Ionic Cohesion and Electron Doping of Thin Carbon Tubules with Alkali Atoms

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Cohesion properties between carbon nanotubules and potassium atoms are studied using a first-principles total-energy and band-structure approach. The present calculations which assume linearly aligned arrangements of K atoms inside and outside of tubules suggest that the classical wetting picture of capillary action is not applicable on a microscopic scale. Charge transfer occurs from the K atoms to the tubule resulting in ionic cohesion. The energy barrier for sliding motion of the K atoms is found to be comparable to that of K diffusion in graphite intercalated compounds. The possibility of superconductivity of doped tubules is also discussed.

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The discovery of tubule forms of graphite sheets [1] and theoretical predictions of their electronic structures [2–4] have stimulated both fundamental and technological interest. Capillary action of molecules into the tubules was theoretically predicted [5], and the capillarity of the tubules for metal has been studied experimentally [6]. The capillary action of metals is of technological interest for fabrication of nanoscaled wires using carbon tubules. Because of confinement, metals inside tubules may form new phases which have not been seen before even for large hydrostatic pressures. When the tubule diameter is microscopic, the confined metal becomes a one-dimensional system in which a Peierls transition may be observed. The capillarity of tubules also raises the possibility of changing the electronic structures of the tubules by doping. In analogy with graphite intercalated compounds (GIC's) [7], injections of electron and hole carriers into tubules are expected for the cases of alkali and halogen dopings, respectively. The doped tubules are expected to show superconductivity as in the cases of GIC's. The curvature of the tubule wall breaks the symmetry of the planer sheet which inhibits the interaction between the π-state electrons and the transverse phonon modes. Hence electron-phonon couplings in tubules are expected to be larger than those in GIC's, and smaller tubules would have larger interactions because of larger curvatures. Another question considered here is whether the doped tubules have high density of states at the Fermi level (E_F), which is another important factor in determining the electron-phonon coupling constant λ and the superconducting T_c.

The surface tension of the liquid phase of metals has been proposed as a key factor in determining whether capillary action (wetting) occurs [8]. From the experimental results, the threshold for the surface tension for wetting has been set around 190 mN/m. According to this criterion, K atoms (with surface tension of $\simeq$395 mN/m [9]) are *not* expected to be captured inside the tubules while Rb atoms (with surface tension of 76 mN/m [9]) are. Recent measurement of electron spin resonance [10] indicates that the K-mixed tubules do not show any signal of electron injections, which is in sharp contrast with the results for the GIC's. To our knowledge, the capillary action of metals [6,8,10] have been examined only in the cases of concentric tubules with diameters larger than 100 Å, even though single-wall tubules with diameters around 10 Å have been fabricated [11,12]. For such small diameters, the captured metal atoms inside the tubules would form an atomic chain of the type shown schematically in Fig. 1. We suggest here that the K atoms could be captured inside the tubule when tubule diameters are microscopic and that the classical model for wetting might be inappropriate for this size. The electronic structures of carbon tubules are well explained based on the rolling of graphite sheets [2,3]. Hence, it is expected that tubules should not have fundamentally different chemical properties from graphite. (For the case of graphite surfaces, a monolayer of adsorbed potassium atoms was observed [13]. However, adsorbed potassium does not evolve to

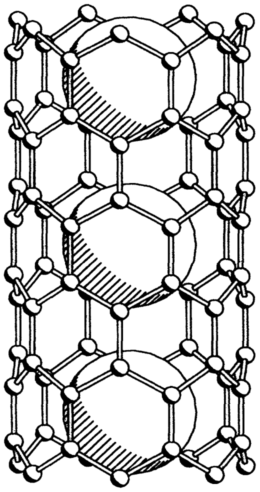

FIG. 1. Schematic picture of a (7,0) carbon tubule having K atoms inside. Large and small circles indicate K and C atoms, respectively.

multiple layers.) The electronic structures of alkali-doped tubules have been calculated within the extended Hückel method on a microscopic scale [14] suggesting the possibility of charge transfer from alkali atoms to tubules. The question remains as to whether the intercalation of alkali atoms is exothermic.

In this study, we demonstrate exothermic cohesion between tubules with diameters less than 1 nm and K chains (linearly aligned K atoms) inside and outside the tubules. The calculated heats of formation are greater than 1 eV per K atom depending on tubule diameters, and the most favorable diameter for cohesion is found to range from 5 to 6 Å. The heat of formation is obtained by subtracting the total energy of a K-doped tubule from the sum of the total energies of separated systems of bulk K metal and an undoped tubule. Charge transfer occurs from the K atom to the tubule wall, suggesting that the origin of the cohesion is an ionic interaction. We conclude that thin tubules react with alkali atoms in a manner which is similar to reactions with graphite sheets. Below, we describe the calculations and give the results for the stabilities and band structures of thin tubules with K atoms.

Total-energy pseudopotential band-structure calculations are done for the K and tubule systems within the framework of the local density approximation using a plane wave basis set with a cutoff energy of 36 Ry. The *ab initio* pseudopotentials are obtained with the Kleinman-Bylander scheme [15] including the core corrections for the exchange-correlation energy [16]. This correction is necessary to reproduce the structural properties of bulk K. The calculations were performed in a supercell geometry with the closest distance between carbon atoms of neighboring tubule walls of 5.5 Å, which was found to be a large enough separation to prevent tubule-tubule interactions.

Before studying the K-doped tubules, we optimized the lattice constant for a one-dimensional linear chain of K atoms. The calculated bond length of the linear chain is 4.09 Å which is smaller than the calculated bond length of 4.38 Å for bcc K. Considering the decrease of the atomic coordination number of the chain compared to that of bcc K, the contraction of the bond length is not surprising [17]. We also investigated the possibility of a Peierls transition of the K chain. We calculated the electronic structure and the total energy by dimerizing the K atoms in the chain. The dimerization results in a Peierls gap and the total energy decreases; however, the amount of the decrease is small, ~ 0.04 meV/atom. So we concluded that a Peierls transition does not occur in the K chain unless temperature is below 0.46 K. The optimized bond length for the nondimerized linear chain is comparable to the lattice constant along the axis of the $(n,0)$ tubules, which is 4.29 Å. (Here, the index notation for the tubules is the same as that given by Hamada, Sawada, and Oshiyama [2].) The K-K distance is therefore set to be the same as the periodic distance along the tubule axis, and the K atoms are assumed to be linearly aligned. Figure 1 illustrates the case for the (7,0) tubule. To achieve self-consistency for the electronic structure calculations, we use two k points in the irreducible part of the Brillouin zone.

Table I lists the calculated heats of formation for the $(n,0)$ tubules having K atoms inside. The heats of formation of the (6,0), (7,0), (8,0), and (9,0) tubules have been calculated with linear K chains at the center of the tubule. In this set of calculations, the position of each K atom of the centered chain is set at the level as shown in Fig. 1 which is found to be the most stable geometry as shown below. For the $(n,0)$ tubules we studied, the maximum heat of formation is obtained in the case of the (7,0) tubule. The diameter of the (7,0) tubule, 5.56 Å, which is close to the interlayer distance of K-doped GIC's of 5.36 Å [18], indicates the similar nature of a K-doped tubule with K-doped GIC's. The (8,0) tubule (diameter of 6.34 Å) also has high heat of formation among the $(n,0)$ tubules. We have confirmed that the K atom is forced back to the center when it is displaced. On the other hand, the (6,0) and (9,0) tubules have rather smaller heats of formation. Compared to the interlayer distance of K-doped GIC's [18], the diameter of the (6,0) tubule (4.78 Å) is too small to have a K atom inside while the diameter of the (9,0) tubule (7.13 Å) is too large for a favorable geometry. In the case of the (9,0) tubule, the K chain would be located away from the center in the most stable geometry. Even if this occurs, the number of nearest-neighboring C atoms for the K atom will be less than those in the (7,0) and (8,0) tubules. We therefore expect that the heat of formation of the (9,0) tubule will still be less than those of the (7,0) and (8,0) tubules.

Figures 2(a) and 2(b) show the band structures of the undoped and K-doped (7,0) tubules, respectively. The features of these band structures are almost identical except for the positions of the E_F and the bands labeled as NFE, α, and β. (Here NFE denotes nearly-free-electron bands which will be described below.) The calculated band structures near E_F are consistent with a rigid shift of E_F induced by K doping which indicates electron injection into the tubule conduction bands. Counting the number of newly occupied states, the amount of charge transfer is estimated to be one electron per K atom. The origin of the cohesion is concluded to be from the charge-transfer energy gain plus an ionic interaction between positively charged K ions and negatively charged tubules. Since these newly occupied states at E_F have large amplitudes for the wave function localized around the

TABLE I. Heats of formation E_h of the $(n,0)$ tubules having K atoms inside. The K-K distance is fixed at 4.29 Å. Diameters of the tubules D are also given.

Tubule	D (Å)	E_h (eV/K atom)
(6,0)	4.78	$\simeq 0.001$
(7,0)	5.56	1.12
(8,0)	6.34	1.07
(9,0)	7.13	0.30

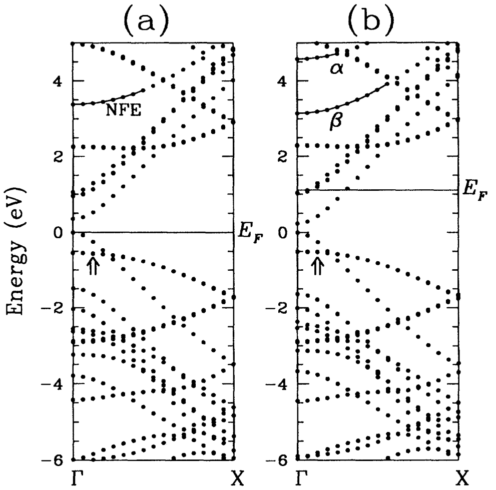

FIG. 2. Calculated band structures of (a) the undoped (7,0) tubule and (b) the K-doped (7,0) tubule. The maximum of the valence bands of the undoped tubules is set as an origin for the energy. The location of the Fermi level E_F is indicated.

tubule circumference, the electron transport is expected to be dominated in tubule walls rather than in the K chain.

For an undoped tubule, the NFE band in Fig. 2(a) has a calculated effective mass of $105 m_0$, where m_0 is the mass of the free electron. The NFE states originate from the sheet states of the graphitic materials which are weakly bonded to the hexagonal sheet [19]. A contour map of the partial charge density corresponding to the NFE state at the Γ point is shown in the panel labeled NFE in Fig. 3. These NFE states are spatially confined at the center of the tubule. When the K atoms are located inside the tubule, the K 4*s* bands and the NFE states hybridize with each other and produce the α and β states shown in Fig. 2(b). The contour maps of the corresponding partial charge densities are also shown in the panels labeled α and β in Fig. 3. From the features of the contour maps, the α states are found to be more weighted by the K 4*s* components than the β states. If the energy levels of the NFE states were located at the bottom of the conduction bands, E_F would cross one of the hybridized states. In that case, the hybridized states of the K 4*s* and the NFE states could contribute to the conductivity of the tubule. For BN tubules, which have been recently proposed [20], the NFE states compose the bottom of the conduction bands for most structural conditions [21]. The present results therefore suggest that when BN tubules are doped with alkali atoms similar hybridization should result. When this occurs, high conductivities of the doped BN tubules in the center of the tube are expected because of contributions from the NFE states.

We have also calculated the total energies and band structures of the (7,0) and (8,0) tubules with the K chain outside the tubule. In both cases, the optimized distance between the K chain and the tubule wall is 2.84 Å which is slightly larger than half of the interlayer distance of the K-doped GIC's (5.36 Å) [18]. The calculated total energies are higher than those for the geometries with the K chain inside. In the present supercell calculations with the chains outside, changing the tubule-tubule distance affects the values of the calculated total energies because the K chain interacts with another tubule of the neighboring unit cell. When the tubule-tubule distance is decreased, the geometry with the K atoms outside becomes more stable than the geometry with the K atoms inside. From these results, we conclude the following: The K atom prefers to be located inside when tubules are isolated, while it prefers to sit in an interstitial site when tubules are condensed. The latter situation is similar to the condensation of K-doped solid C_{60} [22]. From the calculated band structures, which are not shown here, charge transfer is again evident. On the other hand, the hybridization of the α and β bands shown in Figs. 2 and 3 are weakened because the overlap between the NFE wave functions and K 4*s* states is decreased.

The energy barriers for sliding motion of the K chain inside the tubule has been examined for the (7,0) and (8,0) tubules. The calculated values of 0.1–0.3 eV are comparable to those in the K-doped GIC's [23,24]. For

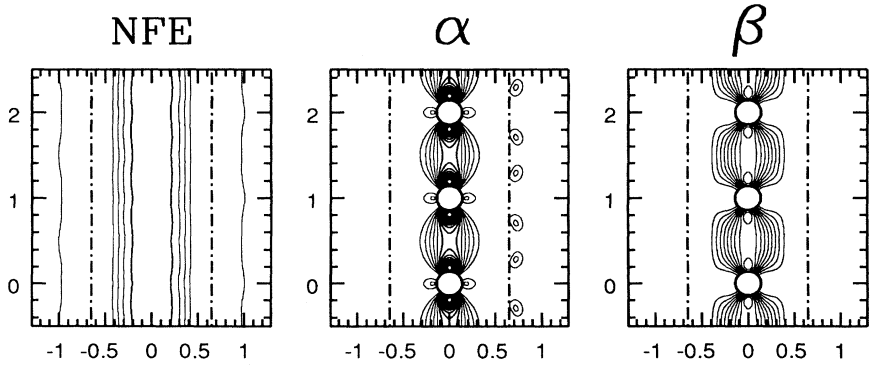

FIG. 3. Contour map of the partial charge density corresponding to the states labeled as NFE, α, and β shown in the band structures of Fig. 2. The contribution from the Γ point is considered. The length scale given in the panels is a unit of the lattice constant along the (7,0) tubule axis, 4.29 Å. The vertical direction is parallel to the tubule axis. Dot-dashed lines denote the positions of the tubules walls, while open circles denote the positions of the K atoms.

open tubules, we expect the K doping of tubules to occur as easy as in the GIC's, even though we have not obtained the theoretical results to explain how K atoms are captured from outside the tubules.

Finally, we briefly remark on the possibility of getting a high density of states at E_F [$N(E_F)$] for the (7,0) tubule for achieving superconductivity. From the calculated band structure in Fig. 2, we do not expect a high $N(E_F)$ in contrast to the case of the K-doped solid C_{60} [22]. Thus we suggest that a high superconducting T_c for K-doped tubules is not likely unless the electron-phonon coupling is particularly strong. (The coupling is expected to be larger than those of GIC's due to the curvature of the tubule walls as mentioned before but not expected to be as large as those of solid C_{60}'s.) However, there is a flat band below E_F, see open arrows in Fig. 2. Hole injection could be realized in the case of halogen doping. According to our estimation, one-hole injection per unit cell of the (7,0) tubules would shift E_F close to the flat band. Although we have not performed any detailed calculations for halogen doping, on the basis of the band-structure calculation, there is the possibility of achieving a high $N(E_F)$ by halogen doping. Contrary to the case of the (7,0) tubule, the (8,0) tubule does not have similar flat bands near E_F, so we do not expect a high $N(E_F)$ for alkali or halogen doping in this case.

In conclusion, we have found cohesion between linearly aligned K atoms and tubules with *angstrom-scale* diameters. The maximum calculated value of the heat of formation is 1.12 eV/(K atom). Since this series of calculations shows exothermic reaction even comparing to bulk K metal, we expect that K intercalation can occur easily when vapor-phase K is used as a source. The energy barrier for the sliding of the K chain inside the tubule is estimated to be of the same order of magnitude as that of K diffusion in the GIC's. Charge transfer of one electron to the tubule conduction bands per K atom occurs, resulting in ionic cohesion between the K atoms and the tubules. The conductivities of the doped tubules are expected to be dominated by carriers on tubule walls rather than on the K chains. In this microscopic situation, the classical wetting model for capillary action is shown to be inappropriate. There is a question as to what tubule diameter gives the transition between macroscopic and microscopic regions. Finally, we hope to motivate experimental examination of tubules with *angstrom-scale* diameters for the possibility of alkali doping.

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