Investigation of the surface bands along the \bar{X} - \bar{M} line of the Cu(100) surface

Daiichiro Sekiba* and Fumio Komori

Institute for Solid State Physics, University of Tokyo, Kashiwanoha 5-1-5, Kashiwashi, Chiba 277-8581, Japan

Pietro Cortona[†]

Ecole Centrale Paris, Laboratoire SPMS, CNRS UMR8580, Grande Voie des Vignes, 92295 Chatenay-Malabry Cedex, France (Received 28 August 2006; revised manuscript received 21 March 2007; published 17 April 2007)

Recent semiempirical linear combination of atomic orbital method (LCAO) calculations for the Cu surfaces of low Miller indices have given surface bands which agree very well with the available experimental data. These calculations indicate the existence of various surface states and resonances, in particular, in the *s*-*d* band region, which have not yet been experimentally observed. We have checked a part of these predictions by performing angle-resolved photoemission measurements along the \bar{X} - \bar{M} direction of the (100) surface, a direction that, to our knowledge, has not yet been investigated. Most of the predicted surface states and resonances have been actually observed and are in good agreement with the calculations. Furthermore, the calculated effective *k*-resolved density of states quantitatively reproduces the experimental photoemission spectra, as it results from the comparison that we have done at the high-symmetry points. The results reported in the present paper confirm the predictive ability of LCAO calculations performed with a carefully chosen parameter set and provide experimental evidence of several previously unknown surface states.

DOI: 10.1103/PhysRevB.75.165410

PACS number(s): 73.20.At, 31.15.Ct, 33.60.Fy

I. INTRODUCTION

The semiempirical linear combination of atomic orbital method (LCAO) was originally developed in order to interpolate the energy bands calculated by first-principles approaches in the early days of the band-structure calculations.¹ Nevertheless, the method is used even today in order to understand the electronic properties of solids and surfaces, mainly because of its physically intuitive character. An important feature of the LCAO method is that it gives energy bands which can be quantitatively compared with results of angle-resolved photoemission spectroscopy (ARUPS) measurements. This is an important advantage of the semiempirical LCAO approach over the *ab initio* methods: the latter, owing to a well-known limitation of the density-functional theory, give energy bands which can only be qualitatively compared with the experimental data. A further advantage is that the LCAO method allows one to treat slabs including a large number of planes. This is useful for at least two reasons. The first one is that a spurious coupling between identical surface states localized on the opposite sides of the slab is avoided. The second one is that the distinction between surface and bulk states becomes easier to draw. For these reasons, the LCAO method is a very convenient tool for the assignment and the interpretation of the peaks observed in ARUPS experiments.

In order to obtain accurate results using LCAO, a good set of parameters describing the system is required. In particular, a careful treatment is necessary in order to reproduce the energy bands at surfaces, where bulk states, surface states, and surface resonances coexist. In the case of Cu, Cortona and Sapet^{2,3} have recently proposed a set of parameters obtained by fitting the bulk bands and a few surface states. They have shown³ that band calculations using these parameters give results in full agreement with the available experimental data^{4–19} obtained by photoemission and inverse photoemission for the (100), (110), and (111) surfaces.

Such parameters have been successively used in order to describe the substrate in a study of the (110) surface partially covered (0.5 monolayer) by oxygen.^{20,21} As well known, this surface reconstructs according to the added row geometry, forming Cu–O–Cu chains in the (001) direction. The electronic structure resulting from the calculations was found to agree very well with the experimental data, and it was possible to locate the p_y antibonding band of the oxygen, a band whose exact position has been intensively searched in the past.^{22,23}

The interest in the present paper is to establish if the parameter set can predict experimental results on a Cu surface. Our calculations have given indications of the existence and of the location of surface states which have not yet been observed experimentally. In the case of the (100) surface, for example, most experimental investigations have concerned the $\overline{\Gamma} \cdot \overline{X}$ and $\overline{\Gamma} \cdot \overline{M}$ directions. The $\overline{X} \cdot \overline{M}$ line, to our knowledge, has never been experimentally investigated. In the present paper, we report the first ARUPS data on Cu(100) along the $\overline{X} \cdot \overline{M}$ line, and we check in this way the reliability of the LCAO parameter set.

II. THE SEMIEMPIRICAL LCAO CALCULATIONS

A. Outline of the LCAO calculations

The LCAO calculations have been performed using a slab geometry comprising 97 planes, taking into account the interactions between first and second neighbors, and allowing nonvanishing overlap integrals. Furthermore, the usual twocenter Slater-Koster¹ approximation has been adopted. In the framework of this approximation, the Hamiltonian matrix elements and the overlap integrals are expressed in terms of diatomic molecularlike quantities, which are, together with the on-site matrix elements, the parameters of the semiempir-

TABLE I. LCAO parameters for the Cu–Cu interactions between nearest neighbors (nn) and next-nearest neighbors (nnn). The Hamiltonian matrix elements and the three on-site integrals (s_0 , p_0 and d_0) are in eV.

	H(nn)	H (nnn)	S (nn)	S (nnn)
ssσ	-1.313	-0.279	0.0729	0
$pp\sigma$	0.861	0.860	-0.2981	-0.035
$pp\pi$	-0.858	-0.320	0.0462	0
$dd\sigma$	-0.367	-0.045	0	0
$dd\pi$	0.167	0	0	0
$dd\delta$	-0.001	0	0	0
$sp\sigma$	1.654	0.650	-0.1587	0
$sd\sigma$	-0.580	-0.113	0	0
$pd\sigma$	-0.795	-0.426	0	0
$pd\pi$	0.323	0.061	0	0
$s_0 = 1.147$	$p_0 = 5.643, d_0$	=-3.043		

ical LCAO method. A typical parameter is indicated by a symbol such as $(pd\pi)$, which stands for the Hamiltonian matrix element (or the overlap integral) between a p orbital on one site and a d orbital on the other, both having a ±1 component of the angular momentum along the axis joining the two sites.

The set of parameters that we have used in our calculations are reported in Table I. As it was discussed in Refs. 2 and 3, adopting the usual procedure and determining the parameters by fitting the experimental bulk bands, various sets of parameters can be found, depending on the (possible) constraints used in the best fit. These sets of parameters give bulk bands having a similar accuracy, but the corresponding surface bands can be strongly different. This ambiguity can be avoided by including a few experimental data for the surface states in the best fit. The parameters reported in Table I were obtained by fitting the bulk bands and five surface states of the (110) surface.²⁴ The criteria used in order to choose the five states were very simple. In the band gaps around the \overline{X} and the \overline{Y} points, there are four (Shockley-like) surface bands. The states belonging to these bands and corresponding to the \overline{X} and \overline{Y} points were used in the fit. Furthermore, a fifth point was chosen in order to better describe the band which extends over a large part of the $\overline{\Gamma} \cdot \overline{X}$ direction. It is worthwhile to notice, however, that the particular choice of the surface states used in the fit is not very important: as it was already mentioned in the Introduction, the resulting parameters give results in good agreement with the experimental data for various Cu surfaces, including the (100) clean surface which is of interest in the present paper.

A special discussion is required by the Tamm states. As it is well known, the physical origin of these states is the different potential seen by atoms on the surface with respect to atoms in the bulk. This change in the potential is accounted for, in semiempirical LCAO calculations, by introducing an energy shift of the on-site integrals. Without this energy shift, the Tamm states are not found by semiempirical LCAO calculations. On the Cu surfaces, the Tamm states are localized



FIG. 1. Calculated energy bands along the \overline{X} - \overline{M} line of the Cu(100) surface. Black and gray circles indicate the energy states localized at the surface (see text), which have even and odd symmetries with respect to the \overline{X} - \overline{M} line, respectively. The dots show the energy states of the whole slab. The surface bands indicated by the black and gray circles are named S8–S21 for convenience in the discussion and for consistence with the notations adopted by Baldacchini *et al.* (Ref. 25). Similarly, the notations G1–G7 indicate the major band gaps, which appear in the calculated band map.

just above the *d* bands. In order to find them by using the parameters reported in Table I, it is sufficient to apply a quite small energy shift. This was shown in Ref. 2 for the (110) surface, and it is also true in the (100) case. The use of a small energy shift (0.15 eV in our calculations) does not degrade, and indeed sometimes improves, the good agreement with the experimental data found without energy shift. The changes induced on the surface states by the energy shift will be discussed in detail in the next subsection.

B. Results of the LCAO calculations along \overline{X} - \overline{M}

In the present paper, we will be concerned with the occupied states in the \overline{X} - \overline{M} direction having energies mainly between the Fermi level and -6 eV. The calculated states are reported in Fig. 1. The surface states are emphasized by the black and gray circles accordingly to their symmetry even or odd with respect to the \overline{X} - \overline{M} line, respectively. The number of them depends on the criterion used in order to select the surface states. In our figures, unless otherwise specified, we have represented as surface states or resonances the states whose contribution to the surface density of states (DOS) is greater than their contribution to the DOS of an inner plane by a factor of 10.

There are seven energy gaps, denoted by G1–G7 in Fig. 1, within the considered energy region. The G1 gap is located in the *sp* bands and contains a Shockley surface band (S1) having its bottom just below the Fermi level at \bar{X} . This band was experimentally observed in the $\bar{\Gamma}-\bar{X}$ direction by Kevan⁷

and, more recently, by Baldacchini *et al.*²⁵ These latter authors named this band S1. More generally, they gave names S1–S7 for the experimental bands of surface states on the $\overline{\Gamma}-\overline{X}$ and $\overline{\Gamma}-\overline{M}$ lines. We adopt similar conventions in the present paper, and we use names S8–S21 for the surface states and resonances found on the $\overline{X}-\overline{M}$ line. The calculations also indicate the existence of a surface resonance at the edge of G1. This band, that we named S8, could be the continuation in the $\overline{X}-\overline{M}$ direction of the S2 band observed by Baldacchini *et al.* along the $\overline{\Gamma}-\overline{X}$ line. However, this conclusion cannot be firmly established from the results of our calculations.

The G2 gap is located between the *sp* bands and the *d* bands along \overline{X} - \overline{M} . The famous Tamm state, S4, around \overline{M} is just above the *d* bands in G2.

There is a long gap (called G3) between -2 and -3 eV which contains two bands of surface states, S9 and S10. The S9 and S10 states have odd and even symmetries with respect to the X-M line, respectively, and they are always close to each other. G4 is a very narrow gap around ~ -3.3 eV near the \overline{X} point. In this gap, there is a surface state S15 having odd symmetry. The G5 gap is located around the center of the \overline{X} - \overline{M} line between -3 and -3.5 eV. A surface resonance S13 (even) is found on the lower edge of G5. The gap G6 is somewhat large and located around -4 eV. It contains two bands of surface states with the odd symmetry, S17 and S18. G7 is a large gap located below -4 eV which extends beyond the \overline{X} point. There are two bands in this gap, S20 (even) and S21 (odd), in the middle and on the lower edge of G7, respectively. The S20 states are probably the continuation along \overline{X} - \overline{M} of the S7 band reported in Refs. 8 and 25.

Apart from these surface states and resonances in the band gaps and on their edges, there are some surface resonances in the projection of the bulk *d* bands: S11 (even), S12 (even), S14 (odd), S16 (even), and S19 (odd). The S11 band seems to cover the whole $\overline{X}-\overline{M}$ line intermittently.

The surface states mentioned above are, in general, insensitive to the precise value of the energy shift used in order to take into account the additional potential due to the surface. While an energy shift of 0.15 eV displaces the Tamm state at the \overline{M} point+0.15 eV toward the Fermi level, this is not the case of the other states. For example, S20 (in G7) is shifted by $\Delta E \sim +0.06$ eV and S18, in the G6 gap, by $\Delta E \sim +0.04$ eV. A particular case is given by S13. Without energy shift, the G5 gap is crossed by the S11 band, which gives rise to a surface band approximately in the middle of the gap. The energy shift pushes the S11 band out of the gap toward the Fermi level, and the S13 resonance appears on the lower edge of the gap.

We have tried to check these calculation results by the first ARUPS measurements along \overline{X} - \overline{M} .

III. EXPERIMENTAL DETAILS

The (100) surface of a Cu single crystal was cleaned by Ar⁺-ion bombardment and 600 °C annealing cycles. Its order

and cleanliness were checked by a sharp 1×1 low-energy electron diffraction pattern and x-ray photoelectron spectroscopy. For ARUPS, we used a Scienta SES100 analyzer. The sample was kept at 130 K during the measurements. Nonpolarized He *i* radiation (SPECS UVS300) was used as an ultraviolet photon source. The photoelectron was detected in the light incidence plane. ARUPS spectra were taken along $\overline{X} \cdot \overline{M}$. We scanned both the polar angle θ with respect to the surface normal and the azimuth angle ϕ with respect to the [110] direction simultaneously (see the inset in Fig. 2). The angle set (θ , ϕ) depends on the focused binding-energy region. We used two angle sets for the binding energies around -4 eV and additionally around -2.5 eV. The base pressure of the analyzer chamber was less than 1×10^{-10} Torr.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the ARUPS spectra taken by changing both the polar and azimuth angles (θ and ϕ , respectively) around the surface normal. The values of these angles were chosen in order to optimize the detection of the bands around -4 eV on the \overline{X} - \overline{M} line. However, the observed energy levels were not sensitive to the focusing binding energy because of the little dispersion of the d band across the \overline{X} - \overline{M} line. The typical intense peaks due to the Cu 3d bands can be seen in the figure within the -2 to -5 eV binding-energy region. As will be discussed later, a few of these peaks can be ascribed to surface states and resonances by comparison with the calculated results. We have indicated these latter peaks by dotted lines in Fig. 2. Figure 3 shows the magnifications of the ARUPS spectra around S20 (A), S17 and S18 (B), and S9 and S10 (C). In Fig. 3, they appear as weak and quite broad peaks. It can be noticed that S9 and S10 seem to be connected, at the \overline{M} point (ϕ =45°), to the band called S5 by Baldacchini et al.

Figure 4 shows ARUPS spectra focused around the Xpoint just below the Fermi level. The acquisition step of the binding-energy sweep was set to 5 meV to collect these spectra. Peaks near the Fermi level, showing an approximately parabolic dispersion, were found around the detection angle $\theta = 36^{\circ}$. These peaks correspond to the bottom of the Shockley band⁷ whose binding energy, in our experiment, was found to be ~ -60 meV. Using in the measurements an acquisition energy step of 20 meV, as we have done in order to collect the spectra reported in Fig. 2, the Shockley band is invisible. A rapid increase of intensity around ~ -0.35 eV below the Shockley state represents the beginning of the bulk band projections. As the edge intensity of this precipicelike feature decreases when the surface is covered by nitrogen atoms (not shown here, see Ref. 26), we believe that there is at least one surface resonance at the edge of these bulk band projections.

The peak positions observed in Figs. 2–4 are displayed in Fig. 5 together with the calculated surface states and resonances reported in Fig. 1. Open circles indicate the experimental results. It can be seen that the agreement is quantitatively good for most surface states and resonances: this is the case for S4 (Tamm state), S9 and S10 in G3, S15 in G4, S18



FIG. 2. ARUPS spectra corresponding to the \overline{X} - \overline{M} line of the Cu(100) surface in the bindingenergy region of -6-0 eV. The inset shows the definition of the photoelectron detection angles θ and ϕ . The correspondence between the Brillouin zone and the crystallographic directions are also shown in the inset. The dotted lines indicate the observed peaks corresponding to the calculated surface states.

in G6, S20 and S21 in G7, and for the resonances S11, S12, and S14. In detailed measurements focused around -2.5 eV with a smaller acquisition energy step [Fig. 3(c)], we were able to distinguish individual peaks corresponding to the S9 and S10 states, while in Fig. 2 they appear as a single broad peak due to the insufficient acquisition energy step. The calculated S20 band starts from the \overline{X} point and continues to



FIG. 3. The magnifications of ARUPS spectra around S20 (a), S17 and S18 (b), and S9 and S10 (c), which are invisible in Fig. 2 due to the weak intensities. The triangles indicate the peaks assigned to S9, S10, S17, S18, and S20. We note that the binding-energy ranges are different in each panel. The angle set (θ, ϕ) in (C) is optimized to the binding energy around -2.5 eV.

approximately the middle of \overline{X} - \overline{M} , whereas we could not observe this band near \overline{X} . Kevan *et al.*⁸ showed that this state has a large cross section for higher photon energy by using synchrotron radiation. Larger photon energy will probably allow us to observe S20 as stronger peaks.

On the other hand, we could not observe in a clear way the surface resonances S13, S16, and S19 because of the



FIG. 4. The ARUPS spectra in the vicinity of the Fermi level around the \overline{X} point of the Cu(100) surface. The peaks showing parabolic dispersion is attributed the bottom of the Shockley state (S1). The precipicelike feature around ~-0.35 eV is assigned to a surface resonance (S8).



FIG. 5. Energy bands determined by ARUPS (open circles) and calculations (black: even symmetry; gray: symmetry) are compared along the \overline{X} - \overline{M} line of the Cu(100) surface. In the experimental bands, all the distinct peaks including bulk's ones are shown.

strong signals originating from the bulk states. As it can be seen in the spectra (Fig. 2), there are always intense peaks in the energy region where these resonances are located. Finally, the broad tail toward smaller binding energies of the S18 peak might indicate the presence of the S17 state in G6, though we did not show it explicitly in Fig. 2. The peaks assigned to the parts of S17 and S18 are reported in Fig. 3(b).

One important advantage of the LCAO method is that it gives realistic k-resolved planar density of states (k-DOS). Although the latter is not directly accessible by photoemission experiments, the main features of the ARUPS spectra can be understood by comparing the observed intensities and an effective k-DOS deduced from the calculated ones. In order to perform a meaningful comparison, we have to take into account the fact that the various planes give a contribution to the photoelectron current which decreases quickly with the depth of the plane within the slab. The effective k-DOS is consequently assumed to be a weighted summation of the planar k-DOS. In the present paper, the weights are set to 100% for the first layer, 50% for the second, 25% for the third, and 15% for the bulk layer. In general, the contribution to the photoemission intensity coming from the various planes decreases exponentially in function of the depth of the plane under the surface. This is expressed by the relation I $=I_l \exp(-l/d)$, where l is the layer number counted from the surface, I_l is the planar k-DOS of the *l*th layer, and *d* is the effective escape depth. Here, d is a unique adjustable parameter. In general, this parameter depends on the various experimental settings such as the photon energy, the photoemission angle, etc. The adopted weights correspond to d ~ 1.5 (layers).

In Fig. 6, we compare the ARUPS spectra and the effective *k*-DOS obtained by our LCAO calculations at the two highly symmetrical points \overline{X} and \overline{M} . The solid lines show the



FIG. 6. The ARUPS spectra (solid line) and the calculated effective *k*-DOS (topmost dotted lines) around the \overline{X} point (left panel) and the \overline{M} point (right panel). The contributions of the first, second, third, and bulk layers to the effective *k*-DOS (see text) are also displayed. The solid line drawn together with the contribution of the first layer (at \overline{X} , left panel) shows as the latter should be modified in order to take into account the different cross sections of 4*s*, 4*p*, and 3*d* electrons. The notations such as S1 indicate the features assigned to surface states or resonances in Fig. 5.

ARUPS spectra, and the dotted lines represent the effective k-DOS (top curves) and the contributions to them coming from the first, second, third, and bulk layers.

We can see that the effective k-DOS reproduce well the experimental spectra at both the \overline{X} and \overline{M} points. This means that our assumption $d \sim 1.5$ was reasonable. The peaks corresponding to the S8 and S1 states are very large in the calculated effective k-DOS, while the features that indicate the presence of these states in the experimental spectrum are quite small. This discrepancy can be understood, at least in part, by taking into account the cross section of each state for a given photon energy. According to the literature, the cross section of the Cu 4s and 4p states for the He I α radiation is 0.47% of the cross section of the Cu 3d states.²⁷ In order to take into account this difference, the contributions of the 4s, 4p, and 3d states to the planar k-DOS should be weighted. This has been done for the first layer, and the result is shown in the figure (solid line) together with the original planar k-DOS. It can be seen that the peaks indicating S8 and especially S1 are considerably smaller, consistent with the experimental observations. Similarly, the intensity of S20 is also decreased by taking into account the cross-section difference. The strong hybridization with the 4sp states can thus explain the weak intensity of S20 in the experiments.

A further discrepancy between the calculated effective *k*-DOS and the experimental spectra is the peak indicating S19 at \overline{M} . The influence of the cross-section difference is, in this case, negligible and cannot explain why S19 is invisible by He I radiation. Nevertheless, various other factors may be



FIG. 7. Band mapping of the surface states and resonances, which are selected by the criterion factors of 100 (full circles) and 10 (open circles), along the \bar{X} - \bar{M} line of the Cu(100) surface.

the cause of this discrepancy. For example, (1) the broadening due to the lifetime of the photoexcited hole, (2) the density of states of the unoccupied band to which the photoelectron is excited, or (3) the photon incidence angle which is related to the selection rules due to the symmetry of the wave functions. One of these factors might explain the negligible experimental intensity of S19, but a full discussion of this aspect is beyond the purpose of the present paper.

Finally, we consider the extension of the surface states and resonances perpendicularly to the surface. Figure 7 shows the calculated bands of surface states and resonances obtained by using two different threshold values in the selection criterion. The filled circles indicate the states selected when the threshold is fixed to 100. The open circles indicate the additional states, which are found when the threshold is lowered to 10 (the value adopted in the present paper). In general, the contribution to the planar *k*-DOS of a given surface state or resonance has a maximum near the surface and decreases continuously when the plane becomes deeper. Let us assume that the decreasing follows an exponential law, $I_l=I_1 \exp(-l/t_s)$, where I_l and I_1 are the contributions to the planar *k*-DOS of the *l*th layer and of the topmost layer, re-

spectively. Then, t_s can be considered a measure of the extension of a given surface state or resonance within the bulk. In our calculations, we have considered surface states or resonances the states for which I_1/I_{bulk} is greater than the chosen threshold. As the slab contains 97 planes, we have defined I_{bulk} by the average of I_{46} , I_{47} , and I_{48} . Thus, the criterion factor is $I_1/I_{bulk} \sim I_1/I_{47}$.²⁸ In this scheme, the of use a threshold equal to 10 means to select states which penetrate into the bulk of ~ 20 layers or less, while fixing the threshold to 100, one selects states for which $t_s \sim 10.2$ layers (or less). In Fig. 7, it can be seen that most bands discussed in the present paper satisfy the selection criterion also if the more striking value of 100 is used for the threshold (indeed one can also use greater values, 1000, for example, without changing significantly the results). The states selected by a threshold equal to 10 play a role in order to just improve the continuity of the bands and to detect some resonances. The analysis reported above is coherent with our experience in this kind of calculations: if the results obtained by using slabs including ~ 20 planes can give a first idea of the localization of the surface states, the use of thicker slabs is highly recommended, in particular, if one is interested not only in the surface states but also in the resonances.

V. CONCLUSIONS

We have performed LCAO calculations based on a recently proposed set of Slater-Koster parameters. The calculated surface bands are in full agreement with the photoemission and inverse-photoemission data reported in the literature for the Cu(100) surface.

The calculations have predicted the existence of many unknown surface and resonance states on the \overline{X} - \overline{M} line. We have made ARUPS measurements along this line, and we have found a quantitatively good agreement between experimental and theoretical band dispersions, as well as between the spectral features observed by ARUPS and the calculated effective *k*-DOS.

The present study confirms the reliability of the parameter set for LCAO calculations and provides experimental evidence of several surface states and resonances. LCAO calculations based on this parameter set will provide a reliable basis for understanding the future experimental results on the various Cu surfaces.

- *Corresponding author. Present address: Institute of Industrial Science, University of Tokyo, Komaba 4-6-1, Meguroku, Tokyo 153-8505, Japan. Electronic address: sekiba@iis.u-tokyo.ac.jp †Electronic address: cortona@spms.ecp.fr
- ¹J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).
- ²P. Cortona and C. Sapet, Surf. Sci. **532-535**, 19 (2003).
- ³P. Cortona and C. Sapet, Int. J. Quantum Chem. 99, 713 (2004).
- ⁴S. L. Hulbert, P. D. Johnson, M. Weinert, and R. F. Garrett, Phys. Rev. B **33**, 760 (1986).
- ⁵P. Heimann, J. Hermanson, H. Miosga, and H. Neddermeyer, Phys. Rev. Lett. **42**, 1782 (1979).

- ⁶S. D. Kevan and D. A. Shirley, Phys. Rev. B 22, 542 (1980).
- ⁷S. D. Kevan, Phys. Rev. B **28**, 2268 (1983).
- ⁸S. D. Kevan, N. G. Stoffel, and N. V. Smith, Phys. Rev. B **31**, 3348 (1985).
- ⁹S. C. Wu, C. K. C. Lok, J. Sokolov, J. Quinn, Y. S. Li, D. Tian, and F. Jona, Phys. Rev. B **39**, 13218 (1989).
- ¹⁰ V. Dose, U. Kolac, G. Borstel, and G. Thorner, Phys. Rev. B 29, 7030 (1984).
- ¹¹W. Jacob, V. Dose, U. Kolac, Th. Fauster, and A. Goldmann, Z. Phys. B: Condens. Matter **63**, 459 (1986).
- ¹²S. Kevan, Phys. Rev. B 28, 4822 (1983).

- ¹³R. A. Bartynski and T. Gustafsson, Phys. Rev. B **33**, 6588 (1986).
- ¹⁴R. A. Bartynski, T. Gustafsson, and P. Soven, Phys. Rev. B **31**, 4745 (1985).
- ¹⁵B. Cord, R. Courths, and H. Wern, Phys. Rev. B **31**, 1164 (1985).
- ¹⁶B. Reihl and K. H. Frank, Phys. Rev. B **31**, 8282 (1985).
- ¹⁷S. D. Kevan, Phys. Rev. Lett. **50**, 526 (1983).
- ¹⁸S. L. Hulbert, P. D. Johnson, N. G. Stoffel, W. A. Royer, and N. V. Smith, Phys. Rev. B **31**, 6815 (1985).
- ¹⁹P. Heimann, J. Hermanson, H. Miosga, and H. Neddermeyer, Phys. Rev. B **20**, 3059 (1979).
- ²⁰P. Cortona and C. Sapet, Surf. Sci. **566-568**, 1102 (2004).
- ²¹P. Cortona and C. Sapet, Surf. Sci. **585**, 155 (2005).
- ²²R. Courths, S. Hufner, P. Kemkes, and G. Wiesen, Surf. Sci. 376, 43 (1997), and references within.
- ²³R. Ozawa, A. Yamane, K. Morikawa, M. Ohwada, K. Suzuki, and H. Fukutani, Surf. Sci. **346**, 237 (1996).
- ²⁴We have used the three states at the \overline{Y} point having energies of -4.72, -0.39, and 2.00 eV and two states belonging to the band which extends in the $\overline{\Gamma} \overline{X}$ direction between 5 and 6 eV. More

precisely, the first of these two states was the one having an energy of 5.40 eV at \overline{X} . The second one was chosen at 6/10 of the $\overline{\Gamma} - \overline{X}$ direction and its energy was 5.84 eV.

- ²⁵C. Baldacchini, L. Chiodo, F. Allegretti, C. Mariani, M. G. Betti, P. Monachesi, and R. Del Sole, Phys. Rev. B 68, 195109 (2003).
- ²⁶D. Sekiba, Y. Yoshimoto, K. Nakatsuji, Y. Takagi, T. Iimori, S. Doi, and F. Komori (unpublished).
- ²⁷J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 1985.
- ²⁸ It is noteworthy that the surface states and the resonances are selected on the basis of their contribution to the planar DOS of the *first* layer. In some cases, this contribution can be too small in order to select a given state, while it would be sufficiently large if we had used the second layer instead of the first. This situation does not arrive frequently but, in the present study, we have an example given by S5 at the \overline{M} point. This state is clearly visible in the experimental spectra and in the effective *k*-DOS reported in Fig. 6, while it does not appear as a calculated resonance in Figs. 1 and 5.