

Effective mass of image-potential states

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Effective masses m^* are determined for the $E(k_{||})$ dispersion of the $n=1$ image-potential state with use of two-photon photoemission. We obtain $m^*/m = 1.3 \pm 0.15$ for Ag(111), $m^*/m = 1.15 \pm 0.1$ for Ag(100), and $m^*/m = 0.9 \pm 0.1$ for Cu(100). The results are explained by a phase-shift analysis which predicts an effective mass larger than unity if the image state is located near the top of the bulk band gap and smaller than unity near the bottom of the gap.

INTRODUCTION

The observation of image-potential states with inverse photoemission¹⁻⁷ and two-photon photoemission^{8,9} has stimulated interest in the fundamental character of these states. Despite intense work on calculating binding energies and wave functions,^{4,5,7,10-16} there remains a problem, i.e., to explain the observation of effective masses significantly different from unity, with deviations as large as 70%. Several attempts have been made relying on a variety of possible mechanisms. The influence of surface corrugation⁵ has been used to calculate effective masses of about 1.2. It requires unreasonably large corrugation potentials after an error of a factor of 4 in the original work is taken into account. This calculation also predicts a correlation between effective mass and binding energy that contradicts the observations.⁹ Coupling with electron-hole pairs and surface plasmons^{15,16} has been considered, but was found to increase the effective mass by at most a few percent.

We offer an alternative (and more rudimentary) explanation of the effective masses based on multiple-reflection theory. There exists a "crystal-induced" modification of the effective mass which arises through the intimate relation between the image-state binding energy and the reflection properties of the bulk band gap. We show that numerical estimates of the effective masses can be obtained from simple "back-of-the-envelope" calculations. These masses are in reasonable agreement with two-photon-photoemission measurements.

TWO-PHOTON-PHOTOEMISSION EXPERIMENTS

The experiments were performed with a frequency-doubled tunable dye laser as described previously.^{8,9} The light was p -polarized. The vacuum level, which is the reference energy for image states, was determined as the turning point of the steplike low-energy cutoff of the (one-photon) photoelectron spectrum taken at $h\nu = 11.83$ eV. The two-photon photoelectron spectra exhibit a sharp peak at the vacuum level which makes it difficult to

define the onset. We find a work function of 4.56 eV for Ag(111), 4.42 eV for Ag(100), and 4.63 eV for Cu(100).

Angle-dependent two-photon-photoemission data are shown in Fig. 1. They are taken in a photon-energy regime where a nonresonant process dominates. (For a dis-

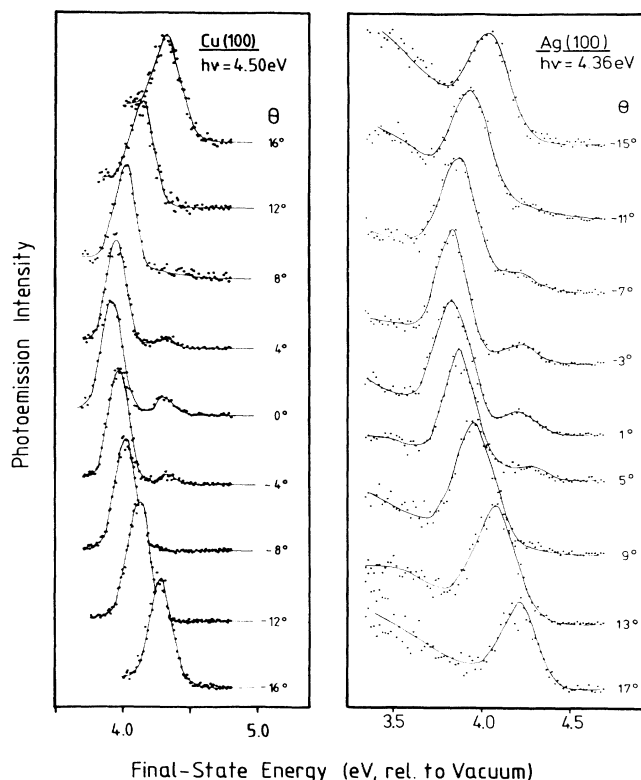


FIG. 1. Angle-dependent two-photon-photoemission spectra showing the dispersion of the $n=1$ image-potential state with $k_{||}$.

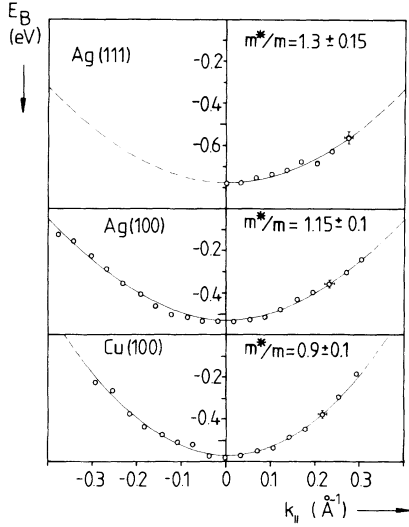


FIG. 2. E vs k_{\parallel} dispersion for the $n=1$ image-potential state on various surfaces as measured with two-photon photoemission. The data points are fitted by parabolas (lines).

cussion of various two-photon-photoemission processes, see Refs. 8 and 9). Thereby, electrons are excited from the continuum of bulk states into the image-potential state with the first photon and become ionized by the second photon. This process is characterized by a kinetic energy of the photoelectrons that increases like $E_{\text{kin}} = h\nu - E_B$ with the photon energy $h\nu$, whereby E_B is the binding energy of the image-potential state below the vacuum level. From the angle dependence of the peak positions, we easily obtain the $E(k_{\parallel})$ band dispersions shown in Fig. 2. The momentum parallel to the surface is given by $k_{\parallel} = \hbar^{-1} \sqrt{2mE} \sin\theta$ with θ measured from the sample normal. The intensity of the emission decreases with increasing θ for Ag(111) but remains constant for the (100) surfaces.

PHASE-SHIFT MODEL

The binding energy of image-potential states can be described in a transparent way by a phase shift model^{4,10-15} in which the electron is reflected back and forth between the crystal and the image-potential barrier. In order to obtain a standing wave, the round-trip phase accumulation must be a multiple of 2π . The phase shift Φ_B at the image-potential barrier is conveniently given by the WKB interpolation formula¹⁷

$$\Phi_B/\pi = \frac{1}{2} [(1 \text{ Ry}) / (E_v - E)]^{1/2} - 1, \quad (1)$$

and depends on the energy of the image state relative to the vacuum level E_v . The phase shift Φ_C on reflection at the crystal-band-gap barrier can be approximated¹¹ by

$$k \tan(\Phi_C/2) = p \tan\delta - q, \quad (2)$$

$$\sin(2\delta) = (\hbar^2/2m)(2pq/V_G), \quad (3)$$

where $\hbar^2 k^2/2m = E$, $2|V_G|$ is the band gap, and δ is a wave-function phase which varies from 0 at the bottom to $\pi/2$ at the top of the gap; p and q are the real and imaginary parts of the electron wave vector within the gap and are given by standard expressions.^{11,18} With these approximations the image-state energies and their dispersions are given by

$$E(k_{\parallel}) = E_v - e_n + \hbar^2 k_{\parallel}^2 / 2m, \quad (4)$$

$$e_n = (1 \text{ Ry}) / 16(n+a)^2, \quad n = 1, 2, 3, \dots$$

$$a = (1 - \Phi_C/\pi) / 2.$$

The mass m in the kinetic-energy term of Eq. (4) is the free-electron mass, but an effective mass $m^*/m = \hbar^2 / (d^2 E / dk_{\parallel}^2)$ different from unity results when the phase Φ_C and, consequently, e_n depends on k_{\parallel} .

Note that the projected gaps considered here are large at $k_{\parallel} = 0$ and decrease with increasing k_{\parallel} . Thus, the lower edge of the gap disperses faster than free-electron-

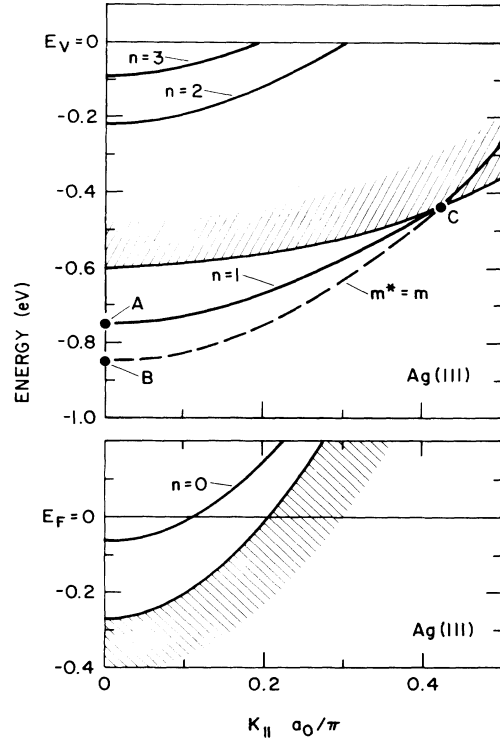


FIG. 3. Band diagram for Ag(111) using a simple phase-shift model. The $n=1$ image-state dispersion intersects the upper edge of the bulk band gap and disperses less than the dashed free-electron parabola. The crystal-induced $n=0$ surface state, on the other hand, intersects the lower edge of the bulk band gap and disperses more strongly than the free electron.

like, whereas the upper edge is relatively flat. As pointed out elsewhere,¹¹ these characteristics are imposed on the surface-state dispersion relations depending on whether the surface state resides in the lower or upper part of the gap.¹³ For a gap centered about $k_{\parallel}=0$ and the lowest ($n=1$) image state, we have binding energies ranging from $e_1=0.85$ eV ($\Phi_C=\pi$) at the top of the gap, to $e_1=0.38$ eV ($\Phi_C=0$) at the bottom of the gap. Many image states observed to date are located near the top of the band gap and cross the upper band edge at finite k_{\parallel} . In such a case the binding energy e_1 increases from a value smaller than 0.85 eV at $k_{\parallel}=0$ to exactly 0.85 eV at the crossing point. Thus, the free-electron-like band dispersion is flattened by the counteracting $e_1(k_{\parallel})$ dispersion, and the effective mass increases. For the intrinsic surface states observed near the bottom of the gap on some surfaces, the situation is reversed: the $e_0(k_{\parallel})$ dispersion adds to the free-electron dispersion and the effective mass decreases.

Numerical estimates for the effective mass can be made by means of the simple geometrical construction shown in Figs. 3 and 4. Outside the gap, the dispersion goes as $m^*/m=1$ originating from point *B*. The crossover point *C* can lie on the upper gap edge, as in Ag(111), or on the lower gap edge,¹⁹ as in Cu(100). This gives rise to the two opposite trends $m^*/m > 1$ or $m^*/m < 1$. For Ag(100) the $n=1$ state is so close to midgap (i.e., 40% up) that no convincing case can be made either way. A more sophisticated calculation with all Fourier components of the potential is called for in order to properly describe the complicated nature of the projected gap near the point where it closes. Our simple model is expected to be most accurate for Ag(111) since the crossover point *C* stays close to $k_{\parallel}=0$, where a single Fourier component gives a reasonable description of the band gap. From the total dispersion within the gap we may define an average effective mass

$$\frac{m^*}{m} = \frac{E_C - E_B}{E_C - E_A}, \quad (5)$$

where E_A is the energy at $k_{\parallel}=0$ determined by the local value of Φ_C . For Ag(111), Ag(100), and Cu(100) one obtains the values given in Table I. Note that the dispersion is not strictly parabolic, so that the experimentally derived m^*/m will depend on the range of the fit. In particular, $m^*/m \rightarrow 1$ if the dispersion is pursued deep into the bulk continuum, or if only the center of the Brillouin zone is considered.¹⁴

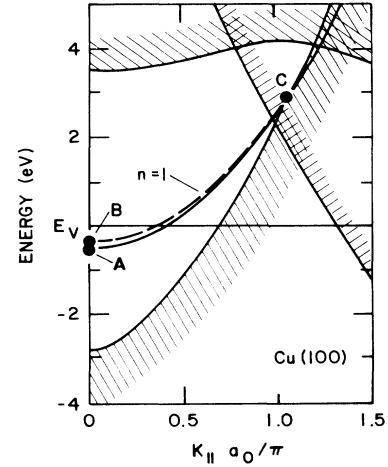


FIG. 4. Band diagram for Cu(100). The $n=1$ image state lies near the middle of the bulk band gap, causing an effective mass near unity (see Table I).

CONCLUDING REMARKS

From Figs. 3 and 4 and Table I one can see that the agreement between the simple phase-shift model and experiment is within the error bars for the effective masses. The absolute binding energies are slightly off due to the approximations made in determining the phase shifts. Only a single Fourier component of the bulk potential was used and the potential in the surface region is imagelike and is embodied in the WKB expression for Φ_B . Also, the position of the image plane needs to be refined. However, these simplifications affect the result on the effective mass to a much smaller degree than the absolute binding energy. We note that our approach for the effective mass works even for the intrinsic ($n=0$, Fig. 3) surface state observed near the bottom of the gap in Ag(111), although our approximations are less reliable in this case. Combining inverse photoemission and photoemission results,^{9,20} the dispersion can be fitted with an effective mass of 0.4–0.5. The phase shift model gives $m^*/m=0.44$. The large effective mass ($m^*/m=1.7$, Ref. 7) for the $n=1$ image state on Ni(110) has been explained by a similar “back-of-the-envelope” construction.¹³

TABLE I. Binding energy E_A and effective mass m^* of the $n=1$ image-potential state. For the definition of the energies E_B and E_C , see Figs. 3 and 4. All energies are in eV.

	Phase model			m^*/m	Experiment	
	E_A	E_B	E_C		E_A	m^*/m
Ag(111)	-0.75	-0.85	-0.45	1.33	-0.77 ± 0.03	1.3 ± 0.15
Ag(100)	-0.53	-0.38 (-0.85) ^a	+2.3 (+2.4) ^a	0.95 (1.11) ^a	-0.53 ± 0.02	1.15 ± 0.1
Cu(100)	-0.50	-0.38	+2.7	0.96	-0.57 ± 0.02	0.9 ± 0.1

^aMarginal due to uncertainties in the crossover point (see text). The numbers in parentheses are for a crossover at the top of the gap.

In summary, we have observed a deviation of the effective mass of image-potential states from unity using two-photon-photoemission and have explained the results semi-quantitatively by a simple phase-shift model. The

underlying mechanism is a k_{\parallel} -dependent phase shift for reflection at the crystal and does not need to invoke the extreme surface corrugation or many-electron effects discussed previously.

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