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Empty surface states, image states, and band edge on Au(111)

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Inverse-photoemission observations on Au(111) reveal the $n=1$ image stage, the L_1 (L_6^+) band edge, and the continuation above the Fermi level E_F of the well-established Shockley surface state. The image-state binding energy (0.60±0.05 eV) is lower than that obtained on Cu(111) or Ag(111), or that expected on the basis of elementary multiple-reflection theory (0.85 eV). The L_1 (L_6^+) level is found to occur 3.6±0.1 eV above E_F.

INTRODUCTION

The work on Au(111) described in this paper completes our **k**-resolved inverse photoemission spectroscopy (KRIPES) survey of the (111) faces of the noble metals. The results are similar to those reported earlier on Cu(111) (Ref. 1) and Ag(111) (Ref. 2) in that we see the $n=1$ image state and the Shockley surface state known from photoemission work.[3–5] The Au(111) surface, however, offers two new results. Firstly, we observe the upper edge of the projected bulk band gap. Secondly, we find, in agreement with Straub and Himpsel,[6] that the binding energy of the $n=1$ image state is significantly lower than the values obtained on Cu(111) and Ag(111), or those predicted by a simple application of multiple reflection theory. $E(k_{\parallel})$ dispersion relations are presented.

INVERSE PHOTOEMISSION EXPERIMENTS

The KRIPES spectra were measured using a refracting monochromator described elsewhere[1,7] and a specially designed low-energy electron gun.[8] The sample was prepared by the usual cycles of ion bombardment and annealing, and displayed a 1×1 low-energy electron diffraction (LEED) pattern.

Figure 1 shows spectra taken at $\hbar\omega=11.0$ eV as a function of angle of electron incidence θ. Three main features are observed: surface states (SS), band edge (BE), and image states (IS). The feature labeled SS is identified as the continuation above E_F of the $n=0$ crystal-induced (or Shockley) surface state, known from angle-resolved photoemission work[3–5] to lie below E_F at $\bar{\Gamma}$. SS first appears strongly near $\theta\sim5°$ and then disperses upward in energy with increasing θ. This peak is also observed at $\theta=0°$ but it is weaker; we attribute this observation [also seen in Cu (Ref. 1) and Ag (Ref. 2)] to the effects of finite angular resolution. The features BE and IS are identified, respectively, as the band edge and the $n=1$ image state.

The peak positions have been reduced to $E(k_{\parallel})$ plots in the usual way and have been superposed in Fig. 2 on the projected bulk band gap. The bulk bands were calculated using a combined interpolation scheme[9] whose parameters had been adjusted for a good fit to the L gap. The position of the L_1 level (L_6^+in double-group notation) is known from piezo-optical,[10] photoemission,[11,12] and tunneling[13] work to lie at $E_F+3.6$ eV. The $L_2'(L_6^-)$ level is known to lie at $E_F-1.0$ eV. The band-edge feature BE seen in KRIPES falls at 3.6±0.1 eV, providing another independent experimental confirmation of the L_1 energy position. The $E(k_{\parallel})$ dispersion of the upper band-edge feature is quite flat, in agreement with the theoretical expectations.

The surface state SS follows reasonably well the extrapolation of the dispersion relation determined below E_F

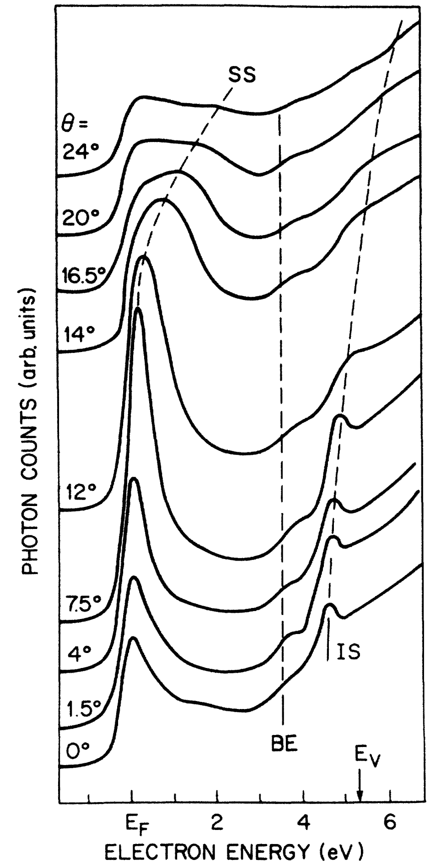

FIG. 1. Inverse photoemission spectra from Au(111) at $\hbar\omega=11.0$ eV as a function of angle of incidence θ. Dashed curves indicate the dispersion of the Shockley surface state (SS), the band edge (BE), and the $n=1$ image state (IS).

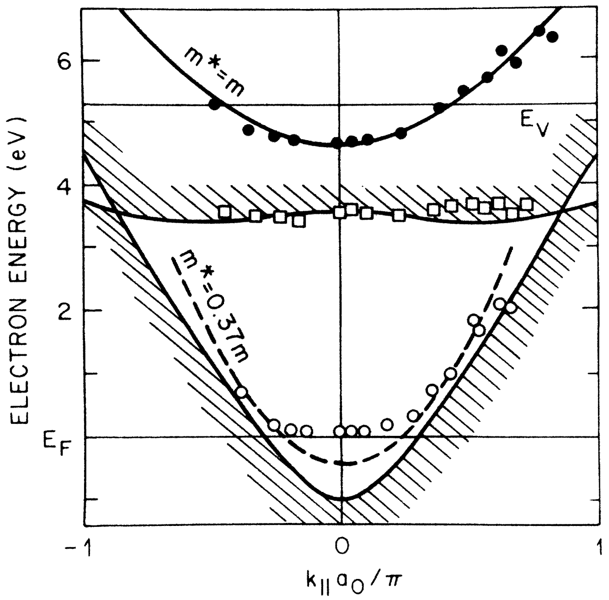

FIG. 2. Experimental $E(k_{||})$ relations for the features SS (open circles), BE (open squares), and IS (solid circles) observed in Fig. 1. Hatching indicates the projected bulk band structure. The dashed curve is the extrapolation of the dispersion relation obtained below E_F in the photoemission data of Ref. 5.

by Hansson and Flodström[5] ($m^*/m=0.37$, energy at $\bar{\Gamma}=E_F-0.45$ eV). At the higher values of $k_{||}$, the experimental dispersion relation approaches the band edge, suggesting the possibility that SS eventually crosses into the bulk continuum becoming a surface resonance, as is believed to be the case in Cu(111) (Ref. 1) and Ag(111) (Ref. 2).

The experimental $E(k_{||})$ dispersion for the $n=1$ image state IS falls close to a free-electron parabola ($m^*/m=1.0\pm0.2$). The IS binding energy $\bar{\Gamma}$ is found to be 0.60±0.05 eV, and will be discussed below.

COMPARISON OF Au WITH Cu AND Ag

We now examine the trends of surface-state formation on the (111) faces of the noble metals using a phase model based on elementary multiple-reflection theory.[14,15] It has been shown[1,16,17] that this theory, in combination with elementary nearly-free-electron (NFE) theory, provides a remarkably good account of the systematics of surface-state formation from gap to gap and from face to face. If $r_Ce^{i\phi_C}$ and $r_Be^{i\phi_B}$ denote the electron reflectivities at the crystal and surface barrier, respectively, bound states occur when the condition $\phi_C+\phi_B=2\pi n$ is satisfied. The "crystal-induced" $n=0$ solutions are identical to the "Shockley states" or "gap states" that occur even for step barriers.[17] The $n\geq1$ solutions constitute a Rydberg series of "image states" converging on the vacuum level E_V, and these occur only when the image potential asymptotic form of the surface barrier is taken into account.

Graphical solutions for the $n=0$ and $n=1$ states are shown for $\bar{\Gamma}$ on Au(111), Cu(111), and Ag(111) in Fig. 3. Here we have used for ϕ_C standard NFE expressions[17] and for ϕ_B the Wentzel-Kramers-Brillouin (WKB) approximation:[18]

$$\phi_B^0/\pi=[(3.4\ \text{eV})/(E_V-E)]^{1/2}-1\ . \qquad (1)$$

In Table I, we list the input data[10-13,19-24] used in these calculations, and we compare the predicted energies with those obtained in photoemission,[3-5,23-26] two-photon photoemission,[23,27,28] and inverse photoemission[1,2,6,29-31] experiments.

In view of the extreme simplicity of the phase model and the use of the WKB approximation ϕ_B^0, the excellence of the quantitative agreement for surface-state energies in Table I should be regarded as fortuitous.[17] Indeed, *exact* agreement, if desired, can be forced for *one* of the states by judicious adjustment of the position z_0 of the image plane. (As in Refs. 1, 16, and 17, we have taken z_0 at half an interlayer spacing beyond the last atomic layer.) The

TABLE I. Energies (in eV) of predicted and experimentally observed image states and surface states at $\bar{\Gamma}$ on the (111) faces of the noble metals.

	Cu(111)	Refs.	Ag(111)	Refs.	Au(111)	Refs.
Input data						
$E(L_1)-E_F$	4.25	10	3.9	10	3.6	10–13
$E(L_{2'})-E_F$	−0.85	17,19	−0.3	10	−1.0	3,10
$E(\Gamma_1)-E_F$	−8.6	19	−7.2	20,21	−9.0	20
Φ	4.94	22	4.56	23	5.31	24
Crystal induced ($n=0$) state						
E_0-E_F predicted	−0.32	This work	−0.06	This work	−0.38	This work
expt.	−0.4	25	−0.12	27	−0.5	3,4
	−0.39	26	−0.08	28	−0.45	5
First image state ($n=1$)						
E_1-E_V predicted	−0.78	This work	−0.77	This work	−0.85	This work
expt.	−0.9	1	−0.9	2	−0.6	This work
	−0.7	6	−0.65	30	−0.42	6
	−0.8	31	−0.6	31		
	−0.83	23,29	−0.77	23,29		

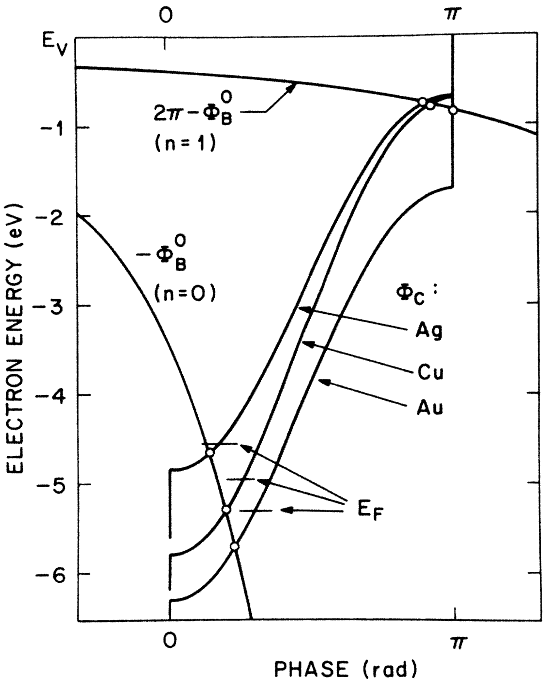

FIG. 3. Graphical solution of the phase model at $k_{\|}=0$ for the energies of the $n=0$ Shockley state and the $n=1$ image states using the WKB approximation for the barrier phase change ϕ_B.

strength of the phase model lies in its ability to predict systematics and trends. The trends for the $n=0$ Shockley state are well reproduced. The binding energy relative to E_F for Au(111) is slightly larger than for Cu(111), whereas that for Ag(111) is significantly smaller.

IMAGE-STATE BINDING ENERGY

The predicted trends are less successful for the image states. We obtain an experimental value of 0.60±0.05 eV for the binding energy e_1 of the $n=1$ image state on Au(111). This value is in agreement, within experimental uncertainty, with the result of Straub and Himpsel,[6] and is significantly smaller than the values ($e_1 \sim 0.8 \pm 0.1$ eV) typically obtained on Cu(111) and Ag(111). It is also smaller than the value 0.85 eV predicted by the elementary multiple-reflection model.

This discrepancy is potentially interesting and important. However, measurement of binding energies using KRIPES suffers from two uncertainties: (1) a resolution uncertainty in knowing where on the leading edge to place E_F; (2) a work-function uncertainty in knowing where to place E_V relative to E_F. We have circumvented these difficulties by calibrating our energy scale for Au(111) against that of the well studied case of Cu(001).

The principles of the calibration are as follows. We assume that the value $e_1=0.57$ eV obtained on Cu(001) using two-photon photoemission by Himpsel and coworkers[23,29] is correct; this is a reasonable assumption since the experimental resolution is superior to KRIPES and the work function was measured *in situ*. We then measure the difference ΔΦ in the work functions of Au(111) and Cu(001) samples attached to the same holder. This is done by monitoring the onset edge of sample current, I, as a function of gun cathode voltage V with a fixed retarding bias (−10 V) on the sample. The results of the energy scale calibration are shown in Fig. 4. Since the two samples are in electrical contact, the Fermi edges in the KRIPES spectra line up. The respective positions for E_V are separated by ΔΦ, so that if e_1 is known for one sample, it is automatically determined for the other. This method for e_1 therefore requires no knowledge of the absolute values of the work functions or the absolute position of E_F. If we *now* use published values for the work functions,[22,24] we obtain the energy scale shown at the bottom of Fig. 4. This same position of the energy scale has been used in Figs. 1 and 2.

The unexpectedly low value for e_1 on Au(111) remains unexplained. The phase model, which accounts so successfully for the systematics of surface-state occurrence in other contexts,[1,17,32] fails in this instance. The main difference with Cu(111) and Ag(111) is that E_V lies well

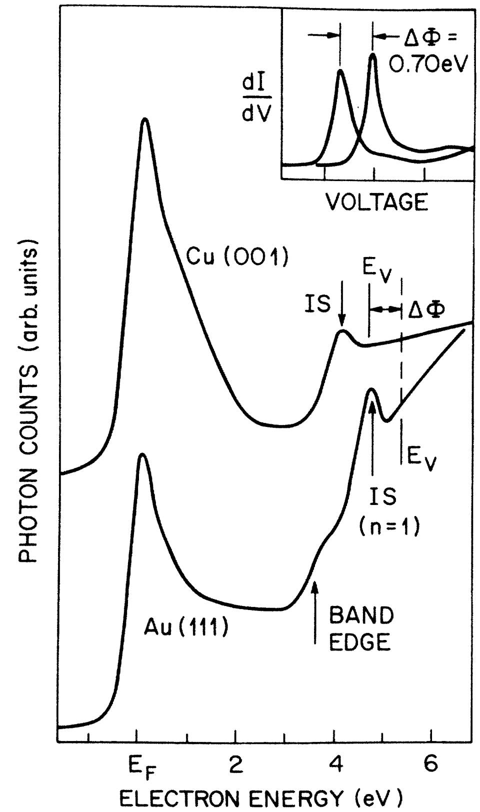

FIG. 4. Normal incidence inverse photoemission spectra ($\hbar\omega = 11.0$ eV) for two samples in electrical contact: Au(111) and Cu(001). The inset illustrates the determination of the work-function difference ΔΦ by differentiation of the sample I-V characteristic. The binding energy of the $n=1$ image state (IS) on Au(111) can then be obtained from that for Cu(001) without knowledge of the absolute values of the respective work functions or the precise Fermi-level location.

above the upper edge of the projected gap, so that the image state is really a surface resonance rather than a surface state. It may therefore be too far removed from the gap for the elementary multiple-reflection model to apply.

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[1] S. L. Hulbert, P. D. Johnson, N. G. Stoffel, W. A. Royer, and N. V. Smith, Phys. Rev. B **31**, 6815 (1985); **32**, 6916(E) (1985).

[2] S. L. Hulbert, P. D. Johnson, N. G. Stoffel, and N. V. Smith, Phys. Rev. B **32**, 3451 (1985).

[3] P. Heimann, H. Neddermeyer, and H. F. Roloff, J. Phys. C **10**, L17 (1977).

[4] Z. Hussain and N. V. Smith, Phys. Lett. **66A**, 492 (1978).

[5] G. V. Hansson and S. A. Flodström, Phys. Rev. B **18**, 1572 (1978).

[6] D. Straub and F. J. Himpsel, Phys. Rev. B **33**, 2256 (1986).

[7] T. T. Childs, W. A. Royer, and N. V. Smith, Rev. Sci. Instrum. **55**, 1613 (1984).

[8] N. G. Stoffel and P. D. Johnson, Nucl. Instrum. Methods A **234**, 230 (1985).

[9] N. V. Smith, Phys. Rev. B **19**, 5019 (1979).

[10] A. B. Chen and B. Segall, Solid State Commun. **18**, 149 (1976).

[11] M. M. Traum and N. V. Smith, Phys. Rev. B **9**, 1353 (1974).

[12] B. Segall and A. B. Chen, Solid State Commun. **17**, 1557 (1975).

[13] R. C. Jaklevic and J. Lambe, Phys. Rev. B **12**, 4146 (1975).

[14] E. G. McRae, Surf. Sci. **25**, 491 (1971).

[15] P. M. Echenique and J. B. Pendry, J. Phys. C **11**, 2065 (1978).

[16] N. V. Smith, Appl. Surf. Sci. **22/23**, 349 (1985).

[17] N. V. Smith, Phys. Rev. B **32**, 3549 (1985).

[18] E. G. McRae and M. L. Kane, Surf. Sci. **108**, 435 (1981).

[19] J. Knapp, F. J. Himpsel, and D. E. Eastman, Phys. Rev. B **19**, 4952 (1979).

[20] H. Eckardt, L. Fritsche, and J. Noffke, J. Phys. F **14**, 97 (1984).

[21] P. S. Wehner, R. S. Williams, S. D. Kevan, D. Denley, and D. A. Shirley, Phys. Rev. B **19**, 6164 (1979).

[22] P. O. Gartland, Phys. Norv. **6**, 201 (1972).

[23] K. Giesen, F. Hage, F. J. Himpsel, H. J. Riess, and W. Steinmann (unpublished).

[24] H. C. Potter and J. M. Blakely, J. Vac. Sci. Technol. **12**, 635 (1975).

[25] P. O. Gartland and B. J. Slagsvold, Phys. Rev. B **12**, 4047 (1975).

[26] S. D. Kevan, Phys. Rev. Lett. **50**, 526 (1983).

[27] H. R. Roloff and H. Neddermeyer, Solid State Commun. **21**, 561 (1977).

[28] G. V. Hansson and S. A. Flodström, Phys. Rev. B **17**, 473 (1978).

[29] K. Giesen, F. Hage, F. J. Himpsel, H. J. Riess, and W. Steinmann, Phys. Rev. Lett. **55**, 300 (1985).

[30] B. Reihl and K. H. Frank (unpublished).

[31] A. Goldmann, V. Dose, and G. Borstel, Phys. Rev. B **32**, 1971 (1985).

[32] R. F. Garrett and N. V. Smith, Phys. Rev. B **33**, 3740 (1986).