PHYSICAL REVIEW B **66**, 245422 (2002)

Unexpected surface sensitivity at high energies in angle-resolved photoemission

Ph. Hofmann, Ch. Søndergaard, S. Agergaard, and S. V. Hoffmann
Institute for Storage Ring Facilities, University of Aarhus, 8000 Aarhus C, Denmark

J. E. Gayone and G. Zampieri
Centro Atómico Bariloche and Instituto Balseiro, Comisión Nacional de Energía Atómica, 8400-Bariloche, Argentina

S. Lizzit
Sincrotrone Trieste, S.S. 14 Km. 163.5, 34012 Trieste, Italy

A. Baraldi
Dipartimento di Fisica, Universitá di Trieste, Via Valerio 2, 34127 Trieste, Italy
and Laboratorio TASC-INFM, S.S. 14 Km. 163.5, 34012 Trieste, Italy

(Received 12 August 2002; published 31 December 2002)

Angle-resolved photoemission data from Al(001) taken with photon energies up to several hundred electron volts show an unexpected surface sensitivity at high energies. The surface state at the center of the surface Brillouin zone can be clearly observed up to photon energies higher than 700 eV. The surface to bulk intensity ratio appears to increase with photon energy, despite the longer inelastic mean-free path of the electrons and the increased vibrational amplitude at the surface. We explain this surprising behavior by considering the effect of phonon excitation in the photoemission event.

DOI: 10.1103/PhysRevB.66.245422 PACS number(s): 79.60.Bm, 63.20.Kr, 72.15.Lh, 73.20.−r

An ubiquitous concept in photoemission, and electron spectroscopy in general, is the electron inelastic mean-free path (IMFP) in solids.[1] Its energy dependence makes it possible to tune the relative contributions of surface and bulk signals to a photoemission spectrum. If one is interested in bulk properties one should work at high photon energies, where the IMFP is long and the surface contribution is expected to be small. Recent progress in instrumentation has made it possible to perform such experiments on valence states with reasonable count rates and energy resolution. In angle-integrated photoemission it has already been shown that the surface contribution is decreasing so much at high energies that valuable information about the bulk can be obtained.[2] Here we are concerned with the case of angle-resolved photoemission spectroscopy (ARPES). Extending ARPES to the high-energy regime is expected to have other advantages, apart from the longer IMFP, such as a simple, free-electron like final state and a wide momentum range perpendicular to the surface. While exploring the high-energy regime of ARPES in a simple metal, however, we found a quite unexpected result. In this paper we present ARPES data from aluminum, taken over a wide photon energy range, which show that the relative surface contribution does not decrease for high energies, in sharp contrast to what would be expected from an IMFP argument. Indeed, the bulk to surface intensity ratio even appears to *decrease* at high energies. This finding is of great importance in electron spectroscopy as it shows that the bulk contribution to a spectrum does not necessarily scale with the IMFP. We explain our observations in terms of phonon excitation and support our ideas with model calculations.

The photoemission experiment was performed at the super-ESCA beamline at the synchrotron radiation source ELETTRA. The base pressure of the experimental chamber was in the mid 10^{-11} mbar region. The Al(001) sample was prepared by standard procedures.[3] The surface was clean and wellordered, as confirmed by the absence of detectable contaminations in x-ray photoemission spectroscopy, the shape of the Al $2p$ core level peaks, and a sharp, low background low-energy electron diffraction (LEED) pattern. Data were taken for photon energies between 125 and 760 eV. This range was covered with one grating of the monochromator and two different harmonics of the undulator (first and third). The total energy resolution of the beamline and the spectrometer was set to vary between 300 meV ($h\nu = 125$ eV) and 900 meV ($h\nu = 760$ eV). The angular resolution of the analyzer can be changed by choosing different apertures. In our experiment it was set to a value of around 1°.

Figure 1 presents the data measured in normal emission at room temperature in two forms. On the right we show a subset of the measured energy distribution curves (EDC's) covering the whole range of photon energies. All spectra have been normalized such that the intensity at a binding energy of 14.1 eV is the same. The image on the left side of Fig. 1 is a plot of the photoemission intensity as a function of binding energy and final state momentum. It was obtained by an interpolation from the whole data set of 111 EDC's (normalized in the same way as above). The final state momentum has been calculated assuming a free-electron-like final state with an inner potential of 11.2 eV. This way of visualizing the data emphasizes the periodicity in the dispersion more clearly, but note that a horizontal cut through the image corresponds only approximately to a spectrum on the right.

A parabolic band dispersing from the band bottom towards the Fermi level is clearly seen in both parts of the figure. It corresponds to the free-electron-like bulk states in the Γ-X direction of the Brillouin zone.[4] The other prominent feature is the peak at 2.5 eV binding energy, caused by the

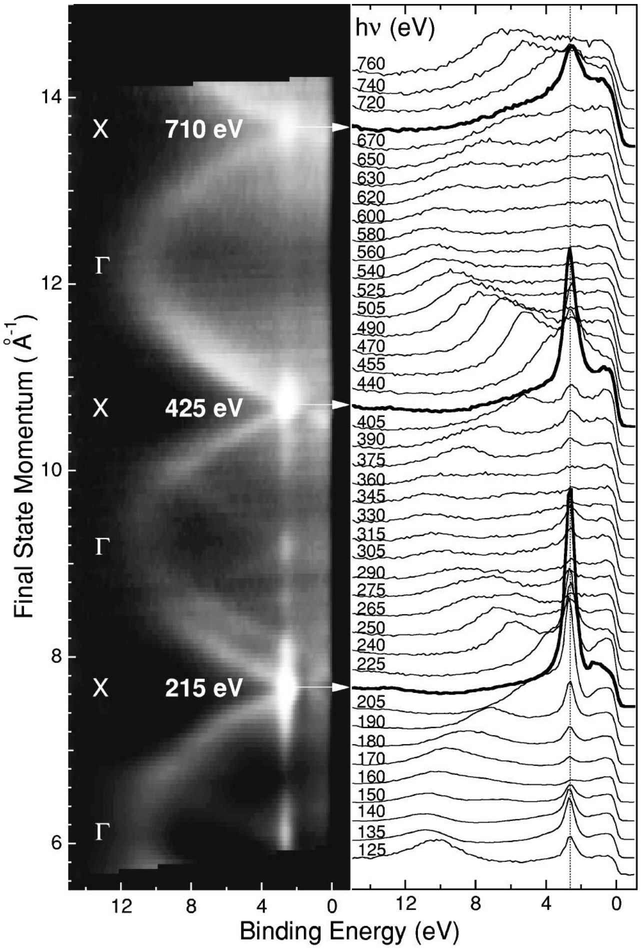

FIG. 1. Photoemission intensity from Al(100) in normal emission at room temperature. Right: raw EDC's normalized to the photoemission intensity at 14.1 eV binding energy and plotted with a vertical offset. Left: photoemission intensity as a function of final state momentum and binding energy (see text). The numbers and the arrows in this part indicate the photon energies at which the states from the *X* point of the Brillouin zone are photoemitted.

Shockley-type surface state on Al(001) which exists in the gap of the bulk band structure at the *X* point point of the Brillouin zone.[4,5] The surface peak is visible at most energies but it is resonantly enhanced when the bulk band reaches the *X* point. This occurs at $h\nu = 215$, 425, and 710 eV. This phenomenon is caused by the fact that the surface state wave function is not entirely two dimensional, but has a remaining depth dependence that is similar to that of the bulk state it is derived from.[6]

To compare the surface and bulk peak intensities on an equal footing, one should consider only the energies where the surface peak resonates. This is because all the bulk peaks are also resonances in the sense that an (almost) k conservation perpendicular to the surface is needed in order to produce a peak. As the photon energy increases, the intensity of the bulk peak decreases at the expense of an increasing background (most clearly seen in the right part of the figure). The intensity of the surface peak in resonance is also decreasing but not as fast as that of the bulk states. This can be seen, for example, by comparing the intensity of the surface peak at and close to the *X* points with that of the bulk peak at the Fermi edge in the same spectra. While the latter is clearly visible at low photon energies, it has completely disappeared at the 710 eV resonance. Therefore, although the IMFP increases in our experiment from about 5 to 20 Å, the bulk peaks never become more intense than the surface peak, and the latter remains to be the most prominent feature even at high energies.

Another reason, besides the increase of the IMFP, to expect a strong decrease of the surface state peak at high energies is related to phonon scattering. According to the work of Shevchik,[7] the temperature-dependent intensity in a direct-transition photoemission peak is given by a Debye-Waller factor of the form $e^{-\Delta k(h\nu)^2\langle u_z^2(T)\rangle}$, where $\Delta k = |\vec{k}_f(h\nu) - \vec{k}_i|$ is the momentum transfer in the photoemission process and $\langle u_z^2(T)\rangle$ is the thermal mean-square displacement of the atoms. This means that the intensity of a peak should decrease when the photon energy and/or the temperature is raised. On Al(001), like on most other surfaces, $\langle u_z^2(T)\rangle$ is larger at the surface than in the bulk[3] and hence one expects the surface peak to be more unstable than the bulk peaks upon an increase of the photon energy.[8]

Given the equivalence of temperature and photon energy in the Debye-Waller factor, we can demonstrate the unexpectedly high stability of the surface state in a more convenient way. Instead of performing an energy scan at a fixed temperature, we fix the energy and change the temperature. An advantage of the temperature scan over the energy scan is that the energy dependence of the photoemission matrix element is irrelevant and, therefore, can be excluded as a possible cause of the high intensity of the surface peak Such data are presented in Fig. 2, which shows a temperature scan at $h\nu = 195$ eV. The data for this scan have not been normalized at all. This is justified because they have been taken within a short time with an almost identical flux of incoming photons and, of course, with the same photon energy. Two bulk-related peaks can be identified in the low-temperature spectra, one at 6.5 eV binding energy and the other one close to the Fermi edge. The surface peak is, as in the other spectra, at 2.5 eV. As mentioned above, it is seen that the intensity of all the peaks decreases when the temperature is raised,[9] but surprisingly the bulk peaks decrease more rapidly than the surface peak. At the highest temperature the two bulk peaks have almost disappeared but the surface peak is still clearly visible, being only decreased to about one third of its original size. Note that the photon energy for this temperature scan was chosen such that the surface state is off resonance in order to have a pronounced bulk peak also close to the bottom of the band. This causes the surface peak to be substantially smaller, but the effect is visible nonetheless.

Figure 3 gives a more quantitative illustration of the same effect. It shows the temperature-dependent intensity of the surface state and of two bulk peaks, all taken with different photon energies. These data have been extracted by analyzing temperature scans similar to that given in Fig. 2. Again, no normalization of the raw data was performed and the intensity was determined by integrating the area of the peak over a linear background. This simple but consistent way to

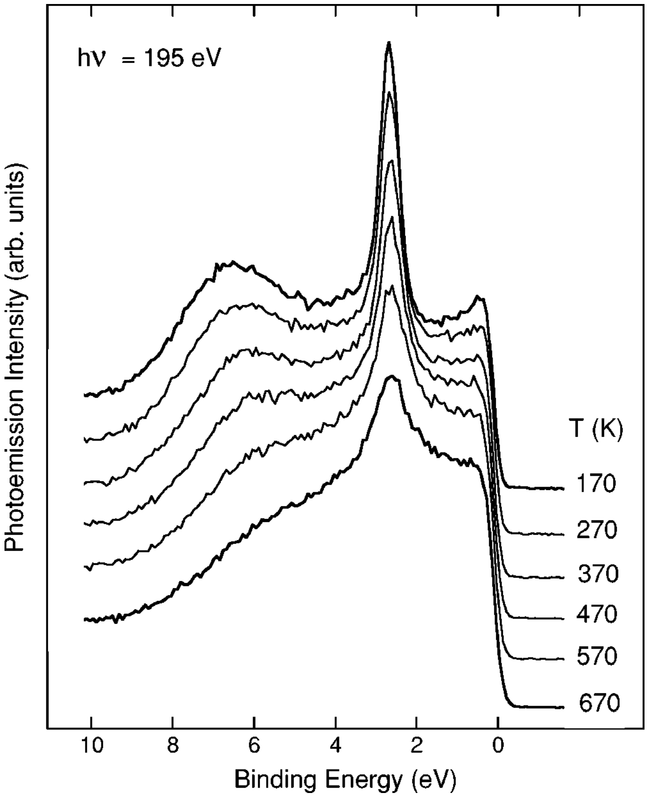

FIG. 2. Photoemission spectra taken in normal emission at $h\nu = 195$ eV as a function of temperature. The series is plotted with a vertical offset between the spectra.

analyze the data has the advantage that no assumptions about the photoemission line shape have to be made. Finally, the resulting intensity versus temperature curves were normalized such that the intensity at the lowest temperature was set to 1. Note that the data for this figure were taken such that all three peaks have been in resonance and hence a quantitative comparison is permitted. The temperature dependence of the two bulk peaks has already been described in Ref. 10. It can be understood qualitatively in terms of Shevchik's model. The peak taken with a photon energy of $h\nu = 567$ eV decays more rapidly than the peak taken with $h\nu = 345$ eV. The decay of the surface state taken with $h\nu = 425$ eV, however, is much slower, even slower than that of the bulk state measured with a lower photon energy.

Two unexpected conclusions can be drawn from the data shown in Figs. 1, 2, and 3: (i) in ARPES the increase of the photon energy does not suppress the surface contribution, contrary to what is observed in angle-integrated experiments,[2] and (ii) the surface peak is more stable towards a temperature increase than the bulk peaks despite the larger atomic vibrations at the surface.

In the following, we explain these observations by the different effect that phonon emission has on the photoemission from surface and bulk states. The basic idea can be presented as follows. The photoemission peaks in ARPES can be viewed as a constructive, coherent superposition of the amplitudes from many emitters. In a first approximation, these emitters are on a three-dimensional lattice for bulk initial states and on a two-dimensional lattice for surface initial states (neglecting the finite penetration of the surface states into the bulk). At finite temperature, each lattice gets disordered by phonons and this affects the coherence that gives rise to the peaks. The loss of coherence due to the thermal disorder increases not only with the temperature but also with the energy because of the smaller wavelength of the photoelectron. We argue that the surface state peak wins over the bulk peaks when going to high energies or high temperatures simply because it is easier to destroy the constructive interference in three dimensions than it is in two dimensions.

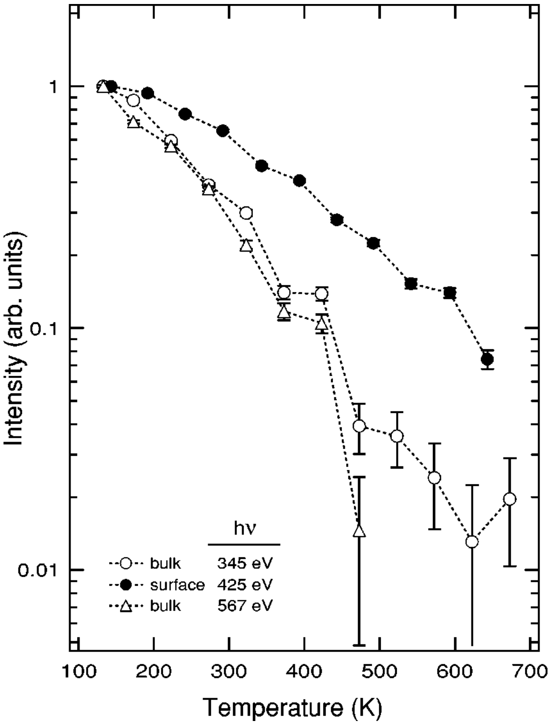

FIG. 3. Photoemission intensity of two bulk peaks and the surface state peak, taken at different photon energies. The points correspond to the integrated intensity of the peak over a linear background. The error bars represent the statistical error in the integration of the peak area. The solid lines are guide to the eye. The peak area at the lowest temperature has been normalized to 1.

To substantiate these ideas we have performed calculations of the probability of photoemission from a valence-band initial state with simultaneous excitation/absorption of phonons using a model described in detail in Ref. 11 In short, the initial state of the electron is composed of two Bloch waves, one propagating towards the surface and one reflected back at the surface, and the final state is the time-reversed LEED wave function. The lattice vibrations are treated within the Debye approximation. We have recently used this model to investigate the temperature dependence of the bulk photoemission peaks of Al.[10] In that work we have found that the so-called direct transition peak in photoemission actually contains a considerable contribution from electrons that have been scattered by one or two phonons. Once this was taken into account, however, the model of Ref. 11 was able to give a good quantitative description of the temperature-dependent intensity of bulk photoemission peaks for a broad range of photon energies.[10] Therefore, all

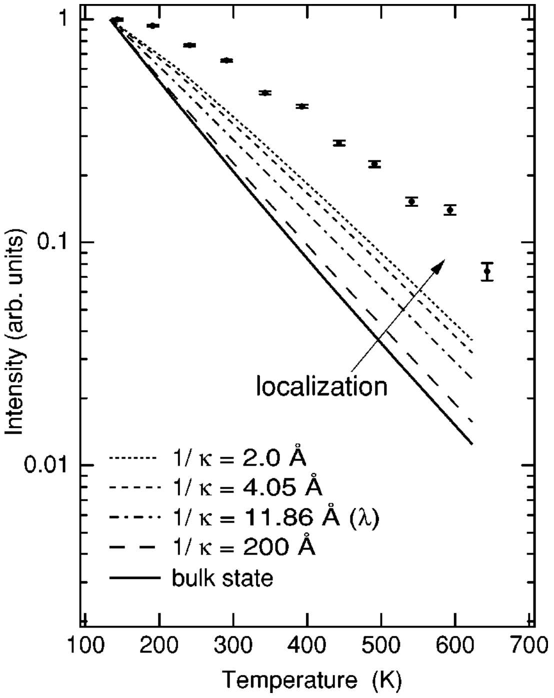

FIG. 4. Calculated photoemission intensities for the Al(001) surface state as a function of the temperature and for different values of the localization parameter $1/\kappa$. The points correspond to the experimental data at $h\nu = 425$ eV. The error bars represent the statistical error in the integration of the peak area.

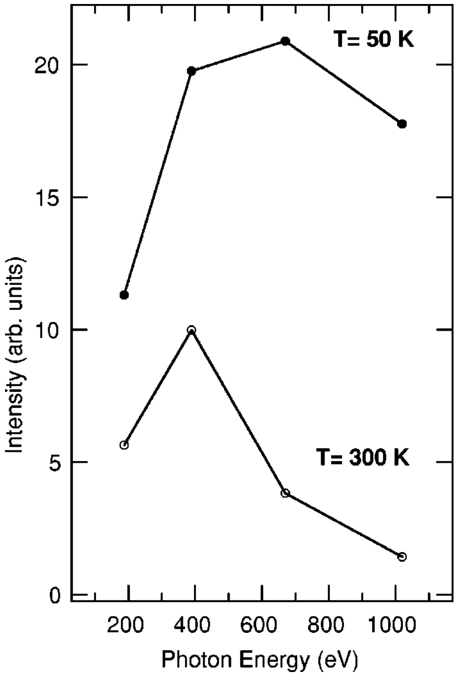

FIG. 5. Calculated photoemission intensities as a function of photon energy for a bulk initial state in the Γ-X line with a binding energy of 8.2 eV. The solid lines are guide to the eye.

the calculated photoemission intensities reported here are the sum of the zero, one, and two phonon-scattered components.

To verify the larger thermal stability of the surface peak we have extended the model of Ref. 11 in order to describe the surface state on Al(001). This state is situated very close to the band edge at the X point in the Brillouin zone and its wave function has a character very similar to these states. We have, therefore, modeled the surface state using a bulk X state and forcing it to decay exponentially into the crystal, with a certain decay length $1/\kappa$. This simple description ignores the true potential change and the enhanced vibrational amplitudes near the surface. We should therefore not expect to get a good quantitative agreement with the experiment with these calculations, but rather a tool to analyze what happens to the temperature or energy dependence of the photoemission peaks as we go from a bulk state (infinite decay length $1/\kappa$) to a surface state (small $1/\kappa$). This is done in Fig. 4, where we show the temperature dependence of the surface peak intensity calculated for different values of $1/\kappa$ and compare this to the experimental result from Fig. 3. As in the experiment, the calculated intensities have been extracted by integrating the peak area over a linear background. After that the calculated intensity at the lowest temperature was set to 1. These intensities, calculated at 439 eV, are compared with the experimental data measured at 425 eV. The two slightly different energies were chosen such that both, theory and experiment, are exactly at the resonance visible in Fig. 1. Figure 4 clearly shows that the higher the localization of the initial state at the surface, the less affected is the intensity by the temperature. This confirms our hypothesis that the stability of the surface peak is, at least in part, explained by the fact that fewer atoms have to emit coherently in order to produce the peak. The calculated intensities are in fair agreement with the experimental data only for $1/\kappa = 2$ Å, a value that is probably too low.[12] Hence there must be other contributions to the high stability of the surface state than those captured in our simple calculation. A possible explanation is that the model lacks a true surface potential barrier and does not take into account the importance of the electric-field gradient at the surface.

One possible problem in the analysis of the experimental data is that, since the spectra have been taken at the X point, there is also a bulk peak at nearly the same position as the surface state peak. This peak cannot be separated in our analysis and might add intensity. However, given the faster decay of the bulk states, a subtraction of its contribution would only lead to a surface state decay which is even slower. In any case, the contribution of bulk states at X is probably only a small source of error because at this high energy the bulk state peaks are already quite small and much broader than the surface state.

To complete the analysis of the thermal stability one should also consider the fact that the localization, besides reducing the effective number of emitters, concentrates them in the region of largest atomic vibrations, which causes a countereffect. Although this cannot be described with our model, the experimental observation that the surface peak is more stable than the bulk peaks suggests that the reduction in the number of coherent emitters is more important than the increase of the atomic vibrations. A different situation can arise in the limit of a very low surface Debye temperature where the effect of increased atomic vibrations would win over the reduction of emitters, leading to a surface peak decay faster than that of the bulk peaks.[8]

Finally, we briefly discuss how the coupling to phonons affects the intensity of the bulk states. In the absence of phonon scattering the intensity of these peaks would increase continuously as a function of photon energy due to the increase of the IMFP. In Fig. 5 we show calculations[13] of the photoemission intensity at two temperatures as a function of photon energy for a bulk state in the Γ-X line with a binding energy of 8.2 eV. Again, the intensity is the integrated peak area over a linear background. The energy and wave-vector selection rules determine that this state is photoemitted at $h\nu = 188$, 390, 670, and 1020 eV. It is seen in the figure that the intensity increases with the photon energy, following the increase of the IMFP, but only up to about 400 eV and 700 eV for $T = 300$ K and 50 K, respectively. Above these energies the intensity begins to decrease due to the loss of coherence induced by the increasing phonon emission. Therefore, in ARPES, unlike in other non-$\vec{k}$-conserving experiments, the phonon excitation sets a limit to the increase of the bulk contributions, impeding thereby to reach high bulk to surface intensity ratios. On the other hand, the figure also illustrates the strong temperature dependence of the absolute peak intensity. As expected from Shevchik's arguments, the intensity is much higher for a low temperature, in particular, at high photon energies. Hence, any bulk-sensitive high-energy ARPES experiment should be performed at low temperature where the peaks are still visible.

In conclusion, we have found that surface states can give a considerable contribution to ARPES spectra at high energies, despite the longer IMFP and the enhanced vibrational amplitude of the surface atoms, and in contrast to what is observed in angle-integrated photoemission. We explain our observations by the different effect that the phonon scattering has on the photoemission from localized, quasi-two-dimensional, surface states and from three-dimensional bulk states. The experimental results described in this paper call for attention in using ARPES at high energies due to fundamental limitations of this approach.

We gratefully acknowledge support by the Danish National Research Council, CONICET (Argentina), and the European Community Access to Research Infrastructure action of the Improving Human Potential Program.

---

[1] C.J. Powell and A. Jablonski, J. Phys. Chem. Ref. Data **28**, 19 (1999), and references therein.

[2] A. Sekiyama, T. Iwasaki, K. Matsuda, Y. Saitoh, Y. Ônuki, and S. Suga, Nature (London) **403**, 396 2000.

[3] J.H. Petersen, A. Mikkelsen, M.M. Nielsen, and D.L. Adams, Phys. Rev. B **60**, 5963 (1999).

[4] H.J. Levinson F. Greuter, and E.W. Plummer, Phys. Rev. B **27**, 727 (1983).

[5] G.V. Hansson and S.A. Flodström, Phys. Rev. B **18**, 1562 (1978).

[6] S.G. Louie, P. Thiry, R. Pinchaux, Y. Pétroff, D. Chanderis, and J. Lecante, Phys. Rev. Lett. **44**, 549 (1980).

[7] N.J. Shevchik, Phys. Rev. B **16**, 3428 (1977); N.J. Shevchik, J. Phys. C **10**, L555 (1977); N.J. Shevchik, Phys. Rev. B **20**, 3020 (1979).

[8] A. Goldmann and R. Matzdorf, Prog. Surf. Sci. **42**, 331 (1993); R. Paniago, R. Matzdorf, G. Meister, and A. Goldmann, Surf. Sci. **336**, 113 (1995); C. Waldfried, D.N. McIlroy, J. Zhang, P.A. Dowben, G.A. Katrich, and E.W. Plummer, *ibid.* **363**, 296 (1996).

[9] The shift of the bulk peaks with the temperature is caused by the lattice expansion.

[10] C. Søndergaard, Ph. Hofmann, C. Schultz, M.S. Moreno, J.E. Gayone, M.A. Vicente Alvarez, G. Zampieri, S. Lizzit, and A. Baraldi, Phys. Rev. B **63**, 233102 (2001).

[11] M.A. Vicente Alvarez, H. Ascolani, and G. Zampieri, Phys. Rev. B **54**, 14 703 (1996).

[12] J.E. Inglesfield and G.A. Benesh, Surf. Sci. **200**, 135 (1988).

[13] Our calculations do not account for the energy dependence of photoemission matrix elements. This is, however, of no consequence here because we only want to study the effect of phonon emission on the intensity and on the probing depth.