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Depolarization and metallization in alkali-metal overlayers

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We study the level shift of the alkali-metal valence resonance with increasing adatom coverage (Θ) with a simple formula based on the Gurney model in which alkali-metal adatoms interact only via the long-range dipole interaction. The calculated level shift is in good agreement with the results of first-principles electronic-structure calculations below the onset of the overlayer "metallization," but breaks down for higher Θ where the orbital overlap among nearby adatoms plays a crucial role in the electronic properties of the overlayer. Our result is also in good accord with the recent experimental data for K/Al(111) at low K coverage.

Alkali-metal-atom adsorption on metal surfaces is one of the simplest chemisorption systems. In the Gurney model[1] the valence *ns* orbital of an isolated alkali-metal atom broadens and shifts upon approaching the surface, resulting—at the equilibrium chemisorption distance—in an *ns*-derived resonance centered ~1 eV above the Fermi energy E_F. The partial filling of the resonance leads to a mostly ionized adatom. A negative screening charge density (image charge) is induced on the metal surface in the vicinity of the adatom, giving rise to a local surface dipole of magnitude $p=e^*d$, where $e^*=1-\sum_\alpha \langle C_\alpha^\dagger C_\alpha \rangle$ (α denotes the alkali-metal-adatom states) is the positive charge on the alkali-metal atom and d is the separation between the alkali-metal core and the image plane. As the alkali-metal-atom coverage (θ) increases, the dipole fields from neighboring adatoms give rise to a local electric field on the alkali-metal-atom site under consideration which shifts the *ns* resonance toward E_F, leading to a larger occupation of this resonance and, hence, to a smaller net alkali-metal-atom charge e^* and to a smaller dipole moment p. Recent first-principles calculations[2,3] have provided new insight into the above-mentioned classical model. (i) The sharp resonance above E_F is a hybridized state of the *ns* and np_z orbitals rather than pure *ns*, whose wave functions strongly polarizes toward the vacuum side of an adatom. It is a strong antibonding state with regard to the adatom-substrate bonding. (ii) The covalency in the adatom-substrate bonding, i.e., $E_c=\sum_{\alpha,\beta} V_{\alpha\beta} \langle C_\alpha^\dagger C_\beta \rangle + \text{c.c.}$, takes a maximum value at the lowest Θ by the maximum use of bonding states. (β denotes the substrate states and $V_{\alpha\beta}$ is the off-diagonal matrix element of the Hamiltonian.) E_c decreases at higher Θ because part of the strong antibonding resonance is occupied, following the strengthening of the adatom-adatom bonding. (iii) The interatomic polarization due to the mixing of adatom and substrate states gives an important contribution to p, and p should be given as

$$p=d\left[1-\sum_\alpha \langle C_\alpha^\dagger C_\alpha \rangle\right]+\left[\sum_{\alpha,\beta} \mu_{\alpha\beta} \langle C_\alpha^\dagger C_\beta \rangle + \text{c.c.}\right] . \tag{1}$$

Consequently, the induced negative charge density on the interface side of adatoms should be partly assigned to a bond charge rather than an image charge. How much weight these two components have in the total dipole moment may vary continuously, depending on the difference in the electronegativity between the adatom and metal substrate.

Since, at present, there is a limit in the lowest Θ value studied by first-principles methods, it is interesting to examine to what extent simplified models can reproduce results of first-principles calculations and experiments. In the present work we study the level shift of the adatom resonance at low Θ using a model based on the Newns-Anderson Hamiltonian as described in Refs. 4 and 5. In these model analyses the interatomic polarization term emphasized in the recent first-principles calculations[2,3,6] was not considered in the expression of p. [The *intra-atomic* polarization term in these model theories is different from the second term of Eq. (1).] However, as far as p includes the first term of Eq. (1) and also as far as adatoms interact via the long-range dipole interaction, the shifted alkali-metal-atom level $\tilde{\varepsilon}_s$ may be given as

$$\tilde{\varepsilon}_s=\varepsilon_s-edE_0 . \tag{2}$$

Here, E_0 is the local electric field at an alkali site from all the other alkali-derived dipoles on the surface. In Eq. (2) we have neglected the Coulomb repulsion term $U^*\langle n_\downarrow \rangle$, where $\langle n_\downarrow \rangle$ is the spin-down occupation of the resonance (we assume spin degeneracy so that $\langle n_\downarrow \rangle = \langle n_\uparrow \rangle$), since it can be argued[5] that U^* is very small for adsorbed alkali-metal atoms and also because the variations in $\langle n_\downarrow \rangle$ are small at those low Θ for which the present model is reasonable. For example, in the study of the K/Cu(100) system in Ref. 4, the quantity $\langle n_\downarrow \rangle$ varied by only 0.1 as Θ varied from zero up to the coverage where the work function takes its minimum. For an adsorbed alkali-metal atom one can estimate U^* from

$$U^*=I-A-e^2/2d , \tag{3}$$

where I is the ionization energy and A the electron affinity of a free alkali-metal atom. Since for alkali-metal atoms $A \approx 0$ and $I = 4-5$ eV, we have, typically, $U^* \approx 1$ eV. Hence the change in $U^* \langle n_\downarrow \rangle$ is typically only ~ 0.1 eV or less as Θ increases from zero to the coverage where the work function takes its minimum. For an ordered lattice of adsorbates,

$$E_0 = Up \ , \tag{4}$$

where the dipole sum (including image dipoles) $U \approx 18 n^{3/2}$, where n is the number of alkali-metal atoms per unit area. The alkali-metal-atom-induced change in the work function is given

$$\Delta\phi = 4\pi nep \ . \tag{5}$$

Hence we can write

$$\tilde{\varepsilon}_s = \varepsilon_s - \frac{18}{4\pi} \Delta\phi\, d n^{1/2} \ . \tag{6}$$

This formula breaks down when the alkali-metal-atom coverage becomes so large that the wave functions on nearby alkali-metal atoms begin to overlap.

Let us now compare the results present above with first-principles calculations. We perform an electronic-structure calculation for hexagonal Na overlayers with varying lattice constants on the semi-infinite jellium with $r_s = 2$, following the method of Ishida.[2] The calculated results are presented in Fig. 1. The theoretical result at zero adatom coverage, $n = 0$, is taken from the work of Lang and Williams.[7] The circles are the theoretical results and the solid lines a guide to the eye. Figure 1(a) shows the full width at half maximum, Γ, of the Na-derived 3s resonance. For $n \le 0.025$ Å^{-2}, the width Γ is practically constant, indicating negligible orbital overlap between nearby Na atoms. For $n \ge 0.025$ Å^{-2}, Γ increases very fast, indicating the onset of "metallization" at $n \sim 0.025$ Å^{-2}. This coverage corresponds to the minimum in the work function [see Fig. 1(c)] and occurs at about $\frac{1}{3}$ of the maximum possible Na monolayer coverage [on Al(111) a Na 2×2 structure is formed at $n = 0.070$ Å^{-2}]. Figure 1(b) shows the variation of the position of the 3s resonance as a function of the alkali-metal-adatom coverage. The dashed curve in this figure is the result obtained from Eq. (6) using the work-function data in Fig. 1(c) and the alkali-metal–image-plane separation $d = 1.64 - 0.83 = 0.81$ Å, where 1.64 Å is the separation between the jellium edge and the nucleus of the alkali-metal atoms,[7] and the 0.83 Å is the distance between the jellium edge and the image plane.[8] The agreement between the "dipole" theory (dashed curve) and the full calculation (solid curve) for $n \le 0.025$ Å^{-2} is remarkably good. The small shift of the s resonance (~ 0.3 eV) as compared with much larger $\Delta\phi$ (~ 1.5 eV) reflects the small d value as well as a factor $n^{1/2}$ in Eq. (6). For $n \ge 0.025$ Å^{-2} the dipole theory breaks down for obvious reasons—here the direct overlap of the 3s orbitals between nearby alkali-metal atoms leads to a strong broadening and to a shift in the resonance position which is not accounted for in the dipole calculation. Hence we reach the important conclusion that the *"dipole picture" is valid up to the coverage corresponding to the work-function minimum, but wave-function–overlap effects must be accounted for at higher* Θ.

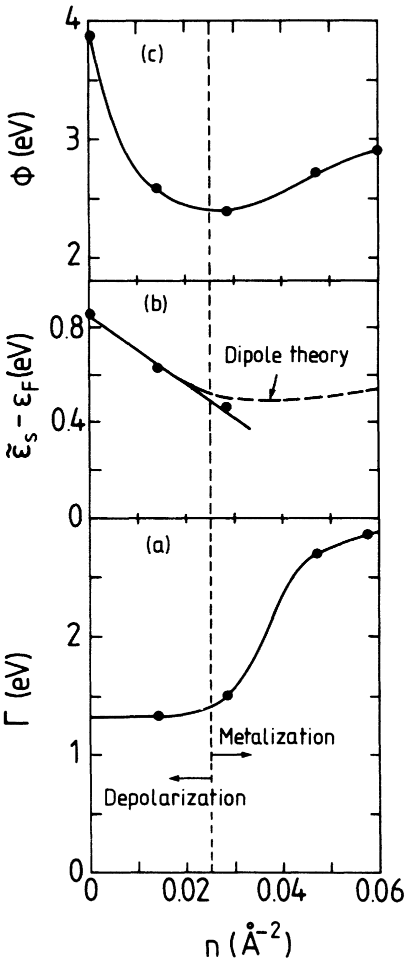

FIG. 1. (a) Full width at half maximum, Γ, of the 3s resonance of Na on a semi-infinite $r_s = 2$ jellium substrate calculated form first principles; see Refs. 2 and 7. (b) Shift of the 3s resonance as a function of alkali-metal coverage. The solid line is the first-principles result, while the dashed curve is based on Eq. (6). (c) Work function as a function of coverage from first principles.

In the dipole model the position of the alkali-metal resonance depends only on the work-function change and on the separation d between the alkali-metal atom and the image plane. Hence it is possible to compare directly the prediction of this theory with experiments. Recently, Frank *et al.*[9] measured the variation of the position of the potassium-derived resonance for K/Al(111) by inverse photoemission. The observed peak may correspond to a hybridized state of K 4s and 4p_z rather than pure K 4s, yet Eq. (6) may be applicable by the appropriate choice of d. The circles in Fig. 2(a) show the result of their measurements, while the solid line is calculated from Eq. (6) using the measured work function as a function of Θ [Fig. 2(b)] as well as the K–image-plane separation $d = 1.6$ Å, deduced from electronic-structure calculations.[10] The experimental data were actually measured at

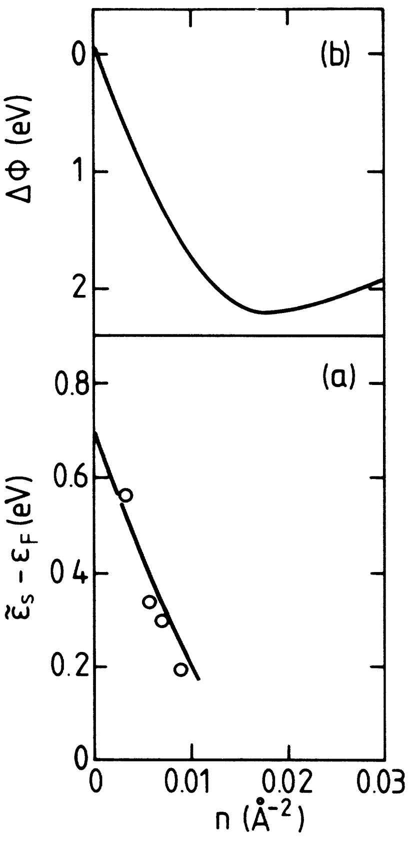

FIG. 2. (a) Circles show the variation of the 4s resonance with K coverage for K on Al(111) (from Ref. 9). The solid curve is calculated from Eq. (6) using the experimentally measured work function in (b).

$k_{\parallel}=0$ (normal emission). Thus the peak position gives the lower edge of the K 4s-4p_z band rather than its center.[11] Yet the width of the K 4s-4p_z band may be very small for $n \leq 0.01$ Å^{-1}. The agreement between theory and experiment lends additional support to the dipole model at low K coverage.

It is not easy to derive quantities such as the occupation number of the ns orbital as used in Newns-Anderson–type model analyses from the results of first-principles calculations. This may especially be the case for alkali-metal atoms, which have the largest valence orbitals of all the elements in the Periodic Table. For example, there is no unique way to divide the occupied part of the Na-induced density of states below E_F, as given in Refs. 2 and 7, into the contributions of the screening charge of the substrate and the true Na valence state. Moreover, these two components cannot be separated, even in experiments such as photoemission, metastable He* deexcitation, core-level shift, and nuclear magnetic resonance. Therefore, model theories based on the Newns-Anderson–type Hamiltonian are successful only if several different experimental observations can be described by the same set of model parameters. Such an attempt was made for K/Cu(100) (Ref. 4), where the work function, optical absorption, and second-harmonic generation were studied for a low-density alkali-metal adsorbate system. Similarly, in the study of mixed-valence systems, where, again, the Anderson model has been frequently used,[12] many different experimental results (involving both "low"- and "high"-energy physics) can be described by the same set of model parameters. In this case some progress has also been made in calculating the model parameters from first-principles calculations.[13]

Muscat and Batra[14] have studied the work-function change of metals upon alkali-metal absorption using the Newns-Anderson model with dipole coupling between the adsorbates. In contrast, in the present work the coverage dependence of the work function was taken as given [from first-principles calculations for Na on jellium and from experiment for K on Al(111)], and from this the variation of the ns resonance with coverage was calculated using dipole-coupling theory and compared with first-principles calculations and with experiment. As pointed out above, for coverages greater than that corresponding to the work-function minimum, direct overlap in alkali-metal wave functions becomes important, and dipole coupling alone cannot be the origin of the alkali-metal-induced work-function changes.

At present, there is debate ensuing over the question of whether the adatom-substrate bonding is covalent or ionic for alkali-metal overlayers on metal and semiconductor[15] surfaces. However, without a strict definition of the ionicity or covalency applicable for real systems, where basis functions for adatom or substrate states as used in the model theory cannot be uniquely determined, such a question is not very meaningful. Imagine the nature of bonding between Na and the elements in the third row of the Periodic Table. The bonding may be covalent for Na—Na, while it may be ionic for Na—Cl. The bonding nature should change continuously with increasing difference in electronegativity, and thus both should contribute to the Na—Al bond. (The jellium with $r_s=2$ studied in the present work corresponds to Al.) The classical Gurney[1] model emphasized the ionic contribution, whereas the recent first-principles calculations[2,3,6] clarified the importance of the covalent contributions, especially for the Θ dependence of the electronic properties.

Finally, we would like to point out that the dipole-induced level shifts discussed above are also important in explaining the Fermi-level pinning by a small concentration of metal atoms on semiconductor surfaces. It has been found that metal atoms adsorbed on semiconductor surfaces often give rise to energy levels in the semiconductor gap which pin the Fermi level at the surface. Since the metal-semiconductor bond usually is strongly polar, large shifts in these levels will occur with increasing metal coverage as a result of the dipole interaction. This gives rise to a Fermi-level–pinning position which varies with alkali coverage and which has been proposed by Klepeis and Harrison[16] as the origin of the experimentally observed[17] variation of the Fermi-level–pinning position at low metal-adatom coverage Θ.

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