Van der Waals density functional study of the structural and electronic properties of La-doped phenanthrene

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(Dated: November 21, 2013)

By the first principles calculations based on the van der Waals density functional theory, we study the crystal structures and electronic properties of La-doped phenanthrene. Two stable atomic geometries of La\textsubscript{1}phenanthrene are obtained by relaxation of atomic positions from various initial structures. The structure-I is a metal with two energy bands crossing the Fermi level, while the structure-II displays a semiconducting state with an energy gap of 0.15 eV, which has an energy gain of 0.42 eV per unit cell compared to the structure-I. The most striking feature of La\textsubscript{1}phenanthrene is that La 5d electrons make a significant contribution to the total density of state (DOS) around the Fermi level, which is distinct from potassium doped phenanthrene and picene. Our findings provide an important foundation for the understanding of superconductivity in La-doped phenanthrene.

I. INTRODUCTION

The recent discovery of superconductivity with T\textsubscript{c} of 18 K in potassium doped picene (C\textsubscript{22}H\textsubscript{11})\textsuperscript{1} has attracted great attention on the aromatic superconductor, a new class of organic superconductor, which was formed by intercalating alkali metal atoms into the interstitial space between aromatic molecules in the molecular crystal. Subsequently, alkali metal doped phenanthrene (C\textsubscript{14}H\textsubscript{10})\textsuperscript{2} and dibenzopentacene (C\textsubscript{30}H\textsubscript{18})\textsuperscript{3} with superconducting transition temperature of T\textsubscript{c} = 5.6 K and 33 K were reported, respectively. In the three kinds of superconductors, the electronic charges are transferred from the doped metal atoms to aromatic molecules and delocalized throughout the molecular crystal. Apart from alkali metal, alkaline earth and rare earth metal are also adopted to synthesize metal-doped phenanthrene crystal to explore their superconductivity. In experiment, the high quality Ba\textsubscript{1.5}phenanthrene \textsuperscript{4} and La\textsubscript{1}phenanthrene \textsuperscript{5} superconductors were obtained with superconducting shielding fractions 40\% and 46\%, and for La\textsubscript{1}phenanthrene, the superconducting transition temperature significantly increases with the pressure and sustains high T\textsubscript{c} in a wide range of pressure \textsuperscript{6}.

The determination of crystal structure of metal doped picene, phenanthrene, and dibenzopentacene is an important prerequisite to understand the electronic behavior and superconducting mechanism in the aromatic superconductors. However, the detailed crystal structures of doped materials have not yet been reported in experiment, especially the metal atomic position, due to the degradation of sample in air and the limit of measurement techniques \textsuperscript{7}. Several theoretical groups have devoted to the researches on the crystal and electronic properties \textsuperscript{2,7,9,4}. For example, Kosugi \textit{et al}. systematically investigated the crystal structure of K-doped picene with different K concentrations, and found that multiple structures exist at the same K concentration; Andres \textit{et al}. fully optimized the geometries of K\textsubscript{3}picene and acquired two distinct structures, one with a herringbone structure and the other with a laminar structure. For tripotassium-intercalated phenanthrene, there also exist the great discrepancy between the optimized structure and the measured one \textsuperscript{15}. Other theoretical researches on the electronic correlation effect and magnetism of K\textsubscript{3}picene were also performed and the lattice parameters were fixed at the measured values \textsuperscript{16} in their first principle calculations.

We notice that van der Waals interactions have not been taken into account in previous theoretical studies. The organic compounds of picene, phenanthrene, and dibenzopentacene are the typical molecular crystals, which have low density and hardness because of the light element and relatively long intermolecular bonds. In these materials, van der Waals interactions existing among molecules play a key role in determining the intermolecular distance and the stacking pattern. Therefore, it is quite necessary to include this factor in simulation of the structural and electronic properties of metal-doped picene, phenanthrene, and dibenzopentacene superconductors.

In this paper, we focus on the structural and electronic properties of rare earth metal La doped phenanthrene, which became a valuable research issue because of the following reasons. Firstly, potassium is an alkali metal element with one electron in the outermost shell. Due to the high metal reactivity, potassium is usually used to intercalate into graphite, C\textsubscript{60}, phenanthrene, picene, and dibenzopentacene to induce superconductivity. Lanthanum belongs to rare earth metal with an electron configuration [Xe]5d\textsuperscript{1}6s\textsuperscript{2} and exhibits two oxidation states, +3 and +2 in general. The metal reactivity of Lanthanum is much lower than potassium
in the reactivity series of metal. Because of such difference, a large discrepancy relative to K-doped phenanthrene can be expected in La-doped phenanthrene. Secondly, the recent report from X. J. Chen group indicated that La-doped phenanthrene displays a significant positive pressure effect of $T_c$ and a sustainable high critical temperature within a wide pressure range, which are unique superconducting features different from K-doped phenanthrene. 

The paper is organized as follows. In Sec. II the computational method is briefly described. In Sec. III the results obtained are described and discussed. In Sec. IV the conclusions are presented.

II. DETAILS OF METHOD

In our calculations the plane wave basis method was used \[17\]. We adopted the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) formula \[18\] for the exchange-correlation potentials. The projector augmented-wave method (PAW) pseudopotentials were used to model the electron-ion interactions. The local-density approximation (LDA) is appropriate for largely homogeneous systems, for example, simple metals and semiconductors. The semilocal-density approximation - GGA works well for inhomogeneous systems, for example, transition metals, ionic crystals, compound metals, surfaces, interfaces, and some chemical systems. However, for sparse systems, including soft matter, van der Waals complexes, and biomolecules, they have inter - particle separations, for which nonlocal, long-ranged interactions, such as van der Waals (vdW) forces, are influential. The van der Waals interaction is considered in the scheme developed by Dion, Thonhauser et al. \[19, 20\] and enclosed in the first principle calculation code Quantum-ESPRESSO \[17\]. In the functional the exchange-correlation energy takes the form of

$$E_{xc} = E_{xc}^{GGA} + E_{xc}^{LDA} + E_{xc}^{nl}$$

where the exchange energy $E_{xc}^{GGA}$ uses the revPBE GGA functional and $E_{xc}^{LDA}$ is LDA to the correlation energy. $E_{xc}^{nl}$ is the nonlocal energy term which accounts approximately for the nonlocal electron correlation effects. The vdW-DF method greatly improves the interaction energies of dispersion bonded systems \[21, 23\], and its application to hard solid can also obtain a systematic improvement in atomization energy and cohesive properties \[24\].

The Gaussian broadening technique was employed and a mesh of $6 \times 6 \times 6$ k-points were sampled for the Brillouin-zone integration. After the full convergence test, the kinetic energy cut-off and the charge density cut-off of the plane wave basis were chosen to be $80$ Ry and $600$ Ry, respectively. In our calculations, the lattice parameters were firstly fixed at the experimental values and the internal atomic coordinates were optimized by the energy minimization. The variable unit cell calculations were performed to compare with the results in the case of fixed lattice constants. The structure relaxation is performed by Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-newton algorithm \[25, 26\] and the maximum and minimum ionic displacement are set to $0.8$ and $0.001$ Bohr. The convergence thresholds of the total energy and force on atom are $10^{-5}$ Ry and $10^{-4}$ Ry/Bohr respectively, and for variable cell calculation, the residual stress on cell is less than $0.5$ KBar.

III. RESULTS AND DISCUSSIONS

Pristine phenanthrene crystallizes in the space group $P2_1$ with the lattice parameters $a = 8.453$ Å, $b = 6.175$ Å, $c = 9.477$ Å, and $\beta = 98.28^\circ$ measured at room temperature \[2\]. The crystal geometry is shown in Fig. 1, where a unit cell contains two molecules arranged in a herringbone structure. After the lattice parameters and the inner atomic coordinates are all fully relaxed, the obtained parameters $a$, $b$, $c$, and $\beta$ are $8.401$ Å, $6.166$ Å, $9.445$ Å, and $97.65^\circ$, which are perfectly consistent with the ones in experiment. If van der Waals interaction is not included in the calculation, the optimized parameters are $8.791$ Å, $6.368$ Å, $9.608$ Å, and $98.66^\circ$. The differences between two sets of computational cell parameters demonstrate that van der Waals force is an important aspect of physics in phenanthrene and related compounds, and it is necessary to take account of this interaction in the first principles simulation for these materials.

The rare earth metal La atoms are intercalated into phenanthrene solid with the ratio of La atom and molecule 1:1 to form La-phenanthrene. La-doped phenanthrene crystallizes in $P2_1$ space group with the lattice parameters $a = 8.482$ Å, $b = 6.187$ Å, $c = 9.512$ Å, and $\beta = 97.95^\circ$. In the relaxation calculations, we have checked most possible configurations to explore the reasonable geometry structure. For La1 phenanthrene, the possible arrangements for two La atoms and two molecules in a unit cell are much reduced compared to...
the situation of K$_3$phenanthrene with six K atoms and two molecules in a unit cell. The following four cases were considered and believed to be sufficient for the arrangement of molecules and La atoms, as shown in Fig. 2 (a) two La atoms are located at two sides of a molecule in a unit cell; (b) two La atoms are located at the same side of a molecule; (c) one La atom sits at the end of molecule (between two molecular layers) and the other at the side of molecule (in the molecular layer); (d) two La atoms sit at the molecular ends. We relaxed the inner atomic positions in the unit cell with cell parameters fixed at the measured ones. The initial configurations (a), (c) and (d) would evolve into the same structure, called the structure-I, whereas the configuration (b) leads to the structure-II.

### 1. La-doped phenanthrene: the structure-I

Fig. 3 shows one of the two stable structures, namely the structure-I. In a molecular layer of La-doped phenanthrene, the aromatic molecules are arranged in a herringbone structure, with an angle about 90° between nearest-neighbor molecular planes. The arrangement of molecules forms a network structure, and La atoms enter into the net hole. For the structure-I, La atoms are distributed more uniformly, i.e. one La atom sited in each hole. The positions of two La atoms in a unit cell are about $\frac{1}{4}c$ and $\frac{3}{4}c$ along the c axis. As for the symmetry of unit cell, the structure-I also keeps P$\bar{2}$$_1$ group symmetry similar to pristine phenanthrene, namely all atomic positions obey the symmetry operation $(x, y, z) \rightarrow (-x, y+0.5, -z)$.

Because of intercalation of La atom, the molecular plane of phenanthrene is distorted. Then the interactions among molecules, especially by the bridge of La atom, are enhanced and lead to a stronger band dispersion, as shown in Fig. 4. Fig. 4(a) clearly shows that there are two bands crossing the Fermi level. The dispersion of bands along $XP$, $FT$ and $ZQ$ (parallel to the axis $b^\ast$). Compared with the band structure of K$_3$phenanthrene in the lower panel of Fig. 2 in Andres’ paper [13], the total width of two bands crossing the Fermi level is about 0.8 eV for La$_1$phenanthrene, which is larger than 0.5 eV in the K doped case. In addition, the two bands below the Fermi level locate around -1.0 eV for La$_1$phenanthrene, lower than -0.5 eV in K$_3$phenanthrene.

An important feature of the electronic structure of La-doped phenanthrene is revealed in Fig. 4(c) that besides the C 2$p$ states, another important contribution to the DOS around the Fermi energy is from La 5$d$ electrons with the weight of about 27%, which is estimated based on the total DOS (3.26 states/eV) and projected DOS on La 5$d$ orbitals (0.44 states/eV $\times$ 2 for two La atoms).

In order to understand this significant feature, we performed Löwdin population calculations to discover the charge transfer from La atom to phenanthrene molecule and resulting electron occupations in atomic orbitals. The calculations indicate that each of two C atoms close to La atom gets about 0.35~0.40 electron from the neighboring H and La atoms. The 6$s$ orbital is empty and 5$d$ orbital has 1.8 electron for La atom. As can be seen from Table. I, the charge transferred from each La atom to a molecule is about 1.0 electron. This result has a great difference from the situation of K-doped phenanthrene. Three K atoms are required for each aromatic molecule in K-doped phenanthrene, picene, dibenzopentacene, coronene[9], as well as fullerene[27, 28], where each molecule can get three electrons from metal atoms. The K 4$s$ states are far higher than the Fermi energy and completely empty in the K-doped system[8], while there exists strong hybridization between La 5$d$ states and C 2$p$ states in La$_1$phenanthrene, which can explain the difference between their band structures. The contribution of La 5$d$ states to the DOS at the Fermi level implies that superconductivity in this compound is intimately related to these La 5$d$ electrons.

The positive pressure effect on $T_c$ is a common feature in the doped aromatic superconductors. Especially for La-doped phenanthrene, application of pressure significantly increases $T_c$ from 4.9 to 8.5 K as the pressure
increases from ambient pressure to 3.2 GPa before the structural phase transition. A similar increase of $T_c$ from 6.1 to 7.6 K with the pressure from ambient pressure to 1.0 GPa was also found by Wang et al. To understand the effect of pressure on the superconductivity in La-doped phenanthrene, we keep the shape of crystal unit cell and decrease the volume to simulate the pressure effect. When the volume changes from 100% to 95%, 90%, and 85%, the corresponding pressure is increased from 2.27 to 3.61, 5.52 and 8.20 GPa, respectively. The total DOS are displayed in Fig. ?? as a function of the volume. The value of DOS at Fermi level increases gradually from 3.2 to 3.6, 3.9, 4.7 states/eV with the volume decreasing. According to the Bardeen-Cooper-Schrieffer (BCS) theory of electron-phonon induced superconductivity, the increase of DOS with pressure will result in an increase of $T_c$, which is in consistent with the experimental measurements.

2. La-doped phenanthrene: the structure-II

For La$_1$phenanthrene, one unit cell includes two La atoms and two molecules. When two La atoms enter the same hole in the network formed by phenanthrene molecules, we obtain the structure-II, as shown in Fig. 5. Because two La atoms do not obey the symmetry operation $(x, y, z) \rightarrow (-x, y+0.5, -z)$, the structure-II does not keep the P2$_1$ group symmetry and it belongs to P1 space group. Compared with the structure-I, the energy is about 0.42 eV lower per unit cell composed of 50 atoms. Hence, the structure-II is more stable from the energetic view. Our results show that the stress of the structure-II with the experimental unit cell is 2.186 GPa, which is comparable to the stress of the structure-I and less than the pressure 3 GPa for tripotassium-intercalated phenanthrene.

Fig. 5 shows the band structure and DOS for the structure-II. The bands are more flat and less dispersive relative to the ones of the structure-I. An remarkable feature revealed by our calculations is that it displays a semiconducting state with an energy gap of 0.15 eV.
percents deviation from 1 in La of superconductor when the concentration of La has few percents deviation from 1 in La phenanthrene, similar to the parent compounds of superconductor LaCuO$_4$\cite{29}, KFe$_{1.5}$Se$_2$\cite{30} and K$_{0.3}$Fe$_{1.6}$Se$_2$\cite{31}.

3. The optimized lattice parameters for the structure-I and structure-II

The simulation of crystal structure of doped phenanthrene or doped picene is a great challenge, because the optimized crystal structures of doped phenanthrene\cite{13} or doped picene\cite{7, 8} reported at present deviate largely from the measurements, even is completely different from the experiment. The variable cell calculations were also performed for La-doped phenanthrene. For structure-I with P$2_1$ group symmetry, the optimized lattice parameters are $a = 8.632$ Å, $b = 6.505$ Å, $c = 9.661$ Å, and $\beta = 108.03^\circ$. Compared with the experimental ones $a = 8.482$ Å, $b = 6.187$ Å, $c = 9.512$ Å, and $\beta = 97.95^\circ$, the corresponding fractional errors are $+1.7\%$, $+5.1\%$, $+1.5\%$, and $+10.3\%$, respectively. For the structure-II with P$1$ group symmetry, the calculated lattice parameters are $a = 9.202$ Å, $b = 6.005$ Å, $c = 9.829$ Å, $\alpha = 86.59^\circ$, $\beta = 103.66^\circ$ and $\gamma = 93.06^\circ$, and the corresponding fractional errors are $+8.5\%$, $-2.9\%$, $+3.3\%$, $-3.8\%$, $+5.8\%$ and $+3.4\%$, respectively ($\alpha = \gamma = 90^\circ$ in the experimental cell with P$2_1$ symmetry). The unit cell volumes for the structure-I and structure-II are $515.8$ Å$^3$ and $525.6$ Å$^3$, very close to the experimental value $494.3$ Å$^3$. With the optimized lattice constants, we have investigated the electronic structure of La$_1$phenanthrene and found that their electronic properties are similar to ones with the experimental lattice parameters. The structure-I is a metal and the structure-II lies in the semiconducting state with a larger energy gap of 0.30 eV. Still, the DOS of La 5$d$ orbital have a substantial contribution to the total DOS around the Fermi level.

There is very small difference of lattice parameters in experiment between pristine and La-doped phenanthrene. However, in our optimized structure-I and structure-II, the errors for some parameters compared to the measurement are larger than 5%. One reason may be that in the compound containing rare earth metal La whose atomic radius is much larger than the ones of C and H atom, it is difficult to deal with the non-bonding interaction between C atom and La atom with available pseudopotentials.

In experiment, the metallic phase of La$_1$phenanthrene was observed, which corresponds to the structure-I. Now the question arising is why the structure-II with lower energy was not observed in measurement? This issue could be addressed in the relaxation calculations. As already mentioned before, the initial configurations (a), (c) and (d) in Fig. 2 evolve into the structure-I, while only the particular configuration (b) results in the structure-II. This demonstrates that it is easier to form the metallic phase during the crystal growing process.

![Image of graph](image-url)

FIG. 6. (Color online) (a) Band structure of La$_1$phenanthrene with experimental lattice parameters for the structure-II. (b) Total DOS per unit cell and orbital-resolved partial DOS per C atom and per La atom. The Fermi level is set to zero.

eV. The lower panel in Fig. 6 shows the partial DOS of La 5$d$ states, which make a great contribution to the total DOS around the Fermi level, similar to the situation for the structure-I. Löwdin population calculations show that each of two C atoms close to La atom gets about 0.35~0.40 electron from the neighbored H and La atoms, and La 6$s$ orbital is empty and La 5$d$ states have about 2.0 electron for La atom. The lost charge per La atom is about 1.0 electron. In experiment, the effect of charge transfer in La-doped phenanthrene was studied by Raman spectroscopy. Based on the similar behavior of phonon softening between La-doped and K-doped phenanthrene, X. F. Wang et al. suggested that three electrons are transferred from a La atom to a phenanthrene molecule\cite{5}. Obviously, our Löwdin population analysis for the structure-I and structure II does not support their deduction. More experiments are needed for clarifying the actual charge transfer in La-doped phenanthrene.

The semiconcuting structure-II phase is not the superconducting phase, but it may be a parent compound of superconductor when the concentration of La has few percents deviation from 1 in La$_1$phenanthrene, similar to...
**IV. CONCLUSIONS**

In summary, by the first principles calculations, we study the crystal structures and electronic properties of pristine and La-doped phenanthrene under considering van der Waals interaction. For La\textsubscript{1}phenanthrene, two stable atomic geometries are obtained with different La atom distributions in the interstitial space among molecules. The structure-I is a metal and two energy bands cross the Fermi level. The structure-II displays the semiconducting state with an energy gap of 0.15 eV. From the energetic viewpoint, the structure-II is more stable because it has an energy gain of 0.42 eV per unit cell compared to the structure-I. The most striking feature of La\textsubscript{1}phenanthrene is that La 5d electrons make a great contribution to the total DOS around the Fermi level, which is obviously distinct from potassium doped phenanthrene and picene. The similar results can be obtained when we carried out the related calculations with the optimized lattice parameters, demonstrating that the electronic property of La\textsubscript{1}phenanthrene is strongly correlated with the specific positions of La atoms. Our findings provide an important information for understanding superconductivity in La\textsubscript{1}phenanthrene.

Whether the superconductivity in these metal doped aromatic crystals is driven by electron-phonon or electron-electron mechanism is still in debate. The value of $x = 3$ is special for K\textsubscript{1}picene, K\textsubscript{2}phenanthrene and K\textsubscript{6}dibenzo[12]annulene, indicating that three electrons doped into each molecule seem to be a key factor to induce superconductivity in K-doped aromatic materials.

For La\textsubscript{1}phenanthrene, La atom is expected to provide three electrons to each phenanthrene molecule. However, only about one electron is transferred from La atom to aromatic molecule, as indicated by Löwdin population. This is drastically different from usual lanthanide compounds and lanthanide complexes, where La takes the valence state of +3 and each La atom loses three electrons. Moreover, La 5d electrons have a great contribution to the DOS around the Fermi level, which might be intimately related to superconductivity, even unconventional superconductivity. All these make La\textsubscript{1}phenanthrene special and rich physical properties can be expected in further research.

**V. ACKNOWLEDGMENTS**

We acknowledge the valuable discussion with Guohua Zhong. This work was supported by MOST 2011CB922200, the Natural Science Foundation of China under Grants Nos.91230203, 91221103, 11174072 and U1204108.

*Note added.* While in the preparation of this manuscript, we learnt of a paper by S. Shahab Naghavi group (Phys. Rev. B 88, 115106 (2013)), which reports that the lowest energy state of La\textsubscript{1}phenanthrene is band insulating and the best metallic structure is slightly higher in energy but retains the $P2_1$ symmetry. The structure-I and structure-II in our results are accordant with the best metallic structure and the lowest energy structure shown in Fig. 3 in Phys. Rev. B 88, 115106 (2013), respectively.

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