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Two-Photon Photoemission via Image-Potential States

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Strong two-photon photoemission is observed from Ag(111) and Cu(111) surfaces with image-potential states as intermediates. Three processes are found: (A) resonant excitation, (B) relaxation into the intermediate state, and (C) energy pooling via collisions between excited electrons. For Ag(111) we find two image-potential states with binding energies of 0.77 ±0.03 and 0.23 ±0.03 eV, close to the hydrogenic values, and an unidentified state 2.57 ±0.05 eV below the vacuum level. The work function is 4.49 ±0.02 eV.

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Electrons can be bound at a surface by the Coulomb attraction to their image charge. The resulting image-potential states form a hydrogenic series converging toward the vacuum level for zero parallel momentum $\mathbf{k}^{\parallel}$ (see Fig. 1). These states offer the possibility to study a two-dimensional electron gas that is confined by a very simple potential. The first application was to trap electrons outside the surface of liquid helium in order to crystallize them into a Wigner lattice.[1] They play a significant role in enhancing the vacuum tunneling rate.[2] Recently, image-potential states were found at metal surfaces by inverse photoemission.[3-5] The electrons are bound close enough to the metal surface that the question arises to what degree the simple Coulombic image potential is modified by the crystal potential.[6-11] The energy resolution of inverse photoemission allows one to resolve a single state only. However, precise binding energies of several series members are needed to probe the shape of the potential.

A high-resolution technique for probing unoccupied states in solids is two-photon photoemission,[12] where intense laser radiation is used to populate a normally unoccupied state with the first photon and to photoionize from this intermediate state with the second photon. Image-potential states are ideally suited as intermediate states because a significant population can be built up. This is expected from their long lifetime,[5,7] which in turn is caused by the fact that they are located outside the solid.

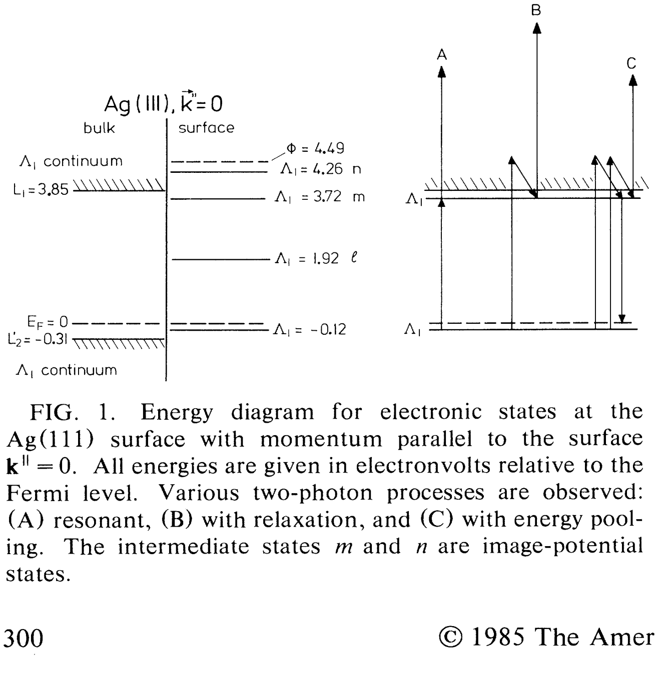

FIG. 1. Energy diagram for electronic states at the Ag(111) surface with momentum parallel to the surface $\mathbf{k}^{\parallel} = 0$. All energies are given in electronvolts relative to the Fermi level. Various two-photon processes are observed: (A) resonant, (B) with relaxation, and (C) with energy pooling. The intermediate states *m* and *n* are image-potential states.

We observe strong two-photon photoemission from the Ag(111) surface with image-potential states as intermediates. Three states are resolved and accurate binding energies are given. Various two-photon excitation mechanisms are found (see Fig. 1) by tuning of the photon energy of the exciting laser: (A) resonant excitation of the intermediate state from an occupied surface state plus ionization with a second photon, (B) excitation into a bulk state, relaxation into the intermediate state, and subsequent ionization, and (C) energy pooling via collisions between two electrons[13] in intermediate states. The occurrence of these second-order processes shows that a high population density of image-potential states is possible. Thus, one can create a two-dimensional electron gas *in vacuo.* The electron mobility is not restricted by phonons and impurities as in semiconductors where the highest quality electron gas is currently achieved. This raises hopes of being able to study new states of matter that possibly occur[14] in a two-dimensional electron system.

The experiments were performed with a frequency-doubled tunable dye laser pumped by a XeCl excimer laser with 10-ns pulse length. The light was *p* polarized. No photoemission was seen with *s* polarization in agreement with selection rules for transitions from Λ_1 to Λ_1 states. Care was taken to avoid a distortion of the spectra by space-charge effects which turned on at about 5×10^4 W/cm^2 power density. Heating of the sample by the laser was negligible at this power. We actually observed a quenching of the two-photon photoemission together with a quenching of the Λ_1 initial state when the sample was heated above $\approx 200\,°\mathrm{C}$. The photoelectrons were detected with an angle-resolving (narrower than ±2°) hemispherical energy

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analyzer capable of 50 meV energy resolution. The Ag(111) surface was cut to better than 0.3°, mechanically and chemically polished, and sputter annealed at 2×10^{-10} Torr vacuum. We obtained a work function of $\phi=4.49\pm0.02$ eV as measured by subtracting the width of the (one-photon) photoelectron spectrum from the photon energy in good agreement with the value of 4.46 ± 0.02 eV[15] reported for clean Ag(111).

The photoelectron spectra in Fig. 2 represent various excitation regimes and give an impression of the richness of the observed structures. The (one-photon) spectrum at $h\nu=11.83$ eV shows the well-known[16] occupied Λ_1 surface state in the $L_{2'}$-L_1 band gap[17] which we use as an initial state (Fig. 1). We measure a width of 52 meV which is to our knowledge the sharpest photoemission feature[18] reported from solids. The spectra shown at the bottom of Fig. 2 are characterized by a quadratic dependence of the photoemission on light intensity. The processes giving rise to the main features in Fig. 2 are identified by use of the photon energy dependence of the peak positions (Fig. 3) and peak intensities (Fig. 4).

Process A is characterized by an intensity resonance when the photon energy is tuned through the transition energy from the initial to the intermediate state. Such resonant behavior is observed in Fig. 4 for the intermediate states m and n at $h\nu=3.84\pm0.02$ eV and $h\nu=4.38\pm0.02$ eV, respectively. The resonance for state l is expected to occur below the two-photon photoionization threshold. By subtracting the binding energy of the initial state (0.12 eV below E_F) we obtain eneriges of 3.72 and 4.26 eV for the intermediate states m and n, respectively (see Fig. 1). Through use of our work function $\phi=4.49$ eV we find that states n and m are bound by 0.77 and 0.23 eV below the vacuum level. A simple hydrogenic model yields (1 Ry)/16=0.85 and (1 Ry)/64=0.21 eV for the $n=1$ and $n=2$ states. An upper limit for the width of the m and n states is given by the width of the resonance curves (for both about 80 meV FWHM). This width is probably dominated by work-function inhomogeneity since the lifetime broadening of the higher state should be much smaller[7] than for the lower state. Another characteristic of process A is its $h\nu$ dependence of the electron kinetic energy (see Fig. 3). With the intermediate state broader than the initial state one expects a peak shift proportional to 2 $h\nu$. Indeed, the slope of the data points for state m in Fig. 3 steepens near the threshold where process A dominates.

For process B with relaxation into an intermediate state one expects a linear dependence of the final-state (kinetic) energy with $h\nu$. The energy of the intermediate state is obtained by subtraction of $h\nu$ from the final-state energy. This process is seen for all three intermediate states l,m,n (Fig. 3). We find not only the proper slope of the data points but also the correct position, which is given by the straight lines labeled B_m,B_n in Fig. 3. These lines have been calculated without adjustable parameters by use of the data from process A as an input. Peak B_l leads to an energy of 1.92 eV above E_F for the intermediate state.

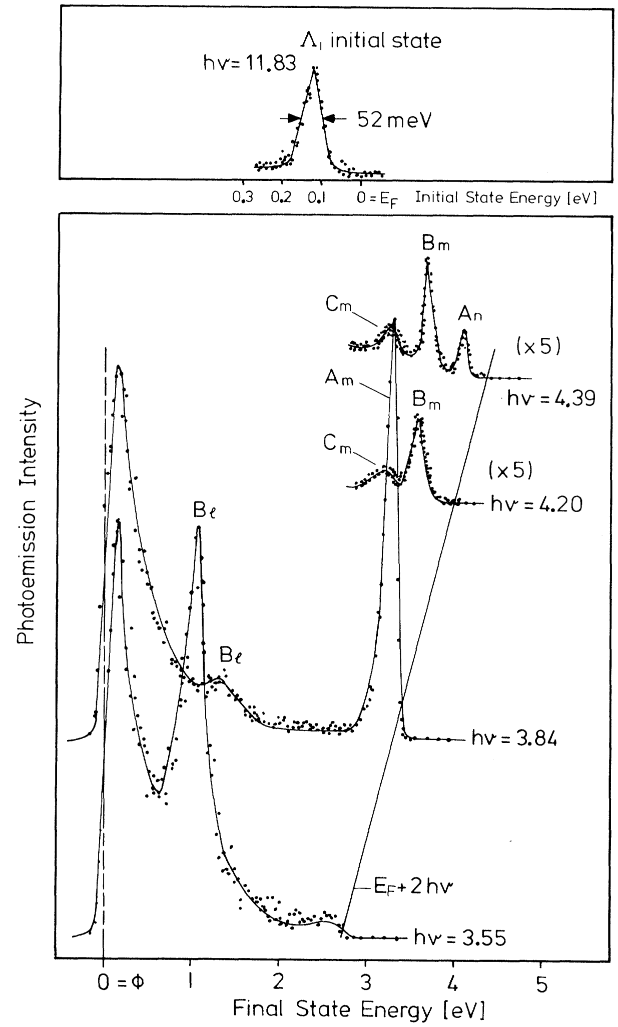

FIG. 2. Single-photon (top) and two-photon (bottom) photoelectron spectra from Ag(111) at $\mathbf{k}^{\parallel}=0$. Various two-photon processes A,B,C are identified for the intermediate states l,m,n (see Fig. 1).

Process C, i.e., energy pooling of two electrons in an intermediate state, should lead to a final-state energy independent of $h\nu$ and equal to twice the intermediate-state energy (relative to E_F). We can identify process C for the state m. The data points for C_m in Fig. 3 lie near the horizontal line predicted by use of the data from process A. This line is a lower limit since process C involves transitions at $\mathbf{k}^{\parallel}\neq0$, where the lowest Λ_1 surface state becomes unoccupied. Thus, all three processes lead to consistent values for the intermediate-state energies.

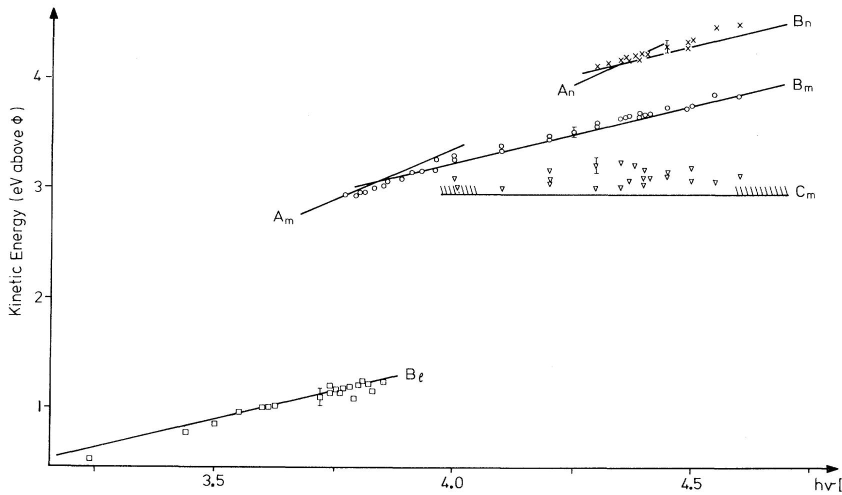

FIG. 3. Final-state energy (above vacuum) vs photon energy $h\nu$ for the two-photon photoemission structures from Ag(111). Straight lines with slope $2h\nu$, $1h\nu$, and 0 are expected for process A, B, and C, respectively.

The energy position of the intermediate states l,m,n can be used to test theoretical models of image-potential states. Two types of corrections to the simple hydrogenic model can occur: (i) modification of the image potential in the z-direction,[6–10] and (ii) corrugation parallel to the surface.[11] For case (i) small corrections have been predicted and our states m and n would keep their assignment as the $n=1$ and $n=2$ states. A phase-shift analysis[7–9] shows that the $n=1$ state shifts toward *lower* binding energy as observed, and only by a small amount since the state lies very close to the upper edge of the bulk band gap.[9] For case (ii) a strong shift of the $n=1$ state toward *higher* binding energy is predicted, which requires an assignment different from the hydrogenic one with l,m,n corresponding to the $n=1,2,3$ states. The magnitude of the shift increases with the surface corrugation. This assignment explains state l, but we suspect that it is incorrect, since state l is not seen in inverse photoemission.[9,19,20] The accuracy of our binding energies should clearly distinguish between these two assignments if more definitive theoretical predictions about the $n=1$ state were made for case (ii). A systematic search using various surfaces is under way. Preliminary data on Cu(111) yield spectra similar to Ag(111) with a binding energy of 0.83 eV below vacuum for the m state. The l state is not seen on Cu(111).

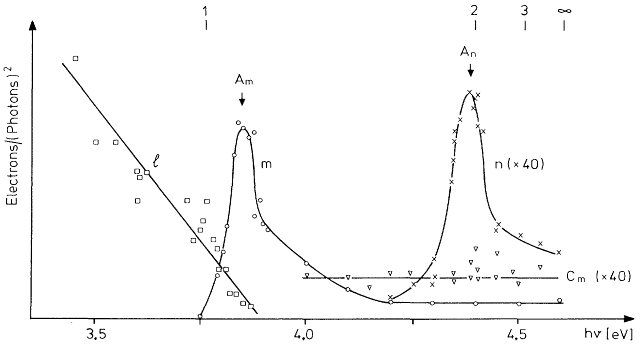

FIG. 4. Intensity vs photon energy for two-photon photoemission features involving the intermediate states l,m,n. The arrows denote the resonance positions for the image-potential states m and n. Tick marks labeled 1,2,3,∞ are for a simple hydrogenic model.

Our best (although not definitive) assignment for the l state is a surface state on Ag(110) facets similar to the one observed[20,21] between 1.6 and 2.5 eV above E_F on Ag(110). This state is located in the same band gap as the other states discussed here. The [111] escape direction on a (110) surface corresponds to a momentum $k^{\parallel}=0.3$ Å^{-1} along [001] at the kinetic energy of about 1 eV for the B_l peak. Silver is known for its tendency to form rough surfaces. For Cu(111) a smoother surface is expected and, indeed, the l state is not seen.

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