Density functional study of alkali metals adsorption on the MgO(1 1 1) surface

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Abstract

The adsorption geometry, binding energy and electronic structure of alkali metals overlayers on the MgO(1 1 1) surface have been studied in the framework of the generalized gradient approximation to the density functional theory. Periodic slabs of MgO with Li, Na, and K atoms adsorbed on both surfaces are considered at 0.5 and 1.0 monolayer coverages. It is found that single monolayers of alkali metals stabilize the oxygen-terminated MgO(1 1 1) surface. This effect is rationalized in terms of the large binding energies of the adsorbates and the charge transfer to the surface oxygen layer. We also demonstrate that, deposition of the Li monolayer leads to the transformation of the electronic structure of the MgO(1 1 1) surface from the metallic-like to an insulator-like one with the energy gap of 1.8 eV.
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1. Introduction

The metal/oxide interface plays an important role in many technological applications. One of the most important examples is a simple metal oxide covered with a simple, noble, or transition metal which can form an efficient supported-metal catalyst. The catalytic role of the metal depends on the structure of the ceramic (oxide) support. On the other hand, from a viewpoint of stability of the deposited layers it is very important to understand the metal–oxide bond and its strength.

Magnesium oxide (MgO) serves as one of the principal model systems for the studies of metal–oxide interfaces. Clean MgO cleaves easily along the (1 0 0) plane. Metal adsorption on the non-polar MgO(1 0 0) surface has been the subject of intensive investigations during the last decade [1–12]. In the case of alkali metal adsorbates it was recognized that low-coverage Na and K films are unstable compared with the three-dimensional metallic bulk-like islands or clusters [10]. In contrast, the Li monolayer films are stable [11]. Another low-index surface, the MgO(1 1 1) is far less investigated. It is well known that a pristine polar MgO(1 1 1) surface, build up of alternating layers of cations and anions, is unstable. One of the ways of achieving stability is a 2×2 reconstruction which often occurs at this surface. Recently

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Cu/MgO(1 1 1) [13], and several transition metal/ MgO(1 1 1) interfaces [14,15] were studied theoretically, and it was suggested [14,15] that adsorption of metals is an efficient way of stabilization of the polar MgO(1 1 1) surface. However, neither copper nor transition metal atoms adsorption leads to an insulating character of the metallic-like MgO(1 1 1) surface as surface reconstructions do [16].

The appearance of the energy gap in surface electronic states around the Fermi level is a principal sign of surface stability of the insulating material, because the energy of interatomic bonding depends directly on the binding energy of valence electrons, and the latter value is equal approximately to the width of the forbidden gap. It seems, that the oxygen-terminated (1 1 1) surface of MgO may be stabilized by the monovalent alkali metals, because each oxygen atom at this surface needs one electron to saturate its valence. Therefore, the central goal of the present work is to study a possibility of stabilization of the MgO-(1 1 1) surface by Li, Na and K overlayers. To our knowledge the adsorption of alkali metal atoms on the MgO(1 1 1) has not been studied so far.

2. Method and details of calculation

The calculations were performed using the FHI96MD simulation code [17] based on the density functional theory, pseudopotential method, and the plane wave basis set. The generalized gradient approximation (GGA) in the Perdew and Wang (PW91) form [18] for the exchange and correlation functional, and fully separable Troullier–Martins pseudopotentials [19] were employed. The pseudopotentials were constructed using the FHI98PP code [20] and were verified to avoid ghost states, and to describe the basic experimental characteristics of the bulk materials. In particular, for Mg and O we used pseudopotential parameters proposed in Ref. [21]. Namely, the core radii chosen for s, p, and d components for oxygen are respectively 1.38, 1.75, and 1.38 Bohrs, while for magnesium the core radius equals to 2.0 Bohr for all three components. The d component of the pseudopotential for oxygen, and the s component for magnesium were adopted as local. Similarly as

in Ref. [21] the Γ point was applied for bulk calculations, whereas for the k-space integrations for slabs we used the (0.25;0.25;0.00) point. The energy cut-off of 44 Ry was applied in all calculations.

The equilibrium lattice constant a_0 and bulk modulus B_0 calculated with the above parameters for MgO, using Murnaghan equation of state [22], are equal to 4.24 Å and 160 GPa. They agree well with the experimental values equal to 4.21 Å [23] and 162 GPa [24], respectively. The above value of the equilibrium lattice parameter was used as an input in further calculations.

For alkali metals we used pseudopotential parameters determined in the literature (Li [25], Na [26], and K [27]). A verification of those parameters yielded calculated values of lattice constants and bulk moduli close to experimental data (in parentheses): for Li—3.41 Å (3.477 Å [28]) and 15.2 GPa (11.6 GPa [29]), for Na—4.23 Å (4.225 Å [30]) and 7.6 GPa (7.3 GPa [31]), and for K—5.14 Å (5.23 Å [23]) and 4.1 GPa (3.7 GPa [32]).

In order to study the alkali metal adsorption, similarly to Refs. [14,15] the MgO(1 1 1) surface was represented by the non-stoichiometric, magnesium- and oxygen-terminated five-layers Mg/O/ Mg/O/Mg and O/Mg/O/Mg/O slabs with the 2×1 surface unit cell. (Such non-stoichiometric systems are formed when one fabricates unreconstructed polar MgO(1 1 1) surfaces.) Oxide slabs were separated by the 20 Å thick vacuum space and repeated periodically. Some test calculations were also done for the MgO(1 0 0) surface. In this case a supercell consisting of four 2×1 layers slab plus 20 Å of the vacuum was used. Studying the surface relaxation effects only the first surface layer atoms of MgO were relaxed in all cases till the maximum forces on atoms were less than 0.01 eV/Å.

Alkali metals were adsorbed symmetrically on both sides of the slab, giving a possibility to compare electronic structures and binding energies for different terminations. We have found that the most favored configuration for the metal adsorption on the MgO(1 1 1) surface is a threefold coordinated hollow site. This is also similar to adsorption of Pd atoms [14] on the MgO(1 1 1). Being placed in on-top positions and allowed to relax, alkali metal atoms move to the threefold

coordinated sites in the process of simulation. For this reason, in our further studies only the three-fold coordinated sites were considered.

The binding energy E_b of alkali adatoms was calculated from the expression:

$$E_b = \frac{1}{N}(E_{M/MgO} - E_{MgO} - NE_M), \qquad (1)$$

where $E_{M/MgO}$ is the energy of the metal/MgO slab, E_{MgO} is the energy of the clean MgO slab, and E_M is the energy of the lone metal atom calculated in a large cubic cell. N is the number of metal adatoms in a surface unit cell, on both sides of the slab.

To study stability of adsorbed alkali metal layers we also calculated the interaction energy E_i for unsupported layers of alkali metal atoms with the geometry corresponding to relaxed layers on the MgO surface. This quantity may be defined as:

$$E_i = \frac{1}{N}(2E_{layer} - NE_M), \qquad (2)$$

where $2E_{layer}$ is the energy of two alkali metal layers without the MgO slab between them.

To construct the densities of states (DOS) we used nine k-points (a $3 \times 3 \times 1$ Monkhorst–Pack mesh [33]) and the 0.2 eV wide Gaussian broadening functions.

3. Results and discussion

3.1. Clean oxide surfaces

For the (1 1 1) surface the relaxation of Mg and O terminations are quite different. We have found a rather small outward relaxation of the Mg surface layer (0.06 Å) and a large inward relaxation of oxygen surface layer: the 0.30 Å shift relative to the bulk position or a contraction of the Mg–O distance by 8%. (The calculated equilibrium interlayer distance in the (1 1 1) direction is 1.22 Å, and the equilibrium distance between Mg and O atoms is 2.12 Å.) The 8% contraction is close to that (10%) obtained from the FP-LAPW calculations [14]. For the Mg-terminated surface the latter results are opposite to ours giving a small (0.02 Å) inward relaxation of Mg atoms (a contraction of the Mg–O distance by 0.5%). Note however, that

the absolute value of this relaxation is very small so the overall agreement is good.

In order to have a firm reference to discuss and compare the changes in the electronic structure introduced by the alkali metals adsorbed on the MgO surface we have calculated the DOS for the bulk MgO, and for the MgO(1 0 0) and MgO(1 1 1) slabs. In the latter case both oxygen and magnesium surface terminations were considered. Results are presented in Fig. 1.

It is clear from Fig. 1 that the existence of the (1 0 0) surface does not significantly perturb the MgO bulk DOS, except of a small reduction of the width of the insulator band gap. In the case of the (1 1 1) surface, however, on both terminations, a strong modification of the DOS takes place. The main effect consists of a downward shift of the conductance band on the Mg termination, and of a strong broadening and splitting of the DOS at the top of the valence band. On the O termination both conduction and valence band are shifted by ≈2–3 eV up in energy. As a result, the surface energy bands are intersected by the Fermi level, which confers a quasi-metallic character to both
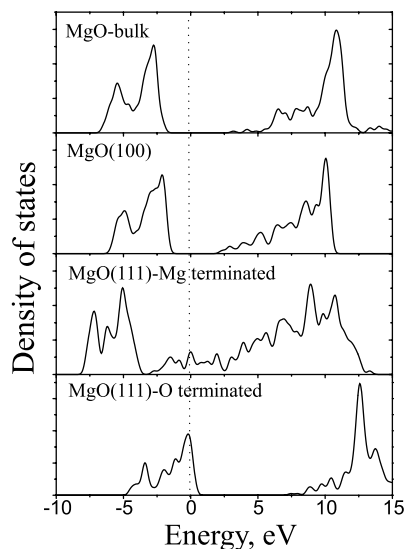

Fig. 1. Density of electronic states (in arbitrary units) for MgO. From top to the bottom: bulk, the (1 0 0) surface, the Mg-terminated (1 1 1) surface, and the O-terminated (1 1 1) surface. Vertical dotted lines show positions of the Fermi level.

terminations. However, the details of the surface oxygen and magnesium bands close to the Fermi level are quite different. The Mg termination is characterized by a metallic-like energy dispersion with a rather low density of states $n(E_F)$ at the Fermi level. At variance, on the O termination, $n(E_F)$ is relatively high, but there is an energy gap of about 7 eV, beginning 0.5 eV above the Fermi level. These results are in a good agreement with the FP-LAPW calculations [14].

3.2. Adsorption on the MgO(111)

The results for the alkali atoms binding properties on both Mg- and O-terminated surfaces are collected in Table 1. For the 0.5 monolayer (ML) coverage the binding energies for all alkali metal atoms (Li, Na, and K) are larger (in the absolute value) on the oxygen-terminated surface than on the magnesium-terminated one. This energy-to-energy ratio is equal roughly to 4 for Li, and increases up to 16, for K. The distance d between the adsorbate and surface atom correlates with the binding energy: the larger d the smaller E_b. This behavior is similar to that described in Refs. [10,11] for alkali metals on the MgO(100).

For the 1.0 ML coverage the binding energies and interatomic distances for the Mg-terminated surface are of the same order of magnitude as those obtained for the 0.5 ML case. The binding energies are larger for the O-terminated surface but we see a significant decrease of E_b for Na, and particularly for K, without changing d. The reason for this is an increased repulsion between adsorbate atoms due to a decrease in the in-plane distance between them. Calculations of the adhesive energy (per atom) performed in Ref. [15] for a group of 27 noble and transition metals show that only for four of them (including Pd) the adhesive bond is stronger at the Mg-terminated surface. Calculations for the 1.0 ML of Pd on the MgO(111) yield −3.8 eV for the Pd binding energy [14], and 2.70 Å for the Pd–substrate-atom distance (for the Mg-terminated surface), and −3.5 eV, and 2.32 Å, respectively for the O-terminated surface. This means that Pd atoms on the Mg-terminated surface are about 1.6 eV stronger bound than Li atoms are, but their bonding with the O-terminated surface is about 3.5 eV weaker than that of Li atoms. Therefore, the energetics of alkali metals on the MgO(111) is quite different from the behavior observed for palladium. As mentioned above, Pd behaves also differently from other transition metals. The calculations of Ref. [15] show a distinct correlation between a strength of the adhesive bond and a valency of transition metal—metals with lowest number of valence electrons are most strongly bound to the O-terminated MgO(111). This agrees qualitatively with our results for (monovalent) alkali metals which are characterized by the large adsorption energies (Table 1). Interestingly, for the adsorption on the Mg-terminated surface the bonding increases, or remains unchanged, with the increased coverage. This is in contrast to the O termination where the binding distinctly decreases for the 1.0 ML coverage, and shows that at high coverage the alkali–alkali interaction becomes much more important than the binding energy to the MgO layer.

Table 1
Characteristics of alkali metal overlayers deposited on the relaxed MgO(111) surface: the binding energy E_b and the distance d from an adatom to a surface atom

	Mg-terminated			O-terminated		
	Li	Na	K	Li	Na	K
0.5 ML coverage						
E_b (eV/atom)	−1.72	−0.78	−0.29	−6.78	−5.40	−4.22
d (Å)	2.86	3.07	3.50	1.90	2.12	2.47
1.0 ML coverage						
E_b (eV/atom)	−2.11	−0.78	+0.29	−6.47	−4.27	−2.80
d (Å)	2.74	3.18	3.56	1.85	2.11	2.48

In order to check the reliability of our single *k*-point (0.25, 0.25, 0.0) calculation that was applied to determine the binding energy, we have carried out test calculations for an increased number of *k*-points. For the Li atom adsorption the calculations with nine *k*-points gave the Li binding energy of 6.36 eV, for the O-terminated surface, and 1.94 eV for the Mg-terminated surface. This is rather close to the corresponding values of 6.47 and 2.11 eV obtained respectively with a single *k*-point.

Figs. 2 and 3 present DOS of the Li, Na, and K half-monolayers and full-monolayers deposited on the MgO(1 1 1). One can see that all DOS for the 0.5 ML coverage have metallic character with a non-zero value of the density of states at the Fermi level. As for the full-monolayer case there is an exception for the Li/O-terminated surface, which
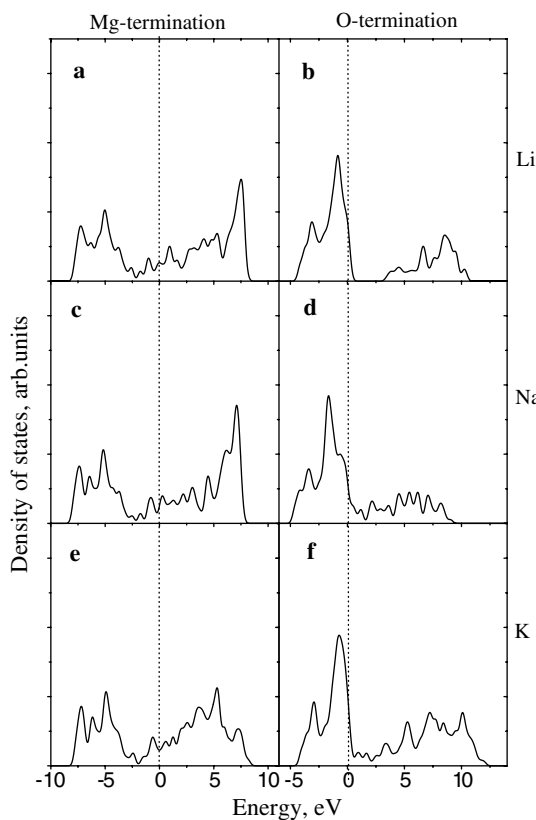

Fig. 2. Density of electronic states for the half-monolayers of lithium, sodium, and potassium on the MgO(1 1 1). The left-column panels correspond to the Mg termination, the right panels present DOS for the O termination.
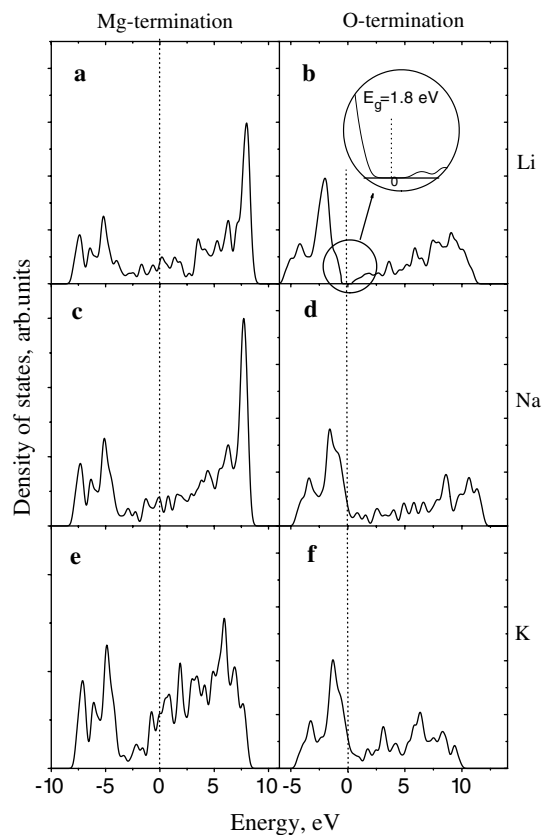

Fig. 3. Density of electronic states for the full-monolayers of lithium, sodium, and potassium on the MgO(1 1 1). The left panels correspond to the Mg termination, the right panels present DOS for the O termination.

has an energy gap of about 1.9 eV. To be sure that the gap is not an artifact, we have carried out an additional calculation for a denser, $4 \times 4 \times 1$ *k*-point mesh (16 *k*-points). This yielded the gap of 1.8 eV which suggests that the energy gap due to surface effect is a real fact. In other words, a monolayer of lithium atoms stabilizes the MgO(1 1 1) surface giving a non-metallic character to it. Thus, only the full-monolayer of Li atoms, and only on the O-terminated surface, leads to the formation of the gap between valence and conduction surface states.

We suspect that the main reason for the appearance of this effect for Li, and not for the other alkali metals, is a smaller atomic size of Li atoms. The interatomic distance in the bulk bcc

Li is 2.97 Å. This value is very close to the Li–Li adatom distance (2.96 Å) in the Li monolayer on the MgO(1 1 1) surface. Thus, Li atoms are in a very natural surrounding, without any stresses present, and their interaction with the surface is very effective. In contrast, the atomic diameter of potassium is 4.53 Å, and the monolayer of K on the MgO(1 1 1) is very compressed. The diameter of Na atom is intermediate between Li and K atom (3.66 Å), and the properties of Na/MgO(1 1 1) interface also have an intermediate character.

A negative influence of stress on the interatomic interaction is seen from the analysis of interaction energy E_i for alkali metals monolayers, corresponding to their geometries on the MgO(1 1 1) surface. The calculated values of E_i for Li, Na, and K monolayers, are −1.52, −0.84, and +0.64 eV, respectively. A positive interaction energy shows that an unsupported K monolayer is unstable. As it is shown in Table 1, on the Mg-terminated surface the binding energy E_b of K is also positive (+0.30 eV). It means that a monolayer of K is repelled from the MgO(1 1 1) surface.

Since the atomic diameter of palladium is 2.80 Å, i.e. it is slightly smaller than that of the lithium atom, one can ask why does the DOS for the Pd/MgO(1 1 1) system not show the energy gap [14] in the valence states band? It seems that not only the atomic size but also the number of valence electrons is decisive here. Palladium has 10 electrons in the valence shell, and the transfer of a small part of them (0.26 electron per atom [15]) to oxygen cannot change drastically the metallic bonding between Pd atoms.

In order to quantify the charge redistribution between the atoms of the slab, we calculated the charge density for the full-monolayers of Li, Na, and K on the oxygen-terminated MgO(1 1 1) surface, and analyzed the electron density profiles $n(z)$ obtained by integration of the electron charge density over the x and y space coordinates (parallel to the surface). The $n(z)$ curves were approximated by the sets of the Gaussians centered on the atoms and the electron numbers on atoms were calculated as the areas under these Gaussians. Examples of such an approximation for the clean MgO(1 1 1) and Li/MgO(1 1 1) slabs, as well as for the bulk
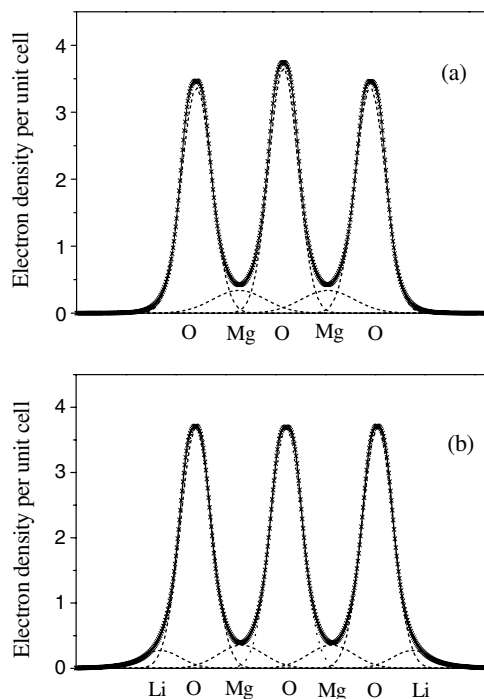

Fig. 4. The electron density profiles across the clean MgO(1 1 1) slab (a) and a slab consisting of 1.0 ML of Li on the MgO(1 1 1) surface (b). Crosses show the computed $n(z)$ profile; dashed lines represent Gaussians centered on the atomic positions; solid lines demonstrate the sum of Gaussians.

MgO, are plotted in Fig. 4. The atomic charges determined from such an analysis (with the computer error of about 0.05 electron per atom) are collected in Table 2.

Analyzing the data of Table 2 one can see that our calculations for bulk MgO and clean MgO surface are in a good accordance with results of Ref. [15], where a similar procedure was applied. Atoms of the Li monolayer are almost half-ionized. A 0.45 electron per atom is transferred from the Li electronic density to a surface oxygen atom to compensate the charge difference between surface and central oxygen atoms. The charge transfer from sodium to oxygen amounts to 0.35 e/atom, and this value is not sufficient to saturate the surface oxygen atom. The minimal charge transfer (0.15 e/atom) is obtained for potassium. Charges on the central oxygen atom and the Mg atoms are not sensitive to the alkali metal deposition within the limits of precision of our calculations. The

Table 2
Charge distribution (electron per atom) between the metal and oxygen atoms in the bulk MgO, at the O-terminated MgO(1 1 1) surface, and in the MgO(1 1 1) slab $Me/O_s/Mg/O_c/Mg/O_s/Me$ covered with a full-monolayer of alkali metal (Me)

System	Me	O_s	O_c	Mg
MgO-bulk			−0.90 (−0.88)	+0.90 (+0.88)
MgO(1 1 1)		−0.45 (−0.47)	−0.90 (−0.89)	+0.90 (+0.91)
Li/MgO(1 1 1)	+0.45	−0.90	−0.90	+0.90
Na/MgO(1 1 1)	+0.35	−0.80	−0.90	+0.90
K/MgO(1 1 1)	+0.15	−0.60	−0.90	+0.90

O_s is the surface oxygen atom, O_c is the central O atom of the slab. For comparison, the atomic charges determined in Ref. [15] from the $n(z)$ profiles are given in brackets.

latter result correlates well with the analogous conclusion of Ref. [15] for transition metals.

To make the electronic structure of the full-monolayers of alkali metals on the O-terminated surface more clear we have calculated the local densities of states (LDOS) on the individual atoms by integrating the squared moduli of the eigen-functions inside the atomic spheres. Values of the sphere radii were chosen to make the integrals of the local valence states equal to the numbers of electrons on atoms obtained from the density profiles $n(z)$ as described above. Fig. 5 shows the LDOS on the metal and surface oxygen atoms in comparison with the DOS of the floating metal layers separated from the substrate. One can see that all of the free metal layers exhibit a metallic character of the electronic structure. A similar, metallic-like DOS is also seen for the oxygen-ter-minated MgO(1 1 1) surface (Fig. 1). However, when the metallic Li layer is contacted with the metallic-like oxygen-terminated Mg(1 1 1) surface, the energy gap is formed between valence and conduction states as a result of the electronic density redistribution. It seems that 0.55 electron per Li atom is not sufficient to create the metallic bonding in the Li adlayer. In other words, the Li monolayer layer looses its metallic character and moreover, it converts the metallic-like character of the substrate structure into a non-metallic one.

The local electronic structure of the Na mono-layer has a tendency to show a band gap near the Fermi level. However, the charge transfer from Na atoms to the surface oxygen atoms is not sufficient to form the energy gap in the local oxygen states. Thus, the total electronic structure retains its me-tallic-like character. In the case of the potassium

adlayer the electron density redistribution is very small, and the adlayer has enough electrons to form the metal bonding. The surface oxygen layer
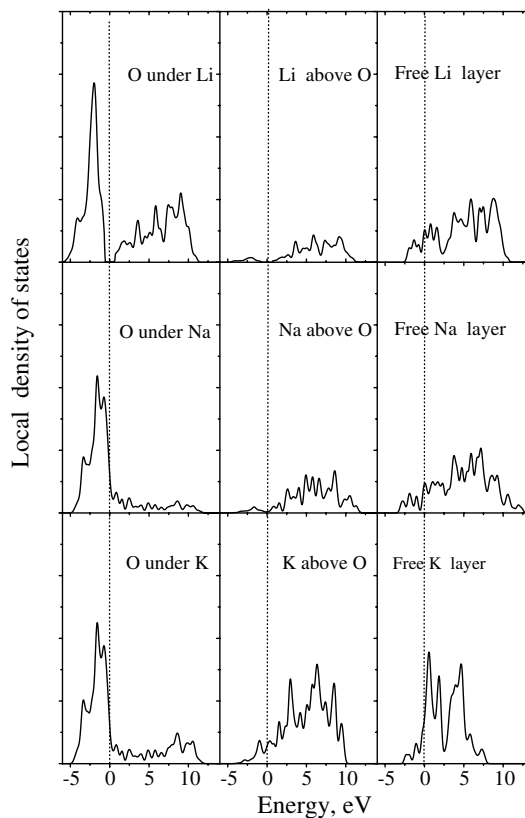

Fig. 5. LDOS (in arbitrary units) for the full-monolayers of lithium, sodium, and potassium on the MgO(1 1 1). The left column correspond to the surface oxygen atoms, the cen-tral column represents the LDOS on metal adlayers. The right column demonstrates the DOS for the free metal layers sepa-rated from the MgO(1 1 1) substrate.

also has a non-zero density of states on the Fermi level. Naturally, the total surface electronic structure is metallic-like.

It was concluded in Refs. [14,15] that palladium stabilizes the oxygen-terminated MgO(1 1 1) surface due to the transfer of 0.26 electron from Pd atom to the surface O atoms and to the large value of the binding energy (−3.5 eV). Taking the same argument for Li adsorption, one finds that the value of the charge transfer for Li atom amounts to 0.45 electron—almost twice as much as for Pd, and the binding energy for the Li monolayer (−6.47 eV, compare Table 1) is larger (in absolute value) than that for the Pd case. Consequently, one can conclude that lithium also stabilizes the oxygen-terminated MgO(1 1 1) surface. From this point of view Na and K stabilize the MgO(1 1 1) surface as well. Their binding energies are rather large (−4.27 and −2.80 eV, respectively) and the charge transfer is not small (0.35 and 0.15 e/atom). However, it seems that the case of Li is more preferable because its deposition leads to the formation of the insulator gap in the energy spectrum of the MgO(1 1 1) surface like surface reconstructions do. The origin of the metallic character of the Na and K monolayers on the MgO(1 1 1) surface has been discussed above.

Coming back to Fig. 2 we can now conclude that the non-zero density of states for the Li half-monolayer, deposited on the oxygen-terminated MgO(1 1 1) surface, results from an insufficient number of the Li atoms. Only one-half of surface oxygen atoms receives the needed electron charge density from lithium. Another half remains unsaturated, thus the total surface DOS does not exhibit any energy band gap at the Fermi level. The same can be said about Na and K. However, in these cases the 0.5 and 1.0 ML coverages do not demonstrate any principal differences in their electronic energy spectra and therefore do not require any additional discussion.

In passing, let us remark that it would be very interesting to compare directly the energetics of the MgO(1 1 1) surface, stabilized by the Li atoms adsorption, with the clean surface, stabilized by the 2 × 2 reconstruction. However, this is a rather difficult task and in order to explore it one has to apply much larger and more complicated slabs than those we employed here. We will try to address this problem in a future work.

4. Summary

We have presented a first-principles study of Li, Na, and K atoms adsorbed on the MgO(1 1 1) surface. On the Mg-terminated (1 1 1) surface the binding energies and interatomic distances for the two (0.5 and 1.0 ML) coverages are similar. For the O-terminated surface the Na, and particularly K atoms are stronger bound for the 0.5 ML coverage. A reason for this is the repelling interaction between adsorbed atoms (Na and K) in compressed 1.0 ML thick films.

All alkali metals considered here prefer to adsorb on the oxygen-terminated surface. In this process a partial electron transfer from alkali atoms to the surface oxygen atoms occurs. The maximum electron transfer (0.45 e/atom) has been found for Li. The density of electronic states of the Li monolayer film deposited on the O-terminated MgO-(1 1 1) surface, exhibits the energy gap of 1.8 eV, which is characteristic for an insulator or a semiconductor. Thus our investigations show that the deposition of 1 ML of Li on the unreconstructed oxygen-terminated MgO(1 1 1) surface manifests in the insulator-like character of the electronic structure and leads to the stabilization of the Mg(1 1 1) surface without a need for the 2 × 2 reconstruction. This stabilization is conditioned by the size and the electronic configuration of Li atoms.

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