

Vinča Institute of Nuclear Sciences

# Understanding trends in lithium binding at two-dimensional materials

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## Introduction

Layered structure and peculiar electronic properties of two-dimensional (2D) materials foster the concept of utilizing them as main components of lithium-ion batteries. Study of Li atoms adsorbed at graphene showed that Li atoms, featuring a long-range electrostatic repulsion, are individually dispersed across the surface [1]. This was a motivation for the further investigation of Li adsorption at various 2D materials. In this study density functional theory was applied to reveal the microscopic picture of Li interaction with fifteen 2D crystals. We found that the general trend in Li binding can be estimated from positions of conduction band minima (CBM) of 2D materials since the energy of the lowest empty electronic states are correlated with the strength of Li adsorption. At variance to the majority of studied surfaces where the electron transferred from Li is spread across the substrate, in monolayers of carbides of Group XIV elements the interaction with Li and the charge transfer are well localized. This gives rise to their capability to accommodate Li structures with a nearly constant binding energy of alkaline atoms over Li coverages ranging from well-separated adatoms to a full monolayer [2].

## Methodology

### Computation

- **Atomic Simulation Environment (ASE)** package for setting up atomistic structures
- **GPW** code for running simulations
- **projector augmented-wave (PAW) method** in real space
- **GGA-PBE** approximation to exchange-correlation potential
- **supercell approach** with periodic boundary conditions within layer and open boundary conditions in direction perpendicular to the surface
- **Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm** for structure relaxation

GPW!

ASE

### Li adsorption on graphene

- Li-2s electron transferred to graphene and delocalized
- no clusterization of Li due to repulsion between Li ions

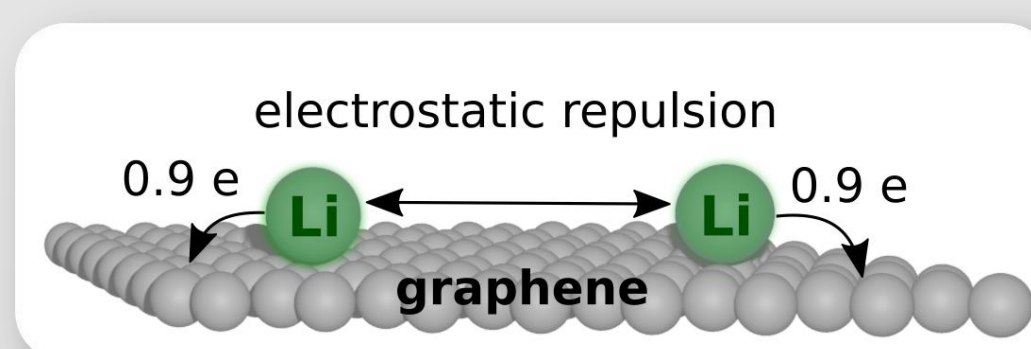


Fig. 1 – Schematic representation of Li atoms on graphene

### Main idea

- Li-2s valence electron will be transferred from Li atom to the lowest unoccupied states of 2D crystal (CBM if it is a semiconductor) if their position on energy scale is lower than the position of 2s state
- the binding of Li atom to 2D crystal is stronger if the difference between the Li-2s state and the CBM is larger

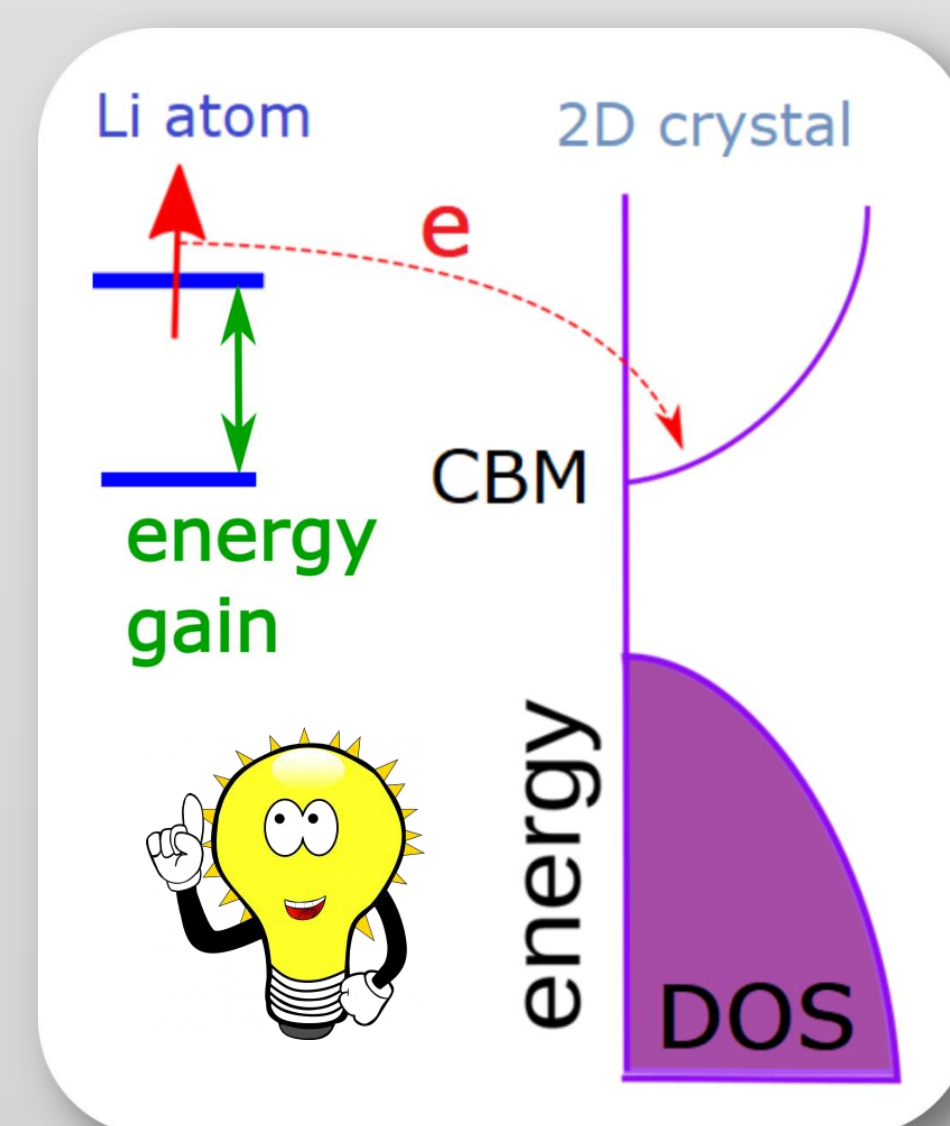
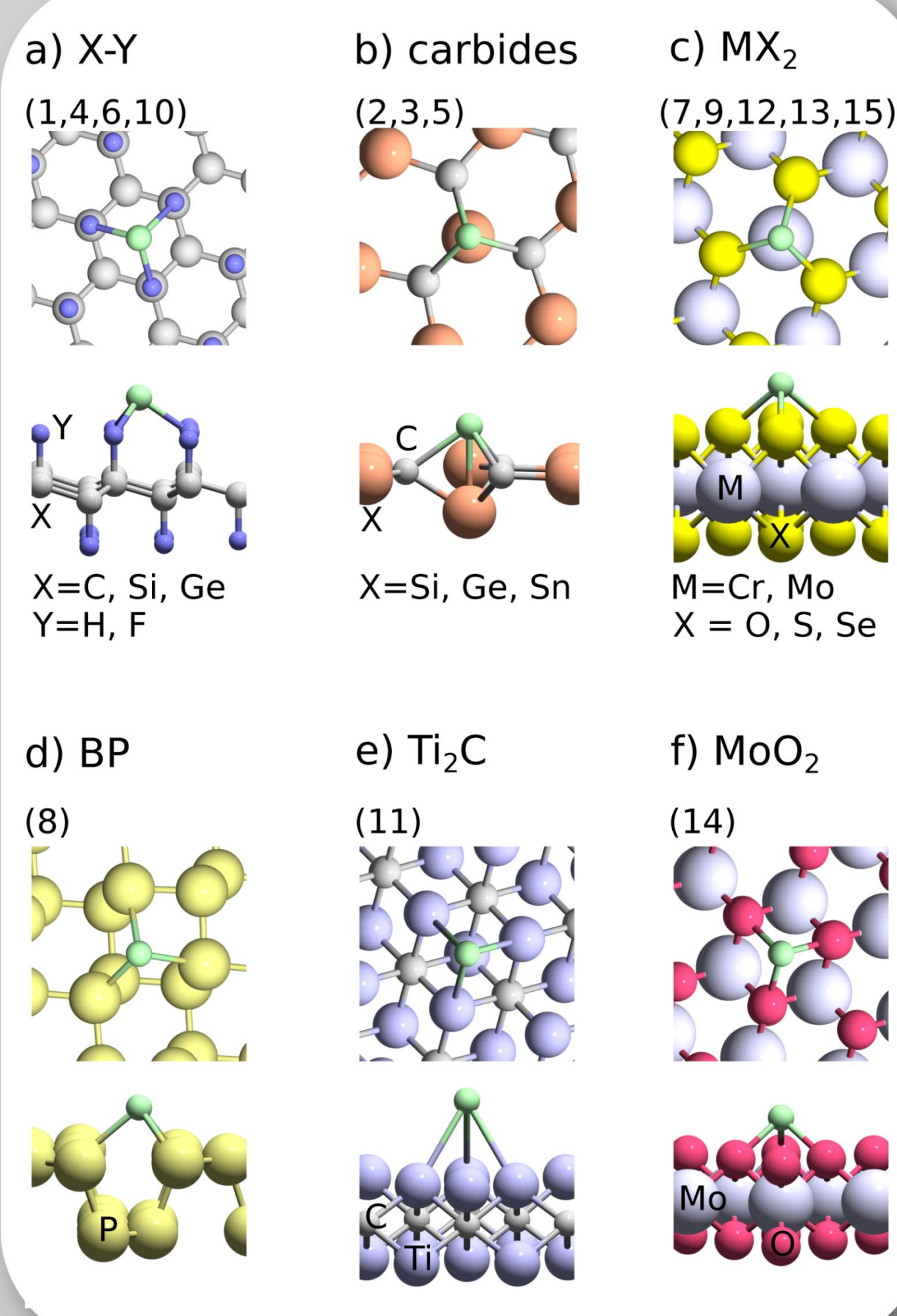


Fig. 2 – Schematic representation of electron transfer from Li to 2D crystal.

Fig. 3 – Top and side view of Li adatom on 2D crystals. Numbers correspond to the list on the left.

### 2D crystals

1. graphene (Gra-H)
2. SiC
3. GeC
4. silicane (Si-H)
5. SnC
6. germanane (Ge-H)
7. MoSe<sub>2</sub>
8. phosphorene (BP)
9. MoS<sub>2</sub>
10. fluorinated graphene (Gra-F)
11. Ti<sub>2</sub>C
12. CrSe<sub>2</sub>
13. CrS<sub>2</sub>
14. MoO<sub>2</sub>
15. CrO<sub>2</sub>



## Results

### Low coverages - Li atom on 2D crystals

- binding energy of Li adatom on 2D crystals can be estimated from the position of the lowest unoccupied states of 2D crystals
- classification of 2D crystals in two groups – **BLUE** and **RED** – is based on the Li adsorption properties

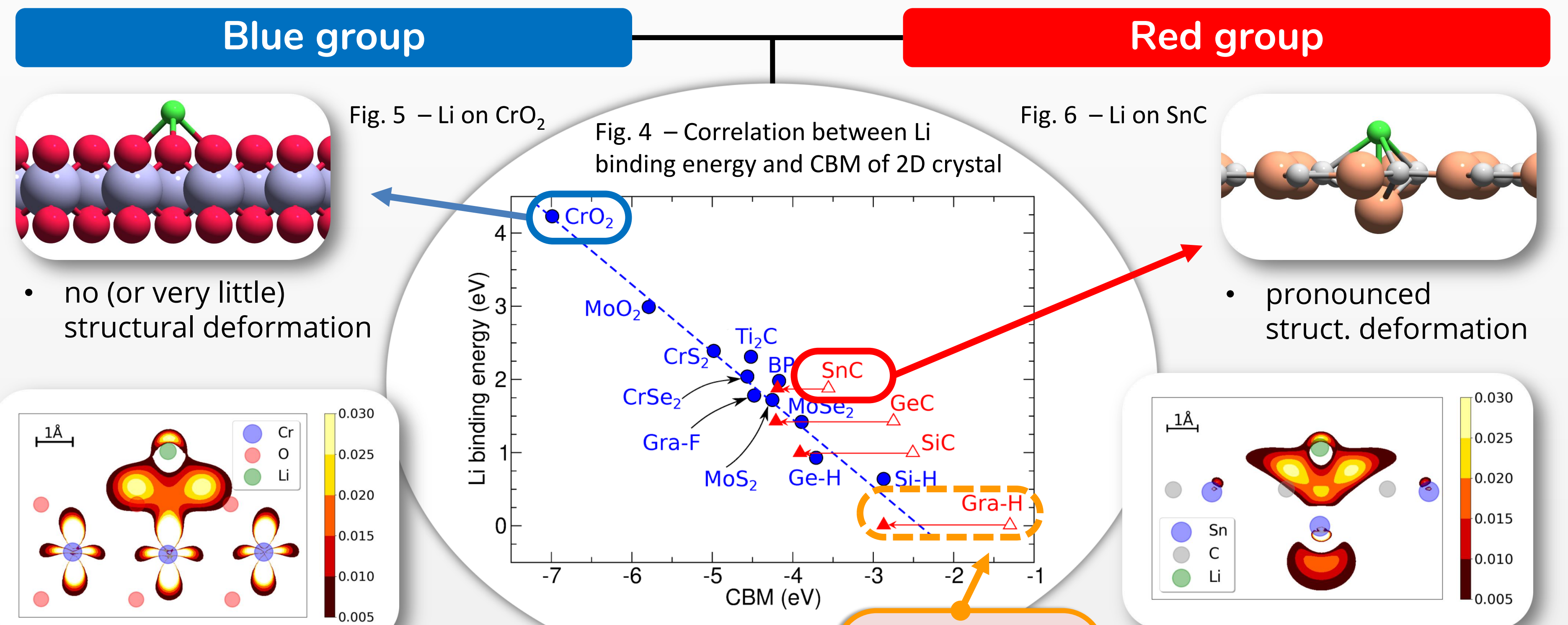


Fig. 7 – Electron density induced upon Li adsorption on CrO<sub>2</sub>

- no (or very little) structural deformation
- transferred electron charge delocalized across the surface
- progressive filling of the lowest unoccupied states upon Li adsorption

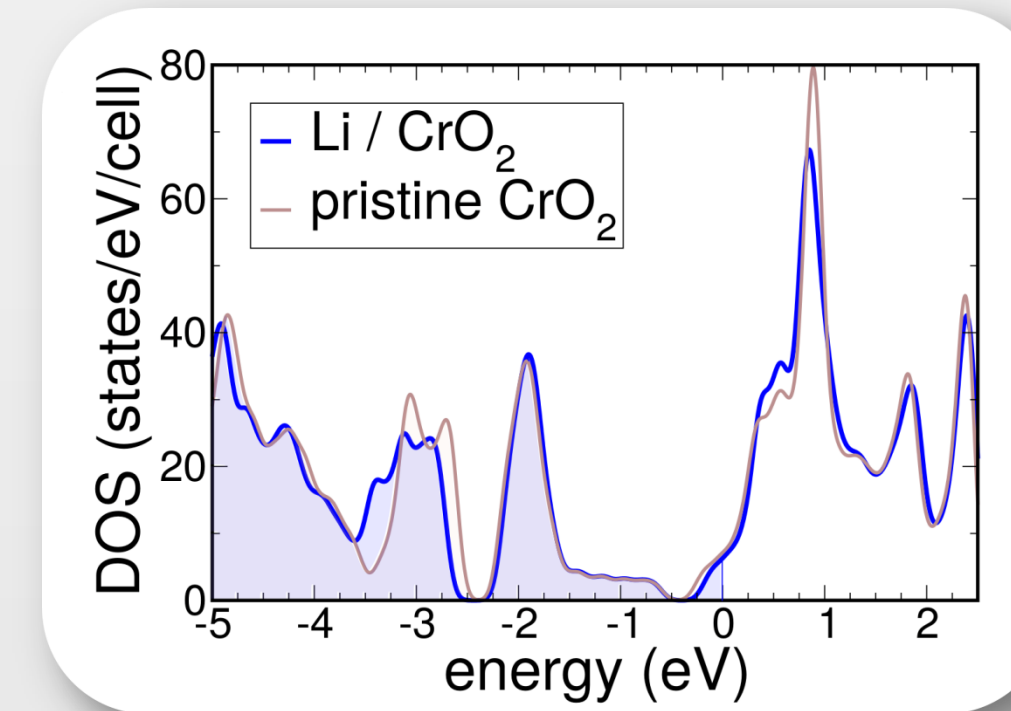


Fig. 9 – Total DOS of pristine CrO<sub>2</sub> and CrO<sub>2</sub> with adsorbed Li atom

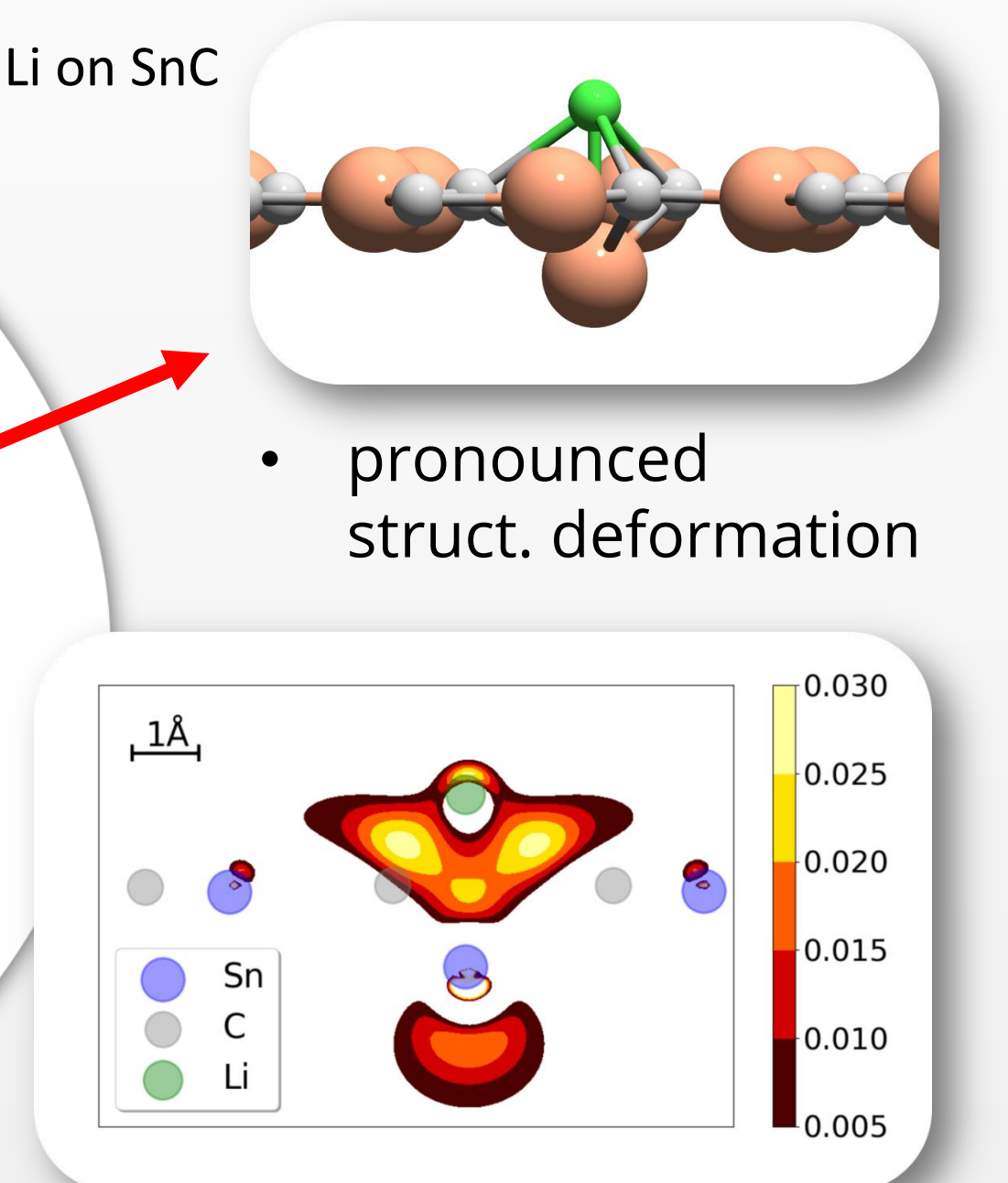


Fig. 8 – Electron density induced upon Li adsorption on SnC

- pronounced struct. deformation
- transferred charge localized in the vicinity of Li atom
- Li electron fills the midgap state of SnC induced upon Li adsorption
- midgap state can accommodate 2 electrons

midgap state is the lowest empty state

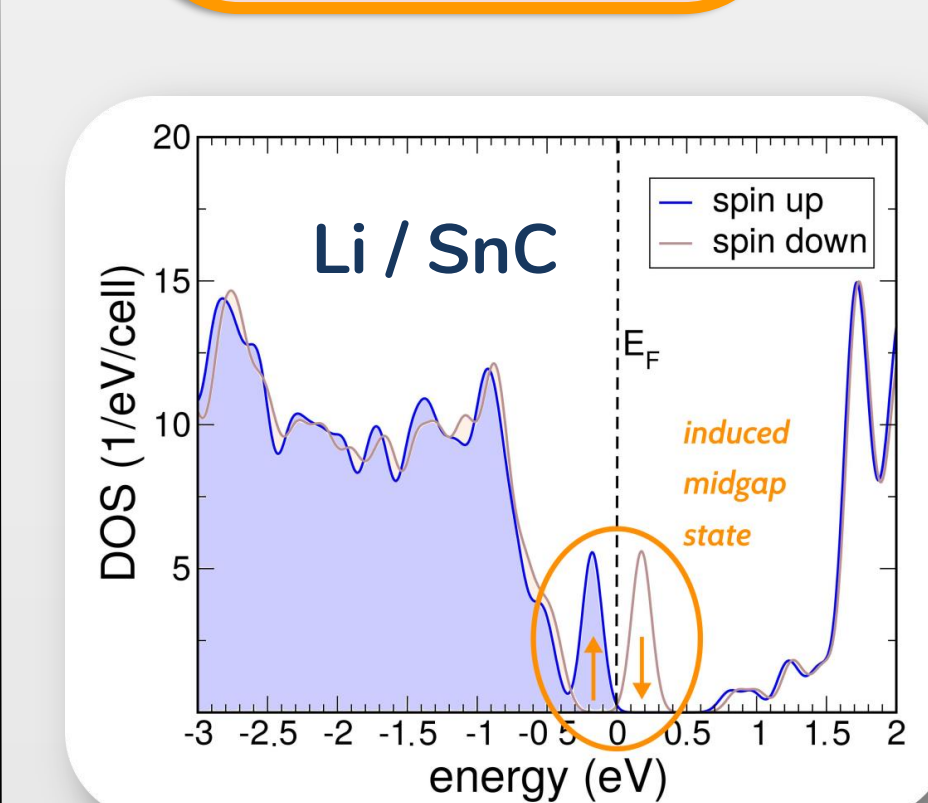


Fig. 10 – Spin-resolved total DOS of SnC with adsorbed Li atom

### High Li coverages of CrO<sub>2</sub> and SnC

- Li atoms on CrO<sub>2</sub> do not show tendency towards clustering while the formation of **Li dimers on SnC** is very favorable

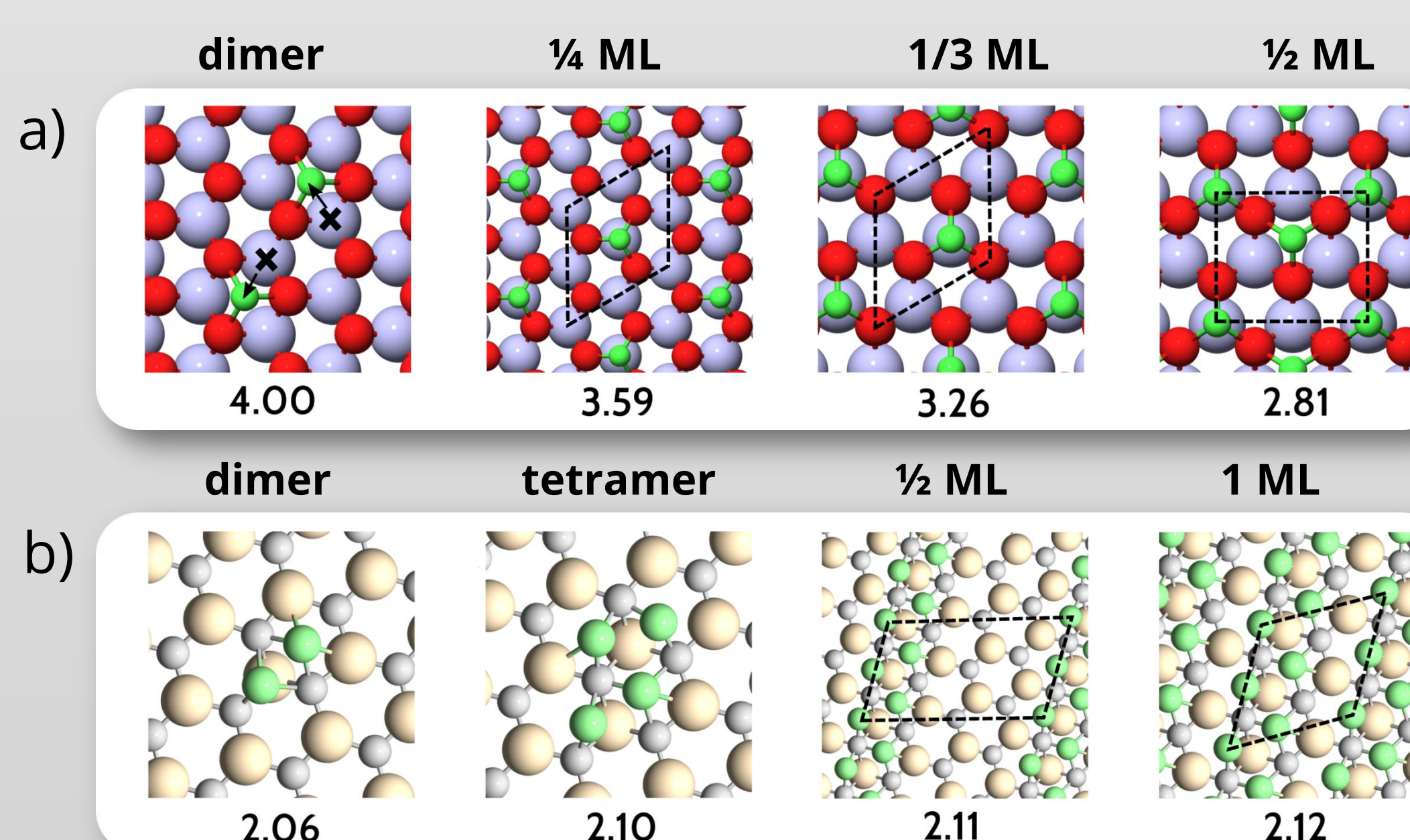


Fig. 11 – The most stable structures of Li on a) CrO<sub>2</sub> and b) SnC with different coverages. Corresponding binding energies (in eV) are presented in the bottom.

- **Li on CrO<sub>2</sub>** - binding energy **steeply decreases** with the increase of Li coverage
- **Li on SnC** - binding energy **nearly constant** as Li coverage increases

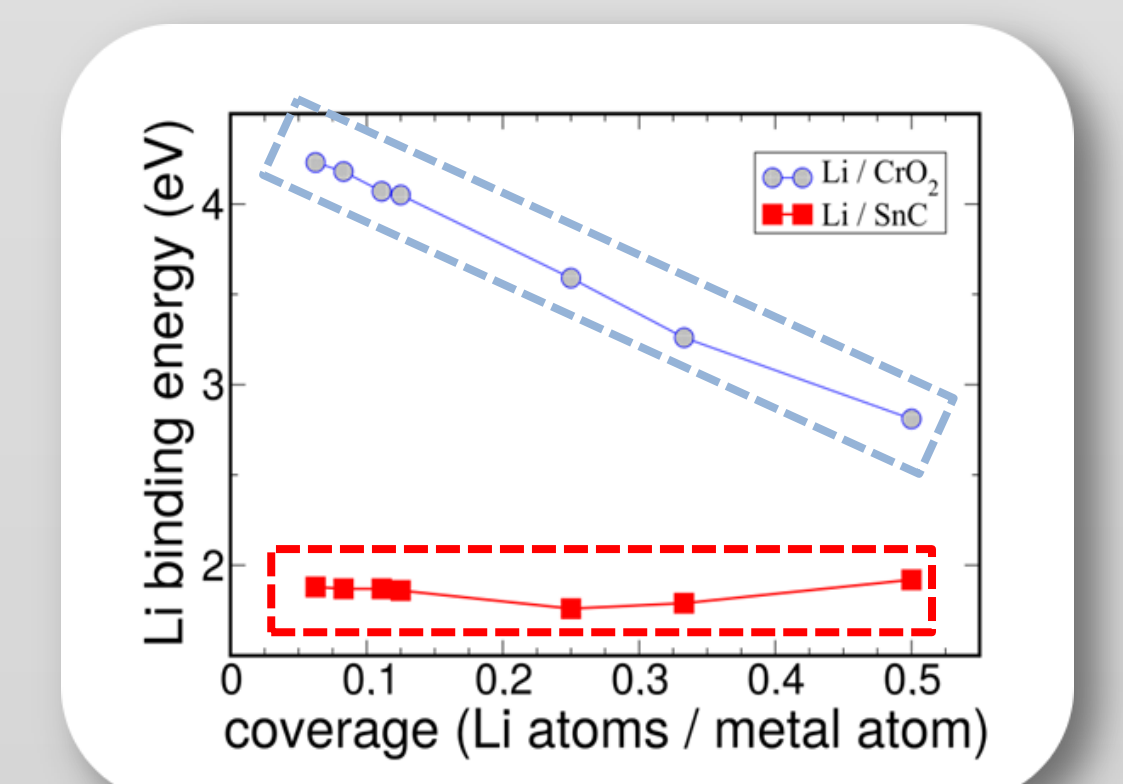


Fig. 12 – Binding energy as a function of coverage for Li adsorbate on CrO<sub>2</sub> (blue dots) and SnC (red squares).

## Conclusion

- Li adsorbed on 2D crystals belonging to the **blue group** causes only minor changes in their structural properties. Moreover, the effect of adsorbate on electronic properties of surfaces is limited to a simple charge transfer. Structures with high Li coverage are unfavorable due to long-range Li-Li repulsion.
- Li binding to 2D crystals from the **red group** causes significant structural deformation of these structures and qualitative changes in their electronic properties as the **midgap states** emerge. Midgap state can accommodate two electrons – this property enables formation of Li dimers on these surfaces.
- Electron transferred from Li-2s state to the midgap state of SnC is localized in the vicinity of Li atom. This suppresses the long-range Li-Li repulsion and enables the formation of **dimerized chains** of Li atoms with a nearly constant value of binding energy from low coverages up to the coverage of 1 ML. In these adsorption configurations the energy penalty for structure deformation is shared between two Li atoms.

## References

- [1] S. Stavrić, M. Belić and Ž. Šljivančanin, Carbon 96, 216 (2016)
- [2] S. Stavrić, Z. S. Popović and Ž. Šljivančanin, Phys. Rev. Mater. 2 (11), 11407 (2018)

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