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Changes in the local surface geometry with conserved adsorbate coverage and long-range order caused by annealing

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The ordered $c(2\times 2)$ Na on Al(100) and $(\sqrt{3}\times\sqrt{3})R30^\circ$ K on Al(111) structures formed at either 100 K or at room temperature are studied by high-resolution core-level spectroscopy. For both systems equal alkali coverages are found at these two temperatures. The core-level spectra, however, show strong changes with temperature. This behavior leads to the surprising conclusion that annealing at room temperature causes an irreversible change in the local geometry, i.e., of the adsorption site, of the overlayer even though neither the long-range order nor the adsorbate coverage changes.

It would seem quite natural and reasonable to assume that if annealing of an adsorbate-covered surface preserves both the low-energy electron-diffraction (LEED) pattern and the adsorbate coverage, then the local geometry of that adsorbate layer remains unaltered by the anneal. Such an assumption is indeed commonly made. It was therefore surprising to discover two different adsorption systems not conforming to such behavior. The investigated systems were Na on Al(100) and K on Al(111). For both of these systems we found ordered overlayer structures where the alkali coverage and the long-range order, as revealed by the LEED pattern, are identical when they are formed at either 100 K or at room temperature (RT), whereas photoelectron spectroscopy shows that the local surroundings of the alkali and the Al surface atoms are quite different, that is, the adsorption site of the alkali atoms changes as a result of the anneal at RT.

In the Na on the Al(100) system, a $c(2\times 2)$ LEED pattern may be formed by adsorption of half a monolayer (ML) (1 ML equals the number of Al surface atoms) of Na at 100 K and also at room temperature,^{1,2} whereas in the K on the Al(111) system, a $(\sqrt{3}\times\sqrt{3})R30^\circ$ (hereafter referred to as $\sqrt{3}$) LEED pattern may be obtained by adsorbing $\frac{1}{3}$ ML of K at 100 K or at RT. Despite the identical LEED patterns at 100 K and at RT for both of these systems, high-resolution core-level spectroscopy reveals that the local geometry is different. The 100-K structures are metastable; annealing at higher temperatures results in an irreversible conversion into the RT structures.

The present results should also be viewed in the light of recent results for the Na on the Al(111) system where RT adsorption, contrary to the accepted view of alkali adsorption, was shown to result in the formation of surface alloys whereas, upon adsorption at 100 K, the alkali atoms stay on the surface as adatoms.^{3,4} For the present systems we find unambiguous evidence for surface alloy formation at RT in the Na on the Al(100) system whereas, for the K on the Al(111) system, no definitive statement can be made on the intermixing issue, although the change in the spectra from 100 K to RT strongly indicates that intermixing occurs. The large change in the

$\sqrt{3}$ K on Al(111) spectra between 100 K and RT are, furthermore, consistent with recent measurements⁵ of LEED intensity versus voltage (I - V) curves which turn out to be very different at these two temperatures.

The experimental apparatus and the methods of sample characterization and preparation have been described in detail in Ref. 4. The RT structures were prepared by either deposition at RT or heating 100-K depositions. These two ways of preparation gave identical results. All measurements of core-level spectra were performed at 100 K in order to reduce vibrational broadening. The total experimental resolution was about 50 and 70 meV for the Al 2p and the alkali core levels, respectively.

The alkali coverage in the $c(2\times 2)$ and the $\sqrt{3}$ structures may be determined from the core-level spectra and the LEED patterns. From the intensity of the core levels of the respective alkali metals, it is found for Na as well as for K that the 100-K and RT structures contain equal amounts of the alkali metal, i.e., the same number of alkali atoms per unit cell. It follows from the size of the respective alkali atoms and of the unit cells of the two surface structures that if there are to be two (or more) alkali atoms per unit cell, these atoms have to be at different distances from the surface. The difference in the surroundings of these two hypothetical alkali sites should result in a difference in the core-level binding energies. Such behavior, for instance, is shown by the 2×2 Na on Al(111) structure, which contains two Na atoms per unit cell and two Na 2p peaks separated by about 0.4 eV.⁴ The present systems, however, show only one component in the alkali core-level spectra, i.e., one alkali atom per unit cell. Thus the ideal coverage, at 100 K and at RT, is 0.5 ML for the $c(2\times 2)$ Na on Al(100) structure and 0.33 ML for the $\sqrt{3}$ K on Al(111) structure.

Any change in the binding energy or intensity in a core-level photoemission spectrum reflects that a change has occurred in the surroundings of the photoemitting atom. The conclusion that the present systems have a different local geometry at 100 K and RT rests solely on this most fundamental property. By analyzing the magnitude of the core-level shifts, information on the change in geometry may sometimes be obtained. The basic idea

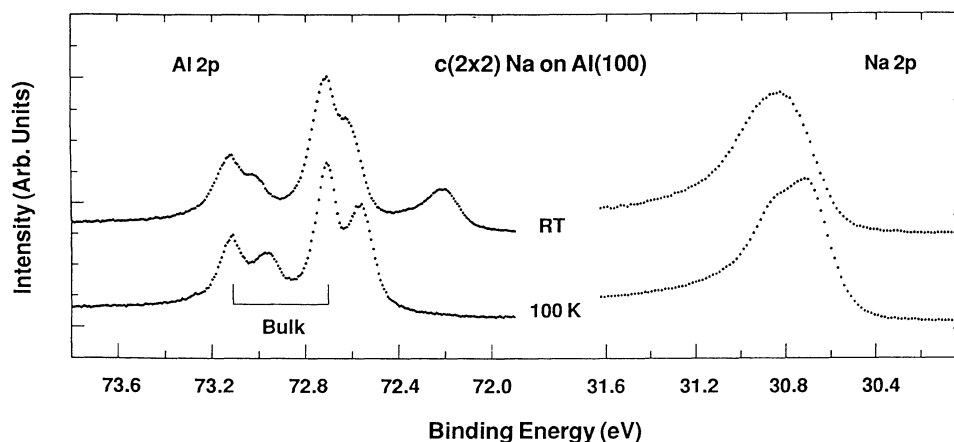


FIG. 1. Al 2*p* and Na 2*p* core-level spectra for $c(2 \times 2)$ Na on Al(100) at 100 K and RT. The bulk Al 2*p* emission is indicated.

behind this in the present systems is that, e.g., the Al atoms experience more alkali-rich surroundings for an intermixed than for a nonintermixed system. Therefore, larger core-level binding-energy shifts are expected for the surface alloy systems. In Ref. 4 we argued that Al 2*p* binding-energy shifts of about -0.4 eV signify that the Al atoms are almost completely surrounded by Na. This estimate was confirmed by measurements⁴ on Al deposited on Na where Al 2*p* shifts of up to -0.5 eV were found to result from the intermixing.

Figures 1 and 2 show Al 2*p*, Na 2*p*, and K 3*p* core-level spectra from the 100-K and RT versions of the $c(2 \times 2)$ Na-Al(100) and $\sqrt{3} \times \sqrt{3}$ K-Al(111) surfaces, respectively. The large difference in the Al 2*p* spectra from the RT and 100-K structures is very obvious from Figs. 1 and 2. This difference immediately shows that the RT and 100-K structures are different; the RT structures contain Al atoms that have surroundings that differ from those in the 100-K surfaces. The alkali core levels from the 100-K and RT structures show different binding energies, reflecting also that the alkali atoms experience different surroundings in these structures. In other words, the alkali adsorption site differs between the 100-K and the RT versions of these ordered structures. It should be noted

that the present behavior is *not* equivalent to the commonly observed sharpening of adsorbate and substrate core levels when a disordered adsorbate layer is ordered by annealing; the 100-K structures in the present case show long-range order similar to the RT structures. Below, we discuss various models for the structures based on a more detailed analysis of the spectra. It should, however, be stressed that the conclusion that the 100-K and RT structures are different is independent of any of these detailed models; it rests solely on the observed difference in the core-level spectra.

Consider first the Na-Al(100) spectra. The 100-K spectra are consistent with expectations for a nonintermixed system with the Na atoms occupying one single site on the surface. The Na 2*p* spectrum consists of one single component, the spin-orbit splitting of the 2*p* level being visible as a shoulder towards higher binding energy. The Al 2*p* spectrum contains two components, one from the bulk atoms and one shifted by -150 meV originating from the Al atoms in contact with Na atoms. The intensity of the -150 meV component is close to that of the surface peak from the clean Al(100) surface.⁶ The present 100-K results are what would be expected from the fourfold-hollow site proposed in early LEED struc-

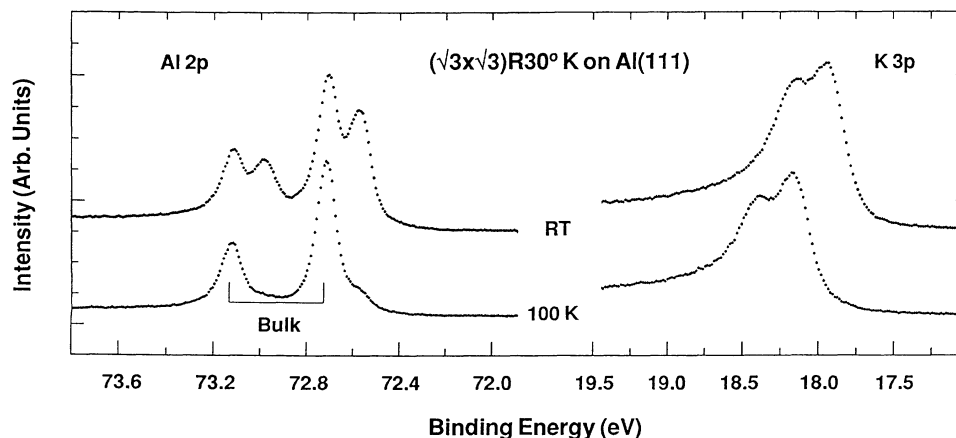


FIG. 2. Al 2*p* and K 3*p* core-level spectra for $(\sqrt{3} \times \sqrt{3}) R30^\circ$ K on Al(111) at 100 K and RT. The bulk Al 2*p* emission is indicated.

ture determinations of $c(2 \times 2)$ Na on Al(100).^{2,7} This is somewhat surprising because these LEED studies used data obtained from samples that had been annealed at 360 K. Our data at RT are, in fact, incompatible with this simple fourfold-hollow site^{2,7} because the Al 2*p* spectrum shows the existence of two inequivalent types of Al surface atoms.⁸ One component, shifted by about -500 meV, originates as discussed above and in Ref. 4 from Al atoms highly coordinated to Na, whereas the other component, shifted by about -115 meV, is due to less Na-coordinated Al atoms in the interface towards the substrate. Thus, the Al 2*p* spectrum demonstrates that the RT version of the $c(2 \times 2)$ structure is a surface Na-Al alloy. The Na 2*p* spectrum from this RT structure consists, just as at 100 K, of one single component, the larger width compared to the 100-K spectrum being attributable to either decreased lifetime and/or vibrational effects, or to the fact that the RT $c(2 \times 2)$ never was as perfect as the 100-K one. Thus, also, the RT structure most likely contains only one single type of Na atoms. This shows that the surface alloy formed in the present system is different from that of the 2×2 Na on Al (111) system which involved two different kinds of Na atoms.⁴ The Na 2*p* binding energy is larger for the RT than for the 100-K structure which, together with the knowledge that the interaction with Al lowers the Na 2*p* binding energy,^{4,9} seems to imply that the Na atoms are less coordinated to Al in the RT than in the 100-K $c(2 \times 2)$. It should, however, be kept in mind that the Al-induced shift of the Na 2*p* is small;^{4,9} thus, changes in these Al-induced shifts might be obscured by shifts resulting from changes in the Na-to-Na coordination. It is no straightforward matter to derive the exact nature of the structural changes from the 100-K to the RT $c(2 \times 2)$ Na on Al(100) structure; that a change occurs is, however, beyond doubt.

Considering, now, the K on Al(111) spectra, perhaps the first observation to be made is the lack of any -400-meV component in the Al 2*p* spectra. With the understanding that K and Na should induce Al 2*p* shifts of similar magnitudes,⁹ this shows that these K-Al(111) structures contain no Al atoms equivalent to the highly Na-coordinated Al atoms from the $c(2 \times 2)$ Na-Al(100) and (2×2) Na-Al(111) structures. Because of the low intensity of the K-induced component of the Al 2*p* spectrum at 100 K, it is very difficult to determine if there is a change in the binding energy or in the width of this component between 100 K and RT; however, the main change from 100 K to RT is a strong change in the intensity of the K-induced feature. The intensity of the shifted component at 100 K is intriguingly low; based on this observation, we suggest that the K atoms occupy on-top sites. The $\frac{1}{3}$ ML of Al atoms directly below the K atoms should show a larger shift than the remaining $\frac{2}{3}$ ML. The difference in these shifts is expected to be small, which would lead to a broad K-shifted component which, in turn, would appear as a low intensity of the K-induced feature. A broadened K-shifted Al 2*p* component could, of course, also be due to considerable disorder in the $\sqrt{3}$ 100-K structure. Such disorder may, however, be ruled out on the basis of the sharpness of the K 3*p* spectra that

shows the K overlayer to be well ordered. The Al 2*p* spectrum from the RT structure is consistent with K atoms occupying a threefold-hollow site on the surface or with a model where one-third of the Al surface atoms in a $\sqrt{3}$ structure has been substituted by K (This is the site of the Na atoms for the $\sqrt{3}$ Na on Al(111) structure³.) We find the substitutional model to be the most likely one. In any model where the difference between the RT and 100-K structures is merely a different adsorption site on an unperturbed (111) surface, it is difficult to imagine any mechanism creating a barrier that keeps the K atoms from choosing the site with lowest total energy (which has to be the RT site) also when they are adsorbed at 100 K. The displacement of Al atoms necessary to obtain a substitutional site would, on the other hand, produce in a natural way such a barrier. Furthermore, a substitutional site at RT would mean that the K atoms have more Al-rich surroundings at RT than at 100 K. With the experimental knowledge that the interaction with Al lowers the binding energy of the K core levels,⁹ one would therefore expect that the K 3*p* binding energy would be lower for the RT structures than for the 100-K ones, which is indeed what is observed.

The transformation from the 100-K to the RT structures may be followed by the development of the core-level spectra as the structures are annealed at subsequently higher temperatures. We have chosen an annealing procedure where the samples were kept 30 sec at the annealing temperature and then cooled to 100 K before measuring the spectra. From these measurements, it was found that for $c(2 \times 2)$ Na on Al(100) the transition starts at around 160 K and is completed around RT, whereas for $\sqrt{3}$ K on Al(111) the temperature range is smaller, starting at 220 K and also ending around RT. Both structures are stable up to at least 450 K. The fact that the transition occurs over such a large temperature range (when the sample is annealed for 30 sec) seems to be consistent with the extensive rearrangements of atoms required by the proposed models. The low transition temperature for Na-Al(100) furthermore means that care has to be exercised when studying the low-temperature $c(2 \times 2)$ phase.¹

In summary, we have shown that for $c(2 \times 2)$ Na on Al(100), as well as for $(\sqrt{3} \times \sqrt{3}) R30^\circ$ K on Al(111), the structures formed at RT and 100 K, respectively, exhibit different local geometries, even though neither the alkali coverage nor the LEED pattern changes. For K on Al(111), it is likely that a substitution reaction occurs at RT, similar to what has been found for $\sqrt{3}$ Na on Al(111). The present results demonstrate that the commonly made assumption of the adsorption site remaining the same if neither the adsorbate coverage nor the LEED pattern changes as a result of annealing need not always be obeyed.

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