Structural, electronic and magnetic properties of vacancies in carbon nanotubes

Walter Orellana
Departamento de Física, Facultad de Ciencias, Universidad de Chile

Financing and support by:

- Millennium Scientific Initiative
- FONDECYT under grant No. 1050197

Motivation

Recent experiments indicate that proton irradiation triggers ferromagnetism in originally non magnetic graphite samples with Curie temperature above room temperature ...

Esquinazi et al., Phys. Rev. Lett. 91, (2003)

These results suggest that similar magnetic propertiers could be found in single-walled carbon nanotubes (CNTs), providing a possible way to obtain controllable metal-free nanomagnets

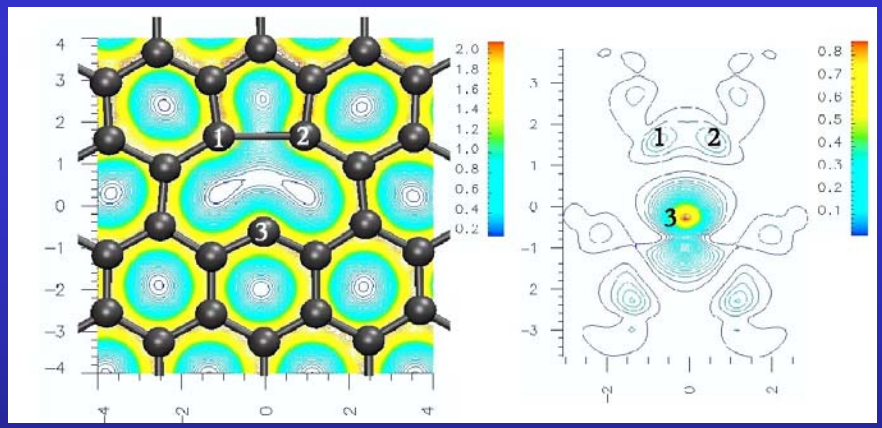
Direct experimental evidence of magnetism in single-walled carbon nanotubes is still lacking due to the presence of metal catalysts in the samples

First-principles calculations can give insigths in the reliability of the magnetism in carbon nanotubes

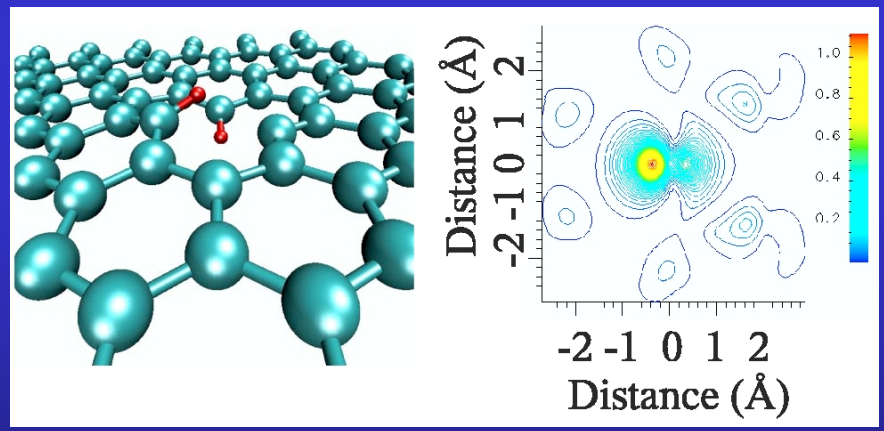
Magnetism in graphite: Theoretical results

Defects like vacancy and vacancy-hydrogen complexes are most likely to appear under irradiation. Both defects exhibit magnetism according to recent DFT calculations

Lehtinen et al., Phys. Rev. Lett. 93, (2004)



$m = 1.0\ \mu_B$

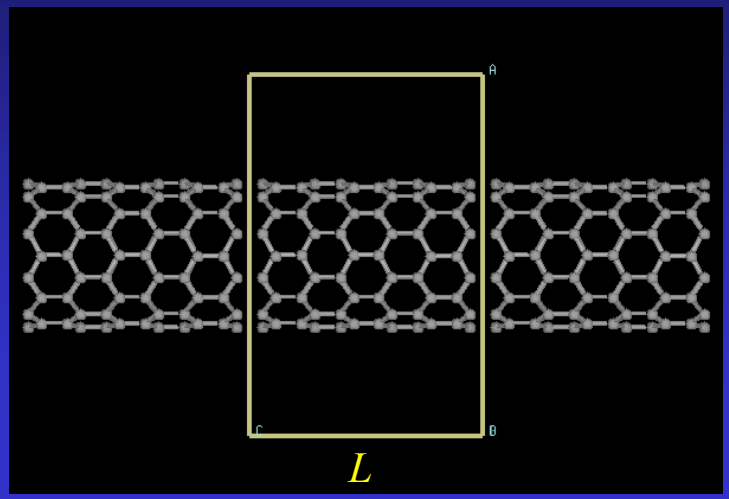


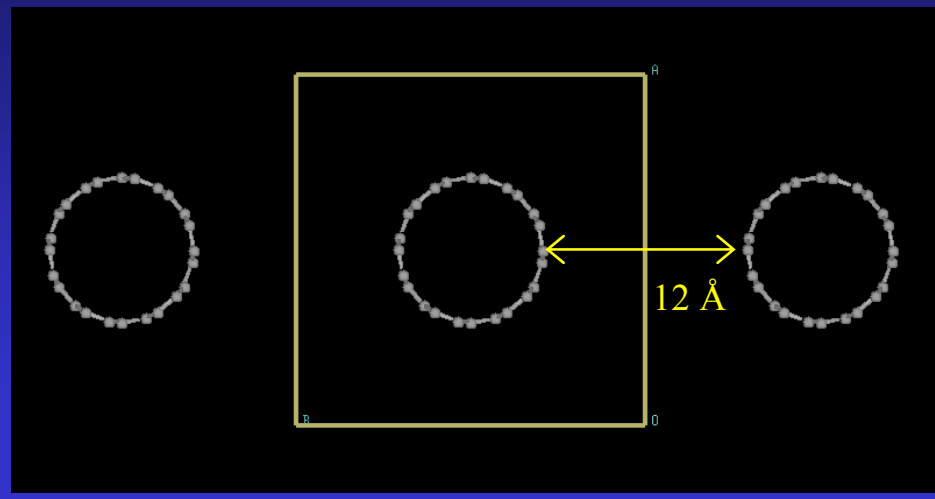
$m = 1.2\ \mu_B$

Theoretical method

- Spin-polarized density functional calculations (DFT+GGA)
- Norm-conserving pseudopotentials
- Basis set of numerical atomic orbitals (DZP, SIESTA code)
- CNTs: armchair [(6,6) & (8,8)] and the zigzag [(10,0) & (14,0)] with diameters of about 8 and 11 Å, respectively
- Two defect concentrations along the tube axis were simulated with supercells of L ~ 13 and 26 Å in length
- The BZ sampling was performed with 6 k points along the tube axis in the 13 Å supercell and the Γ point for the 26 Å supercell
- The structures were fully relaxed until all forces become smaller than 0.05 eV/Å

The supercell approach





- Perfect nanotubes are described as infinites imposing periodic boundary conditions along the tube
- A defective nanotube is described as an infinite tube with a linear concentration of defect (one defect per unit cell)

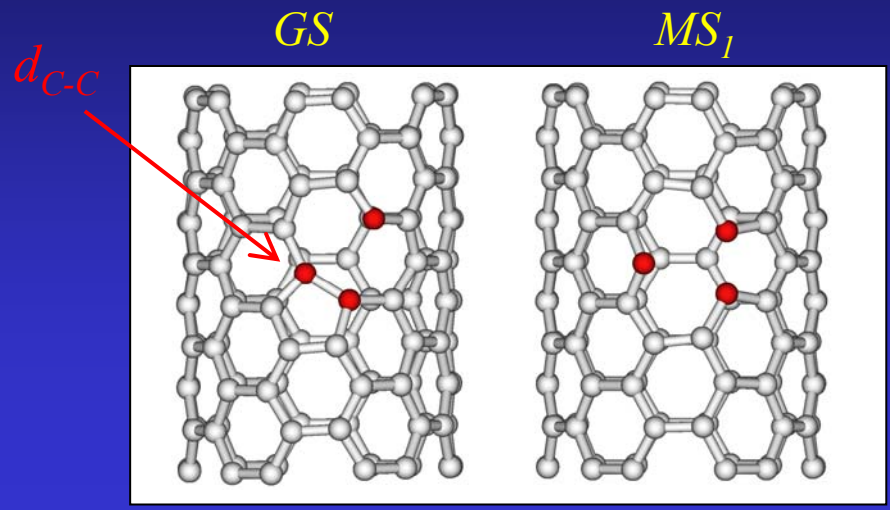
Formation energy: $E_{form}(V) = E_{tot}(CNT) - E_{tot}(CNT + V) - E_{tot}(CNT)/atom$

Spin magnetic moment: $m = 2S\mu_B$

The single vacancy in CNTs

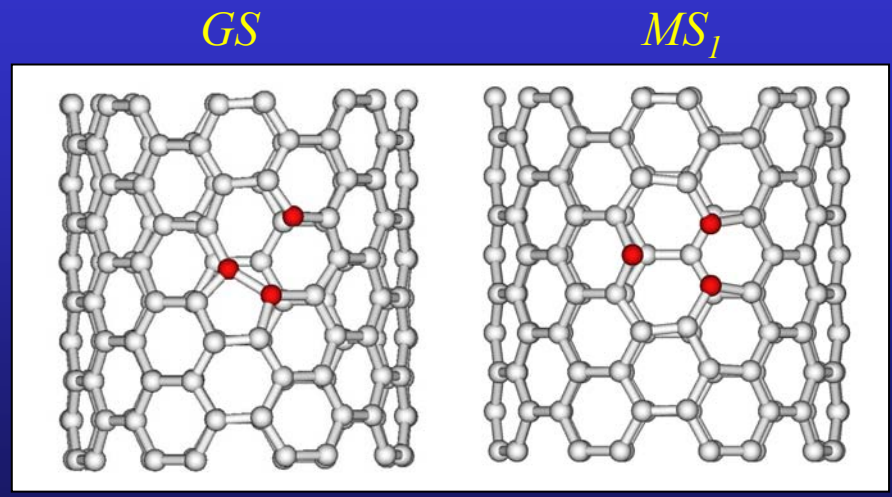
Structural properties of the monovacancy in armchair CNTs

(6,6)+1V	*GS*	MS_1
E_T (meV/atom)	0.0	10.5
m (μ_B)	0.8	1.1
E_{form} (eV)	5.75	7.00
$d_{C\text{-}C}$ (Å)	1.56	1.93



The neighboring atoms reconstruct forming a pentagon, leaving one C atom undercoordinated

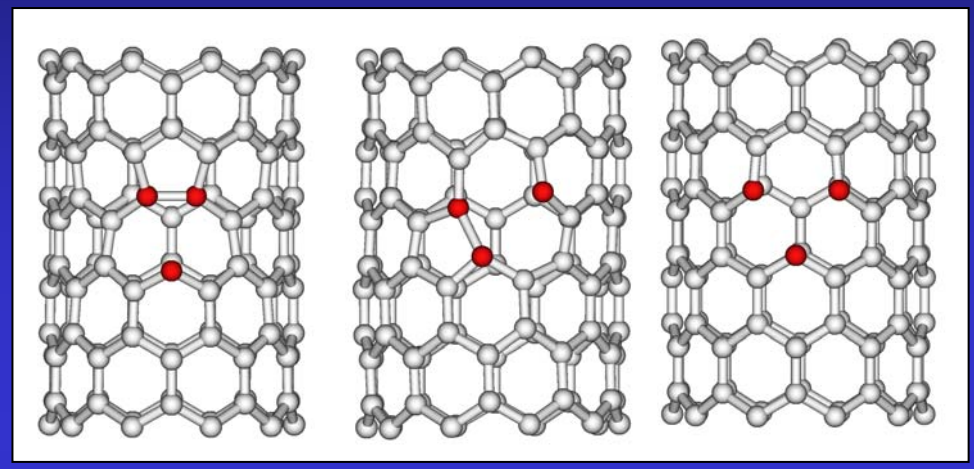
(8,8)+1V	*GS*	MS_1
E_T (meV/atom)	0.0	7.3
m (μ_B)	0.8	1.1
E_{form} (eV)	4.65	5.81
$d_{C\text{-}C}$ (Å)	1.58	1.98



Structural properties of the single vacancy in zigzag CNTs

(10,0)+1V	*GS*	MS_1	MS_2
E_T (meV/atom)	0.0	12.1	17.2
m (μ_B)	0.3	1.0	1.4
E_{form} (eV)	5.67	7.11	7.72
$d_{C\text{-}C}$ (Å)	1.54	1.72	2.50

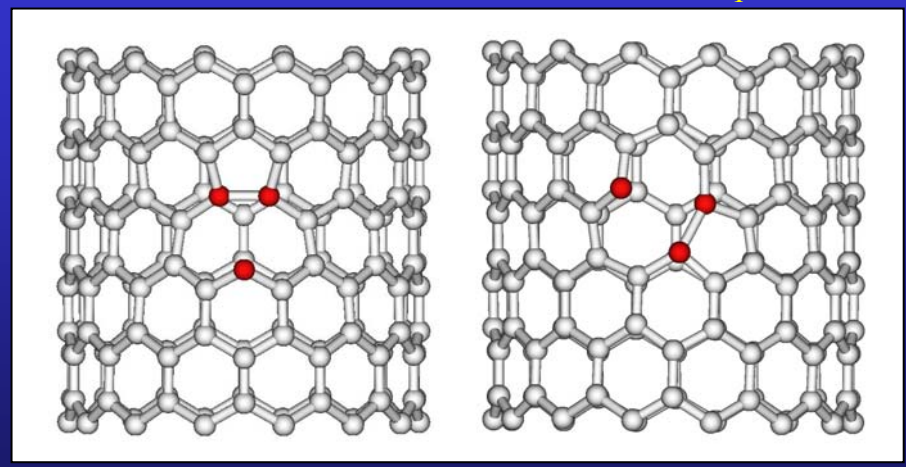
GS MS_1 MS_2 (3db)



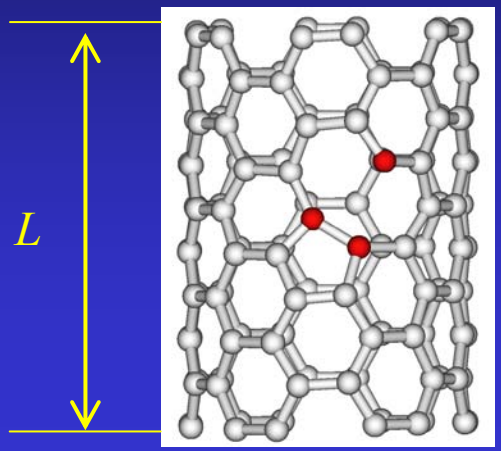
m and $d_{C\text{-}C}$ have a direct proportionality

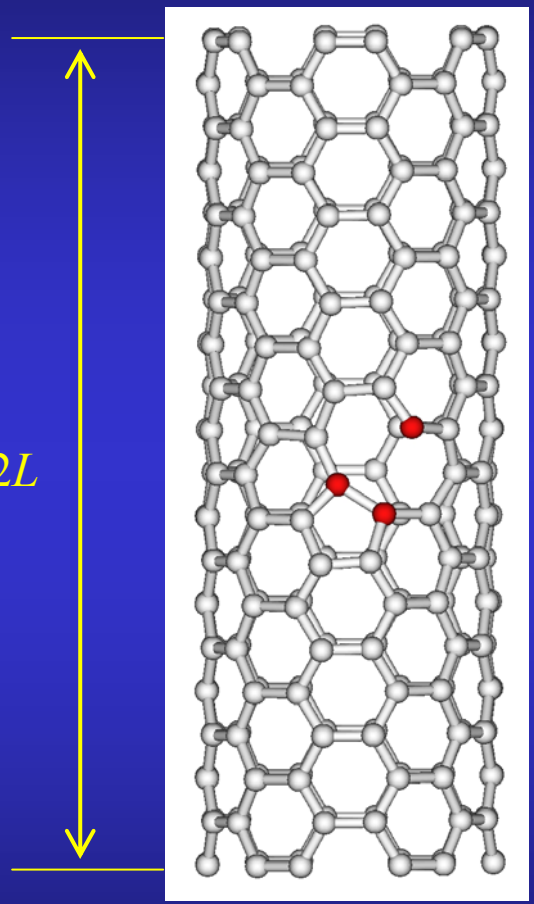
(14,0)+1V	*GS*	MS_1
E_T (meV/atom)	0.0	6.7
m (μ_B)	0.5	1.1
E_{form} (eV)	5.20	6.32
$d_{C\text{-}C}$ (Å)	1.58	1.74

GS MS_1



(6,6)+1V in different concentrations

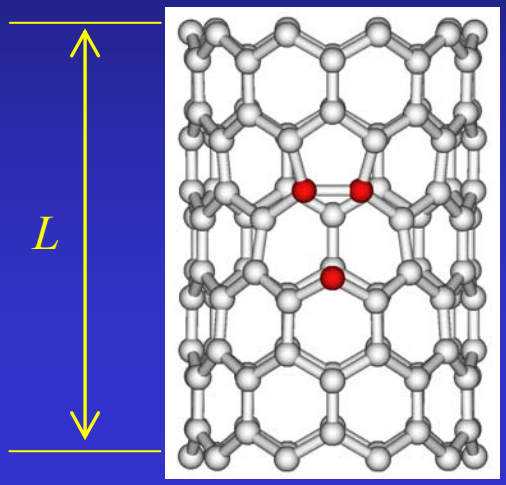


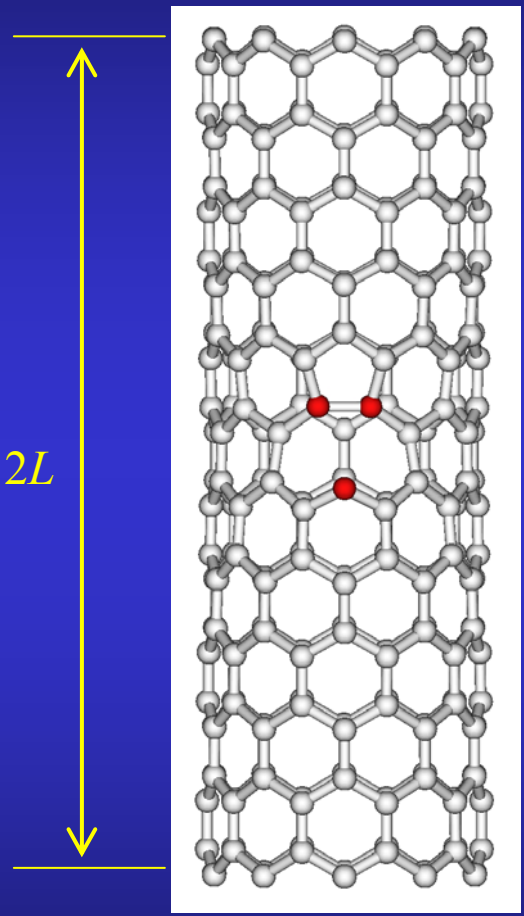


(6,6)+1V	*L*	*2L*
m (μ_B)	0.8	0.6
E_{form} (eV)	5.75	5.85
$d_{C\text{-}C}$ (Å)	1.56	1.57

- There exist small changes in the defective CNTs for a more diluted vacancy concentration
- The magnetic moment tends to decrease

(10,0)+1V in different concentrations



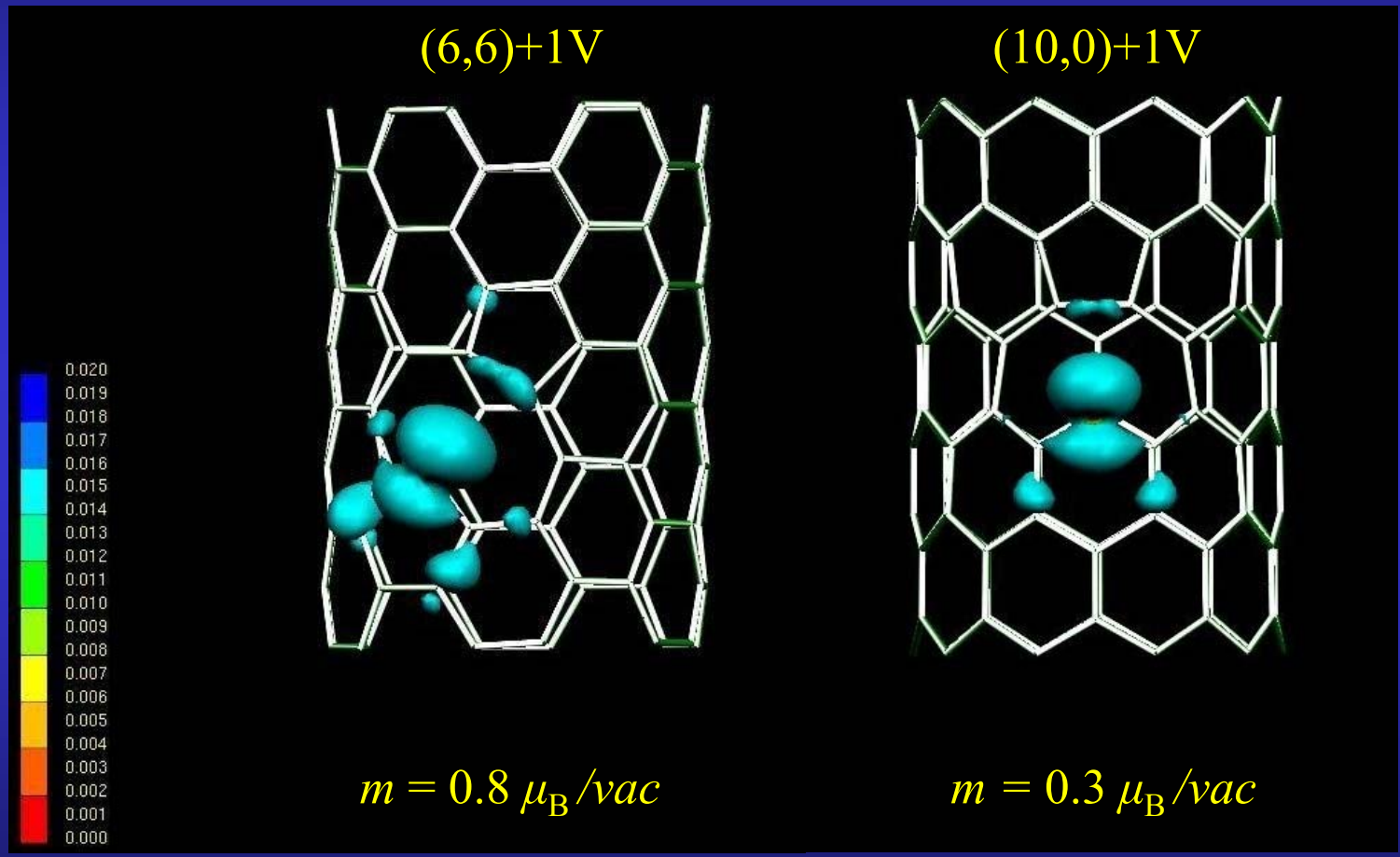


(10,0)+1V	*L*	*2L*
m (μ_B)	0.3	0.5
E_{form} (eV)	5.67	5.65
$d_{C\text{-}C}$ (Å)	1.54	1.53

- The magnetic moment tends to increase
- The magnetic moment tends to change with the distance between defects

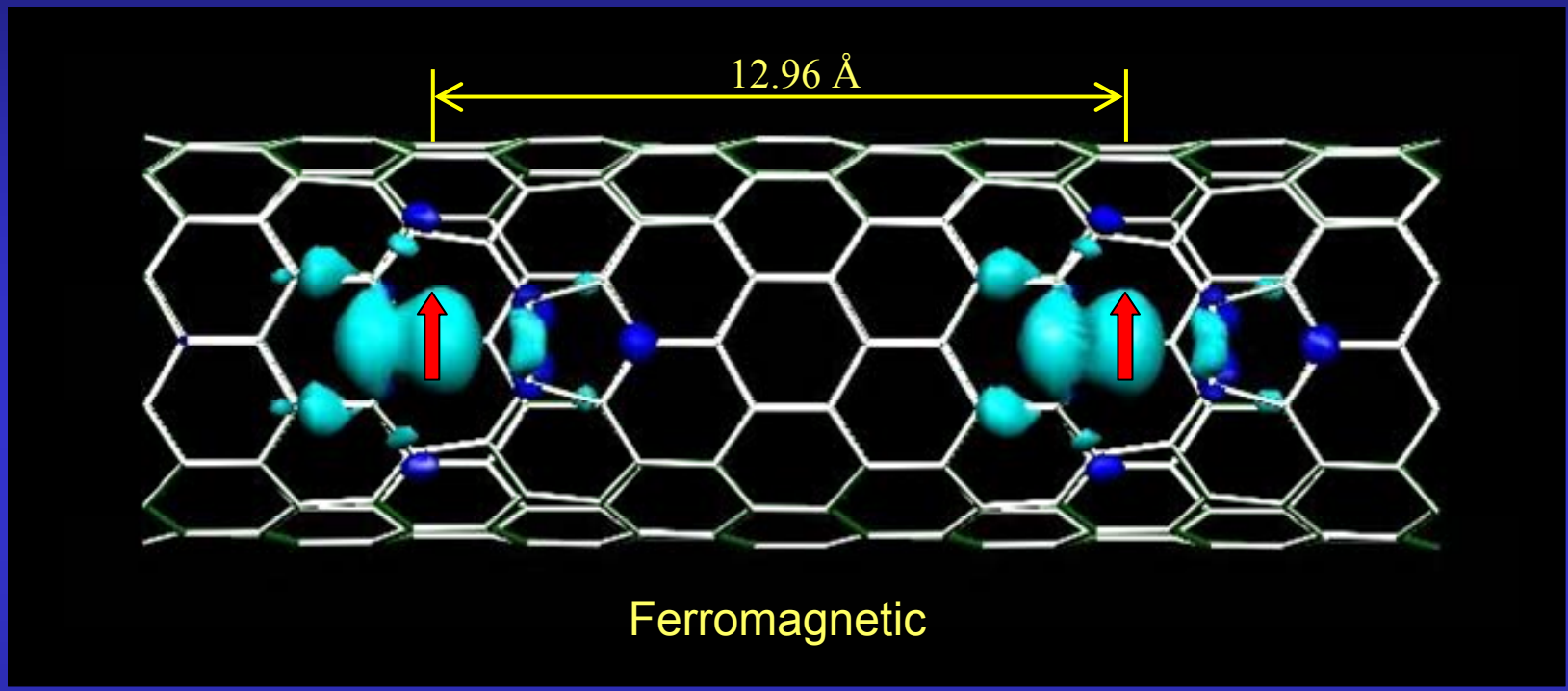
Magnetism in CNTs with a single vacancy

spin density isosurfaces $\rho_{\uparrow} - \rho_{\downarrow}$ [eV/Å^3]



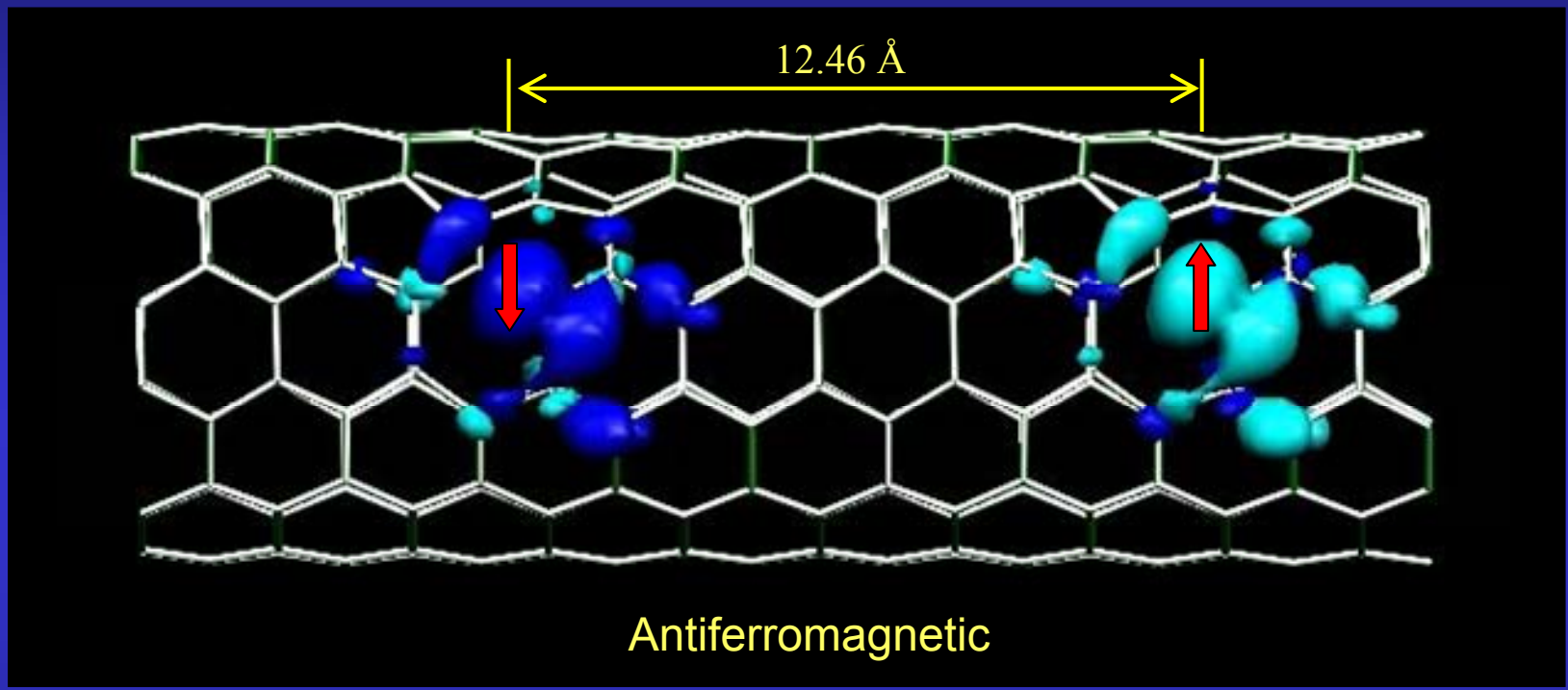
We need to determine the most stable magnetic phase in both defective CNTs …

Doubling the cell $\Rightarrow$ Ferromagnetic order in (10,0)+1V



$E_{FM} - E_{AF} = 6$ meV $\qquad m = 0.4\ \mu_B/vac$

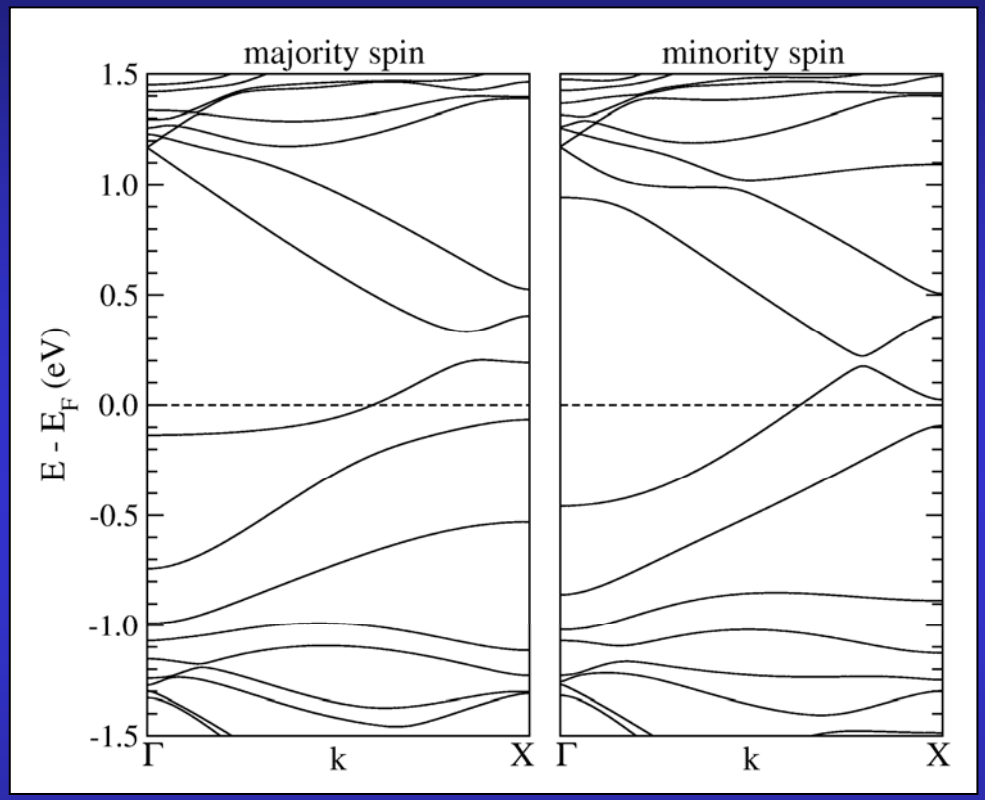
Doubling the cell $\Rightarrow$ Antiferromagnetic order in (6,6)+1V



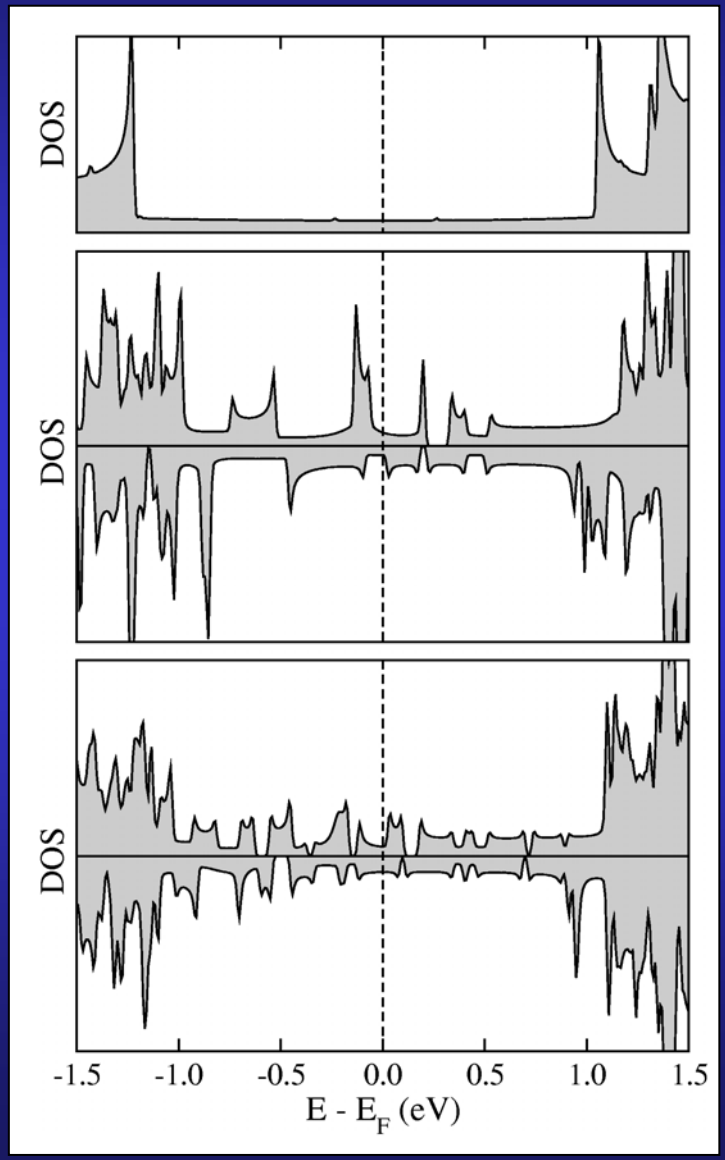
$E_{AF} - E_{FM} = 18$ meV $\qquad m = 0$

Magnetic defects are coupled over long distances by an indirect exchange interaction mediated by π electrons (possible a RKKY interaction)

Electronic structure of (6,6)+1V



L



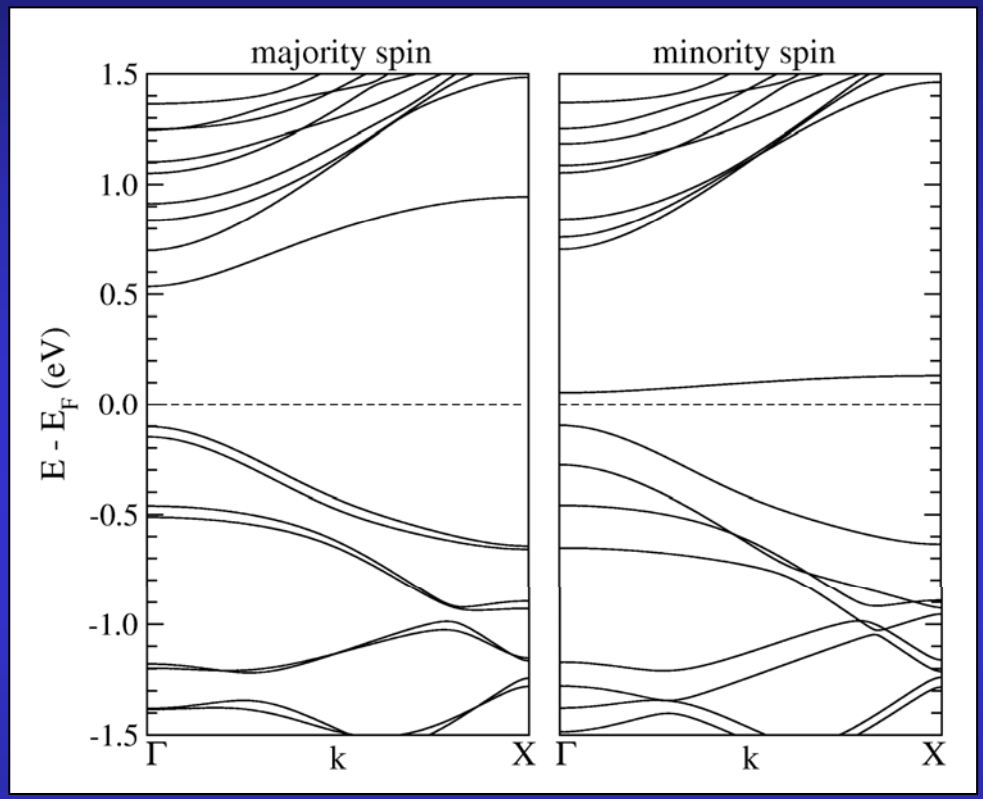
L

L

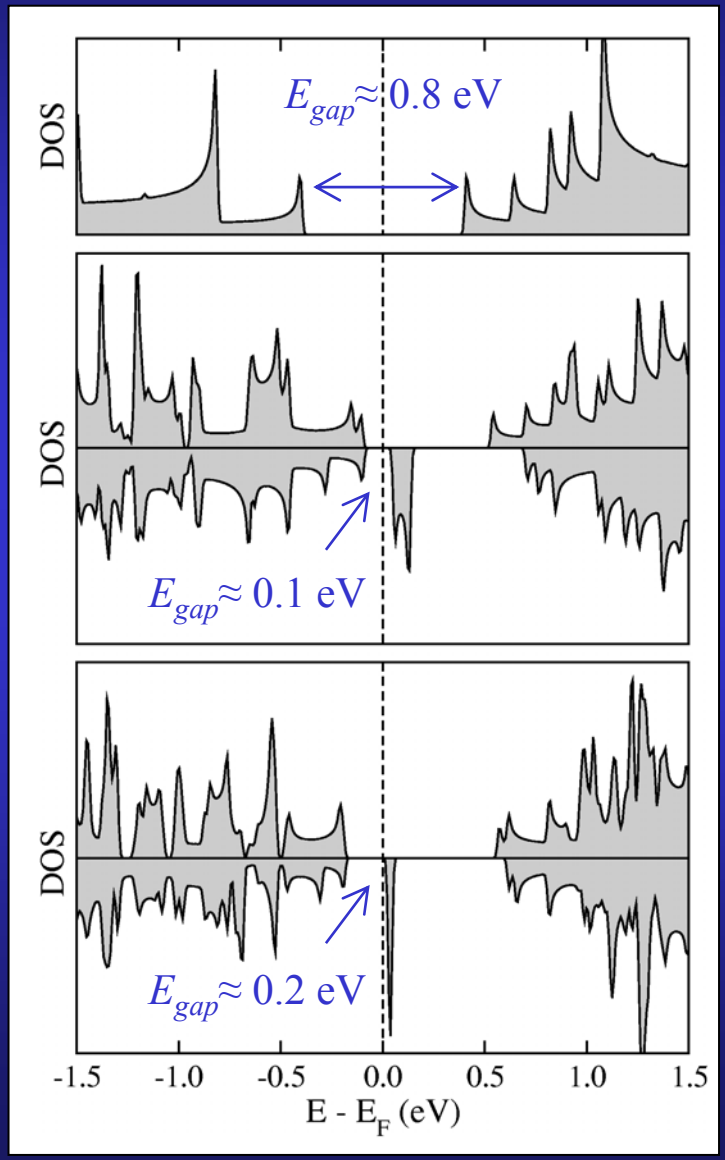
2L

The (6,6) CNT preserves its metallic character with a vacancy.

Electronic structure of (10,0)+1V



L



L

L

2L

The (10,0) CNT preserves its semiconducting character with a vacancy

Comparison with other DFT results

The single vacancy in small CNTs have been previously investigated.
These CNT are the armchairs (3,3)-(6,6) and the zigzags (5,0)-(10,0)

New Journal of Physics 6, 68 (2004)

System	d (Å)	n (vac/Å)	Class	m (μ_B)	Phase
(5,5)+1V	~7	0.20	metal	0.6	ferro
(6,6)+1V	~8	0.20	metal	0.4	ferro
(6,6)+1V	~8	0.08	metal	0.0	antiferro
(6,6)+1V	~8	0.04	metal	0.0	antiferro
(8,8)+1V	~11	0.08	metal	0.0	antiferro
(6,0)+1V	~5	0.08	semi	0.3	ferro
(6,0)+1V	~5	0.06	semi	0.7	ferro
(6,0)+1V	~5	0.04	semi	0.5	ferro
(10,0)+1V	~8	0.08	semi	0.4	ferro
(10,0)+1V	~8	0.04	semi	0.5	ferro
(14,0)+1V	~11	0.08	semi	0.5	ferro

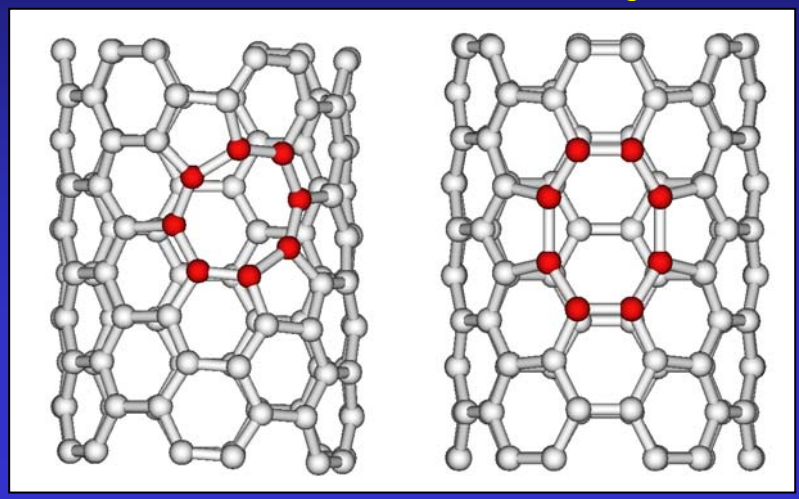
n = linear density of vacancy
d = CNT diameter

The double vacancy in CNTs

Structural properties of the divacancy in CNTs

(6,6)+2V	*GS*	MS_1
E_T (meV/atom)	0.0	30.6
m (μ_B)	0.0	0.0
E_{form} (eV)	4.24	7.84
$d_{C\text{-}C}$ (Å)	1.52	1.78

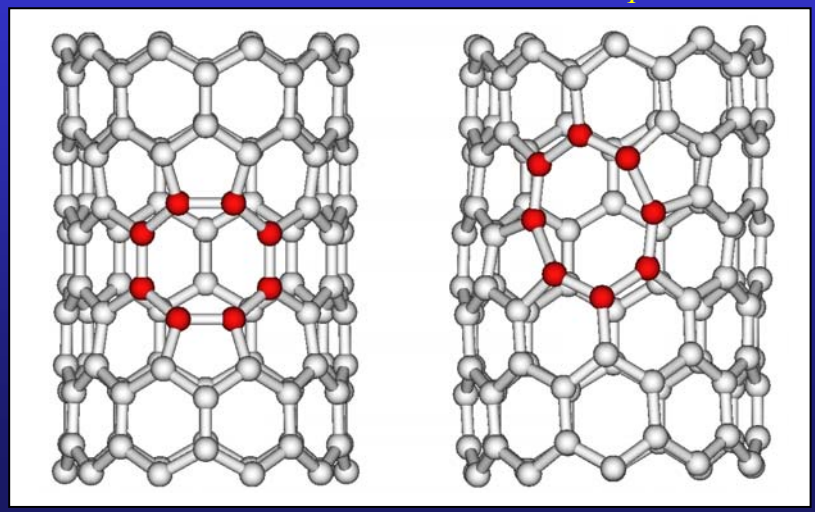
GS MS_1



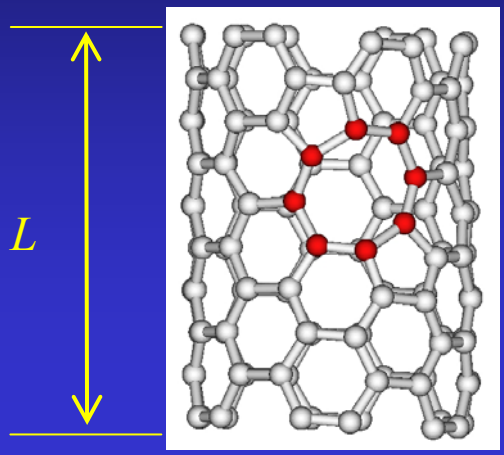
The neighboring atoms reconstruct forming an optagon with two pentagons at opposite directions

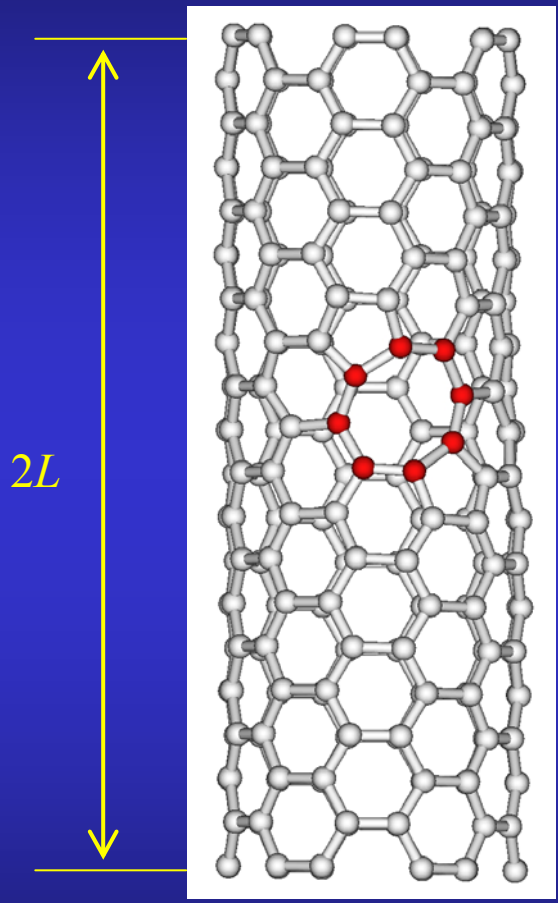
(10,0)+2V	*GS*	MS_1
E_T (meV/atom)	0.0	23.3
m (μ_B)	0.0	0.0
E_{form} (eV)	3.90	6.65
$d_{C\text{-}C}$ (Å)	1.50	1.65

GS MS_1



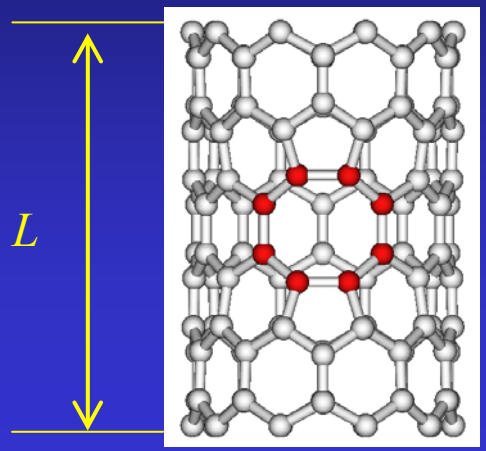
Structural properties of the divacancy in (6,6)

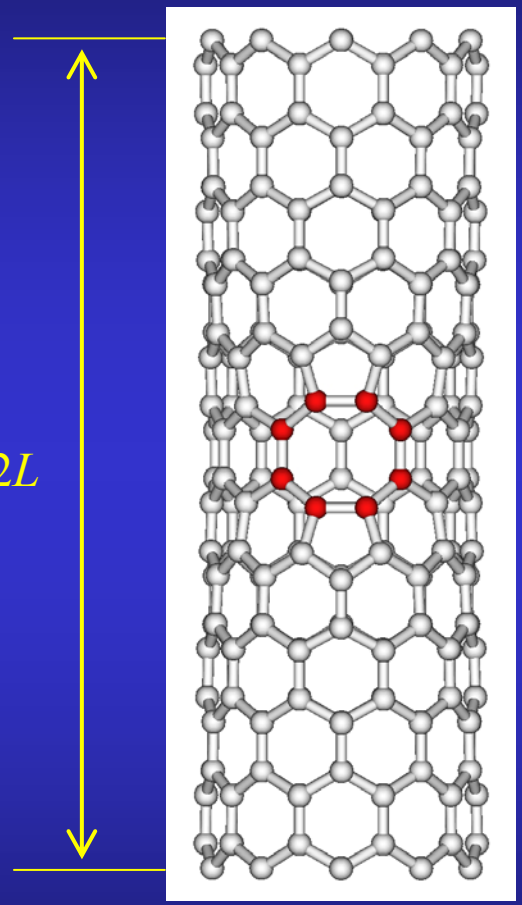




(6,6)+2V	L	$2L$
m (μ_B)	0.0	0.0
E_{form} (eV)	4.24	4.15
$d_{C\text{-}C}$ (Å)	1.53	1.52

Structural properties of the divacancy in (10,0)





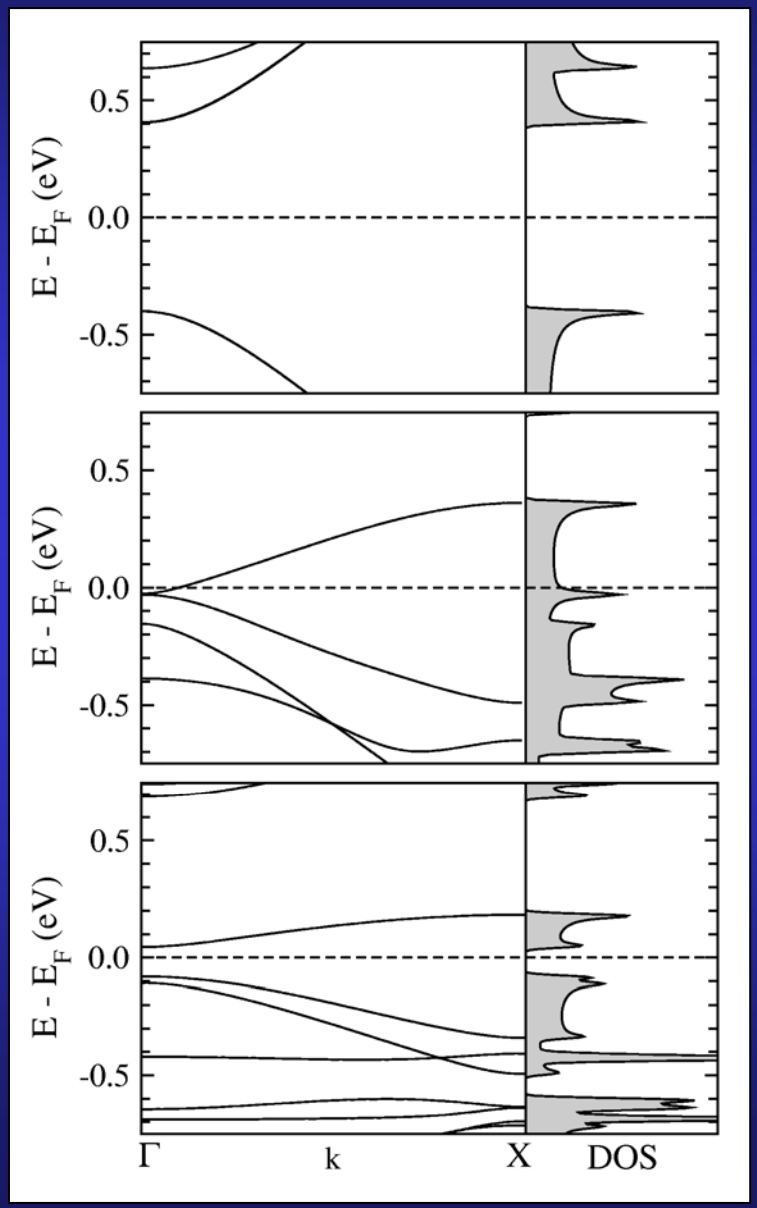
(10,0)+2V	*L*	*2L*
m (μ_B)	0.0	0.0
E_{form} (eV)	3.90	3.95
$d_{C\text{-}C}$ (Å)	1.50	1.49

Electronic structure of (10,0)+2V

L

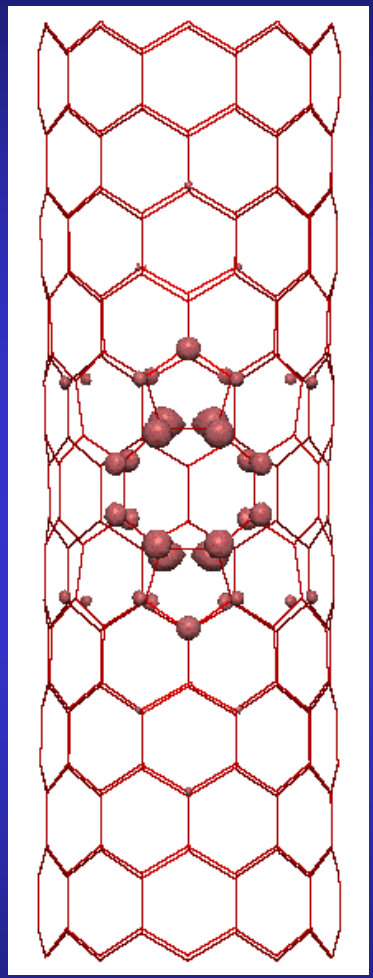
L

2L



$E_{gap} \approx 0.8$ eV

$E_{gap} \approx 0.15$ eV



ρ_{LUMO}

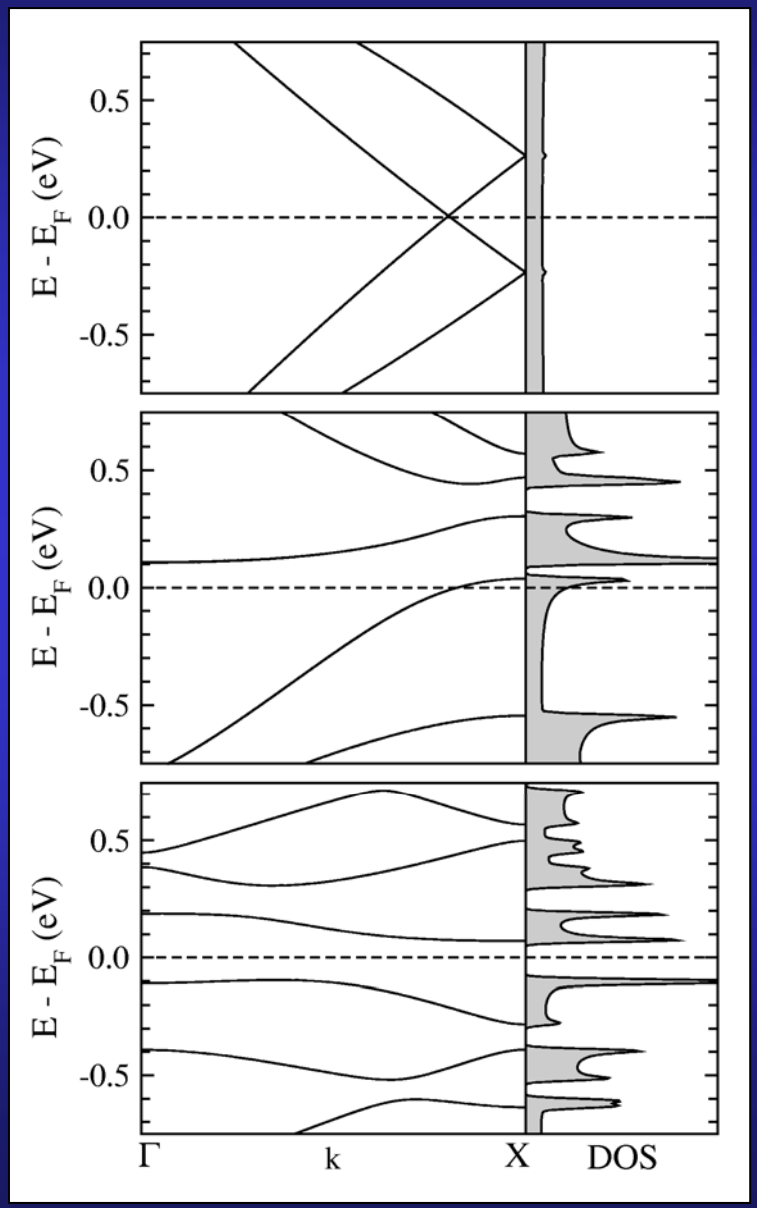
The electronic properties depend on the concentration of defect along the CNT.

Electronic structure of (6,6)+2V

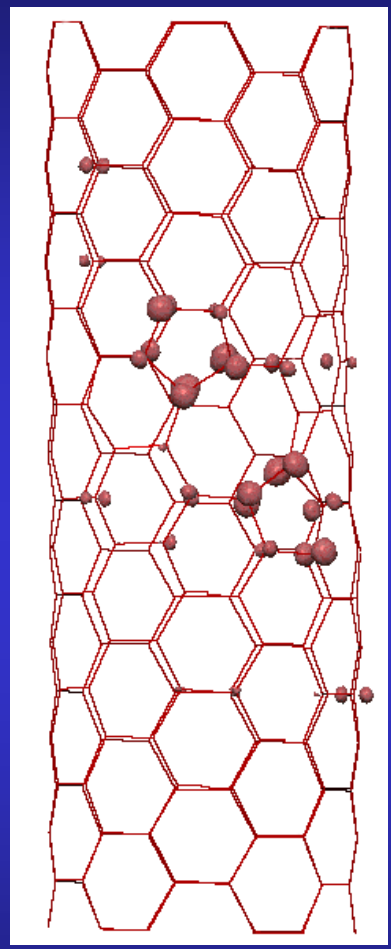
L

L

2L



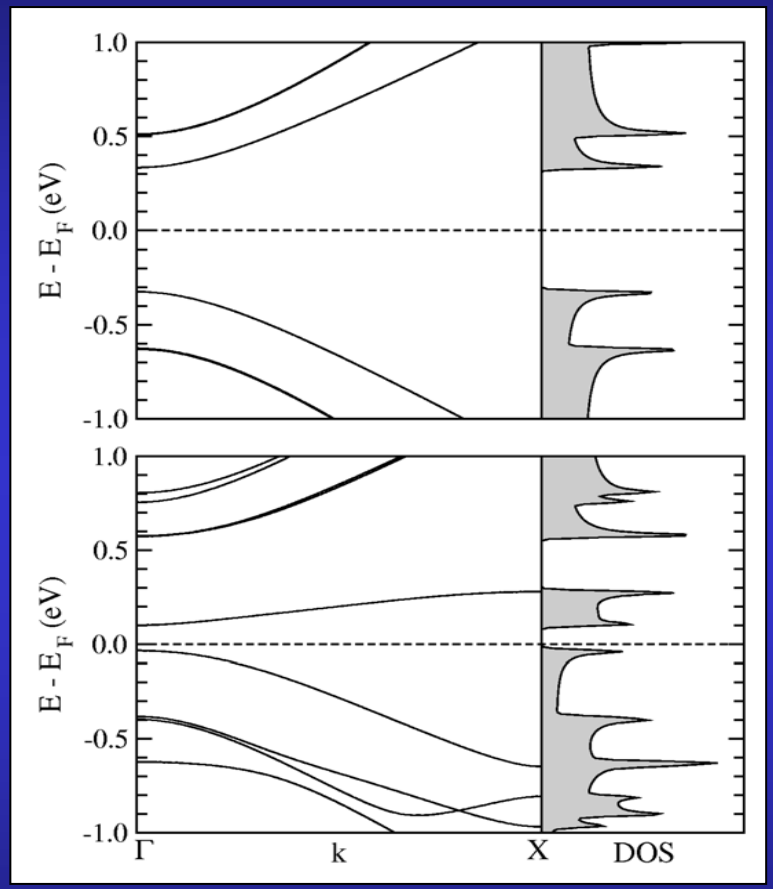
$E_{gap} \approx 0.15$ eV



ρ_{LUMO}

Metallic CNTs become semiconducting at sufficiently diluted concentrations of divacancies

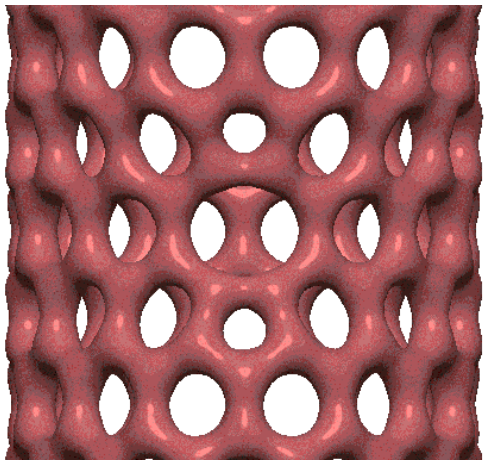
Electronic structure of (14,0)+2V

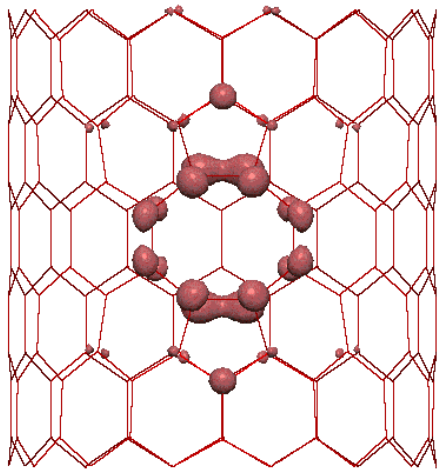


$E_{gap} \approx 0.6$ eV

$E_{gap} \approx 0.1$ eV

ρ_{TOTAL}

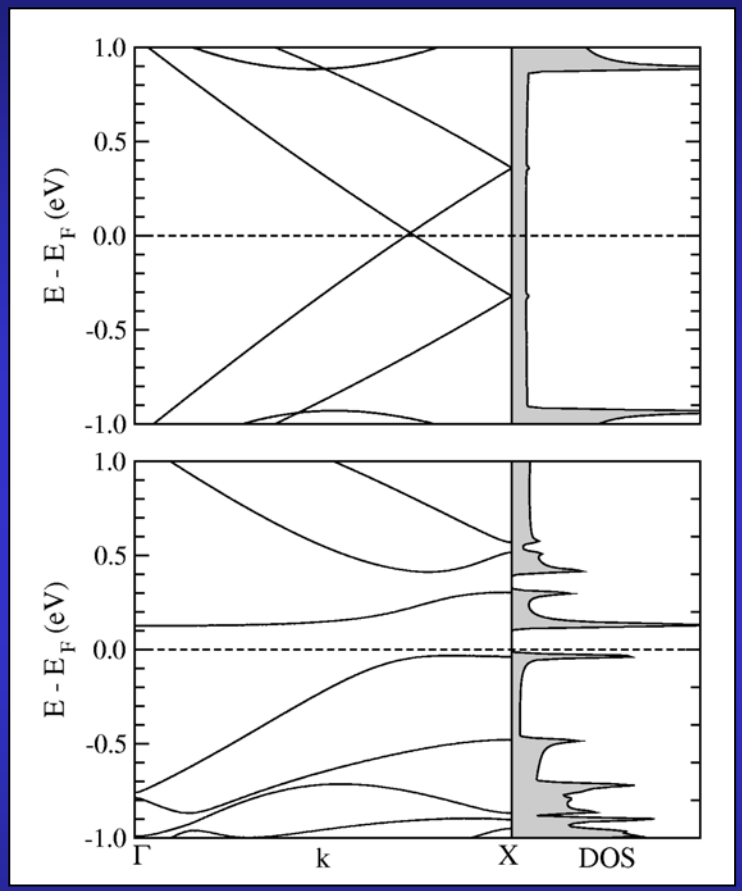




ρ_{LUMO}

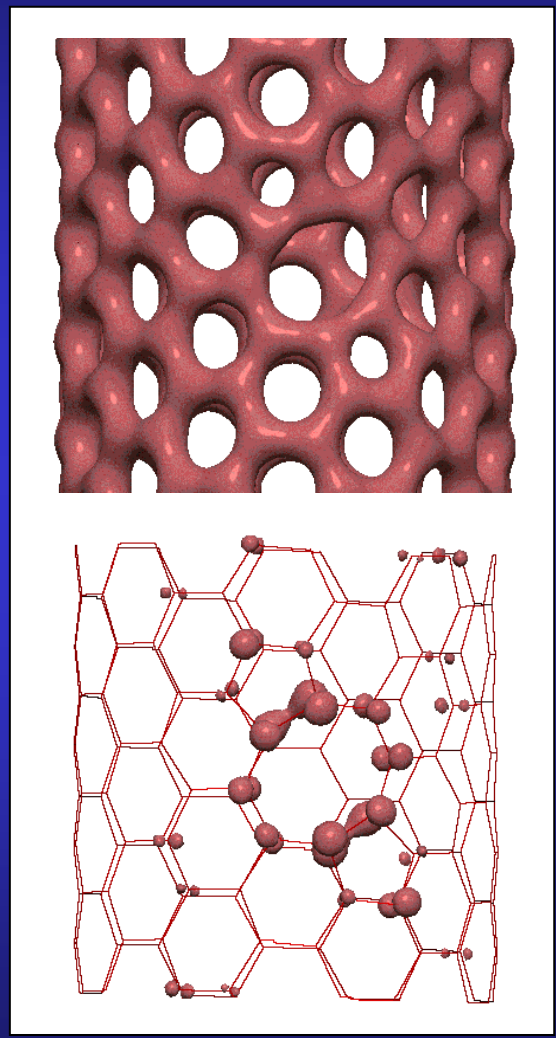
The divacancy promotes a reduction of the gap due to the appearance of a defect state

Electronic structure of (8,8)+2V



$E_{gap} \approx 0.1$ eV

ρ_{TOTAL}



ρ_{LUMO}

The divacancy can change the electronic character of armchair CNTs from metallic to semiconducting

Summary and Conclusions

- Single vacancies trigger magnetism in zigzag and armchair CNTs induced by an unpaired σ electron of an undercoordinated C atom
- Zigzag CNTs with a single vacancy are ferromagnetic whereas armchair CNTs are antiferromagnetic, this would be valid for CNTs with diameter larger than 8 Å
- CNTs with a single vacancy preserve their electronic properties of metal (armchair) and semiconductor (zigzag) CNTs
- The divacancy does not exhibit magnetism due to the full reconstruction of C atoms around the defect (always three fold coordinated)
- The divacancy can change the electronic properties of armchair CNTs from metallic to semiconducting depending on the defect concentration and on the CNT diameter.

For more details please see cond-mat/0510585