Intermixing in the Na on Al(111) System

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Ordered structures formed by Na adsorption on the Al(111) surface are investigated by high-resolution core-level spectroscopy. It is shown that, contrary to the common picture of alkali adsorption, two of the structures formed at room temperature consist of intermixed Na-Al layers. The results for the ($\sqrt{3}\times\sqrt{3}$)-rotated-30° structure are also consistent with intermixing although they do not provide any definite proof. For Na layers deposited at 100 K no intermixing is found.

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Despite the large attention, theoretical and experimental, over the years [1], the nature of the alkali-atom–surface adsorption bond still continues to be a subject of considerable controversy [2-4]. The importance of understanding this bond is not just limited to the subject of alkali adsorption. The original picture of alkali adsorption, put forward by Gurney more than 50 years ago [5], in which the alkali-surface bond is due to the alkali *s* valence level that becomes broadened and partly filled by the interaction with the substrate levels, has had and still has a major influence on descriptions of the adsorption process in general. Also, surface modifications by alkali adsorbates, like, e.g., the promoter effects in heterogeneous catalysis [6], are technologically highly important. When treating alkali adsorption it is common to assume that no intermixing occurs with the substrate; the alkali atoms are assumed to reside *on* the surface. This seems a reasonable assumption from the low solubility of alkali metals in most metals [7]; however, its validity has recently been questioned [8]. Using polarization-dependent surface extended x-ray-absorption fine-structure measurements Schmalz *et al.* showed that the Na atoms of the ($\sqrt{3}\times\sqrt{3}$)-rotated-30° structure formed by adsorbing $\frac{1}{3}$ monolayer (ML) of Na on Al(111) at room temperature occupy an unusual sixfold coordinate site formed by displacing every third Al atom in the Al surface layer [8]. *Ab initio* density-functional calculations furthermore showed this adsorbate geometry to be energetically favorable. Such intermixing would indeed have a major influence on the current picture of alkali adsorption and we have therefore investigated this issue in the Na on Al(111) system using high-resolution core-level spectroscopy. Our results clearly show that some of the overlayers involve intermixing between Na and Al in agreement with the results of Ref. [8] and in contradiction to the generally held belief.

The use of core-level photoemission for investigating intermixing rests on the fact that the core-level binding energy of an atom is dependent upon its surroundings [9,10]. From the core-level spectra it is thus possible to determine the number of different sites that are occupied by a certain element simply by counting the number of peaks, provided, of course, that the shifts are reasonably large and that not too many sites are present. In addition to this basic method of counting components one can also extract further information from the magnitude of the shifts. One way of doing this is to compare the spectra with spectra from samples where the degree of intermixing and the detailed geometry are known beforehand. This, of course, demands that such samples are available. An alternative method is to try to calculate the magnitude of core-level binding-energy shifts between two structures from their geometrical differences, normally using some kind of nearest-neighbor approach [10].

For the Na on Al(111) system it turns out that one need essentially only count the number of chemically shifted peaks to establish that intermixing between Al and Na occurs for two of the overlayer structures. For the rest of the structures, the more involved methods based on the size of the shifts have to be invoked making the conclusions that can be drawn somewhat less definitive.

The experiments were performed at the MAX-I storage ring in Lund, Sweden, using a modified SX700-type monochromator and a large hemispherical electron-energy analyzer [11]. The total resolution for the Al and Na $2p$ spectra was approximately 40 and 60 meV, respectively. All spectra were recorded at a sample temperature close to 100 K in order to reduce the phonon broadening.

The Al(111) crystal was cleaned by a combination of Ar^+ sputtering and annealing at 500 °C. This produced a clean surface which showed very sharp spots in low-energy electron diffraction (LEED). Na was evaporated from SAES getter sources. Even during Na deposition the pressure was in the 10^{-11}-torr range. The purity of the deposited Na layers as well as of the bare Al(111) surface was checked by core-level and valence-band photoemission.

Two different ordered overlayer structures result from Na deposition at room temperature (RT), a ($\sqrt{3}\times\sqrt{3}$)-rotated-30° structure (hereafter denoted $\sqrt{3}$) and at Na saturation at RT, a 2×2 structure [12,13]. These Na overlayers were very well ordered, judging from the

LEED patterns, which showed overlayer spots as sharp as the substrate spots and a low background. Na deposition at around 150 K onto a 2×2 structure leads to the formation of a $(2\sqrt{3}\times2\sqrt{3})$-rotated-30° structure (hereafter denoted $2\sqrt{3}$) [13]. We found it somewhat more difficult to prepare this structure; the LEED spots were not as sharp and the background not as low as for the 2×2 and $\sqrt{3}$ structures. It seems critical to choose exactly the right temperature for deposition of Na so as to attain enough mobility for ordering while avoiding Na reevaporation. Finally, Na deposition on the clean Al(111) surface at 100 K leads to epitaxial growth of Na(111) layers, resulting in the formation of a $\frac{4}{3}\times\frac{4}{3}$ LEED pattern [13]. We use the designation 1 ML for the case where the Al surface is covered by one such (111) Na layer deposited at 100 K.

In Fig. 1 we show Al $2p$ spectra from the clean Al(111) surface and from a number of different Na overlayers.

In order to get an estimate of the expected magnitude of Al $2p$ shifts in Al-Na systems, we first consider spectra from the clean surface and from a surface covered with one (111) layer of Na deposited at 100 K. As the surface core-level shift of Al(111) is very small (less than 15 meV [14]), the clean spectrum exhibits only one spin-orbit split doublet. Deposition of Na at 100 K results in an increasing broadening of the Al $2p$ peaks as the Na coverage is increased due to a Na-induced shift of the surface-atom core levels towards lower binding energy. A number of different coordinations of Al to Na are present when a Na layer is placed on top of the Al(111) surface, which should result in a number of different shifts. However, because of the small magnitude of the shifts they cannot be resolved individually. Nevertheless, from fitting two spin-orbit doublets to the 1-ML spectrum of Fig. 1 it may be concluded that the largest core-level shift of an Al atom caused by placing a Na layer next to it is around −100 meV. It should be noted that this upper estimate of the shift also applies to the low Na coverage regime at 100 K, as evidenced by the absence of any peaks shifted by more than this amount even at the lowest investigated Na coverages (around $\frac{1}{20}$ of that of Fig. 1). According to the model of Ref. [10] the shift induced by surrounding Al completely by Na should be this 1-ML shift of −100 meV multiplied by a factor of 3 to 4. To investigate this estimate further we measured Al $2p$ spectra from samples where Al is placed in a Na environment. These samples were prepared by evaporating small amounts of Al onto thick Na films at 100 K. A spectrum from such a sample is shown in Fig. 1. The Al $2p$ peak is very broad because of the number of different Al to Na coordinations present. The spectrum clearly contains components shifted by about −400 meV from the bulk Al $2p$ binding energy of pure Al. These large shifts are due to the presence of Al atoms with a very high coordination to Na, presumably Al atoms that are completely surrounded by Na. This magnitude of the shift for an Al atom surrounded by Na agrees very well with the above estimate made from the 1-ML spectrum and reasonably well with a value of −0.2 eV calculated by using solution energies [15] obtained by Miedema's scheme.

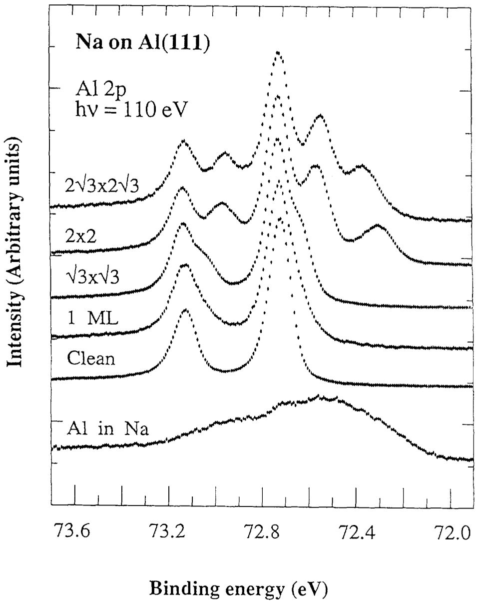

FIG. 1. Al $2p$ spectra from the clean Al(111) surface and from the indicated Na overlayer structures. 1 ML designates an Al(111) surface covered by one layer of Na deposited at 100 K. The Al-in-Na spectrum is from Al deposited on a thick Na film.

With this magnitude of the Na-induced shift in mind the 2×2 and $2\sqrt{3}$ Al $2p$ spectra directly show that intermixing occurs for these structures. The spectrum from both structures contains two clearly resolved Na-shifted components in addition to the bulk peak. The shifts are considerably larger than for the 1-ML surface; for the 2×2 structure they are −170 and −430 meV, for the $2\sqrt{3}$ they are −180 and −360 meV. This existence of two peaks with significantly different binding energies first of all shows that both structures contain, in addition to the bulk Al atoms, two types of Al atoms differing very much in their coordination to Na. Second, from the size of the larger shift, one of these types of Al atoms has to have a much higher coordination to Na than found for any Al atoms in the 1-ML case. From the magnitude of the shift for Al dissolved in Na, discussed above, it is seen that the Al atoms giving rise to the larger shift have to be close to completely surrounded by Na. This is impossible to accomplish without allowing for intermixing. The components shifted by −170 and −180 meV in the 2×2 and the $2\sqrt{3}$ structures, respectively, are due to Al atoms in the interface between the overlayer and the Al crystal. These shifts are larger than the 1-ML shift indicating a larger degree of intermixing at the interface for these two structures than for the 1-ML situation. Finally, it is noticeable that the intensity of the shifted components is comparable to that of the bulk peak showing that for both structures a significant fraction of a (111) layer is taking part in the intermixing.

The $\sqrt{3}$ spectrum unfortunately does not settle the issue of intermixing in this structure. The Na-induced shift is somewhat larger than for the 1-ML situation leading to the appearance of a distinct shoulder. This larger magnitude of the shift is certainly consistent with the suggestion [8] of substitution in the $\sqrt{3}$ structure; however, due to the small magnitude of the shifts this cannot be regarded as conclusive [16].

The Na 2*p* core-level spectra of Fig. 2 [17] shed further light on the nature of the overlayer structures.

Two effects will shift the Na 2*p* binding energy, one being the surface core-level shift of Na, and the other being the Al-induced shift. From the thick-film spectrum the surface core-level shift of Na is found to be +200 meV, in good agreement with Refs. [19] and [20]. By comparison of the binding energy for the surface atoms in the thick film with the 1-ML situation it is seen that changing the underlying layer from Na to Al results in a shift of around −200 meV for the Na 2*p* level. This value is consistent with expectations based on calculated heats of solution [15] and the formalism of Ref. [10]. This gives a shift of about −1 eV when changing the surroundings of a Na atom from Na to Al. For the present situation this value should be reduced by a factor of the order of 4 [10].

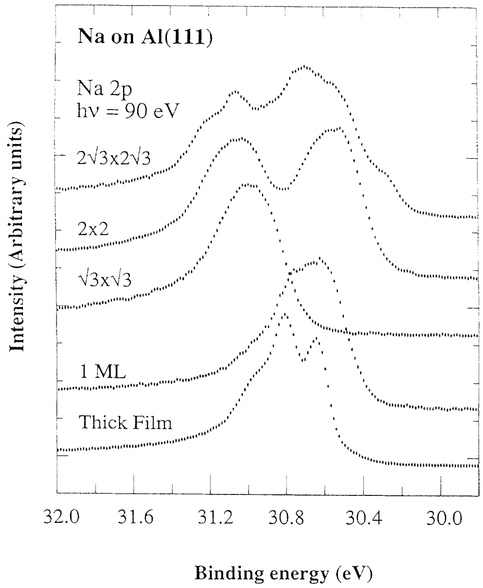

FIG. 2. Na 2*p* spectra from a thick Na film and from the indicated structures formed by Na adsorption on Al(111). 1 ML indicates an Al(111) surface covered by one layer of Na deposited at 100 K.

Both the 1-ML and the $\sqrt{3}$ spectra consist of only one Na 2*p* spin-orbit doublet [17], the binding-energy shift between the two situations being consistent with the well-established trend of decreasing binding energy with increasing coverage of alkali metals [21]. As for the Al 2*p* spectra, it is difficult to draw any conclusions regarding intermixing in the $\sqrt{3}$ structure from the Na 2*p* binding energy other than that it is not inconsistent with intermixing.

As was also the case for the Al 2*p* spectra, the 2×2 and $2\sqrt{3}$ Na 2*p* spectra are qualitatively different from the $\sqrt{3}$ and 1-ML spectra in that now there clearly are more than one component present. The interpretation of these spectra is that both structures contain more than one Na layer. The existence of more than one Na layer is of course also a necessity if Al atoms completely surrounded by Na are to be present. The 2×2 spectrum consists of two components shifted by about 0.5 eV. The high-binding-energy component is due to Na atoms at the surface, the large shift of this component being due to a combination of a surface shift and a decreased coordination to Al compared to that of the underlying Na atoms. The higher binding energy of this layer compared to the surface layer of the thick Na film reflects the lower density of the 2×2 Na layer. Hohlfeld and Horn [13], from LEED results and coverage considerations, suggested that the 2×2 structure consisted of a double Na layer. We agree with this suggestion except for the vital difference that our results show that Al atoms are incorporated into this double Na layer. Keeping in mind the low two-dimensional density of this double Na layer such incorporation seems quite reasonable.

The $2\sqrt{3}$-Na spectra are quite complicated. As a result of the small shifts, the unknown number of components present, and the expectation that these may have different widths, it is not meaningful to try to perform a detailed decomposition into spin-orbit doublets. The component which can be distinguished at high binding energy is attributed to a surface layer of Na. The structure at binding energies around 30.7 eV is due to Na atoms in the bulk of an intermixed Al-Na layer. The shoulder at low binding energy shows that the $2\sqrt{3}$ structure contains Na atoms with even higher coordination to Al than found in the 2×2 structure. Thus the $2\sqrt{3}$ structure is not simply formed by adsorbing a Na layer on top of an otherwise undistorted 2×2 structure. This is also indicated by the binding-energy changes in the Al 2*p* spectra between the 2×2 and the $2\sqrt{3}$ structures.

In summary the present high-resolution core-level spectroscopy and LEED results provide the following picture of the Na on Al(111) system.

When Na is deposited at low temperature (100 K), an epitaxial Na film grows on the surface. There is no sign of intermixing. The Na atoms in the $\sqrt{3}$ structure formed by adsorbing $\frac{1}{3}$ ML of Na at RT are all equivalent; it is not possible to say conclusively whether they are adsorbed on the surface or have substituted one-third of the Al surface atoms as proposed in Ref. [8]. From the results for the 2×2 and $2\sqrt{3}$ structures such substitution is, however, not unexpected. The 2×2 and the $2\sqrt{3}$ structures both contain multilayers of Na. For both structures the existence of two shifted Al components as well as the magnitude of the shifts show that they consist of intermixed Al-Na layers. The detailed structure of these Al-Na layers of course cannot be determined from the present core-level-spectroscopy results but remains to be solved by more traditional structure-determination techniques. Irrespective of this, the present demonstration of intermixing shows that until now the commonly accepted picture of alkali adsorption on close-packed metal surfaces needs modifications; the common assumption that the alkali atoms reside *on* the surface as adatoms may not always be correct.

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[16] One might expect two shifted Al $2p$ components if the Na atoms substitute one-third of the Al surface atoms, one from the remaining Al surface atoms and (a smaller) one from the second-layer Al atoms which are in contact with the Na atoms. In view of the small shift (−100 meV) of the surface Al atoms it is, however, highly questionable if the peak from the second-layer atoms should be resolved from the bulk peak.

[17] A common feature is that the $2p$ peak of Na atoms in contact with Al is broader than in Na metal. This behavior is commonly seen for adsorbed layers of alkali metals and has been attributed to an increase in the lifetime and/or the vibrational broadening [18]. We will not discuss the origins of this effect further.

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