Diffusion and Intercalation of Alkali Atoms in Transition Metal Dichalcogenides

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Abstract

Alkali metal atoms deposited on transition metal dichalcogenides (TMDCs) can either diffuse on the surface or intercalate into the van der Waals gaps of the substrate. In order to understand the interplay between adsorption and intercalation of alkali atoms at these layered crystals, we performed a detailed study of the migration and energetics of Li adatom on $TiSe_2$ (0001) surface, employing total-energy density-functional theory calculations. To get insight into stable and metastable states, diffusion paths and diffusion barriers for the Li adatom, we calculated the adatom's potential energy surface (**PES**), to find e.g. the hcp site energetically slightly preferred over the fcc site. Results are also given for other alkali atoms. To obtain information about the adsorbate-substrate bond, the change in the valence electron density and orbital distribution was studied. The paths of direct intercalation for the alkali atom from the surface through the three layered $TiSe_2$ sandwich into the van der Waals gap were investigated. It was found that the alkali atom has to overcome an energy barrier of at least 3.81 eV to make the direct intercalation possible.

Keywords: Density functional calculations; Diffusion and Migration; Surface diffusion; $TiSe_2$; Transition metal dichalcogenides; Alkali metals

1 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, and structural phase transitions. Special interest is focused on the performance of intercalation driven batteries [1], which has motivated numerous experimental studies dealing with the evaporation of alkali metals on TMDCs surfaces in vacuum. Many alkali metals are found to intercalate [2, 3] but it is also observed that e.g. Rb stays on the surface in form of nanowires [4]. Therefore it is necessary to understand the dynamical properties of these adsorbate-substrate systems in detail.

We present the first *ab initio* structure investigations which try to elucidate the interplay between adsorption and intercalation of alkali atoms at these layered crystals. As a prototype for which vacuum intercalation seems to be experimentally well established [5] mainly the system Li with $TiSe_2$ 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?
- How does the diffusion of Li within the van der Waals gap differ from the surface diffusion?

The $TiSe_2$ crystal is made up of layers also called sandwiches. Each layer consists of a hexagonal transition metal sheet surrounded on adjacent sites by two similar chalcogen sheets. The interaction between adjacent layers is weak of van-der-Waals type, though bandstructure calculations together with angle resolved photoemission results reveal significantly dispersing bands (about 2 eV) along the layer perpendicular direction supported by p_z orbitals with admixtures of d_{z^2}. The z-axis is chosen along the c-direction. Those bands related to layer parallel orbitals show almost no dispersion in this direction.[6, 7]

Intercalation may be difficult for atoms starting at a clean surface, but seems to be possible from a step edge or into a surface fissure as the easy intercalation in solution experiments demonstrates. Especially, from stereochemistry the intercalation of the heavier alkali atoms looks rather improbable at a defect free surface. Thus, data for energy barriers towards diffusion and intercalation at an ideal surface will be a valuable information for the growth by van-der-Waals epitaxy. The latter has become an important tool for the preparation of interfaces and heterojunctions. [8]

The paper is organized as follows. Method and program code of the ab-initio structure optimization are outlined in the next section. The subsequent section presents the results of that optimization, with respect to diffusion first and intercalation second, and discusses possible answers to the above cited questions.

2 METHOD

The calculations employ density-functional theory together with the local-density approximation for the exchange-correlation functional [9, 10], as implemented in the FHI98md code [11]. The nonlinear form of the core-valence exchange-correlation functional is taken into account for the alkali metal atoms [12]. Fully separable norm-conserving pseudopotentials constructed by following the scheme of Troullier and Martins, are used to describe the interaction between electrons and ions.[13] The eigenfunctions are expanded in a plane-wave basis using a cutoff of 40 Ry with three special **k** points in the surface Brillouin zone [14]. Increasing the number of **k** points from 3 to 6 changes the energy *differences* by 0.03 eV. The (0001) surface of $TiSe_2$, clean or with an adatom coverage of $\Theta = 1/3$, is modeled by a $(\sqrt{3}X\sqrt{3})R30^\circ$ unit cell with 3 sandwiches of $TiSe_2$ (9 atomic planes) and a 6.3 Å vacuum region. The alkali metal adatom is adsorbed on one side of the slab, where we let relax the positions of all atoms, except for the $TiSe_2$ atoms in the bottom sandwich, which are fixed at their bulklike positions. Convergence with respect to number of planes and cut-off energy is controlled by increasing their values. Calculations with 4 layers of $TiSe_2$ and a cut-off of 60 Ry show that the adsorption energy *differences* are accurately given, which means that they change by less than 0.03 eV. Surface diffusion is investigated for Li, Na, Rb and Cs whereas in the case of intercalation only Li is considered. The total energy surface of the alkali adatom is determined for its diffusion. It is calculated by fixing the adatom laterally at different positions and allowing all other atoms' and adsorbate's height to relax. The total energy surface for the diffusion is mapped on a (1x1) surface unit cell with a mesh width of one sixth of the unit vectors. For intercalation a non-uniform mesh of points is chosen. The distance between the surface and the middle of the van der Waals gap is divided into 12 planes. The average density of points in each plane corresponds to the diffusion case. For diffusion within the van der Waals gap also an optimization along the c axis was carried through.

3 RESULTS AND DISCUSSION

To answer the question whether an alkali adatom can adsorb on the $TiSe_2$ (0001) surface, we considered four different surface sites, which are especially denoted by hcp, fcc, on-top, and bridge. The first two sites are referred to the stacking of the uppermost Ti plane, the Se plane above, and a full adsorbate plane. The on-top site coincides with the projected Se positions, and the bridge point lies between two of them, see inset of figure 1. For each site we calculated the energy of the system, where the first two $TiSe_2$ layers and the height of the alkali adatom are fully relaxed.

For a Li adatom the hcp site is energetically slightly preferred over the fcc site, see Table 1. The diffusion path, see figure 1, between two hcp sites runs via the direct connection of an adjacent hcp and fcc site over the bridge site, with a diffusion barrier of 0.26 eV, see figure 2. The on-top site represents the maximum in the total energy surface, which is 1.05 eV higher in energy than at the hcp site. 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. As the atomic radius in the alkali metals is the major difference between them ($r^{Li} = 1.51$ Å, $r^{Na} = 1.83$ Å, $r^{Rb} = 2.42$ Å, $r^{Cs} = 2.62$ Å) [15], the lower row atoms have increasing distance to the surface and will experience decreasing substrate electron-density and force-field corrugation. Table 1 lists the respective energies. Without calculations we suggest that K will fit into the same pattern.

To study the diffusion of Li within the van der Waals gap we calculated the energy at four inter-sandwich sites: the octahedral, which is surrounded by six chalcogen atoms, two tetrahedrals, which lie immediately below and above the chalcogen atoms, and a bridge position, which is between an octahedal and a tetrahedral site. The results are listed in the last line of Table 1. The octahedral site is found to be energetically more favorable than the tetrahedral and bridge sites. Both tetrahedral sites have the same energy.

In order to analyze the local relaxations of the $TiSe_2$ substrate along the diffusion path in the van der Waals gap, we performed a structure optimization of bulk $LiTiSe_2$ and bulk $TiSe_2$. We obtained the following lattice constants: $a_{LiTiSe_2} = 6.61$, $c_{LiTiSe_2} = 11.90$, and $a_{TiSe_2} = 6.41$, $c_{TiSe_2} = 10.89$ a_B. This values can be compared to the experimental lattice constants, $a^{exp}_{LiTiSe_2} = 6.88$, $c^{exp}_{LiTiSe_2} = 12.31$, and $a^{exp}_{TiSe_2} = 6.68$, $c^{exp}_{TiSe_2} = 11.34$ a_B [16]. From our results, we notice that Li intercalation gives rise to an increase of the c lattice constant by about 9 %. A subsequent optimization was done for the $TiSe_2$ surface system without guest, using a_{LiTiSe_2} and c_{LiTiSe_2} as lattice constants. We obtained an interlayer distance $d_1 = 6.0$ a_B and intralayer distance $d_2 = 5.9$ a_B. The latter serves as reference for the following results. When the Li adatom diffuses within the van der Waals gap (tetrahedral $\rightarrow$ bridge $\rightarrow$ octahedral), the interlayer distance at each site increases by about 8 %, 6 % and 2 %, respectively. At the octahedral site the Li stays at the middle of the van der Waals gap (about 3.1 a_B to each layers). At the bridge site the Li relaxes closer to the lower layer (3.6 a_B and 2.8 a_B to the upper and lower layers, respectively). At the tetrahedral site, which lies immediately below a chalcogen atom, the Li stays at a distance of 4.3 a_B and 2.2 a_B from the upper and lower layers, respectively. At the other tetrahedral site, the distances are the same but in the opposite order.

In figure 3 the difference between the total electron density when Li is adsorbed on the a) hcp site and b) fcc site on $TiSe_2$ (0001) and that of the clean surface is displayed. In both cases the charge transfer from the adsorbate towards the substrate is clearly visible. 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. This is also true for the fcc position of the adatom but d_{xz} and d_{yz} becoming more important. The perturbation of the system caused by the adsorbate does not reach far into the substrate, thus only the changes in the first $TiSe_2$ sandwich are shown. The charge density is essentially identical to that of the clean surface for layers deeper than the first sandwich. The charge density plots display that the charge transfer from the Li atom to the substrate takes place already at the adsorption positions and not only if it being fully intercalated. Thus, it is hard to believe that the charge transfer process can drive the intercalation as it is found in the literature.

To determine the energetically favorable path of intercalation we calculate the total energy of Li placed in different positions between the surface and the van der Waals gap. For each position of Li all $TiSe_2$ atoms in the first sandwich are allowed to relax. The results are presented in figures 4 and 5. The energy zero of this graphic corresponds to the energy of the hcp adsorption surface site. The Li adatom could reach the first atomic plane from just two surface sites, the hcp and fcc. From our results it is evident that the Li experiences an energy barrier in both cases, with increasing energy when it approaches the Ti plane, reflecting a strongly repulsive interaction. The shown path starts at a point located in the first Se atomic plane directly below the fcc surface site, and continues entirely within the single plane perpendicular to the layers containing the starting point, two Se atoms, and one Ti atom. It represents the path of minimum energy barrier. A saddle point is reached in the middle between two Ti atoms of the Ti plane. From there the energy decreases as the Li moves towards the tetrahedral site in the van der Waals gap with an energy of -0.19 eV, already well below its minimum energy when adsorbed at the surface. From this position Li moves to the octahedral site close to the middle plane of the gap, which exhibits its lowest energy -0.55 eV. This last step experiences a slight energy barrier of 0.06 eV. The reverse moving (ochtahedral $\rightarrow$ bridge $\rightarrow$ tetrahedral) would thus meet a barrier of 0.43 eV showing the stability of the octahedral intercalation site in the van der Waals gap, see Table 1. When the Li is in the first atomic plane, below the fcc surface site, the first layer contracts by 8%. At the saddle point, the first layer expands by 2 %. Both results are relative to d_2.

To resume, intercalation is constituted of the following steps:

1. Li attains the first Se atomic plane via the fcc surface site 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.

In the literature mainly direct intercalation and intercalation via defects are considered. Especially, Li generally was thought to be a candidate for direct intercalation because of its small size. Our calculations show that even this material has a far too high energy barrier for direct intercalation being possible.

4 CONCLUSIONS

We have investigated the energetics of diffusion and intercalation of alkali metals on $TiSe_2$ by means of density functional theory. We found that the energy barriers for alkali metal diffusion range from 0.26 eV for Li to 0.01 eV for Cs. We determined the energetically minimal path of intercalation for Li, with the result of an activation barrier of 3.81 eV, which almost excludes this type of intercalation. The diffusion within the van der Waals gap involves via the bridge position at least 0.43 eV, which is larger than the value for diffusion at the surface.

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Table 1

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.

Alkali Metal	bridge	fcc	on-top
Li	0.26	0.04	1.05
Na	0.12	0.01	0.80
Rb	0.06	0.00	0.55
Cs	0.01	0.00	0.43
	octahedral	bridge	tetrahedral
Li	-0.55	-0.12	-0.19

Figure captions.

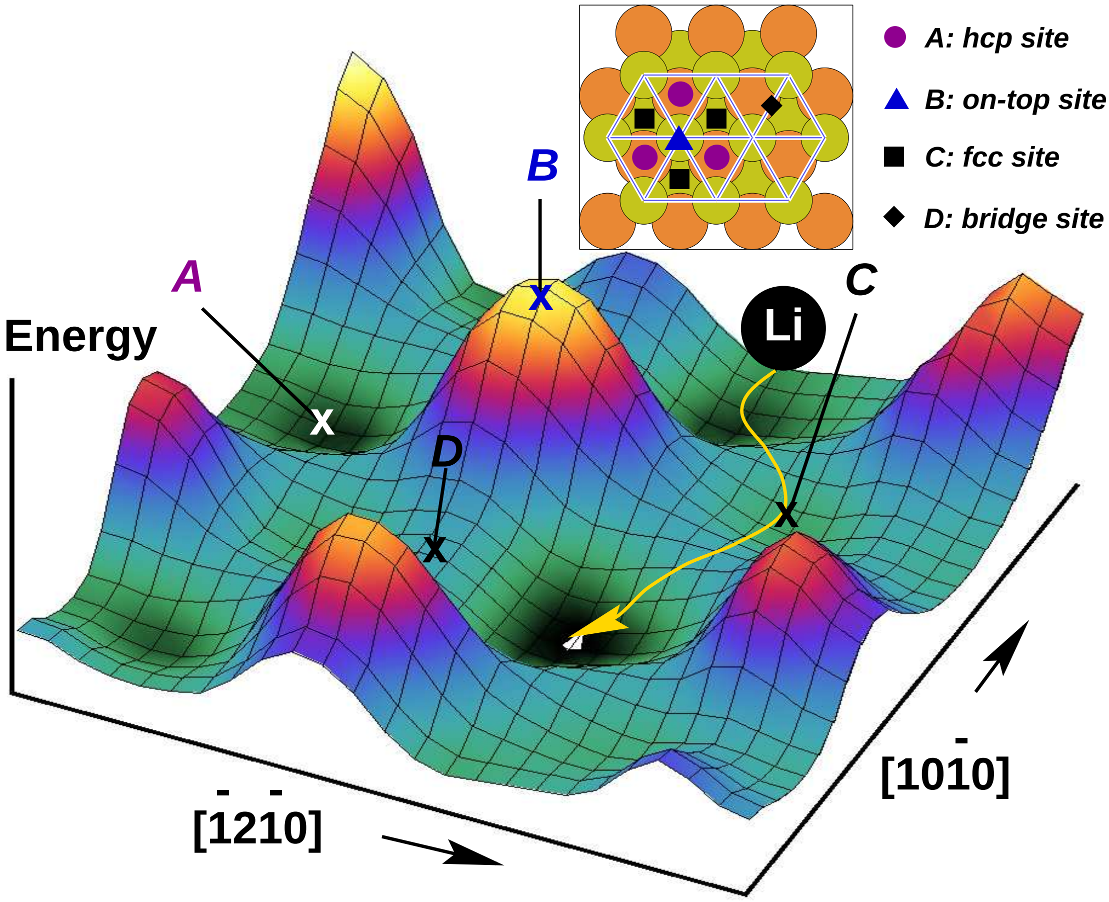
Fig.1 Energy surface of Li diffusion on $TiSe_2$ (0001) with a projection of diffusion path (white solid line) and various adsorption sites given. For the values of the energy axis we refer to the cut in figure 2.

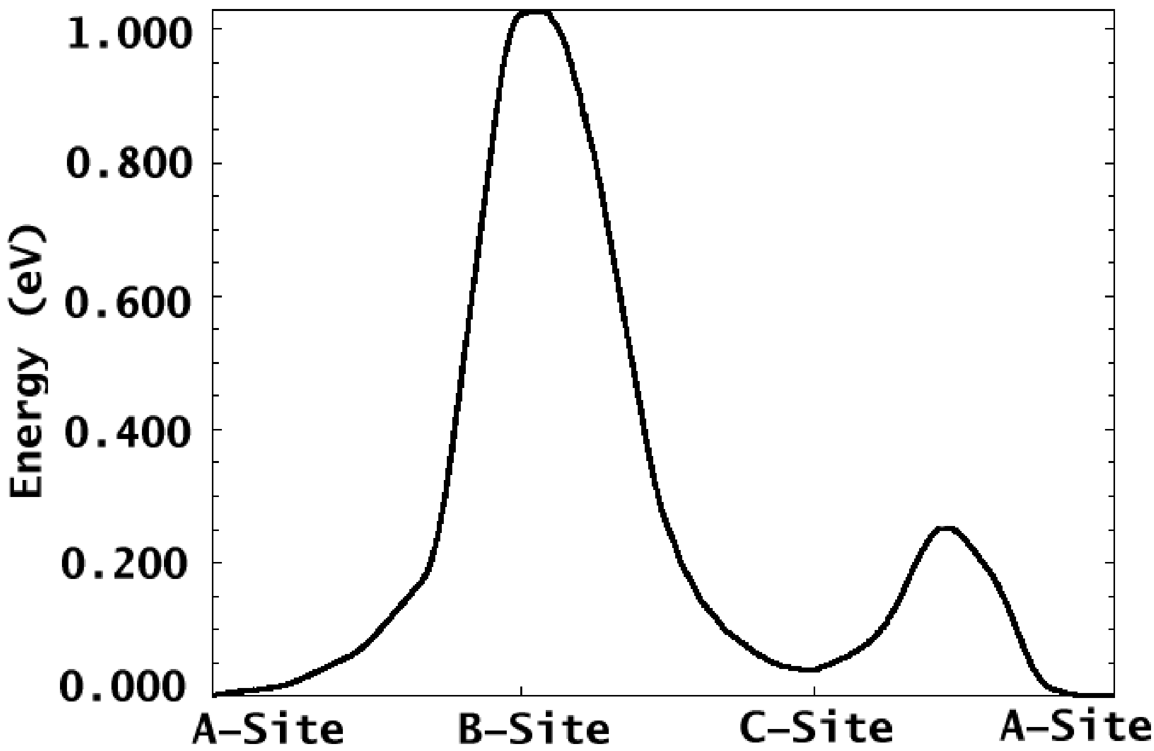
Fig.2 Two-dimensional cut through the energy surface of figure 1 along the diffusion path.

Fig.3 Contour plots of the difference between the total electron density when Li is adsorbed on the a) hcp and b) fcc sites and that of the clean substrate. The figure shows contours in the plane normal to the (0001) surface and the horizontal axis parallel to the $[\bar{1}2\bar{1}0]$ axis. Dark regions correspond to larger density, ion positions as marked. Axis units are a_B, contour units are $10^{-3}\ a_B\ ^{-3}$.

Fig.4 Intercalation energy surface with respect to the position of the intercalant in the intercalation plane; intercalation path denoted by solid line. The y-axis is parallel to the $[\bar{1}1\bar{2}0]$ vector and z-axis normal to the (0001) surface. Energy zero corresponds to the hcp surface adsorption site located at $z = 9.15\ a_B$; center of van der Waals gap at $z = -1.7\ a_B$.

Fig.5 Contour plot of total energy in intercalation plane comprising Se atom of the first, Ti of the second, and Se of the third atomic plane. The y-axis is parallel to the $[\bar{1}1\bar{2}0]$ vector and z-axis normal to the (0001) surface. Energy zero corresponds to the hcp surface adsorption site located at $z = 9.15\ a_B$; center of van der Waals gap at $z = -1.7\ a_B$; contour-line spacing 0.38 eV. The dotted line indicates the energetically favorable intercalation path.

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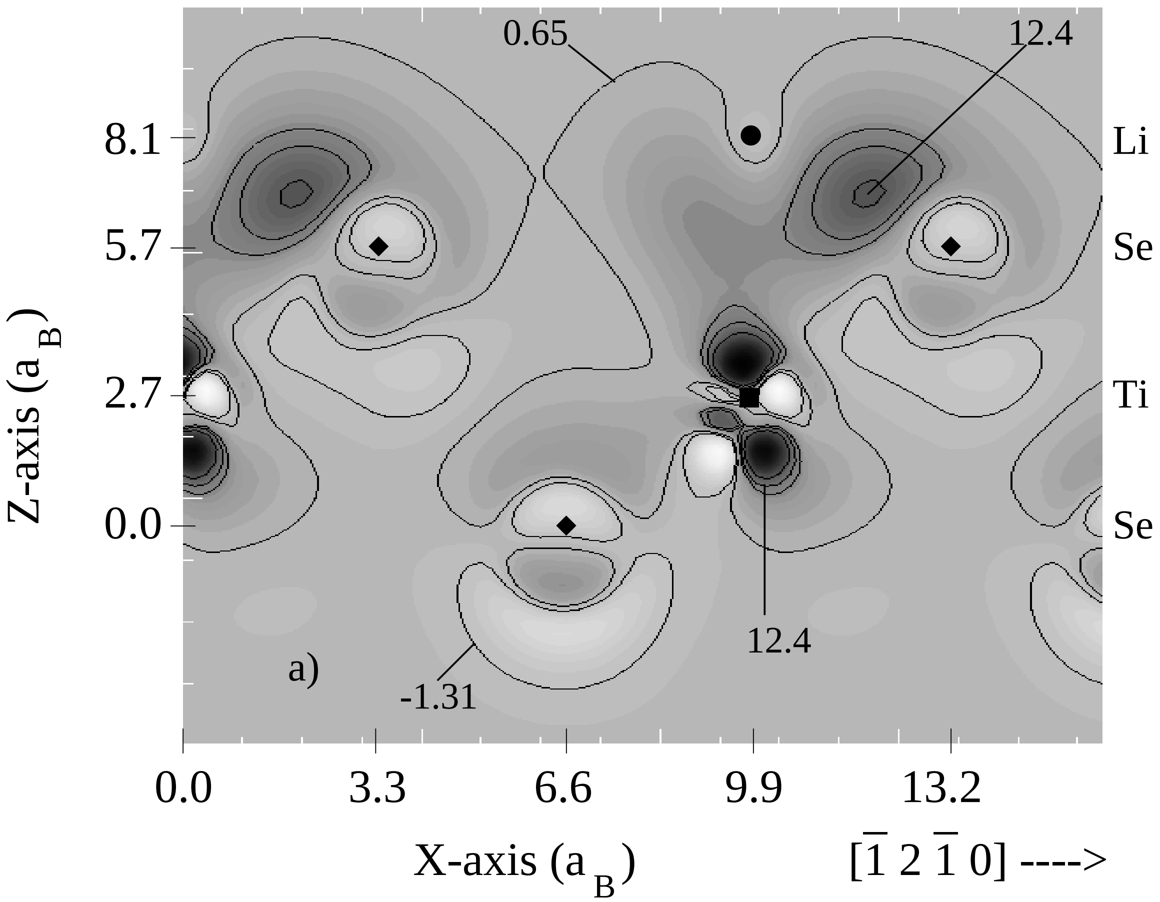
0.800
0.600
0.400
0.200
0.000
A–Site
B–Site
C–Site
A–Site


0.65
12.4
8.1
5.7
2.7
0.0
Li
Se
Ti
Se
Z-axis (a_B)
12.4
a)
-1.31
0.0
3.3
6.6
9.9
13.2
X-axis (a_B)
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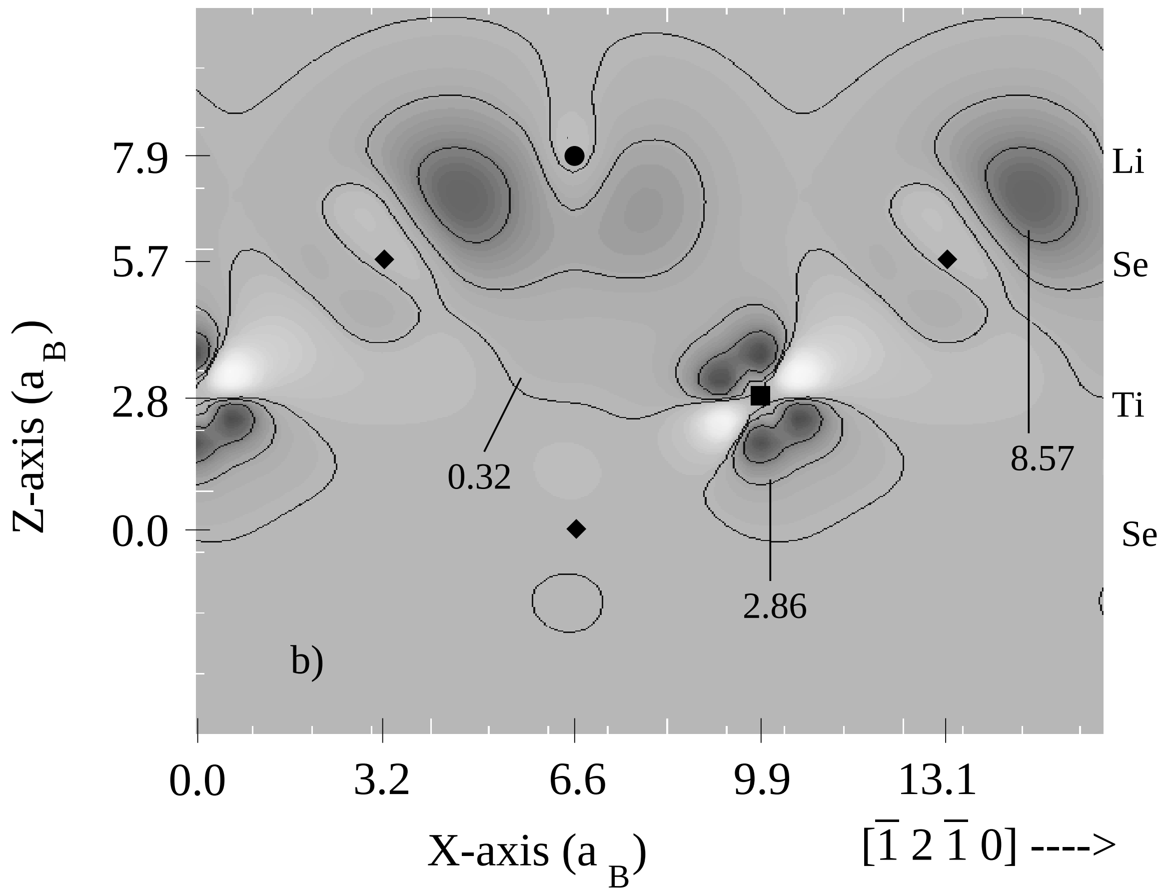
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5.7
2.8
0.0
Z-axis (a B)
Li
Se
Ti
Se
0.32
8.57
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b)
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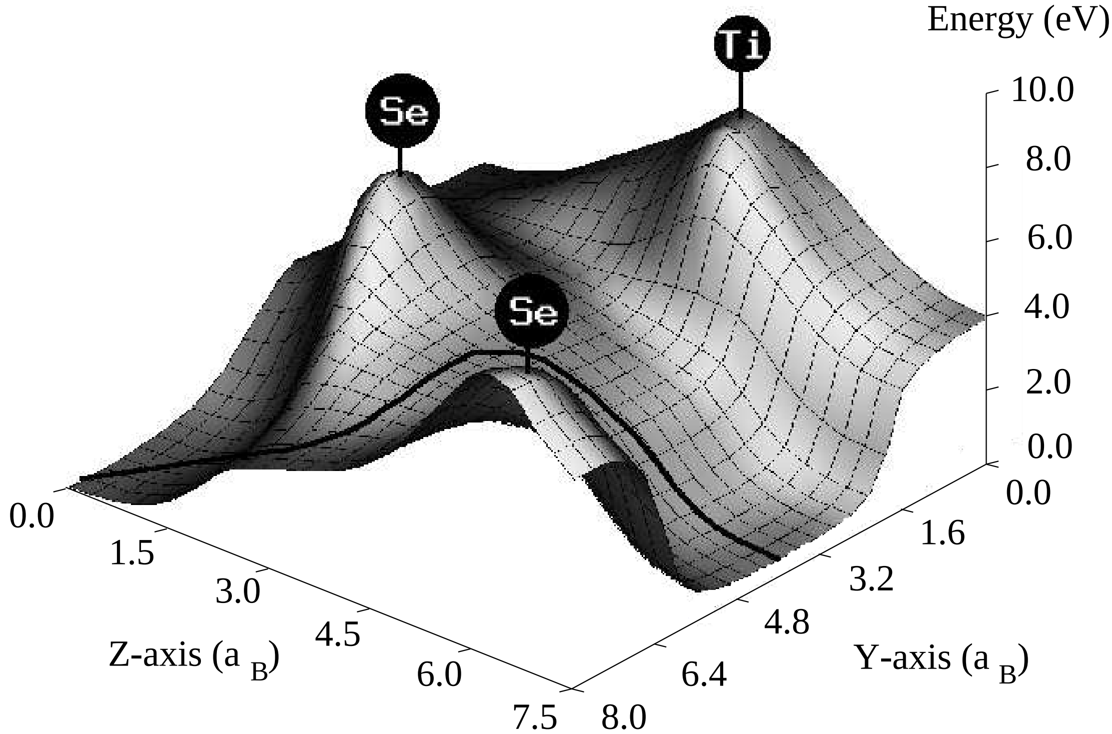
3.2
6.6
9.9
13.1
X-axis (a B)
[$\bar{1}$ 2 $\bar{1}$ 0] ---->


Energy (eV)
Ti
Se
Se
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8.0
6.0
4.0
2.0
0.0
0.0
1.6
3.2
4.8
6.4
8.0
Y-axis (a B)
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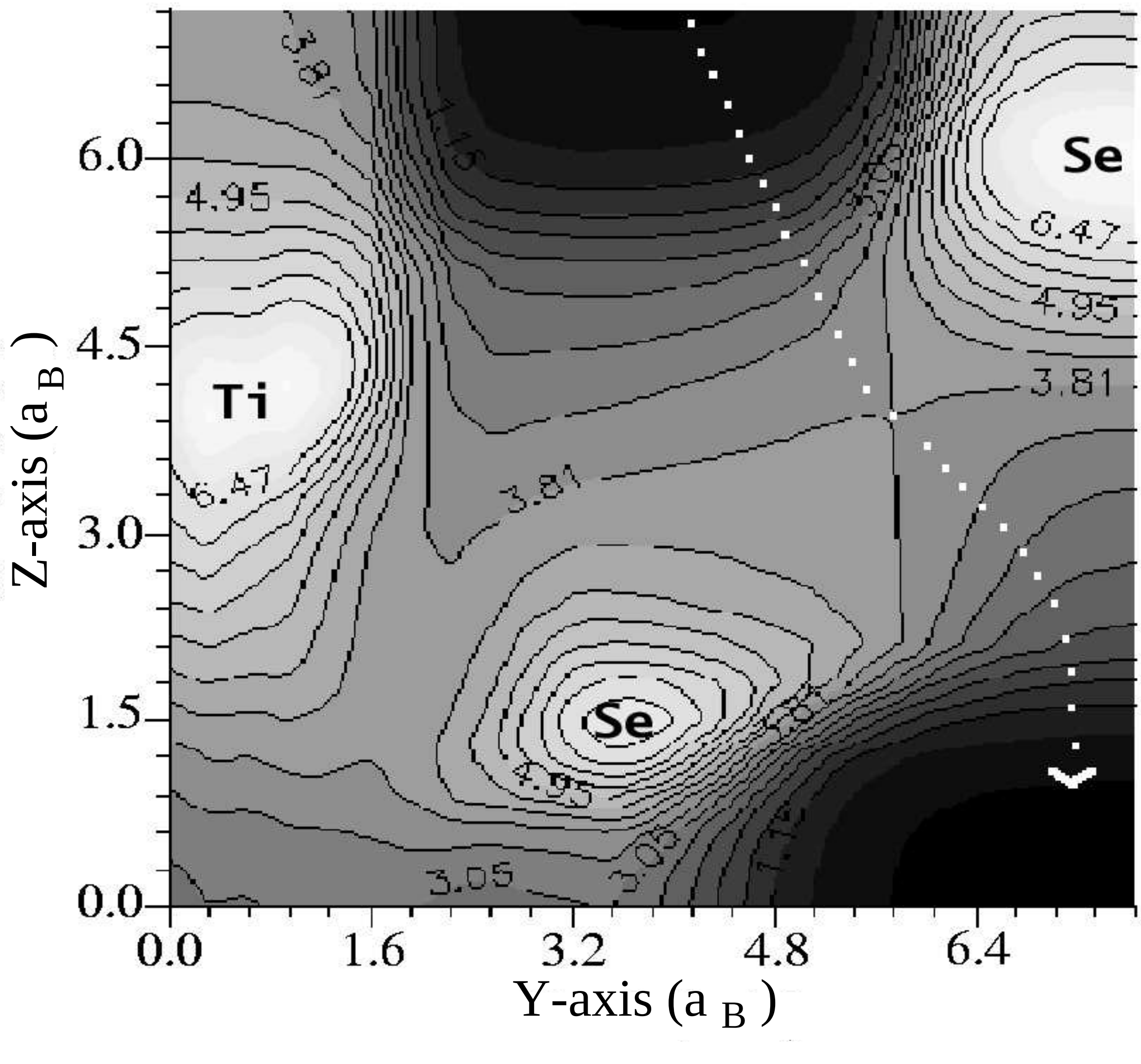
3.0
4.5
6.0
7.5
Z-axis (a B)



Ti
Se
Se
4.95
6.47
3.81
1.15
3.05
Z-axis (a_B)
Y-axis (a_B)
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1.5
3.0
4.5
6.0
1.6
3.2
4.8
6.4