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Ionic metal K_xC_{60}: Cohesion and energy bands

Susumu Saito and Atsushi Oshiyama

Fundamental Research Laboratories, NEC Corporation, Miyukigaoka, Tsukuba 305, Japan

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Microscopic total-energy electronic-structure calculations for K_xC_{60} show that solid C_{60} weakly bonded via van der Waals forces is transformed upon potassium doping into a strongly condensed *ionic metal* in which both Madelung and kinetic energies contribute to its large cohesive energy and bulk modulus. We also find that K doping induces lattice contraction which results in nonrigid energy-band modification. The Fermi level for K_3C_{60} is found to be located close to a peak of the density of states.

Fullerene C_{60} is a soccer-ball-shaped cluster with carbon atoms located at each vertex.[1] The earlier conjecture[2] on the unique shape has been indeed confirmed by success[3] in producing macroscopic quantities of C_{60} from carbon soot and by subsequent photoabsorption,[3,4] nuclear magnetic resonance,[5] and x-ray diffraction measurements.[3,6] In particular, the finding[3] of a close-packed crystalline form of C_{60} has triggered a considerable expansion of research on its solid-state properties: Photoemission[7] and inverse photoemission[8] studies on solid C_{60} have shown its peculiar electron states, and local-density calculations[9,10] have revealed that the C_{60} clusters are condensed by van der Waals forces and that the solid C_{60} is a semiconductor with a direct gap at the Brillouin-zone boundary.[10] Moreover, the recent discovery of superconductivity for the alkali-metal-doped fullerenes, K_xC_{60} (the critical temperature T_c=18 K)[11] and Rb_xC_{60} (T_c=28 K),[12,13] has raised fundamental questions as to mechanisms of superconductivity in these fullerene solids ("fullerites").

In this paper, we report microscopic total-energy electronic-structure calculations for KC_{60}, K_2C_{60}, and K_3C_{60} in which potassium atoms are situated at either or both of tetrahedral and octahedral interstitial sites of face-centered-cubic (fcc) C_{60}. We have found that K doping in fcc C_{60} occurs exothermically with electron transfer from the K atom to the C_{60} cluster and at the same time with hybridization between K 4*s*, C_{60} π, and C_{60} σ orbitals. The resulting K_xC_{60} is shown to be an *ionic metal* in which both the electrostatic and kinetic energies contribute significantly to its larger cohesive energy and bulk modulus than those of undoped solid C_{60}. This feature of the material results from the uniqueness of the C_{60} cluster, i.e., its high electronegativity and closed-shell electron states, showing another possibility of the fullerenes as atomlike units to construct new exotic materials. We have also found that the K doping is accompanied by sizable *lattice contraction* which induces significant modification of the energy bands of fcc C_{60}. The Fermi level for K_3C_{60} is found to be located close to a peak of the calculated density of states (DOS). Although there is no experimental evidence that the fcc lattice[6] of C_{60} is preserved in K_xC_{60},[14] the present results essentially hold in other lattice structures and clarify remarkable features in the modification of cohesive and electronic properties of the solid C_{60} upon alkali-atom doping.

The calculations have been performed with the local-density approximation[15] (LDA) using norm-conserving hard pseudopotentials[16] and the Gaussian-orbitals basis set as reported in Ref. 10. In addition to the Gaussian orbitals at the C sites, three *s* and two *p* Gaussian orbitals, whose exponents are determined by fitting the numerical pseudoatomic orbitals of a K atom, are placed at each K site in the lattice. Technical details of our method have been published elsewhere.[17] The present first-principles calculation describes accurately the structural properties (lattice constants, bulk moduli, and cohesive energies) of diamond and graphite.[10] The predicted cohesive energy of fcc C_{60} has been corroborated by recent experiment,[18] and the calculated DOS is in excellent agreement with the photoemission[7,8] and x-ray emission[19] data.

In fcc C_{60} lattice there are two tetrahedral and one octahedral interstitial sites per C_{60}.[20] The tetrahedral and octahedral sites have sufficient room to accommodate spheres of radius 1.1 and 2.1 Å, respectively. Since the ionic radius of K^+ is about 1.3 Å, the two interstitial sites are candidates to accommodate K atoms. We thus place K atoms at one of these (KC_{60}), at two tetrahedral (K_2C_{60}), and at all of these (K_3C_{60}) interstitial sites in fcc C_{60}, and minimize the total energy by varying the fcc lattice constant. In Fig. 1 the calculated total energies of KC_{60}, K_2C_{60}, and K_3C_{60} as a function of the fcc lattice constant are shown. In the case of KC_{60} we find that the total energy with the K atom at the tetrahedral site is lower than that at the octahedral site by 1.8 eV per K atom. As is seen from the contour map of the valence electron density (Fig. 2), significant electron transfer to the C_{60} cluster from the K atom at any interstitial site occurs. The calculated cohesive energies for KC_{60}, K_2C_{60}, and K_3C_{60} are 10.1 eV per KC_{60}, 19.3 eV per K_2C_{60}, and 24.2 eV per K_3C_{60}, respectively. The preference of the tetrahedral site (i.e., zinc-blende KC_{60}) over the octahedral site (i.e., sodium

chloride KC_{60}) is consistent with an argument based on a simple rigid-sphere model for the crystal structures of ionic materials.[21] Yet the Madelung energy for KC_{60} is estimated to be 3 eV (note the large distance between the K atom and the C_{60} cluster compared with the cation-anion distance in typical ionic materials.) Therefore the large cohesive energy obtained in the present calculation is explained not only by the Madelung energy but also by the kinetic-energy gain. The bulk modulus of KC_{60} obtained from the parabola fitting of the total energies is 77 GPa, and those of K_2C_{60} and K_3C_{60} are larger than that. Since the calculated cohesive energy and the bulk modulus of fcc C_{60} is 1.6 eV per C_{60} and 48 GPa,[22] respectively, the K doping transforms the fcc C_{60} weakly bonded via van der Waals force into a new strongly condensed ionic material. The reaction of K doping is indeed exothermic, and the calculated heats of formation for the reactions, C_{60}(fcc)+K(atom)$\leftrightarrow KC_{60} + \Delta E_1$, KC_{60}+K(atom)$\leftrightarrow K_2C_{60} + \Delta E_2$, and K_2C_{60}+K(atom) $\leftrightarrow K_3C_{60} + \Delta E_3$, are ΔE_1=8.5 eV, ΔE_2=9.2 eV, and ΔE_3=4.9 eV, respectively. Further, phase separation of C_{60}(fcc) and K metal is not likely since the cohesive energy of K metal is small compared with the above heats of formation.

We also find that the K doping is accompanied by sizable contraction of the fcc lattice constant: The calculated lattice constant for fcc C_{60} is 96% of the corresponding experimental value (14.198 Å),[6] whereas the values obtained for K_xC_{60} are about 94% (the inset of Fig. 1). This 2% difference corresponds to 0.3 Å. The LDA calculation gives highly accurate lattice constant (typically with less than 1% error) for condensed materials, whereas it underestimates the lattice constant of van der Waals solid such as graphite or fcc C_{60} by ~5%.[10] Therefore the lattice contraction may be observed more prominently. In any case the obtained lattice contraction by the order of half an angstrom increases the electrostatic energy gain in K_xC_{60} on one hand, and modifies strongly the energy bands (shown below) causing the metallic energy gain in the material on the other. This contraction is in sharp contrast with the case of graphite intercalation compounds[23] (GIC) in which distance between adjacent graphite layers increases by ~50% upon K intercalation. In first-stage GIC, KC_8, the nearest-neighbor distance between K atoms is 4.9 Å whereas in KC_{60} it is 5.7 Å

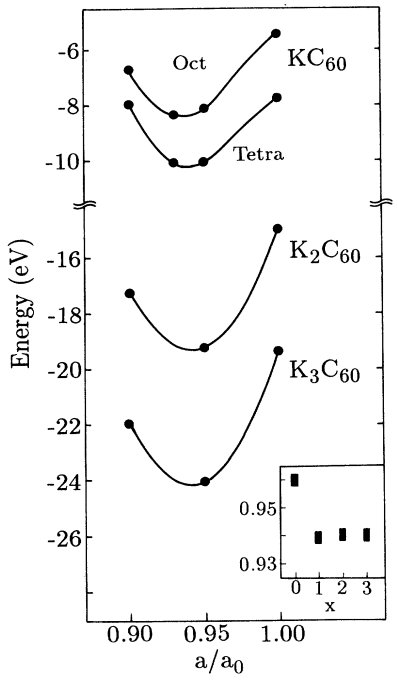

FIG. 1. Calculated total energies of K_xC_{60} as a function of the fcc lattice constant. The total energies are measured from the sum of the energies of isolated C_{60} cluster and of isolated x potassium atoms; i.e., the minus of the cohesive energies. The lattice constant is normalized to the experimental value of fcc C_{60} (a_0=14.198 Å). The inset is the calculated lattice constant as a function of the K composition x.

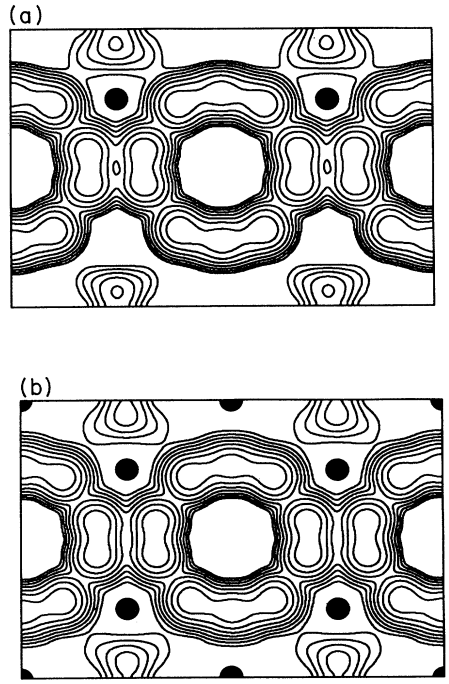

FIG. 2. Contour maps of the valence-electron densities of (a) KC_{60} and of (b) K_3C_{60} on the (110) plane. Solid circles denote the positions of the K atoms at (a) the tetrahedral, or at (b) the tetrahedral and the octahedral interstitial sites. The highest-density contour is 0.90 electron/Å^3, and each contour represents twice or half the density of the adjacent contours. We observe the enhanced bonding between the C_{60} clusters due to the lattice contraction, and the electron transfer from the K atoms to the C_{60} clusters. The density (not shown here) at 2 Å apart from the octahedral site is about 0.002 electron/Å^3.

which is also much larger than the corresponding value 4.6 Å in bcc K metal.

In Fig. 3 the calculated energy bands of K_3C_{60} are shown. The energy bands with π character become significantly dispersive compared to the bands of fcc C_{60}. This is a consequence of the lattice contraction and the resulting increased hybridization. The energy gap of fcc C_{60}, 1.5 eV, is reduced to 0.8 eV in K_3C_{60} according to the present LDA calculation. The Fermi level is at 1.25 eV above the valence-band top and is in the conduction bands. Analysis of the wave functions shows that the states at ~3 eV above the Fermi level have appreciable character of both π orbitals and 4*s* orbitals at the tetrahedral site. On the other hand, a state at 3.9 eV above the Fermi level at the Γ point clearly holds the character of 4*s* at the octahedral site. The antibonding σ bands are also mixed with the π bands. It is noted that this nonrigid modification of the energy bands upon K doping occurs within the fcc structure and is not accompanied with structural phase transition. We also find that the band modification has already occurred for KC_{60} and that further K doping fills the electron in the conduction bands which still preserve the character of π orbitals of the fullerene.

It is clear from Fig. 3 that slight doping of K atoms forms an electron pocket around the *X* point. Yet the Fermi level for KC_{60} is already above the lowest conduction band at the *W* point so that its Fermi surface has holelike orbits around the Γ point near the (001) plane. Further, there are open orbits in the [001] direction.[24] This complexity of the Fermi surface results from the existence of two inequivalent *XW* lines causing unusual splitting and dispersion of the triply degenerate (at the Γ point) conduction bands. This inequivalence is characteristic of fullerites; i.e., the internal atomic structure of the fullerene lowers the symmetry of the lattice system and affects the electron states. In the case of K_3C_{60}, the Fermi level is in the second conduction band so that

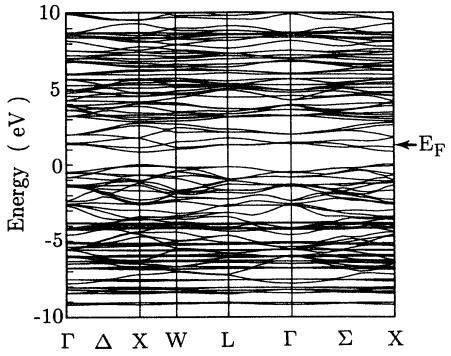

FIG. 3. Energy-band structure of K_3C_{60} along with the Fermi energy E_F. The valence-band top is defined as the zero energy. In addition to the *XW* line shown here, there is another inequivalent *XW* line on which the bands exhibit different dispersions.

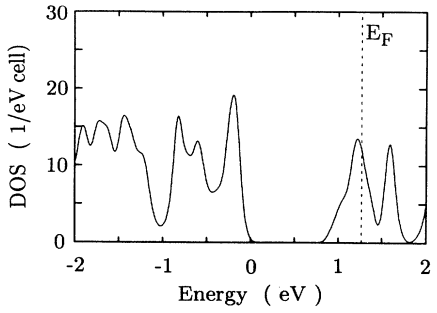

FIG. 4. The calculated electron density of states for K_3C_{60}. A cell contains one K_3C_{60}, and the valence-band top is defined as the zero energy. The Fermi level is close to the DOS peak. Note that the valence-band DOS is higher than the conduction-band DOS.

there occur other electron pockets around the *X* and the *W* points. Therefore K_3C_{60} is a metal characterized as a multicarrier system. The calculated DOS for K_3C_{60} is shown in Fig. 4. There are several DOS peaks originating from the nondispersive conduction bands along the symmetry *k* lines. The Fermi level for K_3C_{60} is found to be close to one of those DOS peaks. A recent experiment[13] has suggested that the composition of the superconducting phase of K_xC_{60} is close to $x=3$. The calculated Fermi-level density of states is $N(E_F)=12$ states/(eV K_3C_{60}). This rather high density of states would be a possible origin of the observed superconductivity in K_xC_{60}.[25]

The lattice contraction upon alkali-atom doping we have found is consistent with the observed variation in the superconducting critical temperature T_c with changing the dopant from K to Rb. The ionic radius of Rb^+ (1.48 Å) is larger than that of K^+ by 11%. The Rb atom at the tetrahedral site is thus unlikely to cause the lattice contraction as the K atom does. Therefore the energy bands become narrower and the $N(E_F)$ higher so that the T_c increases. Another candidate for increasing $N(E_F)$ is the halogen atoms which are expected to dope holes in the valence band of fcc C_{60}. The large ionic radius (1.95 Å for Br^- and 2.16 Å for I^-) prevents the lattice contraction, but still fits in the octahedral site in the fcc lattice. Moreover, the peak of the valence-band DOS is higher than that in the conduction-band DOS (Fig. 4), reflecting the fact[10] that the valence-band effective masses, $1.5m_e$ and $3.4m_e$ (m_e is the bare electron mass), are heavier than the conduction-band effective mass $1.3m_e$ in fcc C_{60}. This favors the higher $N(E_F)$ in the case of halogen-atom doping. It is found that 1.6 states are available between the valence-band top and the first valence-band DOS peak in Fig. 4.

In conclusion, the present calculations have revealed that alkali-atom doping in fcc C_{60} transforms the unique semiconductor C_{60} into a novel form of solid, *ionic metal* K_xC_{60}. Potassium atoms induce the contraction of the fcc lattice constant, thus condensing the fullerenes. In addition, the Fermi level for K_3C_{60} is found to be close to the DOS peak, and the multiple Fermi surfaces exhibit complexity which reflects the internal structure of the

soccer-ball-shaped fullerene.

Note added. After the submission of the present paper, an x-ray diffraction measurement on K_3C_{60} has been reported [P. W. Stephens *et al.*, Nature **351**, 632 (1991)], and the orientation of C_{60} assumed in the present paper is found to be consistent with the experiment. The lattice constant reported there is, however, slightly larger than that of undoped solid C_{60}, in contradiction to the prediction of the present work. The reason for this discrepancy is not clear yet.

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[20] At each fcc lattice site a C_{60} cluster is oriented so that the point group becomes T_h. The bond lengths in the cluster are fixed to the experimental values, 1.46 and 1.40 Å. Actually, the "octahedral" interstitial site in the fcc lattice lacks the octahedral symmetry but has T_h symmetry because of the internal structures of the surrounding C_{60} clusters. Yet we use the term "octahedral" in this paper since it is practical.

[21] In general, ionic materials could have cesium chrolide, sodium chrolide, and zinc-blende structures. According to the rigid-sphere model, when the ionic radius of an anion is larger to some extent than that of a cation, the material is expected to have the zinc-blende structure. See, e.g., F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Wiley, New York, 1972).

[22] In the recent experiments, the bulk modulus of fcc C_{60} is found to be smaller than the calculated value [S. J. Duclos *et al.*, Nature (London) **351**, 380 (1991); J. E. Fischer *et al.*, Science **252**, 1288 (1991)]. The fixed orientation and the fixed size of the C_{60} cluster may give larger bulk modulus in the present calculation.

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[25] See, for electron-phonon matrix elements, J. L. Martins, N. Troullier, and M. Schabel (unpublished). The details of their computational method are different from ours. (They use plane-wave basis set and soft pseudopotential.) Their band width and band gap of solid C_{60} are slightly different from our previous results (Ref. 10).