

Photoelectron driven acoustic surface plasmons in $p(2 \times 2)\text{K}/\text{Be}(0001)$: *Ab initio* calculationsV. M. Silkin,^{1,2,3} B. Hellsing,⁴ L. Walldén,⁵ P. M. Echenique,^{1,2} and E. V. Chulkov^{1,2}¹*Depto. de Física de Materiales and Centro Mixto CSIC-UPV/EHU, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastián/Donostia, Spain*²*Donostia International Physics Center (DIPC), P. Manuel Lardizabal 4, 20018 San Sebastián/Donostia, Spain*³*IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain*⁴*Department of Physics, Göteborg University, Göteborg, Sweden*⁵*Department of Applied Physics, Chalmers University, Göteborg, Sweden*

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We report on low-energy dynamical surface response properties of the $p(2 \times 2)\text{K}/\text{Be}(0001)$ system calculated within a first-principles approach. It is shown that a partly occupied adsorbate-induced quantum-well band dramatically affects the dynamical properties of the beryllium surface. We demonstrate clear evidence that the observed anomalous features in photoemission spectra of this and a similar system can be explained by acoustic surface plasmon excitations.

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Collective electronic excitations play an important role in many dynamical processes near solid surfaces. A well-known example is a surface plasmon—a collective excitation,¹ which for half a century has attracted great attention due to its importance in many applications.^{2–5} The energies of this mode are mainly determined by the average density of valence electrons and in metals lay in the ultraviolet range. Nevertheless, when the wavelength of the surface plasmon is comparable with the wavelength of visible light, the surface plasmon dispersion becomes pronounced and the resulted surface plasmon polariton has a dispersion essentially defined by the velocity of light. In the past few years the field of surfaces plasmons has attracted great attention mainly due to its coupling with light creating a new branch of science—plasmonics.^{6–9}

Recently it has been demonstrated that for atomically flat metal surfaces, supporting partly occupied electronic surface states, a new situation occurs in comparison with more strict two-dimensional (2D) electron systems.^{10–14} Due to the presence of two kinds of carriers (in the bulk states and in a surface band) at the metal surface—a possibility for a novel kind of collective electronic excitation [called acoustic surface plasmon (ASP)] with peculiar soundlike dispersion is introduced.¹⁵ As the electronic surface states indeed present at many surfaces,¹⁶ it is expected that this mode should be a quite general phenomena.¹⁷ Hence new physics and possibilities enter to a field where it is generally believed that the low-energy electronic response is governed by electron-hole pair excitations.⁴

In recent electron-energy-loss measurements the ASP mode has been detected at the $\text{Be}(0001)$ surface in close agreement with *ab initio* calculations.¹⁸ An interesting property of this mode is its quasilinear soundlike dispersion at small momenta, eventually yielding zero frequency for zero momentum. The slope of the dispersion is determined by the surface state Fermi velocity,¹⁵ which might be changed by altering the surface electronic structure. Consequently, the ASP dispersion can be tailored in a wide range.^{5,18}

One way to alter the surface state Fermi velocity consists in adsorption of atomic or molecular species on the surface. At the same time, above a certain coverage, adsorbates can

form their own energy bands—so-called quantum-well state (QWS) bands. For instance, many alkali covered surfaces are known to have a partly occupied free-electron-like QWS band.¹⁹ Based on previous observations of ASP on clean surfaces with partly occupied surface state bands, one would expect that the QWS band would generate similar excitations as well. If so, this clearly opens up the possibility to tune the ASP excitation channel by simply varying both type of alkali atom and its coverage, thereby altering the QWS Fermi velocity and consequently, the ASP dispersion.

Here we show the existence of an ASP spectrum for the system $p(2 \times 2)\text{K}/\text{Be}(0001)$, an order of magnitude more intense than for the clean Be surface. Moreover we show evidence that the anomalous peak, recently observed in photoemission spectroscopy (PES) measurements for both potassium and sodium monolayers adsorbed on $\text{Be}(0001)$ (Ref. 20) as well for a lithium monolayer on $\text{Be}(0001)$ observed some time ago,²¹ most likely is due to ASP excitation originated from the alkali-induced QWS band. This is a first indication that for this type of overlayer systems light can drive a surface localized plasmon, not due to optical transitions but via the ejected photoelectron. The plasmon runs along the surface with a speed proportional to the Fermi velocity of the QWS band.⁵

The PES spectrum (open circles in Fig. 1) shows at the center of the 2D Brillouin zone (2DBZ) additionally to the QWS peak a peak at about 1.2 eV below the Fermi level which cannot be explained by the first-principles band structure calculations (Fig. 2). For this reason it was referred in the work by Algdal *et al.*²⁰ to as “an anomalous peak” appeared due to an energy losses associated with collective oscillations in the overlayer. The same type of features was observed by Watson and co-workers in PES data for a saturated lithium monolayer on $\text{Be}(0001)$ almost two decades ago.²¹ In that case the signature was also almost non-dispersive anomalous peak localized at the 2DBZ center about 0.7 eV below the Li-derived QWS band bottom. The authors argued that its origin was due to folding of an avoided crossing phenomena between the Li QWS band and the Be surface state band at the one Li-reciprocal lattice vector from the $\bar{\Gamma}$ point. In contrast we believe that, as the Li

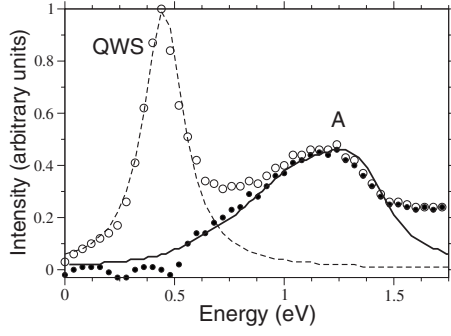


FIG. 1. QWS and anomalous (A) peaks for K/Be(0001) at the $\bar{\Gamma}$ point. The open circles are the experimental data (Ref. 20) and the filled circles are the experimental data with subtraction of the Lorentzian fitted QWS peak. The solid line represents the normalized A peak calculated for a QWS Fermi vector $k_F^{\text{QWS}} = 0.20 \text{ a.u.}^{-1}$ as described in the text.

overlayer is incommensurate with the Be substrate, hybridization between the bands leading to avoided crossing will not take place. Moreover, just as in the case of Na and K on Be(0001),²⁰ the appearance of an anomalous peak at a reciprocal alkali lattice vector from the $\bar{\Gamma}$ point is due to a loss process, described in details below, involving ASP excitations, localized mainly in the alkali overlayer.

We now demonstrate in some details that a so-called anomalous peak in the PES spectrum can be referred to an inelastic scattering process in which a photoexcited electron from QWS has lost energy and momentum due to the ASP excitation. The electron, when leaving the QWS band, can take two routes (as schematically shown in Fig. 3). If the photoelectron starts out with a finite momentum \mathbf{k}_{\parallel} it might leave the surface elastically, i.e., without losing momentum and energy (route I), or it might, with some probability excite an ASP with momentum \mathbf{q}_{\parallel} and energy E . Thus, for $\mathbf{q}_{\parallel} = \mathbf{k}_{\parallel}$, the photoelectron leaves the surface in the normal direction

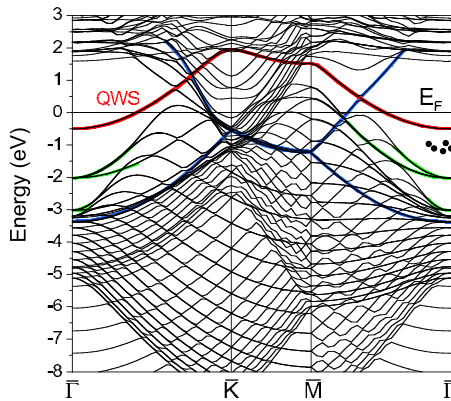


FIG. 2. (Color online) Calculated band structure for $p(2 \times 2)\text{K}/\text{Be}(0001)$ surface along some symmetry directions of the 2DBZ. Red/gray color highlights the potassium-induced QWS band dispersion, whereas others colored lines show beryllium-derived back-folded surface states (Refs. 29–31) down-shifted in energy. The black dots show the experimental PES data points (Ref. 20) yielding the anomalous peak. Zero energy corresponds to the Fermi level, E_F .

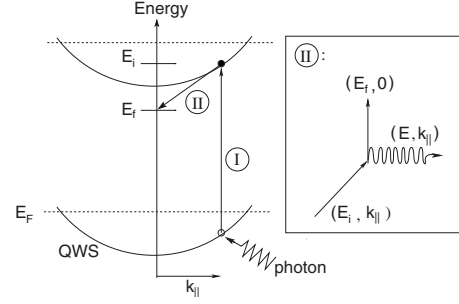


FIG. 3. Scheme of photoemission process from the QWS band. E_F is the Fermi energy. Process I: photoelectron leaves surface with finite emission angle determined by vector \mathbf{k}_{\parallel} . Process II: ASP excitation followed by normal photoemission. The upper parabolic curve pictures the QWS band adding the photon energy $\hbar\omega$. The inset shows the real space ASP excitation process giving rise to a normal electron emission.

having suffered a loss of energy E (route II). From Fig. 2 we note that the potassium-induced QWS band has a parabolic free-electron character, thus we have the initial energy, including the absorbed photon with energy $\hbar\omega$

$$E_i = -\epsilon_b + \frac{\hbar^2 k_{\parallel}^2}{2m^*} + \hbar\omega, \quad (1)$$

relative the Fermi level. The binding energy at the $\bar{\Gamma}$ point, $\epsilon_b \approx 0.56 \text{ eV}$ and effective electron mass, $m^* \approx 1$. The probability for an ASP excitation as a function of energy $E = E_i - E_F$, can be expressed in terms of the surface-loss function, $\text{Im}[g(\mathbf{q}_{\parallel}, E)]$, where g is the surface-response function.²² $\text{Im}[g(\mathbf{q}_{\parallel}, E)]$ yields the distribution of energy loss E for a given parallel momentum \mathbf{q}_{\parallel} . In first-order time-dependent perturbation theory the ASP excitation rate is given by⁵

$$W(E) \sim \frac{4\pi}{S} \sum_{\mathbf{q}_{\parallel}} \frac{1}{q_{\parallel}} \text{Im}[g(\mathbf{q}_{\parallel}, E)], \quad (2)$$

where S is the normalization area. Thus, assuming isotropy in the surface plane, we get

$$W(E) \sim 2 \int_0^{k_F^{\text{QWS}}} \text{Im}[g(q_{\parallel}, E)] dq_{\parallel}, \quad (3)$$

where k_F^{QWS} is the magnitude of the QWS Fermi wave vector.

Our calculation of $\text{Im}[g(\mathbf{q}_{\parallel}, E)]$ is based on the time-dependent density-functional theory²³ in which the nonlocal dynamical density-response function, χ , determines the induced electron density caused by an external potential, v_{ext} . χ is obtained from the integral equation $\chi = \chi^{\circ} + \chi^{\circ}(v + K_{\text{xc}})\chi$. Here K_{xc} accounts for dynamical exchange-correlation effects for which we use the adiabatic extension of the local-density approximation.²⁴ The Fourier transform of the response function for noninteracting electrons, χ° , is determined by the first-principles single particle energies $\epsilon_{n\mathbf{k}}$ and wave functions $\psi_{n\mathbf{k}}$ (expanded in a plane-wave basis up to the energy cutoff of 20 Ry), obtained with the use of lattice parameters from Ref. 20 and self-consistent norm-conserving pseudopotential method.²⁵ The number of Be atomic layers was 16 and vacuum region expanded over 10

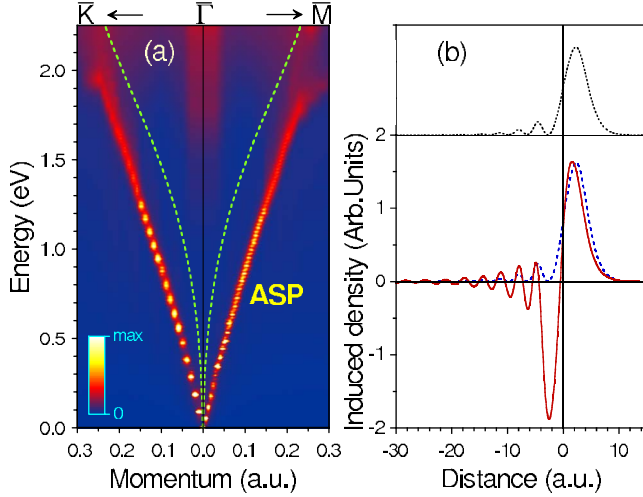


FIG. 4. (Color online) (a) 2D plot of $\text{Im}[g(\mathbf{q}_{\parallel}, E)]$ along the $\overline{\Gamma K}$ (to the left) and $\overline{\Gamma M}$ (to the right) directions. Bright spots show the ASP dispersion and thin dotted line presents dispersion of a 2D plasmon for an unsupported K-derived QWS. (b) Upper panel gives the QWS charge density distribution, n_{QWS} , in the direction perpendicular to the surface. Lower panel shows induced charge density corresponding to the ASP, $\rho_{\text{ASP}}^{\text{ind}}$, (solid line) and the one obtained taking only QWS into account in calculation of the response function, $\rho_{\text{2D}}^{\text{ind}}$, (dashed line) at $q_{\parallel}=0.0569$ a.u.⁻¹. One can see how $\rho_{\text{2D}}^{\text{ind}}$ follows closely to n_{QWS} , while $\rho_{\text{ASP}}^{\text{ind}}$ displays a pronounced oscillatory behavior, mixing with the Be substrate. The K monolayer (Be crystal) is located at $z=0$ (negative z).

Be interlayer spacings. The exchange-correlation potential in form of Ref. 26 was used. The calculation of χ° was performed by summing up over the 30×30 special \mathbf{k}_{\parallel} -point mesh in the $p(2 \times 2)$ K/Be(0001) 2DBZ and one-particle states up to 50 eV above the Fermi level. The surface-response function g is then obtained as

$$g(\mathbf{q}_{\parallel}, E) = -\frac{2\pi}{q_{\parallel}} \int \int dz dz' e^{iq_{\parallel}(z+z')} \chi_{\mathbf{G}=0, \mathbf{G}'=0}(z, z', \mathbf{q}_{\parallel}, E). \quad (4)$$

Further calculation details can be found elsewhere.^{27,28}

The calculated surface-loss function for \mathbf{q}_{\parallel} along two symmetry directions is reported in Fig. 4. At low energies, i.e., below 2 eV, we find here the peaks which correspond to excitations of ASP. The peaks are very sharp in energy comparing with the corresponding mode²⁸ on a bare Be(0001) surface and disperse almost linear with momentum. One can also observe almost isotropic ASP dispersion. Then we approximate the ASP dispersion with

$$\hbar \omega_{\text{ASP}}(\mathbf{q}_{\parallel}) = \hbar c q_{\parallel}, \quad (5)$$

where $c \approx 0.32$ a.u. is the ASP velocity. The function $\text{Im}[g(\mathbf{q}_{\parallel}, \omega)]$ is calculated for fixed momenta \mathbf{q}_{\parallel} and fitted to a parameterized Lorentzian-shaped function

$$\text{Im}[g(\mathbf{q}_{\parallel}, E)] = I_0(q_{\parallel}) \frac{\Delta_{\text{ASP}}}{[E - \hbar c q_{\parallel}]^2 + \Delta_{\text{ASP}}^2}, \quad (6)$$

where $I_0(q_{\parallel})$ is spectral weight and Δ_{ASP} is the mean half-width at a half maximum.

To make connection to the PES data we assume that the contribution to the spectral function, $A(\epsilon)$, from the loss satellite associated with ASP excitations is proportional to the rate of ASP excitations in Eq. (2). With the result in Eq. (6) and ϵ denoting energy relative to the Fermi level we then have

$$A(\epsilon) \sim \int_0^{k_F^{\text{QWS}}} \frac{I_0(q_{\parallel})}{(\epsilon - \epsilon_b + \hbar^2 q_{\parallel}^2 / 2m^* - \hbar c q_{\parallel})^2 + \Delta^2} dq_{\parallel}, \quad (7)$$

where we have taken into account the lifetime broadening due to the initial photoelectron excitation, Δ_{PES} in the full width $\Delta = \Delta_{\text{PES}} + \Delta_{\text{ASP}}$. $\Delta_{\text{PES}} = 0.1$ eV, is the half-width at half-maximum of the QWS peak in Fig. 1 and $\Delta_{\text{ASP}} = 0.05$ eV, is the mean width parameter of the low-energy peaks in the surface-loss function shown in Fig. 4. The calculated spectral function is compared with experiment in Fig. 1. The best fit is obtained with a Fermi wave vector of 0.20 a.u.⁻¹, which agrees with present and previous²⁰ first-principles calculations, and also reasonably well with experimentally measured²⁰ $k_F^{\text{QWS}} = 0.17$ a.u.⁻¹.

Simple energetic reasoning also support our interpretation. The energy difference ΔE between the main normal emission peak and the anomalous peak in Fig. 1 can be estimated as follows. In atomic units we have $\Delta E = c\bar{q} - \bar{q}^2/2$, where \bar{q} is the mean magnitude of the parallel electron wave vector on the circular disk with radius k_F^{QWS} which is given by $2k_F^{\text{QWS}}/3$. As $c \approx 3/2k_F^{\text{QWS}}$ we have $\Delta E \approx (14/9)[(k_F^{\text{QWS}})^2/2] \approx (3/2)\epsilon_b \approx 0.75$ eV which agrees well with the experimental data in Fig. 1. We would like to strength the importance of the linear dispersion of ASP for the appearance of the anomalous spectral feature in PES. If the linear dispersion relation of the ASP is replaced by the dispersion relation of the unsupported QWS [thin dotted line in Fig. 4(a)], the position of the A peak in Fig. 1 is then shifted approximately 1 eV up in energy and thus deviate substantially from experimental data.

Our interpretation that the anomalous peak in the photoemission spectrum refers to excitations of ASPs has additional experimental support. The anomalous peak appears when the QWS band gets occupied during the build up of the K monolayer and shifts down in energy in concert with the QWS band as the K monolayer is completed. Furthermore, the sharp peaks in the calculated surface-loss function disappear as q_{\parallel} exceeds approximately the QWS band wave vector k_F^{QWS} .

It is important to note that the excitation takes place within the surface potential (intrinsic process), as in this case only the parallel momentum of the photoelectron has to be conserved. If the excitation would have taken place outside the surface (extrinsic process), where the potential is flat also the perpendicular momentum has to be conserved. In that case $q_{\parallel}^2/2 = \hbar c q_{\parallel} \Rightarrow q_{\parallel} = 2c > k_F^{\text{QWS}}$, which means no excitation of ASPs would take place. In principle, for any metallic sur-

face with a surface localized band, a photoelectron might excite an acoustic surface plasmon and thus give rise to an anomalous peak in normal PES. However, to be clearly observable, a wide band gap exceeding below the surface state band is required. Furthermore, our study of $p(2 \times 2)\text{K}/\text{Be}(0001)$ clearly demonstrates that the low-energy part of the surface-loss function is enhanced due to the weak coupling to electron-hole pair excitations in the substrate, in comparison with the clean $\text{Be}(0001)$ surface. This is most probably the reason why the anomalous peak was not observed below the surface state band in normal PES for the clean $\text{Be}(0001)$ surface.

In conclusion, we demonstrate, based on *ab initio* calculations a strong impact of the potassium-induced quantum

well state on the low-energy electronic excitations in the $p(2 \times 2)\text{K}/\text{Be}(0001)$ system. In particular we found a long-lived acoustic surface plasmon mode dispersing in a broad energy range from 0 to ~ 2 eV. We clarify that the “anomalous” peaks observed in photoemission spectra for this system and previously studied similar system [$\text{Li}/\text{Be}(0001)$] are explained by photoelectron driven excitations of acoustic surface plasmons.

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