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Linewidth of a cesium adatom resonance on Ag(111)

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Single Cs atoms adsorbed on Ag(111) induce a resonance appearing just below the threshold of the quasi-two-dimensional Shockley-type surface-state continuum. Spectroscopic analysis using a cryogenic scanning tunneling microscope and theoretical modeling are used to identify the importance of the various contributions to the linewidth and to the decay of the resonance: resonant charge transfer, inelastic transitions, and adsorbate vibrations perpendicular to the surface.

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I. INTRODUCTION

The decay of surface-localized electronic excitations has attracted considerable interest from a broad experimental community as well as from theoretical groups. Decay rates may provide valuable insight into quasiparticle interactions, e.g., the electron-electron, electron-phonon, or electron-defect coupling. Angle-resolved photoelectron spectroscopy, scanning tunneling spectroscopy, and time-resolved two-photon photoemission have been used to investigate these decay rates.[1] Several contributions to the decay of surface-localized states were unraveled, among which the most prominent are electron-electron and electron-phonon interactions, as well as charge transfer in the case of localized states.[1,2] In addition, in the case of electronic continua at surfaces, the presence of adsorbates, steps, defects, or ordered overlayers of adsorbates induce scattering phenomena leading to extra broadening effects.[3–7] Scattering by impurities at surfaces has recently received much attention.[8–15] For example, scattering of image potential states by Cu atoms adsorbed on Cu(100) (Refs. 9 and 10) has been shown to contribute significantly and differently to the decay and broadening of these states.

Alkali-metal atoms adsorbed on noble-metal surfaces, e.g., Cu(111)-Na,[16] Cu(111)-Cs,[17,18] and Ag(111)-Cs,[19,20] induce long-lived unoccupied resonances within the surface-projected band gap. These resonances correspond to the transient capture of an electron on an *sp*-hybrid orbital of the alkali-metal atom. The very low decay rates of these resonances have been explained by a quasiblocking of the resonant charge transfer between the resonance and the substrate due to the presence of the surface-projected band gap. While resonant charge-transfer rates for an alkali atom on a free-electron metal may reach 1 eV,[21] it can be reduced to a few meV if a surface-projected band gap is present.[22] Surprisingly, the spectral widths of these resonances are much larger than their decay rate would explain, indicating the existence of extra sources of broadening. In a recent theoretical analysis, the peculiar linewidth and its temperature dependence were traced back to an inhomogeneous broadening due to the distribution of adsorption heights of the alkali adsorbate.[23] Alkali-metal atoms have been predicted to induce also occupied resonances on surfaces as a result of the localization of the two-dimensional surface-state continuum[24,25] when the latter exists. While these states have been reported in the case of noble metal[11,12] and magnetic[12,26] adatoms, they have not been observed for alkali adsorbates until now.

In this paper, we show experimentally and theoretically that an alkali-metal atom adsorbed on Ag(111) induces an occupied localized state deriving from the two-dimensional surface-state continuum. We identify the contributions to the spectroscopic line shape and decay rate of this state. The resonance decays due to both resonant charge-transfer and inelastic processes. In addition, Cs-Ag zero point vibrations, which do not influence the decay rate, contribute to the broadening of the resonance line.

II. EXPERIMENT

Experiments were performed with a scanning tunneling microscope (STM) operated at 7 K and in ultrahigh vacuum with a base pressure of 10^{-9} Pa. The Ag(111) surface and chemically etched W tips were cleaned by annealing and argon ion bombardment. Single Cs atoms were deposited on the cold surface while higher coverages were prepared at room temperature using a commercial source.[27] We define one monolayer (ML) as one adsorbed atom (adatom) per Ag atom. Spectra of the differential conductance (dI/dV) were acquired by superimposing a sinusoidal voltage modulation on the sample voltage (root-mean-square amplitude: 1 mV and frequency: 10 kHz) and measuring the current response with a lock-in amplifier.

III. THEORY

The theoretical study involves two steps. First, a one-electron wave-packet propagation (WPP) approach determines the time evolution of an excited electron interacting with the *static* single adsorbate-substrate system, from which the local density of states (LDOS) and the characteristics (energy, decay rate, and wave function) of the static quasistationary states of the system are extracted.[24,28] The single Cs adsorbate is modeled as a positive ion and the electron-substrate interaction is described by a local potential from Ref. 29. The calculations were performed in cylindrical coordinates, with the z axis perpendicular to the surface and going through the adsorbate center. Some test studies on the

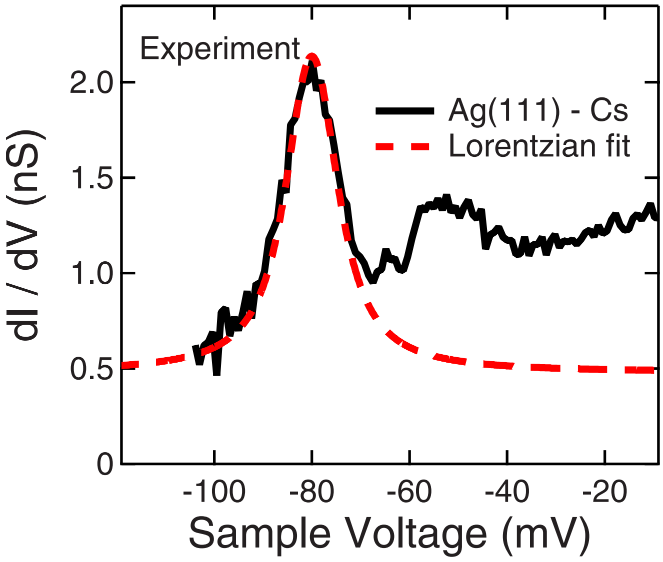

FIG. 1. (Color online) Spectrum of the differential conductance (dI/dV) taken at 7 K on a single Cs atom adsorbed on Ag(111) (solid line). The tunneling gap was defined by opening the feedback loop at 0.1 nA and 50 meV. The dashed line is a Lorentzian fit, which was fit to the resonance.

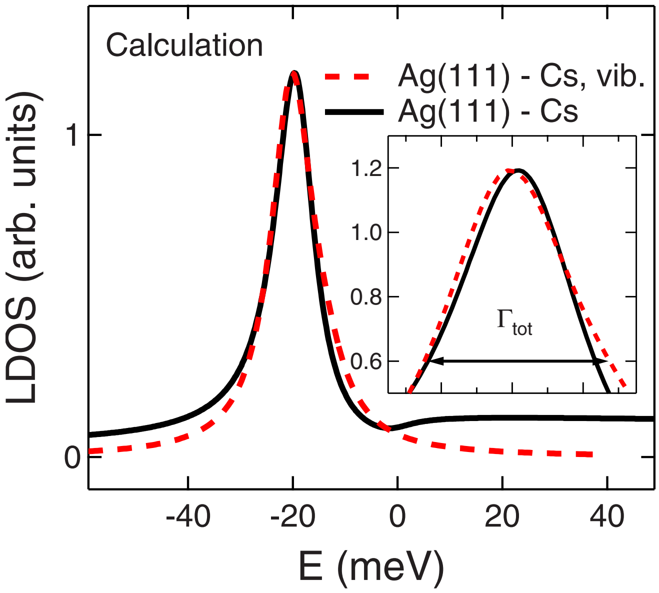

FIG. 2. (Color online) Calculated LDOS of the Cs-induced resonance as a function of energy, E (static adsorbate, black full line). The resonance maximum is located ≈20 meV below the surface-state onset which is set to 0 meV. The linewidth of the resonance (static adsorbate) is 9.1 meV. The red dashed line shows the resonance profile with the adsorbate vibration taken into account ($\Gamma_{\mathrm{tot}} \approx 10.5$ meV). Inset: close-up view to show the different widths of the resonance profiles.

case of a finite Cs coverage were performed using the modeling from Ref. 30. The calculations reveal the existence of a quasistationary state located slightly below the surface-state band bottom. Its energy and width were determined as functions of Z, the adsorbate-surface distance.

In a second step, the evolution of the system in this quasistationary state was treated within the local complex potential (LCP) approximation, in which the LCP as a function of Z was given by the energy and width computed in the first step. The time evolution of the adsorbate in this LCP was studied in a one-dimensional (1D) wave-packet calculation. It describes how the adsorbate vibrates when brought into the excited electronic state. This approach has recently been developed in the context of the resonant photodesorption process;[31] it is similar to the time-dependent treatment of resonant vibrational excitation in electron-molecule collisions.[32] From the analysis of the time dependence of the 1D wave packet, it is possible to extract inelastic transitions induced by the electronic excitation as well as the energy profile of the vibrating resonance for an adsorbate initially in the ground vibrational state.

IV. RESULTS AND DISCUSSION

Experimental dI/dV spectra acquired from single Cs atoms adsorbed on Ag(111) exhibit a prominent peak at ≈−80 meV below the Fermi level, which is located at $V=0$ mV (Fig. 1, black curve). To identify its origin we performed calculations within the wave-packet propagation approach using $m=0$ symmetry (m is the electron momentum projection on the z axis). A sharp peak appears in the local density of states (Fig. 2) below the surface-state threshold, similar to earlier predictions for Cu(111)-Cs.[24]

The resonance wave function for a fixed adsorbate-surface distance has been computed with WPP and is shown in Fig. 3. Except close to the adsorbate center, the resonance wave function looks like the surface-state wave function along the coordinate perpendicular to the surface and exhibits a broad featureless structure parallel to the surface. The resonance decay by the energy-conserving (resonant) electron transfer from the adsorbate-localized state into the continuum of metal states appears in Fig. 3 as an outgoing electron flux inside the bulk, enclosing a finite angle with the surface normal. All this confirms that the state close to and below the surface state originates from the localization of the two-dimensional continuum by the attractive Cs adsorbate. A detailed comparison of the experimental and calculated peak positions is complicated by the presence of a biased STM tip in the experiment. This leads to a modified image potential and a shift of the surface state.[33,34] Since the studied resonance arises from the surface-state continuum localization, it is expected to exhibit a shift similar to that of the surface state, so that the resonance position with respect to the surface-state band bottom should be only weakly influenced by the electric field of the tip of the microscope. Indeed, the calculated resonance position, which is ≈20 meV below the surface-state band bottom, reasonably agrees with the experimental offset of ≈17 meV below the band edge of the unshifted surface state at −63 meV.[35] The influence of the tip on the lifetime is expected to be negligible.[36]

In our experiments, stable spectroscopy of single Cs adatoms on Ag(111) was often hampered by the mobility of the adatoms. Although dI/dV spectroscopy was performed at very low tunneling currents, the signal-to-noise ratio remained below values found for adatoms with stronger coupling to the substrate.[12] Our calculations show that electrons

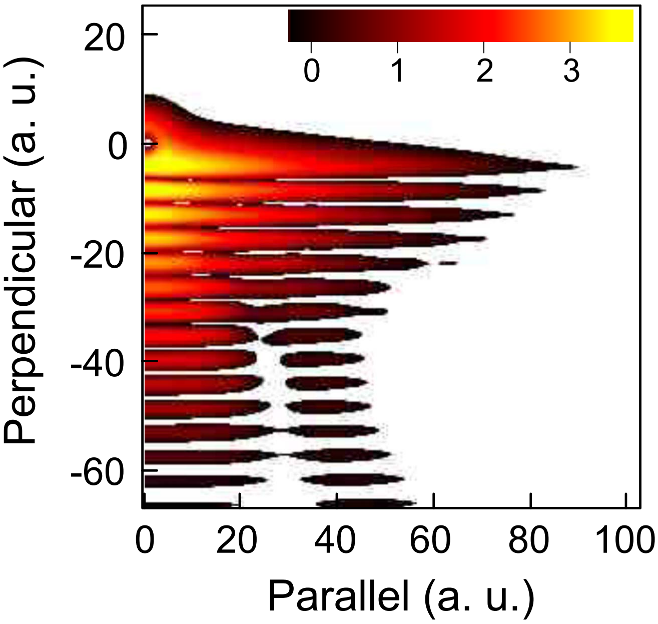

FIG. 3. (Color online) Contour map of the logarithm of the electron density associated with the Cs resonance, which is localized below the surface-state band, as a function of the electron coordinates parallel and perpendicular to the surface. The adsorbate center is at the origin of the coordinates and negative coordinates are inside the substrate. Coordinates are given in atomic units (Bohr radii). The color code is given in the inset: light yellow corresponds to high electron densities, dark to small densities, and white to very low densities.

which tunnel out of the Cs-induced resonance have a high probability for exciting vibrations of the adatom perpendicular to the surface, suggesting a strong resonance-induced adsorbate diffusion, similar to what has been observed for tip-assisted translations of Li atoms adsorbed on Ag(100).[37] To circumvent these problems, we embedded individual Cs atoms in an ultrathin Cs layer.

Our calculations predict that the localized resonance persists at very low coverages, in a few 10^{-3} ML ranges, before the resonances located on the individual Cs adsorbates overlap. The inset of Fig. 4 shows an STM image of a Ag(111) terrace covered with 0.03 ML Cs. It exhibits a nearly uniform hexagonal adsorbate lattice with a nearest-neighbor distance of ≈ 1.5 nm. The peculiar adsorbate superstructure, which is characterized by the coexistence of hexagonal adsorbate arrangements and regions where Cs adatoms exhibit an enhanced mobility, reflects a disorder-to-order transition and will be discussed elsewhere.[38] A typical spectrum acquired on an individual Cs atom residing in the adsorbate layer is presented in Fig. 4. The spectrum exhibits the same characteristics as the spectrum taken on a single adatom (Fig. 1). It is remarkable that the resonance survives in a coverage range where a different regime may be expected. Resonances on different adatoms should start to overlap (Fig. 3) leading to their delocalization, and in that case the resonance cannot be considered as a result of the surface-state localization by an attractive impurity. The additional spectroscopic structures visible at ≈ -50 meV are not visible in spectra of clean Ag(111), which were acquired with the same tip. Consequently, we can rule out tip electronic structure as the origin. Rather, these structures may be a remnant of the Ag(111) surface state or they may be related to additional Cs-induced states.

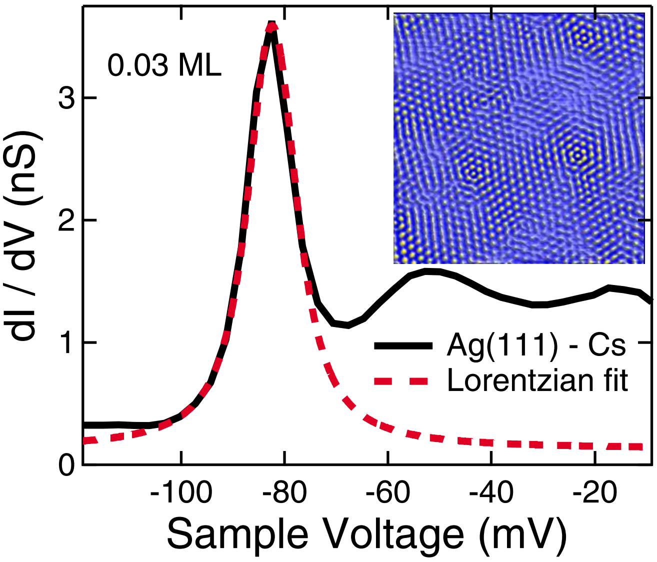

FIG. 4. (Color online) Spectrum of dI/dV acquired on a Cs atom in a 0.03-ML-thick Cs layer on Ag(111). The tunneling gap was defined at 0.1 nA and 200 mV. The dashed line is a Lorentzian fitted to the resonance. Inset: Constant current STM image of a Ag(111) terrace covered with 0.03 ML Cs (0.02 nA, 200 mV, and 24×24 nm^2).

The maximum occurs at ≈ -83 meV in Fig. 4 and is thus lower by ≈ 3 meV than the maximum in the spectrum of the single Cs adatom (Fig. 1). This shift may be partly due to a surface-state shift owing to charge transfer from the alkali-metal layer to Ag(111). Already at small coverages, alkali-metal adsorption is known to induce a considerable charge transfer.[38–41] For Cu(111)-Cs a shift of the Cu(111) surface state to higher binding energies was reported with increasing Cs coverage.[42] Extrapolating these results to low coverages, a surface-state band shift of ≈ 10 meV at 0.03 ML is expected. An additional contribution to the observed energy shift may be due to the electric field of the tip.[33,34]

To extract the intrinsic widths of the Cs-induced resonances a Lorentzian line shape with a full width at half maxi-

TABLE I. Experimental and theoretical linewidths (in meV) of the Cs-induced localized resonance (a width of 1 eV corresponds to a decay rate of 1.52×10^{15} s^{-1}). Γ denotes the FWHM of the resonance measured in spectra of dI/dV, while Γ_0 is the intrinsic FWHM without thermal and instrumental broadening. Γ_{inel} and Γ_{RCT} are the resonance decay rates due to inelastic processes and resonant charge transfer, while Γ_{vib} is the calculated Franck-Condon width of the resonance due to zero-point vibration of the adsorbate perpendicular to the surface. Γ_{tot} is the total theoretical linewidth obtained for a vibrating adsorbate.

Γ	Γ_0	Γ_{inel}	Γ_{RCT}	Γ_{vib}	Γ_{tot}
13.1 ± 2.0	12.0 ± 2.0	6.0	3.1	5.4	10.5

mum (FWHM) Γ_0 was convoluted with functions describing thermal and instrumental broadening. The resulting function was then fit to experimental data. At 7 K the thermal broadening function exhibits a FWHM of ≈ 2.1 meV, while a root-mean-square amplitude of the voltage modulation of 1 mV used for the lock-in detection of the tunneling current gives rise to a FWHM of the instrumental broadening function of ≈ 2.4 mV. As a result we obtain $\Gamma_0 = (12.0 \pm 2.0)$ meV for single Cs adatoms and $\Gamma_0 = (9.5 \pm 0.5)$ meV for Cs atoms embedded in the Cs layer. The convoluted line shapes are depicted as dashed lines in Figs. 1 and 4. A summary of the theoretical and experimental analysis of the linewidth of the Cs-induced resonance is presented in Table I.

The static local density of states in Fig. 2 takes into account the resonance decay by both elastic ($\Gamma_{\mathrm{RCT}} \approx 3.1$ meV) and inelastic processes ($\Gamma_{\mathrm{inel}} = 6.0$ meV). For the latter, we assume that an excited hole in the Cs-induced resonance is subjected to inelastic scattering similar to the Ag(111) Shockley-type surface state. Thus we use the same decay rate as observed for the surface state[35,43,44] as an input for our calculations. This choice is supported by the above-mentioned similarity between the localized state and the surface-state band. The localized state also broadens due to the adsorbate zero-point motion perpendicular to the surface. The corresponding Franck-Condon width amounts to $\Gamma_{\mathrm{vib}} = 5.4$ meV. The total width of the resonances was evaluated from the resonance profile for the adsorbate vibrating perpendicular to the surface, obtained in an additional quantal calculation including the electron-vibration coupling. The resulting total width for a single adsorbate is $\Gamma_{\mathrm{tot}} = 10.5$ meV, which is in good agreement with the experimentally measured width.

Vibrational heating of the Cs adatom induced by inelastically tunneling electrons has been considered. Using the LCP treatment of the vibrating adsorbate, we could evaluate the probability for vibrational excitation induced by the electron injection into the resonance. Based on a Cs vibration decay time of 1.5 ps, which was reported for Pd(111)-Cs,[45] we find a negligible effect of vibrational heating for the presently considered STM current.

V. SUMMARY

In conclusion, single Cs adatoms as well as Cs atoms embedded in ultrathin Cs adsorption layers on Ag(111) localize the two-dimensional surface-state continuum at the adsorbate site. A detailed analysis of the linewidth of this occupied resonance shows that it can be quantitatively accounted by inelastic scattering processes, resonant charge transfer, and vibrations of the adsorbate. The electron-adsorbate vibration coupling associated with the localized resonance split from the surface-state continuum provides another scheme for STM-induced adsorbate excitation.

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[1] P. M. Echenique, R. Berndt, E. V. Chulkov, Th. Fauster, A. Goldmann, and U. Höfer, Surf. Sci. Rep. **52**, 219 (2004).

[2] E. V. Chulkov, A. G. Borisov, J. P. Gauyacq, D. Sánchez-Portal, V. M. Silkin, V. P. Zhukov, and P. M. Echenique, Chem. Rev. (Washington, D.C.) **106**, 4160 (2006).

[3] L. Bürgi, H. Brune, O. Jeandupeux, and K. Kern, J. Electron Spectrosc. Relat. Phenom. **109**, 33 (2000).

[4] H. Jensen, J. Kröger, R. Berndt, and S. Crampin, Phys. Rev. B **71**, 155417 (2005).

[5] S. Crampin, H. Jensen, J. Kröger, L. Limot, and R. Berndt, Phys. Rev. B **72**, 035443 (2005).

[6] S. Crampin, J. Kröger, H. Jensen, and R. Berndt, Phys. Rev. Lett. **95**, 029701 (2005).

[7] C. Corriol, V. M. Silkin, D. Sánchez-Portal, A. Arnau, E. V. Chulkov, P. M. Echenique, T. von Hofe, J. Kliewer, J. Kröger, and R. Berndt, Phys. Rev. Lett. **95**, 176802 (2005).

[8] Ch. Reuß, I. L. Shumay, U. Thomann, M. Kutschera, M. Weinelt, Th. Fauster, and U. Höfer, Phys. Rev. Lett. **82**, 153 (1999).

[9] K. Boger, M. Weinelt, and Th. Fauster, Phys. Rev. Lett. **92**, 126803 (2004).

[10] F. E. Olsson, A. G. Borisov, M. Persson, N. Lorente, A. K. Kazansky, and J. P. Gauyacq, Phys. Rev. B **70**, 205417 (2004).

[11] F. E. Olsson, M. Persson, A. G. Borisov, J.-P. Gauyacq, J. Lagoute, and S. Fölsch, Phys. Rev. Lett. **93**, 206803 (2004).

[12] L. Limot, E. Pehlke, J. Kröger, and R. Berndt, Phys. Rev. Lett. **94**, 036805 (2005).

[13] V. S. Stepanyuk, A. N. Klavsyuk, L. Niebergall, and P. Bruno, Phys. Rev. B **72**, 153407 (2005).

[14] S. Lounis, P. Mavropoulos, P. H. Dederichs, and S. Blügel, Phys. Rev. B **73**, 195421 (2006).

[15] B. Lazarovits, L. Szunyogh, and P. Weinberger, Phys. Rev. B **73**, 045430 (2006).

[16] N. Fischer, S. Schuppler, Th. Fauster, and W. Steinmann, Surf. Sci. **314**, 89 (1994).

[17] M. Bauer, S. Pawlik, and M. Aeschlimann, Phys. Rev. B **55**, 10040 (1997).

[18] S. Ogawa, H. Nagano, and H. Petek, Phys. Rev. Lett. **82**, 1931 (1999).

[19] M. Bauer, S. Pawlik, and M. Aeschlimann, Phys. Rev. B **60**, 5016 (1999).

[20] M. Wessendorf, C. Wiemann, M. Bauer, M. Aeschlimann, M. A. Schneider, H. Brune, and K. Kern, Appl. Phys. A: Mater. Sci. Process. **78**, 183 (2004).

[21] P. Nordlander and J. C. Tully, Phys. Rev. B **42**, 5564 (1990).

[22] A. G. Borisov, A. K. Kazansky, and J. P. Gauyacq, Surf. Sci. **430**, 165 (1999).

[23] A. K. Kazansky, A. G. Borisov, and J. P. Gauyacq, Surf. Sci. **577**, 47 (2005).

[24] J. P. Gauyacq, A. G. Borisov, and A. K. Kazansky, Appl. Phys. A: Mater. Sci. Process. **78**, 141 (2004).

[25] B. Simon, Ann. Phys. (N.Y.) **97**, 279 (1976).

[26] N. Néel, J. Kröger, R. Berndt, and E. Pehlke, Phys. Rev. B **78**, 233402 (2008).

[27] SAES Getters SpA, Viale Italia 77, 20020 Lainate, Italy.

[28] A. G. Borisov, A. K. Kazansky, and J. P. Gauyacq, Phys. Rev. B **59**, 10935 (1999).

[29] E. V. Chulkov, V. M. Silkin, and P. M. Echenique, Surf. Sci. **437**, 330 (1999).

[30] A. K. Kazansky, A. G. Borisov, and J. P. Gauyacq, Surf. Sci. **544**, 309 (2003).

[31] J. P. Gauyacq and A. K. Kazansky, Surf. Sci. **601**, 5473 (2007).

[32] A. K. Kazansky and I. Yu. Sergeeva, J. Phys. B **27**, 3217 (1994).

[33] L. Limot, T. Maroutian, P. Johansson, and R. Berndt, Phys. Rev. Lett. **91**, 196801 (2003).

[34] J. Kröger, L. Limot, H. Jensen, R. Berndt, and P. Johansson, Phys. Rev. B **70**, 033401 (2004).

[35] F. Reinert, G. Nicolay, S. Schmidt, D. Ehm, and S. Hüfner, Phys. Rev. B **63**, 115415 (2001).

[36] M. Becker, S. Crampin, and R. Berndt, Phys. Rev. B **73**, 081402(R) (2006).

[37] V. Simic-Milosevic, M. Heyde, N. Nilius, M. Nowicki, H.-P. Rust, and H.-J. Freund, Phys. Rev. B **75**, 195416 (2007).

[38] M. Ziegler, J. Kröger, R. Berndt, A. Filinov, and M. Bonitz, Phys. Rev. B **78**, 245427 (2008).

[39] S.-Å. Lindgren and L. Walldén, Phys. Rev. B **22**, 5967 (1980).

[40] *Physics and Chemistry of Alkali Metal Adsorption*, edited by H. P. Bonzel, A. M. Bradshaw, and G. Ertl (Elsevier, Amsterdam, 1989).

[41] J. Kröger, D. Bruchmann, S. Lehwald, and H. Ibach, Surf. Sci. **449**, 227 (2000).

[42] M. Breitholtz, V. Chis, B. Hellsing, S.-Å. Lindgren, and L. Walldén, Phys. Rev. B **75**, 155403 (2007).

[43] J. Kliewer, R. Berndt, E. V. Chulkov, V. M. Silkin, P. M. Echenique, and S. Crampin, Science **288**, 1399 (2000).

[44] A. Eiguren, B. Hellsing, F. Reinert, G. Nicolay, E. V. Chulkov, V. M. Silkin, S. Hüfner, and P. M. Echenique, Phys. Rev. Lett. **88**, 066805 (2002).

[45] K. Watanabe, N. Takagi, and Y. Matsumoto, Chem. Phys. Lett. **366**, 606 (2002).