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Energy bands of (111) copper thin films*

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A tight-binding calculation of the energy bands of a 30-layer (111) copper thin film is performed using the same set of 34 Hamiltonian matrix element parameters that we used in our (100) and (110) thin-film calculations. The bands are calculated at 61 points in the irreducible (1/12) two-dimensional Brillouin zone (2D BZ) both with and without a surface parameter shift. The planar and total densities of states are presented. We find a free-electron-like surface state which lies well above the Fermi energy independent of the surface parameter shift. Gartland and Slagsvold have inferred from their photoelectric data that this (or perhaps another surface state in the same region of the 2D BZ) lies below E_F. We present an argument which indicates that their interpretation of their data may be incorrect.

I. INTRODUCTION

In this paper we continue our program of systematically investigating the surface electronic structure of transition metals by means of parametrized linear-combination-of-atomic-orbitals (LCAO) calculations. This method has been successfully applied to semiconductors,[1] and we have previously applied it to the (100),[2] (110),[3] and[4] (111) faces of ferromagnetic iron and to the[5] (100) and[6] (110) faces of copper. In this paper we present the results for (111) copper. Concurrently, we are attempting a self-consistent calculation of a paramagnetic iron thin film having already completed[7,8] an *ab initio* but non-self-consistent supplemented orthogonalized-plane-wave calculation. We believe that, even if we are successful in performing a self-consistent transition-metal thin-film calculation, parametrized LCAO calculations will dominate the theoretical studies of transition-metal surfaces for some time to come for the following reasons. Self-consistent calculations are extremely time consuming and expensive and with current computers can probably not be done for lower-symmetry faces such as the (110) or (111). They are limited to very thin films (about 13 layers), whereas we have done a 47-layer[6] LCAO calculation and when we found a surface state with a decay length of 25 interplanar spacings at a high-symmetry point in the two-dimensional Brillouin zone (2D BZ), we were able to perform the calculation at that 2D BZ point for a 321-layer film.[2] Many surface states are insensitive to the surface potential, making a self-consistent calculation unnecessary, whereas others are so sensitive that their occurrence will depend upon what exchange potential approximation is used in the self-consistent calculation.

Our philosophy is that one obtains the maximum information about transition-metal surfaces if one first obtains bulk LCAO parameters by fitting a bulk energy-band calculation and makes whatever changes seem reasonable in the parameters involving surface atoms. One then repeats the calculation with one or more different sets of surface parameters. Those surface states which are independent of the surface parameters may reasonably be believed to be real. Quite often one finds that as one changes the surface parameters and pulls a surface state out of an energy gap, another surface state is pulled out of the continuum into the gap so that one may again reasonably believe that the gap does contain a surface state. As discussed previously[6] we believe that for copper it is best to keep the surface parameters unchanged from the bulk parameters. We use the same set of 34 parameters, obtained from fitting Burdick's[9] bulk band calculation, as we used for the other two faces[5,6] except that we shifted all the energy bands downward by an additional 0.018 Ry relative to the vacuum (i.e., we shifted all the zero-neighbor parameters by -0.018 Ry) to account for the fact that the (111) work function is approximately that much larger[10,11] than the (100). We have performed this calculation for a 30-layer film which, because of the large interplanar spacing ($a/\sqrt{3}$), is actually somewhat thicker than our 33- and 47-layer (100),[5] and (110),[6] films. Although physically the (111) faces of fcc copper and bcc iron are quite different, it being a close-packed fcc face and being so open a bcc face that there are no first or second neighbors in the plane, symmetrically they are identical. The (111) film unit cell is an hexagonal cylinder containing one atom from every plane of the film. There are three types of planes labeled A, B, and C depending upon whether the atom is located at the center or alternate corners of the hexagon.[12] The film has inversion symmetry but inversion is not a member of the group of the two-dimensional wave vector

$\bar{k}$ except at the $\bar{\Gamma}$ and $\bar{M}$ points of the 2D BZ. This leaves one with a complex matrix. We, therefore, combine planar Bloch basis functions of $+\bar{k}$ and $-\bar{k}$ to obtain nine (one 4*s*, three 4*p*, and five 3*d*) planar standing sine wave basis functions plus nine planar standing cosine basis functions per plane which yield a real Hamiltonian matrix. Because inversion is a member of the group of the combined wave vectors $+\bar{k}$ and $-\bar{k}$, this real Hamiltonian matrix can be reduced to two identical real matrices half as large (270×270 for the case of nine atomic basis functions and a 30-layer film). At high-symmetry points and along symmetry lines we used the symmetrized combinations of atomic basis functions given in Table I of Ref. 4 to block diagonalize the matrix but at a general point in the 2D BZ we had to diagonalize a 270×270 matrix. The bands were calculated at 61 points in the irreducible ($\frac{1}{12}$) 2D BZ.

In Sec. II we present our thin-film energy bands calculated using the bulk LCAO parameters for all the atoms as well as for the case when the zero-neighbor parameters [ss_0, pp_0, dd_0 $(3z^2-r^2)$, and $dd_0(xy)$] of the atoms on the surface plane are made 0.02 Ry more negative than the bulk parameters. We find a large number of gaps many of which contain surface states. In Sec. III the planar (PDS) and total (TDS) densities of states are described. Gartland and Slagsvold,[10] from their photoelectric data, have deduced the existence of a $\bar{\Gamma}$ surface state lying slightly below the Fermi energy. We find a surface state in the same gap but lying far above E_F. In Sec. IV we discuss the location of this surface state in some detail. We also discuss other experimental data which seems to indicate that the structure in their photoemission data cannot be due to a surface state.

II. ENERGY BANDS

In Fig. 1 we present the $\bar{\Sigma}_1-\bar{T}_1'-\bar{T}_1$ bands. The upper bands are the case with the average surface potential the same as in the bulk. The lower bands are for the case with the surface more attractive than the bulk. In Fig. 2 we present the $\bar{\Sigma}_2-\bar{T}_2'-\bar{T}_2$ bands. In both figures we show the extent of all symmetries at the higher symmetry points $\bar{\Gamma}$, $\bar{M}$, and $\bar{K}$. In every case we indicate the bulk bands by dashed lines and the surface states by solid lines. In Fig. 3 we show the composite bands. Gaps in bands of one symmetry which are crossed by bands of another symmetry are called subband gaps. Gaps in the composite bands are called absolute gaps. Since subband gaps exist only on high symmetry lines and points, surface states within subband gaps must become resonances an infinitesimal distance into the 2D BZ. Absolute gaps extend into the interior of the 2D BZ and surface states in these gaps may extend throughout much of the 2D BZ. In discussing the details of Figs. 1–3, we will concentrate on the $\bar{\Sigma}_1-\bar{T}_1'-\bar{T}_1$ and $\bar{\Sigma}_2-\bar{T}_2'-\bar{T}_2$ unshifted bands. As we go we will point out those states which are in absolute gaps and, by comparison, the differences created by shifting the surface potential.

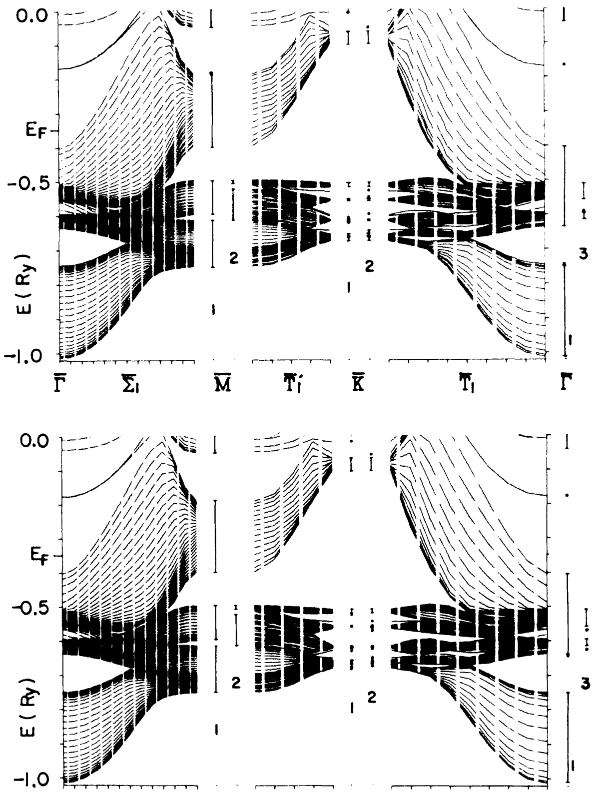

FIG. 1. Two-dimensional ($\bar{\Sigma}_1\bar{T}_1\bar{T}_1'$) energy bands of a 30-layer (111) copper thin film calculated with unshifted surface parameters (upper panel) and shifted surface parameters (lower panel).

Along $\bar{\Sigma}$ the $\bar{\Sigma}_2$ bands have pure *d* character. The three-dimensional Brillouin zone (3D BZ) points which project to give the two-dimensional (2D) $\bar{\Sigma}$ point $(-\alpha,-\alpha,2\alpha)$ are $(\beta-\alpha,\beta-\alpha,\beta+2\alpha)$. Thus the $\bar{\Sigma}$ projection contains $\Sigma(-3\alpha,-3\alpha,0)$, $\Delta(0,0,3\alpha)$, and $\Lambda(-\frac{3}{2}\alpha,-\frac{3}{2}\alpha,\frac{3}{2}\alpha)$ points from the 3D BZ. There is a single $\bar{\Sigma}_2$ gap which has a maximum width on $\bar{\Gamma}$ at -0.59 Ry. This gap pinches off approximately $\frac{1}{3}$ of the way to $\bar{M}$ (i.e., $\alpha\approx 2\pi/9a$) and immediately reopens. This results from an accidental degeneracy between two 3D BZ Σ levels with this value of α. The gap again pinches off and reopens approximately $\frac{2}{3}$ of the way to $\bar{M}$ resulting from a similar degeneracy at Δ.

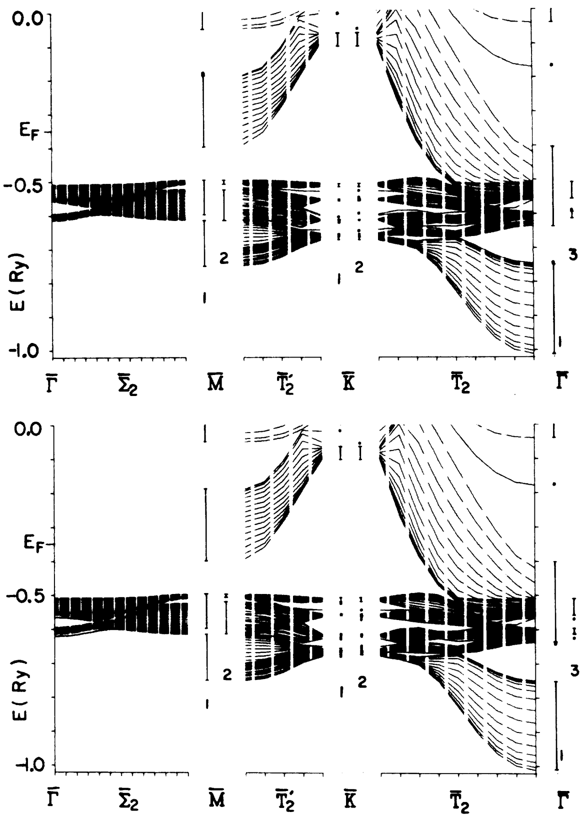

FIG. 2. Two-dimensional ($\bar{\Sigma}_2\bar{T}_2\bar{T}_2'$) energy bands of a 30-layer (111) copper thin film calculated with unshifted surface parameters (upper panel) and shifted surface parameters (lower panel).

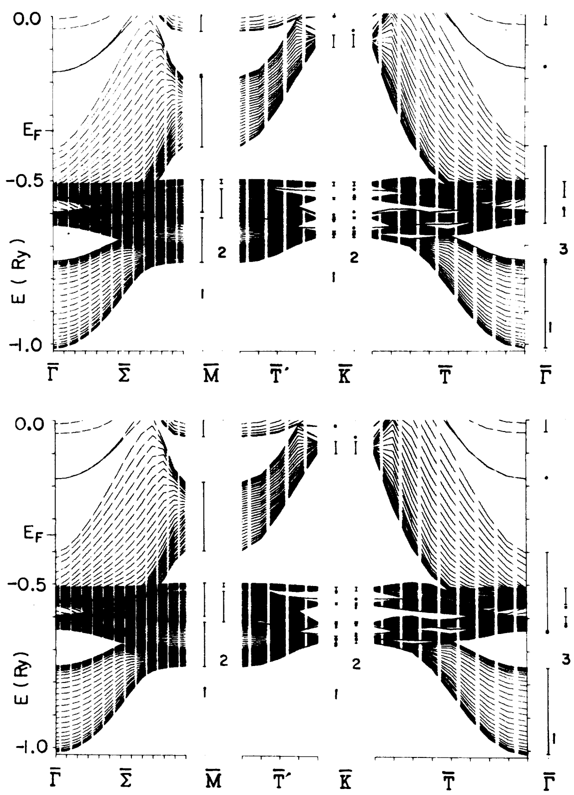

FIG. 3. Two-dimensional composit energy bands of a 30-layer (111) copper thin film calculated with unshifted surface parameters (upper panel) and shifted surface parameters (lower panel).

Between these two pinches the gap is extremely narrow and contains a surface state pair.[13] We have previously discussed[2,3] Tamm[14] and Shockley[15] surface states. The Tamm states arise from a single band, whereas the Shockley surface state pair arises from hybridization between bands and consists of a combination of one state from each band. The concept of Tamm and Shockley states is rigorous only in one dimension. This is demonstrated by the $\bar{\Sigma}_2$ surface state pair which contains one member from the upper and lower continua when it starts at the left-hand pinch off point. The pair then join the lower continuum just before the right-hand pinch off point. Thus this surface state changes continuously from Shockley-like to Tamm-like. With this caveat, we will continue to use Tamm and Shockley as descriptive terms. Because of the narrowness of the gap (0.007 Ry) and the fact that 85% of the amplitude squared of the surface-state wave function is on the surface plane, this $\bar{\Sigma}_2$ surface state disappears after the -0.02-Ry shift of the surface parameters. The $\bar{\Gamma}_3$ Tamm state at -0.59 does not extend into this gap, but merges into the lower bands less than $\frac{1}{12}$ of the way to $\bar{M}$. By making the surface layer more attractive this surface state is lost and two new surface states are created. The first is a new $\bar{\Gamma}_3$ Tamm state at -0.57 Ry which extends 30% of the way to $\bar{M}$. The second is a new $\bar{\Gamma}_3$ Tamm state[16] pulled out of the bottom of the band and extending $\frac{1}{2}$ of the way to $\bar{M}$. All these $\bar{\Sigma}_2$ surface states exist in sub-band gaps; thus none extend off the $\bar{\Sigma}$ line.

Along the $\bar{\Sigma}_1$ band there are many more gaps. A very wide $\bar{\Gamma}_1$ gap between -0.4 and -0.04 Ry extends as a $\bar{\Sigma}_1$ gap $\frac{2}{3}$ of the way to $\bar{M}$ and as a $\bar{T}_{1,2}$ gap more than half of the way to $\bar{K}$. In total this gap covers about 40% of the 2D BZ. In this absolute gap we have a surface state of $\bar{\Gamma}_1-\bar{\Sigma}_1-\bar{T}_{1,2}$ symmetry.[17] This is a Shockley surface state, in the middle of an *sp* gap and is only slightly shifted by the surface-parameter shift. A second $\bar{\Sigma}_1$ gap above E_F has its maximum width on $\bar{M}$ at about -0.1 Ry and extends upward in both the $\bar{\Sigma}_1$ and $\bar{T}_1'$

directions. There is an $\bar{M}_1$ surface state right at the bottom of the gap, which very quickly runs into the bulk bands on either side of $\bar{M}$. Making the surface more negative pulls it completely into the continuum of bulk bands.

Four $\bar{\Sigma}_1$ gaps exist below the Fermi level. The first and third have maximum widths of 0.1 and 0.02 Ry at about -0.5 and -0.6 Ry at $\bar{M}$, respectively. Neither of these gaps contains a surface state, even when the surface potential is made more attractive. But the fourth gap contains a $\bar{\Gamma}_1 - \bar{\Sigma}_1 - \bar{T}_{1,2}$ surface state with an energy of -0.745 Ry at $\bar{\Gamma}$. This gap has a miximum width of 0.12 Ry and extends halfway to $\bar{K}$ and to $\bar{M}$. This absolute gap covers about 25% of the 2D BZ and the surface state exists near the bottom of the gap throughout its entire extent. Making the surface potential more attractive pulls this surface state into the continuum of bulk states. The second gap which is very narrow lies in the middle of the $\bar{\Sigma}_1$ bands at about -0.57 Ry and contains a surface state with and without surface parameter shifts. This gap fails to be connected with the gap which runs to $\bar{M}$ at -0.5 Ry because a three-dimensional (3D) indirect gap closes off over a small but finite range of $\bar{\Sigma}_1$. With a very slight change in the bulk bands these two gaps would be one. All $\bar{T}_1$ ($\bar{T}_1'$) bands are degenerate with $\bar{T}_2$ ($\bar{T}_2'$) bands in an infinitely thick film and therefore are nearly so in a 30-layer film. Thus all gaps along $\bar{T}$ and $\bar{T}'$ are absolute assuring that all surface states in these gaps will remain surface states for at least a short distance into the interior of the 2D BZ.

Most of the gaps not previously discussed have their maximum width at $\bar{K}$. The highest $\bar{K}_1$ and $\bar{K}_2$ surface states which are slightly below the vacuum level quickly run into the top of the bulk continuum as we go away from $\bar{K}$ in either the $\bar{T}$ or $\bar{T}'$ direction. Making the surface potential more attractive makes no change except to lower their energy slightly. Below these there is a very wide $\bar{K}$ gap, from -0.1 to -0.5 Ry. This gap extends along $\bar{T}$ halfway to $\bar{\Gamma}$, and along the entire length of $\bar{T}'$, even extending about $\frac{1}{4}$ of the way from $\bar{M}$ to $\bar{\Gamma}$. There are no surface states in this gap, just as there were no surface states in the similar $\bar{M}$ gap in the (100) bands. Making the surface more attractive does not generate any surface states in this gap. There are four lower and narrower $\bar{K}$ gaps, three of which contain at least one surface state. The highest gap contains two $\bar{K}_2$ surface states. The upper one of -0.53 Ry extends about 60% of the way to $\bar{M}$ and 10% of the way to $\bar{\Gamma}$, and the lower one of -0.55 Ry is right at bottom of the gap and does not extend any appreciable distance in the $\bar{T}$ or $\bar{T}'$ directions. Making the surface more attractive lowers the energy of upper surface state, removes the lower surface state, and pulls a $\bar{K}_1$ surface state into the top of the gap.

The second gap contains (for unshifted surface potential) $\bar{K}_1$ and $\bar{K}_2$ surface states at energy of about -0.6 Ry. These extend only 25% of the way to $\bar{M}$ along $\bar{T}'$, but the $\bar{K}_2$ surface state extends about 65% of the way along $\bar{T}$. By making the surface potential more attractive, these surface states are lost except for a small part of the $\bar{T}$ surface state midway between $\bar{K}$ and $\bar{\Gamma}$, and two new[18] $\bar{K}_2$ surface states appear at the top of the gap. The lower of these extends about 40% of the way to $\bar{\Gamma}$.

The third gap contains a $\bar{K}_1$ surface state at -0.62 Ry and a $\bar{K}_2$ surface state at -0.64 Ry. The gap in which these surface states lie pinches off about $\frac{1}{8}$ of the way along $\bar{T}$, but then opens up again in the middle of the $\bar{T}$ line. A surface state runs essentially the length of the gap beyond the pinch. About $\frac{1}{4}$ of the way along $\bar{T}'$ the gap gets very narrow, but does not pinch off until the end of the $\bar{T}'$ line at $\bar{M}$. A surface state runs through the narrow region of the $\bar{T}'$ gap. The $\bar{K}_1$ surface state disappears almost immediately into the top of the gap along both $\bar{T}$ and $\bar{T}'$, whereas the $\bar{K}_2$ surface state continues as a $\bar{T}'_{1,2}$ or $\bar{T}_{1,2}$ surface state until these gaps get narrow. Upon making surface potential more attractive, new $\bar{K}_1$ and $\bar{K}_2$ surface states appear at the top of the gap with the old surface states only lowered slightly in energy. The surface state in the interior $\bar{T}'$ gap is only slightly lowered in energy while that in the $\bar{T}$ gap is removed and replaced by another $\bar{T}_{1,2}$ pair. A 0.002-Ry $\bar{K}_{1,2}$ gap exists at about -0.66 Ry. It is shown slightly wider in the figures than it actually is simply to make it visible. However, this gap does open up as we go from $\bar{K}$ toward $\bar{\Gamma}$. It exists over about $\frac{1}{2}$ of the line, then pinches off and reopens as the large $\bar{T}_{1,2} - \bar{\Gamma} - \bar{\Sigma}_1$ gap already discussed. A $\bar{T}_{1,2}$ surface state runs a short distance along the bottom of the gap. Making the surface more attractive pulls this surface state out of the gap and pulls another two surface states into the gap. The upper one of the two new surface states runs essentially the entire length of the gap, the other runs along the right-hand bottom of the gap.

We note finally that making the surface more negative pulls a $\bar{K}_1$ Tamm state out of the bottom of the $\bar{K}$ band (at -0.68 Ry) which runs 25% of the way to $\bar{M}$ and $\bar{\Gamma}$.

Whereas for all the faces of iron, but especially the (111), we found bands of surface resonances, in none of the faces of copper are such resonance bands found. The only resonances we found were those which join to surface states in subband gaps and those existed in only the close neighborhood of the symmetry line or point of the 2D BZ. Since

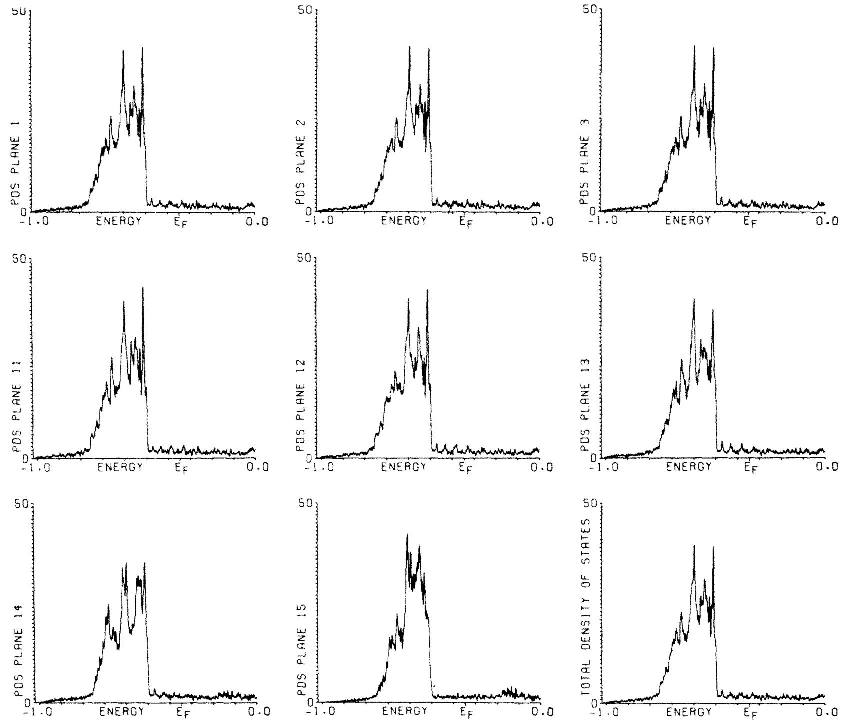

FIG. 4. Planar and total densities of states for 30-layer (111) copper film calculated with unshifted surface parameters.

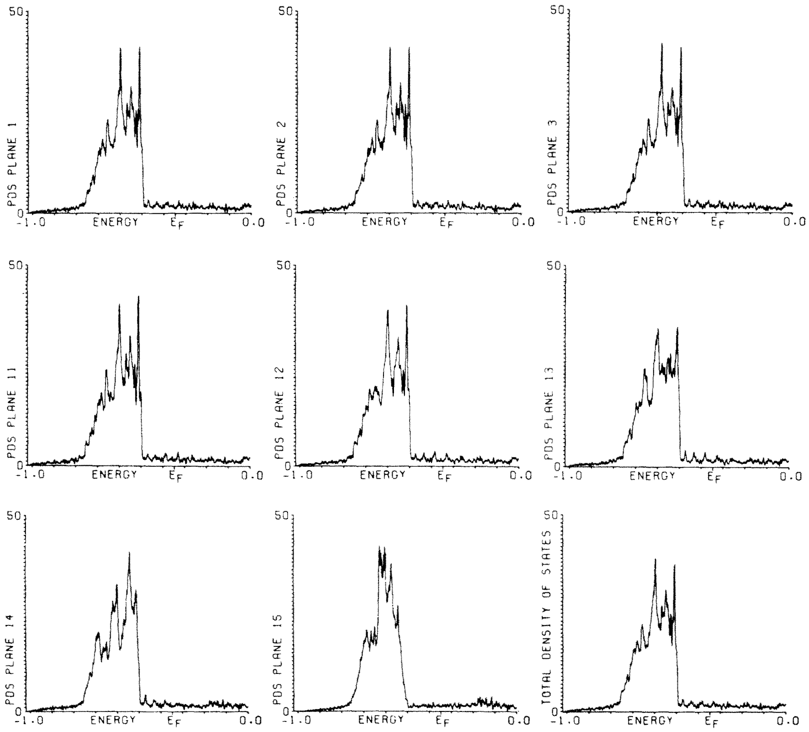

FIG. 5. Planar and total densities of states for 30-layer (111) copper film calculated with shifted surface parameters.

resonances are nothing more than surface states which happen to be degenerate with bulk states of the same symmetry and since copper and iron appear to be equally rich in true surface states (i.e., those in energy gaps), we can give no physical explanation for this disparity.

III. DENSITIES OF STATES

In Figs. 4 (unshifted surface parameters) and 5 (shifted surface parameters) we present the total density of states (TDS) and the planar densities of states (PDS) for several planes. The same energy mesh (0.001 Ry) and smoothing procedure were used as in Refs. 3–6. We see that the PDS for planes 1–3 in the center of the film are all nearly identical with the TDS and are independent of the surface parameter shift. This is because in our 30-layer film, the surface perturbations affect only the outermost four or five layers. The inner layers are quite bulk like as is the TDS. Thus, these PDS are nearly identical to the corresponding ones obtained for the (100) and (110) faces. [The high-energy peak for the (100) face was slightly lower and wider than for the (110) and (111) faces. We attributed[6] this to noise in the calculation.] The TDS for planes near the surface, of course, differ for different surfaces and for different surface parameter shifts. All surface layer PDS have in common that their d bandwidth is narrower (has smaller second moment) than it is for interior planes. The surface atoms on an fcc (111) face are not missing as many neighbors as atoms on (100) or (110) faces so the effect, although still quite appreciable, is not as strong here as it was for the other faces. The structure of the surface plane PDS and that of planes near it also differs from the interior planes's PDS because of surface state contributions. For example the small peak at the high-energy edge of the surface PDS d bands is at -0.527 and -0.541 Ry in Figs. 4 and 5 and can be attributed to the very flat surface state band emanating from $\overline{K}_2$ at -0.531 and -0.543 Ry, respectively. The peak just above the largest peak in Fig. 4 is at -0.594 Ry and can be attributed to the surface state band emanating from $\overline{K}_2$ at -0.599 Ry.

The Fermi energy (for the unshifted surface potential), obtained by summing the TDS up to 11 electrons per atom, is -0.346 Ry in agreement with our results for the other faces (remember all energies here have been lowered by 0.018 Ry to account for the larger work function for this face). Summing the PDS up to E_F, we find a deficit of 0.198 electron/atom on the surface plane and a small excess (which has a maximum value of 0.019 electron/atom on the thirteenth plane) on all the interior planes. This surface deficit is smaller than the 0.269 and 0.354 electron/atom deficit found on the (100) and (110) faces. These deficits arise from a narrowing of the very broad s-p PDS at the surface plane causing states below E_F in the surface PDS. We wish to emphasize again that these deficits should be countered by a flow of charge into the region beyond the surface plane. These deficits are not an indication that the surface potential should be more attractive but simply an indication that the LCAO expansion is incapable of accounting for the charge which extends beyond the surface plane. When the surface potential was made 0.02 Ry more attractive, the surface deficit was reduced to 0.142 electron/atom.

IV. PHOTOELECTRIC DATA

As mentioned in Sec. I, Gartland and Slagsvold[10] have found a large peak in the angle resolved photoemission of (111) copper in the forward direction at 0.4 eV below the Fermi energy. They attribute this to a surface state lying about 0.25 eV above the top of the $\overline{\Gamma}$ continuum (this corresponds to the $L_{2'}$ point in the 3D BZ) and running upward in energy along the $\overline{\Sigma}$ and $\overline{T}$ directions. We do not find this surface state in our calculation. We do find a surface state in the same gap but lying about 2.4 eV *above* E_F. Making the surface parameters 0.27 eV more attractive had a negligible effect on the position of this surface state as can be seen from Fig. 3. We, therefore, attempted to push a state through the top of the $\overline{\Gamma}$ continuum into the gap by making the surface parameters 0.27 eV less attractive. We succeeded in pushing a surface state out of the d bands into the $\overline{\Sigma}$ gap and part of the $\overline{T}'$ gap at about -0.49 Ry, but did not succeed in pushing one out of the s-p bands. Therefore, we must conclude that either the surface state exists and the LCAO method is incapable of reproducing it[19] within what we consider to be a reasonable range of surface parameters or that it does not exist and the interpretation of the experimental data is in error.

We consider first the possibility that our method is deficient. In our original Li calculation[20] we found a surface state near the middle of a gap very similar to this one. Upon making the calculation self-consistent[21] that surface state was pulled down to just above the bottom of the gap while another surface state was pulled out of the upper continuum to replace it in the middle of the gap. The change in potential which induced these surface state shifts was large, our original Li potential having been exceedingly poor. The three good nearly-free-electron metal surface potentials[21] or pseudopotentials[22,23] we know of all have the property of having a planar average through the surface plane of atoms that differs from that through a bulk plane by much less than the range of surface parameters used in this calculation. We must mention that Kar and Soven[24] using the Korringa-Kohn-Rostoker method with a muffin-tin potential with no (x, y) dependence outside of the inscribed spheres have found the copper surface state at the bottom of the gap. Thus, although Li appears to have a surface state at the bottom of the gap and one can be calculated to be there in copper with the appropriate potential, we believe that our parameters span the range within which it is reasonable to believe the self-consistent copper potential exists and that a fully self-consistent copper potential would not produce such a surface state.

We now examine the photoemission data of Gartland and Slagsvold to see if the large peak 0.4 eV below E_F in the forward direction can be interpreted as arising from bulk states rather than surface states. The fact that upon ion bombardment this peak slightly widens but does not disappear whereas a lower energy bulk peak does disappear, we take as a strong indication that this peak does not arise from a surface state. If the surface scattering is so large as to wipe out the bulk peak which exists over a large range of angles it would certainly have a much larger effect on the "surface state" peak which existed over only a small range of angles before ion bombardment, if indeed the ion bombardment did not completely destroy the "surface state." The fact that oxygen exposure destroys this peak is consistent with the peak arising from either bulk or surface states according to the work of Wagner and Spicer[25] who found that the total yield arising from states between E_F and 0.7 eV below E_F in polycrystaline copper was decreased with oxygen exposure. They attributed this to oxygen diffusing into the bulk.

We note that although Burdick's[9] band calculation places $L_{2'}$ 0.6 eV below E_F, Snow's[26] more-recent calculation places it only 0.4 eV below. This result is consistent with the work of Berglund and Spicer[27] who attribute structure in the energy distribution curves of photoemitted electrons from cesiated copper as due to the $L_{2'}$ level lying 0.35 eV below E_F. They also interpret the deviation of the yield curve from the Fowler curve for copper on n-type GaAs (obtained by Mead and Spitzer) as being due to a high density of states located 0.35 eV below E_F. If $L_{2'}$ lies 0.35 eV below E_F then there can be no surface state 0.4 eV below E_F. To try to interpret the structures discussed by Berglund and Spicer as arising from a surface state, one would have to assert that this surface state exists at essentially the same energy at (111) Cu-air, polycrystalline Cu-Ce, and Cu-GaAs interfaces!

Thus although the question of the location of the s-p surface state in copper remains open, we believe that the weight of the evidence indicates that it does not lie below E_F. This leaves the cause of the large peak in the photoemission data unexplained. Kliewer[28] has suggested that nonlocal effects will greatly enhance the photoyield in the forward direction for p-polarized light and the peak of Gartland and Slagsvold did occur only for p-polarized light. However, Kliewer's enhancement occurs only when the frequency of the incident light exceeds the plasma frequency which was not the case for Gartland and Slagvold's experiment.

One of us (L. K.) would like to thank Professor William Spicer for an invaluable discussion concerning the photoelectric data.

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[12] See E. B. Caruthers, L. Kleinman, and G. P. Alldredge [Phys. Rev. B 9, 3330 (1974)] for the crystal structure, reciprocal-lattice vectors, Brillouin zone, symmetry points, and group theory of this face.

[13] Surface states occur in nearly degenerate pairs, having maxima on the two faces and going to a minimum or to zero in the center. In an infinitely thick film these states become exactly degenerate and can be combined to form one state localized on each surface. The degree to which the degeneracy is split depends on the overlap of the states localized on opposite faces. Since we are working with a 30-layer film, visible splitting occurs only when the decay length is very long.

[14] I. Tamm, Z. Phys. 76, 849 (1932); and Phys. Z. Sowjetunion 1, 733 (1932).

[15] W. Schockley, Phys. Rev. 56, 317 (1939).

[16] Since this surface state is pulled out of the bottom of the lowest $\bar{\Sigma}_2$ band, it is not in a gap and perhaps can rigorously be said to be a Tamm state.

[17] In this case there is a pair of surface states, $\bar{\Gamma}_1^{\pm}$, which connect to two $\bar{\Sigma}_1$ surface states and to one $\bar{T}_1$ and one $\bar{T}_2$ surface state. As can be seen from the compatibility relations in Table II of Ref. 4, the degenerate pairs referred to in Ref. 13 will be $\bar{T}_1$, $\bar{T}_2$ pairs along $\bar{T}$ and $\bar{T}_1'$, $\bar{T}_2'$ pairs along $\bar{T}'$.

[18] We count the number of states from the top or bottom of the band to verify whether a surface state appearing after a potential shift is the same one that was there before the shift.

[19] As discussed in Ref. 6, even though the LCAO expansion yields an incorrect surface charge for *s-p* states, it does yield eigenvalues in agreement with those calculated from orthogonalized plane wave expansions as long as one is working in the energy range over which the bulk bands have been fit. We obtained our parameters by fitting the bulk energy bands up to energies 0.19 Ry above the vacuum level.

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