Structural Study of Alkali/Simple Metal Adsorption: Rb and Na on Al(111)

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A quantitative structural study of Na and Rb adsorption on Al(111) using normal incidence standing x-ray wave-field triangulation shows that Rb occupies atop adsorption sites and both systems show a constant adsorbate-substrate bond length over the alkali coverage range 0.12–0.33 monolayer. These results indicate that there is directional local bonding in this simple alkali *s-p* band metal adsorption system, and show that there is no ionic-covalent bonding transition in this coverage range for either system.

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The nature of alkali-atom bonding on metal surfaces and the associated local adsorption geometries, superficially rather simple problems, have recently proved rather controversial. The conventional view of such adsorption is that there is substantial charge transfer from the adsorbed alkali to the substrate metal leading to an essentially ionic adsorbate-substrate bond, with depolarization at high coverage eventually leading to metallic or covalent bonding [1,2]. Evidence believed to support this view includes the measured variation of the work function with alkali coverage [2], and a significant adsorbate-substrate bond-length extension with increasing coverage as the bond becomes less ionic in the Cs/Ag(111) adsorption system [3]. In addition, quantitative structural studies of several such adsorption systems indicate the occupation of maximally coordinated adsorption sites as might be expected for essentially nondirectional bonding [4–9]. By contrast, model calculations of alkali-atom adsorption on jellium lead to a charge redistribution which has been interpreted as characteristic of covalent adsorbate-substrate bonding [10,11], and recent core-level photoemission studies of Cs, K, and Na adsorption of W(110) have been interpreted as consistent with this view [12]. In addition, there are two low-energy electron diffraction (LEED) studies [of Cs on Cu(111) [13] and very recent investigation of K on Ni(111) [14]] which identify *atop* site adsorption, apparently indicating a more directional form of adsorbate-substrate bonding. All of these results supporting this covalent bonding picture are from noble- or transition-metal substrates.

Here we report on quantitative structural studies using a quite different technique [normal incidence standing x-ray wave-field absorption (NISXW) [15,16]] of the adsorption of both Rb and Na on Al(111), a simple *s-p* band metal, over a wide coverage range including phases both with and without long-range order. In the case of Rb on Al(111) we identify the adsorption site as atop, while we find no evidence in either adsorption system for any significant coverage dependence of the adsorbate-substrate bond length. Both of these results support the view that no ionic-to-metallic bonding transition occurs, and suggest that the Rb-Al substrate bonding is highly directional, even for this simple *s-p* band metal substrate. The Na adsorption results differ from those of Rb, however, in indicating that this adsorbate does occupy a high coordination adsorption site, and indeed the results are best explained by the substitutional site recently proposed for this system on the basis of surface-extended x-ray absorption fine-structure (SEXAFS) experiments [9].

The NISXW technique used in this investigation has been described in detail elsewhere [15,16]. The standing x-ray wave-field (SXW) method allows one to determine the spacing between an adsorbed layer and the nearest (extended) substrate scatterer lattice plane associated with the particular Bragg reflection which is excited. By using normal incidence to the Bragg planes the technique becomes rather insensitive to substrate crystal mosaicity and can be applied to normal metal crystals [15,16]. In this experiment we have measured the adsorbate-substrate layer spacings relative to the (111) Bragg reflection with x radiation incident along the Al(111) surface normal, and normal to one of the $(\bar{1}11)$ sets of planes at an angle of 70.5° to the surface. These two layer spacings allow us to locate the adsorption site by simple geometrical triangulation.

The experiments were performed at the Science and Engineering Research Council's Daresbury Laboratory taking x radiation from the Synchrotron Radiation Source on the SEXAFS beam line [17,18]. The Al(111) sample was prepared by the usual combination of x-ray Laue alignment, spark machining, mechanical polishing, and *in situ* argon ion bombardment and annealing cycles until a clean well-ordered surface was obtained as measured by *in situ* Auger electron spectroscopy and LEED. Adsorption of Rb and Na was effected from carefully outgassed SAES "getter" sources [19]. All NISXW measurements were conducted with the sample held at low temperature (approximately 170 K) although in the

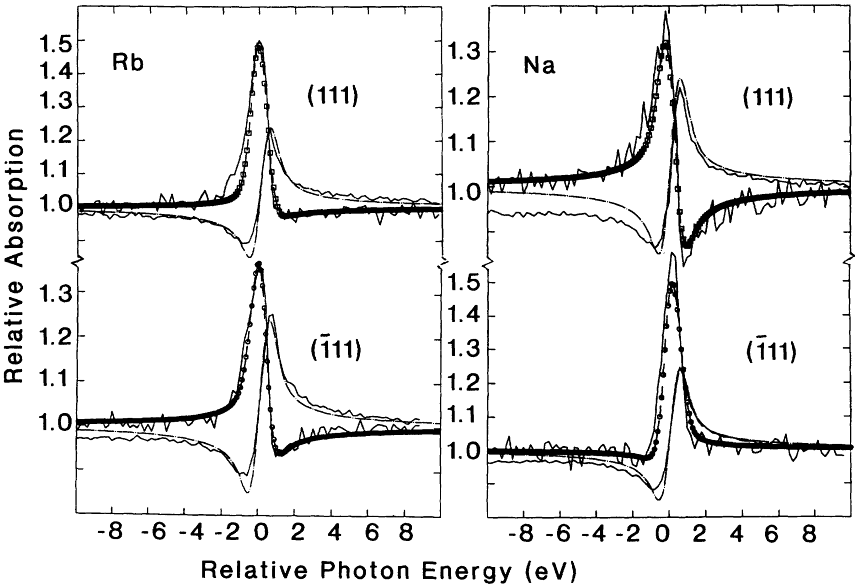

FIG. 1. X-ray absorption, as monitored by Rb and Al Auger electron emission, and by Na 1s photoemission, as a function of the incident photon energy relative to the nominal (111) and ($\bar{1}$11) normal incidence Bragg conditions, from the Al(111)($\sqrt{3}\times\sqrt{3}$)R30°-Rb and Al(111)($\sqrt{3}\times\sqrt{3}$)R30°-Na surfaces. The dash-dotted lines show a theoretical fit to the Al signal assuming absorption at the substrate scatterer planes with the nonstructural parameters optimized. The lines marked by squares (111) and circles ($\bar{1}$11) show theoretical fits to the Rb and Na absorption using optimum layer spacings as described in the text and given in Table I.

case of the Na measurements the alkali dosing was performed at room temperature in order to reproduce the conditions used in the recent SEXAFS study [9]. Rb structures were normally formed at low temperature, although NISXW measurements following room-temperature preparation showed no influence of the preparation temperature. In the case of Rb adsorption, increasing coverage led to (2×2) and ($\sqrt{3}\times\sqrt{3}$)R30° ordered structures [20] assumed to correspond to nominal coverages of 0.25 and 0.33 monolayer (ML). Measurements were made on these two structures and at lower coverages, for which no overlayer long-range order could be observed by LEED. The estimated coverage for these data was 0.12–0.15 ML. In the case of Na adsorption, we report here on results for the ordered ($\sqrt{3}\times\sqrt{3}$)R30° structure (0.33 ML) and for low coverages of approximately 0.12–0.15 ML, although we have also made measurements on the (2×2)Na phase which is obtained by *increasing* the Na exposure beyond that needed to form the ($\sqrt{3}\times\sqrt{3}$)R30°-Na phase; this (2×2) structure is significantly more complex, involving two layers of intermixed Na and Al [21,22].

Representative NISXW results, for the Na- and Rb-induced ($\sqrt{3}\times\sqrt{3}$)R30° structures, are shown in Fig. 1. In each case the SXW absorption in the Al substrate is monitored by measuring the Al *KLL* Auger electron yield at 1390 eV as the photon energy is scanned through the normal incidence Bragg reflection energy for Al(111) at 2660 eV. SXW absorption in Na atoms was measured by monitoring the intensity of the Na 1s photoemission peak, while SXW absorption in the adsorbed Rb atoms was detected through the Rb $L_3M_{4,5}M_{4,5}$ Auger electron yield at 1560 eV. The substrate absorption profiles give an absolute energy scale and allow fitting of nonstructural parameters. The adsorbate signals are then fitted by optimization of two structural parameters, the adsorbate-substrate layer spacing, and the coherent fraction of absorbers. The layer spacings obtained, which were independent of coverage for the two adsorption systems, were Rb, 0.80±0.10 Å for (111) and 1.00±0.10 Å for ($\bar{1}$11); Na, 1.20±0.15 Å for (111) and 0.55±0.15 Å for ($\bar{1}$11). Table I shows how these triangulation values can be compared with the theoretical values for different adsorption sites. Usig the measured (111) layer spacings, we can calculate the associated ($\bar{1}$11) layer spacings which would result for different adsorption sites, and compare these with the experimental value.

Note that there is an ambiguity in all SXW layer spacings in that any integral number of substrate scattering plane layer spacings [2.33 Å in the case of Al(111)] may be added to the measured values without influencing the fit to experiment; because the lateral positions of atoms in the Al(111) atomic layers only repeat every third layer, however, the true ambiguity concerns the addition of zero, one, or two substrate layer spacings to the experimentally determined (111) layer spacing. This is seen clearly in the results of Table I. This ambiguity is overcome by applying physically reasonable constraints to the acceptable effective radius of the adsorbed atom, given as the difference between the implied adsorbate-substrate bond length and the metallic Al radius (see Table I). For example, the Rb data can actually be reconciled with a

TABLE I. Site identification via NISXW triangulation using the (111) and ($\bar{1}11$) reflections for the Na and Rb adsorption structures on Al(111). The measured (111) layer spacings are used to calculate the associated ($\bar{1}11$) layer spacings for atop and hollow sites (hcp above an Al atom in the second layer, fcc above an Al atom in the third layer), and these are compared with the experimental ($\bar{1}11$) layer spacings. Three possible solutions (bold text) are found in each case due to ambiguity associated with adding bulk layer spacings of 2.33 Å but this ambiguity is removed by considering the effective radius, r_{eff}, implied by each of these sites assuming an ideally terminated substrate. The bracketed figures are experimental errors in hundredths of an Å unit. The errors in the theoretical values derive from the experimental errors in the (111) layer spacings.

	Experimental (111) layer spacing (Å)	Theoretical ($\bar{1}11$) layer spacing (Å)			Expt. ($\bar{1}11$) spacing (Å)	r_{eff} (Å)
		atop	fcc hollow	hcp hollow		
Rb	0.80(10)	0.27(3)	1.82(3)	**1.05(3)**	1.00(10)	0.40
	or 3.13(10) (0.80+2.33)	**1.05(3)**	0.27(3)	1.82(3)		1.70
	or 5.46(10) (0.80+4.66)	1.82(3)	1.05(3)	0.27(3)		4.27
Na	1.20(15)	**0.41(5)**	1.96(5)	1.18(5)	0.55(15)	−0.23
	or 3.53(15) (1.20+2.33)	1.18(5)	**0.41(5)**	1.96(5)		2.47
	or 5.86(15) (1.20+4.66)	1.96(5)	1.18(5)	**0.41(5)**		4.66

true (111) nearest substrate plane spacing of 0.80 Å above an hcp hollow adsorption site, 3.13 Å above an atop site or 5.46 Å above a fcc hollow site. Note that this hcp, atop, fcc site ordering is the structural sequence of the bulk fcc solid. These three sites are therefore identical relative to the bulk extended substrate lattice but only the atop site gives an acceptable effective radius for the adsorbed Rb species (1.70 Å compared with the ionic radius of 1.48 Å and the covalent radius of 2.43 Å). In the case of Na adsorption, none of the simple overlayer sites gives an effective radius for the Na which lies in the ionic to metallic radius range (0.97 to 1.91 Å), but a substitutional site with the Na atoms 1.20 Å above the "same layer" Al atoms gives an acceptable effective radius of 1.67 Å. This therefore confirms the substitutional site adsorption already proposed by Schmalz *et al.* [9] on the basis of SEXAFS data.

One further parameter which is obtained from the theoretical fits to the NISXW data is the coherent fraction of absorbers, which provides a measure of the degree of disorder (static and dynamic) perpendicular to the appropriate x-ray scattering planes. For all the (111) reflection data these coherent fraction values were found to be indistinguishable from unity, implying good local order and vibrational amplitudes perpendicular to the Al(111) surface which are small (i.e., smaller than or comparable to those of the substrate Al atoms for which the rms vibrational amplitudes at 170 K are approximately 0.08 Å). In the case of Rb overlayers, however, the ($\bar{1}11$) reflections show a significantly lower value of the coherent fraction indicating disorder parallel to the surface. For both the low coverage and $(\sqrt{3}\times\sqrt{3})R30°$ phases the value obtained (0.8) can be reconciled with vibrational amplitudes parallel to the surface having rms values of approximately 0.18 Å, if we assume the origin of the disorder is dynamic. By contrast, the Na($\bar{1}11$) data show no reduction in coherent fraction. This difference in behavior is consistent with the differences found in the static structures. For Na, the adsorbed atoms are apparently constrained in their motion parallel to the surface, possibly by the adjacent Al atoms if the adsorption site is, indeed, substitutional. By contrast, the atop adsorption site of Rb might be expected to have an associated soft Rb-Al wagging vibrational mode (a frustrated translation) as is found for molecules which adsorb atop via local directional covalent bonds.

These results are significant in three ways: the finding of atop site adsorption for an alkali adsorbate (Rb) on an *s-p* band metallic substrate, the fact that Rb and Na clearly behave differently, and the absence of any alkali coverage dependence of the adsorbate-substrate bond length. Strictly speaking, the NISXW technique does not measure the local bond length but rather the adsorbate location relative to the extended bulk, so a fixed site *could* be reconciled with compensating changes in the nearest-neighbor bond lengths and the outermost substrate layer spacings, although the close-packed fcc (111) surfaces typically show surface layer spacings which differ from the bulk values by substantially less than 0.1 Å [4]. Despite the rather limited precision of our measurements, the coverage independence of the implied bond length is significant; the differences between the ionic and covalent radii of alkali atoms all lie in the range 1.0±0.1 Å so we might expect a bond-length change of several tenths of an angstrom unit in the coverage range 0.12–0.33 ML which we have studied. Previous measurements [20] of the work function change in these adsorption systems show a deviation from a linear coverage dependence beyond approximately 0.1 ML (Rb) and 0.15 ML (Na) so our coverage range should be appropriate to observe the proposed transition. Indeed, Lamble *et al.* [3] have reported a 0.3-Å Cs-Ag bond-length change in a similar coverage range for the Cs/Ag(111) system. Our result that no layer spacing change occurs within ±0.10 Å is therefore significant evidence for the absence of such a transition in either of the systems we have studied.

The different local adsorption structure of Rb and Na on Al(111) in the submonolayer coverage regime appears to be symptomatic of major differences in these systems. In particular, LEED characterization shows that Na/Al(111) shows additional higher coverage phases which are temperature dependent in the range 150–300 K, and which are believed to involve more than one atomic layer of adsorbate [20], while new photoemission data indicate these structures involve Al/Na intermixing [22] [a conclusion supported by our own NISXW study of the (2×2)-Na phase [21]]. These mixed multilayer phases would appear to be a natural extension of the capacity of Na to substitute top-layer Al atoms in the submonolayer coverage range. No such effects are known to occur for Rb adsorption, and the observed sequence of LEED structures is consistent with simple submonolayer overlayer adsorption. Some of these differences may well be attributable to the smaller radius of Na than of Rb. Using SEXAFS Schmalz *et al.* [9] conclude that Na atoms substitute top-layer Al atoms with a Na-Al nearest-neighbor bond length of 3.31 Å, close to the sum of the metallic radii which is broadly consistent with this embedding of the absorbed atom. However, this structure still leaves the Na atom centers some 1.6 Å above the Al atoms of the top layer so the embedding is really rather marginal. If Rb atoms adopted their metallic radii in similar substitutional sites, the Rb-Al top-layer spacing would be 2.6 Å, greater than the Al-Al layer spacing and clearly far less compatible with the idea of metallic embedding. It may be, therefore, that Na adsorption represents a rather special case.

The observation of the atop adsorption site for Rb on Al(111) is perhaps the most surprising result. As remarked above, LEED studies of several alkali-metal adsorption systems [Na/Ni(100) [6,7], Na/Al(100) [5], Cs/Rh(100) [8]] all indicate maximally coordinated hollow site adsorption with an effective alkali radius close to the mean of the appropriate ionic and metallic radii. By contrast, LEED studies of Cs/Cu(111) [13] and K/Ni(111) [14] lead to the conclusion that atop site adsorption is involved with an effective alkali radius within about 0.2 Å of the ionic value. Our result reported here is consistent with this apparent pattern for fcc (111) surface adsorption but is important in using an entirely different investigative technique which gives a far more clearly unique, if somewhat less precise, adsorption site determination for both ordered and disordered phases. Moreover, our result for Al(111) indicates that the effect cannot be related to substrate *d*-band interactions which might be particularly effective in producing directional bonding.

Clearly a proper understanding of the bonding implications of these results necessitates extensive theoretical study. One recent result which may bear on our observation are the calculations of Müller [23] who found that Xe has its lowest-energy configuration on Pt(111) in the atop site. Xe shares with the alkali atoms a high polarizability which dominates its bonding, but its closed-shell configuration is very different from that of the alkalis. One further feature which the Xe/Pt(111), Cs/Cu(111), K/Ni(111), and Rb/Al(111) surfaces do have in common, however, is that the close-packed substrate and large adsorbate size leads to a rather weak geometrical corrugation of the surface; in this situation more subtle lateral interactions may become particularly important in establishing the local bonding geometry.

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