Photoemission from a Ag(111) surface: Failure of the plane-wave, orthogonalized-plane-wave, and augmented-plane-wave final states*

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Photoemission spectra directed along the (111) axis of Ag for $h\nu = 16.8$, 21.2, 26.9, 40.8, and 1254 eV are presented. Simple symmetry considerations are employed to demonstrate that final electron states consisting of a single plane wave, or a combination of plane waves mixed by a weak crystal pseudopotential incorrectly describes the photoemission spectra. It is pointed out that part of the inadequacy of the plane wave is due to its failure to describe the true final state in the region of the atomic cores. Augmented-plane-wave and orthogonalized-plane-wave final states do better than the plane-wave final state, but they predict a vanishing emission for initial states having $m \geq 2$. It is concluded that the above states must be strongly mixed to explain the experimental spectra.

I. INTRODUCTION

A proper description of the nature of the final electron state is important for the interpretation of angle-resolved photoemission spectra from solids and surfaces. In many previous works,[1-7] a final state consisting of a single plane wave has often been employed to calculate the angular dependence of the photoemission spectra, largely because of the simplicity of the analytical results which it yields. However, this model has not yet been tested sufficiently to prove its validity.

Janak *et al.*[8] have suggested that the angle-averaged photoemission spectra of Cu for $h\nu < 20$ eV seemed to be described well by a model in which equal matrix elements connect each initial d band to a free-wave final state. Baird *et al.*[5] have proposed a simplified version of this model, in which only the single-plane-wave final state propagating in the direction of the initial state contributes to the spectra. This model seems to describe the angle-resolved spectra from the noble metals, although the spectra do not exhibit pronounced variations to provide a definitive test for the model.

There are some indications that the plane-wave final-state model is inadequate. Wagner *et al.*[9] have shown by an explicit band structure calculation that the single-plane-wave final state describes incorrectly the angular dependence of the photoionization cross sections of Cu. Rowe and Smith[10] have found that secondary Mahan cones contribute to the photoemission spectra of Cu, indicating the breakdown of the single-plane-wave state due to the crystal potential. Liebsch[11] has pointed out that multiple scattering between atoms can break down the validity of the plane-wave final state. While the mixing of plane waves is expected at low final energies, one expects this mixing to become reduced at high final-state energies, and the plane-wave final state to become valid.

Here, we are concerned primarily with the magnitude of the photoionization cross sections predicted by the plane-wave final-state model in both UPS and XPS regions. We deliberately avoid a calculation such as that made by Wagner *et al.*,[9] and instead rely on simple symmetry arguments to demonstrate the failure of the plane-wave final state for describing the photoemission spectra of Ag along the (111) over a wide range of photon energies. We estimate that inclusion of additional plane waves mixed by the weak crystal pseudopotential provides some, but still not enough, improvement. We argue that the plane-wave final state becomes a worse, not better, approximation for describing the photoionization cross sections as the final-state energy increases. Our analysis indicates that the primary deficiency of the plane-wave final state is one that has been overlooked, namely, its inability to describe properly the charge density of the final state in the region of the core. When the final state in the region of the atomic core makes the dominant contribution to the photoionization cross section, the optical selection rules are governed by spherical symmetry. We also show that the single OPW or single APW final states, which take into account the strong atomic potentials, improve the cross sections greatly, but the OPW's and APW's must be strongly mixed to account for the observed spectra. We conclude that any models for the final state based upon single plane waves, OPW's and APW's are not correct for Ag, and possibly other noble metals, for $h\nu > 20$ eV.

II. d BANDS IN NOBLE METALS

Since the d orbitals of the noble metals are localized about the atomic core, the corresponding d bands are suitably described by the tight-binding approximation.[12] The Bloch wave function cor-

responding to band n and momentum k_i can be written

$$\psi_{n\vec{k}_i} = \sum_l e^{i\vec{k}_i\cdot\vec{R}_l}\phi_{n\vec{k}_i}(r - R_l)\,, \tag{1}$$

where the summation extends over the atomic sites and $\phi_{n\vec{k}_i}(r)$ is an atomic orbital. Along the Λ axis of the fcc structure the d orbitals form three sets of bands having the following symmetry[12-14]:

Λ_3: $2x^2 - y^2 - z^2$, $y^2 - z^2$ (yz, xz);

Λ_3: $2xz - xy - yz$, $xy - zy$ $(xy, x^2 - y^2)$;

Λ_1: $xy + xz + yz$ $(3z^2 - r^2)$.

The orbitals on the left are expressed in terms of the usual crystallographic coordinates while those on the right are expressed in coordinates rotated so that z lies along the (111) axis. The above separation is only approximate since the spin-orbit interaction and crystal-field interaction mix these states somewhat. Calculations by Smith,[15] however, indicate that this decomposition remains valid for Pt, where the spin-orbit interaction is on the order of the bandwidth. In Fig. 1, we have plotted as the top curve the density of states along the (111) direction for the lower six bands taken from the calculation of Smith.[14] Peaks 1 and 2 arise from the upper Λ_3-like band, peaks 3 and 4 from the lower Λ_3 band, and peak 5 from the lowest Λ_1 band.

III. EXPERIMENTAL

Photoemission spectra directed along a (111) axis of Ag were measured in an angle-resolved photoelectron spectrometer (ADES-400 Vacuum Generators). The sample was cleaned and heated by argon-ion bombardment and the quality and orientation of the surface were checked by LEED. The angular acceptance of the electron velocity analyzer was ±2°, so that only a small region of the Brillouin zone was sampled for the final-state energies considered here. The uv photons were provided by a differentially pumped discharge lamp and x-ray photons by a Mg x-ray anode. The energy resolution was 0.15 eV for $h\nu = 16.8$ and 21.2 eV and 0.3 eV for $h\nu = 26.9$ and 40.8 eV, and ~1 eV for $h\nu = 1254$ eV.

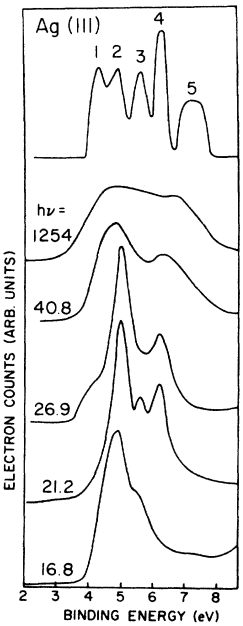

FIG. 1. Photoemission spectra directed along the (111) axis of Ag for $h\nu = 16.8$, 21.2, 26.9, 40.8, and 1254 eV. The uppermost curve is the one-dimensional density of states along the (111) axis of Ag taken from the band structure of Smith (Ref. 14).

IV. RESULTS

The experimental spectra are shown in Fig. 1. We associated the two strong peaks in the spectra observed for $h\nu \geq 21.2$ eV with the two Λ_3 bands. The Λ_1 band ought to appear near a binding energy of 7.5 eV, but it is not visible for $h\nu = 21.2$ and 26.9 eV and is barely visible for $h\nu = 16.8$ and 40.8 eV. The absence of this peak might be due to the fact that the emission is originating from regions in k space near the Γ point, where this band has a predominantly s-like character with a small photoionization cross section. This is also consistent with the fact that peak 1 is not observed, since contributions to it come from the edge of the Brillouin zone. The emission from the lower Λ_3 bands for $h\nu = 16.8$ eV is very weak, and it is even weaker in spectra obtained for $h\nu = 11.8$ eV.[13] A similar behavior has been reported in the directed emission from the (111) faces of Cu, Ag, and Au taken for $h\nu \leq 21.2$ eV.[16] The x-ray photoemission spectra shown in Fig. 1 are similar to those reported by McFeely *et al.*[6] Although our energy resolution is worse (1.0 vs 0.5 eV), our angle resolution (±2° vs ±3°) is somewhat better than theirs.

V. DISCUSSION

Following previous workers,[1-7] it can be shown that the matrix element connecting the tight-binding initial state with a final plane-wave state of momentum $\vec{k}_f$ is

$$M_{fi} = \sum_G \vec{\epsilon}\cdot\vec{k}_f\,\delta(\vec{k}_f - \vec{k}_i - \vec{G})\tilde{\phi}_{n\vec{k}_i}(\vec{k}_f)\,, \tag{2}$$

where

$$\tilde{\phi}_{n\vec{k}_i}(\vec{k}_f) = \int \phi_{n\vec{k}_i}(r)e^{i\vec{k}_f\cdot\vec{r}}\,d^3r\,, \tag{3}$$

ϵ is the direction of polarization of the electromagnetic vector potential and G is a reciprocal-lattice vector. The important feature of this model is that the matrix element depends upon the Fourier transform of the initial-state wave func-

tion, and thus, the angular dependence of the matrix element reflects the angular symmetry of the initial-state wave function. When the electronic charge density of the atomic orbital or the vector potential vanishes in the direction of propagation of the photoelectron, so does the matrix element.

We observe that the two sets of Λ_3 states have a vanishing charge density along the (111) direction. [In general, all states of Λ_2 and Λ_3 symmetry have a vanishing charge density along the (111) axis.] Even if the crystal-field and spin-orbit interaction were to mix the Λ_3 states, this fact would still be true. This means that if the final electron state were a single plane wave propagating along the (111) axis only the Λ_1 initial state ought to contribute to the photoemission spectra.[17,18] [Only Λ_1 states can have plane-wave components directed along the (111) axis.] However, both sets of Λ_3 states appear in the data for all photon energies in Fig. 1. We have found that the strength of emission from the upper Λ_3 bands in Fig. 1 is no weaker than the emission obtained for other angles, where it is not forbidden by the above arguments.

When the initial and final states are written as sums of plane waves,

$$\psi_{n\vec{k}} = e^{i\vec{k}\cdot\vec{r}} \sum_G u_{n\vec{k}}(\vec{G}) e^{i\vec{G}\cdot\vec{r}} , \tag{4}$$

the matrix element connecting them becomes

$$M_{fi} = \delta(\vec{k}_f - \vec{k}_i) \sum_G \vec{\epsilon}\cdot\vec{G} u^*_{n_f\vec{k}_f}(\vec{G}) u_{n_i\vec{k}_i}(\vec{G}) . \tag{5}$$

When the tight-binding wave function in (1) is written as in (4), the $u_{n_i\vec{k}_i}(G)$'s reflect the angular symmetry of the atomic orbital function describing the band.

From Eq. (5) we note that optical excitation of the upper Λ_3 states in the uv regime must take place via components of the final Bloch wave other than the (111), such as the (200) or (220), components. The lower Λ_3 states can make transitions via the (220) or (1-11) components. The strength of the two Λ_3 peaks in the photoemission spectra might be regarded as a measure of the amount of admixture of the primary plane wave propagating in the (111) direction with the above Bloch components. The fact that the upper Λ_3 states appear more strongly than the lower ones for $h\nu \leq 21.2$ eV suggests that the (200) components of the final state are larger than the (1-11) components. Both sets of Λ_3 states appear with comparable magnitudes in the spectra taken for $h\nu = 40.8$, 1254 eV. The spectra obtained from the (111) surfaces of noble metals for $h\nu = 40$–200 eV (Ref. 7) and $h\nu = 1486.6$ eV (Ref. 6) exhibit contributions from the Λ_3 bands that are comparable to the Λ_1 band. Unfortunately in these experiments the finite angular acceptance of the electron velocity analyzer and large final-state momentum of the photoelectron allow initial-state electrons from regions around the (111) axis to contribute to the spectra. Nevertheless, these facts not only indicate the inadequacies of the plane-wave final state, but they imply that the magnitude of the $u_k(G)$'s in the true final state are distributed isotropically. This interpretation holds provided that thermal vibrations are not important in destroying k conservation.[19]

We can estimate the extent to which a single-plane-wave state propagating in the (111) direction with momentum $\vec{k}_0$ is mixed with other plane waves by the lattice pseudopotential. By employing first-order perturbation theory,

$$u_{\vec{k}_0}(\vec{G}) = V_G/[k_0^2 - (\vec{k}_0 - \vec{G})^2] , \tag{6}$$

and Smith's OPW parameters for the potential,[14] we find that for a $\vec{k}_0$ corresponding to the middle of the second free-electron-like band,

$$u_{\vec{k}_0}(200) \sim 0.1 \quad \text{and} \quad u_{\vec{k}_0}(1-11) \sim 0.03 .$$

For this small amount of admixture, the final state is still largely a single plane wave, and the strength of emission of the Λ_3 states ought to be at least an order of magnitude smaller than for the Λ_1 states. Even a more extended calculation of the final state with Smith's OPW parameters would not explain adequately the angular behavior of the cross sections. A mechanism other than the crystal potential is needed that puts more weight into the Bloch components of the final state other than those directed along the axis of emission.

While it is probably true that the part of final-state wave function outside of the atomic cores begins to look more like a plane wave at high photon energies, this portion of the wave function becomes increasingly irrelevant for describing the cross section.[20] Most of the contribution to the cross section comes from the region of the core, where even the high-energy final state looks more like an atomic orbital.[20] The most conspicuous failure of the plane-wave final state is its inability to produce the curvature of the charge density in the region of the core. For this reason the plane-wave final state becomes a *worse* approximation at high final-state energies for describing not only the magnitude of the cross sections, but particularly also their angular dependence. When the emission originates from a localized orbital, such as the d orbitals in Ag, the core part of the final wave function becomes more important at lower photon energies. The plane-wave final state is valid only when it suitably approximates the spatial region of the true final-state wave function that gives the dominant contribution to the

photoionization cross section. We expect this to occur at low final-state energies for initial states that are more delocalized than the d orbitals of the noble metals. Unfortunately, at these low energies, the crystal potential conspires to mix the plane wave making the states Bloch-like. We therefore assert that the plane-wave final state is generally inapplicable for the calculation of angular dependence of the photoionization cross section.

We suggest that an improvement in the description of the cross section occurs when the final-state wave function in the vicintiy of the atomic core is taken into account properly. To see how this comes about, let us consider the simplest correction to the plane-wave final state, the orthogonalized plane wave, which can be written[12]

$$\psi_f = e^{i\vec{k}_f\cdot\vec{r}} - \sum_c \sum_l e^{i\vec{k}_f\cdot\vec{R}_l}\phi_c(r-R_l)\langle\phi_c|\vec{k}_f\rangle\ , \qquad (7)$$

where $\langle\phi_c|k_f\rangle = \int e^{i\vec{k}_f\cdot\vec{r}}\phi_c(r)\,d^3r$, and the summation index c extends over all core states. (In principle, this summation should extend over all states with energies lower than that of the OPW.) Our arguments should also apply to an augmented-plane-wave state, which has a form similar to that of the OPW. The core orbitals which have a nonvanishing overlap integral are those for which $m=0$ about the direction of k_f (we are neglecting the spin-orbit interaction of the core states). Since the core shells are filled, $\langle k_f|\phi_c\rangle$ does not depend upon the direction of k_f, but depends only upon the radial part of the core level.

The photoionization matrix element for the OPW final state becomes[7]

$$M_{fi} = \sum_G \delta(\vec{k}_f - \vec{k}_i - \vec{G}) \times\{\vec{\epsilon}\cdot\vec{k}_f\tilde{\phi}_{n\vec{k}_i} - \langle\phi_c|\vec{k}_f\rangle\langle\phi_c|\vec{p}\cdot\vec{\epsilon}\,|\phi_{n\vec{k}_i}\rangle\}\ . \qquad (8)$$

The first term in brackets corresponds to the result obtained for a single-plane-wave state, and the last term corresponds to atomiclike transitions between the initial-state orbital and the core levels. As the momentum of the final-state electron decreases, the Fourier transform of the more extended initial-state orbital decreases faster than that of the atomic orbitals, and eventually the atomiclike transitions should dominate the photoemission process.

The $\vec{k}_i$ serves to align the orbitals of the initial state. When $\vec{k}_i$ and $\vec{k}_f$ are in the same direction, then the restrictions on the initial states that can make the transition, $\Delta l = \pm 1$, $m = 0, \pm 1$, are much less severe than those given by the single-plane wave final state. Initial states with $|m| \le 1$ (the Λ_1 and upper Λ_3 bands) can make transitions into the OPW. This partly justifies the model suggested by Baird *et al.*[5] in which matrix elements are the same for all initial states. However, the single OPW or APW is still too restrictive, since transitions involving the initial state with $|m| > 1$ (i.e., the lower Λ_3 band) are forbidden. However, the lower set of Λ_3 states are clearly seen in the photoemission data for $h\nu > 20$ eV. This can occur only if the OPW or APW final states are strongly hybridized. If they are strongly hybridized, then more than a single-free-wave band must contribute to the spectra, in contradiction to the model proposed by Baird *et al.*[5]

Some further insight into the nature of the final state is gained when we consider the final state as a linear combination of spherical waves. The initial states are nearly pure d-like, and therefore, atomiclike dipole selection rules provide an additional constraint on the optical excitation process. The $d \to p$ transitions are important for $h\nu < 20$ eV, while $d \to f$ transitions are important for $h\nu > 20$ eV.[16] Using the fact that the final state along the (111) axis has Λ_1 symmetry, the relevant spherical wave components in the final state into which optical transitions from the initial-state d orbitals are allowed are

$$p_1\colon z \quad (Y_{10})\ ,$$
$$f_1\colon z^3 - \tfrac{3}{5}zr^2 \quad (Y_{30})\ ,$$
$$f_2\colon (x^2 - 3y^2)x \quad (Y_{33} + Y_{-33})\ ,$$

where we now take z to be along the (111) axis. The corresponding spherical harmonics are written in parentheses.

When $h\nu < 20$ eV, and only the p_1 component is important in the final state, the upper Λ_3 bands ($m=1$) and Λ_1 band ($m=0$) can make transitions into the p_1 orbital, but the lower Λ_3 bands ($m=2$) cannot, in agreement with the experimental results. We have found that the strength of emission from the lower Λ_3 bands increases for directions off of the Λ axis, where the above restrictions are removed.

As the photon energies increases, the f channels begin to contribute. The upper Λ_3 bands and the Λ_1 band can make transitions into the f_1 component, but not the f_2 component. Conversely, the lower Λ_3 band can make transitions into the f_2 component, while the other bands cannot. Since the OPW and APW states directed along the axis of emission consist of states for which $m=0$, the f_2 wave is not contained within them. (We observe that orthogonalization to the occupied core levels does not open up the $d \to f$ channels. It is necessary to orthogonalize this state to the unfilled f states to open this channel.) We note that

a final state derived solely from the f_2 spherical wave is unable to contribute by itself to emission along the (111) axis, since it has a vanishing charge density along this axis. The f_2 final state must be hybridized with another spherical wave that has a nonvanishing charge density in the direction of emission in order to contribute to the spectra. Therefore, we might consider the f_2 orbital as providing an indirect channel, since the optical excitation and emission steps occur through different spherical waves. The p_1 and f_1 spherical waves provide direct channels, since the excitation and emission steps occur via the same waves.

The similar magnitudes of the emission from both of the Λ_3 bands for $h\nu > 20$ eV implies that the f_1 and f_2 spherical waves occur with nearly equal strengths in the final states. If we consider the final state to be a linear combination of the f_1 and f_2 spherical waves, then the nearly degenerate f waves are easily mixed by a weak crystal potential as k moves away from Γ point. Such a final state predicts that modulations in the relative strength of the two Λ_3 bands ought to occur as the photon energy changes, the lower Λ_3 band being the weakest when k is near the Γ point.

VI. SUMMARY AND CONCLUSIONS

We have shown that the photoionization cross sections for emission from the Ag $3d$ bands along the (111) axis are not described well by a single-plane-wave final state in both the UPS and XPS regimes. Part of the reason for the failure of the plane-wave final state is due to its inability to reproduce the curvature of the true final state in the region of the atomic cores. Single OPW and APW final states, while they take into account the core region, still are not adequate, but then must be thoroughly mixed. A final-state wave function based upon hybridized spherical waves might provide an adequate description for computing the photoionization cross sections in solids.

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