

Hydrogenic image-potential states: A critical examination

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Accurate binding energies E_B of image-potential states are determined with two-photon photoemission. The observed values of E_B [0.83 eV for Cu(111), 0.77 eV for Ag(111), and 0.80 eV for Ni(111)] lie close to the hydrogenic $n=1$ value of $1 \text{ Ry}/16=0.85 \text{ eV}$ and do not depend significantly on the effective mass. This result rules out a recent assignment of the observed image state to an $n=2$ state that is strongly perturbed by surface corrugation. The high accuracy of $\pm 0.03 \text{ eV}$ is used to test various models.

I. INTRODUCTION

The recent observation of image-potential states at metal surfaces¹⁻¹¹ is accompanied by substantial theoretical interest.^{4,5,11-16} These states occur at virtually every metal surface that has been studied and they appear to have a universal binding energy E_B of about 0.7 eV below the vacuum level. The value of E_B is close to $1 \text{ Ry}/16=0.85 \text{ eV}$ which is expected for a purely Coulombic potential. Thus, image-potential states represent a very simple and fundamental class of surface states which are useful to study the two-dimensional electron gas.¹⁷

This simple picture has been questioned by Garcia *et al.*⁵ who conclude that the state seen at about 0.7 eV binding energy actually corresponds to the $n=2$ state and not to the $n=1$ state. We note that the quantum number n is determined uniquely by counting the number of extrema in the wave function outside the image plane (one maximum for $n=1$ and a maximum plus a minimum for $n=2$). Garcia *et al.* find that the $n=2$ state is pulled down by the influence of the corrugation potential parallel to the surface and almost reaches the position of the unperturbed $n=1$ state. Additionally, the effective mass m^* increases, i.e., the dispersion parallel to the surface becomes smaller. A relation between m^* and the binding energy E_B is given:

$$E_B = \epsilon_2 + (1 - m_e/m^*)A/a_s^2 \quad (1)$$

with ϵ_2 being the energy of the $n=2$ state without corrugation [$\epsilon_2=0.19 \text{ eV}$ (Ref. 5) to 0.33 eV (Ref. 8)], m_e the free-electron mass, $A = \pi^2 \hbar^2/m_e = 75.3 \text{ eV \AA}^2$ (corrected for a factor of 4 error in Ref. 5), and a_s as the lattice constant of the surface corrugation which equals $a_0\sqrt{6}/4$ for the (111) face of an fcc lattice.

We test this relation with the recently-developed technique of two-photon photoemission from an occupied surface state⁶ where the first photon excites from an occupied surface state to the image-potential state as intermediate (see Fig. 1) and the second photon ionizes from the image-potential state. This technique has the best energy resolution that is available for probing the binding energy E_B of image-potential states. It is found that E_B is independent of m^* within our error bars of $\pm 0.03 \text{ eV}$.

This result is at variance with the theory by Garcia *et al.* which predicts a dependence of E_B on m^* that is more than an order of magnitude larger than our upper bound. The data are consistent with a hydrogenic picture where the binding energy is only slightly perturbed (about 6%) by the coupling to the crystal. Recent refinements of the hydrogenic model are put to a critical test with unprecedented accuracy.

II. TWO-PHOTON PHOTOEMISSION EXPERIMENT

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 $5 \times 10^4 \text{ W/cm}^2$ power density. Heating of the sample by the laser was negligible at this power. The photoelectrons were detected with an angle-resolving (narrower than $\pm 2^\circ$) hemispherical energy analyzer. The surfaces were cut to better than 0.5° , mechanically and chemically polished, and sputter-annealed in a 2×10^{-10} Torr vacuum. From the width of the (one-photon) photoelectron spectrum taken at $h\nu=11.83 \text{ eV}$ we obtained work functions of 4.88, 4.56, and 5.25 eV for Cu(111), Ag(111) and Ni(111). Similar values were reported previously (4.85, 4.46, and 5.15 eV, respectively^{18,19}).

Various two-photon photoemission processes can be distinguished by following the peak positions in the photoelectron spectra versus photon energy. These have been discussed for Ag(111) in a previous report.⁶ The dominant process is resonant two-photon photoemission with the lowest image-potential state as intermediate (see Fig. 1). This leads to an enhancement of the emission intensity by almost two orders of magnitude when the exciting laser is tuned to the transition energy from the occupied Λ_1 surface state to the lowest image-potential state (Fig. 2). The resonance occurs at $h\nu=4.46, 3.84,$ and 4.69 eV for Cu(111), Ag(111), and Ni(111), respectively. The position of the image-potential state below the vacuum level can be

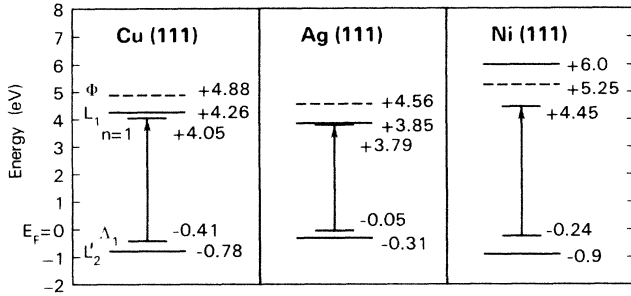


FIG. 1. Energy levels for the three surfaces studied. The positions of the surface states and the work functions Φ are from this experiment (Ref. 19), the bulk band edges (L_2, L_1) from Ref. 20.

determined directly from the photoelectron energy distribution at resonance shown in Fig. 3. The resonance photon energy $h\nu_{\text{res}}$ is subtracted from the kinetic energy of the peak. The vacuum level is given by the turning point at the steplike low-energy cutoff of the one-photon photoelectron spectrum. The two-photon photoelectron spectrum exhibits a sharp peak at the vacuum level. Although the resonance energies differ substantially for the three surfaces, the binding energies of the image-potential states are very similar: $E_B = 0.83, 0.77,$ and 0.80 eV for Cu(111), Ag(111), and Ni(111) with an error of ± 0.03 eV. The effective mass is determined using a nonresonant two-photon photoemission process where electrons are excited from the bulk (e.g., process *B* in Ref. 6). Our result for Ag(111) is $m^*/m_e = 1.35 \pm 0.15$ for the image state and $m^*/m_e = 0.7 \pm 0.2$ for the occupied surface state. For Cu(111) and Ni(111) we are not able to determine m^* due to restrictions in the available photon energy range. Therefore, we have used m^* values from inverse photoemission work by Goldmann *et al.*¹¹ [$m^*/m_e = 1.2 \pm 0.2$ for Cu(111), 1.4 ± 0.3 for Ag(111) and 1.6 ± 0.2 for Ni(111)]. They are consistent with other inverse photoemission work^{4,9,10} and with our own measurement for Ag(111).

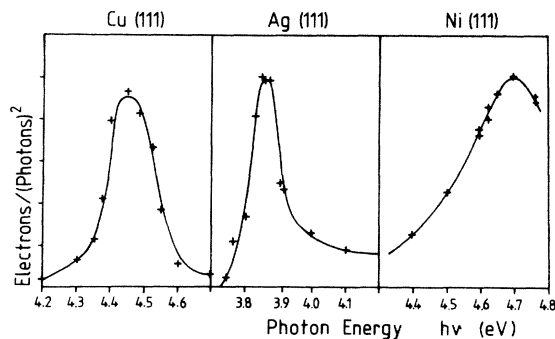


FIG. 2. Intensity of two-photon photoemission versus photon energy. A strong resonance is observed at the transition energy between the occupied Λ_1 surface state (see Fig. 1) and the lowest image-potential state.

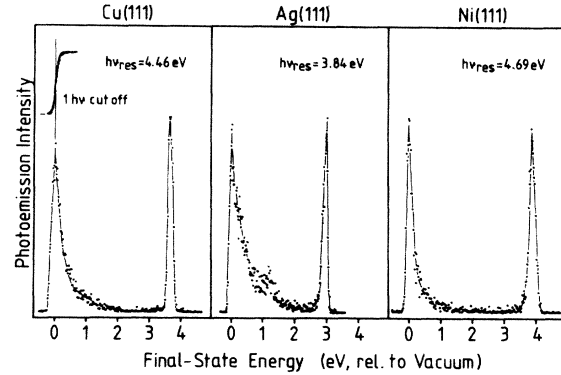


FIG. 3. Energy distribution of photoelectrons at resonance. By subtracting the resonance photon energy from the kinetic energy one obtains the position of the image-potential state relative to the vacuum level.

III. DISCUSSION

Our accurate measurement of the binding energy E_B allows us to test various theoretical models. A strong correlation of E_B with the effective mass m^* has been predicted⁵ in the above-mentioned model where the potential variations parallel to the surface play a dominant role. Most other theories consider the potential perpendicular to the surface only. Smith and others^{4,11,12,15} relate E_B to the position of the vacuum level in the bulk band gap. Since Ni(111) has an effective mass¹¹ and a band gap¹⁸ that differ significantly from Cu(111) and Ag(111), we can use our results to distinguish various models.

First, we discuss the theory by Garcia *et al.*⁵ The correlation between m^* and E_B given by Eq. (1) is shown by three dashed lines in Fig. 4 which differ slightly from each other because of the different lattice constants a_0 . The data are shown by dots with error bars. The Cu(111) data are compatible with the calculation but the Ag(111) and the Ni(111) data fall out of place. No correlation between E_B and m^* is detected within our error bars. Our accuracy in the measurement of E_B is such that even a variation could be detected that is an order of magnitude smaller than predicted.

Most other calculations^{4,11-15} for E_B use a one-dimensional potential. Various empirical potentials have been used which give binding energies for the $n = 1$ state from 0.5 to 2 eV. We note the following two general trends: (i) The level moves up (i.e., E_B is reduced) when the infinitely-deep image-potential well is truncated at a finite depth (typically the inner potential of the solid). (ii) The level moves down with the image plane moving outwards because the effective potential well becomes wider. From our nearly-hydrogenic binding energies we conclude that these counteracting corrections nearly cancel each other. As an example for such calculations we discuss a phase-shift analysis by Smith¹² which explains trends from one material to the other in a transparent way. A simple sinusoidal crystal potential plus a truncated image-potential gives¹² binding energies of 0.78, 0.75, and 0.62 eV for Cu(111), Ag(111), and Ni(111) that are surprisingly close to the experiment. The calculated E_B values are somewhat too small which is likely due to the

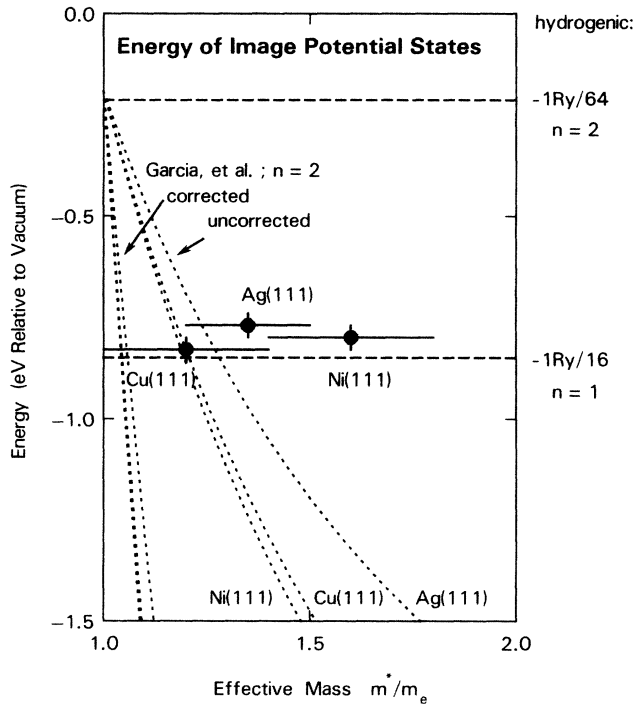


FIG. 4. Relation between the binding energy of the lowest image-potential state E_B and its effective mass m^*/m_e [m^* from Goldmann *et al.* (Ref. 11) for Cu(111) and Ni(111)]. In contrast to the prediction by Garcia *et al.* (Ref. 5) we find E_B close to the hydrogenic value and no significant dependence of E_B on m^* .

fact that the image plane was placed at the jellium edge and not farther outside like required by self-consistent jellium calculations.^{15,21} The expected trend towards lower E_B when going from Cu, Ag, to Ni is not found in the data. The rather critical placement of the image plane or counteracting many-body effects (see below) could be re-

sponsible. Self-consistent calculations of the true surface potential (particularly, the effective image plane for the real lattice) would be very useful in order to become free of fitting parameters.

The influence of many-body effects on E_B has been quantified by Echenique and coworkers¹⁶ who find that E_B increases for higher electron density. The calculated interstitial electron density²² increases from Ag to Cu to Ni (0.022, 0.032, and 0.039 e/bohr^3) and gives a small increase¹⁶ of 0.02 eV in E_B from Ag to Ni. Many-body interactions have also been used to explain effective masses larger than unity¹⁶ but the calculated effect is only a few percent. The key parameter for the strength of many-body interactions is the surface plasmon energy²³ which is correlated with the electron density. Cu and Ni do not exhibit a well-defined plasmon resonance due to damping by d -band transitions but Ag does. The surface plasmon energy [3.6 eV (Ref. 24)] is shifted far below the free electron gas value, though and does not exhibit the canonical ratio of $\sqrt{2}$ to the bulk plasmon energy (3.78 eV). Measurements on simple metals or more sophisticated calculations including d -bands are required for a reliable assessment of many-body effects.

Are, then, image-potential states indeed hydrogenic? Our binding energies are fairly close to the hydrogenic value for the $n = 1$ state with an average deviation of 6% towards lower binding energy. This leads us to conclude that the simple hydrogenic assignment gives a rather good description. In particular, the spatial extent of the wave function into the vacuum (stressed in Ref. 5) should be very similar to the hydrogenic case. The outermost turning point of the wave function (corresponding to the classical turning point) is mainly determined by E_B .

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