Adsorbate-atom-induced relaxation of thin Li(001) films

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First-principles calculations are used to study the effects that adsorbate atoms (Li, Na, Mg, Al) have on the (001) surface of thin body-centered-cubic Li films. The Li, Na, and Mg adsorbates induce a shallow hole on the surface of the substrate at the adsorption site. The Al adsorbate, however, creates a low bump at the adsorption site. For the isolated Li adsorbate the induced surface relaxation of the substrate extends up to second neighbors from the adsorption site. The adsorbed Li atom is able to push its way closer to the surface if the number of atomic layers of the substrate film is increased from 3 to 5. If the distance between the two Li adsorbates is $3a$ (a=lattice parameter of the substrate), both adsorbate atoms lie in their own, completely separate, adsorption holes. When the distance between the adsorbates is decreased to $2a$, the adsorption holes are merged to form a common adsorption valley. [S0163-1829(96)05747-5]

Due to the recent development in crystal-growth techniques and nanotechnology the manufacturing of good quality ultrathin films has become possible.[1-3] The properties of low-dimensional systems differ from those of bulk systems. The reduced dimensionality usually leads to so-called quantum size effects, which means that the change in the size of the system leads to phenomena which are direct consequences of quantum mechanics.

Another class of systems with many interesting properties is the surfaces of bulk objects. Due to the difference in the coordination number of atoms in the bulk and surface environment, relaxations and reconstructions occur in the surface atomic layers. The geometric arrangement of the atoms can significantly affect the physical properties of the surface, thus making the structural determination important for understanding the surface properties. The investigation of the reactions between atoms adsorbed on metal surfaces and also of the adatom-induced surface relaxations has a special importance since there are numerous applications of surface processes in science and technology.

First-principles total-energy calculations provide accurate information of various surface properties (see, e.g., Ref. 4). In this paper, we report a study of the adatom-induced surface relaxations of body-centered-cubic (bcc) Li(001) films. In addition to the surface relaxation, the interactions between the adatoms are important and will be discussed as well. The present calculations are based on the *ab initio* molecular-dynamics method.[5] We studied the effects that the adatoms (Li, Na, Mg, Al) have on the structural properties of thin Li films with (001) surfaces. These systems were selected since the adatoms in question differ from each other in many respects, thus giving a good general idea of the response of Li surfaces to the adsorption of various kinds of atoms.

There have been several investigations on Li films, concentrating, however, on pure Li only. Alldredge and Kleinman[6] studied a 13-layer (001) film of bcc Li. Boettger and Trickey[7] studied hexagonal ultrathin Li films. Quassowski and Hermann[8] studied Li monolayers of hexagonal and square symmetry. We also refer to the systematic investigations into the properties of hexagonal metallic monolayers of Li, Be, Na, Mg, K, Ca, Rb, and Sr.[9]

The first-principles density-functional technique is a powerful tool for studying surfaces.[10] The electronic structure calculations in our work are based on the density-functional method including the local-density approximation,[11,12] with Wigner's interpolation formula[13] for the exchange and correlation. The wave functions of the valence electrons are expanded using the plane-wave basis, and the effects of the ionic cores are introduced using pseudopotentials. Norm-conserving pseudopotentials are obtained by following the prescription of Bachelet, Hamann, and Schlüter,[14] except for the pseudopotentials corresponding to the unoccupied states of the neutral atoms, which are obtained by Hamann's scheme.[15] The d part is treated as a local potential and the pseudopotentials are transformed into a separable form as suggested by Kleinman and Bylander.[16] The partial core correction is included in the pseudopotentials of Li, Na, and Mg.[17] The optimization of the electronic and ionic part is performed using the first-principles structural optimization technique,[18] where the steepest-descent type of algorithm[19] is used to optimize the electronic part. The ionic motions are obtained from ordinary molecular dynamics with Hellmann-Feynman forces.[20]

We use the repeated slab method in the calculations. The slabs consist of three or five layers of Li atoms, and adjacent slabs are separated by vacuum regions. The thickness of the vacuum region (= the distance between the adatoms belonging to the adjacent slabs) was taken to be about 20 a.u., which corresponds to five empty layers between the slabs. The surface orientation of the slabs is (001). Since our computer code assumes inversion symmetry of the unit cell, the adsorbate atom is placed on both sides of the slab. Unit cells with surface areas ranging from $3a \times 3a$ to $5a \times 5a$ are used (a=6.43 a.u. is the calculated lattice parameter for bulk bcc Li).

We refer to our earlier work[21-23] for the determination of suitable computational parameters for these kinds of simulations. In the present work we used 9.0 Ry as a cutoff energy and the number of **k** points was 4 for the 5×5 surface unit cells and 16 for smaller unit cells. The width (half width at half maximum) for the Gaussian-type broadening scheme at the Fermi level was 20 mRy.

TABLE I. Adsorption on frozen and relaxing three-layer Li(001) films using a 3×3 surface unit cell. The first two rows show the results of calculations where the substrate atoms are fixed [either at the bulk Li positions or at the optimized pure three-layer Li(001) slab positions] and only the position of the adsorbate atom is optimized. The third row shows the results of a calculation where the positions of both the substrate and adsorbate atoms are optimized. The fourth row is the same as the third, but for a 5×5 surface cell. The fifth row is the same as the third, but for a five-layer film. d_l and d_a are the atomic surface layer spacing of the film and the distance between the adsorbed atom and the surface (for the relaxing surface the average position of surface atoms is used in evaluating d_l and d_a). E is the total energy of the system.

Adsorbate	Substrate	d_l (a.u.)	d_a (a.u.)	E (Ry)
Li	bulk, frozen	3.22	3.38	-15.128
	relaxed, frozen	3.41	3.42	-15.132
	relaxing	3.41	3.27	-15.132
	relaxing (5×5)	3.42	3.27	-40.200
	relaxing five-layers	3.39	3.08	-24.867
Na	relaxed, frozen	3.41	4.13	-15.093
	relaxing	3.43	4.05	-15.093
Mg	relaxed, frozen	3.41	2.92	-17.670
	relaxing	3.37	2.38	-17.686
Al	relaxed, frozen	3.41	1.77	-22.307
	relaxing	3.49	1.38	-22.330

To study the adsorption of an isolated atom on a surface one has to use large surface unit cells in the calculations. We started our investigation using a 3×3 surface unit cell with an atom adsorbed on the bcc lattice point on the surface. The adsorption of a Li atom on the (001) surface of a three-layer bcc Li film was studied in three different cases. In the first case the three-layer substrate film was constructed by cutting it from bulk bcc Li without any relaxation in the atomic positions, i.e., the atoms of the substrate were frozen in their ideal bulk bcc positions. Then the adsorption process was simulated by keeping the substrate fixed and letting the adsorbate atom find its optimum distance from the surface. The second case was similar to the first one, except that instead of the frozen slice of bulk Li a frozen optimized three-layer Li film was used as the substrate. The optimization of the substrate film in this context means that the atoms are allowed to move perpendicular to the surface to minimize the total energy of the film. In the third case the structure of the whole substrate-adatom system was optimized simultaneously. The atoms of the central layer of the three-layer substrate film were fixed at their ideal bulk bcc positions, but all the other atoms of the system were moved to find the optimum atomic positions, which minimize the total energy of the system.

The distance of the adsorbate atom from the surface was found to depend crucially on the relaxation state of the substrate (Table I). Because in the fully optimized system the surface is not flat anymore (Fig. 1), the position of the surface is not a well-defined quantity. In this work we define the position of the surface to be the average position of the surface layer atoms. The depth of the surface depression under the adsorbed atom is 0.16 a.u. and the distance of the adatom from the bottom of the depression is 3.36 a.u. About half of
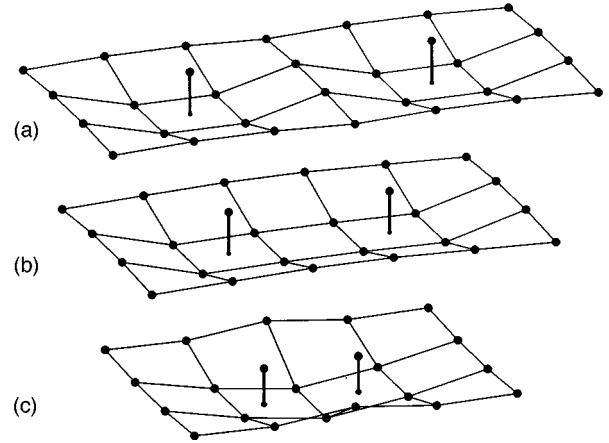

FIG. 1. Surface of a three-layer Li(001) film with two Li atoms adsorbed on it. Figures (from top to bottom) show the situation when the adsorbed atoms are $3a$, $2a$, and $1a$ apart from each other (a = the lattice parameter). In this and the following figures the surface relaxations perpendicular to the surface are scaled by a factor of 10 in order to make the smaller patterns discernible too.

the decrease in the adatom-surface distance is due to the formation of the adsorption hole, and another half comes from the decrease in the distance between the adsorbate atom and the surface atoms near to the adsorption site.

To find out how far from the adsorption site the adatom-induced surface relaxation extends, a calculation for the fully optimized system was also done by using a 5×5 surface unit cell. It was found that there are no drastic changes in the shape of the adsorption hole when the distance between the adatoms is increased from 19.29 to 32.15 a.u. (Fig. 2). Using the 5×5 surface unit cell the depth of the hole under the adsorbed atom is 0.15 a.u. and the distance of the adsorbed atom from the bottom of the hole is 3.36 a.u. This suggests that the 3×3 surface unit cell is large enough to treat the adsorbed Li atoms as isolated adatoms on the surface. This can also be seen by comparing Figs. 1(a) and 2. Hence we conclude that the surface relaxation due to the adsorbed Li atoms extends practically up to the second neighboring atoms from the adsorption site.

To get more insight into the adatom-induced surface relaxations it is interesting to study also the surface effects due to other adsorbates. In the following, we study Na, Mg, and Al adsorption on the Li(001) surface. In comparing the effect due to different adsorbates we restricted our investigation on
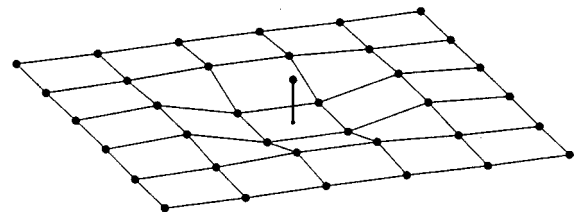

FIG. 2. Li adatom-induced surface relaxations of a three-layer Li(001) film calculated using the 5×5 surface unit cell.
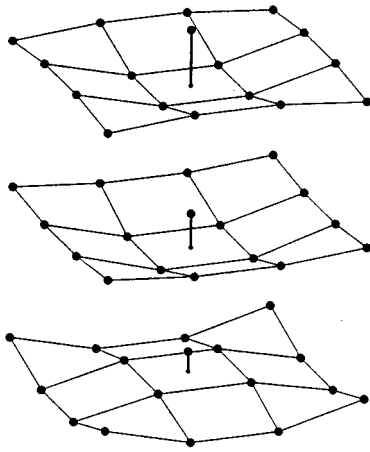
FIG. 3. Surface of a three-layer Li(001) film with Na, Mg, or Al atoms adsorbed on it (from top to bottom).

FIG. 4. Relaxations of the surface (upper) and the next (lower) atomic layers of a five-layer Li(001) film with a Li atom adsorbed on it.

the $\frac{1}{9}$ coverage case. The substrate used in the calculations was the three-layer Li film. The adsorption for each atom was investigated both in the case of the frozen optimized Li film as the substrate and in the case of the fully optimized adatom-substrate system.

In the case of the frozen substrate, the adsorption distance (d_a) is 4.13, 3.42, 2.92, and 1.77 a.u. for the Na, Li, Mg, and Al adsorbates, respectively. For the fully optimized adatom-substrate system d_a is decreased from the above values by 1.9%, 4.4%, 18%, and 22%, correspondingly. The obtained trend in d_a is consistent with the solubilities of these elements in Li and also with the interaction of these atoms with bulk Li crystal.[22] It is also interesting to note that the calculated trend in d_a of these adsorbates correlates with the trend in the number of valence electrons and the electronegativity of the adatom. The results above show that taking into account the relaxation of the whole substrate-adsorbate system in investigating of the adsorption processes is important, especially in the case of Mg and Al adsorption.

Figure 3 shows the surface relaxation patterns due to the adsorption of Na, Mg, and Al on the Li(001) surface. The relaxation induced by the Na adsorbate is similar to that found for the Li adsorbate. The adsorption hole for the Mg adsorbate is larger than that for the Li and Na adsorbates. The Al adsorbate induces a different kind of surface relaxation, it creates a bump not a hole on the surface. This is consistent with the results in the bulk environment where we found that the interaction of both Na and Mg with Li is repulsive, whereas the interaction between Al and Li is attractive.[22] Using the energies of the free atoms[24] and the pure three-layer Li film the desorption energies of the adsorbates can be obtained. The desorption energies for Li, Na, Mg, and Al adsorbates are 120, 104, 79, and 220 mRy, respectively. Using the frozen substrate in the calculations decreases the desorption energies of Mg and Al adsorbates by 8 and 12 mRy from the above fully relaxed substrate-adsorbate values.

In addition to the obtaining of information for ultrathin unsupported Li films, the present results can also be used in estimating the adsorption-induced effects in bulk Li surfaces. To better understand the size effects in slab calculations and
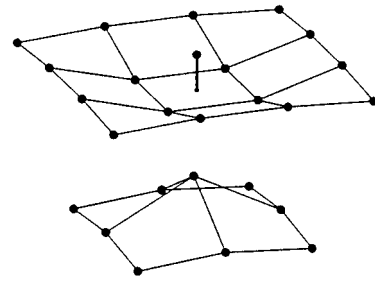
to get more reliable predictions for the physical properties of surfaces of bulk objects we also made calculations for the Li adsorption on a five-layer Li film.

Table I shows that the adsorbed Li atom is able to push its way closer to the surface if the number of the atomic layers in the substrate film is increased from three to five. The increasing of the number of the atomic layers of the substrate film by 2 decreases the adsorbate-surface distance by 6%. This decrease in the adsorbate-surface distance is due to the softening of the surface. In the five-layer film there are two relaxing surface atomic layers under the adsorbed atom compared with only one in the three-layer film. The relaxations of the two surface atomic layers have opposite shapes (Fig. 4). In the first surface layer there is an adsorption hole, but in the second surface layer there is an adsorption bump. It is somewhat surprising that the relaxations of the second surface layer of the five-layer film are larger than the relaxations of the first surface layer of the three-layer film. This may be due to the interactions between the relaxing first and second surface layers in the five-layer film and also to the translational symmetry of the system. For the $\frac{1}{9}$ coverage case in the surface layer the second-neighbor atom from the absorption site is on the surface of the unit cell, which means that its movements are restricted by the symmetry of the system. The second-layer atoms are all inside the unit cell and so their relaxations are not restricted by the translational symmetry of the repeated unit-cell method.

Because the relaxations of the second surface layer of the five-layer film are quite large, one should use much thicker fully relaxing films as substrates when investigating adatom-induced surface relaxations of bulk systems. However, as the results obtained for the three- and five-layer films suggest, the qualitative features of the adsorption-induced surface relaxations of bulk systems can be obtained by using three-layer films.

To investigate growth processes on surfaces it is important to consider interactions between adsorbed atoms. In our calculations the distance between the adatoms is three lattice parameters ($3a$) for the atom adsorbed on the 3×3 surface. In the following we consider the adsorption of a pair of Li adatoms whose mutual distance was taken to be either $1a$ or $2a$. To keep the interaction between the pairs small, the distance between adjacent pairs was taken to be $3a$ in all cases investigated. This means that we have to use 3×4 or 3×5 surface unit cells to investigate adatoms $1a$ or $2a$ apart from each other.

The induced surface relaxations are shown in Figs. 1(b)

TABLE II. Relaxation trends of the Li(001) surface when the adsorbed Li atoms are approaching each other. d_{aa}, d_{ab}, and b are the distance between the adsorption sites, the distance between the adsorbed atom and the bottom of the adsorption hole, and the position of the bottom of the adsorption hole, respectively. d_{aa}, d_{ab}, and b refer to the ideal bcc geometry. Δd_{aa}, Δd_{ab}, and Δb are the changes in these quantities due to the structural optimization process. Δd_{aa} is given in percentage of d_{aa}. Δd_{ab} and Δb are given in percentage of the atomic layer spacing in bulk bcc Li (3.215 a.u.). h is the depth of the adsorption hole and is given in percentage of the atomic layer spacing in bulk bcc Li.

d_{aa}	Δd_{aa}	Δd_{ab}	Δb	h	E/dimer (Ry)
$3a$	0.0	+4.6	+3.2	5.1	-1.028
$2a$	-0.2	+3.8	+3.3	5.9	-1.027
$1a$	-6.3	+0.9	-0.2	9.8	-1.045

FIG. 5. Schematic figure of the adsorption of two Li atoms on the surface of a three-layer Li film. For notations see Table II.

and 1(c). Figure 1(a) shows that if the distance between the adatoms is $3a$, there is a low hill between them and they both lie in their own adsorption hole. When the distance between the adatoms is decreased to $2a$ [Fig. 1(b)] their adsorption holes become merged, forming a $3a$ long common adsorption valley. However, in spite of the formation of the common adsorption valley the interaction between the adatoms is still weak. The distance between the adatoms (d_{aa}) is decreased only by 0.2% compared to the corresponding distance in the ideal bcc Li crystal (Table II, Fig. 5). The differences in the distance of the adatom from the bottom of the adsorption hole (Δd_{ab}), in the position of the bottom of the adsorption hole (Δb) and in the depth of the adsorption hole (h) are also small when comparing the systems with the adatoms $3a$ or $2a$ apart from each other. Decreasing the distance between the adatoms to $1a$ significantly increases the attractive interaction between them. The distance between the adatoms is decreased by 6.3% compared to the lattice parameter a. As Table II shows, the other characteristics of the adsorption site also change drastically. In addition to the reduction in the adsorbate-adsorbate distance the distance of the adatoms from the bottom of the adsorption valley is decreased significantly This means that the bonding of the adatoms both parallel to the surface and perpendicular to the surface is increased. The depth of the adsorption valley is almost doubled, which is mainly due to the decrease of the bottom of the adsorption valley. The interaction between the adatoms also affects the surface relaxation around the adsorbed dimer. As Fig. 1(c) shows, the surface relaxation far from the adsorption center along the dimer axis is decreased from the Fig. 1(b) case, but perpendicular to the dimer axis it is increased.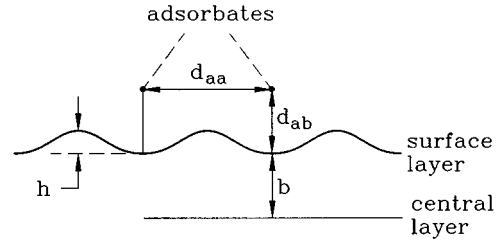 Consideration of the total energies of these three adsorbate-surface systems shows that the configuration of two adatoms closest to each other is energetically most favorable. The energy difference between the $1a$ and $3a$ case is 17 mRy.

As shown above, the interaction between the Li adsorbates on the Li(001) surface is attractive. This suggests that the growth of the Li(001) surface is based on growing islands. The surface relaxation as a function of the size of the adsorbed islands has nonlinear behavior. In the present work we have considered small islands of two different sizes, islands consisting of one and two atoms. The present results can be compared with the results of infinite islands [full monolayer of Li on thick Li(001) film] calculated in our previous work.[21] The distance of the adatom from the bottom of the adsorption hole is 3.36, 3.24, and 3.43 a.u. for one atom, two atoms, and the infinite island, respectively. The results obtained show that there is an island of a certain size, between one and an infinite number of atoms, for which the adsorbate-surface distance gets its minimum value. However, besides the size of the island its shape also affects the surface relaxation.

In conclusion, the adsorption of atoms on a surface can affect the bonding between the substrate atoms in a complex way. The Li, Na, or Mg atoms entering the surface increases the bonding between the surface atomic layer and the second atomic layer below the surface. The Al adsorbate decreases the bonding between the surface atomic layer and the second atomic layer below the surface. The adatom-surface distance is changed significantly due to the relaxation of the substrate film showing that the simultaneous optimization of the adsorbate and substrate atom positions is necessary in these kinds of simulations.

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