Density functional calculations of electronic structure and magnetic properties of the hydrocarbon K₃ picene superconductor near the metal–insulator transition

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New Hydrocarbon Superconductor on the Verge of Metal-Insulator Transition: Electronic Structures and Magnetic Properties of K$_3$picene

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We have investigated the electronic structures and magnetic properties of of K$_3$picene, which is a first hydrocarbon superconductor with high transition temperature $T_c$=18 K. We have shown that the metal-insulator transition (MIT) is driven in K$_3$picene by 5% volume enhancement with a formation of local magnetic moment. Active bands for superconductivity near the Fermi level ($E_F$) are found to have hybridized character of LUMO and LUMO+1 picene molecular orbitals. Fermi surfaces of K$_3$picene manifest neither prominent nesting feature nor marked two-dimensional behavior. By estimating the ratio of the Coulomb interaction $U$ and the band width $W$ of the active bands near $E_F$, $U/W$, we have demonstrated that K$_3$picene is located in the vicinity of the Mott transition.

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Superconductivity has recently been observed in K-doped picene, K$_3$picene, which is a first organic superconductor in the hydrocarbon system. The superconducting transition temperature of K$_3$picene, $T_c$=18 K, is comparable to that of alkali-metal doped fullerene system ($T_c$∼38K). In K$_3$picene, K atoms are intercalated in the stacked picene molecules, as shown in Fig. 1(a). A picene molecule (C$_{22}$H$_{14}$) consists of five connected benzene rings with armchair manner (see Fig. 1(b)). Interestingly, alkali-metal doped A$_3$picenes ($A$=Na, K, Rb, and Cs) exhibit cation $A$ dependent physical properties. With increasing the cation size, the system varies from a Pauli-like paramagnet for $A$=Na to superconductors for $A$=K and Rb, and then to an insulator for $A$=Cs. This feature suggests that A$_3$picene is susceptible to the chemical pressure. This trend is also reminiscent of A$_3$C$_{60}$ ($A$=K, Rb, and Cs), in which changing cation from K to Cs results in 6% volume expansion so as to induce the metal-insulator transition (MIT).

Natural immediate question is what the pairing mechanism is for this organic superconductor K$_3$picene. Unconventional superconductors of recent interest often manifest the incipient MIT and magnetic instability, which provide critical information on the pairing symmetry and the mechanism of superconductivity. Parent compound of cuprate La$_2$−$_x$Sr$_x$CuO$_4$ is an antiferromagnetic (AFM) insulator. Also organic superconductors κ-(BEDT-TTF)$_2$X and A$_3$C$_{60}$ ($A$=K and Cs) show phase transition from AFM insulator to superconductor upon increasing pressure. These examples demonstrate that the investigation of the electronic structures of K$_3$picene under volume change would provide an important clue to the pairing mechanism of superconductivity.

In this Letter, we have explored the volume dependent electronic and magnetic properties of K$_3$picene using the first principles band structure calculation within the density functional theory. We have shown that the MIT and AFM transition is driven in K$_3$picene by 5% volume enhancement with a formation of local magnetic moment. Our results indicate that K$_3$picene itself is on the verge of both MIT and magnetic instability. We have found that the active bands for superconductivity have hybridized character of LUMO and LUMO+1 picene molecular orbitals. Quantitative estimation of $U/W$ ($U$:Coulomb interaction, $W$: band width) also provides that K$_3$picene is near to the Mott transition.

In a unit cell of K$_3$picene, there are two stacked picene molecules and six K atoms (see Fig. 1(a)). The positions of K atoms are still undetermined experimentally. Hence, we first optimized internal atomic positions in K$_3$picene with retaining the observed monoclinic struc-

FIG. 1: (Color online) (a) Crystal structure of K$_3$picene. There are two stacked picene molecules in a unit cell. K atoms are intercalated between the stacked picene molecules. (b) Molecular structure of a picene.
Independent types of picene molecules in a unit cell. Configuration with opposite spin polarizations on the two and AFM phases. Pristine solid picene is a semicon-


correlation potential, the generalized gradient approxi-

employed in WIEN2k package.[12] For the exchange-

earized augmented plane wave (FLAPW) method[11] im-

plemented in VASP package.[7] The sta-

cordance with Ref.[10]. We have also optimized internal

atomic positions of K3picene in order to examine the chemical pressure effect, as is re-

alized in Cs3picene. Then, based on the optimized struc-

tures, we have obtained electronic structures of K3picene

employing the more precise all electron full-potential lin-

earized augmented plane wave (FLAPW) method[11] im-

plemented in WIEN2k package.[12] For the exchange-

correlation potential, the generalized gradient approxi-

mation (GGA)[13] was utilized. To explore the magnetic

properties of K3picene, we have considered the AFM spin

configuration with opposite spin polarizations on the two

independent types of picene molecules in a unit cell.

Figure 2 shows the density of states (DOS) of

K3picene. DOSs of K3picene with original volume (here-

after K3P[OV]) and with +5% volume expansion (here-

after K3P[EV]) are provided in their paramagnetic (PM)

and AFM phases. Pristine solid picene is a semicon-

ductor with wide band gap of 3.3 eV.[14] Figure 2(a)

shows that K3P[OV] also has an energy gap structure

(~ 1.7 eV) between HOMO and LUMO related bands.

In K3picene, three electrons are transferred from three

doped K atoms into one picene, occupying LUMO and

LUMO+1 related bands. For K3P[EV] in Fig. 2(b), the

band widths become narrower to have a larger energy gap

(~ 1.9 eV) between HOMO and LUMO related bands. It

is seen that, for both K3P[OV] and K3P[EV], the DOS at

the Fermi level (EF) is much reduced in the AFM phase

with respect to that in the PM phase. Noteworthy is that

K3P[EV] becomes an insulator in the AFM phase, hav-

ing small energy gap of ~ 0.03 eV. The PM and AFM

phases are almost degenerate. Nevertheless, the mag-

netic moment of one picene, ~0.35 μB, is large enough to

stabilize the magnetic ground state. These features sug-

gest that K3picene (K3P[OV]) is on the verge of magnetic

instability and the MIT. The conceivable AFM state of

K3P[EV] recalls molecular solids with local moment car-

rying 2p electrons. [2] [15, 16] For instance, Cs3C60 has

the AFM spin polarization, which is produced by the

unpaired electrons in the localized molecular orbital.[3]

K-doped pentacene, which is also an alkali-metal doped

hydrocarbon system, has the AFM transition below 0.2

K.[17] In this context, significant enhancement of M/H

observed in Cs3picene below 150 K is most likely to be

related to the AFM state obtained for K3P[EV].[2]

In Fig. 3(a) and (b), PM band structure of K3P[OV]

and AFM band structure of K3P[EV] are plotted, re-

spectively. The former exhibits a metallic state with

two bands crossing EF, while the latter an insulating

state. Metallic band structure of K3P[OV] results from

almost degenerate U and L bands near EF, while the

insulating state in the AFM phase of K3P[EV] emerges
due to shift up and down of respective U and L bands that had become narrowed due to the volume expansion. Notice that the degenerate bands in the PM phase of K$_3$P[OV] at k-points along zone boundary, (100)-(101)-(110) and (111)-(100) directions, are split in the AFM phase of K$_3$P[EV]. This feature indicates that the insulating state in the AFM phase of K$_3$P[EV] is similar to the Slater-type mechanism with unit cell doubling. The degeneracy on the zone boundary is lifted by AFM spin order, which might suggest that K$_3$P[EV] can be categorized into a band insulator. However, similar feature was observed in typical Mott insulating systems such as cuprate and nickel oxides. Therefore, in order to confirm whether K$_3$P[EV] is a band or Mott insulator, one needs to check the $U/W$ value of a system, as will be discussed later.

We have examined orbital characters of U and L bands near $E_F$ that are responsible for superconductivity. The charge densities (CDs) of U and L bands are plotted in Fig. 4(a) and (b), respectively. For comparison, the CDs of LUMO+1 and LUMO of a picene molecule are also provided in Fig. 4(c) and (d), respectively. The CDs in Fig. 4 reveal that U and L bands have mixed character of both LUMO and LUMO+1, even though LUMO+1 character is dominant for U. The energy splitting between LUMO and LUMO+1 of a picene molecule is known to be 0.15 eV.[2] This gap size is comparable to band widths of both LUMO and LUMO+1, even though LUMO+1 character is dominant for U. The energy splitting between LUMO and LUMO+1 of a picene molecule is also provided in Fig. 4(c) and (d), respectively. The CDs in Fig. 4(c) and (d) reveal that U and L bands have mixed character of both LUMO and LUMO+1, even though LUMO+1 character is dominant for U. The energy splitting between LUMO and LUMO+1 of a picene molecule is known to be 0.15 eV.[2] This gap size is comparable to band widths of four conduction bands near $E_F$ (U, L, and two lower bands below L in Fig. 4(b)) which correspond to 0.21, 0.12, 0.12, and 0.13 eV, respectively. The comparable gap size and band widths indicate that the hybridization interaction between LUMO and LUMO+1 is large enough to yield hybridized bands with mixed LUMO and LUMO+1 character near $E_F$. This is contrary to the case of pentacene, in which the energy splitting between LUMO and LUMO+1 ($\sim$ 1.28 eV) is much larger than that in picene.[9]

Fermi surfaces of K$_3$picene in Fig. 5 do not manifest prominent nesting feature. Also the warped Fermi surfaces indicate that this system would not have marked two dimensional behavior. In K$_3$picene, we have found that the Fermi surface geometry is very sensitive to the internal atomic positions in an unit cell. The delicate Fermi surfaces under the small variation of internal atomic positions are expected to arise from the followings: (i) weak binding interaction between picene molecules, and (ii) narrow band widths of two bands crossing $E_F$ (0.30 and 0.15 eV in Fig. 5(a)). Hence, in K$_3$picene, the shape of Fermi surface is not robust, i.e., even small structural disorder would change the geometry of Fermi surface. Indeed, the Fermi surface of the PM phase of K$_3$P[OV] (Fig. 5(a)) is a bit different from that of Ref. [9], although overall band structures are similar.

Figure 5(b) and (c) illustrate explicit effects of AFM spin polarization and volume enhancement on the Fermi surfaces of K$_3$picene, respectively. For the AFM phase of K$_3$P[OV] (Fig. 5(b)), the volume of Fermi surfaces is reduced much, as compared to that of the PM phase of K$_3$P[OV] (Fig. 5(a)). It is because of the reduced DOS near $E_F$ accompanied by the AFM spin-polarization. The remaining Fermi surfaces are mainly on (110) and (110) directions, which correspond to the directions of the nearest neighbor hopping between picene molecules. The volume enhancement also reduces the Fermi surface area, as shown in Fig. 5(c), due to the decreased band width. Warping of the Fermi surfaces in this case is much smaller than that of the PM phase of K$_3$P[OV].

We have calculated electrical conductivity $\sigma$ using the Boltzmann transport theory.[18, 19]. The $\sigma/\tau$ (\(\sigma/\tau\): scattering time) value of the PM phase of K$_3$P[OV] is estimated to be about 0.75 (10$^{19}$ S/m · sec). The calculated anisotropy is about two, which implies that this system is not so anisotropic, as addressed in Fig. 5(a), both volume enhancement and AFM spin polarization significantly suppress the conductivity, as is also consistent with the analysis of the Fermi surfaces in Fig. 5. The $\sigma/\tau$ values of the AFM phase of K$_3$P[OV] and the PM phase of K$_3$P[EV] turn out to be 0.25 and 0.13 (10$^{19}$ S/m · sec), respectively, which are only 33% and 17% of that of the PM phase of K$_3$P[OV]. The conductivity analysis reflects
that both volume enhancement and AFM spin polarization are effective on the MIT. The volume enhancement leads to the heavy effective mass in conductivity by reducing \( W \), while the AFM spin polarization leads to the reduced DOS at \( E_F \) by splitting two bands around \( E_F \) farther.

In general, the volume enhancement of solid decreases the band width \( W \) and increases the Coulomb repulsion \( U \), resulting in larger \( U/W \) value. The increased \( U/W \), when it becomes larger than the critical value \( (U/W)_c \), would drive the MIT through a Mott transition. Indeed, in \( K_3 \)pentacene, the formation of insulating state is experimentally realized.\(^{[20]}\) We have estimated \( U/W \) of \( K_3 \)picene, using the method of Ref.\(^{[21]}\), which was applied to the pentacene solid. The effective Coulomb interaction \( (U_{eff}) \) is given by subtracting the polarization energy \( (E_{pol}) \) from the bare Coulomb interaction \( (U_{bare}) \), \( U_{eff} = U_{bare} - E_{pol} \). \( U_{bare} \) of a charged picene molecule is estimated from the second order Möller-Plesset calculations with 6-31G* atomic orbital basis set for an isolated picene by considering different anionic electron occupations.\(^{[22]} \) \(^{[23]}\) \( E_{pol} \) for a solid \( K_3 \)picene can be determined by using the continuum model, in which a charged molecule is assumed to be surrounded by homogeneous dielectric medium.\(^{[21]}\) We have obtained the dielectric constant and the size of the cavity by fitting the calculated \( E_{pol} \) to the experimental value of the pristine solid picene.\(^{[24]}\) In this way, we have got \( U_{bare} = 2.25 \) eV and \( E_{pol} = 1.40 \) eV, respectively, and thus \( U_{eff} \) is estimated to be 0.85 eV. One can estimate the \( U/W \) for \( K_3 \)P[EV] adopting \( W \) of \( L+U \) bands near \( E_F \) (0.30 eV) for the PM phase of \( K_3 \)P[EV]. Then we have obtained \( U/W = 2.83 \), which is larger than \( (U/W)_c \) value\(^{[27]}\) of 1.73, so that a Mott insulating state is realized in \( K_3 \)P[EV]. This large \( U/W \) value for \( K_3 \)P[EV] suggests that \( K_3 \)P[OV], which exhibits superconductivity, would also be near the boundary of Mott transition.

In a recent report on K atom adsorbed picene molecule,\(^{[28]}\) it was argued that the charge transfer from K atoms to LUMO and LUMO+1 orbitals is not decisive due to the strong Coulomb correlation effect in picene. The above analysis for the Coulomb interaction, however, shows that \( U_{eff} \) in \( K_3 \)picene solid is only about 38% of \( U_{bare} \) in an isolated picene molecule. Therefore, distinctly from the case of picene molecule, the charge transfer from K atoms to LUMO and LUMO+1 related bands will be possible in solid picene due to the reduced effective Coulomb interaction.

In conclusion, we have studied electronic structures and magnetism of a first hydrocarbon superconductor, \( K_3 \)picene, by employing the first principles band structure method within the density functional theory. Active bands for superconductivity are found to have LUMO and LUMO+1 hybridized character. Fermi surfaces of \( K_3 \)picene manifest neither prominent nesting feature nor marked two-dimensional behavior. We have shown that \( K_3 \)picene is on the verge of the MIT and the magnetic instability. Therefore, one needs to consider the strong Coulomb correlation effects to investigate the mechanism of superconductivity in \( K_3 \)picene.

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[25] On the basis of (i) strong hybridized character of LUMO and LUMO+1 for L and U bands near $E_F$, (ii) electron energy loss scattering experiment on pristine solid picene,[26] and (iii) our second order Møller-Plesset calculations, three orbitals (LUMO, LUMO+1, and LUMO+2) are considered to be nearly degenerate. Then by assuming the three-fold degeneracy (LUMO, LUMO+1, and LUMO+2), $(U/W)_c$ for the MIT is given by $(U/W)_c = \sqrt{3} = 1.73$.[27]