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## Note: The role of Peierls-like distortions in the modification of electronic bandgaps of graphene nanoribbons under uniaxial strain

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Microscopic calculations describing the bandgap variations of armchair graphene nanoribbons (AGNRs) subjected to an applied uniaxial strain ( $\epsilon$ ) have been the focus of numerous recent reports.<sup>1–11</sup> Currently, the strain induced bandgap modulation is an important topic as graphene nanoribbons (GNRs) present great interest for applications. Theoretical insights are very valuable as it is difficult for experiment to measure the response of GNRs to external forces.

The principal goal of this *Note* is to clarify that an emblematic mechanism for one-dimensional metal structures—the spontaneous Peierls distortion of the lattice that converts a metal into a semiconductor<sup>12</sup>—is present in AGNRs at selected strain levels. The effect was reported in density functional theory (DFT) calculations carried out in trans-polyacetylene<sup>13</sup> and carbon nanotubes.<sup>14–16</sup> The possibility of a Peierls distortion mechanism was considered in stress-free GNRs with zigzag edges, but found to be suppressed by the strong edge effect.<sup>17</sup> To our knowledge the effect was overlooked till now in the literature of axially elongated and compressed GNRs, including Refs. 1–11.

Here we present evidence for the Peierls effect in a strained AGNR with H-saturated edges and 11 dimer lines, treated with DFT within the generalized gradient approximation. As in one previous investigation,<sup>2</sup> the Becke exchange gradient correction and the Lee-Yang-Parr correlation gradient correction<sup>18,19</sup> implemented in the DMol package<sup>20</sup> were employed. Our basis set consists of the double numerical atomic orbitals augmented by polarization functions. Self-consistent field procedures were carried out with a convergence criterion of  $1.0 \times 10^{-6}$  a.u. in energy and electron density. The strained AGNR was considered optimized when the convergence criteria of  $1 \times 10^{-5}$  in the gradient,  $1 \times 10^{-4}$  in the displacement, and  $1 \times 10^{-7}$  a.u. in energy were met. Medium grid mesh points were employed for the matrix integration procedures. The real-space global cutoff radius was set at 5.5 Å. Calculations considered explicitly only atoms located in one primitive motif under periodic boundary conditions. In order to achieve good convergence in reciprocal space integration, a set of 123  $K$  points uniformly spaced along the one-dimensional Brillouin zone was used. Note that the  $K = 0$  point is included in this set.

The stress-free 11 AGNR considered here is a semiconductor. Its direct bandgap located at  $K = 0$  is solely due to the edge shrinking effect,<sup>21</sup> since the quantum confinement

effect alone predicts a vanishing bandgap.<sup>10</sup> The linear bandgap variation displayed in Fig. 1(a) resembles well the zigzag behavior reported in Refs. 1–9 and attributed to the coupling of  $\epsilon$  to the valence and conduction bands. However, there is also a difference with the metallic state predicted analytically by simple  $\pi$  orbital tight-binding theory<sup>1</sup> and

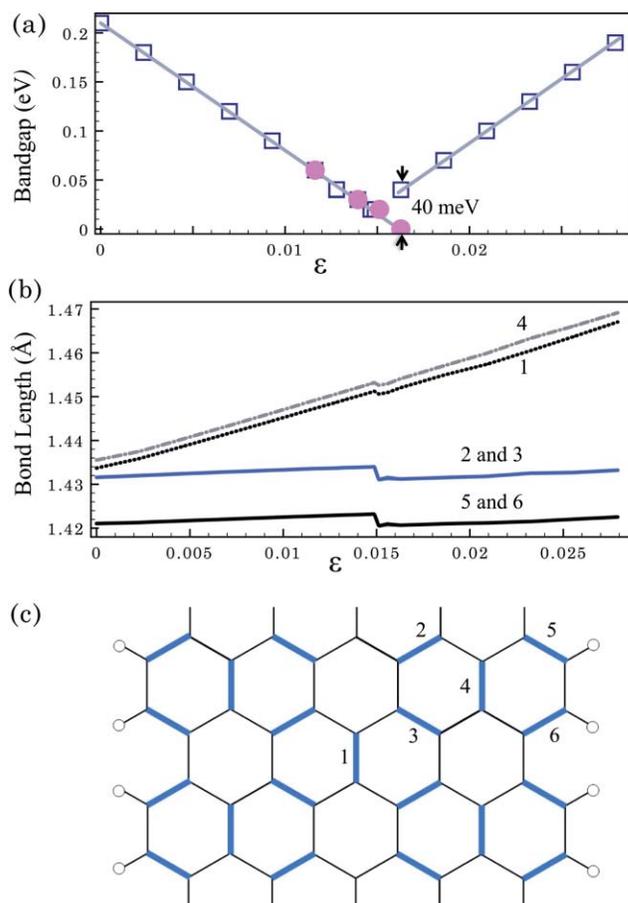


FIG. 1. (a) Bandgap vs. applied  $\epsilon$  in 11 AGNR with H-saturated edges. Empty squares and filled circles represent data from calculations carried out without and with point-symmetry constraints, respectively. (b) Evolution of the selected bond lengths vs.  $\epsilon$ . (c) Schematics of the Kekulé type bond alternation pattern. The thicker (blue) lines identify the bonds that suddenly shrink at  $\epsilon = 0.015$  in (b). The empty circles represent the H atoms. The AGNR long axis is vertical.

obtained by some DFT calculations:<sup>3,9</sup> while the application of  $\varepsilon$  gradually lowers the initial bandgap in a linear manner, we obtain that a metallic state is not really reached. This observation is fully consistent with what was obtained in some other existing DFT investigations.<sup>2,5-8</sup> Unfortunately, the origin of this result has never been addressed.

Here we recognize in our DFT calculations an additional electron-phonon interaction effect emerging in the narrow vicinity of the metallic state. A closer look at Fig. 1(b) reveals that right before the metallic state is expected, the AGNR undergoes a sudden decrease in selected bond lengths. The compressed bonds delineate a clear Kekulé type bond alternation pattern, Fig. 1(c), which is typical for the Peierls effect in a honeycombed lattice.<sup>14,22-24</sup> When the development of this pattern is prevented by using additional point-symmetry constraints, the strain-driven metallic state is still reached at  $\varepsilon = 0.016$ . At this strain level, the bandgap opening due to the Kekulé morphology is of 40 meV. Based on this evidence, we interpret the obtained result as a Peierls effect.

The uncovered electron-phonon interaction effect is the likely mechanism that prevents the onset of the metallic state under  $\varepsilon$  obtained in other DFT calculations employing the same as here<sup>2</sup> and other approximate functionals,<sup>5-8</sup> carried out on slightly wider AGNRs. At the same time, our finding calls for additional first principles studies of strained GNRs that will employ functionals especially constructed for the description of the Peierls distortion.<sup>14</sup> Such calculations could predict more accurately the magnitude of the bandgap opening and thus determine whether the effect is relevant for experiment. Since two dimensional graphene is metallic, qualitatively it can be expected that the Peierls effect is suppressed by an increase in AGNR's width.

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