PHYSICAL REVIEW B, VOLUME 63, 195110

From the Shockley surface state on Cu(111) to *sp*-like surface resonances on $Cu_3Au(111)$

R. Courths,[1] M. Lau,[1] T Scheunemann,[2] H. Gollisch,[2] and R. Feder[2]
[1]*Laboratorium für Festkörperphysik and*
[2]*Theoretische Festkörperphysik Universität Duisburg, D-47048 Duisburg, Germany*

(Received 9 August 2000; revised manuscript received 7 November 2000; published 30 April 2001)

In an angle-resolved ultraviolet photoemission spectroscopy study on ordered $Cu_3Au(111)$ we have observed two *sp*-like surface resonances at 0.4 and 1.0 eV below the Fermi energy around the center of the surface Brillouin zone. Bulk and slab charge densities were calculated self-consistently by a full-potential linearized augmented plane method and employed to construct—via a nonlocal density approximation to exchange and correlation—a real part of the effective one-electron potential, which we subsequently used in relativistic layer Korringa-Kohn-Rostoker calculations to obtain the quasiparticle bulk-band structure, the $k_\parallel$- and layer-resolved density of states and photoemission spectra. For Cu(111), we thus obtained the Shockley surface state and its dispersion in good agreement with experimental data. For $Cu_3Au(111)$, we retrieved our two measured surface features and their dispersions with $k_\parallel$. The feature at 0.4 eV, which corresponds to the Shockley state on Cu(111), is substantially broadened due to hybridization with bulk states. The feature at 1.0 eV, although also degenerate with a bulk band, is comparatively sharp because of different symmetry types.

DOI: 10.1103/PhysRevB.63.195110 PACS number(s): 71.20.−b, 73.20.At, 79.60.−i

I. INTRODUCTION

It is well established that on the (111) surfaces of all three noble metals Cu, Ag, and Au a *sp*-derived surface state (SS), which is commonly referred to as a *Shockley* SS, exists around the center $\bar{\Gamma}$ of the surface Brillouin zone (SBZ) some tenth eV below the Fermi energy.[1] This SS has been extensively studied experimentally by means of angle-resolved photoelectron spectroscopy (ARUPS). To our knowledge, on Cu(111) it was first observed by Gartland and Slagsvold[2] in 1975 and on Au(111) by Heimann *et al.*[3] in 1977. It has served as a prototype for the observation of a variety of phenomena such as two-dimensional surface band structure,[4–8] orbital symmetry[9–11] and photon energy dependence of the photoionization cross section,[9–11,1,12] lifetime effects,[4,5,7,13–15] temperature-induced energy shifts,[16,17] influence of surface morphology[18] and spin-splitting induced by spin-orbit interaction.[8] Properties of Shockley-type surface-state electrons, which form a (quasi-) two-dimensional electron gas have also been studied with scanning tunneling microscopy (STM) by observation of standing surface wave patterns formed in the vicinity of defects such as adsorbates and steps. With STM, dispersion relations of the surface electrons above E_F have been measured recently, too (cf. Ref. 19 and STM-references therein).

The Shockley SS on the noble metal (111) surfaces lies entirely within a gap , which interrupts the bulk *sp*-band near E_F for $\mathbf{k}$ in a region around the Γ-Λ-L line. It is thus a true surface state. On the (111) surface of the ordered alloy Cu_3Au, a low-binding-energy surface state near E_F has been observed by Jordan and Sohal[20] and Lau *et al.*,[21] and its similarity to the Shockley-type state on the noble metal surfaces has been suggested. Its existence on $Cu_3Au(111)$ is surprising because the bulk band structure[21] does *not* show an energy gap in the upper *sp*-like bands near E_F around the bulk Γ-Λ-R line in $\mathbf{k}$ space ([111] direction), which projects onto the center of the SBZ. These facts have motivated us to perform a detailed study—both experimentally using ARUPS *and* theoretically by electronic structure and photoemission calculations—of the surface electronic structure of $Cu_3Au(111)$ in the region of the upper occupied bands. In addition to the expected surface feature at 0.4 eV below E_F, our work revealed a hitherto unknown surface resonance at 1.0 eV. Analogous calculations were performed for Cu(111) with the main purpose of providing a deeper understanding of our $Cu_3Au(111)$ results.

In order to facilitate the presentation and discussion of our results, we show in Fig. 1 a top view of the atomic and

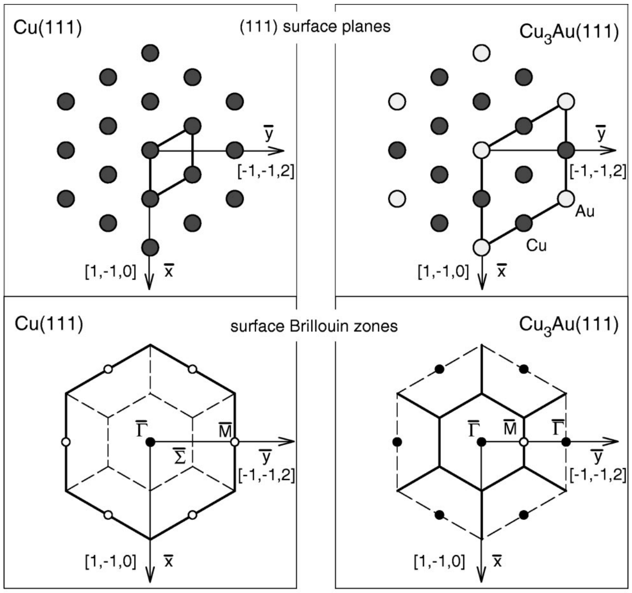

FIG. 1. Top view of the (111) surfaces of Cu (left-hand panels) and Cu_3Au (right-hand panels) in real and reciprocal space (upper and lower panels, respectively), with scales such that the interatomic distances appear the same. The dashed lines indicate the surface Brillouin zones of Cu_3Au in the Cu zone scheme and *vice versa.*

0163-1829/2001/63(19)/195110(8)/$20.00

geometric structure of the (111) surfaces of Cu and Cu_3Au together with the corresponding surface Brillouin zones. The transition from Cu to Cu_3Au is—with scaling to the same interatomic distance—characterized by a doubling of the real space cell and the corresponding reduction of the SBZ.

II. EXPERIMENTAL METHOD

The experiments were performed with an ESCALAB photoelectron spectrometer from Vacuum Generators and ArI ($h\nu = 11.83$ eV), NeI (16.85 eV) and HeI (21.22 eV) resonance radiation. The photon energies given in parentheses correspond to the main lines, which are accompanied by weaker radiation satellites (ArI: 11.62 eV, NeI: 11.67 eV, HeI: 23.09 eV), which also contribute to the photoelectron spectra. Because of the small photon energy differences between main and satellite lines, the spectral ''contaminations'' by the satellites can approximatively be eliminated by subtracting from the raw spectrum a raw spectrum shifted by the photon energy difference and multiplied by the relative satellite radiation intensity I_s with respect to the main line intensity: $N_{corr}(E) = N_{raw}(E) - I_s N_{raw}[E - \delta(h\nu)]$. This satellite correction is not perfect and may cause some weak artificial structures in the corrected spectrum. All spectra shown in this paper are satellite corrected. The electrons were collected around the surface normal in the $(\bar{1},\bar{1},0)$ or $\bar{y}z$ mirror plane of $Cu_3Au(111)$ cutting the surface along the $\bar{\Sigma}$ line of the surface Brillouin zone (SBZ) (see Fig. 1). The exciting light was also incident in this plane. The angle between light incidence direction (polar angle ϑ_{ph} with respect to the surface normal) and the electron detection direction (polar angle ϑ_e) is fixed to $\vartheta_{ph} + \vartheta_e = 38°$. The radiation was used as unpolarized or $p(\bar{y}z)$- or $s(\bar{x})$-polarized light (with $\cong$90% degree of polarization). In our experiments, where ϑ_e was only slightly varied ($-10° \leqslant \vartheta_e \leqslant +10°$), the z and $\bar{y}$ components of the electric field vector of the p light have comparable weight. Only even final states contribute to the photocurrent in a mirror plane and $p(\bar{y}z)/s(\bar{x})$ polarized light thus detects even/odd initial states. The full angular and energy resolutions were about 3° and 80 meV, respectively.

The single crystal of ordered $Cu_3Au(111)$ was cleaned *in situ* by repeated cycles of Ar^+ ion bombardment ($\cong$500 eV beam energy) and subsequent annealing up to 640 K (below the phase transition temperature of 663 K) for several hours. This procedure was repeated until sharp low-energy electron diffraction (LEED) spots indicated a well-ordered surface at room temperature. The intensity and the energetic position of the surface-state emissions to be reported below were also used to check the quality and the orientation of the surface with respect to the analyzer. In order to investigate the surface sensitivity of spectral features, the clean surface was exposed to oxygen. The chemical cleanliness of the surface was checked by means of x-ray excited core-level spectra. In addition, the anisotropy in polar-scanned core-level emissions from copper and gold was used to check the quality of the structural order of the surface.

As for the stoichometry of the surface, we first note that deviations from that of the ideal bulk termination generally affect the energy position and dispersion and even the existence of surface states and resonances. Since the two measured surface-state features are in very good agreement with their theoretical counterparts calculated for a bulklike surface stoichometry, it is very likely that the experimental surface has not been altered stoichiometrically to a significant degree. This is in line with results from Auger spectroscopy,[22] Rutherford backscattering,[24] and reflection high-energy electron diffraction,[23,24] according to which the chemical composition of the surface layer is practically the same as that of the bulk layers. As is cited in a review article on binary-alloy surfaces,[25] an early experimental study[26] however reported a significant Au enrichment at the surface. The available evidence is thus strongly weighted in favor of a bulklike surface composition. In order to settle the issue in a quantitative way, it seems desirable to apply a scanning probe technique (e.g., STM), which would yield a direct image of the surface on an atomic scale.

III. THEORETICAL APPROACH

To calculate the bulk band structures of Cu and of Cu_3Au (for the experimental lattice constants), we employed — in the framework of density functional theory (DFT) — a relativistic self-consistent full-potential linearized augmented plane (FLAPW) method,[27] with the exchange-correlation potential in a local-density approximation (LDA).[29] These band structures are almost indistinguishable from the ones we obtained by using a generalized gradient approximation (GGA),[28] in line with what was found in calculations for Cu by Strocov *et al.*[30]

As a basis for our surface electronic structure and photoemission calculations, we performed self-consistent FLAPW (Ref. 27) supercell calculations with five-layer slabs separated by four vacuum layers. For the distance between the layers we took the bulk interlayer spacing, since surface relaxations on the close-packed (111) surfaces should be negligible. For Cu(111), this is substantiated by LEED analyses.

The thus obtained one-electron potentials are, however, not adequate for photoemission purposes. As will be shown below (cf. Fig. 2), the bulk d bands are about 0.5 eV higher in energy than their experimental counterparts, whereas the sp-like bands are in fairly good agreement. As is well known, there are two sources for this kind of discrepancy: approximations (like LDA or GGA) to the ground-state exchange-correlation energy and the neglect of quasiparticle self-energy corrections. Since a fundamental approach using many-body techniques is presently not yet practicable, one has to resort to introducing corrections to be determined by comparison with experimental energy bands. The simplest and most commonly used type of such correction is a constant shift of the potential (which leads to a constant shift of the calculated bands). In our cases of Cu and Cu3Au, this is however not sufficient, since the DFT sp-bands are already close to experiment and the d bands are about 0.5 eV higher, with intermediate deviations of strong sp-d hybrids. In the following, we put forward a scheme that reproduces the ex-

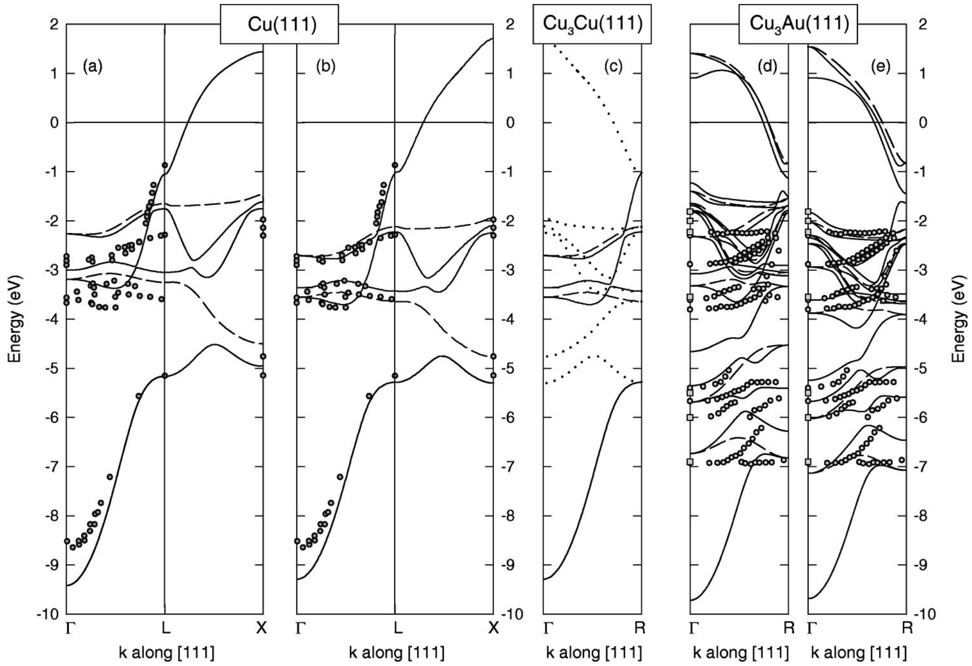

FIG. 2. Bulk band structure $E(k_\parallel, k_z)$ (a) of Cu with k_z along the the (111) direction and $k_\parallel$ corresponding to the $\bar{\Gamma}$ (for ΓL) and $\bar{M}_{\mathrm{Cu}}$ (for LX) points of the surface Brillouin zone (cf. Fig. 1), self-consistently calculated with FLAPW method (Ref. 27) using a local-density approximation (LDA) for the exchange-correlation potential V_{xc}. The solid and the dashed lines correspond to the double group symmetry types Λ_6 and Λ_{45}, respectively. The open circles represent experimental photoemission data (Ref. 36). (b) as (a), but calculated with layer-KKR method using the effective potential V^{eff} [Eq. (5)] with $\beta = 0.05$. (c) Bulk bands of Cu$_3$Cu along (111) with $k_\parallel = 0$ ($\bar{\Gamma}$ point of the SBZ) calculated with V^{eff} [as in (b)]. The solid and dashed lines indicate symmetry types Λ_6 and Λ_{45}, respectively. The dotted lines in the central panel represent the bands ''back-folded'' from the LX part of the left-hand panel. These bands are degenerate having both Λ_6 and Λ_{45} wave functions. (d) Bulk bands of Cu$_3$Au along (111) with $k_\parallel = 0$ of double group symmetry types Λ_6 (solid lines) and Λ_{45} (dashed lines) calculated by FLAPW-LDA [as in panel (a) for Cu(111)], together with experimental photoemission data (circles (Ref. 21), squares (Ref. 41)). (e) as (d) but calculated with V^{eff} [Eq. (5)].

perimental energy bands with the aid of a single adjustable parameter.

Starting from our self-consistent FLAPW-LDA charge densities $\rho(\mathbf{r})$, we construct a one-electron potential V', which in addition to the usual electrostatic parts, involves a nonlocal density approximation (NLDA) exchange-correlation potential

$$V_{xc}(\mathbf{r}) = -\int \left(\frac{\rho(\mathbf{r}')f(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2}\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\frac{\delta f(\mathbf{r},\mathbf{r}')}{\delta \rho(\mathbf{r})} \right) d^3r', \tag{1}$$

where the hole function $f(\mathbf{r},\mathbf{r}')$ is related to the average pair correlation function $g(\mathbf{r},\mathbf{r}')$ by

$$f(\mathbf{r},\mathbf{r}') = 1 - g(\mathbf{r},\mathbf{r}'), \tag{2}$$

and obeys the sum rule

$$\int \rho(\mathbf{r}')f(\mathbf{r},\mathbf{r}')d^3r' = \frac{1}{2}. \tag{3}$$

A derivation and discussion of Eq. (1) as well as ample references to the original literature may be found in the monograph by Dreizler and Gross (1990).[31] In view of practical application, we approximate the hole function by a Gaussian:

$$f(\mathbf{r},\mathbf{r}') = e^{-\lambda(\mathbf{r})|\mathbf{r}-\mathbf{r}'|^2}, \tag{4}$$

where the function $\lambda(\mathbf{r})$ is determined by the sum rule Eq. (3). This form permits a straightforward evaluation of the derivative in the second term of V_{xc}.

The potential V' constructed in the above way yields d bands, which are much lower than the experimental ones. We therefore mix it with the density functional theory (DFT) FLAPW self-consistent potential $V^{DFT\text{-}LDA}$ to obtain an effective potential

$$V^{eff} = (1-\beta)V^{DFT\text{-}LDA} + \beta V'. \tag{5}$$

The resulting d bands are lowered relative to the sp bands by an amount depending on the value of the mixing parameter β. We choose the latter such that the bulk energy bands get closest to their counterparts from our photoemission experiments. The relative lowering of the d bands can be understood by inspecting in detail the radial dependence of the sp- and d-like wave functions.

Subsequently, we use the same procedure to construct from the FLAPW results for the slab (the central layer of which is practically a bulk layer) a layer-dependent potential for the semi-infinite crystal, which we employ in our relativistic layer-KKR code[32] to calculate layer-resolved densities of states and photoemission spectra.

Regarding the surface potential barrier, we first note that the LDA entails the absence of the asymptotic image behavior. Our NLDA scheme in principle produces the latter, but since we have not implemented it in a self-consistency cycle, the overall shape of the barrier cannot be expected to be realistic. We therefore employ in the present study a one-dimensional model form $V(z)$,[33] which provides a smooth transition from the asymptotic image potential to the uniform inner potential V_0 by means of a third-order polynomial in z. The coefficients are chosen such as to reproduce the experimental energy position of the 0.4 eV Shockley surface feature at $k_\parallel = 0$. The second surface feature, which we find for Cu_3Au experimentally at 1.0 eV, is then automatically reproduced at this energy.

The finite lifetimes of the hole and of the photoelectron are taken into account by means of uniform imaginary potential parts. In view of making contact with experimental photoemission data taken at room temperature, we choose for the occupied states a constant value $V_{i1} = -0.025$ eV. For the sp surface state on Cu(111), this implies a natural width full width at half maximum $2|V_{i1}| = 0.05$ eV, which corresponds to the experimentally observed value.[4,7,13] We note that most of this surface-state width arises from phonon contributions with the electron-electron scattering contribution being much smaller. A similar vibration-induced hole lifetime broadening was found in the d-band region of Cu in a theoretical study, in which correlated ion-core displacement configurations were employed on the basis of the adiabatic approximation.[34]

For the unoccupied states of energy E_2 relative to the vacuum level E_{vac}, we use the form $V_{i2} = -2.5/(1 + \exp[-(E_2 - 22.61)/6.78]) + 0.49$ eV which is suggested by LEED experience (cf. Ref. 35, Chapt. 4). For the kinetic energies E_2 from E_{vac} to about 15 eV, which are reached in our present photoemission study, the values of this V_{i2} range from -0.5 to -1.0 eV.

IV. RESULTS AND DISCUSSION

For both Cu(111) and $Cu_3Au(111)$, we first present and discuss calculated bulk band structures and layer-resolved densities of the semi-infinite system. Then we show experimental and calculated photoemission spectra, from which we obtain the dispersion relations of the sp surface-state features.

A. Calculated electronic structure

In Fig. 2 we show occupied bulk energy band structures for Cu(111) and $Cu_3Au(111)$, which we obtained along the lines presented in Sec. 3. The Cu(111) bands, which we obtained by self-consistent DFT-FLAPW (Ref. 27) calculations using an LDA (Ref. 29) for V_{xc}, are presented in panel (a). They are practically identical with the bands from our layer-KKR method using the self-consistent FLAPW potential cast into the muffin-tin form. Comparing them with the bands determined experimentally by photoemission (cf. Ref. 36 and references therein), we mainly notice that the calculated d bands are about 0.5 eV higher in energy than their experimental counterparts. The same displacement was found in a recent calculation,[30] which employed the same FLAPW method, as well as in self-consistent calculations by a full-potential linear muffin-tin orbital LMTO method[37] and by a full-potential KKR method.[38,39]

In contrast, an earlier self-consistent DFT-LDA calculation,[40] in which the Kohn-Sham equations were solved by a ''linearized rigorous cellular method,'' produced Cu bands that agree remarkably well with the experimental data given in Ref. 36 (see also Ref. 41). Since this calculation employed the same specific form of LDA,[29] the prescription for constructing the Kohn-Sham single-particle potential was exactly the same as used in several of the calculations by the other groups. The differences in the results must therefore be due either to the different way of solving the single-particle equations or to the implementation of the self-consistency process, i.e., to purely technical reasons. These technical aspects were handled in three different ways in the recent calculations. Since the latter agree so well with each other, it seems much more likely that they are technically correct rather than the earlier calculation. This conclusion is supported by the fact that the work of Ref. 40 was done with the (far weaker) computing facilities available in 1984. It is therefore most likely that the earlier calculation[40] has been stricken by some error or source of inaccuracy.

Panel (b) of Fig. 2 shows the Cu(111) bulk bands, which we obtained from our potential V^{eff} [Eq. (5)], with the mixing parameter β [cf. Eq. (5)] chosen as 0.05. While the upper part of the sp band is almost the same as in the FLAPW-LDA band structure, which was already compatible with experiment, the d bands are seen to be lowered in energy such that nearly perfect agreement with the experimentally obtained quasiparticle bands is reached.

To elucidate the origin of the band manifold of Cu_3Au along Γ-Λ-R (right panel) from the corresponding bands of Cu along Γ-Λ-L and L-X, we show in Fig. 2(c) the ''intermediary'' band structure of Cu_3Cu. In the latter, the original Cu bands along L-X are seen to be backfolded onto the Γ-R direction (dotted lines). These backfolded energy bands are degenerate and the corresponding wave functions are in general linear combinations of Λ_6 and Λ_{45} symmetry wave functions. Replacement of one Cu atom by an Au atom lifts this degeneracy and produces the Λ_6 and Λ_{45} bands in the right-hand panel.

For Cu_3Au, we first point out [cf. Fig. 2(d)] that the FLAPW-LDA Cu-like d-bands lie about 0.2 eV higher in energy than those from our earlier self-consistent LMTO calculation.[21] In search for reasons of this shift, we note that the FLAPW calculations are of a genuinely full potential nature, while the LMTO calculations were carried out within the atomic sphere approximation. The experimental d-bands were found to lie about 0.3 eV below the LMTO-calculated ones for both $Cu_3Au(111)$ (Ref. 21) and $Cu_3Au(001)$.[42] The FLAPW-LDA bands are thus about 0.5 eV higher in energy than the experimental ones, just like for pure Cu. This is again remedied in the band structure, which we calculated from the potential V_{eff} [Eq. (5)] with the same value 0.05 of the mixing parameter β [see Fig. 2(e)]. In the region of the

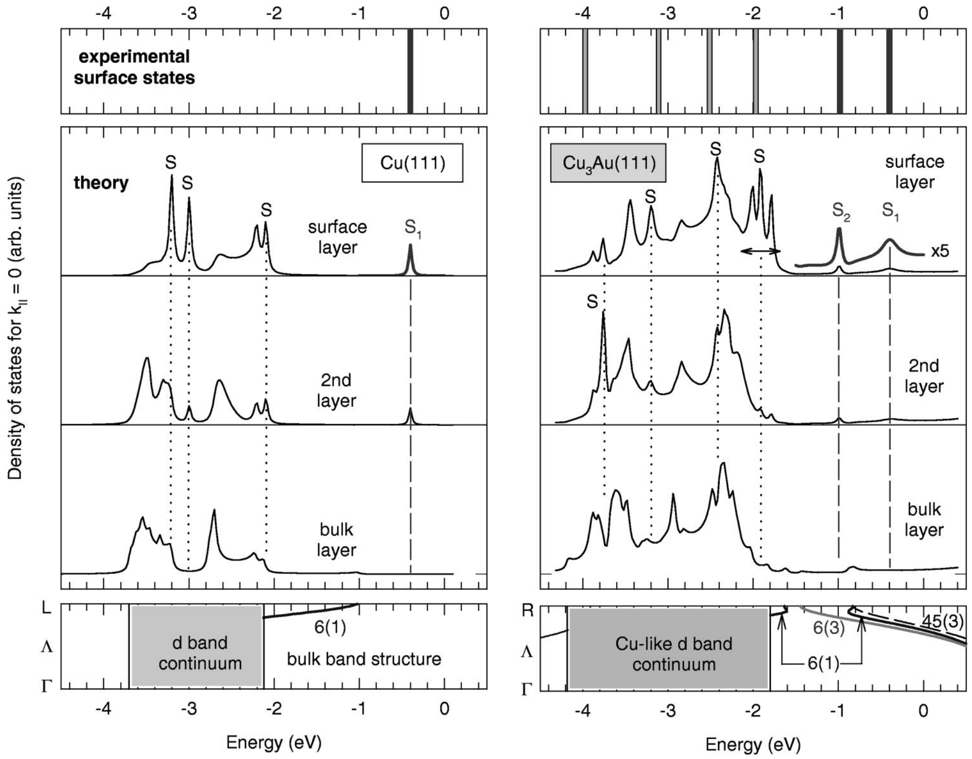

FIG. 3. Layer-resolved densities of states (LDOS) of Cu(111) and Cu$_3$Au(111) for $k_\parallel = 0$ obtained by layer-KKR method with V_{xc} in NLDA. S_1 and S_2 denote the *sp*-derived Shockley surface states/resonances. Surface features with energies in the bulk *d*-band range are summarily denoted by the label *S*. The black (grey) bars in the narrow panels on top inidcate the energies of *sp*-like (*d*-like) surface states, which were observed in photoemission experiments. The bottom panels depict the relevant bulk-band structures with an emphasis on the *sp*-like bands, from which the Shockley surface features originate; in the Cu$_3$Au(111) part the abbreviations 6(3) etc stand for the symmetry types Λ_6^3 etc, where the subscript indicates the double group symmetry and the superscript points to the spatial part (single group symmetry) which dominates in the spin-orbit hybrid.

Cu-like *d* bands between -4 and -2 eV, the agreement with the experimental band data is now very good. Below -4 eV, a significant improvement has been achieved.

Having obtained satisfactory quasiparticle bulk band structures as a prerequisite for the surface electronic structures of Cu(111) and Cu$_3$Au(111), we calculated the layer-resolved densities of states (LDOS) for $\mathbf{k}_\parallel = 0$. Results for the topmost two layers and for a bulk layer are shown in Fig. 3. For Cu(111) (left-hand part) we first note that the bulk LDOS reflects the bulk band structure in the usual way. The surface LDOS exhibits, at -0.4 eV within the bulk *sp* band gap, the Shockley surface state (labeled S_1), which is well known from experiment (cf. references given in the Introduction). Its calculated energy position is seen to coincide with the experimental value (cf. topmost panel). The layer dependence of S_1 is presented in more detail in Fig. 4. There is a quasiexponential decay towards the bulk with a decay depth of about two layers, which clearly demonstrates the true surface-state character of S_1 on Cu(111).

For Cu$_3$Au(111), the calculated LDOS (right-hand part of Fig. 3) reveals *two* surface resonances (labeled S_1 and S_2) in the upper-bulk *sp* region. S_1 at -0.4 eV corresponds to the surface feature already known from experiment[20,21] and is the counterpart of the Shockley state on Cu(111). In contrast to the latter, it is degenerate with three bulk *sp* bands at this energy (cf. bottom panel of the right-hand part of Fig. 3) and, therefore, has a much larger energy width. Its resonance character further manifests itself in an oscillatory decay to the bulk DOS value, which is reached after about 15 atomic layers (cf. Fig. 4).

The second resonance S_2, which we find at -1.0 eV, has not yet been known. It is much sharper in energy because it is located within the gap of the bulk *sp* bands of Δ_6^1 symmetry character and is only degenerate with the *sp* band of Δ_6^3 character bridging the Δ_6^1 gap. This also explains why S_2 decays — compared to S_1 — more steeply from the surface to a lower-bulk value (cf. Fig. 4). Although being a resonance, its surface character is thus much more pronounced.

For both Cu(111) and Cu$_3$Au(111), our calculations also yield some surface-state/resonance-like LDOS features, summarily labeled *S* in Fig. 3, which are located within the bulk *d* band continua. We did not explore them in detail, because they are not the subject of this paper. We only note that there is partial agreement with existing experimental normal photoemission data: (i) For Cu(111), rather surface-sensitive photoemission features in the energy region around -2.0 eV have been reported.[10,11,36] (ii) In our study of the bulk bands of Cu$_3$Au(111) (Ref. 21) we have found several spectral features, the energy locations of which (indicated by the bars in the topmost panels of Fig. 3) are very close to the energies of the surface resonances *S* predicted by our calcu-

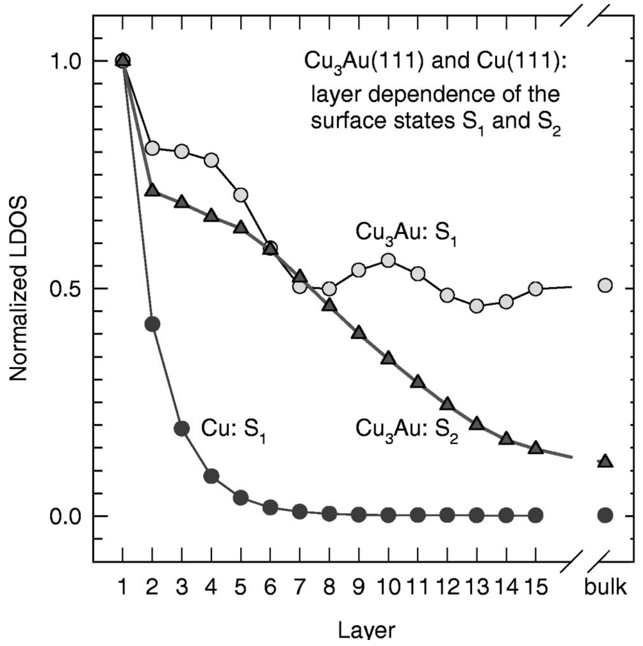

FIG. 4. Layer-resolved densities of states (LDOS) for the Shockley surface state S_1 on Cu(111) and the sp surface resonances S_1 and S_2 on Cu$_3$Au(111).

lation. Since, furthermore, they show *no* dispersion with photon energy, they are likely to originate from the surface electronic structure. An interpretation in terms of bulk DOS transitions is ruled out for the three features below -2 eV, because the experimental band structure [Fig. 2(e)] does not imply a high-bulk DOS at these energies. In a forthcoming detailed study, we also plan to explore the influence of chemical alterations in the surface region, which are mild enough not to significantly affect the sp-like surface states/resonances.

B. Experimental photoemission spectra at normal emission

Figure 5 shows normal emission spectra from Cu$_3$Au(111) and, for comparison, from Cu(111). On the latter surface, the well-known Shockley surface-state appears as a comparatively sharp feature S_1 at energy $E_0 = -0.39(1)$ eV. We note, that the spectral width of S_1 reflects the effective energy resolution of our spectrometer. On Cu$_3$Au(111), its counterpart appears at $E_0 = -0.40(1)$ with comparable peak intensity, however, its sharpness evidently being much less pronounced than on the copper surface. These first findings are in agreement with the results of our calculations discussed above.

Also in agreement with theory, a second Cu$_3$Au(111) surface feature S_2, with an energy width comparable to that of S_1 on Cu(111) but weaker intensity appears at about -1.0 eV. It has *no* counterpart on the Cu(111) surface: the very weak Cu(111) emission at this energy in the HeI excited spectrum is a residual of the bulk excitation from -2.8 eV initial energy with the HeI satellite radiation (23.1 eV photon energy), which could not be eliminated perfectly from the original spectra. Artificial weak structures caused by the satellite correction as described in Sec. II are also visible in the ArI and NeI spectra in between the two surface features S_1 and S_2 and at the high-energy side of S_1. These should not be confused with real features. The existence of S_2 on Cu$_3$Au(111) at constant energy is evidenced by the shown spectra in the photon energy regime between 11.8 and 21.2 eV.

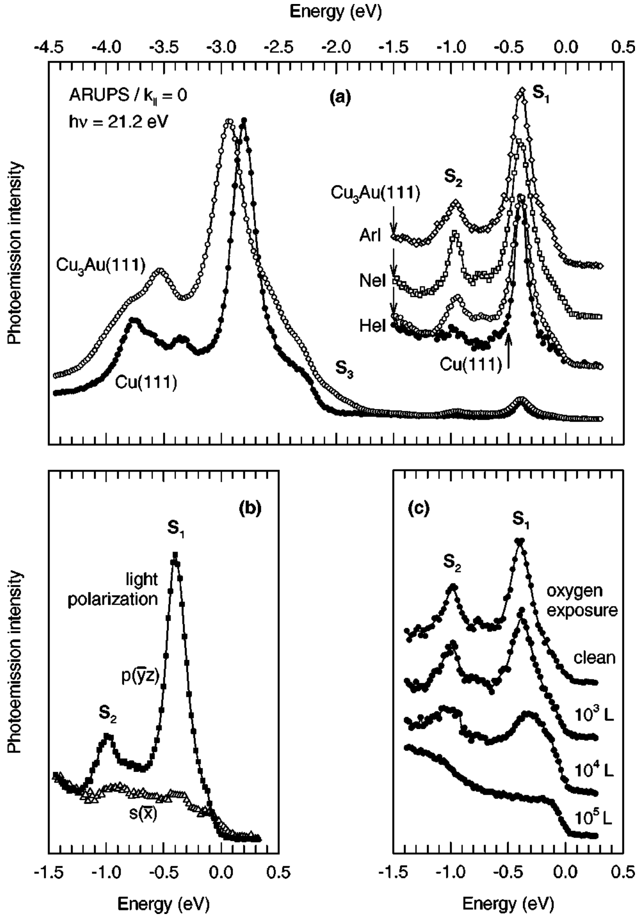

FIG. 5. (a) Comparison of normal emission ARUP spectra from Cu$_3$Au(111) and Cu(111) taken with unpolarized HeI radiation. The region of the Au-like states of Cu$_3$Au at higher binding energy is omitted. The emission from the Shockley-like surface features S_1 and S_2 at about -0.4 and -1.0 eV, respectively, are also shown with an enlarged scale and for excitation with NeI and ArI light. (b) Normal emission ARUP spectra of the Shockley-like surface features on Cu$_3$Au(111) taken with $p(\overline{yz})$ and $s(\overline{x})$ polarized 21.2 eV light, which show that both S_1 and S_2 have even symmetry with respect to the $\overline{yz}$ mirror plane (cf. Fig. 1). (c) as (b) but taken with unpolarized 21.2 eV light as a function of oxygen exposure of the surface.

Measurements to check the symmetry of S_1 and S_2 with polarized light and their surface sensitivity to adsorbates are presented in the lower part of Fig. 6. As necessary for a pronounced surface character, both S_1 and S_2 vanish completely upon the disturbance of the surface by exposure to about 10^5 Langmuir oxygen gas. Also, as in the case for S_1 on Cu(111),[9–11] both surface features on Cu$_3$Au(111) are only excited with $p(\overline{yz})$ light, proving that their symmetry is even with respect to the $\overline{yz}$ mirror plane of the (111) surface

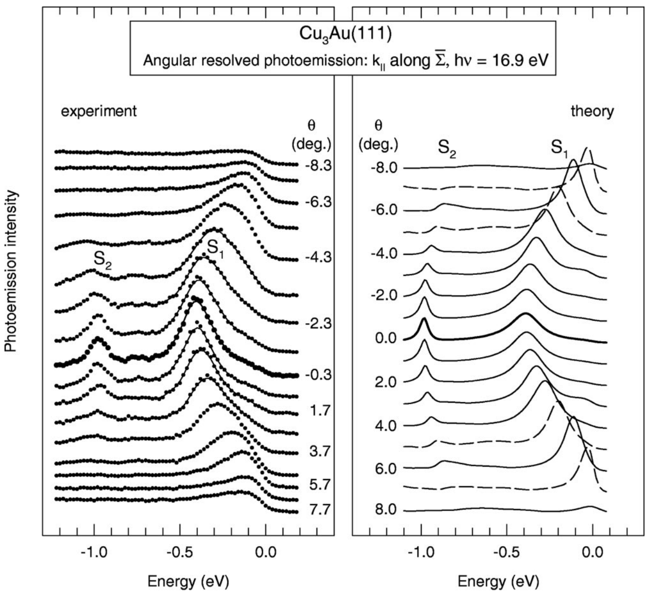

FIG. 6. Experimental (left) and theoretical (right) ARUP spectra of the $Cu_3Au(111)$ Shockley-like surface features S_1 and S_2 as a function of the electron emission angle along the $\bar{\Sigma}$ line in the $\overline{yz}$ plane (see Fig. 1) around the surface normal and excited with unpolarized NeI light.

along the $\bar{\Sigma}$ line (see Fig. 1). These findings are in agreement with our theoretical prediction that one is dealing with surface resonances of Λ_6 symmetry at energies within the bulk-sp continua.

C. Energy dispersion of the surface states

The dispersion of the two surface states on $Cu_3Au(111)$ along the $\bar{\Sigma}$ line around the $\bar{\Gamma}$ point of the SBZ has been measured using HeI, NeI, and ArI radiation. A series of experimental NeI spectra is shown in the left-hand panel of Fig. 6. The right-hand panel shows the corresponding calculated photoemission spectra. From the spectra the $E(k_\parallel)$ relation is easily extracted. It is displayed in the right-hand panel of Fig. 7.

On Cu(111) and Au(111), the observed dispersion of the Shockley-state S_1 is, within the experimental error, parabolic towards the Fermi level E_F:

$$E=E_0+(\hbar^2/2m)\cdot k_\parallel^2=E_0+(300.8\ \text{eV}/a_0^2)\cdot\tilde{k}_\parallel^2/2m^*, \tag{6}$$

where $-E_0$ is the maximum binding energy with respect to E_F measured at the center $\bar{\Gamma}$ of the surface Brillouin zone (SBZ); $k_\parallel$ ($\tilde{k}_\parallel$) is the wave vector along the $\bar{\Sigma}$ line in the SBZ ($\tilde{k}_\parallel$ in units of $2\pi/a_0$: $k=\tilde{k}\cdot 2\pi/a_0$), a_0 the lattice constant in Å (Cu: 3.62 Å, Au: 4.08 Å) and m^* the effective mass in terms of the free electron mass m_0 ($m^*=m/m_0$). On Cu(111) the characteristic parameters at room temperature are $E_0=-0.39(1)$ eV and $m^*=0.46(1)$, on Au(111) $E_0=-0.41(1)$ eV and $m^*=0.28(1)$ (all data taken from Kevan and Gaylord[1]). As can be seen from the left panel of Fig. 7, our theoretical dispersion for the Shockley surface state on Cu(111) ($E_0=-0.40$ eV, $m^*=0.43$) is in nearly perfect agreement with the experimental data (taken from Kevan[4]).

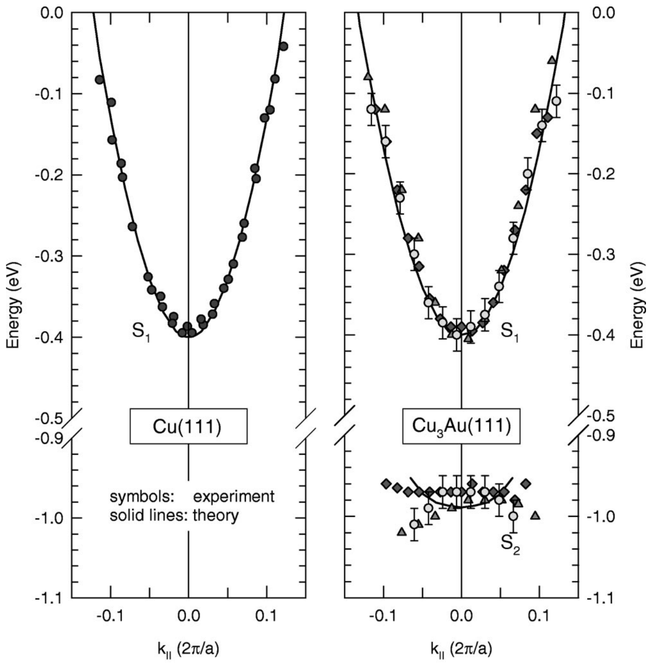

FIG. 7. Experimental and theoretical dispersion relations $E(k_x=0,k_y)$ of the Shockley surface states and resonances for Cu(111) and $Cu_3Au(111)$. The experimental data for Cu(111) have been taken from Kevan (Ref. 4).

As for the noble metals, the dispersion of the corresponding surface resonance S_1 on $Cu_3Au(111)$ is found to be parabolic within the limited region below the Fermi energy. Again, the agreement between theory and experiment, both performed in this paper, is very good. The values of the effective mass, $m^*(\exp)=0.39$ and $m^*(\textit{theor})=0.47$ (as obtained from a parabolic least-squares fit to the experimental and theoretical dispersion curves, respectively), and the energy at the center of the SBZ, $E_0=-0.40(1)$ eV, are very similar to those of Cu(111) and Au(111). The experimental value of m^* is approximately the average of the effective masses of the Shockley states on Cu(111) and Au(111), if one takes the stoichiometry of Cu_3Au into account. This also holds for the lattice constants (Cu_3Au: $a_0=3.76$ Å).

The second Shockley-like surface resonance S_2 on $Cu_3Au(111)$ is found from our experiments at $E_0=-0.97(2)$ eV and from our calculation at a somewhat lower energy $E_0=-0.99$ eV, which is however within the experimental error. The small upward dispersion predicted by theory could not be found experimentally.

V. CONCLUSION AND OUTLOOK

In conclusion, we have discovered—both by photoemission experiments and by surface electronic structure calculations—an electronic surface state on the binary alloy $Cu_3Au(111)$ at -1 eV below the Fermi energy. It resides in a band gap of sp-like bulk states with Λ_6^1 symmetry, which arises in the backfolded Cu bands due to replacing one Cu atom by a Au atom. We have identified the Shockley-like surface feature on $Cu_3Au(111)$ as a surface resonance with the back-folded bands. The experimental dispersion relations of this surface resonance and of the corresponding Shockley surface state on Cu(111) have been perfectly reproduced by our calculations. Work on surface states/resonances, which are predicted by our calculation on top of and within the continuum of the Cu-like *d*-bands of $Cu_3Au(111)$, is in progress.

ACKNOWLEDGMENTS

The present work was performed in the framework of an Advanced Cooperation Program (ACP). It was supported by the Deutsche Forschungsgemeinschaft (DFG). We thank H. Bach (Ruhr-Universitaet Bochum) for supplying the $Cu_3Au(111)$ single crystal. Further, we would like to thank H. Ebert, T. Huhne, and C. Zecha for making available electronic structure results for Cu calculated by their full-potential KKR method.

---

[1] S.D. Kevan and R.H. Gaylord, Phys. Rev. B **36**, 5809 (1987).
[2] P.O. Gartland and B.J. Slagsvold, Phys. Rev. B **12**, 4047 (1975).
[3] P. Heimann, H. Neddermeyer, and H.F. Roloff, J. Phys. C **10**, L17 (1977).
[4] S.D. Kevan, Phys. Rev. Lett. **50**, 526 (1983).
[5] J. Tersoff and S.D. Kevan, Phys. Rev. B **28**, 4267 (1983).
[6] R. Courths, H. Wern, U. Hau, B. Cord, V. Bachelier, and S. Hüfner, J. Phys. F: Met. Phys. **14**, 1559 (1984).
[7] B.A. McDougall, T. Balasubramanian, and E. Jensen, Phys. Rev. B **51**, 13 891 (1995).
[8] S. LaShell, B.A. McDougall, and E. Jensen, Phys. Rev. Lett. **77**, 3419 (1996).
[9] J.A. Knapp, F.J. Himpsel, and D.E. Eastman, Phys. Rev. B **19**, 4952 (1979).
[10] Y. Petroff and P. Thiry, Appl. Opt. **19**, 3957 (1980).
[11] S.G. Louie, P. Thiry, R. Pinchaux, Y. Petroff, D. Chandesris, and J. Lecante, Phys. Rev. Lett. **44**, 549 (1980).
[12] T.C. Hsieh, P. John, T. Miller, and T.-C. Chiang, Phys. Rev. B **35**, 3728 (1987).
[13] R. Matzdorf, G. Meister, and A. Goldmann, Phys. Rev. B **54**, 14 807 (1996).
[14] F. Theilmann, R. Matzdorf, and A. Goldmann, Surf. Sci. **420**, 33 (1999).
[15] G. Nicolay, F. Reinert, S. Schmidt, D. Ehm, P. Steiner, and S. Hüfner, Phys. Rev. B **62**, 1631 (2000).
[16] R. Matzdorf, G. Meister, and A. Goldmann, Surf. Sci. **286**, 56 (1993).
[17] R. Panagio, R. Matzdorf, G. Meister, and A. Goldmann, Surf. Sci. **336**, 113 (1995).
[18] Th. Fauster, Ch. Reuss, I.L. Shumay, M. Weinelt, F. Theilmann, and A. Goldmann, Phys. Rev. B **61**, 16 168 (2000).
[19] L. Bürgi, L. Petersen, H. Brune, and K. Kern, Surf. Sci. **447**, L157 (2000).
[20] R.G. Jordan and G.S. Sohal, J. Phys. C **15**, L663 (1992).
[21] M. Lau, S. Löbus, R. Courths, S. Halilov, H. Gollisch, and R. Feder, Ann. Phys. (Leipzig) **2**, 450 (1993).
[22] H.C. Potter and J.M. Blakeley, J. Vac. Sci. Technol. **12**, 635 (1975).
[23] Y. Ma, S. Lordi, C.P. Flynn, and J.A. Eades, Surf. Sci. **302**, 241 (1994).
[24] S.W. Bonham and C.P. Flynn, Surf. Sci. **388**, L760 (1996).
[25] M.A. Vasiliev, J. Phys. D **30**, 3037 (1997).
[26] C. G. Shaw and S. C. Fain, in *Proceedings of the 7th International Vacuum Congress and the 3rd International Conference on Solid Surfaces (Vienna, 1977)*, edited by R. Dobrozemsky, F.G. Ruedenauer, R.P. Vieboeck, and A. Breth (Elsevier, Amsterdam, 1978), p. 535.
[27] P. Blaha, K. Schwarz and J. Luiz, WIEN97, Vienna University of Technology, 1997. Improved and updated version of the original copyrighted WIEN-code, which was published by P. Blaha, K. Schwarz, P. Sorantin, and S.B. Trickey, Comput. Phys. Commun. **59**, 399 (1990).
[28] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[29] L. Hedin and B. Lundquist, J. Phys. C **4**, 2064 (1971).
[30] V.N. Strocov, Phys. Rev. Lett. **81**, 4943 (1998).
[31] R.M. Dreizler and E.K.U. Gross, *Density Functional Theory* (Springer, Heidelberg, 1990).
[32] S.V. Halilov, E. Tamura, H. Gollisch, D. Meinert, and R. Feder, J. Phys.: Condens. Matter **5**, 3859 (1993).
[33] E. Tamura, R. Feder, J. Krewer, R.E. Kirby, E. Kisker, E.L. Garwin, and F.K. King, Solid State Commun. **55**, 543 (1985).
[34] I. Delgadillo, H. Gollisch, and R. Feder, Solid State Commun. **88**, 789 (1993).
[35] *Polarized Electrons in Surface Physics*, edited by R. Feder (World Scientific, Singapore, 1985).
[36] R. Courths and S. Hüfner, Phys. Rep. **112**, 53 (1984).
[37] A.S. Kheifets, D.R. Lun, and S.Y. Savrasov, J. Phys.: Condens. Matter **11**, 6779 (1999).
[38] T. Huhne, C. Zecha, H. Ebert, P.H. Dederichs, and R. Zeller, Phys. Rev. B **58**, 10 236 (1998).
[39] H. Ebert, T. Huhne, and C. Zecha, private communication.
[40] H. Eckardt, L. Fritsche, and J. Noffke, J. Phys. F: Met. Phys. **14**, 97 (1984).
[41] H. Ibach and H. Lüth, *Solid-State Physics* (Springer, Berlin, 1996).
[42] R. Courths, S. Löbus, S. Halilov, T. Scheunemann, H. Gollisch, and R. Feder, Phys. Rev. B **60**, 8055 (1999).