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Band gaps of primary metallic carbon nanotubes

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Primary metallic or small-gap semiconducting nanotubes are tubes with band gaps that arise solely from breaking the bond symmetry due to curvature. We derive an analytic expression for these gaps by considering how a general symmetry breaking opens a gap in nanotubes with a well-defined chiral wrapping vector. This approach provides a straightforward way to include all types of symmetry-breaking effects, resulting in a simple unified gap equation as a function of chirality and deformations.

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Recently, individual single-wall nanotubes (SWNT's) exhibiting small band gaps of the order of 10 meV were observed for the first time.[1] SWNT's can be classified according to their electronic band gap into three groups: semiconductors, small-gap semiconductors, and real metals. A semiconducting gap arises when the graphite Fermi points are not allowed in the tube's Brillouin zone, which is given by distinct quantization lines according to the tube's circumferential boundary conditions. Such a gap is of the order of 1 eV and was predicted to scale with $1/R$, where R is the tube's radius,[2–4] a prediction that was later verified experimentally by a scanning tunneling microscopy measurement of the density of states.[5–7] The graphite Fermi points lie on a quantization line if $\mathrm{mod}((n-m)/3)=0$,[2,8–10] where n and m are the two integers defining the tube's chiral vector. Tubes that satisfy this condition are called primary metallic. In a real nanotube, however, effects of curvature and deformation break the nearest-neighbor bond symmetry, resulting in a shift of the two distinct Fermi points of graphite that lie at the corners of the hexagonal first Brillouin zone where the bonding and antibonding bands are degenerate (K points). This shift may open a gap depending on the position of the new K points relative to the circumferential quantization line. These gaps are about the value of room temperature and thus coined small-gap semiconductors.

Much interest has been devoted to the study of these small-gap semiconducting tubes, which has led to a good basic understanding. From numerical calculations,[11] it has already been known for a while that only armchair tubes retain zero gap and therefore are truly metallic, while chiral tubes open small gaps because of the intrinsic curvature. These gaps depend on the radius and the chiral angle and were found to be lower than room temperature for tubes with radius exceeding 6 Å . Other numerical studies also examined the effect of structural deformation such as stress[12,13] and twist[13,14] on the electronic band gap of nanotubes, where it was found that the armchair tubes open a gap under twist but are not affected by the uniaxial stress while an opposite response arises in zigzag tubes. Analytic progress was made by Kane *et al.*,[15] where the effects of deformations were modeled as a perturbing vector potential in an effective-mass Hamiltonian. Those calculations were able to verify the numerical findings for the gaps from the intrinsic curvature as well as twists. After the completion of this work, we also became aware of a more recent analytic work by Yang *et al.*[16] where both twist and stress on the nanotubes were considered (but not the intrinsic curvature).

From previous works,[11–16] the gaps can in principle be calculated for almost any shape of nanotube either by using a numerical method or by determining the exact metric and curvature tensors. We now reconsider the effects of deformations on primary metallic nanotubes and formulate the problem in terms of a general symmetry breaking in the tight binding model. This gives a straightforward analysis of the effect, which results in a surprisingly simple and useful formula for the gap. Our compact expression combines the effects from intrinsic curvature, twist, and stress and is only a function of the chiral wrapping vector (n,m) of the tube. This gives a quick and easy way to determine the gap and allows for a good insight into the physical effects, as we will describe below. Our results are a direct consequence of *any* symmetry-breaking effect in the tight-binding model of the graphite sheet in carbon nanotubes.

Our starting point is the observation that the energy separation between the bonding and antibonding bands according to the graphite tight-binding scheme is $2\gamma\Sigma_{i=1}^{3}e^{i\vec{k}\cdot\vec{R}_i}$, where $\vec{R}_i$ are the nearest-neighbor bond vectors and γ is the transfer integral, which is the nearest-neighbor Hamiltonian matrix element.[17] Since at zero temperature the bonding band is occupied and the antibonding empty, the Fermi points $\vec{K}_F$ lie at the band crossings, which are, for the unperturbed graphite, the six corners of the hexagonal first Brillouin zone. If we now break the symmetry of graphite and allow different transfer integrals γ_i depending on the direction of the bonds $\vec{R}_i$, we arrive at a more general equation for the k vectors at which the bands cross,[18]

$$\sum_{i=1}^{3}\gamma_i e^{i\vec{k}\cdot\vec{R}_i}=0, \tag{1}$$

which defines the points of zero gap in k space $\vec{K}'_F$. For small changes $\gamma_i=\gamma+\delta\gamma_i$ we expect small shifts in the band crossing location $\vec{K}'_F=\vec{K}_F+\Delta\vec{k}$. Since we are dealing with primary metallic tubes, we know that $\Sigma_{i=1}^{3}e^{i\vec{K}_F\cdot\vec{R}_i}=0$, where $\vec{K}_F$ are the unperturbed Fermi points. Working in the nanotube coordinates $(\hat{c},\hat{t})$ adopted from Ref. 13, where $\hat{c}$ is the circumferential direction and $\hat{t}$ stands for the translational direction along the axis, the bond vectors are

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$$\vec{R}_1=\frac{a}{2c_h}\left((n+m)\hat{c}-\frac{1}{\sqrt{3}}(n-m)\hat{t}\right),$$

$$\vec{R}_2=\frac{a}{2c_h}\left(-m\hat{c}+\frac{1}{\sqrt{3}}(2n+m)\hat{t}\right), \tag{2}$$

$$\vec{R}_3=\frac{a}{2c_h}\left(-n\hat{c}-\frac{1}{\sqrt{3}}(n+2m)\hat{t}\right),$$

where $a\approx 2.49$ Å is the length of the honeycomb unit vector and $c_h=\sqrt{n^2+nm+m^2}$ is the circumference in units of a. Both inequivalent Fermi points in graphite give the same result when estimating the gap so it is sufficient to consider just one of them. For an unperturbed Fermi point, we write

$$\vec{K}_F=\frac{2\pi}{3ac_h}[(m+2n)\hat{k}_c+m\sqrt{3}\hat{k}_t], \tag{3}$$

where $\hat{k}_c$ and $\hat{k}_t$ correspond to the k vectors along the circumferential and translational directions, respectively.

In order to get the gap, we now need to know the distance between the new Fermi point to the nearest quantization line at the quantized circumferential k_c values. Since the quantization lines are parallel to $\hat{k}_t$, this distance is given by Δk_c, the shift along the circumferential direction $\hat{k}_c$. Expanding Eq. (1) to linear order in the perturbations $\delta\gamma_i\equiv\gamma_i-\gamma$, we find

$$\Delta k_c=\frac{1}{ac_h\gamma\sqrt{3}}[\delta\gamma_1(m-n)+\delta\gamma_2(2n+m)-\delta\gamma_3(n+2m)]. \tag{4}$$

The gap is then obtained by exploiting the fact that close to the Fermi point, the dispersion relation is linear and isotropic,[17]

$$E_g=\sqrt{3}a\gamma|\Delta k_c|. \tag{5}$$

We now want to determine the changes to the transfer integrals $\delta\gamma_i$ due to the curvature and deformations. To first order this change is proportional to the change of the bond length between two neighboring carbon atoms, but may also be created by a misalignment of two neighboring π orbitals. In general, we find that we can always express the change of the nearest-neighbor transfer integrals in terms of a bond deviation matrix **D**,

$$\delta\gamma_i=\vec{R}_i\cdot\mathbf{D}\cdot\vec{R}_i/R_i^2. \tag{6}$$

This deviation matrix is useful for describing the effects of stress, twists, and curvature in a simple unified way as we will see below. All nanotubes have an intrinsic curvature which causes hybridization of the otherwise orthogonal π and σ orbitals. Since the σ bands lie normally far from the Fermi energy, we only consider the curvature effect on the π band, which crosses the Fermi point in primary metallic tubes as long as the tube's radius is $R\gtrsim 2.4$Å .[19]

Following the calculations of Slater and Koster,[20] we can assume that the transfer integrals are proportional to the cosine of the misalignment angle ϕ between two neighboring π orbitals. (A calculation that takes into account the full rehybridization of all orbitals will be considered in a future study.) Using $\cos\phi\approx 1-\frac{1}{8}[(a_{c-c})/\mathrm{R}]^2$, we can immediately express the deformation tensor for the intrinsic curvature in the basis of $\hat{c}$ and $\hat{t}$,

$$\mathbf{D}^{\mathrm{curv}}=\begin{bmatrix}\frac{\gamma}{8}\left(\frac{a_{c\text{-}c}}{R}\right)^2 & 0\\ 0 & 0\end{bmatrix}, \tag{7}$$

where $a_{c\text{-}c}=a/\sqrt{3}$ is the carbon-carbon bond length and $R=ac_h/2\pi$ is the tube's radius. From Eqs. (4)–(7), we find

$$E_g=\frac{\gamma\pi^2}{8c_h^5}(n-m)(2n^2+5nm+2m^2). \tag{8}$$

This formula agrees remarkably well with previous numerical studies[11] if we choose $\gamma=2.5$ eV and also agrees with the results of Ref. 15. Equation (8) gives the energy gap of all primary metallic nanotubes without any applied deformations. One observes that the armchair nanotubes $m=n$ are the only real metallic tubes, while the primary metallic zigzag tubes $(m=0)$, open the highest gaps.

Next we want to examine the effect of a general two-dimensional structural deformation such as twists and stress on the gap in the primary metallic tubes. Our deformation can be written as $\vec{R}\rightarrow(\mathbf{I}+\mathbf{S})\vec{R}$, where $\vec{R}$ is any vector on the tube's surface, **I** is the identity matrix, and **S** is the deformation matrix,

$$\mathbf{S}\equiv\begin{bmatrix}\epsilon_c & \xi\\ 0 & \epsilon_t\end{bmatrix}. \tag{9}$$

Here ϵ_c and ϵ_t are uniaxial stresses along the circumferential and the translational directions and ξ is the strain (nanotube twist). The bond deviation matrix is then given by $\mathbf{D}^{\mathrm{deform}}=|\vec{R}|\,b\,\mathbf{S}$, where $b\simeq 3.5$ eV/Å is the linear change in the transfer integral with a change in the bond length $\gamma_i\rightarrow\gamma_i+b\,|\Delta\vec{R}_i|$ and $|\vec{R}|=a/\sqrt{3}$ is the bond length. We now use $\mathbf{D}^{\mathrm{deform}}$ to obtain the $\delta\gamma_i$ of Eq. (6), and as we did with the curvature, inserting in Eq. (4) and using the dispersion relation, we find

$$E_g=\frac{ab}{4c_h^3}|\sqrt{3}(n-m)(2n^2+5nm+2m^2)(\epsilon_c-\epsilon_t) -9nm(n+m)\xi|. \tag{10}$$

This equation is the response to a two-dimensional linear deformation within the graphite sheet. We notice from Eq. (10) that in the presence of equal uniaxial stresses in both directions $\hat{c}$ and $\hat{t}$, a gap is not opened, as expected since the bonds would maintain their symmetry. The response of armchair and zigzag tubes is complimentary as noticed previously in the numerical studies,[13] i.e., zigzag tubes have the maximum sensitivity for a uniaxial deformation (ϵ_c or ϵ_t) but are insensitive to twists ξ, while the opposite is true for

armchairs, reaffirming that a twist deformation is the only possible source for an energy gap in the armchair tube.

A uniaxial stress ϵ_c around the circumference corresponds to a global change of radius. This effect can come about as a time-dependent deformation due to lattice vibrations in the breathing mode. Realistic static deformations, on the other hand, correspond to the intrinsic curvature, a stress along the tube ϵ_t, and a twist ξ. Therefore, the total gap from static deformations is given by combining Eq. (8) and Eq. (10) with $\epsilon_c = 0$. The total band equation now reads

$$E_g = \left| \left(\frac{\gamma \pi^2}{8 c_h^5} - \frac{ab\sqrt{3}}{4 c_h^3} \epsilon_t \right) (n-m)(2n^2+5nm+2m^2) - \frac{9ab}{4c_h^3} nm(n+m)\xi \right|, \tag{11}$$

which is the main result of our paper.

In some cases, it may be useful to express this formula in terms of the chiral angle α and the radius R of the tube, which gives

$$E_g = \left| \left(\frac{\gamma a^2}{16 R^2} - \frac{ab\sqrt{3}}{2} \epsilon_t \right) \sin 3\alpha - \frac{ab\sqrt{3}}{2} \xi \cos 3\alpha \right|. \tag{12}$$

In this form our results are then consistent with previous calculations,[15] where twists and the intrinsic curvature (but not stress) have been considered as a function of the chiral angle. After the completion of this work, a paper deriving the change in the band gap due to deformations was published,[16] which is also consistent with the angular dependence of the deformation part of Eq. (12) (i.e., without the intrinsic curvature).

We see that Eq. (12) shows an interesting interplay between curvature and deformation effects as plotted in Fig. 1. A very small twist can actually remove the gap due to the intrinsic curvature. For a given radius, the gapless state is therefore moved towards tubes with higher chirality.

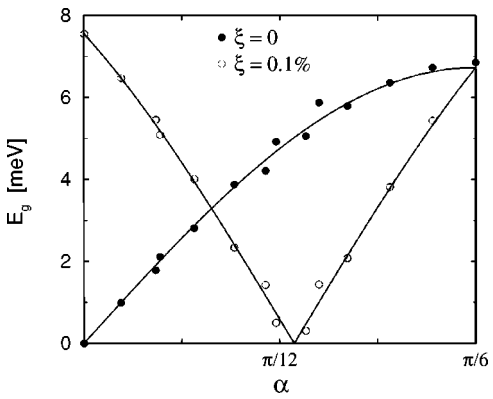

FIG. 1. Energy gaps of primary metallic tubes of radius 12 ±0.5 Å with no twist $\xi = 0$ and a twist $\xi = 0.1\%$ as a unction of chirality. The continuous lines correspond to the average radius (12 Å) while the circles correspond to the actual tubes. A very small twist can thus have a profound effect on the energy gaps.

In summary, we have presented a straightforward procedure to calculate the energy gap induced by a general broken bond symmetry. This leads to a simple analytic expression for the band gaps from both the intrinsic curvature and applied deformations, which provides a quick and reliable way to estimate the physical effects. These gaps have important consequences since they are generally of the same order as room temperature for most primary metallic SWNT's. Only armchair tubes are generically gapless, but a very small twist induces a gap of the order of other small-gap semiconducting nanotubes. Such a small twist, on the other hand, moves the gapless state to tubes with higher chirality.

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[18] In general, we will also consider different bond vectors $\vec{R}_i'$. How-

ever, this simply corresponds to a change of the coordinate system in both real and reciprocal spaces with a conserved dot product $\vec{k}\cdot\vec{R}$. The distance to the quantization lines in Eq. (4) is therefore not affected by different bond vectors, but only by the change in the transfer integrals.

[19] For very small radii ($R \lesssim 2.4$ Å) it was numerically predicted that the σ band is modified to such an extent that it crosses the Fermi point [X. Blase *et al.*, Phys. Rev. Lett. **72**, 1878 (1994)]. However, to the best of our knowledge, the narrowest SWNT ever observed has a diameter of ($R \simeq 3.5$ Å), well above that critical radius.

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