Band structure effects on the Be(0001) acoustic surface plasmon energy dispersion

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We report first-principles calculations of acoustic surface plasmons on the (0001) surface of Be, as obtained in the random-phase approximation of many-body theory. The energy dispersion of these collective excitations has been obtained along two symmetry directions. Our results show a considerable anisotropy of acoustic surface plasmons, and underline the capability of experimental measurements of these plasmons to map the electron–hole excitation spectrum of the quasi two-dimensional Shockley surface state band that is present on the Be(0001) surface.

1 Introduction

The existence of metal surfaces is well known to yield the appearance of conventional surface collective electronic excitations, surface plasmons, predicted by Ritchie 50 years ago [1]. Thereafter, surface plasmons were widely investigated both experimentally and theoretically [2–7]. Another kind of collective excitations that are present at metal surfaces are the so-called multipole surface plasmons predicted theoretically [8] and later detected experimentally [9, 10]. The energy of both these plasmons is a fraction of the bulk plasmon energy, $\omega_p$, typically $(0.7–0.8)\omega_p$ for small momenta.

A qualitatively different surface collective excitation, called acoustic surface plasmon, has recently been predicted theoretically [11] and observed experimentally using angle-resolved electron energy loss spectroscopy [12]. Acoustic surface plasmons are low-energy collective excitations that are confined to solid surfaces where a partially occupied quasi-two dimensional (2D) surface-state band coexists with the underlying three-dimensional (3D) continuum, as occurs in the case of Be(0001) [11] and the (111) surfaces of the noble metals Cu, Ag, and Au [13]. They are called acoustic because their energy dispersion exhibits sound-like linear behaviour at low momenta, contrary to the square-root dispersion expected for a pure 2D electron gas [14].

The calculations that led to the prediction of acoustic surface plasmons [11] assumed translational invariance in the plane of the surface and incorporated the electron dynamics in the direction perpendicular to the surface through the use of a one-dimensional (1D) model potential that describes the main features of the surface band structure [15]. Although acoustic plasmons had previously been
only expected to exist for spatially separated plasmas [16, 17]. 1D model potential self-consistent calculations demonstrated that, contrary to expectations, acoustic plasmons should indeed be present at bare metal surfaces where a 2D surface-state band coexists with the underlying 3D continuum.

In this paper, we report first-principles calculations of acoustic surface plasmons on the (0001) surface of Be, as obtained in the random-phase approximation of many-body theory. First-principles calculations along the \( \Gamma \overline{M} \) symmetry direction were reported before [12], but here we extend those calculations to other symmetry directions and focus on the discussion of the anisotropy of acoustic surface plasmons. Our calculations show that the anisotropy is notable and underline the capability of experimental measurements of these plasmons to map the electron–hole excitation spectrum of the quasi two-dimensional Shockley state band that is present on the Be(0001) surface.

### 2 Calculation details

The rate at which a frequency-dependent external potential \( \phi^{\text{ext}}(r, \omega) \) generates electronic excitations in a many-electron system can be obtained, within lowest-order perturbation theory, as follows [6]

\[
w(\omega) = \sum_{r} \omega(\bar{q}, \omega),
\]

(2)

where the sum extends over the surface Brillouin zone (SBZ) and \( \omega(\bar{q}, \omega) \) denotes the rate at which the external potential generates electronic excitations of frequency \( \omega \) and parallel wave vector \( \bar{q} \):

\[
w(\bar{q}, \omega) = -\frac{2}{A} \int dz \ n_{\text{ind}}(z, \bar{q}, \omega) \phi^{\text{ext}}(z, \bar{q}, \omega),
\]

(3)

\[n_{\text{ind}}(z, \bar{q}, \omega)\text{ and }\phi^{\text{ext}}(z, \bar{q}, \omega)\text{ representing 2D Fourier transforms of the induced electron density }n_{\text{ind}}(r, \omega)\text{ and the external potential }\phi^{\text{ext}}(r, \omega),\text{ respectively, and }A\text{ being the normalization area. If the 2D Fourier transform of the external potential is of the form}

\[
\phi^{\text{ext}}(z, \bar{q}, \omega) = \frac{-2\pi}{\bar{q}} \ \epsilon^{\bar{q}},
\]

(4)

the rate \( \omega(\bar{q}, \omega) \) can be expressed in the following form:

\[
\omega(\bar{q}, \omega) = \frac{4\pi}{\bar{q}A} \ \text{Im} \ g(\bar{q}, \omega),
\]

(5)

where \( g(\bar{q}, \omega) \) represents the so-called surface response function [18]

\[
g(\bar{q}, \omega) = -\frac{2\pi}{\bar{q}} \int dz' dz'' \chi_{\text{G}=0,\text{G}''=0}(z, z', \bar{q}, \omega),
\]

(6)

\( \chi_{\text{G}=0,\text{G}''=0}(z, z', \bar{q}, \omega) \) being the Fourier components of the density response function of the interacting many-electron system. In the random-phase approximation of many-body theory, these Fourier coefficients are easily obtained from the Fourier coefficients \( \chi_{\text{G}=0,\text{G}''=0}(z, z', \bar{q}, \omega) \) of the noninteracting density response function by solving the following matrix equation:

\[
\chi_{\text{G}=0,\text{G}''=0}(\bar{q}, \omega) = \chi_{\text{G}=0,\text{G}''=0}(\bar{q}, \omega) + \sum_{G} \chi_{\text{G}=0,\text{G}''=0}(\bar{q}, \omega) \chi_{G,G''}(\bar{q}, \omega),
\]

(7)

where \( \chi_{\text{G}=0,\text{G}''=0}(\bar{q}, \omega) \) are the Fourier coefficients of the bare Coulomb electron–electron interaction.

For positive frequencies, the imaginary part of the Fourier coefficients \( \chi^{\text{ext}}(\bar{q}, \omega) \) of the noninteracting density response function is easily obtained from the spectral function \( S_{\text{G}=0,\text{G}''=0}(\bar{q}, \omega) \), as follows

\[
\text{Im} \left[ \chi^{\text{ext}}(\bar{q}, \omega) \right] = -\pi S_{\text{G}=0,\text{G}''=0}(\bar{q}, \omega),
\]

(8)

the factor 2 accounting for spin. The sum over \( n(\bar{n}') \) runs over occupied (unoccupied) states of the band structure for 2D wave vectors \( \bar{k} \) in the SBZ. We take \( \bar{q}_G \) and \( \bar{q}'_G \) to be the eigenvalues and eigenfunctions of a first-principles single-particle Kohn–Sham (KS) Hamiltonian of density-functional theory (DFT). For the evaluation of the real part of the Fourier coefficients \( \chi^{\text{ext}}(\bar{q}, \omega) \) of the noninteracting density response function, we perform a Hilbert transform of the corresponding imaginary part.

For a description of the (0001) face of hcp Be from first principles, we employ a repeated-slabs geometry. The slabs periodically repeat in the direction normal to the (0001) surface and every slab consists from 24 atomic Be layers. The distance between slabs is chosen to correspond to 8 Be atomic layers. For the evaluation of the eigenvalues and eigenfunctions entering Eq. (9) we solve the KS equations of DFT self-consistently with the use of norm-conserving pseudopotential [19], the local-density approximation (LDA) for exchange and correlation, and the Perdew–Zunger parametrization of the Ceperley–Alder diffusion Monte Carlo energies of a uniform electron gas [20, 21]. We expand the single-particle wave functions \( \psi_{\bar{k}, n}(r) \) in a plane wave basis, with reciprocal vectors \( G \) up to an energy cut-off of 20 Ry. For the lattice constants, we take the experimental values \( a = 2.385 \ \text{Å} \) and \( c = 3.585 \ \text{Å} \) [22]. The experimental values [23] for the relaxation of surface atomic layers has been taken into account. The sum over 2D wave vectors \( \bar{k} \) in Eq. (9) is taken to run over a \( 108 \times 108 \) mesh, which corresponds to 11664 points in the SBZ. The energy band summations in Eq. (9) include all
occupied energy bands and unoccupied ones up to an energy cut-off of 50 eV above the Fermi level. The integrations involved in the evaluation of the surface response function of Eq. (6) are performed from $-c/2$ up to $c/2$, where $c$ is the unit cell size in the z-direction. Finally, we note that we include the so-called local-field effects in the normal direction only and neglect them along the surface, i.e., only the $G = \mathbf{G}' = 0$ elements of the non-interacting density response matrix $\chi_{\mathbf{q},\omega}(z, z', \mathbf{q}, \omega)$ have been considered in the evaluation of the coefficients $\chi_{\mathbf{q},\omega}(z^*, z'^*, \mathbf{q}, \omega)$ of the interacting density response function; lateral local-field effects were found to be negligible in the case of the Mg(0001) surface [24], and we expect them to be negligibly small, as well, in the case of other simple metal surfaces like Be(0001).

3 Results and discussion

Figure 1 represents the projected electronic structure of the Be(0001) surface, as obtained along the symmetry directions $\Gamma\bar{M}$ and $\Gamma\bar{K}$. The characteristic feature of this surface is the presence of wide energy gaps in the projected bulk band structure, where several strongly localized surface states reside [25–27]. Here we focus our attention on the Shockley surface state that is located around the SBZ center and is marked by SS. According to our present first-principles calculations, the binding energy of this surface state at $\Gamma$ is 2.75 eV in close agreement with the experimental data [25, 26, 28–30] and other ab initio calculations [27, 31]. As for the energy dispersion of this surface-state band, we find that within the occupied part of the band it is almost isotropic and well described by a parabolic-like dispersion with an effective mass $m^*_{SS} = 1.2$, again in good agreement with experiment [26, 32]. However, as seen in Fig. 1, within the unoccupied part, where the surface-state energy approaches the borders of the energy gap, our calculated energy dispersion deviates substantially from the quasi-free-electron-like parabolic behavior and presents notable anisotropy.

Collective excitations created by an external potential of the form dictated by Eq. (4) can be traced to the peaks of the absorption probability $w(\mathbf{q}, \omega)$ of Eq. (5), i.e., to the peaks of the imaginary part of the surface response function $g(\mathbf{q}, \omega)$ of Eq. (6). We have searched for the maxima of $g(\mathbf{q}, \omega)$, as obtained as a function of the frequency $\omega$, for various 2D $\mathbf{q}$ wave vectors, and we have found the low-energy (acoustic) surface-plasmon energy dispersion plotted in Fig. 2 along two distinct symmetry directions: $\Gamma\bar{M}$ and $\Gamma\bar{K}$.

As already shown by the 1D model potential calculations reported previously [11], the energy dispersion of acoustic surface plasmons follows very closely the upper edge of the continuum in the “momentum-energy” phase space where electron–hole pairs excitations within the quasi-2D surface-state band can occur. In its turn, this upper edge is determined by the energy dispersion above the Fermi level and, e.g., in the case of a pure 2D electron gas with parabolic dispersion $E = \mathbf{p}^2/2m^*_c$, is described by $\omega_{\text{upper}} = \sqrt{2}\sqrt{E + \omega^2/2m^*_c}$ [33] (here $v^*_c$ is the surface state Fermi velocity). In the case of the actual Be(0001) surface band structure, the surface state dispersion above the Fermi level deviates substantially from a quasi-free-electron-like parabolic behavior, as discussed above. This is reflected in the momentum-direction dependence of the upper edge of the continuum of electron–hole pairs excitations within the surface state band seen in Fig. 2. The first-principles calculation with all these effects included gives the acoustic surface plasmon energy dispersion which deviates from the previous 1D model potential calculations showing excellent agreement with the available experimental data along the $\Gamma\bar{M}$ direction.

We attribute our predicted anisotropy of acoustic surface plasmons to the fact that the upper edge of the 2D electron–hole pair excitations occurring within the quasi-2D surface-state band depends strongly on the symmetry direction. Our calculations also show that the peaks in the surface loss function are stronger and narrower along the $\Gamma\bar{M}$ than in the case of the $\Gamma\bar{K}$ direction. We attribute this fact to the complicate Be(0001) surface electronic structure, where additionally inter-band transitions involving other surface states are also possible (see Fig. 1). It seems that the destructive role of such transitions on the acoustic surface plasmon properties is more pronounced in the $\Gamma\bar{K}$ direction. Clearly there is no anisotropy in the acoustic surface plasmon dispersion obtained with the use of a 1D model potential [11], simply due to the isotropic surface electronic structure inherent to that approximation. For small momenta, our ab initio acoustic surface plasmon dispersion almost coincides with the dispersion obtained with the use of the 1D model potential and $m^*_{SS} = 1.2$. As the
level, as occurs in the case of the (111) surfaces of the noble metals Cu, Ag, and Au.


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