Formation and Structural Analysis of a Surface Alloy: Al(111)-(2 × 2)-Na

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The Al(111)-(2 × 2)-Na phase formed by adsorption of one-half monolayer Na at 300 K is shown to be a *surface alloy*. Quantitative agreement is achieved between the results of structure determinations by low energy electron diffraction, surface extended x-ray adsorption fine structure, and total energy calculations. The first four layers of the structure are shown to consist of a Na-Al-Na sandwich on a reconstructed Al substrate layer. It is suggested that the formation of the structure involves surface steps as *sources* of Al atoms.

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The adsorption of alkali metals on aluminum surfaces is a favorite testing ground for theories of adsorption [1] because of a presumed simplicity of the electronic and geometrical structures. Recent experimental [2–12] and theoretical [2,13–16] work has revealed, however, that the testing ground is considerably more challenging than was realized in earlier studies. Specifically, a surprising *reconstruction* of the substrate is found to result from the adsorption of one-third monolayer Na, K, or Rb on Al(111) at room temperature [2,3,11,12]. The alkali atoms occupy *substitutional* sites of sixfold coordination in the resulting $(\sqrt{3} \times \sqrt{3})R30°$ phases. In contrast, *metastable* $(\sqrt{3} \times \sqrt{3})R30°$ phases in which the alkalis occupy *on-top* sites on a *rumpled* first Al layer are formed by adsorption of K and Rb at low temperature [3,11]. In the present Letter, a combined experimental and theoretical determination of the structure of Al(111)-(2 × 2)-Na reveals that this phase is much more complex than any of the adsorbed alkali systems studied previously. The structure is shown to consist of a *four-layer surface alloy*, even though bulk alloys of Al and Na are unknown. Quantitative agreement is achieved between the geometrical structures determined for this surface alloy by low energy electron diffraction (LEED), surface extended x-ray absorption fine structure (SEXAFS), and *ab initio* total-energy calculations using density functional theory in the local density approximation (DFT-LDA).

The Al(111)-(2 × 2)-Na phase is formed by adsorption of one-half monolayer Na at room temperature. The structure of this phase is controversial and a number of qualitatively different models have been proposed. The original suggestion by Porteus [17] that the structure consists of three domains of (2 × 1) periodicity was rejected on physical grounds by Hohlfeld and Horn [18], who, in turn, suggested that the structure consists of two layers of Na atoms, each with (2 × 2) periodicity, located on an unreconstructed substrate. The formation of a double Na layer was also concluded more recently in a high-resolution core level spectroscopy (HRCLS) study by Andersen *et al.* [4]. However, in this work it was also argued that Al atoms are incorporated in the double Na layer, resulting in the formation of a multilayer surface alloy. Based on the results of a normal incidence x-ray standing wave (NIXSW) study, Kerkar *et al.* [8] later concluded that the structure contains two composite $NaAl_2$ layers, with Na atoms in the lower layer located in on-top sites on the first Al layer of the substrate. Finally, a very recent scanning tunneling microscope (STM) study by Brune *et al.* [19] concluded that the structure consists of two layers of Na atoms, with the Na atoms in the lower layer adsorbed in substitutional sites on a reconstructed Al layer.

The main features of the structure determined in the present Letter are sketched in Fig. 1. In the following the results of the LEED, SEXAFS, and DTF-LDA studies leading to the structure shown in Fig. 1 are described in that order. .Individual studies will be described in detail elsewhere [20–22].

The Al(111)-(2 × 2)-Na structure was prepared [2] by evaporation of Na from a getter source with the crystal at room temperature. LEED intensity-energy spectra were measured using a video-LEED system [12] at a crystal temperature of 100 K, in the energy range 40–400 eV for 15 symmetry-inequivalent diffracted beams at normal incidence. The surface structure was determined by an iterative minimization of the R factor [12] for the fit between experimental and calculated spectra as a function of the positions and isotropic vibrational amplitudes of atoms in the first seven layers [20]. The results of the refinement of the model of Fig. 1 are given in Table I, together with the corresponding results of the SEXAFS and DFT-LDA analyses. A comparison of experimental LEED intensity-energy spectra with spectra calculated for

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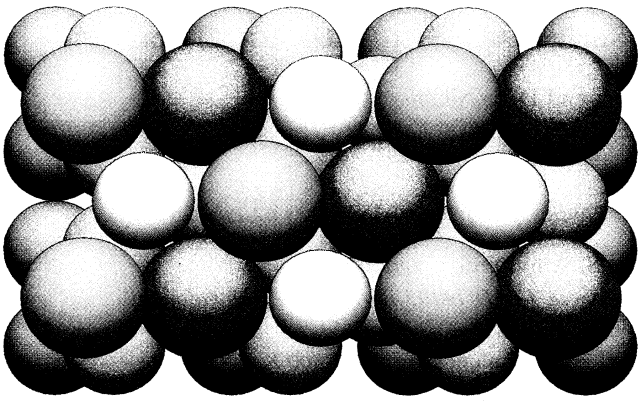
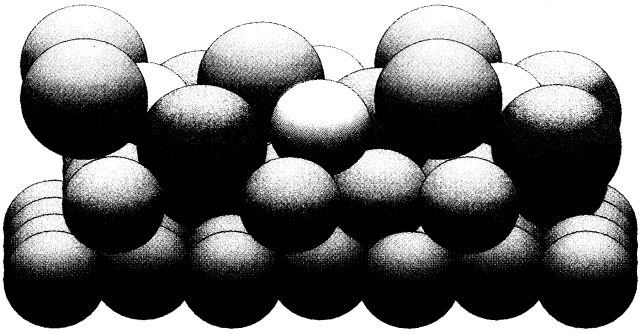


a) top view



b) side view (tilted 10°)

FIG. 1. Model of the Al(111)-(2 × 2)-Na structure. The top four layers, each of (2 × 2) periodicity, consist of a Na-Al-Na sandwich on a reconstructed Al layer with a (2 × 2) vacancy structure. Na atoms (shown in blue) in the lower layer of the sandwich are located in substitutional sites in the reconstructed layer. Al atoms (shown in yellow) in the sandwich layer and Na atoms (shown in red) in the upper layer of the sandwich are located in hcp and fcc sites, respectively, on the reconstructed layer. Al atoms in the reconstructed layer are shown in green. Substrate Al atoms are shown in dark blue. (a) Top view. (b) Side view shown as a central projection on the $(\bar{1}10)$ plane tilted by 10° with respect to the plane of the paper.

the tabulated best-fit parameter values is shown for 5 of the 15 symmetry-inequivalent beams in Fig. 2. The level of agreement between experiment and theory ($R = 0.038$) is not far from the reproducibility of the experimental data ($R = 0.023$ for the comparison of experimental symmetry-equivalent beams) and compares very well with the level of agreement ($R = 0.029$, 0.062, and 0.051) obtained previously for the simpler, room temperature $(\sqrt{3} \times \sqrt{3})R30°$-Na (K, Rb) structures [3,11,12], giving a high degree of confidence in the correctness of the model. In additional calculations, it was found that switching the positions of the Al atoms and upper Na atoms in the sandwich layer (i.e., placing Al atoms in fcc sites and Na atoms in hcp sites) gave a much worse agreement between experimental and calculated LEED intensities. Finally, it was found that intensities calculated for the models derived by NIXSW [8] and STM [19] completely failed to reproduce the experimental measurements [20].

The SEXAFS experiments were performed at the electron storage ring BESSY in Berlin. The Al(111)-(2 × 2)-Na structure was prepared as described above. The sodium K-edge SEXAFS data were taken in the total electron yield mode at normal x-ray incidence ($\theta = 90°$, **E** vector parallel to the surface) and near-grazing incidence ($\theta = 20°$) at a crystal temperature of 120 K. They were analyzed by a conventional Fourier transform method and by a curve-fitting procedure [2]. The interlayer spacings derived from the analysis for the model of Fig. 1 are listed in Table I. The best fits to the SEXAFS χ functions at $\theta = 20°$ and $\theta = 90°$, and to the corresponding Fourier transforms, are shown in Fig. 3. The dominant peak in each Fourier transform is due to the overlap of four different Na-Al distances and one Na-Na distance. However, the strongest contributions, corresponding to d_{34}, $d_{13} = d_{12} + d_{23}$, and $d_{14} = d_{12} + d_{23} + d_{34}$ in Table I, can be determined independently and accurately [21]. We note that good fits were also obtained for a model with a local Al-Na geometry similar to that of Fig. 1, but involving two (2 × 1) Al layers. Thus the present SEXAFS analysis confirms but does not uniquely determine the surface structure. However, the analysis definitely excludes the models derived by NIXSW [8] and STM [19].

Total energy calculations were carried out for a number of possible surface geometries, including the models proposed in earlier studies mentioned above. The calculations [22] were performed using the fhi93cp computer code [23], which uses a plane wave basis set and *ab initio* pseudopotentials. For each structural model, the total energy was minimized with respect to the positions of the Na and Al atoms in the overlayer and Al atoms in the first two or three substrate layers. For the simple overlayer structures the adsorption energy per surface unit cell is equal to the binding energy per unit cell. For the structures with Al atoms in the overlayer, the adsorption energy is calculated assuming the atoms are taken from kink sites at steps, using the fact that in thermal equilibrium the Al chemical potential equals the cohesive energy. The adsorption energies for the structures considered are given in Table II. It can be seen that the structure of Fig. 1 (Table II, E) has the largest adsorption energy (3.08 eV). The geometry leading the minimum total energy for this structure is listed in Table I. It is interesting to note that the structure formed by interchanging the positions of the Na and Al atoms in the first two layers (i.e., placing Na atoms in hcp sites and Al atoms in fcc sites) has an adsorption energy (Table II, D), lower by about 0.20 eV, than that of the optimum geometry. Finally, we note that our DFT-LDA results discriminate against the models proposed

TABLE I. Interlayer spacings d_{ij} (Å) determined by LEED, SEXAFS, and DFT-LDA analyses of the structure of Al(111)-(2 × 2)-Na (see Fig. 1). The layers are numbered from the surface into the bulk. The LEED and DFT-LDA analyses [20,22] also indicate the presence of small (~0.04 Å) lateral displacements of Al atoms in layers 4 and 5, and small (~0.05 Å) vertical displacements of Al atoms in layers 5 and 6. The interlayer spacings given here are with respect to the midpoints of the (bi)layers 5 and 6, which are the first two (almost) perfect bulk layers.

Layer	1	2	3	4	5	6
Atoms	Na	Al	Na	Al	Al	Al
Interlayer spacing		d_{12}	d_{23}	d_{34}	d_{45}	d_{56}
LEED		0.85	0.55	1.52	2.25	2.28
SEXAFS		0.75	0.70	1.50		
DFT-LDA		0.72	0.62	1.46	2.20	2.32

previously by Hohlfeld and Horn [18] (Table II, A or B), by Kerkar *et al.* [8] (Table II, H), and by Brune *et al.* [19] (Table II, C), all of which have smaller adsorption energies than the model of Fig. 1 (Table II, E).

We believe that the present LEED, SEXAFS, and DFT-LDA studies lead to a definitive description of the Al(111)-(2 × 2)-Na structure. As can be seen from Table I, the results of the different methods are in quantitative agreement, which gives a high degree of confidence in the correctness of the model. We consider that the successful experiment and theory comparison reported here breaks new ground in terms of structural complexity. Previously proposed qualitative models [17–19] and one quantitative model [8] for the (2 × 2)-Na structure are shown to be incorrect by all three methods used here. We emphasize, in particular, that the STM study failed to detect the Al layer in the Na-Al-Na sandwich. In fact, the STM images show only a "single protrusion" per unit cell, and the inference that the structure contains two Na layers comes indirectly from the height of this protrusion [19]. We note, however, that the present work confirms the suggestion based on HRCLS measurements [4] that the structure involves a Na-Al-Na sandwich, and that the HRCLS results are straightforwardly accounted for by the structure determined here.

As mentioned above, a structure closely related to that of Fig. 1 is obtained by switching the positions of the Al atoms and the upper Na atoms of the sandwich layer, i.e., placing the Al atoms in fcc sites and the Na atoms in hcp sites on the reconstructed Al layer. Although such a structure might seem intuitively more likely than a structure with Al atoms in hcp sites, both the LEED and DFT-LDA analyses indicate that the structure of Fig. 1

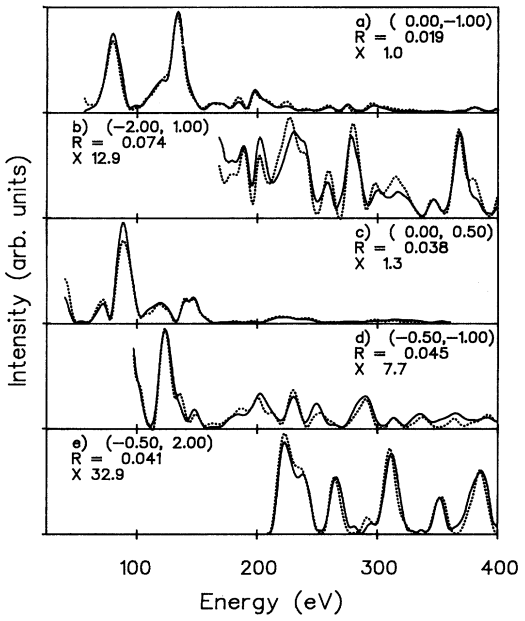


FIG. 2. Experimental intensity-energy spectra (full lines) for 5 of the 15 beams measured at normal incidence compared with spectra (dashed lines) calculated for the model of Fig. 1 with the geometry specified in Table I. A *single* scale factor has been used to normalize the experimental and calculated intensities for all 15 beams. Beam *hk* indices, *R* factors, and plot scale factors are given in the figure.

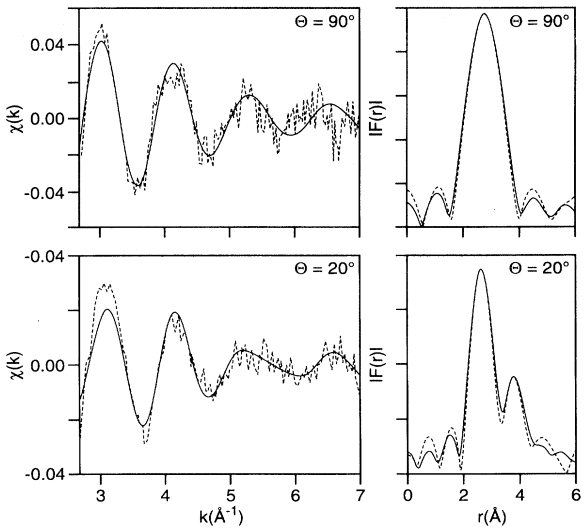


FIG. 3. SEXAFS simulations (left) and their Fourier transforms (right) for $\theta = 90°$ (top) and $\theta = 20°$ (bottom) assuming the model structure of Fig. 1. The simulations are shown as solid lines and the data as dashed lines.

TABLE II. Adsorption energy E^{ad} per unit cell for the surface structures considered. (A) Double Na layer (see Ref. [18]). Na atoms in hcp and on-top sites, respectively, on a bulk Al layer. (B) Double Na layer (see Ref. [18]). Na atoms in fcc and on-top sites, respectively, on a bulk Al layer. (C) Double Na layer (see the STM study of Ref. [19]). Na atoms in substitutional sites and fcc sites, respectively, on a reconstructed Al layer with one vacancy per unit cell. (D) Na-Al-Na sandwich. Na atoms in substitutional sites and hcp sites, respectively, on a reconstructed Al layer. Al atoms on fcc sites. (E) Na-Al-Na sandwich. Na atoms in substitutional sites and fcc sites, respectively, on a reconstructed Al layer. Al atoms on hcp sites. (F) Al-Na-Na sandwich. Al atoms in hcp sites on a bulk Al layer. Na atoms in fcc and on-top sites, respectively. (G) Na-Na-Al sandwich. Na atoms in fcc and hcp sites, respectively, on a bulk Al layer. Al atoms in on-top sites. (H) Double $NaAl_2$ layer (as suggested by the NIXSW study of Ref. [8]).

Structure	A	B	C	D	E	F	G	H
E^{ad} (eV)	2.61	2.60	2.69	2.88	3.08	2.89	2.34	0.18

is in fact preferred. From plots of charge density calculated [22] for the two structures, it can be seen that the overlayer Al atoms experience a larger charge density when in the hcp site as opposed to the fcc site. In fact there is a stronger bonding between Al atoms in the overlayer and their three nearest Al neighbors in the reconstructed Al layer than is between Al atoms in the bulk. Consistent with this stronger bonding of the overlayer Al atoms, the vertical spacing (2.07 Å from the LEED analysis, $d_{23} + d_{34}$ in Table II) between the Al overlayer and the reconstructed Al layer is noticeably less than the interlayer spacing (2.33 Å) in the bulk, corresponding to an Al-Al bond length of 2.65 Å, as compared to the bulk value of 2.85 Å.

The mechanism of formation of the (2×2) structure is an interesting question. Viewed in isolation, it would be natural to conclude that the structure forms without mass transport of Al atoms over the surface, since the Al atoms displaced from the reconstructed Al layer seemingly reappear in the sandwich layer. However, the (2×2) structure forms by adsorption of one-sixth monolayer Na atoms on the $(\sqrt{3} \times \sqrt{3})R30°$ structure. The formation of the latter structure involves the displacement of one-third monolayer Al atoms, which are presumed to diffuse over the surface to be readsorbed at surface steps [2,13]. We conclude, therefore, that formation of the (2×2) structure from the $(\sqrt{3} \times \sqrt{3})R30°$ structure involves a reverse diffusion of one-third monolayer Al atoms from steps and the incorporation of these atoms in the (2×2) structure. The role of surface steps as *sinks* for displaced substrate atoms in reconstructive adsorption has been widely discussed. In light of the present results it seems likely that steps play an equally important role as *sources* of substrate or adsorbed atoms in surface phase transformations.

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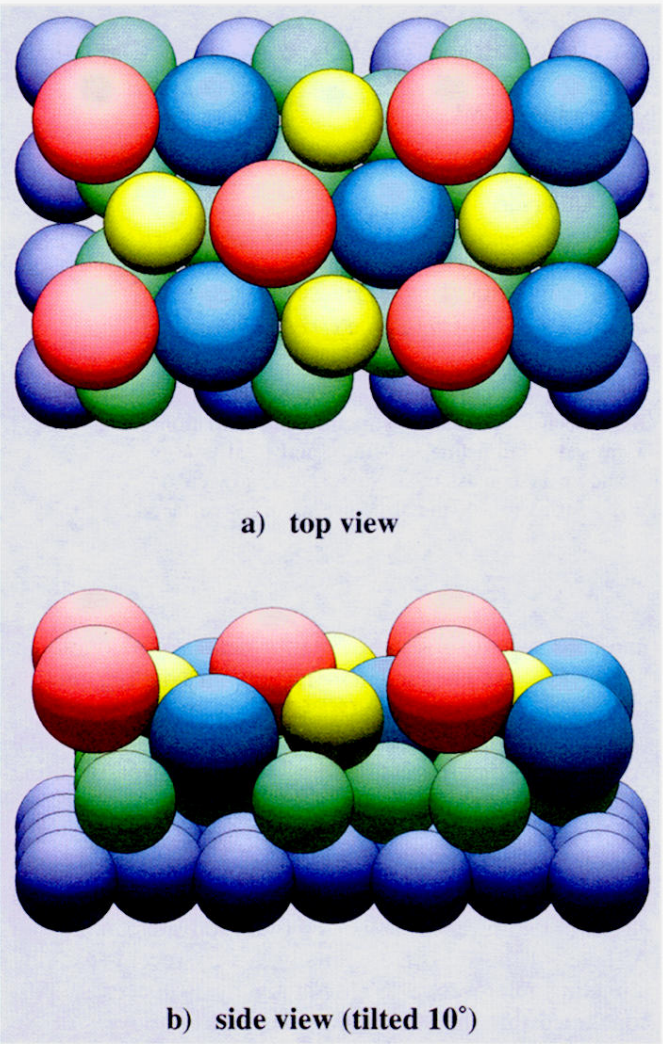

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