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Photoemission spectra and band structures of *d*-band metals. V. The (100) and (111) faces of single-crystal copper

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Photoelectron energy spectra have been measured on the (100) and (111) surfaces of single-crystal copper in the photon energy range 7.7–10.2 eV. The surfaces were prepared by argon-ion sputter-etching and annealing techniques with chemical purity (> 95%) determined by *in situ* Auger-electron spectroscopy. Model band calculations based on direct transitions predict successfully the relative positions of the uppermost *d*-band peak and its splitting on the (100) face. For the (100) face at the lowest photon energy, the calculations predict no emission from the *d* bands, whereas abundant emission is actually observed. The contributions from one of the higher Mahan cones have also been calculated, and are found to be important only for photon energies above 10 eV.

I. INTRODUCTION

The *d*-band noble and transition metals are among the materials whose band structures have been most thoroughly explored by the ultraviolet photoemission technique.[1,2] Most of the experiments, including those reported in an earlier paper of this series,[2] have been performed on evaporated films of unknown crystal orientation. Volume interpretations in terms of one-electron band theory have related the spectra to the energy distribution of the joint density of states[3,4] (EDJDOS) which represents the energy distribution of the photoelectrons excited within the material but takes no account of their directions of propagation. In other words, most theoretical models contain, at some point, an assumption of isotropy. This is true even of the most sophisticated calculation published to date for a *d*-band metal, namely the work of Moruzzi *et al.*[5] on cesiated Cu. Their calculations include the momentum matrix elements for the optical transitions, and also take account of the anisotropy of the group velocity in the transport of the photoelectrons to the surface. Thereafter, however, their model, like others, assumes that the probability of escape of the photoelectron across the surface is independent of its wave vector or direction of propagation.

The aim of the present work was to subject these band-theoretic models to a more severe test by performing experiments and band calculations on (100) and (111) single-crystal faces of Cu. Similar work has been reported by Nilsson and Eastman[6] on single crystals of Ag prepared by epitaxial deposition. Their emphasis was primarily on the emission from the *s*-*p* derived bands just below the Fermi level. We shall be more concerned with the emission from the *d* bands. As well as providing information on the details of the escape process, it is hoped that tests such as these will indicate the relative importance of volume and surface contributions to the measured spectra, and also the possible role of many-body effects in the photoemission process.

II. EXPERIMENTAL DETAILS

A. Apparatus

Photoelectron energy-distribution curves (EDC's) were measured by the ac retarding-field method[7] using a hemispherical diode analyzer. Monochromatic light was produced by a hydrogen discharge lamp of the Hinteregger type (but modified for hot-filament operation[8]) and a McPherson model 225 vacuum ultraviolet monochromator. The light was incident normally upon a multisample holder which permitted the copper (100) and (111) crystals and a nickel reference sample, each with dimensions of 0.5×1 cm^2, to be inserted into the beam in turn. The samples and photoemission analyzer were contained in an ion-pumped stainless steel ultrahigh vacuum chamber which also contained an Auger electron spectrometer, a wide aperture ion gun and leak valves for introducing high-purity argon. The light was admitted to the chamber through a LiF window.

After achieving pressures of $\sim 2\times 10^{-10}$ Torr the samples could be cleaned by argon-ion bombardment (~ 5 μA/cm^2 of 300-eV ions) and annealed at ~ 600 °C to restore crystalline order. As found in previous low-energy-electron-diffraction studies,[9] the main source of surface impurities was not the residual gas but bulk impurities which segregate at the surface during annealing. The most efficient cleaning procedure was to bombard the samples at elevated temperatures. The main bulk impurity was oxygen, and approximately 50 h of argon bombardment were required to reduce the surface contamination below ~ 0.05–0.1 monolayers. This impurity level was estimated by Auger-electron spectroscopy (AES) with an approximation calibration based on the gas adsorption studies of Tracy.[9,10]

After cleaning all three samples simultaneously the EDC's were measured sequentially at a single photon energy. The EDC data was stored in digital form in a PDP-8/L minicomputer which allowed signal averaging to achieve signal-to-noise ratios of 100:1 or better. The photoemission measurements were periodically interrupted and the impurity level checked with AES to ensure that the EDC's were representative of the "clean" surface. From these measurements we determine that a surface coverage of 0.2 monolayers of oxygen or carbon monoxide does not significantly affect the Cu (100) and (111) EDC's for photon energies in the range $\hbar\omega = 7$–11 eV.

B. Results

Typical experimental EDC's are shown in Fig. 1 for copper (100) and (111) single crystals. The energy is taken to be the initial-state energy with the zero at the Fermi energy. The intensity is in arbitrary units with an approximate normalization based on relative photon intensities measured with a sodium salicylate film and photomultiplier. The results for the (111) surface are similar to those obtained on evaporated polycrystalline films by Krolikowski and Spicer.[11]

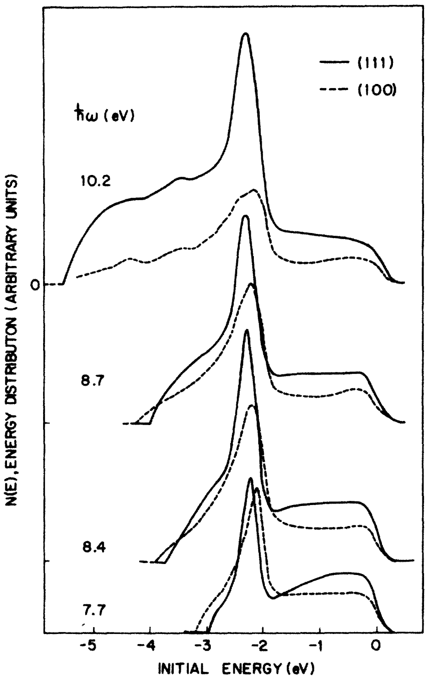

FIG. 1. Experimental photoemission EDC's for single-crystal copper (111) and (100) surfaces. The initial energy zero is taken at the Fermi level, E_F. Note that the leading edge of the d-band peak (near -2 eV) occurs at higher energy on the (100) surface than on the (111) surface.

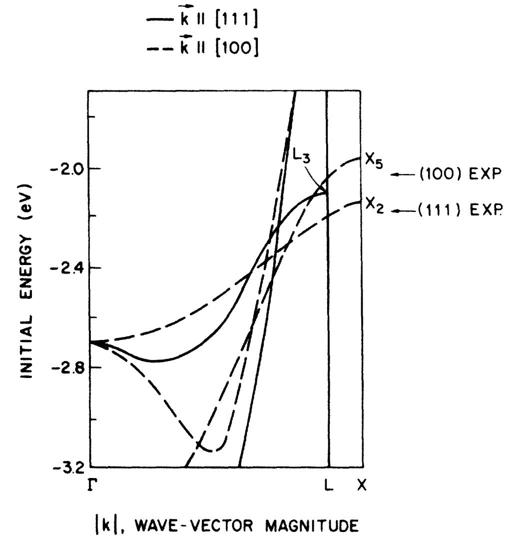

FIG. 2. Energy vs wave vector dispersion relation along directions perpendicular to the (111) surface (solid line) and to the (100) surface (dashed line) as given by Chodorow potential. The experimental d-band peaks at $\hbar\omega = 7.7$ eV are indicated by arrows near the X_5 and L_3 critical points.

The results for the (100) surface differ from the (111) surface in that the leading edge of the d band near -2 eV occurs 0.13 ± 0.05 eV higher in energy and this d-band peak broadens with increasing photon energy. A doublet with components at -2.10 and -2.45 eV is resolved at $\hbar\omega = 10.2$ eV for the (100) sample. Weaker structure at -3.4 and -4.4 eV on the (100) surface and at -3.5 and -4.3 eV on the (111) surface is also resolved.

The experimental work functions determined from these EDC's are $\varphi_{111} = 4.90$ eV and $\varphi_{100} = 4.65$ eV. The higher work function and corresponding lower surface energy for the (111) sample imply that polycrystalline films may have a large fraction of (111) crystallites as suggested by previous work.[11]

The s-band emission observed from 0 to -2 eV is weaker on the (100) surface than on the (111) surface. There is a slight indication of the "square-box" shape predicted by the two-band model[12] for the (111) EDC's but it is masked because of its close proximity to the d-band emission.

III. MODEL CALCULATIONS AND COMPARISON WITH EXPERIMENT

The difference in the position of the leading edge of the d band for the two crystal faces is essentially independent of photon energy. This suggests that it is an initial-state effect which does not require a detailed analysis. We show in Fig. 2 the energy versus wave vector dispersion relation obtained by Burdick[13] for the d bands along the [100] and [111] directions of k space. Also shown in Fig. 2 are the experimental positions of the d-band edge for the (100) and (111) surfaces. There is a good correlation between the d-band energies near the Brillouin zone boundary at X and at L with the experimental values for the (100) and (111) edges, respectively.

A. Joint density of states

We have also attempted a more detailed analysis by performing model band calculations which assume direct transitions. As is customary in such an approach, we relate the measured photoelectron energy spectrum to a Brillouin-zone (BZ) integral of the following form[14]:

$$D(E,\hbar\omega)=\sum_{f,i}\int_{\text{BZ}} d^3k\,|P_{fi}|^2\,T(E_f,\vec{k})\times\delta(E_f-E_i-\hbar\omega)\,\delta(E-E_i)\ . \qquad (1)$$

$E_f(\vec{k})$ and $E_i(\vec{k})$ are the energy eigenvalues in the final and initial state bands, respectively. $|P_{fi}|^2$ is the square of a momentum matrix element representing the optical transition strength. $T(E_f,\vec{k})$ is an over-all escape factor and represents the probability that, after excitation, the photoelectron will reach the surface and escape across it. It is with this latter factor that we shall be concerned here. In the analysis of data from polycrystalline samples, it has been shown[3,4] that it is often sufficient to treat both $|P_{fi}|^2$ and $T(E_f,\vec{k})$ as constants. In this case $D(E,\hbar\omega)$ is called the energy distribution of the joint density of states (EDJDOS). Moruzzi *et al.*[5] have performed calculations on Cu in which the effect on $|P_{fi}|^2$ are included. Their calculations also take account of the anisotropy of the group velocity on the factor $T(E_f,\vec{k})$. However, there appears to be no previous published calculation on a d-band metal which takes into account the effect on $T(E_f,\vec{k})$ of a specific choice of crystal face for the surface of the sample.

The procedure we have adopted in our calculations is to assume that $|P_{fi}|^2$ is constant, but that

$$T(E_f,\vec{k})=1 \text{ if } E_f-E_v\geq\hbar^2k_{\parallel}/2m$$
$$=0 \text{ if } E_f-E_v<\hbar^2k_{\parallel}/2m\ . \qquad (2)$$

E_v is the vacuum level, and $k_{\parallel}$ is the component of $\vec{k}$ parallel to the surface. Equation (2) will be recognized as a simple specular refraction condition. The quanity (E_f-E_v) is the kinetic energy of the photoelectron *in vacuo* and, if it is assumed that $k_{\parallel}$ is conserved on crossing the boundary, must be equal to at least $\hbar^2k_{\parallel}^2/2m$ or, otherwise, the electron will be totally reflected back into the crystal. Extension of Eq. (2) is considered in Sec. III B.

The k-space integral in Eq. (1) was performed by a Monte Carlo sampling of about 375 000 points in the irreducible $\frac{1}{48}$ wedge of the BZ. The energy eigenvalues were generated by a combined interpolation scheme[15] and subsequent quadratic interpolation.[3] The parameters used were arranged to reproduce the first-principles augmented-plane-wave results of Burdick[13] and are given in column (a) of Table I in an earlier paper of this series by Smith and Mattheiss.[15] Spin-orbit splitting and other relativistic effects are not included. The $\frac{1}{48}$ wedges of the BZ are not all equivalent in this problem. The integration can, however, be carried out entirely within a $\frac{1}{48}$ wedge by applying the tests embodied in Eq. (2) several different ways at each $\vec{k}$. These different tests correspond to the different possibilities for the orientation of the $\frac{1}{48}$ wedge with respect to the crystal surface.

Figure 3 shows our results for this weighted EDJDOS at photon energies close to those used in the experiments. As expected, the uppermost d-band peak is predicted to occur at slightly higher

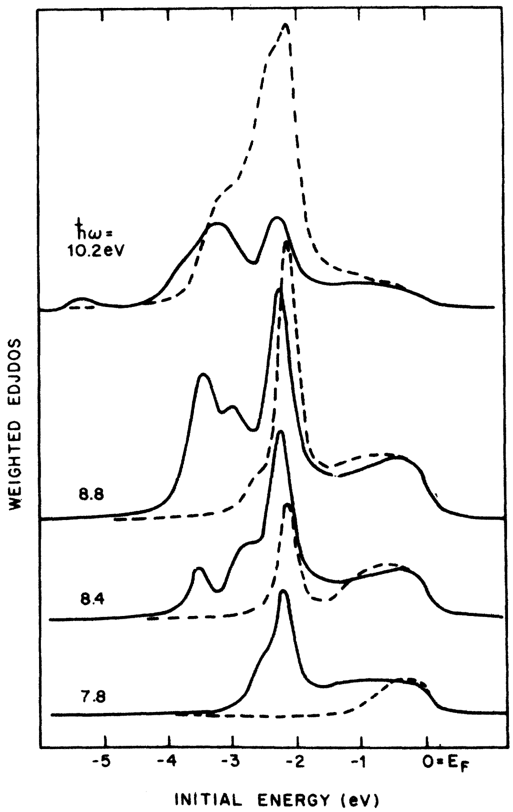

FIG. 3. Calculated photoemission EDC's using a weighting factor as discussed in the text. The curves for $\hbar\omega=10.2$ eV have been reduced by a factor of 5. Full curves are for the (111) face; dashed curves are for the (100) face.

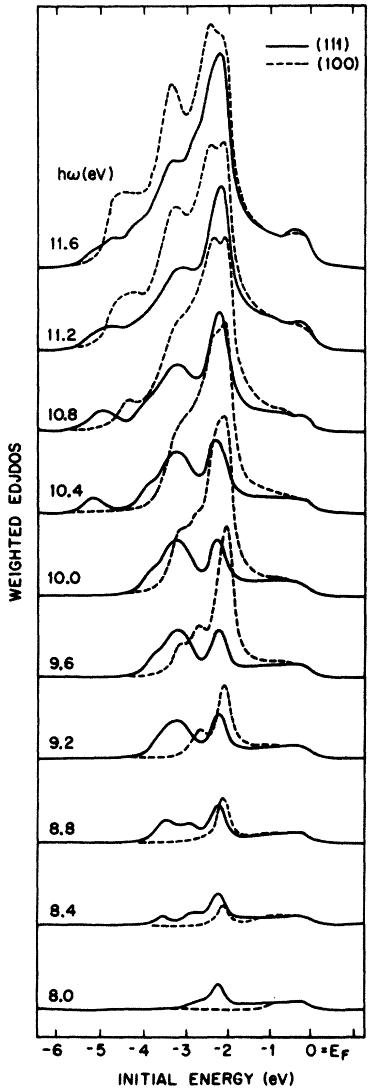

FIG. 4. Evolution of the weighted EDJDOS for Cu as with varying photon energy $\hbar\omega$. Full curves represent the (111) face; dashed curves represent the (100) face.

energies on the (100) face, and this is in good agreement with experiment. Also in agreement is the prediction that, in the $\hbar\omega = 10.2$-eV spectra, the uppermost d-band peak should split into a doublet on the (100) face, but not on the (111) face.

Turning now to the question of peak intensities, rather than peak positions, we find that the agreement between the calculations and experiment is not good. At $\hbar\omega = 10.2$ eV, the total emission from the (100) face is predicted to be considerably greater than that from the (111) face, whereas, in experiment, just the opposite is found. This discrepancy, however, could be due to the assumption of constant matrix elements. A more serious discrepancy occurs at the lower photon energies. At $\hbar\omega = 7.7$ eV, the calculations predict for the (100) face that there should be *no* emission from the d bands, which is in clear contradiction with the experimental results.

The evolution of the weighted EDJDOS with varying $\hbar\omega$ is illustrated in more detail in Fig. 4. Qualitatively, we see that the behavior is quite different for the two crystal faces. In comparison, the differences seen experimentally in Fig. 1 are less pronounced.

B. Higher Mahan cones

An approximation in the calculations which might be thought to be responsible for the absence of d

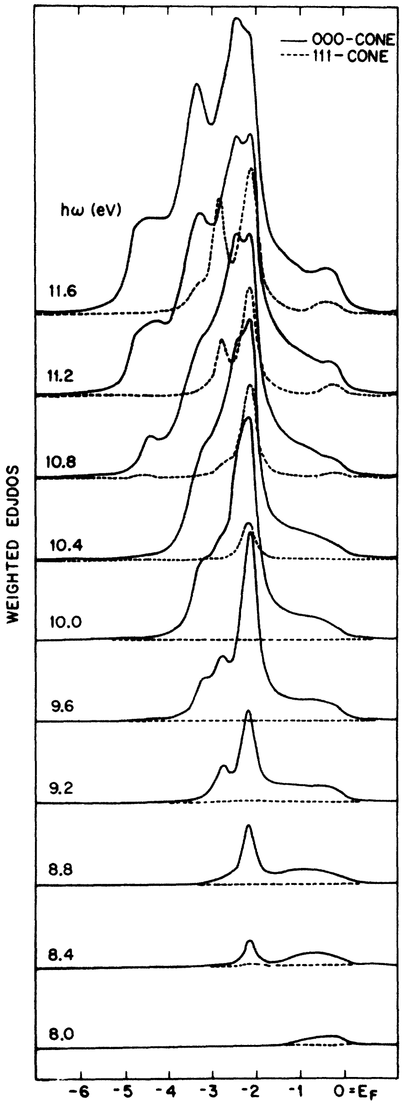

FIG. 5. Weighted EDJDOS for the (100) face of Cu calculated for two alternative "Mahan cones"; the full curves represent the results for the 000 cone and are the same as the dashed curves in Fig. 4; the dashed curves in this figure represent the contributions of the 111 conse on the (100) face.

emission from the (100) face at lower $\hbar\omega$ is our neglect of contributions from higher "Mahan cones."[16] Equation (2) considers only the reduced wave vector $\vec{k}$. The wave functions of the final states in the optical transitions will contain not just the Bloch-wave component with $e^{i(\vec{k}\cdot\vec{r})}$ but also Bloch-wave components of the kind $e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$ where $\vec{G}$ is a reciprocal-lattice vector. Indeed, if the final state lies in band 7, the $\vec{k}+\vec{G}$ components are expected to dominate the $\vec{k}$ component. To assess the importance of such higher components, we have repeated the calculations for the (100) face, but instead of applying the tests of Eq. (2) using the vector $\vec{k}$, we have applied it to the vectors of the kind $\vec{k}+\vec{G}$, where $\vec{G}$ runs over all eight of the $\langle 111\rangle$ reciprocal-lattice vectors. We will refer to the weighted EDJDOS obtained in this way as the contribution from the 111 cones. The results obtained previously, by applying the escape tests to $\vec{k}$ only, will be referred to as the contribution from the 000 cone.[17]

Our numerical results for the 111-cone emission from the (100) face of Cu are shown in Fig. 5. We also show, for comparison, the 000-cone contribution. At the lower photon energies the weighted EDJDOS for the 111 cones is zero or negligible. At about $\hbar\omega = 10.4$ eV, we start to pick up an appreciable contribution from the 111 cones in the d-band region. At photon energies below this, neglect of the 111 cones (and other higher Mahan cones) appears to be quite justified. In particular, the inclusion of higher cones does not remove the dilemma concerning the predicted absence of d emission from the (100) face at low photon energies.

IV. CONCLUDING DISCUSSION

In summary, it has been found experimentally that photoelectron energy spectra measured on the (100) and (111) faces of single-crystal copper differ significantly from each other. Some of these differences can be understood in terms of model band calculations in which the anisotropy of the escape probability is taken into account. The calculations, however, predict additional differences which are not observed. In particular, at the lowest photon energy used in the experiments, the calculations predict no d emission from the (100) face, whereas abundant d emission is actually observed. This discrepancy is not understood at present, and its ultimate explanation may involve one or more of the following possibilities.

(*a*) *Diffuse refraction*. The specular boundary condition may be too restrictive, and there may be appreciable amounts of diffuse refraction, as suggested by Nilsson and Eastman[6] in similar studies on Ag. It is possible that the discrepancies would disappear if the experiments could be performed on ultrasmooth surfaces.

(*b*) *Quasielastic scattering*. There may be scattering processes in which the directions of propagation of the photoelectrons are randomized but their energies are relatively unchanged. Such scattering could occur subsequent to, or as an integral part of, the optical excitation. The latter case would correspond to the Spicer-Doniach nondirect mechanism.[18]

(*c*) *Surface photoelectric effect*. There may be significant contributions from the classic surface photoelectric effect discussed for free-electron metals by Mitchell and others.[19,20] This possibility has been suggested by Feuerbacher and Fitton[21] in connection with directional photoemission experiments on W.

(*d*) *Surface-state emission*. Photoemission from surface states on W has been observed by Waclawski and Plummer[22] and by Feuerbacher and Fitton.[21] The occurence of surface states on d-band metals has been shown by Gurman and Pendry[23] to be of some generality, and emission from such states could be quite strong.[20]

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[17] Strictly speaking, the contribution of a given optical transition to the 000 cone, 111 cones, etc., should be weighted by the extent to which the corresponding plane waves are present in the final state wave function. This has not been done in the present work, since we have generated only energy eigenvalues and not eigenvectors. Consequently, the distinction between "primary" and "secondary" cones made by Mahan in Ref. 16 has little usefulness in the present context. It is more convenient to use the designations: 000 cone, 111 cone, etc.

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