

Copper-rich Intermetallic Compounds $RECu_9Cd_2$ ($RE = La, Ce, Pr, Nd$) with YNi_9In_2 -type Structure

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The YNi_9In_2 -type copper-rich compounds $RECu_9Cd_2$ ($RE = La, Ce, Pr, Nd$) were synthesized directly from the elements in sealed niobium ampoules in an induction furnace and were characterized by powder X-ray diffraction. The structure of $PrCu_9Cd_2$ was refined from single-crystal X-ray diffractometer data: $P4/mbm$, $a = 849.0(3)$, $c = 498.2(3)$ pm, $wR2 = 0.0418$, 374 F^2 values, 23 variables. The structure has two striking polyhedral motifs: $Pr@Cu_{16}Cd_4$ and $Cu_2@Cu_8Cd_4$. The packing of these polyhedra describes the whole structure. The copper and cadmium atoms build up a three-dimensional $[Cu_9Cd_2]$ network with broader ranges of Cu–Cu (246–274 pm) and Cu–Cd (272–288 pm) distances. The cadmium atoms show segregation through pair formation with Cd–Cd distances of 288 pm.

Key words: Cadmium, Transition Metal-rich Intermetallics, Crystal Chemistry

Introduction

Binary transition metal-rich intermetallic compounds often form ternary ordering variants within solid solutions with a main group element on the transition metal sites. Typical examples are the phases $RECu_9Mg_2$ ($RE = Y, La-Nd, Sm-Ho, Yb$) with an ordered $CeNi_3$ structure [1] or the compounds $RENi_9Mg_2$ ($RE = La, Ce, Pr, Nd, Sm, Gd$) with an ordered $PuNi_3$ type [2]. Transition metal-*p*-element ordering is also possible for the $BaCd_{11}$ -type structure, *e. g.* for the silicide $NdCo_9Si_2$ [3]. With the same composition, the structures of YNi_9In_2 [4] and $Ce(Mn_{0.55}Ni_{0.45})_{11}$ [5] have been reported, however, they are not derived from a binary prototype.

Although these compounds are all transition metal-rich, they show varying substructures for the main

group element. The silicon atoms in $NdCo_9Si_2$ are well separated from each other, while the magnesium atoms in $TbCu_9Mg_2$ and $CeNi_9Mg_2$ are arranged in layers where each magnesium atom has three magnesium neighbors at 303, respectively 296 pm, even shorter than the average Mg–Mg distance of 320 pm in *hcp* magnesium [6]. In YNi_9In_2 one observes segregation of In_2 pairs with remarkably short In–In distances of 258 pm.

In the course of our systematic studies on structure-property relationships of $RE_xT_yMg_z$ [7] and $RE_xT_yCd_z$ [8] intermetallic compounds we were interested in cadmium intermetallics with YNi_9In_2 -type structure and with a potential segregation of Cd_2 pairs. Phase-analytical studies in the La–Cu–Cd [9] and Ce–Cu–Cd [10] systems revealed the existence of $LaCu_{7.4}Cd_{3.6}$ [9] and the solid solutions $CeCu_{11-x}Cd_x$ ($x = 2.4–4.8$) [10]. All of these phases were described with Cu/Cd mixing on the four Wyckoff sites. Recent structure refinement of $CaCu_9Cd_2$ [11] showed complete copper-cadmium ordering with Cd_2 dumb-bells with 291 pm Cd–Cd distance. We have now reinvestigated the copper-rich parts of the RE -Cu–Cd systems with the early rare earth elements. Herein we report on the synthesis and structure of the ordered phases $RECu_9Cd_2$ with $RE = La, Ce, Pr, Nd$.

Experimental

Synthesis

Starting materials for the preparation of the $RECu_9Cd_2$ samples were pieces of the rare earth elements (Smart Elements), copper wire (\varnothing 1 mm, Johnson Matthey), and a cadmium rod (Johnson Matthey), all with stated purities better than 99.9%. The moisture-sensitive pieces of the light rare earth elements were kept under dry argon in Schlenk tubes prior to the reactions. The argon was purified with titanium sponge (870 K), silica gel and molecular sieves. The elements were weighed in the ideal 1 : 9 : 2 atomic ratios and sealed in niobium ampoules [12] under an argon pressure of about 700 mbar. The latter were placed in a water-cooled quartz sample chamber of a high-frequency furnace (Hüttinger Elektronik, Freiburg, type TIG 1.5/300) [13] and first rapidly heated to *ca.* 1400 K under flowing argon. The temperature was kept for 10 min and then lowered at a rate of 50 K min^{-1} to 900 K. The tubes were annealed at this temperature for another four hours and then rapidly cooled by switching off the furnace (radiative heat loss). The samples

could mechanically be separated from the ampoules. They are air-stable over months. Larger polycrystalline pieces and small single crystals exhibit metallic luster. Ground powders are dark gray.

X-Ray diffraction

After the annealing sequence all $RECu_9Cd_2$ samples were analyzed by powder X-ray diffraction: Guinier technique (camera equipped with a Fuji-film image plate system, BAS-1800 readout device); $CuK\alpha_1$ radiation; α -quartz

($a = 491.30$, $c = 540.46$ pm) as an internal standard. Least-squares refinements of the powder data led to the tetragonal lattice parameters listed in Table 1. Correct indexing of the patterns was ensured by intensity calculations [14].

Well-shaped single crystals were selected from the crushed $PrCu_9Cd_2$ sample. Several 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 of a suitable specimen 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. The relevant crystallographic data are listed in Table 2.

Table 1. Lattice parameters (Guinier powder data) of tetragonal $RECu_9Cd_2$ samples. Standard deviations are given in parentheses.

Compound	a (pm)	c (pm)	V (nm ³)	Reference
$LaCu_9Cd_2$	852.8(2)	500.9(3)	0.3643	this work
$LaCu_{7.4}Cd_{3.6}$	867.8(10)	514.8(7)	0.3877	[9]
$CeCu_9Cd_2$	850.2(4)	499.2(3)	0.3608	this work
$CeCu_{6.2}Cd_{4.8}$	855.17(2)	506.62(1)	0.3705	[10]
$PrCu_9Cd_2$	849.0(3)	498.2(3)	0.3591	this work
$NdCu_9Cd_2$	847.3(2)	498.1(2)	0.3576	this work

Table 2. Crystallographic data and structure refinement of $PrCu_9Cd_2$.

Empirical formula	$PrCu_9Cd_2$
Molar mass, g mol ⁻¹	937.57
Crystal size, μm^3	$50 \times 50 \times 100$
Space group; Z	$P4/mbm$; 2
Structure type	YNi_9In_2
Lattice parameters (powder data)	
a , pm	849.0(3)
c , pm	498.2(3)
Cell volume V , nm ³	0.3591
Calculated density, g cm ⁻³	8.67
$F(000)$, e	832
Diffractometer	IPDS-II
Radiation; λ , pm	$MoK\alpha$; 71.073
Absorption coefficient, mm ⁻¹	38.4
Transmission (max/min)	0.588/0.350
Detector distance, mm	80
Irradiation time, min	3
ω range; step width, deg	0–180/1.0
Integr. param. A/B/EMS	14.0/2.0/0.030
θ range, deg	3–32
hkl range	$\pm 12, \pm 12, \pm 7$
Total no. reflections	3151
Independent reflections/ R_{int}	374/0.0946
Reflections with $I > 2\sigma(I)/R_\sigma$	285/0.0569
Data/ref. parameters	374/23
$R1/wR2$ for $I > 2\sigma(I)$	0.0335/0.0369
$R1/wR2$ for all data	0.0692/0.0418
Goodness-of-fit (F^2)	1.016
Extinction coefficient	0.0023(3)
Largest diff. peak/hole, e \AA^{-3}	1.51/–1.56

Results and Discussion

Structure Refinement of $PrCu_9Cd_2$

The data set showed a primitive tetragonal lattice. The systematic extinctions were compatible with space group $P4/mbm$, similar to $CaCu_9Cd_2$ [11]. The atomic positions of $CaCu_9Cd_2$ were used as starting parameters, and the structure was refined using the SHELXL-97 (full-matrix least-squares on F_o^2) routine [15] with anisotropic atomic displacement parameters (ADPs) for all atoms. Since our earlier data set of $EuCu_{9.14}Cd_{1.86}$ [11] revealed a small degree of Cu/Cd mixing, the occupancy parameters of all sites were refined in separate least-squares cycles. Similar to the results for $CaCu_9Cd_2$, the praseodymium compound was also observed to feature full ordering and no deviation from the ideal composition. A final difference Fourier synthesis was flat. The refined atomic positions, the ADPs, and the interatomic distances are given in Tables 3–5.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666;

Table 3. Atomic coordinates and anisotropic displacement parameters (pm²) for $PrCu_9Cd_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff site	x	y	z	U_{eq}
Pr	$2a$	0	0	0	118(2)
Cu1	$8j$	0.20828(13)	0.06378(12)	1/2	104(2)
Cu2	$2c$	0	1/2	1/2	130(4)
Cu3	$8k$	0.32152(8)	$x + 1/2$	0.2467(2)	109(2)
Cd	$4g$	0.11979(7)	$x + 1/2$	0	100(2)

Table 4. Anisotropic displacement parameters (pm^2) for PrCu_9Cd_2 .

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pr	119(3)	U_{11}	116(5)	0	0	0
Cu1	109(5)	82(5)	120(6)	0	0	14(4)
Cu2	121(6)	U_{11}	149(11)	0	0	37(8)
Cu3	120(3)	U_{11}	88(5)	0(3)	U_{23}	17(4)
Cd	99(3)	U_{11}	102(5)	0	0	-18(3)

Table 5. Interatomic distances (pm) in the structure of PrCu_9Cd_2 . All distances of the first coordination spheres are listed. Standard deviations are all smaller or equal than 0.2 pm.

Pr:	8	Cu1	310.2	Cu3:	1	Cu3	245.8
	8	Cu3	335.5		1	Cu2	248.7
	4	Cd	338.4		1	Cu3	252.4
Cu1:	1	Cu2	253.5	2	Cu1	253.9	
	2	Cu3	253.9	2	Cu1	259.8	
	2	Cu3	259.8	1	Cd	271.6	
	2	Cu1	261.5	2	Cd	285.9	
	1	Cu1	273.7	2	Pr	335.5	
	2	Cd	292.6	Cd:	2	Cu3	271.6
	2	Pr	310.2		4	Cu3	285.9
Cu2:	4	Cu3	248.7	2	Cu2	287.6	
	4	Cu1	253.5	1	Cd	287.7	
	4	Cd	287.6	4	Cu1	292.6	
				2	Pr	338.4	

E-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html on quoting the deposition number CSD-425067.

Crystal chemistry

YNi_9In_2 -type intermetallic compounds with cadmium had so far only been reported for $\text{LaCu}_{7.4}\text{Cd}_{3.6}$ [9], the solid solutions $\text{CeCu}_{11-x}\text{Cd}_x$ ($x = 2.4-4.8$) [10], CaCu_9Cd_2 , and $\text{EuCu}_{9.14}\text{Cd}_{1.86}$ [11]. The four compounds presented here, RECu_9Cd_2 with $\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$, expand this series of intermetallics. The lattice parameters (Table 1) decrease from the lanthanum to the neodymium compound as expected from the lanthanoid contraction. The CeCu_9Cd_2 cell volume nicely fits in between the lanthanum and praseodymium compounds, indicating trivalent cerium. For comparison we also list the $\text{LaCu}_{7.4}\text{Cd}_{3.6}$ and $\text{CeCu}_{6.2}\text{Cd}_{4.8}$ cell parameters in Table 1. The higher cadmium content (the covalent radii [16] of copper (117 pm) and cadmium (141 pm) differ drastically) in both phases leads to significantly enlarged cell volumes as compared to the ordered phases LaCu_9Cd_2 and CeCu_9Cd_2 . Based on the results

obtained for the cerium system [10], it is most likely that small homogeneity ranges exist also for the other RECu_9Cd_2 phases. Nevertheless, no binary ' RECu_{11} ' phases were found for these four systems. A significant amount of Cd is required for the stabilization of the YNi_9In_2 -type structure. Presumably the 4g site needs full cadmium occupancy, and then part of the remaining copper sites show Cu/Cd mixing on going to higher cadmium substitution.

A view of the PrCu_9Cd_2 structure approximately along the a axis is presented in Fig. 1. The structure contains two striking polyhedral motifs, $\text{Pr}@Cu_{16}Cd_4$ and $\text{Cu2}@Cu_8Cd_4$. The $\text{Pr}@Cu_{16}Cd_4$ polyhedra share common corners, edges, and faces, while only corner- and edge-sharing occurs for $\text{Cu2}@Cu_8Cd_4$. For clarity, only one layer of each type of condensed polyhedra is shown in Fig. 1.

Due to the high copper content one observes a broad range of Cu–Cu distances (246–274 pm), close to the Cu–Cu distances of 256 pm in *fcc* copper [6]. The cadmium atoms are segregated within the copper matrix (Fig. 2), however, not in an isolated form (*i. e.* no Cd–Cd bonding) but as pairs with a Cd–Cd distance of 288 pm, even slightly smaller than the shortest Cd–Cd distances in *hcp* cadmium (6×298 and

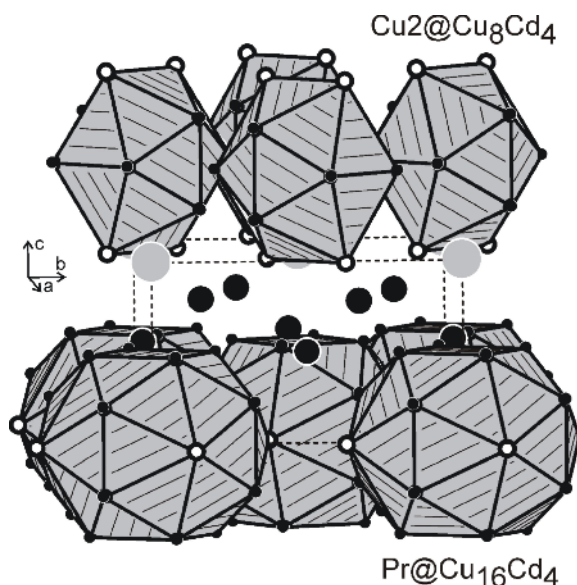


Fig. 1. View of the PrCu_9Cd_2 structure approximately along the crystallographic a axis. Praseodymium, copper, and cadmium atoms are drawn as medium grey, black filled, and open circles, respectively. The two striking polyhedral motifs around the Pr and Cu2 atoms are emphasized.

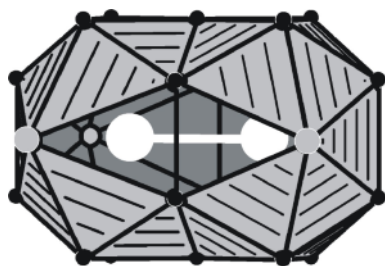


Fig. 2. Coordination of the Cd₂ dumb-bell in PrCu₉Cd₂. Praseodymium, copper, and cadmium atoms are drawn as medium grey, black filled, and open circles, respectively. The Cd₂ pairs correspond to the edges of the Cu₂@Cu₈Cd₄ polyhedra shown in Fig. 1.

6 × 329 pm) [6]. The Cu–Cd distances range from 272 to 288 pm and are much longer than the sum of the covalent radii of 258 pm [16], indicating only weak bonding character.

The YNi₉In₂-type intermetallics show a broad range for their valence electron concentration (VEC). Including all representatives listed in the Pearson data base [17], VEC ranges from 83 for GdFe₉Ti₂ to 108 for LaCu₉In₂. The cadmium compounds reported here have a VEC of 106. The largest influence on VEC is expected for a complete change of the transition metal. First attempts to fully substitute copper by cobalt, nickel, palladium, platinum, or gold were not successful. Further studies of solid solutions of this structure type are in progress in order to establish the stability ranges as a function of VEC and of the size of the elements forming the three-dimensional [T₉X₂] network.

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