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Current progress in understanding alkali metal adsorption on metal surfaces

REVIEW ARTICLE

Current progress in understanding alkali metal adsorption on metal surfaces

R D Diehl† and R McGrath‡

† Department of Physics, Penn State University, University Park, PA 16802, USA
‡ Interdisciplinary Research Centre in Surface Science and Department of Physics, Liverpool University, Liverpool L69 3BX, UK

Abstract. This paper reviews the current situation in the understanding of alkali adsorption on metal surfaces, with particular emphasis on recent structural discoveries. We start by describing the classical 'Langmuir–Gurney' model for alkali adsorption and the challenges to it which arose in the mid 1980s. We then describe the results of structural studies from the early 1990s which provide a whole new set of phenomena to be explicable within the framework of a new paradigm, and discuss whether calculations based on density-functional theory constitute such a paradigm.

1. Introduction

In his famous book *The Structure of Scientific Revolutions* [1], T S Kuhn argued that scientific progress takes place not through incremental advances but through revolutionary breakthroughs. This involves the replacement of one scientific *paradigm* (an accepted scientific theory within which new experimental results are explicable) by a new one. The revolution is considered complete when the new paradigm has been developed so that results once considered anomalous have become expected.

In the field of alkali metal adsorption such a revolution is under way. The existing paradigm is based on the Langmuir–Gurney (LG) model for alkali adsorption. This model was developed in the early 1930s and was essentially the accepted model until the 1980s. It predicted a partial transfer of charge from the alkali metal adatoms to the substrate at very low alkali coverages, and the subsequent depolarization of these adatoms due to their mutual interactions as the coverage is increased. This model was in qualitative agreement with measured work function curves for alkali metal adsorption, and it was widely accepted as describing the essential components of alkali metal chemisorption.

There are several structural implications of this model. First, the alkali adatoms are expected to adsorb in high-coordination sites at least at low coverages because ionic bonds are not directional and generally maximize coordination. Covalent bonds on the other hand are directional bonds, and while the adsorption site would normally be expected to be determined by the details of the chemisorption bond, it is worth noting that generally chemisorbed atoms have been found to bond in high-coordination sites on metal surfaces [2]. Second, since the model predicts a change from an ionic bond at low coverage to a non-ionic bond at monolayer saturation, it would be expected, based on known bondlengths of alkalis in compounds and bulk, that the chemisorption bondlength of the alkali should

increase as the coverage is increased from zero to a saturated monolayer, perhaps by as much as 1 Å [3]. These implications however have been shown to be incorrect in experimental studies carried out during the past 5 years, raising serious doubts about the validity of the LG model.

In this review we first summarize the main issues in the debate over the LG model, and then discuss the new structural observations which have emerged in the past few years.

2. The L–G model

Langmuir and his co-workers developed a simple model based on donation of the alkali valence s electron to the substrate, on the basis of work function and electron emission experiments [4–9]. The idea was clearly stated in his 1932 paper [8]:

'In the case of cesium films we have very direct proof that the adatoms act as dipoles. Adsorption of alkali metal atoms occurs strongly only when the electron affinity of the adsorbent metal exceeds the ionizing potential of the alkali, so the act of adsorption probably involves a transfer of the valence electron to the underlying metal. The force holding the atom may thus be regarded as the attraction of the cesium ion and the negative charge induced in the metallic surface (image force).'

This was based on the fact that the ionization potential for potassium, rubidium and caesium is lower than the work function of tungsten (ϕ_w), so that upon adsorption the valence electron was transferred. This model was extended and given a quantum-mechanical context by R W Gurney in his 1935 paper entitled 'Theory of electrical double layers in adsorbed films' [10]. This work was motivated by experimental observations of barium, calcium and strontium adsorbed on tungsten. These adsorbates behave similarly to the alkalis, but their ionization potentials are larger than ϕ_w. According to Langmuir's criterion, they should not give up their electrons to the metal.

In the Gurney picture the valence s orbital of the alkali atom is lifetime broadened and lowered in energy upon interaction with the substrate, resulting in a partial electron transfer to the substrate and a partially ionic state for the alkali at low coverage (see figure 1). At higher coverages the net charge transfer per adatom decreases due to mutual depolarization of the alkali dipoles and it was proposed that the overlayer becomes metallic and the chemisorption bond ceases to be ionic. Gurney did not discuss the bonding as 'ionic', 'covalent' or 'metallic'; indeed these labels probably did not gain wide usage until the work of Pauling on electronegativity [11]. It is also clear that Gurney envisioned partial rather than total charge transfer:

'An isolated atomic particle in vacuum must be exactly electrically neutral, or else must bear a charge $\pm ne$ where n is an integer. This is not true of an atom forming part of a polar molecule. And . . . there is no reason why this should be true of atoms adsorbed onto a metal surface.'

2.1. Challenges to the LG model

The LG model was later updated by other workers [12–14] in more rigorous theoretical treatments which predicted partial occupancy of this s-level resonance even for a single adatom, but was not seriously challenged until the mid-1980s. In 1983, a theoretical study was performed using self-consistent density-functional theory for a c(2 × 2) 1/2 monolayer of Cs in W [15]. These results were interpreted as showing that the Cs 's' valence electrons are 'polarized' toward the surface, and the Cs-induced changes in charge density are localized outside the surface W atoms. In other words, this study suggested that the LG concept of charge
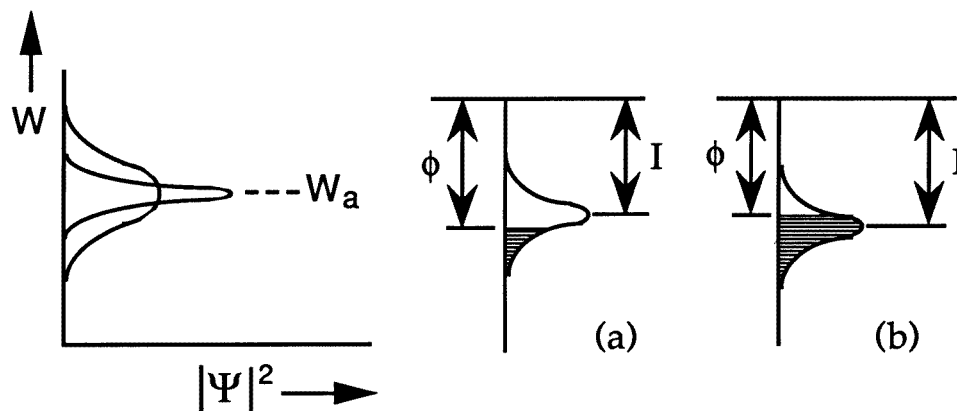
Figure 1. Left, broadening of an energy level as the adsorbed atom approaches the metal surface. Right, representation of the filling of an atomic bond up to the Fermi level (a) for an element of low ionization potential (alkali) and (b) for an element of higher ionization potential. (Figure reproduced from [10].)

transfer from the alkali to the substrate might not be valid. This study covered only the high-coverage regime however, where the LG model implies minimal charge transfer in any case. Nevertheless, some experimental papers also appeared around this time which provided puzzling results: metastable deexcitation spectroscopy (MDS) results [16] for K/Cu(110) suggested that the decrease in ϕ with increasing alkali coverage might not be directly associated with the K 4s resonance occupation, and core-level photoemission of Cs on W(100) [17] did not find the coverage-dependent shifts of the Cs 5p level expected for the LG model. In spite of these early indications that the LG model might not completely describe alkali metal adsorption, in 1989 it was still the basis for understanding alkali metal adsorption [18].

More serious questions of the LG model were prompted by the theoretical work of Ishida and coworkers [19–25] and the core-level photoemission work of Wertheim and coworkers [26]. The calculations for alkalis on jellium and Al surfaces indicated that for alkali coverages down to $\theta = 0.2$ (corresponding to an alkali coverage of $\sim$10%) the adatom region is essentially neutral, and that the dipole moment has a component due to a bond charge (hybridization of atom 's' orbitals with metal p_z orbitals) in addition to the image-charge-type charge transfer implied by the LG model. In this work the decrease of the dipole moment at higher coverage is interpreted as being due to orbital overlap [24] rather than depolarization. Wertheim *et al* [26] used these results to interpret core-level photoemission results for Na, K and Cs adsorption on W(100). Very small alkali-induced surface core-level shifts of the W 4f peaks were found (+5 to −28 meV) in contrast to a large shift to higher binding energy upon O adsorption (+170 meV). The authors cited this as indicative of minimal charge transfer from the alkali. Their interpretation of the results was not uncontentious; other authors subsequently suggested different possible reasons for the lack of a surface core-level shift which were in line with the LG model [27, 28]. Wertheim and co-workers however dismissed the criticism of their interpretation of their work [29–31] and later presented further photoemission results, which they again interpreted in the Ishida framework [30, 31].

At this point a theoretical paper was published by Scheffler and co-workers using a self-consistent Green function method to examine the bonding of Na on Al(100) [32]. This

method allows examination of the bonding at low coverages and differed from most of Ishida's work in that a real substrate was used rather than 'jellium'. They concluded that the adsorbed alkali atom was indeed partially ionized, implying a charge transfer to the metal. The point was reinforced by the close similarity between the charge density contours of a partially ionized Na atom adsorbed on the surface and those of a point charge placed above the surface, showing that alkali orbitals are not playing a significant role in bonding. They also noted that a covalent contribution is present though small. These studies were extended to the case of an isolated adsorbate on Al(111) [33]. Again they concluded that charge transfer takes place and that while the concept of an ionic bond is useful in describing the bonding, the quantitative measurement or definition of charge transfer is ambiguous. They argued that this is due to the fact that the charge transfer is followed by screening, and screening charge is located in front of the metal. Thus the inspection of charge density difference plots does not reveal the origin of charge density differences.

3. New structural results at variance with LG and its perceived implications

While much of the work pertaining directly to the debate has centred on experimental and theoretical studies of electronic structure, several structural studies have attempted to address this issue, either directly or indirectly. In this section we describe the new structural results which have appeared since the early 1990s and how they reflect on the LG model.

3.1. Chemisorption bondlength

As the bondlength in ionic alkali compounds is substantially less than that for covalent or metallic compounds, it was expected to provide an indication of the type of bonding in these systems [3, 11]. The first study to address this possibility was a surface extended x-ray absorption fine-structure (SEXAFS) study of Cs/Ag(111) in 1986 [34, 35] which determined that the bondlength increases by 0.3 Å as the coverage is increased from 0.5 to one saturated layers. Therefore this study supported the notion that there is a change in the character of the chemisorption bond from ionic to something else as the coverage increases.

Later studies, however, did not observe such changes. Chemisorption bondlengths have now been measured as a function of coverage for several systems, as shown in table 1. Several measurements were made of the perpendicular overlayer–substrate spacing rather than the chemisorption bondlength. For example, the perpendicular overlayer–substrate spacing ($d_\perp$) for K/Ni(111) was measured using a specular low-energy electron diffraction (LEED) analysis and was found to be constant over the the coverage range from 0.13 to 0.275 at 2.7 ± 0.1 Å [36]. A later LEED study for Cs/Ru(0001) by Over and coworkers [37] showed that such studies could be misleading since they observed a 0.27 Å bondlength change when the site changed, but that the change in perpendicular spacing was negligible. This change in bondlength was tantalizingly similar to that observed for Cs/Ag(111), but, since it occured at a relatively high coverage, it was interpreted to be due to a coordination effect on the bond, and not a fundamental change in the nature of the bond. Therefore it became clear that any measurement of the chemisorption bondlength must also include the adsorption site.

Later studies included a SEXAFS study of Na/Al(111) which found that the site for Na at room temperature was the substitutional site at coverages of 0.16 and 0.33 and that the bondlength did not change [38]. A normal incidence standing x-ray wavefield (NISXW) study of the Rb/Al(111) system found an atop adsorption site for three coverages in the range 0.12 to 0.33, at 3.13 ± 0.10 Å [39], and a constant chemisorption bondlength. A

Table 1. Coverage dependence of chemisorption bondlengths. $\Delta\theta$ is the coverage range over which measurements were taken, $\Delta\theta/\theta_{\text{sat}}$ is this coverage range relative to the saturation coverage. Δb is the change in chemisorption bondlength in ångströms.

System	Method	$\Delta\theta$	$\Delta\theta/\theta_{\text{sat}}$	Δb	Reference
Na/Al(111)	SEXAFS	0.16–0.33	0.32–0.66	0 ± 0.03	[38]
K/Al(111)	PED	0.05–0.40	0.11–0.89	0.17 ± 0.12	[46]
Rb/Al(111)	NISXW	0.12–0.33	0.36–1.0	0 ± 0.1	[39, 62]
Na, K/Al(111)	DFT		0.14–1.00	< 0.1	[74]
Na/Al(100)	DFT		0.12–1.00	$< 0.1(d_\perp)$	[75]
K/Ni(111)	LEED	0.13–0.275	0.42–0.89	$0 \pm 0.1(d_\perp)$	[36]
K/Ni(100)	DLEED	0.08–0.50	0.16–1.00	-0.075 ± 0.03	[40]
K/Rh(111)	LEED	0.25–0.33	N/A	0 ± 0.05	[44]
Rb/Rh(111)	LEED	0.25–0.33	0.76–1.00	0 ± 0.05	[44]
Cs/Rh(111)	LEED	0.25–0.33	0.76–1.00	0.30 ± 0.05	[44]
Na/Ru(0001)	LEED	0.25–0.33	0.48–0.63	0 ± 0.04	[41]
K/Ru(0001)	LEED	0.25–0.33	0.76–1.00	0.04 ± 0.05	[42]
Rb/Ru(0001)	LEED	0.25–0.33	0.76–1.00	0 ± 0.05	[43]
Cs/Ru(0001)	LEED	0.25–0.33	0.76–1.00	0.27 ± 0.08	[37]
K/Ag(111)	LEED	0.11–0.33	0.28–0.85	0.02 ± 0.03	[45]
Rb/Ag(111)	LEED	0.11–0.33	0.31–0.92	-0.02 ± 0.03	[45]
Cs/Ag(111)	LEED	0.11–0.33	0.33–1.00	-0.03 ± 0.04	[45]
Cs/Ag(111)	SEXAFS	0.15–0.30	0.5–1.00	0.30 ± 0.03	[34, 35]

diffuse LEED study of K/Ni(100) also determined that both the adsorption site and the K–Ni bondlength remained essentially constant in the coverage range from 0.08 to 0.50 [40]. No significant change in bondlength was observed for Na [41] , K [42] or Rb [43] on Ru(0001) between the p(2 × 2) and ($\sqrt{3} \times \sqrt{3}$)R30° coverages where the sites change but their coordination with substrate atoms does not. On Rh(111) similar results were reported, where the bondlength was found to change for the case of Cs where the coordination changes, but not for Na, K or Rb [44]. Finally, a similar situation has been measured for K, Rb and Cs on Ag(111), where the site changes from fcc to hcp in the coverage range 0.11–0.33, but, again, no significant change was observed in the chemisorption bondlength [45]. The results of this last study conflict with the earlier SEXAFS study of Cs/Ag(111) and suggest that the low-coverage measurement in that experiment was in error, probably due to surface contamination. Now the only study where the site stays the same (atop) and which indicates an increase in bondlength (0.17 Å) is the recent photoelectron diffraction (PED) study of K/Al(111) [46], which has not yet been corroborated.

At this point there is no conclusive evidence for a change in bondlength as a function of coverage where the alkali atom has been shown to retain the same coordination. An increase in the bondlength would have been taken to be consistent with the LG model. However while the absence of such an increase is contrary to what is expected in the LG model, it should not be taken as proof that the LG model is incorrect. After all, all of the available information suggests that there *is* a large rearrangement of the charge as the coverage is increased in these systems. For instance, the dynamic dipole moment decreases rapidly with coverage [47–49], large shifts are observed in the surface valence levels [50] and calculations also indicate a large redistribution of charge as the coverage changes [51]. What is surprising is that these large changes in the electronic configuration at the surface are *not* accompanied by a change in the chemisorption bondlength, so, while the measurements of chemisorption bondlengths do not disprove the LG model, they do

disprove the expectation that a large change in the bond should result in a change in the bondlength. What we have learned is that our intuition based on our knowledge of bulk compounds and molecules does not necessarily extend to adsorption systems.

3.2. Anomalous adsorption sites

The preferential occupation of high-coordination sites by alkalis on metal surfaces was a natural expectation within the LG model. High-coordination sites are consistent with ionic bonding, and so would certainly be expected at least at low coverages in the LG model. In addition, it generally has been observed that hollow sites are occupied as part of metal film growth processes [52], and that high-coordination adsorption bonds are the rule in atomic adsorption on metal surfaces [2, 53]. However, a dynamical LEED study of Cs/Cu(111) in 1983 indicated that in the p(2 × 2) structure Cs occupies the low-coordination top site [54]. While there was no public discussion of this unusual and unexpected result, privately it was largely dismissed mainly because it seemed so improbable. A secondary reason may have been that, since dynamical LEED analyses require model calculations and fitting of experimental and theoretical curves, it is difficult for someone who is not a LEED practitioner to evaluate the validity of the result, thereby making the conclusion less convincing. Also, this particular LEED analysis was somewhat unconventional in that it used metric distances to compare spectra instead of more widely used reliability factors, which made comparison with other studies more difficult. By modern standards, the database used in this experiment was rather small, and, in fact, the Cs–Cu bondlength determined in this study is very short, probably too short by at least 0.2 Å based on the results of later studies [55]. Nevertheless, there have been many more reports of top-site structures since 1992, and this particular adsorption site was corroborated in 1994 [56].

Now that top-site adsorption can be considered to be a common occurrence in alkali metal adsorption, the question is why. So far, top-site adsorption has only been observed on close-packed surfaces, suggesting that a relatively smooth surface is a requirement for occupation of the top site. The known adsorption sites for alkali metals adsorbed on close-packed surfaces are shown in table 2. Note that there are several systems for which the adsorption site changes when the symmetry of the overlayer structure changes as the coverage increases. A change in adsorption site was first observed for Cs/Ru(0001), which changes from top-site adsorption in the p(2 × 2) structure to hcp-site adsorption in the $(\sqrt{3} \times \sqrt{3})R30°$ structure [37]. A reason suggested for this change in site was that these sites appear to maximize the screening of adatoms from each other by the substrate. This seemed plausible, since in each of these structures there is a substrate atom located between each two adsorbate atoms, as shown in figure 2. However, there are other systems for which this is not true. For example, Rb/Al(111) occupies the top site in both the p(2 × 2) and $(\sqrt{3} \times \sqrt{3})R30°$ structures. Also, there are several systems in which the adsorption site is a hollow for p(2 × 2) structures and several for which the site is top for the $(\sqrt{3} \times \sqrt{3})R30°$ structure.

The substrate screening idea did however seem to be consistent with the observation that top-site structures are accompanied by substrate rumpling [55]. The effect of this rumpling is to push the substrate atom which is directly beneath the adatom down (inward) relative to the other substrate atoms, thereby allowing the adatom to push deeper into the surface. This rumpling then allows the substrate to be more effective at screening adjacent adatoms. Indeed, it was shown in density-functional theory (DFT) calculations for K/Al(111) [57–59] that the rumpling was a necessary part of the top-site structure, i.e., without the rumpling, the lowest-energy adsorption geometry has occupation of hollow sites. It would then be
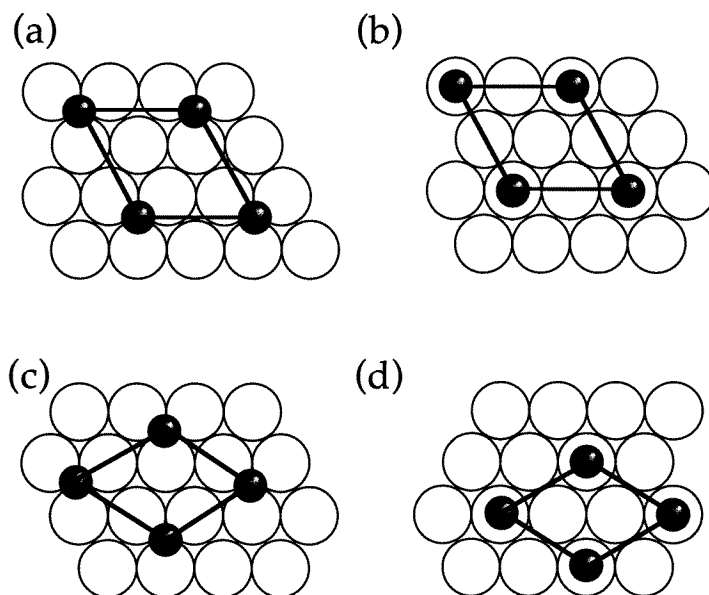
Figure 2. The p(2 × 2) structure for (a) hollow- and (b) top-site geometries, and the ($\sqrt{3} \times \sqrt{3}$)R30° structure for (c) hollow- and (d) top-site geometries.

Table 2. Adsorption sites for alkalis on close-packed substrates.

System	p(3 × 3)	p(2 × 2)	($\sqrt{3} \times \sqrt{3}$)R30°	Bulk modulus	Reference
Cs/Al(111)			top	0.722	[78]
Rb/Al(111)		top	top		[62]
K/Al(111)			top		[57]
Cs/Ag(111)	fcc	fcc	hcp	1.007	[45]
Rb/Ag(111)	fcc	fcc	hcp		[45]
K/Ag(111)	fcc	fcc	hcp		[45]
Cs/Cu(111)		top		1.37	[54]
Rb/Cu(111)		top			[79]
K/Cu(111)		top			[80]
K/Ni(111)		top		1.86	[81]
Cs/Rh(111)		top	hcp	2.70	[44]
Rb/Rh(111)		bridge	hcp		[44]
K/Rh(111)		hcp	hcp		[44]
Na/Rh(111)			hcp		[44]
Cs/Ru(0001)		top	hcp	3.21	[37]
Rb/Ru(0001)		fcc	hcp		[43]
K/Ru(0001)		fcc	hcp		[42]
Na/Ru(0001)		fcc	hcp		[41]
Li/Ru(0001)			hcp		[82]

expected that at very low coverages, where the adatoms are spaced far apart, screening will be less important and therefore the adsorption site should be the hollow. The DFT calculations for K/Al(111) indicate that this should happen [60]. However, the only three studies which have been carried out so far to test this idea, including an experiment on

K/Al(111), have found that the adatoms occupy the top site down to coverages as low as 0.05 [39, 46, 61, 62]. This lack of observation of a crossover from top to hollow sites as the coverage is reduced suggests either that the crossover occurs at a lower coverage than those so far measured or that substrate screening of the adatoms is not the dominant factor in determining top-site adsorption. Since for K/Al(111) at 0.05 coverage the adatoms are already about 13 Å apart, the latter explanation seems more likely.

The effect of rumpling, of course, may be more than just to provide increased screening of the adatoms. Indeed, significant rumpling is observed even in the low-coverage p(3 × 3) structures of K, Rb and Cs on Ag(111) [45] where the adatoms are about 9 Å apart. In such cases, the main role of the rumpling may be to increase the coordination of the adatoms. This hypothesis is consistent with all of the rumpling geometries which have been determined so far, for both top- and hollow-site adsorption [55], and it is still consistent with notion that rumpling is necessary for top-site adsorption to occur. Therefore, one might expect that top-site geometries will be more common on substrates which are more deformable, i.e. those which have lower bulk moduli. While it does seem to be true that top sites are less common on substrates which are stiffer, they are not necessarily observed on substrates which are softer, as indicated by bulk moduli in table 2. Ag(111) in particular seems to provide ample evidence to counter this hypothesis. Therefore at this time we have no simple rule which we can use to predict whether top-site adsorption will occur in any particular system, except to say that top-site adsorption only occurs on close-packed substrates, and that it is more likely for larger adatoms (relative to the substrate spacing).

Although screening of the adatoms by the substrate seems to be a minor consideration at least at low coverages, the effect of coordination does seem to be important, and not just in the top-site structures. This can clearly be seen in the sites and the nature of the rumpling which has been observed for the p(2 × 2) and ($\sqrt{3} \times \sqrt{3}$)R30° structures. For hollow-site adsorption, only the hcp site has been observed in the ($\sqrt{3} \times \sqrt{3}$)R30° geometry, and, except in one case, only the fcc site has been observed in the p(2 × 2) geometry. At first glance there is little to distinguish the two sites. The main difference between the hcp site and the fcc site is whether or not a second-layer substrate atom is present beneath the adatom, and therefore the hcp site may be considered to have a somewhat higher coordination in the absence of other effects. However, the substrate rumpling accompanying these structures also seems to be important, as described below.

Consider first the ($\sqrt{3} \times \sqrt{3}$)R30° structure shown in figure 2(c). For hollow-site adsorption, no rumpling is allowed by symmetry in the top substrate layer, since in this layer all atoms are equivalent with respect to adatoms in either fcc or hcp sites. The preference for the hcp site on the flat substrate already suggests that the presence of the second-layer substrate atom beneath the adatom increases the bonding of the adatom. Rumpling *is* allowed, however, in the second substrate layer, but only for an adatom in the hcp site and not in the fcc site. Therefore, for any rumpling to occur in the top two layers, the adsorption site must be hcp. Now we note that when rumpling has been observed in these systems that the effect of this rumple is to move the second-layer substrate atom which is directly beneath the adatom toward the adatom, i.e. it further increases the coordination of the adatom. So far this rumpling has only been observed for alkalis on Ag(111) [45, 63], which is a particularly soft substrate, and even there its magnitude is comparable to the precision of the measurement.

In the p(2 × 2) structure, shown in figure 2(a), rumpling of the top layer is allowed by symmetry for both fcc and hcp sites. For this structure, all but one of the observed systems listed in table 2 in which the adatom occupies hollow sites has been found to have an fcc site geometry. The rumpling has been measured in most of these systems and the amplitudes

of most observations so far are around 0.1 Å. The geometry of this rumpling is shown in figure 3, and the main effect of it is to push the adatom deeper into the surface than it would be in the absence of rumpling. Therefore this rumple also increases the coordination of the adatom by allowing it to move closer to other substrate atoms. This type of rumple could conceivably occur for hcp site adsorption as well, and in fact is observed for the hcp site geometry found for K/Rh(111) [44]. Why the fcc site is generally preferred over the hcp site for the p(2 × 2) structure is not completely clear, but it may be related to the ease with which the substrate can rumple. Since there is no second-layer atom beneath the fcc site, it is conceivable that a rumpling which pushes the top-layer substrate atoms into the second layer is more easily accomplished.
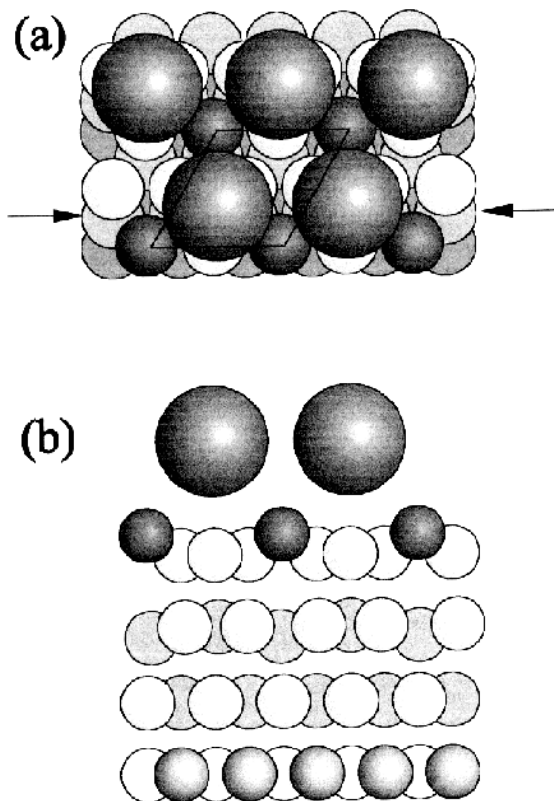

Figure 3. The geometry of the rumpled p(2 × 2) fcc site. (a) top view, (b) side view.

Returning to the question of top sites, it is natural to ask why top-site structures should occur at all if coordination is so important. The answer to this apparently lies in the chemisorption bondlength (also see subsection 3.1). The chemisorption bondlengths for alkali adsorption have been found to depend more on their coordination to the substrate than on any other factor. In order to compare the chemisorption bondlengths for different adsorption systems, it is useful to adjust them for the different alkali and substrate atom sizes by subtracting the ionic radius of the alkali and the metallic radius of the substrate atom. Figure 4 shows these 'excess radii' as a function of the adsorption site coordination for all of the systems studied so far. Clearly the trend is toward higher effective radii for adsorption in higher-coordination sites. On average, there is an increase of about 0.3 Å
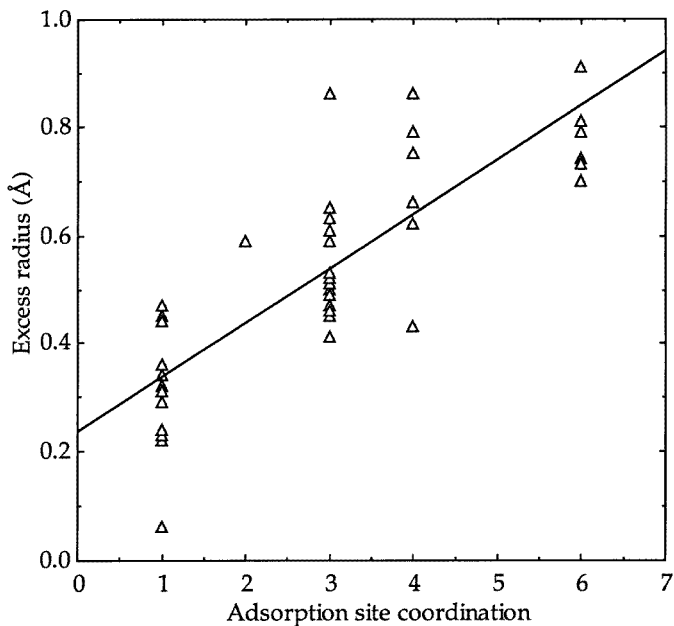
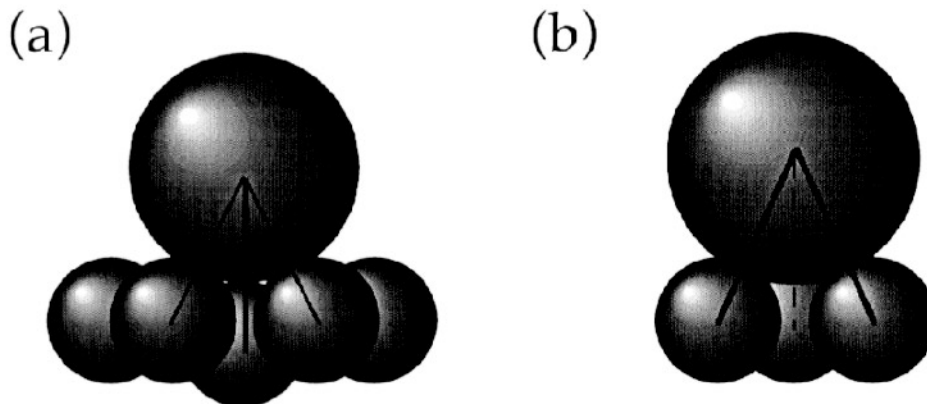**Figure 4.** Effective radius as a function of adsorption site.

Figure 5. A schematic diagram of the increase in chemisorption bondlength in going from the top to the hollow site. (a) shows top-site adsorption. The chemisorption bondlength is shorter and the substrate atom directly beneath the adatom is pushed down slightly, which helps to shorten the distance between the adatom and the six next-nearest substrate neighbours (4 shown). (b) shows hollow site adsorption. Here, the chemisorption bondlength is longer.

in the chemisorption bondlength as the site changes from top to hollow. This situation is shown schematically in figure 5. While the coordination is higher for the hollow site, the alkali adatom is not as close to the substrate atoms as it is in the top site. So an alkali adatom can increase its bonding in two ways: it can increase its coordination at the expense of the bondlength, or it can decrease its bondlength at the expense of the coordination. The energy difference between the two situations is clearly very small in some cases, e.g.

Table 3. Alkali adsorption systems which undergo condensation, along with the coverages at which they condense, the structure they condense into and the temperature. 'HOC' denotes a higher-order commensurate structure.

System	Coverage	Structure	Temp.	NN (Å)	Ref.
Na/Al(111)	0.15	'3 × 3' HOC	LT	~ 4.3	[83]
Na/Al(111)	0.06	$(\sqrt{3} \times \sqrt{3})\text{R}30°$	RT	4.96	[84]
Na/Al(111)	0.15	$(\sqrt{3} \times \sqrt{3})\text{R}30°$	RT	4.96	[83]
K/Al(111)	0.1	$(\sqrt{3} \times \sqrt{3})\text{R}30°$	LT, RT	4.96	[83]
Rb/Al(111)	0.08	p(2 × 2)	LT	5.73	[83]
Rb/Al(111)	0.1	$\begin{pmatrix} 1 & 1 \\ 5 & -6 \end{pmatrix}$HOC	RT	5.5	[83]
Na/Al(100)	0.25	c(2 × 2)	RT	4.05	[85]
Na/Al(100)	0.2	c(2 × 2)	LT	4.05	[86]
Li/Be(0001)	0.20	$(\sqrt{3} \times \sqrt{3})\text{R}30°$	RT	3.97	[87]
Na/Cu(111)	0.18	(3 × 3)HOC	LT	6.01	[88]
Li/Cu(100)	0.25	c(2 × 2)	LT	3.61	[89]
K/Cu(100)	0.18	liquid	RT	5.6	[70]
K/C(0001)	0.02	p(2 × 2)	LT	4.92	[90]
Rb/C(0001)	0.02	p(2 × 2)	LT	4.92	[90]
K/Ag(100)	0.08	c(2 × 2)	RT	4.09	[91]

the DFT calculations for K/Al(111) indicate that the energy difference is less than 50 meV [51]. The reason this situation occurs for adsorbed alkalis and not other adsorbates [64] is apparently due to the exceedingly small variation of the lateral alkali–substrate potential for the larger alkalis on close-packed surfaces. We note here that there have also been reports of top sites and possible site-switching for Xe on close-packed metal surfaces [65, 66]. In these cases again, the lateral variation of the adsorption potential is very small.

The main thing we have learned from these studies is that the energy differences between the various adsorption sites can be exceedingly small for alkali adsorbates, and that subtleties such as substrate rumpling, bondlengths and coordination are important in determining the equilibrium configuration. There is no sure way to predict the adsorption site for any given system, and some sites such as the bridge site found for Rb/Rh(111) [44] are still a complete mystery. The small lateral energy variation can be attributed to the very loosely bound valence electron on the alkali which results both in large adatom sizes relative to the substrate period and in an easily deformed (relative to atomic) surface charge distribution.

3.3. Overlayer condensation

A corollary of the LG model is that adsorbate–adsorbate interactions should be repulsive over a wide range of adsorbate coverages. Even though depolarization begins to occur at a low coverage, the dipole moments of the adatoms are predicted to remain significant even close to monolayer coverage. Repulsive behaviour is indeed observed for many systems with temperature–coverage phase diagrams [55] as evidence. For certain alkali–substrate combinations, however, the alkali overlayers undergo a condensation transition at a relatively low coverage instead of compressing uniformly as the coverage is increased. This condensation transition is intriguing because it resembles a nonmetal to metal transition such as those observed in other metal adsorption systems [67, 68]. The structural result of this condensation is the formation of 2D islands of alkali metal, presumably in equilibrium with a 2D vapour phase. In all cases but one, these islands are solid at room temperature, and

Table 4. Alkali metal adsorption systems where it has been shown using a quantitative technique that a substitutional or alloy structure is formed after dosing at or annealing to room temperature. The temperature quoted is the dosing or annealing temperature; often measurements are taken at considerably lower temperatures. The bondlength quoted is the chemisorption bondlength. N is the coordination number of the alkali adatom. A coordination number denoted by * indicates that, due to surface reconstruction, an unambiguous assignment cannot be made.

System	Θ_{alk}	Structure	Temp.	Site	Method	Bondlength	N	Ref.
Li/Al(111)	0.33	$(\sqrt{3} \times \sqrt{3})R30°$	300	subst.	LEED	2.95	6	[92]
Na/Al(111)	0.33	$(\sqrt{3} \times \sqrt{3})R30°$	300	subst.	SEXAFS, LEED, XSW	3.31	6	[38, 93, 94]
Na/Al(111)	0.5	(2×2)	300	binary alloy	LEED, SEXAFS, DFT	N/A	6	[95, 96]
K/Al(111)	0.33	$(\sqrt{3} \times \sqrt{3})R30°$	90	top	LEED	3.23	1	[57, 59]
	0.33	$(\sqrt{3} \times \sqrt{3})R30°$	300	subst.	LEED	3.58	6	[57, 59]
Rb/Al(111)	0.33	$(\sqrt{3} \times \sqrt{3})R30°$	≲170	top	LEED, XSW	3.13–3.36	1	[62, 97, 98]
	0.33	$(\sqrt{3} \times \sqrt{3})R30°$	300	subst.	LEED, XSW	3.72–3.74	6	[97, 98]
Na + (K, Rb, Cs)/ Al(111)	0.25 +0.25	(2×2)	300	ternary alloy	LEED			[71]
Na/Al(100)	0.5	$c(2 \times 2)$	< 140	hollow	SEXAFS, LEED, DFT	3.20–3.27	4	[85, 99]
	0.5	$c(2 \times 2)$	300	subst./ alloy/ mixture	SEXAFS, DFT, LEED, PED	2.94–3.19	4	[60, 75, 85, 99, 100]
Li/Cu(111)	0.75	(2×2)	300	subst./ hollow	LEED	2.62–3.02	*	[101]
Li/Cu(100)	0.555	(3×3)-5Li	300	subst./ mixed	LEED	N/A	*	[102]
Li/Cu(100)	0.625	(4×4)	300	subst./ other	LEED	N/A	*	[103]

their melting has not been studied. The alkali adsorption systems for which condensation has been observed are shown in table 3. This table neglects any condensation phenomena which might be associated with large reconstructions such as those which occur on fcc (110) surfaces, because of lack of detailed characterization.

The condensation of Na on Al(111) has been studied theoretically [60, 69]. This DFT study indicates that at low coverage the adsorbate–substrate interaction dominates the overlayer, while at higher coverages the attractive, metallic adsorbate–adsorbate bonds are more important and cause the condensation of the overlayer [60, 69]. The reason that condensation occurs for some alkali overlayers and not others is apparently a result of this balance between the adsorbate–adsorbate and adsorbate–substrate interactions. The stronger dipole moments of the heavier alkali atoms upon adsorption and their lower cohesive energies presumably are related to the fact that they have less of a tendency to condense, compared to the lighter ones.

In all of the cases where condensation has been observed, alkali metals condense into commensurate or higher-order commensurate phases, suggesting that the extra energy gained by forming a commensurate structure may tip the balance in favour of condensation. This energy must be quite large in the case of alkalis on Al(111) at room temperature where the site is substitutional (see 3.4). (The case of K/Cu(100) [70], where K has been observed to condense into a liquid phase at 330 K, appears to be quite different from the other systems and deserves further study.)
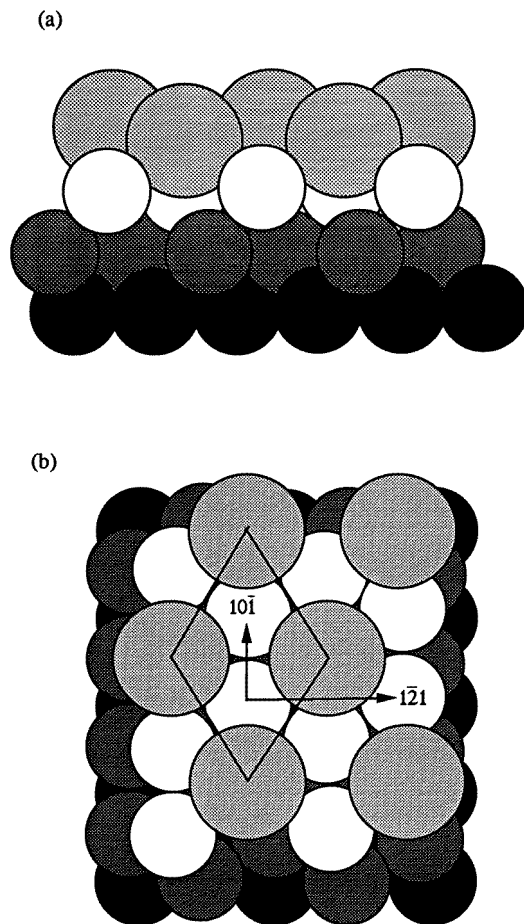
(a)

(b)

Figure 6. The atomic geometry of the substitutional site for Al(111)–($\sqrt{3} \times \sqrt{3}$)R30°–alkali (Li, Na, K, Rb) after [57]. Alkali atoms are shown as larger pale grey circles. (a) A side view of the (111) surface on a (10$\bar{1}$) plane. (b) A top view.

3.4. Intermixing

A recently discovered phenomenon which is outside the LG framework for adsorption is the intermixing of alkali metal atoms with Al and of Li with Cu surfaces at room temperature. (We do not discuss the alkali-induced missing row reconstructions of fcc(110) surfaces where the alkali atoms occupy the troughs on the surface [55], as the alkali atoms tend to be mobile within the troughs and thus do not have a definite adsorption site.)

In the case of Al, the alkali atoms either replace some of the Al atoms on the surface to adsorb in substitutional sites, or penetrate beneath the top Al layer to form what have been termed 'surface binary alloys'. Additionally, a recent report shows that if Na is coadsorbed on Al(111) with other alkalis, a surface ternary alloy can be formed [71]. This is contrary to expectations based on either the conventional ideas of alkali adsorption, where adsorbate–adsorbate repulsion dominates over adsorbate–substrate interaction, or on the fact that no bulk alloys exist between the alkalis (with the exception of Li) and Al or Cu surfaces [72, 73].
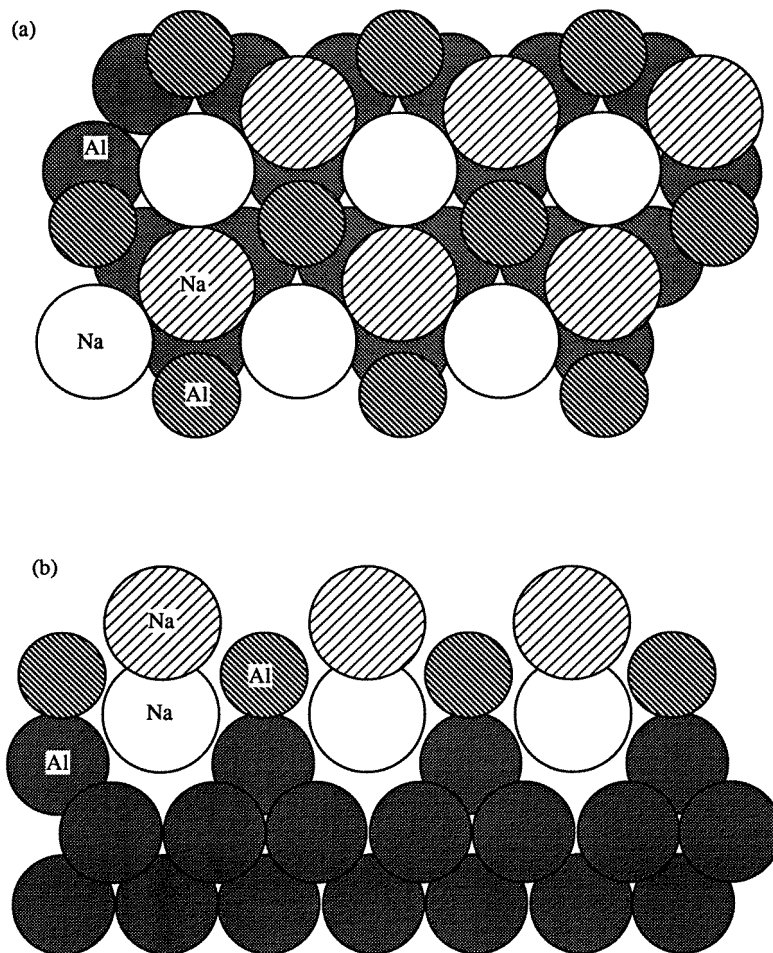
Figure 7. A model of the Al(111)–(2 × 2)–Na structure determined by LEED [96]. The top four layers, each of (2 × 2) periodicity, consist an Na–Al–Na sandwich on a reconstructed Al layer with a (2 × 2) vacancy structure. The Na atoms in the lower layer of the sandwich are located in substituional sites in the reconstructed layer. Al atoms in the sandwich layer and Na atoms in the upper layer of the sandwich are located in hcp and fcc sites, respectively, on the reconstructed layer. (a) A top view. (b) A side view.

Systems where this phenomenon have been observed are listed in table 4. Li, Na, K and Rb all form the same alloy structure on Al(111) at 0.33 coverage. Adsorption at low temperature gives various structures (a higher-order commensurate structure for Na; hollow-site ($\sqrt{3} \times \sqrt{3}$)R30° structures for K and Rb). Upon annealing to 300 K an irreversible transition takes place where the systems forms or retains the ($\sqrt{3} \times \sqrt{3}$)R30° periodicity with adatoms now in substitutional sites. This substitutional structure is shown in figure 6. The same structures can also be formed by dosing at room temperature. There is a large increase in co-ordination with coverage.

For higher coverages of Na (0.5) on both Al(111) and Al(100), a more complex situation pertains where the Na atoms penetrate underneath the top layer Al to form what has been termed a surface binary alloy, which has (2 × 2) symmetry in both cases (figure 7). There

is some disagreement between techniques as to the details of the Na/Al(100) case. For $\theta_{Na} = 0.25$ coadsorption with K, Rb or Cs ($\phi_{alk} = 0.25$), surface ternary alloy structures have been found, each with (2×2) periodicity, consisting of a (K, Rb, Cs)–Al–Na sandwich on a reconstructed Al layer having (2×2) vacancy structure [71]. The lower layer of the sandwich always contains Na, irrespective of the adsorption sequence. Finally, substitutional sites have also been observed for Li adsorbing on Cu(111) and Cu(100) surfaces at room temperature. For $\phi > 0.5$ sequences of structures form as a function of coverage, and the structures formed are characterized by a mixture of substitutional and other adsorption sites.

The formation of the substitutional and alloy structures has been addressed using first-principles DFT calculations by the group of Scheffler [69, 74, 75]. The calculations show that the process occurs due to the favourable energy balance between the energy cost needed to create a surface vacancy ($E_f^{vac} > 0$) and the energy gain from the bonding of the adsorbate in the vacancy sites ($E_b < 0$). If $E_{sub} = E_b + E_f^{vac}$ is lower than the binding energy for the normal, on-surface adsorption, then substitutional adsorption will be favoured. For Al, at least, E_f^{vac} is low. It was also shown that substitutional adsorption is kinetically hindered and requires steps, kinks or some other reservoir for the substrates atoms which have been displaced [69]. Substitutional adsorption only seems to occur at higher coverages on both Al(111) and Al(100), though the physical processes behind the coverage dependence are different [75].

Surface alloys of bulk-immiscible atoms has been studied in the general sense by Tersoff [76]. Using arguments based on energetics and Monte Carlo simulations, he identifies atomic size mismatch as an important parameter which renders minority elements immiscible in the bulk and confines them to the surface regions, and shows that misfitting substitutional surface elements will repel because of strain effects, allowing the formation of ordered alloys.

4. Conclusions

The past 5 years has been a period of intense activity in the study of alkali adsorption on metal surfaces. It appears that the Langmuir–Gurney model can no longer be regarded as the paradigm it once was, though it will perhaps remain a useful starting point in much the same way as the Lennard–Jones potential has served the field of gas–surface dynamics (see e.g. [77]).

The question arises as to whether there is a new scientific paradigm which adequately replaces the LG model. In a sense there is: continuing developments in high-performance computing together with parallel advancements in DFT mean that many if not all problems are now approachable using first-principles calculations. However, although these may yield the correct atomic geometries, the charge density difference plots which contain the information on electronic rearrangements do not indicate the processes contributing to the redistribution and cannot separate 'charge transfer' from screening effects. In intuitive terms, perhaps our best guess at a new paradigm is that the bonding in these systems does not fit comfortably into the 'ionic' or 'covalent' categories but must contain an element of both these extreme 'model' situations.

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