Coverage Dependence of Charge Transfer Between Cs Overlayer and 5*d* Transition Metal Subtrates

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A recently developed embedded cluster scheme is applied to study the coverage dependence of charge transfer between Cs and the (001) surface of all 5d transition metals, which agrees with the jellium-slab model calculation given by the first principle band method. The correlation between the initial drop of work function during cesiation caused by this charge transfer and the unfilled d band of the substrates is revealed

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By using the linearized augmented planewave method and jellium on slab model, Wu *et al.* have investigated the submonolayer adsorption properties of alkali-metal on transition metal substrates.[1] Some general conclusions are drawn from their studies: at low coverage polarization of overlayer electrons toward the substrate is governed by certain localized surface states which hybridize with the overlayer states to some extent; beyond a critical coverage(θ_c) the electron starts to fill the adsorbate states and the overlayer becomes gradually metallized. This critical coverage characterizes the ability of the hybridized surface state to hold extra electrons. However, the jellium model is often debated and cited questionablly in describing the low coverage limit adsorption due to the obvious difference between the model and the physical system.[2]

Very recently, we have developed a semi-empirical embedding cluster scheme to study the alkali metal adsorption on the metal substrate.[3] In our cluster formulation, a bounded planewave basis is introduced to describe the free electron states of the metal substrate while the *d* electron is still represented by the atomic orbitals. In addition, effects from the dangling *d* bonds at the cluster boundary are removed away by a projection technique. Such treatment gives a correct description of the surface electron states and charge transfer in the metal adsorption systems. In this paper, it is applied to study the coverage dependence of the charge transfer between Cs overlayer and 5*d* transition metal substrates. The results given by the cluster model thus provide a comparison and an extension to the jellium-slab model.

To study the coverage dependence of submonolayer Cs adsorption on metal surfaces, explicit geometry of the overlayer is required. A hypothetic structure is used in all calculation. The whole cluster is represented by a Cs_5M_{25} with one Cs atom at the center site and 4 additional Cs atoms sitting on the corners of a square around the center one as shown in Fig. 1. The overlayer coverage is changed by varying the distance between the center and the corner Cs atoms. The center cluster, in which the electron population analysis is made, is chosen as a cubic structure with a surface area equal to the 2 dimensional Wigner-Seitz(WS) cell of the overlayer and a thickness including the atoms in the first two layers of the substrate. A substrate atom is partitioned to different

WS cell of the overlayer according to the overlap between the substrate unit cell and the overlayer WS cell. The center cluster therefore consists of one Cs atom (i.e., one WS cell) and a sum of a few partitioned substrate atoms in first and second layers. The determination of the Fermi level E_f is reformulated as:

$$\sum_i r_i N_i = \sum_i \int_{-\infty}^{E_f} dE\, r_i \rho_i(E) \quad , \tag{1}$$

here $r_i = A_{ai}/A_{WS}$, A_{WS} is the area of the overlayer WS cell (the larger hatched area in Fig. 1 for $\theta = 0.25$), A_{ai} is the overlap between the WS cell and the surface unit cell around substrate atom i (the smaller doubly hatched area), N_i is the total number of valence electrons for atom i and $\rho_i(E)$ is the corresponding local density of states.

The interatomic matrix element given by Harrison can not be directly used to describe the Cs-Cs interaction in the overlayer, because the d^{-2} scaling law for the interaction is only valid near the equilibrium distance. Theoretical analysis predicts a d^{-5} dependence of RKKY type interaction between two adsorbates at surface.[4] In this calculation, we have used an exponential scaling from the viewpoint of quantum chemistry, i.e.,

$$H_{ij}(r) = V_{ij}(d_0)e^{-(r-d_0)\xi} \quad , \tag{2}$$

where d_0 is the equilibrium distance of the cesium crystal and $\xi = 1.06$ is the orbital exponent of Cs: 6*s* atomic wave function. Furthermore $V_{ij}(d_0)$, the hopping integral at the equilibrium distance, is adjusted from the original Harrison parameter (0.39 eV) to 0.16 eV in order to reproduce the correct valence band width 3.2 eV.

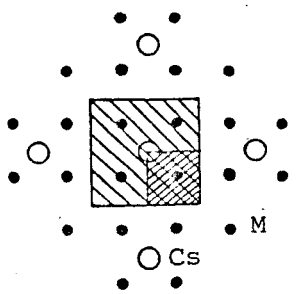

Fig. 1 Schematical structure of cluster of a submonolayer coverage (θ=0.25) for Cs on the (001) surface of a bcc or fcc metal (M).

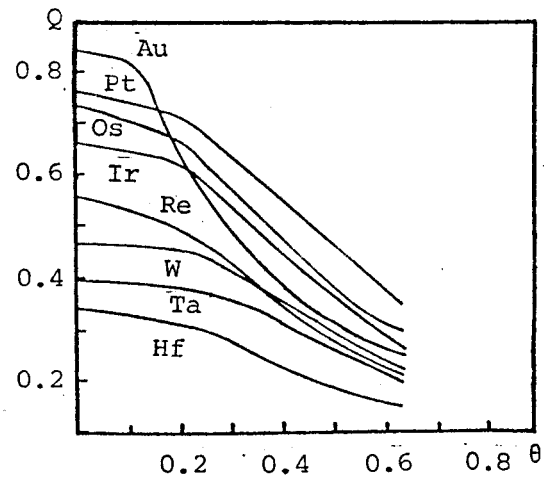

Fig. 2 Charge transfer Q vs coverage $\theta = N_a/N_s$ for Cs on the 5*d* transition metal surface, N_a, N_s are the atomic density of the overlayer and the substrate respectively.

In addition to the earlier treatment, charge self-consistency[5] to simulate electron correlation during charge transfer is adopted in the present calculation. Each level is adjusted according to its electron occupation number of that level. The adjustment is determined by a linear interpolation between atomic and ionic levels. Furthermore, the depolarization fields of the surface dipole layers is also introduced.[6] The diagonal element of the adsorbate level is therefore written as,

$$H_{ii} = -I_i + Q_i \alpha_i + e^2/4d + H_i(\theta) \quad , \tag{3}$$

where the second term comes from charge self-consistency, Q_i is the charge transfer on orbital i and α_i is the difference between the atomic and the ionic levels, e.g., for 6*s* of Cs, α_i=3.2 eV. The third term is the image potential and the last one is the depolarization field. For the substrate orbitals, only the first two terms in Eq. (3) are applied.

The calculated charge transfer vs coverage for Cs adsorption on the (001) surface of Ta, W, Ir, Pt, Au and the (0001) surface of Hf, Re and Os are given in Fig. 2. Quite similar feature is shown by all curves: at lower coverage, there is a relatively flat region where the charge transfer varies slightly with the coverage; beyond this region, the charge transfer drops rapidly and the overlayer is metallized. A critical coverage θ_c is seen for each system, which marks the beginning of the metallization in the overlayer. The flat region shows that continued adsorption of Cs atom donates almost the same amount of electron to adsorption bonding in a certain range of coverage (polarization region). It is found from the electron population that in this region, the transferred electrons from Cs are mainly populated on the hybridized surface *d* states due to strong interaction between the adsorbate and shown in Fig. 2, is wider for Cs on Hf, Ta, W($\theta_c = 0.25 \sim 0.3$), slightly narrower on Ir, Pt, Os(θ_c=0.20), and much narrower on gold (θ_c=0.12) surfaces. This is resulted from the fact that the unfilled surface states on the Hf, Ta, W, Os, Ir, Pt, substrates are much more abundant than those on the Au(001) surface, and therefore they are able to absorb more electrons from the adsorbate. The results in Fig. 2 coincide very well with the adsorbate induced dipole moment $p(\theta)$ given by the jellium-slab model for Cs on the (001) surface of Ta, W, Ir, Pt and Au (Ref. 1). It shows the general feature of the interaction between alkali-metal overlayer and transition metal substrate, although it is not so prominent on the Cs/Re(0001) system.

The charge transfer at (θ=0) for Cs on all 5*d* metals is plotted in the upper panel of Fig. 3, while the work function (experimental) and its derivative[1] are given in the lower panel. It is shown in Fig. 3 that electron transfer from Cs to the substrate ranges from 0.34 on Hf(0001) to 0.84 on Au(001) and increases with the number of *d* electrons of the substrate. This trend agrees quite well with the calculated work function derivative given by the first principle method[1] as shown also in Fig. 3. The work function of the clean metal surface also exhibits similar tendency. Since the work function is used as an input parameter[3] in the determination of the *d* band center E_d, larger work function means lower *d* band, and thus stronger charge transfer. The results in Fig. 3 show that such a choice of matrix elements is reliable in semi-empirical calculation.

It can be inferred from Figs. 2 and 3 that work function change of the adsorption system is determined by two major identities, i. e., the difference between the ionization potential of the adsorbate and the work function of the substrate as well as the surface electron states. The large difference in ionization potential favors the initial charge transfer, while the rich surface states lead to a wider polarization region and hold more extra electrons and thus lead to a greater work function decrease.

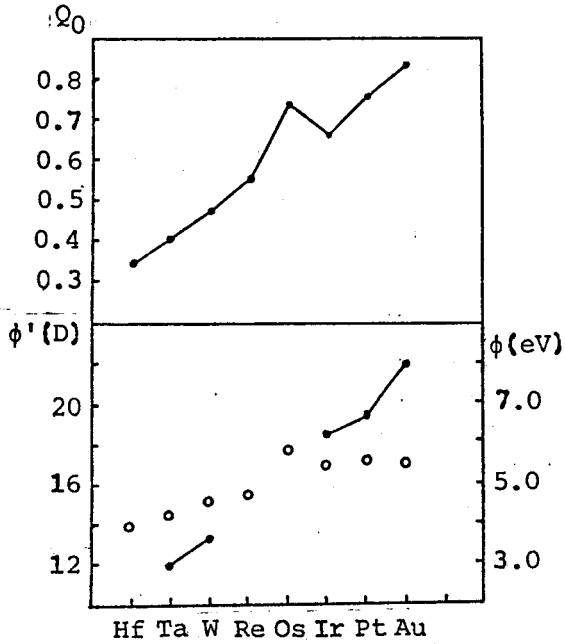

Fig. 3 Upper panel: The initial charge transfer Q_0; Lower panel: The experimental metal work function (circle) and calculated initial work function derivatives (solid curve).

By comparing Fig. 2 with the $P(\theta)$ curves given by the jellium-slab model,[1] it is found that there exist some differences. This is because different quantities (Q and P) are concerned in the two calculations and they are not exactly equivalent. In addition, in the estimation of the length of the dipole moment, we simply let it, referring to other selection,[6] equal to the adsorption height (5.0 a. u.) of Cs atom and remain unchanged for all 5*d* substrates and for all coverages.

The above calculation for coverage dependence of charge transfer for Cs on 5*d* transition metal substrates, which is also valid for other alkali overlayer, provides an evidence that the jellium description for the alkali metal overlayer is tractable even at low coverages. It may be explained as follows: at the low coverage limit, alkali-metal electrons are strongly polarized or transferred to the substrate and the interaction between adsorbates is not important, at least, for determining the nonlocal properties. The surface electron band is dominantly determined by the metal substrate potentials and is therefore insensitive to the structure of the overlayer even at low coverages.

The results given above show that the present embedding cluster scheme does provide a simple and efficient way in studying the interaction and charge transfer in a chemisorption system. We expect this type of study to be extended to even more complicate adsorption systems.

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