

Unusual Chemisorption Geometry of Na on Al(111)

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The adsorption of Na on Al(111) at room temperature has been studied by surface extended x-ray-absorption fine-structure (SEXAFS) experiments as well as by parameter-free calculations. For coverages of $\Theta_{\text{Na}}=0.16-0.33$, the SEXAFS analysis shows that Na atoms occupy an unusual sixfold-coordinated substitutional site. The Na-Al bond length is determined as 3.31 Å, consistent with metallic bonding. *Ab initio* density-functional-theory calculations for several adsorbate geometries show that the substitutional site has the lowest total energy.

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Studies of alkali-metal (AM) adsorption have played an important role in the development of theories of chemisorption. The model for AM adsorption first proposed by Gurney [1], in which the nature of the adsorbate bonding is determined by the energy position and width of a resonance derived from the alkali valence s level, has strongly influenced subsequent theoretical and phenomenological descriptions of adsorption. Much of the interest has centered on the large change in work function, and phenomena related hereto, and on the characteristic dependence of the work function on coverage, found for many metals and semiconductors. Recently, more detailed insight into the nature of the adsorption bond has been obtained from experimental studies [2] using photoemission, inverse photoemission, electron energy loss, and Penning spectroscopies. These studies appear to confirm the main features of the Gurney model in which the resonance derived from the valence s level of the adsorbed atom is mostly unoccupied at low coverage, but moves down in energy through the Fermi level with increasing coverage due to adsorbate-adsorbate interactions. The interpretation that the bonding is largely ionic at low coverages [3] is, however, the subject of considerable current controversy: An alternative description in terms of the dominance of adatom polarization has been proposed [4,5].

With a few exceptions noted below, studies of the adsorbate geometry have not played a central role in discussions of the nature of the adsorption mechanism and very few quantitative determinations of the adatom geometry have in fact been carried out. The recent emphasis of structural studies has rather been, on the one hand, the characterization of the variety of adsorbate phases [6] as a function of temperature and coverage and, on the other hand, studies of the reconstruction [7,8] of fcc (110) and bcc (100) metal surfaces induced by small concentrations of adsorbed AM's. Thus, theoretical models of AM adsorption have almost by default assumed that the adsorption site is one of high symmetry on an unperturbed substrate. In accord with this assumption, self-consistent calculations [5,9,10] for Na adsorption on Al(111) arrived at the conclusion that Na occupies the threefold-

coordinated site. LEED structure determinations [6,11,12] for Ni(100)- $c(2\times 2)$ -Na, Al(100)- $c(2\times 2)$ -Na, and Rh(100)- $c(4\times 2)$ -Cs indicate that for these systems the AM atoms occupy the fourfold sites of highest symmetry. The Cu(111)- $p(2\times 2)$ -Cs structure appears to be exceptional. A LEED study [13] indicates that Cs occupies the on-top site. A recent surface extended x-ray-absorption fine-structure (SEXAFS) study [14] of Cs adsorption on Ag(111) is of particular interest in that bond-length determinations at coverages of 0.15 and 0.30 monolayer revealed that the Ag-Cs bond length is 0.3 Å larger at the higher coverage, consistent with the model of a transition from ionic to metallic bonding with increasing coverage.

In this Letter we present the results of a study of Na adsorption on Al(111) using polarization-dependent SEXAFS measurements as well as parameter-free density-functional-theory calculations for various adsorption geometries. As is well known [15,16], adsorption of Na on Al(111) at room temperature leads to the formation of a $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure at $\Theta_{\text{Na}}=0.33$ monolayer which is followed by a (2×2) structure at $\Theta_{\text{Na}}=0.5$ monolayer. We have studied the adsorption at different coverages but we limit our discussion here to the low-coverage regime up to $\Theta_{\text{Na}}=0.33$. Contrary to previous assumptions concerning the nature of alkali-metal adsorption on close-packed metal surfaces, it is shown that Na adsorption on Al(111) at room temperature leads to a displacement of surface Al atoms from their equilibrium positions and occupation by Na atoms of the sixfold-coordinated hole so created. The determined Na-Al bond length is close to the sum of the hard-sphere metallic radii for Al and Na, suggesting metallic bond character. As opposed to the Cs/Ag(111) system we do not see any change in bond length at lower coverages. At the coverages accessible in this work there is thus no evidence for a change in the nature of the bonding.

The experiments reported here were conducted at the electron storage ring BESSY in Berlin with the grazing-incidence plane grating monochromator [17] SX-700 and with the double-crystal monochromator [18] KMC. The SEXAFS data were taken in the total electron yield mode at normal ($\theta=90^\circ$) and near-grazing ($\theta=20^\circ$) x-ray in-

cidence. The data were analyzed by the conventional Fourier-transform method [19] and by a curve-fitting procedure similar to that used in the EXCURVE program [20]. In both cases linearized Na and Al phase shifts were used. The Al phase shifts were derived from bulk EXAFS measurements. The Na phase shifts were derived from the empirical Al phase shifts by applying [21] the difference between theoretical Na and Al phase shifts taken from the calculations of McKale *et al.* [22]. As a further check on the analysis, a typical SEXAFS spectrum was analyzed using the EXCURVE program. The Al(111) crystal was cleaned by ion bombardment and annealing cycles and characterized by Auger electron spectroscopy (AES) and by low-energy electron diffraction. Na layers were deposited from SAES getter sources [23] with the substrate held at room temperature. They were free from contamination as checked by AES and x-ray-absorption measurements; oxygen contamination was below 5% of a monolayer in all cases. Relative Na coverages were determined from absorption-edge jump ratios.

SEXAFS spectra for the Al(111)-($\sqrt{3}\times\sqrt{3}$)R30°-Na structure at $\theta=90^\circ$ and $\theta=20^\circ$, taken above the K edge of Na and with background subtracted, are shown in Fig. 1 together with their Fourier transforms. The latter are dominated by the nearest-neighbor (nn) Na-Al distance R_1 . For both polarizations the analysis yields a bond length of $R_1=3.31 \text{ \AA}$ ($\pm 0.03 \text{ \AA}$). A second peak, which can be tentatively assigned to the next-nearest-neighbor (nnn) distance R_2 , can be seen in the transform of the data for $\theta=20^\circ$, the analysis of which yields a value for R_2 of roughly 4.4 \AA . A peak related to R_2 is not present

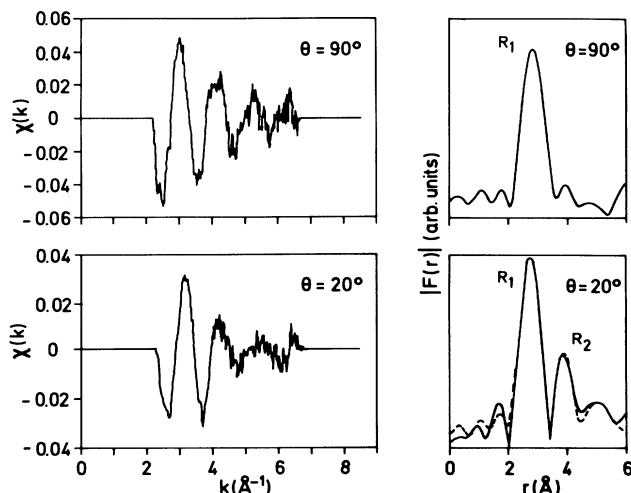


FIG. 1. SEXAFS data for Al(111)-($\sqrt{3}\times\sqrt{3}$)R30°-Na (left) after background subtraction taken at normal (above) and near-grazing (below) incidence and their corresponding Fourier transforms (right). The Fourier transform of a SEXAFS simulation (dashed line) for near-grazing incidence assuming the sixfold-coordinated site of Fig. 2 (see text) on an otherwise unrelaxed Al surface is compared with experiment.

TABLE I. Calculated vs experimental amplitude ratios $A_1(90^\circ)/A_1(20^\circ)$ for Al(111)-($\sqrt{3}\times\sqrt{3}$)R30°-Na. The calculations assumed $R_1=3.31 \text{ \AA}$.

Atop	Threefold hollow	Sixfold subst.	Experiment
0	0.19	1.42	$1.39 \pm 10\%$

in the data for $\theta=90^\circ$. The polarization dependence of the SEXAFS amplitude is given by

$$A(k) \propto N_i^* = 3 \sum_{j=1}^j \cos^2 \alpha_{ij}, \quad \alpha_{ij} = \angle(\mathbf{E}, \mathbf{r}_{ij}), \quad (1)$$

where N_i^* is the effective coordination number for the i th shell and α_{ij} is the angle between the \mathbf{E} vector at the adatom site and the vector \mathbf{r}_{ij} pointing from the absorbing atom to the j th atom in the i th shell. Amplitude ratios $A_1(\theta=90^\circ)/A_1(\theta=20^\circ)$ can be calculated from Eq. (1) for different adsorption sites and compared with the experimental value, with results as shown in Table I. It is evident from the table that occupation of one of the high-symmetry sites usually considered, including the previously suggested [9,10] threefold hollow site, can be excluded. Excellent agreement is obtained, however, for the sixfold-coordinated site depicted in Fig. 2 which is created by the removal of every third Al atom from the outermost layer and its substitution by a Na atom. Thus each Na atom occupies a nearly substitutional site with perpendicular distance to the first layer of Al atoms of 1.67 \AA . This model is clearly consistent with the observation of a ($\sqrt{3}\times\sqrt{3}$)R30° LEED pattern, but it must be noted that it leaves the positions of the displaced Al atoms unspecified. The conclusions above, which result from a straightforward Fourier analysis, are strongly supported by SEXAFS simulations. The Fourier transform of a SEXAFS simulation for $\theta=20^\circ$ assuming the sixfold site of Fig. 2 with a nn Na-Al bond length of $R_1=3.32 \text{ \AA}$ and an unrelaxed substrate is in excellent agreement with the corresponding experimental result as shown in Fig. 1.

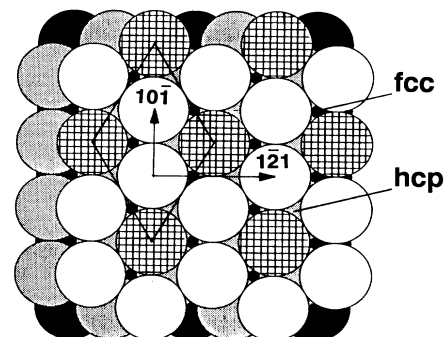


FIG. 2. The atomic geometry of ($\sqrt{3}\times\sqrt{3}$)R30° Na on Al(111) for the substitutional chemisorption. Light-shaded circles are Na atoms. Open, dark-shaded, and solid circles show the top layer, second layer, and third layer of Al. The two metastable on-surface adsorption sites (fcc and hcp) are marked.

The simulation (dashed curve) confirms that the peak R_2 corresponds to the nnn distance of 4.34 Å involving Al atoms in the second layer of the substrate. It follows from Eq. (1) that the peak R_2 should not be observed for $\theta=90^\circ$, in agreement with experiment. It is emphasized that corresponding simulations for $(\sqrt{3}\times\sqrt{3})R30^\circ$ structures involving occupation of threefold hollow, twofold bridge, or onefold on-top sites failed to produce acceptable fits to the data for both polarizations, and that these sites can therefore be excluded. Analysis of SEXAFS measurements taken for $\Theta_{\text{Na}}=0.16$ monolayer, where a (1×1) LEED pattern was observed, leads to the same conclusions. For this coverage the nn bond length was found to be $R_1=3.32\pm 0.04$ Å.

In order to further explore the "unusual" chemisorption we performed self-consistent density-functional-theory calculations of total energies, forces, and electronic structures of some stable and metastable geometries of $(\sqrt{3}\times\sqrt{3})R30^\circ$ Na on Al(111). The local-density approximation for the exchange-correlation functional [24] is used together with fully separable, norm-conserving, *ab initio* pseudopotentials [25]. For the alkali adsorbate a proper treatment of the core-valence exchange-correlation functional is found to be important [26,27]. The total-energy functional is minimized by applying a molecular-dynamics technique for the electronic wave functions [28], simultaneously with an optimized steepest-descent approach for the atomic structure. In order to determine stable as well as metastable adsorbate geometries we started from several different geometries and then allowed the Na adsorbate as well as the top two substrate layers to relax. The basis set consists of plane waves with $E^{\text{cut}}=8$ Ry, and the k_{\parallel} integration is replaced by a sum over six special points in the irreducible part of the surface Brillouin zone. The substrate is described by a ten-layer Al slab. Details will be presented elsewhere [26].

For the "normal" (on-surface) adsorption we find that the two threefold hollow positions represent stable (more accurately, metastable) adsorption sites with a binding energy of 1.7 eV. We also considered strongly distorted surface geometries, by, for example, pushing the three nearest neighbors away from the adsorbate and pulling the second-nearest surface atoms closer, which results in sixfold-coordinated adatoms. The total energy of this geometry is not favorable and the Al atoms are in fact not stable at these positions. The calculated work-function change for the (meta)stable hcp and fcc adsorbate sites is $\Delta\Phi=-1.7$ eV, which agrees with the experimental room-temperature result (-1.7 eV) [16] of the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure and $\Theta_{\text{Na}}=0.33$ monolayer. The calculated Na-Al distances are 3.1 Å for the three nearest and 4.0 Å for the three second-nearest neighbors. Thus, the Al positions are only slightly distorted from the unrelaxed surface geometry, and the Na coordination is clearly threefold. Although the theoretical Na-Al distances compare well with the EXAFS-derived distances,

the coordination number is different. We conclude that the on-surface adsorption is not realized in room-temperature experiments. We therefore considered a replacement reaction, where each Na adsorbate kicks out one Al surface atom, creating as an intermediate step a Na substitutional and an Al adsorbate. This Al adsorbate is then allowed to diffuse to a step, where it is trapped. Taking this reaction into account, the Na adsorption energy is 1.9 eV, and thus by $\Delta E=0.2$ eV more favorable than the normal adsorption. The intermediate step defines the barrier for the reaction. It is calculated to be $E_B=0.8$ eV. We note, however, that other reaction paths than that considered in this work are possible, which may have a smaller barrier height or other sites for the displaced Al. For the local adsorbate geometry we obtain a sixfold coordination with a Na-Al bond length of 3.1 Å and a second-nearest-neighbor Na-Al distance of 4.0 Å. The work-function change for the substitutional $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure (see Fig. 2) is calculated as $\Delta\Phi=-1.6$ eV. We would like to mention that other reactions are also possible, e.g., that the displaced Al atoms have not migrated to steps as we assumed in the calculation. We speculate that they could be placed at the surface, i.e., between the Na adsorbates. Although we are not able to identify the positions of the displaced Al atoms, the fact that we found one reaction which is energetically more favorable than the normal adsorption implies that the displacive mechanism is possible and likely.

In Fig. 3 we show the calculated adsorbate-induced electron-density change for a Na atom occupying a fcc hollow position [Fig. 3(a)], and for the substitutional adsorption [Fig. 3(b)]. The large work-function change for the normal adsorption can be understood in terms of electron transfer from the alkali to the substrate Fermi level. The partially ionized alkali atom is then efficiently screened by an image-charge density induced at the metal surface (outside the top Al layer) [3,29]. For the substi-

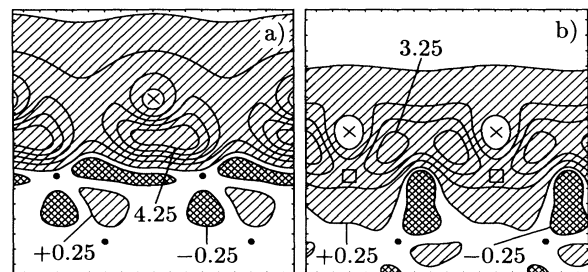


FIG. 3. (a) Electron-density change, $\Delta\rho_{\text{Na-Al}}-\rho^{\text{Al}}$, for $(\sqrt{3}\times\sqrt{3})R30^\circ$ Na on Al for the ("normal") on-surface adsorption at the fcc threefold hollow position. We display the $(\bar{1}\bar{2}1)$ plane. The Na position is marked by a cross and the Al positions are marked by black dots. Units are 10^{-3} bohr $^{-3}$. (b) Same as in (a), but for the electron-density difference between the density of the substitutional Na adsorption and the corresponding vacancy structure. The positions of removed Al atoms are noted by open squares.

tutional adsorption Fig. 3(b) displays the difference between $\rho_2^{\text{Na-Al}}$ and a $(\sqrt{3} \times \sqrt{3})R30^\circ$ vacancy structure, $\rho^{V\text{-Al}}$. It is seen that the adatom does not exactly replace the removed Al, but its position is 1.4 Å above the vacancy. The bonding should now be described as metallic with some covalent contribution. We believe that this change in the bonding character (from partially ionic to more metallic) is the driving mechanism for the substitutional adsorption. Similarly one could say that the higher coordination attained for a substitutional Na drives this process. We speculate that this "unusual" adsorption geometry may be favorable for other metal fcc (111) surfaces as well and that in particular the Cu(111)-(2×2)-Cs and Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -K structures might also involve substitutional occupation of a sixfold-coordinated site. LEED studies [13,30] of these systems led to best, but unconvincing, agreement between experimental and calculated intensities for the on-top site. We note, however, that the calculated energy gain by substitutional adsorption, when compared to the on-surface adsorption, is not very large. Therefore, for other (more open) surfaces and for other materials it is not obvious if this process is relevant as well.

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