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X-Ray Investigation on Rhodium Phosphides. The Crystal Structure of Rh_4P_3

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The rhodium-phosphorus system has been investigated in the range 0–75 atom per cent phosphorus using X-ray and chemical analytical methods. Four intermediate phases have been found, *viz.* Rh_2P, Rh_4P_3, RhP_2 and RhP_3. The structure of Rh_2P is of the anti-fluorite (*C* 1) type, $a = 5.498$ Å, and RhP_3 of the skutterudite (*D* 2) type, $a = 7.996$ Å. The crystal structure of Rh_4P_3 has been determined and refined by single-crystal X-ray methods. The space group is *Pnma*; $a = 11.662$ Å; $b = 3.317$ Å; $c = 9.994$ Å, and the unit cell contains sixteen rhodium atoms and twelwe phosphorus atoms on seven 4(*c*) positions. The structure is related to the Fe_2P (*C* 22) and Co_2P (*C* 23) structures.

The binary system rhodium-phosphorus has been earlier investigated using tensimetric and X-ray powder methods by Faller, Strotzer, and Biltz [1]. They reported four intermediate phases with the following compositions: Rh_2P, $RhP_{0.8}$, RhP_2 and RhP_3. Zumbusch [2] found that the structure of Rh_2P was of the anti-fluorite type. One of the present authors (S.R.) earlier [3] reported the structure of RhP_3 (*D* 2 type), and confirmed the anti-fluorite structure of Rh_2P.

The present paper gives an account of phase-analytical observations on the Rh-P system, and in addition describes the crystal structure determination of the phase Rh_4P_3, which has not been previously characterized properly.

EXPERIMENTAL

The alloys were prepared by heating rhodium metal powder (Heraeus, purity 99.95 %) and red phosphorus (purity 99 % or higher) in evacuated and sealed silica tubes at temperatures between 900°C and 1 100°C. The alloys were prevented from contacting the silica tube walls by placing them in small crucibles of pure aluminium oxide.

Chemical analyses were made at the Department of Analytical Chemistry of this Institute. The analytical work, directed by the head of the department, Dr. F. Nydahl, was performed in the following manner.

The samples were dissolved in hydrochloric acid-chlorine by heating in sealed glass tubes at 300°C for 24—48 h [4-7] (*cf* Ref. [8]). Perchloric acid was used as oxidant for the evolution of chlorine. 1—2 g of sodium chloride was added to the solution, which was evaporated to dryness in order to remove traces of silicic acid. The residue was taken up in hydrochloric acid and filtered. Rhodium was precipitated as sulphide, fired and reduced to metal in hydrogen [8]. In the filtrate from the rhodium sulphide, the phosphoric acid was precipitated after evaporation as ammonium molybdophosphate and weighed as $P_2O_5.24MoO_3$ according to Nydahl [9].

X-Ray powder photographs were taken with Guinier-type focussing cameras using Cu$K\alpha$ and Cr$K\alpha_1$ radiation ($\lambda_{CuK\alpha} = 1.5418$ Å; $\lambda_{CrK\alpha_1} = 2.2896$ 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. The accuracy of the lattice parameter determinations is greater than 0.05 %.

Single crystal intensity data were obtained with an ordinary Weissenberg camera and niobium-filtered MoK radiation. The multiple-film technique was used with thin iron foils between successive films, and the intensities were estimated visually with the aid of a standard intensity scale. The single-crystal specimen of Rh_4P_3, picked from a crushed, arc-melted alloy, was roughly cylindrical and of radius 0.025 mm. An intensity correction for the absorption was applied, the single-crystal being regarded as a perfect cylinder.

Fourier series summations, structure factor calculations, and calculations of interatomic distances were made with the electronic digital computer BESK, using programs developed by M. Edstrand and S. Åsbrink, G. Blomqvist and S. Westman [10]. Atomic scattering factors f_i were introduced as analytical expressions of the type;

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

The constants A_i, B_i, C_i, a_i, b_i and c_i, are based on the atomic scattering factor tables given by Thomas and Umeda [11] for Rh and by Tomiie and Stam [12] for P, and were calculated by Appel [13]. No corrections for dispersion were made. The following constants were used:

	A	B	C	a	b	c
Rh	15.520	16.977	12.024	0.237	2.600	20.057
P	1.447	7.971	5.588	0.001	1.528	37.194

PHASE ANALYSIS AND X-RAY POWDER DATA

The phase-analytical investigation showed that there are four intermediate phases with compositions close to Rh_2P, Rh_4P_3, RhP_2 and RhP_3. Within

Table 1. Phase-analytical data of alloys containing Rh_4P_3.

Alloy	Chemical analysis (weight per cent) Rh	P	Phases detected in powder photographs
$RhP_{0.746}$	81.5	18.29	Rh_4P_3 Traces of Rh_2P
$RhP_{0.753}$	81.4	18.45	Rh_4P_3 Traces of RhP_2

Table 2. Powder data for Rh_4P_3 ($CrK\alpha_1$ radiation).

hkl	$\sin^2\Theta_{obs} \times 10^4$	$\sin^2\Theta_{calc} \times 10^4$	$p \cdot F^2 \times 10^{-3}$	I_{calc}	I_{obs}
101	228	228	2	8	w−
200	385	385	2	5	w−
201	516	517	6	10	w−
002	525	525	4	7	w−
102	—	621	0	0	—
202	911	910	21	16	w
301	—	999	2	2	—
103	1 277	1 277	22	13	w
011	1 322	1 323	209	126	m+
302	1 391	1 392	59	34	w
111	1 418	1 419	172	98	m
400	1 541	1 542	62	32	w
203	1 566	1 566	51	25	w
210	—	1 577	0	0	—
401	1 672	1 673	247	118	m+
211	1 708	1 708	61	29	w
112	—	1 812	3	2	—
303	—	2 048	1	0	—
402	—	2 067	4	2	—
004	2 100	2 099	75	30	m
212		2 102	129	52	
311	2 194	2 190	144	56	m+
104		2 196	213	81	
013	—	2 372	11	4	—
113	—	2 468	19	7	—
204	2 484	2 485	217	78	m
501	2 539	2 541	209	75	m
312	2 583	2 583	96	34	w
404	—	2 723	11	4	—
410	2 733	2 733	685	233	st
213	2 757	2 758	1 306	444	st+
411	2 864	2 864	101	34	w
502	—	2 934	14	5	—
304	2 965	2 967	285	91	m
313	—	3 239	19	6	—
412	—	3 258	0	0	—
105	—	3 377	2	1	—
114	3 386	3 387	203	68	m−
600	—	3 469	22	8	—
503	3 591	3 590	76	30	w
601	—	3 600	5	2	—
404	—	3 641	28	10	—
205	—	3 666	0	0	—
214	3 674	3 676	226	78	m
511	3 732	3 732	233	82	m
413	3 917	3 914	91	34	w
602	3 998	3 994	33	13	w−
512	4 125	4 125	225	88	m
305	—	4 148	43	17	—
314	4 157	4 158	233	86	m
015	4 475	4 472	80	35	w
504	—	4 509	9	4	—
115	—	4 568	16	7	—

(*Table 2. cont.*)

hkl	$\sin^2\Theta_{obs} \times 10^4$	$\sin^2\Theta_{calc} \times 10^4$	$p \cdot F^2 \times 10^{-3}$	I_{calc}	I_{obs}
603	4 651	4 650	739	340	st
610	—	4 661	0	0	—
006	4 724	4 724	244	115	m
020	4 765	4 765	679	319	st
513	—	4 781	11	4	—
611	—	4 791	14	7	—
106	—	4 820	20	10	—
405	—	4 822	4	2	—
414	4 830	4 833	111	58	w
701	—	4 853	0	0	—
215	—	4 857	4	2	—
121	—	4 993	2	1	—

experimental error, (0.05 %), the phases did not show any lattice parameter variations. Some phase-analytical data are given in Table 1 for alloys containing Rh_4P_3. These data show that the composition of the pure phase is $RhP_{0.75}$ rather than $RhP_{0.80}$ as reported by Faller, Strotzer and Biltz [1].

No signs of transitions in the solid state at temperatures between 800°C and 1 100°C were observed in quenched alloys. Some alloys were subjected to higher temperatures by heating in an argon-filled arc furnace. Alloys with a phosphorus content higher than about 50 atom per cent evolved phosphorus vapour on heating, but alloys having phosphorus contents lower than about 40 atom per cent could be melted without serious phosphorus losses. Single-crystals of Rh_4P_3 were obtained from such melts.

The anti-fluorite structure [2] of Rh_2P was confirmed by inspection of the X-ray powder photographs. Measurements of the unit cell edge gave the value 5.498 Å, corresponding to the following interatomic distances: Rh—6 Rh 2.749 Å; Rh—12Rh 3.888 Å; Rh—4P 2.381 Å.

The structure of $Rh_4P_3$was determined by employing single-crystal methods (*vide infra*). Powder data for Rh_4P_3 are presented in Table 2. The unit cell is orthorhombic with the dimensions $a = 11.662$ Å; $b = 3.317$ Å; $c = 9.994$ Å.

Attempts to prepare single-crystals of RhP_2 and RhP_3 were unsuccessful and the powder pattern of RhP_2 could not be interpreted. The powder photographs of RhP_3 could be indexed with the cubic unit cell $a = 7.996$ Å. It seems very probable that RhP_3 is isostructural with $CoAs_3$ (*D* 2 type), the structure of which was determined by Oftedal [14]. According to this author, the structure of $CoAs_3$ is based on the space group $Im3$ (No. 204) with eight cobalt atoms in the 8(*c*) position, and twentyfour arsenic atoms in the 24(*g*) position, having the parameters $y = 0.35$; $z = 0.15$. Assuming that RhP_3 has the *D* 2 structure, a satisfactory agreement between observed and calculated intensities was reached with the parameter values $y = 0.34_7$; $z = 0.13_7$ for the phosphorus atoms. Intensity data are given in Table 3. These parameter

Table 3. Powder data for RhP_3 (Cu*Ka* radiation).

hkl	$\sin^2\Theta_{obs} \times 10^4$	$\sin^2\Theta_{calc} \times 10^4$	$p \cdot F^2 \times 10^{-3}$	I_{calc}	I_{obs}
110	186	186	8	3	w
200	372	372	314	74	st+
211	558	558	29	4	w
220	744	744	480	49	st
310	930	929	29	19	m+
301			204		
222	1 116	1 115	306	21	m+
321	1 302	1 301	1	5	w+
312			81		
400	1 488	1 487	131	7	w+
411	1 673	1 673	7	1	w−
330			17		
420	1 860	1 859	663	51	st
402			500		
332	2 045	2 045	27	1	w−
422	2 230	2 231	839	31	st
510	2 417	2 417	27	9	m
501			16		
431			169		
413			44		
521	—	2 788	0	0	—
512			1		
440	2 974	2 974	134	4	w+
530	3 162	3 160	8	3	w
503			34		
433			46		
600	3 347	3 346	16	8	w+
442			215		
611	—	3 532	0	0	—
532			0		
523			0		
620	3 719	3 718	211	18	m
602			286		
541	*	3 904	1	1	w−
514			18		
622	4 090	4 090	447	18	m
631	4 275	4 275	3	3	w
613			55		
444	4 462	4 462	298	13	m
710	*	4 647	7	1	w−
701			1		
550			2		
640	4 832	4 832	285	24	m+
604			210		

* Too weak for accurate measurement of the diffraction angle.

values for the phosphorus atoms cannot be considered very accurate, but the following approximate interatomic distances may be given:

shortest Rh—P distance 2.33 Å,

shortest P—P distances 2.19 and 2.45 Å.

DETERMINATION OF THE STRUCTURE OF Rh_4P_3

Weissenberg photographs of Rh_4P_3 crystals showed that the symmetry is orthorhombic. The unit cell volume is 386.6 Å^3, indicating a unit cell content of sixteen rhodium atoms and twelve phosphorus atoms. The calculated density is 8.67 g.cm^{-3}. An inspection of the intensity data from the layer lines 0 through 3 around the *b*-axis, showed that the reflexions $hk0$ with $h = 2n + 1$ and $0kl$ with $k + l = 2n + 1$ were absent. The space groups *Pnma* and $Pn2_1a$ were thus probable. Due to the short *b*-axis, the position 8(*d*) in space group *Pnma* must be eliminated. Further inspection of the intensity data showed that the intensity sequences in the 0 and 2 layer lines were equal (allowing for the normal intensity decrease), and the same was true for the 1 and 3 layer lines.

The Patterson sections $P(x0z)$ and $P(x\frac{1}{2}z)$ were calculated. It was possible to explain all maxima in these sections with a structure model based on the space group *Pnma* with sixteen rhodium atoms in four 4(*c*) positions, and twelwe phosphorus atoms in three 4(*c*) positions. Due to extensive overlapping it was difficult to obtain accurate atomic parameters from the Harker peaks alone. However, an analysis of the whole Patterson function using the method

Table 4. Interatomic distances in Rh_4P_3 (Å). (Only distances 3.80 Å or shorter listed.)

	Rh_I	Rh_{II}	Rh_{III}	Rh_{IV}	P_I	P_{II}	P_{III}
Rh_I	2.93_8 (2) 3.31_7 (2)	2.91_3 (2) 3.51_3	2.91_7	2.86_2 3.57_0	2.47 (2)	2.28 2.48 (2)	3.54
Rh_{II}	2.91_3 (2) 3.51_3	3.31_7 (2)	2.91_6	2.79_6 2.87_1 (2)	2.27	2.52 (2)	2.35 (2)
Rh_{III}	2.91_8	2.91_6	2.92_5 (2) 3.31_7 (2)	2.91_5 3.71_5	2.30 (2)	—	2.27 2.52 (2)
Rh_{IV}	2.86_2 3.57_0	2.79_6 2.87_1 (2)	2.91_5 3.71_5	3.31_7 (2)	2.61 (2)	2.30 (2)	2.30
P_I	2.47 (2)	2.27	2.30 (2)	2.61 (2)	3.32 (2)	3.32 3.45 3.78 (2)	3.18 3.74 (2) 3.79 (2)
P_{II}	2.28 2.48 (2)	2.52 (2)	—	2.30 (2)	3.31 3.45 3.79 (2)	3.32 (2) 3.75 (2)	3.25 3.80 (2)
P_{III}	3.54	2.35 (2)	2.27 2.51 (2)	2.30	3.18 3.74 (2) 3.79 (2)	3.25 3.80 (2)	3.32 (2) 3.80 (2)

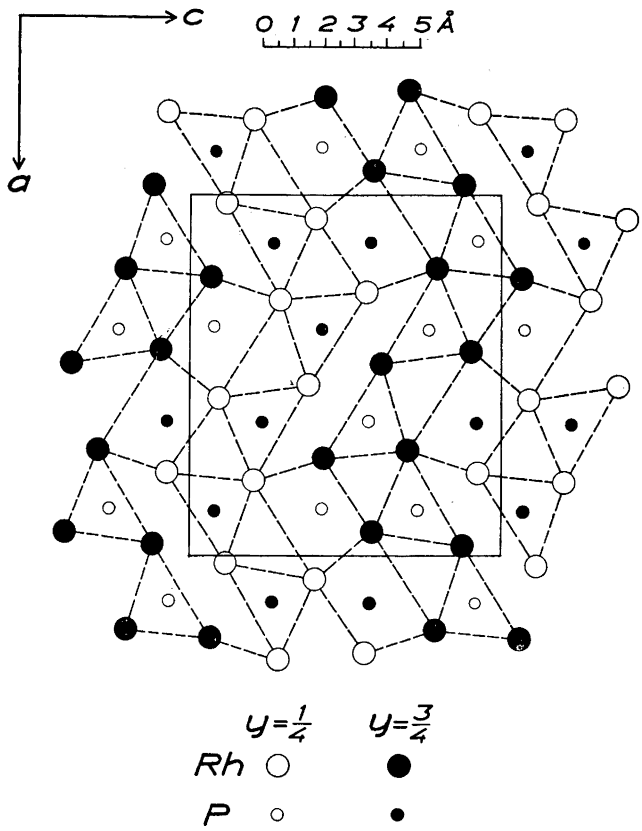

Fig. 1. The structure of Rh_4P_3 projected on (010).

described by Lindqvist [15], provided atomic parameters sufficiently accurate for the determination of a satisfactory number of structure factor signs.

The atomic parameters were refined from electron density projections and difference syntheses in the *ac*-plane. After the last refinement, the *R*-value was found to be 0.105 for the 229 observed $|F(h0l)|$-values. An isotropic, overall temperature factor with $B = 0.20$ Å^2 was applied *. The final structure of Rh_4P_3 is as follows:

Space group *Pnma* — (D_{2h}^{16}), No. 62.
$a = 11.662$ Å; $b = 3.317$ Å; $c = 9.994$ Å; $U = 386.6$ Å^3; $Z = 4$. All atoms on 4(*c*) positions:

* A list of observed and calculated $F(h0l)$-values can be obtained from this Institute on request.

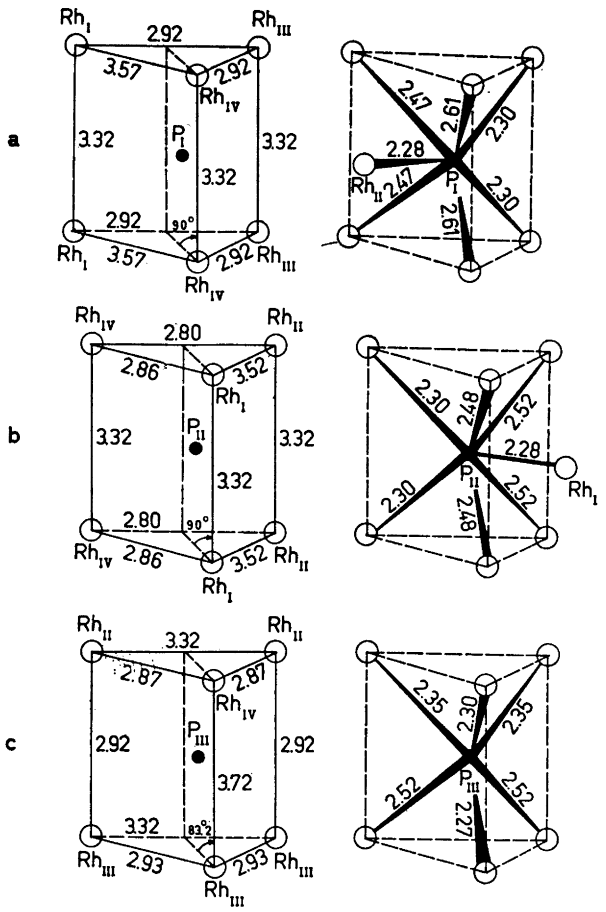

Fig. 2. The environment of the phosphorus atoms in Rh_4P_3.

a. the environment of the P_I atoms
b. the environment of the P_{II} atoms
c. the environment of the P_{III} atoms

	x	*z*
Rh_I	0.0270	0.1172
Rh_{II}	0.2717	0.5696
Rh_{III}	0.0647	0.4059
Rh_{IV}	0.2945	0.2911
P_I	0.3763	0.7616
P_{II}	0.1273	0.9212
P_{III}	0.3704	0.0792

The standard deviation for the rhodium positions, calculated from Cruickshanks [16] formula, is 0.001_9 Å, and for the phosphorus positions 0.007_3 Å. Interatomic distances are listed in Table 4.

DESCRIPTION AND DISCUSSION OF THE Rh_4P_3 STRUCTURE

A projection of the structure onto the *ac*-plane is shown in Fig. 1. The coordination of the phosphorus atoms is shown in greater detail in Fig. 2 a, b and c. The phosphorus atoms are situated at the centres of triangular prisms with rhodium atoms at the corners. This type of nonmetal atom coordination is common with transition metal phosphides, *e.g.* in the (revised) *C* 22 (Fe_2P), and *C* 23 (Co_2P) structures, as well as in transition metal borides and silicides. Each rhodium atom is surrounded by five close phosphorus neighbours, with an average Rh—P distance of 2.41 Å. In the Fe_2P [17] and Co_2P [18] structures, half of the metal atoms are surrounded by four phosphorus atoms in a distorted tetrahedral configuration, and the other half of the metal atoms have five phosphorus neighbours. The rhodium atoms in Rh_4P_3 have on average nine close rhodium contacts with a mean Rh—Rh distance of 3.11 Å.

In transition metal phosphides with a metal content larger than 50 atom per cent, there is no tendency for P—P bond formation [19]. The difference between transition metal phosphides and borides, with respect to the nonmetal-nonmetal bond formation, is clearly illustrated by a comparison of the Rh_4P_3 structure with the orthorhombic Ni_4B_3 structure [20]. The structure of orthorhombic Ni_4B_3 is based on the same space group as Rh_4P_3, the unit cell containing sixteen nickel atoms and twelwe boron atoms distributed on seven 4(*c*) positions. The coordination of the nickel atoms at the corners of triangular prisms around the boron atoms, resembles the coordination of rhodium atoms around the phosphorus atoms in Rh_4B_3; (compare Figs. 1 and 2 in the present paper with Figs. 1 and 3 in Ref.[20]). However, whereas there are no P—P contacts closer than 3.18 Å in Rh_4P_3 two thirds of the boron atoms in Ni_4B_3 are connected in infinite chains with B—B distances of approximately 1.9 Å. Furthermore, each nickel atom in Ni_4B_3 is surrounded by ten or eleven nickel neighbours at an average distance of 2.71 Å, compared with the average coordination of nine rhodium atom neighbours around each rhodium atom in Rh_4P_3 at an average distance of 3.11 Å.

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REFERENCES

1. Faller, F. E., Strotzer, E. F. and Biltz, W. *Z. anorg. Chem.* **244** (1940) 317.
2. Zumbusch, M. *Ibid.* **243** (1940) 322.
3. Rundqvist, S. *Nature* **185** (1960) 31.
4. Gordon, C. L. *J. Research NBS* **30** (1943) 107.
5. Wickers, E., Schlecht, W. G. and Gordon, C. L. *Ibid.* **33** (1944) 363.
6. Wickers, E., Schlecht, W. G. and Gordon, C. L. *Ibid.* **33** (1944) 451.

7. Gordon, C. L., Schlecht, W. G. and Wickers, E. *Ibid.* **33** (1944) 457.
8. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A. and Hoffman, J. I. *Applied Inorganic Analysis*, 2nd ed. N.Y. 1953.
9. Nydahl, F. *Lantbrukshögskol. Ann.* **10** (1942) 110.
10. Åsbrink, S., Blomqvist, G. and Westman, S. *Arkiv Kemi* **14** (1959) 545.
11. Thomas, L. H. and Umeda, K. *J. Chem. Phys.* **26** (1957) 293.
12. Tomiie, Y. and Stam, C. H. *Acta Cryst.* **11** (1958) 126.
13. Appel, K. *Technical Note from the Quantum Chemistry Group, University of Uppsala.*
14. Oftedal, I. *Z. Krist.* **66** (1928) 517.
15. Lindqvist, I. *Arkiv Mineral. Geol.* **2** (1960) 505.
16. Cruickshank, D. W. J. *Acta Cryst.* **2** (1949) 65.
17. Rundqvist, S. and Jellinek, F. *Acta Chem. Scand.* **13** (1959) 425.
18. Nowotny, H. *Z. anorg. Chem.* **254** (1947) 31.
19. Schönberg, N. *Acta Chem. Scand.* **8** (1954) 226.
20. Rundqvist, S. *Ibid.* **13** (1959) 1193.

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