Energetics and electronic structure of a polyacetylene chain contained in a carbon nanotube

G. C. McIntosh,[1] D. Tománek,[2] and Y. W. Park[1]

[1]*School of Physics, Seoul National University, Seoul 151-747, Korea*
[2]*Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824-2320*

Using density-functional theory, we calculate the energy and electronic structure of a polyacetylene chain interacting with various carbon nanotubes. We find that polyacetylene chains are weakly attracted exohedrally or endohedrally to nanotubes. The equilibrium separation between the chain and the wall is close to 3.3 Å, suggesting an energetic preference for polyacetylene to be enclosed in nanotubes wider than the (5,5) tube. The chains are expected to be spontaneously pulled into open nanotubes by forces amounting to a fraction of a nanonewton. Electronic structure calculations reveal the occurrence of a peak at the Fermi level in the electronic density of states, caused by the weak interaction between polyacetylene and the carbon nanotube, which may facilitate the onset of superconductivity in this system.

PACS number(s): 61.46.+w, 73.22.−f, 82.35.Cd

It was noted soon after their initial discovery[1] that carbon nanotubes are hollow cylindrical structures, which could make ideal containers for just a few atoms or small molecules.[2] In this regard, they have been considered for hydrogen storage[3] and as nanosized "test-tubes for manipulating chemical/biological molecules."[4] Filling of carbon nanotubes with molten lead, induced by capillary action, has been demonstrated experimentally.[5] The formation of "peapod" structures is now well established, whereby C_{60} buckyballs readily migrate into a (10,10) nanotube.[6] Further to this, if one is interested in investigating one-dimensional nanosystems, then carbon nanotubes could act as a support structure to contain the nanosystem. For example, nanotubes have been considered for confining a chain of metal atoms,[7] where the interest lies in comparing the properties of the one-dimensional chain with those of the three-dimensional bulk metal.

Even in the absence of contained atoms or molecules, armchair carbon nanotubes are very interesting one-dimensional metallic systems that, for example, have been considered as prime candidates for observing a Luttinger liquid.[8] Another one-dimensional material of considerable interest is polyacetylene (PA). Unlike metallic carbon nanotubes,[9] polyacetylene succumbs to Peierls distortion that causes dimerization in pristine PA, accompanied by a band gap opening at the Fermi level. The charge carriers in lightly doped PA are the somewhat more exotic solitons, which can carry spin and no charge or charge and no spin.[10] In the bulk system, the intrinsic properties of individual PA chains may be obscured by interchain coupling, complicated morphology of the bulk material, or by effects coming from dopant atoms. To avoid these artifacts, we propose to use carbon nanotubes as support structures to keep PA chains straight and to isolate them. Since both nanotubes and highly doped polyacetylene are good metals, the combined nanotube/polyacetylene system may show intriguing transport behavior with wide-scale technological applications.

Two main issues to be addressed are finding the ideal size of a carbon nanotube to comfortably contain just a single PA chain, and to determine the degree of interaction between the carbon nanotube and the enclosed PA chain. On the one

hand, a negligible interaction is desirable if the PA chain is to retain its original properties after insertion into the carbon nanotube. On the other hand, given that both carbon nanotubes and PA are very interesting materials on their own, we are curious as to whether some new phenomena might emerge within the combined system.

In this study, we investigate the binding energy and electronic structure of a polyacetylene chain aligned axially either exohedrally or endohedrally with a nanotube. We find that the polymer chains are weakly attracted towards, and may be spontaneously pulled into, sufficiently wide nanotubes. The undoped polyacetylene/nanotube system is metallic. The weak interaction between the subsystems induces a peak in the electronic density of states at the Fermi level, which may facilitate the onset of superconductivity.

Our calculations are based on density-functional theory (DFT) within the local-density approximation (LDA) and performed using the SIESTA code.[11] Troullier-Martins pseudopotentials were used to represent the nuclei plus core electrons. We used the Perdew-Zunger form of the exchange-correlation potential in LDA.

In all cases, the axes of the PA chain and carbon nanotube were kept parallel. The structural arrangement is illustrated in the insets of Fig. 1(a) as well as in Figs. 2(a) and 2(b). To reduce computing requirements,[12] only armchair nanotubes were considered at this stage. Since the lattice structures of a PA chain and graphitic armchair nanotube are very similar, the PA lattice could be held commensurate with the nanotube lattice, thus reducing the number of atoms required per unit cell. This necessitated the unit cell length of the PA chain to be reduced slightly from 2.475 Å to 2.460 Å, at the negligible energy cost of only ≈1 meV per unit cell.

Depending on the size of the carbon nanotube being considered, the unit cell contained between 20 atoms [for a (4,4) nanotube] and 32 atoms [for a (7,7) nanotube]. Of these, two carbon atoms and two hydrogen atoms were associated with the PA chain, as illustrated in Fig. 2(b). The unit cell size perpendicular to the carbon nanotube axis was set to at least 10 Å, so that there was no interaction between structures in adjacent cells. For total energy calculations, we sampled the irreducible wedge of the one-dimensional Brillouin zone by
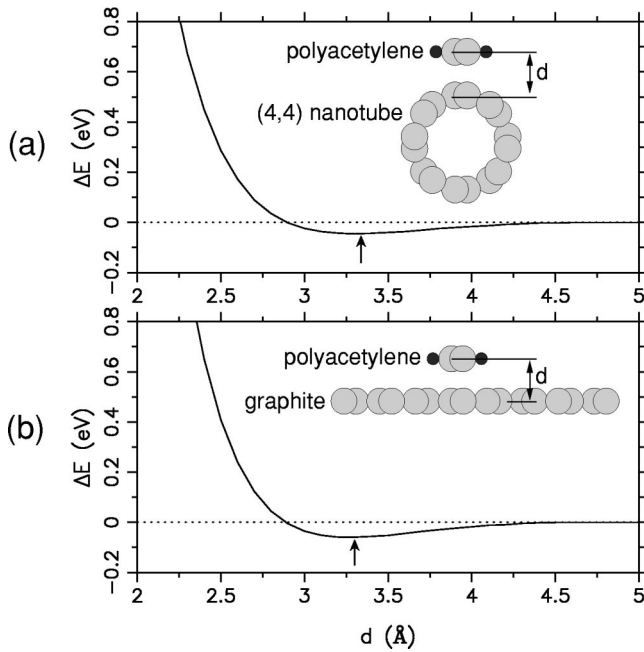
FIG. 1. Interaction energy ΔE between a PA chain and (a) a (4,4) carbon nanotube and (b) a graphite monolayer, representing an extremely wide tube. The schematic geometry, including the definition of the distance d between the chain axis and the graphitic wall, is given in the insets. Energies are given per unit cell, containing two carbon and two hydrogen atoms of the polyacetylene. The equilibrium separations are indicated by arrows.

four k points. To achieve sufficient energy convergence, we used a double-zeta basis,[13] augmented by ghost orbitals, and set the energy cutoff for plane-wave expansion to 100 Ry. We applied the counterpoise correction to account for basis set superposition errors.

As a test case, we have optimized the structure of an isolated PA chain. We obtained an average carbon-carbon bond length of 1.396 Å, which is close to the experimental value of 1.4 Å,[14] and a bond-length alteration (BLA) of 0.051 Å. This value for the BLA is less than the experimental value of 0.08 Å, but underestimation of the BLA has been acknowledged previously for DFT calculations.[15] Resolving this problem requires going beyond the LDA.[16] As another test, we have calculated the equilibrium separation between two graphite sheets. We obtain 3.44 Å, in close agreement with the experimental value.

In our first study, we explored the nature of the binding between a PA chain and a carbon nanotube. Figure 1(a) shows the binding energy ΔE between a (4,4) carbon nanotube and a PA chain that is situated outside the carbon nanotube. We define the binding energy as

$$\Delta E = E(\mathrm{NT} + \mathrm{PA}) - E(\mathrm{NT}) - E(\mathrm{PA}), \qquad (1)$$

where $E(\mathrm{NT})$ and $E(\mathrm{PA})$ are the energies of the isolated nanotube and PA systems while $E(\mathrm{NT} + \mathrm{PA})$ is the energy of the combined system. We find a clear minimum in the ΔE versus d curve with a binding energy of 45.4 meV. Comparing this value to kT, we conclude that the system can be bound at room temperature. The equilibrium separation of
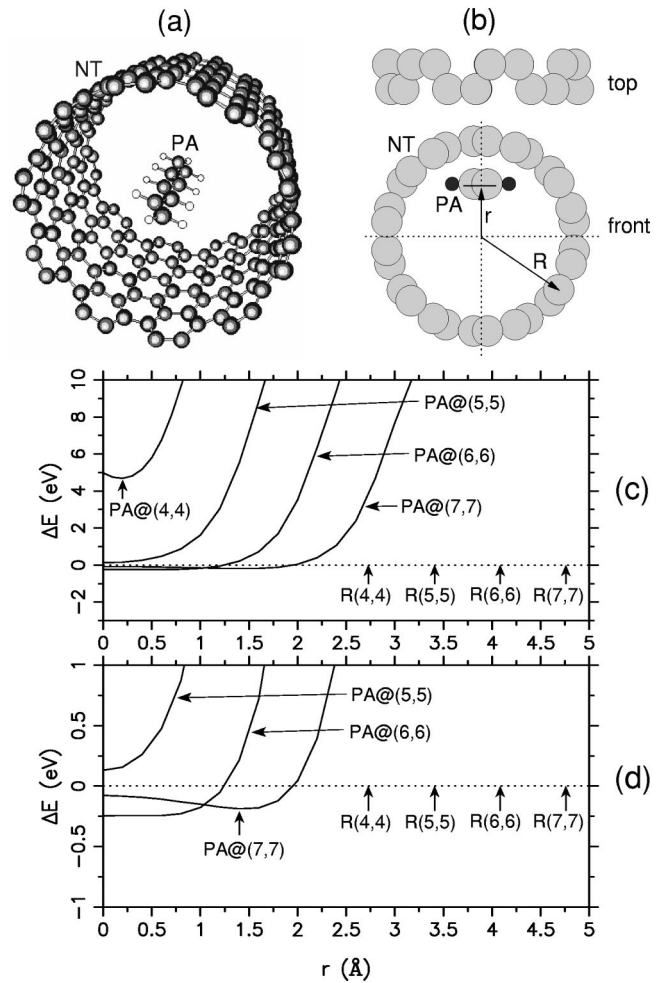

FIG. 2. Interaction between polyacetylene and armchair nanotubes of different diameters. (a) Schematic perspective view of the system. (b) Unit-cell geometry, defining the nanotube radius R and the axial separation r. (c) Interaction energy between a PA chain and various (n,n) nanotubes as a function of the axial separation r. (d) Details of the binding energy, given on an expanded scale. Energies are given per unit cell, illustrated in Fig. 2(b). Vertical arrows for $R(n,n)$ indicate the position of the respective nanotube walls.

3.34 Å turns out to be similar to that between graphite sheets. This is not too surprising, given that the nanotube can be considered as a rolled up graphite sheet and that the carbon backbone of the PA chain is almost commensurate with graphite. For the sake of comparison, in Fig. 1(b) we also show the binding energy between a PA chain and a graphite sheet, representing a nanotube of large diameter. In this case, the binding energy is slightly increased to 59.3 meV and the associated equilibrium separation reduced to 3.30 Å. Evidently, curvature of the graphitic structure plays a role in the binding energy, whereby having more atoms in close proximity to the PA chain increases the binding interaction. Our values for the equilibrium separation also indicate that a carbon nanotube would require a diameter of at least 6.6 Å, before an insertion of a PA chain into the nanotube would become energetically favorable.

Figure 2 shows our main result for a PA chain inside armchair carbon nanotubes of various radii R, as a function
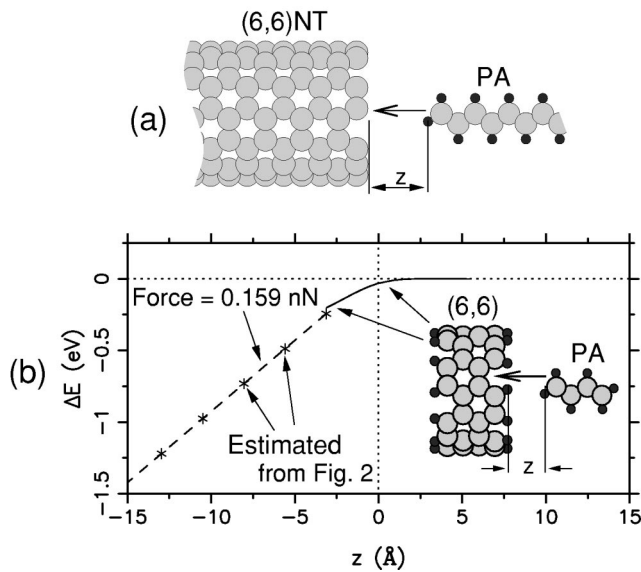
FIG. 3. Energetics of a polyacetylene chain entering a (6,6) nanotube. (a) Schematic diagram, defining the distance z between the ends of the tube and the chain. (b) Energy change associated with a semi-infinite PA chain being pulled into a semi-infinite (6,6) nanotube. The solid curve, based on calculations for the finite cluster shown in the inset, highlights the behavior as the PA chain approaches the open end of the carbon nanotube. The data points (*) at $z<0$ values, as well as the connecting dashed line, are based on the binding energy for the infinite system, presented in Fig. 2. The horizontal spacing of these data points corresponds to the unit-cell size, and their energy is set as a multiple of the binding energy per unit cell.

of the axial separation r. Figure 2(c) shows that on energy grounds, PA is likely to enter nanotubes of sufficiently large diameter and be free for off-axial displacements. For the PA chain inside a (4,4) nanotube the energy never becomes negative, indicating that this configuration is energetically unfavorable.[17] The same holds also for the wider (5,5) nanotube, where the insertion process is only marginally endothermic. For the (6,6) and (7,7) nanotubes, the nanotube diameter is sufficient to allow PA to be bound inside the nanotube, as seen on the expanded energy scale in Fig. 2(d). Comparing the relative stability of the different systems, the (6,6) nanotube appears to be the optimum container for a PA chain. For the (6,6) nanotube, the binding energy minimum is fairly wide, so that a PA chain enclosed inside a (6,6) nanotube would still have some degree of lateral freedom. As compared to larger nanotubes, this system allows PA to interact with more atoms, thus causing further stabilization, as already suggested by the results of Fig. 1. The (7,7) nanotube, with a set of energy minima at $r>0$, is sufficiently wide to accommodate more than one PA chain. We find that insertion of up to seven aligned PA chains, packed in a hexagonal arrangement, is energetically favorable for the even larger (10,10) nanotube.

We next address the possible insertion process of a PA chain into a carbon nanotube, illustrated in Fig. 3(a). Given that the (6,6) nanotube has an appropriate diameter to contain just one PA chain, we consider this as a model system.
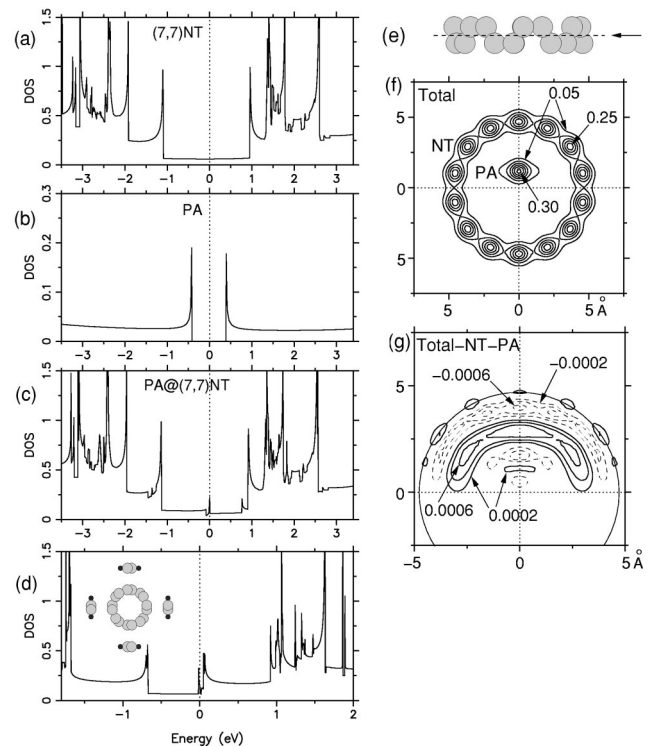

FIG. 4. Electronic structure of a polyacetylene chain interacting with a (7,7) nanotube. The electronic density of states near the Fermi level is shown for (a) an isolated (7,7) nanotube, (b) an isolated PA chain, and (c) for the polyacetylene chain inside a (7,7) nanotube. The density of states of four PA chains surrounding a (4,4) nanotube, with the idealized geometry given in the inset, is shown in (d). $E_F=0$ is used as energy reference in (a)–(d). (f) Charge distribution for the polyacetylene chain inside a (7,7) nanotube within the cross-section plane indicated in (e). Charge density is given in electrons/bohr^3, the equidistant contours being separated by 0.05 electrons/bohr^3. (g) Charge redistribution induced by the nanotube-polyacetylene interaction, obtained by subtracting the charge density of an individual (7,7) nanotube and PA chain from the total charge density in (f). Charge density contours are spaced by 0.0002 electrons/bohr^3; solid (dashed) contours indicate charge enhancement (depletion). The position of the (7,7) nanotube wall is shown by the solid circle. In all cases, the nanotube-PA separation is 3.3 Å, close to the equilibrium separation given in Fig. 1(a).

The energy gain associated with the axial insertion of a PA chain into the (6,6) nanotube is depicted in Fig. 3(b). Since the translation symmetry along the axis is broken in this case, the calculations are performed for finite, hydrogen-terminated clusters representing the nanotube and PA, as shown in the inset of Fig. 3(b), and extrapolated for a semi-infinite PA chain and nanotube. For PA completely outside the nanotube, corresponding to positive z values, the total energy is that of an isolated nanotube and an isolated PA chain and taken as a reference value. We see the energy becoming lowered as the end of the PA chain moves into the carbon nanotube, indicating that the PA chain is likely to be pulled in once it is partially inserted. Of interest is that the PA chain begins to feel the attraction, when it is still ≈ 2 Å outside the carbon nanotube. This suggests that the insertion process should start spontaneously as soon as the PA chain

approaches the open end of the carbon nanotube. For a semi-infinite chain entering a semi-infinite nanotube, the energy gain per segment inserted is constant and can be inferred from Fig. 2. The constant slope of the $\Delta E(z)$ curve in Fig. 3(b) corresponds to a force of 0.159 nN that pulls the PA chain in. This relatively large, capillarity-induced force will likely cause an efficient filling of the available volume by polyacetylene.

We next investigate the degree of electronic interaction between the carbon nanotube and a PA chain. Our model system in the endohedral case is the (7,7) nanotube containing a polyacetylene chain, which has been displaced off the tube axis close to its equilibrium position. The electronic density of states (DOS) of the (7,7) nanotube is shown in Fig. 4(a), that of an isolated PA chain[18] in Fig. 4(b), and that of the combined system in Fig. 4(c). For the sake of comparison, we show the density of states of exohedrally adsorbed PA chains in Fig. 4(d). We find the density of states of the combined system to differ from the superposition of its components, indicating some degree of electronic interaction between the valence systems of the two structures. Comparison between Figs. 4(a) and 4(c) indicates that the presence of PA does not affect the van Hove singularities in the DOS of the nanotube. The most pronounced change occurs in the metallic region in-between the first van Hove singularities of the nanotube, close to E_F. There, we can see a signature of the van Hove singularities of PA, which have been upshifted by the crystal potential. As seen in Figs. 4(c) and 4(d), one of these PA-induced peaks in the DOS coincides with the Fermi level, thus increasing the density of states at E_F for both exohedrally and endohedrally adsorbed polyacetylene. We propose that this change may benefit the possible superconducting behavior of the nanotube/PA system. Our speculation is based on the fact that superconductivity, albeit at low transition temperatures, has been observed in metallic carbon nanotubes.[19] Assuming that the presence of polyacetylene does not affect the strong electron-phonon coupling in nanotubes, the increase in the density of states at E_F should be reflected in a higher T_c of the system.

Figure 4(f) shows the charge distribution through a cross section of the combined (7,7) nanotube/PA system, in a plane defined by Fig. 4(e). To find out the effect of nanotube-PA interaction on the charge distribution, we subtract from the total charge density the superposition of the charge densities of the isolated (7,7) nanotube and PA chain, and present the results in Fig. 4(g). Even though the perturbation is relatively small, reflecting the weak interaction, we can clearly discern a region of increased charge density between the chain and the nanotube wall within the PA-nanotube interaction range. Since this charge stems predominantly from the nanotube, we can talk about PA-induced hole doping of the nanotube, similar to double-walled carbon nanotubes.[20] We conclude that due to the nonvanishing interaction, armchair carbon nanotubes do not act as "perfectly inert" containers for polyacetylene.

In summary, we have performed density-functional calculations to investigate the interaction between polyacetylene chains and armchair carbon nanotubes. We find that polyacetylene chains are weakly attracted exohedrally or endohedrally to nanotubes at an equilibrium separation between the chain and the wall close to 3.3 Å, suggesting the energetic preference for enclosure in sufficiently wide nanotubes. We find the (4,4) nanotube too narrow, but the (6,6) nanotube nearly ideal to contain a single PA chain. Experimentally, such narrow nanotubes may be formed inside zeolites.[21] Wider nanotubes, including the (10,10) nanotube, may contain more than one PA chain. We expect PA chains to be pulled spontaneously into open nanotubes by forces amounting to a fraction of a nanonewton. Electronic structure calculations reveal the occurrence of a peak at the Fermi level in the electronic density of states, caused by the weak interaction between a PA chain and a carbon nanotube. The enhanced density of states may raise the superconducting transition temperature in this system.

[1] S. Iijima, Nature (London) **354**, 56 (1991).

[2] Mark R. Pederson and Jeremy Q. Broughton, Phys. Rev. Lett. **69**, 2689 (1992).

[3] Andrea Quintel, in *Electronic Properties of Novel Material—Molecular, Nanostructures*, edited by Hans Kuzmany, Jörg Fink, Michael Mehring, and Siegmar Roth, AIP Conf. Proc. **544** (AIP, Melville, NY, 2000), p. 537.

[4] Fei Zhang, J. Chem. Phys. **111**, 9082 (1999).

[5] P.M. Ajayan and Sumio Iijima, Nature (London) **361**, 333 (1993).

[6] Susumu Okada, Susumu Saito, and Atsushi Oshiyama, Phys. Rev. Lett. **86**, 3835 (2001).

[7] Angel Rubio, Yoshiyuki Miyamoto, X. Blase, Marvin L. Cohen, and Steven G. Louie, Phys. Rev. B **53**, 4023 (1996).

[8] Marc Bockrath, David H. Cobden, Jia Lu, Andrew G. Rinzler, Richard E. Smalley, Leon Balents, and Paul L. McEuen, Nature (London) **397**, 598 (1999).

[9] J.W. Mintmire, B.I. Dunlap, and C.T. White, Phys. Rev. Lett. **68**, 631 (1992).

[10] Siegmar Roth, *One-Dimensional Metals: Physics and Materials Science* (VCH, Weinheim, 1995).

[11] P. Ordejón, E. Artacho, and J.M. Soler, Phys. Rev. B **53**, R10441 (2000); D. Sánchez-Portal, P. Ordejón, E. Artacho, and J.M. Soler, Int. J. Quantum Chem. **65**, 453 (1997).

[12] Calculations were carried out on a 1.7 GHz Pentium 4 computer.

[13] We found a significant energy difference between the presently used double-zeta and the minimum basis set. Based on calculations for the related ethylene molecule, using a triple-zeta basis would change the binding energy per atom by $\lesssim 3$ meV.

[14] C.R. Fincher, Jr., C.-E. Chen, A.J. Heeger, A.G. MacDiarmid, and J.B. Hastings, Phys. Rev. Lett. **48**, 100 (1982).

[15] Konstantin N. Kudin and Gustavo E. Scuseria, Phys. Rev. B **61**, 16 440 (2000).

[16] M. van Faassen, P.L. de Boeij, R. van Leeuwen, J.A. Berger, and J.G. Snijders, Phys. Rev. Lett. **88**, 186401 (2002).

[17] Asymmetry at $r = 0$ in the $\Delta E(r)$ curve for PA inside the narrow (4, 4) nanotube is due to the strong perturbation of the cylindrical symmetry near the axis by the potential of the tube atoms.

[18] The fundamental band gap of polyacetylene is underestimated in our calculations, a well-documented deficiency of the LDA.

[19] M. Kociak, A.Yu. Kasumov, S. Guéron, B. Reulet, I.I. Khodos, Yu.B. Gorbatov, V.T. Volkov, L. Vaccarini, and H. Bouchiat, Phys. Rev. Lett. **86**, 2416 (2001).

[20] Yoshiyuki Miyamoto, Susumu Saito, and David Tománek, Phys. Rev. B **65**, 041402 (2001).

[21] Z.K. Tang, L. Zhang, N. Wang, X.X. Zhang, G.H. Wen, G.D. Li, J.N. Wang, C.T. Chan, and P. Sheng, Science **292**, 2462 (2001).