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The Crystal Structures of Pd_5B_2, (Mn_5C_2) and Pd_3B

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The crystal structures of Pd_5B_2 and Pd_3B have been determined by single-crystal methods.

Pd_5B_2 has a monoclinic unit cell with the following dimensions: $a = 12.786$ Å, $b = 4.955$ Å, $c = 5.472$ Å, $\beta = 97°2'$. There are four formula units in the unit cell and the space-group is $C2/c$. The twenty palladium atoms are situated in two eightfold positions 8(*f*) with $x_I = 0.0958$, $y_I = 0.0952$, $z_I = 0.4213$ and $x_{II} = 0.2127$, $y_{II} = 0.5726$, $z_{II} = 0.3138$ and one fourfold position 4(*e*) with $y_{III} = 0.5727$. The boron atoms are situated in an 8(*f*) position with $x = 0.106$, $y = 0.311$, $z = 0.077$. Pd_5B_2 is isomorphous with Mn_5C_2.

Pd_3B has the cementite (Fe_3C) structure. The space-group is *Pnma* with $a = 5.463$ Å, $b = 7.567$ Å, $c = 4.852$ Å and the unit cell contains eight palladium atoms in 8(*d*) with $x_I = 0.1798$, $y_I = 0.0700$, $z_I = 0.3276$ and four palladium atoms in 4(*c*) with $x_{II} = 0.0372$, $z_{II} = 0.8446$. Four boron atoms are situated in 4(*c*) with $x = 0.884$, $z = 0.433$.

The literature on the Pd-B system is very scanty. Buddery and Welch [1] report a hexagonal compound occurring at 6.33 wt % B (Pd_3B_2). However, there are reasons to believe that their product, which was obtained by heating palladium and boron in silica tubes, might have been Pd_2Si [2,3]. Recently, Lehrer [4] made a thermal and microscopic analysis in the range 0—6 wt % (0—39 atomic %) B. However, the examination did not yield any definite information on the composition of the intermediate phases.

An X-ray investigation of the Pd-B system has been started at this Institute. In sintered alloys three intermediate phases have been identified. The structures of two of them, Pd_5B_2 and Pd_3B, are described in this paper. Although the structure of the third phase (containing more boron than Pd_5B_2) has not yet been determined, it has been found that it is certainly not identical with the phase reported by Buddery and Welch.

EXPERIMENTAL

The samples were prepared by heating mixtures of palladium powder (claimed purity ca. 99.8 % from Heraeus, Hanau, Germany) and boron powder (claimed purity 99.0—99.7 %, kindly donated by Borax Consolidated, London) in evacuated, sealed silica tubes at temperatures between 800° and 1 100°C. The alloys were prevented from coming into

contact with the walls of the silica tube by placing them in small crucibles of pure aluminium oxide. No appreciable reaction between Al_2O_3 and the palladium borides was detected. However, the compositions of the alloys did not correspond to the nominal compositions, since varying amounts of boron were unavoidably lost during the reactions.

Chemical analyses were made at the Department of Analytical Chemistry of this Institute. For analyses two alloys were chosen in which only the powder diffraction lines of Pd_5B_2 and Pd_3B respectively could be detected.

Results of the chemical analyses.

Phase detected in powder photograph.	Chemical analysis (weight per cent) Pd	B	Formula according to the analysis
Pd_5B_2	93.97	5.84	$Pd_{3.28}B_2$
Pd_3B	96.05	3.44	$Pd_{2.85}B$

The analyses show that no other elements than palladium and boron were present. The large boron contents of the Pd_5B_2-alloy are probably due to unreacted boron.

X-Ray powder photographs were taken with Guinier-type focussing cameras using Cu$K\alpha$ radiation ($\lambda_{CuK\alpha} = 1.5418$ Å). Each powder film used for lattice parameter measurements was calibrated with either silicon ($a = 5.4306$ Å) or calcium fluoride ($a = 5.4630$ Å) as an internal standard.

For the structure determinations, Weissenberg photographs were taken of small single-crystal fragments selected from the crushed alloys with niobium-filtered MoK radiation. The multiple-film technique was used with thin iron foils between successive films, and the intensities were estimated visually by comparison with a standard intensity scale. Fourier series and structure factor calculations were made on the electronic digital computer BESK with programmes (available at BESK) devised by Edstrand and Åsbrink *et al.*[5] In the structure factor calculations the atomic scattering factors were approximated to the following expression:

$$f_i = A_i \exp\left(-\frac{a_i}{\lambda^2}\sin^2\Theta\right) + B_i \exp\left(-\frac{b_i}{\lambda^2}\sin^2\Theta\right) + C_i \exp\left(-\frac{c_i}{\lambda^2}\sin^2\Theta\right) + D_i$$

Appel [6] has calculated the following constants on the basis of the scattering factor tables by Tomas and Umeda [7] (palladium) and Ibers [8] (boron).

	A	B	C	a	b	c
Palladium	15.865	17.354	12.288	0.233	2.565	19.828
Boron	1.644	0.406	2.878	0.6069	4.5832	33.019

The real part of the dispersion correction, (D_i in the above expression), for palladium was taken from the table of Dauben and Templeton [9].

RESULTS

Pd_5B_2 was found to be monoclinic with the unit cell dimensions $a = 12.786$ Å, $b = 4.955$ Å, $c = 5.472$ Å, $\beta = 97°2'$, $U = 344.1$ Å^3. Pd_3B was found to have an orthorhombic unit cell with $a = 5.463$ Å, $b = 7.567$ Å, $c = 4.852$ Å, $U = 200.6$ Å^3.

Neither of these phases displays appreciable variations of lattice parameter, this indicates that both have narrow homogeneity ranges. It should be pointed out that the composition has not been accurately established for either phase, and it is accordingly possible that they show departures from stoichiometry.

For Pd_5B_2 the following conditions for possible reflexions were found: (hkl) only for $h + k = 2n$ and ($h0l$) only for $l = 2n$. This gives Cc or $C2/c$ as possible space-groups. The Patterson section $P(x0z)$ was calculated from the three-dimensional intensity data (700 reflexions). This section contained several large maxima and gave strong indications that the space-group is $C2/c$. Therefore, an attempt was made to interpret the Patterson section in accordance with this space-group.

Large maxima were situated at the following approximate positions: (0, 0, 0); ± (0.21, 0, 0.07); ± (0.19, 0, 0.35); ± (0.19,0, 0.76); ± (0.40, 0, 0.83); ± (0.39, 0, 0.11). The last maximum was unsymmetrically extended in the a direction. It was assumed that all these maxima corresponded mainly to Pd-Pd vectors. Since no maxima were found at ($\frac{1}{2}$, 0, 0), (0, 0, $\frac{1}{2}$) or ($\frac{1}{2}$, 0, $\frac{1}{2}$) the positions 4(a), 4(b), 4(c) and 4(d) were ruled out. Thus 4(e) and 8(f) are the only possible positions. An evaluation of the three-dimensional Patterson function along $P(0, y, \frac{1}{2})$ showed a broad maximum at y 0.16, indicating that the y parameter in the positions 4(e) or 8(f) should be about ± 0.08 or 0.50 ± 0.08. From packing considerations a structure model with the following approximate palladium positions was proposed:

8 Pd_I	in 8(f):	x_I	= 0.10	y_I	= 0.09	z_I	= 0.42
8 Pd_{II}	in 8(f):	x_{II}	= 0.21	y_{II}	= 0.58	z_{II}	= 0.32
4 Pd_{III}	in 4(e):	x_{III}	= 0	y_{III}	= 0.59	z_{III}	= 0.25

With this model all the peaks in the Patterson section $P(x0z)$ could be explained. As atoms belonging to different positions had approximately the same y parameters, vectors between them gave maxima in $P(x0z)$.

The signs of the $F(h0l)$ and the $F(hk0)$ values were computed from the model, and the electron density projections $\varrho(xz)$ and $\varrho(xy)$ were calculated using the intensity data from the zero layer lines around the b and c axes. The coordinates of the palladium atoms were refined from successive difference syntheses. An empirical temperature factor was applied with $B = 0.40$ Å^2 for the $F(h0l)$-values and with $B = 0.42$ Å^2 for the $F(hk0)$-values. In the $(F_o - F_c)$-synthesis, in which only the contribution from the palladium atoms was included for the F_c terms, boron maxima corresponding to one 8(f) position became visible. However, the maxima were too diffuse for an accurate determination of the coordinates, so the boron atoms were placed in the centres of the triangular prisms of palladium atoms. These parameter values were wholly compatible with the experimental intensity data. The final R values obtained were 0.077 for 92 non-equivalent observed $h0l$ reflexions and 0.053 for 52 non-equivalent observed $hk0$ reflexions *. In the final stages of refinement the F_o values of the three strongest $hk0$ reflexions, which were obviously weakened because of extinction, were replaced by the corresponding F_c values.

The final atomic parameters of Pd_5B_2 are:

* A list of calculated and observed structure factors can be obtained from this Institute on request.

Table 1. Interatomic distances in Pd_5B_2 (in Å).

			Average
Pd_I	— 4 Pd_I : 2.85, 2.89 (2), 2.90		
	— 5 Pd_{II} : 2.81, 2.90, 2.90, 2.96, 3.08		2.90
	— 3 Pd_{III}: 2.77, 2.83, 2.97		
	— 4 B : 2.18, 2.18, 2.80, 3.06		
Pd_{II}	— 5 Pd_I : 2.81, 2.90, 2.90, 2.96, 3.08		
	— 5 Pd_{II} : 2.77 (2), 2.77, 2.83 (2)		2.85
	— 1 Pd_{III}: 2.70		
	— 3 B : 2.18, 2.19, 2.60		
Pd_{III}	— 6 Pd_I : 2.77 (2), 2.83 (2), 2.97 (2)		
	— 2 Pd_{II} : 2.70 (2)		2.82
	— 2 Pd_{III}: 2.83 (2)		
	— 4 B : 2.18 (2), 2.19 (2)		
B	— 4 Pd_I : 2.18, 2.18, 2.80, 3.06		
	— 3 Pd_{II} : 2.18, 2.19, 2.60		2.18
	— 2 Pd_{III}: 2.18, 2.19		(six shortest)

(Space-group $C2/c$—(C_{2h}^6); $Z = 4$.)

		x	y	z
8 Pd_I	in 8(f):	0.0958 ± 0.0002	0.0952 ± 0.0003	0.4213 ± 0.0003
8 Pd_{II}	in 8(f):	0.2127 ± 0.0002	0.5726 ± 0.0003	0.3138 ± 0.0003
4 Pd_{III}	in 4(e):	—	0.5727 ± 0.0003	—
8 B	in 8(f):	0.106	0.311	0.077

The standard deviations were calculated from Cruickshank's [10] formula. Interatomic distances are listed in Table 1.

Pd_5B_2 appears to be isomorphous with Mn_5C_2 ($a = 11.66$ Å, $b = 4.573$ Å, $c = 5.086$ Å, $\beta = 97.75°$), reported by Kuo and Persson [11], and with a double carbide of iron and manganese found by Öhman [12] in ferromanganese alloys. In Table 2 the powder data for Mn_5C_2 with observed intensities, reported by Kuo and Persson, are shown together with intensities, calculated assuming the atomic parameters in Mn_5C_2 to be the same as those in Pd_5B_2. Owing to the good agreement it seems quite certain that the two phases are isomorphous.

The powder diffraction lines of Pd_3B, which could be indexed with an orthorhombic unit cell, showed close resemblance to the powder pattern of Pd_3Si [13], which is isostructural with cementite (Fe_3C). Therefore the signs of the $F(h0l)$ and the $F(hk0)$ values were computed from the cementite structure, and the intensity data from the zero layer lines around the b and c axes were used for the refinement of the palladium coordinates with successive difference syntheses. As in the structure determination described above the boron maxima in the difference synthesis were too diffuse to allow any accurate determination of their coordinates. The boron atoms were placed in the centres of the palladium prisms. The final R values obtained were 0.069 for 67 observed $h0l$ reflexions and 0.058 for 54 observed $hk0$ reflexions *; an empirical temperature

* A list of calculated and observed structure factors can be obtained from this Institute on request.

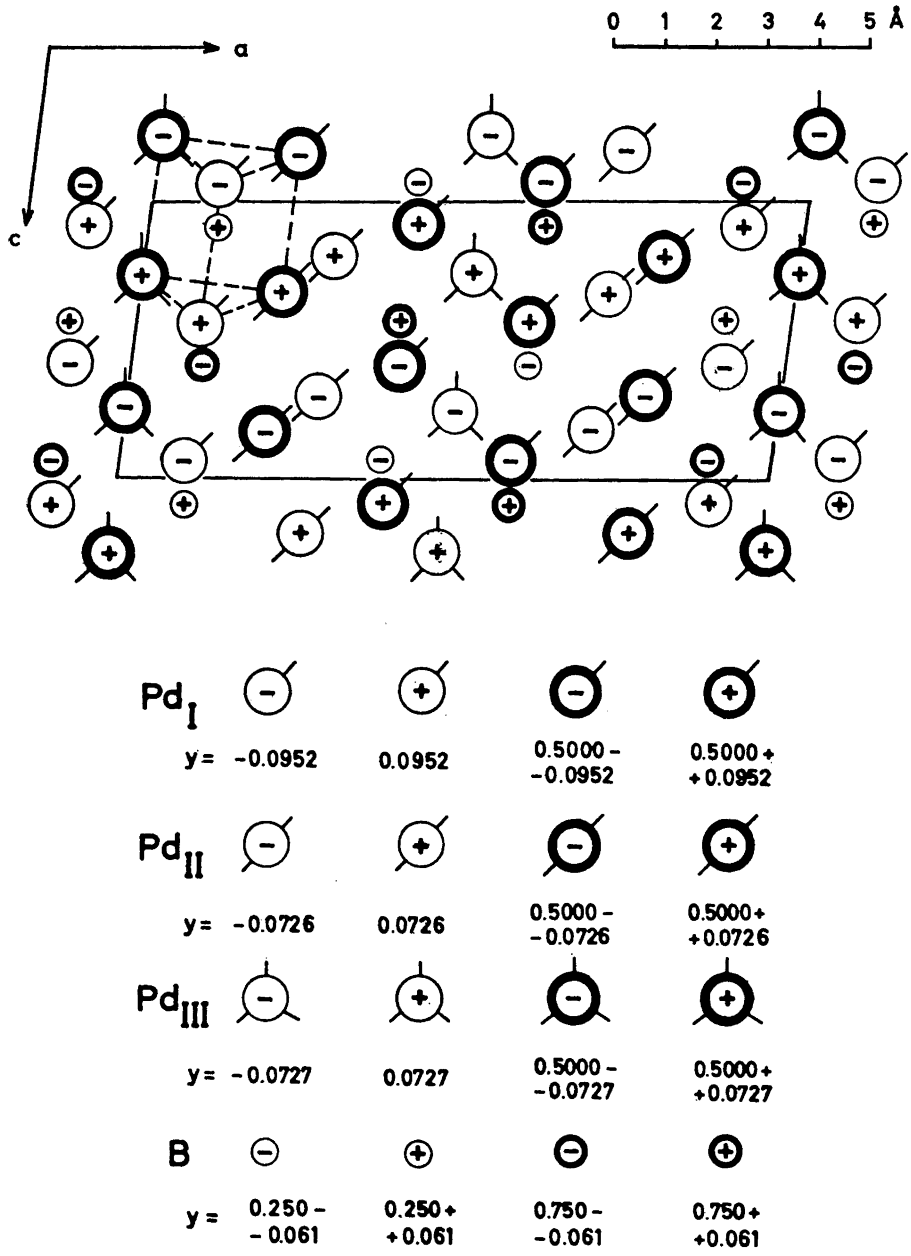

Fig. 1. The structure of Pd_5B_2 projected on the *ac*-plane.

Table 2. Powder data for Mn_5C_2 (CrKa radiation)

hkl	d_{obs} (Å)*	$\sin^2\Theta_{calc}$	I_{obs}*	I_{calc}	$pF^2_{calc} \times 10^{-4}$
200		0.0393		<0.01	0.002
110		0.0726		0.01	0.01
11$\bar{1}$	3.325	0.1182	vw	<0.01	0.001
111		0.1303		0.02	0.04
310	2.938	0.1512	vw	<0.01	0.01
400	2.881	0.1573	vw	0.12	0.23
31$\bar{1}$	2.659	0.1846	m	0.80	1.86
002	2.514	0.2067	m	0.56	1.39
311	2.431	0.2211	m	0.98	2.59
20$\bar{2}$	2.427	0.2217		0.67	1.80
020	2.282	0.2510	st-	2.04	5.67
11$\bar{2}$	2.212	0.2671	st	3.60	10.59
202	2.198	0.2703	st-	2.36	6.94
220		0.2903		0.05	0.14
112	2.117	0.2914	st-	1.37	4.14
021	2.078	0.3026	vst	5.71	17.31
510	2.058	0.3085	st	9.91	30.98
40$\bar{2}$	2.035	0.3153	st-	2.11	6.39
31$\bar{2}$	2.016	0.3214	st	3.65	11.40
51$\bar{1}$	1.990	0.3297	st	1.92	5.81
22$\bar{1}$**		0.3298		1.85	5.60
600	1.972	0.3538	st	0.50	1.46
221**		0.3541		2.82	8.29
511	1.829	0.3905	st-	2.15	5.80
312	1.820	0.3943	st-	3.22	8.69
420		0.4082		0.59	1.52
402	1.779	0.4125	st-	2.66	6.82
42$\bar{1}$	1.732	0.4356	st	2.00	4.76
51$\bar{2}$	1.695	0.4543	st-	1.57	3.57
022	1.690	0.4576	vw	0.93	2.07
22$\bar{2}$	1.663	0.4726	w	0.52	1.10
421		0.4842		0.11	0.23
60$\bar{2}$	1.636	0.4876	m	2.61	5.22

* As reported by Kuo and Persson.

** The 22$\bar{1}$ and 221 reflexions, which have large I_{calc} values, are not reported by Kuo and Persson, but probably they have been overlooked because of the overlap with the 51$\bar{1}$ and 600 reflexions, respectively.

factor with $B = 0.53$ Å^2 was applied in both cases. The final atomic parameters of Pd_3B are as follows:

(Space-group $Pnma$ — (D^{16}_{2h}); $Z = 4$.)

		x	y	z
8 Pd_I	in 8(d):	0.1798 ± 0.0003	0.0700 ± 0.0002	0.3276 ± 0.0003
4 Pd_{II}	in 4(c):	0.0372 ± 0.0005	—	0.8446 ± 0.0005
4 B	in 4(c):	0.884	—	0.433

Interatomic distances are listed in Table 3.

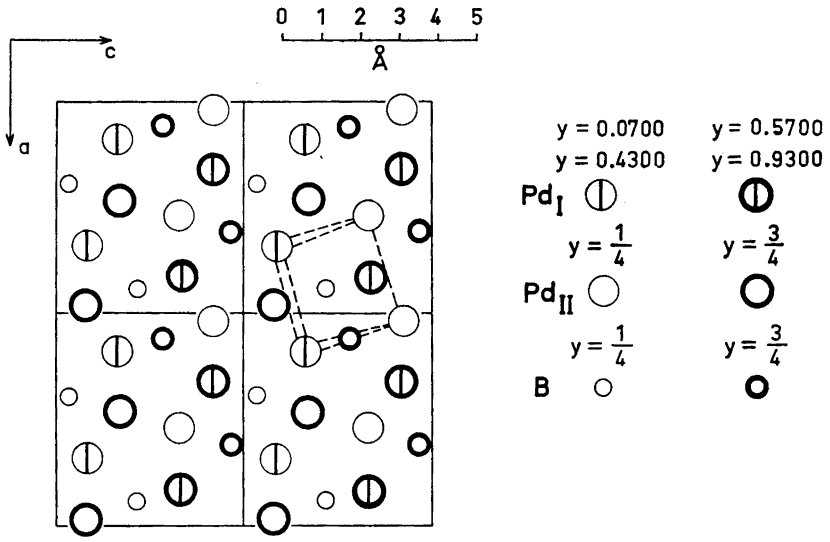

Fig. 2. The structure of Pd_3B projected on the *ac*-plane.

DESCRIPTION OF THE STRUCTURES AND DISCUSSION

Projections of the Pd_5B_2 and the Pd_3B structures are shown in Figs. 1 and 2, respectively.

In both Pd_5B_2 and Pd_3B the palladium atoms are densely packed, and the palladium — palladium contacts are on the average only about 0.10 Å longer than in pure palladium, where they are 2.75 Å.

The Pd_5B_2 structure can be described in terms of corrugated layers of palladium atoms parallel with {010}. The layers are composed of interconnected squares and triangles with metal atoms at the corners (Fig. 3). Similar layers can be found in other borides, as for example in the Me_2B-borides with the $CuAl_2$ structure [14].

The environments of the boron atoms in Pd_5B_2 and Pd_3B are shown in Figs. 4 and 5. The boron atoms are situated in triangular prismatic 'holes' in

Table 3. Interatomic distances in Pd_3B (in Å).

		Average
Pd_I	— 6 Pd_I : 2.72, 2.76 (2), 2.79, 2.83 (2)	2.82
	— 5 Pd_{II} : 2.82, 2.82, 2.86, 2.87, 2.96	
	— 3 B : 2.17, 2.17, 2.71	
Pd_{II}	—10 Pd_I : 2.82 (2), 2.82 (2), 2.86 (2), 2.87 (2), 2.96 (2)	2.87
	— 2 Pd_{II} : 2.88 (2)	
	— 3 B : 2.17, 2.18, 2.97	
B	— 6 Pd_I : 2.17 (2), 2.17 (2), 2.71 (2)	2.17 (six shortest)
	— 3 Pd_{II} : 2.17, 2.18, 2.97	

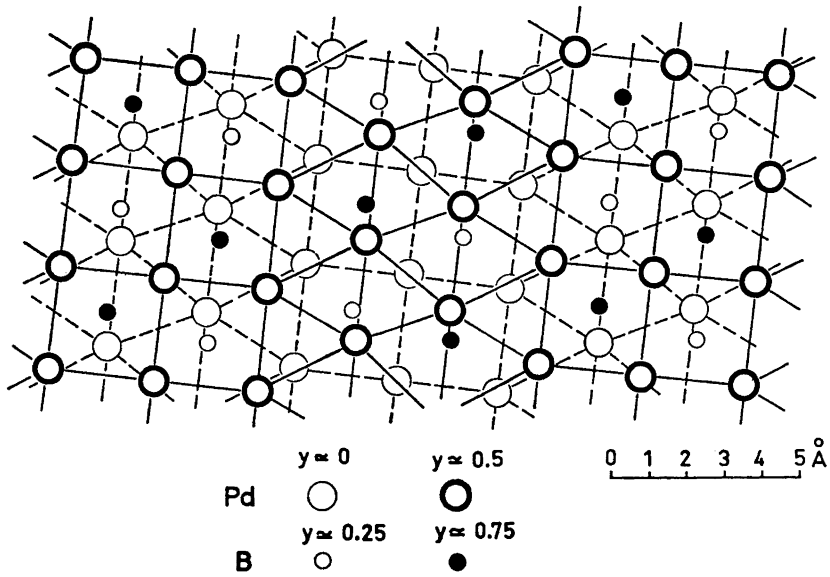

Fig. 3. A schematic picture of the Pd_5B_2 structure as seen along the *b*-axis.

the metal atom lattice, with six metal atoms at the corners of the prism, and three metal atoms, outside each four-sided side of the prism, forming a triangle around the boron atoms. There are no boron-boron contacts in Pd_5B_2 and Pd_3B. The type of non-metal atom coordination found in these borides is shared with many other transition metal borides as well as with several transition metal silicides, carbides and phosphides. The average of the shortest

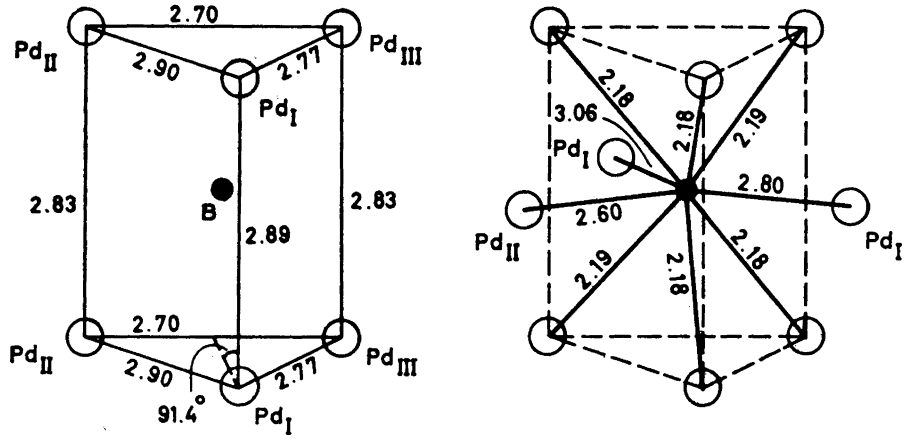

Fig. 4. The environment of the boron atoms in Pd_5B_2.

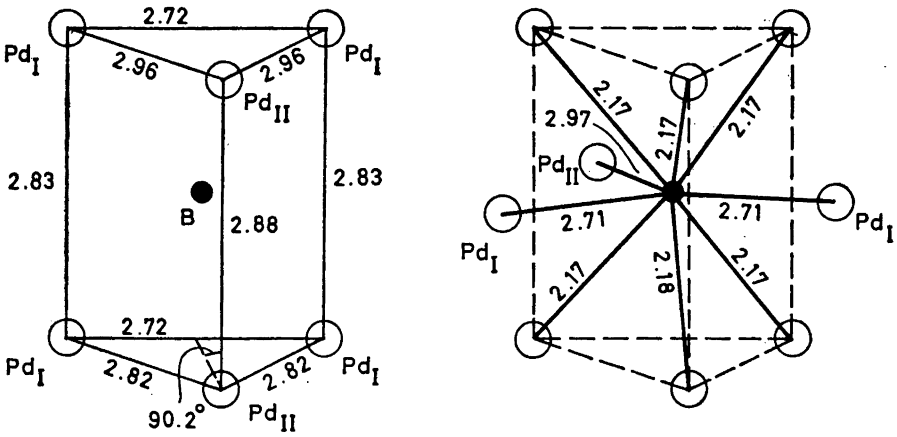

Fig. 5. The environment of the boron atoms in Pd_3B.

palladium-boron distances is 2.18 Å in Pd_5B_2 and 2.17 Å in Pd_3B. If r_{Pd} = 1.38 Å, r_B will be about 0.80 Å. This boron radius is rather small but is in accordance with the Me-B distances found in some other transition metal borides with the same boron environment, *e.g.* Ru_7B_3 (B — 6 Ru 2.16 Å) [15].

Pd_5B_2 and Pd_3B are two new examples of borides which are isostructural with carbides. It has previously been shown that Ni_3B and Co_3B [16], as well as Pd_3B, crystallize with the cementite (Fe_3C) structure and that Ru_7B_3 [15], Rh_7B_3 [17] and Re_7B_3 [17] are structurally very closely related to Cr_7C_3 and Mn_7C_3.

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