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Do carbon nanotubes spin when bundled?

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Using *ab initio* and parametrized techniques, we determine the equilibrium structure of an ordered "bundle" of (10,10) carbon nanotubes. Because of small intertube interaction and lattice frustration, we predict a very soft libration mode to occur at $\nu \approx 12$ cm^{-1}. This mode is predicted to disappear above the orientational melting temperature which marks the onset of free tube rotations about their axis. We discuss the effect of the weak intertube coupling and orientational disorder on the electronic structure near the Fermi level.

I. INTRODUCTION

Among carbon-based materials, fullerenes (such as the C_{60} "buckyball"[1]) and nanotubes[2] have received much attention recently due to their high structural stability and interesting electronic properties. Structurally rigid[3] and highly conducting[4] "ropes" of carbon nanotubes are the molecular counterparts of carbon fibers.[5]

Perfectly spherical C_{60} molecules are known to spin freely at room temperature[6] when crystallized to a solid.[7] One may wonder whether the cylindrical single-wall (10,10) carbon nanotubes,[5] the abundant species[4,8,9] among single-wall tubes, could also rotate relatively freely when forming well-ordered bundles, the "ropes."[4] ^{13}C nuclear magnetic resonance experiments on solid C_{60}[6] have shown that it is only below $T \approx 260$ K that the free C_{60} rotation is hindered by the asphericity of the intermolecular 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 due to orientational dislocations caused by local twists along the tube axis. Due to their large moment of inertia, nanotubes are not expected to spin as fast as the C_{60} molecules. Nevertheless, it is useful to study the soft librational motion of nanotubes and their transition to relatively free tube rotations, marking the onset of orientational disorder in nanotube "ropes."

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[10] that extends to an ≈0.5 eV wide band due to the inter-C_{60} interactions, which in turn depend on the molecular orientation.[10,11] Similarly, interactions between carbon nanotubes in "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 suggested that small deformations may open up a gap at E_F in *isolated* conducting nanotubes.[12] Hence, we expect our results to be of consequence for the conducting behavior of these systems.[13]

In the following, we present theoretical evidence, supported by recent experimental data, about an orientational melting transition in "ropes" consisting of (10,10) nanotubes. We find that even at relatively low temperatures, the hindrance of tube rotations due to discrete atomic positions in the tube walls should lose its significance. This should mark the onset of relatively free rotation or twisting motion about the tube axes. We find that bundling up of nanotubes to "ropes" is accompanied by an ≈7% increase in the density of states near the Fermi level $N(E_F)$, almost independent of tube orientation. The intertube interaction gives rise to an additional band broadening by ≈0.2 eV, which would significantly

diminish the effect of minute tube distortions on states near E_F, predicted for individual tubes.[12]

II. THEORY

To investigate the possibility of rotations in a bundle of nanotubes and their effect on the electronic structure of the system, 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[14] uses an energy cutoff of 50 Rydbergs, describes carbon atoms using soft nonlocal pseudopotentials[15] within a separable approximation,[16] and uses the Ceperley–Alder exchange-correlation potential[17] as parametrized by Perdew and Zunger.[18] This basis had been successfully used to optimize the lattice constant of the C_{60} solid[19] and related systems.[20] Because of the large size of the basis set, which 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.

III. RESULTS AND DISCUSSION

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 very small radial deformation ("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.[4] We also observe a significant decrease of radial tube deformations ("buckling") from $\Delta R \approx 0.03$ Å to $\approx$0.004 Å as the intertube spacing in the "rope" increases by a mere 2.8% from the theoretical equilibrium value $a_{e,th} = 16.50$ Å. Suppression of this radial deformation, which is likely linked to the ability of individual tubes to spin freely, should effectively cause an increase of the equilibrium intertube spacing a_e at the orientational melting temperature. Hence, the 2.8% difference between the observed and calculated value of a_e may be partly due to the fact that the value observed at room temperature,[4] $a_{e,expt}$, was compared to the calculated zero-temperature value $a_{e,th}$.

Even though the agreement between the calculated and observed intertube spacing is very good for a partly Van der Waals system by standards of *ab initio* calculations, we try to understand the minor deviations by calculating the optimized geometry of hexagonal graphite in Figs. 1(b) and 1(c) using the very same basis. Our results for the energy dependence on the inter-layer separation c, presented in Fig. 1(b), show that this value

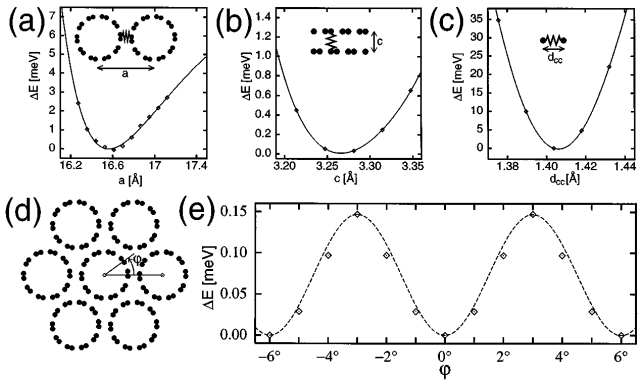

FIG. 1. Density functional results for the relative total energy ΔE of (a) a "rope" of (10,10) carbon nanotubes as a function of the intertube spacing a, (b) hexagonal graphite as a function of interlayer spacing c, and (c) hexagonal graphite as a function of the bond length d_{CC}. (d) Schematic end-on view of the "rope" structure, depicting the tube orientation angle φ. (e) Dependence of the "rope" energy ΔE on the orientation angle φ of individual nanotubes. All energies are given per atom.

is also underestimated by 2.4% when compared to the experimental value. Similar to the tubes, the interatomic distance in graphite is underestimated by only 0.8% with respect to the experimental value.

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 interaction depends not only on the intertube separation a, but also the tube orientation angle φ, defined in Fig. 1(d). The relatively coarse k-point grid, used in the LDA study, was found not to be adequate to describe the minute effect of tube rotations on the intertube hybridization and the density of states near E_F. Therefore, we performed a parametrized calculation of these quantities using 102,400 k-points in the irreducible Brillouin zone for the "rope" lattice and 800 k-points for the tube. Our tight-binding parametrization, which has been used previously to describe superconductivity in bulk C_{60},[10] is based on LDA electronic structure results,[21] and hence should describe correctly the covalent part of the interaction.

These results, in good agreement with the 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 ΔE on the tube orientation φ is comparably weak, as shown in Fig. 1(e). Because of 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 φ, with a period $\Delta\varphi = 6°$ and an activation barrier for rotation of $\Delta E \lesssim 0.15$ meV per atom,[22] 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 depends only weakly ($\Delta E \lesssim 0.07$ meV) on the tube orientation angle φ. We conclude that $\Delta E(\varphi)$ is dominated by the small changes in hybridization between neighboring nanotubes.

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(e), we estimate the libration frequency to lie at $\nu \approx 12$ cm^{-1}. This soft mode lies close to the observed (but not identified) infrared modes of the "rope" at $\nu \approx 15$, 22, 40 cm^{-1}.[23] The librational mode should be infrared silent if the **E**-field were parallel to a perfect bundle of (10,10) nanotubes. This is, however, not the case in real samples where all nanotube orientations coexist, exposing most of the tubes to a nonzero **E**-field component normal to their axis. Also, the majority of rope samples have recently been reported to contain a large fraction of *chiral* (n, m) nanotubes, with a diameter close to that of the achiral (10,10) tubes.[24,25] While the potential energy surface and hence the libration frequency should be very similar, the infrared coupling to the low-frequency modes could be significantly enhanced in this case.

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 is the infinitely high barrier for the entire rigid tube that would lock it in place. In the other extreme of a straight, zero-rigidity tube composed of independent atoms, 0.15 meV/atom activation barrier for rotation would give rise to an orientational melting transition at $T_{OM} \approx 2$ K.

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.[4] As suggested by the potential energy surface for this mode in Fig. 1(e), a local twist by $\varphi > 3°$ results in the nanotube switching locally from one equilibrium orientation to another. Formally, by mapping the orientational coordinate φ onto the position coordinate x, this process can be described using the Frenkel–Kontorova model used to describe dislocations in strained one-dimensional lattices. Under synthesis conditions at temperatures exceeding 1000 K, we expect substantial finite twists to occur in free nanotubes, which are associated with strictly zero energy cost over an infinite length. Upon condensation to a bundle, in an attempt to optimize the interwall interaction while minimizing the torsion energy, orientational dislocations are frozen in at an energy cost of only ≈0.17 meV per atom in a ≈150 Å long strained region,[26] as compared to an optimized straight bundle of nanotubes. Taking a straight, zero-rigidity tube as a reference, we expect T_{OM} to increase from the 2 K value with increasing rigidity. Presence of orientational dislocations, on the other hand, should lower the activation barrier for tube rotations, thus lowering T_{OM} and possibly compensating for the effect of nonzero rigidity.

There are two indications that onset of orientational disorder may occur below room temperature. First, the infrared modes of the "rope" at $\nu \approx 15$, 22, 40 cm^{-1}, some of which may be librations, have been reported to disappear at $T \approx 30$–180 K.[23] The second indication is the transition from nonmetallic to metallic character of the nanotubes, occurring near 50 K,[13] which in our interpretation arises from subtle changes of the electronic density of states near E_F in the presence of increasing orientational disorder, to be discussed below. This is more closely related to the recently proposed mechanism for the temperature dependence of resistivity due to intertube hopping near defects[27] than temperature-induced changes in the weak localization of electrons on individual tubes.[28]

Our results for the electronic structure of an isolated tube and that of the "rope" are presented in Fig. 2. The irreducible Brillouin zone of the triangular tube lattice, shown in Fig. 2(a), collapses to the $\Gamma - A$ line as the intertube separations increase in a system of separating tubes. In this case, the Fermi momentum occurs at the point Δ_F. On the other hand, when nanotubes are bundled in the "rope" lattice, the Fermi point Δ_F expands to a Fermi surface in the hexagonal Brillouin zone that is normal to the $\Gamma - A$ line. This Fermi surface shows a small corrugation, induced by the intertube interaction.

Intertube interactions in the "rope" cause substantial changes in the electronic states that are also reflected in the density of states. Our results, presented in Figs. 2(b) and 2(c), indicate that upon bunching of tubes to a "rope," the density of states near the Fermi level increases by ≈7% from 1.4×10^{-2} states/eV/atom in tubes to 1.5×10^{-2} states/eV/atom in "ropes." We find $N(E)$ near E_F to be nearly independent of the tube orientation angle φ, suggesting that states close to the Fermi level do not couple significantly to tube librations in this marginally metallic system.[4,13] This is similar to the situation in the doped C_{60} solid,[29] where librations also do not play an important role in the superconducting behavior induced by electron-phonon coupling.

An intriguing effect, linked to orientational order within the "rope," is the appearance of a pseudo-gap near E_F in the density of states, as seen in Fig. 2(c). Occurrence of this pseudo-gap in "ropes" of (10,10) nano-

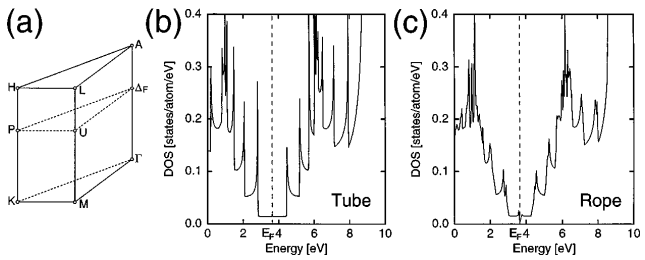

FIG. 2. (a) Irreducible part of the hexagonal Brillouin zone of a nanotube crystal, the "rope." Density of states of (b) an isolated nanotube and (c) a nanotube crystal, the "rope." Dashed lines indicate the position of the Fermi level E_F.

tubes has independently been confirmed in Ref. 30. 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.[31] We expect that in presence of orientational disorder, caused in particular by the twisting motion of (10,10) nanotubes in the "rope" at $T > T_{OM}$, the Brillouin zone should collapse to a point. The resulting reduction of the pseudo-gap should mark the onset of metallic behavior of the "ropes," as discussed above.

IV. CONCLUSIONS

We used *ab initio* and parametrized techniques to determine the orientational ordering in a "bundle" of (10,10) carbon nanotubes and its effect on the electronic properties. The weak intertube interaction and lattice frustration results in a very soft libration mode that occurs at $\nu \approx 12$ cm^{-1}. Because of the small activation barrier for rotation, we predict this mode to disappear at very low temperatures, marking the onset of orientational melting of tubes in the "rope." We suggest that the orientational melting transition in the tube lattice should be accompanied by a significant, possibly discontinuous increase of the equilibrium intertube spacing a_e. The intertube coupling introduces an additional band dispersion of $\lesssim$0.2 eV and opens up a pseudo-gap of the same magnitude at E_F. The pseudo-gap is expected to be significantly reduced in a lattice showing strong orientational disorder, marking the onset of metallic behavior.

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