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Structure and composition analysis of the phases in the system Th–Pd–B–C containing superconductors with $T_c = 14.5$ K and $T_c = 21$ K

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Abstract

Several specimens in the system Th–Pd–B–C with nominal compositions ThPd$_3$B$_2$C and ThPd$_3$B$_3$C (as melted and annealed), containing superconducting phases exhibiting $T_c$'s of 14.5 K and 21 K, have been studied with EPMA, electron diffraction, EDX element analysis and HREM. A number of phases (approximate compositions are given) have been observed: (1) ThPd$_2$B$_2$C, I-centred tetragonal, $a = 0.375$, $c = 1.07$ nm, which can be related to the $T_c$ of 14.5 K; (2) ThPd$_{0.65}$B$_4$, P-type cubic, $a = 0.42$ nm, with a short-range ordered superstructure resulting in diffuse streaks in the electron-diffraction pattern; this phase is suggested to be the 21 K superconducting phase; (3) ThPd$_5$, P-type hexagonal, $a = 0.58$, $c = 0.98$ nm; (4) ThPd$_3$B$_3$, I-centred orthorhombic $a = 0.84$, $b = 0.90$, $c = 1.67$ nm; (5) ThPd$_3$BC, with unknown structure; (6) ThB$_4$, tetragonal $a = 0.72$, $c = 0.41$ nm; (7) graphitic C. Annealing of the specimen ThPd$_3$B$_3$C at 1050°C results in the disappearance of ThPd$_2$B$_2$C and the loss of the $T_c$ at 14.5 K but a strong increase of the 21 K superconducting fraction with a corresponding strong increase of the phases ThPd$_{0.65}$B$_4.7$ and ThPd$_3$. HREM indicates that ThPd$_{0.65}$B$_4.7$ adopts a modified CaB$_6$ structure in which the cube face, $\frac{1}{2}, \frac{1}{2}, 0$, which is vacant in CaB$_6$, is partially occupied by Pd with the removal of some B atoms. The superstructure indicates a short-range ordering (clustering) of the Pd atoms.

1. Introduction

Recently quite a number of intermetallic materials containing boron and carbon have been reported to be superconducting [1–3]. Cava et al. have reported superconductivity at 23 K in the system Y–Pd–B–C [1], and a $T_c$ of 16.6 K in the system Lu–Ni–B–C [2]. The superconducting phase in the latter system could be straightforwardly identified as LuNi$_2$B$_2$C [2]. LuNi$_2$B$_2$C has a fairly simple structure, which is based on the stacking of LuC layers with Ni$_2$B$_2$ blocks [4,5] e.g. (B–Ni$_2$–B–LuC)$_n$. The identification of the 23 K phase in the system Y–Pd–B–C turned out to be difficult. Zandbergen et al. [6] and Fujii et al. [7] have performed electron probe X-ray microanalysis (EPMA), electron diffraction and high-resolution
electron microscopy (HREM) of several superconducting \((T_c = 23 \text{ K})\) and non-superconducting specimens in the Y–Pd–B–C system. They concluded that the superconducting phase is YPd\(_2\)B\(_2\)C having a structure quite similar to that of LuNi\(_2\)B\(_2\)C. Sarrac et al. [3] have reported the presence of two superconducting phases in the system Th–Pd–B–C, one with composition YPd\(_2\)B\(_2\)C having a \(T_c\) of 14.5 K and the LuNi\(_2\)B\(_2\)C structure [3,8] and one with a \(T_c\) of 21 K whose composition and structure are not known. The problem of identifying the 21 K phase in the system Th–Pd–B–C seems to be similar to the identification of the 23 K phase in the system Y–Pd–B–C, since in both cases it is difficult or impossible to synthesize single-phase material.

Similar to the search for the superconducting phase in the system Y–Pd–B–C, we performed an EPMA, electron-diffraction and HREM study of several superconducting \((T_c = 14.5 \text{ K and/or} 21 \text{ K})\) in the Th–Pd–B–C system. Seven different phases could be detected. These investigations confirm that the 14.5 K phase is ThPd\(_2\)B\(_2\)C adopting the LuNi\(_2\)B\(_2\)C structure, and indicate that the 21 K phase is ThPd\(_{0.65}\)B\(_{4.7}\).

2. Experimental

The specimens were prepared by mixing elemental Th, Pd, C and B (all 99.9%) in the appropriate proportions and arc melting on a water-cooled copper hearth. Four melts were performed, with the samples turned over between each melt. Samples were then wrapped in Ta foil, placed in an evacuated quartz tube and annealed at 1050°C for several days.

EPMA, electron-diffraction and HREM were performed on three samples:

1. a nominal composition of ThPd\(_3\)B\(_2\)C, with a \(T_c\) of 14.5 K with a Meissner fraction of 30% and a very small fraction of the phase with a \(T_c\) of 21 K,

2. a nominal composition of ThPd\(_3\)B\(_2\)C as melted, containing \(T_c\)'s of 14.5 K and 21 K both with Meissner fractions of about 2% and

3. a nominal composition of ThPd\(_3\)B\(_2\)C annealed at 1050°C for several days, containing no observable fraction of the phase with a \(T_c\) of 14.5 K and a 30% Meissner fraction of the phase with a \(T_c\) of 21 K. These samples will be coded as 1321, 1331 and 1331a, respectively, in the rest of the paper.

Electron probe X-ray microanalysis (EPMA) was employed for a quantitative assessment of the composition of the various phases present in the three specimens, inhomogeneities in these phases and the fraction of these phases. The specimens were embedded, ground and finally polished using 2.5 μm diamond powder to make them suitable for the EPMA measurements. A Jeol 8621 Superprobe was used, equipped with combined energy dispersive and wavelength dispersive X-ray element analysis systems and JEOL software for instrument control, data acquisition and analysis. Images on a photographic plate were recorded using a 20 keV electron beam energy. The quantitative measurements were performed with 12 keV in the case of Th, Pd and B and 5 keV for C. The beam current was 50 nA. The X-rays of Th Mβ, Pd La and B Kα and C Kα are detected with the wavelength dispersive system. A serious handicap is the overlap of the C Kα line (0.277 keV), the only line for C, with the Pd Mz line (0.284 keV). To overcome this problem, the combined lines (C+Pd) were measured and the intensity of the Pd Mz line, determined from the Pd La line was subtracted. As reference materials are used the ThPd\(_3\) phase present in sample 1 as Th and Pd standard, pure B and pure C (C lamellae in Fe\(_3\)C). The concentrations were calculated using the modified \(\Phi(\rho z)\) approach [9].

For the electron-diffraction and HREM experiments, thin specimens were obtained by crushing under ethanol and mounting the crystal fragments on a Cu grid covered with a carbon coated holey film. In general this method results in particles ranging in size from 0.05 to 5 μm, which are often single phase. Electron microscopy was performed with a Philips CM30ST electron microscope with a field emission gun and a Philips CM30T, both operating at 300 kV and equipped with a Link EDX element analysis system.

Image calculations were carried out for several models using a MacTempas software program, in which the following parameters were used: \(Cs = 1.3 \text{ mm, defocus spread 5 nm, objective aperture 10 nm}^{-1}, \text{ beam convergence 0.1 mrad, and mechanical vibration 0.03 nm. The thickness and defocus were varied.} \)
3. Experimental results

3.1. EPMA, EDX and electron diffraction

EPMA shows that the three specimens contain a large number of phases, which are listed in Table 1. Backscattered electron images of the three specimens are shown in Fig. 1. Most phases are clearly distinguishable in the backscattered electron images, due to their different gray levels, but the phases A3 and A6 (ThPd3 and ThB4) have almost the same appearance. They could be distinguished by using Pd element mapping, since ThB4 does not contain any Pd whereas it is the major component in ThPd3. Also the phases A1 (ThPd2B2C) and A2 (ThPdo.65B4.7) are difficult to distinguish.

The unit cells and the Th/Pd ratios of many crystal fragments were determined by electron diffraction and EDX element analysis. The phases which could be detected in the various specimens are given in Table 1. Electron-diffraction patterns of some of the phases are given in Fig. 2.

It was observed that the fraction of the C-like phase was higher in the electron-microscopy study than in the backscattered electron images. This is probably due to the non-representative sampling in the preparation of the specimens for the electron-microscope study. Because of the low density of this phase it is quite likely that it remains longer in dispersion in the ethanol used to deposit the particles on the carbon film coated Cu grid.

The plate-like phase (A1) is only present in the specimens 1321 and 1331. The composition is determined by EPMA to be ThPd2B2C. The structure as determined by HREM [8] indicates that this phase adopts the LuNi2B2C structure; it is schematically presented in Fig. 3. A [100] diffraction pattern is given in Fig. 2(a). The plate-like morphology is similar to the shapes of the crystals of LuNi2B2C [10] and YPd2B2C [6].

The backscattered electron image of specimen 1331a shows the plate-like remnant of ThPd2B2C which was decomposed during the annealing at 1050°C. The EPMA measurements indicate that ThPd2B2C is decomposed in three phases: A3 (ThPd3), A2 (ThPdo.65B4.7) and a C-rich phase. The C-rich phase is probably pure C, since with electron diffraction no other structures than those of ThPd3, ThPd0.65B4.7, and graphitic C are observed in specimen 1331a.

Diffraction patterns of ThPd0.65B4.7 (A2), are shown in Figs. 2(b) and (c), indicating a primitive cubic unit cell with a = 0.415 nm. EPMA indicates a composition ThPdxBy with x between 0.65 and 0.7

<table>
<thead>
<tr>
<th>Code</th>
<th>Morphology from EPMA</th>
<th>Structural data from electron diffraction</th>
<th>Element ratios according to EPMA</th>
<th>Suggested phase</th>
<th>Specimen</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Plates</td>
<td>Tetr., a = 0.38, c = 1.07</td>
<td>2</td>
<td>ThPd3B2C</td>
<td>1321</td>
</tr>
<tr>
<td>A2</td>
<td>Rounded facets</td>
<td>Cubic, a = 0.42, superstructure</td>
<td>0.65-0.7</td>
<td>ThPd0.63B4.7</td>
<td>1331</td>
</tr>
<tr>
<td>A3</td>
<td>Sharp facets</td>
<td>Hexagonal, a = 0.58, c = 0.97</td>
<td>3</td>
<td>ThPd3</td>
<td>1331</td>
</tr>
<tr>
<td>A4</td>
<td>Matrix</td>
<td>Ort, I-cent, a = 8.4, b = 9.0, c = 1.67</td>
<td>6-9</td>
<td>ThPd5B3</td>
<td>1331a</td>
</tr>
<tr>
<td>A5</td>
<td>Facets</td>
<td>Unknown</td>
<td>3</td>
<td>ThPd3B2C</td>
<td>1321</td>
</tr>
<tr>
<td>A6</td>
<td>Rounded facets</td>
<td>Tetr., a = 0.72, c = 0.41</td>
<td>4-5</td>
<td>ThB4</td>
<td>1331</td>
</tr>
<tr>
<td>A7</td>
<td>Spheres</td>
<td>Hexagonal, graphite-like</td>
<td>- a</td>
<td>C</td>
<td>1331</td>
</tr>
<tr>
<td>A8</td>
<td>Plate-like</td>
<td>Hexagonal, graphite-like</td>
<td>- a</td>
<td>C</td>
<td>1331a</td>
</tr>
<tr>
<td>A9</td>
<td>Lamellae</td>
<td>?</td>
<td>- a</td>
<td>C</td>
<td>1331a</td>
</tr>
</tbody>
</table>

* Large variations occur in the Th, Pd and B content due to the presence of small particles of the other phases in the C matrix.

** Electron diffraction does not allow for a distinction between the phases A7, A8 and A9; therefore all data are given for A8. A7 is also known to be graphite-like because this phase is the only C compound in specimen 1321, in which electron diffraction shows the presence of a graphite-like phase.
Fig. 1. Backscattered electron images. (a) The specimen with a nominal composition ThPd$_3$B$_2$C having a 30% Meissner fraction of the $T_c=14.5$ K phase. (b) The specimen with a nominal composition ThPd$_3$B$_2$C having $T_c$'s of 14.5 and 21 K (2% Meissner fractions). (c) As (b) but annealed at 1050°C showing only a $T_c$ of 21 K (30% Meissner fraction). (d) Enlargement of boxed area in (c). The numbers in the figures refer to the codes for the phases listed in Table 1.
Fig. 2. Diffraction patterns of several phases observed. (a) shows a [100] diffraction pattern of ThPd$_2$B$_2$C (A1). (b) and (c) show [100] and [110] diffraction patterns of the cubic phase (A2); diffuse scattering can be observed in both diffraction patterns. (d) and (e) show the [001] and [100] diffraction patterns of ThPd$_3$ (A3). (f) shows an example of a diffraction pattern of the C-rich phase.

and $y$ between 4 and 5.5. For reasons given in Section 4 the composition is written as ThPd$_{0.65}$B$_{4.7}$. All crystals show the presence of a superstructure, which is reflected in a rather complicated diffuse scattering as can be seen from Figs. 2(b) and (c). The diffuse scattering indicates that the superstructure is only short-range ordered. The large abundancy of this phase and its small and very small volume fraction in the specimens 1321 and 1331, respectively, suggest that this phase is the 21 K superconducting phase.

According to the EPMA measurements the phase ThPd$_3$ (A3) is present in all three specimens with a fraction of at least 10%. Electron diffraction (see Figs. 2(d) and (e)) shows that this phase has a hexagonal unit cell with $a=0.58$, $c=0.95$ nm with 00l, $l\neq 4n$, absent which is in agreement with the structure reported for ThPd$_3$ by Thom et al. [11]. Since this phase is present in the specimens 1321 and 1331 with a fairly large volume fraction (> 15%) it is very un-
likely that this phase is the 21 K superconductor.

The various diffraction patterns of phase A4 could be indexed with an I-centred orthorhombic unit cell with \(a=0.84\), \(b=0.90\) and \(c=1.67\) nm with the approximate composition ThPd\(_4\)B\(_4\). In the Y–Pd–B system, a phase with the same composition and unit cell has been found [6].

We attempted to obtain diffraction information from the phase ThPd\(_3\)B\(_2\)C (A5). Since only the Pd and Th and not the B or C content can be measured by the EDX equipment used, about 100 particles having a Pd/Th ratio of 3 were selected. All these particles showed diffraction patterns of ThPd\(_3\). Either ThPd\(_3\)B\(_2\)C has a structure similar to that of ThPd\(_3\), or none of the crystals investigated were of the intended phase.

The diffraction patterns of phase A6 indicate a P-type tetragonal unit cell with \(a=0.72\), \(b=0.41\) nm. This unit cell and the absence of Pd indicate that this phase is ThB\(_4\) [8].

The two main carbon-rich phases are present as large spherical particles (A7) or platelets (A8) scattered randomly. A typical diffraction pattern is shown in Fig. 3(f), showing rings; the positions of these rings are compatible with graphitic C. In addition to this, some C-rich particles are observed in the backscattered electron images at the decomposed ThPd\(_3\)B\(_2\)C regions in specimen 1331a. The structural nature of these particles could not be detected, because, due to the sample preparation (crushing) for the electron-diffraction investigation, the correlation with the location in the specimen is lost. However, we observed no evidence that this C-rich phase is different from graphitic C.

3.2. High-resolution electron microscopy

A HREM study of ThPd\(_3\)B\(_2\)C has been reported previously [8]. It showed that ThPd\(_3\)B\(_2\)C adopts a LuNi\(_2\)B\(_2\)-like structure, possibly with a deficiency in B. No planar stacking defects could be observed, indicating a strict layer sequence \(\text{B-} \text{Pd}_2\text{-} \text{B-} \text{ThC}_n\). At the edge of wedge-shaped crystals the ThPd\(_3\)B\(_2\)C lattice transforms into a cubic-like structure with \(a=0.41\) nm during the HREM investigation, an example of which is given in Fig. 4. This cubic-like structure is face centred cubic and is consequently different from that of ThPd\(_{0.7}\)B\(_{4.6}\). We have reported previously [6] that the YPd\(_3\)B\(_2\)C lattice also changes into this cubic-like structure by the interaction of the electron beam.

HREM on ThPd\(_3\) showed that the structure as reported for ThPd\(_3\) [11] is adapted. An experimental image and matching calculated image is shown in Fig. 5. It was observed that the structure near the surface was modified when the specimen was exposed to air, making it rather difficult to obtain HREM images of the bulk structure.
HREM on ThPd_{0.65}B_{4.7} shows that this compound has simple HREM images, which can be explained with a cubic structure in which a very strongly scattering atom (Th) occupies the position 0, 0, 0 and a much less scattering atom the position ½, ½, 0 as indicated in Fig. 3(c); the superstructure is not visible in these images, which is logical if one considers that the superstructure is very weak. Fig. 6 shows an experimental [100] image and the corresponding calculated image. For the calculation a model was used which is based on the CaB_{6} structure, in which Ca (position 0, 0, 0) is replaced by Th and Pd is located on the position ½, ½, 0 with an occupancy of 0.22. Due to this Pd some B atoms have to be removed. This results in: Th at 0, 0, 0 with full occupancy, Pd at ½, ½, 0 with 0.22 occupancy and B on 0.21, ½, ½ with an occupancy of 0.78. Because of the low scattering cross-section of B the effect of presence or absence of B is small and cannot be distinguished based on fits with the experimental image. A detailed study of this structure will be presented elsewhere [12].

4. Discussion

In principle, all phases which remained or grew during the annealing at 1050°C could be the 21 K superconducting phase. Evidently ThPd_{3}B_{2}C is destroyed by the annealing and cannot be correlated to the $T_{c}$ of 21 K. The only two phases which grow substantially during the annealing are ThPd_{3} and ThPd_{0.65}B_{4.7}. Furthermore a small volume fraction (< 5%) of ThPd_{3}B_{2}C is formed. The volume fraction of the latter one is insufficient to explain the observed Meissner fraction in the 1331a specimen. The Meissner fraction of about 30% can only be explained assuming ThPd_{3} or ThPd_{0.65}B_{4.7} to be the superconductor. Since ThPd_{3} is also present with a volume fraction of about 15% or more in the specimen 1321, which shows hardly any superconductivity at 21 K, it can be concluded that this phase is not the superconductor. Furthermore the C plates occur with the same volume fraction in specimens 1331 and 1331a, which cannot account for the large difference in Meissner fraction of these specimens. Consequently the 21 K superconductor must be the phase ThPd_{0.65}B_{4.7}.

It is concluded that ThPd_{2}B_{2}C is the phase with a $T_{c}$ of 14.5 K because of the following reasons:

1. the specimen 1321 contains more than 40% of this phase and shows a 14.5 K Meissner fraction of about 30%;
2. this phase is absent in the specimen 1331a which shows no superconducting transition at 14.5 K;
3. the structure as determined by HREM [8] indicates that this phase adopts the LuNi_{2}B_{2}C structure, a structure which has shown superconductivity for many analogous compounds. The plate-like morphology of ThPd_{3}B_{2}C is similar to the shapes of the crystals of LuNi_{2}B_{2}C [10] and YPd_{3}B_{2}C [6]. Since it consists of extended plates, it can easily form an interconnecting network allowing zero resistance and the large magnetic screening below $T_{c}$. In the 1050°C annealed specimen only the remnant of these plates can be observed, which contain ThPd_{3}, ThPd_{0.65}B_{4.7} and C.

Electron-beam induced surface changes are observed for ThPd_{2}B_{2}C (Fig. 4) leading to a cubic-like structure with an $a$-axis of about 0.41 nm, suggesting the formation of an F-centred cubic unit cell (ThPd_{3} without any ordering of Th and Pd and with some B and C at interstitial positions) due to loss of C and B. Apart from this surface change, another change occurs in the structure of ThPd_{2}B_{2}C itself: a decrease
of the c-axis when irradiated by the electron beam of about 0.3 nm. Such a decrease is also observed for ThPd$_2$B$_2$C and ThPd$_3$B$_2$C but in those compounds the decrease is larger, e.g. 0.06 nm. The reason for this decrease is not yet understood.

All phases observed by EPMA can be correlated to the phases observed by electron diffraction and EDX analysis as is evident from Table 1. Some differences in the volume fractions as observed by EPMA and TEM do occur. Partly this can be explained by the non-representative sampling by TEM caused by the preparation method (C phase). The difference in the fraction of ThPd$_{0.65}$B$_{4.7}$ (not observed by EPMA) might be due to a non-random distribution of this phase over the melted button.

The B and C compositions can only be determined from the EPMA measurements. The accuracy of the element analysis by EPMA is quite high for the elements Th and Pd (better than a few % for Th/Pd ratio) but rather low for the elements B and C (about 20% and 40% accuracies, respectively) because of their extremely low X-ray yield and large absorption corrections. The C content contains an extra uncertainty because of the overlap of this X-ray peak with an X-ray peak of Pd. The uncertainty in the contents of these elements is for instance reflected in the composition of ThB$_6$, which in fact is measured by EPMA as approximately ThB$_{5.6}$. This implies that the exact B composition of the 21 K phase, ThPd$_{0.65}$B$_{4.7}$, is not accurately known.

HREM shows that ThPd$_{0.65}$B$_{4.7}$ adopts a cubic structure with a heavy scattering atom on the cube corners and a lesser scattering atom in the faces of the cube. Given the Th/Pd ratio the most likely structure is the one depicted in Fig. 3. Image calculations with this model give a good fit with the experimental image. The presence of Pd on 0.22 of the cube faces must result in a restriction of the number of B atoms because of the too short Pd–B distance. Omitting these B atoms results in a composition ThPd$_{x}$B$_{6-2x}$, giving with $x=0.65$ ThPd$_{0.65}$B$_{4.7}$, which is in good agreement with the composition determined by EPMA. Carbon is not necessary for the structure, but it could be an essential addition to obtain superconductivity. The EPMA measurements indicate that if carbon is present in the structure it is only for a few atomic percent.

The CaB$_6$ structure is reported for several superconductors. For instance, ThB$_6$ [13] is reported to have a $T_c$ of 0.78 K, whereas Matthias et al. [14] report a $T_c$ about 7 K for YB$_6$. This indicates that the CaB$_6$ structure is in principle a structure allowing for a relatively high superconductivity. We have prepared specimens with the nominal composition ThPd$_{0.65}$B$_{4.7}$. These specimens, however, showed to be far from single phase and showed a considerably lower superconducting fraction. This indicates that the chemistry of this system is complicated, in analogy to the system Y–Pd–B–C in which the superconducting phase can only be prepared in a small composition window far from the actual composition of the superconductor YPd$_2$B$_2$C.

The origin of the superstructure of ThPd$_{0.65}$B$_{4.7}$ must be very short-range order, since the superstructure results only in a diffuse intensity in the diffraction patterns. Most probably it is caused by the ordering of the Pd atoms.

The structure of ThPd$_{0.65}$B$_{4.7}$ might be similar to that of YPd$_{1.2}$B$_{3.3}$ [6], which also has a cubic unit cell with $a=0.42$ nm, but with sharp superstructure reflections, indicating long-range order. In the case of similar structure the composition of ThPd$_{1.2}$B$_{3.3}$ should be ThPd$_{1.2}$B$_{3.6}$ because of the composition formula YPd$_{1.2}$B$_{6-2x}$.

It is intriguing that also in the system Y–Pd–B–C a phase with a structure similar to that of ThPd$_{0.65}$B$_{4.7}$ is present: YPd$_{1.2}$B$_{3.3}$ [6], which also has a cubic unit cell with $a=0.42$ nm, but with sharp superstructure reflections, indicating long-range order. This leads to the question whether the 23 K superconductor in the system Y–Pd–B–C is indeed ThPd$_2$B$_2$C or YPd$_{1.2}$B$_{3.3}$, the more because both phases decompose upon annealing at 800°C.

With respect to the preparation of a pure phase there is an important difference between the 21 K superconductor in the system Th–Pd–B–C and the 23 K superconductor in the system Y–Pd–B–C. Whereas the 23 K superconductor decomposes upon annealing at 800°C, the 21 K superconductor, ThPd$_{0.65}$B$_{4.7}$, is stable upon annealing even at 1050°C. The increase of ThPd$_{0.65}$B$_{4.7}$ upon annealing indicates that this phase can in principle be made as a single phase, provided the diffusion rate of all atoms is sufficiently high.
5. Conclusion

Detailed analysis of the phases in the various specimens in the Th–Pd–B–C system indicates that the 14.5 K superconducting phase is ThPd\(_2\)B\(_2\)C and that the 21 K superconductor is ThPd\(_{0.65}\)B\(_{4.7}\). ThPd\(_2\)B\(_2\)C has a structure similar to that of LuNi\(_2\)B\(_2\)C. ThPd\(_{0.65}\)B\(_{4.7}\) adopts a cubic structure with Th on the corners and Pd with a partial occupancy in the faces of the cube. Local ordering of the Pd vacancies results in a short-range superstructure.

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References