Crystal structure search and electronic properties of alkali doped phenanthrene and picene

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Alkali doped aromatic compounds have shown evidence of metallic and superconducting phases whose precise nature is still mysterious. In potassium and rubidium doped phenanthrene, superconducting temperatures around 5 K have been detected, but such basic elements as the stoichiometry, crystal structure, and electronic bands are still speculative. We seek to predict the crystal structure of M$_3$-phenanthrene (M = K, Rb) using ab-initio evolutionary simulation in conjunction with density functional theory (DFT), and find metal but also insulator phases with distinct structures. The original P$_2$1 herringbone structure of the pristine molecular crystal is generally abandoned in favor of different packing and chemical motifs. The metallic phases are frankly ionic with three electrons acquired by each molecule. In the nonmagnetic insulating phases the alkali coalesce reducing the donated charge from three to two per phenanthrene molecule. A similar search for K$_3$-picene yields an old and a new structure, with unlike potassium positions and different electronic bands, but both metallic retaining the face-to-edge herringbone structure and the P$_2$1 symmetry of pristine picene. Both the new K$_3$-picene and the best metallic M$_3$-phenanthrene are further found to undergo a spontaneous transition from metal to antiferromagnetic insulator when spin polarization is allowed, a transition which is not necessarily real, but which underlines the necessity to include correlations beyond DFT. Features of the metallic phases that may be relevant to phonon-driven superconductivity are underlined.

I. INTRODUCTION

The field of organic superconductors has received recent impulse with the discovery of superconductivity in electron doped picene and promptly followed by a broader class of electron-doped polycyclic aromatic hydrocarbons (PAHs). Among them, electron-doped coronene, 1,2,8,9-dibenzopentacene and phenanthrene have been reported. To this date, the metallic and superconducting behavior of many of these exciting systems is proving difficult to reproduce and there is considerable uncertainty, ranging from stoichiometry, mechanism, and precise crystal structure. To clarify the situation, simultaneous efforts of experiment and theory are called for. The lack of knowledge of stoichiometry and of structure poses a starting dilemma to theory, since calculations, either first principles or modeling, obviously depend on both elements. Most theoretical work so far has assumed the nominal three-electron stoichiometry that seemed closest to that of the superconducting cases, assuming or optimizing crystal structures where six alkali-metal atoms fill a bimolecular unit cell of the same herringbone type as the pristine molecular insulator. Based on these reasonable crystal structures, several superconductivity mechanisms have been discussed for electron-doped PAHs. However, even modest changes in the orientation and deformation of the PAHs molecules and in the relative position and distance of alkali metal atoms with respect to them and among themselves can alter the bonding nature of the doped system and its electronic structure making it somewhat risky to build on such insecure foundations. Even assuming without proof the M$_3$-PAHs stoichiometry, a structural search is necessary. The crystal structure searches so far appeared to preserve the pristine herringbone stacking of PAH molecules, limiting the freedom to the alkali atom coordinates and thus exploring only a very small portion of an extensive and complicated phase space. Relaxing this assumption is important, especially as we shall see for small size PAHs.

Predicting crystal structures for organic molecular crystals is not trivial. Intermolecular forces are correlation-dominated and thus hard to determine with confidence by means of standard ab-initio density-functional theory (DFT), where correlations are not automatically dealt with. The problem is aggravated by the weakness of these forces, which gives rise to near degeneracies of a confusing variety of structures. Connected with the latter is frank polymorphism, with many competing and coexisting crystalline structures with the same chemical composition but different symmetries and physico-chemical properties, a possibility likely to be important and that should be seriously considered in alkali-doped PAHs. To explore the variety of low energy structural polymorphs an extensive search over the energy landscape of each compound is essential. To the best of our knowledge, search examples from which criteria and trends could be learned ahead of hopeful future experimental verifications are not yet satisfactorily developed for electron doped PAHs.

This paper deals with crystal structure prediction for the computationally simpler PAH compounds M$_3$-phenanthrene (M$_3$-PA) and by comparison with the best studied compound, namely K$_3$-picene (K$_3$-PC) To
II. COMPUTATIONAL METHODS

Our search of the stable and low-energy metastable structures was carried out using evolutionary algorithm (EA), as implemented in the USPEX code.\textsuperscript{23–27} EA was implemented in conjunction with ab-initio structure relaxations based on density functional theory (DFT) within the Perdew-Burke-Ernzerhof (PBE)\textsuperscript{28} generalized gradient approximation as implemented in VASP (Vienna Ab-initio Simulation Package),\textsuperscript{29} employing all-electron projector-augmented plane wave (PAW) method\textsuperscript{30,31} as well as on QUANTUM ESPRESSO\textsuperscript{32,33} Van der Waals forces were included in two different implementations, and separately compared to a simple hydrostatic pressure between 4 and 10 Kbar whose effects after tuning are found to be roughly equivalent to vdW. The small unit cell size, 54 atoms/cell. That assumption is not unreasonable, but it is unlikely to be of general validity, and therefore we released it. Especially for the smaller size PAH molecules where direct intermolecular forces are weaker the addition of six alkali atoms per bimolecular per cell is a major perturbation that could impact the herringbone structure. In our EA search for M$_3$-PC we explored over two thousands structures within about 60 generations to arrive at the converged stable low energy structures. Fig. 1 shows the energy of approximately 1,500 structures (upper panel) calculated at 45 generations (lower panel). This coarse search was done using straight DFT-PBE.

III. RESULTS

In previous theoretical studies of M$_3$-PA and K$_3$-PC\textsuperscript{4,11–20,35,36} the doped PAHs were generally assumed or in some cases found to retain the herringbone arrangements of $P_{2_1}$ symmetry similar to those of the pristine molecular crystals as in Fig. 2. That assumption is not unreasonable, but it is unlikely to be of general validity, and therefore we released it. Especially for the smaller size PAH molecules where direct intermolecular forces are weaker the addition of six alkali atoms per bimolecular per cell is a major perturbation that could impact the herringbone structure. In our EA search for M$_3$-PA (M = K, Rb) and K$_3$-PC, the molecular arrangement was given freedom to change, and in fact the herringbone arrangement was found to survive in K$_3$-PC but not in M$_3$-PA. Below we present results of M$_3$-phenanthrene, (M = K, Rb) first, and for K$_3$-picene second. We will present structures, their energies, and their electronic structures followed by a conclusive discussion.

A. M$_3$-Phenanthrene (M = K, Rb)

The behavior of K$_3$-PA and of Rb$_3$-PA was found to be totally similar, once a volume expansion of about 8% is considered between the two. Therefore we will mostly...
discuss K₃-PA here, while all conclusions are valid for Rb₃-PA too.

FIG. 2. (Color online) Crystal structures of the M₃-PA low energy structures, obtained assuming two PA molecules and six K or Rb atoms per cell. PS is the previous P2₁ symmetry herringbone structure of de Andres et al.₁¹, chosen as reference. Structure EA1 (metallic) is a first evolution of PS; EA2 (insulating) and EA3 (metallic) are the two lowest energy structural polymorphs. All have a lower P₁ symmetry, but differ by arrangement and shape details of the phenanthrene molecules, and by the positions of the alkalis. Note that approximately defined molecular planes are nearly orthogonal in EA2, but have turned parallel in EA3, which represents our best candidate metallic (possibly superconducting) phase.

We obtained the three lowest energy structures EA1–3 of Fig. 2 with lattice parameters listed in Table 1. Full crystal structure data is given in the Supplementary Information in cif format at the end of this manuscript. The three structures differ in the orientation (and distortion) of the phenanthrene molecules and in the position of the alkali atoms in the bimolecular cell. Each of these structures, generally with P₁ symmetry, represents a “relevant structure”, standing for a multiplicity of nearly degenerate structures differing, e.g., by small displacements of alkali atoms or small distortions of the PA molecules. Later we will provide for the best metallic structure EA3 an example of such a slightly distorted structure which turns the crystal from metallic to semimetallic. Total energies and structural parameters are presented in Fig. 3 also illustrating the uncertainty due to the different vdW functional chosen, as well as a rough equivalence of some vdW forces to a hydrostatic pressure.

The first relevant structure EA1 is a herringbone although a different one from PS, with a 0.4–0.8 eV/cell lower energy, as seen in Fig. 3. Molecules in EA1 are T-shape oriented and are stacked long edge-to-face, with an angle of about 70°. The DFT-PBE electronic structure calculation (Fig. 4) shows that EA1 is metallic, but with much narrower bands and lower symmetry than PS.

In structure EA2 the PA molecules approximately lie on alternating nearly orthogonal planes and are relatively flat, but the six alkali atoms are grouped close enough together to form a sort of loose cluster, sitting between the molecules. The formation energy of M₃-PA compounds relative to the metallic alkali metal plus pristine phenanthrene is definitely negative, which rules out phase separation, which would be surprising here even if in an embryonic form. In order to understand what happens we carried out an analysis of the bonding which is shown in Fig. 5 and of the resulting electronic structure, Fig. 4.

The outcome is that in EA2 the M₆ alkali cluster as a whole donates four of its six s-electrons to the LUMO orbitals of the two PAH molecules in the cell, leaving the LUMO+1 totally empty. The two remaining alkali s-electrons fill up instead a “superatomic” orbital of the alkali cluster, emphasized in Fig. 4, with energy well below the Fermi energy and even below the LUMO band. This electronic configuration gives rise to an insulator with a gap of 0.2–0.4 eV, roughly corresponding to the LUMO-LUMO+1 energy separation. The EA2 structure is therefore not a straight phase separation in an embryonic stage but rather appears to represent, with all
FIG. 4. (Color online) DFT-PBE electronic band structure of various K$_3$-PA crystal structures. Among the two best structures EA2 and EA3, EA2 is a nonmagnetic band insulator, where the two uppermost filled bands have molecular LUMO character, the lowest unfilled bands a LUMO+1 character, and the filled band emphasized in red is a shared orbital within the six alkali atoms in the cell. EA3 instead is the best metallic structure with partly degenerate LUMO+1 half filled bands at Fermi level, not unlike those calculated for La-PA. In analogy to that case, the near-degeneracy at Fermi can be reduced or lifted by a slight intra-cell atomic displacement (here of the K atoms) which takes the system to a semi-metallic state. The insulating antiferromagnetic electronic structure obtained by allowing spin polarization in metallic EA3 is also shown.

the caution and the provisos suggested by assumptions made about cell size and about stoichiometry, a true polymorph of M$_3$-PA. Its structure enhances the crystal volume with a large intermolecular distance between the phenanthrene molecules, yet the mixed ionic-covalent bonding makes it energetically competitive. Of course, unusual as this structure is, it would need checking, e.g., by increasing the simulation cell size, for example by doubling it in the form (2x2x2). However, that would call for a 2$^6$ times large computational effort which is presently beyond the reach of this work. Because of that, and since EA2 is not always the lowest energy structure at least in presence of van der Waals forces, and is not even metallic, we do not pursue it further.

Structure EA3 finally, our best metallic structure, is characterized by a remarkably different, parallel stacking of phenanthrene molecular layers repeating on top of one another (AAA) with alkali atoms spread between the layers as in Fig. 2. The electronic structure of Fig. 4 shows half-filled LUMO+1 bands of width 0.2 eV that are half-filled and somewhat close to electron-hole symmetrical, with near degeneracies and a high density of states near the Fermi level. As was the case in a model previously derived for the hypothetical crystal La-phenanthrene, this situation suggests a potentially strong Fröhlich electron-phonon coupling to zone boundary modes. Among them, a distortion that would reduce the approximate equidistance of atoms and of molecules in the cell, removes this degeneracy and leads to a semimetal. Modifying the structure EA3 of K$_3$-PA by statically displacing the alkali atoms out of their optimal straight-line arrangement (Fig. 6 for example to form an angle of about 174° rather than 180°, the band splitting and the resulting semimetallic behavior obtained are shown in Fig. 4. This is a suggestive element in view of a possible electron-phonon mechanism for superconductivity of electron-
doped PAHs, which is presently under discussion and is being addressed elsewhere. The gap-opening distortion just chosen here is of course somewhat arbitrary, and a proper phonon and electron-phonon calculation will be needed in order to pursue this line.

FIG. 6. (Color online) Top view of the EA3 structure of K$_3$-PA. K atoms are aligned in a slightly deformed straight line with a K$_1$–K$_2$–K$_3$ angle of 174°. An increased zig-zag deformation reducing this angle to 162° transforms the metal into a semi-metal. The distance between the phenanthrene molecular centers is about 5.5 Å, that between the K and center of the nearest benzene ring of PA 2.7 Å. The PA molecules, although not strictly planar, approximately lie on parallel planes, in contrast with the herringbone structure of pristine phenanthrene and of structure EA1.

B. K$_3$-Picene

The genetic crystal structure optimization just conducted for M$_3$-PA led to identify unexpected structures, where the pristine herringbone molecular stacking is abandoned. In view of that, it is worthwhile conducting the same search for K$_3$-PC. Repeating for better confidence the search with a variety of different starting points and both with DFT-vdW and with DFT-PBE at 10 kbars which are roughly equivalent, we invariably found in K$_3$-picene a face-to-edge herringbone packing as the best structure, in contrast to M$_3$-PA. This supports the assumptions and the results, anticipated by previous authors, that the basic herringbone structural motif of pristine picene is preserved.

Previous studies of acenes emphasized the importance of the balance between electrostatic and van der Waals interactions for the packing in molecular crystals. As discussed for pentacene, co-planar stacking essentially results from electrostatic interaction while face-to-edge herringbone is stabilized by dispersion and quadrupole forces. The much larger size of picene implies larger quadrupolar forces, which explains the large stability of herringbone, as opposed to the fragility against doping just shown for phenanthrene.

Both C and D structures, that are energetically the best in presence of van der Waals forces, are face-to-edge herringbone with P2$_1$ symmetry (Fig. 7 and Fig. 8). Similarly to the previously optimized K$_3$-PC-structure the potassium atoms form ordered chains along the c-axis, lying in front of the aromatic ring (Fig. 7). In structure D the chains are uniformly stacked, whereas in the ordering

| Energy and structural data of the best structures of K$_3$-PA and Rb$_3$-PA calculated with DFT-GGA at zero pressure compared with the earlier proposed PS structure. Energy in units of meV.cell$^{-1}$ measured with respect to that of the best structure. Volume is in Å$^3$. Each of these relevant structures generally allows slightly different variants depending on small extra alkali or molecular displacements. |
|---|
| **K$_3$-PA** |
| Sym. | P2$_1$ | P2$_1$ | P1 | P1 | P1 |
| Energy | 1352 | 556 | 70 | 28 | 0 |
| Volume | 586.9 | 648.8 | 786.0 | 693.4 | 725.7 |
| a | 8.24 | 8.95 | 9.63 | 9.96 | 10.20 |
| b | 7.05 | 8.32 | 9.89 | 8.92 | 9.12 |
| c | 10.7 | 8.9 | 9.5 | 9.5 | 9.6 |
| α | 90.0 | 103.0 | 112.6 | 95.1 | 97.2 |
| β | 108.8 | 90.0 | 90.7 | 114.2 | 107.8 |
| γ | 90.0 | 90.0 | 100.7 | 94.9 | 116.2 |
| **Rb$_3$-PA** |
| Sym. | P2$_1$ | P2$_1$ | P1 | P1 | P1 |
| Energy | 1554 | 608 | 0 | 129 | 120 |
| Volume | 631 | 721 | 868 | 765 | 774 |
| a | 8.74 | 9.16 | 9.87 | 10.32 | 10.23 |
| b | 7.10 | 8.64 | 10.12 | 9.13 | 9.18 |
| c | 10.78 | 9.26 | 9.64 | 9.82 | 9.79 |
| α | 90.0 | 100.6 | 113.4 | 94.9 | 96.0 |
| β | 109.4 | 90.0 | 90.8 | 112.2 | 106.2 |
| γ | 90.0 | 90.0 | 99.9 | 63.7 | 115.0 |
FIG. 7. (Color online) The three best structures B, C, D of K$_3$-picene. All structures are herringbone with $P2_1$ symmetry as in pristine molecular picene. D basically coincides with a previously proposed structure, whereas in C alternating lines of potassium atoms are shifted relative to one another, forming a zig-zag network. C and D have basically the same total energy.

FIG. 8. (Color online) Volume (a) and enthalpy (b) of four relevant structures A–D of K$_3$-PC using different functionals and at different pressures. Structure D is closest to earlier established structure in Ref. The two best structures C and D are nearly degenerate in energy and differ by the fractional shift of one alkali line relative to the other line in the unit cell. Note that here vdW corrections are more important than in M$_3$-PA, on account of the larger molecular size. A hydrostatic pressure of about 10 kbars (blue line) has here a similar effect to vdW-DF (cyan and red lines).

We stress here that this kind antiferromagnetic instability of the metallic phases, well known and quite general for these narrow band systems, must be considered with caution. It is surely a signal warning that correlations are very strong, but it needs not imply a true instability of the metallic state. As is independently being shown e.g., in Ref. the inclusion of correlations through a Gutzwiller treatment of a Hubbard $U$ can upset the energetic balance between the metal and the antiferromagnetic insulator, actually favoring a nonmagnetic, metallic and potentially superconducting state at least for small $U$. This background knowledge allows the provisional neglect of the magnetic instabilities, and a serious consideration of crystal structures C and D as genuine candidates describing the metallic phase of K$_3$-PC.

IV. CONCLUSIONS

Electron doped PAHs encompass a larger variety of crystal structure polymorphs than imagined so far. We systematically studied the crystal structure of M$_3$-PA (M = Rb and K), an interesting system where superconductivity has been reported, and of K$_3$-PC, the most studied electron doped and superconducting PAH. By means of an evolutionary algorithm we identified in K$_3$-PA and Rb$_3$-PA at least two possible polymorphs with distinctly different structures that are competing for the ground state. One of them (EA2) is a band insulator, the other (EA3) is metallic, and thus a candidate superconductor. Structurally, the pristine herringbone structural symmetry appears systematically broken by the alkali doping.

The scenario is different in K$_3$-PC, where the larger size molecule allows to the herringbone structure and $P2_1$ symmetry to survive in the stable structure. Here too we still find two essentially degenerate polymorphs, both metallic, whose only difference is the arrangement of the potassium atoms.

Within DFT-PBE all metallic structures are unstable against antiferromagnetism, an instability which leads them to an insulating state in pin-polarized DFT. While
that signals the importance of correlations in the non-magnetic metallic states, it does not imply their irrelevance or non-existence, as recent Gutzwiller calculations have suggested. Should the three-electron stoichiometry which we assumed be confirmed, the present results would also be relevant to the superconductivity of these compounds. The electronic structures of most metallic phases we found, either M₃-PA or K₃-PC, share a common element, namely the near degeneracy among the two LUMO+1 half-filled conduction bands, quite close to the Fermi level. That degeneracy may, as was noted in an earlier calculation for hypothetical La-PA, and as is pointed out above for structure EA3 of K₃-PA be very efficiently split by a zone boundary phonon. That is in broad analogy with MgB₂, potentially interesting as a driving element of phonon-driven superconductivity. Our recent study of a “Hubbard-Frohlich” model derived by idealizing this idea is showing a s± superconducting phase which is especially robust against electron-electron repulsion.

Comparison of our theoretical crystal structures with experiments, problematic at the moment because well defined single phase stoichiometrically defined data are still being sought, will be very interesting suggesting a close cooperation with future structural determinations. We underline the fact that structural work and chemical understanding represent an absolutely vital and urgent necessity for the development and credibility of this field. The present theory work is a basic contribution to this development, that will hopefully encourage future experimental work.

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SUPPLEMENTARY: CRYSTALLOGRAPHIC INFORMATION FILE (CIF)

1. Structure EA1

A. M(3)-phenanthrene

2. Structure EA2

3. Structure EA3(M)
loop
_symmetry_equiv_pos_as_xyz
_symmetry_Int_Tables_number 1
_symmetry_space_group_name_H-M 'P 1'
_cell_angle_alpha 95.07159
_cell_length_c 9.48859

#### STRUCTURE EA3(SM)

#### 4. Structure EA3(SM)

#### 5. Structure PS-K$_3$Phenanthrene
2. Structure B

# CRYSTAL DATA

## STRUCTURE_B

| pd_phase_name | 'EA34' 10.672 7.649 14.576 91.235 105 |
|------------------|------------------------------------------|
| cell_length_a | 9.833379 |
| cell_length_b | 13.84559 |
| cell_length_c | 9.98024 |
| cell_angle_alpha | 106.077 |
| cell_angle_beta | 105.677 |
| cell_angle_gamma | 72.5535 |
| symmetry_space_group_name_H-M | 'P 1' |
| symmetry_cell_number | 1 |

#----------------------------------------------------------------------

## STRUCTURE_C

| pd_phase_name | 'EA188' 7.932 7.540 13.623 97.445 89 |
|------------------|------------------------------------------|
| cell_length_a | 7.3931 |
| cell_length_b | 7.5668 |
| cell_length_c | 13.6552 |
| cell_angle_alpha | 97.4585 |
| cell_angle_beta | 90.2286 |
| cell_angle_gamma | 79.9333 |
| symmetry_space_group_name_H-M | 'P 1' |
| symmetry_cell_number | 1 |

loop

| symmetry_equiv_pos_as_xyz |
|-----------------------------|

| x, y, z |

| atm_site_label | atm_site_occupancy |
|------------------|---------------------|

| atm_site_type_symbol |
|----------------------|

| atm_site_type_symbol |

| atm_site_label | atm_site_occupancy |
|------------------|---------------------|

| atm_site_type_symbol |

| atom site | x | y | z |
|------------------|---|---|---|

3. Structure C

# CRYSTAL DATA

## STRUCTURE_C

| pd_phase_name | 'EA188' 7.932 7.540 13.623 97.445 89 |
|------------------|------------------------------------------|
| cell_length_a | 7.3931 |
| cell_length_b | 7.5668 |
| cell_length_c | 13.6552 |
| cell_angle_alpha | 97.4585 |
| cell_angle_beta | 90.2286 |
| cell_angle_gamma | 79.9333 |
| symmetry_space_group_name_H-M | 'P 1' |
| symmetry_cell_number | 1 |

loop

| symmetry_equiv_pos_as_xyz |
|-----------------------------|

| x, y, z |

| atm_site_label | atm_site_occupancy |
|------------------|---------------------|

| atm_site_type_symbol |
|----------------------|

| atm_site_type_symbol |

| atom site | x | y | z |
|------------------|---|---|---|
4. Structure D

5. Structure PS-K₃Picene
