## Coverage dependence of the work function of metals upon alkali-metal adsorption

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Alkali-metal adsorption on metal substrates leads to changes in the work function  $\Delta\phi$  with changing adsorbate coverage  $\theta$ . The function  $\Delta\phi$  goes through a minimum at a certain coverage. It is demonstrated by an Anderson-model calculation that the experimental data for  $\Delta\phi$  vs  $\theta$  can be successfully explained if metallization is accompanied by a metal-substrate distance relaxation.

Alkali-metal adsorption on metal surfaces has been the object of an ever increasing number of studies, both from an experimental and theoretical viewpoint.<sup>1-3</sup> This increased interest is no doubt due to the many technological applications which these particular chemisorption systems engender in such diverse fields as the preparation of cathodes with low work functions and in the promoting action in heterogeneous catalysis.<sup>4</sup>

Alkali-metal adsorption results in a characteristic variation of the substrate work function  $\Delta \phi$  with adsorbate coverage  $\theta$ , which is made up of a large linear decrease at low coverages, followed by a minimum in  $\Delta \phi$  with a subsequent rise towards the value characteristic of the overlayer. Such a behavior has been observed for all the alkali metals and for many substrate surfaces.<sup>1-4</sup> Amongst the various models introduced to explain this behavior, let us mention the early quantum-mechanical work of Gurney.<sup>5</sup> In the Gurney model, the valence  $|ns\rangle$  level (n = 2, ..., 6) of the alkali-metal adatom is broadened into a resonance as a result of interaction with the metal bands. Owing to the comparable values of the alkali-metal ionization potential and the substrate work function, and also owing to a shift to higher energies as a result of the image force, it is found that the resonance is centered above the Fermi level  $\varepsilon_F$ . However, the tail of the resonance extends below  $\varepsilon_{F}$ , ensuring that the valence level will be partly occupied and thus that the alkali-metal atoms will not be completely ionized. As a result of continued adsorption, an electrostatic potential will result on the surface, whose effect will be to shift the valence  $|ns\rangle$  level of each alkali-metal atom downwards, and will thus result in a progressive neutralization of the adatoms.

This model has gained considerable credence through the recent observation of the  $|4s\rangle$  valence level of adsorbed K atoms on Cu(110) as probed by metastable He deexcitation spectroscopy.<sup>6</sup> It appears from this work that the K  $|4s\rangle$  resonance is partly occupied even in the limit of zero coverage, and that it becomes more pronounced with increasing K coverage. Also reported in this work is the integrated intensity of the K  $|4s\rangle$  peak as a function of the K coverage. Initially, the intensity increases practically linearly with  $\theta$ , but more importantly a break occurs at about  $\theta \sim 0.23$  and the further increase is much stronger. This is qualitatively interpreted in terms of increased metallization of the overlayer.<sup>6</sup>

In the following, we show how the electronic properties of the alkali-metal-substrate complex can be used to obtain realistic work function versus coverage curves. The model we advance recognizes explicitly the fact that metallization of the overlayer is accompanied by a relaxation<sup>7</sup> of the adsorbate-substrate interlayer distance, d. The relaxation upon metallization was obtained earlier<sup>7</sup> in a first-principles calculation. A detailed microscopic analvsis of the work-function lowering upon deposition of cesium on W has been thoroughly discussed by Wimmer, Freeman, Hiskes, and Karo for a fixed coverage.<sup>8</sup> These authors present results for a fixed coverage, but for different values of d, and note a strong dependence of  $\Delta \phi$  on d. We exploit this notion to explain the coverage dependence of  $\Delta \phi$ . Our model can also successfully explain the observed dependence of the integrated K  $|4s\rangle$  intensity on coverage.<sup>6</sup> The two-layer model,<sup>9</sup> proposed for explaining the minimum in  $\Delta \phi$  for Cs/W has already been challenged on other grounds,<sup>10</sup> and is also obviated by our calculation. We shall look at the specific case of K adsorption on metal surfaces. Many recent experimental studies have also used K as the adsorbate, principally because of the role played by this adsorbate in promoting a number of catalytic reactions.4

We treat the problem within the Anderson model in the Hartree-Fock approximation<sup>11</sup>

$$H = \sum_{\sigma} \left( \sum_{k} \varepsilon_{k} n_{k\sigma} + \varepsilon_{s\sigma} n_{s\sigma} + \sum_{k} (V_{ks} c_{k\sigma}^{\dagger} c_{s\sigma} + \text{H.c.}) \right), \quad (1)$$

where

$$\varepsilon_{s\sigma} = \varepsilon_s + U^* \langle n_{s,-\sigma} \rangle + V(\underline{0}) \left( \sum_{\sigma} \langle n_{s\sigma} \rangle - 1 \right) , \qquad (2)$$

 $\varepsilon_s$  is the position of the valence  $|4_s\rangle$  level of the K adatom, renormalized by image effects.  $U^*$  is the intra-atomic Coulomb repulsion between two electrons on the  $|4_s\rangle$  level, also renormalized by image effects.  $\langle n_{s\sigma} \rangle$  is the expectation value of electrons of spin  $\sigma$  on the  $|4_s\rangle$  level.  $V(\underline{0})$ is the electrostatic potential due to all other adatoms in the layer; i.e.,

$$V(\underline{0}) = e^2 \sum_{i} [r_i^{-1} - (r_i^2 + 4d^2)^{-1/2}] , \qquad (3)$$

where the summation is over all sites excluding that described in (1) which we assume at the origin.  $V(\underline{0})$  is clearly dependent upon the adsorbate coverage  $\theta$  and d is

the distance of the adatoms from the effective image plane. The leading term in the Hamiltonian (1) corresponds to the substrate conduction band, while the last term describes a coupling between the metal orbitals and the alkali-metal valence orbital.

The solution of the Hamiltonian (1) is simple.<sup>11</sup> Assuming nonmagnetic solutions  $n = \langle n_{s\sigma} \rangle = \langle n_{s,-\sigma} \rangle$  one finds that the density of states localized on the adatom  $|4s\rangle$  level is given by the relation

$$\rho_s(\varepsilon) = \pi^{-1} \Delta / \{ [\varepsilon - E(\theta)]^2 + \Delta^2 \} , \qquad (4)$$

where

$$\Lambda - i\Delta = \sum_{k} \frac{|V_{ks}|^2}{\varepsilon - \varepsilon_k + i0^+} , \qquad (5)$$

and

$$E(\theta) = \varepsilon_{s\sigma} + \Lambda , \qquad (6)$$

where  $\Delta$  is a weighted density of states, and  $\Lambda$  its Hilbert transform. In the following, we shall assume energy independence of these two functions. If one now integrates  $\rho_s(\varepsilon)$  up to the Fermi energy which is chosen equal to zero, the following relationship will be found:

$$n = \frac{1}{2} - \pi^{-1} \tan^{-1} [E(\theta)/\Delta] , \qquad (7)$$

or equivalently

$$\Delta \cot(\pi n) = E_0 + U^* n + (2n-1)V(\underline{0}) , \qquad (8)$$

and  $E_0 = \varepsilon_s + \Lambda$ . The self-consistent solution of *n* for a given adsorbate coverage  $\theta$  can then be found from a solution of the transcendental equation (8). The solution of (8) is naturally dependent upon the parameters  $E_0, \Delta, U^*$ , and *d* as well as the geometric array of sites available for occupation by the alkali-metal adatoms.  $E_0$  and  $\Delta$  represent the position and width of the adatom valence



FIG. 1. Change in density of states induced by adsorption of a single K atom onto a jellium surface of density  $r_s = 3.1$  a.u. The curves are labeled by the value of the distance of the adatom from the jellium edge (given in a.u.). Also given in parentheses is the width of the resonances (in eV).

 $|4s\rangle$  level and one expects typically that these quantities are dependent on the value of d. In fact, such a relationship is apparent in the theoretical models of the electronic properties of alkali-metal-metal chemisorption systems.<sup>12</sup>

In Fig. 1, are shown the changes in density of states,  $\Delta N(\varepsilon)$ , of a jellium substrate (density  $r_s = 3.1$  a.u.) upon adsorption of a single K atom. The curves are labeled by the value of the distance in a.u. between the adatom and the jellium edge. Also given in the brackets is the width of the K  $|4s\rangle$  resonance in eV. These results were obtained using a wave-function matching technique in which the adatom potential is assumed spherically symmetric within a muffin tin and zero outside, and the jellium surface is represented by a finite barrier potential of height equal to the sum of the Fermi energy and the work function.<sup>12</sup> The results obtained within this simple model were found to be in excellent accord with the results of the first-principles calculations of Lang and Williams<sup>13</sup> for Na adsorption on a jellium surface of density  $r_s = 2.07$  a.u. and one would expect the results for the lower jellium density to be just as reasonable. From Fig. 1, one observes an upwards energy shift of the K  $|4s\rangle$  resonance coupled with a gradual broadening as the adatom is brought closer to the surface.

The use of a jellium substrate is felt to be justified on the grounds that the substrate d band is not expected to be strongly influential in the description of the bonding, owing to the large size of the alkali-metal atoms. This is further supported by the great similarity observed in the work-function variations with adsorbate coverage for a number of substrates with very different d-band properties.<sup>6,14-16</sup> The choice of the jellium density is taken to represent the *sp* band of Ni but should also give a reasonably accurate description of the *sp* bands of such substrates as Fe and Cu. The variation of  $E_0$  and  $\Delta$  with d can thus be extracted from these calculations.

The quantity  $U^*$  is composed of two terms: The Coulomb repulsion U, which is simply given by the difference between ionization potential and electron affinity of the alkali-metal atom, as well as an energy shift owing to the image force

$$U^* = U - e^2/2d . (9)$$

There is thus also a *d* dependence of  $U^*$ . However, for all the alkalis *U* is small (U < 4 eV) and in the *d* range of interest the image term will almost exactly cancel *U*. We have therefore neglected  $U^*$  altogether in the following discussion.

Finally, one must assume a geometric distribution of adatoms on the substrate surface. We have assumed that the adatoms do not cluster and that they are spread uniformly in a square arrangement. The actual geometric network is unimportant as, for instance, very similar results for  $V(\underline{0})$  are obtained for a close-packed hexagonal arrangement.  $V(\underline{0})$  is thus given by the relation

$$V(\underline{0}) = (e^{2}\theta^{1/2}/a) \sum_{l,m} \{ (l^{2} + m^{2})^{-1/2} - [l^{2} + m^{2} + 4(d^{*})^{2}\theta]^{-1/2} \}, \quad (10)$$

and  $d^* = d/a$ , where a is the nearest-neighbor distance for the saturated layer.



FIG. 2. Charge Q on K adatom, as a function of K coverage  $\theta$ , for different values of d. The curves are labeled by the d value given in a.u. Zero coverage values are obtained using a single adatom on the substrate.

One can then solve for *n* self-consistently for different values of *d* and  $\theta$ . Results for the excess positive charge Q = 1 - 2n on a K atom as a function of  $\theta$  are illustrated in Fig. 2 for different values of *d*. One thus sees that there is a progressive neutralization  $(Q \rightarrow 0)$  of the K adatoms as  $\theta$  is increased. One also observes a strong *d* dependence of *Q*. Basically, one finds a sharper and more complete neutralization for larger *d* values, whereas the neutralization is found to be more uniform and less complete for the smaller *d* values. Having solved for *n*, one can then calculate the change in work function through the Helmholtz formula

$$\Delta \phi = 4\pi e \,\theta d \,(2n-1)/a^2 \,. \tag{11}$$

Curves for  $\Delta \phi$  vs  $\theta$  for different values of d are illustrated in Fig. 3. Also shown are experimental points for two typical systems involving K adsorption on metal surfaces.<sup>14,15</sup> A strong d dependence of these curves is observed there which is also apparent in the results of Lang,<sup>17</sup> although in his case d represents the width of the jellium layer which is taken to represent the alkali adlayer. Although all the curves plotted show the expected behavior, i.e., a decrease in  $\Delta \phi$  at small  $\theta$  followed by a minimum and a subsequent rise, one notices that experimental points do not all lie on the same curve. In order to obtain good agreement between theory and experiment over the whole range of coverages, one has to introduce a coverage-dependent adatom-metal separation  $d = d(\theta)$ . In particular, it appears as though, for low coverages a small value of d ( $d \approx 3.2-3.5$  a.u.) gives good results, whereas at higher coverages and in particular beyond the work-function minimum, larger values of d must be invoked ( $d \approx 4-4.5$  a.u.).

We can also explain the break observed<sup>6</sup> in integrated intensity of the K  $|4s\rangle$  resonance at a certain critical coverage if at that coverage d changes<sup>7</sup> by a sensible amount. The  $|4s\rangle$  resonance at this value of d should essentially be the "bulk" potassium level. This is indeed the case as the width of the resonance changes<sup>6</sup> from 3 eV (at low coverage and small d) to the characteristic width of the 4s band, 2.1 eV, at higher coverages and larger d.



FIG. 3. Calculated change in work function  $\Delta \phi$  vs K coverage  $\theta$  for three values of d (curves are labeled by values of d in a.u.). Also given are experimental points for K/Ta(110) ( $\triangle$ , Ref. 15) and for K/Fe(110) ( $\bigcirc$ , Ref. 14).

The variation in d with coverage is a priori reasonable, as one has seen that at low coverages the alkali metals have a consequent charge and that they gradually become neutralilzed as more atoms are adsorbed onto the surface. One would expect the more neutral alkali-metal adatoms at high coverages to be further outside the surface than their charged counterparts at lower coverages. Our model is rather simple but it points to the important fact that a quantitative fit of  $\Delta \phi$  vs  $\theta$  should take into account  $d(\theta)$ variation. A first-principles electronic-structure calculation of metal overlayers on semiconductors has first found important d relaxation upon metallization.<sup>7,18,19</sup> The onset of metallization is accompanied by an increased metalsubstrate interlayer distance. The regain of charge by the overlayer is certainly facilitated if d increases at the coverage where metallization sets in. We thus conclude that in order to reproduce the characteristic variation in work function with alkali-metal coverage, one should impose a coverage-dependent d. We expect this coverage dependence of d to be more generally valid and hope that a quantitative dependence of d on  $\theta$  would soon be worked out. The quantitative description of  $\Delta \Phi$  vs  $\Theta$  is perhaps only one manifestation of *d*-relaxation upon metallization.

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