Density functional calculations of the electronic structure and magnetic properties of the hydrocarbon K₃picene superconductor near the metal-insulator transition

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We have investigated the electronic structures and magnetic properties of a newly discovered hydrocarbon superconductor, K₃picene, having T_c=18 K. We have shown that the metal-insulator transition (MIT) is driven in K₃picene by 5% volume enhancement with the formation of the local magnetic moment. Active bands for the superconductivity near the Fermi level (E_F) have hybridized character of LUMO and LUMO+1 of the picene molecule. Fermi surfaces of K₃picene manifest neither prominent nesting feature nor marked two-dimensional behavior. By estimating the ratio of the Coulomb interaction U and the bandwidth W of the active bands near E_F, we have demonstrated that K₃picene is located in the vicinity of the Mott transition. Our findings suggest that K₃picene is a strongly correlated electron system.

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Recently, the first hydrocarbon superconductivity has been observed in the K-doped picene, K₃picene. Its transition temperature T_c=18 K is comparable to that of the alkali-metal doped fullerene system (T_c≈38 K). In K₃picene, K atoms are intercalated in the stacked picene molecules, as shown in Fig. 1(a). A picene molecule (C₂₂H₁₄) consists of five connected benzene rings with armchair edge (see Fig. 1(b)). Interestingly, alkali-metal-doped A₃picenes (A=Na, K, Rb, and Cs) exhibit the 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 A₃picene is susceptible to the chemical pressure. This trend is also reminiscent of A₃C₆₀ (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).

Unconventional superconductors often manifest the incipient MIT and magnetic instability, which reflect the existence of strongly correlated electrons. The parent compounds of cuprate high T_c superconductors are typically antiferromagnetic (AFM) insulators. Also the organic superconductors κ-(BEDT-TTF)₂X and A₃C₆₀ (A=K and Cs) show the phase transition from an AFM insulator to a superconductor upon increasing pressure. These examples suggest that investigation of the electronic structures of K₃picene under volume change would provide an important clue to the pairing mechanism of superconductivity.

In this report, we have explored the volume-dependent electronic and magnetic properties of K₃picene using the first principles band structure calculation within the density functional theory. We have shown that the MIT and AFM transitions are driven in K₃picene by 5% volume enhancement with the formation of the local magnetic moment. Our results indicate that K₃picene 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 of the picene molecule. Quantitative estimation of U/W (U:Coulomb interaction, W: bandwidth) also provides that K₃picene is near to the Mott transition.

In the unit cell of K₃picene, 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 the internal atomic positions in K₃picene with retaining the observed monoclinic structure (lattice constants: a=5.912, b=8.707, c=12.97 A, and α=92.77°). For this purpose, we have used the pseudo-potential band method of VASP package. For the exchange-correlation potential, the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was utilized. We have used 100 k-points inside the Brillouin zone for the k-point sampling.

FIG. 1: (Color online) (a) Crystal structure of K₃picene. 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.
the first Brillouin zone. The convergence of the total energy with respect to number of k-points was checked to have precision of less than 4 meV per formula unit. For the structural optimization, the atomic relaxations are terminated when the forces in all atomic sites are less than 0.05 eV/Å. The stable positions of K atoms are determined as four above the end benzene rings and two above the center rings with nearly two dimensional stacked arrangement of picene molecules, similarly to the results of Ref. \cite{11,12}. However, the arrangement of picene molecules in Ref. \cite{14} are perpendicular to ab plane losing the conventional herringbone structure of the pristine picene solid. Our optimized structure retains the conventional herringbone structure in accordance with Ref. \cite{14}. We have also optimized the internal atomic positions of K3picene with 5% volume expansion in order to examine the chemical pressure effect, as is realized in Cs3picene. Then, based on the optimized structures, we have obtained the electronic structure of K3picene by employing the more precise all electron full-potential linearized augmented plane wave (FLAPW) band method \cite{15} implemented in WIEN2k package \cite{16}. To explore the magnetic properties of K3picene, we have considered the AFM spin configuration with the opposite spin polarizations of two independent picene molecules in the unit cell.

Figure 2 shows the density of states (DOS) of K3picene. DOSs of K3picene with original volume (hereafter K3P[OV]) and with +5% volume expansion (hereafter K3P[EV]) are provided in their nonmagnetic (NM) and AFM phases. Pristine solid picene is a semiconductor with a wide band gap of 3.3 eV. Figure 2(a) shows that K3P[OV] also has an energy gap structure (∼1.7 eV) between HOMO and LUMO related bands. The stable positions of K atoms are perpendicular to (100)-(101)-(110) directions are split in the AFM phases. Pristine solid picene is a semiconductor with a wide band gap of 3.3 eV. In K3picene, three electrons are transferred from three intercalated K atoms into one picene, occupying LUMO and LUMO+1 related bands, as was pointed out by Kosugi et al. \cite{14}. 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 (E_F) is much reduced in the AFM phase with respect to that of the NM phase. Noteworthy is that K3P[EV] becomes an insulator in the AFM phase, having a small energy gap of ∼0.03 eV. The NM and AFM phases are almost degenerate. Nevertheless, the magnetic moment of one picene, ∼0.35 μ_B, is large enough to stabilize the magnetic ground state. \cite{16,17} These features suggest that K3picene (K3P[OV]) is on the verge of the MIT and magnetic instability. The AFM structure in K3P[EV] with the localized magnetic moment of a picene provides the explanation of the significant enhancement of M/H observed in Cs3picene. Like other molecular solids (KO2, K-doped pentacene, Cs2C60) having local moment carrying 2p electrons, \cite{18,19}, the local moment in K3P[EV] arises from the unpaired electron in the localized molecular orbital.

In Fig. 3(a) and (b), the NM band structure of K3P[OV] and the AFM band structure of K3P[EV] are plotted, respectively. The former exhibits a metallic state with two bands crossing E_F, while the latter shows an insulating state. The metallic band structure of K3P[OV] results from the almost degenerate U and L bands near E_F, while the insulating state in the AFM phase of K3P[EV] emerges due to the 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 NM phase of K3P[OV] at k-points along the (100)-(101)-(110) directions are split in the AFM
bands with mixed LUMO and LUMO+1 character near states that the hybridization interaction between LUMO correspond to 0.21, 0.12, 0.12, and 0.13 eV, respectively. (U, L, and two lower bands below L in Fig. 3(b)), which phase of K$_3$P[OV] while CD of the L band shows hybridized character of 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.

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 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.

phase of K$_3$P[EV]. The overlap of π-π orbitals of adjacent molecules along the (100) direction produces the symmetric hopping along this direction, resulting in the degeneracy on the (100) zone surface for the NM phases. This degeneracy on the (100) zone surface is lifted by the AFM spin ordering for both K$_3$P[OV] and K$_3$P[EV], due to the broken symmetry along the (100) direction. This feature is reminiscent of the Slater-type MIT mechanism accompanied by the cell doubling, and might suggest that K$_3$P[EV] can be categorized into a band insulator. However, similar feature was observed in the typical Mott insulating systems such as cuprate and nickel oxides. Therefore, in order to confirm that 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 the 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 the 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. This gap size is comparable to the 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 size of the gap and band widths indicates that the hybridization interaction between LUMO and LUMO+1 is large enough to yield the hybridized bands with mixed LUMO and LUMO+1 character near $E_F$. Thus, the active bands for superconductivity near $E_F$ have hybridized character of LUMO and LUMO+1 molecular orbitals, in agreement with the earlier report by Kosugi et. al. This is contrary to the case of pentacene, in which the energy splitting between LUMO and LUMO+1 (~ 1.28 eV) is much larger than that of picene.

Fermi surfaces of K$_3$picene are provided in Fig. 5. Note first that there is no prominent nesting feature in the Fermi surfaces of K$_3$P[OV] (Fig. 5(a)), which is in agreement with Ref. 11. Secondly, there is no Fermi surfaces of clear cylindrical shape along the c-axis, indicating that this system would not have marked two dimensional behavior, despite its layered-like crystal structure. This feature is indeed consistent with the band structure in Fig. 3(a), which shows apparent dispersions along the c-axis, (100)-(101) and (001)-(000). Figure 3(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, with respect to that of the NM 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 volume enhancement also reduces the Fermi surface area, as shown in Fig. 5(c), due to the decreased band width.

We have calculated electrical conductivity $\sigma$ using the Boltzmann transport theory. The $\sigma/\tau$ (τ: scattering time) value of the NM phase of K$_3$P[OV] is estimated to be about 0.75 (10$^{19}$S/m·sec). The calculated anisotropy is only about two, which implies that this system is not so anisotropic, as addressed in Fig. 5(a). The reduced Fermi surfaces due to the explicit effects of AFM spin polarization and volume enhancement result in significant drop in the conductivity. The $\sigma/\tau$ values of the AFM phase of K$_3$P[OV] and the NM 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 NM phase of K$_3$P[OV] (0.75×10$^{19}$S/m·sec). The conductivity analysis indicates that both volume enhancement and AFM spin polarization are effective for 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. We have estimated $U/W$ of K$_3$picene, using the method of Ref. which was applied to the pentacene solid. The effective Coulomb interaction ($U_{\text{eff}}$) is given by subtracting the polarization energy ($E_{\text{pol}}$) from the bare Coulomb interaction ($U_{\text{bare}}$).

$$U_{\text{eff}} = U_{\text{bare}} - E_{\text{pol}}.$$  

$U_{\text{bare}}$ 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. $E_{\text{pol}}$ for a solid K$_3$picene can be determined by using the partial continuum model, in which a charged molecule is assumed to be surrounded by a cavity of homogeneous dielectric medium. We have obtained the dielectric constant and the size of the cavity by fitting the calculated $E_{\text{pol}}$ to the experimental value of the pristine solid picene. In this way, we have got $U_{\text{bare}} = 2.25$ eV and $E_{\text{pol}} = 1.40$ eV, respectively, and thus $U_{\text{eff}}$ is estimated to be 0.85 eV. One can estimate the $U/W$ for K$_3$P[EV] by adopting W of L+U bands near $E_F$ (0.30 eV) for the NM phase of K$_3$P[EV]. Then we have obtained $U/W = 2.83$, which is larger than $U/W_{\text{bare}} = 1.75$, 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 the Mott transition.

In a recent report on the K atom adsorbed picene molecule, it was argued that the charge transfer from K atoms to LUMO and LUMO+1 is not decisive due to the strong Coulomb correlation effect in picene. The above analysis for the Coulomb interaction, however, shows that $U_{\text{eff}}$ in K$_3$picene solid is only about 38% of $U_{\text{bare}}$ in an isolated picene molecule. Therefore, distinctly from the case of the 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 the 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. The latter is also supported by the rather small anisotropy in the estimated conductivity. We have demonstrated that K$_3$picene is on the verge of the MIT and the magnetic instability. Therefore, one needs to consider a 3D model with strong Coulomb correlation effects to investigate the mechanism of superconductivity in K$_3$picene.

After submission of the manuscript, we became aware of a related work by G. Giovannietti and M. Capone, Ref. in which the AFM state is found to become stabilized in K$_3$P[OV] by the inclusion of correlation effects. Also recent experiment confirms that the Coulomb interaction ($U$) in solid picene is about 0.85 eV, which is much larger than the band width, Ref. These results are consistent with the present results suggesting that K$_3$picene is a strongly correlated electron system.

Acknowledgments

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in $K_3P[EV]$, the NM and AFM states are nearly degenerate, in view of that the total energy difference is less than the precision of total energy calculation ($\sim 4$ meV). On the other hand, for $K_3P[OV]$, the NM state is more stable than the AFM state by 5 meV per formula unit with similar magnetic moment of $\sim 0.35 \mu_B$ per one picene. The metastable AFM state in $K_3P[OV]$, which has comparable total energy with the NM state, was also reported in Ref.17 by using the pseudo-potential VASP band method.

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