

***Ab initio* electronic and geometrical structures of tripotassium-intercalated phenanthrene**P. L. de Andres,^{1,*} A. Guijarro,² and J. A. Vergés³¹*Donostia International Physics Center (DIPC), Paseo Manuel Lardizabal 4, E-20018 San Sebastian, Spain*²*Departamento de Química Orgánica and Instituto Universitario de Síntesis Orgánica, Universidad de Alicante, San Vicente del Raspeig, E-03690 Alicante, Spain*³*Departamento de Teoría y Simulación de Materiales, Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco, E-28049 Madrid, Spain*

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The geometrical and electronic structure of tripotassium doped phenanthrene, $K_3C_{14}H_{10}$, has been studied by first-principles density-functional theory. The main effect of potassium doping is to inject charge in the narrow phenanthrene conduction band, rendering the system metallic. The Fermi surface for the experimental x-ray unit cell is composed of two sheets with marked one- and two-dimensional character respectively.

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I. INTRODUCTION

There is much interest in the properties of polycyclic aromatic hydrocarbons (PAHs) due to their remarkable potential in a number of fields including electronic devices, energy storage, molecular recognition, etc. Phenanthrene ($C_{14}H_{10}$) is one of the smallest molecules of that family with very interesting electronic properties derived partly from its “armchair” edge termination, as opposed to the “zigzag” termination characteristic of the Acene family (e.g., anthracene, with the same molecular formula). These two different terminations have profound effects in the limit of very large PAHs (i.e., graphene nanoribbons) since anthracene-like strips of material are metallic while phenanthrene-like strips can be either metallic or semiconducting depending on their widths.^{1,2} Furthermore, organic crystals based in different PAHs show an amazingly large number of useful properties that can be easily tuned by the addition of appropriate contaminants. A recent example is the discovery of a whole new family of organic high- T_C superconductors when doped with alkali metals, as reported from experiments in picene,³ phenanthrene,⁴ and most recently coronene.⁵ Interestingly enough, it has been suggested that the superconducting temperature increases with the size of the molecule forming the solid, which, if finally proved, should make these materials of considerable interest.⁴

In an effort to understand these challenging experimental reports, a number of theoretical papers have investigated the nature of pristine and doped related molecular crystals, mostly for picene,^{6–10} but also for pentacene¹¹ and coronene.¹² In this paper, we undertake the theoretical study of tripotassium intercalated phenanthrene ($K_3C_{14}H_{10}$) that has been very recently reported to become superconductor with $T_C = 5$ K.⁴ The mechanism for superconductivity is not yet clear, but a dependence of T_C with external pressure has been found that hints to a nonconventional type of superconductor. To elucidate these questions, it is of paramount importance to gather information about the geometrical and electronic structure of the material, which is the main motivation for this work.

II. METHODS

Theoretical calculations for model systems of interest have been performed using *ab initio* density-functional theory

(DFT).¹³ Wave functions have been expanded in a plane-wave basis up to a cutoff of 680 eV and were sampled on a Monkhorst-Pack $5 \times 7 \times 5$ mesh inside the Brillouin zone. Electronic bands were obtained using a smearing width of $\eta = 0.01$ eV. Carbon and hydrogen atoms have been described by accurate norm-conserving pseudopotentials.¹⁴ For the exchange and correlation (XC) potential, the local density approximation (LDA)^{15,16} has been chosen because of the following reasons: (i) It has been successfully used to describe a large variety of carbonaceous materials; in particular, it describes reasonably well the equilibrium configuration of graphite (unlike GGA that fails to give a reasonable interlayer distance), diamond, the energetic equilibrium between graphite and diamond, and it has been successfully used in many studies of graphene layers, nanotubes, etc. (ii) It yields C-C and C-H distances for many organic molecules within $\sim 2\%$ error or less (e.g., benzene, pentacene, C_{60} , picene, coronene, anthracene, etc., but in particular and most relevant for this work, phenanthrene). (iii) It yields the lattice constant for bcc K within $\sim 5\%$ error, and it brings an appropriate description for the electronic structure of alkali metals. (iv) Finally, it describes reasonably well organic crystals of interest, in particular it yields the phenanthrene unit cell parameters within $\sim 5\%$. Indeed, LDA has been the approximation of choice in many of the *ab initio* DFT studies for these systems so far.^{6,9,10,12,17,18} We notice that in all those examples, LDA yields shorter bond lengths and tends to overestimate binding energies if compared with experimental results, while other approaches, e.g., GGA, tend to result in larger distances and underestimate the interaction. Generally speaking, a local density approximation is conceptually clear and robust, bringing a good compromise between accuracy and computational effort, yielding physically motivated conclusions. Total energies were computed with the CASTEP program,¹⁹ as implemented in Materials Studio.²⁰

III. RESULTS

A monoclinic unit cell (UC) displaying a $P2_1$ symmetry and including two phenanthrene molecules in the basis has been set up with parameters derived from an x-ray analysis (Ref. 21, Fig. 1). Using the formalism and the parameters described

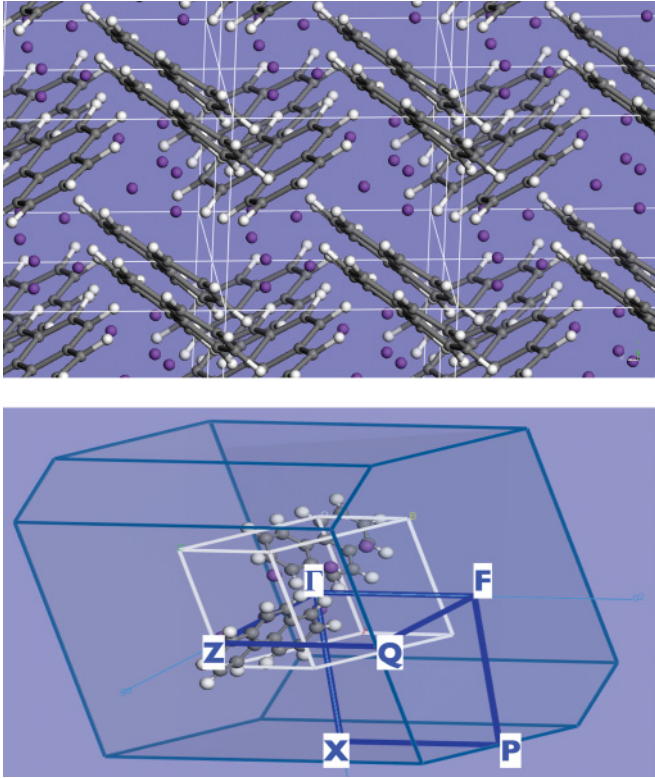


FIG. 1. (Color online) (a) Optimized geometry structure for K_3 doped phenanthrene (upper panel). (b) Brillouin zone with the selected path for the band structure calculation shown in Fig. 2 (lower panel).

above, this system can be optimized to minimize residual forces and stresses. The calculation has been considered converged when the maximum stress on the unit cell has been ≤ 0.2 GPa, the maximum force on any of the atoms on basis in the unit cell has been ≤ 0.02 eV/Å, and the maximum change of the total energy has been ≤ 0.0001 eV. The efficient BFGS method has been used to explore the huge configurational parameter space.²² Convergence against the energy cutoff and the k -points mesh confirm that the enthalpy is accurate to at least 0.01 eV/atom (fractional accuracy is $\approx 0.0001\%$); all these convergence criteria are enough for our purpose of identifying candidate local minima for the structure, and for interpreting the associated electronic structure. The equilibrium unit cell parameters are: $a = 8.46$, $b = 6.16$, $c = 9.47$ in Å, and $\beta = 97.7^\circ$, $\alpha = \gamma = 90^\circ$. These values show (with respect to the x-ray experimental determination²¹) fractional errors of -5% , -3% , and -3% for a , b , and c , respectively. Similarly to the well-known case of graphite, a gradient generalized approximation to the exchange and correlation brings larger errors, in particular 13%, 8%, and 7%, respectively. The optimization of the unit cell to retire residual stress yields a -0.22 eV/unit cell improvement in the total energy. Most of the atomic coordinates in the phenanthrene molecules forming the unit cell basis agree quite well with the experimental ones (i.e., ± 0.05 Å. We notice that different published experimental determinations of the crystal could differ by $\approx \pm 0.02$ Å). The exception comes from the four H atoms participating in the CH- π interaction

between first-neighbors molecules; the theory-to-experiment difference goes up to 0.18 Å. This is not at all surprising, since we are bound to compare a theoretical calculation performed at $T = 0$ K with an experimental structural determination at room temperature where the thermal vibrations should affect more to light atoms like hydrogen, especially if they form part of a weak bond keeping together the two molecules in the unit cell. Finally, the average angle between the planes containing the two molecules stays within 2° of the experimental value. Therefore, these results for pristine phenanthrene confirm the adequacy and set the accuracy of the proposed formalism.

Experimental analysis of the $K_3C_{14}H_{10}$ -doped crystal shows a contraction of the unit cell in the \vec{b} and \vec{c} directions, an expansion in the \vec{a} direction, and a small increase in the angle β . The unit cell volume is overall decreased by -3.5% . From a theoretical point of view, however, intercalation of three potassium atoms creates an internal stress that results in an increase of the unit cell volume by $+9\%$, with a corresponding gain in energy of -0.91 eV/cell. Since the interesting effects are expected to be associated with the basic 2D character of the material, it might be interesting to notice that such an increase is not evenly distributed in the three crystallographic directions; the theoretically predicted area $a \times b$ only increases by $+2\%$, while the increase in c is responsible for the rest. We remark that the theoretical description in the c direction should include long-range interactions that would, however, render *ab initio* self-consistent calculations too costly (this scenario would turn even worse for large molecules). GGA cannot explain the decrease of the unit cell volume, in fact the GGA volume increases by $+37\%$. A crude hard-sphere model for K would predict an increase of the unit cell volume by $+40\%$ to include six interstitial K atoms in the unit cell; this is clearly not a realistic value but nonetheless it explains a positive increase of the volume, not a decrease. To the best of our knowledge, there is not a sensible theoretical explanation for the reported decrease of volume after potassium intercalation. The best x-ray analysis for the doped material was unable to yield a reliable structural determination with the positions of the atoms in the unit cell basis, therefore the particular positions of interstitial potassium, or even the exact stoichiometry in the unit cell, has not been experimentally resolved, and the best we can do is to try different candidates to investigate the one corresponding to the minimum total energy and lower stresses and forces. According to our previous experience with the related system tripotassium-intercalated picene, we have started the optimization of geometrical structures by locating potassium atoms over the hollow positions on the carbon rings forming the molecule. Subsequent geometrical optimization allows all the atoms to relax to the nearest local minima by using an efficient quasi-Newton method. Taking for granted that the x-ray experimental analysis faithfully reproduces a decrease of the volume upon intercalation of potassium, we have explored whether a smaller amount of interstitial atoms could explain this fact—without success. Therefore, our structure should represent, in the worst case, a local metastable minimum intervening with some weight in the appropriate thermodynamical average at a given T . Notice that in all cases the forces on all the atoms in the unit cell have been minimized as explained above. This is the same

course of action as taken before for potassium-doped picene and coronene, and it seems a reasonable one to gather further knowledge on these materials.^{8,12}

We compute the electronic band structure along a selected path on the Brillouin zone (Fig. 1). Our LDA calculation yields for the phenanthrene crystal a direct gap at Γ of 2.75 eV, to be compared with an experimental one of 3.16 eV.^{2,23} Furthermore, we compute a cohesion energy for the crystal of -1.7 eV/cell (with respect to a gas of single phenanthrene molecules), that may be compared with an experimental value (STP) of -1.83 eV/cell.²⁴ Finally, we estimate the CH- π interaction between two molecules as -0.26 eV (attractive). For the experimental x-ray determined unit cell, the important features in the band structure come from the four bands at the top of the valence band and the four bands at the bottom of the conduction band. As has been discussed in similar systems, these show a strong molecular character with weak overlap, and are related to the HOMO and HOMO-1 and LUMO and LUMO + 1 molecular orbitals respectively.¹² The main effect for the crystal intercalated with potassium, $K_3C_{14}H_{10}$, is an effective doping of the conduction band that renders the system metallic (Fig. 2), while the residual stress on the unit cell plays to slightly increase the width and to modify the shape of a few bands near the Fermi energy (Fig. 3); this is most clearly seen in the Fermi surface pictures below. Our calculations show that there is an important charge transfer from the alkali atom to the organic molecules, and the Fermi energy is located in the middle of a narrow band of 0.5 eV width that becomes responsible for the metallic properties of the doped material.

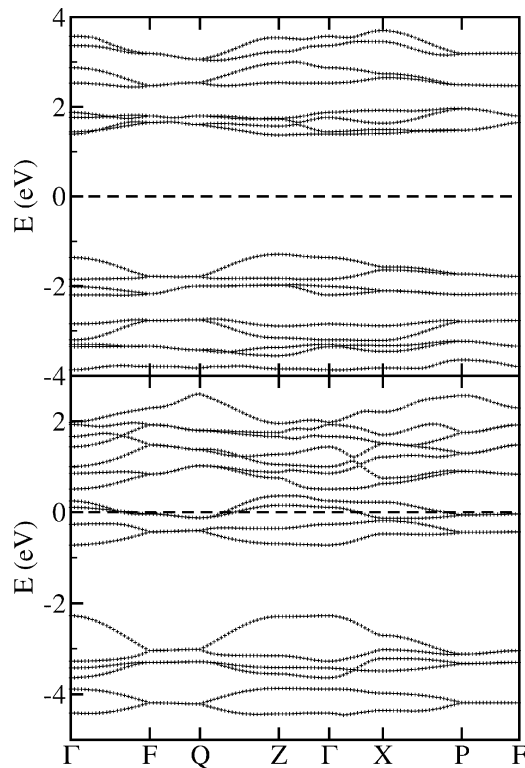


FIG. 2. Upper panel: Band Structure for the phenanthrene crystal. Lower panel: Electronic structure for the K_3 doped crystal corresponding to the x-ray structural determination⁴. The Fermi energy has been taken as origin for energies (dashed lines).

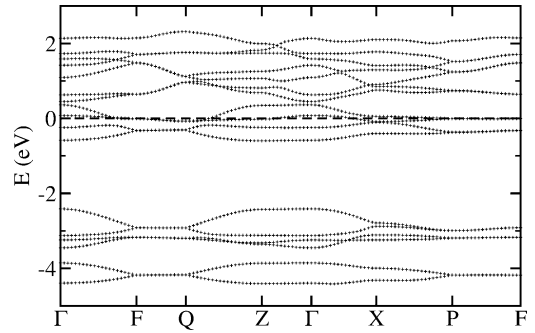


FIG. 3. Band structure for the relaxed structure of the K_3 doped crystal where the unit cell has been optimized to remove stress ($S_{\max} \leq 0.2$ GPa (all symbols as in Fig. 2)).

This band might be sensitive to correlation effects that should be analyzed in a different framework.

The experimental unit cell used for the band structure calculation, however, is under an approximate isotropic pressure of 3 GPa in the present formalism. As the T_C of this material seems to be sensitive to external pressure, we have checked the effect of removing the stress by letting the unit cell relax to a stable equilibrium condition. As the unit cell increases slightly in volume, it decreases the hybridization between the LUMO orbitals of both molecules, and the conduction band crossing the Fermi energy becomes less dispersive. However, no big changes are observed along the chosen path to represent the bands. The Fermi surface, on the other hand, is more sensitive to stress: We have compared the results for the relaxed and unrelaxed unit cells in Fig. 4. The *ab initio* self-consistent Fermi surface has been obtained on a denser Monkhorst-Pack grid in the irreducible part of the Brillouin zone (280 k points), and it has been drawn using XCrysDen.²⁵ A two sheet Fermi surface has been obtained: For the x-ray derived UC, one of the sheets is nearly planar and hints to the strong one-dimensional character of states involved in the metallic conduction on this material. The other sheet is nearly cylindrical and reveals a more two-dimensional character (Fig. 4). After relaxing the unit cell, the planar sheet changes very little, but the cylindrical-like shape becomes a spheroid where the BZ boundaries are now not touched and

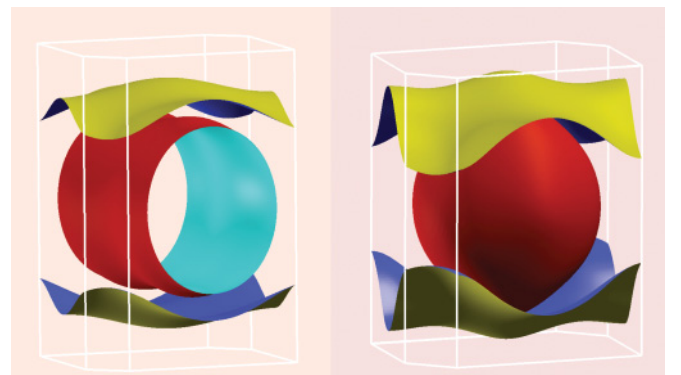


FIG. 4. (Color online) For the doped phenanthrene crystal, the Fermi surface corresponding to the x-ray determination (left panel) is compared to the one related to the relaxed unit cell (right panel).

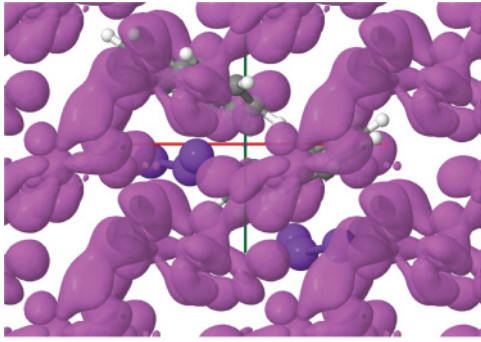


FIG. 5. (Color online) Iso-density corresponding to the four bands nearest the Fermi energy inside the unrelaxed unit cell.

the corresponding gaps occurring near the Fermi energy are closed.

The spatial distribution of electronic density²⁶ confirms the above picture: We draw in Fig. 5 surfaces of iso-density that integrate the four relevant bands close to the Fermi energy. We observe the build-up of extended metallic states based in the overlap of π -like orbitals originating from both phenanthrene molecules. This is consistent with our image of an important

charge transfer from potassium to phenanthrene to build the metallic phase.

In conclusion, we have studied the geometrical and electronic structure of the clean and potassium-doped phenanthrene crystal. The main effect of doping is the population of the phenanthrene conduction band making the system metallic. According to our calculations, the new metallic state is basically related to properties of phenanthrene molecular orbitals. The experimental determination of the UC by x-ray diffraction techniques implies stress since the volume is predicted to shrink by $\approx 3\%$ with respect to the pristine crystal, while all the theoretical models tried have resulted in an expansion of the unit cell volume upon potassium intercalation. The Fermi surface under stress shows a low-dimensional character that can be transformed by allowing the UC to deform to a global equilibrium shape.

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²⁴Only meant as a crude check of the accuracy of the theoretical formalism since experimental values (from NIST database) refer to standard conditions, while theoretical data is for $T = 0$ K and $P = 0$ GPa (no attempt to correct for zero-point vibration has been made), [<http://www.nist.gov/>].

²⁵The Fermi surface has been drawn using XCrysDen [<http://www.xcrysden.org/>].

²⁶To draw the electronic density, we use the program check2xsf by M. J. Rutter [<http://www.tcm.phy.cam.ac.uk/mjr/vis/>].