

Calculations and Analysis of the Electronic Structures of Transition-Metal Phosphosilicides Cu_4SiP_8 , IrSi_3P_3 , CoSi_3P_3 , and FeSi_4P_4

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Electronic structures of phosphosilicides Cu_4SiP_8 , IrSi_3P_3 , CoSi_3P_3 , and FeSi_4P_4 were calculated using the extended Hückel tight-binding method and were analyzed in terms of a modified electron counting scheme. The d -block levels of these compounds appear well below the Fermi level, thereby indicating that the transition-metal atoms exist as d^{10} ions. Except for the case of IrSi_3P_3 , the d -block energy levels of these compounds occur in a narrow energy window less than 1.5 eV wide. The Si $3p$ orbitals act as acceptor orbitals to the transition-metal d orbitals in IrSi_3P_3 , CoSi_3P_3 , and FeSi_4P_4 . © 1999 Academic Press

1. INTRODUCTION

An important role of electron counting schemes in chemistry is to provide insight into the nature of the frontier orbitals (i.e., the highest occupied and lowest unoccupied levels) of a compound under consideration and hence into its physical properties and chemical reactivity. In the covalent electron counting scheme for compounds of main group elements, each atom is assumed to achieve the inert gas electron configuration in the sense of covalent bonding (1, 2). Thus, the valence electrons of an even-electron compound are grouped into bond pairs and lone pairs, thereby providing an approximate ordering of its molecular energy levels (e.g., lone-pair levels are higher lying than bond-pair levels). The covalent electron counting scheme assumes that lone-pair electrons of an atom are not shared with other atoms, while two electrons of each bond pair are equally shared between the two atoms making up the bond. This leads to the concept of formal charge of an atom. For compounds of early transition-metal atoms with electronegative ligands, the ionic electron counting scheme is

invaluable. In this scheme, electronegative ligand atoms are assumed to adopt the inert gas electron configuration in the sense of ionic bonding, and the remaining valence electrons are given to transition-metal atoms. This gives rise to their oxidation states and a clue to the nature of their frontier orbitals. For compounds of late transition-metal atoms with weakly electronegative ligands, the ionic electron counting scheme is not valid because its basic assumption is not justified, and the need to have an alternative electron counting scheme has been recognized (3–7).

Both covalent and ionic components are present in certain classes of compounds so that the description of their electronic structures requires a combined use of the ionic and covalent electron counting schemes, as exemplified by the Zinti–Klemm concept (4b, 8–10). For instance, the oxidation state of LiAl is written as Li^+Al^- by considering a complete electron transfer, and then the occurrence of four Al–Al bonds around each Al is explained in terms of four valence electrons of Al^- based on the concept of covalent bonding. Another combined ionic/covalent electron counting scheme is widely used in describing transition-metal complexes. For example, for a bond between a transition metal M and a functional group CH_3 , the ionic description is applied to the M – C bond with the electron pair of this bond counted as a lone pair belonging to the C atom, but the electron counting for the rest of the CH_3 group is carried out in terms of the covalent electron counting scheme. For the convenience of our discussion, such a combined ionic/covalent electron counting scheme will be referred to as the conventional electron counting scheme.

As first noted in the study of $\text{Cs}_2\text{Au}_2\text{I}_6$ (3), the conventional electron counting scheme leads to an incorrect picture concerning the frontier orbitals of transition-metal

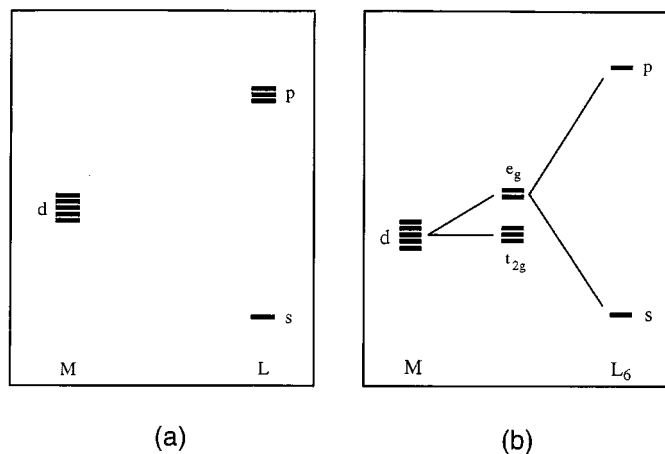


FIG. 1. (a) Relative energy ordering between the d orbital of a transition metal M and the valence s and p orbitals of its ligand atoms L for which the conventional electron counting scheme is not valid. (b) t_{2g} - e_g energy separation expected for a transition metal octahedral complex ML_6 when its relative orbital ordering is given by (a).

compounds for which the ligand atom p orbitals lie considerably higher than the transition-metal d orbital (e.g., Fig. 1a). To correct this problem, we recently proposed a modified electron counting scheme (7): the conventional electron counting scheme is used first to identify the lone-pair levels of the ligand atoms and the occupancy of the transition-metal d -block levels, and then electron transfer is invoked from the highest lying lone-pair levels to all the empty d -block levels. The modified electron counting scheme predicts that the frontier orbitals of such compounds are the highest-lying lone-pair levels of the main group ligand atoms, and the transition-metal atoms have a d^{10} electron count (3, 7). When the transition-metal d orbitals lie between the s and p orbitals of the ligands L in an octahedral complete ML_6 (Fig. 1a), the e_g -block levels are raised by the ligand s orbitals but lowered by the ligand p orbitals (Fig. 1b) (7). As a result of the two opposing effects, the e_g -block levels lie close to the t_{2g} -block levels. Thus, the d -block levels for these compounds should occur in a narrow region of energy (7). These predictions were confirmed by electronic band structure calculations for the phosphosilicides $PtSi_3P_2$ and $NiSi_2P_3$ (7). In the present work, we examine the electronic band structures of the phosphosilicides Cu_4SiP_8 (4b), $IrSi_3P_3$ (11), $CoSi_3P_3$ (12), and $FeSi_4P_4$ (13) by carrying out extended Hückel tight binding (EHTB) calculations (14, 15). Results of our calculations are analyzed from the viewpoint of the modified electron counting scheme.

2. CALCULATIONS

The atomic parameters employed in our calculations (Table 1) were taken and adjusted from results of the first principles calculations on atoms (16, 17). Compared with

their typical values used in the literature, the H_{ii} values for the nd , $(n+1)s$ and $(n+1)p$ orbitals of the transition-metal atoms listed in Table 1 were raised by about 1.5–1.9 eV. This adjustment was made by analyzing the orbital compositions of the d -block levels of the model compounds $[Fe(PH_3)_3(SiH_3)_3]^-$ and $[Co(PH_3)_4]^+$ obtained from our EHTB and density functional theory calculations. EHTB calculations using the atomic parameters in Table 1 give results similar to those obtained from density functional theory calculations (unpublished). As will be discussed below, our EHTB calculations show that the d -block levels of the transition-metal phosphosilicides appear well below the Fermi level. To examine the parameter-dependence of this finding, we carried out EHTB calculations by gradually lowering the H_{ii} values of the nd , $(n+1)s$ and $(n+1)p$ orbitals for the transition-metal atoms to find that the corresponding d -block levels are further lowered from the Fermi level. Thus, the main conclusion of our study, i.e., the d -block levels of the transition-metal phosphosilicides lie well below the Fermi level, remains unaffected by any reasonable variation of the atomic orbital parameters.

3. ANALYSIS OF ELECTRONIC BAND STRUCTURES

a. Cu_4SiP_8

This compound (4b) has two nonequivalent P atoms so that its formula is written as $Cu_4SiP(1)_4P(2)_4$. As depicted in

TABLE 1
Exponents ζ_i and Valence Shell Ionization Potentials H_{ii} of Slater-Type Orbitals χ_i Used for Extended Hückel Tight-Binding Calculation^a

Atom	χ_i	H_{ii} (eV)	ζ_i	c_1^b	ζ_i'	c_2^b
Fe	4s	-7.17	1.925	1.0		
Fe	4p	-3.39	1.390	1.0		
Fe	3d	-10.7	6.068	0.4038	2.618	0.7198
Co	4s	-7.71	2.000	1.0		
Co	4p	-3.79	1.430	1.0		
Co	3d	-11.7	6.386	0.4133	2.745	0.7126
Ir	6s	-9.86	2.457	1.0		
Ir	6p	-3.00	1.810	1.0		
Ir	5d	-10.7	4.680	0.6195	2.490	0.5384
Cu	4s	-9.90	2.200	1.0		
Cu	4p	-4.56	2.200	1.0		
Cu	3d	-12.5	5.950	0.5933	2.300	0.5744
P	3s	-18.9	1.881	1.0		
P	3p	-13.2	1.629	1.0		
Si	3s	-14.7	1.634	1.0		
Si	3p	-8.08	1.428	1.0		

^a H_{ii} 's are the diagonal matrix element $\langle \chi_i | H^{eff} | \chi_i \rangle$, where H^{eff} is the effective Hamiltonian. In our calculations of the off-diagonal matrix elements $H_{ij} = \langle \chi_i | H^{eff} | \chi_j \rangle$, the weighted formula was used. See J. Ammeter, H.-B. Bürgi, J. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.* **100**, 3686 (1978).

^bContraction coefficients used in the double-zeta Slater-type orbital.

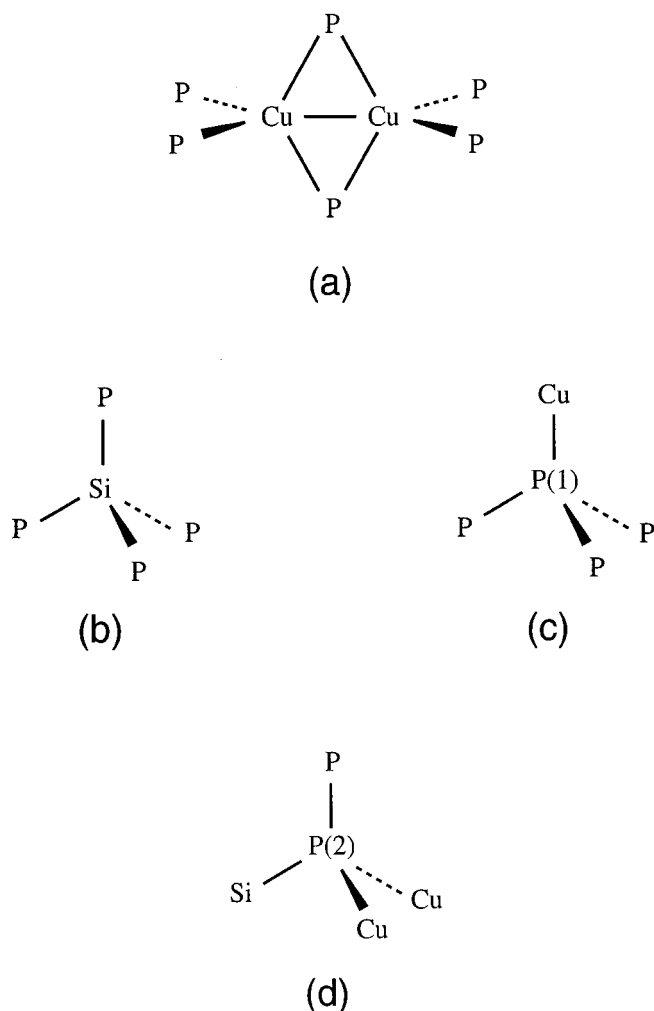


FIG. 2. Coordinate environments of the atoms in Cu_4SiP_8 .

Fig. 2, the Cu atoms are present as Cu–Cu dimer units. The Si, P(1), and P(2) atoms are bonded to four, three, and two main group atoms, respectively, so that their formal charges are 0, 0, and -1 , respectively. Thus, the charge balance of Cu_4SiP_8 is given by $(\text{Cu}^+)_4(\text{Si}^0)(\text{P}^0)_4(\text{P}^-)_4$, and the Si, P(1), and P(2) atoms possess zero, one, and two lone pairs, respectively, according to the conventional electron counting scheme. Kaiser and Jeitschko (4b) described the charge balance of this compound as $(\text{Cu}^+)_4(\text{Si}^{4+})(\text{P}^0)_4(\text{P}^{2-})_4$. The implication of the latter concerning the electron counting will be discussed later (see Section 5).

Given Cu^+ (d^{10}), all the d -block levels of Cu_4SiP_8 should be filled. The unfilled levels of Cu_4SiP_8 are the antibonding levels of the bonds between the main group atoms as well as the $4s$ and $4p$ levels of Cu. Thus, Cu_4SiP_8 should have a band gap. These expectations are borne out in our electronic band structure calculations for Cu_4SiP_8 , results of which are summarized in Fig. 3. The projected

density of states (PDOS) for the Cu $3d$ orbital lies well below the Fermi level, the top portion of the occupied bands are largely represented by the $3p$ orbitals of the P(1) and P(2) atoms, and there is a substantial band gap.

b. IrSi_3P_3

In this compound (11), each Ir is located at an octahedral site made up of four P and two Si atoms (Fig. 4a). The Si and P atoms are each bonded to three main group atoms (i.e., one Si and two P atoms), and hence their formal charges are -1 and 0 , respectively (Figs. 4b and 4c). Thus, the charge balance of IrSi_3P_3 is given by $(\text{Ir}^{3+})(\text{Si}^-)_3(\text{P}^0)_3$, and the Si and P atoms each carry one lone pair according to the conventional electron counting scheme. This implies that each Ir^{3+} (d^6) ion is surrounded by four P lone pairs and two Si lone pairs, and two of the five d -block levels of Ir^{3+} are empty. However, the $5d$ level of Ir lies lower than the $3p$ level of Si (17). Thus, according to the modified electron counting scheme, four electrons of the two Si lone pairs should be transferred to the two empty d -block levels of Ir^{3+} to produce Ir^- (d^{10}). This should lead to a band gap in IrSi_3P_3 , because the Si lone pair level should lie higher in energy than the P lone pairs. These expectations are consistent with results of our electronic band structure calculations for IrSi_3P_3 , which are summarized in Fig. 5. RhSi_3P_3 is isostructural and isoelectronic with IrSi_3P_3 (11), so that the electronic structure of RhSi_3P_3 is similar to that of IrSi_3P_3 (not shown).

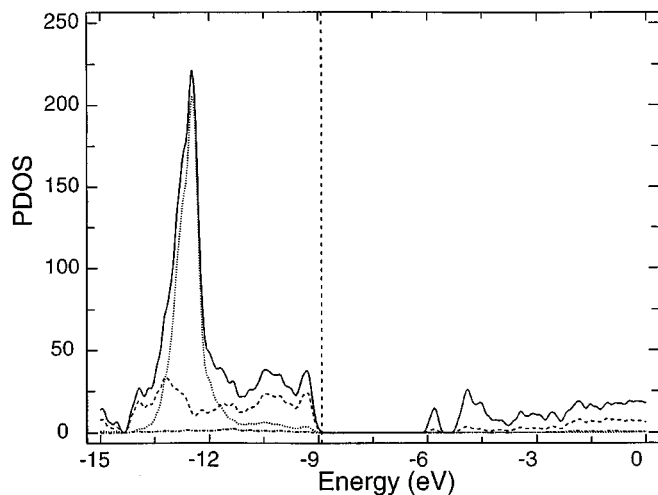


FIG. 3. PDOS plots calculated for Cu_4SiP_8 . The unit of PDOS is electrons per unit cell, $(\text{Cu}_4\text{SiP}_8)_4$. The legends are as follows: the solid line for the total density of states (TDOS), the dotted line for the PDOS of the Cu $3d$ orbitals, the dashed line for the PDOS of the P $3p$ orbitals, and the dash-dot line for the PDOS of the Si $3p$ orbitals. The dashed vertical line refers to the highest occupied energy level.

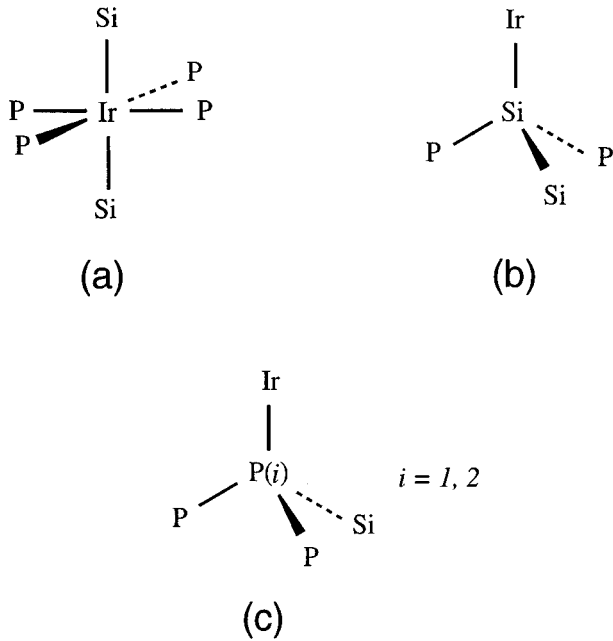


FIG. 4. Coordinate environments of the atoms in IrSi_3P_3 .

c. CoSi_3P_3

In this compound (12), a unit cell has two formula units, i.e., $(\text{CoSi}_3\text{P}_3)_2$, and all atoms of a unit cell are unique. Each Co atom is located at an octahedral site made up of three P and three Si atoms, where the three Si atoms form a triangular face of the octahedral site (Fig. 6a). The Si(1), Si(2), Si(4), and Si(6) atoms are each bonded to three P atoms, so their formal charge is -1 (Fig. 6b). The Si(3) and Si(5) atoms are bonded to two and four main group atoms, respectively, so that their formal charges are -2 and 0 , respectively (Figs. 6c–6d). The P(1), P(3), P(4), and P(5) atoms are each bonded to three main group atoms, so their formal charge is 0 (Fig. 6e). The P(2) and P(6) atoms are bonded to four and two main group atoms, respectively, so their formal charges are $+1$ and -1 , respectively (Figs. 6f–6g). Thus, the charge balance for $(\text{CoSi}_3\text{P}_3)_2$ is written as $(\text{Co}^{3+})_2(\text{Si}^-)_4(\text{Si}^0)(\text{Si}^2)(\text{P}^0)_4(\text{P}^+)(\text{P}^-)$, according to the conventional electron counting scheme.

There is no lone pair on Si(5) and P(2). The Si(3) and P(6) each have two lone pairs, and the remaining Si and P atoms each have one lone pair. Each Co(1) atom is surrounded by Si(3), Si(3), Si(6), P(1), P(4), and P(5), and each Co(2) atom is surrounded by Si(1), Si(2), Si(4), P(3), P(3), and P(6). Each Si(3) is coordinated to two Co(1) atoms, and each P(6) atom to two Co(2) atoms. Thus, each Co^{3+} (d^6) is surrounded by six lone pairs (three from three Si atoms, and three from three P atoms), according to the conventional electron counting scheme.

Since the Co $3d$ level lies lower than the Si $3p$ level (16), four electrons from the three Si lone pairs surrounding each

Co^{3+} should be transferred to its two empty d -block levels, thereby leading to Co^- (d^{10}), according to the modified electron counting scheme. Consequently, the three Si lone-pair levels become incompletely filled. Thus, one might expect the occurrence of a partially filled band, because the three Si lone pairs are degenerate to a first approximation according to the bond orbital picture (18). However, as shown in Fig. 7, the electronic band structure of CoSi_3P_3 shows a substantial band gap. This is so because the three σ -type Si lone pairs in the Si triangle arrangement (Fig. 6a) interact to give the one-below-two energy split pattern (19), as depicted in Fig. 8a.

d. FeSi_4P_4

In this compound (13), all atoms of a unit cell are unique. Each Fe is located at an octahedral site made up of three P and three Si atoms as depicted in Fig. 9a, when three Si atoms form a triangular face of the octahedral site. The Si(1) atom is bonded to four main group atoms (Fig. 9b), so its formal charge is 0 . The Si(2), Si(3), and Si(4) atoms are each bonded to two main group atoms (Fig. 9c), so their formal charge is -2 . The P(1), P(2), and P(4) atoms are each bonded to two main group atoms (Fig. 9d), so their formal charge is -1 . The P(3) atom is bonded to four atoms (Fig. 9e), so its formal charge is $+1$. Consequently, the charge balance of FeSi_4P_4 is given by $(\text{Fe}^{8+})(\text{Si}^{2-})_3(\text{Si}^0)(\text{P}^{2-})_3(\text{P}^+)$, according to the conventional electron counting scheme. No lone pair is present on Si(1) and P(3), but the remaining Si and P atoms each have two lone pairs. Each Fe atom is

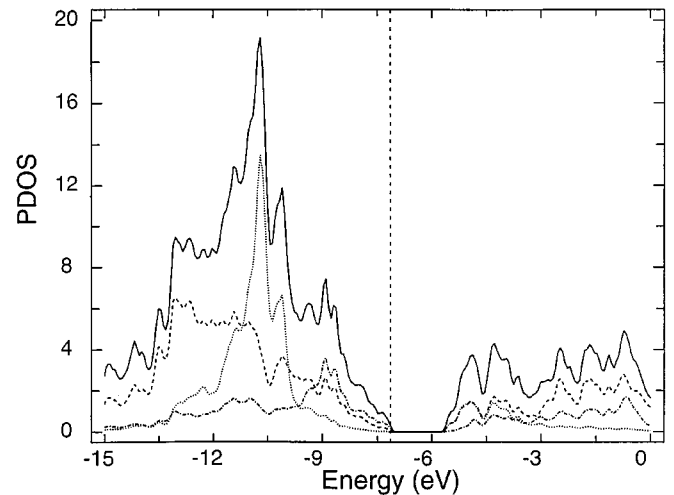


FIG. 5. TDOS and PDOS plots calculated for IrSi_3P_3 . The unit of PDOS is electrons per unit cell, $(\text{IrSi}_3\text{P}_3)_2$. The legends are as follows: the solid line for the TDOS, the dotted line for the PDOS of the Ir $5d$ orbitals, the dashed line for the PDOS of the P $3p$ orbitals, and the dash-dot line for the PDOS of the Si $3p$ orbitals. The dashed vertical line refers to the highest occupied energy level.

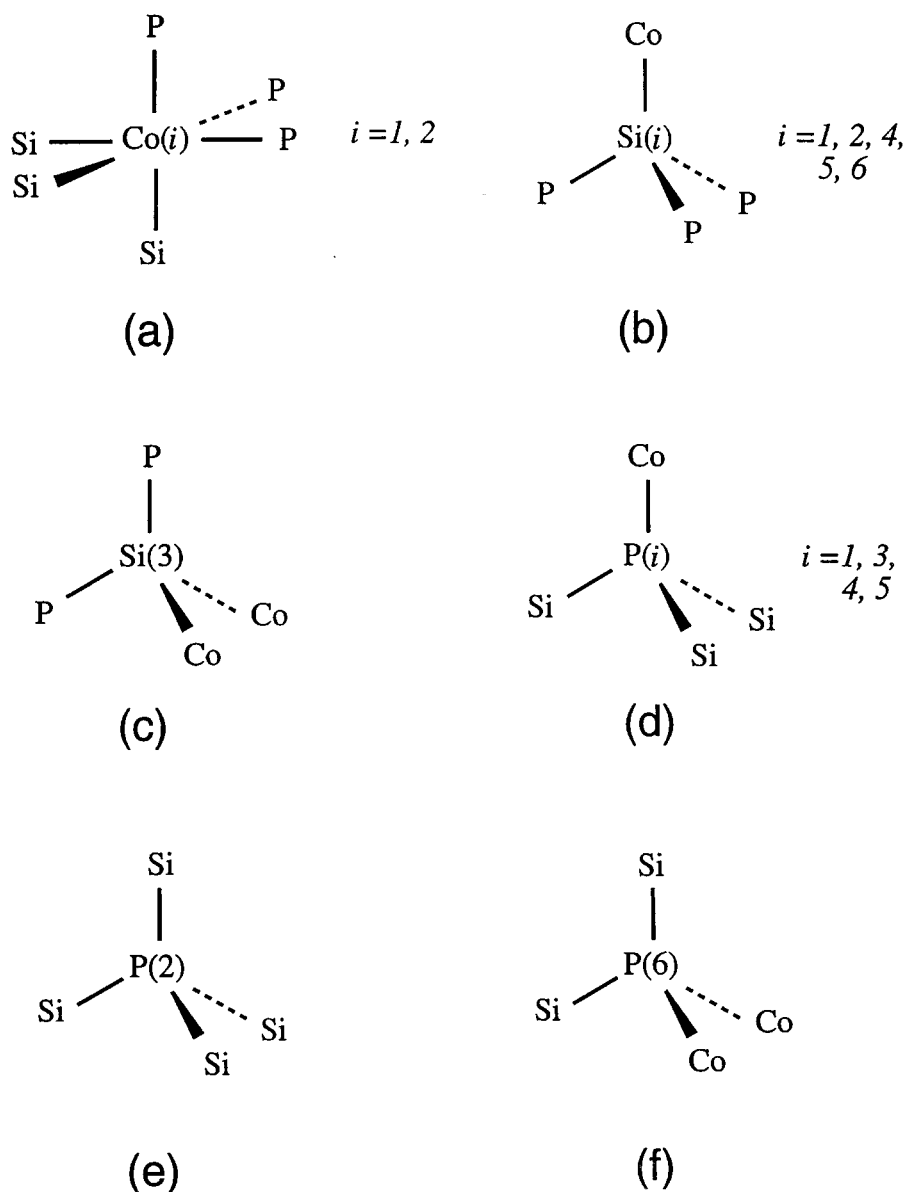


FIG. 6. Coordinate environments of the atoms in CoSi_3P_3 .

surrounded by Si(2), Si(3), Si(4), P(1), P(2), and P(4), so that each Fe^{8+} (d^0) is surrounded by 12 lone pairs.

Since the $3d$ level of Fe lies lower than the Si $3p$ level (16, 17), 10 electrons from the six Si lone pairs surrounding each Fe^{8+} should be transferred to its five empty d -block levels, thereby leading to Fe^{2-} (d^{10}) and making the six Si lone-pair levels incompletely filled, according to the modified electron counting scheme. The latter might suggest the occurrence of a partially filled band from the viewpoint of the bond orbital picture (18). However, as summarized in Fig. 10, the electronic band structure of FeSi_4P_4 shows a substantial band gap. This is explained as follows: Two

sp^3 -type lone-pair orbitals on each Si^- site combine to give rise to one σ -type and one π -type lone-pair orbitals (18), as depicted in Fig. 8b. The π -type lone-pair level is higher in energy than the σ -type lone-pair level. Thus, the interactions among the three π -type lone pairs in the Si triangle arrangement lead to three high-lying levels (19). The interactions among the three σ -type lone pairs in the Si triangle arrangement lead to the one-below-two energy split (Fig. 8a). Namely, there is an energy gap between the lowest-lying and the remaining five lone-pair levels of three Si atoms. Thus, when 10 electrons are removed from the six occupied Si lone-pair levels, there occurs a band gap. RuSi_4P_4 and

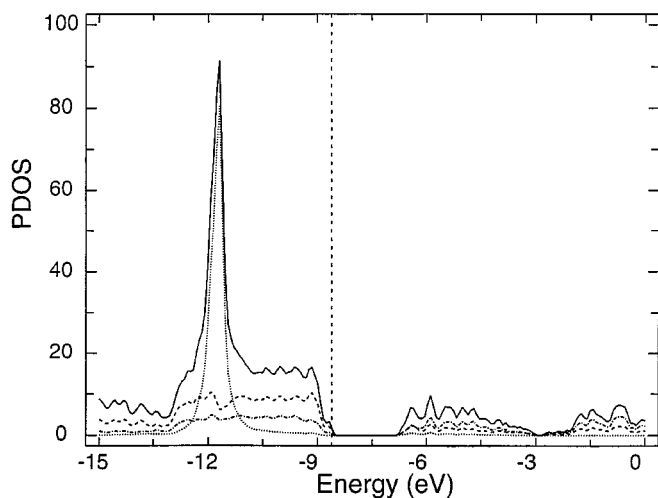


FIG. 7. TDOS and PDOS plots calculated for CoSi_3P_3 . The unit of PDOS is electrons per unit cell, $(\text{CoSi}_3\text{P}_3)_4$. The legends are as follows: the solid line for the TDOS, the dotted line for the PDOS of the Co $3d$ orbitals, the dashed line for the PDOS of the P $3p$ orbitals, and the dash-dot line for the PDOS of the Si p orbitals. The dashed vertical line refers to the highest occupied energy level.

OsSi_4P_4 are isostructural and isoelectronic with FeSi_4P_4 , so that the electronic structures of RuSi_4P_4 and OsSi_4P_4 are similar to that of FeSi_4P_4 (not shown).

4. DISCUSSION

As already pointed out, Kaiser and Jeitschko described the charge balance of Cu_4SiP_8 as $(\text{Cu}^+)_4(\text{Si}^{4+})(\text{P}^0)_4(\text{P}^{2-})_4$. This implies that each Si-P(2) bond is ionic, and the electron pair of this bond is counted as lone pair belonging to P(2). The Si and P atoms are adjacent elements in the Periodic Table, so the difference in their electronegativities (1.8 vs 2.1) is not large (2). Therefore, it is necessary to regard each Si-P bond as polar covalent rather than ionic and thus to write the charge balance of Cu_4SiP_8 as $(\text{Cu}^+)_4(\text{Si}^0)(\text{P}^0)_4(\text{P}^-)_4$. In addition, this picture shows that all the d -block levels and all the bond and lone pairs of the main group atoms are filled, so that Cu_4SiP_8 is predicted to have a band gap. To arrive at the same prediction using the $(\text{Cu}^+)_4(\text{Si}^{4+})(\text{P}^0)_4(\text{P}^{2-})_4$ picture, it is necessary to consider for each S-P(2) bond that the empty lone-pair orbital (i.e., the sp^3 hybrid orbital) of Si^{4+} interacts strongly with the filled lone-pair orbital (i.e., the filled sp^3 hybrid orbital) of P^{2-} to produce a σ bonding and a σ^* antibonding level, with the σ bonding level occupied by two electrons. In essence, this amounts to the $(\text{Cu}^+)_4(\text{Si}^0)(\text{P}^0)_4(\text{P}^-)_4$ picture.

In the phosphosilicide Cu_4SiP_8 (4b), the Si atoms do not carry lone pairs, and each transition metal is found at tetrahedral sites made up of four P atoms. The d -block levels of this compound occur well below the Fermi level as

a peak of width less than 1.5 eV. The occurrence of a narrow d -block peak is not surprising because d -block levels are weakly split at tetrahedral sites. Our earlier work (7) showed that the above discussion also applies to the phosphosilicide NiSi_2P_3 (20).

In the phosphosilicides IrSi_3P_3 , CoSi_3P_3 , FeSi_4P_4 , and PtSi_3P_2 (21), the transition-metal atoms are located at octahedral sites made up of Si and P atoms i.e., two Si and four P atoms in IrSi_3P_3 , three Si and three P atoms in CoSi_3P_3 and FeSi_4P_4 , and four Si and two P atoms in PtSi_3P_2 . Our electronic structure calculations for CoSi_3P_3 , FeSi_4P_4 , and PtSi_3P_2 (7) show that the d -block levels appear well below the Fermi level within an energy window less than 1.5 eV wide. From the viewpoint of the coordination chemistry of a transition-metal atom with σ -donor ligands as discussed in the conventional electron counting scheme, this is surprising. However, the Si $3p$ orbitals surrounding the transition-metal atoms in CoSi_3P_3 , FeSi_4P_4 , and PtSi_3P_2 lie higher in energy than the transition-metal d levels and

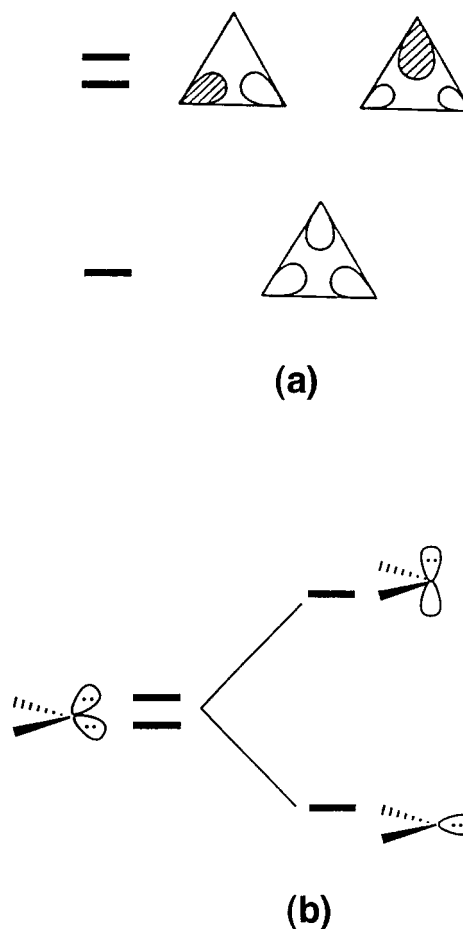


FIG. 8. (a) One-below-two energy split pattern expected for the interaction of three sp^3 -type lone-pair orbitals in a triangular arrangement. (b) Formation of σ - and π -type lone-pair orbitals from two sp^3 -type lone-pair orbitals.

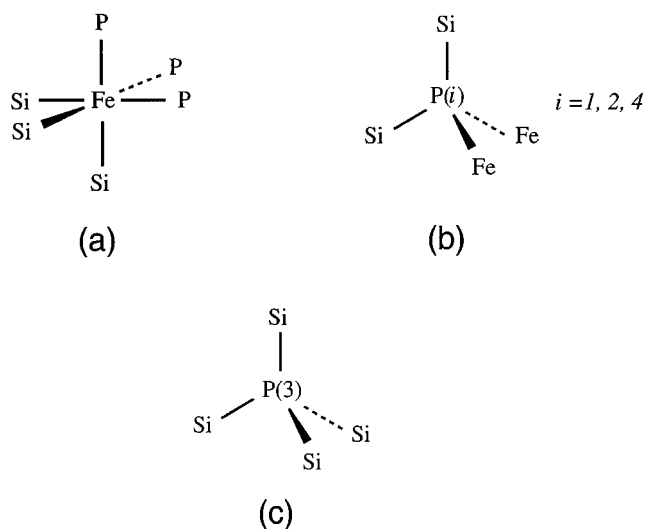


FIG. 9. Coordinate environments of the atoms in FeSi_4P_4 .

hence act as acceptor levels to the transition-metal d orbitals. Consequently, the d -block levels of these compounds are low in energy and occur in a narrow energy region. In contrast, the d -block levels of IrSi_3P_3 , though present well below the Fermi level, are somewhat spread in a wider energy window (Fig. 5). This is accounted for as follows: Each octahedral site of IrSi_3P_3 has two Si atoms (Fig. 4a), while that of CoSi_3P_3 , FeSi_4P_4 , and PtSi_3P_2 has more Si atoms. Thus, the acceptor effect of the Si $3p$ orbitals is weaker in IrSi_3P_3 .

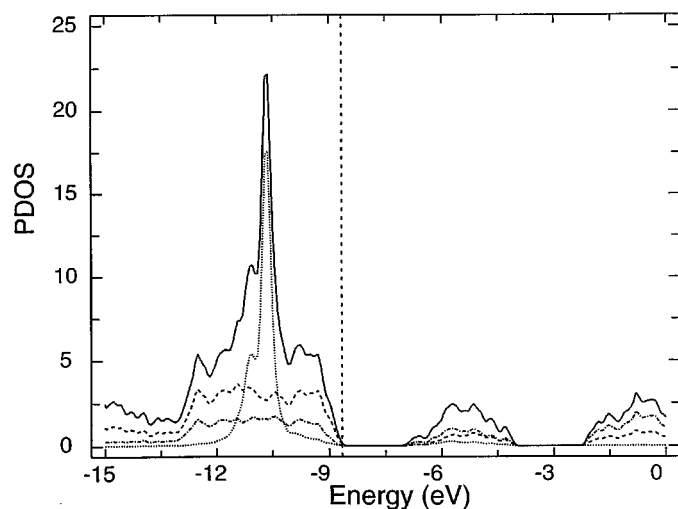


FIG. 10. TDOS and PDOS plots calculated for FeSi_4P_4 . The unit of PDOS is electrons per unit cell, FeSi_4P_4 . The legends are as follows: the solid line for the TDOS, the dotted line for the PDOS of the Fe $3d$ orbitals, the dashed line for the PDOS of the P $3p$ orbitals, and the dash-dot line for the PDOS of the Si $3p$ orbitals. The dashed vertical line refers to the highest occupied energy level.

Vincent *et al.* (12) reported that CoSi_3P_3 is a small band gap semiconductor ($E_g = 0.12$ eV) around room temperature, is diamagnetic around room temperature, and becomes paramagnetic below 65 K. In sharp contrast, our electronic band structure calculations show that CoSi_3P_3 is a large band gap semiconductor ($E_g = 2$ eV). This discrepancy can be easily explained if this compound is slightly nonstoichiometric such that its true composition is given by $\text{CoSi}_{3+x}\text{P}_{3-x}$ or $\text{CoSi}_{3-x}\text{P}_{3+x}$. The excess of Si in $\text{CoSi}_{3+x}\text{P}_{3-x}$ will create acceptor levels close to the top of the valence bands, while the excess of P in $\text{CoSi}_{3-x}\text{P}_{3+x}$ will create donor levels close to the bottom of the conduction bands (22). Then, the activation energies determined from electrical resistivity measurements on such “doped” samples are very small and do not represent the intrinsic band gap of a stoichiometric CoSi_3P_3 sample.

5. CONCLUDING REMARKS

In the electronic structures of the phosphosilicides examined by us (i.e., IrSi_3P_3 , CoSi_3P_3 , FeSi_4P_4 , PtSi_3P_2 , and NiSi_2P_3), the transition-metal atoms have their d -block levels well below the Fermi level and hence can be regarded to exist as “ d^{10} ions.” Except for the case of IrSi_3P_3 , these d -block levels occur in a narrow energy window less than 1.5 eV wide. It should be possible to verify these striking predictions experimentally by using spectroscopic methods e.g., X-ray photoelectron spectroscopy, Mössbauer spectroscopy, and NMR spectroscopy. Essential features of our EHTB electronic band structure calculations are readily explained in terms of the modified electron counting scheme. The d -block levels of CoSi_3P_3 , FeSi_4P_4 , and PtSi_3P_2 exhibit no discernible “ t_{2g} ”–“ e_g ” energy separation, although their transition-metal atoms are located at octahedral sites. This observation arises from the fact that the $3p$ orbitals of the Si atoms surrounding the transition-metal atoms acts as acceptor orbitals to the transition-metal d orbitals. The modified electron counting scheme is useful in analyzing the electronic structures of other late transition-metal compounds containing weakly electronegative ligands (23).

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