

## Ca<sub>2</sub>Pd<sub>2</sub>Cd with W<sub>2</sub>B<sub>2</sub>Co-type Structure

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Ca<sub>2</sub>Pd<sub>2</sub>Cd was synthesized by high-frequency melting of the elements in a sealed niobium ampoule. Its structure was refined from single-crystal X-ray diffractometer data: W<sub>2</sub>B<sub>2</sub>Co type, *Immm*, *a* = 444.58(6), *b* = 590.25(6), *c* = 863.07(10) pm, *wR2* = 0.0252, 305 structure factors, 13 variables. The palladium and cadmium atoms build up two-dimensional [Pd<sub>2</sub>Cd] networks which consist of Pd<sub>4</sub>Cd<sub>2</sub> hexagons and Pd<sub>2</sub>Cd<sub>2</sub> rectangles with 272.7 pm Pd–Pd and 273.2 pm Pd–Cd. The calcium atoms are coordinated by one Pd<sub>4</sub>Cd<sub>2</sub> and one Pd<sub>2</sub>Cd<sub>2</sub> unit. The structure of Ca<sub>2</sub>Pd<sub>2</sub>Cd is compared to that of Ce<sub>2</sub>Pd<sub>2</sub>Cd with its tetragonal Mo<sub>2</sub>B<sub>2</sub>Fe type.

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

### Introduction

The Mo<sub>2</sub>B<sub>2</sub>Fe-type structure [1], a ternary ordered version of U<sub>3</sub>Si<sub>2</sub> [2, 3], has more than 200 representatives for element combinations RE<sub>2</sub>T<sub>2</sub>X (RE = rare earth element, T = transition metal; X = Mg, Zn, Cd, In, Sn, Pb) [4]. Since T elements from the Fe, Co, Ni, and Cu group can be used and the X component can be a di-, tri- or tetravalent element, significant variations of the valence electron concentration (VEC) are possible, leading to a broad variety of magnetic and electric properties in this family of compounds [4]. In the case of indides and stannides it is sometimes even possible to substitute the rare earth atoms by titanium, zirconium or hafnium [5–8]. Synthesis attempts for indides with the divalent alkaline earth elements or europium with lower VEC also led to compounds A<sub>2</sub>Pd<sub>2</sub>In and A<sub>2</sub>Pt<sub>2</sub>In (A = Ca, Sr, Eu) [9–11], however, these intermetallics crystallize with the monoclinic HT-Pr<sub>2</sub>Co<sub>2</sub>Al

type [12, 13], similar to Ca<sub>2</sub>Ir<sub>2</sub>Si [14], with distinctly different polyanionic networks.

In continuation of our systematic studies of AE<sub>2</sub>T<sub>2</sub>X intermetallics (AE = alkaline earth element) we obtained the cadmium compound Ca<sub>2</sub>Pd<sub>2</sub>Cd which again crystallizes with another structure, the orthorhombic W<sub>2</sub>B<sub>2</sub>Co type [15]. Parallel to our work the isotypic phase Ca<sub>2</sub>Pt<sub>2</sub>Cd was published by Samal and Corbett [16]. The synthesis and structure of Ca<sub>2</sub>Pd<sub>2</sub>Cd are reported in this Note.

### Experimental

#### Synthesis

Ca<sub>2</sub>Pd<sub>2</sub>Cd was synthesized directly from the elements. Starting materials were sublimed calcium ingots (Johnson Matthey, >99.5%), palladium plates (Allgemeine Gold- und Silberscheideanstalt, Pforzheim, >99.9%), and a cadmium rod (Johnson Matthey, >99.9%). The moisture-sensitive calcium pieces were kept under argon in a Schlenk tube prior to the reaction. The argon was purified with titanium sponge (870 K), silica gel and molecular sieves. A starting composition of 2Ca : 2Pd : 1Cd was arc-welded [17] in a niobium tube (*ca.* 1.5 cm<sup>3</sup> volume) under an argon pressure of about 700 mbar. The tube was placed in a water-cooled quartz sample chamber of an induction furnace (Hüttinger Elektronik, Freiburg, type TIG 1.5/300) [18] and first rapidly heated to *ca.* 1320 K. The temperature was then lowered to 870 K within 10 min, kept at that temperature for another four hours, followed by rapid cooling (switching off the power supply). The temperature was controlled through a Sensor Therm Methis MS09 pyrometer with an accuracy of ±30 K. The Ca<sub>2</sub>Pd<sub>2</sub>Cd sample could easily be separated from the niobium tube by mechanical fragmentation. Ca<sub>2</sub>Pd<sub>2</sub>Cd is slightly sensitive to moisture and was kept in a Schlenk tube under argon. The powdered sample is dark gray, and single crystals exhibit metallic luster.

#### EDX data

Semiquantitative EDX analyses of several single crystals were carried out in variable pressure mode with a Zeiss EVO<sup>®</sup> MA10 scanning electron microscope with wollastonite, palladium and cadmium as standards. The experimentally observed average compositions were close to the ideal one. No impurity elements were detected, except some niobium traces (only on the surface of some of the polycrystalline pieces) that resulted from a reaction with the crucible material.

Table 1. Crystallographic data and structure refinement of  $\text{Ca}_2\text{Pd}_2\text{Cd}$ .

Empirical formula	$\text{Ca}_2\text{Pd}_2\text{Cd}$
Molar mass, $\text{g mol}^{-1}$	405.36
Structure type	$\text{W}_2\text{B}_2\text{Co}$
Space group; $Z$	$Immm$ ; 2
Lattice parameters, pm (powder data)	$a = 444.58(6)$ $b = 590.25(6)$ $c = 863.07(10)$
Cell volume, $\text{nm}^3$	$V = 0.2265$
Crystal size, $\mu\text{m}^3$	$60 \times 70 \times 100$
Calculated density, $\text{g cm}^{-3}$	5.94
Transmission (max / min)	0.605 / 0.358
Detector distance, mm	60
Irradiation time, sec	5
$\omega$ range; step width, deg	$-59.9-43.9$ ; 0.3
Integr. param. A / B / EMS	7.0 / $-6.1$ / 0.013
Radiation; wavelength, pm	$\text{MoK}\alpha$ ; 71.073
Absorption coefficient, $\text{mm}^{-1}$	14.6
$F(000)$ , e	360
$\theta$ range, deg	4–35
$hkl$ range	$\pm 7, \pm 9, \pm 13$
Total no. reflections	5282
Independent reflections / $R_{\text{int}}$	305 / 0.0305
Reflections with $I > 2\sigma(I)$ / $R_\sigma$	295 / 0.0086
Data / parameters	305 / 13
Goodness-of-fit / $F^2$	1.233
$R1$ / $wR2$ for $I > 2\sigma(I)$	0.0121 / 0.0251
$R1$ / $wR2$ for all data	0.0125 / 0.0252
Extinction coefficient	0.0143(5)
Largest diff. peak / hole, $\text{e \AA}^{-3}$	0.45 / $-0.66$

### X-Ray diffraction

The polycrystalline  $\text{Ca}_2\text{Pd}_2\text{Cd}$  sample was characterized by powder X-ray diffraction on a Guinier camera (equipped with a Fuji-film image plate system, BAS-1800) using  $\text{CuK}\alpha_1$  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. The experimental pattern was compared to a calculated one [19] in order to ensure correct indexing.

Selected single crystals of  $\text{Ca}_2\text{Pd}_2\text{Cd}$  were glued to thin quartz fibers, and their quality was checked by Laue photographs on a Buerger camera (white Mo radiation). Intensity data were collected at room temperature by use of

a Stoe Stadi Vari diffractometer equipped with a Mo micro focus source and a Pilatus detection system and scaled subsequently following the Gaussian-shaped profile of the X-ray source. A numerical absorption correction was applied to the data set. All relevant details concerning the data collection and evaluation are listed in Table 1.

## Results and Discussion

### Structure refinement of $\text{Ca}_2\text{Pd}_2\text{Cd}$

Isotypism of  $\text{Ca}_2\text{Pd}_2\text{Cd}$  with the orthorhombic  $\text{W}_2\text{B}_2\text{Co}$  type was already evident from the Guinier powder data and from our recent investigation of  $\text{Pr}_2\text{Ni}_2\text{Sn}$  [20]. Careful examination of the data set revealed a body-centered orthorhombic lattice and no further systematic extinctions, in agreement with space group  $Immm$ . The atomic sites of  $\text{Pr}_2\text{Ni}_2\text{Sn}$  [20] were taken as starting values, and the structure was refined with anisotropic displacement parameters for all atoms with SHELXL-97 (full-matrix least-squares on  $F_o^2$ ) [21, 22]. Separate refinement of the occupancy parameters revealed no deviation from the ideal composition. All sites were fully occupied within one standard deviation. A final difference Fourier synthesis showed no significant residual peaks. The refined atomic positions, the displacement parameters, and the interatomic distances are given in Tables 2 and 3.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; E-mail: [crysdta@fiz-karlsruhe.de](mailto:crysdta@fiz-karlsruhe.de), [http://www.fiz-karlsruhe.de/request\\_for\\_deposited\\_data.html](http://www.fiz-karlsruhe.de/request_for_deposited_data.html)) on quoting the deposition number CSD-425471.

### Crystal chemistry

$\text{Ca}_2\text{Pd}_2\text{Cd}$  crystallizes with the orthorhombic  $\text{W}_2\text{B}_2\text{Co}$ -type structure, space group  $Immm$ , similar to  $\text{Ca}_2\text{Pt}_2\text{Cd}$  [16] and  $\text{Ca}_2\text{Cu}_2\text{Ga}$  [23]. A view of

Table 2. Atomic coordinates and anisotropic displacement parameters ( $\text{pm}^2$ ) for  $\text{Ca}_2\text{Pd}_2\text{Cd}$ .  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.  $U_{23} = U_{13} = U_{12} = 0$ .

Atom	Wyckoff site	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{\text{eq}}$
Ca	$4j$	1/2	0	0.29864(6)	229(2)	204(2)	192(2)	208(2)
Pd	$4h$	0	0.23098(4)	1/2	190(1)	191(1)	214(1)	198(1)
Cd	$2a$	0	0	0	179(1)	187(1)	275(1)	214(1)

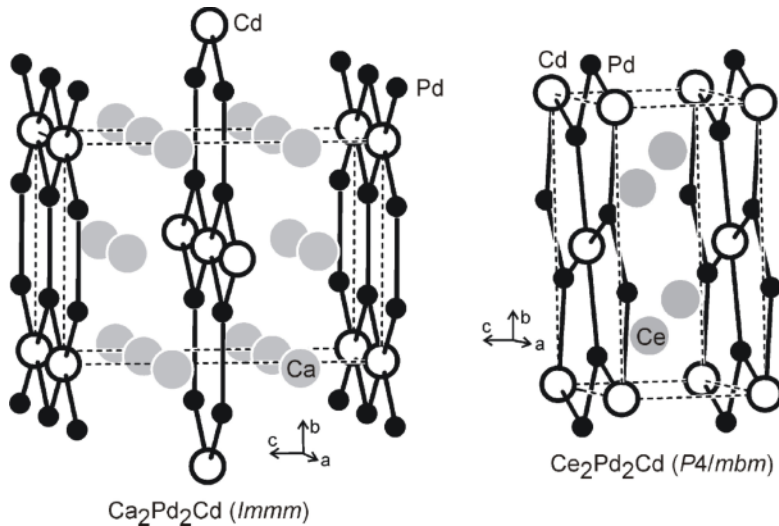


Fig. 1. View of the  $\text{Ca}_2\text{Pd}_2\text{Cd}$  ( $\text{W}_2\text{B}_2\text{Co}$  type) and  $\text{Ce}_2\text{Pd}_2\text{Cd}$  ( $\text{Mo}_2\text{B}_2\text{Fe}$  type) [28] structures approximately along the  $a$  axis. Calcium (cerium), palladium, and cadmium atoms are drawn as medium grey, black filled, and open circles, respectively. The two-dimensional  $[\text{Pd}_2\text{Cd}]$  networks are emphasized.

Table 3. Interatomic distances (pm) in the structures of  $\text{Ca}_2\text{Pd}_2\text{Cd}$  and  $\text{Ce}_2\text{Pd}_2\text{Cd}$  [28]. All distances of the first coordination spheres are listed. Standard deviations are all smaller or equal than 0.2 pm.

$\text{Ca}_2\text{Pd}_2\text{Cd}$			$\text{Ce}_2\text{Pd}_2\text{Cd}$		
Ca:	2 Pd	302.7	Ce:	2 Pd	293.1
	4 Pd	313.4		4 Pd	308.8
	2 Cd	340.4		4 Cd	348.2
	2 Cd	342.5		1 Ce	383.9
	1 Ca	347.6		2 Ce	393.3
	4 Ca	378.9		4 Ce	406.3
Pd:	1 Pd	272.7	Pd:	1 Pd	281.5
	2 Cd	273.2		2 Ce	293.1
	2 Ca	302.7		2 Cd	306.1
	4 Ca	313.4		4 Ce	308.8
Cd:	4 Pd	273.2	Cd:	4 Pd	306.1
	4 Ca	340.4		8 Ce	348.2
	4 Ca	342.5			

the  $\text{Ca}_2\text{Pd}_2\text{Cd}$  structure approximately along the  $a$  axis is presented in Fig. 1. The palladium and cadmium atoms build up two-dimensional networks which are composed of  $\text{Pd}_2\text{Cd}_2$  rectangles and elongated  $\text{Pd}_4\text{Cd}_2$  hexagons. The Pd–Cd distances within these rings are 273 pm long, and they compare well with the sum of the covalent radii of 269 pm [24]. Similar Pd–Cd distances occur in the three-dimensional  $[\text{Pd}_3\text{Cd}]$  network of  $\text{Pr}_6\text{Pd}_{13}\text{Cd}_4$  [25] (274 pm), while they are slightly longer in the  $[\text{PdCd}_2]$  network of  $\text{LaPdCd}_2$  [26] (284–285 pm). Besides the covalent Pd–Cd bonding, the  $[\text{Pd}_2\text{Cd}]$  network is also stabilized by Pd–Pd bonds (272 pm), even slightly shorter than in *fcc* palladium (275 pm) [27]. Due to the body-centered

structure, every other  $[\text{Pd}_2\text{Cd}]$  network is shifted by  $1/2 \ 1/2 \ 1/2$ . The networks are separated and charge-balanced by the calcium atoms.

In contrast to  $\text{Ca}_2\text{Pd}_2\text{Cd}$ , all  $\text{RE}_2\text{Pd}_2\text{Cd}$  intermetallics [28–31] crystallize in the tetragonal  $\text{Mo}_2\text{B}_2\text{Fe}$  type. The  $\text{Ce}_2\text{Pd}_2\text{Cd}$  structure is shown for comparison in Fig. 1. Again the palladium and cadmium atoms build up a two-dimensional  $[\text{Pd}_2\text{Cd}]$  network, however, the latter solely consists of distorted  $\text{Pd}_3\text{Cd}_2$  pentagons with much longer Pd–Cd (306 pm) and Pd–Pd (282 pm) distances [28]. These layers are stacked in AA sequence, and they are separated and charge-balanced by the cerium atoms.

The near-neighbor coordination of the calcium and cerium atoms in both structures is shown in Fig. 2. In total each metal cation has six palladium and

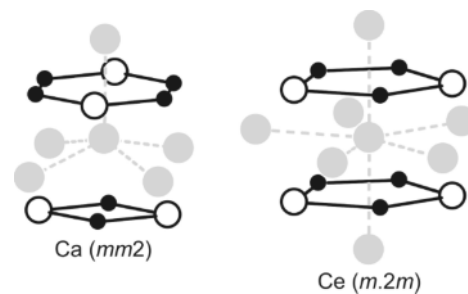


Fig. 2. Coordination of the calcium and cerium atoms in the structures of  $\text{Ca}_2\text{Pd}_2\text{Cd}$  and  $\text{Ce}_2\text{Pd}_2\text{Cd}$  [28]. Calcium (cerium), palladium, and cadmium atoms are drawn as medium grey, black filled, and open circles, respectively. The site symmetries are indicated.

four cadmium neighbors, but with different coordination,  $2 \times \text{Pd}_3\text{Cd}_2$  in  $\text{Ce}_2\text{Pd}_2\text{Cd}$  vs.  $\text{Pd}_4\text{Cd}_2 + \text{Pd}_2\text{Cd}_2$  in  $\text{Ca}_2\text{Pd}_2\text{Cd}$ . This leads to differences in the Ca–Ca vs. Ce–Ce coordinations. The two  $\text{Pd}_3\text{Cd}_2$  pentagons in  $\text{Ce}_2\text{Pd}_2\text{Cd}$  are separated by 393 pm, and we observe five equatorial cerium neighbors and one above and below. The  $\text{Pd}_4\text{Cd}_2$  hexagon and the  $\text{Pd}_2\text{Cd}_2$  rectangle in  $\text{Ca}_2\text{Pd}_2\text{Cd}$  show larger separation of 431 pm, and the calcium atoms react on the smaller size of the  $\text{Pd}_2\text{Cd}_2$  rectangle. They move toward the  $\text{Pd}_2\text{Cd}_2$  rectangle, a puckering effect in order to optimize bonding with these palladium and cadmium atoms.

In summary, the substitution of the rare earth atoms in  $\text{RE}_x\text{T}_y\text{Cd}_z$  phases [32] by alkaline earth metals offers interesting new structural possibilities. The change in size and VEC leads to different structural motifs. Currently we systematically investigate the *AE-T-Cd* systems with respect to phase formation and crystal chemistry. First results show close similarities with the corresponding *AE-T-Mg* systems [33].

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