Crystal structure of $R_3Pd_{25-x}B_{8-y}$, $R = \text{La, Ce}$

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Abstract. New ternary compounds $\text{La}_3\text{Pd}_{25-x}\text{B}_{8-y}$ ($x=1.75$, $y=0.07$) and $\text{Ce}_3\text{Pd}_{25-x}\text{B}_{8-y}$ ($x=1.25$, $y=2.00$) have been synthesized by arc melting. Their crystal structures were determined from X-ray single crystal diffraction data. Both compounds crystallize with a new monoclinic structure type, space group $P 2_1/c$ with $a=1.17567(2)$ nm, $b=1.05757(2)$ nm, $c=1.60664(3)$ nm, $\beta=102.1788(10)$ deg, $R_F^2=0.030$ for 7427 structure factors and 289 variable parameters for $\text{La}_3\text{Pd}_{25-x}\text{B}_{8-y}$ and $a=1.17453(3)$ nm, $b=1.04571(3)$ nm, $c=1.59759(5)$ nm, $\beta=102.132(2)$ deg, $R_F^2=0.035$ for 2805 structure factors and 283 variable parameters for $\text{Ce}_3\text{Pd}_{25-x}\text{B}_{8-y}$. Rietveld refinement for the X-ray powder diffraction patterns for both compounds confirmed the structure models determined from X-ray single crystal diffraction data.

1. Introduction

Exceptional physical properties discovered for CePt$_3$Si [1, 2, 3] prompted us to expand our investigations towards related systems with boron. In continuation of these studies, a series of novel ternary compounds $M_2\text{Pd}_{14+x}\text{B}_{5-x}$ ($M=\text{Th, Ce, Pr, Nd, Sm, Eu, Gd}$) was reported recently [4] of which the crystal structures of $\text{Nd}_2\text{Pd}_{14+x}\text{B}_{5-x}$ and $\text{Th}_2\text{Pd}_{14+x}\text{B}_{5-x}$ were determined from X-ray single crystal data [4] and found to be closely related to the structure type of $\text{Sc}_4\text{Ni}_{29}\text{Si}_{10}$ [5]. The evaluation of X-ray powder diffraction data of the light rare earths containing members (from Ce to Gd) of this series revealed isotypism with the $\text{Nd}_2\text{Pd}_{14+x}\text{B}_{5-x}$ and $\text{Th}_2\text{Pd}_{14+x}\text{B}_{5-x}$ structure. The $\text{La}_2\text{Pd}_8\text{B}_{6}$ sample, initially prepared as non-magnetic counterpart to the magnetic rare earth compounds, however, showed a hitherto unknown X-ray powder diffraction pattern. In the course of our studies of the Ce-Pd-B system at 850 ºC, similar X-ray diffraction patterns were observed for alloys within the concentration range 70-75 at.% Pd. Detailed structural studies of these novel phases became the subject of the present paper.

2. Experimental

$\text{La}_2\text{Pd}_8\text{B}_{6}$ and $\text{Ce}_3\text{Pd}_{25-x}\text{B}_{8-y}$ samples with a total amount of about 1g, were prepared by argon arc-melting elemental pieces of lanthanum and cerium (purity >99.9 mass%, Auer Remy, D), palladium foil (99.9%, Ögussa, A) and crystalline boron (98%, Alfa Aesar, D). For homogeneity, the samples were re-melted several times without significant weight losses (< 1 mass%). The alloy buttons were wrapped in Mo-foil, sealed in an evacuated quartz tube and annealed at 850 ºC for 240 h before quenching in cold water. X-ray powder diffraction data were collected employing a Guinier-Huber image plate system with monochromatic Cu $K\alpha_1$ radiation ($8^\circ<2\theta<100^\circ$). Precise lattice parameters were calculated by least squares fits to the indexed 20 values calibrated with Ge as internal standard ($a_{\text{Ge}}=0.565791$ nm). Single crystals were mechanically isolated from the crushed as cast alloys. Inspections on an AXS-GADDS texture goniometer assured high crystal quality, unit cell dimensions and monoclinic Laue symmetry of the specimens prior to the X-ray intensity data collections on a four-circle Nonius Kappa diffractometer equipped with a CCD area detector employing graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071069$ nm). Orientation matrices and unit cell parameters were derived using the program DENZO [6] (Table 1). No absorption corrections were performed because of the rather regular crystal shapes and small dimensions of the investigated specimens. The
structures were solved by direct methods and were refined with the SHELXL-97 program [7, 8]. Quantitative Rietveld refinements of the X-ray powder diffraction data were performed with the FULLPROF program [9].

**Table 1.** Structural data for R$_3$Pd$_{25-x}$B$_{8-y}$; R=La, Ce (space group $P2_1/c$; No. 14).

| Alloy composition | La$_{9.5}$Pd$_{67}$B$_{23.5}$ | Ce$_{9}$Pd$_{73}$B$_{18}$ |
|-------------------|------------------------------|--------------------------|
| Formula from refinement | La$_{12}$Pd$_{93.09}$B$_{31.75}$ | Ce$_{12}$Pd$_{95.09}$B$_{24}$ |
| Data collection | Nonius KappaCCD | Nonius KappaCCD |
| Radiation | MoK$_\alpha$ | MoK$_\alpha$ |
| 2$\theta$ range | 2.32 < 2$\theta$ < 72.60 | 2.34 < 2$\theta$ < 55.00 |
| Crystal size | 18x18x35$\mu$m$^3$ | 15x15x28$\mu$m$^3$ |
| $a$ [nm] | 1.17567(2) | 1.17453(3) |
| $b$ [nm] | 1.05757(2) | 1.04571(3) |
| $c$ [nm] | 1.60664(3) | 1.59759(5) |
| $\beta$[deg] | 102.1788(10) | 102.132(2) |
| Reflections in refinement | 7427 F$_o$ >4$\sigma$(F$_o$) of 9344 | 2805 F$_o$ >4$\sigma$(F$_o$) of 8593 |
| Mosaicity | <0.55 | <0.45 |
| Number of variables | 289 | 283 |
| $R_p^2 = \Sigma|F_o^2-F_c^2|^2/2F_o^2$ | 0.030 | 0.035 |
| $R_{int}$ | | |
| GOF | 1.030 | 1.036 |
| Extinction (Zachariasen) | 0.00015(1) | 0.00007(2) |
| Residual electron density; max; min in [electrons/Å$^3$] | 3.31; -3.49 | 4.13; -3.95 |

3. Results

3.1. X-ray single crystal diffraction

Single crystal X-ray intensity patterns indicated for both crystals Laue class 2/m and systematic extinctions consistent with space group $P2_1/c$ (no. 14). Intensity statistics unambiguously confirmed the probability of a centrosymmetric space group ($|E^2-1|=0.976$) [10].

3.1.1. La$_3$Pd$_{25}$B$_{8.5}$ structure. Initial atomic positions for heavy atoms La and Pd were found by direct methods whereas eight boron atoms were located from difference Fourier synthesis. The Pd2 and Pd25 sites exhibited an increased ADP (atom displacement parameter) indicating partial occupancy. This structure model was refined to a residual value $R_p^2 = 0.035$ with anisotropic thermal displacement parameters for the metal atoms but isotropic temperature factors for the boron atoms, resulting in the chemical formula La$_9$Pd$_{47.8}$B$_{16}$. An additional peak (13.7 e/Å$^3$) in the difference electron density map at the distance of 0.065 nm from Pd23 and at 0.145 nm from B8 was assigned to a partially occupied Pd24 site. When allowed to refine freely, the occupancy of Pd23/Pd24 and B8 sites converged to 0.923(2)/0.077(2) and 0.923(2), respectively. Replacement of Pd24 by a boron atom resulted in 100(0)% occupancy of this atomic position whereas the occupancy of Pd23 and B8 sites remained unchanged. In case the occupancy parameters of positions filled by mixture of Pd23 and B atoms and only boron were constrained to 1.0, the refinement was unsatisfactory revealing unacceptably small ADP’s of boron atom and two additional peaks of electron density 17 e/Å$^3$ and 13 e/Å$^3$ at the distance 0.012 nm and 0.074 nm respectively from Pd23. This procedure did not improve the distances as well:
still short Pd23-boron atom and boron - boron contacts (0.065 nm and 0.145 nm) prevented the coexistence of all three atoms in the unit cell. The analysis of the coordination figure for this atomic site in case of its occupancy by boron atom showed that due to the smaller atomic radii, the B atom could contact only 4 neighbouring atoms arranged in form of an unusual almost flat and distorted tetrahedron with the central B atom itself staying aside the polyhedron. All these reasons prompted us to remain with the solution of the split sites Pd23/Pd24 with a filling level of 92.3/7.7%. Attempts to attain an ordered structure model in space groups of lower symmetry were unsuccessful. Thus we kept the structure model in space group P21/c finally arriving at the formula La6Pd49-xB16-y with a reliability factor \(R_f^2=3.14\%\). To verify our results and to check on the atom order, X-ray intensity data were collected for a second crystal specimen: the structure solution arrived at an identical arrangement of atomic sites and split sites but refinement converged to a slightly higher value of \(R_f^2 = 3.54\%\).

3.1.2. Ce3Pd25-xB8-y structure. The structure solution in P21/c space group by direct methods revealed 3 atomic positions of cerium and 24 atomic positions of palladium. Although isotypism with the structure model for the La-compound was obvious, the structure refinement (residual value \(R_f^2=12.58\%\) adopting isotropic thermal parameters for all atoms) yielded a significant residual electron density of 69 e/\(\text{Å}^3\) in (1/2,0,0) at a distance of 0.236 nm from Pd26 and large displacement parameters for Pd10 and Pd26 (the atomic numbers correspond to the ones given in table 2). A corresponding atomic site was attributed to Pd28 and occupancy parameters were refined for all three atoms Pd10, Pd26 and Pd28. This procedure improved the R factor to 10.69\% for a partial occupancy of Pd10, Pd26 and Pd28 sites. Six boron atoms were located from difference Fourier syntheses and the structure was refined to \(R_f^2=7.21\%\) adopting anisotropic thermal parameters for heavy atoms and isotropic displacement parameters for borons. Due to a rather significant residual electron density of 22.93 e/\(\text{Å}^3\) observed at (0.2700, 0.4187, 0.4868) in the vicinity of Pd10, this atomic site had also to be refined as split position \(d_{\text{Pd10-Pd27}}=0.089\) nm). The following refinement of ADP’s resulted in a filling level of 80(1)% Pd10 + 20(1)% Pd27 (\(R_f^2=5.28\%\)). Because of unacceptably large displacement parameters for Pd26, i.e. 0.246(9), the Pd26 atomic position was split into (0.6543, 0.1594, 0.0283) (Pd26) and (0.6055, 0.0746, 0.0116) (Pd23). This procedure reduced the residual electron density to acceptable 4.13 e/\(\text{Å}^3\) and a final structure refinement yielded \(R_f^2=3.51\%\) suggesting occupancies as 50(1)% Pd26/Pd28, 30(1)% Pd23 + 20(1)% Pd26.

Comparing the atomic positions of the two structures, we observe that the structure models of Ce3Pd25-xB8-y and La6Pd49-xB16-y differ only by the occupancy of Pd positions within a domain with partially filled atomic sites in the Ce structure, and by the presence of two additional boron positions in the La structure (Table 2). After structural refinement for Ce3Pd25-xB8-y was accomplished, we reconsidered the La structure model assuming that the partially occupied atomic sites observed in the Ce structure are not filled in the La structure. Due to a slightly increased ADP of Pd10 a refinement of the occupancy parameter for this atomic site showed only 93.1\%. As a result, the final difference Fourier map revealed residual peaks as low as 3.31 e\(\text{Å}^3\) at the distance 0.048 nm from Pd23 and the R value was reduced to \(R_f^2=3.00\%\).
Table 2. Atomic coordinates and equivalent isotropic displacement parameters in [10^2 nm^2] for the atoms in R3Pd_{25-x}B_{8-y}.

| Atom | Wyckoff | notation | La_{3}Pd_{25-x}B_{8-y} | Ce_{3}Pd_{25-x}B_{8-y} | La_{3}Pd_{25-x}B_{8-y} | Ce_{3}Pd_{25-x}B_{8-y} | La_{3}Pd_{25-x}B_{8-y} | Ce_{3}Pd_{25-x}B_{8-y} |
|------|---------|----------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
|      |         | Pd1      | 0.0137(4)              | 0.1379(10)             | 0.5646(5)              | 0.5672(10)             | 0.3955(7)              | 0.3983(12)             |
|      |         | Pd5      | 0.0180(4)              | 0.1812(10)             | 0.4940(5)              | 0.4972(10)             | 0.2957(7)              | 0.2987(12)             |
|      |         | Pd6      | 0.0190(4)              | 0.1931(10)             | 0.5142(5)              | 0.5174(10)             | 0.3465(7)              | 0.3497(12)             |
|      |         | Pd9      | 0.0220(4)              | 0.2236(10)             | 0.5501(5)              | 0.5531(10)             | 0.3043(7)              | 0.3075(12)             |
|      |         | Pd13     | 0.0280(5)              | 0.2840(10)             | 0.5901(5)              | 0.5931(10)             | 0.2595(7)              | 0.2627(12)             |
|      |         | Pd14     | 0.0295(5)              | 0.2985(10)             | 0.6109(5)              | 0.6141(10)             | 0.3004(7)              | 0.3036(12)             |
|      |         | Pd15     | 0.0310(5)              | 0.3135(10)             | 0.6309(5)              | 0.6341(10)             | 0.3109(7)              | 0.3141(12)             |
|      |         | Pd16     | 0.0340(6)              | 0.3416(10)             | 0.6509(5)              | 0.6541(10)             | 0.3362(7)              | 0.3394(12)             |
|      |         | B2       | 0.1191(6)              | 0.1231(13)             | 0.6599(6)              | 0.6639(13)             | 0.2059(7)              | 0.2099(14)             |
|      |         | B3       | 0.3166(5)              | 0.3206(12)             | 0.6599(6)              | 0.6639(13)             | 0.2059(7)              | 0.2099(14)             |
|      |         | B4       | 0.3330(6)              | 0.3339(12)             | 0.6599(6)              | 0.6639(13)             | 0.2059(7)              | 0.2099(14)             |
|      |         | B5       | 0.3704(5)              | 0.3744(12)             | 0.6599(6)              | 0.6639(13)             | 0.2059(7)              | 0.2099(14)             |
|      |         | B7       | 0.8117(5)              | 0.8157(12)             | 0.6599(6)              | 0.6639(13)             | 0.2059(7)              | 0.2099(14)             |
|      |         | B8       | 0.6855(5)              | 0.6895(12)             | 0.6599(6)              | 0.6639(13)             | 0.2059(7)              | 0.2099(14)             |

Crystal structure data are standardized using the program Structure Tidy [11].
Analysis of interatomic distances in Ce$_3$Pd$_{25-x}$B$_{8-y}$ showed that the proximity of the positions Pd23 and Pd27 to those of Pd26, Pd28 and Pd10, respectively, precludes all these sites from being simultaneously occupied. For the La structure, short contacts of 0.648(7) Å and 1.449(1) Å were observed for Pd23/Pd24 (92.3%/7.7%) and B8/Pd24 (92.3%/7.7%), respectively.

3.2. X-ray powder diffraction

Full profile Rietveld refinements, performed on powder X-ray diffraction data of alloys La$_2$Pd$_{14}$B$_5$ (Figure 1) and Ce$_3$Pd$_{25}$B$_8$, converged with residual values as low as $R_F=2.56$ and $R_r=2.91$, respectively thus confirming the structure models obtained from single crystals. A small amount of a secondary phase in the La sample was consistent with a new compound La$_2$Pd$_{14}$B$_5$ (space group $I4_1/amd$, $a=0.8612(1)$ nm, $c=1.6643(3)$ nm, $R_F=3.65$) close to the Sc$_4$Ni$_{29}$B$_{10}$ derivative structure [5] and most probably isotypic with the recently determined structure of Nd$_3$Pd$_{14}$B$_{5-x}$ [4].

**Figure 1.** X-ray diffraction pattern of La$_2$Pd$_{14}$B$_5$. The solid line derives from the Rietveld refinement. $Y_{obs}-Y_{calc}$ is the intensity difference between experimental data and Rietveld calculations. Upper pattern of Bragg positions corresponds to La$_3$Pd$_{25-x}$B$_{8-y}$ structure and lower pattern shows Bragg positions of the La$_2$Pd$_{14}$B$_5$ structure.

3.3. Structural analysis

Both La and Ce structures exhibit the same structural arrangement of fully occupied RE, palladium and boron atomic sites with slight shifts in atomic coordinates. Three defect positions of palladium atoms in Ce$_3$Pd$_{25-x}$B$_{8-y}$ do not appear to be filled in La$_3$Pd$_{25-x}$B$_{8-y}$. And vice versa, two atomic sites of boron in the La structure are vacant in the structure with Ce. Several empty polyhedra exist in both structures (see figures 2a and 2b), which show sufficiently large distances from center to the surrounding atoms to eventually host additional boron and/or palladium atoms. From the common architecture both structures can be...
attributed to the same $R_3Pd_{25.3}B_{8.6}$ structural type with the La compound as the Pd-deficient and the Ce compound as the B-deficient members.

Figure 2. Perspective views of $La_3Pd_{25.3}B_{8.6}$ (a) and $Ce_3Pd_{25.3}B_{8.6}$ (b) along [101] axis with outlined vacant polyhedra.

Perspective views of both structures $La_3Pd_{25.3}B_{8.6}$ and $Ce_3Pd_{25.3}B_{8.6}$ along the b direction are given in figures 2a-2b; the coordination polyhedra for atoms are shown in detail in figure 3 to 6 for only $La_3Pd_{25.3}B_{8.6}$ as a representative member of the structure. Each La atom possesses a large coordination sphere formed by palladium and boron atoms. Five boron atoms are found in slightly distorted monocapped and tricapped trigonal prisms whereas B3
and B7 are coordinated by tetragonal antiprisms. The environment of B8 located in the site with partial occupancy has the shape of a distorted heptagonal bi-pyramid with one additional atom (Figure 6).

As the consequence of symmetry, the arrangement of polyhedra in the structure shows a large variety: polyhedra isolated and coupled by common face, edges or vertices; complexes of certain Pd atoms polyhedra arranged along x direction (Figure 7); corrugated (due to the mutual shift for a half of translation unit) columns of connected by common edges coordination units of palladium atoms stretched along z direction, etc. All palladium atoms except Pd2 and Pd25 participate in the formation of coordination spheres for the boron atoms. Boron trigonal prisms axes are oriented in various ways with respect to x, y and z directions (Figure 8). In agreement with the classification of boride structure types with respect to the type of boron-boron aggregation as a function of metal-boron ratio [12], no boron-boron contact was observed in the structure (Table 3).

Figure 3. Coordination polyhedra of lanthanum atoms in La3Pd25-xB8-y. La1 and La3 have two different coordinations depending on which one of the neighbouring sites is occupied: La1(La3) for Pd23/B8 contact (a) and La1(La3) for Pd24 contact (b).

Table 3. Interatomic distances (nm) for boron atoms in La3Pd25-xB8-y.

| Atoms | Distance | Atoms | Distance | Atoms | Distance | Atoms | Distance |
|-------|----------|-------|----------|-------|----------|-------|----------|
| B1 - Pd5 | 0.2108(6) | B3 - Pd7 | 0.2092(7) | B5 - Pd12 | 0.2034(7) | B7 - Pd22 | 0.2101(6) |
| B1 - Pd3 | 0.2153(6) | B3 - Pd15 | 0.2131(7) | B5 - Pd15 | 0.2106(7) | B7 - Pd7 | 0.2135(6) |
| B1 - Pd5 | 0.2249(6) | B3 - Pd14 | 0.2187(6) | B5 - Pd19 | 0.2178(7) | B7 - Pd6 | 0.2177(6) |
| B1 - Pd9 | 0.2270(6) | B3 - Pd19 | 0.2189(6) | B5 - Pd18 | 0.2184(6) | B7 - Pd21 | 0.2224(6) |
| B1 - Pd22 | 0.2281(6) | B3 - Pd21 | 0.2194(7) | B5 - Pd17 | 0.2219(7) | B7 - Pd1 | 0.2231(6) |
| B1 - Pd4 | 0.2299(6) | B3 - Pd9 | 0.2236(6) | B5 - Pd11 | 0.2247(7) | B7 - Pd13 | 0.2233(6) |
| B1 - Pd1 | 0.2361(6) | B3 - Pd17 | 0.2997(7) | B5 - Pd9 | 0.2940(7) | B7 - Pd4 | 0.2895(6) |
| B3 - La1 | 0.3199(7) | B5 - Pd13 | 0.3090(7) | B5 - La3 | 0.3120(7) | B7 - La3 | 0.3082(6) |
| B2 - Pd12 | 0.2108(6) | B2 - Pd6 | 0.2145(6) | B4 - Pd10 | 0.2054(7) | B8 - Pd23 | 0.2096(7) |
| B2 - Pd1 | 0.2146(6) | B4 - Pd23 | 0.2116(8) | B6 - Pd20 | 0.2145(6) | B8 - Pd22 | 0.2140(7) |
| B2 - Pd4 | 0.2182(6) | (or Pd24) | 0.262(1) | B6 - Pd17 | 0.2176(6) | B8 - Pd8 | 0.2156(7) |
| B2 - Pd3 | 0.2228(6) | B4 - Pd18 | 0.2149(8) | B6 - Pd18 | 0.2197(6) | B8 - Pd20 | 0.2189(7) |
| B2 - Pd11 | 0.2232(6) | B4 - Pd16 | 0.2167(8) | B6 - Pd13 | 0.2231(6) | B8 - Pd14 | 0.2230(8) |
| B2 - Pd13 | 0.2965(6) | B4 - Pd11 | 0.2375(8) | B6 - Pd20 | 0.2266(6) | B8 - Pd21 | 0.2443(8) |
| B2 - Pd9 | 0.3112(6) | B4 - Pd15 | 0.2390(8) | B6 - Pd14 | 0.2279(6) | B8 - Pd18 | 0.2941(8) |
| B2 - La1 | 0.3182(6) | B4 - Pd23 | 0.3094(8) | B6 - Pd19 | 0.2376(6) | B8 - La1 | 0.3296(7) |
Figure 4. Coordination polyhedra of palladium atoms in La₃Pd₂₅₋ₓB₈₋ₓ: Pd2₃/B₈ sites are occupied.

Figure 5. Coordination polyhedra of palladium atoms in La₃Pd₂₅₋ₓB₈₋ₓ: Pd2₄ site is occupied.
Figure 6. Coordination polyhedra of boron atoms in La$_3$Pd$_{25-x}$B$_{8-y}$ structure. B$_4$ atoms have two different polyhedra depending on which one of neighbouring sites is occupied, Pd23 (a) or Pd24 (b).

Figure 7. Pd2, Pd6, Pd8 and Pd16 complexes of polyhedra projected onto $bc$ plane (a) separated by columns of coupled mono-capped trigonal prisms of B1 and B6 (b).
3.4. Structural relationships

A comparative analysis of Pd- and Ni-rich ternary rare earth systems is given in figure 9; the concentration range for the formation of new compounds with palladium is shown in the inset. Several structures are found to form within a rather narrow concentration field of R 8-10 at.% - T 60-80 at.% - B 33-10 at.%

Based on the Sc$_4$Ni$_{39}$B$_{10}$ atomic model, first determined by Kuzma et al (1988) for R$_4$Ni$_{39}$B$_{10}$ R=Sc, Tm, Yb, Lu [5], three new Sc$_4$Ni$_{39}$B$_{10}$ derivative structural arrangements have been reported more recently: Y$_3$Pd$_{14}$B$_5$ [13], ErNi$_7$B$_3$ [14] and Nd$_2$Pd$_{14+x}$B$_{5.5}$ [4]; all of them differ from the parent structure by the mode of occupancy of coupled tetragonal antiprisms with Pd and B atoms. All the coordination spheres for boron atoms are tetragonal antiprisms and mono-capped trigonal prisms and the structures show no boron-boron contacts.

Two more structures were found to form with the heavy rare earth ternary borides: Ho$_2$Ni$_{15}$B$_6$ [15] and Ho$_2$Ni$_{10}$B$_5$ [16]. The coordination polyhedra for boron atoms in Ho$_2$Ni$_{15}$B$_6$ (P2$_1$/c, $a=1.4223$ nm, $b=1.0672$ nm, $c=0.9582$ nm, $\beta=94.23^\circ$) all are tetragonal antiprisms; one B-B pair was observed besides seven isolated boron atoms. For the Ho$_2$Ni$_{10}$B$_5$ – type (Pbca, $a=0.9001$ nm, $b=0.9477$ nm, $c=1.7588$ nm), 2 boron-boron pairs form besides three isolated borons. The atomic environments for boron atoms are mono-capped tetragonal antiprisms and bi-capped trigonal prisms.

The most common structural arrangements for the metal rich ternary rare earth borides were observed to be an ordered version of CaCu$_5$ type, CeCo$_3$B$_2$ type and its derivatives with the trigonal prisms as the coordination polyhedra for boron atoms [17].

With respect to the type of boron atom coordination (mono-capped and tri-capped trigonal prisms and tetragonal antiprisms), the La$_3$Pd$_{25-x}$B$_{8-y}$ and Ce$_3$Pd$_{25-x}$B$_{8-y}$ structures are related to Sc$_4$Ni$_{39}$B$_{10}$ – and CeCo$_3$B$_2$ - derivative structures.

Because of the similarities in composition and unit cell dimensions of R$_3$Pd$_{25-x}$B$_{8-y}$ and ErNi$_7$B$_2$ (C2/c space group, $a=1.662$ nm, $b=0.952$ nm, $c=1.068$ nm, $\beta=117.7$ deg) [18], a test for isotypism among both structures was performed. The primitive unit cell of Ce$_6$Pd$_{25}$B$_{8-y}$ was transformed to a C-centered cell with lattice parameters $a=1.77288$ nm, $b=1.04571$ nm, $c=1.17453$ nm, $\beta=118.23$ deg applying the (-a-c, b, a) transformation matrix, however the structure solution in space group C2/c revealed significant violations on systematic absences $hkl$ ($h+k=2n$), $okl$ ($k=2n$) and $h0l$ ($h=2n$, l=2n). These facts clearly show that Ce$_6$Pd$_{25}$B$_{8-y}$ and ErNi$_7$B$_2$ belong to different structure types.
4. Summary
The crystal structures of new ternary compounds La₃Pd₂₅₋ₓB₈₋ₓ (x=1.75, y=0.07) and Ce₃Pd₂₅₋ₓB₈₋ₓ (x=1.25, y=2.00) have been determined from X-ray single crystal data. Both compounds were found to form new monoclinic structural arrangements in space group \(P2_1/c\) with \(a=1.17567(2)\) nm, \(b=1.05757(2)\) nm, \(c=1.60664(3)\) nm, \(\beta=102.1788(10)\) deg, \(R_f^2=0.0300\) for 7427 structure factors and 289 variable parameters for La₃Pd₂₅₋ₓB₈₋ₓ and \(a=1.17453(3)\) nm, \(b=1.04571(3)\) nm, \(c=1.59759(5)\) nm, \(\beta=102.132(2)\) deg, \(R_f^2=0.0495\) for 2805 structure factors and 283 variable parameters for Ce₃Pd₂₅₋ₓB₈₋ₓ. Rietveld refinement for the X-ray powder diffraction patterns for both compounds confirmed the structure models determined from X-ray single crystal data.

Figure 8. B trigonal prism aggregation in the La₃Pd₂₅₋ₓB₈₋ₓ structure.
Figure 9. Formation of compounds in platinum metal subgroup and Ni ternary rare earth boride systems; inset figure shows the range of existence for $R_3Pd_{25-x}B_{8-y}$ and $Nd_2Pd_{14+x}B_{3-x}$ compounds.
Acknowledgements. Research supported by Austrian National Science Foundation FWF project 18054 and M1067-N20.

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