Identification of Stable and Metastable Adsorption Sites of K Adsorbed on Al(111)

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The adsorption of potassium on Al(111) at 90 K and at 300 K has been investigated by low-energy electron diffraction (LEED). Although a $(\sqrt{3} \times \sqrt{3})R30°$ structure is formed at each temperature, a detailed LEED analysis has revealed that the adsorbate positions are quite different and unusual in each case. At 90 K the adatoms occupy on-top sites and at 300 K they occupy substitutional sites. An irreversible phase transformation from the former to the latter structure occurs on warming to 300 K. These results are discussed in the light of recent density-functional-theory calculations.

The adsorption of atoms on crystal surfaces constitutes a wide area of study which still uncovers fundamental questions. Recently alkali-metal adsorption has attracted much attention where the nature of the bond, which changes with alkali coverage, and which is reflected by the well known lowering of the work function, is a subject of current interest and controversy. The adsorption of alkali metals plays an important role in the development of theories of adsorption [1] because, based on previous experimental results [1–4], it was widely believed to result in a relatively simple adsorbate system for close-packed surfaces, i.e., occupation of high-symmetry sites without reconstruction of the substrate. Suprisingly, however, rather few quantitative determinations of the adsorption geometry have been reported [5–10]. A dramatic exception to the notion of simple adsorption has been found very recently by measurements of surface extended x-ray absorption fine structure (SEXAFS) for Na adsorption on Al(111) as well as by density-functional-theory calculations which led to the conclusion that the adsorption produces a reconstruction of the substrate with Na atoms occupying substitutional sites formed by removal of surface Al atoms [11].

The results of the present LEED study show unambiguously that K adsorption at room temperature leads to a $(\sqrt{3} \times \sqrt{3})R30°$ unit cell and a reconstruction of the Al(111) substrate such that K atoms occupy substitutional sites. Unlike the case of Na adsorption, however, adsorption of K at low temperature also results in a $(\sqrt{3} \times \sqrt{3})R30°$ unit cell, but with occupation of on-top sites on a rumpled substrate. An irreversible transformation of the latter, metastable structure to the former structure occurs upon warming to room temperature without change in the 2-D unit cell, which is quite unprecedented and will certainly influence the present understanding of the nature of adsorbate-substrate interactions.

LEED intensity measurements were performed at 90 K for the clean Al(111) surface and for the $(\sqrt{3} \times \sqrt{3})R30°$ structures formed respectively by saturation adsorption at 300 K and by adsorption (not to saturation) at 90 K. Rutherford backscattering measurements have shown that the former structure is formed by adsorption of 1/3 monolayer of K atoms [12] [a monolayer is defined to have the same number of atoms as an Al(111) plane]. Auger electron spectroscopy (AES) measurements in the present work indicated that the structure formed by adsorption at 90 K also corresponds to a coverage of 1/3 of a monolayer. For each structure, intensity-energy curves were measured at normal incidence in the energy range 50–450 eV for 20 diffracted beams, which reduced to four symmetry-inequivalent integral-order and four symmetry-inequivalent fractional-order beams. The measurements were performed using a newly developed video-LEED system [13] which permitted the acquisition of a complete set of data in less than 2 min. AES measurements taken after completion of the LEED measurements indicated that surface contamination was less than 0.01 monolayer.

Comparison of the *experimental* LEED intensity curves for the two structures leads immediately to the conclusion that the corresponding local geometries must be quite different. Furthermore, intensities measured after adsorption at 90 K and warming to 300 K are identical to those measured after adsorption at 300 K alone, indicating the occurrence of an irreversible, order-preserving phase transition.

LEED intensity calculations were performed using the fully dynamical calculation scheme which performs an automatic minimization of a normalized χ^2 function, as a function of the calculational variables, both structural and nonstructural. The R_{DE} factor defined by Kleinle *et al.* [14, 15] was also used to characterize the agreement between experiment and theory in a preliminary

grid search of the parameter space. Scattering from Al and K atoms was described using 10 phase shifts calculated from the muffin-tin band-structure potentials of Moruzzi, Janak, and Williams [16]. Atomic scattering matrices were renormalized for the effects of thermal vibrations using a single Debye temperature Θ_{Al} for the Al substrate and a different Debye temperature Θ_K for the adsorbed K atoms which was taken as a variable in the analysis. The complex electron self-energy $\Sigma = V_0 + iV_{im}$ was taken to be independent of energy. The surface potential barrier was assumed to be a refracting but nonreflecting step of height V_0.

Analysis of intensity curves for the clean Al(111) surface indicated that the first interlayer spacing is expanded by $(1.3 \pm 0.8)\%$ in excellent agreement with the results of previous studies [17]. The analysis, which was carried out for fixed values of $\Theta_{Al} = 490$ K [17] and $V_{im} = 4.0$ eV, led to an optimum value of $V_0 = 6.0 \pm 1.0$ eV (with respect to the muffin-tin zero) and a value of $R_{DE} = 0.20$.

In the analysis of the intensities for each of the two $(\sqrt{3} \times \sqrt{3})R30°$ structures five different adsorption sites were considered as starting points; namely, onefold on-top, twofold bridge, threefold fcc and hcp hollow, and sixfold coordinated substitutional. In the first step of the analysis the K-Al interlayer spacing and the first Al-Al interlayer spacing were optimized together with V_0.

For the structure formed at 300 K the initial analysis showed a clear preference for the substitutional sites. Further refinement involving lateral and vertical relaxations of the substrate and optimization of Θ_K enhanced this preference. The best-fit R factors for the five sites considered are listed in Table I, from which the preference for the substitutional site is evident. (Here, and later in Table II, are also listed the corresponding values of the R factors defined by Pendry [18] and by Zanazzi and Jona [19].) A sketch of the global optimum structure is shown in Fig. 1 where the K atoms are in quasisubstitutional sites formed by the ejection of 1/3 of a monolayer of Al atoms. The K atoms are situated at a vertical distance of 2.16 ± 0.03 Å above the first layer of Al atoms, corresponding to a nearest-neighbor K-Al distance of 3.58 Å. Assuming a hard-sphere metallic radius $r_{Al} = 1.43$ Å yields an effective radius $r_K = 2.15$ Å, lying between the covalent radius of 2.03 Å and the metallic radius of 2.27 Å. The first Al interlayer spacing is contracted by (2

$\pm 1)\%$ with respect to the bulk value, whereas the second Al interlayer spacing is equal to the bulk value within the error of the determination. Optimum values of V_0 $=4.0 \pm 1.5$ eV and $\Theta_K =165 \pm 50$ K were determined in the analysis. A comparison of the experimental intensity curves with those calculated for the optimum geometry is shown in Fig. 2(a), from which a very good agreement is evident. In the analysis the positions of the displaced Al atoms were neglected. In view of the good agreement noted above, it seems unlikely that they form an ordered sublattice, rather they are most probably readsorbed at steps.

For the structure formed at 90 K the initial analysis led to a rejection of the twofold and threefold sites but did not lead to a clear discrimination between the onefold on-top and sixfold coordinated substitutional site. However, further refinement involving lateral and vertical relaxations of the substrate layers and variation of Θ_K did clearly indicate a preference for the on-top site, as is evident from Table II in which the best-fit R factors for all sites considered are listed. For the on-top site the best-fit structure, as sketched in Fig. 3, involves a rumpling of the first layer of Al atoms to form a bilayer, such that Al atoms directly beneath K atoms are displaced towards the bulk by 0.25 ± 0.04 Å. The vertical distance of the K atoms to the first layer of the bilayer was found to be 2.98 ± 0.05 Å, giving a K-Al nearest-neighbor distance of 3.23 Å. The vertical distances of the atoms in the bilayer to the second layer of Al atoms were found to be 2.46 Å and 2.21 ± 0.05 Å as compared to the bulk

TABLE I. The best-fit R factors for each of the sites considered for the Al(111)-$(\sqrt{3} \times \sqrt{3})R30°$-K structure formed at 300 K.

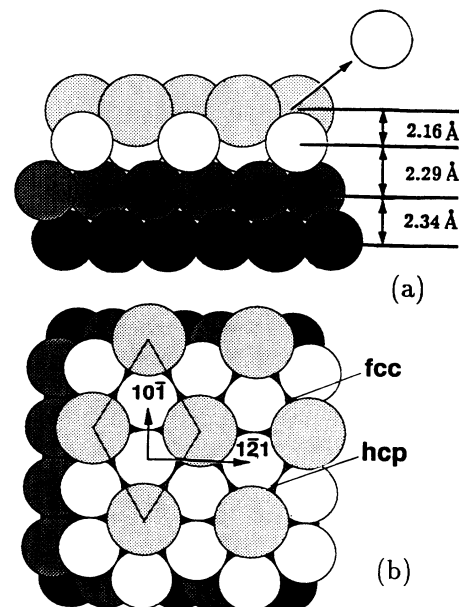| R_{DE}	R_{ZJ}	R_P	Adsorption site
0.284	0.126	0.280	substitutional
0.536	0.213	0.714	on-top
0.590	0.342	0.705	fcc hollow
0.554	0.240	0.686	bridge
0.863	0.353	0.949	hcp hollow

FIG. 1. The atomic geometry of the substitutional site. K atoms are shown as larger pale grey circles; the first, second, and third layers of Al atoms are shown in white, grey, and black, respectively. (a) Side view of the (111) surface on a $(10\bar{1})$ plane. Determined values of the interlayer spacings are indicated on the sketch. (b) Top view.
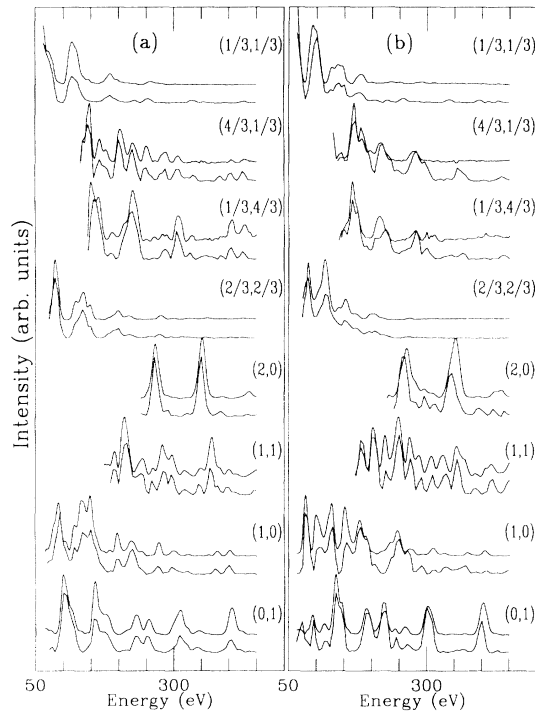
FIG. 2. (a) Experimental and calculated intensity-energy curves for the structure formed by adsorption at 300 K. For each beam the experimental intensities are the upper curves. The calculated intensities are for the best-fit geometry for the substitutional site, as shown in Fig. 1. (b) Experimental and calculated intensity-energy curves for the structure formed by adsorption at 90 K. For each beam the experimental intensities are the upper curves. The calculated intensities are for the best-fit geometry for the on-top site, as shown in Fig. 3.
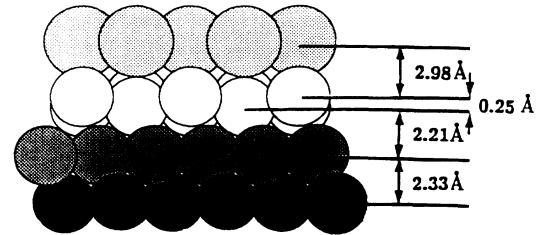

FIG. 3. Side view showing the atomic geometry of the on-top site, where the rumpling of the first Al layer can be seen. For the meaning of the grey code see Fig. 1. The top view of this structure is indistinguishable from Fig. 1(b). Determined values of the interlayer spacings are indicated on the sketch.

interlayer spacing of 2.33 Å. The inward displacement of 1/3 of the Al atoms in the first layer was found to be accompanied by outward lateral shifts of 0.05 Å of the nearest-neighbor Al atoms in the second layer. Assuming again a hard-sphere metallic radius of $r_{Al} = 1.43$ Å yields an effective radius $r_K = 1.80$ Å. The refinement led to optimum values of $V_0 = 6.0 \pm 1.5$ eV and $\Theta_K = 120 \pm 60$ K. A comparison of the experimental and calculated intensities is shown in Fig. 2(b), from which a good agreement is again evident. The occupation of an on-top site after adsorption at low temperature and the occupation of a substitutional site after adsorption at room temper-

TABLE II. The best-fit R factors for each of the sites considered for the Al(111)-($\sqrt{3} \times \sqrt{3}$)$R30°$-K structure formed at 90 K.

R_{DE}	R_{ZJ}	R_P	Adsorption site
0.572	0.259	0.695	substitutional
0.368	0.114	0.326	on-top
0.655	0.327	0.797	fcc hollow
0.607	0.220	0.705	bridge
0.738	0.328	0.904	hcp hollow

ature explains the differences seen in the high-resolution core-level spectroscopy measurements of Andersen et al. [20].

Density-functional-theory (DFT) calculations by Neugebauer and Scheffler [21] for the adsorption of Na and K on Al(111) have been performed. For Na adsorption, the DFT calculations show a clear preference for the quasisubstitutional site, in agreement with SEXAFS results [11]. For K adsorption, however, the calculations show that the adsorption energies for occupation of on-top, fcc, and substitutional sites are practically degenerate. With respect to the substitutional site, it is noted that this energy (1.17 eV) incorporates the energy of 0.41 eV required to displace an Al atom from the first layer and rebond this atom at a surface step. The explanation of the low vacancy-formation energy for the ($\sqrt{3} \times \sqrt{3}$)$R30°$ structure is that for this geometry the group-III Al substrate can form a very favorable sp^2-bonded (graphitelike) surface layer. The calculated [21] nearest-neighbor distances of 3.70 and 3.38 Å for the substitutional and on-top sites, respectively, are in reasonable agreement with the values determined here of 3.58 and 3.23 Å. The significant difference in the bond length of about 0.3 Å between the two different sites reflects the different types of chemical bonds and the different coordination (see Ref. [21]).

The present results shed some light on the nature of the phase transition and the mechanism for the ejection of Al atoms necessary to form the substitutional adsorption. We find that on-top adsorption is metastable for the ($\sqrt{3} \times \sqrt{3}$)$R30°$ structure. Thus, for the periodic layer a structural phase transition to substitutional adsorption becomes possible and it is energetically favorable. Our results indicate that warming to 300 K is sufficient to overcome the activation barrier for this transition. This is consistent with the results of the DFT calculations although it was not possible in these calculations to determine unambiguously if a barrier exists for the transition. The DFT calculations assumed a particular reaction path where the ejected substrate atom moves to a step and is rebonded there. The energy barrier for this reaction path from the on-surface alkali to the surface-substitutional

one is 0.8 eV, namely, the energy of an on-surface alkali minus the energy of the substitutional alkali plus an adsorbed Al atom. This value is in accord with the experimental analysis. A barrier of 0.8 eV implies that the transition could occur with measurable rate at temperatures of the order of 220 K but with negligible rate at 90 K. Clearly a more detailed study of the temperature dependence of the phase transition would be most important.

In summary, a LEED analysis of the $(\sqrt{3} \times \sqrt{3})R30°$ system formed by adsorption of K on Al(111) at two different temperatures (90 and 300 K) shows that the two conditions give rise to the same periodicity but a significantly different local geometry and bonding nature. The structure formed at 90 K contains K atoms in on-top sites on a rumpled first layer of Al atoms. This structure is metastable and converts to a structure containing K atoms in a sixfold coordinated substitutional site on warming to 300 K. It is well known that alkali atoms induce surface reconstructions on open surfaces of metals [22]. For these surfaces the local perturbation of a single adatom suffices to start the reconstruction. The results of the present study, however, show a different and unexpected behavior. Here we have the most close-packed surface and the transition is due to a collective effect of the periodic adlayer. Thus, the adsorbate/metal system which is often described as the most simple, i.e., an adatom with only a single valence electron on the surface of a simple metal, and which is the best candidate for theoretical "jellium," is much more complicated than hitherto assumed.

[1] For a recent review see N. D. Lang, in *Physics and Chemistry of Alkali Metal Adsorption*, edited by H. P. Bonzel, A. M. Bradshaw, and G. Ertl (Elsevier, Amsterdam, 1989).

[2] S. Andersson and J. Pendry, Solid State Commun. **16**, 563 (1975).

[3] J. Demuth, D. Jepsen, and P. Marcus, J. Phys. C **8**, L25 (1975).

[4] B. Hutchins, T. Rhodin, and J. Demuth, Surf. Sci. **54**, 419 (1976).

[5] S. Lindgren, L. Walldén, J. Rundgren, P. Westrin, and J. Neve, Phys. Rev. B **28**, 6707 (1983).

[6] H. Over, H. Bludau, M. Skottke-Klein, G. Ertl, W. Moritz, and C. Campbell, Phys. Rev. B **45**, 8638 (1992).

[7] M. Kerkar, D. Fisher, D. P. Woodruff, R. Jones, R. Diehl, C. McConville, and X. Hu (to be published).

[8] D. Fisher, S. Chandavarkar, I. R. Collins, R. Diehl, P. Kaukasoina, and M. Lindroos, Phys. Rev. Lett. **68**, 2786 (1992).

[9] G. von Eggeling, G. Schmidt, G. Besold, L. Hammer, K. Heinz, and K. Müller, Surf. Sci. **221**, 11 (1989).

[10] C. J. Barnes, P. Hu, M. Lindroos, and D. A. King, Surf. Sci. **251/252**, 561 (1991).

[11] A. Schmalz, S. Aminprooz, L. Becker, J. Haase, J.Neugebauer, M. Scheffler, D. R. Batchelor, D. L. Adams, and E. Bøgh, Phys. Rev. Lett. **67**, 2163 (1991).

[12] H. W. Jørgensen, Ph.D. thesis, Aarhus University, 1976 (unpublished).

[13] D. L. Adams, S. P. Andersen, and J. Burchhardt, in *The Structure of Surfaces III*, edited by S. Y. Tong, M. A. Van Hove, X. Xide, and K. Takayanagi (Springer, Berlin, 1991).

[14] G. Kleinle, W. Moritz, D. L. Adams, and G. Ertl, Surf. Sci. **219**, L637 (1989).

[15] G. Kleinle, W. Moritz, and G. Ertl, Surf. Sci. **238**, 119 (1990).

[16] V. Moruzzi, J. Janak, and A. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[17] H. B. Nielsen and D. L. Adams, J. Phys. C **15**, 615 (1982).

[18] J. B. Pendry, J. Phys. C **13**, 937 (1980).

[19] E. Zanazzi and F. Jona, Surf. Sci. **62**, 61 (1977).

[20] J. N. Andersen, E. Lundgren, R. Nyholm, and M. Qvarford (to be published).

[21] J. Neugebauer and M. Scheffler (to be published).

[22] For a recent review see R. J. Behm, in *Physics and Chemistry of Alkali Metal Adsorption* (Ref. [1]).
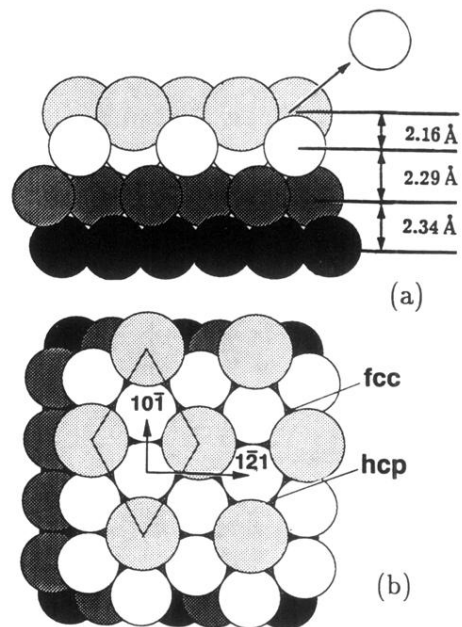
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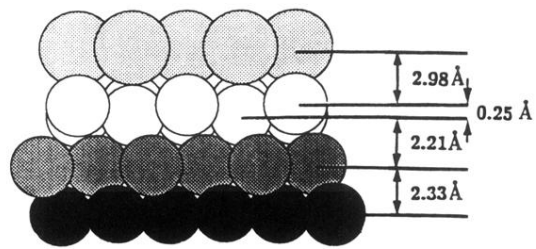
FIG. 3.   Side view showing the atomic geometry of the on-top site, where the rumpling of the first Al layer can be seen. For the meaning of the grey code see Fig. 1. The top view of this structure is indistinguishable from Fig. 1(b). Determined values of the interlayer spacings are indicated on the sketch.