

## Mechanisms of Island Formation of Alkali-Metal Adsorbates on Al(111)

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Using density functional theory total-energy calculations we investigate the chemisorption of Na and K alkali metals on the (111) surface of aluminum from very low coverages ( $\Theta = 1/16$ ) up to a full monolayer. The calculations predict site changes of the adsorbate atoms, as well as a condensation into islands with increasing coverage. Some processes are activated, which implies a possibly irreversible temperature dependence. This is shown to have important consequences for the coverage dependence of the work function change.

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Alkali-metal adsorption on metal surfaces is probably the oldest system studied systematically with respect to the physics, chemistry, and technology of solid surfaces [1,2]. Most phenomena of interest are related to a distinct property of alkali-metal adatoms, namely, that they reduce the work function of the substrate significantly. A first quantum-mechanical explanation of the adsorbate-substrate interaction and the work function change is due to Gurney [3]. In this “electron-transfer model” it is assumed that the electropositive alkali-metal atom donates part of its valence electron to the substrate. There is no question that the *isolated* alkali-metal adatom, when probed by a particle from outside the crystal, looks largely ionized [4,5]. Yet, there is an active controversy about the validity range of the “electron-transfer model” and whether it should be modified or if it should be dismissed (see Refs. [5,6] and references therein). This is not, however, the topic of the present paper. Instead we are interested here in the adsorbate-adsorbate interactions, which are shown to be important already at very low coverages of  $\Theta = 1/16$ . The coverage is defined in this paper such that  $\Theta$  is the ratio of the number of adsorbate atoms to the number of the atoms in the top layer of the unreconstructed substrate. Because the atomic radii of Na and K are bigger than that of the Al substrate, a full, close-packed monolayer of the adsorbate is expected to form at coverages  $\Theta \approx 0.6$  for Na and  $\Theta \approx 0.33$  for K (see also below).

Previous theoretical studies of the coverage dependence of the work function of the alkali-metal adsorption on Al(111) explained the characteristic shape of  $\Delta\Phi(\Theta)$  as a consequence of the continuous decrease of the adsorbate-adsorbate distance (see, for example, Refs. [3,4,7,8]). In fact, the *continuous* increase of the adsorbate density with coverage, i.e., the existence of a homogeneous adlayer, seemed plausible because (at low coverage) the strong dipole moment induced by a single adsorbed alkali-metal atom implies a strong electrostatic adsorbate-adsorbate repulsion.

However, recent experiments are in conflict with this interpretation indicating an attractive interaction between adatoms: Work function,  $\Delta\Phi(\Theta)$ , and low en-

ergy electron diffraction (LEED) pattern measurements by Hohlfeld and Horn [9] for Na adsorbed at  $T = 140$  K on Al(111) show island formation already at a very low coverage of  $\Theta = 0.1$ . This is confirmed by the surface core level and LEED pattern studies of Andersen *et al.* [10]. Room temperature adsorption exhibits a different behavior for  $\Delta\Phi(\Theta)$  and island formation starting at about  $\Theta = 1/8$ . Similar results exist for other alkali-metal adsorbates on Al(111) [9,11] and for alkali-metal adsorbates on silver [12].

A further, so far not fully understood phenomenon concerns the adsorption sites occupied by alkali-metal adatoms on close-packed surfaces. Recent density functional theory using the local density approximation (DFT-LDA) calculations [13,14], a LEED analysis [15], as well as an analysis of the surface core-level shift [10,11] at different temperatures of Na, K, and Rb on Al(111) have shown that in the periodic  $\Theta = 1/3$  adsorbate layer the alkali adatoms kick out surface Al atoms and occupy the substitutional sites. The process is activated, i.e., it starts at a temperature of  $T \approx 220$  K [10,11,14,15]. For a fcc(111) surface the kick-out process and the substitutional adsorption were completely unexpected. Furthermore, it is puzzling that the low temperature adsorption site of Na is the threefold hollow position, whereas K sits on top.

An understanding of these phenomena, in particular what determines the adsorption site and how the phase of the adlayer depends on the temperature and the total coverage, is not yet developed. In order to improve this situation we performed electronic-structure and total-energy calculations using DFT together with the LDA for the exchange-correlation energy. Details of the method are described in Ref. [14]. We use a plane-wave basis set with an energy cutoff of  $E_{\text{cut}} = 8$  Ry and take 6, 6, 3, and 1 special  $\mathbf{k}$  points [16] in the irreducible part of the Brillouin zone for  $\Theta = 1/3, 1/4, 1/12$ , and  $1/16$ , respectively. The adsorbate and the atoms of the two top substrate layers are relaxed using an “optimized steepest descent approach” [17].

As noted above, the substitutional adsorption corresponds to an activated process (see the discussion in Refs.

[14,15]). Therefore we will deal with it below but begin with the nonactivated situation which corresponds to the low-temperature adsorption. Figure 1 summarizes the calculated results for the adsorption energies for Na on Al(111) for various coverages, assuming homogeneous, periodic adlayers. As a consequence of the lateral dipole-dipole repulsion the adsorption becomes energetically less beneficial with increasing coverage. At low coverage the threefold hollow position has the optimal energy. Figure 1 displays that the adsorption energy goes through a maximum. This result implies that the  $\Theta = 1/8$ ,  $\Theta = 1/4$ , and  $\Theta = 1/3$  structures are unfavorable when compared to the densely packed, hexagonal,  $\Theta = 9/16$  adlayer. Thus, the theory predicts a structural phase transition at about  $\Theta = 0.1$  where the adlayer changes from a homogeneous distribution with maximum interatomic distances to adsorbate islands with an interatomic distance only slightly larger than that in bulk Na (see the dashed line in Fig. 1). Whereas at low coverage ( $\Theta < 0.1$ ) the adsorbate-substrate interaction dominates and is well described in terms of the (modified) Gurney model [5], at  $\Theta > 0.1$  it is energetically advantageous to alter the adsorbate-substrate interaction and to build up alkali-metal islands with a metallic, attractive adsorbate interaction. This phase transition may be called a condensation of the adsorbate atoms. In these islands ( $\Theta_{\text{local}} = 0.56$ ) the adsorbate unit cell is a  $4 \times 4$  structure with nine adatoms per cell. Now most adatoms no longer sit at the energetically preferred hollow position, indicating that the adsorbate-substrate interaction is less important than the adsorbate-adsorbate interaction. The analysis of the electron density of the adlayer shows that the islands are very similar to the fcc(111) surface of fcc sodium [18]. Andersen *et al.* [11] recently reported that in the coverage range between the homogeneous adlayer and the  $4 \times 4$  structure there is a precursor, close-packed island structure with a slightly more open geometry, which he calls a distorted  $3 \times 3$  unit cell with a local coverage of  $\Theta_{\text{local}} \approx 0.44$ .

The corresponding results for potassium on Al(111)

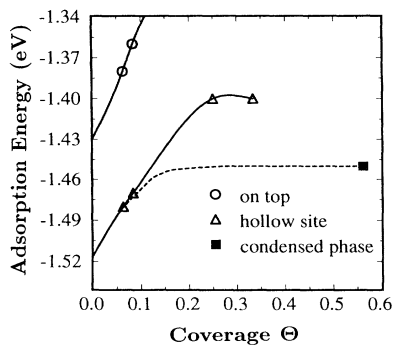


FIG. 1. Adsorption energy versus coverage for on-top and threefold hollow sites. The dashed line marks the phase transition from the homogeneous adlayer into adatom islands.

are given in Fig. 2. At low coverage ( $\Theta \rightarrow 0$ ) the results for Na and K are qualitatively similar. Both adatoms occupy the threefold hollow site where the fcc and hcp surface sites are degenerate within the accuracy of our calculations. With increasing coverage we find that also for K a condensation phase transition should occur starting at about  $\Theta = 0.15$ . The K islands form a  $\sqrt{3} \times \sqrt{3}$  structure which has just an about 5% larger interatomic distance than in K bulk. The interesting point is that we found a change of the adsorption site from the hollow to the on-top position.

We now turn to the substitutional adsorption, already mentioned above, which is an activated process. Thus, this should require some "high" temperature. We are unable to specify at this point what is meant by "high" temperature, because a fully dynamical calculation of the phase transition to the substitutional adsorption is not feasible at this time. It may also be possible that the reaction path and its barriers can be influenced by "impurity" atoms on the surface. The substitutional adsorption is certainly influenced by the quality of the surface, i.e., by the concentration of steps and substrate-atom or vacancy islands. Thus, the reaction path from the "normal" to the substitutional adsorption is uncertain, although a possibility has been suggested [14,15]. For the substitutional adsorption the adsorption energy  $E_{\text{ad}}^{\text{sub}}$  can be written as a sum of two contributions: (i) the creation of a surface vacancy which costs energy (i.e.,  $E_f^{\text{vac}} > 0$ ) and (ii) the bonding of the adsorbate on the surface with the vacancies which is exothermal (i.e.,  $E_b < 0$ ). This gives  $E_{\text{ad}}^{\text{sub}} = E_b + E_f^{\text{vac}}$ .

If this energy is lower, i.e., more favorable, than the binding energy for the normal, on-surface adsorption then the substitutional adsorption will be the ground state. It is obvious that the substitutional adsorption will be favored on such surfaces and for such structures for which the formation energy of a surface vacancy is low [19]. For the Al(111) surface we find a particularly low vacancy formation energy for the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure which is about half the energy of other more open vacancy arrangements. The preference of this vacancy structure is triggered by the covalency of the substrate

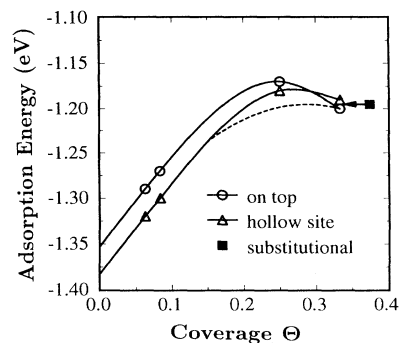


FIG. 2. Same as Fig. 1 but for K on Al(111).

[18].

For Na we find that the substitutional adsorption in the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure is energetically favored over the other adsorption geometries for all coverages. The adsorption energy is  $-1.58$  eV, thus even outside the energy range of Fig. 1. For Na on Al(111) we therefore expect island formation already at very low coverages, provided that the reaction barriers can be overcome. For K, on the other hand, the normal, on-surface adsorption is energetically more favorable at low coverages. The substitutional site becomes energetically possible at monolayer coverages ( $\Theta = 1/3$ ) where all adsorption energies are nearly degenerate (see Fig. 2). The numerical accuracy of the calculation and the fact that we are only able to calculate the static total energy do not allow us to draw conclusions about which structure is the true ground state. In fact, it is possible that the thermodynamic ground state is also controlled by the entropy and then the temperature will determine what the stable phase is.

The first quantitative analysis of the coverage dependence of the work function was attempted by Lang [20] using a jellium overlayer on a jellium substrate. For parameters corresponding to Na on Al he found that  $\Delta\Phi(\Theta)$  should decrease up to a minimum  $\Delta\Phi_{\min} = -1.8$  eV at  $\Theta_{\min} = 0.12$ . Ishida [8] recently treated a homogeneous, atomistic Na adlayer on a jellium substrate, corresponding to Al(111). He obtained  $\Delta\Phi_{\min} = -1.4$  eV at  $\Theta_{\min} = 0.20$ . Although the results of Lang and Ishida are somewhat different they were both interpreted as to support the commonly accepted explanation that the coverage dependence of the work function is a consequence of a continuous adlayer compression linked with a depolarization of the adsorbate induced dipoles. The experimentally determined work function change, measured by Hohlfeld and Horn [9] is, however, significantly different from these calculated results: At low temperature no clear minimum of  $\Delta\Phi(\Theta)$  is found and for room temperature adsorption the experimental minimum is at  $\Theta = 1/3$ , thus much higher than given by Lang's and Ishida's calculations.

We can use the calculated coverage dependence of the dipole moment and of the binding energy in order to evaluate the work function change with coverage from first principles. Again we distinguish the nonactivated ("low temperature") and the activated ("high temperature") adsorption. The possibilities of island formation discussed above (see Figs. 1 and 2) imply that the work function change with coverage is determined by a coexistence of adsorbed "gaslike" adatoms and adatoms in islands with a total coverage  $\Theta_{\text{gas}}$  and  $\Theta_{\text{isl}}$  for each phase. The corresponding dipoles of each phase are  $\mu(\tilde{\Theta}_{\text{gas}})$  and  $\mu(\tilde{\Theta}_{\text{isl}})$ , where  $\tilde{\Theta}_{\text{gas}}$  and  $\tilde{\Theta}_{\text{isl}}$  are the local coverages around the adsorbate, i.e.,  $\tilde{\Theta}_{\text{isl}} \approx 9/16$  for Na and  $\tilde{\Theta}_{\text{isl}} \approx 1/3$  for K. The local coverage  $\tilde{\Theta}_{\text{gas}}$  for the gas phase is calculated under the assumption that the

"gaslike atoms" are homogeneously distributed over the full surface reduced by the area of the islands. The total coverage is  $\Theta = \Theta_{\text{gas}} + \Theta_{\text{isl}}$  and the coverages  $\Theta_{\text{gas}}$  and  $\Theta_{\text{isl}}$  are determined by  $\Theta_i \propto \exp \frac{-E_{\text{ad}}(\tilde{\Theta}_i)}{k_B T}$ , where  $i$  stands for gas or island and  $E_{\text{ad}}$  is the adsorption energy. The work function change is then

$$\Delta\Phi(\Theta) = \frac{-e}{\epsilon_0 A} [\Theta_{\text{gas}} \mu(\tilde{\Theta}_{\text{gas}}) + \Theta_{\text{isl}} \mu(\tilde{\Theta}_{\text{isl}})] \quad (1)$$

Here  $A$  is the area occupied by one adsorbate at  $\Theta = 1$ , and  $e$  and  $\epsilon_0$  are the electron charge and the vacuum dielectric constant. Figure 3(a) shows the corresponding theoretical result for Na on Al(111) for three temperatures ( $T = 0, 70$ , and  $140$  K) together with the experimental  $T = 140$  K result of Hohlfeld and Horn [9]. Our treatment differs significantly from that typically applied but it describes the experimental data satisfactorily.

For the activated, substitutional adsorption our calculations for Na on Al(111) predict island formation with a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure from the very beginning. Figure 3(b) shows the theoretical result in comparison with the measurement. Again we note that this is in clear disagreement with the previous theories. In Fig. 3(b) we only present the coverage range up to  $\Theta = 1/3$  because for higher coverage a second adsorbate layer starts to form and we have not yet determined its atomic structure. It is, however, plausible that the work function will go up with increasing coverage because a thick Na overlayer will have the work function of a Na crystal which corresponds to  $\Delta\Phi = -1.5$  eV. We conclude that the work function minimum observed for Na on Al(111) at room temperatures is a result of a structural change of the adsorbate overlayer and not a result of a depolarization induced by the continuous reduction of the adsorbate-adsorbate distance.

For K on Al(111) the calculations of Fig. 2 together with Eq. (1) give the work function change plotted in Fig. 4, which agrees with the experiment for low temperatures. For high temperatures, for which no experimental data are available, we find no change in the work

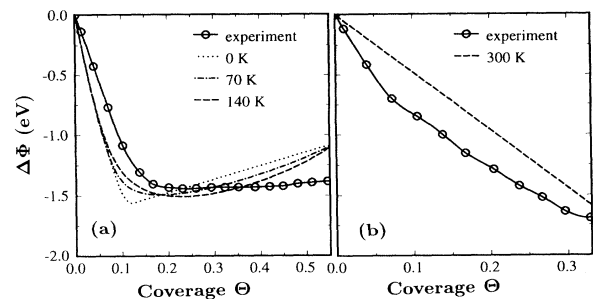


FIG. 3. Calculated (dashed line) and measured Ref. [9] (full line) work function change  $\Delta\Phi$  with coverage for Na on Al(111). (a) for the "normal," on-surface adsorption (nonactivated). (b) for the substitutional adsorption.

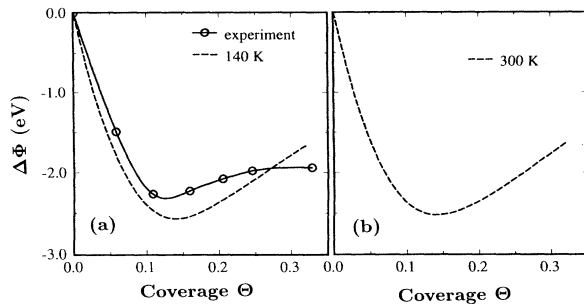


FIG. 4. Same as Fig. 3 but for K on Al(111). The calculated work function changes are practically independent of temperature, therefore in (a) only the  $T = 140$  K curve is plotted.

function shape [see Fig. 4(b)].

In conclusion, we have shown that at very low coverages alkali-metal adatoms repel each other. As a consequence of this repulsion we obtain site changes and island formation. In fact there are two qualitatively different island structures. Assuming a nonactivated adsorption ("low temperature") the island formation is described as an adatom condensation. On the other hand, assuming an activated adsorption ("high temperature") the island formation is triggered by the covalency of the substrate [14], giving rise to a substitutional adsorption which may also be called an ordered surface alloy.

The discussed mechanisms of site changes and island formation for the on-surface adsorption (nonactivated) should be present also on other substrates. However, the substitutional adsorption requires a low vacancy formation energy. Thus, this will be less general. Other substrates where it may occur are, for example, Ag(111) [19], Au(111), and the more open surfaces. Furthermore, we note that the substitutional adsorption is typically kinetically hindered and that it requires steps and kink sites or a reachable and energetically favorable reservoir for the kicked out substrate atoms. The electronic structure of such adsorbate covered surfaces is then largely determined by the created vacancies and only little by the alkali-metal adatoms (see Ref. [21]). We hope that our study will stimulate further experimental and theoretical work with particular attention to the temperature dependence of adsorption and adsorbate-layer phase transitions.

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*Note added.*—Recent experiments show that the de-

scribed concept of condensation is more general than for the adsorbate system studied above. A condensation for Li on Be(0001) was observed by Watson *et al.* [22] and for Mg on Ru(0001) by Over *et al.* [23].

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