

## Temperature-dependent local geometries in the system Al(100)- $c(2\times 2)$ -Na: A surface extended x-ray-absorption fine-structure study

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(Received 21 August 1992)

The adsorption of Na on Al(100) at 140 and 300 K has been studied by surface extended x-ray-absorption fine-structure experiments. An analysis of the measurements shows that the local geometry in the  $c(2\times 2)$ -Na phases formed at each temperature is completely different. At 140 K the Na atoms occupy fourfold hollow sites, whereas at 300 K a model is favored where the Na atoms lie beneath a reconstructed surface Al layer. Warming to 300 K causes an irreversible transformation of the low-temperature structure to the room-temperature structure.

Recent quantitative structural studies<sup>1-6</sup> of the adsorption of alkali metals on fcc (111) and hcp (0001) metal surfaces together with an early low-energy electron diffraction (LEED) study,<sup>7</sup> have revealed a wealth of interesting and unexpected behavior. The main results are (1) occupation of the sites of highest coordination on these most close-packed surfaces is the exception rather than the rule; occupation of onefold on-top sites or of substitutional sites is preferred;<sup>1-7</sup> (2) adsorption at room temperature can lead to reconstruction of the substrate with occupation of substitutional sites and/or subsurface adsorption;<sup>1,5,6</sup> (3) for the same adsorbate/substrate system at a fixed coverage, different surface structures may form at different adsorption temperatures; in one such case an order-preserving phase transition occurs between structures having different local geometry;<sup>5</sup> (4) for the same adsorbate/substrate system at fixed adsorption temperature, different sites may be occupied at different coverages.<sup>2</sup>

In contrast to the above results, studies of alkali-metal adsorption on fcc (100) surfaces<sup>10-13</sup> and a single hcp (1010) surface<sup>14</sup> have been reported to lead to occupation of the fourfold hollow sites of highest symmetry on the unreconstructed substrates. Of particular interest here, an early LEED study<sup>10</sup> of the Al(100)- $c(2\times 2)$ -Na structure formed by adsorption at room temperature suggested occupation of fourfold hollow sites with a nearest-neighbor (NN) Na-Al distance of 2.9 Å.

Complementary to the above results, high-resolution measurements of shifts in core-electron binding energies<sup>8,9</sup> for alkali adsorption on some close-packed surfaces and for Al(100)- $c(2\times 2)$ -Na have also demonstrated the occurrence of order-preserving phase transitions between structures of different local geometry as well as the occurrence of an intermixing of alkali and substrate atom layers.

Here we report on a surface extended x-ray-absorption fine-structure (SEXAFS) study of the Al(100)- $c(2\times 2)$ -Na structure formed both at low temperature (LT), 140 K, and at room temperature (RT). For the  $c(2\times 2)$ -Na phase formed at 140 K, we find that Na atoms occupy

fourfold hollow sites with a NN Na-Al bond length of  $3.21\pm 0.03$  Å. However, the local geometry for the  $c(2\times 2)$ -Na phase formed at room temperature is quite different and involves two close-lying Na-Al bond lengths of 2.9 and 3.2 Å. These results are not compatible with the occupation of fourfold hollow sites on unreconstructed surface as reported in the early LEED study cited above, nor can they be explained in terms of occupation of other sites on an unreconstructed surface. The data can be explained, however, by a model in which Na atoms are located in subsurface sites beneath a reconstructed surface layer of Al atoms. The metastable  $c(2\times 2)$ -Na phase formed at 140 K transforms to the reconstructed  $c(2\times 2)$ -Na phase on heating to room temperature, consistent with the results of measurements of core-electron binding energies mentioned above. Our results show that the adsorption of Na on Al(100) is just as intriguing as that on Al(111).

The experiments reported here were conducted at the electron storage ring BESSY in Berlin with the grazing-incidence plane-grating monochromators<sup>14</sup> SX-700-I and SX-700-IV. The SEXAFS data were taken above the Na  $K$  edge in the total and partial electron yield modes at normal ( $\theta=90^\circ$ , E vector parallel to the surface) and near-grazing ( $\theta=20^\circ$ ) x-ray incidence. They were analyzed by the conventional Fourier transform method and by a curve-fitting procedure<sup>15</sup> using the same phase shifts as in Ref. 1. The Al(100) crystal was cleaned by Ar-ion bombardment and annealing cycles and characterized by LEED and Auger electron spectroscopy (AES). Na layers were deposited from SAES getters<sup>16</sup> with the substrate held at 140 K (LT) or at room temperature (RT). They were free from contamination as checked by AES and x-ray-absorption measurements. A  $c(2\times 2)$ -Na phase was also prepared by heating the LT structure to room temperature. The SEXAFS results for this phase and the RT phase were identical.

Fourier transforms of SEXAFS spectra for the LT and RT  $c(2\times 2)$ -Na phases taken at  $\theta=20^\circ$  and  $90^\circ$  are shown in Fig. 1. It is immediately evident from the differences in the transforms that the local geometry of Na atoms in

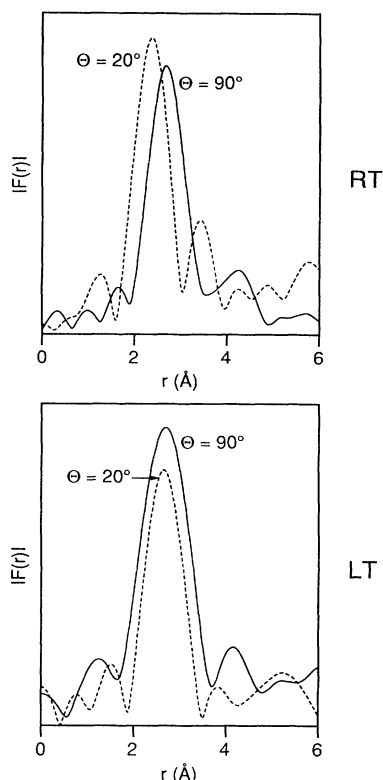


FIG. 1. Fourier transforms of SEXAFS data for Al(100)- $c(2 \times 2)$ -Na taken at normal incidence ( $\theta = 90^\circ$ , solid lines) and near-grazing incidence ( $\theta = 20^\circ$ , dashed lines): top, RT  $c(2 \times 2)$ -Na phase; bottom, LT  $c(2 \times 2)$ -Na phase.

the LT and RT phases is different. It can also be seen that the position of the dominant peak in the Fourier transforms for the LT phase is independent of polarization (Fig. 1, bottom), whereas for the RT phase the dominant peaks at  $\theta = 20^\circ$  and  $90^\circ$  are mutually displaced by

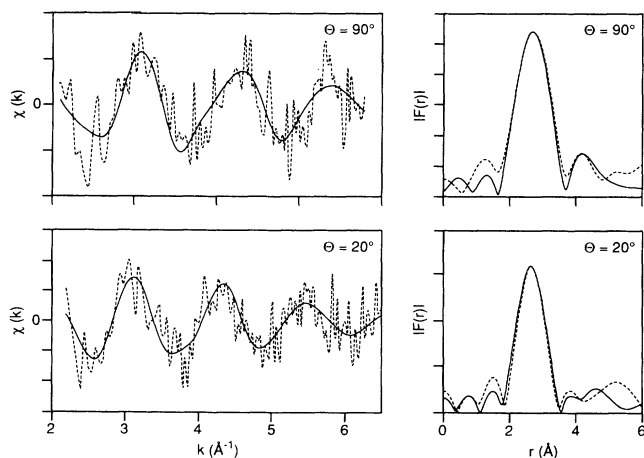


FIG. 2. Experimental SEXAFS spectra  $\chi(k)$  and their Fourier transforms  $|F(r)|$  (dashed lines) for normal incidence ( $\theta = 90^\circ$ ) and near-grazing incidence ( $\theta = 20^\circ$ ) together with simulated spectra and their Fourier transforms (solid lines) for the LT  $c(2 \times 2)$ -Na phase. The simulations are for the structure with Na atoms adsorbed in fourfold hollow sites.

about  $0.3 \text{ \AA}$  (Fig. 1, top). Thus, the RT phase contains (at least) two close-lying Na-Al bond lengths, as opposed to a single dominant Na-Al distance in the LT phase. As noted above, warming the LT  $c(2 \times 2)$ -Na phase to room temperature effects a transformation to the RT  $c(2 \times 2)$ -Na phase with no change in the LEED pattern. This confirms the interpretation of high-resolution core-level spectroscopy measurements by Andersen *et al.*<sup>8</sup> that an order-preserving phase transition occurs for this system.

In the quantitative analysis of the data for each of the two  $c(2 \times 2)$  phases, experimental SEXAFS spectra were compared with spectra calculated for structures involving the following adsorption sites: onefold on-top, twofold bridge, fourfold hollow, and fourfold substitutional. The latter is formed by displacing every second surface Al atom and replacing it by Na. For the RT  $c(2 \times 2)$  phase, structures involving mixed occupation of the sites mentioned were also considered, as were structures involving reconstruction of the substrate and intermixed Na and Al layers. The criteria for acceptance of a structural model include both a good fit of the individual polarization-dependent spectra and the agreement of amplitude ratios for the dominating peak. We note that the latter are only accurate to about 20%. In considering the sensitivity of the fit between calculations and experiment to changes in the local geometry it should be emphasized that although the SEXAFS spectra are dominated by the NN Na-Al bond distances, they also contain contributions from next-nearest-neighbor (NNN) and higher distances.

For the LT  $c(2 \times 2)$ -Na phase an excellent agreement between experiment and calculation is obtained assuming a fourfold hollow site on an unreconstructed substrate. This can be seen from Fig. 2 which shows best fits of calculated SEXAFS  $\chi(k)$  functions and their Fourier transforms (solid lines) with the corresponding experimental spectra and transforms (dashed lines). All other adsorption sites can be definitely excluded. The determined NN Na-Al bond lengths are  $R_1 = 3.20 \pm 0.03 \text{ \AA}$  for  $\theta = 20^\circ$  and  $R_1 = 3.21 \pm 0.03 \text{ \AA}$  for  $\theta = 90^\circ$ .

The SEXAFS spectra for the RT  $c(2 \times 2)$ -Na phase cannot be reproduced by assuming a fourfold hollow site. This is already indicated by the fact that the dominant peaks in the Fourier transforms for  $\theta = 20^\circ$  and  $90^\circ$  yield bond lengths which differ by about  $0.3 \text{ \AA}$ ; namely,  $2.9 \text{ \AA}$  for  $\theta = 20^\circ$  and  $3.2 \text{ \AA}$  for  $\theta = 90^\circ$  (cf. Fig. 1). This result also clearly rules out any other single adsorption site on an unreconstructed Al(100) surface. From the polarization dependence of the SEXAFS amplitude it follows that the structure must contain two interatomic vectors  $\mathbf{r}_i$  and  $\mathbf{r}_k$  (pointing from the absorbing atom to the backscattering atoms), oriented such that one of them,  $\mathbf{r}_i$ , makes a small angle to the surface normal, whereas the other,  $\mathbf{r}_k$ , makes a large angle to the surface normal. Then  $R_i = |\mathbf{r}_i| = 2.9 \text{ \AA}$  dominates the  $\theta = 20^\circ$  SEXAFS spectrum while  $R_k = |\mathbf{r}_k| = 3.2 \text{ \AA}$  dominates the  $\theta = 90^\circ$  spectrum. In general, the structure must involve either occupation by Na atoms of two different adsorption sites or occupation of a single site with two different NN bond lengths to neighboring Al atoms. As discussed below, the latter possibility must involve a reconstruction of the substrate.

Considering first the possibility that the structure contains two inequivalent adsorption sites, we note that the surface coverage of one-half monolayer of Na atoms corresponding to the ideal  $c(2 \times 2)$  structure, and the physical dimensions of the adsorbed atoms, preclude structures with mixed occupation of different sites. Thus, if two different sites are involved they must belong to different domains in each of which only one type of site is occupied. It turns out in fact that simulations based on coexistence of two types of domains with equal concentrations of on-top sites with Na-Al bond length of 2.9 Å and fourfold substitutional sites with Na-Al bond length of 3.2 Å do reproduce the experimental spectra to within the experimental accuracy. We believe nevertheless that this model can be rejected on physical grounds. First, it seems unlikely that the binding energies for the two sites should be so closely degenerate. Second, it is hardly conceivable that adsorption at low temperature would lead to the observed occupation of the fourfold hollow site if in fact occupation of the on-top site was energetically more favorable. The activation barrier for a transition from the fourfold site to the on-top site must surely be very small. Finally, we note that measurements of core-level shifts have been interpreted in terms of the existence of a *single* type of adsorbed Na atom.<sup>8</sup>

Having rejected the possibility that the RT  $c(2 \times 2)$ -Na structure contains two inequivalent adsorption sites, we considered models involving a reconstruction of the substrate, including models with intermixed Na-Al layers. In the light of the analysis described above, it was evident that in the correct model the local environment of the Na atoms must contain the elements both of on-top geometry and of fourfold substitutional geometry.

In considering models involving the adsorption of Na atoms on a reconstructed substrate, two main possibilities arise. First, the reconstruction could consist of a rumpling of the first Al layer to form two  $c(2 \times 2)$  sublattices. Alternately, the reconstruction could consist of a removal of one-half monolayer Al atoms to form a  $c(2 \times 2)$ -Al surface layer. With respect to the first possibility, simulations were performed for a model in which Na atoms are in on-top sites with a bond length of 2.9 Å but where the NNN Al atoms are displaced outwards by 1.5 Å from their bulk positions to form a second  $c(2 \times 2)$  sublattice and to yield a NNN Na-Al distance of 3.2 Å. Although this model apparently includes the main expected ingredients of the correct model, the simulations failed in detail to reproduce the experimental results, evidently because the model does not contain the correct third-nearest Na-Al distances. This conclusion applies generally to models involving adsorption on a rumpled substrate. The second possibility, involving adsorption on a  $c(2 \times 2)$ -Al surface layer, can be ruled out since this class of models cannot contain both of the observed NN Na-Al distances.

Having eliminated models involving adsorption of Na on top of unreconstructed or reconstructed Al surfaces, we considered models for the RT  $c(2 \times 2)$ -Na phase involving intermixed Na-Al layers. Two such models were found to be compatible with the experimental data. The first model, which we favor on physical grounds, is shown

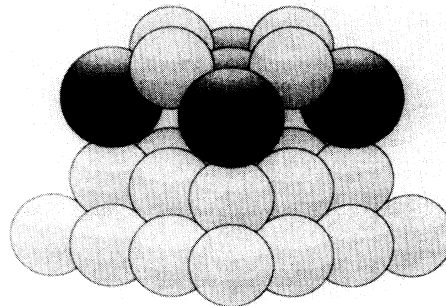


FIG. 3. Structure proposed for the RT  $c(2 \times 2)$ -Na phase. Na atoms are shown as the large, dark circles.

in Fig. 3. It contains Na atoms in on-top sites on an unreconstructed Al layer, but in addition contains a  $c(2 \times 2)$  sublattice of Al atoms adsorbed on top of the Na layer in fourfold hollow sites. The geometry of the top two layers, if inverted, can be seen to be equivalent to adsorption of Na in a fourfold substitutional site. A comparison of simulations (solid lines) for this structure and experiment (dashed lines) is shown in Fig. 4, from which it can be seen that the agreement is very good. Similarly good agreement is obtained for an alternative model in which Na atoms are located in fourfold substitutional sites relative to the substrate and in which Al atoms in a  $c(2 \times 2)$  sublattice are adsorbed on the Na layer in on-top sites. We believe, however, that this model can be rejected because of its extreme surface corrugation.

In summary, an analysis of SEXAFS measurements for the LT  $c(2 \times 2)$ -Na phase leads to a unique identification of the local geometry as consisting of adsorption of Na atoms in fourfold hollow sites on an unreconstructed substrate. The corresponding analysis for the RT  $c(2 \times 2)$ -Na phase leads to the identification of three possible local geometries: (1) a mixture of two domain types involving occupation, respectively, of on-top and fourfold substitutional sites; (2) subsurface adsorption of Na atoms in on-top sites beneath a  $c(2 \times 2)$ -Al layer with Al atoms adsorbed in fourfold hollow sites on the Na layer; (3) subsurface adsorption of Na atoms in fourfold substitutional sites beneath a  $c(2 \times 2)$ -Al layer with Al atoms adsorbed in on-top sites on the Na layer. On physical grounds the second of these three possible local geometries is the most likely and, moreover, yields the best fit. The Na-Al bond distances resulting from the analysis are listed in Table I.

We believe that the above conclusions are internally consistent in the sense that the proposed structures pro-

TABLE I. Measured Na-Al distances for the LT and RT  $c(2 \times 2)$ -Na phases. The experimental accuracy is in all cases  $\pm 0.03$  Å.

$c(2 \times 2)$ -Na phase	$\theta$ (degrees)	$R_1$ (Å)	$R_2$ (Å)
LT	90	3.21	
	20	3.20	
RT	90		3.19
	20	2.94	3.19

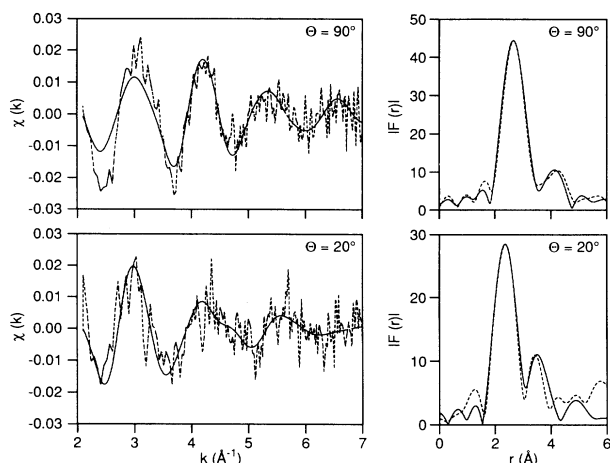


FIG. 4. Experimental SEXAFS spectra  $\chi(k)$  and their Fourier transforms  $|F(r)|$  (dashed lines) for normal incidence ( $\theta=90^\circ$ ) and near-grazing incidence ( $\theta=20^\circ$ ) together with simulated spectra and their Fourier transforms (solid lines) for the RT  $c(2\times 2)$ -Na phase. The simulations are for the structure with subsurface Na atoms shown in Fig. 3.

vide a natural explanation for the observation of an irreversible, order-preserving phase transition between the LT and RT  $c(2\times 2)$ -Na phases. Clearly the restructuring of the surface involved in the formation of the RT  $c(2\times 2)$ -Na phase requires an energy of activation. We believe also that our conclusions are consistent with the core-level spectroscopy measurements of Andersen *et al.*<sup>8</sup> cited previously. We note that the Na  $2p$  spectrum for the  $c(2\times 2)$ -Na phase contains a single component, indicating the existence of a single type of adsorbed Na. Furthermore, we note that the Al  $2p$  spec-

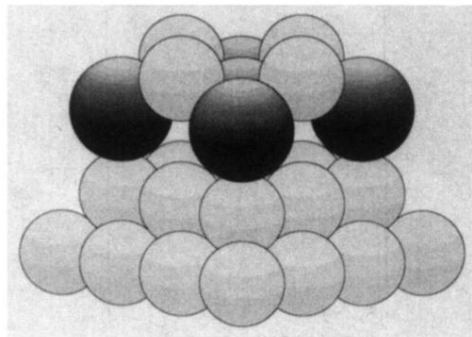
trum contains two components, shifted by 50 and 500 meV, respectively, with respect to the bulk value. Andersen *et al.*<sup>8</sup> suggest that these components can be attributed to Al atoms with different coordinations to the adsorbed Na atoms. Our conclusions for the RT  $c(2\times 2)$ -Na structure are in disagreement with the results of an early LEED study.<sup>10</sup>

It is interesting to compare the structure proposed here for the RT Al(100)- $c(2\times 2)$ -Na phase with the structure determined for Al(111)- $(\sqrt{3}\times\sqrt{3})$ -R $30^\circ$ -Na. For the latter system, *ab initio* density-functional calculations by Neugebauer and Scheffler<sup>17</sup> confirm that the total energy of the system is a minimum for Na atoms adsorbed in six-fold substitutional sites. Neugebauer and Scheffler<sup>17</sup> have suggested that the preference for substitutional sites is a consequence of the ionic nature of the bonding, which can develop strongly because of the efficient screening of dipole-dipole interactions for Na atoms adsorbed in such deep-lying sites. In view of this suggestion it would have been expected that the Al(100)- $c(2\times 2)$ -Na structure might involve occupation of fourfold substitutional sites. We speculate that the structure proposed here involving subsurface adsorption of Na atoms in a fivefold coordinated site gives a more efficient screening of dipole interactions than would be the case for the fourfold substitutional site.

We thank G. Jäkisch for technical assistance throughout the measurements. We thank Jesper Andersen for useful discussions and for communicating results prior to publication. The work has been funded by the German Federal Ministry of Research and Technology (BMFT) under Contract No. 05390 FXB 2 and by the Danish Natural Science Research Council (SNF).

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**FIG. 3.** Structure proposed for the RT  $c(2 \times 2)$ -Na phase. Na atoms are shown as the large, dark circles.