**A Strong Dependence of the P-P Bond Length on the Transition Metal Component in ThCr$_2$Si$_2$-Type Phosphides CaM$_2$P$_2$ (M = Fe, Ni): The Influence of d Band Position and $\sigma_{\pi}$ Mixing**

**Dae-Bok Kang**

Department of Chemistry, Kyungsung University, Busan 608-736, Korea

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An analysis of the bonding situation in CaM$_2$P$_2$ (M=Fe, Ni) with ThCr$_2$Si$_2$ structure is made in terms of DOS and COOP plots. The main contributions to covalent bonding are due to M-P and P-P interactions in both compounds. Particularly, the interlayer P-P bonding by variation in the transition metal is examined in more detail. It turns out that the shorter P-P bonds in CaNi$_2$P$_2$ form as a result of the decreasing electron delocalization into $\sigma_{\pi}$ of P$_2$ due to the weaker bonding interaction between the metal d and $\sigma_{\pi}$ as the metal d band is falling from Fe to Ni.

**Key Words**: Phosphide, ThCr$_2$Si$_2$ structure, Electronic structure

### Introduction

The well-known ThCr$_2$Si$_2$-type structure is the highest number of materials for any crystal structure because of its possibility to adapt to strongly different atomic sizes as well as to a wide range of elements. In these ThCr$_2$Si$_2$ compounds, remarkable differences exist regarding the bonding situation. While in SrFe$_2$P$_2$, e.g., the shortest P-P distance is 3.43 Å, the corresponding value for CaFe$_2$P$_2$ is 2.71 Å and only 2.30 Å for CaNi$_2$P$_2$. The short distance in CaNi$_2$P$_2$ is characteristic of a full P-P single bond. The long contacts of 3.43 Å in SrFe$_2$P$_2$ imply essentially no bonding at all. Hoffmann and Zheng analyzed the underlying nature of the chemical bonding in BaM$_2$P$_2$ with ThCr$_2$Si$_2$ structure by using the extended Hückel (EH) method. They have suggested that the interlayer P-P bonding is promoted by a depletion of the filled P-P $\sigma_{\pi}$ band when going from Fe to Ni compound as a general trend for the transition metal series. However, this $\sigma_{\pi}$ band is high and empty in all these compounds, therefore it cannot be responsible for the trend in the P-P distances. In addition, the influence of M-P interaction on the P-P bonding was not taken into account in their paper.

In the present paper, we will describe the main features of different types of interactions, i.e., the M-P, M-M, and P-P bonding, regarding the ThCr$_2$Si$_2$-type structure represented by the CaM$_2$P$_2$ (M=Fe, Ni) compounds with long and short P-P distances. In order to understand the striking difference of the interlayer P-P distances provided by variation in the transition metal, we present an analysis of the P-P bonding within the M-P interacting framework on the basis of EH tight-binding band calculations. The calculations were performed by using the CAESAR package, which provides useful graphical outputs such as band structure, density of states (DOS), and crystal orbital overlap population (COOP) curves. The atomic orbital parameters used for the calculations are given in Table 1. The theoretical tool we use is perturbation theory and its predictions are confirmed by actual molecular orbital calculations, as will be discussed later. Previous theoretical investigations of these compounds are scarce and confined to calculations using the Linearized Augmented Plane-Wave (LAPW) method.

### Crystal Structure

Figure 1 shows the tetragonal unit cell for CaFe$_2$P$_2$ (or CaNi$_2$P$_2$) with space group I4/mmm and cell parameters $a = 3.855$ (3.916) Å, $c = 9.985$ (9.563) Å. The structural parameters used for the present calculations are taken from ref. 2. The $z$ axes are always parallel to the $c$ axis of the unit cell. The structure consists of M$_2$P$_6$ layers of MP$_4$ tetrahedra and Ca$^2+$ layers, alternately stacked along the $c$ axis. The M$_2$P$_6$ layers contain the strong covalent M-P bonding that is suggested by the short distances comparable to the Pauling single bond radius sums (d$_{M-P}$ = 2.27, d$_{Ca-P}$ = 2.25 Å), whereas the interlayer distances between the P atoms show a great variety of values. In Table 2 we list the P-P distances of some first and second row transition metal phosphides. They decrease strongly as the transition metal moves from the left

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<th>Table 1. Atomic Parameters Used in the Calculations</th>
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*Coefficients in double-$\zeta$ expansion.*
to the right-hand side in the periodic table. An electronic effect governing the observed trend in the P-P distances will be explained in the following section.

Results and Discussion

Electronic structure of CaFe\textsubscript{2}P\textsubscript{2}. In this section we shall see how the electronic structure of the three-dimensional (3D) Fe\textsubscript{2}P\textsubscript{2}\textsuperscript{2−} lattice evolves as we build the 3D solid by putting Fe\textsubscript{2}P\textsubscript{2}\textsuperscript{2−} layers together. First, the interlayer P-P unit may be thought of as being formed by bringing together the P atoms from two layers. The P\textsubscript{2} sublattice of 3D Fe\textsubscript{2}P\textsubscript{2}\textsuperscript{2−} will then be constructed from these units, and finally, the Fe atoms will be introduced into the lattice so that the P atoms can be positioned above and below the four-fold hollows of the Fe square sheet. The square lattice of Fe atoms in this structure is capped by P\textsubscript{2} units from both sides, with a P\textsubscript{2} axis perpendicular to the iron plane.

Crucial to our discussion will be the P\textsubscript{2} bonding unit, sometimes fully formed, sometimes not, in these ThCr\textsubscript{2}Si\textsubscript{2} type structures. The molecular axis of P\textsubscript{2} orients parallel to the \( z \) direction of the cell, and the P-P distance within a P\textsubscript{2} unit is 2.71 Å. In order to understand the bonding relationships in CaFe\textsubscript{2}P\textsubscript{2}, we performed electronic structure calculations of representative molecular fragments and the complete 3D structure. The electronic structure of the P\textsubscript{2} unit is that of a typical homonuclear diatomic molecule. The energy levels of the diatomic orbitals are shown at the left side of Figure 2. What if iron atoms are added to the P\textsubscript{2} sublattice? The shortest Fe-P contact is 2.24 Å, a distance that is well within the iron-phosphorus bonding range. The Fe-P interactions are indeed quite strong, giving an overlap population (OP) of 0.46. The Fe-Fe interatomic distance within the square lattice is 2.73 Å. The schematic diagram in Figure 2 describes the interactions observed for the isolated molecular Fe\textsubscript{2}P\textsubscript{2} cluster (1) cut out of the solid. The energy window of this diagram contains only the valence orbitals of the cluster. At low energy, both \( \sigma \) and \( \pi \) states of P\textsubscript{2} are stabilized by Fe-3d orbitals, mixed in a bonding fashion. The 3d(Fe)-\( \pi(P) \) interaction is relatively small, due to the large energy difference and small coupling overlap of the two, so that the majority of \( \pi \) states remain unchanged. At the highest energy level is primarily \( \sigma \) and \( \sigma' \), antibonding to Fe-3d orbitals. The middle filled levels are slightly more complicated. They are represented by Fe 3d orbitals perturbed by P\textsubscript{2} \( \sigma \) and \( \sigma' \). Since \( \sigma \) and \( \sigma' \) lie at respectively lower and higher energy than Fe 3d levels, P\textsubscript{2} \( \sigma \) mixes in a bonding way to Fe 3d orbitals while \( \sigma \) in an antibonding fashion. Electron density from the filled Fe 3d orbitals will be transferred to the empty P\textsubscript{2} \( \sigma' \).
We next go on to the complete 3D solid. The electropositive element Ca can be considered as an electron donor; it formally transfers two electrons to the sublattice of (Fe,P)2-.

Thus these atoms are presumed not to participate in covalent bonding and are not included in the calculations. Figure 3 displays the total DOS and its decomposition into Fe 3d and P 3p contributions calculated for the 3D Fe3P2- structure. The shape of the DOS can easily be understood starting from the analysis of the orbitals of the cluster Fe3P2, which is the building blocks of this compound. First, the σ and π states of the P4 dimer units appear in the interval −16 to −13 eV in the DOS. Their π* states are associated with two peaks that lie around −12 eV. The bands with strong Fe 3d character are found between −10 and −7 eV. One should notice a P2 3d bonding contribution to Fe 3d for the peak at −10 eV.

The average COOP curves for the bonding interactions present in the structure are plotted in Figure 4a. We can easily identify bonding contributions from the fragment molecular orbitals in Figure 2 and the DOS projections in Figure 3. As expected, the lower part of this energy region is mainly iron-phosphorus bonding. But now the two phosphorus atoms enter the interactions as a P2 pair, whose orbitals are π, σ', and σ''. The antibonding counterparts of 3d-π and 3d-σ" bonding orbitals lie above the Fermi level. The antibonding character between Fe 3d and σ is easily recognized from the peak at −9 eV that falls below the Fermi level. It is generated by the Fe-P antibonding interaction which increases the energy of a P-P σ bonding orbital and places it just below the Fermi level. There is a remarkable σ' contribution at the bottom of the Fe 3d band. The orbital combination at −10 eV is apparently characterized by bonding interaction between the 3d and higher-lying empty σ". Substantial electron filling of σ by mixing with Fe 3d leads to weak interlayer P-P bonding (OP=0.58) in CaFe2P2.

The Fe-Fe distance in CaFe2P2 is 2.73 Å, much longer than that in Fe metal with 2.48 Å. The integrated COOP for the Fe-Fe bonds give small positive values of 0.05, indicating no significant Fe-Fe bonding.

Influence of the transition metal. The substitution of the transition metal component (M=Fe) in CaFe2P2 by Ni leads to drastic changes of the P-P interlayer bonding and small increases (0.04 and 0.05 Å) in the M-M and M-P distances. The CaM2P6 compounds with M=Fe, Co, and Ni form P-P distances of 2.71, 2.45, and 2.30 Å, respectively (see Table 2). It appears that the transition metals from the left side of the periodic table tend to form longer P-P distances. To investigate the effects of transition metal substitution on the interlayer P-P bonding, we have calculated the band structures of CaFe2P2 and CaNi2P2. We substitute Fe in CaFe2P2 by Ni, keeping the geometry of the Fe compound in order to see only the electronic effect. The density of states for CaNi2P2 is essentially the same as for the iron compound, but the Fermi level is lower because the Ni d bond comes down in energy. The P-P σ' band lies so high that it is not occupied in all these compounds. If the interaction between the σ' and the metal d bands is turned on, the weakening of interlayer P-P bonds will be favored by filling the σ' antibonding states. Therefore, a distinctly stronger P-P bond for CaNi2P2 compared to CaFe2P2 cannot be due to the depopulation of the filled P-P σ' states caused by the decreasing transition metal Fermi level.

What else will be the effects of different transition metals
The metal-phosphorus and metal-metal interactions are slightly stronger in the iron compound mainly due to less occupation of their antibonding states. This is in agreement with the experimental observation that the \(\sigma\)-lattice constants for the Fe compound are slightly shorter compared with the Ni compound. For the real CaNi\(_2\)P\(_2\) structure, COOP curves of Ni-P, Ni-Ni, and P-P bonds are plotted in Figure 5. This is analogous to what happened in Figure 4b. The \(\sigma^*\) + metal antibonding states are not shown in the figure because its states with short P-P bonds appear at very high energy of 10 eV.

**Conclusions**

In summary, the interlayer P-P bonding in CaFe\(_2\)P\(_2\) and CaNi\(_2\)P\(_2\) with ThCr\(_2\)Si\(_2\) structure is controlled by the transition metal d band position, but in a way different from previous findings. We do not find the bond formation by the depopulation of filled P-P \(\sigma^*\) orbital when going from Fe to Ni compound. Shorter P-P bonds in the Ni compound are derived from less population of P-P \(\sigma^*\) antibonding states due to the decreasing \(\sigma^*\) mixing with the lowered d band. This effect is working in the shorter P-P bonds on going from left to right in the transition series. If the M\(_2\)P\(_2\) (M=transition element) layers are well separated from each other due to large atoms like Ba or La, it should not be possible to form a short P-P contact by geometric reasons. In any event, it is not reasonable to separate the P-P bond from the metal-phosphorus interaction.

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**References**