PHYSICAL REVIEW B VOLUME 17, NUMBER 10 15 MAY 1978

Free-electron final-state model and angle-resolved photoemission from a Ag(111) surface

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(Received 12 August 1977)

Angle-resolved photoemission spectra from a Ag(111) surface exhibit a strong dependence on photon energy for $h\nu$ extending from 11.6 to 40.8 eV that clearly demonstrates the nonvalidity of the one-dimensional density-of-states model. Trends in the positions of the peaks in the observed spectra are described within the accuracy of our computations by the initial-state band structure and a free-electron-like final state. No evidence is found for surface states nondegenerate with those of the bulk or narrowing of the bulk bands in the vicinity of the surface.

I. INTRODUCTION

Two simplified models have been proposed for which the interpretation of the angle-resolved photoemission spectra can be made easily in terms of the initial states. The first, the one-dimensional density-of-states model (henceforth referred to as ODDOS model) occurs when the density of final-state bands becomes very large so that there is a continuum of states available along any axis of emission into which the initial state can make an optical transition.[1,2] This limit can also be brought about by a destruction of the component of $\vec{k}$ perpendicular to the surface by an elastic escape depth on the order of an interatomic spacing.[1,2] In these cases, the spectra are expected to reveal the one-dimensional density of states associated with the parallel component of $\vec{k}$ along the surface. Aside from the effects of photoionization cross sections, the spectra ought to depend only upon $\vec{k}_{\parallel}$ and not the exciting photon energy. While this model is believed to be most applicable to the x-ray photoelectron spectroscopy (XPS) regime, recent experimental results have indicated that it works well in the ultraviolet photoelectron spectroscopy (UPS) regime for PbS,[3] Bi,[4] and for the (110) face of Ag.[5]

Another simplifying case occurs when the initial states make direct $\vec{k}$ conserving transitions into final states that are free-electron-like.[6-8] [We shall refer to this case as the free-electron-like final-state model(FEFS)]. In any given direction of emission only a single point in $\vec{k}$ space contributes to the spectra at a given energy. Since the energy of the final state is given by a free-electron dispersion, the initial-state band structure is easily deduced from the angle-resolved kinetic-energy distributions if the inner potential is known. Previous angle-averaged photoemission experiments on the noble metals have indicated that the effects of $\vec{k}$ conservation are strong up to ~40 eV, where the spectra appear to resemble the total density of initial states.[9-11] Recent experimental results[12,13] have shown modulations with $h\nu$ which suggest that the FEFS model might apply to the angle-resolved photoemission spectra of the noble metals for photon energies extending as high as a few hundred electron volts.

In a previous paper,[14] we demonstrated that the matrix elements computed from plane-wave final-state wave functions fail to predict the strength of the peaks in the normal emission from the Ag(111) surface. We also stated that atomic cross sections such as are given by orthogonalized and augmented plane waves (OPW's and APW's) seem to do a better job of describing the spectra. However, the conclusion that the OPW's or APW's in the final state must be strongly mixed for $h\nu \leq 26.9$ eV is in error due to an underestimation of the strength of mixing of the d orbitals in the initial-state wave functions. We have traced the failure of the plane-wave final state to describe the photoionization step to its inability to follow the curvature of the true final-state wave function in the vicinity of the atomic core. However, the momentum conservation and transport processes depend more on the phase variation of the wave function from site to site, and thus, the plane wave still might be able to describe this feature of the true final state adequately well.

In this paper, we present more detailed angle-resolved photoemission results than have been presented before[5,14-17] on an Ag(111) surface in the energy regime $h\nu < 40.8$ eV. Our results show that there is a strong dependence of the shape of the angle-resolved spectra upon the photon energy up to 40.8 eV. Within the errors inherent in our initial-state band structure, the position of the peaks observed in over 180 spectra can be described by the FEFS model. We find no reproducible evidence for surface states nondegenerate

with those of the bulk, nor do we find consistent evidence for the narrowing of the local density of states at the surface.[18-20]

Since the basic theory of angle-resolved photoemission has been discussed elsewhere, we briefly state only the points relevant to our present work.

As the photon energy increases from 11.6 to 40.8 eV, the following changes are expected to occur.[1,2,18] (i) The mean free path of the electron becomes shorter, increasing the surface sensitivity and weakening the conservation of $k_\perp$, the component of electron momentum perpendicular to the surface. (ii) The nature of the optical transitions changes from $d \rightarrow p$ for $h\nu < 20$ eV to $d \rightarrow f$ for $h\nu > 20$ eV.[21]

As θ the polar angle of emission increases, the following changes occur. (a) The component of the electron momentum parallel to the surface increases according to

$$k_\parallel = k_0 \sin\theta , \tag{1}$$

where k_0 is the magnitude of free momentum of the electron in the vacuum. (b) The uncertainty in $k_\perp$ increases according to

$$k_\perp = \frac{1}{l \cos\theta_i} , \tag{2}$$

where θ_i is the internal angle of emission, and l is the mean free path of the photoelectron.

According to the FEFS model, the component of momentum inside the solid perpendicular to the surface is

$$k_\perp = (k_i^2 - k_\parallel^2)^{1/2} , \tag{3}$$

where k_i is magnitude of the momentum of the photoelectron inside of the solid, which is given by

$$k_i^2 = k_0^2 + 2mW/\hbar^2 , \tag{4}$$

where W is the inner potential. When momentum is rigorously conserved in the photoemission process, the positions of the peaks in the spectra are determined by the energy eigenvalues of the initial states at the same value of $\vec{k}$ as the final state.

The initial-state d band structure was calculated in the tight-binding approximation using a basis set consisting of five d orbitals, one s orbital, and two spin directions. The parameters were adjusted to bring our band structure into good, but not perfect, agreement with those of Smith[22] and of Christensen.[23] The energy eigenvalues were found at the $\vec{k}$ values specified by the free-electron formulas given above for emission from an initial state having an energy corresponding to the middle of the d bands and $W = 12.3$ eV.

II. EXPERIMENT

The experiments were performed on an angle-resolved photoelectron spectrometer (Vacuum Generators ADES 400) which features a spherical capacitor analyzer mounted on a rotatable table. The sample is mounted vertically and can be rotated in the horizontal plane in order to change the angle of incidence of the excitation sources or about an axis normal to its surface to change the azimuthal angle of emission. The polar angle of the detected electrons emitted from the sample was altered by rotating the analyzer in the horizontal plane.

A spark-cut Ag(111) sample was mechanically polished and etched lightly in nitric acid prior to being inserted into the vacuum chamber. The sample was repeatedly cleaned by argon-ion bombardment and heated by electron-beam bombardment to near the melting point. The quality and orientation of the surface was checked by low- and medium-energy electron diffraction (LEED and MEED) (5 keV). No contamination of the surface was detected with x-ray photoemission. A specially constructed cold cathode discharge lamp mounted on an external $2\frac{3}{4}$-in. flange[24] was operated with Ar, Ne, and He to provide photons of energy $h\nu$ = 11.6, 16.8, 21.2, 26.9, and 40.8 eV at an angle of incidence of 60°. The angular acceptance of the analyzer was ±2° and the energy resolution was 0.15 eV, except for $h\nu = 40.8$ eV where it was 0.3 eV. Typical photoelectron intensities at normal angles of emission of 3×10^4 counts/sec were achieved on the d-band peaks for all photon lines except $h\nu = 40.8$ eV, for which the count rate was 1×10^4 counts/sec. Also, some spectra were taken with radiation emitted from a discharge-lamp monochromator combination[24] that provides an order of magnitude more intensity and better resolution than the combination described earlier.[25] Intensities of 2×10^4 on the d-band peaks were obtained for monochromatrized Ne II radiation with an energy resolution of 0.3 eV. Intensities of 2×10^3, 5×10^2, and 10^2 counts/sec were also obtained for the 30.4, 34.4, and 38.8 eV components of the Ne II spectra.

An overview of the photoelectron spectra of electrons emerging in the ΓLW plane taken for $h\nu$ = 26.9 eV (monochromatized Ne II) and a few polar angles is shown in Fig. 1. The structure in the spectra at first changes quickly but then more slowly as the polar angle of emission increases. The secondary tail shows little structure except near the work function cutoff, indicating that neither the density of final states nor the excape process is contributing much on its own to the angular dependence of the elastically emitted electrons.

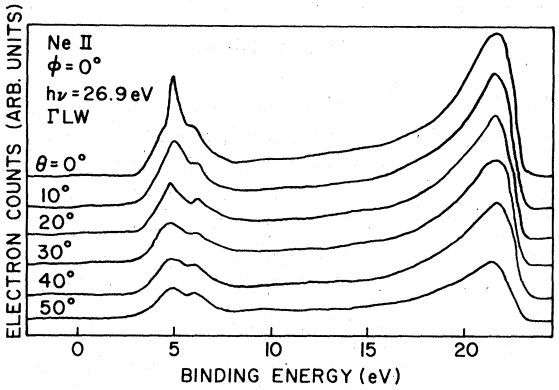

FIG. 1. Photoemission spectra from the ΓLW plane obtained with monochromatized Ne II radiation ($h\nu = 26.9$ eV).

In the remaining figures we present representative photoemission spectra emitted in the ΓLK, ΓLW, and ΓLU planes. We found that the spectra exhibited a similar threefold rotational symmetry that others have noted earlier for the noble metals[8,26-28] and we therefore do not show similar azimuthal data. The vertical lines in the spectra show the peak positions predicted by our tight-binding initial-state band structure and the FEFS model.

The spectra obtained with Ar I ($h\nu = 11.6$ eV) radiation for the ΓLUX plane are shown in Fig. 2. The peak in the s-p band region that is the most intense for normal angles of emission grows weaker and moves slowly with increasing polar angle of emission. The peak occurring near the Fermi enery for $\theta \sim 60°$, which is very similar to the peak observed for emission normal to the (100) surface,[17] is accounted for by the FEFS model. The spectra originating from the d bands do not change shape very much with the angle of emission, in accord with the FEFS model.

The Ne I spectra in Figs. 3–5, show trends with the angle of emission similar to those reported earlier.[26-28] The most dramatic change in the spectra from the ΓLX and ΓLK planes is the rapidly moving s-p band, which emerges through the d bands at $\theta \sim 15°$. This band goes above the Fermi energy for $\theta = 50°$, but retreats below the Fermi energy for the ΓLUX plane at higher angles, in agreement with the behavior predicted by the FEFS model. The d-band portions of the spectra for the ΓLW and ΓLK planes do not show a particularly strong variation with angle. The most notable change is that the peak at 7.1 eV becomes more intense as the emission angle increases. For the ΓLW and ΓLU planes, the peak at 4.5 eV splits into two distinct peaks, the highest-energy peak becoming as narrow as 0.3 eV.

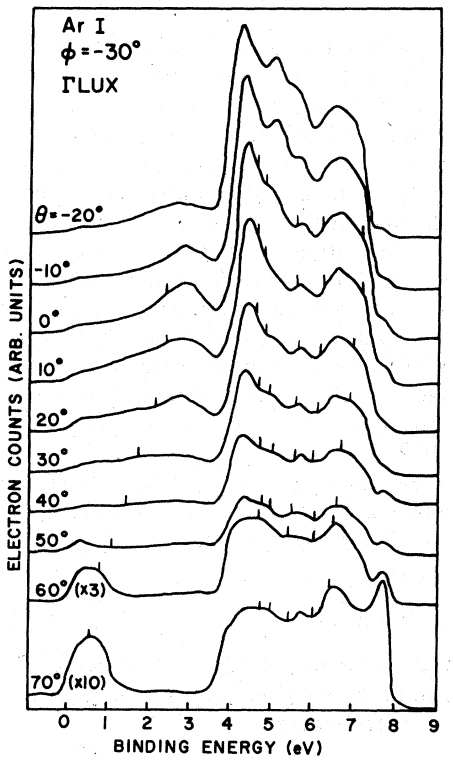

FIG. 2. Photoemission spectra from the ΓLU plane obtained with Ar I ($h\nu = 11.6$ eV) radiation.

The data for $\theta = 80°$ from the ΓLU plane are very similar to those emitted normal to the (100) face at the same photon energy.[16] Also, we note that the data for the ΓLK plane at high angles are very similar to those obtained for emission normal to the (110) face.[16] The clearest prediction of the FEFS model concerning the d bands is the evolution of the spectra for the ΓLK plane with increasing θ into a simple two-peak structure.

A conspicuous feature of the He I spectra for the ΓLU plane in Fig. 6 is the occurrence of two sharp peaks which are separated by ~0.6 eV for $\theta \sim 25$–$40°$. We found that the strength of these sharp peaks decreased by nearly 50% at 750 °C, indicating that they are features due to direct $\vec{k}$ conserving transitions. The emission from the s-p-like band is much weaker than that found at lower photon energies.

The spectra taken for Ne II ($h\nu = 26.9$ eV) in Fig. 7 show structure similar to those taken at lower photon energies. The He II photon spectra, which is split into two lines about 0.6 eV apart, account for some additional broadening of the spectra and for some additional structure when the peaks are sharp. A large number of final-state bands and the decreasing mean free path of the photoelectron introduces additional broadening. Part of the structure observed in the region of the s-p-like bands is a

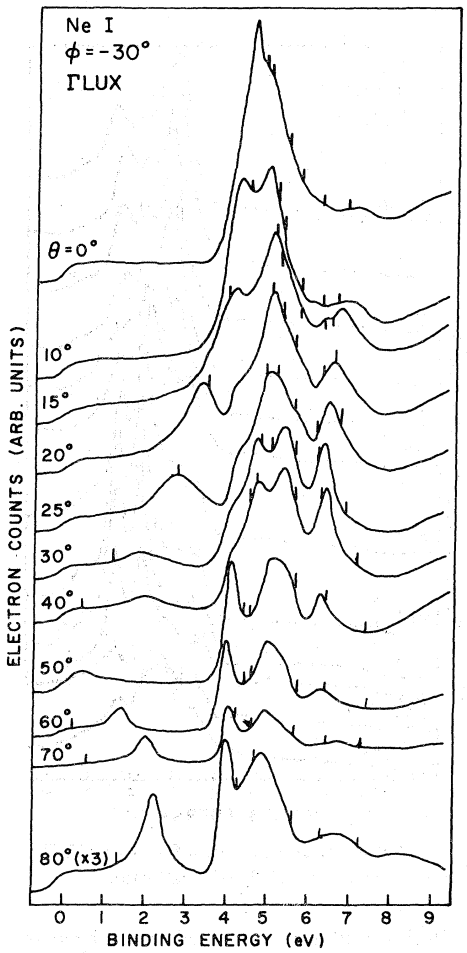

FIG. 3. Photoemission spectra from the ΓLU plane obtained with Ne I ($h\nu = 16.9$ eV) radiation.

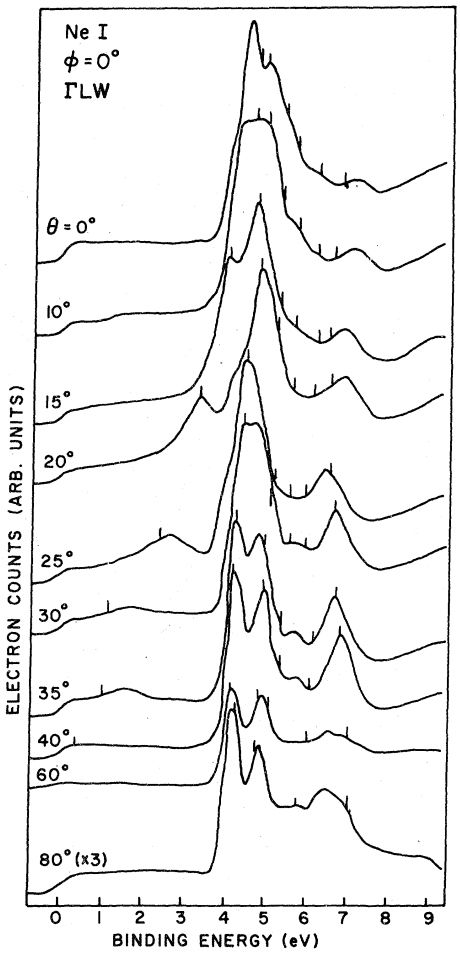

FIG. 4. Photoemission spectra from the ΓLW plane obtained with Ne I ($h\nu = 16.9$ eV) radiation.

replication of the d-band spectra due to the higher-energy satellite lines at $h\nu = 30.4$ eV.

The He II spectra shown in Fig. 8 exhibit considerably less structure than the spectra obtained at lower photon energies. The 0.3-eV energy resolution, the shorter mean free path of the electron, and the worse $\vec{k}$-space resolution are partly responsible for the broadening of the spectra. In contrast to the Ne II spectra, the He II spectra for the ΓLW plane show two broad peaks which move away from one another as the polar angle of emission increases and then begin to move back together again for $\theta > 55°$. The FEFS model reveals that the separation of the two-peak structure roughly follows the dispersion of the two sets of d bands along the Σ axis of the Brillouin zone. All bands appear to contribute to the spectra with comparable strengths at this photon energy, suggesting that the photoionization cross-section effects are not as important as they are at lower photon energies. Similar observations have been made for the angle-averaged photoemission of Ag.[9-11]

III. DISCUSSION

A. FEFS and ODDOS models

In this section, we wish to examine whether the FEFS or ODDOS model provides an adequate explanation for the several features observed in our spectra. Let us first dispose of the ODDOS model.

The ODDOS model predicts that the spectra will exhibit angular variations, but that they ought to have essentially the same shape independent of photon energy for a given $k_{\parallel}$; clearly this model is not adequate for describing the observed spectra for all photon energies, since the spectra from a given plane show a strong dependence upon the photon energy.

A comparison of the spectra emitted from the ΓLK and ΓLU planes provides a good measure of the extent to which either of the FEFS or the

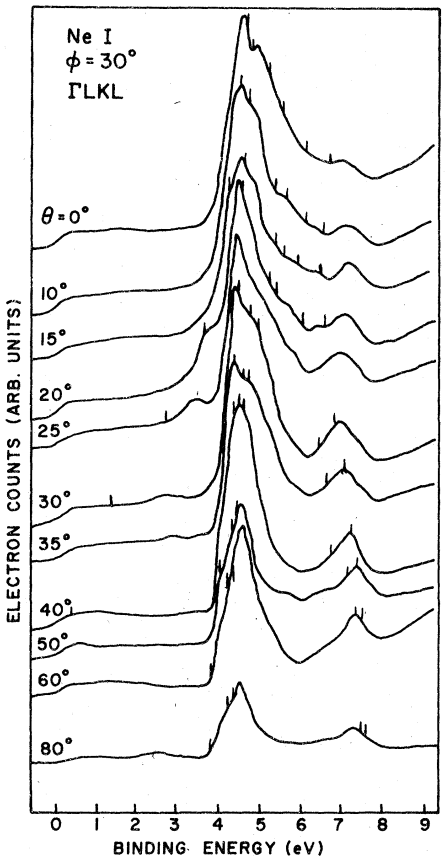

FIG. 5. Photoemission spectra from the Γ*LK* plane obtained with Ne I ($h\nu = 16.9$ eV) radiation.

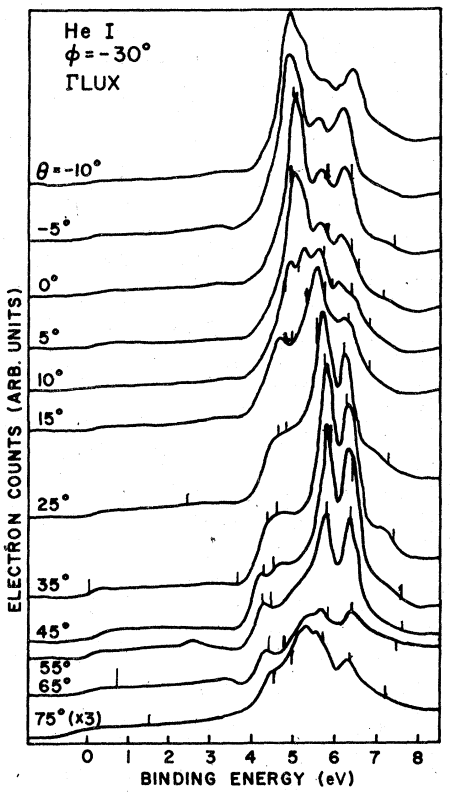

FIG. 6. Photoemission spectra from the Γ*LU* plane obtained with He I ($h\nu = 21.2$ eV) radiation.

ODDOS model is valid. In the limit that the ODDOS model holds, the spectra should exhibit the sixfold rotational symmetry of the Brillouin zone projected onto a plane normal to the [111] axis. A sixfold rotational symmetry requires that the emissions from the Γ*LK* and Γ*LU* planes be identical. The spectra emitted from these planes for $h\nu = 16$ eV are distinctly different, indicating the importance of few or one final-state bands and the maintenance of a strong conservation of $\vec{k}_\perp$. As the photon energy increases to $h\nu = 40.8$ eV, the spectra from the two planes tend to become more similar, although the distinct differences observed suggest that the mean free path of the photoelectron is definitely longer than an interatomic spacing.

An overview of all of the spectra presented shows that the FEFS model is reasonably successful in predicting the trends in the peak positions. (As we shall show in a forthcoming paper,[29] the FEFS model, combined with atomic dipole selection rules, provides a good model for describing the peak shapes and intensities.) The usually small (0.3-eV) discrepancies in locating peak positions are attributed to inadequacies of our sample tight-binding scheme to describe the true initial-state bands and the plane wave to describe the true final-state band. Inspection of the band structures of Smith[22] and of Christensen[23] suggests that the free-electron final state is the least accurate near the Fermi energy, where large gaps exist at the edge of the zone.

A peak from the *s*-*p* band for $h\nu = 21.2$ eV for $\theta = 0°$ occurs at nearly the same position as in the Ar I spectra. The FEFS model shows that at $h\nu = 21.2$ eV, it should have receded even more deeply into the *d* bands than for the Ne I spectra. The occurrence of this weak bump cannot be explained by either the FEFS or the ODDOS model, and it is therefore due to an optical transition that is into a band other than the free-electron final state. Inspection of the free-electron band structure suggests that this peak might be due to contributions from the third, fourth, and fifth free-electron bands along the Λ axis. This small peak is one of the few violations of the FEFS model that we have been able to identify.

B. Surface states and surface narrowing

It has been suggested by several workers that surface states might be present on *d*-band metals

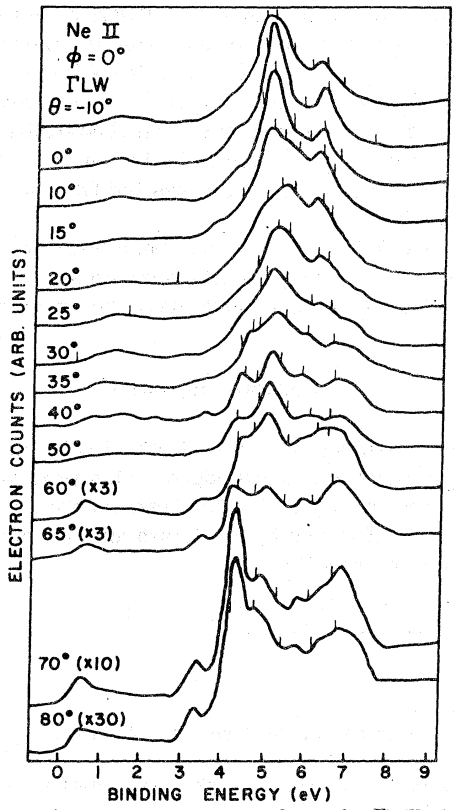

FIG. 7. Photoemission spectra from the $\Gamma L\,W$ plane obtained with Ne II ($h\nu = 26.9$ eV) radiation.

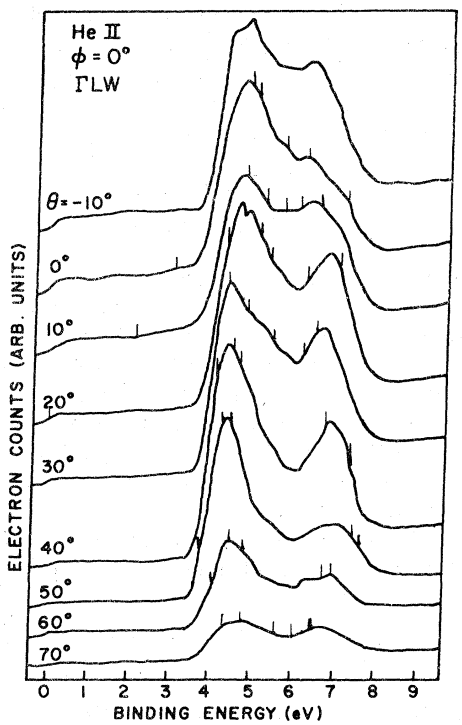

FIG. 8. Photoemission spectra from the $\Gamma L\,W$ plane obtained with He II ($h\nu = 40.8$ eV) radiation.

and that the local density of states near the surface is narrower than that of the bulk.[18-20] A peak near the Fermi energy for electrons emitted normally from a [111] axis has been recently attributed to surface states.[15] We found evidence for such structure near the onset of emission, but its strength was very sensitive to the surface conditions. However, we also point out that since the s-p band reaches the edge of the Brillouin zone at the L point near the Fermi energy,[22,23] this peak might be a one-dimensional density-of-states feature of the bulk bands which has a nonvanishing intensity due to the relaxation of $k_\perp$. This model correctly predicts that this peak disappears rapidly as the polar angle of emission increases.

In none of our photoemission curves have we observed any evidence for d-like surface states that are nondegenerate with those of the bulk, even as the surface sensitivity increased with polar angle. Similar observations have been made for other noble metals.

All of the spectra for $h\nu = 16.8$ and 21.2 eV tend to become broader as θ increases, rather than narrower. The observed behavior can be understood in terms of band-structure effects. For emission normal to the surface, the strongest direct transitions occur for regions near the Γ point, where the bands are the narrowest. Any excursion of $\vec{k}$ away from the Γ point with increasing polar angle should therefore account for a larger band width. Also, as mentioned previously, the broadening might in part be explained in terms of band structure or an increase in the uncertainty of $k_\perp$, which allows more electron states to contribute to the spectra. For the most grazing emission angles, the surface sensitivity for the Ne I and He I spectra increases by only ~50% due to the fact that the maximum internal angle of emission is ~60°.

The He II spectra at the highest polar angles for all azimuthal angles are much narrower than the band width. The spectra taken for $h\nu = 40.8$ eV should be the most sensitive to the surface, since the mean free path is the shortest and the maximum internal angle of emission the greatest. It is clear that surface narrowing effects are not important for $\theta \leq 50°$, since at this angle the spectra achieve their maximum width of 4 eV. However, since the narrowing of the spectra observed for large polar angles is consistent with the predictions of the FEFS model, it is not evidence for narrowing due to surface effects.

IV. SUMMARY AND CONCLUSIONS

The experiments presented here show that the angle-resolve photoemission spectra from Ag

depend strongly upon the photon energy. The lack of structure in the secondary electron tail indicates that the escape process and the final electron states cannot account by themselves for the observed angular variations. Except for a few minor peaks, the FEFS model does provide an adequate description for explaining the observed trends in the positions of the peaks in the spectra over the entire photon-energy range.

Combining this observation with our previously reported results,[14] we conclude that only a single region in the initial Brillouin zone makes the dominant contribution to the spectra emitted in any given direction. This suggests, but does not prove, that the final electron state is described by a single APW or OPW. A calculation of peak intensities appears to be needed to test this possibility further.[29]

We believe that the region of validity of either the FEFS or ODDOS model is strongly material dependent. We suggest that the ODDOS model will be valid near the onset of emission for those elements on the right-hand side of the Periodic Table, where the larger number of valence electrons ensures that a larger number of final-state bands exists near the threshold of emission and the stronger pseudopotential mixes the OPW's thoroughly.

No conclusive evidence has been found for the existence of s-like or d-like surface states nor narrowing of the bulk bands near the surface.

ACKNOWLEDGMENTS

The assistance of Jeffrey Colbert with the band computations is acknowledged. This work was supported in part by the NSF under Grant No. DMR-761-2574 and by the Research Foundation of the State of New York.

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