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Electronic structure and properties of the Fermi surface of the superconductor LaOFeP

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The electronic structure of the superconducting material LaOFeP is investigated by means of *ab initio* calculations using density functional theory. The concept of two-dimensional building blocks as well as Bader analysis are used to obtain more insight about the charge transfer in this layered material. The band structure and the Fermi surface are presented in order to be compared with future experiments. It is found that the intralayer chemical bonding present a significant part of covalency, whereas the interlayer bonding is almost completely ionic. Also, four sheets of the Fermi surface have a significant two-dimensional character.

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I. INTRODUCTION

Since its discovery almost one century ago, superconductivity has always been considered as an extraordinary phenomena, challenging the scientific community through amazing discoveries. Among the breakthroughs made over the last five years, we can cite the superconductivity up to 39 K of magnesium diboride,[1] the unexpected coexistence of ferromagnetism and superconductivity in $ZrZn_2$,[2] the fact that lithium becomes a superconductor under extreme pressures,[3,4] or the surprising superconductivity of $PuCoGa_5$.[5] Not the less important finding is the observation of charge stripes[6,7] for copper-oxide superconductors. All these novelties, together with those made before, are pushing the existing theories to their limits and calling for more efforts on this side. Until now, various degrees of success have been reached: for example, the mechanism involved in MgB_2 is well understood,[8,9] but the one ruling unconventional superconductors has not reached a consensus among scientists. Therefore the discovery of a new superconductor always has a large impact in the condensed matter community since it provides a playground to test existing theories; the first step being to understand the electronic structure using available tools.

Recently, the iron-based layered material LaOFeP has been identified as a superconductor[10] with a critical temperature (T_c) of 3.2 K. Although this low value of T_c prevents it from being used in view of practical applications, the understanding of its electronic properties is interesting by itself in order to obtain insight into the superconductivity mechanism. It is precisely the purpose of this publication to present results concerning *ab initio* calculations on this material. The article is organized as follows: after brief descriptions of the crystal structure and of the computational details, the calculated electronic structure (band structure, density of states, and Fermi surface) of LaOFeP is presented. To have a better understanding of the bonding in this layered material, the concept of two-dimensional (2D) building blocks[11–14] is used together with a Bader analysis[15,16] of the charge density. In the last section of the paper, we offer our conclusions and perspectives.

II. CRYSTAL STRUCTURE

LaOFeP crystallize in a tetragonal layered structure[17] (of the $P4/nmm$ symmetry) made of alternating LaO and FeP layers stacked along the c axis, as presented in Fig. 1. The crystal structure is therefore rather simple with eight atoms (two formula units) in the cell and two internal parameters for the position of the La and Fe atoms. In this geometry, the Fe atoms are coordinated by four P atoms in a distorted tetrahedron geometry, two different P-Fe-P bonding angles being observed in the x-ray diffraction experiments.[10,17] Also, the lanthanum atoms are surrounded by four P atoms and four O atoms in a distorted square antiprism, while the oxygen atoms have four La neighbors arranged in a tetrahedron.

III. COMPUTATIONAL DETAILS

To calculate the relevant quantities, we have used density functional theory (DFT)[18,19] in the framework of the projector augmented waves method[20] as implemented in the code VASP (Vienna *ab initio* simulation package).[21,22] The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof[23] variant was used for the exchange-correlation potential. To ensure convergence of the relevant quantities, a cutoff of 600 eV was used for the plane-wave expansion of the wave function. For Brillouin zone integrations, a mesh of 12×12×6 k points[24] was used within the modified tetrahedron method.[25] The lattice parameters as well as internal positions have been chosen to be those de-

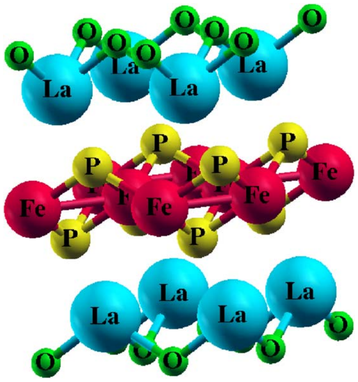

FIG. 1. (Color online) The crystal structure of LaOFeP showing the layered structure LaO-FeP.

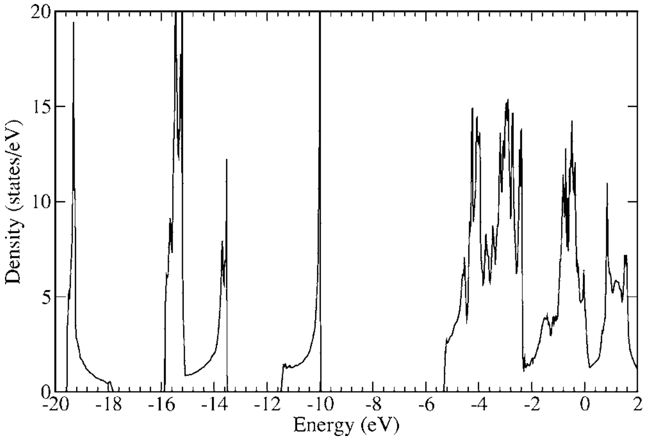

FIG. 2. Total density of states for LaOFeP. The Fermi level is set to 0 eV.

termined experimentally[10] (a=3.964 Å and c=8.512 Å). Also the 5s and 5p electrons of lanthanum have been included as valence states during our calculations.

IV. NUMERICAL RESULTS AND DISCUSSION

In Figs. 2 and 3 the total and partial density states (DOS, PDOS) projected on each atomic species are represented. The total DOS shows alot of structures that can be better understood by looking at the PDOS. From −2 eV to 2 eV the Fe 3d states represent the main contribution to the DOS, together with a contribution from P-p states. For states ranging from −2 eV to −6 eV in energy, all the species are contributing to the DOS, whereas only Fe and P states are responsible for the structure around −11 eV. At high binding energy (−14 eV to −20 eV), the DOS is exclusively made from electronic states of the LaO entity (mainly La-p states together with O-s states, the La-5s states being deeper in energy and are not represented here). The fact that the states at the Fermi level are derived from the FeP block confirms the experimental hypothesis[10] that carriers flows in the 2D FeP layers.

Also, it is noticeable that the La and O atoms are linked not only by a ionic interaction, but also by an important part of covalency: the PDOS of lanthanum and the PDOS of oxygen share common structures around −19 eV, −14 eV, and from −3 to −5 eV, which obviously come from a covalent interaction between the two atoms. The same conclusion can be reached for the Fe and P atoms, which present similar features in their PDOS around −10 eV and around −3 eV. LaOFeP is therefore far from being a purely ionic solid as could be expected at first sight. A weak covalent interaction between the La and the P atoms also exists, as can been seen by the finite value of the La PDOS around −10 eV corresponding to a hybridization with the P-s states. This La-P hybridization can also possibly be seen around −3 eV in their respective PDOS, although it is more hypothetical since all the atoms are contributing to the DOS at this energy.

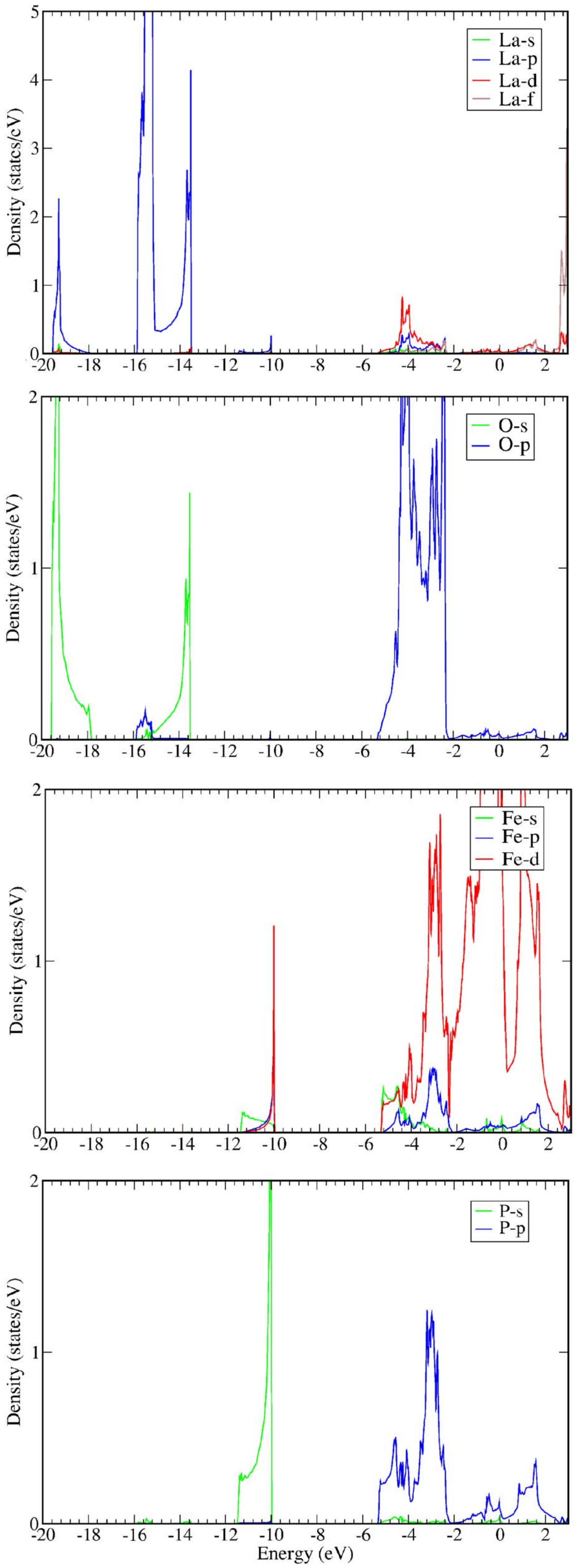

FIG. 3. (Color online) Partial density of states for each atomic species of LaOFeP. The Fermi level is set to 0 eV.

A useful concept to understand the electronic structure of layered systems is the building block concept.[11–14] It permits one to understand the electronic structure of a solid by computing separately the electronic structure of each block that it is made of, and then studying how charge transfer and hybridization effects will alter their properties when building

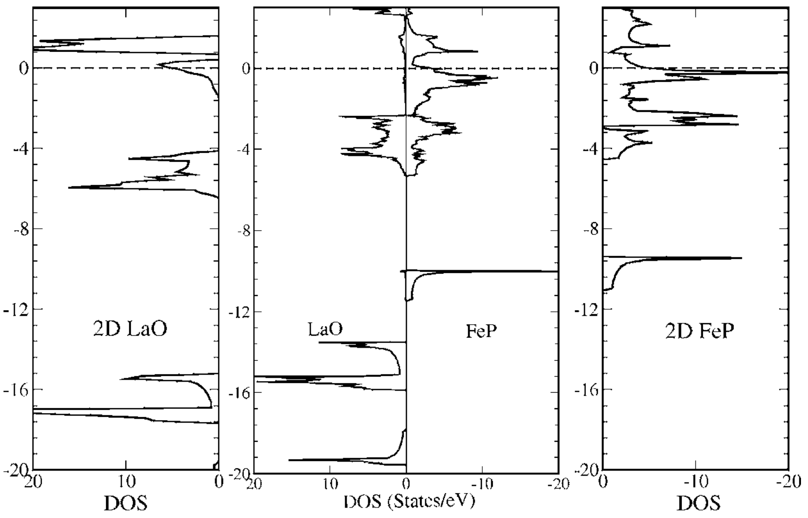

FIG. 4. Comparison of the DOS of the LaO (left) and FeP (right) blocks calculated as isolated entities with the PDOS for LaO (center left) and FeP (center right) in the LaOFeP solid.

the solid from these separated blocks. Therefore, we have calculated the electronic structure of periodic LaO and FeP blocks for the same geometry as in the solid LaOFeP, the corresponding results being presented in Fig. 4. The left and right plots represent, respectively, the DOS of the isolated LaO and FeP blocks, whereas the central diagram represents the PDOS of the LaO and FeP within the solid. When comparing the DOS of the isolated LaO block together with the corresponding one embedded in the solid, we notice that the LaO states are pushed up in energy by approximately 2 eV: the isolated LaO layer is metallic but transfers electrons to the FeP layer to become insulating in the solid. These electrons are transferred to regions that are not covered by the spheres used for the PDOS integration since the position of the Fermi level does not change much for the FeP entity when changing from the isolated layer to the solid. Therefore, we conclude that the LaO-FeP interaction is strongly ionic since the PDOS of LaO and FeP in the solid are very similar to the DOS of their respective 2D counterparts.

In order to further quantify the charge transfer between the two layers, we performed a Bader analysis[15,16] of the charge density. Within this formalism, the gradient paths of the electronic density terminating at an atom define a basin for this particular atom. Then by integrating over each basin, the charge which belongs to the corresponding atom is obtained. The obtained results are presented in Table I and compared with results obtained by integrating the charge within a sphere (the radius is taken to be the one provided as a default by the code) and also compared to the charge for the corresponding purely ionic solid. First, we see the usefulness of the Bader analysis in comparison with an integration over spheres: since it is not possible to cover the whole cell with spheres without making them overlapping, a given amount of electrons (corresponding to the part of the cell not covered by spheres) is always missing (the sum of all charges should be 30). Also in this case the numbers are dependent on the sphere radius and therefore the charge belonging to an atom cannot be given without ambiguity. This results in a large difference between the numbers of the left column and of the central column. Moreover, our previous analysis using the PDOS to determine the balance between covalency and ionicity in LaOFeP is confirmed by the Bader analysis: the La-O and Fe-P bonds differ considerably from ionic ones, whereas the bonding between the LaO and FeP blocks is mostly ionic since the value of the integrated charges almost reach the ones of a perfect ionic solid. The remaining 0.36 electrons probably reflects the La-P covalent interaction noticed before.

In Fig. 5, we show our calculated band structure along some high-symmetry directions computed with the method outlined above. In this range of energy (−2 eV to 2 eV, the

TABLE I. Electronic charges belonging to each atomic specie obtained by various schemes. Left column: integration within a sphere around each atom. Central column: charge obtained from Bader analysis. Right column: charge for a purely ionic solid.

Species	Int. spheres	Bader	Purely ionic
La	8.63	9.05	8 (La^{3+})
O	5.04	7.31	8 (O^{2-})
Fe	7.35	7.59	6 (Fe^{2+})
P	2.49	6.05	8 (P^{3-})
LaO	13.67	16.36	16 (LaO^{+})
FeP	9.84	13.64	14 (FeP^{-})

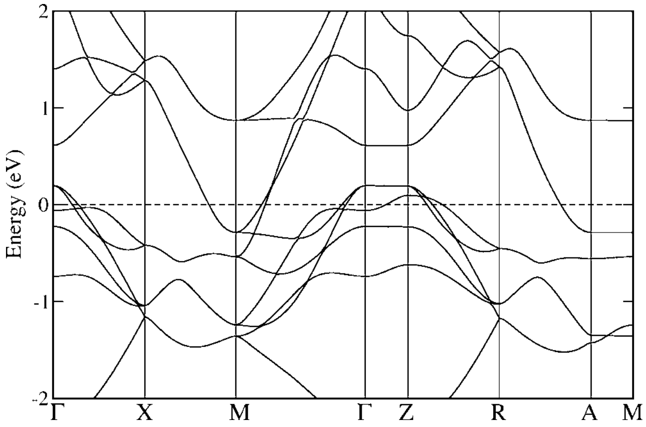

FIG. 5. Calculated band structure of LaOFeP. The Fermi level is at zero energy and is marked by a horizontal dashed line.

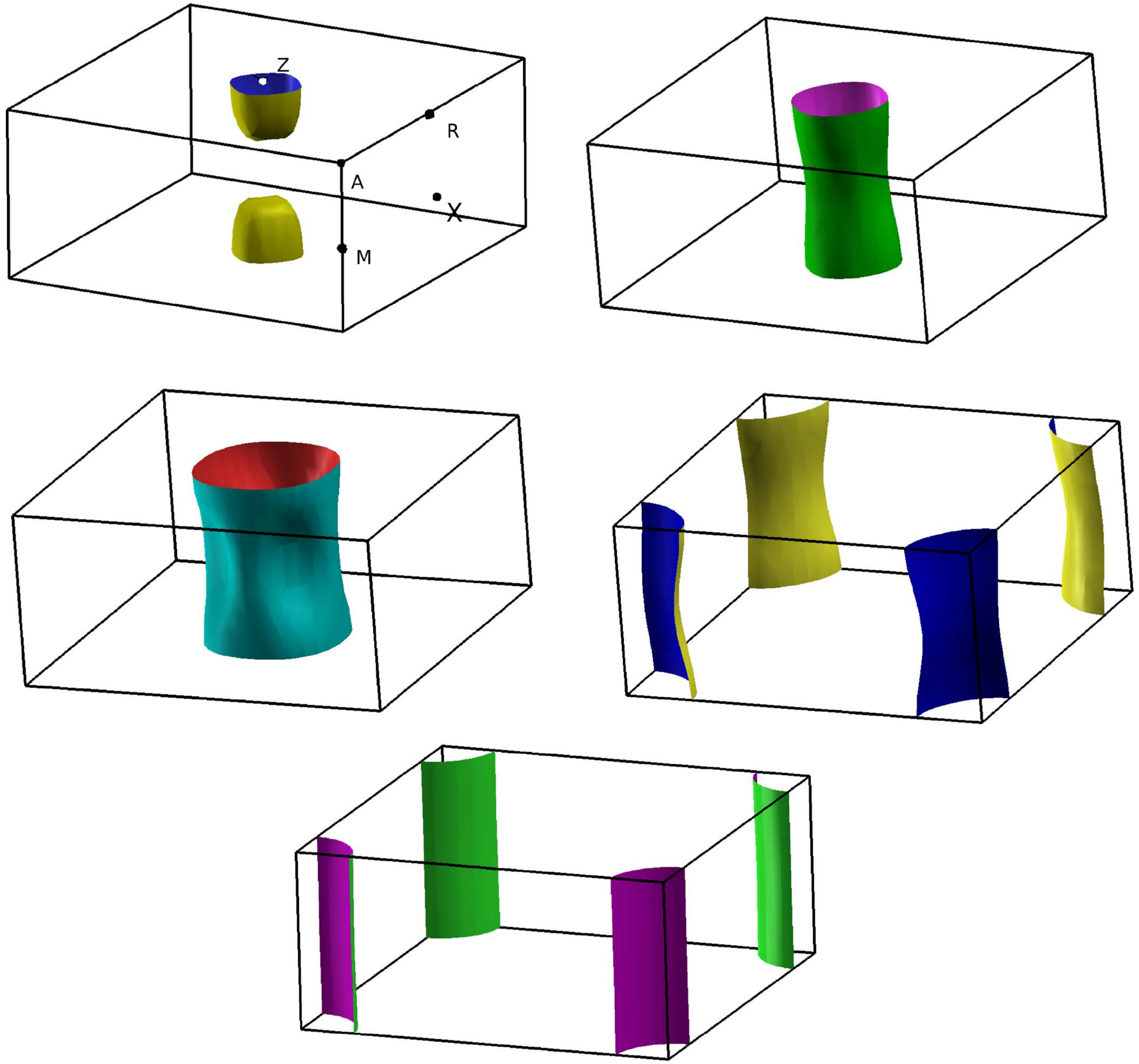

FIG. 6. (Color online) The Fermi surface of LaOFeP, shown in the first Brillouin zone centered around the Γ point.

Fermi level being at 0 eV), the bands are made of Fe states together with a contribution from P states, as seen on the PDOS plots. The main distinguishable features are the flat bands along the $\Gamma-Z$ and $A-M$ high-symmetry directions, which originates from quasi-two-dimensional electronic states (derived from Fe-d_{xy} and Fe-$d_{x^2-y^2}$ orbitals) and are responsible for the peaks in the DOS. However, bands showing a significant dispersion are also present along the same directions, being derived from Fe-d_{xz} Fe-d_{yz}, and Fe-d_{z^2} orbitals.

Since electrons close to the Fermi level are primarily responsible for superconductivity, the Fermi surface (FS) is a key quantity to understand the electronic structure of any metallic material. Fermi surfaces can be probed, for example, using de Haas van Alphen (dHvA) experiments. In this case, the precise determination of the shape of the FS relies on models using simplified geometries to interpret the magnetic field angle dependency of the measured frequencies, but the true shape of the FS can of course be much more complex. Therefore we computed the FS of LaOFeP using the *ab initio* method outlined above. The results are presented in Fig 6. The Fermi surface of LaOFeP is made of five sheets (five bands are crossing the Fermi level as shown by Fig. 5), four of them being cylindrical-like sheets parallel to the k_z direction (two are centered along the $\Gamma-Z$ direction while the two others are centered along the $X-R$ high-symmetry line); the fifth sheet (which is shown at the top of Fig. 6) consists of a distorted sphere centered at the Z high-symmetry point. This spherical sheet corresponds to the band crossing the Fermi level along the $\Gamma-Z$ direction (see the band structure plot

Fig. 5), while the cylindrical shape of the remaining sheets is connected with the two dimensionality of LaOFeP.

Therefore, we can expect the following behavior for the measured dHvA frequencies: there will be four main branches following a $1/\cos\theta$ dependence (where θ is the angle between the magnetic field and the [001] direction) and one branch being approximately constant in function of θ (because a perfect spherical sheet would give a strictly constant behavior). Also, since dHvA frequencies are corresponding to extremal cross-sectional areas of the FS, the branches corresponding to the second, third, and fourth sheets should become divided in two since the corresponding cylinders appear to have two extremal cross-sectional areas. The fifth sheet is very close to a perfect cylinder and therefore the corresponding branch will not appear as doubled in the experiment.

From our calculation, it appears that the superconductivity is primarily associated with electrons of the FeP entity since these states dominate the DOS near the Fermi level. To obtain more insight about the superconductivity mechanism, one can raise or lower the Fermi level by performing doping and then observe, for example, the effect on the critical temperature. This was actually done at the same time as the initial discovery about the superconductivity in LaOFeP:[10] La($O_{0.94}F_{0.06}$)FeP was also synthesized, and it was observed that the additional electrons lead to a significant increase of the transition temperature. This effect can indeed also be observed from our calculations: in a rigid bands picture, shifting the Fermi level for the DOS presented in Fig. 2 will increase the number of states at E_f and therefore increase the transition temperature between normal and superconducting behaviors, in agreement with experiments.[10] Whether the superconductivity of LaOFeP is associated with the iron or the phosphorous sublattice (or both) is more difficult to say since both are contributing to the DOS around the Fermi level.

V. CONCLUSION

In this article, we have reported calculations on the electronic structure of the superconducting material LaOFeP. Our main conclusions concern the covalency of the Fe-P and La-O bonds in opposition to the ionicity of the LaO-FeP interaction, together with the two-dimensional shape of four sheets of the Fermi surface.

Finally, we hope that our investigations will stimulate further experimental work on LaOFeP and related compounds. In particular, our calculated band structure can be compared with angular-resolved photoemission spectras and the Fermi surface can be probed by dHvA experiments. Also, it would be interesting to study both theoretically and experimentally related materials that can be obtained by replacing the La, Fe, and/or P atoms[10] in LaOFeP. This could open the path for a whole new family of superconductors, possibly with higher critical temperatures and properties different from the ones of LaOFeP studied here.

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