

## The Crystal Structure of Pd<sub>5</sub>P

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The crystal structure of Pd<sub>5</sub>P has been investigated by powder diffraction methods. The unit cell is monoclinic of dimensions  $a = 2.837 \text{ \AA}$ ,  $b = 9.441 \text{ \AA}$ ,  $c = 7.695 \text{ \AA}$ ,  $\beta = 90.20^\circ$  and contains 12 palladium and 2 phosphorus atoms. The structure is closely related to the Re<sub>3</sub>B-type structure.

The Pd–P equilibrium diagram has been thoroughly investigated by Gullman.<sup>1</sup> He found two very palladium-rich intermediate phases, Pd<sub>5</sub>P and Pd<sub>3</sub>P, both being formed peritectically at 799°C and 792°C, respectively. Gullman was unable to prepare these compounds in single crystal form, and the powder diffraction patterns were too complex for indexing. Since Pd<sub>5</sub>P and Pd<sub>3</sub>P represent the most metal-rich intermediate phases known in any transition metal-phosphorus system, it would seem to be of great interest to study the properties of these phases more closely. We decided to start an X-ray crystallographic examination of the two phosphides, and in the present paper we give an account of our work on Pd<sub>5</sub>P.

### EXPERIMENTAL DETAILS

*Preparation and X-ray diffraction work.* We prepared Pd–P samples by the silica tube technique in exactly the same manner as described by Gullman,<sup>1</sup> using red phosphorus of purity higher than 99 % and palladium powder (claimed purity 99.9 %) from Johnson, Matthey & Co, Ltd., London, as starting materials. As mentioned by Gullman it is difficult to attain equilibrium conditions in palladium-rich alloys,

and in spite of long and careful heat treatments we could not obtain Pd<sub>5</sub>P samples completely free from palladium or other Pd–P phases. The alloys were very ductile, and the powders used for X-ray diffraction work were prepared by filing with fine-toothed files and sieving. To remove the effects of cold work the filings were annealed at 650°C for one hour. The annealing time and temperature was found to be critical, since the powders sintered at higher temperatures and longer annealing times, and sharp diffraction lines were not obtained for powders annealed at lower temperatures. Attempts to obtain Pd<sub>5</sub>P crystals suitable for X-ray work were unsuccessful. The fragments extracted from the alloys invariably consisted of conglomerates of several crystallites, which were mechanically deformed and exhibited stacking faults and twinning. Annealing treatments of such fragments produced only minor improvements in the crystalline perfection.

Powder diffraction patterns were recorded in Hagg-Guinier-type cameras using CrK $\alpha_1$  or CuK $\alpha_1$  radiation and silicon ( $a = 5.43054 \text{ \AA}$ ) as internal calibration standard. Unit cell dimensions were refined by the least squares method using the local program CELNE<sup>2</sup> on an IBM 1800 computer.

Powder diffraction intensities were measured by two methods. In the first method the intensities were obtained by direct summation on the read-out scaler, using a Philips powder diffractometer PW 1050 with CuK radiation and a lithium fluoride monochromator between the sample and the proportional counter. In the second method Hagg-Guinier photographs, recorded in a Philips XDC 700 camera with strictly monochromatized CrK $\alpha_1$  radiation, were measured by means of an automatic drum densitometer (SAAB model 2) connected to an IBM 1800 computer in the same manner as described by Malmros and Werner.<sup>3</sup> Evaluation of the integrated intensities was made using the program PILT<sup>3</sup> in a locally modified version.<sup>2</sup> This version included the correction factor  $\{1 - \exp - [\mu_t h / \cos(2\theta - \phi)]\}$ , ( $\mu_t$  = absorption coefficient for the film emulsion,  $h$  = thickness of emulsion,  $\theta$  and  $\phi$  as in Ref. 3) allowing for the

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variation of the film blackening due to the oblique incidence of the diffracted beam.<sup>4</sup>

Least squares refinements using the intensity data were performed by means of the program POWOW, originally written by the late W. C. Hamilton, Brookhaven National Laboratory, USA, and modified locally for an IBM 370/155 computer.<sup>5</sup> The program permits the use of sums of intensities for unresolved overlapping reflexions as input data.

### STRUCTURE ANALYSIS

Our powder diffraction data obtained for Pd<sub>3</sub>P were in good agreement with Gullman's results.<sup>1</sup> It was found, however, that some of the weaker diffraction lines listed by Gullman actually belong to the Pd<sub>3</sub>P phase, which was present in small amounts in his Pd<sub>3</sub>P sample.

Table 1. Powder diffraction data for Pd<sub>3</sub>P. (Guinier-Hägg camera, CuK $\alpha_1$  radiation, internal calibration standard silicon  $a = 5.43054 \text{ \AA}$ , intensities from film scanner.)

<i>h k l</i>	$Q \times 10^5$		$d_{\text{obs}}$	$I_{\text{obs}}$
	obs	calc		
0 0 1		1 689		
0 2 0	4 485	4 488	4.722	—
0 2 1		6 177		
0 0 2	6 754	6 756	3.848	—
0 2 2	11 244	11 244	2.982	7
1 1 0	13 543	13 547	2.717	6
1 1 1	15 206	15 204	2.564	40
1 1 1	15 266	15 267	2.559	
0 4 0	17 947	17 951	2.360	41
0 4 1	19 664	19 640	2.255	100
0 2 3		19 689		
1 1 2	20 240	20 240	2.223	73
1 1 2	20 370	20 366	2.216	
1 3 0	22 515	22 522	2.107	33
1 3 1	24 174	24 180	2.034	58
1 3 1	24 248	24 243	2.031	
0 4 2	24 698	24 707	2.012	11
0 0 4	27 018	27 025	1.924	3
1 1 3	28 646	28 653	1.868	9
1 1 3	28 835	28 843	1.862	8
1 3 2	29 207	29 215	1.850	12
1 3 2	29 334	29 342	1.846	8
0 2 4	31 512	31 513	1.781	1
0 4 3	33 155	33 153	1.737	1
1 3 3		37 629		
1 3 3		37 819		
0 6 0		40 390		
1 1 4	40 442	40 445	1.572	5
1 5 0		40 473		
1 1 4	40 702	40 698	1.567	4
0 6 1	42 083	42 079	1.542	4
1 5 1		42 131		

<i>h k l</i>	$Q \times 10^5$		$d_{\text{obs}}$	$I_{\text{obs}}$
	obs	calc		
1 5 1		42 194		
0 4 4		44 976		
0 2 5	46 709	46 714	1.463	3
0 6 2	47 142	47 146	1.456	28
1 5 2		47 166		
1 5 2	47 273	47 293	1.454	
1 3 4		49 420		
1 3 4		49 674		
2 0 0	49 694	49 699	1.418	20
2 2 0		54 187		
1 5 3	55 561	55 580	1.342	49
0 6 3		55 592		
1 1 5	55 749	55 615	1.339	
1 5 3	55 749	55 770	1.339	
2 2 1		55 812		
1 1 5	55 936	55 931	1.337	
2 2 1		55 939		
2 0 2		56 328		
2 0 2		56 582		
0 4 5	60 161	60 178	1.289	5
0 0 6	60 795	60 806	1.282	10
2 2 2		60 816		
2 2 2		61 070		
1 3 5	64 585	64 590	1.244	11
1 3 5	64 901	64 907	1.241	10
0 2 6		65 294		
1 5 4		67 372		
1 7 0	67 379	67 400	1.218	44
0 6 4		67 415		
1 5 4	67 647	67 625	1.216	
2 4 0		67 650		
1 7 1		69 058		
1 7 1		69 121		
2 2 3	69 192	69 198	1.202	24
2 4 1		69 276		
2 4 1		69 402		
2 2 3	69 594	69 578	1.199	19
0 8 0	71 778	71 805	1.180	3
0 8 1	73 471	73 494	1.167	6
1 7 2		74 093		
1 1 6		74 163		
1 7 2		74 220		
2 4 2	74 272	74 280	1.160	4
2 4 2	74 512	74 533	1.158	3
1 1 6		74 543		
2 0 4	76 462	76 470	1.144	2
2 0 4	76 953	76 977	1.140	1
0 8 2	78 542	78 561	1.128	22
0 4 6	78 752	78 757	1.127	
2 2 4		80 958		
2 2 4		81 465		
1 7 3		82 507		
1 5 5		82 542		
0 6 5	82 576	82 617	1.100	36
2 4 3		82 662		
1 7 3		82 697		
1 5 5		82 858		
2 4 3		83 042		
1 3 6		83 138		
1 3 6		83 518		

For identification purposes, revised diffraction data for Pd<sub>3</sub>P as obtained in our study are given in Table 1.

In order to analyze the Pd<sub>3</sub>P structure we started with an attempt to use single crystal methods. As mentioned above, the "crystals" available were of extremely poor quality. However, from the best crystal conglomerates that we found, oscillation films were obtained, which indicated a rotation axis of about 2.8 Å. Weissenberg recordings of the zero, first and second layer lines indicated that Pd<sub>3</sub>P might have an orthorhombic symmetry, with lengths of the remaining two axes of about 9.4 and 7.7 Å. An attempt to index the powder pattern on this basis was partially successful, but at several positions, where we expected to find only one single diffraction line, we observed pairs of closely spaced lines. We therefore tentatively assumed a monoclinic symmetry with the monoclinic angle differing only slightly from 90°. With this assumption all lines in the powder pattern could be accounted for in a very satisfactory manner. The indexed powder data are presented in Table 1.

On re-inspection of the "single crystal" films we found that the distribution of diffraction spots might well be compatible with a monoclinic symmetry. The deviations from orthorhombic symmetry were most probably masked by satellite spots, stacking fault effects, and by the very small deviation from 90° for the monoclinic angle in combination by twinning on (100).

The unit cell dimensions of Pd<sub>3</sub>P at 24 ° C as derived from the powder diffraction data were:  $a = 2.8370(2)$  Å,  $b = 9.4409(6)$  Å,  $c = 7.6945(5)$  Å,  $\beta = 90.198(4)^\circ$  (numbers in parentheses following numerical values are the calculated standard deviations referring to the least significant digits). The standard deviations as returned by the CELNE program include no allowance for systematic errors. The absolute errors are estimated to be less than 0.04 %.

In agreement with Gullman<sup>1</sup> we observed no significant variations in the cell dimensions between samples of different compositions and heat treatments. The cell volume of 206.1 Å<sup>3</sup> is consistent with a cell content of 12 palladium and 2 phosphorus atoms. Both the powder and the "single crystal" diffraction data indicated face centering. Furthermore, no reflexions with  $l = 2n + 1$  were observed among the ( $h0l$ ) reflex-

ions. This indicates  $Cc$  or  $C2/c$  as the most probable space groups. However, among the equivalent positions in these space groups there are no sets of a multiplicity lower than fourfold, while there are only two phosphorus atoms in the unit cell. If the atoms occupy ordered positions in the structure, the space group symmetry can therefore be no higher than  $C2$ ,  $Cm$  or  $C2/m$ .

The numerous overlaps in the powder diffraction patterns and the extremely poor single crystal data precluded the use of X-ray intensities for obtaining an initial structure proposal for Pd<sub>3</sub>P. An attempt was therefore made to derive the atomic arrangement by simple space considerations. Accordingly, we assumed that no Pd-Pd and Pd-P distances in Pd<sub>3</sub>P should be shorter than 2.7 Å and 2.2 Å, respectively, as inferred from the structure data known for Pd<sub>4</sub>3P (Sellberg<sup>6</sup>) and Pd<sub>3</sub>P (Rundqvist and Gullman<sup>7</sup>). Furthermore, we assumed that the atomic arrangement was ordered. An analysis of the various possibilities showed that there was only one principal way of arranging the atoms in accordance with the assumed spatial requirements. This structure proposal had  $C2$  symmetry, with the following approximate atomic positions: 4 Pd in 4c:  $x \sim 0$ ,  $y = 0$  (arbitrarily),  $z \sim 0.32$ ; 4 Pd in 4c:  $x \sim 0$ ,  $y \sim 0.73$ ,  $z \sim 0.19$ ; 2 Pd in 2b:  $y \sim 0.28$ ; 2 Pd in 2a:  $y \sim 0.44$ ; 2 P in 2b:  $y \sim 0.58$ . With this structure proposal as the starting point we proceeded to make refinements based on powder diffraction intensities.

In the powder diffractometer work, we recorded intensities up to a maximum in  $\theta$  of about 45°. For diffraction angles higher than this value the overlapping becomes so extensive that we considered an extension of the intensity measurements to be of very little value. The powder sample used contained small amounts of palladium. Within the  $\theta$ -range recorded, the three palladium reflexions (111), (311), and (222) overlap reflexions from Pd<sub>3</sub>P. From measurements of the intensities of the remaining well resolved palladium reflexions we could calculate the intensities for (111), (311), and (222). In the case of (111) and (222), the calculated intensities amounted only to 4.4 and 8.6 %, respectively, of the total integrated intensities for the overlapping palladium and Pd<sub>3</sub>P reflexions. For each of these two cases of overlap we subtracted the calculated palladium intensity from the total intensity and used the resulting value as the Pd<sub>3</sub>P intensity in the subsequent calculations. The palladium reflexion (311), which overlaps

Table 2. Structure data for Pd<sub>3</sub>P based on space group C2/c.

		<i>x</i>	<i>y</i>	<i>z</i>
8 Pd(1)	in 8 <i>f</i>	0.997(5)	0.133(1)	0.064(2)
4 Pd(2)	in 4 <i>e</i>	0	0.422(2)	$\frac{1}{4}$
2 P(ran- domly)	in 4 <i>e</i>	0	0.715(12)	$\frac{1}{4}$

Isotropic overall temperature factor  $B = 0.8(3) \text{ \AA}^2$ .

the Pd<sub>3</sub>P (081) reflexion, had a calculated intensity which amounted to a considerable fraction of the measured total intensity. Any correction for this overlap would therefore be very uncertain, and accordingly we omitted the Pd<sub>3</sub>P (081) reflexion from the intensity data. The intensity material finally obtained comprised 23 data, seven of which consisting of intensities for single, non-overlapped Pd<sub>3</sub>P reflexions, the remainder being sums of overlapped Pd<sub>3</sub>P reflexions.

For the intensity calculations we assumed the

lithium fluoride monochromator crystal to be ideally imperfect. This leads to the expression

$$(1 + \cos^2 2\theta \cos^2 2\theta_M) / \sin^2 \theta \cos \theta$$

for the Lorentz-polarization correction, where  $\theta$  is the Bragg angle for the sample, and  $\theta_M$  that for the monochromator.<sup>8</sup> The weights  $w$  assigned to the observed intensities in the refinement procedure were based essentially on counting statistics but modified according to the formula

$$w = [N_T + N_B + 0.02(N_T - N_B)^2]^{-1}$$

where  $N_T$  is the total integrated intensity, and  $N_B$  the background intensity, in order to reduce the emphasis on the strongest intensities. In the structure factor calculations, atomic scattering factors for palladium were taken from Cromer and Waber,<sup>9</sup> for phosphorus from Hanson *et al.*<sup>10</sup> and dispersion correction from Cromer.<sup>11</sup>

The refinements based on space group C2 never reached a state of complete convergence, and the parameters oscillated slightly between successive cycles. At the termination of the refinement the weighted agreement factor  $R_w$ , defined as

Table 3. Observed and calculated intensities for Pd<sub>3</sub>P. (Diffractometer data, CuK $\alpha$  radiation).

<i>hkl</i>	$I_o$	$I_c$	<i>hkl</i>	$I_o$	$I_c$	<i>hkl</i>	$I_o$	$I_c$
0 2 2	1 426	1 551	0 2 5	3 648	3 444	$\bar{1} 7 1$	4 016	4 536
$\bar{1} 1 0$	805	688	0 6 2			$\bar{2} 2 3$		
$\bar{1} 1 1$	5 481	5 243	$\bar{1} 5 2$			$\bar{2} 4 1$		
1 1 1			$\bar{1} 5 2$			$\bar{2} 4 1$		
0 4 0	6 415	6 284	$\bar{1} 3 4$	1 739	2 304	2 4 1	349	258
0 4 1	33 410	32 400	1 3 4			$\bar{2} 2 3$		
0 2 3			33 410	32 400	2 0 0	$\bar{2} 0 4$		
$\bar{1} 1 2$	33 410	32 400			$\bar{1} 5 3$	2 0 4		
1 1 2			33 410	32 400	0 6 3	0 8 2		
1 3 0	4 598	4 715			$\bar{1} 1 5$	0 4 6		
$\bar{1} 3 1$			4 598	4 715	1 5 3	$\bar{1} 7 3$		
1 3 1	4 598	4 715			$\bar{2} 2 1$	$\bar{1} 5 5$		
0 4 2			841	759	1 1 5	0 6 5		
0 0 4	841	759			2 2 1	$\bar{2} 4 3$		
$\bar{1} 1 3$			5 638	5 436	$\bar{2} 0 2$	1 7 3		
1 1 3	5 638	5 436			2 0 2	0 0 7		
$\bar{1} 3 2$			5 638	5 436	0 4 5	1 5 5		
1 3 2	5 638	5 436			0 0 6	$\bar{2} 4 3$		
0 2 4			277	202	$\bar{2} 2 2$	$\bar{1} 3 6$		
0 4 3	280	431			$\bar{2} 2 2$	1 3 6		
0 6 0			1 542	1 410	$\bar{1} 3 5$	2 528		
$\bar{1} 1 4$	1 542	1 410			1 3 5		1 989	
1 5 0			1 542	1 410	0 2 6	3 075		
1 1 4	1 542	1 410			$\bar{1} 5 4$		2 830	
0 6 1			446	444	1 7 0	3 916		
$\bar{1} 5 1$	446	444			0 6 4		4 235	
1 5 1			446	444	1 5 4	4 235		
					2 4 0			

$$R_w = \sum w ||I_o| - k|I_c| / \sum |I_o|$$

(where  $k$  is the scale factor and  $I_o$  and  $I_c$  denote intensity values for separate, resolved reflexions or sums of non-resolved, overlapping reflexions) oscillated between 0.11 and 0.12. The good agreement between observed and calculated intensities substantiated the essential features of the proposed structure. It was furthermore observed that the magnitude of the calculated intensities for all  $(h0l)$  reflexions with  $l$  odd was far below the limit of detection in the powder diffractometer measurements.

A study of the correlation matrix revealed strong correlations between some of the parameters refined. This indicates that the oscillatory behaviour of the refinement might be due to the fact that the structure proposed very nearly conforms to an atomic arrangement of higher symmetry. A description in terms of  $C2/c$  symmetry would involve one eightfold and one fourfold palladium position, and one fourfold position randomly occupied by two phosphorus atoms. This would lead to a reduction in the number of positional parameters from eight in  $C2$  symmetry to five in  $C2/c$  symmetry.

A refinement based on  $C2/c$  symmetry converged satisfactorily to a final  $R_w$  of 0.113. The corresponding value for the unweighted agreement factor  $R$  was 0.058. The sign of the  $x$  parameter for the eightfold palladium position remained ambiguous, however, due to the fact that every pair of corresponding  $(hkl)$  and  $(\bar{h}\bar{k}l)$  reflexions was overlapping in the powder diffractometer data. The higher resolution in the Hagg-Guinier films afforded a possibility of resolving this ambiguity. A refinement based

on film scanner intensity data as obtained from  $CrK\alpha_1$  powder films was therefore carried out. The final  $R_w$  and  $R$  values for this refinement were both 0.058, and the value obtained for the  $x$  parameter turned out to be insignificantly different from zero.

The final structure data as obtained from the  $C2/c$  refinements are given in Table 2. Lists of observed and calculated intensities are given in Tables 3 and 4.

## DESCRIPTION AND DISCUSSION OF THE Pd<sub>6</sub>P STRUCTURE

The structure of Pd<sub>6</sub>P is shown in projection on the (100) plane in Fig. 1. Calculated interatomic distances are given in Table 5.

The structure can conveniently be described in terms of triangular prismatic building blocks. Four Pd(1) and two Pd(2) atoms are situated at the corners of a slightly deformed trigonal prism. The phosphorus atoms are situated at the centres of every second Pd<sub>6</sub> prism. The prisms are stacked into a closely packed network, where each palladium atom coordinates 12–15 palladium and phosphorus neighbours. In addition to the six palladium atoms at the corners of the prism, each phosphorus atom has three more remote palladium neighbours situated outside the quadrilateral faces of the prism. The augmented trigonal prismatic nine-coordination for phosphorus is very common with metal-rich transition metal phosphide structures and has been discussed at length earlier.<sup>12,13</sup> In particular, this coordination oc-

Table 4. Observed and calculated intensities for Pd<sub>6</sub>P. (Film scanner data,  $CrK\alpha_1$  radiation).

$hkl$	$I_o$	$I_c$	$hkl$	$I_o$	$I_c$
0 2 2	35	30	1 3 0	156	146
1 1 0	21	22	1 3 1	261	240
1 1 1	84	70	1 3 1		
1 1 1	67	62	0 4 2	44	51
0 4 0	181	175	1 1 3	46	45
0 4 1	470	490	1 1 3	49	43
0 2 3			1 3 2	51	47
1 1 2	182	182	1 3 2	51	50
1 1 2	181	188			

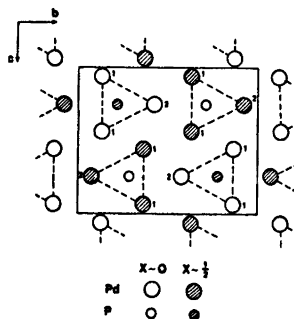


Fig. 1. The crystal structure of Pd<sub>6</sub>P projected on (100). Only half of the phosphorus positions as indicated in the figure are occupied by phosphorus atoms.

Table 5. Interatomic distances (Å) in Pd<sub>5</sub>P. Distances up to 3.8 Å are included. When greater than one, the number of equivalent distances from a central atom to its neighbours precedes the notation for the neighbouring atoms.

Pd(1)–P	2.16(5)	Pd(2)–2P	2.42(10)
P	2.16(5)	P	2.76(12)
Pd(1)	2.69(2)	2Pd(1)	2.83(2)
Pd(1)	2.80(2)	2Pd(1)	2.83(2)
P	2.81(6)	2Pd(2)	2.84(0)
Pd(1)	2.82(2)	2Pd(1)	2.84(1)
Pd(2)	2.83(2)	2Pd(1)	2.86(1)
Pd(2)	2.83(2)	2Pd(1)	3.09(2)
2Pd(1)	2.84(0)		
Pd(2)	2.84(1)		
Pd(2)	2.86(1)	P–	2Pd(1) 2.16(5)
Pd(1)	2.86(2)		2Pd(1) 2.16(5)
Pd(2)	3.09(2)		2Pd(2) 2.42(10)
			Pd(2) 2.76(12)
			2Pd(1) 2.81(6)
			2P 2.84(0)

curs<sup>6,7</sup> in the two palladium phosphides Pd<sub>4,5</sub>P and Pd<sub>3</sub>P.

As regards the twinning observed for the Pd<sub>5</sub>P crystals it is evident from the structural results that twinning on (100) requires very small distortions of the structure at the twin boundaries. The stacking faults may be connected with the distribution of the two phosphorus atoms among the four positions available. The distribution might have a certain degree of order, and it is conceivable that Pd<sub>5</sub>P might ideally crystallize with *C*2 symmetry as we assumed in our preliminary structure analysis. In the real structure, stacking faults may occur among the sheets of filled and unfilled triangular prisms traversing the structure parallel to (001), and the diffraction data would accordingly correspond to *C*2/*c* symmetry.

The atomic arrangement in Pd<sub>5</sub>P resembles very closely that occurring in the boride Re<sub>3</sub>B. This compound crystallizes with the orthorhombic *Cmcm* symmetry.<sup>14</sup> The unit cell contains twelve rhenium and four boron atoms, and the unit cell dimensions: *a* = 2.890 Å, *b* = 9.313 Å, *c* = 7.258 Å, are not much different from those of Pd<sub>5</sub>P. A projection on (100) of the Re<sub>3</sub>B structure would look very nearly the same as Fig. 1, with rhenium atoms at the palladium positions and boron atoms filling all triangular Re<sub>3</sub> prisms.

The Re<sub>3</sub>B-type metal skeleton is apparently very stable with respect to changes in the non-metal sublattice. In the so-called "filled" Re<sub>3</sub>B-type structure, as investigated and discussed thoroughly by Boller and Nowotny,<sup>15–19</sup> the triangular prismatic holes as well as octahedral holes, which also occur between the metal atoms, are filled with non-metal atoms. In contrast, Pd<sub>5</sub>P exhibits an Re<sub>3</sub>B-type metal sublattice with none of the octahedral, and only half of the triangular prismatic holes, filled.

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