Intra-atomic correlation effects and the electronic and magnetic properties in nanotubes

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The Gutzwiller method has been applied to investigate the intra-atomic correlation in the π-band of tubule $B(0,1)n$ versus the number of hexagons on the circumference n. The consequences of the correlation on the electronic (gap) and magnetic (susceptibility) properties have been examined. The critical on-site correlation term U to obtain ferromagnetism or antiferromagnetism has been derived with respect to n. The transition from a paramagnetic to a diamagnetic magnetization obtained by Davids, Wang, Saxena, and Bishop has been studied within the present framework. [S0163-1829(97)09535-0]

Recent synthetic techniques have provided an intensive interest on the physico-chemistry of carbon, particularly C_{60} owing to the superconductivity properties exhibited by C_{60} doped with K and Rb, multishell fullerene, and single (multi) shell nanotubules discovered by Ijima. Tubules have been highly observed with high-resolution electronic microscopy techniques.[1] They have been mostly characterized with electron-energy-loss spectroscopy providing some insights on the π and σ plasmon.[2] Up to now the main experimental difficulty to derive physical data from experiment is due to the random distribution of tubules. However, recently de Heer *et al.* have reported the production of aligned nanotubule films, in which the tubule diameter is 10 ± 5 nm (corresponding to 10–20 concentric cylindrical graphitic sheets) and lengths on the order of 1 μm.[3] They manage to measure angle-dependent conduction-electron spin-resonance and static magnetic susceptibility, so above 40 K, the nanotubule behaves with Pauli susceptibility of 10^{18} spins/cm^3 consistent with a semimetal. Below 40 K, the resistivity, the spin susceptibility and the g factor and their anisotropies can be interpreted like the evidence of charge-carrier localization.[4]

Firstly, let us introduce some notations. Single nanotubule $A(n_1,n_2)$ are formed by rolling a graphite sheet such that the point of coordinates (n_1,n_2) is superposed to the origin. Such tubules display helicity but also chirality for given (n_1,n_2), two ways of rolling are possible leading to two mirror symmetric tubules. In the case with no chirality let us introduce the notation $B(l_1,l_2)n$ instead of $A(n_1,n_2)$ where $n_1=l_1n$, $n_2=l_2n$ and n represents the number of hexagons on the circumference. The first theoretical answer to the electronic character of tubule was reported by Mintmire Dunlop, and White:[5] using a local-density-functional approach and extending these results to a model containing an electron-lattice interaction, they felt that a transition from Peierls-distorted regime to a high-temperature metallic regime could occur below room temperature. Moreover, from a tight-binding band-structure calculation of which the total-energy minimization of the carbon-atom system is described by the Tersoff interaction potential, Hamada, Sawada and Oskigama[6] have predicted an electronic transition in nanotubules from metallic to semiconducting with narrow and moderate band gap highly depending on the diameter of the tubule and on the degree of helical arrangement of the carbon hexagons. However, Blase *et al.*[7] have pointed out using detailed plane-wave *ab initio* pseudopotential local-density calculations the importance of the hybridization of the σ^* and π^* states. As a result their local-density approximation gap compared to their Koster-Slater tight-binding calculation are lowered by more than 50% and even more than one tubule has been found metallic. The variation of the tubule electronic behavior can be understood from a two-dimensional band structure of graphite. Firstly, the main difference between tubule and graphite is that in graphite the wave vector of the Bloch wave function is located in the first Brillouin zone (BZ), as for tubule owing to the finite periodic condition along the circumference the wave vector along the circumference is discretely selected in the BZ.

The aim of the present paper is devoted to the consequences of the intra-atomic correlation on the electronic and magnetic properties. Owing to the difficulty in dealing with correlation both for the σ and π electrons, and noticing that the electronic character and magnetic properties are mainly governed by the π electrons ($sp^2\sigma$ band mixes weakly with p-bonding state) let us investigate only correlation in the π band. Such intra-atomic correlations are classically studied with the Hubbard Hamiltonian H, which has been applied successfully for such studies in fullerene, carbon cluster, and π systems:[8]

$$H=\sum_{k,\sigma}\varepsilon(k)c^{\dagger}_{k\sigma}c_{k\sigma}+U\sum_{i}n_{i\uparrow}n_{i\downarrow} \tag{1}$$

where the first term is the site-to-site hopping contribution and the second the intra-atomic correlation. $c^{\dagger}_{k\sigma}$ ($c_{k\sigma}$) are the creation (annihilation) operators of electon in π band with momentum k and spin σ and $n_{i\sigma}=(c^{\dagger}_{i\sigma}c_{i\sigma})$ is the number operator. The π energy spectra $\varepsilon(k)$ has been derived from a tight-binding calculation involving π and σ electrons described by the following Hamiltonian H^{com}:

$$H^{\mathrm{com}}=\sum_{\substack{i\neq j\\ \gamma,\mu,\sigma}}\beta^{ij}_{\gamma\mu}c^{\dagger}_{\gamma i\sigma}c_{\mu j\sigma}+\sum_{i\gamma\sigma}E_{\gamma}c^{\dagger}_{\gamma i\sigma}c_{\gamma i\sigma}$$
$$+\tfrac{1}{2}\sum_{i\neq j}V(R_i-R_j), \tag{2}$$

where γ,μ label the orbital components of s,p_x,p_y,p_z. The last term describes the core repulsive interaction. The $\beta^{ij}_{\gamma u}$

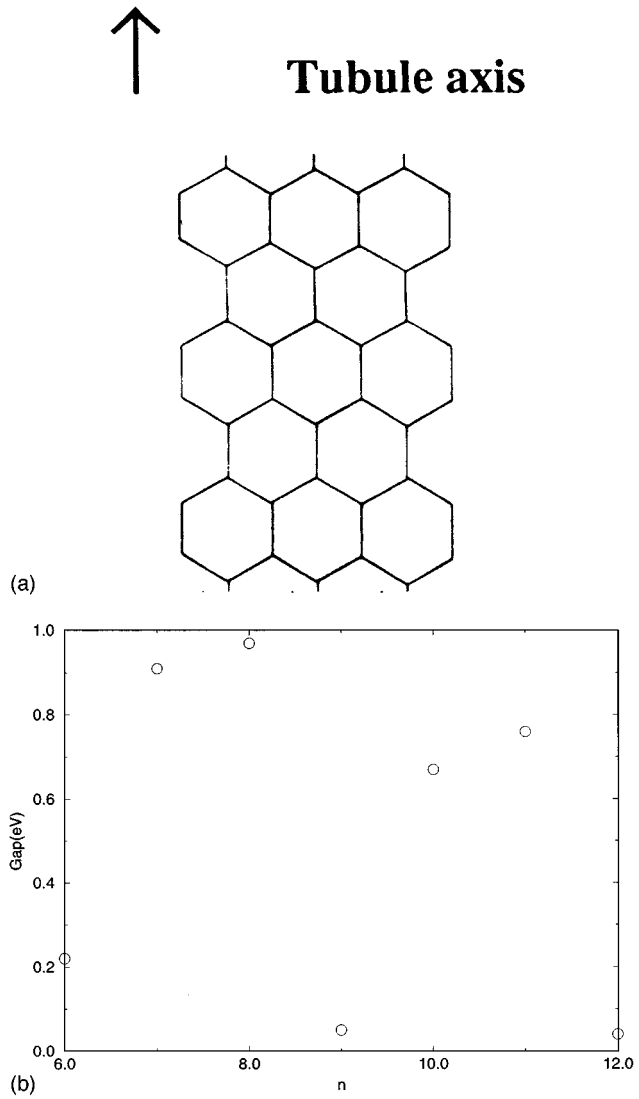

FIG. 1. (a) Geometric configuration for tubule $B(1,0)n$ [the tubule axis is denoted (1,0)]; (b) energy-band gap as a function of the number of hexagons on the circumference for tubules $B(1,0)n$ when the intra-atomic correlations are neglected.

and $V(R)$ are both distance dependent. The atomic relaxation are determined by total-energy minimization given by H^{com} (H^{com} has been previously applied to investigate carbon cluster).[9] Let us illustrate the H^{com} results for the tubules $B(0,1)n$. Figure 1(a) shows the $B(0,1)n$ geometry of the construction unit along the circumference in which a c-c bond is parallel to the tubule axis. The energy-band gap derived from H^{com} (i.e., without intra-atomic correlation) as a function of the number of hexagons on the circumference is displayed in Fig. 1(b). The present results have the same trends as the results of Hamada, Sawada, and Oskigama. In particular, for n multiples of 3 the gap is nearly 0. In the other cases, however, our gap values are smaller; let us say that our following results will quantitatively depend but not qualitatively depend on the electronic structure without correlation.

Let us investigate the effect of the intra-atomic correlation on the band gap. In fullerene and carbon cluster the correlation term U has been assumed equal to 5.5 eV,[8] but in the present work, U will be considered like a parameter. The

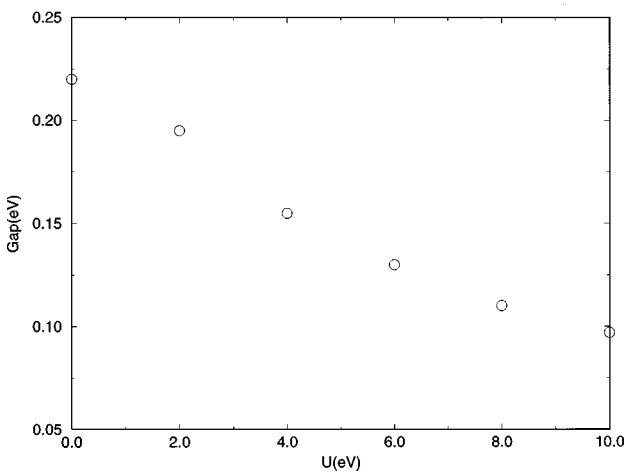

FIG. 2. The energy-band gap of the tubule $B(1,0)$ 6 vs the intra-atomic correlation U.

intra-atomic correlation will be examined in the Gutzwiller framework[10] which is, from the Kotliar and Ruckenstein work,[11] equivalent to the saddle point of the slave boson approach. In the classical Gutzwiller approach in which all the sites are equivalent, a variational N electron function ψ is derived from a Slater determinant $\psi_0 = (1/\sqrt{N!})\det(\psi_1, \ldots, \psi_k)$ built up with the eigenfunctions ψ_k of the unperturbed Hubbard Hamiltonian. ψ is guessed in order to decrease the contribution of the doubly occupied states:

$$|\psi\rangle = \prod_i [1-(1-g)n_{i\uparrow}n_{i\downarrow}]|\psi_o\rangle; \tag{3}$$

here g is a variational parameter that has to be determined so as to minimize the energy.[8]

Let us investigate firstly the case $n=6$, for $U=0$ the gap is small (0.22 eV). Figure 2 plots the evaluation of the gap versus U, the gap is decreasing, for instance if U is equal to 10 eV the gap is quite small $\cong$0.1 eV. Figure 3 displays the trend of the gap versus U for $n=7$, but even for quite larger U the gap remains large. Our results of the gap decreasing with U is in agreement with the result of Horsch, Horsch, and Fulde on diamond.[12] The effect is understood by the fact

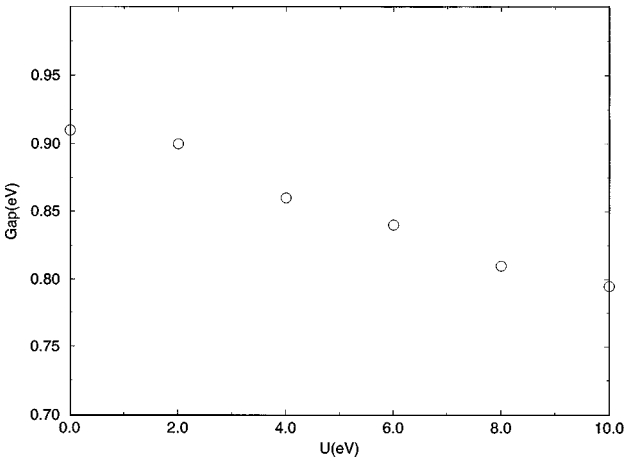

FIG. 3. The energy-band gap of the tubule $B(1,0)$ 7 vs the intra-atomic correlation U.

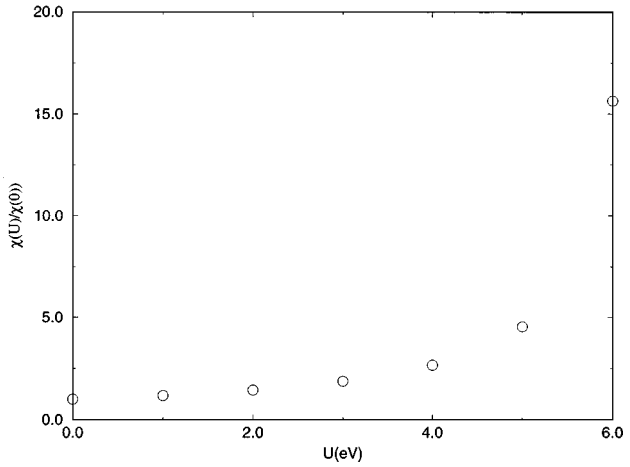

FIG. 4. Evolution of the susceptibility $\chi(U)/\chi/(0)$ vs the intra-atomic correlation U in the tubule $B(1,0)9$.

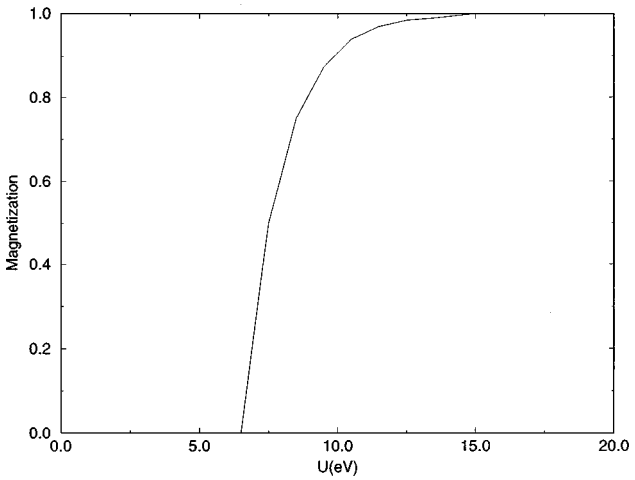

FIG. 5. Magnetization per site vs the intra-atomic correlation U in $B(1,0)6$.

that when an electron is leaving the valence band, the correlations in the valence band are smaller; this effect is not included in the one-electron approximation calculation. The first consequence of our results is that if we assume like Mintmire, Dunlap, and White[5] an electron-lattice interaction, the transition between the metallic and the Peierls distorted regime will be at temperature smaller than the ones deduced by Mintmire, Dunlap, and White.

Previous work has been devoted to the magnetic properties of nanotubes. Tian and Datta[13] have looked at the magnetic susceptibility with a mean-field framework, as for Ajiki and Ando[14,15] they have looked at the effect of magnetic field on band gap.

Finally, let us examine the magnetic properties of tubule. The nonmagnetic and ferromagnetic or partly ferromagnetic can be studied with the previous Gutzwiller method applied with all equivalent site. However, for antiferromagnetic states, it can be investigated with the Gutzwiller approach but the price to pay is to work with the two site Gutzwiller method developed by Takano and Uchinami.[16] The Gutzwiller method has been applied to study the antiferromagnetic spin-wave density as in fullerene,[17] the critical U (6.7 eV) about which the AF SDW are stablized agrees with Hartree-Fock calculations.[18]

Let us study the case where the gap is very small for $U=0$, for instance take $n=9$. The Gutzwiller procedure shows the fully ferromagnetic state is more favorable for $U>7.3$ eV than the nonmagnetic state. The Pauli susceptibility per atom χ at low magnetic field, that is to say, for small magnetization m ($m \ll 1$) where $m=(N\uparrow - N\downarrow)/(N\uparrow + N\downarrow)$ is easily deduced from the variation of the energy $E(m)$ by

$$\chi = \mu^2 \left(\frac{\partial^2 E(m)}{\partial m^2} \right)^{-1}, \tag{4}$$

where μ is the Bohr magneton. χ diverges for $U \cong 7.3$ eV which is the sign of the ferromagnetic transition (Fig. 4).

Let us now investigate the case where the gap is finite for $U=0$. Using the Takano-Gutzwiller method, the case where $n=6$ has been examined, the magnetization per site versus U is plotted in Fig. 5; for $U<6.5$ eV the tubule remains in the diamagnetic state; as for $U>6.5$ eV, antiferromagnetic spin-density wave are stabilized. In both cases, the critical U to obtain magnetic transition is higher than the experimental value. But perhaps one way to investigate the transition will be the use of finite length tubule (in this case the absolute value of the one-electron energy per atom will be smaller than the energy of the infinite tubule and the transition will be occurring with lower U).

Let us finish the paper by examining the effect of the correlation on the magnetic ordering transition described by Davids, Wang, Saxena, and Bishop[19] (DWSB) as the tube radius R is varied. They have shown that as the radius R of a tubule is changed at fixed electron density, a transition is occurring from a paramagnetic ($R<R_c$) to a diamagnetic ($R>R_c$) magnetization for a two dimensional electron-gas model confined on a mesoscopic cylinder but neglecting the Pauli paramagnetization (the critical radius R_c has been estimated to be equal to 6.4 Å). Nevertheless, they have found that the transition nature remains the same if the Pauli paramagnetization is included. In this final part let us investigate if with our model such transition is occurring. Let us consider the tubule in a magnetic field parallel to the tubule axis. Due to the gauge invariance, the hopping term t_{ij} in the Hamiltonian has to be transformed into $t_{ij} \exp i \int A\, dr$. The magnetization including the diamagnetic and the paramagnetic contribution) can be derived straightforwardly from the calculation of the energy of the system versus the flux and U. So for $U=0$, a transition from a diamagnetic to a paramagnetic magnetization is happening for $n=18$. The transition is respectively, for $U=2.2$ and 4.5 eV for $n=24$ and 30. It is due to the fact that the intra-atomic correlation enhances the paramagnetic component and so the transition is displaced to higher n for larger U. By consequence, the phenomena predicted by DWSB is robust versus the intra-atomic correlation.

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