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## Sodium-promoted oxidation of Al(111) studied by core-level photoemission spectroscopy

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**Abstract.** The influence of preadsorbed sodium on the early stages of oxidation of Al(111) has been investigated using synchrotron radiation photoemission measurements of the Al and Na 2p states. There is a strong promotion (by a factor of up to 100 or more) of the rate of oxygen dissociation and formation of the three-dimensional oxide induced by the presence of the sodium. At the highest Na coverage of 0.33 ML (associated with the Al(111) ( $\sqrt{3} \times \sqrt{3}$ )R30°–Na phase), the Al 2p chemically shifted states characteristic of the chemisorption precursor to oxidation seen on the Na-free surface are no longer observed. However, a state of intermediate chemical shift is seen in the Na 2p photoemission peak, at much lower oxygen exposures, and appears to be a characteristic of a new oxidation precursor.

### 1. Introduction

The influence of alkali metal adsorbates on the reactivity of surfaces is a subject that has received considerable attention in the last few years [1,2]. One reason for this is the relevance of the problem to the use of alkali salt promoters and modifiers in heterogeneous catalysis of a number of industrially important reactions. In addition, there has been some interest in the possibility of dry oxidation of semiconductor surfaces through the promotion of the surface oxidation by alkali additives, although the deleterious effect of the alkali metal atoms on the electrical properties of the material, and the difficulty of removing the alkali, may well prevent this interesting phenomenon from being exploited in practice. A small amount of work has also been performed on metal-adsorbate-promoted oxidation of metal surfaces, including the use of rare-earth additives.

A model system which might appear to be particularly simple is the effect of adsorbed sodium on the oxidation of aluminium. The interaction of aluminium surfaces with oxygen has been studied extensively [3], and the oxide films formed on aluminium are especially interesting because of their protective influence on the chemical activity and thus the corrosion of this important structural material. Of the three low-Miller-index faces of aluminium, only the (111) surface shows clear evidence of a chemisorbed phase as a precursor to the formation of a true (3D) oxide phase. The chemisorption phase does not have a different long-range periodicity to that of the substrate, but appears to saturate at a coverage of 1 ML in a (1×1) structure. A combination of low-energy electron diffraction (LEED) [7–13], surface extended x-ray absorption fine structure (SEXAFS) [14–16], and normal-incidence standing x-ray wavefield absorption (NISXW) [6] measurements have emerged with a consensus view concerning the structure of this phase, which involves O atoms in the FCC hollow sites (directly above Al atoms in the third layer) at an outermost O–Al layer spacing of 0.6–0.7 Å. The structure of the oxide phase that nucleates on the surface is,

however, rather less clear, although it seems that O atoms penetrate the surface, possibly leaving overlayer atoms in essentially the same sites as in the chemisorbed layer [6, 16].

A particularly effective 'fingerprint' of the chemisorption and oxidation states is offered by Al core-level spectroscopy performed with a reasonable degree of surface specificity and spectral resolution [17–19]. In particular, synchrotron radiation photoemission, using photons of approximately 100 eV energy, shows Al 2p emission with a range of different chemical shifts which characterize different states of the oxygen–surface interaction [19]. Recent O 1s x-ray photoelectron spectroscopy (XPS) [20] and scanning tunnelling microscopy (STM) [21] investigations have provided confirmation, and further details of, the description of this interaction which was deduced from the Al 2p photoemission data [19].

In this paper we present results of a study of the oxidation of Al(111) in the presence of adsorbed Na atoms, using the same method of synchrotron radiation core-level photoemission, in this case from both the Al 2p and the Na 2p states. We find clear evidence for a very pronounced enhancement of the rate of production of the surface oxide at the expense of the chemisorption phase, and attempt to identify the mechanism associated with this effect.

## 2. Experimental details

The experiments were conducted at the Science and Engineering Research Council's (SERC's) Daresbury Laboratory, taking light from Beamline 6.2 of the Synchrotron Radiation Source (SRS) which is fitted with a Miyake–West grazing-incidence plane grating monochromator [22]. This was operated to provide photons in the energy range 95 eV to 135 eV at a resolution of approximately 150 meV. Photoemission spectra were recorded using a Physical Electronics double-pass cylindrical mirror analyser (CMA) operated at pass energies of 5 eV and 10 eV. The CMA was mounted with its axis in the (horizontal) plane of the electron storage ring, and at 90° to the direction of the incident radiation; the sample was mounted at 45° to each of these directions. The combined energy resolution of the monochromator and analyser (at the lower pass energy) was approximately 180 meV.

The Al(111) sample was prepared by the usual combination of x-ray Laue orientation, spark machining, mechanical polishing and *in situ* cycles of argon-ion bombardment (around 2 keV for 30 minutes) and annealing (650 K for a similar time). A clean well-ordered surface was produced as judged by *in situ* Auger electron spectroscopy and LEED. Sodium was deposited from a well outgassed SAES getter source mounted approximately 5 cm from the sample. Deposition was effected at fixed heating currents (5–6 A) in the getter for varying periods of exposure to the sample, and the coverage was estimated from the relative Al and Na 2p core-level photoemission signals, taking as a calibration point a coverage of 0.33 ML for the phase corresponding to a well-ordered ( $\sqrt{3} \times \sqrt{3}$ )R30° ordered LEED pattern. Oxygen exposures were conducted by introducing oxygen gas into the chamber through a leak valve to pressures in the range  $1 \times 10^{-8}$  to  $2 \times 10^{-7}$  mbar depending on the size of exposure required. All sodium and oxygen exposures were conducted with the sample at room temperature.

## 3. Results and discussions

### 3.1. Oxidation of Al(111) and Al(111)( $\sqrt{3} \times \sqrt{3}$ )R30°–Na

Figure 1 shows a sequence of Al 2p photoemission spectra taken at a photon energy of 100 eV from a clean Al(111) surface following different oxygen exposures. The clean

surface shows the characteristic Al 2p spin-orbit split doublet, but the highest oxygen exposure of 1000 L shows a spectrum in which the largest feature is a broad peak in which the spin-orbit splitting is no longer resolved, and which is chemically shifted by approximately 2.6 eV relative to the metallic (clean surface) peaks; this feature has been widely attributed to the surface oxide. At intermediate exposures several other peaks having intermediate chemical shifts are observed. Previous measurements have shown that there are actually three intermediate states with chemical shifts of approximately 0.5, 1.0 and 1.5 eV [10]. Since these successive chemical shift differences are very similar to the spin-orbit splitting the  $2p_{1/2}$  feature of one state overlaps the  $2p_{3/2}$  peak of the next, leading to the impression that there may only be one or two intermediate states present. These three states have all been attributed to the chemisorption phase, and have been associated with surface Al atoms bonded to 1, 2 or 3 O atoms as the  $(1 \times 1)$  chemisorption structure builds up [19]. O 1s XPS [20] and STM data [21] appear to support this interpretation. We will refer to these three chemically shifted states as chemisorption states 1, 2 and 3. Note that although there is some sequential filling of these states as the chemisorption layer accumulates, it is also clear that some oxide nucleates at exposures much smaller than that needed to saturate the chemisorption phase. The XPS and STM results indicate the formation of saturated  $(1 \times 1)$  chemisorption phase islands on the surface rather than random filling of sites.

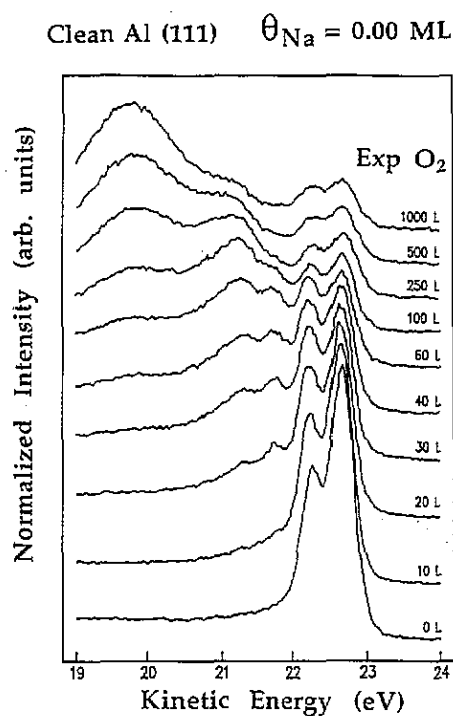


Figure 1. Core-level photoemission spectra in the region of the Al 2p peak, recorded using a photon energy of 100 eV, from Al(111) following different exposures to oxygen.

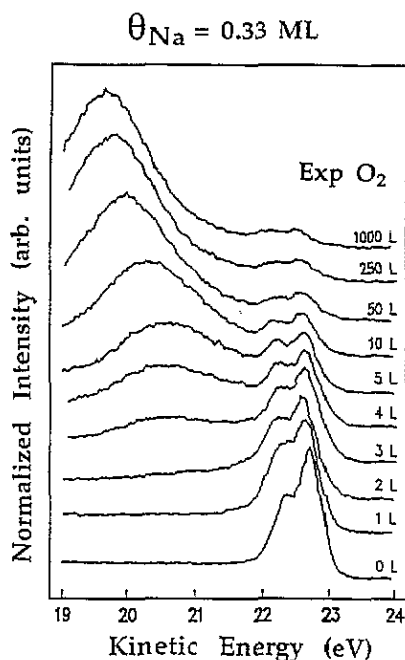


Figure 2. Core-level photoemission spectra in the region of the Al 2p peak, recorded using a photon energy of 100 eV, from Al(111)  $(\sqrt{3} \times \sqrt{3})R30^\circ\text{-Na}$  following different exposures to oxygen.

Contrasting with the clean surface oxidation data of figure 1, figure 2 shows a similar sequence of Al 2p spectra taken during the oxidation of an Al(111)( $\sqrt{3} \times \sqrt{3}$ )R30°-Na surface. These data appear to show no evidence for the formation of any chemisorbed O state, in that there are no intermediate Al 2p chemically shifted peaks, and the broad peak associated with the oxide appears at very low exposure. For example, the relative magnitude of the oxide and metallic peaks after 10 L exposure in figure 2 is similar to that seen in figure 1 after 1000 L, indicating an enhancement in the average oxidation rate of about a factor of 100.

The fact that there is no simple Al-related chemisorption state in this case is not entirely surprising. The 0.33 ML Na coverage believed to be associated with this phase corresponds to a saturation of the surface layer, in that increasing the Na coverage forms a ( $2 \times 2$ ) phase which appears to comprise a double layer of a mixed Al-Na alloy [23, 24]. Moreover, SEXAFS [25] and NISXW [24, 26] measurements both indicate that the ( $\sqrt{3} \times \sqrt{3}$ )R30° phase involves Na substitution of top-layer Al atoms such that each surface Al atom is adjacent to three Na atoms (see figure 3). This means that any simple adsorbed (overlayer) oxygen atom adopting a surface site coordination to three surface metal atoms would have two Al neighbours and one Na neighbour, clearly a very different situation from that of the clean surface. On the other hand, the data of figure 2 indicate that no intermediate state exists, but oxidation occurs essentially immediately. Moreover, the data of figure 2 indicate that in the presence of the 0.33 ML of surface Na, the aluminium oxidizes well below the surface. It is clear from figure 2 that after 1000 L of oxygen exposure, the total area under the broad oxide peak is considerably greater than that under the metallic state peaks seen in the clean surface spectrum. The spectra are normalized to constant incident photon flux, so this effect of a net increase in the total photoemission signal must be attributed to the growth of multilayers of oxide in which the inelastic scattering mean free path is substantially larger than in the metal [27, 28]. This signal enhancement is therefore a signature of multilayer oxidation.

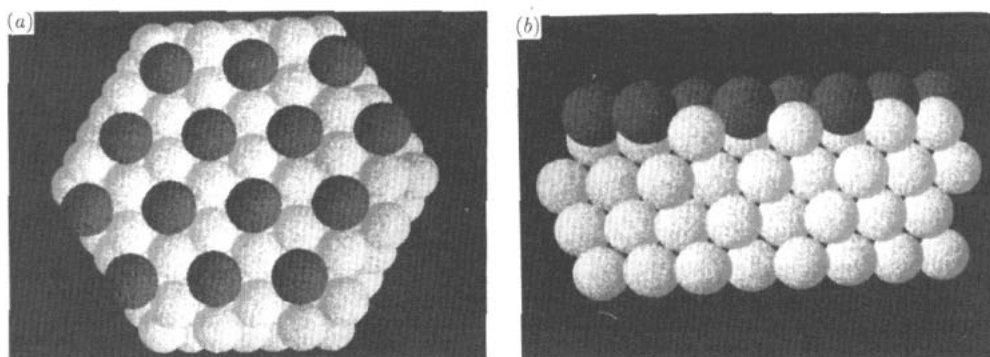


Figure 3. Plan and sectional views of a model of the Al(111)( $\sqrt{3} \times \sqrt{3}$ )R30°-Na structure.

By contrast to this absence of intermediate state in the Al 2p spectra, a similar set of Na 2p photoemission spectra recorded from the Al(111)( $\sqrt{3} \times \sqrt{3}$ )R30°-Na surface following oxygen exposures does show evidence of an intermediate oxidation state as seen in figure 4. For example, the Na 2p spectra taken after 4 or 5 L exposure in figure 4 show that very little intensity remains at the binding energy associated with the original unexposed surface, but the flat top of the spectrum makes it clear that in addition to the fully oxidized state (see

the 50 L exposure spectrum) with a chemical shift of approximately 1.9 eV, an intermediate peak is present with a shift of approximately 0.7 eV. Simple curve fitting confirms that at least one intermediate state is present in these spectra. Comparison of the spectra of figures 2 and 4 at the same oxygen exposure suggests that the intermediate state seen in the Na 2p spectrum passes through its maximum intensity in the phase prior to the acceleration of the true oxidation, in a similar way (but at much lower exposures) to the behaviour of the chemisorption states in the unpromoted Al(111) surface spectra of figure 1. This suggests that a chemisorption precursor may still exist, but the local bonding (or at least the local charge transfer) is between the oxygen and the surface Na atoms rather than between the oxygen and surface Al atoms.

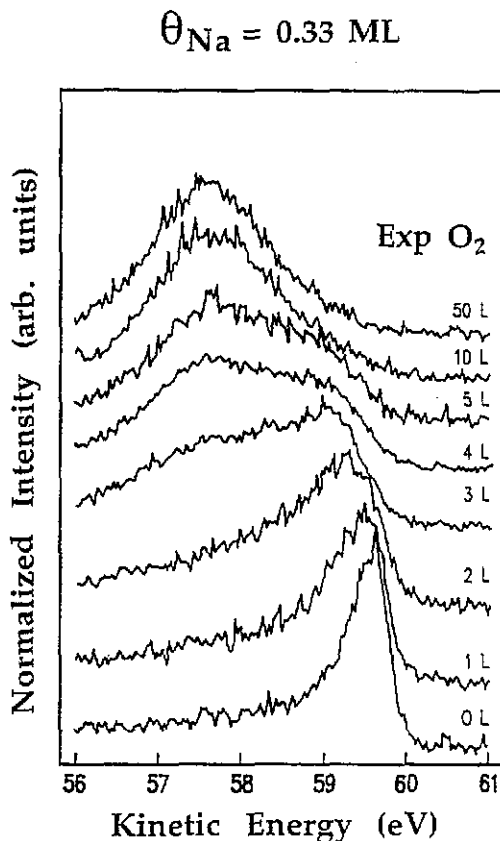


Figure 4. Core-level photoemission spectra in the region of the Na 2p peak, recorded using a photon energy of 95 eV, from Al(111)( $\sqrt{3} \times \sqrt{3}$ )R30°-Na following different exposures to oxygen.

### 3.2. Oxidation of Al(111) with intermediate coverages of Na, and general discussion

Some further information on the interaction of the surface Na and O on the Al(111) surface may be obtained from the results of similar experiments at lower Na coverages. Al 2p spectra obtained from similar experiments conducted on oxygen exposure of Al(111) predosed with coverages of approximately 0.05 ML and 0.20 ML Na are shown in figure 5. Evidently in these experiments there is some presence of the Al chemisorption states seen in the unpromoted surface. This is particularly clear in the case of a 0.05 ML predose of Na (figure 5(a)) in which essentially all the features of the Al/O spectra of figure 1 may be

seen, although after a 0.20 ML predose of Na, only the chemisorption state 3 is clearly resolved. Notice, however, that even at the lowest coverage of Na there is significant enhancement of the rate of uptake of oxygen; figure 6 highlights this point by comparing the Al 2p spectra for zero, 0.05, 0.20 and 0.33 ML Na predose (taken from figures 1, 5 and 2) after exposure to 10 L of oxygen. In the case of the intermediate Na predose levels, there is evidence of an enhancement of the uptake in the chemisorption states as well as in the oxide state. Inspection of the Na 2p spectrum during these same experiments involving oxygen exposure of the 0.05 ML and 0.20 ML Na predosed surfaces reveals spectra very similar to those shown in figure 4. Figure 7 shows the results for the 0.20 ML Na predose; the signal-to-noise ratio for the 0.05 ML Na predose experiment is very poor (and is not shown here), but it is still clear that there is a region of intermediate oxygen exposure in which the Na 2p spectrum broadens and flattens due to the coexistence of the initial, final and intermediate chemically shifted states. We also find the shape of the Na 2p peak is dependent only on the oxygen exposure, and is independent of the Na coverage (including the 0.05 ML coverage state).

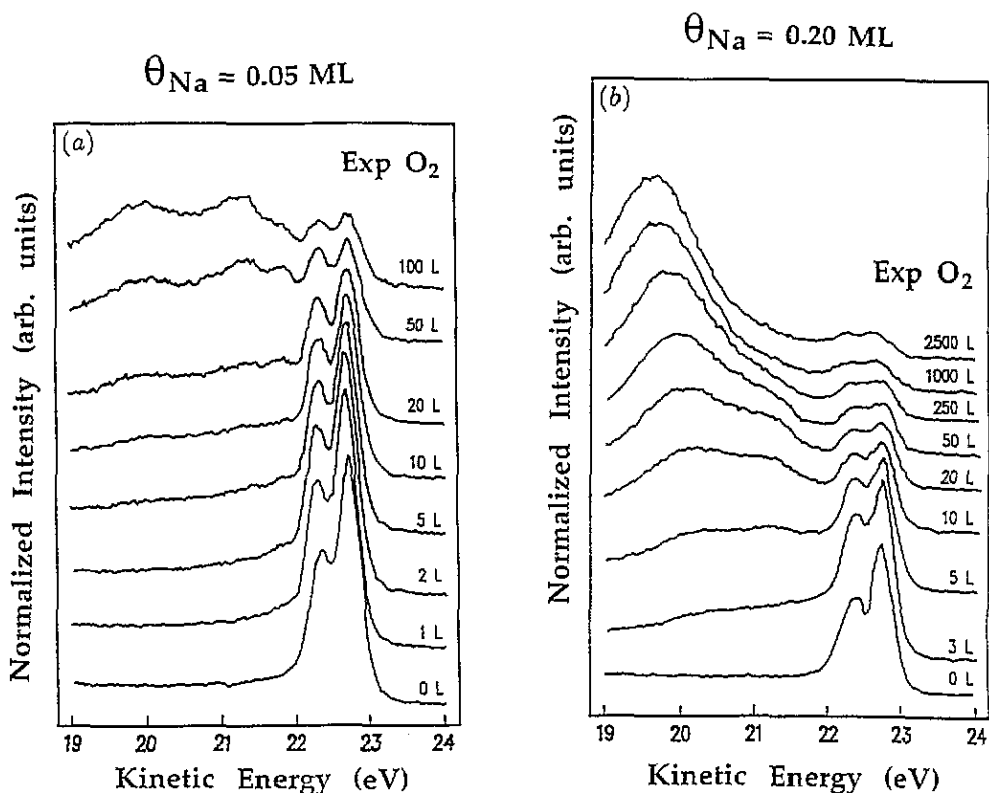


Figure 5. Core-level photoemission spectra in the region of the Al 2p peak, recorded using a photon energy of 100 eV, from Al(111) predosed with (a) 0.05 ML Na and (b) 0.20 ML Na, following different exposures to oxygen.

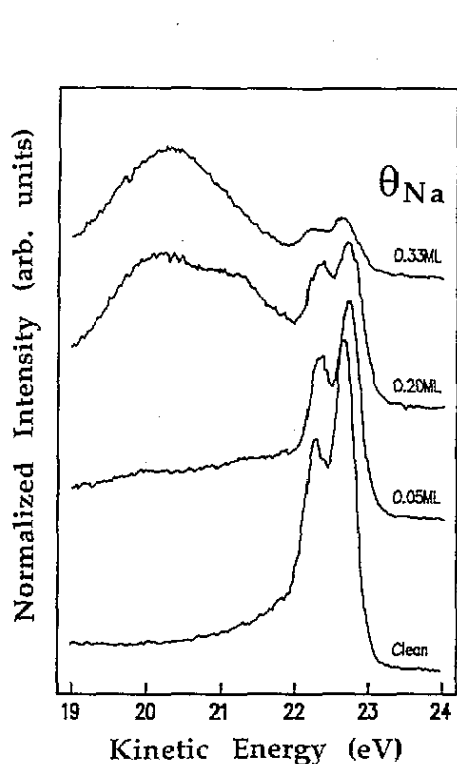


Figure 6. Comparison of core-level photoemission spectra in the region of the Al 2p peak, recorded at a photon energy of 100 eV, from Al(111) with different pre-exposures of Na followed by a 10 L exposure to oxygen.

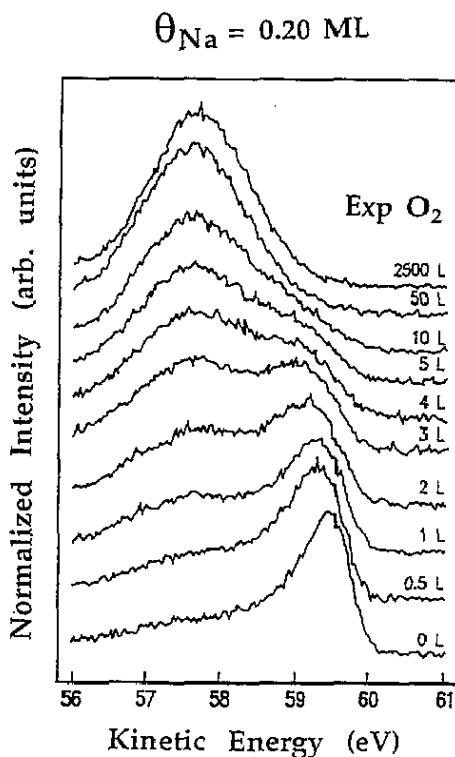


Figure 7. Core-level photoemission spectra in the region of the Na 2p peak, recorded using a photon energy of 95 eV, from Al(111) predosed with 0.2 ML Na, following different exposures to oxygen.

There are two different issues involved in the discussion of mechanisms. Firstly, we would like to understand the oxygen dissociation process itself which is clearly strongly promoted by the presence of the surface Na atoms. Secondly, we need to understand the route to the formation of the 3D oxide; in particular, is there a chemisorbed precursor and, if so, what is its nature? Core-level photoemission cannot give any direct answers to the first question in that we only study the equilibrium state of the surface *after* the dissociation has taken place. On the other hand, the photoemission does appear to give some information on the second question in that the Na 2p photoemission does provide evidence for an oxidation precursor, but one in which the oxygen is more strongly interacting with the surface Na atoms than those of the Al substrate.

One difficulty in interpreting the experiments involving sub-saturation Na predoses, is that we have no explicit information on the spatial distribution of the Na atoms on the surface. In particular, is there islanding of the adsorbates, or not? Generally, we might expect that at low coverages of alkali metal atoms, the large local dipoles at these sites would repel, so the atoms would be approximately equally spaced on the surface. On the other hand, LEED from low coverages of Na on Al(111) at low temperature (100 K)



indicate that clustering can occur at low coverage [29]; no similar evidence exists at room temperature, however, and it does seem that the local adsorption site differs for preparations made at these two temperatures. Even at low coverages, Na atoms substitute top-layer Al atoms at room temperature, but this intermixing is kinetically hindered at 100 K. In the absence of specific information on the Na atom distribution, however, we can consider the consequences of the various possibilities. Imagine, first the rather simple situation in which the Na atoms on the surface at low coverage form islands of the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase (although this is actually contrary to the evidence that no such LEED pattern is seen). In this case the surface could simply behave like a simple mixture of clean regions and ordered Na phase regions. This picture would account largely for the spectra of figure 6 as far as true oxidation is concerned (i.e. the rate of production of the Al 2p oxide peak), but would not predict any enhancement of the rate of uptake of the Al chemisorption states on the bare surface. A minor addition to this model, including the possible role of the edge of the Na phase islands in 'feeding' dissociated oxygen atoms onto the bare Al patches, would overcome this problem. On the other hand, if we imagine the Na atoms to be more widely dispersed (consistent with the lack of ordered LEED structures), then a key question is the apparent range of the influence of the surface Na atoms, and if the effect is non-local, of the mechanism of promotion. For example, if the effect were to be related to the average surface potential change induced by the adsorbed Na, there may be a critical coverage before any significant effect is seen. This is definitely inconsistent with the data. In fact, the enhancement in the rate of oxygen uptake, at least initially, appears to be approximately proportional to the Na coverage, consistent with a local effect. Moreover, the evidence from the Na 2p data support the idea that initial accommodation of oxygen atoms onto the surface is at the Na sites, and the fact that the rate of filling of the Na 2p chemically shifted states is independent of Na coverage indicates that the oxygen dissociation occurs by direct impact of oxygen atoms from the gas phase on the Na sites, indicating a truly local process. Indeed if we assume that the 'oxidic' chemical shift of the Na 2p is coupled to the appearance of the Al 2p oxidic state (perhaps in a mixed oxide), then it appears that the Na sites are probably the nucleation sites for the true 3D oxidation of the Al(111) surface.

Perhaps even more complex than the question of the nature and mechanism of the promotion of the oxidation is the nature of the oxide phases themselves. Notice, for example, that the exact chemical shift associated with the Al 2p level in the 'oxide' state is not unique, but varies by a few tenths of an eV depending on the extent of oxidation, and perhaps on the presence or otherwise of the Na. In fact we have noted previously that if the Al(111) surface interacts with water rather than oxygen, no intermediate chemisorbed oxygen states are seen in the Al 2p spectra, and similar shifts to those seen here occur in the oxide chemical shift. In the case of water adsorption, however, a further possible complication is the possible role of OH species. In general the broad core-level photoemission spectra do not really give us sufficient information to make a real evaluation of this problem. On the other hand, one additional experiment can provide some limited information.

In figure 8 are shown Na 2p spectra recorded after exposing to oxygen a sodium film (deposited on the Al(111) substrate) which is estimated to be 10–20 layers thick. Two important points emerge from these data. Firstly, there is no evidence in these spectra for a simple single-oxygen chemisorption state of intermediate chemical shift. Rather the spectra appear to comprise two features; the metallic state and an oxide state, although again the broad oxide feature shifts by a few tenths of an eV (notice, too, the large enhancement in total photoemitted signal characteristic of multilayer oxidation and an increased mean free path). On the other hand, the chemical shift seen in the oxide state in these spectra is only about 1.5 eV, significantly less than that seen in the sub-monolayer Na film spectra

## Multi-layers of Na

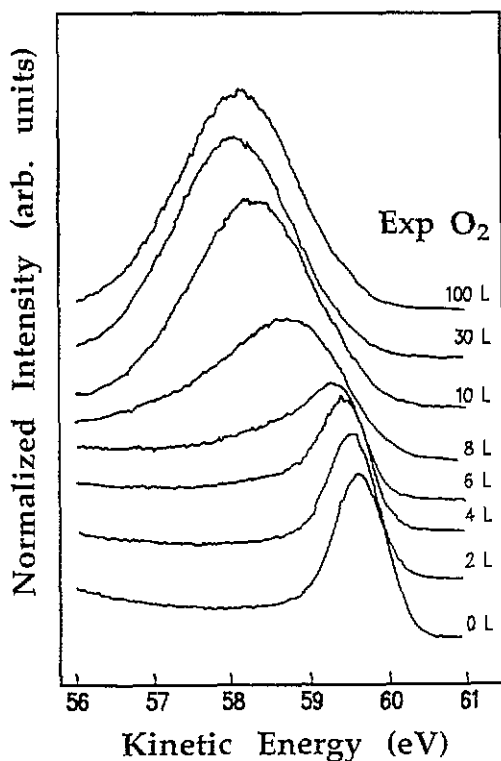


Figure 8. Core-level photoemission spectra in the region of the Na 2p peak, recorded using a photon energy of 95 eV, from a thick film of Na (on Al(111)) following different exposures to oxygen.

of figures 4 and 7. This certainly suggests that either the Na oxide state on the promoted surface comprises a very thin layer which is strongly coupled to the aluminium oxide, or that the oxide formed really does involve both Al and Na atoms as suggested above.

#### 4. Conclusions

Core-level photoemission measurements of the influence of sub-monolayer coverages of Na on Al(111) on the uptake of oxygen by this surface show a strong promotion of both oxygen dissociation and the formation of 3D surface oxide. Al 2p spectra indicate the loss of intermediate chemically shifted states characteristic of a chemisorbed precursor to oxidation; Na 2p spectra, on the other hand, indicate that such a state is still present but the bonding of the surface oxygen is now strongly localized to the Na atoms. It appears that the role of the Na atoms in the promotion is local, and the acceleration oxidation appears to be a direct consequence of the more rapid filling of the precursor state by enhanced oxygen dissociation rates. There is some evidence that the final oxide state involves both Na and Al metal atoms intermixed.

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