

# Palladium-Cadmium Ordering in $REPdCd$ ( $RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb$ ) and Comparison with Isotypic Indium Compounds

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Ternary intermetallic compounds  $REPdCd$  ( $RE = La, Ce, Pr, Nd, Sm, Eu, Tb$ ) were synthesized by reaction of the elements in sealed tantalum tubes in a high-frequency furnace. All compounds were investigated by X-ray diffraction on powders. Those with  $RE = La, Ce, Pr, Nd, Sm$ , and  $Tb$  contain trivalent rare earth metals and they crystallize with the hexagonal  $ZrNiAl$  type structure.  $NdPdCd$  [ $a = 764.8(3)$ ,  $c = 401.3(2)$  pm] and  $TbPdCd$  [ $a = 756.5(2)$ ,  $c = 389.0(1)$  pm] are reported here for the first time as well as  $EuPdCd$ . The compounds with  $La, Ce, Pr$ , and  $Sm$  [J. Alloys Compd. **182**, 87 (1992)] are confirmed. The crystal structure of  $EuPdCd$  was refined from X-ray single crystal diffractometer data:  $TiNiSi$  type,  $Pnma$ ,  $a = 745.9(3)$ ,  $b = 439.8(2)$ ,  $c = 863.7(3)$  pm,  $wR2 = 0.0405$ , 683  $F^2$  values, and 20 variable parameters. The three-dimensional [PdCd] substructure consists of strongly puckered, orthorhombically distorted  $Pd_3Cd_3$  hexagons with Pd-Cd distances ranging from 283 to 285 pm. The europium atoms fill the cavities within the [PdCd] network. Chemical bonding in the series  $REPdCd$  and  $REPdIn$  is compared.

## Introduction

We have recently started a systematic investigation of intermetallic rare earth metal ( $RE$ ) transition metal ( $T$ ) magnesium and cadmium compounds [1, 2, and ref. therein]. Interestingly these intermetallics are isotypic with the corresponding series of indium compounds [3]. The substitution has a drastic effect on (i) the chemical bonding and (ii) on the magnetic properties. To give some examples, in the series  $EuAuIn$  [4],  $EuAuCd$  [5], and  $EuAuMg$  [2, 6], the magnetic ordering temperature increases from 20 K ( $EuAuIn$ ) to 36 K ( $EuAuMg$ ). On the other hand, from  $GdPdIn$  [7, 8] to  $GdPdCd$  [9], the ordering temperature drastically decreases from 102 to 62.5 K. Investigation of chemical bonding in  $La_2Cu_2Mg$  [10] as compared to  $La_2Cu_2In$  [11] on the basis of extended Hückel calculations showed higher crystal orbital overlap populations for the Cu-In contacts as compared to the Cu-Mg contacts. This is also evident from the longer Cu-Mg bond lengths in  $La_2Cu_2Mg$ .

So far, in the series of  $RETCd$  compounds, only the series with gold as transition metal component [5],  $CeCuCd$  [12],  $EuAgCd$ ,  $YbAgCd$  [1] and the palladium based intermetallics  $REPdCd$  ( $RE = La, Ce, Pr, Sm, Gd$ ) [9, 13] have been reported. We have now investigated the palladium compounds in more detail. Herein we report on the synthesis of the new compounds  $NdPdCd$ ,  $EuPdCd$ , and  $TbPdCd$ , the structure refinement of  $EuPdCd$ , and a comparison of these intermetallics with the isotypic indium compounds.

## Experimental Section

### Synthesis

Starting materials for the preparation of  $REPdCd$  were sublimed ingots of the rare earth metals (Johnson Matthey), palladium 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 ingots were cut into smaller pieces in a glove-box and stored under argon prior to the reactions. The argon was purified over titanium sponge (900 K), silica gel, and molecular sieves.

Compound	<i>a</i> (pm)	<i>b</i> (pm)	<i>c</i> (pm)	<i>c/a</i>	<i>V</i> (nm <sup>3</sup> )	Ref.
LaPdCd	775.7(5)	<i>a</i>	412.9(5)	0.532	0.2152	this work
LaPdCd	772.3(1)	<i>a</i>	410.4(1)	0.531	0.2120	[13]
CePdCd	768.1(2)	<i>a</i>	406.37(8)	0.529	0.2076	this work
CePdCd	767.7(1)	<i>a</i>	405.8(1)	0.529	0.2071	[13]
PrPdCd	766.4(2)	<i>a</i>	403.2(1)	0.526	0.2051	this work
PrPdCd	766.2(1)	<i>a</i>	402.9(1)	0.526	0.2048	[13]
NdPdCd	764.8(3)	<i>a</i>	401.3(2)	0.525	0.2033	this work
SmPdCd	761.3(2)	<i>a</i>	396.05(9)	0.520	0.1988	this work
SmPdCd	760.4(3)	<i>a</i>	395.3(2)	0.520	0.1979	[13]
EuPdCd	745.9(3)	439.8(2)	863.7(3)	–	0.2833	this work
GdPdCd	758.2(1)	<i>a</i>	391.78(7)	0.517	0.1950	[9]
GdPdCd	758.2(6)	<i>a</i>	392.9(3)	0.518	0.1956	[13]
TbPdCd	756.5(2)	<i>a</i>	389.0(1)	0.514	0.1928	this work

Table 1. Lattice parameters of *REPdCd* (*RE* = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb) compounds with hexagonal ZrNiAl and orthorhombic TiNiSi type structure.

Due to the low boiling temperature of cadmium, all samples were prepared in sealed tantalum tubes. Pieces of the rare earth metal, the palladium powder, and the cadmium rod were mixed in the ideal 1:1:1 atomic ratio and sealed in small tantalum tubes (tube volume about 1 cm<sup>3</sup>) under an argon pressure of about 800 mbar [14]. The tantalum tubes were placed in a water-cooled quartz glass sample chamber in a high-frequency furnace (KONTRON Roto-Melt, 1.2 kW) under flowing argon [15]. They were first heated for one minute at about 1300 K. Subsequently the tubes were annealed at about 800 K for another two hours. The samples could easily be separated from the tantalum tubes after the annealing procedures. No reactions with the tubes could be detected. Compact pieces are light gray with metallic luster. All *REPdCd* compounds are not stable in moist air. Within a few hours a dark cusp is observed on the surface, most likely due to hydrolyses. The samples were therefore kept under dry argon in Schlenk tubes.

#### X-ray investigations

The samples were characterized through powder diffractograms (Stoe StadiP) using Cu-K<sub>α1</sub> 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. To ensure correct indexing, the patterns were compared with calculated ones [16] taking the atomic positions from the structure refinements of EuPdCd and GdPdCd [9]. For the europium compound the lattice parameters determined from the powder and the single crystal agreed well.

An irregularly shaped silvery single crystal of EuPdCd was taken from the annealed sample. It was examined on a Buerger precession camera equipped with an image plate system (Fujifilm BAS-2500) in order to establish suitability for intensity data collection. Single crystal intensity data were collected at room temperature by use of a four-

Table 2. Crystal data and structure refinement for EuPdCd.

Empirical formula	EuPdCd
Molar mass	370.76 g/mol
Unit cell dimensions	Table 1
Space group	<i>Pnma</i> (No. 62)
Calculated density	8.69 g/cm <sup>3</sup>
Crystal size	40 × 40 × 50 μm <sup>3</sup>
Transm. ratio (max/min)	1.53
Absorption coefficient	35.2 mm <sup>-1</sup>
<i>F</i> (000)	628
$\theta$ Range	3° to 35°
Range in <i>hkl</i>	±12, +7, ±13
Total no. reflections	2578
Independent reflections	683 ( <i>R</i> <sub>int</sub> = 0.0439)
Reflections with <i>I</i> > 2σ( <i>I</i> )	571 ( <i>R</i> <sub>sigma</sub> = 0.0316)
Data / parameters	683 / 20
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.092
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0238 <i>wR</i> 2 = 0.0377
<i>R</i> Indices (all data)	<i>R</i> 1 = 0.0348 <i>wR</i> 2 = 0.0405
Extinction coefficient	0.0198(6)
Largest diff. peak and hole	1.40 and -1.68 e/Å <sup>3</sup>

circle diffractometer (CAD4) with graphite monochromatized Mo-K<sub>α</sub> radiation (71.073 pm) and a scintillation counter with pulse height discrimination. The scans were performed in the ω/2θ 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.

#### Structure refinement of EuPdCd

The isotypism of EuPdCd with EuPdIn [4] (orthorhombic TiNiSi type [17]) was already evident from the X-ray powder data. Consequently, analyses of the systematic extinctions led to space group *Pnma*. The atomic parameters of EuPdIn were taken as starting values and the structure

Table 3. Atomic coordinates and anisotropic displacement parameters ( $\text{pm}^2$ ) for *EuPdCd*. All atoms lie on Wyckoff position  $4c$  ( $x$   $1/4$   $z$ ) of space group *Pnma*.  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [(ha^*)^2 U_{11} + \dots + 2hka^*b^* U_{12}]$ .  $U_{23} = U_{12} = 0$ . The occupancy parameters were refined in a separate series of least squares cycles. In the final run the ideal occupancies were assumed.

Atom	Occupancy	$x$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{13}$	$U_{\text{eq}}$
Eu	1.002(4)	0.03300(4)	0.68027(4)	136(1)	144(2)	133(2)	-6(1)	138(1)
Pd	0.989(6)	0.26510(7)	0.37271(6)	154(2)	151(2)	158(2)	-3(2)	154(1)
Cd	1.004(5)	0.14035(7)	0.06277(6)	155(2)	156(2)	128(2)	7(2)	146(1)

Table 4. Interatomic distances (pm), calculated with the lattice parameters taken from X-ray powder data of *EuPdCd*. All distances within the first coordination spheres are listed. Standard deviations are all equal or less than 0.1 pm.

Eu:	2	Pd	314.1	Pd:	2	Cd	283.3	
	2	Pd	316.1		1	Cd	283.4	
	1	Pd	317.1		1	Cd	285.4	
	2	Cd	338.1		2	Eu	314.1	
	1	Cd	339.9		2	Eu	316.1	
	2	Cd	343.5		1	Eu	317.1	
	1	Cd	360.3		Cd:	2	Pd	283.3
	2	Eu	384.4			1	Pd	283.4
	2	Eu	391.9			1	Pd	285.4
						2	Cd	322.4
			2	Eu		338.1		
			1	Eu		339.9		
			2	Eu	343.5			
			1	Eu	360.3			

was refined using SHELXL-97 (full-matrix least-squares on  $F_o^2$ ) [18] with anisotropic atomic displacement parameters for all atoms. Since palladium and cadmium differ only by two electrons, special care was taken in order to get the correct site assignment for both elements. In the first refinement stage both positions (palladium and cadmium) were refined with the scattering factor of palladium. Refinement of the occupancy parameters revealed an occupancy of 99.0(6)% for the palladium and 106.3(5)% for the cadmium site. Subsequently we refined the cadmium site with the correct scattering factor of cadmium resulting in occupancies of 98.9(6) (palladium) and 100.4(5)% (cadmium). Thus, both sites are fully occupied within two standard deviations and there is no indication for palladium-cadmium mixing. At this point we should keep in mind, that for *EuAgCd* [1], where silver and cadmium differ only by one electron, no silver-cadmium ordering was evident from the single crystal X-ray data. In the final cycles the ideal occupancies were assumed. Final difference Fourier syntheses revealed no significant residual peaks (see Table 2). The positional parameters

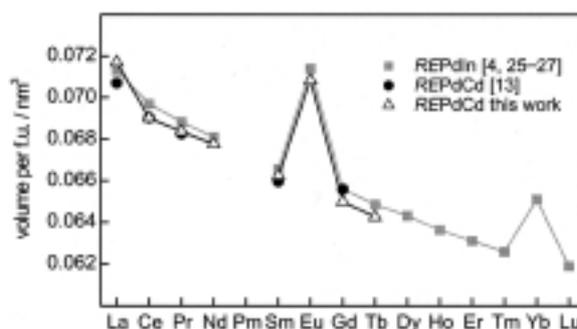


Fig. 1. Plot of the cell volumes per formula unit of *REPdCd* and *REPdIn*. The solid lines serve as a guide to the eye.

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

## Discussion

### Crystal chemistry

The *REPdCd* compounds with neodymium, europium, and terbium as rare earth metal component are reported here for the first time. In Fig. 1 we plot the cell volumes per formula unit of these intermetallics together with those reported previously by Iandelli [13] for *LaPdCd*, *CePdCd*, *PrPdCd*, *SmPdCd*, and *GdPdCd* [9]. The cell volumes decrease from the lanthanum to the terbium compound as expected from the lanthanoid contraction. Due to the divalent europium atoms, *EuPdCd* shows a large positive deviation from this plot. For *CePdCd*, *PrPdCd*, *SmPdCd*, and *GdPdCd* our lattice parameters are in excellent agreement with the data given by Iandelli [13]. For *LaPdCd*, however, we find a

\*Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD 412311.

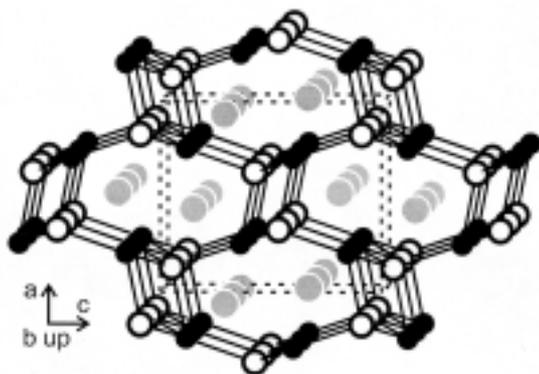


Fig. 2. View of the  $\text{EuPdCd}$  structure along the  $b$  axis. The europium, palladium, and cadmium atoms are drawn as gray, filled, and open circles, respectively. The three-dimensional  $[\text{PdCd}]$  network is emphasized.

slightly larger cell volume. This may be due to a homogeneity range  $\text{LaPd}_{1+x}\text{Cd}_{1-x}$  as it was recently observed for the series of isotypic gold compounds  $\text{REAuCd}$  [5]. In all cases, the transition metal atoms partially substitute the cadmium positions. In view of these results, the  $\text{LaPdCd}$  sample of Iandelli [13] most likely has the higher palladium content, since palladium is smaller than cadmium. The quality of single crystals from our  $\text{LaPdCd}$  sample was not sufficient for a structure refinement which would reveal the definite composition. Experiments with the heavier and higher melting rare earth metals revealed different X-ray powder patterns. So far it was not possible to investigate the structures on the basis of single crystal data.

The  $\text{REPdCd}$  compounds with a trivalent rare earth metal crystallize with the hexagonal  $\text{ZrNiAl}$  type structure [19 - 21], space group  $P62m$ . We have repeatedly discussed this structure type in previous papers concerning  $\text{RETMg}$  and  $\text{RETCd}$  compounds [5, 6]. For details we refer to these publications.

In Fig. 2 we present a view of the  $\text{EuPdCd}$  structure along the  $y$  axis.  $\text{EuPdCd}$  crystallizes with the orthorhombic  $\text{TiNiSi}$  type structure, similar to  $\text{EuAgMg}$  [22],  $\text{EuAuMg}$  [6], and  $\text{EuAuCd}$  [5]. The

palladium and cadmium atoms build a three-dimensional  $[\text{PdCd}]$  network in which the europium atoms are located. Each palladium atom has four cadmium neighbors in a strongly distorted tetrahedral coordination at Pd-Cd distances from 283 to 285 pm, slightly longer than the sum of the covalent radii of 269 pm [23]. We can therefore assume a significant degree of Pd-Cd bonding. The electronic structure of isotypic  $\text{EuAgMg}$  [2] was recently investigated by the TB-LMTO-ASA method. This pattern of chemical bonding can safely be applied also to  $\text{EuPdCd}$ . Within the  $[\text{PdCd}]$  network we observe Cd-Cd distances of 322 pm, only slightly longer than the average Cd-Cd distance of 314 pm in *hcp* cadmium [24].

Finally we compare the cadmium compounds with the series of isotypic indides [25 - 27]. Although the covalent radius of cadmium (141 pm) is significantly smaller than the radius of indium (150 pm) [23], we find almost the same cell volumes for  $\text{EuPdCd}$  ( $0.2833 \text{ nm}^3$ ) and  $\text{EuPdIn}$  ( $0.2856 \text{ nm}^3$ ) [4]. The same holds true also for the hexagonal compounds with  $\text{ZrNiAl}$  type structure (Fig. 1). From this behavior we can conclude that Pd-In bonding is stronger than Pd-Cd bonding. A quite similar situation occurs for the isotypic compounds  $\text{EuAuIn}$  [4],  $\text{EuAuMg}$  [6], and  $\text{EuAuCd}$  [5].  $T$ -In bonding is also stronger than  $T$ -Cd bonding in the series of  $\text{RE}_2\text{T}_2\text{Mg}$  and  $\text{RE}_2\text{T}_2\text{Cd}$  compounds [10, 28, 29]. This was recently investigated by extended Hückel calculations on  $\text{La}_2\text{Cu}_2\text{Mg}$  [10] and  $\text{La}_2\text{Cu}_2\text{In}$  [11]. The Cu-In crystal orbital overlap populations were higher than the Cu-Mg COOP's.

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