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Charge transfer and positron states at alkali-metal-covered nickel surfaces

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We report calculations of the positron surface state on clean and alkali-metal- (Na,Cs) covered Ni surfaces. It is shown that the alkali adsorption increases the surface-state binding energy. With the lowering of the electron work function, this leads to positronium desorption energies which are weakly dependent on the alkali coverage, in agreement with the recent experiments of Gidley, Köymen, and Capehart. It is shown that the positron becomes mainly localized between the substrate and the overlayer, and that the lifetime is shorter for positrons on the alkali-metal-covered surface.

The interaction of positrons with solid surfaces gives rise to a host of fascinating phenomena, which have been under intensive detailed investigations during the last few years.[1] Like electrons, positrons can be bound to metal surfaces by "image" correlation interactions. However, in contrast with electrons, for which the long-range image-potential dominates and leads to a series of Rydberg-type levels, the positron surface state is critically dependent on the short-range "correlation well" in the proximity of the surface atoms. The bound state is the result of the interplay between repulsion from the surface ionic cores and the attractive electron-positron correlations just outside the surface. Ever since its introduction[2] to account for anomalously long positron lifetimes in metals containing large irradiation-induced voids, the description of the positron surface state has been the subject of several theoretical studies.[3−9]

The positron binding energies E_b to the surface state are experimentally[10] deduced from the activation energies E_a required to thermally desorb positronium (Ps) atoms from the surface:

$$E_a = E_b + \phi_- - B , \qquad (1)$$

where ϕ_- is the electron work function of the surface and $B = 6.8$ eV is the binding energy of a Ps atom in vacuum. The values of E_b obtained from experimental values of E_a and ϕ_- using Eq. (1) typically cluster around 2–3 eV for metals, with the exception that the alkali metals are not expected to support a stable surface state.[4] The most extensive and quantitative calculations[7] for the positron surface state are based on an image-potential model, which combines the atomistic nature of the potential with a matching of the short-range (local-density) correlation potential to the long-range (nonlocal, image) potential. These calculations have been successful in analyzing the appearance and the stability of the surface state, but the capability of the model to accurately predict the surface-state lifetime and angular correlation pattern is still a matter of debate.[8,9,11,12]

Recently, Gidley, Köymen, and Capehart[13] have undertaken a very interesting study of the positron surface state.

By adsorbing alkali metals (Li, Na, K, Cs) on well-characterized Ni surfaces they have systematically lowered the electron work function ϕ_- and measured the activation energies E_a. While the work function ϕ_- is lowered[14] by up to several eV with submonolayer coverages, Gidley, Köymen, and Capehart found surprisingly small reductions in E_a, with a typical E_a of around 0.7–0.8 eV diminishing to zero only at coverages near a physical monolayer. By Eq. (1), this indicates that the binding energy E_b to the surface state is increasing almost as fast as the electron work function is lowered. At first sight this would seem unexpected, and has prompted other, alternative models[9,13] for the surface state. These emphasize the composite nature of the surface state either as a "physisorbed" Ps atom or as a Ps$^+$ "ion," the binding and subsequent desorption of which is less sensitive to the underlying surface.

The purpose of the present paper is to show that the results of Gidley, Köymen, and Capehart[13] *are* consistent with the image-induced surface state model. Our calculation is based on the analogy with a steady-state chemical reaction, whose activation energy is calculated as the total energy difference between initial and final states. The latter is free Ps outside the surface and the former the system of metal electrons and surface positrons. The alkali-metal chemisorption leads to charge rearrangement and the well-known lowering of the electron work function by reducing the electrostatic surface barrier for electrons. The same effect also leads to an *increase* in the positron binding energy via a mechanism where the positron actually becomes localized in the region *between* the substrate and the alkali-metal overlayer. The increased stabilization of the positron surface state together with the decreasing electron work function result in an activation energy which is a weak function of the alkali-metal coverage, in agreement with the experiment.

The calculations are based on the three-dimensional atomistic approach,[7] where an effective potential $V^+(\mathbf{r})$ acting upon the positron is first constructed. This is then fed into a Schrödinger equation solved by numerical relaxation techniques. The boundary conditions imposed for

the computational unit cell assure that the positron is in the lowest-lying Bloch state parallel to the surface. The annihilation characteristics of the ground state can then be calculated from the positron and electron densities. The potential contains an electrostatic (Hartree) part $V_C(\mathbf{r})$ and a correlation component $V_{corr}(\mathbf{r})$:

$$V^+(\mathbf{r}) = V_C(\mathbf{r}) + V_{corr}(\mathbf{r}) . \qquad (2)$$

The correlation part is constructed by using the local-density approximation where $V_{corr}(\mathbf{r})$ becomes a function[15] of the electron density $n(\mathbf{r})$. Outside the surface, V_{corr} is joined to the image potential

$$V_{im}(\mathbf{r}) = -1/4[z - z_0(\mathbf{r})] , \qquad (3)$$

where z is the coordinate perpendicular to the surface and $z_0(\mathbf{r})$ defines the image surface. This is the corrugated-mirror model,[7] where the image potential is constructed to have the same constant value contours as the electron density outside the surface.

A simple yet reasonably accurate prescription[16] for $V_C(\mathbf{r})$ and $n(\mathbf{r})$ is based on the superposition of atomic Coulomb potentials and charge densities. This leads to a good representation[17] of the positron distribution inside bulk materials and in point defects of them. At the surface, however, the electrostatic potential differs somewhat from the atomic superposition which is reflected in the fact that the calculated positron ground-state-energy parameters E_∞ for bulk differ from the measured positron work functions ϕ_+: If the superposition were accurate throughout the crystal, one would have $E_\infty = -\phi_+$. One can mimic the additional dipolar effect by adding the missing step $\Delta V_0 = -\phi_+ - E_\infty$ in the potential construction. For clean surfaces, this is relatively unimportant as the properties of the surface state are largely determined by the depth of the correlation well, i.e., the position of the image surface. In the present case, however, it is exactly the *changes* in the dipolar potential in the surface region that determine the important trends. Consequently, we incorporate both ΔV_0 and the alkali-metal-induced change ΔD in the dipolar step into the electrostatic potential $V_C(\mathbf{r})$. In practice, this is done in the form of a ramp potential $V_{surf}(z)$:

$$V_C(\mathbf{r}) = V_C^{AS}(\mathbf{r}) + V_{surf}(z) , \qquad (4)$$

where AS denotes the atomic superposition and

$$V_{surf}(z) = \begin{cases} \Delta V, & z < z_1, \\ \Delta V(z - z_2)/(z_1 - z_2), & z_1 < z < z_2, \\ 0, & z > z_2. \end{cases} \qquad (5)$$

Above, $\Delta V = \Delta V_0 + \Delta D(\theta)$ is the surface dipolar step height dependent on the alkali-metal coverage θ. The coordinates z_1 and z_2 define the spatial extent of the surface dipolar barrier (see below). The atomic superposition approximation is used for the electron charge density. This is justified, as both the local-density correlation potential $V_{corr}(n(\mathbf{r}))$ and the rate function[18] $\Gamma(n(\mathbf{r}))$ are slowly varying functions of the density and thus not sensitive to small relaxations, in contrast with the electrostatic potential. The rate function appears in the expression for the annihilation rate λ:

$$\lambda = \int d\mathbf{r} |\psi_+(\mathbf{r})|^2 \Gamma(n(\mathbf{r})) , \qquad (6)$$

where $\psi_+(\mathbf{r})$ is the positron wave function. The core electron contribution to the annihilation rate is treated within the independent-particle model, with prefactors discussed in Ref. 17.

For a clean surface the charge rearrangement relative to the atomic superposition takes place primarily in the region just outside the topmost layer of atoms,[19] and thus a reasonable choice for z_1 is to coincide with the outermost plane (which we take to reside at $z = 0$). The value of z_2 corresponds to the extent of the electron density into the vacuum and is taken to be half the interlayer spacing. The value of $z_0 = 1.23$ Å (along the calibration line [100], see Ref. 7) is determined so that the experimental binding energy $E_b = 2.33$ eV for a *clean* Ni(100) (Ref. 20) is reproduced for the model with the added step. The step height ΔV_0 is -2.0 eV; this reproduces the observed[1] positron work function $\phi_+ = -1.3$ eV for Ni(100). The results for the binding energy and the annihilation lifetime $\tau = 1/\lambda$ are included in Table I, which shows that the inclusion of the additional step is relatively unimportant for the clean surface. This reflects the fact that the positron wave function primarily resides outside the surface. The influence of the surface dipole on the positron surface state has also been examined by Brown, Walker, and

TABLE I. Calculated properties of positron surface states on clean and alkali-metal-covered Ni(100) surfaces. θ is the coverage, ϕ_- the electron work function, and $\Delta V(\theta)$ the dipolar step at the surface [see Eqs. (4) and (5)]. E_b is the binding energy in the surface state and E_a the activation energy for Ps desorption. Two estimates are given for the lifetime: τ is the local-density result and τ_c includes the cutoff in the image-potential region (Ref. 8).

Adsorbate	θ	ϕ_- (eV)	ΔV (eV)	z_2 (Å)	E_b (eV)	τ (psec)	τ_c (psec)	E_a (eV)
Clean		5.22	−2.0	0.88	2.33	331	565	0.75
		5.22	0	· · ·	2.23	352	660	0.65
Na	0.125	2.5	−4.9	2.2	4.2	298	343	−0.1
	0.25	2.1	−5.3	2.2	4.2	307	343	−0.5
	0.5	2.9	−4.5	2.2	3.4	361	461	−0.5
Cs	0.125	1.6	−5.8	3.8	6.0	309	338	0.8
	0.25	1.6	−5.8	3.8	5.8	298	299	0.6
	0.5	1.9	−5.5	3.8	5.0	264	264	0.1

West,[21] employing a jellium model, with similar conclusions.

For alkali-metal covered surfaces, the dipolar heights $\Delta D(\theta)$ are directly obtained from the measured electron work-function changes.[13,14] Self-consistent slab calculations[22] for Cs on W and Mo have demonstrated that the change in the electrostatic potential associated with the charge rearrangement is concentrated in the region *between* the topmost substrate layer and the overlayer. Guided by this result, we position the dipolar step so that $z_1 = 0$ and $z_2 = z_a$, where z_a is the perpendicular distance of the chemisorbed layer.

We have performed calculations for Na and Cs on Ni(100) at coverages [defined relative to the Ni(100) surface atom density] of $\theta = 0.125$ [$c(4 \times 4)$ structure], $\theta = 0.25$ [$p(2 \times 2)$ structure], and $\theta = 0.5$ [$c(2 \times 2)$ structure]. The coverage of 0.5 corresponds to one physical monolayer (the maximum coverage within a single layer) for Na on Ni,[22] whereas the physical monolayer coverage is about 0.35 for Cs on Ni.[23] The adsorbate positions are taken from the experimental LEED values: $z_a = 2.2$ Å (Ref. 24) and 3.8 Å (Ref. 25) for Na and Cs, respectively. The image plane position z_0 in the [100] direction is taken to be 1.8 and 2.1 Å outside the adsorbate layer for Na and Cs, respectively. These distances are based on the jellium calculations[26] for image plane positions. The electron work-function change $\Delta D(\theta)$ is taken from Gidley, Köymen, and Capehart,[13] with a value of 5.2 eV for the work function of clean Ni(100).[27] The input data and the calculated results for the binding energy E_b and the lifetime $\tau = 1/\lambda$ are collated in Table I.

Figure 1 shows the effective potential and the ground-state positron wave function for a representative case of an alkali-metal-covered Ni surface. Instead of being trapped in the image-correlation well just outside the surface, the positron now becomes mainly localized in the region between the substrate and the overlayer. One implication of this result is that the description of the positron-surface interaction in the region of the image-correlation well outside the surface becomes relatively unimportant. For example, the positioning of the image surface outside the overlayer is not critical. The positron localization is mainly driven by the electrostatic and geometric effects at the overlayer.

The other important result is that the positron binding energy E_b with respect to vacuum is substantially larger than for the clean surface (see Table I). For low coverages there is an increase in the binding energy similar in magnitude to the decrease in the electron work function. This leads to activation energies E_a that depend weakly on coverage. For higher coverages, the binding energy saturates and eventually will fall off slowly. Figure 2 shows the calculated activation energies as functions of the alkali-metal coverage, in comparison with the recent experimental data of Gidley, Köymen, and Capehart. We find a good qualitative agreement for the *slopes*. The simplified account of the surface dipole effects employed here excludes detailed quantitative comparison, but the calculated activation energies differ from the experimental values by no more than 0.3–0.5 eV. It is also significant that the alkali-metal-induced surface step ΔD
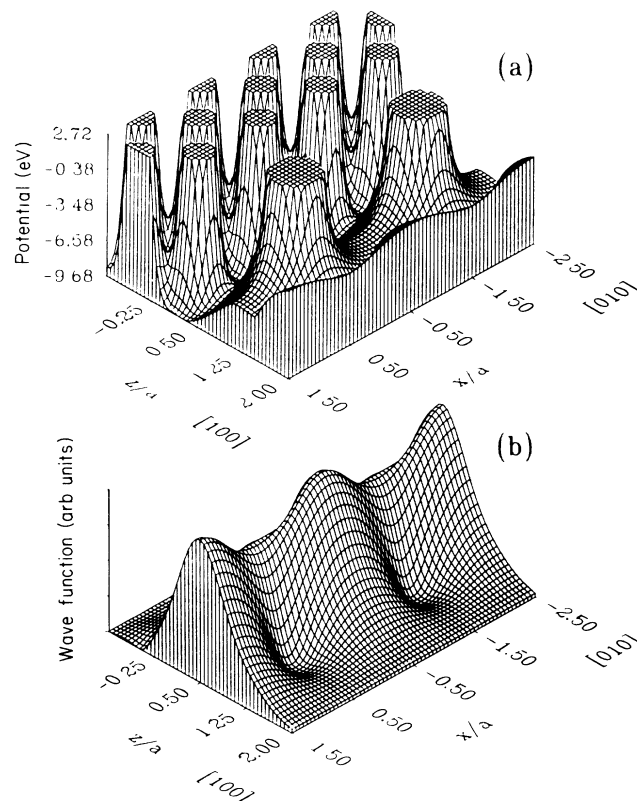

FIG. 1. (a) The effective positron potential on a Cs $p(2 \times 2)$/Ni(100) surface. (b) The ground-state positron wave function for the surface state on Cs $p(2 \times 2)$/Ni(100). The length a is the Ni lattice constant (3.52 Å).

leads to much larger binding energies than the pure AS model, typically 2.5 eV for Cs and 0.7 eV for Na. This shows that the charge rearrangement associated with the alkali-metal adsorption is of crucial importance in explaining the trends in the surface state.

The calculated lifetimes are also given in Table I. Two columns are included. The first one corresponds to the
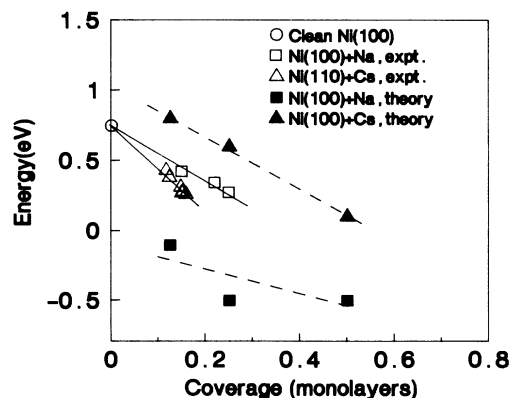

FIG. 2. The positronium activation energy E_a as a function of coverage for Na and Cs on Ni(100) (solid symbols). The experimental points for Ni(100) + Na and Ni(110) + Cs are taken from Ref. 13. All coverages are given in terms of the Ni(100) surface atomic density. The dashed lines correspond to least-squares fits to the theoretical results.

local-density formula for Γ, while the other contains the cutoff[8] in the image-potential region where the positron becomes decoupled from its screening cloud. These two models are related to the ongoing discussion[8,9,11] of the surface lifetime. While the two approaches give substantially different values for clean metal surfaces, they become much closer to each other for the alkali-metal-covered case. This again reflects the fact that, for alkali-metal-covered surfaces, the positron stays largely within the overlayer and does not enter the image-potential region. It is also noteworthy that the calculations predict a clear *decrease* of the lifetime simultaneously with an *increase* in the binding energy in going from a clean to an alkali-metal-covered surface. Usually, in the case of positron defect trapping,[17] a deeper trap (large binding energy) is associated with a longer lifetime.

The calculations have been restricted to coverages larger than 0.125. For lower coverages, the charge rearrangement tends to become localized around individual adatoms[28] and thus the representation of the dipolar step by a one-dimensional function becomes less accurate. Also the computational unit cell becomes so large that it is difficult to handle with the present calculational scheme.

In summary, we have performed calculations for the positron surface state on Ni(100) surfaces covered by ordered layers of Na and Cs adsorbates. The charge transfer associated with the chemisorption, which is also manifest in the lowering of electron work function, leads to a dipolar field which strongly stabilizes the positron surface state so that the activation energy for Ps desorption decreases only weakly with coverage. The positron is mainly localized in the region between the substrate and the overlayer. We predict lifetimes which are substantially shorter than for clean surfaces.

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