

## The Crystal Structure of $\text{Re}_3\text{P}_4$

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The crystal structure of  $\text{Re}_3\text{P}_4$  has been determined and refined from X-ray powder diffraction data.  $\text{Re}_3\text{P}_4$  crystallizes with the  $\text{Fe}_3\text{Se}_4$ -type structure and the monoclinic unit cell dimensions (space group  $C2/m$ ) are:  $a = 12.179 \text{ \AA}$ ,  $b = 3.012 \text{ \AA}$ ,  $c = 6.042 \text{ \AA}$ ,  $\beta = 114.07^\circ$ . The structure of  $\text{Re}_3\text{P}_4$  is compared with that of the isostructural compound  $\text{Cr}_3\text{S}_4$ , and some notable differences are discussed.

The information about the rhenium-phosphorus system is still rather meagre. On the basis of tensimetric and X-ray powder diffraction studies, Haraldsen<sup>1</sup> concluded that four rhenium phosphides:  $\text{Re}_2\text{P}$ ,  $\text{ReP}$ ,  $\text{ReP}_2$ , and  $\text{ReP}_3$ , occur. Rundqvist<sup>2</sup> prepared  $\text{Re}_2\text{P}$  and solved its crystal structure from powder diffraction data. Recently, Hulliger<sup>3</sup> reported the occurrence of a phosphide of composition  $\text{Re}_3\text{P}_7$ . He stated that the structure of  $\text{Re}_3\text{P}_7$  is different from that of  $\text{Re}_3\text{As}_7$ , which crystallizes with the  $\text{Ir}_3\text{Sn}_7$ -type structure.

Evidently, the Re—P system needs further clarification. In the present communication, the occurrence of a compound of composition  $\text{Re}_3\text{P}_4$  is reported. A crystal structure determination of this compound is described, and in addition some phase-analytical observations of the Re—P system are presented.

### PREPARATION AND PHASE ANALYSIS

Rhenium phosphide samples were prepared by heating rhenium powder (Heraeus, claimed purity 99.8 %) and red phosphorus (purity higher than 99 %) in evacuated and sealed silica tubes at different temperatures between 700° and 1100°C for times varying from a few days up to several weeks. The reaction between rhenium and phosphorus was found to proceed rather slowly, particularly in the more phosphorus-rich preparations, and small amounts of elemental phosphorus often remained even after very long heat-treatments. Phase analyses of the products were made by the powder diffraction technique employing Guinier-Hägg focussing cameras.

In samples containing up to about 58 at% phosphorus, only two intermediate phases were observed. The most rhenium-rich compound was found to be  $\text{Re}_2\text{P}$  in agreement with earlier results.<sup>1,2</sup>  $\text{Re}_2\text{P}$  forms a two-phase region with a phase of higher phosphorus content at all temperatures covered in the

present study. This two-phase region was mentioned in an earlier investigation<sup>2</sup> and the higher phosphide was then denoted ReP, following Haraldsen's original report. However, the present phase analysis showed that the higher phosphide is in fact homogeneous at a phosphorus content higher than 50 at%, and a composition of  $\text{ReP}_{1.33}$  is indicated. As described below, the ideal crystallographic formula of this phase is  $\text{Re}_3\text{P}_4$ , and the compound is therefore denoted  $\text{Re}_3\text{P}_4$  in the following. For identification purposes, powder diffraction data for  $\text{Re}_3\text{P}_4$  are given in Table 1.

Table 1. Powder diffraction data for  $\text{Re}_3\text{P}_4$ . Guinier-Hägg type camera,  $\text{CrK}\alpha_1$  radiation. Internal calibration standard: Si ( $a = 5.43054 \text{ \AA}$ ).

$hkl$	$\sin^2\theta_{\text{obs}} \times 10^4$	$\sin^2\theta_{\text{calc}} \times 10^4$	$p F_{\text{calc}} ^2 \times 10^{-4}$	$I_{\text{obs}}$
200	424.1	424.0	17.2	m+
001	431	430.7	0.6	w-
$\bar{2}01$	506.0	506.1	37.8	st
201	1203.1	1203.3	54.1	st
$\bar{4}01$	1429.3	1429.6	10.0	w
$\bar{2}02$	1449.4	1449.6	69.9	st
110	1551.0	1550.9	25.6	w+
400	1695.8	1695.9	75.3	st
002	—	1722.8	1.2	—
$\bar{1}11$	1807.5	1807.2	171.6	st+
$\bar{4}02$	2024.3	2024.3	18.6	w+
$\bar{1}11$	2155.6	2155.9	41.2	m-
$\bar{3}11$	2306	2306.6	3.9	w-
310	2399.0	2398.8	62.2	st-
401	—	2823.9	1.6	—
202	2844.5	2844.0	61.9	st-
$\bar{1}12$	—	2925.0	2.8	—
$\bar{3}12$	3075.8	3075.8	99.6	st
$\bar{6}01$	3200	3200.8	20.2	w-
$\bar{2}03$	3253	3254.4	11.7	w-
311	3352.7	3352.5	153.2	st
$\bar{6}02$	3447.4	3447.1	85.3	m+
$\bar{4}03$	3480.3	3480.5	76.8	m+
112	3621.8	3622.3	133.2	st
$\bar{5}11$	3653.6	3654.1	199.1	st
600	—	3815.9	6.1	—
003	3876.3	3876.3	77.3	m+
$\bar{5}12$	—	4074.5	0.9	—
$\bar{5}10$	—	4094.8	0.0	—
$\bar{6}03$	—	4554.6	0.6	—
$\bar{3}13$	4706.4	4706.3	99.9	m+
402	—	4813.2	0.1	—

The phase relationships at phosphorus contents higher than about 58 at% were not examined in detail. A preliminary survey indicates the occurrence of more than one phase in this region. A sample of the  $\text{Re}_3\text{P}_7$  phase described in Ref. 3 was kindly put at the author's disposal by Dr. Hulliger. The diffraction pattern of this compound was found to be identical with diffraction patterns obtained in the present study. A more detailed analysis of the phase relationships in the phosphorus-rich part of the Re—P system is in progress.

In summarizing the available information about the rhenium phosphides, it can be stated that there is conclusive evidence for the occurrence of the two compounds  $\text{Re}_2\text{P}$  and  $\text{Re}_3\text{P}_4$ . It is very likely that the compound denoted  $\text{ReP}$  by Haraldsen is identical with  $\text{Re}_3\text{P}_4$ . Haraldsen's powder diffraction data are compatible with this suggestion, and his tensimetric results indicate that the phosphorus content of the compound is in fact larger than 50 at %.

#### THE STRUCTURE DETERMINATION OF $\text{Re}_3\text{P}_4$

Attempts to prepare  $\text{Re}_3\text{P}_4$  single-crystals suitable for X-ray examination were not successful. Heat treatments for very long times and experiments with the halogen transport technique were tried but very finely divided polycrystalline material was invariably obtained. The crystallographic examination therefore had to be performed by powder diffraction methods.

It is possible to index the powder diffraction pattern on the basis of a *C*-centred monoclinic cell (see Table 1). A least-squares refinement of the data yielded the following cell dimensions and standard deviations:  $a = 12.1787 \pm 4$  Å,  $b = 3.0118 \pm 1$  Å,  $c = 6.0418 \pm 1$  Å,  $\beta = 114.073 \pm 2^\circ$ . The unit cell volume indicates a cell content of six rhenium and eight phosphorus atoms. The most probable space-groups are *C2*, *Cm*, or *C2/m*.

Intensities for the reflexions were measured on photometer tracings of films taken with  $\text{CuK}\alpha$  radiation in a Guinier-Hägg camera covering the angular range up to  $45^\circ$ . The intensities were corrected for Lorentz-polarization factors in the manner described earlier.<sup>2</sup> The overlaps among the reflexions were rather numerous and only 41 of the accessible 105 reflexions could be measured with acceptable accuracy.

Using these 41 reflexions, the Patterson section  $P(x0z)$  was calculated. The strongest maxima in this section were compatible with an arrangement of two Re atoms in position  $2a$  and four Re atoms in position  $4i$  of space group *C2/m*. An electron density section  $\rho(x0z)$  was calculated using signs of the structure factors determined by the rhenium contributions. In addition to the expected rhenium maxima, the section was found to contain further maxima, which could readily be interpreted as arising from two sets of phosphorus atoms in  $4i$  positions. The positional parameters and the individual isotropic temperature factors were refined by the least-squares method on a CDC 3600 computer using the full-matrix program LALS written by Gantzel, Sparks and Trueblood and modified by A. Zalkin in Berkeley and by C.-I. Brändén, R. Liminga and J. O. Lundgren in Uppsala. Atomic scattering factor values were taken from *International Tables III*<sup>4</sup> and the weights assigned to the structure factors were according to the scheme proposed by Hughes.<sup>5</sup> The refinement converged rapidly and the final *R*-value for the 41 reflexions was 0.079.

The structure analysis described above is based on the assumption that the space group symmetry is *C2/m*, but the lower symmetries *C2* or *Cm* cannot be completely excluded. However, the good agreement between observed and calculated structure factors, and the reasonable atomic arrangement obtained indicates that the deviation from the symmetry *2/m* cannot be very large.

Further refinements based on the lower symmetries were not considered profitable in view of the large number of parameters compared with the limited intensity material.

The final structure data for  $\text{Re}_3\text{P}_4$ , subject to the limitations mentioned above, are as follows:

		$\text{Re}_3\text{P}_4$					
Space group $C2/m$ ; $Z = 2$ .		$x$	$\sigma(x)$	$z$	$\sigma(z)$	$B$	$\sigma(B)$
2	$\text{Re}_I$ in 2 $a$					2.27	0.40
4	$\text{Re}_{II}$ in 4 $i$	0.2618	0.0006	0.3186	0.0009	2.87	0.40
4	$\text{P}_I$ in 4 $i$	0.3559	0.0050	0.0320	0.0066	3.89	1.23
4	$\text{P}_{II}$ in 4 $i$	0.1000	0.0029	0.4458	0.0047	1.57	1.13

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

Interatomic distances and standard deviations are given in Table 2.

Table 2. Interatomic distances and their standard deviations ( $\text{\AA}$  units) in  $\text{Re}_3\text{P}_4$ . Distances shorter than 4  $\text{\AA}$  listed.

	Dist.	S.d.		Dist.	S.d.
$\text{Re}_I$ — 4 $\text{P}_I$	2.380	0.043	$\text{Re}_{II}$ — 2 $\text{P}_{II}$	2.274	0.023
— 2 $\text{P}_{II}$	2.462	0.026	— 1 $\text{P}_{II}$	2.389	0.032
— 2 $\text{Re}_{II}$	2.977	0.006	— 1 $\text{P}_I$	2.435	0.046
— 2 $\text{Re}_I$	3.012	0.000	— 2 $\text{P}_I$	2.517	0.033
— 4 $\text{P}_{II}$	3.890	0.017	— 2 $\text{Re}_{II}$	2.769	0.009
			— 1 $\text{Re}_I$	2.977	0.006
$\text{P}_I$ — 2 $\text{Re}_I$	2.380	0.043	— 2 $\text{Re}_{II}$	3.012	0.000
— 1 $\text{Re}_{II}$	2.435	0.046	— 2 $\text{P}_{II}$	3.845	0.020
— 2 $\text{Re}_{II}$	2.517	0.033	— 2 $\text{P}_I$	3.873	0.029
— 2 $\text{P}_I$	2.874	0.097	— 1 $\text{P}_I$	3.983	0.036
— 2 $\text{P}_I$	3.012	0.000			
— 2 $\text{P}_{II}$	3.336	0.039	$\text{P}_{II}$ — 2 $\text{Re}_{II}$	2.274	0.023
— 2 $\text{P}_{II}$	3.361	0.051	— 1 $\text{Re}_{II}$	2.389	0.032
— 2 $\text{P}_{II}$	3.486	0.043	— 1 $\text{Re}_I$	2.462	0.026
— 1 $\text{P}_{II}$	3.640	0.053	— 1 $\text{P}_{II}$	2.768	0.063
— 1 $\text{P}_I$	3.685	0.111	— 2 $\text{P}_{II}$	3.012	0.000
— 2 $\text{Re}_{II}$	3.873	0.029	— 2 $\text{P}_I$	3.336	0.039
— 1 $\text{Re}_{II}$	3.983	0.036	— 2 $\text{P}_I$	3.361	0.051
			— 2 $\text{P}_I$	3.486	0.043
			— 1 $\text{P}_I$	3.640	0.053
			— 2 $\text{P}_{II}$	3.754	0.060
			— 2 $\text{Re}_{II}$	3.845	0.020
			— 2 $\text{Re}_I$	3.890	0.017

#### DESCRIPTION AND DISCUSSION OF THE $\text{Re}_3\text{P}_4$ STRUCTURE

After the completion of the structure analysis of  $\text{Re}_3\text{P}_4$  it was realized that the atomic arrangement corresponds to the  $\text{Fe}_3\text{Se}_4$ -type structure.<sup>6</sup> This structure was originally described with  $I2/m$  symmetry. A projection of the  $\text{Re}_3\text{P}_4$  structure along the monoclinic axis is given in Fig. 1. The  $C$ -centred and the  $I$ -centred cells are both indicated.

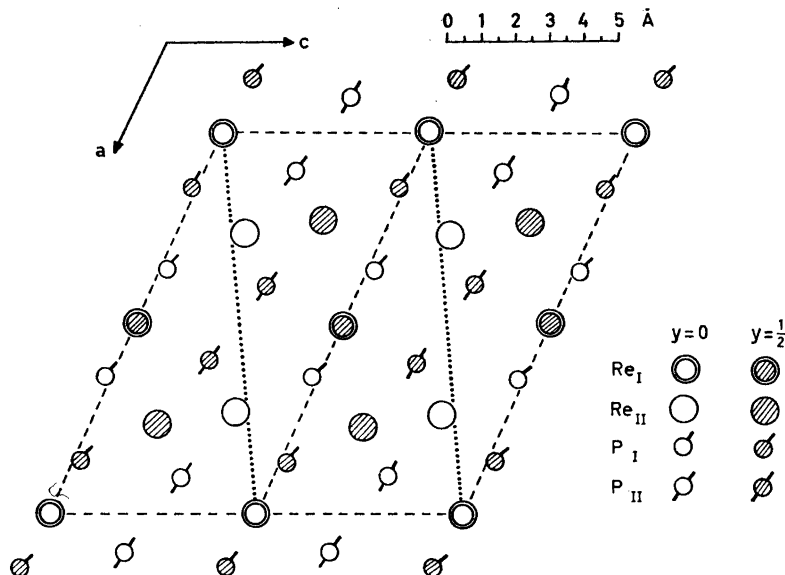


Fig. 1. The structure of  $\text{Re}_3\text{P}_4$  projected along the monoclinic axis. The  $C$ -centred cell is indicated by dashes, the  $I$ -centred cell by dots.

The  $\text{Fe}_3\text{Se}_4$ -type structure has been thoroughly described elsewhere (see, *e.g.*, Refs. 6, 7, and 8), and its classification as a member of the NiAs structure family is well known. Representatives for this structure type have hitherto been found mainly among the transition metal chalcogenides.<sup>8</sup> While the general atomic arrangement in  $\text{Re}_3\text{P}_4$  closely resembles that in the chalcogenides, some details in the arrangement are appreciably different and are briefly discussed below. It appears suitable to compare  $\text{Re}_3\text{P}_4$  with  $\text{Cr}_3\text{S}_4$ . The radius ratios for the two compounds are nearly the same, and the atomic positions in  $\text{Cr}_3\text{S}_4$  have been accurately determined by Jellinek.<sup>7</sup>

The coordination about the non-metal atoms (X) in the two compounds are closely similar,  $X_I$  having five and  $X_{II}$  four metal atom (Me) neighbours. The  $X_I$ -Me distances are on the average somewhat larger than the  $X_{II}$ -Me distances, in  $\text{Re}_3\text{P}_4$ :  $P_I$ -5 Re = 2.45 Å;  $P_{II}$ -4 Re = 2.35 Å; in  $\text{Cr}_3\text{S}_4$ :  $S_I$ -5 Cr = 2.44 Å;  $S_{II}$ -4 Cr = 2.38 Å. The S-S distances in  $\text{Cr}_3\text{S}_4$  exceed 3.25 Å, while in  $\text{Re}_3\text{P}_4$  the shortest P-P distances are only about 2.8 Å. This value, however, greatly exceeds the normal P-P bond distance of 2.2 Å. In both compounds the metal atoms are surrounded by six non-metal neighbours in slightly deformed octahedral arrangements.

The most conspicuous difference between the two compounds is observed for the Me-Me distances. The shortest Cr-Cr distance in  $\text{Cr}_3\text{S}_4$ , 2.97 Å, exceeds the Goldschmidt metal diameter for 12-coordination (2.56 Å) by more than 16%. In  $\text{Re}_3\text{P}_4$ ,  $\text{Re}_I$  has four rhenium neighbours at an average distance of 2.99 Å (9% larger than the Goldschmidt diameter of 2.74 Å)

and  $\text{Re}_{II}$  has five rhenium neighbours at an average distance of 2.91 Å (6 % larger than the Goldschmidt diameter). The shortest Re—Re distance, 2.77 Å, is very close to the Goldschmidt diameter.

The importance of metal-metal contacts in sulphide structures has been stressed by Jellinek,<sup>9</sup> who regards the metal-metal interaction as an essential factor in determining the structures and the physical properties. The comparison of  $\text{Re}_3\text{P}_4$  and  $\text{Cr}_3\text{S}_4$  made above shows that the tendency towards the formation of metal-metal bonds is stronger in  $\text{Re}_3\text{P}_4$  than in  $\text{Cr}_3\text{S}_4$ . Analogous observations can be made in more general comparisons of the crystal chemistry of phosphides with that of sulphides. The difference between phosphides and sulphides as regards metallic bond character has also been noted by Samsonov,<sup>10</sup> who explains this effect in a qualitative way by considering the difference in ionization potentials between phosphorus and sulphur.

It appears, however, that the theories about the chemical bond in the compounds under discussion are still rather unsatisfactory, and in particular the metal-metal bonds remain to be accounted for in a quantitative way.

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