

Electron Counting Scheme Relevant for Late Transition Metal Compounds with Weakly Electronegative Ligands. Electronic Band Structure Study of Phosphosilicides PtSi₃P₂ and NiSi₂P₃[†]

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The conventional electron counting scheme often leads to erroneous predictions for late transition metal compounds with weakly electronegative main group ligand atoms. The cause for this deficiency was analyzed, and a modified electron counting scheme was proposed for predicting the frontier orbitals of such compounds. The modified scheme predicts that the transition metal atoms of such compounds have a d^{10} electron count, and their frontier orbitals are represented by the highest-lying lone pair levels of the main group ligand atoms. These predictions were tested by carrying out electronic band structure calculations for phosphosilicides PtSi₃P₂ and NiSi₂P₃. The relevance of nonstoichiometric compositions of these phases was also discussed.

1. Introduction

For extended solids composed of transition metal and electronegative main group elements, the concept of oxidation state can be used to predict the qualitative nature of their frontier orbitals. In such compounds, main group atoms L are much more electronegative than transition metal atoms M, so that the valence s and p levels of each ligand atom L lie lower in energy than the d level of M (Figure 1a). Thus their electronic structures are well described by the approximation that the main group atoms adopt the inert gas electron configuration in the sense of ionic bonding, and the remaining valence electrons occupy the d-block levels. In this ionic electron counting scheme, each atom is given its oxidation state, and each two-electron M–L bond is described as ionic with the electron pair counted as a lone pair belonging to the atom L. Compounds composed of only main group elements are described by the covalent electron counting scheme. This scheme assumes that each atom achieves the inert gas electron configuration in the sense of covalent bonding, and 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. In the covalent electron counting scheme, each atom is given its formal charge, and an approximate ordering of molecular energy levels is given (e.g., bond pair levels lie lower than lone pair levels).^{1,2}

The bonding in a number of compounds has both ionic and covalent character, so their description requires the use of both the ionic and covalent electron counting schemes, as first exemplified by the Zintl–Klemm concept.^{3–7} For example, the

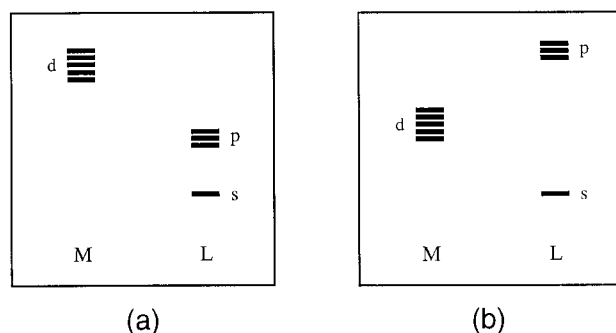


Figure 1. Relative energy ordering between the d orbital of a transition metal M and the valence s and p orbitals of its ligand atoms L. The conventional electron counting scheme is valid for (a) but not for (b).

tetrahedral lattice of the Al atoms in LiAl is explained by considering the oxidation state Li^+Al^- ,^{3a} which results from a complete electron transfer from Li to Al. Then the occurrence of four Al–Al bond pairs around each Al is readily accounted for in terms of covalent bonding, because each Al^- has four valence electrons. The Zintl–Klemm concept is applicable to a large number of compounds and anions,^{6,7} known as Zintl compounds and Zintl anions, respectively. Another combined ionic/covalent electron counting scheme is widely used in describing transition metal complexes. For instance, for a metal–ligand bond such as $M-CH_3$, the ionic description is

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[†] Dedicated to Professor S. Wolfe on the occasion of his 65th birthday.

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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. This combined ionic/covalent electron counting scheme will be referred to as the conventional electron counting scheme.

For compounds of late transition metals with weakly electronegative ligands, the conventional electron counting scheme is not adequate in predicting the qualitative nature of their frontier levels, and a need for a modified electron counting scheme has been recognized.^{8–11} Use of either the ionic or the conventional electron counting scheme to such compounds can lead to a picture inconsistent with experiment and theory. For example, the compound $\text{Cs}_2\text{Au}_2\text{I}_6$ contains linear AuI_2 and square planar AuI_4 units so that on the basis of the oxidation states Cs^+ and I^- , the Au oxidation states in the AuI_2 and AuI_4 units are often regarded as +1 and +3, respectively.¹² Likewise, the Au oxidation state of the square planar AuTe_4 units found in $(\text{Et}_4\text{N})_4\text{KAuAs}_4\text{Te}_8$,¹¹ $(\text{Et}_4\text{N})_3\text{AuTe}_7$,¹³ and $(\text{Et}_4\text{N})_4\text{Au}_2\text{Te}_{12}$ ¹⁴ is considered as +3. By analogy with the chemistry of the Ni^{2+} (d^8) ions, the Au^{3+} (d^8) picture provides a ready rationalization for the square planar structure of the AuI_4 and AuTe_4 units. However, studies of electronic structure calculations^{8,11} and X-ray photoelectron spectroscopy¹² for these compounds indicate that all their d-block levels are completely filled, thereby indicating a d^{10} electron count for Au (i.e., the Au^+ oxidation state). Another interesting example is AuTe_2 , which has an incommensurate structural modulation such that the coordination number of Au varies continuously two to four. All the Au atoms of this compound are found to be in the oxidation state +1.^{15,16} The primary cause for this inconsistency of the Au^{3+} picture is that the 5d orbital of Au lies below the 5p orbitals of Te and I,^{17,18} which prevents electron transfer from the Au 5d to the 5p level of I or Te (Figure 1b).

A similar difficulty arises for transition metal phosphosilicides, MSi_xP_y (M = transition metal).^{19–25} For example, noting

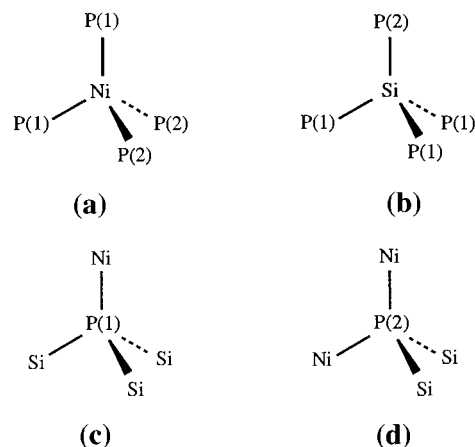


Figure 2. Coordinate environments of the atoms in NiSi_2P_3 .

that P and Si are the most and least electronegative elements of NiSi_2P_3 , respectively, Wallinda and Jeitschko assigned the oxidation state $(\text{Ni}^+)(\text{Si}^{4+})_2(\text{P}^{3-})_3$ for NiSi_2P_3 .^{22b} A similar analysis for platinum phosphosilicide PtSi_3P_2 leads to the oxidation state $(\text{Pt}^{6-})(\text{Si}^{4+})_3(\text{P}^{3-})_2$ and hence a highly unlikely electron configuration $(5d)^{10}(6s)^2(6p)^4$ for Pt. There are several reasons for this difficulty. First, the ionic electron counting scheme completely neglects the presence of covalent bonding between P and Si. Second, the electronegativity difference between Si and P is smaller than that between C and N (2.5 vs 3.0),² so that Si–P bonds should be described as polar covalent rather than ionic as implied by the ionic description Si^{4+} and P^{3-} . Third, the Si 3s level does not lie well above the Pt 5d level,^{17,18} so a complete electron transfer from the Si 3s to the Pt 5d and the P 3p levels is a poor approximation. For compounds of late transition metals for which the metal d levels lie between the valence s and p levels of its ligand atoms (Figure 1b), there is a need to have a modified electron counting scheme useful for predicting the qualitative nature of their frontier orbitals. In the present work, we probe this question and examine, as examples, the electronic structures of the phosphosilicides PtSi_3P_2 ²¹ and NiSi_2P_3 ²² using the extended Hückel tight binding (EHTB) method.²⁶ We note that the single-crystal X-ray diffraction data for NiSi_2P_3 are equally well refined as $\text{Ni}_{1.282(4)}\text{Si}_{1.284(5)}\text{P}_3$,^{22b} and the earlier study of NiSi_2P_3 reported the composition as $\text{Ni}_{1.68}\text{Si}_{0.88}\text{P}_3$.^{22a} These nonstoichiometric compositions were considered unacceptable,^{22b} partly because they lead to an unreasonably high oxidation state for Ni (from the viewpoint of ionic electron counting based on Si^{4+} and P^{3-}). In the following, we carry out calculations for the stoichiometric composition NiSi_2P_3 primarily and comment on the validity of the nonstoichiometric compositions in Section 5.

2. Coordinate Environments in and Conventional Electron Counting for NiSi_2P_3 and PtSi_3P_2

To find a modified electron counting scheme appropriate for NiSi_2P_3 and PtSi_3P_2 , it is necessary to first examine the coordinate environments of their atoms. The unit cell of NiSi_2P_3 has two formula units, i.e., $(\text{NiSi}_2\text{P}_3)_2$, in which all atoms are in tetrahedral sites.²² There are two kinds of P atoms, so the NiSi_2P_3 formula can be written as $\text{NiSi}_2[\text{P}(1)]_2\text{P}(2)$. Each Ni atom is bonded to four P atoms (Figure 2a), and so is each Si atom (Figure 2b). Thus the Ni and Si sites are similar. Each P(1) atom is bonded to one Ni and three Si atoms (Figure 2c), and each P(2) atom to two Ni and two Si atoms (Figure 2d).

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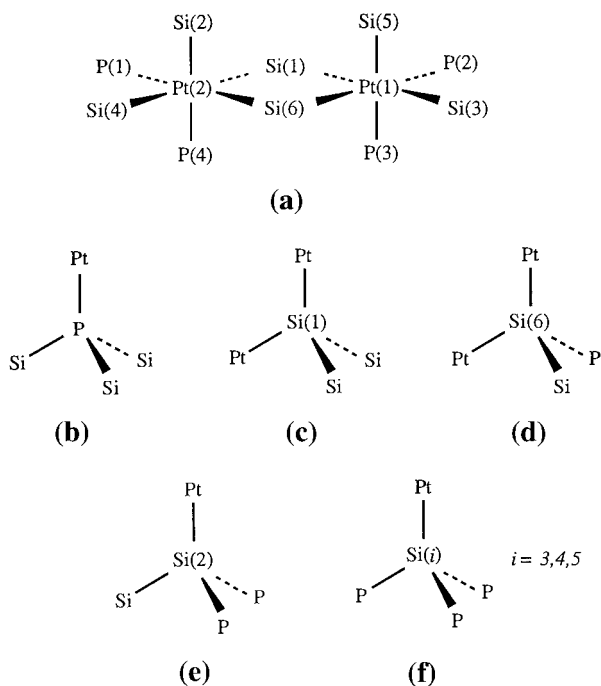


Figure 3. Coordinate environments of the atoms in PtSi_3P_2 .

The unit cell of PtSi_3P_2 has two formula units, i.e., $(\text{PtSi}_3\text{P}_2)_2$, in which all atoms are unique.²¹ Each Pt atom is in an octahedral site made up of four Si and two P atoms (Figure 3a). Each P atom is bonded to one Pt and three Si atoms (Figure 3b), the Si(1) and Si(6) atoms are each bonded to two Pt and two main group atoms (Figures 3c and 3d), and the Si(2), Si(3), Si(4), and Si(5) atoms are each bonded to one Pt and three main group atoms (Figure 3e and f).

In the conventional electron counting scheme, each Ni–P, Pt–P or Pt–Si bond of NiSi_2P_3 and PtSi_3P_2 is regarded as ionic with the electron pair counted as an electron pair belong to the main group element. Then from Figure 2a–d, the Si, P(1) and P(2) atoms of NiSi_2P_3 have the formal charges 0, 0 and -1 , respectively, so that the charge balance of NiSi_2P_3 is given by $(\text{Ni}^+)(\text{Si}^0)_2(\text{P}^-)_2(\text{P}^-)$. Thus, as for the Ni oxidation state of the stoichiometric composition NiSi_2P_3 , the ionic and the conventional electron counting schemes are in agreement. The Ni^+ oxidation state implies a d^9 electron count, which predicts that there are nine electrons in the five d-block bands of NiSi_2P_3 per formula unit. As will be discussed in Section 5, the ionic and the conventional electron counting schemes lead to very different Ni oxidation states for the nonstoichiometric compositions $\text{Ni}_{1.282(4)}\text{Si}_{1.284(5)}\text{P}_3$ and $\text{Ni}_{1.68}\text{Si}_{0.88}\text{P}_3$.

For PtSi_3P_2 , the coordinate environments of Figure 3b–f show that the formal charge of the P atoms is 0, that of the Si(2), Si(3), Si(4), and Si(5) atoms is -1 , and that of the Si(1) and Si(6) atoms is -2 . Thus PtSi_3P_2 has the charge balance $(\text{Pt}^{4+})_2(\text{Si}^{2-})_2(\text{Si}^-)_4(\text{P}^0)_4$. The Pt^{4+} oxidation state implies a d^6 electron count, which predicts that there are six electrons in the five d-block bands of PtSi_3P_2 per formula unit. Concerning the Pt oxidation state, the ionic and the conventional electron counting schemes provide very different pictures (i.e., Pt^{6-} versus Pt^{4+}).

3. Modified Electron Counting Scheme

Atomic electronic structure calculations^{17,18} show that the P 3p levels lie higher than, but not far from, the Ni 3d and Pt 5d levels. However, the Si 3p level lies significantly higher than the Ni 3d and Pt 5d levels.^{17,18} Thus, the ionic description of

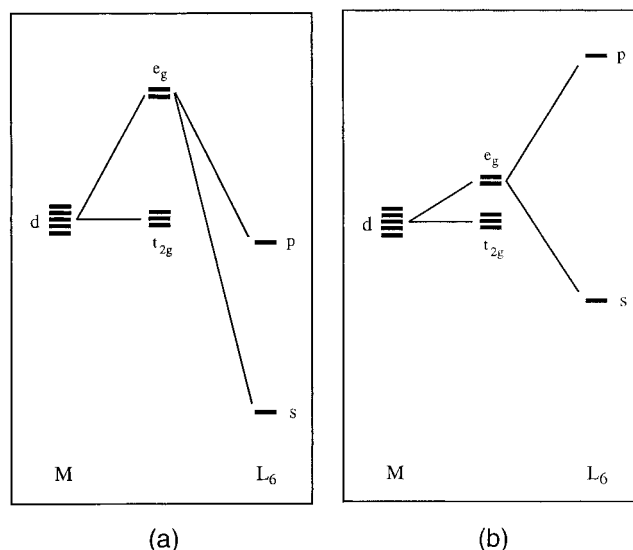


Figure 4. t_{2g} – e_g energy separation expected for a transition metal octahedral complex ML_6 when its relative orbital ordering is given by Figure 1a in (a) and by Figure 1b in (b).

the ionic and the conventional electron counting scheme is a poor approximation for the Ni–P and Pt–P bonds, and is an unreasonable one for the Pt–Si bond. Given the energy ordering, $\text{Pt } 5d \ll \text{Si } 3p$, it would be more reasonable to consider each two-electron Pt–Si bond as ionic with the electron pair counted as a lone pair belonging to Pt.

The formal charge Pt^{4+} for PtSi_3P_2 given by the conventional electron counting scheme implies that the t_{2g} -block levels are filled with six electrons, and the e_g -block levels are empty, if the compound adopts the low-spin electron configuration. In this scheme, each Pt^{4+} ion is considered as surrounded with six lone pairs (i.e., four from four Si atoms, and two from two P atoms). As discussed above, it is more realistic to regard the two-electron Pt–Si bond as ionic with the electron pair counted as belonging to Pt. Thus, per formula unit PtSi_3P_2 , four electrons from the four Si lone pair levels should be transferred to the empty e_g -block levels of each Pt, provided that the e_g -block levels do not lie high in energy. To check the latter point, we examine the t_{2g} – e_g energy separation in an octahedral ML_6 complex with σ donor ligands L. When the metal d level lies higher than the valence s and p levels of its ligand atoms (Figure 1a), the e_g -block levels lie much higher than the t_{2g} -block levels as depicted in Figure 4a. For the metal d orbitals of e_g symmetry (i.e., z^2 and x^2-y^2 orbitals) are raised by the ligand group orbitals of e_g symmetry constructed from the ligand s orbitals (Figure 5a) and also by those constructed from the ligand p orbitals (Figure 5b). If the metal d level lies between the valence s and p levels of its ligand atoms (Figure 1b), the metal d orbitals of e_g symmetry are raised by the ligand orbitals of Figure 5a, but are lowered by those of Figure 5b. Consequently, as depicted in Figure 4b, the t_{2g} – e_g energy separation becomes small, and the e_g level may even lie below the t_{2g} level if the energy lowering by the ligand p orbitals is strong enough. To test this prediction, we carried out EHTB calculations for the hypothetical octahedral compounds $(\text{PtP}_6)^{14-}$, $[\text{Pt}(\text{PH}_3)_6]^{4+}$, $(\text{PtSi}_6)^{20-}$, and $[\text{Pt}(\text{SiH}_3)_6]^{2-}$, for which the Pt–P and Pt–Si distances were taken to be the average Pt–P and Pt–Si distances found for PtSi_3P_2 . The e_g -block level lies about 5 eV above the t_{2g} -block level in $(\text{PtP}_6)^{14-}$ and $[\text{Pt}(\text{PH}_3)_6]^{4+}$. However, the e_g -block level lies 0.9 eV above the t_{2g} -block level in $(\text{PtSi}_6)^{20-}$ and 0.6 eV below the t_{2g} -block level in $[\text{Pt}(\text{SiH}_3)_6]^{2-}$.

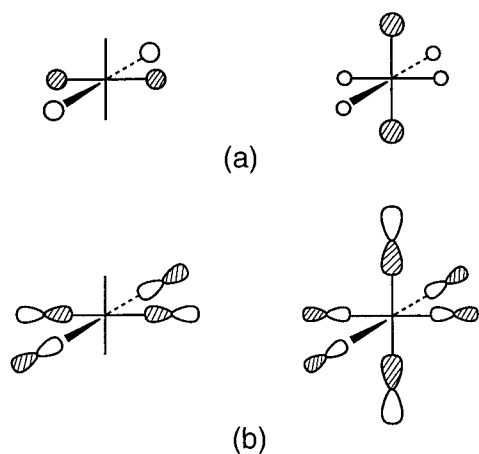


Figure 5. Ligand group orbitals of e_g symmetry in an octahedral ML_6 complex constructed from the ligand s orbitals in (a) and from the ligand p orbitals in (b).

The electron pairs of the main group elements in PtSi₃P₂ are expected to have the energy ordering, P–Si bond pair < P lone pair < Si lone pair, namely, the Si lone levels are the highest lying occupied ones. As discussed above, the e_g -block levels lie as low as the t_{2g} -block levels. Therefore, it would be energetically favorable to transfer, per formula unit PtSi₃P₂, four electrons from the four Si lone pair levels to completely fill the e_g -block levels of each Pt thereby leading to a d^{10} electron count for Pt. This leaves four electrons in the four Si lone pair levels. Thus, the frontier energy levels of PtSi₃P₂ should be represented by the Si lone pair levels. In reaching this prediction, we first employed the conventional electron counting scheme and then considered electron transfer from the highest lying lone pair levels of the main group ligand atoms to all the empty d -block levels so as to correct the erroneous prediction of the conventional electron counting scheme. This modified approach will be referred to as the “modified electron counting scheme” to distinguish it from the conventional one.

Let us examine NiSi₂P₃ in terms of the modified electron counting scheme. The formal charge Ni⁺ of NiSi₂P₃ implies a d^9 electron count, i.e., there are nine electrons in the five d -block levels of each Ni that is surrounded with four P lone pairs (Figure 2a). If the P lone pair levels lie higher than the d -block levels of each NiP₄ unit, it would be reasonable to consider one electron transfer from the P lone pair levels to the empty d -block level of Ni. Then the frontier energy levels of NiSi₂P₃ will be represented by P lone pair levels.

4. Electronic Band Structures of NiSi₂P₃ and PtSi₃P₂

The predictions of the modified electron counting scheme described above were tested by calculating electronic band structures of PtSi₃P₂ and NiSi₂P₃ using the EHTB method. The atomic parameters employed for these calculations are summarized in Table 1.²⁷

The total density of state (TDOS) plot calculated for PtSi₃P₂ is presented in Figure 6a, which shows a substantial band gap.

(27) 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 Pt and Ni listed in Table 1 are about 1.5 eV higher. Concerning the orbital compositions of the d -block levels of the Ni(PMe₃)₄⁺ cation,³⁰ extended Hückel molecular orbital calculations using the Ni and P parameters of Table 1 give results similar to those obtained from our density functional theory calculations (unpublished work). Certainly, our conclusions remain the same when the H_{ii} values of Pt and Ni are lowered. This is also the case when they are raised within a chemically reasonable range (e.g., up to about 1.5 eV).

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
Pt	6s	-7.08	2.51	1.0		
Pt	6p	-5.48	1.84	1.0		
Pt	5d	-12.6	4.851	0.6314	2.588	0.5288
Ni	4s	-7.67	2.08	1.0		
Ni	4p	-3.65	1.47	1.0		
Ni	3d	-12.0	6.706	0.4212	2.874	0.7066
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 elements $\langle \chi_i | H^{\text{eff}} | \chi_i \rangle$, where H^{eff} is the effective Hamiltonian. In our calculations of the off-diagonal matrix elements $H^{\text{eff}} = \langle \chi_i | H^{\text{eff}} | \chi_j \rangle$, the weighted formula was used. See: Ammeter, J.; Bürgi, H.-B.; Thibault, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. ^b Contraction coefficients used in the double- ζ Slater-type orbital.

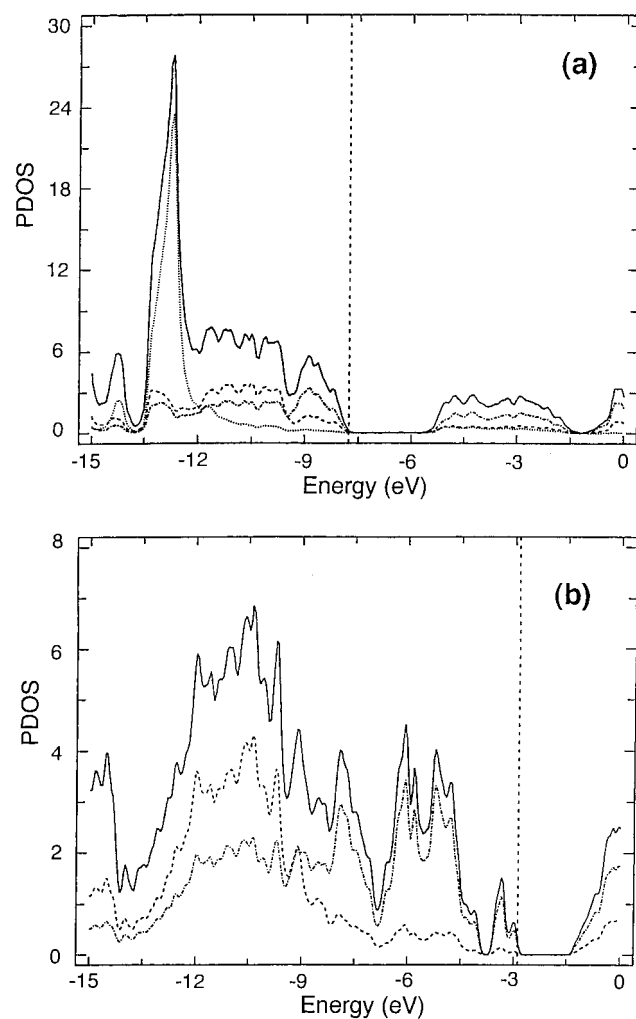


Figure 6. TDOS and PDOS plots calculated for (a) PtSi₃P₂ and (b) the Si₃P₂⁴⁻ lattice of PtSi₃P₂: (—) TDOS; (···) PDOS of the Pt 5d orbitals; (---) PDOS of the P 3p orbitals; (-·-) PDOS of the Si 3p orbitals.

Therefore, PtSi₃P₂ should not be metallic, although it was reported to be metallic.²¹ A possible reason for this observation will be discussed in the next section. The projected density of state (PDOS) plots calculated for the 5d orbitals of Pt and the 3p orbitals of P and S are also included in Figure 6a. All the Pt 5d orbital contributions lie well below the Fermi level in a narrow energy region of about 1.5 eV in width, and their average

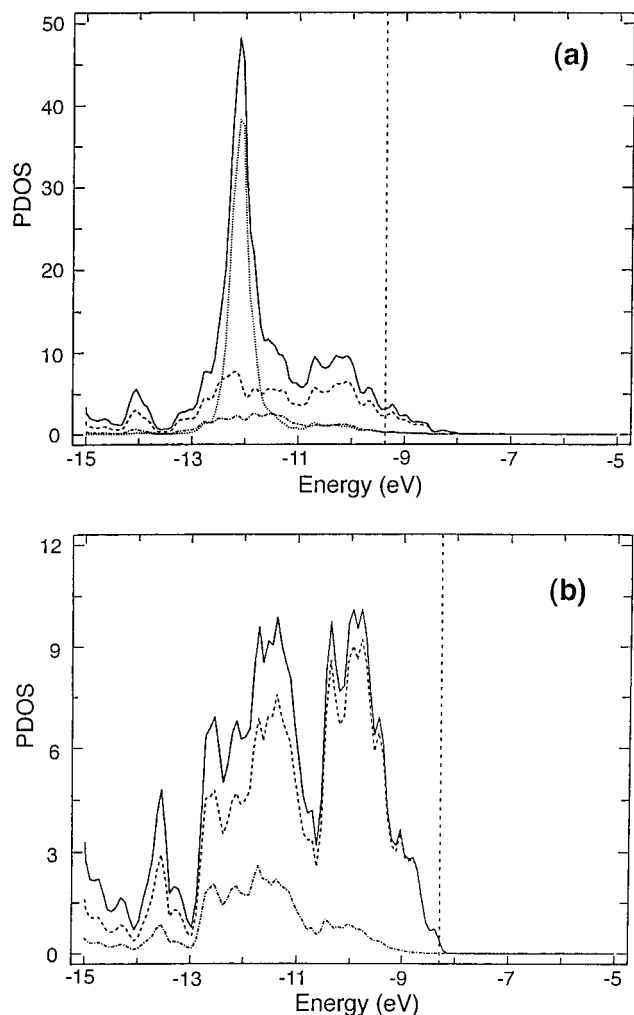


Figure 7. TDOS and PDOS plots calculated for (a) NiSi_2P_3 and (b) the Si_2P_3^- lattice: (—) TDOS; (···) PDOS of the Ni 3d orbitals; (---) PDOS of the P 3p orbitals; (-·-) PDOS of the Si 3p orbitals.

energy lies slightly lower than the d-orbital energy of the Pt atom. The TDOS and PDOS plots calculated for the hypothetical $\text{Si}_3\text{P}_2^{4-}$ lattice (resulting from PtSi_3P_2 by removing Pt^{4+}) are presented in Figure 6b, which shows clearly that the Si lone pairs lie very high in energy. Consequently, Figure 6a and b supports the two primary predictions of the modified electron counting scheme that the Pt atom of PtSi_3P_2 has a d^{10} electron count, and the t_{2g} - e_g energy separation is small.

Figure 7a shows the TDOS and PDOS plots calculated for NiSi_2P_3 . As in the case of PtSi_3P_2 , Figure 7a shows that all the Ni 3d orbital contributions lie well below the Fermi level in a narrow region of energy, and their average energy lies slightly lower the d-orbital energy of the Ni atom. The TDOS and PDOS plots calculated for the hypothetical Si_2P_3^- lattice (resulting from NiSi_2P_3 by removing Ni^+) are given in Figure 7b. The top portion of the PDOS for the P 3p orbitals lies high in energy due to overlap repulsion among the P lone pairs surrounding each empty Ni site.²⁸ Thus, electron transfer from the P lone pair levels to lower-lying empty levels, when available, would be energetically favorable. Thus, Figure 7a and b shows that the Ni atom of NiSi_2P_3 has a d^{10} electron count.

5. Discussion

Our electronic structure calculations support the predictions of the modified electron counting scheme that the transition

metals of PtSi_3P_2 and NiSi_2P_3 have a d^{10} electron count. Figures 6a and 7a show that the d-block bands of PtSi_3P_2 and NiSi_2P_3 are about 1.5 eV wide with no clear-cut distinction between the “ t_{2g} ” and “ e_g ” block bands. From the viewpoint of the conventional electron counting scheme, this result is surprising for PtSi_3P_2 in which the Pt atoms are located at the octahedral sites made up of four Si and two P atoms. In essence, the “surprising” result originates from the fact that the Pt 5d level lies below the Si 3p level. Thus the Si lone pair levels do not act as donor levels but as acceptor levels to the Pt 5d levels.²⁸ This is also the reason, in average, the d-block bands of PtSi_3P_2 lie lower in energy than the Pt 5d levels.

Let us now consider a probable origin of the observed metallic property of PtSi_3P_2 .²¹ Stoichiometric PtSi_3P_2 samples do not have partially filled bands. Thus one has to consider a slight nonstoichiometry in PtSi_3P_2 that will either remove some electrons from the highest occupied (i.e., valence) bands or add some electrons to the lowest unoccupied (i.e., conduction) bands of stoichiometric PtSi_3P_2 . Since Pt has a d^{10} electron count, some vacancy in the Pt sites will not create partially filled bands. However, substitutional defects in the P and Si sites leading to either $\text{PtSi}_{3+x}\text{P}_{2-x}$ or $\text{PtSi}_{3-x}\text{P}_{2+x}$ will do. The former creates holes in the valence bands, while the latter creates electrons in the conduction bands. Since the conduction bands lie substantially higher than the valence bands, it would be energetically more favorable to have holes in the valence bands. The observed metallic property of PtSi_3P_2 implies that the true stoichiometry of the samples studied is probably $\text{PtSi}_{3+x}\text{P}_{2-x}$.

Perrier et al. reported the structure of another platinum phosphosilicide PtSi_2P_2 ,²¹ in which each Pt atom is located at an octahedral site made up of three Si and three P atoms. Though not presented, our electronic structure calculations for PtSi_2P_2 show the same trends as found for PtSi_3P_2 , namely, the Pt d-block levels occur in a narrow region of energy well below the Fermi level so that the d-electron count for the Pt atoms should be considered as d^{10} .

Given the stoichiometry of NiSi_2P_3 , the top portion of the valence bands are empty (Figure 7a). To completely fill the valence bands, one extra electron per formula unit NiSi_2P_3 is needed. NiSi_2P_3 has 17 valence levels per formula unit (i.e., five d-block levels, four P lone pair levels, and eight Si–P bond pair levels) but has only 33 valence electrons per formula unit. All 17 valence levels become completely filled for the composition NiSiP_4 , which is obtained from NiSi_2P_3 by replacing 50% of the Si sites with P. This composition would lead to an unreasonably high oxidation state for Ni from the viewpoint of the ionic electron counting based on Si^{4+} and P^{3-} (i.e., +8). However, Figure 2b shows that each P atom replacing a Si site gets the +1 formal charge, so that the charge balance for NiSiP_4 is given by $(\text{Ni}^0)(\text{Si}^0)(\text{P}^+)(\text{P}^0)_2(\text{P}^-)$ according to the conventional electron counting scheme. Namely, the Ni oxidation state in the NiSiP_4 composition (i.e., 0) is smaller than that in the NiSi_2P_3 composition (i.e., +1) if the presence of the covalent Si–P bonds is recognized.

We now consider the validity of the nonstoichiometric compositions $\text{Ni}_{1.282(4)}\text{Si}_{1.284(5)}\text{P}_3^{22b}$ and $\text{Ni}_{1.68}\text{Si}_{0.88}\text{P}_3$.^{22a} These compositions can be rewritten as $\text{Ni}_{1.382}\text{Si}_{1.384}\text{P}_{3.234}$ and $\text{Ni}_{1.813}\text{Si}_{0.95}\text{P}_{3.237}$, respectively, to normalize the total number of atoms per formula unit to six as in NiSi_2P_3 . Therefore, the nonstoichiometric compositions are obtained by replacing appropriate portions of the Si sites with Ni and P atoms. As already mentioned, the Si and Ni sites of NiSi_2P_3 are equivalent in that they are surrounded by four P atoms (Figure 2a and b). In addition, each P atom replacing a Si site will get the formal

(28) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; Chapter 2.

charge +1 (Figure 2b). Thus, according to the conventional electron counting scheme, Ni_{1.382}Si_{1.384}P_{3.234} has the charge balance (Ni^{0.552+})_{1.382}(Si⁰)_{1.384}(P⁺)_{0.236}(P⁰)₂(P⁻), and Ni_{1.813}-Si_{0.950}P_{3.237} has the charge balance (Ni^{0.421+})_{1.813}(Si⁰)_{0.950}(P⁺)_{0.237}(P⁰)₂(P⁻). Consequently, the Ni oxidation state is not larger but smaller in the nonstoichiometric compositions Ni_{1.282(4)}Si_{1.284(5)}P₃ and Ni_{1.68}Si_{0.88}P₃ than in NiSi₂P₃ (i.e., +0.552, +0.421, vs +1.000) once the presence of Si-P covalent bonding is taken into consideration. Thus, as far as the Ni oxidation state is concerned (based on the conventional electron counting scheme), the nonstoichiometric compositions Ni_{1.282(4)}Si_{1.284(5)}P₃ and Ni_{1.68}Si_{0.88}P₃ are, if not more than, as acceptable as the stoichiometric composition NiSi₂P₃. The true composition of this phase may depend from experiment to experiment. From the viewpoint of entropy and more fully filling all the valence orbitals, the nonstoichiometric compositions are more favorable than the stoichiometric composition.

Finally, it should be mentioned that when the modified electron counting scheme is applied to the nonstoichiometric compositions Ni_{1.282(4)}Si_{1.284(5)}P₃ and Ni_{1.68}Si_{0.88}P₃, we reach the same conclusions as in the case of the stoichiometric composition NiSi₂P₃ (see Section 3).

6. Concluding Remarks

For late transition metal compounds with weakly electronegative ligands for which the relative energy ordering of Figure 1b applies, the conventional electron counting scheme incorrectly predicts that the empty d-block levels of the transition metal atoms lie below the highest-lying lone pair levels of the main group ligand atoms. This deficiency of the conventional electron counting scheme is easily corrected by introducing

electron transfer from the highest-lying lone pair levels of the main group ligand atoms to the empty d-block levels. Such an electron transfer is energetically favorable because the t_{2g}-e_g energy separation is negligible in cases when the relative energy ordering of Figure 1b is applicable. As a consequence, the highest-lying lone pair levels of the main group ligand atoms become the frontier orbitals of such compounds, and the transition metal atoms have a d¹⁰ electron count. Our EHTB electronic band structure calculations for PtSi₃P₂ and NiSi₂P₃ support these two predictions. The modified electron counting scheme proposed in this work is also applicable to other transition metal phosphosilicides²⁹ and should also be useful for a wide range of compounds for which the relative energy ordering of Figure 1b applies. Our discussion also suggests that the true compositions of the PtSi₃P₂ and NiSi₂P₃ phases can be nonstoichiometric.

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