

Interference between Bulk and Surface Photoemission Transitions in Ag(111)

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The direct-transition photoemission peak from the *sp* valence band of Ag(111) shows a pronounced asymmetry. The emission intensity on the lower binding energy side of this peak is considerably higher, and extends to a cutoff at the band edge just below the Fermi level. This extra emission is derived from indirect transitions induced by the surface. A linear combination of the direct (bulk) and indirect (surface) channels results in the asymmetric line shape. [S0031-9007(96)00851-4]

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Angle-resolved photoemission is the only general tool for probing the occupied band structure of solids. Its application in recent years has covered a variety of materials, including (high-temperature) oxide superconductors [1], fullerenes [2], *f*-electron compounds [3], ferromagnets [4], etc., all with a great deal of success. One would think that the basic photoemission processes should be well understood by now. This is actually not so, even in the case of the noble metals which played a key role as model systems in the early days of the development of the photoemission technique. In this paper, we will reinvestigate the photoemission properties of Ag(111). The focus of this study is to examine the line shape of a direct band-to-band transition in the bulk derived from the nearly-free-electron-like Ag *sp* states [5]. The standard three-step model for photoemission would predict a simple symmetric peak with a width determined by lifetime broadening [6]. As we will show below, the experimental line shape is far more interesting. The peak has an asymmetric tail on the lower binding energy side extending over a wide range to a cutoff at the valence band edge just below the Fermi level. This extra emission does not resemble the density of states, and can be attributed to indirect transitions caused by the change in dielectric response at the surface. Interference between the direct (bulk) and indirect (surface) transitions results in the asymmetric line shape for the direct-transition peak. An analysis of the line shape yields a quantitative measure of this surface effect. This interference phenomenon is fairly similar to the Fano resonances seen in atomic and molecular spectra for autoionization processes.

Our experiment was done at the Synchrotron Radiation Center, University of Wisconsin-Madison, Stoughton, Wisconsin. Figure 1 shows three spectra taken with photon energies of $h\nu = 7, 8,$ and 9 eV from a sample kept at room temperature using a normal emission geometry. The incident light was *p* polarized and had an angle of incidence of 45° with respect to the surface normal. The major spectral features are labeled in the figure. The energy reference is the Fermi level. To facilitate

the discussion, we show in Fig. 2 the band structure of Ag along the [111] direction. The intense peak in Fig. 1 with an energy just below the Fermi level is derived from a Shockley surface state located in the *sp* band gap at the *L* point in the Brillouin zone [5,7]. The direct-transition peaks as labeled in Fig. 1 correspond to the vertical band-to-band transitions indicated by the arrows in Fig. 2. As the photon energy changes, a different point in *k* space is probed, and the peak moves relative to the Fermi level correspondingly. This peak movement has been employed for band mapping [5]. The above-mentioned *sp*-derived states are excited only by the electric field component perpendicular to the surface. The *d* states of Ag, with binding energies greater than about 4 eV, give rise to intense peaks. A tail of this *d* emission can be

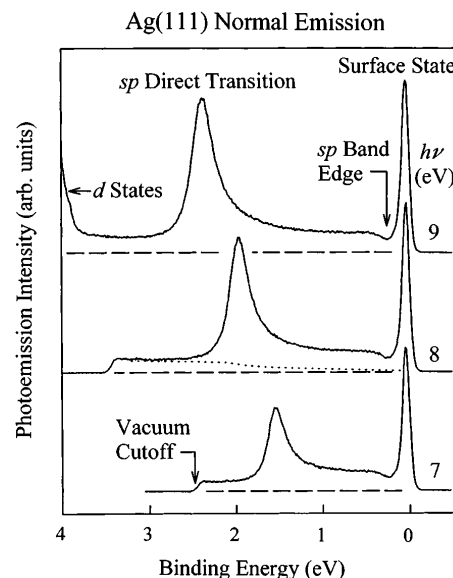


FIG. 1. Normal emission spectra from Ag(111) taken with photon energies of 7, 8, and 9 eV as indicated. The main spectral features are indicated. The dashed horizontal lines indicate zero intensity levels for the three spectra, and the dotted curve for the middle spectrum shows the inelastic background function.

seen in the spectrum for $h\nu = 9$ eV. For the other two spectra, these d states are not excited due to the vacuum cutoff.

The dashed horizontal lines in Fig. 1 indicate the zero intensity level for each spectrum. It is clear that the direct-transition peak is asymmetric, with the emission intensity on the lower binding energy side being significantly higher. This extra emission, referred to as the indirect transition, extends to a cutoff at the sp band edge. Each spectrum also contains a small background caused by inelastic scattering of the photoelectrons. The inelastic scattering is a cascading process, with more secondary electrons generated at higher binding energies. The dotted curve for the 8 eV spectrum in Fig. 1 is an estimate of this background. It is constructed according to the "Shirley criterion" [8]; namely, the background function at each point is taken to be proportional to the integral of the area under the spectrum to the right. The proportional constant is determined in the present case by matching the calculated background function to the measured background just above the vacuum cutoff. Because the inelastic background is necessarily a monotonically increasing function of binding energy, much of the asymmetric tail of the direct-transition peak on the lower binding energy side is due to elastic events. The 8 eV spectrum, after subtraction of this background, is shown in Fig. 3 using small circles.

The standard three-step model of photoemission suggests that the direct transition should be characterized by a Lorentzian with a width determined by the electron and hole lifetimes [6]. This is certainly not the case for the spectrum in Fig. 3. Furthermore, the emission on the

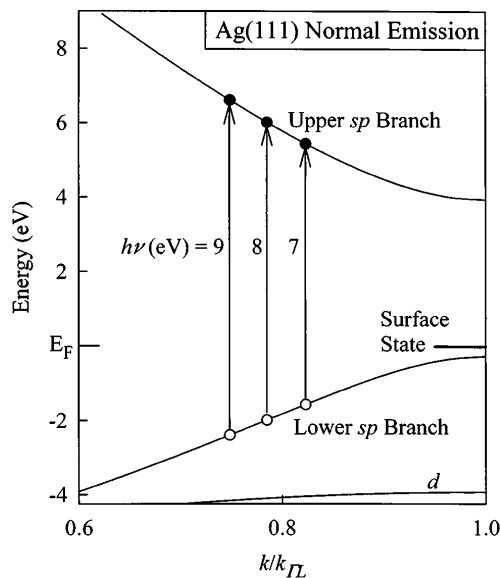


FIG. 2. Band structure of Ag along the [111] direction. The horizontal axis is the wave vector normalized to the distance between the zone center and the zone boundary. Direct transitions for photon energies of 7, 8, and 9 eV are indicated by vertical arrows.

lower binding energy side of this peak is too flat and extends too far to be accounted for by an extension of the direct-transition process; it must be derived from a different channel. Overall, the observed line shape resembles a Fano profile, and strongly implies an interference between two channels: a direct channel, which as a narrow spectral distribution, and an indirect channel, which has a wide spectral distribution.

To understand the observed line shape, and to determine the origin of the indirect channel, we have made a model calculation, incorporating all of the essential physics that are known to apply for the present system. The model begins with a two-band fit to the nearly-free-electron-like Ag sp band dispersions. In addition to the pseudopotential V_{111} , two effective masses, one each for the two sp branches separated by the L gap, are introduced to account for higher-order hybridization effects [9]. An excellent fit is obtained. The corresponding Bloch waves are then constructed, and, at each energy, the initial wave function is formed by a linear combination of two Bloch states, one traveling toward $+z$, and the other traveling toward $-z$. For the Ag-vacuum interface, we assume a step potential determined by the work function of Ag. The position of this potential step z_0 extends beyond the classical surface due to electrons spilling over into the vacuum side, and is determined in our calculation by fitting to the known energy of the Shockley surface state.

For the photoemission final state, we employ a time-reversed low-energy-electron-diffraction (LEED) state in accordance with a one-step description of the photoemis-

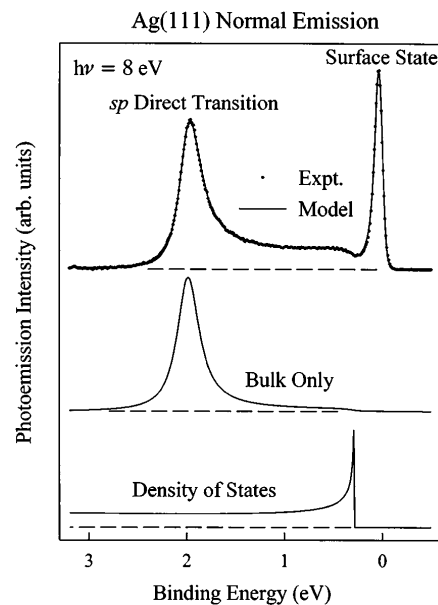


FIG. 3. The top curve is a model fit to the experimental spectra (circles) taken with a photon energy of 8 eV; the inelastic background function has been removed for the experimental spectra. The middle curve shows the result of the same model calculation but with the surface contributions removed. The bottom curve shows the density of valence states.

sion process [6,10]. The damping of the final state due to inelastic scattering in Ag is modeled by an exponential envelope function with a decay length of 2ξ , where ξ is the mean free path. This effectively leads to a complex final wave vector, or a complex energy (the imaginary part corresponds to a lifetime broadening). The momentum matrix element $\langle\psi_f|\mathbf{A}\cdot\nabla|\psi_i\rangle$ is then calculated using the above described wave functions, and the initial and final density of states are computed using the dispersion relations. These are combined using Fermi's golden rule to yield a photoemission spectrum. The results, not surprisingly, show a fairly symmetric direct-transition peak. This is because ξ is fairly large at these low energies, and, consequently, the transition is dominated by the bulk integral. The results are thus well described by the three-step model [11].

What is missing up to this point is the surface effect on the photon field. The transition matrix element actually consists of two terms, $\langle\psi_f|\mathbf{A}\cdot\nabla+(\nabla\cdot\mathbf{A})/2|\psi_i\rangle$, where the second term, although often ignored, is really not negligible [6,12]. Classically, there is a discontinuity in the dielectric function ε at the surface, which, upon differentiation, leads to an extra term proportional to $\delta(z-z_0)$. This delta function is somewhat broadened, phase shifted, and otherwise modified (Friedel-like oscillations) when the quantum mechanical response function of the system is taken into account. This problem is computationally challenging, and, as far as we know, has only been worked out for the simplest possible system, the jellium [12]. Nevertheless, it is clear that the contribution from this surface term to the transition matrix element will be proportional to the amplitudes of the wave functions at the surface, namely, of the form $C\psi_f^*(z_0)\psi_i(z_0)$, with the coefficient C being on the order of $\partial A/\partial z|_{z_0}d$, where d is the atomic layer spacing (approximate range of the surface effect). The gradient of the vector potential at the surface should be on the order of $k\Delta A$, where $\Delta A=(\varepsilon-1)A$ is the difference between the internal and external fields, and $k=\pi/d$ is the wave vector at the zone boundary. Combining these equations, we obtain $C/A\approx(\varepsilon-1)\pi=-1.8+4.3i$ for $h\nu=8$ eV using the known optical constant of Ag [13]. Putting this value into our calculation results in a significantly asymmetric line shape, which bears some resemblance to the experimental one.

The solid curve overlapping the data points in Fig. 3 is a fit to the experimental curve using C as an adjustable parameter (with A normalized to 1). The value of C from this fit is $-3.1+3.5i$, which is of the same order of magnitude as our rough estimate. For comparison, the middle curve in Fig. 3 is a result of the same calculation but with C set to zero, in other words, with the surface term ignored (the surface state is also ignored in this calculation). The line shape is a fairly symmetric peak, as mentioned above. The difference between the two model curves shows the significance of the surface

contribution. Other parameters involved in constructing the fitting function include the known full width at half maximum of 75 meV for the surface state peak [14], and an instrumental resolution of 55 meV. The width of the direct-transition peak is determined mostly by the damping of the time-reversed LEED state and, to a lesser extent, by the broadening of the hole state. The latter quantity is 100 meV from our fit, which is somewhat larger than the surface state broadening, as expected. The mean free path for the final state is 30 Å from the fit—a very reasonable value [6]. The intensity of the surface state peak in Fig. 3 can be related to the coherence length of the hole state, which is on the order of 10^2 Å. None of these parameters have anything to do with the asymmetry of the direct-transition peak, or the magnitude of the indirect-transition contribution.

The traditional view of the photoemission process would suggest that the indirect transition should resemble the density of valence states. The *sp* band edge at the zone boundary is a saddle point singularity, which gives rise to a divergent density of states in one dimension, as shown by the bottom curve in Fig. 3. Both the experiment and our calculation reveal no such divergent behavior. Rather, the indirect transition is bounded by a rounded cutoff at the band edge. The reason for this behavior can be related to the behavior of the matrix element. The initial wave function can be characterized by a rapid oscillation with a wave vector near the zone boundary modulated by a long-period envelope function. This envelope function is pinned at the surface by a node. For energies near the band edge, the period of the envelope function becomes long, and, consequently, the wave function becomes depleted near the surface. As a result, the matrix element diminishes, which effectively quenches the divergent singularity of the density of states. This rounded cutoff is thus a result of constraints on the initial wave function imposed by the surface boundary condition.

In summary, Ag(111) is a simple system, but its detailed photoemission line shape has remained unexplained over a long time. The direct transition is characterized by an asymmetric line shape, accompanied by a significant indirect emission at low binding energies with a rounded cutoff at the band edge. These spectral features can be related to surface effects. The interference between the direct and indirect transitions causes the direct-transition peak to assume an asymmetric profile. The indirect transition can be attributed to the $\nabla\cdot\mathbf{A}$ term in the transition matrix element, which becomes important at a surface. A simple estimate of the magnitude of this surface contribution yields a value consistent with the experimental results. The effects discussed in this study are fairly general in nature, and are likely to be important for other systems as well. The mean free path is 30 Å for the present experiment, but can become as short as ~ 5 Å at higher photon energies. The importance of the surface term will increase

correspondingly, and its amplitude can become comparable to that of the bulk contribution. Clearly, these surface effects cannot be ignored in quantitative materials studies using photoemission spectroscopy.

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