Influence of the adsorbed layer randomness on charge transfer in alkali-metal adsorption on metal surfaces

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We investigate theoretically the effects of the adlayer randomness at low coverages on the charge state of alkali adatoms within the Muscat-Newns model [Solid State Commun. **11**, 737 (1972)]. The fluctuating electrostatic potential at an adatom site due to a random arrangement of all the other atoms in the adlayer is modeled in analogy to Holtsmark's theory of static broadening of spectral lines in plasmas. We find that these fluctuations induce a stronger depolarization of the adlayer with increasing coverage than in the Muscat-Newns model, corresponding to a slower drop of the effective work function.

Although an extensively studied subject of surface science (for recent reviews, see Refs. 1–4), alkali-atom adsorption on metal surfaces still presents a challenging problem, as regards both the electronic[5] and atomic[6] structure of the adlayer at submonolayer coverages. In particular, the characteristic dependence of the effective work function (WF) on the adatom coverage has been the subject of many theoretical investigations (a detailed list of references can be found in Refs. 1–4). We shall study here this problem in the low-coverage regime, using the microscopic model due to Muscat and Newns (MN),[7] which is based on the Anderson Hamiltonian in the Hartree-Fock approximation. According to this model, the $|ns\rangle$ valence level of an isolated adatom is broadened into a resonance as a result of the interaction with the metal bands, and the width of the corresponding Lorentzian shape is determined by the chemisorption function Δ (which is, actually, a constant for a flat and wide metal band). When the adatom is placed at a distance d from the image plane, the resonance center ε_a is placed well above the Fermi level, owing to rather low ionization potential I and the upwards image shift $1/(4d)$ of the $|ns\rangle$ valence level. (Atomic units are used, unless otherwise explicitly indicated.) As a result, the average electron population $\langle n_a\rangle$ of the resonance is rather small, that is, an isolated adatom is largely ionized, with the effective (positive) charge $Q = 1 - 2\langle n_a\rangle$ (neglecting the spin polarization and the intra-atomic Coulomb repulsion[7]). Neglecting further the intra-atomic charge polarization,[7] one can associate with each adatom a dipole, formed by the charge Q and its image, with the dipole moment $\mu = 2dQ$. With increasing adatom coverage ρ, a dipole layer is formed on the surface, resulting in a decrease of the effective WF ϕ, according to

$$\phi = \phi_0 - 2\pi\rho\mu \ , \tag{1}$$

where ϕ_0 is the WF of the clean surface.

More important for the MN model is that the dipole layer induces a local electrostatic potential lowering at each adatom site, so that the $|ns\rangle$ resonance shifts downwards and becomes more and more populated by electrons as the coverage increases. As a result, ionic-to-neutral change of adatoms occurs, leading to a reduction of the dipole moment μ, so that the ϕ dependence on ρ becomes no longer linear, as implied by Eq. (1). This depolarization of the adlayer leads to a characteristic minimum in ϕ, occurring typically at about one half, or less, of the monolayer coverage. In the MN model,[7] the charge on adatom is obtained, in the simplest form, as

$$Q = \frac{2}{\pi}\arctan\left(\frac{\varepsilon_a + V}{\Delta}\right) , \tag{2}$$

where $\varepsilon_a = \phi_0 - I + 1/(4d)$ is the valence level of an isolated adatom, referred to the Fermi level (neglecting the temperature effects on the Fermi-Dirac distribution), and V is the electrostatic potential at the adatom site, due to all other adatoms in the adlayer. In fact, V is the parameter of the microscopic model, which contains an information about the atomic arrangement of the adlayer. Assuming a homogeneous distribution of charges Q on adatoms,[8] and taking the classical form of the dipole potential for each adatom

$$V_d(\mathbf{r}) = Q\left(\frac{1}{r} - \frac{1}{\sqrt{r^2 + 4d^2}}\right) \tag{3}$$

(where r is a distance across the surface), one can obtain V as a function of Q, so that Q results from (2) self-consistently. To do so, one has to specify the geometric configuration of atoms within the adlayer, and this is an extremely complex requirement. Usually, one assumes that the adlayer forms a regular (square or hexagonal) lattice at *all* coverages and temperatures, with the lattice spacing scaled by the mean adatom-adatom spacing $\sim 1/\sqrt{\rho}$, and takes for V an average value V_l by means of a lattice sum of the dipole potential terms.[7]

However, it has been demonstrated experimentally (see, e.g., Ref. 9), using low-energy electron diffraction (LEED), that, at room temperatures and low coverages (below the WF minimum), alkali atoms are uniformly dispersed over the surface, due to the mutual dipole-dipole repulsion, forming a two-dimensional "gas" phase.

At coverages around the WF minimum, the depolarization of the adlayer is accompanied by a reduction of the dipole-dipole repulsion between the adatoms, which allows a condensation of the "gas" phase into a "liquid" phase, corresponding to the onset of the short-range order in the adlayer. At high coverages, towards the monolayer, a direct adatom-adatom interaction dominates and leads to a long-range order in the adlayer, with corresponding increase of the WF towards the value characteristic for a regular lattice of an alkali-metal film. Since the MN model ignores the direct adatom-adatom interaction, its applicability is limited only to the low coverages (roughly, up to the work function minimum), where the dipole interactions determine both the arrangement of adatoms and their charge state, and, therefore, cannot describe the increase of the WF at higher coverages. Obviously, using the lattice sum is an adequate description of the adlayer structure at temperatures below the ordering temperature for a given coverage, which turns out to be much lower than the room temperature in the low-coverage regime.[10] While a regular lattice implies negligible fluctuation of V around the value V_l in (2), we wish here to check the assumed[7] validity of the lattice sum description at low coverages and temperatures above the ordering temperature, since, in this regime, one expects large fluctuations of the value of V in (2), owing to the randomness of the corresponding "gas" or "liquid" phases. Namely, in such a situation, each adatom experiences a different configuration of other atoms, and all these configurations form an ensemble. Consequently, the expression (2) for the charge Q on an adatom should be taken rather as an ensemble average

$$Q = \frac{2}{\pi}\int_{-\infty}^{\infty} dV\, P(V)\, \arctan\left(\frac{\varepsilon_a + V}{\Delta}\right), \qquad (4)$$

where $P(V)$ is the probability distribution function (normalized to unity) of the electrostatic potential at the adatom site, due to random positions of all other adatoms within the adlayer.

A useful basis for obtaining the distribution P is the Holtsmark's theory for the spectral line broadening in plasmas in the static limit (for details see, e.g., Ref. 11). Assuming a perfectly smooth surface, that is, a homogeneous adlayer, we obtain, to the lowest order in coverage,

$$P(V) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt \times \exp\{itV + \rho\int d^2r\, g(r)\,[e^{-itV_d(r)} - 1]\}. \qquad (5)$$

Since $P(V)$ is evaluated at a charged site,[12] we need in (5) the pair distribution function $g(r)$ of the adlayer, which is difficult to model, but provides substantial flexibility to our theory. For instance, at low coverages, one may describe the adlayer as a "nonideal gas" by using for $g(r)$ a Boltzmann factor, involving a dipole-dipole potential, and study the effects of increased temperature. However, we prefer to make a closer connection with the ring-shaped LEED patterns, observed at room temperatures for coverages up to about half a monolayer.[10,13] These ring patterns, whose radii are proportional to $\sqrt{\rho}$, are characteristic of a liquid phase. Consequently, $g(r)$ should be normalized as

$$\rho\int d^2r\,[1 - g(r)] = 1 \qquad (6)$$

in order to reflect the tendency of adatoms to stay away from each other, due to the electrostatic repulsion between them. The simplest form of $g(r)$, which satisfies the above requirements and generates an appropriate LEED structure factor, is a step function of the interadatom distance r, placed at $1/\sqrt{\pi\rho}$.

Using the dipole potential (3) in (5), and introducing the parameter $W = (\pi\rho)^{3/2}\mu d$, which has the dimension of energy, one can express the distribution function as $P(V) = p(v,c)/W$, where $p(v,c)$ is a function of the reduced electrostatic potential $v = V/W$ and the reduced coverage $c = 4\pi\rho d^2$. In Fig. 1, we show the universal function $p(v,0)$, which describes the low-coverage case, $c \ll 1$, together with the corresponding Gaussian approximation (GA). It follows from the $p(v,0)$ curve that $P(V)$ peaks at about $V_p = -1.68W$, which is, within several percents, equal to the low-coverage value from the lattice sum, $V_l \approx -9\rho^{3/2}\mu d$.[7,9] Note that the GA generally peaks at the value of the first moment $\bar{V}$ of the distribution $P(V)$, which is $= -2W$ in the case $c \ll 1$. More important is that, for $c \ll 1$, the full width at half maximum (FWHM) of both the distribution $P(V)$ and the corresponding Gaussian is $1.66W$. This means that the lowering of the $|ns\rangle$ resonance in a proportion to W is inevitably accompanied by its broadening by a comparable amount of W. In other words, the original width of the $|ns\rangle$ resonance Δ is increased, through the convolution (4), by the randomness broadening, leading to a stronger depolarization of the adlayer with increasing coverage, than expected from the MN model.[7,9,14] Consequently, since Δ is essentially a free parameter of the MN model, its choice by fitting to experimental data[9,14] should be influenced by the effect of the adlayer randomness. Also presented in Fig. 1. are the function $p(v,1)$ and its GA

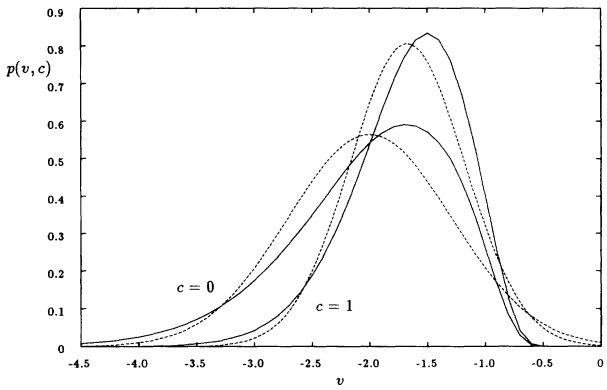

FIG. 1. Solid lines represent the probability distribution function $p(v,c)$ of the reduced electrostatic potential v for reduced coverages $c = 0$ and 1, while the dashed lines are the Gaussian approximations for these two functions (see the text). The broader pair of curves correspond to $c = 0$ and the narrower to $c = 1$.

for medium coverages, $c = 1$, showing a reduction of both the peak shift and the FWHM in terms of W. These curves also show that the accuracy of the GA improves with increasing coverages, and we have verified numerically that it suffices to use this approximation for $P(V)$ in Eq. (4). In order to study how the drop of the effective WF, $\Delta\phi = 2\pi\rho\mu$ [cf. Eq. (1)], is influenced by the randomness effect, we choose the system K/Cu(100) (Refs. 9 and 14) and solve Eq. (4) self-consistently for $d = 3.6$ and $d = 4.1$, with the corresponding values $\Delta = 0.48$ eV and $\Delta = 0.78$ eV, chosen to reproduce the zero-coverage dipole moment per adatom $\mu_0 = 6.2 = 15.8$ D.[9] The results for the $\Delta\phi$ dependence on the coverage θ (defined as the number of adatoms per number of surface atoms) are displayed on Fig. 2. These results are compared in Fig. 2. with the results from the standard MN model,[7,9,14] obtained as the self-consistent solution of Eq. (2) with $V = \bar{V}$, which contains no broadening due to adlayer randomness. As expected, the stronger depolarization of the adlayer due to randomness broadening of the $|ns\rangle$ resonance leads to a slower drop of the effective WF with increasing coverage at temperatures well above the ordering temperature, than in the standard MN model. This randomness effect appears already at coverages well below the WF minimum [note that the experimentally observed WF minimum occurs at $\theta = 0.17$ (Ref. 9) or $\theta = 0.13$ (Ref. 14) for the adsorption system K/Cu(100)]. A similar effect of the increasing disorder of the adlayer on the work function has also been obtained from the lattice-gas model.[15]

In a conclusion, let us note that the present theory offers only qualitative description of the randomness effect at low coverages, because we have neglected the intraatomic charge polarization in the microscopic model, which is known to reduce the dipole moment per adatom with increasing coverage.[7,9] Since this polarization results from the hybridization of the $|ns\rangle$ and $|np_z\rangle$ alkali valence orbitals, which is mediated by the normal component the local electrostatic field at an adatom site, it is important to consider also the fluctuations of this field, which are statistically correlated with the fluctuations of the electrostatic potential at the same site.

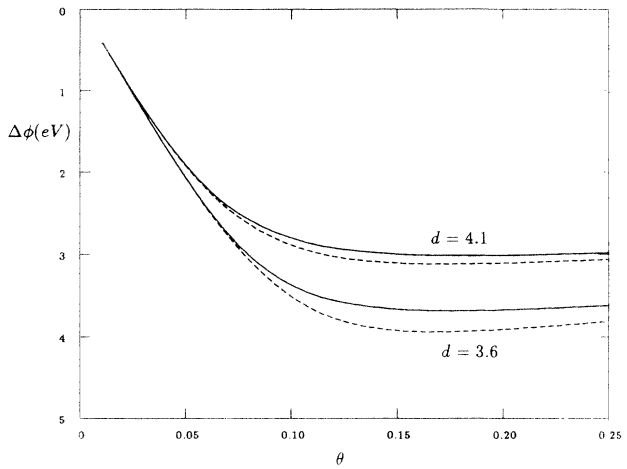

FIG. 2. Drop of the effective work function $\Delta\phi$ as a function of the coverage θ for the system K/Cu(100) (see the text). Solid lines are the results with the randomness effect, while the dashed lines are the results from the standard Muscat-Newns (Refs. 7, 9, and 14) model. The upper pair of curves correspond to the adatom distance from the image plane $d = 4.1$ and the lower to $d = 3.6$.

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