

Electron-phonon coupling and temperature-dependent shift of surface states on Be(10 $\bar{1}$ 0)

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(Received 11 February 2002; published 18 June 2002)

The temperature dependence of two Shockley surface states ($S1$ and $S2$) on Be(10 $\bar{1}$ 0), located in a wide bulk projected band gap from \bar{A} to $\bar{\Gamma}$, has been investigated with angle-resolved photoemission spectroscopy. The electron-phonon coupling of the surface states $S1$ and $S2$ at the zone boundary (\bar{A}) were determined using both Debye and Einstein phonon models. Based on fitting, this analysis indicates that the surface optical phonon mode located around 64 meV contributes most strongly to the electron-phonon coupling of the $S1$ surface state, which is highly localized in the surface layer. The determined electron-phonon coupling parameter λ of $S1$ and $S2$ (0.647 and 0.491, respectively) is distinct from the bulk value ($\lambda_{\text{bulk}}=0.24$). Both surface states $S1$ and $S2$ are observed to shift linearly with the temperature, but in opposite directions at the rates of $(-0.61 \pm 0.3) \times 10^{-4}$ eV/K and $(1.71 \pm 0.8) \times 10^{-4}$ eV/K, respectively. The different behavior of the two surface states, with respect to both the electronic-phonon coupling and temperature-dependent shift of initial energy, is attributed to the higher surface charge localization of $S1$ than $S2$.

DOI: 10.1103/PhysRevB.65.235428

PACS number(s): 73.20.At, 71.38.-k, 79.60.Bm

I. INTRODUCTION

Cleaving a bulk crystal results in broken symmetry and consequent rearrangement of the electronic charge in the selve region and generates a surface with static and dynamic properties that are quite different from its bulk counterpart. The unique, reduced-dimensional properties of metal surfaces are reflected in the ensuing surface electronic structure (e.g., surface states); hence, probing the electronic properties provides a window to understanding the fundamental properties of this three-dimensional to two-dimensional (3D-to-2D) world. In the present study, we focus on elucidating unique properties of two Shockley surface states located at the same point in the surface Brillouin zone (SBZ) on Be(10 $\bar{1}$ 0). Specifically, the differences between the electron-phonon coupling properties dictated by the quasiparticle screening of these two surface states, with quite different charge distributions into the bulk, will be determined.

Beryllium is a *sp*-bonded “simple metal” with unusual properties. Whereas the bulk, having a nonideal *c/a* ratio, attenuated density of states (DOS) at E_F (i.e., semimetal), and a large degree of covalent bonding, can be considered far from ideal, the surface has been shown, both experimentally and theoretically, to be a nearly-free-electron system. For example, because surface states in Be(0001) account for roughly 80% of the local DOS at E_F in the outermost layer, the surface has been considered as the best model to investigate the purely 2D electronic system. Experimentally, this peculiarly large surface-to-bulk ratio of the local DOS (LDOS) at E_F has been shown to contribute to many observed surface properties which deviate substantially from the bulk, including abnormally large surface core level shifts and giant surface Friedel oscillations.^{1,2} In addition, other unique many-body effects at the surface of Be(0001) have also been reported. For example, a *threefold* increase, relative to the bulk value, in the surface mass enhancement coupling parameter λ_s , which expresses the strength of the

electron-phonon interaction, has been reported from high-resolution angle-resolved photoemission (ARUPS) studies.^{3,4,5,6}

In contrast to the close-packed Be(0001) surface, the *near*-surface properties of the more open Be(10 $\bar{1}$ 0) surface, although qualitatively similar to that of the Be(0001),^{7,8} reveal it to be less free-electron like and more covalent like. In a series of experimental papers which explored the atomic,⁹ dynamic,¹⁰ and electronic¹¹ structure of Be(10 $\bar{1}$ 0), Hoffman *et al.* concluded that, while surface states dominate the DOS at E_F , the bonding in the underlying layers is progressively more covalent like. Specifically, a covalent model of directional backbonding was invoked to explain the large contraction between the first and second layers when the Be(10 $\bar{1}$ 0) surface relaxes. Furthermore, Cho *et al.*¹² attributes the observed surface core-level shifts, persisting down to the fifth layer in Be(10 $\bar{1}$ 0), to the increased “stiffness” of electrons and consequent screening attenuation in underlying layers. In light of this, the expectation is that the electron-phonon coupling at the Be(10 $\bar{1}$ 0) surface may be quite different from that of Be(0001), which is purely free-electron like. However, Balasubramanian *et al.* determined, from temperature-dependent ARUPS data of one specific surface state, that the electron-phonon coupling parameter of the Be(10 $\bar{1}$ 0) surface [$\lambda_{S1, \text{Be}(10\bar{1}0)} = 0.648 \pm 0.03$ (Ref. 13)]. This experimental value is equal, within uncertainty, to that of the close-packed surface [$\lambda_{S, \text{Be}(0001)} = 0.7 \pm 0.1$ (Ref. 5)]. Both values are nearly 3 times larger than the bulk value of $\lambda_B = 0.24$.

In the present study, the Be(10 $\bar{1}$ 0) surface is reinvestigated with high-resolution ARUPS to determine the temperature dependence of the surface state linewidth (electron-phonon coupling) and peak position. Specifically, we focus on the difference in the electron-phonon coupling for two surface states at the same point in the SBZ. Both Shockley-like surface states are centered at the surface zone boundary

(\bar{A}) and disperse within a wide bulk projected band gap (see inset in Fig. 1). Theoretically, Silkin and Chulkov¹⁴ have shown, using self-consistent pseudopotential calculations, that the symmetry and degree of surface charge localization of these two surface states ($S1$ and $S2$) are quite different. Whereas 70% of the charge associated with $S1$ ($E_{B,S1} \sim 0.6$ eV at \bar{A}) is located in the top atomic layer, $S2$ ($E_{B,S2} \sim 2.9$ eV at \bar{A}) is less localized at the surface (only 50% of charge is in first layer) and extends deeper into the selvage region. Both $S1$ and $S2$ extend throughout large sections of the surface Brillouin zone (along both $\bar{A}\bar{\Gamma}$ and $\bar{A}\bar{L}$ directions) and hence contribute a large fraction of the total density of states. The contribution of the LDOS of $S1$ near E_F makes the surface nearly free-electron like. Taking advantage of the distinct charge localization differences between $S1$ and $S2$, probing their individual character (temperature dependence of width and energy) of these surface states will give insight into the dissimilar surface versus bulk properties. Specifically, the supposition is that the bonding becomes more covalent as one goes into the bulk; thus, properties of $S2$, being less localized at the surface, should be more “covalent like” than $S1$.

Before presenting results, a brief review of how the electron-phonon coupling parameter λ is extracted from ARUPS data is warranted. Specifically, it is important to question the assumptions used in the prior analyses.⁴ In the case of a 2D band, the inverse lifetime of the photohole is proportional to the deconvoluted ARUPS peak width. The temperature dependence of the photohole lifetime (τ) is dictated primarily by electron-phonon interactions at energies close to E_F (electron-defect and electron-electron interactions are assumed to be nontemperature dependent and/or small). In general, the electron-phonon interaction (e - p) contribution to the inverse-lifetime width at any temperature is given by the expression¹⁵

$$W_{e-p}(\omega) \frac{\hbar}{\tau_{e-p}} = 2\pi\hbar \int_0^{\omega_{\max}} \alpha^2 F(\omega') [1 - f(\omega - \omega') + 2n(\omega') + f(\omega + \omega')] d\omega', \quad (1)$$

where $\alpha^2 F(\omega)$ is the Eliashberg coupling function, ω_{\max} is the maximum phonon frequency, and n and f are the Bose-Einstein and Fermi distribution functions, respectively. Within a Debye model, the electron-phonon coupling constant λ is linearly related to the Eliashberg coupling function $\alpha^2 F(\omega) = \lambda(\omega/\omega_D)^2$ if $\omega < \omega_D$, where ω_D is the Debye frequency. Previous ARUPS studies of Be surface states, as well as other systems,^{4,16} have employed this assumption: namely, that above one-third of the Debye temperature (Θ_D), Eq. (1) can be simplified to yield a linear relationship between the linewidth, as determined from an ARUPS spectrum, and temperature. The slope of this relationship yields λ_s for a given band in k space. Using this assumption, the determined value of λ_s is extracted solely from the high-temperature data, wherein the linearity of Eq. (1) is most valid and is independent of the detailed shape and dimensionality of the phonon spectrum. In the case of materials

with low Debye temperatures (e.g., $\Theta_D \lesssim 400$ K), employing this linear approximation has been shown to be quite valid.

In the case of Be, which has a large Debye temperature ($\Theta_{D,\text{bulk}} = 1000$ K), using the “high-temperature linear approximation” is inadequate because it limits the extent of information that can be extracted. For example, it is well known^{15,17} that for $T \ll \Theta_D$, the inverse lifetime due to electron-phonon 3D scattering varies as T^3 . This “textbook” example clearly indicates the breakdown of the linear approximation model. Because of beryllium’s large Debye temperature, including relative lower-temperature data ($T \lesssim \Theta_D/3$) in the analysis is experimentally undemanding and, hence, enables, through full use of Eq. (1), better elucidation of fundamental information, such as the detailed shape and dimensionality of the phonon spectrum, of the many-body e - p mechanism. For example, including data over a large temperature range facilitates the ability to test, through goodness of fitting, the choice of a phonon spectra model for the Eliashberg coupling function. In other words, if we invoke a given phonon spectra model (e.g., Debye or Einstein) in Eq. (1) which can fit the extended temperature range better than other models, it would add insight into which specific phonons (e.g., a major phonon branch) interacts most strongly with the screening process of the given surface state photohole. As recently reported,¹⁸ this concept has been shown to be the case in close-packed noble metal surfaces, wherein a specific Rayleigh mode dominated the electron-phonon interaction.

In this paper, we will show that this is indeed correct for the two Shockley surface states $S1$ and $S2$, centered about the same high-symmetry k point (\bar{A}) on Be($10\bar{1}0$). Namely, our fitting analysis of ARUPS data indicates that the temperature dependence of the $S1$ and $S2$ peak widths is phonon model dependent. In the case of $S2$, which has more bulklike attributes than $S1$, a Debye phonon model best fits the data with an electron-phonon coupling parameter of $\lambda_{S2} = 0.491$, a factor approximately 2 times larger than the bulk value. However, ARUPS data of $S1$, whose charge is localized almost exclusively in the first layer, are best fit with a model which assumes that the electrons in this state interact most strongly with a surface optical phonon mode (i.e., Einstein model with $\omega_E = 64$ meV). We will also show that an analysis of the $S1$ and $S2$ energy peak position versus temperature supports the assertion that the former is more localized at the surface. Specifically, $S1$ shows a fundamentally different behavior (i.e., $\Delta E_{S1}/\Delta T < 0$), which indicates that its bulk character (i.e., $\Delta E_{S2}/\Delta T > 0$, due to thermal expansion) is small. These results will be discussed in light of their respective binding energies within the bulk wideband gap at \bar{A} in Be($10\bar{1}0$).

II. EXPERIMENTAL DETAILS

The experiments were performed at the CAMD synchrotron facility. All data presented here were acquired in an UHV system ($P_{\text{base}} = 9 \times 10^{-11}$ Torr) equipped with a Scienta 200 hemispherical energy analyzer in combination with an Omicron He discharge lamp. In order to achieve an ac-

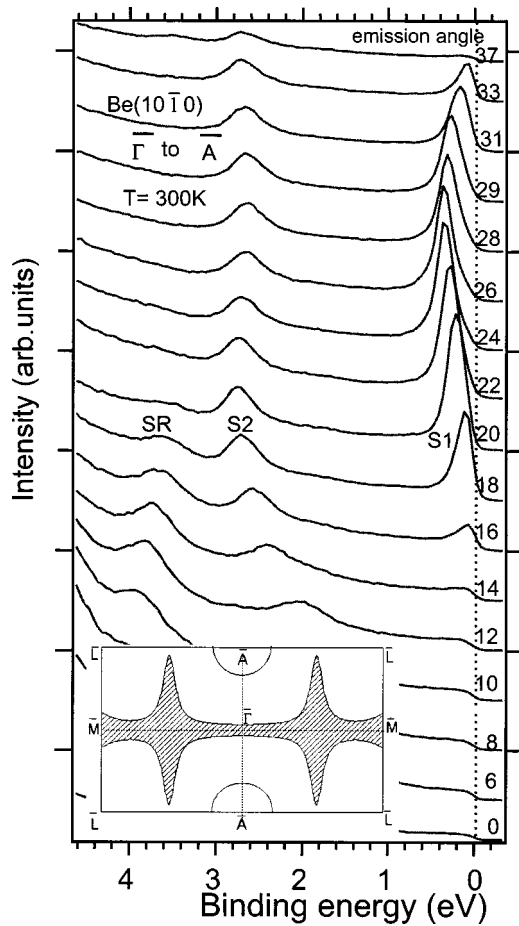


FIG. 1. Energy distribution curves of $S1$ and $S2$ surface-state dispersion from Γ to \bar{A} at room temperature. The emission angle corresponding to \bar{A} is 25.2° for $S1$ and 28° for $S2$. SR is the surface resonance state, which disperses deeply in the bulk band from Γ toward the bulk band edge at \bar{A} . The inset at the bottom is the surface Brillouin zone on the $(10\bar{1}0)$ plane. The shaded area indicates the projection of the bulk Fermi surface, and the solid curves around \bar{A} are the Fermi lines contributed from $S1$ surface state.

ceptable surface-state photoelectron signal, the entrance slit of the analyzer was chosen so that the overall experimental energy resolution was 50 meV, as confirmed through deconvolution of the Gaussian width from the Fermi edge. A clean $\text{Be}(10\bar{1}0)$ sample was prepared using methods described earlier.⁴ Based on Laue diffraction data, the sample was mounted with the scattering plane along the $\Gamma\bar{A}$ direction. A sample manipulator (button heater attached to the head of an open-cycle He cryostat) was used to control temperature. The cleanliness of the sample was confirmed by the sharp and intensive surface-state peak in the spectra. All the spectra presented here were taken with He I photons (21.2 eV).

III. RESULTS AND DISCUSSION

A. ARUPS spectra

Figure 1 shows the energy distribution curves (EDC's) as a function of emission angle along the $\Gamma\bar{A}$ direction. The

bottom spectrum (0° emission angle) corresponds to normal emission (Γ point) and the increasing angle corresponds to increasing parallel momentum across the surface Brillouin zone, which has a large bulk projected band gap. At room temperature, the binding energies of $S1$ and $S2$ at \bar{A} are 0.37 and 2.62 eV, respectively. The third peak, observed at higher binding energy, is a surface resonance (SR) that disperses deeply in the bulk band from Γ toward the bulk band edge at \bar{A} .¹¹ The temperature dependence of the two surface states $S1$ and $S2$ at \bar{A} are shown in Figs. 2(a) and 2(b), respectively. After removing a Shirley background for each temperature EDC, the $S1$ peak was fitted with a Lorentzian line shape to extract both peak and width energies. Because $S2$ has an asymmetrical shape due to the bulk band edge at higher binding energy, the peak was partially fit with a Lorentzian line shape (full low- E_B side and partial high- E_B side of the peak) after the Shirley background was removed. From this fitting procedure, one can immediately see that, as expected, the linewidth increases with temperature; however, quite surprisingly, the peak positions of $S1$ and $S2$ shift in opposite directions. We will first discuss the temperature-dependent widths to extract electron-phonon coupling constants and then return to the peak shifts.

B. Peak widths

Figure 3(a) shows results of this analysis procedure for the $S1$ peak width versus temperature, along with a fitting curve of Eq. (1) employing a Debye phonon model. The solid line corresponds to a fit of the data between a temperature range of 303 and 700 K using a surface Debye energy 60 meV obtained from previous low-energy electron diffraction (LEED) I - V measurements.⁹ The result of this fitting yields $\lambda_{S1} = 0.657 \pm 0.03$, which is equal, within the error, to the result $\lambda = 0.642 \pm 0.031$ obtained from a previous experimental study.¹³ This agreement adds credibility to the results of both studies; an equivalent electron-phonon coupling parameter is determined upon fitting ARUPS data over an equivalent temperature range and Debye energy. However, when the fitted line is extrapolated (dashed line) using Eq. (1) to lower temperatures, specifically, 303–45 K, one can see that the overall fit to the extended data range is no longer adequate. Although previous studies have employed this methodology, in the present case it is found that using a Debye phonon model is insufficient to fit the data from this extended temperature range and indicates a breakdown in the approach.

This breakdown can be seen more clearly from the fit (dashed line) found in Fig. 3(b). As opposed to the limited temperature range fitting and subsequent extrapolation that was shown in Fig. 3(a), this time all temperature range data are used in the fitting analysis. The dashed line corresponds to a fit, employing a Debye phonon model ($\omega_D = 60$ meV) in Eq. (1), yielding $\lambda_{S1} = 0.476 \pm 0.0243$. As seen by eye, the best-fitted line, as determined from a χ^2 analysis, does not adequately reproduce the high-temperature data. Figure 3(c) (open circles) shows the results of the goodness of fit (χ^2) using the Debye phonon model over the extended tempera-

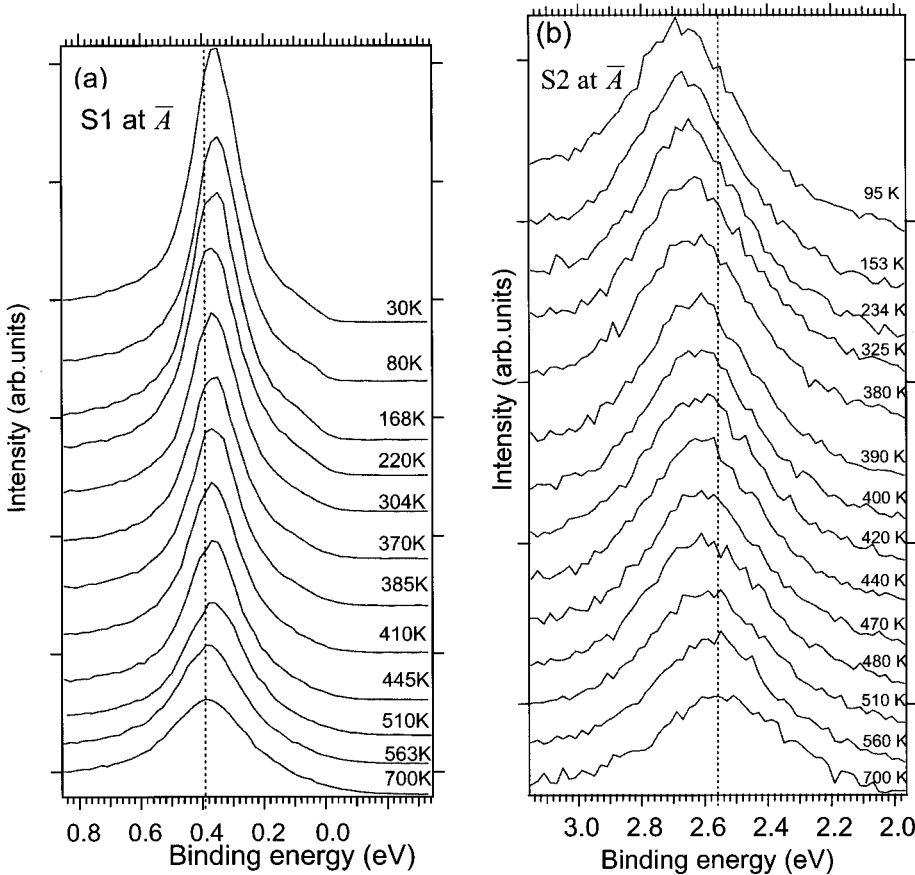


FIG. 2. (a) Temperature dependence of S1 state at \bar{A} from 50 to 700 K. (b) Temperature dependence of S2 at \bar{A} from 95 to 730 K.

ture range as a function of the Debye energy (ω_D). Here we only consider the range of Debye energy between 60 and 100 meV where the resulting peak width offset, which represents the temperature-independent contribution from e - e interactions and e -defect scattering, are physically reasonable (30–100 meV).¹⁹ From this figure, it is evident that the overall fit to the ARUPS data is optimized when the Debye energy increases and approaches 100 meV. However, even when fitting parameters are optimized, this approach does not adequately, as judged by the χ^2 reliability factor, reproduce the temperature-dependent linewidth data. This leads to the conclusion that a Debye phonon model is not appropriate in determining the electron-phonon coupling parameter of the S1 surface state.

Although this approach has been widely used for other systems, the failure of the Debye model as applied to the S1 state is not unexpected, due to the strong 2D charge localization of this state in the top layer. In the Debye phonon model, the phonon density of states is taken to be a smooth, continuous function up to the cutoff energy (ω_D). As stated above, the model is independent of the detailed shape and dimensionality of the phonon spectrum; basically, the electron-phonon interaction is smoothed out in energy and, more importantly, momentum space. However, in the present case, because of the high 2D localization of this surface state, there may be a limited number of phonon modes at the surface that dominate the electron-phonon coupling mechanism. In other words, a phonon density of states more akin to an Einstein phonon model, instead of a Debye phonon model, is

perhaps a more appropriate approach for properly describing the electron-phonon interaction in the present case.

If this type of approach is assumed, a different functional form of the coupling constant in Eq. (1) must be used. In the case of an Einstein phonon model, the Eliashberg coupling function in Eq. (1) takes the form $\alpha^2 F(\omega) = (\lambda \omega_E/2) \delta(\omega - \omega_E)$. Assuming this model can be used, Fig. 3(c) (solid circles) shows the results of the goodness of fit (χ^2) using the Einstein phonon model over the extended temperature range as a function of the frequency parameter ω_E . As seen, throughout a wide range of ω_E (50–70 meV),¹⁹ this model yields overall better fits to the extended temperature range data than the Debye phonon model described above [i.e., $\chi^2(\omega)$ is a factor of 2 lower than the corresponding fit from Debye model]. This indicates that an Einstein phonon model methodology indeed better describes the S1 electron-phonon interaction.

Because there is no distinct minima in χ^2 [Fig. 3(c)], a proper choice of ω_E , which consequently yields a value of λ , must be made with additional input. From bulk properties and prior electron-phonon studies of Be, one would expect that if an Einstein phonon model were invoked, which models the density of states with a δ function at one frequency, the physically reasonable range of ω_E should be between 50 and 80 meV.²⁰ The justification for using an Einstein model in the present case is that the known high 2D localization of this surface state and thus the electron-phonon coupling mechanism are limited to phonon modes localized to the

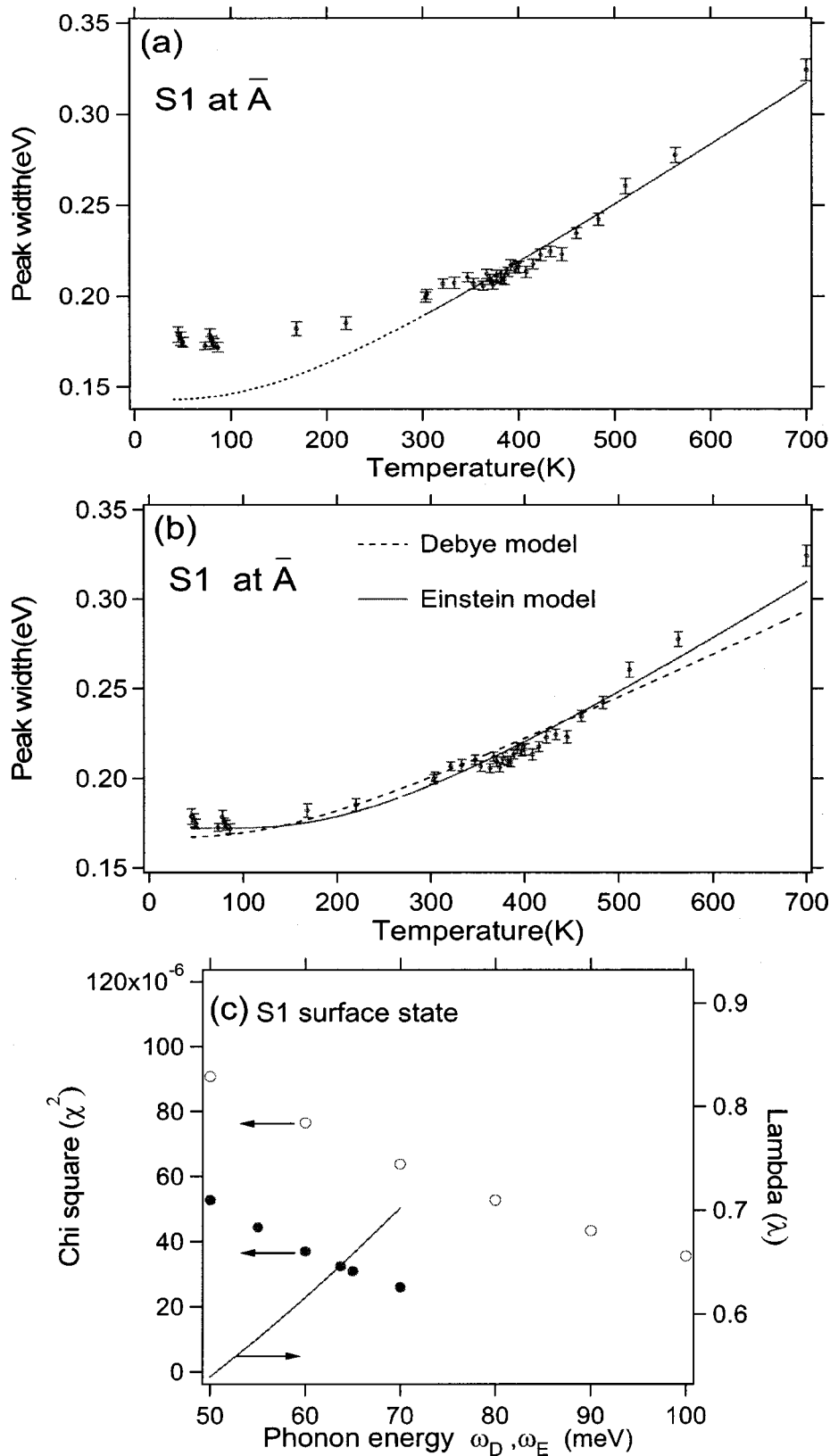


FIG. 3. Surface-state $S1$ peak-width at \bar{A} vs temperature: (a) The solid line corresponds to a fit using Eq. (1) (Debye phonon model with $\omega_D=60$ meV) over a limited temperature range 303–700 K, resulting in $\lambda=0.657 \pm 0.03$. The dashed line is an extrapolation of this fit to a lower-temperature range: (b) The dotted line corresponds to fit of all data (45–700 K, Debye phonon model with $\omega_D=60$ meV), resulting in $\lambda=0.476 \pm 0.0243$. The solid line corresponds to fit of all data (45–700 K, Einstein phonon model with $\omega_E=64$ meV), resulting in $\lambda=0.646 \pm 0.0209$. The error bar for each data point corresponds to statistical fitting uncertainties. (c) Left axis: χ^2 of fit versus ω_D (ω_E) for the fitting of whole temperature range by the Debye (Einstein) model as indicated with open (solid) circles. Right axis: λ vs Einstein energy for the Einstein model as indicated with the solid curve. The intersection of the solid curve and solid circles indicates the chosen fitting parameter ($\omega_E=64$ meV).

surface. In accordance, Lazzeri and De Gironcoli²¹ have calculated the theoretical surface phonons on Be(10 $\bar{1}0$) using a 104-layer slab model. Results of this study indicate that at the \bar{A} point of the surface Brillouin zone, the density of states is dominated by two acoustic modes at 26.4 and 32.3 meV,

polarized mainly perpendicular to the surface, and more importantly, one surface optical mode at 64 meV polarized along the surface. The latter mode, which disperses weakly through the SBZ, has a shear-horizontal character and 50% of the total displacement localized in the first two layers.¹⁰ If

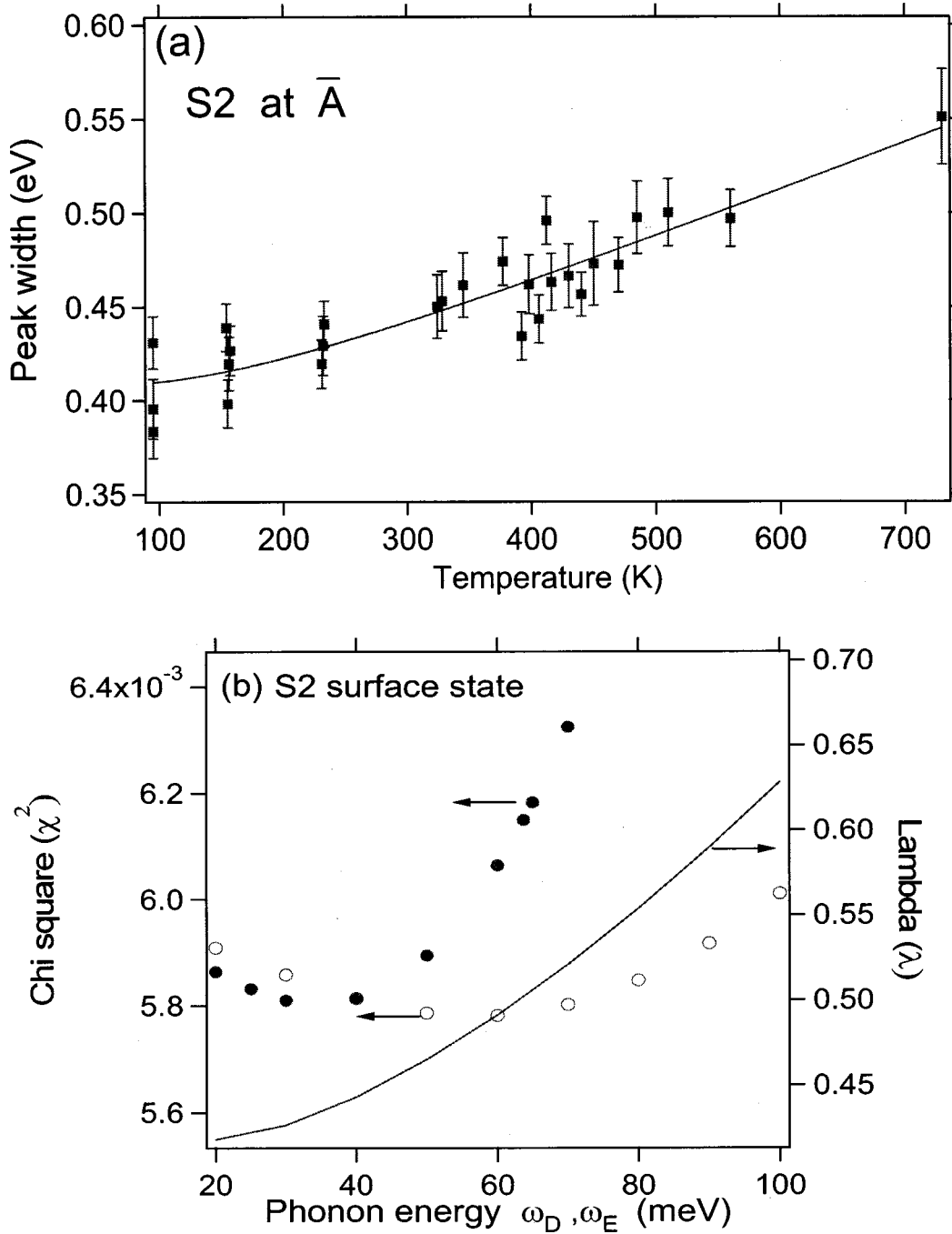


FIG. 4. Surface-state $S2$ peakwidth at \bar{A} vs temperature: (a) The solid line corresponds to a fit using Eq. (1) of all data (95–730 K, Debye phonon model with $\omega_D = 60$ meV), resulting with $\lambda = 0.491 \pm 0.04$. The error bar for each data point corresponds to statistical fitting uncertainties. (b) Left axis: χ^2 of fit vs ω_D (ω_E) for the fitting of whole temperature range by the Debye (Einstein) model as indicated with open (solid) circles. Right axis: λ vs ω_D for the Debye model as indicated with the solid curve. The intersection of the solid curve and open circles indicates the optimal fitting parameter ($\omega_D = 60$ meV).

we assume that this surface-localized optical phonon mode dominates the electron-phonon interaction, fitting the $S1$ data over the extended temperature range yields a value of $\lambda_{S1} = 0.646 \pm 0.021$. As seen in Fig. 3(b) (solid line), this goodness of fit is much better than the Debye model approach (dashed line).

If the fitting methods applied to $S1$ are now applied to the $S2$ state, the results indicate a fundamental difference in the

physics associated with the coupling of the surface states to different phonon modes. Specifically, the phonon model used to characterize the interaction is different between $S1$ and $S2$. Figure 4(a) shows the analyzed temperature-dependent peakwidth data [Fig. 2(b)] of the $S2$ surface state. Compared to the $S1$ state, there is more scatter in the data, primarily due to the lower signal to noise and the intrinsic asymmetric line shape, alluded to above. Figure 4(b) shows, similar to

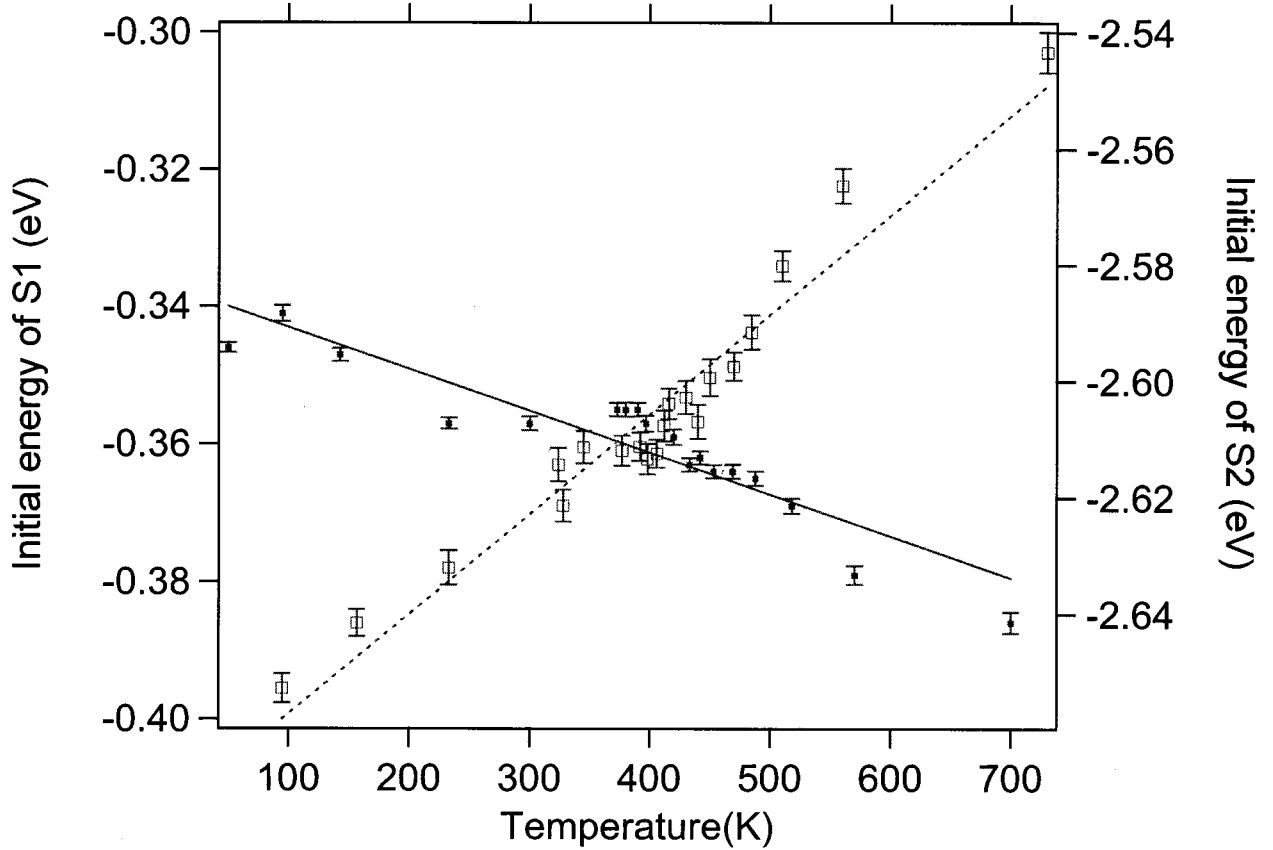


FIG. 5. Temperature dependence of the initial-state energy E_0 of the surface state $S1$ (solid square, left axis) and $S2$ (open square, right axis) at \bar{A} . The solid and dashed lines are the linear fit; the resulting slopes are $(-0.61 \pm 0.3) \times 10^{-4}$ eV/K for $S1$ and $(1.71 \pm 0.8) \times 10^{-4}$ eV/K for $S2$, respectively. The error bar for each data point corresponds to statistical fitting uncertainties.

Fig. 3(b), the goodness of fit (χ^2) to the data [Fig. 4(a)] for a broad range of phonon energies (ω_E and ω_D) for both Einstein and Debye phonon models. In the case of $S2$, the Debye phonon model results in a better reliability factor for all phonon parameter frequencies. Moreover, in spite of the somewhat large scatter in the data, using a Debye model yields a broad minimum in χ^2 near $\omega_D = 60$ meV, a value equivalent to that extracted from a LEED I - V study.⁸ Using this parameter, the resulting electron-phonon coupling is determined to be $\lambda = 0.49112 \pm 0.04$ and is shown in Fig. 4(a) (solid line). For comparison, the χ^2 value of the fit employing an Einstein model ($\omega_E = 64$ meV), as used in the analysis of the $S1$ state, is larger and does not adequately fit the ARUPS temperature-dependent data. The offsets (e - e and e -defect contribution) from the fitting of $S2$ peak width versus temperature via both Debye and Einstein models are, in general, large (~ 300 meV) compared to the $S1$ data. Because the $S2$ state is less localized at the surface and penetrates into the bulk states, its extra broadening is attributed to consequent scattering into bulk states.²²

C. Energy shift

In addition to the temperature-dependent peakwidth, the initial energies of both surface states shift with temperature. Figure 5 shows the initial energy (peak position) of both

surface states as a function of temperature. As seen, the $S1$ and $S2$ states shift in opposite direction with the temperature at the rate of $(-0.61 \pm 0.3) \times 10^{-4}$ eV/K and $(1.71 \pm 0.8) \times 10^{-4}$ eV/K, respectively. Just for reference, due to thermal expansion, the bandwidth of typical bulk states decreases with temperature (i.e., $\Delta E_{\text{bulk}}/\Delta T > 0$), which is in agreement with what is observed for the $S2$ state only. This particular surface state lies energetically close to the bulk band edge at \bar{A} and 40% of its charge distribution lies below the second atomic layer.^{11,14} Similar to what has been observed with zone-centered, Schockley surface states on noble metals,²³ the temperature-dependent initial state of $S2$ is dictated by bulk band properties. In contrast to $S2$, the $S1$ surface state is centered in a bulk gap at \bar{A} and its charge density, as detailed above, is extremely localized in the first atomic layer. Needless to say, the strange negative temperature dependence (i.e., $\Delta E_{S1}/\Delta T < 0$) of $S1$ is intimately tied to the unique static and dynamic properties of the Be(10 $\bar{1}$ 0) surface. This phenomenon has been observed in other systems. For example, previous ARUPS studies on Cu(100) (Ref. 24) have shown that a Tamm surface state centered at \bar{M} shifts to lower binding energy when the temperature decreases ($\Delta E_{\text{Cu}(100)}/\Delta T = -0.6 \times 10^{-4}$ eV/K). This Tamm state, with d -band symmetry, is known to be highly localized in the top surface layer. Although the $S1$ on Be(10 $\bar{1}$ 0) and

the Tamm surface state on Cu(100) are quite different overall, their 2D charge localization and corresponding temperature binding energy properties are similar.

The somewhat strange $\Delta E_{S1}/\Delta T$ observation on this surface must correlate with the corresponding static relaxation in the near-surface atomic structure. Based on ten-layer slab calculations, Hjorstam *et al.*²⁵ compared the differences between the surface projected density of surface states of the relaxed and unrelaxed atomic configuration for Be(10 $\bar{1}$ 0). Upon relaxation, they found that the large first-layer contraction affects the LDOS near E_F , specifically that states near E_F are pushed to higher binding energy (lower initial energy). Extending this argument, knowing the $S1$ surface state dominates the LDOS near E_F ,¹⁴ the binding energy of $S1$ should correspondingly increase upon contraction. Based on a LEED I - V experimental study, Ismail *et al.*²⁶ showed that the first layer in Be(10 $\bar{1}$ 0) indeed contracted with increasing temperature toward 500 K ($\Delta d_{12}/\Delta T < 0$). Our observations are in agreement with these prior theoretical and experimental results. The contraction, due to the *negative* thermal expansion and the negative thermal shift of $S1$ ($\Delta E_{S1}/\Delta T < 0$), is indeed correlated due to the large surface localization. In other words, the temperature-dependent shift of $S1$ is dictated by the localized nature of the surface charge and the observed thermal contraction of the surface. The exact details of this mechanism are not yet known: however, there is a consistent argument for the shift of $S1$ with temperature with other experimentally determined surface properties (e.g., negative thermal relaxation). However, they certainly involve the dynamic interplay between the anharmonic potential of the surface atomic lattice and corresponding surface energy dictated by the degree of 2D localization and corrugation of the surface. The detailed coupling between the surface-state(s) charge density, the surface phonons, and the resulting thermal expansion is a challenging many-body problem and requires further theoretical input.

IV. CONCLUSIONS

In summary, ARUPS has been used to measure the temperature-dependent peak width and binding energy of two surface states on Be(10 $\bar{1}$ 0). Based on extended temperature range data, model-dependent electron-phonon coupling parameters have been determined for the photohole decay of both $S1$ and $S2$, which are both Schockley-like surface states centered at the same point in the surface Brillouin zone. The extensive data set of this study facilitated an analysis, through comparison of χ^2 reliability factors, of the specific phonon model that best describes the Eliashberg coupling function of the electron-phonon interaction mechanism. To our knowledge, this is the first time this type of enhanced analysis has been applied to such a system. In addition, because the analysis is applied to both surface states,

it affords the ability to directly compare the degree of surface localization of each state with its ensuing properties. Based on this analysis, the resulting electron-phonon coupling strength λ for $S1$ and $S2$ are 0.646 ± 0.0209 (Einstein model, $\omega_E = 64$ meV) and 0.49112 ± 0.04 (Debye model, $\omega_D = 60$ meV), respectively. In the case of $S1$, which is primarily 2D localized to the surface layer, the better fitting (i.e., smaller χ^2) of the extended temperature range data with an Einstein phonon model indicates a strong e - p coupling dominated by an interaction with a highly localized, surface optical phonon mode. This latter assertion, which is quite unique, should be tested theoretically. A main conclusion from the analysis of the $S1$ data is that the typical use of Eq. (1) with a standard Debye phonon model should be questioned. With extended temperature range data, this is possible and provides a better fundamental understanding of the e - p interaction. A recent publication¹⁸ showed that there is a distinct difference in e - p coupling between bulk and surface phonons with zone-centered surface states on Cu(111) and Ag(111). In the case of Be(10 $\bar{1}$ 0), we have shown that the e - p decay of 2D $S1$ state is dominated by very localized, surface optical phonon modes. The suggested 2D localization of the $S1$ surface state is further confirmed by the unique temperature dependence of its initial energy. In the case of $S2$, whose charge extends into the underlying selvage region, the lower value of λ , determined more appropriately with a Debye phonon model, along with the bulklike, positive $\Delta E_{S2}/\Delta T$ value suggests it is distinctly different from $S1$.

As outlined in the Introduction, the electronic structure of bulk Be is quite unique and the bonding is best described as covalent like; the surface layer, however, is grossly different, being better described as a simple metal. In accordance, this study has shown distinct differences between the two surface states, due primarily to their respective degree of charge penetration into the bulk. $S1$ has been shown, in agreement with prior studies,¹³ to have an abnormally high electron-phonon coupling compared to the bulk, largely due to its surface localization. Because $S2$ is not purely 2D localized in the surface layer, there should be strong relation between this surface state and the covalentlike property in the Be(10 $\bar{1}$ 0) surface region. Indeed, Hoffman *et al.*⁹ have suggested that surface state provides backbonding (covalent) of the underlying atomic layers and consequent contribution to the large inward contraction of the surface. We also believe this is indeed correct and additional support of this argument will be presented elsewhere.²⁷

ACKNOWLEDGMENTS

The authors wish to acknowledge the discussions and technical help of X. Gao and J. Topolancik. This research was supported by U.S. DOE contract No. DE-FG02-98ER45712 and NSF Contract No. DMR-0105232

- ¹L. I. Johansson, H. I. P. Johansson, J. N. Andersen, E. Lundgren, and R. Nyholm, *Phys. Rev. Lett.* **71**, 2453 (1993).
- ²P. T. Sprunger, L. Petersen, E. W. Plummer, E. Lægsgaard, and F. Besenbacher, *Science* **275**, 1764 (1997).
- ³M. Hengsberger *et al.*, *Phys. Rev. Lett.* **83**, 592 (1999); M. Hengsberger, R. Fresard, D. Purdie, P. Segovia, and Y. Baer, *Phys. Rev. B* **60**, 10 796 (1999).
- ⁴T. Balasubramanian, E. Jensen, X. L. Wu, and S. L. Hulbert, *Phys. Rev. B* **57**, 6866 (1998).
- ⁵S. Lashell, E. Jensen, and T. Balasubramanian, *Phys. Rev. B* **61**, 2371 (2000).
- ⁶E. Jensen, R. A. Bartynski, T. Gustafsson, and E. W. Plummer, *Phys. Rev. Lett.* **52**, 2172 (1984).
- ⁷H. I. P. Johansson and L. I. Johansson, *Phys. Rev. B* **49**, 17 460 (1994).
- ⁸Ph. Hofmann, B. G. Briner, M. Doering, H.-P. Rust, E. W. Plummer, and A. M. Bradshaw, *Phys. Rev. Lett.* **79**, 265 (1997).
- ⁹Ph. Hofmann, K. Pohl, R. Stumpf, and E. W. Plummer, *Phys. Rev. B* **53**, 13 715 (1996).
- ¹⁰Ph. Hofmann and E. W. Plummer, *Surf. Sci.* **377**, L330 (1997).
- ¹¹Ph. Hofmann, R. Stumpf, V. M. Silkin, E. V. Chulkov, and E. W. Plummer, *Surf. Sci.* **355**, L278 (1996).
- ¹²J.-H. Cho, K. S. Kim, S.-H. Lee, M.-H. Kang, and Z. Zhang, *Phys. Rev. B* **61**, 9975 (2000).
- ¹³T. Balasubramanian, P.-A. Glans, and L. I. Johansson, *Phys. Rev. B* **61**, 12 709 (2000).
- ¹⁴V. M. Silkin and E. V. Chulkov, *Phys. Solid State* **37**, 1540 (1995).
- ¹⁵G. Grimvall, *The Electron-Phonon Interaction in Metals* (North-Holland, New York, 1981).
- ¹⁶B. A. McDougall, T. Balasubramanian, and E. Jensen, *Phys. Rev. B* **51**, 13 891 (1995).
- ¹⁷N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College, Philadelphia, 1976).
- ¹⁸A. 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).
- ¹⁹The range of phonon frequencies were selected based on reasonable physical properties which were both input and output from the fitting. For example, bulk Be has a Debye energy of 86 meV and thus the range of phonon energies input to the fit must be nearly equivalent (<100 meV). Moreover, an additional variable in the fit is the offset, specifically the contribution of e - e and e -defect interactions, which cannot be unphysically negative. In Ref. 3, the contribution of both these effects to the localized surface state in Be(1000) is 75 meV. In accordance, we believe an offset range between 30 and 100 meV is physically reasonable for their contribution to the $S1$ peak width.
- ²⁰R. Stedman, Z. Amilius, R. Pauli, and O. Sundin, *J. Phys. F: Met. Phys.* **6**, 157 (1976).
- ²¹M. Lazzeri and S. De Gironcoli, *Surf. Sci.* **454**, L442 (2000).
- ²²S. D. Kevan, *Phys. Rev. Lett.* **50**, 526 (1983).
- ²³R. Paniago, R. Matzdorf, G. Meistter, and A. Goldmann, *Surf. Sci.* **336**, L113 (1995).
- ²⁴R. Paniago, R. Matzdorf, A. Goldmann, and R. Courths, *J. Phys.: Condens. Matter* **7**, 2095 (1995).
- ²⁵O. Hjortsam, J. Trygg, J. M. Wills, B. Johansson, and O. Eriksson, *Surf. Sci.* **355**, L214 (1996).
- ²⁶Ismail *et al.* (private communication).
- ²⁷S. J. Tang, Ismail, P. T. Sprunger, and E. W. Plummer (unpublished).