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The Crystal Structure of Pd_2B

LARS-ERIK TERGENIUS AND TORSTEN LUNDSTRÖM

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

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The crystal structure of Pd_2B has been investigated by X-ray powder diffraction and single-crystal diffractometry. There are strong indications that Pd_2B crystallizes with the anti-$CaCl_2$ type structure (C 35), space group *Pnnm* (No. 58), $a = 4.6918(4)$ Å, $b = 5.1271(4)$ Å, and $c = 3.1096(3)$ Å, but the extent to which the boron atoms assume ordered positions cannot be determined precisely with X-ray diffraction methods alone.

Introduction

Stenberg reported the occurrence of three intermediate phases in the Pd–B system (*1*) and determined the structures of the most metal-rich phases, namely, Pd_3B and Pd_5B_2. In the present paper we report the results from an X-ray investigation of the third phase of composition Pd_2B. On reinspection of Stenberg's unpublished material (deposited at this institute), we found that his X-ray data for the third phase are in complete agreement with our own for Pd_2B. Stenberg had even indexed the powder pattern with cell dimensions in agreement with those reported here.

Experimental

Preparation and phase analysis. Several alloys in the nominal composition range $Pd_{0.74}B_{0.26}$–$Pd_{0.33}B_{0.67}$ were prepared by arc-melting pellets of palladium powder (claimed purity, 99.8%; Heraeus, Hanau, Germany) and crystalline boron powder (analyzed purity, 98.9% boron, with 0.3% iron as the main metallic impurity; H. C. Starck, Goslar, Germany). The alloys were examined in a Guinier-Hägg focusing powder camera equipped with a germanium monochromator yielding $CuK\alpha_1$ radiation. The phase studied gave a powder pattern with very broad and diffuse reflections, indicating nonhomogeneity and/or distorted crystals (the boride is ductile). The samples were therefore heat-treated for 1 week at 900°C under an atmosphere of 13-kPa argon (claimed purity, minimum 99.998%; ALFAX AB, Malmö, Sweden) using crucibles of boron nitride. No changes in the powder films were obtained. After pulverization, the samples were stress-relieved for 15 min (conditions as above) and then gave sharp reflections. All heat treatments were performed in silica-free furnaces, in order to avoid interchange between boron and silicon.

Two specimens, $Pd_{0.67}B_{0.33}$ and $Pd_{0.62}B_{0.38}$, only gave reflections from Pd_2B, while the more boron-rich specimens also gave reflections of β-rhombohedral boron, probably with small amounts of dissolved palladium. The specimen of nominal composition $Pd_{0.74}B_{0.26}$ gave only powder lines of Pd_3B. The two-phase equilibrium $Pd_5B_2 + Pd_2B$ was obtained in a powdered

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sample, which was stress-relieved in a vacuum furnace at 530°C during 30 min. However, Pd_5B_2 was not obtained at 900°C (as reported by Stenberg (*1*)), which might indicate that it is stable only at lower temperatures. The weight losses during the arc-melting and the heat treatment were, on the average, 1.2% for samples of about 1.2 g. For the $Pd_{0.55}B_{0.45}$ sample, which besides the Pd_2B pattern also gave β-boron reflections, the weight loss was 1.26%. If this weight loss is solely due to palladium, the composition is changed insignificantly. Thus, this investigation clearly indicates a lower boron content for the investigated phase than the equiatomic composition.

The cell dimensions were determined using silicon ($a = 5.431065$ Å) (*2*) as the internal calibration standard. The method of least squares was adopted in the refinements of the cell dimensions. No significant cell volume variation was observed, indicating that the homogeneity range is small. The powder intensities were measured with a SAAB Mark II film scanner (*3, 4*). To facilitate identification of the phase, X-ray powder data are presented in Table I.

Single-crystal work. Fragments from the two crushed alloys $Pd_{0.67}B_{0.33}$ and $Pd_{0.62}B_{0.38}$ were examined using a Weissenberg single-crystal camera. Since the phase is ductile, the fragments gave very diffuse X-ray reflections together with satellite spots. A fragment of nominal composition $Pd_{0.62}B_{0.38}$ was heat-treated at 840°C for 6 hr under pure argon together with powder of the same nominal composition. After the heat treatment, this fragment gave fairly sharp reflections, but

TABLE I

POWDER DIFFRACTION DATA (Cu$K\alpha_1$ RADIATION) FOR Pd_2B^{a-c}

		$Q \cdot 10^5$ (Å^{-2})		Intensity	
hkl	d_{obs}(Å)	Obs.	Calc.	Obs.	Calc.
110^d	—	—	8,347	<1	0.39
011	2.659	14,146	14,145	36	30
101^d	—	—	14,884	≪3	0.14
020	2.564	15,214	15,216	7	5
200	2.347	18,152	18,170	41	35
111	2.314	18,682	18,688	100	100
120	2.250	19,758	19,759	60	58
210^d	—	—	21,975	—	0.00
121^d	—	—	30,101	≪1	0.08
211	1.759	32,314	32,316	31	23
220	1.731	33,387	33,387	8	5
130^d	—	—	38,780	—	0.03
002	1.555	41,348	41,366	17	13
221^d	—	—	43,729	—	0.00
031	1.498	44,582	44,578	25	22
310^d	—	—	44,689	—	0.02
131	1.427	49,120	49,121	2	2
112^d	—	—	49,714	—	0.04
301^d	—	—	51,227	—	0.02
230^d	—	—	52,408	—	0.00
311	1.348	55,013	55,030	35	24
320	1.335	56,113	56,101	21	15
022	1.329	56,620	56,582	7	2
202	1.296	59,541	59,536	18	16
040	1.282	60,861	60,865	9	4
122	1.279	61,147	61,125	34	29
231	1.262	62,754	62,749	37	29
212^d	—	—	63,342	—	0.00
140	1.236	65,418	65,408	10	8
321^d	—	—	66,443	≪1	0.03
400	1.173	72,693	72,683	10	9
222	1.157	74,748	74,753	6	5
330^d	—	—	75,122	—	0.02
141^d	—	—	75,751	—	0.03
410^d	—	—	76,489	—	0.00
240	1.125	79,016	79,036	8	10
132^d	—	—	80,147	—	0.03

[a] Space group *Pnnm* (No. 58).

[b] Cell dimensions: $a = 4.6918(4)$ Å, $b = 5.1271(4)$ Å, and $c = 3.1096(3)$ Å.

[c] Cell volume: 74.80(1) Å^3. $Z = 2$; $D_{calc} = 9.93$ g/cm^3.

[d] Superstructure reflection.

the number of satellite reflections had increased considerably. The fragment was therefore treated in *aqua regia* for about 15 sec. This treatment improved the Weissenberg zero-level photograph considerably, so that the crystal fragment could be used for intensity data collection.

The intensities were measured with a Stoe-Philips computer-controlled four-circle single-crystal diffractometer equipped with a graphite monochromator to yield Mo$K\alpha$ radiation. An ω-2θ step scan technique was used, and three test reflections were measured at regular intervals to check the crystal orientation and instrumental stability. Up to an angular limit of $2\theta = 60°$, all reflections corresponding to a primitive lattice were measured. Since on inspection of the intensity data, the noncentered reflections were found to have insignificant intensities, it was decided to measure centered reflections only during the remaining data collection. For $60° < 2\theta < 120°$, all reflections except those inaccessible by the geometrical limitations of the instrument were measured, corresponding to the intervals $-10 \leqslant h \leqslant 6$, $-12 \leqslant k \leqslant 12$, and $-7 \leqslant l \leqslant 7$. A total number of 1610 reflections was measured, of which 333 were symmetry independent (centered reflections only).

The calculations were performed on IBM 1800, NORD-10, and IBM 370/155 computers using crystallographic programs described in Ref. *5*. The single-crystal intensities were corrected for Lp and absorption effects, using Gaussian grid technique. The shape of the crystal was irregular and the size was rather small, so that an examination by scanning electron microscopy was made in order to get a good geometrical description. The crystal, being wedge shaped with a maximum extension of about 50 μm, was approximated to a polyhedron with 10 boundary planes and a calculated volume of $1.3 \cdot 10^{-5}$ mm^3. The transmission factor varied between 0.53 and 0.77 for a calculated linear absorption coefficient of 228 cm^{-1}.

Structure Determination

The palladium atom arrangement is centered, since the single-crystal data exhibit the systematic absences $k + l$ odd for hkl and h odd for $h0l$ reflections. The possible space groups are then $Ama2$, $Ama2_1$, and $Amam$. $Amam$ was chosen for the calculations.

The only possible palladium position in the space group assumed is the 4(*c*) position. The other two four-fold sites can be disregarded since they would give too short distances of 2.3459 Å ($=a/2$). The only possible boron position is 4(*a*). This structure proposal involves two nonequivalent Pd–B distances, and by putting these two equal, one obtains a *y* coordinate of 0.342 for Pd. A preliminary refinement was made on powder data with the calculated *y* coordinate as the initial value. One scale factor, one positional parameter, and two temperature factors were varied, and the refinement terminated with a conventional agreement factor of 8.6% for 21 reflections. The *y* coordinate remained unchanged. Full occupancy was assumed for the two atomic positions.

The initial single-crystal refinement of the structure, based on F and on averaged absorption-corrected single-crystal data, converged to $R(F) = 0.032$. The atomic scattering factors (*6*) used were corrected for anomalous dispersion (*7*). For the strongest reflections, F_0 was systematically lower than F_c, and the temperature factor for the boron atom was very high. Refinement of the occupancy factor for the boron position and introduction of anisotropic temperature factors gave the residual $R(F) = 0.020$. In order to make a proper extinction correction, the whole material was included, resulting in $R(F) = 0.022$ (1610 reflections) when refining on F^2. The maximum extinction correction was 32%. The occupancy of the boron position was refined to 48.4(1.4)%.

The internal consistency factor for symmetry-related reflections (defined analogously to the conventional agreement factor), which had decreased from 2.53 to 2.19 after the absorption correction, was now reduced to 1.71%. In the following refinements based on F^2 and on averaged extinction-corrected data, the occupancy of the boron position was set to 50%. One scale factor, one positional parameter, anisotropic temperature factors for palladium, and an isotropic temperature factor for boron were refined, yielding $R(F^2) = 0.024$, $R_w(F^2) = 0.030$, and $R(F) = 0.019$ (333 reflections). The agreement factors given above are defined as

$$R(F^n) = \sum \left\| F_o^n \right| - \left| F_c^n \right\| / \sum \left| F_o^n \right|$$

and

$$R_w(F^n) = \left[\sum w(|F_o^n| - |F_c^n|)^2 / \sum w |F_o^n|^2 \right]^{1/2}, \quad n = 1 \text{ or } 2.$$

In the last formula w denotes the individual weight of each reflection, defined as

$$w^{-1} = \sigma_c^2 + (p_n \cdot F_o^n)^2.$$

σ_c is the standard deviation of F_o^n based on counting statistics, and p_n modifies the weight to account for systematic errors. p_n was selected to make the weighting scheme as even as possible, and the value chosen for p_2 was 0.027.

A ΔR plot (*8*) after the refinement of the whole data set (1610 reflections) gave a least-squares line with a slope of 0.75 and an intercept of −0.10 in the range of ±4 around the mean (17 reflections outside).

In the refinement described, the boron atoms were randomly distributed on the available boron positions in an orthorhombic distortion of the L'3 type of structure. The question of ordering has, however, to be considered. Yvon *et al.* (*9*) presented various ordering schemes for filling octahedral holes in hexagonal close-packed structures, as well as orthorhombic distortions of such structures. Using this information, structure factors and powder intensities were calculated for four different types of ordering, namely, anti-$CaCl_2$, deformed anti-CdI_2, ζ-Fe_2N, and ξ-Nb_2C. As in the case of carbides (*9, 10*), neutron diffraction has to be used in order to solve the problem of ordering unambiguously, but this technique would, in the case of borides, require the use of boron enriched with ^{11}B (*11*).

A reinvestigation of the powder data strongly indicated that the structure is of the anti-$CaCl_2$ type. Among the superstructure reflections expected for an anti-$CaCl_2$-type ordering, the four strongest could indeed be observed in heavily overexposed powder films (see Table I). For the strongest reflection, (110), the visually estimated intensity agreed within 20% with the value calculated for the anti-$CaCl_2$-type ordering. The single-crystal data also supported the assumed ordering hypothesis, the intensities for the strongest superstructure reflections exceeding the background by 6σ. However, since the effects of multiple reflection might well be of the same magnitude, the powder diffraction data probably give more reliable information regarding the ordering.

The ordered anti-$CaCl_2$-type structure crystallizes with *Pnnm* symmetry (*12*). Attempts to refine the structure by the least-squares method assuming this symmetry invariably failed, indicating that the palladium positions deviate insignificantly from the centered arrangement. This supports indirectly the interpretation of the superstructure reflections made above, since their intensities depend solely on the boron atom ordering and not on any deviation from centering for the palladium atoms.

In Table II, the structure data are accordingly presented in terms of *Pnnm* space group symmetry, although the values were actually obtained from refinements in the space group *Amam*. Observed and calculated structure factors have been reported elsewhere.[1]

Description and Discussion of the Structure

The structure of Pd_2B can be described as an orthorhombically distorted hexagonal close-packing of palladium atoms, with boron atoms filling half of the octahedral holes in an ordered manner. The ordering corresponds to the anti-$CaCl_2$-type structure. The unit cell dimensions are $a = 4.6918(4)$ Å, $b = 5.1271(4)$ Å, and $c = 3.1096(3)$ Å. The deviation from hexagonal symmetry for Pd_2B is 4.8%, if defined as $[(c \cdot 3^{1/2} - b)/c \cdot 3^{1/2}] \cdot 100\%$. The a axis corresponds to the hexagonal c axis. A literature survey of compounds crystallizing in the C35-type structure has been made. All representatives found have been collected in Table III, which also gives the cell dimensions, the deviations from hexagonal symmetry, and the references. As seen from the table, only two ionic compounds isostructural to $CaCl_2$ are known. Furthermore, four C35 anti-type metallic compounds are known, namely, Pd_2B, Co_2C, Co_2N, and η-Fe_2C. Although discovered some time ago, the C35-type structure thus has very few representatives. $PtGe_2$ was also reported to be of the $CaCl_2$ type, but was later corrected by the same author (*17*) to be of the löllingite type, which was corroborated in the present investigation.

A stereoscopic view of the structure is shown in Fig. 1. The boron atom is surrounded by six palladium atoms, situated at the corners of a slightly deformed octahedron. The palladium atoms are surrounded by 12 other palladium atoms and by boron atoms situated at three of the corners of a triangular prism. It is very likely that this ordering is responsible for the deviation from hexagonal symmetry.

The interatomic distances in Pd_2B are presented in Table IV. The Pb–B distances, 2.104 and 2.122 Å, are very short compared to the atomic radius sum of 2.25 Å. Other platinum metal borides also have short metal–boron distances, for instance, $IrB_{0.9}$(t) (*18*), with Ir–B distances of 2.11_3 and 2.13_2 Å (radius sum = 2.24 Å). Another example is $IrB_{\sim 1.35}$ (*19*), where the shortest Ir–B distances are between 2.04 and 2.07 Å. However, one must keep in mind that in most of these cases, the boron sites are only

TABLE II

STRUCTURE DATA FOR Pd_2B^{a-d}

		Positional parameters			$U_{ij} \cdot 10^5$ (Å^2)^e		
Atom	Position	x	y	z	U_{11}	U_{22}	U_{33}
Pd	4(g)	1/4	0.34489(3)	0	700(5)	798(5)	675(5)
B	2(a)	0	0	0	—^{f}		

[a] Refinement based on F^2.
[b] Space group *Pnnm* (No. 58).
[c] Standard deviations are given in parentheses.
[d] Full occupancy for both atoms.
[e] The anisotropic temperature factor is of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2})]$; $U_{12} = U_{13} = U_{23} = 0$.
[f] $U_{iso} = 90(6) \cdot 10^{-4}$ Å^2.

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[1] See NAPS document No. 03415 for two pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017.

TABLE III

SURVEY OF COMPOUNDS CRYSTALLIZING WITH THE C35-TYPE STRUCTURE

Compound	Cell dimensions (Å) a	b	c	Deviation from hexagonal symmetry (%)	Reference
$CaCl_2$	6.24	6.43	4.20	11.6	(*13*)
$CaBr_2$	6.584±6	6.871±6	4.342±4	8.6	(*14*)
$YbBr_2$	6.63(2)	6.93(2)	4.37(2)	8.4	(*15*)
Co_2C	4.3707±10	4.4465±10	2.8969±5	11.4	(*12*)
Co_2N	4.3443±10	4.6056±10	2.8535±5	6.8	(*12*)
η-Fe_2C	4.318±5	4.704±16	2.830±6	4.0	(*16*)
Pd_2B	4.6918(4)	5.1271(4)	3.1096(3)	4.8	This work

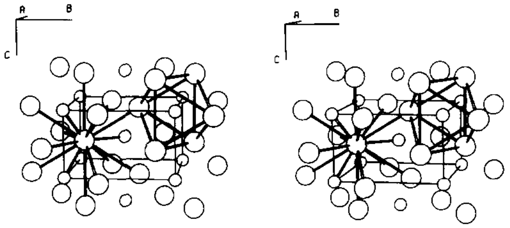

FIG. 1. Stereoscopic view of the structure of Pd_2B.

partially occupied. There are no B–B contacts in the Pd_2B structure.

It is interesting to note the increasing mean Pd–Pd distance with increasing boron content for the phases in the binary system: Pd–2.75 Å, Pd_3B—2.84 Å, Pd_5B_2—2.85 Å, and Pd_2B—2.98 Å.

TABLE IV

INTERATOMIC DISTANCES IN Pd_2B (Å UNITS)[a,b]

Pb–2 B	2.104	B–4 Pd	2.104
–1 B	2.122	–2 Pd	2.122
–2 Pd	2.834		
–4 Pd	2.978		
–4 Pd	2.998		
–2 Pd	3.110		

[a] Distances shorter than 3.5 Å are listed. No boron–boron contacts exist.

[b] The estimated deviations are all less than 0.001 Å.

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