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New Hydrocarbon Superconductor on the Verge of Metal-Insulator Transition: Electronic Structures and Magnetic Properties of K_3picene

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We have investigated the electronic structures and magnetic properties of of K_3picene, which is a first hydrocarbon superconductor with high transition temperature T_c=18K. We have shown that the metal-insulator transition (MIT) is driven in K_3picene 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_3picene 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_3picene is located in the vicinity of the Mott transition.

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Superconductivity has recently been observed in K-doped picene, K_3picene, which is a first organic superconductor in the hydrocarbon system.[2] The superconducting transition temperature of K_3picene, T_c=18 K, is comparable to that of alkali-metal doped fullerene system (T_c ∼38K).[3] In K_3picene, 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_3picenes (A=Na, K, Rb, and Cs) exhibit cation A dependent physical properties.[2] 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_3picene is susceptible to the chemical pressure. This trend is also reminiscent of A_3C_{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).[4]

Natural immediate question is what the pairing mechanism is for this organic superconductor K_3picene. 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 $La_{2-x}Sr_xCuO_4$ is an antiferromagnetic (AFM) insulator.[5] Also organic superconductors κ-(BEDT-TTF)$_2$X and A_3C_{60} (A=K and Cs) show phase transition from AFM insulator to superconductor upon increasing pressure.[3, 6] These examples demonstrate that the investigation of the electronic structures of K_3picene 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_3picene 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_3picene by 5% volume enhancement with a formation of local magnetic moment. Our results indicate that K_3picene 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_3picene is near to the Mott transition.

In a unit cell of K_3picene, 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_3picene with retaining the observed monoclinic struc-

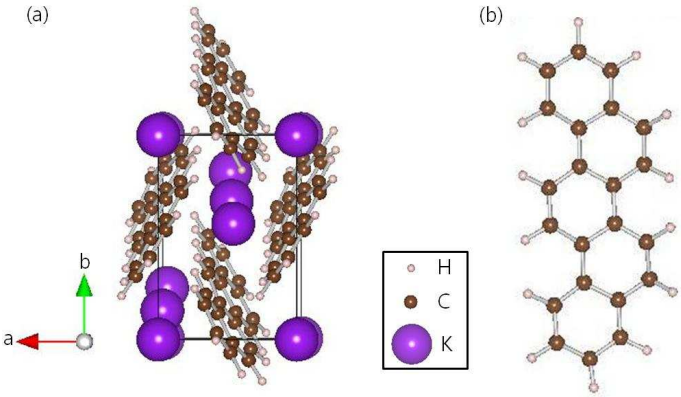

FIG. 1: (Color online) (a) Crystal structure of K_3picene. There are two stacked picene molecules in a unit cell. K atoms are intercalated between the stacked picene molecules. (b) Molecular structure of a picene.

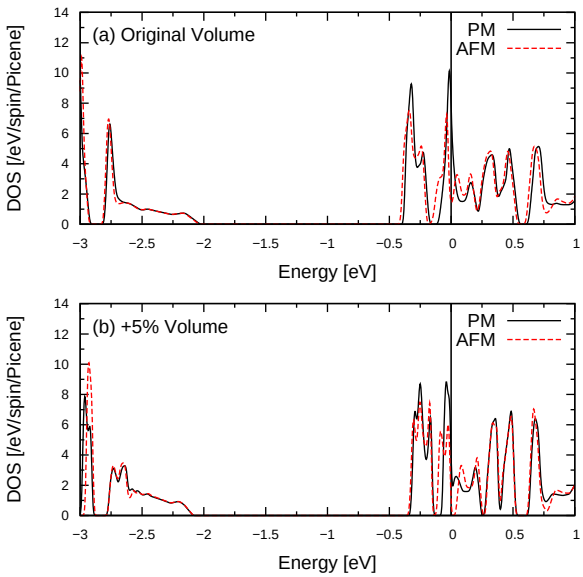

FIG. 2: (Color online) Density of states for PM (black solid lines) and AFM (red dotted lines) phases of K_3picene. (a) K_3picene with original volume (K_3P[OV]), and (b) K_3picene with +5% volume expansion (K_3P[EV]).

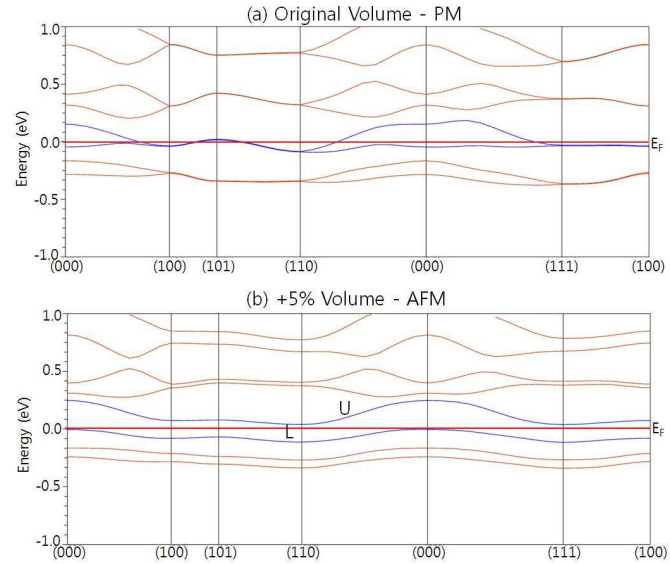

FIG. 3: (Color online) (a) Band structure for PM phase of K_3picene with original volume (K_3P[OV]). (b) Band structure for AFM phase of K_3picene with +5% volume expansion (K_3P[EV]). Notice that two bands near E_F are split into U and L which are represented by blue (dark) color.

ture (lattice constants: a=8.707, b=5.912, c=12.97 $\AA$, and β=92.77°).[2] For this purpose, we have used the pseudopotential method of VASP package.[7] The stable positions of K atoms were determined to be four K's above the end benzene rings and two K's above the center rings,[8] similarly to those of Ref.[9, 10]. However, the arrangement of picene molecules in Ref. [9] are perpendicular to *ab* plane losing the conventional herringbone structure of the pristine picene solid. Our optimize structure retains the conventional herringbone structure in accordance with Ref.[10]. We have also optimized internal atomic positions of K_3picene with 5% volume expansion in order to examine the chemical pressure effect, as is realized in Cs_3picene. Then, based on the optimized structures, we have obtained electronic structures of K_3picene employing the more precise all electron full-potential linearized augmented plane wave (FLAPW) method[11] implemented in WIEN2k package.[12] For the exchange-correlation potential, the generalized gradient approximation (GGA)[13] was utilized. To explore the magnetic properties of K_3picene, 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 K_3picene. DOSs of K_3picene with original volume (hereafter K_3P[OV]) and with +5% volume expansion (hereafter K_3P[EV]) are provided in their paramagnetic (PM) and AFM phases. Pristine solid picene is a semiconductor with wide band gap of 3.3 eV.[14] Figure 2(a) shows that K_3P[OV] also has an energy gap structure ($\sim$ 1.7 eV) between HOMO and LUMO related bands. In K_3picene, three electrons are transferred from three doped K atoms into one picene, occupying LUMO and LUMO+1 related bands. For K_3P[EV] in Fig. 2(b), the band widths become narrower to have a larger energy gap ($\sim$ 1.9 eV) between HOMO and LUMO related bands. It is seen that, for both K_3P[OV] and K_3P[EV], the DOS at the Fermi level (E_F) is much reduced in the AFM phase with respect to that in the PM phase. Noteworthy is that K_3P[EV] becomes an insulator in the AFM phase, having small energy gap of $\sim$ 0.03 eV. The PM and AFM phases are almost degenerate. Nevertheless, the magnetic moment of one picene, $\sim$0.35 μ_B, is large enough to stabilize the magnetic ground state. These features suggest that K_3picene (K_3P[OV]) is on the verge of magnetic instability and the MIT. The conceivable AFM state of K_3P[EV] recalls molecular solids with local moment carrying $2p$ electrons.[3, 15, 16] For instance, Cs_3C_{60} 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 Cs_3picene below 150 K is most likely to be related to the AFM state obtained for K_3P[EV].[2]

In Fig. 3(a) and (b), PM band structure of K_3P[OV] and AFM band structure of K_3P[EV] are plotted, respectively. The former exhibits a metallic state with two bands crossing E_F, while the latter an insulating state. Metallic band structure of K_3P[OV] results from almost degenerate U and L bands near E_F, while the insulating state in the AFM phase of K_3P[EV] emerges

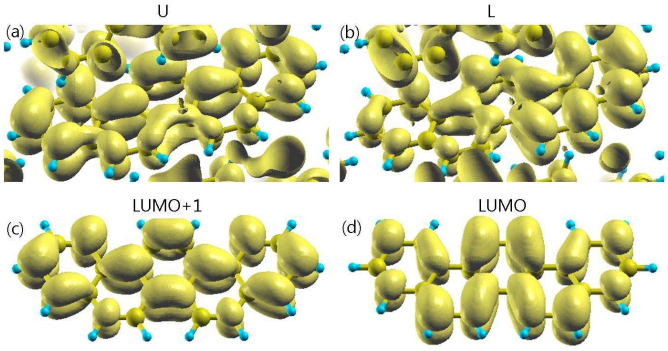

FIG. 4: (Color online) Charge densities (CDs) of (a) U and (b) L bands in Fig. 3. CDs of (c) LUMO+1 and (d) LUMO orbitals of a picene molecule. CD of the U band shows mostly LUMO+1 character with small hybridization with LUMO, while CD of the L band shows hybridized character of LUMO and LUMO+1.

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_3P[OV] at **k**-points along zone boundary, (100)-(101)-(110) and (111)-(100) directions, are split in the AFM phase of K_3P[EV]. This feature indicates that the insulating state in the AFM phase of K_3P[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_3P[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_3P[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 four conduction bands near E_F (U, L, and two lower bands below L in Fig. 3(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_3picene 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_3picene, 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. 3(a)). Hence, in K_3picene, 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_3P[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_3picene, respectively. For the AFM phase of K_3P[OV] (Fig.5(b)), the volume of Fermi surfaces is reduced much, as compared to that of the PM phase of K_3P[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 $(1\bar{1}0)$ 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_3P[OV].

We have calculated electrical conductivity σ using the Boltzmann transport theory.[18, 19]. The σ/τ (τ: scattering time) value of the PM phase of K_3P[OV] is estimated to be about 0.75 ($10^{19} S/m \cdot sec$). 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 σ/τ values of the AFM phase of K_3P[OV] and the PM phase of K_3P[EV] turn out to be 0.25 and 0.13 ($10^{19} S/m \cdot sec$), respectively, which are only 33% and 17% of that of the PM phase of K_3P[OV]. The conductivity analysis reflects

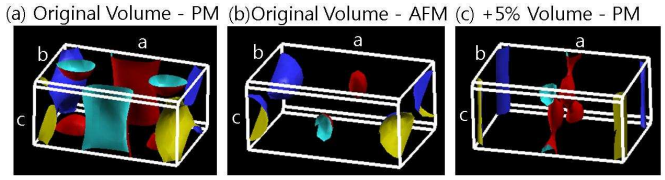

FIG. 5: (Color online) Fermi surfaces of K_3picene. (a) PM phase of K_3P[OV], (b) AFM phase of K_3P[OV], and (c) PM phase of K_3P[EV].

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_1pentacene, the formation of insulating state is experimentally realized.[20] We have estimated U/W of K_3picene, 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 Møller-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_3picene 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_3P[EV] adopting W of L+U bands near E_F (0.30 eV) for the PM phase of K_3P[EV]. Then we have obtained $U/W = 2.83$, which is larger than $(U/W)_c$ value[25] of 1.73, so that a Mott insulating state is realized in K_3P[EV]. This large U/W value for K_3P[EV] suggests that K_3P[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_3picene 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_3picene, 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_3picene manifest neither prominent nesting feature nor marked two-dimensional behavior. We have shown that K_3picene 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_3picene.

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[2] R. 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).
[3] Y. Takabayashi, A. Y. Ganin, P. Jeglić, D. Arćon, T. Takano, Y. Iwasa, Y. Ohishi, M. Takata, N. Takeshita, K. Prassides, and M. J. Rosseinsky, Science **323**, 1585 (2009).
[4] M. -Z. Huang, Y. -N. Xu, and W. Y. Ching, Phys. Rev. B **46**, 6572 (1992).
[5] A. Aharony, R. J. Birgeneau, A. Coniglio, M. A. Kastner, and H. E. Stanley, Phys. Rev. Lett. **60**, 1330 (1988).
[6] S. Lefebvre, P. Wzietek, S. Brown, C. Bourbonnais, D. Jérome, and C. Mézière, Physica. B **312**, 578 (2002).
[7] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[8] We have checked that the other possible K_3picene structure, in which K atoms are out of the stacked planar picene molecules, is unstable by more than 1 eV per picene, as compared to the structure considered in the present study.
[9] T. Kosugi, T. Miyake, S. Ishibashi, R. Arita, and H. Aoki, J. Phys. Soc. Jpn. **78**, 113704 (2009).
[10] P. L. Andres, A. Guijarro, and J. A. Vergés, arXiv:1010.6168v1 (2010);
[11] M. Weinert, E. Wimmer, and A. J. Freeman, Phys. Rev. B **26**, 4571(1982).
[12] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kavasnicka, J. Luitz, WIEN2k (Karlheinz Schwarz, Technische Universitat Wien, Austria, 2001).
[13] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[14] H. Okamoto, N. Kawasaki, Y. Kaji, Y. Kubozono, A. Fujiwara, and M. Yamaji, J. Am. Chem. Soc. **130**, 10470 (2008).
[15] M. Labhart, D. Raoux, W. Känzig, and M. A. Bösch, Phys. Rev. B **20**, 53 (1979).
[16] F. J. Disalvo, W. E. Falconer, R. S. Hutton, A. Rodriguez, and J. V. Waszczak J. Chem. Phys. **62**, 2575 (1974).
[17] T. Mori, and S. Ikehata, J. Appl. Phys. **82**, 5670 (1997).
[18] P. B. Allen, W. E. Pickett, and H. Krakauer, Phys. Rev. B **37**, 7482 (1988).
[19] BOLTZTRAP code by G. K. H. Madsen and D. J. Singh, Comput. Phys. Commun. **175**, 67 (2006).
[20] M. F. Craciun, G. Giovannetti, S. Rogge, G. Brocks, A. F. Morpurgo, and J. van den Brink, Phys. Rev. B **79**, 125116 (2009).

[21] G. Brocks, J. Chem. Phys. **112**, 5353 (2000).
[22] C. Møller and M.S. Plesset, Phys. Rev. **46**, 618 (1934).
[23] P. J. Knowles, J. S. Andrews, R. D. Amos, N. C. Handy, and J. A. Pople, Chem. Phys. Lett. **186**, 130 (1991).
[24] N. Sato, K. Seki, and H. Inokuchi, J. Chem. Soc. Faraday Trans. **77**, 1621 (1981).
[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]
[26] F. Roth, M. Gatti, P. Cudazzo, M. Grobosch, B. Mahns, B. Büchner, A. Rubio, and M. Knupfer, arXiv:1009.4052v1 (2010);
[27] O. Gunnarsson, E. Koch, and R. M. Martin, Phys. Rev. B **54**, 11026 (1996).
[28] T. A. Baker, and M. Head-Gordon J. Phys. Chem. A **114**, 10326 (2010).