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Abstract
We report an *ab initio* study of the electron–phonon (e–ph) interaction and its contribution to the lifetime broadening of excited hole (electron) surface states on Al(001). The calculations based on density-functional theory were carried out using a linear response approach in the plane-wave pseudopotential representation. The obtained results show that both the electron–phonon coupling and the linewidth experience a weak variation with the energy and momentum position of a hole (electron) surface state in the energy band. An analysis of different contributions to the e–ph coupling reveals that bulk phonon modes turn out to be more involved in the scattering processes of excited electrons and holes than surface phonon modes. It is also shown that the role of the e–ph coupling in the broadening of the Rayleigh surface phonon mode is insignificant compared to anharmonic effects.

1. Introduction

The study of electron and hole dynamics at metal surfaces has been of considerable interest [1–12] because of the important role of electron excitations in photochemical reactions [13], in particular, in photodissociation and photodesorption processes [14], in catalytical reactions as well as in charge and spin transport in bulk metals, across interfaces, and at surfaces [15, 16]. One of the key quantities of the excited electrons is its lifetime, which sets the duration of the excitation. The inverse lifetime (linewidth) Γ is determined by electron–electron (e–e), electron–phonon (e–ph), and electron–defect (e–df) interactions, $\Gamma_{tot} = \Gamma_{e-e} + \Gamma_{e-ph} + \Gamma_{e-df}$. At low temperatures and for large excitation energies inelastic e–e scattering is the most important process that limits the excitation lifetime. The e–e contribution to the lifetime broadening has been studied within a GW approximation [3–5, 17]. The elastic e–df scattering can be either avoided [1, 3, 4, 6] or strongly reduced [3] in many experimental measurements but it is not the case at elevated temperatures where thermally excited defects turn out to be very important [18]. As for the e–ph coupling, Γ_{e-ph} becomes comparable with Γ_{e-e} close to the Fermi level, within a typical phonon energy $\hbar\omega_D$ (ω_D is the Debye cutoff energy) [3, 17, 19], and at room temperature the e–ph contribution can even exceed the e–e part [20]. A theoretical description of the e–ph coupling needs the phonon spectrum, electron wavefunctions and the screened deformation potential to evaluate the e–ph matrix elements. Up to now, the influence of the e–ph coupling on the electron lifetime in surface states has been usually evaluated by assuming a constant e–ph matrix element [4, 21–23] and using the Debye model for the phonon spectrum [24]. In this case, the Eliashberg spectral function $\alpha^2 F(\omega)$ and the e–ph coupling parameter λ, which measure the contribution of phonons to the scattering of electrons and the strength of the e–ph interaction, do not depend on an electronic state. Fully *ab initio* calculations of the e–ph interaction for excited electrons and holes have been recently reported for the $\overline{\Gamma}$ surface electronic states on Be(0001) [25], Mg(0001) [26], and Al(001) [18]. Both $\alpha^2 F(\omega)$ and λ can also be extracted from the measured slope of the real part of self-energy at the Fermi level using photoemission spectroscopy (PES) [27, 28]. For hole states located far from the Fermi energy, λ can be deduced from PES measurements of the temperature dependence of the linewidth [23, 29, 30]. The linewidth of the $\overline{\Gamma}$ surface electronic state on Al(001) was recently

measured at different temperatures using photoemission spectroscopy [18]. The obtained data were then interpreted in terms of the e–ph coupling and thermally excited defects. Information concerning e–ph interactions can also be obtained from the measured phonon linewidths because the phonon characteristics are influenced by the e–ph coupling [31, 32]. On Al(001), the linewidths of surface Rayleigh phonons have been measured with high-resolution helium-atom scattering over a wide range of wavevectors [33].

Here we focus on the e–ph coupling and its contribution to the decay of the electron lifetime and present an analysis for electronic surface states on Al(001). The *ab initio* calculations were performed for both the $\overline{\Gamma}$ surface state and the occupied and unoccupied surface states at the Brillouin zone boundary. The obtained Eliashberg spectral function $\alpha^2 F(\omega)$, e–ph coupling parameter λ, and the phonon-induced contribution to the excited hole (electron) lifetime broadening (linewidth) Γ_{e-ph} are presented as both energy-and momentum-resolved. It is shown that the e–ph coupling depends rather weakly on the energy and momentum of a surface electronic state. We have also evaluated the contributions to the spectral function from different phonons, particularly from the Rayleigh surface mode.

2. Theory

The phonon-induced lifetime broadening of a hole (electron) state with momentum $\mathbf{k}_i$ and energy $\epsilon_{\mathbf{k}_i}$ is defined as [24]:

$$\Gamma_{e-ph}(\epsilon_{\mathbf{k}_i}) = 2\pi \int_0^{\omega_m} \alpha^2 F^E(\epsilon_{\mathbf{k}_i}; \omega)[1 + n(\omega) - f(\epsilon_{\mathbf{k}_i} - \omega)]$$
$$+ \alpha^2 F^A(\epsilon_{\mathbf{k}_i}; \omega)[n(\omega) + f(\epsilon_{\mathbf{k}_i} + \omega)]d\omega. \tag{1}$$

Here, f and n are the Fermi and Bose distribution functions, respectively, and ω_m is the maximum phonon frequency. The electron state dependent Eliashberg spectral function corresponding to phonon emission (E) and adsorption (A) processes is written as

$$\alpha^2 F^{E(A)}(\epsilon_{\mathbf{k}_i}; \omega) = \sum_{\mathbf{q}, \nu, f} \delta(\epsilon_{\mathbf{k}_i} - \epsilon_{\mathbf{k}_f} \mp \omega_{\mathbf{q}, \nu})$$
$$\times |g(\mathbf{k}_i, \mathbf{k}_f, \mathbf{q}, \nu)|^2 \delta(\omega - \omega_{\mathbf{q}, \nu}), \tag{2}$$

where $g(\mathbf{k}_i, \mathbf{k}_f, \mathbf{q}, \nu)$ is the e–ph matrix element. The sum is carried out over final electron states $\mathbf{k}_f$ and all possible phonon modes $(\mathbf{q}, \nu)$. The electron state dependent e–ph coupling parameter is given by [24]:

$$\lambda(\epsilon_{\mathbf{k}_i}) = \int_0^{\omega_m} \frac{\alpha^2 F^E(\epsilon_{\mathbf{k}_i}; \omega) + \alpha^2 F^A(\epsilon_{\mathbf{k}_i}; \omega)}{\omega} d\omega. \tag{3}$$

When $\lambda(\epsilon_{\mathbf{k}_i})$ is averaged over all initial electron states on the Fermi surface one obtains the e–ph coupling parameter $\lambda(\epsilon_F)$ which determines the electronic mass enhancement [31].

The calculations were performed by using density-functional perturbation theory [34, 35] and the *PWSCF* code [36], taking both phonon emission and phonon adsorption into account. The electron–ion interaction was described by a nonlocal norm-conserving pseudopotential generated following von Barth and Car [36]. The plane-wave basis-set
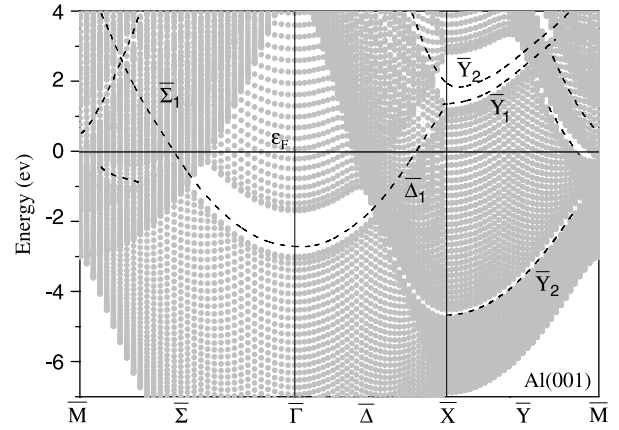

Figure 1. Calculated bulk Al bands projected onto the (001) plane (in gray), dashed lines denote surface electronic states.

cutoff was restricted to 16 Ryd. The surface Brillouin zone (SBZ) integrations were performed using 45 special points in the irreducible SBZ and the first-order Hermite–Gaussian smearing technique [37] with a width of 0.02 Ryd. To describe the surface a periodically repeated slab geometry of the fully relaxed 11-layer Al slabs separated by seven atomic layers of vacuum was used. The calculations were performed at the lattice constant $a = 7.5$ au determined from the total energy minimization within the local density approximation (LDA). The difference between the evaluated and experimental ($a = 7.63$ au) values is typical for LDA calculations [38]. Since the Al(001) surface is not reconstructed, the atomic positions inside the plane maintain the symmetry of the bulk and the lattice parameter is kept. Forces between the layers of atoms which tend to relax in the direction normal to the surface were minimized and checked to be smaller than 10^{-4} Ryd au^{-1}. The relaxation consists of an expansion of the first and second interlayer spacings relative to the bulk distance: these are $\Delta d_{12} = +1.4\%$ and $\Delta d_{23} = +0.7\%$, respectively. These values are close to both experimental $\Delta d_{12} = (+1.8 \pm 0.3)\%$ [39] and *ab initio* results: $\Delta d_{12} = +1.2\%$ and $\Delta d_{23} = +0.2\%$ [40].
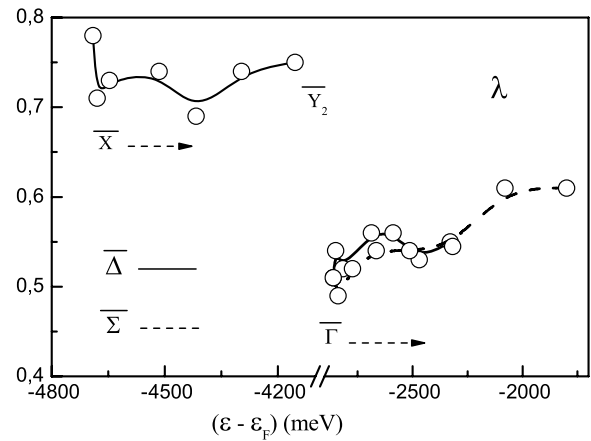
3. Calculation results

Figure 1 shows the calculated bulk bands projected onto the (001) plane and surface electronic states indicated by dashed lines. As a consequence of the slab geometry, all surface states appear pairwise, one from each surface of the slab. In the limit of an infinitely thick slab the pairs of states will be degenerate. However, for finite slabs there is a splitting which depends on the slab thickness and penetration depth of a given surface state. So, the surface states in the figure represent an average of a pair of states arising from two surfaces of an 11-layer Al slab. First, we have considered the surface electronic state in the SBZ center associated with the sp band gap around the X point in the bulk Al. The maximum binding energy (at the $\overline{\Gamma}$ point) is found to be 2.86 eV, which agrees well with the experimental value of 2.8 ± 0.2 eV [41] and with other *ab initio* calculation results [42, 43]. To see how the surface electronic
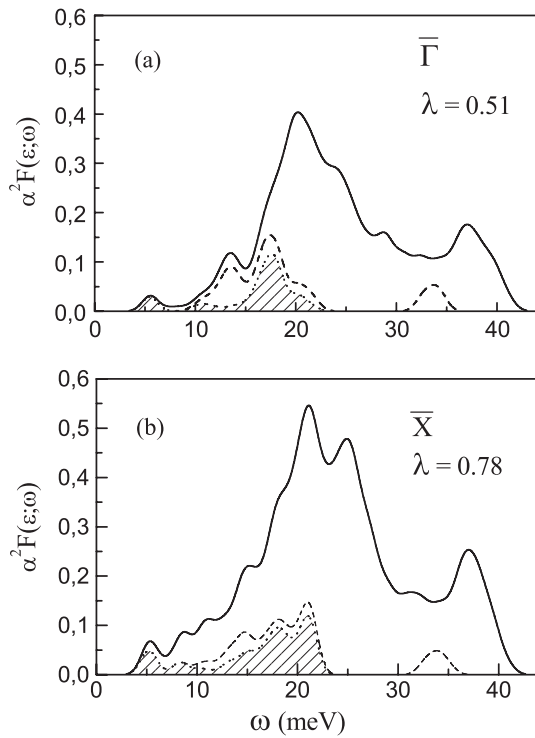
Figure 2. Electron–phonon spectral function $\alpha^2 F(\epsilon_{\mathbf{k}_i}; \omega)$ for hole states at the $\overline{\Gamma}$ (a) and $\overline{X}$ (b) symmetry points. The contributions from surface phonons (including the Rayleigh surface mode scattering—the hatched area) are indicated by dashed lines.

Figure 3. Electron–phonon coupling parameter λ as a function of hole energy and momentum for the $\overline{\Gamma}$ surface electronic state and the occupied surface state in the $\overline{Y}$ symmetry direction.

state couples to phonons, we have calculated the Eliashberg spectral function for different hole energies and momenta. The summation over the phonons ($\mathbf{q}$, ν) in equation (2) was carried out over 256 wavevectors in the surface BZ. The delta function with electron energies was approximated by the first-order Hermite–Gaussian function with a smearing width in the range of 0.01–0.03 Ryd. Figure 2(a) shows $\alpha^2 F(\epsilon_{\mathbf{k}_i}; \omega)$ for a surface hole state at the $\overline{\Gamma}$ point. The spectral function represents an average of the emission and adsorption parts which in the case of Al nearly coincide. As can be seen, the low- and middle-energy phonons are more involved in the scattering processes of electrons than the high-energy modes. On the contrary, for bulk Al, as well as for another simple metal Be, the lower-energy part of the phonon spectrum is strongly suppressed by e–ph matrix elements [20]. The low-energy contributions to the spectral function partly come from scattering of electrons with surface phonons. A small peak at energies of 12–15 meV is mainly determined by scattering with transverse in-plane polarized modes splitting off the bulk phonon bands at the SBZ boundary. An appreciable contribution also comes from the Rayleigh surface mode the polarization of which coincides with the surface electron state symmetry (sp_z). It represents about 15% of the total contribution to the spectral function independently of the energy and momentum position of a hole state: at the $\overline{\Gamma}$ point or close to the Fermi level. In general, the role of surface phonons is not so important compared to the contribution coming from bulk phonon modes. The surface phonon part represents less than 30%. A similar

conclusion can be drawn from an analysis of the Rayleigh mode linewidths. The Rayleigh surface phonon widths have been measured with high-resolution helium-atom scattering as a function of wavevector along the $\overline{\Delta}$ direction [33]. The phonon linewidths of 0.2–0.6 meV obtained at room temperature are restricted to small $\mathbf{q}$ values. The measured phonon widths were found to be in good agreement with the data obtained in a molecular-dynamics simulation carried out to mimic anharmonic interactions. We have evaluated the linewidth of the Rayleigh surface mode due to the e–ph coupling for all $\mathbf{q}$ vectors. As is known, the e–ph contribution to phonon linewidths can be obtained from the e–ph coupling at the Fermi energy [24]. In particular, the e–ph mass enhancement parameter $\lambda(\epsilon_F)$ is simply a weighted average of the phonon linewidths. The obtained values of 0.06–0.10 meV are small compared to the experimental data. So, the role of the e–ph coupling in the broadening of the Rayleigh phonon mode is insignificant compared to the anharmonic effects.

Figure 3 represents the e–ph coupling parameter λ for the $\overline{\Gamma}$ surface electronic state as a function of energy in two symmetry directions: $\overline{\Delta}$ and $\overline{\Sigma}$. As is evident from the figure, $\lambda(\epsilon_{\mathbf{k}_i})$ shows a slight dependence on hole energy and momentum. It varies from 0.5 to 0.55 along $\overline{\Delta}$ and reaches 0.6 in the $\overline{\Sigma}$ symmetry direction. The calculated $\lambda(\overline{\Gamma}) = 0.51 \pm 0.01$ is somewhat higher than the e–ph coupling parameter evaluated both at the Fermi level of bulk Al, $\lambda(\epsilon_F) = 0.43$, and at the Fermi energy of the Al(001) surface, $\lambda(\epsilon_F) = 0.45$.

At the SBZ boundary (the $\overline{Y}$ symmetry direction) there are three surface electronic states. The occupied surface band located at the bottom of the lower-energy gap at $\overline{X}$ was measured experimentally at -4.55 eV with respect to the Fermi energy [44]. The binding energy (at the $\overline{X}$ point) obtained for this state in the present calculation is 4.69 eV. Its p_x, p_y polarization alternates with symmetry sp_z from layer to layer. Figure 2(b) shows $\alpha^2 F(\epsilon_{\mathbf{k}_i}; \omega)$ for this surface state at the $\overline{X}$ point. As one can see, it is similar in shape to the e–ph spectral function for a hole state at $\overline{\Gamma}$. The surface phonon contribution remains and, like the previous case, depends slightly on the binding energy of a hole state.

Another peak associated with the Rayleigh mode contribution appears at 20–22 meV. It is determined by the coupling of electrons with the Rayleigh surface modes from the vicinity of the $\overline{M}$ symmetry point. These phonon modes hardly participate in the scattering processes of the zone center surface electronic state because they cannot couple to the opposite symmetry bulk states in the $\overline{\Sigma}$ direction [45]. The next distinctive feature is connected with the bulk phonon mode contribution, which increases significantly compared to the case of the $\overline{\Gamma}$ surface state. Being located at the edge of the bulk electronic bands, this surface state decays very slowly inside the slab. The increasing overlap with final bulk electronic states results in a considerable contribution to the scattering processes from bulk phonon modes. The e–ph coupling parameter $\lambda(\overline{X}) = 0.78 \pm 0.04$ is half as much again as $\lambda(\overline{\Gamma})$. On moving along the $\overline{Y}$ symmetry direction $\lambda(\epsilon_{\mathbf{k}_i})$ exhibits a slight dependence on hole energy, varying between 0.7 and 0.8 (figure 3). Similar results have been obtained for the upper unoccupied surface state of the same symmetry ($\overline{Y}_2$) where λ changes between 0.65 at the $\overline{X}$ point and 0.7. The e–ph coupling parameter for the lower unoccupied surface state ($\overline{Y}_1$) which is a continuation of the surface state at $\overline{\Gamma}$ is somewhat smaller, ranging from 0.59 to 0.65.

As is obvious, the obtained state dependent e–ph coupling parameters are hardly sensitive to the energy and momentum position of a hole (electron) surface state in the energy band. In particular, the variation range of $\lambda(\epsilon_{\mathbf{k}_i})$ does not exceed 0.1. However, the strength of the e–ph coupling for excited electrons at the $\overline{\Gamma}$ surface band is less by half than the values of $\lambda(\epsilon_{\mathbf{k}_i})$ obtained for the surface electronic bands in the $\overline{Y}$ symmetry direction. Therefore, one could say that the e–ph coupling at Al(001) depends strongly on the electronic band rather than on the energy and momentum position of the excited electron in the energy band. A similar result has been obtained in bulk Al where the behavior of the momentum-resolved e–ph coupling as a function of excitation energy is found to depend appreciably on the electronic energy band. In contrast, the e–ph coupling in bulk Pd and Be is very sensitive to the energy and momentum position of an excited electron and, at the same time, varies strongly from one electronic band to another [20, 32]. An unusually strong anisotropy of the e–ph coupling was also reported for the Fermi surface of MgB_2 [46]. As regards to surface electronic states, the available information on Eliashberg spectral function and the e–ph contribution to the lifetime broadening of excited electrons shows that the e–ph coupling at Be(0001) and Bi(001) surfaces exhibits a dramatic energy dependence. Also, the behavior of λ as a function of energy is very sensitive to the surface electronic band considered [47, 48].

The phonon-induced lifetime broadening of excited holes (electrons) as a function of energy and momentum at $T = 0$ is shown in figure 4. The top panel (a) gives $\Gamma_{e-ph}(\epsilon_{\mathbf{k}_i})$ for the $\overline{\Gamma}$ surface state while panels (b) and (c) show the data for the surface states in the $\overline{Y}$ symmetry direction. At the SBZ center, $\Gamma_{e-ph}(\overline{\Gamma}) = 35$ meV at $T = 0$ and increases up to 90 meV at room temperature. The calculated e–e contribution $\Gamma_{e-e} = 131$ meV [8] is much bigger than the e–ph part at such excitation energies. However, at room
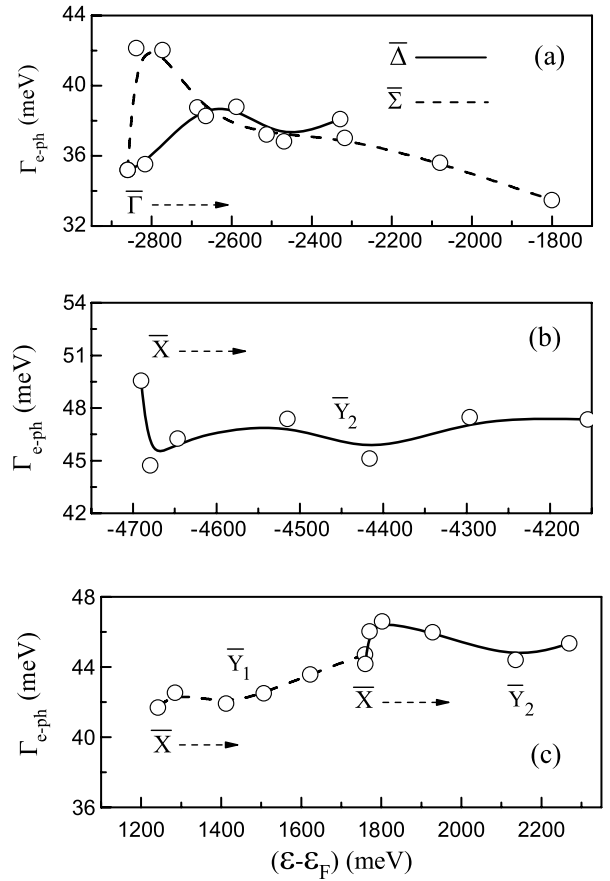
Figure 4. Phonon-induced lifetime broadening Γ_{e-ph} as a function of hole energy and momentum for the $\overline{\Gamma}$ surface electronic state (a), and for the surface electronic states in the $\overline{Y}$ symmetry direction ((b), (c)).

temperature they become comparable. The measured linewidth at $\overline{\Gamma}$ extrapolated to 0 K is 267 meV [18] whereas the calculated e–e and e–ph contributions taken together give only 166 meV. As is shown [18] besides the e–ph coupling which becomes increasingly important at elevated temperatures thermally excited defects can have a significant influence on the lifetime of electronic surface states. The e–ph contribution to the linewidth of the surface hole state at $\overline{\Gamma}$ has also been studied using a model calculation [49]. Eiguren *et al* obtained $\lambda(\overline{\Gamma}) \approx 0.23$ and $\Gamma_{e-ph}(\overline{\Gamma}) \approx 18$ meV. Both values are nearly half as large as those obtained in the present calculation. However, in the model calculation the gradient of the one-electron potential is represented by the Ashcroft pseudopotential screened within the Thomas–Fermi approximation. This approximation can be applied successfully to sp_z surface states on simple and noble metal surfaces only near the Fermi energy. Thus, the value of λ obtained for this surface state at the Fermi level comes up to 0.55 and $\Gamma_{e-ph}(\epsilon_F) \approx 37$ meV [49]. As follows from our calculations, figure 4, the energy dependence of the broadening is rather weak. On moving along the $\overline{\Sigma}$ and $\overline{\Delta}$ symmetry directions Γ_{e-ph} varies slightly with the position of a hole state in the energy band coming up to 42 meV ($\overline{\Sigma}$) and, then, slowly decreasing with energy. The data also show an additional momentum dependence of the e–ph coupling

because the linewidth values for the same energy can differ from each other depending upon the hole momentum. For the surface electronic states in the $\overline{Y}$ symmetry direction the phonon-induced linewidth changes smoothly between 40 and 50 meV, figures 4(b) and (c). For the occupied surface state at the $\overline{X}$ symmetry point, $\Gamma_{e-ph} = 50$ meV at $T = 0$ and increases up to 135 meV at room temperature.

4. Conclusion

In summary, we have presented the results of an *ab initio* study of the e–ph interaction and its contribution to the lifetime broadening of excited hole (electron) surface states on Al(001). The obtained data show that while the strength of the e–ph coupling for hole states at the $\overline{\Gamma}$ surface band is slightly higher than the e–ph coupling parameter evaluated at the Fermi level of both bulk Al and the Al(001) surface, the values of $\lambda(\epsilon_{\mathbf{k}_i})$ for the occupied surface electronic state in the $\overline{Y}$ symmetry direction are half as much again. An analysis of different contributions to the spectral function reveals that the low-energy phonons turn out to be more involved in the scattering processes of excited electrons and holes than the high-energy modes, unlike the case of bulk Al where the lower-energy part of the phonon spectrum is strongly suppressed by e–ph matrix elements. The scattering of electrons with surface phonons represents ~30% of the total contribution to the spectral function independently of the energy and momentum position of a hole (electron) state. The role of the e–ph coupling in the broadening of the Rayleigh surface phonon mode is found to be insignificant compared to anharmonic effects. The obtained results also show that both the electron–phonon coupling parameter and the linewidth experience rather weak variations with the energy and momentum position of a hole (electron) surface state and depend first of all on the surface electronic band. In particular, the variation range does not exceed 0.1 for $\lambda(\epsilon_{\mathbf{k}_i})$ and 10 meV for $\Gamma_{e-ph}(\epsilon_{\mathbf{k}_i})$.

Acknowledgments

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