthey, > 99.9 %), palladium powder (Degussa-Hüls, ca. 200 mesh, > 99.9 %), nickel powder (Johnson-Matthey), and a cadmium rod ( $\varnothing 8$  mm, Johnson-Matthey), all with stated purities better than 99.9 %. Pieces of the three elements were weighed in the ideal 1 : 1 : 2 atomic ratios and sealed in tantalum ampoules under an argon pressure of about 600 mbar [9]. The argon was purified over molecular sieves, silica gel and titanium sponge (900 K). The tantalum tubes were then put in a water-cooled quartz sample chamber [10] of an induction furnace (Hüttinger Elektronik, Freiburg, Typ TIG 1.5/300).

The tubes were first rapidly heated to ca. 1640 K under flowing argon and kept for one minute. Subsequently the temperature was lowered to ca. 950 K and the sample was annealed for four hours at this temperature followed by quenching. The temperature was controlled through a Sensor Therm Metis MS09 pyrometer with an accuracy of  $\pm 30$  K. The samples could easily be separated from the tubes. No reaction with the crucible material was observed.  $\text{LaPdCd}_2$  and  $\text{PrNi}_{0.951(4)}\text{Cd}_2$  are slightly sensitive to moisture. The samples were kept under dry argon in Schlenk tubes. The polycrystalline samples are medium gray; single crystals exhibit metallic luster.

The bulk samples and the single crystals investigated on the diffractometers were analyzed by EDX using a LEICA 420 I scanning electron microscope with  $\text{LaB}_6$ ,  $\text{PrF}_3$ , Pd, and Cd as standards. The single crystals mounted on the quartz fibres were coated with a thin carbon film. The EDX analyses ( $25 \pm 1$  at.-% La:  $25 \pm 1$  at.-% Pd:  $50 \pm 1$  at.-% Cd and  $26 \pm 1$  at.-% Pr:  $23 \pm 1$  at.-% Ni:  $51 \pm 1$  at.-% Cd) revealed no impurity elements and were in agreement with the ideal 1 : 1 : 2 composition. For the nickel based crystal, the tendency for smaller nickel content was already evident from the EDX data.

### X-Ray powder and single crystal data

Both samples were characterized through X-ray powder patterns (Guinier technique) using  $\text{CuK}\alpha_1$  radiation and  $\alpha$  quartz ( $a = 491.30$ ,  $c = 540.46$  pm) as an internal standard. The Guinier camera was equipped with an imaging plate system (Fujifilm BAS-1800). The lattice parameters (Table 1) were obtained from least-squares fits of the Guinier data. The correct indexing was ensured through comparison of the experimental patterns with calculated ones [11] using the atomic positions obtained from the structure refinements.

Table 1. Crystal data and single crystal structure refinement of LaPdCd<sub>2</sub> and PrNi<sub>0.951(4)</sub>Cd<sub>2</sub>, MgCuAl<sub>2</sub>-type, orthorhombic space group *Cmcm*, Pearson code oC16, *Z* = 4.

Empirical formula	LaPdCd <sub>2</sub>	PrNi <sub>0.951(4)</sub> Cd <sub>2</sub>
Formula weight [g mol <sup>-1</sup> ]	470.11	424.42
Unit cell dimensions (Guinier data)		
<i>a</i> [pm]	431.9(1)	420.26(8)
<i>b</i> [pm]	1015.7(4)	981.0(2)
<i>c</i> [pm]	835.7(2)	815.3(1)
Cell volume <i>V</i> [nm <sup>3</sup> ]	0.3666	0.3361
Calculated density [g cm <sup>-3</sup> ]	8.52	8.39
Crystal size [μm <sup>3</sup> ]	10 × 30 × 45	80 × 100 × 100
Transm. ratio [max/min]	0.781/0.383	—
Absorption coefficient [mm <sup>-1</sup> ]	27.4	31.9
<i>F</i> (000) [e]	796	732
<i>θ</i> Range [°]	4–31	4–40
Range in <i>hkl</i>	±6, ±14, ±11	±7, ±17, ±14
Total no. of reflections	1901	4101
Independent reflections	326	604
	( <i>R</i> <sub>int</sub> = 0.0300)	( <i>R</i> <sub>int</sub> = 0.0754)
Reflections with <i>I</i> ≥ 2σ( <i>I</i> )	296	541
	( <i>R</i> <sub>σ</sub> = 0.0161)	( <i>R</i> <sub>σ</sub> = 0.0319)
Data/parameters	326/16	604/17
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.203	1.205
Final <i>R</i> indices		
<i>R</i> 1/ <i>wR</i> 2 ( <i>I</i> ≥ 2σ( <i>I</i> ))	0.0200/0.0422	0.0192/0.0394
<i>R</i> 1/ <i>wR</i> 2 (all data)	0.0239/0.0436	0.0239/0.0404
Extinction coefficient	0.0034(3)	0.0026(1)
Largest diff. peak / hole, [e Å <sup>-3</sup> ]	1.65/–0.92	1.78/–1.39

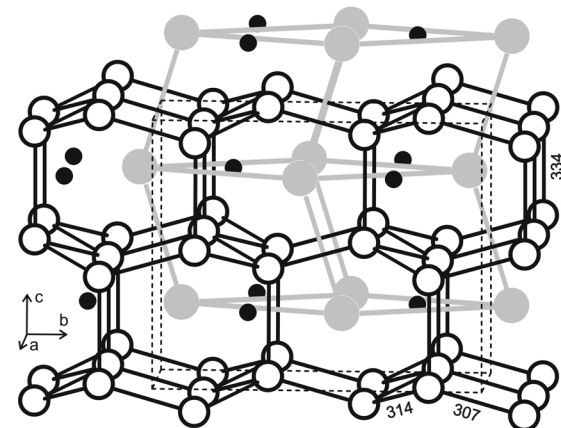


Fig. 1. Cutout of the LaPdCd<sub>2</sub> structure. Medium gray, open, and black filled circles represent lanthanum, cadmium, and palladium atoms, respectively. Selected bond lengths within the cadmium substructure are given in pm.

The lattice parameters of the powders and the single crystals agreed well.

Irregularly shaped single crystals of LaPdCd<sub>2</sub> and PrNi<sub>0.951(4)</sub>Cd<sub>2</sub> were selected from the annealed samples and examined by Laue photographs on a Buerger precession camera (equipped with an imaging plate system Fujifilm BAS-1800) in order to establish suitability for in-

Table 2. Atomic coordinates and isotropic displacement parameters (pm<sup>2</sup>) for LaPdCd<sub>2</sub> and PrNi<sub>0.951(4)</sub>Cd<sub>2</sub>. *U*<sub>eq</sub> is defined as one third of the trace of the orthogonalized *U*<sub>ij</sub> tensor. Note that the nickel site is occupied only by 95.1(4) %.

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> / <i>B</i>
LaPdCd <sub>2</sub> :					
La	4 <i>c</i>	0	0.06378(4)	1/4	126(2)
Pd	4 <i>c</i>	0	0.77904(6)	1/4	130(2)
Cd	8 <i>f</i>	0	0.35461(4)	0.05001(6)	131(2)
PrNi <sub>0.951(4)</sub> Cd <sub>2</sub> :					
Pr	4 <i>c</i>	0	0.06012(3)	1/4	93(1)
Ni	4 <i>c</i>	0	0.77686(7)	1/4	116(2)
Cd	8 <i>f</i>	0	0.35187(2)	0.05160(3)	98(1)

Table 3. Interatomic distances (pm), calculated with the powder lattice parameters of LaPdCd<sub>2</sub> and PrNi<sub>0.951(4)</sub>Cd<sub>2</sub>. Standard deviations are all equal or less than 0.1 pm. All distances within the first coordination spheres are listed.

LaPdCd <sub>2</sub>				PrNi <sub>0.951(4)</sub> Cd <sub>2</sub>			
La:	1	Pd	289.2	Pr:	1	Ni	277.9
	2	Pd	307.3		2	Ni	298.9
	2	Cd	339.4		2	Cd	328.8
	4	Cd	341.1		4	Cd	334.7
Pd:	4	Cd	346.0	Ni:	4	Cd	334.8
	2	La	431.9		2	Pr	420.3
	2	La	437.5		2	Pr	424.4
	4	Cd	283.7		4	Cd	275.2
Cd:	2	Cd	285.1	Cd:	2	Cd	276.4
	1	La	289.2		1	Pr	277.9
	2	La	307.3		2	Pr	298.9
	2	Pd	283.7		2	Ni	275.2
	1	Pd	285.1		1	Ni	276.4
	1	Cd	307.0		2	Cd	302.0
	2	Cd	314.3		1	Cd	302.6
	1	Cd	334.3		1	Cd	323.5
	1	La	339.4		1	Pr	328.8
	2	La	341.1		2	Pr	334.7
	2	La	346.0		2	Pr	334.8

tensity data collection. Single crystal intensity data of the PrNi<sub>0.951(4)</sub>Cd<sub>2</sub> crystal were collected at room temperature on a CAD4 four-circle diffractometer with graphite monochromatized MoK<sub>α</sub> radiation (71.073 pm) and a scintillation counter with pulse height discrimination. The scans were performed in the ω/2θ mode. The LaPdCd<sub>2</sub> crystal was measured on a Stoe IPDS-II diffractometer with MoK<sub>α</sub> radiation in oscillation mode. A numerical absorption correction was applied to this data set. All relevant crystallographic data for the data collections and evaluations are listed in Table 1. Examination of the systematic extinctions of both data sets was compatible with space group *Cmcm*. The atomic parameters of LaNi<sub>0.958(6)</sub>Cd<sub>2</sub> [5] were taken as starting values and the structures were refined using SHELXL-97 (full-matrix least-squares on *F*<sub>o</sub><sup>2</sup>) [12] with anisotropic atomic displacement parameters for all sites. As a check for possible

defects, the occupancy parameters were refined in a separate series of least-squares cycles. Except for the nickel site in the praseodymium compound, all sites were fully occupied within two standard uncertainties. In the final cycles the nickel occupancy parameter was refined as a least-squares variable. Final difference Fourier syntheses revealed no significant residual peaks (see Table 1). The positional parameters and interatomic distances are listed in Tables 2 and 3.

Further details on the structure refinements may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No.'s. CSD-417029 (LaPdCd<sub>2</sub>) and CSD-417030 (PrNi<sub>0.951(4)</sub>Cd<sub>2</sub>).

## Discussion

The cadmium compounds LaPdCd<sub>2</sub> and PrNi<sub>0.951(4)</sub>Cd<sub>2</sub> crystallize with the orthorhombic MgCuAl<sub>2</sub>-type structure. As an example, a drawing of the LaPdCd<sub>2</sub> unit cell is presented in Fig. 1. The structure can be considered as a transition metal filled, orthorhombically distorted variant of the well known Zintl phase CaIn<sub>2</sub> [13]. The strongly distorted hexagonal subcell is emphasized in the figure.

The cadmium atoms build up three-dimensional networks that resemble the structure of hexagonal dia-

mond, lonsdaleite [14]. The Cd–Cd distances range from 302 to 334 pm, similar to the Cd–Cd distances in *hcp* cadmium ( $6 \times 298$  and  $6 \times 329$  pm) [14]. Together, the palladium (nickel) and cadmium atoms build up three-dimensional [PdCd<sub>2</sub>] and [Ni<sub>0.951(4)</sub>Cd<sub>2</sub>] networks in which the lanthanum (praseodymium) atoms fill distorted hexagonal channels. The Ni–Cd (275–276 pm) and Pd–Cd (284–285 pm) distances are slightly longer than the sums of the covalent radii (256 pm Ni + Cd and 269 pm Pd + Cd) [15], similar to LaNi<sub>0.958(6)</sub>Cd<sub>2</sub> [5], indicative of substantial Ni–Cd and Pd–Cd bonding. For further crystal chemical details we refer to the previous work on LaNi<sub>0.958(6)</sub>Cd<sub>2</sub> [5].

Both LaNi<sub>0.958(6)</sub>Cd<sub>2</sub> [5] and PrNi<sub>0.951(4)</sub>Cd<sub>2</sub> reveal small nickel deficits. The nature of this defect formation is still unclear, since the electronic structure calculations [5] have shown, that the Fermi level cuts a region of bonding states, and even further bonding states could have been filled.

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