

Are Fullerene Tubules Metallic?

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We have calculated the electronic structure of a fullerene tubule using a first-principles, self-consistent, all-electron Gaussian-orbital based local-density-functional approach. Extending these results to a model containing an electron-lattice interaction, we estimate that the mean-field transition temperature from a Peierls-distorted regime to a high-temperature metallic regime should be well below room temperature. Such fullerene tubules should have the advantages (compared to other conjugated carbon systems) of a carrier density similar to that of metals and zero band gap at room temperature.

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New synthetic techniques have yielded macroscopic amounts of a series of the all-carbon fullerenes C_{60} and C_{70} [1]. Recently, elongated ellipsoidal structures have been observed in transmission electron microscopy images of fullerene materials [2], which were interpreted as larger all-carbon fullerene cages containing roughly 130 carbons. Other workers have also considered the possibility of obtaining fullerene tubules [3,4], while work on carbon fibers has demonstrated that tubular graphitic filaments can be synthesized with filament diameters as small as 10 nm [5]. We have examined a hollow fullerene tubule using a first-principles local-density-functional (LDF) band-structure approach [6], and show herein that these structures, if synthesized, should have a carrier density comparable to a good metal without doping.

The base fullerene C_{60} has a soccer-ball structure (a truncated icosahedron) formed from twelve pentagons and twenty hexagons [7-10]. Experimental evidence [8,11] implies that the larger fullerene, C_{70} , has a D_{5h} structure that can be constructed by orienting the C_{60} along one of its C_5 axes, and then inserting five new hexagons by equatorially adding a planar ring of ten carbon atoms. As discussed by several workers [3,4], an extended structure can be formed by continuing to add such rings, each one rotated one-half full turn from the last. We depict a section of such an extended structure in Fig. 1. The transverse dimensions of this tubule are consistent with the observed ellipsoidal structures [2] having a cross-section diameter of ~ 0.7 nm, roughly that of the diameter of C_{60} .

We have calculated the electronic structure of an infinitely long tubule using a first-principles, all-electron, self-consistent method originally developed to treat chain polymers [12] and recently adapted for helical symmetry [6]. This method calculates the total energy and the electronic structure using local Gaussian-type orbitals within a one-dimensional band-structure approach. The structure considered herein was generated by a planar ring of ten carbon atoms with D_{5h} symmetry arranged in five pairs; the distance between interior members of adjacent pairs was fixed at twice the nearest-neighbor separation

typical of fullerenes and other graphitic systems of 0.142 nm. The tubule structure was generated with a screw operation having a twist of π rad and a translational shift of 0.123 nm chosen to yield nearest-neighbor separations between rings equal to the in-ring values. The one-electron states are Bloch functions generated by repeated application of the screw operation, and belong to irreducible representations of the screw symmetry group with a dimensionless analog of the wave vector k . In the calculations we used twenty evenly spaced points in the one-dimensional Brillouin zone ($-\pi < k \leq \pi$) and a carbon $7s3p$ Gaussian basis set.

We depict our calculated valence band structure in Fig. 2. All of the operations of the C_{5v} point group commute with the screw-symmetry space group. We thus label all bands according to the four irreducible representations of the C_{5v} group: the rotationally invariant a_1 and a_2 representations, and the doubly degenerate e_1 and e_2 representations. For this lattice structure we find the tubule is a metal, with the a_1 bands and a_2 bands crossing at a posi-

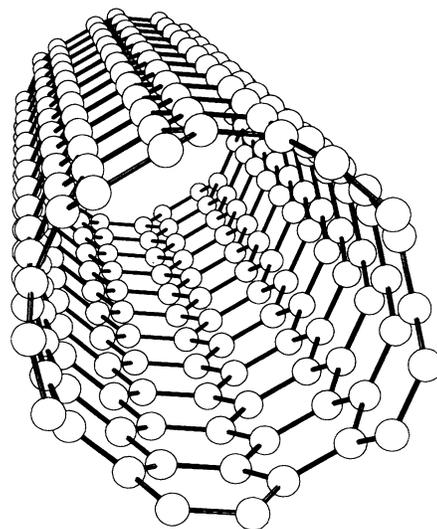


FIG. 1. Depiction of fullerene tubule constructed from C_{10} rings with D_{5h} symmetry.

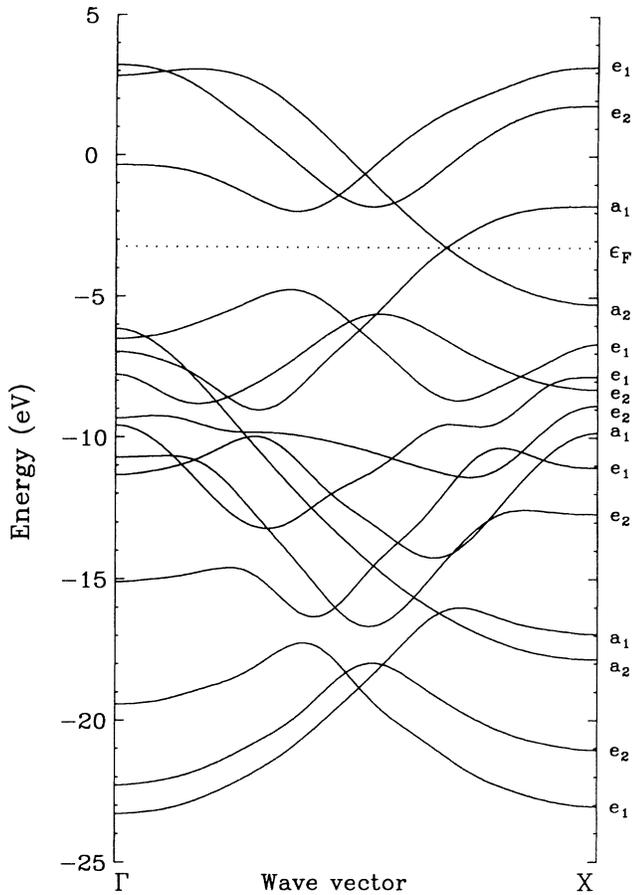


FIG. 2. Local-density-functional valence band structure of a fullerene tubule. The Fermi level ϵ_F is depicted with the dotted line. Γ and X correspond to dimensionless "wave vector" coordinate k of 0 and π , respectively.

tion in the Brillouin zone roughly 0.69 of the width of the half Brillouin zone from the origin. The Fermi level ϵ_F coincides with this crossing. These states are analogous to those we would obtain for a single sheet of graphite—generated by unrolling the tubule and repeating to generate a two-dimensional periodic structure—if we impose Born-von Karmann boundary conditions over a width equivalent to the circumference around the tubule for a single axis direction in the graphitic system. Continuing this analogy, we find that the a_1 and a_2 states in the vicinity of ϵ_F are predominantly p -orbital states aligned with the local normal of the tubule surface, similar to the π -like states in graphite. We obtain four states at the Fermi level (a_1 and a_2 states at k_F and $-k_F$), which are related to the four inequivalent (by translational symmetry) states at ϵ_F found in two-dimensional graphite.

We find, in fact, that the a_1 and a_2 bands near ϵ_F can be well reproduced by a tight-binding model using only states constructed from the set of p orbitals aligned normal to the tubule surface. The a_1 and a_2 states associated with each ring l (denoted herein as $|a_1^l\rangle$ and $|a_2^l\rangle$, re-

spectively) are then constructed from the rotationally invariant (under the C_5 rotations) combinations of symmetric and antisymmetric sums of p orbitals for each of the five pairs of nearest neighbors in the ten-carbon ring. Given a constant matrix element V_0 between all nearest-neighbor carbon pairs both within and between rings, the Hamiltonians for the a_1 and a_2 bands can then be written (within a constant carbon on-site term) as H_0^+ and H_0^- , respectively:

$$H_0^\pm = \pm V_0 \sum_{l,\sigma} [n_{l\sigma} + (c_{(l+1)\sigma}^\dagger c_{l\sigma} + \text{H.c.})], \quad (1)$$

where for H_0^+ (H_0^-) $c_{l\sigma}^\dagger$ creates an electron of spin σ in the state $|a_1^l\rangle$ ($|a_2^l\rangle$), and $n_{l\sigma}$ is the corresponding number operator. The band energies are then given by $\epsilon(k) = \pm V_0(1 + 2\cos k)$. This model predicts a bandwidth in each band of $4|V_0|$, total bandwidth of $6|V_0|$, separation of bands at the Brillouin zone edge of $2|V_0|$, and crossing of the bands at $k = 2\pi/3$. The Fermi level is pinned to the crossing of the a_1 and a_2 bands, with more complex treatments (such as the LDF calculation) shifting the crossing slightly from $k = 2\pi/3$ in the Brillouin zone. Similar results can be obtained for analogous larger structures, which for a structure constructed from rings with M carbon pairs (i.e., $2M$ carbon atoms per ring) can be generated with a helical twist angle of π/M radians. All such structures will have bands crossing the Fermi level equivalent to the a_1 and a_2 bands, leading to four states at the Fermi level. Because these bands are of different point-group symmetries, deformations which do not break the symmetry of the lattice will not open a gap at the Fermi level unless they are severe enough to shift the relative positions of the bands by several eV's. Using the LDF bandwidth for the a_1 band at ϵ_F of 9.6 eV (taking into account the avoided crossing) we estimate an effective hopping matrix element of $|V_0| \sim 2.4$ eV. This value is slightly less than the corresponding hopping matrix elements found in polyacetylene systems of 2.5–3.0 eV, which is explained by the tubule curvature. We find that all of the predictions of this tight-binding model are in good agreement with our first-principles results, noting that the a_2 bandwidth in Fig. 2 is slightly lessened by another avoided crossing with an a_2 at higher energies that is not included in the figure. In particular, we note that ϵ_F —pinned at the crossing of the a_1 and a_2 bands—crosses these bands almost exactly at the value of $k = 2\pi/3$ predicted by the tight-binding model.

Peierls [13] pointed out long ago that any one-dimensional metal should break the initial translational symmetry (his argument applies equally well to the screw-symmetry group) to produce a gap at ϵ_F . The Fermi-level crossing at $k = 2\pi/3$ indicates that the symmetry breaking will be one that changes the repeat unit from a single ten-carbon ring to a three-ring unit. A conventional Kekulé structure that breaks symmetry in this way can be constructed from three ten-carbon rings in each periodic unit cell: one ring with double bonds (a

double-bond ring) between nearest-neighbor carbon pairs, and two rings having singly bonded carbon pairs (single-bond rings). The rings are then interconnected by single bonds between single- and double-bond rings, and with double bonds between adjacent single-bond rings. This distortion not only opens a gap at ε_F but also satisfies the local valence requirements of carbon—two single bonds and one double bond attached to each carbon site in the tubule. At some temperature, however, thermal effects will be sufficient to diminish this bond distortion and hence eliminate the gap at ε_F . We can estimate these

effects using mean-field techniques [14–17] for a Fröhlich Hamiltonian analogous to the Su-Schrieffer-Heeger (SSH) model for polyacetylene [18].

As is usual for conjugated systems, we assume that the change in bond length, δd , resulting from the formation of double and single bonds leaves the average of a single- and double-bond hopping matrix element V_0 unchanged. To first order in δd , the nearest-neighbor matrix elements are then $V = V_0 \pm t$ (where $t = -a|\delta d|$, with a the electron-lattice coupling constant), so that the distortion leads to a perturbation of H_0^\pm for the a_1 and a_2 bands given by

$$H_{\text{pert}}^\pm = \pm t \sum_{l,\sigma} \left[n_{(3l+1)\sigma} + n_{(3l+2)\sigma} - n_{(3l+3)\sigma} + \sum_{m=0}^2 [(-1)^m c_{(3l+m)\sigma}^\dagger c_{(3l+m+1)\sigma} + \text{H.c.}] \right] \quad (2)$$

with the same notation as in Eq. (1). The perturbation in Eq. (2) opens a gap of $4t$ at ε_F in the tight-binding model for both bands. Thus if t were comparable to the value estimated for polyacetylene, then this gap would be roughly 1–2 eV and the tubule would be a semiconductor. However, the electron density of states per carbon at ε_F driving this distortion is roughly one-fifth that of polyacetylene, while the elastic energy per carbon resisting the distortion is a factor of 1.5 times larger in the tubule. These differences lead us to expect that the tubule is not a semiconductor at room temperature, but rather has a carrier density comparable to that of a good metal.

More explicitly, the electronic contribution per ten-carbon ring to the free energy can be written (within an unimportant constant for our tight-binding model) as

$$F_{\text{el}} = - (2/\pi\beta) \int_0^\pi \ln[1 + \cosh\beta\varepsilon(k)] dk,$$

where $\beta = 1/k_B T$ and $\varepsilon(k)$ is the band energy of either the a_1 or a_2 band. To obtain F_{el} we have used the particle-hole symmetry of the two-band system, which remains conserved in the presence of the distortion, to fix the chemical potential at ε_F , chosen to equal zero in the tight-binding model. We have also used the fact that the perturbation conserves the C_{5v} point-group symmetry, and thus introduces intraband but not interband coupling. Using perturbation theory we can then show to first order in $k - k_F$ that $\varepsilon(k)$ entering F_{el} can be replaced by $\varepsilon(k) = \varepsilon_k = - [3V_0^2(k - 2\pi/3)^2 + 4t^2]^{1/2}$. Because we seek an upper bound on t we approximate $\varepsilon(k)$ over the half zone with this expression, which is accurate in the neighborhood of ε_F and produces an enhanced energy lowering for the distortion compared to that predicted using the exact dispersion relation. Next we add to F_{el} (which favors the distortion) a lattice contribution per ring (which resists the distortion) of $15Kt^2/2a^2$, where K is an effective spring constant for distorting one carbon-carbon bond. This lattice contribution is analogous to a corresponding term in the traditional SSH model for polyacetylene [18]. Finally, minimizing the resulting total expression with respect to t , we obtain a self-consistent

gap equation of the usual form:

$$\frac{8a^2}{15\pi K} \int_0^\pi \frac{\tanh(\beta\varepsilon_k/2)}{\varepsilon_k} dk = 1. \quad (3)$$

Solving Eq. (3) for t in the limit $\beta \rightarrow \infty$ yields a mean-field gap at zero temperature,

$$E_g = 4t = \frac{8\pi|V_0|}{\sqrt{6}} \exp\left(\frac{-R|V_0|K}{a^2}\right), \quad (4)$$

with $R = 15\pi\sqrt{3}/16 \approx 5$, while solving this equation in the limit $t \rightarrow 0$ yields a mean-field transition temperature from a distorted insulator to a metallic state given by $k_B T_c = (e^\gamma/2\pi)E_g$, where γ is Euler's constant. This result for T_c represents an upper-bound estimate for the thermal stability of the Peierls-distorted state, not only because of our earlier approximations, but also because of the neglect within the mean-field approximation of fluctuations which will smear out any true phase transition in one dimension.

For *trans*-polyacetylene, we note that the SSH model [18] predicts $E_g = (16|V_0|/e) \exp(-\pi|V_0|K/4a^2)$, using the above parameters. As we noted above, we find V_0 for the tubule slightly smaller than typically used for polyacetylene, but of the same magnitude. Reasonable values of the parameters for polyacetylene yield $E_g \approx 1.5$ – 2.0 eV, with a resulting mean-field transition temperature [also given by $k_B T_c = (e^\gamma/2\pi)E_g$] to a metallic state well above both room temperature and the decomposition temperature for the material. For the fullerene tubule, however, we find that for a comparable ratio $|V_0|K/a^2$ the much larger effective exponent factor $R \approx 5 \gg \pi/4$ leads to a mean-field transition temperature orders of magnitude below room temperature, with estimates based on the above model being less than 1 K. Because T_c overestimates the thermal stability of the Peierls distortion, this material should not require doping to enhance conductivity at room temperature as in the polyacetylene systems.

For graphite, the reason for low conductivity is the low

carrier density, of the order of 10^{18} cm^{-3} compared to typical metallic carrier densities of $\sim 10^{22} \text{ cm}^{-3}$. From the tight-binding model, we calculate a carrier density for an array of parallel-packed tubules of $n_e \approx 8\sqrt{3}m|V_0|a/\hbar^2\Omega$, where a is the translation distance for each screw operation and Ω is the cross section for each tubule. Assuming a cross-sectional area of 1 nm^2 , we estimate the carrier density at $\sim 10^{22}\text{--}10^{23} \text{ cm}^{-3}$. As we expect the carrier mobility along the tubule axis to be comparable to the high mobilities found in graphitic systems, we consequently expect a conductivity along the tubule axis comparable to good metals. Analogous larger-radius tubules would also have a room-temperature metallic regime, although with decreasing carrier densities resulting from larger effective values of Ω .

These fullerene tubules as well as other analogous structures of different diameter represent a conjugated carbon network intermediate between the more well-known polyacetylene and the graphitic systems, but with a high conductivity as a result of the small diameter. We have calculated its electronic structure using an all-electron Gaussian-orbital based local-density-functional approach. Using a Fröhlich Hamiltonian for the electron-lattice interaction, we estimate that the mean-field transition temperature from a Peierls-distorted regime to a high-temperature metallic regime should be well below room temperature, in contrast to the room-temperature Peierls-distorted regime for polyacetylene. Compared to other conjugated systems, the fullerene tubules considered herein would appear to have the advantages of a carrier density similar to metals (as opposed to graphite) and a simple metallic phase (i.e., zero band gap) at room temperature (as opposed to polyacetylene), with a concomitant relatively high conductivity.

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