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# Chemical Bonding Topology of Binary and Ternary Transition-Metal Polyphosphides

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Edge-localized models are presented for the chemical bonding topologies of the low-coordination-number binary transition-metal polyphosphides $MP_4$ (M = Fe, Ru, Os, Mn, Tc, Re, Cr, Mo, W, V), $MP_3$ (M = Co, Tc, Re), $MP_2$ (M = Ni, Pd, Pt, Co, Rh, Ir, Fe, Ru, Os), $Re_2P_5$, and $Re_6P_{13}$, which provide simple rationalizations of their electrical properties (i.e., semiconducting versus metallic). Similar models can be used for related ternary metal polyphosphides such as $M'M_2P_{12}$ (M' = Ti, Nb, Mo, W; M = Mn, Fe) and $Ln_6Ni_6P_{17}$. Extension of such models to the ternary metal phosphide superconductors $LnM_4P_{12}$ (Ln = lanthanide; M = Fe, Ru, Os) suggests porous delocalization similar to that found in ternary metal boride superconductors such as $LnRh_4B_4$.

## Introduction

Solid-state transition-metal phosphides have been classified into two types on the basis of the coordination numbers of the component atoms. Jeitschko and co-workers[1] consider phosphides with high coordination numbers to be those in which the transition metal atoms are surrounded by more than six phosphorus atoms and at least some of the phosphorus atoms have more than four nearest neighbors. Metal phosphides with low coordination numbers are considered to be those with six or less phosphorus neighbors around each transition-metal atom and tetrahedral coordination of all phosphorus atoms. In general, such low-coordination metal phosphides have relatively high phosphorus/metal ratios and some direct phosphorus–phosphorus bonding.

This classification of transition-metal phosphides based on coordination numbers of the component atoms is closely related to their skeletal chemical bonding topology.[2-5] Thus, edge-localized models are sufficient to account for the key features of the chemical bonding in low-coordination-number metal phosphides whereas delocalized models approaching those of metals and their alloys are required for understanding the chemical bonding in the high-coordination-number metal phosphides.

This paper summarizes the key aspects of the chemical bonding topology of low-coordination-number transition-metal phosphides. Understanding in detail the chemical bonding topology of such phosphides is important for the development of new types of superconductors in view of the previously established[6-8] relationship between edge-localized bonding, "porous delocalization", and superconductivity. In this connection the 7.2 K superconductor $LaRu_4P_{12}$[9] is shown to be an example of a metal phosphide exhibiting edge-localized bonding and porous delocalization.

## Background

The two extreme types of skeletal chemical bonding in metal clusters and other types of infinite solid-state structures may be called edge-localized and globally delocalized.[2-5] An edge-localized skeleton has two-electron two-center bonds along each edge of the skeleton and is favored when the numbers of vertex internal orbitals match the vertex degrees (the *vertex degree* is the number of edges meeting at the vertex in question). A globally delocalized skeleton is constructed by fusion of polyhedra containing multicenter bonds in the polyhedral cavities and is favored when the numbers of internal orbitals do not match the vertex degrees. Since

the chemical bonding manifolds of the transition metals forming the phosphides of interest can contain no more than nine bonding orbitals (i.e., $sp^3d^5$), transition-metal phosphides with more than nine atoms within bonding distance of the transition-metal atom must necessarily exhibit delocalized skeletal bonding. Such high-coordination-number transition-metal phosphides, which include all derivatives with P/M < 2, will not be considered in this paper.

Now consider the nature of the phosphorus vertices in metal phosphide structures using molecular species such as (alkylphosphinidene)metal carbonyl complexes[10] as models. Normal phosphorus vertices are bonded to four other atoms, which may be either other phosphorus atoms or transition-metal atoms in the species of interest. Since a neutral phosphorus atom has 5 valence electrons, a four-coordinate phosphorus atom bonded to $m$ metal atoms and $4 - m$ phosphorus atoms will furnish $[5 - (4 - m)]/m = (m + 1)/m$ electrons to each metal atom, making the central phosphorus atom in neutral $PMP'_3$, $PM_2P'_2$, $PM_3P'$, and $PM_4$ units donors of totals of 2, 3, 4, and 5 skeletal electrons, respectively, or donors of 2, $3/2$, $4/3$, and $5/4$ skeletal electrons per metal atom, respectively. The central phosphorus atoms in the $PMP'_3$, $PM_2P'_2$, $PM_3P'$, and $PM_4$ units in the structures of solid-state metal phosphides thus correspond to tertiary phosphines, $\mu_2$-dialkylphosphido groups, $\mu_3$-alkylphosphinidene groups, and $\mu_4$-phosphido groups, respectively, in molecular organophosphorus metal complexes.

The electronic configurations of edge-localized metal phosphides can be evaluated most readily by considering the environment around a single neutral metal atom. In this connection an $MP_{n/m}$ structural unit refers to a metal bonded to $n$ phosphorus atoms that are each shared with $m$ metal atoms. Structural units in which the central atom has the 18-electron-favored rare-gas configuration are favored in edge-localized metal phosphides just as in discrete molecular metal complexes and lead to diamagnetic semiconductors (e.g., $FeP_4$).[11] In other cases some direct metal–metal bonding in addition to metal–phosphorus bonding is required to give the central metal atom the favored 18-electron rare-gas configuration. If the metal–metal bonds are isolated, the metal phosphide remains a diamagnetic semiconductor (e.g., $MnP_4$).[12] However, if the metal–metal bonds form an infinite chain, the metal phosphide can exhibit metallic properties (e.g., $CrP_4$ and $VP_4$).[13] Globally delocalized transition-metal phosphides with high coordination numbers also generally exhibit metallic properties in accord with delocalization similar to that found in free metals. These ideas are fully equivalent to the models presented by Möller and Jeitschko[14] in which "optimal use is made of transition-metal d orbitals which are either fully occupied with

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nonbonding electrons or utilized for metal–phosphorus and metal–metal bonding".

## Binary Transition-Metal Polyphosphides

In most of the low-coordination-number metal phosphides discussed in this paper the central metal atoms are surrounded by six phosphorus atoms. If the metal and phosphorus atoms are all considered to be neutral, the aggregations of six phosphorus atoms donate totals of 10, 9, and 8 electrons to the central metal atoms in the $MP_4$, $MP_3$, and $MP_2$ structures, respectively, making $FeP_4$, $CoP_3$, and $NiP_2$ the derivatives having the favored 18-electron rare-gas configurations of the transition metals without supplemental metal–metal bonding. More detailed discussions on these systems are presented below.

**(A) $MP_4$.** The fundamental structural units in $MP_4$ derivatives are $MP_{4/2}P_2$ units in which half of the phosphorus atoms ($P_{4/2}$) are bonded to two metal atoms and two phosphorus atoms whereas the other half of the phosphorus atoms ($P_2$) are bonded to one metal atom and three phosphorus atoms, leading to infinite phosphorus subnetworks in the three-dimensional structure. The metal atoms in the iron compound $FeP_4$[15] as well as its ruthenium and osmium analogues[16,17] have the favored 18-electron rare-gas configuration as follows:

| | |
|---|---|
| neutral Fe atom | 8 electrons |
| 2 P atoms in $PMP'_3$ units: (2)(2) | 4 electrons |
| $^4/_2$ $\mu_2$-P atoms in $PM_2P'_2$ units: $(^4/_2)(3)$ | 6 electrons |
| total valence electrons for the Fe atom | 18 electrons |

The manganese, technetium, and rhenium compounds $MnP_4$,[12,16,18] $TcP_4$,[19] and $ReP_4$[20] require one metal–metal bond per $MP_{4/2}P_2$ octahedron to attain the favored 18-electron rare-gas configuration, leading to isolated M–M pairs (Mn–Mn = 2.94 Å in $MnP_4$ compared with 2.90 Å in $Mn_2(CO)_{10}$;[21] Tc–Tc = 3.00 Å in $TcP_4$[19] compared with 3.04 Å in $Tc_2(CO)_{10}$;[22] Re–Re = 3.01 Å in $ReP_4$[20] compared with 3.02 Å in $Re_2(CO)_{10}$[23]). The chromium, molybdenum, and tungsten compounds $CrP_4$,[24] $MoP_4$,[24] and $WP_4$[25] require two metal–metal bonds per $MP_{4/2}P_2$ octahedron to attain the favored 18-electron rare-gas configuration, leading to infinite chains of metal–metal bonds (Cr–Cr = 3.18 Å in $CrP_4$[24]). Similar infinite chains of metal–metal bonds are also found in $VP_4$[26] (V–V = 3.25 Å). The infinite chains of metal–metal bonds in $VP_4$, $CrP_4$, $MoP_4$, and $WP_4$ lead to metallic conductivity, as indicated by band-structure calculations,[13] whereas $MnP_4$, $TcP_4$, $ReP_4$, $FeP_4$, $RuP_4$, and $OsP_4$ without such infinite chains of metal–metal bonds are diamagnetic semiconductors.

**(B) $MP_3$.** The fundamental structural unit of $CoP_3$[27] with the skutterudite structure[28] is $CoP_{6/2}$ in which each phosphorus atom is bonded to two metal atoms and two phosphorus atoms, leading to a phosphorus subskeleton consisting of isolated $P_4$ rings.[27] The neutral cobalt atoms in $CoP_3$ receive $(^6/_2)(3) = 9$ electrons from the six $\mu_2$-P atoms, leading to the favored 18-electron rare-gas configuration without any direct Co–Co bonds. The compound $CoP_3$ is thus a diamagnetic semiconductor. The compounds $TcP_3$[29]

and $ReP_3$[29] have the less symmetrical $MPP_{2/2}P_{3/3}$ structural units with two metal–metal bonds for each such structural unit (e.g., Tc–Tc = 3.09 Å in $TcP_3$), leading to the favored 18-electron rare-gas configuration as follows:

| | |
|---|---|
| neutral Tc or Re atom | 7 electrons |
| 1 P atom in $PMP'_3$ unit: (1)(2) | 2 electrons |
| $^2/_2$ $\mu_2$-P atom in $PM_2P'_2$ units: $(^2/_2)(3)$ | 3 electrons |
| $^3/_3$ $\mu_3$-P atom in $PM_3P'$ units: $(^3/_3)(4)$ | 4 electrons |
| 2 M–M bonds | 2 electrons |
| total valence electrons for the Tc or Re atom | 18 electrons |

**(C) $MP_2$.** The fundamental structural units of most $MP_2$ derivatives are $MP_{6/3}$ units in which all of the phosphorus atoms ($P_{6/3}$) are bonded to three metal atoms and one phosphorus atom, leading to isolated $P_2$ units. Such structures correspond to the pyrite and marcasite structures, which have been treated in detail elsewhere.[30–33] The nickel derivative $NiP_2$ has the pyrite structure[34] in which the nickel atoms have the favored 18-electron rare-gas configuration without any direct Ni–Ni bonding. In addition, an alternative structure for $NiP_2$ and $PdP_2$ is possible based on $MP_{4/2}$ structural units in which the metal atoms have square-planar coordination and the phosphorus atoms are bonded to two metal atoms and two other phosphorus atoms, leading to zigzag chains of phosphorus atoms.[35] In this structure the metal atoms have the 16-electron configurations characteristic of square-planar complexes with an eight-orbital $sp^3d^4$ manifold.[36] The cobalt, rhodium, and iridium phosphides $MP_2$ (M = Co, Rh, Ir) have the arsenopyrite structure based on $MP_{6/3}$ structural units with one metal–metal bond from each $MP_{6/3}$ coordination sphere (Co–Co in $CoP_2$ = 2.67 Å)[26] corresponding to the 18-electron rare-gas configuration with isolated bonded metal pairs in the infinite lattice, namely short (bonding) and long (nonbonding) metal–metal distances alternating along a metal chain.[37] The iron, ruthenium, and osmium phosphides $MP_2$ (M = Fe, Ru, Os) have the marcasite structure,[38] in which each metal atom in an $MP_{6/3}$ structural unit is bonded to two other metal atoms (Fe–Fe = 2.72 Å in $FeP_2$; Ru–Ru = 2.87 Å in $RuP_2$; Os–Os = 2.92 Å in $OsP_2$), leading to the favored 18-electron rare-gas configuration.

**(D) $Re_2P_5$.** The structure of $Re_2P_5$ is very complicated, containing 10 different types of phosphorus atoms and 4 different types of rhenium atoms.[39] Each rhenium atom is bonded to six phosphorus atoms. Half of the rhenium atoms are directly bonded to two other rhenium atoms whereas the other half of the rhenium atoms are directly bonded to three other rhenium atoms, leading to isolated $Re_4$ rhomboidal ("butterfly") clusters of the following type:



**1**
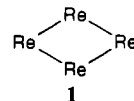
The average rhenium electronic configuration in $Re_2P_5$ can be shown to be the favored 18-electron rare-gas configuration as follows, labeling for clarity the rhenium atoms as they are labeled in the original paper:[39]

(a) Rhenium 1: $RePP_{2/2}P_{2/3}P_{1/4} = ReP_{35/12}$

| | |
|---|---|
| neutral Re atom | 7 electrons |
| 1 P atom in a $PMP'_3$ unit: (1)(2) | 2 electrons |
| $^2/_2$ P atoms in $PM_2P'_2$ units: $(^2/_2)(3)$ | 3 electrons |
| $^2/_3$ P atom in $PM_3P'$ units: $(^2/_3)(4)$ | $2^2/_3$ electrons |
| $^1/_4$ P atom in a $PM_4$ unit: $(^1/_4)(5)$ | $1^1/_4$ electrons |

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| 2 Re–Re bonds | 2 electrons |
|---|---|
| total valence electrons for rhenium 1 | $17^{11}/_{12}$ electrons |

(b) Rhenium 2: $RePP_{1/2}P_{2/3}P_{2/4} = ReP_{8/3}$

| | |
|---|---|
| neutral Re atom | 7 electrons |
| 1 P atom in a $PMP'_3$ unit: (1)(2) | 2 electrons |
| $^1/_2$ P atom in a $PM_2P'_2$ unit: $(^1/_2)(3)$ | $1^1/_2$ electrons |
| $^2/_3$ P atom in $PM_3P'$ units: $(^2/_3)(4)$ | $2^2/_3$ electrons |
| $^2/_4$ P atom in $PM_4$ units: $(^2/_4)(5)$ | $2^1/_2$ electrons |
| 3 Re–Re bonds | 3 electrons |
| total valence electrons for rhenium 2 | $18^2/_3$ electrons |

(c) Rhenium 3: $ReP_{2/2}P_{3/3}P_{1/4} = ReP_{9/4}$

| | |
|---|---|
| neutral Re atom | 7 electrons |
| $^2/_2$ P atom in $PM_2P'_2$ units: $(^2/_2)(3)$ | 3 electrons |
| $^3/_3$ P atom in $PM_3P'$ units: $(^3/_3)(4)$ | 4 electrons |
| $^1/_4$ P atom in a $PM_4$ unit: $(^1/_4)(5)$ | $1^1/_4$ electrons |
| 2 Re–Re bonds | 2 electrons |
| total valence electrons for rhenium 3 | $17^1/_4$ electrons |

(d) Rhenium 4: $ReP_{1/2}P_{5/3} = ReP_{13/6}$

| | |
|---|---|
| neutral Re atom | 7 electrons |
| $^1/_2$ P atom in a $PM_2P'_2$ unit: $(^1/_2)(3)$ | $1^1/_2$ electrons |
| $^5/_3$ P atoms in $PM_3P'$ units: $(^5/_3)(4)$ | $6^2/_3$ electrons |
| 3 Re–Re bonds | 3 electrons |
| total valence electrons for rhenium 4 | $18^1/_6$ electrons |

Average stoichiometry:

$$^1/_2(ReP_{35/12} + ReP_{8/3} + ReP_{9/4} + ReP_{13/6}) = Re_2P_5$$

Average rhenium valence electrons:

$$^1/_4(17^{11}/_{12} + 18^2/_3 + 17^1/_4 + 18^1/_6) = 18 \text{ electrons}$$

The closed-shell 18-electron rhenium configuration coupled with the absence of a connected infinite network of rhenium–rhenium bonds is consistent with the observed[39] diamagnetism and semiconductivity of $Re_2P_5$.

(E) $Re_6P_{13}$. The structure of $Re_6P_{13}$[40,41] is closely related to that of $Re_2P_5$ in that each rhenium atom is bonded to six phosphorus atoms and the rhenium atoms form isolated $Re_4$ rhomboidal units (1) in which half of the rhenium atoms are directly bonded to two other rhenium atoms and the other half of the rhenium atoms are directly bonded to three other rhenium atoms. There are five different types of phosphorus atoms and two different types of rhenium atoms in this structure, leading to the following electron-counting scheme:

(a) Rhenium 1: $ReP_{2/2}P_{1/3}P_{3/4} = ReP_{25/12}$

| | |
|---|---|
| neutral Re atom | 7 electrons |
| $^2/_2$ P atom in $PM_2P'_2$ units: $(^2/_2)(3)$ | 3 electrons |
| $^1/_3$ P atom in $PM_3P'$ units: $(^1/_3)(4)$ | $1^1/_3$ electrons |
| $^3/_4$ P atom in $PM_4$ units: $(^3/_4)(5)$ | $3^3/_4$ electrons |
| 3 Re–Re bonds | 3 electrons |
| total valence electrons for rhenium 1 | $18^1/_{12}$ electrons |

(b) Rhenium 2: $ReP_{2/2}P_{3/3}P_{1/4} = ReP_{9/4}$

| | |
|---|---|
| neutral Re atom | 7 electrons |
| $^2/_2$ P atom in $PM_2P'_2$ units: $(^2/_2)(3)$ | 3 electrons |
| $^3/_3$ P atom in $PM_3P'$ units: $(^3/_3)(4)$ | 4 electrons |
| $^1/_4$ P atom in a $PM_4$ unit: $(^1/_4)(5)$ | $1^1/_4$ electrons |
| 2 Re–Re bonds | 2 electrons |
| total valence electrons for rhenium 2 | $17^1/_4$ electrons |

Total stoichiometry:

$$3(ReP_{25/12} + ReP_{9/4}) = Re_6P_{13}$$

Average rhenium valence electrons:

$$^1/_2(18^1/_{12} + 17^1/_4) = 17^2/_3$$

The average deficiency of $^1/_3$ electron in the 18-electron closed-shell configuration for each rhenium atom corresponds to holes in the valence band in accord with the observed metallic behavior

of $Re_6P_{13}$. Thus, $Re_6P_{13}$ with edge-localized chemical bonding and holes in the valence band is an interesting porously delocalized system that might be predicted to exhibit superconductivity with $T_c$ in the range 5–15 K like the similarly porously delocalized Chevrel phases,[6,42] certain ternary metal borides such as $LnRh_4B_4$ (Ln = lanthanide),[7,43] and $LaRu_4P_{12}$[9] discussed below.

## Ternary Transition-Metal Phosphides

(A) $M'M_2P_{12}$ (M' = Ti, Nb, Mo, W; M = Mn, Fe). The $M'M_2P_{12}$ derivatives have stoichiometries corresponding to mixed-metal tetraphosphides $M'P_4 \cdot 2MP_4$. All of the phosphorus atoms are four-coordinate as in the case of the other low-coordination-number transition-metal polyphosphides. However, the early transition metals (M') are surrounded by eight phosphorus atoms in contrast to the manganese or iron atoms, which are surrounded by six phosphorus atoms as in their "simple" $MP_4$ (M = Fe, Mn) derivatives discussed above. The structures of the $M'M_2P_{12}$ derivatives can be dissected into $MPP_{5/2}$ and $M'P_2P_{6/2}$ structural units with twice as many $MPP_{5/2}$ units as $M'P_2P_{6/2}$ units, leading to the observed stoichiometry. The average transition-metal electronic configuration of $MoFe_2P_{12}$[44] and $WFe_2P_{12}$[44] can be shown as follows to be the favored 18-electron rare-gas configuration in accord with their observed diamagnetism:

(a) Iron: $FePP_{5/2} = FeP_{7/2}$

| | |
|---|---|
| neutral Fe atom | 8 electrons |
| 1 P atom in a $PMP'_3$ unit: (1)(2) | 2 electrons |
| $^5/_2$ P atoms in $PM_2P'_2$ units: $(^5/_2)(3)$ | $7^1/_2$ electrons |
| total iron valence electrons | $17^1/_2$ electrons |

(b) Molybdenum: $MoP_2P_{6/2} = MoP_5$ (similar for tungsten in $WFe_2P_{12}$)

| | |
|---|---|
| neutral Mo atom | 6 electrons |
| 2 P atoms in $PMP'_3$ units: (2)(2) | 4 electrons |
| $^6/_2$ P atoms in $P_2MP'_2$ units: $(^6/_2)(3)$ | 9 electrons |
| total molybdenum valence electrons | 19 electrons |

Average transition-metal valence electrons:

$$^1/_3[(2)(17^1/_2) + 19] = 18 \text{ electrons}$$

The molybdenum–manganese compound $MoMn_2P_{12}$[45] requires one Mn–Mn bond per $MnPP_{5/2}$ octahedron for the metal atoms to attain a similar favored average 18-electron rare-gas configuration, leading to isolated Mn–Mn pairs (Mn–Mn = 2.88 Å) in accord with its observed diamagnetism. The niobium–manganese compound $NbMn_2P_{12}$[45] also has bonded Mn–Mn pairs (Mn–Mn = 2.85 Å) but no Nb–Nb or Nb–Mn bonding so that the average metal electron configuration is $17^2/_3$, corresponding to one unpaired electron for each $NbMn_2P_{12}$ formula unit in accord with its observed paramagnetism of 1.96 $\mu_B$. A similar model can be used for $TiMn_2P_{12}$[45,46] with bonded Mn–Mn pairs (Mn–Mn = 2.83 Å), no Ti–Ti or Ti–Mn bonding, and 16-electron configurations for the titanium atoms leading to a diamagnetic species.

(B) $LnM_4P_{12}$. Ternary transition-metal phosphides of the type $LnM_4P_{12}$ (M = Fe, Ru, Os; Ln = lanthanide) are of particular interest because of their superconducting properties leading to $T_c$'s as high as 7.2 K for $LaRu_4P_{12}$.[9] The ruthenium–phosphorus subskeleton in $LaRu_4P_{12}$ has the skutterudite structure[47] similar to $CoP_3$ discussed above. The structural unit $RuP_{6/2}^-$ has the 18-electron closed-shell configuration like the $CoP_{6/2}$ structural unit in $CoP_3$. However, since a trivalent lanthanide can only contribute $^3/_4$ electron to each of four neutral $RuP_{6/2}$ units, the effective valence electron count of each ruthenium atom is $17^3/_4$. The deficiency of $^1/_4$ electron in the 18-electron closed-shell configuration of each ruthenium atom corresponds to holes in the valence band. Thus, $LaRu_4P_{12}$ is a porously delocalized system with a transition-metal electronic configuration similar to that

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of the ternary lanthanide rhodium boride superconductors[43] discussed in a previous paper.[7]

**(C) $Ln_6Ni_6P_{17}$.** An attempt to prepare nickel analogues of $LnM_4P_{12}$ (M = Fe, Ru, Os) led instead to products of the stoichiometry $Ln_6Ni_6P_{17}$.[48] This stoichiometry may be dissected into equal numbers of $NiP_{4/2}$ and $LnP_{2/3}P_{1/6}$ structural units by considering the nearest phosphorus neighbors of the nickel atom (P(1) in ref 48) and allocating the phosphorus atoms not within bonding distance of any nickel atom to a lanthanide atom. The phosphorus atoms of the $NiP_{4/2}$ units are bonded to one other phosphorus atom (P(2) in ref 48) but are donors of only two rather than four skeletal electrons since these phosphorus atoms are bonded to only two rather than three nickel atoms thereby being regarded as "pseudotricoordinate" excluding P–Ln bonds. Thus, in effect each phosphorus atom (P(1)) in the $NiP_{4/2}$ structural unit is using a lone pair to coordinate to the lanthanide atoms. The geometry of the nickel atom in a $NiP_{4/2}$ unit in $Ln_6Ni_6P_{17}$ is intermediate between tetrahedral with a favored 18-electron configuration and square planar with a favored 16-electron configuration. Since the lanthanides are tripositive, the actual Ni–P structural unit is $NiP_{4/2}{}^{3-}$ with an intermediate 17-electron configuration as follows:

| neutral Ni atom | 10 electrons |
|---|---|
| $^4/_2$ P atoms in $PNi_2P'$ units: $(^4/_2)(2)$ | 4 electrons |
| –3 charge | 3 electrons |
| total valence electrons for the nickel atom | 17 electrons |

**Summary**

This paper shows how edge-localized models suffice to account for the chemical bonding in low-coordination-number binary transition-metal polyphosphides of the stoichiometries $MP_4$, $MP_3$, and $MP_2$ as well as the more complicated rhenium derivatives $Re_2P_5$ and $Re_6P_{13}$. Such models explain the occurrence of direct metal-metal bonding in species such as $MP_4$ (M = Mn, Re, Cr, V), $MP_3$ (M = Tc, Re), and $MP_2$ (M = Co, Rh, Ir, Fe, Ru, Os) and provide simple rationalizations of their electrical properties (i.e., semiconducting versus metallic). Similar edge-localized models can be applied to ternary model polyphosphides such as $M'M_2P_{12}$ (M' = Ti, Nb, Mo, W; M = Mn, Fe) and $Ln_6Ni_6P_{17}$ (Ln = lanthanide). Application of such models to the ternary phosphide superconductors $LnM_4P_{12}$ (Ln = lanthanide; M = Fe, Ru, Os) suggests porous delocalization similar to that found in ternary metal boride superconductors such as $LnRh_4B_4$.

(48) Braun, D. J.; Jeitschko, W. *Acta Crystallogr. B* **1978,** *B34,* 2069.

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# Calculation of the Theoretical Magnetic Susceptibility of the Four $S = {}^5/_2$ Spin System. Application to Tetranuclear Manganese(II) Complexes

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The calculation of the theoretical magnetic susceptibility of the four $S = {}^5/_2$ spin system has been carried out by exact diagonalization of the effective spin Hamiltonian in the 1296 uncoupled spin states basis set. The temperature-dependent magnetic susceptibility data of more than 60 hypothetical tetranuclear manganese(II) complexes, presented as $\chi T$ vs $T$ plots, have been calculated for the first time, by varying the $J$, $D$, and $g$ parameters within reasonable limits: $-2.5 \leq J_i \leq 0.25$ cm$^{-1}$; $-0.5 \leq D \leq 0.5$ cm$^{-1}$; $1.9 < g_i < 2.1$. Systematic variations of these parameters have shown that, within these limits, the effect of the variation of $D$ is negligible except at low temperature, when the $J$ values are very small. The effect of the variation of the $g$ parameters is observable down to 10–20 K, although more pronounced in the high-temperature range. As expected, the variation of the magnetic susceptibility is strongly affected by the variation of the $J$ parameters. On the basis of these results the experimental magnetic susceptibility data of a tetranuclear manganese(II) complex, $(C_{12}H_{14}N_3OMn^{II})_4(ClO_4)_4\cdot2H_2O$, have been least-squares fitted with assumed $S_4$ or $T_d$ symmetry, isotropic $g$, and $D = 0$ cm$^{-1}$, yielding $J_A = J_B = J = -0.51$ cm$^{-1}$ and $g = 1.954$. The results obtained indicate that in the present case a small distortion from the $T_d$ to the $S_4$ symmetry does not induce measurable differences between the two sets of exchange integrals.

**Introduction**

The calculation of the theoretical magnetic susceptibility, $\chi$, of a compound in a magnetic field, $H$

$$\chi = -\frac{N}{H}\left(\sum_i \frac{\partial E_i}{\partial H} e^{-E_i/kT}\right) \Big/ \left(\sum_i e^{-E_i/kT}\right) \qquad (1)$$

implies the determination of all energy levels, $E_i$, of this compound. The most common approaches are approximated methods that deal with magnetic susceptibility at zero magnetic field.[1] In this respect, the Van Vleck method[2] is the most commonly used for fitting experimental temperature-dependent magnetic susceptibility data.

A more rigorous method based on the exact diagonalization of the effective spin Hamiltonian has been used in a few examples.[3] In that case, the results remain valid even when the zero-field splitting and exchange parameters have the same order of magnitude. However, when the number, $N$, of interacting magnetic centers and/or when the value of the spin, $S_i$, increases, the dimension of the problem

$$\prod_{i=1}^{N}(2S_i + 1)$$

becomes extremely large, resulting in lengthy calculations that are not always justified.

Recent progress in the knowledge of the water oxidation site of photosystem 2 brings a new justification for work in this di-

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