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## Correlation between work function changes and core-level shifts in alkali overlayers

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**Abstract.** We have measured the work function changes and Na 2p core-level shifts for the systems Na/Cu(111), Na/Ni(111), and Na/Cu(110) as a function of alkali coverage. We find that the coverage dependence of the core-level shift in the first layer is well correlated with the work function change. We suggest that these quantities are related through the coverage dependence of the alkali dipole moment and the position of the centroid of the alkali valence charge density. In order to confirm this relationship, we use a simple fitting procedure which is able to reproduce the work function changes from the core-level shifts for all three systems.

### 1. Introduction

During the past few years, a substantial amount of theoretical and experimental effort has gone into studying the electronic (and other) properties of alkali atoms adsorbed on metal and semiconductor surfaces [1]. The interest in these systems is due in large part to the expectation that the alkalis serve as good model systems for studying metal adsorption and the metallization of overlayers on surfaces. Among the large amount of work that has been done on these systems, measurements and interpretations of work function changes date back to the very early work of Langmuir and Gurney [2], and are still continued to this day. On the other hand, detailed and systematic measurements of alkali core level shifts, and theoretical modelling of these shifts, is very recent [3–9]. It is the apparent relationship we have observed between these two rather different quantities that is the subject of this paper.

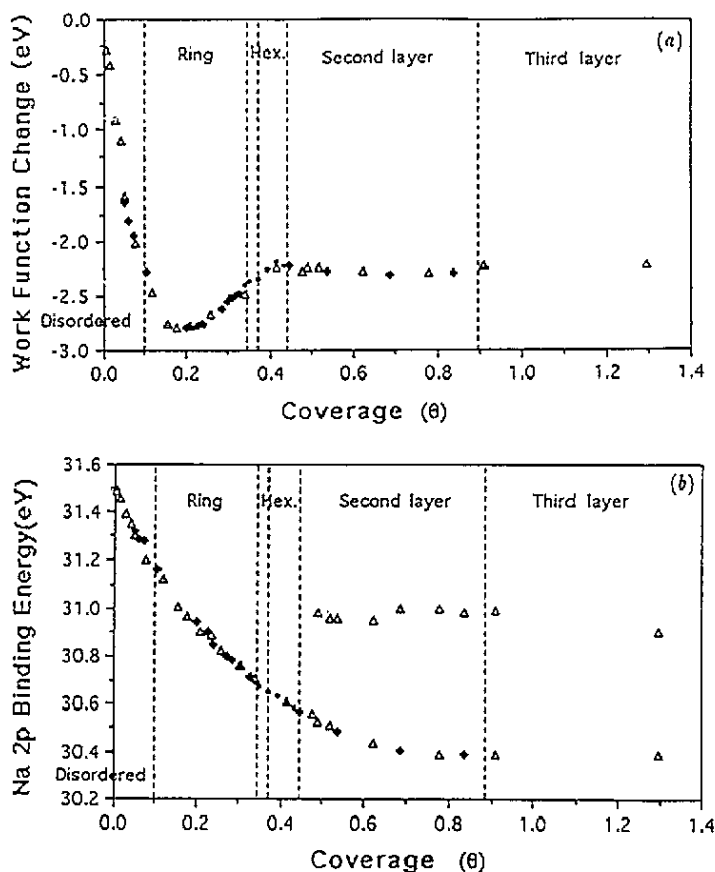
The work function change,  $\Delta\Phi$ , due to alkali adsorption can be written in the following general form [1, 10–12]:

$$\Delta\Phi = D(\theta)\theta\sigma_{\text{ML}}/\epsilon_0 \quad (1)$$

where  $D(\theta)$  is the (coverage-dependent) dipole moment per alkali adatom in units of Debye (Db);  $\theta$  is the coverage in monolayers;  $\sigma_{\text{ML}}$  is the alkali adatom monolayer density (which is  $8.4 \times 10^{14}$  atoms  $\text{cm}^{-2}$  for 1 ML of Na on the Cu(110) and Cu(111) [4, 13] surfaces and  $8.2 \times 10^{14}$  atoms  $\text{cm}^{-2}$  for 1 ML of Na on the Ni(111) surface [10]); and  $\epsilon_0$  is the permittivity constant ( $= 2.655 \times 10^{14}$  Db  $\text{V}^{-1} \text{cm}^{-2}$ ). Ishida *et al* have shown [14–17], based on first principles local density functional calculations of alkalis on

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jellium, that the characteristic work function changes induced by alkali adsorption on metal surfaces (as an example, see figure 1(a) for the results of work function measurements of Na/Cu(111) [3, 13]) can be well reproduced by a coverage-dependent dipole moment which is a monotonically decreasing and more or less linear function of increasing alkali coverage. The result of Ishida's calculation for a jellium substrate with  $r_s = 3$  is presented in figure 2. In his calculation, the valence charge density around the alkali adatoms becomes less polarized and more symmetric with increasing coverage due to the increasing importance of alkali-alkali interactions. This reduction in polarization leads to the dipole moment decrease and corresponding work function change. In addition, Ishida predicts a close correlation between the alkali dipole moment and the adsorption energy [14], both of which decrease with increasing alkali coverage. In this paper, we will demonstrate such a correlation between the dipole moment and the binding energies of alkali core levels.



**Figure 1.** (a) The work function change and associated LEED patterns of Cu(111) as a function of Na coverage. (b) The binding energy of the Na 2p core level of Na/Cu(111) as a function of Na coverage. The photon energy used was 70 eV, and the binding energy is referenced to the Fermi level. For both figures, which were taken from [3], the different symbols represent the results from different experimental runs.

In figure 1(b), we present as an example of core-level shifts the results of our measurements of the binding energy of the Na 2p core level of Na/Cu(111) as a function of

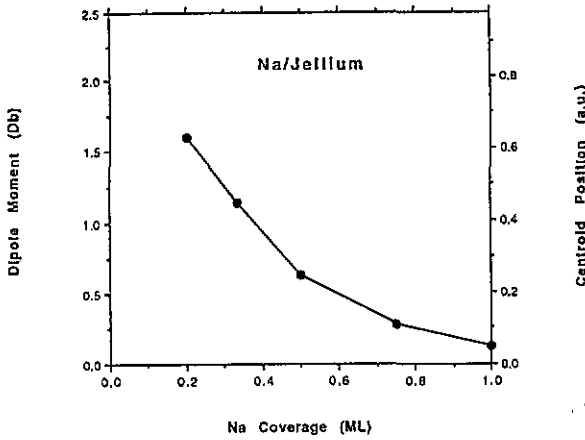


Figure 2. Theoretical results of the dipole moment and the position of the centroid of the planar average of the alkali-induced ground-state charge density for Na/Jellium with  $r_s = 3$  as a function of alkali coverage. Results taken from [17].

Na coverage [3]. Core-level shifts in general are due to a combination of initial and final state changes. Therefore, to fully understand coverage-dependent alkali core-level shifts, both initial and final-state effects must be considered. We have recently demonstrated [3], using a local density functional calculation, that at least a significant part of the overall magnitude (but not the detailed shape) of the decrease in the binding energies of the Na 2p core levels of Na/Cu(111) and Na/Ni(111) up to the completion of one monolayer can be accounted for as an initial-state shift associated with coverage-dependent changes in the electrostatic potential around the alkali nucleus.

Part of this initial-state effect, which was not separated out in this calculation, is a contribution due to coverage-dependent changes in the dipole field at the alkali core due to the alkali dipole-dipole interaction in the overlayer. Persson and Ishida [16] have estimated this dipole shift for the valence 4s level of K/Al(111) to be  $\simeq 0.5$  eV to higher binding energy (towards  $E_F$  for the unoccupied 4s state) for low alkali coverage up to  $\simeq 0.5$  monolayer, but *in the opposite direction* from measured alkali core-level shifts (as for Na/Cu(111) in figure 1(b):  $\simeq 1$  eV shift to lower binding energy). Since dipole-dipole interactions are also associated with work function changes, any connection between core level and work function shifts is not obvious from these theoretical results of Persson and Ishida.

Based on a comparison of experimental and theoretical results, we attributed [3] the initial-state shift in the electrostatic potential which gives rise to much of the alkali core-level shift to changes in the alkali valence charge distribution as a function of alkali coverage. In particular, as the alkali coverage increases, the centroid of the planar averaged charge density shifts from a position between the substrate and the alkali nucleus to a position much closer to the nucleus [3, 14, 17]. This centroid position is plotted in figure 2 for Na adsorption on jellium with  $r_s = 3$ , from a calculation by Ishida and Liebsch [17]. We can see from this figure that the centroid position, since it is proportional to the dipole moment per atom discussed above [17], is also quite linear with alkali coverage over much of the alkali coverage range. The relationship of centroid position to dipole moment makes sense since a centroid shift away from the nucleus implies a certain degree of polarization of the alkali valence charge, and the dipole moment is only sensitive to the charge polarization perpendicular to the surface. These connections suggest that alkali core-level shifts are correlated to some degree with the work function change through the dipole moment

change. In the following section, we will examine this relationship by comparing core-level photoemission results to work function measurements for the systems Na/Cu(111), Na/Ni(111) and Na/Cu(110) (see references [3] and [4] for experimental details).

## 2. Results and discussion

We have previously found that Na 2p core-level net shifts from low coverage up to one monolayer are 1.1 eV, 0.9 eV and 0.55 eV for the systems Na/Ni(111) [3], Na/Cu(111) [3], and Na/Cu(110) [4], respectively. The corresponding maximum work function decreases (from low coverage to the minimum point) are 3.05 eV, 2.75 eV, and 2.15 eV [3,4,14]. In addition, the core level shifts for Na/Cu(111) and Na/Ni(111) (but not Na/Cu(110)) are monotonic and nearly linear with alkali coverage (see figure 1(b) for the case of Na/Cu(111)). Their general shape resembles both the calculated dipole moment and centroid position curves presented in figure 2. These similarities suggest a possible connection between these different properties of alkali overlayers.

To examine this relationship more closely, we have first subtracted offset energies from the core-level binding energy curves of the three systems discussed here to match them at an energy of 0.2 eV at one monolayer coverage, as illustrated in figure 3. (To produce the curves in figures 3, we subtracted energies of 30.15 eV, 30.4 eV, and 30.35 eV for Na/Ni(111) Cu(111), and Cu(110), respectively.) For now, the choice of 0.2 eV is arbitrary. From this figure, we can again see the similarities and differences between these systems, as discussed above. We should point out that the Na/Cu(110) system is a special case; we have attributed the non-monotonic behaviour of the binding energy curve at low coverage to the onset of an Na-induced ( $1 \times 2$ ) missing row reconstruction of the surface [4].

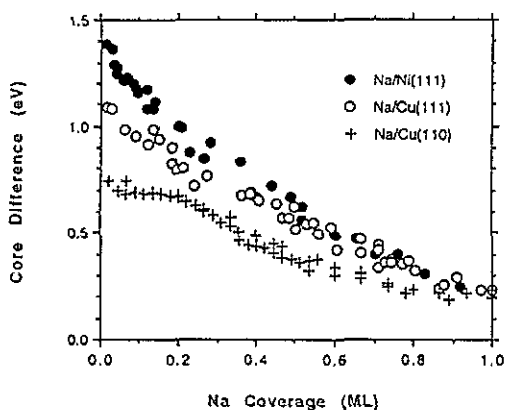
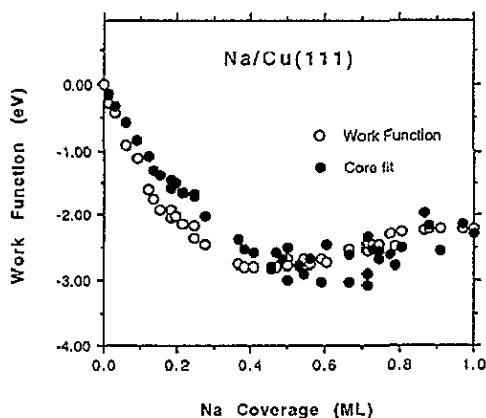


Figure 3. The binding energies of the Na 2p core levels (minus offsets in each case) for the systems Na/Ni(111), Na/Cu(111), and Na/Cu(110) as a function of Na coverage up to the completion of the first layer (see text for details). Data taken from [3] and [4].

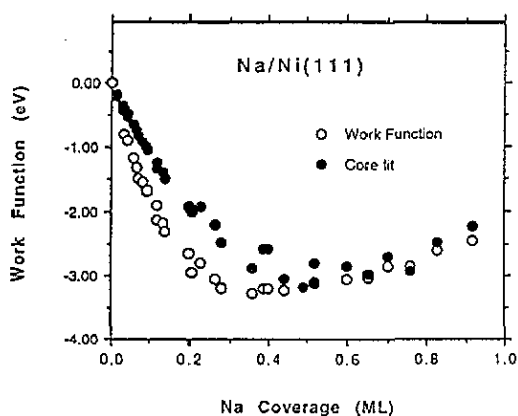
We note again the similar shape of the core-level curves of Na/Cu(111) and Na/Ni(111) to the calculated dipole moment curve displayed in figure 2. To take this a step further, we will now equate the *shape* of the measured core-level binding energy curves in figure 3 with the dipole moment curves, starting with Na/Cu(111). Using the formula in equation (1) and



**Figure 4.** A comparison of the work function change of Na/Cu(111) with the results of a fitting procedure using a convolution of the Na 2p core-level binding energy shift (see text for details).

an adjustable scale factor, we will attempt to reproduce the measured work function change of this system, and then extend the procedure to Na/Ni(111) and Na/Cu(110). First, we multiply the Na/Cu(111) curve in figure 3 (with offset subtracted) by the coverage. Second, we scale the resulting curve so that we reproduce the value of the work function at its minimum. This turns out to require a scale factor of 9.655.

The results of this simple 'fitting' procedure, along with our measured work function results, are displayed in figure 4. The agreement is fairly good, including a similar overall shape and a similar value at one monolayer. On the other hand, the fitted curve does not line up particularly well at low coverage, is very scattered at high coverage, and the coverage corresponding to the minimum value is somewhat higher than for the measured data.



**Figure 5.** A comparison of the work function change of Na/Ni(111) with the results of a fitting procedure using a convolution of the Na 2p core-level binding energy shift (see text for details).

We next use the same procedure to convolute the core-level binding energy curves of Na/Ni(111) and Na/Cu(110) from figure 3 into work function curves. The results are displayed in figures 5 and 6. The agreement in both cases is again fairly good, with obvious

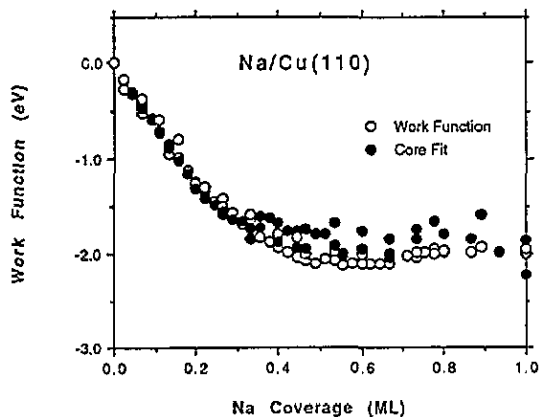


Figure 6. A comparison of the work function change of Na/Cu(110) with the results of a fitting procedure using a convolution of the Na 2p core-level binding energy shift (see text for details).

features of similarity and difference. The important point to note about these results, which we feel lends considerable support to the idea of the correlation discussed in this paper, is that the starting points (0.2 eV for the binding energy curves in figure 3) and the scale factor (9.655) selected to obtain the best fit for Na/Cu(111) were the *same values* used to produce the convolutions of Na/Ni(111) and Na/Cu(110). In other words, once the two parameters were derived for Na/Cu(111), *no adjustable parameters* were used to obtain the fits for Na/Ni(111) and Na/Cu(110) in figures 5 and 6.

Overall, we find the core-level convolutions to reproduce the work function results quite well in all cases, especially considering the simplicity of the 'recipe' and the fact that the same parameters were used for all three systems. Obviously the fits are not exact, and there are even some qualitative differences between Cu(111), Ni(111) versus Cu(110). The convolutions agree better with the work function measurements of the (111) systems at higher coverage, better with Cu(110) at lower coverage. Perhaps there is some significance to this, but at this level of analysis, it is not worth pursuing in our opinion.

Regarding the choice of offset (0.2 eV) used to fit the Na/Cu(111) data, we found that this was rather sensitive in terms of obtaining reasonable agreement with the work function results. A difference of more than  $\approx 0.05$  eV from this end point resulted in a qualitatively poorer fit. There is some physical significance to this value. The ratio of this end point at one monolayer to the energy at low coverage (in figure 3) is equivalent in our fitting scheme to the ratio of the alkali dipole moment at one monolayer versus low coverage. In the present analysis, these ratios are 0.15, 0.18, and 0.26 for Na/Ni(111), Cu(111), and Cu(110), respectively, which are reasonable but somewhat higher than the dipole moment ratios in the calculations of Ishida *et al* [14–17] ( $\approx 0.05$  in figure 2, for example).

We would like to point out that we do not expect this analysis to work as well for all systems. For alkalis/aluminium, for example, island formation is observed at intermediate coverage [5, 18]. Once islands start to form, the correspondence between work function and core-level binding energy should no longer be valid. Departures from this relationship may be indicative of differences in the structure or other properties of the alkali overlayers.

Another important point that should be mentioned is that no discussion of final-state shifts was presented in the above analysis. In our LDA calculation of Na/Jellium [3], we were only able to consider initial-state effects through the electrostatic potential change. However, we did not obtain good agreement between the *shape* of the curve of the calculated

electrostatic potential as a function of coverage with the measured core-level shifts. This suggests that final-state effects must also be considered to fully describe alkali core-level shifts. In fact, the shape of the centroid position versus coverage (figure 2) resembles quite well the core-level shift curves of Na/Cu(111) and Na/Ni(111) (figure 3). Since changes in core hole screening which produce final-state shifts in core-level binding energies are also related to the valence charge distribution, our analysis suggests that the centroid position change provides a good first-order guide to the combination of initial- and final-state effects in alkali core-level shifts. Finally, the centroid position change discussed above does not directly include any changes in the *lateral* distribution of the alkali valence charge, which will also contribute to both types of core-level shifts. However, lateral charge redistribution will generally be accompanied by changes in the perpendicular polarization of the valence charge. Therefore, again, the centroid position may provide a first-order estimate of the changes that lead to alkali core-level shifts.

The motivation for the presentation above was our observation that quantitative differences in alkali core-level binding energy shifts correspond to quantitatively different work function changes. Our analysis tends to support this connection and suggests a relationship between core-level shifts and alkali dipole moments. We believe that the most likely basis for this correlation is through the similar behaviour of the coverage dependence of the alkali dipole moment and the position of the centroid of the valence charge density with respect to the alkali nucleus. Both quantities are related to the degree of polarization of the valence charge, and have been shown to be primarily responsible for the work function change and the initial-state core-level shift through the electrostatic potential change, respectively. We hope to examine these issues in other alkali and related systems, and we feel these correlations are worth considering in future discussions of alkali adsorption.

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