Electronic structure and bonding in 
\textbf{BaNi}_2\textbf{P}_4

\begin{abstract}
The electronic structures of the \((\text{Ni}_2\text{P}_4)^2^-\) subnet of \(\alpha-\) and \(\beta\)-\(\text{BaNi}_2\text{P}_4\) have been investigated by means of electronic band structure calculations using the semiempirical extended Hückel tight-binding method. Molecular and chain models of the \((\text{Ni}_2\text{P}_4)^2^-\) subnet comprising \(\text{Ni}_2\text{P}_2\) rings have also been analyzed. Although the electronic structure for the solid is more complicated than those of the molecular and one-dimensional models, the use of the Framework Electron Counting (FEC) rules based on a molecular orbital analysis of related molecules is useful for the rationalization of the chemical bonding in the solid. The basic feature of this system is a three-dimensional network of edge-sharing \(\text{NiP}_4\) tetrahedra, linked through \(\text{P}_4\) squares. There are less than eight valence electrons in each \(\text{Ni}_2\text{P}_2\) ring; different \(\text{Ni} \cdots \text{Ni}\) contacts in the nonequivalent rings can be rationalized from this electron-deficient filling of the framework orbitals. While a simple one-dimensional model suggests a Peierls distortion as the origin of the observed phase transition in \(\text{BaNi}_2\text{P}_4\), a detailed look shows that this mechanism is not operative in this metallic compound.

\textbf{Key words} Electronic structure - Transition-metal phosphides - Chemical bonding
\end{abstract}

\begin{resumen}
La estructura electrónica de la red aniónica \((\text{Ni}_2\text{P}_4)^2^-\), presente en las estructuras \(\alpha-\) y \(\beta\)-\(\text{BaNi}_2\text{P}_4\), ha sido estudiada mediante cálculos de bandas, usando el método semiempírico “extended Hückel tight-binding”. También se han analizado modelos moleculares y en cadena de la subred \((\text{Ni}_2\text{P}_4)^2^-\) que contienen anillos \(\text{Ni}_2\text{P}_2\). Aunque la estructura electrónica del sólido es más complicada que la de los modelos, el cálculo del número de electrones del esqueleto (Framework Electron Counting, FEC), basado en un análisis de orbitales moleculares de moléculas relacionadas, es útil para la comprensión del enlace químico en el sólido. La característica principal de este sistema es la red tridimensional de tetraedros \(\text{NiP}_4\) que comparten aristas, conectados a través de anillos cuadrados \(\text{P}_4\). En cada anillo \(\text{Ni}_2\text{P}_2\) hay menos de ocho electrones de valencia, y la existencia de diferentes contactos \(\text{Ni} \cdots \text{Ni}\) en los anillos no-equivalentes pueden ser atribuidos a esta ocupación deficiente en electrones de los orbitales del esqueleto. Aunque un simple modelo monodimensional sugiere una distorsión de Peierls como el origen de la transición de fase observada en \(\text{BaNi}_2\text{P}_4\), un análisis más detallado muestra que este mecanismo no es operativo en dicho compuesto metálico.
\end{resumen}

\begin{introduction}
At temperatures over 100°C, \(\text{BaNi}_2\text{P}_4\) crystallizes in a tetragonal structure \([1]\) formed by condensation of relatively large \(\text{Ni}_8\text{P}_{16}\) cages each of which contains a single barium atom in its interior (Fig. 1). The same crystal structure has also been reported \([2]\) for \(\text{BaPd}_4\text{P}_4\). An alternative view of this structure is to consider the phosphorus-nickel sublattice as being composed of linear chains \((1a)\) of edge-sharing \(\text{NiP}_4\) tetrahedra running along the [001] direction in the
\end{introduction}
crystal. These chains are arranged in such a way that four phosphorus atoms belonging to four distinct chains form square P₄ rings with short P-P distances (2.23Å) that can be identified as single P-P bonds. Similar square P₄ rings have also been found in binary MP₃ transition-metal phosphides with the skutterudite structure and for the related RM₄P₁₂ filled skutterudites, and have been of theoretical interest to identify as single P-P bonds.

On lowering the temperature, the tetragonal α-BaNi₄P₄ phase undergoes a gradual transition to a lower symmetry, orthorhombic β-BaNi₄P₄ phase. The structure of this low temperature phase is essentially the same as that found for α-BaNi₄P₄, its main difference being that now the NiP₄ tetrahedra are distorted, resulting in chains of edge-sharing tetrahedra with alternating Ni-Ni distances (1b). As a side effect, the P₄ rings are now slightly compressed, with practically the same P-P distance as in the high temperature phase.

In this contribution we will use the semiempirical extended Hückel method (see Appendix for computational details) to analyze the bonding in the (Ni₃P₂)³⁻ subnet of BaNi₄P₄. Our main aim is to look for simple electron counting rules that explain the presence of short Ni-Ni distances across the Ni₃P₂ rings in the low temperature phase. The elegant synthetic work reporting the original structure and its deformations was accompanied by a theoretical analysis, in fact using a methodology similar to ours. However, as we will see, there are certain problems in the reported theoretical modeling. This and the inherently intriguing structure has led us to undertake an independent study of the electronic structure of this material.

### Framework Electron Counting

The nickel atoms in both phases of BaNi₄P₄ have tetrahedral environments. By sharing the vertices (and edges) of the NiP₄ tetrahedra one can build up the chains present in these two structures. An alternative view of these chains is as an array of alternating, mutually perpendicular NiP₄ diamonds. Such basic M₂X₂ building blocks are very common in organometallic chemistry; there are large families of L₂M₄(µ-XR₂)₁₂ molecules with a wide range of metal-metal separations across the ring. A workable rationalization of the different bonding situations encountered in these compounds is provided by the Framework Electron Counting (FEC) rules [5, 6]. These rules, based on a molecular orbital analysis of the σ-type bonds in the diamond-shaped M₂X₂ framework, provide a simple tool to predict the existence or absence of M–M interactions across the rings, which in turn lead to more or less squeezed diamonds.

Let us take a simple model L₄M₄(µ-XR₂)₁₂ compound to illustrate these electron counting rules. Each XR₂ bridging ligand can contribute two orbitals to framework bonding. If we consider M to be a d¹⁰ metal ion (i.e., Cu⁺ or Ni⁺), where it is likely that we may neglect participation of d orbitals in the M₂X₂ ring bonding, the metal atom is left with two empty sp³ orbitals available for framework bonding. The orbitals of the XR₂ and ML₅⁻ fragments interact as shown in the diagram presented in Fig. 2. Four M-X bonding orbitals and their corresponding antibonding counterparts result. If each bridging XR₂ ligand is able to contribute four electrons to the framework, as in the case of PH₃⁻, the four M-X bonding framework orbitals will be totally occupied and the framework electron count (FEC) is eight. If we analyze more carefully the shape of the four M-X bonding framework orbitals (2a-d), we may easily convince ourselves that no net M–M or X–X bonding interactions can be expected. The FEC = 8 case corresponds thus to the canonical situation of four localized M-X bonds, as found in cyclobutane.
Another interesting situation occurs when we consider XR₃ ligands, such as phosphine. In this case each bridging ligand can only contribute to framework bonding through its lone pair or radical σ-orbital. The net result is that we only will have two M-X bonding framework orbitals (aₙ and bₚ) and two non-bonding, metal centered orbitals (bₜₐ and bₚₐ). Filling the framework orbitals for this electron count (FEC = 6), leads to a net attractive M···M interaction across the ring since both orbitals are M···M bonding. This situation, four atoms sharing four electrons with delocalized bonding in the ring, is the same as in the archetypal diborane molecule.

An intermediate case is provided by L₄M₂(µ-XR₂)₂, with FEC = 7. By removing two electrons from the four bonding framework orbitals a net M···M or X···X interaction can be created. For this case two different minima appear in a plot of the energy as a function of the X-M-X angle, corresponding to geometries with either short M···M or X···X distances. For a more detailed account of the application of the framework electron counting rules to a large set of organometallic compounds, the reader is referred to the original formulation of these rules [5, 6].

Let us now try to apply the FEC rules to the basic Ni₃P₄, building units in BaNi₂P₄. A reasonable molecular model for these units can be obtained by taking two edge-sharing NiP₄ tetrahedra and saturating all the dangling bonds with hydrogen atoms to obtain the (PH₃)₄Ni₂(µ-PH₂)₂ compound shown in 3. That fixes the periphery of the model, but how many electrons should we have in the ring to represent properly the bonding situation found in BaNi₂P₄? If we consider that the barium atoms act merely as electron donors we are led to a -2 charge on the Ni₃P₄ subnet. One way to reach the appropriate electron count is to first complete the octet at each four-membered ring P. That would give a P₄⁺ (as in 4), or a Ni₃P₄⁺. Of course we have two electrons less, i.e. Ni₃P₄²⁻, indicating that each P is on average half electron short of an octet (or there is a half electron hole in the Ni 3d block, unlikely because of the tetrahedral coordination of typical four-coordinated Ni⁰). The result is that in the Ni₃P₂, ring the FEC is not 8, but 7. The appropriate model in which we replace the “terminal” P on each Ni by PH₃ and the bridging P by PH₂ is [Ni₂(PH₃)₄(PH₂)₂]⁺.

A plot of the energy as a function of the P-Ni-P angle (Fig. 3) has a single minimum at 98°, a value very close to that found in α-BaNi₂P₄ (99.3°). The intermediate situation
between FEC = 6 (double minimum) and FEC = 8 (single minimum, no interactions across the ring) is evident in the hump that is found in the energy curve for angles close to 80°, a feature which is a typical sign of level crossing. Analysis of bonding in the Ni₃P₄ rings (see Table 1) shows that, as expected, framework Ni-P bonding is weakened upon removing electrons, while weak Ni···Ni bonding interactions across the ring are only expected for the FEC = 6 case. The Ni···Ni distance of 2.92 Å found for the FEC = 7 case is significantly longer than twice the metallic radius of nickel. This, together with the negative Ni···Ni overlap population computed in this case, indicates that there is no Ni···Ni bonding in the present FEC = 7 case.

**Electronic structure of BaNi₄P₄**

The preceding discussion sets the framework for an analysis of the fascinating network in BaNi₄P₄. In this section we will turn our attention to the specific aspects of bonding in the two crystalline phases of BaNi₄P₄. We will proceed in two steps, starting with the electronic structure of a single chain of edge-sharing NiP₄ tetrahedra. After analyzing framework bonding for this relatively simple model, we will move to a more precise model for the solid phases, the 3D (Ni₃P₄)₂⁻ subnet.

**Framework bonding in a chain of edge sharing tetrahedra**

To identify the relevant bonding features in the complex solid state structure of BaNi₄P₄ consider the simple chain of edge-sharing tetrahedra shown in 5. The dangling bonds on the bridging phosphorus atoms have been saturated by hydrogen atoms. Again the electron count for the extended polymer is not obvious, but needs to be reasoned out carefully. The essential feature of the (Ni₃P₄)₂⁻ system in the full three-dimensional system is that each P bridging nickel atoms is not a closed octet (P₃⁻ or PH₂⁻), but rather is one half of an electron short per PH₂⁻. To get the same number of electrons per Ni₃P₄ ring as in the solid state compound we have to assign in this one-dimensional model to each unit cell a 2- charge, i.e. [Ni₃(PH₂)₄]⁻. The plot of the total energy of the chain as a function of the P-Ni-P angle (not shown) is practically identical to that found for the molecular model (Fig. 3), with a single minimum at 101.9°, close to the experimental value in α-BaNi₄P₄ (99.3°). For this experimental angle, both overlap populations and net charges on the P atoms are very close to the ones found for the molecular model with FEC = 7.

The analysis of the calculated density of states (DOS) curve and its atomic projections for this model structure (Fig. 4) allows us to identify three qualitatively different types of bands in the region around the Fermi level. The peak that appears between -15 and -16 eV is basically due to P-H bonding in the bridges. The projected DOS curve for the H atoms (not shown in the Figure) allows us to rule out important contributions of these atoms in the other regions of the DOS curve (except for high lying P-H antibonding bands), so that we can be confident that the atoms used for saturating the dangling bonds in our model are not introducing significant perturbations in Ni-P framework bonding.

The sharp peak at -14.5 eV is mainly due to the 3d orbitals of the Ni atoms; it is clear that our initial assumption of neutral Ni atoms with a d⁰ configuration is essentially correct. The wide band of levels stretching from -13.0 to -8.0 eV is basically built up by Ni 4s and 4p orbitals, together with important contributions from the phosphorus atoms. These levels may be identified with the framework orbitals discussed for our molecular model. A more careful analysis shows that the lowest lying framework bands, those coming from the a₄ framework orbital, appear in the same region as the 3d bands of nickel.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Ring geometry and overlap populations for the [PH₃]₃Ni₃[μ-PH₂]₃P⁻ model compound with different framework electron counts</th>
</tr>
</thead>
<tbody>
<tr>
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<td>n = 2</td>
</tr>
<tr>
<td>FEC</td>
<td>8</td>
</tr>
<tr>
<td>P-Ni-P (°)</td>
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</tr>
<tr>
<td>Ni-Ni (Å)</td>
<td>3.09</td>
</tr>
<tr>
<td>OP (Ni-P)</td>
<td>0.655</td>
</tr>
<tr>
<td>OP (Ni-Ni)</td>
<td>-0.071</td>
</tr>
</tbody>
</table>
The band structure for the model \([\text{Ni}_2(\text{PH}_2)_4]^2-\) chain is shown in Fig. 5a, where the framework bands have been highlighted. The same symmetry labels that were used for the molecular model have been adopted to indicate the framework orbital from which each band is derived. Notice, however, that because of the presence of a \(4_2\) screw-axis relating the two \(\text{Ni}_2(\text{PH}_2)_2\) rings in the unit cell, the framework orbitals of one \(\text{Ni}_2\text{P}_2\) ring combine in the same band with \(1t\)-type orbitals of the neighboring ring, as illustrated in 6 for the case of the \(b_{3u}\) band. Another consequence of the existence of a screw axis is seen in the dispersion diagram (Fig. 5a); the bands are doubled, presenting two branches that are degenerate at the edge of the Brillouin zone (Z point in Fig. 5a). In the case of the \(b_{3u}\) and \(b_{2g}\) bands, the band doubling cannot be appreciated in Fig. 5a because the two branches are degenerate along the \(\Gamma Z\) line. The Fermi level for this model structure is located at the point where the two \(b_{1u}\) branches meet, thus giving a half-filled framework band, which is consistent with a FEC of 7 per \(\text{Ni}_2(\text{PH}_2)_i\) ring. For later discussion it is important to realize that the \(a\) and \(b_{1u}\) bands are strongly dispersed because of their \(\sigma\) character along the chain direction (2), whereas the \(b_{3u}\) and \(b_{2g}\) band show little dispersion. A study of chains of edge-sharing tetrahedra present in the \(\text{AFeS}_2\) compounds (A = K, Rb or Cs) has been reported previously by Silvestre and Hoffmann [7]. However, that work focused on the partially filled metal 3d bands, which are less important in the present case in which the metal 3d bands are fully occupied (below \(-14\) eV in Fig. 5a).

The partially filled \(b_{1u}\)-type band in this 1D model immediately suggests a potential structural distortion of the Peierls type [8, 9]. Since this band is half-filled, a unit cell doubling distortion, such as the one found in the \(\alpha\)-\(\text{BaNi}_2\text{P}_4\) to \(\beta\)-\(\text{BaNi}_2\text{P}_4\) phase transition (1a-b), is in principle a good candidate for opening up a gap between the two \(b_{1u}\)-type branches. That in turn should result in a lowering of the system's total energy. The extent of the distortion can be monitored by a single parameter defined as the difference between the two P-Ni-P angles in the distorted chain, \(\Delta \alpha = \alpha_1 - \alpha_2\). (5). The effect of the distortion on the band structure of our 1D model is shown in Fig. 5 for two different values of \(\Delta \alpha\). Three important features should be noticed in these dispersion diagrams: (1) as expected, the distortion opens a gap at the Fermi level, separating the two \(b_{1u}\)-type branches; (2) the Fermi level is lowered by the distortion; and (3) the degeneracy of the \(b_{2g}\) and \(b_{3u}\)-type branches is removed by the distortion. As a consequence, one might expect that a Peierls distortion lies at the origin of the experimentally detected phase transition in \(\text{BaNi}_2\text{P}_4\). A more thorough analysis will show, however, that the situation is not so simple.

If one calculates the total energy of the system, the distortion is found to be destabilizing. Why is this happening? The answer can be found in the behavior of the \(b_{2g}\) and \(b_{3u}\)-type bands. When the degeneracy of their two branches is lifted by the distortion, the total energy of the system is increased. For these two bands the change in ring geometry favors M-P bonding in one of the two rings while weakening it in the other one (7a-b), resulting in the removal of degeneracy. The energy loss due to the destabilization of one branch is not compensated by the energy gain in the other branch, and the combined effect is energetically unfavorable. If one plots the contribution of each band to the energy change as a function of \(\Delta \alpha\) (as...
Table 2  Ring geometry and overlap populations for the undistorted (Δα = 0°) and distorted (Δα = 20°) [Ni3(PH2)4]z- chains

<table>
<thead>
<tr>
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<th>Δα = 0°</th>
<th>Δα = 20°</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-Ni-P (°)</td>
<td>99.3</td>
<td>109.3</td>
</tr>
<tr>
<td>Ni-Ni (Å)</td>
<td>2.88</td>
<td>2.58</td>
</tr>
<tr>
<td>OP (Ni-P)</td>
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<tr>
<td>OP (Ni-Ni)</td>
<td>-0.012</td>
<td>0.056</td>
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shown in Fig. 6) it is clear that the opening of the gap at the Fermi level is much smaller than the destabilization provided by the loss of degeneracy in the b2g- and b3u-type bands.

How does the distortion affect framework bonding in the Ni2P4 rings of our model? This question can be easily answered by examining the Ni-P and Ni···Ni overlap populations of the distorted chain (Table 2). The distortion localizes the occupied, stabilized b1u-type branch at the rings with long Ni···Ni distances and the empty, destabilized b1u-type branch at those with short Ni···Ni distances. The effect of this localization of the b1u-type band is an increased Ni-P overlap population and a decreased Ni···Ni overlap population for the rings with long Ni···Ni distances. Rings with short Ni···Ni distances experience just the opposite changes in their overlap populations. From the framework bonding point of view, the distortion corresponds to converting a chain of identical FEC = 7 rings into a chain of alternating FEC = 6 (short Ni···Ni distances) and FEC = 8 (long Ni···Ni distances) Ni2P4 rings.

The second major problem that one finds in accepting the Peierls distortion as the origin of the phase transition in BaNi2P4 is the validity of the ID model in representing the actual electronic structure of the BaNi2P4 crystals. In pseudo one-dimensional compounds (where Peierls-type distortions have been observed) the 3D crystal structure is built up from weakly interacting ID units that can be, to a first approximation, considered independently. As it has already been mentioned, this is not the case in BaNi2P4. In this compound the Ni2P4 chains are disposed in such a way that four phosphorus atoms belonging to four distinct chains form square P4 rings with short P-P bonds, an interaction that cannot be considered as weak. A careful investigation of the band structure of the complete Ni2P4z- sublattice is thus necessary before accepting (or rejecting) the Peierls' distortion hypothesis as the origin of the phase transition in BaNi2P4.

Let's be a little more specific about this. The polymer model we used was Ni8(PH2)10-. If we strip off the H's from the phosphido groups, we must take them off as protons, otherwise octets at P are not preserved. So we would claim that an appropriate model would be (Ni2P4)10- (H+)8. It is this model which would retain the essential electronic feature of the Ni2P4 rings, i.e. that they have 7 framework electrons per ring. The lower dimensional model of Keimes et al. is thus quite electron poor - this may be seen by comparing the filling of electrons in their 1D polymer, which is much less than in their (and our) 3D sublattice.

Band structure of the 3D (Ni2P4)z- sublattice

As found above for the 1D model, the calculated one-electron energy of the 3D sublattice (Ni2P4)z- does not decrease upon distortion (Fig. 7). Hence, the driving force for the distortion cannot be explained at the one-electron level, although Fig. 7 suggests that distortions of a few degrees in Δα require little energy. Let us recall that the distortion found in the experimental structure of β-BaNi2P4 corresponds to Δα = 7.5°, for which we calculate a
destabilization of only 0.13 eV (i.e., 3.0 kcal/mol or 12.5 kJ/mol). Similar results were obtained when the Ba$^{2+}$ ions were included in the calculation.

Even if the extended Hückel calculations do not allow us to unravel the driving force for the distortion, we can analyze those changes in the electronic structure and bonding which are related to orbital topology and symmetry and therefore well evaluated by such calculations. The band structure for the 3D (Ni$_2$P$_4$)$^2$ net in the high temperature α-BaNi$_2$P$_4$ phase is shown in Fig. 8a. The first feature evident in this dispersion diagram is the 3D metallic character of this compound, with a complicated Fermi surface arising from the crossing of the Fermi level by multiple bands in different directions of the first Brillouin zone. Clear evidence for the 3D character of this compound can be found in the $\Gamma$-X direction, perpendicular to the Ni$_2$P$_4$ chains. Interchain coupling through the P$_4$ rings in this direction is responsible for the important dispersion found for the bands near the Fermi level along this symmetry line. An important difference from the one-dimensional model studied above is that not only the $b_{1u}$, but also the $b_{3u}$ band crosses the Fermi level. Let us recall that the $b_{3u}$ orbital gave rise to a flat band in the 1D model (Fig. 5). Hence, it is interesting to analyze the differences between the band structures of the 1D model and the 3D α-structure along the chain direction (the ΓZ direction of the Brillouin zone). In Fig. 9 we have abstracted the levels corresponding to the $b_{1u}$ and $b_{3u}$ bands in that direction to simplify the discussion.

In order to understand the dispersion patterns of the $b_{1u}$ and $b_{3u}$ bands (Fig. 9) we must recall that there are two chains per unit cell and that they combine a framework orbital of one Ni$_2$P$_4$ ring with a π orbital of the neighboring ring, because of the presence of a screw axis. Hence, the number of bands is twice that found in the 1D model (Fig. 5), formed in-phase and out-of-phase combinations of the crystal orbitals of the two chains in the unit cell. Since the chains are connected through P-P bonds of P$_4$ rings, one of the $b_{1u}$ bands is stabilized, the other one destabilized as seen in Fig. 9. As for the $b_{3u}$ bands, there are three important differences with the one-dimensional model. First, these bands appear at higher energy as a result of changing its character from $\sigma_{PH}$ of the PH$_2$ bridging groups to $\sigma_{pp}$ of the...
Table 3 Ring geometry and overlap populations for the undistorted (Δα = 0°) and distorted (Δα = 20°) [Ni₂P₄]²⁻ solid

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<td>P net charge</td>
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Table 4 Atomic parameters used for the extended Hückel calculations

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<tr>
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</table>

P₄ rings in the 3D structure. In second place, as a result of the unit cell doubling, each of the b₃u bands (b₃u and b'₃u) is doubled giving rise to two branches. The lowest levels of these bands (1b₃u and 1b'₃u) at Δα = 20° are built up from in-phase combinations of the b₃u framework orbitals of one Ni₂P₂ ring in each of the two chains and are allowed by symmetry to mix with the π-bonding orbitals of the perpendicular Ni₂P₂ rings (8a). The highest levels (2b₃u and 2b'₃u) are out-of-phase combinations (8b) and mix with π² orbitals of the alternate rings. Finally, at the Z point the framework orbitals mix with π non-bonding orbitals (9), and the two branches are degenerate, resulting in the overall folded band aspect [9]. The partial filling of these bands can be roughly represented by an (a₉)²(b₁g)²(b₃u)²(b₁u) configuration (the numbers given are only for the purpose of illustration and should not be taken in a numerical sense) for the framework orbitals, consistent with the relatively long experimental through-ring Ni–Ni distance of 2.89 Å.

In the α-BaNi₂P₄ to β-BaNi₂P₄ phase transition, two different Ni₂P₂ rings result, one with short, another one with long Ni–Ni distance, labelled as A and B (10), respectively. Upon distortion, the band structure is modified (Fig. 8b), but no gap appears at the Fermi level. This result indicates that the distortion cannot be attributed to a Peierls effect, a result that could be anticipated from the strong three-dimensional character of the undistorted structure. The most salient changes in the band structure appear along the ΓZ direction close to the Fermi level, where the b₃u bands lose their degeneracy and are split in energy.

The effect of distortion 10 on the b₁u and b₃u bands along the ΓZ line is shown in Fig. 9, where the splitting of the b₃u set at Δα = 20° can be clearly appreciated. One of the two b₃u bands becomes mostly localized at the A rings (10), and is stabilized due to its σ(P···P) and π(Ni···Ni) properties. The other band, localized at the B rings (10) is destabilized. The overall effect is schematically shown in the block diagram 11. As a result, the band centered on rings A increases its population upon distortion, whereas the one centered on rings B is partially depopulated. The differences in electron population between the two types of Ni₂P₂ rings can be seen in the calculated charge for the corresponding P atoms (Table 3). An indirect result of all this is that the Fermi level is lowered and the population of the b₁u band also decreases. Although we have seen above that it is not appropriate to talk in terms of integer FEC numbers in the present case, one can clearly identify a trend towards a configuration of the type (a₉)²(b₁g)²(b₃u)²(b₁u) for the A rings and...
The 3D structure were severely distorted. Notice that the Ni–Ni distances in both rings (2.77 and 3.02 Å for rings A and B, respectively) are still relatively long, compared with those in binuclear complexes of tetrahedrally coordinated Ni with phosphido bridges with a FEC of 6 (2.50–2.56 Å) [10-13].

A consequence of the electron transfer from rings B to A is that the overall population of the framework bonding orbitals decreases upon distortion for B and increases for A. Hence, the Ni-P bonds are slightly but significantly longer in the B rings (2.240(2) Å) than the corresponding bonds in A (2.219(2) Å). All the trends in bond distances are nicely followed by the calculated interatomic overlap populations (Table 3).

Conclusions

In this work we have analyzed the electronic structure of the recently synthesized \( \text{BaNi}_2\text{P}_4 \) compound, in an attempt to understand the complicated bonding relations that hold together a complex 3D net of nickel and phosphorus rings. Special attention has been devoted to the experimentally detected phase transition that this compound undergoes at approximately 100°C.

Our results indicate that the basic structure of the \( \text{Ni}_2\text{P}_4 \) \(^2\)-subnet found in this compound can be rationalized by using a simple molecular model and applying the recently proposed framework electron counting rules. These qualitative rules can be applied consistently to the \( \text{Ni}_2\text{P}_4 \) rings found in both the high and low temperature structures of \( \text{BaNi}_2\text{P}_4 \). Different through-ring Ni–Ni distances in the two non-equivalent \( \text{Ni}_2\text{P}_4 \) rings found in the low temperature \( \beta\text{-BaNi}_2\text{P}_4 \) phase can be rationalized from the filling of the framework bonding bands.

Although a simple 1D model suggests the appealing hypothesis of a Peierls distortion as the origin of the phase transition in this compound, a careful examination of the electronic structure of \( \text{BaNi}_2\text{P}_4 \) makes it clear that the Peierls distortion mechanism is not responsible for the observed deformation. Instead, \( \text{BaNi}_2\text{P}_4 \) is predicted to be a 3D metal in both its high and low temperature phases. The driving force for the distortion cannot be explained at the one-electron level of theory, although the difference in the calculated energies for both phases is small. Hence, two-electron effects or entropic factors might be at the origin of the phase transition.

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Appendix

Computational details

All the molecular orbital calculations were of the extended Hückel type [14, 15] and all band structure calculations presented in this work were obtained by using the extended Hückel tight-binding method [15-17]. The off-diagonal elements of the Hamiltonian matrix were evaluated with the modified Wolfsberg-Helmholz formula [18], Extended Hückel computations were performed using the YaeHMOP package [19]. The atomic parameters used in these calculations are shown in Table 4. The geometries adopted for the model compounds were as follows: \( \text{PH}_4 \) groups were used for the molecular model as terminal ligands, with Ni-P = 2.227 Å and P-H = 1.350 Å and with tetrahedral angles. The bridging groups \( \text{PH}_3 \) were used with Ni-P = 2.227 Å (experimental value for \( \alpha\text{-BaNi}_2\text{P}_4 \)) and P-H = 1.350 Å, and were oriented preserving a \( D_2h \) symmetry for the \( \text{Ni}_2\text{P}_4 \) core for the molecule and chain models, with H-P-H = 109.5 degrees.

References