

Crystal structure and electronic states of tripotassium picene

P. L. de Andres

Departamento de Nanoestructuras, Superficies y Recubrimientos, Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco, 28049 Madrid, Spain

A. Guijarro

Departamento de Química Orgánica and Instituto Universitario de Síntesis Orgánica, Universidad de Alicante, San Vicente del Raspeig, 03690 Alicante, Spain

J. A. Vergés*

Departamento de Teoría y Simulación de Materiales, Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco, 28049 Madrid, Spain

(Received 28 October 2010; published 21 June 2011)

The crystal structure of potassium-doped picene with an exact stoichiometry ($K_3C_{22}H_{14}$, K_3 picene from here onwards) has been theoretically determined within density functional theory allowing complete variational freedom of the crystal structure parameters and the molecular atomic positions. A modified herringbone lattice is obtained in which potassium atoms are intercalated between two paired picene molecules displaying the two possible orientations in the crystal. Along the c -axis, organic molecules alternate with chains formed by three potassium atoms. The electronic structure of the doped material resembles pristine picene, except that now the bottom of the conduction band is occupied by six electrons coming from the ionized K atoms (six per unit cell). Wavefunctions remain based mainly on picene molecular orbitals getting their dispersion from intralayer *edge-to-face* CH/ π bonding, while eigenenergies have been modified by the change in the electrostatic potential. The small dispersion along the c -axis is assigned to small H–H overlap. From the calculated electronic density of states, we expect metallic behavior for potassium-doped picene.

DOI: [10.1103/PhysRevB.83.245113](https://doi.org/10.1103/PhysRevB.83.245113)

PACS number(s): 71.15.Mb, 61.66.Hq, 71.20.Rv

I. INTRODUCTION

Recently, Mitsuhashi *et al.*¹ have shown the existence of superconductivity at relatively high temperatures for alkali-metal-doped picene. In particular, $K_{3.3}$ picene shows a critical temperature of $T_c = 18$ K. This work opens the door to a new class of materials that promise improved T_c values. While the structure of the organic picene crystal is well known since 1985,² the best possible structural determination using synchrotron radiation on K-doped samples has been indecisive about the actual positions of interstitial atoms.³ No further advance in the understanding of the superconductivity is possible until a successful detailed structural determination exists. Once the atomic structure is known, both the electronic states and the phonons can be quantitatively studied and the usual ideas to understand superconductivity followed. A preliminary theoretical determination of the crystal structure of pristine and potassium-doped picene (K_3 picene) has been reported by Kosugi *et al.*⁴ by a first-principles calculation which adheres strictly to experimentally determined crystal parameters for the unit cell vectors length (see also comment in Ref. 5). Kosugi *et al.* find that potassium-doped picene molecules show an *edge-to-face* intralayer ordering but stay almost perpendicular to the ab plane, losing the conventional herringbone interlayer stacking [see Fig. 4(a) of Ref. 4]. In our work, to circumvent the difficulties found in the experimental determination of the structure of $K_{2.9}$ picene (small and disordered samples, possible existence of more than one structural phase, etc.¹), we have adopted a more general strategy to the structural search of the crystalline structure of highly doped picene; we rely on the best available *ab initio* methods based on density

functional theory (DFT) to get a stable structure that provides at least a local minimum of the free energy of a precise stoichiometry. We study the case of three potassium atoms per picene molecule because it is the one showing the higher critical temperature. Therefore, in our calculation, atomic positions and parameters defining the unit cell (including the symmetry group) have been fully optimized to reach a total energy minimum configuration subject to minimum forces and stresses. The resulting crystalline structure shows enough internal consistency and symmetry to be theoretically appealing. We remark that the calculated structure differs significantly from two different structures published for a smaller K doping of a similar material (pentacene crystal).^{6,7}

The rest of the paper is organized as follows: Sec. II gives details for the computational procedure followed in this work. Section III presents our optimized crystalline structure and the corresponding electronic band structure and density of states. Finally, Sec. IV summarizes our conclusions.

II. NUMERICAL PROCEDURE

A full experimental determination of the doped picene crystal structure based on x-rays diffraction data has not been possible so far because of the large background and the small number of useful measured peaks. However, a basic Le Bail determination of the structure has been performed to obtain approximate values for the unit cell parameters,³ yielding values quite similar to the ones derived for pristine picene. Therefore, we propose to complement the presently limited experimental information with a pure numerical

procedure based in DFT to define realistic candidates for the actual crystalline structure. One important advantage is that polycyclic aromatic hydrocarbons (PAHs) show a robust geometry even in the presence of alkali metals and translate and rotate almost rigidly during the total energy minimization. However, the position of the dopant atoms is a complex problem not fully understood, as shown by previous theoretical studies concluding different alternative models.⁸ In order to get a plausible crystalline structure for K_3 picene, we have minimized the free energy per unit cell using a DFT scheme at the local density approximation (LDA) level. Both atomic positions and cell parameters ($a, b, c, \alpha, \beta, \gamma$) are free to change to minimize forces on atoms and stresses on the unit cell get. Some more technical parameters of the computation are as follows. We use norm-conserving pseudopotentials,⁹ an energy cutoff of 660 eV, and Monkhorst-Pack¹⁰ meshes of $4 \times 6 \times 3$ or $5 \times 5 \times 3$ depending on the unit cell being under consideration. Actual calculations have been performed with the CASTEP program allowing for spin polarization of different bands of the doped crystal.^{11,12} To describe the exchange and correlation potential, we use Kohn and Sham's local density approach as computed by Ceperley and Alder.^{13,14} Maximum forces and stresses on the system are converged to target thresholds of 0.1 eV/Å and 0.1 GPa.

The whole procedure has been applied to pure picene as an overall check. The optimization was started using the complete structural determination provided by the Cambridge Crystallographic Data Centre (CSD_CIF_ZZZOYC01). Cell parameters (a, b, c, β) change from 8.480 Å, 6.154 Å, 13.515 Å, 90.46° to 8.373 Å, 6.043 Å, 13.390 Å, 90.18°, respectively, improving the cell total energy in merely 0.12 eV. The unit cell volume shrinks about 4%, but the change in the molecule structure is imperceptible. Therefore, the test is quite satisfactory and we assume that the differences between experimental and computational values provide an estimate for the errors involved in our structural search.

III. RESULTS AND DISCUSSION

A. Crystal structure

Previous work on K-doped pentacene⁶ and on K_3 picene⁴ has proven that when large enough amounts of alkali atoms are introduced in a herringbone organic structure, the preferred positions for the dopants is intralayer, i.e., in between planes defined by PAH molecules. The other possibility, K atoms in the planes between PAH layers, is energetically less favorable but it has also been considered for K_1 pentacene.⁷ Since we are mainly interested in the case of very high doping (K_3 picene) because it shows promising results as a new superconducting material, we have assumed from the beginning that K occupies sites between picene molecules. As a starting crystal structure, we use pristine crystalline picene with K atoms in the centroids of next-nearest-neighbors picene molecules.¹⁵ Subsequently, the system is allowed to freely evolve under atomic forces obtained from a series of fully converged DFT calculations to drive the molecules to equilibrium positions. We have performed three sets of different calculations: (i) we froze the unit cell parameters to the values obtained from a Le Bail x-ray analysis, (ii) values similar to the

ones deduced from a Le Bail x-ray analysis, but relaxed by less than 10% in order to diminish the structural stress, and (iii) fully optimized values for the unit cell lengths and angles. The optimum configuration for the first case allows us to minimize the maximum component of forces on any atom below $F_{\max} = 0.03$ eV/Å, but the maximum component of the tensor stress is $S_{\max} = 5$ GPa, and the total energy is above the global minimum found later by 1.42 eV. The second case allows us to decrease $S_{\max} = 2$ GPa, but the total energy is still above the best configuration by 0.97 eV. Finally, the fully optimized structure ($a = 7.359$ Å, $b = 7.361$ Å, $c = 14.018$ Å, $\alpha = 90^\circ$, $\beta = 105.71^\circ$, and $\gamma = 90^\circ$) allows us to decrease the maximum force and stress below 0.1 eV/Å and 0.1 GPa, respectively. The LDA cell volume increases from 669 Å³, for clean picene, to 730 Å³ after doping with potassium. Even after a full optimization, the system belongs to the space group $P2_1$ and remains monoclinic within a ± 0.01 Å error in the atomic positions. Also $a = b$ at the precision of our computation. A more detailed analysis shows that picene molecules acquire a small regular curvature that contrasts with the structure of the free molecule which is completely planar. Figure 1(a) shows how K atoms are intercalated between the picene molecules that form a layer. The high symmetry of the arrangement is clear. Precise structural information is given in a supplemental material *cif*-like file.¹⁶

To understand the effect of different starting atomic configurations on the final equilibrium structure, we have looked at a laminar structure resembling intercalated graphite. The unit cell is made with two picenes and six potassium atoms too, but now the picene molecules are parallel. Potassium goes to centroids between corresponding hexagonal rings. Starting from this configuration, DFT forces lead to a locally stable structure in which picene molecules form a global plane whereas intercalated potassium completes a structure resembling the well known KC_8 . The total energy of this structure is more than 2 eV per cell higher than the previous herringbone one. Consequently, from a strict energetic point of view, it is clearly inferior. Figure 1(b) schematically shows this laminar structure. Again, precise structural information is given in a supplemental material *cif*-like file.¹⁶

The ultimate justification of a crystal structure should come from experiment, typically from x-ray diffraction. Mitsuhashi *et al.*¹ provide the x-ray diffraction pattern of a $K_{2.9}$ picene sample obtained with synchrotron radiation of $\lambda = 0.99937$ Å in the supplemental material of their paper. We have used the mercury program¹⁷ to calculate a powder pattern for any well-defined crystal structure. Our results are shown in Fig. 2. First, we have checked that both the original picene crystal and the one refined by DFT at the LDA level provide spectra similar to the one given in Ref. 1. Second, we have used the same program to get the pattern for our predicted K_3 picene structure (see Fig. 2). It can be observed that the small angle part of the spectrum of doped picene resembles the one obtained for pristine picene in the herringbone structure. This is easily explained since the arrangement of picene molecules is still close to the original one. Until here, there is some agreement with experiment since Mitsuhashi *et al.* comment that x-ray diffraction pattern of $K_{2.9}$ picene shows a good correspondence with that of pristine picene (supplemental Figs. S7(a) and S7(b) of Ref. 1). Nevertheless, our well-ordered array of K atoms

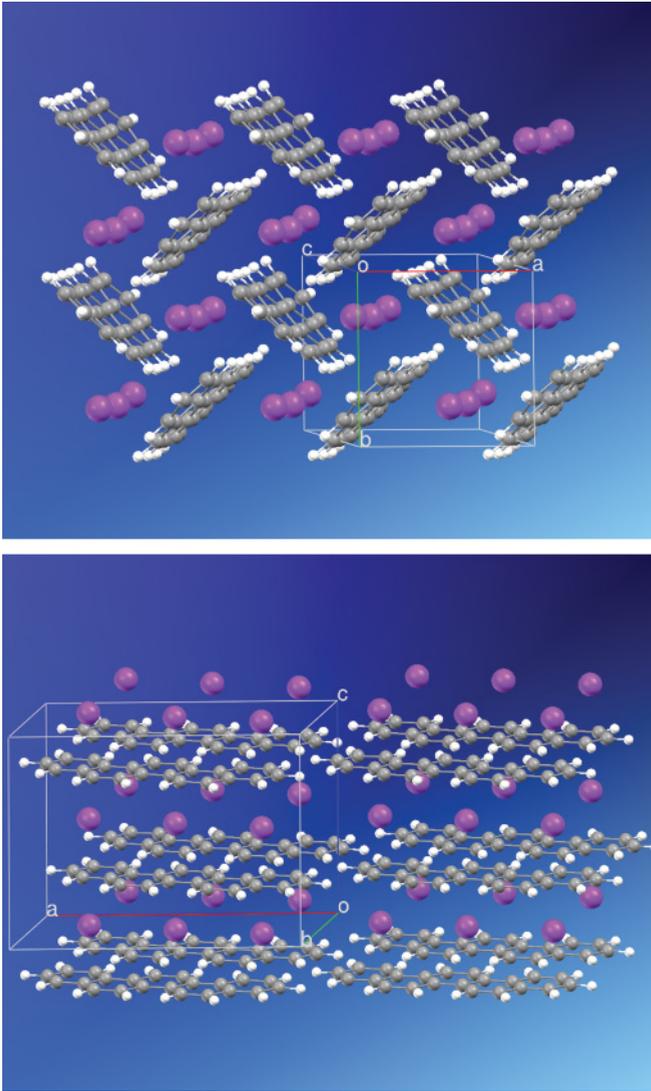


FIG. 1. (Color online) Upper panel shows the optimized atomic structure of K_3 picene as obtained with CASTEP for a completely free lattice structure. The $P2_1$ spatial symmetry of pristine picene is conserved. Notice that although only one atomic layer is displayed, the positions of the next-layer picene molecules are on the top of potassium atoms. Lower panel shows an alternative structure obtained starting the geometrical optimization from a lamellar arrangement of picene molecules intercalated by K atoms in a global configuration based on intercalated graphite.

produces important peaks at larger angles that have not been experimentally observed. We believe that K disorder, phase mixing, etc. prevent a better experimental determination of dopant positions and demand more research in the future.

On the other hand, calculated powder pattern spectra allow us to discard alternative lamellar structures because they systematically show the extinction of the (0,0,1) low angle peak. It is easy to check that the spectrum of potassium-intercalated graphite (KC_8) shows a similar property.

B. Electronic structure

The motivation behind the structural work is to better understand the electronic properties of the material. We

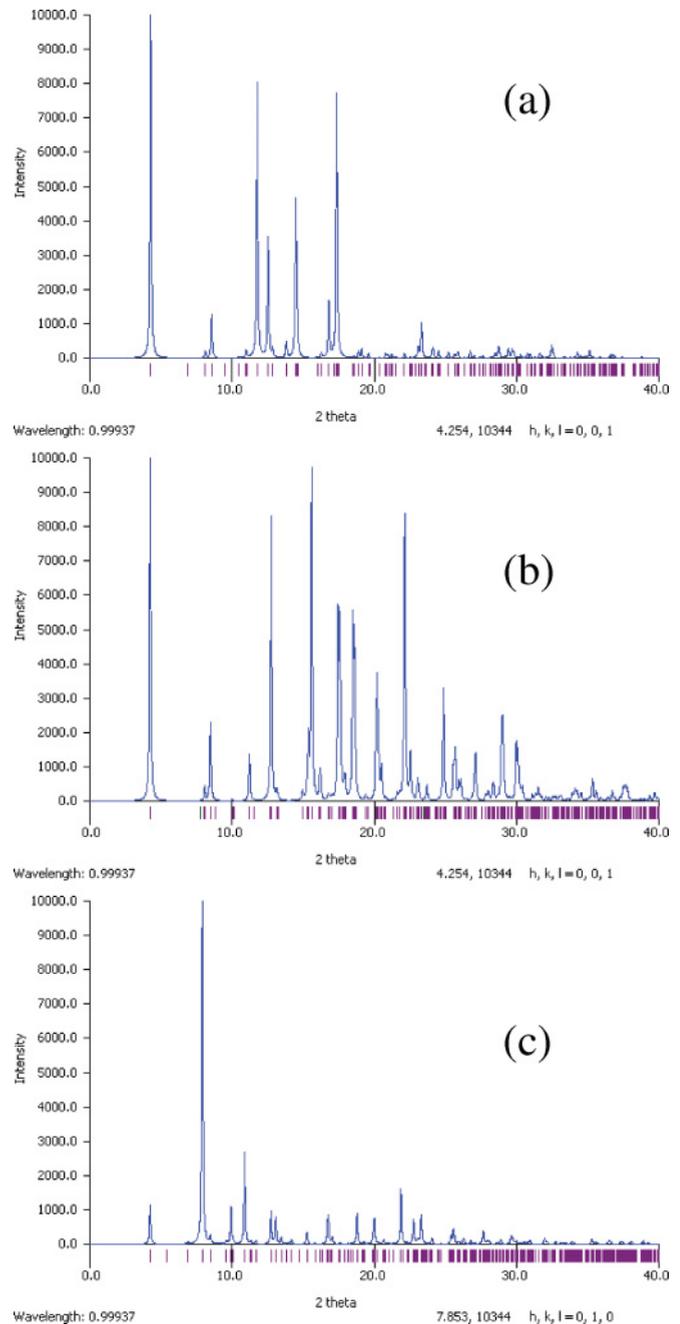


FIG. 2. (Color online) Calculated powder x-ray diffraction pattern of the optimized theoretical structure of pristine picene (upper panel), K-doped picene in the optimized herringbone structure (medium panel), and K-doped picene in the alternative lamellar structure (lower panel). Intensity is given in arbitrary units while diffraction angle is measured in degrees.

compute the electronic density of states and the band structure for the optimized configuration using standard procedures in DFT. Figure 3 gives some details of the Brillouin zone form and orientation relative to the crystal lattice. Also the path used to calculate the band structure is shown. Figure 4 gives results corresponding to the LDA clean picene crystal (upper panels) and doped K_3 picene in the LDA herringbone crystalline structure (lower panels). The most significant feature of picene electronic structure is the opening of a wide gap (about

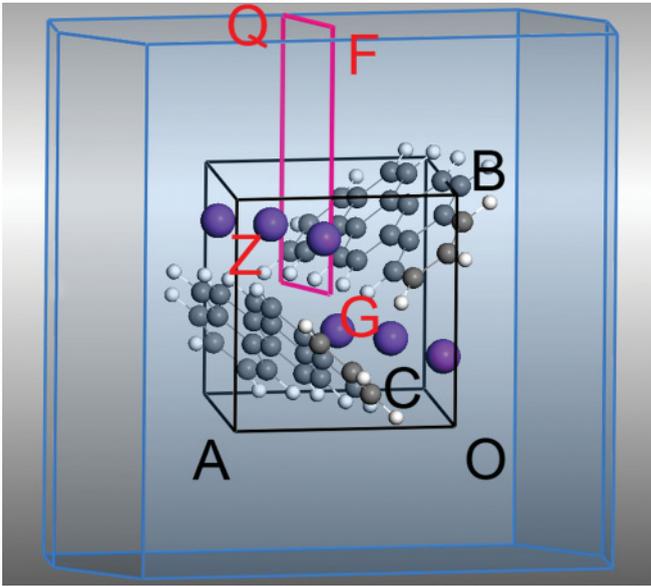


FIG. 3. (Color online) Brillouin zone obtained for K-doped picene showing the crystalline unit cell and molecules therein. The GFQZG path followed to calculate the band structure is shown by a continuous (red) line.

2.5 eV in our approximation) separating occupied (valence) states from empty (conduction) states. The upper right panel shows the bands that are close to the chemical potential. This result is in accordance with the insulating character of picene although the gap is underestimated in the LDA. After adding six potassium atoms per cell and assuming that the theoretically proposed crystalline structure is correct, the

material presents the electronic structure shown in the lower panels of Fig. 4. Both valence and conduction bands are globally similar to the previous ones except for two new peaks appearing in the valence band, the first just above -30 eV and the second around -13 eV. They correspond to the fully occupied $3s$ and $3p$ states coming from potassium atoms. The valence electrons of K atoms have been transferred to the conduction band as the Fermi level position indicates (we have checked that the integral below the occupied part of the conduction band is precisely six). Consequently, the potassium $4s$ states lie well above in the conduction band (but are not shown in the figure) and are completely empty. A closer look to the states that are occupied by K electrons in doped picene is given by Fig. 5. It is clear that the dispersion of the bands is larger in the doped material and consequently, the separation to the valence bands is smaller. Notice also that dispersion along FQ and Z Γ directions (both parallel to \mathbf{k}_3 -axis (c^* -axis) is more or less similar. Although the assignment of wavefunctions weight to particular atoms or molecules is beyond the scope of this contribution, we believe that extended states of the doped material are similar to pristine picene wavefunctions but their energies are shifted by the new electrostatic potential induced from the transference of electrons from potassium to organic molecules. Therefore, assuming that $4s$ K orbitals do not have a significant weight in the conduction band states, the existence of several weak CH/π bonds^{18,19} among perpendicular picene molecules can explain the existence of extended states. On the other hand, the smaller H–H overlaps should provide the smaller delocalization along the c -axis.

Once changes in the electronic structure of picene due to the doping by K have been analyzed, some conclusions

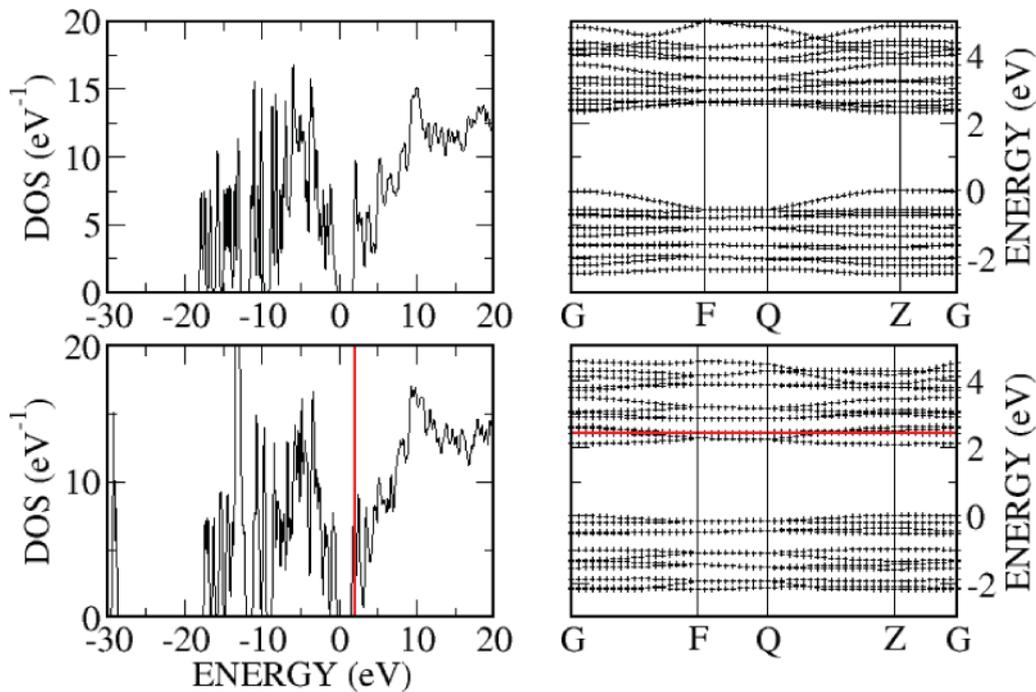


FIG. 4. (Color online) Density of states and bands around the Fermi level for pristine picene as described by the LDA DFT scheme use in this work (upper panels) and the corresponding one after doping with potassium and relaxing the herringbone original structure (lower panels). The top of the valence band of both compounds has been aligned to facilitate the comparison. Solid (red) lines indicate the Fermi level position for the metallic system at 2.45 eV, approximately.

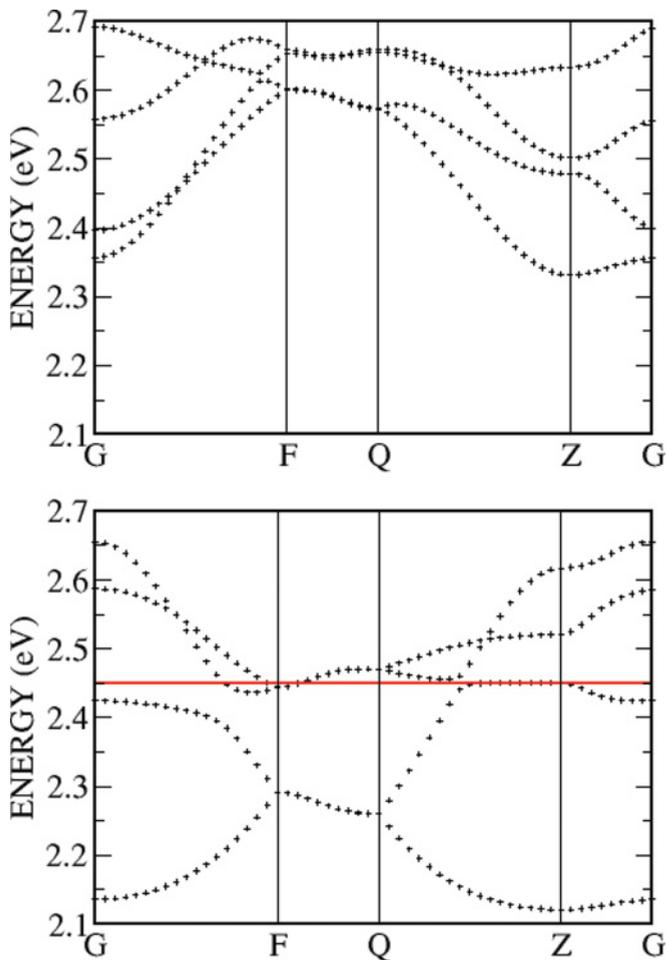


FIG. 5. (Color online) Detail of the conduction bands occupied by K doping. Upper panel shows the bands of pristine picene and lower panel shows the bands changed by the presence of potassium.

can be inferred. First, the introduction of potassium gives rise to an ionic system in which long range Coulomb forces contribute an important percentage of the whole cohesive energy. Second, the broadening of the molecular levels of individual picene molecules likely comes from the original edge-to-face interactions of any herringbone arrangement plus the smaller interlayer coupling mediated by H-H overlap. Consequently, the doped system presents extended states covering the whole crystal, but showing a reduced dispersion along the k_3 -axis. This characteristic implies a smaller electric conductivity parallel to the c -axis in comparison with conductivities in the a and b directions. Measurements mentioned by Mitsuhashi *et al.*¹ for doped pentacene share this property although physical grounds are quite different. In the last case, conductivity shows a two-dimensional character because doping occurs in a - b planes allowing extended two-dimensional wavefunctions for the alkali metals.

C. Intercalation of K

Intercalation of K atoms inside the picene crystal is crucial to modify some properties of interest, e.g., superconductivity. In this subsection, we use our structural and electronic calculations to compute diffusion barriers for K atoms moving inside

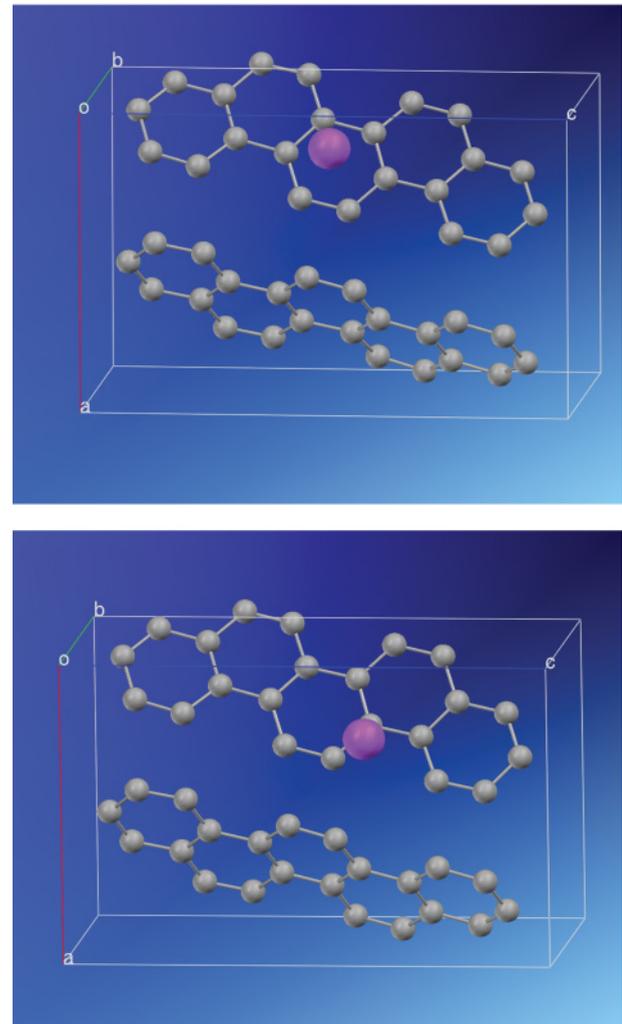
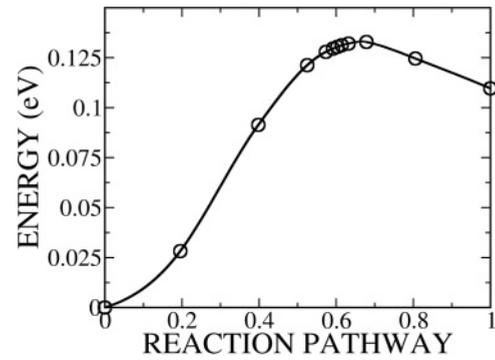


FIG. 6. (Color online) Diffusion barrier (eV) for one K atom diffusing inside the frozen clean picene unit cell. Configurations for the initial and final states are shown in the upper and lower panels, respectively (hydrogens have been removed from the picture for the sake of clarity).

the unit cell. The starting point are local equilibrium adsorption sites computed for a common unit cell that we choose to be the experimental one for clean picene;² this is a reasonable choice because of the low amount of potassium involved in these calculations. Barriers are estimated from a linear synchronous transit (LST) transition state search, followed by a quadratic synchronous transit (QST) refinement.²⁰

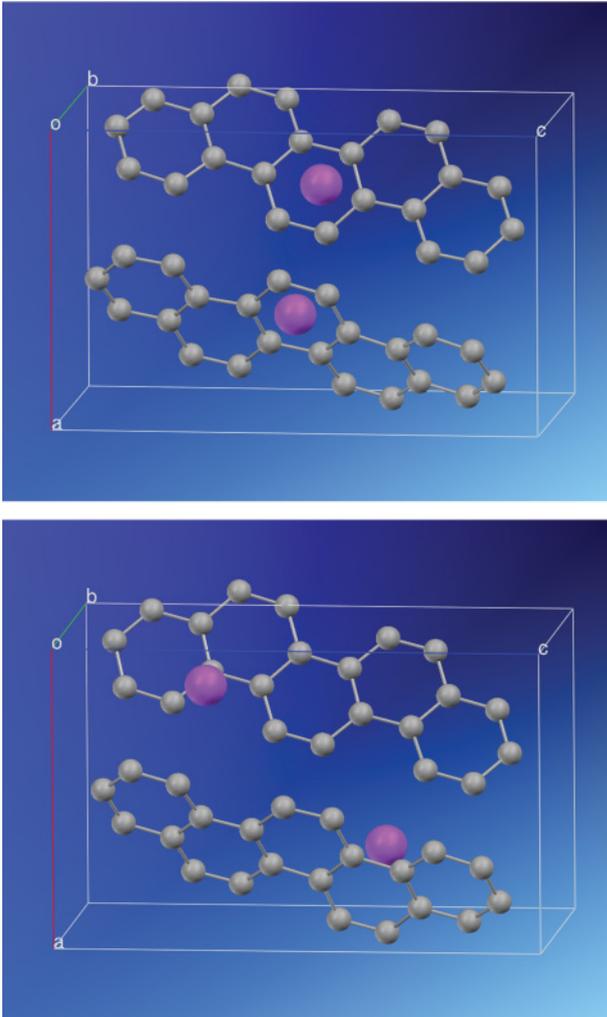
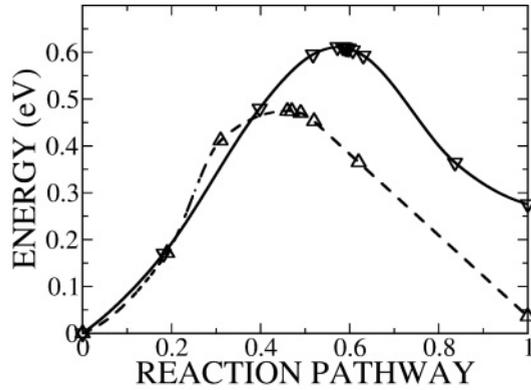


FIG. 7. (Color online) Diffusion barriers (eV) for two K atoms moving in the same direction (triangles pointing down, continuous lines) and in the opposite direction (triangles pointing up, dashed line). Configurations for the initial and final states are shown in the upper and lower panels, respectively.

The global energy minimum for a single K in the picene unit cell is close to the central part of the channel defined by four picene molecules [Figs. 1(a) and 6]. We compute the diffusion barrier to move the K atom along the channel (the displacement introduces new forces making the atom to get closer to one of the picene molecules by 0.6 \AA). The energy of reaction when moving between these two local adsorption sites

TABLE I. Barriers from the initial (B_I) and final (B_F) states, and energy of reaction ($\Delta E = E_F - E_I$) for one and two K atoms diffusing in the unit cell (primarily along the c direction). For two K atoms, two different cases have been considered: a symmetric (antisymmetric) diffusion mode (S or A, respectively) where both atoms move along the same (opposite) directions.

System	B_I	B_F	ΔE
One K	0.13	0.02	0.11
Two K (S)	0.61	0.33	0.28
Two K (A)	0.47	0.44	0.04

is 0.11 eV and the highest barrier (from the initial position to the transition state) is 0.13 eV (Table I). This barrier is small enough to predict a large diffusivity of K inside the picene crystal: we estimate this value from $W e^{-B/k_B T}$, where W is a typical attempt frequency that we take as the frequency of a plausible phonon (e.g., 1 THz), B is the diffusion barrier for this particular hop from site I to site F, T is temperature, and k_B is the Boltzmann constant. This simple estimate shows that the potassium atom is making about 10^9 hops per second at room temperature, making macroscopical diffusion in a reasonable amount of time possible.

For two K, simultaneously diffusing in the unit cell, many more configurations need to be explored making an extremely complex energy landscape. We show in Fig. 7, two representative cases: starting out from the global minimum configuration where both K atoms stay near the center of the unit cell, both atoms diffuse either along the same or opposite directions (mostly, both along the $+c$, or the $+c$ and $-c$ axis, respectively). The lower barrier corresponds to the K atoms moving away from each other: 0.47 and 0.44 eV from the initial and final states, respectively. For the *concerted* diffusion, barriers are 0.61 and 0.33 eV, respectively, and the initial and final states have a larger energy difference: 0.28 eV (Table I).

IV. CONCLUDING REMARKS

Systematic use of DFT allows the prediction of a plausible crystalline structure for heavily doped picene (K_3 picene). Potassium is absorbed in the square prism space defined by four equivalent picene molecules. The original herringbone structure formed by the organic molecules is only weakly deformed. This justifies the similarity of the x-ray powder spectra of the doped material and the pristine picene. Nevertheless, our predicted structure does not quantitatively reproduce the experimental spectrum, mainly because the larger angle peaks originating in K are not present in the experiment. The metallic character of the doped material comes from the occupation of picene wavefunctions due to the transfer of electrons from potassium to the organic molecules. The presence of K cations induces a modified electrostatic potential that broadens the lower part of the conduction band without appreciably changing the wavefunctions based on molecular orbitals of picene. Therefore, the reason for the intralayer dispersion of the bands is the CH/ π interaction responsible for the herringbone PAH arrangement. We should comment that this delocalization effect will be lost for separated parallel picene molecules, providing an important argument against

alternative laminar structures. In view of these results, we assume that superconductivity might be triggered by electron-phonon coupling *within* individual picene molecules.

ACKNOWLEDGMENTS

The authors are grateful to E. Gutiérrez for helping us with the interpretation of x-ray spectra. We are also grateful

to A. Hansson for providing us with the structural data of the two phases of Kpentacene shown in Fig. 1 of Ref. 6. Financial support by the spanish “Ministerio de Ciencia e Innovación MICINN” (Grant Nos. CTQ2007-65218, CSD2007-00006, MAT2008-1497, and FIS2009-08744) is gratefully acknowledged. We also acknowledge support from the DGUI of the Comunidad de Madrid under the R&D Program of activities MODELICO-CM/S2009ESP-1691.

*jav@icmm.csic.es

¹R. Mitsuhashi, Y. Suzuki, Y. Yamanari, H. Mitamura, T. Kambe, N. Ikeda, H. Okamoto, A. Fujiwara, M. Yamaji, N. Kawasaki, Y. Maniwa, and Y. Kubozono, *Nature* **464**, 76 (2010).

²A. De, R. Ghosh, R. Roychowdhury, and P. Roychowdhury, *Acta Crystallogr. Sect. C* **41**, 907 (1985).

³Supplemental material of Ref. 1 suggests intralayer intercalation of potassium based on the variation of the lattice constants.

⁴T. Kosugi, T. Miyake, S. Ishibashi, R. Arita, and H. Aoki, *J. Phys. Soc. Jpn.* **78**, 113704 (2009).

⁵Two of the authors of Ref. 4 (T.M. and S.I.), speak on the possible existence of several metastable structures in private communications.

⁶A. Hansson, J. Böhlin, and S. Stafström, *Phys. Rev. B* **73**, 184114 (2006).

⁷M. F. Craciun, G. Giovannetti, S. Rogge, G. Brocks, A. F. Morpurgo, and J. van den Brink, *Phys. Rev. B* **79**, 125116 (2009).

⁸References 6, 7, and 4 detail quite different possibilities for K insertion into organic crystals formed by large polycyclic aromatic hydrocarbons (PAH) that share an initial herringbone crystalline structure.

⁹Opium, as described in [<http://opium.sourceforge.net/>].

¹⁰H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).

¹¹S. Clark, M. D. Segall, C. Pickard, P. Hasnip, M. J. Probert, K. Refson, and M. C. Payne, *Z. Kristallogr.* **220**, 567 (2005).

¹²Materials Studio 4.4 as described in [<http://www.accelrys.com>].

¹³W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1964).

¹⁴D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).

¹⁵Initial positions for the six K atoms per cell are obtained calculating the centroids of corresponding hexagonal rings of parallel molecules. First, third, and fifth rings between parallel molecules separated by *a* were chosen although the centroids corresponding to the closer stacking (*b*) provide almost the same initial positions.

¹⁶See supplemental material at [<http://link.aps.org/supplemental/10.1103/PhysRevB.83.245113>] for crystal structures described by *cif*-like files in Fig. 1. The first one called “herringbone.cif” precisely defines the herringbone structure of K-doped picene shown in the upper panel of Fig. 1 and the second one, called “laminar.cif”, gives the laminar structure shown in the lower panel of the same figure.

¹⁷Mercury – Crystal Structure Visualisation and Exploration Made Easy by [<http://www.ccdc.cam.ac.uk/products/mercury>].

¹⁸M. Nishio and M. Hirota, *Tetrahedron* **45**, 7201 (1989).

¹⁹J. Cornil, J. Ph. Calbert, and J. L. Brédas, *J. Am. Chem. Soc.* **123**, 1250 (2001).

²⁰T. A. Halgren and W. N. Lipscomb, *Chem. Phys. Lett.* **49**, 225 (1997).