Diffusion and Intercalation of Alkali Atoms in Transition Metal Dichalcogenides

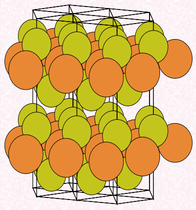
C. Ramírez and W. Schattke
Institut für Theoretische Physik und Astrophysik, CAU Kiel, Germany

Introduction

Many interesting physical properties which also yield applications in various technical fields are connected to the quasi two-dimensional behavior of the ***transition-metal dichalcogenides*** such as Fermi surface nesting, charge density waves, structural phase transitions, and intercalation.
Experimentally extensively investigated, questions are still open to be answered by theory. Here, the first ***ab-initio*** structure investigations are presented which try to elucidate the interplay between **adsorption** and **intercalation** of alkali atoms at these layered crystals.
As a prototype for which intercalation seems to be experimentally well established the system ***Li*** with ***TiSe₂*** has been explored with ***ab-initio*** calculations to yield:

- What are the adsorption positions on the surface?
- How does ***Li*** diffuse on the surface and what are the energy barriers?
- Which geometrical paths do lead to intercalation and which are the energy barriers the alkali atom has to overcome to make the direct intercalation possible?
- Which differences from surface diffusion ***Li*** does experience within the van der Waals gap?

Crystal Structure



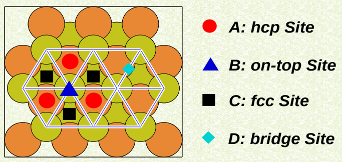
TiSe₂ with ***1T-CdI₂*** structure is made up of a plane of **titanium** atoms surrounded on adjacent sites by two **seleniums** planes.

Method

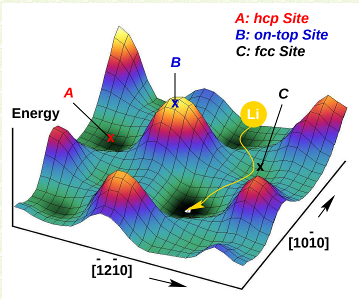
- Our calculations employ Density Functional Theory using the Local Density Approximation (**LDA**) for the exchange-correlation functional as implemented in the **FHImd98 [1]** code.
- Fully separable norm-conserving pseudopotential constructed following the scheme of **Troullier** and **Martins [2]**, are used to describe the interaction of electrons and ions.
- The eigenfunctions of the Kohn-Sham operator are expanded in a plane-wave basis set using a cutoff of **40 Ry**.
- Simultaneous relaxation of electronic and ionic degrees of freedom using a first order iterative technique.
- Supercell with **3** layers of ***TiSe₂*** and a **6.3Å** vacuum region.

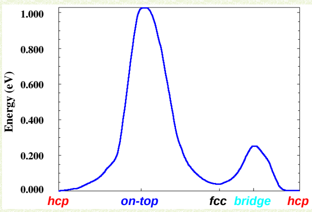
Diffusion of Li on $TiSe_2$ (0001)

Where can Li adsorb on $TiSe_2$ (0001) ?



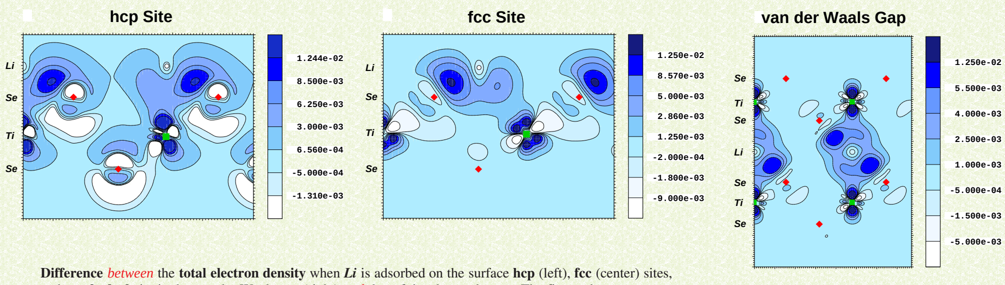
Four different surface sites are especially denoted by ***hcp***, ***fcc***, ***on-top***, and ***bridge*** referring to the stacking of the uppermost ***Ti*** plane, the ***Se*** plane above, and a full adsorbate plane.





- Two adsorption sites on ***TiSe₂*** (0001): ***hcp*** and ***fcc***.
- For a **Li** adatom the ***hcp*** site is energetically slightly preferred over the ***fcc***.
- The energetically lowest transition site (corresponding barrier: 0.263 eV) is the ***bridge*** position.
- The migration over the ***on-top*** position is energetically unfavorable.

Electron Density differences



Difference *between* the **total electron density** when ***Li*** is adsorbed on the surface **hcp** (left), **fcc** (center) sites, and **octahedral-**site in the van der Waals gap (right) *and* that of the clean substrate. The figure shows contours in the plane normal to the surface and parallel to the [1120] axis. The contour lines are given in $bohr^{-3}$.

- The electron density is accumulated in the region between ***Se*** and ***Li*** as well as in the ***Ti*** position.
- When the adatom is adsorbed on the ***hcp*** site the ***Ti 3d*** orbitals, a mixture of d_{z^2} , d_{xz}, and d_{yz} with prominence of the first one, point to the ***Li*** position, as they do also for the ***fcc*** position of the adatom but d_{xz}, and d_{yz} becoming more important.
- At the van der Waals gap the same charge transfer from ***Li*** to ***Ti*** is observed as in the surface.

Surface

Alkali Metal	*bridge*	*fcc*	*on-top*
Li	0.263	0.041	1.05
Na	0.123	0.008	0.80
Rb	0.059	0.003	0.55
Cs	0.012	0.000	0.43

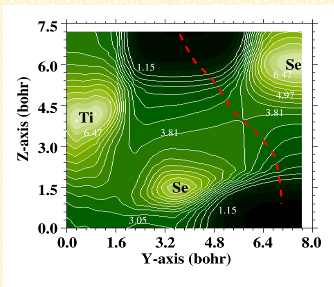
van der Waals gap

	octahedral	*bridge*	*tetrahedral*
Li	-0.55	-0.12	-0.19

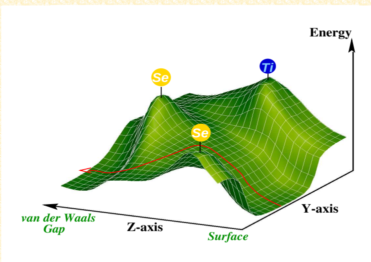
Energy differences (in eV) of the ***bridge***, ***fcc***, and ***on-top*** sites with respect to the ***hcp*** site at the surface, and, last line, in the van der Waals gap.

- In contrast to the results for ***Li***, we found for ***Na***, ***Rb*** and ***Cs*** adsorption that the calculated energies for the ***hcp*** and ***fcc*** sites are equal within the accuracy of our method.

Intercalation



Contour plot of the total energy (eV) in the intercalation plane comprising ***fcc*** adatom site, ***Se*** of the first, ***Ti*** of the second and ***Se*** of the third atomic plane. The y-axis is parallel to the [1120] vector. Energy zero corresponds to the ***hcp*** surface adsorption site located at z = 9.15 a. u. The center of the van der Waals gap is at z = -1.7 a. u. The dashed line indicates the intercalation path.



The lithium has to overcome a barrier of **3.88 eV** to make the **direct intercalation** possible.

Less energetically unfavorable direct intercalation path.

1. ***Li*** attains the fcc site on the first ***Se*** atomic plane with a **cost** of **1.15 eV**.
2. It moves to a bridge position between two ***Ti*** ions at the second atomic plane with a **cost** of **3.81 eV**.
3. It goes through the tetrahedral hole constituted by the ***Se*** ion of the first atomic plane and three ***Se*** ions of the third atomic plane with an energy **gain** of **0.19 eV**.
4. It finishes intercalation via a bridge position symmetric to that at the surface by reaching the octahedral hole made of six ***Se*** ions surrounding the van der Waals gap with an energy **gain** of **0.55 eV**.

References

[1] M. Bockstedte, A. Kley, J. Neugebauer and M. Scheffler, Comp. Phys. **107**, 187 (1997).

[2] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

http://www.theo-physik.uni-kiel.de/theo-physik/schattke/