# Surface states at the (001) surface of CuAu*I*

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We report calculations of the electronic structure in the neighborhood of the (001) surface of CuAu*I* using the self-consistent-field, linear muffin-tin orbital method within the atomic sphere approximation, with a slab geometry and including the surface dipole terms. We focus our attention on the vicinity of the $\bar{M}$ point in the surface Brillouin zone and we identify the two (Tamm-type) surface states reported recently in photoemission measurements. The overall agreement between the theoretically determined dispersions of these states and those observed experimentally is very good and provides strong support for our calculational scheme. We show also that measurements of the surface core level shifts should allow a determination of the termination. [S0163-1829(97)02912-3]

Recently, Xu and Jordan[1] reported the occurrence of two Tamm-type surface states at the $\bar{M}$ point on the (001) and (100) surfaces of equiatomic CuAu*I*, with binding energies in the ranges 1.3–1.6 and 6.1 eV, i.e., just above the $d$-band continuum and in a gap within the Au-related $d$-band complex, respectively. They measured the dispersion relations but since there had been no previous theoretical investigations of these particular surfaces — nor of any surface of CuAu*I* for that matter — they limited their discussion to the similarity of the surface states at the lower binding energies to those previously observed at the $\bar{M}$ point of Cu(100) (Refs. 2–6) and Au(100) (Ref. 7) and to a related surface state on Cu$_3$Au(100).[8,9] These particular states are split off from the top of the $d$-band continuum by a tenth of an eV or so. In addition, through comparisons of the dispersions of the surface states with the larger binding energies, Xu and Jordan[1] were able to draw some conclusions about the atomic spacings on the (100) and (001) surfaces of CuAu *I*.

At about the same time, Jordan *et al.*[10] demonstrated the suitability of the self-consistent-field, linear muffin-tin orbital (SCF-LMTO) method within the atomic sphere approximation (ASA), using a slab geometry and including the surface dipole terms,[11] to the calculation of the electronic structure in the vicinity of the (100) surface of Cu. They showed, for example, that two surface states exist at the $\bar{M}$ point, one about 0.2 eV above the $d$-band continuum and the other in a spin-orbit induced gap near the top of the $d$-band continuum, in good agreement with experiments.[2–6] In addition, they showed that the layer-by-layer potential functions generated by this method could be used in first-principles photocurrent calculations, and the resulting spectra were in excellent agreement with the photoemission measurements of Kevan and Shirley.[4] Jordan *et al.*[10] concluded therefore that their approach was reliable and realistic.

In this paper, we extend the calculational scheme described in Ref. 10 to investigate the electronic structure at the (001) surface of CuAu*I*. Initially, we concentrate on surface states at the $\bar{M}$ point of the surface Brillouin zone. We show that surface states exist whose dispersions in $\vec{k}_{\parallel}$ space are in very good agreement with those obtained by Xu and Jordan[1] in their photoemission measurements and we show that the occurrence of the surface states depends critically on the composition of the terminating (i.e., surface) layer. In addition, we examine the dependence of the surface core level shifts on the termination.

Equiatomic CuAu*I* has the $L1_0$ (layered tetragonal) structure and so the planes normal to the [001] direction comprise alternate layers of Cu and Au atoms. Thus, in the absence of segregation, the (001) surface is either Cu or Au terminated; careful compositional analysis by Auger electron spectroscopy (AES) revealed that the surface layer is essentially 100% Au.[12] Therefore, in the spirit of Ref. 10 we calculated the electronic structure in the vicinity of the (001) surface of CuAu*I* using the SCF-LMTO-ASA method and a 16-layer slab consisting of 11 (alternating Cu and Au) metal layers and five vacuum layers. With this arrangement there are a total number of six inequivalent metal atoms and, hence, layers — which we label $M1$ (the central layer of Cu atoms) through $M6$ (the surface layers of Au atoms) — and three inequivalent vacuum layers (of ''empty'' spheres) — labeled V1 (the layers in contact with the $M6$ layer) through V3 (the central vacuum layer). The calculation was carried out for 56 $k$ points in the tetragonal Brillouin zone with a Wigner-Seitz radius of 2.88 au for each sphere — the equilibrium value for CuAu*I* determined from a previous self-consistent, ''bulk'' calculation using the experimentally measured $c/a$ ratio (0.9251).

Inspection of the charge transferred between the innermost Cu and Au atomic spheres (in layers $M1$ and $M2$, respectively), see Table I, indicates that we have included a sufficient number of layers in the slab since the magnitudes differ by $<0.02\%$ and are within 0.2% of the value from the ''bulk'' calculation. In addition, the amount of charge in the middle vacuum layer, $V3$, is negligibly small. Furthermore, in another set of calculations with two fewer metal layers

TABLE I. The loss ($-$) or gain ($+$) of electronic charge in each atomic sphere in layers $M1$, $M2$, and $V3$ (equal radii). In the third column the charge transferred between the Cu and Au atomic spheres in a bulk calculation is shown.

| Layer | Charge transferred | "Bulk" value |
|---|---|---|
| $M1$ (Cu) | $+0.330571$ | $+0.329893$ |
| $M2$ (Au) | $-0.330517$ | $-0.329893$ |
| $V3$ (vacuum) | $+0.000027$ | $-$ |

(i.e., nine metal plus five vacuum layers), we obtained essentially the same results as those shown in Table I.

In Figs. 1(a) and 1(b) we show the dispersion of surface states, indicated by points, in the vicinity of the $\bar{M}$ point together with the projected relativistic (bulk) band structure; the energy ranges correspond to the regions where Xu and Jordan[1] observed surface states in their photoemission measurements. In Fig. 1(a) a surface state can be seen that is split off from the top of the $d$-band complex, which corresponds to one of the states observed experimentally; in Figs. 2(a) and 2(b) we compare the measured and calculated dispersions of this state. There are several points that should be made.

(i) Because the calculated equilibrium lattice constants of CuAu*I* are a little larger than those measured experimentally, the positions of the $\bar{M}$ point are slightly different in the two plots; the corresponding experimental and theoretical values of $|\bar{\Gamma}\bar{M}|$ are 1.62 Å$^{-1}$ and 1.57 Å$^{-1}$, respectively.

(ii) The calculations actually show two very closely lying surface state bands ($A$ and $B$ shown by the solid triangles and open squares, respectively) that certainly could not be resolved separately in the photoemission experiments.

(iii) Both surface states are of $d$ character at the $\bar{M}$ point, with about 79% of $A$ and 91% of $B$ arising from layer $M6$, i.e., the surface layer, with most of the balance in each case originating from the next layer ($M5$).

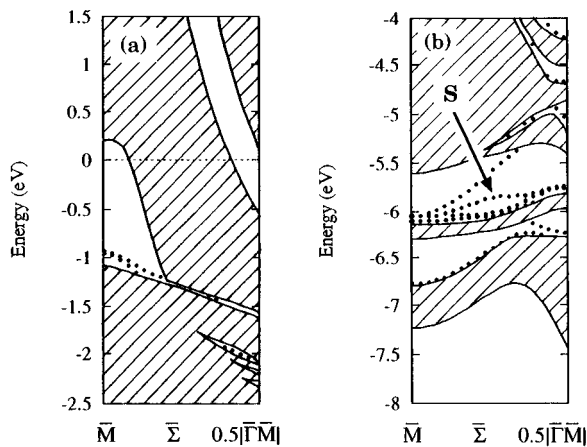(iv) There is a difference of some 0.6 eV between the



FIG. 1. The dispersion of surface states (points) along $\bar{\Sigma}$ in the band gaps of the projected (relativistic) band structure near $\bar{M}$ (shaded regions), (a) at the top of the $d$-band continuum and (b) in the predominantly Au-related $d$ bands, for an Au terminated surface. Note that the energy scale is in eV relative to the Fermi level.
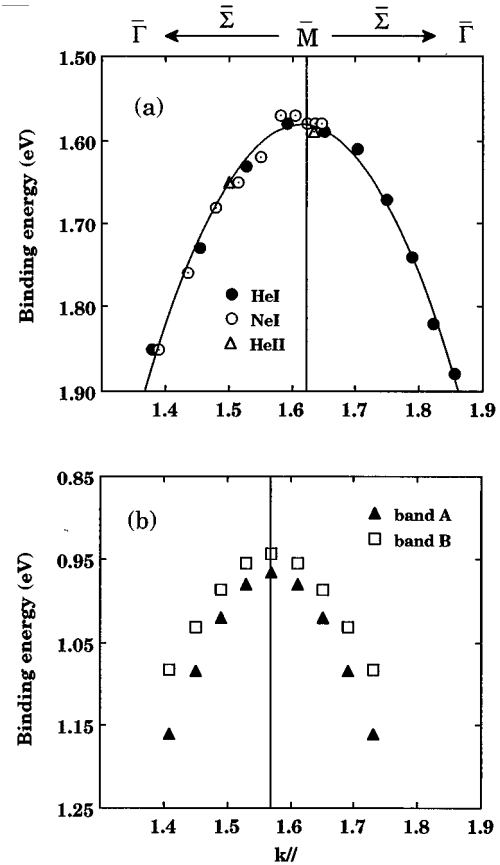


FIG. 2. (a) The experimentally measured and (b) the calculated dispersion of the surface state along $\bar{\Sigma}$ located just above the $d$-band continuum near $\bar{M}$. The energy scale is in eV relative to the Fermi energy. The experimental data in (a) are from Ref. 1; the open circles, closed circles, and triangles are for NeI, HeI, and HeII radiations, respectively.

theoretical and experimental binding energies. Such discrepancies are not uncommon with these types of comparisons involving Cu-based alloys in this energy range, and may well be due to self-energy effects in the photoemission process that are not included in our (ground state) calculations.

(v) From parabolic fits of the form

$$E_B(\vec{k}_{||}) = E_0 + \frac{\hbar^2}{2m^*}(\vec{k}_{||} - \vec{k}_0)^2,$$

where $E_B$ is the binding energy of the state and $\vec{k}_0$ is the position of the $\bar{M}$ point, we find that the calculated effective electron masses ($m^*/m_e$) actually depend on the $|\vec{k}_{||}|$ range chosen, but for $\pm 0.2$ Å on either side of the $\bar{M}$ point the values for bands $A$ and $B$ are $-0.49 \pm 0.02$ and $-0.68 \pm 0.05$, respectively. The experimental value determined over a similar $|\vec{k}_{||}|$ range is $-0.73 \pm 0.03$.

(vi) According to the calculations the surface state is split off by 0.15 eV from the top of the $d$ band continuum, which is in good agreement with that estimated from experiment, i.e., $\sim 0.2$ eV.

Overall, therefore, the agreement between the calculations and the photoemission measurements of this surface state is very satisfactory.
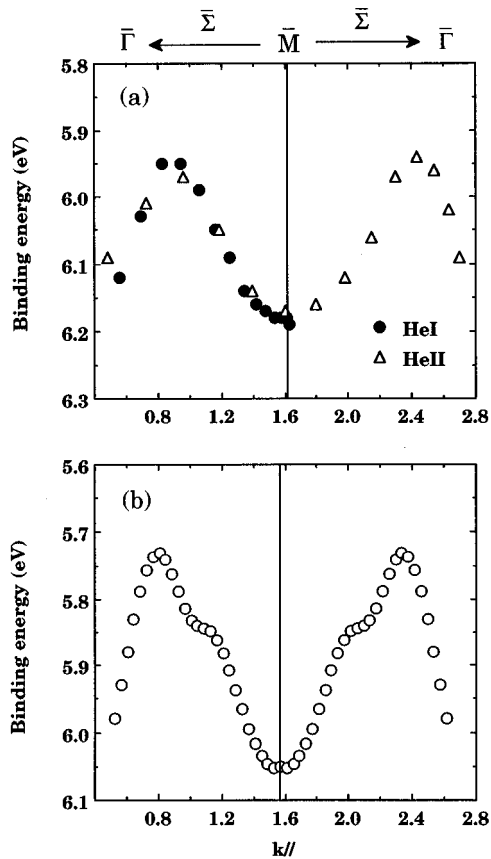
FIG. 3. (a) The experimentally measured and (b) the calculated dispersion of the surface state along $\bar{\Sigma}$ located in the predominantly Au-related bands near $\bar{M}$. The energy scale is in eV relative to the Fermi energy. The experimental data in (a) are from Ref. 1; the closed circles and triangles are for HeI and HeII radiations, respectively.

In Figs. 1(b) we see that there are a number of surface state bands in the projected bulk band gap at the $\bar{M}$ point between $-5.5$ and $-6.1$ eV. However, a close inspection of the dispersion of these states indicates that the band labeled $S$ is the one that closely resembles the experimental result, as shown in Figs. 3(a) and 3(b). In fact, the agreement is very good indeed. Our calculations indicate that this surface state is almost entirely of $d$ character with a weight of 84% from layer $M6$.

We carried out also a similar 16-layer slab calculation for the (001) surface but with a Cu terminating layer. In Figs. 4(a) and 4(b) we show the results that are complementary to those shown in Figs. 1(a) and 1(b). It is interesting to note that the calculations do not produce either of the surface states obtained previously and observed in the photoemission spectra. Thus, we must conclude that the appearance of these two surface states is a direct consequence of an Au termination. It is certainly encouraging to note that this is completely consistent with the surface composition determined experimentally by AES.[12]

The nature of the termination appears to have other implications as well; for example, in the calculated shifts of the core level eigenvalues in the surface region. In Fig. 5(a) we show the shift of several Au core level eigenvalues in layers $M4$ and $M6$ (the surface layer) for an Au terminated slab,
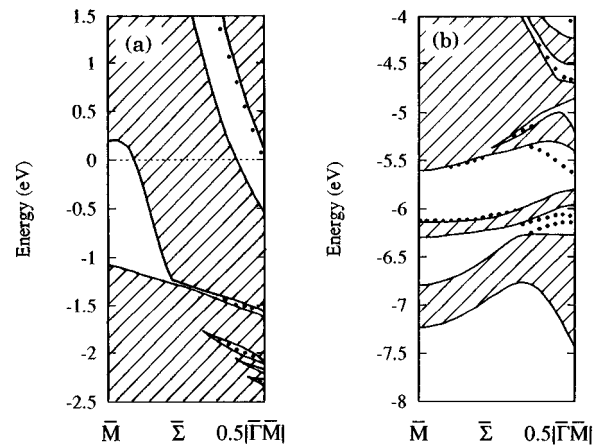


FIG. 4. The dispersion of surface states along $\bar{\Sigma}$ in the band gaps of the projected (relativistic) band structure near $\bar{M}$ (shaded regions), (a) at the top of the $d$-band continuum and (b) in the predominantly Au-related bands, for a Cu terminated surface. Note that the energy scale is in eV relative to the Fermi level.

with reference to layer $M2$ (the ''bulklike'' layer). In Fig. 5(b) we show a set of Cu eigenvalues, relative to layer $M1$, for the same slab. We note that all the Au shifts are very similar, and likewise the Cu shifts. We see that there is a surface core level shift (SCLS) of the Au eigenvalues of $-0.5$ to $-0.6$ eV, whereas in the case of Cu the eigenvalues in layer $M5$ show a very small positive shift ($\sim 0.02$ eV). In
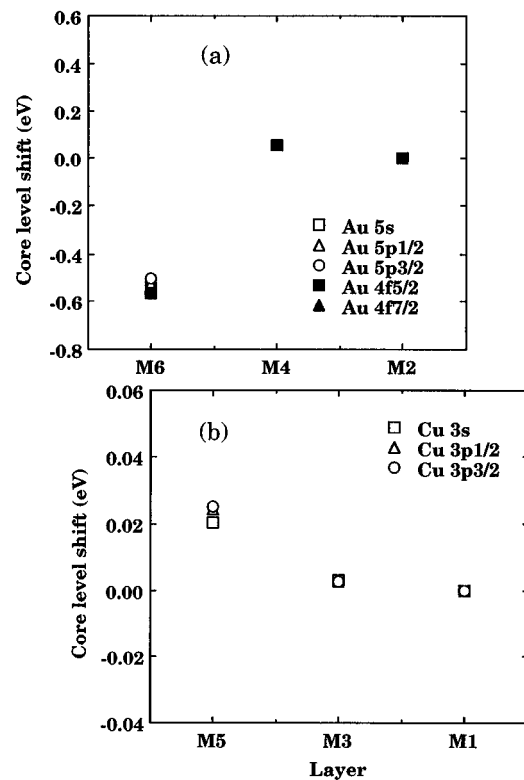


FIG. 5. The calculated core level shifts for the Au terminated surface. The Au eigenvalue shifts (a) are relative to the innermost Au layer ($M2$) and the Cu eigenvalue shifts (b) are relative to the central Cu layer ($M1$). $M6$ is the surface layer.
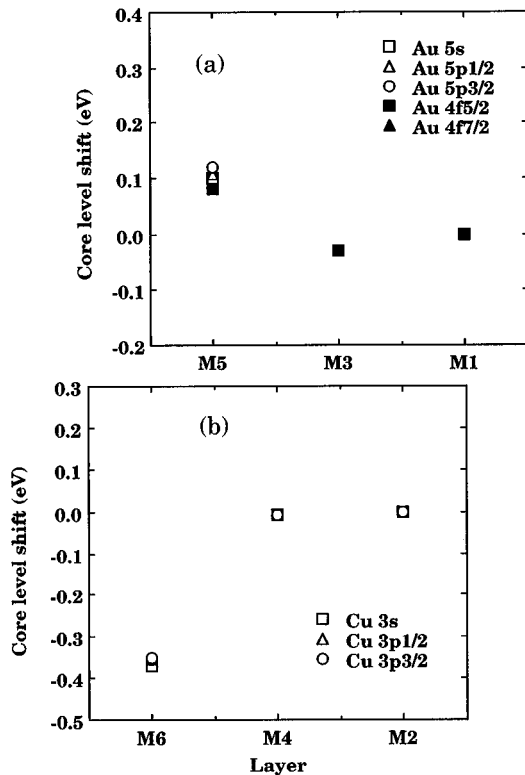
FIG. 6. The calculated core level shifts for the Cu terminated surface. The Au eigenvalue shifts (a) are relative to the central Au layer ($M1$) and the Cu eigenvalue shifts (b) are relative to the innermost Cu layer ($M2$). $M6$ is the surface layer.

Figs. 6(a) and 6(b) we show the shifts for a Cu terminated slab. In contrast to the case of the Au terminated slab, the Au atoms in layer $M5$ now show a small positive shift ($\sim 0.1$ eV) and the Cu atoms show a negative SCLS of about $-0.35$ eV. Thus, the *signs* of the SCLS of Au and Cu are sensitive to the type of termination. The reason for this sensitivity is due to the fact that the first vacuum layer (V1) gains electrons in both cases — about $+0.35e$ and $+0.2e$ for the Au and Cu terminated surfaces, respectively — and the metal atoms in the surface layer ($M6$) lose electrons — about $-0.5e$ and $-0.1e$ for the Au and Cu terminated surfaces, respectively. In the case of the Au terminated slab all of the Au spheres experience a decrease in electron count — as indeed the Au atomic spheres do in a bulk calculation as shown in Table I — and since the $M6$ layer contains Au atoms, we could describe the situation as ''normal'' for the Au atoms in that layer. However, with a Cu terminated surface the Cu spheres in the $M6$ layer *lose* charge and so now we have a ''non-normal'' situation for those Cu atoms. The

net result is that atoms in the surface layer experience a negative SCLS no matter whether that layer contains Au or Cu atoms. Hence, a measurement of the sign of the Au and/or Cu SCLS will indicate whether the (001) surface of CuAu*l* is Au or Cu terminated. Unfortunately, this experiment has not been performed but we speculate that since surface states occur and AES measurements suggest an Au termination, then a negative SCLS for Au will be observed.

As we show in Table I, on the assumption of equal atomic sphere radii, the charge is transferred from the Au spheres to the Cu spheres in the bulk. This redistribution of charge results in a shift of the Au and Cu core level eigenvalues of about $+0.5$ eV and $-0.4$ eV, respectively, values which, incidently, are consistent with experimental measurements of the binding energy shifts on alloying.[13] Therefore one *might* conclude that a decrease (increase) in charge in the atomic sphere leads to an increase (decrease) in the core level binding energies. However, the results of our slab calculations show that at the surface, a *loss* of charge in the atomic spheres actually occurs along with a *negative* SCLS for both the Au and Cu terminations. Thus, the signs of the SCLS's are determined by location, i.e., geometry, rather than the loss or gain of charge in the atomic sphere.

In summary, therefore, we have calculated the electronic structure in the vicinity of the (001) surface of CuAu*l* using the SCF-LMTO-ASA method and a 16-layer slab geometry. We can account for the two surface states reported previously at the $\bar{M}$ point; one above the top of the $d$-band continuum and the second within a gap in the predominantly Au-related $d$ bands. The occurrence of these states confirms that the (001) surface has an Au termination since calculations assuming a Cu termination do not produce the surface states. In addition, we show that the sign of the SCLS is sensitive to the termination; if the (001) surface is Au terminated, as we believe it is, then the Au SCLS will be negative and the Cu SCLS will be small but positive. If the surface is Cu terminated, the Cu SCLS will be negative and the Au SCLS small and positive. We plan to use the layer-by-layer potential functions generated by our calculations in first-principles (relativistic) photocurrent calculations, similar to those recently carried out by Ginatempo *et al.*,[14] in order to provide more direct and detailed comparisons with the photoemission measurements.

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