Surface-electronic-state effects in electron emission from the Be(0001) surface

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We study the electron emission produced by swift protons impinging grazingly on a Be(0001) surface. The process is described within a collisional formalism using the band-structure-based (BSB) approximation to represent the electron-surface interaction. The BSB model provides an accurate description of the electronic band structure of the solid and the surface-induced potential. Within this approach we derive both bulk and surface electronic states, with these latter characterized by a strong localization at the crystal surface. We found that such surface electronic states play an important role in double-differential energy- and angle-resolved electron emission probabilities, producing noticeable structures in the electron emission spectra.

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I. INTRODUCTION

Beryllium has been chosen as plasma-facing material for the international nuclear fusion experiment ITER, currently under construction in Cadarache, France [1]. Most of the inner walls of the plasma vessel of this facility will be covered with beryllium, while the plasma will mainly consist of hydrogen isotopes. Even though plasma ions will be confined within the nucleus of the fusion reactor, collisions against the beryllium walls cannot be completely avoided. Therefore, the study of scattering processes involving the impact of protons on Be surfaces is of particular interest.

In the last two decades a large number of works has investigated the properties of beryllium crystals and their collisional interaction with other elements [2–5]. At the static limit, first-principles calculations of the interaction of protons with beryllium surfaces have been performed, involving the description of the adsorption, defect formation, and diffusion mechanisms [6–8]. A wide variety of articles were also devoted to studying the surface electronic structure of different faces of Be, such as the (0001) face [9–13] and others [14–17]. In the case of the Be(0001) surface, in the vicinity of the Fermi level this surface presents surface electronic states displaying an exceptionally high electron-density localization near the surface atomic layers [11]. As a result, it is expected that the presence of this kind of partly occupied surface states will affect the inelastic transition probabilities for this material. Indeed, it has recently been demonstrated that partly occupied surface electronic states can dramatically modify the dielectric properties of metal surfaces [18,19].

In this article we investigate the dynamic interaction of a proton with a beryllium surface in the intermediate- and high-energy range, for which theoretical and experimental studies are scarce. More specifically, we study the electron emission from the valence band of the Be(0001) surface under grazing impact of fast protons by employing the binary collisional formalism [20,21]. A crucial point in this approach is the proper description of the electron-surface interaction [22]. A simple representation of this potential can be obtained by considering that conduction electrons are bounded to the surface by a finite step potential (a jellium model) [20,21,23–26]. However, for a more realistic description, we use here the band-structure-based (BSB) model [27], which incorporates information about the electronic band structure of the solid. In the BSB approach the surface interaction is described by a one-dimensional model potential [28] that reproduces the width and position of the projected bulk energy gap, the energies of the surface states, and the first image state [29–32]. The dynamic response of the medium is derived in a consistent way from the unperturbed electronic states by using a linear-response theory. The BSB approximation has already been successfully employed to evaluate energy loss and electron emission from Al surfaces [27,33].

This paper is organized as follows: Sec. II gives a brief explanation of the theoretical model used to calculate the electron emission probability. In Sec. III, results are presented and discussed. The conclusions are summarized in Sec. IV. Atomic units are used unless otherwise stated.

II. THEORETICAL METHOD

Within the binary collisional formalism, the differential probability per unit path for the electronic transition $i \to f$ reads [20]

$$P_{if}(Z) = \frac{2\pi}{v_s}\delta(\Delta) \mid T_{if} \mid^2 , \tag{1}$$

where Z is the projectile distance to the surface, v_s is the component of the projectile velocity parallel to the surface plane, and the Dirac delta $\delta(\Delta)$expresses the energy conservation, with

$$\Delta = \vec{v}_s \cdot (\vec{k}_{fs} - \vec{k}_{is}) - (E_f - E_i), \tag{2}$$

where $\vec{k}_{is}$ ($\vec{k}_{fs}$) is the initial (final) electron momentum parallel to the surface and E_i (E_f) is the initial (final) electron energy.

In Eq. (1) T_{if} represents the T-matrix element, which is evaluated with a first-order perturbation theory. It reads

$$T_{if} = \langle \Phi_f | V_{Pe} | \Phi_i \rangle, \tag{3}$$

where V_{Pe} denotes the Coulomb projectile-electron interaction shielded by the other valence electrons and Φ_i (Φ_f)is the initial (final) unperturbed electronic state.

By assuming translational invariance in the plane parallel to the surface, the unperturbed states can be expressed as

$$\Phi_{\vec{k}_s,n}(\vec{r}) = \frac{1}{2\pi} \exp(i\vec{k}_s \cdot \vec{r}_s)\phi_n(z), \tag{4}$$

where $\vec{r} = (\vec{r}_s, z)$ is the position vector of the active electron, with $\vec{r}_s$ and z being the components of $\vec{r}$ parallel and perpendicular, respectively, to the surface plane. The frame of reference is here placed on the topmost atomic layer, with $\hat{z}$ perpendicular to the surface, toward the vacuum region.

In Eq. (4) $\phi_n(z)$ is the eigenfunction of the one-dimensional Schrödinger equation associated with the surface potential of Ref. [28] with eigenenergy ε_n. To derive the one-dimensional functions $\phi_n(z)$ we employ slab geometry by considering the following representation:

$$\phi_n(z) = \frac{1}{\sqrt{L}} \sum_{j=-N}^{N} a_n(j) \exp\left(i \frac{2\pi j}{L} \tilde{z}\right), \tag{5}$$

where L is a normalization length, $2N+1$ is the number of basis functions, and the coefficients $a_n(j)$ are numerically evaluated. The coordinate $\tilde{z} = z + d_s$is measured with respect to the center of the slab, which is placed at a distance d_s from the surface.

The potential V_{Pe} is expressed as the sum $V_{Pe} = V_{pe}^{\text{Coul}} + V_{\text{ind}}$, where V_{Pe}^{Coul} is the Coulomb projectile interaction and V_{ind} represents the surface potential induced by the incident ion moving at a distance Z from the surface plane. The potential V_{ind} is obtained from the two-dimensional Fourier transform of the density-density response function, which is calculated [34,35] within the linear-response theory by employing the BSB electronic states given by Eq. (4).

The differential probability of electron transition to a given final state f with momentum $\vec{k}_f$, $dP/d\vec{k}_f$, can be derived from Eq. (1) by integrating along the classical projectile trajectory $Z(X)$, after adding the contributions coming from the different initial states. That is,

$$\frac{dP}{d\vec{k}_f} = \int_{-\infty}^{\infty} dX \sum_i \rho_e \Theta(E_F - E_i) P_{if}(Z(X)), \tag{6}$$

where $\rho_e = 2$ takes into account the spin states, the unitary Heaviside function Θ restricts the initial states to those contained inside the Fermi sphere, and E_F is the Fermi energy. Furthermore, since the final electronic states $\Phi_f(\vec{r})$ present a well-defined momentum only in the direction parallel to the surface plane, to determine $\vec{k}_f = (\vec{k}_{fs}, k_{fz})$ it is necessary to define an *effective* electron momentum perpendicular to the surface as $k_{fz} = \sqrt{2\varepsilon_{n_f}}$, where ε_{n_f} is the eigenenergy associated with the final one-dimensional wave function $\phi_{n_f}(z)$. More details of the BSB approximation can be found in Ref. [27].

III. RESULTS

We confined our study to a collision system composed of 100-keV protons impinging on a Be(0001) surface with a glancing angle ($\alpha = 1^\circ$) . At this impact energy, protons can be treated as bare ions along the whole trajectory. The parameters used to describe beryllium are the following: the Fermi energy is $E_F = 14.3$eV, and the work function is $E_W = 5.35$eV. The energy of the surface states is close to -8.1 eV, measured with respect to the vacuum level. In our framework, the final electron momentum can be expressed as $\vec{k}_f = k_f(\cos\theta_e \cos\varphi_e, \cos\theta_e \sin\varphi_e, \sin\theta_e)$,where $\theta_e$is the elevation angle with respect to the surface and φ_e is the azimuthal angle between the direction of emission and the scattering plane.

To derive the one-dimensional wave functions ϕ_n we followed the same procedure as in Ref. [27]. We used a basis formed by 421 plane waves, the width of the unit cell was $L = 338.7338$ a.u., and the distance between the surface and the slab center was $d_s = 135.48$a.u. Once the differential probability of electron emission was obtained from Eq. (1), further integration on the trajectory given by Eq. (6) was solved by interpolating 23 values of the X coordinate. To evaluate the projectile trajectory we employed the Ziegler-Biersack-Litmark (ZBL) potential plus the BSB-induced potential given in Ref. [28].

In the BSB model, two wave functions $\phi_{n_f}(z)$ (the symmetric one and the antisymmetric one) are associated with the same positive energy ε_{n_f}, where symmetry properties are determined with respect to a plane parallel to the surface and placed in the middle of the slab. Therefore, these wave functions do not allow us to distinguish electrons emitted inside the solid from those ejected toward the vacuum semispace. As a first estimate we considered that ionized electrons emitted to the vacuum region represent approximately 50% of the total ionized electrons from the conduction band [27].

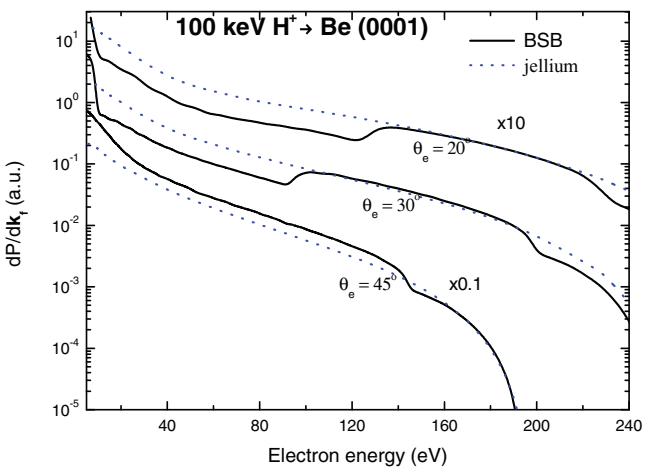

FIG. 1. (Color online) Double-differential probability of electron emission from the valence band of a Be(0001) surface as a function of the electron energy for 100-keV protons impinging with an angle of $\alpha = 1^\circ$. Three different grazing electron ejection angles in the scattering plane, measured with respect to the surface, are considered: $\theta_e = 20^\circ, 30^\circ$, and 45°. Solid line, BSB results; dashed line, results derived with the jellium model from [19].

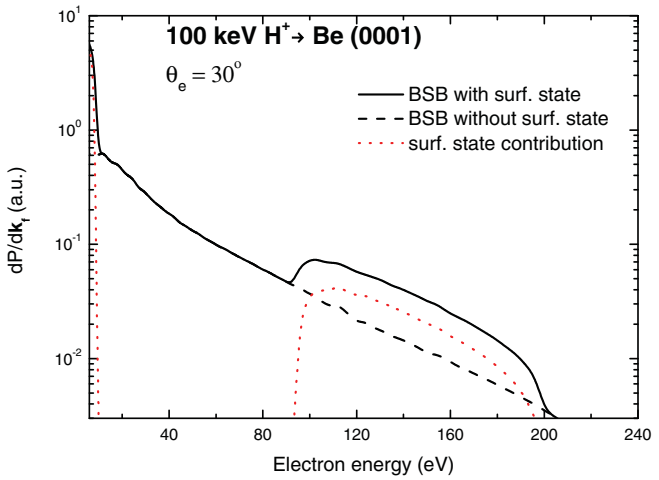

FIG. 2. (Color online) Influence of the surface state in the differential electron emission probability for the ejection angle $\theta_e = 30^\circ$. Dotted line, surface-state contribution; dashed line, BSB electron emission spectrum excluding the surface-state contribution; solid line, BSB electron emission spectrum (including surface-state contribution).

In Fig. 1 we show the differential probability of electron emission as a function of the electron energy for three different ejection angles in the scattering plane. All the electron spectra decay to zero for energies beyond a maximum energy that depends on the emission angle. This behavior originates in the restriction imposed by the Δ function in Eq. (2), i.e., $\Delta = \vec{v}_s \cdot (\vec{k}_{fs} - \vec{k}_{is}) - (E_f - E_i) = 0$, which determines the energy conservation during the electronic transition. From this expression the maximum energy $E_{f\,\max} = k^2_{f\,\max}/2$ reached by the ejected electrons is obtained from the condition

$$k_{f\,\max} = v_s \cos\theta_e \cos\varphi_e \pm \left[v_s^2(\cos^2\theta_e \cos^2\varphi_e - 1) + R^2_{\max}\right]^{1/2}, \tag{7}$$

where $R^2_{\max} = (v_s + k_F)^2 - 2V_0$, with k_F being the electronic momentum corresponding to the Fermi energy and V_0 being the minimum of the surface electronic potential.

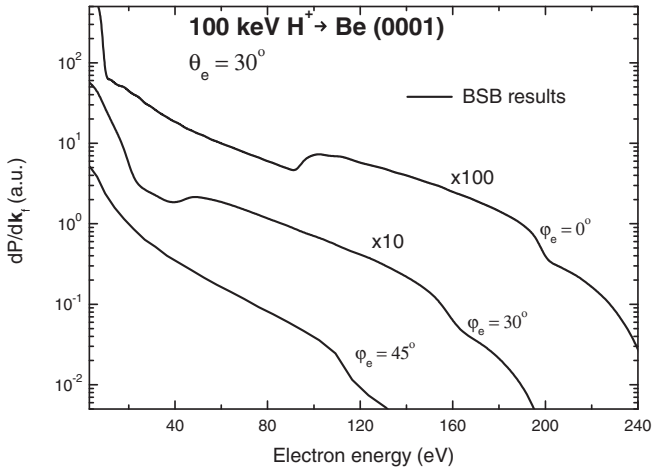

FIG. 3. Similar to Fig. 1 for the emission angle $\theta_e = 30^\circ$ and three different azimuthal angles measured with respect to the scattering plane: $\varphi_e = 0^\circ, 30^\circ$, and 45°.

From Fig. 1 we observe that the electronic distributions display pronounced shoulders at intermediate energies. The positions of these shoulders gradually shift toward lower electron energies as the emission angle increases. In addition, for small θ_e values a sharp maximum at low electron energies is present in the BSB distribution. But this peak grows smoother as the emission angle augments, as is the case for $\theta_e = 45^\circ$. Both effects, the low-energy peak and the shoulders, are related to the electronic band structure of the solid, and when the electron-surface interaction is represented in a simpler way by using the jellium model [20], $dP/d\vec{k}_f$ becomes a uniformly decreasing function of the energy, without displaying any superimposed structure.

In order to investigate the band-structure effects observed in the spectra of Fig. 1, in Fig. 2 we plot the contribution of the occupied surface states to the BSB electron emission probability for the ejection angle $\theta_e = 30^\circ$. Results are compared with the BSB energy distributions obtained with and without including surface states. Note that again, as a consequence of the energy conservation imposed by the Δ function in Eq. (2), electrons ionized from the surface states

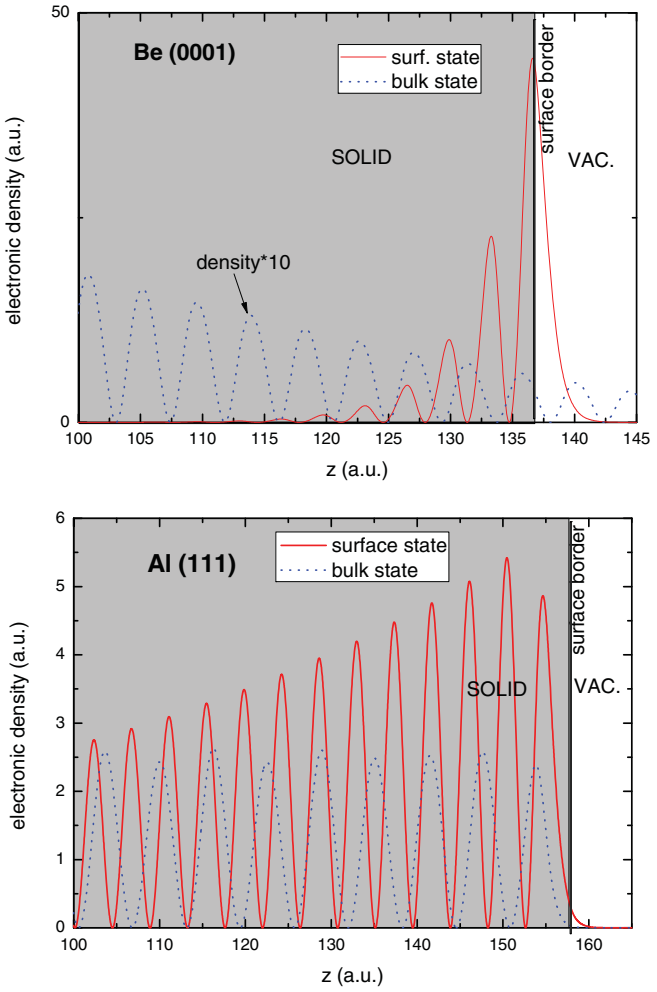

FIG. 4. (Color online) Comparison between the surface-state contribution to the electron density (solid line) and the contribution of a bulklike state of a close energy value (dotted line) for (a) Be(0001) and (b) Al(111) surfaces.

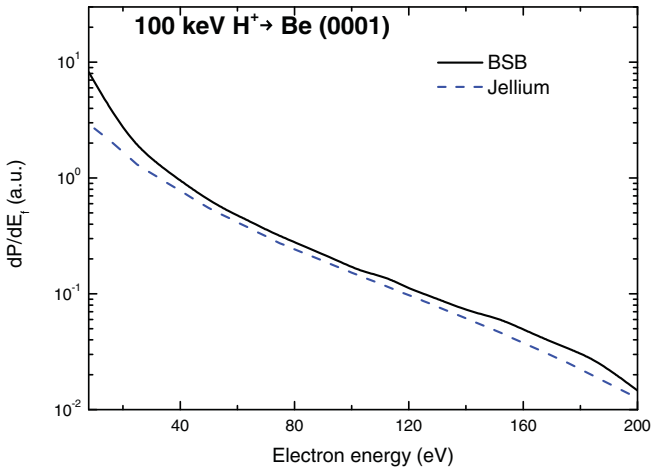

FIG. 5. (Color online) Probability of electron emission from the valence band as a function of the electron energy for 100-keV protons impinging on a Be(0001) surface with an angle of $\alpha = 1^\circ$. Solid line, BSB results; dashed line, results derived within the jellium model, as in Ref. [26].

present final momenta confined within a spherical region [20], which includes the well-known "binary ridge."

In this energy region, the emission probability from the surface states is much higher than the one corresponding to the remaining bound states. Therefore, this high contribution is visible as a superimposed structure in the BSB electron distribution, as shown in Fig. 2.

The structures due to the contribution of the surface electronic states are also present for emission angles out of the scattering plane. In Fig. 3 we plot electron distributions for the ejection angle $\theta_e = 30^\circ$ considering three different azimuthal angles: $\varphi_e = 0^\circ, 30^\circ$, and 45°, where $\varphi_e = 0^\circ$ corresponds to emission in the scattering plane. When emitted electrons depart from the scattering plane by increasing the value of φ_e, the shoulders of the electron spectrum begin to shift to lower values of E_f, as also observed in Fig. 1 in relation to the dependence on the polar angle θ_e. In particular, we found that for the azimuthal angle $\varphi_e = 45^\circ$, surface-state structures vanished almost completely. In this case, the presence of occupied surface states produces only a weak shoulder at energies near 120 eV.

To understand why the influence of occupied surface states is much stronger for beryllium than for aluminum surfaces, where surface-state effects were found to play a minor role [27], we analyze the surface-state contribution to the electron density for both elements. In Fig. 4 the electronic density corresponding to the surface state is compared to the one associated with a different initially occupied state, with a close energy value, considering Be(0001) [Fig. 4(a)] and Al(111) [Fig. 4(b)] surfaces. In both cases, in the subsurface region, the electronic density of the surface state is higher than the one corresponding to any other bound state, especially near the crystal border, which is placed at a distance $d/2$ in front of the topmost atomic layer, with d being the interplanar separation. But for beryllium this difference reaches more than one order of magnitude at the surface edge, while for Al(111) both densities differ by a factor smaller than 2. Therefore, the highly peaked electron density of the surface state of Be at the surface border gives rise to noticeable effects in the double-differential electron distribution.

Finally, we evaluate the single-differential electron emission probability dP/dE_f, which was obtained from $dP/d\vec{k}_f$ integrating over the corresponding emission solid angle. To perform such an integration we have used a Monte Carlo numerical technique. The BSB energy spectrum for beryllium is shown in Fig. 5, compared with results derived with the jellium model. Remarkably, the band-structure effects almost completely disappear when the BSB angular distributions are integrated to derive the simple differential energy-resolved emission probability. This is due to the fact that in the BSB angular spectra the positions of the surface-state structures vary strongly with the ejection direction. BSB and jellium models provide similar energy distributions, the main differences being observed at low electron energies, where the BSB results are larger than jellium results by a factor of more than 2.

IV. CONCLUSION

We have evaluated electron emission spectra for Beryllium (0001) surfaces bombarded with swift protons by employing the BSB approach, which incorporates information about the electronic band structure of the solid. BSB double-differential electron probabilities display noticeable structures related to the presence of occupied surface states, which are completely missed when a simpler model, like the jellium model, is used to describe the electron-surface interaction. Surface-state contribution arises as a superimposed structure in the electron spectrum, being restricted to an angular and electron energy range determined by the energy conservation.

In the subsurface region of the Be(0001) crystal, the electronic density associated with the surface state is much higher than the one corresponding to the remaining occupied bound states. This is why surface-state effects are visible in the double-differential electron emission probabilities. However, these band-structure effects tend to disappear when the angular distribution is integrated to derive the electron energy spectrum, with differences with the jellium model being only observed in the low-energy region. In the future it would be interesting to investigate if the description of such effects is affected by the incorporation in our model of more realistic wave functions, such as the ones obtained from *ab initio* band-structure calculations.

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