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## Enhanced Surface Vibrations and Reconstruction of the Al(111) Surface Induced by Rb Adsorption

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The bond geometries of Rb atoms in two different  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structures, formed by adsorption on Al(111) at 100 and 300 K, have been determined by low energy electron diffraction. Adsorption at 300 K leads to occupation by Rb atoms of a quasisubstitutional, sixfold coordinate site formed by displacing every third Al atom in the first layer of the substrate. Adsorption at 100 K leads to occupation of an on-top site on a rumpled Al layer in which the vibrational amplitudes of Al atoms are anomalously large. An irreversible, order-preserving phase transition from the 100 K to the 300 K structure occurs on annealing.

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Studies of the adsorption of alkali metals on metals have played an important role in the development of theories of adsorption. However, until recently, very few quantitative *structural* results were available for these systems, with the result that theoretical models have assumed adsorption to occur on sites of high symmetry on unperturbed substrates [1,2]. That this assumption is not generally valid was first demonstrated by a surface extended x-ray absorption fine structure (SEXAFS) study [3] of the adsorption of Na on Al(111) at room temperature, which showed that the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure involves a *reconstruction* of the substrate. This completely unexpected [4] result was confirmed [3,6] by *ab initio*, total-energy calculations using density-functional theory (DFT). Further confirmation has been provided more recently via high-resolution core level spectroscopy [7] (HRCLS), normal incidence standing x-ray wave field [8] (NISXW), and low energy electron diffraction [9] (LEED). The observed reconstruction of a close-packed fcc(111) surface has added a new dimension to the discussion of alkali metal adsorption and has stimulated recent studies in which the possibility of strong perturbations of the substrate structure has been considered. Thus it has been shown that adsorption of K on Al(111) and Na on Al(100) leads to a reconstruction of the substrate [10–12]. For all of the above systems, adsorption at *low temperature* is found to lead to chemisorbed structures with no, or relatively minor, perturbation of the substrate structure. Irreversible, order-order phase transitions from the chemisorbed phases to the reconstructed phases occur on annealing to room temperature.

The results above raise the question as to whether reconstruction of the substrate is a general feature of alkali metal adsorption on metals. Recent studies of the adsorption of K on Ni(111) [13] and Ni(100) [14], K and Cs on Ru(0001) [15,16], and Na on Ni(100) [17], indicate that for these systems, at least, adsorption at room temperature leads to chemisorbed structures, al-

though for the Ni(111)-(2×2)-K and Ru(0001)-(2×2)-Cs structures, occupation of an unusual on-top site is accompanied by a small rumpling of the first layer of the substrate, as also occurs in the Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -K structure produced by adsorption at low temperature [10].

In the case of adsorption on Al surfaces, the question arises as to whether reconstruction of the substrate is limited to the adsorption of Na and K. It is known from LEED and HRCLS studies [10,12] that the Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -K structures formed at 100 and 300 K are different, and that the latter involves a reconstruction of the substrate. The suggestion has been made based on HRCLS measurements that the corresponding two  $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Rb structures are also different and that the 300 K structure involves a reconstruction of the substrate [18]. This suggestion conflicts with the conclusions of a NISXW study [8], in which it was reported that Rb adsorbs in an on-top site at 170 K, but that measurements following room-temperature preparation show no influence of the preparation temperature. In this regard it is interesting to note that the DFT calculations [6] for Na and K adsorption on Al(111) show that the quasisubstitutional site is favored energetically for Na, whereas threefold hollow, on-top, or substitutional sites are essentially degenerate for K. For Rb, the first results [19] of ongoing DFT calculations indicate that the calculated internal energies at 0 K favor adsorption on the surface rather than substitutional adsorption. Nevertheless, it is shown in the present work that adsorption of Rb at room temperature does in fact lead to a reconstruction of the Al(111) substrate.

A detailed account of the experimental and calculational procedures used in this work will be given elsewhere [20]. LEED intensity-energy spectra were measured using a video-LEED system [10,21] for each of the two  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structures, at 100 K, at normal incidence, in the energy range 40–400 eV for 49 diffracted

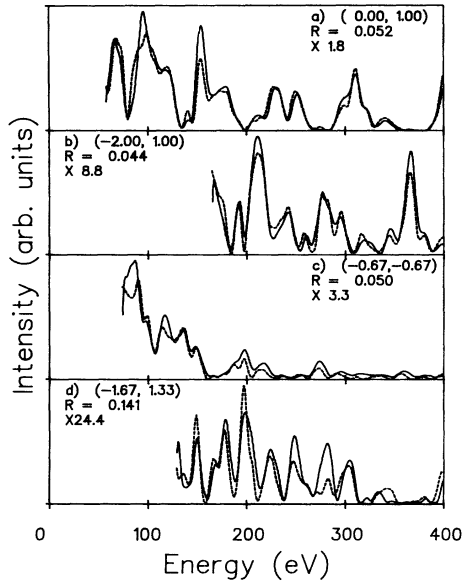


FIG. 1. Experimental intensity-energy spectra (full lines) for 4 of the 12 beams measured after adsorption at 300 K, compared with spectra (dashed lines) calculated for Rb adsorbed in the quasisubstitutional site. A single scale factor has been used to normalize the experimental and calculated intensities for all 12 beams. Note that the good agreement between experiment and calculations extends also to the relative beam intensities which differ by an order of magnitude. Beam  $hk$  indices,  $R$  factors, and plot scale factors are given in the figure.

beams. Averaging of symmetry-equivalent beams led to 5 integral-order and 7 fractional-order symmetry-inequivalent beams. Normal incidence was set by minimizing the discrepancy, as measured by the  $R$  factor defined below, between intensity spectra for (nominally) symmetry-equivalent beams. The resulting values of  $R = 0.017$  and  $0.029$  for the data sets for the 300 and 100 K structures, respectively, can be compared with the final values for the comparison of experimental and calculated spectra of  $0.051$  and  $0.066$ .

A comparison of the experimental spectra for adsorption at 100 and 300 K shows conclusively (see Figs. 1 and 2) that the geometrical structure is different in the two  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phases. The  $R$  factor for this comparison was  $0.54$ . Spectra taken after adsorption at 100 K and annealing to 300 K were closely similar ( $R = 0.07$ ) to spectra taken after adsorption at 300 K, revealing the occurrence of an order-preserving phase transition from the 100 K structure to the 300 K structure.

The geometry of the two different structures was determined by minimizing the  $R$  factor for the comparison of experimental  $I_{hk,i}^{\text{exp}}(E)$  and calculated  $I_{hk,i}^{\text{cal}}(E)$  intensity-energy spectra, as a function of the structural and non-structural variables of the calculations. The  $R$  factor is defined [22,23] as

$$R = \sum_{hk,i} \left( \frac{I_{hk,i}^{\text{exp}} - c I_{hk,i}^{\text{cal}}}{\sigma_{hk,i}} \right)^2 / \sum_{hk,i} \left( \frac{I_{hk,i}^{\text{exp}}}{\sigma_{hk,i}} \right)^2,$$

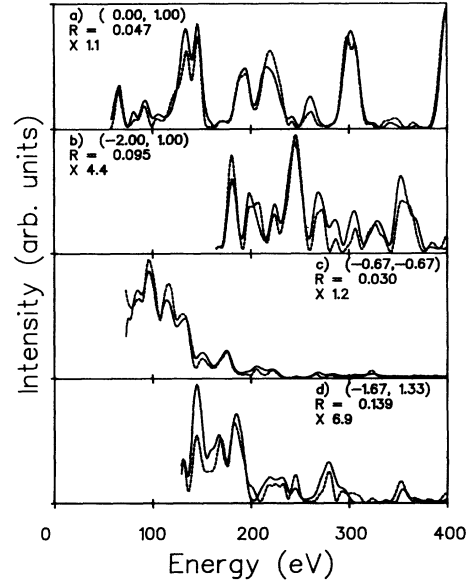


FIG. 2. Experimental intensity-energy spectra (full lines) for the same 4 beams as in Fig. 1, but measured after adsorption at 100 K, compared with spectra (dashed lines) calculated for Rb adsorbed in the on-top site on a rumpled Al layer. See caption to Fig. 1.

where  $\sigma_{hk,i}$  is the experimental uncertainty at the  $i$ th energy point for the beam  $hk$ , and  $c$  is a single, global scaling constant between the experimental and calculated intensities, determined by the requirement that  $\partial R / \partial c = 0$ . We emphasize that this definition of  $R$  takes into account essentially the full information content of the measurements including, *inter alia*, relative  $hk$  beam intensities.

LEED intensities were calculated using the full dynamical theory of LEED. Atomic scattering matrices were calculated using 14 phase shifts, calculated from band-structure potentials [24] for Al and Rb, and were renormalized for thermal vibrations using root-mean-square (isotropic) vibrational amplitudes  $u_{\text{Rb}}$  for Rb atoms, and  $u_{\text{Al},1}$  and  $u_{\text{Al,bulk}}$  for Al atoms in the first Al layer and bulk, respectively. The complex electron self-energy  $\Sigma = V_0 + iV_{\text{im}}$  was taken to be independent of energy.

In order to determine the gross features of the Rb adsorption site, an initial survey was carried out of models involving threefold hollow, onefold on-top, or sixfold substitutional sites, compatible with the experimentally observed symmetry. For the 300 K structure, this led directly to the identification of the quasisubstitutional site, as sketched in Fig. 3(b). A full refinement of the model parameters gave very good agreement between experimental and calculated intensity spectra and gave an  $R$ -factor value of  $0.051$ . Inclusion in the model of an  $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Al overlayer, formed from the displaced Al atoms, in various orientations with respect to the Rb layer, destroyed the fit and could therefore be ruled out. For the 100 K structure, satisfactory agreement was not achieved for adsorption in any of the simple high-

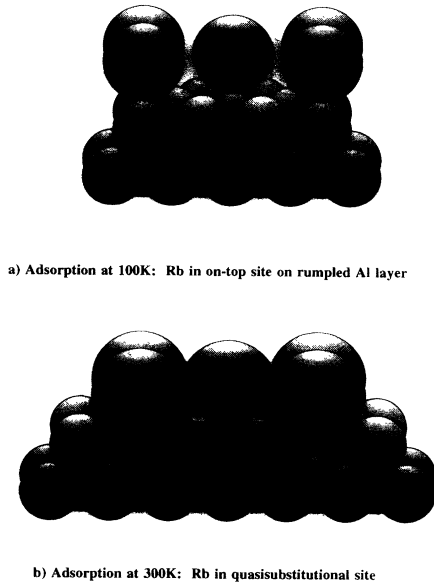


FIG. 3. Sketches of the structures formed by adsorption of Rb, shown from the side as central projections on the  $[1\bar{1}2]$  plane tilted by  $10^\circ$  with respect to the plane of the paper. Rb atoms are shown as the large, dark circles. (a) The on-top-rumpled structure formed by adsorption of Rb at 100 K. Note that the Al atoms directly beneath adsorbed Rb atoms are displaced towards the bulk with respect to the other Al atoms in the first layer. (b) The quasibulk structure formed by adsorption of Rb at 300 K. Rb atoms are located in sixfold coordinated sites formed by displacing Al atoms from the first layer.

symmetry sites. However, a convincing improvement in the fit was obtained for a model with Rb atoms adsorbed in on-top sites on a rumpled first Al layer, as sketched in Fig. 3(a), in which the Al atoms directly beneath adsorbed Rb atoms are displaced inward with respect to the remaining atoms of the layer. A refinement of the model parameters in which Al atoms in all layers were given the same vibrational amplitudes  $u_{\text{Al,bulk}}$  led to  $R=0.18$  for a vertical separation of  $\Delta r=0.29$  Å between the two sublattices of the rumpled layer, and  $u_{\text{Al,bulk}}=0.09$  Å. However, a further refinement, in which both the vibrational amplitudes  $u_{\text{Al,1}}$  of Al atoms in the rumpled Al layer and  $u_{\text{Al,bulk}}$  were varied, produced a dramatic improvement [25] in the fit, reducing the  $R$  factor by nearly threefold to  $R=0.066$ , for optimum values  $\Delta r=0.265$  Å and  $u_{\text{Al,1}}=0.18$  Å. A subsequent independent variation of the vibrational amplitudes of the Al atoms in each sublattice of the rumpled layer indicated that they have the same amplitudes,  $u_{\text{Al,1}}=0.18$  Å. It is possible that inclusion of anisotropic vibrations would further improve the fit, but that has not been investigated here [26]. The values for  $u_{\text{Al,1}}$  and  $u_{\text{Al,bulk}}$  given here can be compared with the corresponding values of  $0.13 \pm 0.02$  Å and  $0.08 \pm 0.01$  Å determined recently [9] for clean Al(111). A comparison of experimental and calculated intensity-energy spectra for 4 of the 12 symmetry-inequivalent beams used in the

TABLE I. Best-fit parameters for Rb adsorption at 300 K in the quasibulk site, and for Rb adsorption at 100 K in the on-top site on a rumpled Al layer.  $\Delta r$  is the rumpling, i.e., the vertical separation of the two sublattices in the rumpled layer.  $d_{ij}$  is the spacing between layers  $i$  and  $j$  in the surface-normal direction.  $d_{01}$  is the Rb-Al spacing. For the on-top structure, the layer spacings are with respect to the midpoint of the rumpled layer.  $r_{\text{Rb}}$  is the effective hard-sphere radius for Rb, assuming  $r_{\text{Al}}=1.426$  Å.  $u_{\text{Rb}}$ ,  $u_{\text{Al,1}}$ , and  $u_{\text{Al,bulk}}$  are the root-mean-square vibrational amplitudes for Rb atoms, and for Al atoms in the first layer and bulk, respectively. For both structures,  $d_{23}$  and  $d_{34}$  were equal to the bulk value to within 0.01 Å. The “bulk” values for  $d_{12}$  and  $r_{\text{Rb}}$  are calculated from the tabulated [28] lattice constants. The bulk values for  $u_{\text{Rb}}$  and  $u_{\text{Al,bulk}}$  are calculated from tabulated [29] Debye temperatures of 56 and 428 K, respectively.

	Quasibulk	On-top-rumpled	Bulk
$d_{01}$	$2.41 \pm 0.02$ Å	$3.22 \pm 0.03$ Å	
$\Delta r$		$0.265 \pm 0.02$ Å	
$d_{12}$	$2.27 \pm 0.02$ Å	$2.33 \pm 0.02$ Å	2.33 Å
$r_{\text{Rb}}$	2.31 Å	1.93 Å	2.47 Å
$V_{\text{im}}$	$3.2 \pm 0.3$ eV	$3.5 \pm 0.3$ eV	
$u_{\text{Rb}}$	$0.22 \pm 0.03$ Å	$0.22 \pm 0.03$ Å	0.40 Å <sup>a</sup>
$u_{\text{Al,1}}$	$0.14 \pm 0.02$ Å	$0.18 \pm 0.02$ Å	
$u_{\text{Al,bulk}}$	$0.10 \pm 0.01$ Å	$0.08 \pm 0.01$ Å	0.11 Å <sup>a</sup>
$R$	0.051	0.066	

<sup>a</sup>At 100 K.

analysis is given in Figs. 1 and 2 for the quasibulk and on-top-rumpled models, respectively. The detailed results of the refinement are summarized in Table I.

The main conclusions of this work are as follows. The  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structures formed by adsorption of Rb at 100 and 300 K are different. The structure formed at 100 K contains Rb atoms adsorbed in on-top sites on a rumpled Al bilayer. The vibrational amplitudes of Al atoms in the rumpled layer are anomalously large. The structure formed at 300 K contains Rb atoms adsorbed in quasibulk sites formed by displacement of Al atoms. The displaced Al atoms are not incorporated in the structure but are presumably readsorbed at steps. An irreversible phase transition occurs on annealing the 100 K structure to 300 K. The structure so formed is very similar to if not completely identical to the structure formed directly by adsorption at 300 K. It contains perhaps a small fraction of trapped Al atoms.

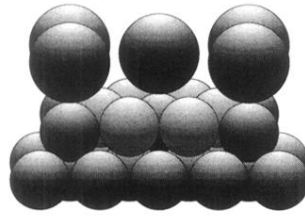
The present determination of the geometry of the two  $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Rb structures confirms the suggestions [18] made on the basis of HRCLS that they are different and that the 300 K structure involves a reconstruction of the substrate. It is now established that adsorption of Na, K, and Rb on Al(111) at room temperature leads to a reconstruction of the substrate. Thus the suggestion [8] that Na adsorption represents a special case in this respect can be rejected. The occupation by Rb of an on-top site in the 100 K structure is similar to that found

previously [10] for K, and confirms the conclusion for Rb based on a NISXW study [8].

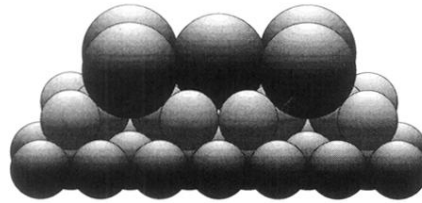
Finally we emphasize that the reconstruction of Al(111) by adsorption of Rb is far from obvious from the results of the *ab initio* calculations [6] for Na and K, and is in conflict with initial calculations [19] of internal energy at 0 K for Rb. It also contradicts the intuitive notion that Rb would be too large to substitute Al atoms in the Al(111) surface. The fact that reconstruction does occur suggests that the role of the adsorbed alkalis is rather one of stabilizing a  $(\sqrt{3}\times\sqrt{3})R30^\circ$  vacancy structure, than one of participating in surface alloy formation *per se*. Such a picture is consistent with the suggestion by Neugebauer and Scheffler [6] that a  $(\sqrt{3}\times\sqrt{3})R30^\circ$  vacancy structure can be stabilized by  $sp^2$  hybridization of the Al atoms. *A novel feature of the present study is the observation of large vibrations for Al atoms in the ruffled Al layer of the on-top structure.* Since the first step in the phase transition between the two structures presumably involves a place exchange of Al and Rb atoms, it is interesting to speculate that this involves the softening of an Al-Rb vibrational mode. It is also conceivable that the vibrations of surface atoms play a role in tipping the free energy balance between occupation of the on-top and substitutional sites in favor of the latter. We anticipate that ongoing DFT-molecular dynamics calculations [19] will clarify the possible roles of vibrational energy and entropy in the choice of the stable structure for this system.

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- [26] We plan in future work to investigate the extent of possible anisotropy in the vibrations of surface atoms by implementing Eq. 6.50 in Ref. [27] for the temperature-dependent atomic scattering matrix. We note that an *approximate* treatment of anisotropic vibrations was carried out in Ref. [10] for the adsorbed K atoms in the corresponding Al(111)- $(\sqrt{3}\times\sqrt{3})R30^\circ$ -K on-top structure, but the vibrational amplitudes of first layer Al atoms were not varied in that study.
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a) Adsorption at 100K: Rb in on-top site on ruffled Al layer



b) Adsorption at 300K: Rb in quasisubstitutional site

FIG. 3. Sketches of the structures formed by adsorption of Rb, shown from the side as central projections on the  $[1\bar{1}\bar{2}]$  plane tilted by  $10^\circ$  with respect to the plane of the paper. Rb atoms are shown as the large, dark circles. (a) The on-top-ruffled structure formed by adsorption of Rb at 100 K. Note that the Al atoms directly beneath adsorbed Rb atoms are displaced towards the bulk with respect to the other Al atoms in the first layer. (b) The quasisubstitutional structure formed by adsorption of Rb at 300 K. Rb atoms are located in sixfold coordinated sites formed by displacing Al atoms from the first layer.