SEMICONDUCTOR-METAL TRANSITIONS IN CARBON NANOTUBES

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Introduction

We first present the π electron density of states (DOS) of two particular, high symmetry types of carbon nanotubes, designated zigzag and armchair tubules. We have used the Green's function method within the framework of a simple, tight-binding scheme based on a 1 dimensional (1D) tubule model. We have computed an analytic expression of the DOS ρ(E) and discuss the main features according to the type of tubule. Next, we particularly treat the effects of compressive and tensile, uniaxial stress on the DOS and the bandgaps. This seems of interest since such effects of stress on the electronic properties of carbon tubules have to date received little attention in spite of references to the predicted interesting mechanical properties.

The density of states

The "graphene model" does not take into account the effect of curvature and predicts that the zigzag tubules for which n is a multiple of 3 are metallic. In fact, the curvature of small diameter tubes transforms the predicted metallic behaviour into that of a small-gap semiconductor due to σ-π hybridisation. In the present case, to introduce the effects of curvature on the electronic properties, we use a simple deformation potential as a perturbation in a tight-binding model near the Fermi level. Using a 1-D Green's function technique, we then computed an analytic expression of ρ(E) for $0 \leq E \leq 10$ eV in the cases of both types of nanotubes studied here. We observe the formation of discrete energy levels E_m corresponding to DOS discontinuities (δ-like variations). Furthermore, we obtain analytical expressions of the DOS ρ(E), which can be expressed in the following form:

$$\rho(E) = \sum_m \frac{|E|}{\sqrt{E^2 - E_m^2}\sqrt{E_m'^2 - E^2}} \quad (1)$$

where E_m-and E'_m are discrete energy values.

Effects of uniaxial stress

We now examine the effects of a uniaxial, homogeneous deformation of the tubules along their axes. We have computed the $\pi-$electron band structure and DOS, under both uniaxial traction ($\sigma \succ 0$) and compression ($\sigma \prec 0$) using a semi-empirical tight-binding approach, adapted to take into account the modifications of both direct and reciprocal lattice structures and two-center integrals with stress. We have used the following graphite values $S_{11} = 0.98\ 10^{-12} Pa^{-1}$ et $S_{12} = -0.16\ 10^{-12} Pa^{-1}$.

We find that the discrete DOS energy levels and the gaps for zigzag tubules are very deformation sensitive. For uniaxial strain, ρ(E) is analytically expressed in the case of (n,0) tubule by :

$$\rho(E,\sigma) = \frac{1}{2\pi\sqrt{3}} \frac{(1+S_{12}\sigma)}{(1+S_{11}\sigma)} A \qquad (2)$$

$$A = \sum_{(m)} \frac{|E| \times \theta(|E|, E_m^-) \times \theta_{inv}(|E|, E_m^+)}{\sqrt{E^2 - (E_m^-)^2}\sqrt{(E_m^+)^2 - E^2}} \qquad (3)$$

where the discrete energy levels E_m, displaced by the deformation, are given by :

$$E_m^{\pm}(\sigma) = t_3 \left| \left[1 \pm 2 \left(\frac{t_{12} + V_{12}}{t_3} \right) \cos \frac{m\pi}{N} \right]_c \right| \qquad (4)$$

$\theta(|E|, E_m^-)$ and $\theta_{inv}(|E|, E_m^+)$ are respectively Heaviside and inverse Heaviside functions defined by $\theta(|E|, E_m^-) = 1$ if $|E| > E_m^-$ and 0 elsewhere; and $\theta_{inv}(|E|, E_m^+) = 1$ if $|E| < E_m^+$ and 0 elsewhere. We obtain similar expressions for $\rho(E)$ and E_m in the case of armchair (n,n) tubules. These results are of less importance since these tubules remain metallic under all strains studied here.

Let us examine the (n,0) zigzag tubules. It is always possible to define the zigzag tubules in one of the following forms: (3q,0), (3q+1,0) or (3q-1,0) where q is an integer. The electronic band gap is obtained by putting $m = q$ in the formula (??).

In the case of the (3q+1,0) nanotubes the gap increases under traction whereas in the case (3q-1,0) it decreases. These different kinds of behaviour can be understood in the 2D representation by examining the effects of stress on the allowed lines in the Brillouin zones. In the (3q+1,0) case, the corner nearest allowed line moves away from the K point whereas for the (3q-1,0) case it becomes closer.Furthermore, we observe that compression should lead to a semiconductor to metal transition in the case of (3q,0) and (3q+1,0) and the same kind of transition is obtained with traction in the case of (3q-1,0) tubules, at a diameter dependent stress σ_t(d).

In summary, we have shown that a uniaxial stress applied parallel to the axis of carbon nanotubes can significantly modify the band gap and induce a semiconductor-metal transition.

References

see R. Heyd, A. Charlier, E. Mc Rae. Phys Rev B, in press ,1997, Vol 55, March .