al modes shown in Fig. 1, but the characteristic wave-vector scale is increased from 1 $cm^{-1}$ to a few hundred inverse centimeters. In particular, at long wavelengths, the lowest transverse mode will have a frequency reduced from the bare phonon frequency $\omega_t(q)$ by the square root of $m^*/m$.

It should be noted that the calculations in the present paper have assumed small displacements of the electrons. At high driving powers, the electron displacement may be large compared to the lattice constant and the electron velocities may be large compared to the phase velocities of the ripplons. Under such conditions, the electrons will leave the ripplons behind, and excitations may be seen at the bare phonon frequencies $\omega_l(q)$ and $\omega_t(q)$.

We are deeply indebted to Dr. C. C. Grimes for discussions of the emerging experimental data and of the possible theoretical explanations, throughout the course of this investigation. This work has been supported, in part, by the National Science Foundation through Grant No. DMR-77-10210 and a graduate fellowship to one of us (D.S.F.).

[1]R. W. Hockney and T. R. Brown, J. Phys. C 8, 1813 (1975); D. J. Thouless, J. Phys. C 11, L189 (1978); C. C. Grimes, Surf. Sci. 73, 379 (1978).

[2]P. M. Platzman and H. Fukuyama, Phys. Rev. B 10, 3150 (1974); L. A. Bonsall and A. A. Maradudin, Phys. Rev. B 15, 1959 (1977).

[3]C. C. Grimes and G. Adams, preceding Letter [Phys. Rev. Lett. 42, 795 (1979)].

[4]In a real experimental geometry, the plasmon dispersion is modified by the presence of the capacitor plates and is linear at wavelengths large compared to the helium depth [C. C. Grimes and G. Adams, Surf. Sci. 58, 292 (1971)].

[5]P. M. Platzman and G. Beni, Phys. Rev. Lett. 36, 626, 1350(E) (1976); V. B. Shikin and Yu. P. Monarkha, J. Low Temp. Phys. 16, 193 (1974).

[6]For $q < 40$ $cm^{-1}$, the renormalized shear frequency is less than the linewidths in GA ($\cong 1$ MHz). For $q > 500$ $cm^{-1}$, the electron motion is primarily in the highest mode with $\omega_l(q) > \omega_d \cong 6 \times 10^8$ $sec^{-1}$. On physical grounds, we expect the cutoff $q_c$ to lie between these limits.

[7]Yu. P. Monarkha and V. B. Shikin, Zh. Eksp. Teor. Fiz. 68, 1423 (1975) [Sov. Phys. JETP 41, 710 (1976)].

# Occupied Surface-State Bands in *sp* Gaps of Au(112), Au(110), and Au(100) Faces

P. Heimann and H. Miosga
*Sektion Physik der Universität München, D-8000 München 22, Federal Republic of Germany*

and

H. Neddermeyer
*Institut für Experimentalphysik der Ruhr-Universität, D-4630 Bochum, Federal Republic of Germany*

(Received 27 November 1978)

We have identified occupied surface-state bands from angle-resolved photoelectron energy distribution curves of Au(112), Au(100), and Au(110), which are located in *sp* gaps of the projected bulk band structure. An approximate criterion for their possible experimental existence is given.

It is now experimentally well established that the (111) faces of the noble metals exhibit occupied surface states in the center of the two-dimensional Brillouin zone (2D BZ).[1-6] Dispersion of the surface-state bands has been determined by angle-resolved photoelectron spectroscopy showing that these surface states exist in the gap at point $L$ of the bulk band structure. The energetical minimum of these surface-state bands occurs in the [111] direction, around which a fairly symmetrical distribution in $\vec{k}$ space is observed.

Recently Williams *et al.* investigated a (211) face of Cu,[7] which consists of three-atom terraces of (111) orientation separated by one-atom steps of (100) orientation $\{(S)\text{-}[3(111)\times(100)]$ structure$\}$. They found surface states pointing into the [111] direction of the (211)-oriented single crystal from which they concluded that these surface states are associated with the (111) terraces of Cu.

In the present Letter we report on photoemission results from a (211) face of Au, which cannot be explained by the interpretation given in Ref. 7. Instead, the occurrence of surface states on the (211) face of Au appears as a general property of the *sp* gap around the $L$ point of the three-

 

dimensional Brillouin zone (3D BZ) and is not associated with the arrangement of (111) steps. We demonstrate that similar surface states exist for the (110) and (100) faces. The necessary condition for the existence of these surface states is that the projected bulk band structure has a gap extending below $E_F$ for the face in question. An approximate criterion for the occurrence of such a gap is that the line $\vec{k}_{\parallel}$ = const must lie entirely inside the (111) neck of the Fermi surface; otherwise there are bulk band states extending to $E_F$ for this $\vec{k}_{\parallel}$. Since the range of $\vec{k}_{\parallel}$ thus defined is not in the center of the 2D BZ, in general, and surface states are expected to occur at fixed values of $\vec{k}_{\parallel}$ the angles of emission from these surface states must change with photon energy. This fact is actually seen in our results.

Our observation seems to be important in several respects. Most interesting is certainly the possibility to observe surface states of the same gap in different directions. Differences in position and dispersion of the surface-state bands might then reflect differences in the projected bulk band structure and the potential associated with each surface. From an experimental point of view the occurrence of surface states in photoemission spectra of clean metal single crystals might be more general than was believed previously, especially for low photon energies, where the intensity of surface-state emission may become comparable with the bulk features of the angle-resolved photoelectron-energy distribution curves (AREDC's).[3,8]

The AREDC's have been measured by means of a photoelectron spectrometer,[9] which has an energy and angle resolution of better than 0.06 eV and 2°, respectively. A low-energy electron-diffraction (LEED) system allows the control of surface geometry. From Auger spectra we estimated the contamination of the clean surface to be at most a few percent of a monolayer. Special care was taken for the preparation of the (112) orientation to obtain a smooth surface. We did not attempt to determine the surface geometry of Au(112) in detail since the photoemission data did not show irregular behavior which might be related to the existence of Au(111) terraces, whose existence could be qualitatively deduced from the LEED pattern. The angular distributions corresponding to states of the $(1\bar{1}0)$ mirror plane were obtained by rotating the sample around an axis, keeping the angle between incident light[10] and electron takeoff always constant. Since at present we are only interested in the existence of surface states and not in their intensity, variations of the angle of incident light are not considered here.

Some of our results are displayed in Figs. 1(a)–1(d), 2(a), and 2(b), which show AREDC's in the vicinity of the Fermi level $E_F$ for different Au single crystals and photon energies. In each family of AREDC's, where the polar angle $\theta$ and consequently $\vec{k}_{\parallel}$ has been varied, a peak near $E_F$ emerges at a certain polar angle on top of the steplike background of emission from bulk $sp$, bands, becomes more intense with increasing $\theta$, and finally disappears on further increasing $\theta$. As will be shown below these peaks always correspond to occupied surface states located in the $sp$ gap.

A careful analysis of the AREDC's from Au(112) [see Figs. 1(d), 2(a), and 2(b)] shows that the intensity and energetical behavior of the conspicuous peak is symmetrical around $k_{\parallel} = 0.445$ Å$^{-1}$ for all photon energies. In Fig. 2(c) the normalized intensity of this peak is plotted for different

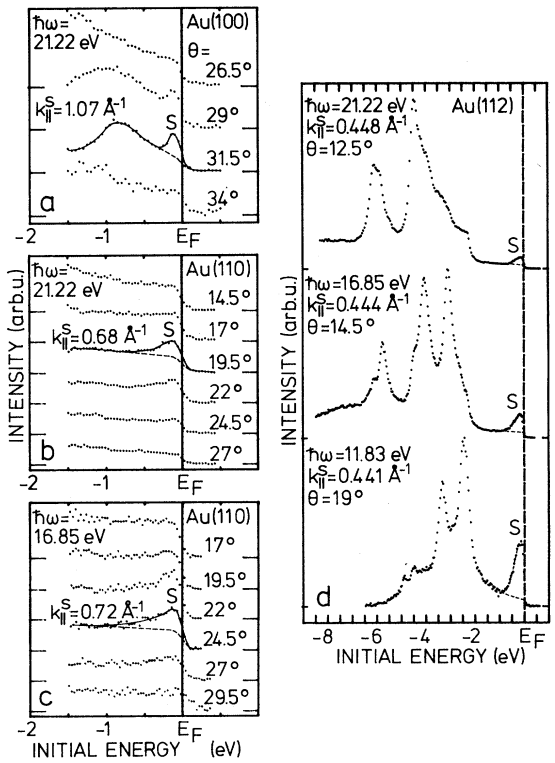


FIG. 1. AREDC's from Au single crystals using different photon energies. The photoelectrons have been measured in the $(1\bar{1}0)$ mirror plane. The polar angle is referred to the surface normal. The wave-vector components parallel to the surface ($\vec{k}_{\parallel}^S$) of transitions from surface states (labeled $S$) are also given.

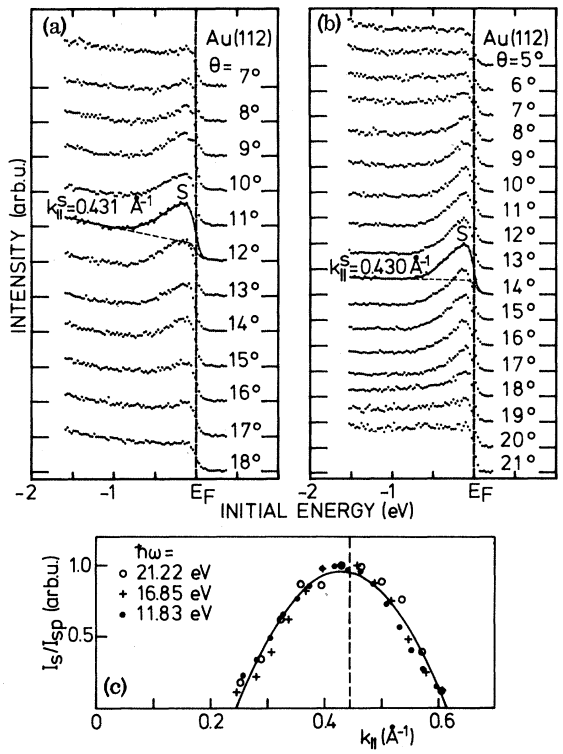


FIG. 2. (a) AREDC's from Au(112) using a photon energy (a) of 21.22 eV and (b) of 16.85 eV. (c) Intensity ratio between surface-state emission and bulk $sp$-band transitions [indicated by the dashed lines in (a) and (b) vs $\vec{k}_{\parallel}$. The dashed line corresponds to the boundary of the 2D BZ of Au(112).

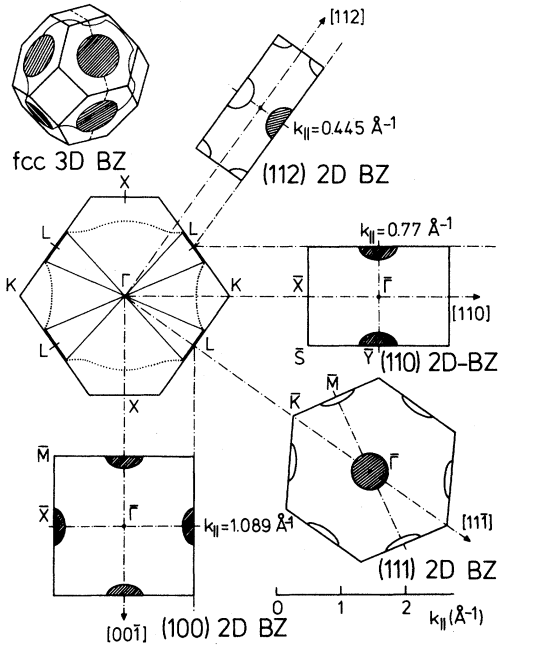


FIG. 3. 3D BZ and 2D BZ's of Au. The perspective drawing of the 3D BZ (upper left) shows the $L$ necks of the Fermi surface by the shaded areas (not drawn to scale). The dotted lines schematically indicate the cut through the Fermi surface. In the 2D BZ's the projection of the $L$ neck is shown by the elliptical and circular lines, respectively. The shaded areas included by these lines show the regions in $\vec{k}_{\parallel}$ space, where we found occupied surface states. Values for $\vec{k}_{\parallel}$ of zone boundaries are also given.

photon energies versus the parallel component of the wave vector.[11] The measured values have been fitted with a parabola. The intensity variation is very similar for each photon energy and only dependent on $\vec{k}_{\parallel}$. Therefore one necessary condition to assign the observed features as due to emission from surface states is fulfilled. As a consequence the maximum intensity is observed under different polar angles, when different photon energies are used [Fig. 1(d)]. For Au(112), emission from these states does not point into the [111] direction, in general, and therefore cannot be explained by surface states of the (111) terraces. For Au(110) a similar peak is emitted for $k_{\parallel} \cong 0.7$ Å$^{-1}$ and for Au(100) a peak near $E_F$ appears around $k_{\parallel} \cong 1.07$ Å$^{-1}$ for a photon energy of 21.22 eV.

To understand the occurrence of these peaks as being due to surface states we have to consider projections of the bulk band structure on the corresponding 2D BZ's and to examine in which range of $\vec{k}_{\parallel}$ the $sp$ gap appears in the different directions. This has approximately been done in Fig. 3, where a cut through the 3D BZ is shown together with 2D BZ's of the orientations used in the present measurements.[12] The $sp$ gap in the 3D BZ is indicated by the heavy lines centered around the $L$ points. It is evident from Fig. 3 that this gap appears in various parts of the individual 2D BZ's. For the possible existence of surface states we have only to consider values of $\vec{k}_{\parallel}$ falling into one of these areas and once knowing the photon energy are able to determine the angle, where emission from surface states can be expected. The values for $\vec{k}_{\parallel}$ at the boundaries of the 2D BZ's are included in Fig. 3. The agreement with the experimental values of $\vec{k}_{\parallel}$, which approximately correspond to emission from the zone boundaries (as given by the AREDC's) is remarkably good.

We have also attempted to identify surface states in the corners of the 2D BZ of Au(112) but could not definitely conclude on their existence because of an overlap with bulk transitions. Emis-

sion from surface states on the opposite side of the surface normal from Au(112) in the (1$\bar{1}$0) plane has also not been observed, which can eventually be explained by the opposite group velocity of the bulk states leading to this gap. It has to be noted that the *sp* gap of Au(112) is not absolute since on the opposite side of the 3D BZ states up to $E_F$ are occupied. The surface states of Au(112) are therefore, in fact, surface resonances contrary to those of Au(100) and Au(110), where absolute gaps exist in the vicinity of $E_F$ at $\bar{X}$ and $\bar{Y}$, respectively.[13]

Another criterion for the identification of surface states of Au(112) may be the intensity variation of the observed peaks as a function of photon energy [Fig. 1(d)]. The intensity ratio to the *d*-electron transitions closely follows the $\hbar\omega$-dependent photoionization cross section of the *sp* surface state on Cu(111).[3,8]

Sensitivity to gas adsorption of the surface-state emission has not been investigated systematically. However, accidental contamination of the surface did not show drastic effects relative to those of bulk features, which also showed intensity reductions due to an increase of diffuse scattering.

We have attempted to determine the dispersion of the Au(112) surface-state band. However, because of overlap with bulk emission from *sp* bands the results are not very reliable. At the zone boundary the surface-state band is observed at an initial energy of $-0.15$ eV and probably showing a weak dispersion towards $E_F$, when $\vec{k}_{\parallel}$ approaches the center of the 2D BZ.

In summary, we have demonstrated that the *sp*-gap surface states of Au previously seen on the (111) face are also observed for other orientations of the single crystal. It has to be concluded that emission from surface states may be always possible if the parallel component of the wave vector falls into this gap of the projected band structure. We believe that a similar behavior should be considered for every material exhibiting surface-state bands in nearly-free-electron energy gaps.[14]

We acknowledge a stimulating discussion with Dr. J. Pendry, which led to this investigation. We thank Professor J. Hermanson for carefully reading the manuscript and valuable comments. Support by the Deutsche Forschungsgemeinschaft through special funds of "Sonderforschungsbereich 128" is gratefully acknowledged. We are indebted to Professor J. Peisl for making possible the use of the facilities of the Institute.

[1]P. O. Gartland and B. J. Slagsvold, Phys. Rev. B 12, 4047 (1975).

[2]P. Heimann, H. Neddermeyer, and H. F. Roloff, J. Phys. C 10, L17 (1977).

[3]J. A. Knapp, F. J. Himpsel, and D. E. Eastman, to be published.

[4]P. Heimann, thesis, University of Munich, 1977 (unpublished).

[5]Z. Hussain and N. V. Smith, Phys. Lett. 66A, 492 (1978).

[6]G. V. Hansson and S. A. Flodström, Phys. Rev. B 17, 473 (1978), and 18, 1572 (1978).

[7]R. S. Williams, P. S. Wehner, S. D. Kevan, R. F. Davis, and D. A. Shirley, Phys. Rev. Lett. 41, 323, 520(E) (1978).

[8]J. B. Danese and P. Soven, Phys. Rev. B 16, 706 (1977).

[9]H. Neddermeyer, P. Heimann, and H. F. Roloff, J. Phys. E 9, 756 (1976).

[10]Resonance radiation from Ar, Ne, and He was used.

[11]For details of the numerical analysis see P. Heimann, H. Miosga, and H. Neddermeyer, to be published.

[12]For the construction of the (112) 2D BZ we have assumed a two-dimensional periodicity of the lattice according to the outermost atomic layer.

[13]Š. Pick and M. Tomášek, Czech. J. Phys. B 28, 781 (1978).

[14]Recently, M. W. Holmes and D. A. King have observed on a W(110) face for a polar angle of 65° a feature near $E_F$ which was sensitive to hydrogen adsorption [Proceedings of the First European Surface Science Conference, Amsterdam, The Netherlands, 5-9 June 1978 (unpublished)]. This feature can obviously be explained by emission from surface states, which exist in the same gap as is responsible for the surface states appearing normal to W(100). Results of G. V. Hansson and S. A. Flodström [Phys. Rev. B 18, 1562 (1978)] on different Al faces further demonstrate this general existence criterion for surface states. We also believe that the emission from Cu(211) (Ref. 7) is associated with the *sp* gap projected on the (211) face. In our opinion, the observation of Williams *et al.* (Ref. 7) that they see the surface states of Cu(211) pointing into the [111] direction depends on the photon energy. The effects should be comparable with our measurements of Au(112) [Fig. 1(d)], where we also see surface-state emission pointing into the [111] direction for a photon energy of 11.83 eV. Finally, we found an analog behavior for Cu(110) and Ag(100).