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Dependence of work function on the order-disorder phase transition in chemisorbed layers

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The effect of the order-disorder phase transition in chemisorbed layers on the change of work function is studied within the tight-binding approximation. Charge transfers are calculated using the first terms in a continued-fraction series for the electronic Green's function. A sizable decrease in the work function with respect to the disordered phase at a given coverage is found. This leads to a minimum in the work-function versus coverage curve not found for the random nonequilibrium distribution.

I. INTRODUCTION

It is a well known fact that chemisorbed gases may form ordered surface structures which depend upon the nature and concentration of the adsorbed species and upon the orientation and nature of the crystal substrate.[1,2] It is expected that the formation of ordered surface structures play an important role in heterogeneous catalysis since the potentials of sites available for chemisorption would change as a function of the degree of order at the surface. Low-energy-electron-diffraction (LEED) experiments have shown ordered structures for H and alkali metals adsorbed on metallic substrates.[1] In such systems the bond between adatom and substrate is predominately ionic and the ad atoms are partially polarized through a transfer of electronic charge to the substrate.

Order-disorder phase transition at the surface of binary alloys and on chemisorbed layers have been studied recently.[3-6] In this paper we study the effect of ordering on the change in work function produced by the substrate-adsorbate dipole layer. Here, we show that the ordered structure lowers the repulsive electrostatic interaction between adatoms by increasing the distance between ions of the same sign. At the same time the overlap between adatoms is reduced causing a strong decrease in the bandwidth. These effects lead to an increase of the charge transfer and ionicity of the surface bond. We find a sizable decrease in the work function with respect to the disordered arrangement of adatoms at a given coverage leading to a minimum in the work function versus coverage curve not found for the random nonequilibrium distribution.[7]

In Sec. II we present the model to treat order-disorder effects on the work function. The calculations are presented in Sec. III. Our results are given in Sec. IV and discussed in Sec. V.

II. MODEL

We will study here only the simple case of alkali-metal adsorption on noble-metal surfaces. Similar qualitative behavior can be expected for transition-metal surfaces. We use the single-band tight-binding model which is well suited to describe changes in local environment on the surface. The Hamiltonian for the layer of N_A atoms of metal A on the surface of metal B containing N atoms is then

$$H=\sum_{i} \epsilon_i |i\rangle\langle i| + \sum_{i\neq j} t_{ij} |i\rangle\langle j| . \tag{1}$$

Here $|i\rangle$ is the Wannier state of a given spin at a site i. The single-site energies ϵ_i depend on the type of atom located at the site i and include Coulomb interactions between electrons located on the same site as well as Coulomb interactions between charges located on different sites in the Hartree approximation[8]

$$\epsilon_i = \epsilon_i^0 + U_0 \Delta n_i + 2 \sum_{j\neq i} V_{ij} \Delta n_j . \tag{2}$$

Here ϵ_i^0 is the single-site energy for the pure metal atom. U_0 is the value of the interatomic interaction, whereas V_{ij} is the Coulomb interaction between electrons on different sites. The hopping term t_{ij} allows electrons to overlap between different sites and form bands. The adatoms can give or accept electrons of the substrate thereby changing the number n_i of electrons on a site by $\Delta n_i = n_i - n_i^0$, n_i^0 being the valence of the metal atom A or B sitting on the site in question. A charge $2e\Delta n_i$ is found then on i. We simplify the model by considering coverages $\theta = N_A/N$ in the vicinity of $\theta = 0.5$ and adsorption of adatoms in the top position only of a simple cubic lattice (Fig. 1). An ordered $c(2\times 2)$ structure can then by simulated by dividing the lattice plane into an α and β sublattice such that each α site is surrounded by β sites and each β site by only α sites.[9,10] We then assign the same value of charge transfer Δn_A^α to the adatoms on the α sublattice and Δn_A^β to adatoms on the β sublattice. Similarly Δn_I^α is the charge on the site of the first plane of the substrate immediately below the α-adatom site and Δn_I^β below the β site. In the second and

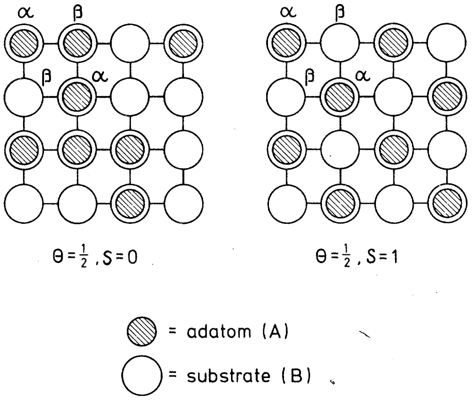

FIG. 1. Illustration for the chemisorption of N_A adatoms A on the top position of N substrate atoms B, the coverage is $\theta=0.5$. (a) Disordered phase ($S=0$); (b) ordered phase ($S=1$).

lower planes of the substrate the requirement of charge neutrality within the metal prevents charge transfer within the bulk. In the disordered state of the adatom layer, α and β sites are occupied with equal probability. At temperatures below the order-disorder transition temperature, α sites are preferred over β sites. We introduce the long-range order parameter S to define the probability P_α (P_β) to find an α (β) site occupied by an adatom:

$$P_\alpha=\begin{cases}\theta(1+S) & \text{for } \theta\leqslant 0.5\ ,\\ \theta+(1-\theta)S & \text{for } \theta\geqslant 0.5\ ,\end{cases}$$
$$P_\beta=\begin{cases}\theta(1-S) & \text{for } \theta\leqslant 0.5\ ,\\ \theta-(1-\theta)S & \text{for } \theta\geqslant 0.5\ .\end{cases} \tag{3}$$

The disordered state is defined by $S=0$, the completely ordered state by $S=1$. In the case of half-coverage, in the completely ordered phase ($S=1$) all chemisorbed atoms are on the α sublattice and all β sites are unoccupied. This corresponds to the $c(2\times2)$ structure[1] [Fig. 1(b)]. If $S=0$ (the complete disordered phase) there are as many chemisorbed atoms on α sites as on β sites [Fig. 1(a)]. Values of S between 1 and 0 correspond to intermediate degrees of order. We can now study the charge transfer as a function of the order parameter S in the vicinity of $\theta=0.5$.

III. CALCULATIONS

We calculate the number of electrons assigned to a site i from the local electronic density of states $N_i(E)$:

$$n_i=\int^{E_F} N_i(E)\,dE\ . \tag{4}$$

The density of states is obtained from the single-site electronic Green's function $G_{ii}(E)$,

$$N_i(E)=-(1/\pi)\,\mathrm{Im}\langle G_{ii}(E)\rangle \tag{5}$$

where $\langle\ \rangle$ denotes the ensemble average over adatom configurations and

$$G_{ii}(E)=1/(E-\epsilon_i-\Delta_i)\ . \tag{6}$$

The electronic self-energy Δ_i results from hopping of electrons between sites and is calculated from the expansion[11,12]

$$\Delta_i=\sum_{j\neq i}\frac{t_{ij}t_{ji}}{E-\epsilon_j-\Delta_j^i}+\cdots\ . \tag{7}$$

Here Δ_j^i includes only hops from site j which avoid i:

$$\Delta_j^i=\sum_{l\neq i,j}\frac{t_{jl}t_{lj}}{E-\epsilon_l-\Delta_l^{ij}}+\cdots\ , \tag{8}$$

where similarly sites i and j are avoided in Δ_l^{ij}. We simplify by neglecting the higher-order terms in the expansion and closing the set of equations by use of[13] $\Delta_l^{ij}\simeq\Delta_l^j$. These approximations give results for the density of states comparable to the coherent-potential approximation and moment methods in the case of alloys and alloy surfaces.[14] To obtain the ensemble average over adatom configurations we make use of

$$\langle G_{ii}(E)\rangle=P_\alpha(E-\epsilon_A-\Delta_{A,\alpha})^{-1}+P_\beta(E-\epsilon_A-\Delta_{A,\beta})^{-1}\ ,$$

and similarly for Eqs. (7) and (8). These approximations are justified in a calculation of charge transfers which do not depend sensitively on the exact shape of the density of states.

We restrict to nearest neighbor hopping and study the three uppermost layers in detail. In our model we then have five self-energies to calculate from (7) and (8): $\Delta_{A,\alpha(\beta)}$ for an adatom α (β) site, $\Delta_{\mathrm{I},\alpha(\beta)}$ for an atom of the first layer just below an α (β) site, and Δ_{II} for atoms in the second layer. The value of the single site energy also depends whether the site is of α or β type because of the charge transfer and resulting electrostatic interaction with neighboring sites.[10] In the tight-binding method this leads to a shift of the bands relative to the neutral state. For A atom an α site in the adatom layer we find

$$\epsilon_{A,\alpha}=\epsilon_A^0+U_0\Delta n_A^\alpha+P_\alpha\Delta n_A^\alpha 2e^2\sum_{A'\ \mathrm{on}\ \alpha}\frac{1}{r_{AA'}}+P_\beta\Delta n_A^\beta 2e^2\sum_{A'\ \mathrm{on}\ \beta}\frac{1}{r_{AA'}}+\Delta n_I^\alpha 2e^2\sum_{B\ \mathrm{on}\ \alpha}\frac{1}{r_{AB}}+\Delta n_I^\beta 2e^2\sum_{B\ \mathrm{on}\ \beta}\frac{1}{r_{AB}}\ , \tag{9}$$

and similarly for β sites and for sites of the B-metal surface just below the α and β sites. P_α and P_β are the probabilities defined in Eq. (2). $\epsilon^0_{A(B)}$ are the values of the single-site energies for the pure metals A (B). The lattice sums $\sum(1/r_{ij})$ in the point-charge approximation are calculated with Ewald summation techniques.[15] The first two sums in Eq. (8) are the contributions coming from the adatoms on α and β sublattices at distance $r_{AA'}$ from the adatom A. The last two are the contributions coming from the substrate B-type atoms situated below α and β sites, at distance r_{AB} from the A atom.

Below the first layer of B metal, charge neutrality requires that for monovalent metals the center of the local density of states remains pinned to the Fermi energy.

Combining (7), (8), and (9) we find the self-energy of an α site in the adatom layer to be given by

$$\Delta_{A,\alpha} = Z_0 \frac{P_\beta t^2_{\alpha\beta}}{E-\epsilon_{A,\beta}-\Delta^{A,\alpha}_{A,\beta}} + Z_1 \frac{t^2_{\alpha I}}{E-\epsilon_{I,\alpha}-\Delta^{A,\alpha}_{I,\alpha}} \tag{10}$$

and

$$\Delta^{A,\alpha}_{A,\beta} = (Z_0-1) \frac{P_\alpha t^2_{\alpha\beta}}{E-\epsilon_{A,\alpha}-\Delta^{A,\beta}_{A,\alpha}} + Z_1 \frac{t^2_{\alpha I}}{E-\epsilon_{I,\beta}-\Delta^{A,\beta}_{I,\beta}} \ . \tag{11}$$

Here Z_0 denotes the number of nearest-neighbor sites lying also in the chemisorbed layer and Z_1 is the number of nearest-neighbor atoms in the first layer. ($Z_0=4$ and $Z_1=1$ for a simple cubic lattice.) The adatom disorder is accounted in the probabilities P_α and P_β. Note that $\Delta^i_j \equiv \Delta^{A,\alpha}_{A,\beta}$ if i and j refer to atomic sites on the α and β sublattice of the chemisorbed layer. Similarly, $\Delta^i_j \equiv \Delta^{A,\alpha}_{I,\alpha}$ if i refers to an α site of the chemisorbed layer and j to a site in the first substrate layer just below an α site. $t_{\alpha\beta}$, $t_{\alpha I}$, and $t_{\beta I}$ are the hopping integrals between states centered on α and β sites, on α sites and first layer and on β sites and first layer, respectively.

The equations for the other self-energies follow by analogy. These equations are solved simultaneously and the charge transfer is calculated self-consistently from the resulting density of states. Charge conservation puts a further requirement on the charge transfers which must fulfill the condition

$$P_\alpha \Delta n^\alpha_A + P_\beta \Delta n^\beta_A = -(\Delta n^\alpha_I + \Delta n^\beta_I) \ . \tag{12}$$

IV. RESULTS

The calculations were performed for a system of two monovalent metals of equal s-bandwidth $2W$. Nearest-neighbor hopping was assumed to have the same value between all neighboring sites and was estimated from the bandwidth of the pure metals. The single-site energies ϵ^0_i of the neutral metal atoms can be approximated by the Fermi energies in the pure metals and the relative positions obtained from the contact potential or from the difference in work functions. We have used $(\epsilon^0_A - \epsilon^0_B)/W = 0.1$ and $U_0/W = 1.0$ for the intra-atomic Coulomb interaction.

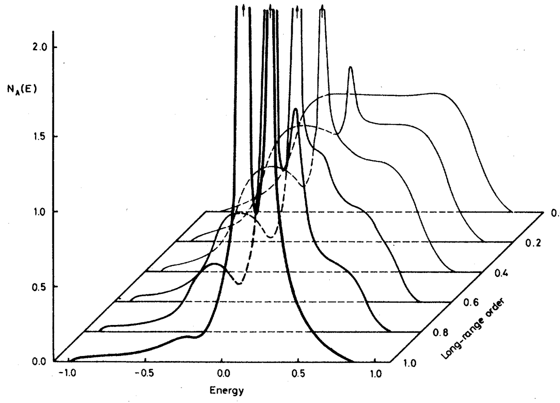

FIG. 2. Average local density of states on a site in the chemisorbed layer for different degrees of order. We used $\theta=0.5$, $\delta=(\epsilon^0_A-\epsilon^0_B)/W=0.1$, and $U_0/W=1.0$. The energy is given in units of half-bandwidth W.

In Fig. 2 we show the local electronic density of states on the adatoms averaged over α and β sites: $N_A(E) = P_\alpha N^\alpha_A(E) + P_\beta N^\beta_A(E)$ for $\theta = 0.5$ and various values of order parameter S. The decrease in bandwidth and the formation of bonding and antibonding peaks are typical of a decrease in the number of nearest neighbors. This causes a slight shift to higher energies of the Fermi energy. The average density of states of the first layer of the substrate is less effected by ordering as shown in Fig. 3 since most of the bandwidth comes from interactions with neighbors in the bulk metal which

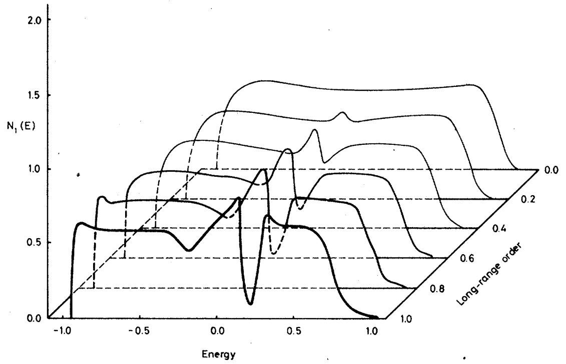

FIG. 3. Average local density of states on a site in the first substrate layer for different degrees of order. The parameters used are the same as in Fig. 2.

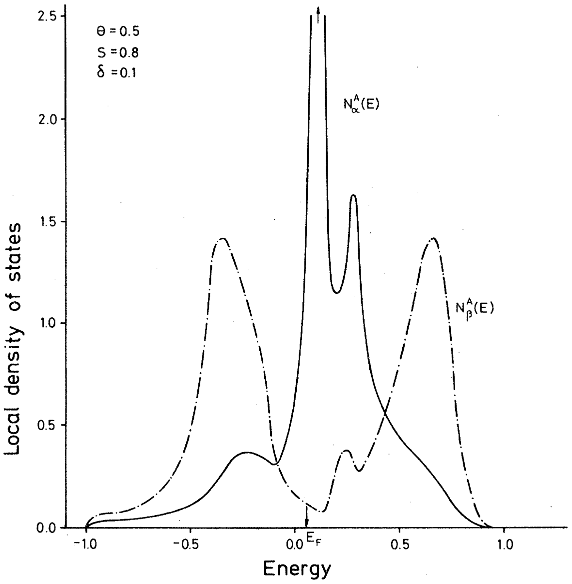

FIG. 4. Local density of states on α and β sites of the chemisorbed layer. The Fermi energy is marked by the arrow. We used $\theta = 0.5$, $S = 0.8$, and $\delta = 0.1$.

masks effects due to changes in the configuration of the adatoms. In Fig. 4 we show the local density of states on α and β sites of the adatom layer for $S = 0.8$, $\theta = 0.5$, and $\delta = (\epsilon_A^0 - \epsilon_B^0)/W = 0.1$. The local density of states on sites in the first substrate layer below α and β sites are shown in Fig. 5. The parameters used are the same as in Fig. 4. In Fig. 6 we plot the average charge on the adatom layer $2e\theta\,\Delta n_A = 2ep_\alpha\,\Delta n_A^\alpha + 2ep_\beta\,\Delta n_A^\beta$ in units of electronic charge. This quantity is positive and increases quadratically with increasing order so that the adatoms obtain a progressively larger value of ionic charge. We also show the charge on an α site $2e\,\Delta n_A^\alpha$ and on a β site $2e\,\Delta n_A^\beta$. The ions on adatoms α sites are always positively charged but it is interesting to note that for increasing order in the adatom layer the charge on a β site changes sign and becomes negative. At high values of S the β sites are occupied with small but nonvanishing probability and it is then possible to obtain both electropositive and electronegative states of the adatoms. On the other hand, the average charge $2e\Delta n_{\rm I} = e\Delta n_{\rm I}^\alpha + e\Delta n_{\rm I}^\beta$, the charge on sites in the first layer below α-sites $2e\Delta n_{\rm I}^\alpha$ and below β sites $2e\Delta n_{\rm I}^\beta$ as well as 1 remain negative independent of the order present in the adatom layer. This is also shown in Fig. 6. To illustrate the dependence of the charge transfer on converage we have carried out calculations for $\theta = 0.4$, 0.5, and 0.6 and various values of order parameter. [In the random situation ($S = 0$) the charge transfer was calculated in all the coverage range.[7] For low and high coverages and $S \neq 0$ the charge transfer is extrapolated.] The results are shown in Fig. 7. A maximum in the charge transfer appears as the adatom layer approaches a completely ordered structure. For $\theta = 1$ only an ordered adatom structure is possible and the charge transfer must reach the saturation value of monolayer coverage. At $\theta = 0$, $\theta\Delta n_A = 0$. The resulting change in work function due to adsorption on the surface is found from the potential drop through the dipole layer

$$\Delta\phi = 4\pi e^2 (2\theta\Delta n_A d)\nu_s \,. \tag{13}$$

Here d denotes the distance of the adatoms to the first layer of the substrate and ν_s being the number density of ions on the substrate layer. Disre-

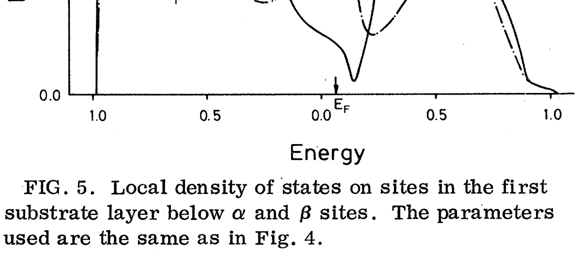

FIG. 5. Local density of states on sites in the first substrate layer below α and β sites. The parameters used are the same as in Fig. 4.

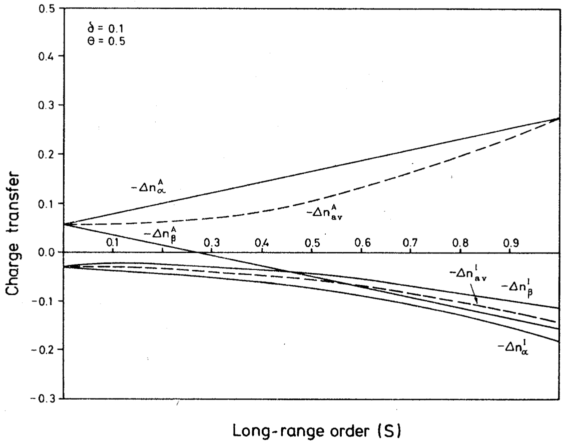

FIG. 6. Charge transfers per site and per spin in units of electric charge e. Δn_α^A, Δn_β^A, and $\Delta n_{\rm av}^A$ refer to the charge transfer on chemisorbed atoms sitting in α sites, β sites, and average sites, respectively. $\Delta n_\alpha^{\rm I}$ and $\Delta_\beta^{\rm I}$ refer to the charge transfer on sites in the first substrate layer below α and β sites; $\Delta n_{\rm av}^{\rm I}$ is the average charge transfer in the first layer.

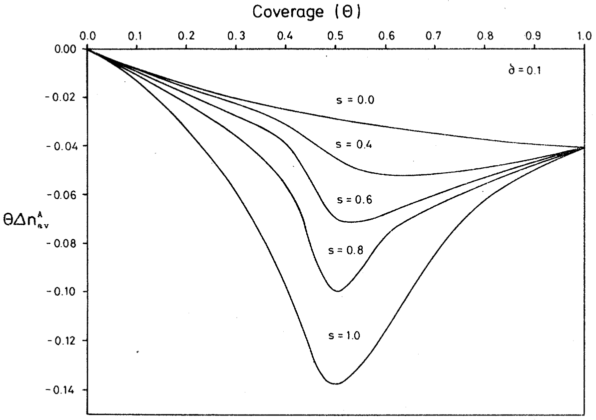

FIG. 7. Coverage dependence of the work function difference (units of electronic charge e) for various degrees of order. We used $\delta = 0.1$.

garding for the moment a possible decrease in d with coverage due to increasing charge transfer, $\Delta\phi$ will also follow the θ dependence of Fig. 7. A minimum in the work function as a function of coverage[16] signals then the appearance of an adatom phase of highest possible order for adsorption on a given crystal plane, allowing much higher values of charge transfer than would be otherwise possible. This would explain the absence of a minimum for work function measurements performed before the thermal equilibrium distribution on polycrystalline samples where presumably no long-range order can be achieved.[18]

As suggested by Klemperer,[19] this would also explain why the work-function-coverage curves during Ce deposition on tantalum carbide show a minimum when Ce^+ ions were used and no minimum when Ce atoms were used,[20] assuming that charge transfer is relatively slow in this system. In this case, an overlayer of Ce^+ will be ordered, whereas an overlayer of Ce atoms will be disordered until they get charged.

V. DISCUSSION

Many different ordered structures are possible for adsorption on a given crystal plane and it would be of interest to calculate the spatial distribution of adatoms self-consisently for all coverages. For example, LEED data[21] for Na adsorption on Ni(100) suggests the existence of uniformly spaced adatoms with a complete monolayer at $\theta = 0.5$. On the (110) surface various ordered structures are formed as the coverage is increased. Unfortunately not all such distributions can easily be described within the model presented here, mainly in the low coverage limit where it has been found that in some cases the chemisorbed atoms try to form islands.[22] In this case a better description of the order would be achieved by the short-range order. The island dissolution will be studied in a future publication.

An effect of charge transfer would be to reduce the distance d of the adatom to the surface due to the increasing Coulomb attraction. This would lead to greater overlap of the adatoms and the substrate and wider adatom bands than obtained for fixed values of d. Somewhat smaller values of charge transfer will be the consequence. This will also be the result of a more careful study of dielectric screening effects which reduce the values of the bare interatomic Coulomb interactions.[23] We have neglected the difference in nearest-neighbor distance and therefore of hopping integrals of the pure substances A and B. For the simple systems studied here this is of minor importance and we simply note that small values of nearest neighbor hopping between adatoms encourages charge transfer. In substrates of transition metals with narrow d bands,[24] the dependence of hopping integral on position, orbital and crystal symmetry will be much more sensitive and require a more careful study than is possible within our simple model. We can point out though that the screening of s electrons by d electrons on the same site will diminish the tranfer of charge and weaken the bond between adatoms and substrate. A study of this question would require a self-consistent calculations of the charge transfer below the first layer.[25,26] In any case, the neglect of perturbation beyond the second layer should not be serious. From calculations within the jellium model, we expect charge neturality already within the second layer as we have assumed here.

The charge-transfer values obtained here are of the same order of magnitude as in the jellium model of alkali adsorption.[16] This model cannot distinguish between ordered and disordered phases but permits a self-consistent calculation of the equilibrium electronic charge distribution. A minimum in the work function occurs as suggested by the earlier ideas of Langmuir[27] when the decrease in the dipole moment, due to depolarization by the other dipoles on the surface, is balanced by the increase in the number of adsorbed atoms. In contrast, the charge transfers obtained here do not decrease steadily with increasing coverage but show a maximum at that coverage for which an ordered adatom phase exists with maximum distance between like charges.

In summary, we have shown that ordering in the adatom layer increases the charge transfer by lowering repulsive Coulomb interactions between the adatoms. This assists the indirect interactions[28,29] between adatoms mediated by the substrate in creating ordered adatom phases. In the completely ordered or completely disordered phases only positively charged adatoms are found. For small deviations from complete order, we find that the state of adatoms can be electropositive or electronegative depending whether the adsorption site corresponds to the ordered structure or not. This would qualitatively explain results on adsorption of H and Pt where it is found that H can be adsorbed in both the electropositive α as well as the electronegative β state.[30] Finally we have shown that an ordered adatom phase can be cause of the minimum in the work function with coverage when a transition metal is covered by a layer of alkali metal.

It would be of interest to also study the effect of adatom ordering on magnetic properties of the covered transition metal surfaces[30,31] and to extend this work to alloys.

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