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Electronic and crystallographic properties of reconstructed and nonreconstructed Au{001}

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Low-energy-electron-diffraction analyses of Fe-, Mn-, and Rh-stabilized Au{001}1×1 surfaces find the atomic structure to be a relaxed bulk termination. The first and the second interlayer spacings are contracted by about (2±2.8)% and (2.8±2.8)%, respectively, of the bulk spacing along ⟨001⟩. Photoemission experiments with synchrotron radiation on reconstructed Au{001}5×20 find a surface-resonance band above the bulk d bands which exhibits dispersion with photon energies between 14 and 24 eV, in accordance with the buckled character of the hexagonal overlayer responsible for the surface reconstruction. All remaining features in the photoemission spectra from Au{001}5×20 can be explained on the basis of the self-consistent relativistic calculation of Eckardt, Fritsche, and Noffke to within 0.4 eV. Photoemission from Rh-stabilized Au{001}1×1 is similar to that from the reconstructed surface except for the surface resonance, which is markedly reduced on the 1×1 surface, and a shift of one band which points toward a transfer of s-like charge from the Rh to the Au atoms in the surface region.

I. INTRODUCTION

It is well known that clean {001} surfaces of the metals Ir, Pt, and Au are reconstructed, i.e., they have a structure different from that corresponding to bulk termination. The reconstructions have been denoted 1×5 or 5×20 and have long been ascribed to the formation of a hexagonal close-packed overlayer on top of the regular {001}1×1 net.[1] This atomic arrangement has been confirmed for Ir{001} and Pt{001} with quantitative analysis of low-energy electron-diffraction (LEED) intensities.[2] The 5×20 reconstructions are usually destroyed by strongly bound adsorbates in favor of a nonreconstructed, or 1×1, geometry.[3] Various impurities have been reported to cause this structural rearrangement in the case of Au{001}.[4]

Neither the reconstructed nor the unreconstructed {001} surface of Au has been subjected to quantitative structure analysis, although the corresponding electronic properties have been studied by photemission. Heimann *et al.*,[5] using UV-lamp photons with energies of 21.22 and 16.85 eV, reported the observation of surface-state bands on the 5×20 and the 1×1 surface; these bands are located above the bulk d bands and disappear when the surface structure is changed. In the work reported herein we study the atomic structure of a nonreconstructed {001} surface of Au as stabilized with small amounts of three different metallic impurities (Fe, Mn, and Rh), and we establish for the first time that such a structure is that of a slightly relaxed bulk termination. We also study the electronic properties of both the reconstructed and the Rh-stabilized unreconstructed surface by means of photoemission with synchrotron radiation. We find, in particular, that the strong feature found by Heimann *et al.* in the photoemission spectrum of the reconstructed surface with photon energy $h\nu=21.2$ eV exhibits dispersion with varying photon energy between 14 and 24 eV. This feature, located at 2.8 eV below the Fermi energy, is surface sensitive, since it is strongly attenuated by a surface coverage by Rh of about 0.2 layer equivalents, and would therefore not be expected to change its energy position with varying photon energy. However, the observed dispersion is consistent with the buckled character of hexagonal overlayer, as determined by atom diffraction.[6] We also find that the photoemission spectrum of Au{001}5×20 can be well explained by the relativistic self-consistent band structure of Au as calculated by Eckardt, Fritsche, and Noffke[7] (EFN), suggesting that the reconstruction is limited to the top atomic layer on the surface. On the impurity-stabilized bulklike unreconstructed surface the data indicate that emission from the surface resonance is markedly decreased, in agreement with Heimann *et al.*,[5] and that the interaction between Rh and Au is dominated by a flow of s-like charge from Rh to Au, rather than by the expected d-d interactions. The experimental evidence for all these results is given below.

This paper is organized as follows. Section II gives experimental details of both the LEED and the photoemission work; Sec. III describes the LEED intensity analyses of unreconstructed 1×1 surfaces of Au{001} as obtained with Fe, Mn, and Rh impurities; Secs. IV and V report results of photoemission experiments on Au{001}5×20 and Rh-stabilized Au{001}1×1 surfaces, respectively; and Sec. VI summarizes the conclusions.

II. EXPERIMENTS

The experimental tools used in the present work were LEED, Auger-electron spectroscopy (AES) and angle-

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resolved ultraviolet photoemission spectroscopy (ARUPS). LEED was used both qualitatively for the identification of the Au{001}5×20 and the Au{001}1×1 structure, and quantitatively for the determination of the atomic arrangement on the 1×1 surface. AES was used for monitoring surface cleanness, composition and coverage, while ARUPS was used for the study of the electronic structure in the valence band of both the 5×20 and the 1×1 surface.

For both the LEED and the ARUPS experiments the sample was prepared *ex situ* with conventional methods, i.e., first by orientation of the surface perpendicular to a ⟨001⟩ direction of Au to within 0.5°, then by mechanical grinding and polishing of the surface with abrasives of decreasing particle size (1, 0.3, and 0.05 μm) and finally by electrolytic polishing in order to remove the damage produced by the abrasives. In all experiments the sample was mounted on a manipulator that allowed rotations around three mutually perpendicular axes,[8] thus allowing precise orientation of the sample for normal incidence in the LEED experiments, and for measurements with *s*- or 25% *p*-polarized radiation in the photoemission experiments. After introduction into the experimental chamber and attainment of base pressure (1×10^{-10} Torr), the {001} surface was cleaned *in situ* by cycles of Argon-ion bombardments (5×10^{-5} Torr, 400 eV, 10 μA) and anneals at about 500 °C.

The LEED experiments and the collection of intensity data were done at different times extending over a period of about two years. The original aim of the experiments was to study the epitaxial growth of various metals on a {001} surface of Au. The metals (Fe, Mn, and Rh) were vaporized *in situ* from sources consisting of a thin wire of the appropriate metal wrapped around a tungsten spiral which was electrically heated. The coverage of the substrate surface was estimated from the ratio of the AES line of the deposited metal to the AES line of the substrate, and was converted to units of layer equivalent (LE) using known interlayer distances.

In the initial stages of metal deposition it was found (as already reported by others[4]) that minute amounts of metal impurities (of the order of 0.1 to 0.2 LE) destroyed the 5×20 reconstruction of Au{001} and replaced it with a 1×1 structure. In the LEED experiments, intensity data were collected in the electron-energy range from 40 to 400 eV for the 10, 11, 20, and 21 beams with a video system described elsewhere.[9] These data were then corrected for elimination of the background and normalized to constant incident electron current for use in the LEED intensity analyses described below. (In the course of the analysis of the Rh-stabilized Au{001}1×1 data an accident destroyed the file of the 21 spectrum, which was therefore not used in that case.)

The photoemission experiments were done on beamline U7B of the National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory. A plane-grating monochromator was used to disperse the synchrotron radiation, and the experiments were carried out in the photon-energy range between 14 and 24 eV. The energies of the photoelectrons were measured with a double-pass cylindrical mirror analyzer fitted with a special slit providing an angular resolution of 2°. As mentioned above, photoemission spectra could be collected both for *s*- and for 25% *p*-polarized radiation.

III. LEED INTENSITY ANALYSIS OF IMPURITY-STABILIZED Au{001}1×1

The calculations of LEED intensities versus energy of the incident electrons [so-called $I(V)$ curves] were done with Jepsen's computer program CHANGE.[10] Ten relativistic Au phase shifts and 69 beams were used up to 360 eV, with inner potential $V_0=(10+5i)$ eV (real part adjustable in the fitting process), and isotropic root-mean-square amplitude of thermal vibrations of 0.145 Å. Evaluation of the agreement between theory and experiment was done both visually and by R-factor analysis using the Van Hove–Tong R_{VHT} (Ref. 11), the Zanazzi-Jona r_{ZJ} (Ref. 12) and the Pendry R_{P} (Ref. 13) factors. Test calculations were also made with the Van Hove–Tong computer program[14] and the results compared with those obtained with CHANGE. The corresponding $I(V)$ curves were found to be very similar, but not identical, mostly

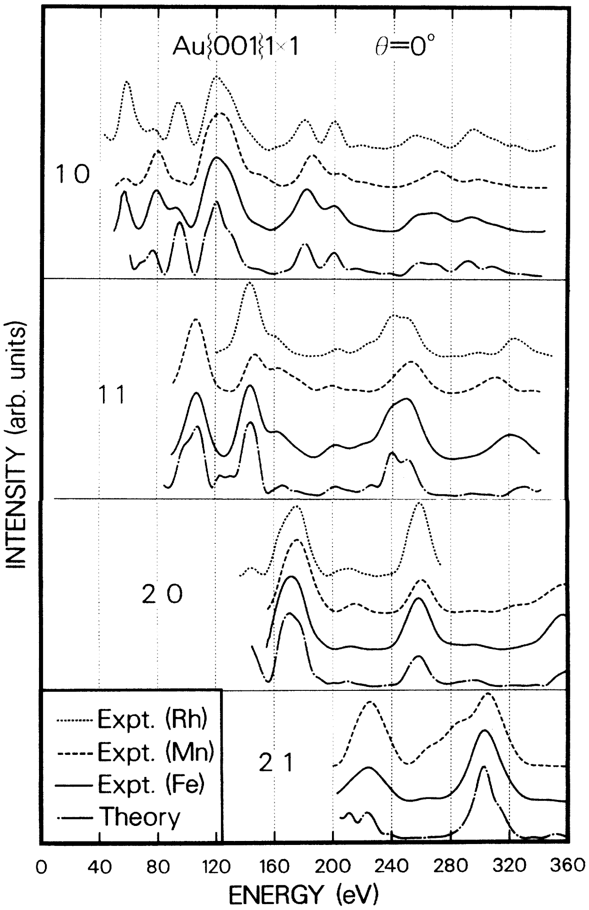

FIG. 1. Comparison between calculated and experimental $I(V)$ spectra from Rh-stabilized (dotted curves), Mn-stabilized (dashed curves), and Fe-stabilized (solid curves) Au{001}1×1. In each panel the bottom curve (dash-dotted) is the calculated curve.

with differences in peak intensities detectable.

The calculations were done for a number of different values of the first and the second interlayer spacing on the surface. With the notation Δd_{ik} for the change in spacing between layers i and k, the value of Δd_{12} was varied from -0.175 to $+0.025$ Å in steps of 0.025 Å, and for each of these values Δd_{23} was varied from -0.08 to $+0.08$ Å in steps of 0.02 Å. The analysis was carried out independently for each of the three sets of experimental intensity data, one set for each impurity, i.e., the R factors were minimized separately for the three sets. The best-fit parameters thus obtained were then averaged.

The averaged structural parameters are $\Delta d_{12} = -0.03\pm0.04$ Å [corresponding to $(2\pm2.8)\%$ contraction of the first interlayer spacing with respect to the bulk spacing along ⟨001⟩] and $\Delta d_{23} = -0.04\pm0.04$ Å [corresponding to $(2.8\pm2.8)\%$ contraction of the second interlayer spacing]. The corresponding R-factor values were $R_{\mathrm{VHT}}=0.37$, $r_{\mathrm{ZJ}}=0.26$, and $R_{\mathrm{P}}=0.38$.

The fit between theory and each one of the three experimental data can be judged from the plot in Fig. 1. The correspondence is not as good as one may find for stable 1×1 metal surfaces (as confirmed also by the relatively high R-factor values), but is considered satisfactory in view of the metastable character of the Au{001}1×1 surface structure and the likely possibility that some areas of the surface still had the 5×20 structure. The results indicate therefore that the impurity-stabilized Au{001}1×1 surface is only slightly relaxed from bulk termination, a property common to most stable nonmagnetic fcc{001} surfaces ($\Delta d_{12}/d_{\mathrm{bulk}}$ in percent is 0 for Ag and Al, -1.1 ± 0.4 for Cu and -8 ± 1.2 for Pb).

IV. PHOTOEMISSION STUDY OF Au{001}5×20

Normal-emission angle-resolved electron distribution curves (AREDC) were collected from clean Au{001}5×20 in the photon-energy range from 14 to 24 eV with both s- and 25% p-polarized radiation, and are depicted in Figs. 2 and 3, respectively. The features marked A, B, C, D, E, and F identify photoemission peaks due to bulk direct interband transitions, and the associated dashed lines show their dispersion with varying photon energy.

In Figs. 2 and 3, peak S, which disperses from 1.8 eV at $h\nu=15$ eV to 2.9 eV at $h\nu=22$ eV, is due to photoelectrons emitted from a surface-resonance band of the close-packed hexagonal overlayer that produces Au{001}5×20.[5] We will see that this peak is markedly attenuated when minute amounts of impurities are added to the surface, converting the structure to 1×1 (see Figs. 5 and 6 below), thus confirming the surface character of this peak. Figures 2 and 3 show that this peak S disperses with photon energy—a new finding. The previous photoemission study[5] could not detect this dispersion because it was done with UV-lamp light, hence with constant photon energy. Peak S is sensitive to s-polarized light, hence should have Δ_7 symmetry. We attribute it to a surface resonance, rather than to a surface state, because it is not located inside a gap of the bulk band structure. The observed dispersion is surprising at first be-

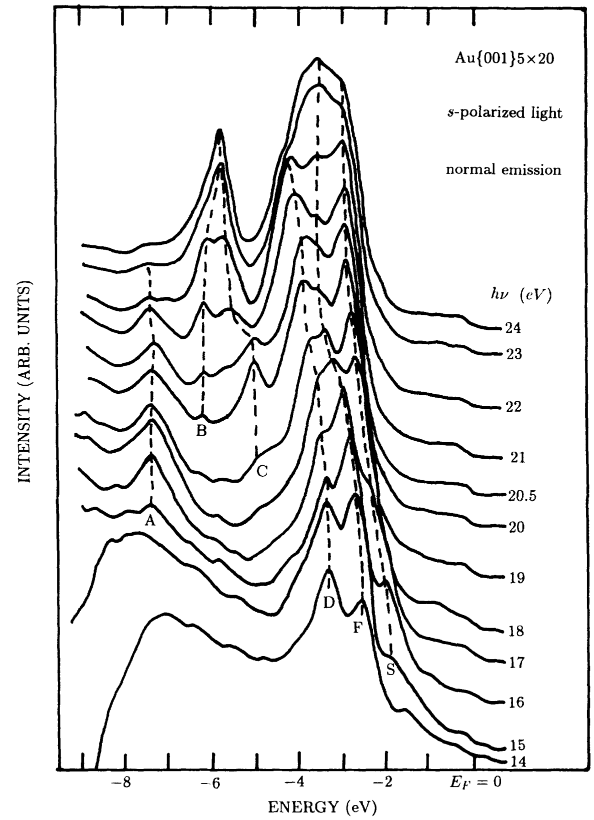

FIG. 2. Angle-resolved electron distribution curves (AREDC) measured from Au{001}5×20 for normal emission with s-polarized light.

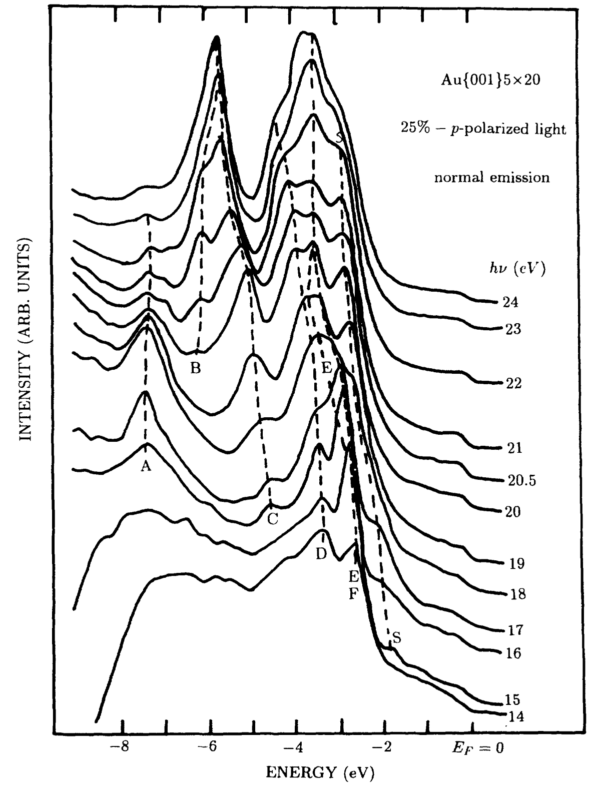

FIG. 3. AREDC's measured from Au{001}5×20 for normal emission with 25% p-polarized light.

cause a surface resonance, owing to its two-dimensional nature, is not expected to exhibit dependence on the perpendicular momentum $k_\perp$. But we note that the top (hexagonal close-packed) atomic layer on Au{001}5×20 is not flat, hence is not two-dimensional—buckling of the order of 0.5 Å has been detected on this surface.[6] Thus, the dispersion of the surface resonance is consistent with the buckled character of the hexagonal close-packed overlayer on the surface.

From the observed interband transitions (peaks A through F in Figs. 2 and 3) we have mapped the bulk-bands dispersion depicted in Fig. 4. In this figure, the solid curves are the initial and final energy bands calculated relativistically and self-consistently by EFN.[7] The crosses and the centered circles on dashed lines are experimental results: The former were found to be sensitive to *s*-polarized light, the latter, to *p*-polarized light, hence they have Δ_7 and Δ_6 symmetry, respectively. These experimental initial states were obtained by first subtracting the value of the photon energy from the measured kinetic energy E_{kin} of the final state (relative to the Fermi level E_F) and then determining the perpendicular momentum $k_\perp$ along the $\Gamma\Delta X$ line with the final Δ_6 band calculated by EFN.[7]

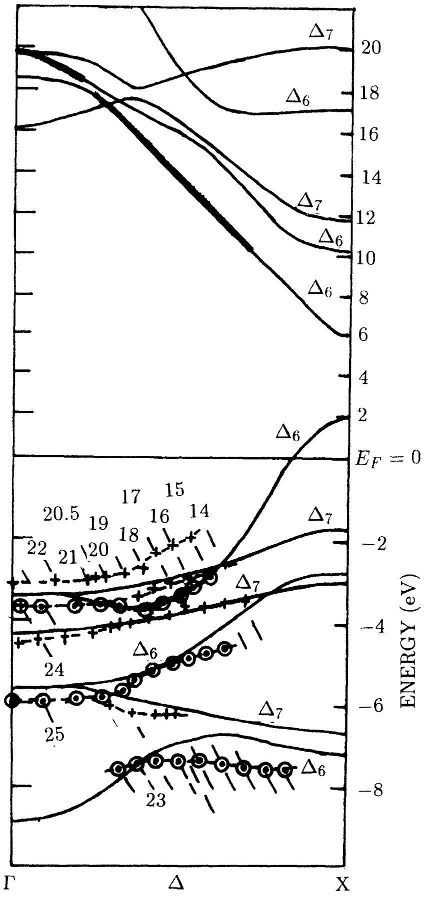

FIG. 4. Band structure of Au along the $\Gamma\Delta X$ line. Solid curves are calculated by Eckardt, Fritsche, and Noffke (Ref. 7). Dashed curves are experimental as measured from reconstructed {001}5×20, the data being drawn as crosses (*s* sensitive) and dotted circles (*p* sensitive). The numbers refer to photon energies.

We note here that in the final-state energy range below 24 eV there are three Δ_6 bands in the EFN calculation. In the present work, for the determination of $k_\perp$ we have chosen the portions of the Δ_6 bands which have been drawn thick in Fig. 4. The reason for this choice is that in those portions the dispersion is closest to the dispersion of free-electron-like bands. One expects, therefore, that the surface-transmission factors are larger in these regions than elsewhere.[15]

The experimental energy bands shown with dashed lines in Fig. 4 are in overall satisfactory agreement with EFN's calculations to within 0.4 eV, except for the middle part of the lowest Δ_6 band,where the discrepancy between theory and experiment is closer to 0.8 eV. We note that in Fig. 4 there is no theoretical counterpart of the experimental band associated with peak S in Figs. 2 and 3—a fact that is consistent with the origin of peaks S from the reconstructed close-packed hexagonal overlayer on the surface.[5] In this regard, it may also be worth noting in Figs. 2 and 3 that the peaks denoted with A through F, which are due to bulk direct interband transitions, have comparable intensities with peak S from the surface-resonance band. Given that the mean free path of the photoelectrons measured in these experiments may be only about 5–9 Å long,[16] this fact suggests that the 5×20 reconstruction is probably confined to the first atomic layer only.

In their study of Au{111}, Courths *et al.*[15] report that the experimental valence bands along the $\Gamma\Lambda L$ line deviate by about −0.3 eV from the calculation of EFN, which is consistent with the present results on the (reconstructed) {001} surface. Our measurements yield the following values of critical points: $\Gamma_8^+ = -3.6\pm0.1$ eV, $\Gamma_7^+ = -4.5\pm0.1$ eV, and $\Gamma_8^+ = -5.9\pm0.1$ eV, to be compared with EFN's calculated values; $\Gamma_8^+ = -3.38$ eV, $\Gamma_7^+ = -4.33$ eV, and $\Gamma_8^+ = -5.75$ eV.

V. PHOTOEMISSION STUDY OF Au{001}1×1-Rh

ARDEC's were collected from a Au{001}1×1 surface (produced by minute amounts, approximately 0.2 LE, of Rh) in the photon-energy range from 14 to 24 eV with both *s*- and 25% *p*-polarized radiation, and are depicted in Figs. 5 and 6, respectively. Comparison with the curves collected from Au{001}5×20 invites several comments:

(1) Peak S is dramatically decreased in the 1×1 surface (as mentioned above and seen in Fig. 7), confirming its surface-resonance character. To be sure, peak S is still detectable in the photon-energy range between 17 and 21 eV, but this observation may be explained by the fact that the small surface coverage by Rh may not have eliminated completely the 5×20 reconstruction of the surface.

(2) The peaks marked with A through F, which are due to bulk direct interband transitions, have the same energy positions and similar intensities in Figs. 5 and 6 as in Figs. 2 and 3, with one exception: The uppermost Δ_6-symmetry band is shifted by approximately 0.6 eV to-

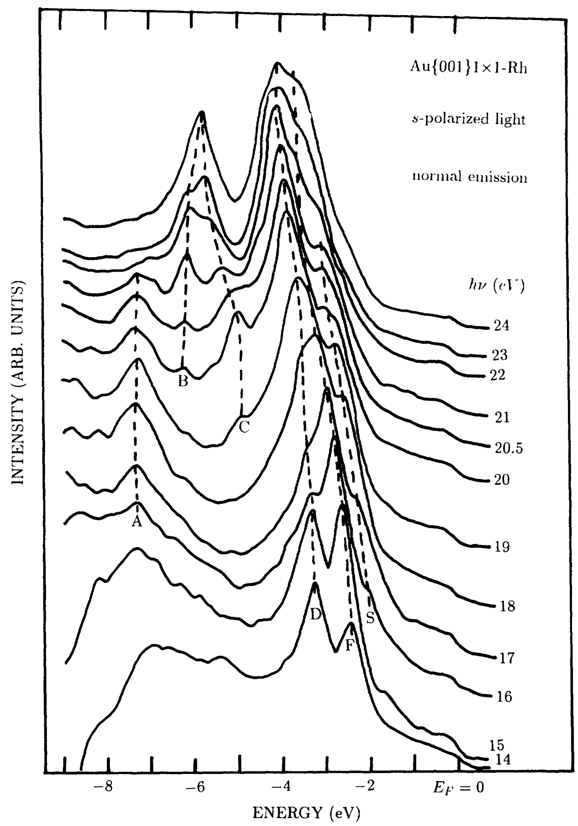

FIG. 5. AREDC's measured from Au{001}1×1 for normal emission with s-polarized light.

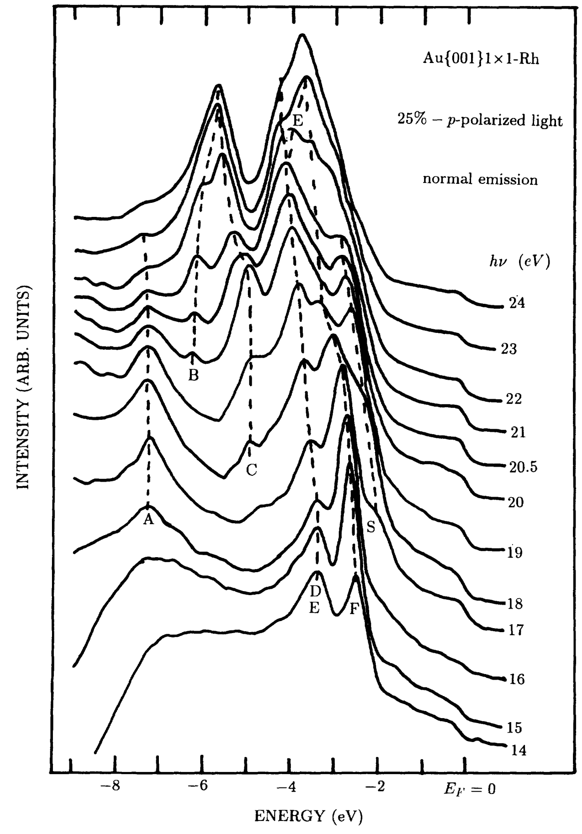

FIG. 6. AREDC's measured from Au{001}1×1 for normal emission with 25% p-polarized light.

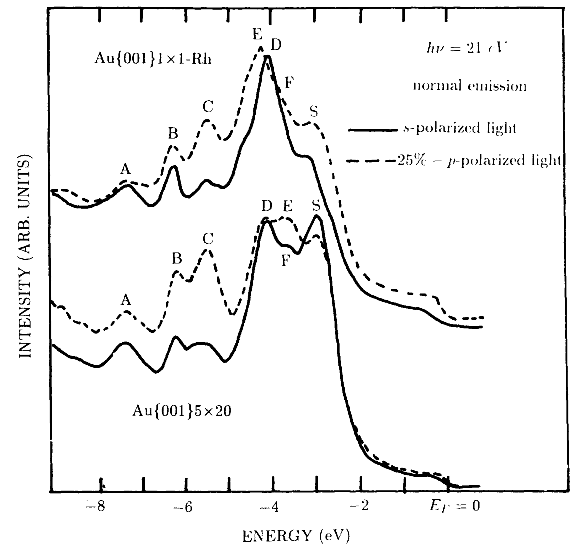

FIG. 7. Detailed comparison between normal-emission AREDC's from Au{001}5×20 (bottom set) and normal-emission AREDC's from Au{001}1×1 (top set). In both cases, solid and dashed curves were collected with s- and 25% p-polarized light, respectively. As far as energy positions are concerned, the only difference between the two sets is in peak E due to the top Δ_6 band.

ward higher binding energy in the middle part of the $\Gamma\Delta X$ line. This shift can be seen more clearly in Fig. 7, chosen as an example for the case in which $h\nu=21$ eV. The p-sensitive peak E is shifted from about -3.6 eV on the 5×20 surface to about -4.2 eV on the 1×1 surface. This shift will be discussed below. The observation that all other peaks (A,B,C,D,F) maintain their energy positions and have similar intensities in the two structures (a fact clearly visible in Fig. 7) confirms their origin from bulk direct interband transitions and confirms, in particular, the fact that the positions of the final-state bands are the same in the two structures. We have therefore used the same mapping procedure and the same final-state positions as used above for Fig. 4 in order to determine the bulk-band dispersion on the 1×1 surface from the data in Figs. 5 and 6. The results are depicted in Fig. 8, which again shows that the experimental bands of Au{001}1×1 have very similar energy positions and dispersion as their counterparts on Au{001}5×20, with the exception of the uppermost Δ_6 band.

(3) The shift in energy position of the uppermost Δ_6 band can be explained as follows. The interaction between the foreign impurity Rh and the Au atoms in the surface region is dominated by s-electron flow from Rh to the Au sites, in accordance with the different electronegativities of Rh and Au (Rh 2.2, Au 2.4, see Ref. 17). The shift of the Δ_6-symmetry band toward larger binding energy confirms the fact that the Au atoms on the 1×1 surface have more s-like electrons than those on the 5×20 surface. (Since the density of states in k space is constant and the band is not fully occupied in Fig. 4, a shift downwards means that there are more electrons in the band than before the shift.) But we need to explain why this charge transfer affects only the uppermost Δ_6 band and

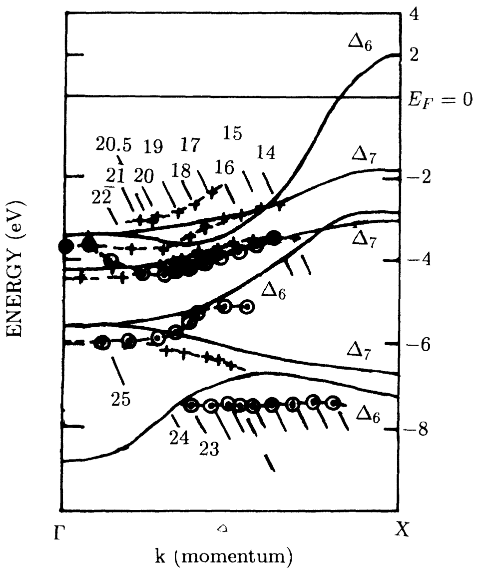

FIG. 8. Band structure of Au along the $\Gamma\Delta X$ line. Solid curves are calculated by Eckardt, Fritsche, and Nofke (Ref. 7). Dashed curves are experimental as measured from unreconstructed Au{001}1×1-Rh, the data being drawn as crosses (*s* sensitive) and dotted circles (*p* sensitive). The numbers refer to photon energies.

not the other bands. Group theory tells us that the interaction between two-electron bands occurs only if the two bands have the same symmetry. Since *s*-like electrons have Δ_6 symmetry, then a transfer of *s*-like charge from Rh to Au will only be reflected in the energy position of the top Δ_6-symmetry band of the Au 5*d*-6*s* hybridized band. No shift is observed in the lowest band with Δ_6 symmetry because the energy of *s*-like electrons in Rh is much higher than that of this band, hence the interaction between them is small. Also, no shift is observed in the intermediate band with Δ_6 symmetry either. But this band originates from the Δ_5 band (d_{xz} and d_{yz}) in the nonrelativistic calculation, hence it should not be sensitive to *s*-charge transfer, i.e., to change in *s*-*d* hybridization.

VI. CONCLUSIONS

The main conclusions of the present work may be summarized as follows.

(a) The unreconstructed {001}1×1 surface of Au prepared by depositing minute amounts of Fe, Mn, or Rh impurities on a clean Au{001}5×20 surface has a slightly relaxed bulklike structure. The relaxation consists in small contractions of both the first and the second interlayer spacing by about 2–2.8% of the bulk interlayer spacing.

(b) A photoemission peak located above the Au *d* bands and due to a surface-resonance band from the hexagonal close-packed overlayer on Au{001}5×20 exhibits some energy dispersion with varying perpendicular momentum $k_\perp$. This observation is consistent with the buckling found by atom diffraction[6] in the hexagonal overlayer.

(c) Other features in the photoemission spectra from Au{001}5×20 are well explained by bulk direct transitions between initial and final energy bands along the $\Gamma\Delta X$ line as calculated relativistically and self-consistently for a 1×1 surface by EFN.[7] The initial-band positions found experimentally are generally in satisfactory agreement, to within 0.4 eV, with EFN's calculations. This result suggests that the 5×20 reconstruction exists only in the first layer, so that the photoemission response of a Au{001}5×20 surface can be well understood on the basis of a 1×1 calculation.

(d) The deposition of minute amounts of Rh (and, by inference from the LEED study, of other impurities as well) on an Au{001}5×20 surface destroys the 5×20 reconstruction and yields a 1×1 structure. The photoemission spectra from this surface show that the features caused by bulk direct transitions remain the same as on the 5×20 surface with the exception that the top Δ_6-symmetry band is shifted toward higher binding energy by about 0.6 eV in the middle portion of the $\Gamma\Delta X$ line. This shift suggests that the interaction between the Rh and the Au atoms on the surface is dominated by *s*-like charge transfer from the Rh to the Au sites, and not, as may have been expected, by *d*-*d* effects.

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