

## A structural study of the $\text{Al}(111)(\sqrt{3} \times \sqrt{3})R30^\circ$ phase at different temperatures

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 1869

(<http://iopscience.iop.org/0953-8984/6/10/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.147

The article was downloaded on 12/05/2010 at 17:49

Please note that [terms and conditions apply](#).

## A structural study of the Al(111) ( $\sqrt{3} \times \sqrt{3}$ ) R30°–Rb phase at different temperatures

G Scragg†, B C C Cowie†, M Kerkar‡, D P Woodruff†, A Daimellah§, S Turton¶ and R G Jones¶

† Physics Department, University of Warwick, Coventry CV4 7AL, UK

‡ SERC Daresbury Laboratory, Warrington WA4 4AD, UK

§ Metallurgy Department, Ecole Nationale Polytechnique, Alger, Algeria

¶ Chemistry Department, University of Nottingham, Nottingham NG7 2RD, UK

Received 16 November 1993

**Abstract.** Normal-incidence standing x-ray wavefield (NISXW) measurements have been made of the local adsorption site of Rb on Al(111) surfaces, particularly in an ordered ( $\sqrt{3} \times \sqrt{3}$ )R30° phase, as a function of the sample temperature during adsorption or subsequent annealing. The results confirm the atop-site occupation for low-temperature (around 150 K) preparation, but show that room-temperature preparation leads to a structure having Rb atoms in surface substitutional sites. The overall structural situation is therefore essentially the same as that found previously by low-energy electron diffraction LEED for the Al(111)( $\sqrt{3} \times \sqrt{3}$ )R30°–K phases. However, experiments involving annealing of the low-temperature prepared surface to room temperature indicate that only a small part of the surface easily transforms to the higher-temperature form, and indeed there is evidence that even in room-temperature preparations some fraction of the adsorbed atoms may remain in atop sites. The apparent conflict of this result with that from recent photoemission core-level shift and LEED data is discussed.

### 1. Introduction

During the last 5–10 years or so there has been a considerable revival of interest in the properties of alkali-metal adsorption on surfaces (see, e.g., [1, 2]), due partly to controversy over the nature of the adsorbate–substrate bond (see, e.g., [3–7]) (especially for metallic substrates), as well as to the interesting chemical property changes that these adsorbates can make to the reactivity of the surface [8]. Insofar as aluminium is often thought of as a free-electron-like metal (in common with the less experimentally convenient alkali metals), alkali adsorption on the close-packed Al(111) surface might be expected to be a particularly simple case, but the results of many experiments during this recent period have made it clear that this is not the case. In particular, the structural aspects of these adsorption systems have proved rather surprising [9–17].

Until recently most structural studies of alkali adsorption on metal surfaces indicated adsorbate occupation of the maximally coordinated overlayer hollow sites (see, e.g., [18]), as might be expected for non-directional bonding of physically large adsorbate atoms. In the case of Al(111), the first clear evidence that this was not the case came from a SEXAFS study of the room-temperature Al(111)( $\sqrt{3} \times \sqrt{3}$ )R30°–Na structure, which showed that this involves Na atoms in top-layer *substitutional* sites [9]. A second result involved the use of the normal-incidence standing x-ray wavefield (NISXW) absorption technique; these

experiments [11–13] confirmed the substitutional site assignment for the room temperature-prepared Al(111)–Na system, but found that for Rb adsorption on this surface at low temperature, the alkali occupies an *atop* site over a wide range of coverages. In fact atop site adsorption has also been found for K and Cs adsorption on several close-packed transition- and noble-metal surfaces [19–21], but there had been suggestions that this surprisingly low-coordination adsorption site might be related to substrate d-band interactions, an explanation not possible for Al. A further twist to the Al(111)–alkali story emerged from high-resolution core-level photoemission studies of Na, K, Rb and Cs adsorption at low temperature and at room temperature [10, 14, 16]. Particularly conspicuous in these measurements is the presence of a quite strongly chemically shifted component of the Al 2p signal in the case of Na adsorption when the sample was prepared at room temperature, a result seen as a fingerprint of the local intermixing of the substitutional site found in SEXAFS. In addition, however, these photoemission studies also showed similar temperature-dependent effects for the other alkalis, and particularly for K and Rb. Direct confirmation of this change, and indeed of a potential behaviour pattern, was subsequently obtained by quantitative LEED studies of the Al(111)( $\sqrt{3} \times \sqrt{3}$ )R30°–K phases prepared at low temperature and at room temperature, which showed that there are actually two quite different structural phases with the same long-range periodicity [15]. At low temperature the K adsorbates occupy atop sites, as in the low-temperature Rb phase, whereas at room temperature they occupy substitutional sites, as in the room temperature Na phase.

The purpose of the present study was to extend our earlier studies of the Al(111)–Rb adsorption system to the full temperature range over which a similar irreversible phase transition is seen to occur in the photoemission core-level shift work, and to see if the stable room-temperature Al(111)–Rb phase also involves substitutional sites, as is implied by the photoemission data. This work was also undertaken to check an NISXW result of the earlier measurements; although these studies concentrated on the low-temperature adsorption phase, brief tests indicated that no site change appeared to occur if the sample was dosed at higher temperatures. This earlier result appears to conflict with the evidence of temperature-dependent core-level shift measurements, which show a transition temperature for the irreversible transformation to the room temperature structure of approximately 240 K [22]. In a first set of new measurements (autumn 1992) made by dosing Al(111) with Rb at different coverages at low temperature followed by short heating cycles to around room temperature, always measuring the NISXW at low temperature, we again found no evidence of a major structural transition, and indeed a few data taken from a room-temperature preparation appeared to confirm the persistence of the atop-site occupation. In a final set of measurements (autumn 1993), however, we have concentrated on the ordered ( $\sqrt{3} \times \sqrt{3}$ ) phase, and included several room-temperature preparations as well as the effect of heating on the low temperature phase. This allowed us to make some reasonably direct comparisons with a parallel LEED study that came to our notice [23]. We therefore address in this paper the local adsorption structure of the Al(111) system when formed at low temperature, when formed at high (room) temperature and when formed at low temperature and subsequently subjected to various heating treatments.

## 2. Experimental details and NISXW methodology

The basic approach to the NISXW measurements and data analysis was as used in our earlier study of the low-temperature Al(111)–Rb and room-temperature Al(111)–Na phases [11–13]. In particular, we set up (111) or ( $\bar{1}11$ ) Bragg scattering conditions at normal incidence

to the appropriate scattering planes (and thus at incidence angles of  $0^\circ$  and  $70.5^\circ$  to the (111) surface). Adsorbate- and substrate-specific emission signals (Rb LMM and Al KLL Auger electron peaks at 1560 eV and 1390 eV respectively) were then recorded as a function of incident photon energy around the Bragg energy (2660 eV); these provide characteristic absorption profiles of these atoms in the standing x-ray wavefields, from which we can determine the layer spacing of the adsorbing atoms relative to the (extended) scatterer plane locations (see, e.g., [24]–[26]).

The measurements were performed at the Science and Engineering Research Council's (SERC's) Daresbury Laboratory, taking x-rays from the Synchrotron Radiation Source (SRS) on beamline 6.3, which is equipped with an in-vacuum double crystal monochromator [27,28]. The Al(111) sample was prepared by the usual combination of x-ray Laue alignment, spark machining, mechanical polishing and *in situ* Ar-ion bombardment and annealing until a clean and well ordered surface was produced as judged by Auger electron spectroscopy and LEED. Rb dosing was from a well outgassed SAES getter source [29]. In the case of studies of the  $Al(111)(\sqrt{3} \times \sqrt{3})R30^\circ\text{-Rb}$  phases, observations were made not only of the LEED pattern, but also of the energies at which some of the lowest-index diffraction beams (particularly the  $(\frac{1}{3}\frac{1}{3})$  beams) had their maximum intensities. The parallel LEED study [23] of these phases had shown very marked differences in the 'I-V' (intensity-voltage) curves of these beams for the low-temperature and room-temperature phases, so these values gave a simple guide to which LEED phase we were studying. Note that the sample cooling, via a liquid-nitrogen-filled tank and copper braid, led to a minimum sample temperature of approximately 150 K, and this is the 'low' temperature referred to hereafter in this paper.

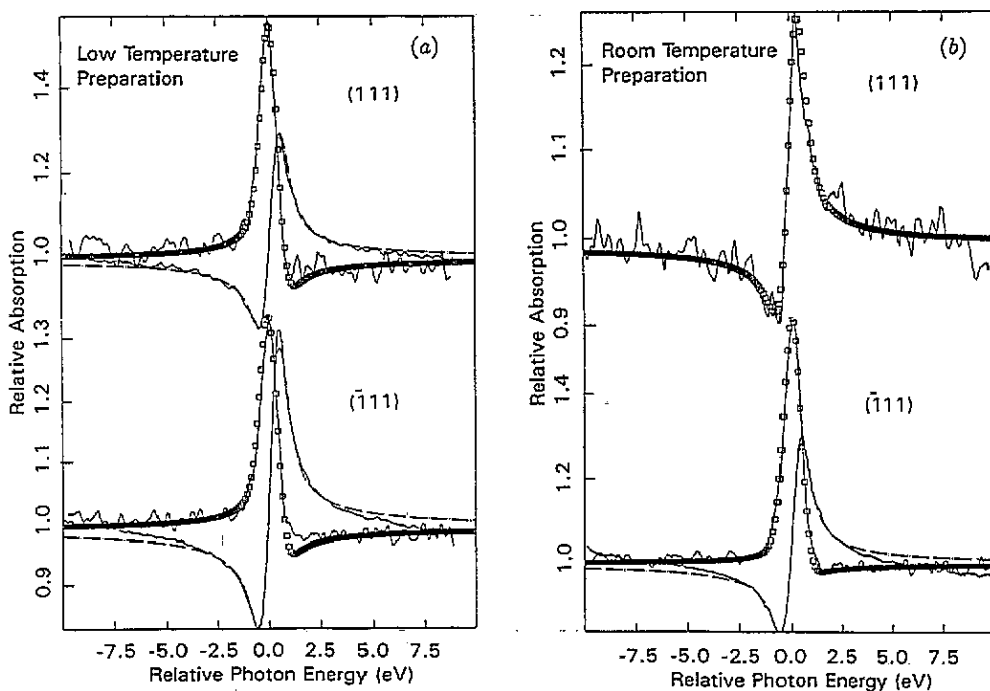
The method of data analysis, as in previous studies [11–13, 25, 26], may be summarized as follows. First, the Al absorption profile was used to establish the non-structural parameters of the absolute energy and the instrumental broadening, assuming that these atoms lie on the scatterer planes (although the possibility that the coherent fraction may be less than unity is included). The Rb absorption profiles were then fitted keeping the non-structural (instrument) parameters fixed, and varying only the (Rb) layer spacing and the associated coherent fraction. Note that in cases in which the coherent fraction is significantly less than unity, (but only in these cases), there is an ambiguity in the fits in that some mixtures of alternative layer spacings at high coherent fractions are also possible. A profile that apparently corresponds to a low coherent fraction can be fitted by a range of combinations of layer spacing and coherent fraction distributions. In such cases, a unique fit for more than one layer spacing requires the imposition of additional constraints, such as the specific layer spacing values that may contribute to the profile. We will address this point specifically in discussing the structural models. Notice, however, that the combination of the layer spacings relative to the (111) and  $(\bar{1}\bar{1}\bar{1})$  planes uniquely defines the atomic positions by simple real-space triangulation, and any structural model involving multiple sites must also be consistent with the NISXW data collected in both directions.

### 3. Results and discussion

#### 3.1. Equilibrium structures

The results of the NISXW measurements of the low-temperature-prepared and room-temperature-prepared  $(\sqrt{3} \times \sqrt{3})$  phases are shown in figure 1. These show the Al and Rb absorption profiles for both the (111) and  $(\bar{1}\bar{1}\bar{1})$  reflections for each structure. All these data were recorded with the sample cooled to low temperature (to minimize the effects of thermal vibrations), but measurements were also made at room-temperature of the room

temperature-prepared phase, with essentially identical results (after correcting for changes in substrate Debye–Waller factors). Best-fit theoretical curves using single layer spacings are also shown in figure 1, and the Rb layer spacings obtained are summarized in table 1 along with a comparison of the predicted (111) layer spacings compatible with the observed (111) layer spacings and different possible adsorption sites. Because there are three inequivalent (111) atom layers that make up an FCC crystal, there is some ambiguity concerning the exact adsorption site, but some approximate knowledge of the adsorbate atom size removes this doubt. For example, a site above an ‘HCP’ hollow site in the top layer is also directly above (i.e. atop) an atom in the second layer, and also occupies an ‘FCC’ hollow site relative to the third layer. As the NISXW technique is not sensitive to the presence (or absence) of these intermediate substrate layers, removing them from the model would not change the NISXW lineshape; on the other hand, in this example occupation of the FCC hollow implies a real Rb–Al layer spacing  $4.66 \text{ \AA}$  (two bulk layer spacings) greater than that implied by the HCP hollow, so it is easy to distinguish these because there is a huge difference in the implied nearest-neighbour distance to the substrate atoms. Note also that a substitutional site is, from the point of view of table 1, equivalent to an atop site, in that the substituting atom actually sits atop the site that was occupied by an Al surface atom. Of course, the substitutional site implies a layer spacing much smaller than would be consistent with a real atop site.



**Figure 1.** NISXW results taken at the (111) and  $(\bar{1}\bar{1}\bar{1})$  reflections from both the low temperature-prepared (a) and room-temperature-prepared (b)  $\text{Al}(111)(\sqrt{3} \times \sqrt{3})R30^\circ\text{-Rb}$  structures, recorded at low temperature. Experimental Al and Rb absorption profiles are both shown as full lines, together with theoretical fits to the Al profiles (dash-dot line) achieved by adjusting non-structural parameters, and to the Rb profiles (squares) using layer spacings and coherent fractions described in the text and used in table 1.

**Table 1.** Site identification via NISXW triangulation using the (111) and  $\bar{1}\bar{1}\bar{1}$  reflections for the Al(111)( $\sqrt{3} \times \sqrt{3}$ )R30°-Rb structures formed at low temperature and at room temperature. The measured (111) layer spacings are used to calculate the associated  $\bar{1}\bar{1}\bar{1}$  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  $\bar{1}\bar{1}\bar{1}$  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 bondlength considerations (see text). The bracketed figures are experimental errors in hundredths of an Ångström. The errors in the theoretical values derive from the experimental errors in the (111) layer spacings.

Experimental (111) layer spacing (Å)	Theoretical $\bar{1}\bar{1}\bar{1}$ layer spacing (Å)			Experimental $\bar{1}\bar{1}\bar{1}$ spacing (Å)	$r_{\text{eff}}$ (Å) (site)
	atop	FCC hollow	HCP hollow		
Low-temperature phase					
0.90(10)	0.30(3)	1.85(3)	<b>1.08(3)</b>	} 1.00(10)	0.45 (HCP)
or 3.23(10) (0.90+2.33)	<b>1.08(3)</b>	0.30(3)	1.85(3)		1.80 (atop)
or 5.56(10) (0.90+4.66)	1.85(3)	<b>1.08(5)</b>	0.30(3)		(or 2.88 (sub)) 4.29 (FCC)
Room-temperature phase					
0.05(10)	0.02(3)	1.57(3)	<b>0.80(3)</b>	} 0.75(10)	0.22 (HCP)
or 2.38(10) (0.05+2.33)	<b>0.80(3)</b>	0.02(3)	1.57(3)		0.95 (atop)
or 4.71(10) (0.05+4.66)	1.57(3)	<b>0.80(5)</b>	0.02(3)		(or 2.29 (sub)) 3.56 (FCC)

Also shown in table 1 are the values of the adsorbate effective radius,  $r_{\text{eff}}$  implied by each of the possible sites (assuming that there are no changes in the substrate layer spacings induced by the adsorption). If we recall that the outer limits of reasonable values for  $r_{\text{eff}}$  are defined by the ionic and metallic radii for Rb (1.48 Å and 2.43 Å), it is clear from table 1 not only that the low-temperature atop site found earlier is confirmed (with a layer spacing of  $3.23 \pm 0.10$  Å—to be compared with our earlier determination of  $3.13 \pm 0.10$  Å—and an effective radius, 1.80 Å, close to the ionic value), but also that the room temperature phase can only reasonably be reconciled with the substitutional site (with a larger effective radius, 2.29 Å, closer to the metallic value). The overall similar pattern of behaviour between K and Rb adsorption indicated by the photoemission core level shift results [16] is therefore given quantitative confirmation. This structure is also in good agreement with that of the parallel LEED study [23]. Note that our NISXW data provides no direct information on the location of the substrate Al atoms; we determine the adsorbate atom sites relative to the extended substrate lattice. We are therefore unable to determine any adsorbate-induced changes in the outermost substrate layer spacing, or any possible 'rumpling' of these substrate layers; these parameters can be obtained from other methods, especially LEED.

Although these conclusions appear to be entirely satisfactory in terms of the consistent pattern of behaviour that emerges, one surprising feature of the parameter values involved in the fit to the room-temperature-phase data shown in figure 1(b) is the low value (0.6) of the coherent fraction for the (111) reflection. Measurements of several different room-temperature preparations gave values for this coherent fraction in the range 0.6–0.8; i.e. all significantly below unity. The complete set of coherent fraction values used in the fits of figure 1 were 1.0 for all Al absorption profiles, 1.0 and 0.5 for the (111) and  $\bar{1}\bar{1}\bar{1}$  Rb profiles for the low-temperature phase, and 0.6 and 1.0 for these same parameters for the room-temperature phase. Typical error estimates in fitting these coherent fractions are  $\pm 0.1$ . In the case of the low-temperature phase, we have noted in our earlier study [11, 12] that the  $\bar{1}\bar{1}\bar{1}$  reflection shows a low coherent fraction, and this can be reconciled with the large amplitude of thermal vibrations parallel to the surface that can be expected (and observed

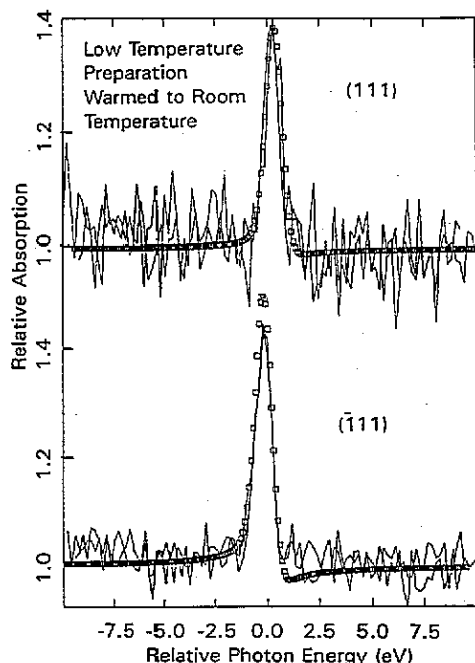
in other techniques—notably photoelectron diffraction [30–32], but also SEXAFS [33]) for an atop species.

The low (111) coherent fraction for the room temperature phase *could* be attributed to large amplitude vibrations perpendicular to the surface but there seems little reason to anticipate this effect; certainly we would expect the vibrations parallel to the surface to be much smaller for the substitutional site, but there is no obvious reason for very soft modes perpendicular to the surface. We note too that there is no significant difference between the values of this fitting parameter obtained from data recorded at low and room temperature, suggesting the disorder is not dynamic in origin; the same inference may be drawn from the scatter in coherent fraction values found in different preparations. An alternative explanation is that the true structure involves two or more different (111) layer spacings; we will return to this idea in the next section.

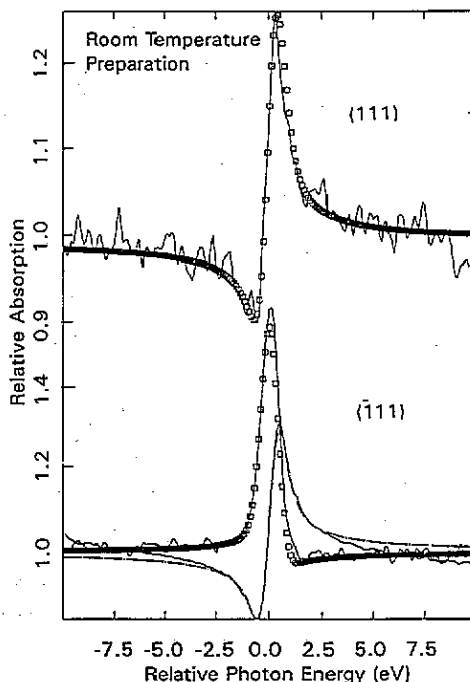
### 3.2. Transformations to the high temperature phase, and phase coexistence

We now summarize the results of the extensive measurements recorded from surfaces prepared at low temperature but subsequently subjected to various elevated-temperature heat treatments. In these experiments our original intention had simply been to produce the 'room-temperature phase' for study by the convenient device of briefly annealing a surface prepared at low temperature. Core-level photoemission studies of the change in Rb 4p lineshape induced by similar annealing indicate that the complete transformation of the surface from low-temperature to room-temperature phase can be achieved in probably no more than 1 min at a temperature of 300 K, and is 80% complete after 20 min at a temperature as low as 244 K [22]. Our NISXW measurements taken after briefly heating a cold-prepared sample to nominal temperatures in excess of 300 K for a few minutes, however, indicated very little change had occurred in the local structure of the adsorbed Rb. Of course, when heating a sample mounted on a liquid-nitrogen-cooled stage, there are significant temperature gradients in the area of the sample, so although care was taken to attach the thermocouple to a point that should monitor the true sample temperature, there is always the possibility that this is not the case. It is therefore certainly possible that the temperatures recorded in these experiments may differ from those recorded in similar annealing experiments by Andersen *et al* [22].

After many failures to observe any substantial change in NISXW lineshape in these experiments, we eventually ran a test of the effect of allowing the complete sample, cooling stage and manipulator system to warm up by removing the liquid nitrogen supply. After some 3–4 hours when all temperatures in the system were at nominal room temperature, new NISXW data were collected, and these measurements were repeated the following morning (some 12 h later). Auger electron spectra recorded after this extended anneal showed no contaminant peaks above the noise. Figure 2 shows the NISXW spectra measured in this experiment; there is no discernible difference between the spectra recorded after 3–4 h warming, and those recorded after a further 12 h anneal, and in both cases the overall line shapes are far more like those of the low-temperature phase than those of the room temperature-prepared phase when compared with figure 1. Interestingly, after this free warming process, measurements of the ( $\sqrt{3} \times \sqrt{3}$ ) LEED pattern indicated that the  $\frac{1}{3}$  order beams peaked in intensity at energies characteristic of the room-temperature phase, not the low temperature phase. Although no systematic observations of the LEED intensities were made in the short annealing experiments, at least one careful measurement of this kind after a succession of short anneals indicated  $\frac{1}{3}$  order beam intensity maxima consistent with a persistent low-temperature phase.



**Figure 2.** NISXW Al and Rb adsorption profiles taken at the (111) and ( $\bar{1}11$ ) reflections from a low-temperature-prepared  $\text{Al}(111)(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-Rb}$  structure subsequently allowed to warm to room temperature over a period of 3–4 h; a second set of spectra recorded 12 h later is overlaid. Theoretical fits based on a mixture of (70%) atop and (30%) substitutional adsorption sites are shown as described in the text.



**Figure 3.** NISXW Al and Rb adsorption profiles taken at the (111) and ( $\bar{1}11$ ) reflections from the room-temperature-prepared  $\text{Al}(111)(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-Rb}$  structure as shown in figure 1, but compared with theoretical fits based on a mixture of (20%) atop and (80%) substitutional adsorption sites as described in the text. For clarity, the (111) Al adsorption profile for the room-temperature-prepared phase is omitted from the figure.

Also shown in figure 2 are theoretical fits to these spectra. There are some changes in the detailed shape and amplitude, especially those of the (111) NISXW scan, relative to the low-temperature phase, and the fits are based on a model comprising a mixture of atop and substitutional adsorption sites at structural parameter values essentially the same as those listed in table 1 and found to fit the data of figure 1. In particular, the layer spacings and coherent fractions used for the low temperature phase are identical to those used to fit the profiles from this phase in figure 1, but some small change in the layer spacing for the room-temperature phase (to 2.30 Å) has been incorporated into the fits with a coherent fraction for both reflections of unity. This is consistent with the alternative two-site model interpretation of the room-temperature spectra of figure 1 described below. The fits shown in figure 2 are based on 70% of the Rb atoms in the (low-temperature) atop sites and 30% in the (high-temperature) substitutional sites. In this context we return to the possible interpretation of the low (111) Rb coherent fraction in the room-temperature-prepared  $\sqrt{3}$  phase in terms of mixed sites; in particular, we consider the possibility that some fraction of the Rb atoms even in this preparation occupies the (low-temperature) atop sites. Notice that the ( $\bar{1}11$ ) layer spacings of the two different structures are quite similar, so a mixture of these phases has relatively little effect on this lineshape; in particular, a modest concentration of atop-site occupation coexisting with the substitutional site can be expected to have only a



very modest effect in reducing the apparent coherent fraction for the  $(\bar{1}11)$  reflection. By contrast, the (111) atop site lineshape is qualitatively similar to the incoherent (reflectivity) lineshape component, so this same fraction of atop sites will lead to a substantial apparent drop in the apparent (111) coherent fraction. Confirmation of this argument is given in figure 3, which shows a fit of the room-temperature-prepared-phase NISXW (from figure 1) fitted to an 80% mixture of a substitutional site (at the slightly modified layer spacing of 2.30 Å) and 20% atop at a layer spacing of 3.23 Å; the coherent fractions of each component are the same as those used in the fits to the data collected in the free warming experiments shown in figure 2.

At this point we should also mention some experimental NISXW data recorded in the autumn of 1992 on an Rb adsorption phase prepared at room temperature with a coverage lower than that of the  $(\sqrt{3} \times \sqrt{3})$  phase; this surface showed the 'complex' LEED pattern described later in this section. Superficial inspection of these data indicated only atop site occupation, but more careful fitting of these data now reveals a mixture of 15% substitutional and 85% atop is consistent with the results. This result reinforces those of our original study of the Al(111)-Rb system [11, 12] in which a small number of room temperature preparations at arbitrary coverages gave similar NISXW profiles to the low-temperature preparations; it suggests that the reconstruction may be a special property of the  $(\sqrt{3} \times \sqrt{3})$  ordered phase.

In isolation, therefore, our own data can be interpreted consistently by a model in which even a room-temperature preparation of a nominal  $\frac{1}{3}$  ML phase of Rb on Al(111) leads to some fraction of the surface having atop Rb atoms, coexistent with the dominant substitutional-site occupation; for surface concentrations below 0.33 ML the occupation of the substitutional sites may be far lower. Moreover, the results imply that the thermal transformation of a low-temperature-prepared (nominal 0.33 ML coverage) phase is far from facile, and that at room temperature, at least, the transformation is not completed over a period of many hours. Our LEED observations appear to confirm the idea that the component of the surface that transforms to the substitutional site is the one that has good  $(\sqrt{3} \times \sqrt{3})$  long-range order; presumably the untransformed part has less good long-range order and thus contributes little to the LEED diffracted beam intensities. The fact that good LEED patterns can be obtained from only small parts of a surface, which are well ordered, is well known, but insofar as one can anticipate difficulty in effecting the structural phase transition, one might anticipate that large domains of long-range order would cause the greatest obstruction, because of the problem of disposing of the ejected surface Al atoms as Rb atoms move from atop to substitutional sites. On the other hand, theoretical calculations [15] suggest that one of the reasons for the preferred substitutional sites for K on Al(111) is the particularly low creation energy for surface vacancies in a  $(\sqrt{3} \times \sqrt{3})$  ordered phase, indicating that it is precisely the ordered parts of a transformed surface that do have the associated reconstruction. Thus one might argue that effecting the transition in domains of well ordered  $(\sqrt{3} \times \sqrt{3})$  phase in the atop state will have the greatest kinetic problems because of the difficulty of disposing of 0.33 ML of excess Al atoms within the domain, but if the transition does start to occur the energetics favour the transformation only when it does produce regions of  $(\sqrt{3} \times \sqrt{3})$  long-range order.

One further piece of relevant information concerning this question of local site transformations is the pattern of behaviour of the long-range order in the Al(111)/Rb system. In particular, although at low temperature a  $(2 \times 2)$  phase at a coverage of 0.25 ML precedes the 0.33 ML  $(\sqrt{3} \times \sqrt{3})$  phase, both of which involve atop site occupation [11, 12], at room temperature the  $(2 \times 2)$  phase is not seen. Instead, a rather complex LEED pattern is observed with rings of diffracted beams around the  $\frac{1}{3}$ -order positions, which Andersen *et al* [16] have identified as having a mesh described in the matrix notation as  $\begin{pmatrix} 1 & 1 \\ 5 & -6 \end{pmatrix}$  and

which they point out is most reasonably understood in terms of a coverage of 0.27 ML corresponding to three Rb atoms per unit surface mesh. A possible model for this structure which we can propose is shown in figure 4, and comprises strips of a local ( $\sqrt{3} \times \sqrt{3}$ ) phase separated by regular antiphase domain boundaries. The Rb atoms are shown in sites that may be regarded as either atop or substitutional (the plan view does not distinguish these sites). This simple model suggests that the favoured ( $\sqrt{3} \times \sqrt{3}$ ) phase is formed locally, rather than the larger average separation implied by the (2×2) phase at almost exactly the same average coverage. Of course, if the ( $\sqrt{3} \times \sqrt{3}$ ) phase is indeed the favoured state for the substitutional reconstruction, one might then suppose that these local ( $\sqrt{3} \times \sqrt{3}$ ) strips in this 'complex' phase are reconstructed. Indeed it is tempting to wonder whether the antiphase boundary regions in which the local Rb coverage is lower in the structure of figure 4 is where the excess Al atoms are deposited. Unfortunately, it is only possible to dispose of two, rather than the required three, Al atoms per surface unit mesh in this region if the Al atoms simply form an extra layer in the bulk Al structure; this modified version of the structure is also shown in figure 4. Unfortunately, this picture appears to be at variance with the experimental NISXW results reported above which point to a dominant atop-site occupation of a surface showing this LEED pattern (unless the long-range ordered component of the surface is again the minority phase).

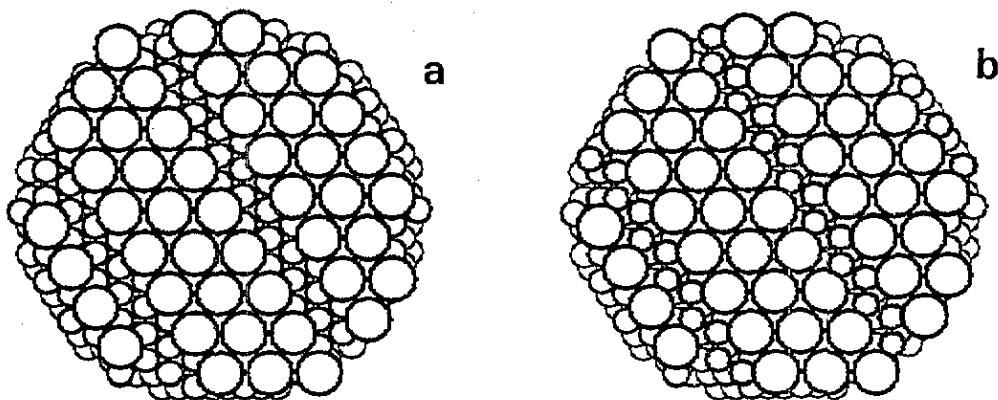


Figure 4. A schematic plan view of two possible models of the 0.27 ML, room temperature Rb overlayer phase on Al(111) described in the matrix notation as  $\begin{pmatrix} 1 & 1 \\ 5 & -6 \end{pmatrix}$ . The larger circles represent Rb atoms in either atop or substitutional sites, the smaller circles Al atoms. (a) shows an Rb overlayer structure only; (b) includes excess Al atoms (removed from the surface layer by Rb atom substitution), which occupy extra layer sites along the antiphase domain boundaries separating strips of local ( $\sqrt{3} \times \sqrt{3}$ ) R30° structure. Note that both structures contain three Rb atoms per surface unit mesh (coverage 0.27 ML) but in (b) there are only two excess Al atoms per unit mesh.

Of course, we know in general from STM studies of several 'missing-row' reconstructions of surfaces that the problem of disposing of ejected top layer substrate atoms is far less of a problem than was previously supposed, and that steps, for example, can act as sources or sinks of 'spare' atoms. In other cases, islands of one atomic thickness can form to 'dispose' of such atoms. On the other hand, our NISXW data for the Al(111)/Rb system do point to some problems in executing this thermally activated phase transition. One final factor in this case could also be the presence of steps. If the driving force for the reconstruction is an attempt to put the surface alkali atoms in more highly coordinated sites, atop Rb atoms

adjacent to step edges (but on the lower terrace) may be favoured relative to terrace sites, so that the generation of extra steps by the transformation of some parts of a surface could stabilize other parts to higher temperature. Clearly, the problem is complex, and our limited data are insufficient to go beyond this structured speculation.

Although the arguments presented above provide a consistent if incomplete picture of the relative stability of the two local Rb sites and the transformation to the lower-energy state, the results appear to be in conflict with the previously reported core level photoemission studies which indicate rapid and complete passage to the higher-temperature structure at temperatures well below room temperature [22]. There are basically two alternative possible interpretations of this conflict. Either there are key differences between the two experiments (e.g. sample surface perfection or exact coverage), or there is some ambiguity in the interpretation of one or both of the experiments. Experimental differences are difficult to resolve, although our free warming experiment excludes the possibility of gross error in sample temperature measurement. We have also observed the difficulty of transforming to the substitutional site in experiments conducted over a range of coverages and on at least two different samples; the similar behaviour of the two samples suggests that surface order could only be a factor if the transformation is only facile on especially perfect samples. The one remaining possibility is that the complete transformation only occurs on surfaces on which the coverage is almost exactly the ideal  $0.33 \text{ ML}$  of the  $(\sqrt{3} \times \sqrt{3})$  phase.

On the issue of interpretation, we have already discussed some ambiguities in the interpretation of our data; what is clear, however, is that our free warming experiments do not lead to a structure in which all Rb atoms adopt the substitutional sites found in the ordered room-temperature-prepared  $(\sqrt{3} \times \sqrt{3})$  phase found both in our NISXW measurements and in the parallel LEED study. The final possibility is that there is some ambiguity in the interpretation of the photoemission data. The published photoemission data following the phase transition are unfortunately too sparse to allow careful reanalysis; it is clear, however, that the exact core-level shifts seen in the adsorbate photoemission peaks depend on both the overall coverage and the local adsorption coordination, so it may be that a single core-level binding energy is not a unique fingerprint of a single structural model. Indeed, we note that the observed Rb 4p binding energies of the 'complex' phase are very similar to those of the low-temperature  $(\sqrt{3} \times \sqrt{3})$  phase [16], lending some support to the idea that it is only the room-temperature ordered  $(\sqrt{3} \times \sqrt{3})$  phase that is reconstructed.

#### 4. Conclusions

NISXW measurements of ordered  $\text{Al}(111)(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-Rb}$  formed at low temperature confirm the previous assignment of an atop adsorption site, but similar measurements of a phase having the same long-range order prepared at room temperature indicate that the majority of the Rb atoms, at least, occupies substitutional sites in the surface. The main parameters of these structures are given in table 1, although we should note that the mixed-site interpretation of the room-temperature phases (i.e. prepared at, or warmed to, room temperature) indicates an Rb-Al layer spacing of  $2.30 \text{ \AA}$  rather than the  $2.38 \text{ \AA}$  given in table 1 (which corresponds to the fit to the room-temperature-prepared phase based on a low coherent fraction and only the substitutional site). The effective radii of the Rb adsorbates in these two sites are approximately  $1.8 \text{ \AA}$  and  $2.2 \text{ \AA}$  respectively, and these may be compared with the ionic radius of  $1.48 \text{ \AA}$  and the metallic radius of  $2.43 \text{ \AA}$ . This result agrees well with an independent LEED study [23], and the behaviour is very similar to that found for the  $\text{Al}(111)(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-K}$  structures studied by LEED [15].

Attempts to study the transformation of the low temperature ( $\sqrt{3} \times \sqrt{3}$ ) phase to the higher-temperature state by heating to room temperature, however, indicate that this transition is not simple, although the part of the surface that does transform (approximately 30% in our case of a free warming to room temperature) has good ( $\sqrt{3} \times \sqrt{3}$ ) long-range order as witnessed by the LEED beam intensities, indicating that the atop atoms do not have such good long-range order. We also have evidence that even in a simple room temperature preparation, some fraction of the Rb atoms may occupy the atop sites characteristic of the low-temperature phase; in the case of a nominal 0.33 ML coverage phase (i.e. one showing a ( $\sqrt{3} \times \sqrt{3}$ ) LEED pattern), the apparent concentration of atop sites is low, but at lower coverages the atop site may remain the majority state.

We are not able to account fully for the apparent disagreement between these conclusions and those of a recent photoemission core level shift study [22]. Clearly further studies of the phase transition are warranted, but a microscopic method such as STM could prove especially revealing. Finally, we should remark on that the fact that although there is now evidence that Na, K and Rb all have some tendency to substitute the top-layer substrate atoms in Al(111), there is now increasing evidence that this occurs far more readily for Na (which even forms a double-layer alloy phase [13, 14]) than for Rb. In view of the very much larger physical size of the Rb atom, and the fact that even when it substitutes an Al atom, its centre lies a full Al substrate layer spacing above the surrounding Al atoms of the 'same' layer, this does not seem too surprising.

## Acknowledgments

The authors are pleased to acknowledge the support of the SERC in the form of SRS beamtime allocation, a research grant, a studentship for GS and a visiting fellowship for MK.

## References

- [1] Bonzel H P, Bradshaw A M and Ertl G (ed) 1989 *Physics and Chemistry of Alkali Adsorption* (Amsterdam: Elsevier)
- [2] Aruga T and Murata Y 1989 *Prog. Surf. Sci.* **31** 61
- [3] Ishida H and Terakura K 1988 *Phys. Rev. B* **38** 5752
- [4] Ishida H 1991 *Surf. Sci.* **242** 341
- [5] Riffe D M, Wertheim G K and Citrin P H 1990 *Phys. Rev. Lett.* **64** 571
- [6] Lambie G M, Brooks R S, King D A and Norman D 1988 *Phys. Rev. Lett.* **61** 1112
- [7] Benech G A and King D A 1992 *Chem. Phys. Lett.* **191** 315
- [8] King D A and Woodruff D P (ed) 1993 *Coadsorption, Promoters and Poisons (The Chemical Physics of Solid Surfaces 6)* (Amsterdam: Elsevier)
- [9] Schmalz A, Aminpirooz S, Becker L, Haase J, Neugebauer J, Scheffler M, Batchelor D R, Adams D L and Bogh E 1991 *Phys. Rev. Lett.* **67** 2163
- [10] Andersen J N, Qvarford M, Nyholm R, van Acker J F and Lundgren E 1992 *Phys. Rev. Lett.* **68** 94
- [11] Kerkar M, Fisher D, Woodruff D P, Jones R G, Diehl R D and Cowie B 1992 *Phys. Rev. Lett.* **68** 3204
- [12] Kerkar M, Fisher D, Woodruff D P, Jones R G, Diehl R D, McConville C F and Cowie B 1992 *J. Vac. Sci. Technol. A* **10** 2148
- [13] Kerkar M, Fisher D, Woodruff D P, Jones R G, Diehl R D and Cowie B 1992 *Surf. Sci.* **278** 246
- [14] Andersen J N, Lundgren E, Nyholm R and Qvarford M 1992 *Phys. Rev. B* **46** 12784
- [15] Stampf C, Scheffler M, Over H, Burchhardt J, Nielsen M, Adams D L and Moritz W 1992 *Phys. Rev. Lett.* **69** 1532
- [16] Andersen J N, Lundgren E, Nyholm R and Qvarford M 1993 *Surf. Sci.* **289** 307
- [17] Neugebauer J and Scheffler M 1993 *Phys. Rev. Lett.* **71** 577

- [18] MacLaren J M, Pendry J B, Rous P J, Saldin D K, Somorjai G A, Van Hove M A and Vvedensky D D 1987 *Surface Crystallographic Information Service: A Handbook of Surface Structures* (Dordrecht: Reidel)
- [19] Lindgren S A, Wallden L, Rundgren J, Westrin P and Neve J 1983 *Phys. Rev. B* **28** 6707
- [20] Fisher D, Chandavarkar S, Collins I R, Diehl R D, Kaukasoina P and Lindroos M 1992 *Phys. Rev. Lett.* **68** 2786
- [21] Over H, Bludau H, Skotte-Klein M, Ertl G, Moritz W and Campbell C T 1992 *Phys. Rev. B* **45** 8638
- [22] Andersen J N, Lundgren E and Nyholm R 1993 *MAX-LAB Activity Report 1992* p 50; and to be published
- [23] Adams D L private communications; Nielsen M, Burchhardt J, Adams D L, Lundgren E and Andersen J N to be published
- [24] Batterman B W 1964 *Phys. Rev. A* **133** 759
- [25] Woodruff D P, Seymour D L, McConville C F, Riley C E, Crapper M D, Prince N P and Jones R G 1987 *Phys. Rev. Lett.* **58** 1460
- [26] Woodruff D P, Seymour D L, McConville C F, Riley C E, Crapper M D, Prince N P and Jones R G 1988 *Surf. Sci.* **195** 237
- [27] MacDowell A A, Norman D, West J B, Campuzano J C and Jones R G 1986 *Nucl. Instrum. Methods A*, **246** 131
- [28] MacDowell A A, Norman D and West J B 1986 *Rev. Sci. Instrum.* **57** 2667
- [29] SAES Getters SpA, Milano, Italy
- [30] Fritzsche V, Schindler K-M, Gardner P, Bradshaw A M, Asensio M C and Woodruff D P 1992 *Surf. Sci.* **269/270** 35
- [31] Dippel R, Weiss K-U, Schindler K-M, Gardner P, Fritzsche V, Bradshaw A M, Asensio M C, Hu X-M, Woodruff D P and Gonzalez-Elise A R 1992 *Chem. Phys. Lett.* **199** 625
- [32] Davis R, Hu X-M, Woodruff D P, Weiss K-U, Dippel R, Schindler K-M, Hofmann Ph, Fritzsche V and Bradshaw A M 1994 *Surf. Sci.* at press
- [33] Adler D L, Collins I R, Liang X, Murray S, Leatherman G S, Ysuei K-D, Chandavarkar S, McGrath R, Diehl R D and Citrin P H to be published