Structural, electronic and magnetic properties of vacancies in carbon nanotubes

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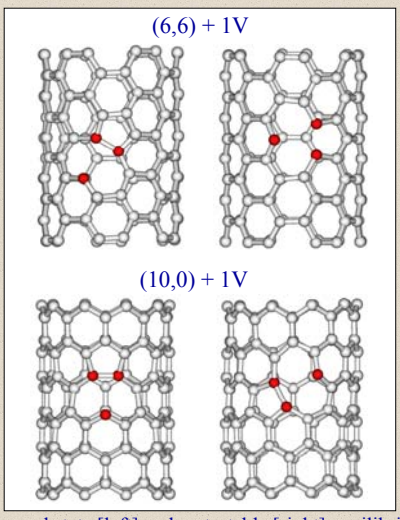
Abstract

The single vacancy and the divacancy in single-walled carbon nanotubes (CNTs) are addressed by first-principles calculations. We study both defects in armchair and zigzag CNTs with 8 and 11 Å in diameter and also considering two defect concentrations along the CNT axis. Our results show that in the equilibrium geometries, both armchair and zigzag CNTs containing a vacancy exhibit ferromagnetism with magnetic moments ranging from 0.3 to 0.8 μ_B, which are due to a twofold coordinated C atom. On the other hand, CNTs with a divacancy do not exhibit magnetism due to a full reconstruction around the defect where all C atoms are threefold coordinated. We observed that the single vacancy does not change drastically the CNT electronic properties, which preserve their corresponding metallic or semiconducting characters. However, for the divacancy both armchair and zigzag CNTs become semiconductors, exhibiting a energy gap of about 0.15 eV. The defect formation energies in the ground state and in metastable geometries are also discussed.

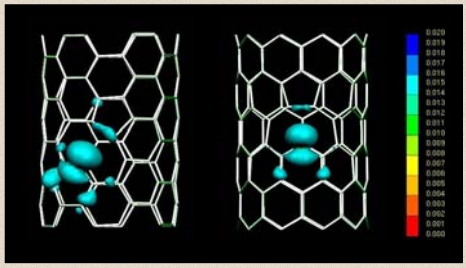
Theoretical approach

- ✓ Spin-polarized density functional calculations (DFT+GGA).
- ✓ Norm-conserving fully-separable pseudopotentials.
- ✓ Basis set of numerical atomic orbitals (DZP, SIESTA code).
- ✓ The CNTs under study are the armchair [(6,6) & (8,8)] and the zigzag [(10,0) & (14,0)] which have 8 and 11 Å in diameters, respectively.
- ✓ Two defect concentrations along the tube axis were simulated by using supercells with lengths of L ≈ 13 and 26 Å.
- ✓ The BZ sampling was performed with 6 k points along the tube axis in the 13 Å supercells and the Γ point for the 26 Å supercells.
- ✓ The systems are fully relaxed until the forces become smaller than 0.05 eV/Å.

The single vacancy in CNTs



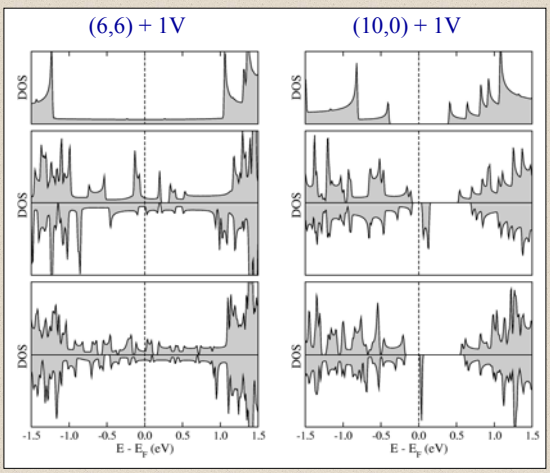
Ground state [left] and metastable [right] equilibrium geometries for the (6,6) and (10,0) CNTs with a vacancy. Red balls are C atoms around the defect



Spin density isosurfaces for the (6,6) [left] and (10,0) [right] CNTs with a single vacancy (units in $e/Å^3$).

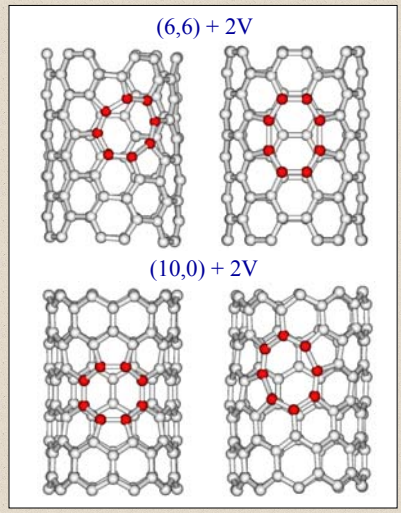
System	L (Å)	m (μ_B)	E_{form} (eV)
(6,6)+1V	12.46	0.82 (1.10)	5.75 (7.00)
(6,6)+1V	24.92	0.63	5.85
(10,0)+1V	12.96	0.32 (1.04)	5.67 (7.11)
(10,0)+1V	25.92	0.49	5.65
(8,8)+1V	12.46	0.77 (1.10)	4.65 (5.81)
(14,0)+1V	12.96	0.53 (1.10)	5.20 (6.32)

Magnetic moment (m) and formation energies (E_{form}) for CNTs with a vacancy in two concentrations or supercell lengths (L). In parenthesis are shown the results for the metastable geometries.

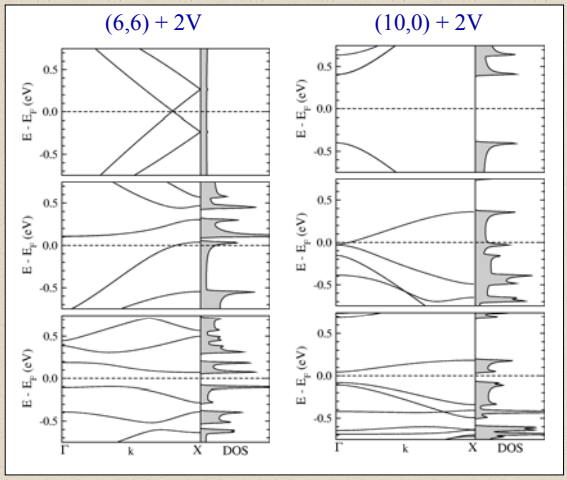


Spin-resolved density of state (DOS) for the (6,6) [left] and (10,0) [right] CNTs with a vacancy. [upper panel] Perfect CNT. [center] The vacancy in a ~13 Å supercell. [lower panel] The vacancy in a ~26 Å supercell.

The divacancy in CNTs



Ground state [left] and metastable [right] equilibrium geometries for the (6,6) and (10,0) CNTs with a divacancy



Band structure and density of state (DOS) for the (6,6) [left] and (10,0) [right] CNTs with a divacancy. [upper panel] Perfect CNTs. [center] The divacancy in a ~13 Å supercell. [lower panel] The divacancy in a ~26 Å supercell.

System	L (Å)	m (μ_B)	E_{form} (eV)
(6,6)+2V	12.46	0.0 (0.0)	4.24 (7.84)
(6,6)+2V	24.92	0.0	4.17
(10,0)+2V	12.96	0.0 (0.0)	3.90 (6.65)
(10,0)+2V	25.92	0.0	4.06
(8,8)+2V	12.46	0.0	2.09
(14,0)+2V	12.96	0.0	2.33

Magnetic moment (m) and formation energies (E_{form}) for the divacancy in armchair and zigzag CNTs with different supercell lengths (L). In parenthesis are shown the results for the metastable geometries

Acknowledgments

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