

The Crystal Structure of Re_2P

STIG RUNDQVIST

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The crystal structure of Re_2P has been determined by X-ray powder methods. The structure belongs to the $C23$ type. The dimensions of the orthorhombic unit cell are: $a = 5.540 \text{ \AA}$; $b = 2.939 \text{ \AA}$; $c = 10.040 \text{ \AA}$. The space group is $Pnma$, with 4Re_I in $4(c)$: $x = 0.829_5$; $z = 0.065_8$; 4Re_{II} in $4(c)$: $x = 0.852_0$; $z = 0.785_0$; and 4P in $4(c)$: $x = 0.395$; $z = 0.110$. The Re_2P structure is compared with that of Ru_2P , and notable differences are indicated.

In previous communications ¹⁻⁵ on the crystal chemistry of phosphides of the Group VIII metals, the structures of several phosphides with the composition Me_2P have been described. Among the phosphides of the Group VII transition metals, Mn_2P is known to be isostructural with Fe_2P (the revised $C22$ type ¹), but the structure of Re_2P has not been determined previously. The present investigation was undertaken in view of the possible structural relationships between Re_2P and the phosphides of the platinum metals.

EXPERIMENTAL

Rhenium phosphides were prepared by heating rhenium powder (Heraeus, Hanau, Germany, claimed purity 99.8 %) and red phosphorus (purity higher than 99 %) in evacuated and sealed silica tubes at temperatures up to 1100°C . No attack on the tube walls was detected and chemical analysis was not carried out. Powder photographs were taken in Guinier-type focussing cameras using $\text{CuK}\alpha$ radiation. For the lattice parameter measurements, silicon ($a = 5.4306 \text{ \AA}$) was used as an internal calibration standard and the accuracy obtained was estimated to be greater than 0.05 %. Intensities of the powder lines were measured on photometer records of the films using methods similar to those described by Hägg and Regnström ⁶. Relative $|F|$ -values were calculated from the equation derived by Hägg ⁷. No absorption correction was applied. Fourier summations were made on an analogue computer of the Hägg-Laurent type, constructed by T. Lundström ⁸. Structure factor calculations were made on the electronic digital computer BESK using a program devised by Åsbrink *et al.* ⁹ For the calculations of the atomic scattering factors, expressions of the type

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

were used. The constants A_i , B_i , C_i and a_i , b_i , c_i have been calculated by Appel¹⁰ on the basis of scattering factor tables given for rhenium by Thomas and Umeda¹¹ and for phosphorus by Tomiie and Stam¹². The following constants were used:

	A_i	B_i	C_i	a_i	b_i	c_i
Re	25.854	28.303	19.925	0.170	1.885	15.175
P	1.447	7.971	5.588	0.001	1.528	37.194

For rhenium, the real part of the dispersion correction, calculated by Dauben and Templeton¹³ to be -6 units, was inserted as the constant D_i in the above expression.

THE RHENIUM-PHOSPHORUS SYSTEM

The rhenium-phosphorus system was investigated earlier by Haraldsen¹⁴. He found four intermediate phases with the compositions Re_2P , ReP , ReP_2 and ReP_3 . No crystallographic data were reported.

In the present investigation, alloys with phosphorus contents varying from 0 to 50 atom % were prepared. The products were obtained as blue-black powders which oxidized slowly in air.

The powder photographs showed the existence of Re_2P and ReP , and furthermore the existence of the two-phase regions $\text{Re} + \text{Re}_2\text{P}$ and $\text{Re}_2\text{P} + \text{ReP}$ was established. This shows that Re_2P and ReP are the only intermediate phases in the region 0–50 atom % phosphorus (at least at temperatures between 800° and 1100°C). Within the limits of experimental errors (less than 0.05 %) the lattice parameters of Re_2P were unchanged in two-phase $\text{Re} + \text{ReP}$ and $\text{Re}_2\text{P} + \text{ReP}$ alloys. It is therefore concluded that Re_2P has a narrow homogeneity range.

Re_2P alloys were heated for several weeks at 1000°C in silica tubes, but single-crystals suitable for X-ray work were not formed. Re_2P alloys were also heated at temperatures up to the melting point in an argon-filled arc furnace, but they decomposed rapidly, evolving phosphorus fumes. The powder method was therefore the only possible means for the structure determination.

THE STRUCTURE DETERMINATION OF Re_2P

The reflexions in the powder pattern of Re_2P were indexed on the basis of an orthorhombic unit cell with the dimensions: $a = 5.540$ Å; $b = 2.939$ Å; $c = 10.040$ Å. The cell volume of 163.5 Å³ indicates that the unit cell contains eight rhenium and four phosphorus atoms. Accordingly a value of 16.4 g·cm⁻³ is obtained for the calculated density. The experimental value quoted by Haraldsen¹⁴ is 15.5 g·cm⁻³.

($hk0$) reflexions were observed only for $h = 2n$ and ($0kl$) reflexions for $k + l = 2n$. It was noted further that the intensity distribution of the ($h0l$) reflexions was closely similar to that of the ($h2l$). These observations, combined with the small value of 2.939 Å for b strongly suggest that the Re_2P structure is based on the space group $Pnma$ with all the atoms in the 4(c) positions.

Table 1 X-Ray powder data for Re_2P ($\text{CuK}\alpha$ radiation, $\lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA}$)

<i>hkl</i>	$\sin^2\theta_{\text{obs}} \times 10^4$	$\sin^2\theta_{\text{calc}} \times 10^4$	$ F _{\text{obs}}$	F_{calc}	I_{obs}	I_{calc}
002	236	236	41.1	- 47.6	11.2	15.0
101	252	252	109.4	113.3	153.5	164.3
102	430	429	39.6	45.0	12.7	16.5
103	725	724	29.7	- 31.2	3.8	4.2
011	746	746	98.0	102.9	38.8	42.8
200	774	774	177.6	-173.8	61.0	58.5
201	832	832	112.9	-106.9	45.7	41.1
111	} 939	939		191.7	} 288.0	235.5
004		942		84.6		11.5
202	1 008	1 009	29.9	- 21.5	2.7	1.4
112	-	1 116		8.5	} 259.5	0.4
104	1 136	1 136	310.9	298.1		238.5
013	1 216	1 217	383.6	-381.0	371.0	376.0
203	1 303	1 304	343.1	336.9	282.5	273.0
113	1 411	1 410	26.6	- 29.0	3.2	3.8
210	1 460	1 461	381.5	377.8	320.0	313.5
211	1 520	1 519	13.9	- 17.0	0.8	1.2
105	1 666	1 666	76.9	81.2	11.3	12.7
212	1 697	1 696	46.0	- 48.3	8.0	8.8
204	1 715	1 716	26.6	- 33.1	1.3	2.1
301	1 800	1 800		-191.3	} 156.3	65.8
114	1 820	1 823		-158.6		90.5
302	1 976	1 976		- 62.4	} 56.5	6.4
213	1 992	1 991		121.0		48.0
006	2 121	2 120	177.9	-190.9	24.7	28.4
015	2 161	2 160	67.0	- 63.1	6.8	6.1
205	2 243	2 246	42.4	42.3	2.7	2.7
303	2 270	2 271	32.0	35.1	1.5	1.8
106	2 313	2 314	18.7	- 22.6	0.5	0.8
115	2 354	2 353	62.2	66.4	10.9	13.0
214	2 404	2 403	60.5	62.5	10.9	11.6
311	2 489	2 487	24.2	- 18.7	1.7	1.0
312	2 662	2 663		40.5	} 4.4	4.4
304	-	2 683		20.5		0.6
020	2 748	2 748	343.1	-333.4	78.8	74.3
206	2 895	2 894	58.4	70.3	4.5	6.5
215	2 934	2 933		53.9	} 9.3	7.7
313	2 956	2 958		- 23.0		1.4
022	-	2 984		28.2	} 13.1	1.0
121	} 3 000	3 000		- 67.5		11.8
116		3 001		23.5	1.4	
107	3 079	3 079		-156.3	} 57.4	31.8
400	3 092	3 094		-204.7		27.2
401	3 154	3 153		32.4	} 2.9	1.4
122	3 178	3 177		- 27.6		2.0
305	3 212	3 213	53.8	- 62.5	3.8	5.1
402	3 332	3 330		62.5	} 174.5	5.1
314	3 371	3 370		235.7		146.3
123	3 470	3 471	20.0	19.1	1.1	1.0
220	3 522	3 522	103.9	106.5	14.5	15.3
017	-	3 573		- 14.5	} 59.4	0.3
221	} 3 580	3 580		65.7		11.8
216		3 581		-134.2	49.0	
403	3 625	3 625	156.0	-163.2	33.6	36.7

Table 1. Cont.

<i>hkl</i>	$\sin^2\theta_{\text{obs}} \times 10^4$	$\sin^2\theta_{\text{calc}} \times 10^4$	$ F _{\text{obs}}$	F_{calc}	I_{obs}	I_{calc}
207	—	3 660		9.4	4.1	0.1
024	3 690	3 690		— 52.2		3.8
222	—	3 757		13.4		0.5
117	} 3 767	3 766		—219.5	206.0	137.0
008		3 770		—136.4		13.4
410	3 780	3 781		—180.1	} 139.2	46.1
411	3 839	3 840		— 71.7		15.0
306	3 860	3 861		— 30.7	} 14.2	1.4
124	3 883	3 884		—188.5		104.0
315	3 898	3 900		65.0	} 153.5	12.4
108	3 963	3 963	97.3	94.2		13.3
412	—	4 017		— 13.8	} 64.3	0.6
404	4 035	4 037		— 44.8		3.1
223	4 053	4 052		—216.9	} 13.9	145.3
413	4 312	4 311		146.8		71.3
217	—	4 347		23.7	} 71.8	1.9
125	4 416	4 414		— 54.3		10.1
224	4 465	4 464		22.1	} 100.0	1.7
208	} 4 548	4 543		74.2		9.8
316		4 548	4 548		— 26.9	2.6
321	4 548	4 548		126.6	} 13.8	57.0
405	4 571	4 567		— 69.4		8.5
307	4 627	4 627		225.6	} 41.1	93.3
118	4 648	4 650		— 72.5		19.6
322	} 4 725	4 724		42.8	} 7.0	6.8
414		4 724		— 42.3		34.0
026	4 866	4 868		129.6	} 12.1	12.1
501	4 891	4 894		77.5		

In order to determine the atomic parameters, the Patterson sections $P(x0z)$ and $P(x\frac{1}{2}z)$ were calculated. On account of overlaps only 32 reflexions were clearly resolved on the photometer curves. For most of the remaining lines, individual $|F|^2$ values were calculated using the sum of the intensities obtained from the photometer curves and the ratio of the intensities estimated visually on the powder films.

Table 2. Interatomic distances in Re₂P (Å). (Distances shorter than 3.5 Å listed)

	Re _I	Re _{II}	P
Re _I	2.73 (2) 2.939 (2)	2.74 (2) 2.82, 2.83(2)	2.4 ₅ , 2.6 ₁ (2) 3.1 ₇ , 3.2 ₈
Re _{II}	2.74 (2) 2.82, 2.83 (2)	2.86 (2) 2.939 (2)	2.2 ₇ (2) 2.6 ₉ (2)
P	2.4 ₅ , 2.6 ₁ (2) 3.1 ₇ , 3.2 ₈	2.2 ₇ (2) 2.6 ₉ (2)	2.9 ₀ (2) 2.939 (2)

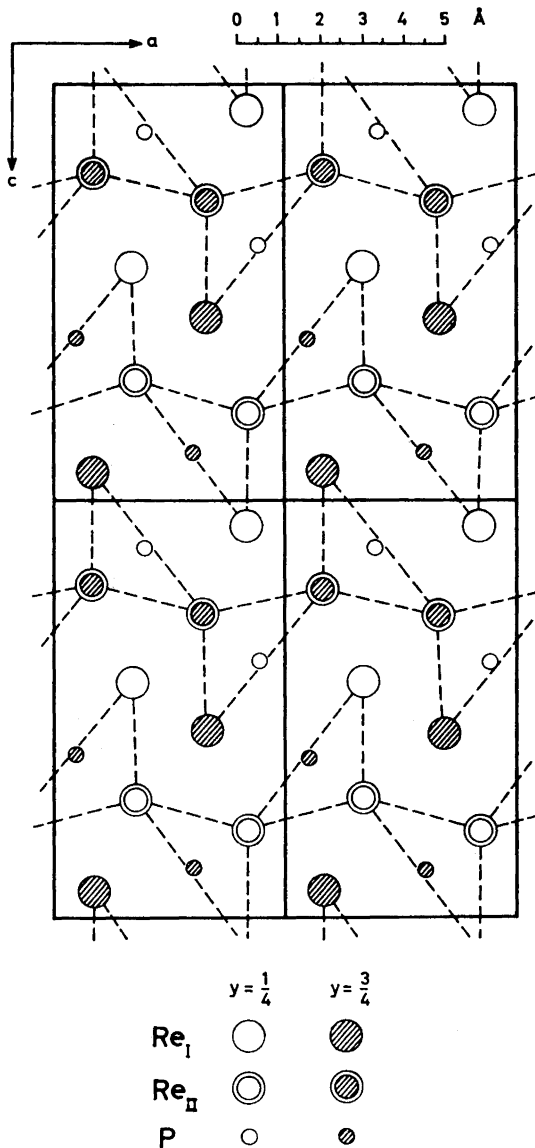


Fig. 1. The structure of Re_2P projected on (010).

All strong maxima in the two Patterson sections can be interpreted as arising from eight rhenium atoms situated in two sets of $4(c)$ positions of space-group $Pnma$. On the basis of parameter values obtained from the Patterson maps, the signs of most of the structure factors were determined, and the

electron density function was calculated in the section $\rho(x\frac{1}{4}z)$. In addition to the expected rhenium maxima, positive regions corresponding to a 4(c) set of phosphorus atoms were discernible.

The structure was then refined by successive difference syntheses. After two cycles, the signs of the structure factors became constant. In the further refinements, only the $|F|$ values of the 32 well resolved reflexions were used, and the final R -value for these reflexions was found to be 0.047. An isotropic temperature factor with $B = 1.52 \text{ \AA}^2$ was applied. X-ray powder data for Re_2P are given in Table 1.

The final structure data of Re_2P are as follows:

Space group $Pnma$ — (D_{2h}^{16}) No. 62

$$a = 5.540 \text{ \AA}; \quad b = 2.939 \text{ \AA}; \quad c = 10.040 \text{ \AA}; \quad U = 163.5 \text{ \AA}^3$$

All atoms are in 4(c) positions with the parameter values:

	x	z
Re_I	0.829 ₅	0.065 ₅
Re_{II}	0.852 ₀	0.785 ₀
P	0.395	0.110

An estimation of the errors in the atomic positions using Cruickshanks¹⁵ equation indicated the following standard deviations: rhenium positions 0.02 \AA ; phosphorus positions 0.07 \AA .

Interatomic distances are listed in Table 2.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Fig. 1 shows a projection on the ac -plane of the Re_2P structure. As seen from the general arrangement of the atoms, the structure can be classified as belonging to the $C23$ type. In a previous paper⁵ the structures of Co_2P and Ru_2P , both of which have the $C23$ structure, were treated. The atomic radius of ruthenium is not very different from that of rhenium. Nevertheless, the structures of Re_2P and Ru_2P show significant differences, which are clearly seen when the interatomic distances are compared.

As a basis for the comparison, the following atomic radii may be taken, for phosphorus the tetrahedral covalent radius $r_P = 1.10 \text{ \AA}$, for rhenium and ruthenium the Goldschmidt radii for 12-coordination $r_{\text{Re}} = 1.37_5 \text{ \AA}$ and $r_{\text{Ru}} = 1.33_5 \text{ \AA}$ (as given by Hume-Rothery and Raynor¹⁶). Details of the atomic coordination in Re_2P and Ru_2P are summarized below. Only distances less than 3.5 \AA are considered.

Compound	Atom	Number of close metal neighbours	Average distances
Re_2P	Re_I	9	$2.81 = 2r_{\text{Re}} + 0.06$
	Re_{II}	9	$2.84 = 2r_{\text{Re}} + 0.09$
	P	9	$2.67 = r_{\text{Re}} + r_P + 0.19$
Ru_2P	Ru_I	8	$2.82 = 2r_{\text{Ru}} + 0.15$
	Ru_{II}	10	$2.93 = 2r_{\text{Ru}} + 0.26$
	P	9	$2.49 = r_{\text{Ru}} + r_P + 0.05$

(It should be noted that whilst the accuracy of individual Re—P distances is not great, the average value is more reliable.)

It is evident that by comparison with the values quoted for the atomic radii of Ru, Re and P, the average Me—Me distances are shorter and the Me—P distances longer in Re_2P than in Ru_2P .

Acknowledgements. This work has been financially supported by the *Swedish State Council of Technical Research* and by the *Air Force Office of Scientific Research of the Air Research and Development Command, United States Air Force*, through its European Office under Contract No. AF 61(052)—40. Facilities for the use of the electronic digital computer BESK were granted by the *Swedish Board for Computing Machinery*.

The author is much indebted to professor G. Hägg for valuable comments on the manuscript. The author also wishes to thank Mr. S. Wahlgren for taking the photometer records, and Dr. B. Aronsson for interesting discussions.

REFERENCES

1. Rundqvist, S. and Jellinek, F. *Acta Chem. Scand.* **13** (1959) 425.
2. Rundqvist, S. and Larsson, E. *Ibid.* **13** (1959) 551.
3. Rundqvist, S. *Nature* **185** (1960) 31.
4. Rundqvist, S. and Hede, A. *Acta Chem. Scand.* **14** (1960) 893.
5. Rundqvist, S. *Ibid.* **14** (1960) 1961.
6. Hägg, G. and Regnström, G. *Arkiv Kemi, Mineral. Geol.* **18 A** (1944) Nr. 5.
7. Hägg, G. quoted in Berger, S. *Acta Chem. Scand.* **7** (1953) 612.
8. Lundström, T. and Klimecki, V. *J. Sci. Instr.* *In print*.
9. Åsbrink, S., Blomqvist, G. and Westman, S. *Arkiv Kemi* **14** (1959) 545.
10. Appel, K. *Technical Note from the Quantum Chemistry Group, University of Uppsala*.
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. Dauben, C. H. and Templeton, D. H. *Ibid.* **8** (1955) 841.
14. Haraldsen, H. *Z. anorg. Chem.* **221** (1935) 397.
15. Cruickshank, D. W. J. *Acta Cryst.* **2** (1949) 65.
16. Hume-Rothery, W. and Raynor, G. *The structure of metals and alloys*. The Institute of Metals, London 1954.

Received October 5, 1960.