On the formation and crystal structure of the Pd₆B phase

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In commemoration of the 100th anniversary of Fritz Laves' birthday

Received February 1, 2005; accepted November 11, 2005

*X-ray diffraction / Electron diffraction /
Neutron diffraction / Palladium–boron alloys /
Order-disorder transformations /
Powder diffraction structure analysis*

Abstract. The crystal structure of the Pd₆B phase has been elucidated employing selected-area electron diffraction and X-ray and neutron powder diffraction methods. It is based on a cubic close packed arrangement of Pd with B occupying $\frac{1}{6}$ of the interstitial octahedral sites in an ordered way, such that a monoclinic (*C2/c*) superstructure results. The crystal structure contains isolated [BPd₆] octahedral entities providing large distances between nearest neighbour boron atoms. Depending on the way of preparation, the same Pd₆B phase can occur for the same composition in two different ‘manifestations’ having considerably different lattice parameters, which has a microstructural origin. Various phase equilibria between the ordered Pd₆B phase and the disordered interstitial solid solution of boron in cubic close packed palladium have been investigated to clarify the corresponding regions in the phase diagram Pd–B.

1. Introduction

The structural principle underlying binary interstitial phases (terminal solid solutions and intermediate phases) of transition metals with B, N, C, O is simple [1]: a relatively rigid metal partial structure exhibiting usually a dense arrangement of the metal atoms (cubic close packed, hexagonal close packed or body centred cubic) serves as a host for light non-metal atoms (usually H, B, C, N, O) which occupy octahedral or tetrahedral interstices, the so-called interstitial sites. This building principle ensures metal-metal bonding as well as metal-interstitial atom bonding, whereas the interstitial atoms are too far apart to exhibit significant direct bonding interaction.

In spite of their simple basic building principle, the structural details of interstitial phases can be both rather

complex and revealing with respect to chemical bonding and properties of these materials. One of the most interesting structural aspects is the formation of long-range order of the interstitials (ordering of interstitial atoms vs. vacancies; a typical low-temperature phenomenon) and the accompanying structural distortions of the metal host structure (see *e.g.* [2–7]). Since interstitial phases are important constituents of many important materials (*e.g.* steels), knowledge and understanding of these structural aspects is desired, because thereby interpretation and modelling of phase transformations involving such interstitial phases becomes possible.

Of the above-mentioned interstitial atoms boron is the least common one. This can largely be understood on the basis of its high atomic radius, which makes it difficult to fit into octahedral sites of close packed metals (see discussion in Ref. [8]). Palladium is one of the few exceptions: it forms a *hcp* based interstitial boride phase Pd₂B [9], as well as an extended interstitial terminal solid solution of boron in palladium, Pd[B]. The latter may be regarded a remarkable model system for the study of the character of metallic interstitial phases. In the crystal structure of Pd[B] the B atoms occupy octahedral interstitial sites of a cubic close packed (*ccp*) partial structure of Pd atoms [8, 10, 11] in a disordered fashion, such that both the Pd sites and the octahedral sites form *fcc* type arrays. The maximum interstitial solubility above about 450 °C in Pd[B] has been reported to correspond to an atomic fraction of ~20 at% B [12], which is the largest one known for any metal-boron system [8]. In the sequel the *atomic ratio* *y* will be used to quantify the composition of the solid solution (and for the ordered phases derived from it) in the form of the formula PdB_{*y*} (*e.g.* PdB_{0.25} for ~20 at% B); *y* also corresponds to the average occupancy of the octahedral sites. Except for very low B contents, the solid solution is only stable at elevated temperatures, but it can be retained by quenching.

For the solid solution PdB_{*y*} ordering of *y* B vs. (1 – *y*) vacancies can occur on the *fcc* type array of octahedral sites (often referred to as the ‘*fcc* sublattice’ of octahedral sites).

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The low-temperature region of the Pd–B phase diagram in the composition range Pd–PdB_{0.25} appears to consist of low-temperature phases and of several two-phase regions. The literature is contradictory, but since X-ray powder diffraction patterns of the low-temperature phases are always dominated by the typical ‘fcc-type pattern’ of *fundamental reflections*, which are already observed for the solid solution, it is generally accepted that the metallic partial structure of the parent solid solution with the *ccp* arrangement of Pd atoms is largely retained as the mean crystal structure of the low-temperature phases.

One single low-temperature phase was reported in Ref. [13] (Fig. 1a), having the assigned composition PdB_{0.188} (‘Pd₁₆B₃’). The X-ray powder diffraction patterns showed no splitting of the fundamental reflections, which would hint at (but which would not be required for) a symmetry lower than cubic. Observed superstructure reflections were ascribed to a not specified B ordering on the octahedral sites and were indexable (with integral indices) according to a face-centred cubic superstructure cell with $a' = 2a_{fcc}$, where a_{fcc} denotes the lattice parameter of the *fcc* parent solid solution. With respect to the parent a_{fcc} cell these superstructure reflections are indexable as $\frac{h}{2} \frac{k}{2} \frac{l}{2}$ with odd h, k, l . For similar compositions (PdB_{0.18}–PdB_{0.20}) a low-temperature phase Pd₅B was reported to form from the solid solution upon annealing below 380 °C [14]. XRD patterns were similar to those of the solid solution and no additional superstructure reflections were detected, but observed splitting of fundamental reflections was interpreted in terms of a slightly tetragonally distorted variant

of the solid solution phase having a face-centred tetragonal (*fcc*) unit cell with a_{fcc} , $c_{fcc} \approx a_{fcc}$ and $c_{fcc} < a_{fcc}$. A phase diagram for the system Pd–B published in Ref. [15] (Fig. 1b) showed two different low-temperature phases: ‘Pd₆B’ which would form congruently from the solid solution at 440 °C and ‘Pd₅B’ which would form peritectically from the solid solution at 372 °C; further crystallographic information was not given.

No one of the mentioned previous works [13–15] concerning the low-temperature phases (formed from the solid solution PdB_y) is indicating the way in which B is distributed on the *fcc*-type array formed by the octahedral sites.

Ordering of different species (different types of atoms or vacancies and atoms) within a partial structure formed by an *fcc*-type array of sites has been observed for various types of phases [16]: The most elementary case of this type of ordering concerns ordering substitutional solid solutions $M_yM'_{1-y}$ with M and M' being different metals with *ccp* structure; e.g. see the classical system Au–Cu [17]. The PdB_y alloys are interstitial alloys in which the ordering partial structure (*i.e.* the octahedral sites) is embedded in a host partial structure of metal (Pd) atoms with *ccp* arrangement, which is usually fully occupied by one type of atoms, so that ordering cannot occur on this partial structure. Thus, PdB_y can be compared with many interstitial transition metal nitrides and carbides, $MX_y\Box_{1-y}$ (M : transition metal, X : C, N, less frequently O; $\Box$: vacancy on ordering partial structure). In contrast with PdB_y most representatives of these phases are known for relatively large values of y : $0.5 \leq y \leq 1$; they are often referred to as defect-NaCl (rock salt) type interstitial phases. Furthermore, there are many, basically ionic (sometimes with some additional metallic bonding for low-valent transition metals) metal chalcogenides ($X = O, S, \dots$) and halides ($X = F, Cl, \dots$), $M_yM'_{1-y}X$ or $M_y\Box_{1-y}X$ which are derived from the rock-salt structure: a complete close packed cubic partial structure of chalcogenide/halide anions, X , with the *fcc* type array of octahedral sites being occupied by different types of cations (M, M') or cations and vacancies ($\Box$); examples are anatase-type $Ti\Box O_2$ [18], $Sc_2\Box S_3$ [19], $U\Box_4Cl_5$ [20] (*i.e.* $y = 0$), $LiFeO_2$ and Li_5ReO_6 [21].

The crystal structures of all phases mentioned above, exhibiting rather different chemical bonding character, attract interest because the ordering type chosen by nature out of an infinite number of possibilities reflects the nature of the interaction and the magnitude of the interaction energies between the ordering species, and thus the type of ordering provides profound insight into the thermodynamics of the system considered. Hence, investigation of, in particular, such systems for which the state of order varies as a function of temperature and/or composition, e.g. by order-disorder phase transitions, can be rewarding scientifically. Usually the atomic interactions leading to the observed state of order are expressed in terms of pair-interaction energies between the different species (atom types and vacancies) on the ordering partial structure. On the basis of such pair-interaction energies it is possible to calculate ‘ordering phase diagrams’ if additionally models for the configurational entropy are adopted, e.g. in a Gorsky–Bragg–Williams approach [22] or by employing the cluster variation method [23, 24].

Fig. 1. Phase diagrams for the Pd–B system as proposed in Ref. [13] (a) and Ref. [15] (b).

The interatomic interactions determining the state of order are of various types. For *metallic* interstitial or substitutional solid solutions the interactions are often subdivided into strain-induced interactions (mainly due to size of the atoms leading to local distortions in the crystal structure) and into so-called chemical interactions [25]. For *ionic* phases usually Coulomb approaches (Madelung energy) are applied, together with polarisation and strain (size) effects [26, 27].

In the following the crystal structure of the ordered low-temperature phase Pd₆B as determined in this work by electron, X-ray and neutron diffraction analyses will be presented. Furthermore, the existence of different two-phase equilibria of Pd₆B with a disordered PdB_y solid solution will be established, leading to specification of the Pd₆B phase field in the Pd–B phase diagram. In this work the formula Pd₆B will be used for this phase irrespective of the actual, experimentally determined composition of this phase in a specific specimen, which is specified by *y* in the formula PdB_y, likewise applied also for the solid solution.

2. Experimental

2.1 Preparation of the Pd–B alloys

The three PdB_y alloys investigated in this study were prepared from weighed amounts of about 1.5 g–3.5 g Pd foils (Heraeus, 99.9 wt%) and an appropriate amount of crystalline B pieces (isotope enriched boron: Eagle Picher, 99.29% ¹¹B, chemical purity 99.97 wt%; or B with isotopes in natural abundance: Johnson Matthey, chemical purity 99.5 wt%) by arc melting under argon (550 hPa; Messer Griesheim, 99.999 vol%). For an overview of the prepared alloys, see Table 1. For alloy 2 intended for neutron diffraction measurements the pure isotope ¹¹B was used instead of B with the natural mixture of its isotopes (about 20 at% ¹⁰B), because ¹⁰B has an extremely high neutron absorption cross section [28] and by its use the diffracted neutron beam intensity would decrease dramatically.

The homogeneity of the reguli and their compositions were checked by measuring the cubic lattice parameters by X-ray diffraction (XRD; cf. Section 2.3.). The compositions were calculated by application of [8]:

$$a = 3.8920 \text{ \AA} + 0.6882 \text{ \AA } y. \quad (1)$$

In the following the actual compositions, described by PdB_y, are used to identify the alloys used in the experiments (Table 1).

For the homogeneity measurements, small parts of the as-cast bulk samples were removed by filing from the top and bottom of the reguli using a diamond rasp.¹ The filings were sealed under vacuum in quartz capsules, annealed at 800 °C for 5 min and subsequently quenched in water. The heat treatment was performed in order to relieve deformation stresses due to the filing procedure. If homogeneity had not been achieved, the corresponding regulus was remelted and the X-ray test procedure was repeated. The samples listed in Table 1 contain apparently a little less B than corresponding to the composition aimed at; experience with the preparation of other Pd–B alloys has suggested that some B loss can happen during the arc beam melting.

For the structural and thermal analyses, heat treated powder and pieces of bulk specimen were prepared starting from the homogeneous reguli. The powder specimens (for XRD) were obtained by filing the reguli as described above for the homogeneity verification, and bulk pieces (for transmission electron microscopy, TEM and differential thermal calorimetry, DSC) were cut from the reguli by electrical discharge machining. The thus obtained powder filing batches and bulk pieces were encapsulated in evacuated quartz tubes and stress relieved at 800 °C for 5 min followed by water quenching (including, for the bulk pieces, immediate subsequent crushing of the quartz tubes to obtain a higher cooling rate). For further heat treatments at lower temperatures, leading to the ordered and/or two-phase states (see Sections 4.2 and 4.3), filings and bulk pieces were re-encapsulated (as above) and again quenched (including crushing of the quartz tube for the bulk pieces) after annealing.

For the neutron diffraction measurements a larger amount of powder than for the XRD measurements was required. To this end, the homogeneous regulus was filed entirely. The resulting powder (ca. 2.5 g) was encapsulated under helium (at about 500 hPa; Westfalen Reinstgase, 99.999 vol%) in a quartz tube, stress relieved and water quenched. The He atmosphere (instead of vacuum) was chosen in order to achieve a fast cooling rate for the relatively large batch size.

2.2 DSC Measurements

Differential scanning calorimetry (DSC) measurements were carried out using a power compensated Perkin Elmer DSC Pyris-1. The samples in form of one bulk piece of

¹ The filing with the diamond rasp introduced diamond as an impurity phase as revealed by corresponding reflections in diffraction patterns, which are particularly visible in the neutron diffraction patterns.

Table 1. Overview of prepared Pd–B alloys, measured cubic lattice parameters by X-ray powder diffraction (XRD) and calculated compositions (cf. Eq. (1)) from homogeneity tests, and techniques applied for further structure and constitution characterisation (XRD, transmission electron microscopy (TEM), neutron powder diffraction (NPD) and differential scanning calorimetry (DSC)).

Alloy no.	Composition from weighing	Lattice parameter XRD data at room temperature (Å)	Calculated composition using Eq. (1)	Characterisation technique
1	PdB _{0.150}	3.9913(1)	PdB _{0.144}	XRD, TEM
2	Pd ¹¹ B _{0.163}	4.0010(1)	Pd ¹¹ B _{0.158}	XRD, NPD
3	PdB _{0.177}	4.0040(1)	PdB _{0.163}	DSC, TEM

20–40 mg of Pd–B were put into an open gold pan, whereas the reference pan was empty. A protective gas atmosphere of pure argon was employed. The used heating/cooling rate was 20 °C/min. Since only the qualitative thermal behaviour of the samples was of interest here, the DSC measurements were performed without separate precise calibration involving an uncertainty of about ± 5 °C for all indicated temperatures.

2.3 X-ray diffraction measurements

X-ray powder diffraction (XRD) patterns were recorded at a Philips X'Pert MPD diffractometer applying Bragg-Brentano geometry and a primary beam monochromator to select the K_{α_1} component of the employed copper radiation (wave length of 1.54056 Å). The samples consisted of a thin layer of the PdB_y alloy powders mixed with silicon powder (with lattice parameter $a = 5.43102$ Å) as internal standard (only used for lattice-parameter measurements), deposited onto single-crystalline silicon wafers with a (510) plane parallel to the surface.

Since a large amount of powder from the neutron-diffraction measurements was available, the solid-solution sample Pd¹¹B_{0.158} was prepared for XRD as a 'backloaded' specimen with a thickness of 2 mm and a diameter of 15 mm.

For the homogeneity measurements, all fundamental reflections (*i.e.* reflections expected from the *fcc* lattice of the solid solution phase) in the range of $25^\circ < 2\theta < 100^\circ$ (*i.e.* *hkl* from 111_{fcc} to 222_{fcc}) were recorded by measuring over 2θ ranges sufficiently large to determine the background at both sides of each reflection. The reflection positions were obtained by fitting the reflections with symmetrical pseudo-Voigt functions [29, 30]. The thus obtained 2θ values of the PdB_y reflections were corrected using the positions of the Si reflections in the same 2θ range for calibration. The lattice parameters of the PdB_y phase were subsequently determined by using the programme CELREF [31]. Similar procedures were applied for lattice-parameter determinations of phases pertaining to more complicated low-temperature states involving occurrence of two-phase mixtures and/or non-cubic phases.

2.4 Neutron diffraction measurements

Neutron powder diffraction (NPD) on Pd¹¹B_{0.158} powder (alloy 2) as quenched from 800 °C was performed at the HRPT powder diffractometer [32] installed at the spallation neutron source SINQ (Paul Scherrer Institute, Villigen, CH) employing the high-intensity mode of the instrument. The present measurements were conducted in the same way as those presented earlier in Ref. [11]. The wavelength of the neutron beam was $\lambda = 1.1966$ Å. The Pd¹¹B_{0.158} powder was kept in a closed vanadium cylinder ($d = 4$ mm). To avoid frozen air in the vanadium cylinder and thus avoiding bad thermal contact, the powder had been put into the cylinders in a glovebox under helium atmosphere. The sample was measured for about 8 h at 15 K (using a closed cycle CTI refrigerator). Absorption due to the sample was shown to be negligible; see Ref. [11].

Rietveld refinement on the basis of the NPD data was performed using the program Jana2000 [33]. A fixed

background was estimated from measured intensities at a series of 2θ values in between occurring reflections and subtracted from the intensity profile. In the subsequent Rietveld refinement allowance was made for a residual background described by a Legendre function with fitted coefficients. A possible zero-point shift was refined as well. The reflection profiles were fitted with pseudo-Voigt functions according to the Thompson–Cox–Hastings version [34].

2.5 TEM sample preparation

Transmission electron microscopy (TEM) and electron diffraction was performed to investigate the superstructure of the ordered low-temperature phase and microstructural phenomena related with the ordering. Plates with a thickness of a few hundred μm were cut from the arc-beam-melted bulk samples by electrical discharge machining. These plates were cleaned and polished to achieve a thickness of about 100 μm . Subsequently, conventional Ar⁺ ion-milling was performed at an acceleration voltage of 4 kV on a BalTec RES010 instrument for up to 35 h applying an angle of incidence of 6°. If necessary, the samples were additionally thinned at a modified [35] BalTec RES010 for 30 minutes applying a voltage of 1 kV until they were electron transparent. To avoid sample heating during the milling the sample was cooled with liquid nitrogen. The TEM measurements were carried out using JEOL 2000 FX (200 kV), Philips CM 30 (300 kV) and Philips CM 200 (200 kV) transmission electron microscopes.

3. Possible ordering patterns for B in Pd₆B

The determination of the crystal structure of the ordered Pd₆B (ideal composition: $y = 1/6$ with respect to PdB_y) phase on the basis of selected-area electron diffraction patterns (*cf.* Section 4.3) was facilitated by a successful conjecture of three main candidate structure types. Good guesses can be made by looking at already known ordered phases like those discussed in the introduction in which the two species (say X and Y) on the ordering *fcc* type array of sites occur in a 1:5 ratio, *i.e.* with compositions $X_{1/6}Y_{5/6}$ or $X_{5/6}Y_{1/6}$. Considering first the crystal structures of interstitial phases with the formula $MX_{1/6}Y_{5/6} = MX_{1/6}\square_{5/6}$ as candidate structures for Pd₆B (= PdB_{1/6}□_{5/6}), no example was found in literature.

However, the crystal structures of the interstitial phases with the formula $MX_{1/6}Y_{5/6} = M\square_{1/6}Y_{5/6}$ may also be candidate structures for Pd₆B, where the roles of interstitial atom X and vacancy $\square$ are interchanged. This implies that analogous types of ordering can occur for MX_y with $y = 1/2 + \delta$ and $y = 1/2 - \delta$. Ordered defect-NaCl type interstitial phases of the type $MY_{5/6}\square_{1/6}$ are known for interstitial transition metal carbides ($M = \text{V, Nb}$; $Y = \text{C}$): $MY_{5/6}$ or M_6C_5 . Three different, closely related superstructure types have been described for these carbides [36], in terms of idealised atomic coordinates (including those of the empty octahedral sites) and in terms of the basis vectors of the superlattices, as follows:

Fig. 2. Crystal structure of *pseudocubic* Pd₆B (space group $C2/c$) as obtained by Rietveld refinement of NPD data: (a) view along $[110]_{fcc}$; alternate sequence of layers of octahedral interstitial sites (looked upon ‘edge on’) within the cubic close packed arrangement of Pd with average occupancies for B of $y_{av} = 1/3$ and 0. The stacking direction corresponds to $[111]_{fcc}$ (see Table 2). One *fcc* unit cell has been highlighted in the upper part of the figure, and one monoclinic unit cell at the bottom. (b) view along $[111]_{fcc}$; arrangement of B atoms with the surrounding Pd atoms within one of the occupied octahedral layers, vacant octahedral sites within this layer are indicated by squares, □. (c) One BPd₆ entity with shortest distances B–Pd. Orientation like in (a).

1. trigonal, space group $P3_1$, $\mathbf{a}_{tr} = 1/2[21\bar{1}]_{fcc}$, $\mathbf{b}_{tr} = 1/2[112]_{fcc}$, $\mathbf{c}_{tr} = 2[1\bar{1}1]_{fcc}$, $V_{tr} = 4.5V_{fcc}$
2. monoclinic, space group $C2$, $\mathbf{a}'_{m1} = 1/2[11\bar{2}]_{fcc}$, $\mathbf{b}'_{m1} = 3/2[110]_{fcc}$, $\mathbf{c}'_{m1} = [1\bar{1}2]_{fcc}$, $V_{m1} = 6V_{fcc}$, $\beta'_{m1} = \arccos(-1/3) = 109.47^\circ$
3. monoclinic, space group $C2/m$, $\mathbf{a}_{m2} = 1/2[11\bar{2}]_{fcc}$, $\mathbf{b}_{m2} = 3/2[110]_{fcc}$, $\mathbf{c}_{m2} = 1/2[1\bar{1}2]_{fcc}$, $V_{m2} = 3V_{fcc}$, $\beta_{m2} = \arccos(-1/3) = 109.47^\circ$

However, the space groups of the superstructures of types 1 and 2 have to be revised. According to Refs. [37, 38] the actual symmetry of type 1 is $P3_112$ (or $P3_212$) rather than $P3_1$ ($P3_2$). Furthermore, structures which exhibit the same ordering patterns of species on an ordering *fcc* type array of sites like that one occurring for type 2 were discussed (i) in the course of considerations on the hypothetical cation ordering in ionic NaCl derivative crystal structures (e.g. structure candidates for Li₅ReO₆ [21]), and (ii) in the course of a systematic derivation of possible crystal structures for octahedral molecules MX_6 which adopt an *fcc* type array of X [39]. In these works the structures were conceived to be centrosymmetric ($C2/c$ rather than $C2$), suggesting that this is also the case for the corresponding M_6C_5 superstructure of type 2. Moreover, a basis transformation can be applied in order to bring the monoclinic angle β of the type 2 superstructure closer to 90° [21, 39]. The thus resulting idealised superlattice basis vectors and the atomic coordinates for the three candidate structure types for Pd₆B have been listed in Table 2 (superstructure of type 2) and in the Appendix (superstructures of types 1 and 3).

Table 2. Idealised structure parameters for the type 2 superstructure candidate for Pd₆B: space group $C2/c$; $\mathbf{a}_{m1} = 1/2[11\bar{2}]_{fcc}$ ($a_{m1} = \sqrt{6}/2a_{fcc}$), $\mathbf{b}_{m1} = 3/2[110]_{fcc}$ ($b_{m1} = 3\sqrt{2}/2a_{fcc}$), $\mathbf{c}_{m1} = 1/2[332]_{fcc}$ ($c_{m1} = \sqrt{22}/2a_{fcc}$), $V_{m1} = 6V_{fcc}$, $\beta_{m1} = \arccos(-1/\sqrt{33}) = 100.03^\circ$.

Atom	Wyckoff site	x_{id}	y_{id}	z_{id}
B	4e	0	$1/12$	$1/4$
Pd1	8f	$1/8$	$1/4$	$1/8$
Pd2	8f	$1/8$	$7/12$	$1/8$
Pd3	8f	$1/8$	$11/12$	$1/8$

It should be noted here that all three ordering types give rise to superstructure reflections indexable as $\frac{h}{2} \frac{k}{2} \frac{l}{2}_{fcc}$ with odd h, k, l with respect to the *fcc* unit cell of the

solid solution (the indices with respect to the different supercells vary from type to type) [36, 40]. Such superstructure reflections have been observed previously for ‘Pd₁₆B₃’ [13]. However, in Ref. [13] a *cubic* $a' = 2a_{fcc}$ supercell² was proposed with unspecified ordering pattern for B. In addition to these superstructure reflections common to the three superstructure types, further superstructure reflections occur in different ways for the three superstructure types, which should allow distinction between the three superstructure types. However, distinction of superstructure types 1 and 3 on the basis of powder diffraction patterns only may not be straightforward [40].

4. Experimental results

4.1 Thermal analysis; phase transition ordered Pd₆B $\rightleftharpoons$ disordered PdB_{1/6}

A bulk piece of PdB_{0.163} was annealed at 800 °C for 5 min and subsequently quenched in water by crushing the quartz capsule. In this way the disordered state occurring at high temperature should be retained. Subsequently, in the DSC the sample was heated up to 500 °C and cooled down, for three times in succession (Fig. 3a). Only the first of these DSC cycles showed upon heating an exothermic signal in the range of 100 °C to 230 °C with the maximum at about 160 °C (Fig. 3b). This is followed by an endothermic signal with an onset temperature for the heating runs of about 440(5) °C (Fig. 3a). In the following heating runs only the latter signal is observed. In all cooling runs an exothermic signal occurs with onset tempera-

² This supercell structure proposal is reasonable because no splitting of the fundamental reflections was observed which would hint at a crystal system of lower symmetry than cubic. See further results obtained in the present work.

Fig. 3. DSC scans recorded from a PdB_{0.163} (alloy 3) bulk piece (after annealing for 5 min at 800 °C followed by water quenching thereby retaining the disordered solid solution). During the first heating run the exothermic signal observed at about 160 °C (b) indicates the (at this temperature) irreversible ordering of B atoms leading to Pd₆B. Upon further heating and subsequent cooling, at 440(5) °C the (reversible) transition ordered Pd₆B $\rightleftharpoons$ disordered PdB_{0.163} occurs, in this and in all following heating and cooling cycles (a).

ture of about 440(5) °C, *i.e.* the same temperature at which the endothermic signal occurring in all three heating runs is observed.

The exothermic signal at about 160 °C during only the first heating run is ascribed to ordering of the as-quenched disordered alloy, disordered PdB_{0.163} $\rightarrow$ ordered Pd₆B. The signal at about 440 °C observed upon heating and cooling in all cycles is attributed to the reversible order-disorder phase transition, ordered Pd₆B $\rightleftharpoons$ disordered PdB_{0.163}, in agreement with earlier results [15].

It was found that samples which were quenched from 800 °C *without* immediate subsequent crushing (see Section 2.1), led to absence of the initial exothermic signal at about 160 °C upon heating in the first cycle. This implies that crushing is essential to realise efficacious quenching to retain the disordered solid solution state.

4.2 Electron diffraction; type of B ordering in the Pd₆B phase

Electron diffraction patterns recorded from PdB_{0.163} (alloy 3) annealed for 1 week at 360 °C showed not only the funda-

Fig. 4. Electron diffraction pattern negatives of a thin foil prepared from (a) PdB_{0.163} (alloy 3) quenched and annealed for 1 week at 360 °C and (b–d) PdB_{0.144} (alloy 1) quenched and annealed for 3 weeks at 280 °C. The fundamental reflections and zone axes of each pattern except (d) have been indicated according to the *fcc* average structure (black numbers) and to the monoclinic type 2 superstructure (white numbers, see Table 2). The directions of the incident electron beams have been indicated; (d) can be understood as a superposition of patterns (b) and (c). Weak streaks parallel to $[1\bar{1}1]_{fcc}$ hint at faults in the stacking sequence of partially occupied (by B) layers of octahedral interstitial sites of the close packed cubic arrangement of Pd, and have been indicated in the enlarged part of pattern (b). The circle in (d) indicates the (superstructure) reflections used to record the dark-field image shown in Fig. 5.

mental reflections pertaining to the mean *fcc*-type arrangement of the Pd atoms but also many reflections ascribed to the occurrence of a superstructure (see Fig. 4a). A comparison of the recorded diffraction patterns with diffraction patterns simulated [41] on the basis of the three candidate structures (see Section 3 and the Appendix) showed that all observed superstructure reflections can be explained by the exclusive occurrence of type 2 ordering (*C2/c*, Table 2); diffraction patterns requiring the (additional) presence of ordering types 1 and 3 were not observed.

Since the *monoclinic* superstructure of type 2 is formed from a *cubic* high-temperature phase, different orientations of the superlattice with respect to the *fcc* lattice of the parent high temperature phase are possible, and thus differently oriented domains are expected to occur. Indeed some diffraction patterns were observed which could be explained as superpositions of diffraction patterns from differently oriented (with respect to the incident electron beam) domains, as shown in Fig. 4d.

Whereas the annealed PdB_{0.163} (alloy 3, a week at 360 °C) apparently consists of only one single phase, TEM of the annealed PdB_{0.144} (alloy 1, 3 weeks at 280 °C followed by quenching) reveals plates of a second phase in a matrix consisting of Pd₆B with the superstructure of type 2 (for plates see Fig. 5, for diffraction patterns see Figs. 4b–d). According to the selected-area electron diffraction performed, these plates (typical thickness <100 nm) have – with respect to the fundamental reflections – the same crystallographic orientation as the surrounding matrix, but the superstructure reflections lack. Indeed, the plates appear dark in dark-field images re-

Fig. 5. Dark field image (positive) taken using the superstructure reflections of the ordering of type 2 encircled in Fig. 4d. The plate-like dark regions (visible as dark bands) are the areas of the solid solution disordered with respect to B.

corded from the superstructure reflections of the surrounding matrix (Fig. 5). The superstructure reflections used for the dark field images have been indicated in Fig. 4d.

Certain diffraction patterns pertaining to $\langle 211 \rangle_{fcc}$ zones showed besides the superstructure reflections corresponding to the type 2 ordering additional diffuse streaks parallel to $[\bar{1}1\bar{1}]_{fcc}$ directions in these patterns (Fig. 4b; see Section 5). Note that for the monoclinic Pd_6B phase specific directions $[uvw]_{fcc}$ or planes $(hkl)_{fcc}$ are defined according to Table 2.

4.3 X-ray powder diffraction; identification of two-phase equilibria

X-ray diffraction measurements on powder samples quenched from the solid solution phase field (*i.e.* from 800 °C) were used to determine the lattice parameters of the fcc unit cell of the solid solution. Subsequent application of Eq. (1) led to determination of the B contents (cf. Table 1).

Inspection of the XRD patterns obtained from the $\text{Pd}^{11}\text{B}_{0.158}$ (alloy 2) and $\text{PdB}_{0.163}$ (alloy 3) powders quenched from 800 °C revealed the presence of $\frac{h}{2} \frac{k}{2} \frac{l}{2}_{fcc}$ superstructure reflections with odd h, k, l (Fig. 6) as reported previously for ‘ Pd_{16}B_3 ’ [13], and which are also consistent with the $C2/c$ (type 2) superstructure (as confirmed for this specimen by NPD, see Section 4.4.). This indicates that the quenching for these powder samples was not sufficiently drastic; the quenched sample already reveals ordering of B, although splitting of the fundamental reflections does not occur, *i.e.* the fundamental reflections can be indexed on the basis of a fcc lattice with lattice parameter a_{fcc} ; Pd_6B in fact is monoclinic with ‘true’ lattice parameters which can easily be calculated from a_{fcc} using the relations given in Table 2. Thus in the following the presently observed form of the ordered Pd_6B phase is designated as *pseudocubic*.

Upon annealing this batch of quenched $\text{Pd}^{11}\text{B}_{0.158}$ powder for 70 h at 360 °C or for 96 h at 280 °C, according to

Fig. 6. Part of the neutron (NPD) and X-ray powder diffraction (XRD) patterns of $\text{Pd}^{11}\text{B}_{0.158}$ (quenched from 800 °C) and the XRD pattern of $\text{PdB}_{0.144}$ (annealed for 70 h at 360 °C; see also Fig. 7), all in the range between the 200_{fcc} and 220_{fcc} reflections. The patterns have been scaled and shifted in order to allow easier comparison of the patterns. The $\frac{h}{2} \frac{k}{2} \frac{l}{2}_{fcc}$ superstructure reflections with odd h, k, l have been indicated by stars (*); further superstructure reflections have been indicated by diamonds (◆).

the XRD analysis, decomposition into two apparently — according to the fundamental reflections — face-centred cubic phases occurred: a majority high-B content phase showing the same superstructure reflections as observed already for the sample quenched from 800 °C and a minority low-B content phase showing no superstructure reflections (Fig. 7a). Thus it appears that low-B solid solution has precipitated from the initial ordered Pd_6B phase leading to a slight increase of the B content of the latter (which remains *pseudocubic*). Single peak fitting of selected fundamental reflection pairs, of the solid solution phase and of the *pseudocubic* Pd_6B phase (originating from the 111_{fcc} , 200_{fcc} , 220_{fcc} , 311_{fcc} and 222_{fcc} reflections of the sample quenched from 800 °C), provided the lattice parameters of the fcc unit cells as well as the integrated intensities of the different reflections. The mole fractions of the two phases (referring to formula PdB_y) were then calculated adopting that the mole fractions are proportional with the corresponding integrated intensities³. This was done separately for the above-mentioned five reflection pairs of the two phases and the averaged results have been given in Table 3. The average B content of the samples ($\text{PdB}_{0.153}$ for the annealing at 280 °C and $\text{PdB}_{0.152}$ for the annealing at 360 °C), as calculated on the basis of the mole fractions and the B contents of the two phases, is close to the expected value of the alloy $\text{Pd}^{11}\text{B}_{0.158}$ (Table 3).

The XRD patterns recorded from the $\text{PdB}_{0.144}$ powder (alloy 1) showed no superstructure reflections after quenching from 800 °C, indicating that the solid solution had been fully retained. Upon annealing for 70 h at 360 °C and 70 h at 280 °C new weak reflections and splitting of the fundamental reflections occur. For both annealing temperatures the reflection groups originating from the fundamental reflections of the solid solution can be interpreted in terms of formation of an fcc low-B content solid solution phase and an apparently face-centred tetragonal

³ This is justified because the unit-cell volumes, the structure factors and the absorption coefficients are very similar for both phases.

Fig. 7. Part of X-ray diffraction patterns of (a) quenched Pd_{0.158}B (alloy 2, already ordered after quenching) and (b) quenched Pd_{0.144}B (alloy 1) after annealing at 280 °C (leading to decomposition into ordered Pd₆B + disordered Pd_{B~0.01}) and at 360 °C (leading to decomposition into ordered Pd₆B + disordered Pd_{B~0.13}). Starting from Pd_{0.158}B the *pseudocubic* manifestation, and starting from Pd_{0.144}B the *pseudotetragonal* (*fct* = face-centred tetragonal) manifestations of Pd₆B are found (cf. Table 3). The patterns have been scaled and shifted in order to allow easier comparison of the patterns. The perpendicular, dashed lines indicate the positions of the reflections of quenched Pd_{0.158}B and quenched Pd_{0.144}B.

(*fct*) high-B content phase. The latter shows unsplit fundamental reflections $hhhf_{ct}$ (originating from 111_{fcc} and 222_{fcc} of the initial solid solution) and split (doublets) hhl_{fct} and lhh_{fct} of intensity ratio 2:1 or 1:2 (originating from 200_{fcc} , 220_{fcc} , 311_{fcc} , Fig. 7b). For both annealing temperatures the lattice parameter of the cubic low-B content phase (depending on the annealing temperature, see Fig. 7b) largely corresponds to that observed for the disordered low-B content phase that developed upon annealing

of Pd¹¹B_{0.158} (see above and Table 3). The according to the fundamental reflections face-centred tetragonal high-B content phase has $c_{fct} > a_{fct}$; its B content is estimated on the basis of Eq. (1) by substituting the lattice parameter a_{fcc} in Eq. (1) by $(a_{fct}^2 \times c_{fct})^{1/3}$. Analogously to the findings for the low-B content phase, the resulting B content of the *pseudotetragonal* Pd₆B is about equal to the one of the *pseudocubic* Pd₆B (with superstructure of type 2) developing upon annealing of (already *pseudocubic*) Pd¹¹B_{0.158} at the same annealing temperatures (see Table 3). TEM analysis of Pd_{0.144}B (alloy 1) annealed at 280 °C indicated the presence of a two-phase state with a disordered solid solution minority component and an ordered majority component showing type 2 superstructure (see Section 4.2). Hence, it is concluded, that the two phases observed by XRD are the same: the *fcc* low-B content component is the disordered solid solution, and the apparently face-centred tetragonal component is indeed the (same) monoclinic Pd₆B phase exhibiting now different lattice parameters (*pseudotetragonal* Pd₆B) than the Pd₆B produced by annealing Pd_{0.158}B (*pseudocubic* Pd₆B). The *pseudotetragonal* unit cell suggested by inspection of the fundamental reflections in the XRD patterns can be related to the monoclinic supercell as described in Table 2 by choosing $\mathbf{c}_{fct} = [001]_{fcc}$ ($\mathbf{a}_{fct} = [100]_{fcc}$ and $\mathbf{b}_{fct} = [010]_{fcc}$). The two other alternatives, $\mathbf{c}_{fct} = [100]_{fcc}$ and $\mathbf{c}_{fct} = [010]_{fcc}$, would lead to lattices with lattice parameters incompatible with monoclinic symmetry. In fact, if the monoclinic lattice parameters for a type 2 superstructure (Table 2) are calculated on the basis of the *pseudotetragonal* cell parameters and the choice $\mathbf{c}_{fct} = [001]_{fcc}$, the weak reflections observed in the XRD patterns of annealed Pd_{0.144}B (alloy 1) can be indexed with respect to this monoclinic cell; most of these superstructure reflections are observed (with the same Miller indices) in the XRD patterns of the *pseudocubic* Pd₆B produced from Pd¹¹B_{0.158} (alloy 2). This confirms that indeed the *pseudotetragonal* Pd₆B produced from Pd_{0.144}B (alloy 1) and the *pseudocubic* Pd₆B pro-

Table 3. Lattice parameters (measured by XRD at ambient temperatures) and mole fractions (referring to the formula Pd₆B_y) of the high B component (ordered Pd₆B) and low B component (disordered solid solution) obtained by decomposing Pd_{0.144}B (alloy 1) and Pd¹¹B_{0.158} (alloy 2) both at 280 °C and 360 °C.

Annealing temperature (°C)	Annealing time (h)	Calculated composition of low-B content solid solution phase using Eq. (1)	Lattice parameters of Pd ₆ B phase a_{fcc} or a_{fct} , c_{fct} (Å)	Calculated composition using Eq. (1) ^a	Mole fraction Pd ₆ B	Calculated average B content y_{av} of the whole sample
starting material Pd ¹¹ B _{0.158} (alloy 2, unsuccessfully quenched from 800 °C, see Section 4.3)						
280 ^a	96	Pd _{0.008} B	$a_{fcc} = 4.0020(1)$ <i>pseudocubic</i>	Pd _{0.160} B	0.95(1)	0.153(2)
360	70	Pd _{0.127} B	$a_{fcc} = 4.0022(1)$ <i>pseudocubic</i>	Pd _{0.160} B	0.75(0)	0.152(0)
starting material Pd _{0.144} B (alloy 1, successfully quenched from 800 °C, see Section 4.3)						
280	70	Pd _{0.010} B	$a_{fct} = 3.9971(2)$ $c_{fct} = 4.0133(3)$ <i>pseudotetragonal</i>	Pd _{0.161} B	0.86(1)	0.140(4)
360	70	Pd _{0.125} B	$a_{fct} = 3.9960(2)$ $c_{fct} = 4.0146(2)$ <i>pseudotetragonal</i>	Pd _{0.160} B	0.42(1)	0.140(1)

a: For *pseudocubic* Pd₆B a_{fcc} , for *pseudotetragonal* Pd₆B the cubic root of the volume of the *pseudotetragonal* unit cell is taken as the lattice parameter in Eq. (1); see text.

Fig. 8. Rietveld refinement on the basis of the neutron diffraction pattern recorded at 15 K from the quenched $\text{Pd}^{11}\text{B}_{0.158}$ sample after annealing for 5 min at 800 °C (alloy 1): measured data points, calculated intensity profile and difference curve. The reflection markers indicate reflection positions of diamond (top of marker bar), an impurity (see Section 2.1) and of ordered Pd_6B . Regions excluded from the refinement have been shaded; the corresponding 2θ ranges 80–85° and 87–89° 2θ were excluded as well due to the accidental occurrence of electronic interfering signals.

duced from $\text{Pd}^{11}\text{B}_{0.158}$ (alloy 2) are just different forms of the same phase which will be called *manifestations* here (see Section 5.1). Furthermore, the superstructures as revealed for alloys 1 and 3 by electron diffraction are also the same as deduced from the corresponding XRD patterns. It follows that the ordered Pd_6B phase forming in all three alloys is the same and of ordering type 2.

Mole fractions of the low- and high-B content components of decomposed $\text{PdB}_{0.144}$ (alloy 1) were obtained as described above for $\text{PdB}_{0.158}$. To this end, for the *pseudotetragonal* high-B Pd_6B component the integrated intensities of all reflections originating from a certain hkl_{fcc} were summed up. Again, good agreement between the calculated average B content and the value determined for the initial solid solution was obtained ($\text{PdB}_{0.140}$ as calculated for both annealing temperatures vs. the initial boron content of $\text{PdB}_{0.144}$, cf. Table 3).

4.4 Neutron diffraction; structure parameters of Pd_6B

As compared to the corresponding XRD pattern taken at ambient temperatures, the NPD pattern (Figs. 6 and 8) of the $\text{Pd}^{11}\text{B}_{0.158}$ sample taken at 15 K⁴ shows much stronger superstructure reflections relative to the intensities of the fundamental reflections: the effect of ordering of B is more pronounced in NPD patterns because the scattering power of B is higher than that of Pd in NPD (as can be expressed in terms of the coherent scattering lengths; see Table 4), whereas for XRD the scattering power (expressed in terms of the atomic form factors, or basically in terms of the number of electrons) is much smaller for B than for Pd.

Table 4. Experimental details for the neutron powder diffraction data taken at 15 K from ordered Pd_6B phase powder of the composition $\text{Pd}^{11}\text{B}_{0.158}$ (alloy 2 powder quenched from 800 °C), containing diamond impurities from filing. Figure of merits for the performed Rietveld analysis have been indicated. For the refined fractional coordinates of the Pd_6B phase see Table 5.

Wave length (Å)	1.1966
Diffraction angle range used (°)	12–162
Stepwidth (°)	0.05
Excluded regions (°) ^a	80–85, 87–89
Phase 1	Pd_6B (composition $\text{Pd}^{11}\text{B}_{0.158}$)
Space group	$C2/c$
Coherent scattering lengths [28], b (barn)	
Pd	5.91
^{11}B	6.65
a_{m1} (Å)	$\sqrt{6}/2a_{\text{fcc}}$
b_{m1} (Å)	$3\sqrt{2}/2a_{\text{fcc}}$
c_{m1} (Å)	$\sqrt{22}/2a_{\text{fcc}}$
β_{m1} (°)	$\arccos(-1/\sqrt{33})$
a_{fcc} (Å) ^b	3.99279(4) Å
Phase 2	diamond
Crystal system	cubic
Space group	$Fd\bar{3}m$
Fractional coordinates: C	$1/8 \ 1/8 \ 1/8$
Coherent scattering lengths [28], b (barn)	
C	6.646
a (Å)	3.56692(8)
Weight fraction diamond	0.0082(3)
R_{wp} [42]	0.0569
R_{B} [42]	0.0579
R_{wp} and R_{B} with ideal fractional coordinates from Table 2: $R_{\text{wp}} = 0.0624$; $R_{\text{B}} = 0.0746$	

a: Due to accidental occurrence of interfering signals

b: Lattice parameters are restricted to be *pseudocubic*, so that a_{fcc} constitutes effectively the only refined lattice parameter of the Pd_6B phase.

⁴ The sample temperature of 15 K has no influence on the B ordering in the phase. The measurements were recorded at 15 K in the course of a series of other measurements of that sample at that temperature [4].

Fig. 9. (a) Enlarged part of Fig. 8. Fundamental reflections have been indicated by hkl_{fcc} , superstructure reflections $\frac{h}{2} \frac{k}{2} \frac{l}{2}_{fcc}$ with odd h, k, l by stars (*) and further (noticeable) superstructure reflections by diamonds (◆). (b) shows the same region after a Rietveld refinement using fixed ideal fractional coordinates according to Table 2, demonstrating the influence of the Pd atom displacements from their ideal sites on the intensities of the superstructure reflections (compare Fig. 9a (allowing for displacements) with Fig. 9b (Pd atoms on ideal positions)).

In agreement with the XRD data (Section 4.3), the $\frac{h}{2} \frac{k}{2} \frac{l}{2}_{fcc}$ superstructure reflections with odd hkl are the strongest superstructure reflections. Additionally, peculiar broad intensity humps occur in the NPD pattern (e.g. at about $2\theta = 44^\circ$, in Fig. 9a marked with diamonds). Rietveld refinement was performed adopting ordering according to superstructure of type 2 (Sections 4.2 and 4.3). The monoclinic lattice parameters were taken consistent with

the *pseudocubic* lattice as indicated by the unsplit fundamental reflections in the NPD data (and also in XRD data of the same specimen showing narrower reflections than the NPD data) by fixing the ratios of a_{m1} , b_{m1} , c_{m1} as well as by fixing the value of β_{m1} to 100.03° (Table 2). Rietveld refinement was initially performed with the fixed fractional coordinates from Table 2 which already gives a reasonable fit to the experimental profile (Fig. 9b), implying that the above-mentioned intensity humps are superstructure reflections additional to the indexed $\frac{h}{2} \frac{k}{2} \frac{l}{2}_{fcc}$ reflections with odd hkl , and being thus characteristic for the superstructure of type 2. In a next step refinement of the fractional coordinates of the Pd and B atoms led to a significant improvement of the fits (Fig. 9a), in particular to the superstructure reflections, although considerable correlations occur between the refined fractional coordinates, in particular for the Pd atoms. The final coordinates are listed in Table 5. Comparison of the finally calculated diffraction pattern with the observed diffraction pattern suggests that some superstructure reflections are relatively broad, whereas others are relatively sharp (in particular the $\frac{h}{2} \frac{k}{2} \frac{l}{2}_{fcc}$ reflections with odd hkl) (see Section 5.1).

Test refinements show that partial occupation of other than the presently considered octahedral sites cannot be excluded; however, the minor improvement of the fit does not justify the consideration of these additional parameters.

5. Discussion

5.1 The ordered arrangement of B in Pd₆B

The here observed ordering pattern of B on the octahedral interstices of the *ccp* arrangement of Pd atoms (superstructure of type 2) corresponds to that of vacancies on the octahedral interstices of the *ccp* arrangement of V atoms in a superstructure reported for V₆C₅ [43].

The formation of superstructures of types 1–3, i.e. including the observed one of type 2 (see Fig. 2), from the disordered solid solution can basically be understood qualitatively considering repulsive pair interactions B...B:

Table 5. Refined fractional coordinates of ordered Pd₆B^a (composition Pd¹¹B_{0.158}; *C2/c*; ideal structure model, see Table 2) as obtained by Rietveld analysis of the neutron powder diffraction data taken at 15 K (see also Table 4).

Atom	Wyckoff site	$x = x_{id} + \delta x^b$	$y = y_{id} + \delta y^b$	$z = z_{id} + \delta z^b$	$\langle u^2 \rangle$ (Å ²) ^c	occupancy
B	4e	0	0.0807(10)	0.25	0.0071(–)	0.954(–) ^d
Pd1	8f	0.125(3)	0.2507(7)	0.1200(6)	0.0026(1)	1
Pd2	8f	0.120(2)	0.5819(7)	0.1244(4)	$= \langle u^2(\text{Pd1}) \rangle$	1
Pd3	8f	0.128(3)	0.9104(7)	0.1223(4)	$= \langle u^2(\text{Pd1}) \rangle$	1

a: Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-415013, the name of the author, and the citation of the paper.

b: The fractional coordinates are regarded as the sum of the ideal coordinates (see Table 2) modified by displacements δx , δy , δz .

c: The atomic displacement parameter for B was fixed at the same value used for a series of PdB_y alloys at 15 K [11]. The atomic displacement parameters of Pd were assumed to be the same for the three different Pd sites.

d: The occupancy of the B site was fixed at the value expected from the composition Pd¹¹B_{0.158} and the assumption that all B atoms are located on this site.

The superstructure avoids the occurrence of (i) nearest neighbour B···B pairs (*i.e.* avoids ‘edge-sharing’ Pd₆B octahedra using the terminology of the Pauling rules [44], for which $d = 2^{1/2}/2a_{fcc}$, where d is the distance between the pair of B atoms considered, if distortions with respect to the initially disordered *fcc* structure are neglected) and of (ii) next-nearest neighbour B···B pairs (*i.e.* avoids ‘corner-sharing’ Pd₆B octahedra for which $d = a_{fcc}$). This is achieved by keeping each second layer of octahedral sites perpendicular to one $[111]_{fcc}$ direction (*i.e.* $[\bar{1}\bar{1}\bar{1}]_{fcc}$ in the Pd₆B structure as given in Table 2) devoid of B atoms, whereas the other half of the octahedral layers is occupied by B with an (average) occupancy⁵ of $1/3$ (Fig. 2a). By this type of incorporation of B atoms into only each second layer of octahedral sites, the occurrence of next-nearest neighbour pairs B···B is excluded. Furthermore, a specific ordering of B atoms exists within the occupied layers, as indicated in Fig. 2b, ensuring that also no nearest-neighbour pairs B···B occur, and leads to the occurrence of isolated [BPd₆] (formally molecular) entities. The composition PdB_y with $y = 1/6$ is the one with the highest B content for which this is possible.

The superstructures of types 1–3 differ only in the way of stacking of the (partially) occupied layers of octahedral interstices [36]. In all these superstructures nearest and next-nearest neighbour B···B pairs are absent. The relative stability of the three superstructure types is determined by (subtle) longer distance (pair-)interactions. This makes faulting in the stacking sequence discussed likely. The occurrence of faulting is indeed suggested by the diffraction streaks (see Section 4.2) along $[11\bar{1}]_{fcc}$, *i.e.* parallel to the stacking direction of the alternately (partly) occupied and unoccupied layers of octahedral sites; a similar phenomenon was observed for V₆C₅ [45]. Moreover, the line-broadening of certain weak superstructure reflections as observed in the NPD data (see Section 4.4) also suggests faulting; see similar phenomena in NPD patterns observed for Nb₆C₅ (for which type 1 superstructure occurred) [46].

According to the fundamental reflections the average lattice of the Pd₆B phase of the Pd¹¹B_{0.158} as quenched from 800 °C is apparently not distorted: it is *pseudocubic* (cf. Section 4.2). This means that systematic overlap between inequivalent Bragg reflections occurs in the NPD data, in particular for the fundamental reflections. Yet, the Rietveld refinement on the basis of the NPD data is able to reveal (Table 5, and comparison of Fig. 9a and b) that shifts of the Pd and B atoms with respect to their ideal fractional coordinates occur (Table 2). In the undistorted structure (as described by the ideal fractional coordinates given in Table 2) with the refined *pseudocubic* lattice parameter $a_{fcc} = 3.993$ Å, (cf. Table 4) all distances Pd–B within the isolated Pd₆B entities would be $a_{fcc}/2 = 1.996$ Å. However, the refined fractional coordinates indicate significantly larger Pd–B distances within these entities ranging from 2.02(1) to 2.05(1) Å (Fig. 2c). The angles B–Pd_{ideal}–Pd

(where Pd_{ideal} corresponds to Pd sites with the ideal fractional coordinates from Table 2) vary between 138° and 166° for Pd1, Pd2 and Pd3, indicating that the displacements of the Pd atoms from their ideal sites occur largely radially away from the B atom (for purely radial displacements the angle B–Pd_{ideal}–Pd would be 180°). For the disordered solid solution such Pd atom displacements were observed and described in terms of a static displacement contribution to the overall atomic displacement parameters [11]. The shortest Pd–B distances in Pd₆B, 2.02 to 2.05 Å (at 15 K), are about equal to or somewhat shorter than those observed for other compounds with octahedral coordination of B by Pd, *e.g.* $d(\text{Pd}–\text{B}) = 2.04$ Å for YbPd₃B [47], 2.10–2.12 Å for Pd₂B [48] or 2.13 Å for Li₂Pd₃B [49].

The displacements of the Pd atoms in Pd₆B lead to Pd–Pd distances ranging from 2.74(1) to 2.91(1) Å (see Fig. 10; the twelve nearest Pd neighbours of Pd1, Pd2 and Pd3 were considered, leading to 36 Pd–Pd pairs), whereas the Pd–Pd nearest neighbour distances would be equal to $a_{fcc}/2^{1/2} = 2.82$ Å for an undistorted *ccp* structure of Pd atoms with lattice parameter a_{fcc} . As follows from the radial displacements of the Pd atoms surrounding octahedrally a B atom, the Pd–Pd distances which form the edges of [BPd₆] octahedra are the longest nearest neighbour distances for Pd, *i.e.* all longer than 2.855 Å (12 distances, see Fig. 10), whereas the other ones (being edges of only unoccupied Pd₆ octahedra) are shorter than 2.855 Å (24 distances). The present observations concerning Pd–Pd nearest neighbour distances agree well with results from EXAFS measurements on disordered Pd_{0.16} [10]. The EXAFS signals were interpreted by fitting to the experimental data two different shortest Pd–Pd distances of 2.782(5) Å and 2.897(5) Å, respectively, which are smeared due to static displacements in a Gaussian fashion (see Fig. 10). The distance of 2.897(5) Å was attributed to edges of Pd₆ octahedra occupied by B, and the distance of

Fig. 10. Histogram showing the distribution of Pd–Pd distances shorter than 3 Å for the coordination spheres of one Pd1, one Pd2 and one Pd3 atom in Pd₆B. The 24 distances shorter than 2.855 Å (limit indicated by dashed line) correspond to edges of empty Pd₆ octahedra, whereas the 12 longer ones correspond to Pd₆ octahedra occupied by B ([BPd₆] entities). The arrows indicate the maxima of two Gaussian Pd–Pd distance distributions located at 2.782(5) Å and 2.897(5) Å fitted to EXAFS data for Pd–Pd distances [10]. The standard deviation ranges 2σ of these distance distributions have been indicated by horizontal bars.

⁵ Note that complete occupation of the latter octahedral layers leads to the CdCl₂ type structure as occurring for a couple of hemi-carbides, M₂C [51].

2.782(5) Å was attributed to edges of unoccupied Pd₆ octahedra.

The observed deviations of the fractional coordinates of Pd in Pd₆B from the geometrically ideal ones can be understood recognising the relative large size of B with respect to the size of the octahedral sites of Pd [8], as also evidenced by the strong dependence of the lattice parameter of the PdB_y solid solution on the B content, as given by Eq. (1).

Formation of the Pd₆B phase from disordered PdB_{0.144} led to a considerably distorted, *pseudotetragonal* lattice (according to the fundamental reflections), whereas Pd₆B obtained by the not sufficiently drastic quenching of Pd¹¹B_{0.158} from 800 °C is *pseudocubic*, and remains *pseudocubic* even after annealing treatments comparable to those subjected to PdB_{0.144}. Although the observed lattice parameters of the Pd₆B generated in these two ways are different, the volumes of the *pseudocubic* and of the *pseudotetragonal* cells are practically the same, and thus the estimated compositions are the same (see Table 3). Further, the electron and X-ray diffraction evidence attained in this work demonstrates that the type of ordering in both cases is also the same (superstructure of type 2).

The occurrence of the *pseudocubic* and *pseudotetragonal* manifestations for the same Pd₆B phase is a striking observation, because, if equilibrium occurs, at the same measuring temperature, pressure and composition the same lattice parameters should occur for a crystalline phase irrespective of the way of preparation. Hence, the occurrence of different lattice parameters for the same phase must have a microstructural origin. Due to the monoclinic symmetry of the Pd₆B phase usually anisotropic ordering strain [50], with respect to the original *fcc* solid solution, is expected, reflecting a long-range accumulation of the local atomic displacements due to the ordering. If monoclinic domains are formed initially coherently in an initially cubic crystallite, the ordering strain can be accommodated by a special arrangement of ordered domains and/or elastic/plastic deformation. Possibly remaining coherency stresses counteracting the ordering strain will elastically distort the domains so that lattice parameters different from the equilibrium ones are measured. Therefore, the different lattice parameters of the *pseudocubic* and of the *pseudotetragonal* manifestations of Pd₆B are likely due to their different domain microstructures caused by different initial alloy compositions and thus different ‘ways’ of formation (Section 5.2). Probably, neither the *pseudocubic* nor the *pseudotetragonal* manifestation exhibit the ‘true’ (stress free) lattice parameters of ordered Pd₆B (of the considered composition).

5.2 Consequences for the constitution of the binary system Pd–B

The experimental results presented in this work are compatible with a tentative phase diagram for the Pd–B system (Pd-rich side) as proposed in Fig. 11. The compositions of the three PdB_y alloys investigated have been indicated (Table 1). The composition PdB_{0.163} (alloy 3) apparently lies within the homogeneity range of the Pd₆B phase, because it was possible to transform the whole quenched sample into

Fig. 11. Proposed phase diagram of the Pd–B system (Pd-rich side) indicating the observed phases, their respective compositions and the initial compositions of the alloys investigated in this work. The shaded region indicates that upon moderately fast cooling of the PdB_y solid solution in that range a homogeneous (ordered) Pd₆B phase (of unchanged B content) develops, which upon annealing decomposes by diffusion according to the two-phase regions as indicated (see open circles).

this phase upon annealing at 360 °C (Section 4.2). The same quenched alloy was analysed by DSC, which indicated that the congruent transformation, ordered Pd₆B $\rightleftharpoons$ disordered PdB_{1/6}, occurs at about 440(5) °C (Section 4.1).

The not sufficiently drastic quenching of Pd¹¹B_{0.158} (alloy 2) led to, also, an apparently homogeneous Pd₆B phase (Sections 4.3 and 4.4). However, the Pd₆B phase with this composition is not stable at the annealing temperatures of 360 °C and 280 °C because it is decomposed into the Pd₆B phase with the composition PdB_{0.160} and a disordered PdB_y solid solution (of composition about PdB_{0.008} at 280 °C and of composition about PdB_{0.127} at 360 °C; Table 3). These results are compatible with the presence of a miscibility gap with a critical temperature of 410 °C and a monotectic temperature at 312 °C adopting values as given in Ref. [13].

Evidently, the ordered phase Pd₆B is easily formed upon cooling by ordering of the B atoms on the octahedral interstices of *ccp* Pd as suggested by the difficulties to retain the solid solution upon quenching of the PdB_{0.163} (alloy 3) bulk material (end of Section 4.1) and the relatively large powder batch of Pd¹¹B_{0.158} (alloy 2, Sections 4.3 and 4.4). Clearly, the subsequent decomposition of the latter alloy upon annealing (into the ordered phase Pd₆B of composition PdB_{0.160} and the solid solution PdB_y of lower B content) requires much more time at the same temperature since long-range diffusion is necessary.

The rapid formation of the ordered Pd₆B phase from the solid solution even during quenching has only been observed in a limited composition range below about $y = 1/6$, as indicated in Fig. 11 by the shaded region: the solid solution of the composition PdB_{0.144} could be retained (Section 4.3). Subsequent annealing of PdB_{0.144} produced the same equilibrium phases as annealing of quenched Pd¹¹B_{0.158}. This suggests that the Pd₆B phase cannot be formed with the composition PdB_{0.144}. Thus, in the PdB_{0.144} alloy, long-range diffusion is required leading to the enrichment of B in parts of the alloy where the ordered Pd₆B phase develops (now in its *pseudotetragonal* manifestation; see Sections 4.2 and 4.3, and Fig. 5).

Because of coincidence of the lattice parameter of $a_{fcc} = 4.005 \text{ \AA}$ of the apparently cubic 'Pd₁₆B₃' phase (PdB_{0.188}) [13] with the value of $a_{fcc} = 4.001\text{--}4.002 \text{ \AA}$ as observed for *pseudocubic* Pd₆B as generated from alloy 2 of the average compositions Pd¹¹B_{0.158} (see Section 4.3) and because of the compatibility of the superstructure reflections $\frac{h}{2} \frac{k}{2} \frac{l}{2}$ with odd hkl observed for the 'Pd₁₆B₃' phase with similar reflections observed in this work for the Pd₆B phase (exhibiting the superstructure of type 2) for compositions close to PdB_{1/6}, it seems very likely that both phases, in fact, are the same. The difference between the assigned compositions — PdB_{0.188} [13] and PdB_{0.163} (this work) — probably originates from the different methods used to assign compositions to alloys, and their possible systematic errors: The good agreement of the reported lattice parameter values (see above), in fact, suggests that the composition of 'Pd₁₆B₃' from Ref. [13] in reality is close to the composition of the presently observed Pd₆B phase. In this context, it must be mentioned that in the present work all compositions, of both the solid solution phase and the Pd₆B phase were obtained by application of Eq. (1), which was determined on the basis of measured lattice parameters of an extensive series of PdB_y solid solution samples and chemical analyses of the corresponding samples [8]. In Ref. [13] a different equation was proposed.⁶ Finally, in any case the occurrence of an ordering pattern based on the avoidance of nearest-neighbour and next-nearest-neighbour B···B pairs (leading to isolated Pd₆B entities) strongly suggest that the B content in the Pd₆B phase cannot be higher than as indicated by PdB_{1/6}.

A deeper discussion of the phase diagram Pd–B in the context of recent experimental results including the present ones can be found in Ref. [52].

6. Conclusions

(i) The crystal structure of the Pd₆B phase can be described as an ordered low-temperature phase, originating from the PdB_y solid solution, with *fcc* arrangement of Pd and with B on the octahedral interstices. The observed occupational ordering pattern (space group *C2/c*) of the B atoms avoids the occurrence of nearest and next-nearest neighbour pairs B···B. The crystal structure can be regarded as built from 'isolated' BPd₆ entities, conserving the basic cubic close-packed arrangement of Pd. The same ordering pattern as observed for the B atoms in Pd₆B□₅ has been observed previously for vacancies in defect-NaCl type V₆C₅□ in which V takes the places of Pd, C those of □, and □ those of B.

(ii) The same ordered Pd₆B phase can occur, for the same composition, in different *manifestations* with respect to its lattice parameters, a *pseudocubic* one, which forms

upon direct formation of B ordering from the solid solution which has the same composition as the Pd₆B phase, and a *pseudotetragonal* one, which forms when the Pd₆B precipitates from a (quenched) solid solution of significantly lower B content than the Pd₆B phase. The occurrence of these two different manifestations has probably microstructural origin.

(iii) The phase equilibria between the ordered Pd₆B phase and the disordered PdB_y solid solution of (much) lower B content have been established.

Appendix

Table A1. Idealised structure parameters for the type 1 superstructure candidate for Pd₆B: space group *P3₁12*: $\mathbf{a}_{tr} = \frac{1}{2}[1\bar{1}2]_{fcc}$ ($a_{tr} = \sqrt{6}/2a_{fcc}$), $\mathbf{b}_{tr} = \frac{1}{2}[\bar{1}12]_{fcc}$ ($b_{tr} = \sqrt{6}/2a_{fcc}$), $\mathbf{c}_{tr} = 2[111]_{fcc}$ ($c_{tr} = 2\sqrt{3}a_{fcc}$), $V_{tr} = 4.5V_{fcc}$.

Atom	Wyckoff site	x_{id}	y_{id}	z_{id}
B	3a	$\frac{1}{9}$	$\frac{8}{9}$	$\frac{1}{3}$
Pd1	6c	$\frac{1}{9}$	$\frac{8}{9}$	$\frac{7}{12}$
Pd2	6c	$\frac{4}{9}$	$\frac{5}{9}$	$\frac{7}{12}$
Pd3	6c	$\frac{7}{9}$	$\frac{2}{9}$	$\frac{7}{12}$

Table A2. Idealised structure parameters for the type 3 superstructure candidate for Pd₆B: space group *C2/m*: $\mathbf{a}_{m2} = \frac{1}{2}[1\bar{1}2]_{fcc}$ ($a_{m2} = \sqrt{6}/2a_{fcc}$), $\mathbf{b}_{m2} = \frac{3}{2}[110]_{fcc}$ ($b_{m2} = 3\sqrt{2}/2a_{fcc}$), $\mathbf{c}_{m2} = \frac{1}{2}[1\bar{1}2]_{fcc}$ ($c_{m2} = \sqrt{6}/2a_{fcc}$), $V_{m2} = 3V_{fcc}$, $\beta_{m2} = \arccos(-\frac{1}{3}) = 109.47^\circ$.

Atom	Wyckoff site	x_{id}	y_{id}	z_{id}
B	2a	0	0	0
Pd1	4i	$\frac{1}{4}$	0	$\frac{3}{4}$
Pd2	8j	$\frac{1}{4}$	$\frac{2}{3}$	$\frac{3}{4}$

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⁶ A considerable lattice volume shrinkage of $\Delta V/V = 0.75\%$ was reported [6] to occur upon ordering. The present data cannot confirm this due to the lack of solid solution lattice parameters for these alloys. Yet the good consistency of the B content considerations in Table 4 and Section 4.3 seems to contradict the magnitude of this shrinkage.

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