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Crystal Growth, Properties, and Structure Refinements of Some Rhenium Phosphides and Arsenophosphides

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Small single crystals of Re_2P and Re_3P_4 were grown in a tin flux. Their crystal structures were refined from single crystal diffractometer data to residuals of $R = 0.055$ and $R = 0.049$, respectively. The new compound $ReP_{2.3}$ was prepared. Re_6P_{13} forms an extended solid solution with As up to $Re_6As_{10.7}P_{2.3}$. Re_3P_4 is diamagnetic. ReP_4 is a diamagnetic semiconductor with a band gap of 0.54 eV. Systematic trends in the structural chemistry of rhenium phosphides are discussed.

Introduction

The system rhenium–phosphorus was first studied by Haraldsen (*1*) by the tensimetric technique of thermal decomposition. He found the four compositions $ReP_{0.56}$, $ReP_{1.18}$, $ReP_{2.06}$, and $ReP_{2.98}$ to which he assigned the tentative formulas Re_2P, ReP, ReP_2, and ReP_3. The two phosphorus-rich compositions were characterized as Re_6P_{13} (*2, 3*) and ReP_4 (*4*). Two other rhenium polyphosphides Re_2P_5 (*5*) and ReP_3 (*6*) were recently prepared and characterized by us. Rundqvist has determined the crystal structures of the two metal-rich composition from X-ray powder data and established their ideal formulas as Re_2P (*7*) and Re_3P_4 (*8*). For Re_2P he found a $PbCl_2$ (Co_2P) type structure with very unusual axial ratios (*9*). Therefore, and because of the relatively small scattering power of the phosphorus atoms, this structure determination was somewhat questionable. Apart from the considerably higher accuracy of the present refinements, however, we confirm Rundqvist's work on these compounds. In addition we report on phase equilibria and physical properties of some rhenium phosphides, on the preparation of a new rhenium phosphide with the approximate composition $ReP_{2.3}$, and on some ternary compositions of rhenium with arsenic and phosphorus.

Sample Preparation

According to our previous experiences (*3–6*) the direct reactions of the elemental components in evacuated silica tubes are very slow and thermodynamic equilibria

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are practically unachievable. With the addition of about 1–5% iodine as a mineralizer or by working in a tin flux the reactions are much faster, although with annealing temperatures below about 900°C (iodine mineralizer) and 800°C (tin flux) we have repeatedly observed three phase products, indicating that thermodynamic equilibria were not achieved.

Starting materials were rhenium powder (Ventron, 99.997, 325 mesh), semiconductor-grade red phosphorus (Hoechst-Knapsack, "ultrapure"), iodine (Merck, 99.99), arsenic, and tin (both from Merck, "rein"). The arsenic (As) was further purified by us through fractional sublimation.

The overall sample compositions were usually higher in phosphorus content than the desired compositions. In the samples with iodine as a mineralizer this is needed to build up some phosphorus pressure in the tubes (A total of 10–50 mg P, sealed in tube volumes of about 5 cm^3); more excess P is needed for high and less for low annealing temperatures. In samples prepared in the tin flux the activity of P is reduced by the formation of Sn phosphides. The phosphorus containing tin-rich matrix of these samples was dissolved in moderately diluted, hot hydrochloric acid. In the samples with iodine the excess P was driven to a cooled end of the tubes prior to quenching in cold water. Annealing times and temperatures varied between 12 hr at 1200°C and 2 weeks at 600°C. To prevent reaction with the silica tubes, samples which were to be annealed above 1000°C were enclosed in alumina containers.

In agreement with previous experiences (*7*) we found it very difficult to obtain single crystals of Re_2P which were suitable for diffraction work. The sample from which we finally isolated a single crystal of Re_2P had a starting composition of Re : P : Sn = 2 : 1 : 12. It was annealed at 900°C (7*d*) and slowly cooled (within 5 days) to room temperature. The crysal of Re_3P_4 used for the structure refinement was taken from a sample with the starting composition Re : P : Sn = 1 : 1 : 6 which was annealed for 7 days at 800°C and quenched.

Phase Equilibria in the Re–P System

In agreement with previous results (*1*, *7*, *8*) we find only one compound with a high rhenium content: Re_2P; and it is in equilibrium with Re and Re_3P_4. The phosphorus-rich part of the Re–P system, however, is much more complicated than Haraldsen's tensimetric study (*1*) suggested. Our results are summarized in Figs. 1 and 2. They show the starting compositions, the annealing temperatures, and the resulting phases which were identified through their Guinier powder patterns. Besides Re_3P_4 and the recently characterized compounds Re_6P_{13} (*2*, *3*), Re_2P_5 (*5*), ReP_3 (*6*), and ReP_4 (*4*) we find another phase ReP_x which is in equilibrium with Re_6P_{13} and Re_2P_5 (= Re_6P_{15}). We therefore estimate its composition to be in between and close to Re_6P_{14}, i.e., $x \sim 2.3$.

Although the results of Figs. 1 and 2 are not sufficient to draw the complete phase diagram of the Re–P system, we can deduce the stability regions of most compounds: at high temperatures and in equilibrium with P vapor we find the compounds ReP_4, Re_6P_{13}, Re_3P_4, and Re_2P. Since their powder patterns also resemble the diagrams listed by Haraldsen (*1*) we conclude that these are the four phases characterized by him. ReP_3 is found only in samples annealed at relatively low temperatures, whereas Re_6P_{13} can only be synthesized at high temperatures.

The synthesis in the tin flux proceeds faster and thermodynamic equilibria where reached for lower temperatures than in the reactions catalized by iodine. Re_2P_5 was obtained only through the tin flux synthesis. Its energy dispersive analysis and the structure determination (*5*) did not give any indication for it being stabilized by tin. At tem-

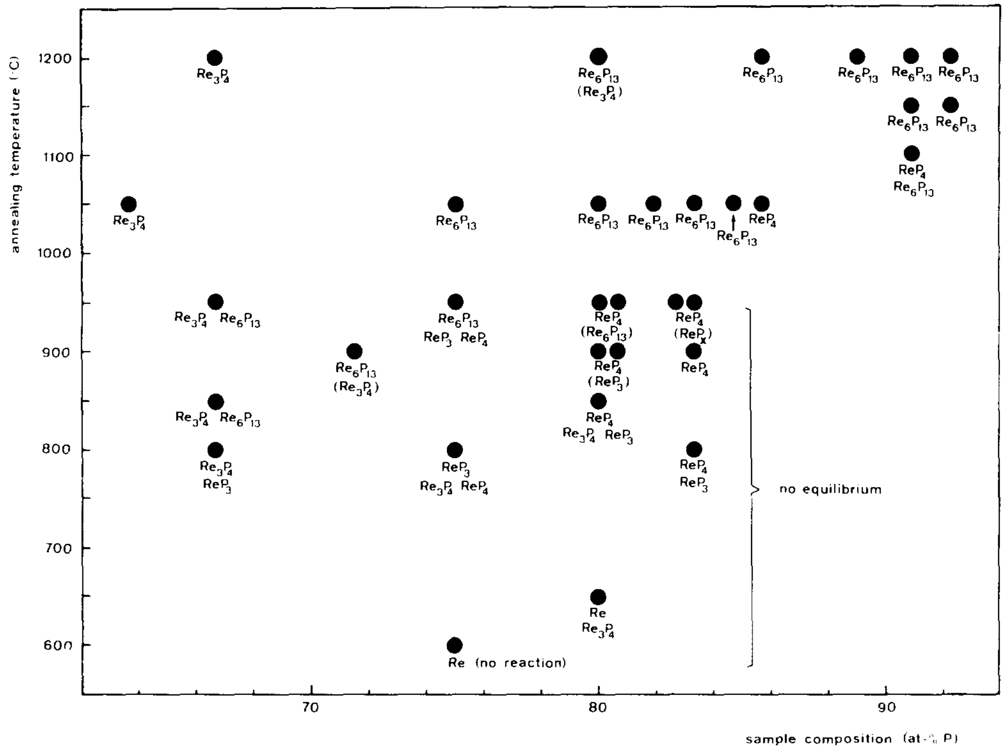

FIG. 1. Phase analytical results of phosphorus-rich rhenium phosphide samples prepared with iodine as mineralizer. Formulas written side by side indicate about equal amounts. The formula of the minority compound is set under the formula of the major compound. Formulas in parenthesis indicate trace amounts.

peratures of 600°C or less the reactions were too slow to be observable.

Structure Refinements of Re_2P and Re_3P_4

Only very small crystals of Re_2P were obtained. The crystal used for the structure refinement had square-prismatic shape ($4 \times 5 \times 8\ \mu m^3$). The crystal of Re_3P_4 had similar habit with dimensions $25 \times 25 \times 75\ \mu m^3$. Because of the small size of the Re_2P crystal conventional single crystal film data could not be collected. The systematic extinctions and symmetry of the diffraction data set, however, were fully compatible with the space group *Pnma* deduced earlier from the powder data (*7*). Weissenberg photographs of Re_3P_4 confirmed the C-centered monoclinic cell of this Fe_3Se_4 (Cr_3S_4) type structure (*8*). Lattice constants were refined from Guinier powder data using α-quartz (a = 4.9130 Å, c = 5.4046 Å) as standard.

The diffraction data were collected in a four-circle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation, a scintillation counter, and a pulse-height discriminator. Scans were recorded along theta with background counts at both ends of each scan.

The positional parameters deduced from the powder data (*7, 8*) were used as starting parameters for the full matrix least-squares refinements. Scattering factors for neutral atoms (*10*), corrected for anomalous dispersion (*11*), were used. Weights were as-

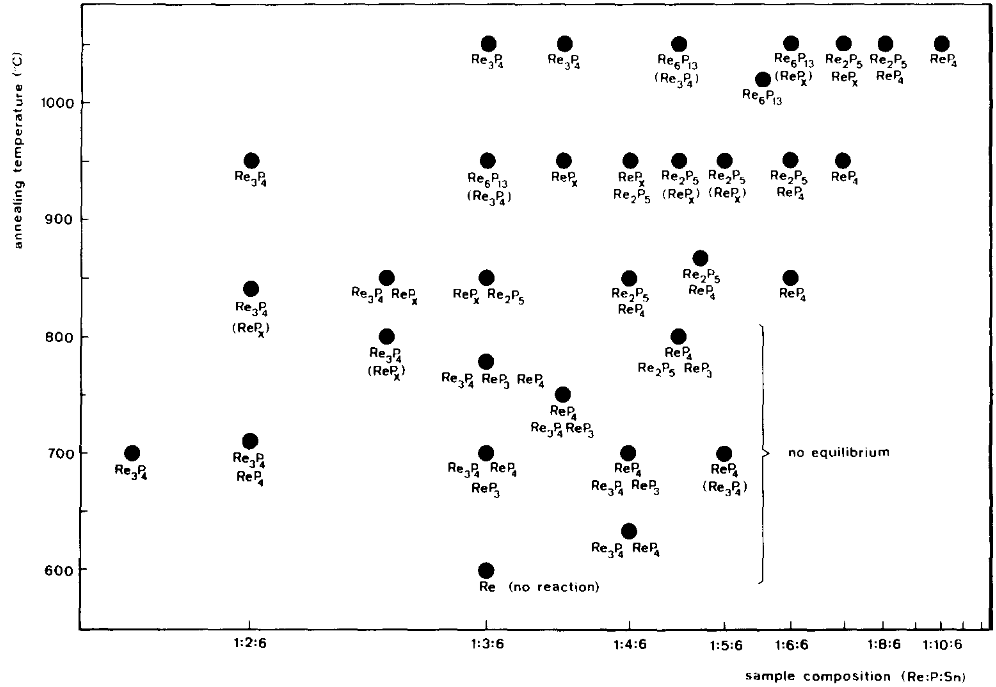

FIG. 2. Rhenium phosphides in samples prepared by the tin flux technique. For explanations see Fig. 1.

signed according to counting statistics. A secondary extinction parameter was refined and applied to the calculated structure factors. The highest and lowest peaks in the final difference Fourier syntheses were +16.8 and −12.0 e/Å^3 in Re_2P and +10.5 and −19.8 e/Å^3 in Re_3P_4. Most of these peaks were close to the Re positions and are probably due to insufficient absorption correction. None of the peaks higher than 6 e/Å^3 was at a potential interstitial site. Further details and results of the structure refinements are summarized in Table I. Listings of structure factor tables can be obtained from the authors. Positional and thermal parameters, and interatomic distances are listed in Tables II–V.

The New Phase $ReP_{\sim 2.3}$

$ReP_{\sim 2.3}$ was obtained more easily from the tin flux than in samples with iodine as a mineralizer. Its powder patterns (Table VI) consist always of diffuse and sharp diffraction lines and have some resemblence to those of Re_6P_{13}. Notably the sharp line with d_0 = 2.763 Å corresponds to the 003 reflection (hexagonal indexing) of Re_6P_{13}. Scanning electron micrographs showed a needle-like prismatic habit with diameters of up to 3 μm and heights of up to 15 μm. In view of the diffuse scattering observed in the powder patterns the crystals were judged not to be large enough for single crystal X-ray diffraction. Even though the powder patterns resemble those of Re_6P_{13}, they cannot be rationalized as originating from poorly crystalized Re_6P_{13} and/or from Re_6P_{13} crystals with strongly preferred orientation. It seems more likely that the structure of $ReP_{2.3}$ is some kind of stacking variant of Re_6P_{13} with lower rhenium content and considerable disorder in the stacking sequences. We are reminded of the dif-

TABLE I

CRYSTAL DATA AND SOME RESULTS OF THE STRUCTURE REFINEMENTS OF Re_2P AND Re_3P_4

Compound	Re_2P	Re_3P_4
Structure type	$PbCl_2(Co_2P)$	$Fe_3Se_4(Cr_3S_4)$
Space group	$Pnma$-D_{2h}^{16}	$C2/m$-C_{2h}^{3}
a (Å)	5.540(3)	12.169(4)
b (Å)	2.940(2)	3.015(1)
c (Å)	10.039(4)	6.043(2)
β	—	114.13(2)
V (Å^3)	163.5	202.3
Formula units/cell Z	4	2
Calculated density (g/cm^3)	16.39	11.20
Linear absorption coefficient $\mu_{MoK\alpha}$ (cm^{-1})	1423.5	872.0
Portion of reciprocal space measured up	$\frac{1}{2}$	$\frac{1}{4}$
to $(\sin \theta)/\gamma$	0.7	1.0
Intensity data collected	833	952
Internal R value	0.073	0.023
Final conventional R	0.055	0.049
For F values $>3\sigma$	163	845
Variable parameters	20	30

fraction patterns described for NbP_{1-x} which can be considered as a disordered stacking variant derived from the WC and NbAs type structures (*12*).

TABLE II

POSITIONAL AND THERMAL PARAMETERS OF Re_2P^a

	Re(1)	Re(2)	P
x	0.8263(3)	0.8532(4)	0.4076(29)
y	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
z	0.0646(2)	0.7864(2)	0.1027(17)
U_{11}	0.0035(9)	0.0036(9)	0.0106(27)
U_{22}	0.0058(14)	0.0043(15)	U_{11}
U_{33}	0.0028(9)	0.0046(11)	U_{11}
U_{12}	0	0	0
U_{13}	0.0001(7)	0.0008(8)	0
U_{23}	0	0	0
B (Å^2)	0.29(5)	0.31(5)	0.80(21)

[a] All atoms are in position 4c of space group $Pnma$-D_{2h}^{16}. The standard deviations of the least significant digits are given in parentheses. The ellipsoidal thermal parameters are defined by $T = \exp\{-2\pi^2 (U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)\}$. The last row contains the B values as obtained in a least-squares refinement where all atoms were allowed only isotropic thermal parameters.

Physical Properties

All rhenium phosphides are black with metallic luster. Magnetic and electrical conductivity data for Re_6P_{13}, Re_2P_5, and ReP_3 were reported earlier (Table VII). For the other compounds we have obtained the following results, all from samples prepared by the tin flux technique.

Magnetic susceptibilities were determined with the Faraday method at room temperature. Re_3P_4 is diamagnetic with a susceptibility of $\chi = -343 \times 10^{-6} \pm 20 \times 10^{-6}$ cm^3/mol. A polycrystalline sample of $ReP_{2.3}$ with a small amount of (diamagnetic) Re_2P_5 as impurity was paramagnetic. Single crystals of ReP_4 are diamagnetic: $\chi = -89 \times 10^{-6} \pm 20 \times 10^{-6}$ cm^3/mol.

Electrical conductivities of Re_3P_4 were determined by cycling pressed pellets between 75 and 500 K as described earlier (*13*).

TABLE III

POSITIONAL AND THERMAL PARAMETERS OF $Re_3P_4{}^a$

	Re(1)	Re(2)	P(1)	P(2)
$C2/m$	$2a$	$4i$	$4i$	$4i$
x	0	0.26376(3)	0.3513(2)	0.0836(2)
y	0	0	0	0
z	0	0.31897(6)	0.0255(4)	0.4354(5)
U_{11}	0.0013(2)	0.0011(1)	0.0041(7)	0.0031(7)
U_{22}	0.0032(2)	0.0021(2)	0.0035(8)	0.0043(8)
U_{33}	0.0039(2)	0.0034(1)	0.0056(8)	0.0053(8)
U_{12}	0	0	0	0
U_{13}	0.0017(1)	0.0017(1)	0.0036(6)	0.0012(6)
U_{23}	0	0	0	0
B (Å^2)	0.19(1)	0.14(1)	0.31(3)	0.33(3)

[a] Concerning standard deviations, the definition of the ellipsoidal thermal parameters, and the isotropic B value see footnote of Table II.

TABLE IV

INTERATOMIC DISTANCES IN Re_2P^a

Re(1):	1 P	2.351	Re(2):	2 P	2.343
	2 P	2.581		2 P	2.705
	2 Re(1)	2.747		2 Re(1)	2.748
	2 Re(2)	2.748		1 Re(1)	2.797
	1 Re(2)	2.797		2 Re(1)	2.847
	2 Re(2)	2.847		2 Re(2)	2.865
	2 Re(1)	2.940		2 Re(2)	2.940
P:	2 Re(2)	2.343			
	1 Re(1)	2.351			
	2 Re(1)	2.581			
	2 Re(2)	2.705			

[a] Listed are all Re–Re distances shorter than 4 Å. The shortest nonbonding Re–P distance is 3.243, the shortest P–P distance is 2.731 Å. Standard deviations are 0.003 Å for Re–Re distances and 0.018 Å for Re–P distances.

TABLE VI

GUINIER POWDER PATTERN OF $ReP_{\sim 2.3}{}^a$

d_0 (Å)	I_0	d_0 (Å)	I_0
7.928	vw, diffuse	2.004	s
5.284	s, diffuse	1.985	m
4.529	m, diffuse	1.864	w
3.505	s, diffuse	1.848	s
3.401	s, diffuse	1.826	m
2.825	w, diffuse	1.810	m
2.763	vs, sharp	1.651	m
2.592	s, sharp		

[a] From the second half of the diagram only relatively sharp reflections are listed.

The conductivity curves are flat with maxima around room temperature. This may be interpreted as semimetallic behavior: at high temperatures the conductivities decrease as is typical for metals and at low temperatures they decrease because of a decreasing carrier concentration as it is known for semiconductors. The results should, however, be regarded with some caution because they were obtained from polycrystalline samples and the conductivities may have been dominated by surface effects.

Electrical conductivities were also determined for small single crystals of ReP_4. They show semiconducting behavior. The band gap as determined from the slope of the ln R vs $1/T$ plot at high temperatures according to the relation $R = R_0 \exp(E_a/2kT)$ is $E_a = 0.54 \pm 0.04$ eV.

Rhenium Arsenophosphides

Only one compound is reported to form in the Re–As system (*14*, *15*). It has the composition Re_3As_7 and crystallizes with

TABLE V

INTERATOMIC DISTANCES IN $Re_3P_4{}^a$

Re(1):	2 P(2)	2.402	P(1):	2 Re(1)	2.408
	4 P(1)	2.408		1 Re(2)	2.413
	2 Re(2)	2.994		2 Re(2)	2.487
	2 Re(1)	3.015		2 P(1)	2.797
Re(2):	2 P(2)	2.381	P(2):	2 Re(2)	2.381
	1 P(1)	2.413		1 Re(1)	2.402
	2 P(1)	2.487		1 P(2)	2.459
	1 P(2)	2.562		1 Re(2)	2.562
	2 Re(2)	2.788			
	1 Re(1)	2.994			
	2 Re(2)	3.015			

[a] All Re–Re and Re–P distances shorter than 3.8 Å are listed. The shortest not listed P–P distances are 3.015 Å. Standard deviations are 0.002 Å for Re–Re, 0.004 Å for Re–P, and 0.006 Å for P–P distances.

TABLE VII

PHYSICAL DATA OF RHENIUM PHOSPHIDES

Compound	Magnetic behavior	Electrical conductivity	Literature
Re_2P	Paramagnetic?	Metallic?	
Re_3P_4	Diamagnetic	Semimetallic	This work
Re_6P_{13}	Paramagnetic	Metallic	(*2*, *5*)
$ReP_{2.3}$	Paramagnetic	?	This work
Re_2P_5	Diamagnetic	Semiconducting	(*5*)
ReP_3	Diamagnetic	?	(*6*)
ReP_4	Diamagnetic	Semiconducting	This work

Ru_3Sn_7 (Ir_3Ge_7) type structure (*16–19*). We have prepared samples of the arsenic- and phosphorus-rich part (<35 at% Re) of the ternary system Re–As–P to see whether any additional rhenium arsenides can be prepared or whether they can be "stabilized" by the substitution of some As by P. They were all prepared with iodine as mineralizer and annealed at temperatures between 900 and 950°C.

No additional binary rhenium polyarsenide was found. However, the phosphide Re_6P_{13} (hexagonal, $a = 15.665$, $c = 8.320$ Å, $V = 1768$ Å^3) (*3*) forms a continuous solid solution $Re_6As_xP_{13-x}$ up to $a = 16.282$, $c = 8.629$ Å, $V = 1981$ Å^3. The composition of this limit of the solid solubility was estimated from Vegard's rule assuming the atomic volume increment of an As atom to be 3.3 Å^3 greater than that of a P atom.[1] This results in a composition of about $Re_6As_{10.7}P_{2.3}$. Intensity calculations (*24*) for the powder patterns of various compositions within the solid solution show, that the first P atoms which are substituted by As atoms in Re_6P_{13} (*3*) are those of position P(1); the last P atoms which cannot be substituted entirely by As atoms are those of position P(3). This was actually expected by us because the P(1) atoms have by far the greatest distances to their neighbors, and can therefore most easily be replaced by the larger As atoms. For the P(3) atoms the situation is inverse; especially the very short P(3–P(3) distance of 2.142 Å makes these positions least suitable for a replacement by As atoms. In a more quantitative way this can be expressed by the calculation of "mean fictive atomic radii," MEFAR (*25*). The compositions $Re_3As_4P_3$, $Re_3As_3P_4$, and Re_3P_7 were reported (*16*) to be isotypic. In view of the present results it seems likely that they correspond to the solid solution $Re_6As_xP_{13-x}$ described here.

One new compound with high As content was also prepared in the ternary system Re–As–P. It has a noticeable homogeneity range, but does not extend into the binary Re–As system. It is characterized by the following *d* spacings (Å) and intensities: 9.90 vw, 7.85 m, 6.72 w, 5.98 w, 4.87 vs, 4.17 s, 4.09 w, 3.79 s, 3.37 s, 3.24 w, 3.07 w, 3.00 m, 2.84 s, 2.83 s, 2.77 vs, 2.69 w, 2.65 vs.

Discussion

Our structure refinements of Re_2P and Re_3P_4 confirm Rundqvist's (*7, 8*) structure determinations especially for the Re positions. None of the Re–Re distances of our refinements differ by more than 0.02 Å from the corresponding distances in the earlier refinements from powder data. Due to the much weaker scattering power of P, however, the P positions could not be determined very accurately in the earlier work. Of the bonding distances of interest the greatest differences occur for the following distances (with the corresponding distance of the earlier structure determination in parentheses) in Re_2P:Re(1)–P 2.351 Å (2.4$_5$ Å); in Re_3P_4: Re(2)–P(2) 2.562 Å (2.39 Å), P(2)–P(2) 2.459 Å (2.77 Å).

Although Re_2P formally has (anti-)$PbCl_2$ type structure, the near-neighbor coordinations are quite different from those in other binary and ternary compounds with this structure type, e.g., in Ru_2P (*26*), or in the many compounds with TiNiSi structure (*9, 27–31*). For instance, the two different Re atoms in Re_2P have three and four P neighbors, some of which at rather large distances. In contrast the two different metal atoms in the many other binary and ternary metal-rich compounds with this structure have five, respectively, four metalloid neighbors, all at very short distances. As a corollary, considerable differences also occur in metal–metal bonding. This has al-

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[1] This value is obtained by comparing the cell volumes of various transition metal diphosphides and diarsenides, e.g., MoP_2 and WP_2 (*20, 21*) with $MoAs_2$ and WAs_2 (*22, 23*).

TABLE VIII

INTERATOMIC DISTANCES, AVERAGE DISTANCES (Å), AND COORDINATION NUMBERS IN RHENIUM PHOSPHIDES

	Range P–P	$\overline{\text{P–P}}$	Range Re–P	$\overline{\text{Re–P}}$	Range Re–Re	$\overline{\text{Re–Re}}$	Coordination numbers	
							P	Re
Re_2P[a]	(2.731)	—	2.343–2.705	2.516	2.747–2.940	2.831	7 Re	12 (3P + 9Re) and 13 (4P + 9Re)
Re_3P_4[a]	2.459	2.459	2.381–2.562	2.437	2.788–3.015	2.946	5 (5Re) (4Re + 1P)	10 (6P + 4Re) and 11 (6P + 5Re)
Re_6P_{13} (3)	2.142–2.291	2.211	2.290–2.699	2.421	2.761–2.941	2.853	4[b]	8 (6P + 2Re) and 9 (6P + 3Re)
Re_2P_5 (5)	2.095–2.265	2.208	2.280–2.587	2.411	2.852–2.960	2.899	4[b]	8 (6P + 2Re) and 9 (6P + 3Re)
ReP_3 (6)	—	—	—	—	3.122	3.122	4[b]	8 (6P + 2Re)
ReP_4 (4)	2.177–2.251	2.202	2.347–2.521	2.402	3.012	3.012	4[b]	7 (6P + 1Re)

[a] This work.

[b] In ReP_4: 2Re + 2P and 1Re + 3P, in other Re polyphosphides also 4Re and 3Re + 1P.

ready been noted from the comparison of Re_2P with Ru_2P (*26*).

In Table VIII we have summarized bonding distances and coordination numbers of all structurally characterized rhenium phosphides. There are consistent trends in the average P–P and Re–P distances and also in the coordination numbers. With decreasing coordination numbers the average P–P and Re–P bond distances also decrease. This is of course a well-known correlation, however, it is remarkable that this trend persists also for the P–P bonds in Re_6P_{13}, Re_2P_5, and ReP_4, even though the P atoms in these compounds have all the same coordination number and only the metal–metal bonding is decreasing. The metal–metal bond lengths do not follow this trend of decreasing bond length with decreasing coordination number. This has to do with the directional character of the Re–P and P–P bonds: optimal (shorter) bond lengths in the polyphosphides cannot be obtained because this would require too great distortions of the ReP_6 octahedra and too great deviations from the tetrahedral Re–P–Re bond angles.

The magnetic and electrical conductivity data of Re_6P_{13}, Re_2P_5, ReP_3, and ReP_4 can be completely rationalized on the basis of classical two-electron bonds (*3–6*, *32*). The semiconductivity of ReP_4, reported here for the first time, was fully expectable from the structural characteristics of this compound. Such rationalizations of the physical properties are not as easily possible for Re_3P_4 and Re_2P. In these compounds the number of near neighbor interactions exceeds the corresponding number of valence electrons available. This is well known for typical intermetallic compounds. Nevertheless Re_3P_4 is diamagnetic and probably semimetallic. Thus bond saturation occurs, but the concept of the two-electron bond will have to be supplemented by counting procedures for multicenter bonds. Semiconductivity is not limited to compounds with two-electron bonds as is demonstrated by semiconducting $CrSi_2$ (*33*) and $RuAl_2$ (*34*). Because of the high metal-content of Re_2P, we do however expect paramagnetism and metallic conductivity for this compound.

Acknowledgments

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