

Cesiation of W(001): Work Function Lowering by Multiple Dipole Formation

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Rigorous, self-consistent, all-electron, full-potential linearized augmented plane wave studies reveal that the lowering of the W(001) work function upon cesiation arises from a complex multiple dipole formation mechanism: Essentially, Cs forms a metallic overlayer with its valence electrons strongly polarized and its $5p$ semicore shell polarized oppositely.

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Cesiated metal surfaces are important both for their prototypical properties and for their technological applications. Thus the lowering of the work function by the deposit of an overlayer of Cs on a metal surface like W, first discovered by Kingdon and Langmuir¹ in 1923 and still widely used in a host of experiments, has widespread applicability in such areas as thermionic conversion,² ion propulsion,³ and recently as negative hydrogen (deuterium) ion sources for magnetic fusion reactors.^{4,5} Despite its long history and obvious importance, the mechanism for the work-function lowering still remains a challenge for theoretical treatment—as does an in-depth understanding of the electronic structure so essential for optimization of negative H (or D) yields^{4,5} and for determination of thermionic conversion efficiencies.² Because of the complexity of rigorous calculations for this type of system, only calculations on a “jellium” model have been carried out to describe the work-function changes induced by alkali adsorption.⁶ Although these calculations give a qualitatively correct description of the work-function changes, important structures due to the atomistic nature of the surface and interface atoms are not included in these calculations. In particular, an understanding of the role played by the rich localized Wd surface states⁷ requires a more detailed description of the surface.

In this Letter, we present results of the first rigorous, fully self-consistent, all-electron calculation of Cs chemisorbed on a W(001) surface using our highly accurate full-potential linearized augmented plane wave (FLAPW) method for

thin films.⁸ The chemisorption process is characterized by comparing the results of independent self-consistent calculations for (1) a five-layer W(001) slab, (2) an unsupported Cs monolayer, and (3) Cs in a $c(2 \times 2)$ coverage on W(001) at distances ranging from 2.6 to 2.9 Å. We find that the reduction in the work function, Φ , upon cesiation, arises from a multiple dipole formation at the surface and interface layers. A characteristic feature of the clean W(001) surface is the pronounced spill-out of electrons from the surface layer into the vacuum which leads to the formation of a strong surface dipole. This surface dipole is reduced in the cesiated system: Cs forms a metallic overlayer with its valence electrons polarized toward the W surface, thus reducing the spill-out into the vacuum. Correlated with the polarization of the Cs valence electrons, the Cs semicore $5p$ electrons are markedly counterpolarized. Because of the strong metallic screening, changes in the electronic environment are localized to the Cs overlayer and the Cs/W interface layer. The net result of these polarizations is a reduction of the effective electrostatic surface barrier. As a result, all W states, and also the Fermi level, are shifted to smaller binding energies with respect to the vacuum and consequently the work function is reduced by 2.0–2.5 eV, depending on the Cs-W distance used.

Although crucial for determination of the lowering of the work function upon cesiation, there are no accurate experimental determinations of the distance between the Cs and W atoms. It is

therefore necessary to carry out the electronic structure studies for various assumed Cs-W distances. Since the lowering of Φ is greatest for reduced Cs coverage, we first study the $c(2 \times 2)$ coverage (which corresponds to one Cs atom per two W atoms) as the lowest coverage which is still computationally tractable (12 atoms per unit cell) for varying Cs-W separations. [The $p(2 \times 2)$ structure at which the minimum in Φ occurs⁹ requires 22 atoms per unit cell for a five-layer W substrate.]

In our FLAPW studies, we use the same W-W distances as in bulk W (lattice constant 3.161 Å) and distances between the planes of the Cs and surface W atoms which vary from 2.6 to 2.9 Å. In each iteration, the wave functions for each of the 19 k points in the irreducible wedge of the first Brillouin zone are expanded in about 2×450 LAPW basis functions. For the valence electrons all relativistic effects, except spin-orbit splitting, are taken into account. The core electrons are calculated fully relativistically in each iteration. Electronic exchange and correlation effects are treated within the local density functional formalism using the Wigner exchange-correlation potential. Self-consistency was assumed when the input and output potentials differed on the average by less than 1.5 mRy. (The eigenvalues had then converged to better than 0.1 mRy.)

Important to an in-depth understanding of the mechanism of the lowering of the work function is the spill-out of the electrons on a clean sur-

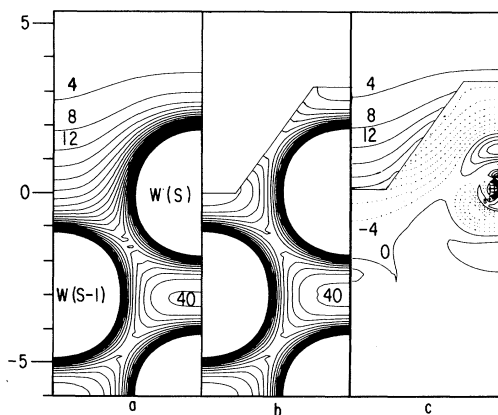


FIG. 1. Total charge density on (a) a clean W(001) surface, (b) an "ideal" surface, and (c) the difference between (a) and (b), showing the spill-out of electrons into the vacuum. The units are $10^{-3}e/a_0^3$. Dotted contour lines indicate loss of electrons. The vertical scale at the left gives the distance from the surface W atoms in atomic units.

face and the associated dipole layer which is modified and reduced upon cesiation. One way to monitor this dipole layer is a comparison of the calculated charge density [Fig. 1(a)] and that of an "ideal" surface formed by cleaving a bulk crystal along the boundaries of Wigner-Seitz cells without allowing any redistribution of the charge density. In our case we have constructed the ideal surface from the charge density in a Wigner-Seitz cell of the bulklike atoms in the center of the clean W(001) film [Fig. 1(b)]. The difference between the charge densities of the calculated and the ideal surfaces [Fig. 1(c)] reveals that the electronic environment of essentially only the surface atoms is affected by the spill-out of electrons into the vacuum. The electrostatic dipole barrier associated with the spill-out, shown in Fig. 1(c), is found to be 5.5 eV.¹⁰ The resultant Φ , 4.77 eV, of the five-layer W(001) slab agrees quite well with experiment (4.63 ± 0.02 eV); the Φ of an independent FLAPW calculation for a seven-layer W(001) slab (4.63 eV) gives excellent agreement with experiment.

Let us now focus on how the charge density at the W surface is modified upon cesiation since this will give us insight into the dipoles which counteract and reduce the original "spill-out dipole." To this end, we subtract from the total

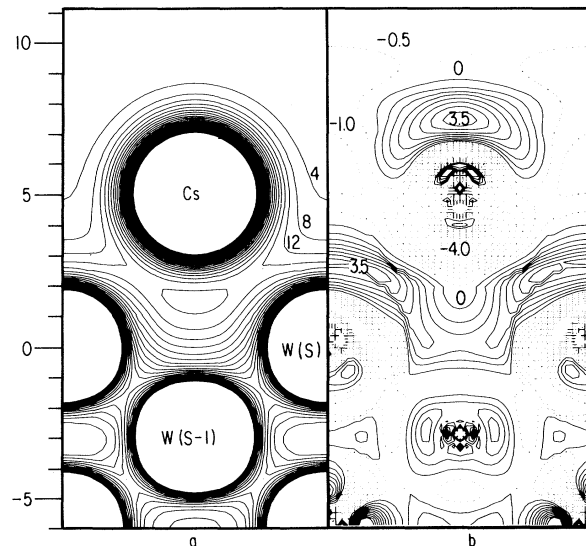


FIG. 2. (a) Total electronic charge density for Cs $c(2 \times 2)$ on W(001) and (b) the difference charge density between that of Cs/W and the superposed density of clean W(001) and a Cs monolayer (in units of $10^{-3}e/a_0^3$). The vertical scale at the left gives the distance from the surface W atoms in atomic units.

charge density of the cesiated W surface [Fig. 2(a)] the charge density of the clean W surface and the charge density of a Cs monolayer [with the same Cs-Cs spacings as in Cs $c(2 \times 2)$ on W]. The resulting charge-density difference [Fig. 2(b)] reveals the charge redistribution upon cesiation. Two main effects become obvious: (1) a loss of electrons in the region between and outside the Cs atoms combined with a pronounced increase in electronic charge near the surface W atoms and (2) a dramatic polarization of the Cs $5p$ semicore electrons. Both effects are associated with the formation of dipole layers which influence the work function of the system. The region between and outside the Cs atoms is the domain of Cs valence electrons (originating in the bulk from the atomic $6s$ functions). Upon deposition of the Cs overlayer on the W surface, the Cs valence electrons are polarized towards the W surface leading to an increase of electronic charge in the interface region between the Cs and surface W atoms. An analysis of the projected density of states by atom type and orbital angular momentum for the clean and cesiated W surface reveals that the contribution from the surface W atoms remains the dominant component near the Fermi energy and that the Cs- d character of the states near E_F is greatly enhanced compared with that of an unsupported Cs monolayer. Together these observations indicate a polarized metallic bond with a tendency towards the formation of a covalent bond between Cs and the surface W atoms.

We are now in a position to understand the changes in the electrostatic potential induced by the cesiation of the W surface. This potential is most conveniently displayed in the form of the Coulomb potential averaged over planes parallel to the surface. In Fig. 3 (lower panel) we show this averaged potential for the clean (solid lines) and the cesiated (broken lines) W surface together with their corresponding Fermi energies and work functions for a Cs-W distance of 2.6 \AA . The analysis of these results shows that the Coulomb potential near the W atoms is shifted by almost the same constant amount (2.00 eV) by which the work function is reduced [$\Phi = 2.77 \text{ eV}$ for the cesiated W(001) surface]. This shift is caused by the change in the effective surface dipole layer: The polarization of the Cs valence electrons towards the surface W atoms gives rise to a dipole barrier which counteracts the original spill-out dipole and thus reduces the work function. By contrast, the dipole layer associated with the polar-

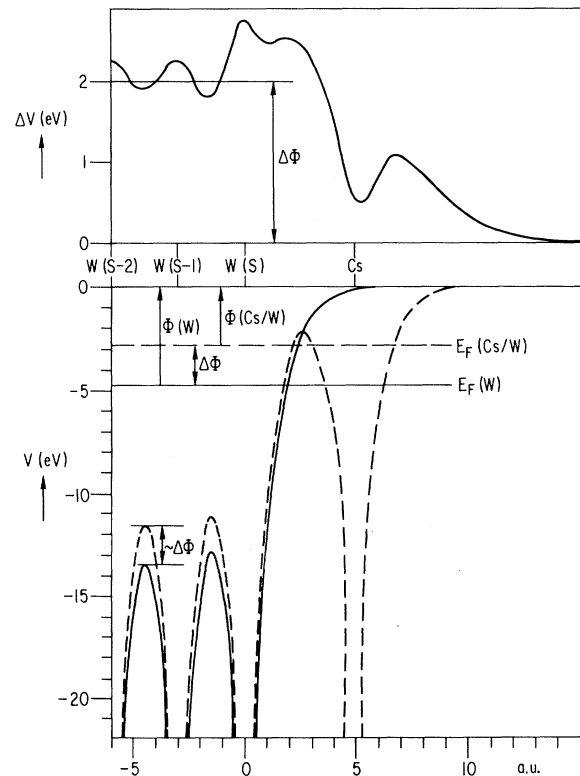


FIG. 3. Lower panel: Average Coulomb potential (\bar{V}), averaged in planes parallel to the surface, for the clean (solid lines) and cesiated (broken lines) W(001) surfaces. Top panel: $\bar{V}(\text{Cs/W}) - [\bar{V}(\text{clean W}) + \bar{V}(\text{Cs monolayer})]$. $\Phi(\text{W})$ and $\Phi(\text{Cs/W})$ denote the W and the cesiated-W work functions and $\Delta\Phi$ is their lowering.

ization of the Cs $5p$ semicore electrons acts in the same direction as the spill-out dipole and tends to increase the work function.

The resulting effect of these multiple dipole formations is a net reduction of the effective surface dipole and hence a lowering of the work function. The Cs-induced changes in the electrostatic potential, i.e., the formation of a dipole layer which counteracts the spill-out dipole, is shown in the upper panel of Fig. 3 in the form of the difference between the (planar-averaged) Coulomb potential of the cesiated system and the superposed Coulomb potentials of the clean W and the unsupported Cs monolayer. One observes clearly a dipole barrier due to the polarization of the Cs valence electrons and a superposed structure due to the Cs semicore $5p$ polarization. The net result is an almost constant shift by 2 eV inside the Cs/W interface region. Further, as found from independent self-consistent calculations for

increased W-Cs distances from 2.6 to 2.75 and to 2.90 Å, there is an increase of the spatial extension of the polarized Cs overlayer and hence an enhancement of the counteracting dipole. As a result the work function is further reduced to 2.55 and 2.28 eV, respectively.

In conclusion, these rigorous, self-consistent, all-electron, FLAPW studies have revealed in detail the complex nature of the multiple dipole formation mechanism by which the work function is lowered when a transition metal like W is cesiated. Unlike simple models, which ionize the Cs overlayer atoms by electron transfer into the W surface, Cs forms a metallic overlayer, which has its valence electrons strongly polarized and its 5*p* semicore shell dipole polarized oppositely. The charge redistribution is localized to the interface atoms and shows an enhancement of the electronic charge on the Cs side of the interface W atoms. The admixture of the directional character of Cs *d*-like charge and the persistent dominance of W *d*-like surface states near E_F indicates a tendency towards a covalent Cs(*s,d*)-W(surface,*d*) bond. Together, these effects reduce the effective surface dipole barrier and bring about the dramatic reduction in the observed work function.

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