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Ni_2C formation at the graphene/Ni(111) interface: first-principles investigation

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Outline

- State-of-the-art
- Simulating and comparing (epitaxial & rotated)-graphene/carbide/Ni(111)
  - Structural models & thermodynamics
  - Electronic properties
- From graphene/Ni interface towards carbide formation

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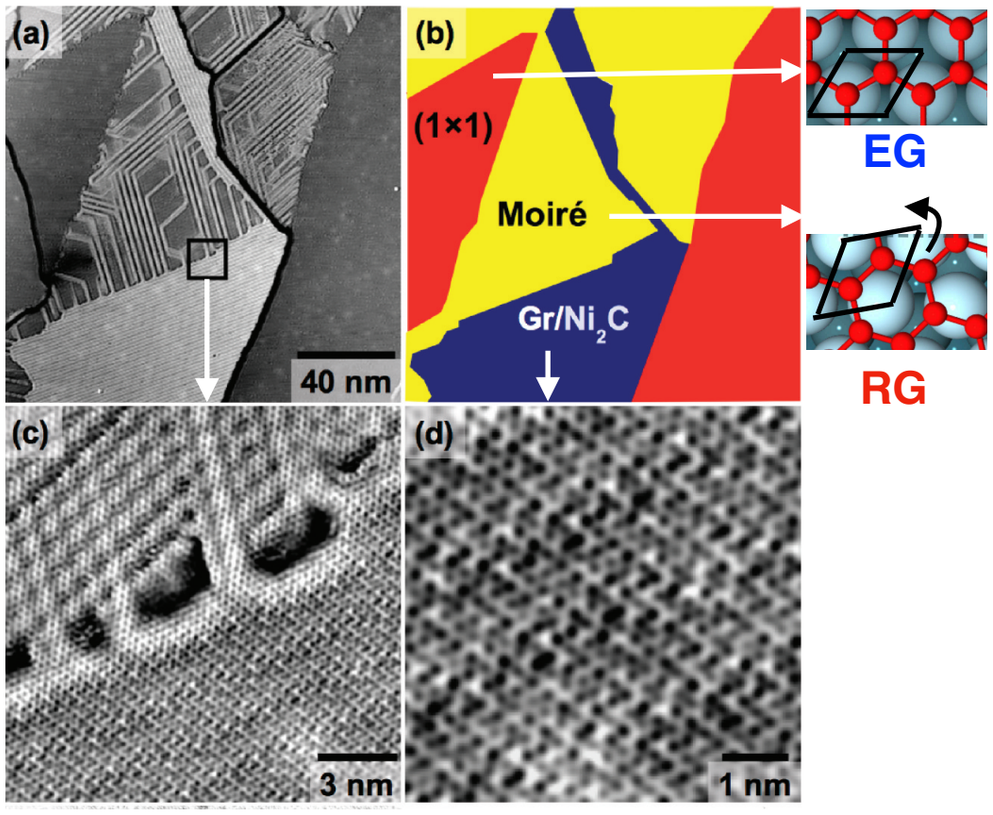
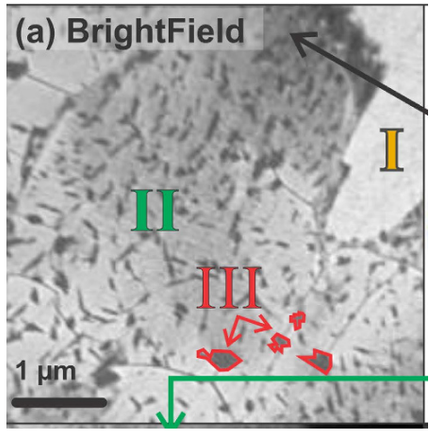
State-of-the-art: Experimental facts

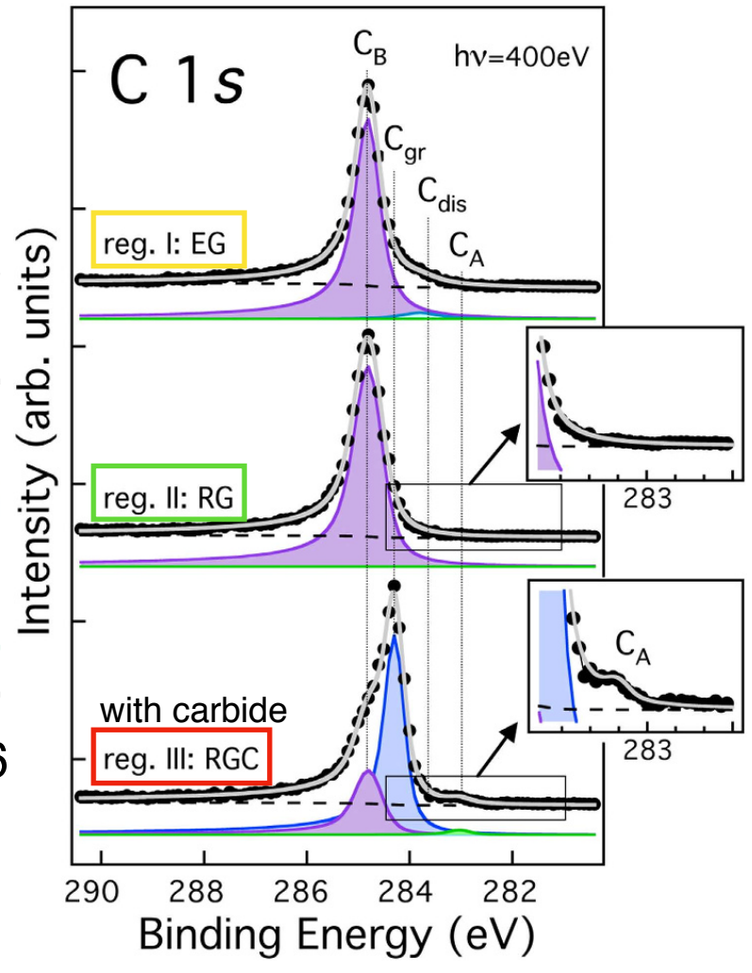
1) **Coexistence of EPITAXIAL Graphene (EG) and ROTATED Graphene (RG) on Ni(111)**
2) **Carbide (Ni_2C)** can form only **under RG (not EG !)** through surface segregation of C atoms dissolved in Ni bulk, and temperature controls its formation/dissolution



Jacobson et al., ACSNano 2012



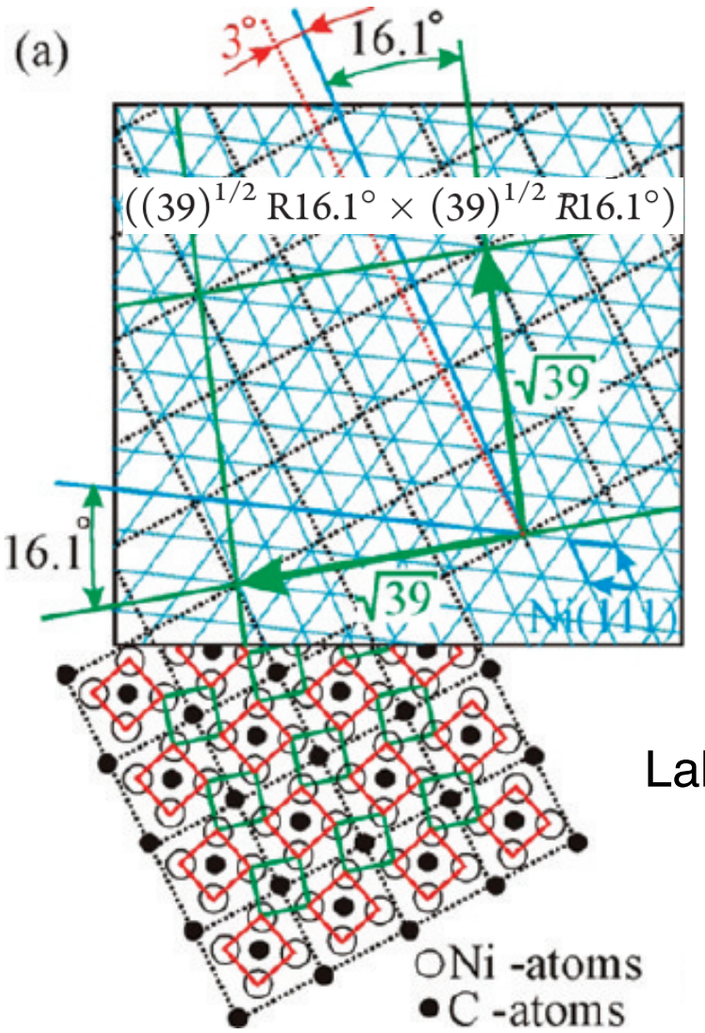
Africh et al., SciRep 2016



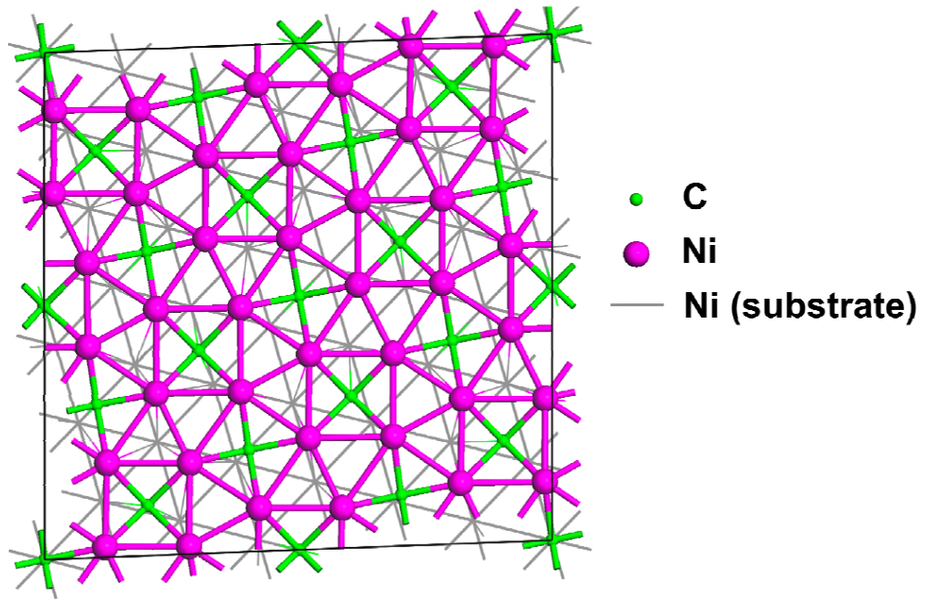
Why carbide form only under RG?

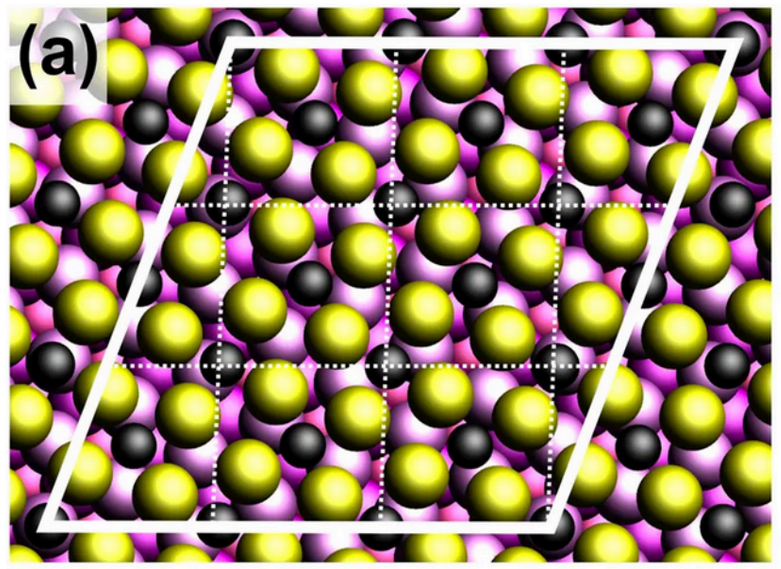
=> investigate and compare EG/Ni_2C/Ni(111) and RG/Ni_2C/Ni(111) (if existing) by quantum mechanical numerical simulations

State-of-the-art:
Models for numerical simulations



Lahiri, NanoLett 11 (2011) 518



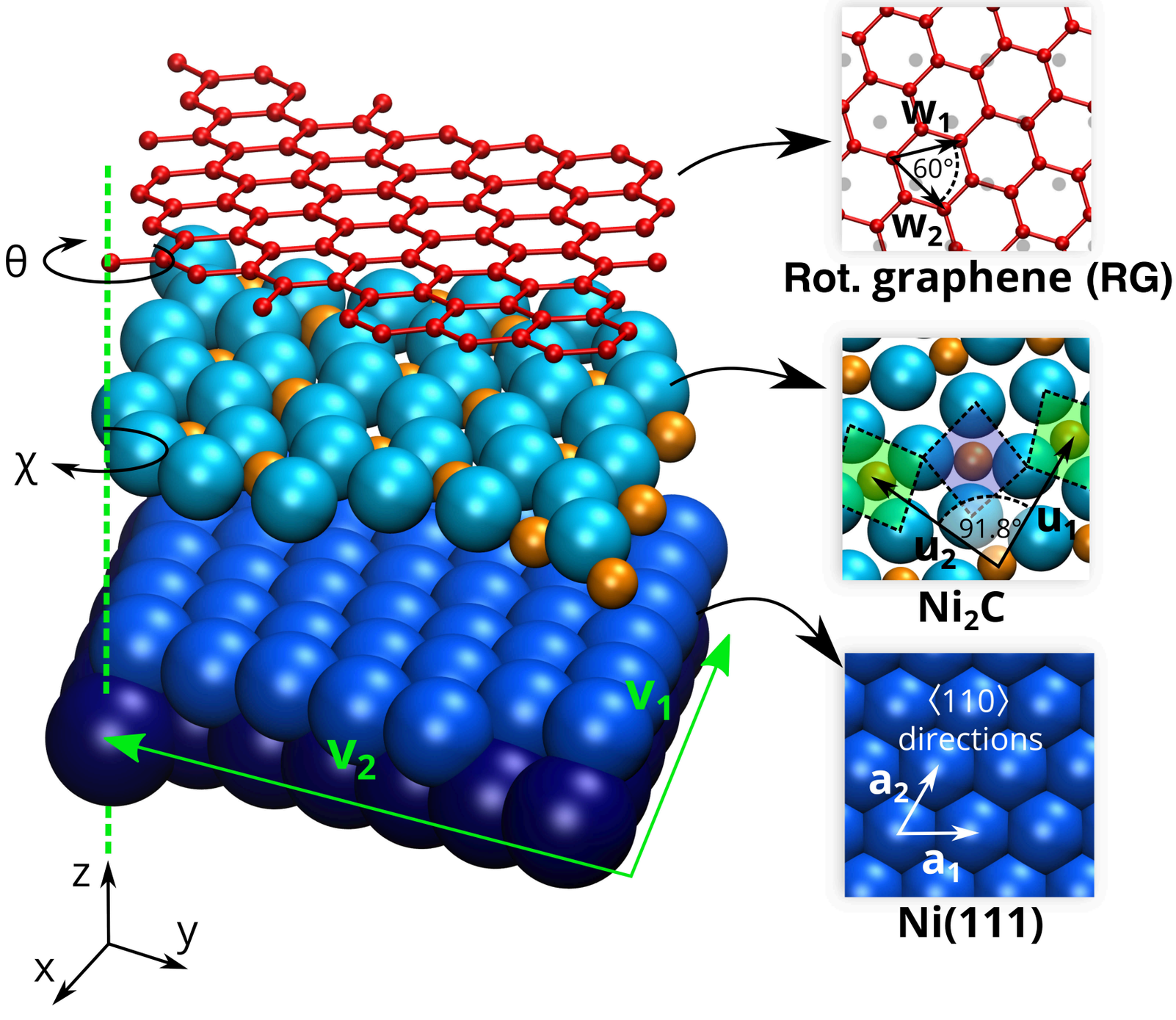


Rameshan et al., Sci Rep. 2018

Models matching Ni_2C/Ni(111) have been proposed,
also valid for EG/Ni_2C/Ni(111) (EG has a (1x1) matching with Ni(111))

but not valid for RG/Ni_2C/Ni(111)

$RG/Ni_2C/Ni(111)$: Matching three lattices



A big challenge:

a coincidence moiré cell matching **three** different lattices ?

A large cell to be investigated using ab-initio density functional theory (DFT)

QUANTUMESPRESSO

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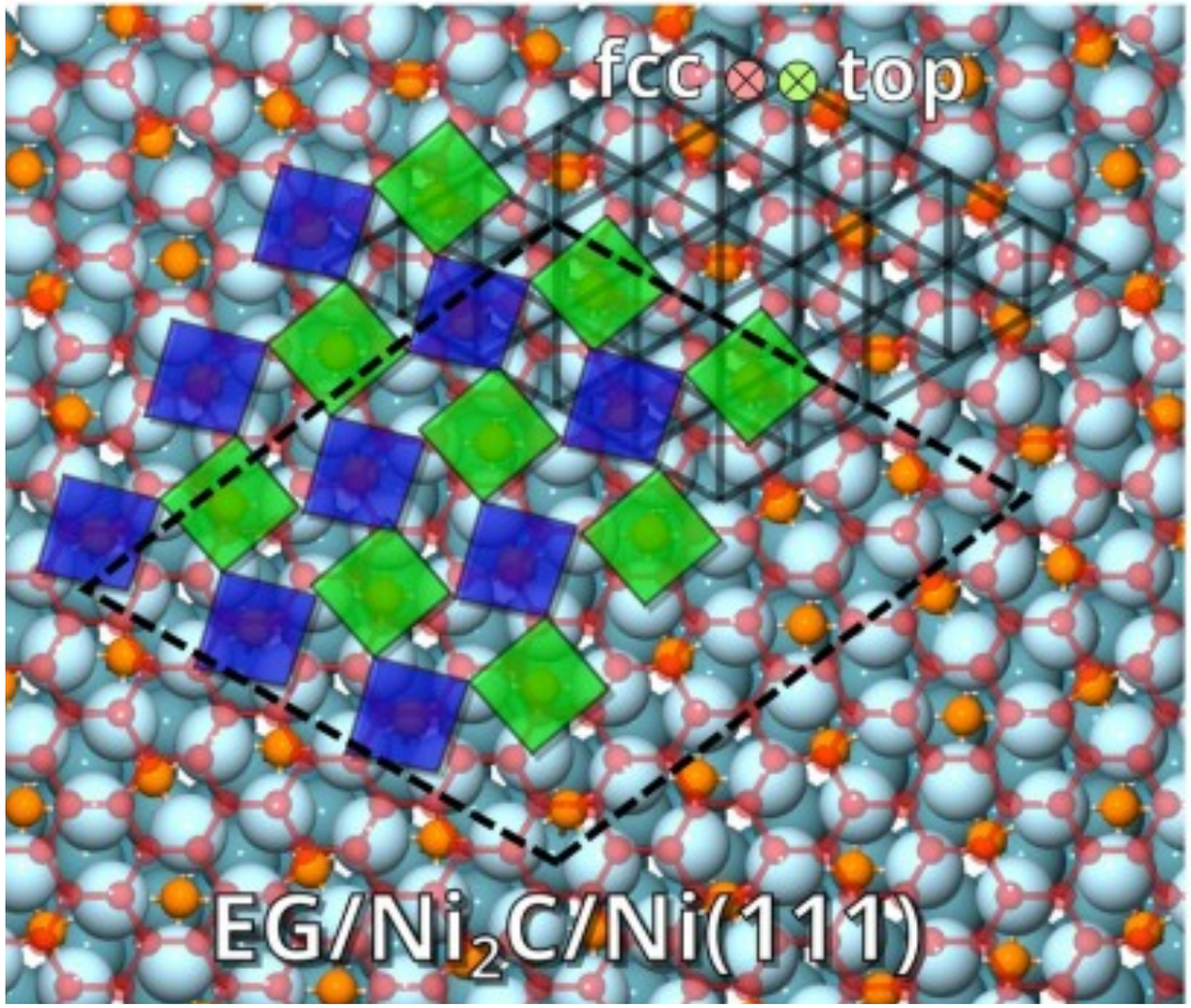
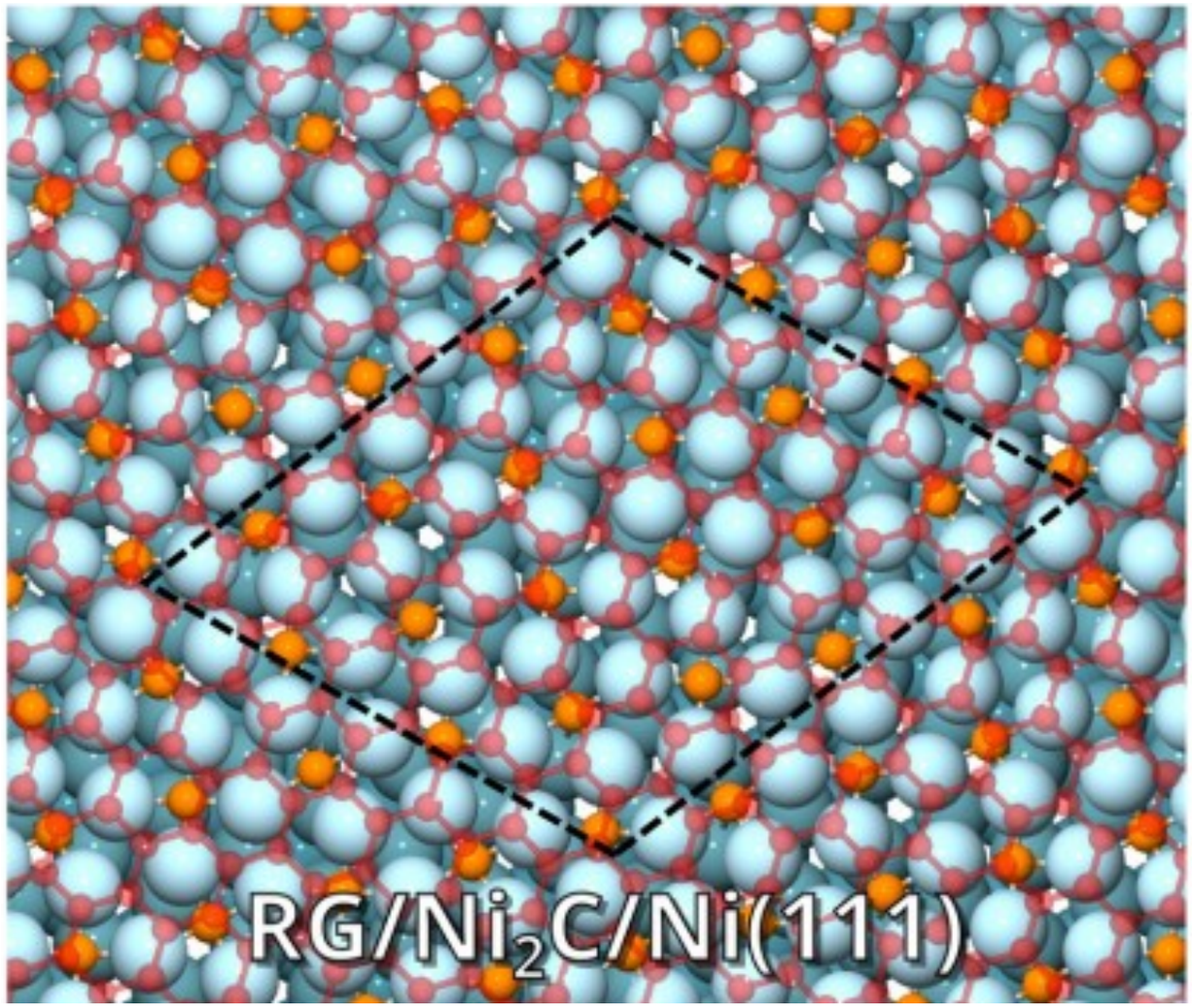
RG/Ni_2C/Ni(111) and EG/Ni_2C/Ni(111): Structural models

cell 6x(√43 R7.6) accommodating all the three different lattices (RG rotated by ~17°)





EG (top-fcc registry w.r.t. Ni) — 222 atoms:
Ni(111): 42 Ni / layer (2 layers)
Ni_2C: 18 C + 36 Ni
EG: 84 C

RG — 226 atoms:
Ni(111): 42 Ni / layer (2 layers)
Ni_2C: 18 C + 36 Ni
RG: 88 C (slightly compressed)

RG/Ni_2C/Ni(111) and EG/Ni_2C/Ni(111): Structural properties & thermodynamics

From DFT simulations:

- Ni_2C is thermodynamically stable under both EG and RG
- Ni_2C detaches both EG and RG from the substrate:

$h(Gr\text{-}Ni_2C) = 3.08$ Å ($h(Gr\text{-}Ni(111)) = 2.10$ Å)

$E_{ads} = -0.10$ eV/C_{gr}

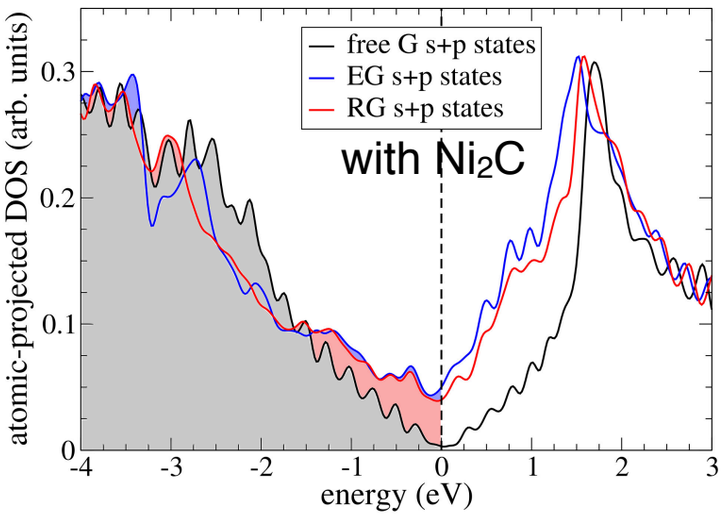
=> Open question:

if Ni_2C is stable under both EG and RG, what makes the difference?

$RG/Ni_2C/Ni(111)$ and $EG/Ni_2C/Ni(111)$: Electronic properties

Also very similar for EG and RG:

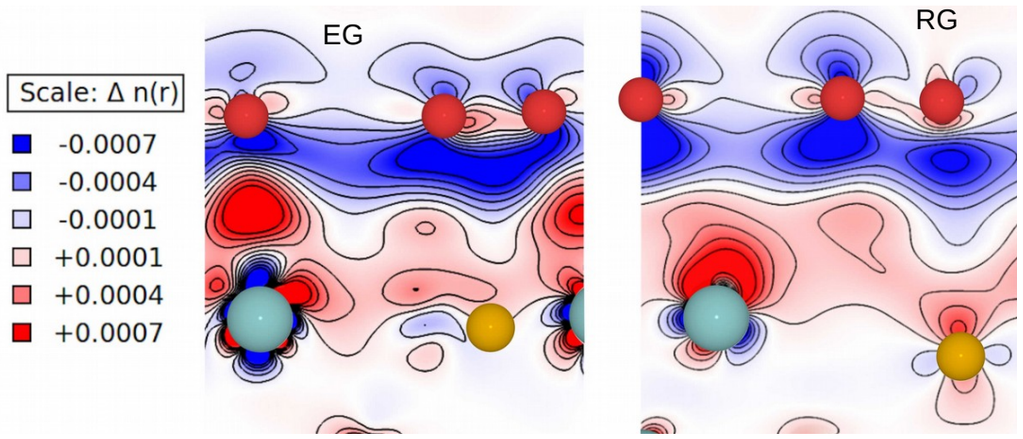
- **Graphene DOS** suggests a weak interaction with the substrate



similar to free G (Dirac cone restored); consistent with exp. observation of switching from metallic to semi-metallic behaviour

- small **electron transfer** from G to substrate

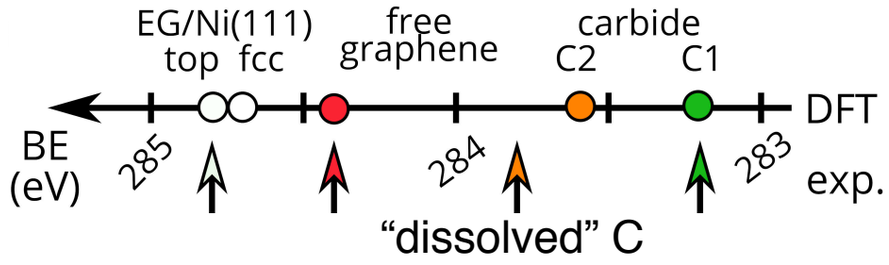
(differential density plots: whole system - constituents)

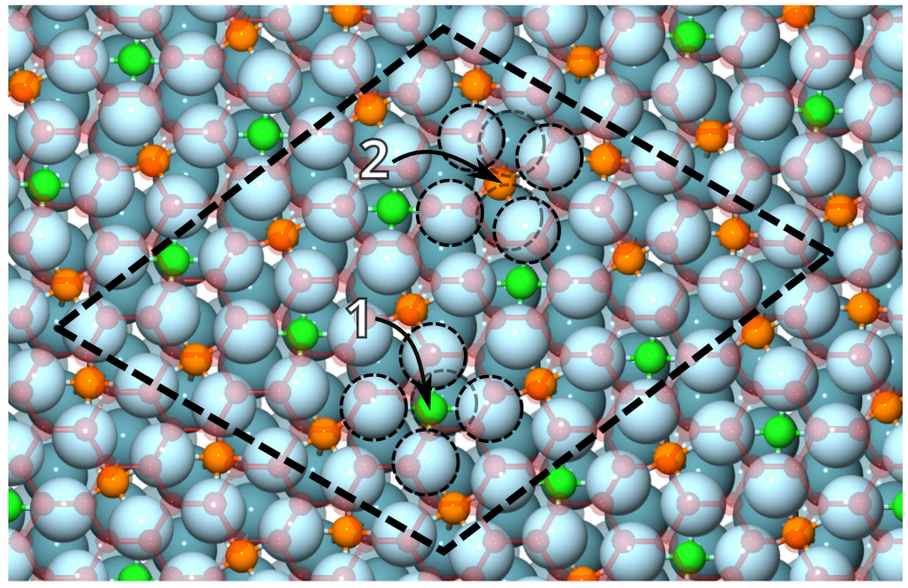


- Calculated **C1s binding energies**

(core level shifts: fingerprints of different C configurations)

allow to interpret the experimental XPS peaks





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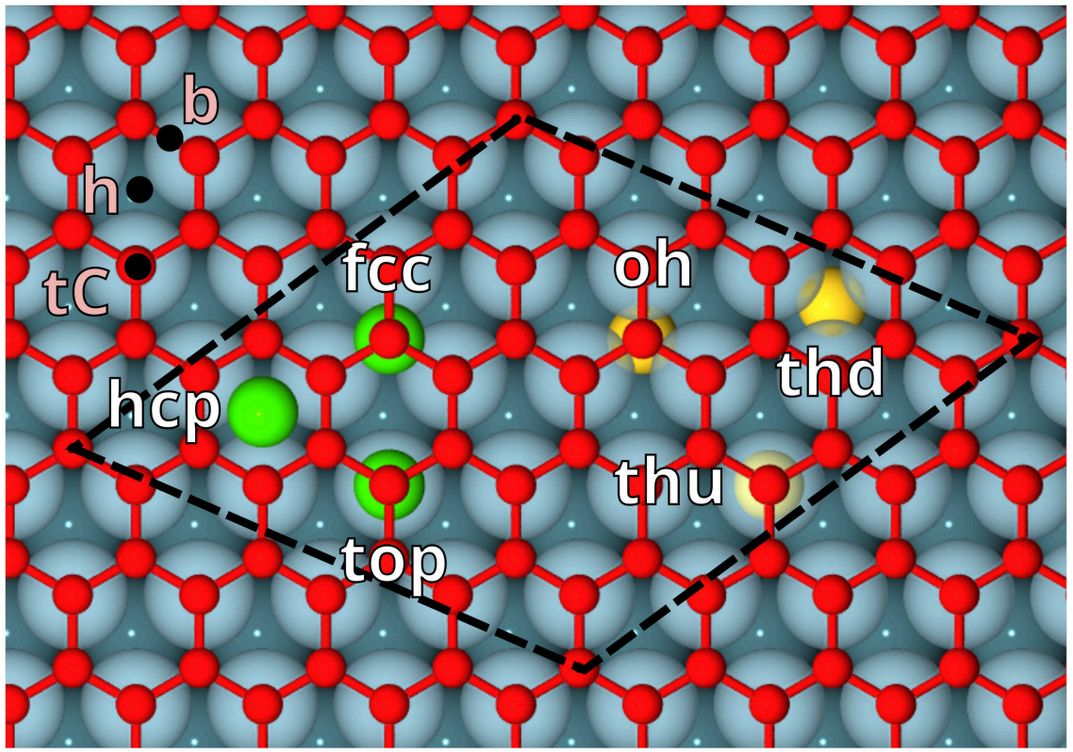
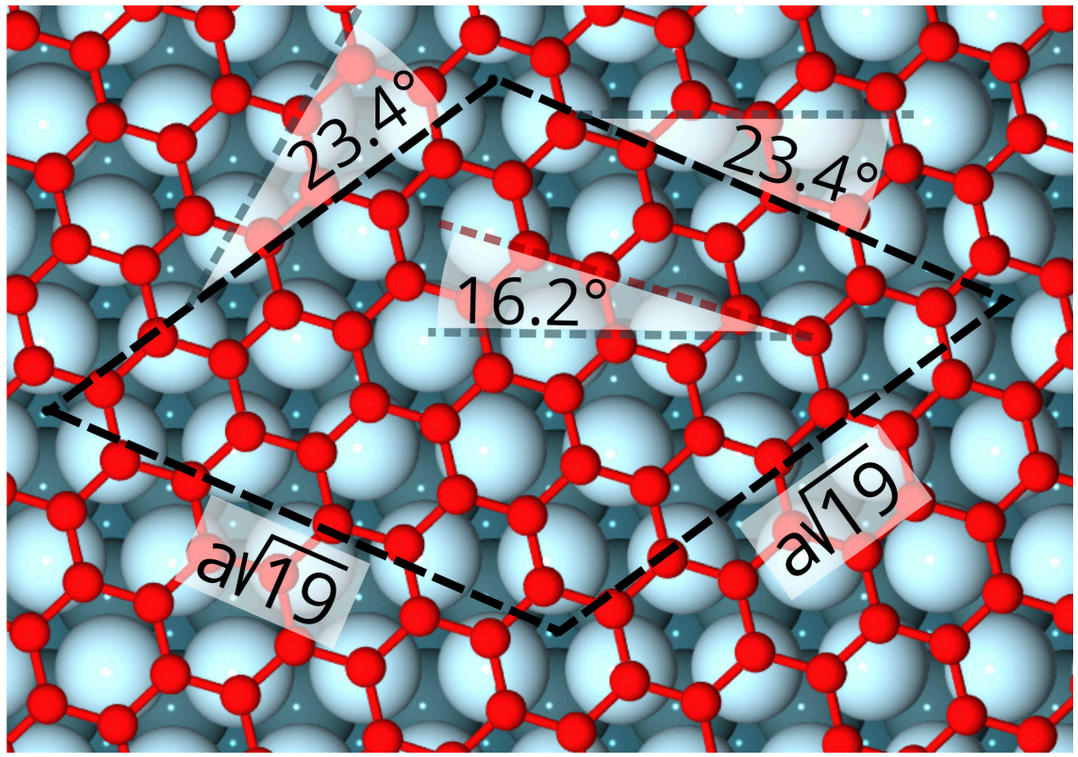
RG/Ni(111) and EG/Ni(111): Structural models and properties

Smallest coincidence cell for RG/Ni(111) (RG rotated by ~17º)

$$(\sqrt{19} \times \sqrt{19})\, R\, 23.4°$$

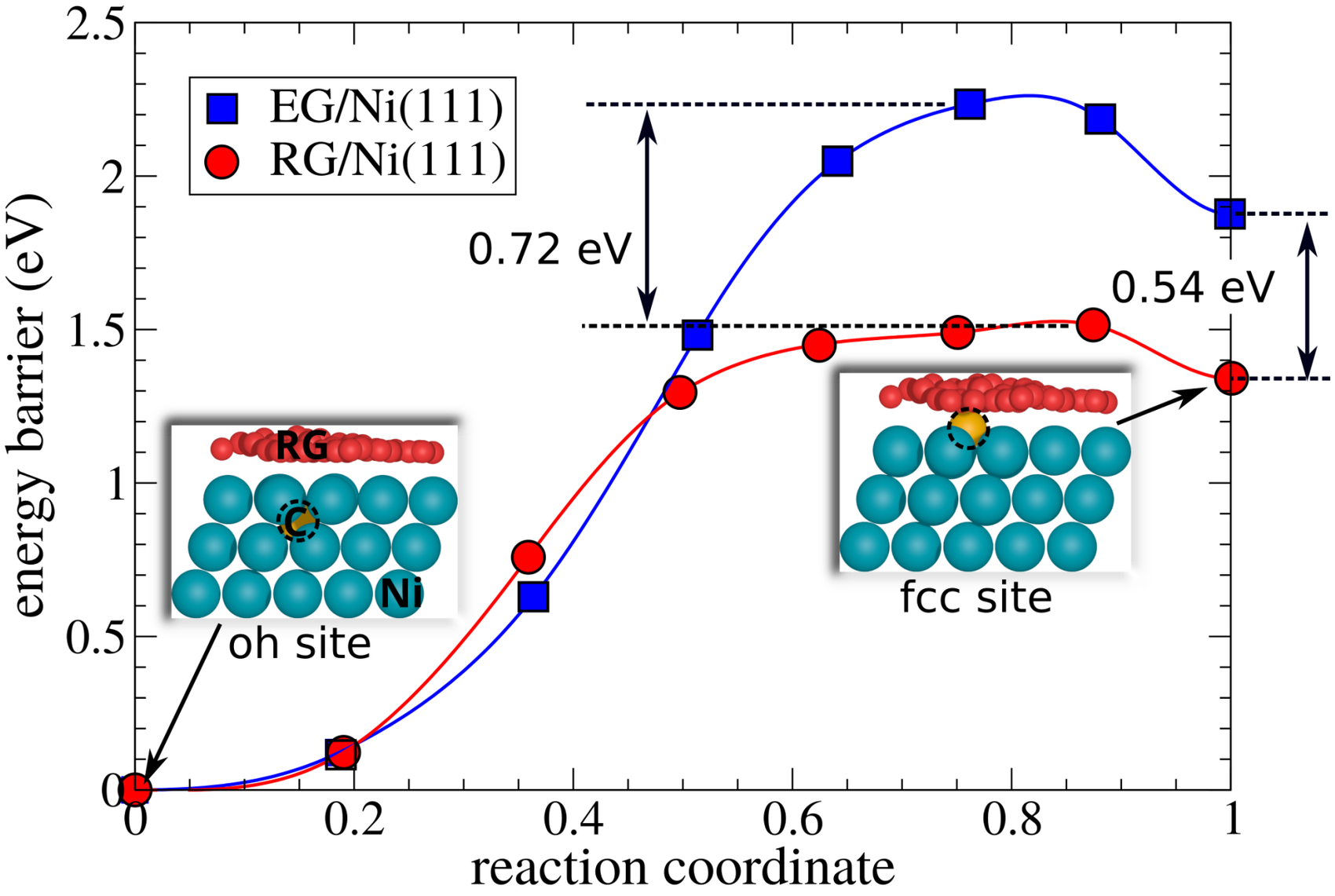




Starting from these structures, investigate the segregation of C atoms dissolved in Ni bulk towards different surface/subsurface positions:

- oh : the most stable subsurface
- fcc: the most stable on surface

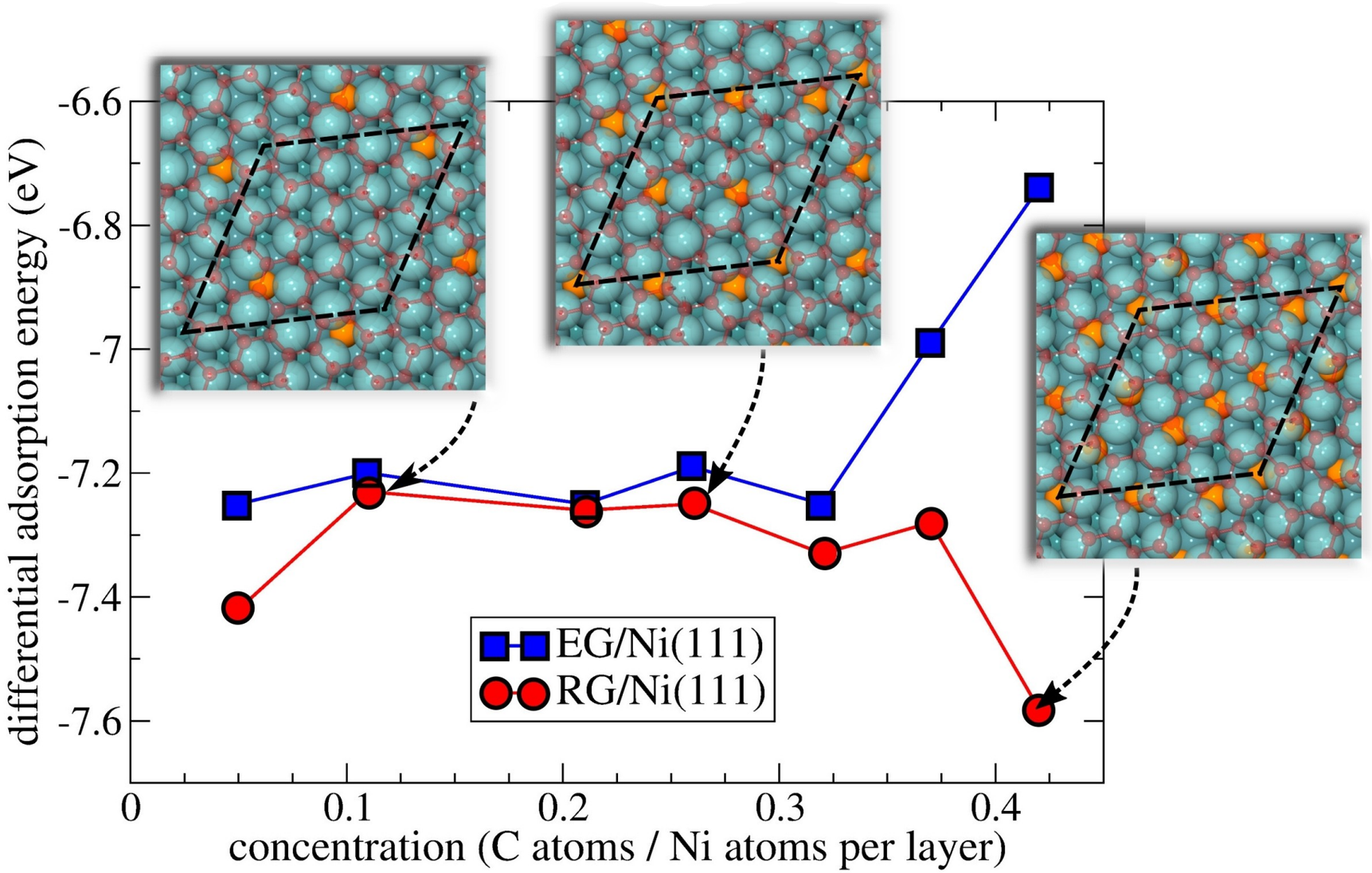
Towards Ni_2C formation under RG/Ni(111) and EG/Ni(111)



Segregation of one individual C atom at a time:

- subsurface o*h* sites are the most stable for dissolved C in Ni both under **RG** and **EG** (compatible with Ni2C formation !)
- for small dissolved C concentration, surface segregation is an activated process with high energy barriers (higher for **EG**, but this **does not make a big difference**)

Towards Ni_2C formation under RG/Ni(111) and EG/Ni(111)



Segregation of further C atoms:

- C concentration < 0.35 ML: similar chemical potential in **RG** and **EG**
- C concentration > 0.35 ML (towards the characteristic C concentration of 0.5 ML in Ni_2C): segregation much easier under **RG** than **EG -** this **does make the difference!**

Conclusions

- From thermodynamics, Ni_2C should be stable at the interface graphene/Ni(111) both under EPITAXIAL and ROTATED G domains, but it is observed only under RG
- Calculated structural and electronic properties of graphene/Ni_2C/Ni(111) are also very similar for both EG and RG domains (G detached by Ni_2C from the surface, recovering ~free-standing features)
- Kinetics arguments for surface segregation of individual C atoms dissolved in Ni bulk do not explain the difference between EG and RG domains for blocking/favouring Ni_2C formation
- **Substantial differences between the chemical potentials for high concentration of C atoms segregated on Ni surface under EG and RG explain the observed Ni_2C formation only under RG**

Thank you for your attention

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