

## Effect of intertube coupling on the electronic structure of carbon nanotube ropes

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We calculate the structural and electronic properties of an ordered “bundle” of (10,10) carbon nanotubes. Our results indicate that intertube coupling causes an additional band dispersion of  $\leq 0.2$  eV and opens up a pseudogap of the same magnitude at  $E_F$ . Soft librations at  $\nu \approx 12$  cm $^{-1}$  are predicted to occur below the orientational melting temperature which marks the onset of tube rotations about their axis. Whereas the density of states near  $E_F$  increases by 7% due to intertube coupling and by one order of magnitude due to K doping in  $KC_8$ , these states do not couple to tube librations. [S0163-1829(98)52340-5]

Carbon nanotubes<sup>1,2</sup> are promising candidates for the next generation of nanometer-scale electronic devices.<sup>3-5</sup> So far, theoretical studies of electronic and structural properties of *isolated* nanotubes<sup>6-9</sup> have by far outweighed those for nanotube “ropes.”<sup>10-12</sup> Very little is known about the effect of intertube coupling on the electronic structure of nanotube ropes that form naturally under synthesis conditions.<sup>13</sup> Since the graphitic bonding is very similar in solids composed of  $C_{60}$  molecules and nanotubes, we expect that also the effect of inter-molecular interactions on the electronic structure of these molecular crystals should be similar.

Electronic states involved in the superconducting behavior of the alkali-doped  $C_{60}$  solid derive from this molecule’s degenerate lowest unoccupied  $t_{1u}$  molecular orbital<sup>14</sup> that extends to an  $\approx 0.5$  eV wide band due to the inter- $C_{60}$  interactions, which in turn depend on the molecular orientation.<sup>14,15</sup> Similarly, interactions between nanotubes in pure or alkali-doped ropes, which depend on the mutual orientation of adjacent tubes, are expected to affect states at the Fermi level to an important degree. This point is especially intriguing, since recent calculations suggest that small deformations may open up a gap at  $E_F$  in *isolated* conducting nanotubes.<sup>16</sup> Hence, intertube interactions and orientational disorder may play an important role in the conducting (and superconducting) behavior of these systems.

Perfectly spherical  $C_{60}$  “buckyball” molecules<sup>17</sup> are known to spin freely at room temperature<sup>18</sup> when crystallized to a solid.<sup>19</sup> One may wonder, whether the homogeneous, perfectly cylindrical single-wall carbon nanotubes<sup>9,13,20</sup> could also rotate relatively freely when forming well-ordered bundles, the ropes.<sup>13</sup>  $^{13}C$  nuclear magnetic resonance experiments on solid  $C_{60}$  (Ref. 18) have shown that it is only below  $T \approx 260$  K that the free  $C_{60}$  rotation is hindered by the asphericity of the inter-molecular potential, due to the discrete atomic positions. In bundles of nanotubes, we expect the barrier for rotation to be even lower due to the frustration

introduced by triangular packing of tubes that have a  $D_{10h}$  symmetry and orientational dislocations (local twists) along the tube axes. Even though nanotubes, due to their large moment of inertia, will not spin as fast as  $C_{60}$  molecules in the lattice, it is useful to consider the effect of orientational disorder and rotations on the electronic structure of these systems.

In the following, we present theoretical evidence that the electronic structure of (10,10) nanotubes, especially near the Fermi level, changes significantly when the tubes are bundled to ropes. We find that the intertube interaction gives rise to an additional band dispersion of  $\approx 0.2$  eV near  $E_F$ , which would significantly diminish the effect of minute distortions on states near  $E_F$ , predicted for individual tubes.<sup>16</sup> Even though the intertube interaction is weak, it causes a buckling of the Fermi surface and an  $\approx 0.2$  eV wide pseudogap to open at  $E_F$  in undoped systems. Occurrence of this pseudogap in ropes of (10,10) nanotubes has independently been reported in Ref. 11. Due to the intertube interaction, the density of states  $N(E)$  is found to increase by  $\approx 7\%$  near the Fermi level (outside the pseudogap region), almost independent of the tube orientation. Potassium doping to the composition  $KC_8$  increases  $N(E_F)$  by one order of magnitude, again independent of tube orientation, in close agreement with the observed conductivity increase by one order of magnitude in this system upon doping.<sup>21</sup> Due to the small intertube interaction and high degree of lattice frustration, we predict a very soft librational mode to occur at  $\nu \approx 12$  cm $^{-1}$ . This mode is expected to disappear above the orientational melting temperature which marks the onset of tube rotations about their axis. This rotational motion, however, does not couple strongly to the electronic states near  $E_F$ . As in the doped  $C_{60}$  solid,<sup>14</sup> we do not expect librational phonons to play an important role in Bardeen-Cooper-Schrieffer (BCS) based superconductivity of nanotube ropes.

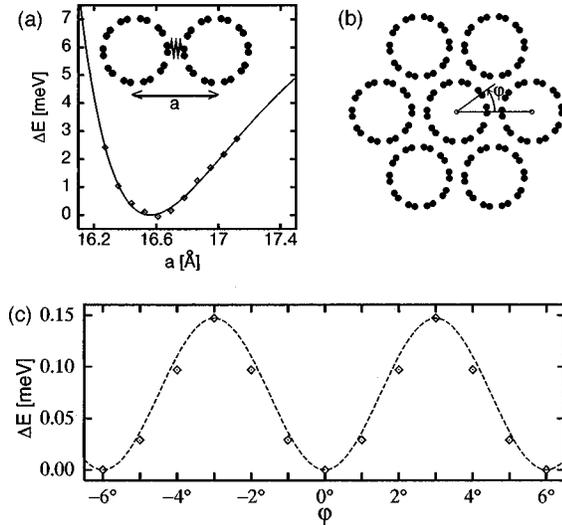


FIG. 1. (a) Density-functional results for the relative total energy  $\Delta E$  of a rope of (10,10) carbon nanotubes as a function of the intertube spacing  $a$ . (b) Schematic end-on view of the equilibrium rope structure, depicting the tube orientation angle  $\varphi$ . (c) Dependence of the rope energy  $\Delta E$  on the orientation angle  $\varphi$  of individual nanotubes. All energies are given per atom.

To investigate the effect of intertube coupling in a bundle of librating nanotubes on its electronic structure, we first optimize the geometry of an ordered nanotube lattice, the rope, using the density functional formalism within the local density approximation (LDA). Our plane-wave code<sup>22</sup> uses an energy cutoff of 50 Ryds, describes carbon atoms using soft nonlocal pseudopotentials<sup>23</sup> within a separable approximation,<sup>24</sup> and uses the Ceperley-Alder exchange-correlation potential<sup>25</sup> as parametrized by Perdew and Zunger.<sup>26</sup> This basis had been successfully used to optimize the lattice constant of the  $C_{60}$  solid<sup>27</sup> and related systems.<sup>28</sup> Due to the large size of the basis set, that contains nearly 200 000 plane waves, we restrict our sampling of the irreducible part of the Brillouin zone to 4  $k$  points when determining the optimum intertube spacing and the equilibrium tube geometry.

The interatomic distances in the tubes, optimized within the LDA, are  $d_{CC} = 1.397$  Å for bonds perpendicular to the tube axis (“double” bonds) and  $d_{CC} = 1.420$  Å for the other (“single” bonds). The weak intertube interaction in the rope, shown in Fig. 1(a), causes only a very small radial deforma-

tion (“buckling”) of the tubes with an amplitude of  $\Delta R \approx 0.03$  Å. As shown in Fig. 1(a), the calculated equilibrium intertube separation  $a_{e,th} = 16.50$  Å lies only 2.8% below the observed value  $a_{e,expt} = 16.95 \pm 0.34$  Å.<sup>13</sup>

We found the  $k$ -point sampling used in the LDA calculation sufficient to describe the details of intratube and general features of intertube interactions. This relatively coarse  $k$ -point grid is, however, not adequate to describe the minute effect of tube rotations on the intertube hybridization and states near the Fermi level. Therefore, we performed a parametrized calculation of this quantity using 102 400  $k$  points in the irreducible Brillouin zone for the rope lattice and 800  $k$  points for the tube. The tight-binding parametrization, based on LDA electronic structure results,<sup>29</sup> has been used successfully to describe superconductivity in bulk  $C_{60}$ .<sup>14</sup> The band structure energy functional is augmented by pairwise interactions describing both the closed-shell interatomic repulsion and the long-range attractive Van der Waals interaction, to correctly reproduce the interlayer distance and the  $C_{33}$  modulus of graphite.

This is discussed more quantitatively in Fig. 2, where we compare the band structure of an isolated tube to that of the rope in equilibrium. The irreducible Brillouin zone of the triangular tube lattice, shown in Fig. 2(a), collapses to the  $\Gamma - A$  line at large intertube separations corresponding to isolated tubes. In this case, depicted in Fig. 2(b), the Fermi momentum occurs at the point  $\Delta_F$ . On the other hand, when nanotubes are bundled in the rope lattice, the Fermi point  $\Delta_F$  expands to a Fermi surface that is normal to the  $\Gamma - A$  line in the hexagonal Brillouin zone. This Fermi surface shows a small corrugation, which is induced by the intertube interaction, and hence depends both on the intertube separation  $a$  and the tube orientation angle  $\varphi$ , defined in Fig. 1(b).

The effect of intertube interactions on the electronic structure is easily seen by comparing the band structure of an isolated tube and the equilibrium rope along the  $\Gamma - A$  line in Figs. 2(b) and (c), respectively. An even more pronounced effect can be observed in the band dispersion perpendicular to the tube axis in Fig. 2(d). In the following, we will focus on a precise description of the changing hybridization as a function of the tube orientation  $\varphi$ , which describes the coupling of electronic states to tube librations. We note that if a strong electron-libration coupling were present, it should lead to superconducting behavior that could be described using the Bardeen-Cooper-Schrieffer formalism.

Our parametrized results, in good agreement with the

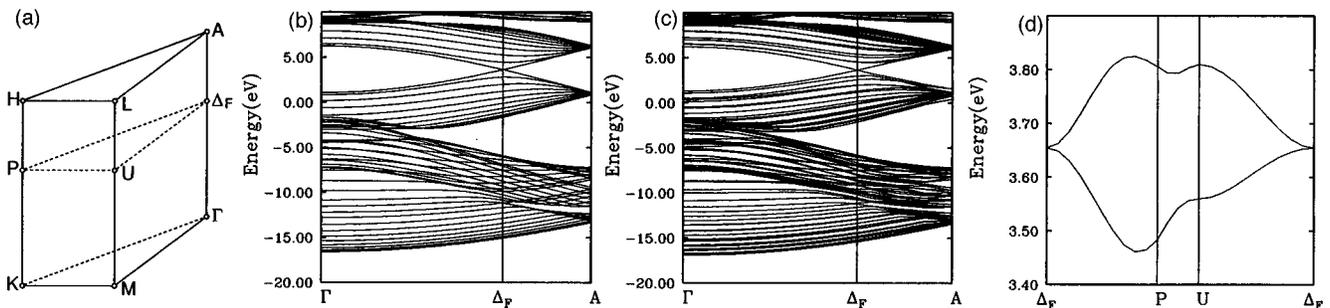


FIG. 2. (a) Irreducible part of the hexagonal Brillouin zone of a nanotube crystal, the rope. Band structure of (b) an individual nanotube and (c) the rope, along the tube axis. (d) Dispersion of the top valence and bottom conduction bands of the rope, in a plane perpendicular to the tube axis, containing the point  $\Delta_F$  depicted in (c).

LDA data presented in Fig. 1(a), indicate that nanotubes gain  $\Delta E_b \approx 9$  meV per atom when bunching up to a rope. The calculated dependence of the binding energy  $\Delta E$  on the tube orientation  $\varphi$  is comparably weak, as shown in Fig. 1(c). Due to the high degree of frustration in a system of tubes with  $D_{10h}$  symmetry that are bundled to a triangular lattice, we find  $\Delta E(\varphi)$  to be periodic in  $\varphi$ , with the equilibrium tube orientation  $\varphi_e = 0^\circ$ , a period  $\Delta\varphi = 6^\circ$ , and an activation barrier for rotation of  $\Delta E \approx 0.15$  meV per atom.<sup>30</sup> This is in good agreement with our LDA results for the equilibrium tube orientation and the rotational barrier of  $\Delta E \approx 0.3$  meV per atom. At the relatively large equilibrium separation  $d_w \approx 3.4$  Å between the walls of neighboring nanotubes, the repulsive part of the interaction (originating in the kinetic energy increase of a compressed electron gas) shows only a small ( $\Delta E \approx 0.07$  meV) dependence on the tube orientation angle  $\varphi$ . The orientational dependence of the total energy thus reflects both the changing intertube hybridization and Van der Waals interaction between adjacent tubes, also discussed in Ref. 12.

At very low temperatures, we expect nanotubes to perform mostly librational motion in the shallow potential wells. We should think of tube librations or rotations within the rope as of a twisting motion of tube segments rather than a spinning motion of rigid tubes. Approximating the periodic, but strongly anharmonic potential  $\Delta E(\varphi)$  by the sinusoid shown in Fig. 1(c), we estimate the libration frequency to be  $\nu \approx 12$  cm<sup>-1</sup>. This soft mode lies close to the observed (but not identified) infrared modes of the rope at  $\nu \approx 15, 22$ , and  $40$  cm<sup>-1</sup>.<sup>31</sup>

An infinitely rigid and straight nanotube, when part of an ordered rope, has only two degrees of freedom, namely for axial and angular motion. Even though the activation barrier *per atom* for any of these motions may be small, the relevant quantity in this case it is the infinitely high barrier for the entire rigid tube that would lock it in place and inhibit any rotation.

A more realistic estimate of the onset of orientational disorder must consider that nanotube ropes, when synthesized, are far from being straight over long distances.<sup>13</sup> As suggested by the potential energy surface for this mode in Fig. 1(c), a local twist by  $\varphi > 3^\circ$  results in the nanotube switching locally from one equilibrium orientation to another, like in the Frenkel-Kontorova model of dislocations in strained lattices. Taking into account the actual tube rigidity,<sup>32</sup> we have found that the energy cost for such an orientational dislocation is only  $\approx 0.17$  meV per atom in the  $\approx 150$  Å long strained region.<sup>33</sup> Due to the high tube rigidity,<sup>32</sup> we expect  $T_{OM}$  for a perfect, dislocation-free rope to be significantly higher than the few degrees Kelvin, suggested by the 0.15 meV/atom high activation barrier for rotation in the unphysical zero-rigidity limit. Presence of orientational dislocations and tubes of other chiralities, on the other hand, would reduce the level of commensurability and lower the activation barrier for tube rotations, thus resulting in a finite value of  $T_{OM}$ .

There are two indications that onset of orientational disorder may be significantly below room temperature. First, low-frequency infrared modes of the rope at  $\nu \approx 15, 22$ , and  $40$  cm<sup>-1</sup>, some of which may be librations, have been reported to disappear at  $T \approx 30 - 180$  K.<sup>31</sup> The second indica-

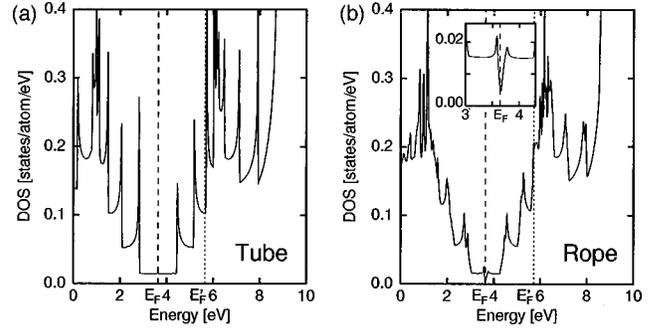


FIG. 3. Density of states of (a) an isolated nanotube and (b) a nanotube crystal, the rope. The structure of the pseudogap in the rope is displayed in the inset on an expanded energy scale. Dashed and dotted lines indicate the position of the Fermi level  $E_F$  for the undoped and  $E'_F$  for the  $KC_8$  doped systems, respectively.

tion is the transition from nonmetallic to metallic character of the nanotubes, occurring near 50 K,<sup>34</sup> which in our interpretation arises from subtle changes of the electronic density of states near  $E_F$  in presence of increasing orientational disorder. This is more closely related to the recently proposed mechanism for the temperature dependence of resistivity due to intertube hopping near defects<sup>35</sup> than temperature-induced changes in the weak localization of electrons on individual tubes.<sup>36</sup>

As discussed above and in Fig. 2, intertube interactions in the rope cause substantial changes in the electronic states which are also reflected in the density of states. Our results, presented in Fig. 3, indicate that upon bunching of tubes to a rope, the density of states close to the Fermi level increases by  $\approx 7\%$  from  $1.4 \times 10^{-2}$  states/eV/atom in tubes to  $1.5 \times 10^{-2}$  states/eV/atom in ropes, nearly independent of the tube orientation angle  $\varphi$ . Hence we find that states at the Fermi level do not couple significantly to tube librations, similar to the situation in the doped  $C_{60}$  solid.<sup>37</sup> We do not expect librations to play an important role in potentially superconducting behavior induced by electron-phonon coupling in this marginally metallic system.<sup>13,21,34</sup>

An intriguing effect, outlined in the inset of Fig. 3(b), is the occurrence of a pseudogap near  $E_F$  in the density of states of the rope. This feature results from breaking the  $D_{10h}$  tube symmetry by the triangular lattice, and should be less significant in the highly symmetric ordered lattice of (6,6) nanotubes.<sup>10</sup> We expect that in presence of orientational disorder, caused by the presence of different tubes, or a twisting motion of individual nanotubes in the rope at  $T > T_{OM}$ , the Brillouin zone should collapse to a point. We also expect an increase of the intertube spacing at  $T > T_{OM}$ , in analogy to  $C_{60}$  crystals. The resulting reduction of the pseudogap should mark the onset of metallic behavior of the ropes, as discussed above.

In a situation analogous to graphite intercalation compounds, the electronic structure of a system doped by potassium to the composition  $KC_8$  can be described by a rigid-band model,<sup>38</sup> where each K atom transfers its  $4s$  electron to the (otherwise unmodified) electronic structure of the nanotube crystal. This shifts the Fermi level from  $E_F$  to  $E'_F$ , as indicated in Figs. 3(a) and 3(b). Upon doping to this degree, the density of states increases by a factor of  $\approx 12$  with respect to the undoped system. This has been confirmed ex-

perimentally by a corresponding increase in conductivity by one order of magnitude.<sup>21</sup> As in the undoped solid, characterized by  $E_F$ , we do not observe a significant dependence of the density of states at  $E'_F$  on tube orientation. This suggests that even in this doped system, librational modes should not couple significantly to states at the Fermi level. This situation is very similar to alkali-doped  $C_{60}$  solid, where librational modes were shown not to couple to states at  $E_F$  (Ref. 37) and not to play any significant role in the electron-phonon coupling that causes superconductivity in these systems.<sup>14</sup>

Our LDA results indicate a significant decrease of radial tube deformations (“buckling”) from  $\Delta R \approx 0.03 \text{ \AA}$  to  $\approx 0.004 \text{ \AA}$  as the intertube spacing in the rope increases by a mere 2.8% from the theoretical equilibrium value  $a_{e,th} = 16.50 \text{ \AA}$ . Suppression of this radial deformation, which is likely to occur in rotating tubes, should effectively lead to an increase of the equilibrium intertube spacing  $a_e$ . The 2.8% difference between the observed and calculated value of  $a_e$  may be partly caused by the fact that we were comparing a room-temperature value<sup>13</sup> of  $a_{e,expt}$  to a zero-temperature value of  $a_{e,th}$ . We suggest that orientational melting of the tube lattice should be accompanied by a significant, possibly discontinuous increase of the equilibrium intertube spacing  $a_e$ .

In summary, we used *ab initio* and parametrized techniques to determine the structural and electronic properties

of an ordered bundle of (10,10) carbon nanotubes. The intertube coupling introduces an additional band dispersion of  $\leq 0.2 \text{ eV}$  and opens up a pseudogap of the same magnitude at  $E_F$ . The weak intertube interaction and lattice frustration results in a very soft libration mode at  $\nu \approx 12 \text{ cm}^{-1}$ . Due to the small activation barrier for tube rotations and the presence of frozen-in orientational dislocations in the rope, we expect the “twisting” motion of finite tube segments to turn into an orientational melting process within the rope even at very low temperatures. We do not observe any significant coupling of librational motion to states near  $E_F$  in the undoped system, nor in the doped  $KC_8$  system with a one-order-of-magnitude higher conductivity. As in the alkali-doped  $C_{60}$  solid, we do not expect significant influence of tube libration modes on a potentially superconducting behavior of an ordered lattice of carbon nanotubes.

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- <sup>1</sup>S. Iijima, *Nature (London)* **354**, 56 (1991).  
<sup>2</sup>For a general review, see M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996), and references therein.  
<sup>3</sup>Sander J. Tans *et al.*, *Nature (London)* **386**, 474 (1997); J. W. G. Wildöer *et al.*, *ibid.* **391**, 59 (1998).  
<sup>4</sup>T. W. Odom *et al.*, *Nature (London)* **391**, 62 (1998).  
<sup>5</sup>Marc Bockrath *et al.*, *Science* **275**, 1922 (1997).  
<sup>6</sup>J. W. Mintmire *et al.*, *Phys. Rev. Lett.* **68**, 631 (1992).  
<sup>7</sup>R. Saito *et al.*, *Appl. Phys. Lett.* **60**, 2204 (1992).  
<sup>8</sup>N. Hamada *et al.*, *Phys. Rev. Lett.* **68**, 1579 (1992).  
<sup>9</sup>Young Hee Lee *et al.*, *Phys. Rev. Lett.* **78**, 2393 (1997).  
<sup>10</sup>J.-C. Charlier *et al.*, *Europhys. Lett.* **29**, 43 (1995).  
<sup>11</sup>P. Delaney, H. J. Choi, J. Ihm, S. G. Louie, and M. L. Cohen, *Nature (London)* **391**, 466 (1998).  
<sup>12</sup>Jian Ping Lou, *Phys. Rev. Lett.* **79**, 1297 (1997).  
<sup>13</sup>A. Thess *et al.*, *Science* **273**, 483 (1996).  
<sup>14</sup>M. Schluter *et al.*, *Phys. Rev. Lett.* **68**, 526 (1992).  
<sup>15</sup>Susumu Saito *et al.*, *Phys. Rev. Lett.* **66**, 2637 (1991).  
<sup>16</sup>C. L. Kane *et al.*, *Phys. Rev. Lett.* **78**, 1932 (1997).  
<sup>17</sup>H. W. Kroto *et al.*, *Nature (London)* **318**, 162 (1985).  
<sup>18</sup>C. S. Yannoni *et al.*, *J. Phys. Chem.* **95**, 9 (1991); R. Tycko *et al.*, *ibid.* **95**, 518 (1991).  
<sup>19</sup>W. Krätschmer *et al.*, *Nature (London)* **347**, 354 (1990).  
<sup>20</sup>P. Nikolaev *et al.*, *Chem. Phys. Lett.* **266**, 422 (1997).  
<sup>21</sup>R. S. Lee *et al.*, *Nature (London)* **388**, 255 (1997).  
<sup>22</sup>O. Sugino *et al.*, *Phys. Rev. Lett.* **68**, 1858 (1992).  
<sup>23</sup>N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).  
<sup>24</sup>L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).  
<sup>25</sup>D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).  
<sup>26</sup>J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).  
<sup>27</sup>J. H. Weaver *et al.*, *Phys. Rev. Lett.* **66**, 1741 (1991).  
<sup>28</sup>S. Okada *et al.*, *Phys. Rev. B* **55**, 4039 (1997).  
<sup>29</sup>D. Tománek *et al.*, *Phys. Rev. Lett.* **67**, 2331 (1991).  
<sup>30</sup>Rather than using a fixed cutoff distance in our parametrized scheme, which would cause artifacts in the energy due to a changing neighbor map during tube rotations, we obtained the potential energy surface by carefully integrating over energy differences due to small rotations, during which the neighbor map was kept fixed.  
<sup>31</sup>W. Holmes, J. Hone, P. L. Richards, and A. Zettl, *Bull. Am. Phys. Soc.* **43**, 629 (1998).  
<sup>32</sup>G. Overney, W. Zhong, and D. Tománek, *Z. Phys. D* **27**, 93 (1993).  
<sup>33</sup>Y.-K. Kwon *et al.* (unpublished).  
<sup>34</sup>J. E. Fischer *et al.*, *Phys. Rev. B* **55**, R4921 (1997).  
<sup>35</sup>A. B. Kaiser *et al.*, *Phys. Rev. B* **57**, 1418 (1998).  
<sup>36</sup>L. Langer *et al.*, *Phys. Rev. Lett.* **76**, 479 (1996).  
<sup>37</sup>C. Christides *et al.*, *Phys. Rev. B* **46**, 12 088 (1992).  
<sup>38</sup>The electronic structure calculation must, of course, account for the expansion of the intertube spacing  $a$  upon intercalation. We expect the electron-libration coupling to further decrease in such an expanded lattice.