Positron-annihilation-induced Auger-electron-spectroscopy studies of properties of an alkali-metal overlayer on the Cu(100) surface

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Positron-annihilation-induced Auger-electron spectroscopy (PAES) employs positrons trapped at the surface to create core-holes and to initiate the Auger process in atoms in the topmost layer of the surface. The results of experimental and theoretical investigations of the attenuation of the positron-annihilation-induced Cu $M_{2,3}VV$ Auger signal with Cs coverage on the Cu(100) surface at low and high temperatures are discussed. They reveal that at 163 K the normalized intensity of the positron-annihilation-induced Cu $M_{2,3}VV$ Auger signal remains nearly constant at the clean-surface value until the Cs coverage reaches approximately 0.7 physical monolayer, at which point the signal intensity drops precipitously. We present an analysis of this unusual behavior using a model that treats the positron as trapped in a double-well potential in the direction perpendicular to the surface: one well is associated with the Cu substrate and the other with the Cs adsorbate. The sharp drop in the Cu PAES intensity which occurs over a small change in the Cs coverage is attributed to a migration of positrons trapped at low Cs coverages at the Cs/Cu interface to the positron surface state on the vacuum side of the alkali-metal overlayer at high Cs coverages. This migration can be accounted for in terms of a structural phase transition in the Cs overlayer from a disordered distribution of adsorbate atoms to adsorbate metallic islands with an ordered hexagonal close-packed structure.

I. INTRODUCTION

Like electrons, positrons have quantum-mechanical states at surfaces on a number of metals. These surface states are critically dependent on the short-range "correlation well" in the vicinity of the surface atoms and are the consequence of the interplay between repulsion from the surface ionic cores and the attractive electron-positron correlations just outside the surface. The existence of positron surface states has been demonstrated by the observation that positrons could be thermally desorbed from clean metal surfaces at elevated temperatures as positronium.[1] While the trapping of electrons at metal surfaces may be interpreted on the basis of a simple long-range image potential, truncated at the surface, there is still much controversy on the modeling of the positron surface state.[2] This is due to the fact that positrons reside so close to metal surfaces that the electron-positron correlations strongly affect the nature of the positron surface states.

Recently, the interaction of positrons with solid surfaces has become the subject of extensive experimental studies using positron-annihilation-induced Auger-electron spectroscopy (PAES).[3-7] PAES employs positrons trapped at the surface state to annihilate with the neighboring core-level electrons, creating core-hole excitations and so initiating the Auger processes almost exclusively in atoms in the topmost layer. Thus PAES experiments can be used to selectively obtain chemical information from the topmost atomic layer and in the characterization of the initial stages of epitaxial growth, interdiffusion, and alloy formation.[3-7] In addition, since the PAES intensities are quite sensitive to the spatial distribution of the positron density at the surface, PAES can

be applied to clarify the nature of the positron surface state.

In this paper, we present PAES studies of the effect of the adsorption of Cs on the (100) surface of copper. Properties of the alkali-metal overlayer are investigated, and the localization of the positron surface states is examined from very low Cs coverages up to a full monolayer. It is found in measurements performed at 163 K that the normalized intensity of the positron-annihilation-induced Cu $M_{2,3}VV$ Auger signal drops sharply almost to zero when the Cs coverage reaches approximately 0.7 physical monolayer significantly deviating from the predictions of the existing theoretical model.[8,9] [One physical monolayer of a hexagonal close-packed array of Cs atoms on the (100) surface of copper corresponds[10] to 0.416×10^{15} atoms/cm^2.] The observed behavior of the normalized intensity of the positron-annihilation-induced Cu $M_{2,3}VV$ Auger signal with Cs coverage is explained within a simple model that treats the positron as trapped in a double-well potential in the direction perpendicular to the surface (one well is located just outside the Cu substrate and the other is located on the vacuum side of the alkali-metal adsorbate metallic islands).[11] The sharp drop in the normalized Cu $M_{2,3}VV$ PAES intensity observed at 163 K for the Cs/Cu(100) system is attributed to a rapid growth in the population of the positron surface state on the vacuum side of the Cs overlayer. The positron surface state on the vacuum side of the Cs overlayer appears over a small change in the Cs coverage at the critical alkali-metal coverage of approximately 0.70 physical monolayer.[11] According to the results of computer simulations of the deposition of Cs atoms on the (100) surface of copper[12] as well as from observations of the development of the low-energy electron

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diffraction (LEED) pattern,[10,13] at these Cs coverages the overlayer experiences a structural phase transition from a disordered distribution of adatoms to adsorbate islands with an ordered hexagonal close-packed structure.

II. EXPERIMENTAL PROCEDURE

The measurements were performed using the PAES apparatus at the University of Texas at Arlington described previously.[14] It consists of three major parts: a magnetically guided low-energy monoenergetic positron beam, an ultrahigh vacuum (UHV) sample chamber for surface preparation and analysis, and a trochoidal energy analyzer. The low-energy positron beam was derived from a 10-mCi ^{22}Na positron source and a tungsten-foil moderator. The positron beam was incident onto the sample surface at approximately 30 eV. The UHV chamber included a precision manipulator, a conventional cylindrical mirror analyzer (CMA) for routine surface characterization, a trochoidal energy analyzer[15] (equipped with a microchannel plate to detect and measure the energy of electrons in the single-particle counting mode), LEED optics, and a sputter ion gun for sample cleaning and characterization. A Sm-Co permanent magnet was mounted behind the sample to reduce the angular spread of the Auger electrons at the spectrometer and improve the energy resolution of the measurements.[14,16] The effective energy resolution for the spectrometer was set at ~ 10 eV full width at half maximum. Crossed electric and magnetic fields acted as velocity selectors for the beam, both in the source and sample chambers, and were used to direct the low-energy positrons onto a sample surface and to collect the Auger electrons. Three NaI(Tl) scintillators mounted near the sample and coupled to photomultipliers were used to detect annihilation gamma rays emitted in coincidence with the annihilation-induced Auger electrons. The NaI(Tl) scintillators were used also to monitor the incident-beam intensity. Electron-stimulated Auger spectroscopy (EAES) measurements were performed using the same experimental apparatus as described above by substituting an electron beam for the positron beam.

The Cu(100) single crystal was mechanically polished using standard techniques and oriented parallel to the (100) face to within ±1° as determined using Laue diffraction. The sample surface was prepared by a combination of repeated cycles of 3 keV Ne$^+$ ion sputtering and annealing at 923 K to remove contaminants from the surface. Conventional Auger-electron and LEED techniques were used to characterize the structure and cleanness of the sample surface. A LN$_2$ cooling stage and a button heater were attached to the sample holder. Computer controls were used to keep the sample temperature constant to within ±1 K during the measurements. The sample was biased to −5 V to attract the slow reemitted positrons back to the sample.

The Cs deposition on the Cu(100) substrate was performed at room temperature using resistively heated SAES Cs getters. After outgassing, the pressure in the UHV chamber was maintained at ~5.0×10^{-10} Torr during evaporation and at less than 2.0×10^{-10} Torr during the PAES and EAES measurements. The Cs coverage was determined by using a single-pass CMA to measure the ratio R of the Cs (563 eV) EAES Auger peak to the Cu (920 eV) EAES Auger peak, and by observation of the evolution of the LEED pattern. The Cs coverage is approximately proportional to R. At room temperature, saturation coverage of Cs on the (100) surface of copper is one physical monolayer.[5] The PAES, EAES, and LEED data were taken at each Cs coverage at 163 K and then repeated after warming the sample to 303 K without changing the amount of Cs deposited.

The change in electron work function ($\Delta\Phi_-$) as a function of Cs coverage was measured by determining the sample voltage at which the positron beam was reflected.[17] The positronium fraction (f_{Ps}), which is defined as the fraction of the incident positrons leaving the surface as positronium, was measured as a function of Cs coverage for both 163 and 303 K by analyzing the pulse-height spectrum from a NaI γ-ray detector.[18]

III. EXPERIMENTAL RESULTS

The positron-annihilation-induced Auger-electron spectra of clean Cu and of Cu for different Cs coverages at 163 K are shown in Figs. 1(a)–1(d). The spectra were obtained from the detection of electrons in coincidence with annihilation gamma rays from the samples. The data are the sum of four loops in which the energy range was increased by 1-eV steps with an accumulation time of 30 s per point for each loop (total 120 s per point). The primary peaks for the Cu spectra correspond to the $M_{2,3}VV$ (~60 eV) Auger transitions. The sharp rise in counts below ~30 eV observed in the spectra shown in Fig. 1 is due to the collisionally excited secondary electrons. Plots of the normalized intensity of the positron-annihilation-induced Cu $M_{2,3}VV$ Auger signal I_P as a function of the ratio R of the Cs (563 eV) to the Cu (920 eV) EAES peaks at 163 and 303 K are shown in Figs. 2(a) and 2(b), respectively. The PAES intensities were extracted from the spectra shown in Fig. 1 along with others taken at intermediate coverages using a least-square fit to a reference Cu $M_{2,3}VV$ line shape.[6] The intensities were divided by the quantity $\delta(1-f_{Ps})$, where δ is a constant chosen to normalize the clean surface intensity to unity. Such a normalization has been shown to account for the depopulation of the surface state due to positronium emission.[4]

The most striking effect of the Cs overlayer is a sharp drop almost to zero in the normalized Cu $M_{2,3}VV$ PAES intensity at 163 K in a range of less than 0.02 monolayer wide at the critical Cs coverage of 0.70 physical monolayer. In contrast to the PAES results, it follows from Fig. 3(a) that the intensity of the electron-annihilation-induced Cu Auger-electron signal I_E decreases linearly to about 55% of the clean surface value at 0.9 physical monolayer of Cs coverage, consistent with attenuation due to inelastic scattering of the outgoing Auger electrons in the Cs overlayer. The positronium fraction f_{Ps} as a function of Cs coverage for both 163 and 303 K is shown in Fig. 3(b). From Figs. 3(b) and 3(c), the isothermal (303 K) desorption of positrons as positronium
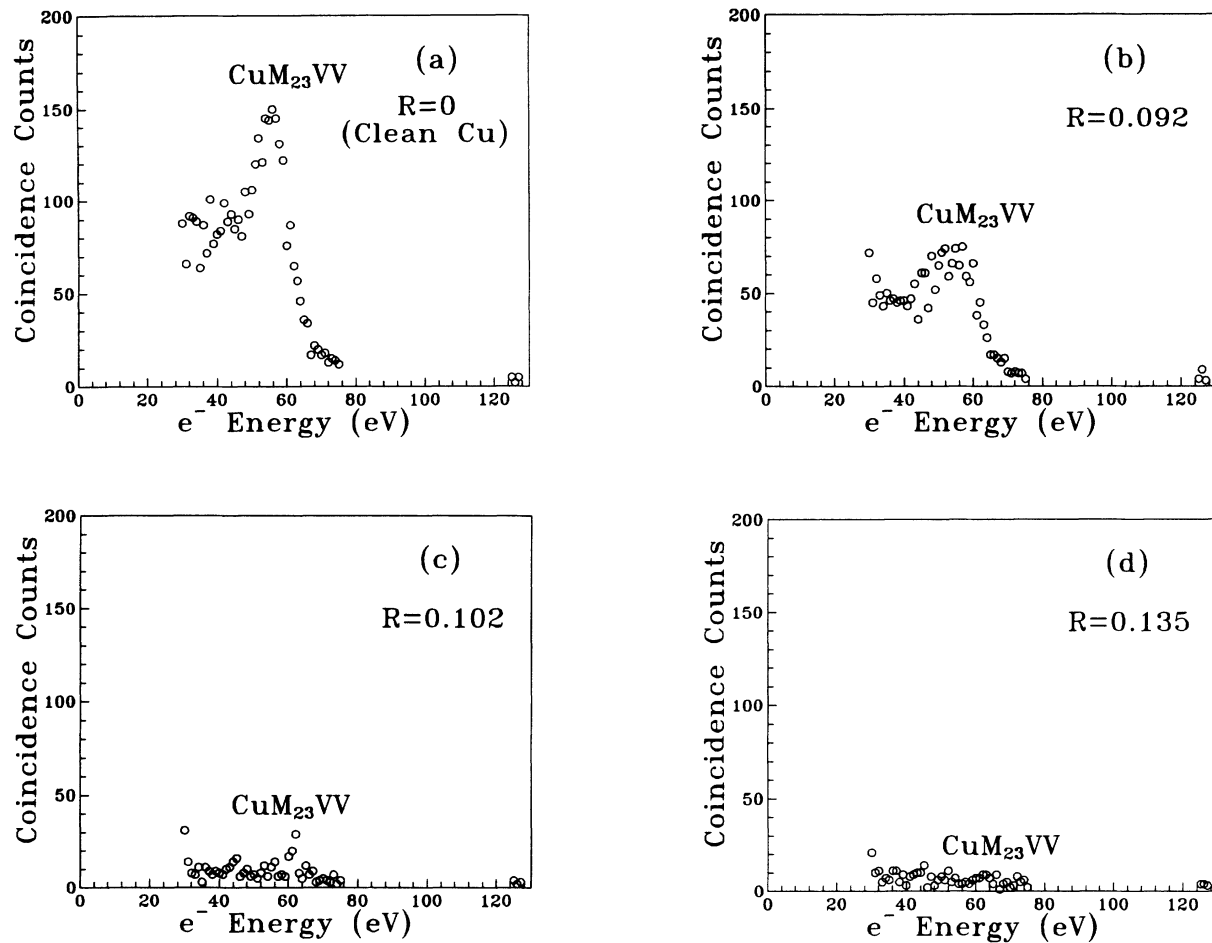
FIG. 1. Positron-annihilation-induced Auger spectra obtained from a Cu(100) surface at 163 K for four different values of the ratio R of the Cs (563 eV) to the Cu (920 eV) Auger peaks for a system Cs/Cu(100). The Cu $M_{2,3}VV$ peak is labeled in each panel. The Cs coverage is approximately proportional to R. A ratio of 0.14 corresponds to one physical monolayer.
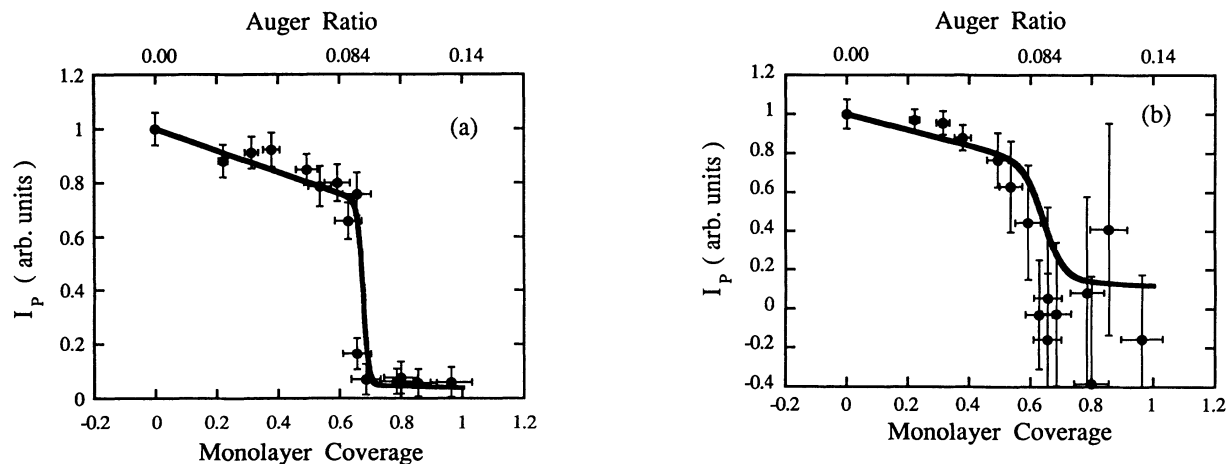

FIG. 2. The normalized Cu $M_{2,3}VV$ PAES intensity I_P as a function of the ratio of the Cs (563 eV) to the Cu (920 eV) Auger peaks and the Cs coverage for a Cs/Cu(100) system at (a) 163 K and (b) 303 K. Some data points in (b) go below zero due to counting statistics and the fact that a small constant background has been subtracted from I_P (which is very close to zero at high Cs coverages). The deviations from zero were exaggerated by dividing by $(1-f_{Ps})$, which is also close to zero at 303 K for high Cs coverages. The solid line in (a) and (b) is a theoretical curve for I_P obtained from Eq. (2) multiplied by the attenuation factor $(1-0.4c)$ for the following values of the parameters: $c^* \cong 0.70$, $\alpha \cong 116$ for 163 K and $\alpha \cong 30$ for 303 K, $\Delta E \cong 0.038$ eV.

from the Cs/Cu(100) system takes place after $\Delta\Phi_-$ has dropped by 3 eV and when the Cs overlayer reaches approximately 0.5 monolayer. The Cs coverage dependence of the Cu $M_{2,3}VV$ PAES intensity normalized to the clean Cu value I_P correlates strongly with the positronium fraction f_{Ps} as it should: for coverages, at which f_{Ps}

changes rapidly, the suppression of the desorption of positronium causes a corresponding increase in the Cu PAES signal, and, when the positronium fraction increases most rapidly, I_P drops most sharply. As seen from Figs. 2(a) and 2(b), the drop in I_P is sharper at 163 than at 303 K and starts at higher Cs coverages.

IV. DISCUSSION

The Nieminen-Jensen (NJ) theory[8] predicts that the charge rearrangement that leads to the lowering of the electron work function causes the positron to become localized in the region between the substrate and the alkali-metal overlayer up to the coverage of one physical monolayer, producing an increase in the positron binding energy. Thus, according to this theory the Cu PAES signal should remain close to the clean-surface value after deposition of Cs. A relatively modest amount of attenuation is expected due to the fact that the outgoing Cu Auger electrons must traverse the Cs overlayer. This effect was measured by obtaining the EAES spectra using the same spectrometer and the same geometry as was used in the PAES measurements. The Cs overlayer should have almost no effect on the efficiency with which the 3-keV electron beam used in EAES excites Auger electrons. Thus, a measured reduction in the EAES intensity to about 55% of the clean-surface value at 0.9 physical monolayer of Cs can be assumed to be due solely to attenuation caused by the inelastic scattering of outgoing Auger electrons as they traverse the Cs overlayer. Calculations based on the NJ theory indicate that the decrease in the Cu core annihilation probability caused by a decrease in the overlap of the positron wave function with the Cu substrate should have a comparatively smaller effect (less than 16%).[5] However, calculations of the Cu PAES signal intensity based on the NJ theory and the measured attenuation of the outgoing electrons are in reasonable agreement with the experimental data only below the critical coverage of approximately 0.7 physical monolayer, they do not reproduce the sharp drop in the PAES intensity at 163 K and the PAES intensity coverage dependence observed for higher Cs coverages.

We attribute the failure of the NJ theory[8,9] in explaining the observed Cu PAES intensity dependence on the Cs coverage to the following.

(a) The image-potential-induced positron surface state on the alkali-metal-covered (100) surface of copper was found[5] by numerical solution of a single-particle Schrödinger equation. The calculations[5] of the effective surface potential acting upon the positron were performed using the corrugated-mirror model[8] which is an approximation to a rather complicated dynamic and non-local image interaction and does not take fully into account the correlations between the positron and electrons in the system. Furthermore, the effective surface potential experienced by a positron in the theoretical model[8,9] was constructed[5] from the superposition of Coulomb potentials from neutral atoms, which may not be appropriate taking into consideration the possible charge transfer or polarization effects in the alkali-metal–transition-metal system, i.e., the effective surface potential was not
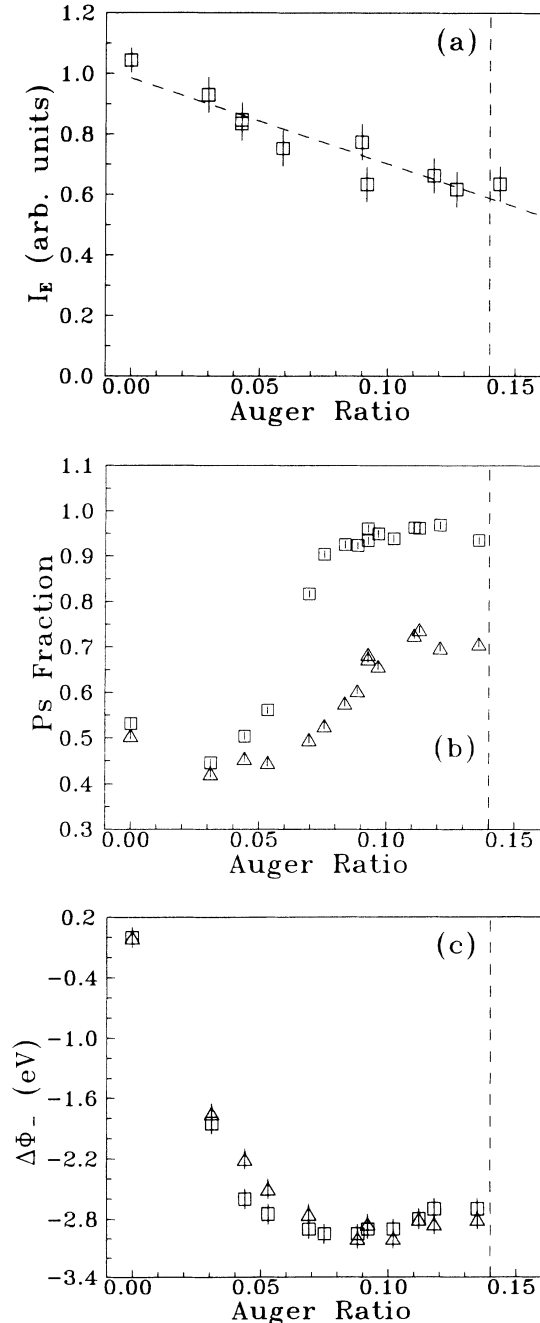

FIG. 3. (a) The normalized EAES intensity I_E at 303 K, (b) the positronium fraction f_{Ps}, and (c) the change in electron work function $\Delta\Phi_-$ as a function of the ratio of the Cs (563 eV) to the Cu (920 eV) Auger peaks for a Cs/Cu(100) system. The inclined dashed line shown in (a) was determined from a least-squares fit to the EAES data. The vertical dashed lines in (a), (b), and (c) indicate the value of the ratio corresponding to one physical monolayer. Data in (b) and (c) were obtained both at 163 (triangles) and at 303 K (squares).

self-consistent. A theoretical study of the nature and the mechanism of the bonding of an alkali metal (Cs) on a transition-metal surface [W(001)] based on all-electron local-density-functional results obtained with the self-consistent full-potential linearized augmented-plane-wave method[19] shows that consideration of the above-mentioned factors may significantly change the final theoretical results. (b) The calculations of the positron surface state based on the NJ theory were performed using a small cell size and for certain assumed regular periodic surface structures in the alkali-metal overlayer, which did not correspond to experimentally observed structures either for low or for high Cs coverages,[10,13] and they did not take fully into consideration the actual structural changes in the alkali-metal overlayer with increasing coverage.

To study the formation of and possible structural changes in the alkali-metal overlayer with increasing Cs coverage we performed computer simulations of the distribution of Cs atoms randomly deposited on the (100) surface of copper.[12] The simulations were performed on the basis of a model in which each Cs atom, including the landing one, was allowed to move on the two-dimensional surface due to the forces experienced by each adatom from the other adatoms and from the substrate, characterized by a periodic crystal potential with a period of a lattice of Cu. The adatoms were allowed to move till the system of Cs adatoms formed a configuration corresponding to the lowest potential energy of the overlayer. It was assumed that at low alkali-metal coverages the adsorbed Cs atoms experienced adsorbate-adsorbate repulsion due to polarization effects while at higher Cs coverages the interaction between adatoms was screened by conduction electrons. These simulations[12] show that below 0.6 monolayer alkali-metal coverage, Cs atoms deposited on the Cu(100) surface are distributed uniformly so that the standard deviation of the average distance between nearest neighbors is small and there are no areas with close-packed Cs atoms. The results of the computer simulations described above are consistent with studies of the spectrum of collective and single-particle excitations of the Cs/Cu system using electron-energy-loss spectroscopy (EELS) at these coverages.[20] According to Linddgren and Wallden,[20] the electronic structure of the Cs adsorbate appears to change in a gradual manner: a small change in coverage produces a small change of excitation energy, suggesting rather uniform distribution of adatoms. Our computer simulations also show that Cs atoms deposited on the Cu(100) surface start clustering at coverages of approximately 0.6 physical monolayer. From approximately 0.7 and up to one physical monolayer, Cs atoms in the overlayer start to form adsorbate islands increasing in area with a locally hexagonal close-packed structure. For a Cs coverage of 0.7 physical monolayer, approximately 25% of the overlayer area has an ordered hexagonal close-packed structure with the nearest Cs-Cs distance on Cu(100) of 5.26 Å. For a Cs coverage of 0.75 physical monolayer, approximately 55% of the overlayer area consists of islands with a locally close-packed structure. The calculations indicate that at least 80% of the overlayer area is close packed for the Cs

coverage of 0.84 physical monolayer. Thus, as it follows from computer simulations, over a small change in the alkali-metal coverage at the critical Cs coverage of approximately 0.7 physical monolayer the Cs adsorbate in the Cs/Cu(100) system experiences a structural phase transition from a disordered distribution of adatoms to adsorbate islands with an ordered hexagonal close-packed structure.

The results of the computer simulations are supported by LEED observations. Studies[13] of the deposition of Cs on the Cu(100) surface for coverages varying between 0.0 and 1.0 monolayer by LEED at low temperatures (below 160 K) revealed that the Cs adatoms occupy hollow sites with fourfold symmetry for coverages up to 0.7 monolayer. These results were deduced in the LEED work[13] by comparing the obtained LEED patterns with the calculated and measured LEED intensities for the system alkali-metal/Ni(100).[21] Above 0.7 monolayer coverage, the Cs overlayer is formed by two kinds of domains with quasihexagonal meshes rotated by 90°.[10,13] At room temperature a hexagonal close-packed LEED pattern due to the Cs overlayer appears at 0.8 monolayer and is completed by 1.0 monolayer.[10,13]

The EELS studies and investigations of coverage-dependent binding energies by ultraviolet photoelectron spectroscopy[20] revealed that a characteristic feature of the Cs overlayer is the large difference in the effect of the adsorbate at low and high coverage. Studies of the charge transfer between adsorbate and substrate at different Cs coverages by measuring the threshold energy for alkali core-level excitations using EELS (Ref. 20) revealed that the threshold for Cs $5p$ excitations decreases from 13.2 eV for the more ionic Cs adsorbate at low coverage to 11.6 eV for the nearly neutral adsorbate at high coverage. Such changes in the character of the Cs adsorbate with coverage correlate with the Cs coverage dependence of the electron work function. A depletion of electronic charge on the vacuum side of the adsorbate and increase of electronic charge in the Cs/Cu interface region at low coverages produces the rapid initial drop of the electron work function. The change in the electron work function at low coverage is equated with the potential drop across a dipole layer at the surface created by the polarized adatoms. The variation of the work function with the Cs coverage suggests that the alkali overlayer is essentially neutral at coverages close to a full monolayer. Similar results for the work function changes due to adsorption of alkali-metal overlayers on transition-metal surfaces are obtained in the experimental investigations by Riffe, Wertheim, and Citrin[22] and in the theoretical calculations.[19,23,24]

Thus, at low coverages the Cs adsorbate can be regarded as an array of polarized adatoms, whereas at high coverages its behavior is that of a metal. As the Cs coverage reaches the value of approximately 0.7 physical monolayer, the areas with an ordered hexagonal close-packed structure of Cs atoms appear in the Cs overlayer signaling the onset of a structural phase transition. In these close-packed areas, Cs atoms lose their atomic character and form the two-dimensional metallic adsorbate.

In our model we assume that the positron surface state

is localized in the region between the substrate and the alkali-metal overlayer, and that, as the Cs coverage reaches 0.7 physical monolayer and the Cs overlayer becomes metallic, the positron surface state also appears on the vacuum side of the alkali-metal overlayer. As a consequence of this assumption, we treat the positron as trapped in a double-well potential in the direction perpendicular to the surface: one well is associated with the Cu substrate and the other well is associated with the Cs adsorbate. The positron surface state at the Cs/Cu interface is characterized by the binding energy E_{1b}. The positron surface state on the vacuum side of the areas of alkali-metal adsorbate with the hexagonal close-packed structure of Cs atoms is characterized by the binding energy E_{2b}. The calculated value for the binding energy of the positron surface state associated with the Cu substrate and located at the Cs/Cu interface is equal to 5.29 eV at the Cs coverage of 0.92 physical monolayer.[9] The calculated value for the binding energy of the positron surface state on the vacuum side of the Cs overlayer on the Cu(100) surface is not available.

In our model we also assume that the energy level E_{2b} associated with the positron surface state on the vacuum side of the Cs overlayer lies lower than the energy level E_{1b} associated with the positron surface state at the Cs/Cu interface. As a result, as soon as the positron surface state appears on the vacuum side of the alkali-metal overlayer with the close-packed structure of Cs atoms, it would become occupied by positrons. We assume that the relative number of positrons that can occupy the surface state on the vacuum side of the Cs overlayer can be regarded to be a sharp function of the Cs coverage c on the Cu(100) surface:

$$n(c) = \exp(-E_{2b}/kT)/\{1 + \exp[-\alpha(c - c^*)]\} \ , \quad (1)$$

where $c^* \cong 0.7$, $\alpha \cong 116$ for 163 K, and $\alpha \cong 30$ for 303 K. This assumption is consistent with LEED observations[10,13] as well as with the results of our computer simulations[12] which indicate that a structural phase transition from a disordered distribution of adsorbate atoms to adsorbate metallic islands with an ordered hexagonal close-packed structure takes place over a remarkably small change in the Cs coverage at the critical Cs coverage of approximately 0.7 physical monolayer. The parameter c^* defines the Cs coverage at which the positron surface state appears on the vacuum side of the Cs overlayer, its value is determined from computer simulations and the LEED spectra.[10−13] The parameter α defines the sharpness of the coverage dependence of $n(c)$, its value is determined by the fitting of the theoretical curve for the Cs coverage dependence of the normalized Cu PAES intensity to the experimental data. The relative number of positrons that can occupy the positron surface state at the Cs/Cu interface is defined by $\exp(-E_{1b}/kT)$. Due to the fact that the wave function of a positron in a surface state decays rapidly into the bulk of a metal[9] it is possible to neglect the annihilation of a positron in a surface state on the vacuum side of the Cs overlayer with the Cu core electrons. Then the normalized Cu PAES intensity would be proportional to the probability of the positron to occupy the bound state at the Cs/Cu interface,

which is given by the following expression:

$$f = 1/[1 + n(c)\exp(-\Delta E_b/kT)] \ , \quad (2)$$

where $\Delta E_b = E_{2b} - E_{1b}$ is the difference between the binding energies of the positron states associated with the Cs adsorbate and the Cu substrate, E_{2b} and E_{1b}, respectively. (For simplicity we neglect the possible Cs coverage dependence of ΔE_b.) The value for $\Delta E_b \cong 0.04$ eV is found by the fitting of the theoretical curve for the Cs coverage dependence of the normalized Cu PAES intensity to the experimental data. This implies that the value for the binding energy E_{2b} for the positron surface state on the vacuum side of the Cs overlayer on the (100) surface of copper is equal to 5.33 eV at the Cs coverage of 0.92 physical monolayer.

With increasing temperature, the probability for the positron to desorb from the surface increases.[25] This will cause an increase in the positronium emission from the surface, a decrease in the number of positrons annihilating at the positron surface state, and a subsequent suppression of the PAES intensity. The change in the normalized Cu PAES intensity at 303 K as compared to its value at 163 K due only to the temperature effect on the positron thermal desorption from the surface affecting the Auger-electron process can be taken into consideration multiplying each term in the expression for f by the functions ξ_i $(i = 1,2)$ with appropriate parameters, corresponding to the positron surface states located at the Cs/Cu interface and on the vacuum side of the Cs overlayer, following a thermal activation curve of the form[26]

$$\xi_i = \lambda_i/\{\lambda_i + \Gamma\exp(-E_a^i/k_B T)\} \ , \quad (3)$$

where λ is the positron-annihilation rate at the surface and E_a is the activation energy for positron desorption as positronium. The latter is related to the binding energy E_b of the positron at the surface by[1,17]

$$E_a = E_b + \Phi_- - R/2 \ , \quad (4)$$

where Φ_- is the electron work function, and $R/2 = 6.8$ eV is the ground-state binding energy of the positronium. The prefactor Γ is calculated to be[25]

$$\Gamma = 4k_B T(1 - \langle \beta_{Ps} \rangle)/\hbar \ , \quad (5)$$

where $\langle \beta_{Ps} \rangle$ is the velocity-averaged positronium reflection coefficient, and $\hbar$ is Plank's constant. In our calculations of the coverage dependence of the attenuation of the PAES Cu $M_{2,3}VV$ normalized peak intensity we assumed that the temperature effect on the positron thermal desorption from the positron surface states in the Cs/Cu interface and on the vacuum side of the Cs overlayer is the same.

The results of the theoretical calculations for the Cs coverage dependence of the normalized Cu PAES intensity multiplied by an attenuation factor determined from the attenuation of the normalized Cu EAES intensity from Fig. 3(a), to take into consideration inelastic scattering of the outgoing Auger electrons, are presented in

Figs. 2(a) and 2(b).

As can be seen from Fig. 2, the model correctly describes the behavior of the experimental Cu PAES signal with the Cs deposition at both low and high temperatures. At 163 K the calculated normalized Cu PAES intensity remains nearly constant at the clean-surface value until the Cs coverage reaches approximately 0.7 physical monolayer at which the theoretical curve drops sharply in agreement with the experimental results. According to the proposed model this drop occurs due to the fact that above the critical Cs coverage a structural phase disorder-order transition takes place in the alkali-metal overlayer. As a consequence of this structural phase transition the Cs overlayer becomes metallic and the positron surface state appears on the vacuum side of the Cs overlayer.

Due to the fact that the energy level associated with this positron surface state lies lower than the energy level associated with the positron bound state in the region between the substrate and the alkali-metal overlayer, the positron surface state localized at the Cs/Cu interface becomes depopulated as a result of occupation by positrons of the surface state localized on the vacuum side of the CS overlayer. This leads to a sharp drop in the Cu PAES intensity. The nonzero value of the Cu PAES intensity at Cs coverages exceeding the critical coverage is due to partial population of the positron bound state at the Cs/Cu interface.

The predicted positron-annihilation probabilities with core-level electrons are very small for the Cs core levels. For example, calculations of bulk core annihilation rates[9] indicate that of the levels giving Auger transitions in the experimental range currently available, the two highest probabilities are 0.078% for $4p$ and 0.26% for $4d$ as compared to approximately 6% for the $3p$ level of Cu.[9] Thus, the expected intensity of the Cs PAES signal is of the order of 0.04 of the clean Cu $M_{2,3}VV$ PAES peak intensity. A detailed discussion of the positron-annihilation probabilities with the Cs core-level electrons and data consistent with the observation of a small Cs PAES signal will be presented in another paper. Additional evidence that the positron is bound in a surface state at high Cs coverages can be found in the fact that the positronium fraction increases from $\sim 70\%$ to $\sim 100\%$ as the temperature is increased from 163 to 303 K indicating thermal desorption from a state with low activation energy which must be at or near the surface. The fact that the normalized Cu PAES intensity approaches zero at high Cs coverages indicates that this state is on the vacuum side of the Cs overlayer.

V. CONCLUSIONS

A sharp drop in the normalized Cu $M_{2,3}VV$ PAES intensity almost to zero for the system Cs/Cu(100) is observed at 163 and 303 K which occurs over a small change in the Cs coverage at the critical alkali-metal coverage of 0.7 physical monolayer. We deduce from the results of computer simulations of the deposition of Cs atoms on the (100) surface of copper, as well as from observations of the development of the LEED pattern, that there is a structural phase transition in the Cs overlayer. Over a small range in alkali-metal coverage at the critical Cs coverage it transforms from a disordered distribution of adatoms to an arrangement of adsorbate islands with an ordered hexagonal close-packed structure. It is assumed that in these islands with locally hexagonal close-packed structure Cs atoms lose their atomic character and form a two-dimensional metallic adsorbate, and that a new positron surface state appears on the vacuum side of the Cs overlayer.

A simple model which treats the positron as trapped in a double-well potential in the direction perpendicular to the surface (one well located just outside the Cu substrate and the other located on the vacuum side of the Cs adsorbate), explains the observed behavior of the normalized Cu $M_{2,3}VV$ PAES intensity at 163 and 303 K with the Cs coverage. A drop in the normalized Cu $M_{2,3}VV$ PAES intensity at 163 and 303 K for the system Cs/Cu(100) which occurs over a small change in the Cs coverage at the critical Cs coverage of approximately 0.7 physical monolayer is attributed to a rapid growth of population of the positron surface state as it appears on the vacuum side of the Cs overlayer. The model has provided a good fit to the experimental data.

PAES has provided clear evidence for a shift of positrons trapped initially at the Cs/Cu interface to the vacuum side of the alkali-metal overlayer as a function of the Cs coverage.

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