Electronic and Geometrical Structure of Potassium doped Phenanthrene

P.L. de Andres *,1 A. Guijarro,2 and J.A. Vergés3

1 Donostia International Physics Center (DIPC), Paseo Manuel Lardizabal 4, 20018 San Sebastian, Spain.
2 Departamento de Quimica Organica and Instituto Universitario de Sintesis Organica, Universidad de Alicante, San Vicente del Raspeig, 03690 Alicante, Spain.
3 Departamento de Teoria y Simulacion de Materiales, Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco, 28049 Madrid, Spain.

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Abstract

The geometrical and electronic structure of potassium doped phenanthrene, K3C14H10, have 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-rays structure is composed of two sheets with marked one and two dimensional character respectively.

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* On leave of absence from Instituto de Ciencia de Materiales de Madrid (CSIC) 28049 Madrid (Spain)
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\textsubscript{14}H\textsubscript{10}) is one of the smallest molecules of that family with very interesting electronic properties derived partly from its “arm-chair” 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.\textsuperscript{1,2} Furthermore, organic crystals based in different PAHs show an amazing 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\textsubscript{c} superconductors when doped with alkali metals.\textsuperscript{3–7} In particular, recent reports show that potassium doped phenanthrene in a stoichiometry K\textsubscript{3}C\textsubscript{14}H\textsubscript{10} is a superconductor with \(T\textsubscript{C} = 5\) K.\textsuperscript{4} The mechanism for superconductivity is not clear yet, but a dependence of \(T\textsubscript{C}\) with external pressure has been found that hints to a non-conventional 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.

Theoretical calculations for model systems of interest have been performed using ab-initio density functional theory (DFT).\textsuperscript{5} Wavefunctions have been expanded in a plane-wave basis set up to a cutoff of 680 eV and were sampled on a Monkhorst-Pack \(8 \times 10 \times 7\) 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.\textsuperscript{6} For the exchange and correlation (XC) potential the local density approximation (LDA) has been chosen, owning to its well-known success dealing with these kind of systems.\textsuperscript{10} All these choices have been proven in different occasions adequate to reproduce experimental geometrical parameters. Total energies were computed with the CASTEP program,\textsuperscript{11} as implemented in Materials Studio.\textsuperscript{12}

A monoclinic unit cell (UC) displaying a P\textsubscript{2}\textsubscript{1} symmetry and including two phenanthrene molecules in the basis has been set up with parameters derived from an X-rays analysis (ref\textsuperscript{13}, Fig. \textsuperscript{1}). Using the formalism and the parameters described above we have optimized the system to minimize residual forces and stresses; the corresponding parameters for the UC are
FIG. 1: (a) Optimized geometry structure for K$_3$ doped phenanthrene (upper panel). (b) The phenanthrene molecule displaying its arm-chair like edges (lower left panel). (c) Brillouin zone with the selected path for the band structure calculation shown in Fig. 2 (lower right panel).
TABLE I: Unit cell parameters for clean and potassium doped phenanthrene determined either from X-rays structural analysis or by DFT full optimization of forces and stresses (distances in Å and angles in degrees)

|                  | a   | b   | c   | β  | V  |
|------------------|-----|-----|-----|----|----|
| C_{14}H_{10}     | 8.05| 5.96| 9.16| 96.8| 437|
| K_{3}C_{14}H_{10}| 8.04| 6.54|10.09|102.6|517|
| C_{14}H_{10} \text{[L3]} | 8.46| 6.16| 9.47| 97.7| 489|
| K_{3}C_{14}H_{10} \text{[L1]} | 8.65| 5.96| 9.30| 100.2| 472|

displayed in Table I and the coordinates of all the atoms in the basis can be retrieved from the complementary material. According to the well known tendency of LDA to underestimate bond lengths the size of the UC is reduced in the three crystallographic axis with respect to the experimental values by \( \approx 5 - 3\% \) resulting in an overall decrease of the unit cell volume of 11\%. Most of the atomic coordinates in the phenanthrene molecules forming the unit cell basis agree quite well with the experimental ones (i.e. \( \pm 0.05 \text{ Å} \), we notice that different published experimental determinations of the crystal could differ by \( \pm 0.02 \text{ Å} \)). The exception comes from the four H atoms participating in the CH-\( \pi \) interaction between first-neighbors molecules; the theory to experiment difference in these can reach 0.18 Å. This is not at all surprising since the X-rays analysis of H is itself so difficult, and because we are bound to compare a theoretical calculation performed at T=0 K with an experimental structural determination performed at room temperature where the thermal vibrations should affect more to light atoms like hydrogen, especially if they form part of a sensitive 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 confirm the adequacy and set the accuracy of the proposed formalism.

Experimental analysis of K_{3}C_{14}H_{10} doped crystal shows a contraction of the unit cell in the \( \vec{b} \) and \( \vec{c} \) directions, a expansion in the \( \vec{a} \) direction, and a small increase in the angle \( \beta \). The unit cell volume is overall decreased by -3.5\%. From a theoretical point of view, however, intercalation of potassium creates an internal stress that results in an increase of the unit cell volume by +18\%. Optimizing the unit cell to remove the stress field yields an energy improvement of 0.9 eV/unit cell. \( \left( \max(S_{ij}) \leq 0.1 \text{ GPa}, \max(F) \leq 0.1 \text{ eV/Å} \right) \). At
the present moment there is no a reliable structural determination that could yield all the positions of the atoms in the unit cell basis, therefore our best knowledge on the particular positions of interstitial potassium is limited to a procedure like the one employed here, that in the worst case should represent at least a local metastable one intervening with a given weight in the appropriate thermodynamical average at a given T.

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 $\Gamma$ of 2.75 eV, to be compared with an experimental one of 3.16 eV.\cite{214} 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 it has been discussed in similar systems, these show a strong molecular character with weak overlap, and should be related to the HOMO and HOMO-1 and LUMO and LUMO+1 molecular orbitals respectively.\cite{6} 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). 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 that becomes responsible for the metallic properties of the doped material.

The experimental unit cell used in these calculations, 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 an stable equilibrium condition. The unit cell increases slightly in volume, decreasing the hybridization between the LUMO orbitals of both molecules and the conduction band crossing the Fermi energy becomes less dispersive, but no big changes are observed along the chosen path to represent the bands. The Fermi surface, however, is more sensitive to small geometrical details: we have compared the results for the relaxed and unrelaxed unit cells (Fig. 3). To improve the sampling in k-space and the representation of surfaces in the Brillouin zone, a 4x4 tight-binding hamiltonian describing the first four conduction bands has been derived by fitting the electronic bands on a dense Monkhorst-Pack grid in the irreducible part of the Brillouin zone (280 k-points). A two sheet Fermi surface has been obtained that is compatible with the ab-initio determination in a coarse k-space grid. For the X-rays 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.
FIG. 2: Band Structure for the phenanthrene crystal (upper panel) and for the K₃ doped crystal corresponding to the X-rays structural determination (lower panel). The Fermi energy has been taken as origin for energies (dashed lines).
FIG. 3: For the doped phenanthrene crystal the Fermi surface corresponding to the X-rays determination (left panel) is compared to the one related to the relaxed unit cell (right panel).

The other sheet is nearly cylindrical and reveals a more two-dimensional character (Fig. 3). After relaxing the unit cell, the planar sheet changes very little, but the cylindrical-like shape becomes an spheroid where the BZ boundaries are now not touched and corresponding gaps happening near the Fermi energy are closed.

The spatial distribution of electronic density confirm the above picture: we draw in Fig. 4 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 \( \pi \)-like orbitals originated from both phenanthrene molecules. This is consistent with our image of an important charge transfer from potassium to phenanthrene to build the metallic phase.

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 the properties of molecular orbitals. The experimental determination of the UC by X-rays diffraction techniques implies stress since the UC volume is predicted to shrink by \( \approx 10\% \) with respect to the pristine crystal. The Fermi surface under stress shows a low-dimensional character that can be transformed by allowing the UC
FIG. 4: Iso-density corresponding to the four bands nearest the Fermi energy inside the unrelaxed unit cell.

to deform to a global equilibrium shape.

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I. APPENDIX: ADDITIONAL MATERIAL
TABLE II: Fractional coordinates for the atoms forming the basis in the potassium-doped fully relaxed structure (the corresponding UC has been defined in Table I).

| ATOM | u    | v    | w    |
|------|------|------|------|
| H    | 0.2801 | 0.1603 | -0.3413 |
| H    | 0.0165 | -0.0229 | -0.4506 |
| H    | -0.1379 | -0.2386 | -0.3076 |
| H    | -0.0311 | -0.2629 | -0.0625 |
| H    | 0.0314 | -0.2411 | 0.1399 |
| H    | 0.1042 | -0.1898 | 0.3868 |
| H    | 0.3438 | 0.0317 | 0.4950 |
| H    | 0.5360 | 0.1894 | 0.3535 |
| H    | 0.7555 | 0.2884 | 0.1222 |
| H    | 0.4811 | 0.2557 | -0.1280 |
| H    | -0.2802 | 0.6623 | 0.3408 |
| H    | -0.0161 | 0.4803 | 0.4506 |
| H    | 0.1382 | 0.2634 | 0.3081 |
| H    | 0.0312 | 0.2379 | 0.0634 |
| H    | -0.0313 | 0.2580 | -0.1393 |
| H    | -0.1038 | 0.3085 | -0.3861 |
| H    | -0.3431 | 0.5293 | -0.4949 |
| H    | -0.5364 | 0.6875 | -0.3540 |
| H    | -0.5761 | 0.7881 | -0.1230 |
| H    | -0.4818 | 0.7863 | 0.1272 |
| C    | 0.2110 | 0.0720 | -0.2768 |
| C    | 0.0583 | -0.0287 | -0.3395 |
| C    | -0.0288 | -0.1423 | -0.2604 |
| C    | 0.0377 | -0.1604 | -0.1194 |
| C    | 0.1408 | -0.1409 | 0.1823 |
| C    | 0.1825 | -0.1139 | 0.3247 |
| C    | 0.3241 | 0.0000 | 0.3861 |
| C    | 0.4273 | 0.0913 | 0.3047 |
| C    | 0.4772 | 0.1858 | 0.0760 |
| C    | 0.4162 | 0.1845 | -0.0683 |